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SILICON-THE SILICON-CARBON BOND: ANNUAL SURVEY FOR THE YEAR 1989*

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I. INTRODUCTION

This section of the annual survey of organosilicon chemistry covers material appearing in volumes 110 and 111 of Chemical Abstracts. It is the intent of the author to be as thorough as possible without being redundant in presenting the results of the chemistry of the silicon-carbon bond and carbofunctional organosilanes. Liberal use of abbreviations is used. These should, however, be familiar to the practiced chemist. An honest attempt has been made to arrange the subject matter into categories, but due to the multiple nature of much of the chemistry this is not always possible, thus the reader is advised to peruse all sections.

II. REVIEWS

A total of 25 reviews were found. Not all of these were directly related to the silicon-carbon bond, but are noted here nevertheless. The number of references cited in each review is indicated in parentheses. The Annual Survey for the Silicon-Carbon Bond for 1986 appeared (617). [1] A history of the development of organosilanes and silicones with no references was published. [2] The literature on the use of sonochemical reactions of organosilanes was reviewed (61). [3] Several reviews dealt with the structure and reactivity of organosilanes, these included aspects of the reactivity of hypervalent silicon species in organic synthesis (15) [4], selective transformations of pentacoordinate silanes (21) [5], organosilanes having specific valence states (17) [6], organosilanes with nonstandard coordination types (111) [7], and the electronic structure of 1-halosilatranes (59) [8]. Others were on the structure and reactions controlled by strong sigma-pi interactions, which deals with the conjugation of the Si-Si bond with C-C double and triple bonds (18) [9], the influence of silyl groups on the reactivity and formation of metal-carbon bonds (32) [10], and ^{29}Si-^{15}N spin-spin coupling as a probe for structural studies of nitrogen containing organosilanes (26) [11]. Reviews dealing with mechanistic questions were examples of the contribution of gas kinetic studies to the understanding of organosilicon reaction mechanisms (38) [12], and radical thermochemistry using silanes as free-radical reducing agents (9) [13]. The remainder of the reviews dealt with the use of

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organosilanes in synthesis and these included the oxidation of silicon-carbon bonds (21) [14], development of new synthetic reactions using organosilicon and organotin chemistry (44) [15], silylated and stannylated thiazoles and oxazoles in synthesis (48) [16], silanes as reducing agents in organic chemistry (18) [17], diastereofacial selectivity in nucleophilic additions to chiral acylsilanes (6) [18], dipolar additions of nitrones with organosilanes (71) [19], 1-alkoxy-1-siloxycyclopropanes as homoenolate nucleophiles of esters (18) [20], 1-siloxycyclopropanes as homoenolate ion precursors (12) [21], synthesis and reactions of functionalized silyl enol ethers (78) [22], nucleophilic activation of silyl enol ethers and esters (32) [23], donor-acceptor substituted cyclopropanes as synthetic building blocks with special attention to methyl 1-trimethylsiloxycyclopropane-carboxylates (115) [24], and the steric influence of the trimethylsilyl group in organic reactions (145) [25].

III. DISSERTATIONS

A total of 16 dissertations were abstracted in 1989 with the majority dealing with synthetic aspects of organosilicon chemistry. These included the synthesis of allylsilanes and β-silyl ketones from 1-alkynyltrialkylborates [26] , synthesis and reactions of allylsilanes [27], synthesis of highly substituted arylsilanes [27], 1-arylsulfonyl-4-trimethylsilyl-1- and -2-butenes as synthetic equivalents for 1-(1,3-butadienyl) anion and 1,1-(1,3-butadienyl) dianion [28], silylfuran oxidations applied to the synthesis of the antibiotic patulin [29], allylsilane initiated carbocyclizations including the diastereo-selectivity and the total synthesis of hirsutene [30], studies on the development of organosilicon reagents [31], synthesis and studies of silyl methyl ketals of quinones [32], and trimethylsilyl ethers of ethynyl alcohols as latent drugs [33] Mechanistic emphasis was found in a mechanistic and kinetic study of thermally-induced α- and β-elimination of alkoxysilanes [34], synthesis and reactions of bis(trimethylsilyl) compounds a search for the mechanism of the Peterson olefination reaction [35], kinetic and mechanistic aspects of the thermal decomposition of silylketenes, -thioketenes and -ketenimines [36], and reactions of silylenes with various reactants [37]. Organometallic chemistry of organosilanes included silyl substituted iron alkyl complexes [38], transition metal complexes involving the 1,5-bis(trimethylsilyl)pentadienyl ligand [39], and synthesis of some late transition metal and main group organosilyl compounds [40]. Finally the synthesis and application of alkyldihydrochlorosilanes for surface modification of porous silicon was published. [41]

IV. ALKYLSILANES

A. Preparation

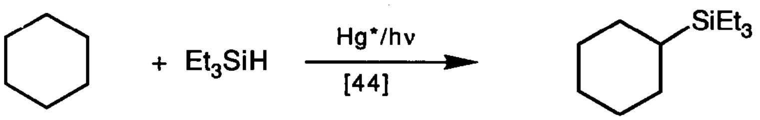
A convenient preparation of bis(trimethylsilyl)methane from dibromomethane was reported. (Eqn. 1) Trimethylsilylcyclopropanes were prepared as illustrated by the example in Eqn. 2.

$$CH_2Br_2 + 2\ Me_3SiCl + 4\ Li \xrightarrow[\text{-50°C} \atop [42]]{Et_2O/THF} CH_2(SiMe_3)_2 \qquad (1)$$

(CH_2ClBr also works well, but not CH_2Cl_2)

(2)

The cross dehydrocoupling of cyclohexane and triethylsilane was reported. (Eqn. 3) The reaction runs with ethanol to give the α-hydroxysilane. (Eqn. 4)



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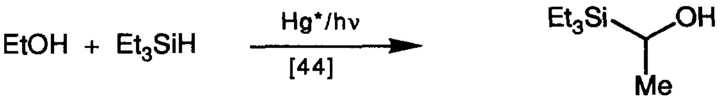

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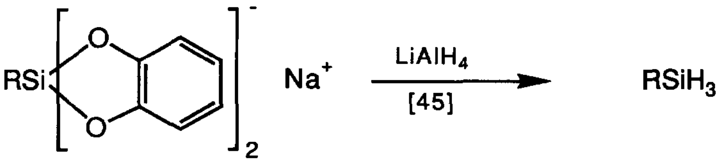
The reaction of nucleophilic reagents with pentavalent silicon complexes **1** result in alkyl as well as aryl, ethynyl or vinylsilanes. (Eqns. 5-8)



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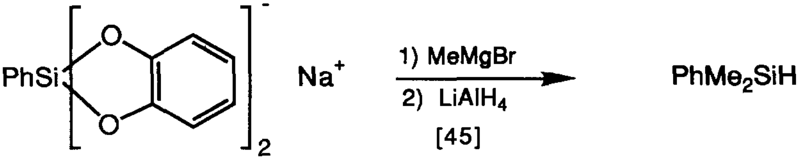

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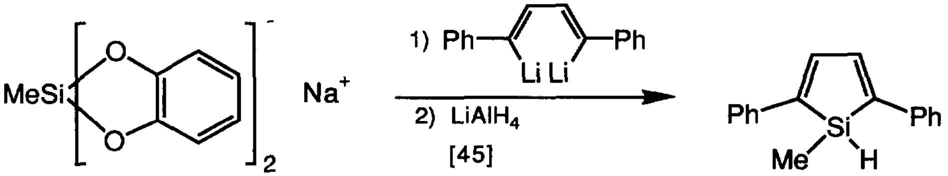

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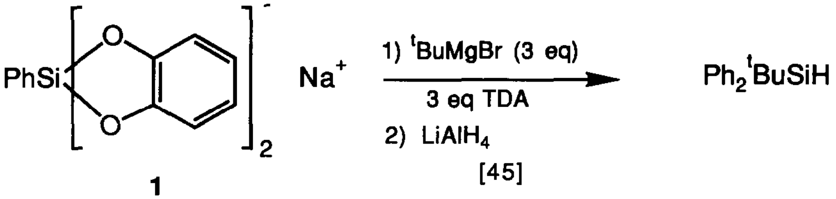
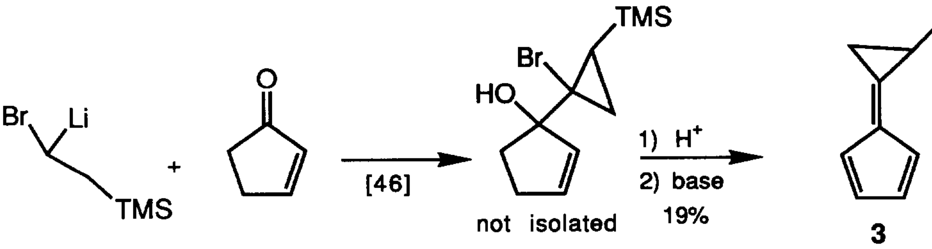


1

(8)

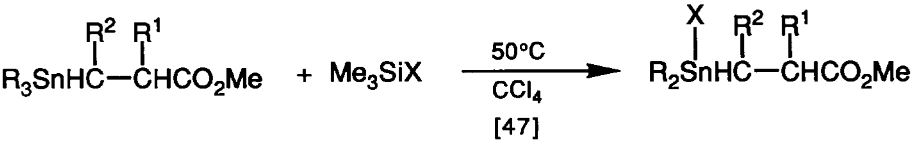
(TDA = tris(3,6-dioxaheptyl)amine, which together with $LiAlH_4$ causes disproportionation)

The trimethylsilyl substituted cyclopropyllithium reagent **2** was used to prepare **3**. (Eqn. 9)



(9)

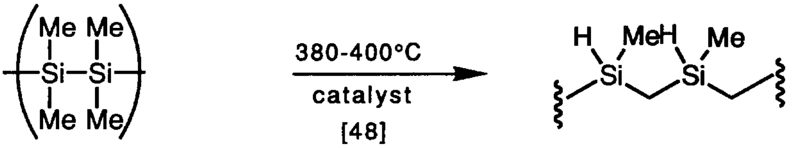
The tin-silicon exchange reaction shown in Eqn. 10 was reported. It is essentially an irreversible reaction.



$$\mathrm{R_3SnH}\overset{\mathrm{R^2}}{\overset{|}{\mathrm{C}}}-\overset{\mathrm{R^1}}{\overset{|}{\mathrm{C}}}\mathrm{HCO_2Me} + \mathrm{Me_3SiX} \xrightarrow[\mathrm{CCl_4}\ [47]]{50°\mathrm{C}} \mathrm{R_2}\overset{\mathrm{X}}{\overset{|}{\mathrm{Sn}}}\mathrm{H}\overset{\mathrm{R^2}}{\overset{|}{\mathrm{C}}}-\overset{\mathrm{R^1}}{\overset{|}{\mathrm{C}}}\mathrm{HCO_2Me} \qquad (10)$$

R = Me, ^{n}Bu, Ph; X = Cl, Br, I

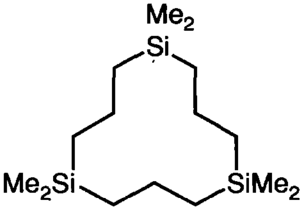
Certain boron catalysts were found to convert polydimethylsilanes to polycarbosilanes. (Eqn. 11)



(11)

catalyst = $B(OMe)_3$, $B(OTMS)_3$, $B(NEt_2)_3$ or TMS_2BNMe_2; yields 35-63%

The 12-silacrown **4** was prepared in a 9 step iterative process starting from chloropropyltrimethoxysilane. [49]



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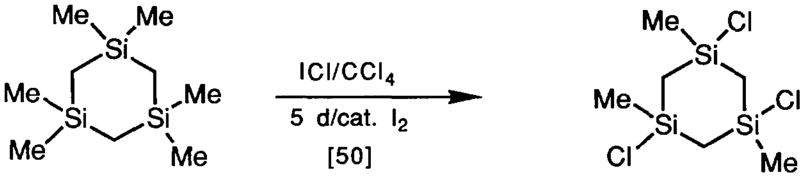
B. Reactions

The carbosilane **5** was shown to react with idoine monochloride to give chlorodemethylation in a rather clean reaction. (Eqn. 12) Carbosilane **6** reacts with aluminum bromide to give **7** and the all cis isomer **8**. (Eqn. 13)



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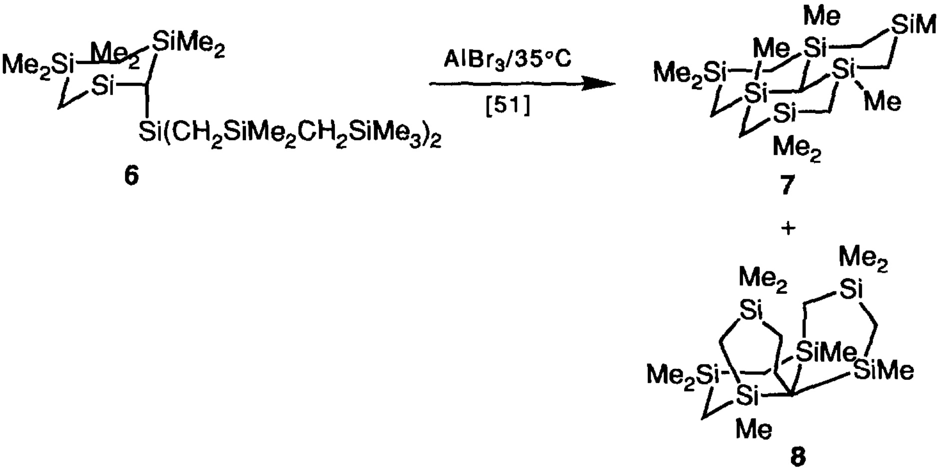
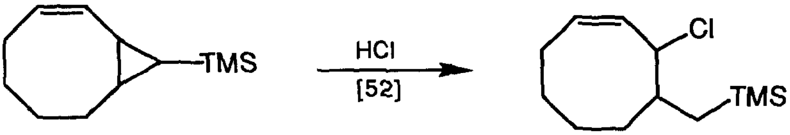


(13)

Trimethylsilylcyclopropanes were ring opened with acid. (Eqns. 14 and 15)



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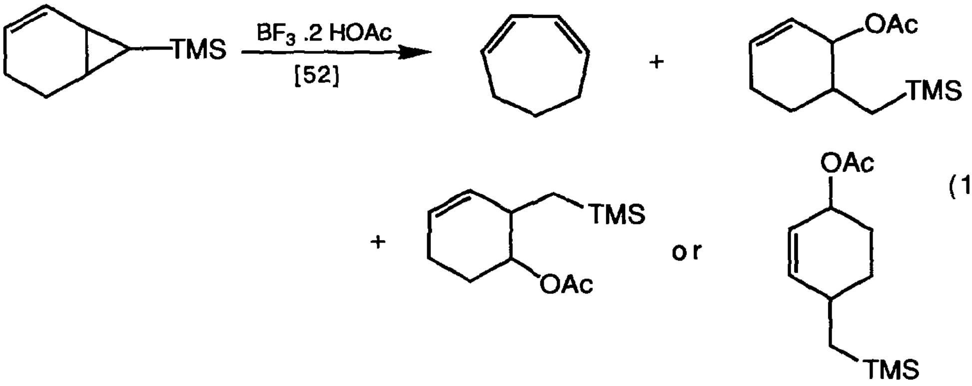
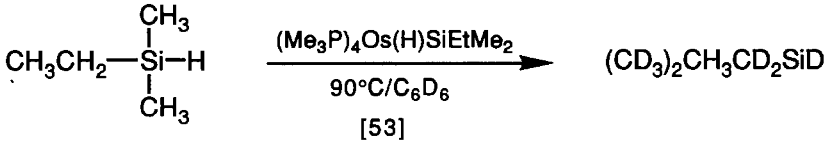


(15)

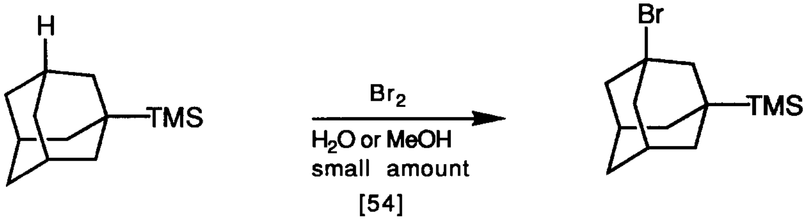
The total selection H/D exchange of the α-CH bonds of alkylsilanes was reported. (Eqn. 16)



$$CH_3CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-H \xrightarrow[\substack{90°C/C_6D_6 \\ [53]}]{(Me_3P)_4Os(H)SiEtMe_2} (CD_3)_2CH_3CD_2SiD$$

(16)

1-Trimethylsilyl- and 1,3-bis(trimethylsilyl)adamantane undergo bromination at the C-H bond and not at a C-Si bond. (Eqns. 17 and 18)



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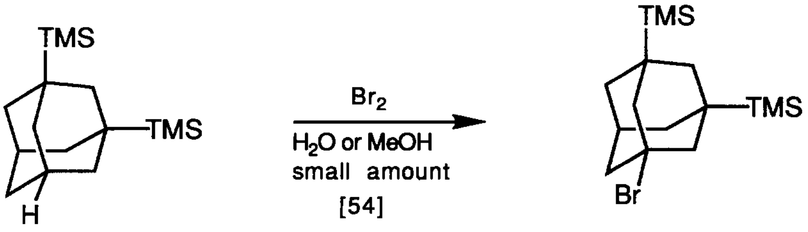
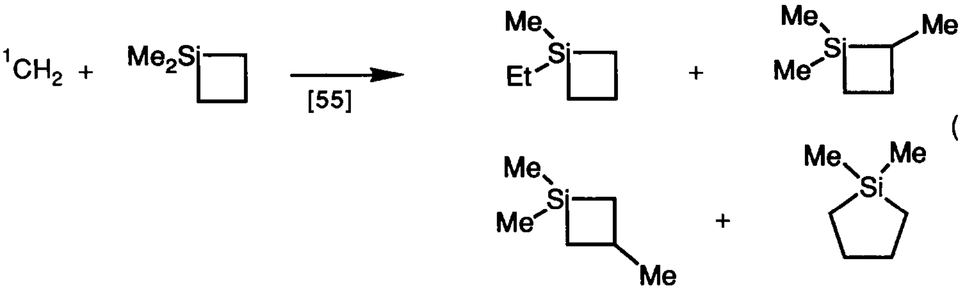


(18)

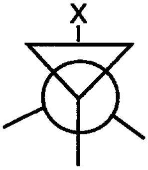
The reaction of singlet methylene with 1,1-dimethyl-1-silacyclobutane gives both C-H and C-Si insertion. (Eqn. 19)



(19)

C. Other Studies

The enthalpies of formation of Me_3SiX systems was found to linearly correlate with the ionization potential of X. [56] The favored conformation of c-$C_3H_5SiH_2X$ (X = F, Cl, Br, I) was found to be the syn **9** and not the gauch **10**. [57] A study of long range hyperfine splitting of substituted (including silyl substituted) adamantanes was reported. [58]



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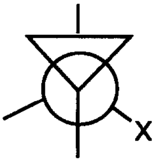

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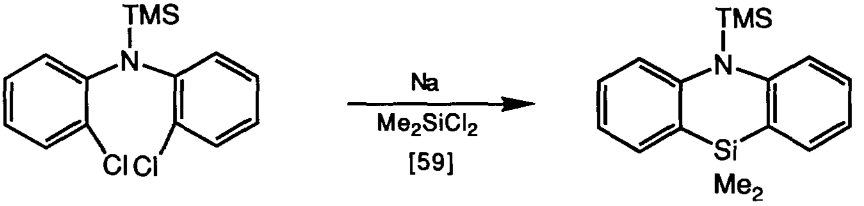
V. ARYLSILANES

A. Preparation

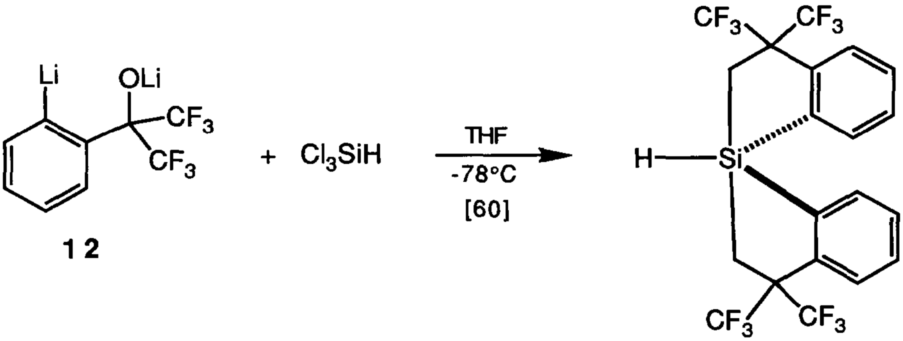
Various derivatives of 9,9-dimethyl-9-silaacridines **11** were prepared by the direct reaction of N-trimethylsilyl bis(2-halophenyl)amines with sodium and dimethyldichlorosilane. (Eqn. 20)



11

(20)

The pentavalent organosilane **12** was prepared from two equivalents of dilithium reagent **13** and trichlorosilane. (Eqn. 21) Compound **13** was shown to reduce aldehydes and ketones (Eqn. 22) as was the PPN (PPN = $Ph_3P{=}NPPh_3^+$) salt.



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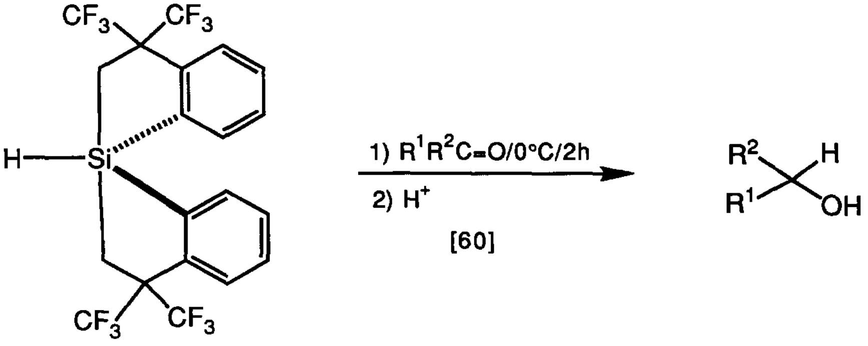
13

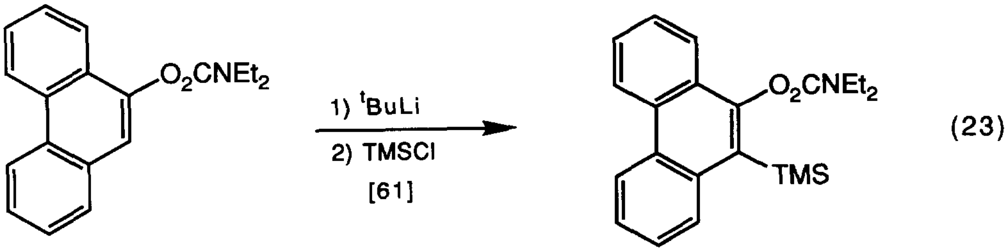
(21)



13

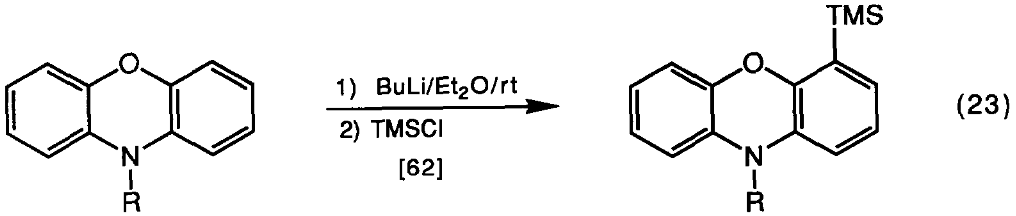
(22)

Metalation-trimethylsilylation of phenanthryl diethylcarbonate gives the ortho silylated product **14**. (Eqn. 23)

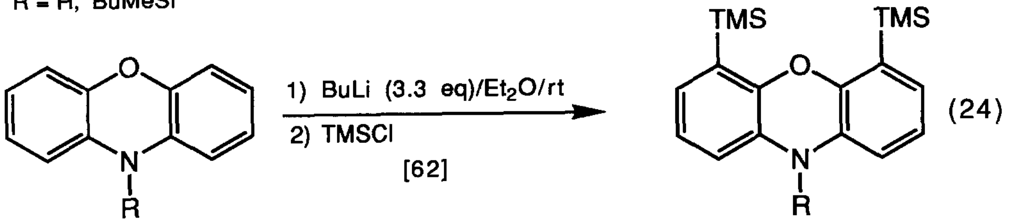


14 88 %

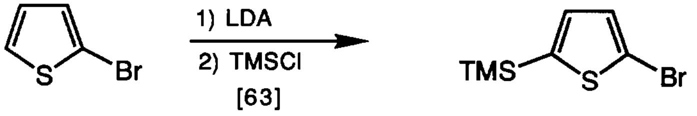
Metalation-trimethylsilylation of phenoxazine gives the 4-trimethylsilyl derivative or the 4,6-disilyl derivative depending on the amount of lithiating agent employed. (Eqns. 24 and 25)



R = H, ^{t}BuMeSi



Metalation-trimethylsilylation of 2-bromothiophene gives the 5-trimethylsilyl derivative. (Eqn. 25) This was coupled with the iodo bisthiophene **15** to give the α-terthienylsilane **16**. (Eqn. 26)



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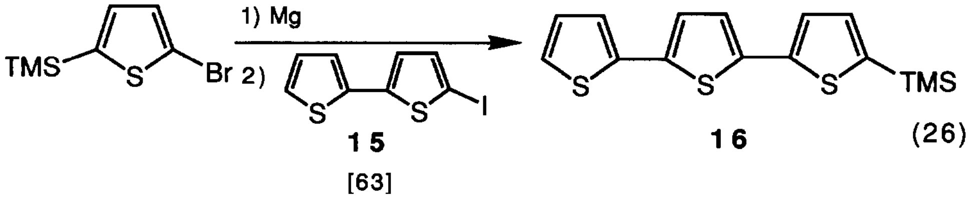
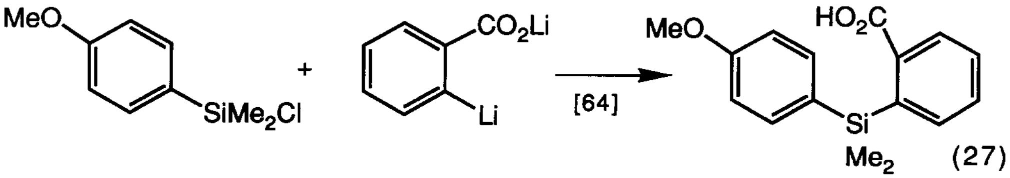


(26)

Ortho lithio lithium benzoate was reacted with p-anisyldimethylchlorosilane. (Eqn. 27) A number of 1-silaindolinone systems were prepared starting from **17**. These conversions are shown in Eqns. 28 through 32. Although the product of **17** with ammonia is structurally similar to saccharin it exhibits no sweet taste.



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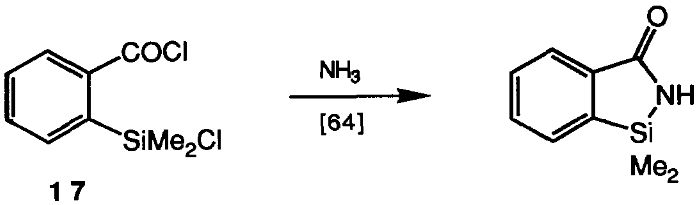

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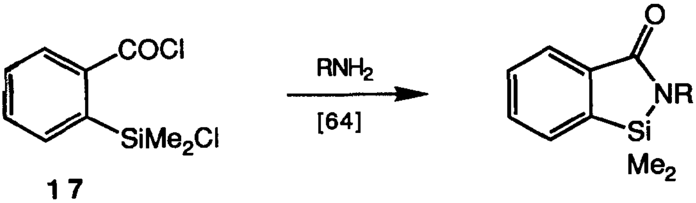

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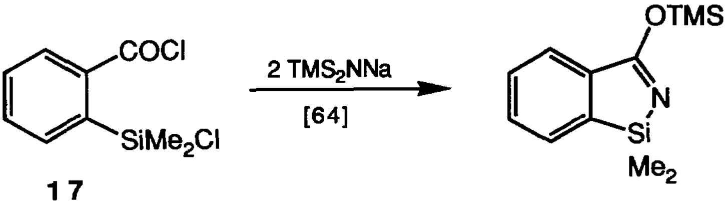

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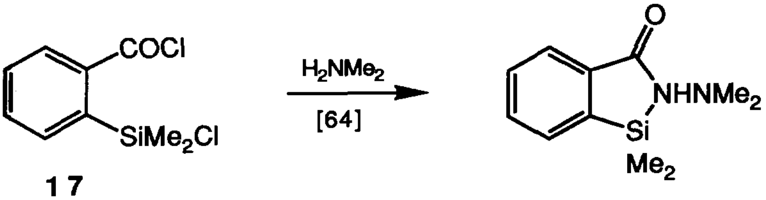

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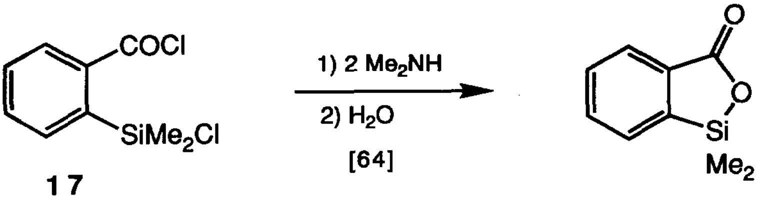
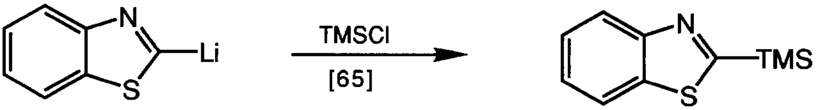


17

(32)

Benzothiazole was lithiated and trimethylsilylated as shown. (Eqn. 33) Lithiation-trimethylsilylation of benzothiazine **18** proceeds as shown in Eqn. 34.



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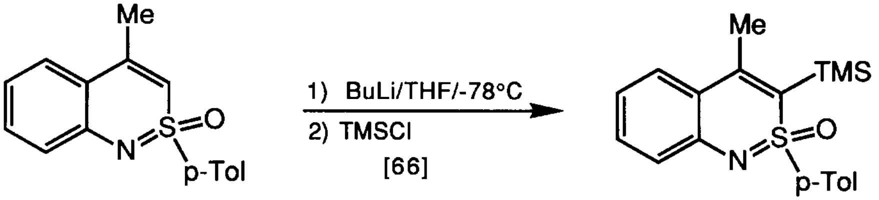


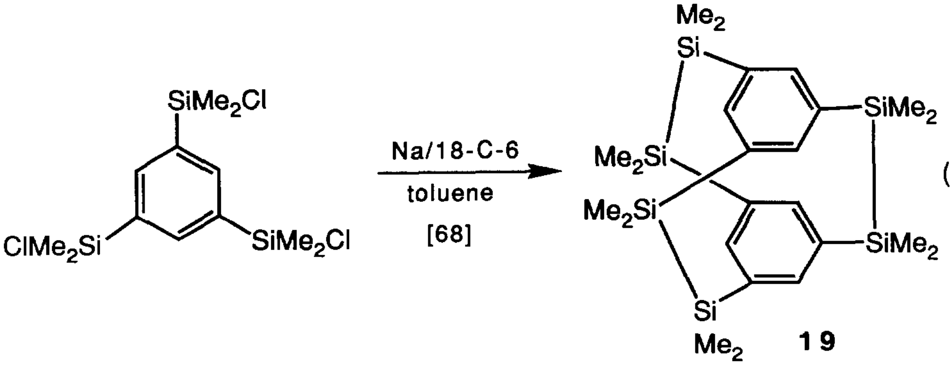
18

(34)

A full account of the preparation of arylsilanes from aroyl chlorides appeared. (Eqn. 35)

$$\mathrm{PhCOCl} + \mathrm{ClMe_2SiSiMe_2Cl} \xrightarrow[\substack{\mathrm{R_3P} \\ [67]}]{(\mathrm{PhCN})_2\mathrm{PdCl_2}} \mathrm{PhSiMe_2Cl} + \mathrm{PhCOCOPh} + \mathrm{PhCHO} + \mathrm{Me_2SiCl_2} + \mathrm{CO} \qquad (35)$$

Treatment of 1,3,5-tris(chlorodimethylsilyl)benzene gives **19** in 0.22 % yield. (Eqn. 36) This material is stable to at least 300°C, but is oxidized to the disiloxane with trimethylamine N-oxide. (Eqn. 37)



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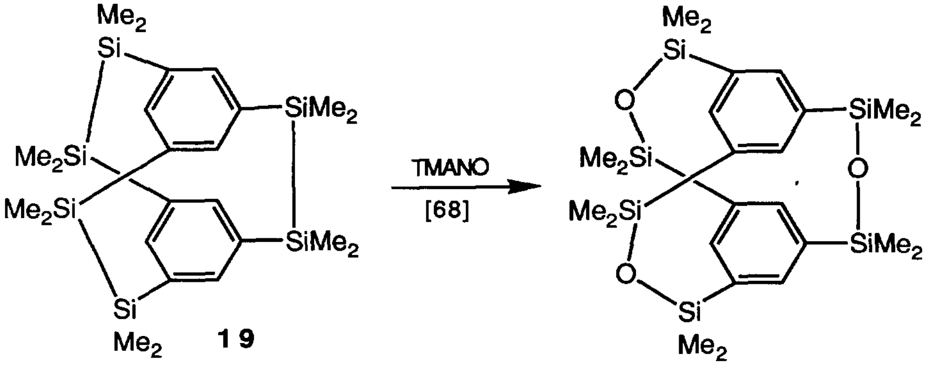

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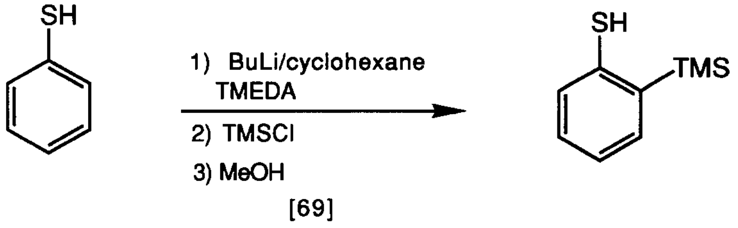
(37)

(TMANO = trimethylamine-N-oxide

Thiophenol can be doubly deprotonated and the dilithium reagent reacted with chlorosilanes to give, after desilylation of the mercapto group, the ortho silyl thiophenol. (Eqn. 38) The product from the reaction with dimethyldichlorosilane was oxidized to **20**. (Eqn. 39) Similar results were obtained with 2-pyridinethiols. (Eqn. 40) In this system the second deprotonation occurs at the 6 position. (Eqn. 41) These materials were used to form complexes with Cu(I) and Ag(I).



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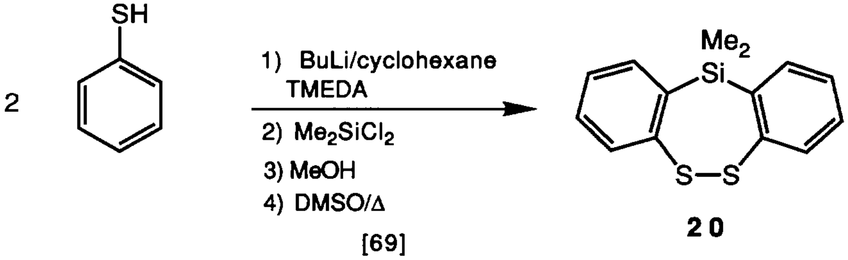

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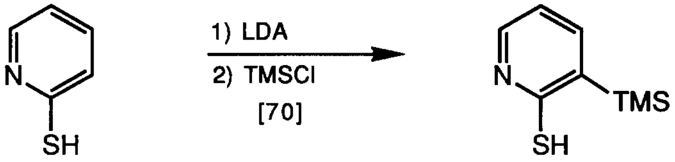
(39)



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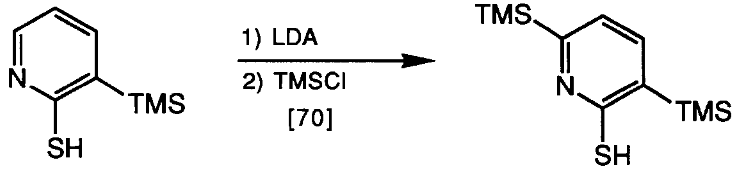
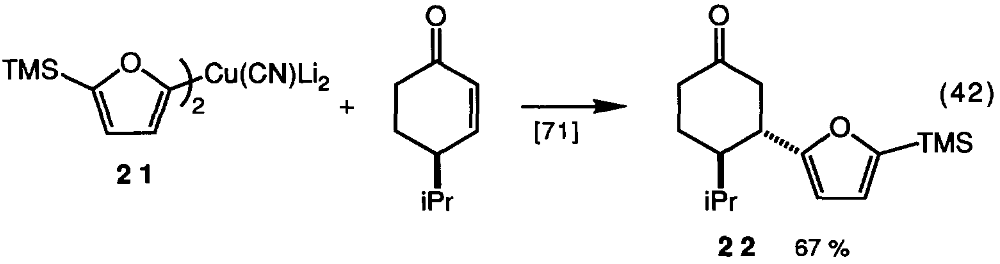


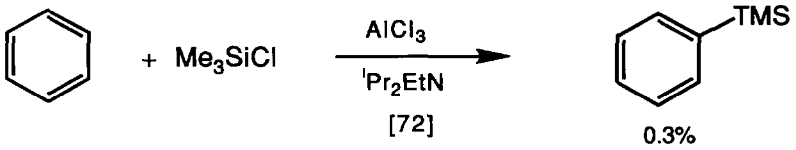
(41)

The silylated copper reagent **21** was reacted with enones to give **22**. (Eqn. 42)



(42)

By incorporating the presence of a hindered tertiary amine to trap the HCl liberated and therefore prevent protodearylation it proved possible to electrophilically trimethylsilylate, albeit in low yield, benzene with trimethylchlorosilane/aluminum chloride. (Eqn. 43)



(43)

Et_3SiCl gave 1.2% and $^iPr_3SiCl$ gave 1.6%

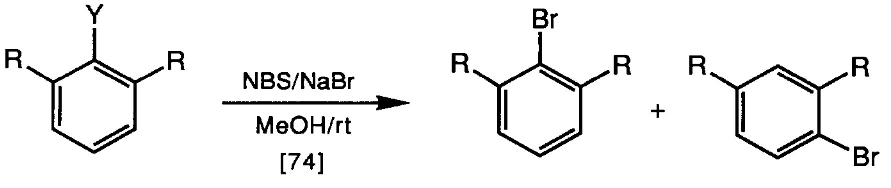
B. Reactions

The facile dephenylation of phenylsilanes with triflic acid was reported. (Eqns. 44 and 45)

$$PhMe_2SiSiMe_2Ph \xrightarrow[\text{1 h/rt}\ [73]]{CF_3SO_3H} CF_3SO_3Me_2SiSiMe_2O_3SCF_3 \qquad (44)$$

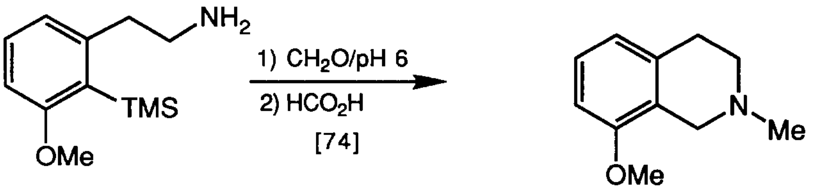
$$Ph_2SiMe_2 \xrightarrow[\text{1 h/rt}\ [73]]{CF_3SO_3H} (CF_3SO_3)_2SiMe_2 \qquad (45)$$

The bromodesilylation of arylsilanes was again shown to be much better than the reaction with simple arenes. (Eqn. 46) The selective protodesilylation was employed in a regioselective Pictet-Spangler reaction. (Eqn. 47)



(46)

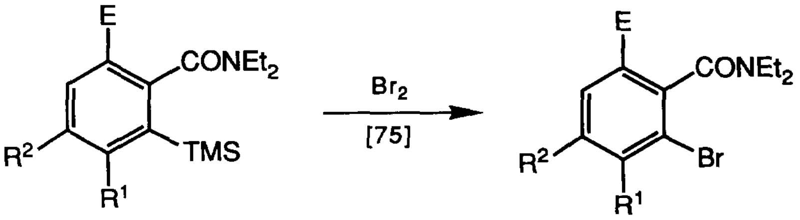
R = MeO Y = H	4 %	96 %
R = MeO Y = TMS	100 %	0 %
R = Me Y = H	4 %	96 %
R = Me Y = TMS	100 %	0 %



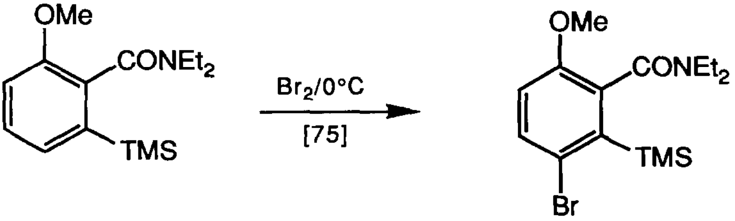
(47)

(72 % versus 22 % for H compound)

Bromodesilylation of ortho trimethylsilylbenzamides is possible, but when a methoxy group is present on the aromatic ring it will direct the regioselectivity of the bromination. (Eqns. 48 and 49)

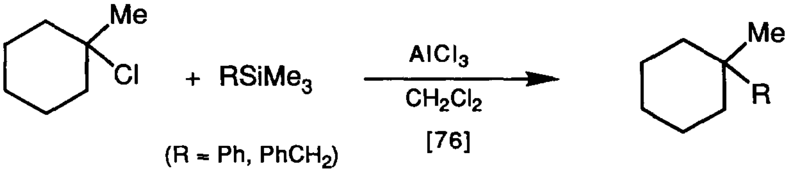


(48)



(49)

Phenyl and benzylsilanes were shown to react with tertiary chlorides in the presence of aluminum chloride to give phenylation or benzylation of the alkane. (Eqn. 50)



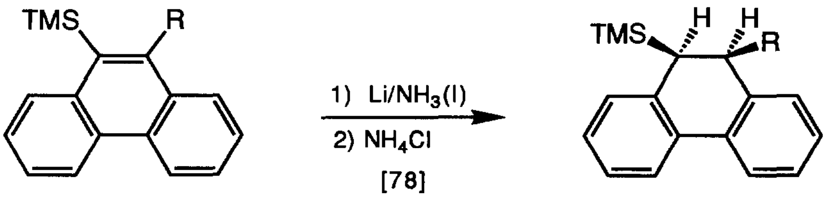
(50)

Perfluoroarylsilanes give the corresponding diaryl system when treated with xenon difluoride in the presence of a metal fluoride salt. (Eqn. 51)

$$R_nSiMe_{4-n} + XeF_2 \xrightarrow[\text{[77]}]{\text{MF}} R\text{-}R \qquad (51)$$

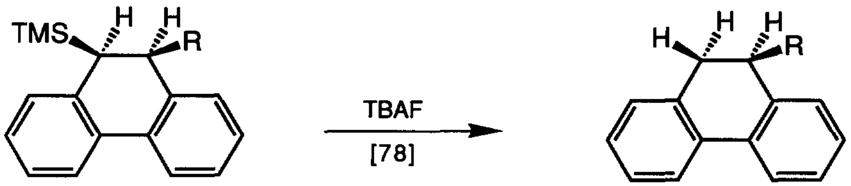
(R = C_6F_5; p-$F_3CC_6H_4$; 2,3,5,6-tetrafluoropyridyl; M = K, Cs, Rb)

The trimethylsilyl group was used to control the regiochemistry of the reduction of phenanthrenes. (Eqn. 52) The trimethylsilyl group can be protolytically removed (Eqn. 53) or used to specifically alkylate the dihydrophenanthrene (Eqn. 54).

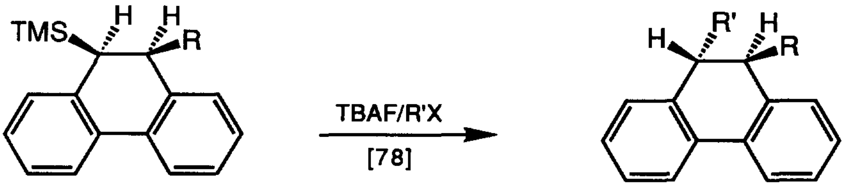


(52)

(R = H, Me, Et)



(53)



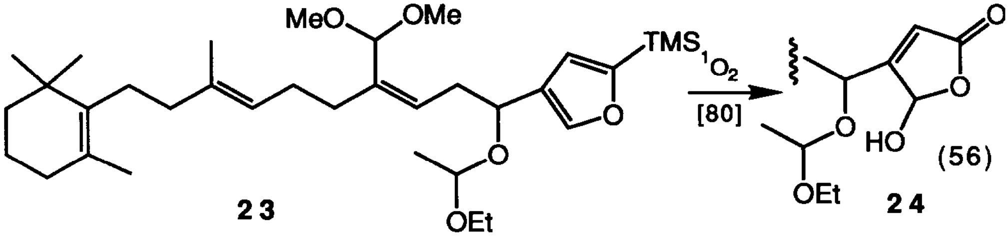
(54)

Arylfluorosilanes were cleaved by mercury(II) salts to give the arylmercuric halide, cyanide or acetate. (Eqn. 55) The reaction was, as expected, facilitated by electron donation in the ring.

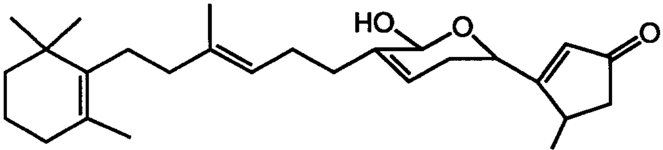
$$4\text{-Y-C}_6\text{H}_4\text{SiF}_3 + \text{HgX}_2 \xrightarrow[{[79]}]{} 4\text{-Y-C}_6\text{H}_4\text{HgX} \qquad (55)$$

(Y = H. Me, Cl, Br, NO_2; X = Cl, Br, I, CN, OAc)

Furylsilane **23** was oxidized with singlet oxygen to secomanoalide **24**. (Eqn. 56) A similar reaction was used to synthesize manoalide **25**.

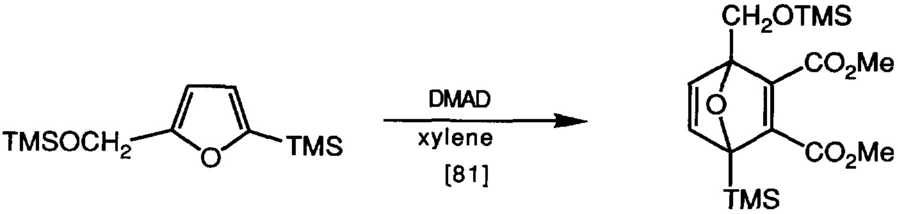


23 **24** (56)



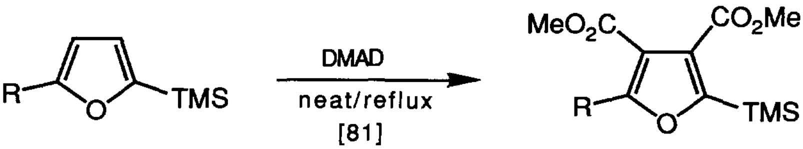
25

At lower temperatures 2-trimethylsilylfurans react with dimethylacetylene dicarboxylate to give the expected adduct **26**. (Eqn. 56a) At higher temperatures the reaction leads to extrusion of acetylene to give furan **27**. (Eqn. 57)



26

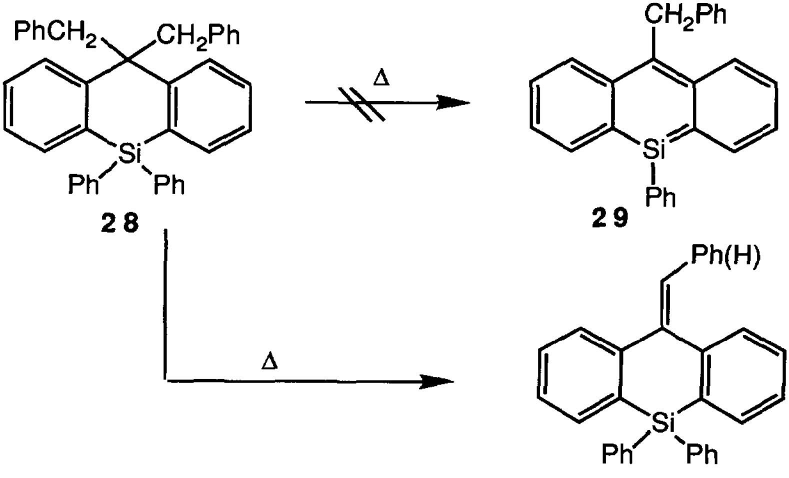
(56a)



27

(57)

Thermolysis of **28** does not give the silaanthracene **29** as hoped, but rather the benzylidene derivative **30**. (Eqn. 58)

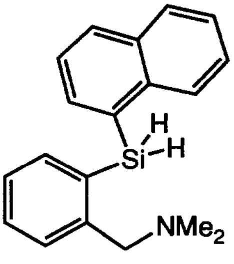


28 **29** **30**

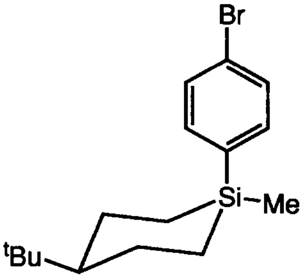
(58)

C. Other Studies

An x-ray study of **31** shows the Si-N distance to be 244 nm. [83] An x-ray analysis of **32** was carried out. [84] The analogous phenyl derivatives were halodesilylated with predominant retention of configuration. The fragmentation of 2-thienylsilanes in the mass spectrometer was studied. [85] The π-donor ability of furylsilanes was investigated. [86] The conformations of dibenzochalcogenosilacins and -silanins were studied spectroscopically. [87]



31



32

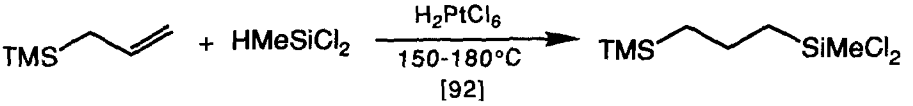
VI. HYDROSILATION

A. New Developments

The synthesis of polyvinylsiloxane-platinum complexes and their catalytic acitivity for hydrosilation was investigated. In addition to the addition of monomeric silanes to multiple bonds with these catalysts the hydrosilation of olefins with polyhydrosiloxanes was studied. [88] Vinylazole complexes of some platinum and rhodium salts were employed successfully in hydrosilations. [89] A poly-ω-diphenylphosphinoundecylsiloxane platinum complex was used to catalyze the hydrosilation reaction. [90] A poly(phosphino-organosiloxane)silicate-supported rhodium(I) catalyst was employed in the hydrosilation reaction. [91]

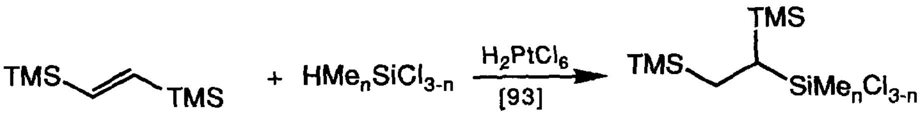
B. Hydrosilation of Alkenes

Allyltrimethylsilane was found to be 3 to 10 times less reactive than vinyl (or butenyl)silanes towards the hydrosilation reaction. (Eqn. 59)

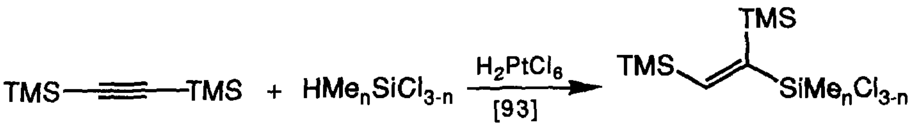


(59)

The hydrosilation of (E) 1,2-bis(trimethylsilyl)ethene and bis(trimethylsilyl)-acetylene was reported. (Eqns. 60 and 61) Both give trisilylated systems.

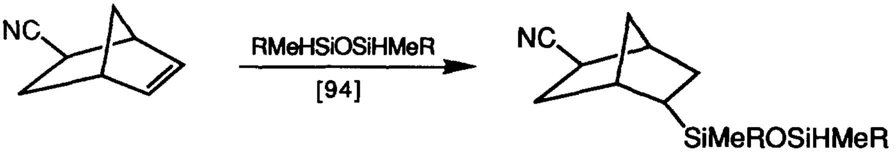


(60)



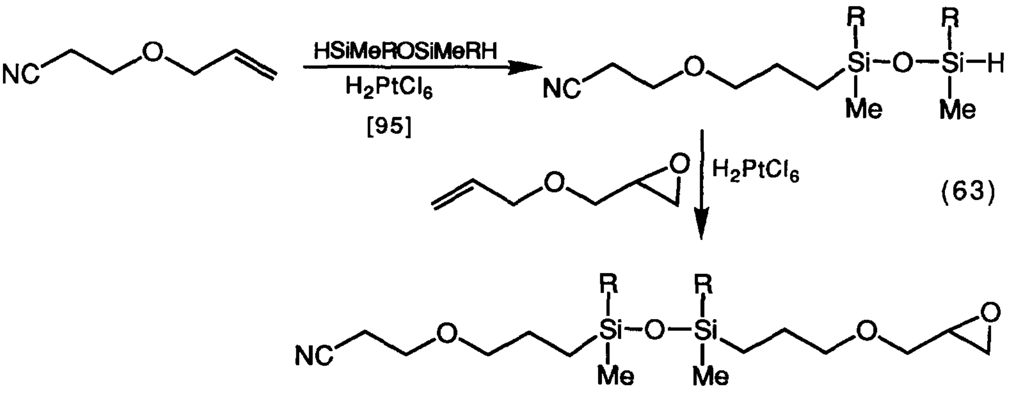
(61)

Functional organosilanes were prepared by the hydrosilation of functionalized systems. Thus, hydrosilation of 2-cyanobicyclo[2.2.1]hept-5-ene gives the expected cyanofunctional organosilane. (Eqn. 62)



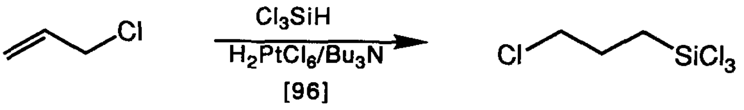
(62)

The hydrosilation of cyanoethylallyl ether with 1,3-dihydrodisiloxanes followed by the hydrosilation of allylglycidyl ether gives difunctional disiloxanes. (Eqn. 63)



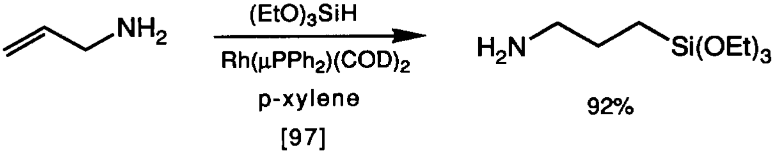
(63)

Various chloroplatinic acid/amine systems were investigated for the hydrosilation of allyl chloride. Chloroplatinic acid/tri-butylamine is reported to give 85% yield of the commercially important chloropropyltrichlorosilane. (Eqn. 64)



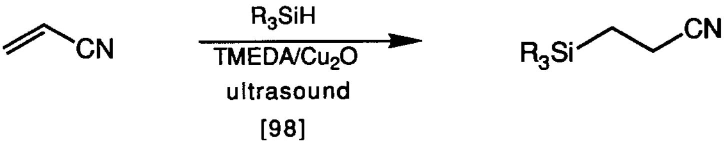
(64)

The hydrosilation of allylamine with rhodium phosphite catalysts was reported to give up to 92 percent of aminopropyltriethoxysilane with very little of the β-adduct. (Eqn. 65)



(65)

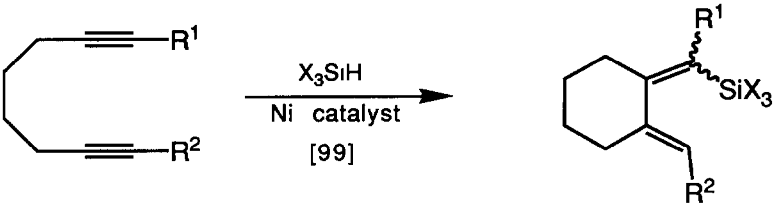
The reaction of several tri- or dichlorosilanes with acrylonitrile in the presence of Copper(I) oxide and N,N,N',N'-tetramethylethylene diamine (TMEDA) together with ultrasound was reported. (Eqn. 66) Dimethyl- and diphenylchlorosilane reacted very poorly under these conditions.



(66)

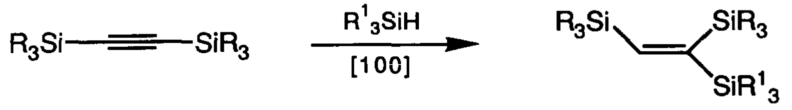
C. Hydrosilation of Acetylenes

The hydrosilation of 1,7-diynes in the presence of a nickel catalyst gives hydrosilation-oxidation. (Eqn. 67)



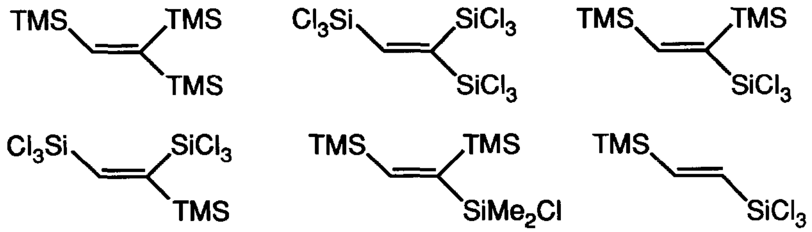
(67)

Tris(silyl)ethenes were prepared by the hydrosilation of bis(silyl)acetylenes. (Eqn. 68) These materials were studied extensively by NMR. Some of the chloro derivatives were reduced to the silanes.

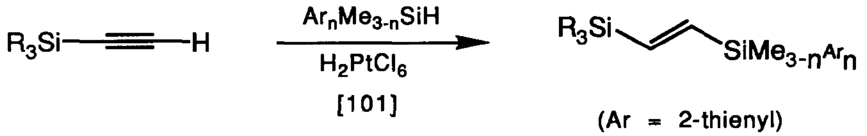


(68)

Prepared were:



Various ethynylsilanes were subjected to hydrosilation by thienylmethylsilanes. (Eqn. 69)



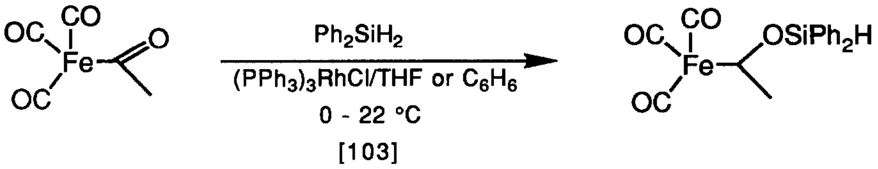
(69)

(Ar = 2-thienyl)

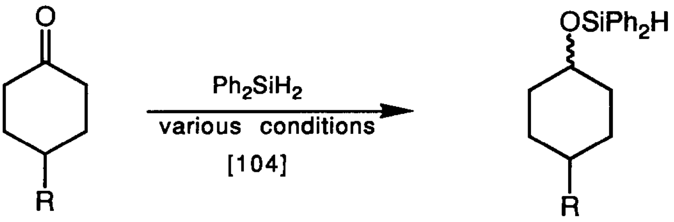
D. Hydrosilation - Reductions

Benzaldehyde was reacted with triethylsilane in the presence of a ruthenium catalyst. (Eqn. 70) Dihydrosilanes were used to reduce acyl iron complexes (Eqn. 71) and 4- and 2-substituted cyclohexanones (Eqn. 72).

$$PhCHO + Et_3SiH \xrightarrow[\substack{C_6D_6/h\nu \\ [102]}]{\substack{Ru(CO)_3(PPh_3)_2 \\ \text{or } Ru(CO)_4(PPh_3)}} PhCH_2OSiEt_3 \qquad (70)$$



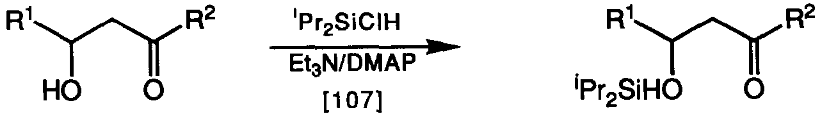
(71)



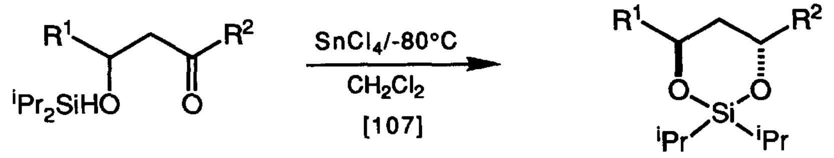
(72)

A total of 58 different prochiral ketones were reacted with diphenylsilane in the presence of $[Rh(COD)Cl]_2$ and various chiral ligands. The highest ee value for the resulting alcohols found was 88.5 percent. [105] A further report was submitted on this topic by the same researchers in which 21 different 2-(2-pyridyl)oxazolines as ligands were investigated. [106]

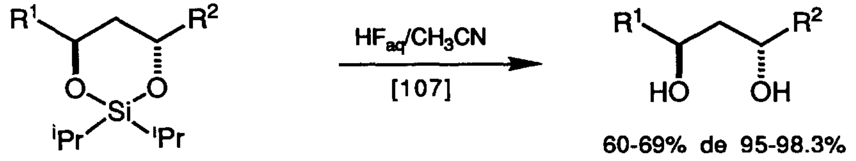
Anti-selective 1,3-diols can be prepared by a silylation-hydrosilation-desilylation sequence on β-hydroxy ketones with diisopropylsilane. (Eqns. 73 - 75)



(73)



(74)



(75)

E. Other Studies

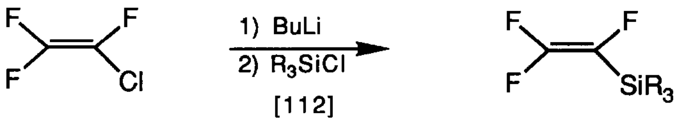
The $(Ph_3)_3RhCl$ catalyzed hydrosilation of olefins, acetylenes and carbonyls with 1,2-bis(dimethylsilyl)ethane gives only the mono adducts. [108] The mechanistic aspects of the hydrosilation of styrene with triethylsilane were reported. [109] The rates and α/β ratio of the hydrosilation of some acrylates and methacrylates were reported. [110] The disproportionation of methyldichlorosilane with Speier's catalyst was reported. [111]

VII. VINYLSILANES

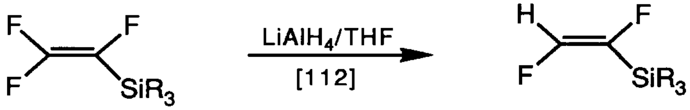
A. Preparation

The reaction of vinylmetallic reagents with chlorosilanes provided some interesting vinylsilanes. For example, chlorotrifluoroethylene suffers metal-halogen exchange with n-butyllithium and the resulting vinyllithium reagent can be silylated.

(Eqn. 76) These vinylsilanes can be reduced and metalated to lead to other derivatives. (Eqns. 77 - 79) Coupling reactions were also reported. (Eqns. 80-81)



(76)



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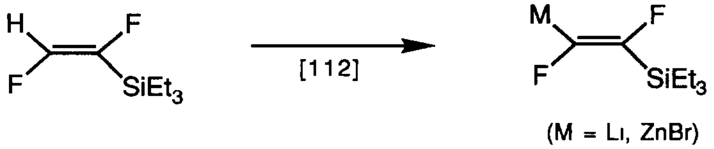
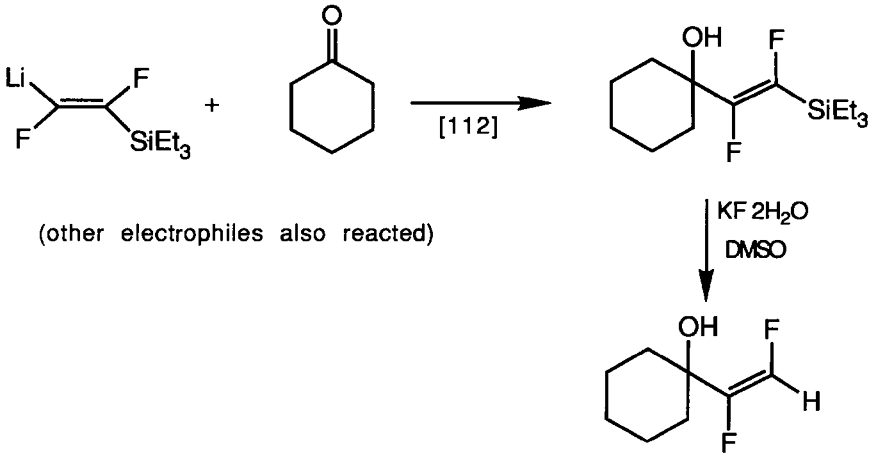


(78)



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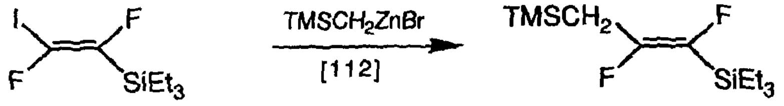
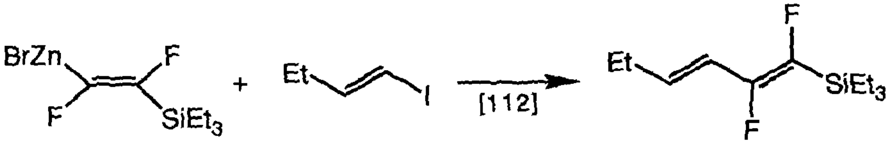
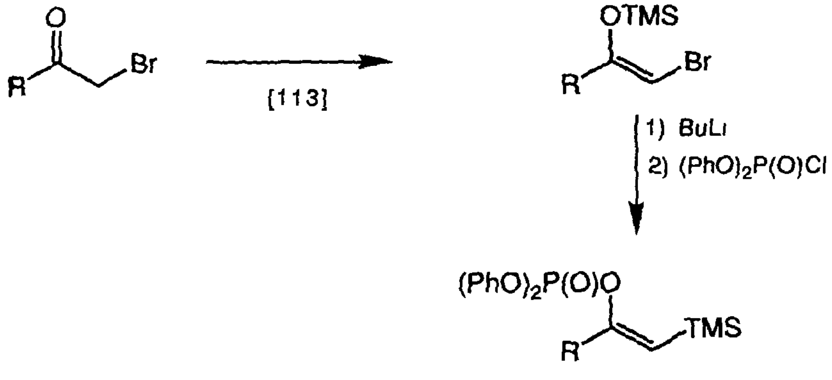


(80)



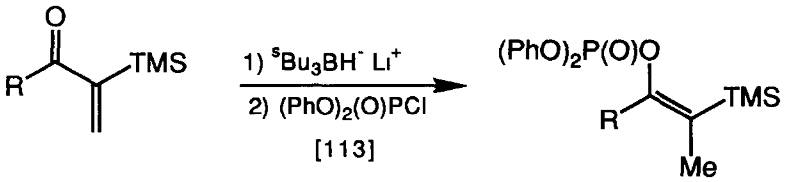
(81)

Vinylsilane phosphonates were prepared as shown in Eqn. 82 starting from α-bromo ketones. Other routes to these systems involve deprotonation-phosphorylation of β-ketosilanes (Eqn. 83) or conjugated addition-enolate trapping of *α-silyl-α,β-unsaturated ketones* (Eqn. 84).



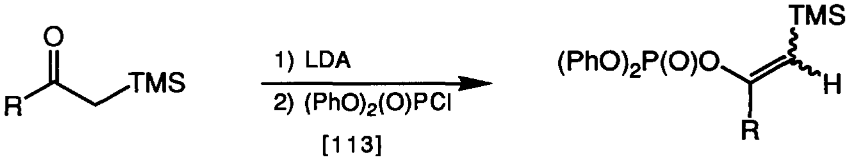
(82)

4 examples: 64 - 87 %



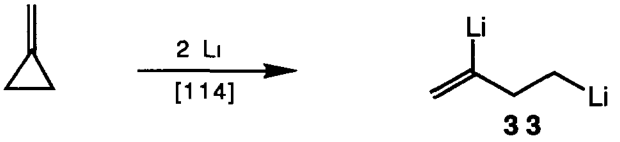
R = Me (8%), Ph (67%)

(83)



(84)

Methylenecyclopropane reacts with lithium metal to give dilithium system **33**. The more reactive Li-C bond is that of the sp^3 carbon. (Eqns. 85 - 87)



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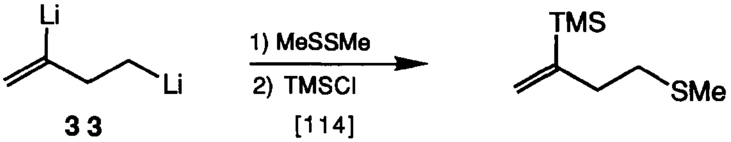

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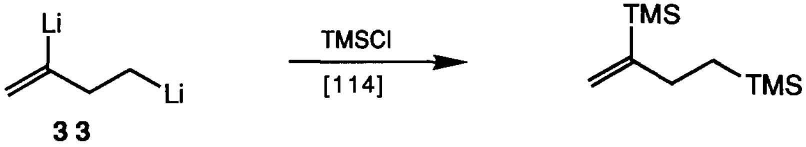
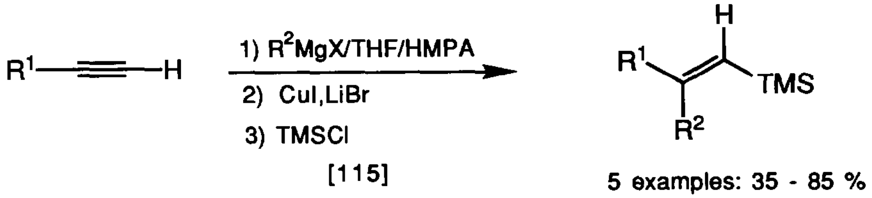
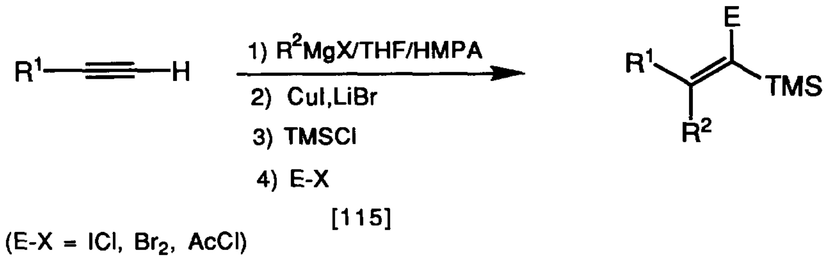


(87)

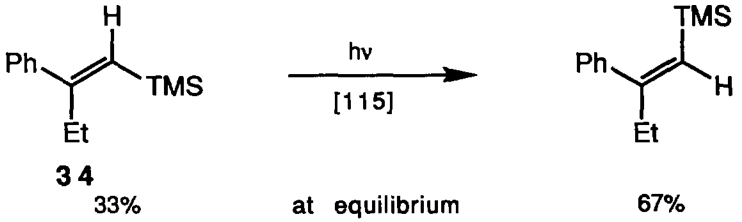
The addition of organomagnesium halides to acetylenes followed by trimethylsilylation provides a regio- and stereoselective synthesis of vinylsilanes. (Eqns. 88 and 89) The photochemical isomerization of **34** was reported in the same paper. (Eqn. 90)



(88)



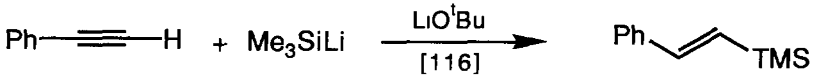
(89)



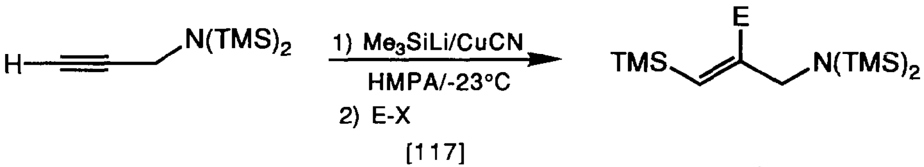
(90)

The addition of silylmetallic reagents to triple bonds was used to prepare vinylsilanes. The reaction of trimethylsilyllithium to phenylacetylene in the presence of lithium tert-butoxide gives (E) β-trimethylsilylstyrene. (Eqn. 91) Protected propargyl-amine reacts with trimethylsilyllithium and then electrophiles to give 1-

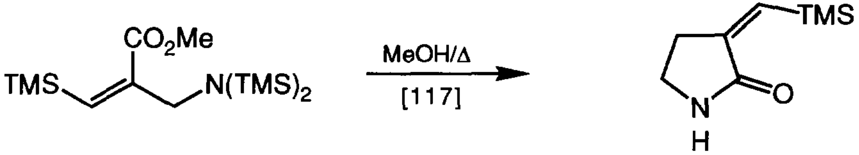
trimethylsilyl-2-substituted allyl amines. (Eqn. 92) The carbomethoxy derivative was converted to the corresponding silylmethylidene lactam. (Eqn. 93)



(91)



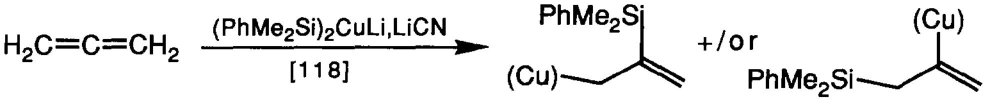
(92)

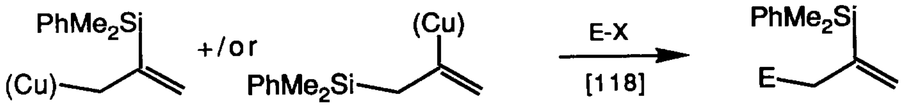


(93)

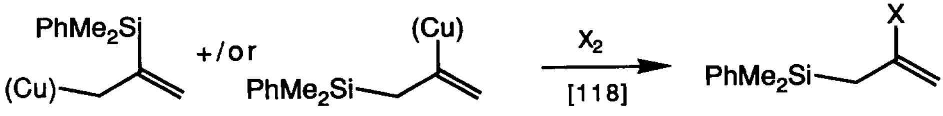
Lithium bis(phenyldimethylsilyl)cuprate was added to allene followed by the addition of an electrophile to give either substituted vinylsilanes or allylsilanes. (Eqns. 94 - 96)

(94)



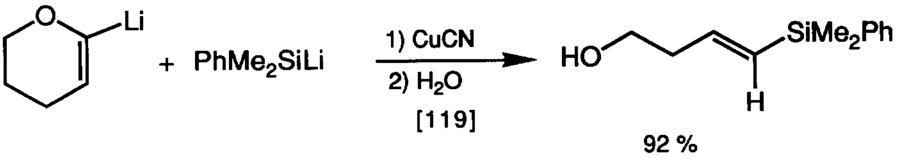

(95)

(E-X = NH_4Cl, MeI, AcCl, ethylene oxide, cyclohexenone, Cl_2)

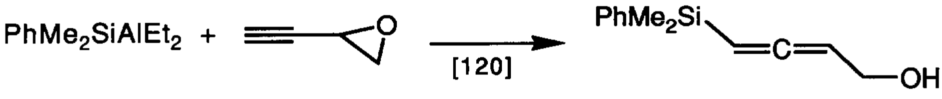

(96)

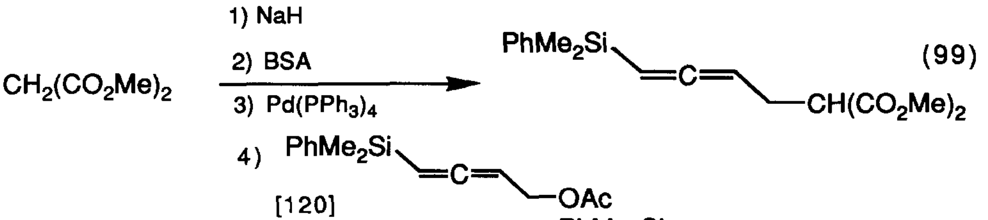
(X_2 = Br_2 or I_2)

Phenyldimethylsilyllithium was reacted with α-lithiated cyclic enol ethers to give ω-hydroxyvinylsilanes. (Eqn. 97)

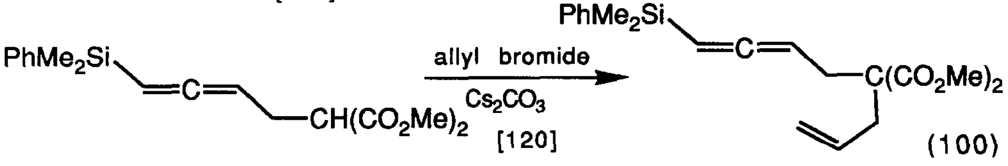

(97)

Phenyldimethylsilyldiethylaluminum was reacted with 3,4-epoxybutyne to give 4-(dimethylphenylsilyl)-2,3-dien-1-ol (Eqn. 98), which was used in alkylations with active carbanions (Eqns. 99 and 100).


(98)

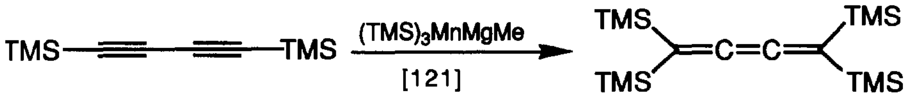


(99)



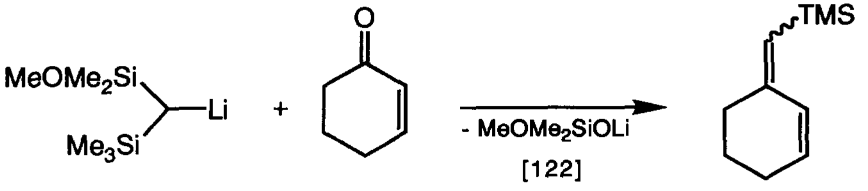
(100)

[Tris(trimethylsilyl)manganese]methylmagnesium was reacted with bis(trimethyl-silyl)-1,3-butadiyne to give 1,1,4,4-tetrakis(trimethylsilyl)-1,2,3-butatriene. (Eqn. 101) An x-ray structure determination showed the internal C=C to be 127.6 nm and the terminal C=C's to be 131.9 nm.



(101)

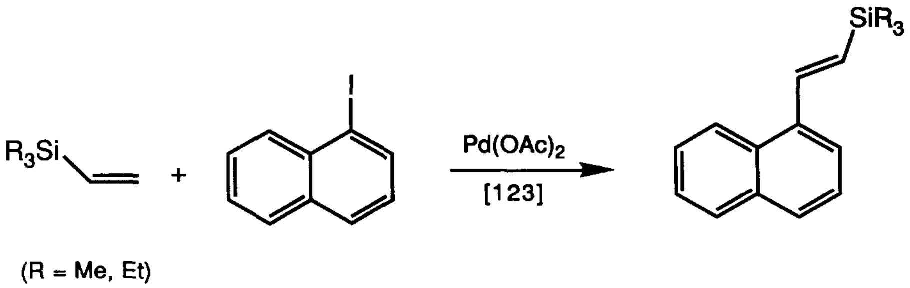
The reaction of (methoxydimethylsilyl)trimethylsilylmethane with tert-butyllithium gives lithium reagent **35**. This reacts with ketones and aldehydes to give exclusively vinyltrimethylsilanes with loss of the methoxydimethylsilyl group. (Eqn. 102)



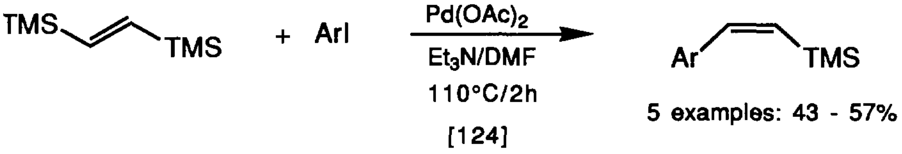
35

(102)

A variety of coupling reactions were employed in the preparation of vinylsilanes. Vinyltrimethyl(or triethyl)silanes were coupled with aryl iodides to give β-aryl vinylsilanes. (103) A similar reaction leading to the same class of product is seen with (E) 1,2-bis(trimethylsilyl)ethylene and aryl iodides. (Eqn. 104)

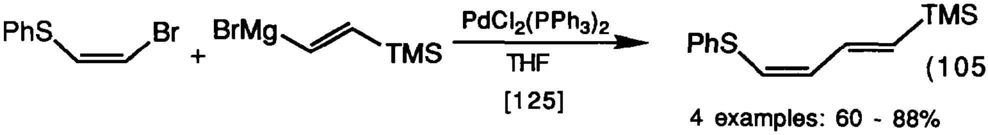


(103)

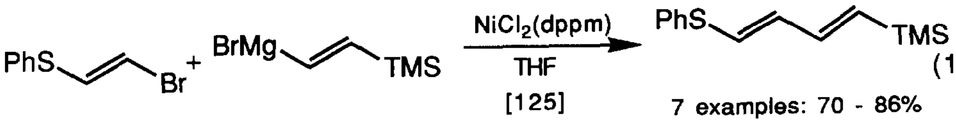


(104)

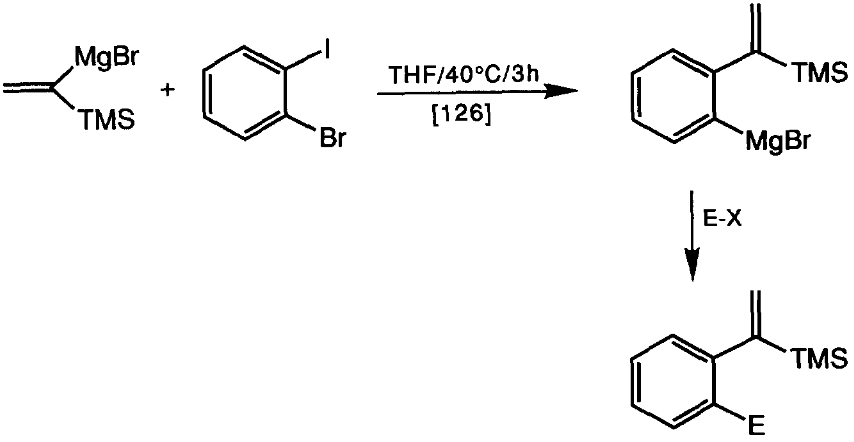
The cross-coupling of silicon containing vinylmetallic reagents leads to vinylsilanes as seen from the examples shown in Eqns. 105 - 111.



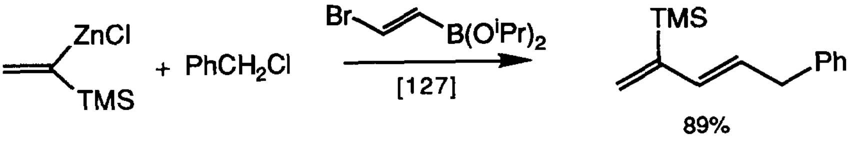
(105)



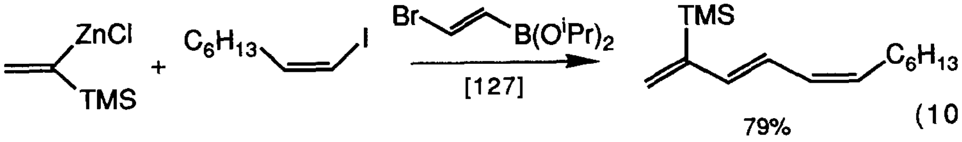
(106)



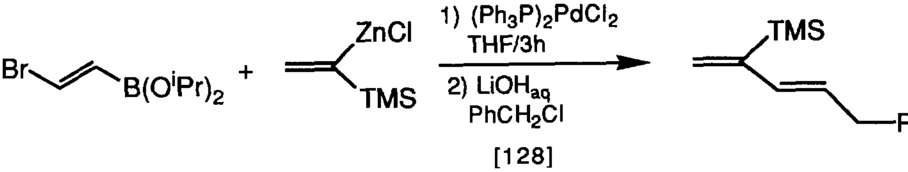
(107)



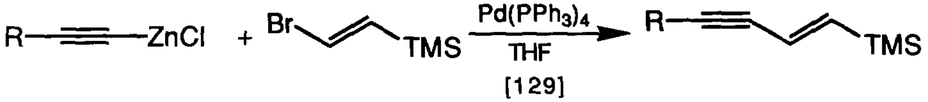
(108)



(109)

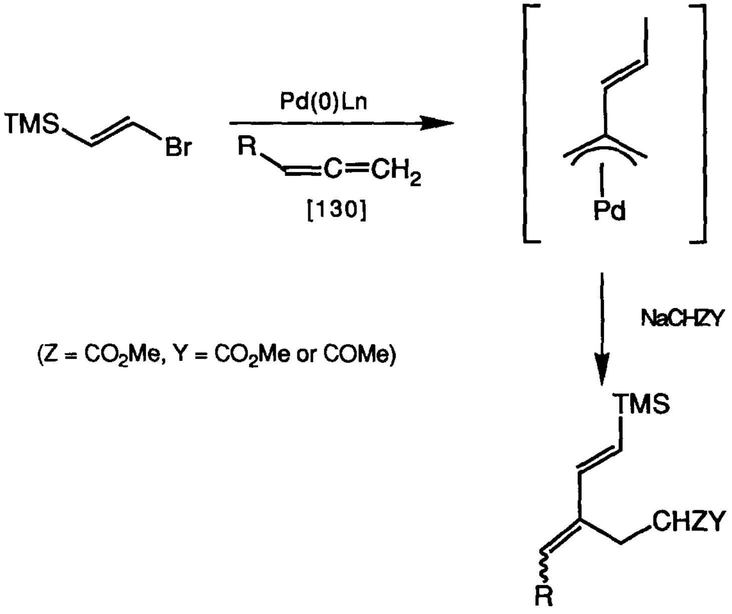


(110)



(111)

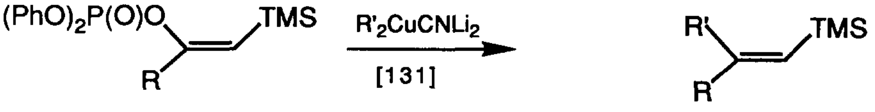
Trimethylsilylated 1,3-dienes were prepared by carbopalladation of allenes followed by treatment of the π-allyl palladium complex with a stabilized carbanion. (Eqn. 112)



(112)

(Z = CO_2Me, Y = CO_2Me or COMe)

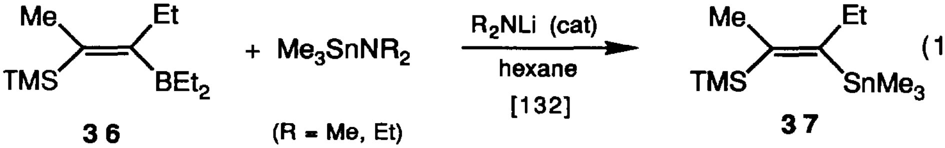
The addition of organocuprates to vinylsilane phosphates (see Eqns. 82 - 84 for the preparation of these materials) gives vinylsilanes in a stereospecific manner. (Eqn. 113)



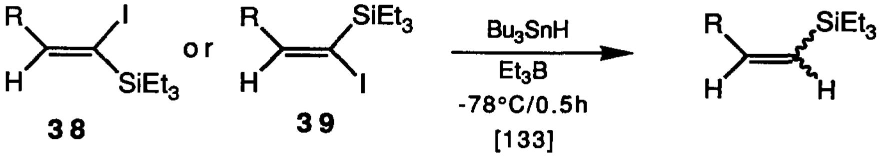
(113)

22 examples: trace - 90%

Vinylsilane **36** was reacted with aminostannanes to give **37**. (Eqn. 114) Reduction of **38** or **39** gives a Z:E mixture of vinylsilanes. (Eqn. 115)

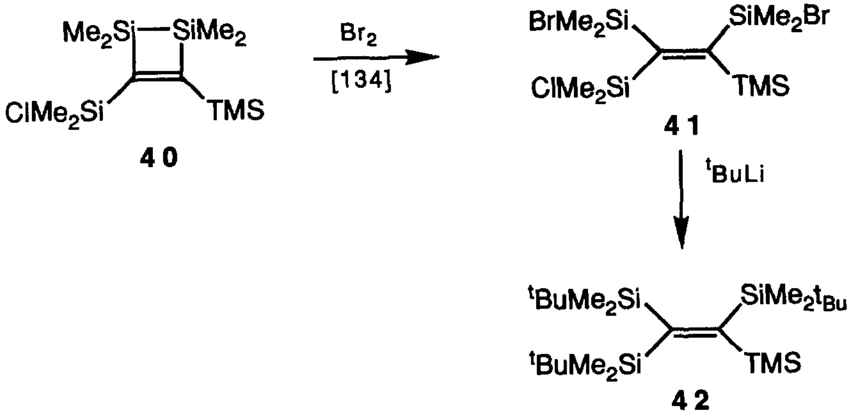


(114)



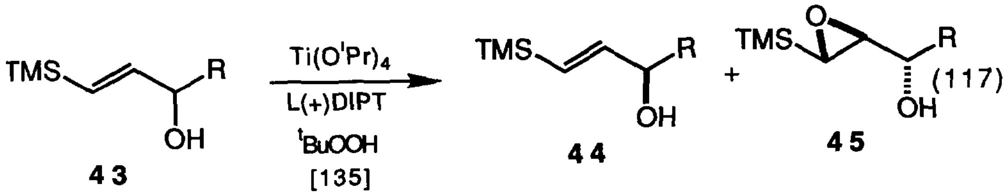
(115)

Vinylsilane **40** was converted *via* known chemistry to vinylsilanes **41** and **42**. (Eqn. 116)



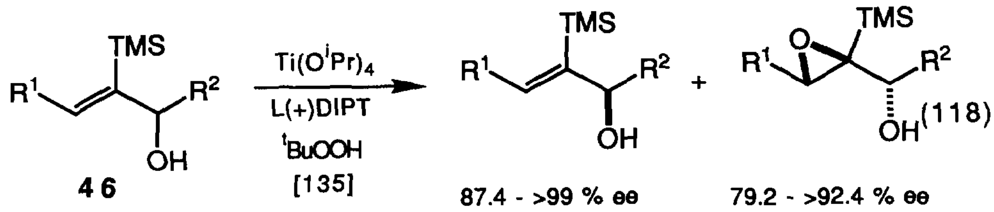
(116)

The Sharpless kinetic resolution technique was applied to racemic **43** to give vinylsilanes **44** and epoxysilanes **45** in good to excellent ee. (Eqn. 117) The 2-trimethylsilyl derivatives **46** were also looked at with somewhat less impressive results, however. (Eqn. 118)



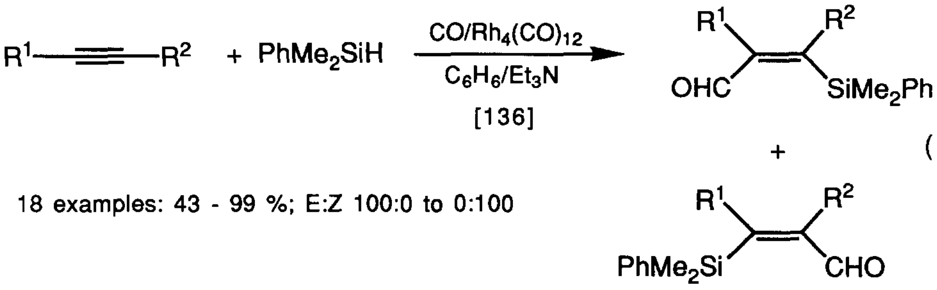
(117)

9 examples: ee usually >99% for each product



(118)

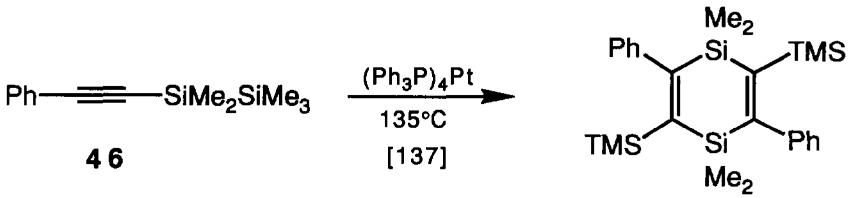
Acetylenes and acetylenic silanes provided the starting materials for vinylsilanes. The silyl formylation of acetylenes gives β-silyl acroleins. (Eqn. 119)



(119)

18 examples: 43 - 99 %; E:Z 100:0 to 0:100

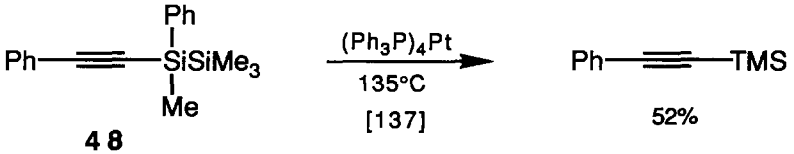
Treatment of phenylethynylpentamethyldisilane with platinum(0) gives **47**. (Eqn. 120) On the other hand the phenyl derivative **48** eliminates phenyltrimethylsilane. (Eqn. 121)



46

47 36%

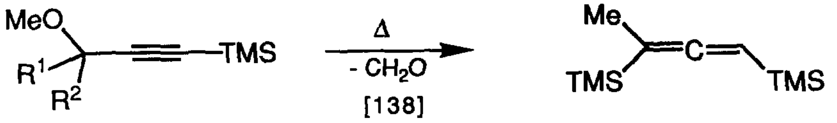
(120)



48

(121)

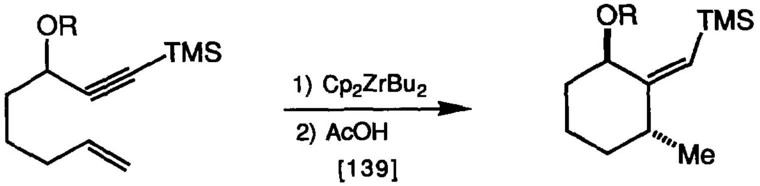
Retro cleavage of 1-trimethylsilylpropargyl methyl ethers produces, *via* loss of formaldehyde, allenylsilanes. (Eqn. 122)



(122)

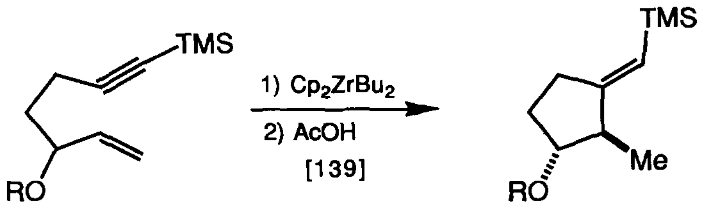
6 examples: 79 - 99 % by GC and 50 - 83 % isolated

Suitably unsaturated ethynylsilanes are cyclized to vinylsilanes with zirconium complexes. (Eqns. 123 - 125)



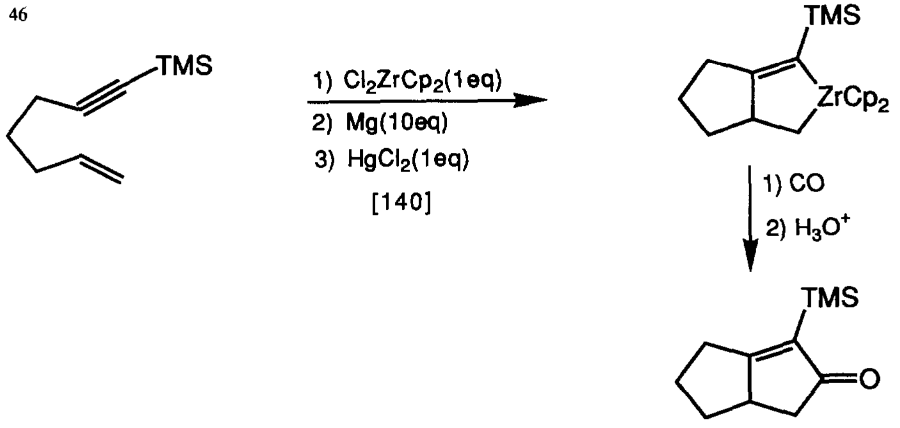
(123)

R = ${}^tBuMe_2Si$ 79%
R = H 70%



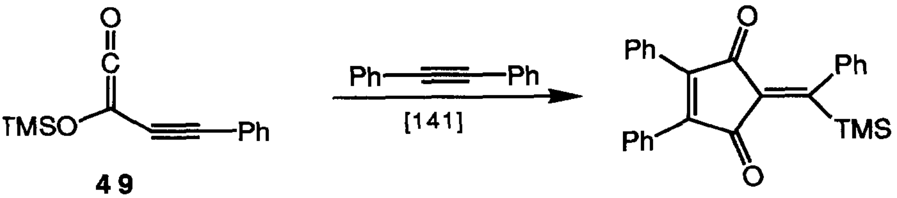
(124)

R = ${}^tBuMe_2Si$ 78%
R = H 81%



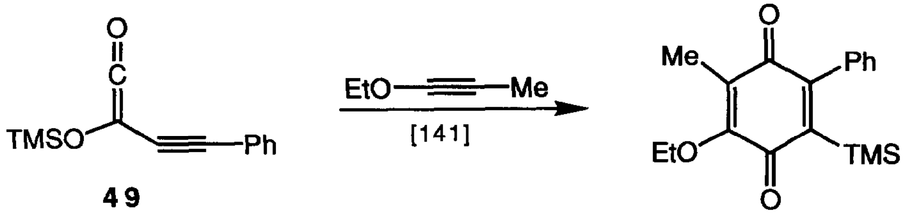
(125)

Trimethylsiloxyethynyl ketenes **49** react with acetylenes to give silylated quinones. (Eqns. 126 and 127)



49

(126)

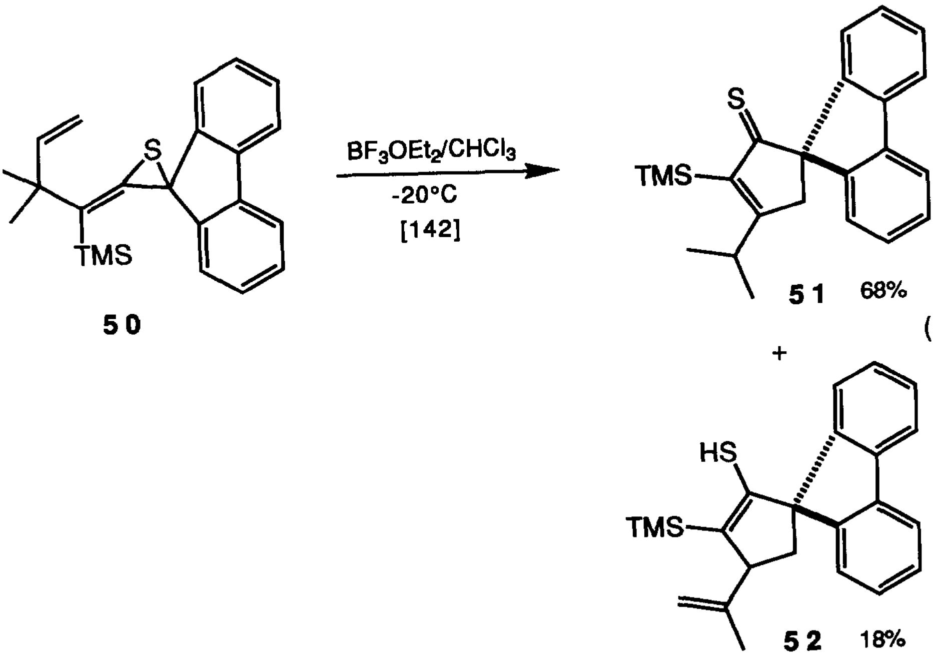


49

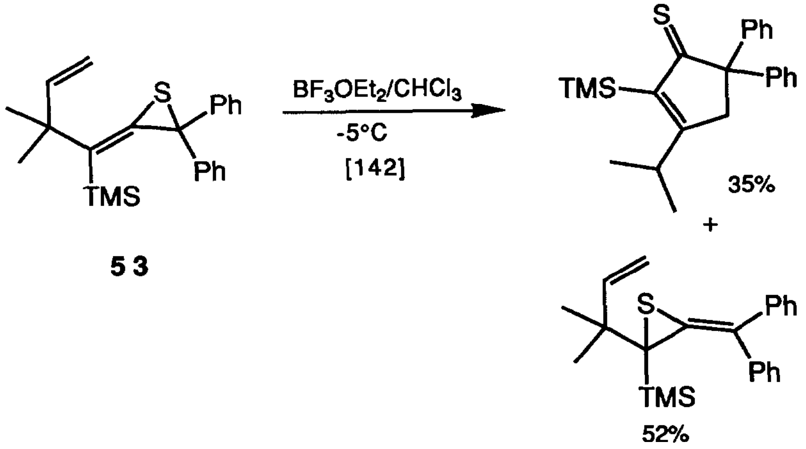
45%

(127)

Vinylsilane **50** was reacted with boron fluoride etherate to give **51** and **52**. (Eqn. 128) A similar reaction occurred with **53**. (Eqn. 129)


50
BF3OEt2/CHCl3
-20°C
[142]
S
TMS
51 68%
+
HS
52 18%

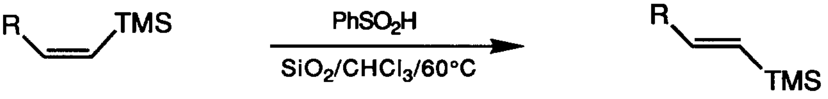
(128)


53
BF3OEt2/CHCl3
-5°C
[142]
S
Ph
TMS
35%
+
52%

(129)

B. Reactions

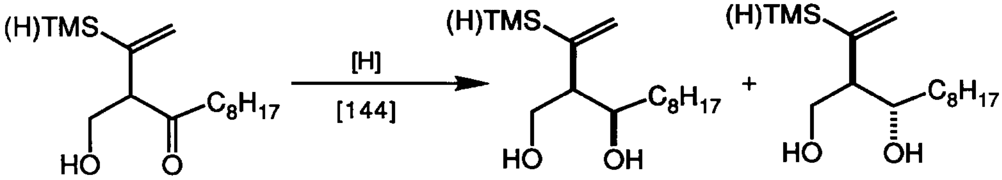
Two (Z) vinylsilanes were isomerized to the (E) isomers with a weak acid in the presence of silica gel, which greatly reduced the protodesilylation process. (Eqn. 130)



(130)

R = $PhCH_2$ 86% E:Z = 93:7
R = $PhCH_2CH_2$ 97% E:Z = 93:7

The vinylsilane **54** showed greatly enhanced stereoselectivity in reduction of the carbonyl group compared to the protonated derivative. (Eqn. 131)

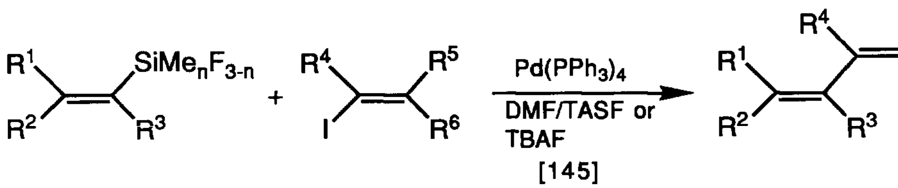


54

(131)

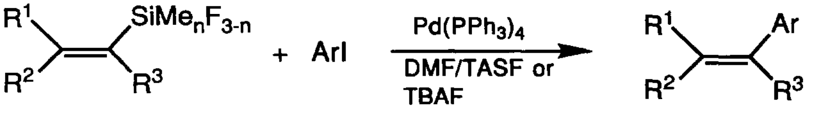
$LiEt_3BH$	>99% (66%)	<1% (34%)
DIBAL	81% (37%)	19% (63%)

Alkenylfluorosilanes were used to couple with vinyl iodides to give 1,3-dienes. (Eqn. 132) These vinylsilanes also were coupled with aryl iodides. (Eqn. 133) These reactions are better with the fluorine ligand on silicon as opposed to the simple trimethylsilyl group.



(132)

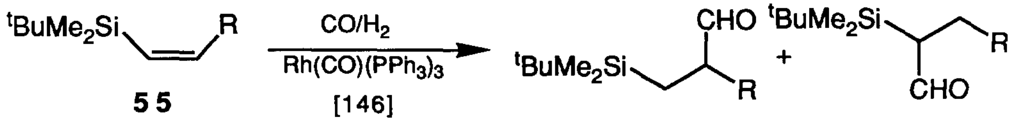
7 examples: 55 - 89%



(133)

8 examples: 43 - 85%

The hydroformylation of (Z) vinylsilanes **55** gives predominantly the β-formylation product. (Eqn. 134) The (E) vinylsilane gives the enol silyl ether upon hydroformylation. (Eqn. 135)

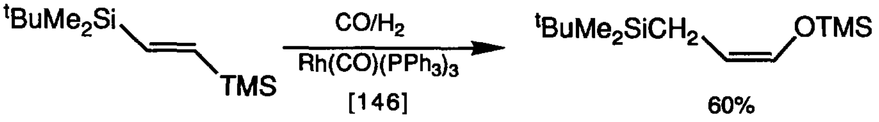


R = Bu, CH_2OMe, CH_2OTMS, CH(OMe)Me, CH(OH)Me, CH(OH)Pr

>96% <4%

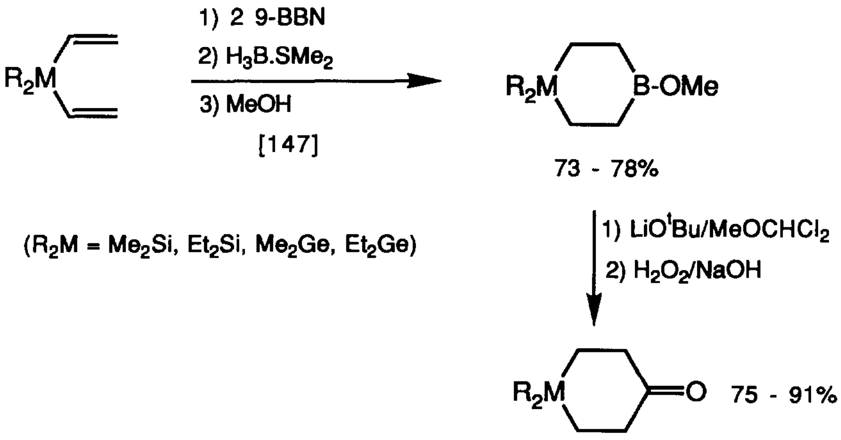
(134)

6 examples: 17 - 80%



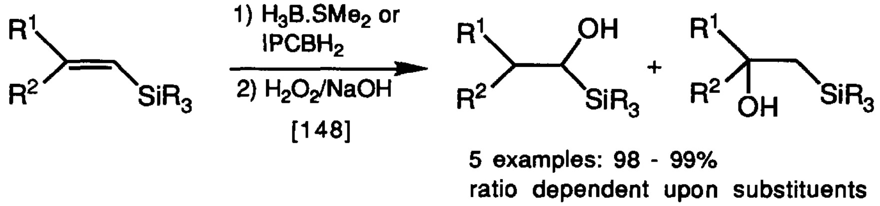
(135)

Divinylsilanes and germanes were cleverly converted to 4-sila- and 4-germacyclohexanones by first treating with 9-borabicyclo[3.3.1]nonane (9-BBN) to ensure clean β-hydroboration, then transborylation with borane methylsulfide complex, methanolation and carbonyl insertion as shown. (Eqn. 135A)



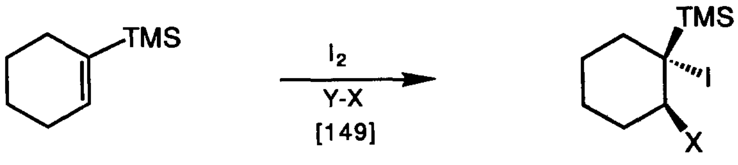
(135A)

A detailed study of the hydroboration of β-substituted vinylsilanes by both borane methyl sulfide complex and isopinocampheylborane was reported. (Eqn. 136) For the optically active isopinocampheylborane hydroboration ee's up to 40% were observed.



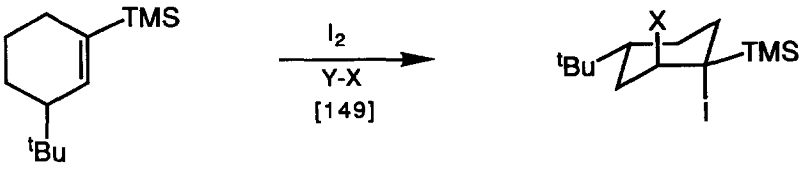
(136)

Vinylsilanes were treated with iodine in the presence of a nucleophile to give α-iodo-β-substituted silanes. (Eqns. 137 - 139) Vinylsilane **56** was reacted with iodine chloride to give vinyl iodide **57**. (Eqn. 140)

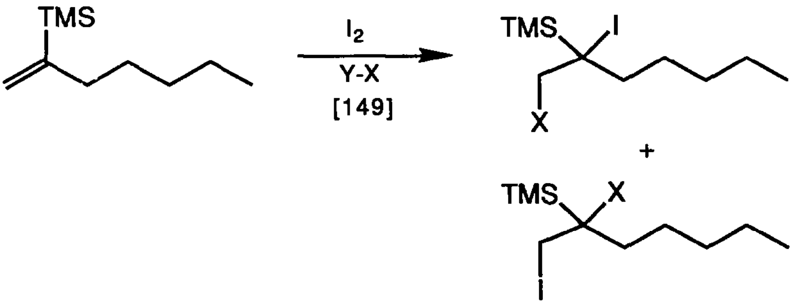


(137)

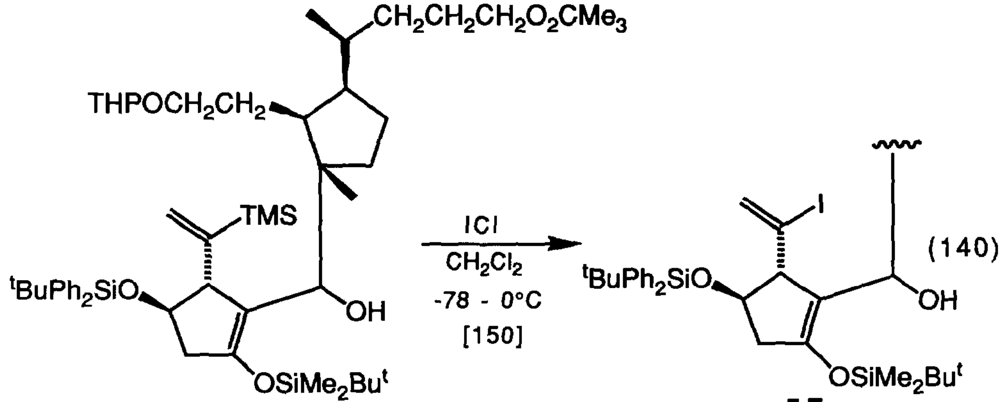
(Y-X = MeOH, LiN_3, LiSCN, LiOAc)



(138)



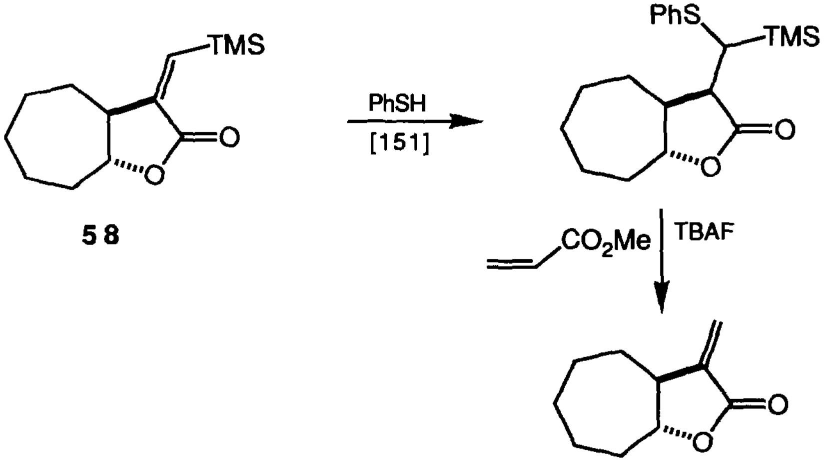
(139)



56 **57**

(140)

α-Trimethylsilylmethylene lactone **58** was converted to α-methylene lactone **59** as shown. (Eqn. 141)

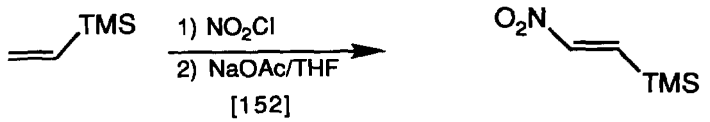


58

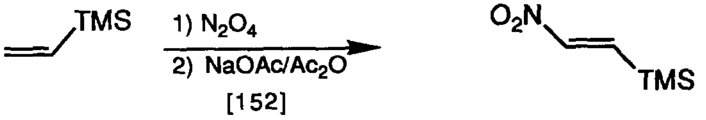
59

(141)

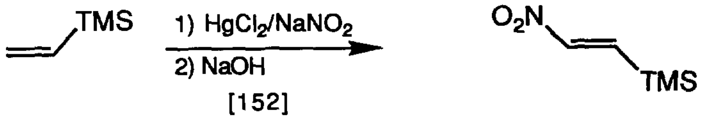
Three routes to (E) 2-nitroethylenyltrimethylsilanes were investigated. These were the addition of NO_2Cl to vinyltrimethylsilane followed by treatment with sodium acetate (Eqn. 142), the reaction of vinyltrimethylsilane with N_2O_4 and then sodium acetate/acetic anhydride (Eqn. 143) and nitromercuration of vinyltrimethylsilane followed by treatment with base (Eqn. 144).



(142)



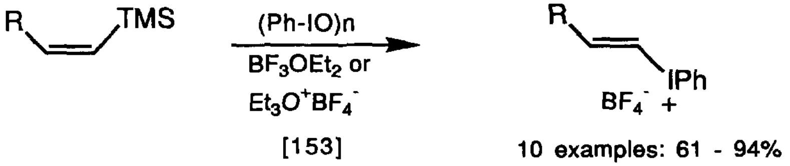
(143)



(144)

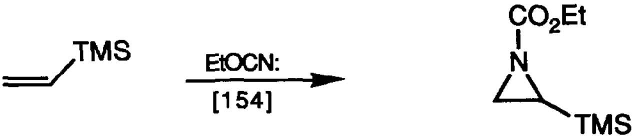
(E)

Vinylsilanes react with iodosylbenzene in the presence of a Lewis acid catalyst to give vinylphenyl iodonium tetrafluoroborates. (Eqn. 145) The (Z) isomers do not react under these conditions.



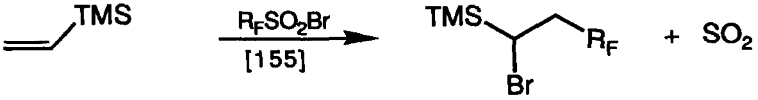
(145)

Ethoxycarbonylnitrene was added to vinyltrimethylsilane to give the silylated aziridine. (Eqn. 146)



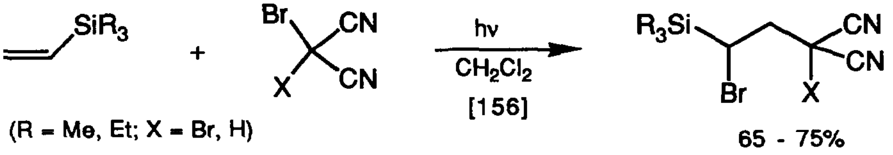
(146)

Perfluoroalkanesulfonyl bromides were added to vinyltrimethylsilane. (Eqn. 147)

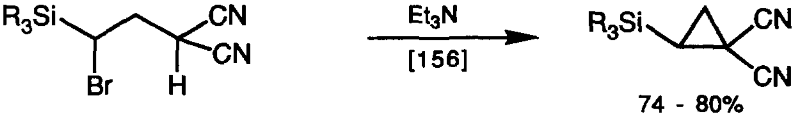


(147)

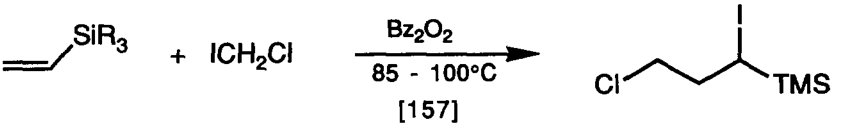
Brominated malonitriles were added to vinylsilanes. (Eqn. 148) Cyclization of the adducts gave silylated dicyanocyclopropanes. (Eqn. 149) Vinyltrimethylsilane was reacted with iodochloromethane to give 1-iodo-3-chloropropyltrimethylsilane. (Eqn. 150)



(148)

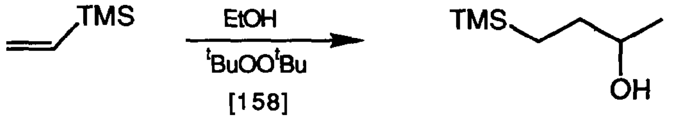


(149)



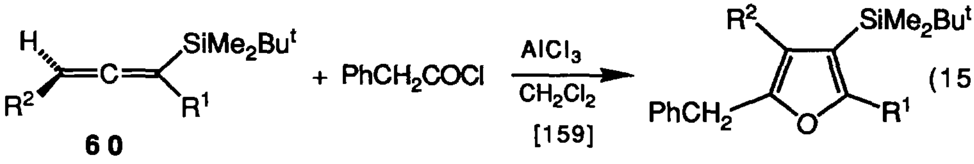
(150)

Free radical addition of the α-C-H bond of ethanol to vinyltrimethylsilane was reported. (Eqn. 151)



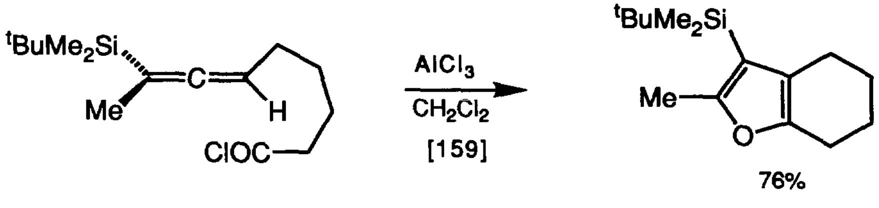
(151)

Allenylsilanes **60** were shown to react with acid chlorides to give silylated furans. (Eqn. 152) The reaction was also carried out in an intramolecular fashion. (Eqn. 153)



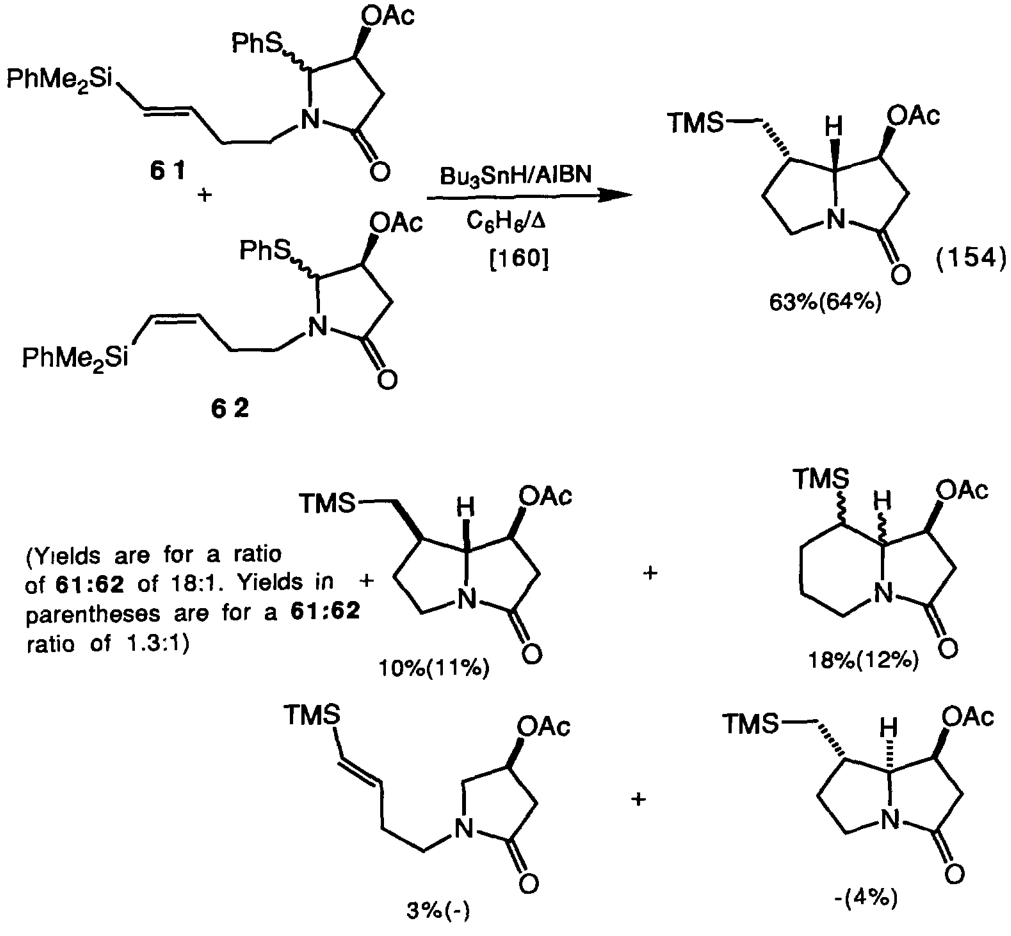
(152)

6 examples: 35 - 79%



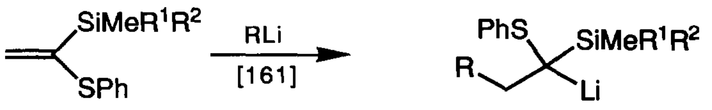
(153)

The intramolecular cyclization of vinylsilanes **61** and **62** was applied towards the synthesis of (+)-heliotridine and (-)-dihydroxyheliotridine. (Eqn. 154)

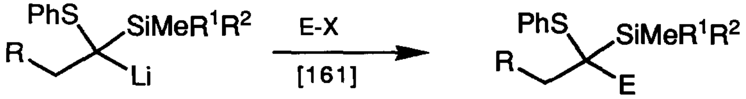


(Yields are for a ratio of **61**:**62** of 18:1. Yields in parentheses are for a **61**:**62** ratio of 1.3:1)

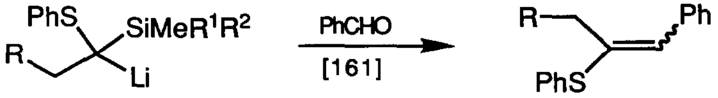
1-Silylethenyl sulfides and sulfoxides suffer Michael addition of lithium reagents to give an intermediate, which can be substituted or used for Peterson olefinations. (Eqns. 155 - 158) Treatment of the sulfide with two equivalents of phenyllithium gives a cyclopropane. (Eqn. 159)



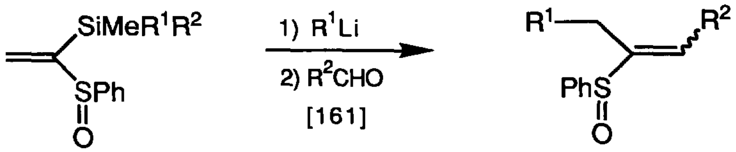
(155)



(156)

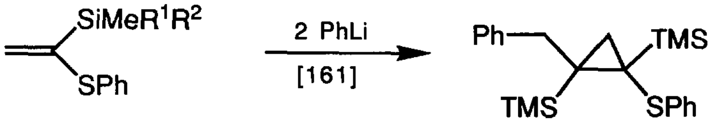


(157)



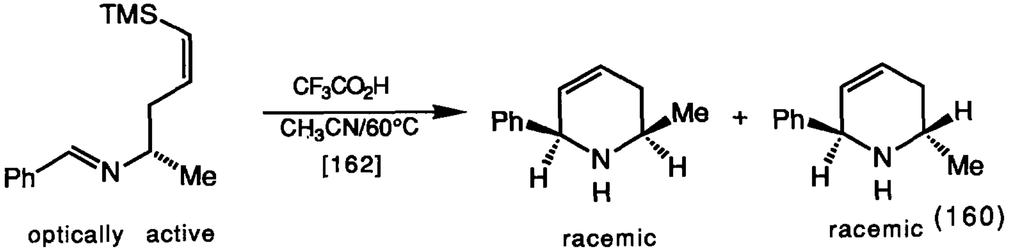
(158)

17 examples: 26 - 92%

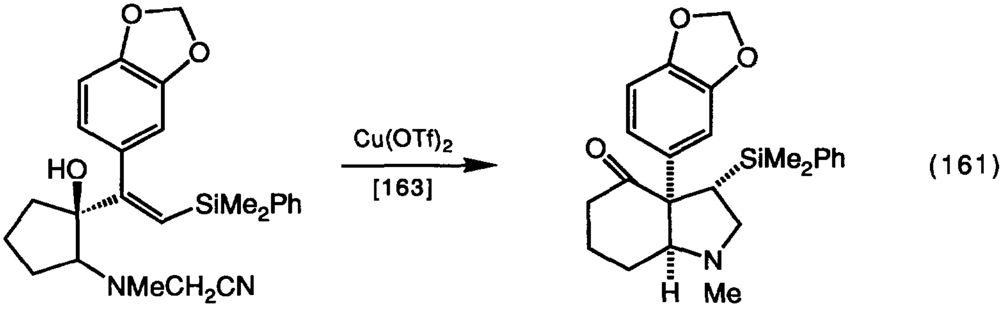


(159)

Intramolecular cyclization of vinylsilanes with iminium ions was used to prepare tetrahydropyridines. (Eqn. 160) Unfortunately, the reaction occurs with racemization.



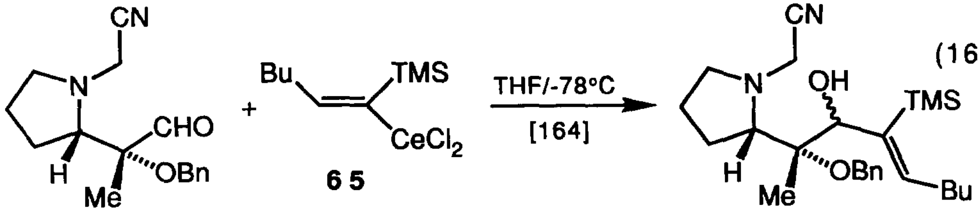
Copper(II) triflate brought about the cyclization-rearrangement of **63** to **64**. (Eqn. 161) Compound **64** was further converted to 6a-epipretazettine.



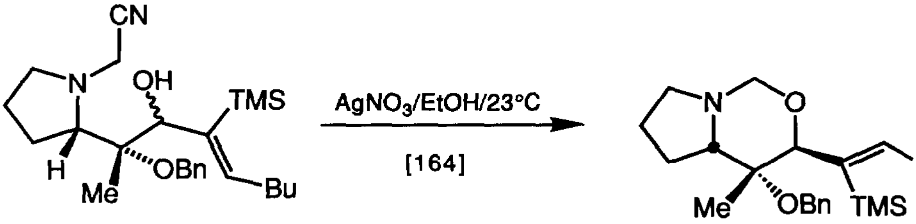
63

64

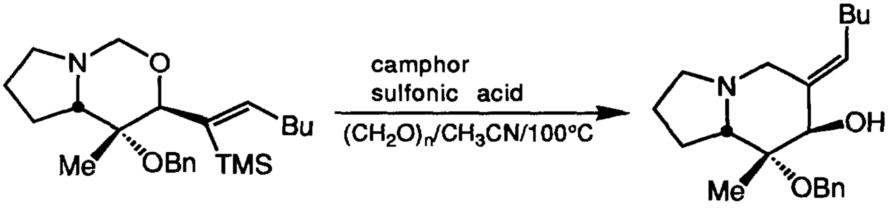
The vinylsilane cerium reagent **65** was used in a key manner in the synthesis of allopumiliotoxin A. (Eqns. 162 - 164)



(162)

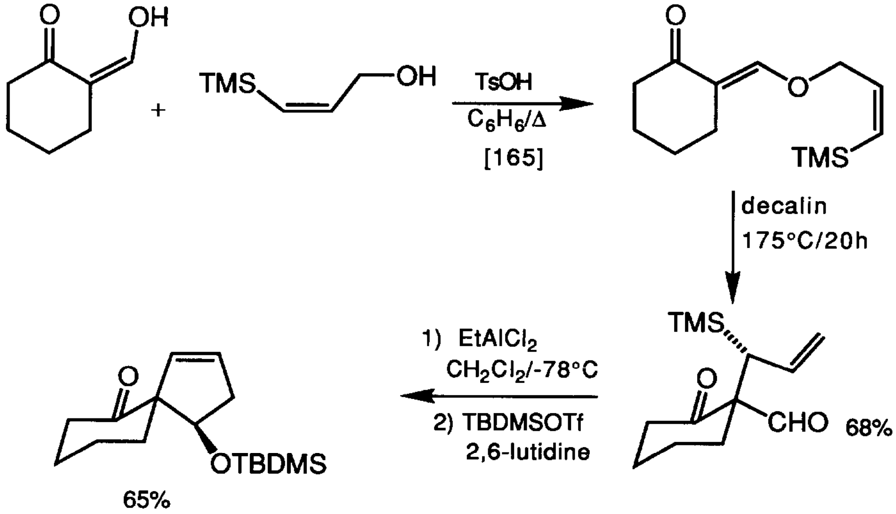


(163)



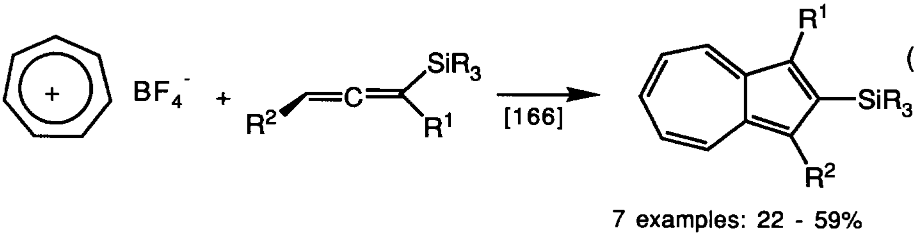
(164)

3-Trimethylsilylpropen-1-ol was used to prepare silylated vinyl allyl ethers for Claisen rearrangements leading to allylsilanes. (Eqn. 165)



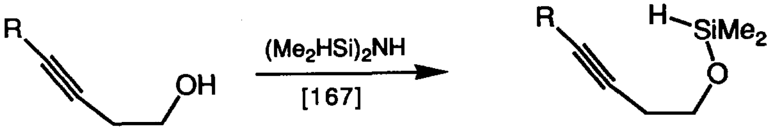
(165)

Tropylium tetrafluoroborate was reacted with allenylsilanes to give azulenes. (Eqn. 166)

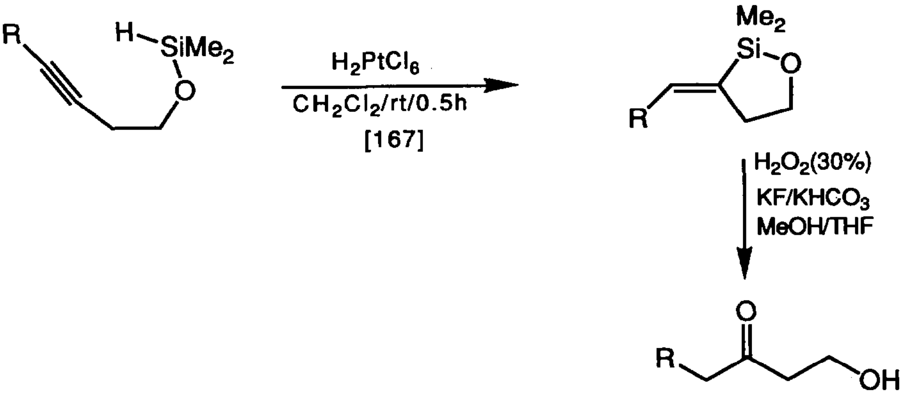


(166)

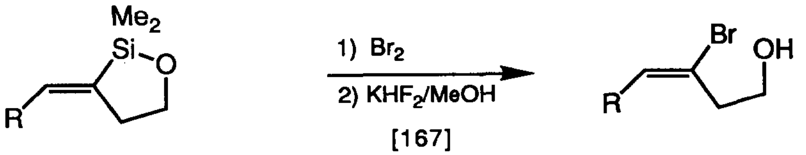
Ethynyl substituted alcohols were silylated and then intramolecularly hydrosilylated to give vinylsilanes, which were oxidized to keto alcohols. (Eqns. 167 and 168) In one case the vinylsilane was brominated. (Eqn. 169)



(167)



(168)



(169)

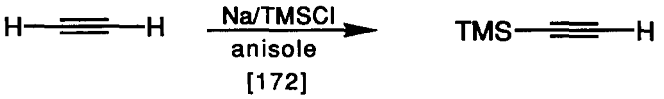
C. Other Studies

The kinetic parameters of the Diels-Alder reaction of certain 1-silacyclopentadienes with maleic anhydride were determined by ^1H NMR. [168] A ^1H, ^{13}C, and ^{29}Si NMR study of α- and β-silyl styrenes was carried out as was a similar study on their dichlorocarbene adducts. [169] A comprehensive theoretical study of the dissociation pathways of vinylsilane was reported. [170] The vibrational-rotational analysis of vinylsilane was reported. [171]

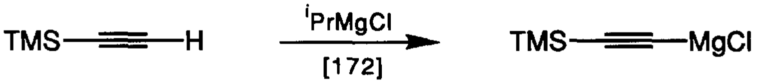
VIII. ETHYNYLSILANES

A. Preparation

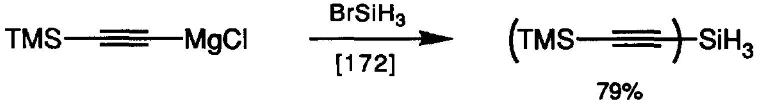
Reaction of acetylene, sodium and trimethylchlorosilane in the presence of anisole gives trimethylsilylacetylene. (Eqn. 170) The Grignard reagent of this was reacted with various halosilanes to give mono- bis-, tris- and tetrakis(trimethylsilylethynyl)silane. (Eqns. 171 - 175)



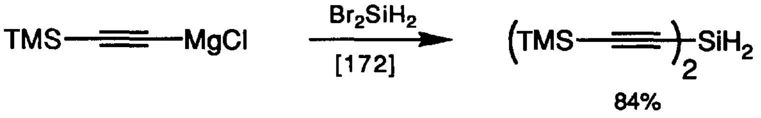
(170)



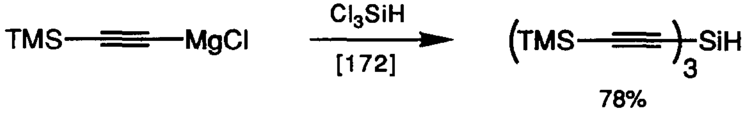
(171)



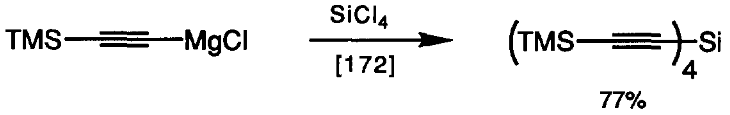
(172)



(173)

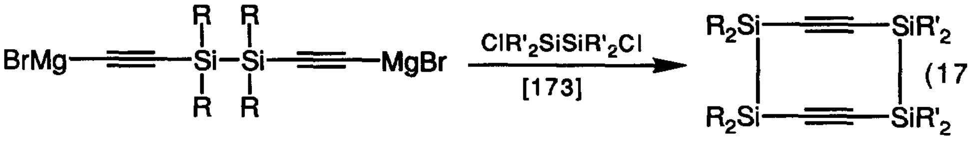


(174)



(175)

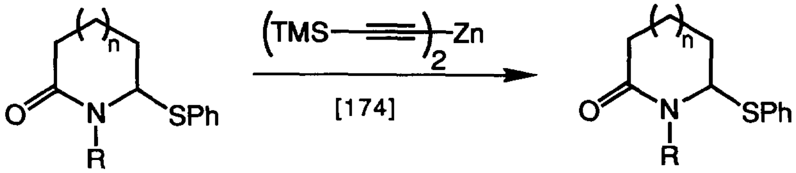
The di-Grignard reagent of 1,2-diethynyldisilanes was reacted with 1,2-dichlorodisilanes to give 1,2,5,6-tetrasilacycloocta-3,7-diynes in good yields. (Eqn. 176)



(176)

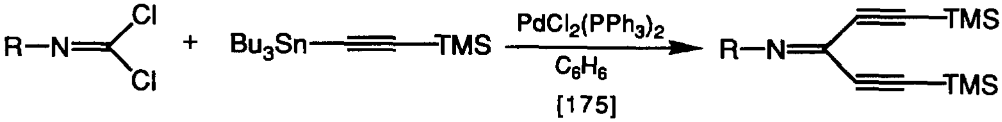
R,R' = Me,Me (67%); Bu,Bu (73%); Me,Bu(62%)

Bis(trimethylsilylethynyl)zinc was shown to react with α-phenylthiolactams to give silylethynylation. (Eqn. 177)

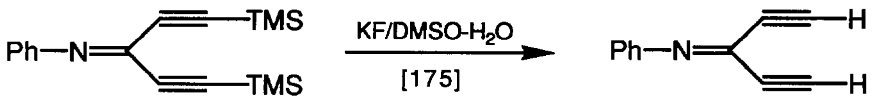


(177)

Trimethylsilyl(tributylstannyl)ethyne was reacted with isonitrile dichlorides to give diethynyl imines and ketones. (Eqns. 178 - 180)



(178)



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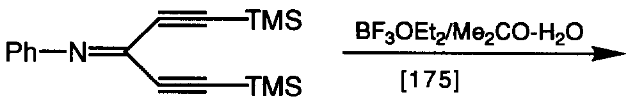
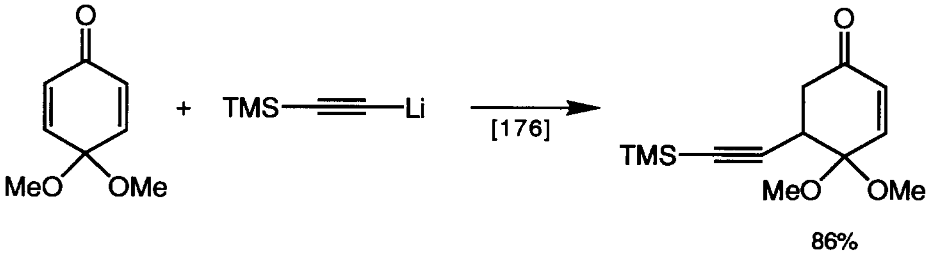


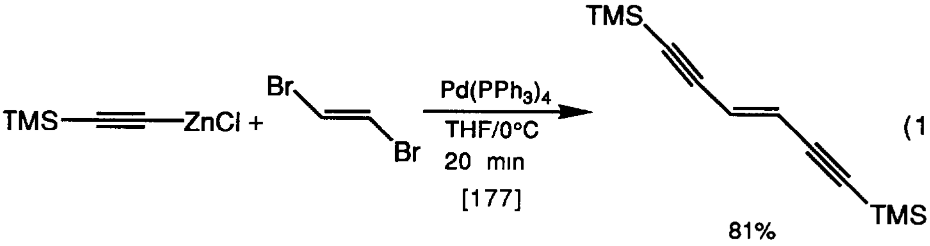
(180)

Trimethylsilylethynyllithium was reacted with quinone monoketals. (Eqn. 181)



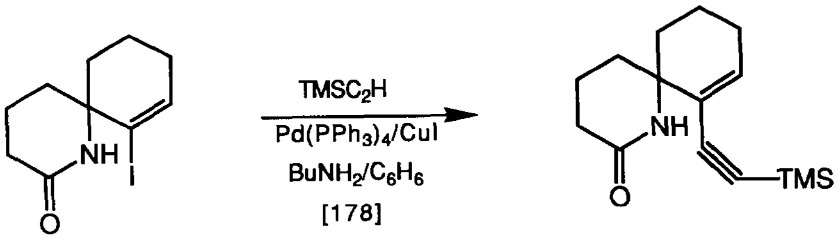
(181)

Trimethylsilylethynylzinc chloride was coupled with 1,2-dibromoethylene. Only the (E) dibromoethylene reacts. (Eqn. 182)



(182)

The coupling of trimethylsilylacetylene with vinyl iodide **66** was used in an approach to histrionicotoxins. (Eqn. 183)



66

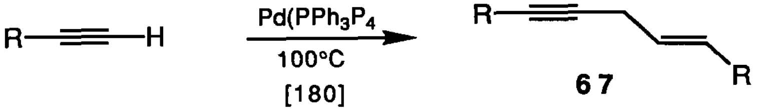
(183)

The coupling of ethynyldisilanes with aryl halides gives the arethynyl disilanes. (Eqn. 184) These were subjected to studies of their absorption and emission spectra.

$$\mathrm{H{-}{\equiv}{-}SiMe_2SiMe_3} \; + \; \mathrm{Y\text{-}Ar\text{-}X} \; \xrightarrow[\mathrm{CuI/Et_2NH}]{\mathrm{(Ph_3P)_2PdCl_2}} \; \mathrm{Y\text{-}Ar{-}{\equiv}{-}SiMe_2SiMe_3} \qquad (184)$$

[179]

Silylacetylenes give 1,4-bis(trimethylsilyl)enyne **67**. (Eqn. 185)

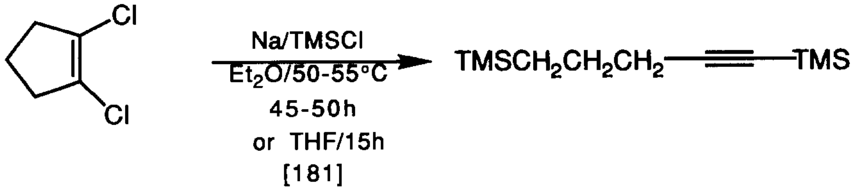


67

(R = $Me_3SiPhMeSi$-, $PhMe_2Si$-, Ph_2MeSi-)

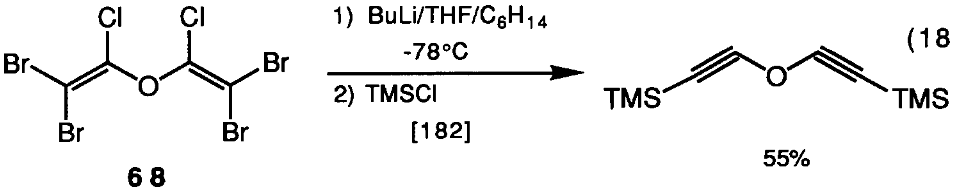
(185)

1,5-Bis(trimethylsilyl)pentyne was prepared from 1,2-dichlorocyclopentene. (Eqn. 186)



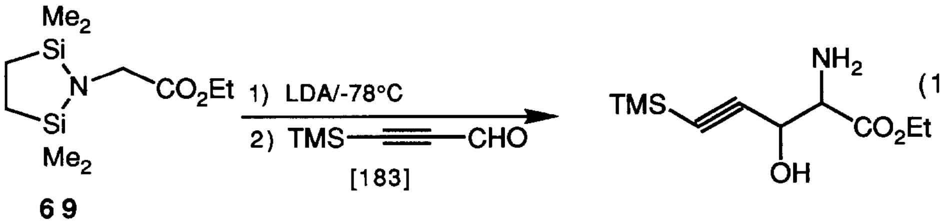
(186)

Bis[(trimethylsilyl)ethynyl]ether was prepared from divinyl ether **68** in good yield. (Eqn. 187)

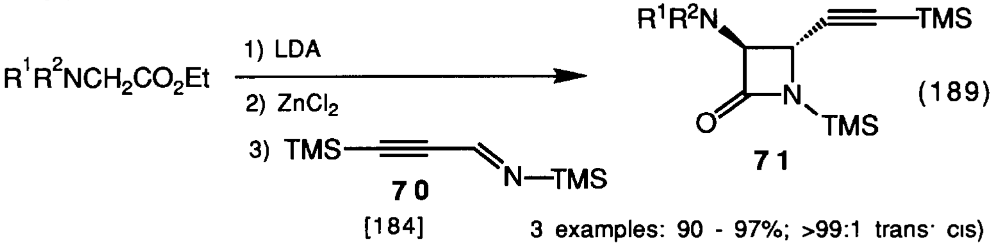


(187)

Trimethylsilylpropional was treated with the enolate of protected glycine to give ethynylsilane **69**. (Eqn. 188) Bis silylated ynimine **70** was used to prepare β-lactams **71**. (Eqn.189)

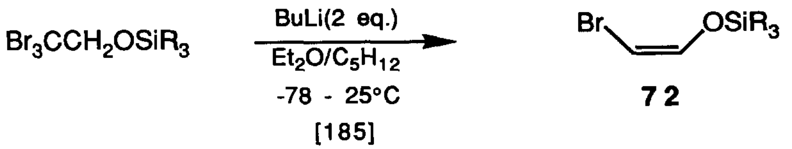


(188)

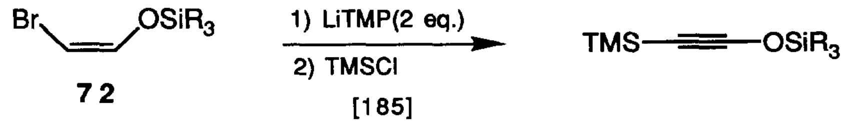


(189)

Treatment of β-bromo enol silyl ethers **72**, available as shown (Eqn. 190), with lithium diisopropylamide and then trimethylchlorosilane gives the bis silylated ynoates (Eqn. 191).

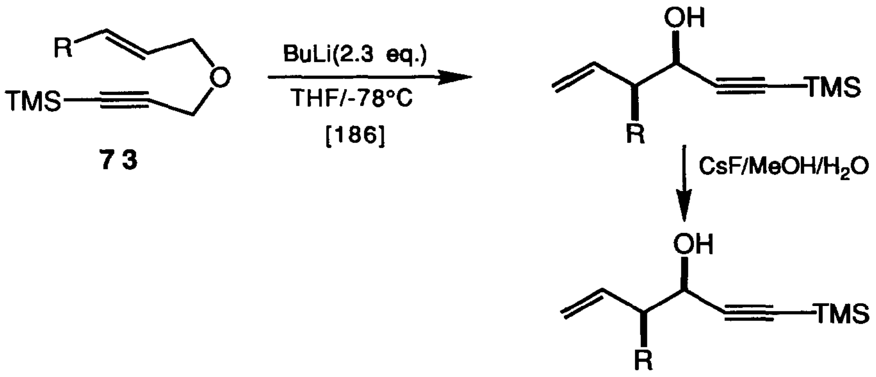


(190)



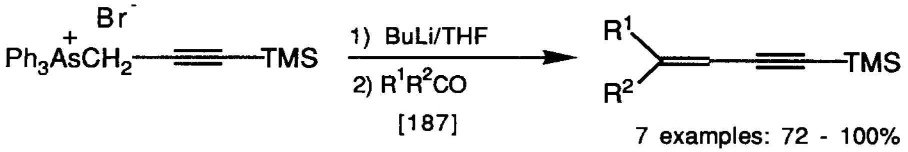
(191)

Whereas other 1-substituted propargyl allyl ethers undergo [1,2] and [1,4] sigmatropic rearrangements upon treatment with butyllithium, the silylated material **73** gives only the [2,3]-Wittig rearrangement. (Eqn. 192) Protodesilylation is readily achieved with fluoride ion.



(192)

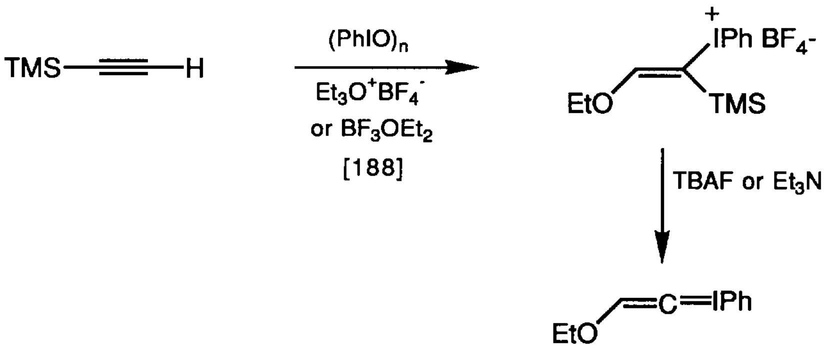
1-Trimethylsilylenynes were prepared from silylated propargyl arsonium ylide and ketones or aldehydes. (Eqn. 193)



(193)

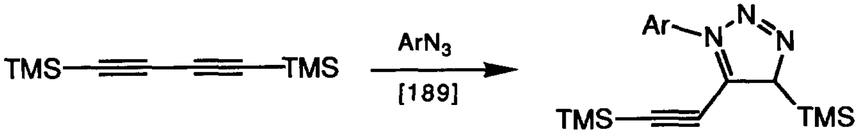
B. Reactions

Ethynyltrimethylsilane was reacted with iodosobenzene to give vinylphenyl iodonium tetrafluoroborates. (Eqn. 194) Desilylation is possible with fluoride ion.

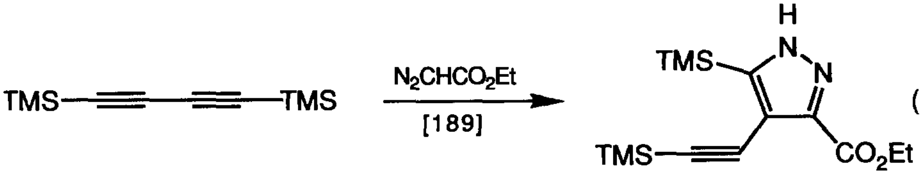


(194)

Bis(trimethylsilyl)butadiyne was reacted with aryl azides to give triazenes. (Eqn. 195) The silylated hexatriyne reacts similarly at the silylated triple bond. (Eqn. 196)

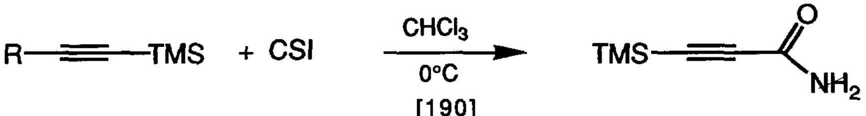


(195)



(196)

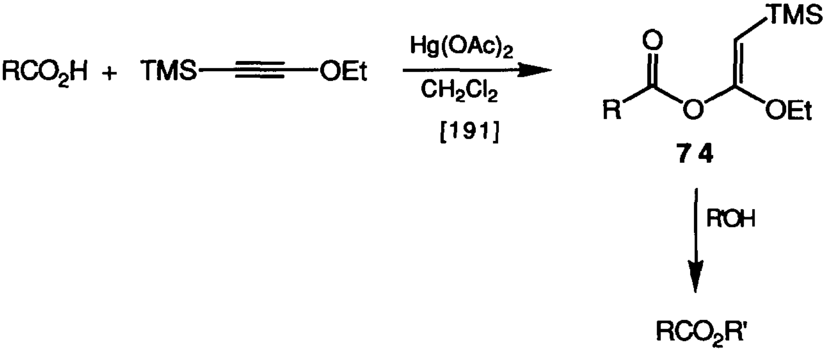
Alkynamides were prepared from alkynylsilanes by treatment with chlorosulfonyl isocyanate (CSI). (Eqn. 197)



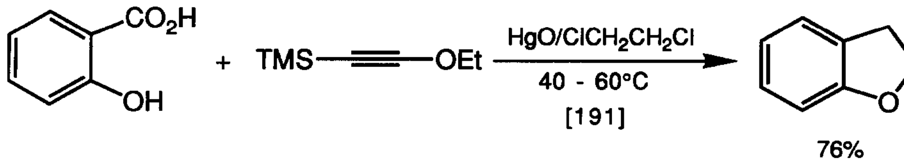
4 examples: 54 - 71%

(197)

Ethoxyethynyltrimethylsilane was reacted with carboxylic acids in the presence of mercury(II) acetate ketene acetals **74**, which were converted to esters. (Eqn. 198) The reaction was used to prepare certain lactones (Eqn. 199) and in peptide synthesis.

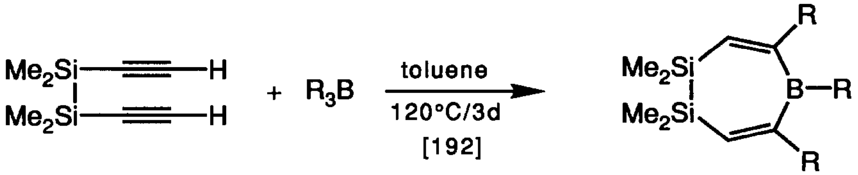


(198)



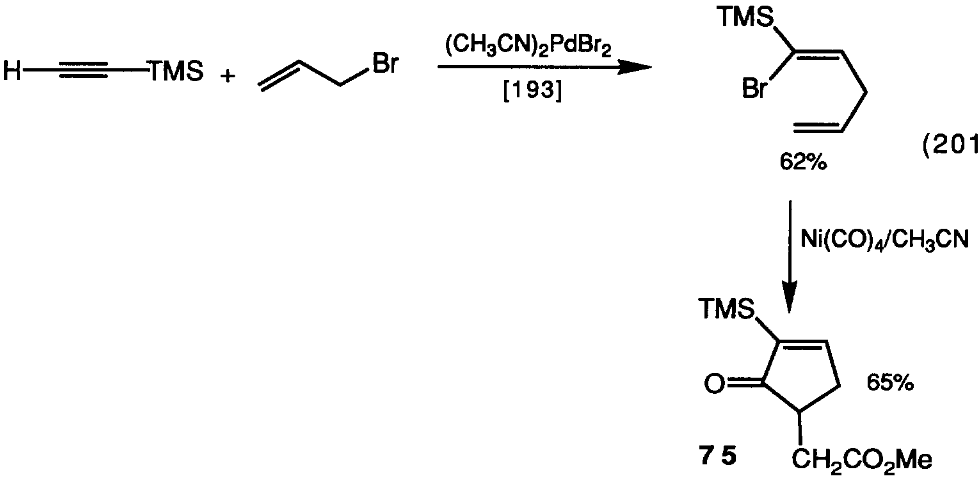
(199)

1,2-Diethynyltetramethyldisilane was reacted with trimethyl- or triethylborane to give boradisilacycloheptadienes. (Eqn. 200)



(200)

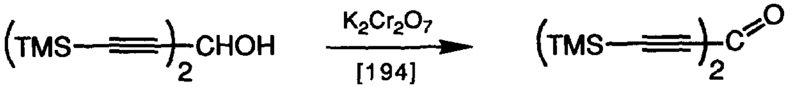
Bromoallylation of trimethylsilylacetylene followed by carbonylation gave cyclopentenone **75**. (Eqn. 201)



(201)

75

Bis(trimethylsilylethynyl)carbinol was oxidized to the ketone (Eqn. 202), which was cyclized with phosphorous pentabromide (Eqn. 203) and converted to tris(trimethylsilyl-ethynyl)carbinol (Eqn. 204). The tris(trimethylsilylethynyl)carbinol was coupled (Eqn. 205) and reacted with triethyl- or tris(trimethylsilylethynyl)aluminum (Eqn. 206).



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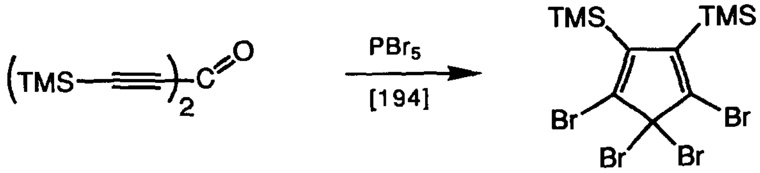

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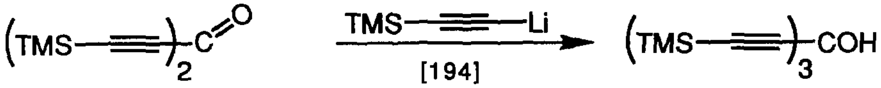

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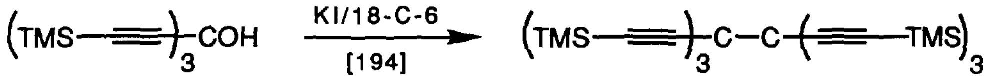

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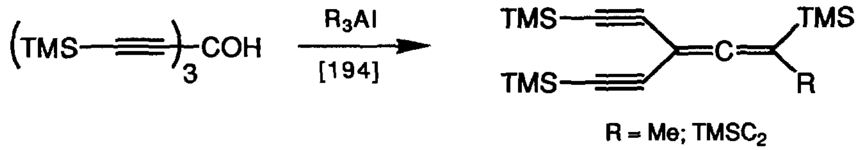
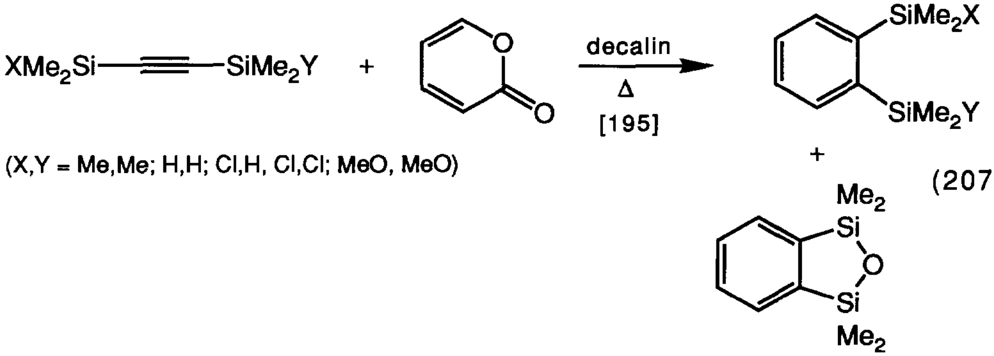


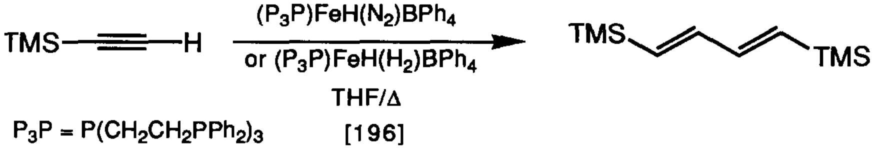
(206)

Various bis silyl acetylene derivatives were reacted with α-pyrone to give, after decarboxylation, ortho-disilyl benzenes. (Eqn. 207)



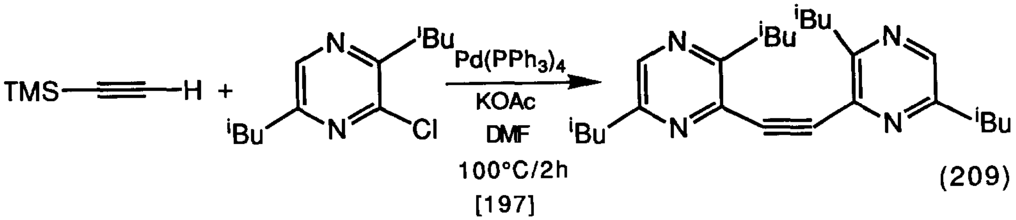
(207)

Trimethylsilylacetylene was coupled to give (E,E)-1,4-bis(trimethylsilyl)-1,3-butadiene. (Eqn. 208)



(208)

Trimethylsilylacetylene was coupled with chloropyrazines to give bis adduct (Eqn. 209) or monoadduct, which could be arylated (Eqn. 210).



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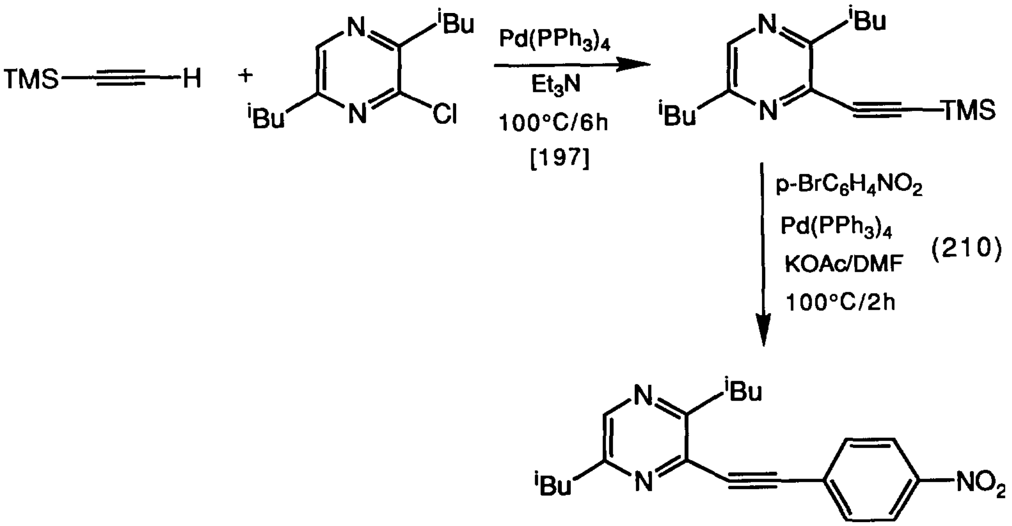
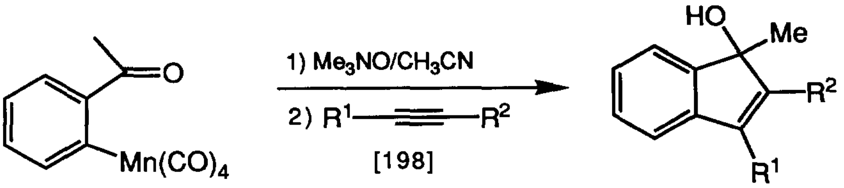


(210)

Indenols were prepared by the reaction of various ethynylsilanes with manganese complex **76**. (Eqn. 211)

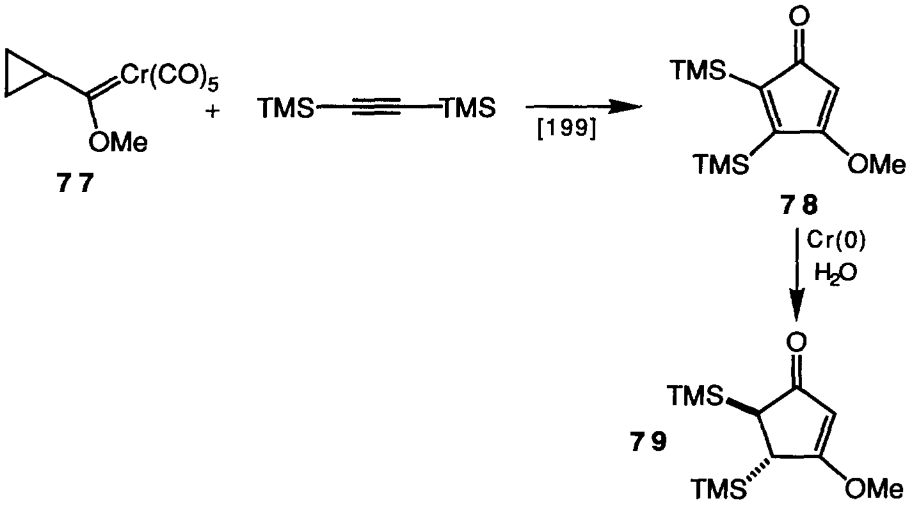


(211)

76

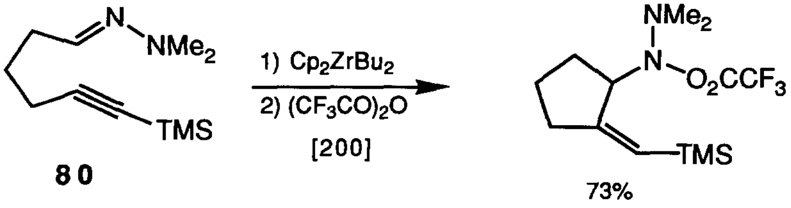
(R^1,R^2 = H,TMS; Bu, TMS; EtO,TMS; Me,TMSCH$_2$; Et, TMSCH$_2$: 31 - 70%)

The chromium carbene complex **77** was reacted with bis(trimethylsilyl)acetylene to give cyclopentadienone **78** and upon oxidation cyclopentenone **79** (Eqn. 212).



(212)

Cyclization of ethynylsilane **80** proved possible. (Eqn. 213)



(213)

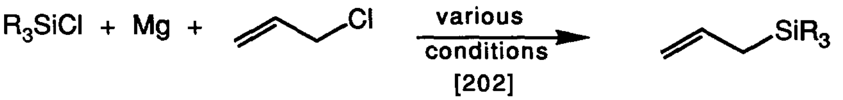
C. Other Studies

A theoretical investigation of the primary dissociation pathways of ethynylsilane was reported. [201]

IX. ALLYLSILANES

A. Preparation

Fifteen different allylsilanes were prepared by reacting a chlorosilane with magnesium and allyl chloride. (Eqn. 214) Various conditions and their effect on the yield of the reaction were studied.



(214)

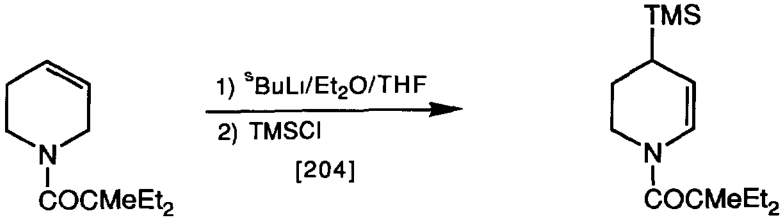
The allylzinc reagent **81** did not react with alkyl halides, but can be silylated. (Eqn. 215)

81

(215)

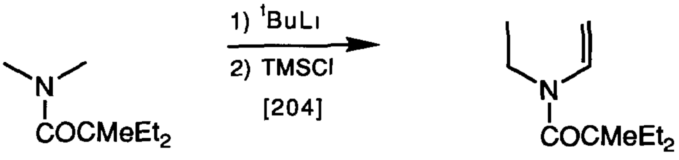
Deprotonation-trimethylsilylation of **82** and **83** gives allylsilanes. (Eqns. 216 and 217) The 5-tert-butyl system silylates away from the tert-butyl group. (Eqn. 218)

Other 5-substituted systems give mono- or bis silylation depending on the reaction conditions. (Eqn. 219)



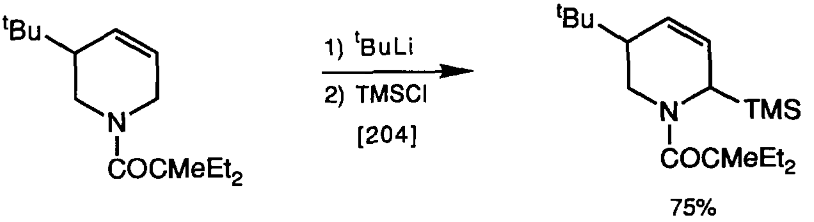
82

(216)



83

(217)



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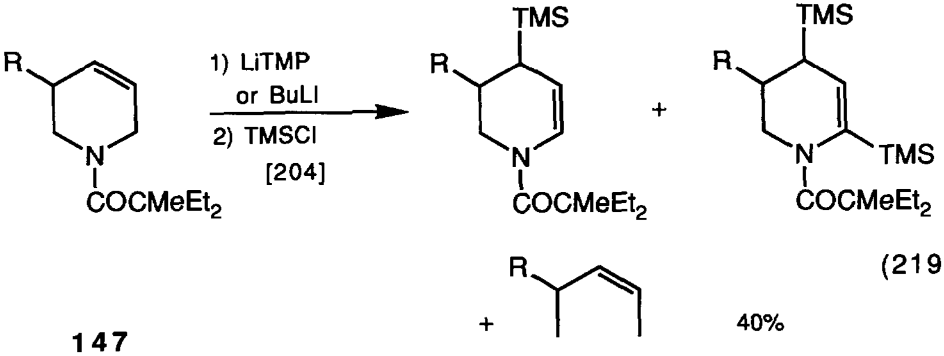
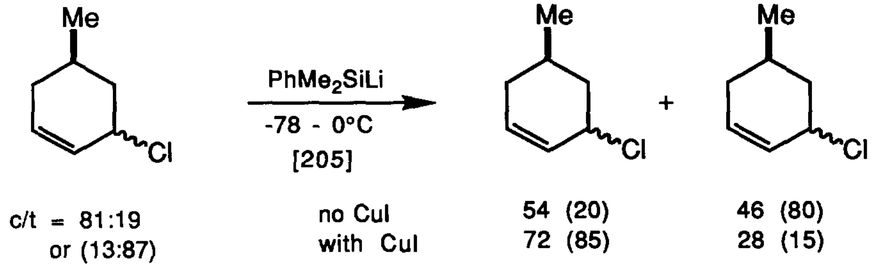


147

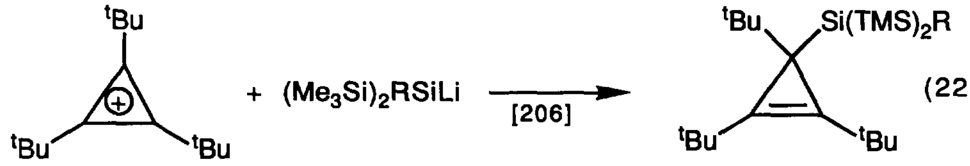
(219)

Silyl organometallic reagents were used to prepare allylsilanes. Phenyldimethylsilyllithium was reacted with 3-chlorocyclohexenes in the absence and presence of copper(I) iodide. In the presence of copper(I) iodide the reaction occurs with clean anti S_N2' attack. (Eqn. 220)



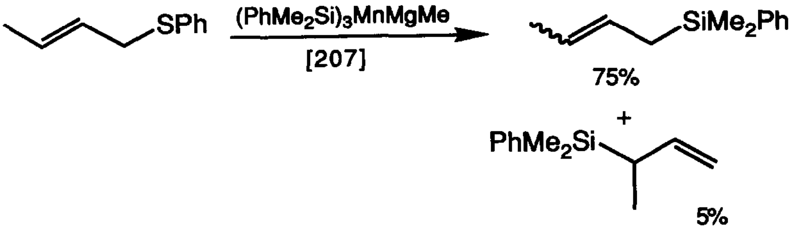
(220)

Various silyllithium reagents were reacted with tri-tert-butylcyclopropenium tetrafluoroborate to give the silylated cyclopropene. (Eqn. 221) These materials were found to be very stable thermally and chemically.



(221)

The reagent formed from 3 equivalents of a silyllithium, methylmagnesium iodide and manganese(II) chloride reacts with allylphenyl sulfides to give allylsilanes. (Eqn. 222) These same reagents also couple with vinyl halides to give vinylsilanes. (Eqn. 223) Silyl aluminum reagents react with allyl phosphonates give allylsilanes. (Eqn. 224)



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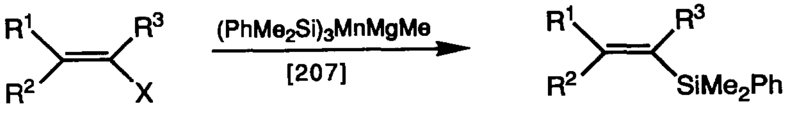
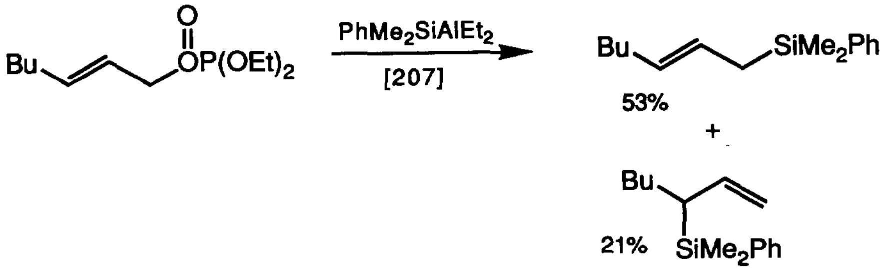


(223)

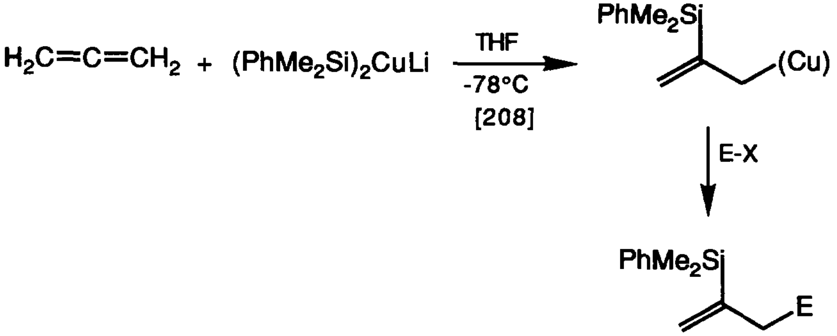
20 examples: 40 - 100%

(X = Br, I, SMe, $OP(O)(OPh)_2$, $OP(O)OEt)_2$, OSO_2CF_3, SPh)

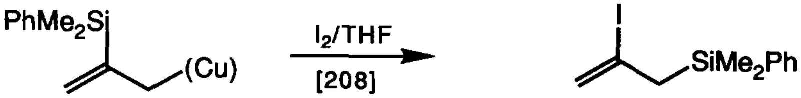


(224)

Silylcupration of allene leads to a 2-(trimethylsilyl)allylcopper reagent, which when reacted with typical electrophiles gives the allylsilane. (Eqn. 225) When reacted with iodine it gives the 2-iodoallylsilane **84** (Eqn. 226), which can be converted to the lithium reagent and then reacted with various electrophiles. (Eqn. 227)

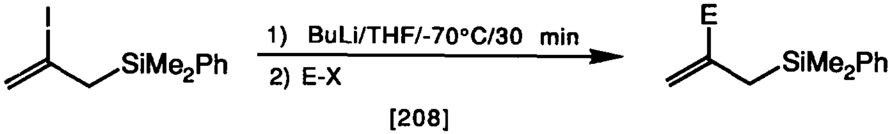


(225)



84

(226)

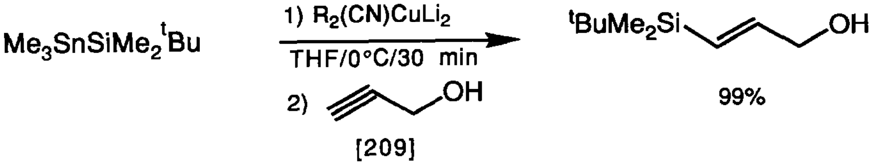


(227)

(E-X = D_2O, MeI, CH_2O, $CH_3CH{=}CHCHO$, acetone)

68 - 92%

The reagent formed from tert-butyldimethyl(trimethylstannyl)silane and a higher order cuprate was reacted with various electrophiles. (Eqns. 228 - 230) The thexyl-dimethylsilyl reagent was also thusly prepared and reacted. (Eqns. 231 - 233) This type of reagent does not form from trimethyl(trimethylstannyl)silane due to reaction at silicon rather than at tin.



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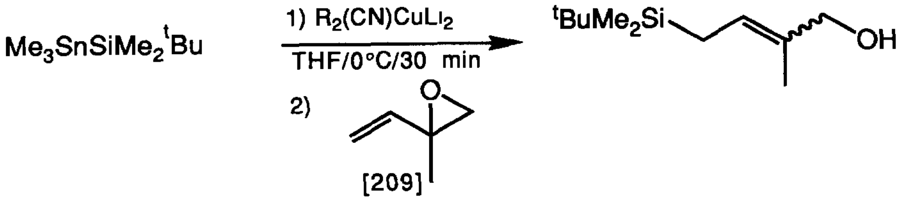

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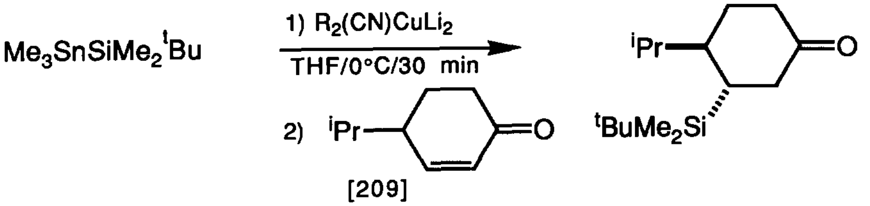
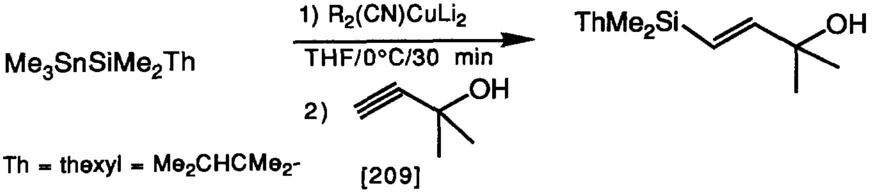
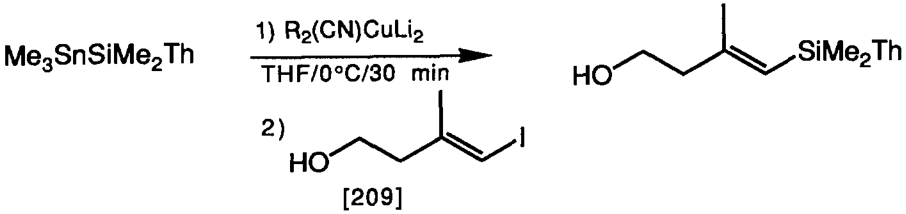


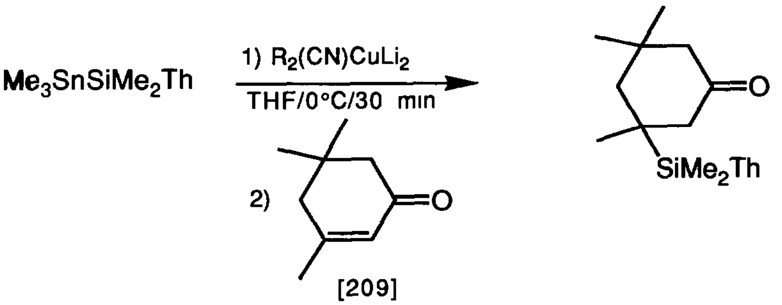
(230)



(231)

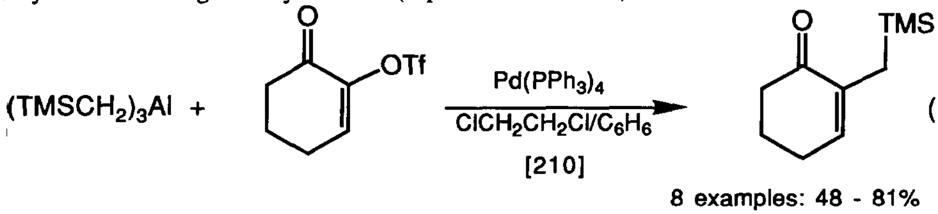


(232)

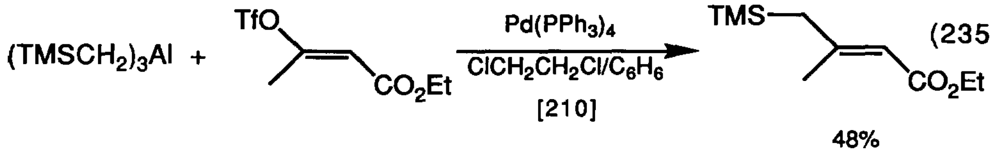


(233)

Silylmethyl organometallic reagents were also employed in the preparation of allylsilanes. Tris(trimethylsilylmethyl)aluminum, which was generated without isolation from trimethylsilylmethyllithium and aluminum trichloride, was reacted with vinyl triflates to give allylsilanes. (Eqns. 234 and 235)

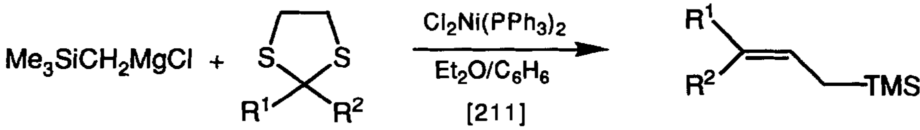


(234)



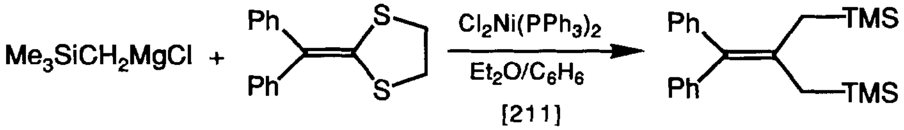
(235)

Trimethylsilylmethylmagnesium chloride was reacted with dithioketals in the presence of nickel(II) to give allylsilanes by a process of addition-elimination. (Eqns. 236 and 237) The reaction of trimethylsilylmethylmagnesium chloride with esters gives allylsilanes *via* a double addition-Peterson elimination sequence. (Eqns. 238 and 239)

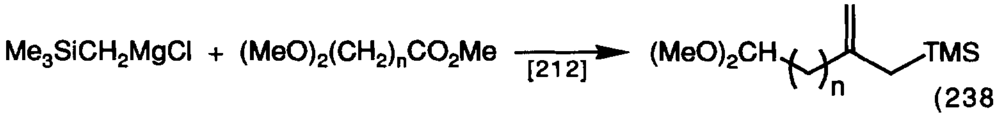


(236)

9 examples: 48 - 89%

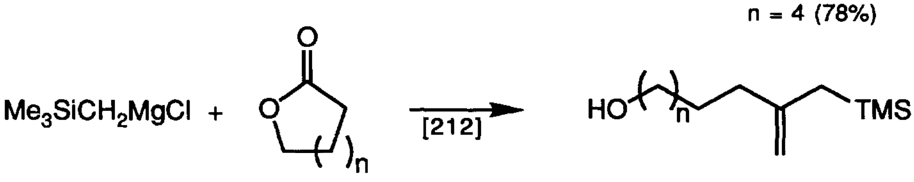


(237)



(238)

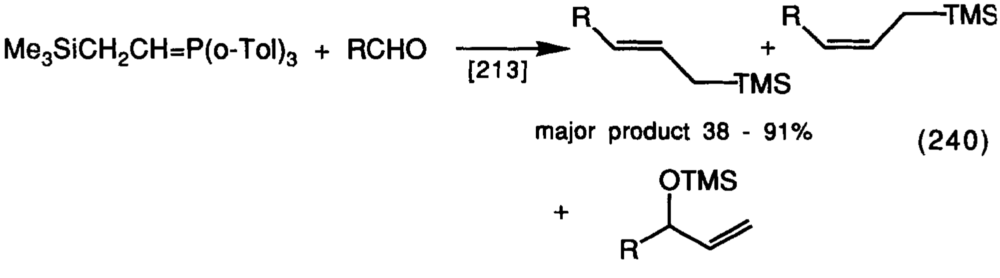
n = 3 (42%)
n = 4 (78%)



(239)

n = 1 (74%)
n = 2 (60%)

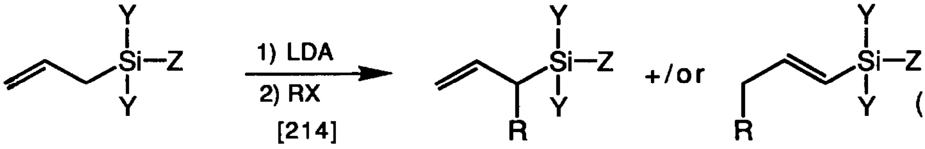
The reaction of aldehydes with a modified Seyferth-Wittig reagent gives predominantly the (E) allylsilane in addition ot the (Z) isomer and the silylated allyl alcohol. (Eqn. 240)



major product 38 - 91%

(240)

The deprotonation-methylation of several allylsilanes with different groups on the silicon atom was carried out in order to investigate the effect of the ligands on silicon on the α to β methylation ratio. (Eqn. 241) The amount of α product was observed to greatly depend on the ligands and the solvent of the reaction.



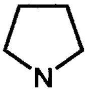
(241)

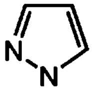
Y,Z = OMe,OMe; OEt,OEt; OCH_2CH_2OMe,OCH_2CH_2OMe; Me, CH_2NEt_2; Me, OCH_2CH_2OMe; Me, $OCH_2CH_2NMe_2$; Me, $OCH_2CH_2OCH_2CH_2OMe$.

Also looked at Y = Me and Z = CH_2-G where G =

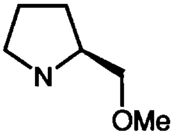
NEt_2; $MeNCH_2VH_2NMe_2$; $N(CH_2CH_2OMe)_2$

$N(CH_2CH_2OEt)_2$;

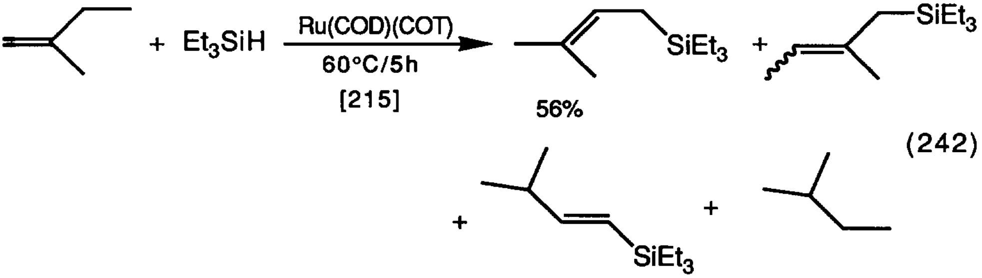




and



The ruthenium catalyzed reaction of olefins with silanes gives allylsilanes. (Eqns. 242 and 243)



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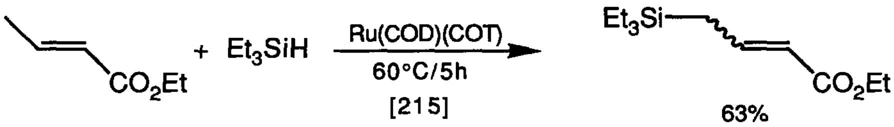
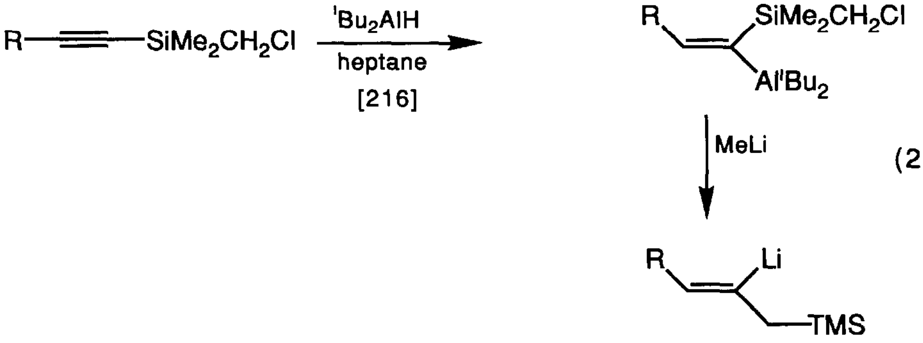


(243)

Chloromethylethynylsilanes react with diisobutylaluminum to give the α-alumino vinylsilane, treatment of which with methyllithium gives a rearrangement t a 2-lithio allylsilane system. (Eqn. 244) This was trapped with several electrophiles. (Eqn. 245) The intermediate organoalane can also be trapped. (Eqn. 246)



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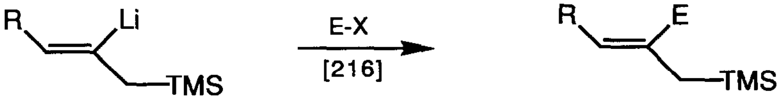

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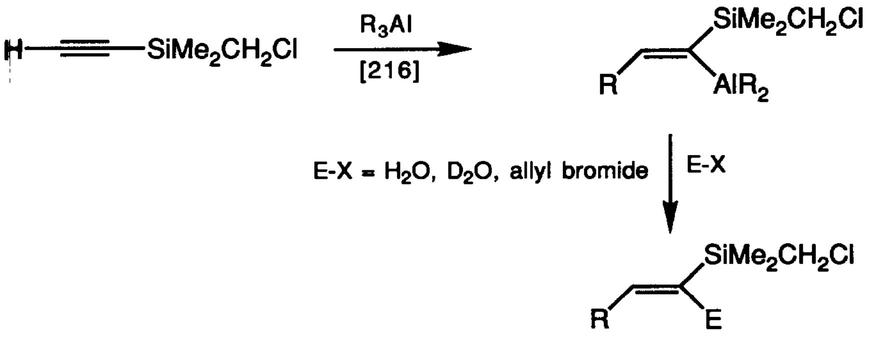
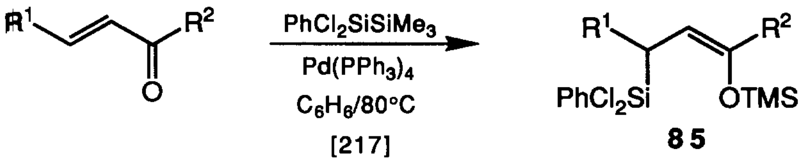


(246)

Enones were reacted with 1,1-dichloro-1-phenyl-3,3,3-trimethyldisilane and palladium(0) to give 1,4-disilylation and allylsilane **85**. (Eqn. 247) This reacts as an enol silyl ether towards alkylation or solvolysis. (Eqn. 248) Oxidation of the Si-C bond was also carried out. (Eqn. 249)



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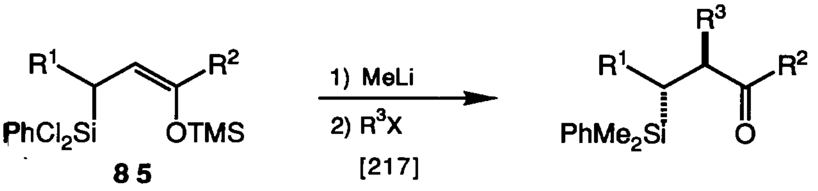
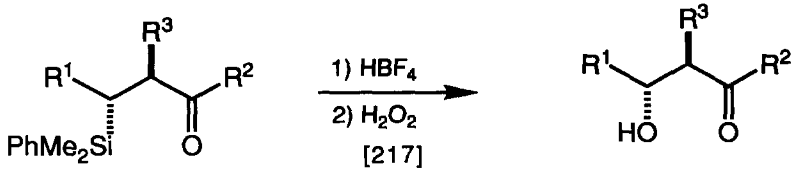
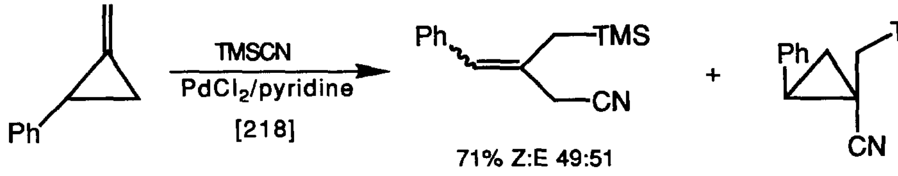


(248)

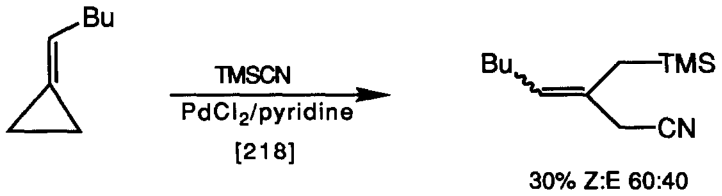


(249)

Alkylidenecyclopropanes were reacted with trimethylsilyl nitrile to give cyano functional allylsilanes. (Eqns. 250 and 251)

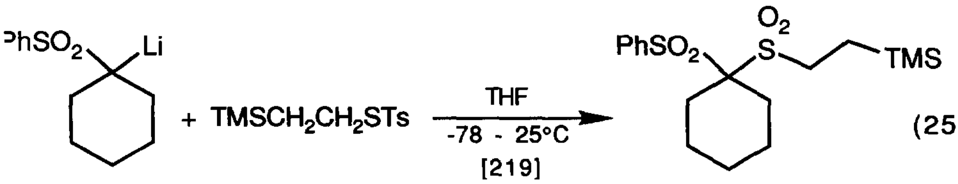


(250)

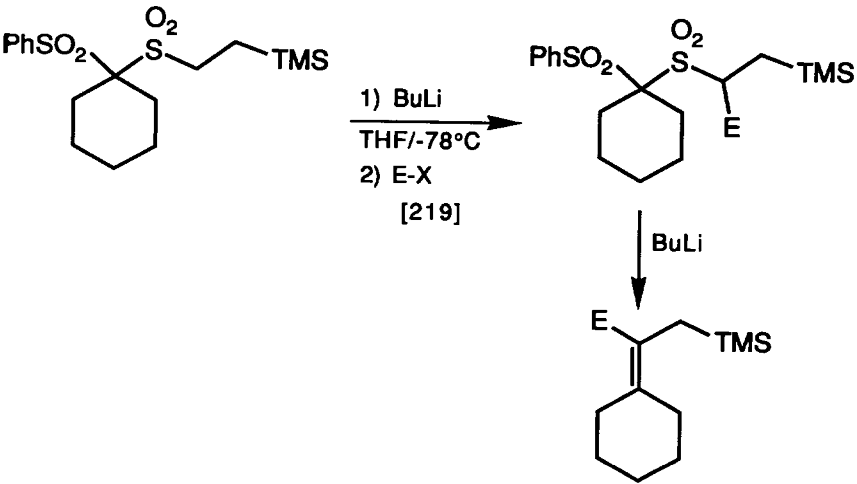


(251)

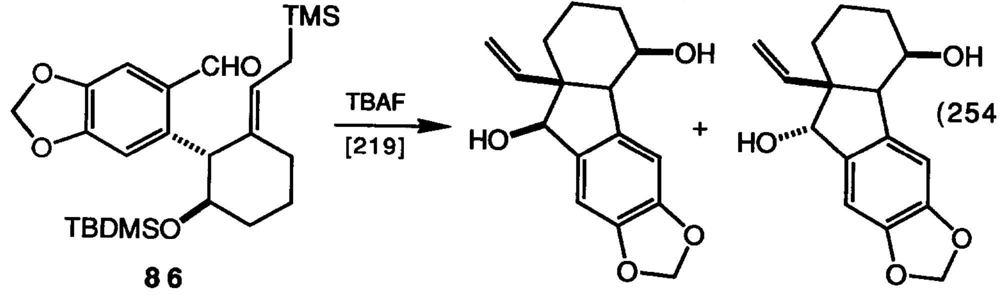
In a clever route to allylsilanes β-trimethylsilylethyl thiosulfonate was reacted with α-lithiosulfones. (Eqn. 252) These could in turn be alkylated and then subjected to a Ramberg-Baecklund reaction to give allylsilanes. (Eqn. 253) This approach was used to set up allylsilanes **86** and **87** for cyclization reactions. (Eqns. 254 and 255)



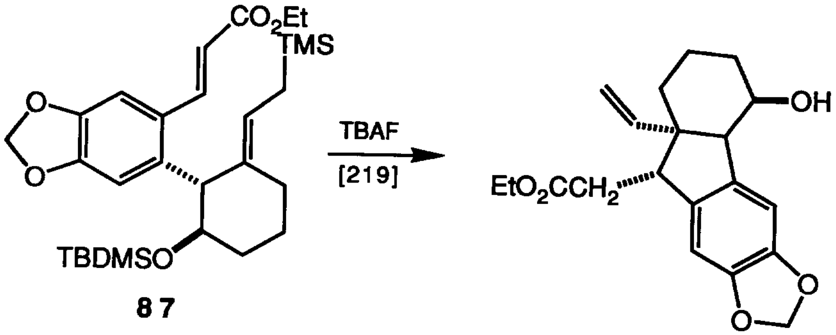
(252)


PhSO2
O2
S
TMS
1) BuLi
THF/-78°C
2) E-X
[219]
PhSO2
O2
S
TMS
E
BuLi
E
TMS

(253)


TMS
CHO
O
O
TBDMSO
86
TBAF
[219]
OH
HO
O
O
+
OH
HO
O
O

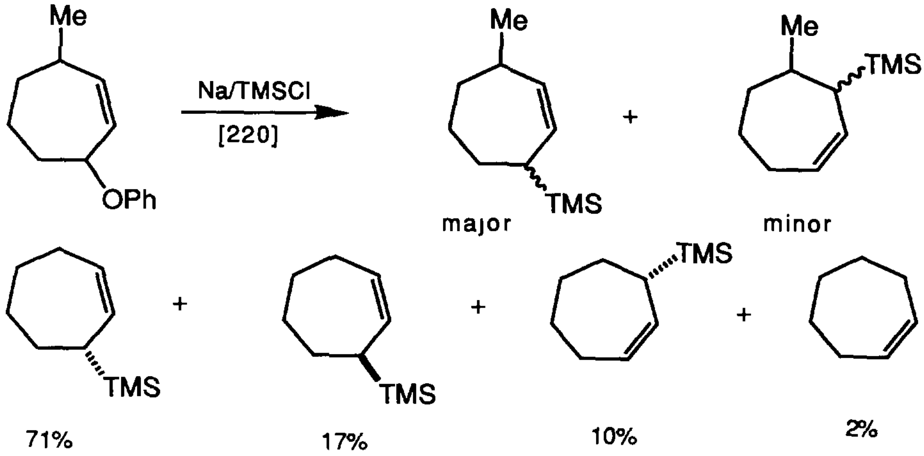
(254)


CO2Et
TMS
O
O
TBDMSO
87
TBAF
[219]
OH
EtO2CCH2
O
O

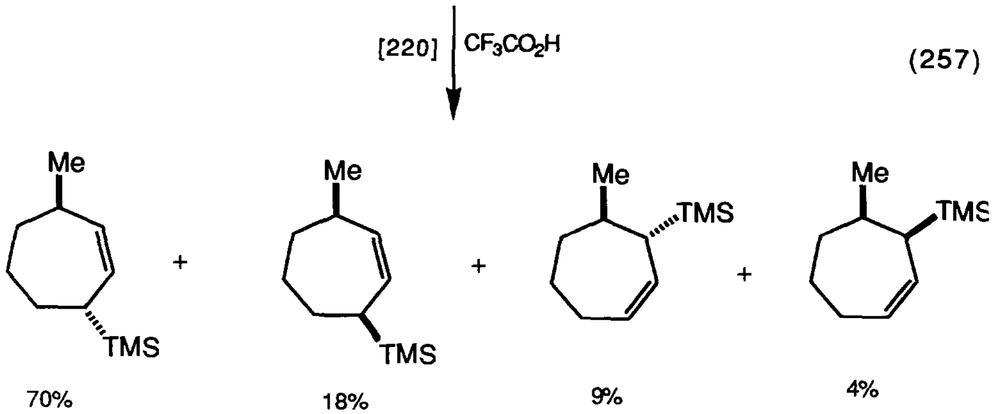
(255)

B. Reactions

The preparation and a study of the stereochemistry of the acidolysis of some cycloheptyl-2-enylsilanes (and stannanes) was reported. (Eqns. 256 and 257) The electrophile is delivered in an anti-S_E' mode.

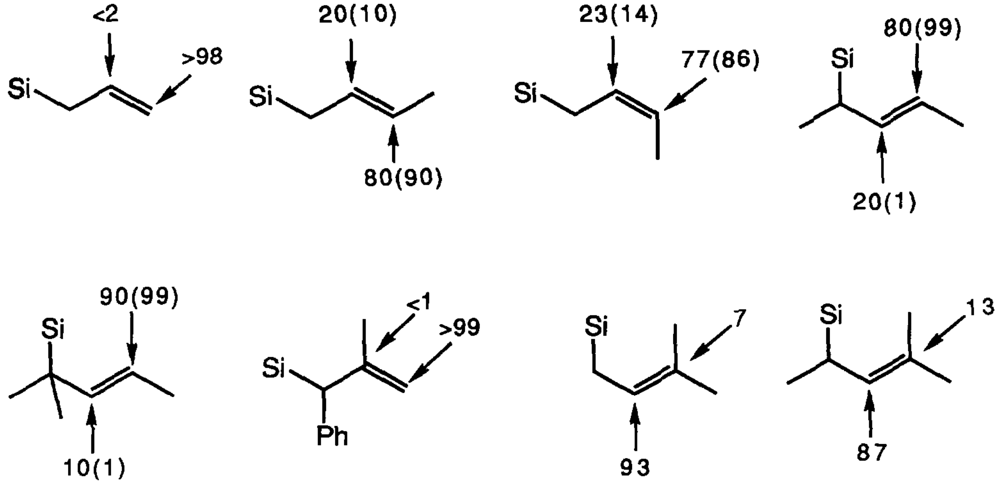


(256)



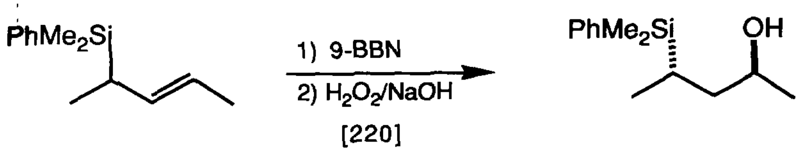
(257)

The regioselectivity of the hydroboration of allylsilanes was determined for a number of systems. The results are indicated below. [221]

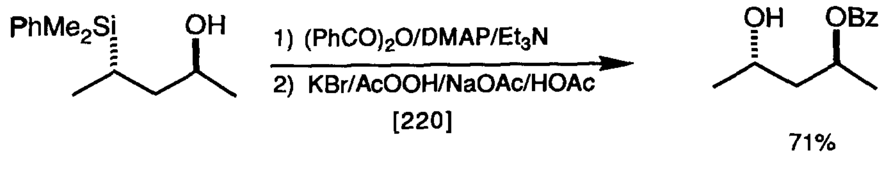


(Si = $PhMe_2Si$; numbers are for borane in THF, numbers in parentheses are for 9-BBN)

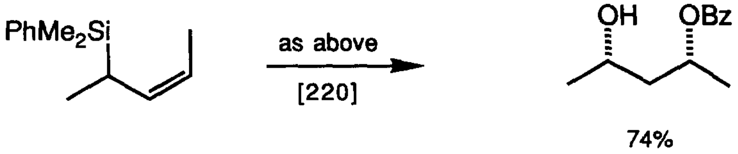
The stereochemistry of the hydroboration of allylsilanes was also studied by this same group. Utilization of the dimethylphenylsilyl group allows for both oxidation of the C-B and C-Si bonds leading to diols of fixed stereochemistry. (Eqns. 258 - 261)



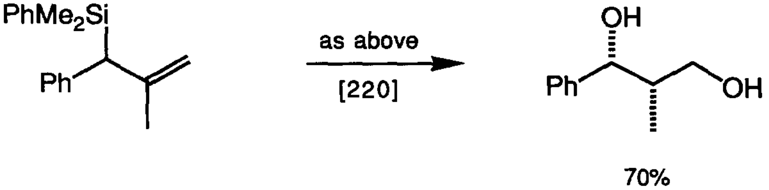
(258)



(259)

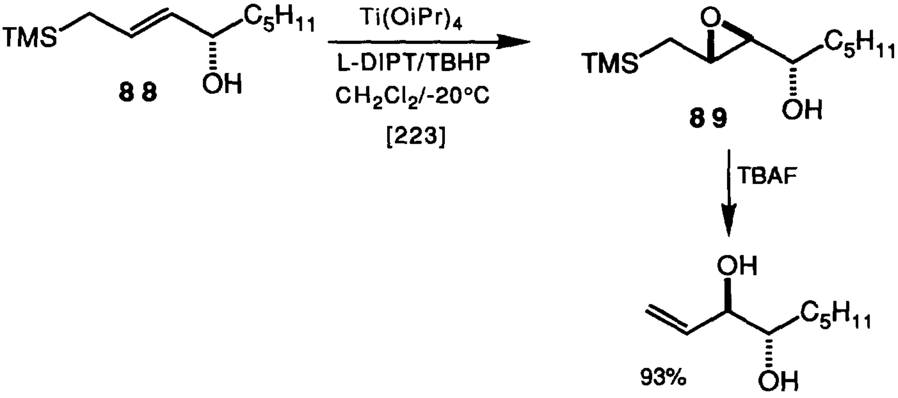


(260)

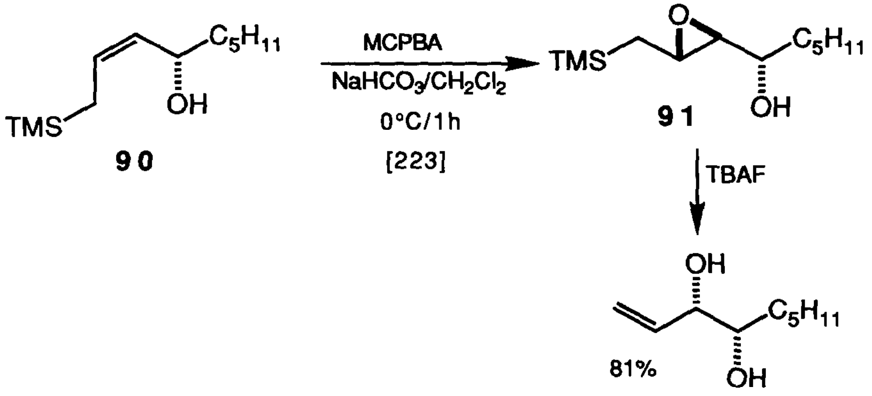


(261)

(E) 4-Hydroxyallylsilane **88** was prepared and subjected to the Sharpless epoxidation procedure. Treatment with fluoride ion gave the optically active diol **89**. (Eqn. 262) The (Z) isomer **90** was oxidized and ring opened to give **91**. (Eqn. 263)

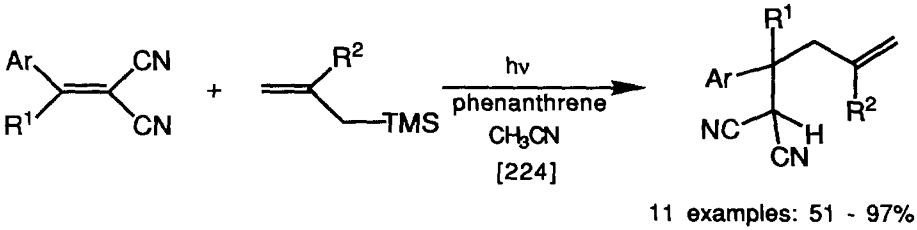


(262)

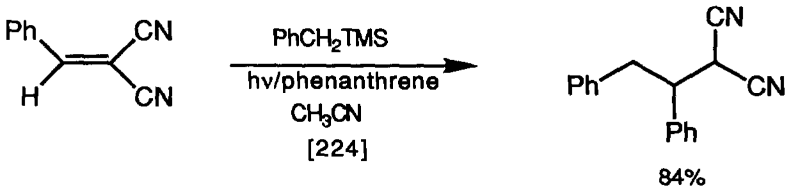


(263)

Allylsilanes photochemically allylate 1,1-dicyanoalkenes. (Eqn. 264) Benzylation is similarly possible. (Eqn. 265)

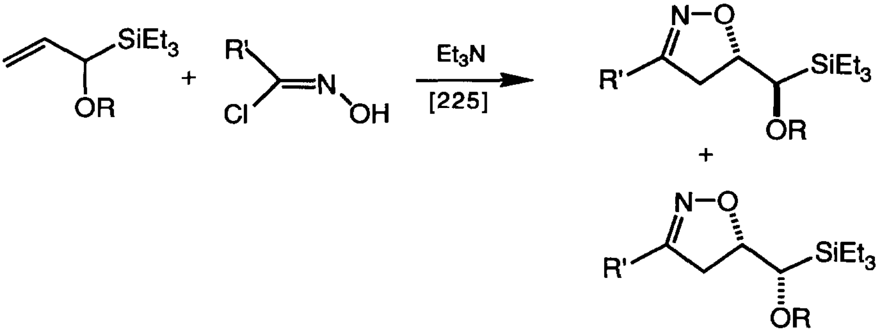


(264)



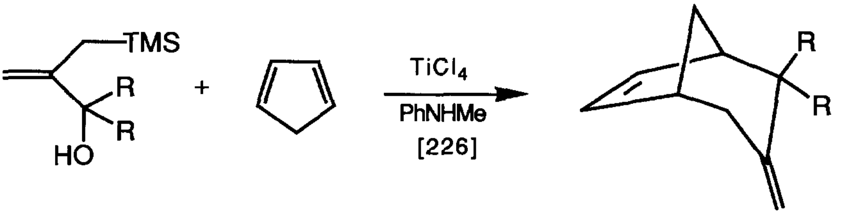
(265)

Chiral α-alkoxyallylsilanes were shown to react with nitrile oxides to give the products of dipolar addition. (Eqn. 266)

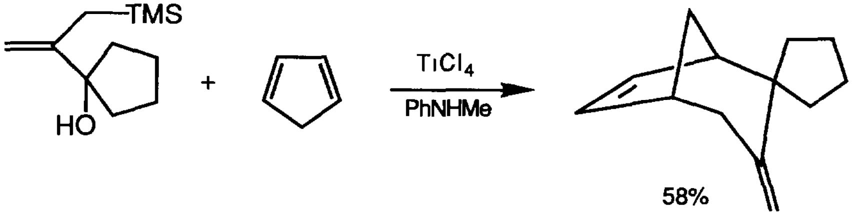


(266)

Trimethylsilylmethylallyl alcohols were shown to react with cyclopentadiene under the influence of a Lewis acid. (Eqns. 267 and 268)

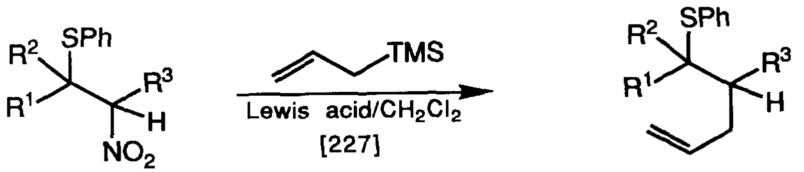


(267)



(268)

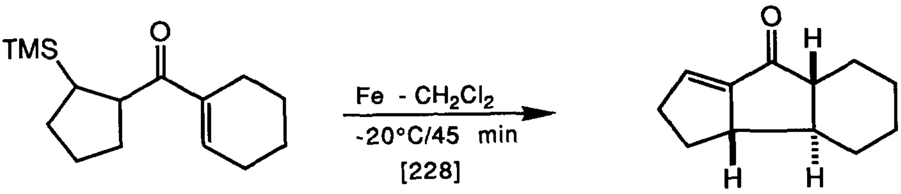
Whereas normal nitroalkanes do not react with allylsilanes, β-nitro sulfide do react to give allylation. (Eqn. 269) Trimethylsilylnitrile reacts similarly to give cynation.



11 examples: 44 - 79%

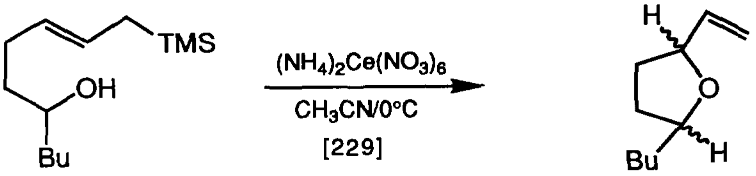
(269)

The silicon-directed Nazarov reaction was employed in the preparation of linearly fused tricyclic ring systems. (Eqn. 270)



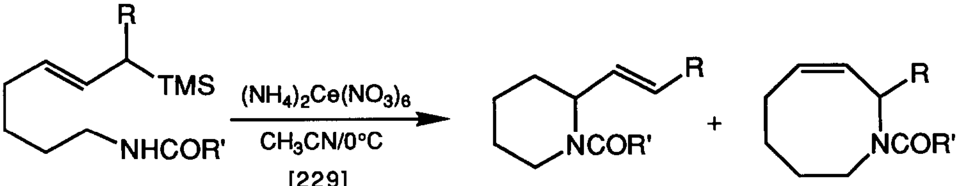
(270)

The oxidative ring closure of hydroxy and amido substituted allylsilanes was accomplished. (Eqns. 271 and 272)



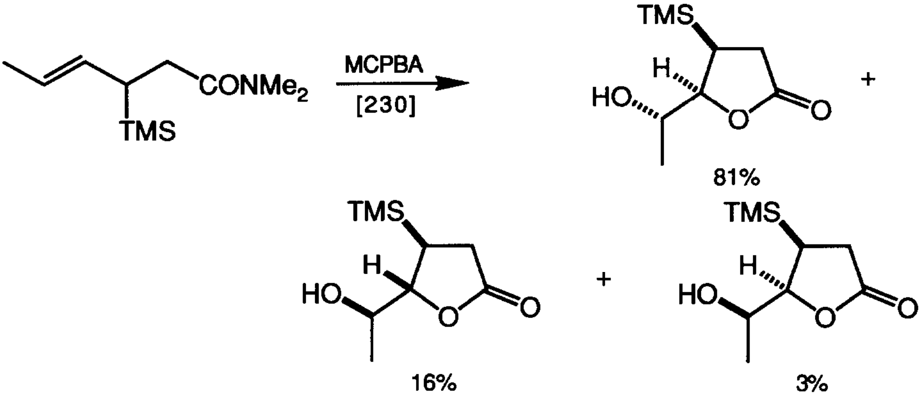
three other products also observed
yields of 43 - 92% on 6 examples

(271)



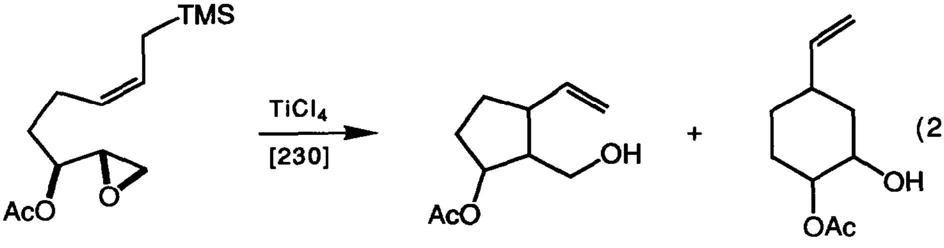
(272)

Epoxidation of some substituted allylsilanes lead to silylated tetrahydrofuranones. (Eqn. 273)



(273)

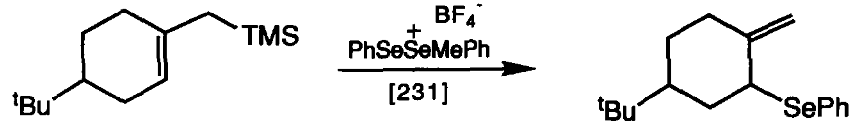
The allylsilyl **92** was cyclized with titanium tetrachloride. (Eqn. 274)



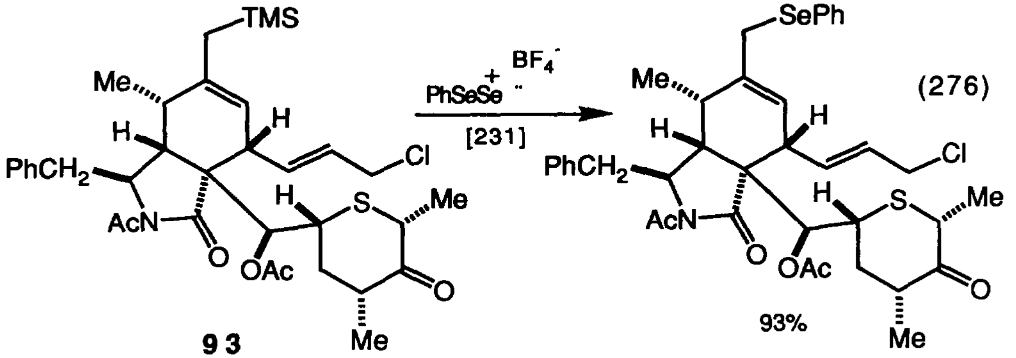
92

(274)

Allylselenides were prepared from allylsilanes. (Eqn. 275) The procedure was used in the synthesis of cytochalasin isoindolone utilizing allylsilane **93**. (Eqn. 276)



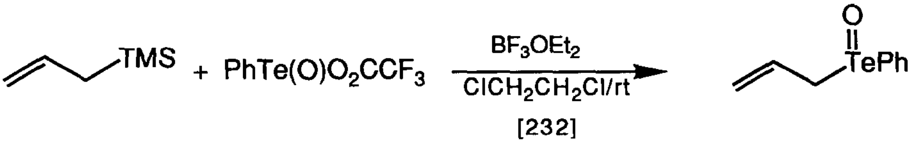
(275)



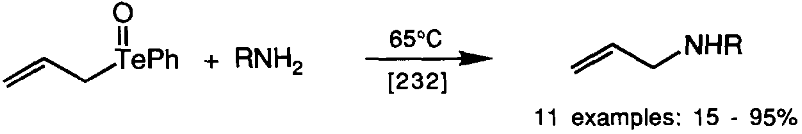
93

(276)

Phenyltellurinylation of allylsilanes is possible as shown in Eqn. 277. The allyl tellurium oxides can be converted directly to amines. (Eqn. 278)

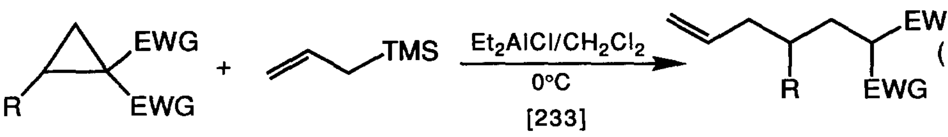


(277)



(278)

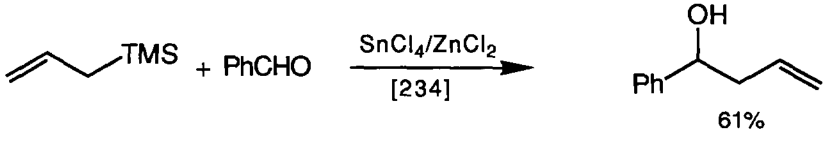
The conjugate addition of allylsilanes to electrophilic cyclopropanes was observed. (Eqn. 279)



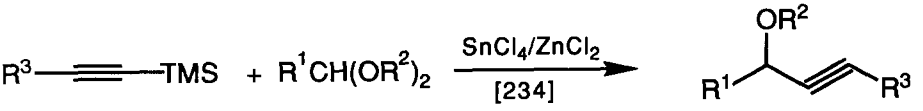
(279)

EWG = electron withdrawing group; R = H or Me

Allylsilanes were shown to react with aldehydes and ketones under both acid catalyzed and fluoride ion promoted conditions. Allyltrimethylsilane reacts with aldehydes in the presence of tin(IV) chloride and zinc chloride. (Eqn. 280) Similar conditions give the ethynylation of ketals utilizing ethynylsilanes. (Eqn. 281) 1,1-Difluoro-3-trimethylsilylpropene was reacted with aldehydes and ketones to give β,β-difluoro alcohols **94** in the presence of fluoride ion. (Eqn. 282)

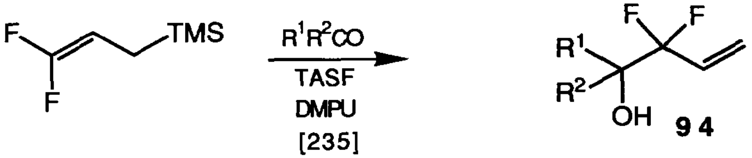


(280)



(281)

12 examples: 15 - 85%

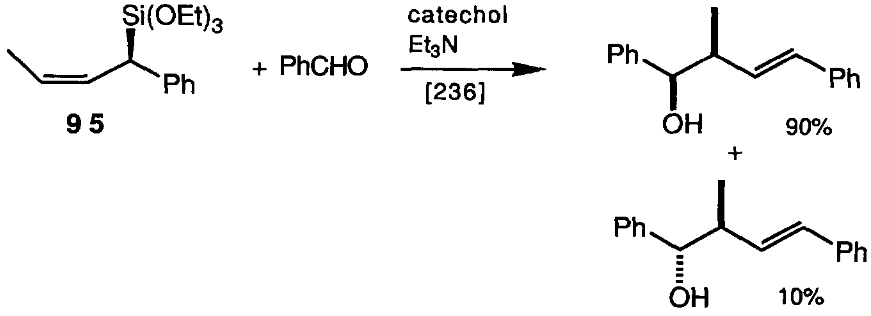


94

(282)

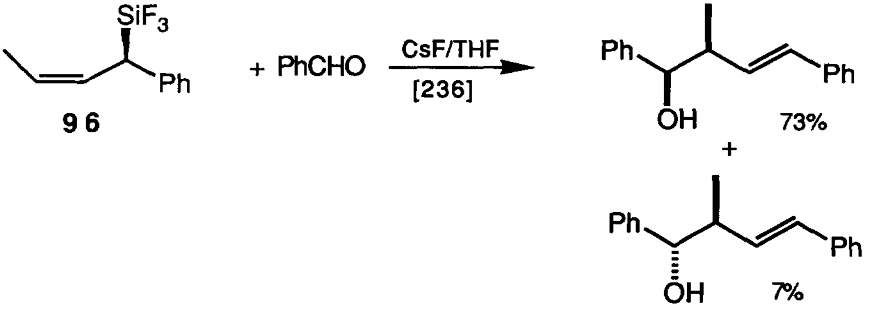
6 examples 34 - 100%

The stereochemistry and the mechanism of the allylation of ketones and aldehydes with allylsilanes **95** and **96** was studied. The results are consistent with a six-memebered ring transition state for the reaction. (Eqns. 283 and 284)



95

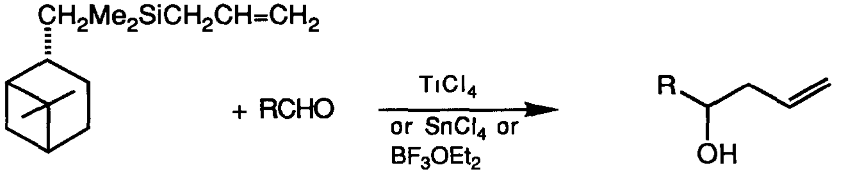
(283)



96

(284)

The allylsilane **97** was utilized in efforts to convert aldehydes into optically active homoallylic alcohols. (Eqn. 285) The configuration of the homoallylic alcohol depends on the Lewis acid catalyst used for the allylation reaction.



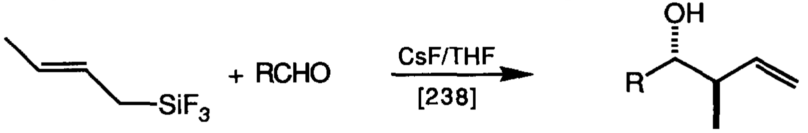
97

[237]

(285)

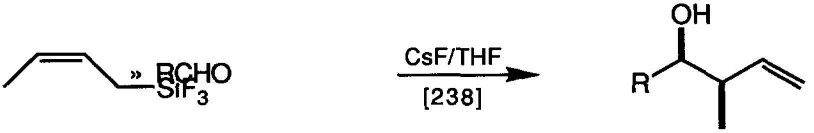
R configuration from $TiCl_4$
S configuration from $SnCl_4$ or BF_3OEt_2

Stereodefined crotyltrifluorosilanes were shown to react stereoselectively with aldehydes under the influence of fluoride ion. (Eqns. 286 and 287)



(286)

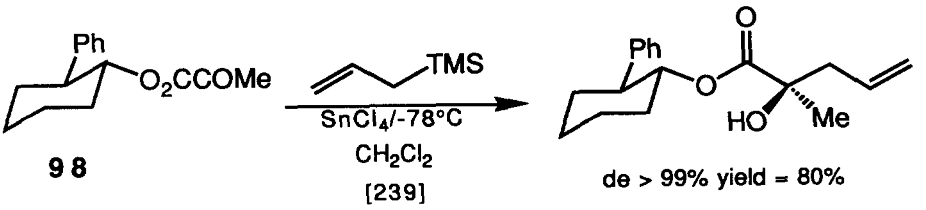
> 98% with < 2% of syn isomer
5 examples: 68 - 96%



(287)

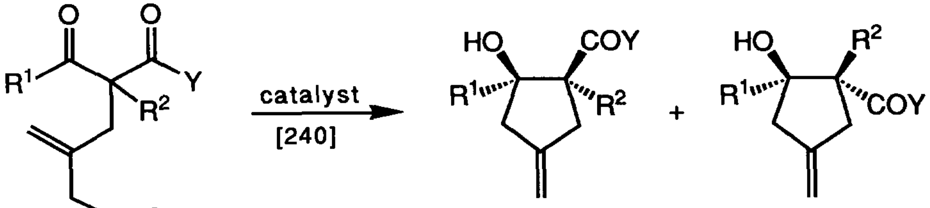
9% with 10% of anti isomer
5 examples· 77 - 96%

Chiral pyruvate **98** was allylated with allyltrimethylsilane with high diastereoselectivity. (Eqn. 288)



(288)

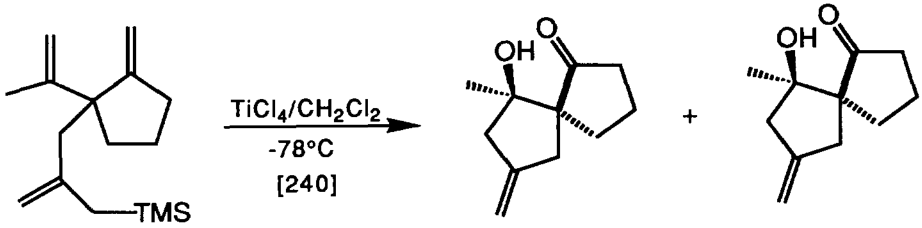
1,3-Dicarbonyl containing allylsilanes of the type **99** were cyclized under chelation control with titanium tetrachloride to give very high stereoselectivity as compared with the results from non-chelation control. (Eqns. 289 and 290)



(289)

99

For Y = CO_2Et	major	minor
$TiCl_4$	>200	<1
BF_3OEt_2	1	1.2
TBAF	2	1



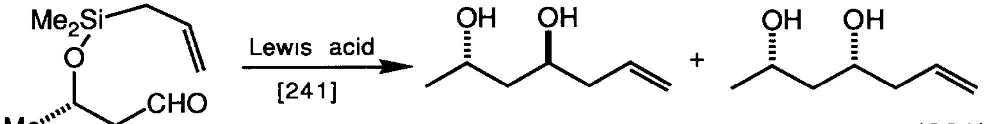
(290)

10 parts 1 part

An interesting twist to the concept of intramolecular allylation *via* allylsilanes was to utilize siloxy aldehydes in which the silyl group contains the allyl group as well

This was applied in 1,3-asymmetric inductions of chiral silylated β-hydroxy aldehydes.

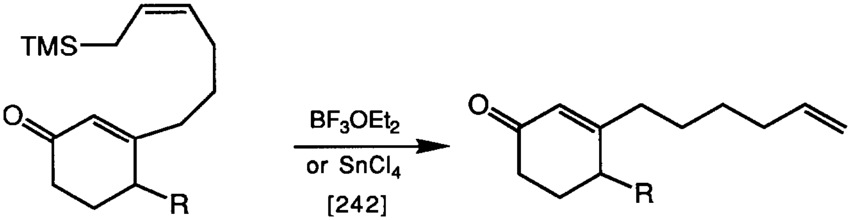
(Eqn. 291)



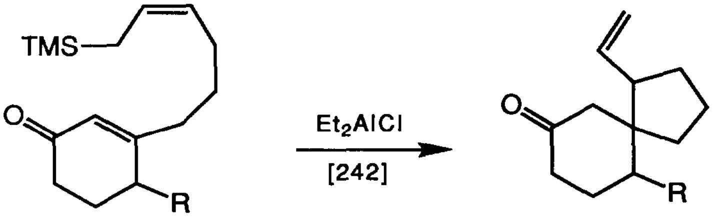
(291)

Lewis acid		
TiCl$_4$	8%	92%
SnCl$_4$	92%	8%
BF$_3$OEt$_2$	70%	30%

As has been the case for the recent past several intramolecular cyclizations involving the reaction of an allylsilane group with an enone were reported. Some of these proceed best with fluoride ion while others are better with Lewis acid. Examples are shown in Eqns. 292 - 297.

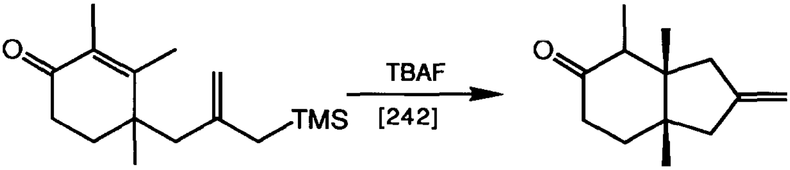


(292)

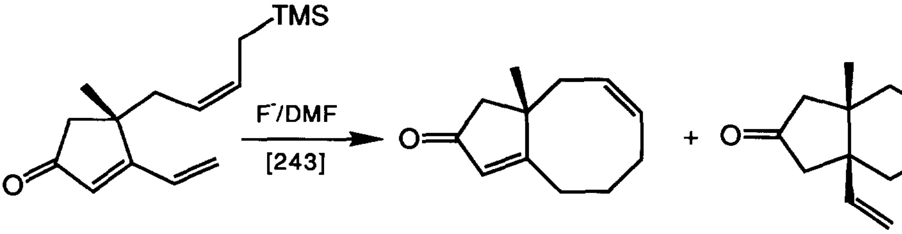


R = H, Me, both diastereomers formed

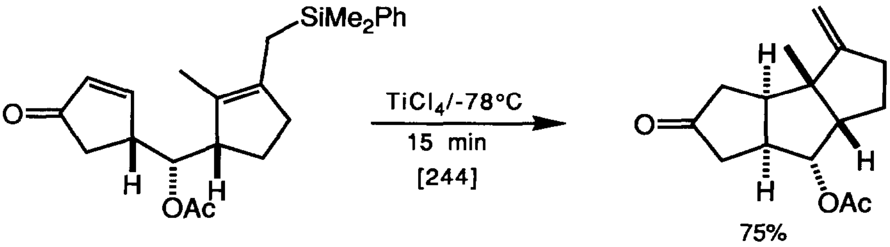
(293)



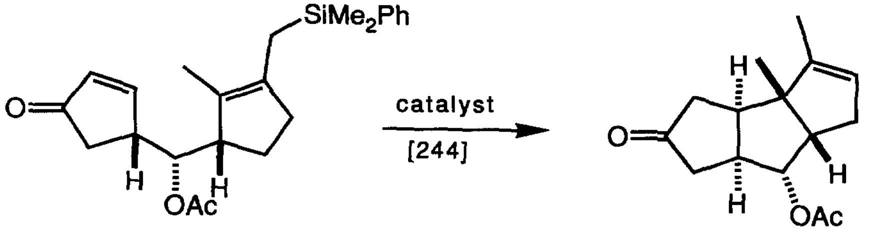
(294)



(295)



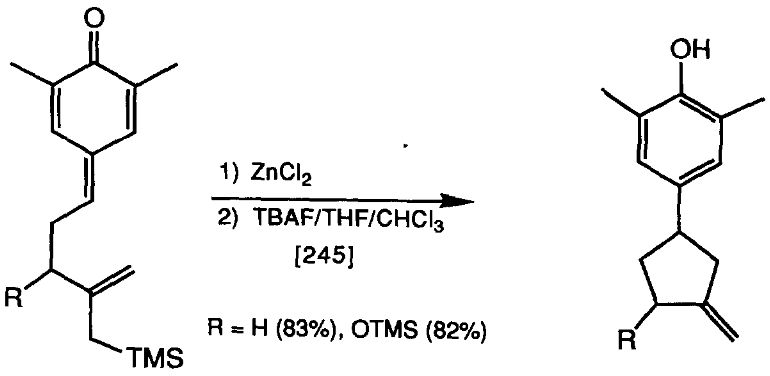
(196)



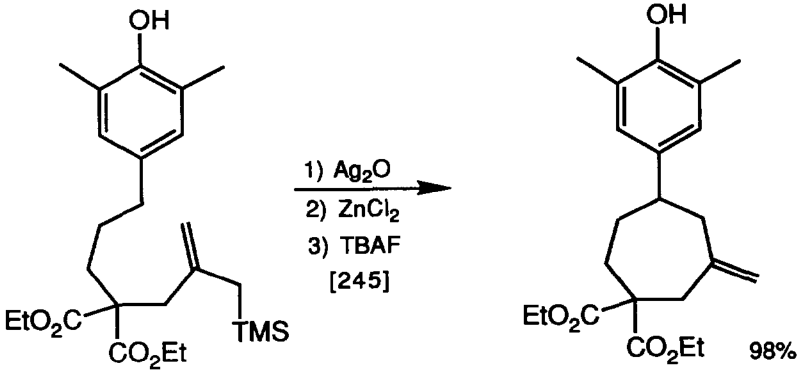
(297)

catalyst = BF_3OEt_2 (94%); $SnCl_4$ (77%); $EtAlCl_2$ (32%)

Allylsilanes were employed in an intramolecular cyclization procedure involving para-quinone methides. (Eqns. 298 and 299)

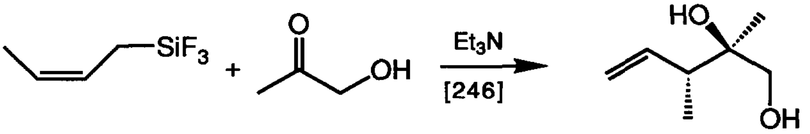


(298)



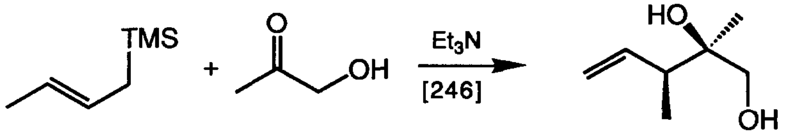
(299)

Allylsilanes were used to allylate α-hydroxy ketones. The stereo chemistry is explained by a chelated bicyclic transition state. (Eqns. 300 and 301)



(300)

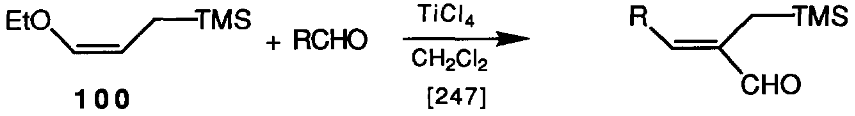
5% of diastereomer formed



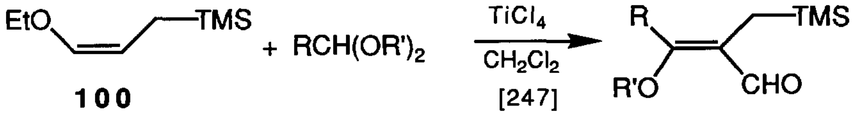
(301)

3% of diastereomer formed

Allylsilane **100**, prepared by hydrogenation of the appropriate propargylsilane, was reacted with aldehydes and acetals to give products retaining the silicon group. (Eqns. 302 and 303) A [2+2] cycloaddition is proposed to explain the results.

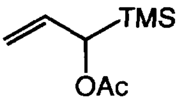


(302)

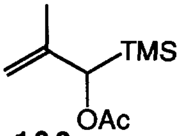


(303)

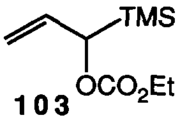
Allylations with allylsilane **101** gives vinyl acetates as a result of the double bond transposition that occurs during the allylation reaction. The allylsilanes **102** and **103** were also employed in the allylations, with the relative reactivity being **102**>**103**>**101**. (Eqn. 304)



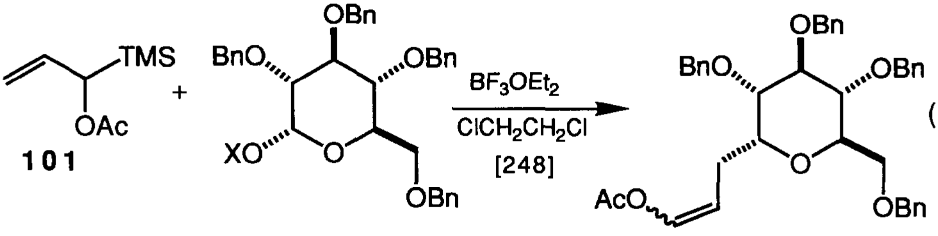
101



102



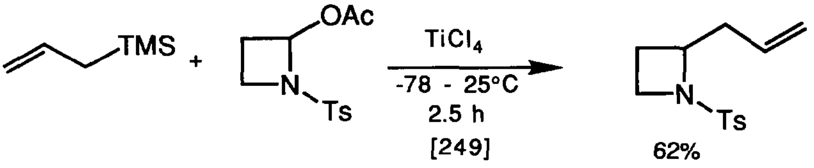
103



(304)

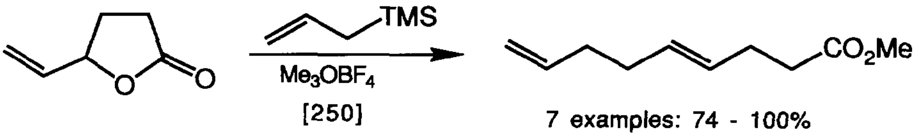
6 examples: 50 - 81%

The allylation of 2-acetoxy azetidines with allyltrimethylsilane was reported. (Eqn. 305)

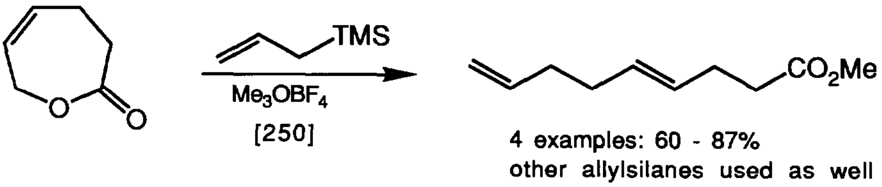


(305)

The reaction of γ-vinyl-γ-butyrolactones with allyltrimethylsilane results in a clever preparation of 4,8-alkadienoates. (Eqns. 306 and 307)

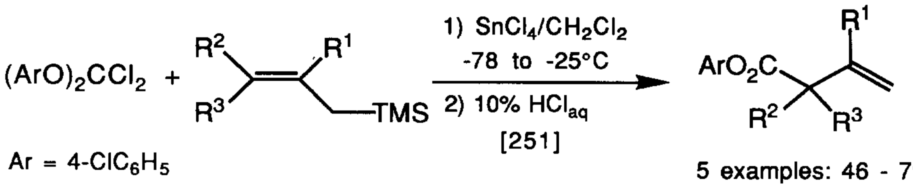


(306)

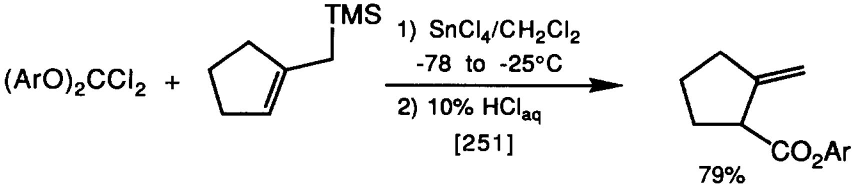


(307)

β,γ-Unsaturated carboxylic acid esters were prepared *via* allylation of diaryloxydichloromethanes. (Eqns. 308 and 309)

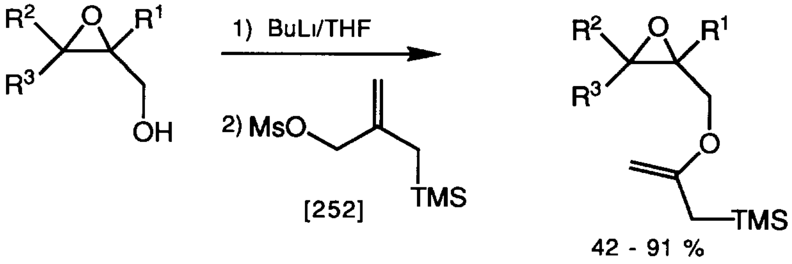


(308)

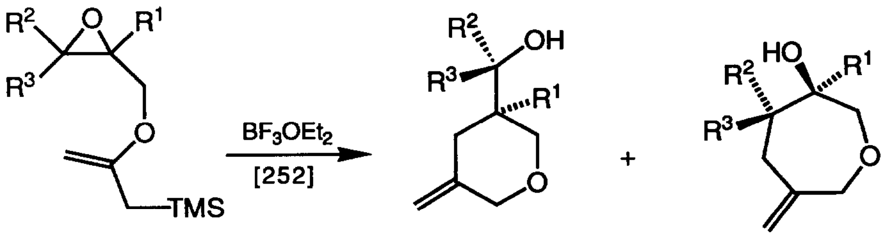


(309)

Epoxy functionalized allylsilanes, prepared as shown in Eqn. 310, were converted to oxepanes upon treatment with Lewis acids. (Eqn. 311)



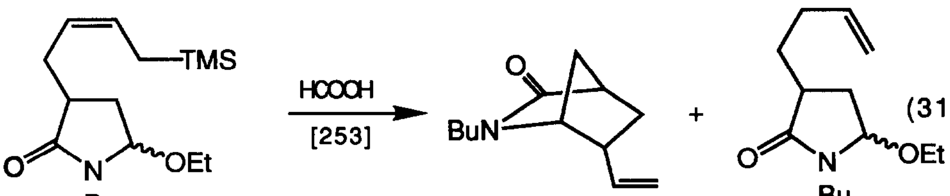
(310)



(311)

7 examples: 63 - 82%; ratios from 1. to 7:1
with $TiCl_4$ 6 examples: 48 - 95% only 7 membered ring.

The allylsilane **104** was cyclized *via* the aminal group. (Eqn. 312) Several other examples were reported.



(312)

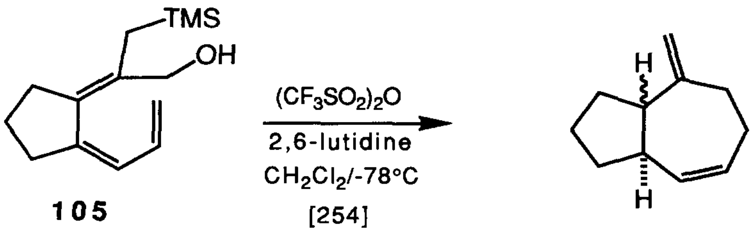
104

66%

27%

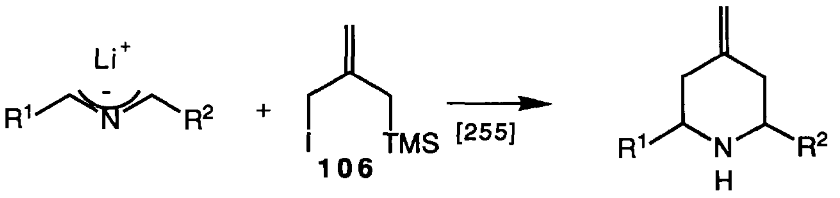
8 other examples: 73 - 98%

Hydroazulene were prepared via a [3+4] cycloaddition involving allylsilane **105**. (Eqn. 313)



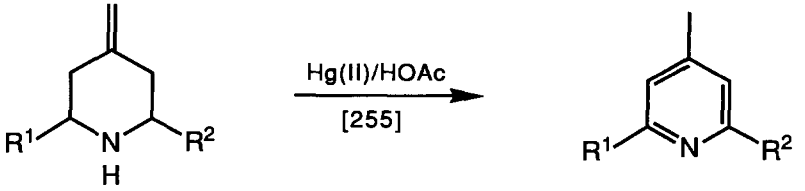
(313)

2-Azaallyl anions were reacted with allylsilane **106** to give piperidines and pyridines. (Eqns. 314 and 315)



(314)

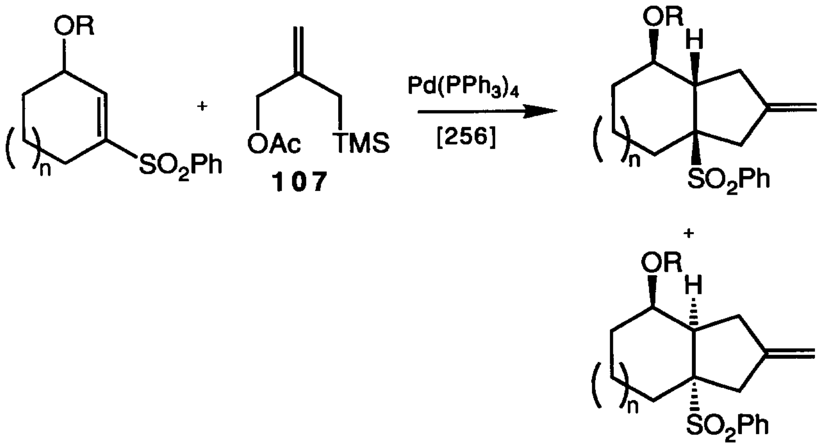
3 examples: 66 - 75%



(315)

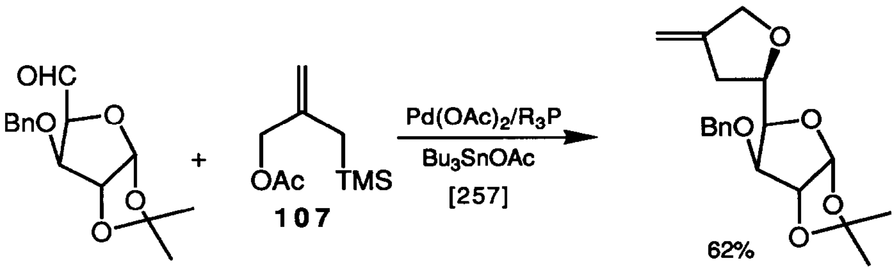
5 examples: 14 - 73% over both steps

γ-Alkoxy-α,β-unsaturated sulfones were shown to react with allylsilane **107** to give a stereocontrolled cyclopentenone synthesis. (Eqn. 316)

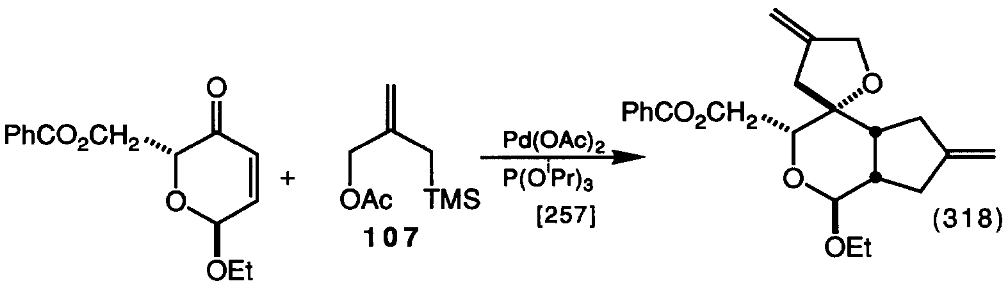


(316)

The palladium-catalyzed trimethylenemethane reaction was applied to aldehydes with the aid of a tin cocatalyst to give tetrahydrofurans. (Eqn. 317) In one instance both the double bond and the carbonyl were reacted. (Eqn. 318)

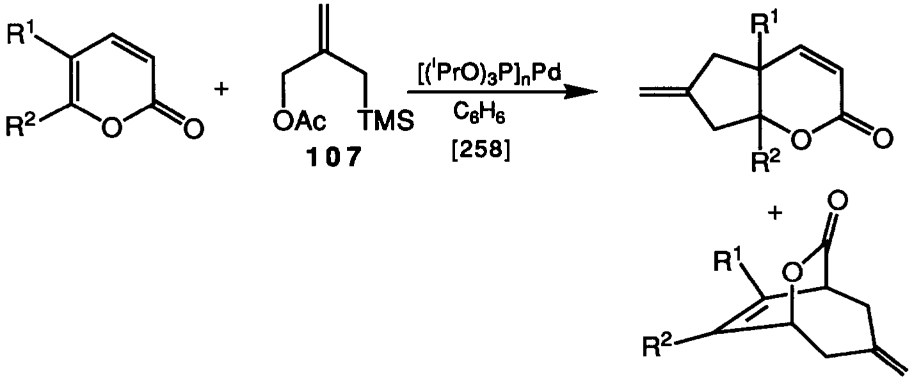


(317)



(318)

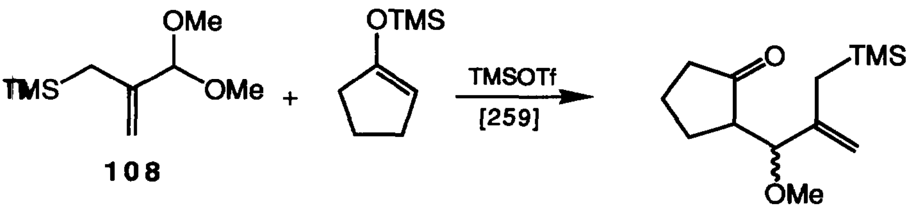
The same allylsilane, **107**, was reacted with pyrones to give the products of [4+3] cycloaddition. (Eqn. 319)



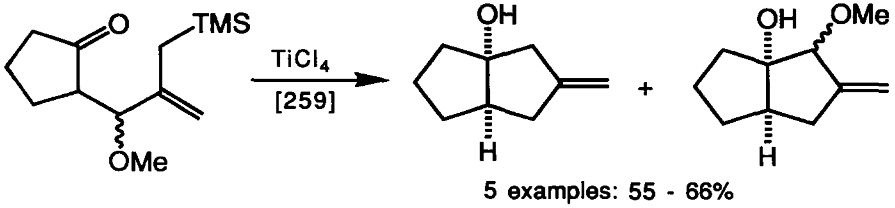
(319)

major product: 7 examples: 23 - 92%

The allylsilane **108** was reacted with enol silyl ethers to give keto allylsilanes, which could be cyclized upon treatment with a Lewis acid. (Eqns. 320 and 321)

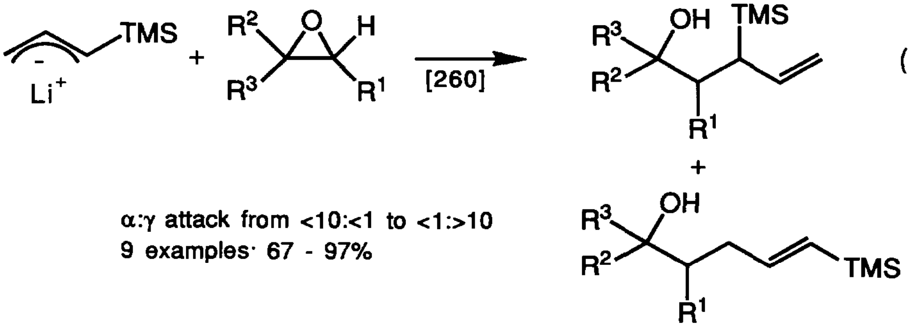


(320)

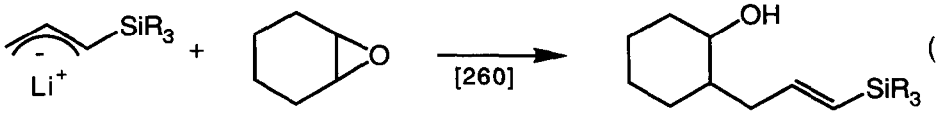


(321)

The lithium reagent derived from allyltrimethylsilane was reacted with epoxides to give both α and γ attack. (Eqns. 322 and 323)



(322)

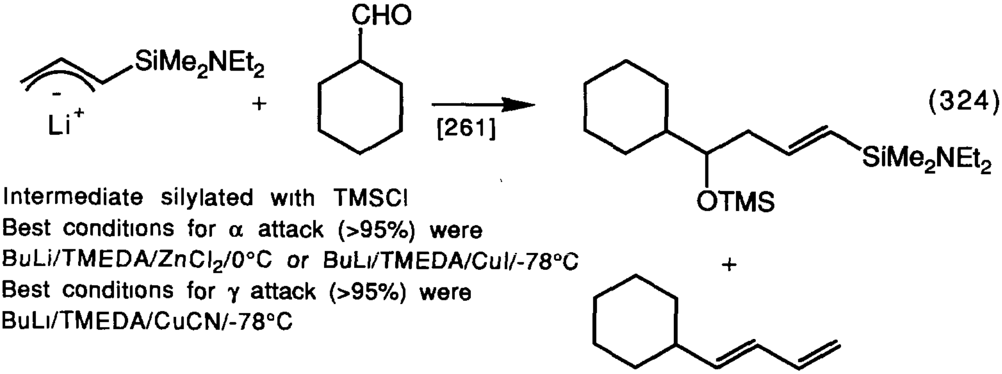


(323)

$SiR_3 = Me_3Si, Ph_3Si, Ph_2MeSi, Me_2CHCMe_2Me_2Si$

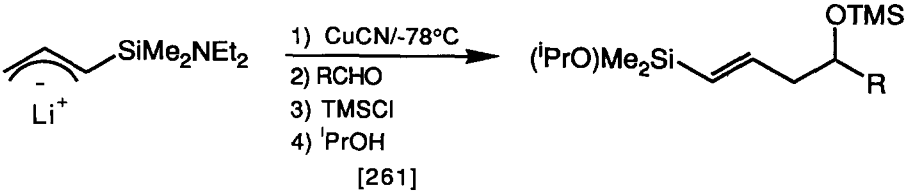
major product

The anion of (diethylamino)allyldimethylsilane was reacted with aldehydes under various conditions to enhance the α or γ attack. (Eqns. 324 and 325) The resulting silanes could be oxidized. (Eqn. 326)

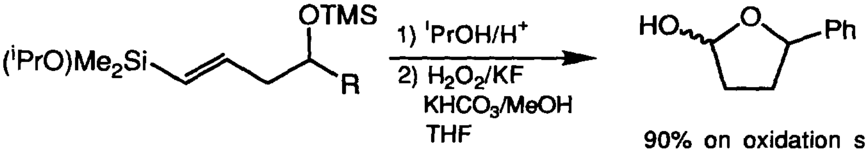


(324)

Intermediate silylated with TMSCl
Best conditions for α attack (>95%) were
$BuLi/TMEDA/ZnCl_2/0°C$ or BuLi/TMEDA/CuI/-78°C
Best conditions for γ attack (>95%) were
BuLi/TMEDA/CuCN/-78°C



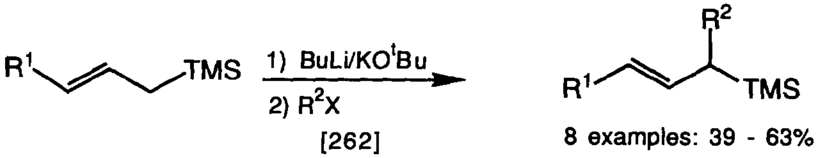
(325)



(326)

90% on oxidation step
for R = Ph

Deprotonation-alkylation of 1-substituted allylsilanes gives the product of α-alkylation predominantly. (Eqn. 327)



(327)

8 examples: 39 - 63%
γ attack ranged from 0 - 39%

(Pentamethylcyclopentadienyl)trimethylsilane was shown to be a good reagent for the transfer of the pentamethylcyclopentadienyl ligand to other metals. (Eqn. 328)

$$Cp^*SiMe_3 + MX_4 \xrightarrow[{[263]}]{} Cp^*MX_3 + TMSX \qquad (328)$$

(MX_4 = $TiCl_4$, $TiBr_4$, TiI_4, $ZrCl_4$ and $HfCl_4$: yields 95.2 - 99%

C. Other Studies

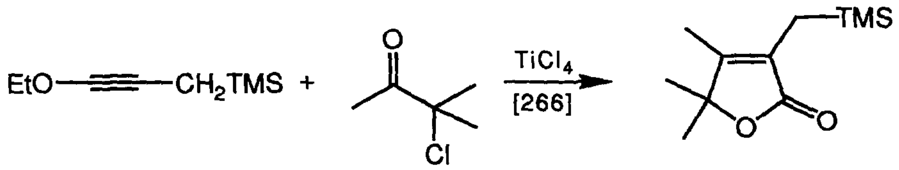
An x-ray study of 3,3,6,6-tetrakis(trimethylsilyl)-1,4-cyclohexadiene was reported. It has a shallow boat conformation with rather long (192 pm) Si-C bonds, which form an angle of about 34° with the π axis contributing to the HOMO destabilization of this compound. [264] An ab initio study of 7-silanorbornadiene and 7,7-dimethyl-7-silanorbornadiene was carried out. [265]

X. PROPARGYLSILANES

1-Ethoxy-3-trimethylsilylpropyne was shown to react with α-chloroketones in the presence of titanium tetrachloride to give dienic esters. (Eqn. 329) When the α-chloro ketone is disubstituted cycliztion occurs with retention of the trimethylsilyl group. (Eqn. 330)

(329)

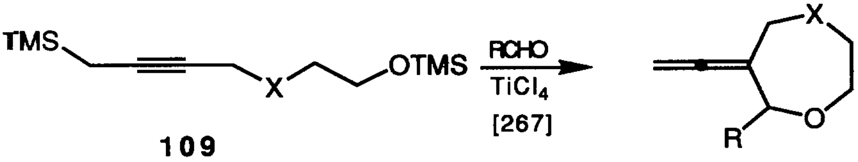
10 examples: 37 - 71%



(330)

44%

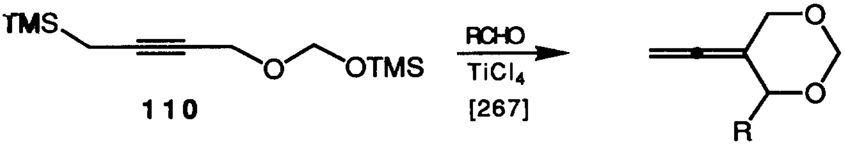
Propargylsilanes **109** and **110** were reacted with aldehydes to give exocyclovinylidene hedterocycles. (Eqns. 331 and 332)



109

(331)

X = O 5 examples: 40 - 87%; X = S 5 examples: 20 - 85%; X = ^{i}PrN 2 examples: 57 - 86%

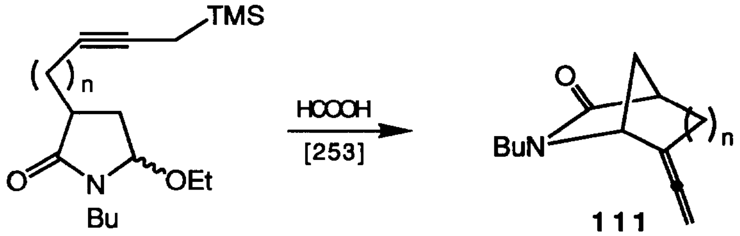


110

(332)

7 examples: up to 95%

Intramolecular cyclizations of propargylsilanes were also reported. The bridged azabicyclic systems **111** were thusly prepared. (Eqn. 333)

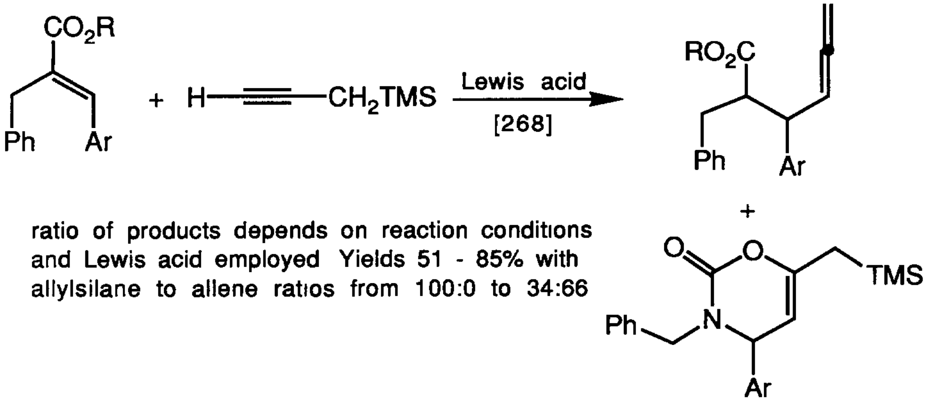


111

(333)

n = 1 82%; n = 2 98%

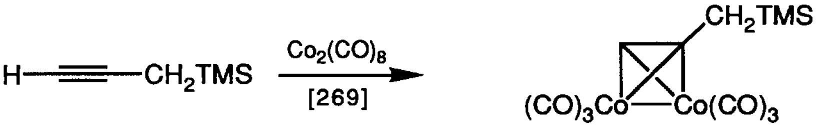
Propargyltrimethylsilane was reacted with N-(alkoxycarbonyl)iminium salts. (Eqn. 334)



(334)

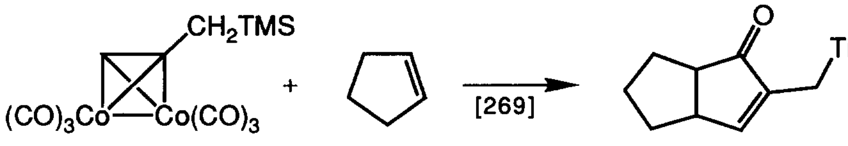
ratio of products depends on reaction conditions and Lewis acid employed Yields 51 - 85% with allylsilane to allene ratios from 100:0 to 34:66

Propargyltrimethylsilane was reacted with dicobalt octacarbonyl to give complex **112**, which was reacted with olefins to give 2-trimethylsilylmethylcyclopentenones. (Eqns. 335 - 337)



112

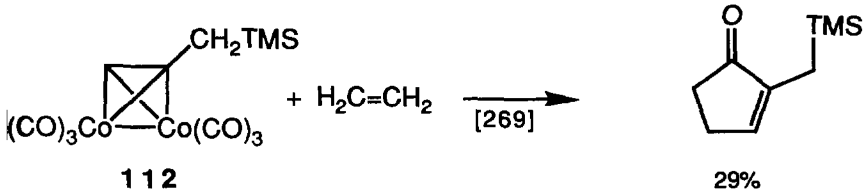
(335)



112

28%

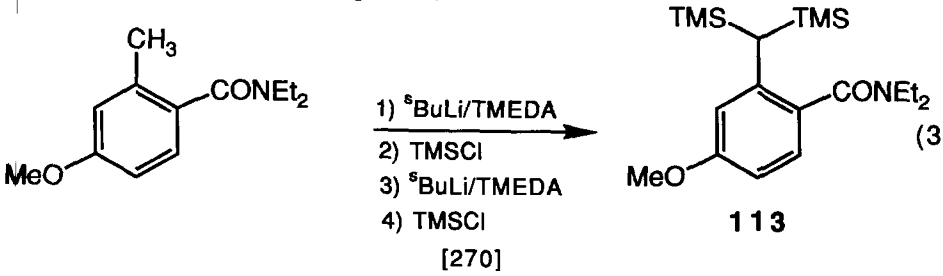
(336)



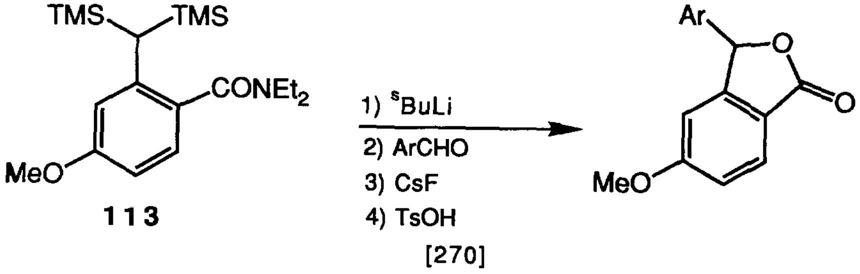
(337)

XI. BENZYLSILANES

1,1-Bis(trimethylsilyl)toluene **113** was formed as shown (Eqn. 338) and then deprotonated again and the anion reacted with aromatic aldehydes. Desilylationa nd cyclizations gives lactones. (Eqn. 339)

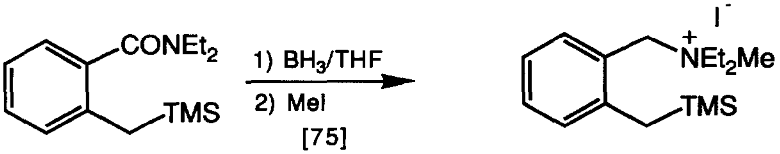


(338)

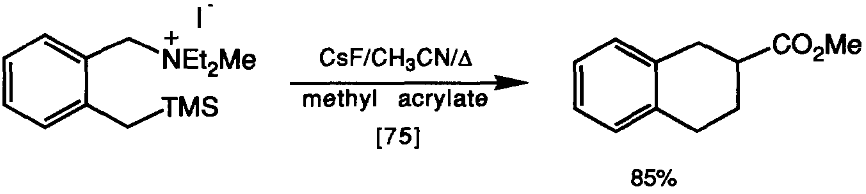


(339)

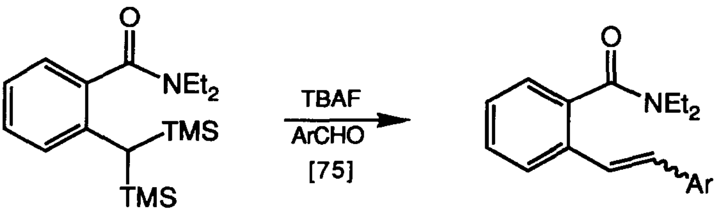
Ortho-trimethylsilylmethyl benzamides were reduced with borane and alkylated with methyl iodide. Treatment of the resulting ammonium salt with fluoride ion in the presence of methyl acrylate gave the Diels-Alder adduct expected from the ortho xylylene. (Eqns. 340 and 341) Treatment of ortho bis(trimethylsilyl)methyl benzamides with fluoride ion in the presence of al aldehyde gives the product of a Peterson olefination. (Eqn. 342)



(340)



(341)

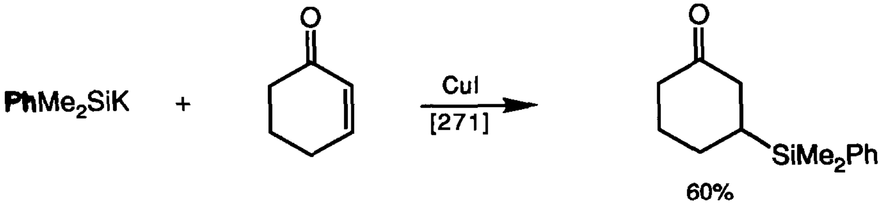


(342)

ArCHO = 3,5-dimethoxybenzaldehyde 74%

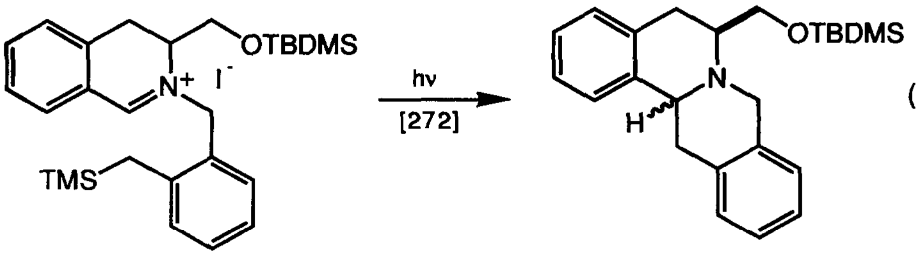
Benzylsilanes were formed by the reaction of a chlorosilane with potassium on graphite followed by the addition of benzyl bromide. (Eqn. 343) A similar silylation occurs with cyclohexeneone in the presence of Cu(I) to enhance the conjugate addition. (Eqn. 344)

$$\mathrm{PhMe_2SiCl} + \mathrm{C_8K} \xrightarrow[\text{[271]}]{} \mathrm{PhMe_2SiK} \xrightarrow{\mathrm{PhCH_2Br}} \underset{90\%}{\mathrm{PhMe_2SiCH_2Ph}} \qquad (343)$$



(344)

The effect of solvent and reaction conditions on the cyclization shown in Eqn. 345 was studied.



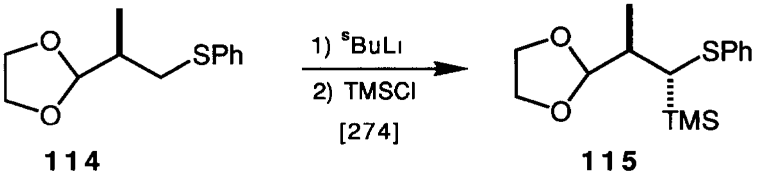
(345)

The sigma value of the Me_3SiCH_2 group was determined from the pKa's of trimethylsilylmethyl substituted benzoic acids. [273]

XII. α-FUNCTIONAL ORGANOSILANES

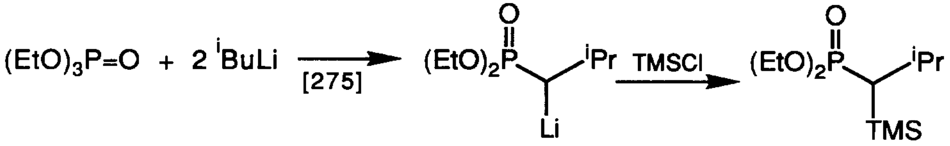
A. Preparation

Sulfide **114** was converted to α-trimethylsilyl sulfide **115** with high diastereoselectivity. (Eqn. 346)



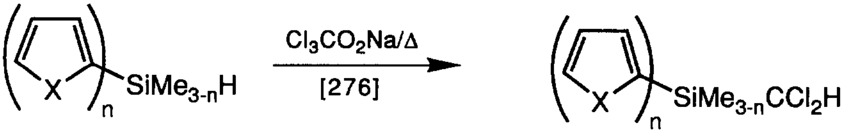
(346)

Triethylphosphate was reacted with two equivalents of isobutyllithium and then trimethylchlorosilane to give the α-silyl phosphonate. (Eqn. 347)



(347)

Sodium trichloroacetate derived dichlorocarbene was inserted into an Si-H bond to give the α,α-dichloromethylsilane. (Eqn. 348)



(348)

X = O, S

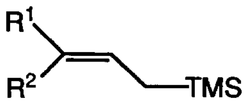
The reaction of chlorosilanes with bromotrifluoromethane in the presence of tris(diethylamino)phosphine gives the corresponding trifluoromethylsilane. This was used to prepare **116**. (Eqn. 349)

$$\mathrm{Cl_2SiHNR_2} + \mathrm{CF_3Br} \xrightarrow[\text{[277]}]{\mathrm{(Et_2N)_3P}} \underset{\textbf{116}}{\mathrm{(CF_3)_2SiHNR_2}} \qquad (349)$$

Trimethylsilylmethyl azide was reduced with lithium aluminum hydride to trimethylsilylmethyl amine, which was reacted with ketones and aldehydes to give α-trimethylsilyl imines. (Eqns. 350 and 351)

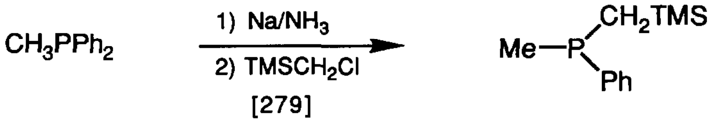
$$\mathrm{TMSCH_2N_3} + \mathrm{LiAlH_4} \xrightarrow[\text{[278]}]{} \mathrm{TMSCH_2NH_2} \qquad (350)$$

$$\mathrm{TMSCH_2NH_2} + \mathrm{R^1R^2C{=}O} \xrightarrow[\text{[278]}]{} \qquad (351)$$

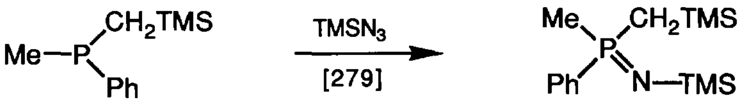


4 examples. 85 - 91%

Methyldiphenylphosphine was metalated and trimethylsilylmethylated. (Eqn. 352) Reaction of the trimethylsilylmethyl derivative with trimethylsilyl azide was carried out as well. (Eqn. 353)

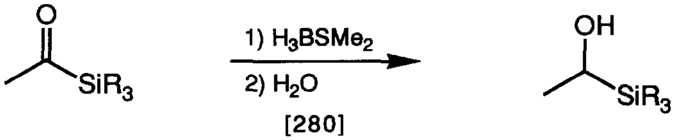


(352)



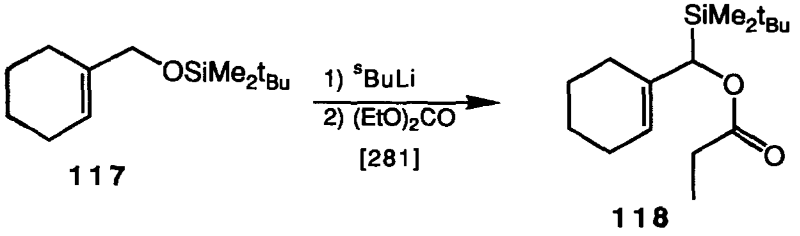
(353)

The borane reduction of acylsilanes was used to give α-hydroxysilanes. (Eqn. 354)

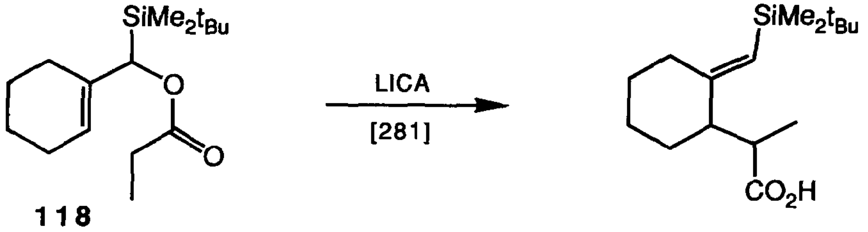


(354)

The tert-butyldimethylsilyl allyl alcohol **117** was treated with sec-butyllithium and then diethyl carbonate to give the α-silyl ester **118**, which underwent a Claisen rearrangement upon treatment with base. (Eqns. 355 and 356)



(355)



(356)

B. Reactions

The gas phase thermolysis of (chlormethyl)arylmethylsilanes resulted in the preferential migration of the hydrogen atom from silicon with a lesser amount of aryl migration. (Eqn. 357) On the other hand the aryl group migrates preferentially to the methyl group. (Eqn. 358)

$$\mathrm{ArMeHSiCH_2Cl} \xrightarrow[\text{gas phase}]{\Delta} \underset{\text{major}}{\mathrm{ArMe_2SiCl}} + \underset{\text{minor}}{\mathrm{MeClHSiCH_2Ar}} \quad (357)$$

[282]

$$\mathrm{ArMe_2SiCH_2Cl} \xrightarrow[\text{gas phase}]{\Delta} \underset{\text{major}}{\mathrm{ClMe_2SiCH_2Ar}} + \underset{\text{minor}}{\mathrm{ArMeClSiCH_2CH_3}} \quad (358)$$

[282]

Esters of hydroxymethylsilanes were thermolyzed as well. In this case a hydrogen migrates from silicon in preference to a trimethylsilylmethyl group. (Eqn. 359)

$$\mathrm{(TMSCH_2)H_2SiCH_2O_2CR} \xrightarrow[\text{[283]}]{\Delta} \mathrm{(TMSCH_2)H(RCO_2)SiCH_3} \qquad (359)$$

The reaction of iodomethyltrimethylsilane with alkoxide ion gives alkoxytrimethylsilanes as a result of attack at silicon and cleavage of the Si-C bond with loss of methyl iodide, which is converted to the methyl ether. (Eqn. 360)

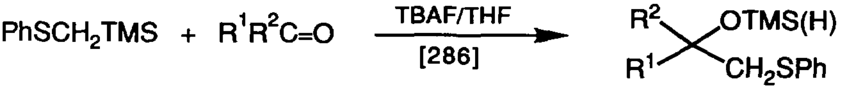
$$\mathrm{TMSCH_2I + RONa} \xrightarrow[\text{[284]}]{} \mathrm{TMSOR + ROMe} \qquad (360)$$

Interestingly, the reaction of phenoxy or anilino chloromethylsilanes with fluoride ion results in the migration of the phenoxy or anilino group from silicon to carbon. (Eqn. 361)

$$\mathrm{PhEMe_2SiCH_2Cl} \xrightarrow[\text{[285]}]{\mathrm{KF/CH_3CN}} \mathrm{FMe_2SiCH_2EPh} \qquad (361)$$

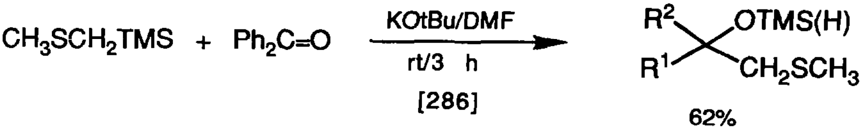
E = O 85%; NMe 90%

Several reactions of α-functional organosilanes with fluoride as an initiator or mediator were reported. Thiophenoxymethyltrimethylsilane was reacted with ketones and aldehydes in the presence of fluoride ion to igve thiophenoxymethylation of the carbonyl. (Eqn. 362) (Trimethylsilylmethyl)methyl sulfide gives a similar reaction with benzophenone in the presence of tert-butoxide. (Eqn. 363)



(362)

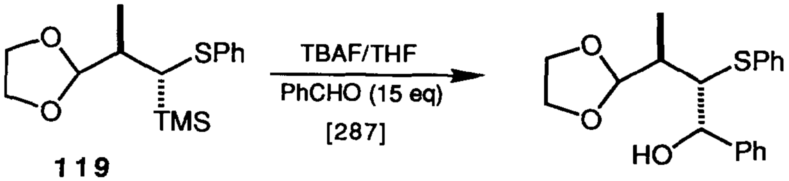
7 examples: 45 - 96%



(363)

62%

A similar reaction was used with the α-thiophenoxysilane **119** and **120** with benzaldehyde. The stereoselectiviyt of the reaction is very high. (Eqns. 364 and 365)

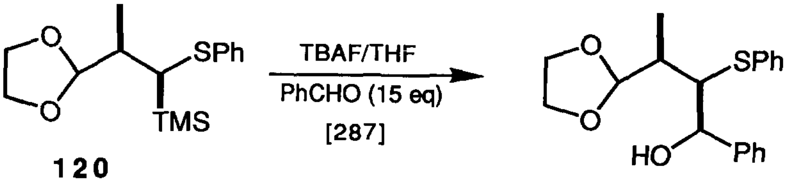


(364)

119

anti:syn = 97·3

anti:syn = 94:6



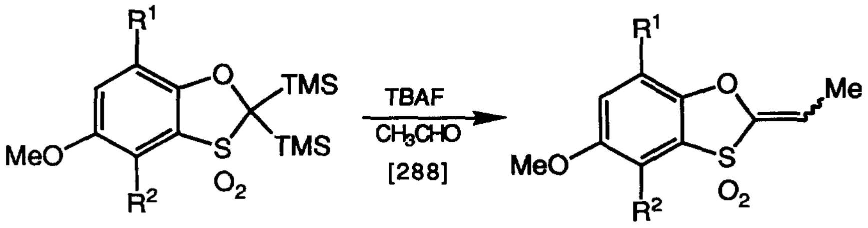
(365)

120

anti:syn = 25:75

anti:syn = 25:75

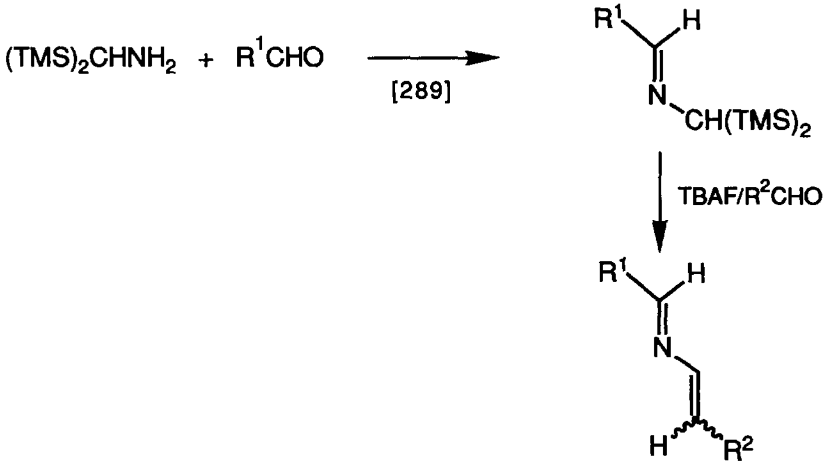
Reaction of the α,α-bis(trimethylsilyl)sulfone **121** with fluoride ion in the presence of acetaldehyde gives the product of addition followed by Peterson elimination. (Eqn. 366)



121

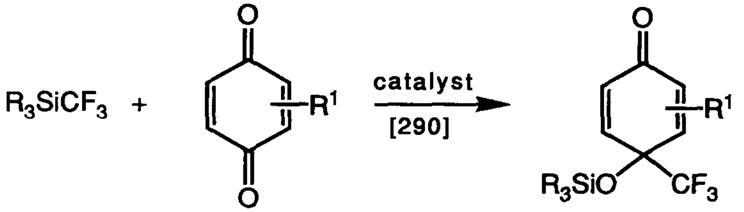
(366)

Bis(trimethylsilyl)methylamine was converted to the corresponding imines, which upon treatment with fluoride ion in the presence of an aldehyde gives 2-aza-1,3-dienes. (Eqn. 367)



(367)

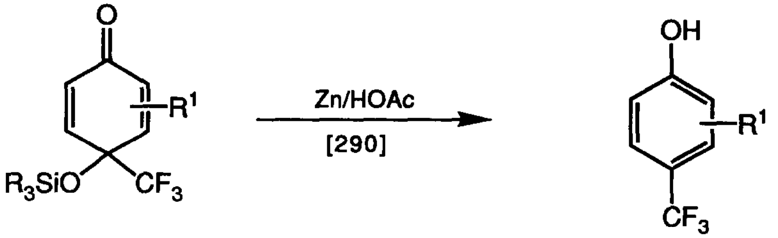
Trifluoromethylsilanes were shown to react with quinones in a route to trifluoromethyl substituted phenols and anilines. (Eqns. 368 - 370)



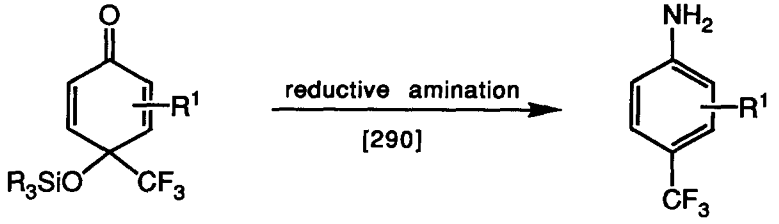
(368)

7 examples: 44 - 90%

(several catalysts used including CsF, KHF_2, NaCN, NaOH, LiN_3, and others)

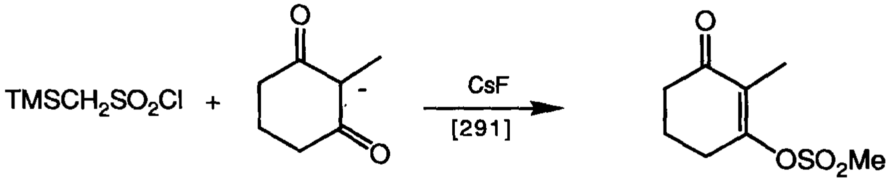


(369)



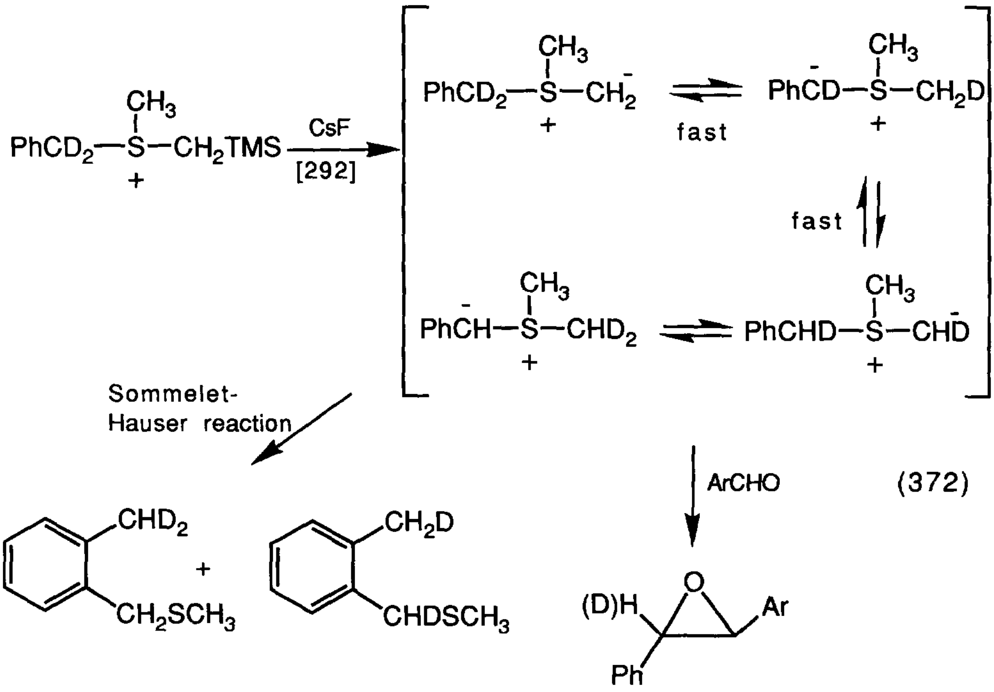
(370)

The attempted interception of $CH_2{=}SO_2$, generated from trimethylsilylmethylsulfonyl chloride and fluoride ion, by the enolate of 2-methylcyclohexane-1,3-dione gave only the methyl sulfonate. (Eqn. 371) Similar results were obtained with other 1,3-diketone enolates.



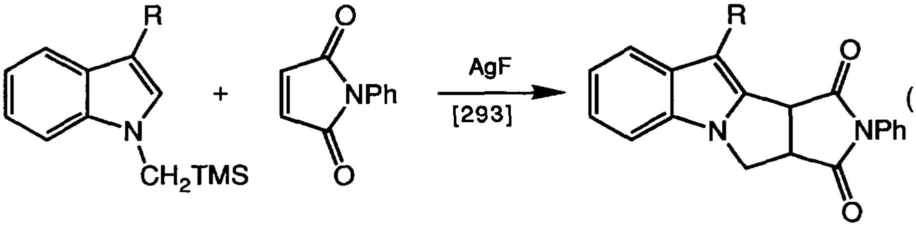
(371)

Desilylation of (trimethylsilylmethyl)benzylmethyl sulfonium salts with fluoride ion gives sulfur ylides. These were shown to equilibrate with the more stable phenyl stabilized ylides. (Eqn. 372)



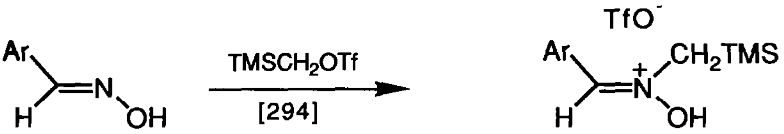
(372)

Treatment of N-trimethylsilylmethyl substituted indoles with fluoride ion in the presence of dipolarophiles gives the dipolar addition product. (Eqn. 373)

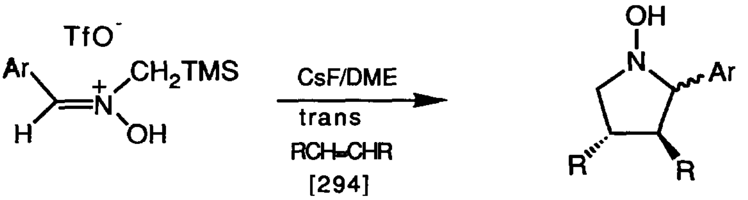


(373)

The reaction of aryl substituted oximes with trimethylsilylmethyl triflate gives the corresponding silyl iminium salt, which upon treatment with cesium fluoride in the presence of an appropriate olefin gives the cycloadduct. (Eqns. 374 and 375) A mechanism involving deprotonation and silyl migration is proposed to explain the reaction.

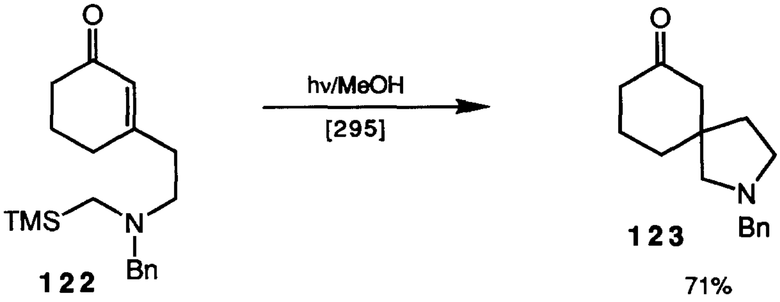


(374)



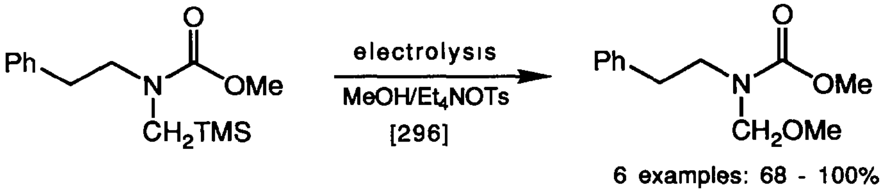
(375)

Photolysis of **122** gives **123** *via* a single electron transfer cyclization process. (Eqn. 376)



(376)

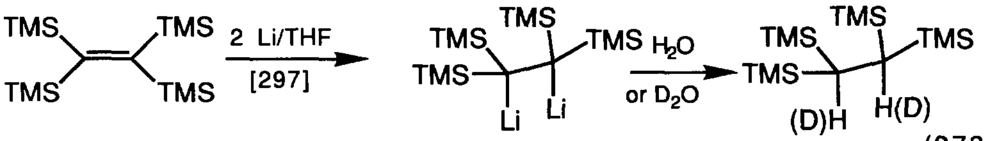
N-Trimethylsilyl carbamates were shown to give N-methoxymethyl carbamates upon electrolysis in methanol. (Eqn. 377)



(377)

C. α-Metalated Organosilanes

Tetrakis(trimethylsilyl)ethylene was shown to react with lihtium metal in tetrahydrofuran to give the dilithio derivative. (Eqn. 378)



(378)

Thermolysis of trimethylsilyllithium results in elimination of tetramethylsilane and formation of α,α-dilithiotrimethylsilylmethane. (Eqn. 379) The same reaction with bis(trimethylsilyl)methyllithium gives bis(trimethylsilyl)dilithiomethane. (Eqn. 380)

$$\mathrm{TMSCH_2Li} \xrightarrow[\substack{-\mathrm{Me_4Si} \\ {[298]}}]{150^\circ\mathrm{C}} \mathrm{TMSCHLi_2} \xrightarrow{\mathrm{MeOD}} \mathrm{TMSCHD_2} \qquad (379)$$

$$\mathrm{(TMS)_2CHLi} \xrightarrow[\substack{-\mathrm{Me_4Si} \\ {[298]}}]{150^\circ\mathrm{C}} \mathrm{(TMS)_2CLi_2} \xrightarrow{\mathrm{MeOD}} \mathrm{(TMS)_2CD_2} \qquad (380)$$

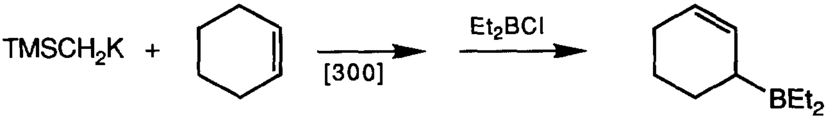
The reaction of bis(trimethylsilyl)dichloromethane with sublimed lithium metal or with 4,4'-di-tert-butylbiphenyl (LiDBB) gives bis(trimethylsilyl)dilithiomethane, which was reacted with seveal electrophiles. (Eqn. 381)

$$\mathrm{(TMS)_2CCl_2} + \mathrm{Li\ (or\ LiDBB)} \xrightarrow[{[299]}]{} \mathrm{(TMS)_2CLi_2} \longrightarrow \mathrm{(TMS)_2CE_2} \qquad (381)$$

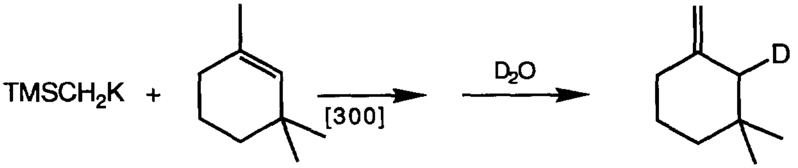
E^+ = EtOD, MeI, EtI, TMSCl, Me_3GeCl, Me_3SnCl, Me_2SO_4, PhCHO, cyclohexanone gives proton transfer

Trimethylsilylmethylpotassium was prepared from the reaction of bis(trimethylsilylmethyl)mercury and potassium metal. It was shown to deprotonate olefins. (Eqns. 382 - 384) In one application the thusly deprotonated olefins were reacted with diethylboron chloride to give an allylborane which was reacted with acetaldehyde to give homoallylic alcohols. (Eqn. 385)

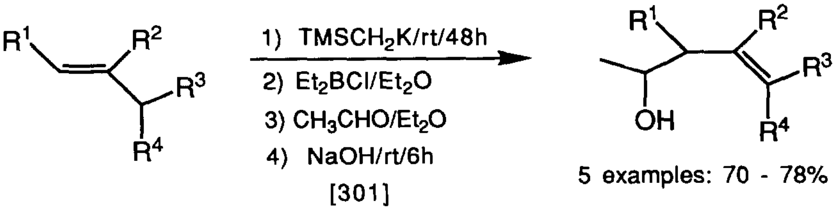
$$(TMSCH_2)_2Hg + K \xrightarrow[{[300]}]{} 2\,TMSCH_2K \qquad (382)$$



(383)



(384)



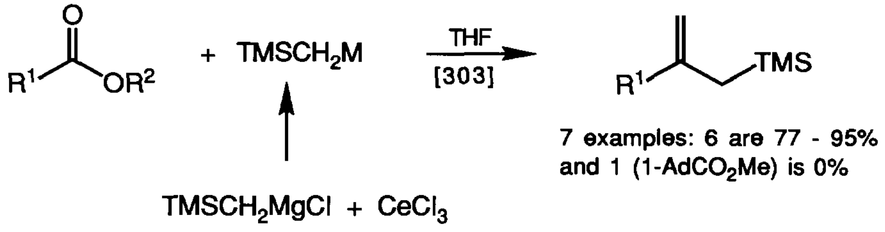
(385)

Trimethylmethoxysilane was shown to react with tert-butyllithium in cyclopentane to give deprotonation of a silyl methyl group rather than substitution. (Eqn. 386) A similar reaction takes place with methoxymethyltrimethylsilane. (Eqn. 357)

$$\text{TMSOMe} \xrightarrow[\text{[302]}]{{}^{t}\text{BuLi/c-C}_5\text{H}_{10}} \text{MeOSiMe}_2\text{CH}_2\text{Li} \xrightarrow{\text{TMSCl}} \text{MeOSiMe}_2\text{CH}_2\text{TMS} \qquad (386)$$

$$\text{MeOCH}_2\text{TMS} \xrightarrow[\text{[302]}]{{}^{t}\text{BuLi/c-C}_5\text{H}_{10}} \text{MeOCH}_2\text{SiMe}_2\text{CH}_2\text{Li} \longrightarrow \text{MeOCH}_2\text{SiMe}_2\text{CH}_2\text{D} \qquad (387)$$

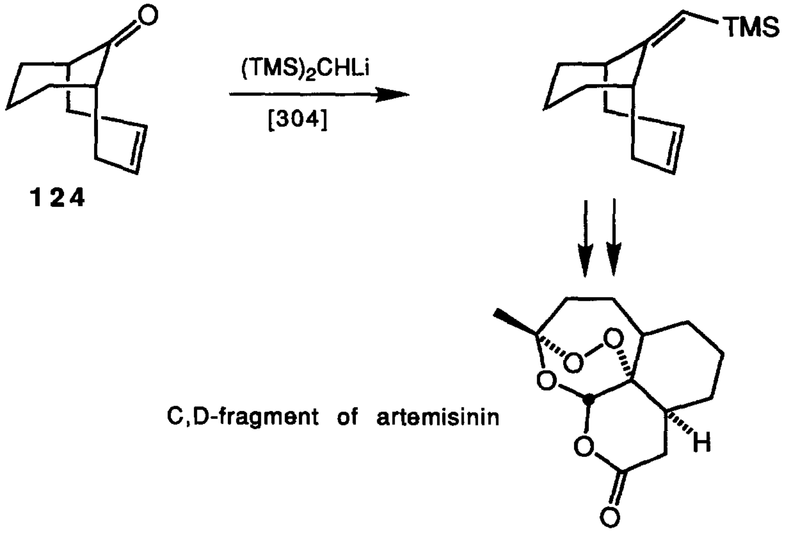
The organometallic derivative formed from the reaction of trimethylsilylmethylmagnesium chloride and cerium(III) chloride reacts with esters to give allylsilanes, presumably *via* the intermediacy of an α-silyl ketone. (Eqn. 388)



7 examples: 6 are 77 - 95% and 1 (1-AdCO$_2$Me) is 0%

(388)

The reaction of bis(trimethylsilyl)methyllithium with ketone **124** was used in the preparation of the C,D-ring fragment of artemisinin. (Eqn. 389)



124

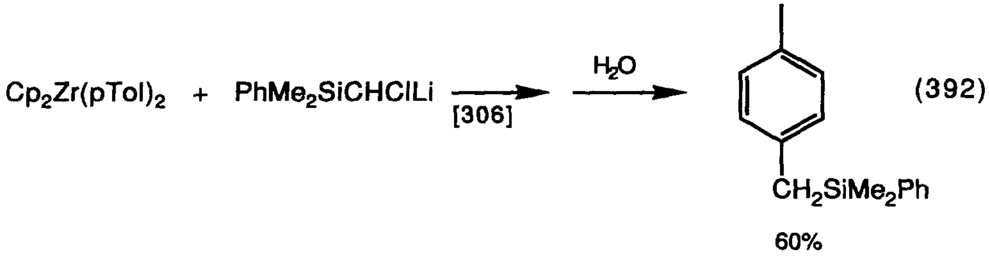
(389)

Bis(trimethylsilyl)methyllithium was reacted with aluminum trichloride to give bis(trimethylsiyl)methylaluminum chloride, reduction of which with potassium gives the dialane. (Eqn. 390) The x-ray structure shows it to be nearly planar with an Al-Al bond length of 266.0 pm.

$$\begin{tikzcd}
(TMS)_2CHLi + AlCl_3 \arrow[r, "Et_2O", "{[305]}"'] & {[(TMS)_2CH]_2AlCl} \arrow[d, "2\ K"] \\
 & {[(TMS)_2CH]_2Al\text{-}Al[CH(TMS)_2]} \\
 & 59\%
\end{tikzcd} \qquad (390)$$

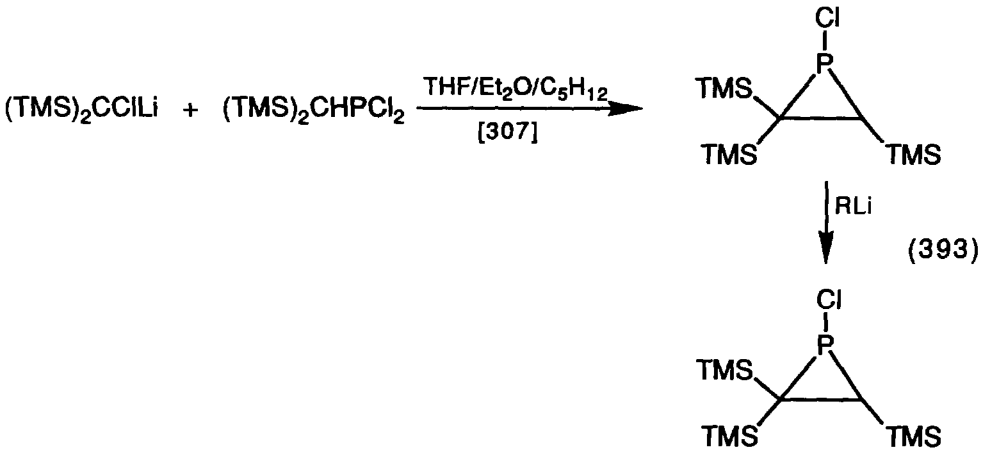
(Trimethylsilyl)chloromethyllithium and (phenyldimethylsilyl)chloromethyllithium were used to probe the migratory insertion reactions of various transition metal organometallics. (Eqns. 391 and 392)

$$Bu_2Mn + PhMe_2SiCHClLi \xrightarrow[\text{[306]}]{} \xrightarrow{H_2O} \underset{88\%}{BuCH_2SiMe_2Ph} \qquad (391)$$



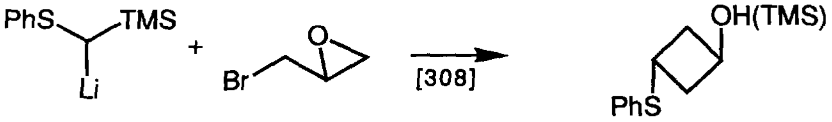
(392)

Bis(trimethylsilyl)chloromethyllithium was reacted with bis(trimethylsilyl)-methyldichlorophosphine to give a 1-chlorophosphirane, which could be substituted without ring opening. (Eqn. 393)



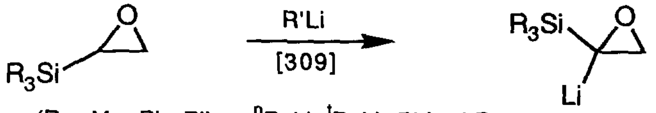
(393)

Lithiated thiophenoxymethyltrimethylsilane was reacted with the epoxide of allyl bromide to give phenylthiocyclobutanols *via* a 1,4-silyl migration of silicon from carbon to oxygen. (Eqn. 394)



(394)

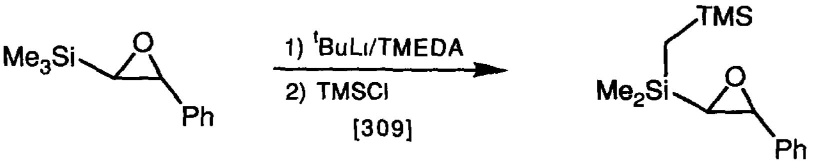
α-Epoxysilanes were shown to be deprotonated at the α-position with several strong bases. The lithium reagent was quenched with several electrophiles. (Eqn. 395) The presence of a β-phenyl group, however lead to deprotonation of one of the silicon methyl groups. (Eqn. 396)



(395)

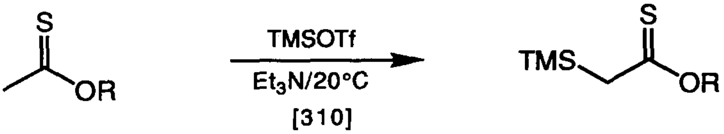
(R = Me, Ph; R'Li = ^{n}BuLi, ^{t}BuLi, PhLi, LDA)

quenched with H_2O, D_2O, TMSCl, MeI, Me_3SnCl benzoylaziridine

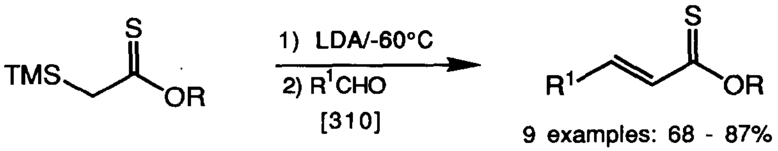


(396)

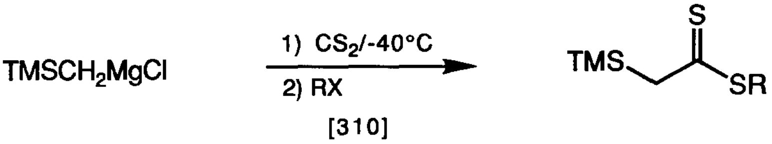
α-Trimethylsilyl thiono and dithiono esters, prepared as shown were deprotonated and the lithium reagent condensed with aldehydes and ketones to give α,β-unsaturated thiono and dithio esters. (Eqns. 397 - 400)



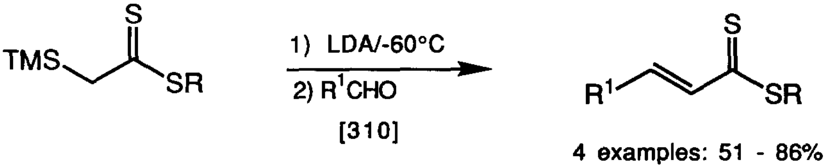
(397)



(398)

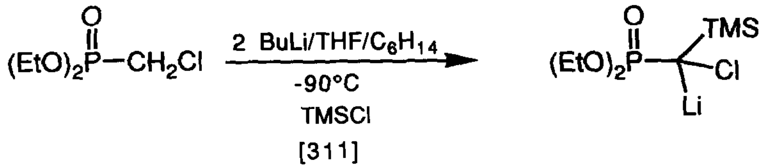


(399)

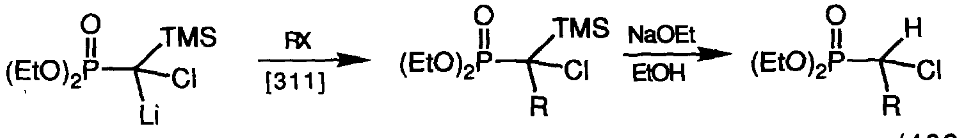


(400)

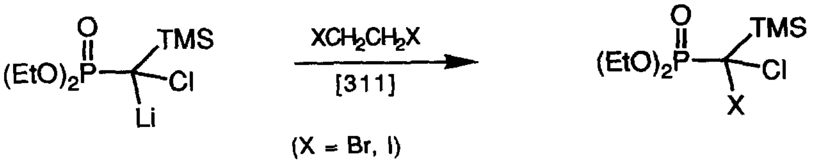
(Chloromethyl)diethylphosphonate was deprotonated and trimethylsilylated to give as an intermediate (trimethylsilylchloromethyl)diethylphosphonate, which was further deprotonated by the presence of a second equivalent of base. The resulting lithium reagent was reacted with various electrophiles. (Eqns. 401 - 404)



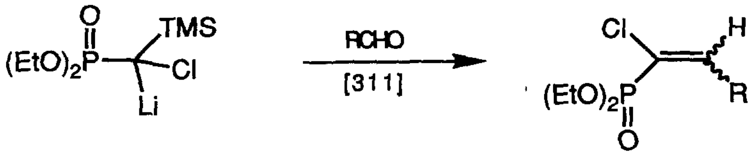
(401)



(402)

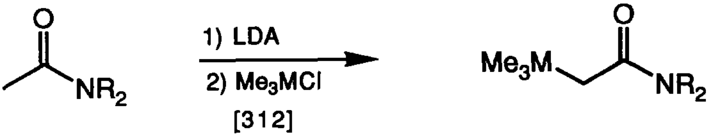


(403)

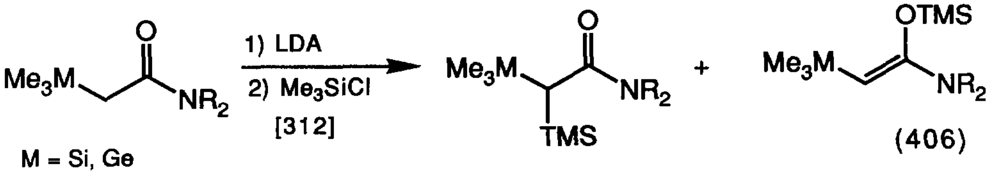


(404)

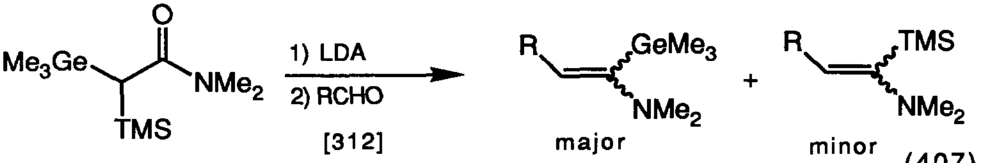
N,N-Dialkylacetamides were deprotonated and metalated with trimethylchlorosilane and trimethylchlorogermane. (Eqn. 405) The α,α-bis(trimethylsilyl)acetamides were also present mixed with the tautomeric O-silylated material. (Eqn. 406) Deprotonation of the α-trimethylsilyl-α-trimethylgermyl acetamide followed by condensation with an aldehyde gave principally the product of loss of the trimethylsilyl group rather than the trimethylgermyl group. (Eqn. 407)



(405)

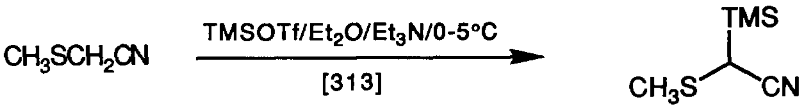


(406)

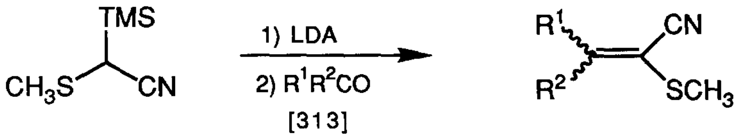


(407)

α-Cyano substituted vinyl sulfides were prepared starting from cyanomethylmethyl sulfide and proceding through an α-trimethylsilyl lithium reagent as shown below. (Eqns. 408 and 409)



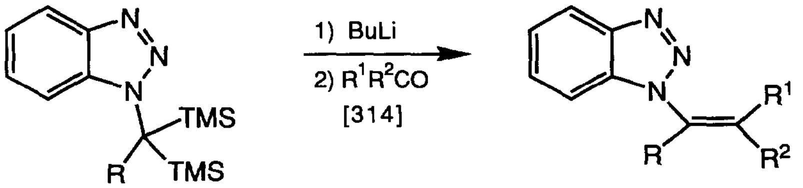
(408)



15 examples: 41 - 95%
E>Z

(409)

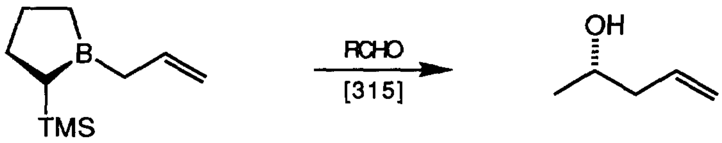
The bis(trimethylsilyl)benzotriazole **125** was reacted with butyllithium to remove one of the trimethylsilyl groups. The resulting α-trimethylsilyllithium reagent was condensed with aldehydes and ketones to give the Peterson olefination product. (Eqn. 410)



125

(410)

The α-borylsilane **126** was shown to allylate aldehydes with very high enantiomeric excess and yield. (Eqn. 411) The R enantiomer was also prepared and studied.



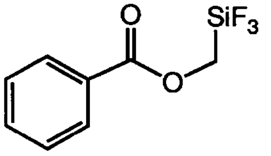
126

7 examples. 92 - 97% ee and 80 - 92% yield

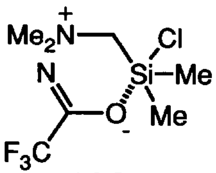
(411)

D. Other Studies

A differential scanning calorimetry study was carried out on the thermal rearrangement of α-substituted silanes. [316] The crystal and molecular structures of a variety of trifluoromethylsilanes were determined. [317] The infrared spectrum of **127** was reported with an analysis in terms of Si-O interaction. [318] The synthesis and structure of **128** were reported. [319]



127

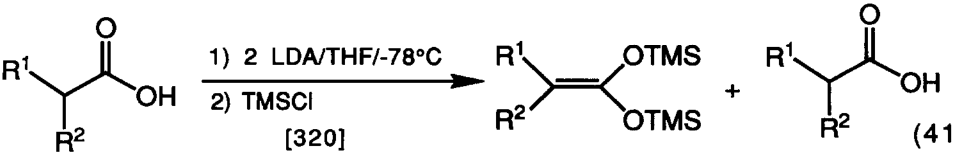


128

XIII. β-FUNCTIONAL ORGANOSILANES

A. Preparation

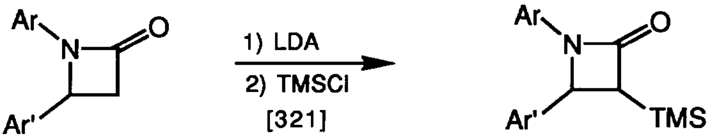
α-Trimethylsilyl trimethylsilyl esters were prepared directly from carboxylic acids. The ratio of C-O silylation depends on the structure of the carboxylic acid with the more hindered acids giving more C-silylation. (Eqn. 412) A combination of thermodynamics and steric effects are presented to explain the results.



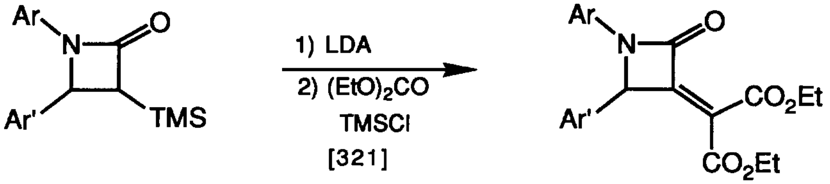
(412)

R¹	R²			% Yield
H	H	100	0	70
Me	H	80	20	65
Et	H	50	50	56
Me	Me	24	76	84
^{i}Pr	H	0	100	79
^{t}Bu	H	0	100	60

The direct C-silylation of azetidinones was used to prepare ylidene azetidinones. (Eqns. 413 and 414)

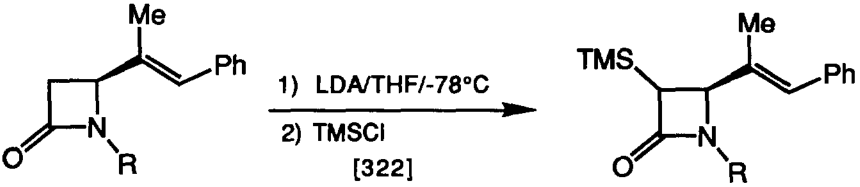


(413)



(414)

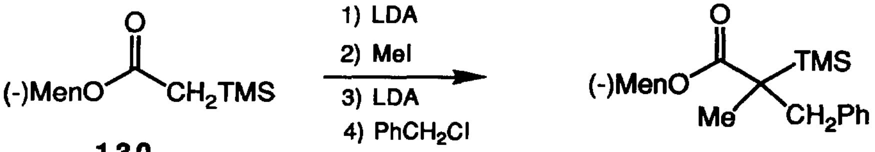
The C-silylation of **129** was used in the synthesis of carbapenum antiobiotics. (Eqn. 415)



129

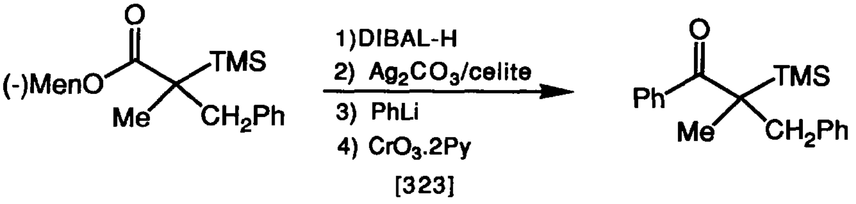
(415)

The α-silyl ester **130** was alkylated and then methylated to give **131** as a mixture of diastereomers. (Eqn. 416) The same materials, but with a different diastereomeric ratio, could be obtained by a silylation-alkylation sequence on menthyl propionate. The purified diastereomers were converted to α-silyl ketones which were subjected to Haller-Bauer cleavage. This occurred with retention at the carbon. (Eqns. 417 and 418)

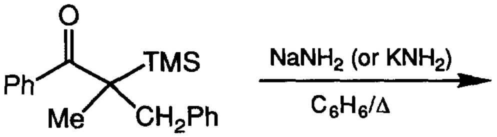


130 **131**

(416)

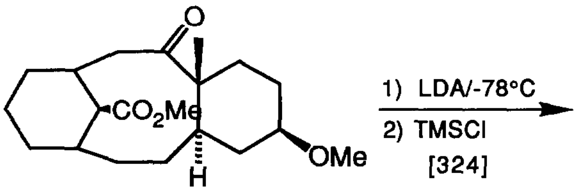


(417)



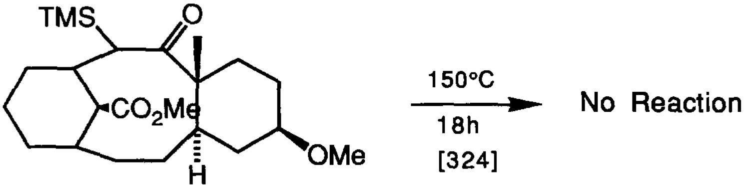
(418)

The deprotonation-trimethylsilylation of **132** gives the α-trimethylsilyl ketone rather than the silyl enol ether. This is the first report of the direct C-silylation of the enolate of a ketone. (Eqn. 419) Moreover the α-silyl ketone was not rearranged at 150°C for 18 h, conditions which are known to convert α-silyl ketones to their enol silyl ethers within 1 h. (Eqn. 420)



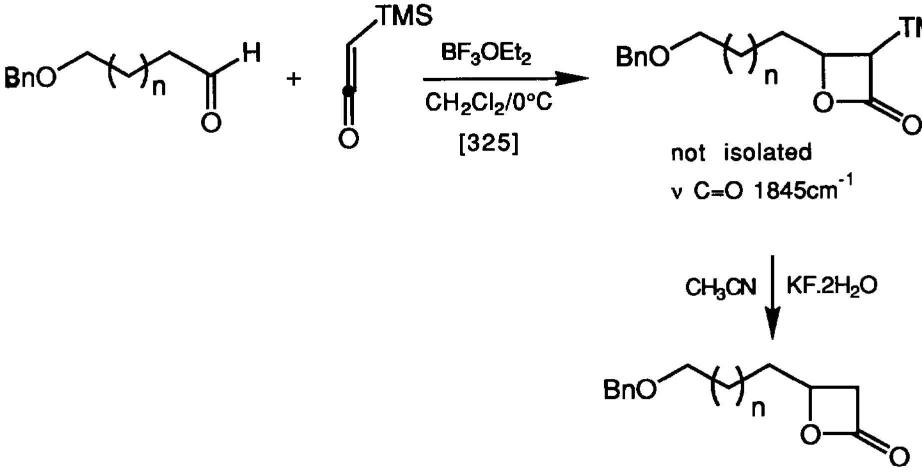
132

(419)



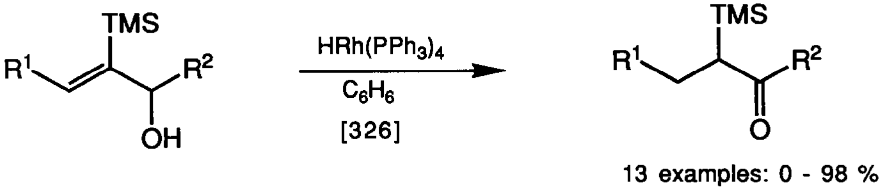
(420)

The acid catalyzed reaction of aldehydes with trimethylsilyl ketene gives α-trimethylsilyl β-lactones. These were not isolated, but desilylated with fluoride ion. (Eqn. 421)

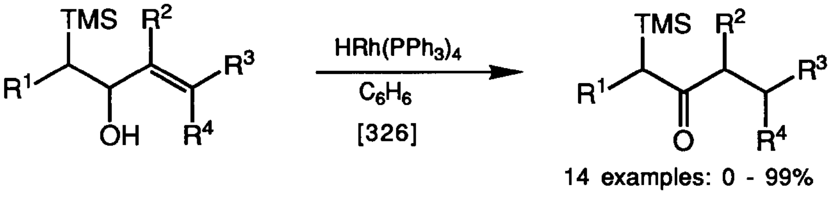


(421)

A full account of the rearrangement of 2-trimethylsilyl-3-hydroxy alkenes to α-silyl ketones was published. The general reaction is shown in Eqns. 422 and 423.

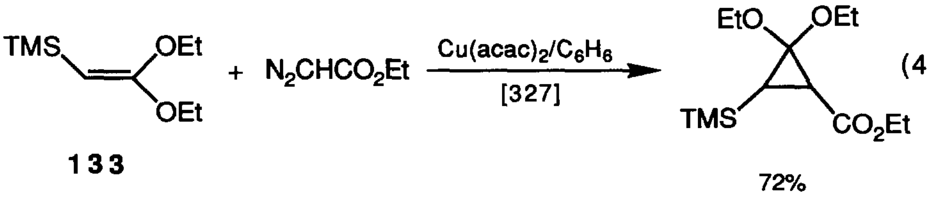


(422)



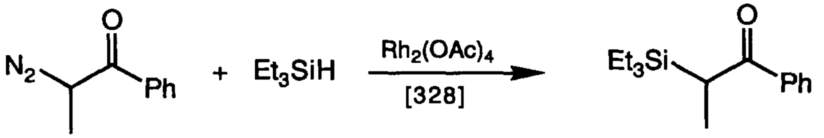
(423)

Diazo compounds served well for the formation of α-silyl carbonyl systems. The reaction of ethyl diazoacetate with **133** the α-silylcyclopropanone as the ketal. (Eqn. 424)



(424)

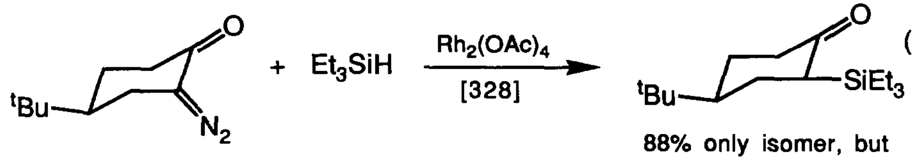
The reaction of silanes with α-diazo ketones or esters was shown to give the α-silyl carbonyl compound in good yields. (Eqns. 425 - 427)



(425)

90% including 10% of the silyl enol ether

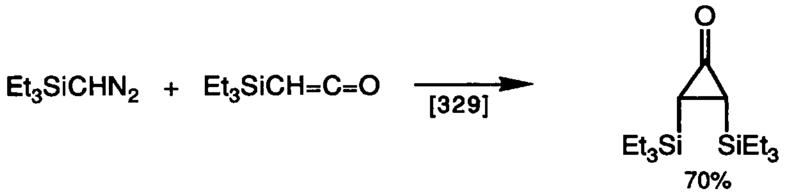
$$N_2CHCO_2Et + Me_3SiH \xrightarrow[{[328]}]{Rh_2(OAc)_4} TMSCH_2CO_2Et \qquad (426)$$



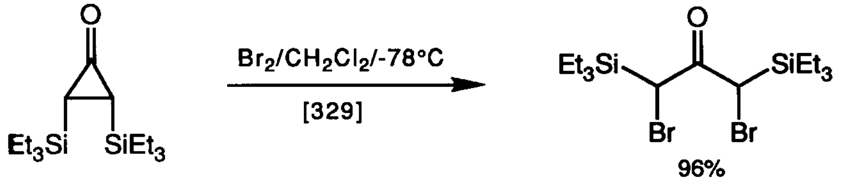
(427)

88% only isomer, but 10 % of silyl enol ether also present

The reaction of triethylsilyldiazomethane with triethylsilyl ketene was reported to give the α,α'-bis(triethylsilyl)cyclopropanone. (Eqn. 428) This was reacted with bromine to give ring cleavage without desilylation. (Eqn. 429)

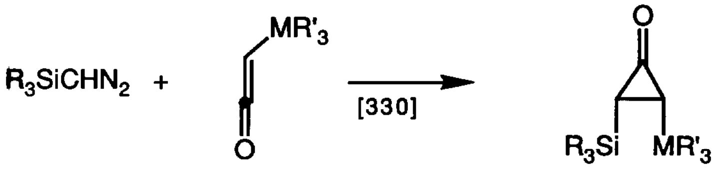


(428)

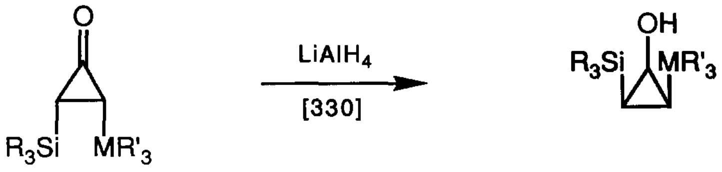


(429)

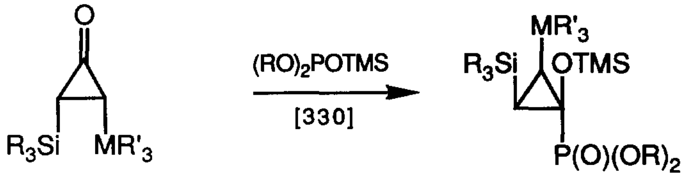
Trialkylsilyldiazomethanes were reacted with silyl (or germyl) ketenes to give again the α-silylcyclopropanones. (Eqn. 430) These were subjected to some other reactions. (Eqns. 431 and 432)



(430)

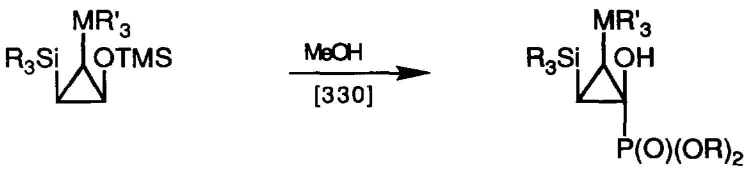


(431)



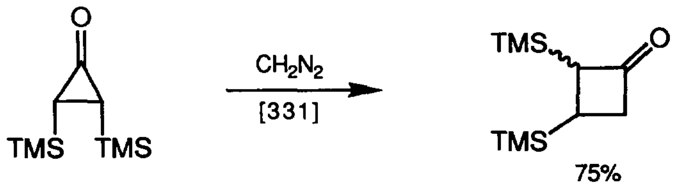
(432)

(R_3Si = Me_3Si, $MeEt_2Si$; R'_3M = Me_3Si, $MeEt_2Si$, Et_3Ge)

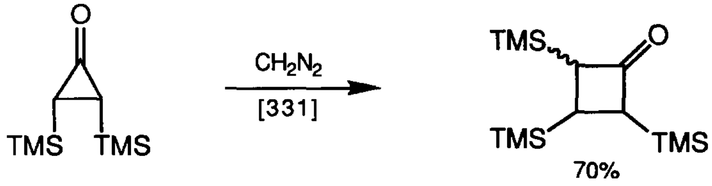


(433)

The reaction of α-silylcyclopropanones with diazomethane gives the ring expanded α-silyl cyclobutanone. (Eqn. 434) The reaction with trimethylsilyldiazomethane gives the silylated derivative. (Eqn. 435)



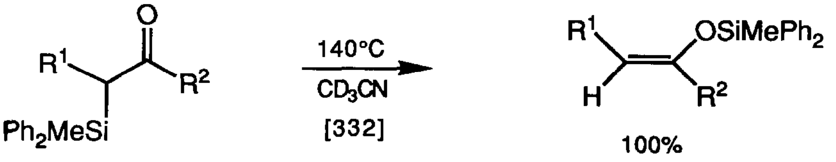
(434)



(435)

B. Reactions

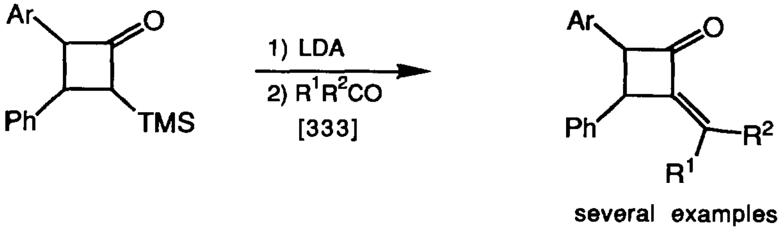
It was shown that α-(methyldiphenylsilyl)ketones could be rearranged in a stereospecific manner to the (Z) enol silyl ethers in CD_3CN. (Eqn. 436) When carried out in the absence of solvent or other solvents a mixture of isomers was obtained.



(436)

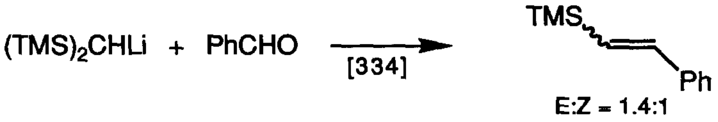
$R^1 = Me, {}^nC_8H_{17}$; $R^2 = Et, Ph, {}^tBu, Pr$

α-Trimethylsilyl azetidiones were deprotonated and reacted with ketones and aldehydes to give α-alkylidene azetidinones. (Eqn. 437)

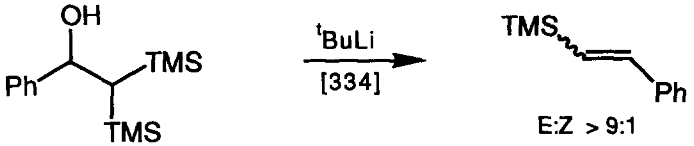


(437)

It was found that the intermediate β-oxidosilane derived from bis(trimethylsilyl)methyllithium and benzaldehyde gives Z and E β-trimethylsilyl styrene in a ratio of 1.4:1, whereas that derived from 2,2-bis(trimethylsilyl)-1-phenylethano and tert-butyllithium gives > 90% E β-trimethylsilylstyrene. (Eqns. 438 and 439) It is argued that in the Peterson olefination there is not a well defined β-oxidosilane.

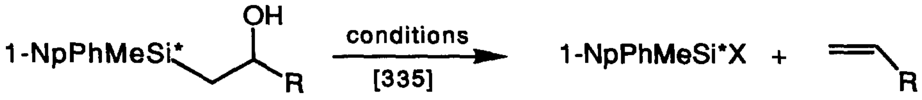


(438)



(439)

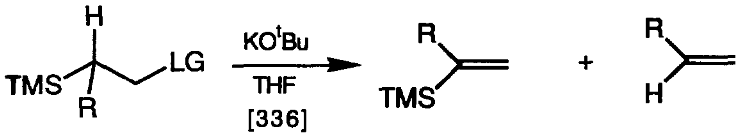
β-(1-naphthylphenylmethylsilyl) alcohols, optically active at silicon were prepared from the silylmethyllithium reagent and aldehydes. (Eqn. 440) These were subjected to various elimination conditions and the stereochemistry at silicon determined for each. The observed inversion at silicon for acid catalyzed elimination and retention with base catalyzed elimination is consistent with expectations.



(440)

conditions	X	Stereochemistry
BF_3OEt_2	F	Inversion
HOAc/NaOAc	OAc	Inversion
H_2SO_4/THF/H_2O	OH	Inversion
KH/THF/then H_2O	OH	Retention

The treatment of various trimethylsilyl alkanes with leaving groups in the b-position with potassium tert-butoxide leads to loss of either a proton or the trimethylsilyl group. (Eqn. 441)



(441)

LG	k_{obs}(rel)	%Si attack	% H attack
PhS	1	32	68
PhS	0.55	57	43
PhS	2x104	100	0
$PhSO_2$	34	90	10
CH	v. fast	100	0
CN	0.3	100	0
OAc	v. fast	100	0

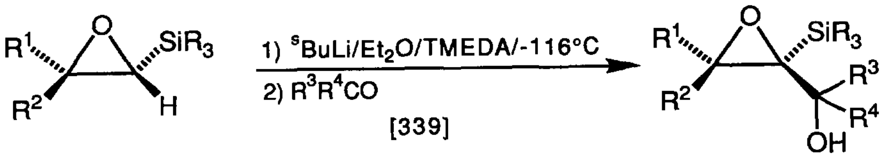
C. Other Studies

A quantum chemical and x-ray study was done on β-chloroethylsilanes. Calculations were carried out to determine the potential energy surface for the b-elimination reaction. [337] Diphenylphosphinoethyltriethoxysilane was bonded to monmorillonite and then reacted with $Pd(PhCH_2CN)_2Cl_2$ to give a catalyst that was employed in the hydrogenation of alkynes to give cis alkenes in high yields and nearly complete stereoselectivity. [338]

XIV. MISCELLANEOUS FUNCTIONAL ORGANOSILANES

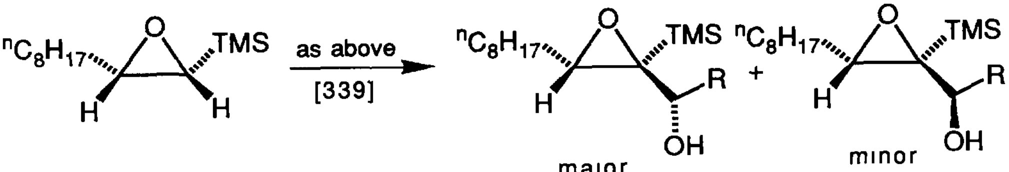
A. Epoxysilanes

The preparation and reactions of trimethylsilyl substituted oxiranyl lithium reagents was reported. The stereoselectivity of the reactions of these reagents was also investigated. (Eqns. 442 and 443)



(442)

13 examples. 0 - 83%

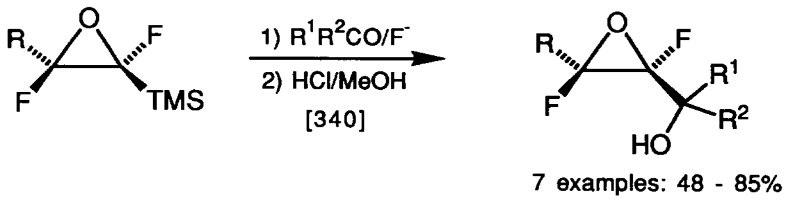


major

(ratios from 2:1 to 7.7:1)

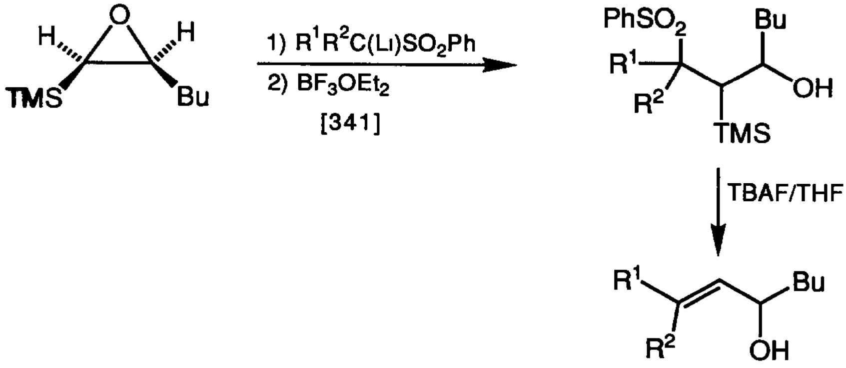
(443)

The reaction of certain epoxysilanes with fluoride ion in the presence of an aldehyde or ketone gives the product of the oxiranyl anion derived from loss of the silicon. (Eqn. 444)



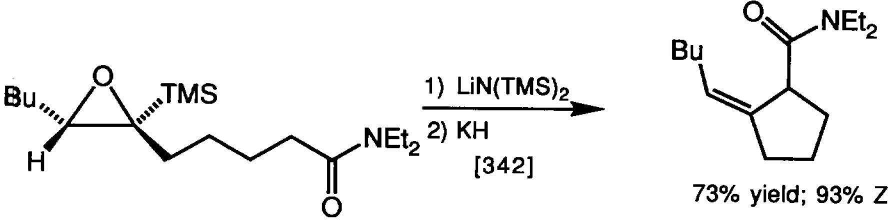
(444)

Lithiated aryl sulfones were reacted with epoxysilanes leading to allyl alcohols after β-elimination of trimethylsilylphenylsulfone. (Eqn. 445)

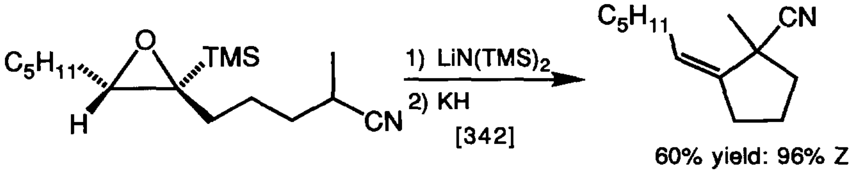


(445)

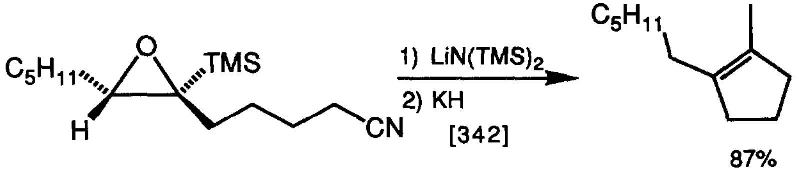
An intramolecular version of the attack of anions on epoxysilanes followed by elimination was employed in the preparation of alkylidene cyclopentanes. (Eqns. 446 448) Isomerization to the internal double bond can occur as seen in Eqn. 448.



(446)

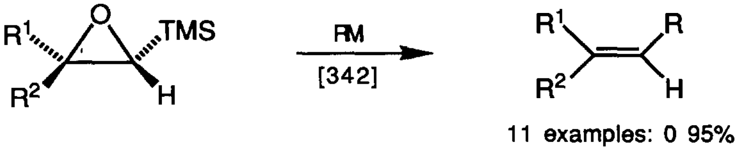


(447)



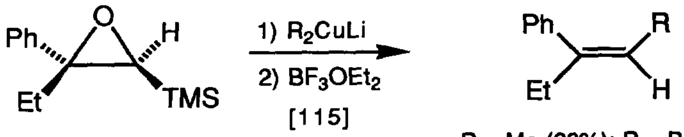
(448)

Epoxysilanes were reacted with various organometallic reagents as a route to substituted olefins. (Eqn. 449) The stereochemistry of the olefin coul be controlled by the elimination procedure. (Eqns. 450 and 451)



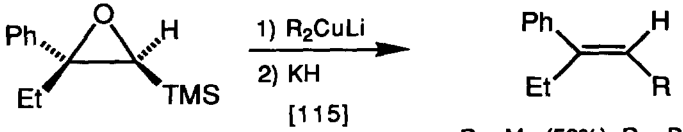
(449)

(RM = Li_2CuPh_2CN; PhLi; thienyllithium; hexynyllithium; $Li_2CH_2CONEt_2$; lithiodithiane)



R = Me (60%); R = Bu (65%)

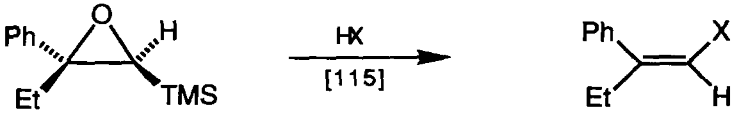
(450)



R = Me (50%); R = Bu (50%)

(451)

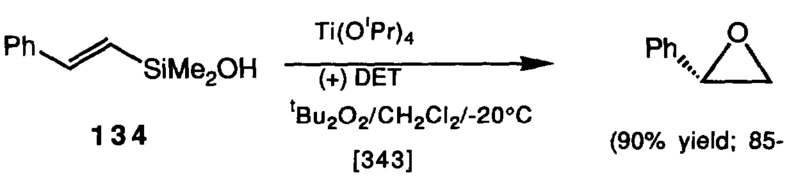
The reaction of epoxysilanes with hydrogen halides was used to prepare vinyl halides with fixed geometry. (Eqn. 452)



X = I (70%); Br (60%); Cl (50%)

(452)

In an interesting extension of the Sharpless epoxidation of allyl alcohols, the vinylsilanol **134** (a silaallyl alcohol) was reacted with the Sharpless reagent and then desilylated to give the epoxide of styrene as the S enantiomer in 90% yield and from 85 to 95 % ee. (Eqn. 453)



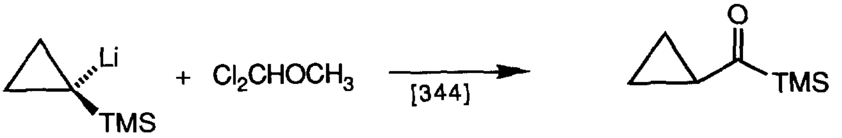
134

(90% yield; 85-95% ee)

(453)

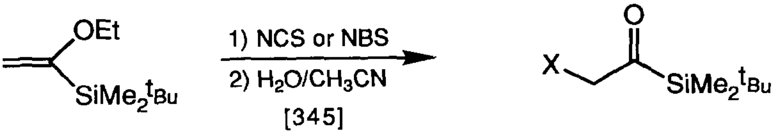
B. Acylsilanes

Cyclopropyltrimethylsilyl ketones were prepared by the reaction of 1-trimethylsilylcyclopropyllithium with methyl(dichloromethyl)ether. (Eqn. 454) The acylsilanes were subjected to several reactions.

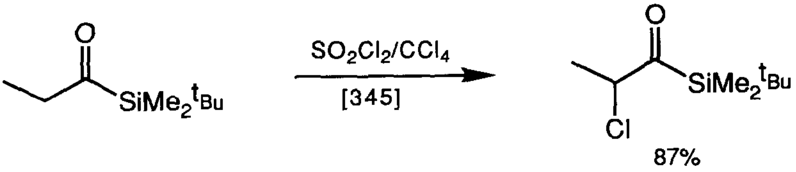


(454)

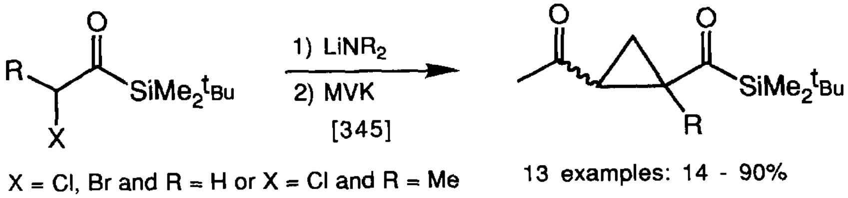
Halogenation of 1-silyl enol ethers leads to α-halo acylsilanes. (Eqn. 455) These were also available via reaction of the enolate of an acylsilane with surfuryl chloride. (Eqn. 456) α-Halo acylsilanes were deprotonated and reacted with methylvinyl ketone to give cyclopropyl acylsilanes (Eqn. 457) Cycyloprop yl acylsilanes were also prepared as shown in Eqn. 458.



(455)



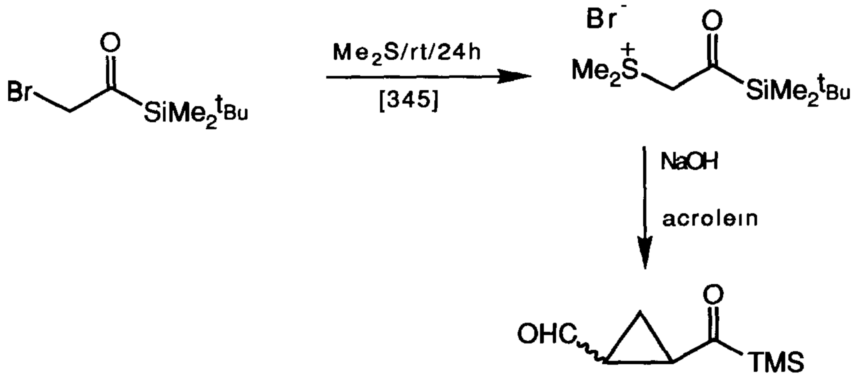
(456)



(457)

X = Cl, Br and R = H or X = Cl and R = Me

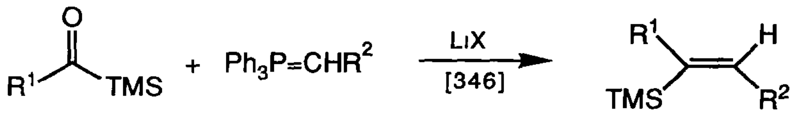
13 examples: 14 - 90%



5 examples: 40 - 89%

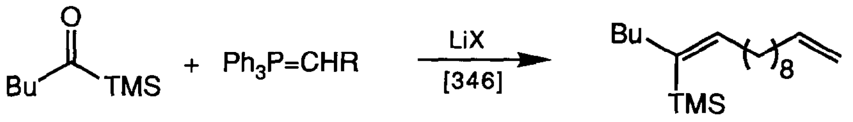
(458)

Acylsilanes were reacted with Wittig reagents to provide a highly stereoselective synthesis of (Z) vinylsilanes. (Eqn. 459) Deprotonation of the acylsilane is a major side reaction. This methodology was employed in the synthesis of E-11-hexadecen-1-ol acetate and example of a pure trans insect pheromone. (Eqns. 460 and 461) Interestingly the protodesilylation of a vinylsilane with acetyl chloride in acetonitrile is very highly stereoselective.



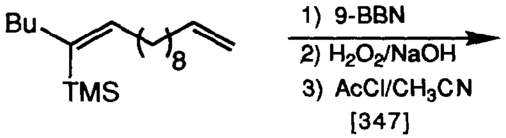
9 examples: 0 - 82%
Z.E > 96·4 except for
R^1 = Me, R^2 = OMe 78:22

(459)



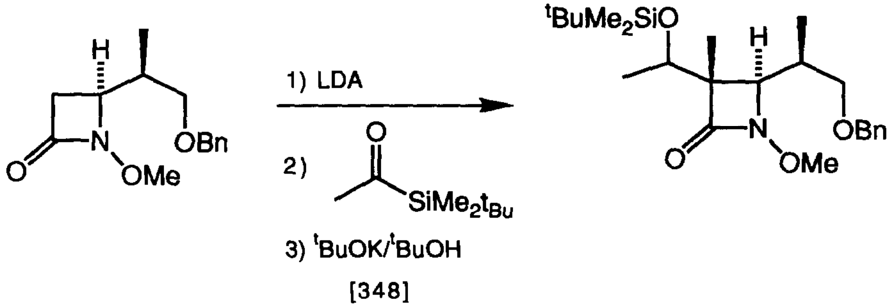
(460)

R = $(CH_2)_8CH=CH_2$



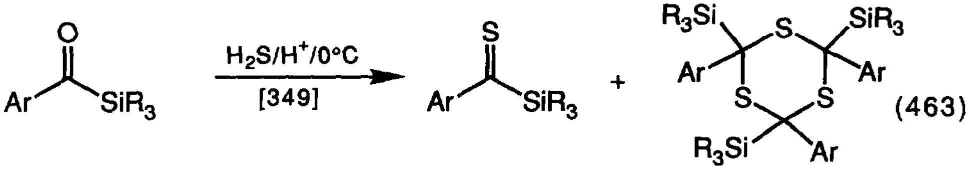
(461)

Acyl tert-butyldimethylsilane was used to react with the enolate of a β-lactam tc give, after a Brook rearrangement, the lactam with the protected hydroxyethyl side chain present. (Eqn. 462)

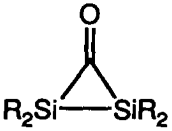


462)

Aryl acylsilanes were converted to their thiones by reaction with hydrogen sulfide. (Eqn. 463) The trimer of the thione was also produced in these reactions. They were protodesilylated with fluoride ion.



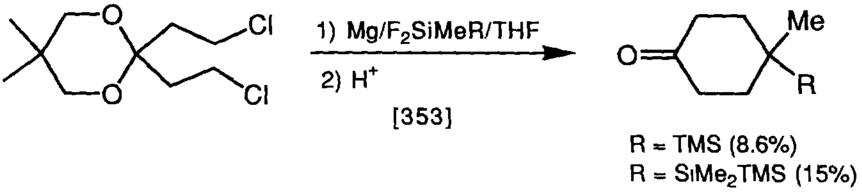
The acylsilane **135** was subjected to MO calculations to determine whythey are colored. It was concluded that the LUMO has a large negative hydperconjugation stabilization of the chromophoric antibonding orbitals suggesting excited state geometries to be more like the corresponding ground state so that long wavelength UV absorption due to vertical axcitation energies are nearly equal to adiabatic excitation energies. [350] The ^{29}Si isotope effect on the photolysis of acylsilanes was studied. [351] The esr spectra of anion radicals of seven different acylsilanes were reported. [352]



135

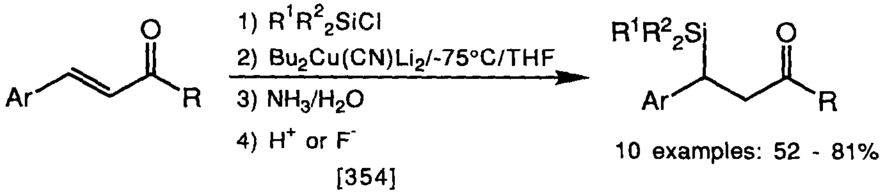
C. Other Functional Organosilanes

An interesting di-Grignard approach to 4-silacyclohexanones was reported starting with the protected 1,5-dichloro-3-pentanone. (Eqn. 464)



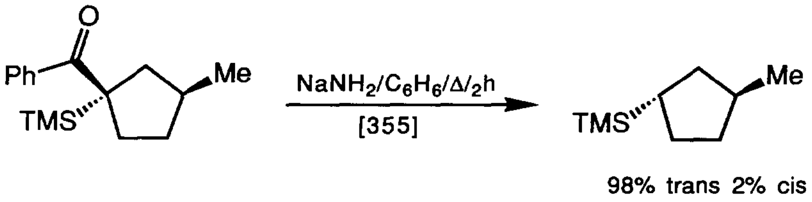
(464)

γ-Ketosilanes were conveniently prepared by treatment of α,β-unsaturated ketones with copper(I) cyanide, butyllithium and a chlorosilane. (Eqn. 465)

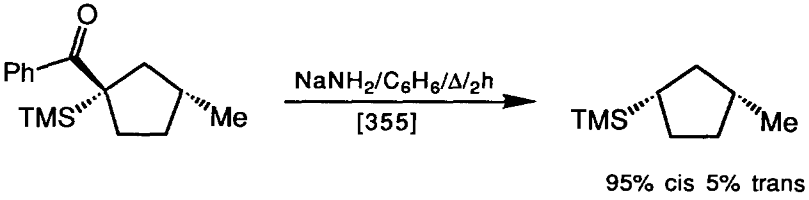


(465)

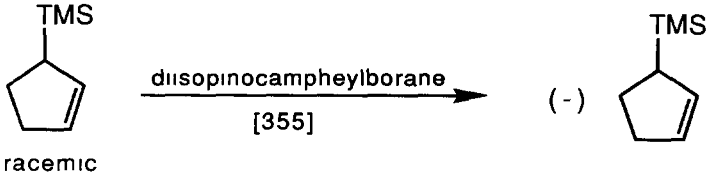
It was shown that chiral α-silyl benzoylcycloalkanes undergo base-catalyzed cleavage with retention of configuration within limits of steric crowding. (Eqns. 466 and 467) The chiral starting materials had their origin in 3-trimethylsilylcyclopentene, which was converted by kinetic hydroboration of the racemic mixture to (-) 3-trimethylsilylcyclo-pentene. (Eqn. 468)



(466)

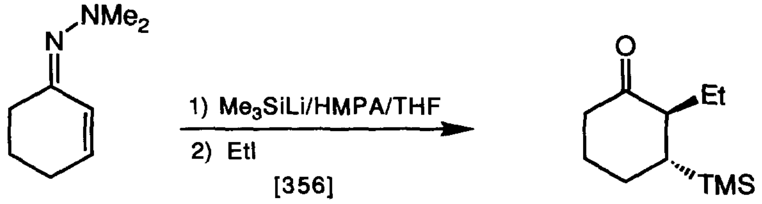


(467)

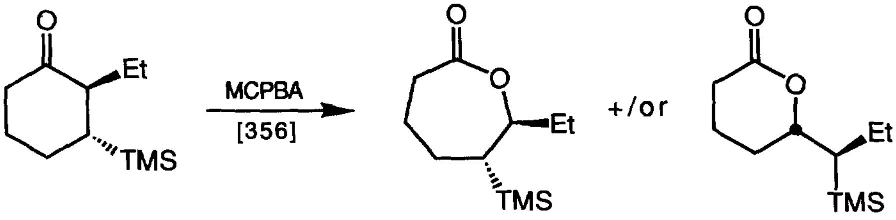


(468)

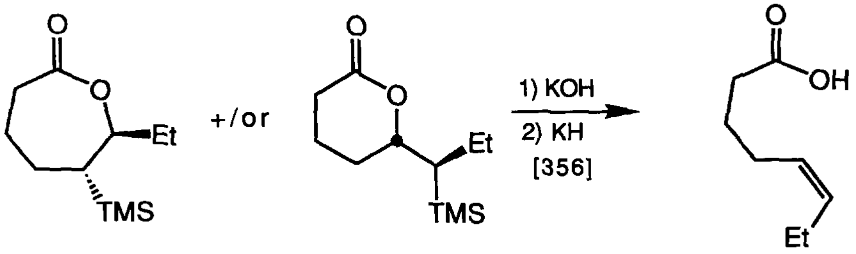
Z-δ,ε-Unsaturated carboxylic acids were prepared by addition of trimethylsilyl lithium to the dimethylhydrazone of cyclohexenone followed by alkylation, Bayer-Villiger oxidation and elimination. (Eqns. 469 - 471) Both exo- and endo-brevicomin were prepared utilizing this chemistry as a key ingredient.



(469)

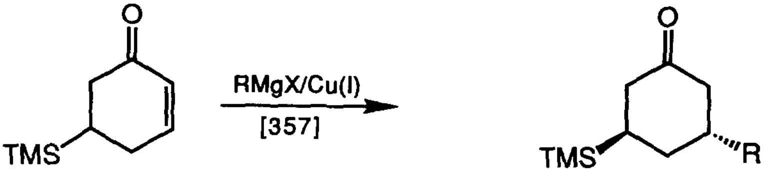


(470)



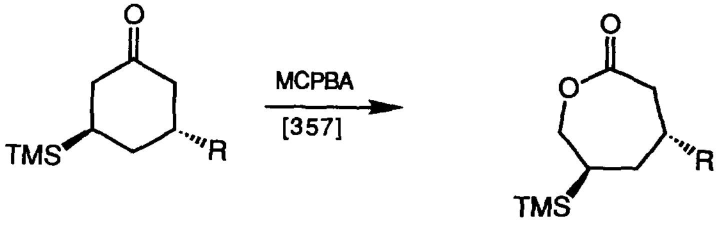
(471)

5-Trimethylsilyl-2-cyclohexenone was the source of 3-substituted-γ-butyrolactones. (Eqns. 472 -476) The preparation of (-) enterolactone **137** was accomplished from optically active cyclohexenone **136**. (Eqn. 477)



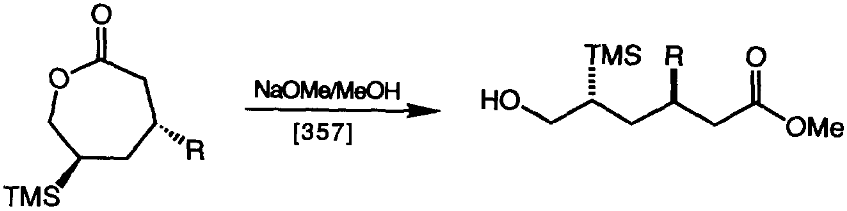
(472)

9 examples: 74 - 92%

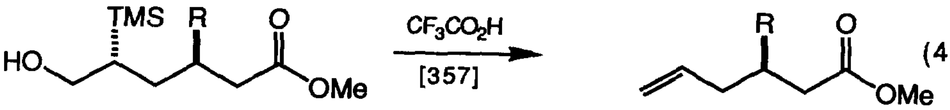


(473)

9 examples: 88 - 95%

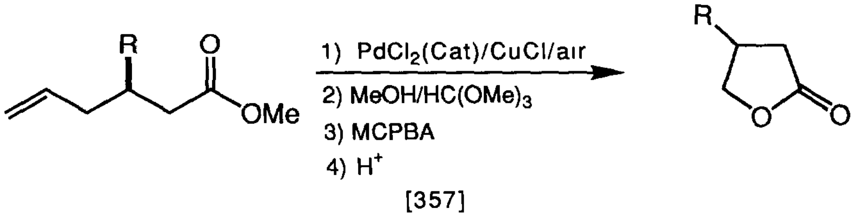


(474)

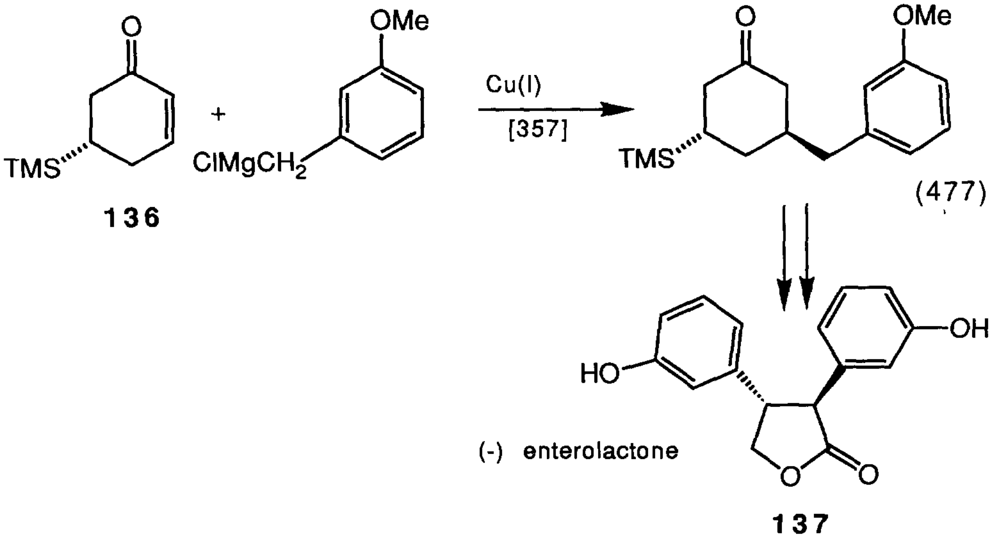


(475)

79 - 99%

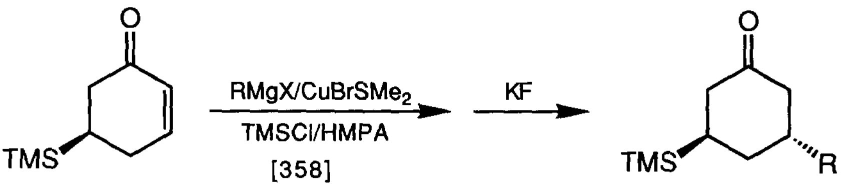


(476)

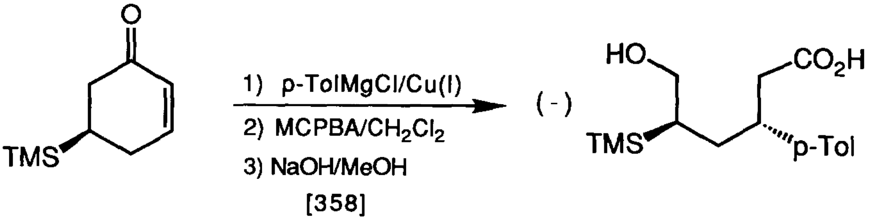


(477)

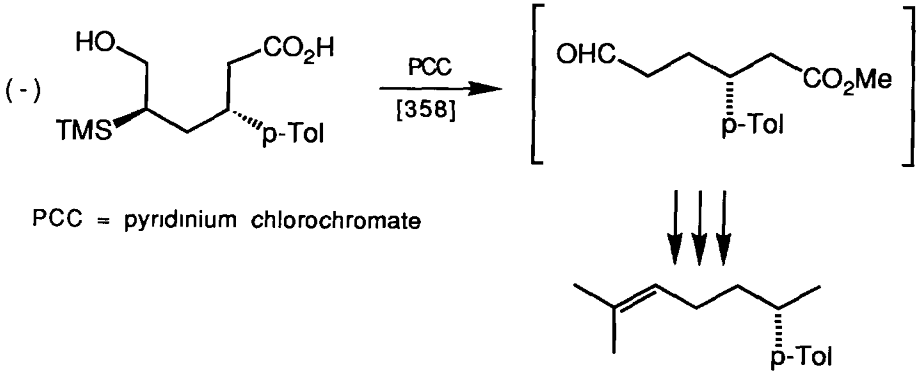
The optically active R-5-trimethylsilyl-2-cyclohexenone was used to prepare optically active 3-substituted-5-trimethylsilylcyclohexanones. (Eqns. 478 and 479) The methodology was applied to the synthesis of (+) α-curcumene, (+) α-curcumone, and (-) methyl citronellate. The syntheses of (+) α-curcumene and (+) α-curcumone are shown. (Eqns. 4780 and 481)



(478)



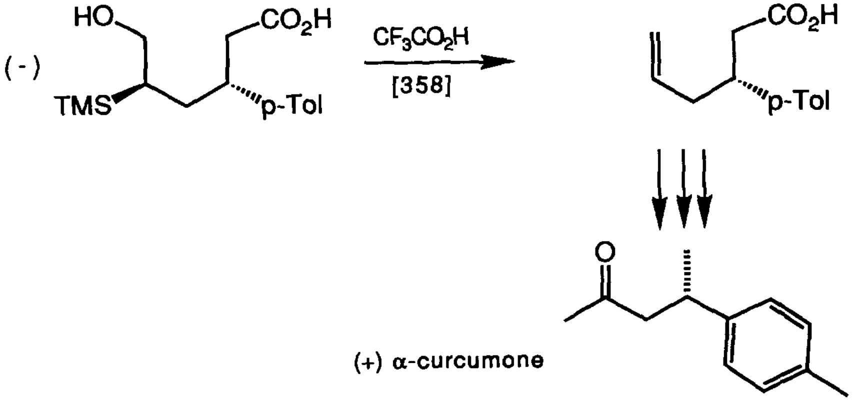
(479)



(480)

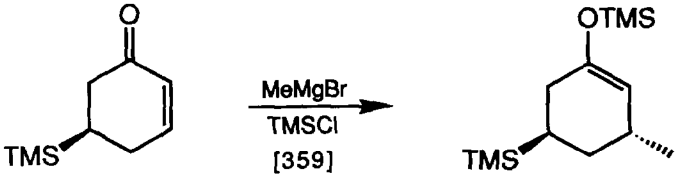
PCC = pyridinium chlorochromate

(+) α-curcumene

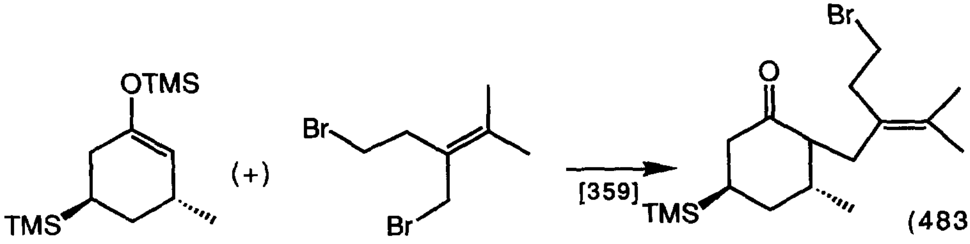


(481)

The above methodology was also applied to the preparation of (-) β-vetivone as shown in Eqns. 482 -485.

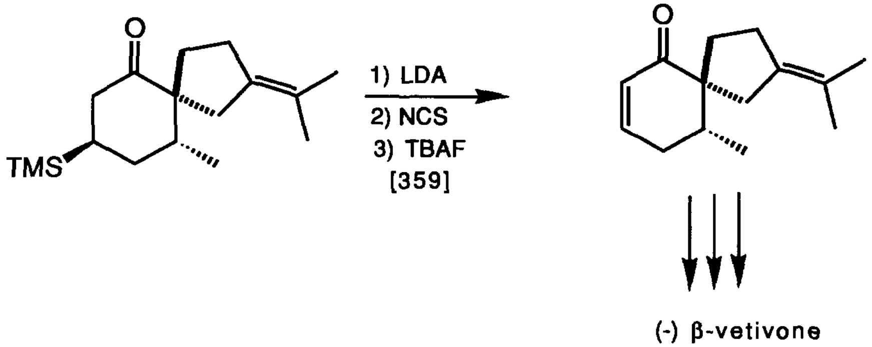


(482)



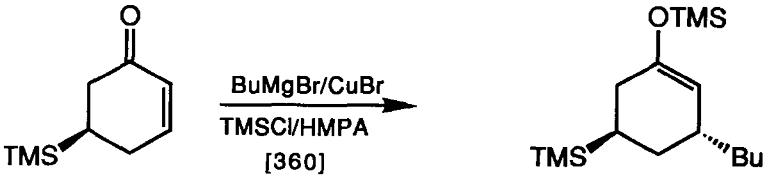
(483)

(484)

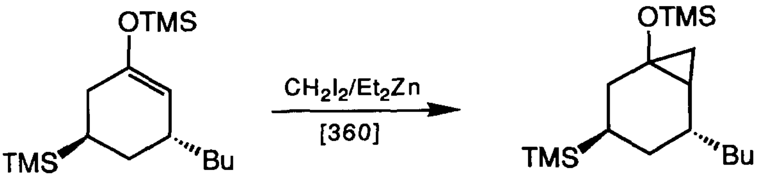


(485)

This useful starting material was also used to prepare R (+) 4-butyl-2,6-cycloheptadienone, a constituent of marine algae. (Eqns. 486 - 489)



(486)



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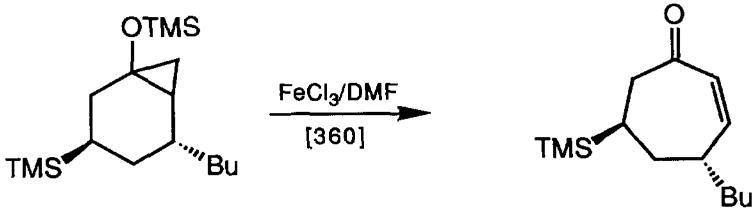
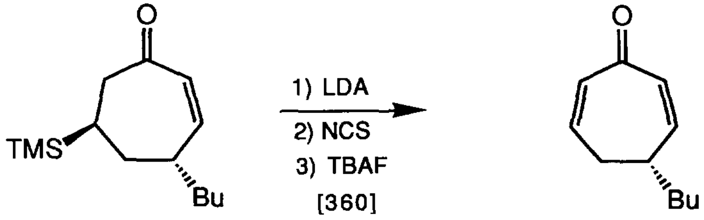
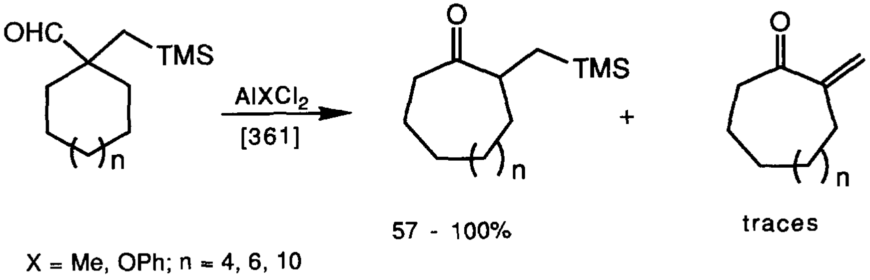


(488)

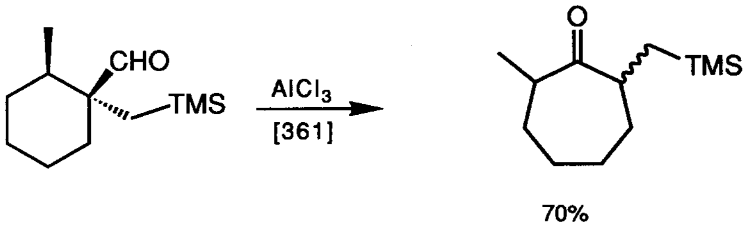


(489)

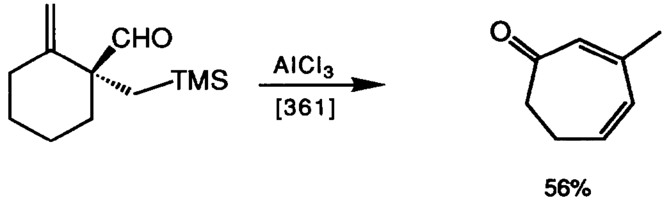
Cyclic β-trimethylsilyl contining aldehydes were ring expanded upon treatment with Lewis acids. (Eqns. 490 and 491)



(490)

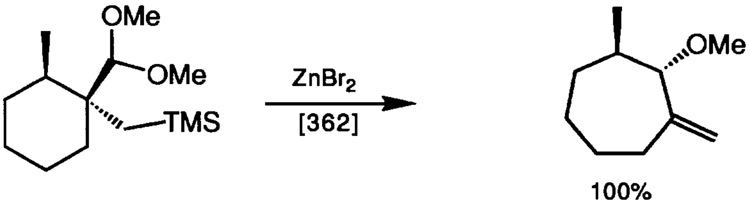


(491)

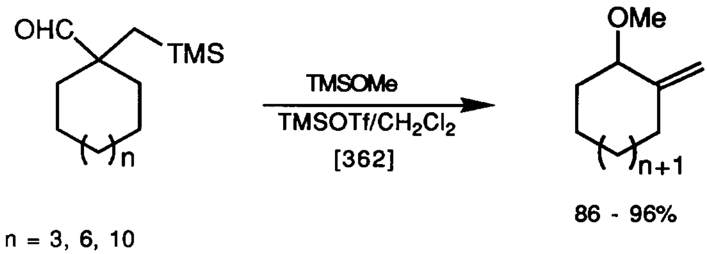


(492)

The ketals of this type of silyl substituted aldehyde is also ring expandable. (Eqn. 493) The same products, allyl methyl ethers, are available from the aldehyde with trimethylmethoxysilane as a reagent and trimethylsilyl triflate as the catalyst. (Eqn. 494)

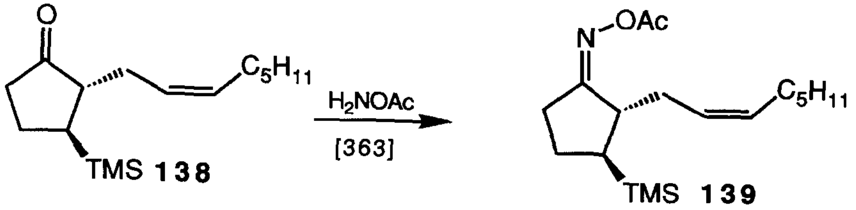


(493)

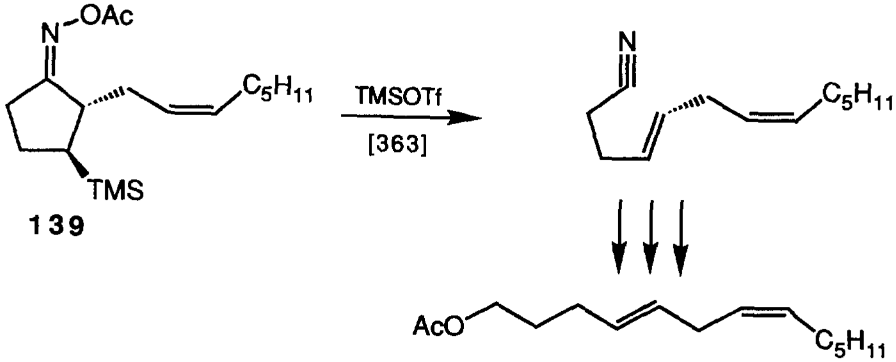


(494)

β-Trimethylsilylcyclopentanone **138** was converted to the acetoxy oxime and 1,4- eliminated to give the unsaturated nitrile **139**, which was used to prepare a component of the sex pheromone of the potato tuberworm. (Eqn. 495)

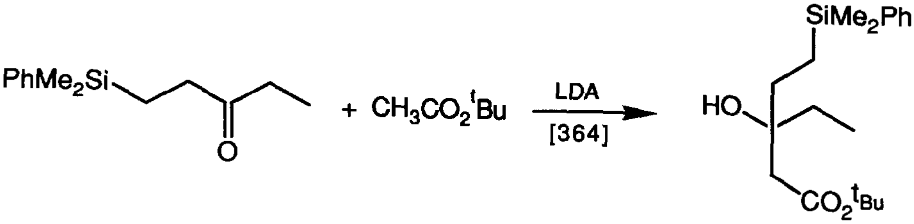


(495)

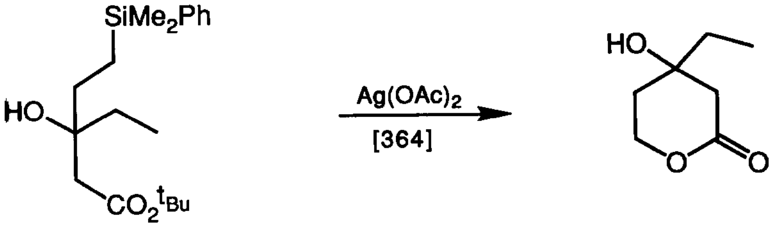


(496)

The synthesis of 3-ethyl-3-hydroxy-γ-valerolactone, a homolog of mevonolactone, was prepared from β-silyl ketone. (Eqns. 497 and 498)

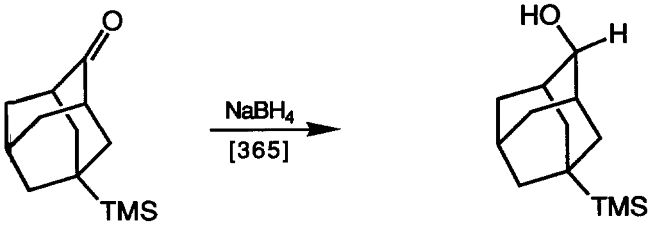


(497)



(498)

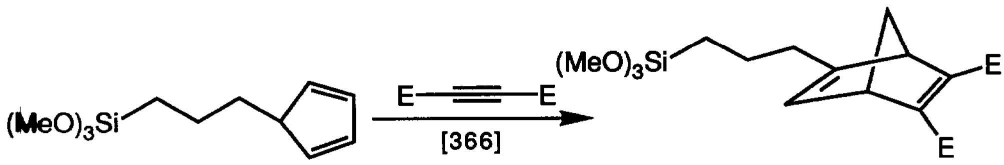
The reduction of ketone **140** gave a slight preference for the anti isomer. (Eqn. 499)



140

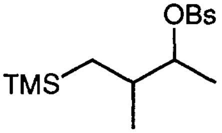
(499)

Trimethoxysilylpropylcyclopentadiene was reacted with acetylene dicarboxylates and fumaronitrile to give materials that could be attached to silica gel and complexed to transition metal complexes to provide solid supported catalysts. (Eqns. 500 and 501)

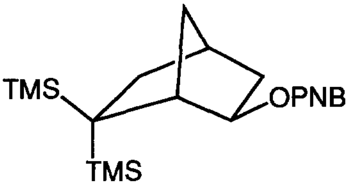


E = CO_2Me (57%), CO_2Et (62%) (500)

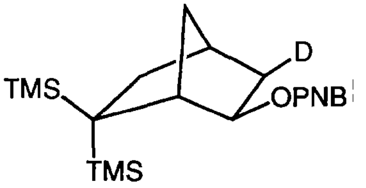
The solvolysis of **141** was studied in order to study the γ-silicon stabilization of carbocations. Some acceleration was observed. [370] The effect of trimethylsilyl groups on the solvolysis of 2-norbornyl systems was studied using **142** and **143**. [371] The stereochemical course of the solvolysis of γ-substituted silanes was studied using **144** and **145**. [372]



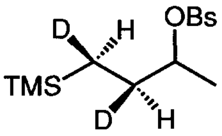
141



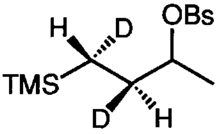
142



143



144

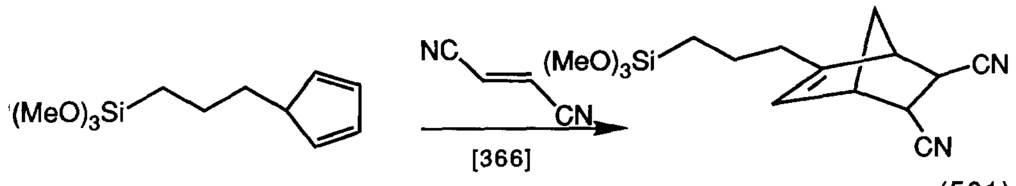


145

XV. REACTIVE SPECIES

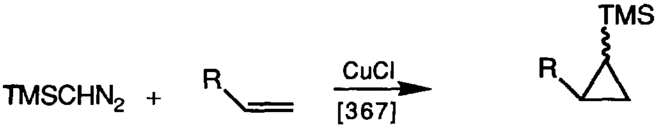
A. Radicals

In a study of the reactivities of silanes with tert-butyoxy radical it was found that trimethylsilyl groups activate the Si-H bond towards radical cleavage. Thus one finds a relative reactivity of Et_3SiH < $TMSMe_2SiH$ < $(TMS)_3SiH$. [373] The rates of reaction of $(TMS)_3Si$ radical with alkyl halides compared to those of Et_3Si and Bu_3Si radicals was made. For examples for the reaction with benzyl bromide the rates were $Et_3Si\cdot$ (2.4x109), $Bu_3Si\cdot$ (1.5x109) and $(TMS)_3Si\cdot$ (9.6x108). In general the $(TMS)_3Si$ radical towards alkyl halides is not as strong as other silyl radical, but as good or better than the tri-butyltin radical. [374]



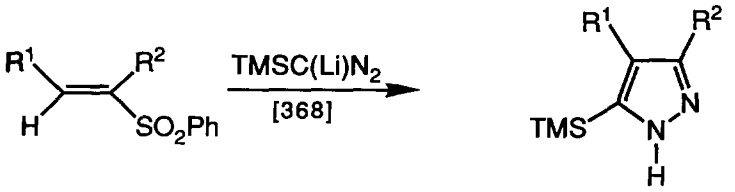
(501)

Trimethylsilyldiazomethane was reacted with olefins under the influence of copper(I) chloride. (Eqn. 502)



(502)

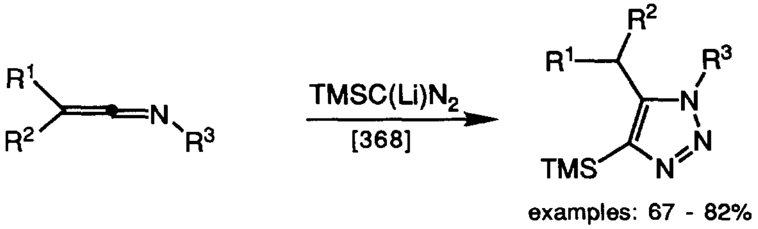
Unsaturated sulfones were reacted with lithio trimethylsilyldiazomethane to give pyrazoles in good yield. (Eqn. 503)



13 examples: 36 - 98%

(503)

Ketenimines were reacted with lihtio trimethylsilyldiazomethane to give triazoles, again in good yield. (Eqn. 504)



(504)

The gas-phase acidities of organosilanes and electron affinities of organosilyl radicals were determined. These are given below for various silanes. [375]

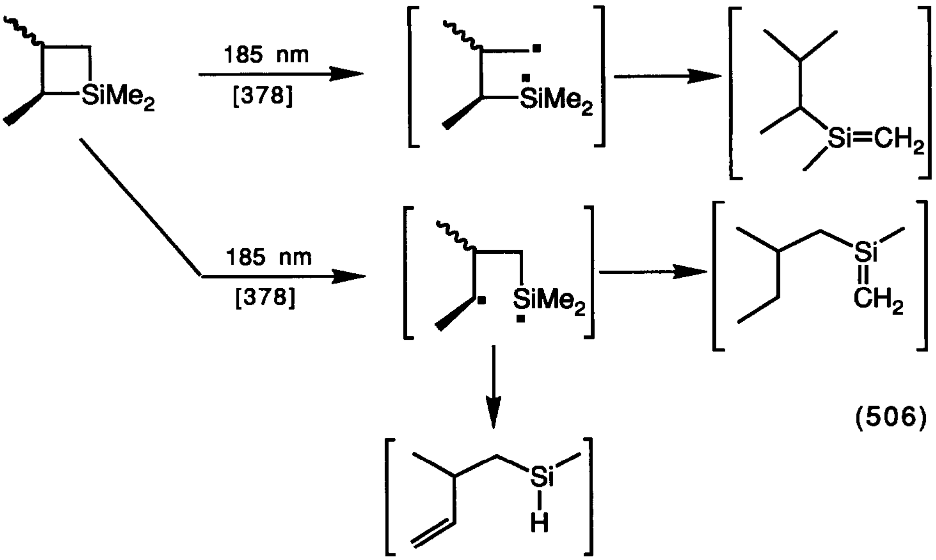
Silane	ΔH°acid	EA(for $RH_2Si\cdot$)	Si-H (diss. energy)
SiH_4	372.8	32.4	91.6
$PhSiH_3$	370.7	33.1	90.2
$PhMeSiH_2$	374.2	30.7	91.3
$MeSiH_3$	378.3	27.5	92.2
Me_3SiH	382.8	22.4	>91.0

A study of the reaction of triethylsilyl radcial, generated by laser flash photolysis of a 1:1 solution of triethylsilane and di-tert-butyl peroxide, with sulfides was reported. The reaction gives carbon centered readical *via* attack at sulfur by the silyl radical. (Eqn. 505)

$$Et_3Si\bullet + R\text{-}S\text{-}R \xrightarrow[{[376]}]{} Et_3Si\text{-}R + R\bullet \qquad (505)$$

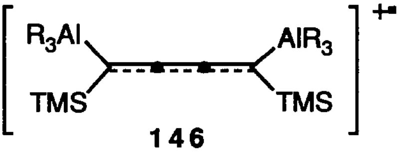
Silacyclobuty-1-yl radicals were generated and studied. ESR studies showed the radicals to have non-planar rings and the SOMO on Si to be pseudo-equatorial. A substantial long range coupling of 16.4 G to the pseudo-equatorial γ-proton was found

[377] It was shown that mechanistically silacyclobutanes undergo Si-C bond cleavage upon photolysis at 185 nm. (Eqn. 506)



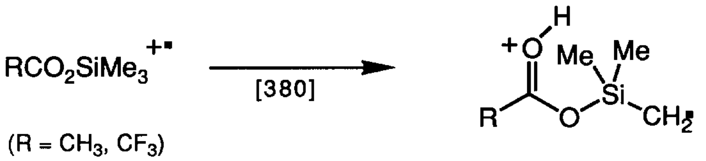
(506)

The reaction of 1,4-bis(trimethylsilyl)-1,3-butadiyne with R3Al and potassium metal led to the first observation of persistent radical di-ate complexes **146**. [379]



146

An ESR study of the radical cation of trimethylsilyl acetate and trimethylsilyl trifluoroacetate showed the unpaired electron to be on silicon. Upon annealing one finds a rearrangement taking place to give the silylmethyl radical. (Eqn. 507)



(507)

B. Silylenes

Bis(pentamethylcyclpentadienyl)dichlorosilane was reduced with naphthalene-lithium, sodium or potassium to give a stable decamethylsilicocene. (Eqn. 508) The silylene could be further reduced to silicon metal and the pentamethylcyclopentadienyl-metallic, but treatment of the dichlorosilane with four equivalents of the naphthalene-metal system did not give total reduction to metallic silicon. (Eqn. 509) The silylene can be sublimed and the NMR data support a π-bonded rather than a σ bonded system.

$$(Me_5C_5)_2SiCl_2 + 2\ C_{10}H_8M \xrightarrow[{[381]}]{} (Me_5C_5)_2Si\colon \qquad (508)$$

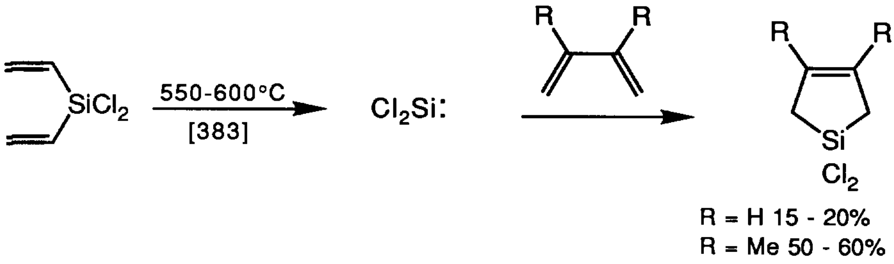
$$(Me_5C_5)_2Si\colon\ \ 2\ C_{10}H_8M \xrightarrow[{[381]}]{} Si^{\circ} + 2\ Me_5C_5M \qquad (509)$$

Laser flash photolysis of pentamethyldisilane or octamethyltrisilane was used to generate dimethylsilylene, which was then reacted with various unsaturated systems. (Eqn. 510)

$$Me_3SiMe_2H \text{ or } Me_3SiSiMe_2SiMe_3 \xrightarrow[\text{photolysis}]{\text{laser flash}} \underset{}{Me_2Si:} \qquad (510)$$

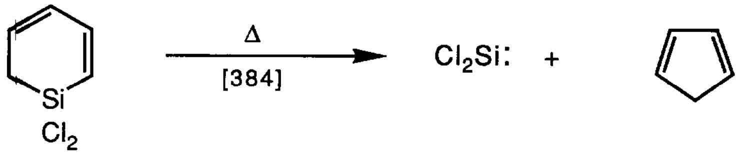
$$\text{[382]}$$

Thermolysis of divinyldichlorosilane yields dichlorosilylene, which was trapped with 2,3-dimethylbutadiene. (Eqn. 511)



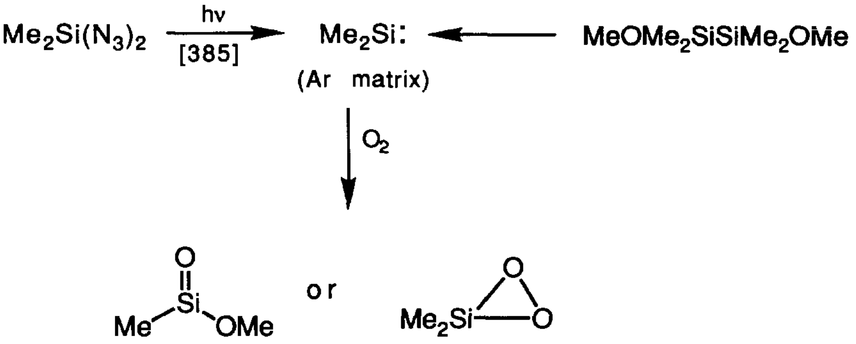
(511)

Thermolysis of 1,1-dichloro-1-silacyclohexa-2,4-diene gives cyclopentadiene and dichlorosilane. (Eqn. 512)



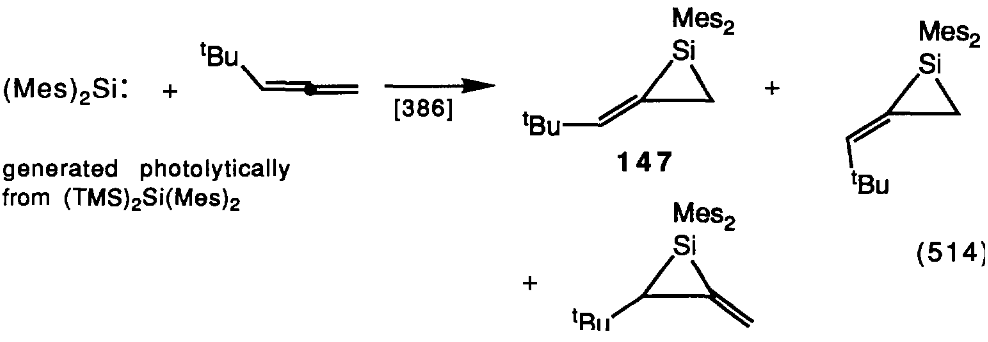
(512)

Photolysis of dimethyldiazidosilane gives dimethylsilylene in a matrix as did the thermolysis of sym-tetramethyldimethoxydisilane. (Eqn. 513) The reaction of the matrix iisolated silylene with oxygen under different conditions gave either methyl 1 sila-acetic acid or dimethyldioxasilirane.



(513)

The reaction of dimesitylsilylene with allenes was reported to give alkylidene-silacyclopropanes. (Eqns. 514 and 515) These were shown to undergo a number of interesting reactions. (Eqns. 516 - 522)



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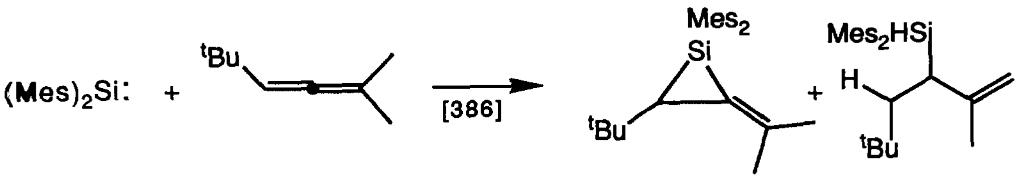

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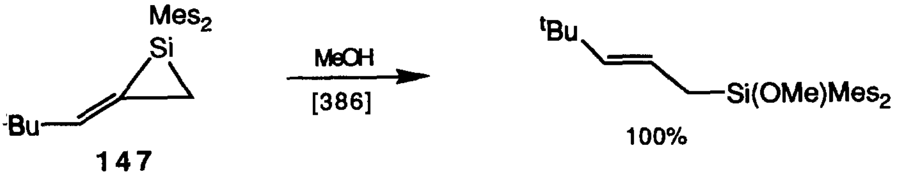

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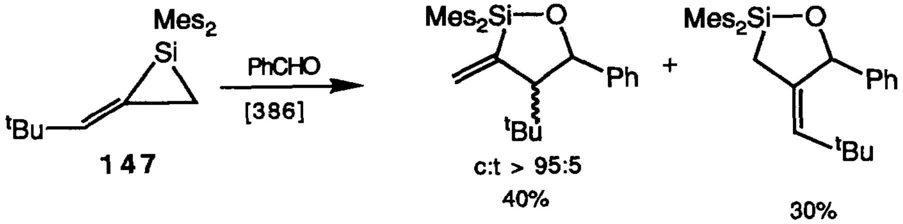

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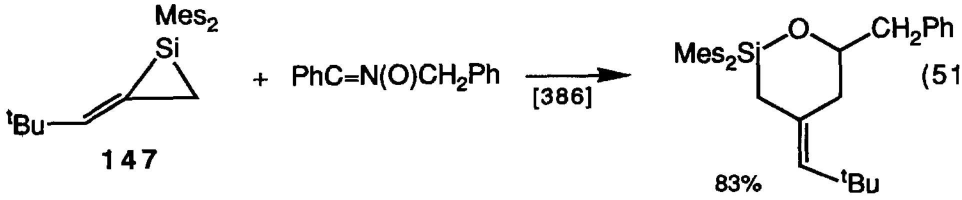

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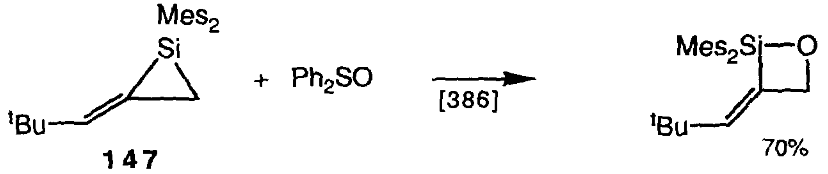

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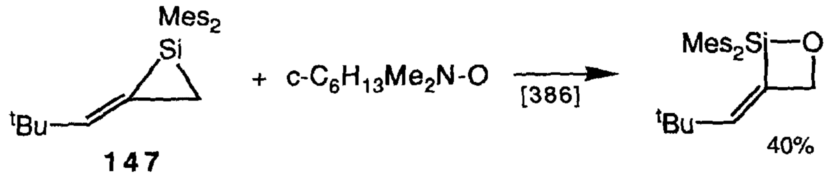

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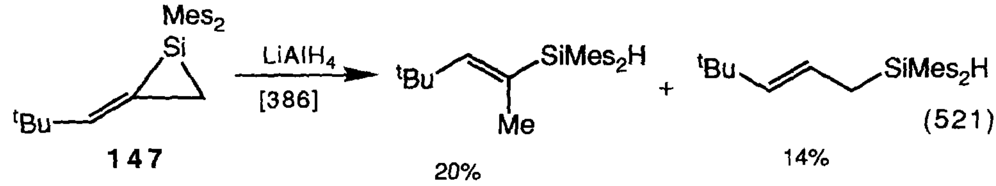

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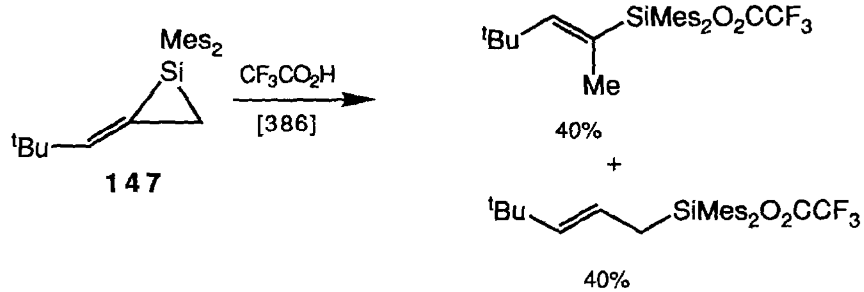


(522)

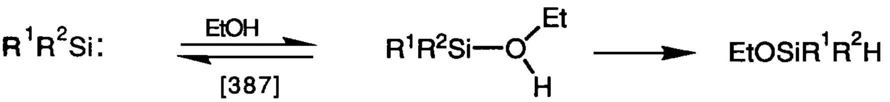
Three different silylenes were generated by the photolytic extrusion of hexamethyldisilane from trisilanes and subjected to reactions with various donors. (Eqns. 523 and 524) The reaction with ethanol was shown to proceed through a complex which then upon warming gives the OH insertion product. (Eqn. 525)

$$R^1R^2Si(TMS)_2 \xrightarrow[[387]]{h\nu} R^1R^2Si: \tag{523}$$

R^1R^2 = Mes; R^1 = Mes, R^2 = ^tBu;
R^1 = Mes, R^2 = 2,6-diisopropylphenoxy

$$R^1R^2Si: \xrightarrow[[387]]{donor} R^1R^2Si\text{-Donor} \tag{524}$$

(donor = R_2O, R_2S, Bu_3P, R_3N)

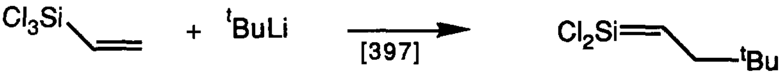


(525)

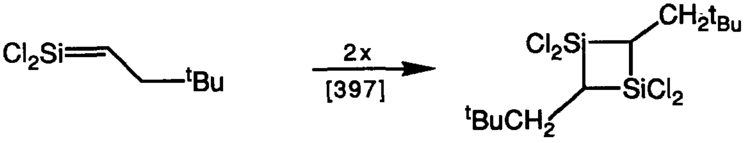
The kinetics of the formation of dimethylsilylene from the pyrolysis of pentamethyldisilane and heptamethyltrisilanes were determined. [388] The mechanism of addition of silylenes to 1,3-butadiene was reported. [389] It was concluded that the main cyclic adduct results from initial 1,2-addition to form a vinylsilacyclopropane followed by a 1,3-silyl shift, rather than Si-C bond rupture. The rearrangement reactions of 1-methyl-2-vinylsilacyclopropane were studied by deuterium labelling. [390] The heats of formation of methylsilylene and dimethylsilylene were predicted based on MP2/6-31G(d,p) level of computation. The values given are 49.2 kcal/mol for dimethyl-silylene and 32-33 kcal/mol for methylsilylene [391] The heats of formation of silylene, methylsilylene and dimethylsilylene were determined kinetically. The values are 64 kcal/mol 48 kcal/mol and 32 kcal/mol, respectively. [392] The latter two numbers are in close agreement to those predicted by theory. The uncertainties involved in the determination of the heats of formation silylenes was discussed. [393] The thermal decomposition kinetics of sym-tetramethyldisilane and 1,1-dimethyldisilane were reported. [394] The eight competing decomposition pathways for methylsilane were evaluated theoretically. [395] The kinetics of the reactions of laser flash photolytically generated dimethylsilylene with alcohols, olefins, acetylenes Si-H and Sn-H were reported. [396]

C. Silenes

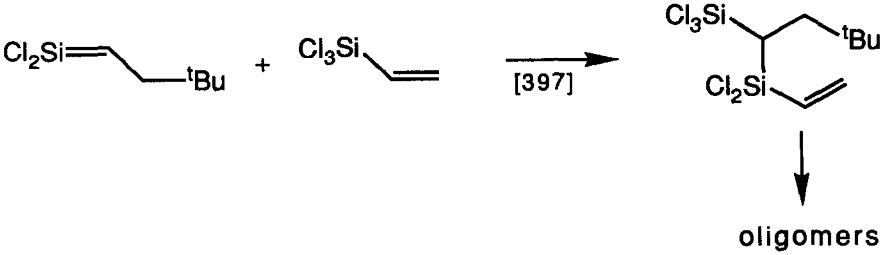
The addition of tert-butyllithium to vinyltrichlorosilane results in the generation ofdichloro(neopentyl)silene. (Eqn. 526) Some of the reactions of this silene are given below. (Eqns. 527 - 529)



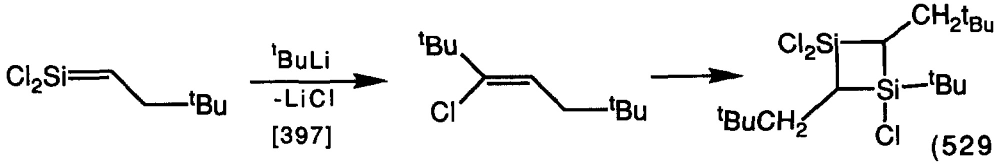
(526)



(527)

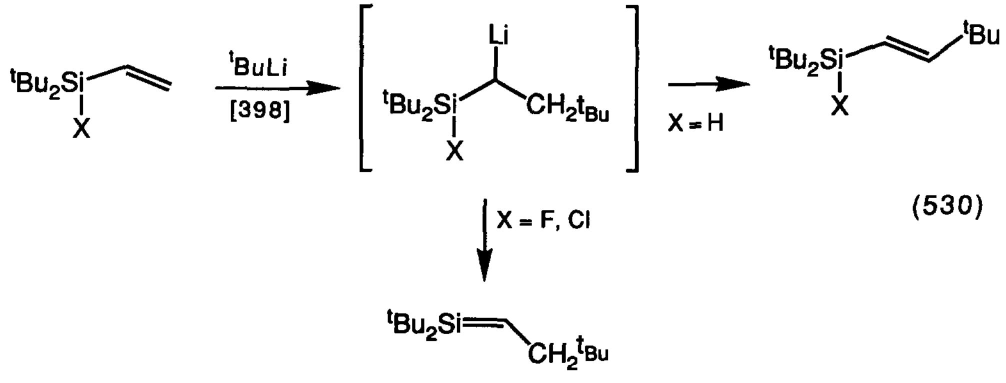


(528)



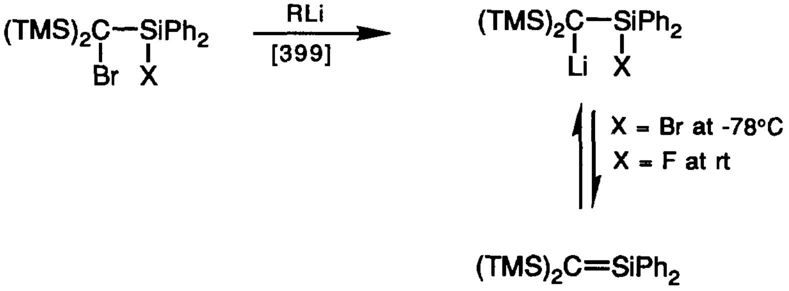
(529)

Di-tert-butylneopentylsilaethene was prepared as shown below. (Eqn. 530)



(530)

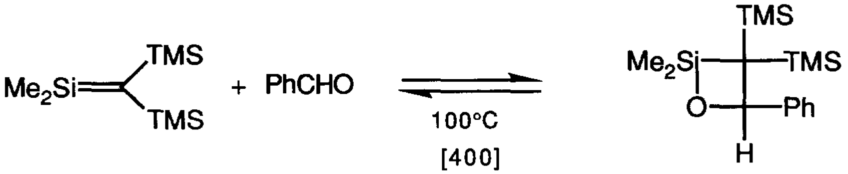
An organolithium route was employed in the synthesis of 1,1-diphenyl-1-sila-2,2-bis(trimethylsilyl)ethene. (Eqn. 531) This silene was trapped with organolithium reagents, $Ph_2C{=}NTMS$, and $^tBu_2MeSiN_3$.



$$(TMS)_2\underset{Br}{C}-\underset{X}{Si}Ph_2 \xrightarrow[{[399]}]{RLi} (TMS)_2\underset{Li}{C}-\underset{X}{Si}Ph_2 \xrightleftharpoons[X\,=\,F\text{ at rt}]{X\,=\,Br\text{ at }-78^\circ C} (TMS)_2C{=}SiPh_2$$

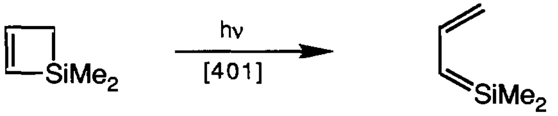
(531)

1,1-Dimethyl-1-sila-2,2-bis(trimethylsilyl)ethene can be stored as its benzaldehyde adduct and regenerated therefrom at 100°C. (Eqn. 532)



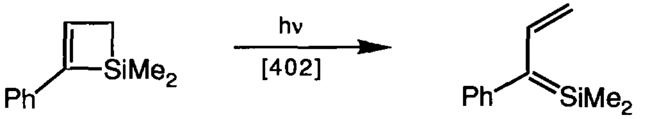
(532)

The photolysis of 1,1-dimethyl-1-silacyclobut-2-ene was studied and found to be consistent with the intermediacy of **148**. (Eqn. 533) Another silabutadiene **149** was photolytically generated. (Eqn. 534)



148

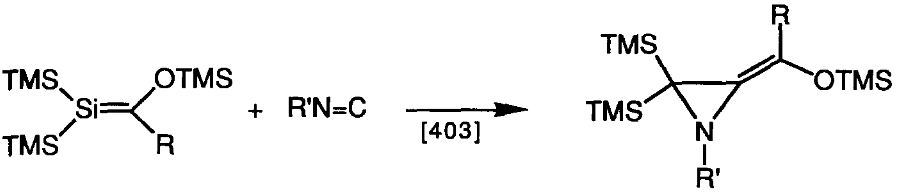
(533)



149

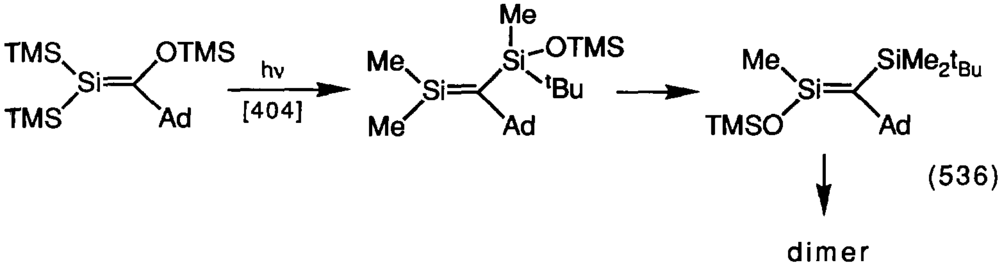
(534)

The insertion of a silene into an isonitrile was shown to give a silaaziridine. (Eqn. 535) The photochemical rearrangements of stable silenes was studied. (Eqn. 536) Silacyclopropanes were shown to be produced from the reaction of silenes with Wittig reagents. (Eqn. 537)

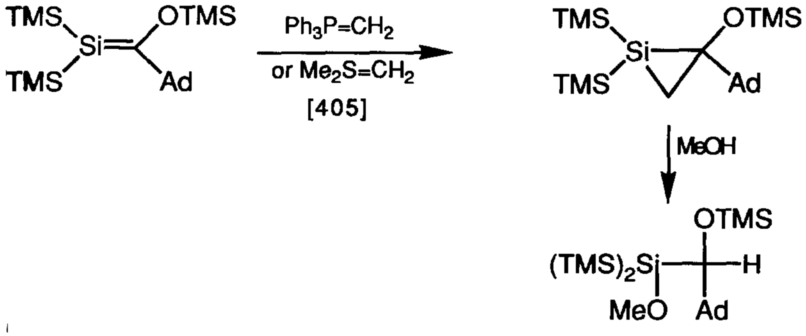


(535)

(R = 1-adamantyl, mesityl; R' = 2,6-dimethylphenyl)



(536)

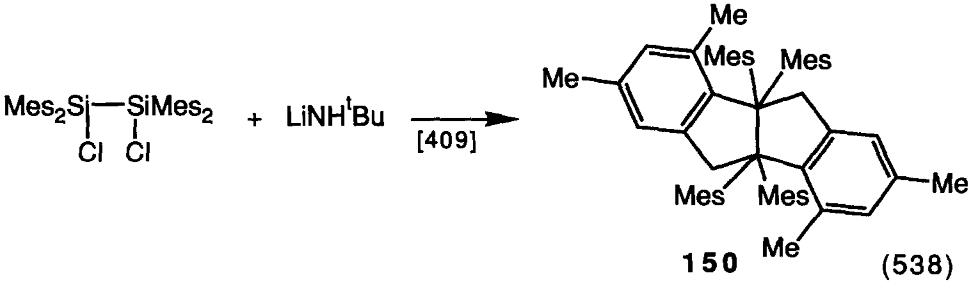


(537)

A study of the microwave transitions for transient dimethylsilene lead to values of 1.692 pm for the Si=C bond length in agreement with theory. [406] The crystal structures of four sterically crowded 1,3-disilacyclobutanes generated from the silenes, were determined. [407] All four contained essentially planar disilacyclobutane rings. The generation of Si=C in the coordination sphere of iron carbonyl complexes was accomplished. [408]

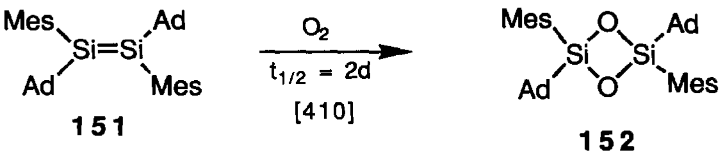
D. Disilenes

Sym-tetramesityldichlorodisilane was reacted with lithium tert-butylamine to give a disilene, which *via* insertion gives a bicyclic disilene **150**. (Eqn. 538)



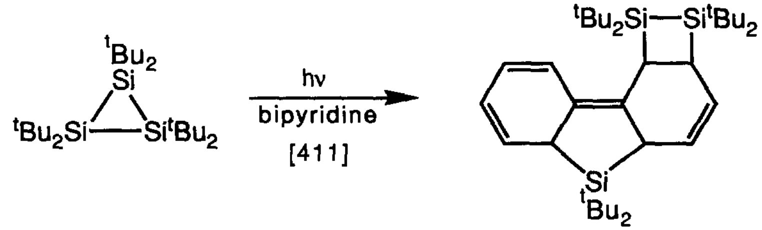
150 (538)

The disilene **151** was subjected to x-ray analysis and was shown to react with oxygen to give **152**. (Eqn. 539)



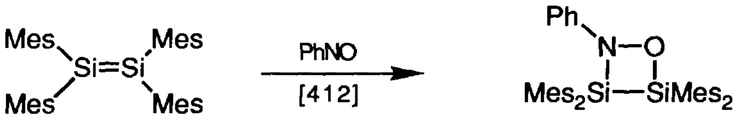
(539)

Di-tert-butylsilylene and tetra-tert-butyldisilene were generated from the tri-silacyclopropane and added to bipyridine. (Eqn. 540)

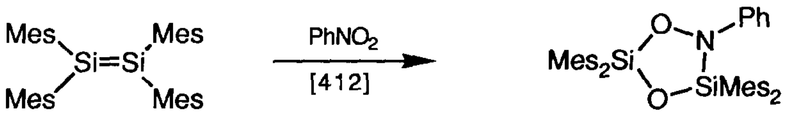


(540)

Tetramesityldisilene was reacted with phenyl nitrite and phenyl nitrate to give the cycloadducts. (Eqns. 541 and 542)

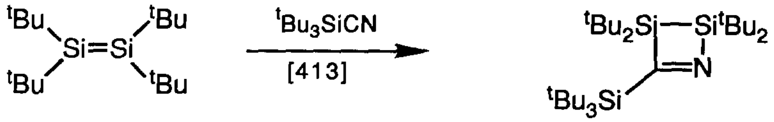


(541)

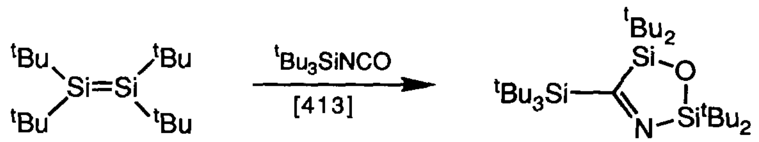


(542)

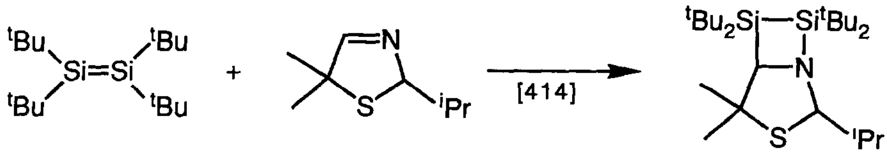
Tetrakis tert-butyldisilene was reacted with tri-tert-butylsilyl nitrile and tri-tert-butyl isocyanate. (Eqns. 543 and 544) This same disilene was added to a cyclic imine. (Eqn. 545)



(543)

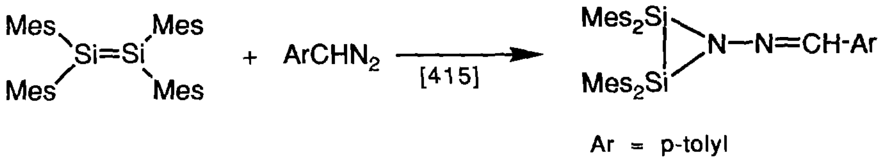


(544)

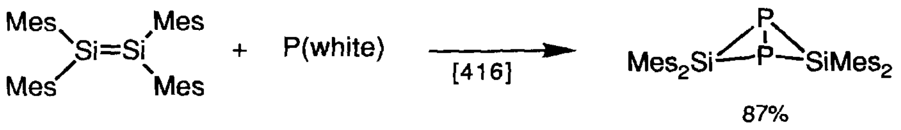


(545)

tetrakismesityldisilene was reacted aryldizomethanes to give disilaaziridines. (Eqn. 546) It was also reacted with white phosphorus. (Eqn. 547)



(546)

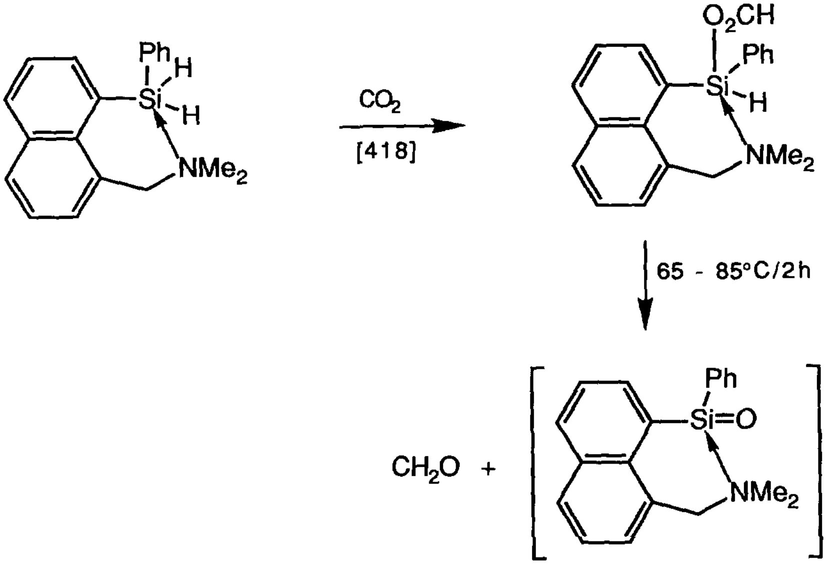


(547)

The transition state kinetic parameters for the isomerization of1,2-di-tert-butyl 1,2-di-mesityldisilene were determined by calculations and found to be in agreement with those found experimentally. [417]

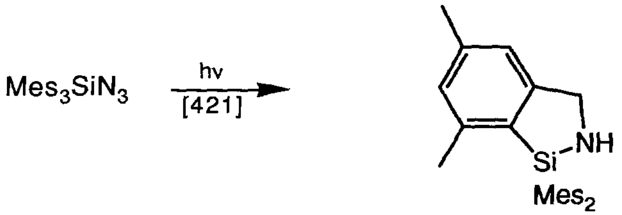
E. Silanones and Silaimines

The reaction of carbon dioxide with a pentavalent silicon hydride splits out formaldehyde and a silanone, which was trapped with $(Me_2SiO)_3$. (Eqn. 548) Dimethoxysilanone was matrix isolated and subjected to infrared analysis. [419] Dimethylsilanone and dimethylsilanone-d_6 were matrix ixolated and subjected to infrared analysis. [420]

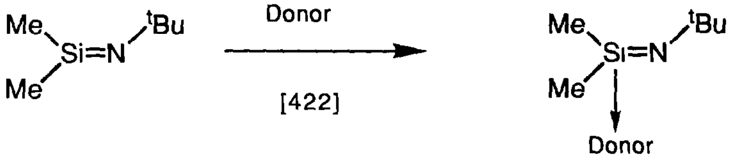


(548)

Trimesitylsilyl azide as well as other hindered silyl azides were photolyzed to give silanimines. (Eqn. 549) N-Tert-butyldimethylsilaimine was reacted with various donors in the presence of trimethylsilyl triflate as a catalyst. (Eqn. 550) The donor strenghts were found to be F^- > NMe_2Et > Cl^- = Et_3N > THF > Et_2O.



(549)

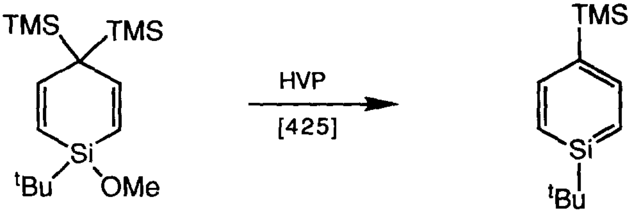


Donor = Et_2O, THF, Et_3N, NMe_2Et, F^-

(550)

F. Other Reactive Species

The conformational structures of 1-phenylsilabenzene, 1,4-disilabenzene and 2,2'-bis-1,3-disilabenzene were studied by the ab initio STO-3G method. All have high conformational mobility and are preferentially planar. [423] The aromatic energies of some heteroaromatic systems were calculate including that of silabenzene. [424] High vacuum pyrolysis of **153** gives **154**. (Eqn. 551)

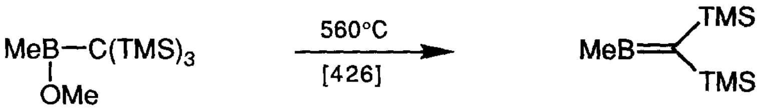


153

154

(551)

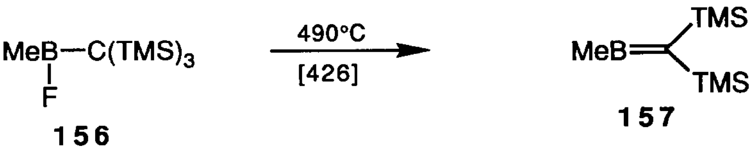
Thermolysis of **155** or **156** gives loss of trimethylmethoxysilane and the alkylalkylidene-borane **157**. (Eqns. 552 and 553) It was shown to dimerize in a head to tail fashion, react with pyridine, benzophenone and a boraimine. (Eqns. 554 - 557)



155

157

(552)



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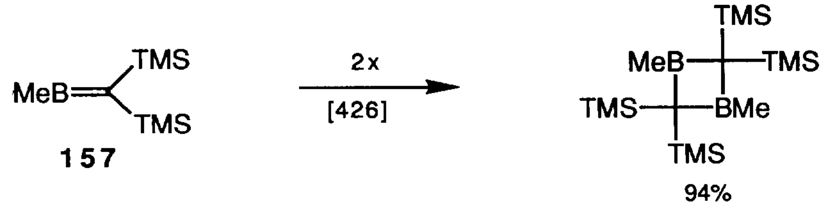

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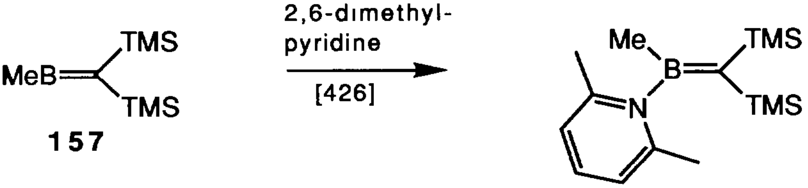
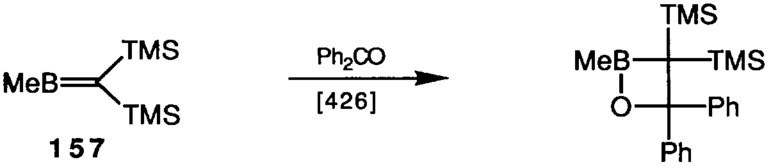


(555)



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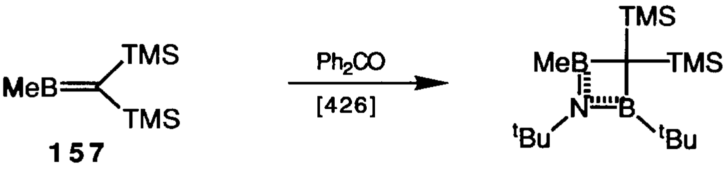

(557)

Theoretical studies on various disila three-membered rings (containing CH_2, O, NH_2, SiH_2, PH, and S) gave the heats of formation and the thermodynamics of the insertion reactions of X + $H_2Si{=}SiH_2$. [427]

The trimethylsilyl anion was shown to give loss of H_2, loss of a hydrogen radical, loss of methyl radical, loss of methane and loss of ethane and a hydrogen radical in its gas phase decomposition. [428]

Aromatic electrophilic substitution by trimethylsiyl cation in the gas phase was studied. A sigma complex is suggested from the data. [429] The preparation of trimethylsilyl perchlorate in dichloromethane was accomplished by the reaction of trimethylsilane and trityl perchlorate. It showed a molar conductance of 0.65 $ohm^{-1}cm^{2}mol^{-1}$ compared to trityl perchlorate itself with 43.5. It did show higher values in sulfolane (10.7) and acetonitrile (175.9). [430] Ion cyclotron resonance spectroscopy has been used to compare the relative stabilities of carbocations and silyl cations in the gas phase. [431] The generation and rearrangement of some β-silyl cations in the gas phase showed the formation of silyl cations among other things. [432] The hydrolysis of α-metalloidal vinyl ethers undergo a rate-limiting protonation to produce α-metal carbocations. Comparative data indicate the order of stabilization of the cation to be C>Sn>Ge>Si>H. [433] In a study of the stereochemical dependence of a β-trimethylmetal group on the stability of a carbocation it was found that tin and germanium are about 10 times as interactive as silicon. [434] Ab initio calculations show that a secondary cation with a β-silyl group is more stable than that without the silyl group by about 22.1 kcal/mol and for a tertiary cation the extra stabilization is 15.9 kcal/mol. A batch, stirred-flow technique for the kinetic study of organosilane reactions in the gas phase was presented. [436]

XVI. ACKNOWLEDGEMENTS

I wish to thank my editors, Professors D. Seyferth and John Oliver for their help and support during the writing of this survey for the past ten years. I hope you, the readers have benefited from the efforts.

XVII. REFERENCES

1. G.L. Larson, J. Organometal. Chem., **360**, 39 (1989).
2. G. Proserpio, Prod. Chim. Aerosol Sel., **29**, 42 (1988). Chem. Abstr., **111**:153872w.
3. Yu.S. Gol'dberg, R.Ya. Sturkovich, E. Lukevics, Appl. Organomet. Chem., **2**, 215 (1988).
4. R. Corriu, Pure Appl. Chem., **60**, 99 (1988).
5. Anonymous, Nachr. Chem. Tech. Lab., **37**, 28 (1989). Chem. Abstr., **110**:57701y.
6. H. Sakurai, K. Sakamoto, K. Sato, Kagaku (Kyoto) **42**, 842 (1987). Chem. Abstr., **110**:8243s.
7. V.E. Shklover, Yu.T. Struchkov, M.G.Voronkov, Usp. Khim., **58**, 353 (1989). Chem. Abstr., **111**:174157g.
8. M.G. Voronkov, V.P. Baryshok, L.P. Petukhov, V.I. Rakhin, R.G. Mirskov, V.A. Pestunovich, J. Organometal. Chem., **358**, 39 (1988).
9. H. Sakurai, Pure Appl. Chem., **59**, 1637 (1987).
10. U. Schubert, J. Organometal. Chem., **358**, 215 (1988).
11. E. Kupce, E. Lukovics, J. Organometal. Chem., **358**, 67 (1988).
12. I.M.T. Davidson, J. Organometal. Chem., **341**, 255 (1988).
13. D. Griller, D.D.M. Danial, Pure Appl. Chem., **61**, 717 (1989).
14. Anonymous, Nachr. Chem., Tech. Lab., **37**, 263 (1989). Chem. Abstr., **110**:211686f.
15. M. Ochiai, Yakugaku Zasshi, **108**, 271 (1988). Chem. Abstr., **110**:153389y.
16. A. Dondoni, G. Fantin, M. Fogagnolo, A. Mastellari, A. Medici, E. Nagrini, Gazz. Chim. Ital., **118**, 211 (1988).
17. C. Chatilialoglu, NATO ASI Ser., Ser. C **260**, 115 (1989). Chem. Abstr., **111**:214522f.
18. W.R. Roush, Chemtracts: Org. Chem., **1**, 382 (1988).
19. P. Deshong, S.W. Lander, Jr., J.M. Leginus, Adv. Cycloaddit., **1**, 87 (1988).
20. I. Kuwajima, Pure Appl. Chem., **60**, 115 (1988).
21. E. Nakamura, Kenkyu Hokoku Asahi Garasu Kogyo Gijutsu Shoreikai, **52**, 27 (1988). Chem. Abstr., **111**:6529m.
22. J.M. Poirier, Org. Prep. Proced. Int., **20**, 317 (1988).
23. C. Chuit, R.J.P. Coprriu, C. Reye, J. Organometal. Chem., **358**, 57 (1988).
24. H.U. Reissig, Top. Curr. Chem., **144**, 73 (1988).
25. J.R. Hwu, N. Wang, Chem. Rev., **89**, 1599 (1989).
26. K.E. Yang, Diss. Abstr. Int. B **49**, 1186 (1988).
27. S. Dhumrongvaraporn, Diss. Abstr. Int. B **49**, 4821 (1989).
28. T.P. Meagher, Diss. Abstr. Int. B **49**, 1707 (1988).

29. M.S. Beeson, Diss. Abstr. Int. B **49**, 2189 (1988).
30. J.M. Defauw, Diss. Abstr. Int. B **49**, 4821 (1989).
31. K. Hoy, Diss. Abstr. Int. B **49**, 1703 (1988).
32. A.J. Stern, Diss. Abstr. Int. B **49**, 3770 (1989).
33. E.R. O'hare, Diss. Abstr. Int. B **49**, 4327 (1989).
34. S. Bain, Diss. Abstr. Int. B **49**, 411 (1988).
35. A.L.O. Agwaramgbo, Diss. Abstr. Int. B **49**, 3187 (1989).
36. G.C. Paul, Diss. Abstr. Int. B **49**, 3768 (1989).
37. J.R. Fisher, Diss. Abstr. Int. B **49**, 2667 (1989).
38. B.R. Landrum, Diss. Abstr. Int. B **49**, 2652 (1989).
39. R.W. Gedridge, Jr., Diss. Abstr. Int. B **49**, 404 (1987).
40 T.M. Elkins, Diss. Abstr. Int. B **49**, 4811 (1989).
41. R.ED. Golding, Diss. Abstr. Int. B **49**, 3721 (1989).
42. J. Auge, Synthetic Commun., **18**, 85 (1988).
43. A.A. Kamyshova, E.Ts. Chukovskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 938 (1988). Chem. Abstr. **110**:135307r
44. S.H. Brown, R.H. Crabtree, J. Amer. Chem. Soc., **111**, 2946 (1989).
45. A. Boudin, G. Cerveau, C. Chuit, R.J.P. Corriu, Bull. Chem. Soc. Jpn., **61**, 101 (1988).
46. A. Weber, R. Galli, G. Sabbioni, U. Staempfli, S. Walther, M. Neuenschwander, Helv. Chim. Acta, **72**, 41 (1989).
47. J.C. Podesta, A.B. Chopa, A.D. Ayala, L.C. Koll, J. Organometal. Chem., **333**, 25 (1987).
48. F. Duboudin, M. Birot, O. Babot, J. Dunogues, R. Calas, Synthetic Commun., **341**, 125 (1988).
49. M. Jung, H. Xia, Tetrahedron Lett., **29**, 297 (1988).
50. G Fritz, J. Harold, Z. Anorg. Allg. Chem., **556**, 23 (1988).
51. G. Fritz, H. Volk, M. Straub, H.G. Von Schering, K. Peters, E.M. Peters, J. Organometal. Chem., **341**, 109 (1988).
52. M. Grignon-Dubois, J. Dunogues, M. Ahra, Recl. Trav. Chim. Pays-Bas, **107**, 216 (1988).
53. D.H. Berry, L.J. Procopio, J. Amer. Chem. Soc., **111**, 4099 (1989).
54. C.A. Grob, P. Sawlewics, Helv. Chim. Acta, **71**, 1508 (1988).
55. H.M. Frey, R. Walsh, I.M. Watts, J. Chem. Soc., Chem. Commun., 284 (1989).
56. C.G. Screttas, M. Micha-Screttas, J. Org. Chem., **54**, 5132 (1989).
57. R. Stoelevik, P. Bakken, J. Mol. Struct., **196**, 285 (1989).
58. M. Kira, M. Akiyama, M. Ichinose, H. Sakurai, J. Amer. Chem. Soc., **111**, 8256 (1989).
59. U. Wannagat, D. Wiese, Z. Naturforsch., B: Chem. Sci. **43**, 104 (1988).
60. M. Kira, K. Sato, H. Sakurai, Chem. Lett., 2243 (1987).

61. J.M. Fu, M.J. Sharp, V. Snieckus, Tetrahedron Lett., **29**, 5459 (1988).

62. Y. Antonio, P. Barrera, O. Contreras, F. Franco, E. Galeazzi, J. Garcia, R. Greenhouse, A. Guzman, E. Velarde, J.M. Muchowski, J. Org. Chem., **54**, 2159 (1989).

63. A.M. Eachern, C. Sacy, L.C. Leitch, J.T. Arnason, P. Morand, Tetrahedron, **44**, 2403 (1988).

64. U. Wannagat, R. Schrader, J. Organometal. Chem., **341**, 95 (1988).

65. H. Chikashita, M. Ishibaba, K. Ori, K. Ito, Bull. Chem. Soc. Jpn., **61**, 3637 (1988).

66. M. Harmata, Tetrahedron Lett., **29**, 5229 (1988).

67. J.D. Rich, Organometallics, **8**, 2609 (1989).

68. A. Sekiguchi, T. Yatabe, C. Kabuto, H. Sakurai, Angew. Chem., **101**, 778 (1989).

69. E. Block, V. Eswarakrishnan, M. Gernon, G. Ofori-Okai, C. Saha, K. Tang, J. Zubieta, J. Amer. Chem. Soc., **111**, 658 (1989).

70. E. Block, M. Gernon, H. Kang, J. Zubieta, Angew. Chem., **100**, 1389 (1988).

71. J.S. Ng, J.R. Behling, A.L. Campbell, N. Duy, B. Lipshutz, Tetrahedron Lett., **29**, 3045 (1988).

72. G.A. Olah, T. Bach, G.K. S. Prakash, J. Org. Chem., **54**, 3770 (1989).

73. K. Matyjaszewski, Y.L. Chen, J. Organometal. Chem., **340**, 7 (1988).

74. R.B. Miller, T. Tsang, Tetrahedron Lett., **29**, 6715 (1988).

75. R.J. Mills, N.J. Taylor, V. Snieckus, J. Org. Chem., **54**, 4372 (1989).

76. G.I. Bolestova, Z.N. Parnes, M.E. Vol'pin, Zh. Org. Khim., **24**, 1071 (1988). Chem. Abstr., **110**:212224r.

77. V.V. Bardin, I.V. Stennikova, G.G. Furin, T.V. Leshina, G.G. Yakobson, Zh. Obshch. Khim., **58**, 2580 (1988). Chem. Abstr., **111**:134254e.

78. P.W. Rabideau, Z. Marcinow, Tetrahedron Lett., **29**, 3761 (1988).

79. M.G. Voronkov, N.F. Chernov, E.M. Perlova, J. Organometal. Chem., **341**, 225 (1988).

80. S. Katsumura, S. Fujiwara, S. Isoe, Tetrahedron Lett., **29**, 1173 (1988).

81. A. Tanaka, Y. Harigaya, N. Nishino, K. Nakayama, Heterocycles, **27**, 1115 (1988).

82. Y. Van den Winkel, O.S. Akkerman, F. Bickelhaupt, Main Group Met. Chem. **11**, 91 (1988).

83. J. Boyer, C. Breliere, F. Carre, R.J.P. Corriu, J. Chem. Soc. Dalton Trans., 43 (1989).

84. H. Sakarai, M. Murakami, K. Takeuchi, C. Kabuto, J. Organometal. Chem., **341**, 133 (1988).

85. S. Rozite, I. Mazeika, A. Gaukhman, N.P. Erchak, E. Lukovics, J. Organometal. Chem., **348**, 169 (1988).

86. A.N. Egorochkin, M.A. Lopatin, G.A. Razuvaev, N.P. Erchak, Dokl. Akad. Nauk SSSR **298**, 895 (1988). Chem. Abstr., **110**:95327p.
87. S.N. Tandura, Yu.A. Strelenko, S.I. Androsenko, E.E. Masterov, N.V. Alekseev, V.I. Rakiskaya, O.G. Rodin, Zh. Obshch. Khim., **58**, 398 (1988). Chem. Abstr., **110**:95335q
88. G. Yuan, C. Li, S. Yan, Z. Xie, Cuihua Xuebo, **9**, 52 (1988). Chem. Abstr., **110**:135314r.
89. L.I. Kopylova, N.D. Ivanova, V.N. Voropaev, E.N. Satsuk, N.I. Shergina, L.V. Sherstyannikova, M.G. Voronkov, Zh. Obshch. Khim., **58**, 806 (1988).
90. C. Xiao, Y. Lın, C. Luo, Z. Tian, Wuhan Daxue Xuebao Zir n Kexueban, 81 (1988). Chem. Abstr., **110**:231731v.
91. B. Marciniec, Z. Foltynowicz, W. Urbaniak, Appl. Organomet. Chem., **1**, 459 (1987).
92. V.I. Zhun, A.L. Tsvetkov, V.N. Sheludyakov, Zh. Obshch. Khim., **59**, 390 (1989). Chem. Abstr., **111**:134261e.
93. O.G. Yarosh, V.B. Modonov, M.G. Voronkov, Metalloorg. Khim., **1**, 712 (1988).
94. K.M. Rustamov, R.A. Sultanov, G.A. Saryev, R.I. Mamedova, M. Sh. Sultanova, Dokl. Akad. Nauk Az SSR, **43**, 39 (1987). Chem. Abstr., **110**:135303m.
95. R.A. Sultanov, K.M. Rustamov, Z.M. Pashaev, R.I. Mamedova, Azerb. Khim. Zh., 78 (1987). Chem. Abstr., **110**:95336r.
96. C. Hu, R. Yang, Y. Jiang, Fenzi Cuihua, **2**, 38 (1988). Chem. Abstr., **111**:78085m.
97. K. Takatsuna, M. Tachikawa, K. Shiozawa, N. Okamoto, Y. Okumura, EP 302,672 (C1. C07F7/18). Chem. Abstr., **111**:154099m.
98. A.B. Rajkumar, P. Boudjouk, Organometallics, **8**, 549 (1989).
99. K. Tamao, K. Kobayashi, Y. Ito, J. Amer. Chem. Soc., **111**, 6478 (1989).
100. H. Schmidbaur, J. Ebenhoech, Z. Naturforsch., B: Chem. Sci., **42**, 1543 (1987).
101. E. Lukevics, O. Pudova, R. Sturkovich, J. Organometal. Chem., **346**, 297 (1988).
102. E.M. Gordon, R. Eisenberg, J. Mol. Cat., **45**, 57 (1988).
103. E J. Crawford, P.K. Hanna, A.R. Citler, J. Amer. Chem. Soc., **111**, 6891 (1989).
104. K. Felfoldı, I. Kapocsi, M. Bartok, J. Organometal. Chem., **362**, 411 (1989).
105. H. Brunner, A. Kuerzinger, J. Organometal. Chem., **346**, 413 (1988).
106. H. Brenner, U. Obermann, Chem. Ber., **122**, 499 (1989).
107. S. Anwar, A.P. Davis, Tetrahedron, **44**, 3761 (1988).
108. H. Nagashima, K. Tatebe, T. Ishibashi, J. Sakakibara, K. Itoh, Organometallics, **8**, 2495 (1989).
109. W. Caseri, P.S. Pregosin, J. Organometal. Chem., **356**, 259 (1988).
110. X. Lin, M. Hong, Q. Cai, Xiamen Daxue Xuebao, Ziran Kexueban, **27**, 558 (1988).

111. N.R. Belyakova, V.P. Mileshkevich, Zh. Obshch. Khim., **59**, 724 (1989). Chem. Abstr. **111**:78103r.

112. P. Martinet, R. Sauvetre, J.F. Normant, J. Organometal. Chem., **367**, 1 (1989).

113. F.L. Koerwitz, G.B. Hammond, D.F. Weimer, J. Org. Chem., **54**, 738 (1989).

114. A. Maercker, K.D. Klein, Angew. Chem., **101**, 63 (1989).

115. S.S.P. Chou, H.L. kuo, C.J. Wang, C.Y. Tsai, J. Org. Chem., **54**, 868 (1989).

116. A.V. Seleznev, D.A. Bravo-Zhivotovskii, I.D. Kalikhman, V.Yu. Vitovskii, O.B. Bannikov, M.G. Voronkov, Metalloorg. Khim., **1**, 689 (1988). Chem. Abstr., **111**:134244b.

117. L. Capella, A. Degl'innocenti, G. Reginato, A. Ricci, M. Tadei, G. Seconi, J. Org. Chem., **54**, 1473 (1989).

118. I. Fleming, M. Rowley, P. Cuadrado, A.M. Gonzalez-Nogal, F.J. Pulido, Tetrahedron, **45**, 413 (1989).

119. P. Kocienski, S. Wadman, K. Cooper, J. Amer. Chem. Soc., **111**, 1363 (1989).

120. B.M. Trost, J.M. Tour, J. Org. Chem., **54**, 484 (1989).

121. Y. Morimoto, Y. Higuchi, K. Wakamatsu, K. Oshima, K. Utimoto, N. Yasuoka, Bull. Chem. Soc. Jpn., **62**, 639 (1989).

122. T.F. Bates, R.D. Thomas, J. Org. Chem., **54**, 1784 (1989).

123. N.M. Christovalova, I.S. Akhrem, V.F. Sizoi, V.V. Bardin, M.E. Vol'pin, Izv. Akad. Nauk SSSR Ser. Khim., 1180 (1988). Chem. Abstr., **110**:95337s.

124. K. Karabelas, A. Halberg, J. Org. Chem., **54**, 1773 (1989).

125. V. Fiandanese, G. Marchese, G. Mascolo, F. Naso, L. Ronzini, Tetrahedron Lett., **29**, 3705 (1988).

126. T.K. Vinod, H. Hart, Tetrahedron Lett., **29**, 885 (1988).

127. Y. Naruta, Y. Nishigaichi, K. Maruyama, Chem. Lett., 135 (1988).

128. S. Hyuga, N. Yamashina, S. Hara, A. Suzuki, Chem. Lett., 809 (1988).

129. B.P. Andreini, A. Carpita, R. Rossi, Tetrahedron Lett., **29**, 2239 (1988).

130. B. Cazes, V. Colovray, J. Gore, Tetrahedron Lett., **29**, 627 (1988).

131. F.L. Koerowitz, G.B. Hammond, D.F. Weimer, J. Org. Chem., **54**, 743 (1989).

132. B. Wrackmeyer, K. Wagner, Chem. Ber., **122**, 857 (1989).

133. K., Miura, Y. Ichinose, K. Nozaki, K. Fugami, K. Oshima, K. Utimoto, Bull. Chem. Soc. Jpn., **62**, 143 (1989).

134. H. Sakurai, K. Eabata, K. Sakamoto, Y. Nakadaira, C. Kabuto, Chem. Lett., 965 (1988).

135. Y. Kitano, T. Matsumoto, F. Sato, Tetrahedron, **44**, 4073 (1988).

136. I, Matsuda, A. Ogiso, S. Sato, Y. Izumi, J. Amer. Chem. Soc., **111**, 2332 (1989).

137. J. Ohshita, M. Ishikawa, Chem. Express, **3**, 179 (1988). Chem. Abstr., **110**:231690f.

138. H. Hopf, E. Naujoks, Tetrahedron Lett., **29**, 609 (1988).

139. E.C.Lund, T. Livinghouse, J. Org. Chem., **54**, 4487 (1989).

140. E. Negishi, S.J. Holmes, J.M. Tour, J.A. Miller, F.E. Cederbaum, D.R. Swanson, T Takahashi, J. Amer. Chem. Soc., **111**, 3336 (1989).

141. M. Fernandez, D.J. Pollart, H.W. Moore, Tetrahedron Lett., **29**, 2765 (1988).

142. N. Tokitoh, N. Choi, M. Goto, W. Ando, J. Org. Chem., **54**, 4660 (1989).

143. M. Ochiai, Y. Takaoka, T. Ukita, Y. Nagao, E. Fujita, J. Org. Chem., **54**, 2346 (1989).

144. K. Suzuki, M. Miyazawa, M. Shimazaki, G. Tsuchihashi, Tetrahedron, **44**, 4061 (1988).

145. Y. Hatanaka, T. Hiyama, J. Org. Chem., **54**, 268 (1989).

146. M.M. Doyle, W.R. Jackson, P. Perlmutter, Tetrahedron Lett., **30**, 233 (1989).

147. J.A. Soderquist, A. Negron, J. Org. Chem., **54**, 2462 (1989).

148. J.A. Soderquist, S.-J. Hwang Lee, Tetrahedron, **44**, 4033 (1988).

149. E.J. Grayson, G.H. Whitham, Tetrahedron, **44**, 4087 (1988).

150. M. Rowley, M. Tsukamoto, Y. Kishi, J. Amer. Chem. Soc., **111**, 2735 (1989).

151. M.D. Bachi, E. Bosch, Tetrahedron Lett., **29**, 2581 (1988).

152. R.F. Cunico, Synth. Commun., **18**, 917 (1988).

153. M. Ochiai, K. Sumi, Y. Takaoka, M. Kunishima, Y. Nagao, M. Shiro, E. Fujita, Tetrahedron, **44**, 4095 (1988).

154. V. Dirnens, Yu.Sh. Gol'dberg, E. Lukevits, Dokl. Akad. Nauk SSSR **298**, 116 (1988). Chem. Abstr., **110**:8270y.

155. W.Huang, J. Chen, Huaxue Xuebo, **46**, 895 (1988). Chem. Abstr., **110**:94474x.

156. O.E. Nasakin, P.M. Lukin, A.L. Shevnitsyn, V.D. Sheludyakov, E.A. Chernyshov, Zh. Obshch. Khim., **58**, 1168 (1988). Chem. Abstr., **110**:192906j.

157. R.A. Amriev, F.K. Velichko, Izv. Akad. Nauk SSSR Ser. Khim. 485 (1989). Chem. Abstr., **111**:214546s.

158. A.B. Terect'ev, Izv. Akad. Nauk SSSR Ser. Khim. 2179 (1988). Chem. Abstr., **111**:78082h.

159. R.L. Danheiser, E.J. Stone, H. Koyama, D.S. Yamashita, C.A. Klade, J. Amer. Chem. Soc., **111**, 4407 (1989).

160. J.M. Dener, D.J. Hart, Tetrahedron, **44**, 7037 (1988).

161. S. Kanemasa, H. Kobayashi, J. Tanaka, O. Tsuge, Bull. Chem. Soc. Jpn., **61**, 3957 (1988).

162. G.W. Daub, D.A. Heerding, L.E. Overman, Tetrahedron, **44**, 3919 (1988).

163. L.E. Overman, H. Wild, Tetrahedron Lett., **30**, 647 (1989).

164. R.M. Lett, L.E. Overman, Tetrahedron Lett., **29**, 6541 (1988).

165. L.A. Paquette, G. Ladouceur, J. Org. Chem., **54**, 4278 (1989).

166. D.A. Becker, R.L. Danheiser, J. Amer. Chem. Soc., **111**, 389 (1989).

167. K. Tamao, K. Maeda, T. Tanaka, Y. Ito, Tetrahedron Lett., **29**, 6955 (1988).
168. G.K. Henry, R. Shinimoto, Q. Zhou, W.P. Weber, J. Organometal. Chem., **350**, 3 (1988).
169. E. Liepins, Yu. Gol'dberg, I. Iovel, E. Lukevics, J. Organometal. Chem., **335**, 301 (1988).
170. J.S. Francisco, J. Amer. Chem. Soc., **111**, 7353 (1989).
171. J.K. McDonald, V.F. Kalasinsky, J.A.S. Smith, T.J. Geyer, J.R. Durig, J. Mol. Struct., **174**, 291 (1988).
172. H. Schmidbaur, J. Ebenhoech, G. Mueller, Z. Naturforsch., B: Chem. Sci. **43**, 49 (1988).
173. T. Iwahara, R. West, J. Chem. Soc., Chem. Commun., 954 (1988).
174. S. Mori, H. Iwakura, S. Takechi, Tetrahedron Lett., **29**, 5391 (1988).
175. Y. Ito, M. Inouye, M. Murakami, Tetrahedron Lett., **29**, 5379 (1988).
176. A.J. Stern, J.S. Swenton, J. Chem. Soc., Chem. Commun., 1255 (1988).
177. B.P. Andreini, M. Benetti, A. Carpita, R. Rossi, Gazz. Chim. Ital. **118**, 469 (1988).
178. R.J. Butlin, A.B. Holmes, E. McDonald, Tetrahedron Lett., **29**, 2989 (1988).
179. K.A. Horn, R.B. Grossman, J.R.G. Thorne, A.A. Whitenack, J. Amer. Chem. Soc., **111**, 4809 (1989).
180. M. Ishikawa, J. Oshita, Y. Ito, A. Minato, J. Organometal. Chem., **346**, C58 (1988).
181. G. Nagendrappa, Tetrahedron Lett., **30**, 121 (1989).
182. I.H. Ooi, R.H. Smithers, J. Org. Chem., **54**, 1479 (1989).
183. G. Guanti, E. Baldaro, L. Banfi, A. Guaragna, E. Narisano, U. Valcavi, Tetrahedron, **44**, 3685 (1988).
184. F.H. Van der Steen, H. Kleijn, J.T.B.H. Jastrzebski, G. Van Koten, Tetrahedron Lett., **30**, 765 (1989).
185. R.L. Danheiser, A. Nishida, S. Savariar, M.P. Trova, Tetrahedron Lett., **29**, 4917 (1988).
186. K. Hayakawa, A. Hayashida, K. Kanematsu, J. Chem. Soc., Chem. Commun., 1108 (1988).
187. Y. Shen, Q. Liao, J. Organometal. Chem., **346**, 181 (1988).
188. M. Ochiai, M. Kunishima, K. Fuji, M. Shiro, Y. Nagao, J. Chem. Soc., Chem. Commun., 1076 (1988).
189. R.M. Bettison, P.B. Hitchcock, D.R.M. Walton, J. Organometal. Chem., **341**, 247 (1988).
190. P.C.B. Page, S. Rosenthal, R.V. Williams, Synthesis, 621 (1988).
191. Y. Kita, S. Akai, M. Yamamoto, M. Taniguchi, Y. Tamura, Synthesis, 334 (1988).
192. B. Wrackmeye, J. Chem. Soc., Chem. Commun., 1624 (1988).

193. F. Camps, J.L. Coll, J.M. Moreto, Tetrahedron Lett., **29**, 5811 (1988).
194. A.H. Alberts, H. Wynberg, J. Chem. Soc., Chem. Commun., 748 (1988).
195. P.R. Jones, T.E. Albanesi, R.D. Gillespie, P.C. Jones, S.W. Ng, Appl. Organomet. Chem., **1**, 521 (1987).
196. C. Bianchini, A. Meli, M. Peuzzini, F. Vizza, F. Zanobini, P. Frediani, Organometallics, **8**, 2080 (1989).
197. Y. Akita, H. Kanekawa, T. Kawasaki, I. Shiratori, A. Ohta, J. Heterocycl. Chem. **25**, 975 (1988).
198. L.S. Liebeskind, J.R. Gasdaska, J.S. McCallum, S.J. Tremont, J. Org. Chem., **54**, 669 (1989).
199. J.W. Herndon, S.U. Tumer, Tetrahedron Lett., **30**, 295 (1989).
200. M. Jensen, T. Livinghouse, J. Amer. Chem. Soc., **111**, 4495 (1989).
201. J.J.W. McDouall, H.B. Schlegel, J. Amer. Chem. Soc., **111**, 4622 (1989).
202. V.D. Sheludyakov, V.I. Zhun, V.V. Strukova, Khim. Prom-st 401 (1987). Chem. Abstr., **109**:93103t.
203. N. El Alami, C. Belaud, J. Villieras, J. Organometal. Chem., **353**, 157 (1988).
204. P. Beak, B. Lee, J. Org. Chem., **54**, 458 (1989).
205. B. Laycock, I. Maynard, G. Wickham, W. Kitching, Aust. J. Chem., **41**, 693 (1988).
206. D.B. Puranik, P.M. Johnson, M.J. Fink, Organometallics, **8**, 770 (1989).
207. K. Fugami, J. Hibino, S. Nakasukasa, S. Matsubara, K. Oshima, K. Utimoto, H. Nozaki, Tetrahedron, **44**, 4277 (1988).
208. P. Cuadrado, A.M. Gonzalez, F.J. Pulido, I. Fleming, Tetrahedron Lett., **29**, 1825 (1988).
209. B.H. Lipshutz, D.C. Reuter, E.L. Ellsworth, J. Org. Chem., **54**, 4975 (1989).
210. M.G. Sauinier, J.F. Kadow, M.M. Tun, J. Amer. Chem. Soc., **111**, 8320 (1989).
211. Z.J. Ni, T.Y. Luh, J. Chem. Soc., Chem. Commun., 1011 (1988).
212. T.V. Lee, J.R. Porter, F.S. Frances, Tetrahedron Lett., **29**, 5009 (1988).
213. H. Iio, M. Ishii, M. Tsukamoto, T. Tokoroyama, Tetrahedron Lett., **29**, 5965 (1988).
214. R.F. Horvath, T.H Chan, J. Org. Chem., **54**, 317 (1989).
215. Y. Hori, T. Mitsudo, Y. Watanabe, Bull. Chem. Soc. Jpn., **61**, 3011 (1988).
216. H. Shiragami,T. Kawamoto, K Imi, S. Matsubara, K. Utimoto, H. Nozaki, Tetrahedron, **44**, 4009 (1988).
217. T. Hayashi, Y. Matsumoto, Y. Ito, Tetrahedron Lett., **29**, 4147 (1988).
218. N. Chotani, T. Takeyasu, T. Hanafusa, Tetrahedron Lett., **29**, 3979 (1988).
219. M.G. Ranasinghe, P.L. Fuchs, J. Amer. Chem. Soc., **111**, 779 (1989).
220. W. Kitching, K.G. Penman, B. Laycock, I. Maynard, Tetrahedron, **44**, 3819 (1988).
221. I. Fleming, N.J. Lawrence, Tetrahedron Lett., **29**, 2073 (1988).

222. I. Fleming, N.J. Lawrence, Tetrahedron Lett., **29**, 2077 (1988).
223. T. Matsumoto, Y. Kitano, F. Sato, Tetrahedron Lett., **29**, 5685 (1988).
224. K. Mizuno, O. Munehiro, Chem. Lett., 1507 (1988).
225. D.P. Curren, S.A. Gothe, Tetrahedron, **44**, 3945 (1988).
226. H.M.R. Hoffmann, U. Eggert, U. Gibbels, K. Giesel, O. Koch, R. Lies, J. Rabe, Tetrahedron, **44**, 3899 (1988).
227. A. Kaminura, H. Sasatani, T. Hashimoto, N. Ono, J. Org. Chem., **54**, 4998 (1989).
228. S.E. Denmark, R.C. Klix, Tetrahedron, **44**, 4043 (1988).
229. S.R. Wilson, C.E. Augelli-Szafran, Tetrahedron, **44**, 3983 (1988).
230. G.R. Procter, A.T. Russell, P.J. Murphy, T.S. Tan, A.N. Mather, Tetrahedron, **44**, 3953 (1988).
231. E. Vedejs, J.D. Roberts, S.J. Wittenberger, Tetrahedron Lett., **29**, 2287 (1988).
232. N.X. Hu, Y. Aso, T. Otsubo, F. Ogura, Tetrahedron Lett., **29**, 4949 (1988).
233. R. Bambai, R.D.W. Kemmitt, J. Chem. Soc., Chem. Commun., 734 (1988).
234. M. Hayashi, A. Inubushi, T. Mukaiyama, Bull. Chem. Soc. Jpn., **61**, 4037 (1988).
235. M. Fujita, M. Obayashi, T. Hiyama, Tetrahedron, **44**, 4135 (1988).
236. T. Hayashi, Y. Matsumoto, T. Kiyoi, Y. Ito, S. Kohra, Y. Tominaga, A. Hosomi, Tetrahedron Lett., **29**, 5667 (1988).
237. G. Yi, D. Wong, T.H. Chen, Youji Huaxue **8**, 115 (1988). Chem. Abstr., **110**:75615c.
238. M. Kira, T. Hino, H. Sakurai, Tetrahedron Lett., **30**, 1099 (1989).
239. J.K. Whitesell, K. Nabona, D. Deyo, J. Org. Chem., **54**, 2258 (1989).
240. G.A. Molander, S.W. Andrews, Tetrahedron, **44**, 3869 (1988).
241. M.T. Reetz, A. Jung, C. Bolm, Tetrahedron, **44**, 3889 (1988).
242. D. Shinzer, C. Allagiannis, S. Wichmann, Tetrahedron, **44**, 3851 (1988).
243. G. Majetich, K. Hull, Tetrahedron Lett., **29**, 2773 (1988).
244. G. Majetich, J. Defauw, Tetrahedron, **44**, 3833 91988).
245. S.R. Angle, K.D. Turnbull, J. Amer. Chem. Soc., **111**, 1136 (1989).
246. K. Sato, M. Kira, H. Sakurai, J. Amer. Chem. Soc., **111**, 6429 (1989).
247. J. Pornet, A. Rayadh, L. Migniac, Tetrahedron Lett., **29**, 4717 (1988).
248. J.S. Panek, M.A. Sparks, J. Org. Chem., **54**, 2034 (1989).
249. T. Shono, Y. Matsumura, K. Uchida, F. Nakatani, Bull. Chem. Soc. Jpn., **61**, 3029 (1988).
250. M. Kawashima, T. Fujisawa, Bull. Chem. Soc. Jpn., **61**, 4051 (1988).
251. H. Mayr, A. Cambanis, E. Baeuml, Synthesis, 962 (1988).
252. G.A. Molander, S.W. Andrews, J. Org. Chem., **54**, 3114 (1989).
253. W.J. Klaver, H. Hiemstra, W.N. Speckamp, Tetrahedron, **44**, 6729 (1988).

254. R.J. Giguere, S.M. Duncan, J.M. Bean, L. Purvis, Tetrahedron Lett., **29**, 6071 (1988).
255. T.W. Bell, L.Y. Hu, Tetrahedron Lett., **29**, 4819 (1988).
256. B.M. Trost, P. Seoane, S. Mignani, M. Acemoglu, J. Amer. Chem. Soc., **111**, 7487 (1989).
257. B.M. Trost, S.A. King, T. Schmidt, J. Amer. Chem. Soc., **111**, 5902 (1989).
258. B.M. Trost, S. Schneider, Angew. Chem., **101**, 215 (1989).
259. T.V. Lee, R.J. Boucher, J.R. Porter, D.A. Taylor, Tetrahedron, **44**, 4233 (1988).
260. E. Schaumann, A. Kirschning, Tetrahedron Lett., **29**, 4281 (1988).
261. K. Tamao, E. Nakajo, Y. Ito, Tetrahedron, **44**, 4007 (1988).
262. A. Mordini, G. Palio, A. Ricci, M. Taddei, Tetrahedron Lett., **29**, 4991 (1988).
263. G. Hidalgo Llinas, M. Mena, F. Palacios, P. Royo, R. Serrano, J. Organometal. Chem., **340**, 37 (1988).
264. H.D. Hausen, C. Bessenbacher, W. Kaim, Z. Naturforsch., B: Chem. Sci. **43**, 1087 (1988).
265. M.N. Paddon-Row, K. Jordan, J. Chem. Soc., Chem. Commun., 1508 (1988).
266. J. Pornet, A. Rayadh, L. Migniac, Tetrahedron Lett., **29**, 3065 (1988).
267. D. Damour, J. Pornet, L. Migniac, J. Organometal. Chem., **349**, 43 (1988).
268. P.M. Esch, H. Hiemstra, W.N. Speckamp, Tetrahedron Lett., **29**, 367 (1988).
269. D.C. Billington, W.J. Kerr, P.L. Pauson, J. Organometal. Chem., **341**, 181 (1988).
270. R.J. Mills, V. Snieckus, J. Org. Chem., **54**, 4386 (1989).
271 A. Fuerstner, H. Wiedmann, J. Organometal. Chem., **354**, 15 (1988).
272. I.S. Cho, C.P. Lee, P.S. Mariano, Tetrahedron Lett., **30**, 799 (1989).
273. A.J. Stern, J.S. Swenton, J. Org. Chem., **54**, 2953 (1989).
274. P.G. McDougal, B.D. Condon, M.D. Laffose, Jr.; A.M. Lauro, D. Van Derveer, Tetrahedron Lett., **29**, 2547 (1988).
275. M.P. Teulade, S.P. Savignac, Janssen Chim Acta, **6**, 3 (1988). Chem. Abstr., **110**:95397m.
276. E. Lukovics, R. Sturkovich, Yu. Gol'dberg, A. Gaukhman, J. Organometal. Chem , **345**, 19 (1988).
277. H. Beckers, H. Buerger, R. Eujen, Z. Anorg. Allg. Chem., **563**, 38 (1988).
278. M. Letellier, D.J. McPhee, D. Griller, Synthetic Commun., **18**, 1975 (1988).
279. W. Wolfsberger, Z. Naturforsch., B: Chem Sci. **43**, 295 (1988).
280. J.A. Soderquist, I. Rivera, A. Negron, J. Org. Chem., **54**, 4051 (1989).
281. M.A. Avery, C. Jennings-White, W.K.M. Chong, J. Org. Chem., **54**, 1789 (1989).
282. M.P. Clarke, R. Damrauer, I.M.T. Davidson, R. Simon, Organometallics, **8**, 2031 (1989).
283. R. Tacke, R. Rohr-Aehle, J. Organometal. Chem., **354**, 139 (1988).

284. T.K. Reddy, G.V. Reddy, J. Chem. Soc., Chem. Commun., 251 (1989).
285. J.J. Eisch, C.S. Chiu, J. Organometal. Chem., **358**, C1 (1988).
286. J. Kitteringham, M.B. Mitchell, Tetrahedron Lett., **29**, 3319 (1988).
287. P.G. McDougal, B.D. Condon, Tetrahedron Lett., **30**, 789 (1989).
288. W. Meichle, H.H. Otto, Arch. Pharm. **322**, 263 (1989). Chem. Abstr., 111:134025f.
289. J. Lasarte, C. Palomo, J.P. Picard, J. Dunogues, J.M. Aizpurua, J. Chem. Soc., Chem. Commun., 72 (1989).
290. G.P. Stahly, D.R. Bell, J. Org. Chem., **54**, 2873 (1989).
291. S.R. Ramadas, S.R. Jayanthi, W. Walter, Sulfur Lett., **7**, 159 (1988).
292. A. Padwa, J.R. Gasdaska, Tetrahedron, **44**, 4147 (1988).
293. A. Padwa, G.E. Fryxell, J.R. Gasdaska, M.K. Venkatramanan, G.S.K. Wong, J. Org. Chem., **54**, 644 (1989).
294. A. Padwa, W.H. Dent, A.M. Schoffstall, P.E. Yeske, J. Org. Chem., **54**, 4430 (1989).
295. W. Xu, Y.T. Yoon, E. Hasegawa, U.C. Yoon, P.S. Mariano, J. Amer. Chem. Soc., **111**, 406 (1989).
296. J. Yoshida, S. Isoe, Tetrahedron Lett., **28**, 6621 (1987).
297. A. Sekiguchi, T. Nakanishi, C. Kabuto, H. Sakurai, J. Amer. Chem. Soc., **111**, 3748 (1989).
298. B.C. manley, R.J. Lagow, Polyhedron, **7**, 2023 (1988).
299. N.J.R. Van Eikema Hommes, F. Bickelhaupt, G.W. Klumpp, Tetrahedron Lett., **29**, 5237 (1988).
300. M. Zaidlewicz, C.S. Panda, Synthesis, 645 (1987).
301. M. Zaidlewicz, Synthesis, 701 (1988).
302. T.F. Bates, R.D. Thomas, J. Organometal. Chem., **359**, 285 (1989).
303. B.A. Narayanan, W.H. Bunnelle, Tetrahedron Lett., **28**, 6261 (1987).
304. M.A. Avery, C. Jennings-White, W.K.M. Chong, J. Org. Chem., **54**, 1789 (1989).
305. W. Uhl, Z. Naturforsch., B: Chem. Sci., **43**, 1113 (1988).
306. E. Negishi, K. Akiyoshi, B. O'Connor, K. Takagi, G. Wu, J. Amer. Chem. Soc., **111**, 3089 (1989).
307. E. Niecke, M. Leuer, M. Nieger, Chem. Ber., **122**, 453 (1989).
308. P.L. Coe, A.S. Jones, A. Kumar, R.T. Walker, Tetrahedron Lett., **29**, 835 (1988).
309. J.J. Eisch, J.E. Galle, J. Organometal. Chem., **341**, 293 (1988).
310. K. Hartke, O. Kunze, LIebigs Ann. Chem., 321 (1989).
311. M.P. Telaude, P. Savignac, J. Organometal. Chem., **338**, 295 (1988).
312. S. Urayama, S. Inoue, Y. Sato, J. Organometal. Chem., **354**, 155 (1988).
313. D.I. Han, D.Y. Oh, Synthetic Commun., **18**, 2111 (1988).

314. A.R. Katritzky, R.J. Offerman, P. Cabildo, M. Soleiman, Recl. Trav. Chim. Pays-Bas, **107**, 641 (1988).

315. R.P. Short, S. Masamune, J. Amer. Chem. Soc., **111**, 1892 (1989).

316. S. Sare, H.K. Cammenga, B. Becker, R. Rohr-Aehle, R. Tacke, J. Therm. Anal., **33**, 1185 (1987).

317. H. Beckers, H. Buerger, C.J. Wilke, J. Organometal. Chem., **356**, 31 (1988).

318. G.A. Gavrilova, T.N. Aksamentova, N.A. Khlopenko, N.N. Chipanina, Yu.L. Frolov, V.B. Modonov, L.I. Gubanova, M.G. Voronkov, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk 81 (1989). Chem. Abstr., **110**:231710n.

319. A.A Macharashvili, B.A. Gostevskii, V.E. Shklover, Yu.T. Struchkov, M.G. Voronkov, B.A. Gostevskii, I.D. Kalihman, O.B. Bannikova, V.A. Pestunovich, J. Organometal. Chem., **340**, 23 (1988).

320. M. Bellassoued, J.E. Dubois, E. Bertounesque, Bull. Sic. Chim. Belg., **97**, 263 (1988).

321. S. Guertler, H.H. Otto, Arch. Pharm. **322**, 3 (1989).

322. F.P. Cossio, J.M. Odriozola, M. Oiarbide, C. Palomo, J. Chem. Soc., Chem. Commun., 74 (1989).

323. J.P. Gilday, J.C. Gallucci, L.A. Paquette, J. Org. Chem., **54**, 1399 (1989).

324. J.D. Winkler, C.S. Lee, L. Rubo, C.L. Muller, P.J. Squattrito, J. Org. Chem., **54**, 4491 (1989).

325. K.T. Mead, B. Samuel, Tetrahedron Lett., **29**, 6573 (1988).

326. S. Sato, I, Matsuda, Y. Izumi, J. Organometal. Chem., **344**, 71 (1988).

327. G.S. Zaitseva, O.P. Novikova, L.I. Livantsova, A.V. Kisin, Yu.I. Baukov, Zh. Obshch. Khim., **58**, 1675 (!988).Chem. Abstr., **110**:172712q.

328. V. Bagheri, M.P. Doyle, J. Taunton, E.E. Claxton, J. Org. Chem., **53**, 6158 (1988).

329. G.S. Zaitseva, O.P. Novikova, L.I. Livantsova, Yu.I. Baukov, Zh. Obshch. Khim., **58**, 1676 (1988).Chem. Abstr., **110**:172713r.

330. G.S. Zaitseva, I.F. Lutsenko, A.V. Kisin, Yu.I. Baukov, J. Lorberth, J. Organometal. Chem., **345**, 253 (1988).

331. G.S. Zaitseva, A.V. Kisin, O.P. Novikova, L.I. Livansova, Yu.I. Baukov, Zh. Obshch. Khim., **58**, 1677 (1988). Chem. Abstr., **110**:172720r.

332. G.L. Larson, R. Berrios, J.A. Prieto, Tetrahedron Lett., **30**, 283 (1989).

333. S. Guertler, H.H. Otto, Arch. Pharm., **322**, 105 (1989).

334. P.F. Hudrlik, E.L.O. Agwaramgbo, A.M. Hudrlik, J. Org. Chem., **54**, 5613 (1989).

335. G.L. Larson, J.A. Prieto, E. Ortiz, Tetrahedron, **44**, 3781 (1988).

336. S.L. Jones, C.J.M. Stirling, J. Chem. Soc., Chem. Commun., 1153 (1988).

337. N.A. Avdyukhina, E.B. Chuklanova, I.A. Abronin, A I. Gusev, V.I. Zhun, V.D Sheldyakov, Metalloorg. Khim., **1**, 878 (1988).

338. B.M. Choudary, K. Mukkanti, Y.V.S. Rao, J. Mol. Catal., **48**, 151 (1988).
339. G.A. Molander, K. Mautner, J. Org. Chem., **54**, 4042 (1989).
340. T. Dubuffet, R. Sauvetre, J.F. Normant, Tetrahedron Lett., **29**, 5923 (1988).
341. M. Masnyk, J. Wicha, Tetrahedron Lett., **29**, 2497 (1988).
342. Y. Zhang, J.A. Miller, E. Negishi, J. Org. Chem., **54**, 2043 (1989).
343. T.H. Chan, L.M. Chen, D. Wang, J. Chem. Soc., Chem. Commun., 1280 (1988).
344. T. Nakajima, M. Segi, S. Suga, Kenkyu Hokoku - Asahi Garasu Kogyo Gijutsu Shoreikai **51**, 243 (1987). Chem. Abstr., **111**:23568r.
345. J.S. Nowick, R.L. Danheiser, Tetrahedron, **44**, 4113 (1988).
346. J.A. Soderquist, C.L. Anderson, Tetrahedron Lett., **29**, 2425 (1988).
347. J.A. Soderquist, C.L. Anderson, Tetrahedron Lett., **29**, 2777 (1988).
348. F. Shirai, T. Nakai, Chem. Lett., 445 (1989).
349. B.F. Bonini, G. Mazzanti, P. Zani, G. Maccagnani, E. Foresti, J. Chem. Soc. Perkin Trans.1, 1499 (1988).
350. R.S. Grev, H.F. Schaefer, III., J. Amer. Chem. Soc., **111**, 6137 (1989).
351. E.N. Step, V.F. Tarasov, A.L. Buchachenko, Chem Phys. Lett., **144**, 523 (1988).
352. K. Mochida, K. Yamamoto, Bull. Chem. Soc. Jpn., **61**, 2933 (1988).
353. M. Kira, K. Takeuchi, C. Kabuto, H. Sakurai, Chem. Lett., 353 (1988).
354. W. Amberg, D. Seebach, Angew. Chem., **100**, 1786 (1988).
355. L.A. Paquette, G.D. Maynard, C.S. Ra, M. Hoppe, J. Org. Chem., **54**, 1408 (1989).
356. P.F. Hudrlik, A.M. Hudrlik, T. Yimenu, M.A. Waugh, Tetrahedron, **44**, 3791 (1988).
357. M. Asaoka, N. Fujii, K. Shima, H. Takei, Chem. Lett., 805 (1988).
358. M. Asaoka, K. Shima, N. Fujii, H. Takei, Tetrahedron, **44**, 4757 (1988).
359. M. Asaoka, K. Takenouchi, H. Takei, Chem. Lett., 1225 (1988).
360. M. Asaoka, K. Takenouchi, H. Takei, Chem. Lett., 921 (1988).
361. K. Tanino, T. Katoh, I. Kuwajima, Tetrahedron Lett., **29**, 1815 (1988).
362. T. Katoh, K. Tanino, I. Kuwajima, Tetrahedron Lett., **29**, 1819 (1988).
363. H. Nishiyama, K. Sakuta, N. Osaka, H. Arai, M. Matsumoto, K. Itoh, Tetrahedron, **44**, 2413 (1988).
364. I. Fleming, S.K. Armstrong, R.J. Pollitt, J. Chem. Res. Synop., 19 (1989).
365. M. Xie, W.J. Le Noble, J. Org. Chem., **54**, 3836 (1989).
366. J.A. Adeleke, B.L. Booth, J. Organometal. Chem., **339**, 223 (1988).
367. T. Aoyama, Y. Iwamoto, S. Nishigaki, T. Shioiri, Chem. Pharm. Bull., **37**, 253 (1989).
368. T. Asaki, T. Aoyama, T. Shioiri, Heterocycles, **27**, 343 (1988).
369. T. Aoyama, S. Katsuta, T. Shioiri, Hetercycles, **28**, 133 (1989).

370. V.J. Shiner, Jr.; M.W. Ensinger, J.C. Huffman, J. Amer. Chem. Soc., **111**, 7199 (1989).

371. W. Kirmse, F. Soellenboehmer, J. Amer. Chem. Soc., **111**, 4127 (1989).

372. J. Coope, V.J. Shiner, Jr., J. Org. Chem., **54**, 4270 (1989).

373. C. Chatgilialoglu, S. Rossini, Bull. Soc. Chim. Fr., 298 (!988).

374. C. Chatgilialoglu, D. Griller, M. Lesage, J. Org. Chem., **54**, 2492 (1989).

375. D.M. Wetzel, K.E. Salomon, S. Berger, J.I. Brauman, J. Amer. Chem. Soc., **111**, 3835 (1989).

376. N. Soundararajan, J.E. Jackson, M.S. Platz, J. Phys. Org. Chem., **1**, 39 (1988).

377. R.A. Jackson, A.K. Zarkadis, J. Organometal. Chem., **341**, 273 (1988).

378. M.G. Steinmetz, H. Bai, Organometallics, **8**, 1112 (1989).

379. W. Kaim, J. Organometal. Chem., **339**, 253 (1988).

380. C.J. Rhodes, J. Organometal. Chem., **336**, 317 (1987).

381. P. Jutzi, U. Holtmann, D. Kanne, C. Krueger, R. Blom, R. Gleiter, I. Hyla-Kryspin, Che, Ber., **122**, 1629 (1989).

382. J.E. Baggott, M.A. Blitz, H.M. Frey, P.D. Lightfoot, R. Walsh, J. Chem. Soc., Faraday Trans. 2 **84**, 515 (1988).

383. E.A. Cheryshev, N.G. Komalenkova, M.Ya. Kel'man, V.N. Bochkarev, A.N. Polivanov, V.I. Zhun, Zh. Obshch. Khim., **58**, 1166 (1988).

384. E.A. Chernyshev, N.G. Komalenkova, D.A. Zagorets, M.Ya. Kel'man, Zh. Obshch. Khim., **57**, 2732 (1987).

385. A. Patyk, W. Sander, J. Gauss, D. Cremer, Angew. Chem., **11101**, 920 (1989).

386. H. Saso, W. Ando, K. Ueno, Tetrahedron, **45**, 1929 (1989).

387. G.R. Gillette, G.H. Noren, R. West, Organometallics, **8**, 487 (1989).

388. M.P. Clarke, I.M.T. Davidson, M.P. Dillon, J. Chem. Soc., Chem. Commun., 1251 (1988).

389. M.P. Clarke, I.M.T. Davidson, J. Chem. Soc., Chem. Commun., 241 (1988).

390. M.P. Clarke, I.M.T. Davidson, M.P. Dillon, J. Chem. Soc., Chem. Commun., 1139 (1988).

391. M.S. Gordon, J.A. Boatz, Organometallics, **8**, 1978 (1989).

392. H.E. O'Neal, M.A. Ring, W.H. Richardson, G.F. Licciardi, Organometallics, **8**, 1968 (1989).

393. R. Walsh, Organometallics, **8**, 1973 (1989).

394. K.E. Nares, M.E. Harris, M.A. Ring, H.E. O'Neal, Organometallics, **8**, 1964 (1989).

395. M.S. Gordon, T.N. Truong, Chem. Phys. Lett., **142**, 110 (1987).

396. G. Levin, P.K. Das, C. Bilgrien, C.L. Lee, Organometallics, **8**, 1206 (1989).

397. N. Auner, Z. Anorg. Allg.. Chem., **558**, 55 (1988).

398. N. Auner, Z. Anorg. Allg.. Chem., **558**, 87 (1988).

399. N. Wiberg, M. Link, G. Fischer, Chem Ber., **122**, 409 (1989).

400. N. Wiberg, G. Preiner, K. Schurz, G. Fischer, Z. Naturforsch., B: Chem. Sci., **43**, 1468 (1988).
401. M.G. Steinmetz, B.S. Udayakumar, M.S. Gordon, Organometallics, **8**, 530 (1989).
402. R.T. Conlin, S. Zhang, M. Namavari, K.L. Bobbitt, Organometallics, **8**, 571 (1989).
403. A.G. Brook, A.K. Saxena, J.F. Sawyer, Organometallics, **8**, 850 (1989).
404. K.M. Baines, A.G. Brook, R.R. Ford, P.D. Lickiss, A.K. Saxena, W.J. Chatterton, J.F. SAwyer, B.A. Behnam, Organometallics, **8**, 693 (1989).
405. A.G. Brook, A. MacMillan, J. Organometal. Chem., **341**, C9 (1988).
406. H.S. Gutowsky, J. Chen, P.J. Hajduk, J.D. Keen, T. Emilsson, J. Amer. Chem. Soc., **111**, 1901 (1989).
407. K.M. Baines, A.G. Brook, P.D. Lickiss, J.F. Sawyer, Organometallics, **8**, 709 (1989).
408. N. Auner, J. Grobe, T. Schaefer, B. Krebs, J. Organometal. Chem., **363**, 7 (1989).
409. Y. Pan, K. Peters, H.G. Von Schnering, Chem Ber., **122**, 1483 (1989).
410. B.D. Shepherd, D.R. Powell, R. West, Organometallics, **8**, 2664 (1989).
411. M. Weidenbruch, A. Schaefer, H. Marsmann, J. Organometal. Chem., **354**, C12 (1988).
412. G.R. Gillette, J. Maxka, R. West, Angew. Chem., **101**, 90 (1989).
413. M. Weidenbruch, B. Flintjer, S. Pohl, W. Saak, Angew. Chem., **101**, 89 (1989).
414. M. Weidenbruch, B. Flintjer, S. Pohl, D. Haase, J. Martens, J. Organometal. Chem., **338**, C1 (1988).
415. H. Piana, U. Schubert, J. Organometal. Chem., **348**, C19 (1988).
416. M. Driess, A.D. FAnta, D. Powell, R. West, Angew. Chem., **101**, 1087 (1989).
417. G. Ju, Y. Yang, Huaxue Xuebao, **46**, 639 (1988). Chem. Abstr., **110**:231702m.
418. P. Arya, J. Boyer, R.J.P. Corriu, G.F. Lanneau, M. Perot, J. Organometal. Chem., **346**, C11 (1988).
419. V.N. Khabasheskii, Z.A. Kerzina, O.M. Nefedov, Izv. Nauk SSSR, Ser. Khim., 2187 (1988).
420. V.N. Khabasheskii, Z.A. Kerzina, E.G. Baskir, A.K. Maltsev, O.M. Nefedov, J. Organometal. Chem., **347**, 277 (1988).
421. S.S. Zigler, L.M. Johnson, R. West, J. Organometal. Chem., **341**, 187 (1988).
422. N. Wiberg, K. Schurz, J. Organometal. Chem., **341**, 145 (1988).
423. H.J. Hofmann, R. Cimiraglia, M. Persico, Chem. Phys. Lett., **146**, 249 (1988).
424. M.J.S. Dewar, A.J. Holder, Hetercycles, **28**, 1135 (1989).
425. P. Jutzi, M. Meyer, H.P. Reisenauer, G. Maier, Chem Ber., **122**, 1227 (1989).
426. R. Boese, P. Paetzold, A. Tapper, R. Ziembinski, Chem. Ber., **122**, 1057 (1989).

427. J.A. Boatz, M.S. Gordon, J. Phys. Chem., **93**, 3025 (1989).
428. J.H. Bowie, P.C.H. Eichinger, J. Chem. Soc. Perkin Trans.2, 1263 (1988).
429. F. Cacace, M.E. Crestoni, S. Fornarini, R. Gabrielli, Int. J. Mass Spectrom. Ion Processes **84**, 17 (1988).
430. J P. Lambert, J.A. McConnell, W. Schilf, W.J. Schulz, Jr., J. Chem. Soc., Chem. Commun., 455 (1988).
431. S.K. Shin, J.L. Beauchamp, J. Amer. Chem. Soc., **111**, 900 (1989).
432. G. Angelini, Y. Keheyan, G. Laguzzi, L. Gaetano, Tetrahedron Lett., **29**, 4159 (1988).
433. J.A. Soderquist, A. Hassner, Tetrahedron Lett., **29**, 1899 (1988).
434. J.B. Lambert, G.T. Wang, D.H. Teramura, J. Org. Chem., **53**, 5422 (1988).
435. M.R. Ibrahim, W.L. Jorgensen, J. Amer. Chem. Soc., **111**, 819 (1989).
436. I.M.T. Davidson, G. Eaton, K.J. Hughes, J. Organometal. Chem., **347**, 17 (1988).