SILICON - THE SILICON-CARBON BOND

Annual Survey for the year 1982

Gerald L. Larson
Department of Chemistry
University of Puerto Rico
Río Piedras, Puerto Rico 00931 (USA)

I. INTRODUCTION

This section of the annual survey of organosilicon chemistry covers material reported in volumes 96 and 97 of Chemical Abstracts. It is intended to cover the carbon-silicon bond and carbofunctional organosilanes. In many cases the reader will note that equations are written in a general form utilizing the designations R and Ar for alkyl and aryl groups, respectively. Some overlap of material with other sections of the survey is inevitable, but preferable to omissions.

Although the survey is arranged in sections, other examples of each particular class of compounds will be found in other sections as well due to the "dual" nature of much of the chemistry. This has been separated out whenever possible, but to do so in every case would fragment and lengthen the survey excessively.

II. REVIEWS

Thirty six review articles appeared in volumes 96 and 97 of Chemical Abstracts. These are given below with the number of references cited in each given in parentheses. Thus, review articles appeared on the structure and properties of organocyclodisilazanes (164) [1], 1-silacyclohexa-2,4-dienes as ligands (20) [2], preparation and properties of organosilicons (0) [3], industrial preparation of organosilicons (23) [4], cyclic polysilanes (27) [5], the silicon-hydrogen bond in organosilanes (193) [6], thiophene derivatives of silicon, germanium, tin and lead (46) [7], heats of formation of organosilicon compounds (76) [8], silyl groups as leaving groups (86) [9], and organosilicons with unusual structures (31) [10]. Several reviews dealt with the topic of organosilicons in synthesis (26) [11], applications of organosilicons in organic synthesis (29) [12], applications of allylsilanes to organic synthesis (30) [13], allylsilanes as allyl cation equivalents (29) [14], reactions of allylsilanes with synthetic applications (52) [15], allylsilanes as synthons of allyl alcohols (41) [16], chemistry of cyclopropylsilanes (47) [17], silyl methods for the modification of penicillin and cephalosporin (121) [18], silylation of functional groups (70) [19], and the use of organosilicons in the synthesis of naturally occurring compounds (36) [20]. Five reviews deal with silicon reagents. These are organosilicon reagents (86) [21], organopseudohalides (282) [22], syntheses with trimethylsilyl cyanide (9) [23], trialkylsilyl triflates in organic synthesis (77) [24], and trialkylsilyl perfluoroalkanesulfonates in organic synthesis (191) [25]. Five of the reviews deal with biologically active organosilicons. These are systematic sila substitution of drugs (127) [26] sila substitutions (17) [27], bioactive organosilicon compounds (53) [28], biologically active silicon compounds (23) [29], and novel achievements in organosilicon chemistry : its application to organic syntheses, catalytic possibilities and biological activity (54) [30]. The topic of reactive silicon species was reviewed as the reaction of silicon atoms and silylenes (234) [31], the chemistry of silacyclopropenes (30) [32], and silylene, germylene and stannylene (19) [33]. Hydrosilylation was reviewed regarding the stereochemistry and mechanism (book) [34], polymer supported metal catalysts (23) [35], and the synthesis of vinylsilanes from olefins and hydrosilanes (23) [36].

III. DISSERTATIONS

Doctoral dissertations, which are available from Dissertation Abstracts, Ann Arbor, Michigan, are given in this section. These include the chemistry of silenes, silenoids and 2-silanorbornenes [37], synthesis of unsaturated silacycles [38], mechanism of shock-initiated decomposition of disilane [39], chemistry of silylsilylenes [40], reaction of halomethylsilanes with alkoxides [41], reduction of α-chlorosilanes with tri-n-butyltin hydride [42], regio- and stereochemical studies of organosilanes [43], internal dynamics of tri-tert-butylsilanes [44], sterically hindered silyl enol ethers [45], permethylated polysilanes [46], secondary mass spectrometry of organosilane films [47], reactions of trialkylsilyl metal carbonyls with aldehydes and ketones [48], trimethylsilylmethyl substituted organotin compounds [49], and trimethylsilylmethyl indium(III) compounds [50].

IV. ALKYLSILANES

This section includes silicon-carbon systems wherein the carbon ligands contain no or remote functionality.

A. Preparation

The preparation of adamantylalkyl(aryl)allyloxysilanes has been reported. [51] A study of the catalytic activity of steam and pressure-cured copper in the direct synthesis of methylchlorosilanes has been made. [52] Tetraalkylsilanes were prepared by treatment of silicon tetrahalides or alkyl silicon trihalides with two or more organometallic compounds. (Eqn. 1) The mixtures were useful as lubricants and hydraulic fluids.

$$ {}^{n}C_8H_{17}MgBr + {}^{n}C_{10}H_{21}MgBr + MeSiCl_3 \xrightarrow[{[53]}]{} MeSi({}^{n}C_8H_{17})_m({}^{n}C_{10}H_{21})_{3-m} \quad (1) $$

m= 3	28.0%
= 2	48.0%
= 1	21.7%
= 0	2.3%

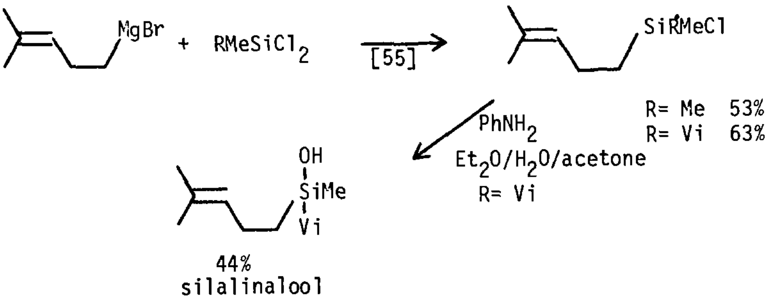
The nucleophilic substitution at silicon was employed in the preparation of some potential sila perfumes. (Eqn. 2)

$$\begin{tikzcd} MeSiCl_3 + R^1MgCl \arrow[r, "{[54]}"'] & R^1MeSiCl_2 \arrow[r, "R^2MgCl"] & R^1R^2MeSiCl \arrow[d, "NaOH"] \\ & & R^1R^2MeSiOH \end{tikzcd} \quad (2)$$

65-89%

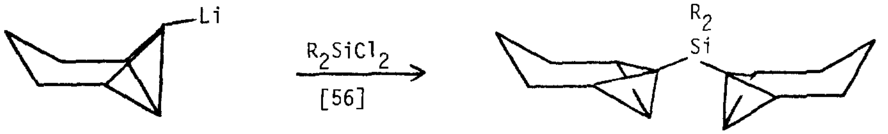
R^1	R^2
Me	$PhCH_2$
Et	$PhCH_2$
Me	$PhCH_2CH_2$
Et	$PhCH_2CH_2$
Vi	$PhCH_2CH_2$

In another synthesis of sila perfumes, the silicon analog of linalool was prepared. (Eqn. 3)



(3)

The intriguing disila[4.1.1]propellanes were prepared as shown below. (Eqns. 4-7)



(4)

1

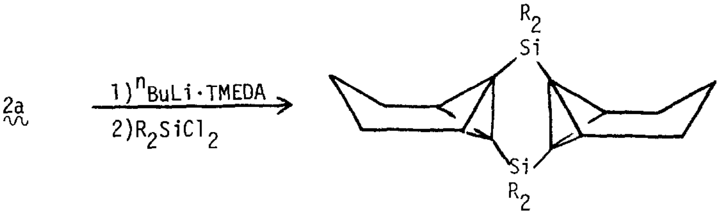
2a R= Me 100%
2b R= Ph 66%

$$1 \quad + \quad RSiCl_3 \xrightarrow[{[56]}]{} R\text{-}SiR'_3 \qquad (5)$$

R= H 37%
R= Me 33%

$$1 \quad + \quad SiCl_4 \xrightarrow[{[56]}]{} R'_4Si \qquad (6)$$

74%



(7)

R= Me 23%
R= Ph 8%

The preparation of β-trimethylsilylmethyl carboranes was accomplished. (Eqns. 8,9)

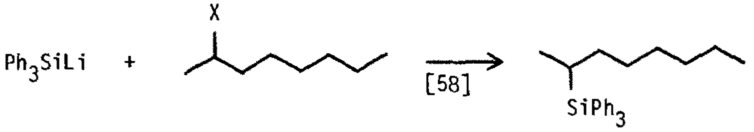
$$9\text{-I-o-}C_2B_{10}H_{11} \quad + \quad TMSCH_2MgCl \xrightarrow[{Et_2O \atop [57]}]{(Ph_3P)_2PdCl_2} 9\text{-}(TMSCH_2)\text{-o-}C_2B_{10}H_{11} \qquad (8)$$

83%

$$9\text{-I-m-}C_2B_{10}H_{11} \quad + \quad TMSCH_2MgCl \xrightarrow[Et_2O]{(Ph_3P)_2PdCl_2} 9\text{-}(TMSCH_2)\text{-m-}C_2B_{10}H_{11} \qquad (9)$$

71%

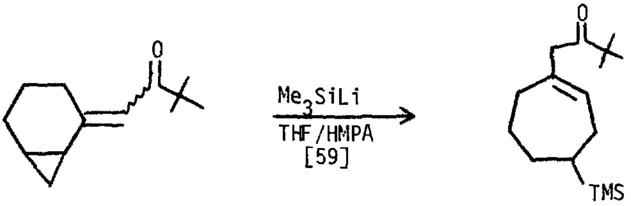
The stereochemistry of the reaction of triphenylsilyllithium with 2-octyl tosylate, chloride and bromide was studied. The resulting 2-octyltriphenylsilanes were optically active, but not necessarily optically pure, as a result of net inversion. (Eqn. 10) The reaction is not a clean S_N2 reaction.



(10)

X	Addition	e,e of silane
OTs	normal	93.7
Cl	normal	71
Br	normal	25
OTs	inverse	100
Cl	inverse	75
Br	inverse	25

The addition of trimethylsilyllithium with the cyclopropyl enone below gives the remotely functionalized, ring expanded system. (Eqn. 11) A single electron transfer mechanism is postulated.



(11)

72%

B. Reactions

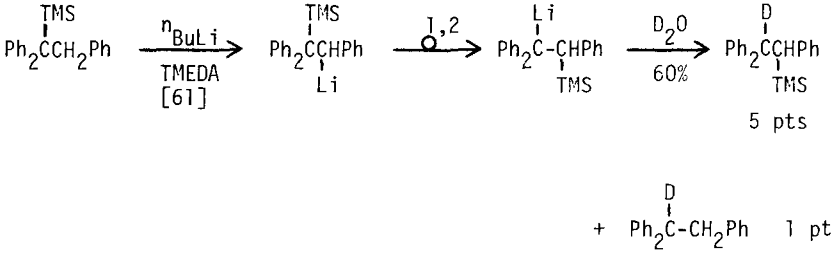
Tertiary alcohols are methylated with tetramethylsilane in the presence of $AlBr_3$. (Eqn. 12) 1-Adamantanol gave a mixture of mono, di, tri and tetramethylated adamantanes, with the methyl groups on the tertiary positions.

$$R_3COH + Me_4Si \xrightarrow[{[60]}]{AlBr_3} R_3CMe \qquad (12)$$

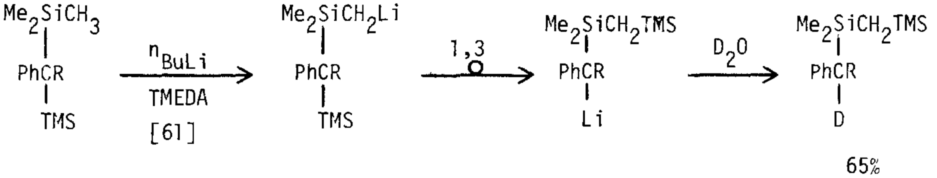
$R_3COH=$

1-Ad-OH

It was shown that silyl substituted organolithium compounds can undergo 1,2; 1,3 or 1,4 triorganosilyl migrations as seen below. (Eqns. 13-15).

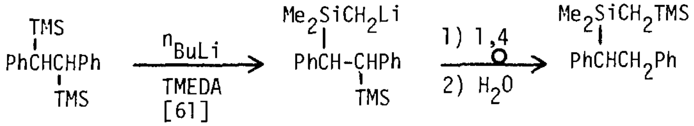


$$\mathrm{Ph_2\overset{TMS}{C}CH_2Ph} \xrightarrow[\text{TMEDA [61]}]{^{n}\mathrm{BuLi}} \mathrm{Ph_2\overset{TMS}{C}\underset{Li}{C}HPh} \xrightarrow[\circ]{1,2} \mathrm{Ph_2\overset{Li}{C}\text{-}\underset{TMS}{C}HPh} \xrightarrow[60\%]{D_2O} \underset{\text{5 pts}}{\mathrm{Ph_2\overset{D}{C}\underset{TMS}{C}HPh}} + \mathrm{Ph_2\overset{D}{C}\text{-}CH_2Ph}\ \text{1 pt} \quad (13)$$



$$\mathrm{\underset{TMS}{\underset{|}{\overset{Me_2SiCH_3}{\overset{|}{PhCR}}}}} \xrightarrow[\text{TMEDA [61]}]{^{n}\mathrm{BuLi}} \mathrm{\underset{TMS}{\underset{|}{\overset{Me_2SiCH_2Li}{\overset{|}{PhCR}}}}} \xrightarrow[\circ]{1,3} \mathrm{\underset{Li}{\underset{|}{\overset{Me_2SiCH_2TMS}{\overset{|}{PhCR}}}}} \xrightarrow{D_2O} \underset{65\%}{\mathrm{\underset{D}{\underset{|}{\overset{Me_2SiCH_2TMS}{\overset{|}{PhCR}}}}}} \quad (14)$$

R= Me, ^{n}Bu



$$\mathrm{Ph\overset{TMS}{C}H\underset{TMS}{C}HPh} \xrightarrow[\text{TMEDA [61]}]{^{n}\mathrm{BuLi}} \mathrm{\overset{Me_2SiCH_2Li}{\overset{|}{PhCH}}\text{-}\underset{TMS}{C}HPh} \xrightarrow[\text{2) } H_2O]{\text{1) } 1,4\ \circ} \mathrm{\overset{Me_2SiCH_2TMS}{\overset{|}{PhCH}}CH_2Ph} \quad (15)$$

C. Spectral and Other Studies

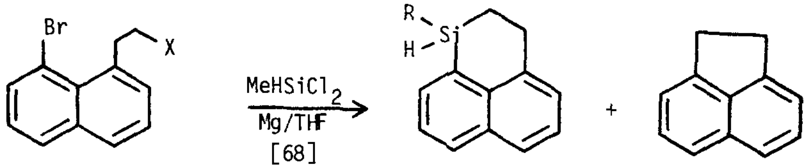
The asymmetry of the methyl group in CH_3SiH_2F has been determined by ab initio gradient computation, the results differing from those determined by microwave spectroscopy. [62] The single crystal X-Ray structure of $(Me_3Si)_3CSiMe_2Ph$ shows a rather long C_1-Si distance of 1.920 Å, small Si-C-Si angles of 105.2° and large C_1-Si-C angles of 113.5°. [63]

Strained cyclosilanes were the subject of some studies. Thus, the MM2 program for molecular mechanics has been applied to several cyclic and polycyclic silanes. The procedure gives good results with moderately strained systems, but should be used with caution for highly strained (e.g. silacyclobutanes) systems. [64] Electron impact fragmentation of dimethyl silacyclobutanes shows a ring expansion rearrangement involving the methyl groups on silicon. [65] Ring puckering in silacyclobutanes has been studied by infrared spectroscopy [66] and calculations. [67]

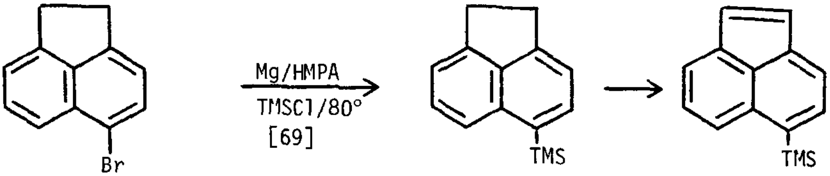
V. ARYLSILANES

A. Preparation

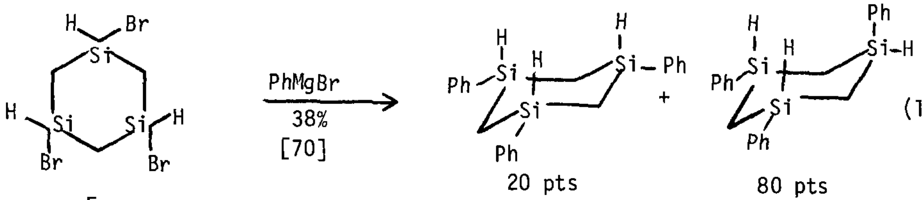
As expected the reaction of an aryllithium reagent or aryl Grignard reagent with halosilanes remains the most popular route to arylsilanes. Several examples, which need no further comment, are given below. (Eqns. 16-25)



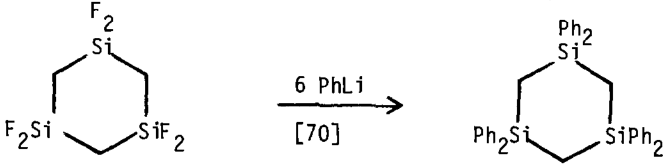
(16)



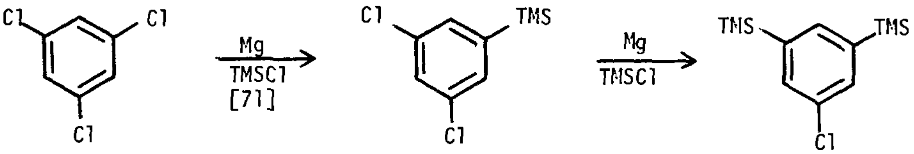
(17)



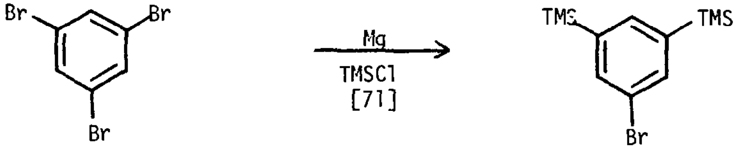
(18)



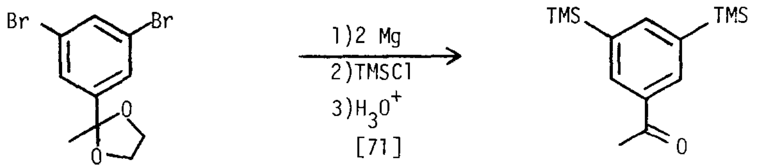
(19)



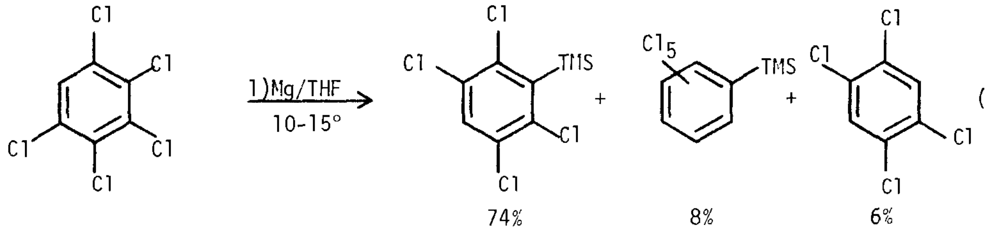
(20a)



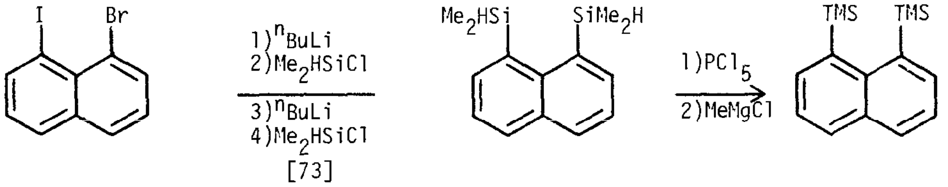
(20b)



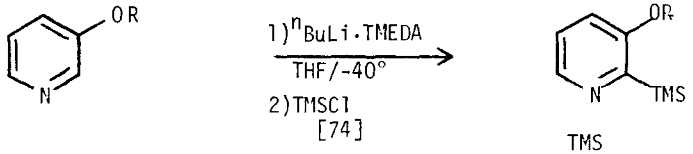
(21)



(22)

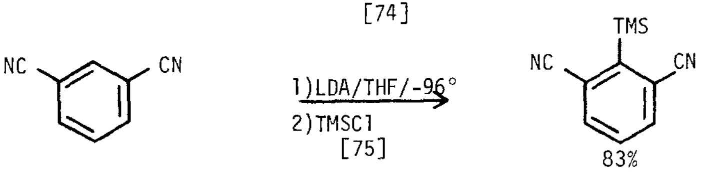


(23



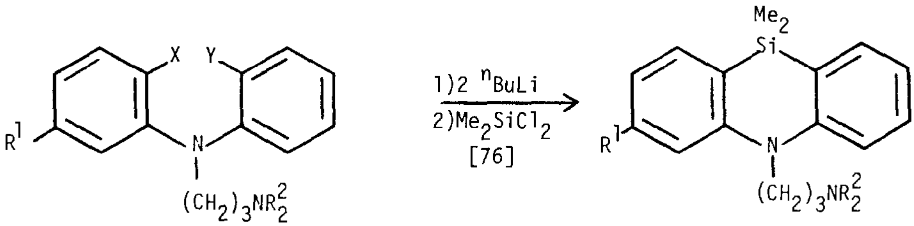
R= Et 83%
R= PhCH$_2$ 44%

(24)



(25)

The silicon analog of the psychotropic drug dimetacrine, 3, was prepared as shown below. (Eqn. 26)

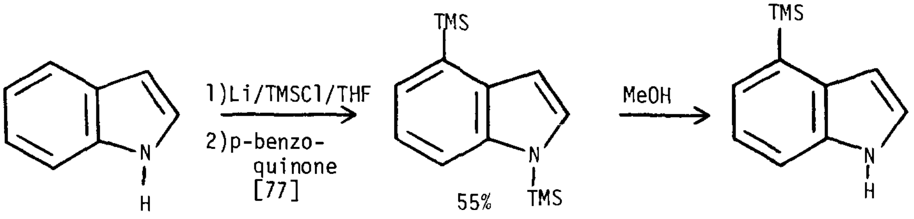


(26)

X= Y= Br R^1= H
X= Y= Cl R^1= H
X= Y= Br R^1= Cl

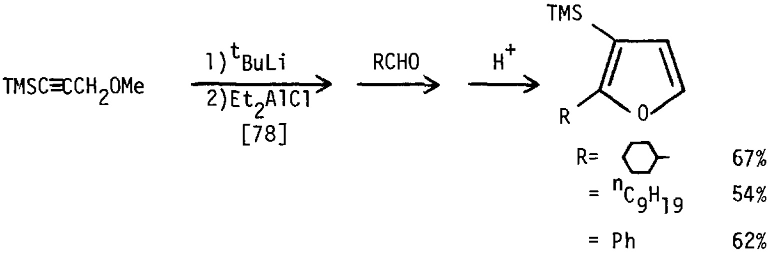
R^1= H, R^2= Me 70%
R^1= Cl, R$^2_2$= Me, Et or Me$_2$

A reductive silylation-oxidation procedure was used to prepare 4-(trimethylsilyl)indole. (Eqn. 27)



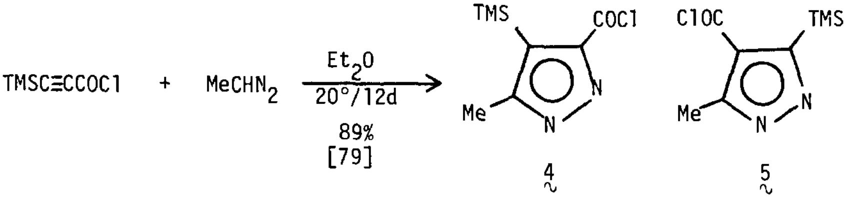
(27)

A cyclization was employed to prepare 3-(trimethylsilyl)furans from aldehydes. (Eqn. 28)



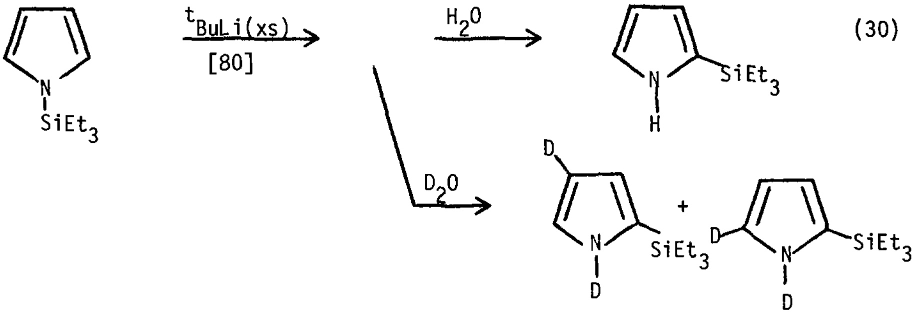
(28)

The silylated pyrazoles, 4 and 5 were prepared from the ethynylsilane and methyldiazomethane. (Eqn. 29)

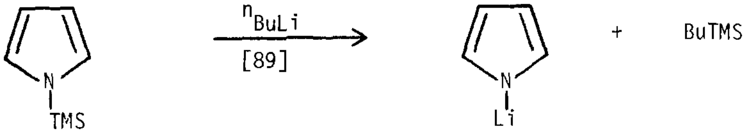


(29)

An interesting rearrangement provides 2-silylpyrroles from N-silylpyrroles. (Eqn. 30) The possibility of cleaving the silicon-nitrogen bond directly is seen in Eqn. 31.



(30)



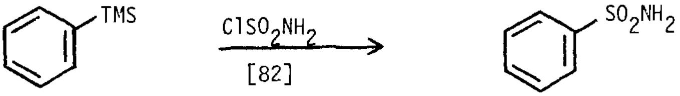
(31)

The disilane residue from the direct synthesis of methylchlorosilanes has been successfully arylated with aryl halides in the presence of Pd(0). (Eqn. 32) This article contains 96 references and as such constitutes an excellent review of the subject.

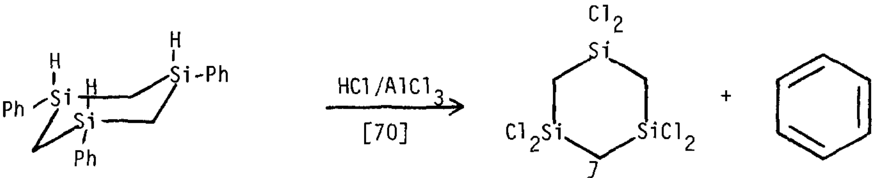
$$\mathrm{Ar(X)} \quad + \quad (\mathrm{Me_nCl_{3-n}Si})_2 \xrightarrow[\text{[81]}]{\mathrm{Pd(0)}} \mathrm{ArSiMe_nCl_{3-n}} \qquad (32)$$

B. Reactions

Examples of electrophilic substitution of arylsilanes appeared. The reaction of arylsilanes with sulfamoyl chloride gives the corresponding aryl sulfamide. (Eqn. 33) Treatment of 6 with HCl/AlCl$_3$ gives benzene and the chlorosilane 7. (Eqn. 34) Acylation of 4-(trimethylsilyl)indole, 8, gives the 4-acyl derivative. (Eqn. 35) The arylation of 1-adamantanoyl chloride was accomplished. (Eqn. 36) The acid catalyzed reaction of phenyltrimethylsilane with benzhydrol gives triphenylmethane. (Eqn. 37)

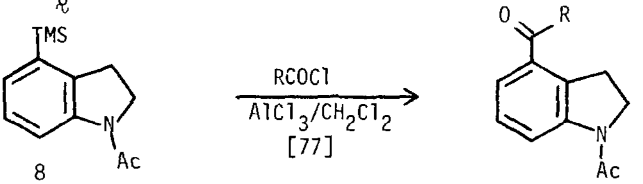


(33)



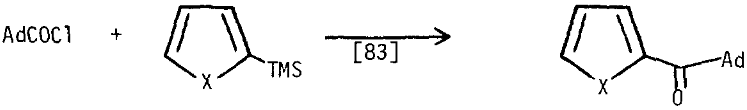
6

(34)

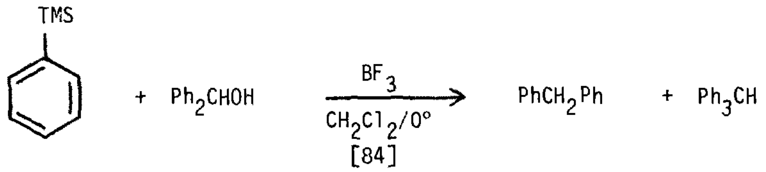


8

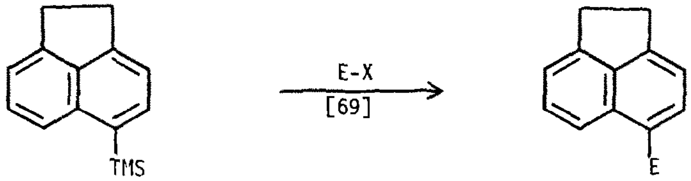
R= Me 95%
R= ClCH$_2$CH$_2$ 70% (35)



X= O 61%
X= S 82% (36)



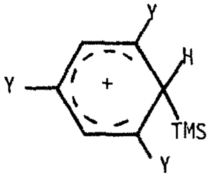
(37)



(38)

E-X= ICl (94%); $TMSOSO_2Cl$ (88%); $AcCl/AlCl_3$ (80%); $ClCH_2COCl/AlCl_3$ (65%)

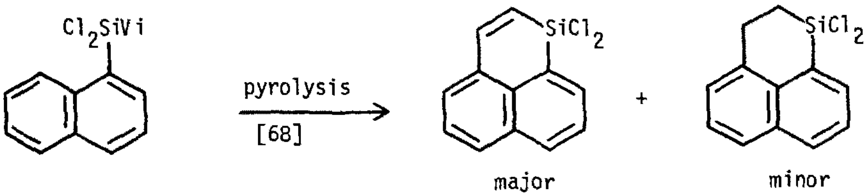
It was determined that the protodesilylation of phenyltrimethylsilane with $HClO_4$/MeOH proceeds via the sigma complex **9** with the rate determining step being protonation of the arylsilane to form **9**. The reaction showed a secondary deuterium effect of 0.79 (k_H/k_D). [85]



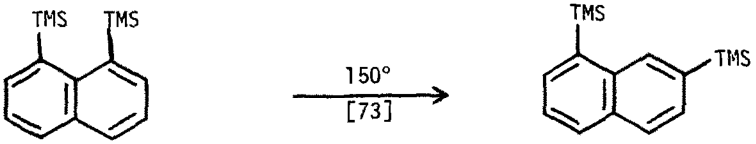
9 Y= H
Y= D

The relative rates of nitrodesilylation of o, m and p-bis(trimethylsilyl)benzenes were determined. The reaction proceeds to nitrodesilylate the trimethylsilyl groups. The rates followed the order $k_m > k_o > k_p$. [86]

The pyrolysis of (1-naphthyl)vinyldichlorosilane gives the products shown in Eqn. 39. The thermolysis of 1,8-bis(trimethylsilyl)naphthalene gives the 2,8 isomer. (Eqn. 40)

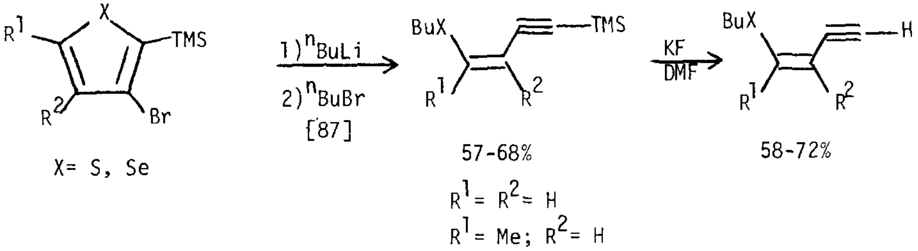


(39)



(40)

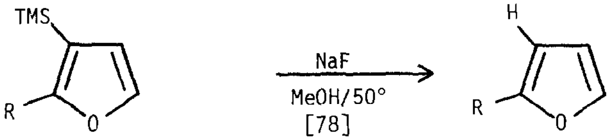
The presence of a trimethylsilyl group on the 2 position of thiophenes and selenophenes facilitates the ring opening of the 3-lithio derivatives. (Eqn. 41)



(41)

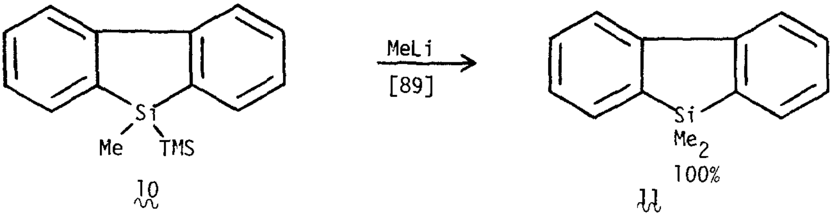
The base cleavage of a variety of ortho substituted arylsilanes employing KOH/DMSO/H_2O was carried out and the results show that the rate determining step is formation of the aryl anion, which is then protonated. [88]

Treatment of(3-trimethylsilyl)furans with NaF gives protodesilylation. (Eqn. 42)

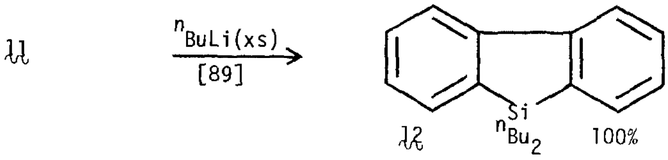


(42)

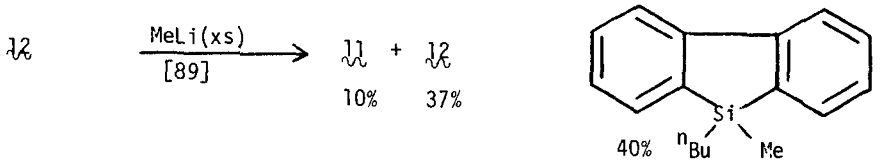
Treatment of dibenzosilole 10 with lithium reagents give substitution at silicon. (Eqn. 43) The same is true for the dialkyl species 11 and 12. (Eqns. 44-45). A pentavalent silicon intermediate is proposed.



(43)

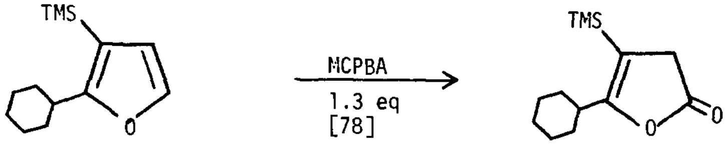


(44)

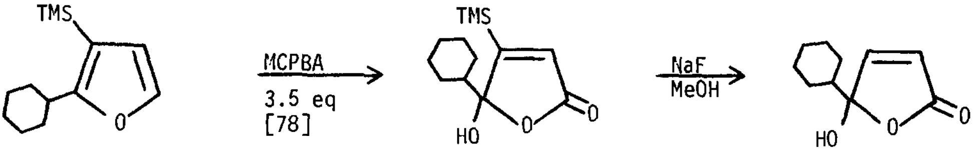


(45)

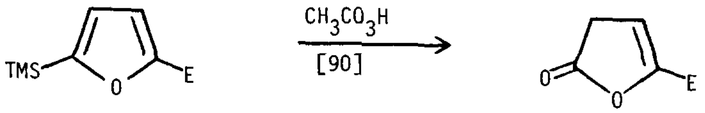
The oxidation of silylated furans proved to be a useful entry into unsaturated lactones as shown below. (Eqns. 46-49)



(46)

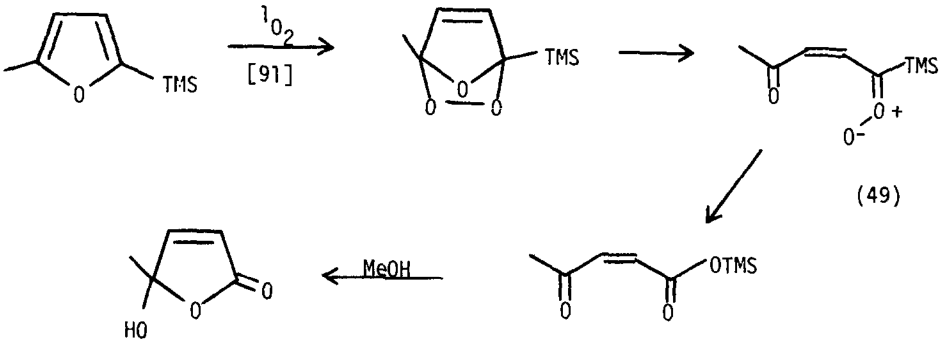


(47)



(48)

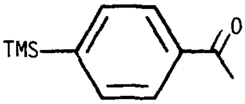
10 examples
(N.R.→84%)



(49)

C. Spectroscopic and Theoretical Studies

Spectral studies (UV, IR, NMR) on **13** indicate that the TMS group has a weak +I effect. [92]



13

The effect of solvent on the absorption and fluorescence spectra of 1-arylsilatranes has been studied. [93] The degrees of electron transfer from N to Si were calculated to be 0.07 to 0.10 electron. A series of arylsilanes were investigated as to the effect of attached silyl group. Thus, using the general series 14, it was found via dipole moment, IR, NMR, pKa and ΔH complexation data that the Me_2ClSi group is a π-acceptor and the $Me_2(Et_2N)Si$ group is a weak π-acceptor or strong π-donor depending on R. [94]

$R^1C_6H_4SiMe_2R^2$ $\qquad$ R^2= Cl, NEt_2

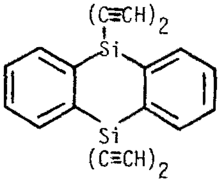
14

The electronic structures of a series of phenylethynylsilanes have been studied with the compounds 15-18. The effective charge on silicon increased in the order 15 (n=0) < 15 (n=1) $\sim$ 16 < 17 < 15 (n=2) $\sim$ 18 < 15 (n=3). [95] X-ray fluorescence spectra, photoelectron emission and MO(CNDO/2) calculations were carried out on $Ph_{4-n}SiH_n$ (n= 0-4). [96] The extent of delocalization in several silanes including $PhSiH_3$ was calculated. [97] Rayleigh scattering has been used to study the electronic effects in $PhSiMe_3$. [98]

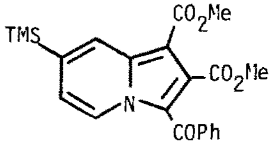
$Ph_{4-n}Si(C{\equiv}CH)_n$ $\qquad$ $Ph_2Si(C{\equiv}C\text{-}C{\equiv}C)_n$ $\qquad$ $(Ph_2SiC{\equiv}C)_n$

15 $\qquad$ 16 $\qquad$ 17

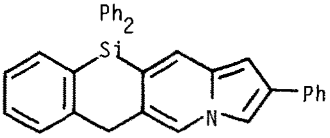
n= 0-4



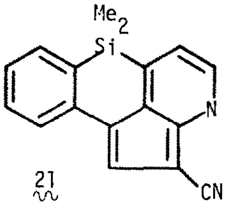
The mass spectra for the silylindoolizines 19-21 have been measured. [99]



19



20



21

VI. HYDROSILYLATION

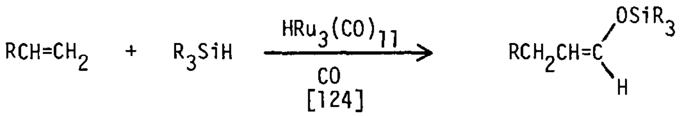
A. New Catalysts

The rate constants for the hydrosilylation of 1-heptene with ion-exchange bound hexachloroplatinic acid as a function of the sorbtion on the catalyst were obtained. The first step in the reaction is complexation of the silane with the catalyst. [100] Several ketones were photolytically hydrosilylated or hydrosilylated with a variety of transition metal carbonyl complexes. [101] A highly active and selective hydrosilylation catalyst was prepared as a SiO_2 supported poly(γ-aminopropylsiloxane)platinum complex, with $H_2PtCl_6 \cdot 6H_2O$ being the platinum source. This catalyst gives higher yields, faster reactions and can be reused. [102]

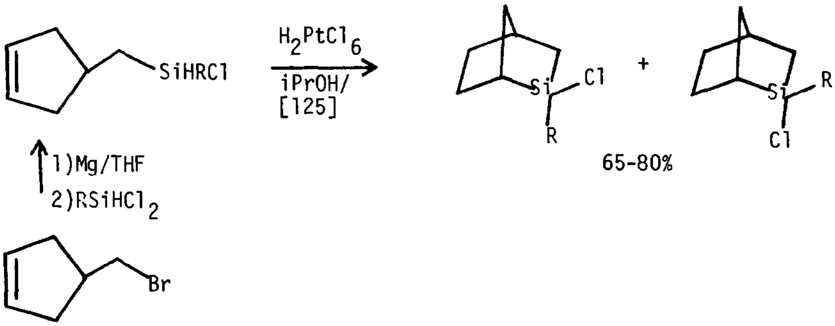
B. The Hydrosilylation of Alkenes, Alkynes and Carbonyls

Several examples of hydrosilylation were reported. These are given in Table I.

Two examples bear further mention. These are the silacarbonylation of ethylene and propylene shown in Eqn. 50 and the intramolecular hydrosilylation leading to 2-silanorbornanes. (Eqn. 51) The 2-silanorbornanes represent a new class of compounds.



$$RCH{=}CH_2 \quad + \quad R_3SiH \xrightarrow[\substack{CO \\ [124]}]{HRu_3(CO)_{11}} RCH_2CH{=}C\begin{matrix} OSiR_3 \\ H \end{matrix} \qquad (50)$$



(51)

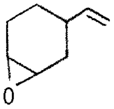
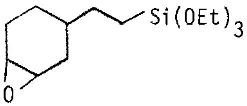
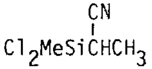
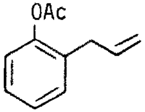
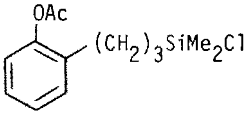
VII. VINYLSILANES

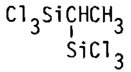
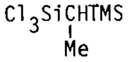
A. Preparation from Vinylmetallics and Related Reactions

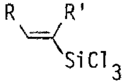
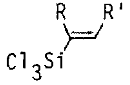
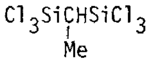
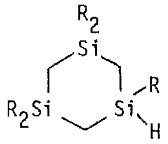
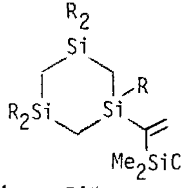
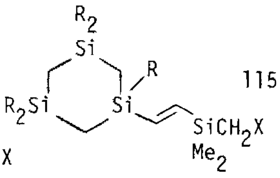
The disilane residue from the direct synthesis of methylchlorosilanes has been coupled with vinylchloride to give vinylsilanes. (Eqn. 52)

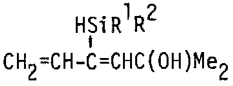
$$CH_2{=}CHCl \quad + \quad (Me_nCl_{3-n}Si)_2 \xrightarrow[{[81]}]{Pd(0)} CH_2{=}CH{-}SiMe_nCl_{3-n} \qquad (52)$$

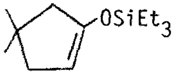
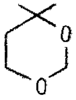
TABLE I: HYDROSILYLATION OF ALKENES, ALKYNES AND KETONES

ENTRY	SILANE	SUBSTRATE	CATALYST/CONDITIONS	PRODUCT	REF.
1	$(EtO)_3SiH$		$H_2PtCl_6 \cdot 6\ H_2O$ 1.4 h/rt		103
2	Cl_3SiH	$ClCH_2CH{=}CH_2$	H_2SiCl_6/R_3X X= N, P, As R= alkyl	$Cl(CH_2)_3SiCl_3$	104
3	$MeCl_2SiH$	$ClCH_2CH{=}CH_2$	same	$Cl(CH_2)_3SiCl_2Me$	104
4	$(EtO)_3SiH$	$H_2NCH_2CH{=}CH_2$	$(Ph_3P)_2PtX_2$ X= Cl, I or $(Ph_3P)_4Pt$ or H_2PtCl_6 4-26 h/120°	$H_2N(CH_2)_3Si(OEt)_3$	105
5	Cl_2MeSiH	$CH_2{=}CHCN$	Ni-containing catalyst	$Cl_2MeSiCH_2CH_2CN$	106
6	Cl_2MeSiH	$CH_2{=}CHCN$	Fe or Co-containing catalyst	 $Cl_2MeSi\overset{CN}{\overset{\vert}{C}}HCH_3$	106
7	Me_2ClSiH		H_2PtCl_6		107

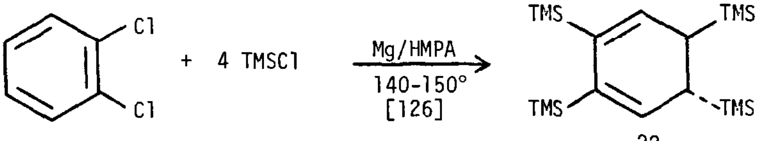
ENTRY	SILANE	SUBSTRATE	CATALYST/CONDITIONS	PRODUCT	REF.
8	Cl_3SiH	$(CH_2{=}CHCH_2)_2S$	L_2Ni L= acac, R_3P	$CH_2{=}CHCH_2S\ (CH_2)_3SiCl_3$ + $^nPrS(CH_2)_3SiCl_3$ + $S[(CH_2)_3SiCl_3]_2$	108
9	$MeCl_2SiH$	$RCH{=}CH_2$	NiL_2X_2/120°/10 h X= Br, NO_3, Cl L= R_3P, $R_3P{=}O$	$RCH_2CH_2SiMe_2Cl$ + $RCH_2CH_2SiHClMe$	109
10	Cl_3SiH	$Cl_3SiCH{=}CH_2$	$H_2PtCl_6{\cdot}6\ H_2O$	$Cl_3SiCH_2CH_2SiCl_3$ +  $Cl_3Si\underset{SiCl_3}{\underset{\vert}{C}}HCH_3$	110
11	Cl_3SiH	$Me_3SiCH{=}CH_2$	$(TMSCH{=}CH_2)Fe(CO)_4$	 $Cl_3Si\underset{Me}{\underset{\vert}{C}}HTMS$ 3 pts + $Cl_3SiCH_2CH_2TMS$ 0.3 pts + $Cl_3SiCH{=}CHTMS$ 1 pt	111
12	various	various	NiL_2X_2 X= Cl, Br L= phosphine oxides	organosilanes	112

ENTRY	SILANE	SUBSTRATE	CATALYST/CONDITIONS	PRODUCT		REF.
13	Cl_3SiH	$RCH{=}CH_2$	H_2PtCl_6	$RCH_2CH_2SiCl_3$		113
14	Cl_3SiH	$RC{\equiv}CR'$	H_2PtCl_6		+ 	113
15	Cl_3SiH	$Cl_3SiCH{=}CH_2$		 $Cl_3S\underset{\mathrm{Me}}{\underset{\mid}{i}}CHSiCl_3$	+ $Cl_3SiCH_2CH_2SiCl_3$	114
			$(Ph_3P)_4Pd$/60°	70	6	
			" /120°	81	4	
			" /reflux	96	2	
			H_2PtCl_6/60°	0	65	
			" /120°	0	92	
			" /reflux	0	97	
			$(Ph_3P)_3RhCl$/120°	0	96	
16	 R= Me, Ph	$HC{\equiv}CSiMe_2CH_2X$ X= Br, Cl	H_2PtCl_6	 R= Me 54%	 46%	115

ENTRY	SILANE	SUBSTRATE	CATALYST/CONDITIONS	PRODUCT	REF.
17	R_3SiH	$R'CH=CH_2$	$^tBuOO^tBu$	$R'CH_2CH_2SiR_3$	116
	R= Et, ^nPr, Ph				
	(Reaction is best with a large excess (ca. 30 fold) of the silane to avoid telomerization)				
18	$R^1R^2SiH_2$	$CH_2=CHC\equiv CC(OH)Me_2$	$H_2PtCl_6/80°$	 $CH_2=CH-\overset{HSiR^1R^2}{\overset{\mid}{C}}=CHC(OH)Me_2$	117
	R^1= Me; R^2= $Ph(CH_2)_n$ (n= 0-3), $PhCHMeCH_2$, $^nC_6H_{13}$, $^nC_7H_{15}$, $^iC_7H_{15}$, $^nC_8H_{17}$, $ClCH_2$, $Cl(CH_2)_3$				
	R^1= R^2= Et, Ph				
19	Cl_3SiH	$ClCH_2Me_2SiC\equiv CH$	-	$ClCH_2Me_2SiCH=CHSiCl_3$	118
20	$RHSiCl_2$	$HC\equiv CH$	$(PPh_3)_4Pt$; $(PPh_3)_4Pd$; $PdCl_2(PPh_3)_2$ $RuCl_2(PPh_3)_4$	$CH_2=CHSiClHR$	119
21	$R^1R^2R^3SiH$	$HC\equiv CH$	$AlCl_3$	$CH_2=CHSiR^1R^2R^3$	120
	(R^1= R^2= Me, R^3= $^nC_5H_{11}$; R^1= R^2= Me, R^3= $^nC_3H_7$; R^1= R^2= R^3= Et)				
22	$(R_3Si)_2$	$HC\equiv CH$	$(Ph_3P)_4Pd$	$R_3SiCH=CHSiR_3$	121
	R_3Si= Cl_2MeSi, $ClMe_2Si$, others		+ others		

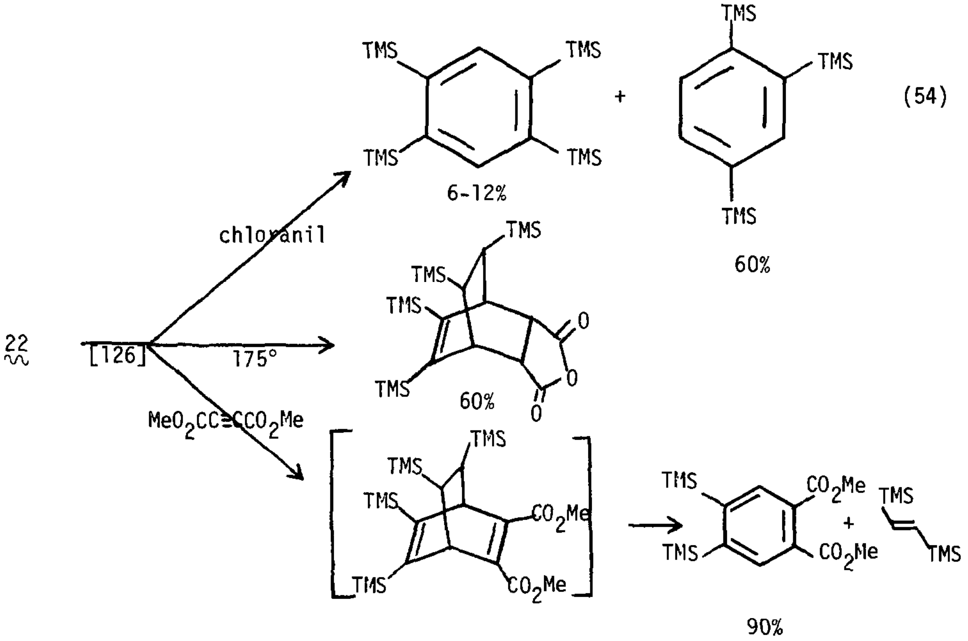
ENTRY	SILANE	SUBSTRATE	CATALYST/CONDITIONS	PRODUCT	REF.
23	Et_3SiH		H_2PtCl_6		123
24	Et_3SiH		$ZnCl_2$/100°	$Me_2CHCH_2CH_2OCH_2OSiEt_3$ + $Et_3SiOCMe_2CH_2CH_2OMe$ + $MeOCMe_2CH_2CH_2OSiEt_3$	123

The TMSCl/Mg/HMPA reductive silylation reaction has been employed to prepare the silylated cyclohexadiene, **22** (Eqn. 53), which was aromatized and also used in Diels-Alder reactions. (Eqns. 54-56)



22

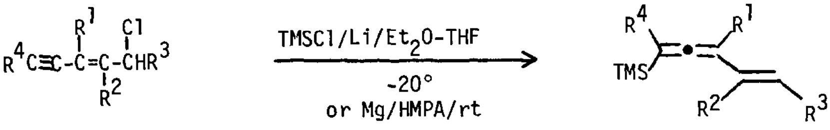
(53)



(54)

(56)

In a similar approach the chloroenynes, **23**, gave the allenylsilanes **24**. (Eqn. 57) The ethynylsilane **25** was the only example to give the ethynyl product in addition to the allenyl product. (Eqn. 58)

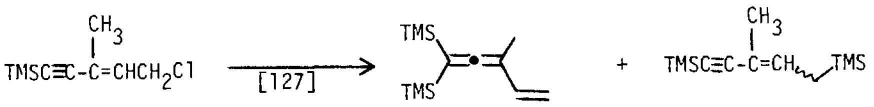


23

24

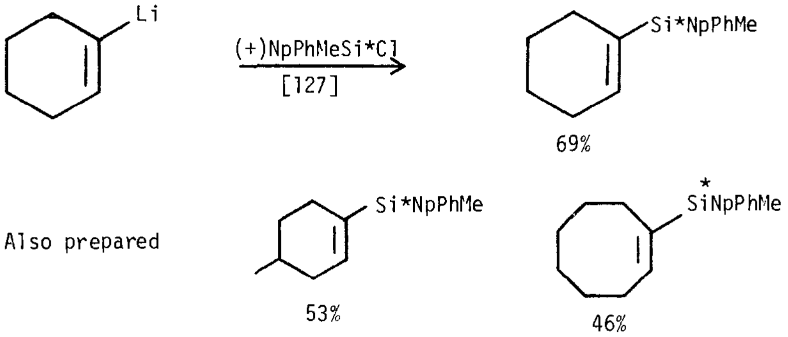
5 examples
50-80%

(57)



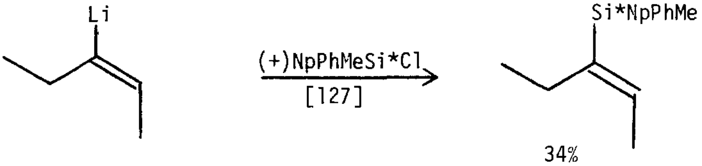
25 65% 30% (58)

The Shapiro reaction was used to prepare a variety of vinylsilanes optically active at silicon. These are shown in Eqns. 59-60 below.



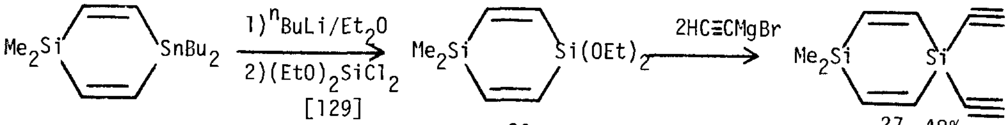
69% (59)

Also prepared 53% 46%



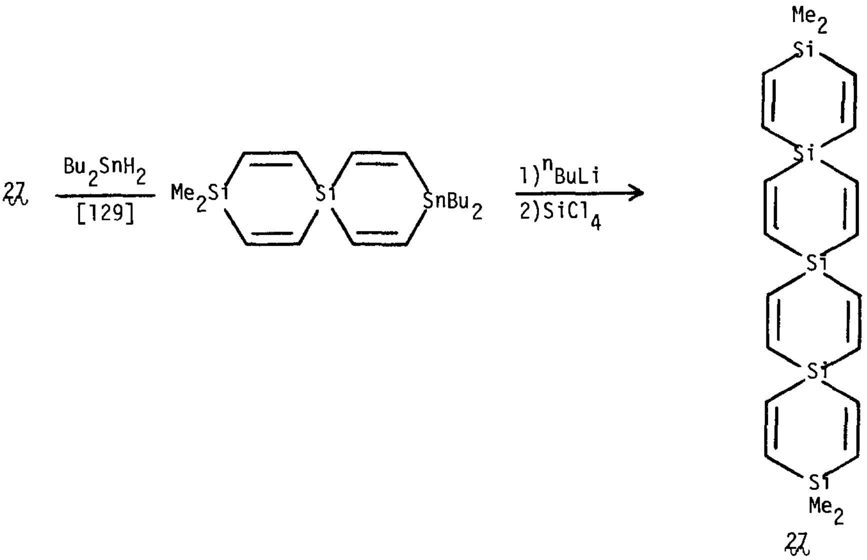
34% (60)

The intriguing polyspirodisilacyclohexadienes below were prepared from the appropriate lithium reagents as shown. (Eqns. 61-64) A red shift is seen in the UV spectra going from **28**→**29**→**27**. The compounds form anion radicals upon treatment with K/DME at -90°.



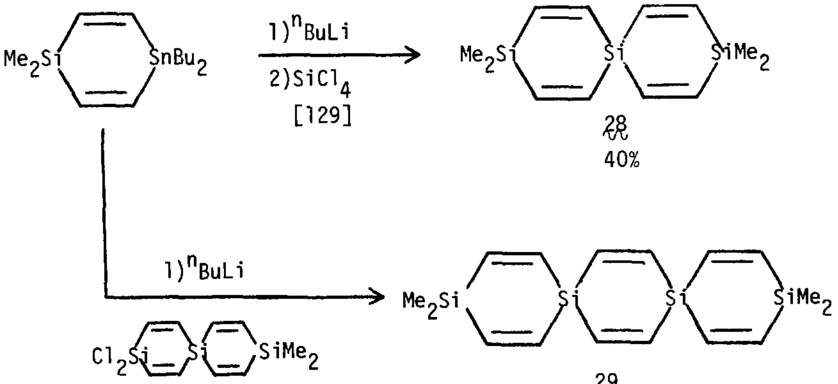
26 30% **27** 48%

(61)



27

(62)



28
40%

(63)

29
7.6%

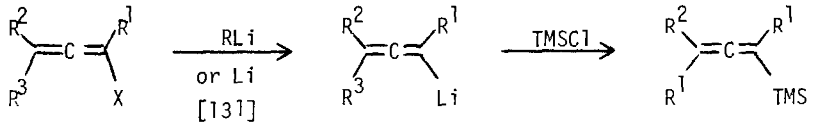
(64)

The silyl Wittig reagents 31 were prepared via the "vinyllithium" 30. (Eqn. 65)

$$\overset{+}{\mathrm{Ph_3PCH_3}}\ \mathrm{I^-} \xrightarrow[\text{[130]}]{2\ {}^{s}\mathrm{BuLi}} \underset{\mathbf{30}}{\mathrm{Ph_3P{=}CHLi}} \xrightarrow{\mathrm{R_3SiCl}} \underset{\mathbf{31}}{\mathrm{Ph_3P{=}CHSiR_3}} \qquad (65)$$

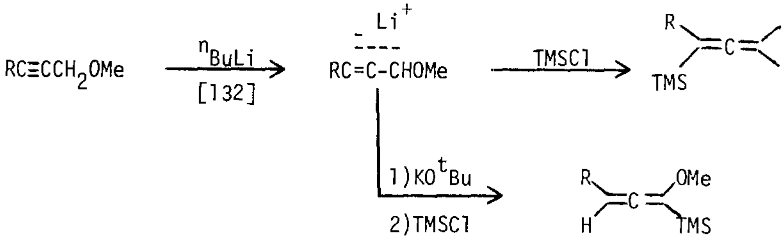
(R_3Si= various)

Several allenylsilanes have been prepared from the appropriate allenyllithium reagents. These are shown below. (Eqns. 66-70)

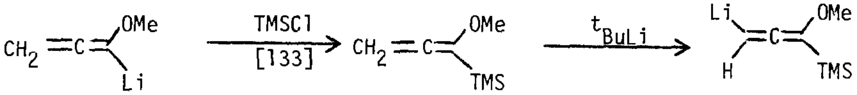


(66)

R^1	R^2	R^3	
H	H	^{n}Pr	90%
H	H	$^nC_8H_{17}$	85%
^{n}Bu	Me	Me	95%

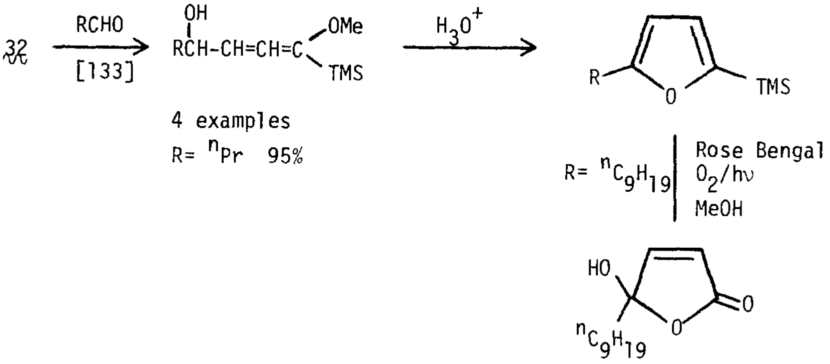


(67)



(68)

32

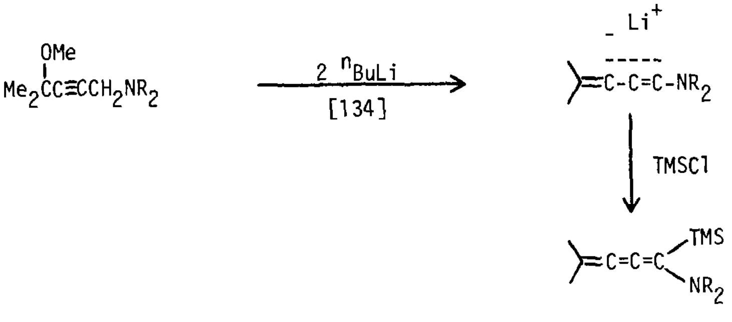


4 examples

R= ^{n}Pr 95%

R= $^nC_9H_{19}$

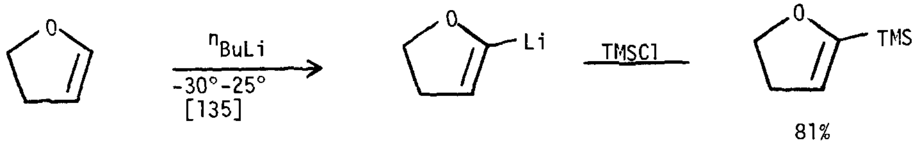
(69)



R= Me, Et

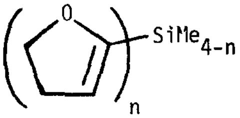
(70)

Lithiation of 4,5-dihydrofuran followed by silylation gives the 4,5-dihydro-2-furylsilane in good yield. (Eqn. 71) The bis and tris compounds **33** and **34** were prepared similarly.



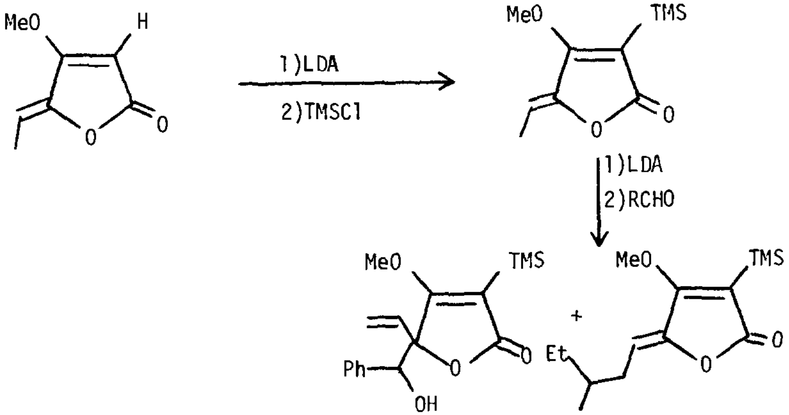
81%

(71)



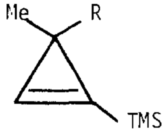
n= 2 **33**
n= 3 **34**

The 4-methylidene tetronic acids can be directly metalated and silylated as seen in Eqn. 72. The silylated material deprotonates, but reacts at both γ and ε sites.



70% (PhCHO) 17% (EtCHO)

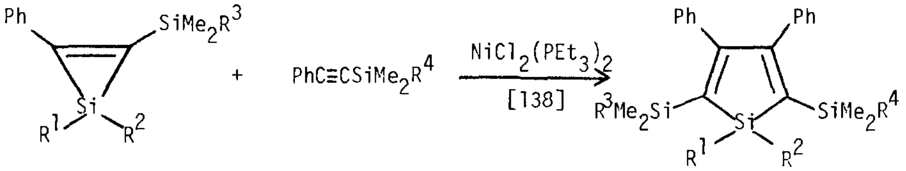
The synthesis of the cyclopropenylsilanes 35 has been reported. [137]



35

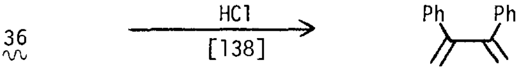
B. Preparation From Silicon-Containing Molecules

Ethynylsilanes continued to be an excellent source of vinylsilanes. Silacyclopropenes were shown to react with ethynylsilanes to give siloles 36. (Eqn. 73) These react with HCl to give the diene. (Eqn. 74)



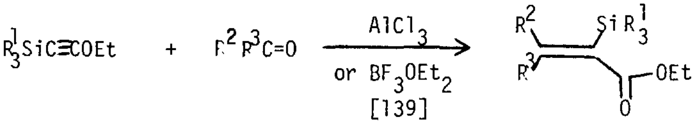
(73)

36
7 examples
(N.R. ($R^1 = R^2 = Me_3$) - 99%)



(74)

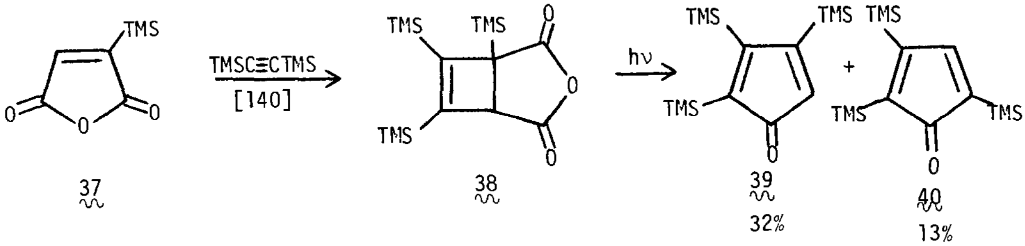
Ethoxyethynylsilanes react with aldehydes and ketones to give the α-carboethoxyvinylsilanes in good yield. (Eqn. 75)



(75)

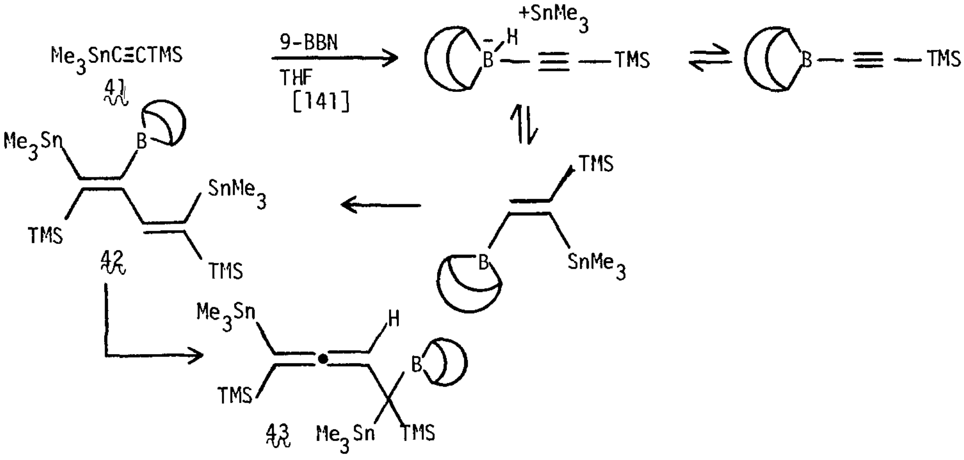
21-96%

The cycloaddition of the furandione, 37, with bis(trimethylsilyl)acetylene gives 38 photolysis of which gives the silylated cyclopentadienones 39 and 40. (Eqn. 76)



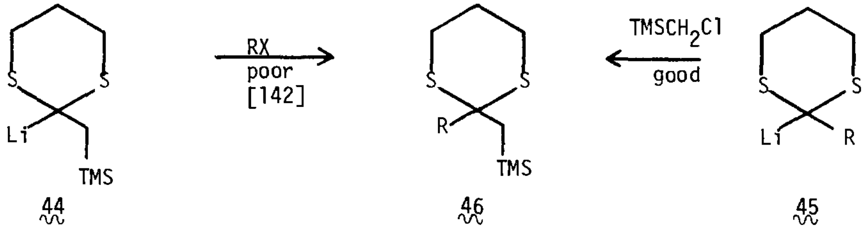
(76)

The ethynylsilane **41** can be hydroborated with 9-BBN to give the vinylsilane **42** which rearranges to the final product **43**. (Eqn. 77)

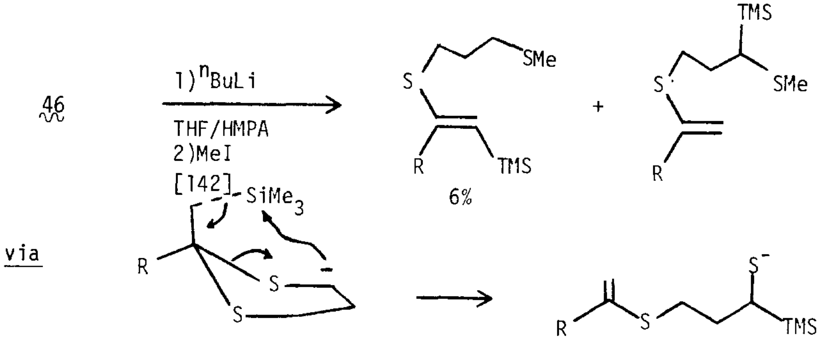


(77)

The metalation of certain organosilanes can lead, via the reaction of these metalated derivatives, to vinylsilanes. The metalated dithiane **44** followed by alkylation gives a substituted dithiane **46** though in poor yield. A better route to this system is via the silylmethylation of anion **45**. (Eqn. 78) These systems upon treatment with n-butyllithium open to give the vinylsilanes. (Eqn. 79)

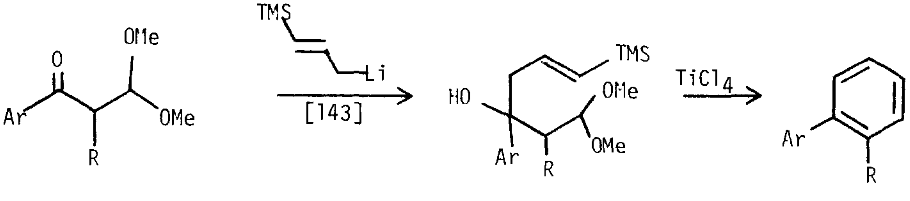


(78)



(79)

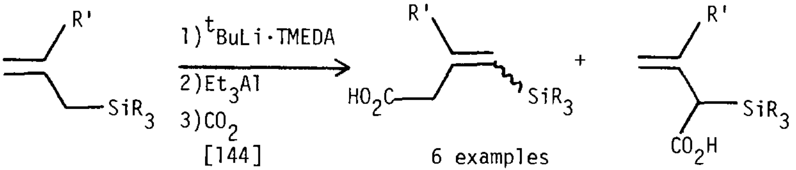
Trimethylsilyllithium reacts with protected β-keto aldehydes to give highly functionalized vinylsilanes which are molecularly condensed to give aromatic compounds. (Eqn. 80)



(80)

5 examples
12-59%

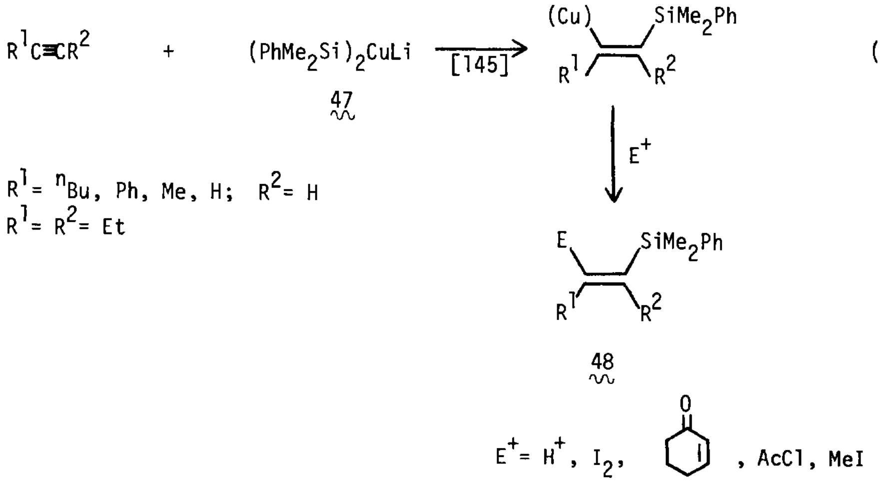
Other silylallyllithiums were converted to carboxylic acids via their aluminum complexes. (Eqn. 81) The allylsilanes are the primary product of this reaction.



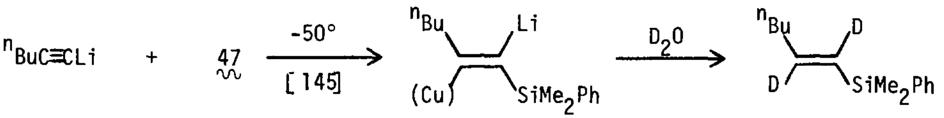
(81)

6 examples
20-85%

Two silylmetallic reagents were useful in the preparation of vinylsilanes. The addition of the silyl cuprate 47 to acetylenes followed by introduction of an electrophile gives the vinylsilanes 48. (Eqn. 82) Even the ethynyllithium reagent reacts. (Eqn. 83)

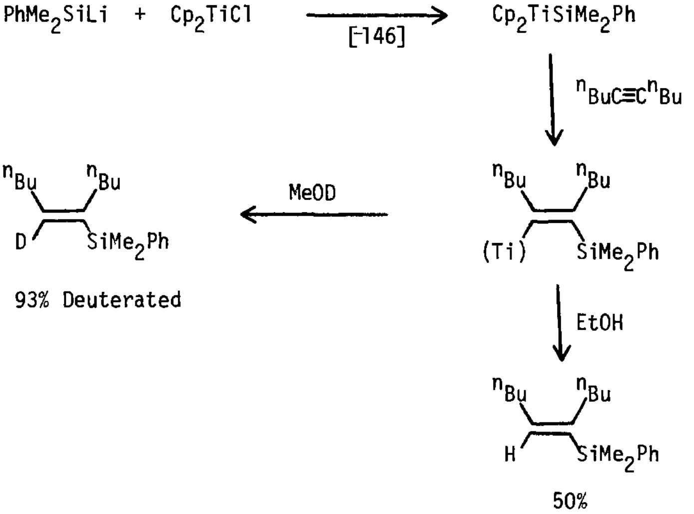


(82)



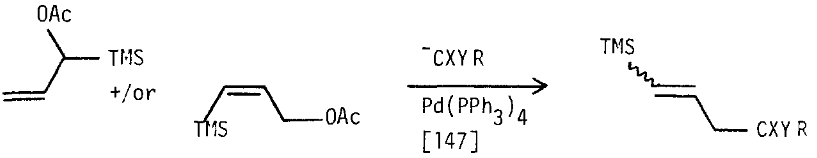
(83)

In a related approach the silyltitanium compound 49 was prepared and added to acetylenes. (Eqn. 84)



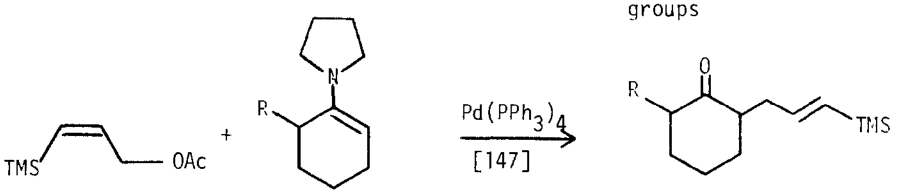
(84)

Malonate anions react with either 1- or 3-trimethylsilyl allyl acetate to give the substituted vinylsilane. (Eqn. 85) The reaction also proceeds with enamines. (Eqn. 86)



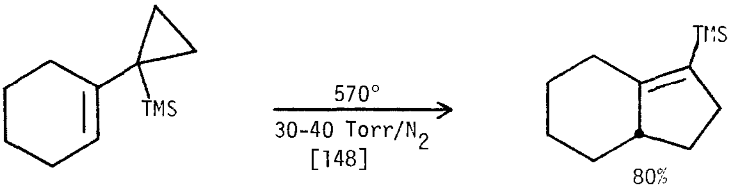
(85)

X and Y electron withdrawing groups

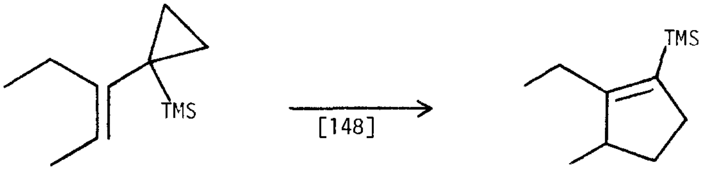


(86)

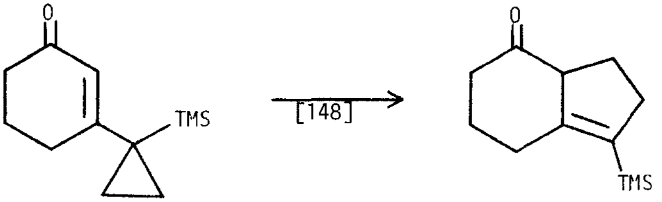
A number of 1-alkenyl-1-trimethylsilylcyclopropanes were thermolyzed to give 1-trimethylsilylcyclopentenes. (Eqns. 87-89)



(87)



(88)

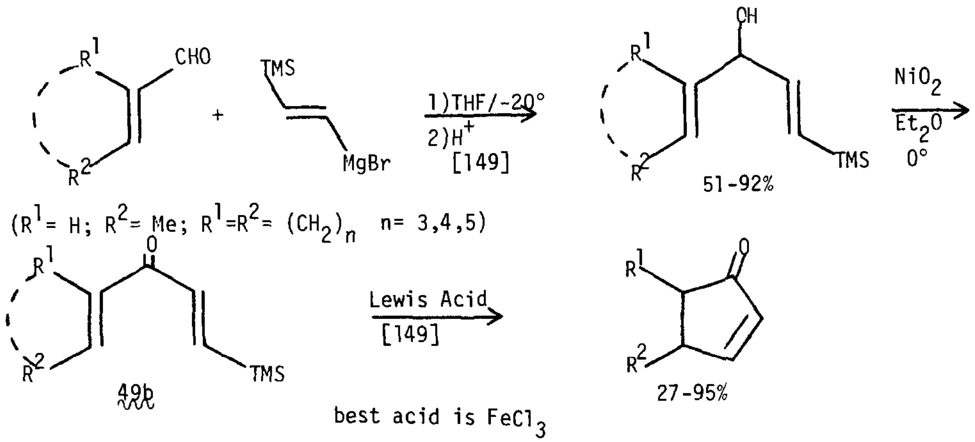


(89)

C. Reactions

1. Reactions of Silylated Vinylmetallics

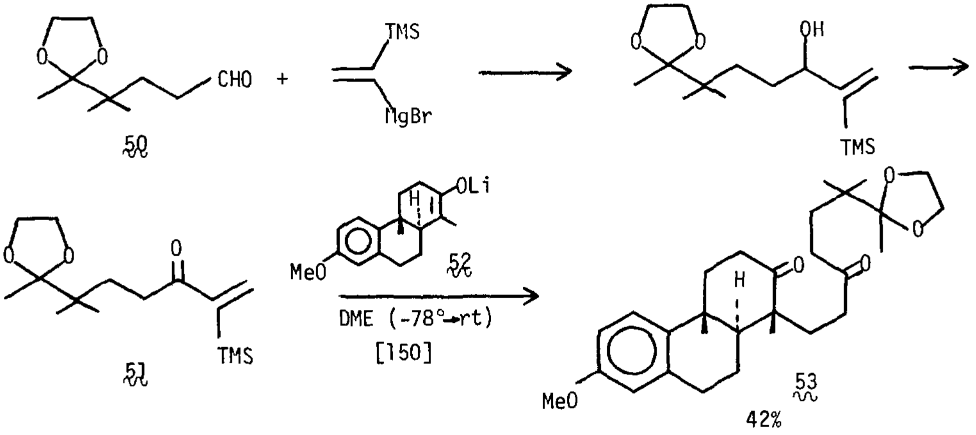
A silicon-mediated Nazarov cyclization was carried out on the dienones 49b, prepared from β-(trimethylsilyl)vinylmagnesium bromide as shown. (Eqn. 90) This leads to the alternate double bond isomer to that obtained from the unsilylated dienones.



(R^1 = H; R^2 = Me; R^1=R^2= $(CH_2)_n$ n= 3,4,5)

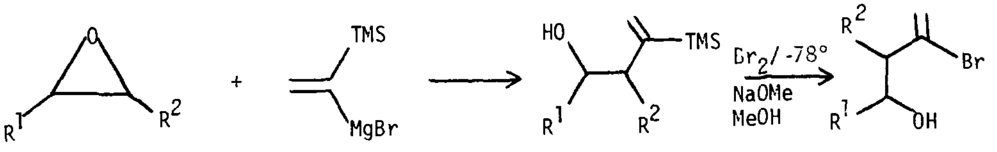
best acid is $FeCl_3$

The Grignard of 1-(trimethylsilyl)-bromoethylene was reacted with the protected keto aldehyde 50 to give an alcohol which was oxidized to the enone 51. Reaction of the enone with the enolate 52 gave the monoprotected trione 53. (Eqn. 91)



(91)

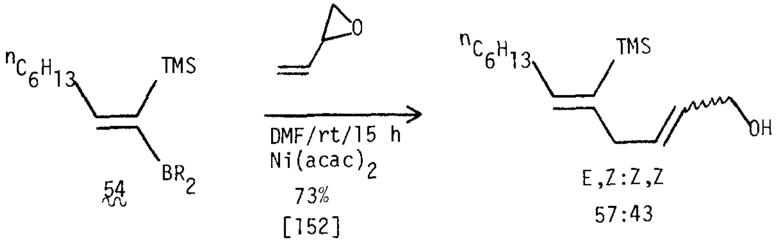
This same Grignard reagent was reacted with epoxides in the presence of Cu(I). The resulting vinylsilane was bromodesilylated to give the vinylbromide. (Eqn. 92)



(92)

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

The α-trimethylsilylvinylborane, 54, was reacted with vinylepoxide to give the products shown in Eqn. 93.

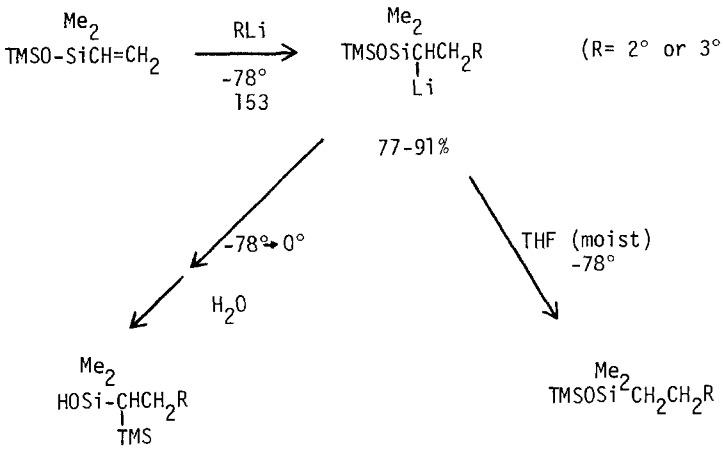


(93)

2. Addition of Anions

One example of this type of reaction of vinylsilanes is to be found in Eqn. 91.

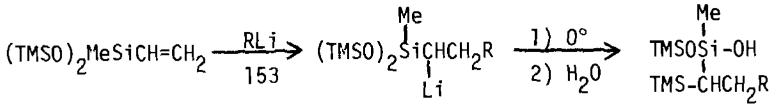
Alkyllithium reagents were added to silyloxyvinylsilanes. The α-lithiosilanes undergo a 1,3-silicon migration at ca. 0° as shown below. (Eqns. 94-95) Less hindered organolithium reagents tend to attack silicon leading to displacement.



(R= 2° or 3° but not 1° or Ph)

(94)

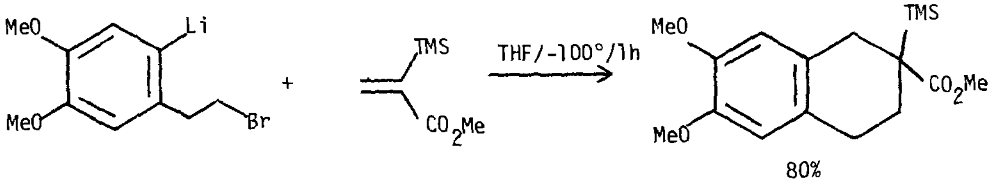
R= ^{s}Bu 100%
= iPr 95%
= ^{n}Bu 86% (reaction at rt)



$$\mathrm{(TMSO)_2MeSiCH{=}CH_2} \xrightarrow[153]{\mathrm{RLi}} \mathrm{(TMSO)_2\overset{Me}{Si}\underset{Li}{C}HCH_2R} \xrightarrow[2)\ \mathrm{H_2O}]{1)\ 0^\circ} \begin{array}{l}\mathrm{\quad\ \ Me}\\ \mathrm{TMSOSi{-}OH}\\ \mathrm{TMS{-}CHCH_2R}\end{array} \qquad (95)$$

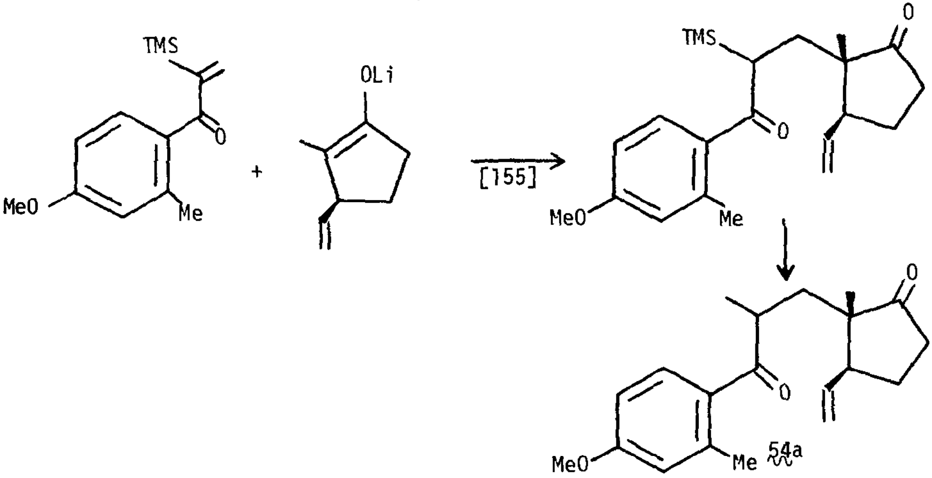
R= ^{s}Bu	95% (after hydrolysis)	95
= ^{i}Pr	91% " "	100
= ^{t}Bu	75 " " (plus 25% rearranged)	-
= ^{n}Bu	---- (plus 52% attack at Si)	40

A clever cyclization was accomplished as shown in the addition of the aryllithium reagent to methyl α-trimethylsilylacrylate and subsequent intramolecular alkylation of the formed α-silyl enolate. (Eqn. 96) Disecoestrenone, 54a was

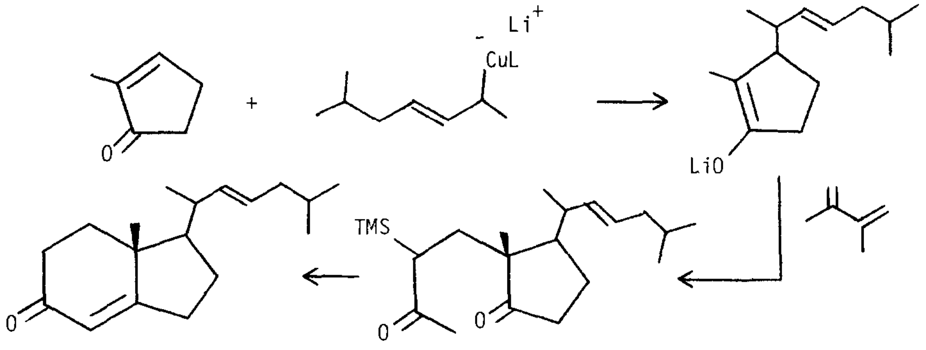


(96)

prepared via a Michael addition to an α-silylvinylketone as shown in Eqn. 97. A similar reaction is shown in Eqn. 98.



(97)

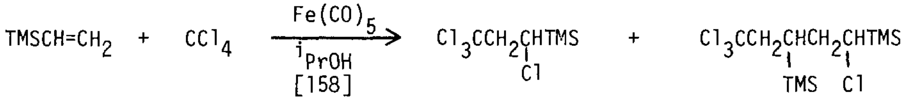


(98)

3. Electrophilic Addition Reactions

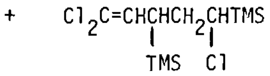
The relative rates of oxidation of some vinylsilanes with meta-chloroperbenzoic acid have been determined. It was found that trimethylsilyloxydimethylvinylsilane oxidizes very slowly, that trimethylsilyldimethylvinylsilane gives mostly the epoxide and that trimethylsilyldimethylallylsilane gives both oxidation of the Si-Si bond and the double bond. [157]

The reaction of trimethylvinylsilane with CCl_4 gives an equimolar mixture of five products, four of which are dimeric. (Eqn. 99)



$$\mathrm{TMSCH{=}CH_2 + CCl_4 \xrightarrow[{}^{i}PrOH\ [158]]{Fe(CO)_5} Cl_3CCH_2\underset{Cl}{C}HTMS + Cl_3CCH_2\underset{TMS}{C}HCH_2\underset{Cl}{C}HTMS}$$

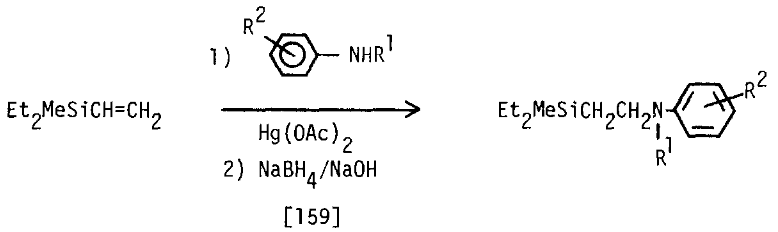
erythro and threo (99)



$$+ \mathrm{Cl_2C{=}CH\underset{TMS}{C}HCH_2\underset{Cl}{C}HTMS}$$

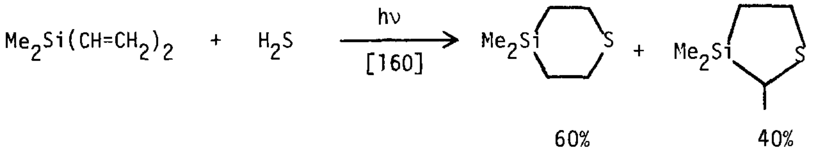
erythro and threo

The aminomercuration-demercuration of vinylsilanes has been accomplished. (Eqn. 100)

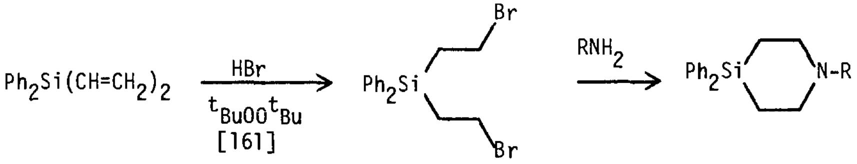


(100)

Dimethyldivinylsilane undergoes photocatalyzed addition of H_2S to give the five and six membered heterocycles. (Eqn. 101) Diphenyldivinylsilane added two equivalents of HBr in the presence of peroxide. The resulting dibromide could be substituted by a secondary amine. (Eqn. 102)

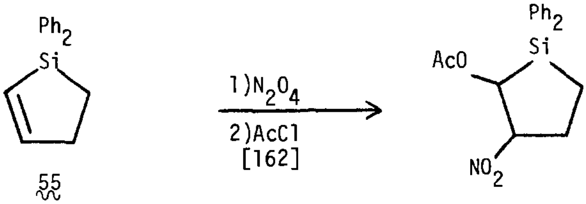


(101)



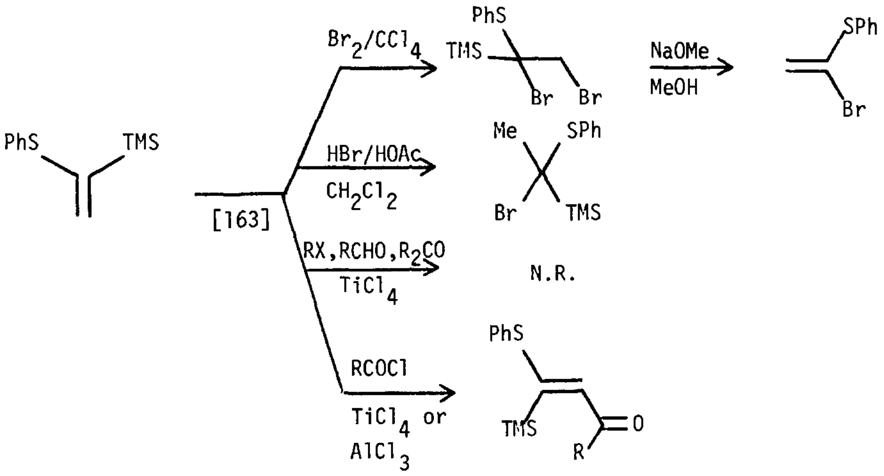
(102)

The silacyclopentene 55 undergoes electrophilic addition in N_2O_4. Acetylation gives the acetyl product. (Eqn. 103)



(103)

The addition of electrophiles to 1-phenylthio-1-trimethylsilylethene is governed by the sulfur group and not the silyl group. (Eqns. 104-107)



(104)

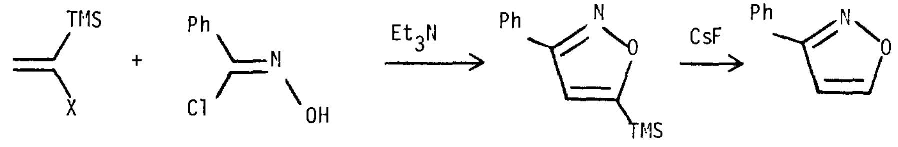
(105)

(106)

(107)

4. Cycloadditions

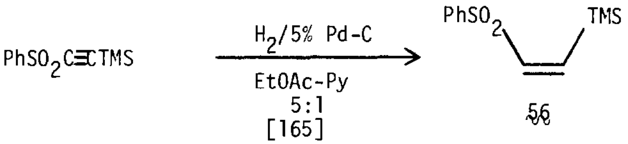
Silylated isoxazoles were prepared as shown in Eqn. 108.



(108

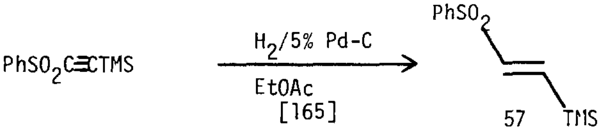
X= Br, -S-

Cis or trans-1-benzenesulfonyl-2-(trimethylsilyl)ethylene, prepared by reduction of the acetylene (Eqns. 109-110) have been employed as an acetylene equivalent in Diels-Alder reactions. (Eqns. 111-115) The intermediate can be further elaborated before elimination to form the double bond as seen in the anthracene case. (Eqn. 113)



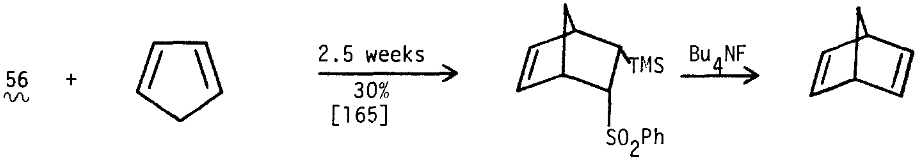
56

(109)

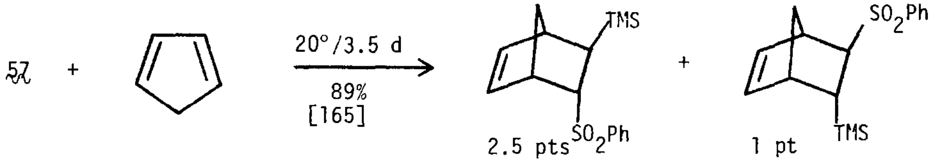


57

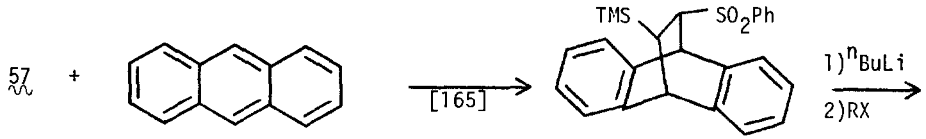
(110)

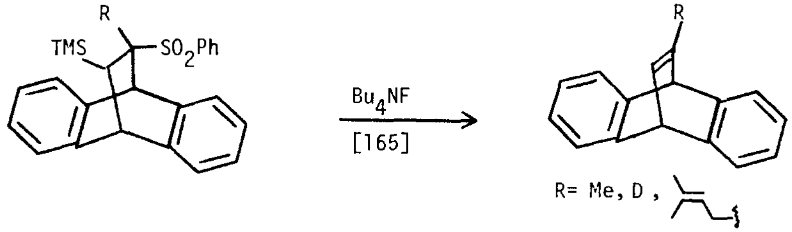


(111)

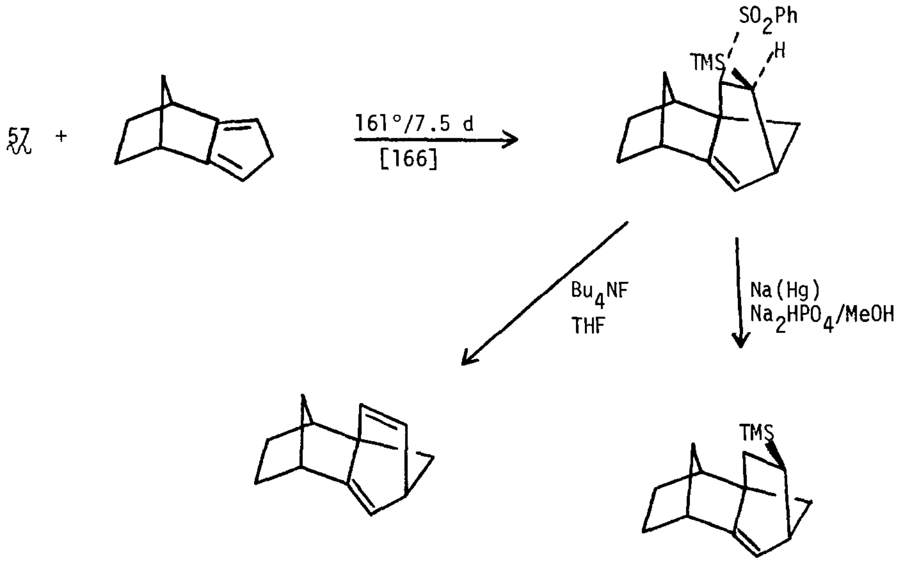


(112)



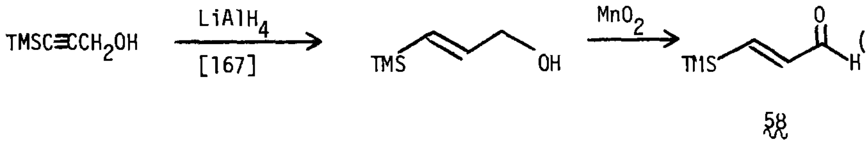


(114)

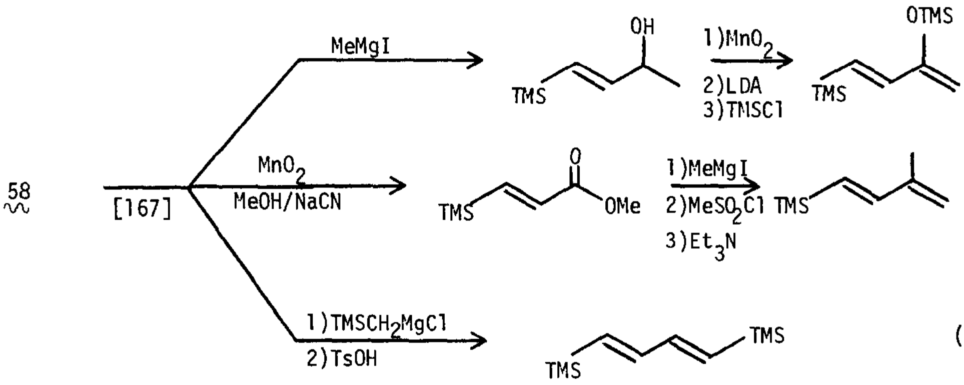


(115)

Silylated butadienes were shown to be excellent reagents for Diels-Alder cyclizations. The products are allylsilanes and, therefore, useful in the further elaboration of the newly formed six membered ring. Representative examples from this complete study are given. (Eqns. 119-124) The syntheses of some of the dienes employed are given in Eqns. 116-118.



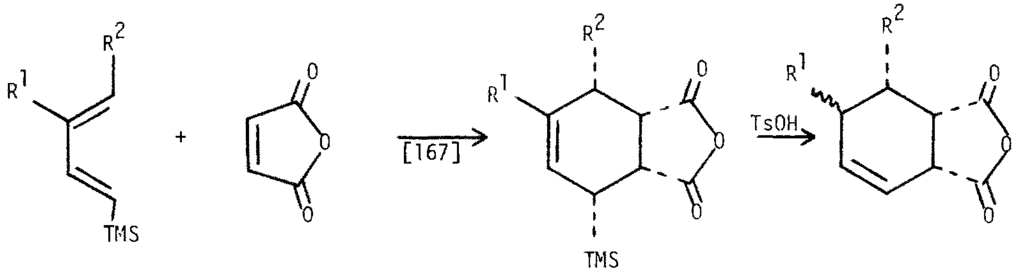
(116)



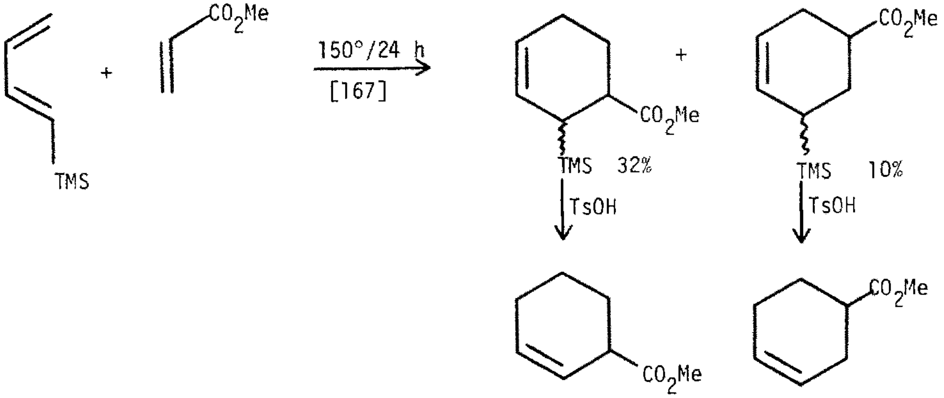
(117)

(118a)

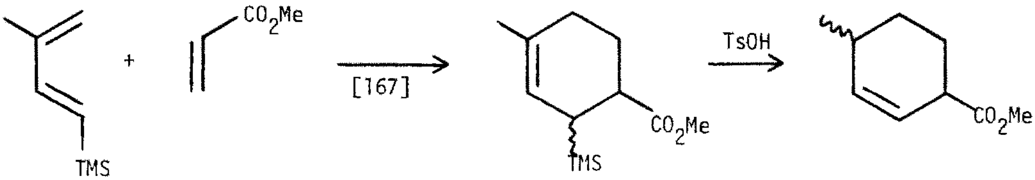
(118b)



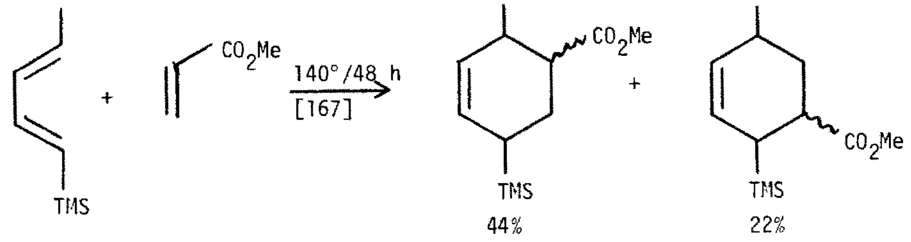
(119)



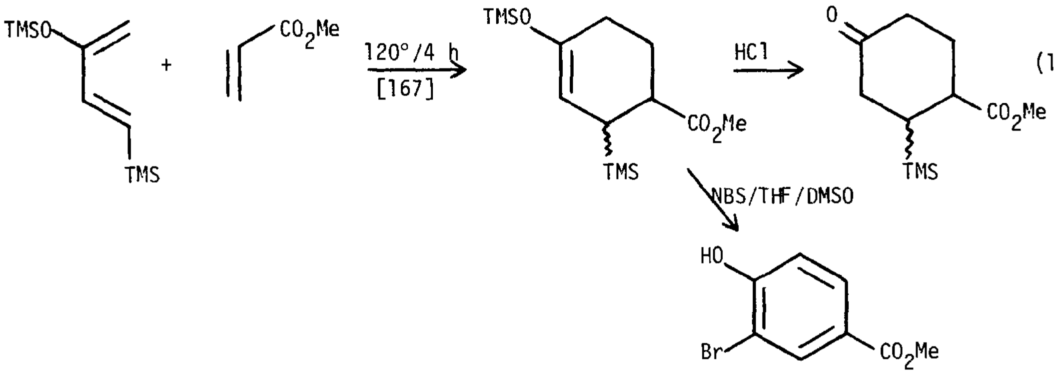
(120)



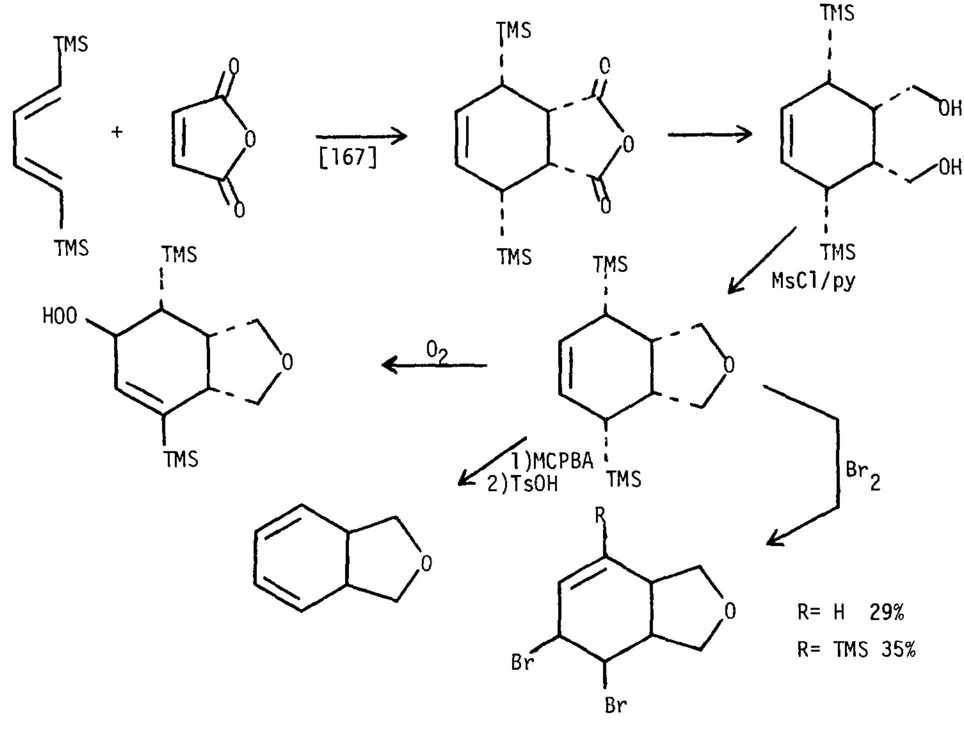
(121)



(122)



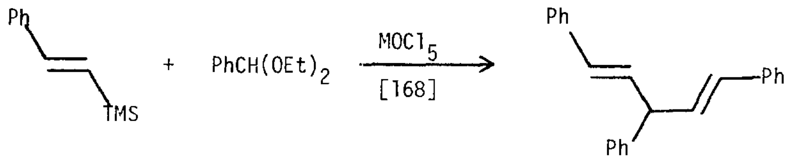
(123)



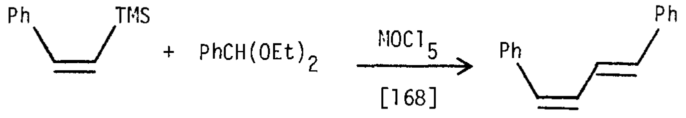
(124)

5. Electrophilic Substitution

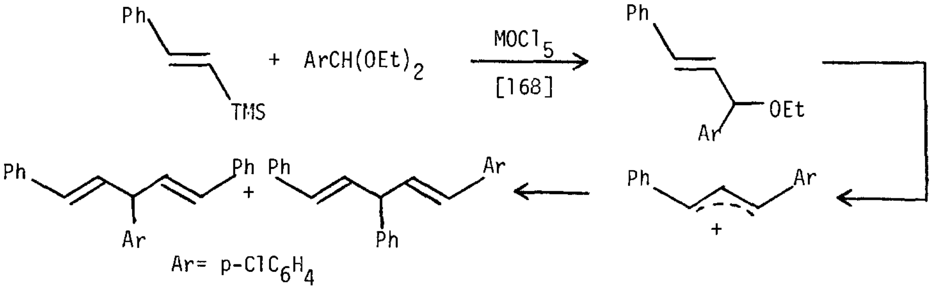
The electrophilic substitution of vinylsilanes produced some interesting transformations. These are given in Eqns. 125-127. Cis and trans β-trimethylsilylstyrene react with the diethylacetal of benzaldehyde to give the product of bisaddition. (Eqns. 125-126) When this was carried out with the acetal of p-chlorobenzaldehyde it was shown that the second step proceeds via an allylcation which can react at either terminus. (Eqn. 127) The reaction is stereospecific.



(125)

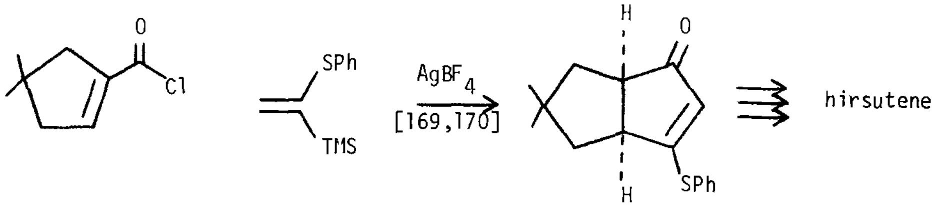


(126)



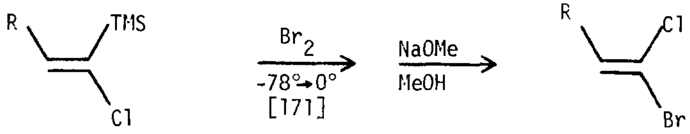
(127)

The reaction of acyl chlorides with 1-phenylthio-1-trimethylsilylethylene was employed in a key step to the total synthesis of hirsutenes. (Eqn. 128) See also Eqns. 97-100 for other reactions of this vinylsilane.

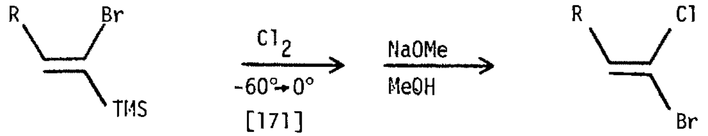


(128)

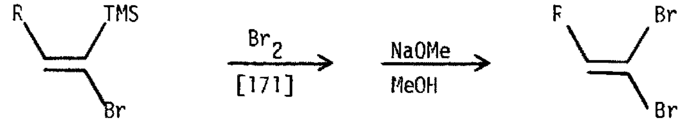
The addition of bromine or chlorine to α-halovinylsilanes has been reported. The resulting dehalosilylation results in the overall electrophilic substitution of the vinylsilane. (Eqns. 129-131)



(129)

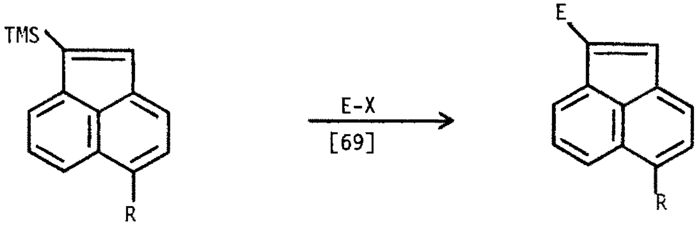


(130)



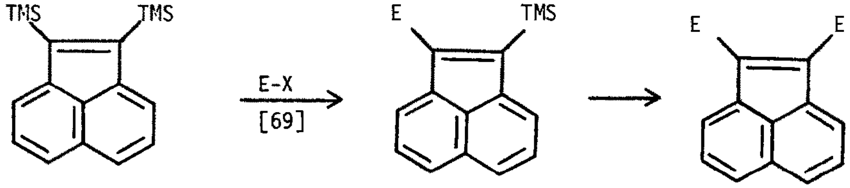
(131)

The electrophilic substitution of 1-trimethylsilylacenaphthylene and 1,2 bis(trimethylsilyl)acenaphthylenes were investigated. (Eqns. 132-133)



(132)

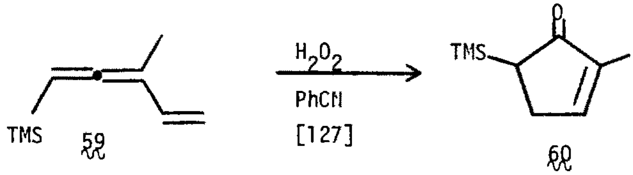
EX= ICl; $TMSOSO_2Cl$; AcCl; EtCOCl



(133)

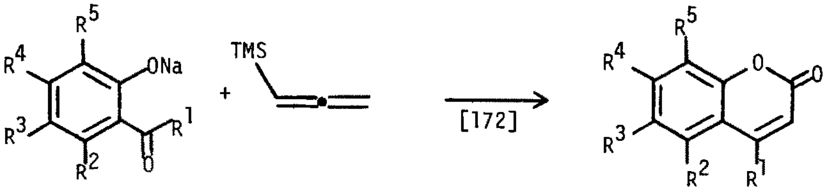
6. Miscellaneous Reactions

The (vinylallenyl)silane, 59, undergoes oxidation to give the cyclopentenone 60. (Eqn. 134)



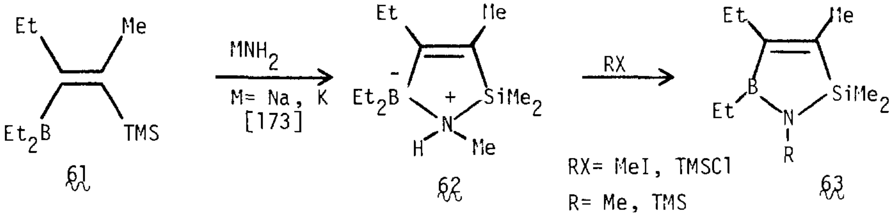
(134)

The reaction of o-acylphenols as their sodium salts with trimethylsilylketene leads to coumarins. (Eqn. 135)



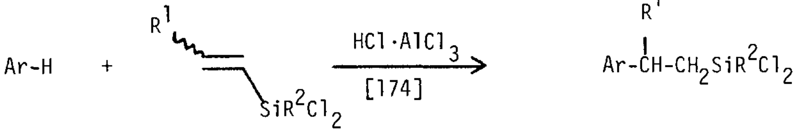
(135)

Reaction of the β-borylvinylsilane, **61**, with sodium or potassium amide gives the cyclic system **62** which could be N methylated or silylated to give **63**. (Eqn. 136)



(136)

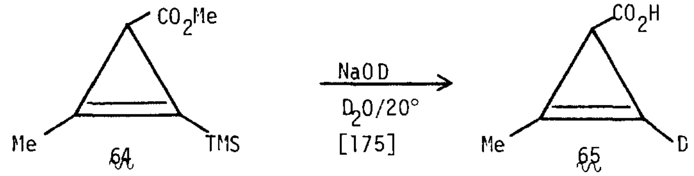
Vinylsilanes were used to silylalkylate aromatic rings with $HCl/AlCl_3$ catalysis. (Eqn. 127)



(137)

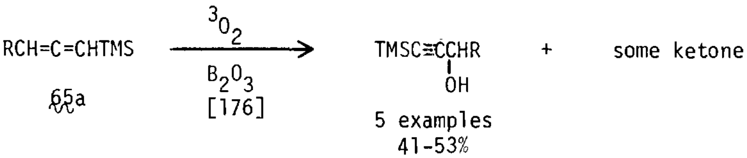
R^1= H, R^2= Cl
R^1= trans Et, R^2= Me
R^1= cis + trans Et, R^2= Cl

The cyclopropenylsilane **64** was deuterodesilylated to give **65**. (Eqn. 138)

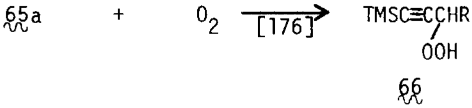


(138)

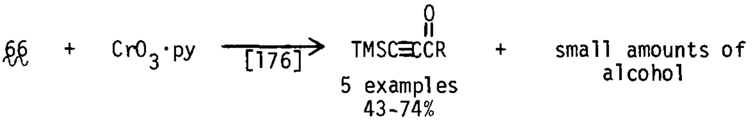
The oxidation of allenylsilanes gives silylated propargyl alcohols (Eqn. 139), or silylated propargylhydroperoxides (Eqn. 140) which can be oxidized to the silylated acylacetylenes. (Eqn. 141)



$$\underset{\textbf{65a}}{RCH{=}C{=}CHTMS} \xrightarrow[\begin{subarray}{c} B_2O_3 \\ [176] \end{subarray}]{{}^3O_2} \underset{\begin{subarray}{c} \text{5 examples} \\ 41\text{-}53\% \end{subarray}}{TMSC{\equiv}C\underset{\underset{OH}{|}}{C}HR} + \text{some ketone} \qquad (139)$$

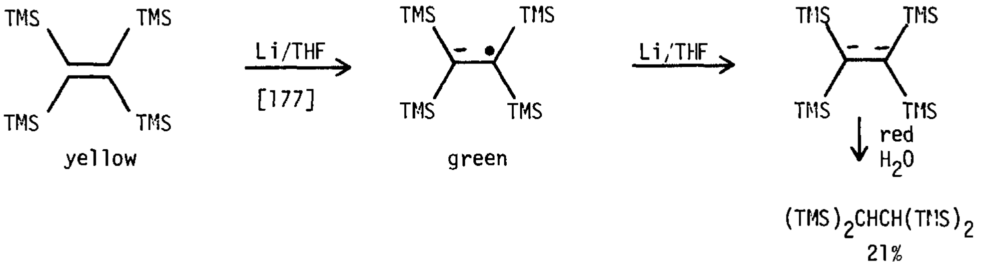


$$\textbf{65a} + O_2 \xrightarrow[{[176]}]{} \underset{\textbf{66}}{TMSC{\equiv}C\underset{\underset{OOH}{/}}{C}HR} \qquad (140)$$



$$\underset{\sim}{66} + CrO_3\cdot py \xrightarrow[{[176]}]{} \underset{\substack{\text{5 examples}\\ 43\text{-}74\%}}{TMSC{\equiv}C\overset{\overset{O}{\|}}{C}R} + \text{small amounts of alcohol} \qquad (141)$$

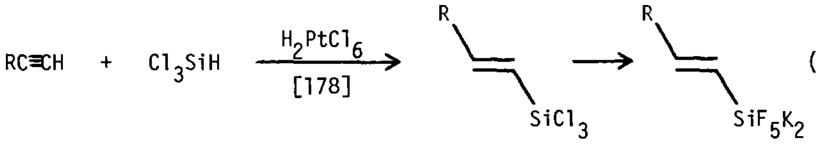
Tetrakis(trimethylsilyl)ethylene, can be reduced with lithium metal in THF. The initially produced, green anion radical is further reduced to the red dianion. Quenching of the dianion with water gives 1,1,2,2-tetrakis(trimethylsilyl)ethane. (Eqn. 142) The ^{29}Si-NMR of the dianion shows the silicon resonance to be at -17.27 ppm.



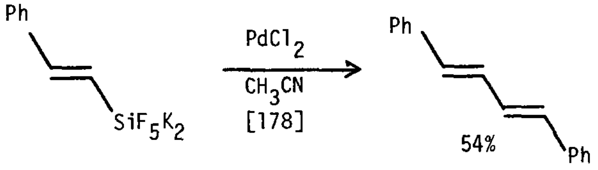
(142)

7. Organofluorosilicates

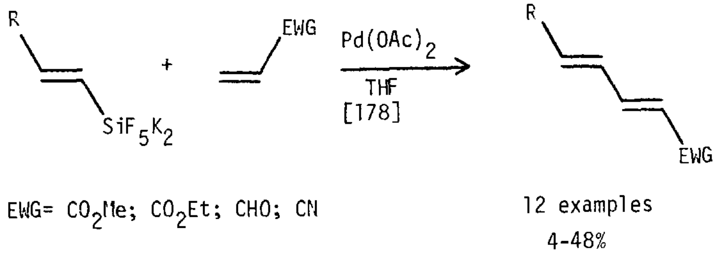
Potassium vinylfluorosilicates, available via the hydrosilylation of acetylenes and subsequent treatment with potassium fluoride,(Eqn. 143) undergo a variety of coupling reactions as shown in Eqns. 144-148. Treatment of the vinylfluorosilicate with $PdCl_2$ results in the direct coupling of the vinyl group (Eqn. 144). Treatment with Michael acceptors in the presence of Pd(II) gives Michael addition of the vinyl group. (Eqn. 145) Coupling with allyl halides gives 1,4-dienes (Eqn. 146). The coupling with aryl iodides leads to arylation of the vinyl group. (Eqn. 147) Finally, carbonylation leads to α,β-unsaturated esters. (Eqn. 148) Arylfluorosilicates react somewhat similarly. (Eqns. 149-150)



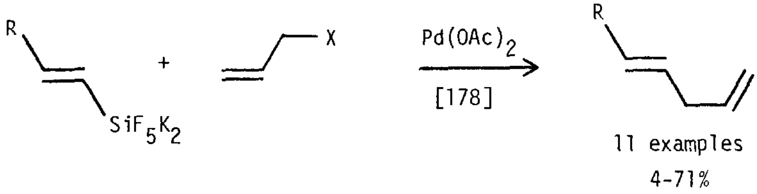
(143)



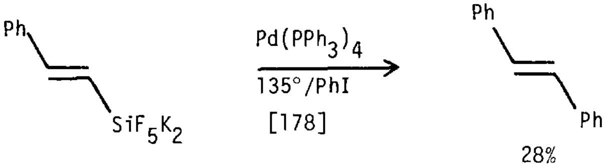
(144)



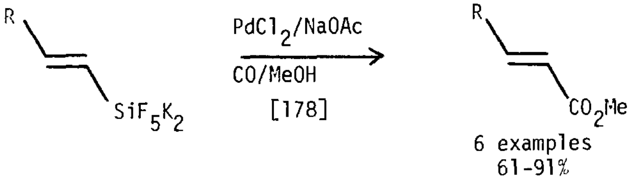
(145)



(146)



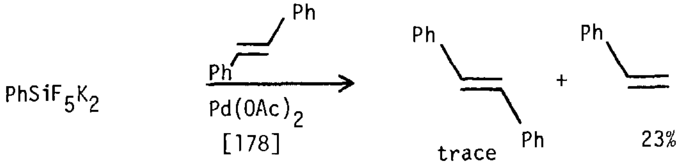
(147)



(148)

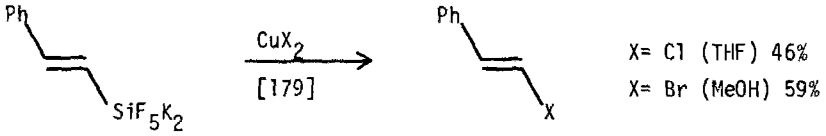
$$PhSiF_5K_2 \xrightarrow[\substack{CH_3CN \\ [178]}]{PdCl_2} \text{Ph-Ph} \quad 48\%$$

(149)

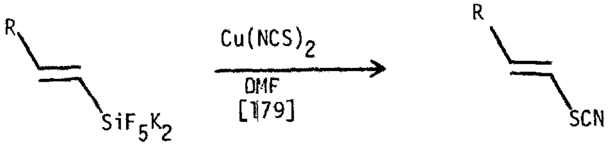


(150)

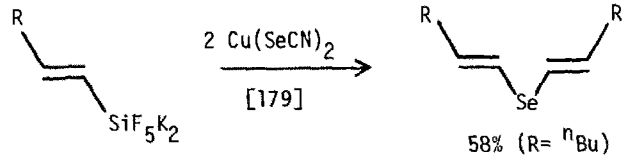
The copper (II) oxidation of vinylfluorosilicate leads to a variety of organic systems. (Eqns. 151-154) These reactions also work with alkylfluorosilicates. (Eqns. 155-157)



(151)

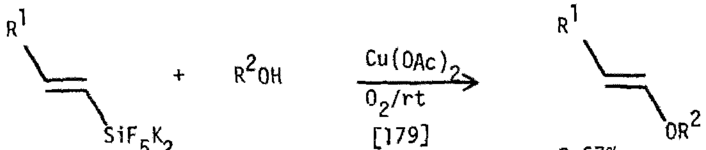


(152)



58% (R= ^{n}Bu)

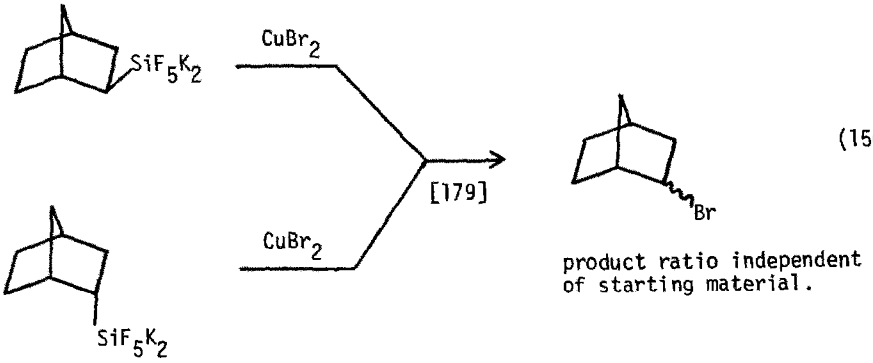
(153)



0-67%

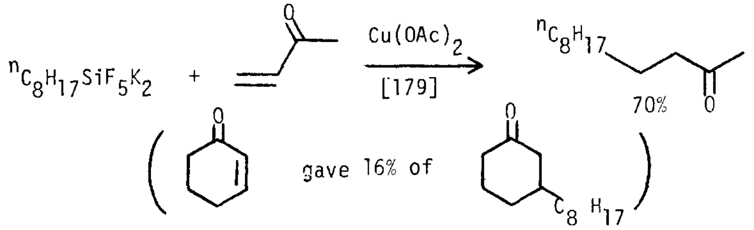
(154)

$$^{n}C_8H_{17}SiF_5K_2 \xrightarrow[O_2/MeOH \; [179]]{CuCl_2} {}^{n}C_7H_{15}CHO \qquad (155)$$



product ratio independent of starting material.

(156)

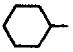


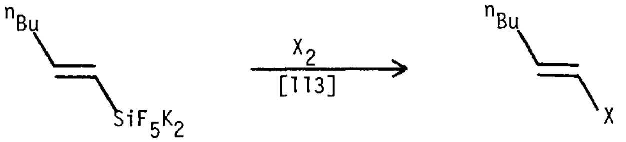
(157)

Halogenation of alkenyl or alkylfluorosilicates leads to the corresponding halides. (Eqns. 158-160) The stereoselectivity in the vinyl systems is high, but solvent dependent, in the alkyl systems as seen from the reaction of the norbornyl systems **67**. (Eqn. 160) Thus in polar solvents such as MeOH or THF predominant inversion is noted. NBS is more stereoselective than Br_2.

$$\mathrm{RSiF_5K_2} \xrightarrow[\text{[113]}]{X_2} \text{R-X} \qquad (158)$$

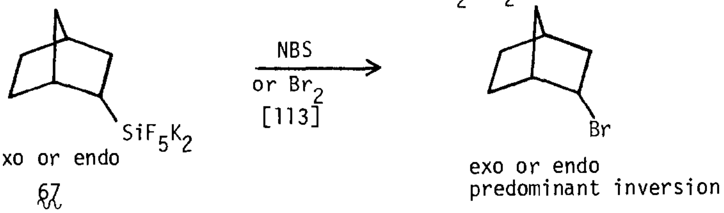
$X_2= Br_2$	X= Br	4 examples	59-74%
$X_2= I_2$	X= I	2 examples	32 and 73%
$X_2= Cl_2$	X= Cl	2 examples	54 and 73%

R= $^nC_8H_{17}$; $^tBuCH_2CH_2$; ; Ph



(159)

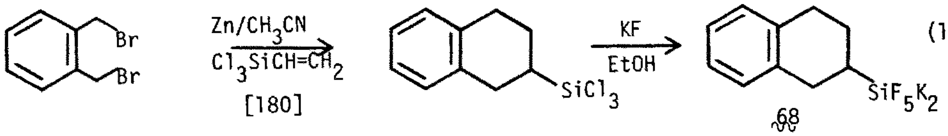
$X_2= Br_2$	X= Br	61%	(E:Z 67:33)
$X_2= I_2$	X= I	48%	(E:Z 100:0)



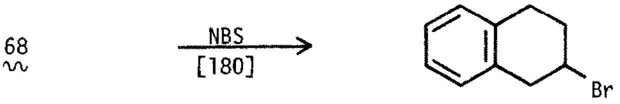
67

(160)

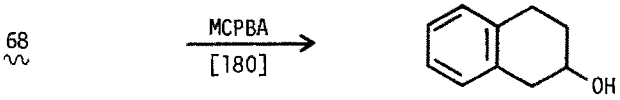
Some further alkylfluorosilicate reactions are given here even though they are not vinyl systems, but because they are fluorosilicates. (Eqns. 162-167).



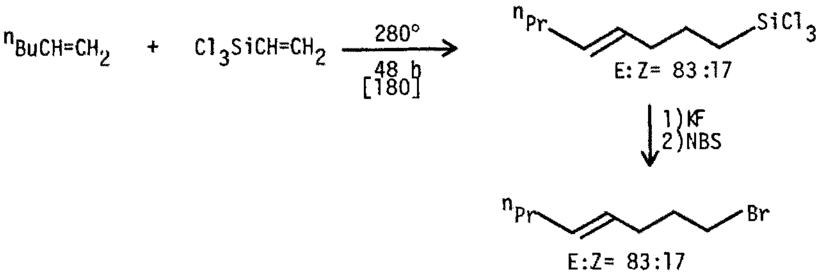
(161)



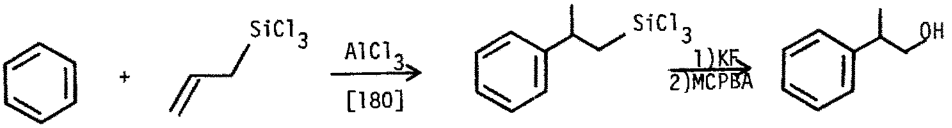
(162)



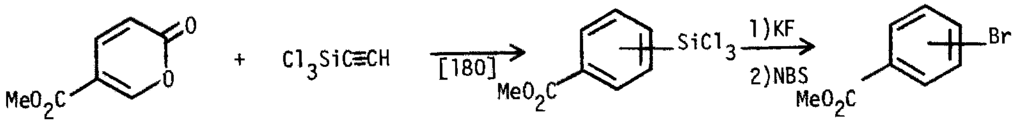
(163)



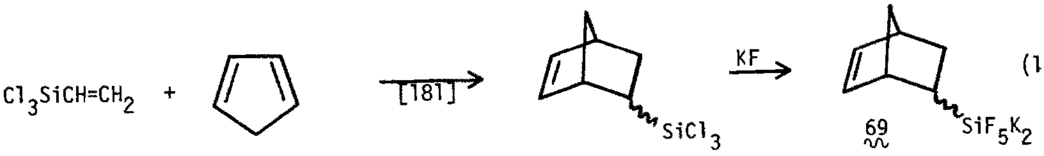
(164)



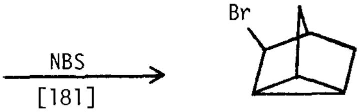
(165)



(166)

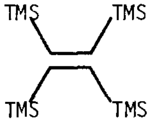


(167)

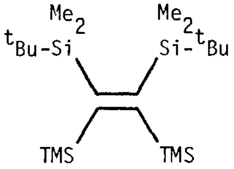
69  (167)

8. Spectral and Theoretical Studies

An X-ray crystal structure has been carried out on tetrakis(trimethylsilyl)ethylene, 70. The C=C is a rather long 1.368 Å, the =C-Si bonds are 1.915 Å and the =C-Si angle is a wide 124.10°. Although each end of the molecule is planar the two planes form a dihedral angle of 29.5° due to the steric bulk. The molecule shows reversible thermochromism being colorless at -70° and orange at ca. 200°. It shows an isosbestic point at 389 nm. [182] The X-ray crystal structure of 71 shows the structure to be similar to that of 70 with the dihedral angle between the two planes formed by Si_2C units at either end of the molecule being 49.6°. [183]



70



71

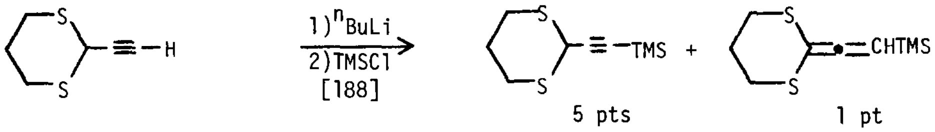
The microwave spectra of vinylsilane and its twelve isotopically substituted species (^{29}Si, ^{33}Si, ^{13}C, D) have been recorded: structure, dipole moments and internal rotation are discussed. [184]

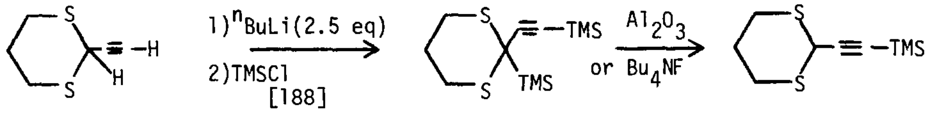
The photoelectron spectra of some vinylsilanes show a slight increase in the dπ-pπ overlap in vinyldisilanes as compared to vinylsilanes. [185] Electron transmission spectroscopy of vinyltrimethylsilane indicates that the π MO's of the negative ion state is stabilized (with respect to $^{t}BuCH{=}CH_2$) by interaction with the d orbitals of silicon. [186] The effect of an α-silyl group on the stability of vinyl cations was the subject of a study involving ab initio calculations. [187]

VIII. ETHYNYLSILANES

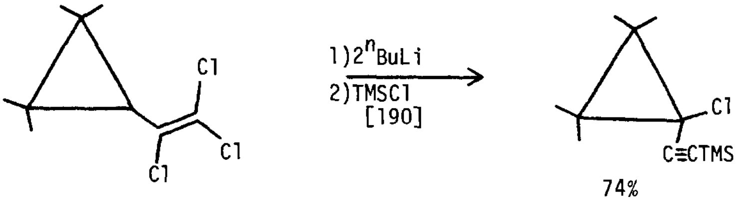
A. Preparation From Ethynylmetallic Reagents

Not surprisingly the reaction of readily available ethynylmagnesium halides or ethynyllithium reagents with halosilanes represents the single most popular entry into ethynylsilanes. Examples that appeared are shown below and are presented without further comment. (Eqns. 168-175)


(168)


(169)

$$CH_3C{\equiv}CLi \quad + \quad iPr_3SiOT \quad \xrightarrow[{[189]}]{} \quad CH_3C{\equiv}CSi^iPr_3 \qquad (170)$$


(171)

$$HOCMe_2C{\equiv}CH \quad \xrightarrow[\substack{2)TMSCl\\ 3)HCl\\ [191]}]{1)EtMgBr} \quad ClCMe_2C{\equiv}CTMS \qquad (172)$$

$$ClCH_2Me_2SiC{\equiv}CMgBr \quad + \quad ClSi(OMe)_3 \xrightarrow[{[118]}]{} ClCH_2Me_2SiC{\equiv}CSi(OMe)_3 \qquad (173)$$

47.4%

$$PhCHMeOCH_2C{\equiv}CMgBr \quad + \quad TMSCl \quad \xrightarrow[{[192]}]{} \quad PhCHMeOCH_2C\ CTMS \qquad (174)$$

$$BrMgOCH_2C{\equiv}CMgBr \quad + \quad PhCH_2Me_2SiCl \quad \xrightarrow[{[193]}]{} \quad HOCH_2C{\equiv}CSiMe_2CH_2Ph \qquad (175)$$

The reaction of ethynylstannanes and halosilanes gives the ethynylsilane and tin halide. (Eqns. 176-179)

$$CF_3C{\equiv}CSnMe_3 + TMSCl \xrightarrow[[194]]{HMPA} CF_3C{\equiv}CTMS + Me_3SnCl \qquad (176)$$

$$NCC{\equiv}CSnEt_3 + TMSBr \xrightarrow[[194]]{HMPA} NCC{\equiv}CTMS \qquad (177)$$

$$HC{\equiv}CSnEt_3 + TMSI \xrightarrow[[194]]{HMPA} HC{\equiv}CTMS \qquad (178)$$

$$RSC{\equiv}CSnMe_3 + TMSBr \xrightarrow[[195]]{} RSC{\equiv}CTMS \qquad (179)$$

R= Et 82%

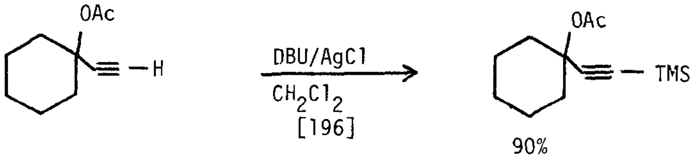
R= Me 79%

Hindered tertiary amines can be used to form the acetylene anion in the presence of the chlorosilane as opposed to preparing the anion separately. (Eqn. 180) This method tolerates certain groups. (Eqn. 181)

$$R\text{-}C{\equiv}CH + TMSCl \xrightarrow[\substack{AgCl\ (cat)\\ CH_2Cl_2\\ [196]}]{DBU} RC{\equiv}C\text{-}TMS \qquad (180)$$

5 examples

84-94%



(181)

B. Preparation From Silicon Containing Acetylenes

The metalation of 1-silylpropynes served as an entry into a variety of ethynylsilanes. Lithiation of 1-Triisopropylsilylproyne gave the bissilyl compound **72** upon silylation. (Eqn. 182) Compound **73** could be metalated and the anion **74** reacted with aldehydes as shown. (Eqns. 183-184)

$$CH_3C{\equiv}CTIPS \xrightarrow[\text{or } {}^{t}BuLi/Et_2O\text{-}Pentane/-10°\ \text{ or } {}^{n}BuLi/THF/-20°\ [189]]{1)\ {}^{n}BuLi/TMEDA/-15°} LiCH_2C{\equiv}CTIPS \quad (182)$$

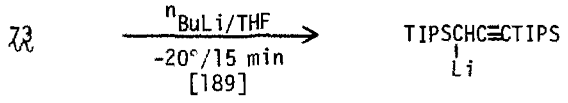
TIPS= iPr_3Si

72

$$LiCH_2C{\equiv}CTIPS \xrightarrow{TIPS\text{-}Cl} TIPSCH_2C{\equiv}CTIPS$$

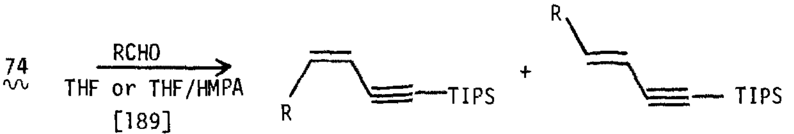
73

100%



$$73 \xrightarrow[-20°/15\ min\ [189]]{{}^{n}BuLi/THF} TIPS\underset{Li}{C}HC{\equiv}CTIPS \quad (183)$$

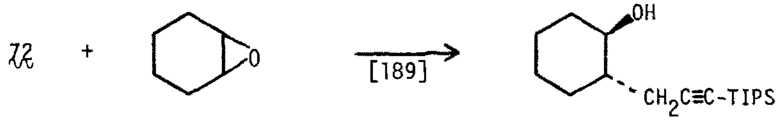
74



(184)

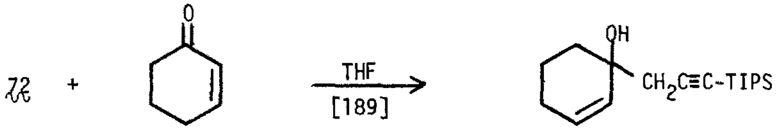
major product in THF major product in THF/HMPA

The lithium reagent 72 was reacted with cyclohexene oxide (Eqn. 185) and cyclohexenone. (Eqns. 186-187) Alkylation of 72 gave the silylated acetylenes shown. (Eqn. 188)

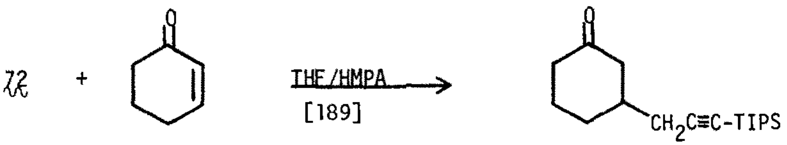


(185)

82% (4.5% of the allene)



(186)



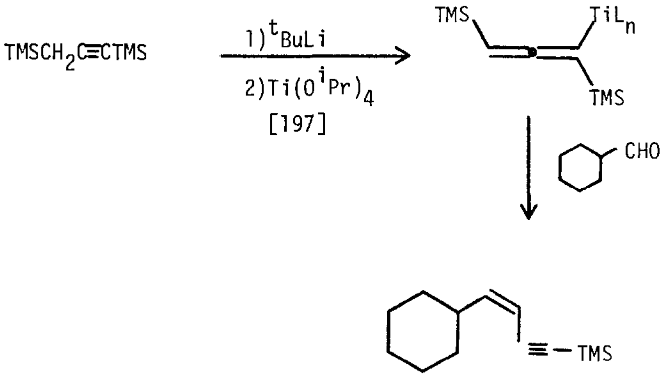
(187)

$$\underset{\sim}{72} \quad + \quad RBr \quad \xrightarrow{[189]} \quad RCH_2C\equiv C\text{-}TIPS \qquad (188)$$

$R = PhCH_2CH_2$ 96%

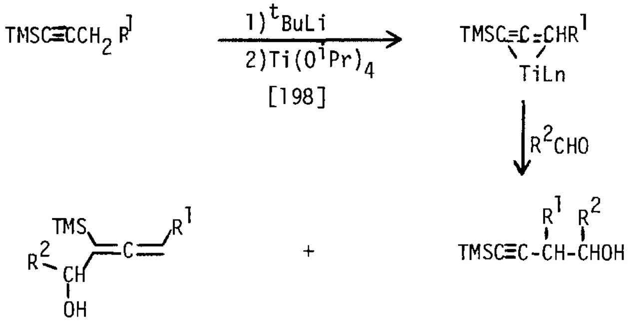
R= geranyl 78%

In a related study bistrimethylsilylpropyne was deprotonated and the resulting lithium reagent reacted with $Ti(O^iPr)_4$ to form the titanium reagent, which gives only the acetylenic product with cyclohexylcarbaldehyde and none of the allenyl product. (Eqn. 189) Similar reaction with 1-trimethylsilylacetylenes including the stereoselectivity are given in Eqns. 189-190.



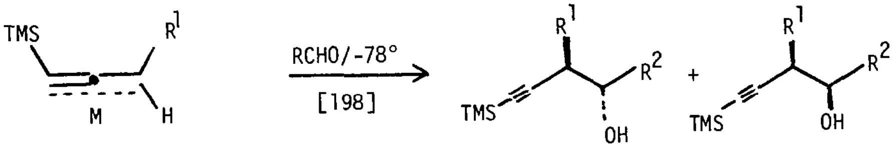
87% (Z:E > 20:1)

(189)



(190)

R^1	R^2			
H	C_6H_{11}	99	1	93%
H	Ph	99	1	87%
Me	C_6H_{11}	1	99	69%
Me	Ph	1	99	79%

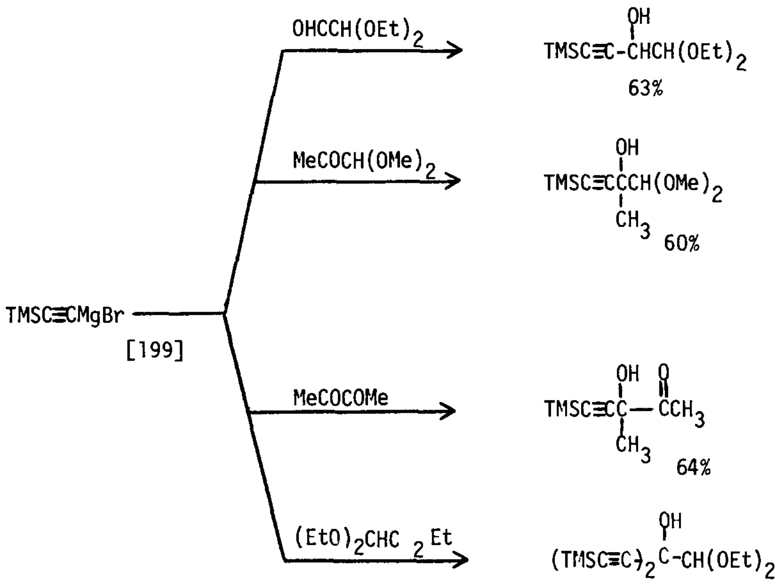


(191)

M	R^1	R^2			
Li	Me	C_6H_{11}	62	38	48%
Mg	Me	C_6H_{11}	65	35	42%
Ti	Me	C_6H_{11}	89 (93*)	11 (7*)	69%
Ti	Me	Ph	84	16	79%
Zn	OTHP	C_6H_{11}	71	29	51%
Ti	OTHP	C_6H_{11}	90	10	67%
Ti	OTHP	$^nC_5H_{11}$	88	12	65%

*(at -100°)

Trimethylsilylethynylmagnesium bromide was reacted with aldehydes, ketones and esters. (Eqns. 192-195)



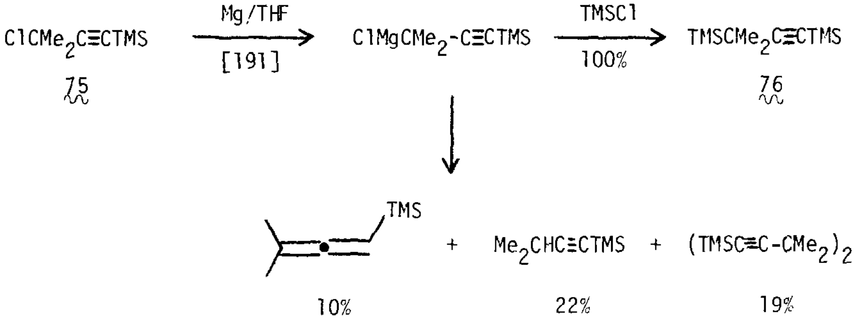
(192)

(193)

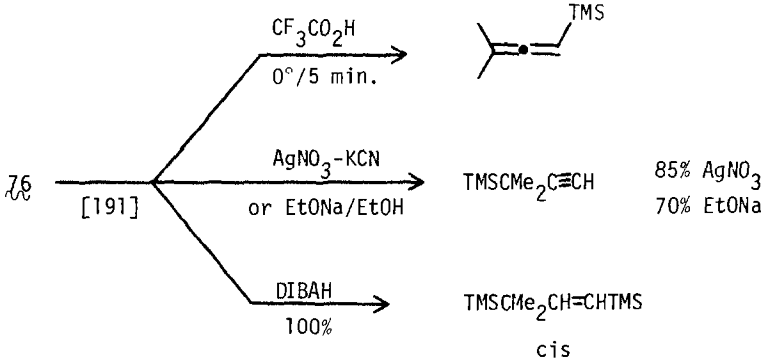
(194)

(195)

The propargyl chloride 75, prepared according to Eqn. 172, can be converted to the Grignard reagent, which can be silylated to give 76. (Eqn. 196) Protonation gives a mixture of products. Some reactions of 76 are also given below. (Eqns. 197-199)



(196)



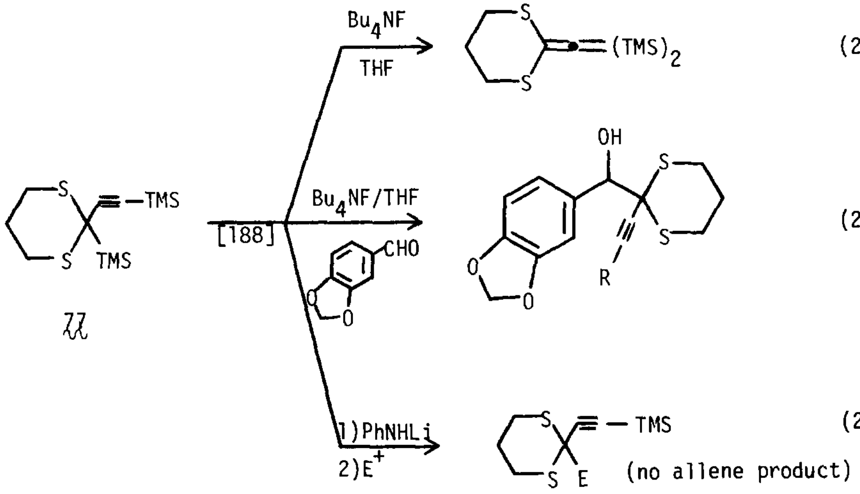
(197)

(198)

(199)

The ethynylsilane 77, prepared according to Eqn. 169, undergoes the reactions shown below. (Eqns. 200-202)

Iodocarboranes were coupled with TMSC≡CMgBr to give the β-ethynylcarboranes. (Eqn. 203) These were hydrolyzed to the acetylene with KOH/MeOH.



77

(200)

(201)

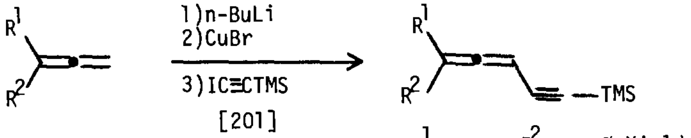
(202)

$$(o)\ \text{or}\ (m)\ C_2B_{10}H_9I\ +\ \text{TMSC}{\equiv}\text{CMgBr}\ \xrightarrow[{[200]}]{}\ (o)\ \text{or}\ (m)\ C_2B_{10}H_9C{\equiv}\text{CTMS}\qquad(203)$$

90%

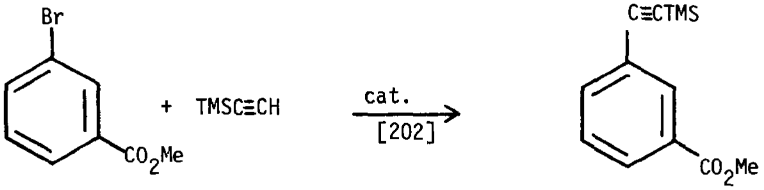
E$^+$= H$_2$O, D$_2$O, MeI, TMSCl, aldehydes, ketones, enones

Allenylcuprates were coupled with 2-iodotrimethylsilyl acetylene according to Eqn. 204. Aryl halides have been coupled with trimethylsilylacetylene as seen in Eqn. 205.



(204)

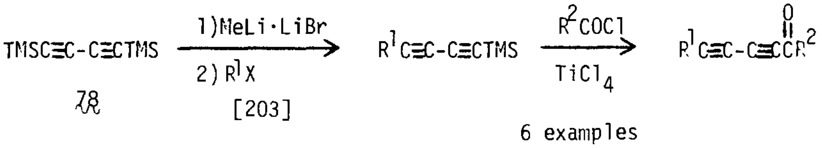
R^1	R^2	% Yield
H	H	85
^{t}Bu	H	77
Me	Me	80



(205)

cat.= Ar$_3$P, Pd(OAc)$_2$; or Pt(OAc)$_2$ or Ni(OAc)$_2$ and Et$_3$N.

The bissilylated butadiyne, **78**, can undergo metal-metal exchange to give the monosilylated lithium reagent which can be alkylated. The remaining ethynylsilane bond can be electrophilically acylated to produce diynones. (Eqn. 206)

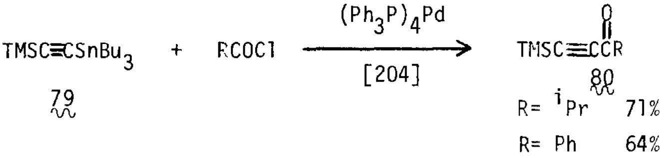


$$\underset{\mathbf{78}}{TMSC\equiv C\text{-}C\equiv CTMS} \xrightarrow[2)\,R^1X]{1)\,MeLi\cdot LiBr} R^1C\equiv C\text{-}C\equiv CTMS \xrightarrow[TiCl_4]{R^2COCl} R^1C\equiv C\text{-}C\equiv C\overset{O}{\overset{\|}{C}}R^2 \qquad (206)$$

[203]

6 examples

The ethynylsilane bond is inert to conditions in which the ethynyltin bond is reactive. Thus, acylation of **79** to give the silylated ynone **80** is possible. (Eqn. 207)



$$\underset{\mathbf{79}}{TMSC\equiv CSnBu_3} + RCOCl \xrightarrow[{[204]}]{(Ph_3P)_4Pd} \underset{\mathbf{80}}{TMSC\equiv C\overset{O}{\overset{\|}{C}}R} \qquad (207)$$

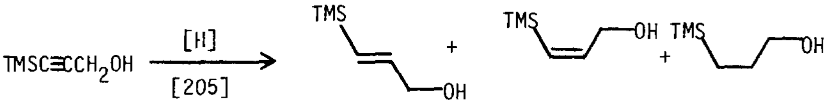
R= ${}^iPr$ 71%

R= Ph 64%

C. Reactions

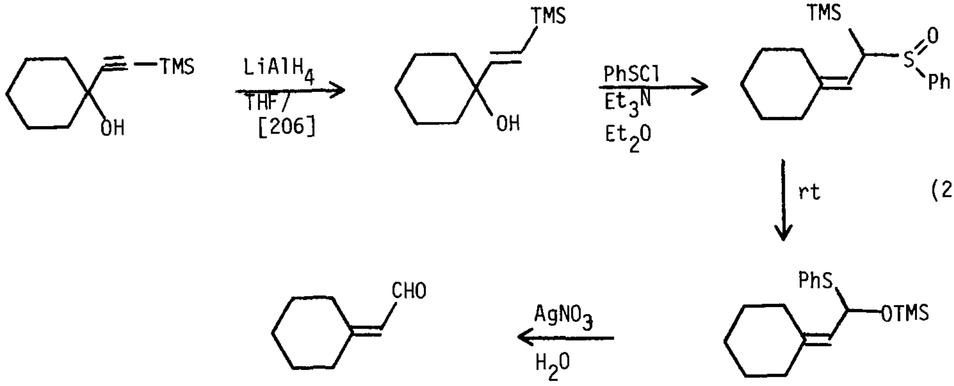
1. Additions to the C≡C

The lithium aluminum hydride reduction serves as an excellent entry into (E)-3-(trimethylsilyl)-2-propen-1-ol. (Eqn. 208) Best results were obtained with $NaAlH_2(OCH_2CH_2OMe)_2$ in ether. Other reducing agents and conditions than those shown gave poorer yields and product mixtures. A similar reaction is shown in Eqn. 209, the resulting vinylsilane being converted to the unsaturated aldehyde in this case.



(208)

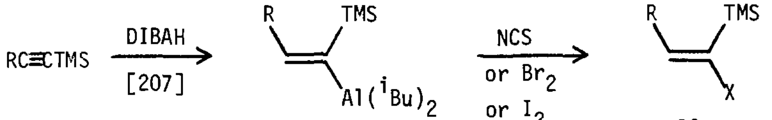
$LiAlH_4$/THF/0°	95	3	2
$LiAlH_4$/DME/0°	98	1.5	0.5
$NaAlH_2$ (O⁀OMe)$_2$ Et_2O, 0 25°	100	0	0



68%
3 other examples

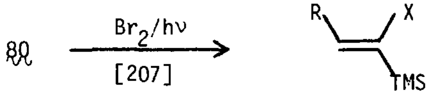
(209)

Diisobutylaluminum hydride undergoes cis addition to ethynylsilanes placing the aluminum atom geminal to the silicon group. These vinylalane intermediates can be converted to α-halovinylsilanes. (Eqns. 210-212)

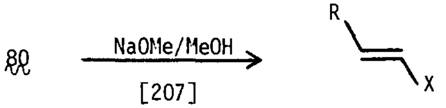


80

(210)



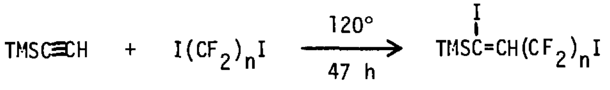
X= Cl, Br, I (211)



12 examples
68-93% from **80**

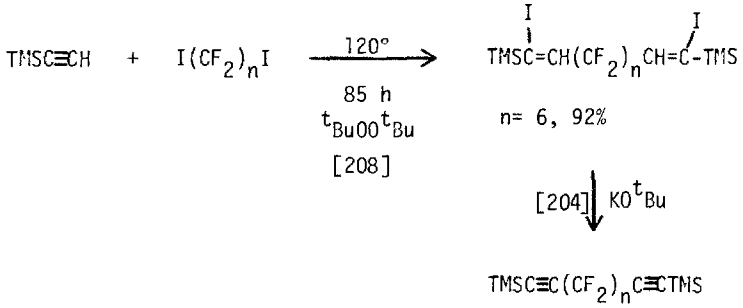
X= Cl, Br, I (212)

Several examples of the addition of perfluoroalkyl iodides to ethynylsilanes have been reported. (Eqns. 213-216)



$$\mathrm{TMSC{\equiv}CH} \quad + \quad \mathrm{I(CF_2)_nI} \xrightarrow[\text{47 h}]{120°} \mathrm{TMS\overset{I}{C}{=}CH(CF_2)_nI} \qquad (213)$$

^{t}BuOO^{t}Bu n= 6 73%
[208]



$$\mathrm{TMSC{\equiv}CH} \;+\; \mathrm{I(CF_2)_nI} \xrightarrow[\substack{85\ \mathrm{h}\\ {}^t\mathrm{BuOO}{}^t\mathrm{Bu}\\ [208]}]{120°} \mathrm{TMS\overset{I}{C}{=}CH(CF_2)_nCH{=}\overset{I}{C}\text{-}TMS} \qquad (214)$$

$$n = 6,\ 92\%$$

$$\Big\downarrow\ [204]\ \mathrm{KO^tBu}$$

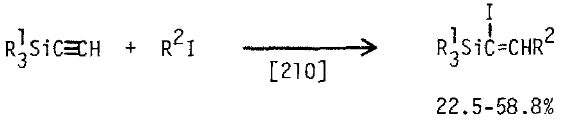
$$\mathrm{TMSC{\equiv}C(CF_2)_nC{\equiv}CTMS}$$

$$\mathrm{I(CF_2)_nI} \;+\; \mathrm{TMSC{\equiv}CTMS} \xrightarrow[{[208,209]}]{\mathrm{-TMSI}} \mathrm{TMSC{\equiv}C(CF_2)_nC{\equiv}CTMS} \qquad (215)$$

$$n = 8,\ \ 86\%$$

$$\Big\downarrow\ \mathrm{KF\cdot 2\ H_2O/MeOH}$$

$$\mathrm{HC{\equiv}C(CF_2)_8C{\equiv}CH}$$



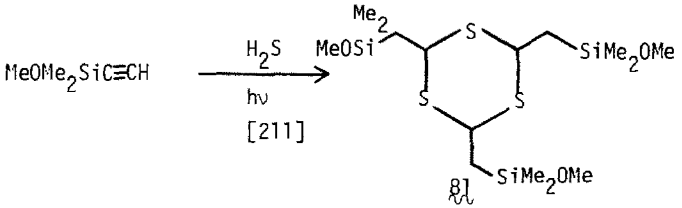
$$\mathrm{R^1_3SiC{\equiv}CH} \;+\; \mathrm{R^2I} \xrightarrow[{[210]}]{} \mathrm{R^1_3Si\overset{I}{C}{=}CHR^2} \qquad (216)$$

$$22.5\text{-}58.8\%$$

$\mathrm{R^1_3Si}$= variety of $\mathrm{RO_nMe_{3-n}Si}$ groups

$\mathrm{R^2}$= $\mathrm{CF_3}$, $\mathrm{C_3F_7}$, $\mathrm{(CF_2)_4H}$

The photochemical addition of H_2S to methoxydimethylsilylacetylene gives the trimer 81 (Eqn. 217) whereas the addition to triethylsilylacetylene gives the corresponding monoadduct, 82. (Eqn. 218)



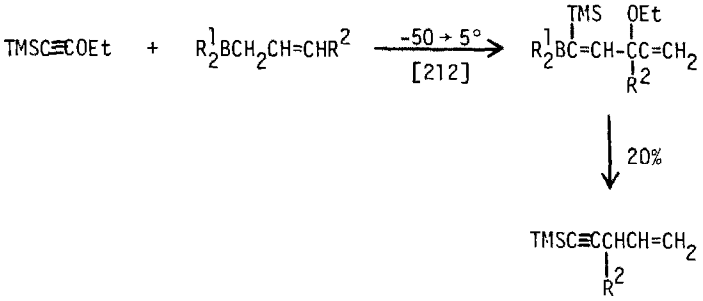
81

(217)

$$\mathrm{Et_3SiC{\equiv}CH} \xrightarrow[\substack{h\nu\\ [211]}]{\mathrm{H_2S}} \mathrm{(Et_3SiCH{=}CH)_2S} \qquad (218)$$

82

The allylboronation of ethynylsilanes has been reported. (Eqn. 219)



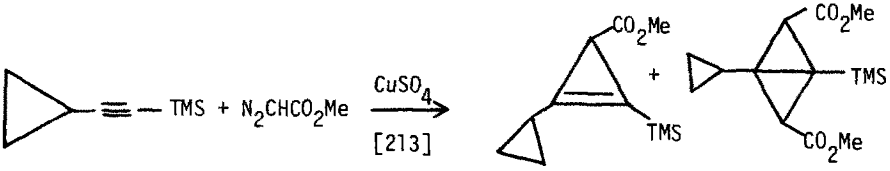
(219)

R^2= H, R^1= ^{n}Bu 86%

R^2= H, R^1= allyl 59%

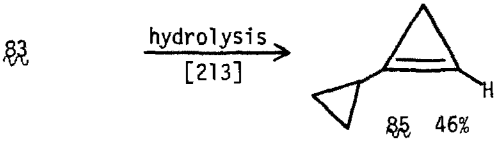
R^2 Me, R^1= $CH_2CH=CHMe$ 86%

The thermal cyclocondensation of trimethylsilylcyclopropylacetylene with methyldiazoacetate in the presence of $CuSO_4$ gives 83 and 84. Hydrolysis of 83 gives 85 and cycloaddition of 83 or 85 with cyclopentadiene gives 86 and 87, respectively. (Eqns. 220-222)



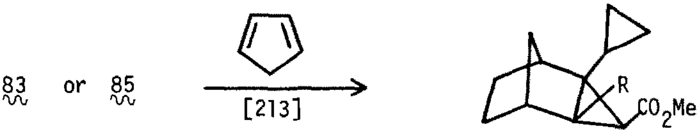
(220)

83 65% 84 8%



(221)

85 46%

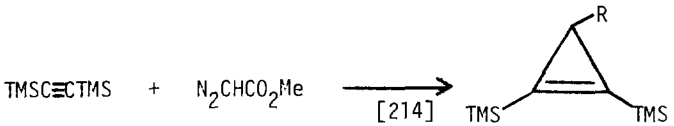


(222)

R= M 93% 86

R= TMS 70% 87

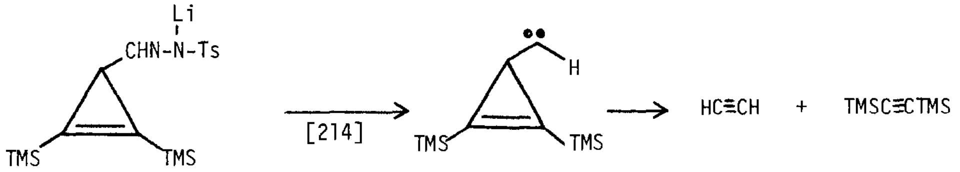
Bistrimethylsilylacetylene reacts with diazo esters to give the silylated cyclopropenes 86. The ester functionality can be converted to other functional groups. The resulting carbene splits out acetylene and bistrimethylsilylacetylene. (Eqns. 223-224)



(223)

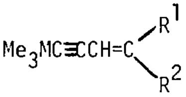
86a

R= CO_2Me (H)
R= CH_2OH (O)
R= CHO
R= CHN_2



(224)

The kinetics of the addition of MeSCl to 1-silylated-enynes of the general structure 87a have been studied. [215]



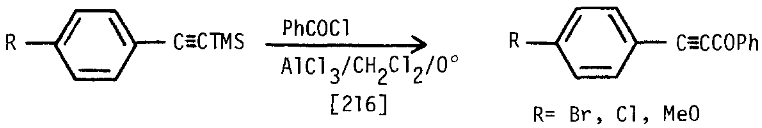
$Me_3MC\equiv CCH=C(R^1)(R^2)$

87a

M= C, Si
R^1= H, Me
R^2= Ac, CO_2Et, CN

2. Electrophilic Substitution Reactions

The acylation of ethynylsilanes remains a popular route to ethynyl ketones as seen from the examples below. (Eqns. 225-229)



(225)

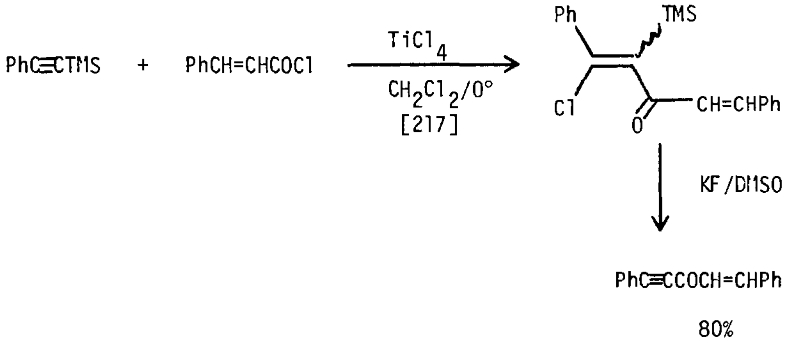
R= Br, Cl, MeO

$$ArC\equiv CTMS + Ar'CH=CHCOCl \xrightarrow[CH_2Cl_2]{AlCl_3} ArC\equiv CCOCH=CHAr' \qquad (226)$$

[217]

7 examples

38-60% crude
30-40% recrystallized

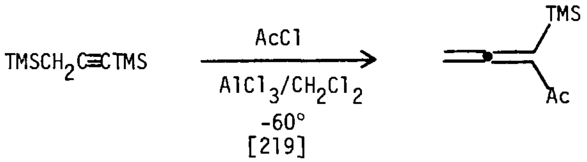


(227)

$$R^1_3SiC{\equiv}C\text{-}NR^2R^3 \;+\; R^4COCl \xrightarrow[\text{[218]}]{CH_3CN} R^4COC{\equiv}CNR^2R^3 \qquad (228)$$

R^1 = Me, Ph

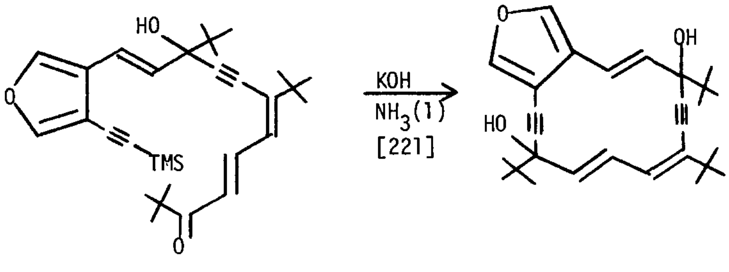
6 examples
21-73%



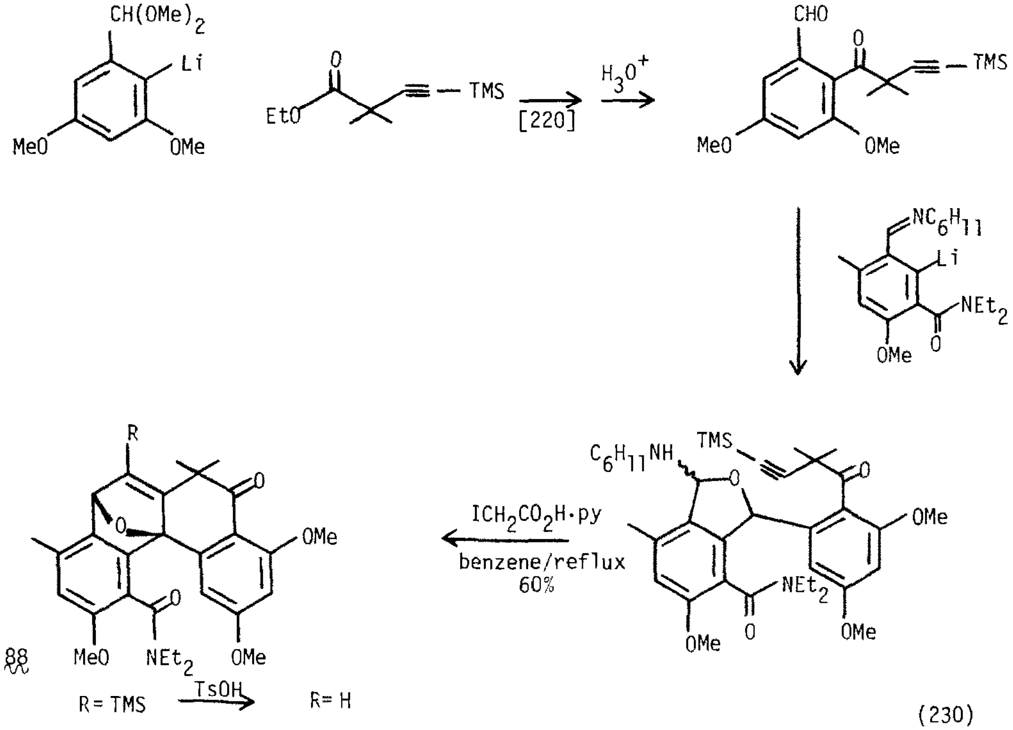
(229)

An electrophilic reaction of an ethynylsilane was used as the key step in the synthesis of resistomycin. This produced the vinylsilane 88 which had to be protodesilylated. (Eqn. 230)

It is noted that a similar transformation, although it is not electrophilic in nature, is possible under base catalysis, wherein the acetylene anion is generated directly from the ethynylsilane. This has been used in the formation of annulenes. (Eqn. 231) For another example see reference 222.



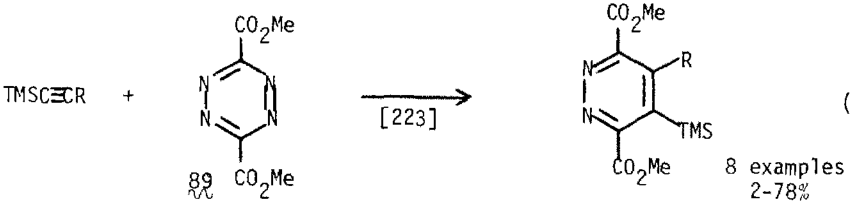
(231)



(230)

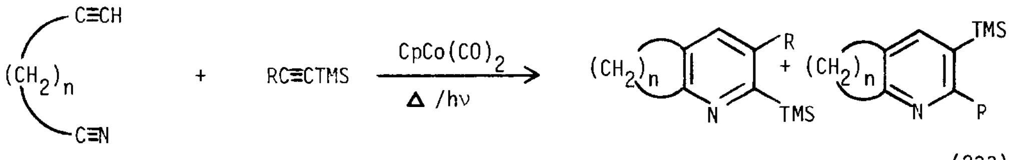
3. Cycloadditions

The cycloaddition of the tetrazine **89** with ethynylsilanes gives the silyl derivatives of pyrazines. (Eqn. 232)



(232)

The cobalt catalyzed cyclization of acetylenic nitriles with ethynylsilanes leads to 2-silylated pyridines. (Eqn. 233) A complete product analysis of the reaction of 1,6-bistrimethylsilyl-1,5-hexadiyne with CpCo(CO)$_2$ has been done. [225]



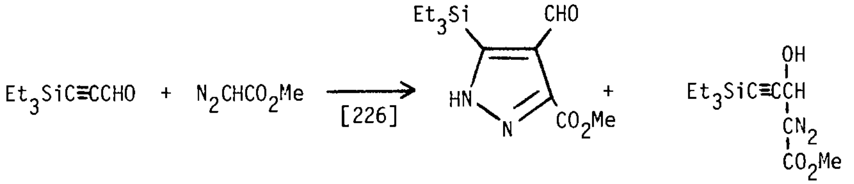
(233)

major product

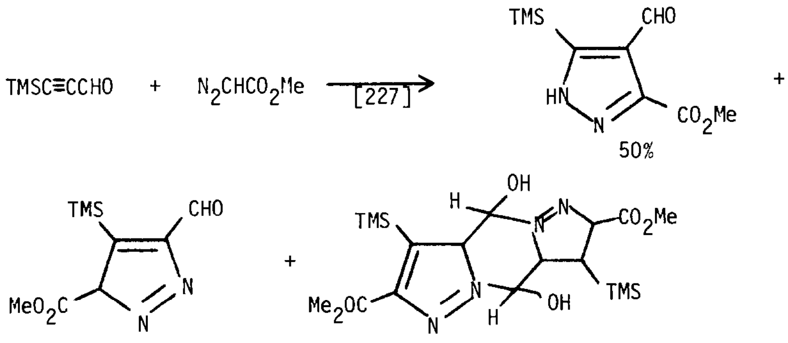
n	R	% Yield	
3	TMS	77	-
3	Me	70	0
4	TMS	77	-
4	Me	70	0
4	^{n}Bu	56	0
4	H	29	0
5	TMS	25	-
5	Me	66	0

4. Reactions of Functional Ethynylsilanes

Trialkylsilylpropynals were reacted with several reagents. These reactions are shown below. (Eqns. 234-238)



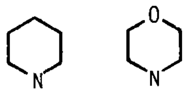
(234)



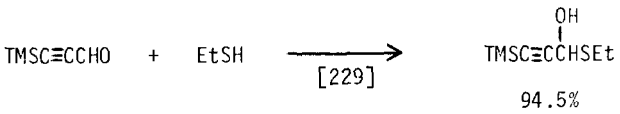
(235)

$$TMSC{\equiv}CCHO + HNR_2 \xrightarrow[20\ d,\ rt,\ [228]]{(TMS)_2NH} TMSC{\equiv}CCH(NR_2)_2 \qquad (236)$$

$R_2N=$



50% 60%



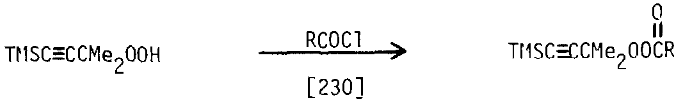
$$\mathrm{TMSC{\equiv}CCHO} + \mathrm{EtSH} \xrightarrow[{[229]}]{} \mathrm{TMSC{\equiv}C\overset{OH}{\overset{|}{C}}HSEt} \quad 94.5\% \qquad (237)$$

$$\mathrm{TMSC{\equiv}CCHO} + 2\ \mathrm{EtSH} \xrightarrow[{[229]}]{} \mathrm{TMSC{\equiv}CCH(SEt)_2} \qquad (238)$$

The silylated propargylic hydroperoxides can be alkylated and acylated. (Eqns. 239-240)

$$\mathrm{TMSC{\equiv}CCMe_2OOH} \xrightarrow[{[230]}]{\mathrm{RC(OH)Me_2}} \mathrm{TMSC{\equiv}CCMe_2OOCMe_2R} \qquad (239)$$

R= Ph, PhC≡C



$$\mathrm{TMSC{\equiv}CCMe_2OOH} \xrightarrow[{[230]}]{\mathrm{RCOCl}} \mathrm{TMSC{\equiv}CCMe_2OO\overset{O}{\overset{\|}{C}}R} \qquad (240)$$

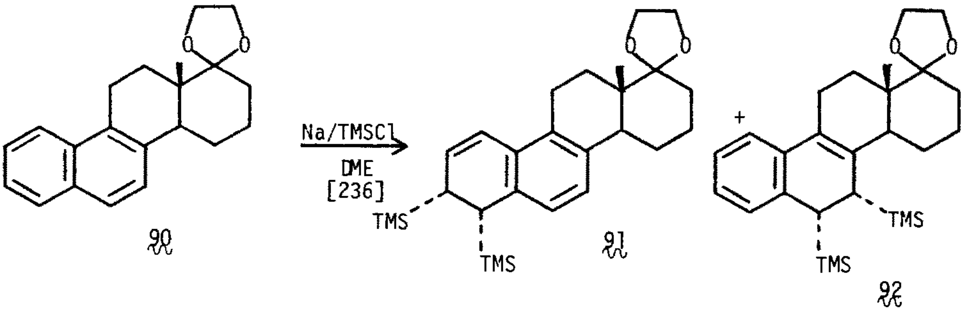
D. Spectroscopic and Theoretical Studies

The gas-phase molecular structure of silylmethylacetylene has been determined by electron diffraction. [231] ^{13}C-NMR and CNDO/2 MO calculations have been done on silylated enynes and the data compared to the analogous carbon systems. [232] The structure and donor activity of ethynylsilanes has been investigated via dipole moment, IR and NMR measurements together with quantum mechanical calculations. [233] The photoelectron spectral bands were discussed for $Me_3MC{\equiv}CH$ and $Me_3MC{\equiv}C\text{-}CH{=}CH_2$ (M= C, Si, Ge). [234] The photoionization of silylacetylenes and related acetylenes were measured. [235]

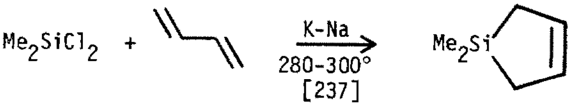
VIII. ALLYLSILANES

A. Preparation from Allylmetallics

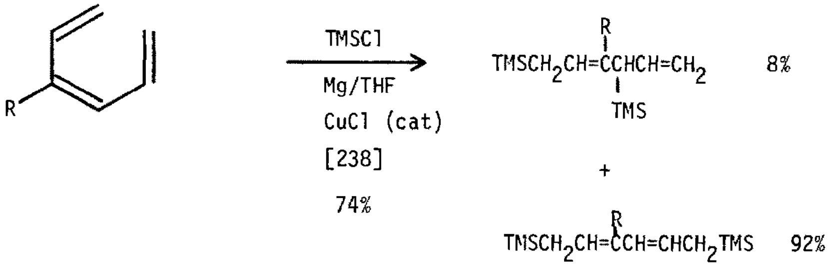
The reductive silylation of **90** gives the silanes **91** and **92**, presumably via the corresponding allylsodium species. (Eqn. 241) Treatment of dimethyldichlorosilane and 1,3-butadiene with fused K-Na at 280-300° gave 1,1-dimethyl-1-silacyclopent-3-ene. (Eqn. 242) Reductive silylation of conjugated trienes gives allylsilanes. (Eqn. 243) The resulting silylated dienes were used in Diels-Alder reactions. (Eqn. 244-245)



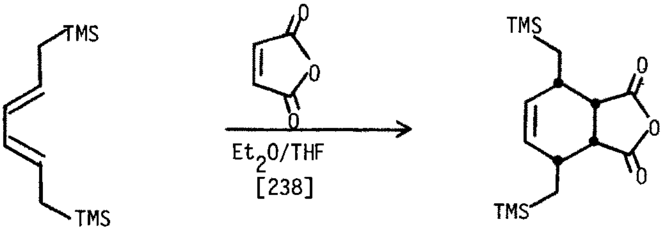
(241)



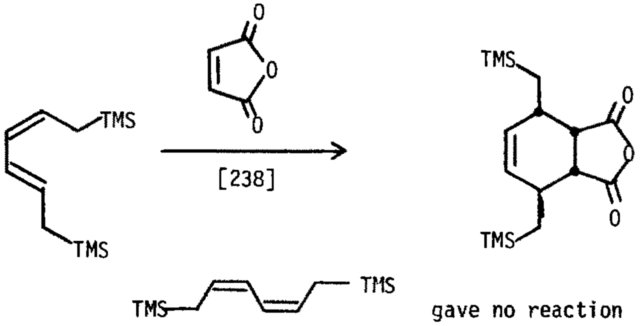
(242)



(243)

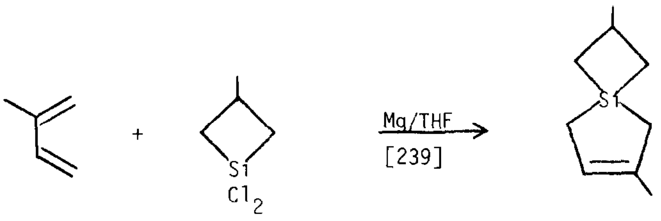


(244)



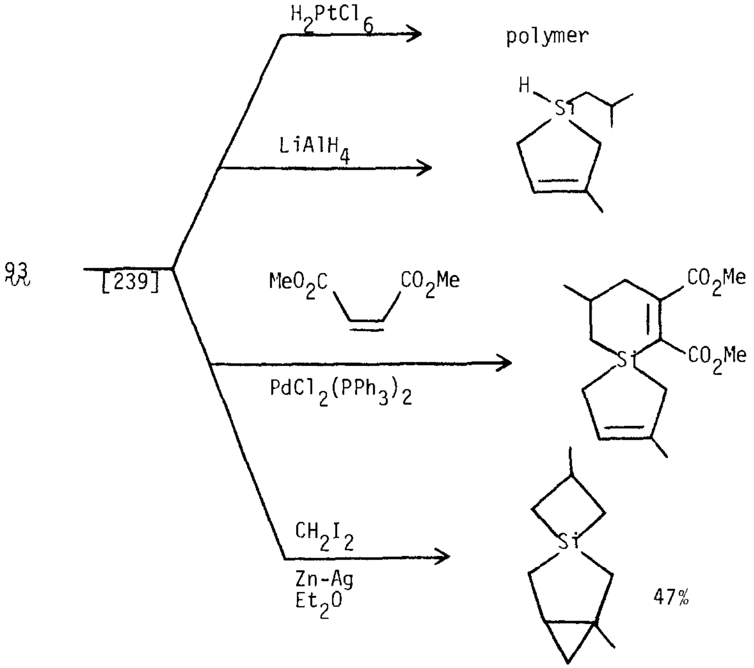
(245)

Reductive silylation of 2-methyl-1,3-butadiene leads to the silaspiro-octene, 93. Some reactions of 93 are shown. (Eqns. 246-250)



93

(246)



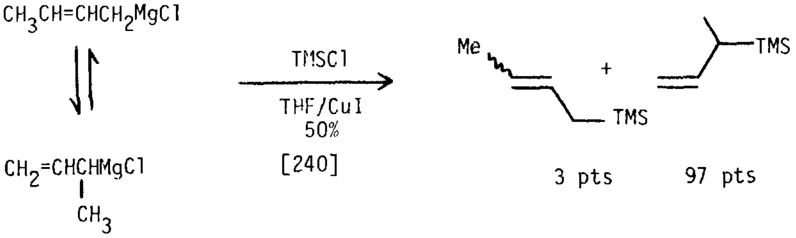
(247)

(248)

(249)

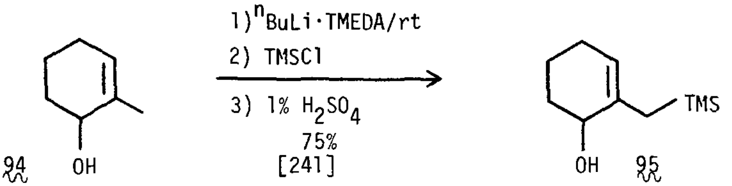
(250)

Crotylmagnesium chloride was reacted with trimethylchlorosilane in order to find best conditions for the preparation of 3-trimethylsilylbutene over the isomeric 1-trimethylsilyl-2-butene. The best conditions are shown below. (Eqn. 251)

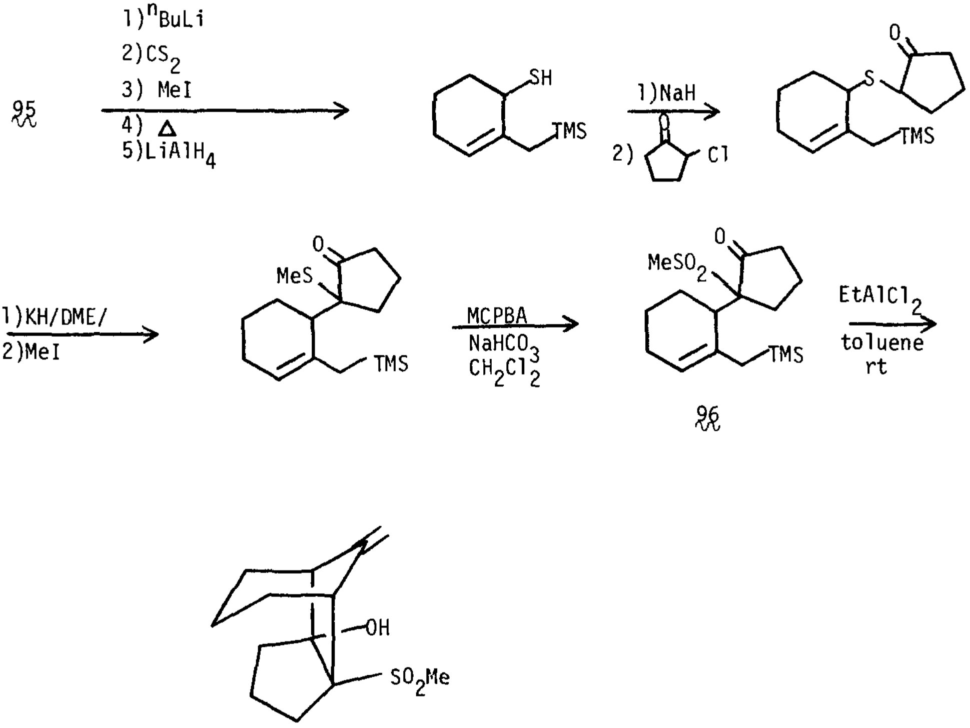


(251)

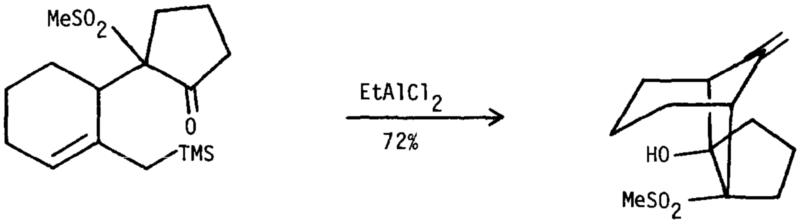
Double deprotonation of cyclohexanol 94 followed by silylation and selective hydrolysis gives the functional alkylsilane, 95. This compound is a useful synthon as shown. (Eqns. 252-254) The other isomer of 96 gives the other bicycloundecyl system. (Eqn. 254)



(252)

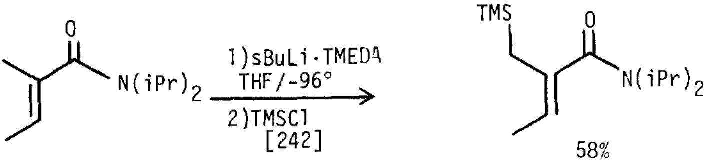


(253)



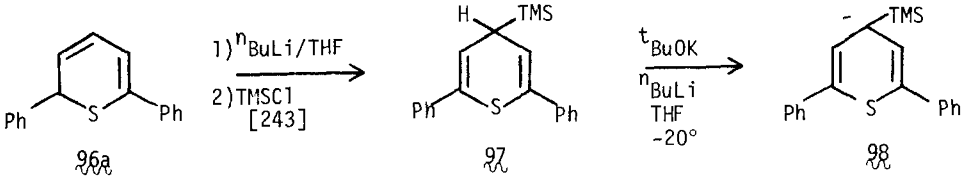
(254)

Metalation-silylation of tertiary unsaturated amides leads to functionalized allylsilanes. (Eqn. 255)

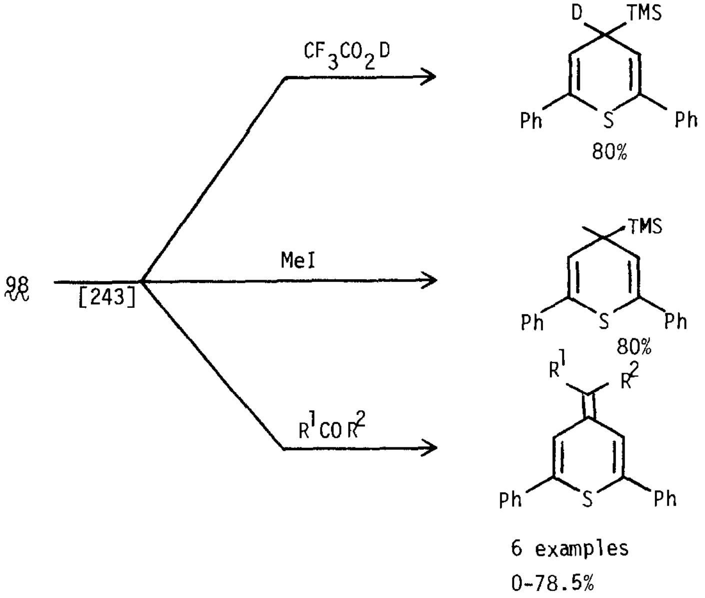


(255)

Metalation-silylation of 96a and 97, which can be metalated and reacted to give several interesting systems. (Eqns. 256-259)



(256)

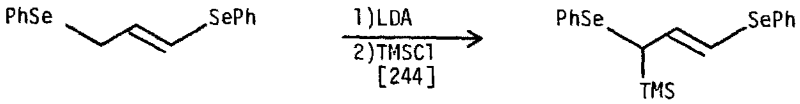


(257)

(258)

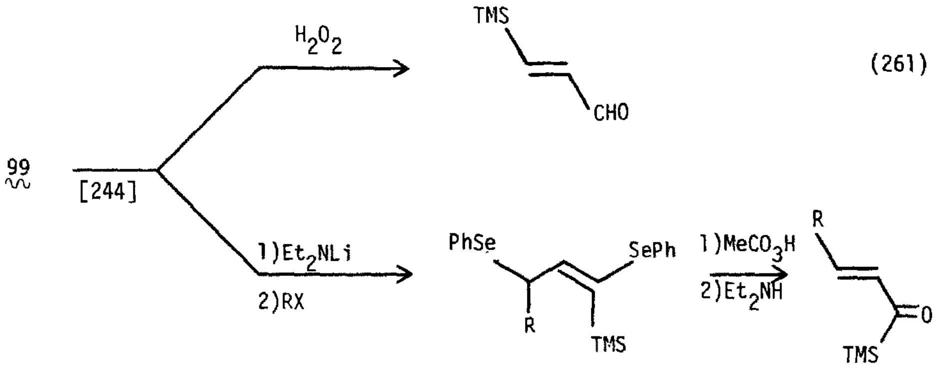
(259)

The metalation-silylation of 1,3-bis(phenylseleno)propene gives the allylsilane 99, which is the precursor to aldehydes and acylsilanes. (Eqns. 260-262)



99

(260)

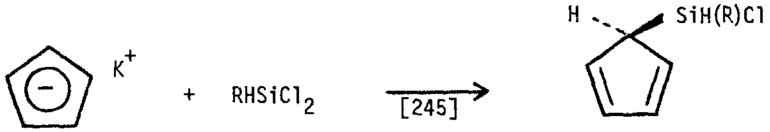


(261)

(262)

RX= iPrBr (75%); ^{s}BuBr (68%); ^{i}BuBr (65%)

The asymmetric cyclopentadienylsilanes 100 were prepared from potassium cyclopentadienide. (Eqn. 263).



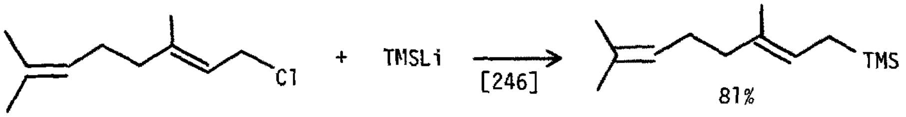
100

R= Me, nBu, $TMSCH_2$

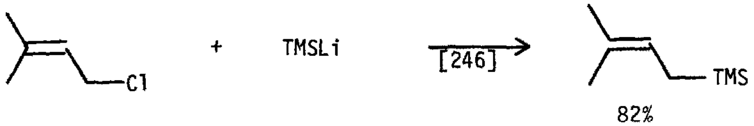
(263)

B. Preparation from Silyl Anions

The reaction of trimethylsilyllithium and allylic halides gives allylsilanes. (Eqns. 264-265)



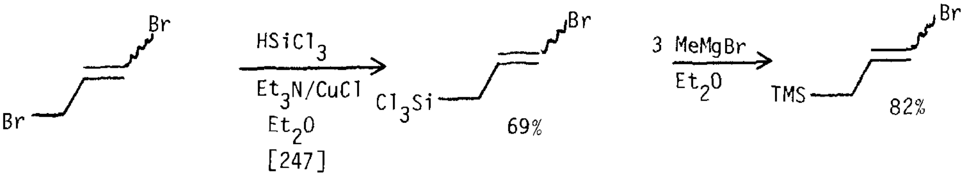
(264)



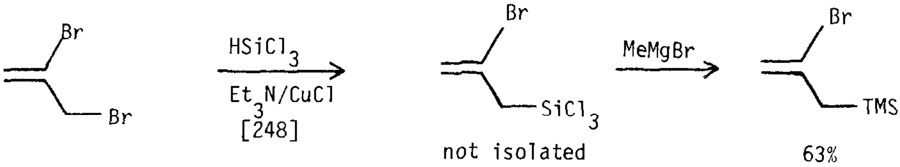
82%

(265)

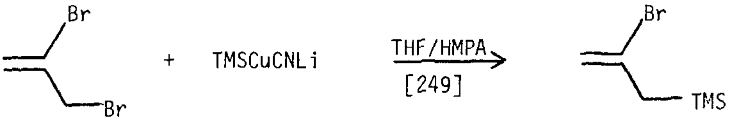
The Benkeser generation of trichlorosilyl anion carried out in the presence of allylbromides gave the corresponding allylsilanes. (Eqns. 266-267) Trimethylsilylcyanocuprate reacts with 2,3-dibromopropene to give the allylsilane. (Eqn. 268)



(266)



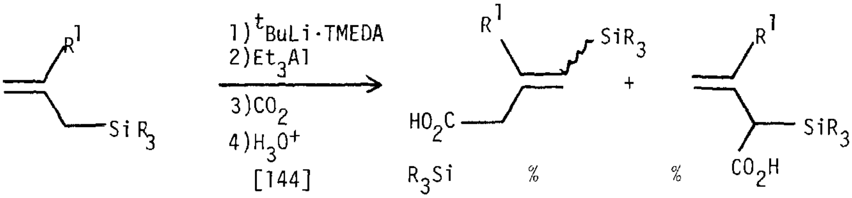
(267)



(268)

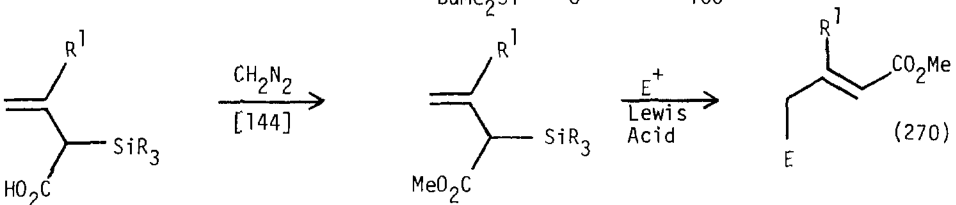
C. Preparation from Silylated Organometallics

Allylsilanes were deprotonated, converted to the aluminum complex and carboxylated to give mixtures of the vinylsilane and the allylsilane with the allylsilane predominating. (Eqn. 269) These new allylsilanes were useful synthetic units. (Eqn. 270)



(269)

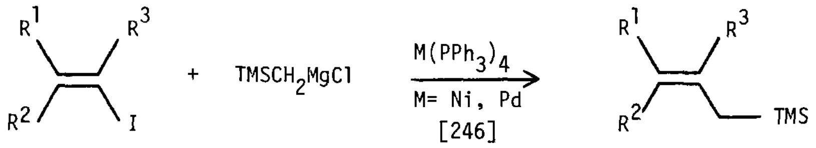
R_3Si	%	%
Ph_3Si	30	70
Me_3Si	35	75
$PhMe_2Si$	0	100
$TolMe_2Si$	0	100
$^tBuMe_2Si$	0	100



(270)

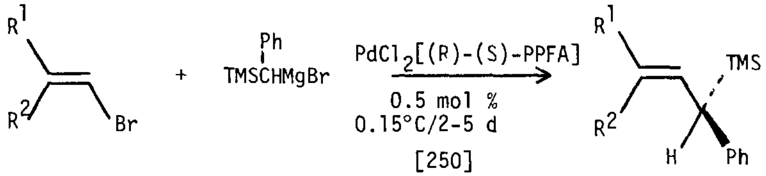
E^+= aldehydes, ketones, ketals, PhSCH(Cl)Me, RCOCl.

Trimethylsilylmethylmagnesium chloride couples with vinyl iodides to give allylsilanes. (Eqn. 271) A similar coupling is seen in Eqn. 272 except that this is carried out in the presence of a chiral phosphine palladium complex and gives an optically active allylsilane.



4 examples
70-85%

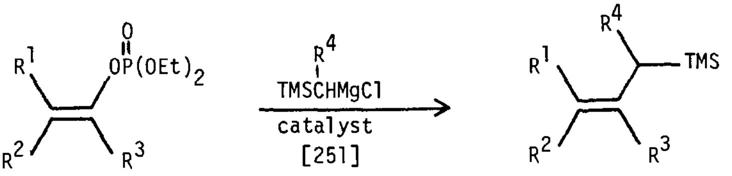
(271)



(272)

R^1	R^2	% e,e	% Yield
H	H	95	42
Me	H	85	77
H	Me	24	38
Ph	H	95	93
H	Ph	13	95

Enol phosphates couple with α-silyl Grignard reagents to give allylsilanes in good yield. (Eqn. 273)

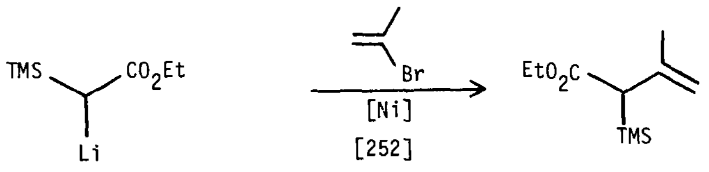


(273)

catalyst= Ni(acac)$_2$; NiBr$_2$; Pd(PPh$_3$)$_4$

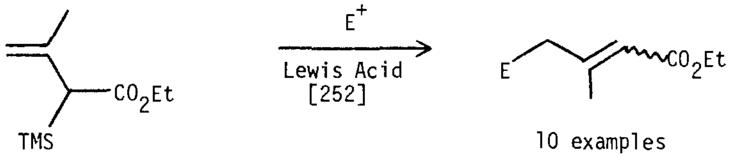
10 examples (47-92%)

Ethyl lithio(trimethylsilyl)acetate was coupled with 2-bromopropene to give the α-silylated-β,γ-unsaturated ester, which was used to direct electrophiles to the γ position. (Eqns. 274-275)



62%

(274)



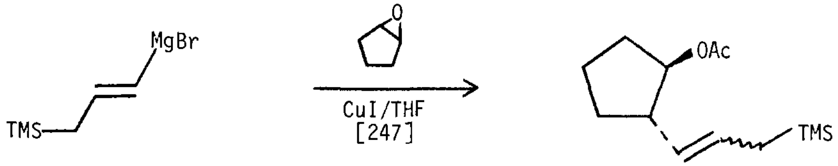
(275)

E^+= aldehydes, ketones, acetals, acid chlorides, PhSCH2Cl

10 examples
(71-100%)

Lewis Acids= $TiCl_4$, TMSOTf

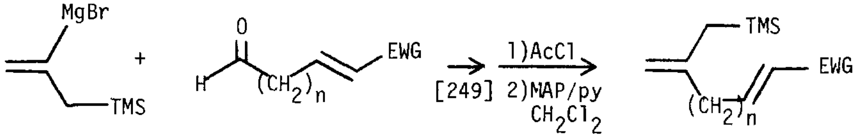
3-Trimethylsilyl-1-propenylmagnesium bromide reacts with epoxides in the presence of Cu(I) to give the corresponding allylsilanes. The alcohol is best isolated as the acetate. (Eqn. 276) The related reagent 3-trimethylsilyl



(276)

6 examples
(57-97%)

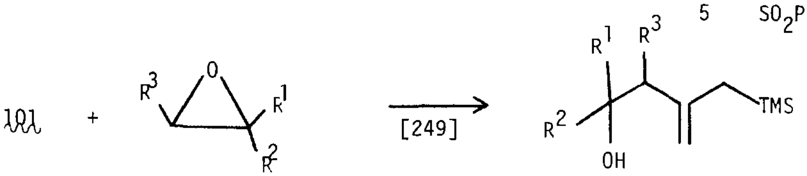
2-propenylmagnesium bromide 101 proved to be a highly useful precursor to a variety of allylsilanes. (Eqns. 277-279)



101

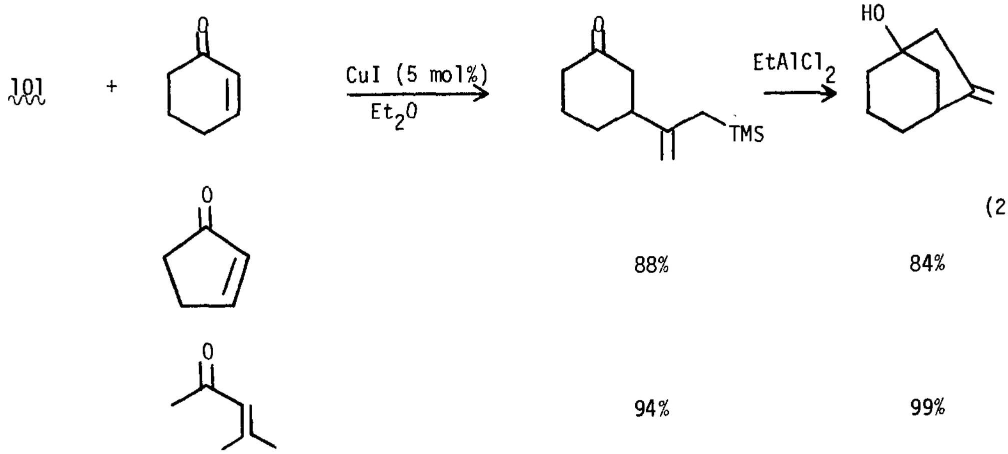
(277)

n	EWG
3	CO_2Et
3	SO_2Ph
4	SO_2Ph
5	SO_2Ph



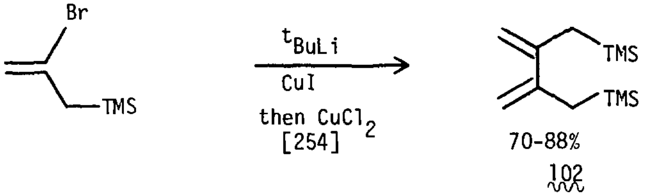
(278)

5 examples
(82-95%)



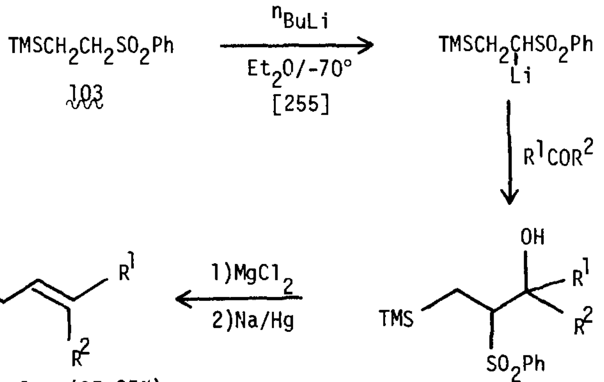
(279)

In a related reaction the diene 102 was prepared. (Eqn. 280)



(280)

β-(Trimethylsilylethyl)phenylsulfone 103 can be deprotonated, reacted with a ketene and the β-hydroxy sulfone converted to a double bond giving the allylsilane. (Eqn. 281)

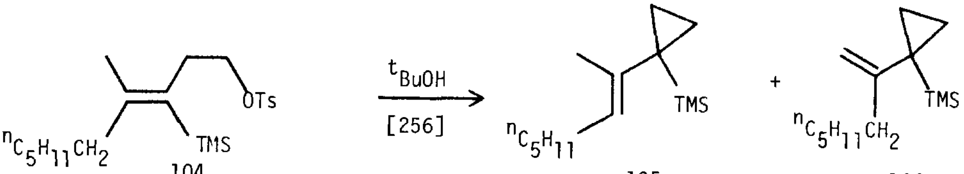


(281)

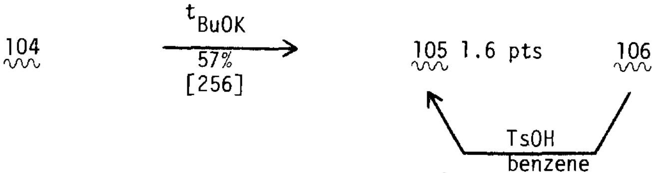
8 examples (85-95%)

D. Miscellaneous Preparations

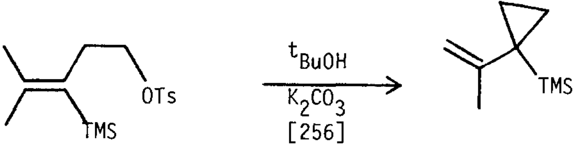
Evidence for the silicon enhanced solvolysis of the tosylate 104 has been presented. The intermediate β-silyl carbenium ion does not desilylate, but loses a proton to give predominantly 105 instead. (Eqn. 282) The base catalyzed solvolysis results in the abstraction of a proton from the less hindered methyl group to give the terminal olefin 106. (Eqn. 283) An additional example is given in Eqn. 284.



104 105 106 (282)



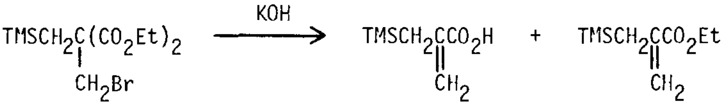
(283)



(284)

A malonic ester approach was used to prepare the allylsilanes 107 as shown in Eqn. 285.

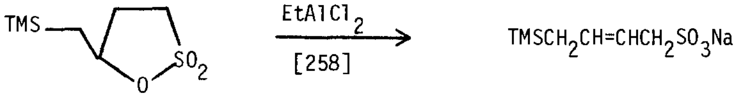
$$\mathrm{CH_2(CO_2Et)_2} \xrightarrow[\text{2)TMSCH}_2\text{Cl* [257]}]{\text{1)Na/EtOH}} \underset{81\%}{\mathrm{TMSCH_2CH(CO_2Et)_2}} \xrightarrow[\text{2)CH}_2\text{Br}_2]{\text{1)NaH/benzene}} \qquad (285)$$



$$\underset{84\%}{\mathrm{TMSCH_2\underset{\substack{|\\ CH_2Br}}{C}(CO_2Et)_2}} \xrightarrow{\text{KOH}} \underset{107\ 82\%}{\mathrm{TMSCH_2\underset{\substack{\|\\ CH_2}}{C}CO_2H}} + \mathrm{TMSCH_2\underset{\substack{\|\\ CH_2}}{C}CO_2Et}$$

84% 107 82%

Treatment of the sulfone, 108 with a Lewis Acid gives the allylsilane 109. (Eqn. 286)



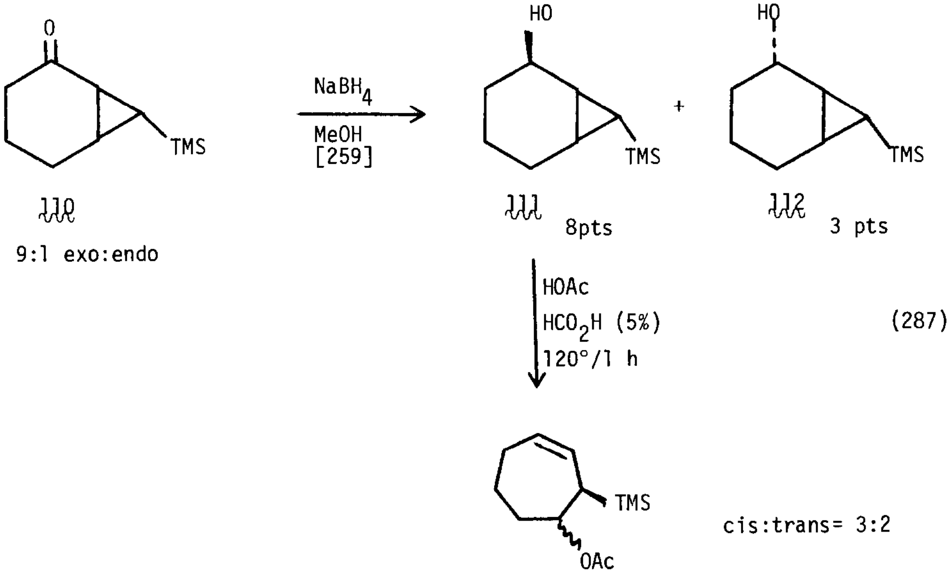
(286)

108 109

---

*(The abstract indicated that TMSCl was used. This must be an error. Since this is in the patent literature it could not be checked).

The cyclopropylsilane **110** was reduced to the mixture of epimeric alcohols **111** and **112**, which can be ring expanded to give allylsilanes. The mixture of β-silyl acetates is due to epimerization of the cyclopropylsilane. (Eqns. 287-288)



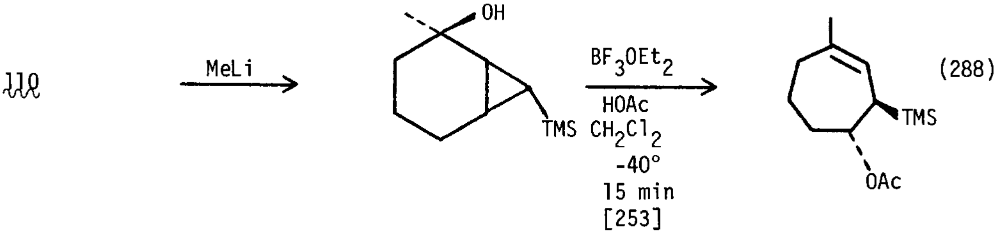
110 9:1 exo:endo

111 8pts

112 3 pts

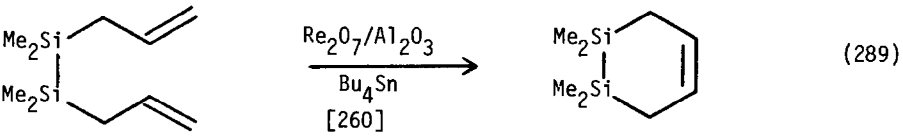
cis:trans= 3:2

(287)



(288)

The cyclization of the allylsilane **113** under metathesis conditions gives ethylene and the cyclic allyl disilane **114**. (Eqn. 289)

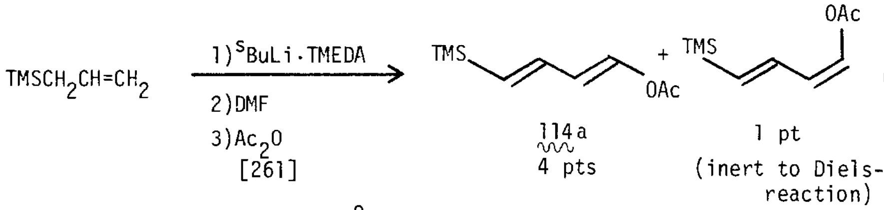


113

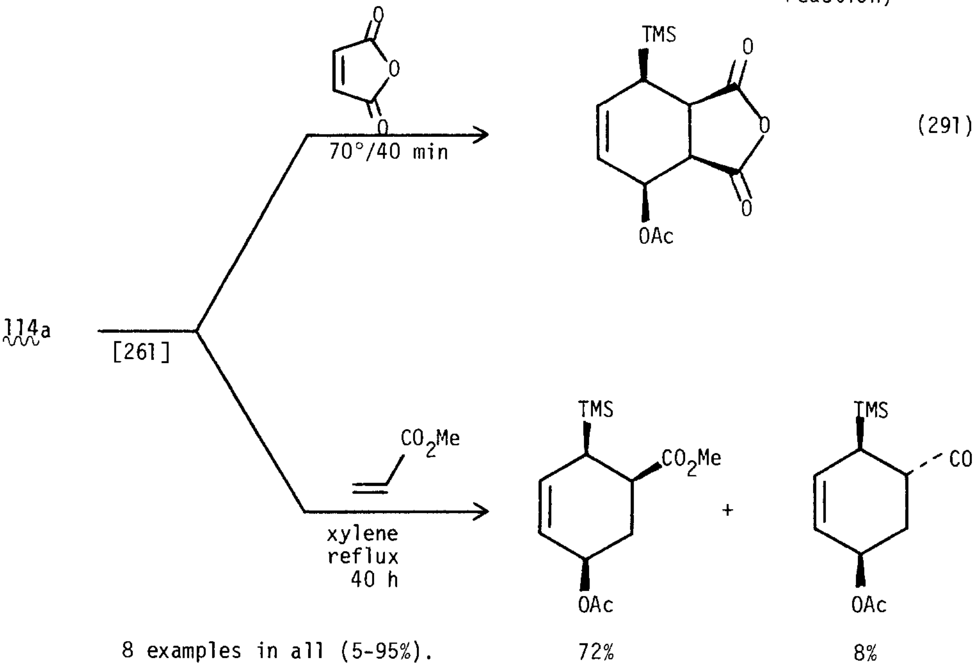
114

(289)

The silylated butadiene **114a** prepared according to Eqn. 290, gives allylsilanes upon Diels-Alder cyclization as shown in Eqns. 291-292.



(290)

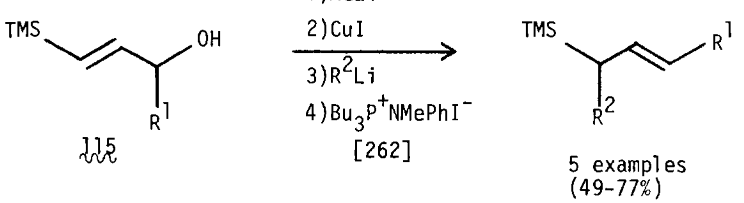


(291)

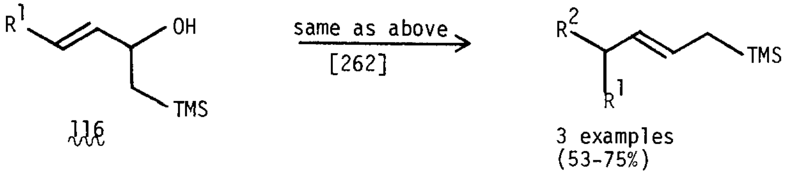
(292)

8 examples in all (5-95%).

γ-Hydroxyvinylsilanes 115 and the β-hydroxysilanes 116 were converted to allylsilanes according to Eqns. 293-294.



(293)



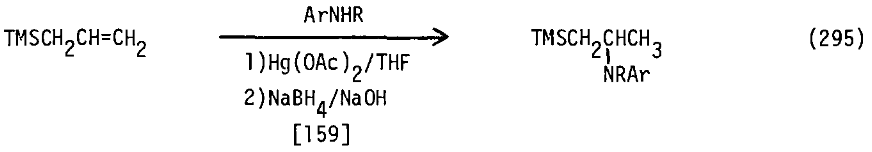
(294)

E. Reactions

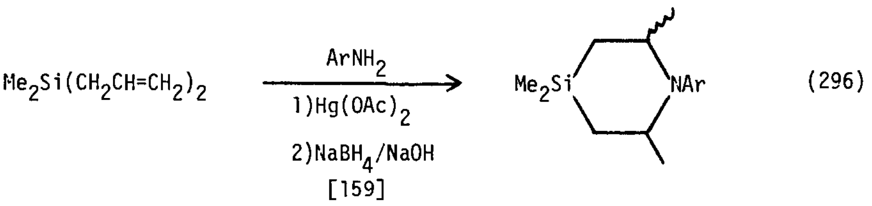
1. Addition Reactions

In this section are found additions to the C=C of allylsilanes with no loss of the silicon group.

The aminomercuration-demercuration of allylsilanes leads to β-aminosilanes in moderate to good yield. (Eqn. 295) It is possible to prepare the heterocycles with primary amines and bisallylsilanes. (Eqn. 296)

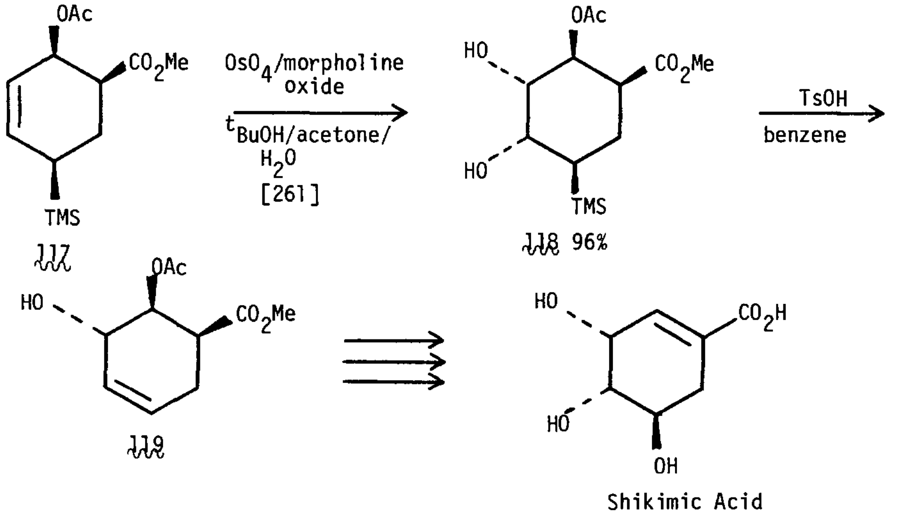


$$\mathrm{TMSCH_2CH{=}CH_2} \xrightarrow[\substack{\text{1)Hg(OAc)}_2\text{/THF} \\ \text{2)NaBH}_4\text{/NaOH} \\ \text{[159]}}]{\text{ArNHR}} \mathrm{TMSCH_2\underset{NRAr}{\underset{|}{C}}HCH_3} \qquad (295)$$



(296)

The allylsilane 117 prepared according to Eqn. 273 was reacted with OsO_4 to give the diol 118 in excellent yield. Dehydroxysilylation with acid gave the allylic alcohol 119, which was converted to Shikimic Acid. (Eqn. 297)



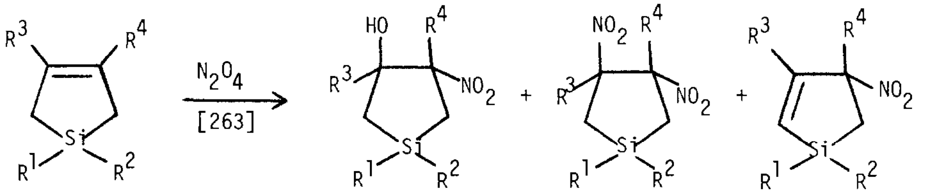
117

118 96%

119

(297)

1-Sila-3-cyclopentene reacts with N_2O_4 to give predominantly the bis nitro or the hydroxy nitro compound and the vinylsilane as shown in Eqn. 298.

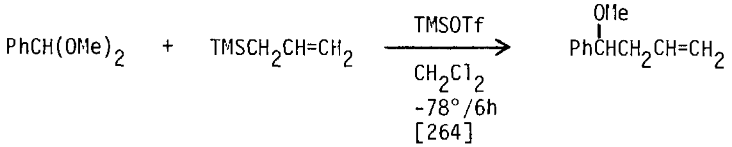


(298)

2. Electrophilic Desilylations

The most important reactions of allylsilanes in terms of synthetic utility are the electrophilic cleavage of allylsilanes with double bond transposition. Several examples of this general reaction appeared.

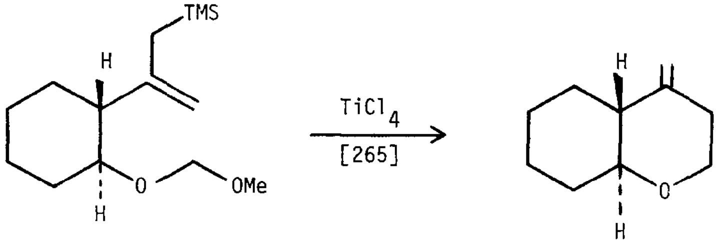
Acetals react with allylsilanes in the presence of Lewis Acids. Examples of this now familiar reaction are given below. (Eqns. 299-301) The reaction is regioselective as seen in Eqns. 300-301 where the methoxy group is lost preferentially.



$$PhCH(OMe)_2 + TMSCH_2CH{=}CH_2 \xrightarrow[\substack{CH_2Cl_2 \\ -78°/6h \\ [264]}]{TMSOTf} Ph\overset{OMe}{\overset{|}{C}}HCH_2CH{=}CH_2 \qquad (299)$$

$$RO\text{-}CH_2OMe + TMSCH_2CH{=}CH_2 \xrightarrow[[265]]{TiCl_4} ROCH_2CH{=}CH_2 + MeOH \qquad (300)$$

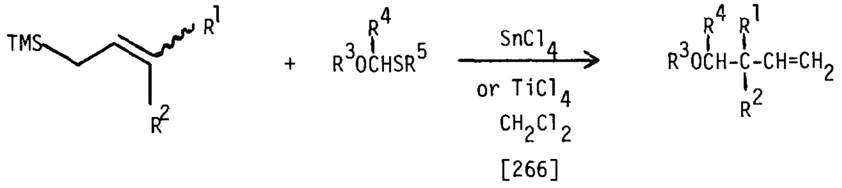
6 examples
86-96%



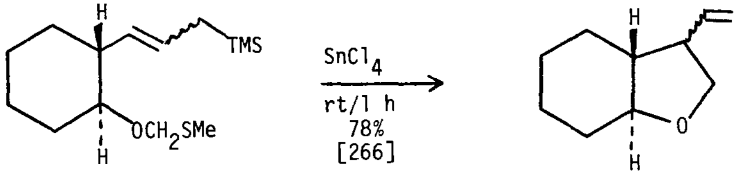
(301)

other examples given

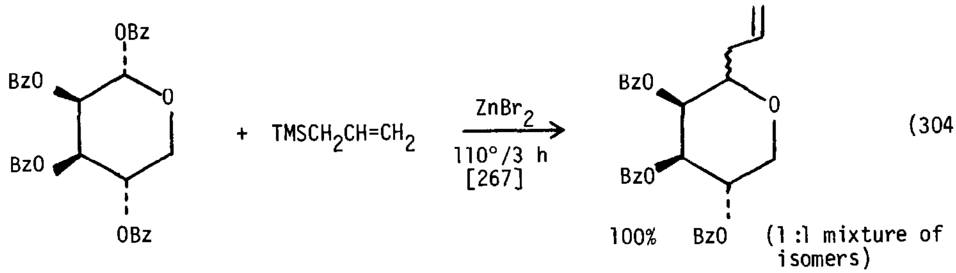
Monothioacetals react in a similar manner to lose the thiol or the alcohol of the molecule depending on the structure of the monothioacetals. (Eqn. 302) Cyclization in this type of reaction is also possible. (Eqn. 303)



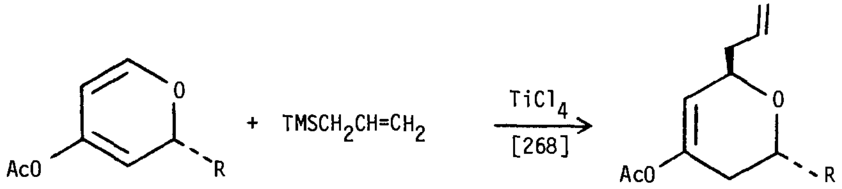
(302)



(303)

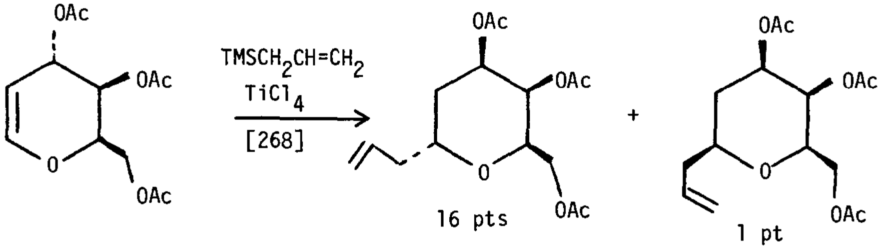


(304)

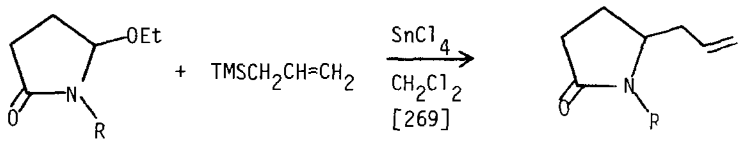


(305)

R= CH_2OBz (99%), Ph (60%), CH_2SPh (95%), $^nC_3H_7$ (82%)

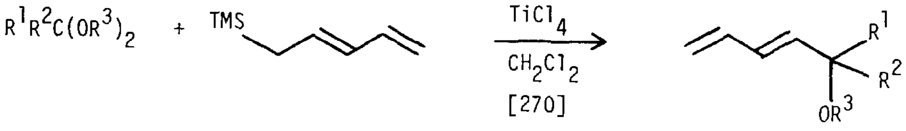


(306)



(307)

R= H 69%
Bz 66%
CH_2CH_2Br 75%

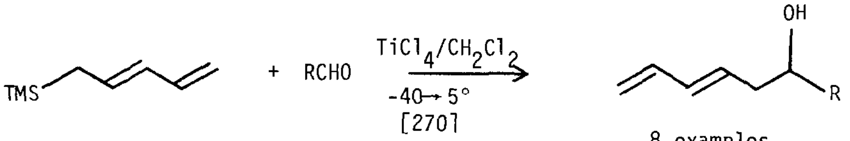


(308)

R^3= Me, Et

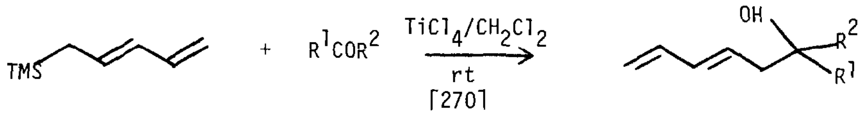
4 examples
(40-79%)

The Lewis Acid catalyzed reaction of allylsilanes with aldehydes and ketones remains popular. 2,4-Dienylsilanes were employed in the dienemethylation of aldehydes and ketones. (Eqns. 309-311) The reaction of these allylsilanes with α,β-unsaturated aldehydes and ketones gives cyclic products. (Eqns. 312-313) This implies that the carbenium ion can be trapped internally before undergoing desilylation.

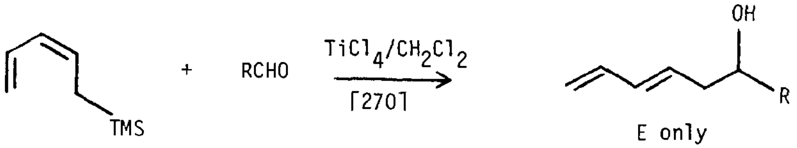


(309)

8 examples
(51-80%)

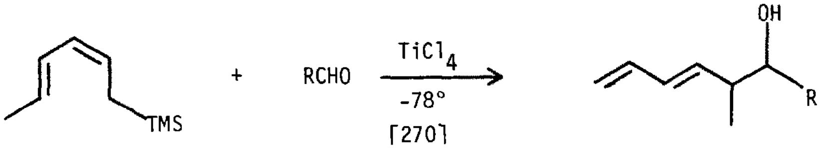


(310)



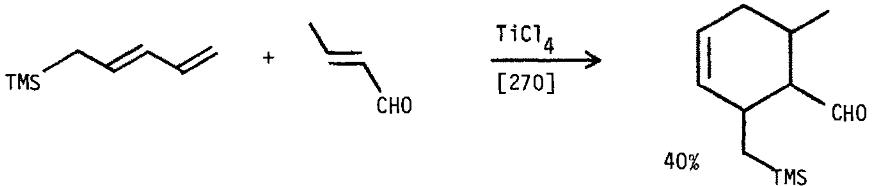
(311)

E only

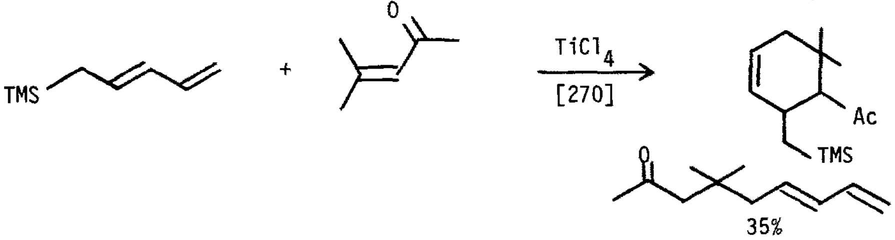


(312)

R	erythro	threo
Me	66	34
Et	74	26
^{i}Pr	84	16

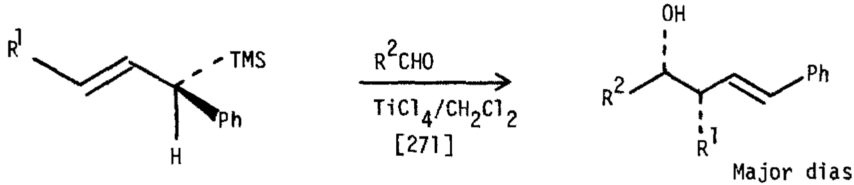


(312)



(313)

The potential of this allylation reaction in the preparation of optically active allyl derivatives has been investigated in some very elegant chemistry. Starting with the optically active allylsilane **120** prepared according to Eqn. 272 allylations were carried out on aldehydes. (Eqns. 314-315) The Z isomers **121** were not so selective. (Eqn. 315) Other electrophilic reactions also give high stereoselectivity. (Eqns. 316-317)



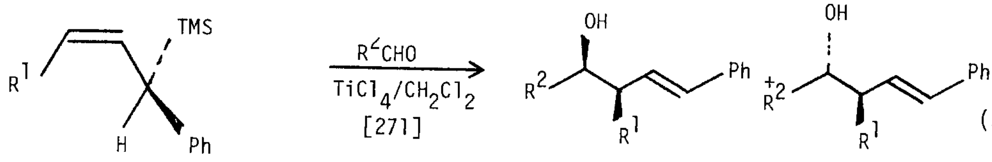
(314)

120

Major diastereomer

R^1	R^2
Me	^{t}Bu, ^{i}Pr, Me
Ph	^{t}Bu

85% e,e in all cases

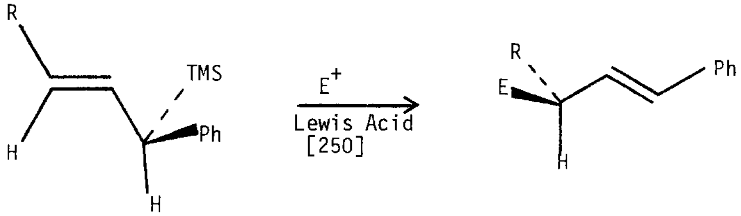


(315)

121
R^1= Me, Ph; R^2= ^{t}Bu

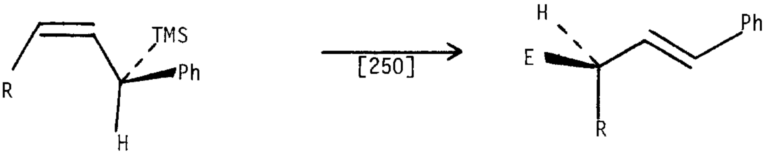
e,e 14-28%

e,e 22-29%



(316)

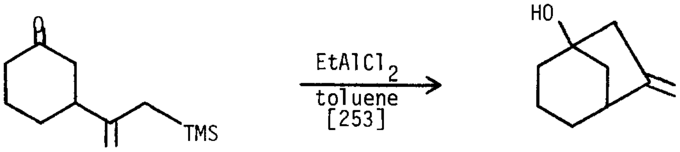
R= Me,	85% e,e	E= ^{t}Bu	87% e,e
R= Ph,	95% e,e	E= ^{t}Bu	93% e,e
R= Me,	85% e,e	E= Ac	53% e,e
R= Me,	85% e,e	E= CH_2OH	86% e,e



(317)

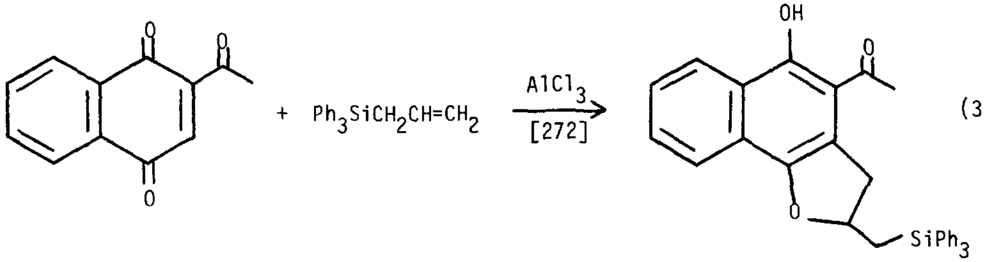
R= Me	24% e,e	E= ^{t}Bu	27% e,e
R= Ph	13% e,e	E= Ac	19% e,e
		E= ^{t}Bu	15% e,e

One example of an intramolecular allylation of a ketone was reported. (Eqn. 318)



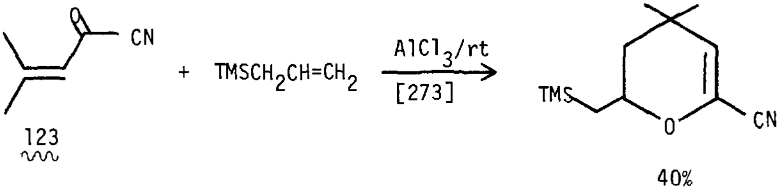
(318)

The allylation of the naphthoquinone, 122, takes an unusual course where the carbenium ion is trapped before desilylation as shown. (Eqn. 319)



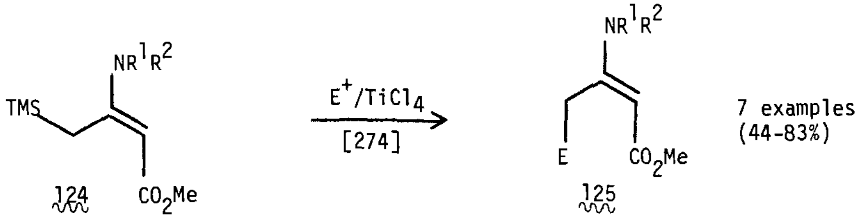
(319)

Allylation of the α,β-unsaturated acyl nitrile 123 takes a similar course. (Eqn. 320)

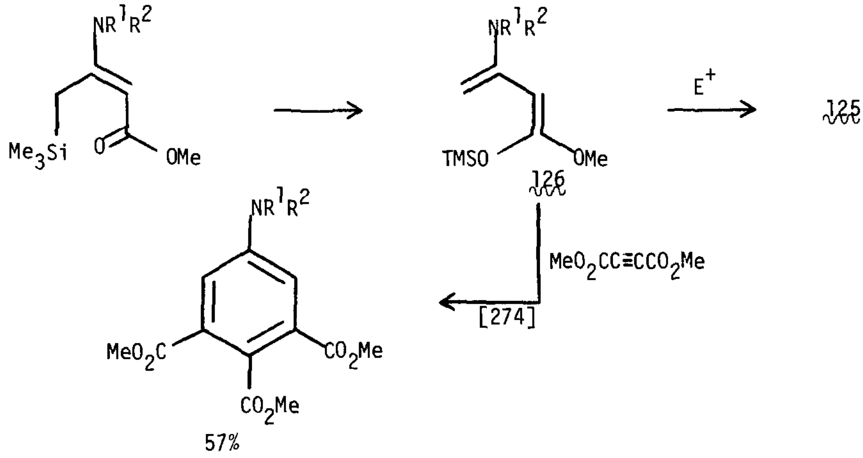


(320)

The enaminyl allylsilanes 124 reacts with electrophiles to give the unexpected γ regioisomers 125. (Eqn. 321) This is explained by a 1,5-silyl migration to give the silyl ketene acetal 126 which is in fact the reactive species. This was shown by the Diels-Alder reaction given in Eqn. 323.



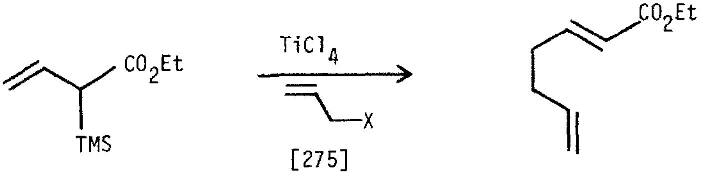
(321)



(322)

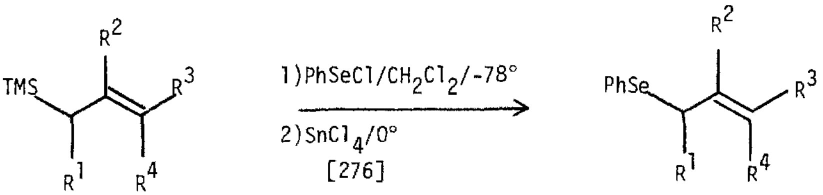
(323)

γ-Allylation of esters from ethyl 2-trimethylsilyl-3-butenoate is possible. (Eqn. 324)



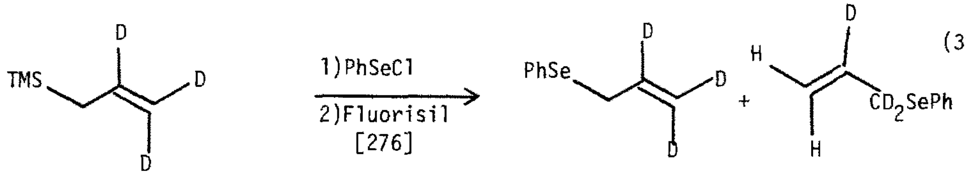
(324)

Selenium compounds represented the electrophile in three studies. These are given below. (Eqns. 325-328) The regioselectivity of the reaction is not high. (Eqn. 326) The selenyl oxide rearranges to give the allyl alcohol with no net double bond transformation. (Eqn. 328)

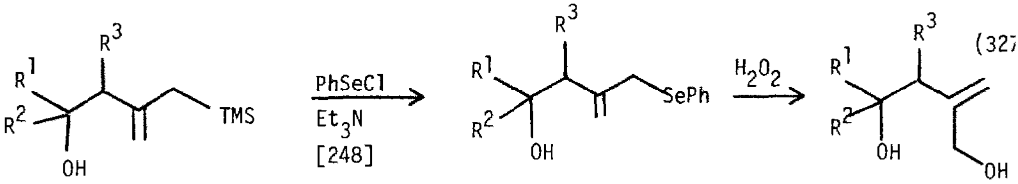


(325)

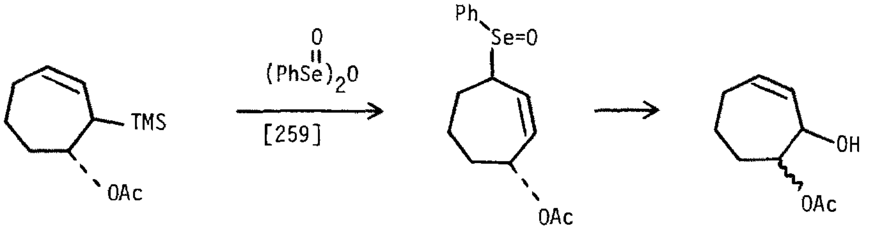
9 examples (65-97%)



(326)

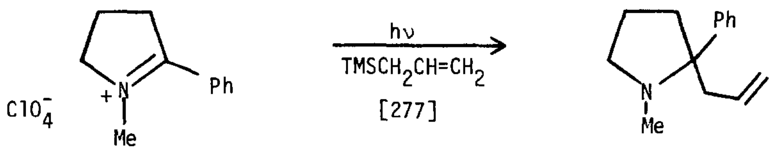


(327



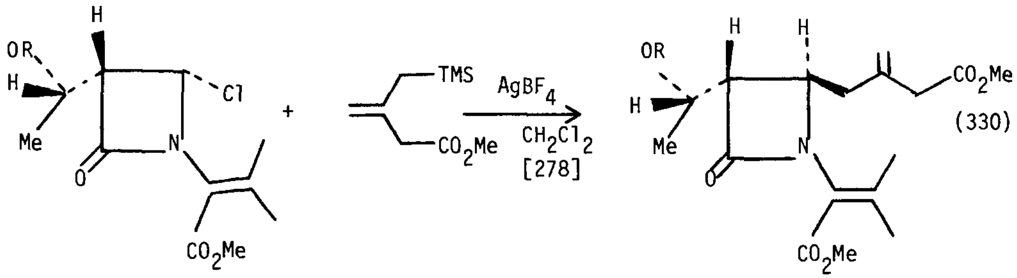
(32

Other allylation reactions involving allylsilanes include the allylation of pyrollinium ions, (Eqn. 329), β-chloro-β-lactams (Eqn. 330), the cobalt complexes **127** (Eqns. 331-332), benzhydrol and related alcohols (Eqn. 333) and aromatics (Eqns. 334-336).

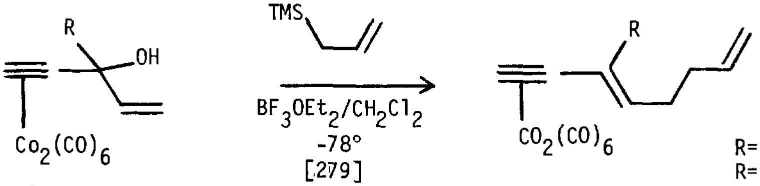


(329)

(2 other examples 47 & 85%)



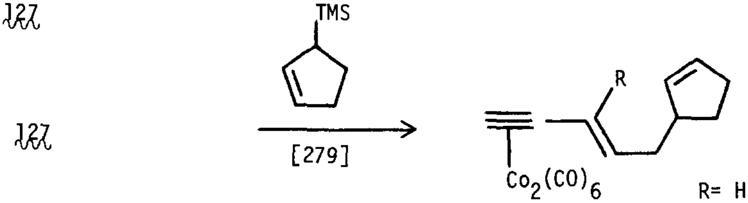
(330)



127

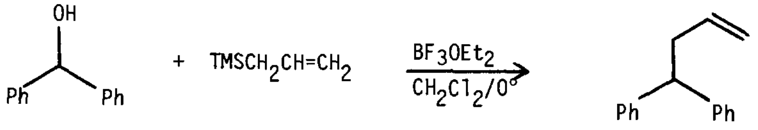
(331)

R= H 81%
R= Me 76%



(332)

R= H 80%



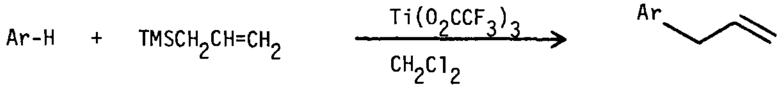
(333)

100%

8 other examples

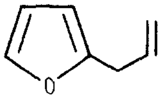
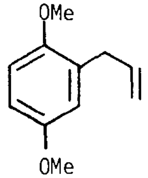
cyclohexanol and t-butanol gave N.R.

(22-100%)

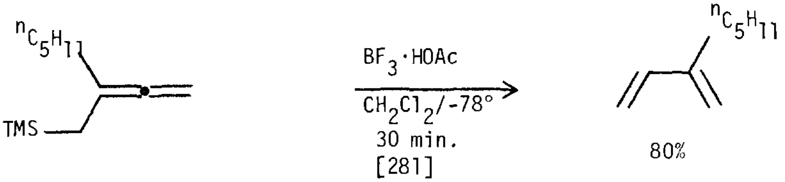


(334)

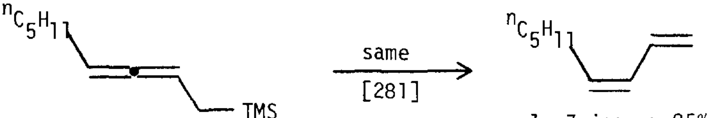
6 examples
19-89%

For example  (83%)  (83%)

Protodesilylation of allylsilanes results in double bond transposition. Some examples are given in Eqns. 335-339.

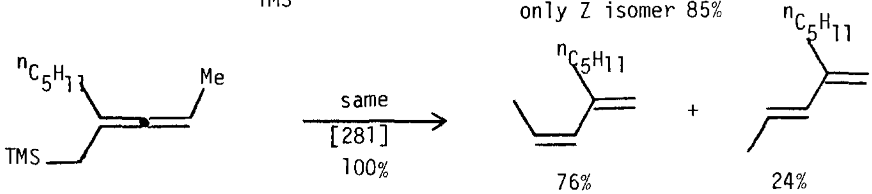


(335)

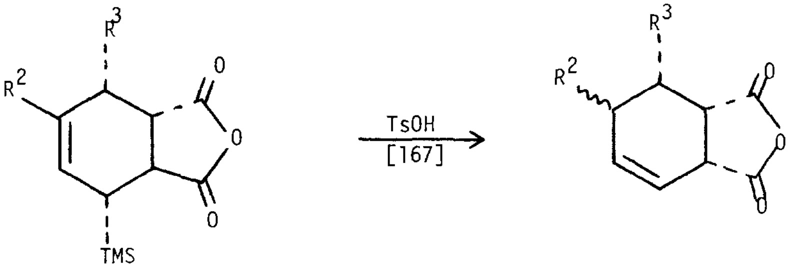


only Z isomer 85%

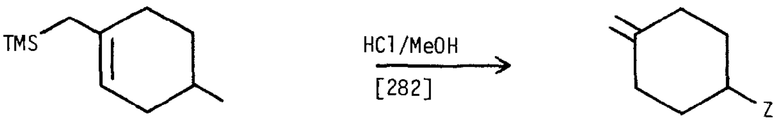
(336)



(337)



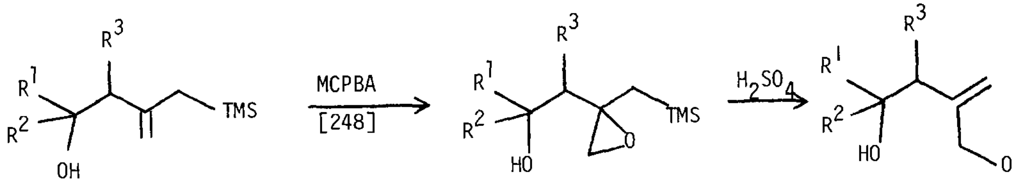
(338)



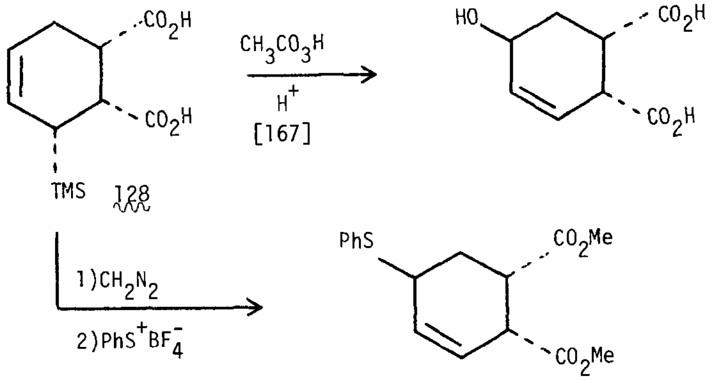
(339)

Z= CO_2Me, CO_2Et, CHO, COMe, etc.

Epoxidation-protonation results in the overall electrophilic hydroxylation with double bond transposition. (Eqns. 340-341) The allylsilane 128 (as the methyl ester) also underwent phenylsulfenylation. (Eqn. 342)



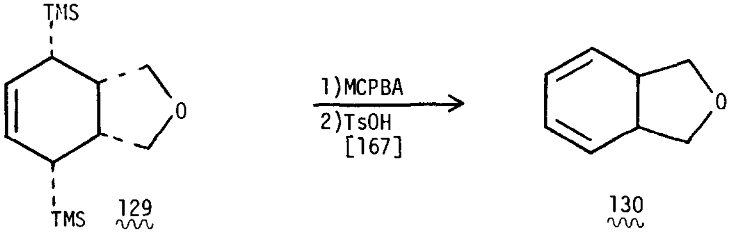
(340)



(341)

(342)

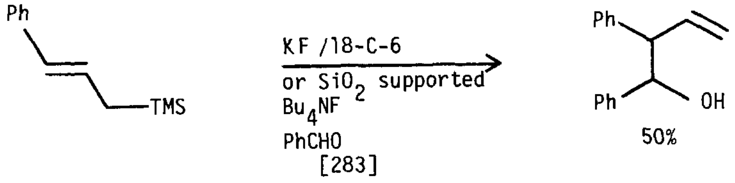
Peracid oxidation of 129 followed by acid treatment results in formation of the cyclohexadiene 130. (Eqn. 343)



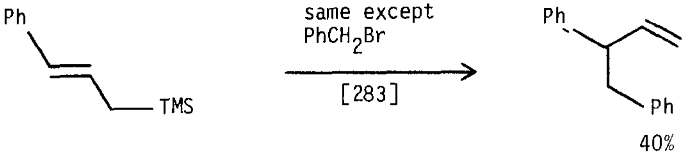
(343)

3. Other Reactions

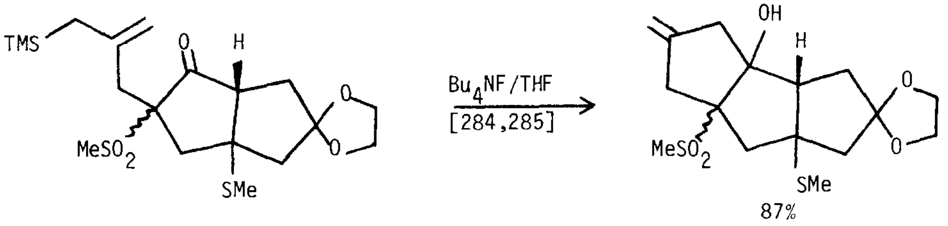
The reaction of fluoride ion with allylsilanes in the presence of electrophiles gives allylation of the electrophile.Three examples are given one of which involves a cyclization. (Eqns. 344-346)



(344)



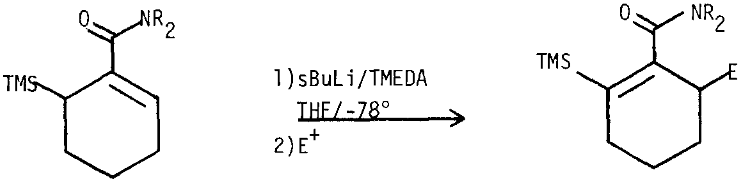
(345)



(346)

see also ref. 278

Metalation of the unsaturated, silylated amides 131 gave a series of functional vinylsilanes 132. (Eqn. 347)



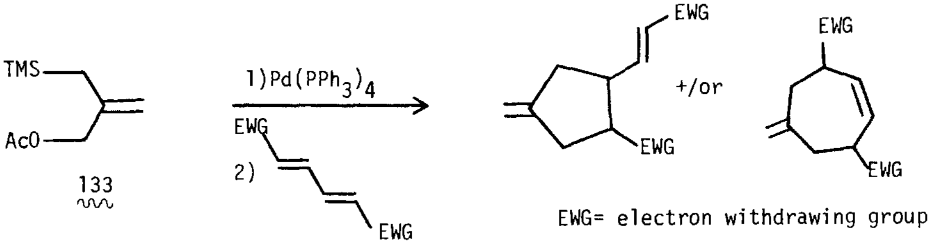
(347)

131 132

E^+= EtI, $PhCH_2Cl$, Me_2CO, Ph_2CO, $PhCONMe_2$, PhCHO

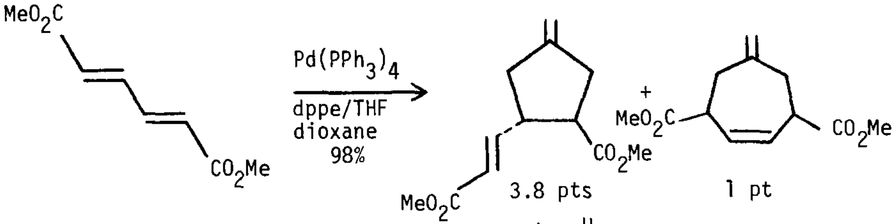
60-90% yield

Allylsilane 133 proved to be an excellent precursor to trimethylenemethane palladium complexes, which are useful in cycloadditions. (Eqns. 348-349) The reaction is also possible in an intramolecular sense. (Eqn. 350)

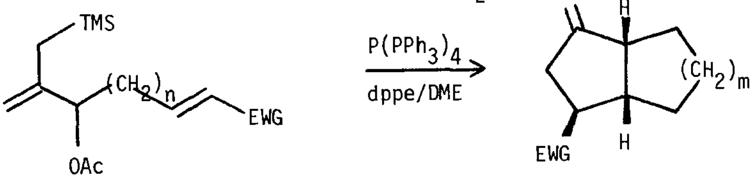


(348)

EWG= electron withdrawing group



(349)



(350)

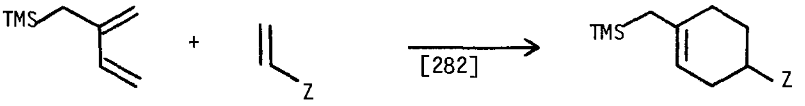
n= 3 EWG= CO_2Et

n= 3,4,5 EWG= SO_2Ph

30% m= 1 EWG= CO_2Et, SO_2Ph

70% m= 2 EWG= SO_2Ph

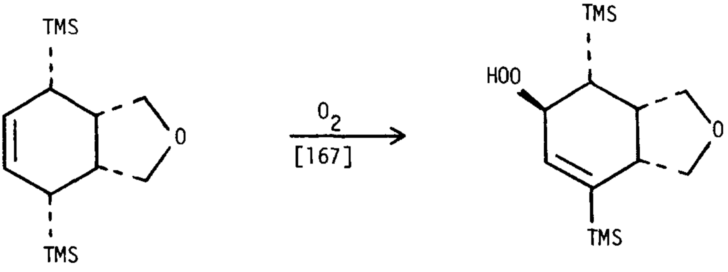
2-Trimethylsilylmethyl-1,3-butadiene undergoes catalyzed Diels-Alder reactions to give the cyclic allylsilanes. (Eqn. 351)



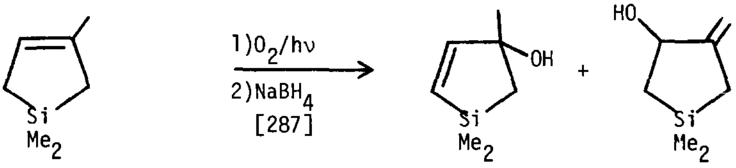
(351)

(see also Eqn. 339)

Photooxygenation of allylsilanes gives ene reactions without loss of the silyl group. (Eqn. 352-353)

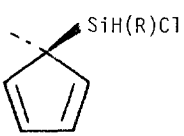


(352)

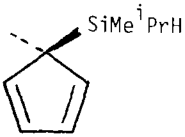


(353)

The stereochemically nonrigid silylcyclopentadienes 134 and 135, were found to undergo 1,2 migrations as the lowest energy pathway. [245]



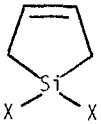
134



135

F. Spectroscopic and Theoretical Studies

The photoelectron spectra of the silacyclopentenes 136 show an increase in the ionization potential in the order of electron acceptor ability of the silyl group. [185]



136

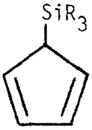
= Et, Me, TMSO, EtO, MeO, Cl

1.88 eV 9.67 eV

The high field NMR spectra of 137 have been studied. [288] The three isomeric forms of 138 and 139 have been studied by MNDO approximation calculations. [289]

$(H_2C{=}CHCH_2Me_2Si)_2Hg$

137



R= H, Me

138

$\eta^5C_5H_5SiR_3$

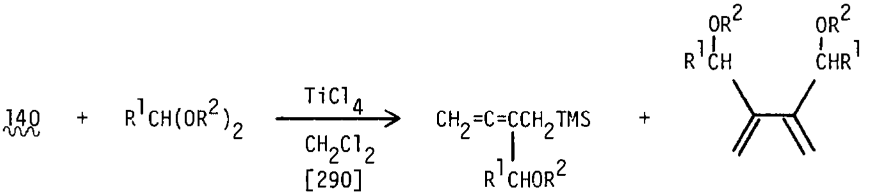
139

IX. PROPARGYLSILANES

The 1,4-bistrimethylsilyl-2-butyne was prepared according to Eqn. 354. It proved to be useful in the preparation of the allenes and 1,3-dienes as shown. (Eqn. 355) A 3:2:1 ratio of acetal:140:$TiCl_4$ gives mostly 141 whereas a ratio of 5:2:2 gives mostly 142.

$$TMSCH_2C\equiv CH \xrightarrow[\substack{2)TMSCH_2I \\ 20\ h/50° \\ [290]}]{1)^nBuLi} TMSCH_2C\equiv CCH_2TMS \qquad (354)$$

140



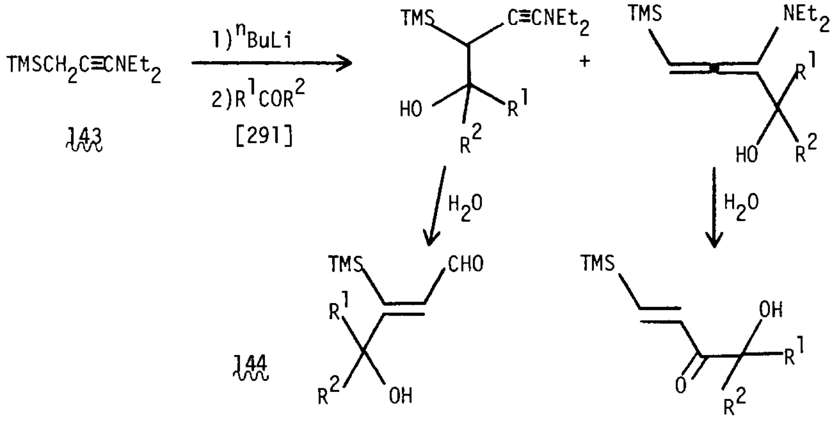
140 + $R^1CH(OR^2)_2$ $\xrightarrow[\text{CH}_2\text{Cl}_2\ [290]]{\text{TiCl}_4}$ 141 + 142 (355)

7 examples

141 25-77%

142 49-95%

Deprotonation of the propargylsilane 143 followed by quenching of the anion with aldehydes or ketones gives mixtures of allenyl and propargyl products. These can be hydrolyzed to the functionalized vinylsilanes. (Eqn. 356)



143

144

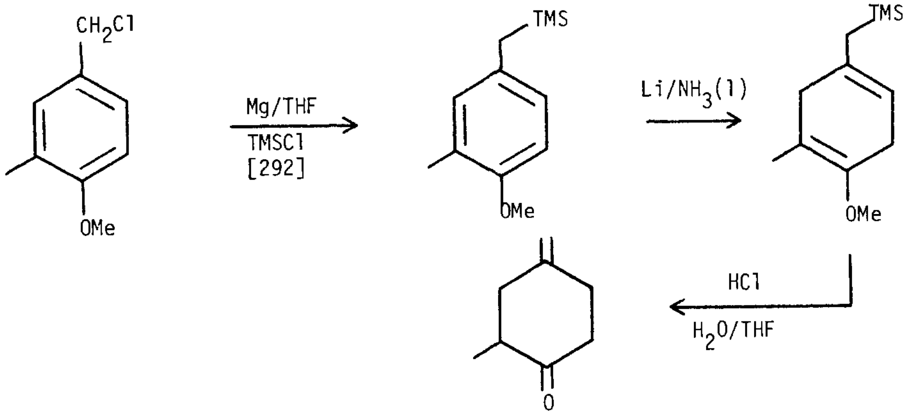
145

(356)

R^1	R^2	% 144	%145	% Yield
Ph	H	74	26	77
Ph	Me	76	24	85
Ph	Et	75	25	81
Me	Me	72	28	75

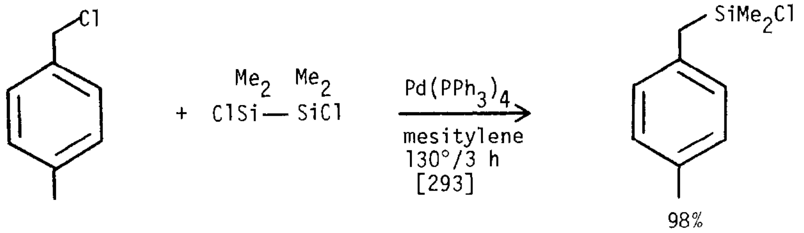
X. BENZYLSILANES

Benzylsilanes were prepared by the Mg/THF/TMSCl method. (Eqn. 357) These were reduced with $Li/NH_3(l)$ and the resulting allylsilanes protodesilylated.



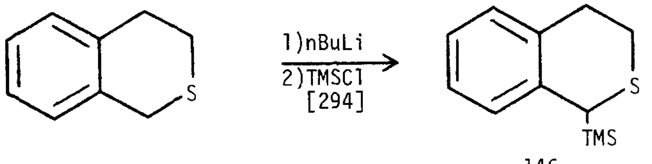
(357)

Benzyl chlorides were coupled with disilanes to give benzylsilanes. (Eqn. 358).



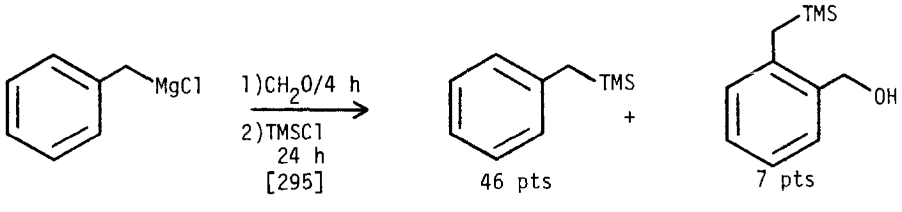
(358)

Isothiochromanyl lithium was silylated to give the benzylsilane 146. (Eqn. 359) Trimethylchlorosilane trapping of the initial product of benzylmagnesium chloride with monomeric formaldehyde to give the benzylsilanes shown. (Eqn. 360)



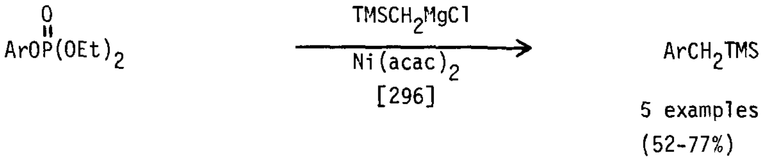
146

(359)



+ other nonsilylated products

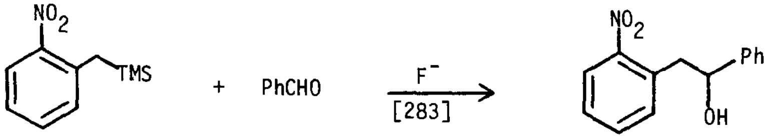
Arylphosphates can be coupled to trimethylsilylmethylmagnesium chloride to give benzylsilanes. (Eqn. 361)



$$ArO\overset{O}{\overset{\|}{P}}(OEt)_2 \xrightarrow[Ni(acac)_2\ [296]]{TMSCH_2MgCl} ArCH_2TMS \quad (361)$$

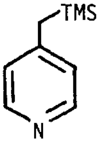
5 examples
(52-77%)

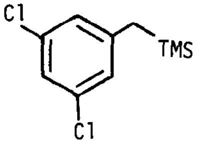
Benzylsilanes can be reacted with fluoride ion in the presence of electrophiles to give the products of reaction of benzyl anion with the electrophile. (Eqn. 362)



(362)

Also used benzyl bromide and propylene oxide as electrophiles

and 

and 

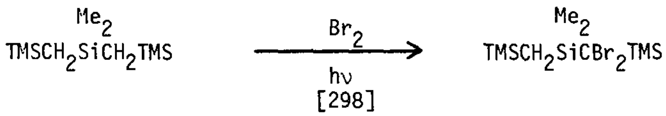
as benzylsilanes

The charge-transfer frequencies of some TCNE-benzylsilane complexes were measured. The photoelectron spectra and ^{13}C-NMR spectra of the benzylsilanes were also recorded. [297]

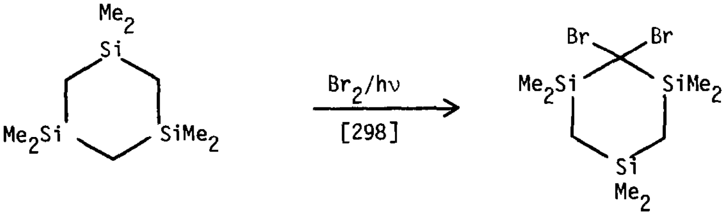
XI. α-FUNCTIONAL ORGANOSILANES

A. Preparation

Direct bromination of α-silylmethylenes leads to α,α-dibromosilanes as shown in the examples below. (Eqns. 363-364) As expected the second bromine reacts preferentially at the already brominated carbon.



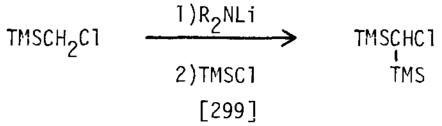
$$TMSCH_2\overset{Me_2}{Si}CH_2TMS \xrightarrow[h\nu\ [298]]{Br_2} TMSCH_2\overset{Me_2}{Si}CBr_2TMS \quad (363)$$



(364)

Also reacted $(BrMe_2Si)_2CH_2$ and $(Me_2SiCH_2)_4$

Silylation of trimethylsilylchloromethyllithium gives the bissilylated chloromethane. (Eqn. 365) A more practical route to this same compound begins with dichloromethane. (Eqn. 366)

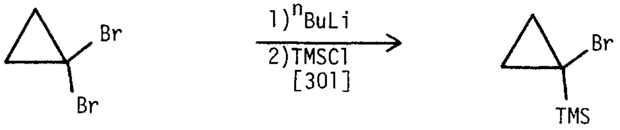


$$\mathrm{TMSCH_2Cl} \xrightarrow[\text{2)TMSCl [299]}]{\text{1)}R_2\text{NLi}} \underset{\mathrm{TMS}}{\mathrm{TMSCHCl}} \qquad (365)$$

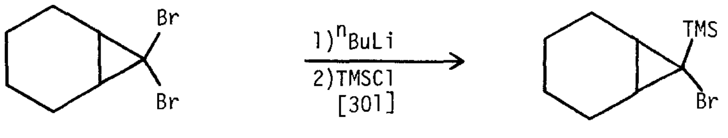
(Yields increased in the order R= Et$<$iPr$<$$C_6H_{11}$)

$$\mathrm{CH_2Cl_2} + 2\ \mathrm{TMSCl} + 2\ {}^{n}\mathrm{BuLi} \xrightarrow[\text{-100° rt [300]}]{\mathrm{THF/Et_2O/pentane}} \mathrm{(TMS)_2CCl_2} \xrightarrow[\text{2)EtOH}]{\text{1)}{}^{n}\text{BuLi/-100°}} \mathrm{(TMS)_2CHCl} \qquad (366)$$

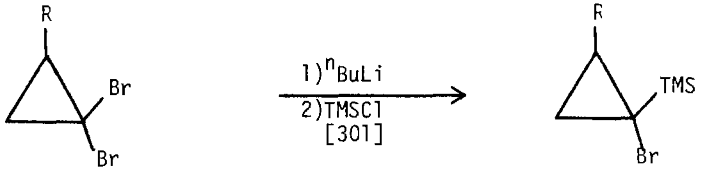
α-Bromocyclopropylsilanes are best prepared from the corresponding dibromocyclopropanes. (Eqns. 367-370). Related reactions are given in Eqns. 371-372.



(367)

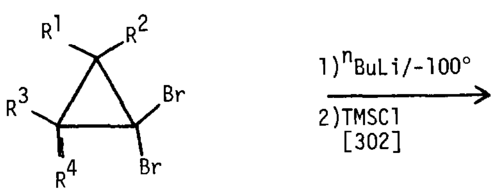


(368)

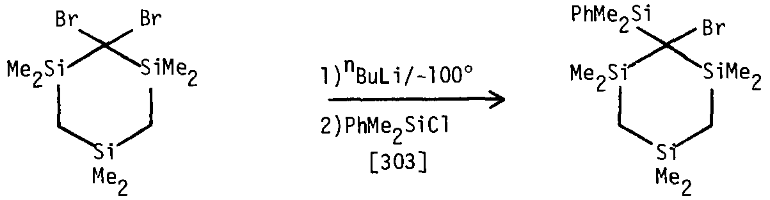


(369)

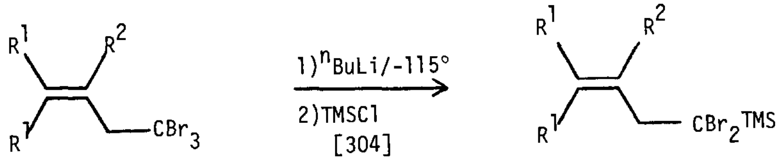
R= Ph 95-97% cis TMS
R= $PhCH_2OCH_2$ 50% cis TMS



(370)



(371)



(372)

$R^1 = R^2 = H$ 69%

$R^1 = Me, R^2 = H$ 76%

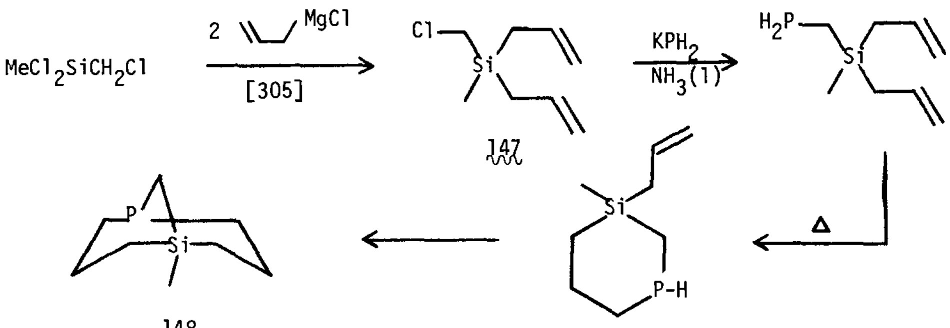
$R^1 = H, R^2 = Me$ 50%

The coupling of disilanes with carbon tetrachloride gives the trichloromethylsilane in good yield. (Eqn. 373)

$$(MeCl_2Si)_2 + CCl_4 \xrightarrow[\text{[81]}]{Ph_3P} Cl_3CSiCl_2Me \qquad (373)$$

62%

The chloromethylsilane 147 was prepared via direct allylation. It was then converted to the phosphinyl derivative cyclization of which gave the phosphasilabicyclo[3.3.1]nonane 148. (Eqn. 374)

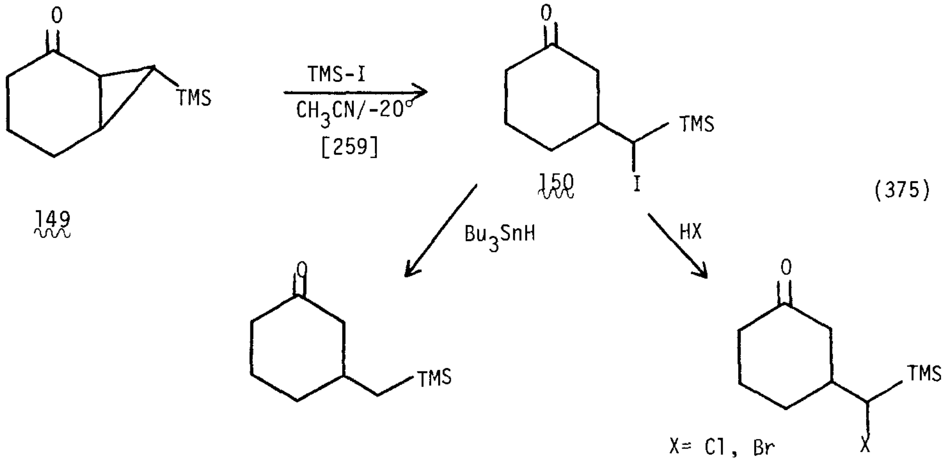


147

148

(374)

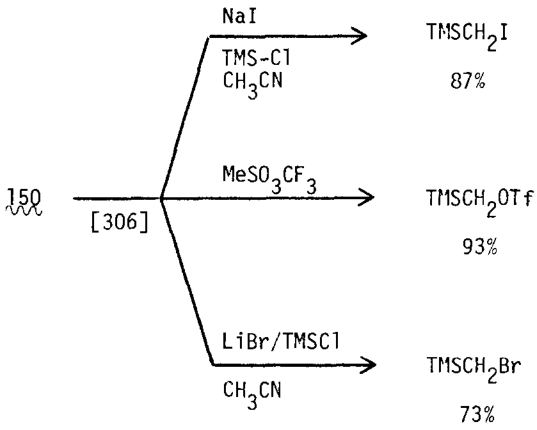
Iodotrimethylsilyl iodide opening of the silylcyclopropane **149** gives the α-iodosilane **150**. (Eqn. 375) The α-iodosilane can be reduced or substituted.



(375)

Chloromethylmethyl ether readily forms methoxymethyllithium, which is silylated to give the methoxymethylsilane. (Eqn. 376) The methoxymethylsilane is an excellent precursor to the iodo, bromo and triflate derivatives. (Eqns. 377-379)

$$\mathrm{MeOCH_2Cl} \xrightarrow[\text{DMM [306]}]{\text{Li}} \mathrm{MeOCH_2Li} \xrightarrow{\text{TMSCl}} \underset{\textbf{150a}}{\mathrm{MeOCH_2TMS}} \qquad (376)$$

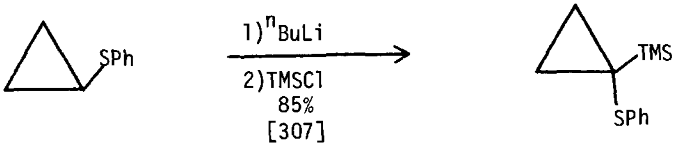


(377)

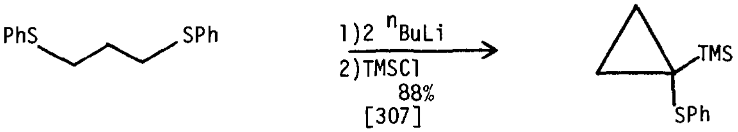
(378)

(379)

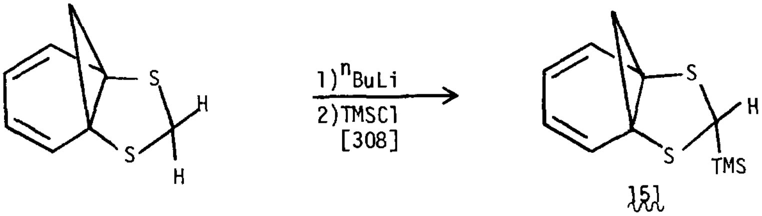
α-Thiophenylcyclopropyltrimethylsilane is prepared from the corresponding lithium reagent prepared as shown in Eqns. 380 and 381. The interesting silylated dithiane 151 was prepared according to Eqn. 382. A similar reaction is shown in Eqn. 383.



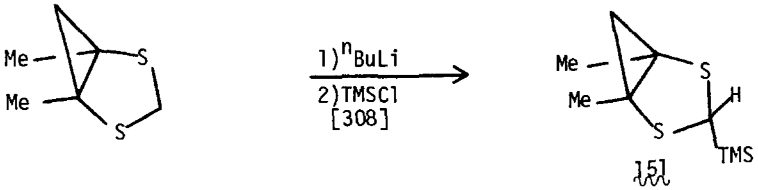
(380)



(381)

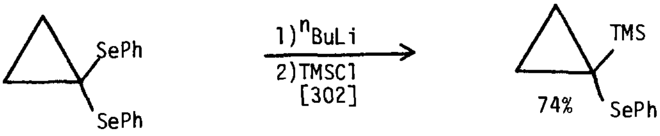


(382)



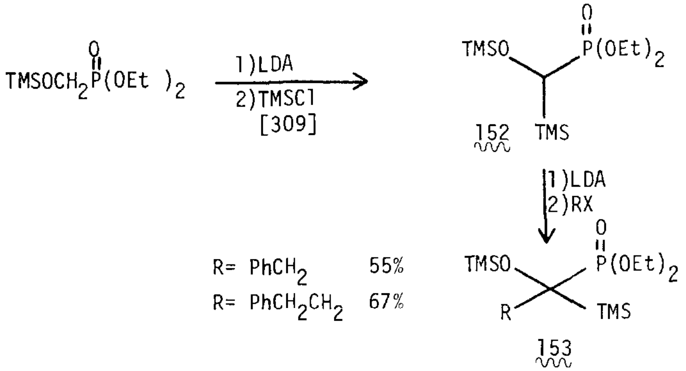
(383)

Metal-metal exchange of your diselenocyclopropanes followed by silylation gives the α-selenephenylsilane. (Eqn. 384)



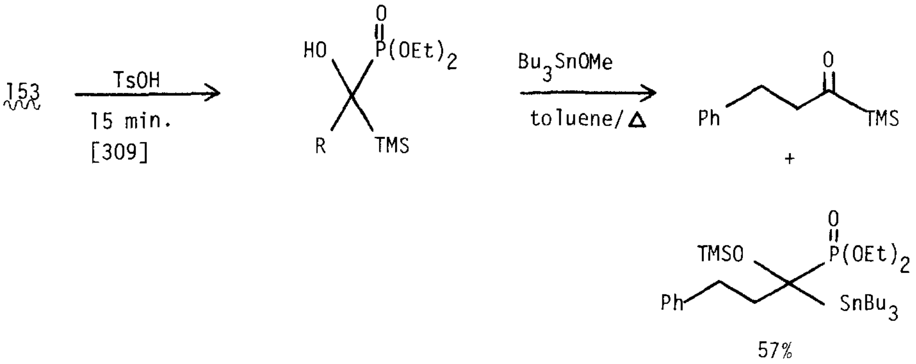
(384)

α-Phosphorylsilanes were prepared. (Eqn. 385) They are entries into α-hydroxy-α-phosphorylsilanes and acylsilanes. (Eqn. 386)



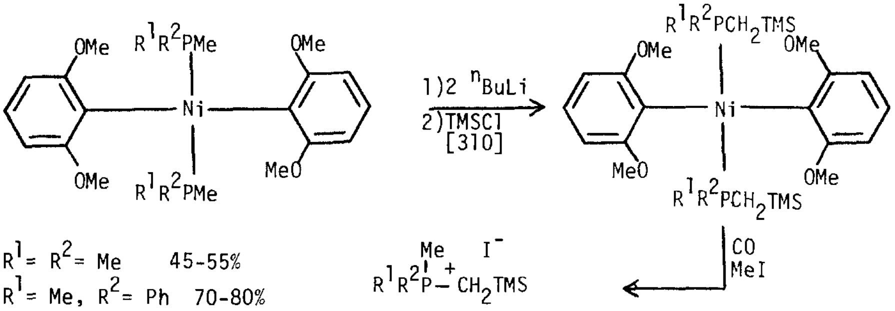
R= $PhCH_2$ 55%
R= $PhCH_2CH_2$ 67%

(385)



(386)

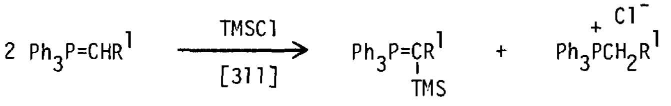
Direct metalation of a methylphosphine ligand bond to nickel is possible. Silylation gives the silylmethylphosphine, which remains bound to the nickel. (Eqn. 387) The ligand can be removed by treatment with CO and MeI.



$R^1 = R^2 = Me$ 45-55%
$R^1 = Me, R^2 = Ph$ 70-80%

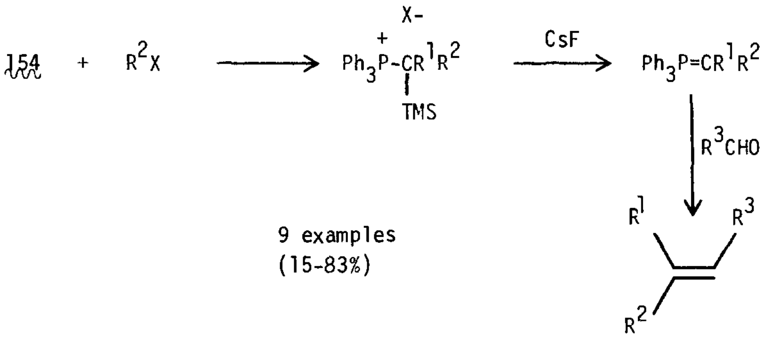
(387)

Trimethylsilylation of Wittig reagents gives the silylated Wittig reagent 154. (Eqn. 388) These can be alkylated and then treated with fluoride to generate the disubstituted ylid, which reacts with aldehydes. (Eqn. 389)



$$2\ Ph_3P{=}CHR^1 \xrightarrow[\text{[311]}]{TMSCl} \underset{TMS}{Ph_3P{=}CR^1} + Ph_3\overset{+}{P}CH_2R^1\ Cl^- \qquad (388)$$

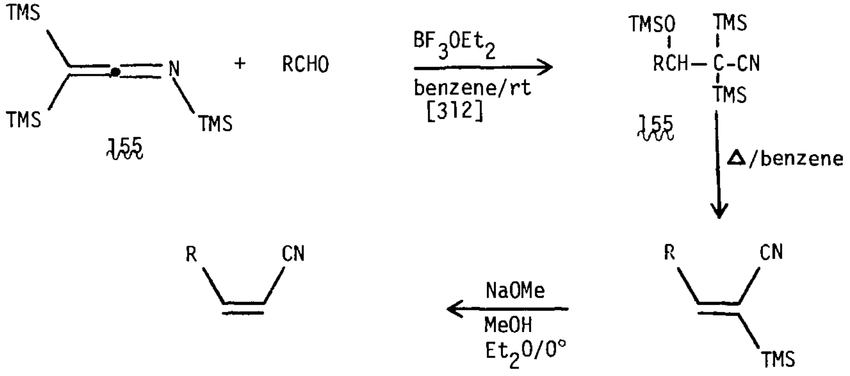
154



(389)

9 examples
(15-83%)

The α-cyanosilanes 155 were prepared in an interesting condensation reaction. These lead thermally to α-cyanovinylsilanes and via protodesilylation to Z-vinylnitriles. (Eqn. 390)

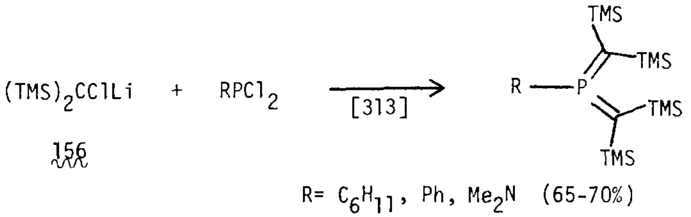


(390)

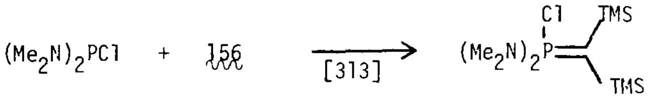
B. Reactions

1. Reactions of α-Silyl Organometallic Reagents

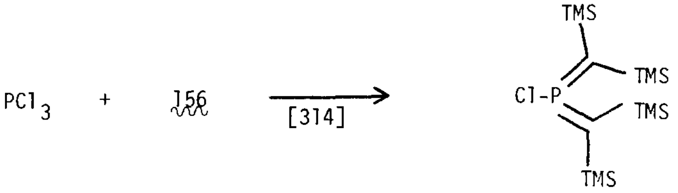
Bis(trimethylsilyl)chloromethyllithium reacts with chlorophosphines to give methylidene phosphoranes. (Eqns. 391-393)



(391)

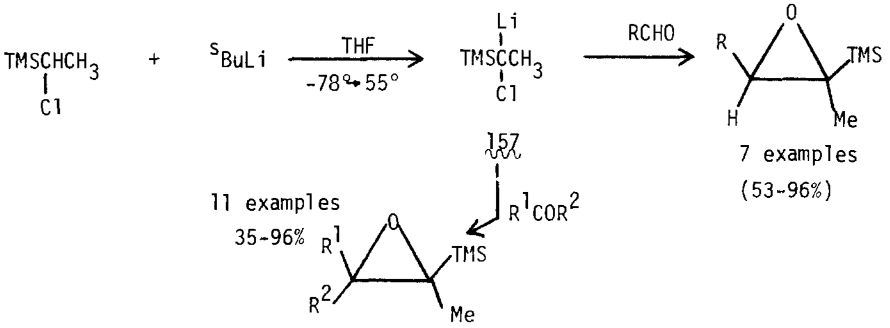


(392)



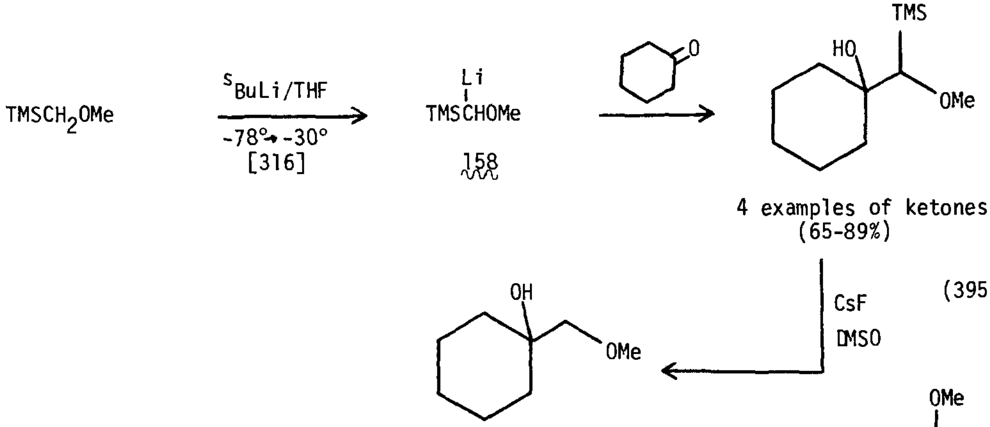
(393)

(α-Chloroethyl)trimethylsilane can be deprotonated to give the lithium reagent **157**, reaction of which with aldehydes or ketones leads to α,β-epoxysilanes rather than a Peterson reaction to give vinyl chlorides. (Eqn. 375)

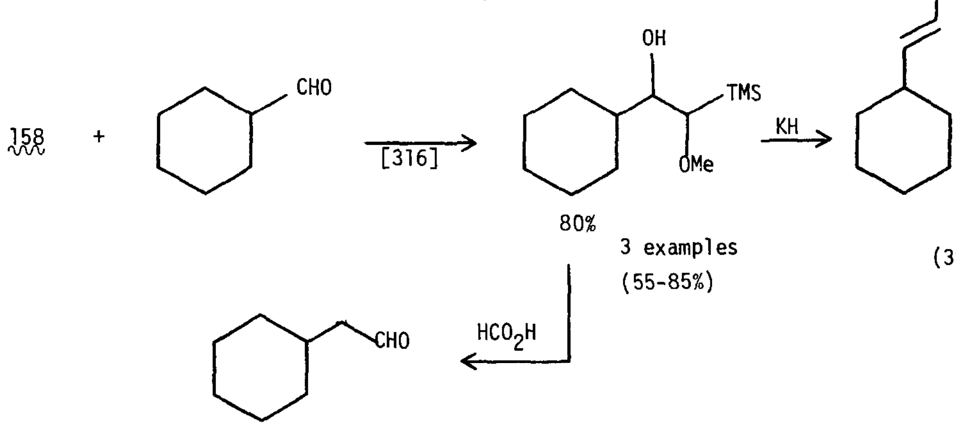


(394)

A similar deprotonation of methoxymethyltrimethylsilane gives lithium reagent **158**, which reacts with aldehydes and ketones to give α-methoxy-β-hydroxy silanes. These are converted to aldehydes, β-methoxy alcohols and enol ethers. (Eqns. 395-396).

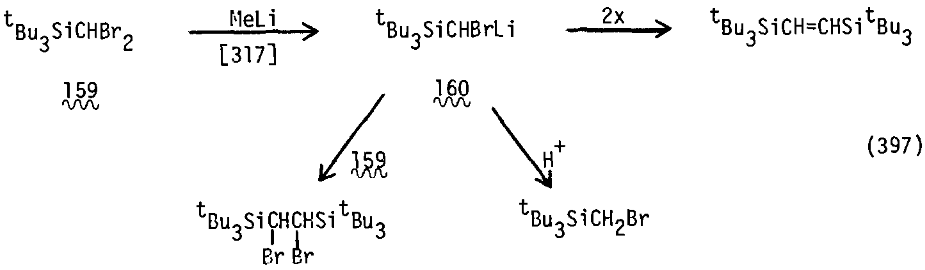


(395)



(396)

The α-bromo-α-silyllithium reagent 160 gave the reactions shown below. (Eqn. 397) The corresponding dichloromethylsilane 161 gave metal-hydrogen exchange. (Eqn. 398)

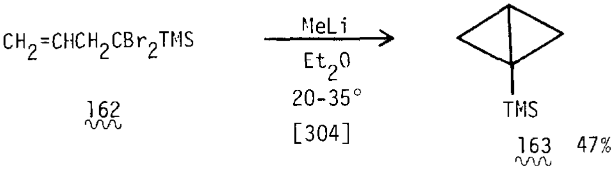


(397)

$$ {}^{t}Bu_3SiCHCl_2 \xrightarrow[{[317]}]{MeLi} {}^{t}Bu_3SiCCl_2Li \xrightarrow{2x} {}^{t}Bu_3SiCCl{=}CClSi{}^{t}Bu_3 \qquad (398) $$

161

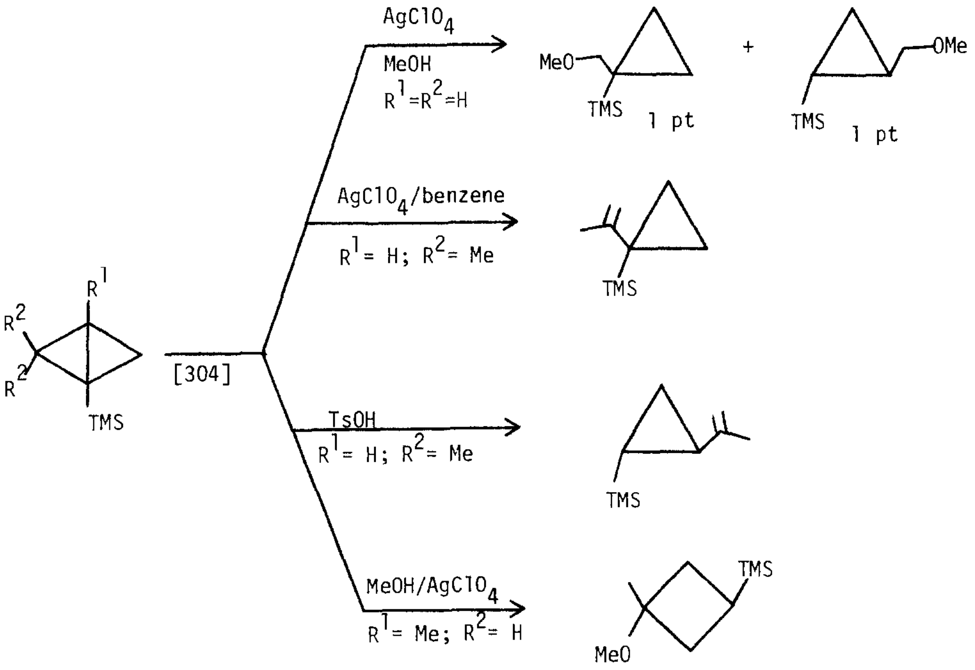
The α,α-dibromosilane 162 prepared according to Eqn. 372 reacts with methyllithium to give the bicyclobutane 163. (Eqn. 399) Some reactions of 163 and related systems are given. (Eqns. 400-403)



162

163

(399)



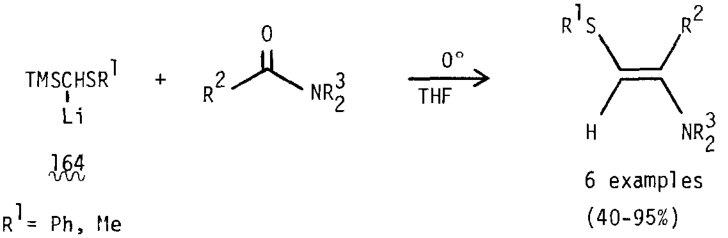
(400)

(401)

(402)

(403)

The α-thio trimethylsilylmethyllithium reagents 164 react with amides to give functionalized enamines. (Eqn. 404) The reaction of the sulfones follows a similar path. (Eqn. 405) The reaction products with esters, urea and ethylcarbonate were hydrolyzed to the α-thio carbonyl systems. (Eqns. 406-408)



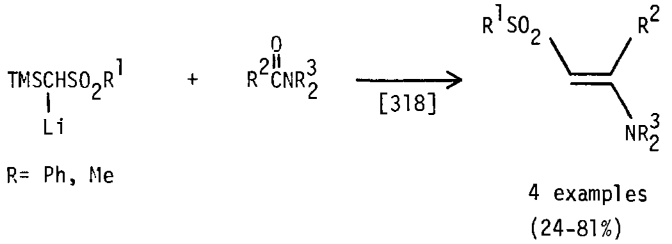
164

R^1= Ph, Me

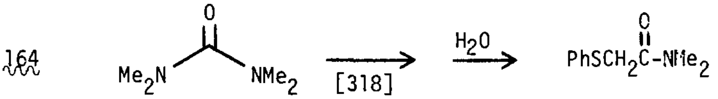
6 examples

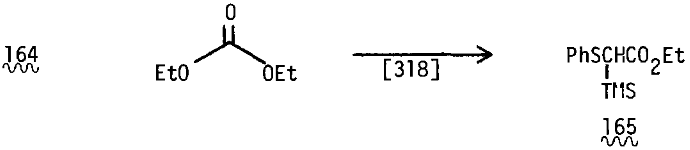
(40-95%)

(404)

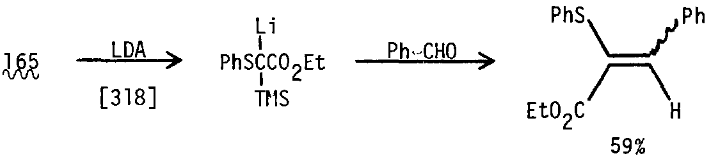

(405)

$$164 + PhCO_2Et \xrightarrow[2)\,H_2O \\ [318]]{1)\,0°/THF} \underset{60\%}{PhSCH_2COPh} + \underset{38\%}{PhSCH_2TMS} \qquad (406)$$

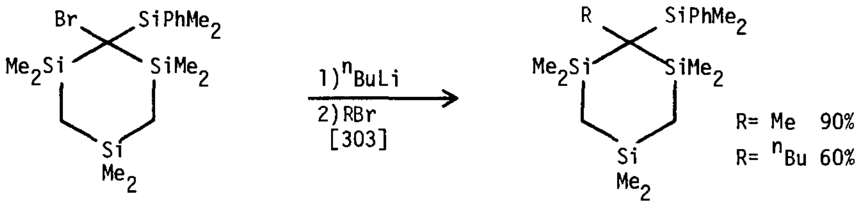

(407)


(408)

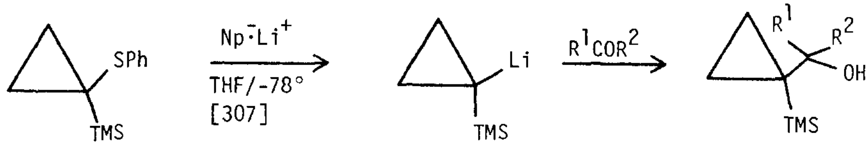
The α-silyl ester **165** can be further deprotonated and reacted with benzaldehyde to give the unsaturated ester. (Eqn. 409)


(409)

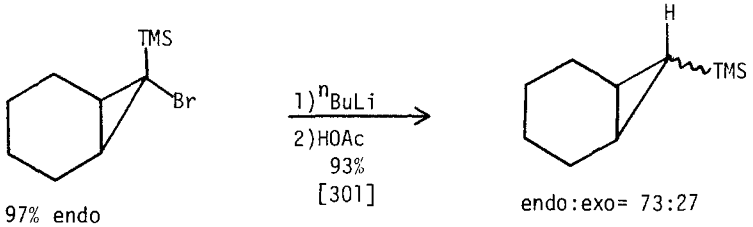
Metal-bromine exchange of **166** gives the lithium reagent which could be alkylated as shown. (Eqn. 410)


(410)

α-Trimethylsilylcyclopropyllithium reagents received some attention. Examples of their synthesis and reactions are given below. (Eqns. 411-415)



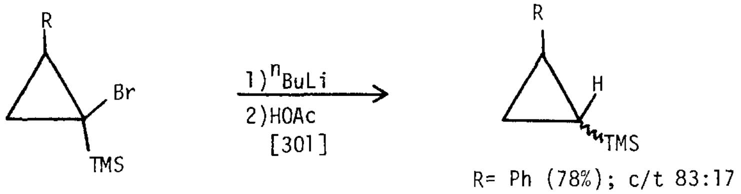
(411)



97% endo

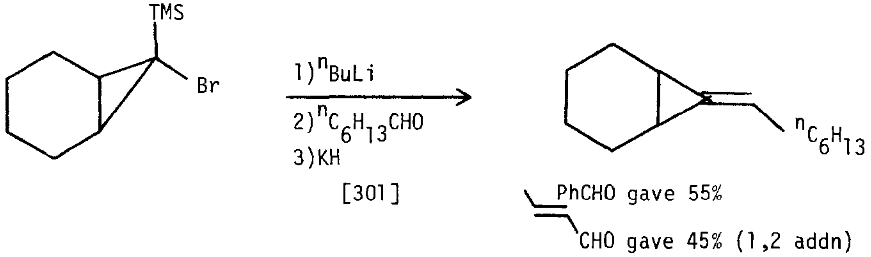
endo:exo= 73:27

(412)



R= Ph (78%); c/t 83:17

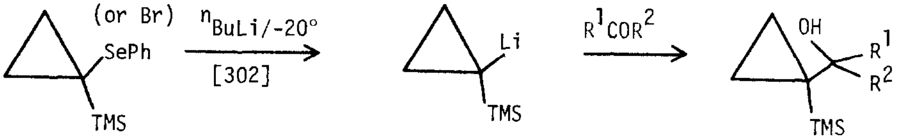
(413)



PhCHO gave 55%

CHO gave 45% (1,2 addn)

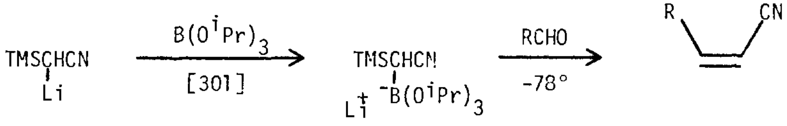
(414)



11 examples
(10-85%)

(415)

(Cyanomethyl)trimethylsilyllithium was converted to the borate complex 167, which was reacted with aldehydes to give α,β-unsaturated nitriles with high stereoselectivity. (Eqn. 416)



167

(416)

(Ph_3Si and ${}^tBuMe_2Si$ systems also looked at)

Trimethylsilylmethyllithium was reacted with $AlBr_3$ to give the tris(trimethylsilylmethyl)alane in excellent yield. (Eqn. 417) This reacts with KH to form the hydride in good yield.

$$3\ TMSCH_2Li \;+\; AlBr_3 \xrightarrow[\underset{[319]}{\text{reflux/12 h}}]{\text{hexane}} \underset{85\%}{(TMSCH_2)_3Al} \xrightarrow{KH} K^+HAl(CH_2TMS)_3 \qquad (417)$$

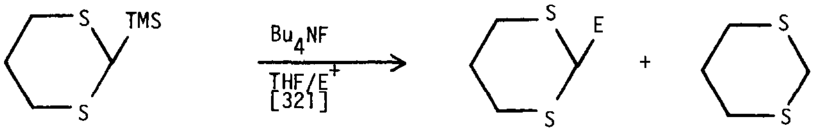
Tris(trimethylsilyl)methyltrimethyllead, **168**, undergoes electrophilic cleavage of the methyllead bond rather than the silylmethyllead bond. (Eqns. 418-419)

$$\begin{tikzcd}
\underset{\mathbf{168}}{(TMS)_3CPbMe_3} \arrow[r, "X_2", "\underset{[320]}{X=Cl,Br}"'] & (TMS)_3CPbMe_2X \arrow[r, "X_2"] & (TMS)_3CPbMeX_2 \arrow[d, "X=\ Br"] \\
 & & (TMS)_3CBr + MeBr + Pb
\end{tikzcd} \qquad (418)$$

$$\mathbf{168} \xrightarrow[{[320]}]{X_3CCO_2H} \underset{X=\ Cl,\ Br,\ H}{(TMS)_3CPbMe_2O_2CCX_3} \xrightarrow[\Delta]{X=\ Cl,Br} (TMS)_3CPbMe_2X + CO_2 + :CX_2 \qquad (419)$$

2. Reactions with Nucleophiles and Electrophiles

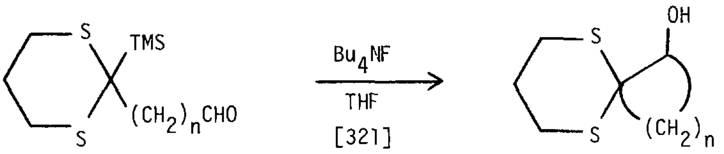
The trimethylsilyldithiane **169** was used as a way to generate the dithianyl anion "in situ" in the presence of a variety of electrophiles. The reactions proceed only moderately well. (Eqn. 420) Good yields of cyclic materials are however, possible. (Eqn. 421)



(420)

169

E^+= RX (5-30%); PhCHO (40-70%)



(421)

n	% Yield
3	5
4	56-65
5	60-76
6	57-61
7	10-20

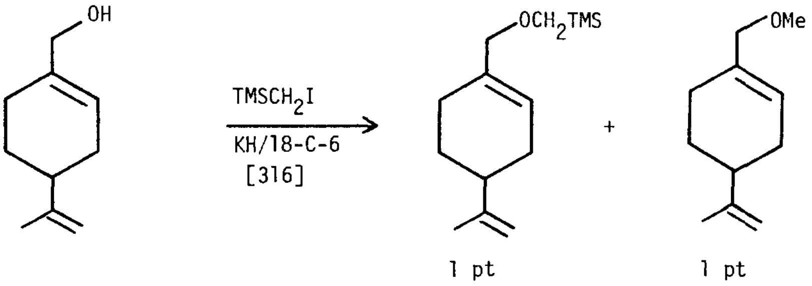
Attempts to utilize dihalomethylsilanes as entries into monohalocarbenes under phase transfer conditions resulted in protodesilylation only. (Eqn. 422)

$$Me_3SiCX_2R \xrightarrow[Q^+X^-]{NaOH\ (50\%)} (Me_3Si)_2O + X_2CHR \qquad (422)$$

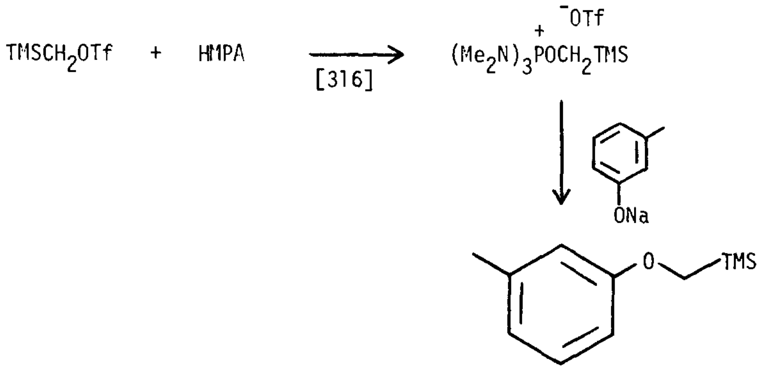
[322]

R= H, alkyl

The solvolysis of trimethylsilylmethyl tosylate and triflate is faster than the corresponding neopentyl systems in ethanol but slower in trifluoroethanol. A direct S_N2 displacement is argued. [323] A kinetic study of the alcoholysis of various $R_3Si(CH_2)_nNMe_2$ systems was carried out as a function of n. [324] Trimethylsilylmethyl iodide or triflate are good reagents for the trimethylsilylmethylation of alcohols. (Eqns. 423-424)

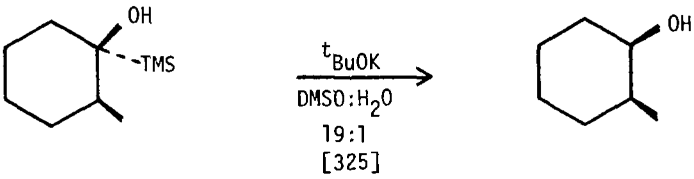


(423)

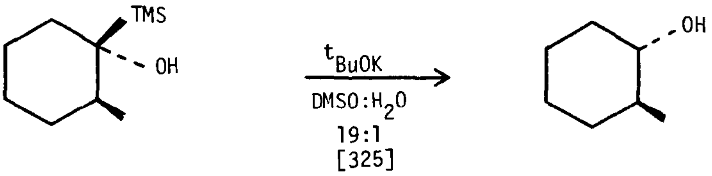


(424)

Under specific conditions the Brook rearrangement can be made to go with retention of configuration at carbon as shown in the isomeric silylcyclohexanols below. (Eqns. 425-426)

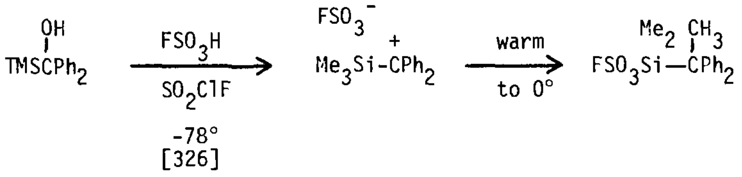


(425)



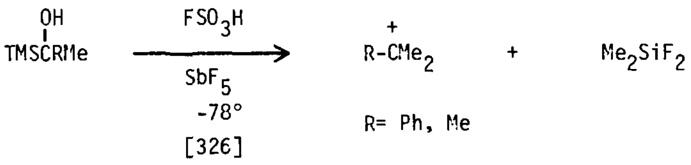
(426)

α-Hydroxysilanes which contain groups capable of stabilizing a carbenium ion undergo loss of water in the presence of acid followed by methyl migration from silicon to carbon upon warming. (Eqns. 427-428)



$$\mathrm{TMS}\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\mathrm{Ph_2} \xrightarrow[\substack{\mathrm{SO_2ClF}\\ -78^\circ\\ [326]}]{\mathrm{FSO_3H}} \overset{\mathrm{FSO_3^-}}{\overset{+}{\mathrm{Me_3Si\text{-}CPh_2}}} \xrightarrow[\text{to } 0^\circ]{\text{warm}} \mathrm{FSO_3}\overset{\mathrm{Me_2}}{\mathrm{Si}}\text{—}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{Ph_2}$$

(427)

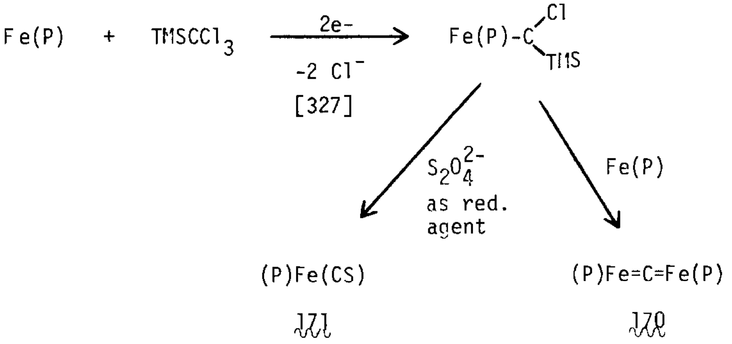


$$\mathrm{TMS}\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\mathrm{RMe} \xrightarrow[\substack{\mathrm{SbF_5}\\ -78^\circ\\ [326]}]{\mathrm{FSO_3H}} \overset{+}{\mathrm{R\text{-}CMe_2}} + \mathrm{Me_2SiF_2}$$

R= Ph, Me

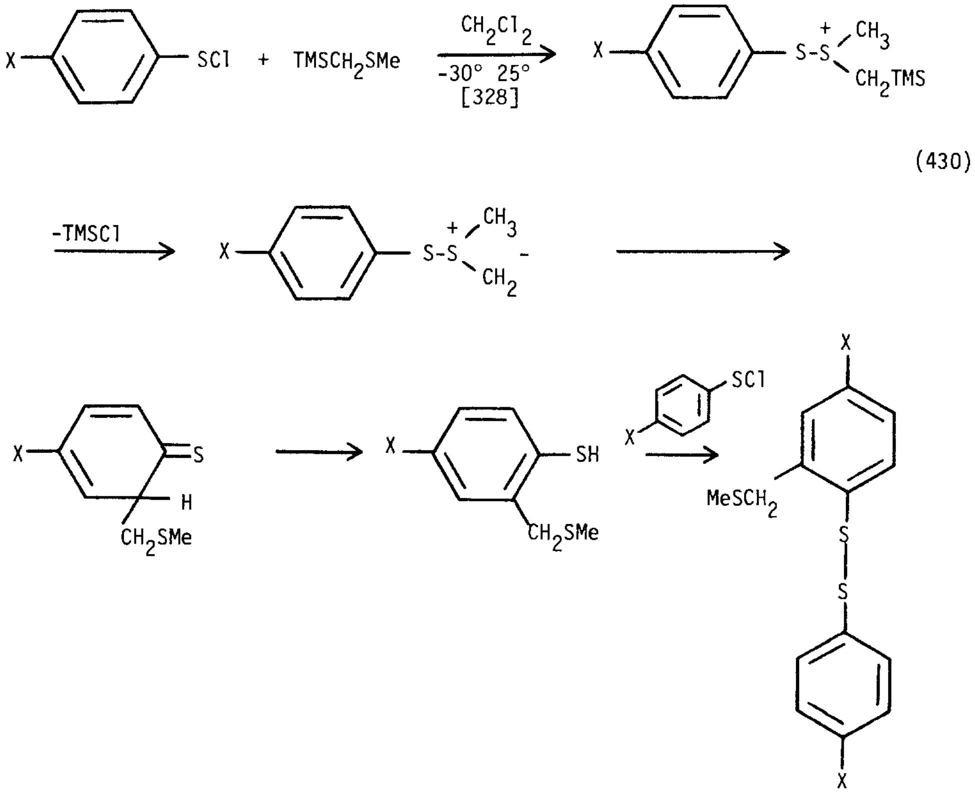
(428)

Trichloromethyltrimethylsilane was reacted with ferrotetraphenylporphyrins ($Fe^{II}(P)$) under reducing conditions to give silacarbene complexes which lose trimethylchlorosilane to give the complexes **170** or in the presence of dithionate **171**. (Eqn. 429)



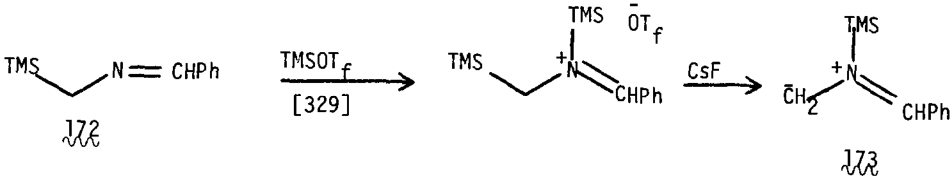
(429)

Treatment of methylthiomethyltrimethylsilane with arylsulfenyl chlorides gives thiomethylation of the aryl ring via a novel [2,3] sigmatropic rearrangement of a thiosulfonium ylid intermediate. (Eqn. 430)

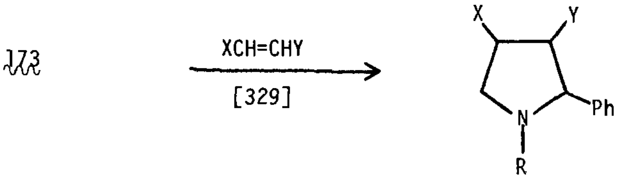


(430)

The α-silyl imine, 172, is a precursor for a highly useful 1,3-dipole 173 which can lead to pyrrolidines as illustrated in Eqns. 431-432.

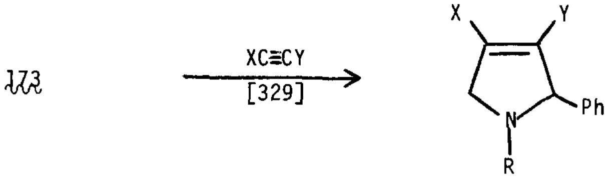


(431)



(432)

R= H, TMS
9 examples
high yields



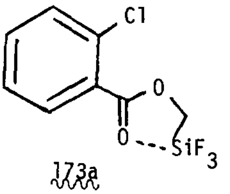
(433)

X= Y= CO_2Me 92%

The configurations of o (or p) tolylbenzylmethylsilylmethylamine were determined by conversion to known systems via standard reactions. [330]

C. Spectroscopic Studies

The X-ray crystal structure of (2-chlorobenzyloxymethyl)trifluorosilane 173a showed it to have a trigonal bipyramidal silicon atom. [331]



173a

The infrared spectra of chloromethyl and bromomethylsilanes 174 and 175, respectively, revealed that the SiH bonds are gauche and trans to the halogen and that this conformational effect accounts for the doublet seen in earlier work. [332]

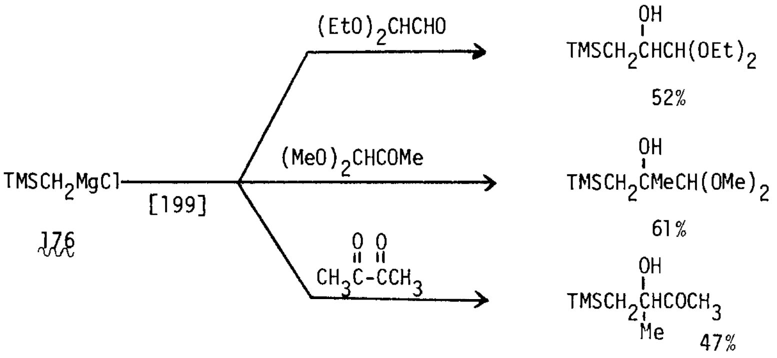
$HSiD_2CH_2Cl$ **174**　　　$HSiD_2CH_2Br$ **175**

XIII. β-FUNCTIONAL ORGANOSILANES

A. β-Hydroxy and Related Organosilanes

The preferred method of preparing β-hydroxyorganosilanes is via the reaction of a silylmethyllithium or magnesium reagent with an aldehyde or ketone. The resulting β-hydroxysilane is often converted to an olefin. Examples of this process are given in Eqns. 434-438.

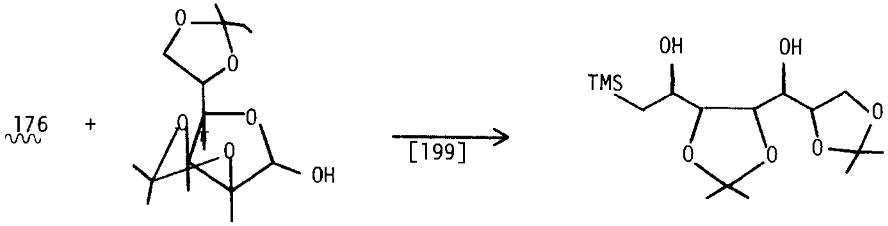
Reactions of the trimethylsilylmethyltitanium reagent **177** and the chromium reagent **178** with aldehydes, but not ketones, were reported. The intermediate β-oxidosilane undergoes spontaneous elimination as the titanium salt (Eqn. 441) but not as the chromium salt. (Eqn. 442)



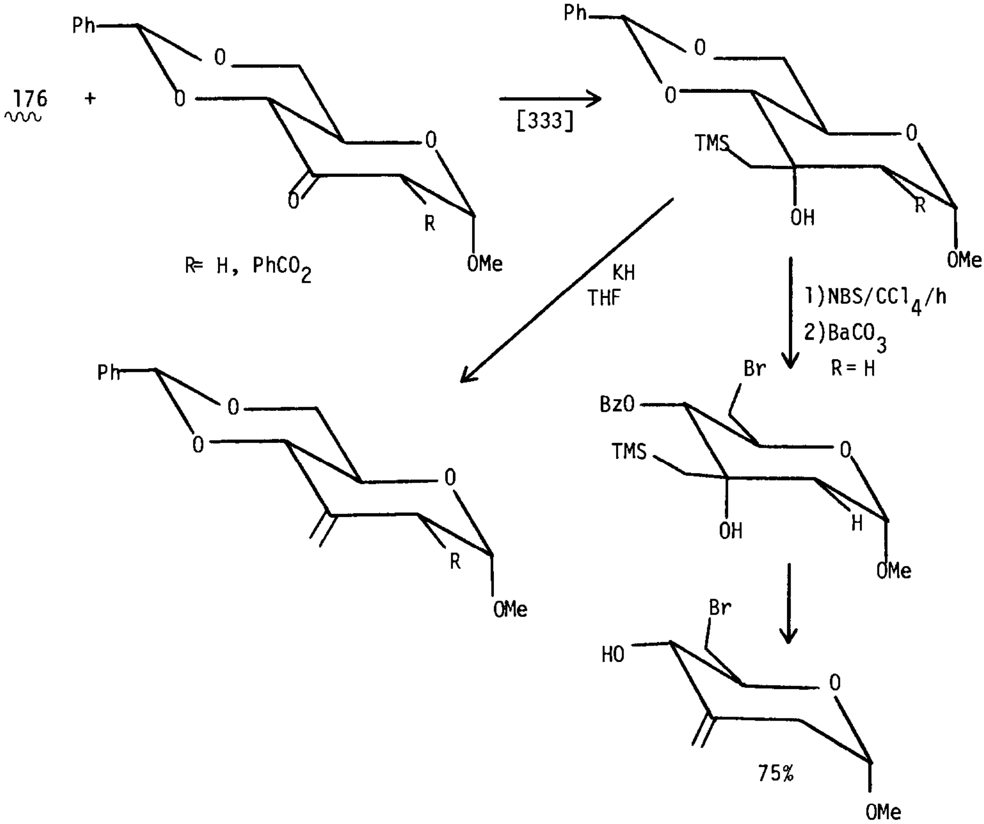
(434)

(435)

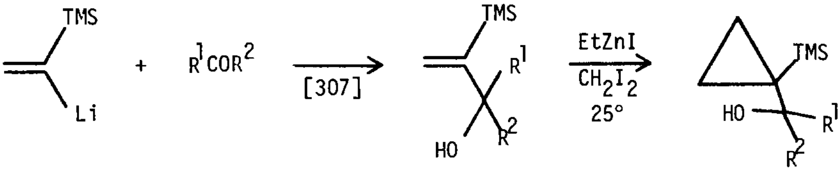
(436)



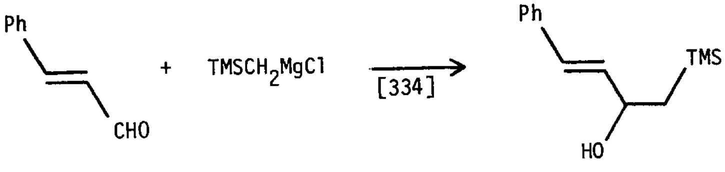
(437)


176
+
Ph
O
O
O
O
R
OMe
R= H, PhCO$_2$
[333]
Ph
O
O
O
TMS
OH
R
OMe
KH
THF
1)NBS/CCl$_4$/h
2)BaCO$_3$
R = H
Ph
O
O
O
R
OMe
Br
BzO
TMS
O
OH
H
OMe
Br
HO
O
75%
OMe

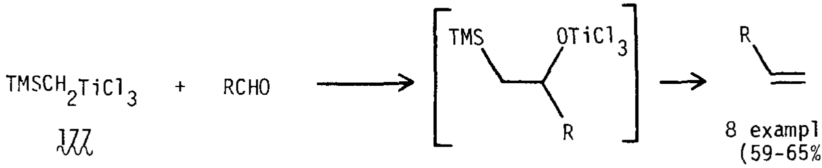
(438)


TMS
Li
+
R^{1}COR^2
[307]
TMS
R^1
HO
R^2
EtZnI
CH$_2$I$_2$
25°
TMS
HO
R^1
R^2

(439)

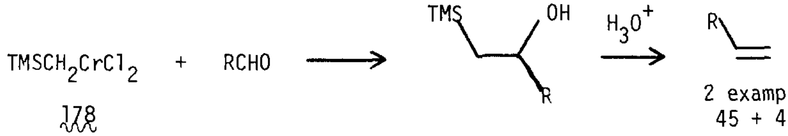

Ph
CHO
+
TMSCH$_2$MgCl
[334]
Ph
TMS
HO

(440)



(441)

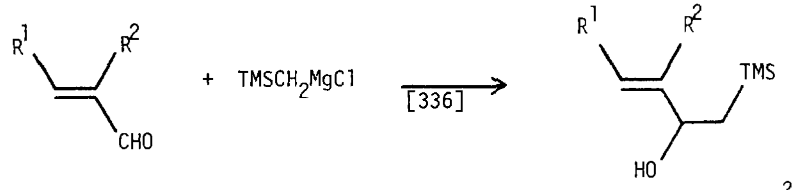
8 examples
(59-65%)
3 ketones (0-8%)



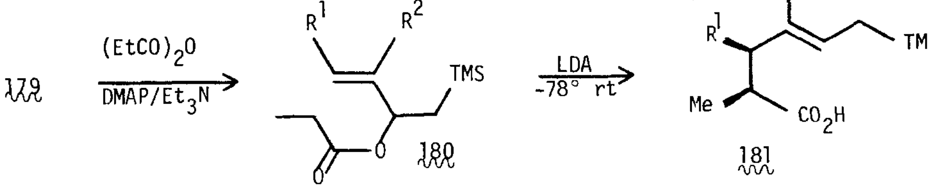
(442)

2 examples
45 + 47%

The β-hydroxysilane 179 was converted to the propionate ester, which undergoes a silicon-mediated homo-Claisen rearrangement to give an allylsilane, 181, 182, which can be further reacted to give protodesilylation. (Eqns. 443-447). The protodesilylation must occur intramolecularly via 183 to account for the stereochemistry observed.

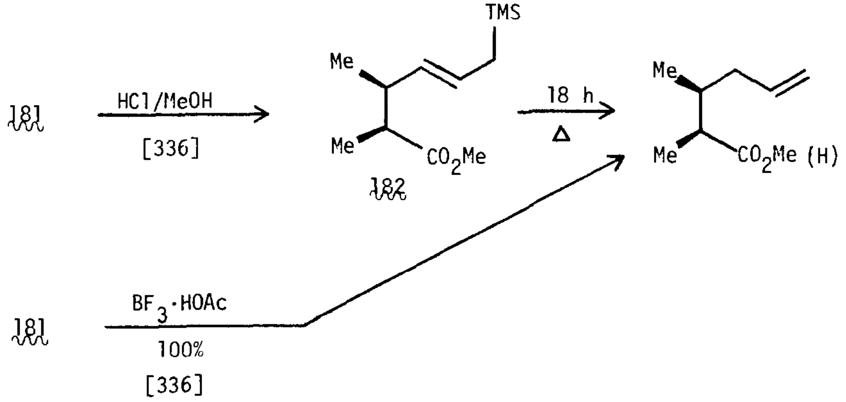


(443)



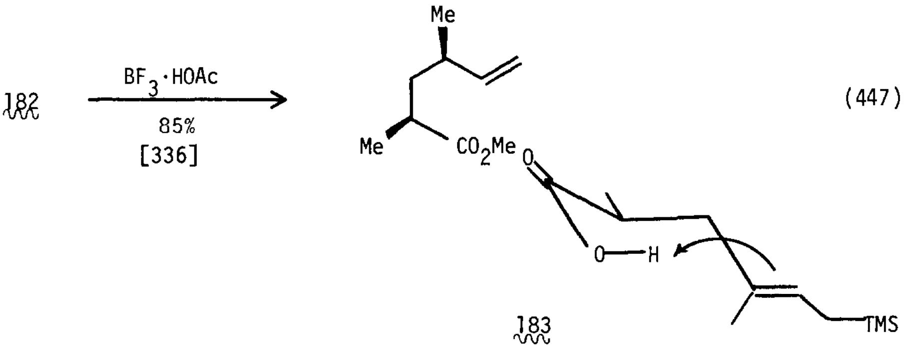
R^1= Me, R^2= H 80%
R^1= H, R^2= Me 95%

R^1= Me 61% 9:1 trans-erythro
R^2= Me 53% 95% E



(445)

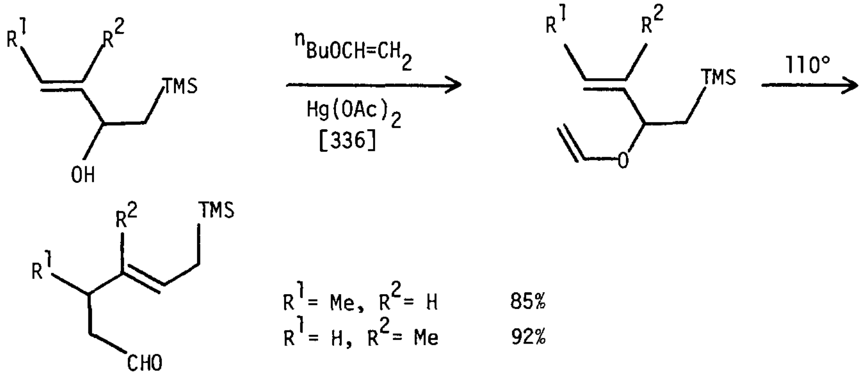
(446)



183

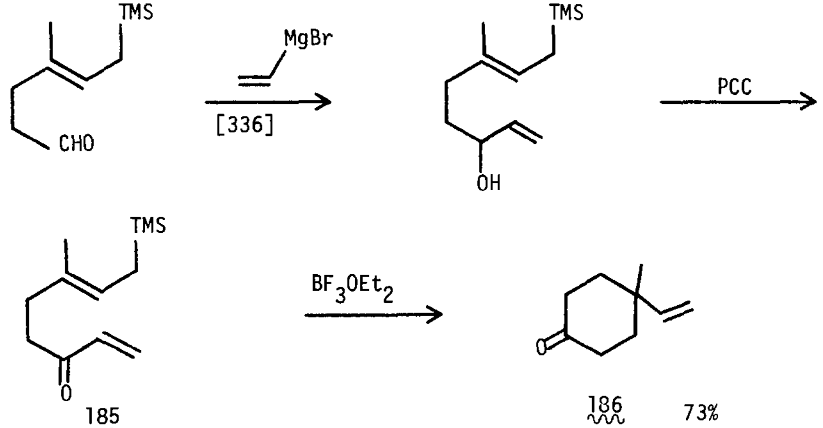
(447)

The oxy-Cope rearrangement of 184 was also carried out to give allylsilanes. The allylsilane 185 undergoes an intramolecular cyclization to give 186. (Eqns. 448-449)



(448)

R^1= Me, R^2= H 85%
R^1= H, R^2= Me 92%

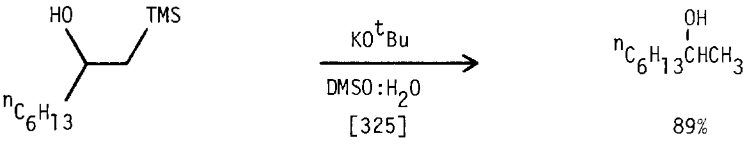


(449)

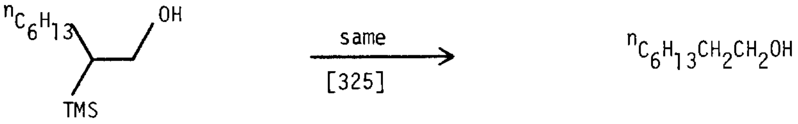
185

186 73%

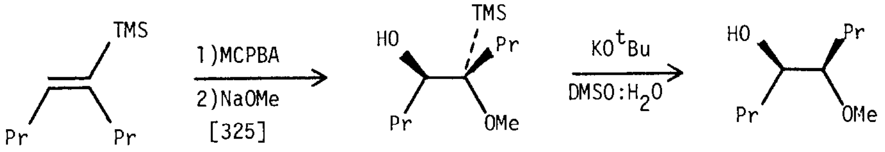
Conditions were found wherein it is possible to protodesilylate β-hydroxysilanes, in what is in effect, a homo-Brook rearrangement. The reaction occurs with retention of configuration at carbon. (Eqns. 450-454) Some β-elimination does occur in these reactions.



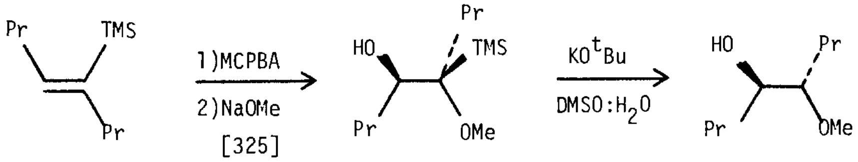
(450)



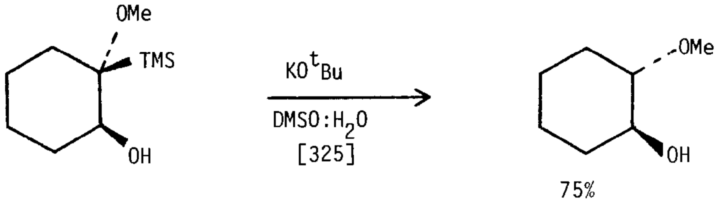
(451)



(452)

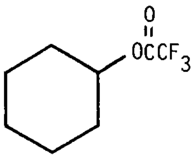


(453)

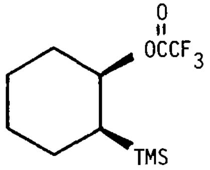


(454)

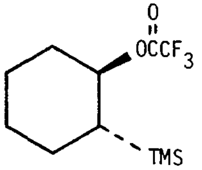
The solvolysis rates of 187, 188 and 189 in trifluoroethanol were carried out and the values obtained are given below. It is argued that in the cis isomer 188 a through bond effect of the silyl group enhances the rate whereas in the trans isomer 189 both a through bond effect and neighboring group participation are rate enhancing. [337]



187
rel. rates 1.0



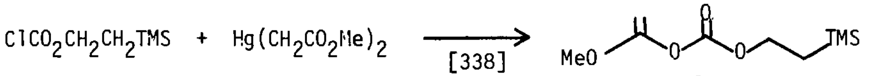
188
3.35 x 10^4



189
2.47 x 10^6

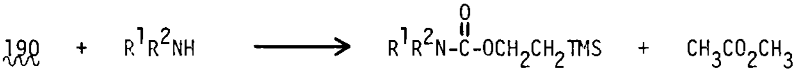
(455)

β-(Trimethylsilylethyl) esters, useful protecting groups for carboxylic acids, were employed in the protection of amines as shown in Eqns. 455-456.



190
65%

(455)

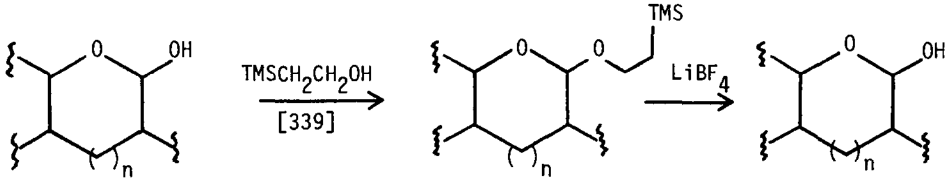


$$190 + R^1R^2NH \longrightarrow R^1R^2N\text{-}\overset{\overset{O}{\|}}{C}\text{-}OCH_2CH_2TMS + CH_3CO_2CH_3 \quad (456)$$

7 examples 60-87%

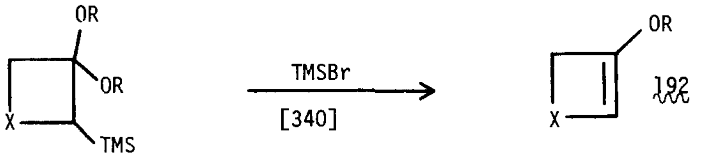
R^1= H, R^2= CH_2CO_2H 99%

2-Trimethylsilylethanol found use as a reagent for the protection of the anomeric center in pyranosides as shown in Eqn. 457.



(457)

The α-silylated ketals 191 react with TMSBr to give cyclobutenes 192. (Eqn. 458)



191

192

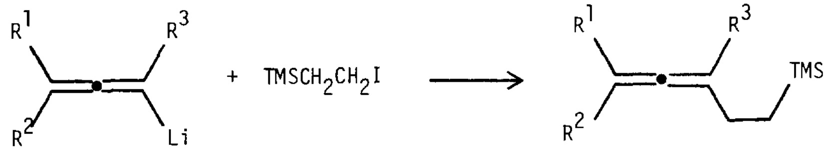
X= CO, R= Et 77%
X= SO_2, R= Me 53%

(458)

2-Trimethylsilylethanol can be converted to the β-bromo or β-iodosilanes 193. The β-iodoethylsilane reacts with allenyllithium reagents to give β-silylallenes. (Eqns. 459-460)

$$\mathrm{TMSCH_2CH_2OH} \xrightarrow[\text{[341]}]{\mathrm{Ph_3PX_2}} \underset{\mathbf{193}}{\mathrm{TMSCH_2CH_2X}} \qquad (459)$$

X= Br 45%
X= I 42%

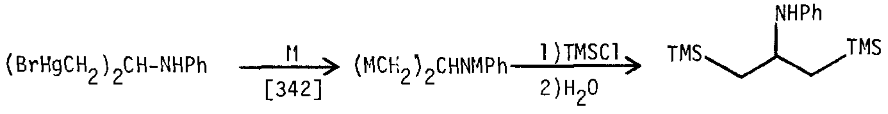


(460)

5 examples
(0-70%)

The trianions 194 can be quenched with TMSCl to give the β-aminosilanes. (Eqn. 461) The reaction of n-propylamine with trimethylvinylsilane in the presence of ^{n}BuLi gives the β-aminosilane. (Eqn. 462)

β-Silylenamines were prepared as shown in Eqn. 463.

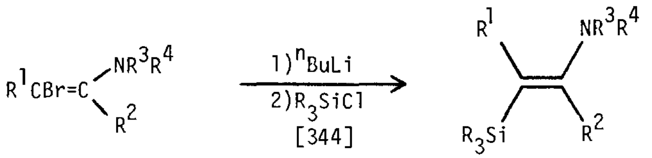


(461)

M= Li, Na, K

194

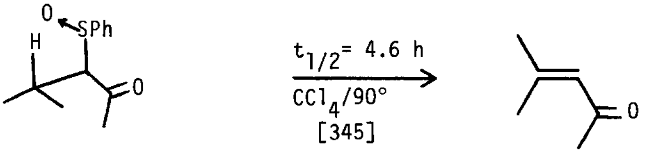
$$\mathrm{TMSCH{=}CH_2} \quad + \quad {}^n\mathrm{PrNH_2} \xrightarrow[\substack{60\text{-}65^\circ/\mathrm{THF} \\ 10\ \mathrm{h} \\ [343]}]{{}^n\mathrm{BuLi}} \mathrm{TMSCH_2CH_2NHPr} \qquad (462)$$



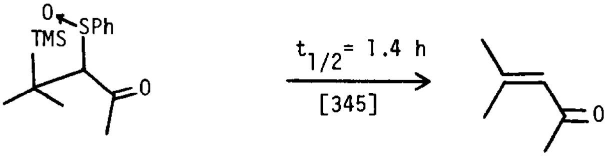
(463)

10 examples
(27-89% Z:E mixtures)

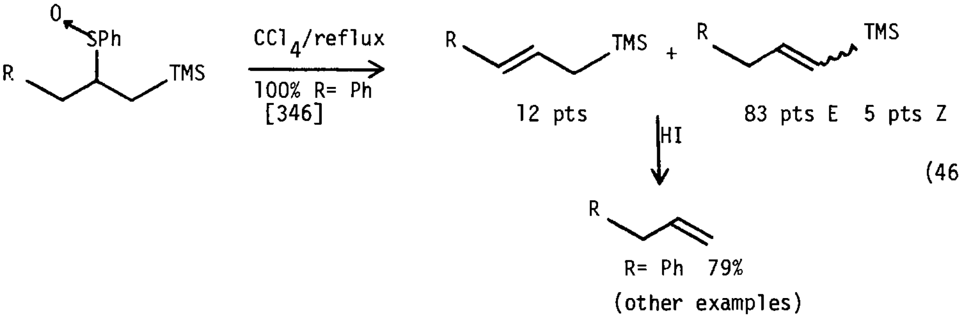
Organosilanes containing the β-sulfoxy group can undergo loss of the silicon or a β-hydrogen. In the prsence of a β-silyl group loss of silicon is seen and in fact is faster than the corresponding loss of H. On the other hand when both β-silyl and β-H are present, loss of H is observed. (Eqns. 464-469)



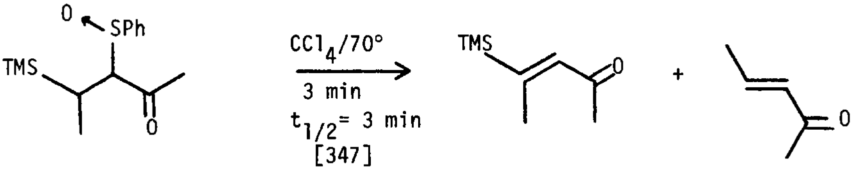
(464)



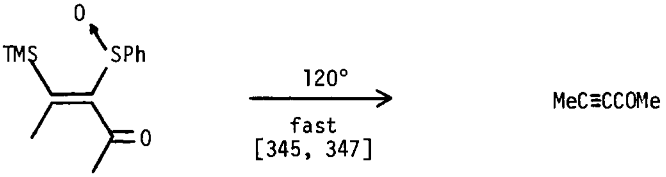
(465)



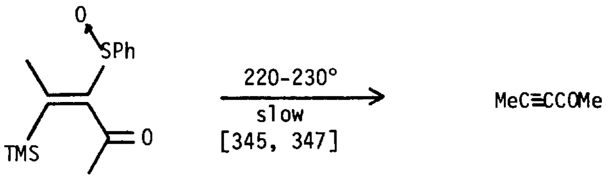
(466)



(467)



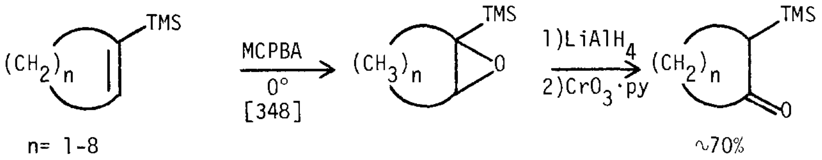
(468)



(469)

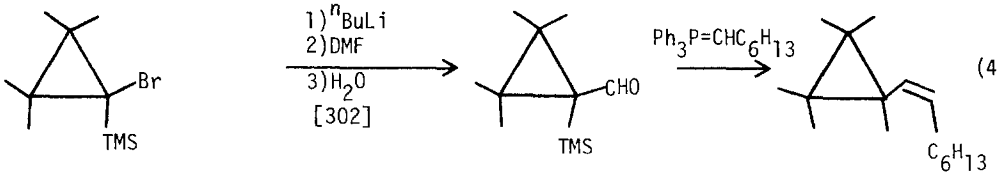
B. β-Carbonyl and Related Organosilanes

β-Ketosilanes, more commonly and hereafter referred to as α-silyl ketones, were prepared by a variety of methods. Examples of both the synthetic approaches and the subsequent reactions of the α-silyl ketones where applicable are given below. Cyclic α-trimethylsilyl ketones were prepared in three steps from cycloalkenylsilanes. (Eqn. 470)



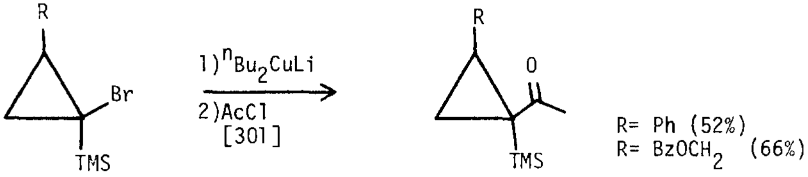
(470)

1-Trimethylsilyl-1-formyl or acylcyclopropanes were prepared as shown in Eqns. 471-472. Wittig reaction on this aldehyde gives the corresponding allylsilane. (Eqn. 471)



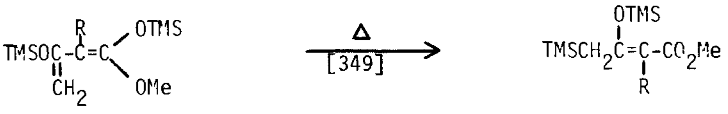
(see Eqn. 351)

(471)



(472)

The diene **195** thermally rearranged to the α-silyl ketone where the ketone is in the form of its silyl enol ether. (Eqn. 473)



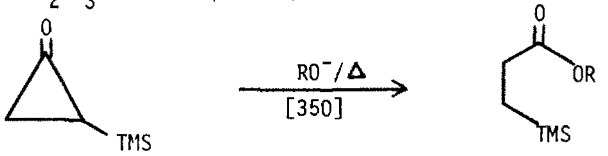
(473)

195

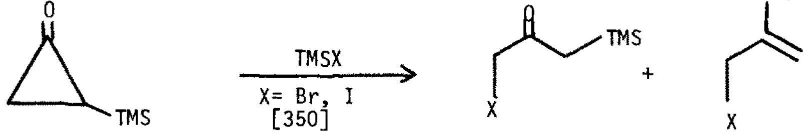
R= H 50%

R= Me 38%

Trimethylsilylcyclopropanores undergo reactions with nucleophiles to give cleavage of the C_1-C_2 bond. (Eqn. 474) and with TMSBr or TMSI to give cleavage of the C_2-C_3 bond. (Eqn. 475)

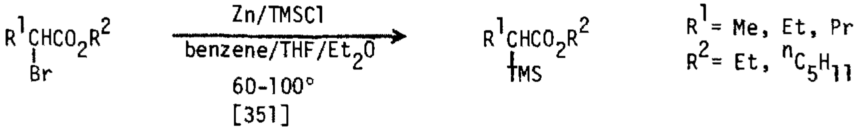


(474)



(475)

α-Silyl esters were prepared by a Reformatsky procedure. (Eqn. 476) Ethyl α-silylacetates were reacted with Grignard reagents and the resulting β-hydroxysilanes eliminated to give 1,1-disubstituted olefins in good yield. (Eqn. 477)

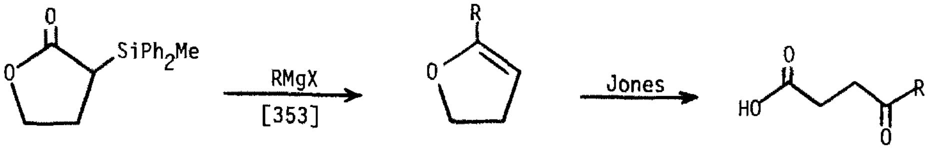


$$R^1\underset{\displaystyle Br}{C}HCO_2R^2 \xrightarrow[\substack{60\text{-}100°\\ [351]}]{\substack{Zn/TMSCl\\ benzene/THF/Et_2O}} R^1\underset{\displaystyle TMS}{C}HCO_2R^2 \qquad \begin{array}{l} R^1= Me, Et, Pr\\ R^2= Et, {}^nC_5H_{11}\end{array} \qquad (476)$$

$$R^1_2MeSiCH_2CO_2Et \xrightarrow[\substack{2)H_2SO_4/THF\\ or\ BF_3OEt_2/CH_2Cl_2\\ [352]}]{1)2\ R^2MgX} \underset{0\text{-}98\%}{CH_2{=}CR^2_2} \qquad (477)$$

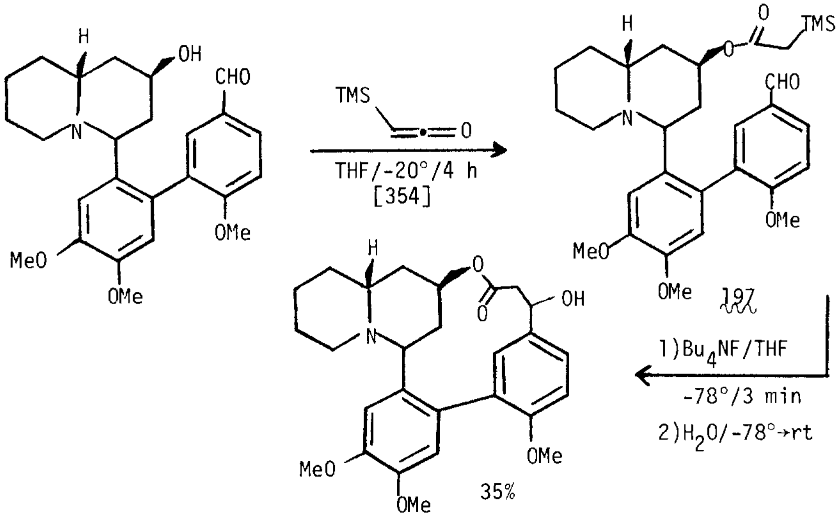
R^1= Me, Ph

In a related reaction α-(diphenylmethylsilyl)-γ-butyrolactone was reacted with Grignard reagents to give 4,5-dihydrofurans 196, which were converted directly to 4-oxocarboxylic acids. (Eqn. 478) The α-silyl ester 197, prepared from trimethylsilylketene, undergoes an intramolecular condensation upon treatment with fluoride ion. (Eqn. 479)



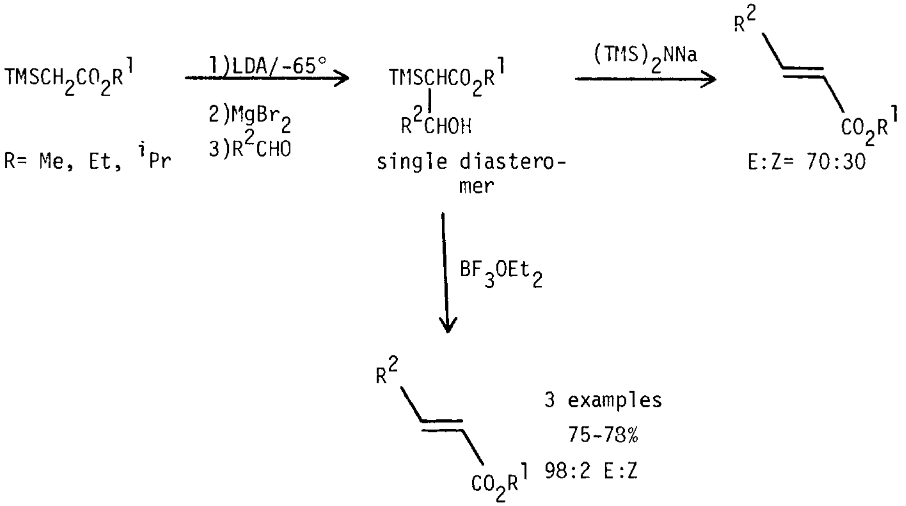
196

(478)

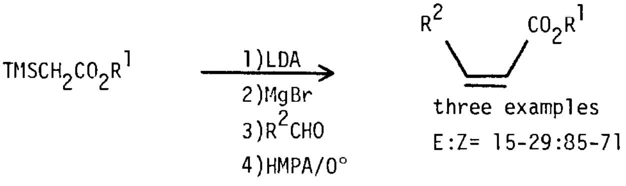


(479)

Deprotonation of α-silyl esters followed by condensation with aldehydes leads to α,β-unsaturated esters or β-hydroxysilanes, which can be converted to α,β-unsaturated esters. The stereochemistry of the process depends on the reaction conditions. (Eqns. 480-481) It is argued that the base catalyzed elimination is stepwise allowing for loss of stereoselectivity.

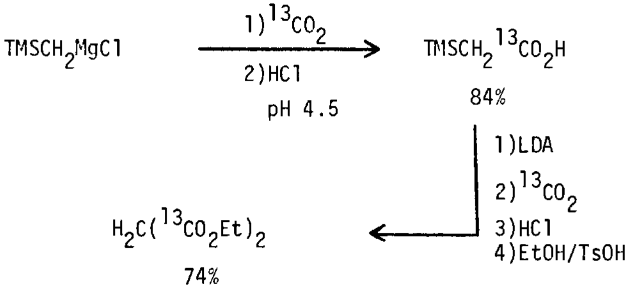


(480)



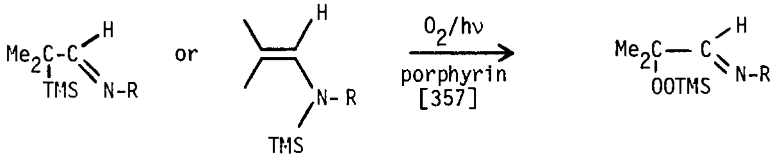
(481)

A trimethylsilyl route to labelled diethylmalonate is shown in Eqn. 482.



(482)

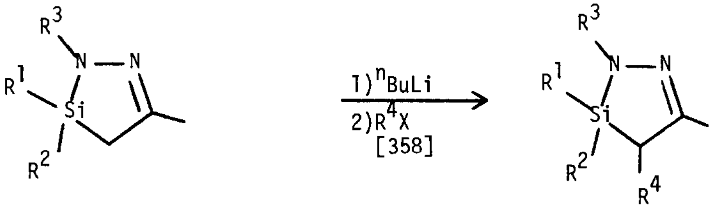
The α-silylated imines or the N-silylated isomers are photooxidized to the α-silylperoxy imines. (Eqn. 483)



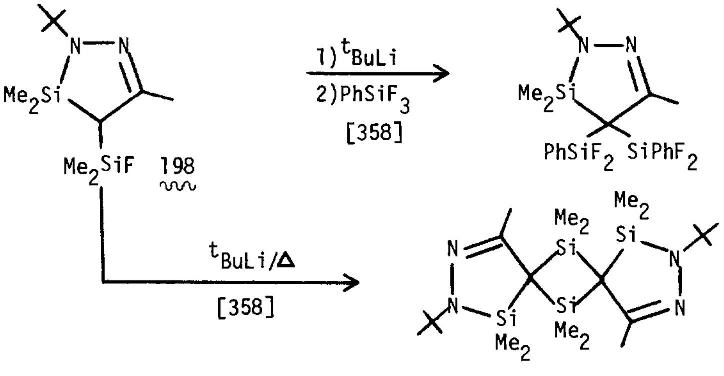
(483)

R= Me, Et, ^{i}Pr, ^{i}Bu, ^{t}Bu

Deprotonation-silylation of 1,2-diaza-3-sila-5-cyclopentenes gives the 4-alkylated derivatives. (Eqn. 484) Other reactions are shown in Eqns. 485-487.

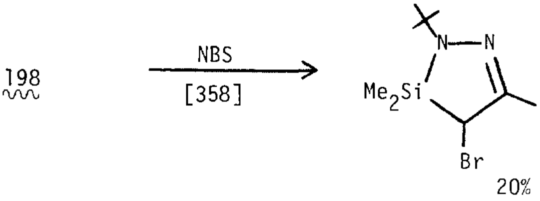


(484)



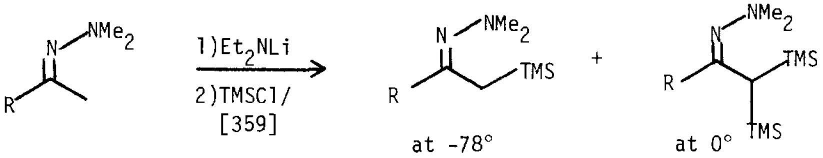
(485)

(486)



(487)

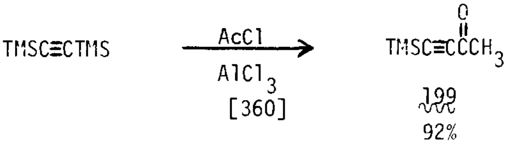
Silylation of the anions of ketone N,N-dimethylhydrazones gives the α-silyl hydrazone (-78°) or the α,α-bis(silyl) hydrazone (0°). (Eqn. 488)



(488)

C. γ-Functional Organosilanes

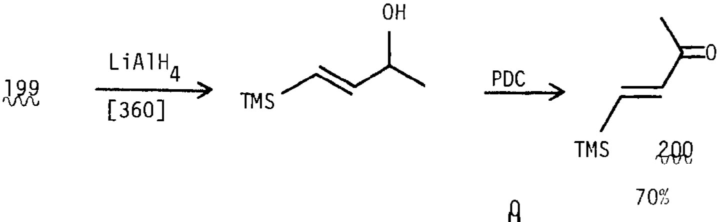
Trimethylsilylbutyn-3-one 199 and trimethylsilylbuten-3-one 200 were prepared as shown in Eqns. 489 and 490, respectively. Some reactions are given. (Eqns. 491-494)



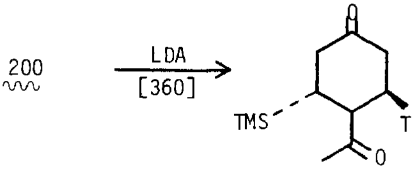
$$\mathrm{TMSC{\equiv}CTMS} \xrightarrow[\mathrm{AlCl_3}\ [360]]{\mathrm{AcCl}} \mathrm{TMSC{\equiv}C\overset{\overset{O}{\|}}{C}CH_3}$$

199
92%

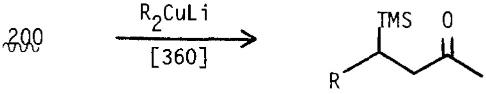
(489)



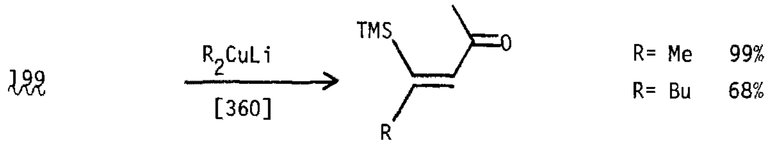
(490)



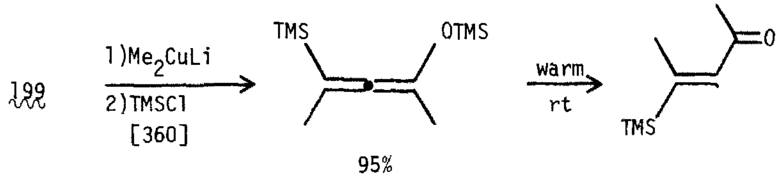
(491)



(492)

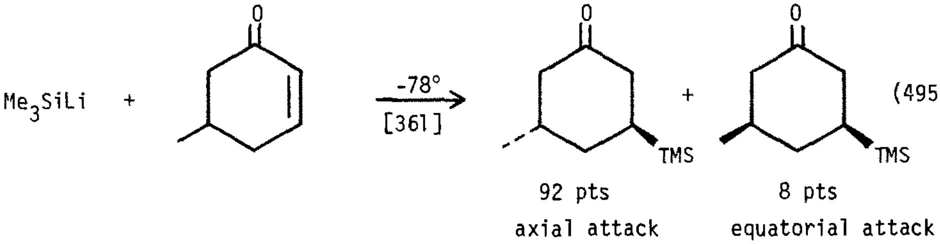


(492)

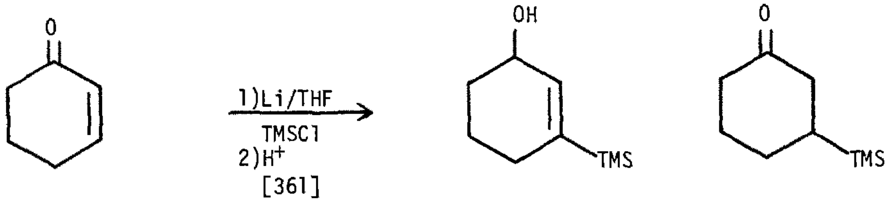


(493)

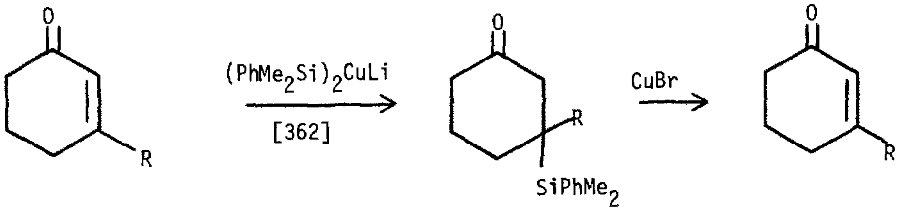
Other syntheses of β-silyl ketones are given in Eqns. 495-500. As can be noted the conjugate addition of a silylmetallic reagent is an excellent route to these systems.



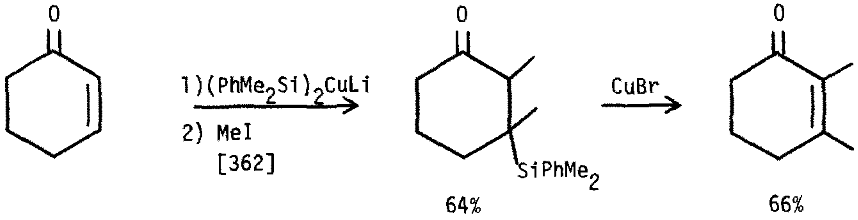
(495)



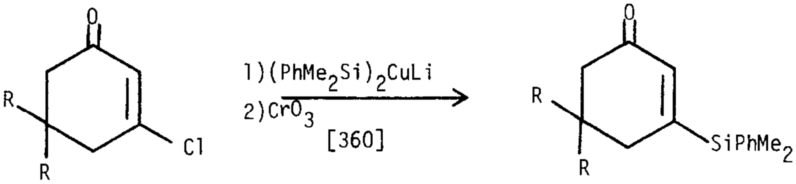
(496)



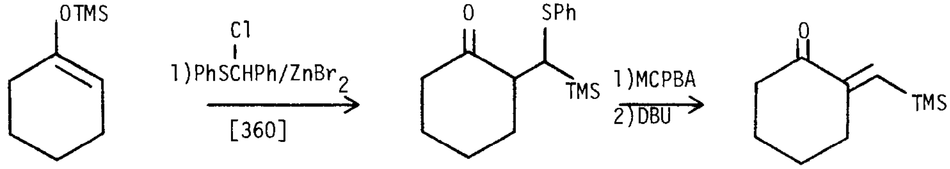
(497)



(498)

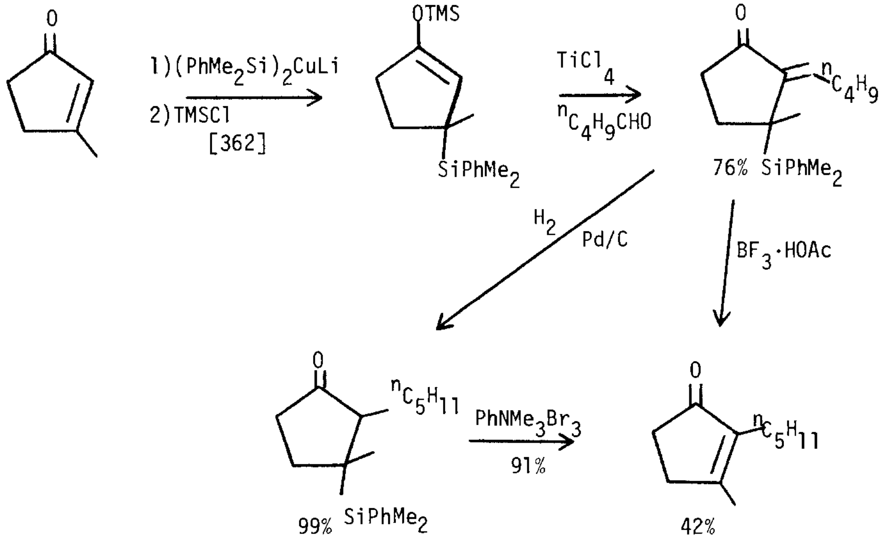


(499)



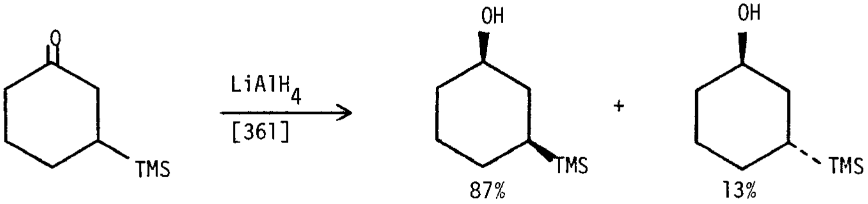
(500)

This methodology was applied to a synthesis of dihydrojasmone. (Eqn. 501)

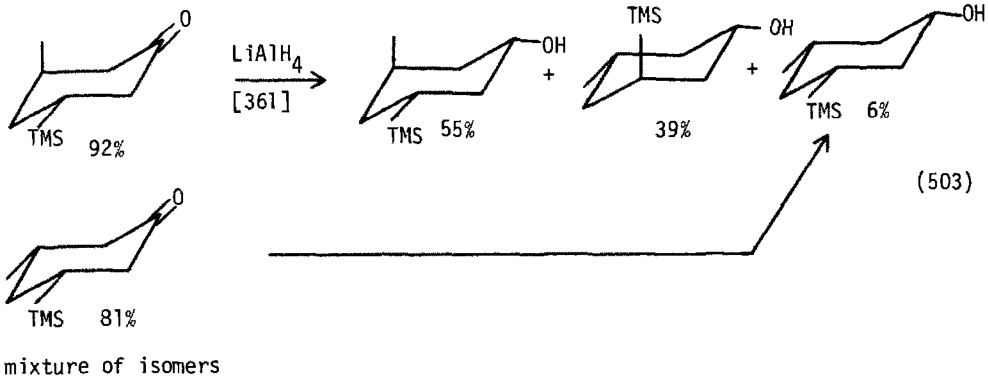


(501)

The reduction of 3-trimethylsilylcyclohexanones with $LiAlH_4$ was found to be only moderately stereoselective. (Eqns. 502-503)

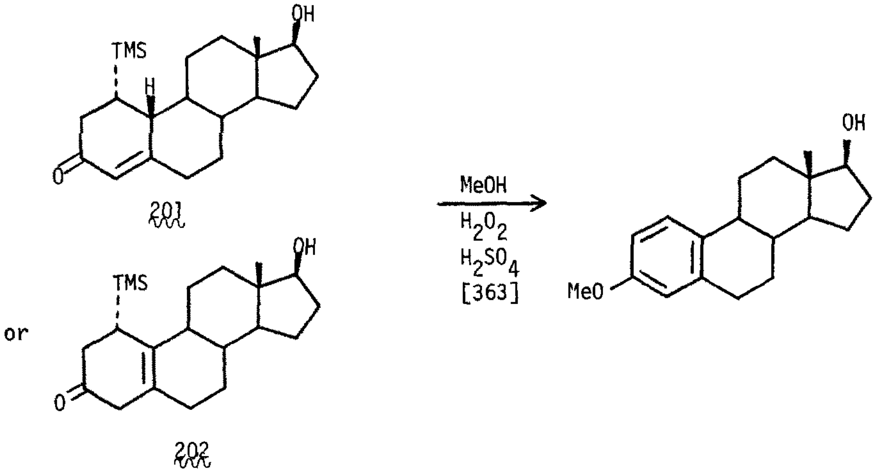


(502)



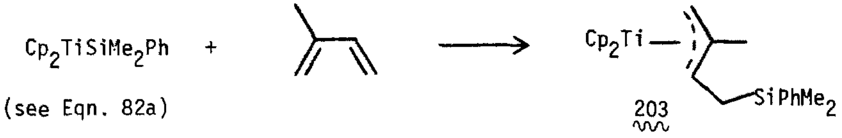
(503)

The β-silylketones **201** and **202** aromatize upon oxidation in methanol to give the estradiol methyl ethers. (Eqn. 504)

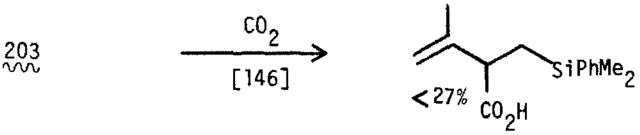


(504)

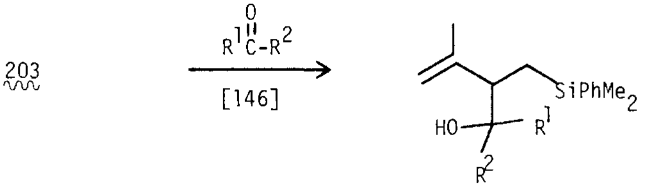
The titanium reagent **203** (Eqn. 505) can be carboxylated to give the β-silyl carboxylic acid or treated with acetaldehyde or acetone to give the γ-hydroxysilanes. (Eqns. 506-507) Protonation gives the olefin. (Eqn. 508)



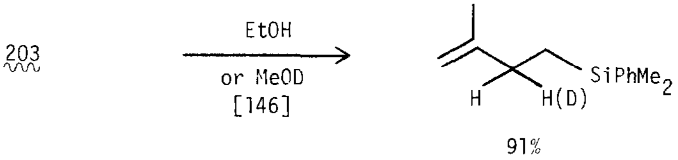
(505)



(506)



(507)



(508)

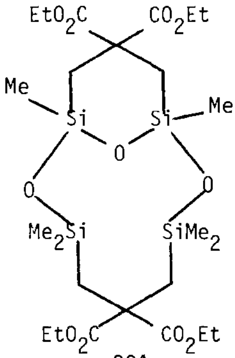
3-(Trimethylsilyl)propionic acid reacts with mercuric acetate to give the mercury salt, which can be decarboxylated to give a β-silylethylmercury salt. (Eqn. 509)

$$\begin{tikzcd}
TMSCH_2CH_2CO_2H \arrow[r, "Hg(OAc)_2", "{[364]}"'] & (TMSCH_2CH_2CO_2)_2Hg \arrow[d, "h\nu \text{ or } BzOOBz", "Cl^-"'] \\
& TMSCH_2CH_2HgCl
\end{tikzcd}$$

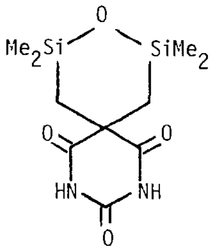
$\sim$ 50%

(509)

The crystal structure of the unusual γ-silyl ester 204 and the amide 205 were determined. [365]

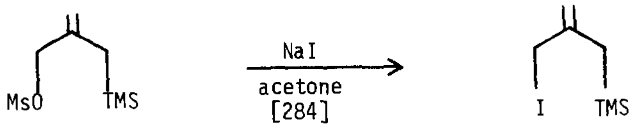


204



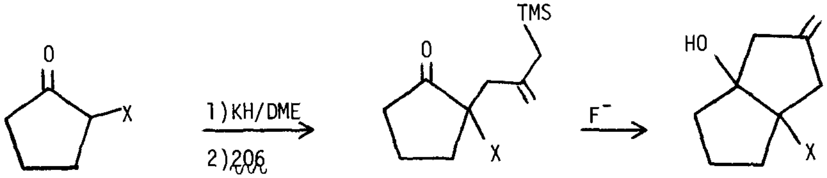
205

The γ-iodosilane 206 was prepared from the corresponding mesylate. (Eqn. 510) It serves as an alkylating agent. (Eqn. 511) Its reactivity is much lower than that of the nonsilylated derivative 207, (Eqn. 512) but better than the tert-butyl analog 208. [366]



206

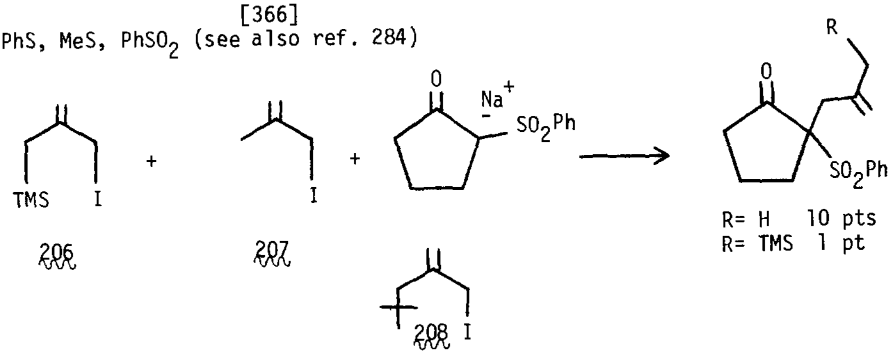
(510)



[366]

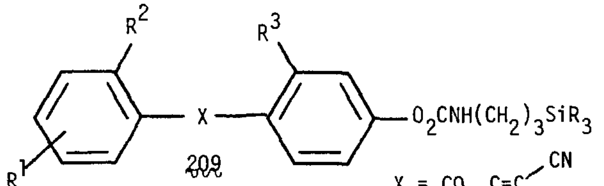
(512)

X= PhS, MeS, $PhSO_2$ (see also ref. 284)



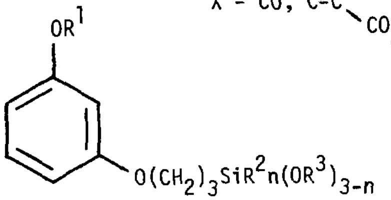
R= H 10 pts
R= TMS 1 pt

The γ-functional silanes 209 [367], 210 [368], and 211 [369] and related systems were reported. Compounds of the type 209 and 210 are ultraviolet absorbers.

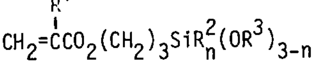


209

X = CO, $C{=}C(CN)CO_2R$



210

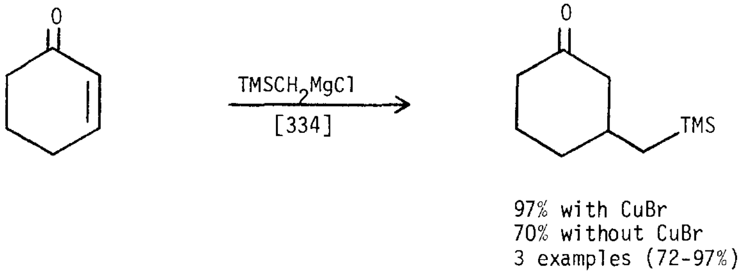


$$CH_2{=}C(R^1)CO_2(CH_2)_3SiR^2_n(OR^3)_{3-n}$$

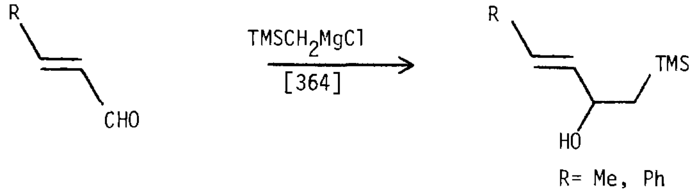
211

XIV. MISCELLANEOUS FUNCTIONAL ORGANOSILANES

Cyclohexenone reacts with trimethylsilylmethylmagnesium chloride in a Michael fashion (Eqn. 513) whereas the reaction with crotonaldehyde or cinnamaldehyde proceeds in a 1,2 fashion (Eqn. 514).

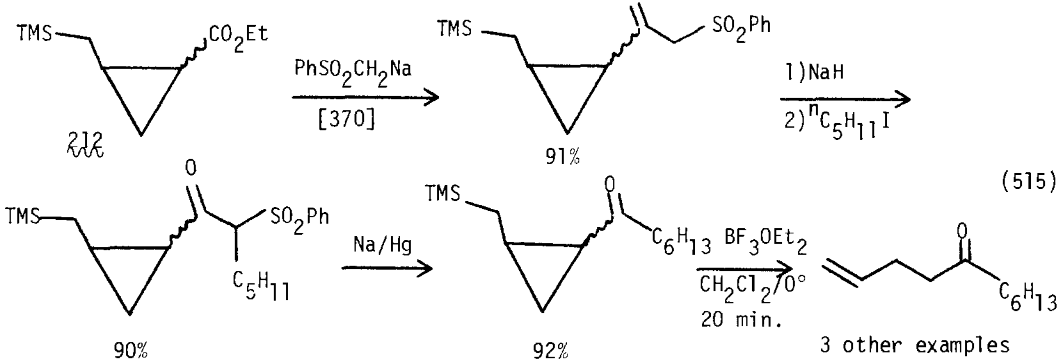


(513)



(514)

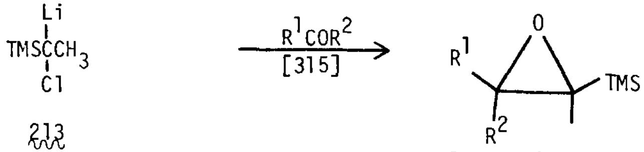
(Trimethylsilylmethyl)cyclopropyl ester 212 was converted to γ,δ-unsaturated ketones according to Eqn. 515.



(515)

XV. α,β-EPOXYSILANES

Excellent yields of α,β-epoxysilanes were obtained from the α-chloro-α-silyllithium reagent 213 and aldehydes and ketones. (Eqn. 516) This approach



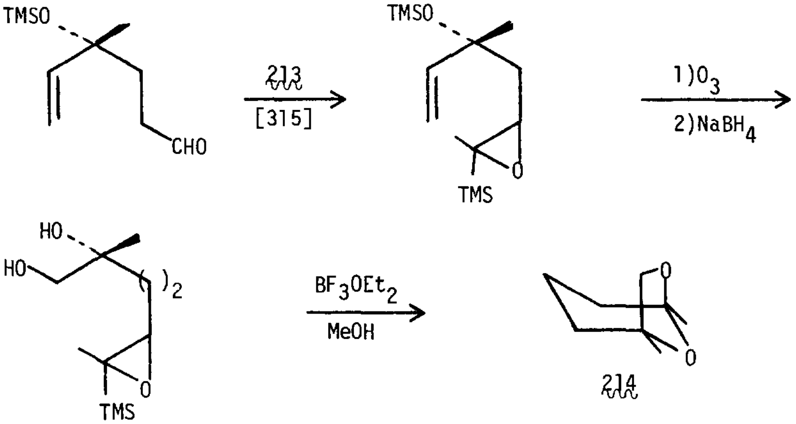
213

(see Eqn. 375)

R^1 and $R^2 \neq$ H 11 examples (35-96%)
R^1 or $R^2 =$ H 7 examples (53-96%)

(516)

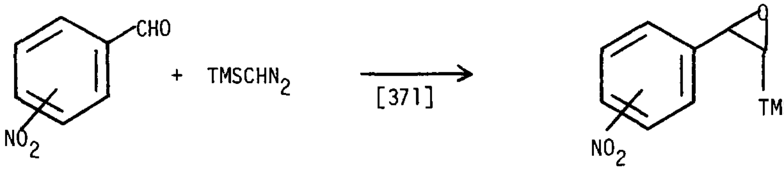
was used to prepare R(+) Frontalin, the aggregation pheromone of the southern pine beetle, 214 (Dendroctonus frontalis). (Eqn. 517)



214

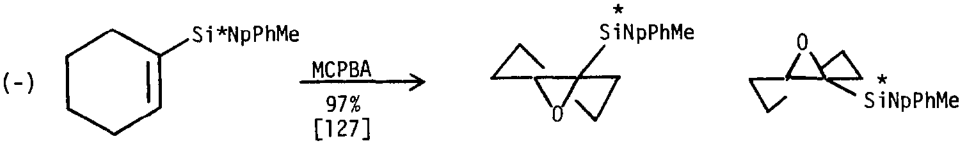
(517)

Silylated styrene oxides were prepared from aryl aldehydes and trimethylsilyldiazomethane. (Eqn. 518)



(518)

The optically active vinylsilane 215 gave the corresponding epoxysilanes, but with very poor asymmetric induction. (Eqn. 519)



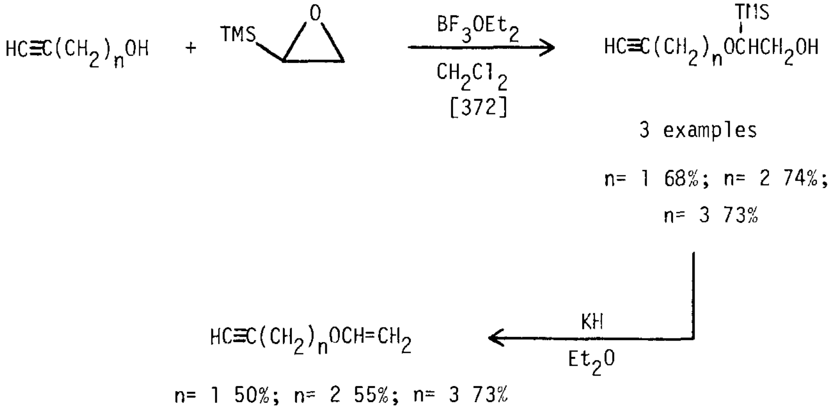
215

43 pts

57 pts

(519)

Acetylenic vinyl ethers were prepared from acetylenic alcohols and epoxysilanes as shown in Eqn. 520. Acetylenic vinyl esters were also prepared. (Eqn. 521)



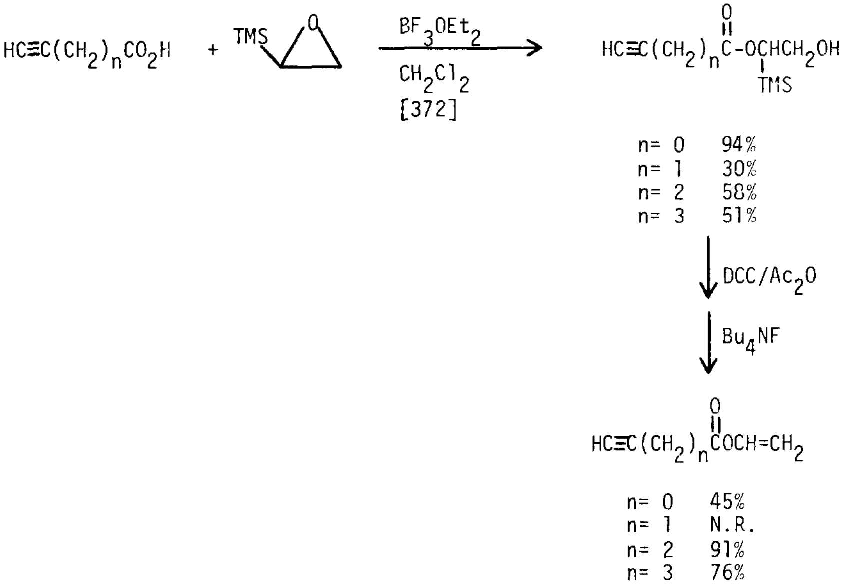
$$HC{\equiv}C(CH_2)_nOH + \text{TMS-oxirane} \xrightarrow[\substack{CH_2Cl_2 \\ [372]}]{BF_3OEt_2} HC{\equiv}C(CH_2)_nO\overset{\text{TMS}}{C}HCH_2OH \quad (520)$$

3 examples

n= 1 68%; n= 2 74%; n= 3 73%

$$\xrightarrow[Et_2O]{KH} HC{\equiv}C(CH_2)_nOCH{=}CH_2$$

n= 1 50%; n= 2 55%; n= 3 73%



$$HC{\equiv}C(CH_2)_nCO_2H + \text{TMS-oxirane} \xrightarrow[\substack{CH_2Cl_2 \\ [372]}]{BF_3OEt_2} HC{\equiv}C(CH_2)_n\overset{O}{\overset{\|}{C}}\text{-}O\underset{\text{TMS}}{C}HCH_2OH \quad (521)$$

n= 0	94%
n= 1	30%
n= 2	58%
n= 3	51%

$$\downarrow DCC/Ac_2O$$

$$\downarrow Bu_4NF$$

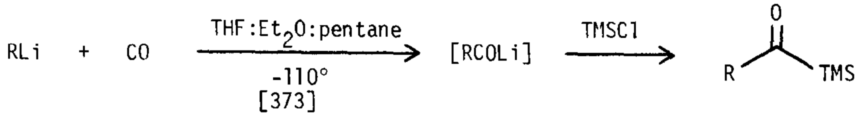
$$HC{\equiv}C(CH_2)_n\overset{O}{\overset{\|}{C}}OCH{=}CH_2$$

n= 0	45%
n= 1	N.R.
n= 2	91%
n= 3	76%

XVI. ACYLSILANES

A. Preparation

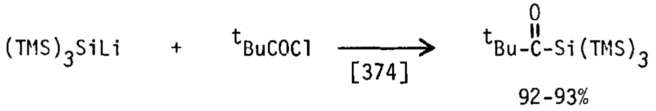
The most direct approach to acylsilanes to appear is the direct generation of an alkyllithium reagent in the presence of trimethylchlorosilane. (Eqn. 522)



(522)

R	% Yield (GLC)	% Yield (distilled)
^{n}Bu	77	45
^{n}C$_5$H$_{11}$	71	45
^{n}C$_6$H$_{13}$	80	71
^{i}Bu	75	50
(CH$_3$)$_2$CHCH$_2$CH$_2$	87	65
^{i}Pr	28	-
^{t}Bu	50	-
^{s}Bu	30	-

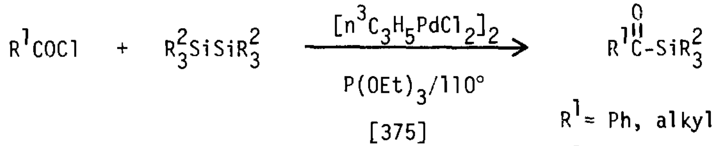
Tris(trimethylsilyl)silyllithium was reacted with pivaloyl chloride to give the corresponding acylsilane in high yield. (Eqn. 523)



$$(\mathrm{TMS})_3\mathrm{SiLi} \quad + \quad {}^t\mathrm{BuCOCl} \xrightarrow[{[374]}]{} {}^t\mathrm{Bu}\text{-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{-}\mathrm{Si}(\mathrm{TMS})_3 \qquad (523)$$

92-93%

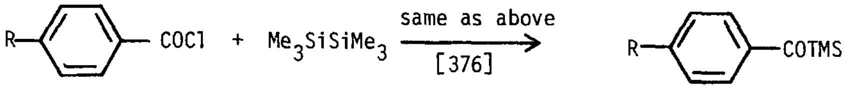
The coupling of disilanes with acyl chlorides gives acylsilanes. (Eqn. 524) This methodology was applied to the preparation of benzoylsilanes in particular. (Eqn. 525)



$$\mathrm{R^1COCl} \quad + \quad \mathrm{R^2_3SiSiR^2_3} \xrightarrow[\mathrm{P(OEt)_3/110^\circ}\ [375]]{[\eta^3\mathrm{C_3H_5PdCl_2}]_2} \mathrm{R^1}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{-}\mathrm{SiR^2_3} \qquad (524)$$

R^1= Ph, alkyl, furyl

R^1= Ph, 97.5% yield

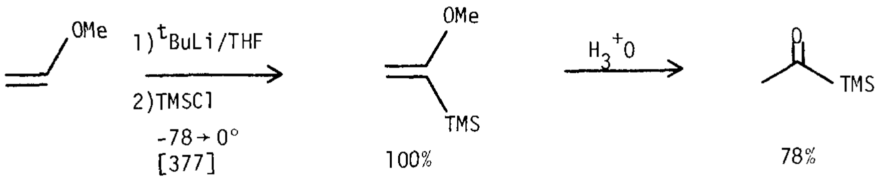


(525)

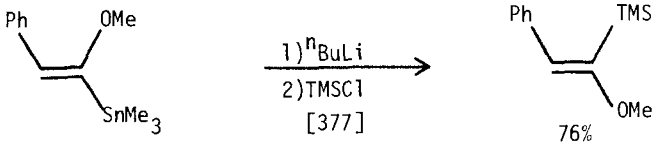
R= Cl, Br, NO$_2$, CO$_2$Me

R= Cl 71%

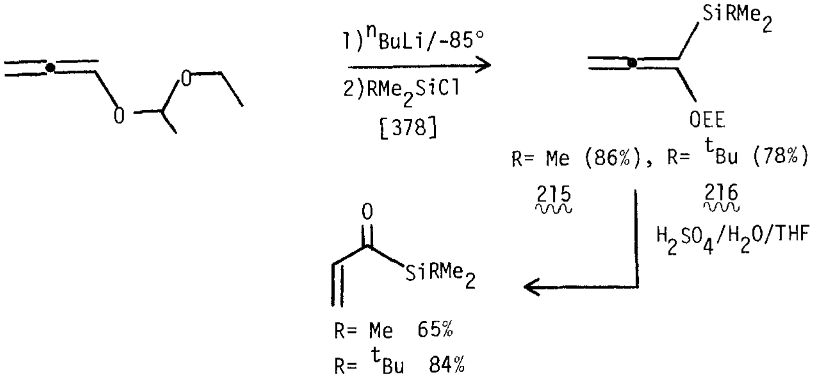
The metalation-silylation of vinyl ethers gives the acylsilane in the protected state. Hydrolysis of the α-silylvinyl ether gives the acylsilane. Examples of this useful approach are given below. (Eqns. 526-532)



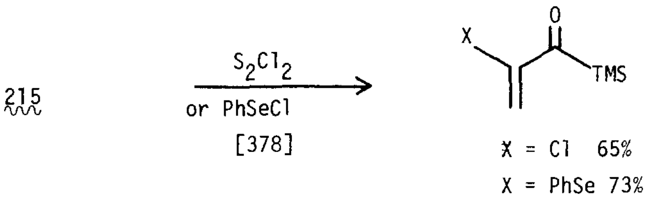
(526)



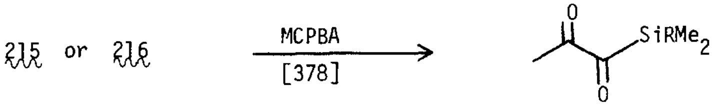
(527)



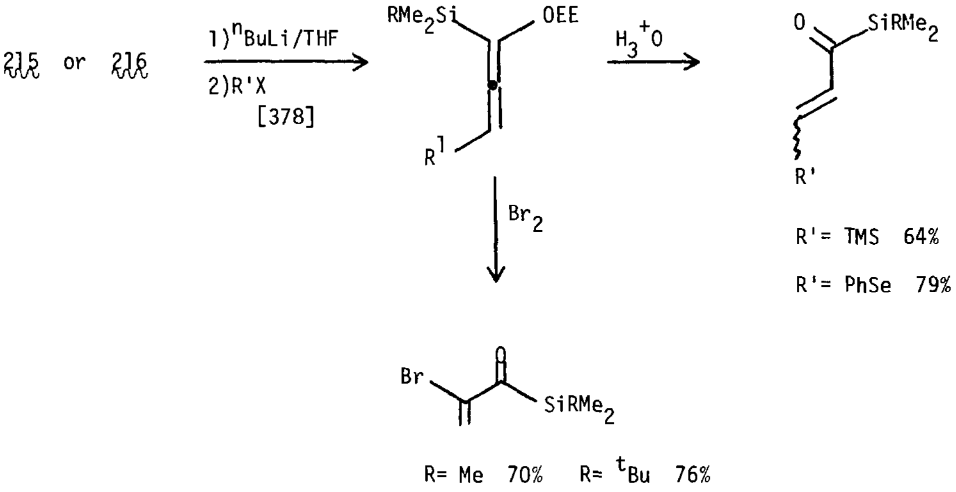
(528)



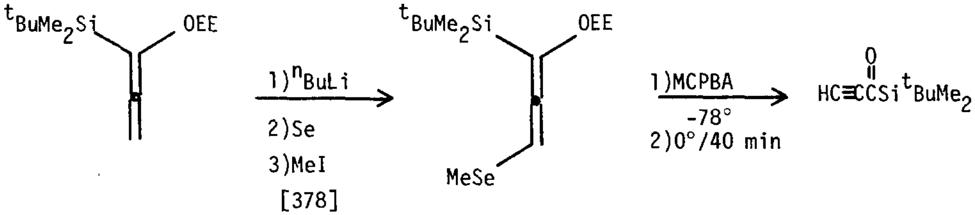
(529)



(530)

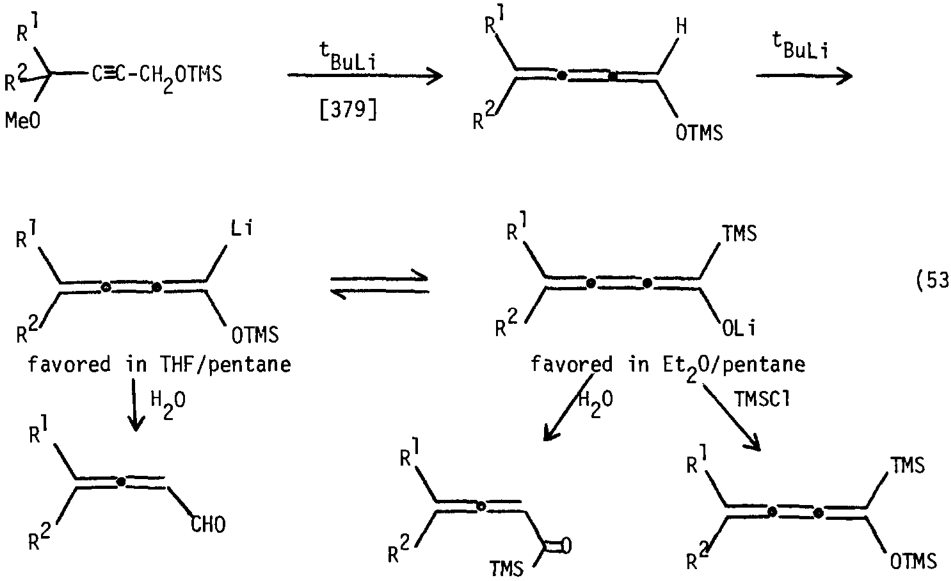


(531)



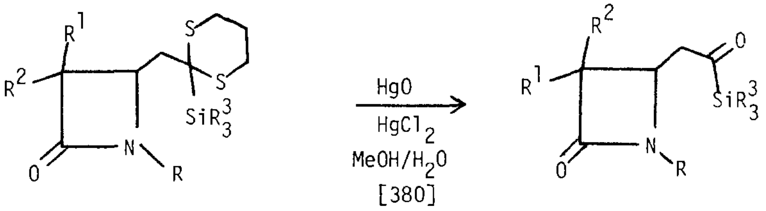
(532)

In a related reaction the product distribution was solvent dependent.



(533)

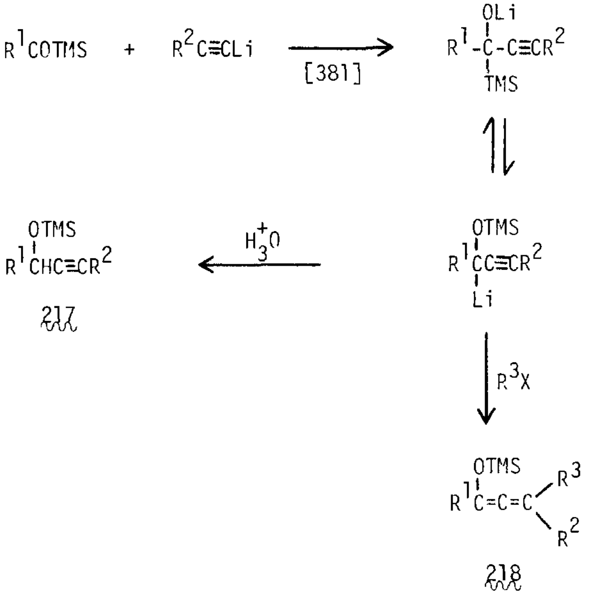
Acylsilane derivatives of carbapenenes were obtained via deprotection of the α-silyl-1,3-dithianes. (Eqn. 534)



(534)

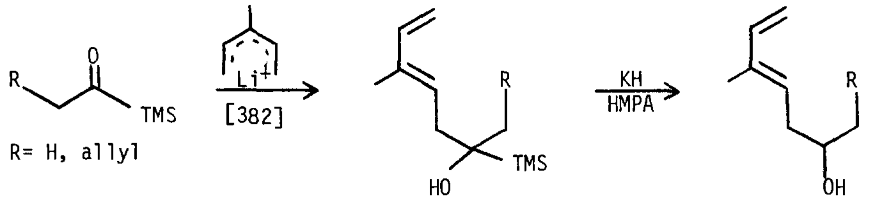
B. Reactions

Acylsilanes react with nucleophiles at the carbonyl carbon to give α-oxidosilanes, which can undergo a Brook rearrangement to give the silyloxymethyllithium derivative. Some examples are given below. (Eqn. 535) The reaction of an acylsilane with an alkynyllithium reagent gives a Brook rearrangement to give the propargyllithium reagent, which is in equilibrium with the allenyllithium reagent. (Eqn. 535) Protonation gives the silylated propargyl alcohol **217**. Alkylation leads to the allenyloxysilane **218**.

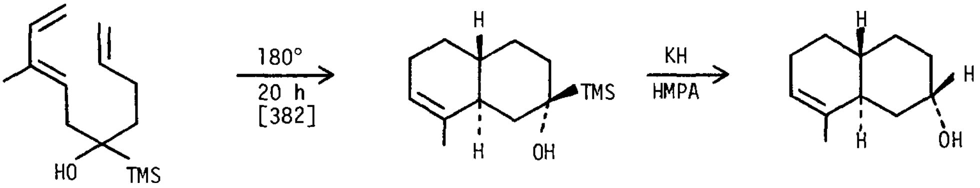


(535)

The reaction of 3-methylpentadienyllithium with acylsilanes was used to prepare a precursor for intramolecular Diels-Alder reaction. (Eqn. 536-537) Note that the Brook rearrangement in Eqn. 537 occurs with retention at carbon.

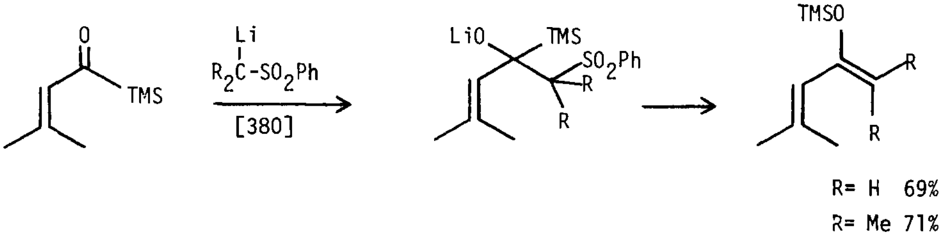


(536)

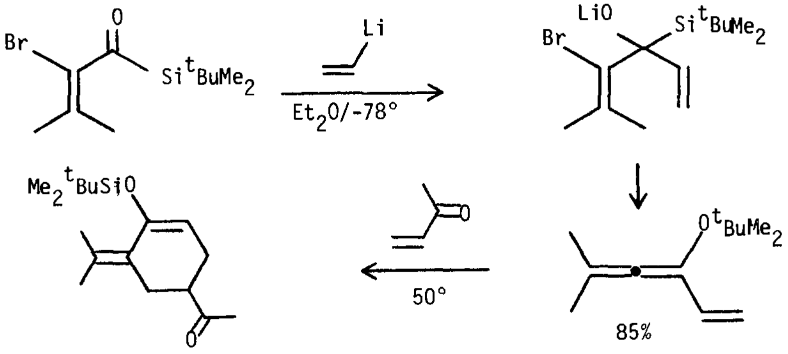


(537)

Some interesting and useful dienes were generated from acylsilanes as shown in Eqns. 538-539.

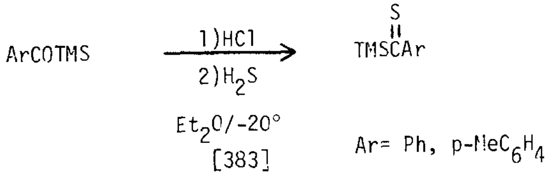


(538)



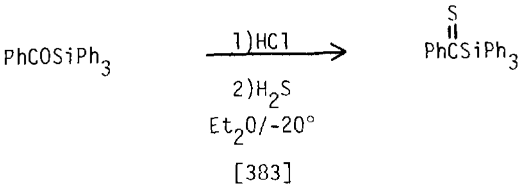
(539)

Benzoyltrimethylsilanes were reacted with H_2S in the presence of acid to give the thioacylsilanes, which were too unstable to isolate. (Eqn. 540) The triphenylsilyl system gave a product, which was also unstable. (Eqn. 541)



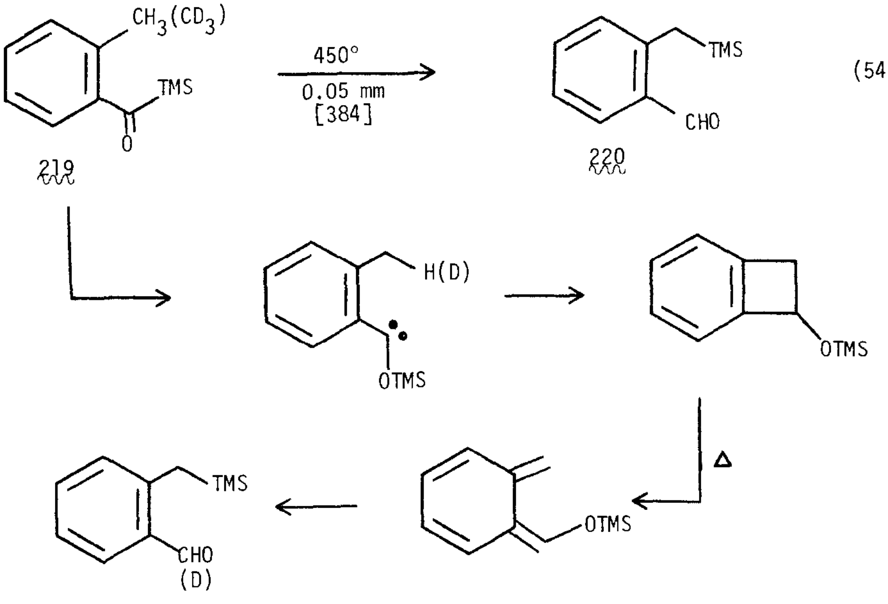
$$\mathrm{ArCOTMS} \xrightarrow[\substack{2)\,\mathrm{H_2S} \\ \mathrm{Et_2O}/-20^\circ \\ [383]}]{1)\,\mathrm{HCl}} \mathrm{TMS}\overset{\overset{\displaystyle S}{\|}}{\mathrm{C}}\mathrm{Ar} \qquad (540)$$

$$\mathrm{Ar} = \mathrm{Ph},\ p\text{-}\mathrm{MeC_6H_4}$$

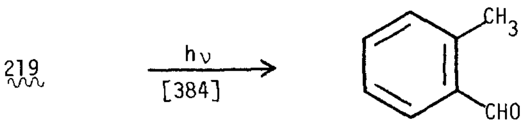


$$\mathrm{PhCOSiPh_3} \xrightarrow[\substack{2)\,\mathrm{H_2S} \\ \mathrm{Et_2O}/-20^\circ \\ [383]}]{1)\,\mathrm{HCl}} \mathrm{Ph}\overset{\overset{\displaystyle S}{\|}}{\mathrm{C}}\mathrm{SiPh_3} \qquad (541)$$

The benzoylsilane 219 was vacuum pyrolyzed to give the benzylsilane 220. A carbene intermediate is proposed. (Eqn. 542) Photolysis of 219 gives protodesilylation. (Eqn. 543)

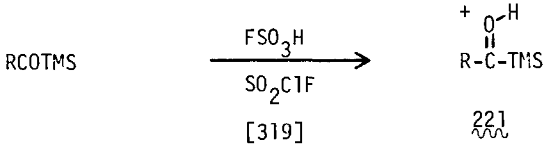


(542)



(543)

Protonation of acylsilanes gave carbenium ions that show significant deshielding of the carbonyl carbon in 221 in the NMR compared to the carbon analog. (Eqn. 544)



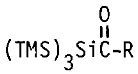
$$RCOTMS \xrightarrow[SO_2ClF]{FSO_3H} R\overset{\overset{+}{O}-H}{\overset{\|}{C}}-TMS \qquad (544)$$

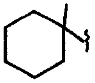
[319]

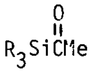
221 R= Me, Ph

C. Spectroscopic Studies

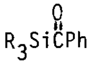
A complete NMR (^{13}C, ^{29}Si) of a series of acylsilanes has been reported. The systems studied are listed below. [385]



$(TMS)_3Si\overset{O}{\overset{\|}{C}}-R$ R= ^tBu, Et_3C,  , 1-Ad, Ph, $pMeOC_6H_4$, $oMeOC_6H_4$, CF_3, C_6F_5, OH, $OSiPh_3$



$R_3Si\overset{O}{\overset{\|}{C}}Me$ R= Me, Ph



$R_3Si\overset{O}{\overset{\|}{C}}Ph$ R= Me, Et, Ph

XVII. REACTIVE INTERMEDIATES

A. Silicon Radicals

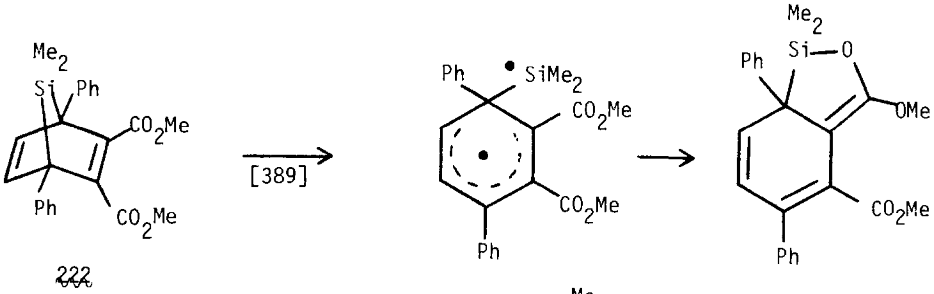
The Arrhenius parameters for the abstraction of H· from trimethylsilane with $^tBu\cdot$ have been determined and the results with those for the abstraction from 2-methylpropane. The parameters could be expressed by the following rules: log A= 8.4 ± 0.5 L/mol-5 per H and Ea (kcal/mol)= 0.42 ΔH + 8.7 (±0.7). [386] A low pressure technique was used to measure the rate constants of the equilibrium shown in Eqn. 545 between trimethylsilane and bromine radical.

$$Br\cdot + Me_3SiH \xrightarrow[k_{-1}]{k_1} Me_3Si\cdot + HBr \qquad (545)$$

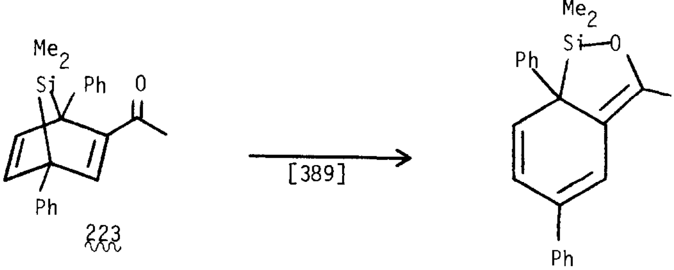
[387]

Triphenylsilylanion reacts with p-terphenyl when photolyzed to produce the p-terphenyl anion radical and triphenylsilyl radical, which dimerizes to give hexaphenyldisilane. [388]

Thermolysis of the 7-silanorbornadiene 222 was shown to proceed via silyl radicals and not via silepin or silanorcaradiene as previously proposed. (Eqn. 546) Compound 223 reacts analogously. (Eqn. 547)



(546)



(547)

The reaction of triethylsilyl radicals with alkyl halides using laser flash photolysis. Some of the rate constants at 300°K are given below. Arrhenius parameters were determined for a few cases. The data obtained were combined with literature data to calculate a rate of inversion of silyl radicals of $6.8 \times 10^{-9}\ s^{-1}$ at 80°, $t_{1/2}$ 104 ps or a 5.6 kcal/mol barrier. [390]

EtI	PhBr	^tBuCl	$PhCH_2F$	
4.3×10^9	1.1×10^8	1.7×10^6	$< 10^5$	$M^{-1}s^{-1}$

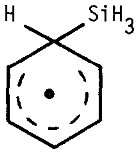
Triethylsilyl radicals were employed in the dehydrobromination of exo and endo-2-bromonorbornenes. [391]

The addition of triethylsilyl radicals to carbonyls is subject to polar effects and, therefore, show a wide range of reactivities. Some of the data obtained is shown below.

carbonyl	$k(M^{-1}s^{-1})$ at 300 K
duroquinone	2.5×10^9
benzil	3.3×10^8
Propionic anhydride	1.6×10^6
3-pentanone	2.8×10^5
ethylformate	3.5×10^4

The relative rates of addition of $Cl_3Si\cdot$ to alkenes were determined. All monosubstituted olefins react at nearly the same rate whereas isobutene is somewhat faster, especially at lower temperatures. [393] The kinetics of the gas-phase addition of $Cl_3Si\cdot$ to cis and trans-2-butene imply a fairly loose transition state. The $Cl_3Si\cdot$ is electrophilic and subject to steric factors. [394] In another study of the reaction of cis and trans-2-butene with $Cl_3Si\cdot$ the rate of the cis-trans isomerization was also measured. [395]

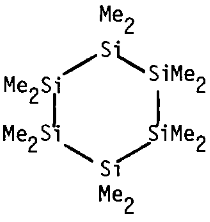
An ab initio optimized geometry of the intermediate 6-silylcyclohexadienyl radical 223a, obtained from radical addition to benzene, shows it to have 4.3° out-of-plane angle. [396]



223a

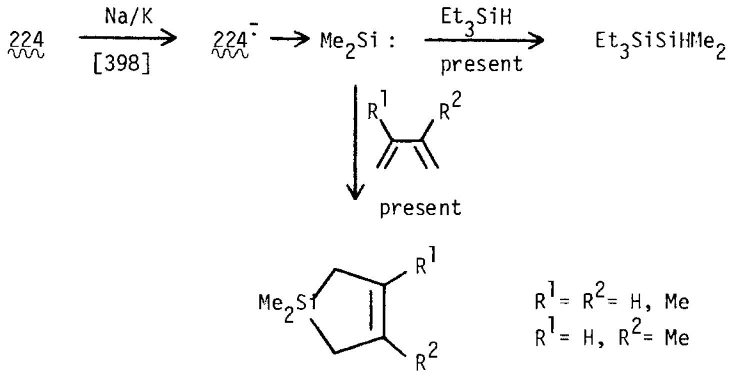
B. Silylenes

Dimethylsilylene generated photochemically from 224, was inserted into OH, OSi and SiH bonds. The relative reactivities are OH > SiH ∿ SiO. [397]



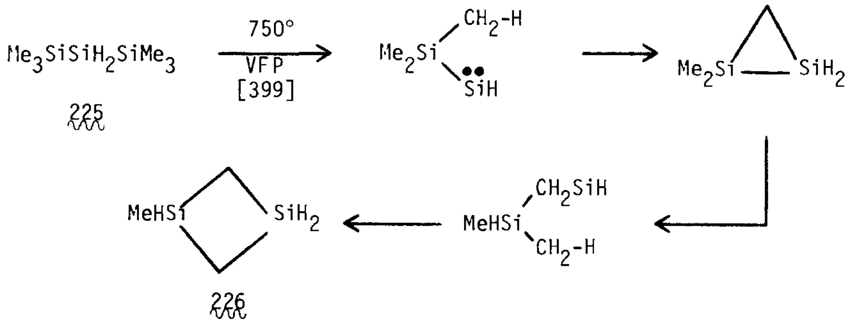
224

Treatment of 224 with Na/K in THF is a source of dimethylsilylene as seen from Eqn. 548.



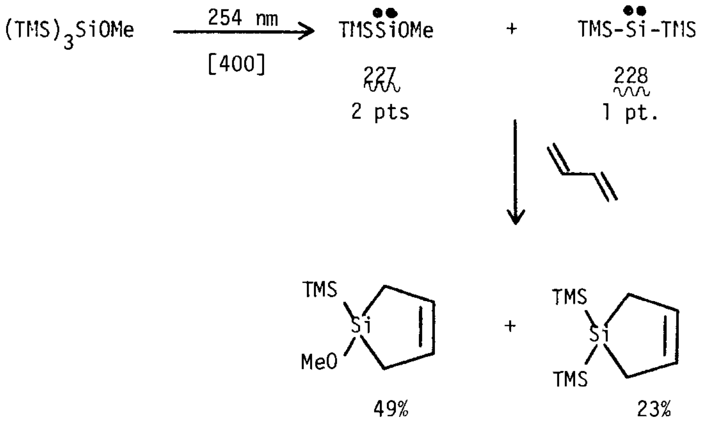
(548)

The pyrolysis of trisilane 225 leads to disilacylobutane 226 via the silylene as shown. (Eqn. 549) The reaction of recoiling silicon atoms with trimethylsilane gives 225 among other products.



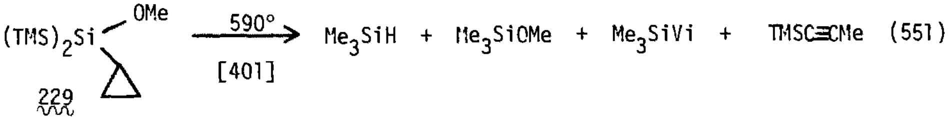
(549)

Photolysis of tris(trimethylsilyl)methoxysilane gives two trimethylsilylsilylenes 227 and 228. In the presence of 1,3-butadiene the corresponding silacyclopentenes are obtained.

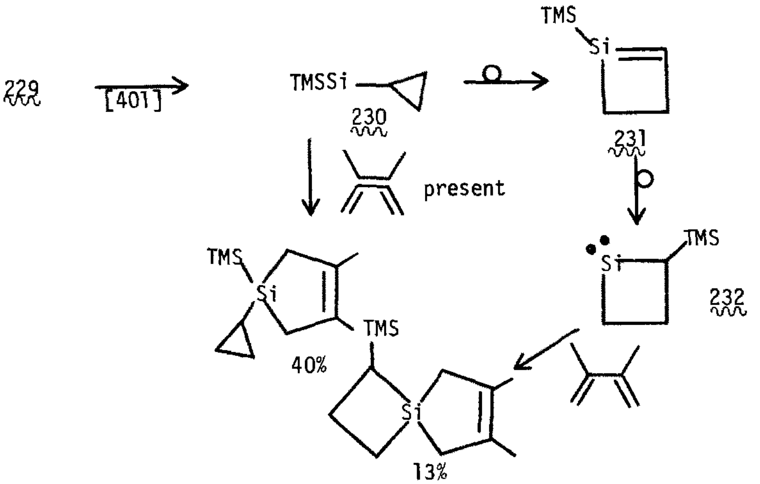


(550)

Pyrolysis of methoxycyclopropylsilane 229 produces trimethylsilylcyclopropylsilylene, 230, which gives several products. It will add to dienes as such or rearrange to silane 231 and then to a new silylene 232 before addition to the diene. (Eqn. 552) The pyrolysis of bis(trimethylsilyl)allylylmethoxysilane leads to similar results. [401]

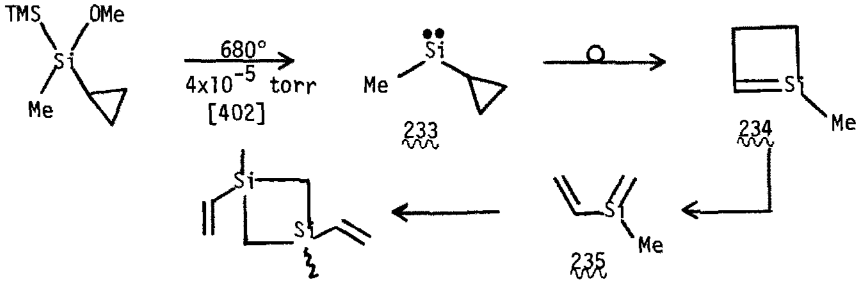


$$\text{(TMS)}_2\text{Si} \xrightarrow[\text{[401]}]{590^\circ} \text{Me}_3\text{SiH} + \text{Me}_3\text{SiOMe} + \text{Me}_3\text{SiVi} + \text{TMSC}{\equiv}\text{CMe} \quad (551)$$



(552)

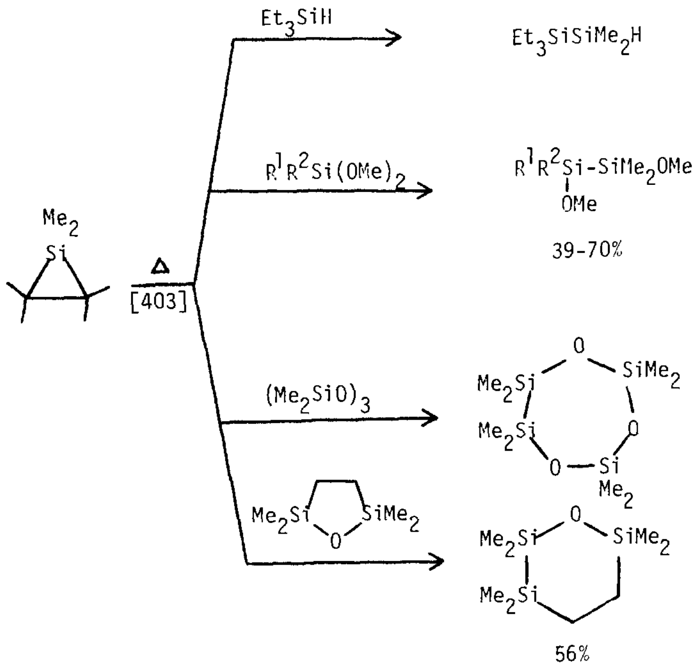
In a related system the silylene to silene rearrangement (233→234) occurs; the silane does not undergo migration to a new silylene but opens to another silene 235. (Eqn. 553)



(553)

1:1 cis:trans

Thermolysis of hexamethylsilirane gives dimethylsilylene. This generation of dimethylsilylene was carried out in the presence of a variety of reagents. (Eqns. 554-557)



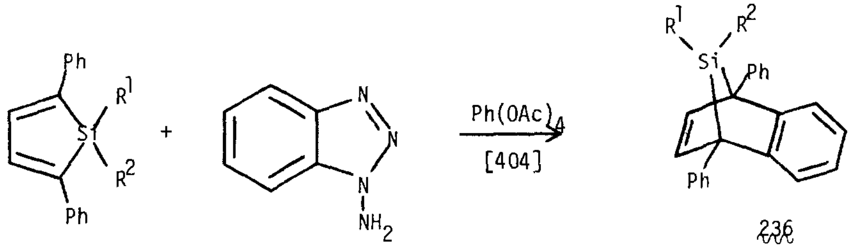
(554)

(555)

(556)

(557)

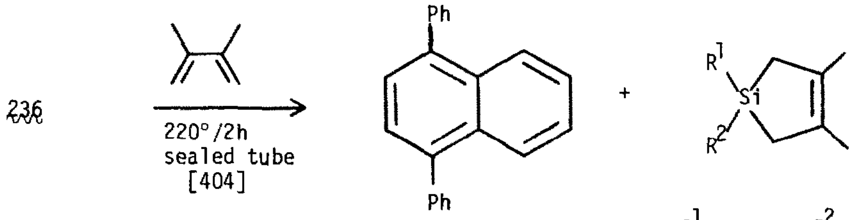
Thermolysis of a series of benzo-7-silanorbornadienes 236 (Eqn. 558) gives silylenes. (Eqn. 559) In particular compound 237 provides evidence for a silylene to disilene rearrangement. (Eqn. 560)



(558)

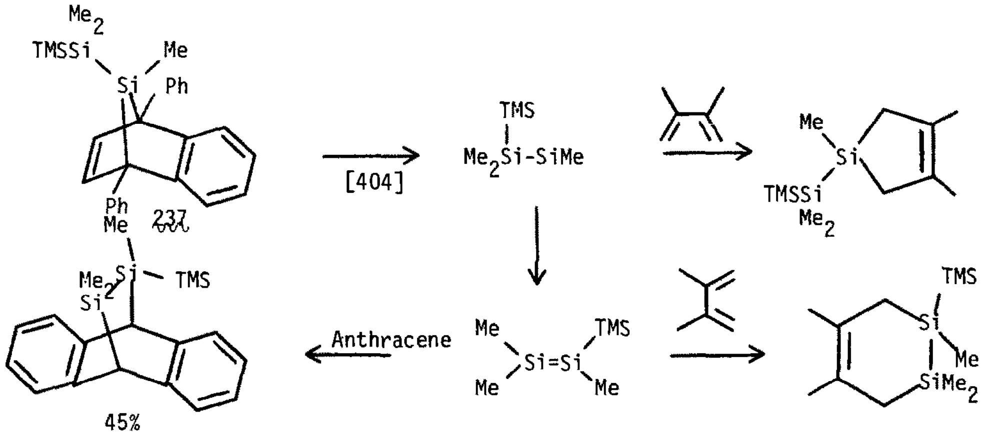
236

R^1	R^2	% Yield
Me	Me	38
Me	TMS	63
Me	$PhMe_2Si$	30
TMS	TMS	39
Me	$TMSSiMe_2$	79



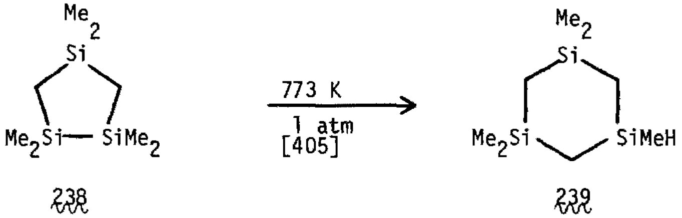
(559)

R^1	R^2	% Yield
Me	Me	40
Me	TMS	40
Me	$PhMe_2Si$	44
TMS	TMS	50

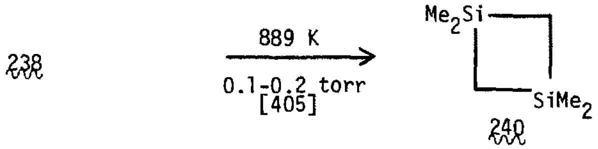


(560)

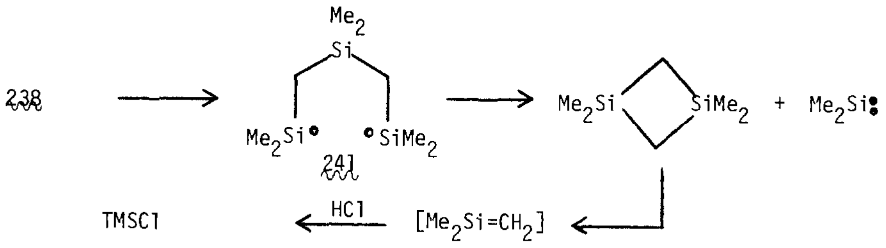
The pyrolysis of the trisilacyclopentane, 238 leads to the trisilacyclohexane 239 at high pressures in a radical reaction and to mostly disilacyclobutane 240 at lower pressures. Trapping (HCl) experiments indicate that the disilacyclobutane does not arise solely from silene formation, but rather at least in part from the free radicals 241 which lose dimethylsilylene. (Eqns. 561-563)



(561)

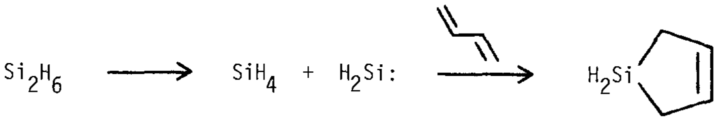


(562)



(563)

The single-pulse shock tube technique has been applied to the decomposition of disilane. Two primary processes are observed. (Eqns. 564-565) The silylene produced in Eqn. 564 is efficiently trapped by butadiene.

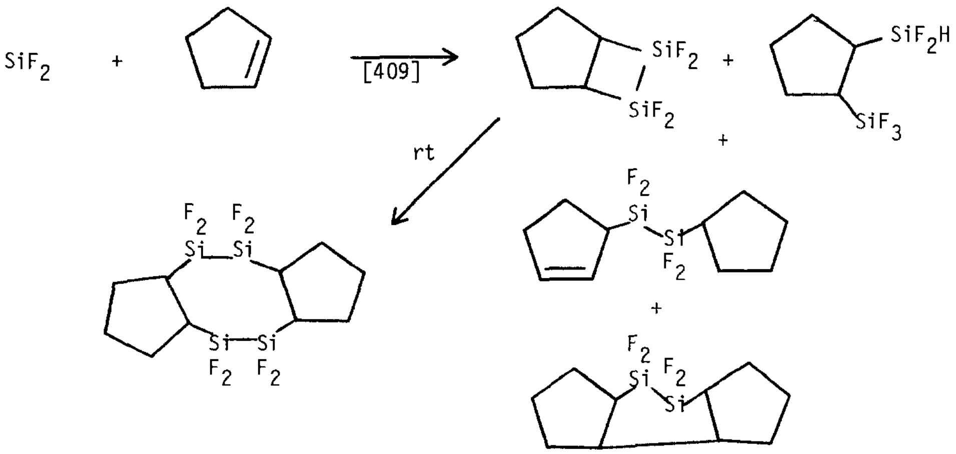


(564)

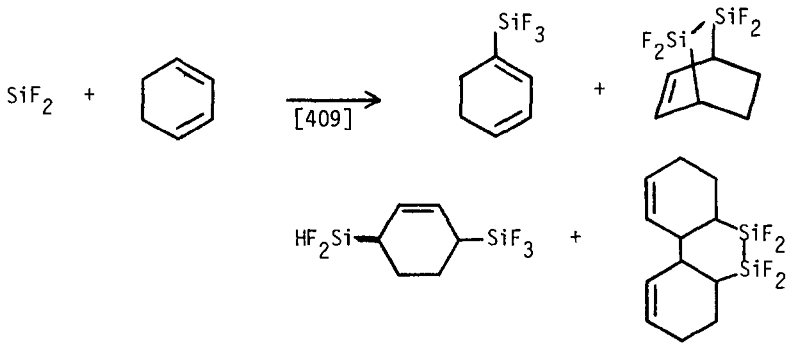
$$Si_2H_6 \longrightarrow H_2Si{=}SiH_2 \quad + \quad H_2 \qquad (565)$$

Calculations indicate that the insertion of silylene into dihydrogen requires 36 kJ/mol compared to the insertion of carbene, which has no activation barrier. [407]

Two studies of difluorosilylene were reported. The reaction with isonitriles polymerization was induced via radicals generated in the attack of the isonitrile or the difluorosilylene. [408] In the second study difluorosilylene was allowed to react with cyclopentene and 1,3-cyclohexadiene to give the products shown below. (Eqns. 566-567) A radical mechanism is argued.



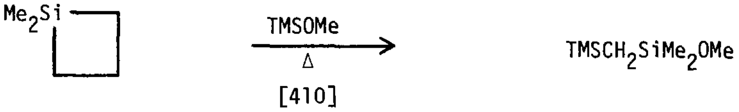
(566)



(567)

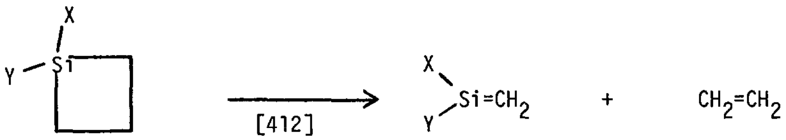
C. Silenes

The generation of silenes from silacyclobutanes or disilacyclobutanes remained popular. These are presented first. Dimethylsilene was shown to add regiospecifically to trimethylmethoxysilane. (Eqn. 568) The kinetics of this reaction have been studied. [411]



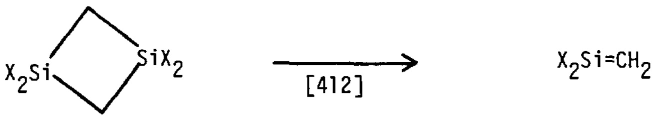
(568)

Halogenated silenes were generated from the appropriately halogenated silacyclobutanes and disilacyclobutanes. (Eqns. 569-570) The results are compared with those obtained from mass spectral studies. The thermal degradation of 1,1-dichloro-1-silacyclobutane was studied by impulse pyrolytic chromatography-mass spectroscopy. [413]



(569)

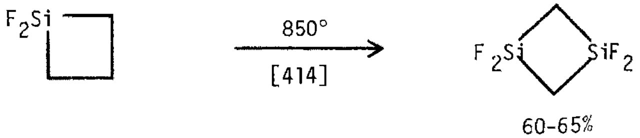
X= Y= F, Cl
X= F, Y= Me
X= Cl, Y= Me



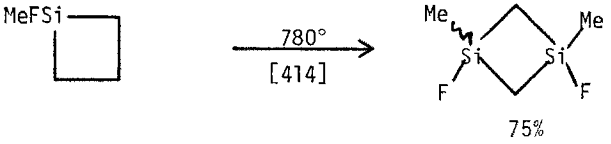
(570)

X= F, Cl

Thermolysis of 1,1-difluoro-1-silacyclobutane and 1-methyl-1-fluoro-1-silacyclobutane gives the head to tail dimers of the resulting silene. (Eqns. 571-572.

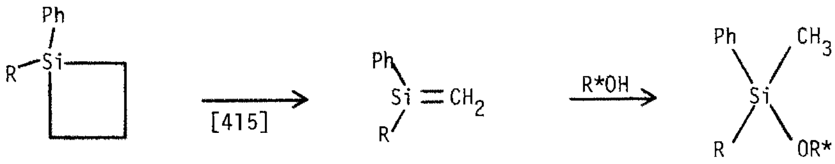


(571)



(572)

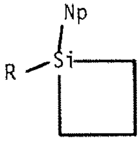
The generation of prochiral silenes and their insertion into optically active alcohols. In most cases there was no asymmetric induction. (Eqn. 573)



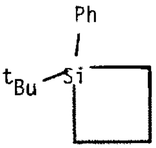
(573)

R= H, Vi, Et, ^{t}Bu

R*OH= menthol, borneol, isoborneol

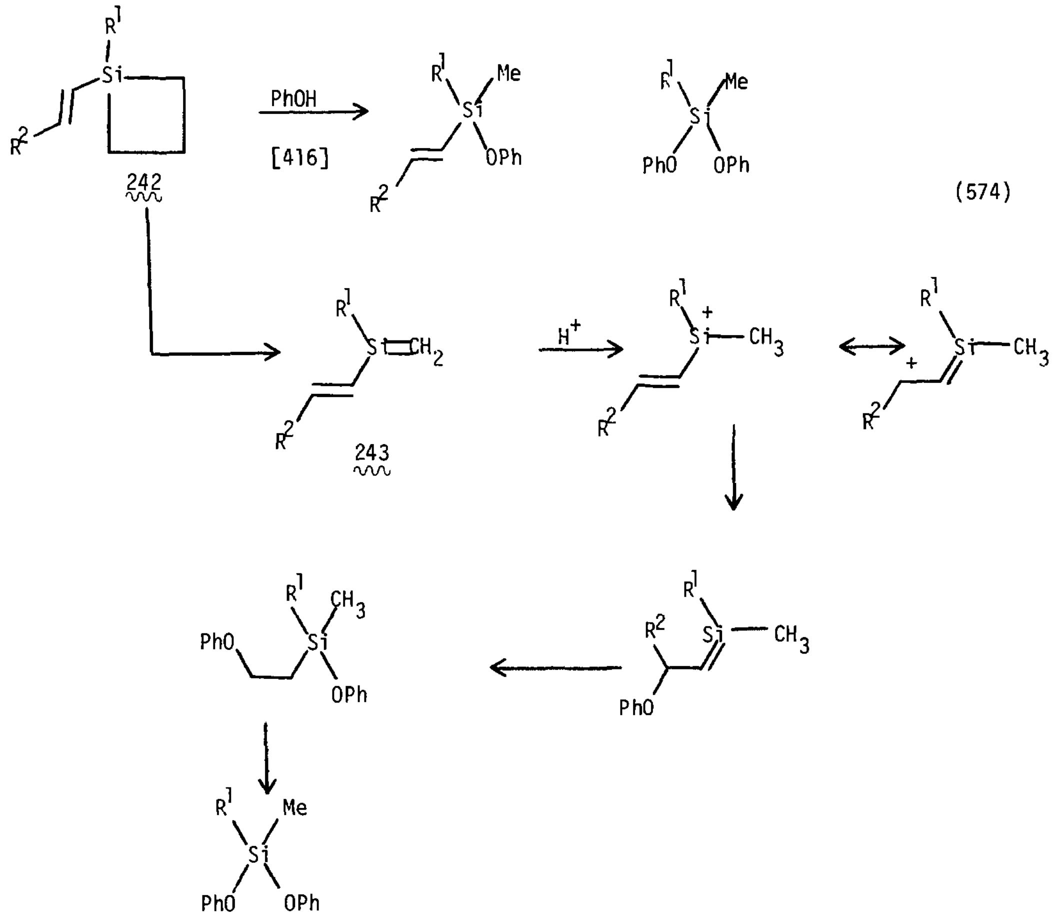


did not react

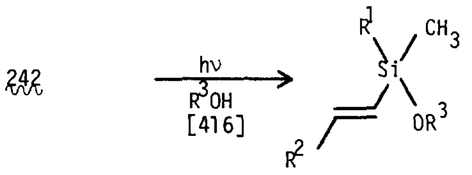


with isoborneol gave 65:35 mixture of diastereomers

The vinylsilacyclobutane 242 is pyrolyzed to give vinylsilanes, 243. The pyrolysis in the presence of phenol gives both phenoxy and diphenoxysilanes. An allylic silicenium ion is argued. (Eqn. 574) The photolysis proceeds normally. (Eqn. 554)

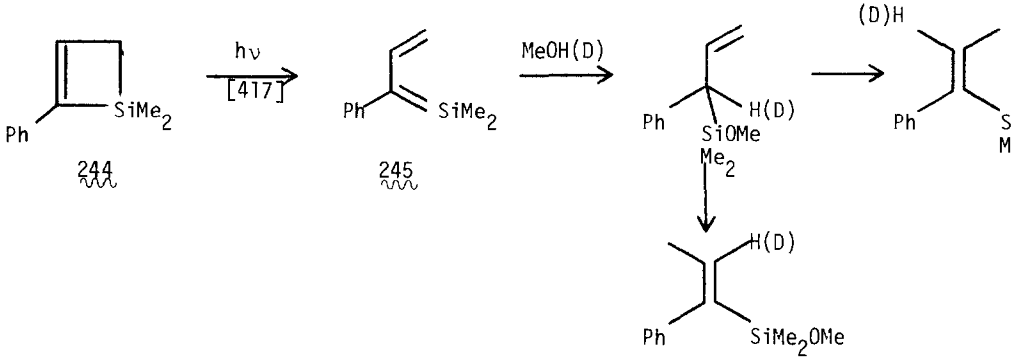


(574)

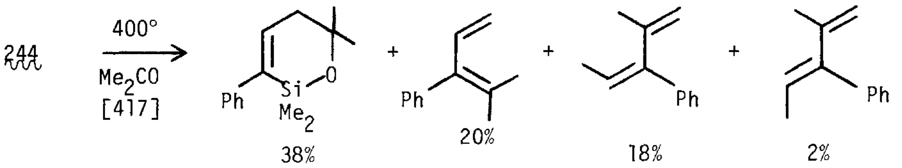


(575)

A 1-sila-1,3-butadiene 245 is the proposed intermediate from the photolysis of 244. (Eqn. 576) Pyrolysis in the presence of acetone gave the results in Eqn. 577.

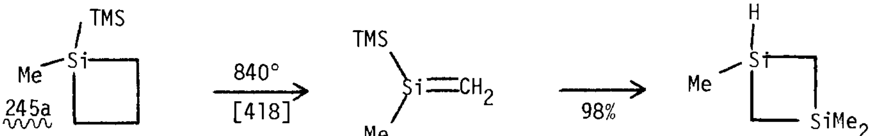


(57



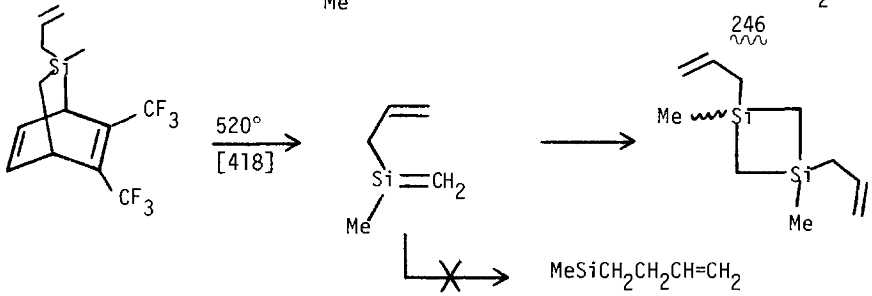
(577)

In order to further test the silene to silylene rearrangement of trimethylsilylsilenes, these species were generated from silacyclobutane 245a. This gave disilacyclobutane 246 in 98% yield. (Eqn. 557) The allylsilene 247, however, did not undergo the silene to silylene rearrangement. (Eqn. 579)



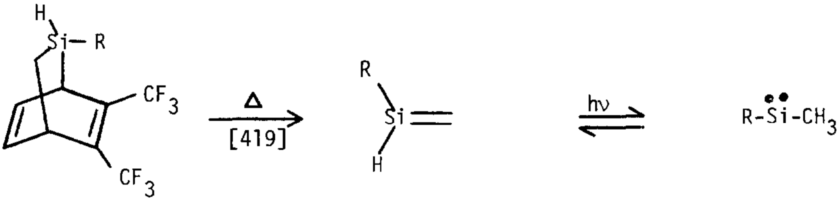
246

(578)



(579)

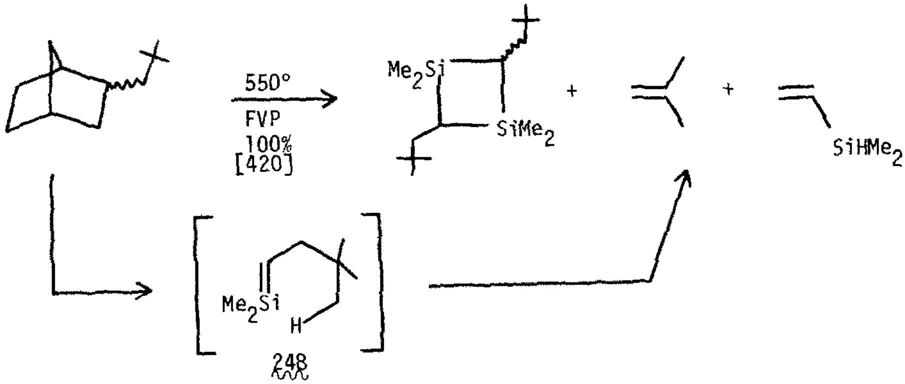
Thermally generated silenes were found to undergo reversible photoisomerization with their isomeric silylenes. (Eqn. 580)



(580)

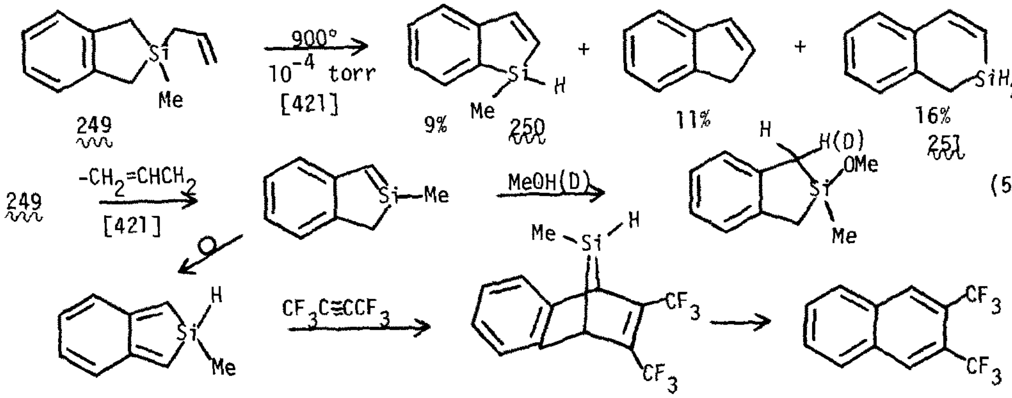
matrix isolation

An intramolecular silene ene reaction has been reported via the silene 248. (Eqn. 581) Thus, the formation of equal amounts of isobutene and dimethylvinylsilane are used as an indication of the silene ene reaction.



(581)

The pyrolysis of silaindene 249 generates silaindene 250, which undergoes a 1,5-hydrogen shift to give the benzosilole 251. This can be trapped. (Eqn. 583)



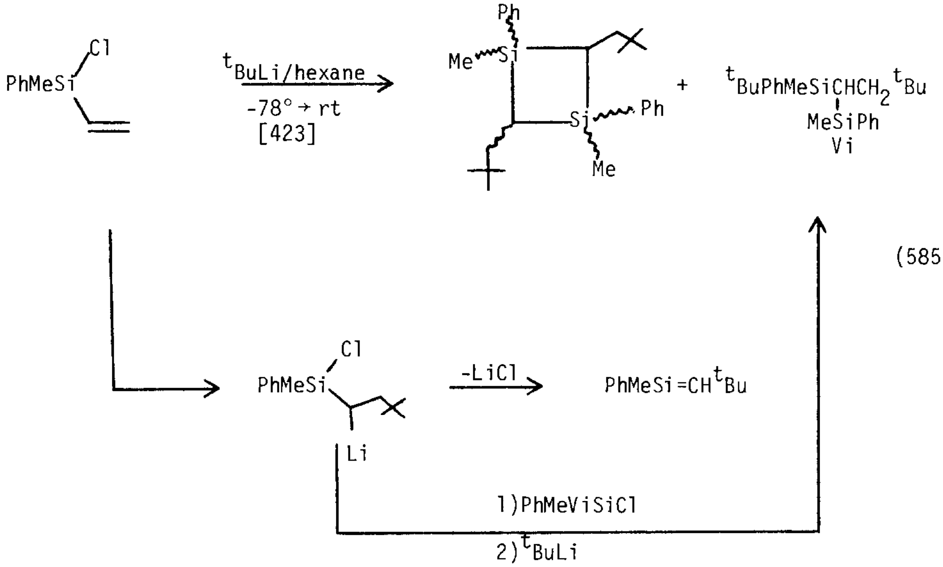
(582)

(583)

The mercury sensitized photolysis of tetramethylsilane gives trimethylsilylmethyl radical, which loses a methyl radical to form dimethylsilene. (Eqn. 584) The activation energy of the reaction and the heat of formation of dimethylsilene were determined. The π bond energy was established to be 189 kJ/mol.

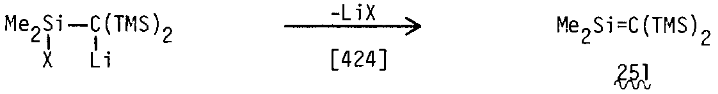
$$\begin{tikzcd}
Me_4Si + Hg(^3P_1) \arrow[r, "{[422]}"'] & Hg(^1S_0) + H\cdot + Me_3SiCH_2\cdot \arrow[d, "-CH_3\cdot"] \\
& Me_2Si{=}CH_2
\end{tikzcd} \qquad (584)$$

The reaction of tert-butyllithium with phenylmethylvinylchlorosilane in hexane gives six products. (Eqn. 564) The products arise from addition of the lithium reagent to the double bond followed by elimination of LiCl to give the silene, which then gives the disilacyclobutanes. The acyclic compound arises from straightforward substitution chemistry.



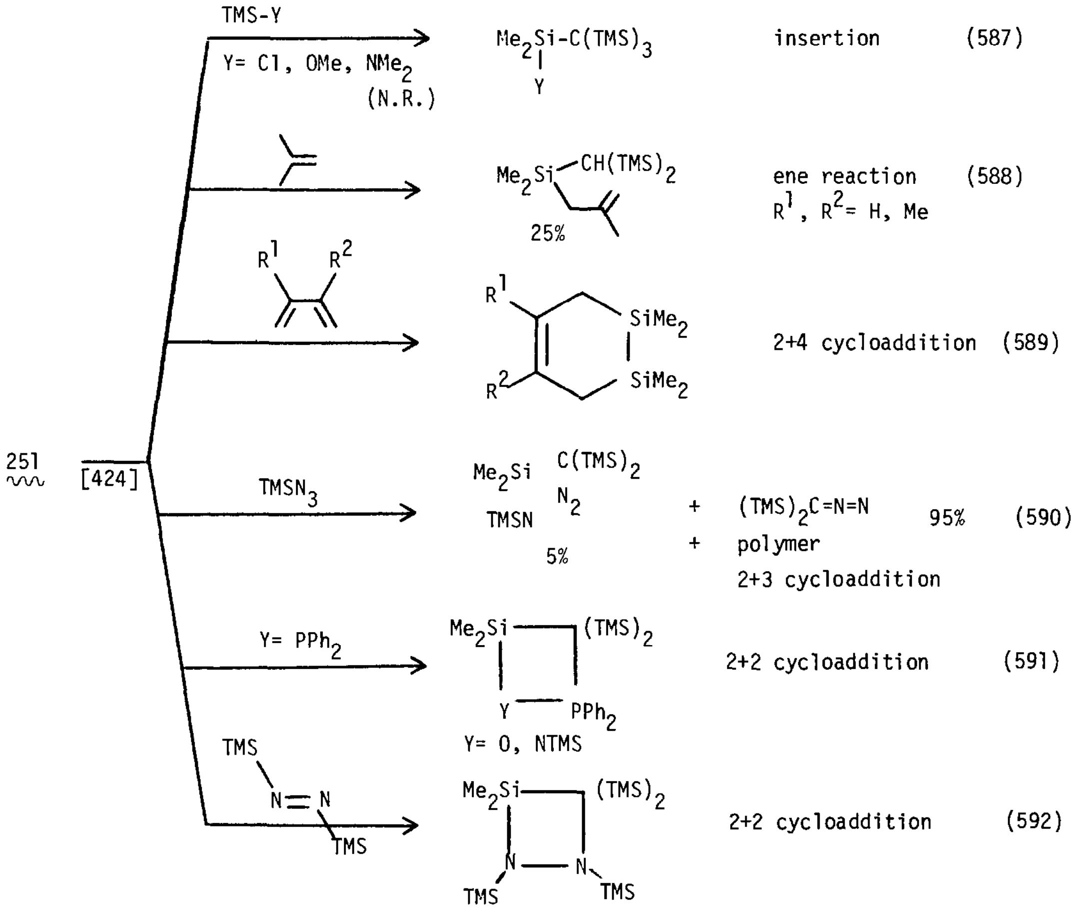
(585)

In a similar approach the silaethylene **251** was prepared via loss of LiX as shown. Silene **251** was trapped by a variety of compounds. (Eqns. 586-592) In a study of Eqn. 586 it was found that the elimination occurred in the order X= TsO > Cl > Br > I > Ph_2PO_4 > SPh F > Ph_2PO_2. [425]



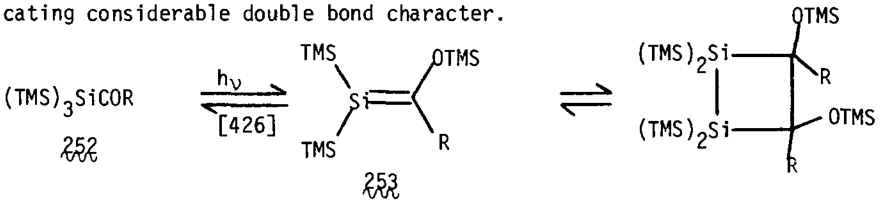
$$\underset{X}{Me_2Si}-\underset{Li}{C}(TMS)_2 \xrightarrow[\text{[424]}]{-LiX} \underset{\mathbf{251}}{Me_2Si{=}C(TMS)_2} \qquad (586)$$

X= Ph_2PO_4



(587)
(588)
(589)
(590)
(591)
(592)

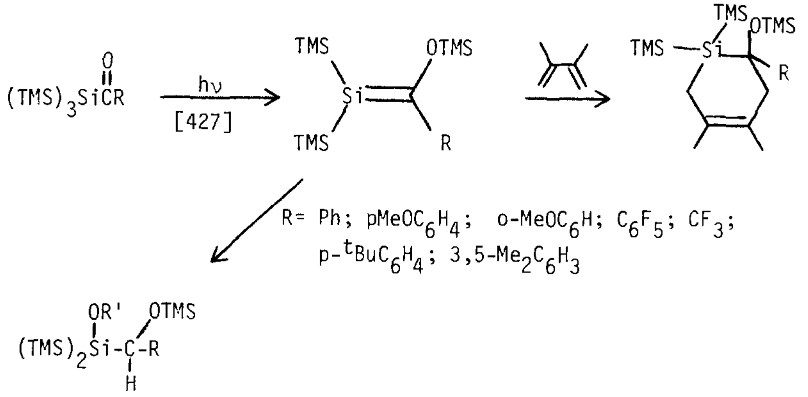
Stable, solid silaethylenes 253 were further studied. They were prepared photochemically from the bulky acylsilanes 252. (Eqn. 593) The crystal structure of 253 (R= 1-Ad) shows a Si=C bond of 1.764 Å and a 14.6° angle between the planes. Furthermore at +60° three ^{29}Si resonances are still evident indicating considerable double bond character.



(593)

R= ^{t}Bu, Et$_3$C, 1-Ad

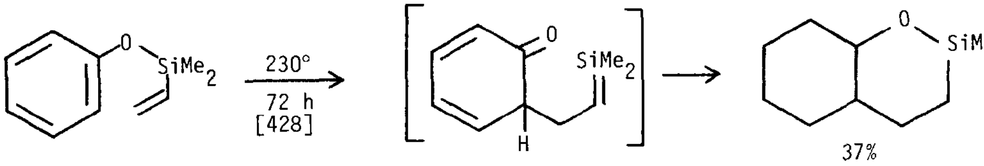
Attempts to prepare stable silaethylenes by placing aryl substituents on central carbon failed to give stable systems indicating that steric bulk is more important than electronic factors in the stability of silaethylenes. The synthesis of these species is given in Eqn. 594.



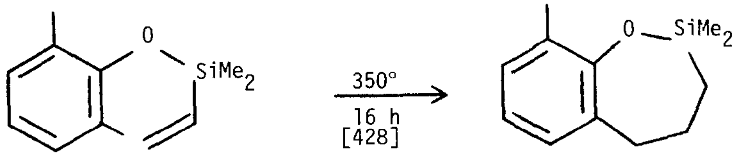
R= Ph; $pMeOC_6H_4$; $o\text{-}MeOC_6H$; C_6F_5; CF_3; $p\text{-}{}^tBuC_6H_4$; $3,5\text{-}Me_2C_6H_3$

(594)

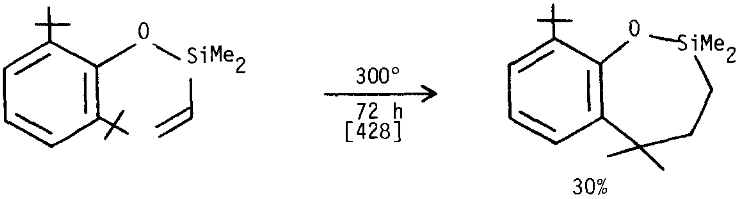
A silaethylene intermediate is involved in a Claisen rearrangement of allylphenoxysilanes. (Eqn. 595) When the ortho positions are substituted a radical process takes over. (Eqns. 596-597).



(595)



(596)



(597)

Direct spectroscopic evidence of dimethylsilene was made as well as that of the trideutero derivative. The band at 1016.5 cm^{-1} was assigned to the Si=C stretch and that at 817.5 cm^{-1} to the CH_2 out of plane vibration. [429]

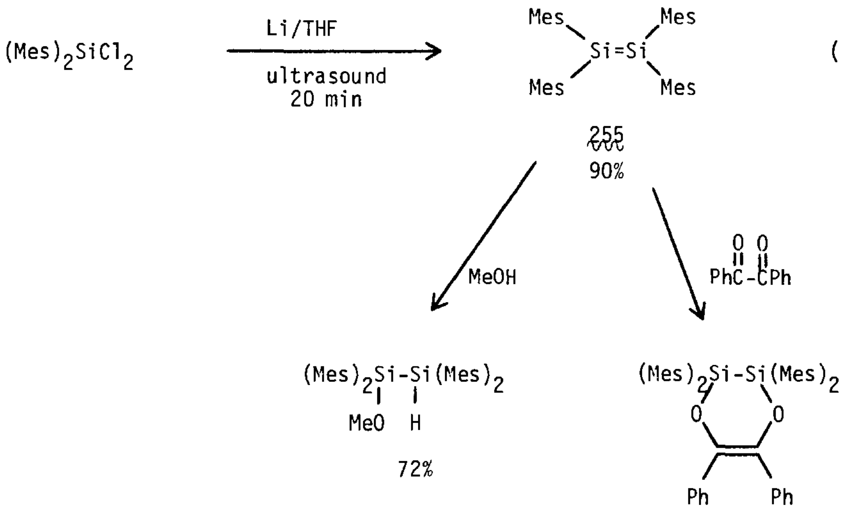
Ab initio calculations on Si-C multiple bonds indicates that $FSi{\equiv}CH$ is the most stable structure of HCSiF, $F_2Si{=}CH_2$ is much more stable than $FSiCH_2F$, that CH_3SiF is 14.4 kcal/mol more stable than $H_2C{=}SiHF$ but $FH_2C\text{-}SiH$ 49.4 kcal/mol less stable than $H_2C{=}SiHF$. In addition the calculations showed that $H_2C{=}SiF_2$ more stable than H_2FCSiF by 38 kcal/mole and $HF_2C{-}CH$ more stable than CHF=SiHF. [430]

The barrier between silaethylene and methylsilylene, which involves a 1,2-hydrogen shift, has been calculated to be greater than 25 kcal/mol, whereas experimental evidence indicates this to be about 5 kcal/mol. The authors suggest that other interpretations of the experimental data be considered, although they themselves offer no alternative explanation. This appears to further murky the waters of the silaethylene-silylene rearrangement question. [431]

The heat of formation of 1,1-dimethylsilaethylene was determined by pulsed in cyclotron double resonance spectroscopy. A value of the π energy of 38 kcal/mole was estimated. [432]

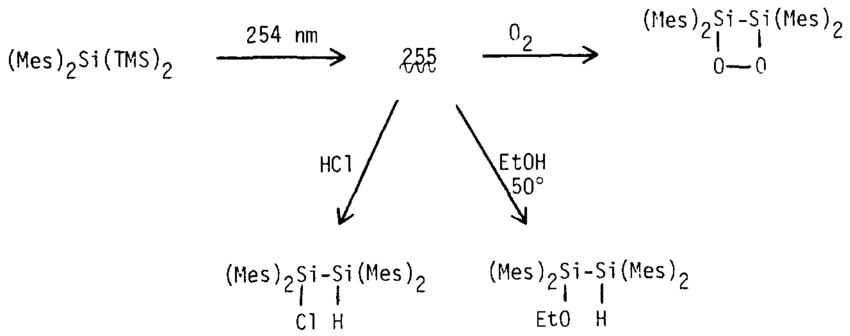
D. Disilenes

A novel and convenient synthesis of the stable disilene 255 from dimesityldichlorosilane is shown in Eqn. 598. The half-wave potential of 255 was found to be -2.8 V vs. Ag/Ag^+.



(598)

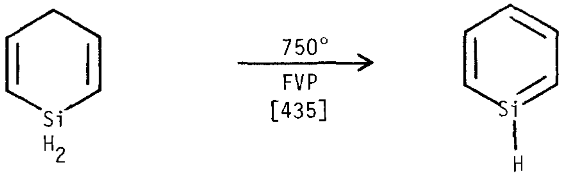
Irradiation of bis(mesityl)bis(trimethylsilyl)silane 256 gives 255. (Eqn. 599) Additions to the Si=Si bond are possible.



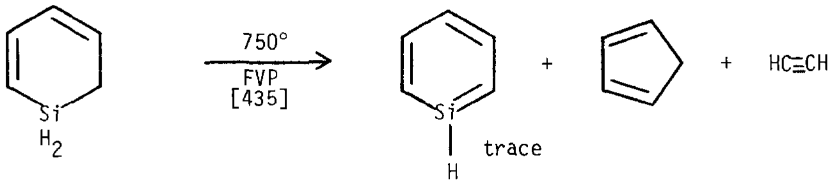
(599)

E. Silabenzenes

Thermal dehydrogenation of 1-sila-2,5-cyclohexadiene gives silabenzene. (Eqn. 600) This material was matrix isolated. Under identical conditions 1-sila-2,3-cyclohexadiene gave only traces of silabenzene.

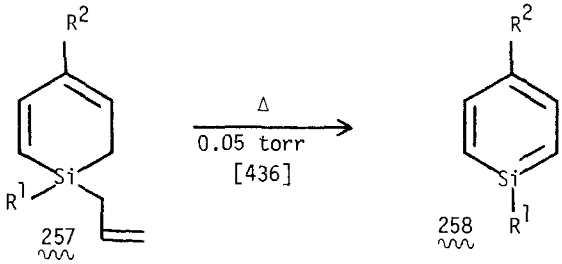


(600)



(601)

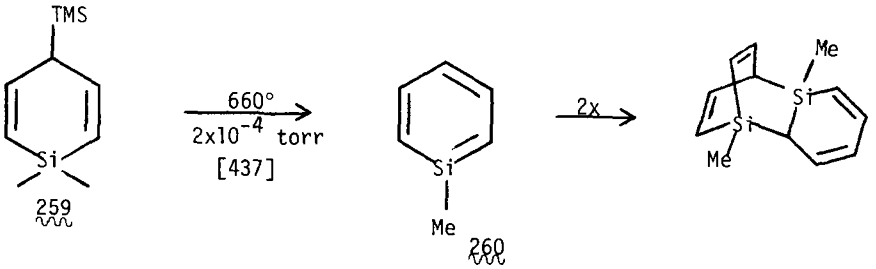
Pyrolysis of the 1-sila-2,3-cyclohexadienes 257 leads to substituted silabenzenes 258. (Eqn. 602) The photoelectron spectra were recorded for both these and the germanium analogs.



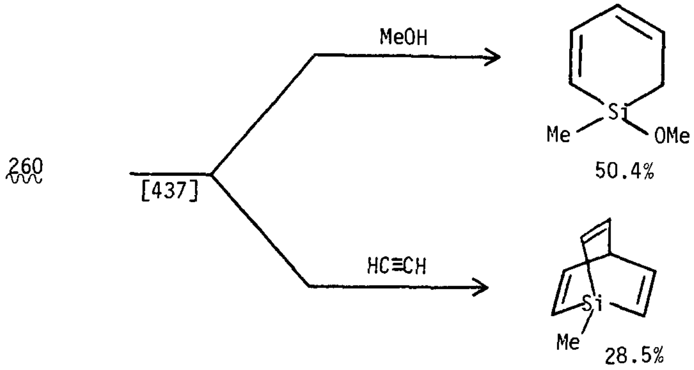
R^1= Me R^2= ^{t}Bu
R^1= Me R^2= Me
R^1= H R^2= ^{t}Bu

(602)

A rearrangement-elimination sequence was used to generate 1-silatoluene from 259. (Eqn. 603) Silatoluene 260 was trapped with methanol and acetylene. (Eqns. 604-605) Evidence for the rearrangement is seen from Eqns. 606-607.

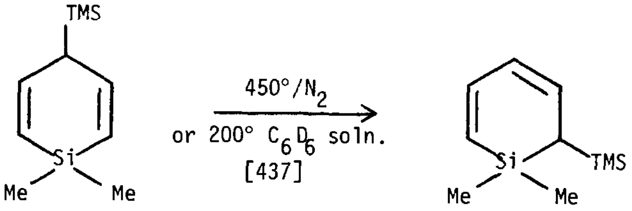


(603)

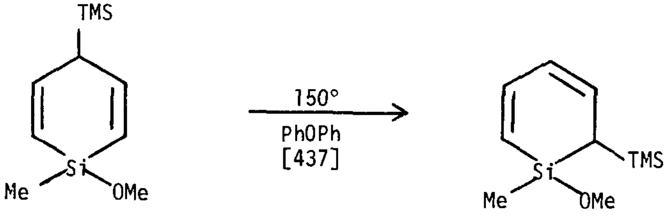


(604)

(605)

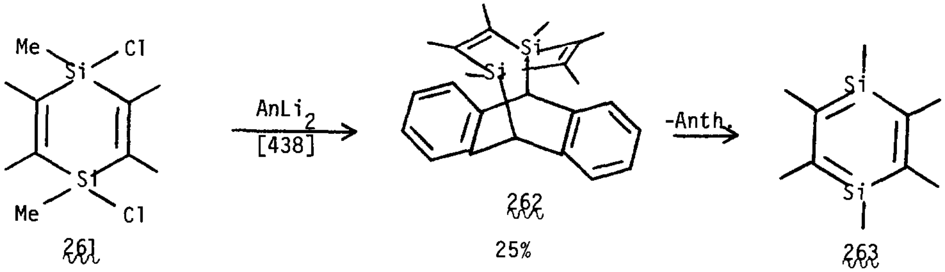


(606)

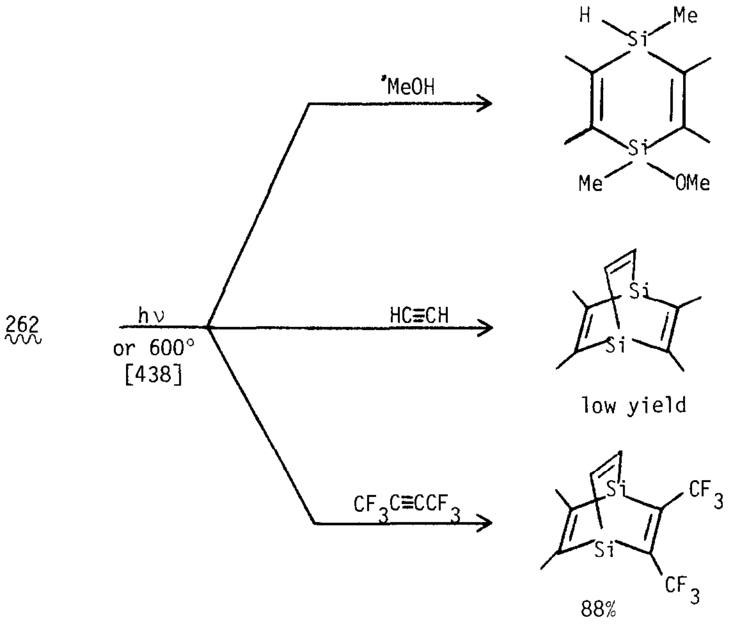


(607)

Treatment of 261 with dilithioanthracene gives 262, which thermally leads to anthracene and 1,4-disilabenzene 263, which can be trapped with methanol, acetylene or hexafluoro-2-butyne. (Eqns. 608-611)



(608)



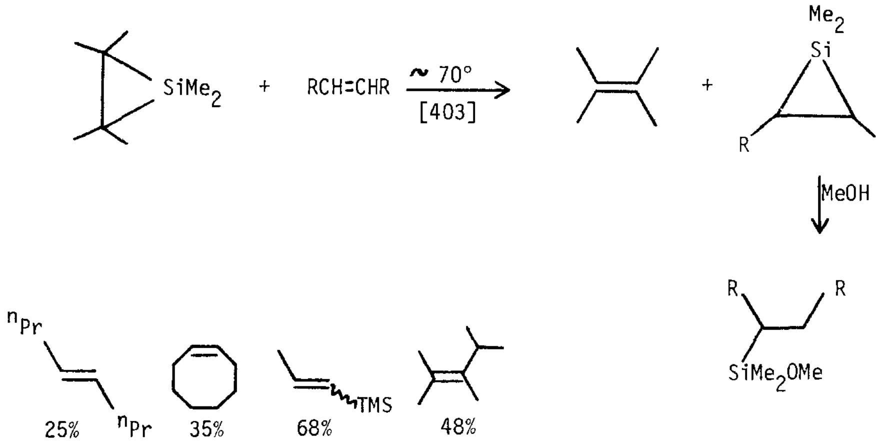
(609)

(610)

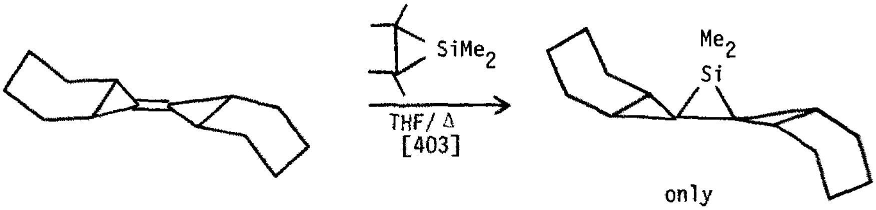
(611)

F. Silacyclopropanes

A clever synthesis of siliranes was achieved starting with hexamethylsilirane as a source of dimethylsilylene, which added to olefins present in the reaction mixture. Only internal olefins reacted. As the products are not stable they were isolated as their methanol addition product. (Eqns. 612-613) The reaction is stereospecific as seen from Eqn. 613.

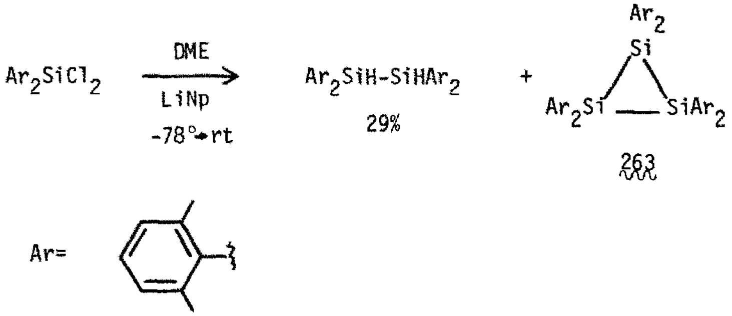


(612)



(613)

Bis(2,6-dimethylphenyl)dichlorosilane reacts with lithium naphthalenide in DME to give the trisilacyclopropane **263** (Eqn. 614). An X-ray structure of **263** was determined. It is stable to O_2, heat and water, but it reacts with halogens. Photolysis of **263** gives the disilene **264**. (Eqn. 615)

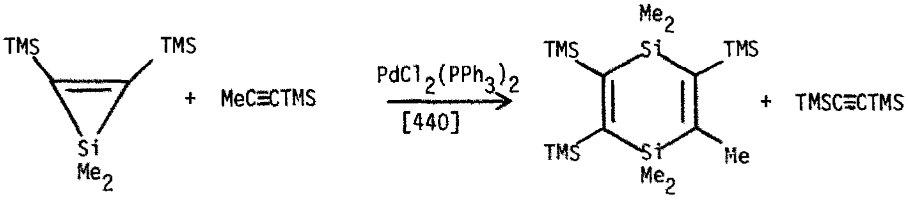


263

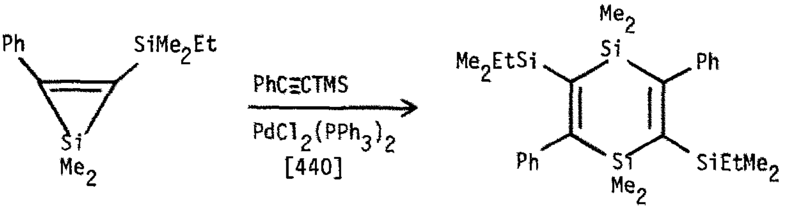
(614)

$$\mathbf{263} \xrightarrow{h\nu} \underset{\mathbf{264}}{Ar_2Si{=}SiAr_2} \qquad (615)$$

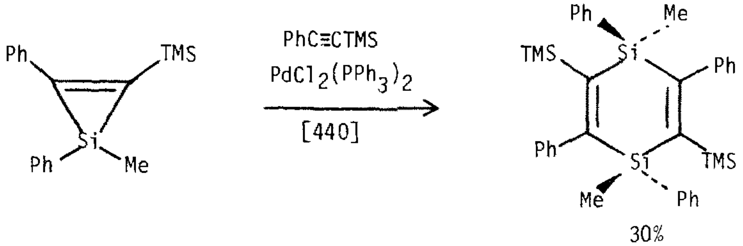
Silacyclopropenes react with acetylenes or dimerize when treated with palladium (II) catalyst. (Eqns. 616-618)



(616)



(617)



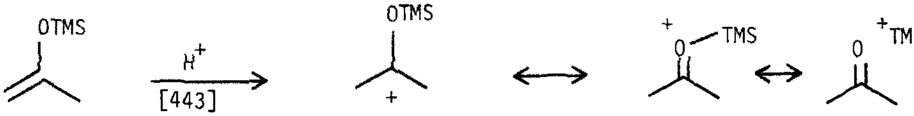
(618)

F. Miscellaneous Reactive Intermediates

The ^{29}Si NMR of TMS-X (X= Cl, Br, I) with Lewis acids BX_3 and AlX_3 were measured and the chemical shift difference taken as a measure of positive charge on silicon. No full silicenium ion was seen, but with TMSI (BI_3) and TMSBr (BBr_3, $AlBr_3$) considerable positive charge on silicon was seen. A predicted value of 225-275 ppm for the silicenium ion was given. [441]

Chloride and hydride exchange reactions of the trimethylsilicenium ion were measured in the gas-phase with pulsed ion cyclotron resonance mass spectrometry. The heat of formation of trimethylsilicenium ion is estimated to be 154±4 kcal/mol, which is 10-20 kcal/mol more stable than tert-butylcarbenium ion. [442]

Ion cyclotron resonance spectroscopy was used to study the protonation of 2-trimethylsilicenium acetone adduct is found to have 42 kcal/mol stabilization. The silicon carries a large percentage of the positive charge. (Eqn. 619)

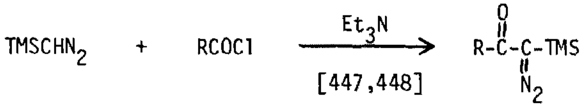


(619)

Vinyl ethers and alkoxy ketones were allowed to react with trimethylsilicenium ion. The reaction is at saturated oxygen. [444]

The esr spectrum of tetramethylsilyl cation radical shows it to C_{2v} symmetry rather than D_{2d} or T_d as allowed by John-Teller distortions. [445] MNDO-MO calculations were carried out on various silicon cation radicals, $SiH_3Y^{+\cdot}$. Substantial distortions are predicted. [446]

Trimethylsilyldiazomethane and related compounds provided some interesting and useful chemistry. The Arndt-Eistert synthesis was carried out with $TMSCHN_2$ rather than the more dangerous diazomethane. Examples are given below. (Eqns. 620-622).



$$TMSCHN_2 + RCOCl \xrightarrow[\text{[447,448]}]{Et_3N} R\text{-}\overset{O}{\overset{\|}{C}}\text{-}\underset{N_2}{\underset{\|}{C}}\text{-}TMS \qquad (620)$$

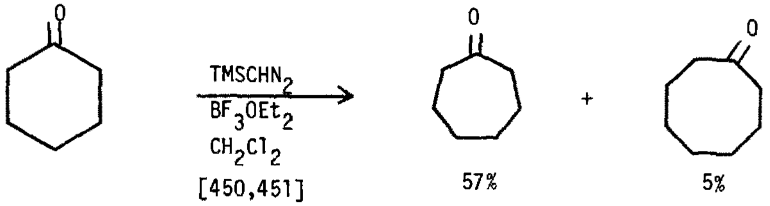
265

$$\mathbf{265} + PhCH_2OH \xrightarrow[\text{[447,448]}]{} RCH_2\text{-}CO_2CH_2Ph \qquad (621)$$

R= Ph, 62.8% [442]

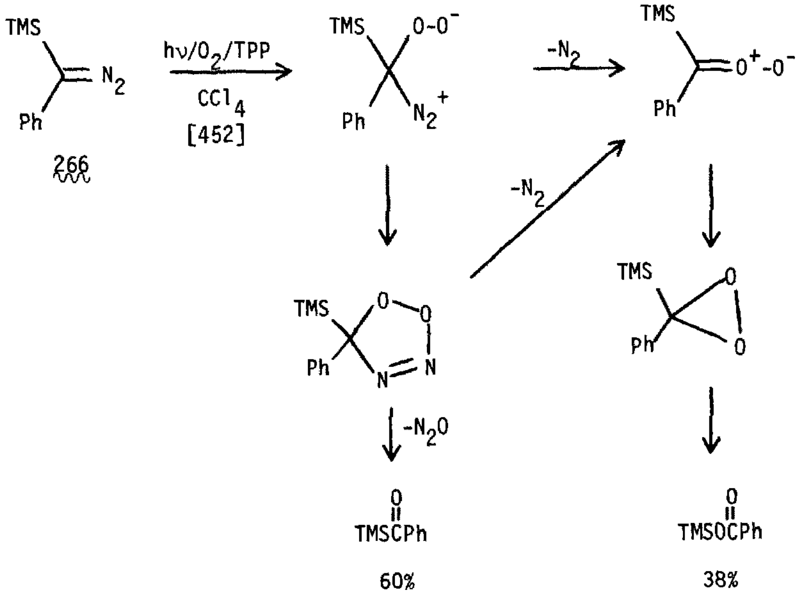
$$\mathbf{265} + PhNH_2 \xrightarrow[\text{[449]}]{180\text{-}85°} RCH_2CONHPh \qquad (622)$$

Trimethylsilyldiazomethane reacts readily with ketones in the presence of BF_3OEt_2 to give homologated ketones. (Eqn. 623).



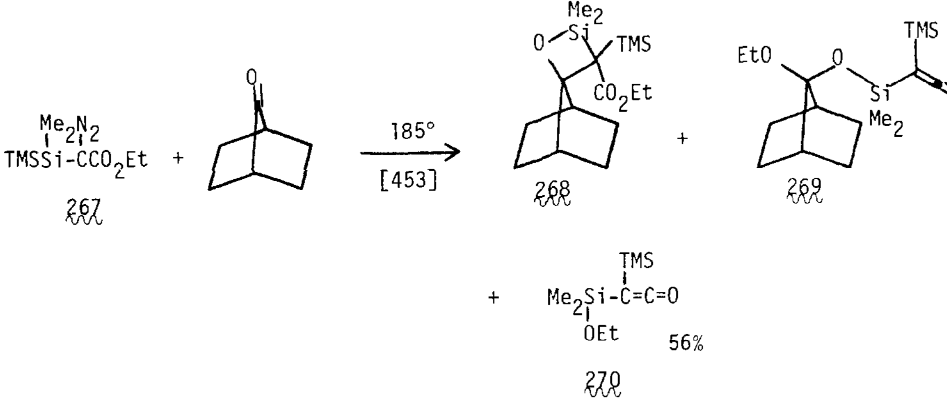
(623)

Photooxygenation of silyl diazo compound 266 gives benzoyltrimethylsilane and trimethylsilyl benzoate. The proposed mechanism is shown below. (Eqn. 624)

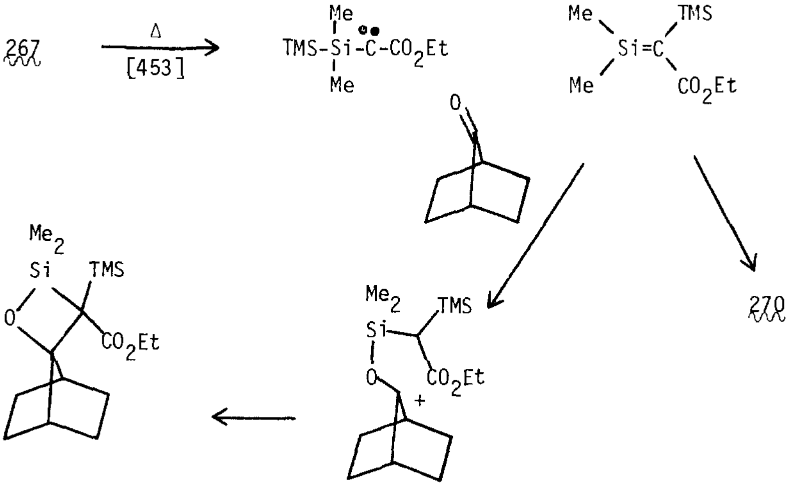


(624)

Thermolysis of silyl diazo compound 267 in the presence of 7-norbornanone gives the 1,2-silaoxetane 268. The reaction proceeds through the α-silyl carbene and the silaethylene. (Eqn. 625-626) Benzophenone and adamantanone gave no silaoxetane and enolizable ketones gave enol ethers.

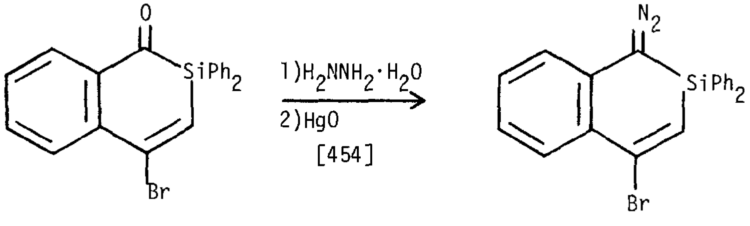


(625)

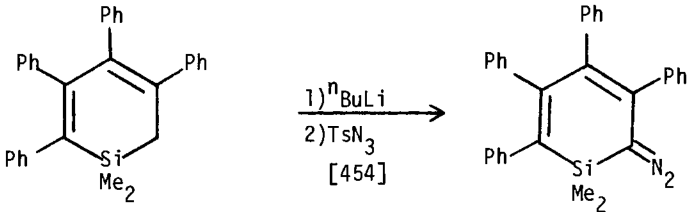


(626)

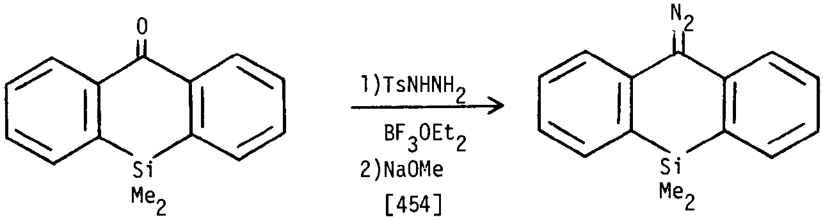
The synthesis of some cyclic silyl diazo compounds was achieved. (Eqns. 627-629)



(627)



(628)



(629)

Earlier reports on the thermolysis of hydridosilyl peroxides to give silanones has been shown to be better interpreted as intramolecular rearrangement of the intermediate peroxy intermediates instead. [455]

Acknowledgements: I wish to express my thanks to Ms. Linda Vega for typing this manuscript and to Professor John A. Soderquist, graduate students Juan Suárez and Rosa Betancourt de Pérez for proofreading.

REFERENCES

1. Yu.M. Varezhkin, D.Ya. Zhinkin, M.M. Morgunova, Usp. Khim., 50 (1981) 2212. Chem. Abst. 96:69062w.

2. O.B. Afanasova, N.G. Komalenkova, E.A. Chernyshev, Nov. Napravleniya Khim. Kremniiorg. Soedin, (1981) 21. Chem. Abst. 97:163043h.

3. B. Zelei, Termeszet Vilaga, 113 (1982) 358. Chem. Abst. 97:163041f.

4. M. Arai, Yuki Gosei Kagaku Kyokaishi, 40 (1982) 567. Chem. Abst. 97:163040e.

5. R. West, Pure Appl. Chem., 54 (1982) 1041.

6. M.G. Voronkov, V.B. Pukhnarevich, Izv. Akad. Nauk SSSR, Ser. Khim. (1982) 1056. Chem. Abst. 99:92339w.

7. O.A. Pudova, E. Lukevics, Latv. PSR Zinat. Akad. Vestis, Khim. Ser. (1982) 259. Chem. Abst. 97:92350t.

8. A.M. Mosin, Deposited Doc., (1981) SPSTL 216 Khp-D81. Chem. Abst. 97:216256p.

9. J. Donogues, Chemtech, 12 (1982) 373.

10. H. Sakurai Yuki Gosei Kagaku Kyokaishi, 40 (1982) 472. Chem. Abst. 97:198235z.

11. I. Fleming, Kem.¯Kemi, 9 (1982) 365. Chem. Abst. 97:198234y.

12. X. Huang, Z. Chem. Huaxue Tongbao (1982) 257. Chem. Abst. 97:143888

13. H. Sakurai, Fundam. Res. Organomet. Chem. Proc. China-Jpn.¯U.S. Trilateral Semin. Organomet. 1st, (1982) 259. Chem. Abst. 97:110046e.

14. M. Ochiai, E. Fujita, Yuki Gosei Kagaku Kyokaishi, 40 (1982) 508. Chem. Abst. 97:110059m.

15. H. Sakurai, Pure Appl. Chem. 54 (1982) 1.

16. H. Niskiyama, K. Itoh, Yuki Gosei Kagaku Kyokaishi, 40 (1982) 518. Chem. Abst. 97:110062g.

17. L.A. Paquette, Isr. J. Chem., 21 (1981) 128. Chem. Abst. 96:52341p.

18. G. Veinbergs, L. Petrulanis, E. Lukevics, Khim. Geterotsikl. Soedin, (1982) 147. Chem. Abst. 96:181018n.

19. H. Sakurai, Y. Okamoto, Yuki Gosei Kagaku Kyokaishi, 40 (1982) 525 Chem. Abst. 97:109577x.

20. H. Sakurai, A. Hosomi, Kagaku (Kyoto), 36 (1981) 1036. Chem. Abst. 96:181325k.

21. X. Huang, Z. Chen, Huaxue Shiji, (1982) 161. Chem. Abst. 97:216255n.

22. R.M. Pike, M.F. Mangano, J. Organometal. Chem. Libr. 12 (1981) 53.

23. S. Huenig, Chimia, 36 (1982) 1.

24. M. Suzuki, R. Noyori, Yuki Gosei Kagaku Kyokaishi, 40 (1982) 534. Chem. Abst. 97:127683h.

25. H. Emde, D. Domsch, H. Feger, U. Frick, A. Goetz, H.H. Hergott, K. Hofmann, W. Kober, K. Kraegeloh, T. Oesterle, W. Steppan, W. West, G. Simchen, Synthesis, 1 (1982) 1.

26. A. Bentlage, Gov. Rep. Announce Index, 82 (1982) 1891. Chem. Abst. 97:182493w.

27. U. Wannagat, Yortr. Rheinisch-Westfael. Akad. Wiss., Nat., Ing.¯Wirtschaftswiss, 302 (1981) 55. Chem. Abst. 96:69060u.

28. T. Inoi, Y. Nagai, Yuki Gosei Kagaku Kyokaishi, 40 (1982) 582. Chem. Abst. 97:140341q.

29. G. Wu, Huaxue Shiji, 112 (1982) 78. Chem. Abst. 97:92337u.

30. A. Ricci, Kem. Kozl., 57 (1982) 243. Chem. Abst. 97:110065k.

31. Y.N. Tang, React. Intermed. (Plenum), 2 (1982) 297.

32. M. Ishikawa, Yuki Gosei Kagaku Kyokaishi, 40 (1982) 484. Chem. Abst. 97:163039m.

33. W.P. Neumann, Nachr. Chem., Tech. Lab, 30 (1982) 192.

34. V.P. Yur'ev, I.M. Salimgareeva, "Reaktsiya Gidrosililirovaniya Oletinov: Metallokompleksnyi Kataliz v Protsessakh Gidrosililirovaniya, Stereokhimiya i Mekhanism Reaktsii" Nanka, Moscow, USSR (1982) Chem. Abst. 97:72573q.

35. Z. Zhou, Y.Li, L. Wang, Y. Jiang, Y.Y. Chiang, Fundam. Res. Organomet. Chem. Proc. China-Jpn-U.S. Trilateral Semin. Organomet. Chem. 1st. (1982) 77. Chem. Abst. 97:71589n.

36. Y. Seki, K. Kawamoto, S. Murai, N. Sonoda, Yuki Gosei Kagaku Kyokaishi, 40 (1982) 501. Chem. Abst. 97:110058k.

37. R.A. Pierce, Diss. Abstr. Int. B. 42 (1982) 4429. Chem. Abst. 97:92391g.

38. G.T. Burns, *Ibid*, 42 (1982) 4419. Chem. Abst. 97:72428w.

39. J.E. Dzarnoski, Jr. *Ibid*, 42 (1982) 4411. Chem. Abst. 97:72478n.

40. Y.S. Chen, *Ibid*, 42 (1982) 3264. Chem. Abst. 96:217920s.

41. E.A. Sans, *Ibid*, 42 (1981) 1897. Chem. Abst. 96:52382c.

42. F.G. Belmonte, *Ibid*, 42 (1982) 4789. Chem. Abst. 97:127703q.

43. R.G. Daniels, *Ibid*, 43 (1982) 137. Chem. Abst. 97:182513c.

44. R.J. Wroczynski, *Ibid*, 42 (1982) 4434. Chem. Abst. 97:72429x.

45. P.A. Manis, *Ibid*, 43 (1982) 428. Chem. Abst. 97:198266k.

46. R.T. Smart, *Ibid*, 42 (1981) 1883. Chem. Abst. 96:52381b.

47. M.R. Ross, *Ibid*, 42 (1981) 2357. Chem. Abst. 96:69093g.

48. D.L. Johnson, *Ibid*, 42 (1981) 1456. Chem. Abst. 96:35389t.

49. A.J. Zapata Vilera, *Ibid*, 42 (1982) 3699. Chem. Abst. 97:6435v.

50. R.N. Rusinko, *Ibid*, 42 (1982) 3681. Chem. Abst. 97:6367z.

51. S.S. Novikov, B.I. No, T.K. Korchagina, Yu.V. Popov, L.G. Magnitskaya, Ref. Zh. Khim. Abst. No. 10S489 (1982) Chem. Abst. 97:216285w.

52. E.S. Starodubtsev, L.M. Khananashvili, G.N. Kozlova, L.V. Gasanova, N.I. Tsomaya, T.P. Geleishvili, D.F. Kalanov, Soobshch. Akad. Nauk. Cruz SSR, 105 (1982) 321. Chem. Abst. 97:163081u.

53. C. Tamborski, C.E. Snyder, U.S. Pat. Appl. US 336, 474. Chem. Abst. 97:198373t.

54. D. Wrobel, R. Tacke, U. Wannagat, U. Harder, Chem. Ber., 115 (1982) 1694.

55. D. Wrobel, U. Wannagat, Liebigs Ann. Chem. (1982) 734.

56. H.G. Zoch, G. Szrimies, T. Butkowskyj. M. Van Meerssche, G. Germain, J.P. Declereq, Chem. Ber. 114 (1981) 3896.

57. L.I. Zakharhin, A.I. Kovredov, I.S. Savel'eva, E.V. Safranova, Zh. Obshch. Khim. 51 (1981) 2383. Chem. Abst. 96:20148q.

58. K.W. Lee, J. San Filippo, Jr., Organometallics, 1 (1982) 1496.

59. R.T. Taylor, J.G. Galloway, Tetrahedron Lett., 23 (1982) 3147.

60. G.I. Bolestova, Z.N. Parnes, D.N. Kursanov, Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 2839. Chem. Abst. 96:142319s.

61. J.J. Eisch, M.R. Tsai, J. Organometal. Chem., 225 (1982) 5.

62. J.E. Boggs, M. Von Carlowitz, S. Von Carlowitz, J. Phys. Chem., 86 (1982) 157.

63. C. Eaborn, P.B. Hitchcock, P.D. Lickiss, J. Organometal. Chem., 221 (1981) 13.

64. F.K. Cartledge, Ibid, 225 (1982) 131.

65. L.E. Gusel'nikov, V.V. Volkova, N.A. Tarasenko, A.V. Tishenkov, U.G. Zaiken, E.I. Eremina, N.S. Nametkin, Org. Mass Spectrom., 16 (1981) 242.

66. M.A. Harthcock, J.M. Cooke, J. Laane, J. Phys. Chem., 86 (1982)4335

67. M.A. Harthcock, J. Laane, J. Mol. Spectrosc. 91 (1982) 300.

68. P. Boudjouk, J.S. Kiely, R. Sooriyakumaran, J. Organometal. Chem., 221 (1981) 33.

69. G. Felix, M. Laguerre, J. Donogues, R. Calas, J. Organometal Chem., 47 (1982) 1423.

70. G. Fritz, K. Gompper, H. Wilhelm, Z. Anorg. Allg. Chem., 478 (1981) 20.

71. D. Wrobel, U. Wannagat, J. Organometal Chem., 225 (1982) 203.

72. M.T. Rahman, Ibid, 225 (1982) 25.

73. R. Sooriyakumaran, P. Boudjouk, Organometallics, 1 (1982) 218.

74. F. Marsais, G. LeNard, G. Queguiner, Synthesis, (1982) 235.

75. T.D. Krizan, J.C. Martin, J. Org. Chem., 47 (1982) 2681.

76. D. Wiese, R. Tacke, U. Wannagat, Liebigs Ann. Chem., (1981) 1285.

77. A.G.M. Barrett, D. Dauzonne, D.J. Williams, J. Chem. Soc., Chem. Commun., (1982) 636.

78. M. Ishiguro, N. Ikeda, H. Yamamoto, Chem. Lett., (1982) 1029.

79. M.M. Demina, L.P. Safranova, A.S. Medvedeva, N.S. Vyazankin, Izv. Akad. Nauk SSSR Ser. Khim. (1982) 220. Chem. Abst. 96:162805a.

80. D.J. Chadwick, S.T. Hodgson, J. Chem. Soc., Perkin Trans. I., (1982) 1833.

81. R. Calas, J. Dunogues, G. Deleris, N. Duffaut, J. Organometal Chem., 225 (1982) 117.

82. P. Babin, J. Donogues, G. Felix, P. Lapouyade, R. Calas. J. Chem. Res. Synop. (1982) 16.

83. T. Sasaki, A. Nakanishi, M. Ohno, J. Org. Chem. 47 (1982) 3219.

84. J.A. Cella, Ibid, 47 (1982) 2125.

85. I. Szele, Helv. Chim. Acta, 64 (1981) 2733.

86. Z.S. Salih, T.H. Al-Khayat, Iraqi J. Sci., 22 (1981) 319. Chem. Abst. 97:163079z.

87. S. Gronowitz, T. Frejd, O. Karlsson, K. Lawitz, P. Pedaja, K. Petterson, Chem. Ser. 18 (1981) 192. Chem. Abst. 96:104346r.

88. G. Seconi, M. Taddei, C. Eaborn, J.G. Stamper, J. Chem. Soc., Perkin Trans 2 (1982) 643.

89. M. Ishikawa, K. Nishimura, H. Sugisawa, M. Kumada, J. Organometal Chem., 218 (1981) C21.

90. I. Kuwajima, H. Urabe, Tetrahedron Lett., 22 (1981) 5191.

91. W. Adam, A. Rodriguez, Ibid, 22 (1981) 3505.

92. J.C. Marie, J. Marrot, R. Nabet, Bull. Soc. Chim. Fr., (1981) 429.

93. M.G. Voronkov, E.I. Brodskaya, V.V. Belyaeva, V.P. Baryshok, Dokl. Akad. Nauk SSSR, 261 (1981) 1362 Chem. Abst. 96:142125a.

94. Yu. V. Kolodyazhnyi, M.G. Gruntfest, V.K. Dmitrieva, O.A. Osipov, Zh. Obshch. Khim., 52 (1982) 632. Chem. Abst. 97:6389h.

95. M.M. Tatevosyan, A.T. Shuvaev, N.N. Nharabaev, A.P. Zemlyanov, Yu. A. Taterin, A.S. Baev, A.M. Sladkov, N.A. Zemlyanov, Deposited Doc, (1980) Chem. Abst. 96:84919z.

96. A.T. Shuvaev, M.M. Tatevosyan, A.P. Zemlyanov, N.N. Kharabaev, V.M. Kopylov, Ibid, (1980) Chem. Abst. 96:69096k.

97. R. Ponec, L. Dejmek, V. Chvalovsky, Collect. Czech. Chem. Commun., 46 (1981) 2663.

98. J. Bordeau, E. Frainnet, C. Clement, J. Organometal. Chem. 233 (1982) 149.

99. N.S. Prostakov, N. Saxena, P.I. Zakharov, A.V. Varlamov, D.A. Fesenko, Ibid, 228 (1982) 37.

100. T.N. Zaslavskaya, N.A. Filippov, V.O. Reikhsfel'd, Zh. Obshch. Khim., 52 (1982) 80. Chem. Abst. 96:142946u.

101. R.L. Yates, U.S. Pat. US 4, 332,654 (Cl.204-158R;CO 7F 7/18) Chem. Abst. 97:163243y.

102. L. Wang, Y. Jiang, Cuihua Xuebo, 2 (1981) 236. Chem. Abst. 96:68095x.

103. Jpn. Kokaid Tokkyo Koho JP 81 90,092 (Cl.C07F7/18) Chem. Abst. 96:6859r.

104. M. Capka, Czech. CS 187, 167 (Cl.C07F7/12). Chem. Abst. 96:6863n.

105. P. Svoboda, V. Vybiral, J. Hetfles, Czech. CS 193, 448 (Cl.C0787/06). Chem. Abst. 96:218019s.

106. V.V. Kaverin, L.Kh. Khalilov, I.N. Brui, Deposited Doc. (1980) Chem. Abst. 97:216281t.

107. V.A. Sergeev, V.K. Shitikov, G.U. Abbasov, M.R. Bairamov, A.A. Zhdanov, T.V. Astapova, S.M. Aliev, Zh. Obshch. Khim. 52 (1982) 1846. Chem. Abst. 97:216295a.

108. V.V. Kaverin, I.M. Salimgreeva, I.V. Kovaleva, V.P. Yur'ev, Izv. Akad. Nauk SSSR Ser. Khim., (1981) 2119. Chem. Abst. 96:69082c.

109. N.A. Moldavskaya, N.K. Skvortsov, N.F. Voloshina, V.O. Reikhsfel'd Zh. Obshch. Khim., 51 (1981) 1621. Chem. Abst. 96:69173h.

110. V.D. Sheludyakov, V.I. Zhun, S.D. Vlasenko, V.N. Bochkarev, T.F. Slyusarenko, A.V. Kisin, V.M. Nosova, G.N. Turkel'taub, E.A. Chernyshev, Ibid, 51 (1981) 2022. Chem. Abst. 96:6782k.

111. G.V. Nurtdinova, G. Gailiunas, V.P. Yur'ev, Izv. Akad. Nauk SSSR Ser. Khim. (1981) 2652. Chem. Abst. 96:104353r.

112. N.A. Moldavskaya, N.K. Skvortsov, V.O. Reikhsfel'd, V.E. Aleshin, E.D. Ageeva, N.F. Voloshina, Yu.N. Kukuskkin, Otkrytiya Izobret. Prom. Obraztsy, Tovarnye Znaki, (1981) 109 Chem. Abst. 96:199871v.

113. K. Tamao, J. Yoshida, H. Yamamoto, T. Kakui, H. Matsumoto, M. Takahashi, A. Kurita, M. Murata, M. Kumada, Organometallics, 1 (1982) 355.

114. B. Marciniec, J. Gulinski, W. Urbaniak, Synth. React. Inorg. Met.-Org. Chem., 12 (1982) 139.

115. G. Fritz, H. Wilhelm, A. Oleownik, Z. Anorg. Allg. Chem., 478 (1981) 97.

116. N.M.K. El-Durini, R.A. Jackson, J. Organometal. Chem., 232 (1981) 117.

117. S.I. Sadykh-Zade, P.M. Mustafaev, L.G. Kulieva, Dokl. Akad Nauk Az. SSR, 37 (1981) 51. Chem. Abst. 96:20158t.

118. M.G. Voronkov, T.D. Burnashova, O.G. Yarosh, Zh. Obshch. Khim., 52 (1982) 614. Chem. Abst. 97:38988u.

119. Jpn. Kokai Tokkyo Koho Jp 81,133,296 (Cl.C07F7/12) Chem. Abst. 96:143069x.

120. Voronkov, M.G., S.N. Adamovich, V.B. Pukhnarevich, Zh. Obshch. Khim., 51 (1981) 2385. Chem. Abst. 96:6796t.

121. J pn. Kokai Tokkyo Koho Jp 81,122,390 (Cl.C07F7/14). Chem. Abst. 96:162933r.

122. G.D. Annis, L.A. Paquette, J. Am. Chem. Soc., 104 (1982) 4504.

123. I.V. Mironov, I.A. Mel'nitshii, I.N. Siraeva, T.K. Kiladze, E.A. Kantor, D.L. Rakmankulov, Zh. Obshch. Khim., 51 (1981) 2700. Chem. Abst. 96:104361s.

124. G. Suess-Fink, J. Reiner, J. Mol. Catal. 6 (1982) 231.

125. S.E. Cremev, C. Blankenship, J. Org. Chem., 47 (1982) 1626.

126. J. Dunogues, D. N'Gabe, M. Laguerre, N. Duffaut, R. Calas, Organometallics, 1 (1982) 1525.

127. J.P. Dulcere, J. Grimaldi, M. Santelli, Tetrahedron Lett., 22 (1981) 3179.

128. R.G. Daniels, L.A. Paquette, Organometallics, 1 (1982) 1149.

129. H. Sakurai, T. Koyama, M. Kira, A. Hosomi, Y. Nakadaira, Tetrahedron Lett., 23 (1982) 543.

130. E.J. Corey, J. Kang, J. Am. Chem. Soc., 104 (1982)4724.

131. J.C. Clinet, G. Linstrumelle, Synthesis, (1981) 875.

132. H.D. Verkruijsse, W. Verboom, P.E. Van Rijn, L. Brandsma, J. Organometal. Chem., 232 (1982) C1.

133. P. Pappalardo, E. Ehlinger, P. Magnus, Tetrahedron Lett., 23 (1982) 309.

134. P.E. Van Rijn, L. Brandsma, J. Organometal. Chem., 233 (1982) C25.

135. N.P. Erchak, J. Popelis, I. Pihler, E. Lukevics, Zh. Obshch. Khim., 52 (1982) 1181. Chem. Abst. 97:110079t.

136. N.G. Clemo, G. Pattenden, Tetrahedron Lett., 23 (1982) 581.

137. N.I. Yakushkina, G.R. Zhurina, L.S. Surmina, Yu.K. Grishin, D.V. Bazhenov, V.V. Plemenkov, I.G. Bolesov, Zh. Obshch. Khim., 52 (1982) 1604. Chem. Abst. 97:182567y.

138. M. Ishikawa, H. Sugisawa, O. Harata, M. Kumada, J. Organomet. Chem., 217 (1981) 43.

139. Yu.I. Baukov, G.S. Zaitseva, L.I. Livantsova, R.A. Bekker, I.A. Savast'yanova, G.I. Oleneva, I.F. Lutsenko, Zh. Obshch. Khim., 51 (1981) 1304.

140. G. Maier, H.W. Lage, H.P. Reisenauer, Angew. Chemie., 93 (1981) 1010.

141. B. Wrackmeyer, C. Bihlmayer, J.Chem. Soc., Chem. Commun., (1981) 1093.

142. T.A. Hase, L. Lahtinen, Tetrahedron Lett., 22 (1981) 3285.

143. M.A. Tius, Ibid, 22 (1981) 3335.

144. Y. Naruta, H. Uno, K. Maruyama, Chem. Lett., (1982) 961.

145. I. Fleming, T.W. Newton, F. Roessler, J. Chem. Soc., Perkin Trans. I (1981) 2527.

146. K. Tamao, M. Akita, R. Kanatani, N. Ishida, M. Kumada, J. Organomet. Chem., 226 (1982) C9.

147. T. Harao, J. Enda, Y. Ohsiro, T. Agawa, Tetrahedron Lett., 22 (1981) 3079.

148. T. Hiyama, A. Kanakura, Y. Morizawa, H. Nozaki, Ibid, 23 (1982) 1279.

149. S.E. Denmark, T.K. Jones, J. Am. Chem. Soc., 104 (1982) 2642.

150. J.W. Apsimon, R.P. Sequin, C.P. Huber, Can. J. Chem., 60 (1982) 509.

151. L.D. Martin, J.K. Stille, J. Org. Chem. 47 (1982) 3630

152. N. Miyaura, Y. Tanabe, H. Suginome, A. Suzuki, J. Organomet. Chem., 233 (1982) C13.

153. H.A. Firgo, W.P. Weber, Organometallics, 1 (1982) 649.

154. A.P.S. Narula, D.I. Schuster, Tetrahedron Lett., 22 (1981) 3707.

155. G. Quinkert, W.D. Weber, U. Schwartz, H. Stark, H. Baier, G. Duerner, Liebigs Ann. Chem., (1981) 2335.

156. T. Takahashi, H. Yamada, Y. Naito, J. Tsuji, Tennen Yuki Kagobutsu Toronkai Koen Yoshishu, 24th (1981) 379. Chem. Abst. 96:163041k.

157. T.A. Dixon, K.P. Steele, W.P. Weber, J. Organomet. Chem., 231 (1982) 299.

158. F.G. Yusupova, G.V. Nurtdinova, I.N. Brui, A.N. Nizamova, K.M. Khalilov, G. Gailiunas, V.P. Yur'ev, Zh. Obshch. Khim., 51 (1981) 1807. Chem. Abst. 96:6784n.

159. J. Barluenga, C. Jimenez, C. Najera, M. Yus, Synthesis, (1982) 414.

160. M.G. Voronkov, N.N. Vlasova, S.U. Kirpichenko, E.N. Suslova, M. Yu. Adamovich, V.V. Keiko, Zh. Obshch. Khim., 52 (1982) 712. Chem. Abst. 97:39135a.

161. M. Gerlach, P. Jutzi, J. Stasch, H. Przuntek, Z. Naturforsch., B: Anorg. Chem. Org. Chem., 37B (1982) 657.

162. V.V. Pevekalin, V.M. Berestovitskaya, E.V. Trukhin, N.G. Komalenkova, S.A. Bashkirova, E.A. Chernyshev, Zh. Obshch. Khim., 52 (1982) 922. Chem. Abst. 97:72415q.

163. D.J. Ager, Tetrahedron Lett., 23 (1982) 1945.

164. A Padwa, J.G. MacDonald, Ibid, 23 (1982) 3219.

165. L.A. Paquette, R.V. Williams, Ibid, 22 (1981) 4643.

166. L.A. Paquette, R.V. Williams, J. Org. Chem., 47 (1982) 4566.

167. M.J. Carter, I. Fleming, A. Percival, J. Chem. Soc., Perkin Trans 1. (1981) 2415.

168. T. Harao, S. Kohno, J. Enda, Y. Ohshiro, T. Agawa, Tetrahedron Lett., 22 (1981) 3633.

169. P. Magnus, D.A. Quagliato, Organometallics, 1 (1982) 1243.

170. P. Magnus, D.A. Quagliato, J.C. Huffman, Ibid, 1 (1982) 1240.

171. R.P. Fisher, H.P. On, J.T. Snow, G. Zweifel, Synthesis, (1982) 127.

172. R.T. Taylor, R.A. Cassell, *Ibid*, (1982) 672.

173. R. Koester, G. Seidel, Angew. Chemic., 93 (1981) 1009.

174. I.T. Farkhieva, Ya. Kh. Bieshev, Yu. B. Monakov, S.R. Rafikov, Izv. Akad. Nauk SSSR, Ser. Khim., (1982) 907. Chem. Abst. 97:55880v.

175. D.A. Donaldson, R.P. Hughes, Synth. Commun, 11 (1981) 999.

176. T. Yogo, J. Koshino, A. Suzuki, *Ibid*, 11 (1981) 769.

177. H. Sakurai, Y. Nakadaira, H. Tobita, Chem. Lett., (1982) 771.

178. J. Yoshida, K. Tomao, H. Yamamoto, T. Kakui, T. Uchida, M. Kumada Organometallics, 1 (1982) 542.

179. J. Yoshida, K. Tamao, T. Kakui, A. Kurita, M. Murata, K. Yamada, M. Kumada, *Ibid*, 1 (1982) 369.

180. K. Tamao, J. Yoshida, M. Akita, Y. Sugihara, T. Iwahara, M. Kumada, Bull. Chem. Soc., Jpn., 55 (1982) 255.

181. K. Tamao, M. Mishima, J. Yoshida, M. Takahashi, N. Ishida, M. Kumada, J. Organomet. Chem., 225 (1982) 151.

182. H. Sakurai, Y. Nakadaiva, H. Tobita, T. Ito, K. Toriumi, H. Ito, J. Am. Chem. Soc., 104 (1982) 300.

183. H. Sakurai, H. Tobita, Y. Nakadaira, C. Kabuto, *Ibid*, 104 (1982) 4288.

184. Y. Shiki, A. Hasegawa, M. Hayashi, J. Mol Struct. 78 (1982) 185.

185. V.I. Khvostenko, B.G. Zykov, V.P. Yur'ev, V.F. Mironov, G.T. Kovel'zon, A.A. Panasenko, V.D. Sehludyakov, I. Gailiunas, J. Organomet. Chem., 218 (1981) 155.

186. A. Modelli, D. Jones, G. Distefano, Chem. Phys. Lett., 86 (1982) 434.

187. Y. Apelog, A. Stanger, J. Org. Chem., 47 (1982) 1462.

188. N.H. Anderson, A.D. Denniston, D.A. McRae, *Ibid*, 47 (1982) 1145.

189. E.J. Corey, C. Ruecker, Tetrahedron Lett., 23 (1982) 719.

190. T. Liese, A. De Meijere, Angew. Chemie., 94 (1982) 65.

191. B. Bennetau, J.P. Pillot, J. Dunogues, R. Calas, J. Chem. Soc., Chem. Commun., (1981) 1094.

192. M.E. Askerov, G. Janes, S.F. Karaev, Azerb. Khim. Zh., (1982)36 Chem. Abst. 97:182484u.

193. S.F. Karaev, R.M. Kuliev, Sh. O. Guseinov, M.E. Askerov, M.M. Mousumzade, Zh. Obshch. Khim., 52 (1982) 1160. Chem. Abst. 97:92385h.

194. E.T. Bogaradovskii, V.S. Zavgorodnii, B.V. Polozov, A.A. Petrov, Ibid, 52 (1982) 455. Chem. Abst. 96:181343q.

195. E.T. Bogoradovskii, V.S. Zavgorodnii, A.V. Moshinskaya, A.A. Petrov, Ibid, 51 (1981) 2144. Chem. Abst. 96:6821x.

196. Y. Taniguchi, J. Inanaga, M. Yamaguchi, Bull. Chem. Soc. Jpn., 54 (1981) 3229.

197. R. Haruta, M. Ishiguro, K. Furuta, A. Mori, N. Ikeda, H. Yamamoto, Chem. Lett., (1982) 1093.

198. M. Ishiguro, N. Ikeda, H. Yamamoto, J. Org. Chem. 47 (1982) 2225.

199. L. Birkofer, D. Wundram, Chem. Ber, 115 (1982) 1132.

200. L.I. Zakharkin, A.I. Kovredov, V.A. Ol'shevskaya, Zh. Obshch. Khim., 51 (1981) 2807. Chem. Abst. 96:85633p.

201. K. Ruitenberg, J. Meijer, R.J. Bullee, P. Vermeer, J. Organomet. Chem., 217 (1981) 267.

202. Eur. Pat. EP 50, 428 (Cl.C07B27/00) Chem. Abst. 97:109711m.

203. G.E. Jones, A.B. Holmes, Tetrahedron Lett., 23 (1982) 3203.

204. M.W. Logue, K. Teng, J. Org. Chem., 47 (1982) 2549.

205. S.E. Denmark, T.K. Jones, Ibid, 47 (1982) 4595.

206. I. Cutting, P.J. Parsons, Tetrahedron Lett., 22 (1981) 2021.

207. H.P. On, W. Lewis, G. Zweifel, Synthesis, (1981) 999.

208. K. Baum. C.D. Bedford, R.J. Hunad, J. Org. Chem., 47 (1982) 2251.

209. K. Baum, C.D. Bedford, R.J. Hunad, Gov. Rep. Announce. Index (US) 82 (1982) 2782. Chem. Abst. 97:126958q.

210. M.G. Voronkov, O.G. Yarosh, L.N. Il'icheva, Izv. Akad. Nauk, SSSR, Ser Khim., (1982) 1424. Chem. Abst. 97:163080t.

211. M.G. Voronkov, G. Yu. Zhila, O.G. Yarosh, A.I. Albanov, N.N. Vlasova, Zh. Obshch. Khim., 52 (1982) 1207. Chem. Abst. 97:23872c.

212. S.F. Ponomarev, Yu.N. Bubnov, B.M. Mikhailov, Izv. Akad. Nauk SSSR, Ser Khim., (1981) 1859. Chem. Abst. 96:20155q.

213. E.A. Shapiro, G.V. Lun'kova, A.O. Nefedov, I.E. Dolgii, O.M. Nefedov, Ibid, (1981) 2535. Chem. Abst. 96:142932m.

214. G. Maier, M. Hoppe, H.P. Reisenauer, C. Krueger, Angew. Chem., 94 (1982) 445.

215. N.N. Belyaev, E.V. Komissarova, M.D. Stadnichuk, Zh. Obshch. Khim., 52 (1982) 2084. Chem. Abst. 97:216305d.

216. M. Ali, A. Razzaq. S.H. Kabir, M.M. Shafiuddin, Dacca Univ. Stud., Part B. 29 (1981) 79. Chem. Abst. 96:199769t.

217. P. Babin, P. Lapouyade, J. Dunogues, Can. J. Chem., 60 (1982)379.

218. G. Himbert, M. Feustel, M. Jung, Liebigs Ann. Chem., (1981) 1907.

219. J.P. Pillot, B. Bennetau, J. Dunogues. R. Calas, Tetrahedron Lett., 22 (1981) 3401.

220. B.A. Keay, R. Rodrigo, J. Am. Chem. Soc., 104 (1982) 4725.

221. H. Ebe, T. Nakagawa, M. Iyoda, M. Masazumi, Tetrahedron Lett., 22 (1981) 4441.

222. Y. Yoshikawa, M. Iyoda, M. Nakagawa. S. Nakatsuji, Ibid, 22 (1981) 5209.

223. L. Birkofer, E. Haensel. Chem. Ber. 114 (1981) 3154.

224. D.J. Brien, A. Naiman, K.P.C. Vollhardt, J. Chem. Soc., Chem. Commun., (1982) 133.

225. E.R.F. Gesing, P.C. Vollhardt, J. Organomet. Chem., 217 (1981)105.

226. A.S. Medvedeva, M.M. Demina, A.I. Borisova, I.D. Kalikhman, Zh. Obshch. Khim., 51 (1981) 1324. Chem. Abst. 96:35372g.

227. A.S. Medvedeva, M.M. Demina, A.I. Borisova, O.I. Margorskaya, I.D. Kalikhman, E.I. Brodskaya, N.S. Vyazankin, J. Organomet. Chem., 231 (1982) 109.

228. A.S. Medvedeva, A.I. Borisova, N.S. Vyazankin, Zh. Obshch. Khim., 51 (1981) 2804. Chem. Abst. 96:85646v.

229. A.I. Borisova, A.S. Medvedeva, N.S. Vyazankin, Ibid, 51 (1981) 1920. Chem. Abst. 96:6786q.

230. M.R. Vilenskaya, G.A. Petrovskaya, A.N. Karpenko, Visn. L'viv Politekh Inst., 149 (1981) 47. Chem. Abst. 96:104364v.

231. S. Cradock, J. Koprowski, D.W. H. Rankin, J. Mol. Struct. 77 (1981) 113.

232. N.N. Belyaev, V. Ya. Komarov, E.V. Komissarova, M.D. Stadnichuk, Zh. Obshch. Khim., 52 (1982) 679. Chem. Abst. 97:5701s.

233. Yu. V. Kolodyazhnyi, N.I. Sizova, I.G. Lorents, L.I. Kuznetsova, A.P. Sadimento, L.I. Ol'khovskaya, N.V. Komarov, Ibid, 52 (1982) 1855. Chem. Abst. 97:216296b.

234. N. Villem, Tartu Riikliku Ulik. Toim., 588 (1981) 133. Chem. Abst. 97:92452c.

235. V. Takhistov, N. Khlebnikova, V. Orlov, Org. React. (Tartu) 17 (1980) 449. Chem. Abst. 96:142097t.

236. O.M. Minailova, V.M. Rzheznikov, K.K. Piunitskii, Zh. Obshch. Khim., 52 (1982) 408. Chem. Abst. 96:218104r.

237. I.E. Gusel'nikov, Z.A. Kerzina, Yu. P. Polyakov, N.S. Nametkin, Izv. Akad. Nauk SSSR, Ser Khim., (1982) 219 Chem. Abst. 96:162804z.

238. L. Birkofer, M. Buchorst, A. Steigel, D. Eichstaedt, J. Organomet. Chem., 233 (1982) 291.

239. D. Terunuma, Shibuya, H. Nohira, Bull. Chem. Soc., Jpn., 55 (1982) 2287.

340. A. Hosomi, H. Iguchi, H. Sakurai, Chem. Lett., (1982) 223.

241. B.M. Trost, H. Hiemstra, T. Am. Chem. Soc., 104 (1982) 886.

242. D.J. Kempf, K.D. Wilson, P. Beak, J. Org. Chem., 47 (1982) 1610.

243. C.H. Chen. J.J. Duney, G.A. Reynolds, Ibid, 47 (1982) 680.

244. H.J. Reich, M.C. Clark, W.W. Willis, Jr., Ibid, 47 (1982) 1618.

245. A. Bonny, R.D. Holmes-Smith, G. Hunter, S.R.Stobart, J.Am. Chem. Soc., 104 (1982) 1855.

246. E. Negishi, F.-T. Luo, C.L. Rand, Tetrahedron Lett., 23 (1982)27.

247. H. Nishiyama, S. Narimatsu, K. Itoh, Ibid, 22 (1981) 5289.

248. H. Nishiyama, H. Yokoyama, S. Narimatsu, K. Itoh, Ibid, 23 (1982) 1267.

249. B.M. Trost, M.J. Dominic. J. Am. Chem. Soc., 104 (1982) 3733.

250. T. Hayashi, M. Konishi, H. Ito, M. Kumada, Ibid, 104 (1982)4962.

251. T. Hayashi, T. Fujiwa, Y. Okamoto, Y. Katsuro, M. Kumada, Synthesis, (1981) 1001.

252. P. Albaugh-Robertson. J.A. Katzenellenbogen, Tetrahedron Lett., 23 (1982) 723.

253. B.M. Trost, B.P. Coppola, J. Am. Chem. Soc., 104 (1982) 6879.

254. B.M. Trost, M. Shimizu, Ibid, 104 (1982) 4299.

255. C.N. Hsiao, H. Shecter, Tetrahedron Lett., 23 (1982) 1963.

256. B.B. Snider, M. Karras, J. Org. Chem., 47 (1982) 4588.

257. H. Sakurai, Jpn Kokai Tokkyo Koho JP 81, 110, 693 (Cl.C07F7/08). Chem. Abst. 96:35532j.

258. G. Sonnek, G. Mueller, Z. Chem., 22 (1982) 102.

259. P. Magnus, F. Cooke, T. Sarkar, Organometallics, 1 (1982) 562.

260. N.V. Ushakova, E.Sh. Finkel'shtein, E.B. Portnykh, V.M. Vdovin, Izv. Akad. Nauk SSSR Ser. Khim. (1981) 2835. Chem. Abst. 96:122864n.

261. M. Koreeda, M.A. Ciufolini, J. Am. Chem. Soc., 104 (1982) 2308.

262. Y. Tanigawa, Y. Fuse, S. Murahashi, Tetrahedron Lett., 23 (1982) 557.

263. E.V. Trukhin, V.M. Berestovistkaya, V.V. Perekalin, Zh. Obshch. Khim., 52 (1982) 1167. Chem. Abst. 97:144905z.

264. Jpn. Kokai Tokkyo Koho Jp 81, 118, 032 (Cl.C07C43/03). Chem. Abst. 96:84742m.

265. H. Nishiyama, K. Itoh, J. Org. Chem., 47 (1982) 2496.

266. H. Nishiyama, S. Narimatsu, K. Sakuta, K. Itoh, J. Chem. Soc., Chem. Commun., (1982) 459.

267. A.P. Kozileowski, K.L. Sorgi, Tetrahedron Lett., 23 (1982) 2281.

268. S. Danishefsky, J.F. Kerwin, Jr., J. Org. Chem., 47 (1982) 3803.

269. G.A. Kraus, K. Neuenschwander, J. Chem. Soc., Chem. Commun, (1982) 134.

270. D. Seyferth, J. Pornet, R.M. Weinstein, Organometallics, 1 (1982) 1651.

271. T. Hayashi, M. Konishi, M. Kumada, J. Am. Chem. Soc., 104 (1982) 4963.

272. Y. Naruta, H. Uno, K. Maruyama, Tetrahedron Lett., 22 (1981)5221.

273. Z.M. Ismail, H.M.R. Hoffmann, Angew. Chem., 94 (1982) 862.

274. T.H. Chan, G.J. Kang, Tetrahedron Lett., 23 (1982) 3011.

275. Y. Morizawa, S. Kanemoto. K. Oshima, H. Nozaki, Ibid, 23 (1982) 2953.

276. H. Nishiyama, K. Itagaki, K. Sakuta, K. Itoh, Ibid, 22 (1981) 5285.

277. K. Ohga, P.S. Mariano, J. Am. Chem. Soc., 104 (1982) 617.

278. M. Hashimoto, M. Aratani, K. Sawada, Eur. Pat. Appl. EP 35,689 (Cl.C07D205/08). Chem. Abst. 96:68708z.

279. S. Padmanabhan, K.M. Nicholas, Tetrahedron Lett., 23 (1982)2555.

280. M. Ochiai, M. Arimoto, E. Fujita, Ibid, 22 (1981) 4491.

281. B. Psaume, M. Montury, J. Gore, Synth. Commun., 12 (1982) 409.

282. A. Hosomi, H. Iguchi, J. Sasaki, H. Sakurai, Tetrahedron Lett., 23 (1982) 551.

283. A. Ricci, A. Degl'Innocenti, M. Fiorenza, M. Taddei, M.A. Spartera, D.R.M. Walton, Ibid, 23 (1982) 577.

284. B.M. Trost, D.P. Curran, J. Am. Chem. Soc., 103 (1981) 7380.

285. B.M. Trost, J.E. Vincent, U.S. US 4, 307,241 (Cl.556-428C0F7/08). Chem. Abst. 96:162934s.

286. B.M. Trost, T.N. Nanninga, D.M.T. Chan, Organometallics 1 (1982) 1543.

287. A. Laporterie, G. Manuel, J. Dubac, P. Mazerolles, Nouv. J. Chim., 6 (1982) 67.

288. R. Benn, H. Guenther, A. Maercker, V. Menger, P. Schmitt, Angew. Chem., 94 (1982) 314.

289. A.F. Cuthbertson, C. Glidewell, J. Organomet. Chem., 221 (1981)19.

290. J. Pornet, N.B. Kolani, Tetrahedron Lett., 22 (1981) 3609.

291. S.I. Pennanen, Synth. Commun., 12 (1982) 209.

292. R.G. Salomon, M.F. Salomon, M.G. Zagorski, J.M. Reuter, D.J. Coughlin, J. Am Chem. Soc., 104 (1982) 1008.

293. H. Matsumoto, M. Kasahara, I. Matsubara, M. Takahashi, T. Nakano, Y. Nagai, Chem. Lett., (1982) 399.

294. H. Boehme, P.M. Sutoyo, Phosphorus Sulfur, 13 (1982) 235.

295. R.A. Benkeser, D.C. Snyder, J. Org. Chem., 47 (1982) 1243.

296. T. Hayashi, Y. Katsuro, Y. Okamoto, M. Kumada, Tetrahedron Lett., 22 (1981) 4449.

297. C. Eaborn, A.R. Hancok, W.A. Stanczyk, J. Organometal. Chem., 218 (1981) 147.

298. G. Fritz, U. Finke, W. Speck, Z. Anorg. Allg. Chem., 481 (1981)51.

299. A. Oliva, A. Molinari, G. Maulen, Bol. Soc. Chil. Quim., 27 (1982) 221. Chem. Abst. 97:23868f.

300. A.H. Cowley, R.A. Kemp. Synth. React. Inorg. Met. Org. Chem., 11 (1981) 591.

301. L.A. Paquette, K.A. Horn, G.J. Wells, Tetrahedron Lett., 23 (1982) 259.

302. S. Halazy, W. Dumont, A. Krief, Ibid, 22 (1981) 4737.

303. G. Fritz. W. Speck, Z. Anorg. Allg. Chem., 481 (1981) 60.

304. M.S. Baird, S.R. Buxton, M. Mitra, Tetrahedron Lett., 23 (1982) 2701.

305. U. Kuehne, F. Krech, K. Issleib, Phosphorus Sulfur, 13 (1982) 153.

306. R.F. Cunico, H.S. Gill, Organometallics, 1 (1982) 1.

307. L.A. Paquette, G.J. Wells, K.A. Horn, T.-H. Yan. Tetrahedron Lett., 23 (1982) 263.

308. R. Okazaki, M. Ooka, T. Akiyama, N. Inamoto, Heterocycles, 18 (1982) 241.

309. M. Sekine, A. Kume, T. Hata, J. Chem. Soc., Chem. Commun., (1981) 969.

310. M. Wada, J. Chem. Soc., Chem. Commun, (1981) 680.

311. H.J. Bestmann, A. Bomhard, Angew. Chem., 94 (1982) 562.

312. Y. Sato, Y. Niinomi, J. Chem. Soc., Chem. Commun., (1982) 56.

313. R. Appel, J. Peters, A. Westerhaus, Angew. Chem., 94 (1982) 76.

314. R. Appel, A. Westerhaus, Tetrahedron Lett., 23 (1982) 2017.

315. F. Cooke, G. Roy, P. Magnus, Organometallics, 1 (1982) 893.

316. P. Magnus, G. Roy, Organometallics, 1 (1982) 553.

317. M. Weidenbruch, H. Flott, Angew. Chem., 94 (1982) 384.

318. T. Agawa, M. Ishikawa, M. Komatsu, Y. Ohshiro, Bull. Chem. Soc. Jpn., 55 (1982) 1205.

319. O.T. Beachley, Jr., C. Tessiere-Youngs, R.G. Simmons, R.B. Hallock, Inorg. Chem., 21 (1982) 1970.

320. F. Glockling, N.M.N. Gowda, Inorg. Chim. Acta, 58 (1982) 149.

321. N.H. Anderson, D.A. McRae, D.B. Grotjahn, S.Y. Gabne, L.J. Theodore, R.M. Ippolito, T.K. Sarkar, Tetrahedron, 37 (1981)4069.

322. G.L. Larson, C. Cádiz, J. Organomet. Chem., 232 (1982) 113.

323. P.J. Stang, M.D. Schiavelli, M.R. Hughey, J.Am. Chem. Soc., 104 (1982) 6852.

324. I.E. Saratov, I.V. Shpak, S.A. Markov, S.Ya. Lazarev, V.O. Reikhsfel'd, Zh. Obshch. Khim., 51 (1981) 2030. Chem. Abst. 96:34173f.

325. P.F. Hudrlik, A.M. Hudrlik, A.K. Kulkarni, J. Am. Chem. Soc., 104 (1982) 6809.

326. G.A. Olah, A.L. Berrier, L.D. Field, G.K.S. Prakash, J. Am. Chem. Soc., 104 (1982) 1349.

327. J.P. Bettioni, D. Dupre, D. Mansuy, J. Organomet. Chem., 214 (1981) 303.

328. P.G. Gassman, T. Miura, Tetrahedron Lett., 22 (1981) 4787.

329. K. Achiwa, M. Sekiya, Ibid, 23 (1982) 2589.

330. D. Terunuma, K. Senda, M. Sanazawa, H. Nohira, Bull. Chem. Soc. Jpn, 55 (1982) 924.

331. E.A. Zel'bst, V.E. Shklover, Yu. T. Struchkov, A.A. Kashaev, L.I. Gubanova, V.M. Dyakov, Yu.L. Frolov, Dokl. Akad Nauk SSSR, 259 (1981) 1369. Chem. Abst. 96:6788s.

332. D.C. McKean, I. Torto, A.R. Morrison, J. Organomet. Chem.,226 (1982) C47.

333. F.A. Carey, W.C. Frank, J. Org. Chem., 47 (1982) 3548.

334. R.T. Taylor, J.G. Galloway, J. Organomet. Chem., 220 (1981) 295.

335. T. Kauffmann, R. Koenig, C. Pahde, A. Tannert, Tetrahedron Lett., 22 (1981) 5031.

336. S.R. Wilson, M.F. Price, J. Am. Chem. Soc., 104 (1982) 1124.

337. J.P. Lambert, R.B. Finzel, Ibid, 104 (1982) 2020.

338. Y. Kita, J. Haruta, H. Yasuda, K. Fukunaya, Y. Shirouchi, Y. Tamura, J. Org. Chem., 47 (1982) 2697.

339. B.H. Lipshutz, J.P. Pegram, M.C. Morey, Tetrahedron Lett., 22 (1981) 4603.

340. A.G. Shipov, L.I. Livantsova, G.S. Zaitserva, Yu. I. Baukov, I.F. Lutsenko, Zh. Obshch. Khim., 52 (1982) 713. Chem. Abst. 97:72413n.

341. B. Psaume, J. Gore, C.R. Seances Acad. Sci., Ser 2 294 (1982) 177.

342. J. Barluenga, J. Villamana, F.J. Fananas, M. Yus, J. Chem. Soc ., Chem. Commun., (1982) 355.

343. V.N. Perchenko, G.L. Kamneva, N.S. Nametkin, Zh. Obshch. Khim., 52 (1982) 362. Chem. Abst. 97:6375a.

344. S. Kuno, Y. Sato, J. Organometal. Chem., 218 (1981) 309.

345. I. Fleming, D.A. Perry, Tetrahedron Lett., 22 (1981) 5095.

346. M. Ochiai, S. Tada, K. Sumi, E. Fujita, J. Chem. Soc., Chem. Commun., (1982) 281.

347. I. Fleming, J. Goldhill, D.A. Perry, J. Chem. Soc., Perkin Trans 1, (1982) 1563.

348. H. Beisswenger, M. Hanack, Tetrahedron Lett., 23 (1982) 403.

349. P.R. Brook, B. Devadas, P.G. Sammes, J. Chem. Res. Synop., (1982) 134.

350. G.S. Zaitseva, G.S. Krylova, O.P. Perelygina, Yu.I. Baukov, I.F. Lutsenko, Zh. Obshch. Khim., 51 (1981) 2252. Chem. Abst. 96:35384n.

351. F.G. Saitkulova, V.V. Fotin, U.S.S.R. SU 792, 889. (Cl.C07F7/08) Chem. Abst. 97:92550h.

352. G.L. Larson, D. Hernández, Tetrahedron Lett., 23 (1982) 1035.

353. L.M. Fuentes, G.L. Larson, Ibid, 23 (1982) 271.

354. D.E. Seitz, R.A. Milius, J. Quick, Ibid, 23 (1982) 1439.

355. M. Larcheveque, A. Debal, J. Chem. Soc., Chem. Commun., (1981) 877.

356. H. Thiese, W. Franke, H. Schwartz, Synthesis, (1982) 587.

357. M. Fourtinon, B. DeJeso, J.C. Pommier, C.R. Seances Acad. Sci, Ser. 2, 293 (1981) 153.

358. U. Klingebiel, S. Pohlmann, P. Werner, Z. Anorg. Allg. Chem., 482 (1982) 65.

359. A. Oliva, S. Stegen, Bol. Soc. Chil. Quim., 27 (1982) 218. Chem. Abst. 97:23867e.

360. I. Fleming, D.A. Perry, Tetrahedron, 37 (1981) 4027.

361. G. Wickham, H.A. Olszowy, W. Kitching, J. Org. Chem., 47 (1982) 3788.

362. D.J. Ager, I. Fleming, S.K. Patel, J. Chem. Soc., Perkin Trans 1, (1981) 2520.

363. O.N. Minailova, K.K. Piunitskii, Zh. Obshch. Khim., 51 (1981) 1437. Chem. Abst. 96:6930g.

364. Yu. A. Ol'dekop, N.A. Maier, A.A. Erdman, Z.P. Zubreichuk, I.A. Shingel, Vestsi Akad Navuk BSSR Ser. Khim. Navuk, (1982) 102. Chem. Abst. 97:72416r.

365. I.L. Dubchak, V.E. Shklover, T.V. Timofeeva, Yu.T. Struchkov, A.A. Zhdanov, E.A. Kashutina, O.I. Shchegolikhina, Zh. Strukt. Khim, 22 (1981) 147. Chem. Abst. 96:69094h.

366. B.M. Trost, D.P. Curran, Tetrahedron Lett., 22 (1981) 5023.

367. B.A. Ashby, Fr. Demande FR 2, 483, 421 (C1.C07F7/08) Chem. Abst. 96:218020k.

368. R.H. Chung, W.D. Kray, Fr. Demande FR 2, 487,837 (C1.C07F7/18). Chem. Abst. 97:6517y.

369. Jpn. Kokai Tokkyo Koho JP 81, 104, 890 (C1.C07F7/18). Chem. Abst. 96:52496t.

370. M. Ochiai, K. Sumi, E. Fujita, Chem. Lett., (1982) 79.

371. Jpn. Kokai Tokkyo Koho JP 82, 14,593 (C1.C07F7/08) Chem. Abst. 97:6516x.

372. M.C. Croudace, N.E. Schore, J. Org. Chem., 46 (1981) 5357.

373. D. Seyferth, R.M. Weinstein, J.Am Chem. Soc., 104 (1982) 5534.

374. G. Guntekunst, A.G. Brook, J. Organomet. Chem., 225 (1982) 1.

375. Jpn. Kokai Tokkyo Koho JP 81, 125,395 (C1.C07F7/08) Chem. Abst. 96:69202s.

376. Jpn. Kokai Tokkyo Koho JP 81,125,320 (C1.C07C7/08) Chem. Abst. 96:69203t.

377. J.A. Soderquist, G.J.H. Hsu, Organometallics, 1 (1982) 830.

378. H.J. Reich, M.J. Kelly, J.Am. Chem. Soc., 104 (1982) 1119.

379. R.G. Visser, L. Brandsma, H.J.T. Bos, Tetrahedron Lett., 22 (1981) 2827.

380. B.G. Christensen, R.W. Ratcliffe, T.N. Salzmann, Eur. Pat. Appl. EP 37, 082 (C1.C07D487/04). Chem. Abst. 96:142559v.

381. K.J.H. Kruithof, G.W. Klumpp, Tetrahedron Lett., 23 (1982) 3101.

382. S.R. Wilson, M.S. Haque, R.N. Misra, J. Org. Chem., 47 (1982)747.

383. B.F. Bonini, G. Mazzanti, S. Sarti, P. Zanirato, G. Maccagnani, J. Chem. Soc., Chem. Commun, (1981) 822.

384. C. Shih. J. Swenton, J. Org. Chem., 47 (1982) 2668.

385. A.G. Brook, F. Abdesaken, G. Gutekunst, N. Plavac, Organometallics, 1 (1982) 994.

386. C.R. Park, S.A. Song, Y.E. Lee, K.Y. Choo, J. Am. Chem. Soc., 104 (1982) 6445.

387. M. Choe, K.Y. Choo, Chem. Phys. Lett., 89 (1982) 115.

388. O. Ito, T. Aruga, M. Matsuda, J. Chem. Soc., Faraday Trans 1, 78 (1982) 2259.

389. T.J. Barton, W.F. Goure, J.L. Witiak, W.D. Wulff, J. Organomet. Chem., 225 (1982) 87.

390. C. Chatgilialoglu, K.U. Ingold, J.C. Scaiano, J.Am. Chem. Soc., 104 (1982) 5123.

391. A.S. Dneprovskii, B.Z. Pertsikov, T.I. Temnikova, Zh. Org. Khim., 18 (1982) 1482.

392. C. Chatgilialoglu, K.U. Ingold, J.C. Scaiano, J.Am. Chem. Soc., 104 (1982) 5119.

393. T. Dohmaru, Y. Nagata, Bull. Chem. Soc. Jpn., 55 (1982) 323.

394. T. Dohmaru, Y. Nagata, J. Chem. Soc., Faraday Trans 1, 78 (1982) 1141.

395. T. Dohmaru, Y. Nagata, J. Phys. Chem., 86 (1982) 4522.

396. M. Kira, H. Sakurai, Chem. Lett., (1982) 221.

397. K.P. Steele, D. Tzeng, W.P. Weber, J. Organomet. Chem., 231 (1982) 291.

398. R.T. Conlin, L.L. Peterson, Ibid, 232 (1982) C71.

399. S.H. Mo, P.P. Gaspar, J. Am. Chem. Soc., 104 (1982) 1424.

400. P.P. Gaspar, Y.S. Chen, A.P. Helfer, S. Konieczny, E.C.L. Ma, S.H. Mo, Ibid, 103 (1981) 7344.

401. S. Burns, G.T. Burns, T.J. Barton, Ibid, 104 (1982) 6140.

402. T.J. Barton, G.T. Burns, W.F. Goure, W.D. Wulff, Ibid, 104 (1982) 1149.

403. D. Seyferth, D.C. Annarelli, D.P. Duncan, Organometallics, 1 (1982) 1288.

404. H. Sakurai, H. Sakaba, Y. Nakadaira, J. Am. Chem. Soc., 104 (1982) 6156.

405. I.M. T. Davidson, F.T. Lawrence, G. Fritz, E. Matern, Organometallics, 1 (1982) 1453.

406. J. Dzarnoski, S.F. Rickborn, H.E. O'Neal, M.A. Ring, Ibid, 1 (1982) 1217.

407. M.S. Gordon, J. Chem. Soc., Chem. Commun., (1981) 890.

408. M.T. Hsu, C.Y. Lee, C.S. Liu, Proc. Natl. Sci. Counc., Repub. China, Part B, 5 (1981) 344. Chem. Abst. 96:51553x.

409. Y.M. Pai, C.K. Chen, C.S. Liu, J. Organomet. Chem., 226 (1982) 21.

410. P. John, B.G. Gowenlock, P. Groome, J. Chem. Soc., Chem. Commun, (1981) 806.

411. I.M.T. Davidson, I.T. Wood, Ibid, (1982) 550.

412. N. Auner, J. Grobe, J. Organomet. Chem., 222 (1981) 33.

413. L.E. Gusel'nikov, V.M. Sokolova, E.A. Volnina, Z.A. Kerzina, N.S. Nametkin, N.G. Komalenkova, S.A. Bashkirova, E.A. Chernyshev Dokl. Akad. Nauk SSSR 260 (1982) 348.

414. N. Auner, J. Grobe, Z. Anorg. Allg. Chem., 485 (1982) 53.

415. G. Bertrand, J. Dubac, P. Mazerolles, J. Ancelle, Nouv.J. Chim., 6 (1982) 381.

416. G. Bertrand, G. Manuel, P. Mazerolles, G. Trinquier, Tetrahedron, 37 (1981) 2875.

417. D. Tzeng, R.H. Fong, H.S.D. Soysa, W.P. Weber, J. Organomet. Chem., 219 (1981) 153.

418. T.J. Barton, S.A. Burns, G.T. Burns, Organometallics, 1 (1982)210

419. H.P. Reisenauer, G. Mihm, G. Maier, Angew. Chem., 94 (1982) 864.

420. R.T. Conlin, M.P. Bessellien, P.R. Jones, R.A. Pierce, Organometallics, 1 (1982) 396.

421. T.J. Barton, G.T. Burns, Ibid, 1 (1982) 1455.

422. P. Potzinger, B. Reimann, R.S. Roy, Ber. Bunsenges Phys. Chem., 85 (1981) 1119.

423. P.R. Jones, M.E. Lee, J. Organomet. Chem., 232 (1982) 33.

424. N. Wiberg, G. Preiner, O. Schieda, Chem. Ber., 114 (1981) 3518.

425. N. Wiberg, G. Preiner, O. Schieda, G. Fisher, Ibid, 114 (1981) 3505.

426. A.G. Brook, S.C. Nyberg. F. Abdesaken, B. Gutekunst, G. Gutekunst, R. Krishna, M.R. Mallory, Y.C. Poon, Y.M. Chang, W.N. Winnie, J.Am. Chem. Soc., 104 (1982) 5667.

427. A.G. Brook, R. Krishna, M.R. Kallury, Y.C. Poon, Organometallics, 1 (1982) 987.

428. G. Bertrand, P. Mazerolles, J. Ancelle, Tetrahedron 37 (1981) 2459.

429. A.K. Maltsev, V.N. Khabashesku, O.M. Nefedov, J. Organomet. Chem., 226 (1982) 11.

430. M.S. Gordon, J. Am. Chem. Soc., 104 (1982) 4352.

431. Y. Yoshioka, H.E. Schaefer, III, Ibid, 103 (1981) 7366.

432. W.J. Prieto, W.J. Hehre, Ibid, 104 (1982) 4329.

433. P. Boudjouk, B.H. Han, K.R. Anderson, Ibid, 104 (1982) 4992.

434. R. West, M.J. Fink, J. Michl, Science, 214 (1981) 1343.

435. G. Maier, G. Mihm, H.P. Reisenhauer, Chem. Ber., 115 (1982) 801.

436. G. Maerkl, D. Rudnick, R. Schultz, A. Schweing, Angew. Chem., 94 (1982) 211.

437. T.J. Barton, M. Vuper, J. Am. Chem. Soc., 103 (1981) 6788.

438. J.D. Rich, R. West, Ibid, 104 (1982) 6884.

439. S. Masamune, Y. Hanzawa, S. Murakami, T. Bally, J.F. Blount, Ibid, 104 (1982) 1150.

440. M. Ishikawa, H. Sugisawa, M. Kumada, T. Higuchi, K. Matsui, K. Hirotsu, Organometallics, 1 (1982) 1473.

441. G.A. Olah, L.D. Field, Ibid, 1 (1982) 1485.

442. J.R. Eyler, G. Silverman, M.A. Battiste, Ibid, 1 (1982) 477.

443. M.L. Hendewerk, D.A. Weil, T.L. Stone, M.R. Ellenberger, W.E. Farneth, D.A. Dixon, J. Am. Chem. Soc., 104 (1982) 1794.

444. M.F. Dottore, V.C. Trenerry, D.J. Stone, J.M. Bowie, Org. Mass Spectrom., 16 (1981) 339.

445. B.W. Walter, F. Williams, J. Chem. Soc., Chem. Commun., (1982) 270.

446. C. Glidewell, Inorg. Chim. Acta., 64 (1982) L59.

447. T. Aoyama, T. Shioiri, Chem. Pharm. Bull., 29 (1981) 3249.

448. Jpn. Kokai Tokkyo Koho JP 82 14, 556 (Cl.C07C67/14). Chem. Abst. 97:5988r.

449. Ibid, JP 82 64,620 (Cl.C07B29/00). Chem. Abst. 97:127299n.

450. N. Hashimoto, T. Aoyama, T. Shioiri, Chem. Pharn. Bull., 30 (1982) 119.

451. Jpn. Kokai Tokkyo Koho JP 82 14,550 (Cl.C07C45/68). Chem. Abst. 96:199169x.

452. A. Sekiguchi, Y. Kabe, W. Ando, J. Org. Chem., 47 (1982) 2900.

453. W. Ando, A. Sekiguchi, T. Sato, J. Am. Chem. Soc., 104 (1982) 6830.

454. A. Sekiguchi, W. Ando, Bull. Chem. Soc., Jpn., 55 (1982) 1675.

455. T.J. Barton, S.K. Kent, S.A. Burns, Organometallics, 1 (1982) 721.