SILICON — THE SILICON-CARBON BOND; ANNUAL SURVEY FOR THE YEAR 1984[*]

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[*] Previous review see J. Organomet. Library 17, Elsevier Science Publ., Amsterdam, 1985, p. 1-162.

I. INTRODUCTION

This section of the annual survey of organosilicon chemistry covers material appearing in volumes 100 and 101 in Chemical Abstracts. It is the intention of this author to report on the silicon-carbon bond and carbofunctional organosilicons. It will be noted that in many instances equations are written in general form with liberal use of R, Ar, and TMS for the alkyl, aryl, and trimethylsilyl groups, respectively. In an attempt to convey more information in this year's version, several tables have been reproduced directly from the literature with special thanks due to those authors and publishers who gave permission for their reproduction. Although effort has been made to arrange the material into sections, the reader is advised to peruse all sections since the multiple nature of much of the chemistry does not permit complete categorization of all the material.

II. REVIEWS

A total of thirty nine reviews appeared, not all of which are directly aligned with this chapter, but which are listed nevertheless. The number of references to be found in each review is given in parentheses.

The synthesis and reactivity of silicon compounds were the topics of a number of reviews. These dealt with silafunctional compounds (531 and 506) [1,2], organosilicon reaction mechanisms (290) [3], hyperconjugation of organosilicons (40) [4], steric effects (200) [5], intramolecular interactions (219) [6], organosilicons as alkylating agents (16) [7]. The silylation reaction was the topic of two reviews one dealing with hydroxyl-containing compounds (41) [8] and the other with nucleosides and nucleotides (80) [9]. The hydrosilylation with silicon ion complexes of platinum was reviewed (10) [10]. Dioxosilaheterocycles (101) [11] and the reactions of organopolysilanes with organic peroxides (75)[12] were reviewed. A review on a new phase of organosilicon chemistry dealing with new silicon compounds including formal polymers appeared (0) [13]. Silicon-containing odorous compounds were reviewed (26) [14].

Reviews on the uses of organosilicons continue to appear. These include the use of organosilicons in synthesis (15) [15], selective syntheses with organosilicons (11) [16], organosilicon synthesis of isocyanates (71 and 111) [17, 18], new synthetic chemistry of transition metal trialkylsilane complexes (71) [19], important organosilicon reagents (14) [20] and applications of chlorotrimethylsilane-sodium iodide to synthesis (16) [21]. The synthetic applications of fluordesilylation was reviewed (5) [22].

Reactive silicon species was the topic of several reviews including divalent organosilicon species (32) [23], the formation and reactions of silylene (28) [24], a new look at the chemistry of difluorosilylene (36) [25], gas phase reactions of dichlorosilylene (43) [26], studies of silaethene (40) [27], small ring doubly bonded organosilicons (2) [28], silyl anions (113) [29] and silacyclohexadienyl anions (35) [30].

In addition to the reviews listed above several useful reviews, which are not abstracted, were published by Petrarch Systems, Inc. These deal with general organosilicon chemistry (4) [31], acylsilanes (66) [32], and silylcarbonyl compounds (68) [33], silene chemistry (68) [34], organopolysilanes (49) [35], organofluorosilicate chemistry (53) [36], silane blocking agents (57) [37], silane coupling agent chemistry (3) [38], and a compilation of infrared data of organosilicons (3) [39].

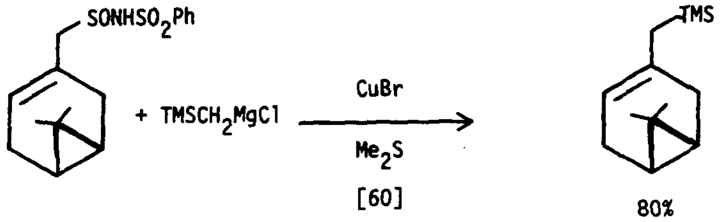
III. DISSERTATIONS

Twenty dissertations appeared in Dissertation Abstracts during the year. These are available from University Microfilms, Ann Arbor, Michigan. The topics dealt with in these theses are the reaction of α,β-unsaturated ketones with iodosilanes [40], the development of new organosilicon reagents [41], reduction and carbometalation of alkynylsilanes [42], synthesis and reactions of α,β-unsaturated silyl ketones [43], polyolefin allylsilane cyclizations [44], the use of trimethylsilylketene in the synthesis of coumarins and in cyclization eliminations [45], silylcyclopropanes as synthetic intermediates [46], carbon-carbon bond formation using metallo derivatives of organosilicons [47], bromovinylsilanes in synthesis [48], reactions of metal vapors with bis(trimethylsilyl)acetylene [49], synthesis and structures of dihydrosilaanthracenes and dihydrosilaheteroanthracenes [50], synthesis and structural chemistry of organosilicon compounds [51], trimethysilylmethylgallium compounds [52], cyclic silanes [53], silylenes, disilenes and cyclodisiloxanes [54], synthesis and mechanistic studies of silaoxetanes and silanones [55], synthesis and polymerization of trialkylsilylstyrenes [56], mechanism and kinetics of shock-induced decomposition of ethylsilane, vinylsilane and dimethylsilane [57], some chemistry of dimethylsilylene [58], and evidence for a silylenium ion in solution [59].

IV. ALKYLSILANES

A. Preparation

The reaction of allyl sulfonamides with trimethylsilylmethylmagnesium chloride in the presence of cuprous bromide gives homoallylic silanes. (Eqns. 1-3) The reaction occurs in an S_N2 and an S_N2' manner.



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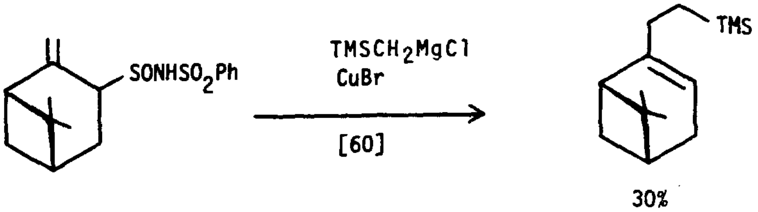

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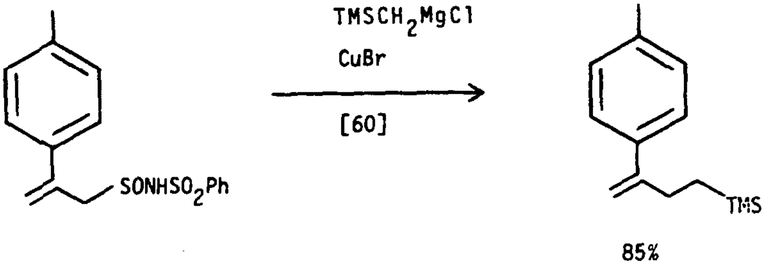

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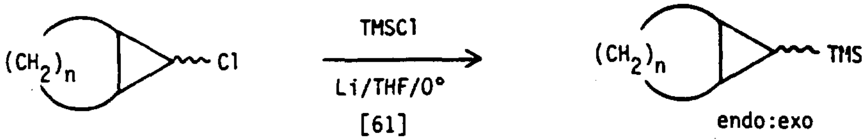
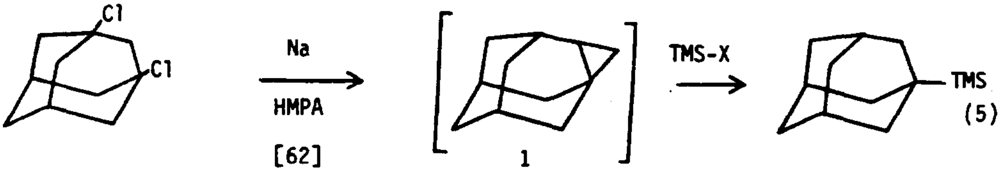
Chlorocyclopropanes were converted to trimethylsilylcyclopropanes with the TMSCl/Li/THF reagent. (Eqn. 4)



(4)

n		endo:exo
n = 3	80%	45:55
4	85%	40:60
5	85%	48:62

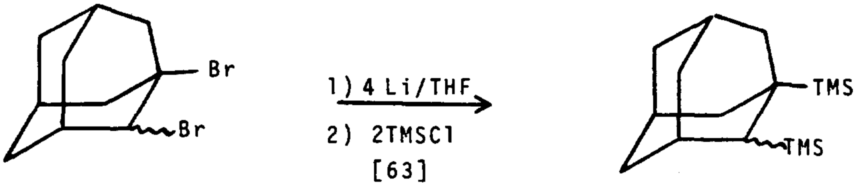
1-Trimethylsilyladamantane can be prepared from 1,3-dichloroadamantane, sodium and certain silanes in hexamethylphosphoric triamide. (Eqn. 5) The reaction is postulated as passing through the cyclopropane 1.



(5)

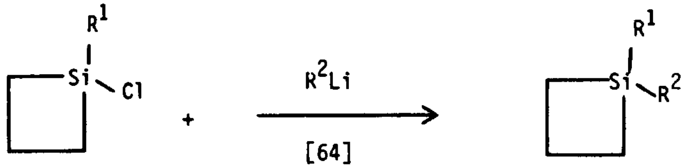
X =			
H	48%	Cl	14%
TMS	52%	NEt_2	95%
OTMS	50%		

The isomeric bis-trimethylsilyladamantanes were prepared from the corresponding dilithium reagents. (Eqn. 6)



(6)

The 1-carboranyl-1-silacyclobutanes **2** and **3** were prepared from the corresponding chlorosilacyclobutanes and the lithiated carboranes. (Eqn. 7).



(7)

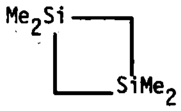
2 R^1 = Me, R^2 = 1-methyl-m-carboran-7-yl

3 $R^1 = R^2$ = 1-methyl-O-carboran-2-yl

The reaction of diethyl(trimethylsilyl)phosphite with carbon tetrachloride gives several compounds including chlorotrimethylsilane, trichloromethyltrimethylsilane and 1,1,3,3-tetramethyl-1,3-disilacyclobutane. (Eqn. 8) The dimethyl and di-n-propyl derivatives react similarly.

$$(EtO)_2POTMS + CCl_4 \xrightarrow[{[65]}]{} (EtO)_2P(O)Cl + (EtO)_2P(O)CCl_3 + TMSCl + TMSCCl_3 + HCCl_3 \qquad (8)$$

$+$



B. Reactions

Tetrasubstituted organosilicons undergo redistribution reactions in the presence of trichlorosilane and chloroplatinic acid. The smallest groups tend to exchange most readily. (Eqn. 9) The results are shown in Table I.

The hydromethylation of olefins can be accomplished by treatment with tetramethylsilane and aluminum chloride in the presence of hydrochloric acid. (Eqns. 10, 11). In other examples, 2-methyl-2-butene gave 2,2-dimethylbutane in 92 percent yield and 1-methylcyclopentene gave 1,1-dimethylcyclopentane in 40 percent yield.

$$R^1R^2R^3R^4Si + SiHCl_3 \xrightarrow[[66]]{H_2PtCl_6} R^2R^3R^4SiCl + R^1SiHCl_2 \qquad (9)$$

TABLE 1

EXCHANGE REACTIONS BETWEEN ORGANOSILANES AND TRICHLOROSILANE

Organosilanes	Reaction conditions (°C/h)	Products $ClSiRR'_2$ (Yield %)+$HSiCl_2R$
1. Et_2Si-n-Pr_2	153/72	$ClSiEt$-n-Pr_2 (81) $HSiCl_2Et$ $ClSiEt_2$-n-Pr (9) $HSiCl_2$-n-Pr
2. Et_2Si-i-Pr_2	161/72	$ClSiEt$-i-Pr_2 (85) $HSiCl_2Et$
3. Et_2Si-n-Bu_2	164/72	$ClSiEt$-n-Bu_2 (83) $HSiCl_2Et$
4. n-Pr_2Si-i-Pr_2	165/72	mixture of $HSiCl_2$-n-Pr + $(C_3H_7)_3SiCl$ isomers
5. n-Pr_4Si	166/24	$ClSi$-n-Pr_3 (78) $HSiCl_2$-n-Pr
6. (*p*-tolyl)$_4$Si	145/48	ClSi-*p*-tolyl$_3$ (65)[a]

[a] Based on ClSi-*p*-tolyl$_3$/(*p*-tolyl)$_4$Si ratio in product mixture.
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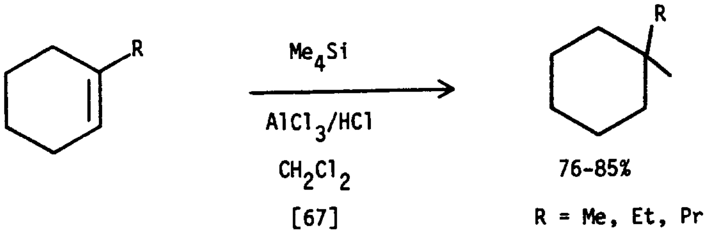

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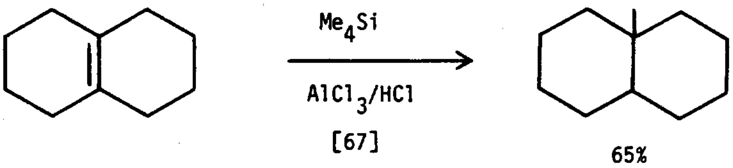


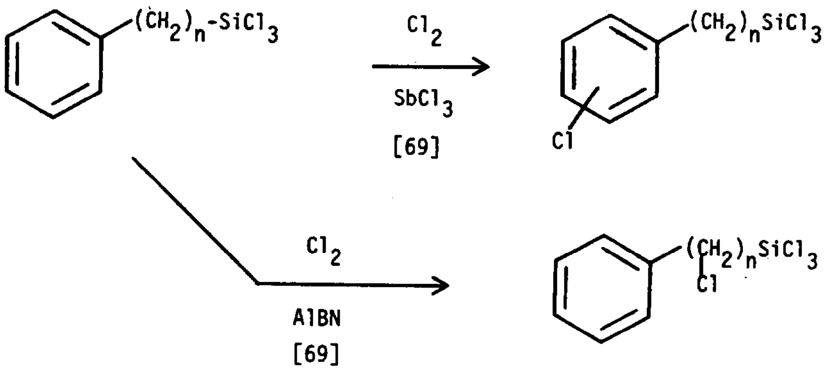
(11)

The chlorination of tetramethylsilane with chlorine in the presence of 5 mol percent iodine provides a quantitative yield of chlorotrimethylsilane. (Eqn. 12). The reaction was applied to other tetraalkylsilanes as well.

$$Me_4Si \xrightarrow[30°/CCl_4]{Cl_2/I_2(cat)} Me_3SiCl \qquad (12)$$

[68]

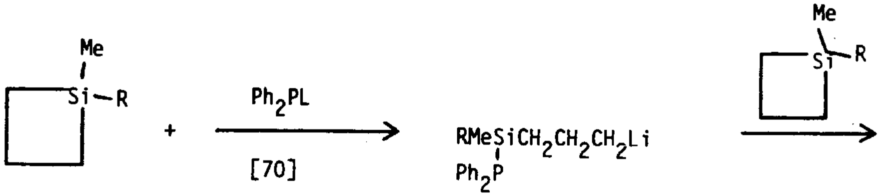
Chlorination of ω-phenylalkyltrichlorosilanes in the presence of antimony trichloride proceeds at the aromatic ring, whereas in the presence of AIBN chlorination takes place on the chain. In the absence of a catalyst both sites are chlorinated. (Eqns. 13, 14)



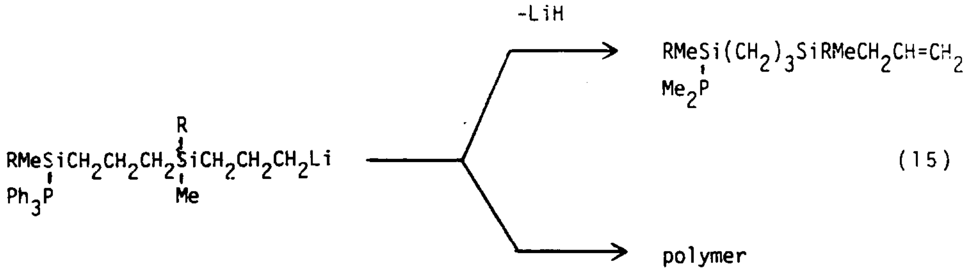
(13)

(14)

Diphenylphosphoryllithium opens silacyclobutanes via nucleophilic attack at silicon to produce a γ-silylpropyllithium reagent, which can itself attack another silacylobutane leading eventually to allyldisilapentanes, via loss of lithium hydride, or to polymers. (Eqn. 15)



R = Me, m-tolyl

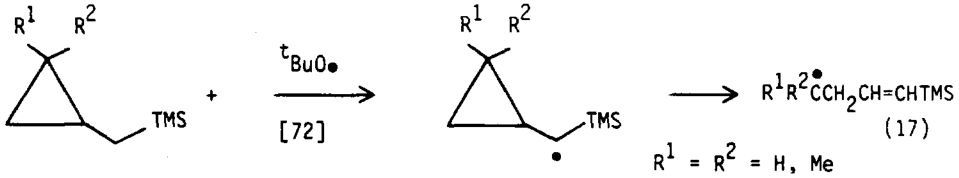


$$\underset{Ph_3P}{RMeSi}CH_2CH_2CH_2\overset{R}{\underset{Me}{Si}}CH_2CH_2CH_2Li \xrightarrow{-LiH} \underset{Me_2P}{RMeSi}(CH_2)_3SiRMeCH_2CH{=}CH_2 \quad + \quad \text{polymer} \qquad (15)$$

The reaction of substituted trimethylsilanes with hydroxide ion in the gas phase was used to obtain the relative gas phase acidities of alkanes as obtained from the ratio of Me_3SiO^- to RMe_2SiO^- produced according to Eqn. 16.

$$Me_3SiR \ + \ HO^- \xrightarrow[\text{[71]}]{} Me_3SiO^- \ + \ RH \ + \ RMe_2SiO^- \ + \ CH_4 \ . \qquad (16)$$

Trimethylsilylmethylcyclopropanes, when reacted with the tert-butoxy radical, proceeds to give the cyclopropylmethyl radical, which opens to the homoallylic radical. (Eqn. 17) In the trimethylsilylcyclopropanes **4** and **5** the stereochemistry of the substituents determines the pathway of the ring opening. (Eqn. 18) The cyclopropyl group activates the methylene group better than does the trimethylsilyl group. (Eqn. 19) The 1,1-bistrimethylsilyl[n.2.0]-cycloalkanes **6** react to give the α-silyl radicals and not the ring expanded β-silyl radicals. (Eqn. 20)



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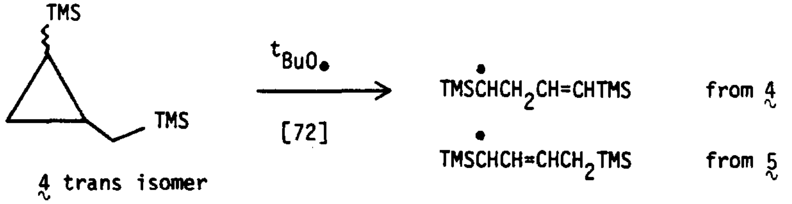
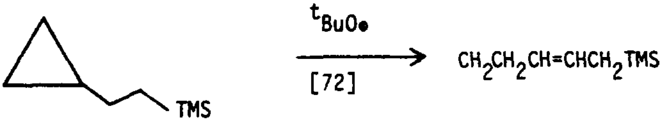


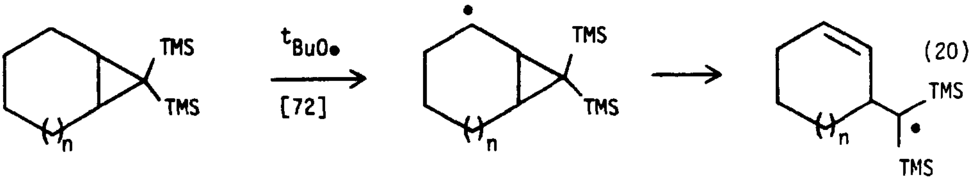
(18)

4 trans isomer

5 cis isomer



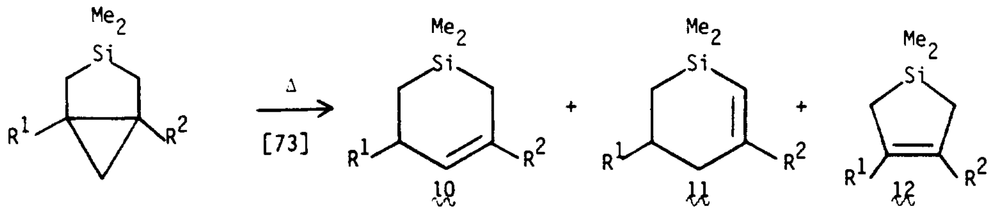
(19)



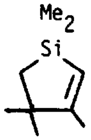
(20)

6 n = 1,3

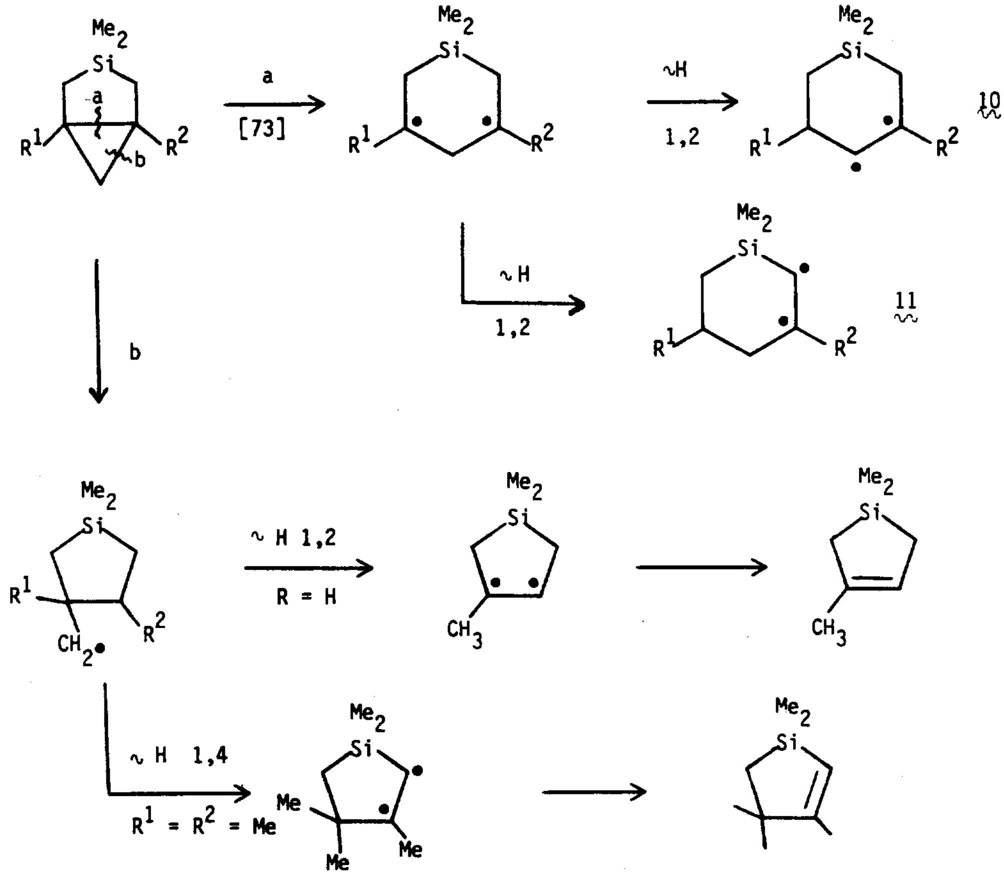
The thermal isomerization of 3-sila[3.1.0]hexanes was carried out on compounds 7, 8 and 9 to give silacyclohexenes and silacyclopentenes. (Eqn. 21) The proposed mechanism is that shown in Scheme I.



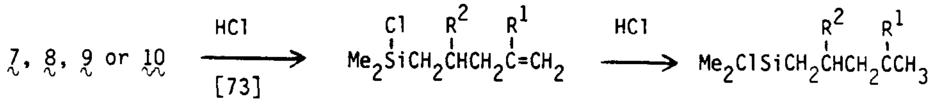
(21)

Compound	Conditions	10	11	12
7 $R^1 = R^2 = H$	560°/flow system	90%	5%	5%
8 $R^1 = H$; $R^2 = Me$	410°/sealed tube	45%	45%	10%
9 $R^1 = R^2 = Me$	330°/sealed tube	40%	40%	 (20%)

SCHEME I



Compounds **7**, **8**, and **9** react with HCl to give ring cleavage products, presumably via a β-silyl carbocation. Compound **10** reacts similarly. (Eqn. 22)



$$\mathbf{7},\ \mathbf{8},\ \mathbf{9} \text{ or } \mathbf{10} \xrightarrow[{[73]}]{HCl} Me_2\overset{Cl}{Si}CH_2\overset{R^2}{C}HCH_2\overset{R^1}{C}{=}CH_2 \xrightarrow{HCl} Me_2ClSiCH_2\overset{R^2}{C}HCH_2\overset{R^1}{C}CH_3 \quad (22$$

It has been shown that a variety of alkylmethylsilanes containing from one to three electronegative ligands,X (where X=H, Cl, F, EtO, NEt_2) can be oxidized to the corresponding alkanols. (Eqn. 23) The electronegative ligand can be disguised as an allyl or phenyl group if these are first converted to the fluoride prior to oxidation. (Eqn. 24)

$$RSiMe_nX_{3-n} \xrightarrow[\substack{KHCO_3 \\ \text{or } NaHCO_3 \\ [74]}]{30\%H_2O_2} \underset{68\text{-}100\%}{ROH} \qquad (23)$$

n = 0-2

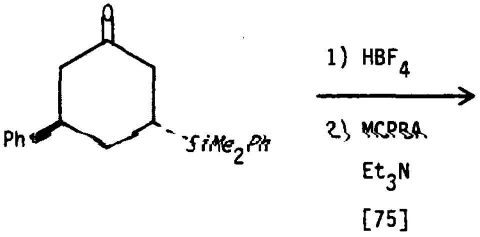
X = H, Cl, F, OEt, NEt_2

R = $^nC_8H_{17}$

$$R^1SiMe_2R^2 \xrightarrow[\substack{2)\ KHF_2/MeOH \\ 3)\ 30\%H_2O_2 \\ KHCO_3 \\ [74]}]{1)\ CF_3CO_2H} R^1OH \qquad (24)$$

R^2 = allyl or phenyl

A similar approach to the oxidation of alkylphenyldimethylsilanes, wherein the phenyl group acts as a disguised fluoride ligand, is shown in Eqns. 25 and 26. The reaction proceeds with retention of configuration at carbon.



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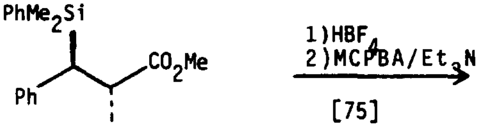
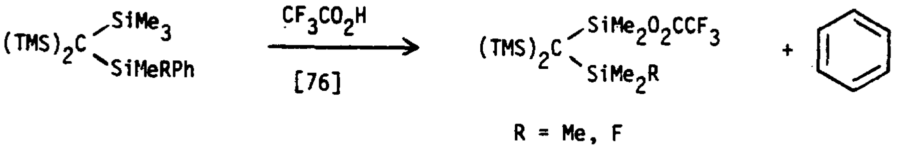


(26)

The cleavage of the silicon-carbon bond in tris(trimethylsilyl)methylsilicon compounds was studied. The reaction proceeds with rearrangement and anchimeric assistance. (Eqns. 27-29)



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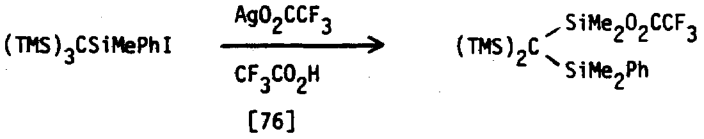
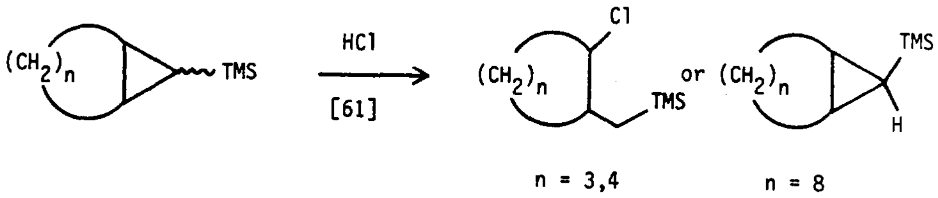


(28)

$$(TMS)_3CSiMe_2OMe \xrightarrow[25°/30\ min.]{CF_3CO_2H} (TMS)_2C(SiMe_2O_2CCF_3)_2 \qquad (29)$$

[76]

The 1-trimethylsilyl[n.1.0]cycloalkanes (n=3, 4) react with HCl to give cleavage of the C-1 - C-2 bond, where n=8 the endo isomer isomerizes to the exo isomer under these conditions. (Eqn. 30) The reaction with $BF_3 \cdot (HOAC)_2$ depends on the value of n. (Eqns. 31-33).



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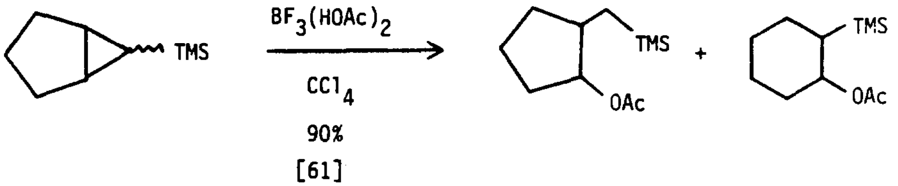

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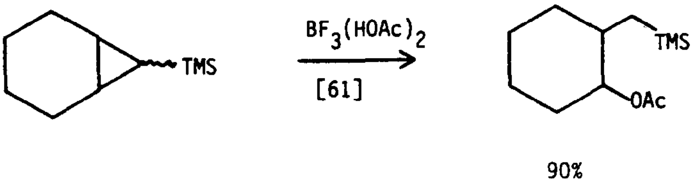

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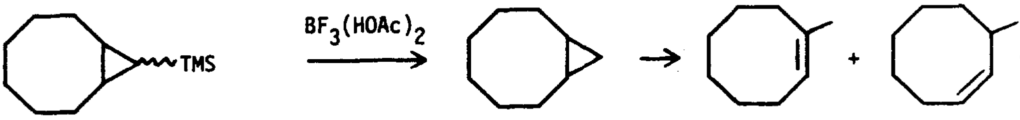

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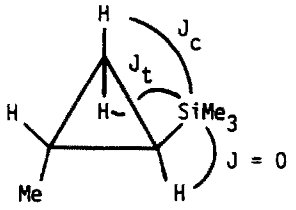
C. Spectral and Other Studies

The ^{13}C- and ^{29}Si-NMR spectra of a number of silylcyclopropanes have been reported. The ^{13}C chemical shifts are intermediate between those of vinyl and ethylsilanes. The ^{29}Si chemical shifts do not show any evidence for back bonding between the ring and the silicon atom. [77] A microcomputer was used to calculate the ^{1}H-^{29}Si coupling constants in silicon- containing molecules. [78] Silicon-29 NMR spectroscopy employing selective population inversion was used to determine the stereochemistry of silylcyclopropanes via the ^{1}H-^{29}Si coupling constants. Some of the coupling constants are shown in structures **13** and **14**. [79] The study was extended to exo- and endo-1-trimethylsilyllbicyclo[3.1.0]-hexanes, **15** and **16**. [80]



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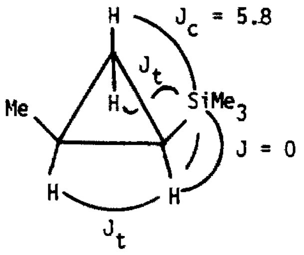
J_t = 3.9; J_c = 6



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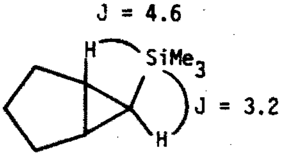
J_t = 3.2 and 3.5



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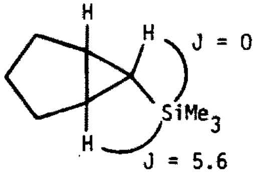
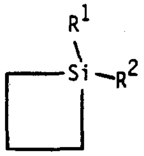


16

values in Hz

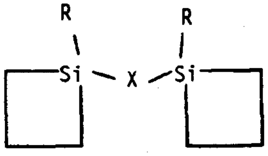
The mass spectra of a series of silacyclobutanes **17** and **18** have been reported. [82] The far-IR spectra of 1-silacyclopent-3-ene and its 1-deutero and 1,1-dideutero derivatives have been reported. This provided evidence of not only the normal ring puckering, but also for a ring twisted excited state. [83] Fluorine-19 NMR has been employed in studying the conformations of **19**. The conformations for R = H are shown in Eqn. 34. [84] The x-ray silicon K spectrum of tetramethylsilane has been reported. [85]



R^1 = Me, ${}^tBu$, Ph, $PhCH_2$, cC_6H_{11}, $pMeC_6H_4$, $\alpha C_{10}H_7$

R^2 = Ph, $PhCH_2$, $pMe_2NC_6H_4$, $\alpha C_{10}H_7$

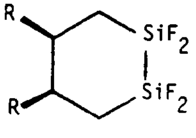
17



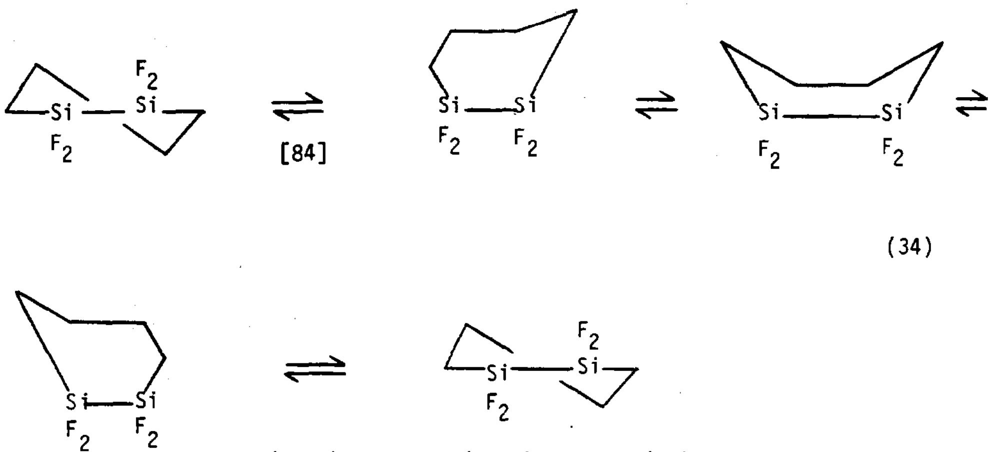
X = bond, R = $\alpha C_{10}H_7$

X = O R = Ph, $\alpha C_{10}H_7$

18



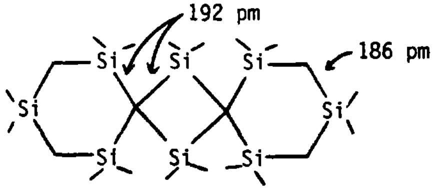
19



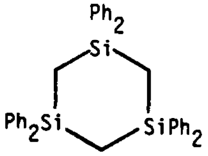
(34)

R	ΔH (kcal)	ΔG (kcal)	ΔS (eu)
Cl	7.17	12.14	-18.9
Br	7.77	12.72	-18.2
Me	5.22	8.40	-17.8
H		6.3	

The crystal structure of **20** shows it to have flattened chair six-membered rings and elongated Si-C bonds (192 pm) at the strained spiro center. [86] The crystal structure of **21** shows it to have a flattened twist-boat conformation with a Si-CH_2 distance of 187.1 pm, a ring C-Si-C angle of 110.0^{o} and a Si-C-Si angle of 117.9^{o}. [87]



20



21

The electronic structures for disilane, ethane, methylsilane, pentasilane, tetrasilylmethane and pentane were calculated. It was found that coulombic stabilization of the Si-C bond compensates for lower overlap so that the compounds are stable to disproportionation and that bonding differences can be explained on the basis of local interactions indicating that the delocalization in silanes is due to second order interactions involving low lying excited states. [88] Ab-initio and electron diffraction studies on cyclobutylsilane indicate a slight preference for the equatorial silyl group. [89]

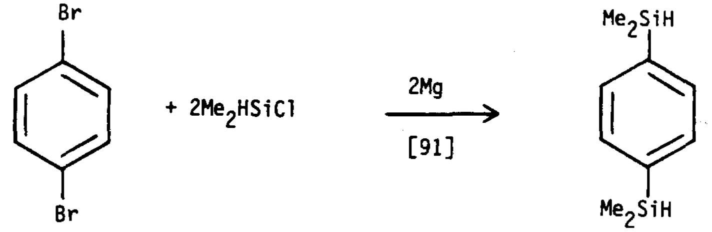
The multiple-IR-photon decomposition of alkysilanes proceeds via a four-center mechanism involving hydrogen atoms β to silicon. (Eqn. 35)

$$H_3SiCH_2CH_3 \xrightarrow[\text{[90]}]{\text{MIRPD}} H_4Si \quad + \quad CH_2{=}CH_2 \qquad (35)$$

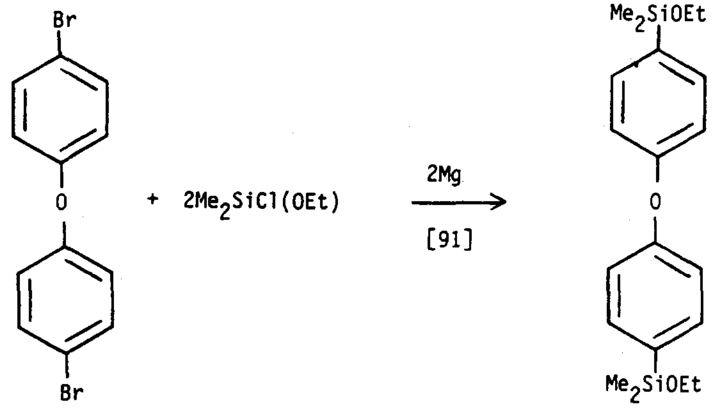
V. ARYLSILANES

A. Preparation

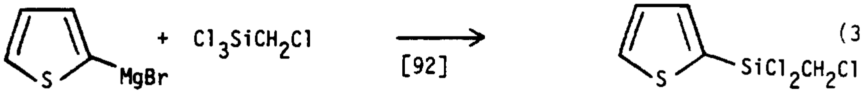
Arylsilanes were prepared from arylmagnesium halides or aryllithium reagents and chorosilanes. Some examples are presented without further comment, except to point out that Eqns 43-45 nicely illustrate the concept of utilizing the trimethylsilyl group to block a more reactive position. (Eqns. 36-46)



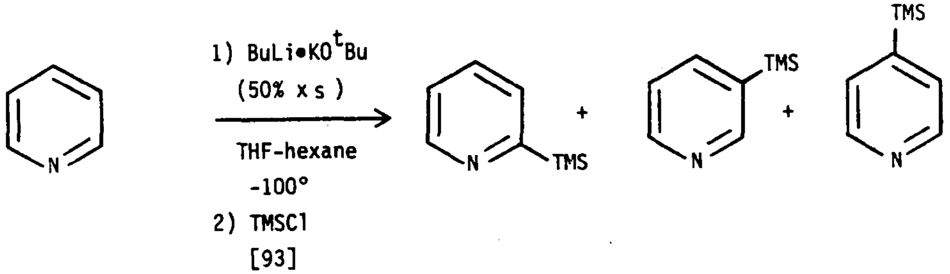
(36)



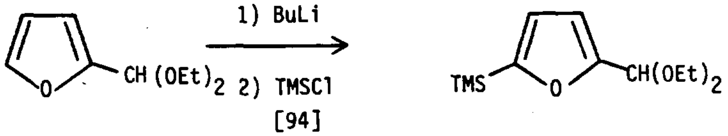
(37)



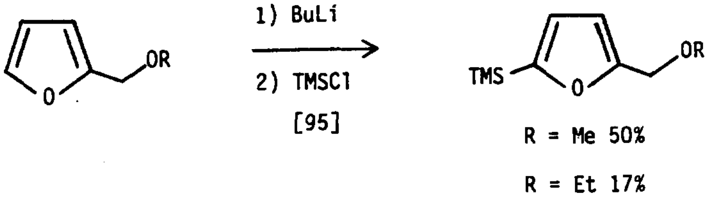
(38)


1) BuLi•KO^{t}Bu
(50% xs)
THF-hexane
-100°
2) TMSCl
[93]
N
TMS
+
TMS
+
TMS

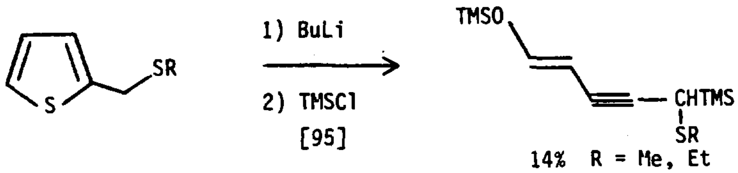
(39)


O
CH(OEt)$_2$
1) BuLi
2) TMSCl
[94]
TMS
O
CH(OEt)$_2$

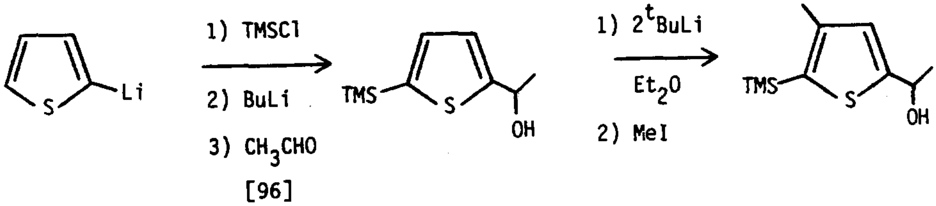
(40)


O
OR
1) BuLi
2) TMSCl
[95]
TMS
O
OR
R = Me 50%
R = Et 17%

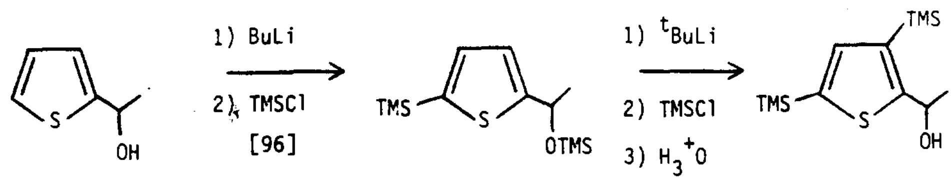
(41)


S
SR
1) BuLi
2) TMSCl
[95]
TMSO
CHTMS
SR
14% R = Me, Et

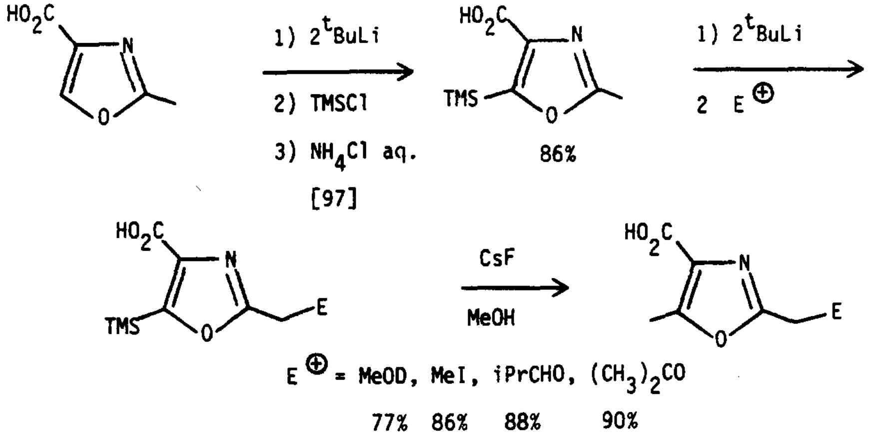
(42)


S
Li
1) TMSCl
2) BuLi
3) CH$_3$CHO
[96]
TMS
S
OH
1) 2^{t}BuLi
Et$_2$O
2) MeI
TMS
S
OH

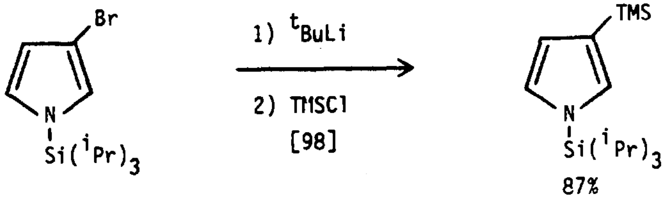
(43)



(44)

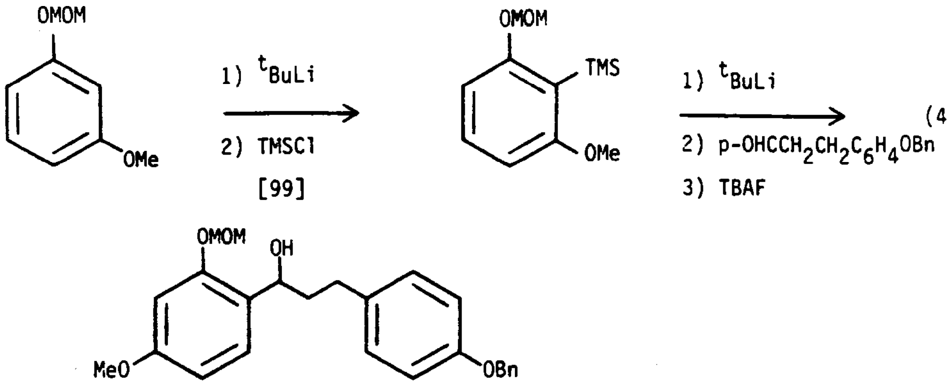


(45)

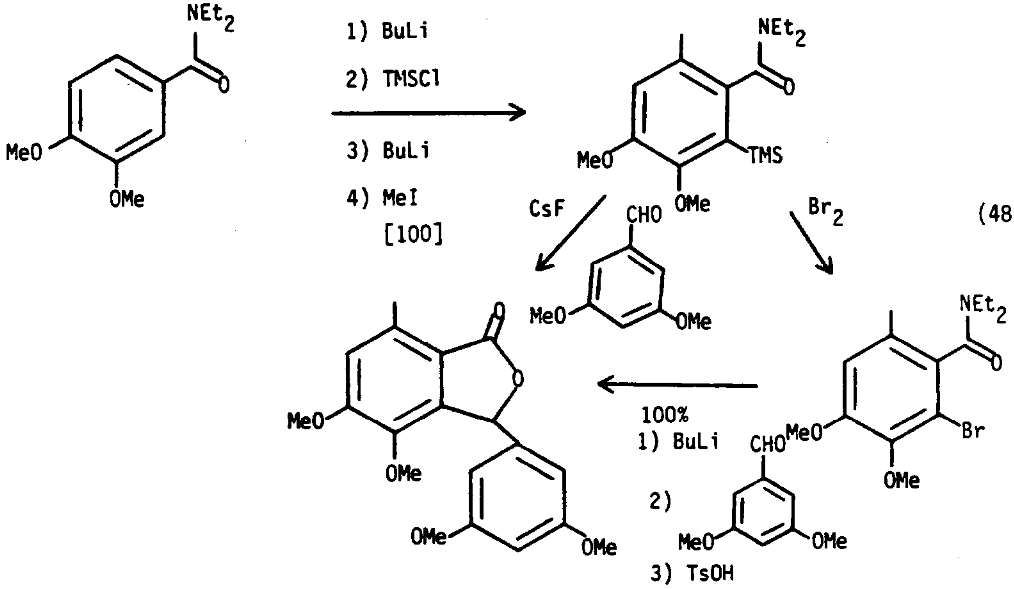


(46)

The concept of ortho-lithiation-silylation has been put to good use in synthetic strategy. In the example shown in Eqn. 47 the trimethylsilyl group is used to block a more reactive site to allow lithiation at C-6. The trimethylsilyl group is then removed with fluoride ion to give, in this example, the protected precursor to the flavanoid brousonin A. A second example, shown in Eqn. 48, employs the trimethylsilyl group to both protect the more reactive site and provide a regiospecific introduction of bromine in a route towards naturally-ocurring anthraquinones. The trimethylsilyl group can be a direct precursor to the anion as well.

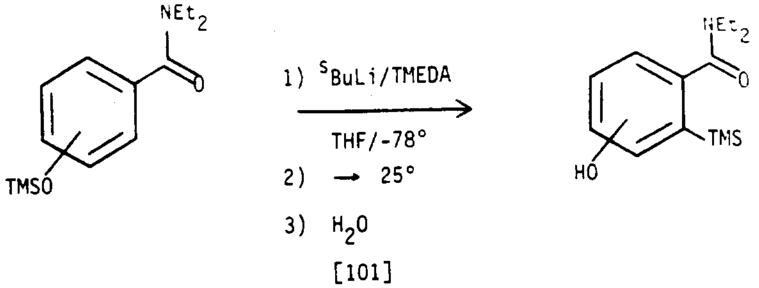


(47)



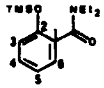
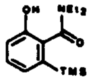
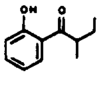
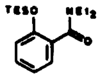
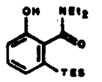
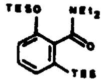
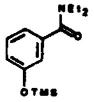
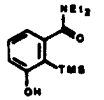
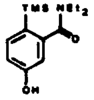
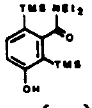
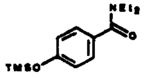
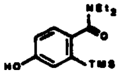
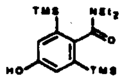
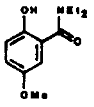
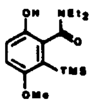
(48)

Certain trimethylsilylated phenols can be lithiated. This is followed by a rearrangement of the trimethylsilyl group from oxygen to carbon to give arylsilanes (Eqns. 49-51) Additional results concerning Eqns. 49 and 50 are given in Tables II, III and IV. In the case of m-trimethylsilyloxybenzamides this was turned into a convenient route to products from a benzyne intermediate. (Eqn 50) Para-methoxybenzaldehyde was deprotonated and silylated ortho to the methoxy group. (Eqn. 51)



(49)

Table II: Anionic Silicon Rearrangements of Silyloxy Benzamides.[a]

Benzamide	Products[b] yield,[c] %		
 4a	 6a 68[d]	 2	
 4b	 6b 47 (45)	 10 (30)	
 4c	 6c 58 (62)	 6d 5 (16)	 4 (11)
 4d	 6e 78 (82)		 11 (10)
 4e	 6f (76)		

[a] TMS = $SiMe_3$, TES = $SiEt_3$. [b] All products showed analytical and spectral (IR, NMR, MS) data consistent with the assigned structures. 6a, 6c, and 6f were chemically correlated (MeI/K_2CO_3/acetone) with silylated anisamides prepared by directed ortholithiation-silylation.[11] [c] Yields are of purified (chromatographed, distilled) materials. Yields in brackets correspond to those obtained by in situ preparation of 4a-d and the TMS derivative of 4e. [d] 21% of starting 4a was recovered.

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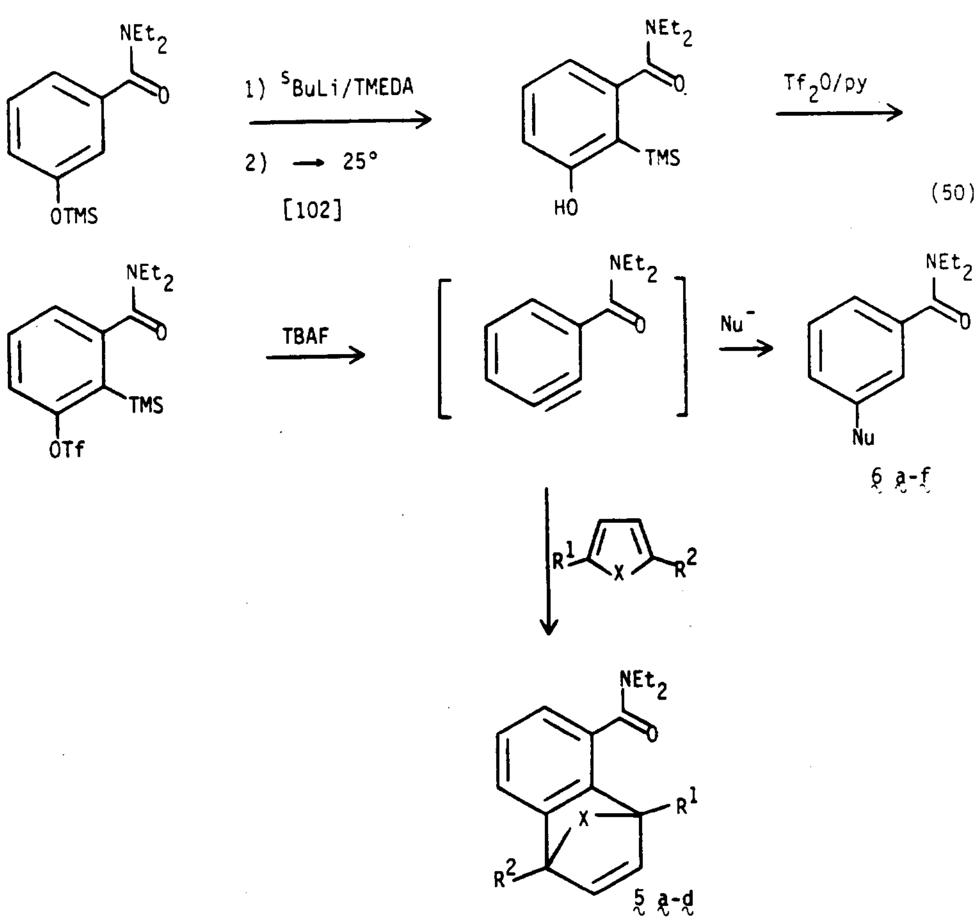

(50)

Table III: Reaction of the Benzyne of N,N-Diethylbenzamide with Nucleophiles.

Nu$^-$	Product	Nu	Yield, %
HOMe	**6a** [b]	OMe	41
HOPh	**6b**	OPh	43
LiSPh	**6c** [c]	SPh	62
TMSNHPh[d]	**6d** [e]	NHPh	70
TMSN(Me)Ph[d]	**6e** [c,e]	N(Me)Ph	83
 **TMSO** **O**	**6f** [e]	CH(COMe)$_2$	22

---

[a] See footnote a, Table 1. All products were oils with the exception of **6d**, mp 97-98°C (CH_2Cl_2-hexane). [b] Found to be identical with an authentic sample by direct comparison of spectroscopic and hplc properties. [c] Compounds **6c** and **6e** were shown to be different by spectroscopy (IR, NMR) and hplc behavior with the corresponding authentic o-isomers obtained by treatment of ortho lithiated N,N-diethylbenzamide with $(PhS)_2$ (Doadt, E.G.; Snieckus, V. unpublished results) and LiCu(CN)MeNPh (Iwao, M.; Reed, J.N.; Snieckus, V. J. Am. Chem. Soc. **1982**, **104**, 5531). [d] Prepared by modification of a literature method: Walton, D.R.M. J. Chem. Soc. C, **1966**, 1706. [e] Reaction was carried out in anhydr THF using 6 equiv of TBAF.

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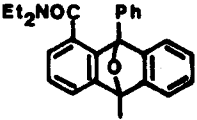
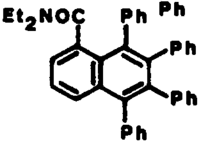
Table IV. Cycloaddition Reactions of the Benzyne of N,N-Diethylbenzamide [a]

Product	X	R^1	R^2	Yield,%	mp,°C
5a	O	H	H	63	75-76 (Et_2O-hexane)
5b	O	Me	Me	60	66 (Et_2O-hexane)
5c	O	H	Me	30	oil[b]
5d	O	Me	H	30	
7				56	61-62 (CH_2Cl_2-hexane)
8[c]				47	211-212 (EtOAc-hexane)

[a] All new compounds show analytical and spectral (IR, NMR, MS) data consistent with the assigned structures. Preparative tlc (SiO_2/pet ether-EtOAc, 65:35) was used for most purifications. Yields have not been optimized. [b] Unresolved 1:1 mixture of **5c** and 5d (NMR ($CDCl_3$) δ 1.86, 1.92 for the bridgehead methyl groups). [c] Product of decarbonylation of the initial cycloadduct during ptlc.

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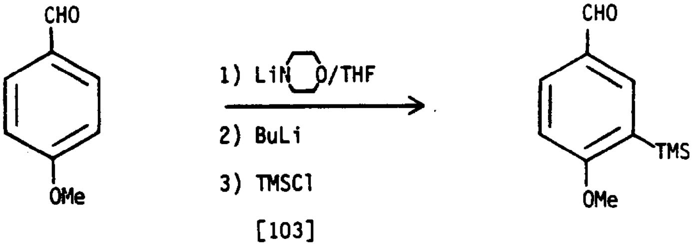
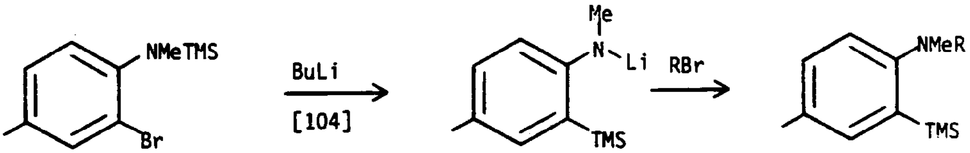


(51)

A similar rearrangement was observed in an ortho-lithiotrimethylsilylaniline. (Eqn. 52)



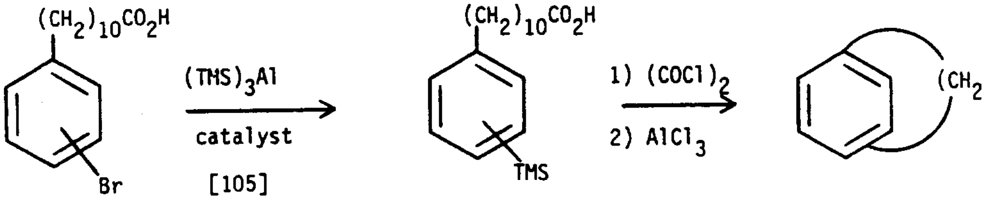
(52)

R = ^{n}Bu, Me

Tris-(trimethylsilyl)aluminum reacts with aryl bromides under catalytic conditions to give the corresponding arylsilanes. This has been used to prepare meta- and para-bridged aromatics. (Eqns. 53, 54)

$$\mathrm{ArBr} + (\mathrm{TMS})_3\mathrm{Al} \xrightarrow[\text{[105]}]{\text{"catalyst"}} \underset{\substack{\text{7 examples} \\ \text{51-79\%}}}{\text{Ar-TMS}} \qquad (53)$$

catalyst = $(Ph_3P)_2NiCl_2$ or $(Ph_3P)_4Pd$



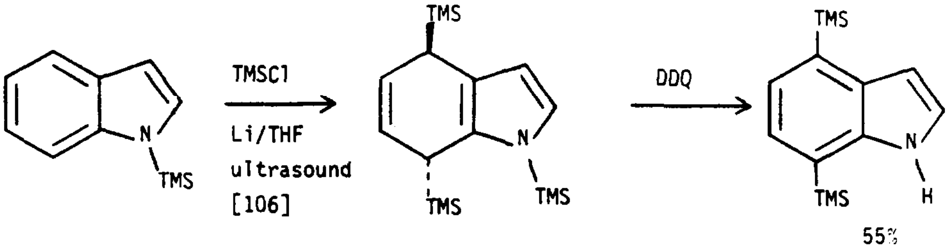
(54)

para 58%

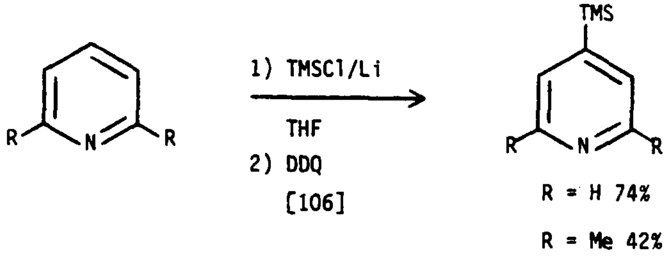
meta 23%

Other routes to arylsilanes were published. For example aromatic systems were subjected to the TMSCL/Li/THF reagent and ultrasound to give the bis-allylsilane, which was then rearomatized. (Eqns. 55, 56)

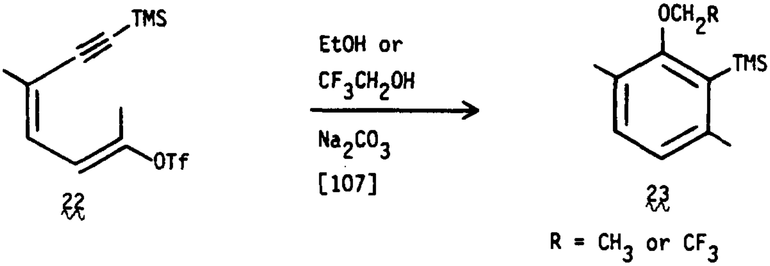
The dienynyl triflate **22** cyclized to the arylsilane **23** under basic conditions. (Eqn. 57). 4-Methyloxazole can be deprotonated and silylated. The reaction proceeds via an α-isocyano enol silyl ether **24** (Eqn. 58) Lithiated trimethylsilyldiazomethane reacts with α,β-unsatured nitriles to give 3-trimethylsilylated pyrazoles. (Eqn. 59)


TMS
TMSCl
Li/THF
ultrasound
[106]
TMS
TMS
TMS
DDQ
TMS
TMS
H
55%

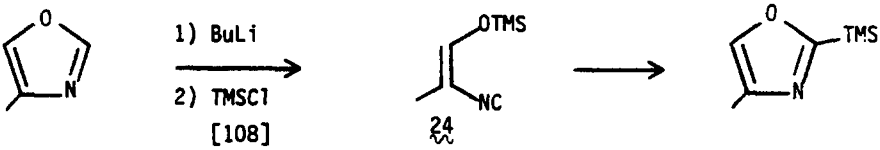
(55)


R
N
R
1) TMSCl/Li
THF
2) DDQ
[106]
TMS
R
N
R
R = H 74%
R = Me 42%

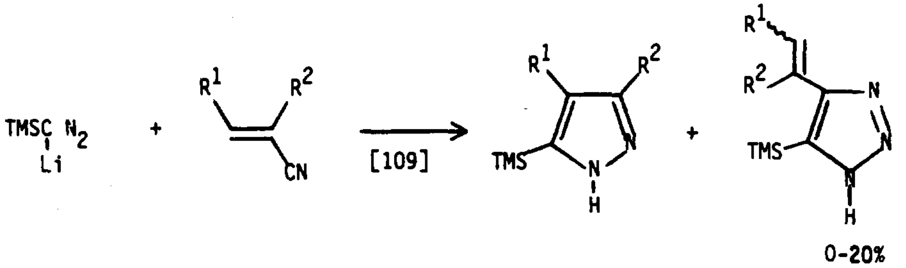
(56)


TMS
OTf
22
EtOH or
CF3CH2OH
Na2CO3
[107]
OCH2R
TMS
23
R = CH3 or CF3

(57)


O
N
1) BuLi
2) TMSCl
[108]
OTMS
NC
24
O
TMS
N

(58)


TMSC N2
Li
+
R1
R2
CN
[109]
R1
R2
TMS
N
N
H
+
R1
R2
N
N
TMS
N
H
0-20%

(59)

B. REACTIONS

The protiodesilylation of arylsilanes provided a route to chlorosilanes. (Eqn. 60) Arylsilanes are hydrolytically cleaved in the presence of palladium (II). (Eqn. 61) The kinetics of the reaction has been studied.

$$\mathrm{R^1MePhSi(CH_2)_4SiR^2MePh} \xrightarrow[\substack{\mathrm{AlCl_3} \\ {[110]}}]{\mathrm{HCl}} \mathrm{R^1MeClSi(CH_2)_4SiR^2MeCl} \qquad (60)$$

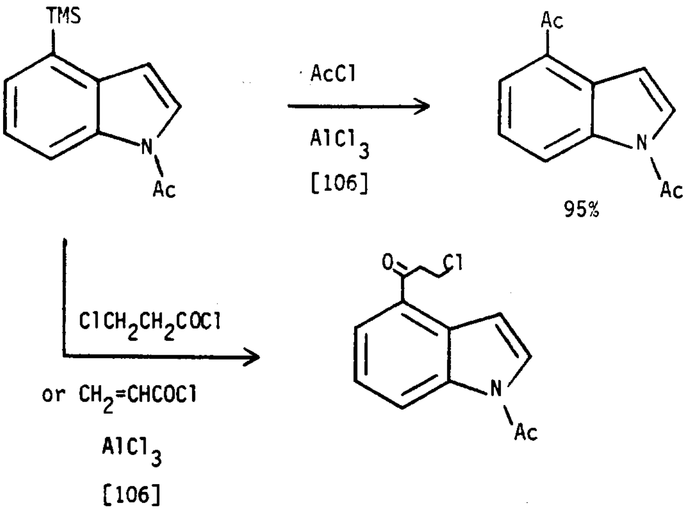
$$\mathrm{Ar\text{-}TMS} \xrightarrow[\substack{\mathrm{DMF} \\ 0.7\%\ \mathrm{H_2O} \\ {[111]}}]{\mathrm{Li_2PdCl_4}} \mathrm{Ar\text{-}H} + \mathrm{(TMS)_2O} \qquad (61)$$

$$\mathrm{Ar} = \mathrm{C_6H_5},\ m\text{-}\mathrm{Me\text{-}C_6H_4},\ p\text{-}\mathrm{MeC_6H_4},\ p\mathrm{Cl\text{-}C_6H_4},\ p\mathrm{MeOC_6H_4}$$

The electrophilic cleavage of the aryl-silicon bond continues to be an excellent way to selectively functionalize an aromatic ring. A number of arylations were reported. (Eqns. 62-68) Other electrophilic reactions were reported, notably condensation with benzaldehyde (Eqn. 69) and phenylsulfenation (Eqn. 70).

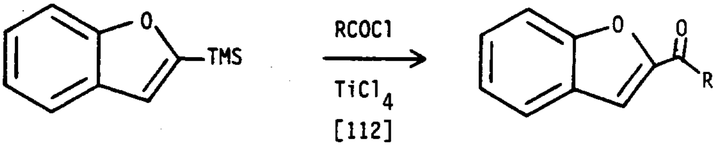
Trimethylsilyl substituted pyrazoles were subjected to a variety of electrophilic cleavage reactions. (Eqns. 71-77). Nucleophilic reactions are also possible with 3-trimethylsilylpyrazoles. (Eqns. 78-79).

2-Trimethylsilyl substituted furans were oxidized to butenolides with peracetic acid. (Eqns. 80, 81).



(62)

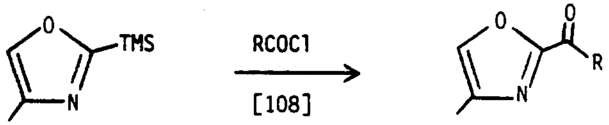
(63)



(64)

R = 1°, 2°, 3°

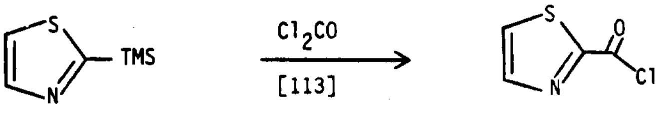
6 examples 74-92%



(65)

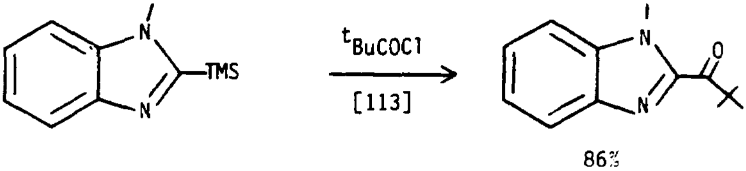
8-84%

R = Me, Ph, OEt, CO_2Me

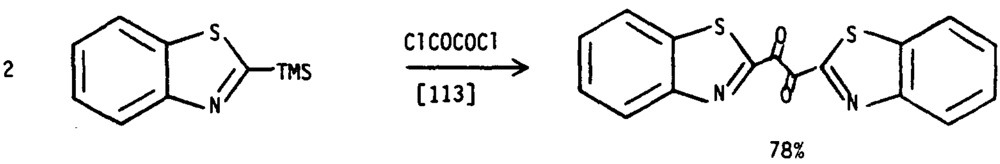


(66)

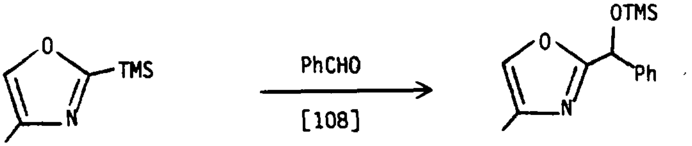
68%


TMS
N
N
tBuCOCl
[113]
N
N
O
86%

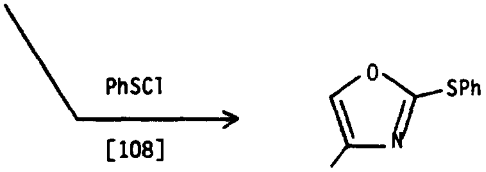
(67)


2
S
N
TMS
ClCOCOCl
[113]
S
N
O
O
S
N
78%

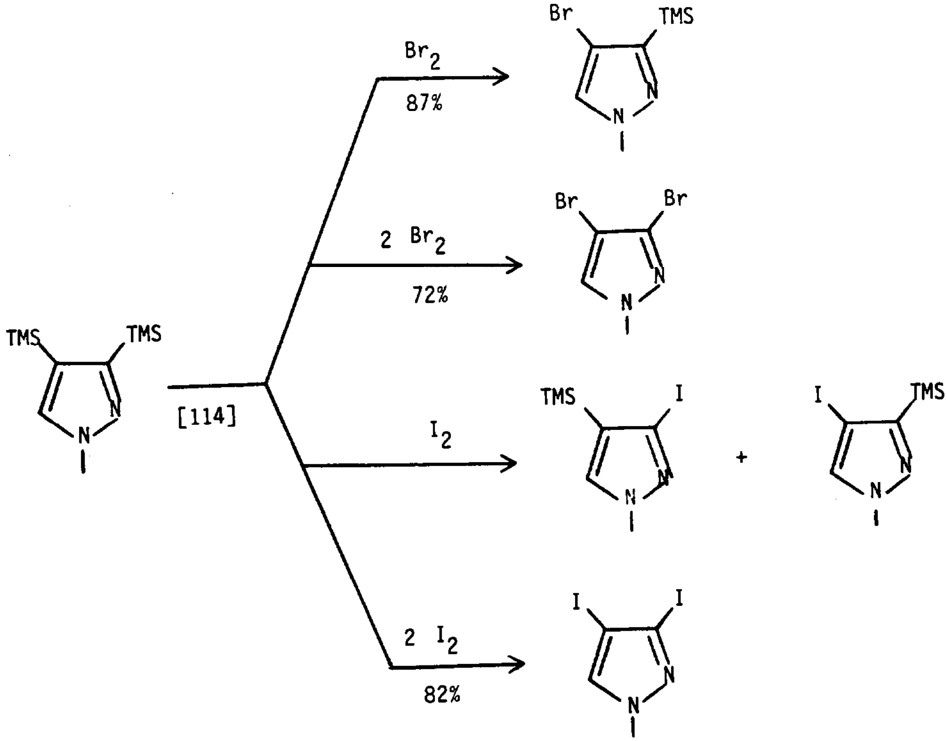
(68


O
N
TMS
PhCHO
[108]
OTMS
O
N
Ph

(69)


PhSCl
[108]
O
N
SPh

(70)

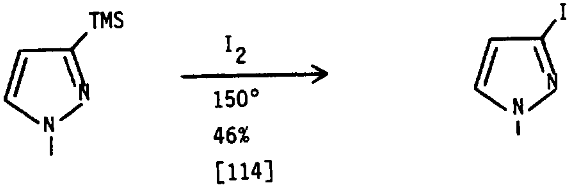


(71)

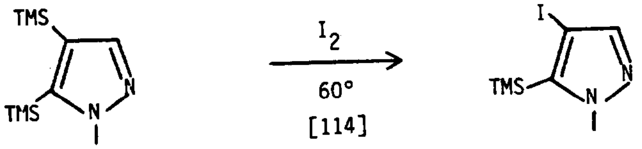
(72)

(73)

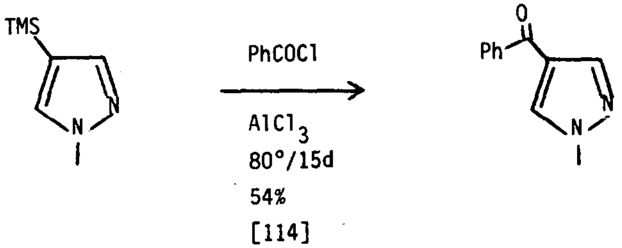
(74)



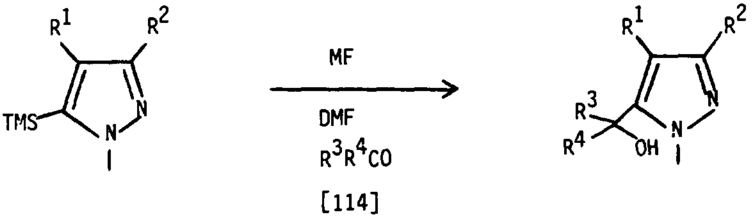
(75)



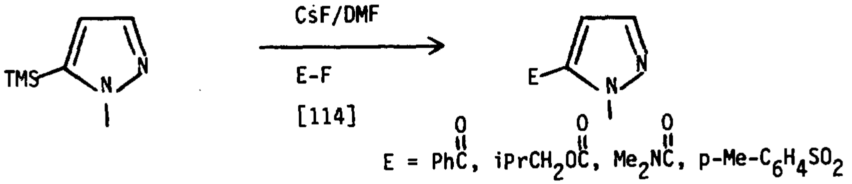
(76)



(77)

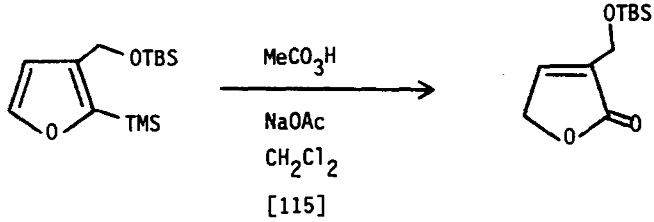


(78)

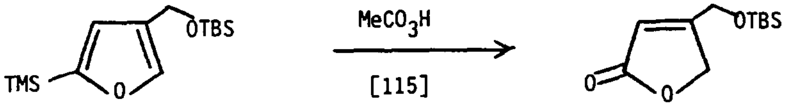


$E = Ph\overset{O}{\overset{\|}{C}},\ iPrCH_2O\overset{O}{\overset{\|}{C}},\ Me_2N\overset{O}{\overset{\|}{C}},\ p\text{-}Me\text{-}C_6H_4SO_2$

(79)

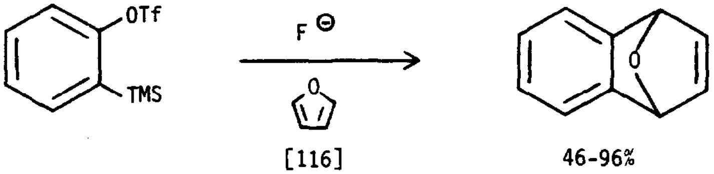


(80)



(81)

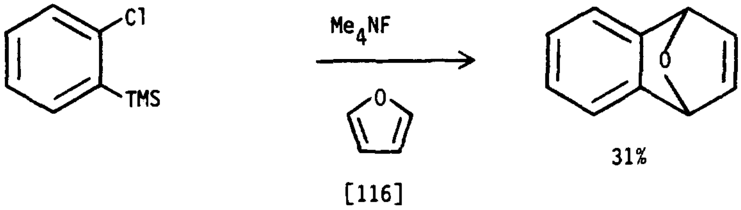
Ortho-trimethylsilylaryl triflates react with fluoride ion to give benzyne. (Eqn. 82). The ortho chloro system also provides benzyne. (Eqn. 83)



(82)

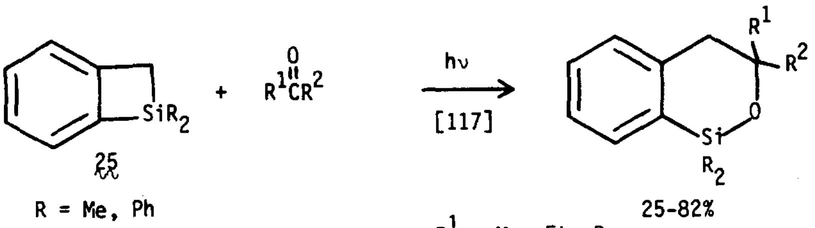
F⊖ sources Me_4NF/HMPA; KF/HMPA; CsF/HMPA; TBAF/HMPA

KF/18-crown-6 gave no reaction



(83)

The benzosilacyclobutene 25 reacts photochemically with aldehydes and ketones to give insertion into the aliphatic silicon-carbon bond. (Eqn. 84)



25

(84)

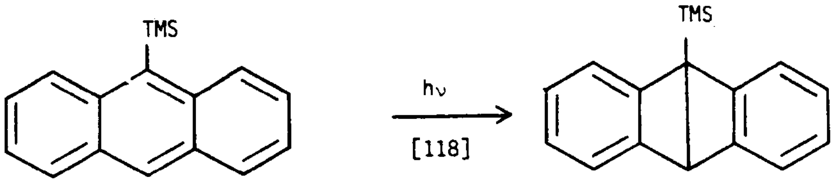
R = Me, Ph

R^1 = Me, Et, Pr

R^2 = H, Me, Et, Ph

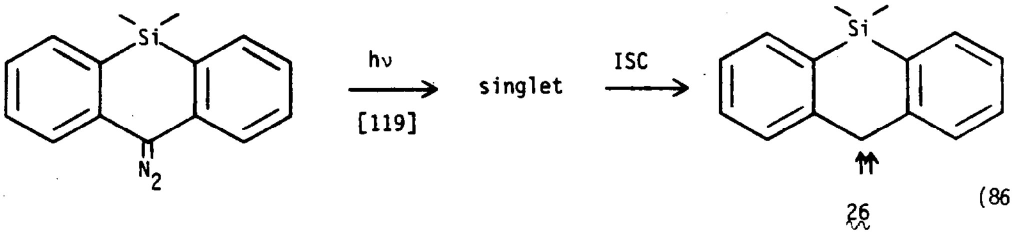
R^1, R^2 = $-(CH_2)-_4$

Photolysis of 9-trimethylsilylanthracene gives the Dewar isomer. (Eqn. 85)

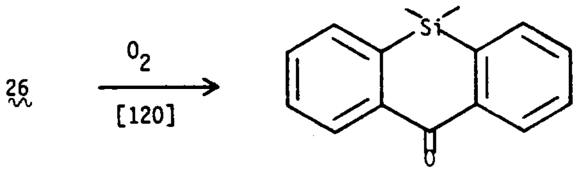


(85)

Photolysis of 9,9-dimethyl-9-sila-10-diazoanthracene gives the triplet carbene via intersystem crossing (Eqn. 86) The triplet carbene was observed spectroscopically and trapped with oxygen. (Eqn. 87)



(86)

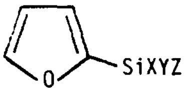


(87)

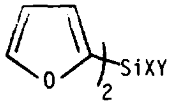
Ortho-silyl phenoxyl radicals dimerize and disproportionate depending on the silyl groups. [121] Phenylsilane produces ethylene, acetylene, silane and ethylsilane upon multiple-IR-photon decomposition. [90]

C. Spectroscopic and Other Studies

The vibrational spectra and IR dichroism of tetraphenylsilane in solution, in the melt and in the solid state have been measured. [122] The photoelection spectra of 2-silylfurans **27** and bis-2-furanylsilanes **28** have been recorded and the results compared with CNDO/2 calculations. It is argued that the importance of $d\pi$-$p\pi$ interaction must be considered. [123]

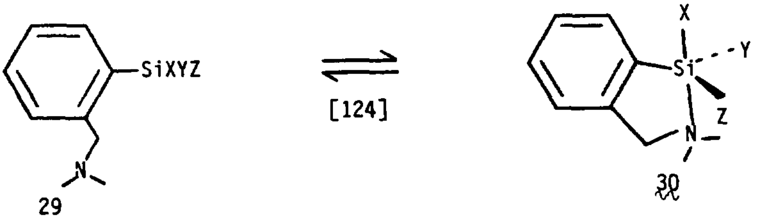


27



28

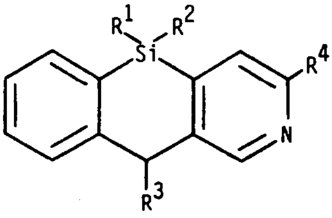
Variable temperature ^{29}Si-NMR spectra were recorded on the ortho-silyl benzylamines **29** to determine the amount of pentavalent structure **30** as a function of the ligands on silicon. (Eqn. 88) No pentavalent structure was found for the trimethoxysilyl and trimethylsilyl groups.



(88)

X	Y	Z	K
F	F	F	8.1
Me	F	F	1.6
Me	H	F	2.5
o-$C_6H_4CH_2MMe_2$	F	F	1.0

The mass spectra of a series of 9-substituted-10-sila-2-azaanthracenes **31** were recorded. [125] In an attempt to measure the $d\pi$-$p\pi$ bonding in 2-silylfurans and 2-silylthiophenes, these compounds were mixed with phenol and the $\Delta\nu$ of the OH stretch measured. They were also mixed with TCNE and the charge transfer band measured. [126] The inductive, hyperconjugative and d-orbital effects of trimethyl- phenylsilane, phenylsilane and trifluorophenylsilane were studied by comparing CNDO/5 with HOMO and LUMO levels. All three effects have important roles with d-orbitals being most important with trifluorophenylsilane and hyperconjugation with the other two silanes studied. [127] Some 5-trimethylsilylfurans containing azomethine and vinyl groups on the ring were tested for antitumor and bactericidal activity. [128]



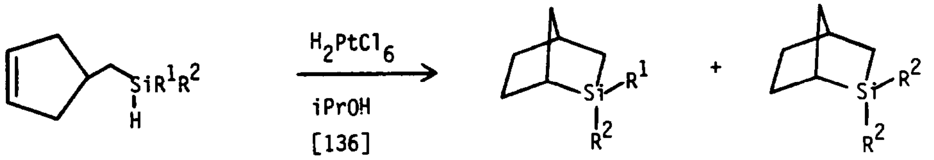
31

VI. HYDROSILYLATION

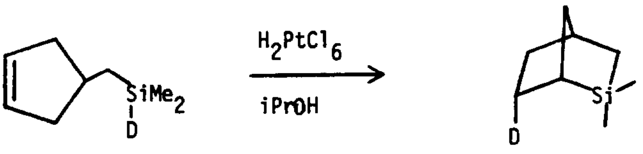
A. New Developments

The hydrosilylation of styrene with Rh (I) catalysis depends on the ratio of Rh (I) to the silane used. At a ratio 10^{-4} addition to the double bond occurs whereas at a ratio of 10^{-3} the β-silylstyrene is observed. At intermediate concentrations both pathways are operative. [129] Ruthenium (II) and ruthenium (III) catalysts were found to be best for terminal olefins and vinylsilanes and not as good for substitued olefins and unsaturated esters. [130] Triphenylsilylmanganese pentacarbonyl was found to be a hydrosilylation catalyst. Thermal activation proceeds via tiphenylsilyl radical generation and initiation whereas photochemical activation proceeds via a coordinative mechanism. This is the first example of a mechanistic difference between photochemical and thermal activation of a hydrosilylation catalyst. [131] The hydrosilylation of olefins in the presence of metal carbonyl clusters has been reported. [132] The hydrosilylation of terminal acetylenes in the presence of boron-containing platinum and palladium complexes has been carried out. [133] The 1,5-cyclooctadiene complex of methyliodoplatinum (II) catalyzes the hydrosilylation of triphenylvinylsilane. [134] The catalytic activity of $RhCl(PPh_3)_2L$ (L=CO, PPh_3) is enhanced by the addition of oxidizing agents such as hydrogen peroxide, tert-butylhydroperoxide and meta-chloroperbenzoic acid. Similar results were found with transition metal hexacarbonyl catalysts (metal=Cr, Mo, W). [135]

Intramolecular hydrosilylation of 4-(dialkylsilylmethyl)-cyclopentenes provides 2-sila [2.2.1] heptanes. (Eqn. 89) The hydrosilylation occurs from the endo side (Eqn. 90)



(89)



(90)

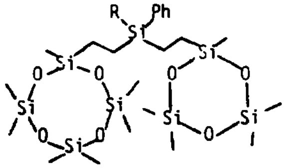
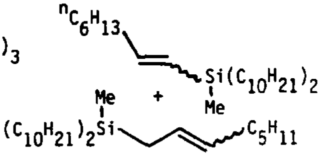
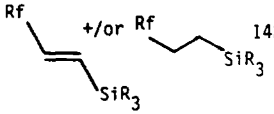
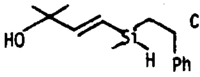
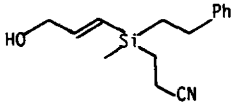
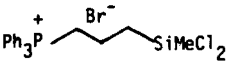
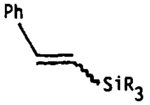
The hydrosilylation of 1-hexene and trimethylvinylsilane with some cobalt and rhodium carbonyl catalysts was studied by IR. [137] The hydrosilylation of phenylacetylene with $H_2O\ Cl_6\ 6H_2O$ THF was studied spectroscopically. [138]

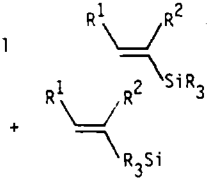
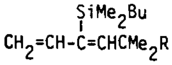
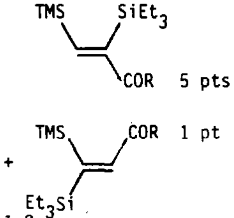
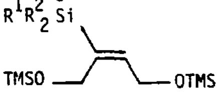
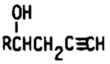
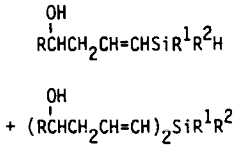
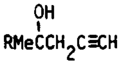
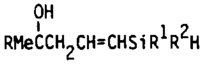
B. Hydrosilylation of Alkenes and Alkynes

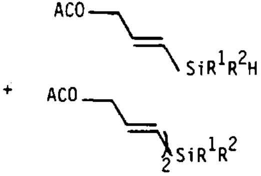
As usual a number of hydrosilylation reactions were reported during the year. These are given in Table V. These are presented without further comment.

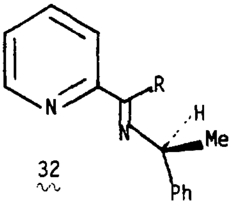
The enantioselective hydrosilylation of prochiral ketones was the topic of three reports. Rhodium and platinum catalysts with the chiral ligands **32**, **33** and **34** among others were used to hydrosilylate acetophenone, phenylacetone and pinacolone with diphenylsilane and α-naphthylphenylsilane. (Eqn. 91) The hydrosilylation of acetophenone with diphenylsilane and rhodium catalysis in the presence of asymmetric iminophosphine ligands gave low (3-17% ee) enantioselectivity. [155] on the other hand the $[Rh(COD)Cl]_2$ catalyzed reduction of prochiral ketones in the presence of an optically active thiazolidine gave up to 96 percent ee. The best thiazolidine ligand was **35**. (Eqn. 92)

Table V: Hydrosilylation of Alkenes and Alkynes

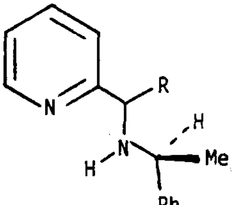
Entry	Silane	Alkene(Alkyne)	Conditions	Product	Ref.
1	$Me_{3-n}Cl_nSiH$	$PhCH_2CH=CH_2$	$H_2PtCl_6.PPh_3$	$Ph(CH_2)_3SiMe_{3-n}Cl_n$	139
2	$RPhSiH_2$ (R = Me, Ph)	D_4-$CH=CH_2$ then D_3-$CH=CH_2$	H_2PtCl_6		140
3	$(^nC_{10}H_{21})_2MeSiH$	1-octene	$RhCl(PPh_3)_3$		141
4	R_3SiH R = alkyl, Cl, OEt	$R_fCH=CH_2$ $R_f=CF_3$ & C_6F_5	$RhCl(PPh_3)_3$ or $Ru_3(CO)_{12}$		142
5		$CH_2=CHCN$			143
6	$MeCl_2SiH$	$Ph_3\overset{+}{P}CH_2CH=CH_2$ Br^-	H_2PtCl_6/Δ $CHCl_3$		144
7	R_3SiH R = Cl, Et, EtO	$PhC\equiv CH$	H_2OsCl_6		145

Entry	Silane	Alkene(Alkyne	Conditions	Product	Ref.
8	R_3SiH R = Et, alkyl	$R^1C\equiv CR^2$	$Rh(acac)_3/Et_3Al$		146
9	$BuMe_2SiH$	$RMe_2CC\equiv CCH{=}CH_2$ R = glycidyloxy, CO_2Me	H_2PtCl_6	$CH_2{=}CH\text{-}\overset{SiMe_2Bu}{C}{=}CHCMe_2R$	147
10	Et_3SiH	$TMSC\equiv CCOR$ R = H, Me, Ph	H_2PtCl_6		148
11	$R^1R^2_2SiH$ R^1R^2 = Me, Et, Ph	$TMSOCH_2C\equiv CCH_2OTMS$	H_2PtCl_6		149
12	$R^1R^2SiH_2$	$R\overset{OH}{C}HCH_2C\equiv CH$		$R\overset{OH}{C}HCH_2CH{=}CHSiR^1R^2H$ $+\ (R\overset{OH}{C}HCH_2CH{=}CH)_2SiR^1R^2$	150
13	$R^1R^2SiH_2$	$RMe\overset{OH}{C}CH_2C\equiv CH$	H_2PtCl_6	$RMe\overset{OH}{C}CH_2CH{=}CHSiR^1R^2H$	151

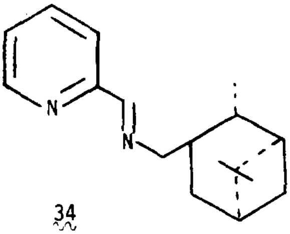
Entry	Silane	Alkene(Alkyne)	Conditions	Product	Ref.
14	$R^1R^2SiH_2$	$AcOCH_2C{\equiv}CH$	H_2PtCl_6		152
15	$R^1_2R^2SiH$	$HO(CH_2)_4OCH_2C{\equiv}CH$		$R^1_2R^2SiCH{=}CHCH_2O(CH_2)_4OH$	153



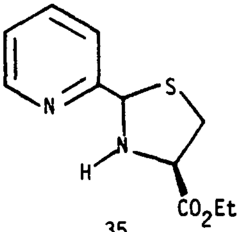
32



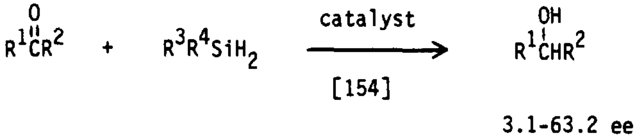
33



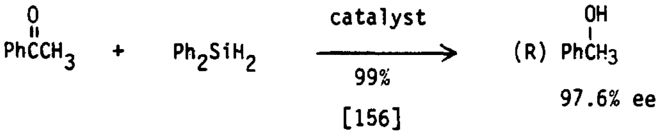
34



35

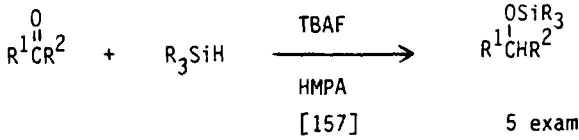


$$R^1\overset{O}{\overset{\|}{C}}R^2 \quad + \quad R^3R^4SiH_2 \xrightarrow[\text{[154]}]{\text{catalyst}} \underset{\text{3.1-63.2 ee}}{R^1\overset{OH}{\overset{|}{C}}HR^2} \qquad (91)$$



$$Ph\overset{O}{\overset{\|}{C}}CH_3 \quad + \quad Ph_2SiH_2 \xrightarrow[\substack{99\% \\ \text{[156]}}]{\text{catalyst}} \underset{\text{97.6\% ee}}{(R)\ Ph\overset{OH}{\overset{|}{C}}H_3} \qquad (92)$$

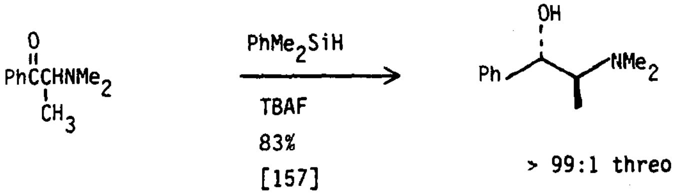
The silane reduction of aldehydes and ketones was accomplished in a nucleophilic manner with fluoride ion. (Eqn. 93) This was done in a diestereoselective manner as shown in Eqns 94 and 95. The acid catalyzed reduction gives the opposite stereoselectivity. (Eqn. 96)



$$R^1\overset{O}{\overset{\|}{C}}R^2 + R_3SiH \xrightarrow[\text{HMPA [157]}]{\text{TBAF}} R^1\overset{OSiR_3}{\overset{|}{C}}HR^2 \qquad (93)$$

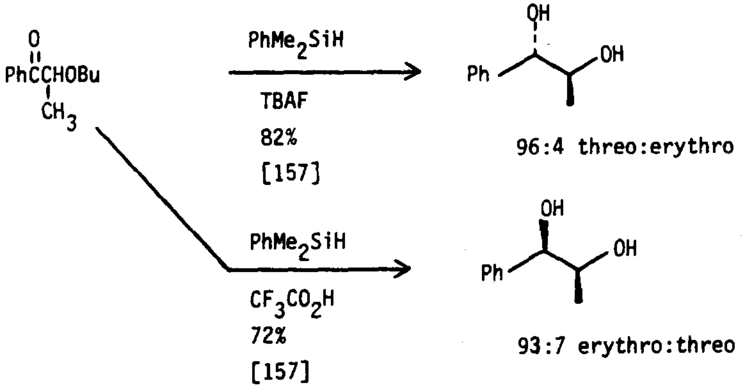
5 examples

57-100%



(94)

> 99:1 threo



(95)

96:4 threo:erythro

(96)

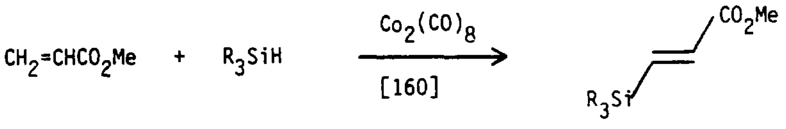
93:7 erythro:threo

The reaction of ethers with triethylsilane in the presence of colloidal nickel results in reduction. (Eqn. 97) Ketals react with triethylsilane in the presence of zinc iodide and a variety of additives (I_2, Br_2, Cl_2, HCl, HI) to give ethers. (Eqn. 98) The kinetics of the reaction shown was studied.

$$Me_2CHOR + Et_3SiH \xrightarrow[\text{Nickel (colloidal) [158]}]{100\text{-}120^\circ} CH_3CH_2CH_3 + ROSiEt_3 \qquad (97)$$

$$\mathrm{MeCH(OPr)_2} \quad + \quad \mathrm{Et_3SiH} \quad \xrightarrow[\substack{\text{additive}\\ [159]}]{\mathrm{ZnI_2}} \quad \mathrm{MeCH_2OPr} \quad + \quad \mathrm{PrOSiEt_3} \qquad (98)$$

Methyl acrylate reacts with silanes with dicobalt octacarbonyl catalysis to give 3-silyl acrylates. (Eqn. 99).



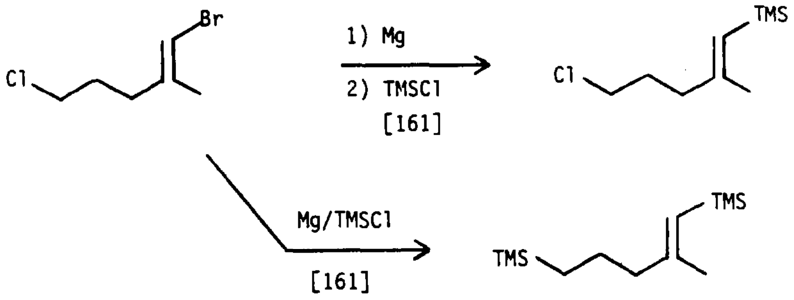
(99)

R_3Si = Et_2MeSi (86%); Me_3Si (65%); $PhMe_2Si$ (69%)

VII. VINYLSILANES

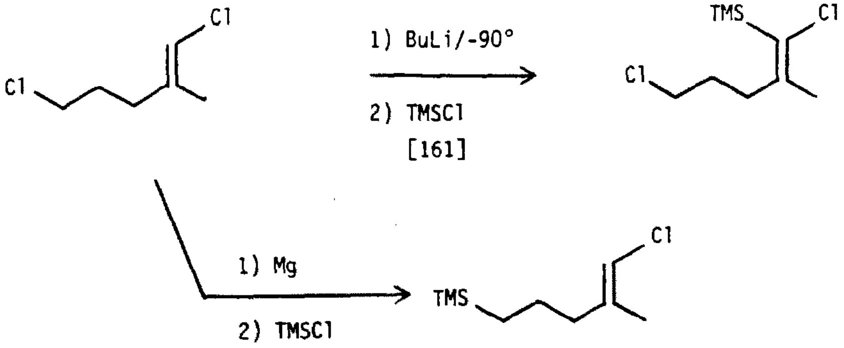
A. Preparation

The reaction of vinyl organometallics with chlorosilanes produces the corresponding vinylsilane as seen in Eqns. 100-108. The reactions shown in Eqns. 100-103 show interesting chemoselectivity as do Eqns. 107-108.



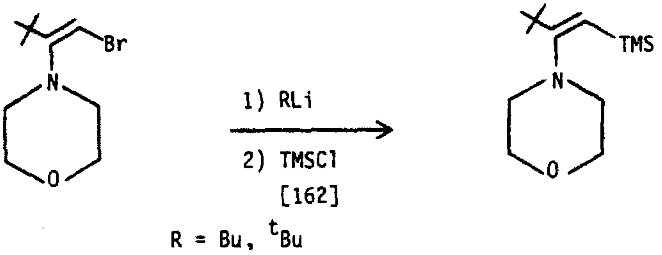
(100)

(101)

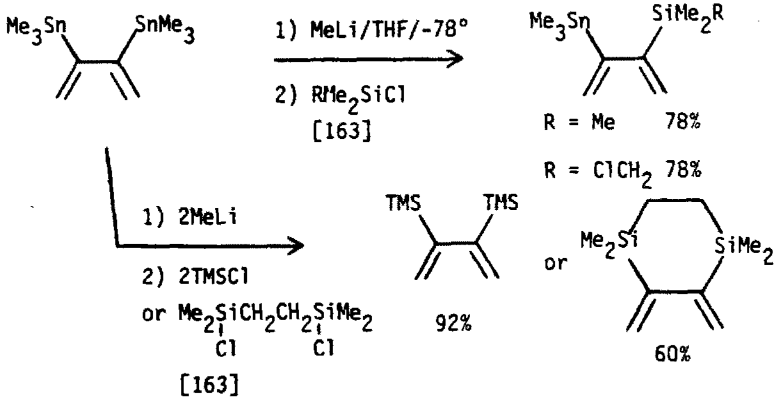


(102)

(103)

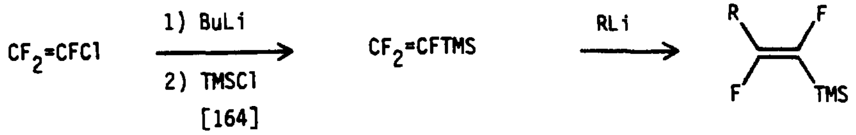


(103a)

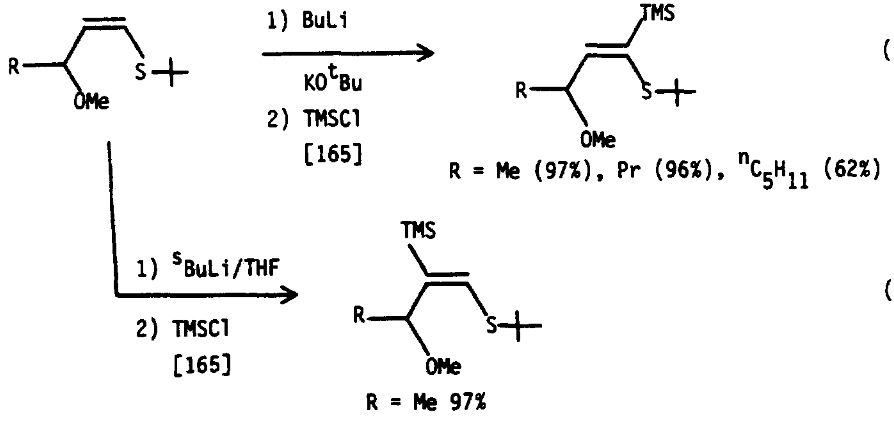


(104)

(105)



(106)

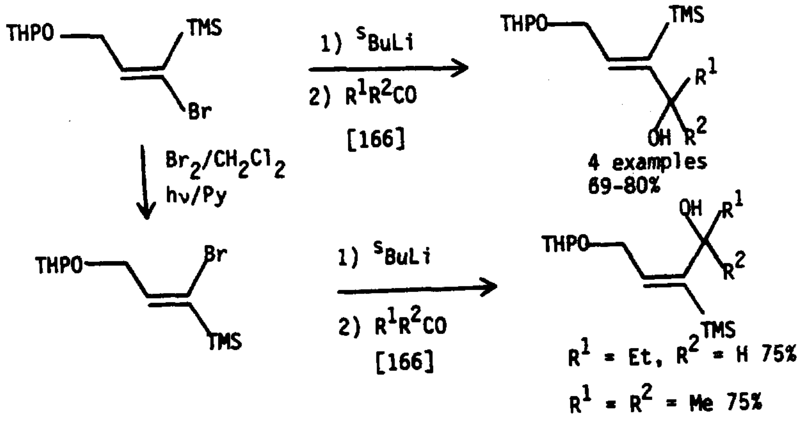


(107)

(108)

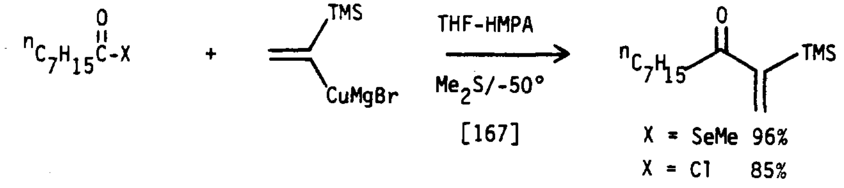
α-Trimethylsilylated vinyl organometallics are excellent sources of functionalized vinylsilanes as seen from Eqns. 109-116. (E) - 1,3-bistrimethylsilylpropene was deprotonated and the anion condensed with aldehydes and ketones to give, after elimination, trimethylsilyl-1,3-dienes. (Eqn. 115)

Lithiated allyltrimethylsilane reacts with α-oxo-ketenethioacetals to give vinylsilanes. (Eqn. 116).

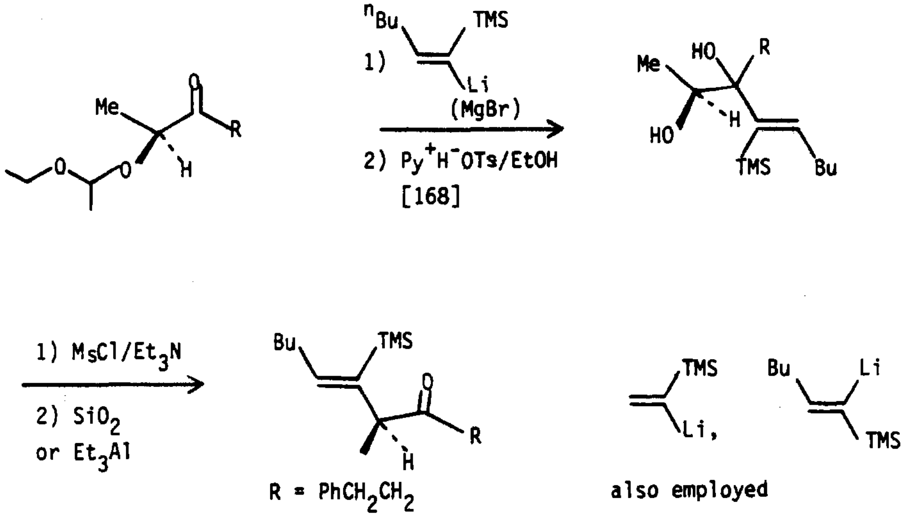


(109)

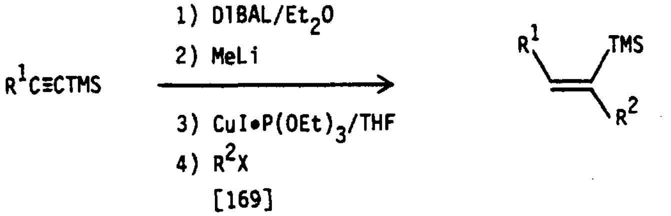
(110)


$^nC_7H_{15}C(=O)$-X
+
TMS
CuMgBr
THF-HMPA
Me_2S/-50°
[167]
$^nC_7H_{15}$
O
TMS
X = SeMe 96%
X = Cl 85%

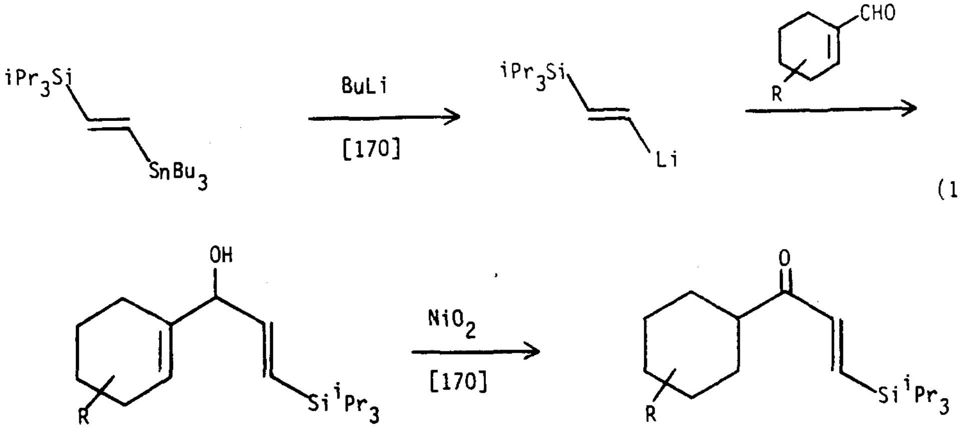
(111)


Me
O
R
O
O
H
1)
^{n}Bu
TMS
Li
(MgBr)
2) Py^+H^-OTs/EtOH
[168]
Me
HO
R
H
HO
TMS
Bu
1) MsCl/Et_3N
2) SiO_2
or Et_3Al
Bu
TMS
O
R
H
R = $PhCH_2CH_2$
TMS
Li,
Bu
Li
TMS
also employed

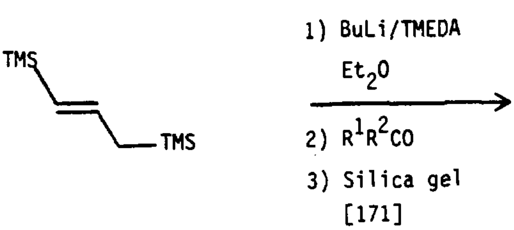
(112)


$R^1C{\equiv}CTMS$
1) DIBAL/Et_2O
2) MeLi
3) CuI•P(OEt)$_3$/THF
4) R^2X
[169]
R^1
TMS
R^2

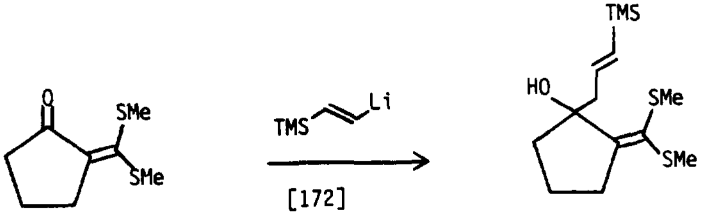
(113)



(114)



(115)

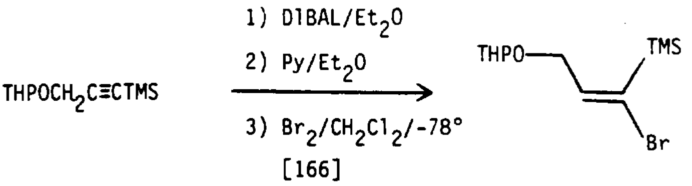


(116)

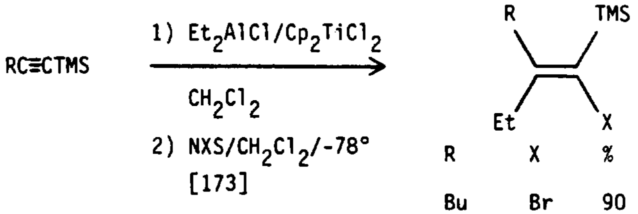
89%

other examples

Trimethylsilylacetylenes were converted to vinylsilanes, normally by addition reactions (Eqns. 117-120) but also via the propargyllithuim reagent (Eqn. 121). Clean cis and trans reductions of 1-trimethylsilylbutyn-3-ol was accomplished. (Eqn. 120)

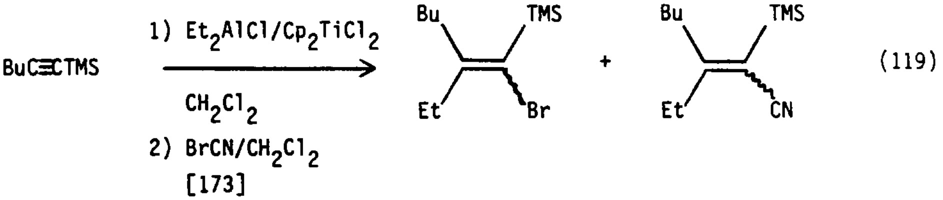


(117)

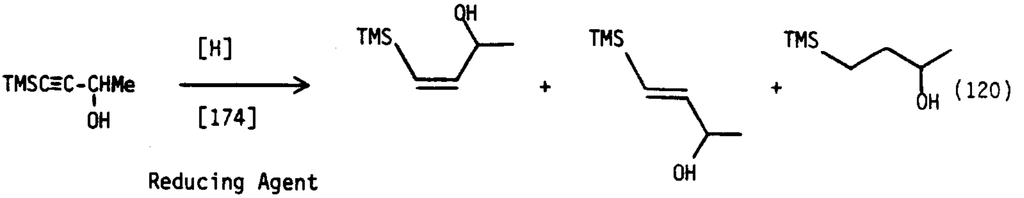


(118)

R	X	%	Z:E
Bu	Br	90	97:3
Bu	Cl	85	-
Bu	I	86	99:1
cC_6H_{11}	Br	80	95:5

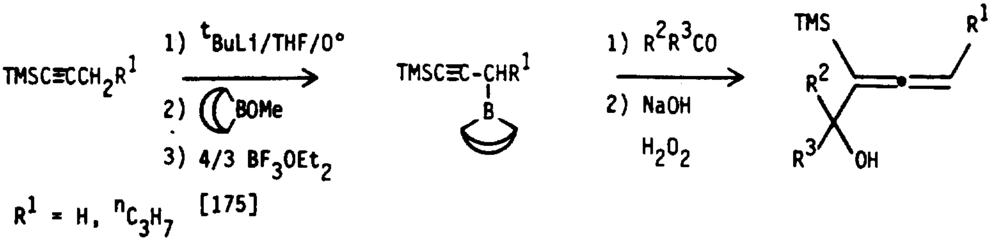


(119)



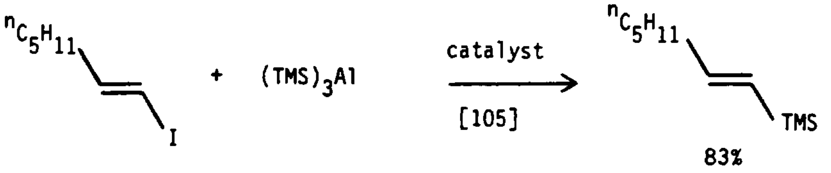
(120)

Reducing Agent			
$LiAlH_4/THF$	4	94	2
$NaAlH_2(O\frown\smile OMe)_2$	0	100	0
H_2/NiB	98	2	0
$LiAlH_4/Et_2O/$	99	1	0

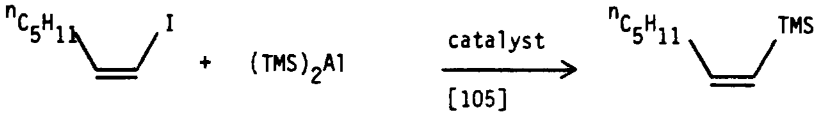


(121)

Tris(trimethylsilyl)aluminum reacts with vinyl iodides in the presence of a catalyst to stereospecifically give the corresponding vinylsilanes. (Eqns. 122, 123) (Phenyldimethylsilyl)methylmagnesium chloride adds to ω-tosyl-, mesyl- or bromoacetylenes in the presence of cuprous iodide to give phenyldimethylsilylmethylidenecycloalkanes. (Eqns. 124-127) A related transannular cyclization is shown in Eqn. 127. The silylmetalation of allenes has been reported. (Eqns. 128-130) Both regioisomers are obtainable. (Eqns. 128)

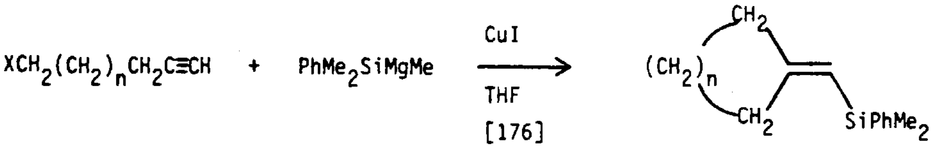


(122)



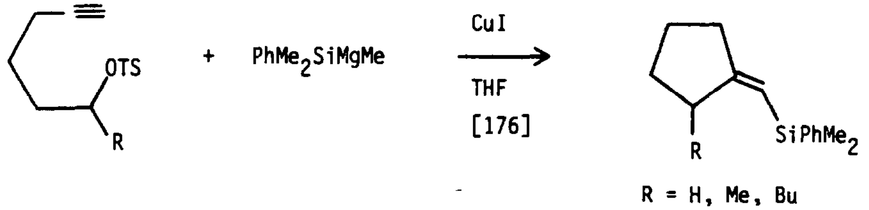
(123)

catalyst $(Ph_3P)_2NiCl_2$ or $Pd(PPh_3)_4$

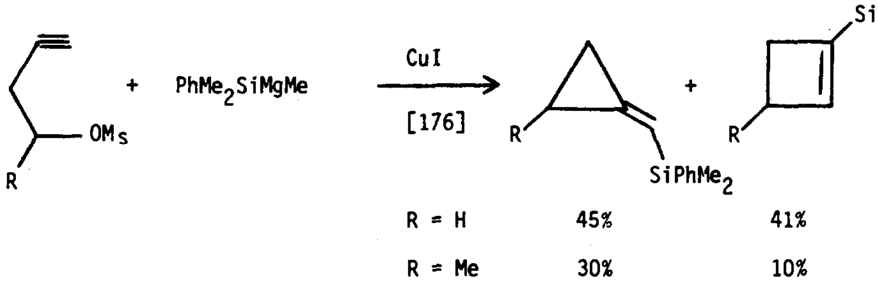


(124)

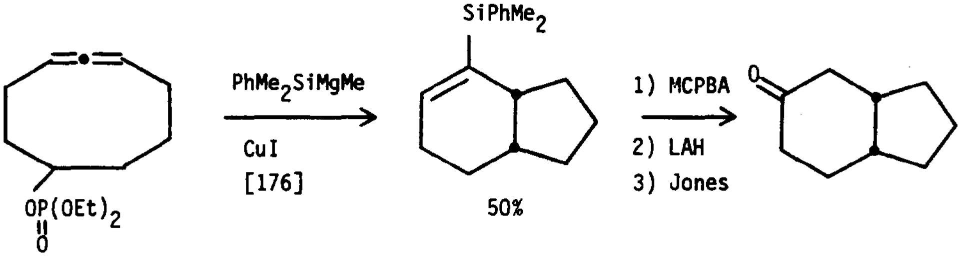
n	X	%
2	OTs	91
3	OMs	60
1	OTs	28



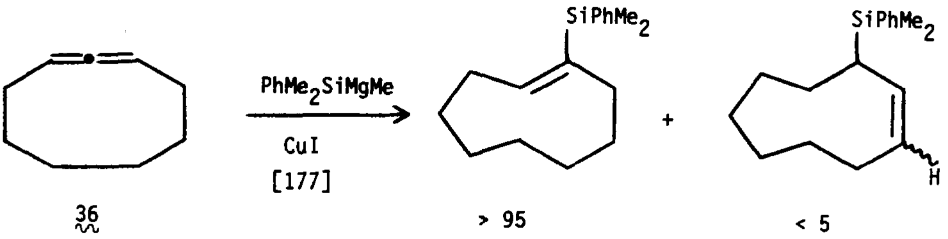
(125)



(126)



(127)



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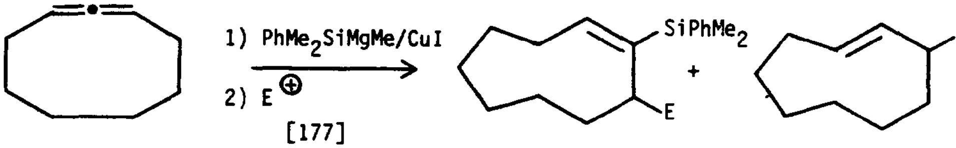

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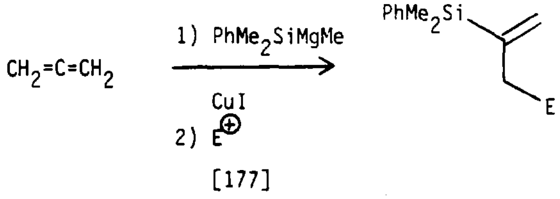
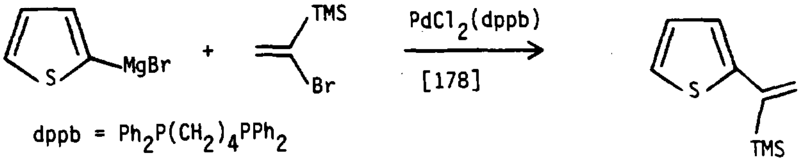


(130)

Heteroaryl Grignard reagents were reacted with α-bromovinyltrimethylsilane and a palladium (II) catalyst to give 1-heteroarylvinyltrimethylsilane. (Eqn. 131) The respective roles of the reagents can be reversed. (Eqn. 132) Vinylsulfones provide (Z) or (E) vinylsilanes as illustrated in Eqns. 133-134.



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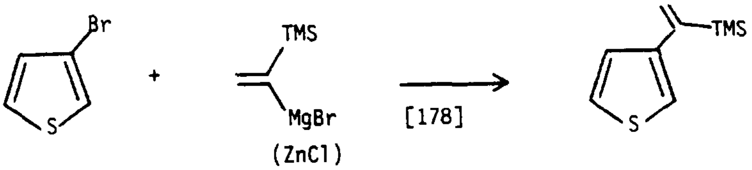

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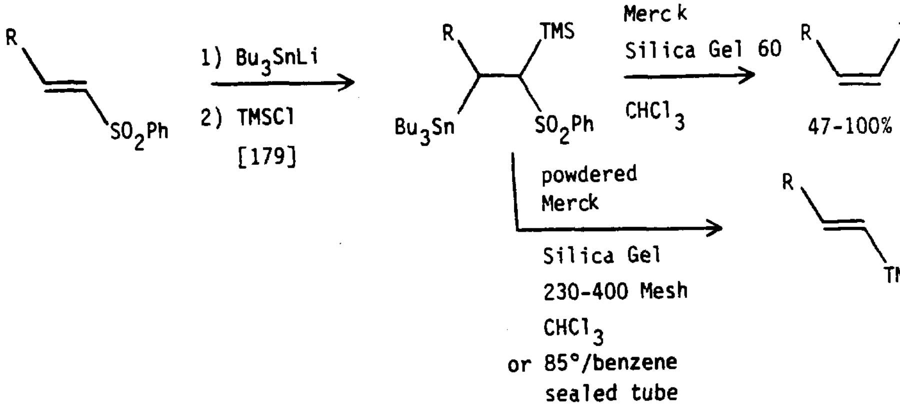
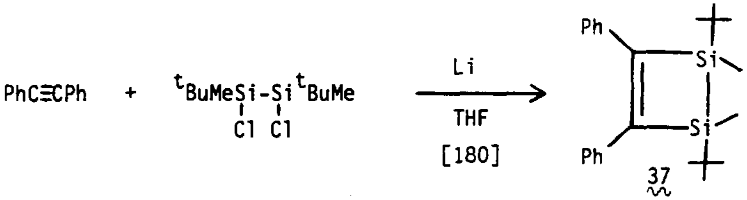


(133)

(134)

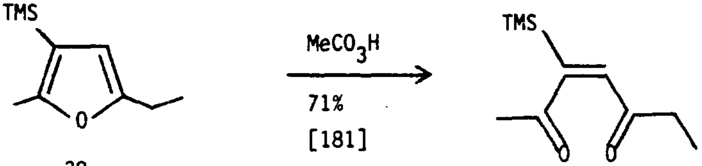
Sym-di-tert-butyldichlorodimethyldisilane reacts with lithium and diphenylacetylene to give the disilacyclobutene **37**. (Eqn. 135) The trimethylsilylfuran **38** is oxidized to **39** in good yield. (Eqn. 136) Trimethyldiazomethane reacts with sulfonyl chlorides to give vinylsilanes. (Eqn. 137)



37

61%

(135)



38

39

(136)

$$\mathrm{RCH_2SO_2Cl} + \mathrm{TMSCHN_2} \xrightarrow[\mathrm{Et_3N}\ [182]]{\mathrm{THF}} \mathrm{RCH{=}CHTMS} \qquad (137)$$

16-80%

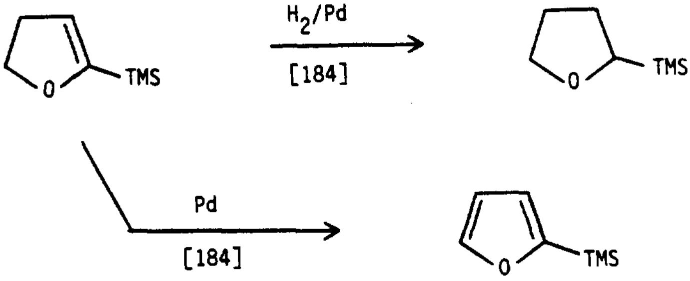
(mostly E)

B. Reactions

Several addition reactions of vinylsilanes were reported. It was found that a "nickel-silane" catalyst would hydrogenate the double bond of chlorovinylsilanes without reduction of the chlorine-silicon bond. (Eqn. 138) Hydrogenation of 2-trimethysilyl-4,5-dihydrofuran in the presence of palladium gives 2-trimethylsilyltetrahydrofuran. (Eqn. 139) In the absence of hydrogen the reaction gives 2-trimethylsilylfuran. (Eqn. 140) Similar reactions take place with the bis-dihydrofuryl system **40**. (Eqns. 141, 142)

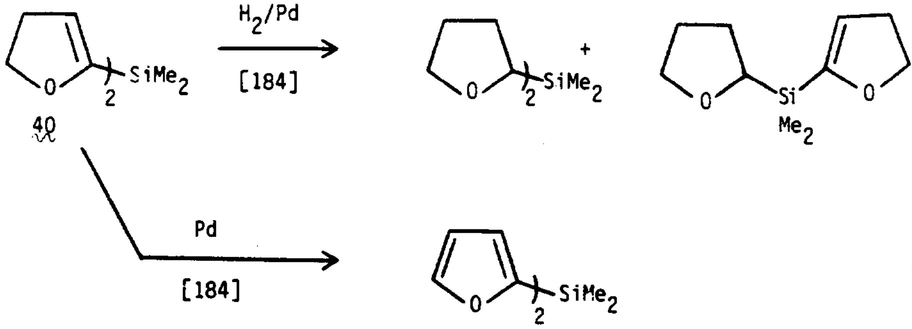
Methyldichloroazocarboxylate **41** adds to the double bond of vinyltrimethylsilane (Eqn. 143) Treatment of the product with bisulfite and base under phase transfer conditions leads to the trimethylsilylaziridine. (Eqn. 144) Phenylsulfuryl chloride adds to vinyltrimethylsilane. (Eqn. 145) Elimination of the HCl gives the trans-1-(phenylsulfonyl)-2(trimethylsilyl)ethylene **43**. The cis is isomer **44** is obtained as shown in Eqn. 146. These are excellent ethylene, substitued ethylene and acetylene equivalents in [4 + 2] cycloadditions. (Eqns. 147-151) Phenylselenenyl chloride and bromide add to vinyltrimethylsilanes. Treatment of this product in "in situ" with silver nitrite gives the β-nitrosilane **46**. Oxidative elimination leads to (E) β-nitrovinylsilane **47** in the unsubstituted case and to the (Z) product **48** in the substituted case. (E)-2-nitro-1-(trimethylsilyl)ethylene is an excellent dienophile. (Eqns. 153-155)

$$Me_nCl_{3-n}SiCH{=}CH_2 \xrightarrow[\text{"Ni/SiH"}\ [183]]{H_2(1\ atm.)} Me_nCl_{3-n}SiEt \qquad (138)$$



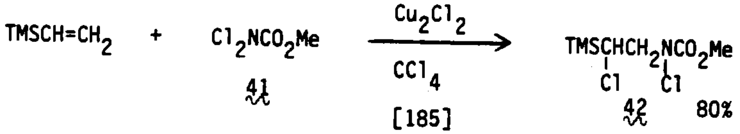
(139)

(140)

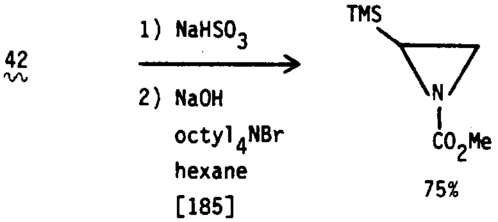


(141)

(142)



(143)



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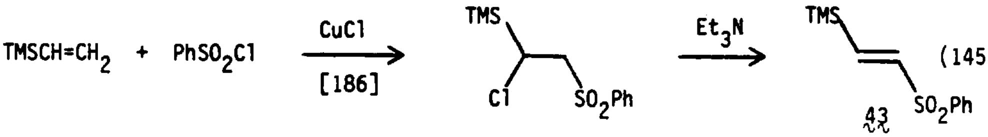

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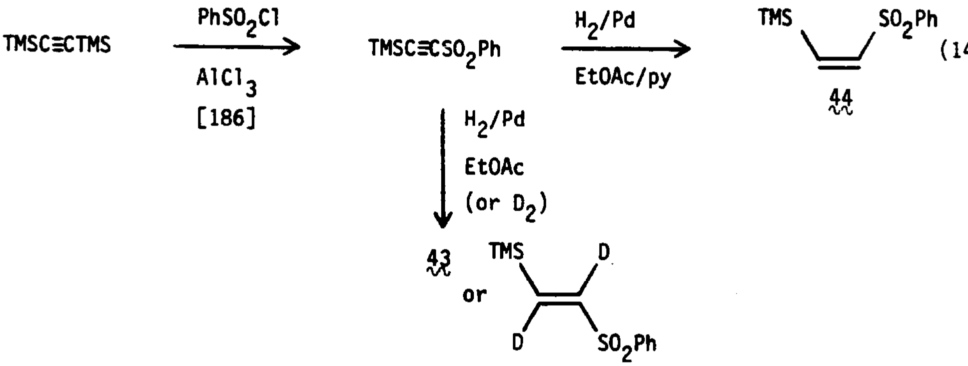

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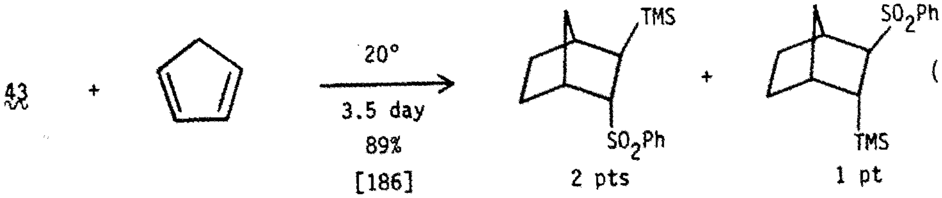

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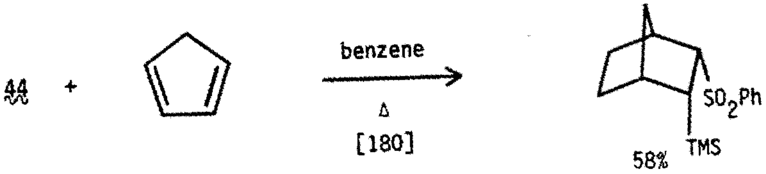

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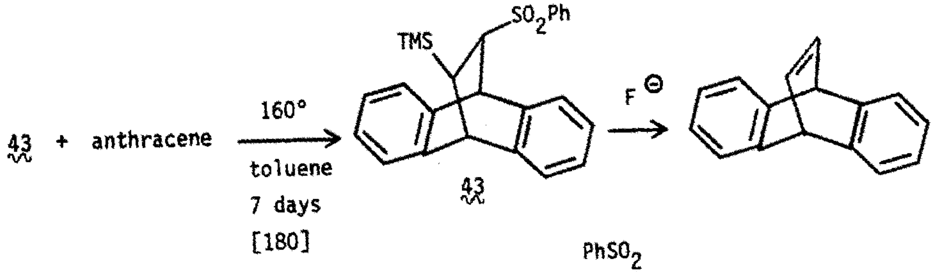

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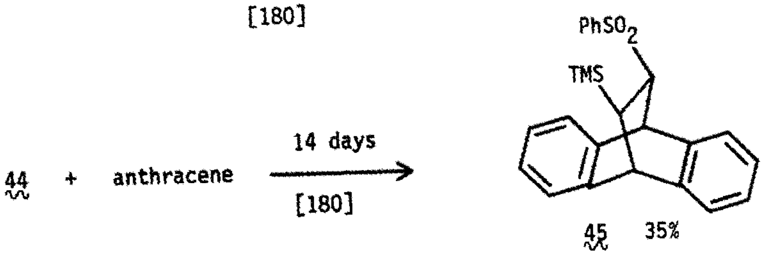

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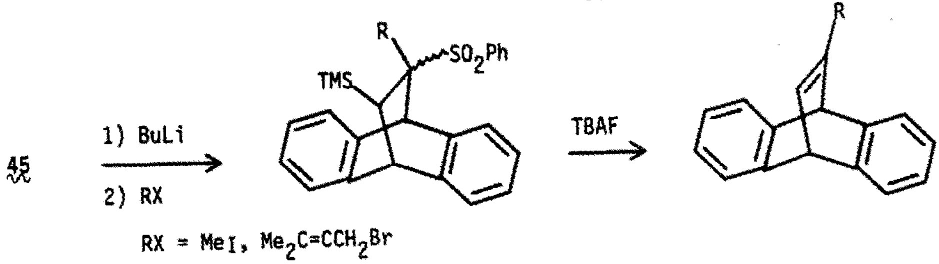

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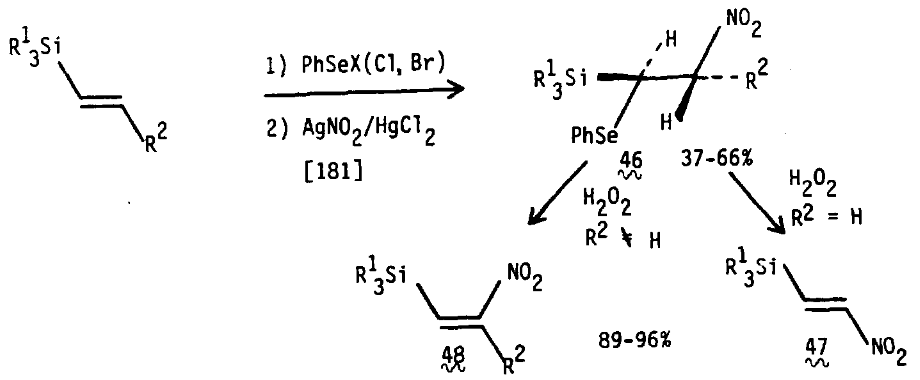

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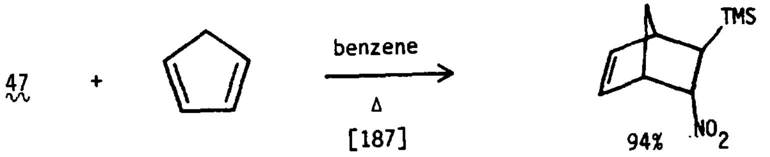
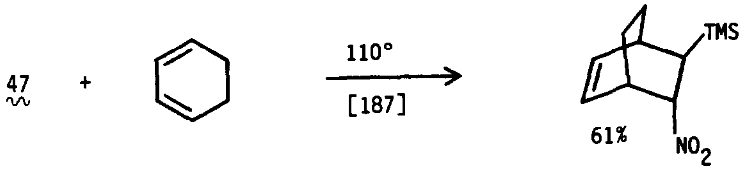


(153)



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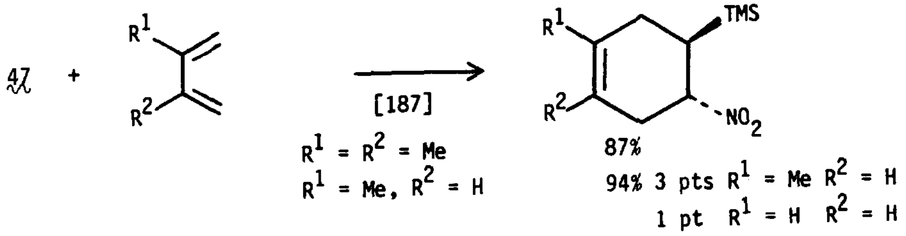
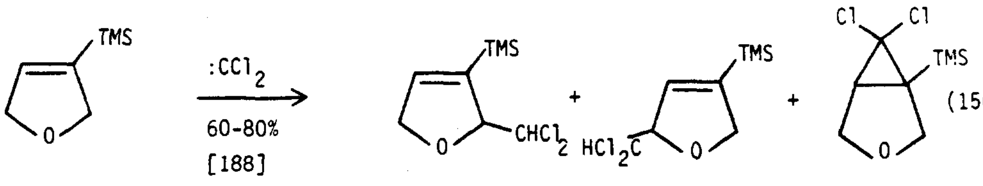


(155)

3-Trimethylsilyl-2,5-dihydrofuran reacts with dichlorocarbene, generated by various phase transfer routes, to give addition to the double bond or insertion into an allylic C-H bond. (Eqn. 156) The reaction of dichlorocarbene with 2-trimethylsilyl-4,5-dihydrofuran gives ring expansion. (Eqn. 157)



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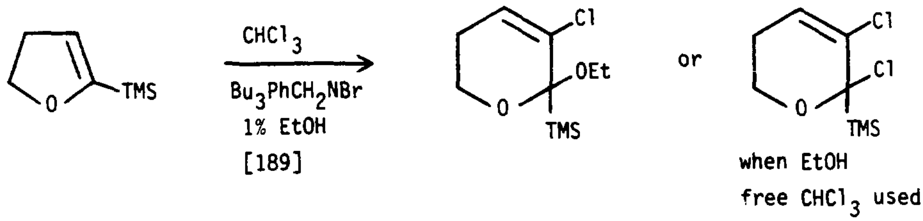
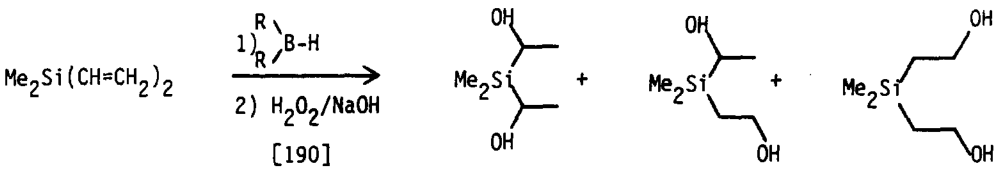


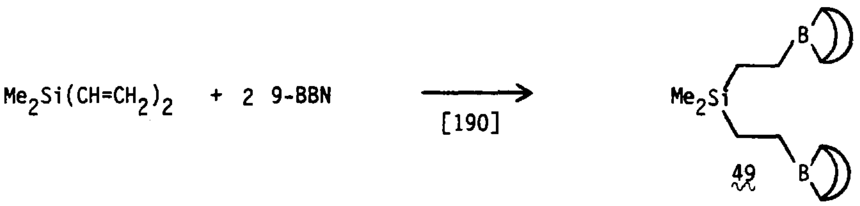
(157)

A detailed study of the hydroboration of dimethyldivinylsilane has been carried out with a variety of hydroborating agents (Eqn. 158) with 9-BBN giving exclusively the 1,5-diboryl adduct. (Eqn. 159) This diboryl derivative can be exchanged with borane methylsulfide to give 1,1-dimethyl-1-sila-4-boracyclohexane **49** (Eqn. 160) This material serves as an excellent precursor to 1,1-dimethyl-1-silacyclohexan-4-one, **50**, a compound difficult to prepare by other methods. (Eqn. 161)

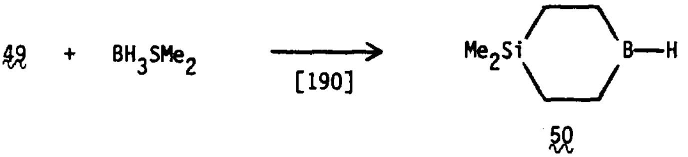
Hydroboration-oxidation of the unsaturated vinylsilane **51** selectively reacts at the terminal double bond. Oxidation to the acid and epoxidation of the vinylsilane leads to β-hydroxysilane **53**, which can be eliminated to ylidene lactone **54**. (Eqn. 162) Epoxidation of the alcohol **52** gives the ylidene tetrahydrofuran **55** (Eqn. 163) Application of this methodology to a partial prostaglandin precursor **56** is shown in Eqn. 164. Trans-1-trimethylsilyl-3-propenol undergoes asymmetric epoxidation to give (E)-(2S, 3S)-3-trimethylsilylglycidol, **57** which was converted to (-) propanolol. (Eqn. 165) (E)-α-Bromovinylsilanes **58** have been shown to be acyl anion or aryl cation equivalents in the synthesis of ketones. A key reaction in the sequence is the epoxidation-opening of a vinylsilane. (Eqns. 166, 167)



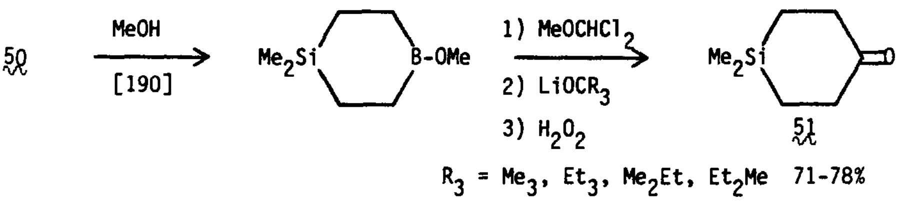
(158)



(159)



(160)



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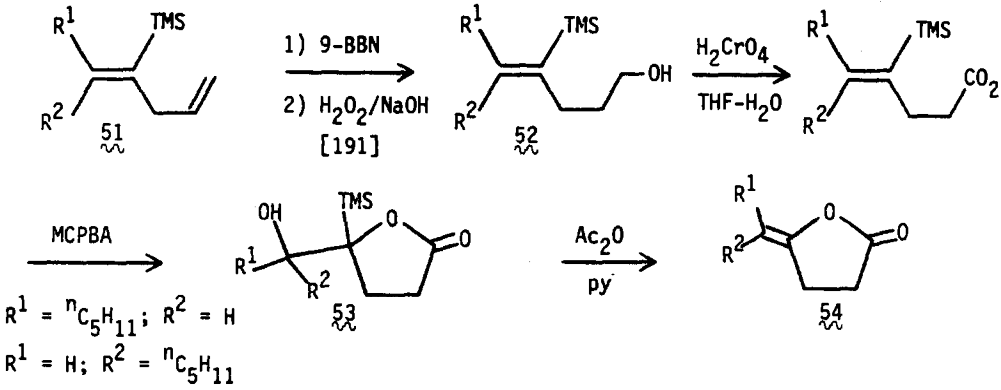
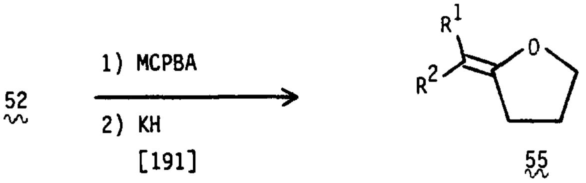
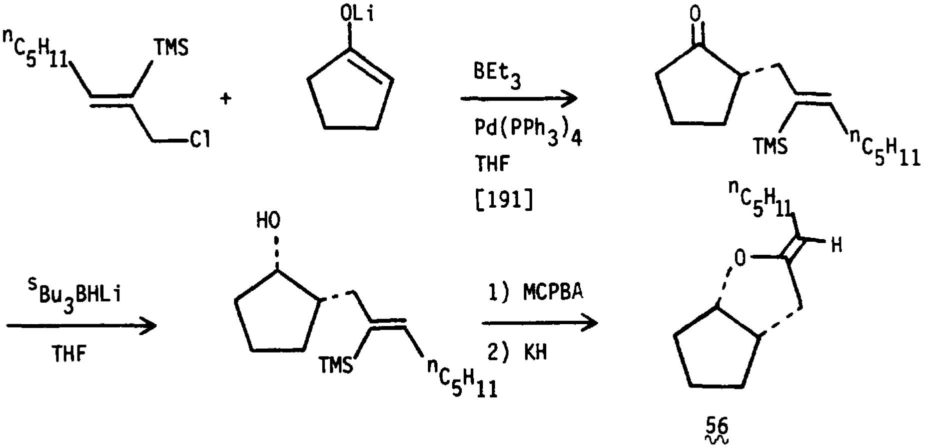


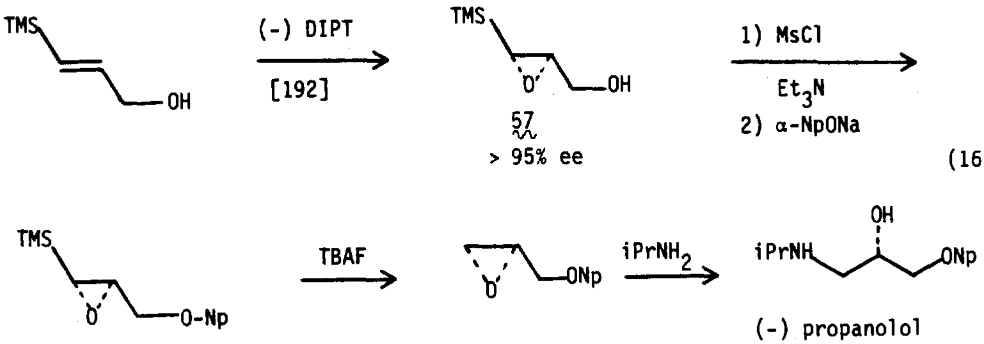
(162)


52
1) MCPBA
2) KH
[191]
R1
R2
O
55

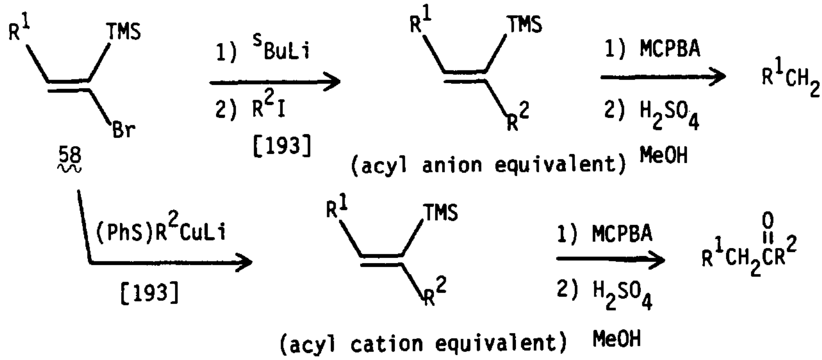
(163)


nC5H11
TMS
Cl
+
OLi
BEt3
Pd(PPh3)4
THF
[191]
O
TMS
nC5H11
sBu3BHLi
THF
HO
TMS
nC5H11
1) MCPBA
2) KH
nC5H11
H
O
56

(164)


TMS
OH
(-) DIPT
[192]
TMS
O
OH
57
> 95% ee
1) MsCl
Et3N
2) α-NpONa
TMS
O
O-Np
TBAF
O
ONp
iPrNH2
OH
iPrNH
ONp
(-) propanolol

(165)

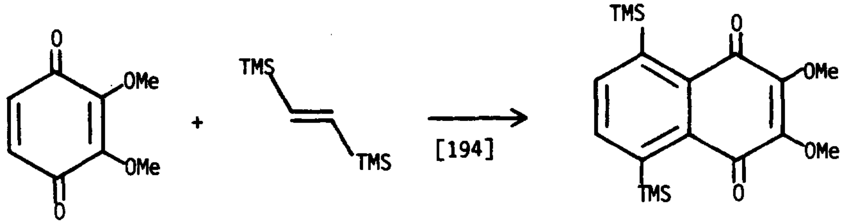


58

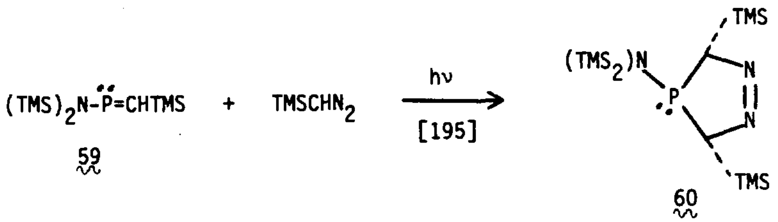
(166)

(167)

In other reactions of the addition type 1,4-bistrimethylsilyl-1,3-butadiene cycloadds with 2,3-dimethoxybenzoquinone. (Eqn. 168) The unusual vinylsilane **59** photolytically cycloadds with trimethylsilyldiazomethane to give **60**, which gave the phosphacyclopropane **61** upon extrusion of nitrogen and conrotatory ring closure. (Eqn. 169) Silylketenes react with ynamines to give cyclobutenones and allenenyl amides, which rearrange to the propargylic amides. (Eqn. 170) The allenenyl amide could be "trapped" when a phenyl group was on the nitrogen. (Eqn. 171)



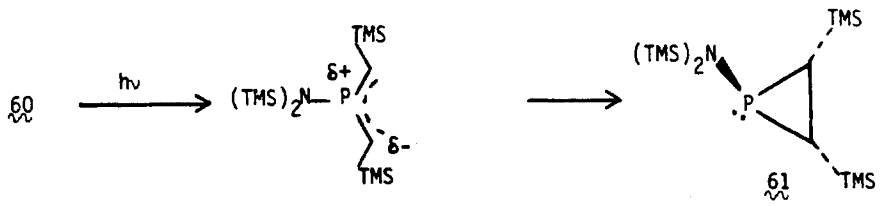
(168)

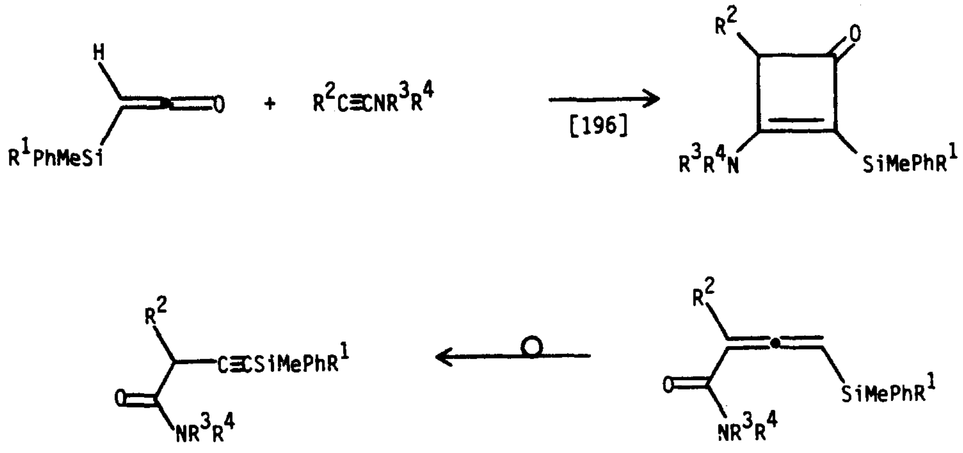


59

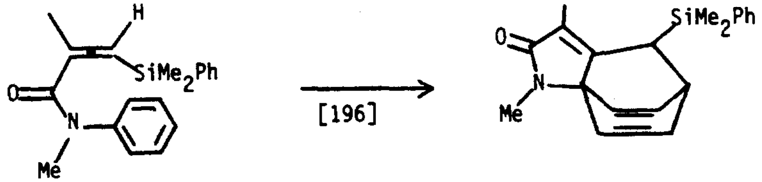
60

(169)



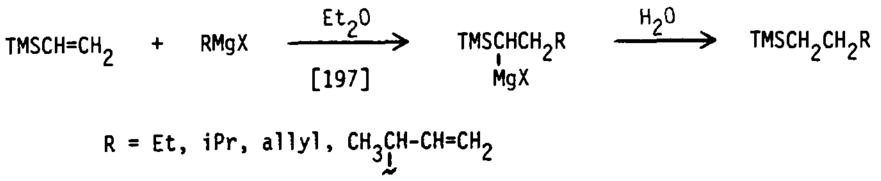


(170)



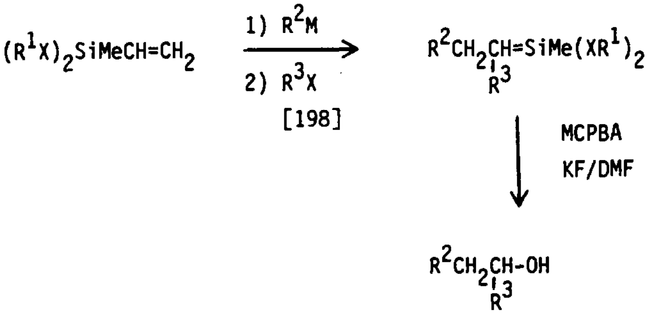
(171)

The addition of organometallic reagents to vinylsilanes provides useful synthetic intermediates. The addition of Grignard reagents to vinyltrimethylsilane followed by protonation was carried out. (Eqn. 172) Organolithium and Grignard reagents add to vinylmethyldialkoxy (or diamino) silanes. The resulting products can be oxidized to the corresponding alcohols. (Eqn. 173) The oganometallic can add to the double bond or substitute the silicon atom as seen in Eqn. 174 It is further possible to prepare optically active alcohols via use of the chiral ligands and silicon as seen in Eqn. 175.

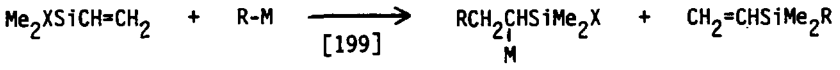


$$\mathrm{TMSCH{=}CH_2} + \mathrm{RMgX} \xrightarrow[\text{[197]}]{\mathrm{Et_2O}} \mathrm{TMS\underset{MgX}{C}HCH_2R} \xrightarrow{\mathrm{H_2O}} \mathrm{TMSCH_2CH_2R} \qquad (172)$$

R = Et, iPr, allyl, $\mathrm{CH_3\underset{\sim}{C}H{-}CH{=}CH_2}$



$$\mathrm{(R^1X)_2SiMeCH{=}CH_2} \xrightarrow[\text{2) } \mathrm{R^3X}\ \text{[198]}]{\text{1) } \mathrm{R^2M}} \mathrm{R^2CH_2\underset{R^3}{C}H{=}SiMe(XR^1)_2} \xrightarrow{\mathrm{MCPBA},\ \mathrm{KF/DMF}} \mathrm{R^2CH_2\underset{R^3}{C}H{-}OH} \qquad (173)$$



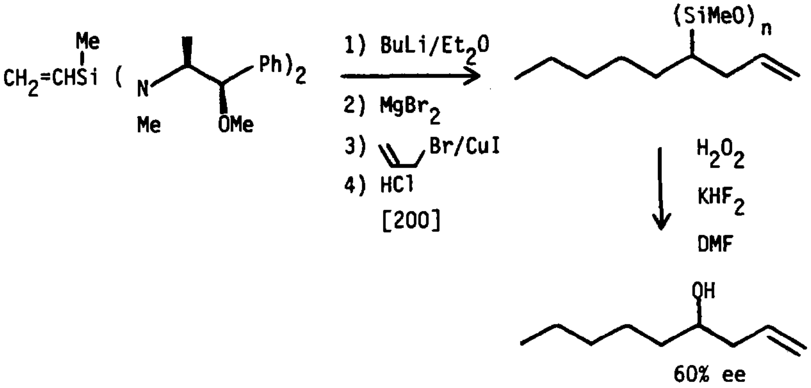
$$\mathrm{Me_2XSiCH{=}CH_2} + \mathrm{R{-}M} \xrightarrow[\text{[199]}]{} \mathrm{RCH_2\underset{M}{C}HSiMe_2X} + \mathrm{CH_2{=}CHSiMe_2R} \qquad (174)$$

^{n}BuLi gives substitution

iPrMgCl gives addition with $\mathrm{MeSi(OR)_2}$(R = Me, iPr)

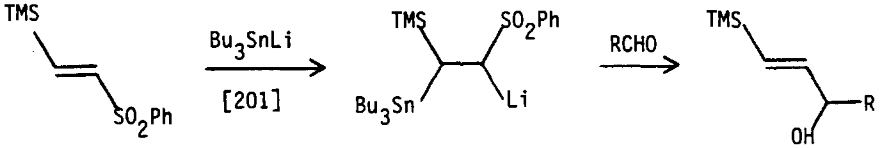
and $\mathrm{Me_2Si(O{\sim}N\langle\ )}$

iPrMgCl gives substitution with $\mathrm{MeSi(O{\sim}N\langle)_2}$



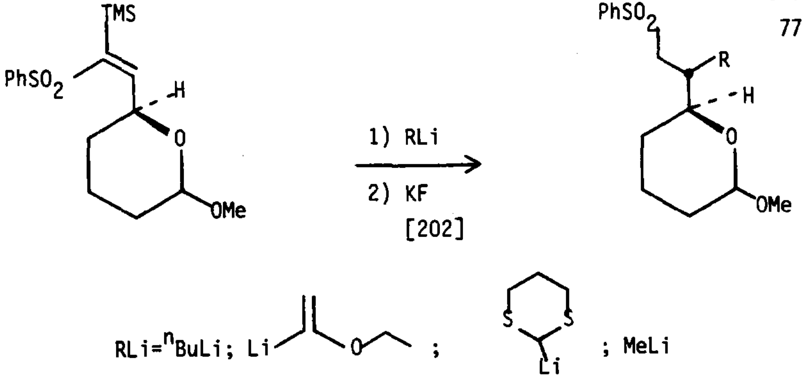
(175)

Vinylsilanes, which are also vinylsulfones, undergo addition of organolithium reagents to place the metal α to the sulphone group. These reactions are synthetically useful. (Eqns. 176-178)

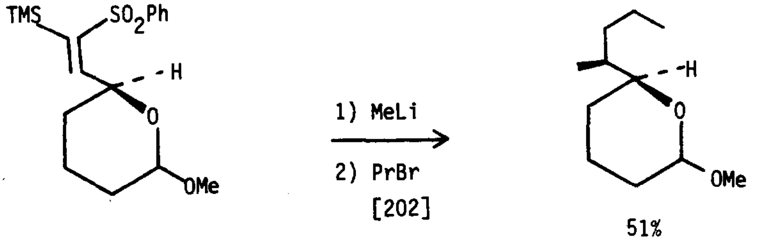


3 examples
77-93%

(176)



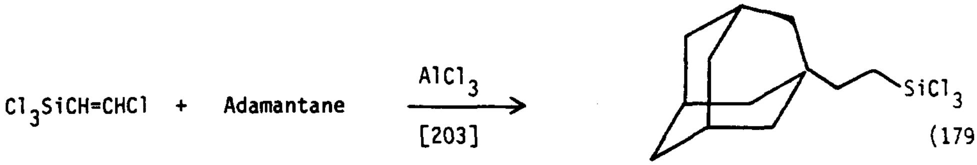
(177)



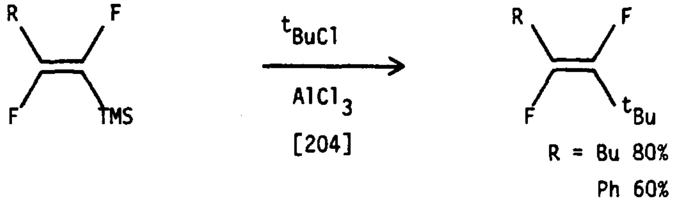
51%

(178)

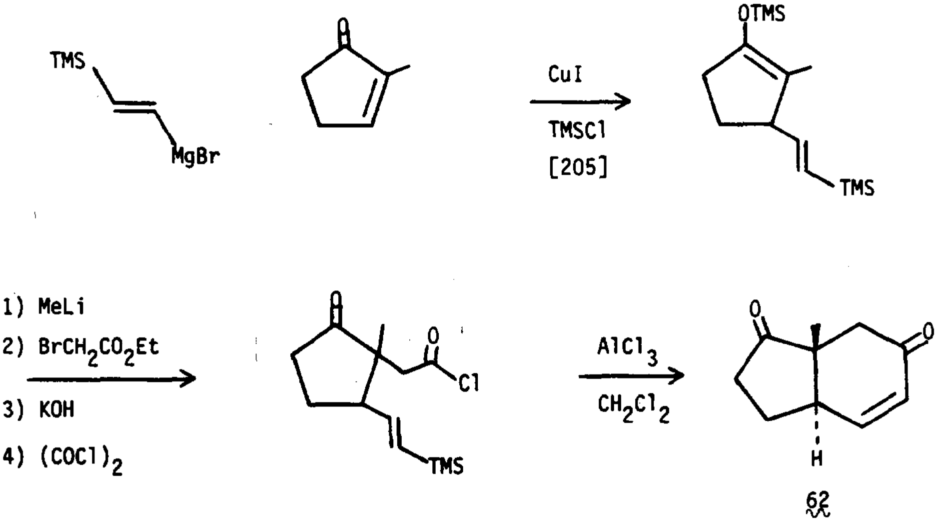
The reaction of β-chlorovinyltrichlorosilane with adamantane and aluminum chloride gives 1-(2-trichlorosilylethyl)adamantane. (Eqn. 179) The trimethylsilyl group of fluorinated vinylsilanes can be electrophically replaced (Eqn. 180) Examples of the intramolecular electrophilic reaction of vinylsilanes appeared. A synthesis of trans-7a-methylhydrin-4-ene-1,6-dione **62** is shown in Eqn. 181. The intramolecular cyclization of vinylsilanes and iminium ions was accomplished. (Eqn. 182) The trimethylsilyl group was used to direct the regioselective introduction of the double bond in the Nazarov reaction. (Eqns. 183-189) The requisite precursors were prepared according to Eqns. 183 and 184. A comparison of the results shown in Eqn. 187 and those in 188 and 189 demonstrate a considerable effect of larger ligands on silicon for the 6-methylated system **63**.



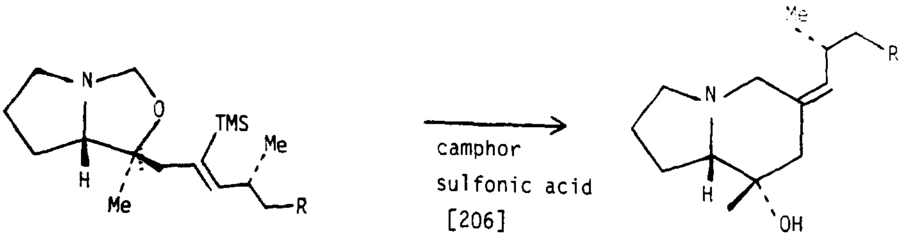
(179)



(180)

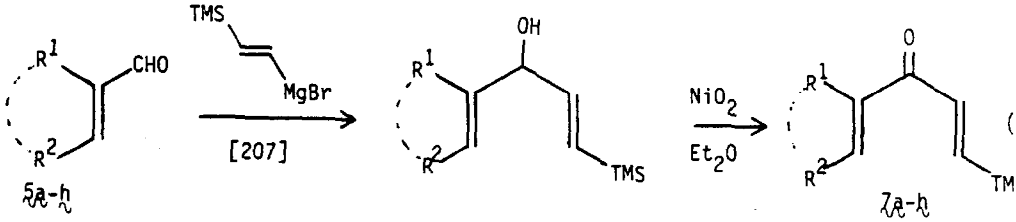


(181)



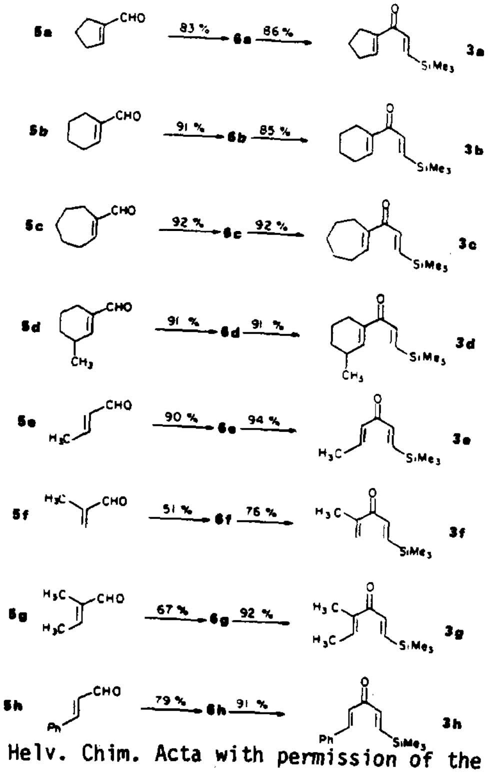
(182)

R = Pr, CH_2OCH_2Ph



(183)

Table VI: Divinyl Ketones from Enals According to Eqn. 183.



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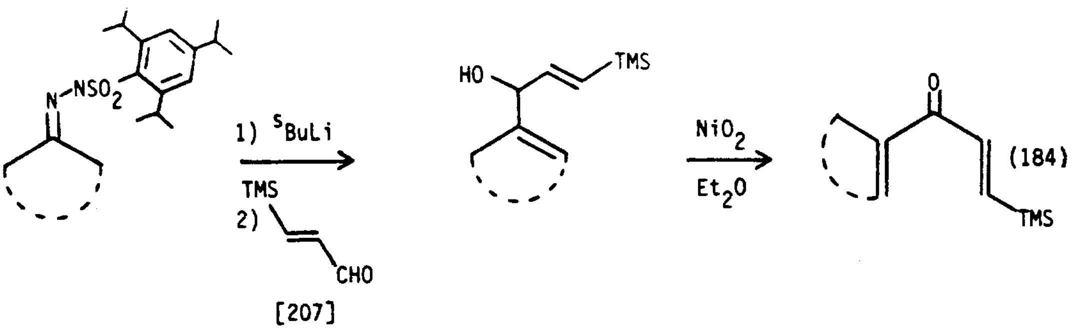
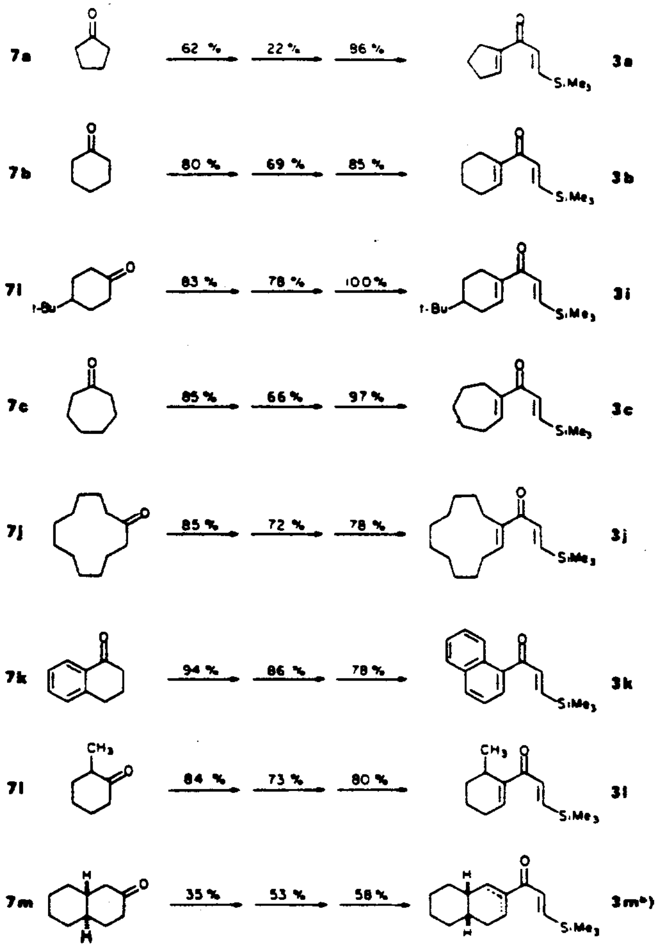


(184)

Table VII: β-Trimethylsilyl Divinyl Ketones According to Eqn. 184.



Ketone				Dienone
7a	62 %	22 %	96 %	3a
7b	80 %	69 %	85 %	3b
7i	83 %	78 %	100 %	3i
7c	85 %	66 %	97 %	3c
7j	85 %	72 %	78 %	3j
7k	94 %	86 %	78 %	3k
7l	84 %	73 %	80 %	3l
7m	35 %	53 %	58 %	3m[b]

---

[a] Yields for conversion ketones 7 to hydrazones 8 to alcohols 6 to dienones 3.

[b] An inseparable 2:1 mixture of isomers.

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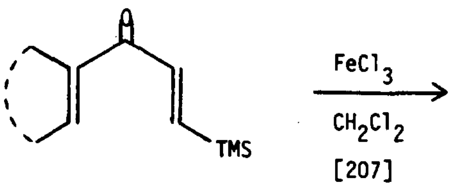
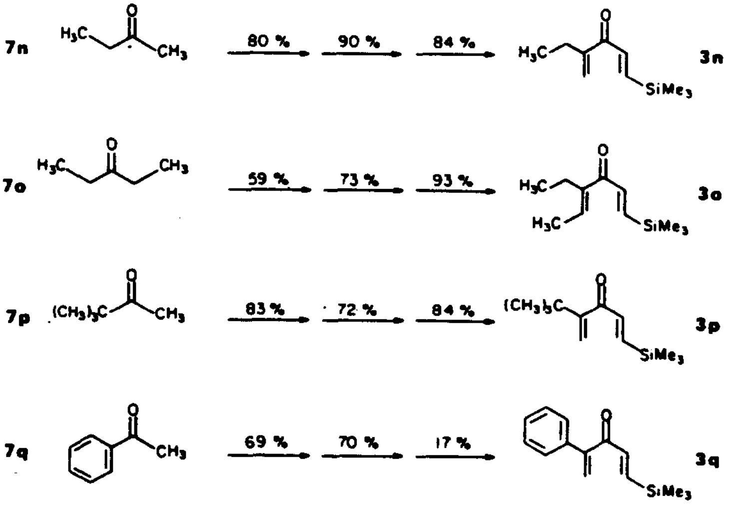


(185)

Table VIII: Acyclic Divinyl Ketones form Ketones According to Eqn. 185



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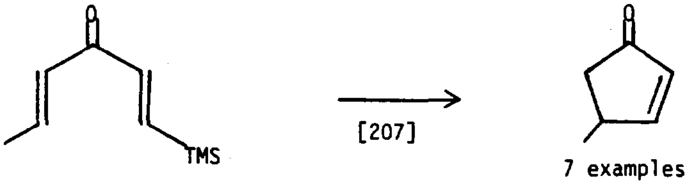
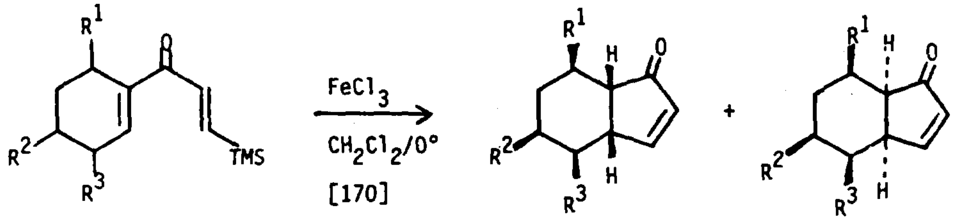


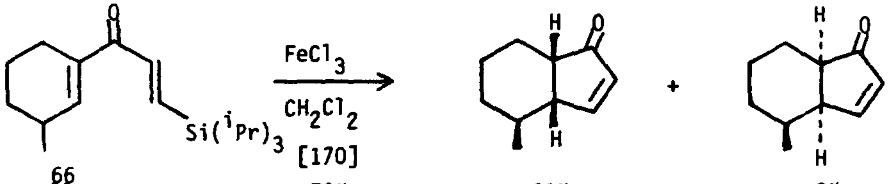
7 examples
27-95%

(186)



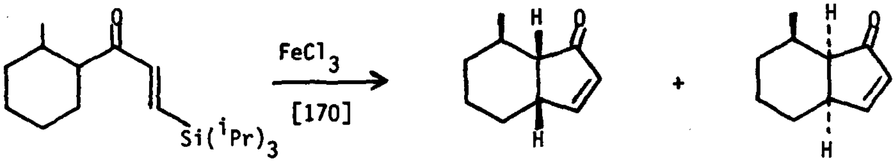
(187)

	R^1	R^2	R^3		
63	Me	H	H	72	28
64	H	${}^tBu$	H	76	24
65	H	H	Me	78	22



(188)

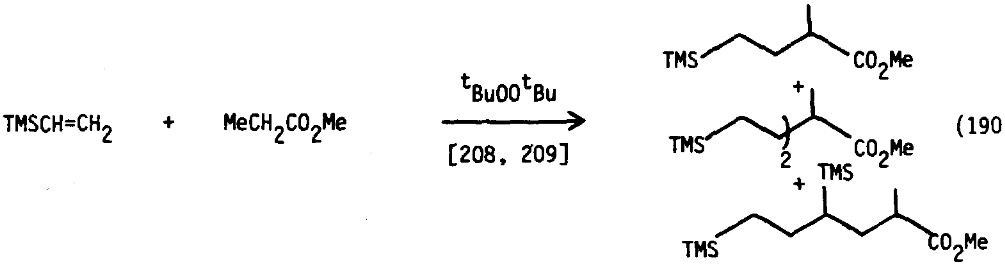
66 70% 91% 9%



(189)

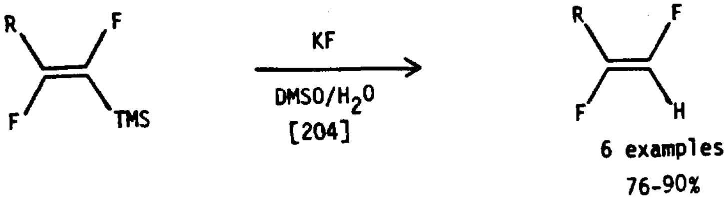
78 % 22 %

The telomerization of vinyltrimethylsilane with methyl propionate has been studied. (Eqns. 190)

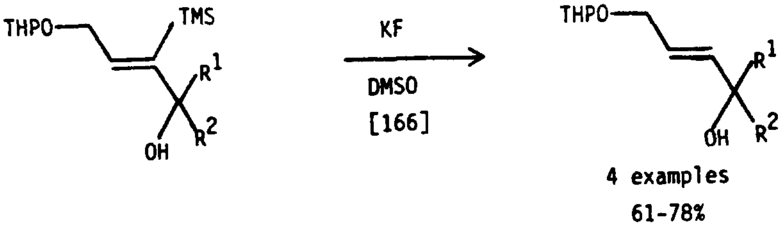


(190)

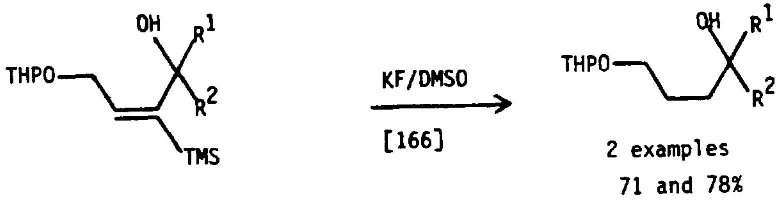
Examples of the fluoride ion-induced protiodesilylation of vinylsilanes are given in Eqns. 191-193. Vinylsilanes react with aldehydes under the influence of fluoride ion (Eqn. 194). α-Trimethylsilyl vinyl triflates react with fluoride ion to give the alkylidene carbene. (Eqn. 195)



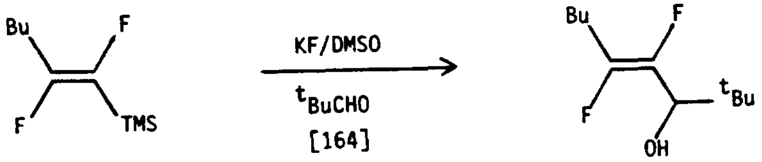
(191)



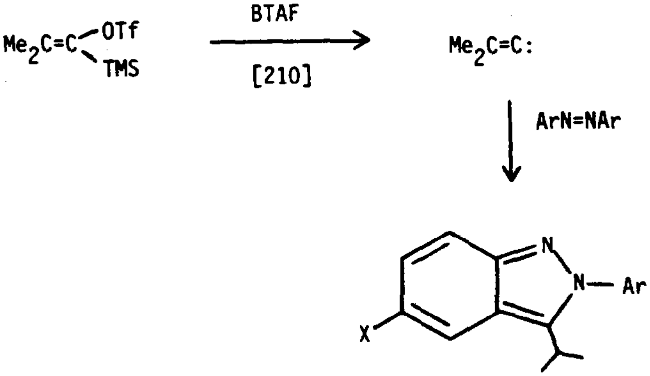
(192)



(193)

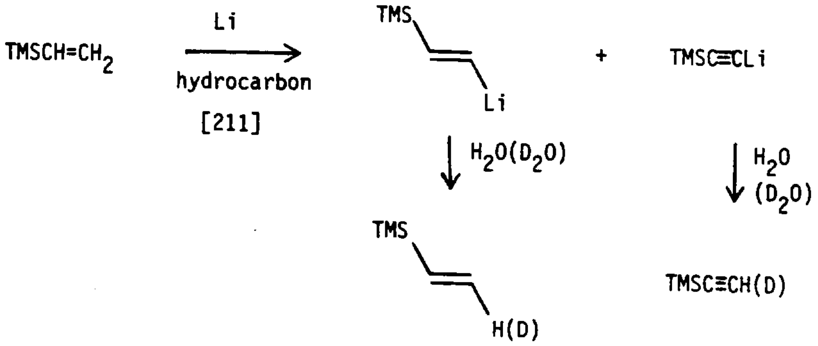


(194)

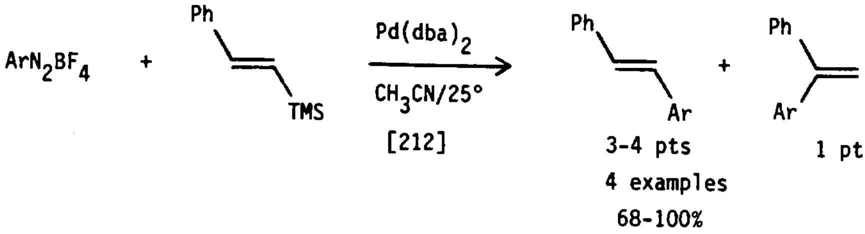


(195)

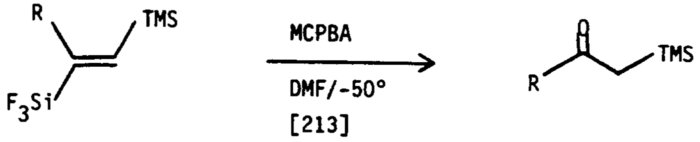
Several other reactions, which are difficult to classify, were reported. Vinyltrimethylsilane reacts with lithium metal in a hydrocarbon medium to give a mixture of trans-2-trimethylsilylvinyllithium and trimethylsilylethynyllithium. (Eqn. 196) Aryldiazo tetrafluoroborates couple with vinylsilanes in the presence of palladium (0). (Eqn. 197) The direct oxidation of trifluorovinylsilanes has been reported. (Eqns. 198, 199) The trimethylsilyl group in vinylsilanes was shown to have an effect on the regiochemistry of the ene reaction. (Eqns. 200,201) It is argued that in **70** transition state **71** prevails whereas in **68** transition state **72** competes. Vinylsilanes **73** can be cyclized to the dihydrofurans **74**. (Eqn. 202) The silylated cyclopropene **75** can be protiodesilylated in the presence of fluoride ion. (Eqn. 203) The vinylsilane **77** oxidizes at both carbon-boron bonds. (Eqn. 204) The silylation of 1-tert-butyl-1-sila-2,4-cyclohexadienes can be achieved at the 2, 4 and 6 positions. (Eqn. 205) The first reported methylene phosphorane **79** was prepared by ozonolysis of **78**. (Eqn. 206) An x-ray structure of **79** was carried out. Methylene phosphine **80** cycloadds to **81** to give **82** in low yield. (Eqn. 207)



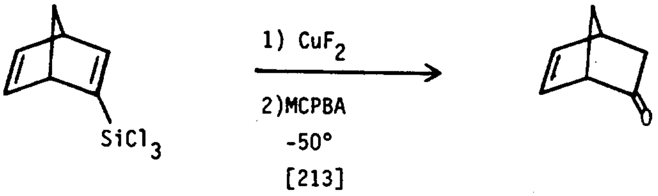
(196)



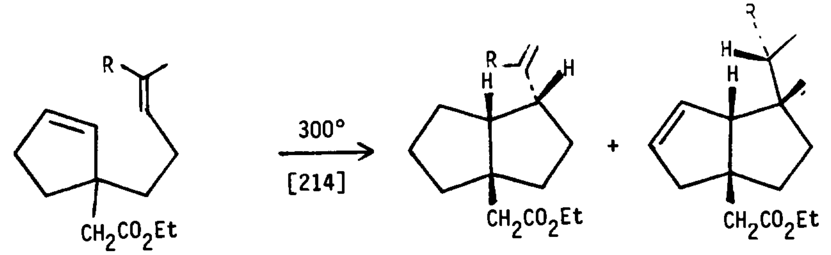
(197)



(198)

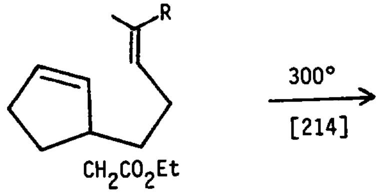


(199)



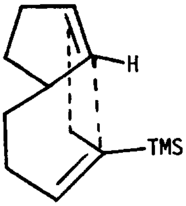
(200)

67	R = H	1	1
68	R = TMS	1	1

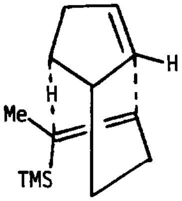


(201)

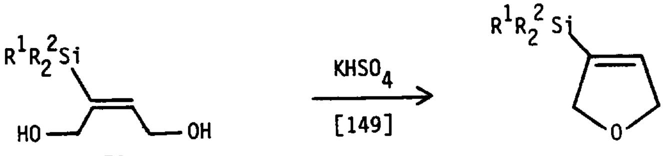
69	R = H	3	1
70	R = TMS	100	0



71



72



(202)

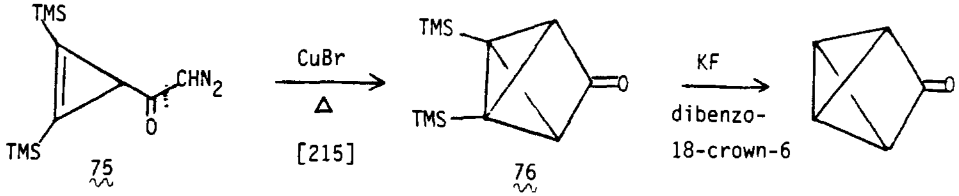
73

$R^1 = R^2 = Me, Et$

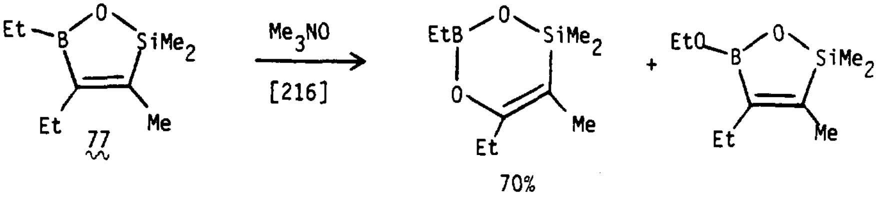
$R^1 = Ph; R^2 = Me$

74

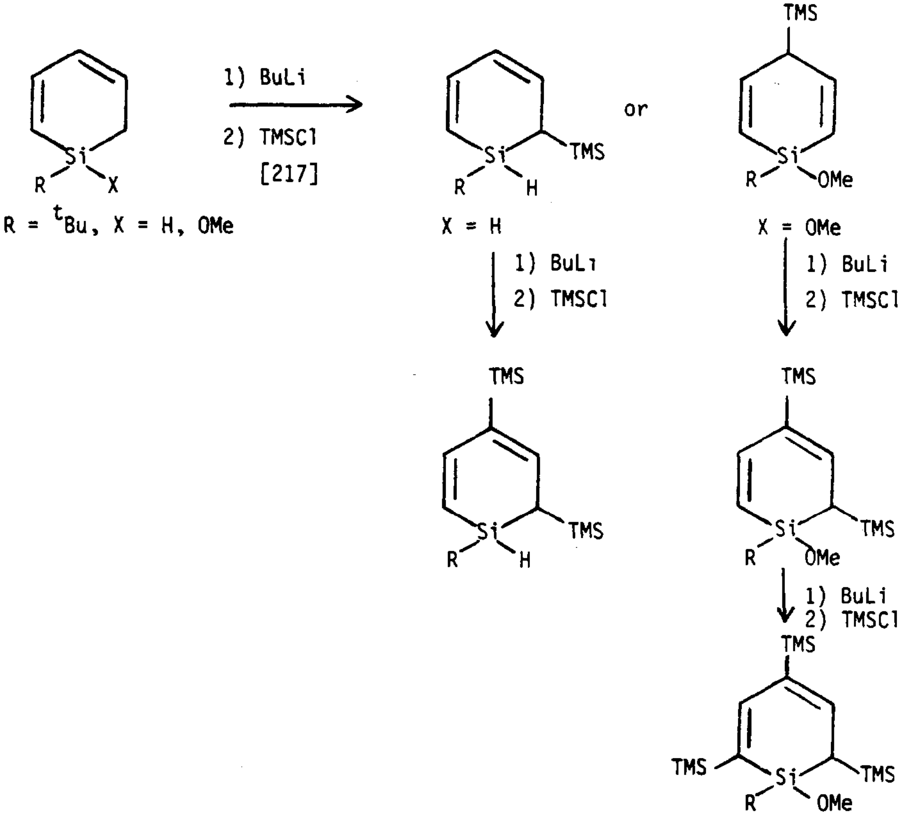
68-80%


TMS
CHN2
O
TMS
75
CuBr
Δ
[215]
TMS
TMS
O
76
KF
dibenzo-
18-crown-6
O

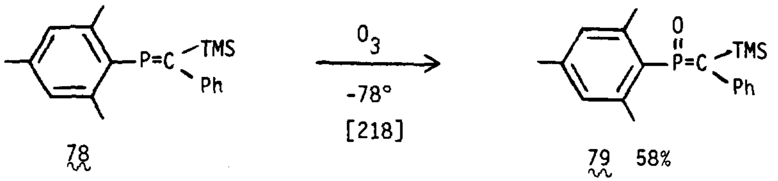
(203)


Et
B
O
SiMe2
Et
Me
77
Me3NO
[216]
EtB
O
SiMe2
O
Et
Me
70%
+
EtO
B
O
SiMe2
Et
Me

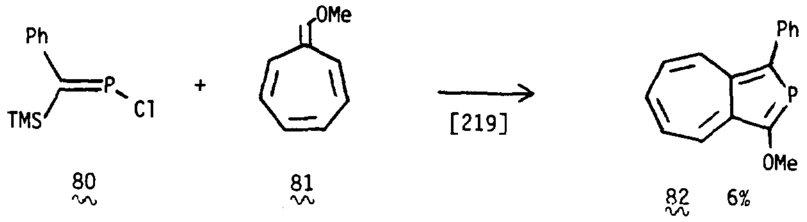
(204)


Si
R
X
R = tBu, X = H, OMe
1) BuLi
2) TMSCl
[217]
Si
R
H
TMS
X = H
or
TMS
Si
R
OMe
X = OMe
1) BuLi
2) TMSCl
TMS
TMS
Si
R
H
1) BuLi
2) TMSCl
TMS
TMS
Si
R
OMe
1) BuLi
2) TMSCl
TMS
TMS
TMS
Si
R
OMe

(205)



(206)

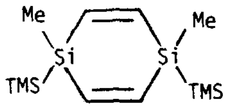


(207)

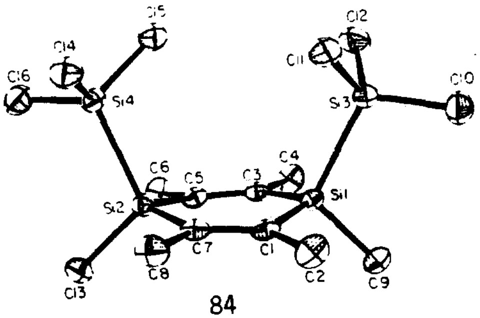
C. Spectroscopic and Other Studies

The ^{13}C - ^{13}C coupling constants in vinyltrimethylsilane were determined. [220] The ^{13}C-NMR spectra of trans-1-(alkylthio)-2-(trimethylsilyl)ethylenes were recorded. [221] It is argued that the pπ-dπ conjugation is governed by the steric effect of the alkylthio group and the resonance effect of the silyl group.

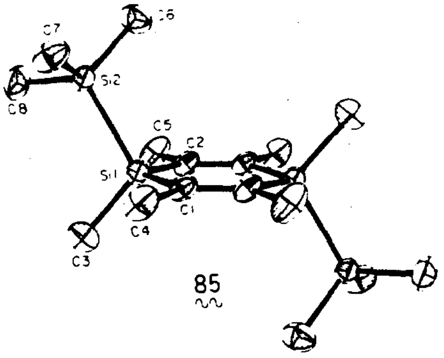
The geometries of the cis and trans 1,4-disilacyclohexadienes **83** were determined by x-ray analysis. [222] The trans system is nearly planar **85** and the cis form a twisted boat with the trimethylsilyl groups slightly pseudoaxial **84**. The E/Z equilibrium of 1-trimethylsilylvinyllithium was studied by NMR. A half-life of between 0.5 and 15 min at -70^{o} was calculated from the results with aΔH of activation of 7.4 (1.5) kcal/mol and a ΔS of activation of -32 (4) entropy units. [223]



83



84



85

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VIII. ETHYNYLSILANES

A. Preparation

The reaction of ethynyl organometallic reagents with chlorosilanes provided entries into ethynylsilanes. (Eqns. 208-214) Trimethylsilylethynyl organometallics provided entries into various functionalized ethynylsilanes. (Eqns. 213, 218, 219-222). The aldehyde **86** was converted to the 1,3-dioxolane **87** which was deprotonated and reacted with several electrophiles. (Eqns. 214-216) Reagent **89** proved an excellent precursor to the propiolate anion equivalent. (Eqn. 219) Trimethylsilylethynylzinc chloride adds to the stannylated propargyl chloride **90** in an SN2' fashion to give the allenyltin system **91**. (Eqn. 222) Tris(trimethylsilylethynyl) aluminum reacts with cycloalkylamino carbonates via a rearrangement alkylation sequence to give the ethynyl nitrogen heterocycle. (Eqn. 223)

Other organometallic derivatives of ethynylsilanes are useful in the preparation of ethynylsilanes. For example, 1-(triisopropylsilyl)propargylmagnesium bromide was reacted with an epoxide and allyl phosphates to give the propargylated product. This was monohydroborated and oxidized to the acid, which was esterified in a synthesis of perannulenes. (Eqn. 224)

Methyl diazoacetate reacts to insert the carbene into the terminal C-H bond of terminal ethynylsilanes except when an SiH bond is present when insertion takes place at this bond. (Eqns. 226, 227)

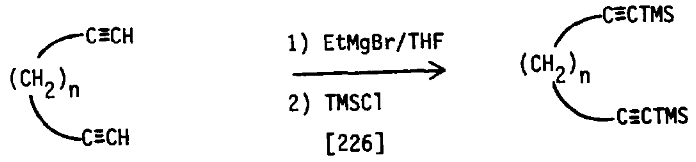
$$\mathrm{RC{\equiv}C\text{-}C{\equiv}CLi} + \mathrm{TMSCl} \xrightarrow[{[224]}]{} \mathrm{RC{\equiv}C\text{-}C{\equiv}C\text{-}TMS} \qquad (208)$$

R = Bu, Ph

$$\mathrm{RC{\equiv}CCH{=}CHCl} \xrightarrow[\text{2) TMSCl } [225]]{\text{1) NaNH}_2/\text{NH}_3(\text{l})} \mathrm{RC{\equiv}C\text{-}C{\equiv}C\text{-}TMS} \qquad (209)$$

R = $^nC_6H_{13}$ 70%

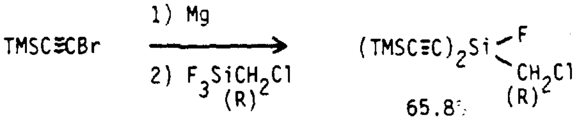
R = Ph 71%



(210)

n	% Yield
2	99
3	98
4	98
5	97
6	96
14	94

$$\mathrm{HO(CH_2)_4OCH_2C{\equiv}CH} \xrightarrow[\text{2) } R^1R^2_2\text{SiCl } [153]]{\text{1) EtMgBr}} \mathrm{HO(CH_2)_4OCH_2C{\equiv}CSiR^1R^2_2} \qquad (211)$$



$$\text{TMSC}\equiv\text{CBr} \xrightarrow[\text{2) F}_3\text{SiCH}_2\text{Cl (R)}^2]{\text{1) Mg}} (\text{TMSC}\equiv\text{C})_2\text{Si}(\text{F})\text{CH}_2\text{Cl (R)}^2 \qquad (212)$$

[227]

65.8%

12 examples

24.5-76.5%

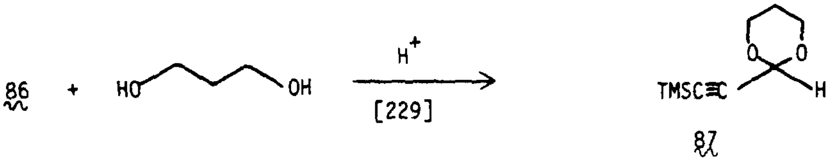
$$\text{PhZC}\equiv\text{CH} \xrightarrow[\text{2) ClMe}_2\text{SiCH}_2\text{Cl}]{\text{1) EtMgBr}} \text{PhZC}\equiv\text{CSiMe}_2\text{CH}_2\text{Cl} \qquad (213)$$

[228]

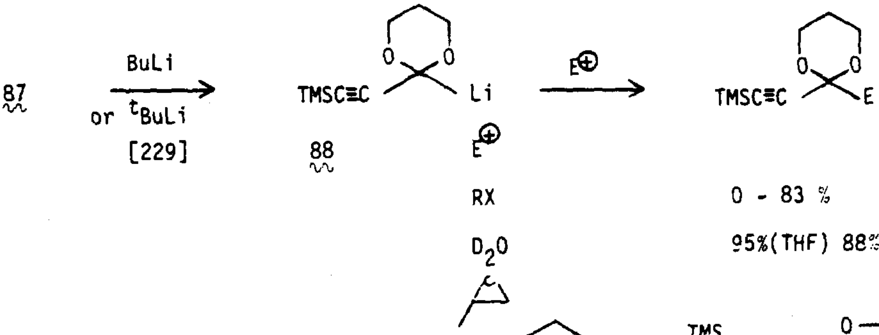
Z = O, S

$$\text{TMSC}\equiv\text{CH} \xrightarrow[\text{2) DMF}]{\text{1) EtMgBr}} \underset{\mathbf{86}}{\text{TMSC}\equiv\text{CCHO}} \qquad (214)$$

[229]



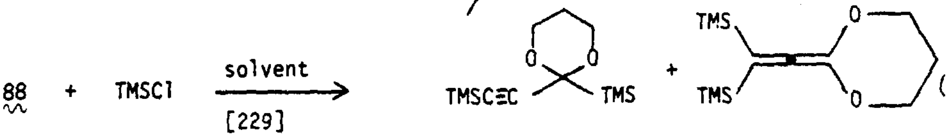
(215)



(216)

0 - 83 %

95%(THF) 88%(Et$_2$O)



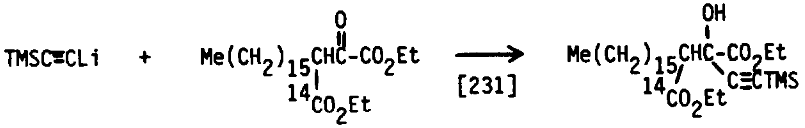
(217)

solvent		
THF	60	40
Et$_2$O	35	65
HMPA	100	0

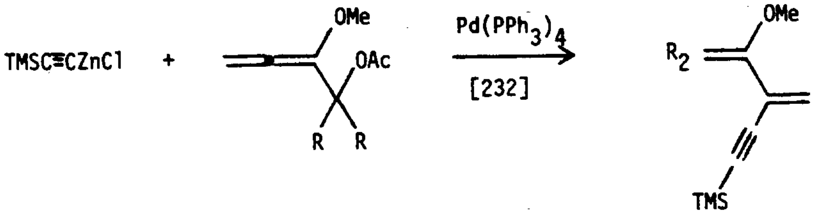
$$\mathrm{TMSC{\equiv}CH} \xrightarrow[\text{2) (EtO)}_3\text{C}^+\text{BF}_4^-\ [230]]{\text{1) BuLi}} \underset{\mathbf{89}}{\mathrm{TMSC{\equiv}CC(OEt)_3}} \qquad (218)$$

$$\mathbf{89} \xrightarrow[\text{2) BuLi}\ [230]]{\text{1) NaOH/EtOH}} \mathrm{LiC{\equiv}CC(OEt)_3} \xrightarrow{E^{\oplus}} \mathrm{EC{\equiv}CC(OEt)_3} \qquad (219)$$

11 examples
52-94%

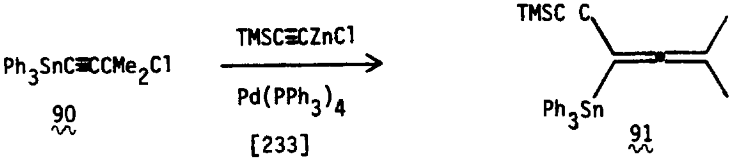


$$\mathrm{TMSC{\equiv}CLi} + \mathrm{Me(CH_2)_{15}\underset{^{14}CO_2Et}{CH}\overset{O}{\overset{\|}{C}}{-}CO_2Et} \xrightarrow[{[231]}]{} \mathrm{Me(CH_2)_{15}\underset{^{14}CO_2Et}{CH}\overset{OH}{\overset{|}{C}}(C{\equiv}CTMS){-}CO_2Et} \qquad (220)$$

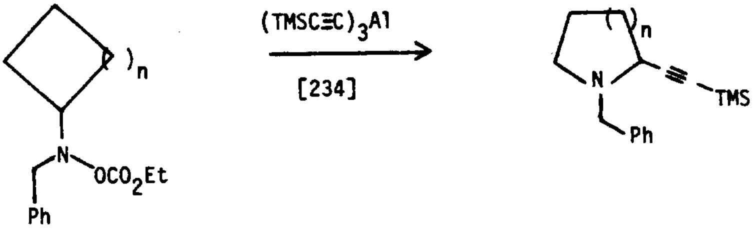


(221)

R = H (85%), Me (95%)

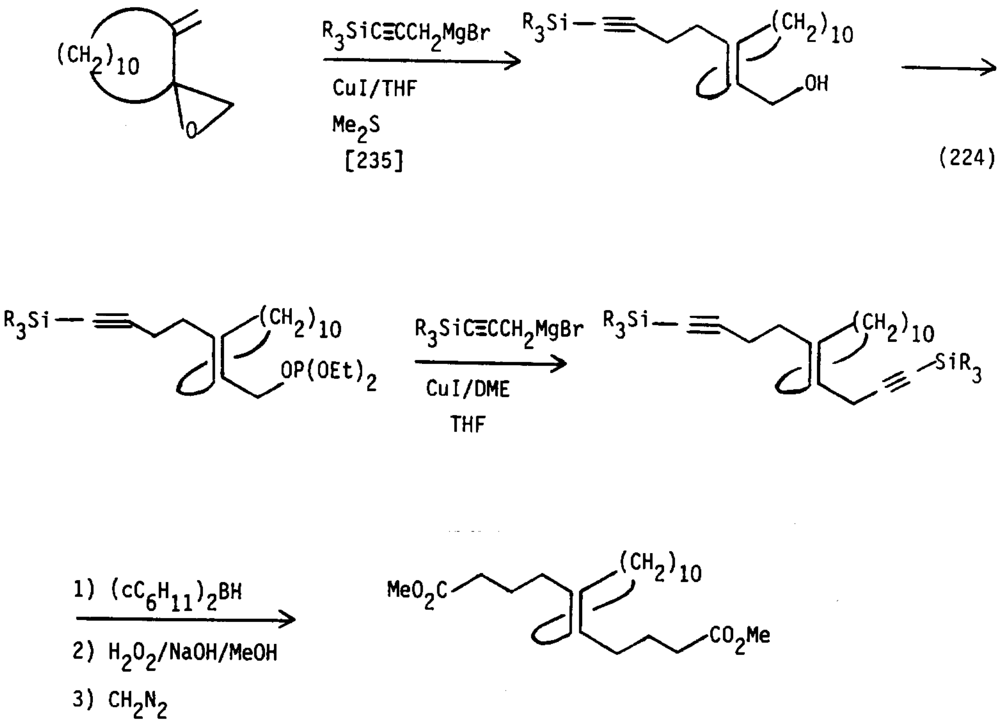


(222)

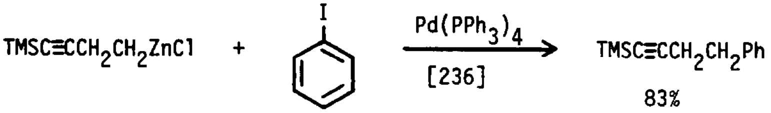


(223)

n = 1 (98%); n = 2 (71%)

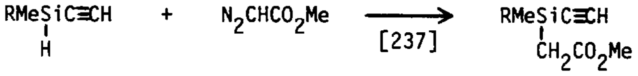


(224)



$$\mathrm{TMSC{\equiv}CCH_2CH_2ZnCl} + \mathrm{PhI} \xrightarrow[\text{[236]}]{\mathrm{Pd(PPh_3)_4}} \underset{83\%}{\mathrm{TMSC{\equiv}CCH_2CH_2Ph}} \tag{225}$$

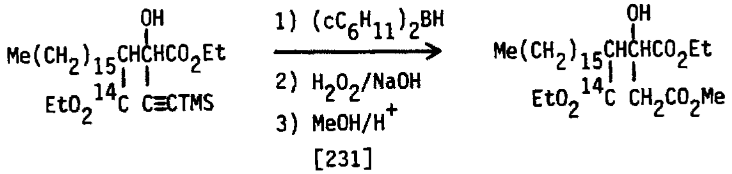
$$\mathrm{RMe_2SiC{\equiv}CH} + \mathrm{N_2CHCO_2Me} \xrightarrow[\substack{\text{or CuCl} \\ \text{or CuSO}_4 \\ 80\text{-}100° \\ [237]}]{\text{Cu}} \mathrm{RMe_2SiC{\equiv}CCH_2CO_2Me} \tag{226}$$



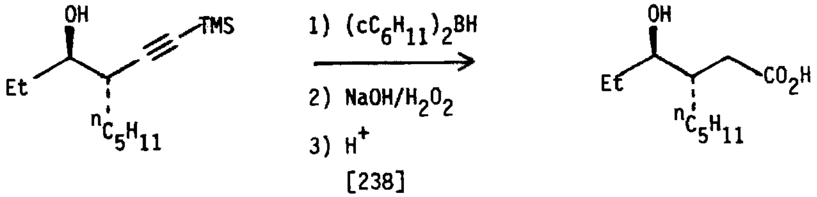
$$\mathrm{RMe\underset{H}{Si}C{\equiv}CH} + \mathrm{N_2CHCO_2Me} \xrightarrow[\text{[237]}]{} \mathrm{RMe\underset{CH_2CO_2Me}{Si}C{\equiv}CH} \tag{227}$$

B. Reactions

Additions to ethynylsilanes were reported. The monohydroboration-oxidation gives carboxylic acids. (Eqns. 228, 229) The addition of the boron-boron bond to ethynylsilanes has been reported. (Eqn. 230) An apparent rearrangement occurs in the substituted ethynylsilanes. Trimethylsilylacetylene gives the 1,2-bisboryl adduct. (Eqn. 231) The ethynylimine **92** adds thiophenol at both the imine and triple bond. (Eqn. 232) The enyne **93** suffers addition to the double bond in an 1,2 fashion and to the enyne in a 1,4 fashion. (Eqn. 233) The silylated ethynyl ethers **94** cycloadd to ketenes. (Eqn. 234)



(228)



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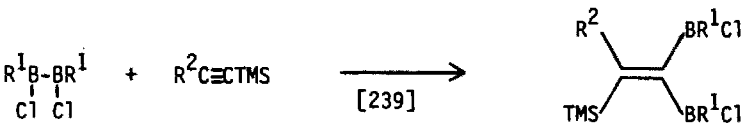
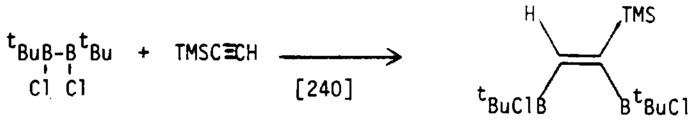


(230)

R^1 = ^{t}Bu, Me_2N

R^2 = TMS, Ph, $^tBuCH_2$, Me



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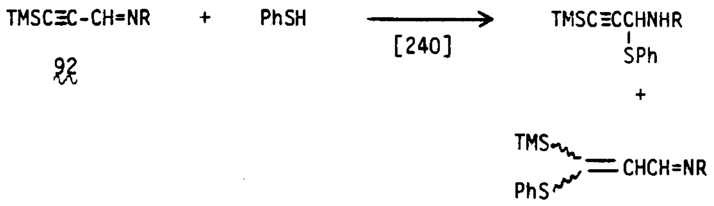

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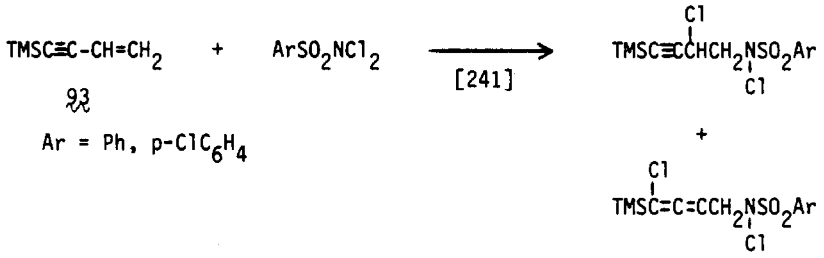

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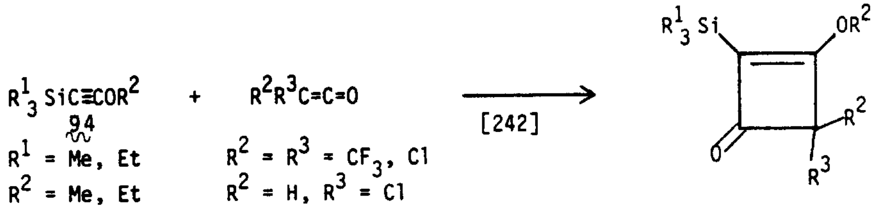
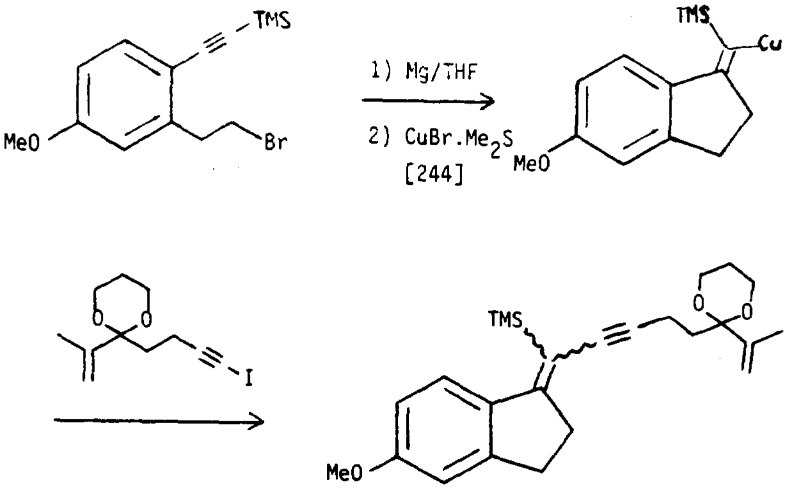


(234)

The addition of organometallics to ethynylsilanes was reported. It was reported that 1-trimethylsilylpropyne and trimethylsilylphenylacetylene are stable to Grignard reagents as determined by ^{13}C and ^{29}Si-NMR. [243] However Grignard reagents were added to ethynylsilanes in intramolecular reactions in two cases one with copper catalysis. (Eqns. 235, 236) More examples are given in Eqns. 237-240. Allylzinc bromide adds to ethynylsilanes. (Eqn. 241) Additional results of this reaction are given in Table IX.



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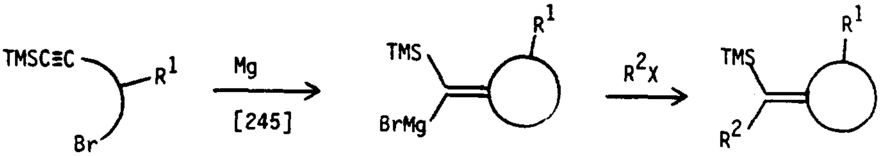
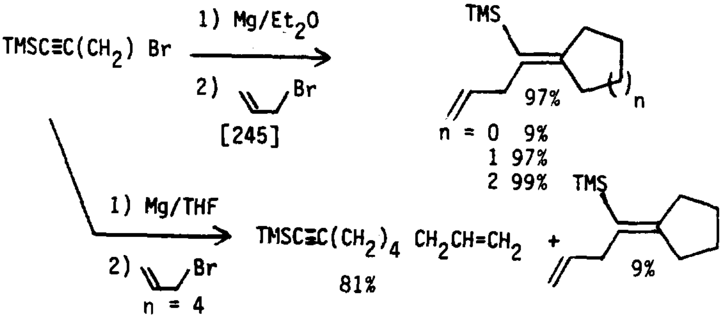


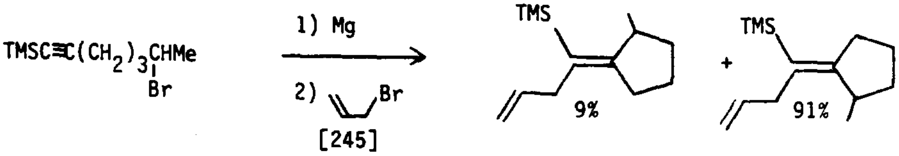
(236)

several examples



(237)

(238)



(239)

(240)

Table IX: Allylzincation of 1-(Trimethylsilyl)-1-alkynes with Allylzinc Bromide According to Eqn. 241.[a]

alkynylsilane	product[b]	% GC yield (isolated)	stereochemical purity[c]
1-(trimethylsilyl)-1-hexyne (**2a**)	1-(trimethylsilyl)-2-(2-propenyl)-1-hexene (**4a**)	85 (70)	85[e]
1-(trimethylsilyl)-5-chloro-1-pentyne (**2b**)	1-(trimethylsilyl)-2-(3-chloropropyl)-1,4-pentadiene (**4b**)	88 (63)	81[e]
1-(trimethylsilyl)-2-phenylethyne[d] (**2c**)	1-(trimethylsilyl)-2-phenyl-1,4-pentadiene (**4c**)	78	>95[e]
1-(trimethylsilyl)-3-(benzyloxy)-1-hexyne (**2d**)	1-(trimethylsilyl)-2-(2-propenyl)-3-(benzyloxy)-1-hexene (**4d**)	74	>95[f]
1-(trimethylsilyl)-3-(trimethylsiloxy)-1-hexyne (**2e**)	1-(trimethylsilyl)-2-(2-propenyl)-3-(trimethylsiloxy)-1-hexene (**4e**)	52	>95[f]
4-(trimethylsilyl)-2-methyl-1-buten-3-yne (**2f**)	1-(trimethylsilyl)-2-isopropenyl-1,4-pentadiene (**4f**)	57	>95[f]
1-(trimethylsilyl)-3,3-dimethyl-1-butyne (**2g**)	no reaction	0	

[a] Unless otherwise indicated, reactions were performed in refluxing THF for 16–25 h by using 2.5 equiv of **1** per equiv of **2** and then quenched with saturated NH_4Cl. [b] Satisfactory ^1H NMR, ^{13}C NMR, IR, and mass spectral data were obtained for all products. [c] Determined by ^{13}C NMR. [d] Reaction was run at room temperature for 2 days in THF. [e] Predominant net cis carbometalation. [f] Predominant net trans carbometalation.

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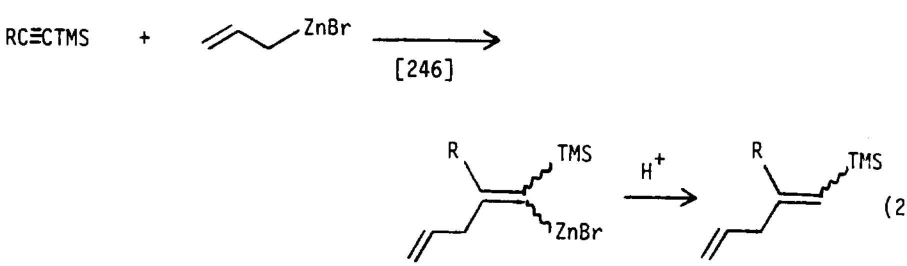
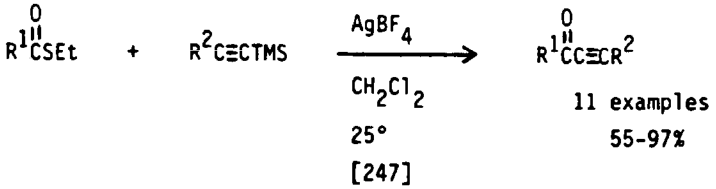


(241)



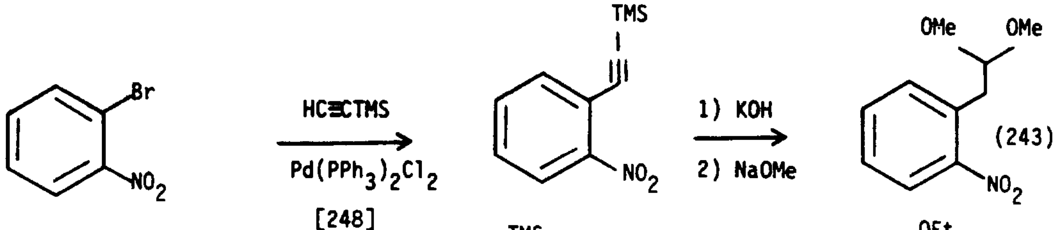
$$R^1\overset{O}{\overset{\|}{C}}SEt \quad + \quad R^2C{\equiv}CTMS \xrightarrow[\substack{CH_2Cl_2 \\ 25° \\ [247]}]{AgBF_4} R^1\overset{O}{\overset{\|}{C}}C{\equiv}CR^2$$

11 examples
55-97%

(242)

Thiol esters react with ethynylsilanes in the presence of silver tetrafluoroborate to give ethynyl ketones in good yield. (Eqn. 242) Ethynyltrimethylsilane can be cross-coupled with aryl chlorides, bromides and iodides. (Eqns. 243, 244)

Deprotonation of the propargylic position of ethynylsilanes has provided some useful chemistry. A key step in the synthesis of α-ethynylhistamine was condensation of dianion **95** with epibromohydrin. (Eqn. 245) Trimethylsilylated propargyl allyl ethers were subjected to the [2.3] Wittig rearrangement. (Eqns. 246-248) In these examples the trimethylsilyl group serves to protect the acidic terminal position.



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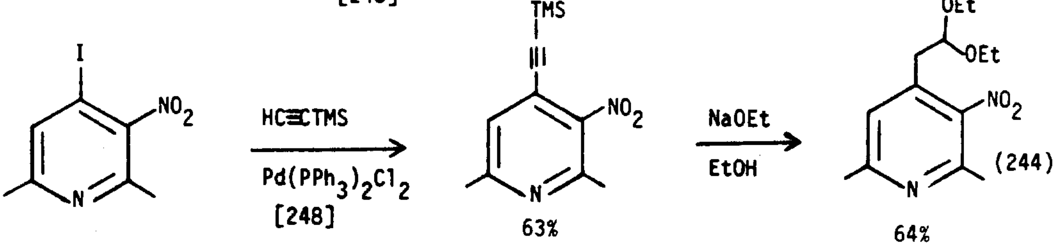

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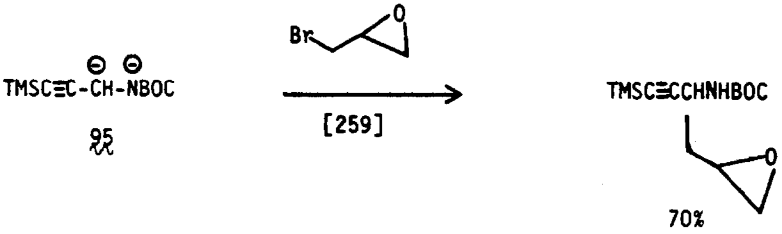
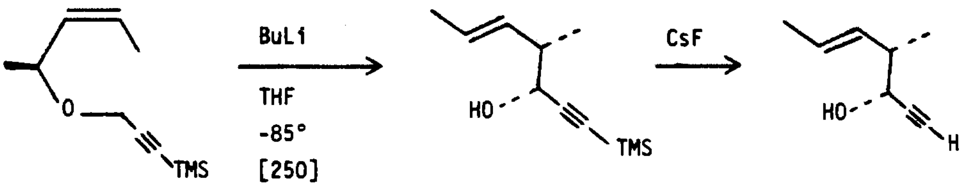


(245)



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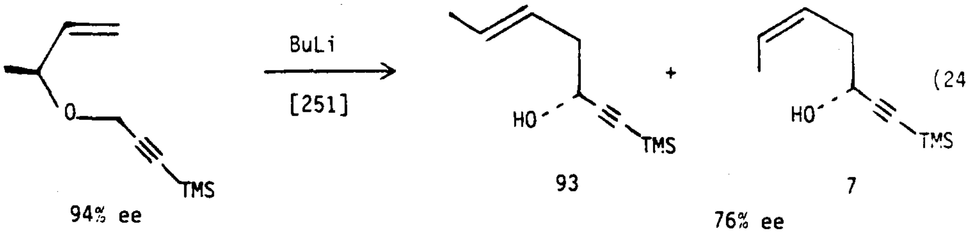

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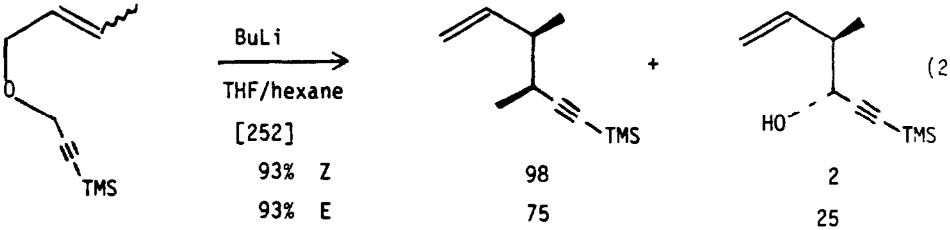
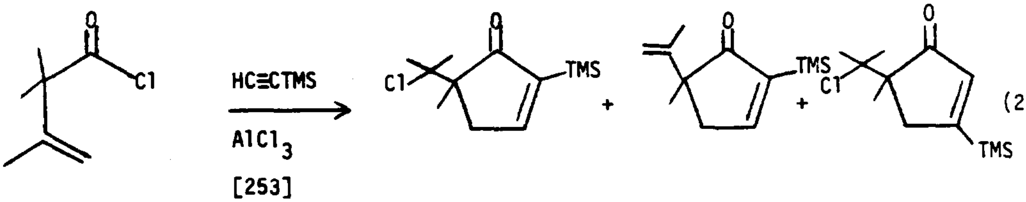


(248)

In other reactions ethynyltrimethylsilane was added to α,β-unsaturated acid chlorides under Friedel-Crafts conditions. (Eqns. 249, 250) 1-Trimethylsilyl propiolic chloride reacts with methyl diazoacetate at the triple bond. (Eqn. 251) Trimethylsilylpropargyl ethers were subjected to cobalt catalyzed cyclizations. (Eqns. 252, 253) Trimethylsilylated conjugated diynes can be metalated. (Eqn. 254) Ethynyltrimethylsilane can be dimerized in the presence of titanium (IV) and a Grignard reagent. (Eqn. 255) Trimethylsilyl alkynone **96** photoadds to tetramethylethylene (Eqn. 256) Intermediate carbene **97** is postulated. The tert-butyl analog 97a proceeds via a singlet carbene, which cyclizes to a cyclopropene. (Eqn. 257)



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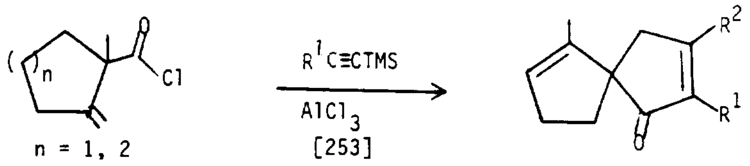
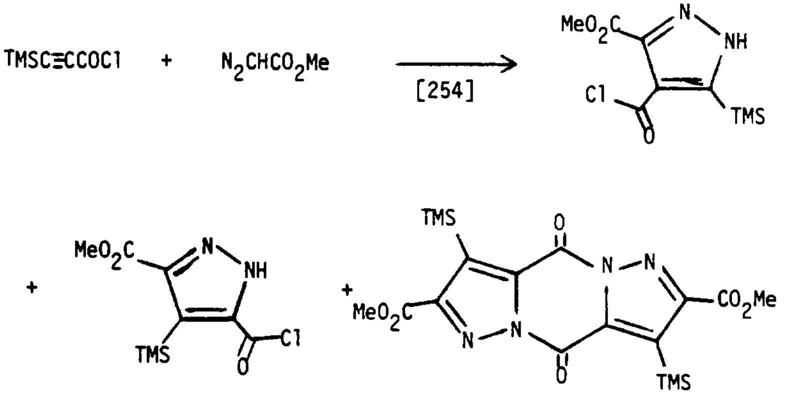


(250)

n	R^1	R^2	% Yield
1	H	TMS	57
1	TMS	H	13
2	H	TMS	71
2	TMS	H	17
1	Me	TMS	62
1	TMS	Me	14
2	Me	TMS	57
2	TMS	Me	24



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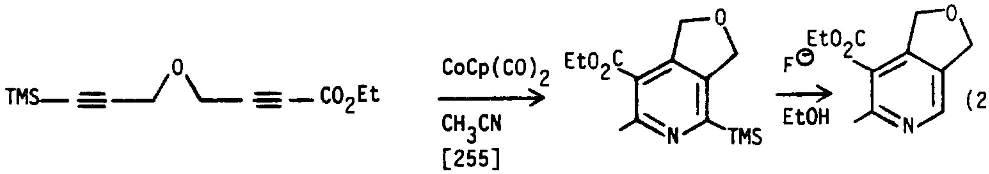

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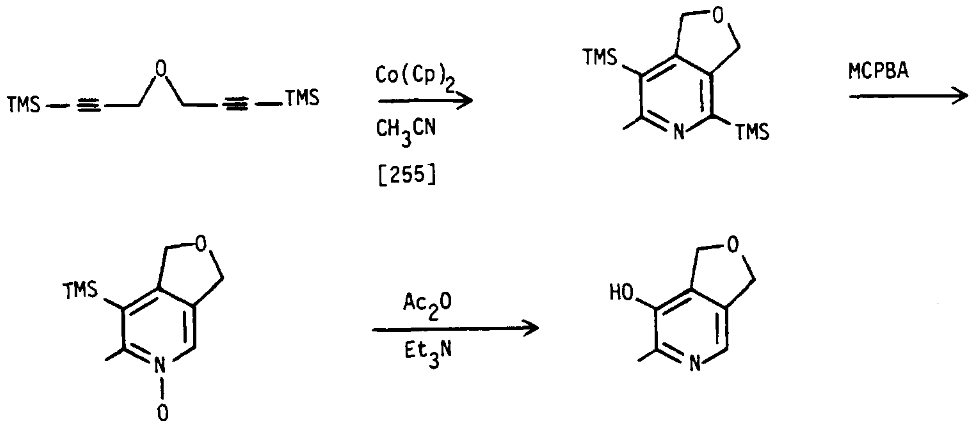

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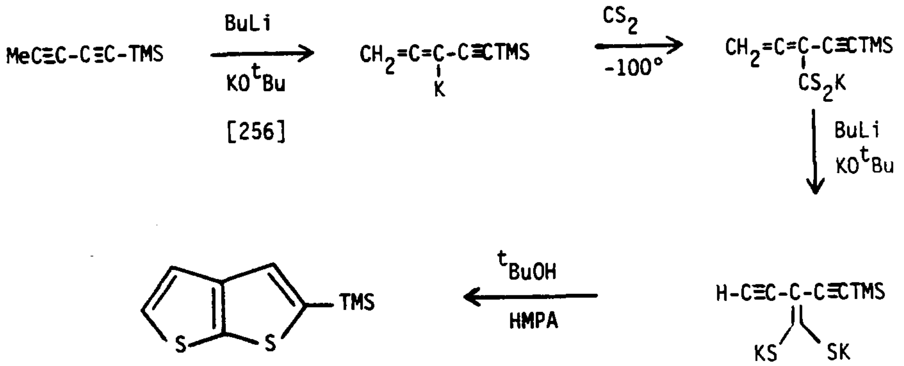

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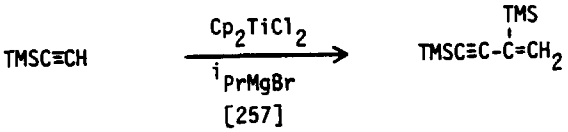
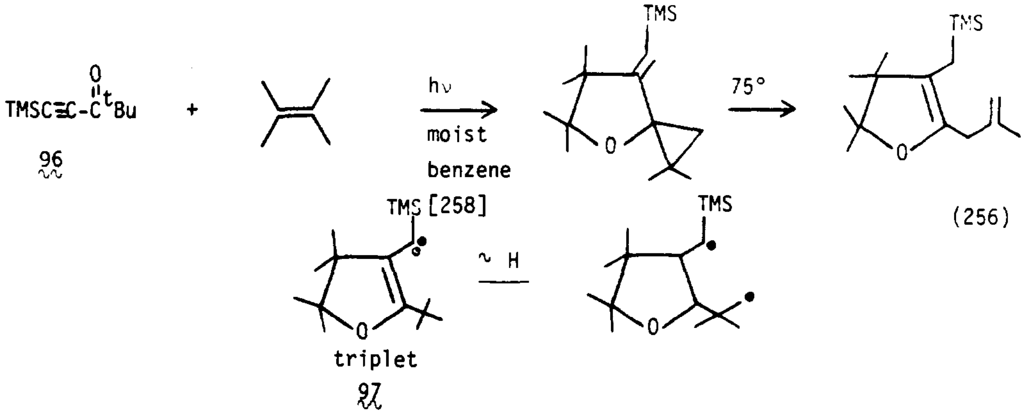


$$\mathrm{TMSC{\equiv}CH} \xrightarrow[\substack{^{i}\mathrm{PrMgBr} \\ [257]}]{\mathrm{Cp_2TiCl_2}} \mathrm{TMSC{\equiv}C{-}\overset{TMS}{C}{=}CH_2}$$

(255)



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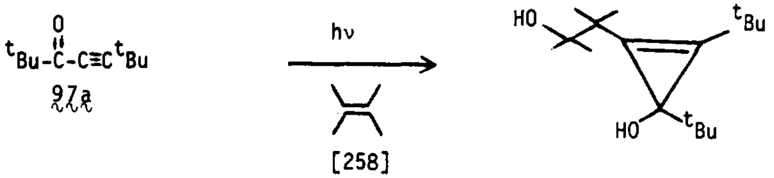


(257)

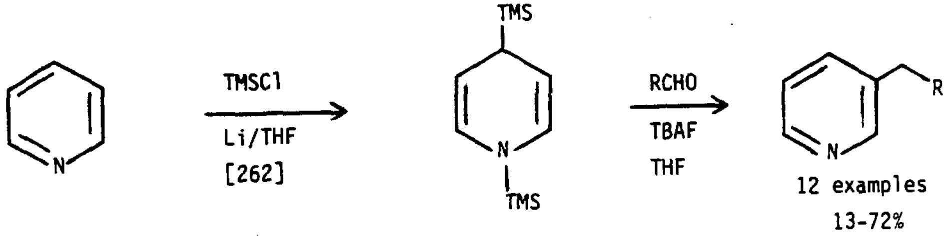
C. Spectroscopic and Other Studies

Several spectroscopic studies of silyltrifluoroacetylene and its trideuterio derivative were carried out, including MS, IR, Raman, microwave and electron diffraction. [259] The vibrational relaxation and molecular dynamics of liquid ethynyltrimethylsilane and 1-deuterioethynyltrimethylsilane were studied. [260]. The ^{13}C-^{13}C coupling constants were determined for ethynylsilanes, including triethylsilyllithioacetylene. [261]

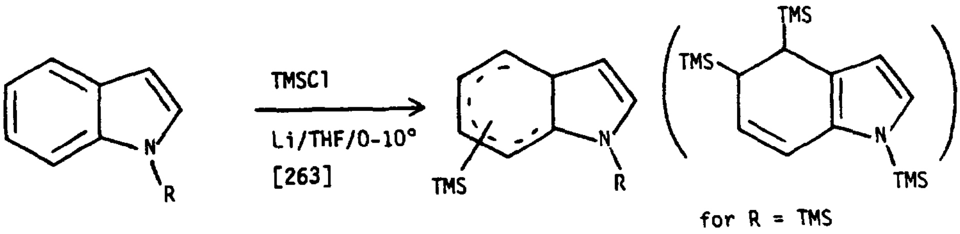
IX. ALLYLSILANES

A. Preparation

The TMSCl/Li/THF reagent nicely silylates pyridines. (Eqn. 258) The allylsilane products react with aldehydes under the influence of fluoride ion to give 3-alkylated pyridines. (Eqn. 258) Allylsilanes are produced from the reaction of the TMSCl/Li/THF reagent and indoles and benzothiophene. (Eqns. 259, 260) Benzofuran gives arylsilanes. (Eqn. 261) The TMSCl/Li reagent was applied to an allylsulfide to provide an allylsilane. (Eqn. 262)



(258



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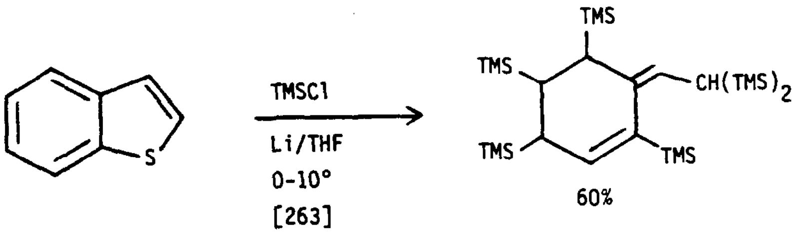

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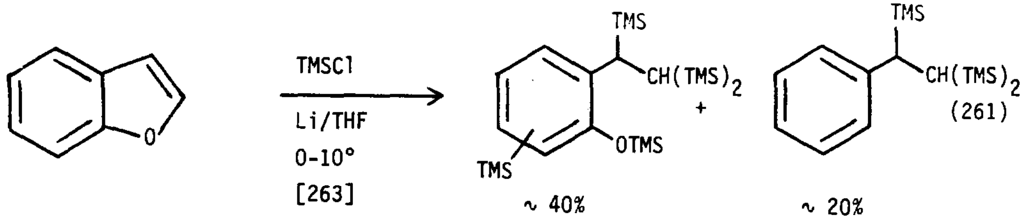

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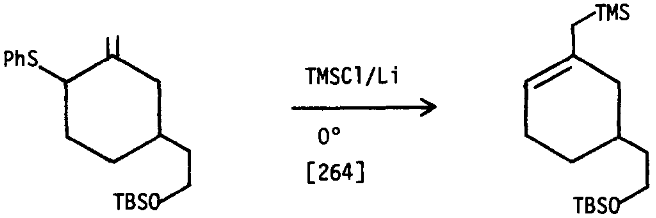
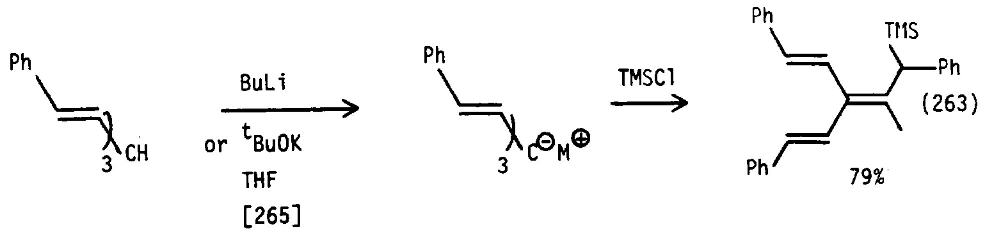


(262)

Allylorganometallic reagents were reacted with chlorosilanes to produce allylsilanes. The tristyrylmethyllithium reagent was silylated. (Eqn. 263) Lithium reagents **98** and **99** were quenched with trimethylchlorosilane to give the α-chloroallylsilanes. (Eqns. 264, 265) 1-(Diethoxyphosphoxyl)-1-dimethylamino allyllithium reagents were prepared and silylated. (Eqns. 266, 267) Bisallylation is also possible. N-allylpyrollidine can be metalated and trimethylsilylated to give esters, the enamine or the α-pyrollidylallylsilane. (Eqns. 268, 269) These products can in turn be metalated and silylated. (Eqns. 270, 271) 1-Tert-butyl-3-methoxy-1-alkenes were metalated and silylated to provide the α-tert-butylthioallylsilanes, (Eqn. 272) hydrolysis and oxidation-elimination of which provided the β-trimethylsilyl α,β-unsaturated ketones. (Eqn. 273) The dianion of the boracyclopentene **100** can be silylated to give the allylsilane **101**. (Eqn. 274) Allyl Grignard reagents react with silanes under catalysis with nickel complexes. (Eqn. 275) Lithiated allyltrimethylsilane was reacted with benzaldehyde, butyraldehyde, isobutyraldehyde and acetophenone in the presence and absence of triethylaluminum. The Lewis acid brought about increased reaction at the α-position. (Eqn. 276)



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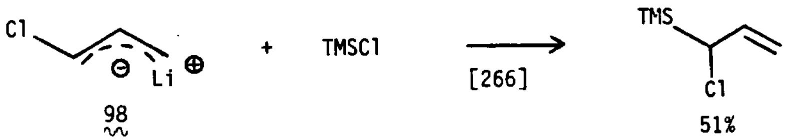

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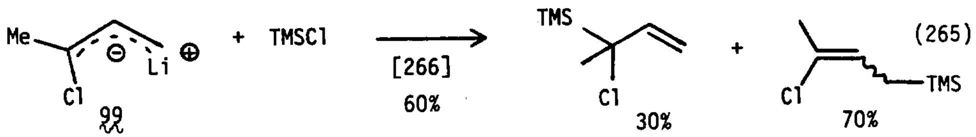

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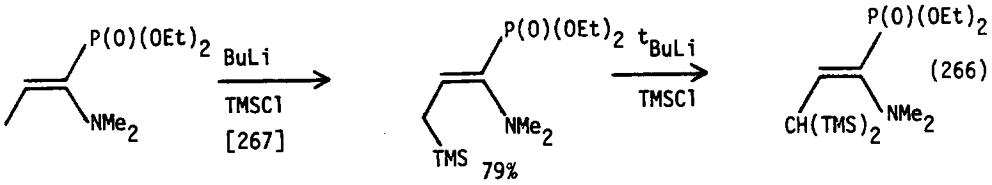

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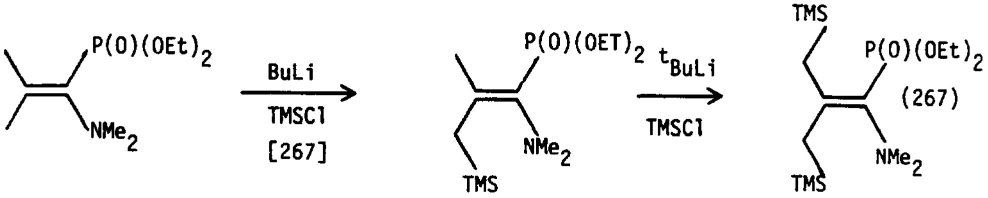

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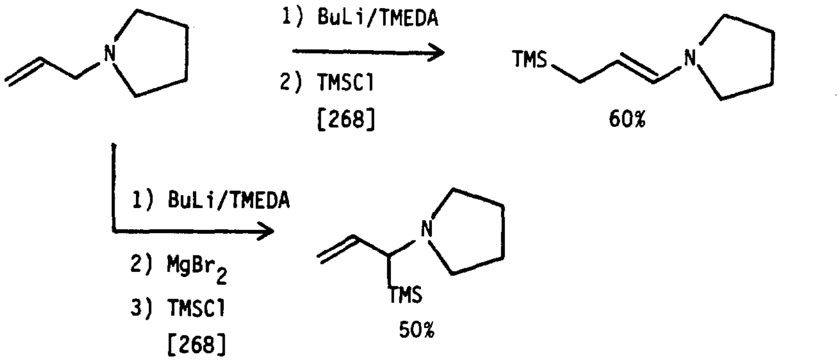
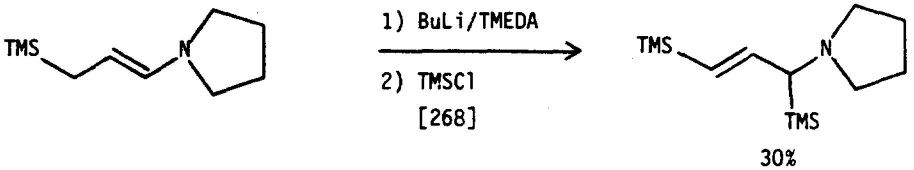
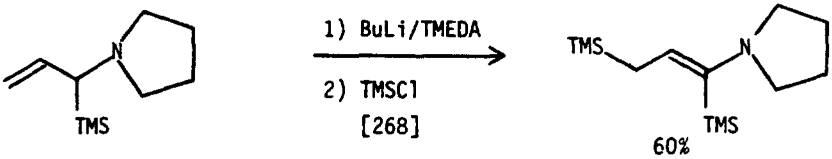


(268)

(269)



(270)



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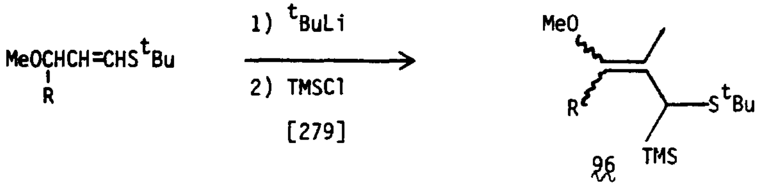
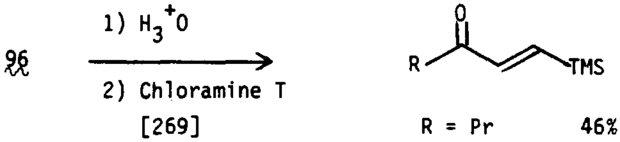


(272)

R = Me (92%) E:Z 27:73

R = Pr (87%) E:Z 17:83

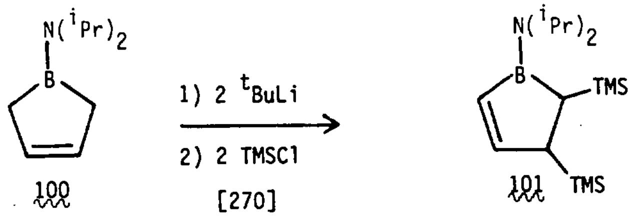
R = $^nC_5H_{11}$ (95%) E:Z 20:80



(273)

R = Pr 46%

R = $^nC_5H_{11}$ 52%



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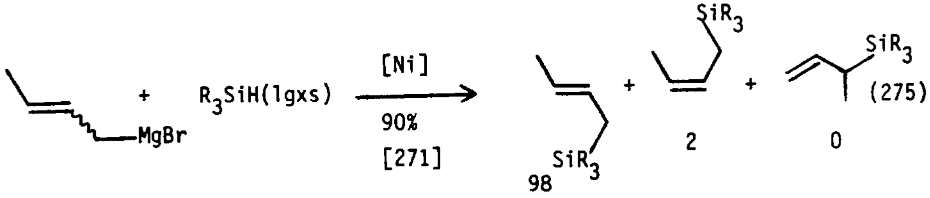
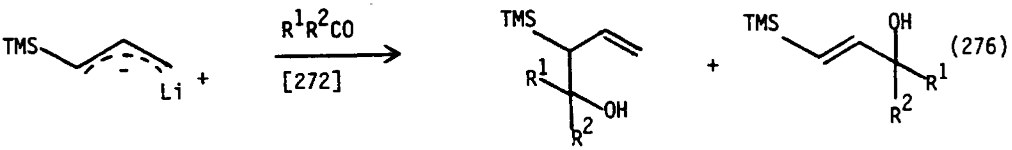


(275)

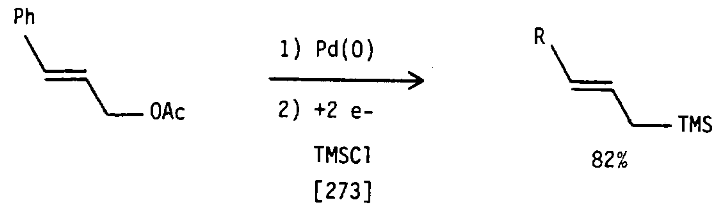
R_3Si = Ph_2MeSi; $PhMe_2Si$ [Ni] = $NiCl_2$(dppt) and others



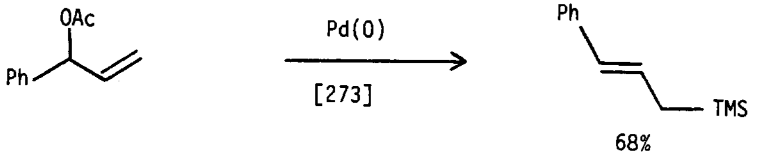
(276)

R^1	R^2	Et_3Al		
Pr	H	Yes	94	6
Pr	H	No	10	90
^{i}Pr	H	Yes	50	15
^{i}Pr	H	No	10	90
Ph	H	Yes	43	20
Ph	H	No	17	83
Ph	Me	Yes	24	76
Ph	Me	No	0	100

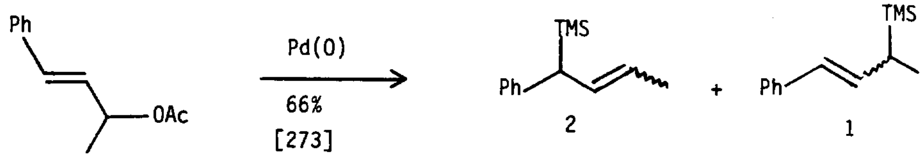
The palladium (0) catalyzed electroreductive silylation of allyl acetates has been achieved. (Eqns. 277-279)



(277)

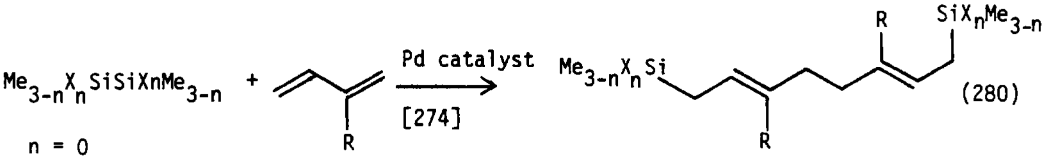


(278)



(279)

Disilanes have been coupled to 1,3-dienes to give allylsilanes. (Eqn. 280) Hexamethyldisilane can be coupled with allyl esters to give allylsilanes together with vinylsilanes. (Eqns. 281, 282) The Grignard reagent of 2-bromothiophene reacts with 2-bromo-3-trimethylsilylpropene to give the allylsilane **102**. (Eqn. 283)



(280)

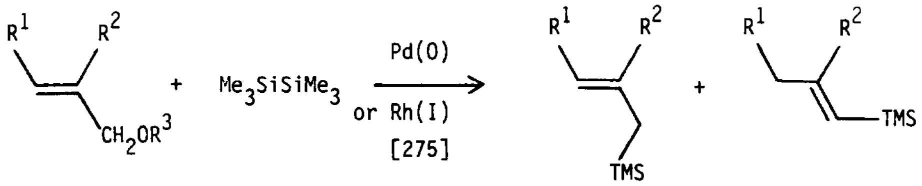
n = 0

n = 1 X = Cl, OMe

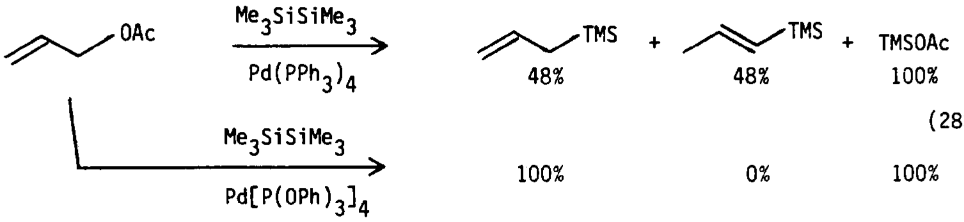
n = 2 X = Cl, OMe

R = H, Me

0-87% under a variety of conditions



(281)



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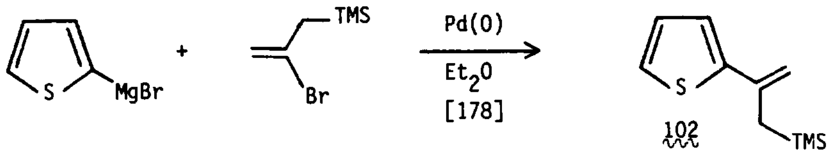
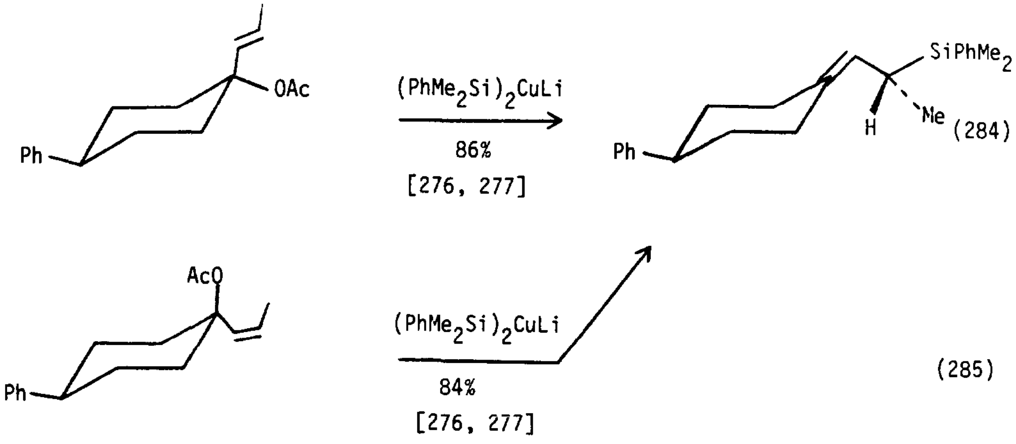


102

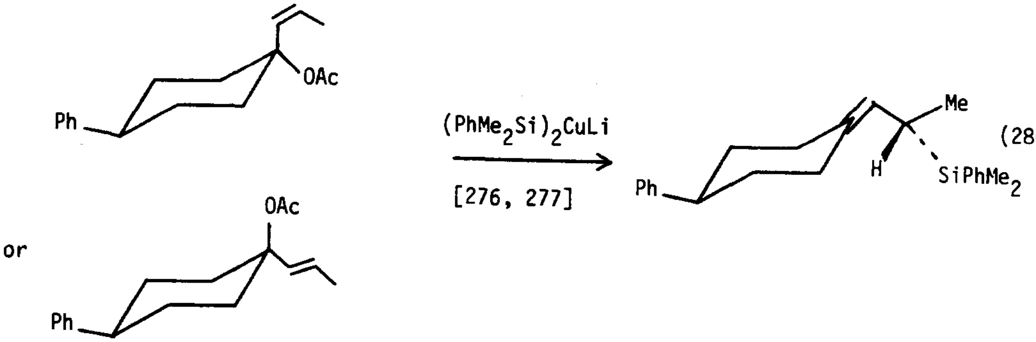
(283)

The reaction of silylmetallic reagents with suitable allyl substrates produces allylsilanes. Lithium bis(phenyldimethylsilyl) cuprate reacts with allyl acetates to give allylsilanes with double bond transposition. (Eqns. 284-286) The reaction is stereospecific. Trimethylsilyllithium reacts with allyl chlorides and bromides to give allylsilanes. (Eqns. 287, 288) In a like manner phenyldimethylsilyllithium reacts with 3-chlorocyclohexenes. (Eqns. 289-291) The reaction occurs with double bond transposition and stereospecifically. (Eqn. 291) The addition of cuprous iodide enhances the substitution. The chiral naphthyl-oxazoline **103** reacts with trimethylsilyllithium to give the chiral 1,2-dihydronaphthalene **104**, which can be converted to aldehyde **105**. (Eqn. 292)

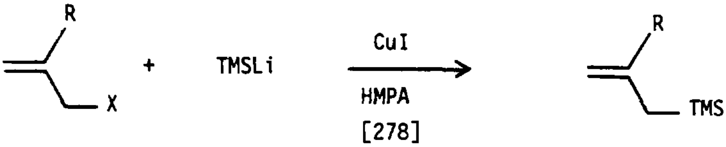


(284)

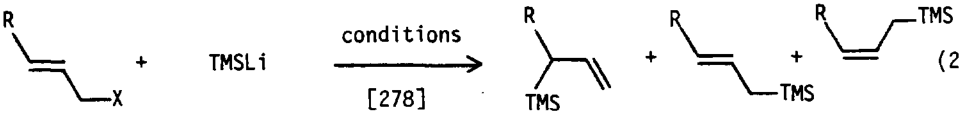
(285)



(286)



(287)



(288)

Table X: Conversion of Allylic Halides to Allyl Trimethylsilanes According to Eqn. 288.

Entry	Compound	Reagent	Solvent	Temp.	Product 3:4:5[c]	Yield[d]
1	1a	$(CH_3)_3SiLi$ + CuI[a]	HMPA	7-25°	87:13:0	80%
2	2a	$(CH_3)_3SiLi$ + CuI[a]	HMPA	7-25°	60:13:27	80%
3	1a	$(CH_3)_3SiLi$ + CuI[a]	HMPA-ether[b]	-60°	98:2:0	87%
4	2a	$(CH_3)_3SiLi$ + CuI[a]	HMPA-ether[b]	-60°	77:5:18	79%
5	1a	$(CH_3)_3SiLi$	HMPA-ether[b]	-60°	4a only	78%
6	2a	$(CH_3)_3SiLi$	HMPA-ether[b]	-60°	4a only	76%
7	1b	$(CH_3)_3SiLi$ + CuI[a]	HMPA-ether[b]	-60°	94:6:0	80%
8	2b	$(CH_3)_3SiLi$ + CuI[a]	HMPA-ether[b]	-60°	68:32:0	97%
9	2b	$(CH_3)_3SiLi$	HMPA-ether[b]	-60°	30:68:2	38%

[a] **Copper (I) iodide was added to the reaction mixture as a solution in dimethyl sulfide.**

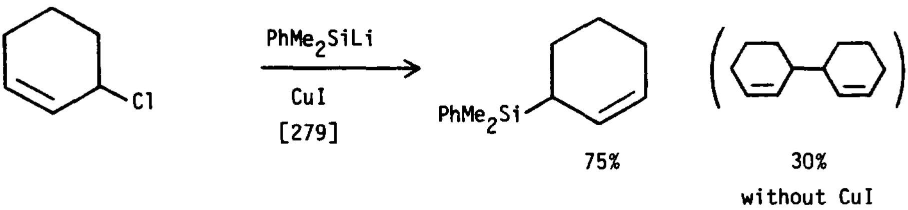
[b] **The solution was approximately 25% HMPA in ether.**

[c] **Ratios were determined by gas chromatography using an OV-17 column at 110°.**

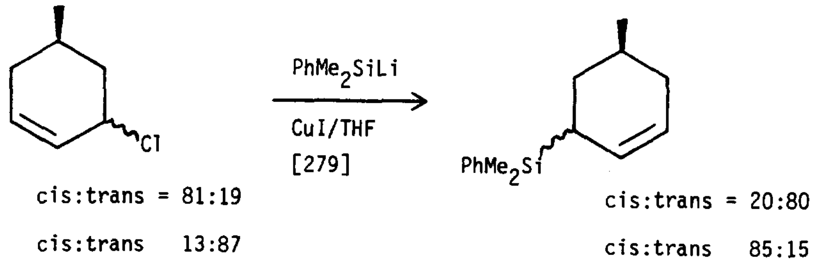
[d] **Yields refer to isolated products purified by distillation or column chromatography.**

Reprinted from Synth. Commun. 13, 778 (1983), Smith, J.G., Quinn, N.R., Viswanathan, M. and Marcel Dekker, Inc., N.Y.

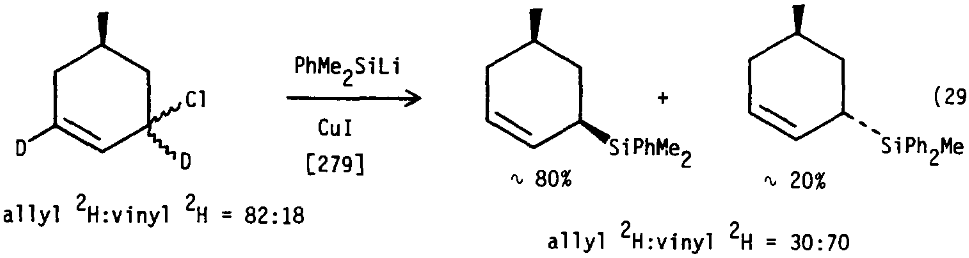
1a, R=C_6H_{13}, X=Cl; 2a, R=C_6H_{13}, X=Br; 1b, R=Ph, X=Cl; 2b, R=Ph, X=Br.



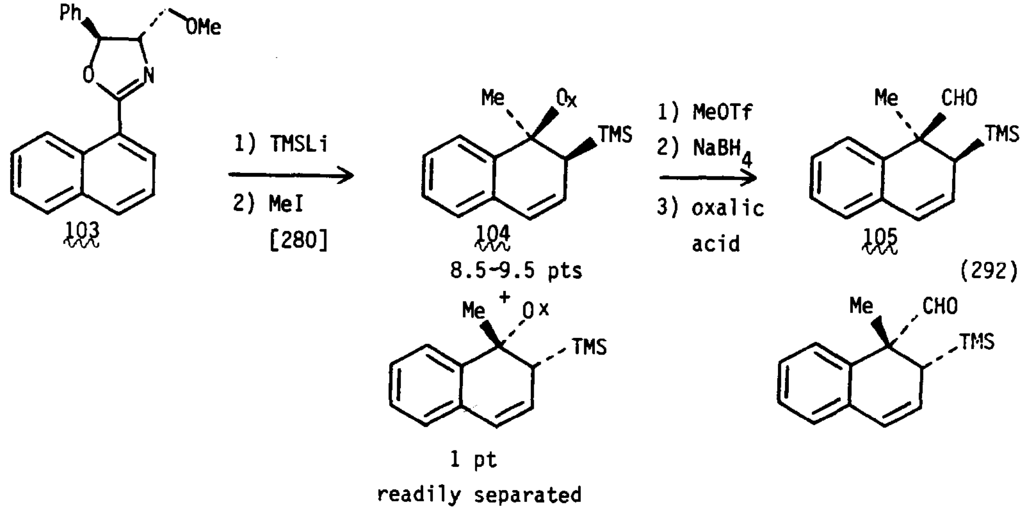
(289)


PhMe$_2$SiLi
CuI/THF
[279]
Cl
PhMe$_2$Si
cis:trans = 81:19
cis:trans 13:87
cis:trans = 20:80
cis:trans 85:15

(290)

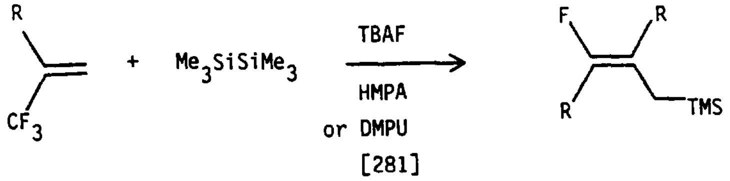

Cl
D
D
PhMe$_2$SiLi
CuI
[279]
SiPhMe$_2$
+
SiPh$_2$Me
~ 80%
~ 20%
allyl ^{2}H:vinyl ^{2}H = 82:18
allyl ^{2}H:vinyl ^{2}H = 30:70

(291)

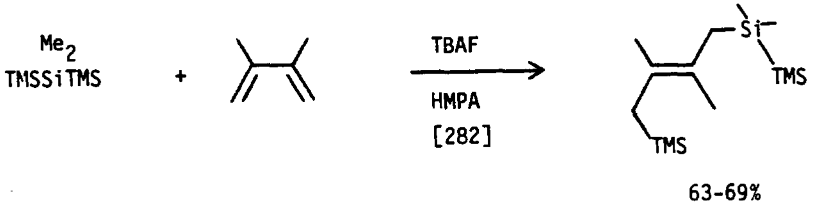

Ph
OMe
O
N
103
1) TMSLi
2) MeI
[280]
Me
Ox
TMS
104
8.5–9.5 pts
+
1) MeOTf
2) NaBH$_4$
3) oxalic acid
Me
CHO
TMS
105
1 pt
readily separated

(292)

An "in situ" form of the trimethylsilyl anion can be generated from disilanes or trisilanes. Thus hexamethyldisilane reacts with trifluoromethylethylenes in the presence of fluoride ion to give 1,1-difluoroallylsilanes. (Eqn. 293) Octamethyltrisilane reacts with 1,3-dienes in the presence of fluoride ion to give allylsilanes. (Eqn. 294)

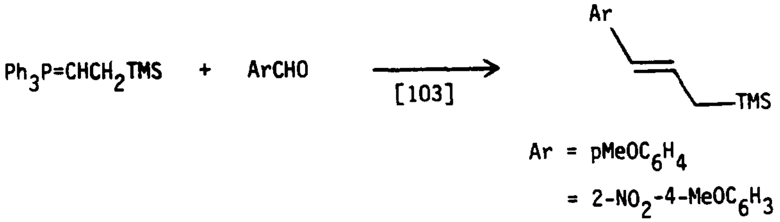


(293)

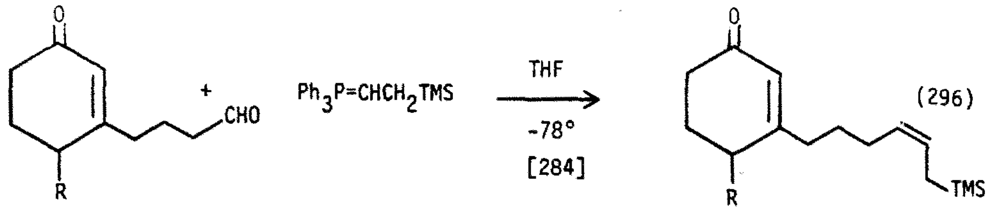


(294)

The ylid of (2-trimethylsilyl)triphenylphosphonium bromide (Seyferth's Reagent) was reacted with aromatic aldehydes to give allylsilanes. (Eqn. 295) This same reagent was reacted with an aliphatic aldehyde in the presence of a ketone. (Eqn. 296)

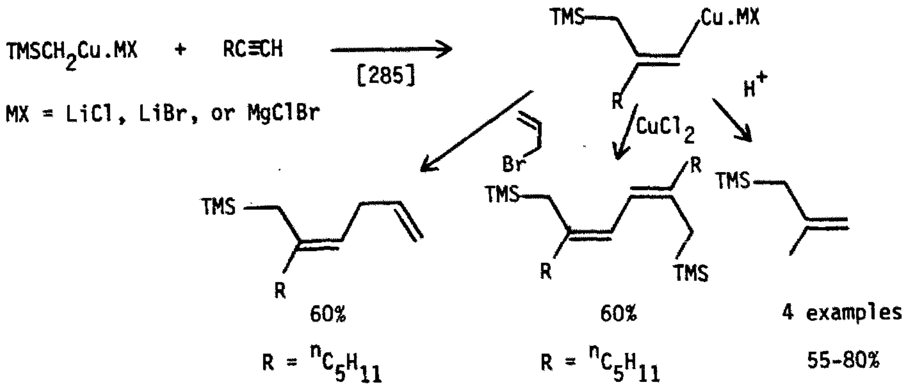


(295)

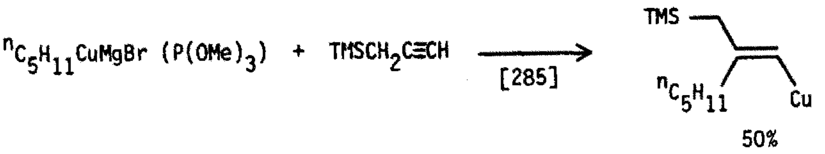


(296)

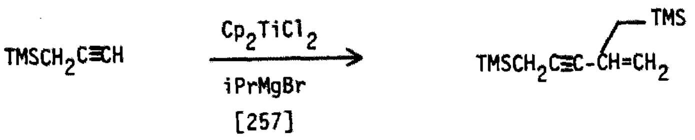
Trimethylsilylmethylcopper reagents were added to terminal acetylenes to give 1-metallo allylsilanes, which are useful reagents for further elaboration. (Eqn. 297) The roles of the reagents and the stereochemistry can be reversed as seen in the reaction of pentylcopper to 3-trimethylsilylpropyne. (Eqn. 298) Propargyltrimethylsilane was dimerized according to Eqn. 299.



(297)



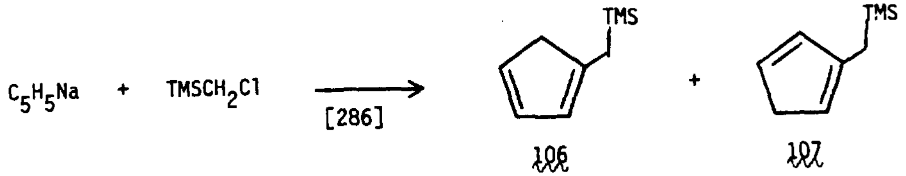
(298)



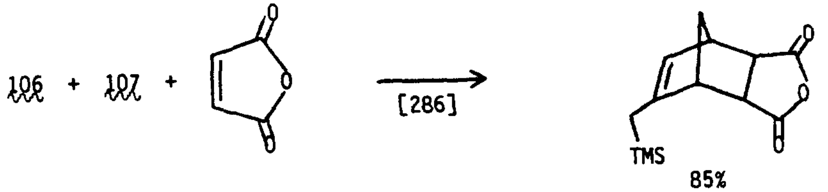
$$\mathrm{TMSCH_2C{\equiv}CH} \xrightarrow[\substack{\text{iPrMgBr}\\ [257]}]{\mathrm{Cp_2TiCl_2}} \mathrm{TMSCH_2C{\equiv}C\text{-}\overset{\text{TMS}}{C}H{=}CH_2}$$

(299)

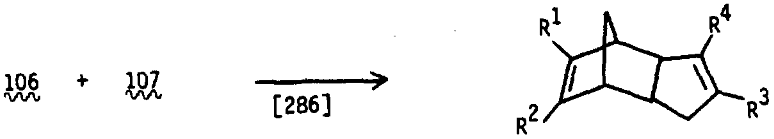
Cyclopentadienyl sodium reacts with chloromethyltrimethylsilane to give allylsilanes **106** and **107** in equal amounts. (Eqn. 300) These undergo Diels-Alder reactions and a thermal rearrangement. (Eqns. 301-303)



(300)



(301)

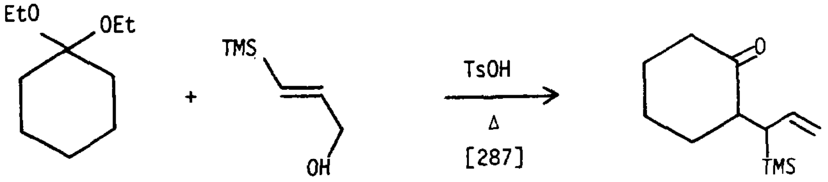


(302)

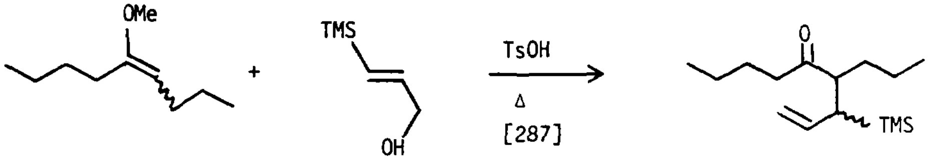
$R^1 = R^4 = H$; $R^2 = R^3 = CH_2TMS$
$R^1 = R^3 = CH_2TMS$; $R^2 = R^4 = H$
$R^1 = R^3 = H$; $R^2 = R^4 = CH_2TMS$
$R^1 = R^4 = CH_2TMS$; $R^2 = R^3 = H$

$$\underset{\sim\sim}{106} + \underset{\sim\sim}{107} \xrightarrow[[286]]{625°} \underset{30\%}{PhTMS} \qquad (303)$$

Trans-1-trimethylsilylpropenol reacts with ketals and enol ethers to produce keto allylsilanes. (Eqns. 304, 305)

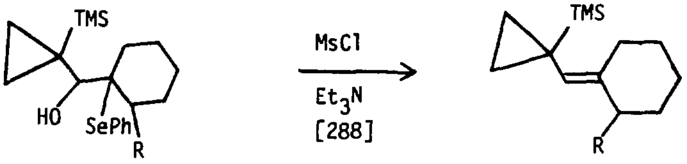


(304)



(305)

The α-hydroxyselenide **108** was eliminated to give allylsilane **109**. (Eqn. 306)



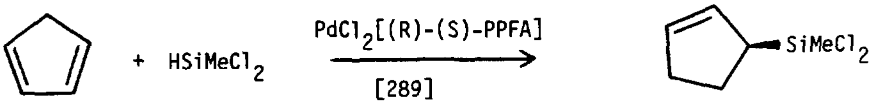
108

109

(306)

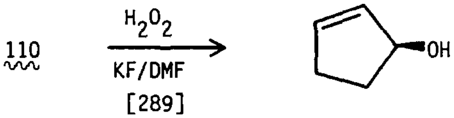
R = H, Me

Hydrosilylation of cyclopentadiene with an optically active palladium complex provided 3-silylcyclopentenes in optically active form. (Eqns. 307-309)

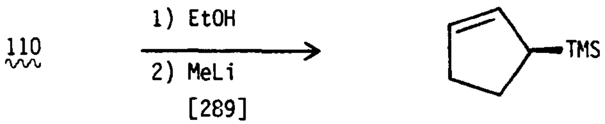


110 22-25% ee

(307)

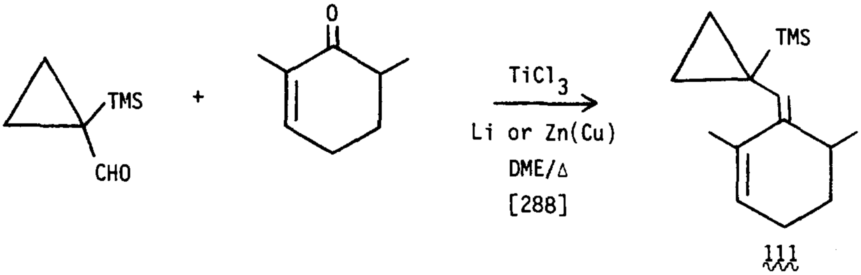


(308)

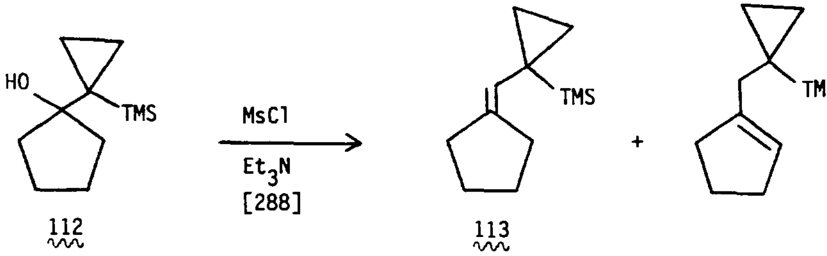


(309)

1-Trimethylsilylcyclopropyl carbaldehyde was reductively coupled with 2,6-dimethylcyclohexenone to give allylsilane **111**. (Eqn. 310) Elimination of β-hydroxysilane **112** gives allylsilane **113**. (Eqn. 311)



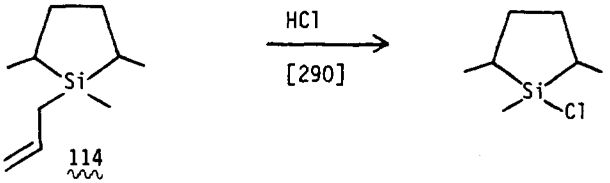
(310)



(311)

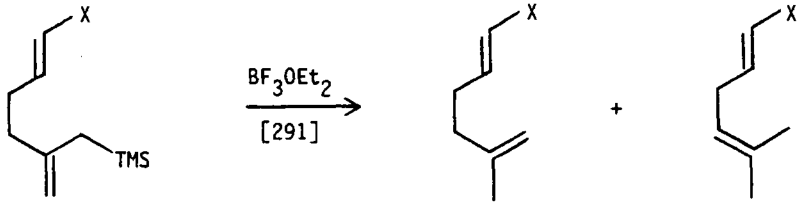
B. Reactions

The protiodesilylation of allylsilanes is a common reaction. This occurs with transposition of the double bond. The cleavage of allylsilane **114** with HCl occurs with inversion at silicon. (Eqn. 312) The cleavage with mercuric chloride proceeds with retention and with trifluoroacetic acid a mixture of retention and inversion is found. Protiodesilylation can be brought about by boron trifluoride as seen in Eqns. 313, 314. The trifluoroacetolysis of 3-methyl-but-2-enyltrimethylsilane indicates that the β-trimethylsilyl carbocation is favored over the tertiary carbocation. (Eqn. 315) The stereochemistry of the protiodesilylation has been investigated. It is predominantly anti. (Eqns. 316-318)



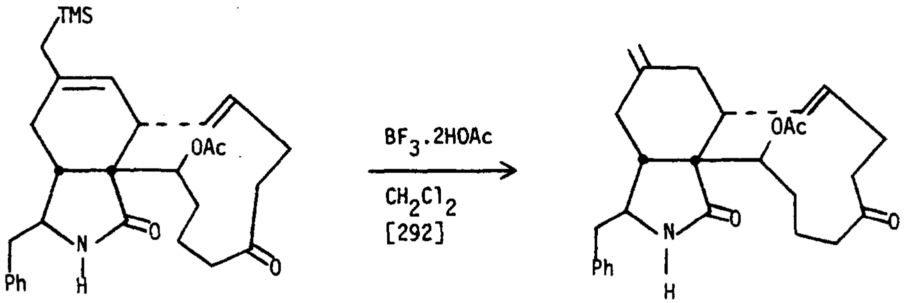
(312)

E,Z/Z,E : Z,Z : E,E gives E,Z/Z,E : E,E : Z,Z
54 15 31 54 16 30

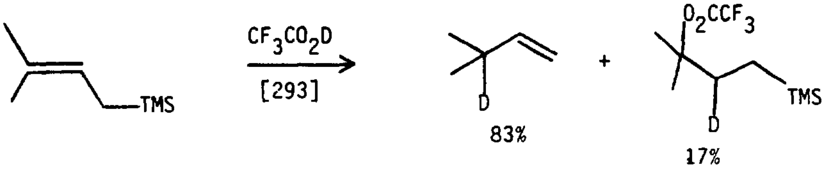


(313)

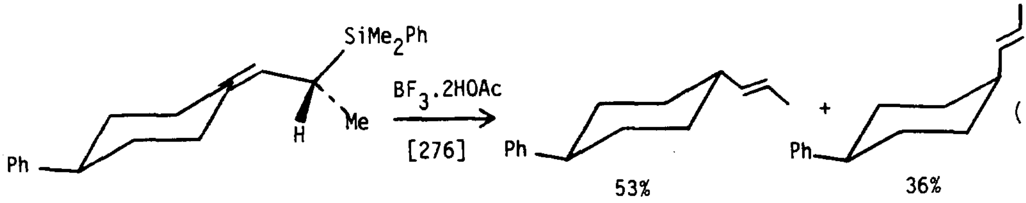
X = CO_2Bu, CN



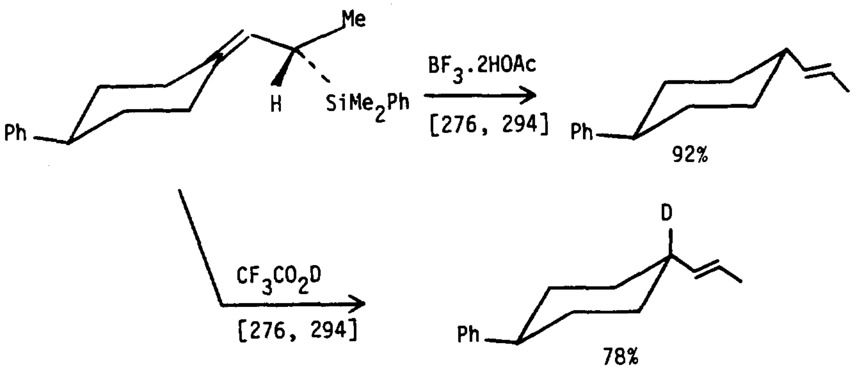
(314)



(315)



(316)

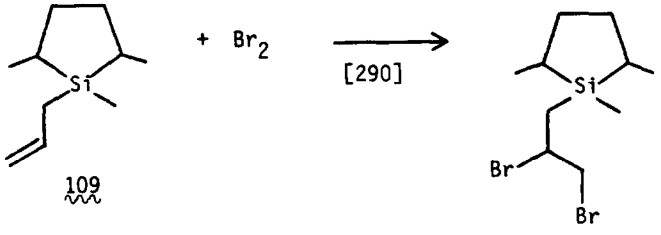


(317)

(318)

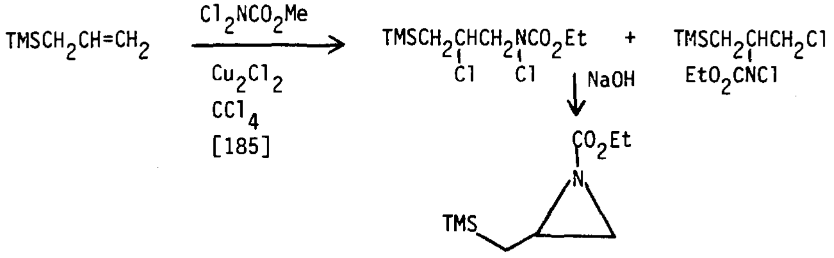
Hydrogenation of allyltrichlorosilane without reduction of the Si-Cl bond is possible. (Eqn. 319) Bromine adds without cleavage of the allyl-silicon bond. (Eqn. 320) Chloroamines add to allylsilanes and lead ultimately to aziridines. (Eqn. 321) Diallylsilane adds H_2S photolytically. (Eqn. 322) Elemental sulfur was added to silacyclopentene **115** to give the products shown. (Eqn. 323)

$$Cl_3SiCH_2CH{=}CH_2 \xrightarrow[\text{"Ni/SiH"}\ [183]]{H_2} Cl_3SiCH_2CH_2CH_3 \qquad (319)$$

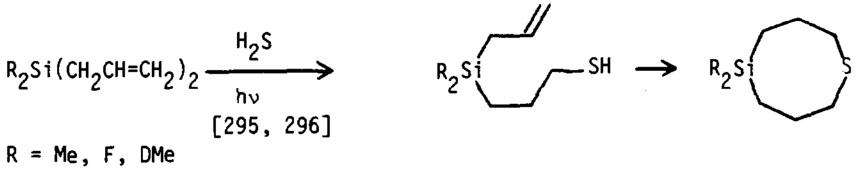


109

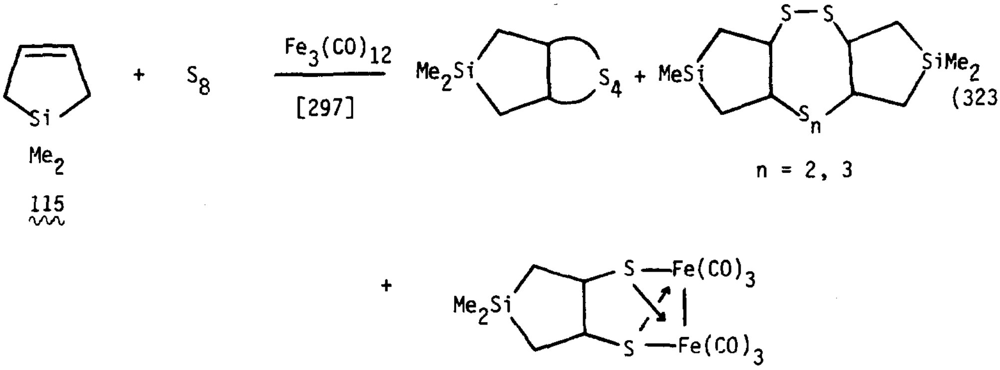
(320)



(321)

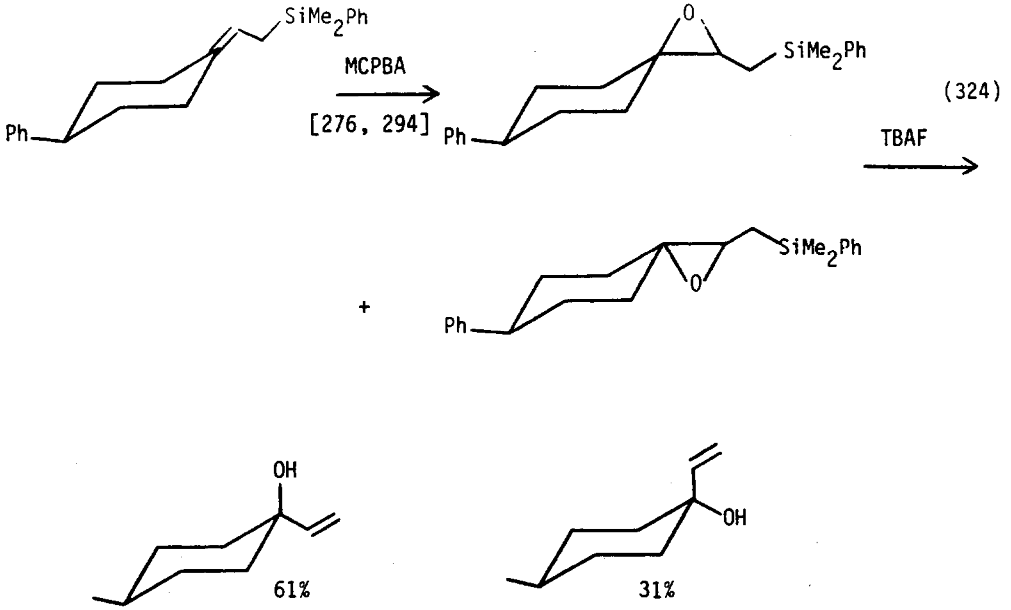


(322)

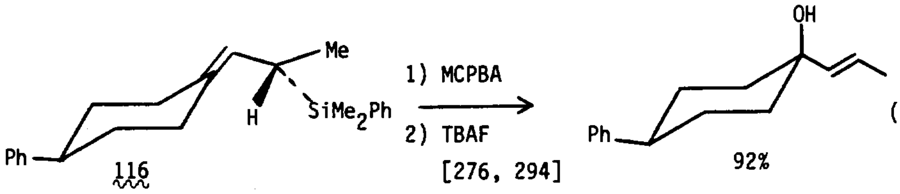


(323)

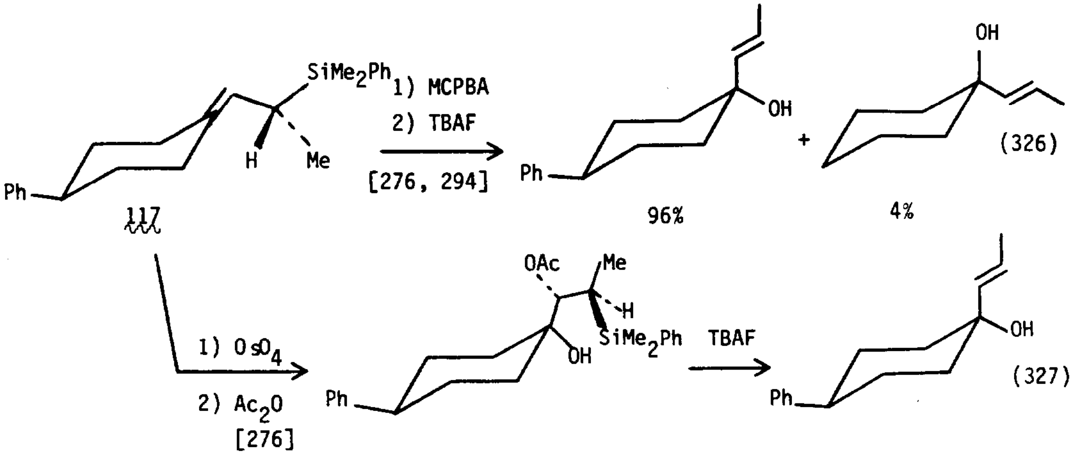
The stereochemistry of the epoxidation of some allylsilanes was studied. In the alkylidene cyclohexane series anti attack predominates (Eqns. 324, 325), but can he overridden by the allylsilyl group. (Eqn. 326). Similar results were observed in the osmylation reaction. (Eqns. 327, 328) Again the products were analyzed by fluoride-mediated elimination. The epoxidation of optically active allylsilanes has been studied (Eqn. 329-331) Anti attack was also demonstrated in the acyclic system.



(324)

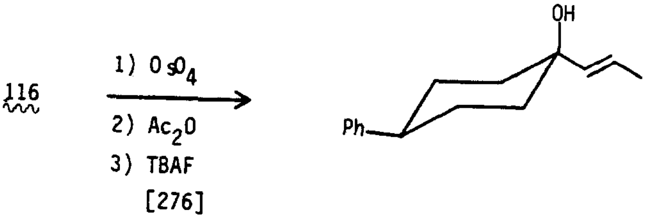


(325)

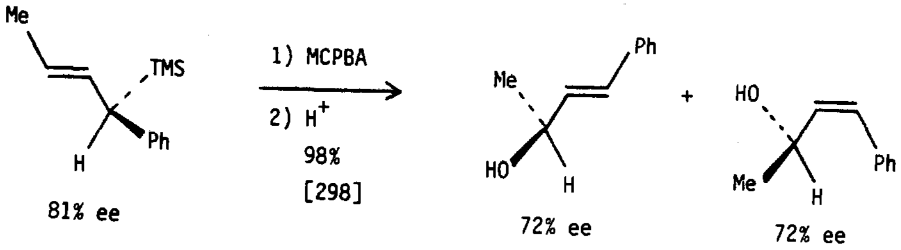


(326)

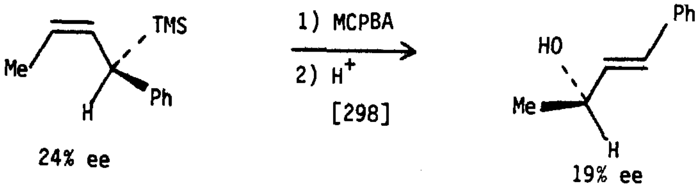
(327)



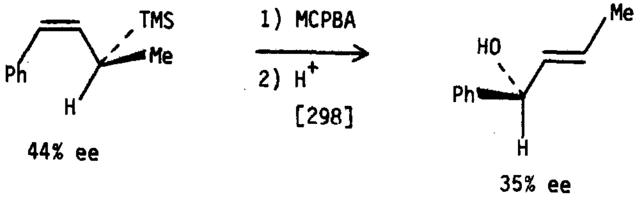
(328)



(329)

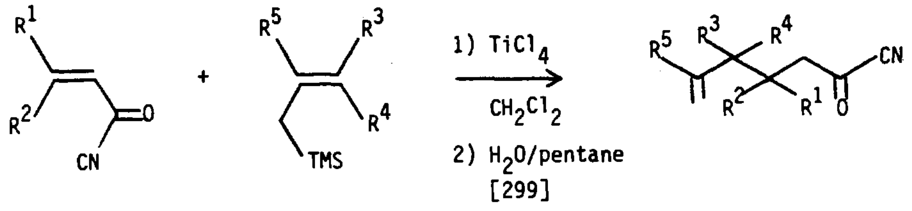


(330)



(331)

Lewis acid catalyzed electrophilic reactions of allylsilanes continue to be highly useful synthetically. The reaction of allylsilanes with α,β-unsaturated acyl nitrides gives α,β-unsaturated acylnitriles via a Michael addition. (Eqn. 332) The acylation of **116** and **117** gave a mixture of products. (Eqns. 333, 334) The allylation of β thiophenyl chlorides with allyltrimethylsilane takes place with stereospecific displacement of the chlorine. (Eqn. 335) Benzylmethyl ethers and benzyl chlorides were allylated with allylsilanes. (Eqn. 336) Chloromethylpropargyl ethers were allylated. (Eqn. 337) A series of α-trimethylsilyl-α, β- unsaturated esters were used to prepare γ-substituted α,β-unsaturated esters as shown in the example in Eqn. 338. The results are given in Tables XII and XIII. The bis-silylated diene **118** was reacted with acetaldehyde. (Eqn. 339) The product of this reaction was converted to racemic muscone. Ketones can be converted to ketals with silyl ethers in the presence of iodotrimethylsilane. If allyltrimethylsilane is added to the reaction mixture, direct allylation occurs. (Eqn. 340) The same transformation is possible employing alcohols, allyltrimethylsilane and iodine. (Eqns. 341, 342)



(332)

with :

$R^1 = CH_3,\ R^3 = CH_2Si(CH_3)_3,\ R^2 = R^4 = R^5 = H$ **a**

$R^1 = R^5 = CH_3,\ R^2 = R^3 = R^4 = H$..............**b**

$R^1 = R^2 = R^5 = CH_3,\ R^3 = R^4 = H$ ....**c**

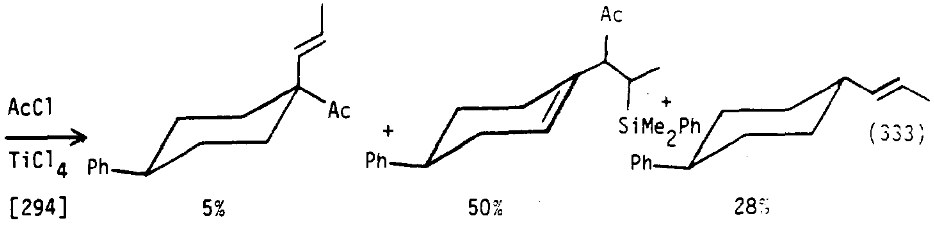
$R^1 = R^5 = CH_3,\ R^3 = CH_2Si(CH_3)_3,\ R^2 = R^4 = H$ **d**

$R^1 = R^2 = R^5 = CH_3,\ R^3 = CH_2Si(CH_3)_3,\ R^4 = H$ **e**

$R^1 = R^4 = R^5 = CH_3,\ R^3 = CH_2Si(CH_3)_3,\ R^2 = H$ **f**

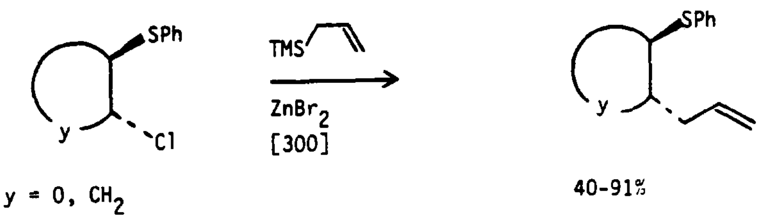
$R^1 = R^2 = R^4 = R^5 = CH_3,\ R^3 = CH_2Si(CH_3)_3$....**g**

$\underset{\sim}{116}$ (Eqn. 325)



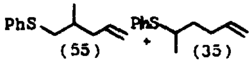
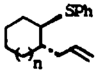
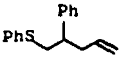
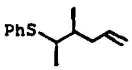
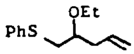
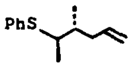
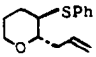
(333)

$\underset{\sim}{116} \xrightarrow{\text{AcCl}}$ 15% 32% 16% (334)



(335)

Table XI: Allylation According to Eqn. 335.

Entry	Alkene	Adduct (% yield^a)	Entry	Alkene	Adduct (yield^a)
1		n = 0 (91)	6^c		 (55) + (35)
2		n = 1  (78)^b	7		 (74)
3		n = 2 (50)	8		 (85)
4		 (92)	9		 (83)
5		 (40)	10		 (73)^b

^{a}Yields refer to isolated products thoughout. $^b J_{viz}$ 11-12 Hz. ^{c}Reaction conditions: 70°C, 16 h.

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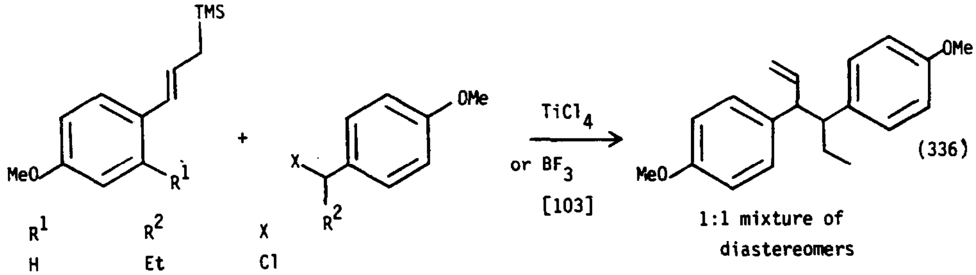
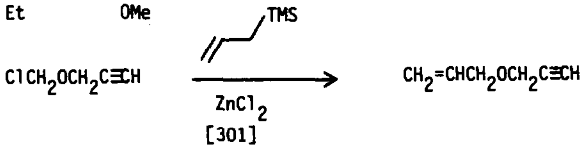
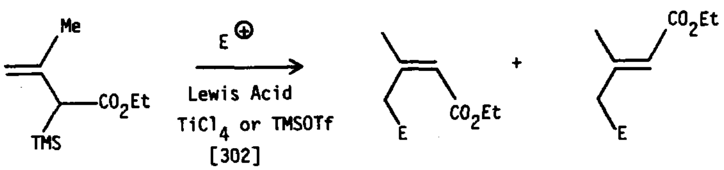


R^1	R^2	X
H	Et	Cl
H	Et	OMe
NO_2	Me	OMe
NO_2	Et	OMe

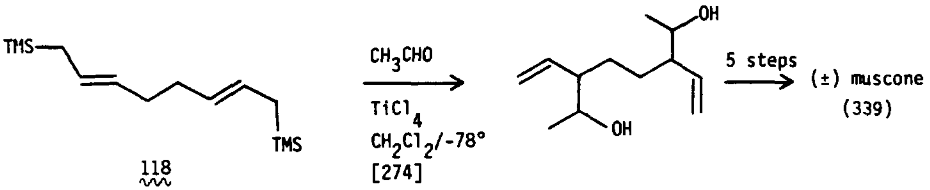
(336)



(337)

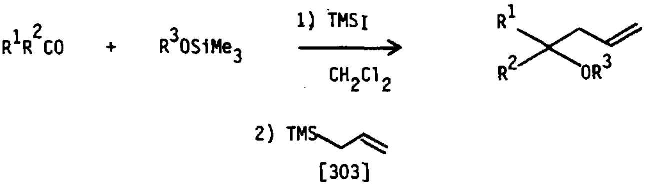


(338)



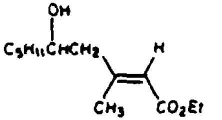
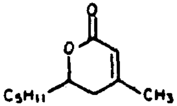
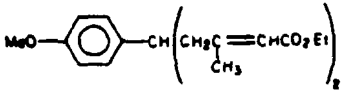
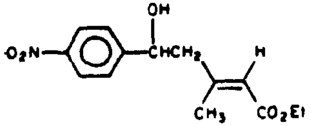
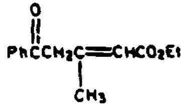
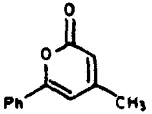
118

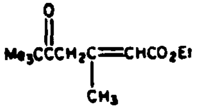
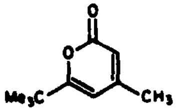
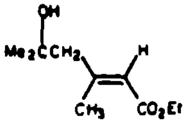
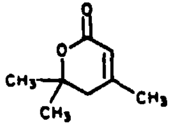
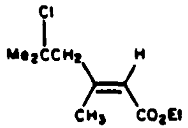
(339)



(340)

Table XII: Reaction of 117a with Carbonyl Compounds in the Presence of $TiCl_4$ According to Eqn. 338.[a]

entry	electrophile	temp, °C, time		products (ratio)[b]	yield, % (crude, purified)[c]
1	$C_5H_{11}CHO$	−78, 12 h, −30, 3 h	21	 (92)	86, 22[d]
			22	 (8)	
2	*p*-$MeOC_6H_4CHO$	−78, 24 h	23	 (*E*,*E*:*E*,*Z* = 82:18)	72, *e*
3	*p*-$O_2NC_6H_4CHO$	−78, 16 h	24	 (*E* = >95)[f]	89, 65
4	PhCOCl	room temp, 33 h	25	 (28)[g]	~100, 49
			26	 (72)	

5	Me$_3$CCOCl	room temp, 23 h	27	 $\mathrm{Me_3C\overset{O}{\overset{\|}{C}}CH_2\underset{CH_3}{\underset{\mid}{C}}{=}CHCO_2Et}$	(82)[g]	86, 58
			28		(18)	
6	(CH$_3$)$_2$CO	room temp, 24 h	29		(76)	71, *e*
			30		(10)	
			31		(14)	

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[a] In a typical procedure 1.1 equiv of an electrophile is added to a solution of TiCl$_4$ (0.181 mL, 1.65 mmol, 1.1 equiv) in 2 mL of CH$_2$Cl$_2$ at -78 °C, followed by a solution of 7 (301 mg, 1.5 mmol, 1.0 equiv) in 2 mL of CH$_2$Cl$_2$. The reaction was stirred at -78 °C for 15 min and then stirred under the conditions stated in the table. [b] Determined by GLC before purification. [c] Sum of yields of all components after isolation by chromatography. [d] No attempt was made to maximize yield. [e] Not determined. [f] Only one isomer detected by ^{1}H NMR. [g] Mixture of isomers contained a nonseparable, unidentified component.

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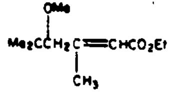
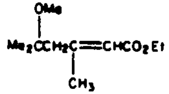
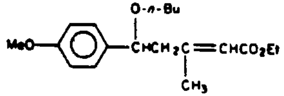
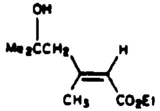
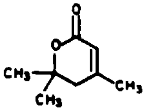
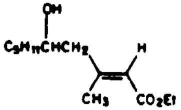
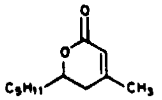
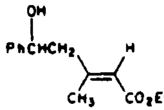
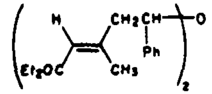
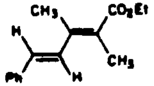
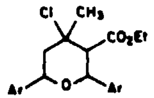
Table XIII: Reaction of 117a with Electrophiles Promoted by Various Lewis Acids According to Eqn. 338.

entry	electrophile	Lewis acid	temp, °C, time	products (ratio)	yield, % (crude, purified)[b]
1	$Me_2C(OMe)_2$	$TiCl_4$	−78, 22 h, 0, 9 h	**32**  $Me_2C(OMe)CH_2C(CH_3)=CHCO_2Et$ (*E*:*Z* = 91:9)[c]	~100,[d] *e*
2	$Me_2C(OMe)_2$	Me_3SiOTf	−78, 26 h	**32**  $Me_2C(OMe)CH_2C(CH_3)=CHCO_2Et$ (*E*:*Z* = 86:14)[c]	~100, 83
3	*p*-$MeOC_6H_4CH(O\text{-}n\text{-}Bu)_2$	Me_3SiOTf	−78, 2 h	**33**  (*E*:*Z* = 97:3)[c]	~100, 81
4	$(CH_3)_2CO$	TiF_4	−32, 5 h, 0, 5 h, room temp, 15.5 h	**29** 	16, *c*
				30 	
5	$C_5H_{11}CHO$	TiF_4	−78, 5 h, room temp, 22 h	**21**  (84)[f]	88, 31[g]

				22		(16)[f]	
6	PhCHO	TiF_4	−78, 90 min, −32, 90 min, room temp, 7 h	34		(19)[f]	~100, 83
				35		(77)[f]	
				36		(4)[f]	
7	p-$O_2NC_6H_4CHO$	$FeCl_3$	−78, 4 h, room temp, 13.5 h	37			~100, 86[h]

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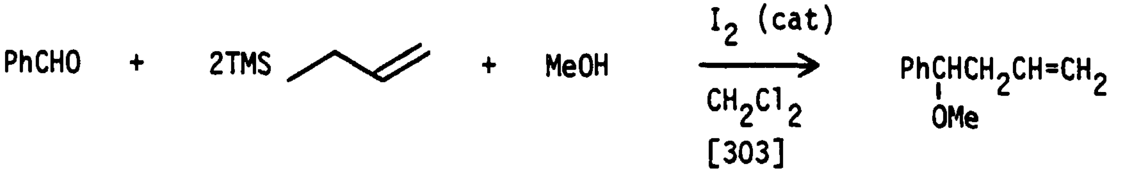
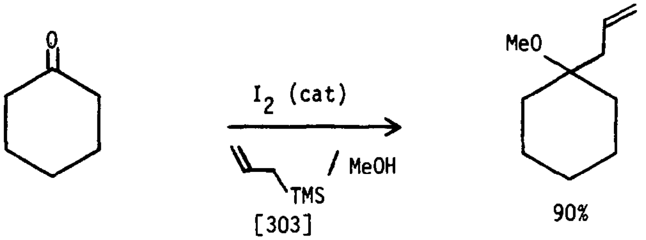
[a] For a typical reaction see footnote a of Table I, with $TiCl_4$, Me_3SiOTf (17 mg, 0.05 equiv), or TiF_4 (204 mg, 1.1 equiv) as promoter. [b] Sum of yields of all components after isolation by chromatography. [c] Determined by GLC before purification. [d] Crude material contained starting material and other unidentifiable components. [e] Not determined. [f] Ratio of isolated yields. [g] Another major component was isolated but could not be identified. [h] Mixture of diastereomers.

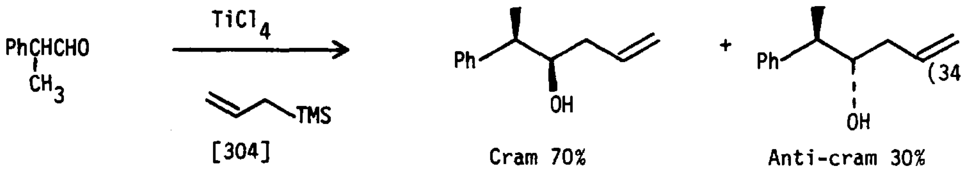


$$PhCHO + 2TMS\text{(allyl)} + MeOH \xrightarrow[CH_2Cl_2\ [303]]{I_2\ (cat)} PhCH(OMe)CH_2CH{=}CH_2 \qquad (341)$$

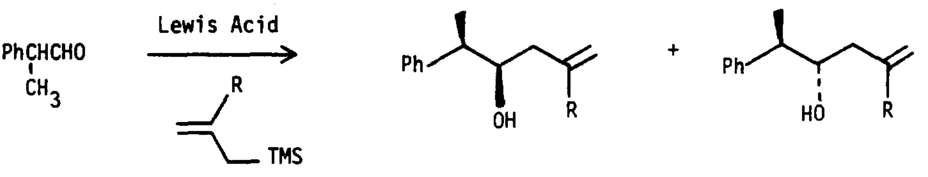


(342)

The diastereoselectivity of the allyltrimethyslsilyl allylation of several aldehydes has been studied. The allylation of 2-phenylpropanal gives predominantly Cram attack. (Eqn. 343) The diastereoselectivity of the allylation of a number of chiral aldehydes was studied. A representative sampling is given in Eqns. 344-347. A chelate effect is argued for the enhanced diastereoselectivity in the benzyloxy systems. (Eqn. 345-347) Chiral β-benzyloxy aldehydes were allylated with allyltrimethylsilane. (Eqn. 348) The diastereoselectivity in this reaction is opposite to that shown in Eqn. 347. The allylation of optically active 1,3-dioxolane-4-ones to give optically active homoallylic esters was reported. (Eqn. 349) Optically active allylsilane 119 reacts with pivaldehyde (Eqn. 350) and ethylene oxide (Eqn. 351) to give the optically active products indicated.



(343)

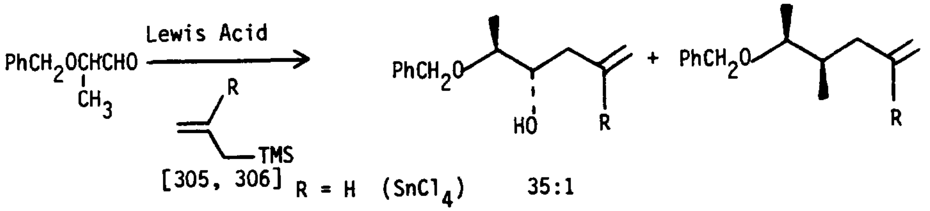


(344)

[305]

R = H 1.3 - 2.2:1

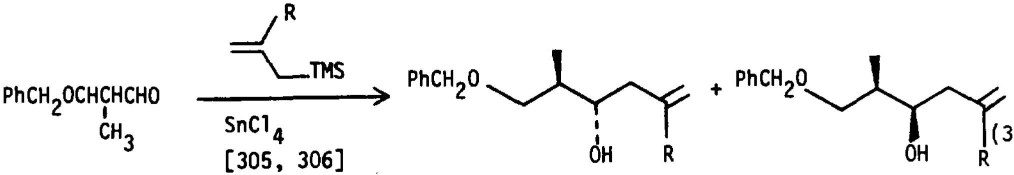
R = Me 1.3 - 7:1



(345)

R = H (SnCl$_4$) 35:1

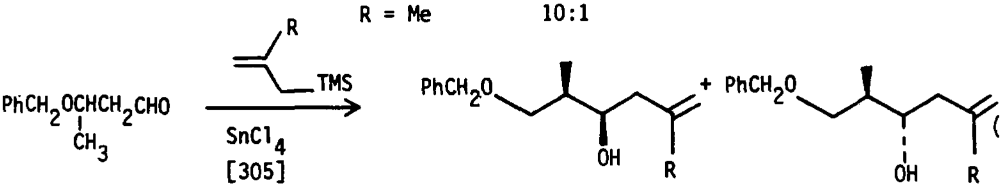
R = Me (SnCl$_4$) 45:1



(346)

R = H 12:1

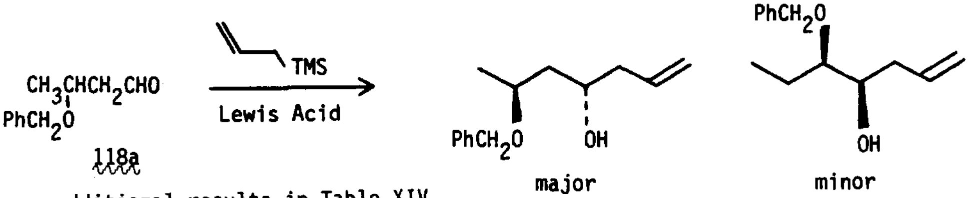
R = Me 10:1



(347)

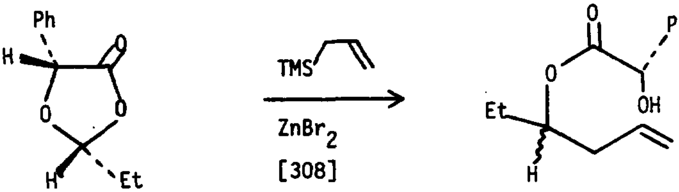
R = H 9:1

R = Me 7:1



(348)

see additional results in Table XIV



(349)

72% (S)

28% (R)

Table XIV: Reaction of 118a with Allyltrimethylsilane and Various Lewis Acids According to Eqn. 348.

Lewis acid	Temp. of Lewis acid addn. (°C)	Temp. of reaction (°C)	Solvent	Time (h)	2 : 3
$TiCl_4$	-78	-78	CH_2Cl_2	2	95 : 5
$SnCl_4$	-78	-78	CH_2Cl_2	2	95 : 5
$BF_3 \cdot OEt_2$	-78	-78	CH_2Cl_2	2	85 : 15
$BF_3 \cdot OEt_2$	-78	-78	THF	2	--[b)]
2 BF_3 (g)[c)]	-78	-78	CH_2Cl_2	2	91 : 9
$AlCl_3$[d)]	-78	-78	CH_2Cl_2	2	--[b)]
$AlCl_3$[d)]	+22	-78	CH_2Cl_2	2	--[e)]
$AlCl_3$[f)]	-76	-78	CH_2Cl_2	2	89 : 11
$ZnCl_2$[d)]	-78	-78	CH_2Cl_2	2	--[b)]
$ZnCl_2$[d)]	+22	+22	CH_2Cl_2	2	--[b)]
$SbCl_5$[g)]	-78	-78	CH_2Cl_2	2	--[e)]
$SbCl_5$[g)]	-100	-100	CH_2Cl_2	0.25	--[e)]
$SnCl_2$[h)]	+22	+22	CH_2Cl_2	2	--[b)]

a) Ratio of Lewis acid to 1 was 1:1, except as stated; time for complexation: ~10 min; conversion to 2/3 >85%, except as stated.

b) No reaction.

c) BF_3 gas was bubbled through solution of 1 at -78 °C for 10 min., i.e., probably two BF_3 molecules attached to 1.

d) Much of Lewis acid did not dissolve.

e) Extensive decomposition of substrate.

f) Time for complexation : 2 h ; much of $AlCl_3$ dissolved, but solution was somewhat cloudy.

g) Time for complexation: 1 minute.

h) Time for complexation: 2 h; solution was still very milky.

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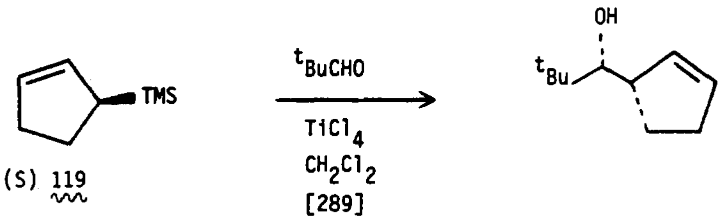
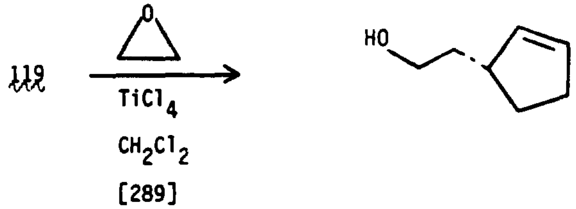
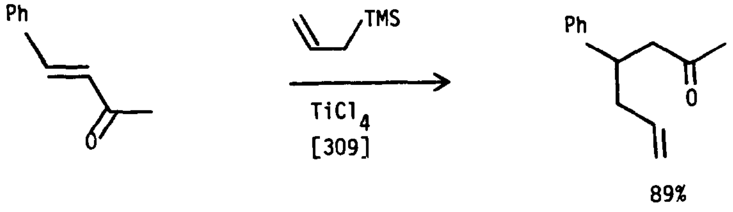


(350)

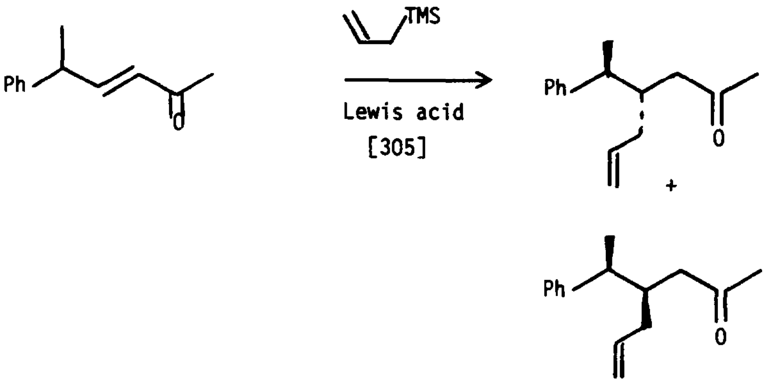


(351)

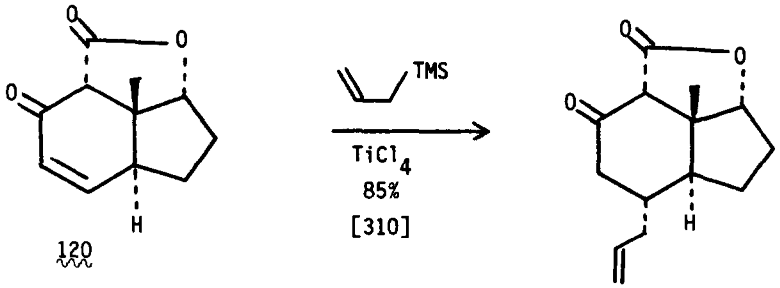
The conjugative allylation of αβ-unsaturated ketones by allylsilanes has been studied. (Eqns. 352-354) When Lewis acid catalyzed the reaction proceeds well with ketones but poorly with esters, nitriles and amides. (Eqn. 352) The reaction is only moderately diastereoselective. (Eqn. 353) The allylation of cyclohexanone **120** was used in an approach to prostanoid and corticosteroid synthons. (Eqn. 354)



(352)



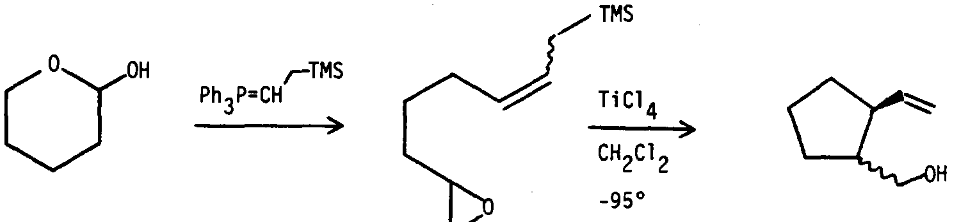
(353)



120

(354)

Several cyclizations employing the intramolecular allylation via allylsilanes have been reported. (Eqns. 355-257) Thus, treatment of epoxide **121** with titanium tetrachloride results in a five-exo-tet cyclization to give the cyclopentanes **122** and **123**. (Eqn. 355) Cyclohexenone **124** gives the spiro [4.5] decanone **125** in a five-endo-trig process. (Eqn. 356) The stereochemistry of cyclization of allylsilane **126** was studied. (Eqn. 357)



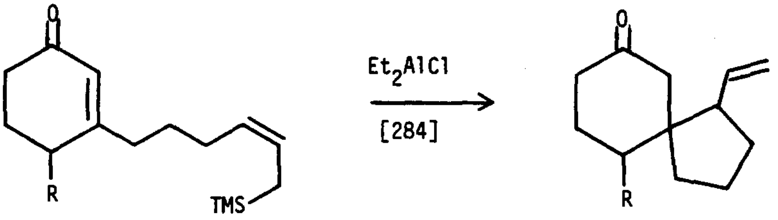
55% [311]

121

cis 122 4 pts

trans 123 1 pt

(355)

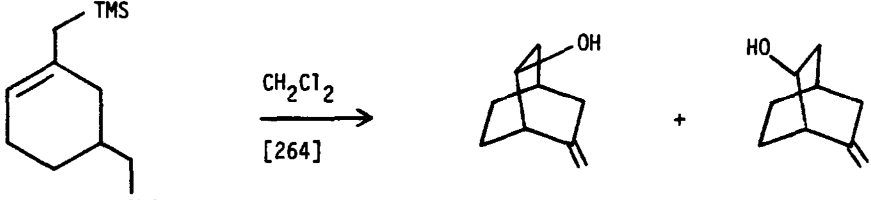


124

125

R = H, Me

(356)

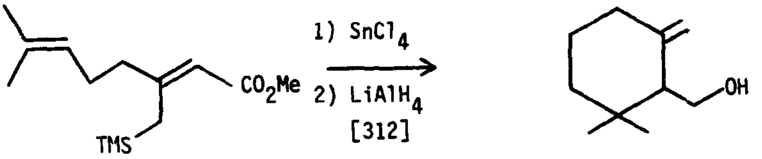


126

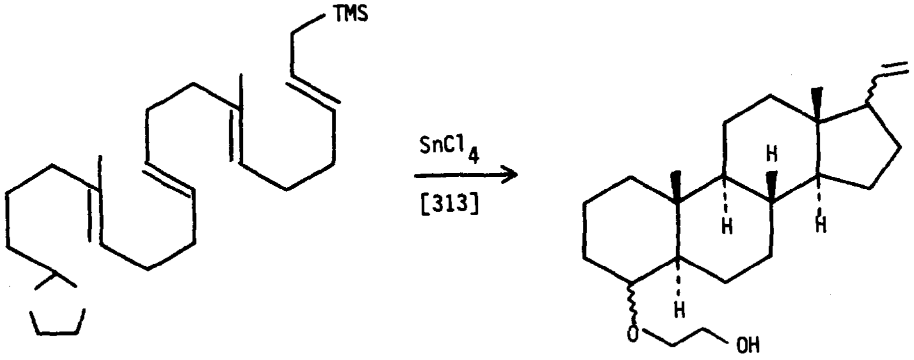
(357)

Catalyst		
SnCl$_4$	49	51
Et$_2$AlCl	66	34
FeCl$_3$	70	30
AlCl$_3$	79	21
BF$_3$OEt$_2$	80	20
TBAF/THF	30	70

Under acid conditions the product from a synclinal transition state is favored. The fluoride-mediated reaction gives the anti product as a result of an antiperiplanar transition state. The intramolecular cyclization with olefins is also possible. (Eqns. 358, 359)

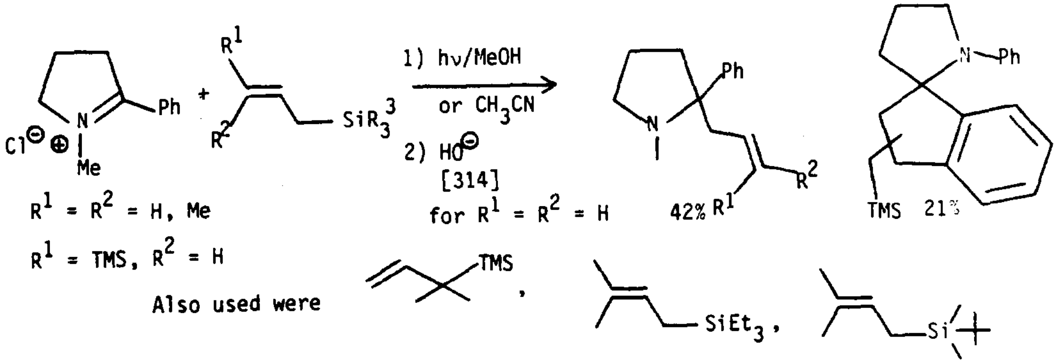


(358)

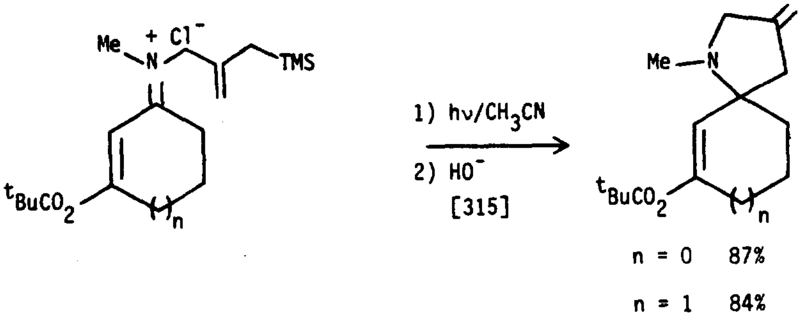


(359)

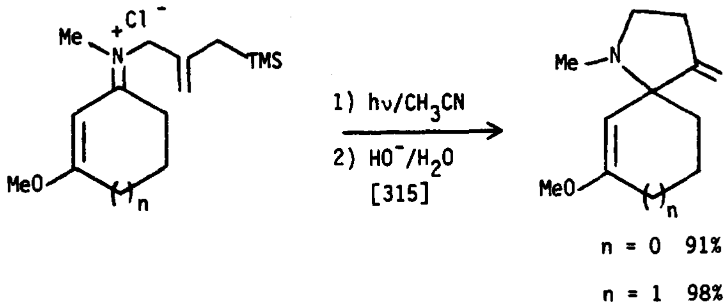
Allylsilanes react with iminium salts upon photolysis to give homoallyl amines. (Eqn. 360) The reaction can also be carried out intramolecularly. (Eqns. 361, 362)



(360)

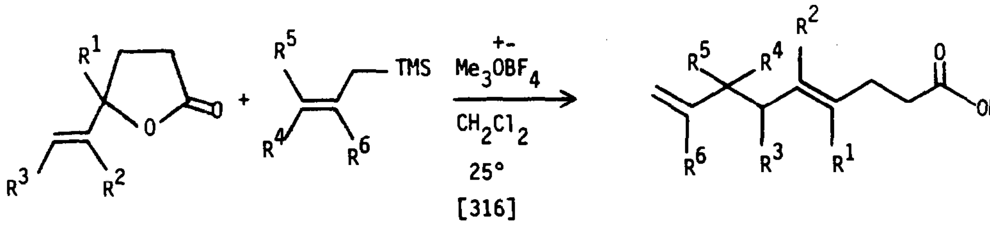


(361)

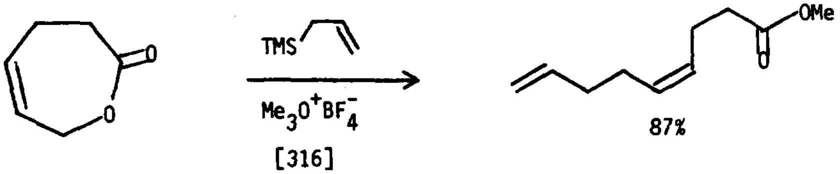


(362)

The fluoride-induced reaction of allylsilanes with electrophiles constitutes an increasingly useful synthetic method for nucleophilic allylation. Examples are shown in Eqns. 363-374. Trimethyloxonium tetrafluoroborate brings about the reaction of allylsilanes with lactones. The reaction can be done in an S_N2' (Eqn. 363) or S_N2 (Eqn. 364) fashion.

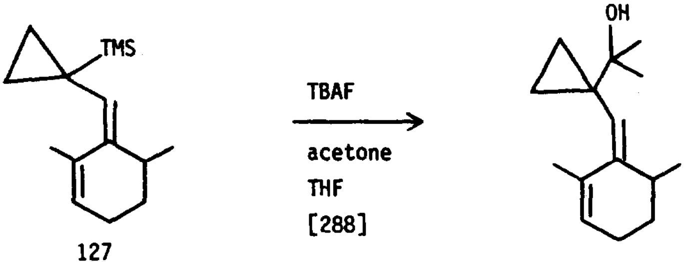


(363)



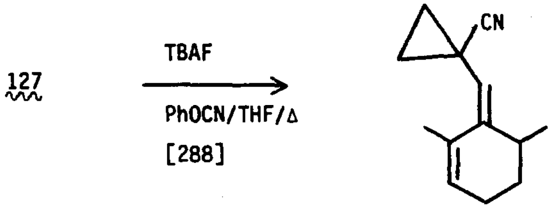
(364)

The allylsilane **127** reacts with acetone and phenylisocyanate under the inducement of fluoride ion. (Eqns. 365, 366) The fluoride-induced reaction of 1, 3-bistrimethylsilylpropane with aldehydes and ketones gives homoallylic alcohols which are also vinylsilanes. (Eqn. 367) The pyrollidinoallylsilane **128** reacts with ketones or aldehydes in the presence of fluoride ion to give α-pyrollidino-tetrahydrofurans. (Eqns. 368, 369)

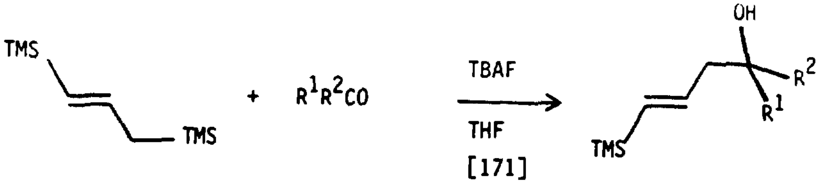


127

(365)

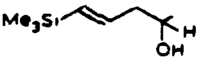
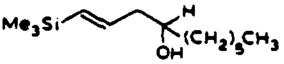
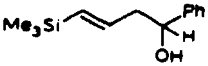
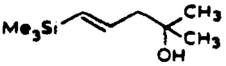
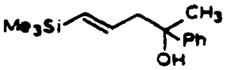
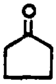
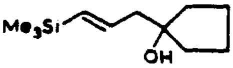
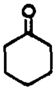
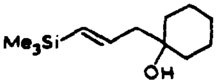


(366)

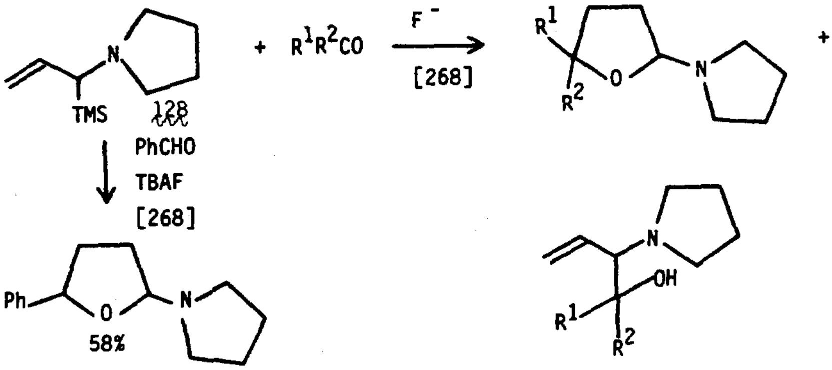


(367)

Table XV: Reaction of Carbonyl Compounds with 127a According to Eqn. 367.

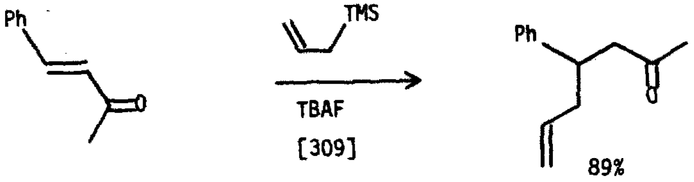
RCOR'	Reaction conditions[a]	Products[b] (%)	
CH_3CHO	25°C, 3h		(70)
$CH_3(CH_2)_5CHO$	25°C, 3h		(75)
PhCHO	40°C, 5h		(90)
$(CH_3)_2CO$	25°C, 16h		(45)
PhCO—CH_3	25°C, 24h		(60)
	25°C, 16h		(65)
	25°C, 16h		(62)

a. Together with the normal products were observed products of crotonization, produced by the fluoride ion. b. Yield of product purified by thin layer chromatography (silica gel eluting with chloroform).

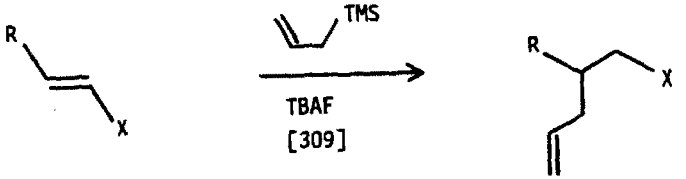


(368)

The fluoride-induced allylation can also be done in a Michael fashion. (Eqns. 370, 371) and in fact has been done in a Michael fashion intramolecularly. (Eqns. 372, 373)



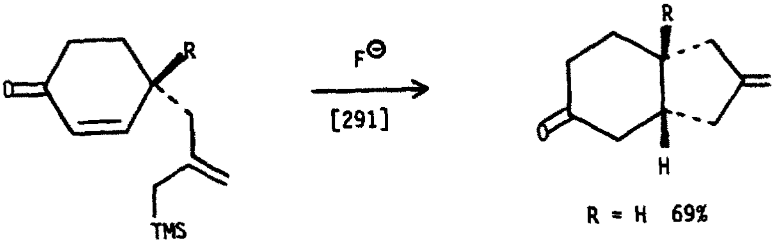
(370)



(371)

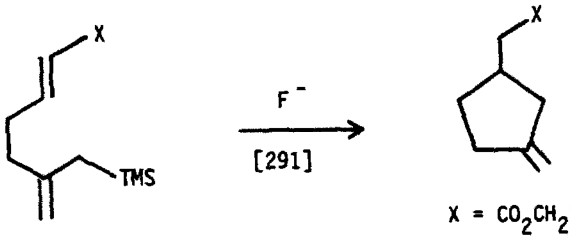
X = CO_2Me, CN, $CONEt_2$, CO_2CH_2Ph

$TiCl_4$ catalysis does not work on this reaction.



R = H 69%

R = Me 63%

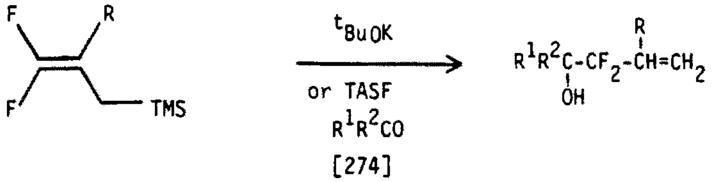


(373)

X = CO_2CH_2Ph 66%

X = CN 64%

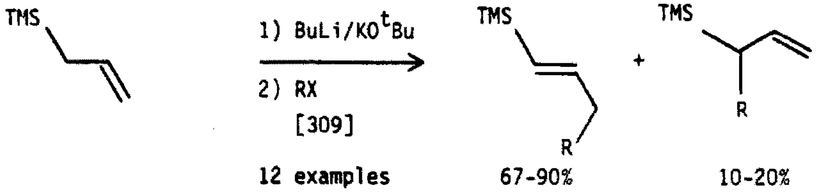
Potassium tert-butoxide or tris(triethylamino)sulfonium difluorotrimethylsilicate induce the reaction of 1,1-difluoroallylsilanes with aldehydes and ketones. (Eqn. 374)



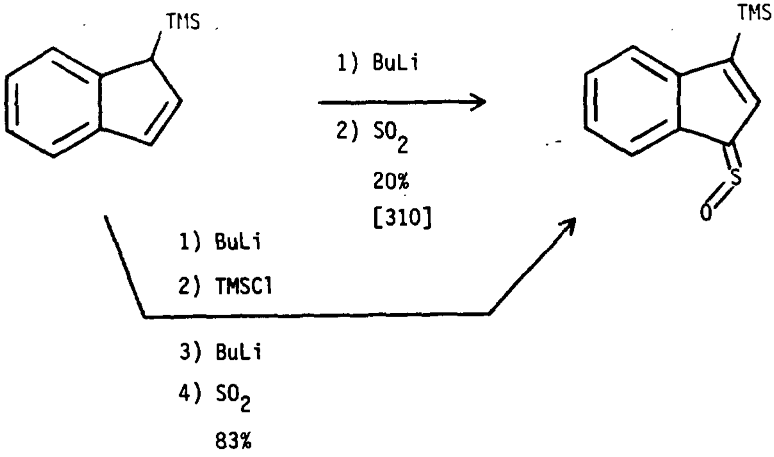
(374)

TASF = $(Et_3N)_3S^+Me_3\bar{S}iF_2$

Trimethylsilylallyl anions have been formed and reacted with various electrophiles. (Eqns. 375-382) Schlosser's base gives an anion from allyltrimethylsilane that gives more γ-alkylation (Eqn. 375) Deprotonation of 3-trimethylsilylindenes gives an anion which reacts with sulfur dioxide to give sulfines. (Eqns. 376-378) The allylsilane **129** was deprotonated and alkylated to give predominantly γ-alkylation and some α-alkylation. (Eqn. 379) Alkylation was observed at the γ-position of the anion of **130**. (Eqn. 380) A titanium (III) salt of the anion of 1,3-bistrimethylsilylpropene reacts with propanal to give γ-attack. (Eqn. 381) The products lead to (E,E) or (E,Z) 1-trimethylsilyl-1,3-dienes consistent with the intermediate β-hydroxysilane being threo.

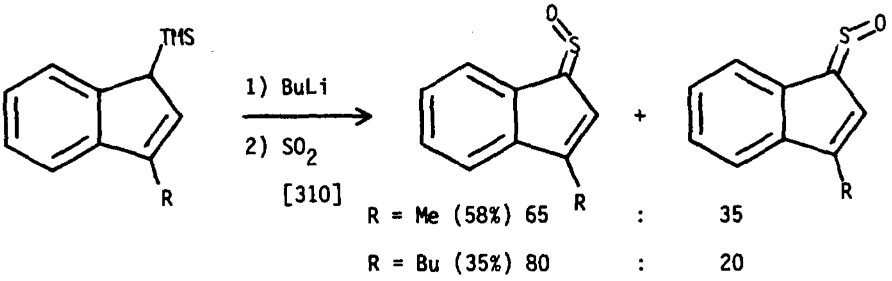


(375)

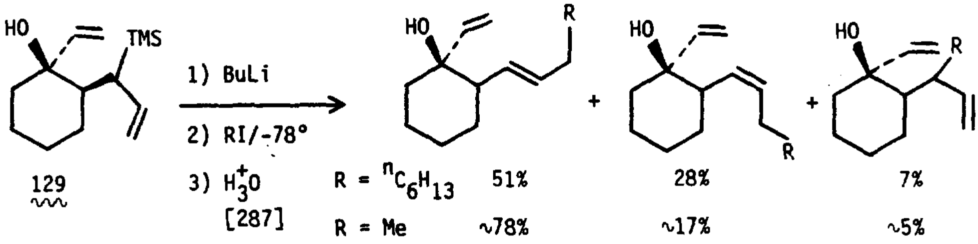


(376)

(377)

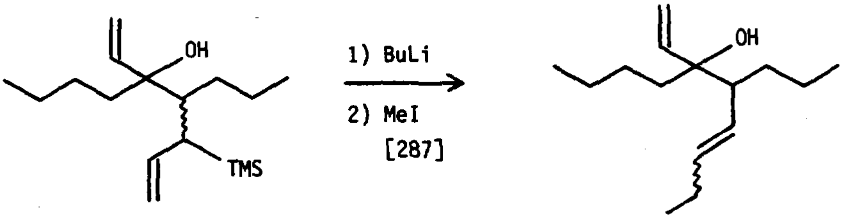


(378)



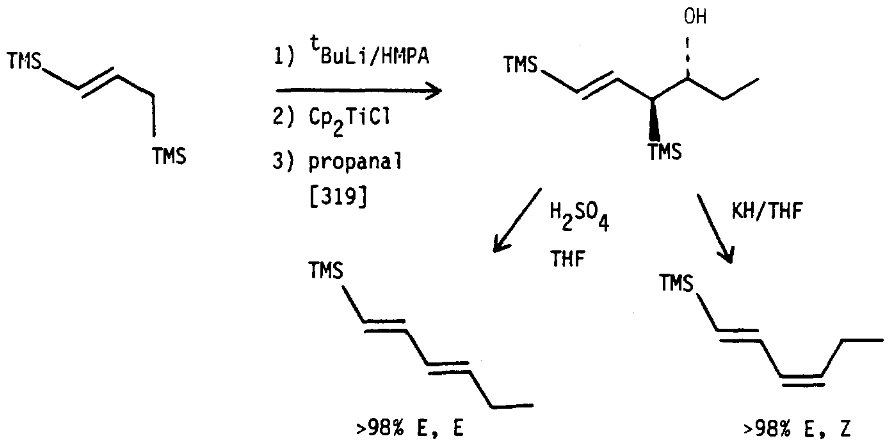
129

(379)



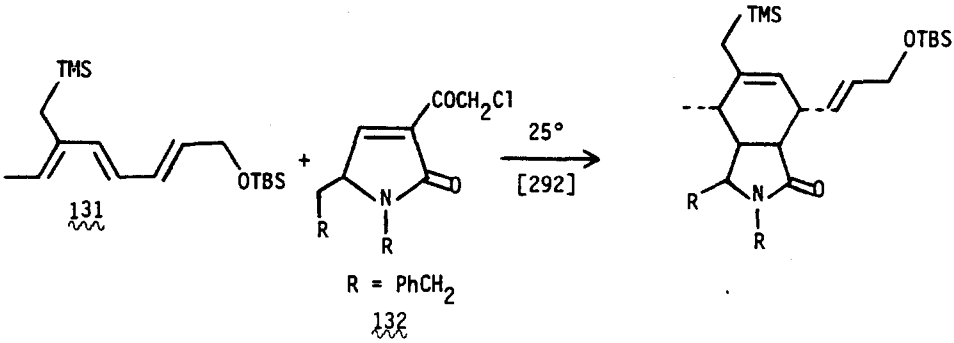
130

(380)

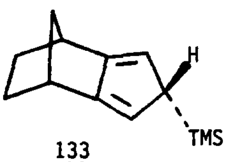


(381)

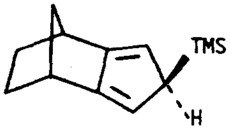
Allylsilanes were involved in electrocyclic reactions. The allysilane **131** undergoes a regioselective cycloaddition with dienophile **132**. (Eqn. 382) The Diels-Alder reactions of allylsilanes **133**, **134** and **135** were studied. (Eqns. 383-386) Isomer **133** reacts cleanly with dimethylacetylene dicarboxylate. (Eqn. 383) but gives three products when isomerized at 140° prior to addition of the dienophile. Isomer **134** also reacts cleanly. (Eqn. 385) Isomer **135** reacts much more slowly than the **133** and **134**. (Eqn. 386)



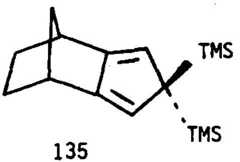
(382)



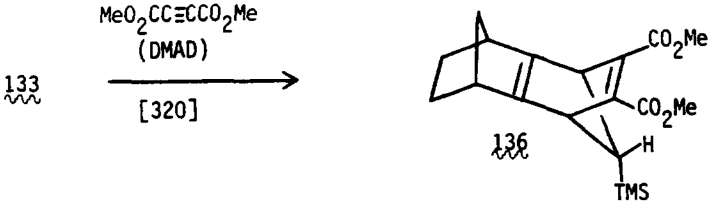
133



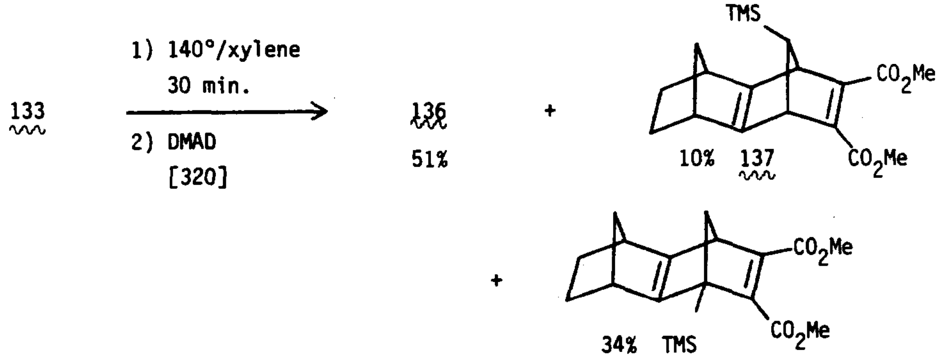
134



135

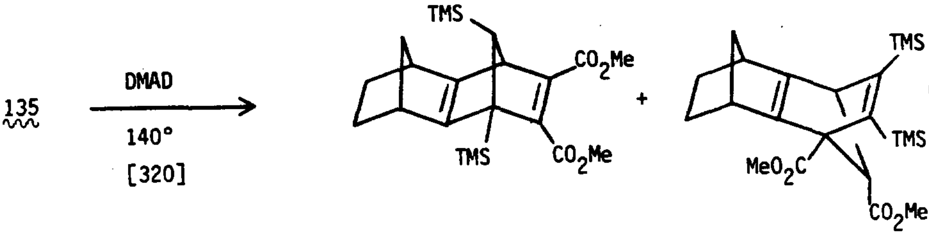


(383)



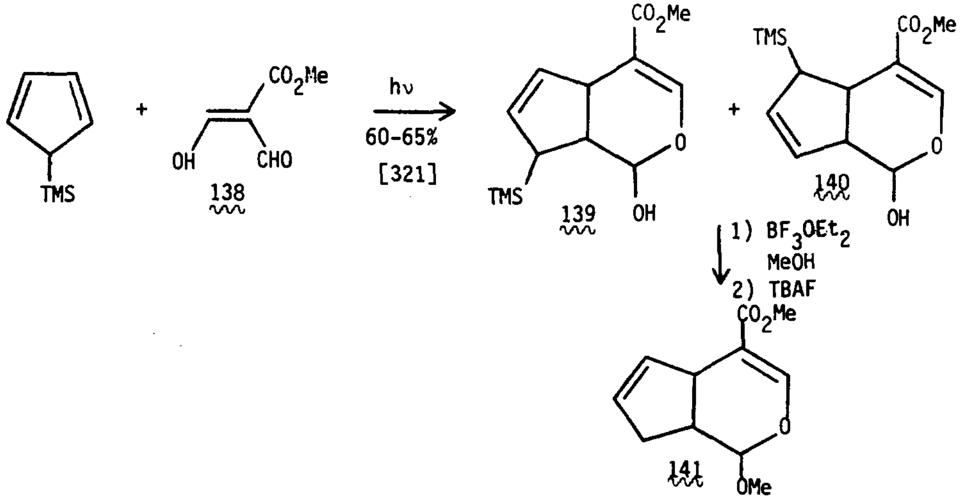
(384)

$$134 \xrightarrow[\text{[320]}]{\text{DMAP}} \underset{77\%}{137} \qquad (385)$$



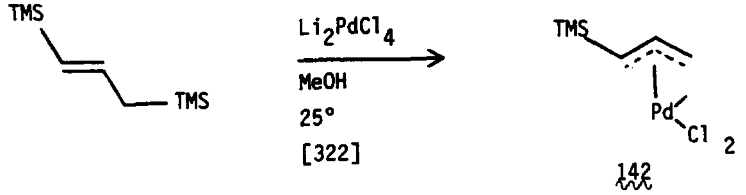
(386)

1-Trimethylsilylcyclopentadiene reacts with **138** in a Paterno-Buchi photoannulation to give lactols **139** and **140**, which were methylated and protiodesilylated to give **141**. (Eqn. 387)

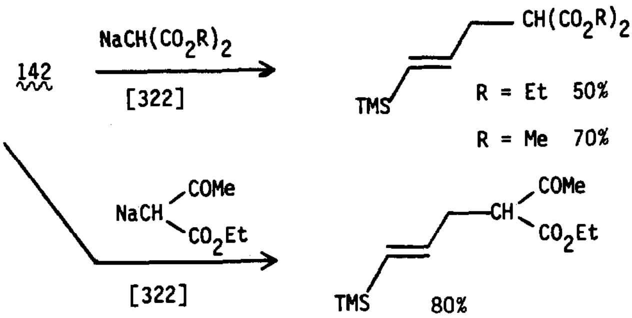


(387)

1,3-Bistrimethylsilylpropene reacts with dilithium tetrachloropalladate to give the π-allyl complex **142**, which reacts with malonate type anions to give E-vinylsilanes. (Eqns. 388-390) The optically active allysilanes **143** or **144** reacts with the above palladium reagent (or its bromo counterpart to give the optically active π-allyl palladium complex **145** as a result of anti attack of the palladium. (Eqn. 391) Allylsilanes react with perfluoroalkyl halides to give the corresponding perfluoroalkyl allyl systems. (Eqn. 392)

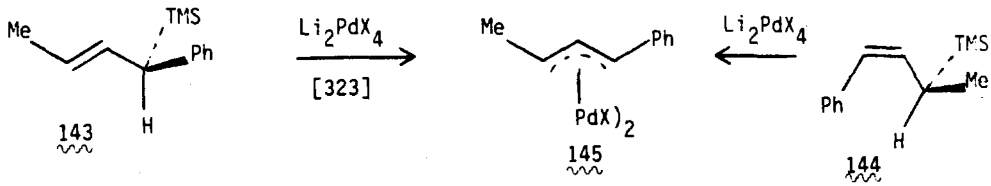


(388)

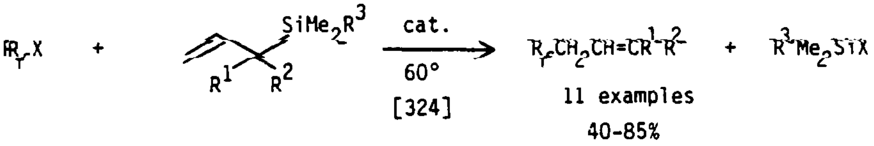


(389)

(390)



(391)



(392)

Cat. = $Fe_3(CO)_{12}$ or $Ru_3(CO)_{12}$

Table XVI: Reaction of Polyfluoroalkyl Halides with Alkylsilanes According to Eqn. 392.

Entry	R_f	X	R^1	R^2	R^3	Cat.[a] (mol%)	EA[b] (mol%)	Temp. (°C)	Time (h)	Product[c] (% yield)
1	C_3F_7	I	H	H	Me	Fe_3(2.0)		60	12	3a (80)
2	C_8F_{17}	I	H	H	Me	Ru_3(0.3)		60	19	3b (71)
3	CF_2CF_2Br	I	H	H	Me	Fe_3(1.3)	(12)	60	3	3c (85)
4	$CFClCF_2Cl$	I	H	H	Me	Fe_3(1.3)	(12)	60	4	3d (85)
5	$CFHCF_2Cl$	I	H	H	Me	Fe_3(1.3)	(12)	60	3	3e (75)
6	$CFClCF_2Br$	Br	H	H	Me	Ru_3(0.3)		60	6	3f (59)
7	$CF(CF_2Br)CF_3$	Br	H	H	Me	Fe_3(1.3)	(12)	60	20	3g (40)
8	$CFClCF_2Cl$	I	H	CH_2CF_3	Me	Fe_3(2.0)	(15)	60	2	3h (85)
9	$CFClCF_2Cl$	I	H	Me	H	Ru_3(0.6)		60	3	3i (82)
10	$CFClCF_2Cl$	I	H	H	Me	hν[d]		0	3	3d (65)
11	$CFClCF_2Cl$	I	H	H	Me	AIBN[e](12)		80	8	3d (40)

[a] Fe_3=$Fe_3(CO)_{12}$, Ru_3=$Ru_3(CO)_{12}$. [b] EA=ethanolamine. [c] Determined by GLC. [d] Irradiated externally with 400 W high-pressure Hg lamp. [e] AIBN=azobisisobutyronitrile.

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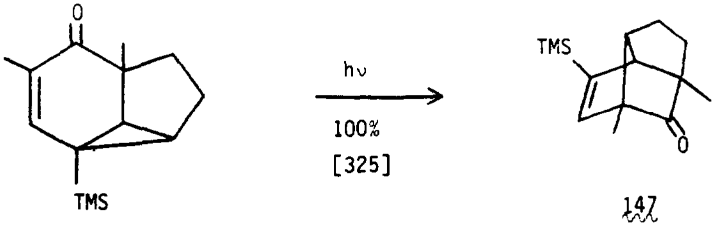
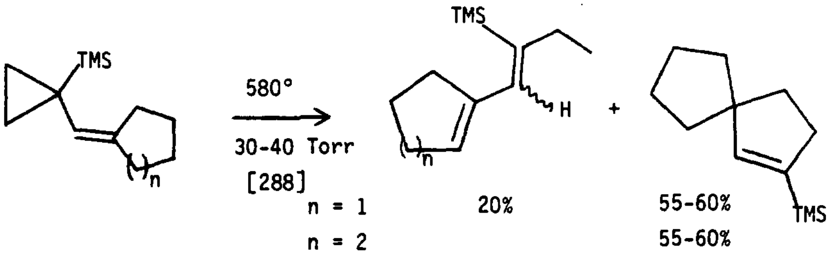
The allylsilane **146** photorearranges to **147**. (Eqn. 393) The thermal vinylcyclopropane to cyclopentene rearrangement was carried out with trimethylsilyl substitution at C-1 of the cyclopropyl group. (Eqn. 394, 395)

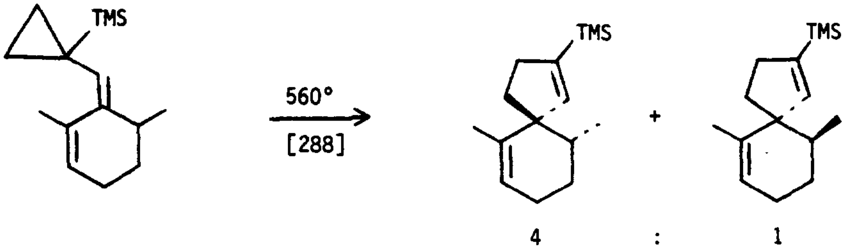


146 147

(393)



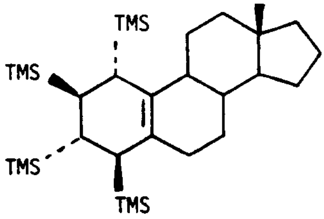
(394)



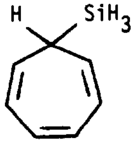
(395)

C. Spectroscopic and Other Studies

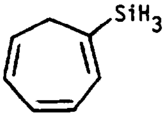
The crystal structure of **148** was determined. The A ring is in the chair conformation whereas the B and D rings are in half-chair conformations. [326] The microwave spectrum structures, dipole moment and internal rotation of allylsilane were determined. [327] The structures **149-153** were analyzed by MNDO calculations. The monohapto structure **149** is much more stable than the heptahapto structure **153**. Structures **150**, **151** and **152** are lower in energy than **149**. No energy minima could be found for di-or pentahapto structures. Only a [1,5] shift could be found. [328]



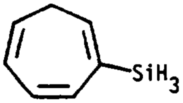
148



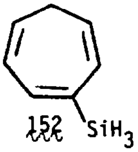
149



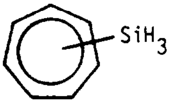
150



151



152



153

X. PROPARGYLSILANES

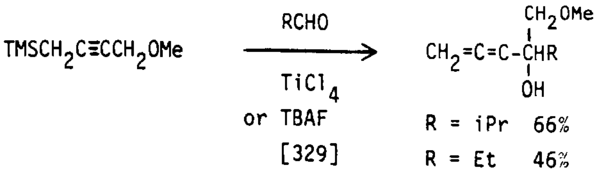
The reaction of propynyllithium reagents with iodomethyltrimethylsilane give propargylsilanes. (Eqn. 396) Propargyltrimethylsilane was deprotonated and reacted with paraformaldehyde. (Eqn. 397) The propargylsilanes formed in Eqn. 396 react with aldehydes under electrophilic or nucleophilic conditions (Eqns. 398-400)

$$\mathrm{ROCH_2C{\equiv}CH} \xrightarrow[\substack{\text{2) TMSCH}_2\text{I} \\ [329]}]{\text{1) BuLi}} \mathrm{ROCH_2C{\equiv}CCH_2TMS} \qquad (396)$$

R = H, Me, TMS

$$\mathrm{TMSCH_2C{\equiv}CH} \xrightarrow[\substack{\text{2) (CH}_2\text{O)}_n \\ [329]}]{\text{1) EtMgBr}} \mathrm{TMSCH_2C{\equiv}CCH_2OH} \qquad (397)$$

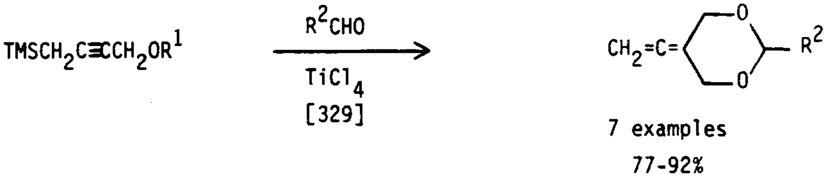
50%



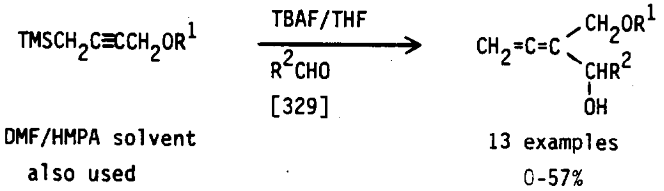
$$\mathrm{TMSCH_2C{\equiv}CCH_2OMe} \xrightarrow[\substack{\mathrm{TiCl_4}\\ \text{or TBAF}\\ [329]}]{\mathrm{RCHO}} \mathrm{CH_2{=}C{=}C{-}\underset{\underset{OH}{|}}{\overset{\overset{CH_2OMe}{|}}{C}}HR}$$

R = iPr 66%
R = Et 46%

(398)



(399)



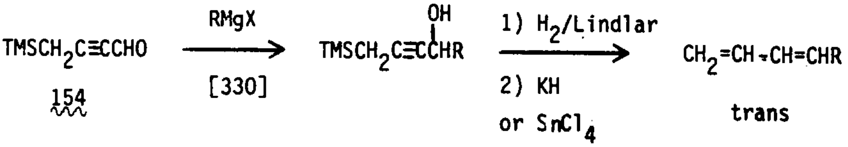
$$\mathrm{TMSCH_2C{\equiv}CCH_2OR^1} \xrightarrow[\substack{\mathrm{R^2CHO}\\ [329]}]{\mathrm{TBAF/THF}} \mathrm{CH_2{=}C{=}C}\begin{matrix}\nearrow \mathrm{CH_2OR^1}\\ \searrow \mathrm{\underset{\underset{OH}{|}}{C}HR^2}\end{matrix}$$

DMF/HMPA solvent also used

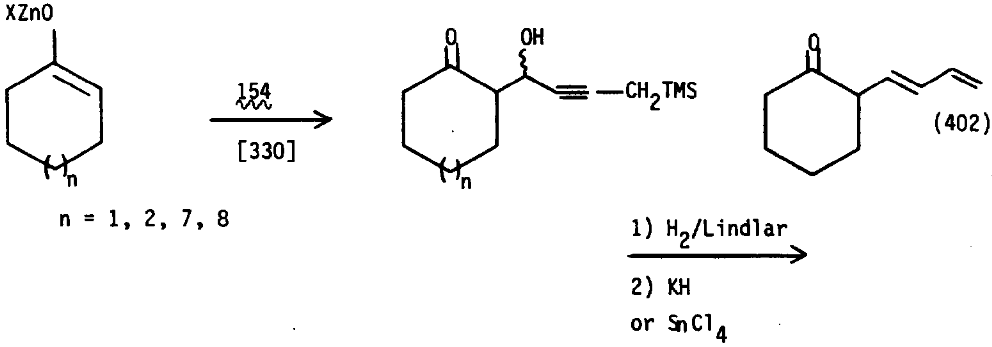
13 examples
0-57%

(400)

4-(Trimethylsilyl)but-2-ynal **154** proved to be an excellent synthon for (E) 1,3-dienes. (Eqns. 401-402) Propargylsilanes react with diisobutylaluminum hydride nonregiospecifically, but the mixture of intermediates can be protonated to give (Z) allylsilanes. (Eqns. 403, 404) A similar result is obtained via hydroboration-protonation. (Eqn. 405) Trans-4-trimethylsilylbut-2-en-1-ol was prepared according to Eqn. 406. This alcohol was used as a new protecting group for carboxylic acids, the acid being released upon treatment with palladium (0). (Eqn. 407) The reaction of propagylsilanes with suitable electrophiles in the presence of a Lewis acid gives allenenylation (Eqns. 408, 409) The reaction has been carried out in an intramolecular, asymmetric cyclization as illustrated in Eqn. 410. Propargyltrimethylsilane was dimerized with a Ti(0) isopropylmagnesium bromide catalyst. (Eqn. 411)

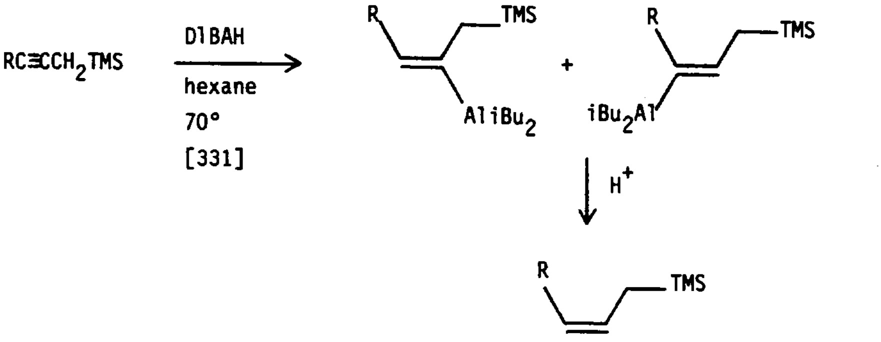


(401)



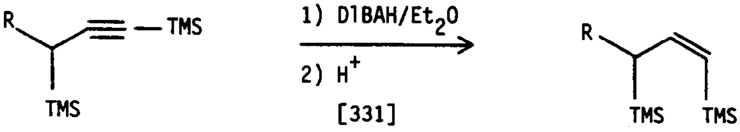
n = 1, 2, 7, 8

(402)



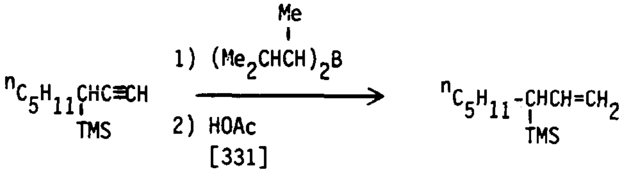
(403)

R = Bu (85%), $^{n}C_6H_{11}$ (85%), ^{t}Bu (83%)



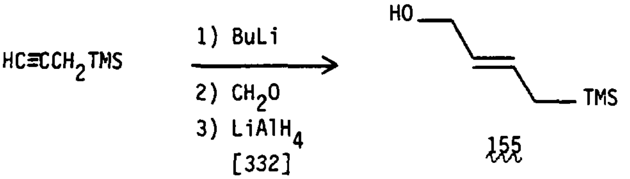
(404)

R = $^{n}C_5H_{11}$ (89%), iC_6H_{11} (82%), Ph (75%)



$$ {}^{n}C_5H_{11}\underset{TMS}{CH}C\equiv CH \xrightarrow[\text{2) HOAc [331]}]{\text{1) }(Me_2CH\overset{Me}{CH})_2B} {}^{n}C_5H_{11}\text{-}\underset{TMS}{CH}CH=CH_2 $$

(405)



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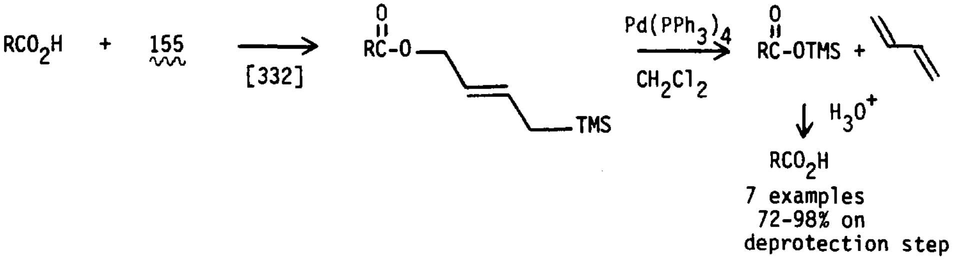

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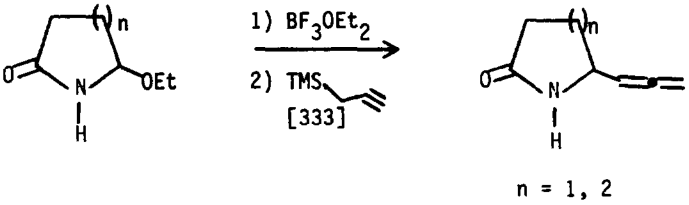

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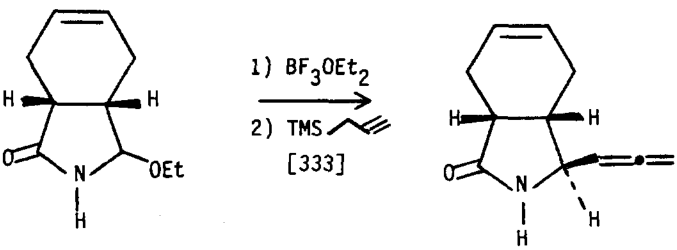

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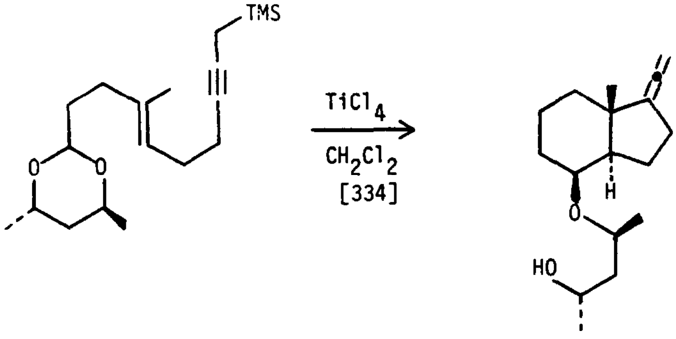
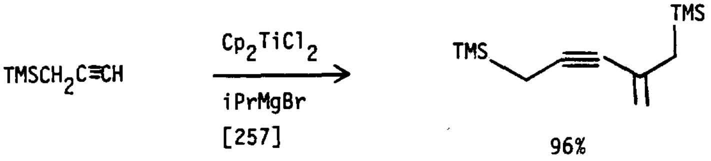


(410)

87

82% isolated

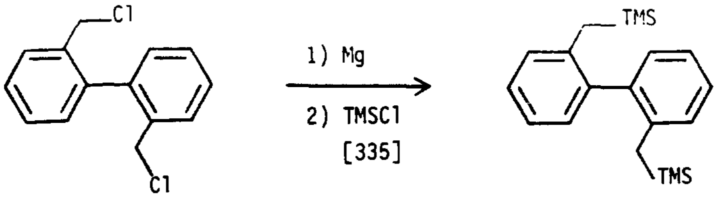


(411)

XI. BENZYLSILANES

A. Preparation

The reaction of benzylmagnesium chlorides with chlorosilanes was used to prepare benzylsilanes. Some examples are shown in Eqns. 412, 413. As seen in Eqn. 413 this can be done in an "in situ" manner. The lithiation-silylation of the benzylic position is a useful route to benzylsilanes and also allows elaboration of benzylsilanes (Eqns. 415-419) The bis-trimethylsilylpicoline **156** forms a dimeric species with Cu(I) or Li. (Eqn. 415) Metal-bromine exchange is better than benzylic deprotonation and deprotonation of a benzylsilane better than a tolylmethyl group. (Eqn. 418). Benzyl deprotonation-silylation is possible even in systems where ortho metalation is a viable alternate pathway. (Eqn. 419). This process has been used to protect the methyl group utilizing the fact that the benzylsilyl groups can be protiodesilylated. (Eqn. 419) It has also been used to further metalate benzylsilanes. (Eqns. 420-423)



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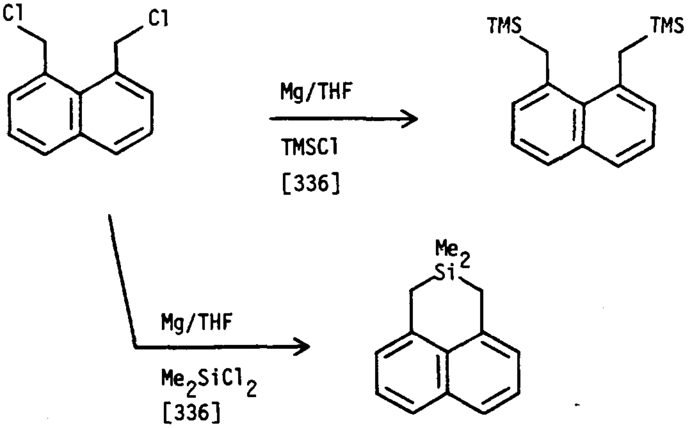
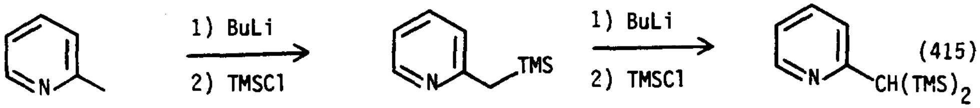


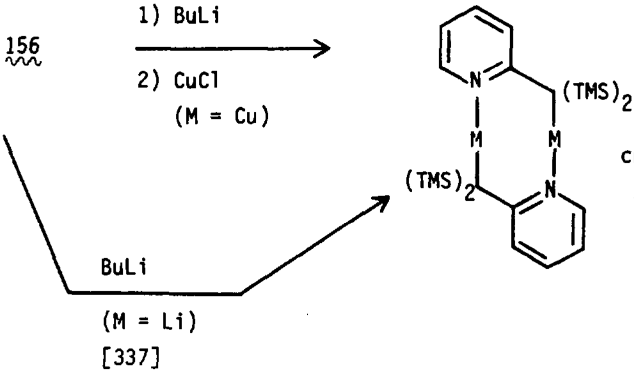
(413)

(414)



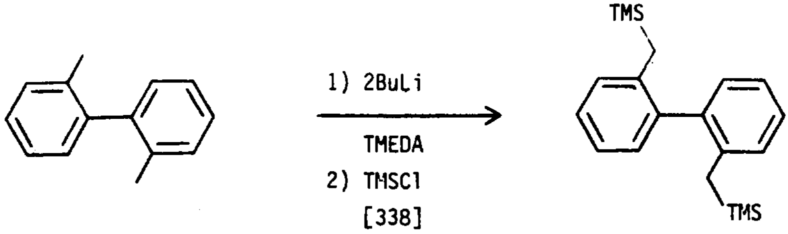
(415)

156



(416)

characterized by
X-ray



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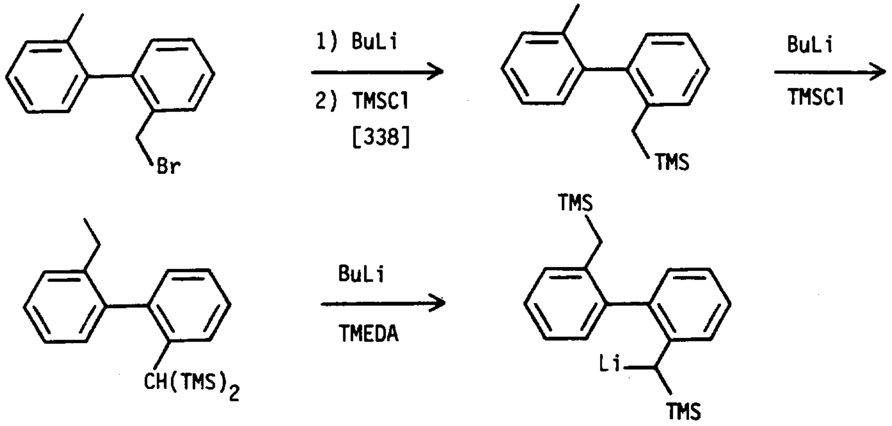

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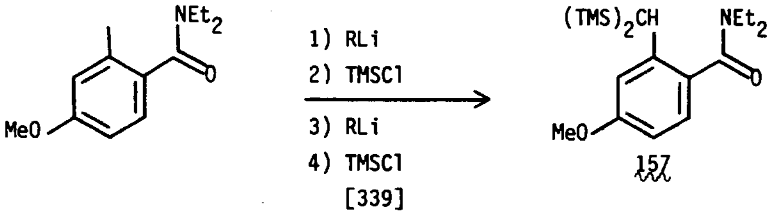

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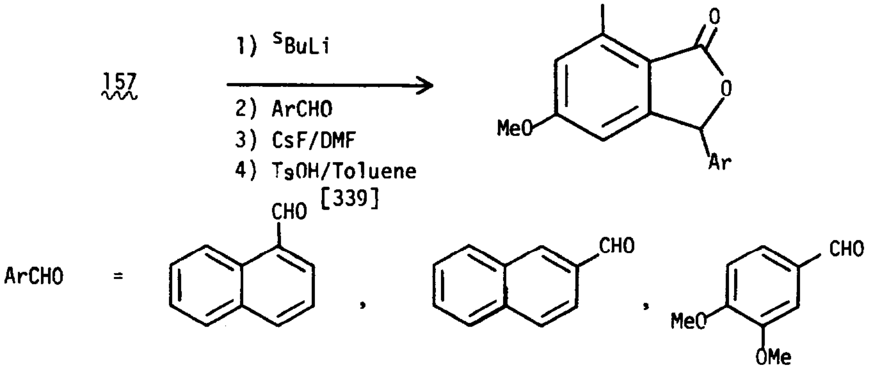

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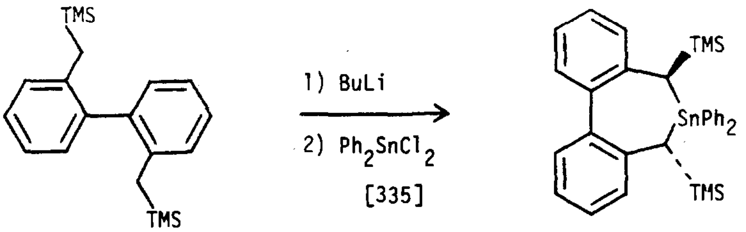

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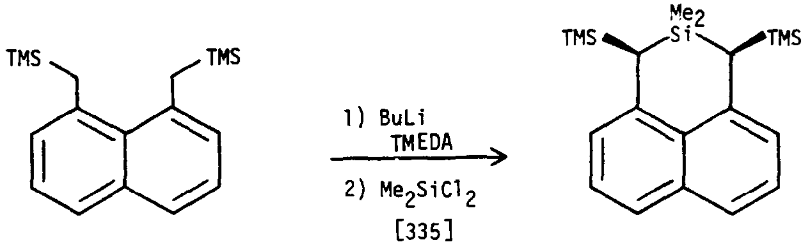
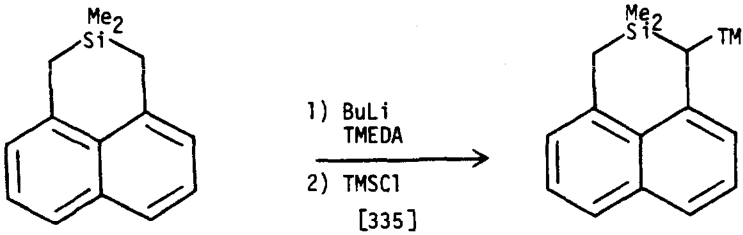
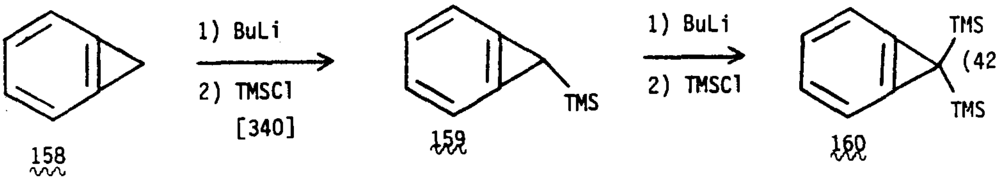


(422)



(423)

Cyclopropabenzene **158** can be deprotonated and silylated to give **159**, deprotonation and silylation of which gives **160** (Eqn. 424) A similar reaction occurs with cyclopropanaphthalene **161** although the monosilylated material is not isolated in this system. (Eqn. 425) Both **160** and **162** are excellent precursors to the corresponding alkylidenecyclopropaarenes **163** and **164**, respectively. (Eqns. 426, 427)



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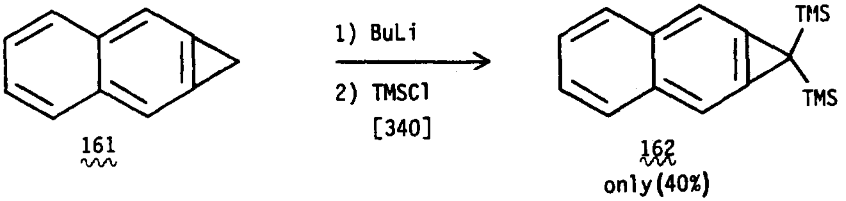

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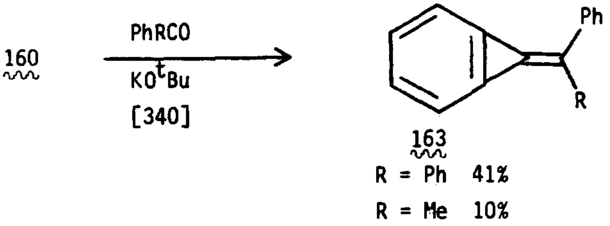
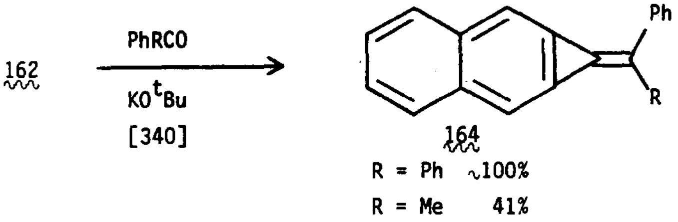
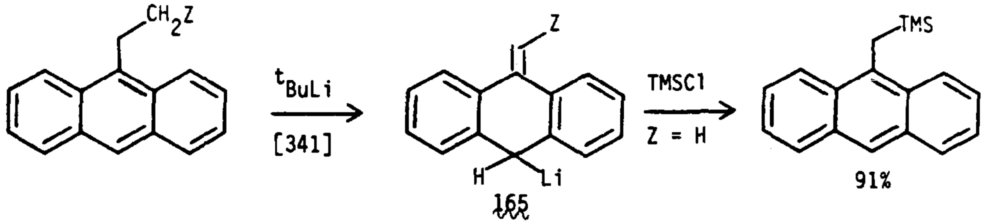


(426)

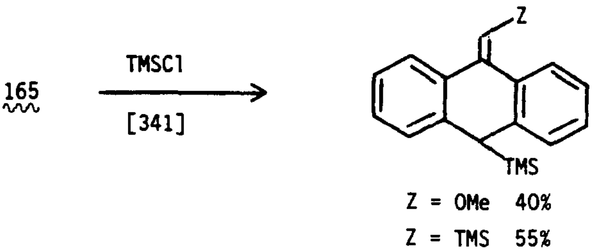


(427)

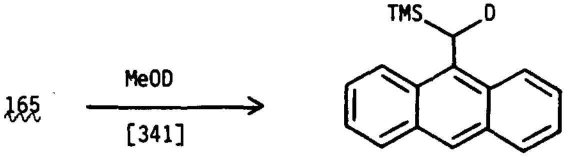
Some 9-anthranylmethyl anions were generated and silylated. A rearrangement occurs to give 9-yliden-10-anthranyl carbanions. (Eqns. 428-430)



(428)

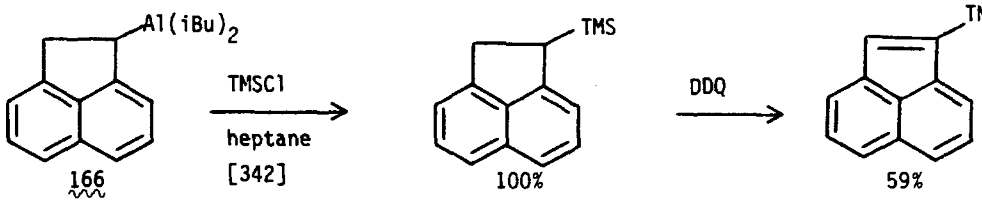


(429)



(430)

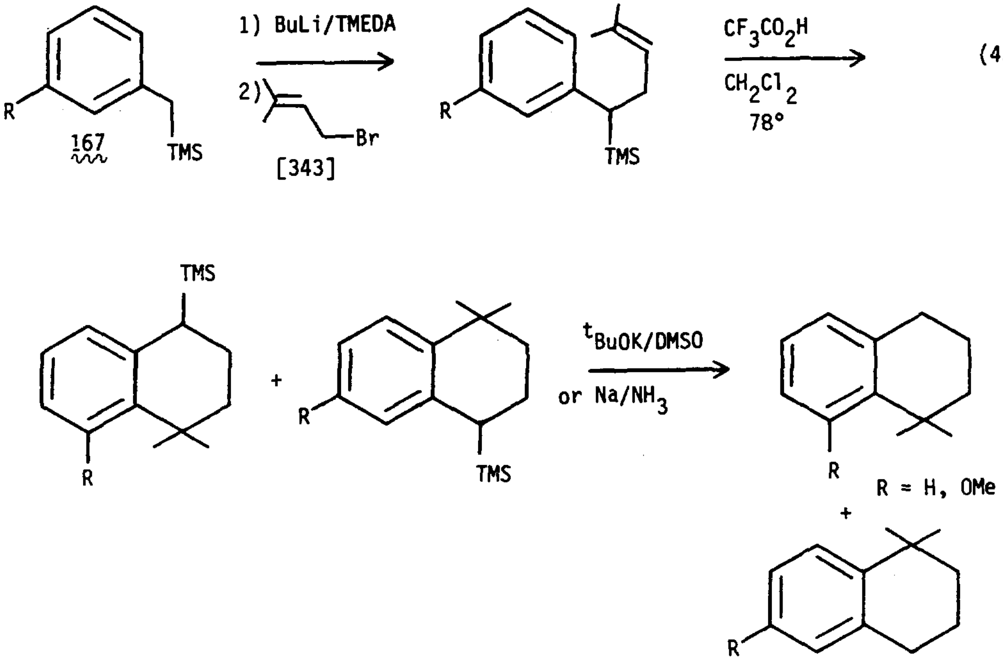
Diisobutylacenaphthenylaluminum **166** reacts with chlorotrimethylsilane to give acenaphthenyltrimethylsilane in excellent yield. This reacts with DDQ to give the acenaphthylenylsilane. (Eqn. 431)



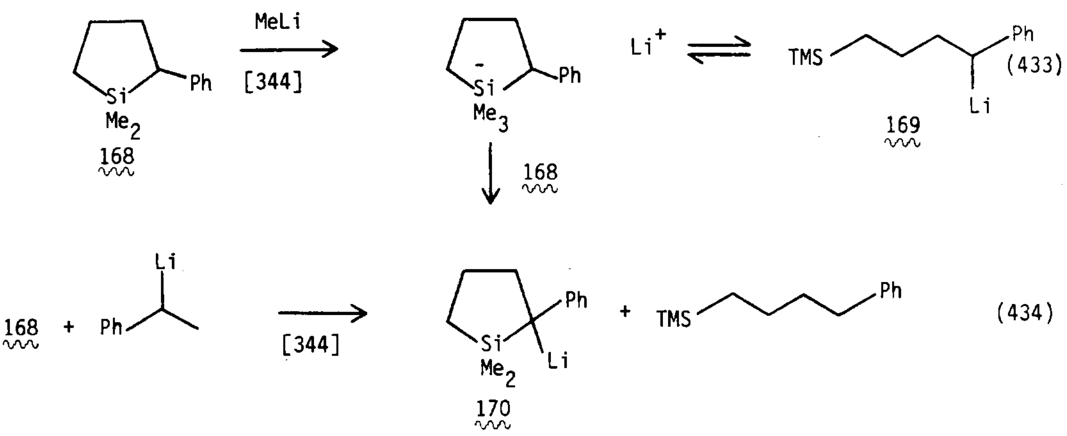
(431)

B. Reactions

Benzylsilanes are readily deprotonated as seen by some examples already presented and the resulting carbanions are useful for further elaboration. Benzylsilanes of the structures **167** were deprotonated and the anion reacted with prenyl bromide. The resulting product was cyclized and protiodesilylated. (Eqn. 432) Benzylsilane **168** reacts with methyllithium to form lithium reagent **169** via a pentavalent silicate. This anion can react with **168** to give furan **170**, which can also be formed from **168** and 1-phenylethyllithium. (Eqns. 433- 434)



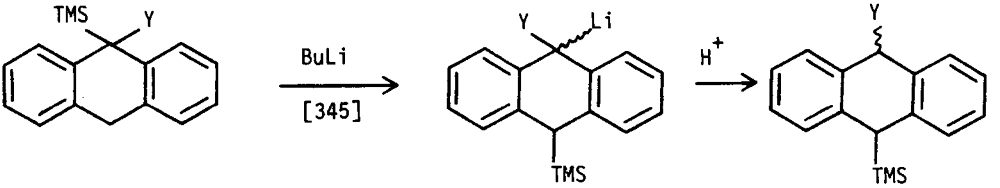
(432)



(433)

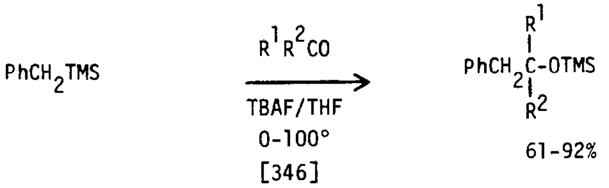
(434)

9-Trimethylsilylanthracenes react with butyllithium to give the products of trimethylsilyl migration. (Eqn. 435)



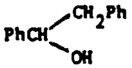
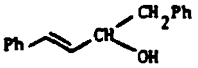
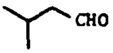
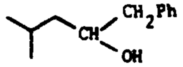
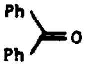
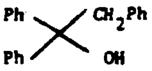
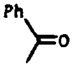
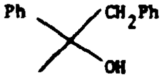
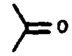
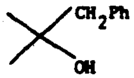
(435)

Benzyltrimethylsilane reacts with aldehydes and ketones in the presence of fluoride ion. (Eqn. 436) Benzylsilanes react photochemically with iminium salts both intermolecularly (Eqn. 437) and intramolecularly (Eqn. 438) The benzylsilane is clearly better than the corresponding toleune for these reactions.



$$\mathrm{PhCH_2TMS} \xrightarrow[\substack{\mathrm{TBAF/THF} \\ 0\text{-}100° \\ [346]}]{\mathrm{R^1R^2CO}} \mathrm{PhCH_2C(R^1)(R^2)\text{-}OTMS} \quad 61\text{-}92\% \qquad (436)$$

Table XVII: Reaction of Benzyltrimethylsilane with Carbonyl Compounds in the Presence of Fluoride Ion According to Eqn. 436.

Carbonyl Derivative	Reaction Temperature		Product obtained after hydrolysis (or silica gel filtration in last 2 cases)	% Yield
PhCHO	12 h	Addition at room temp. followed by reflux in THF		92
	12 h	"		85
	3 h	"		68
	4 h	Addition at o° followed by warming to room temp.		85
	4 h	"		75
	4 h	"		61

The results require the following comments °the benzylsilane reacts like a true organometallic, but one that is distillable and thus easily purified. °the benzylation whose yield has not yet been optimized is done avoiding the secondary reactions normally observed with classical organometallic reagents (formation of bibenzyl). °The judicial choice of benzylsilanes and other carbonyl substrates since it allows subsequent cyclizations opens new perspectives in the chemistry of polycyclic derivatives.

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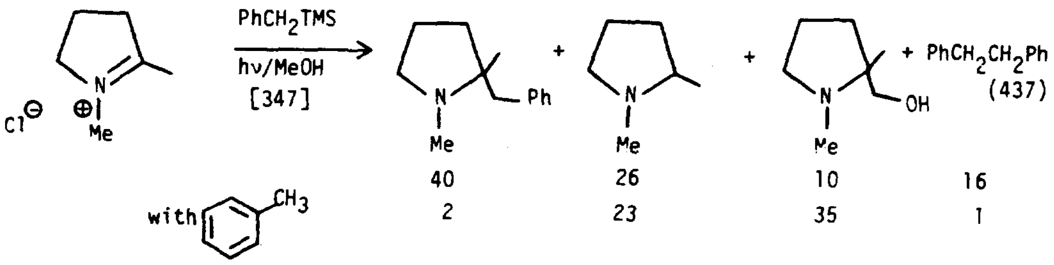
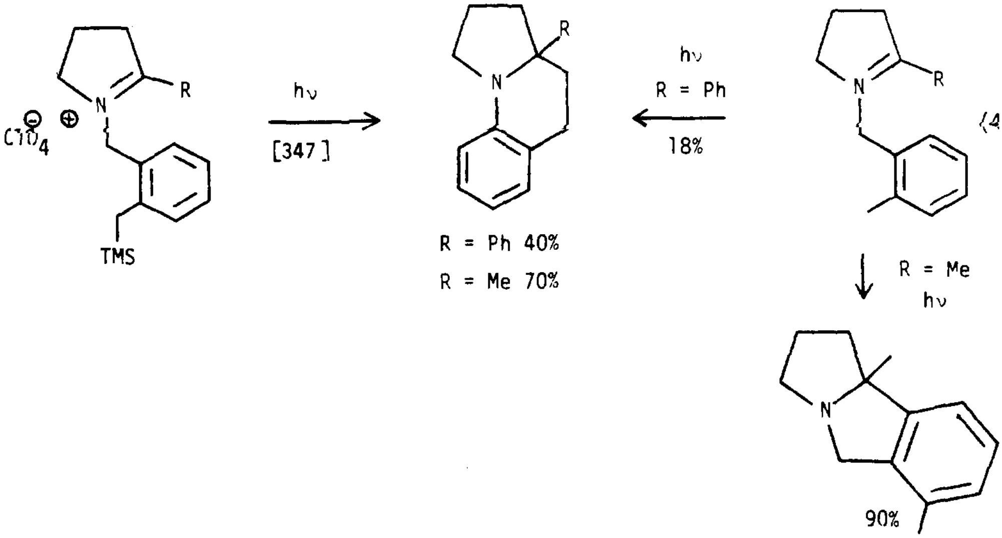
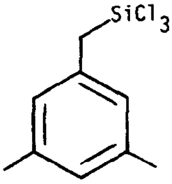


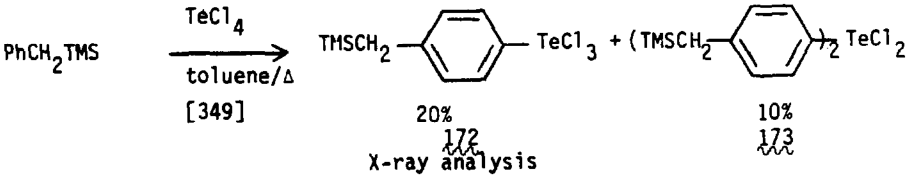


(438)

α-(Trichlorosilyl)mesitylene **171** reacts with $Cl_2/FeCl_3$ to give ring chlorination and with chlorine in the presence of a radical initiator (AIBN) to give methyl and methylene chlorination. [348] Benzyltrimethylsilane reacts with tellurium (IV) chloride to give **172** and **173**. (Eqn. 439)



171



(439)

XII. α-FUNCTIONAL ORGANOSILANES

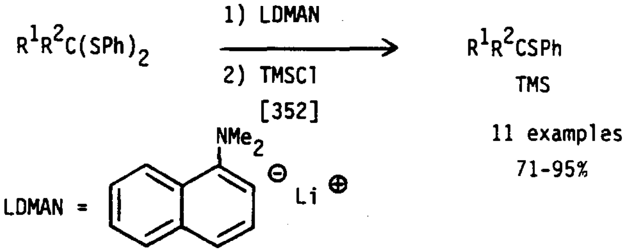
A. Preparation

The preparation of α-functional organosilanes are to be found throughout this survey in addition to those that are placed in the section. The silylation of α-functional organolithium reagents provides an excellent entry into α-functional organosilanes. Several examples follow. (Eqns. 440-445)

Chlorotrimethylsilane reacts with phosphorus trichloride and oxygen to give dimethylchlorophosphonic acid derivatives (Eqn. 446) The reaction of (chloromethyl)dimethylchlorosilane with **174** gives the morpholine derivative **175** (Eqn. 447) Chloromethylsilanes react with α-chloro esters in the presence of ethanol amines to give silylmethyl esters. (Eqn. 448) The 1,3-butadiene **176** can be converted to the lithium reagent, which when reacted with selenium gives **177**. (Eqn. 449) Chloro(phenylthio)methylsilane reacts with lead (II) isocyanate to give **178**. (Eqn. 450) α,α-Dichlorosilanes react with dimethyl(trimethylsilyl)phosphine to give ylides, which undergo further reaction as shown in Eqns. 451, 452)

$$Me_2PCH_2Li \quad + \quad Me_{4-n}Cl_nSiCl \xrightarrow[{[350]}]{} Me_{4-n}Si(CH_2PMe_2)_n \qquad (440)$$

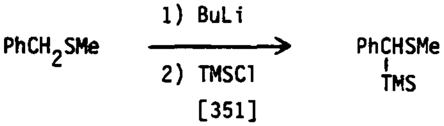
$n = 1\text{-}4$



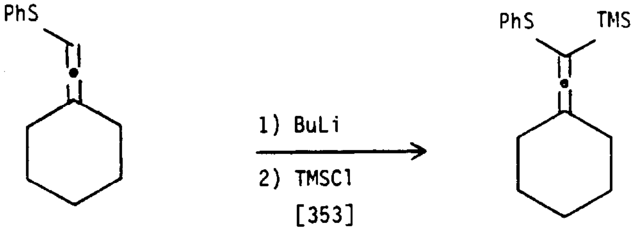
$$R^1R^2C(SPh)_2 \xrightarrow[\text{2) TMSCl} \; [352]]{\text{1) LDMAN}} R^1R^2C(SPh)(TMS) \qquad (441)$$

11 examples

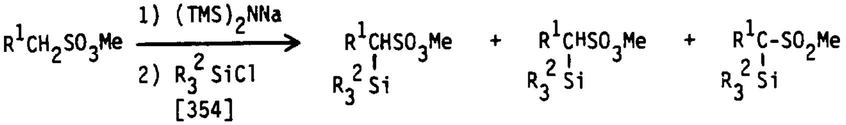
71-95%



$$PhCH_2SMe \xrightarrow[\text{2) TMSCl} \; [351]]{\text{1) BuLi}} PhCH(SMe)(TMS) \qquad (442)$$



(443)

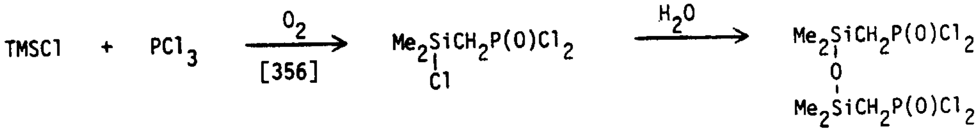


$$R^1CH_2SO_3Me \xrightarrow[\text{2) } R_3^2SiCl \text{ [354]}]{\text{1) } (TMS)_2NNa} \underset{R_3^2Si}{R^1CHSO_3Me} + \underset{R_3^2Si}{R^1CHSO_3Me} + \underset{R_3^2Si}{R^1C\text{-}SO_2Me} \quad (444)$$

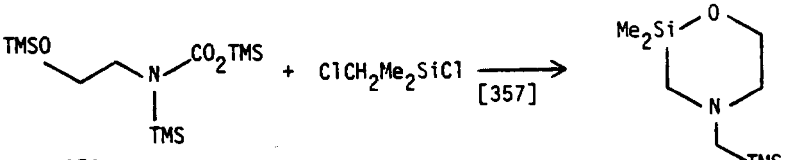
R = Me, Et

R = H, Me, Et, Pr

$$CH_3N{\equiv}C \xrightarrow[\text{2) TMSCl, -95° [355]}]{\text{1) BuLi/DMM}} \underset{45\text{-}50\%}{TMSCH_2N{\equiv}C} \quad (445)$$



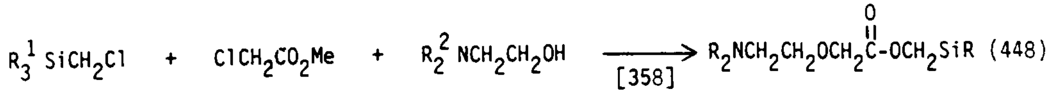
$$TMSCl + PCl_3 \xrightarrow[\text{[356]}]{O_2} \underset{Cl}{Me_2SiCH_2P(O)Cl_2} \xrightarrow{H_2O} \begin{array}{c} Me_2SiCH_2P(O)Cl_2 \\ | \\ O \\ | \\ Me_2SiCH_2P(O)Cl_2 \end{array} \quad (446)$$



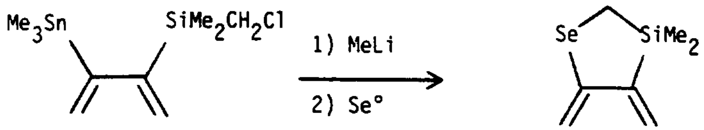
174

175

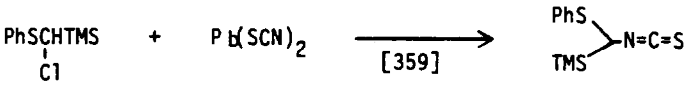
(447)



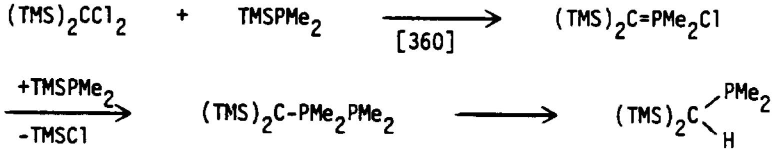
$$R^1_3SiCH_2Cl + ClCH_2CO_2Me + R^2_2NCH_2CH_2OH \xrightarrow[{[358]}]{} R_2NCH_2CH_2OCH_2\overset{O}{\overset{\|}{C}}-OCH_2SiR \quad (448)$$



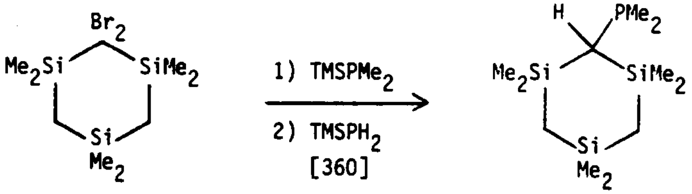
176 177 (449)



178 (450)

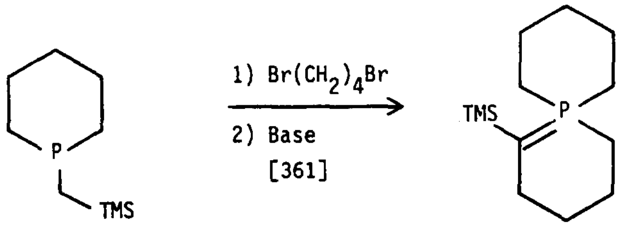


(451)

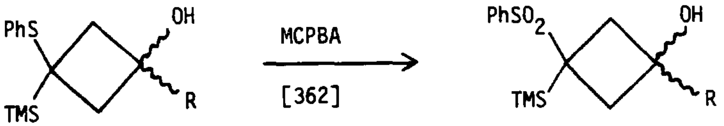


(452)

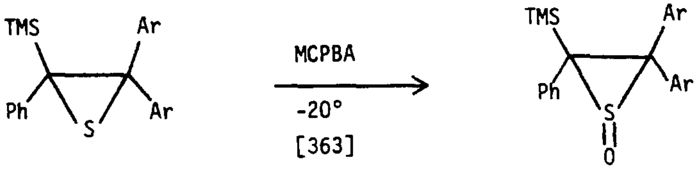
Certain α-functional organosilicons were oxidized to other α-functional organosilicons. Examples are given in Eqns. 453-455. Other α-functional organosilicon were converted to different α-functional organosilicons via a substitution pathway. Trimethylsilyl triflate reacts with pyridines to form the trimethylsilylmethyl pyridinium salts. (Eqns. 456) Trimethylsilylmethyl azide reacts with phosphines to give **179** "in-situ", which can be reacted with aldehydes to give α-trimethylsilyl imines and with carbon dioxide or carbon disulfide to giveα-trimethylsilyl isocyanates or thioisocyanates. (Eqns. 459)



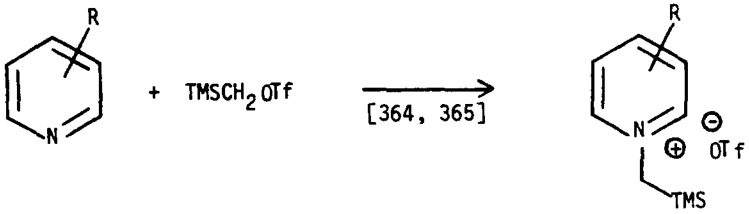
(453)



(454)



(455)



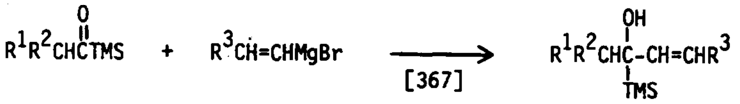
(456)

$$\mathrm{TMSCH_2N_3} \quad + \quad \mathrm{R_3P} \quad \xrightarrow[{[366]}]{} \quad \underset{\mathbf{179}}{\text{"}\mathrm{TMSCH_2N{=}PR_3}\text{"}} \qquad (457)$$

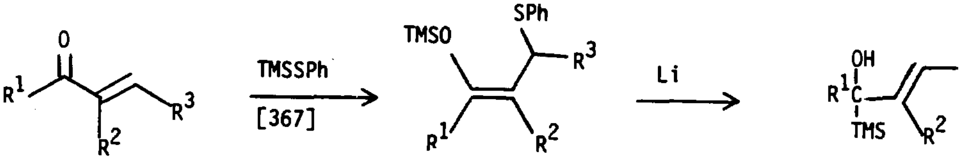
$$\text{"}\mathbf{179}\text{"} \quad + \quad \mathrm{PhCHO} \quad \xrightarrow[{[366]}]{} \quad \mathrm{TMSCH_2N{=}CHPh} \qquad (458)$$

$$\text{"}\mathbf{179}\text{"} \quad + \quad \underset{(X\,=\,O,\ S)}{\mathrm{CX_2}} \quad \xrightarrow[{[366]}]{} \quad \mathrm{TMSCH_2NCX} \qquad (459)$$

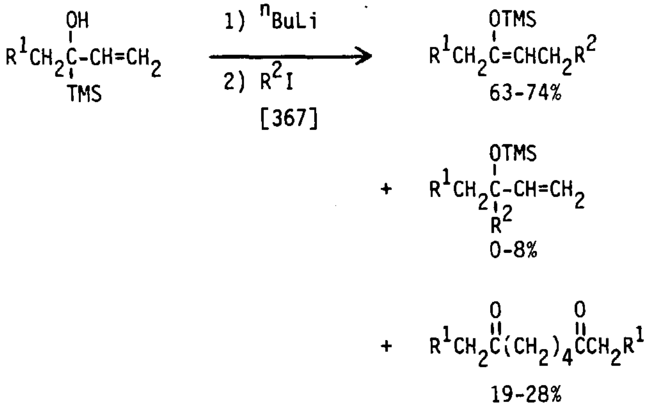
Acylsilanes were reacted with vinyl Grignard reagents to give α-hydroxysilanes. (Eqn. 460) These same systems could be arrived at via the reaction of thiophenoxytrimethylsilane with enones followed by treatment with lithium metal. (Eqn. 461) Studies were carried out on the rearrangement of the lithium alkoxide of the α-hydroxysilanes. (Eqns. 462, 463)



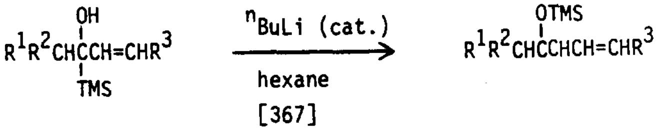
$$\mathrm{R^1R^2CH\overset{\overset{\large O}{\|}}{C}TMS} \quad + \quad \mathrm{R^3CH{=}CHMgBr} \quad \xrightarrow[{[367]}]{} \quad \mathrm{R^1R^2CH\underset{\underset{TMS}{|}}{\overset{\overset{OH}{|}}{C}}\text{-}CH{=}CHR^3} \qquad (460)$$



(461)

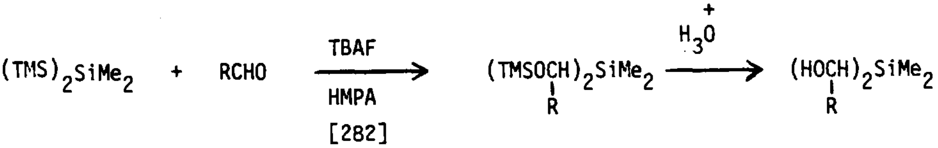


$$R^1CH_2\overset{OH}{\underset{TMS}{C}}\text{-}CH{=}CH_2 \xrightarrow[2)\ R^2I\ [367]]{1)\ ^nBuLi} \underset{63\text{-}74\%}{R^1CH_2\overset{OTMS}{C}{=}CHCH_2R^2} + \underset{0\text{-}8\%}{R^1CH_2\overset{OTMS}{\underset{R^2}{C}}\text{-}CH{=}CH_2} + \underset{19\text{-}28\%}{R^1CH_2\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}CH_2R^1} \quad (462)$$

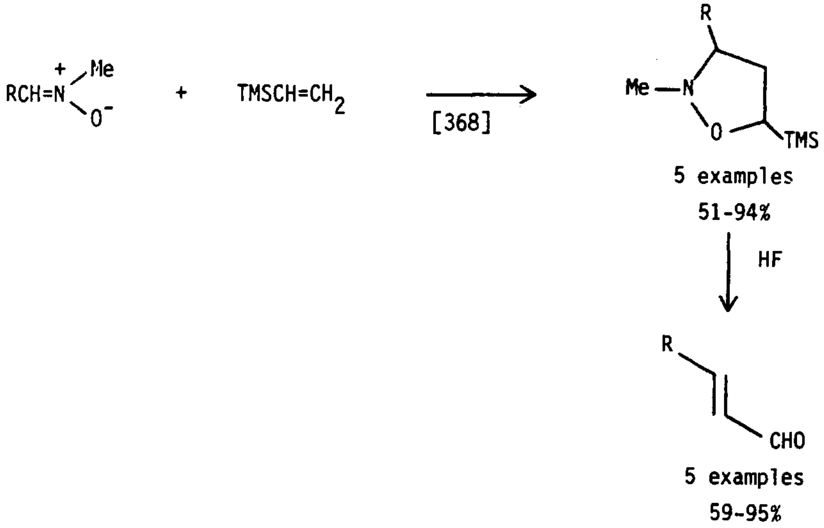


$$R^1R^2CH\overset{OH}{\underset{TMS}{C}}CH{=}CHR^3 \xrightarrow[\text{hexane}\ [367]]{^nBuLi\ (cat.)} R^1R^2CH\overset{OTMS}{C}HCH{=}CHR^3 \quad (463)$$

Octamethyltrisilane reacts with fluoride ion in the presence of aldehydes to give α-silyloxysilanes, which can be hydrolyzed to α-hydroxysilanes (Eqn. 464) Vinyltrimethylsilane reacts with nitrones to give α-alkoxysilanes, which are precursors to α,β-unsaturated aldehydes. (Eqn. 465)



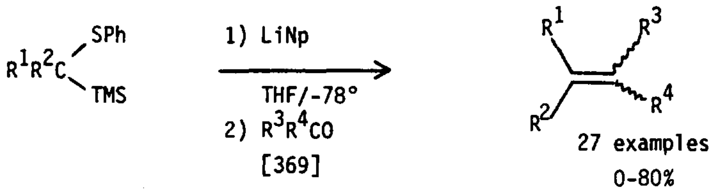
$$(TMS)_2SiMe_2 + RCHO \xrightarrow[\text{HMPA}\ [282]]{\text{TBAF}} (TMSO\underset{R}{C}H)_2SiMe_2 \xrightarrow{H_3O^+} (HO\underset{R}{C}H)_2SiMe_2 \quad (464)$$



(465)

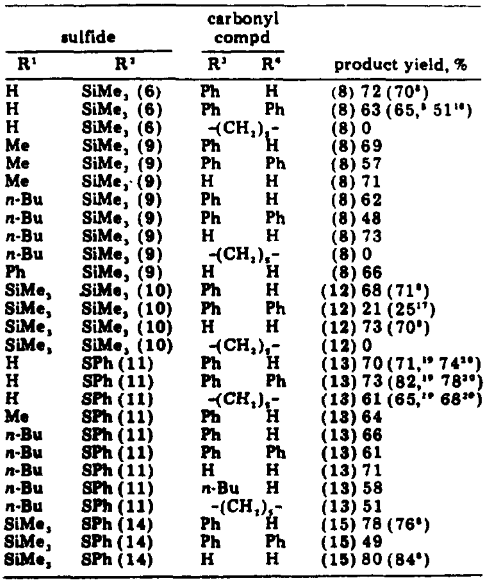
B. α-Metallated Organosilicons

Several α-metallated organosilicons were prepared and reacted resulting in a variety of highly useful and novel reactions. α-Thiophenoxysilanes were converted to α-lithiosilanes, which were then reacted with aldehydes and ketones. (Eqns 466, 467) The reaction also works well with 1-thiophenoxy-1-trimethylsilyl allenes. (Eqns. 468, 469) α-Silyllithium reagents were reacted with sulfur dioxide to form sulfines (Eqn. 470) and with sulfines to form olefins (Eqn. 471) Sulfinylanilines were also reacted with bisilyllithium reagents. These give thione S-imides. (Eqn. 472) The reaction of trimethylsilylpicolyllithium with oxime ethers gives aziridines and enamines. (Eqn. 473)



(466)

Table XVIII: Preparation and Reaction of α-Silylcarbanions with Carbonyl Compounds According to Eqn. 466.



sulfide		carbonyl compd		
R^1	R^2	R^3	R^4	product yield, %
H	$SiMe_3$ (6)	Ph	H	(8) 72 (70[8])
H	$SiMe_3$ (6)	Ph	Ph	(8) 63 (65,[8] 51[16])
H	$SiMe_3$ (6)	$-(CH_2)_5-$		(8) 0
Me	$SiMe_3$ (9)	Ph	H	(8) 69
Me	$SiMe_3$ (9)	Ph	Ph	(8) 57
Me	$SiMe_3$ (9)	H	H	(8) 71
n-Bu	$SiMe_3$ (9)	Ph	H	(8) 62
n-Bu	$SiMe_3$ (9)	Ph	Ph	(8) 48
n-Bu	$SiMe_3$ (9)	H	H	(8) 73
n-Bu	$SiMe_3$ (9)	$-(CH_2)_5-$		(8) 0
Ph	$SiMe_3$ (9)	H	H	(8) 66
$SiMe_3$	$SiMe_3$ (10)	Ph	H	(12) 68 (71[9])
$SiMe_3$	$SiMe_3$ (10)	Ph	Ph	(12) 21 (25[17])
$SiMe_3$	$SiMe_3$ (10)	H	H	(12) 73 (70[9])
$SiMe_3$	$SiMe_3$ (10)	$-(CH_2)_5-$		(12) 0
H	SPh (11)	Ph	H	(13) 70 (71,[19] 74[20])
H	SPh (11)	Ph	Ph	(13) 73 (82,[19] 78[20])
H	SPh (11)	$-(CH_2)_5-$		(13) 61 (65,[19] 68[20])
Me	SPh (11)	Ph	H	(13) 64
n-Bu	SPh (11)	Ph	H	(13) 66
n-Bu	SPh (11)	Ph	Ph	(13) 61
n-Bu	SPh (11)	H	H	(13) 71
n-Bu	SPh (11)	*n*-Bu	H	(13) 58
n-Bu	SPh (11)	$-(CH_2)_5-$		(13) 51
$SiMe_3$	SPh (14)	Ph	H	(15) 78 (76[8])
$SiMe_3$	SPh (14)	Ph	Ph	(15) 49
$SiMe_3$	SPh (14)	H	H	(15) 80 (84[8])

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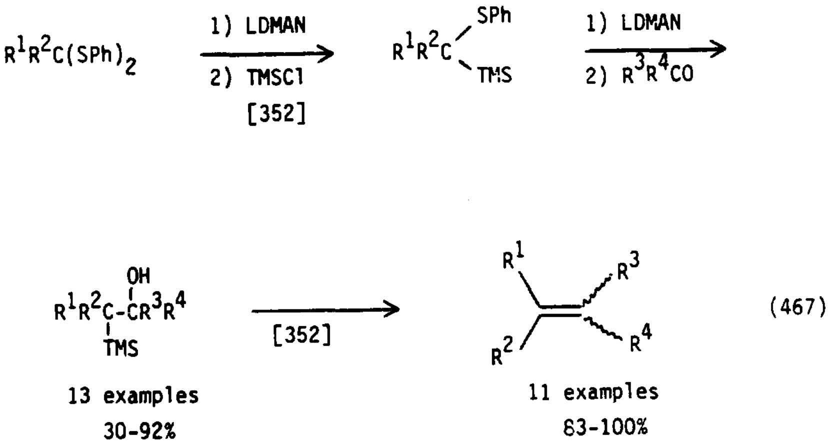
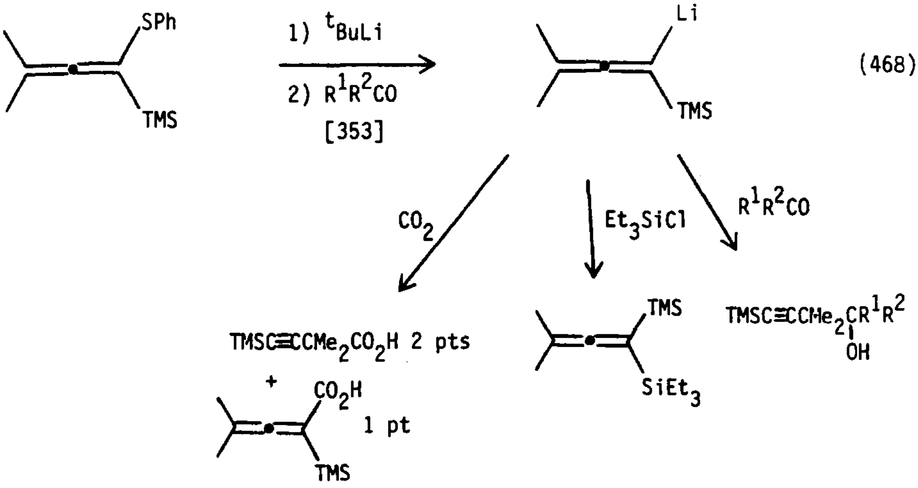
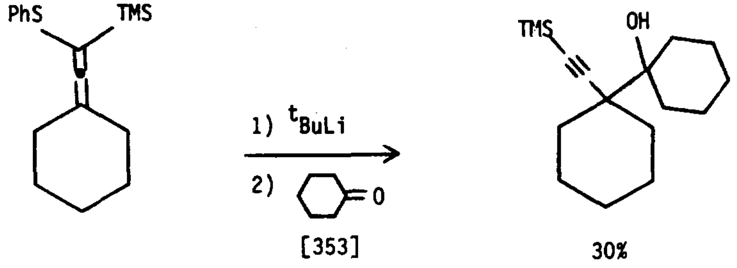


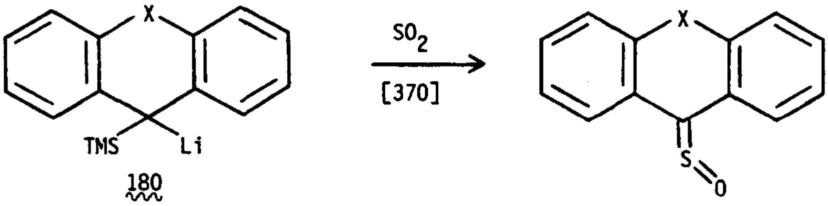
(467)



(468)



(469)

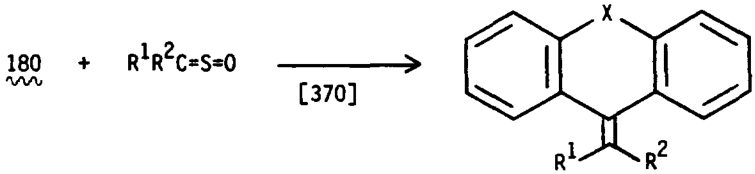


180

X = bond, O

8 examples
41-80%

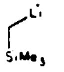
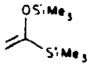
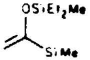
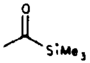
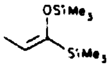
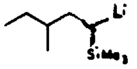
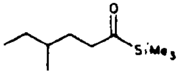
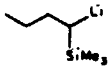
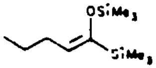
(470)

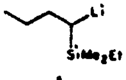
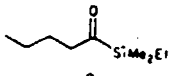
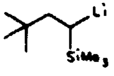
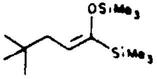
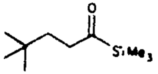
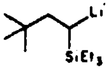
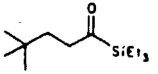
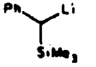
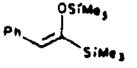
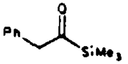


5 examples
34-50%

(471)

Table XIX: Preparation of Acylsilanes and Their Enol Silyl Ethers According to Eqn. 474.[a]

run	substrate	solvent	electrophile	product	yield, %[b]
1[c]	 **1a**	Et_2O	Me_3SiCl	 **5**	86 (75)
2			$Et_2MeSiCl$		80
3			H_2O		72
4[c]	 **1b**	Et_2O	Me_3SiCl		88 (E = ~100)[d]
5[e]	 **1c**	Et_2O	H_2O	 **7**	68
6[e]	 **1d**	THF	Me_3SiCl		(63) (E = ~100)[d]

7[e]	 **1e**	THF	H_2O	 **8**	(66)
8[e]	 **1f**	Et_2O	Me_3SiCl		96 (*E* = ~100)[d]
9			H_2O		(80)
10[e]	 **1g**	Et_2O	H_2O		73 (61)
11[f]	 **1h**	TMEDA	Me_3SiCl		92 (*E*/*Z* = 89/11)[d]
12			H_2O		94

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[a] Unless otherwise stated, all reactions were performed at 15 °C for 1-1.5 h on a 5-mmol scale using concentration of 0.2-1.1 M of lithium compounds. [b] Determined by GLC. Isolated yields are in the parentheses. [c] Prepared from silylmethyl chlorides and Li dispersion; see ref 7. [d] Determined by ^1H NMR of vinylic hydrogen; generally, the vinylic H of *E* isomers resonate at higher fields. [e] Prepared from vinylsilanes and RLi (Et_2O or THF, −20 °C, 1-4 h); see: Hudrlik, P. F.; Peterson, D. *J. Am. Chem. Soc.* 1975, *97*, 1464. Mulvaney, J. E.; Gardlund, Z. G. *J. Org. Chem.* 1965, *30*, 917. [f] Prepared from benzylsilane and *n*-BuLi (TMEDA, 0 °C, 0.5 h); see: Chan, T. H.; Chang, E. *J. Org. Chem.* 1974, *22*, 3264.

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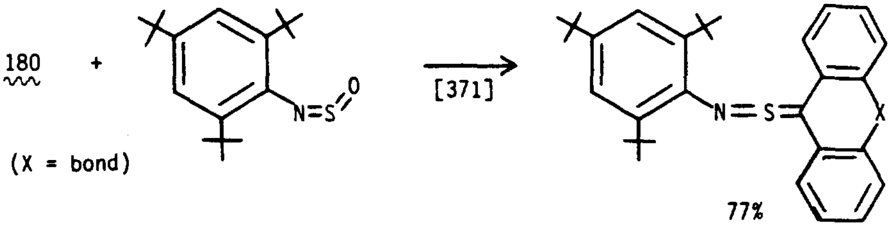
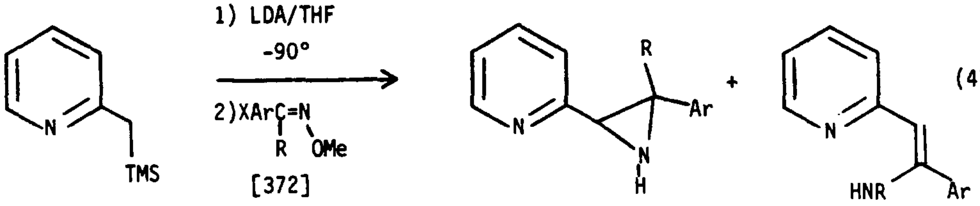


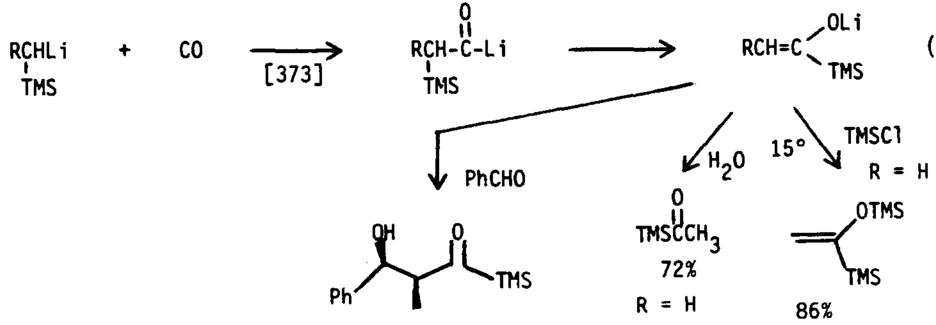
(472)



(473)

X	R			%
H	H	78	22	49
Cl	H	29	71	42
Me	H	33	67	45
MeO	H	38	62	45
H	Me	--	--	
H	Me	--	--	

The reaction of α-silyllithium reagents with carbon monoxide produces the lithium enolate of an acylsilane after intramolecular rearrangement of the initial α-silylallithium species. (Eqn. 474).



(474)

R = Me

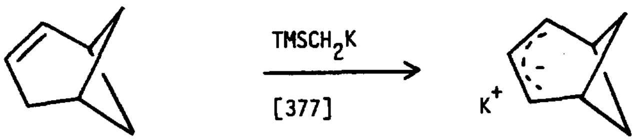
erythro 93

threo 7

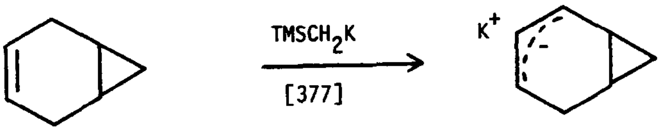
Tris(trimethylsilyl)methyllithium has been prepared by an improved route [374]. It has been reacted with trifluorosilanes. (Eqn. 475) Monodeuterated tetramethylsilane was prepared from trimethylsilyllithium. (Eqn. 476) Trimethylsilylmethylpotassium has been employed to deprotonate olefins. (Eqns. 477-479)

$$(TMS)_3CLi \quad + \quad F_3SiR \xrightarrow[\text{[375]}]{} (TMS)_3C\text{-}SiF_2R \qquad (475)$$

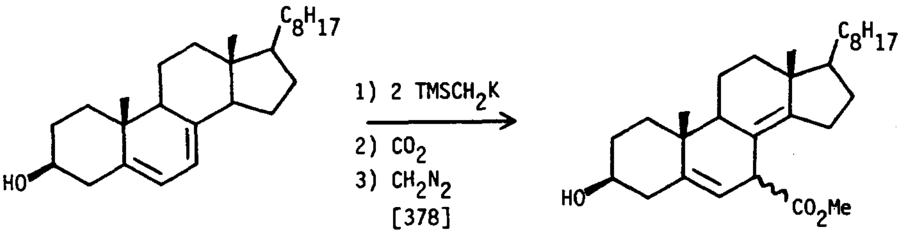
$$TMSCH_2Cl \xrightarrow[\substack{\text{2) purity} \\ \text{3) } D_2O \\ \text{[376]}}]{\text{1) 2Li}} \underset{96\%}{TMSCH_2D} \qquad (476)$$



(477)



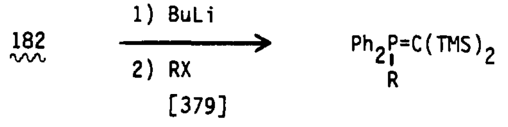
(478)



(479)

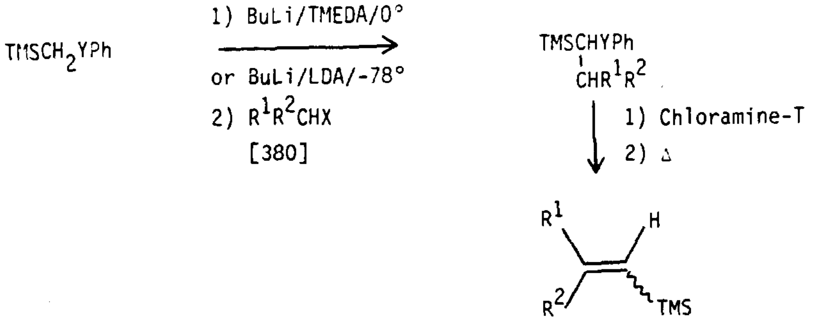
A number of α-functional-α-silylmethyllithium reagents have been reported. The α-diphenylphosphinylsilane **181** can be lithiated and silylated to give **182** (Eqn. 480), which can be lithiated and reacted with electrophiles to give methylene phosphoranes (Eqn. 481). Trimethylsilylmethyllithium reagents containing thio, seleno and telluro groups have been prepared and reacted with alkyl halides. Treatment of the products with chloramine-T gives vinylsilanes. (Eqn. 482) Lithiated 2-trimethylsilyl-1,3-dithiane with **183** gives the dithianylidenephosphine **183a**. (Eqn. 483) α-Trimethylsilyl-α-amine nitriles were prepared and lithiated and the lithium reagent condensed with benzaldehyde. (Eqn. 484) Bis(trimethylsilyl)chloromethyllithium was prepared and reacted with difluorodialkylsilanes. (Eqn. 485) α-chlorobenzyltrimethylsilane can be deprotonated and alkylated or silylated. (Eqn. 486) (Dichloromethyl)trimethylsilane can be deprotonated and quenched with aldehydes to give 1,1-dichloroalkenes. (Eqn. 487) The epoxide is formed from the reaction of α-iodo-α-(diphenylsilyl)methyllithium and benzaldehyde. Treatment of the epoxide with phenyllithium provides cis stilbene. (Eqn. 488) Deprotonation of **184** gives **185**, which serves as an ester homologation unit. (Eqn. 489) α-Lithiotrimethylsilyl acetonitrile reacts with enones in a Michael fashion much better than lithio acetonitrile itself. (Eqn. 490)

$$\underset{181}{Ph_2PCH_2TMS} \xrightarrow[\substack{2)\ TMSCl \\ [379]}]{1)\ BuLi} \underset{182}{Ph_2PCH(TMS)_2} \qquad (480)$$



$$182 \xrightarrow[\substack{2)\ RX \\ [379]}]{1)\ BuLi} Ph_2\underset{R}{P}{=}C(TMS)_2 \qquad (481)$$

R = Ph_2P; $^{t}Bu_2P$; $(cC_6H_{11})_2P$; Me; Et; ·Pr; ^{i}Pr; ^{n}Bu; $TMSCH_2$; PhCO; $^{t}BuCO$; MesCO

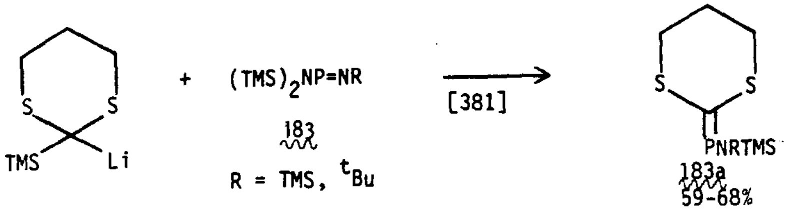


(482)

Y = S 6 examples 30-92%

Y = Se 5 examples 24-82%

Y = Te 4 examples 56-64%



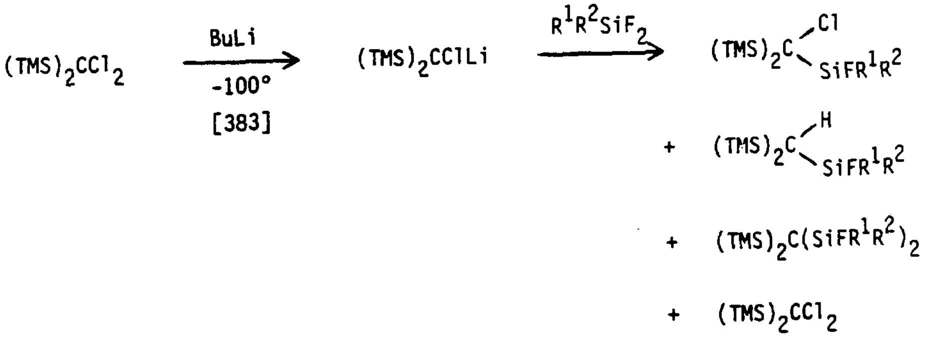
183

183a

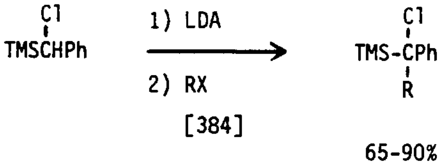
59-68%

(483)

(484)



(485)



$$\mathrm{TMS}\overset{\mathrm{Cl}}{\mathrm{C}}\mathrm{HPh} \xrightarrow[\substack{\text{2) RX}\\ [384]}]{\text{1) LDA}} \mathrm{TMS\text{-}}\underset{\mathrm{R}}{\overset{\mathrm{Cl}}{\mathrm{C}}}\mathrm{Ph} \qquad (486)$$

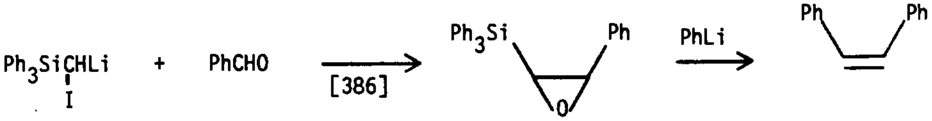
65-90%

R = TMS, Me, Et, Bu, ^{i}Pr, allyl

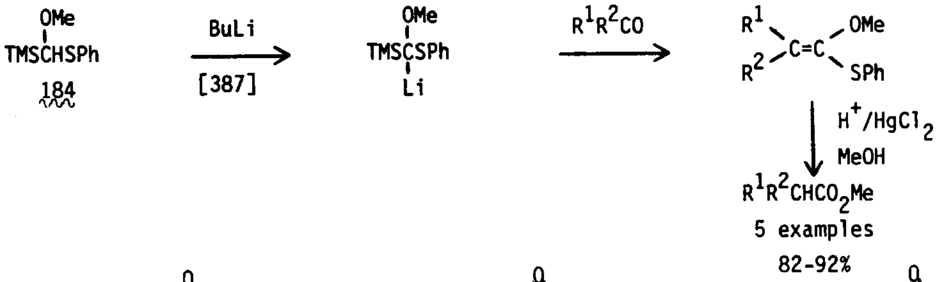
$$\mathrm{TMSCHCl_2} \xrightarrow[\substack{\text{or LDA}\\ \text{THF/-100°}\\ \text{2) RCHO}\\ [385]}]{\text{1) BuLi}} \mathrm{RCH{=}CCl_2} \qquad (487)$$

6 examples

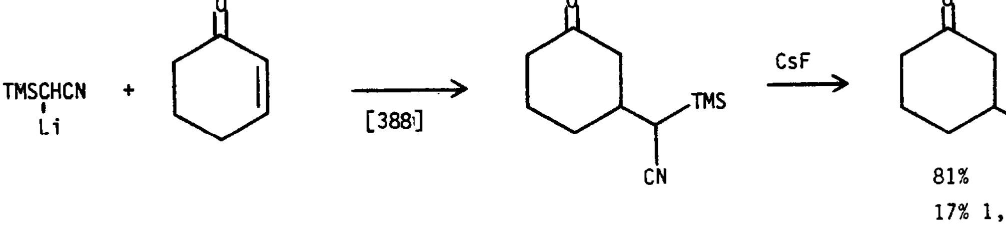
64-97%



(488)



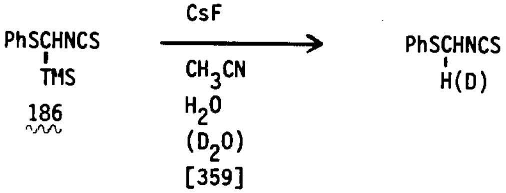
(489)



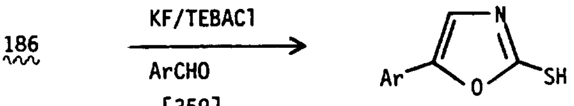
(490)

C. Reactions

One of the more exciting and useful developments in the applications of organosilicons to synthesis to emerge has been the treatment of α-functional organosilicons with fluoride ion to generate, via nucleophilic desilylation, a functionalized carbanion. The isothiocyanate **186** reacts with fluoride ion in the presence of water to give protio (or deuterio with D_2O) desilylation (Eqn. 491) and in the presence of aryl aldehydes to give oxazolethiols (Eqn. 492) Trimethylsilylmethylaziridines containing a carbanion stabilizing group undergo ring opening upon treatment with fluoride ion. (Eqn. 493, 494) The reaction is proposed as proceeding via the enolate anion of an imine. (Eqn. 494) Trimethylsilylmethylpyridinium triflates undergo a 1,3-dipolar addition to dimethylacetylene dicarboxylate in the presence of fluoride ion. (Eqns. 496, 497) Further examples of this silicon-mediated 1,3 dipolar cycloaddition of acylic systems are shown in Eqns. 498-500. The last example is that of an azomethine ylide.

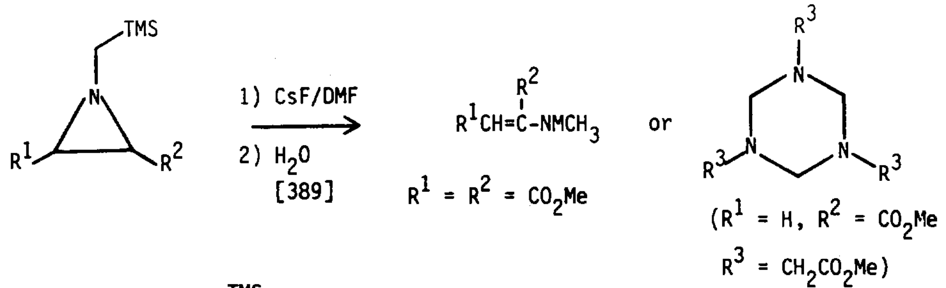


$$\underset{\underset{186}{\text{TMS}}}{\text{PhSCHNCS}} \xrightarrow[\substack{CH_3CN \\ H_2O \\ (D_2O) \\ [359]}]{CsF} \underset{\text{H(D)}}{\text{PhSCHNCS}} \qquad (491)$$

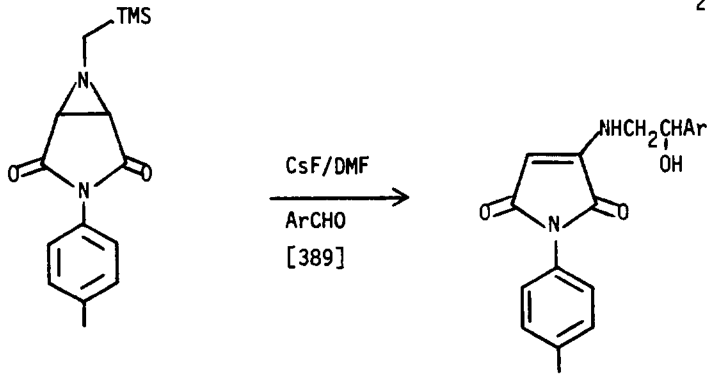


3 examples
71-79%

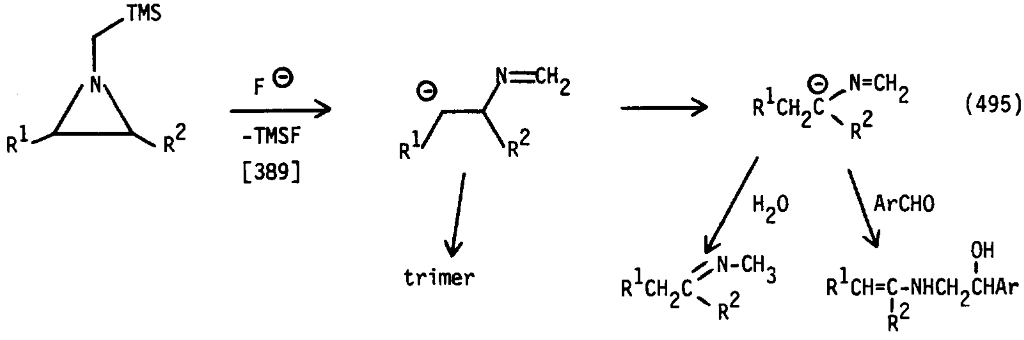
(492)



(493)

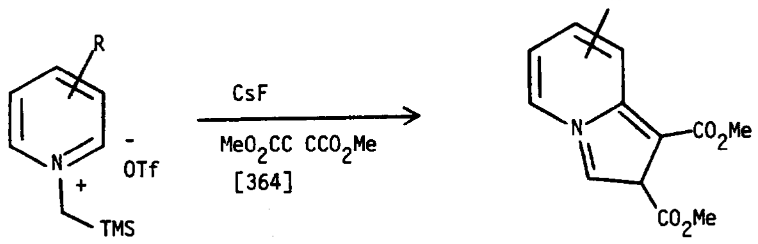


(494)



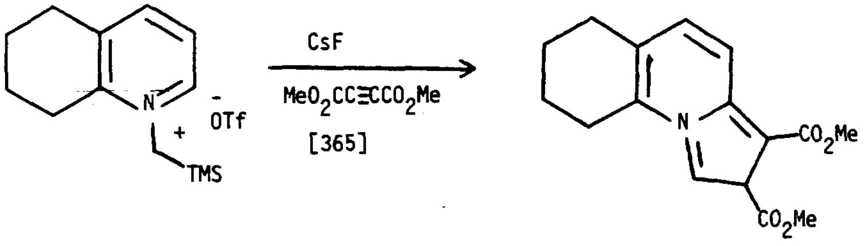
(495)

R^1 = anion stabilizing group

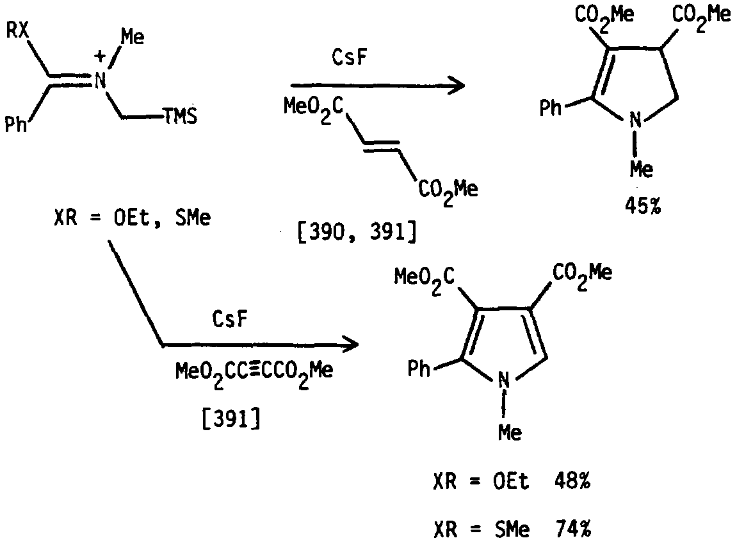


(496)

5 examples
83-100%

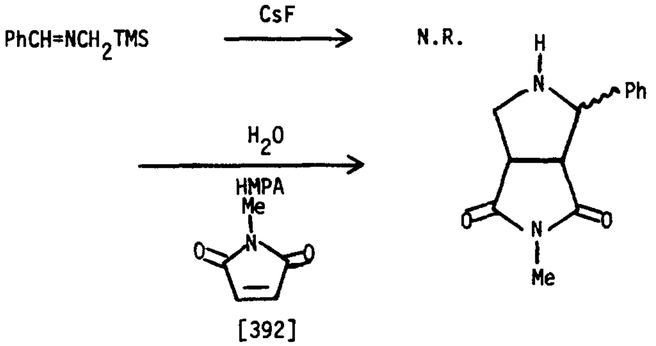


(497)



(498)

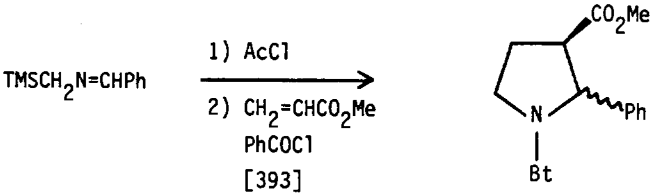
(499)



(500)

also with other unsaturated esters and nitriles

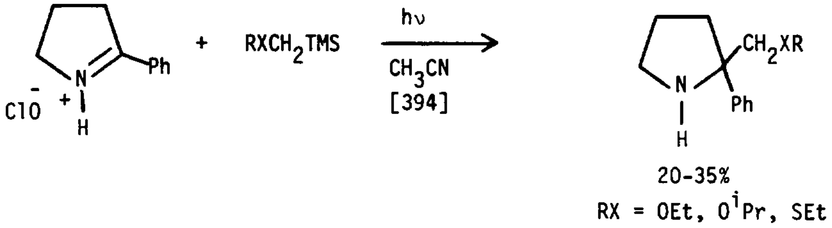
Pyrollidines were prepared from α-silylated imines upon treatment with acetyl chloride and then methyl acrylate in the presence of benzoyl chloride (Eqn. 501)



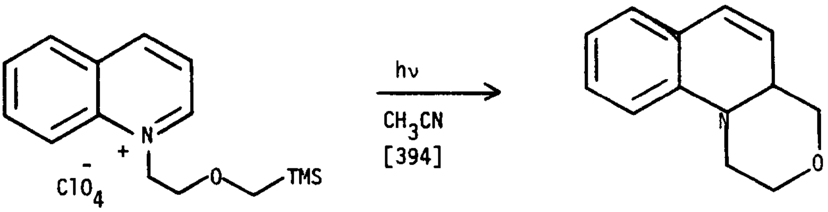
(501)

Pyrolinium and quinolinium salts react with α-alkoxy and α-thioethoxysilanes upon photolysis (Eqns. 502) In the quinolinium case the reaction was carried out in an intramolecular sense. (Eqns. 503-505)

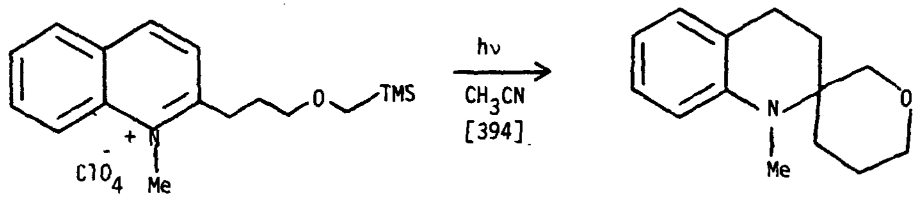
Unsaturated bromomethylsilanes cyclize upon treatment with tri-n-butyltin hydride. This concept was utilized in the preparation of diols as shown in Eqns. 506, 507.



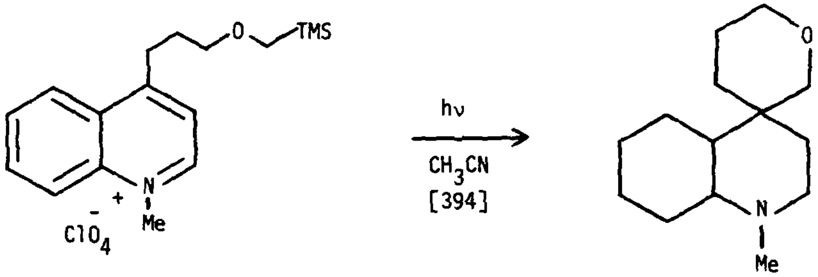
(502)



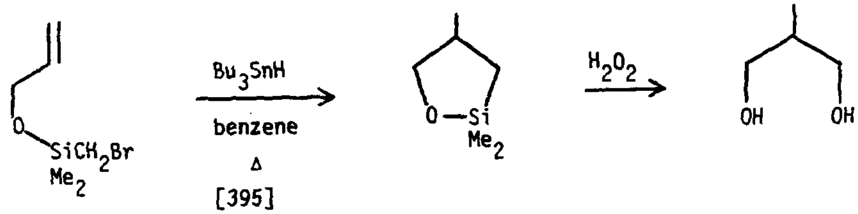
(503)



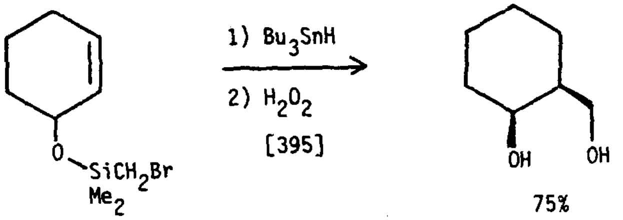
(504)



(505)

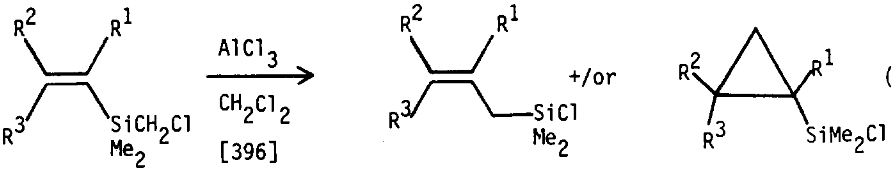


(506)



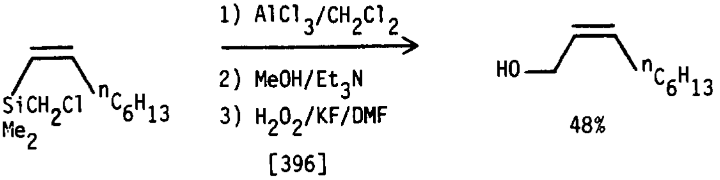
(507)

Chloromethylvinylsilanes rearrange upon treatment with aluminum chloride. The geometry of the vinyl group is maintained. (Eqn. 508) Again the product can be oxidized to the alcohol. (Eqn. 509)α,α-Dichlorobenzylsilanes react with hexamethyldisilane in the presence of palladium (0) to give silylated stilbenes. (Eqn. 510) The reaction of dichloromethyl- or dibromomethyl-tris(tert-butyl)silane with organolithium reagents or LDA gives several products. (Eqn. 511)

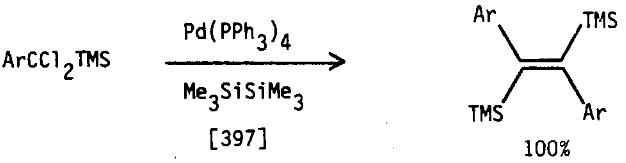


(see table XXI previous page)

(508)

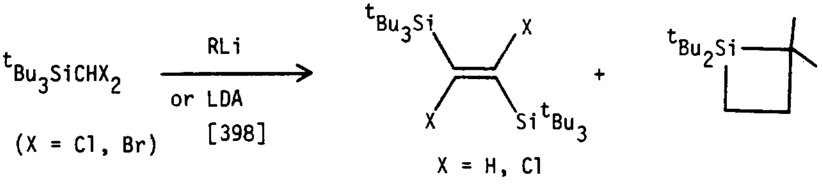


(509)



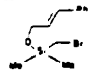
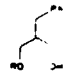
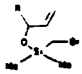
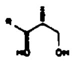
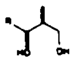
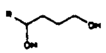
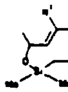
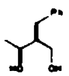
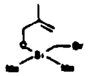
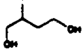
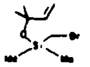
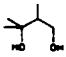
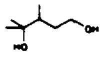
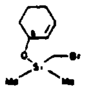
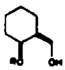
Ar = Ph, pClC6H4

(510)



(511)

Table XX: Synthesis of 1,3 Diols According to Eqn. 507.[a]

run	substrate 1	yield,[b] %	products [ratio,[c] %]		
					
1	1a	85	3a, R = H [100]		
2	1a	80	3b, R = Ac [100][d]		
					
3	1b, R = Me	95	3c [69]	3d [15]	4a [16]
4	1c, R = *i*-Pr	90	3e [82]	[~0]	4b [18]
5	1d, R = *t*-Bu	91	3f [71]	[0]	4c [29]
6	1e, R = CH_2=CH	85	3g [61]	3h [11]	4d [28]
7	1f, R = Ph	88	3i [54]	3j [5]	4e [41]
					
8	1g, R¹ = H; R² = Ph	85	3k [84]	3l [16]	
9	1h, R¹ = Ph; R² = H	94	3k [100]	3l [0]	
					
10	1i	52	3m [35]		4f [65]
					
11	1j	83	3n [91]		4g (9)
					
12	1k	75	3o, R = H [100]		
13	1k	78	3o, R = Ac[100][d]		

[a] To a solution of 1 (2 mmol) in 36 mL of benzene was added dropwise a mixture of *n*-Bu_3SnH (1.2-1.5 mmol) and AIBN (0.03 mmol) in 4 mL of benzene at reflux over a 2-h period followed by heating for an additional 1-2 h. The reaction can be carried out in 0.025-0.05 M solution. After evaporation of benzene under reduced pressure (under atmospheric pressure for 3, 4, 6, 10, and 11), the residual oil was treated with 1.2 mL of 30% H_2O_2 (method A) in 5 mL of DMF and KF (10 mmol) at 60 °C for 7-8 h (run 1, 2, 7, 8, and 9) or (method B) in 3 mL of MeOH and 3 mL of THF and Na_2CO_3 (2 mmol) at reflux for 5 h (run 3-6 and 10-13). After the usual workup, purification was achieved by column chromatography (silanized SiO_2, Merck 7719; ether-hexane). Structures were determined by ^1H NMR (90 MHz) after purification of HPLC. Stereochemical assignment of the 1,3-diols for runs 3-9 was determined by ^1H NMR data of the diols and their ketals; see supplementary material for their spectral data. For run 12, the cis configuration was assumed since the diol was not identical with the trans product from the Prins reaction with cyclohexene; see ref 8.

[b] Isolated yields. [c] After separation of 1,4-diols, the ratio was determined by HPLC of their ketals with acetone and cyclohexanone (run 3, 8, and 9), ^1H NMR of a mixture of 1,3-diols (run 7, see ref 7), or ^1H NMR of the benzoates of a mixture (run 4 and 6). [d] Acetylation was performed with acetic anhydride in pyridine and KF at 40 °C for 2 days.

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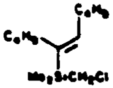
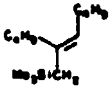
Table XXI: $AlCl_3$ Rearrangement of Alkenyl(chloromethyl silanes According to Eqn. 508.

alkenyl(chloromethyl)silane	rearrangement product(s)[b]		yield,[c] %	allyl/cyclopropyl ratio[d]
 1	 7		89	100/0
 5	 14	 15	83	93/7
 3	 10	 11	65	87/13
 2	 8	 9	58	78/22
 4	 12	 13	93	77/23
 6		 16	44	0/100

[a] Carried out in dry CH_2Cl_2 at room temperature in the presence of $AlCl_3$ (10 mol %) for 5-25 min. [b] After methylation. [c] Isolated yield. [d] Determined by ^1H NMR.

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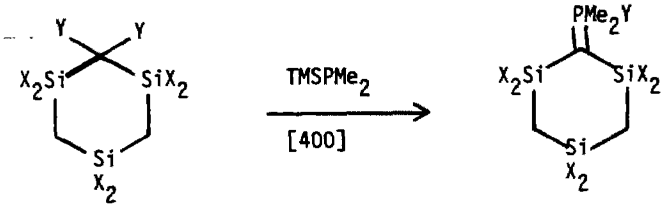
Trimethylsilylazide reacts with arylmagnesium bromides and aryllithium reagents to give anilines. (Eqn. 512, 513) The α,α-dihalosilanes **187** react with trimethylsilyldimethylphosphine to give the ylides **188**. (Eqn. 514) This class of compounds reacts with phosphorus trichloride to cleave the silicon carbon bond. (Eqns. 515, 516)

$$\mathrm{ArMgBr} \xrightarrow[\text{2) } H_2O \quad [399]]{\text{1) } TMSCH_2N_3} \mathrm{ArNH_2} \quad \begin{array}{c}\text{5 examples}\\ \text{69-92\%}\end{array} \tag{512}$$

$$\mathrm{ArLi} \xrightarrow[\text{2) } H_2O \quad [399]]{\text{1) } TMSCH_2N_3} \mathrm{ArNH_2} \quad \begin{array}{c}\text{5 examples}\\ \text{69-92\%}\end{array} \tag{513}$$

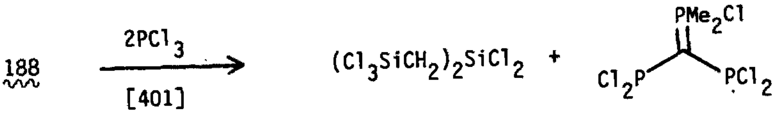


187 **188**

(514)

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

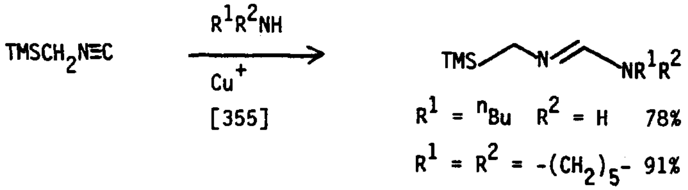
$$(Cl_3Si)_2C{=}PMe_2Cl \xrightarrow[{[401]}]{2PCl_3} (Cl_2P)_2C{=}PMe_2Cl + 2SiCl_4 \tag{515}$$



(516)

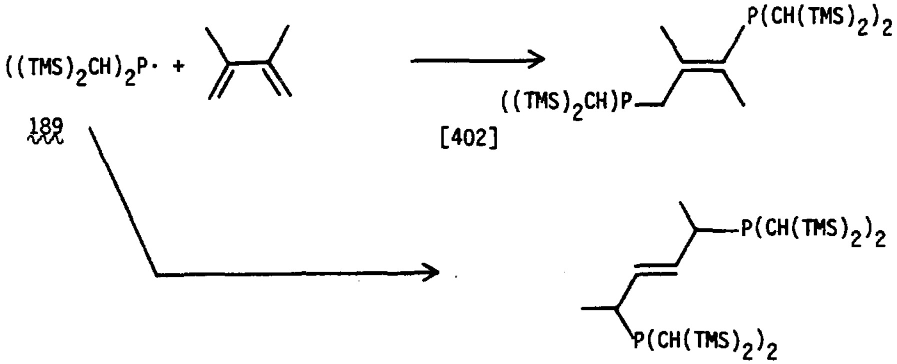
Trimethylsilylisocyanide was reacted with alcohols to give protiodesilylation (Eqn. 517) and with primary or secondary amines to give formamidines. (Eqn. 518)

$$\mathrm{TMSCH_2N{\equiv}C} \xrightarrow[\mathrm{Cu^+}\ [355]]{\mathrm{ROH}} \mathrm{CH_3N{\equiv}C} \qquad (517)$$



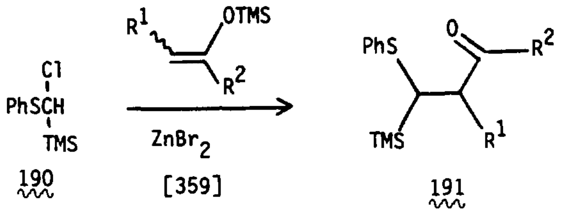
(518)

The stable phosphoryl radical 189 was reacted with conjugated dienes to give 1,4 addition. (Eqns. 519, 520) The α-functional organosilane 190 reacts with enol silyl ethers with displacement of the chloride. (Eqn. 521) The product of this reaction can be converted to β-trimethylsilyl enones. (Eqn. 522)

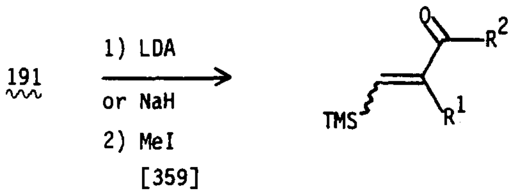


(519)

(520)



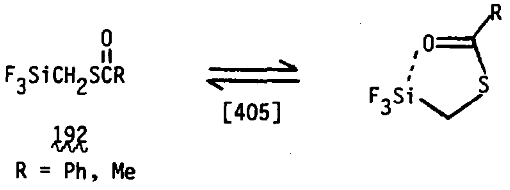
(521)



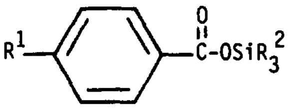
(522)

D. Spectroscopic and Other Studies

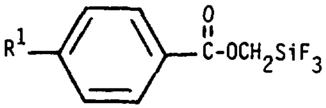
The acetolysis of the chloromethyl group in siloxanes was studied. [403] The relative nucleophilicities of 9-trimethylsilyl-9-lithiofluorene with respect to other 9-substitued-9-lithiofluorenes was determined. [404] The conformational isomerism in **192** was studied in the solid state and in solution. (Eqn. 523) The structure of 3,3-dimethyl-3-silathiethane was determined by election diffraction. [406] The silyl esters **193** were subjected to dipole moment studies [407] as well as ^{13}C-NMR studies [408]. The closely related system **194** was the subject of a ^{17}O-NMR study. [409] Halomethylsilanes comprised the subject of an NQR study. [410] The bis(silylmethyl)mercury systems **195** were studied by 'H, ^{29}Si and ^{199}Hg NMR. [411] The trimethylsilylmethyltin compounds **196** were studied by ^{119}Sn, ^{13}C, and ^{1}H NMR. [412] The mass spectra of α-thiosilanes **197**, **198** and **199** were reported. [413] The crystal structures of **200** [414] and **201** [415] have been determined. Compound **200** is monomeric and **201** is dimeric.



(523)



193



194

$(Me_{3-n}X_nSiCH_2)_2Hg$

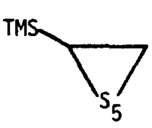
n = 0-3

195

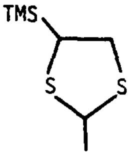
$(TMSCH_2)_nMe_{3-n}Sn$

n = 1-3

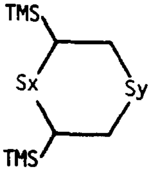
196



197



198



199

X = 2, Y = 1
X = 2, Y = 2

$Li[C(SiMe_2Ph)_3]THF$

200

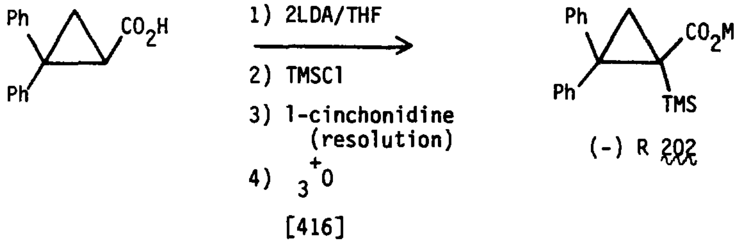
$[Li(thf)_4][LiC(TMS)_3]_2$

201

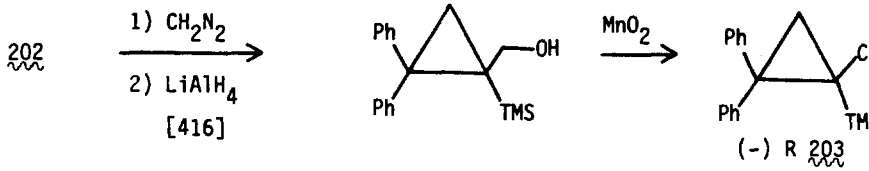
XIII. β-FUNCTIONAL ORGANOSILANES

A. Preparation

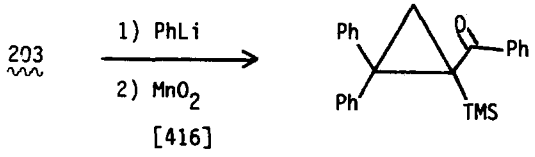
Several organosilanes containing the β-carbonyl group were reported. The trimethylsilylcyclopropane carboxylic acid **202** was prepared and resolved. (Eqn. 524) This served as a percursor to the aldehyde (Eqn. 525) and the phenyl ketone (Eqn. 526). It was used to study the stereointegrity of the α-silyl radical (Eqn. 527) and α-silyl anion (Eqn. 528). It was found that silyl ketene acetals rearrange to α-silyl esters at high pressure. The reaction is intermolecular. (Eqns. 529, 530) Hexafluoroactone reacts with trimethylsilylketene to give α-trimethylsilyl-β-lactones via reaction with the monomer and the dimer. (Eqn. 531) The rhodium catalyzed rearrangement of 2-trimethylsilyl allyl alcohols gives β-ketosilanes, which are rearranged to their enol silyl ethers. (Eqn. 532) In a like manner 4-trimethylsilyl allyl alcohols are rearranged to β-ketosilanes. (Eqn. 533) The reaction of α-(diphenylmethylsilyl) esters with Grignard reagents gives β-ketosilanes. (Eqn. 534) The reaction proceeds via the enolate of the β-ketosilane. (Eqn. 538) Vinylmagnesium bromide adds twice, the second addition on a Michael fachion. (Eqn. 536) Treatment of 2-alkoxy-1-bromo trimethylsilylcyclopropanes with base and subsequent hydrolysis of the acetal or ketal gives α-trimethylsilyl α,β-unsaturated aldehydes of ketones (Eqns. 537, 538)



(524)

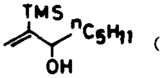
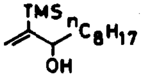
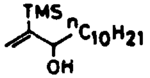
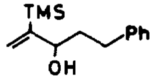
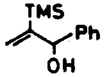
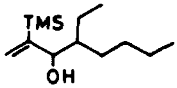
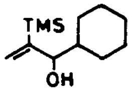
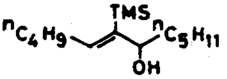
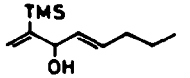


(525)



(526)

Table XXII: Formation of β-Ketosilanes According to Eqn. 532.

Entry	Allyl alcohol (1)	Reaction time (h)	Conversion (%)	Yield of 2[b)] (%)
1	 (1a)	1	100	60
2	 (1b)	0.5	100	90
3		1.5	0	0[c)]
4		20	100	0 (82)
5	 (1c)	0.25	100	96
6		20	100	0 (80)
7	 (1d)	0.5	100	94
8		20	100	0 (61)
9	 (1e)	0.08	100	56 (17)
10		20	100	0 (83)
11	 (1f)	1	100	82
12	 (1g)	0.25	100	81
13	 (1h)	1.25	100	60 (34)
14		0.5	100	87[d)]
15		45	100	0 (66)
16	 (1i)	1	100	82[e)]

a) Reactions were carried out in 0.5 mmol scale at 105°C.

b) Isolated yields. Values in parentheses show the yield of trimethylsilyl enol ether 3.

c) Reaction was carried out at 75°C.

d) Ten mol % of $HRh(PPh_3)_4$ was used and filtered from the reaction mixture before distillation.

e) About 7% of 2-trimethylsilyl-1-octan-3-one was included.

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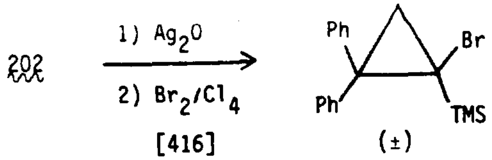

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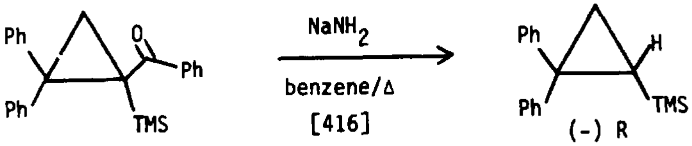

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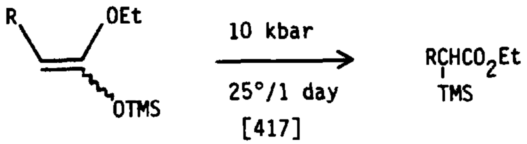

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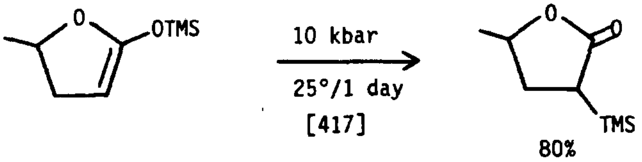

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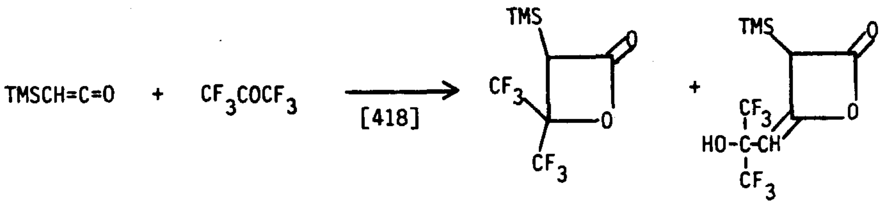
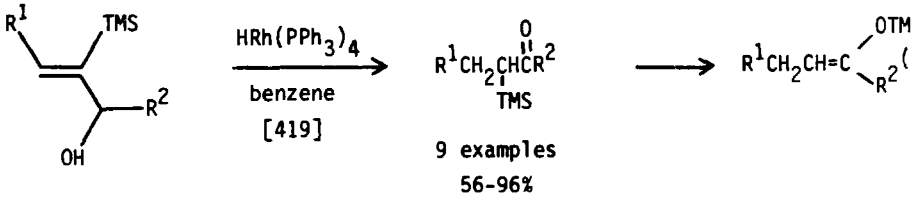
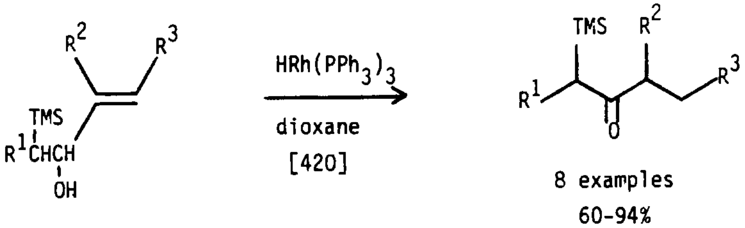


(531)



(532)



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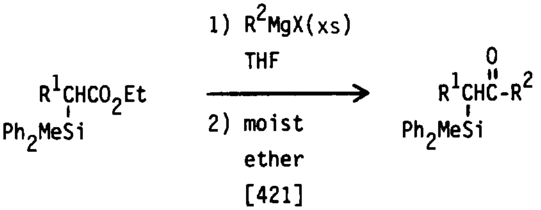
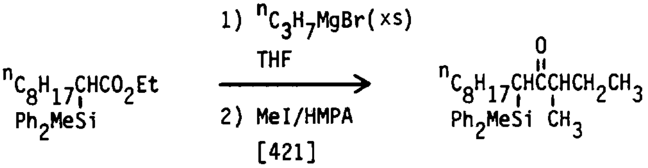


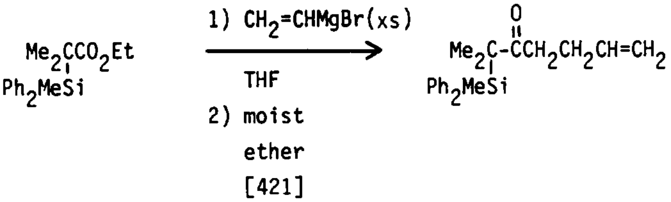
$$\underset{\displaystyle Ph_2MeSi}{R^1CHCO_2Et} \xrightarrow[\text{2) moist ether [421]}]{\text{1) } R^2MgX\text{(xs) THF}} \underset{\displaystyle Ph_2MeSi}{R^1CH\overset{O}{\overset{\|}{C}}\text{-}R^2}$$

(534)



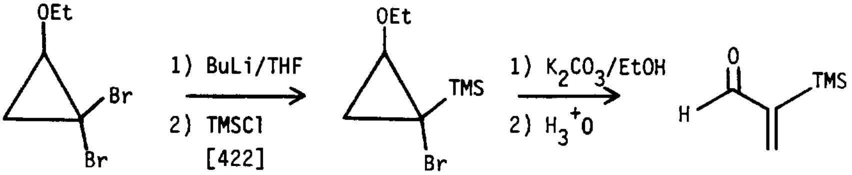
$$\underset{\displaystyle Ph_2MeSi}{{}^nC_8H_{17}CHCO_2Et} \xrightarrow[\text{2) MeI/HMPA [421]}]{\text{1) } {}^nC_3H_7MgBr\text{(xs) THF}} \underset{\displaystyle Ph_2MeSi\ \ CH_3}{{}^nC_8H_{17}CH\overset{O}{\overset{\|}{C}}CHCH_2CH_3}$$

(535)



$$\underset{\displaystyle Ph_2MeSi}{Me_2CCO_2Et} \xrightarrow[\text{THF 2) moist ether [421]}]{\text{1) } CH_2\text{=}CHMgBr\text{(xs)}} \underset{\displaystyle Ph_2MeSi}{Me_2C\text{-}\overset{O}{\overset{\|}{C}}CH_2CH_2CH\text{=}CH_2}$$

(536)



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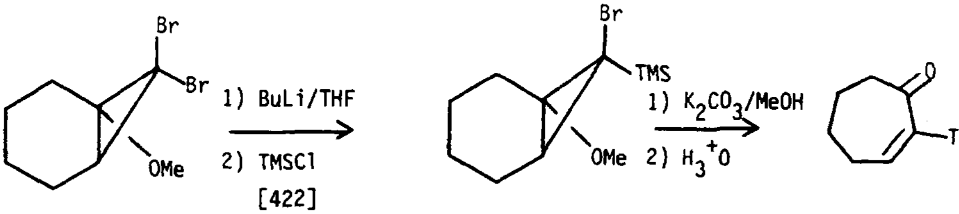
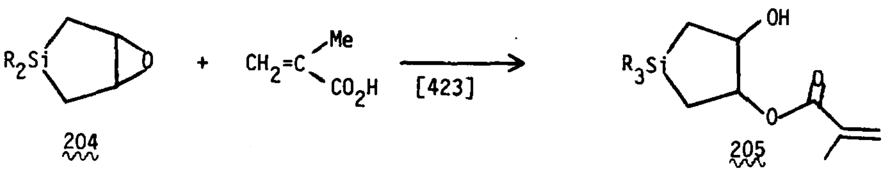


(538)

The β-epoxysilane **204** was reacted with methacrylic acid to give the β-hydroxysilane **305**. (Eqn. 539) Several β-functional organosilanes were prepared from 1-trimethylsilylvinylmagnesium bromide as seen below. (Eqn. 540-545)



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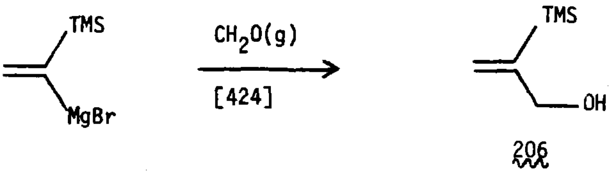
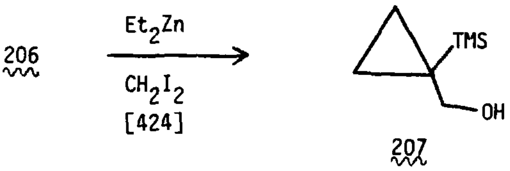


(540)



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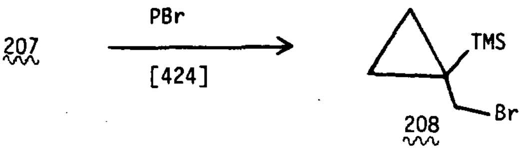

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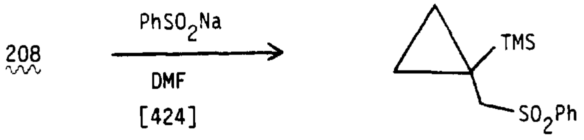

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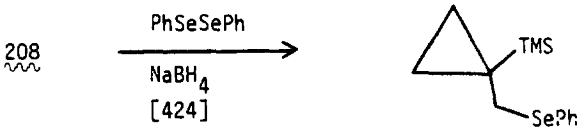

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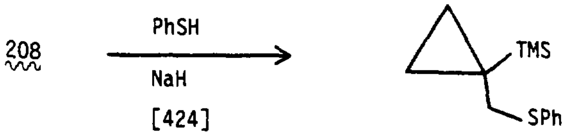
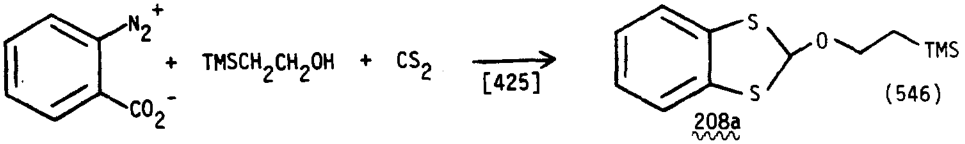


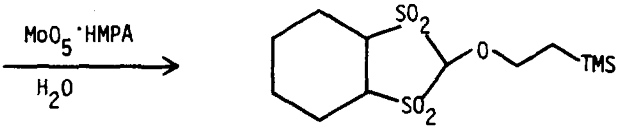
(545)

B. Reactions

A carbonyl 1,2 dipole synthon was fashioned from the β-alkoxysilane **208a**, prepared as shown in Eqn. 546. The carbanion nature of the synthon is seen from the alkylations (Eqn. 547) and Michael additions (Eqn. 549). The acylonium nature proceeds via a reactive acylating species which reacts with oxygen or nitrogen nucleophiles (Eqn. 550) or intramoleculary with carbon nucleophiles (Eqn. 551). Alkylation of **209** followed by reductive removal of the bissulfane and the trimethylsilylethyl units makes this a $HOCH_2^{\ominus}$ synthon as well. (Eqn. 552) An indirect approach to hemisuccinates was reported as shown in Eqn. 553.

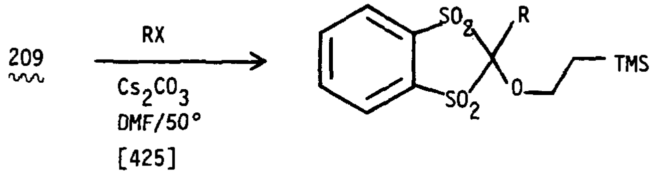


(546)



209

(546)



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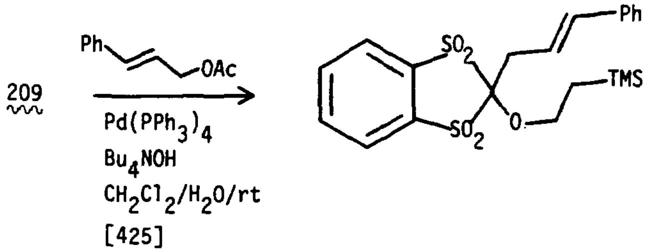

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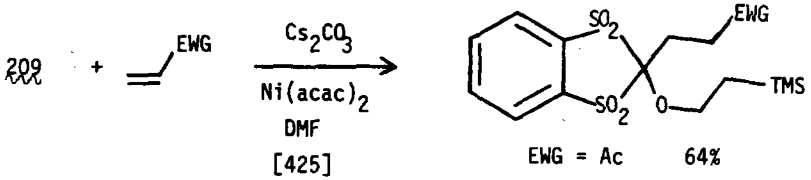
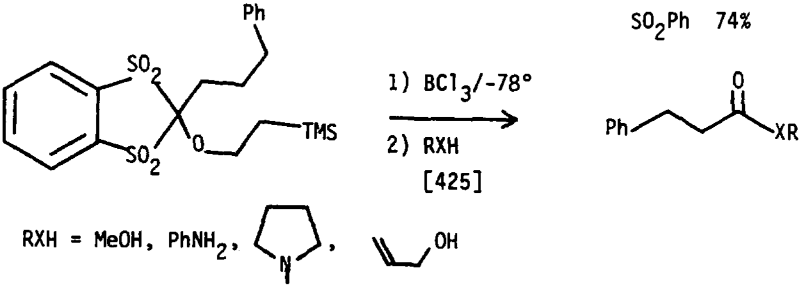
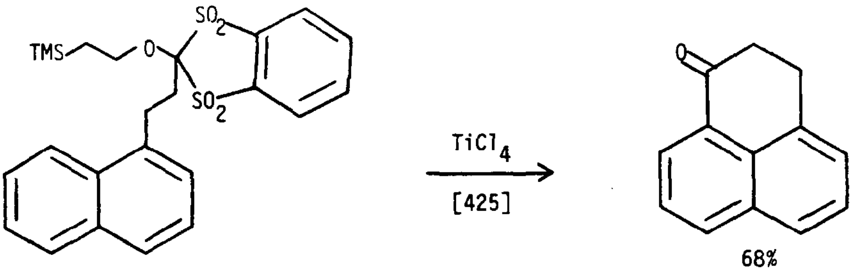


(549)

EWG =		
EWG =	Ac	64%
	CN	46%
	SO_2Ph	74%

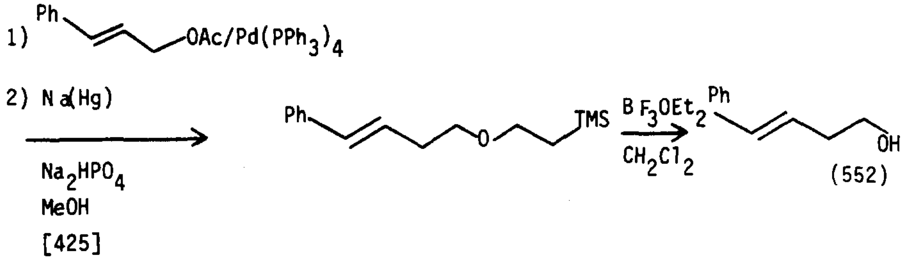


(550)



(551)

209



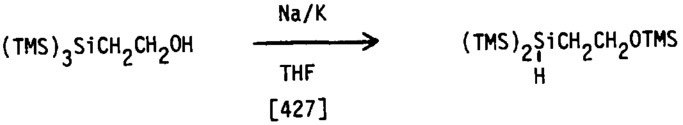
(552)

$$HO_2C(CH_2)_2CO_2CH_2CH_2TMS \xrightarrow[\text{2) } Bu_4NF \text{ [426]}]{\text{1) ROH}} RO_2C(CH_2)_2CO_2H \qquad (553)$$

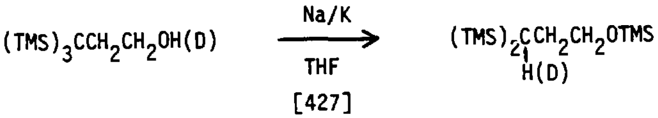
6 examples

83-92%

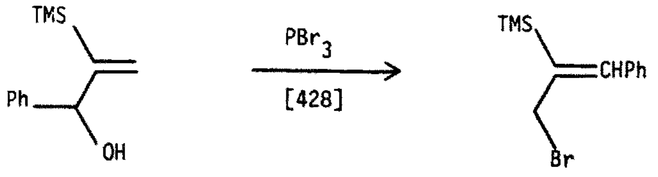
A new anionic rearrangement of silicon from silicon to oxygen was reported. (Eqn. 554) A similar rearrangement was observed for the carbon system. The proton that replaces the migrating silicon group originates from the OH group. (Eqn. 555) Treatment of β-hydroxysilane **210** with phosphorus tribromide gives the rearranged allyl bromide **211**. (Eqn. 556)



$$(TMS)_3SiCH_2CH_2OH \xrightarrow[\text{THF [427]}]{\text{Na/K}} (TMS)_2\underset{H}{Si}CH_2CH_2OTMS \qquad (554)$$



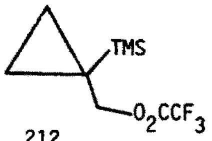
$$(TMS)_3CCH_2CH_2OH(D) \xrightarrow[\text{THF [427]}]{\text{Na/K}} (TMS)_2\underset{H(D)}{C}CH_2CH_2OTMS \qquad (555)$$



210 211

(556)

The solvolysis of a series of trimethylsilyl substituted cyclopropyl carbinyl trifluoroacetates was studied. These systems **212-214** solvolyze some 25-45 times faster than the parent systems. [429]



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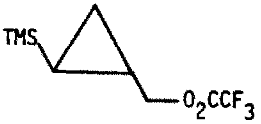

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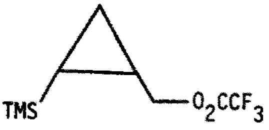
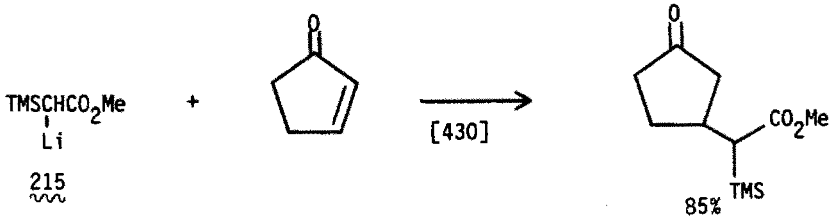


214

Methyl lithiotrimethylsilylacetate was added to enones. The reagent gives 1,4 addition to cyclopentenone. (Eqn. 557) The reaction with cyclohexenone and trans-4-phenyl-3-buten-2-one gives only 1,2 addition. [430] This reaction was utilized in two approaches to methyl jasmonate. (Eqns. 558, 559) Better results were obtained with the diphenylmethylsilyl ester **215a**, however. (Eqn. 559)



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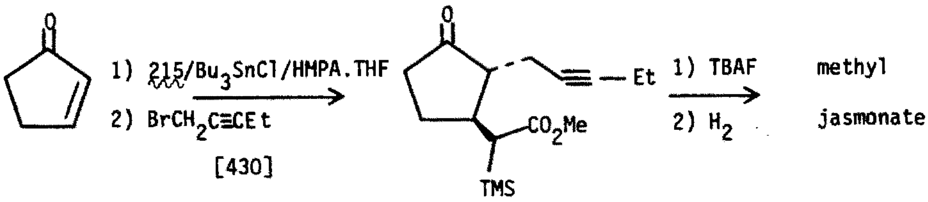

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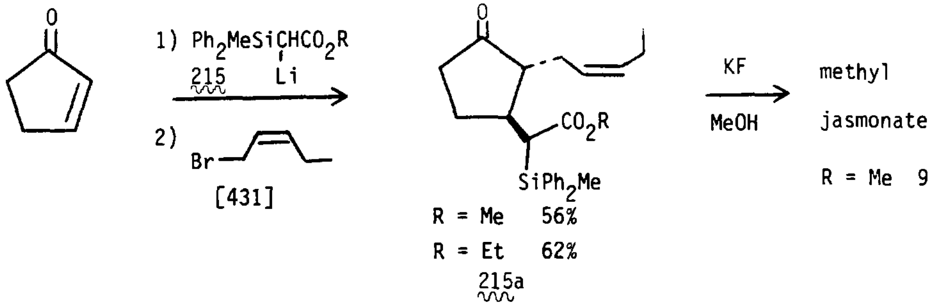
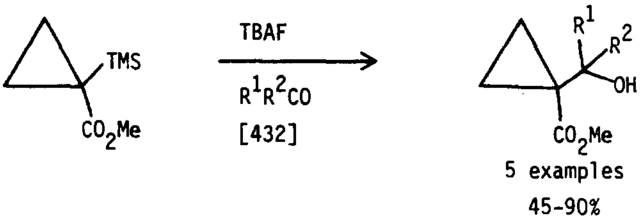


(559)

α-Trimethylsilylcyclopropyl esters, nitriles, and ketones are useful sources of the corresponding enolate ion via reaction with fluoride ion. (Eqns. 560-562) Vinylogous systems also react in a similar manner. (Eqns. 563, 564)



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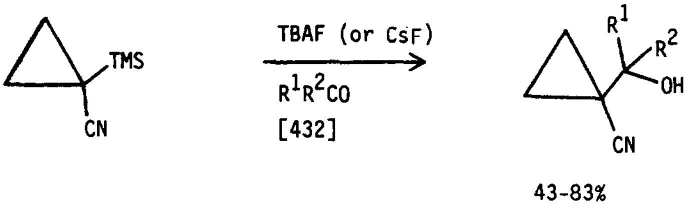

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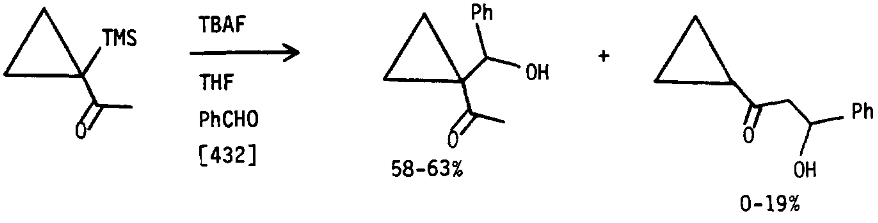
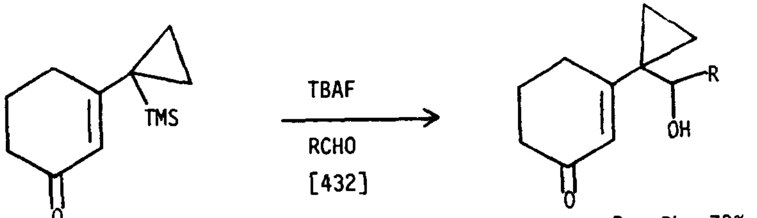
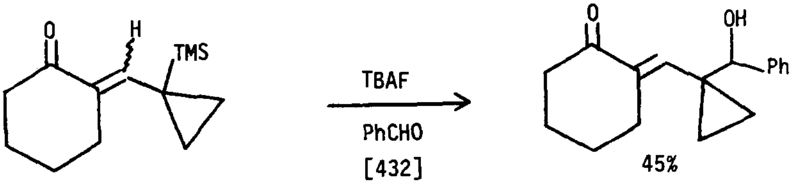


(562)



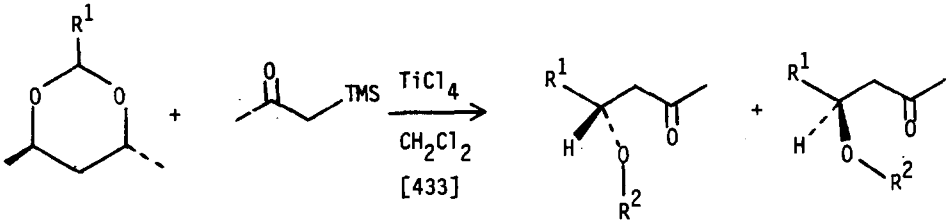
(563)

R = Ph 73%
iPr 27%
H 70%

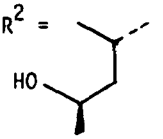


(564)

Trimethylsilylacetone was used to prepare optically active β-alkoxyl ketones via condensation with the cyclic acetals of (R, R) -2,4-pentanediol. (Eqn. 565) The reaction proceeds as well with the β-ketosilane as it does with the isomeric enol silyl ether.

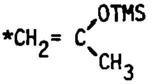


(565)

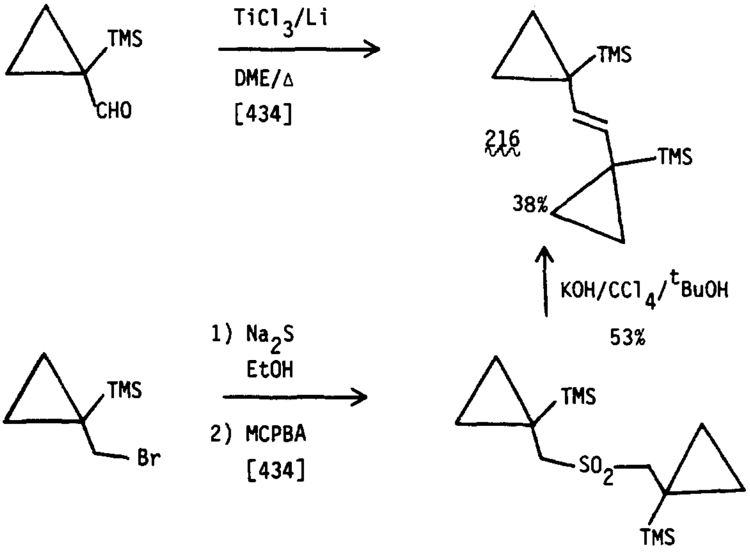
(R² =


)

R^1 = $^nC_8H_{17}$	92%	97	3
R^1 = CH_2=$CHCH_2CH_2$	93%	97	3*
R^1 = cC_6H_{11}	93%	98	2

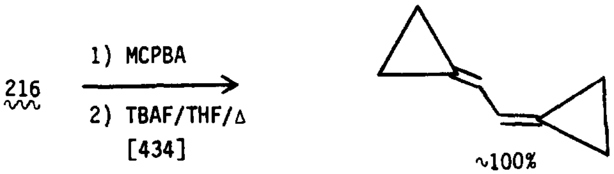

$*CH_2=C(OTMS)CH_3$ gives 89% 97:3 ratio

1-Trimethylsilylcyclopropylcarbaldehyde can be coupled with Ti(0). (Eqn. 566) This same allylsilane can be prepared via a Ramberg-Backland elimination. (Eqn. 567) Treatment of the epoxide of the allylsilane gives dicyclopropylidenethanes. (Eqn. 568)



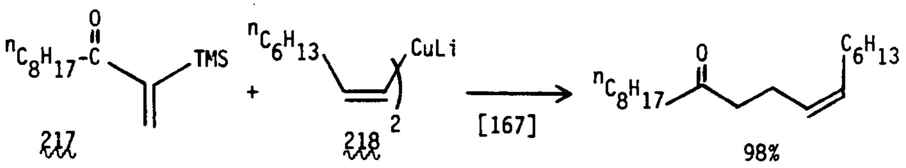
(566)

(567)

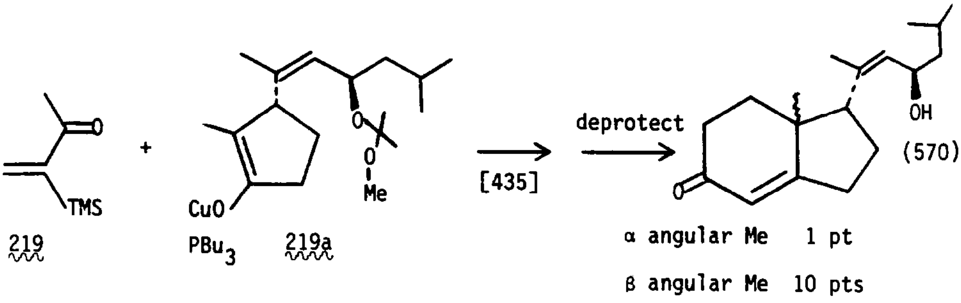


(568)

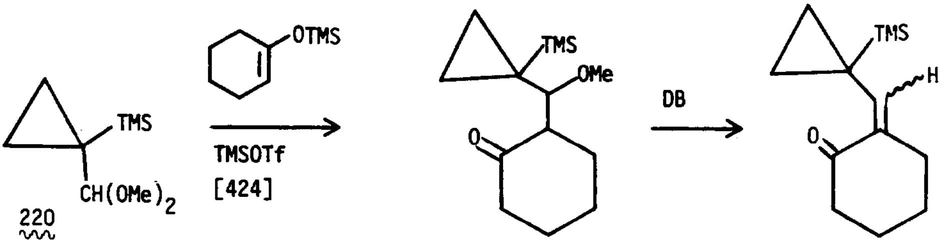
α-Trimethylsilyl enones **217** reacts with the divinylcuprate **218** in a 1,4 manner with loss of the silyl group. (Eqn. 569) An enantioselective double Michael addition was accomplished between copper enolate 219a and α-trimethylsilyl enone **219**. (Eqn. 570) The dimethylacetal of 1-trimethylsilylcylopropylcarbaldehyde was shown to undergo some interesting reactions. (Eqns. 571-573)



(569)



(570)



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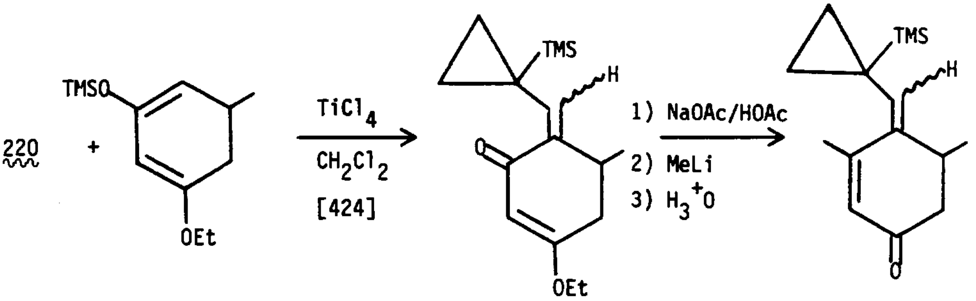

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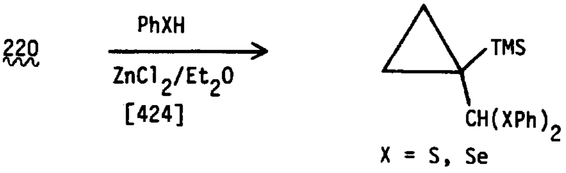
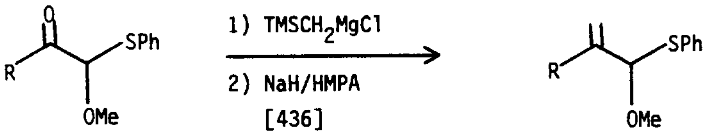


(573)

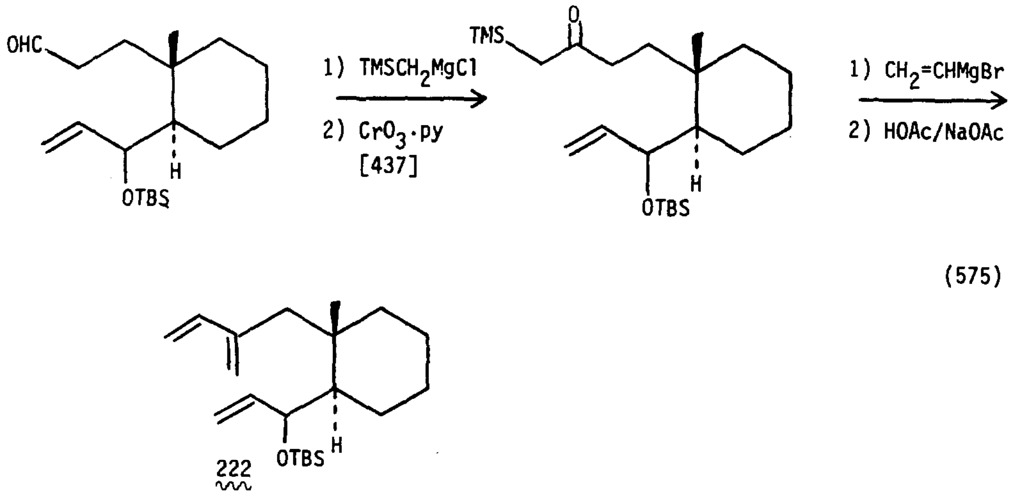
C. Olefins from β-Functional Organosilanes

The reaction of α-trimethylsilyl carbanions with aldehydes and ketones gives β-hydroxysilanes which are readily dehydroxysilylated (Peterson olefination) to give olefins although examples of this reaction are to be found elsewhere in this survey, this section is devoted to the olefination procedure. Examples of the use of trimethylsilylmethylmagnesium chloride in the methylenation of ketones and aldehydes are shown in Eqns. 574-577. A preparation of the α-methylenated aryl anion equivalent **221** was reported. (Eqn. 574) A sequential approach passing through a β-ketosilane was employed to prepare **222**, which was subjected to an intramolecular Diels-Alder reaction. (Eqn. 575) The pentacyclic dione **223** was sequentially treated to Peterson reaction conditions. The first olefination proceeded without problems, but the second required conversion to the β-chlorosilane. (Eqn. 576) The interesting allylsilane **224** was prepared by bis addition of trimethylsilylmethylmagnesium chloride to ethyl trifluoroacetate and acid catalyzed elimination. (Eqn. 577) This allylsilane serves as an excellent source of the 2-trifluoromethylallyl anion. (Eqn. 578) Treatment of hydroxysilane **225** with butyllithium and phenylsulfurylation leads to rearrangement to sulfoxide **226**. Oxidation of **226** gives primarily (E) sulfone **227**, which can be alkylated in the α-position. Fluoride-induced elimination occurs in a vinylogous fashion leading to terminal 1,3-dienes.(Eqns. 579, 580)

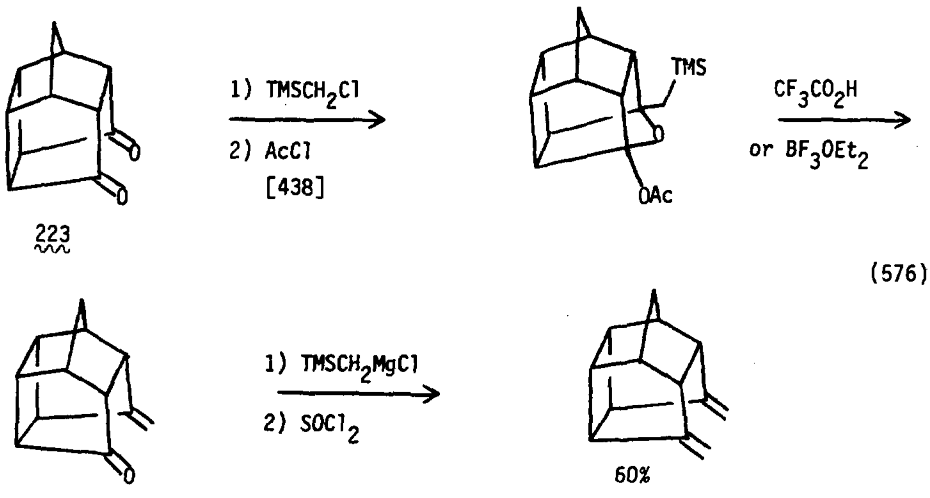


221
4 examples
~90%

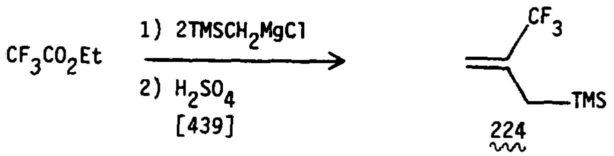
(574)


OHC
OTBS
H
1) TMSCH₂MgCl
2) CrO₃·py
[437]
TMS
O
OTBS
H
1) CH₂=CHMgBr
2) HOAc/NaOAc
OTBS
H
222

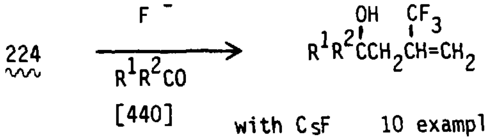
(575)


O
O
223
1) TMSCH₂Cl
2) AcCl
[438]
TMS
O
OAc
CF₃CO₂H
or BF₃OEt₂
O
1) TMSCH₂MgCl
2) SOCl₂
60%

(576)


CF₃CO₂Et
1) 2TMSCH₂MgCl
2) H₂SO₄
[439]
CF₃
TMS
224

(577)

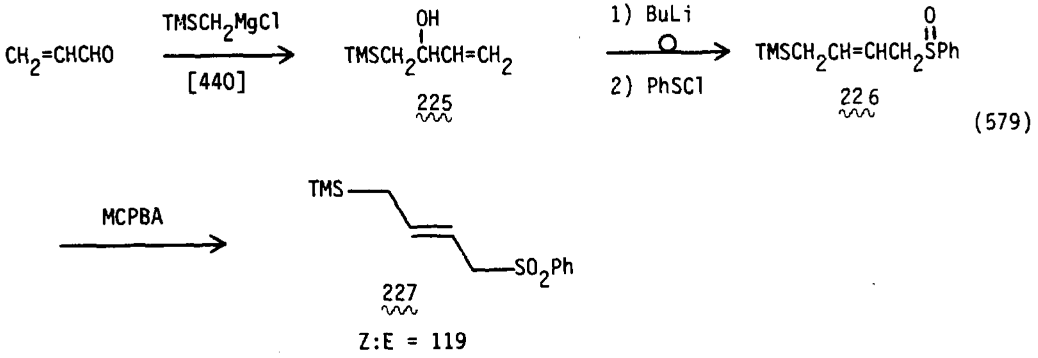


$$224 \xrightarrow[R^1R^2CO]{F^-} R^1R^2\overset{OH}{C}CH_2\overset{CF_3}{C}HCH{=}CH_2 \qquad (578)$$

[440]

with CsF 10 examples 31-99%

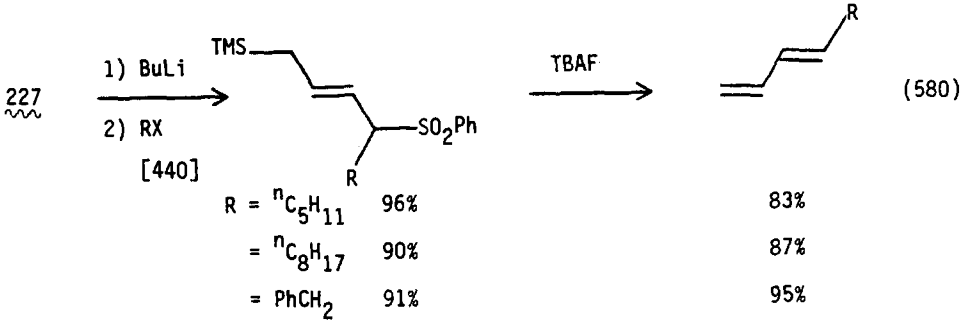
with TBAF 7 examples 48-89%



$CH_2{=}CHCHO \xrightarrow[[440]]{TMSCH_2MgCl} TMSCH_2\overset{OH}{C}HCH{=}CH_2$ (225) $\xrightarrow[2)\ PhSCl]{1)\ BuLi} TMSCH_2CH{=}CHCH_2\overset{O}{S}Ph$ (226) (579)

227

Z:E = 119

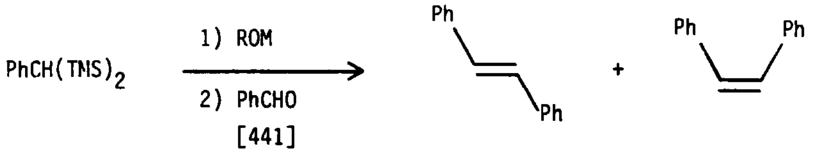


R = $^nC_5H_{11}$ 96% 83%

= $^nC_8H_{17}$ 90% 87%

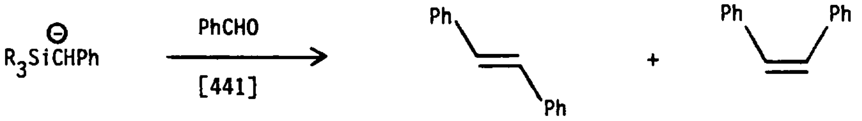
= $PhCH_2$ 91% 95%

The effect of reaction conditions and steric crowding on the Peterson olefination was studied as shown in Eqns. 581, 582). The reaction medium has no real effect on the reaction whereas the bulk of the silyl group leads to more (Z) product.



(581)

R	M	Z:E	%
^{t}Bu	Li	1:1.43	100
Me	Na	1:1.32	99
^{t}Bu	K	1:1.30	100
TMS	Na/MgI$_2$	1:1.81	50

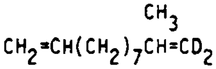


(582)

R$_3$Si	Z:E
Me$_3$Si	1:1.30
Et$_3$Si	1:1.24
Me(cC$_6$H$_{11}$)$_2$Si	1:1.14
Me$_2$^{t}BuSi	1:1.04
Ph$_2$^{t}BuSi	1:0.65
Ph$_3$Si	1:0.52

The reduction of α-silyl esters gives β-hydroxysilanes which upon elimination were used to prepare deuterated terminal olefins. (Eqn. 583) In a similar vane α-silyl esters were sequentially reacted with organomagnesium and organolithium reagents to give, after elimination, tri-and tetrasubstituted olefins. (Eqn. 584)

Table XXIII: Preparation of Terminal Olefins from Esters According to Eqn. 583.

R	X	Y	Product	% Yield[a]
$^{n}C_8H_{17}$	H	H	1-decene	85
$CH_2{=}CH(CH_2)_7$-	H	H	1,10-undecadiene	85
$CH_2{=}CH(CH_2)_7$-		H	2-methyl-1,10-undecadiene	80
$^{n}C_8H_{17}$-	H	D	$^{n}C_8H_{17}$-$CH{=}CD_2$	57
$^{n}C_8H_{17}$-		D	 $CH_2{=}CH(CH_2)_7\overset{CH_3}{C}H{=}CD_2$	83
$^{n}C_8H_{17}$-	D	D	$^{n}C_8H_{17}CD{=}CD_2$	54
$^{n}C_8H_{17}$-	D	H	$^{n}C_8H_{17}CD{=}CH_2$	67
D	D	-	$Ph_2C{=}CD_2$	67

a. Isolated by preparative GLC.

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Table XXIV: Tri- and Tetrasubstituted Olefins from α-Silyl Esters According to Eqn. 584.

entry (cmpd)	R^1	R^2	R^3M	R^4M	olefin	yield,[a] %
1 (**11**)	Me[b]	H	PhMgBr	PhMgBr	MeCH═CPh$_2$	85
2 (**12**)	Me[b]	H	*n*-C$_5$H$_{11}$MgBr	*n*-C$_5$H$_{11}$MgBr	MeCH═C(*n*-C$_5$H$_{11}$)$_2$	54
3 (**13**)	Me	H	*n*-C$_6$H$_{13}$MgBr	*n*-C$_6$H$_{13}$MgBr	MeCH═C(*n*-C$_6$H$_{13}$)$_2$	66
4 (**14**)	Me	H	PhCH$_2$MgCl	PhCH$_2$MgCl	MeCH═C(CH$_2$Ph)$_2$	37
5 (**15**)	Et	H	PhMgBr	PhLi	EtCH═C(Ph)$_2$	55
6 (**16**)	*n*-C$_8$H$_{17}$	H	PhMgBr	PhLi	*n*-C$_8$H$_{17}$CH═C(Ph)$_2$	20
7 (**17**)	*n*-C$_8$H$_{17}$	H	MeMgI	MeMgI	*n*-C$_8$H$_{17}$CH═C(Me)$_2$	39
8 (**17**)	*n*-C$_8$H$_{17}$	H	MeMgI	MeLi	*n*-C$_8$H$_{17}$CH═(Me)$_2$	54
9 (**18**)	*n*-C$_8$H$_{17}$	H	EtMgI	EtMgI	*n*-C$_8$H$_{17}$CH═C(Et)$_2$	9
10 (**19**)	*n*-C$_8$H$_{17}$	H	*n*-C$_3$H$_7$MgBr	*n*-C$_3$H$_7$MgBr	*n*-C$_8$H$_{17}$CH═C(*n*-C$_3$H$_7$)$_2$	8
11 (**20**)	*n*-C$_8$H$_{17}$	H	C$_3$H$_5$MgBr	C$_3$H$_5$MgBr	*n*-C$_8$H$_{17}$CH═C(allyl)$_2$[c]	84
12 (**21**)	*n*-C$_8$H$_{17}$	H	*n*-C$_4$H$_9$MgBr	*n*-C$_4$H$_9$Li	*n*-C$_8$H$_{17}$CH═C(*n*-C$_4$H$_9$)$_2$	19
13 (**22**)	*n*-C$_8$H$_{17}$	H	*n*-C$_3$H$_7$MgBr	MeLi	*n*-C$_8$H$_{17}$CH═C(*n*-C$_3$H$_7$)Me[d]	55
14 (**23**)	CH$_2$═CH(CH$_2$)$_7$	H	MeMgBr	MeLi	CH$_2$═CH(CH$_2$)$_7$CH═C(Me)$_2$	56
15 (**24**)	Me	Me[e]	PhMgBr	PhLi	Me$_2$C═C(Ph)$_2$	70
16 (**25**)	Me	Me[e]	*n*-C$_4$H$_9$MgBr	*n*-C$_4$H$_9$Li	Me$_2$C═C(*n*-C$_4$H$_9$)$_2$	60
17 (**26**)	Me	Me[e]	*n*-C$_6$H$_{13}$MgBr	*n*-C$_6$H$_{13}$MgBr	Me$_2$C═C(*n*-C$_6$H$_{13}$)$_2$	44
18 (**27**)	*n*-C$_8$H$_{17}$	Me[f]	MeMgI	MeLi	(*n*-C$_8$H$_{17}$)MeC═CMe$_2$	12

[a] Isolated yields. [b] Ethyl (trimethylsilyl)propionate prepared via methylation of ethyl (trimethylsilyl)acetate used in these reactions. [c] The allyl Grignard has been shown to add twice to other hindered esters. [d] Product is greater than 99:1 *E*:*Z* when elimination is carried out with KO-*t*-Bu. [e] Prepared by methylation of the lithium enolate of 4 (R = Me). [f] Prepared by methylation of 4 (R = *n*-C$_8$H$_{17}$).

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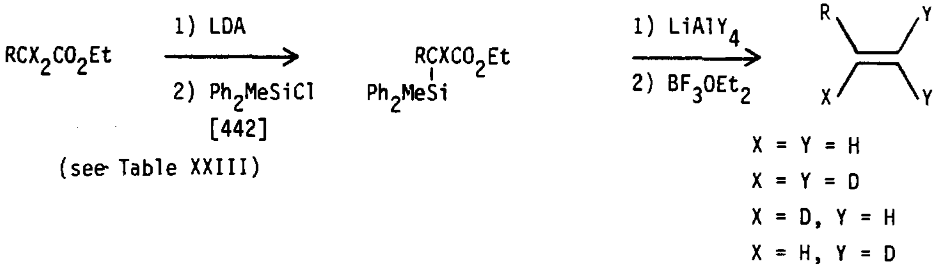

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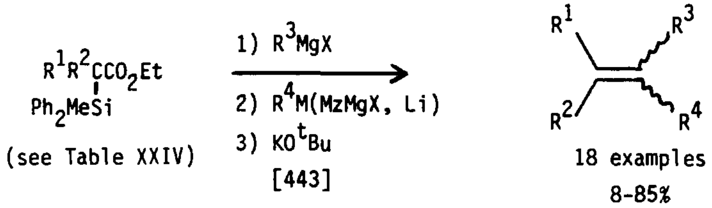
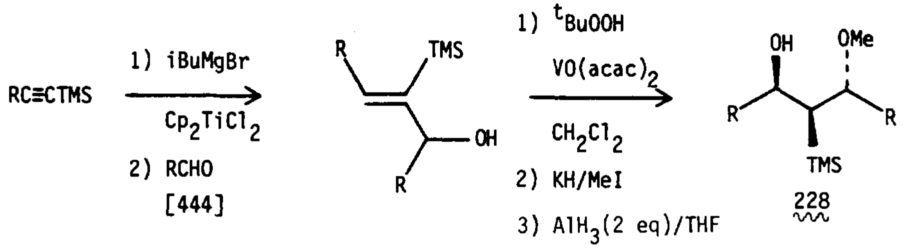


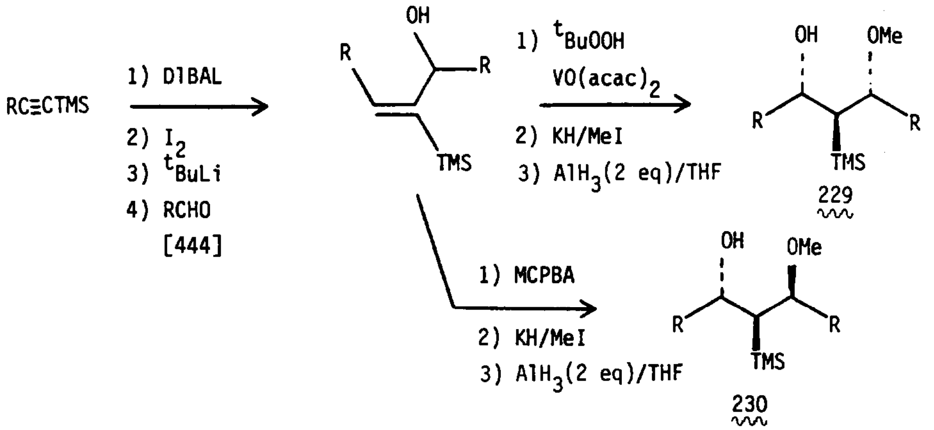
(584)

Further information on the mechanism of the base catalyzed elimination of β-hydroxysilanes was deduced from the potassium hydride catalyzed elimination of the β-hydroxy- β-methoxysilanes **228**, **229** and **230**, prepared according to Eqns. 585-587. It was found that both a syn loss of silanol and an anti elimination of methoxide were possible. (Eqn. 588) An initial attack at silicon by the alkoxide to form a pentacoordinate silicate was postulated.



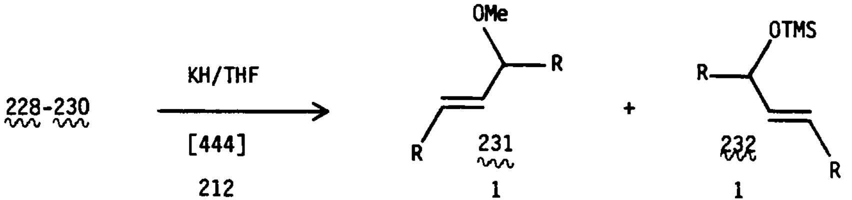
228

(585)



(586)

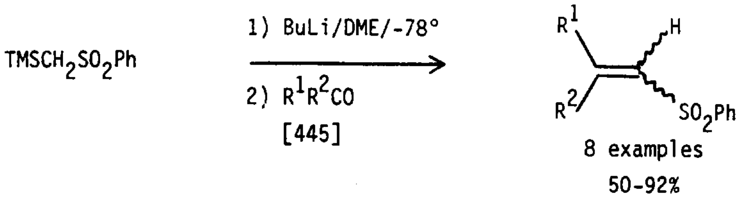
(587)



(588)

[444]	231	232
212	1	1
213	1	4
214	5.8	1
214 (with $PhMe_2Si$ group instead of Me_3Si group)	7	1

Carbanions containing an α-silyl and an α-functional group were employed in the Peterson olefination. This approach was used to prepare α,β-unsaturated sulfones. (Eqns. 589, 590) In the bicyclic system **233** vinylallenes were ultimately prepared. The Regioselectivity of deprotonation of **233** is interesting. Deprotonation of α-substituted α-silyl esters followed by condensation with aldehydes and ketones gives α-substituted α,β-unsaturated esters. (Eqn. 591) The enolate anion of α-trimethylsilyl-β-lactam **234** was reacted with propynal to give **235**. (Eqn. 592)



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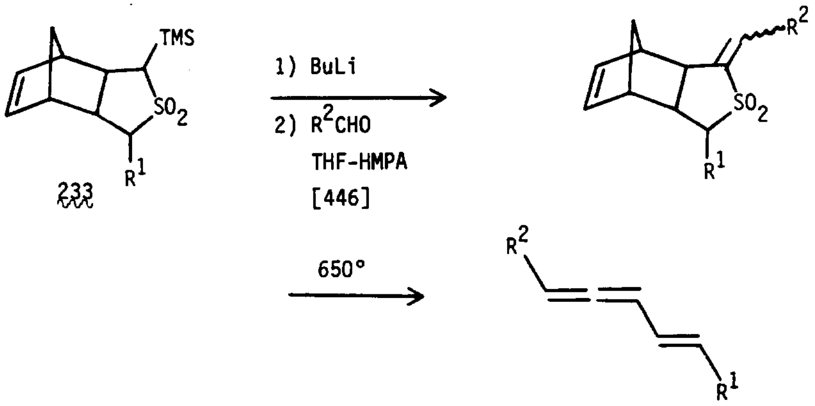

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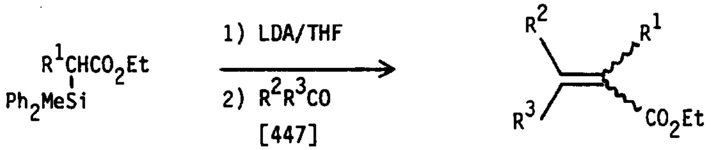

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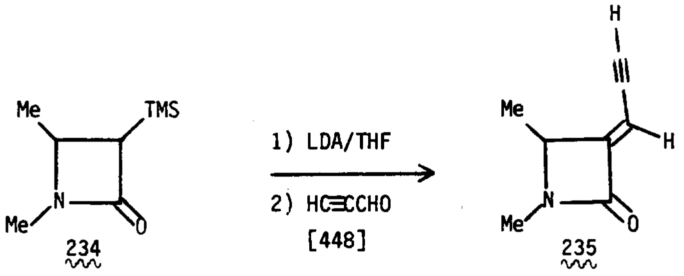
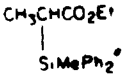
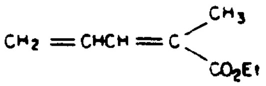
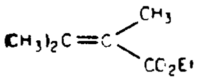
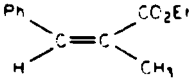
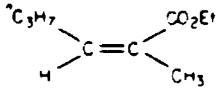
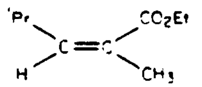
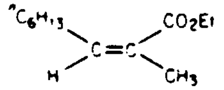
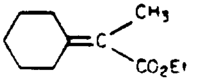
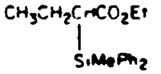
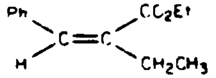
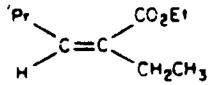
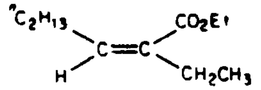
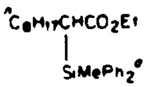
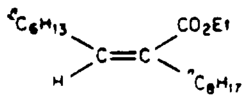


(592)

D. Spectroscopic and Other Studies

The unstable trimethylsilylacetaldehyde was detected spectroscopically. [449] The degree of intramolecular coordination of **236** was studied. [450] It was found that there was more coordination in nonpolar solvents and at lower temperatures. The mass spectra of the β-thiosilanes **237** and **238** were recorded [413]

Table XXV: α-Substituted α,β-Unsaturated Esters According to Eqn. 591.

entry	ester	carbonyl compd	product	% yield[b] (*Z*:*E* ratio)
1	 $CH_3CH(SiMePh_2^{a})CO_2Et$	**acrolein**		65 (77:23)
2		**acetone**		54
3		**benz-aldehyde**		65 (78:22)
4		**1-butanal**		57 (75:25)
5		**2-methyl-propanal**		60 (90:10)
6		**1-heptanal**		69 (75:25)
7		**cyclo-hexanone**		77
8	 $CH_3CH_2CH(SiMePh_2)CO_2Et$	**benz-aldehyde**		73 (80:20)
9		**2-methyl-propanal**		55 (82:18)
10		**1-heptanal**		67 (78:22)
11	 $^{n}C_8H_{17}CH(SiMePh_2^{a})CO_2Et$	**1-heptanal**		62 (71:29)

[a] SiMePh$_2$ = diphenylmethylsilyl. [b] Isolated yields, *Z*:*E* ratios determined by ^{1}H NMR.[13]

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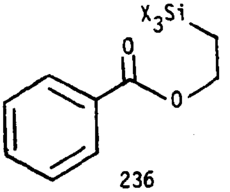
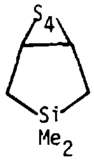
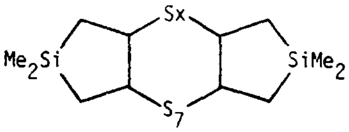


236

X = F, Cl, OMe, $(O\frown\smile)_3N$



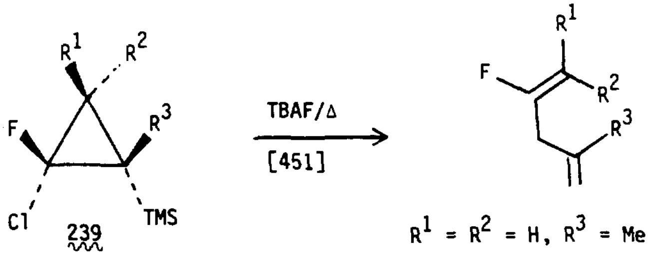
237



238

XIV. MISCELLANEOUS FUNCTIONAL ORGANOSILANES

The β-chlorocyclopropylmethylsilanes **239** produce dienes with inversion at the carbon bearing the chlorine upon treatment with fluoride ion. (Eqn. 593) Thiasilacycloalkanes were prepared from unsaturated γ-chlorosilanes. (Eqn. 594) The cyclization did not take place for the long chain system **240** (Eqn. 595) Elimination of γ-silyl sulfoxides and γ-silyl sulfilimines produces γ,δ-unsaturated silanes. (Eqns. 596, 597)



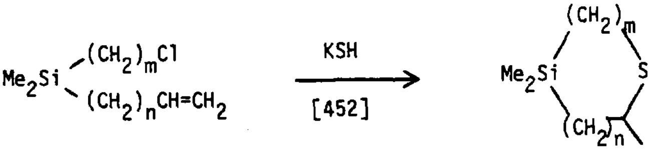
239

$R^1 = R^2 = H, R^3 = Me$

$R^1 = H, R^2 = R^3 = Me$

$R^1 = H, R^2 = Me, R^3 = Et$

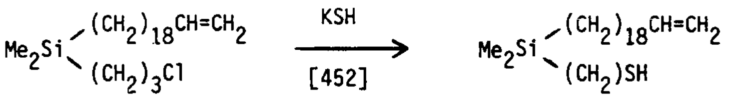
(593)



m = n = 1 60%

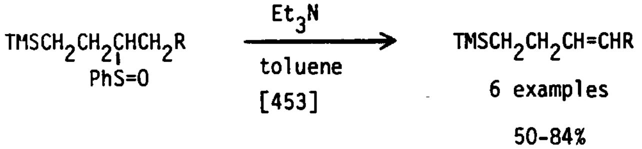
m = 3, n = 0 35%

(594)



$$\mathrm{Me_2Si}\begin{cases}\mathrm{(CH_2)_{18}CH{=}CH_2}\\ \mathrm{(CH_2)_3Cl}\end{cases} \xrightarrow[\text{[452]}]{\text{KSH}} \mathrm{Me_2Si}\begin{cases}\mathrm{(CH_2)_{18}CH{=}CH_2}\\ \mathrm{(CH_2)SH}\end{cases} \qquad (595)$$

240



$$\mathrm{TMSCH_2CH_2\underset{PhS=O}{C}HCH_2R} \xrightarrow[\substack{\text{toluene}\\ \text{[453]}}]{\mathrm{Et_3N}} \mathrm{TMSCH_2CH_2CH{=}CHR} \qquad (596)$$

6 examples

50-84%

Table XXVI: Synthesis of 3-Alkenylsilanes According to Eqn. 596.

Entry	RX	Reaction time/h[a]	Sulfoxide (4) (% yield)[b]		3-Alkenylsilane (1)[c] (% yield,[b] E/Z[d])
1	$n\text{-}C_8H_{17}Br$	7	$Me_3Si(CH_2)_2CH\text{-}n\text{-}C_8H_{17}$ (4b) PhS=O	(55)	$Me_3Si(CH_2)_2CH{=}CH\text{-}n\text{-}C_7H_{15}$ (74, 1.3/1)
2	$n\text{-}C_8H_{17}Br$	5	4b	(60)[e]	
3	$n\text{-}C_8H_{17}I$	23	4b	(61)	
4	$n\text{-}C_4H_9Br$	7	$Me_3Si(CH_2)_2CH\text{-}n\text{-}C_4H_9$ (4c) PhS=O	(84)	$Me_3Si(CH_2)_2CH{=}CH\text{-}n\text{-}C_3H_7$ (50, 1/1)
5	$n\text{-}C_4H_9Br$	5	4c	(51)[e]	
5	Me_2CHCH_2Br	12[f]	$Me_3Si(CH_2)_2CHCH_2CHMe_2$ PhS=O	(50)	$Me_3Si(CH_2)_2CH{=}CHCHMe_2$ (22, 2/1)
6	$CH_2{=}CMeCH_2Cl$	9	$Me_3Si(CH_2)_2CHCH_2CMe{=}CH_2$ PhS=O	(44)	$Me_3Si(CH_2)_2CH{=}CHCMe{=}CH_2$ (34, 5/1)
7	$PhCH_2Cl$	8	$Me_3Si(CH_2)_2CHCH_2Ph$ PhS=O	(57)	$Me_3Si(CH_2)_2CH{=}CHPh$ (78, 1/0)
8	$p\text{-}CH_3\phi CH_2Cl$	14	$Me_3Si(CH_2)_2CHCH_2\phi CH_3\text{-}p$ PhS=O	(64)	$Me_3Si(CH_2)_2CH{=}CH\phi CH_3\text{-}p$ (62, 1/0)

a) Metalation of the sulfoxide 4a was conducted with n-BuLi-TMEDA in THF[7] at -70-0 °C for 1 h. Then alkyl halide was added at -78 °C and the reaction mixture was stirred for a given time at 0 °C. b) Yield after isolation by TLC. c) Pyrolysis was conducted in toluene in the presence of Et_3N at reflux for 4-6 h. After that, the mixture was stirred in MeOH including CF_3SO_3H as a catalyst at 70 °C for 2 h. d) Determined by NMR. e) Metalation[4] of the sulfide 8a with t-BuLi-HMPA was conducted in THF at -78 °C for 2 h. After alkyl halide was added, the mixture was stirred at -20 °C and worked up as usual. The alkylated sulfide 8 was isolated by TLC and oxidized with MCPBA in CH_2Cl_2. Overall yield is shown. f) s-BuLi-TMEDA was used as a metalating reagent.

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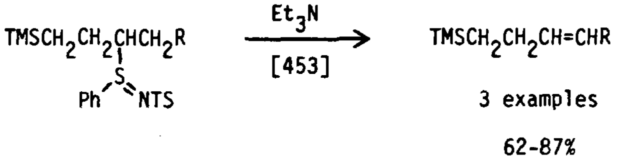


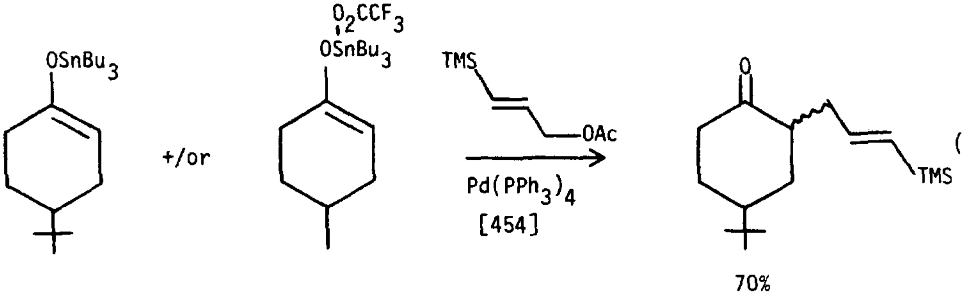
$$\mathrm{TMSCH_2CH_2\underset{\underset{Ph\diagup\ \diagdown NTS}{\overset{|}{S}}}{C}HCH_2R}\ \xrightarrow[\text{[453]}]{\mathrm{Et_3N}}\ \mathrm{TMSCH_2CH_2CH{=}CHR}$$

3 examples

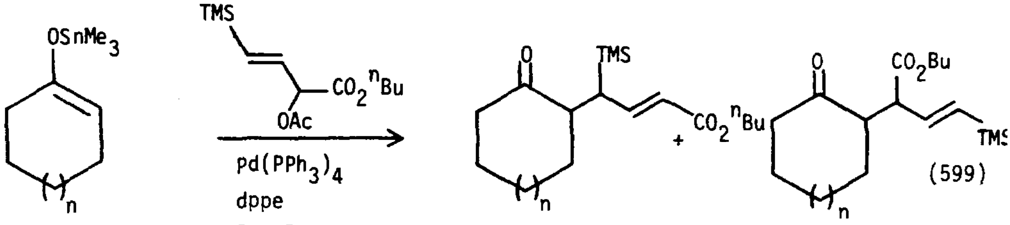
62-87%

(597)

3-Acetoxvinylsilanes were coupled with enol stannyl trifluoroacetates to give ketovinylsilanes. (Eqns. 598, 599) γ-Bromovinylsilanes react with organo cuprates to give S_N2 substitution (Eqn. 600), but with the monoalkylated copper (I) to give both S_N1 and S_N2 attack. (Eqn. 601)



(598)

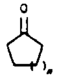
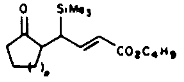
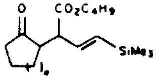
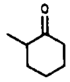
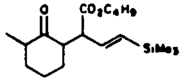
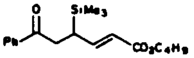
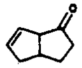
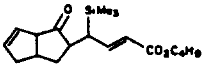
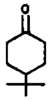
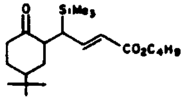
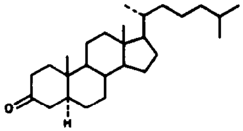
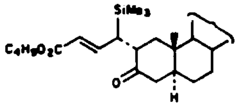


(599)

n = 1 37% 82 : 18

n = 0 55% 67 : 33

Table XXVII:[a] Palladium Catalyzed Alkylation of Trimethyl Tin Enolates According to Eqn. 599.

entry	ketone	product		isolated yield, %
		 **8**	 **9**	
1	$n = 1$	82	18	55
2	$n = 2$	67	33	37
3		 **10**		49
4	$PhCOCH_3$	 **12**		52
5		 **13**		26
6		 **14**		61
7		 **15**		61

[a] All reactions were performed using 1-7 mol % of $(Ph_3P)_4Pd$ + dppe in THF at room temperature.

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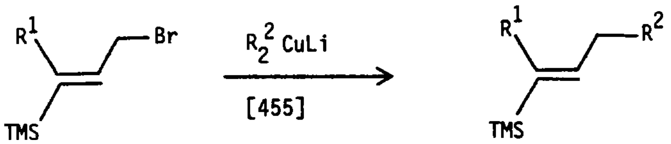
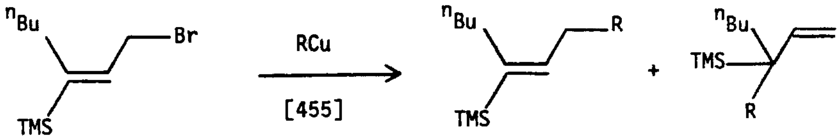
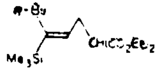
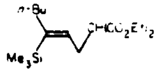
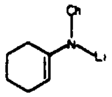
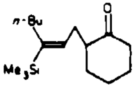
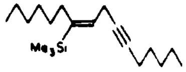
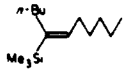
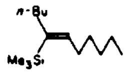
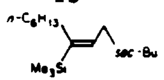
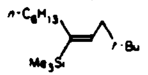
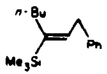


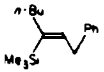
(600)



(601)

Table: XXVIII: Reaction of 3-(Trimethylsilyl)allyl Bromides with Nucleophiles Eqn. 600.

entry	starting material (R)	reaction condition	product^b	(yield, %)
1	6 (*n*-Bu)	NaCH(CO$_2$Et)$_2$ (1.2 equiv) 0→23 °C (3 h), THF	 **8**	(60)
2	7 (*n*-Bu)		 **9**	(79)
3	6 (*n*-Bu)	 (**10**) (1.5 equiv) −15→23 °C (3 h), THF	 **11**	(86)^c
4	6 (*n*-C$_6$H$_{13}$)	Li$_2$(*n*-C$_5$H$_{11}$C≡C)$_2$CuCN (**12**) (1.0 equiv), 0 °C (0.5 h), THF	 **13**	(85)
5	6 (*n*-Bu)	LiCu(*n*-Bu)$_2$ (2.2 equiv), -78→-40 °C (2 h), ether	 **14**	(100)
6	7 (*n*-Bu)		 **15**	(100)
7	6 (*n*-C$_6$H$_{13}$)	*sec*-BuCu (3.0 equiv), -78→-40 °C (2 h), ether	 **16**	(100)
8	6 (*n*-C$_6$H$_{13}$)	*t*-BuCu (2.0 equiv), -78→-40 °C (2 h), ether	 **17**	(100)
9	6 (*n*-Bu)	LiCuPh$_2$ (2.5 equiv), -78→-0 °C (3 h), ether	 **18**	(76)

10	7 (*n*-Bu)	 **19**	(85)

[a] All reactions were carried out (0.1-0.3 M concentration) under rigorous exclusion of moisture and oxygen. Reaction was monitored by TLC, and, when complete, extractive workup was performed in the usual way. [b] The product was isolated pure by chromatography on silica gel and fully substantiated by spectral data. [c] After hydrolysis in 4% aqueous oxalic acid (23 °C, 1 h).

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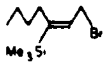
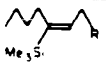
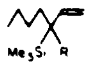
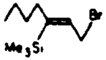
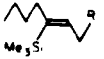
Table XXIX: Reaction of 3-(Trimethylsilyl)allyl Bromides with Organocopper Reagents Eqn. 601.

starting material (R = *n*-Bu)	alkylcopper RCu (equiv)	products and yield,[b] %	
		 **20**	 **21**
	n-BuCu (2)	0	100
	n-BuCu·BF$_3$ (2)	0	100
	PhCu (2)	16[c]	82[c]
	sec-BuCu (3)	100	0
	t-BuCu (2)	100	0
		 **22**	 **21**
	n-BuCu (2.5)	0	100

[a] Reactions were done under the identical conditions (with those in Table I). [b] The products were isolated pure by chromatography unless otherwise noted. [c] Determined by NMR.

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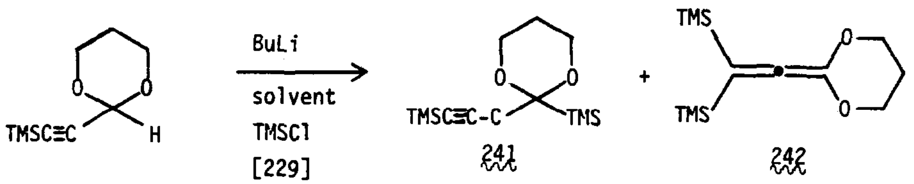
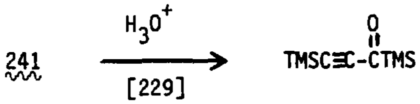
Acylsilanes were prepared according to Eqns. 602-604. The protected ethynyl acylsilane was mixed with its allenyl isomer. (Eqn. 602) Treatment of α-silyloxynitriles with lithium and trimethylchloroilme leads to the enamine of acylsilanes (Eqn. 604)

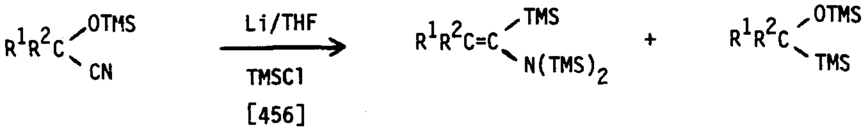


(602)

solvent		
THF	60	40
Et_2O	35	65
HMPA	100	0

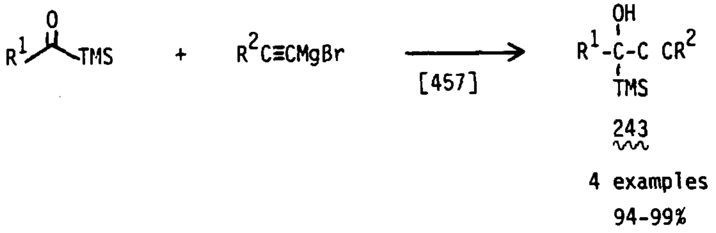


$$\mathbf{241} \xrightarrow[{[229]}]{H_3O^+} TMSC{\equiv}C\text{-}\overset{O}{\overset{\|}{C}}TMS \qquad (603)$$

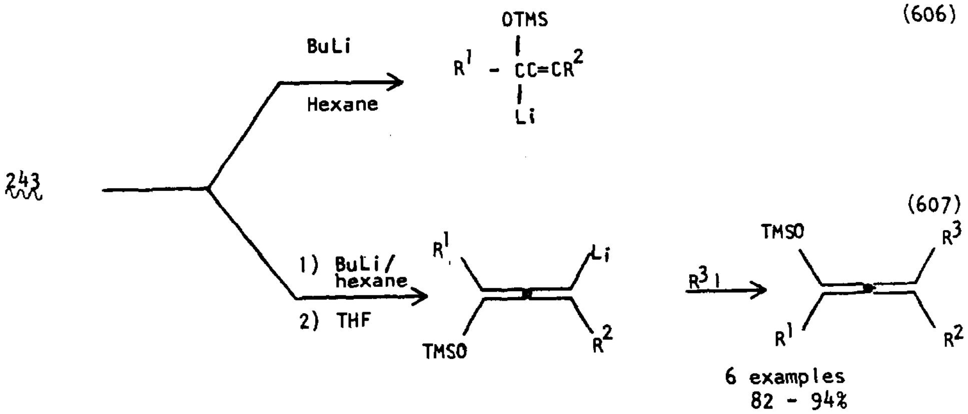


(604)

The reaction of acylsilanes with ethynylmagnesium bromides gives α-trimethylsilyl propargyl alcohols. (Eqn. 605) These, upon treatment with butyllithium, produce the α-silyloxy propargyllithium reagent in hexane and the allenyllithium reagent in THF. (Eqns. 606, 607) Acylsilanes were photolytically reacted with disulfides to give α-silyloxy-α-mercapto radicals.

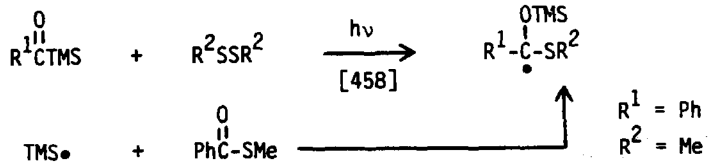


(605)



(606)

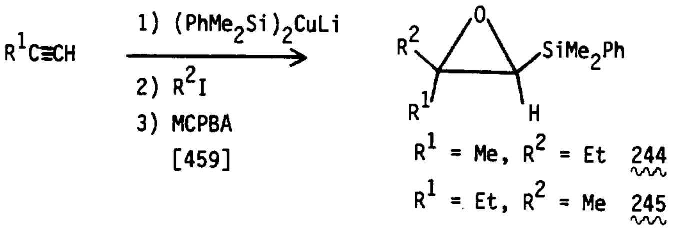
(607)



(608)

Epoxysilanes, readily available from unsaturated organosilanes, were the subject of several studies. The stereochemistry of the boron trifluoride catalyzed rearrangement of α,β-epoxysilanes to enol silyl ethers was studied. The results are consistent with rotation of the molecule so as to place the silyl group in a position to stabilize the carbocation formed. Thus epoxide **244** gives (Z) enol silyl ether **246** and epoxide **245** gives **247**. (Eqns. 610, 611)

The epoxides were prepared according to Eqn. 609. The boron fluoride catalyzed opening of β-hydroxy-αβ-epoxysilanes gives α,β-unsaturated ketones or aldehydes. The ring opening appears to proceed to place the positive charge to the trimethylsilyl group. (Eqn. 612) The epoxide ring-opening of 1-trimethylsilylcyclohexene oxide was compared to the electrophilic additions to 1-trimethylsilylcyclohexene. In the epoxide the attack is at the α-carbon. (Eqn. 613) Oxymercuration of 1-trimethylsilylcyclohexenes gives the anti-Markovnikov product exclusively, whereas HOCl or NBS/H_2O give mixtures. (Eqns. 614-616) The reaction of α,β-epoxysilanes with benzaldehyde in the presence of dimolybdenum tetraacetate gives the enone. (Eqn. 617) N-Trimethylsilyl amides react with epoxysilanes to give β-carboxamide silyloxides. (Eqns. 618, 619)



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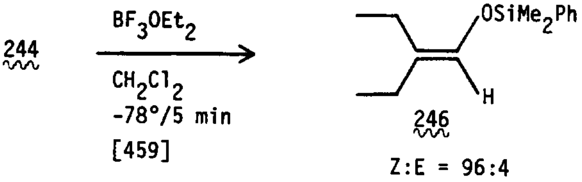

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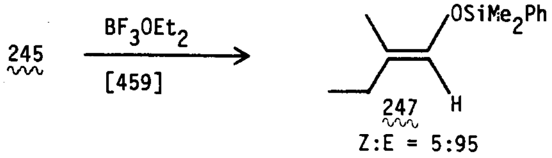

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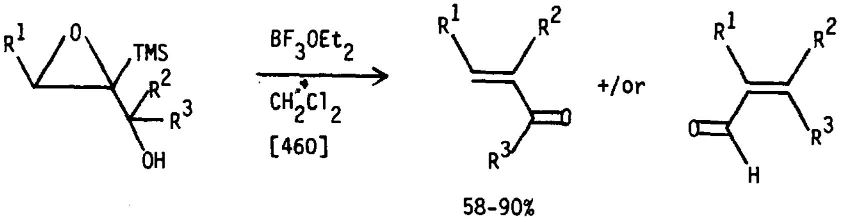

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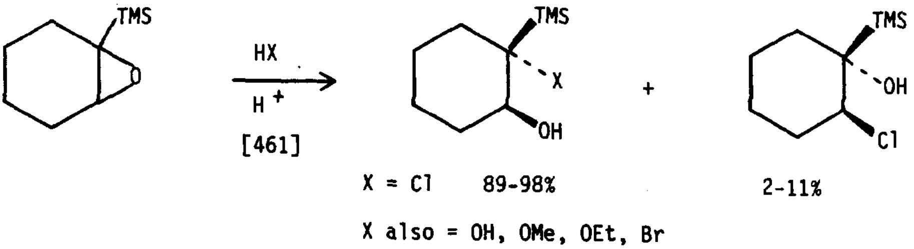

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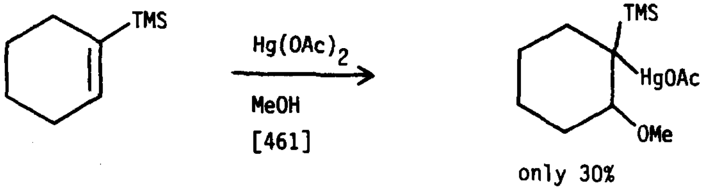
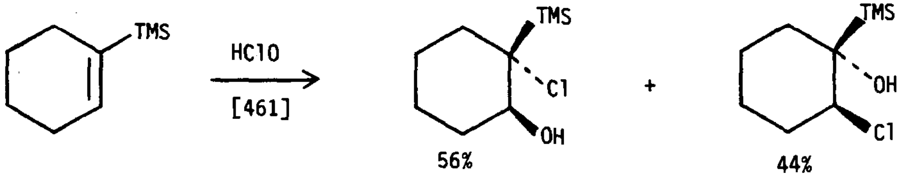


(614)



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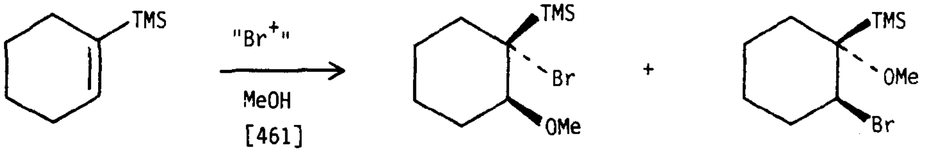
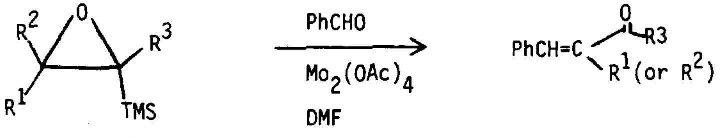


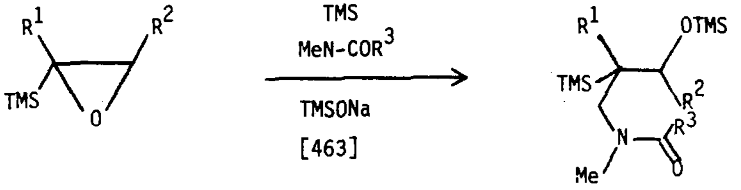
(616)

NBS/MeOH	67	33
$Br_2/CaCO_3/MeOH$	81	19



(617)

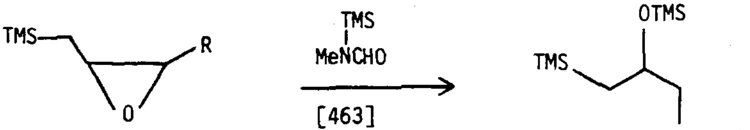
R^1 +/or R^2 = H



(618)

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

R^3 = H, Me

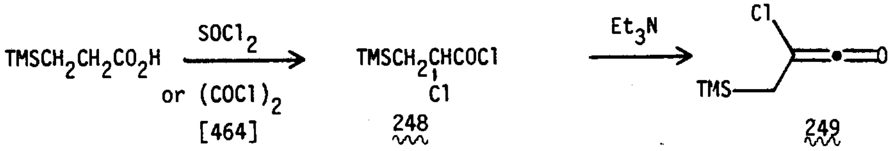


(619)

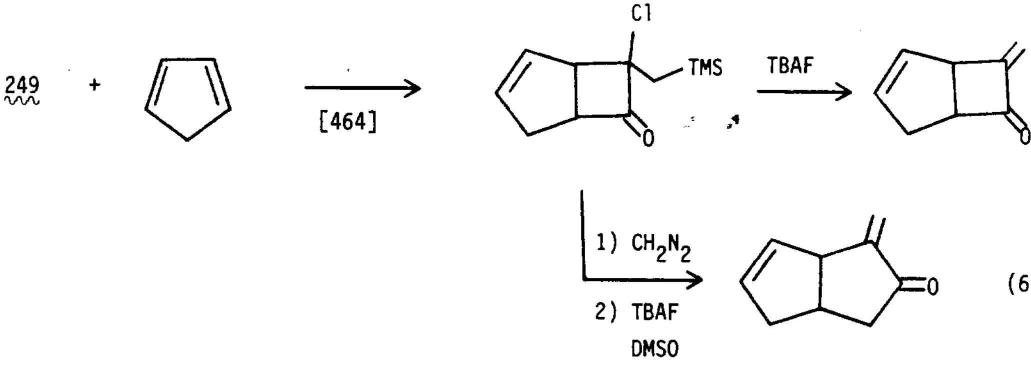
R = H, Ph

R = Ph no reaction

Several γ-carbonyl organosilanes were reported. γ-Trimethylsilyl propionic acid was converted to α-chloro acid chloride **248** which was converted to ketene **249**. Ketene **249** undergoes 2 + 2 cycloadditions leading, by virtue of the β-chlorosilane produced, to enones. (Eqns. 620-624) The 2-trimethylsilycyclopropane carboxylic acid **250** was prepared and resolved. This was used to show that β-silylcyclopropyl anions are stable. (Eqn. 625) A series of γ-silyl propionic acids was protiodesilylated (Eqn. 626) The γ-trimethylsilyl adamantanones **251** and **252** were prepared. (Eqn. 627) Lithium reduction of **253** in the presence of trimethylchlorosilane gives γ-silyl ketone **254** upon hydrolysis. (Eqn. 628) Lithium bis(dimethylphenylsilyl)cuprate adds to α,β-unsaturated esters and ketones to give enolates which methylate with high diastereoselectivity. (Eqn. 629, 630) The structure assignments were confirmed by silicon-directed Baeyer-Villiger oxidation of the γ-silyl ketones and stereospecific elimination of the β-acetoxysilanes. (Eqns. 631-633) Fluoride derived trimethylsilyl anion was added to fused cyclopentenone **254a** to give γ-trimethylsilyl ketone **255**. This was reduced and eliminated with rearrangement to **256**. (Eqn. 634) Cyclic (E)-β-trimethylsilylketoximine acetates are cleaved to unsaturated nitriles with trimethylsilyl triflate. (Eqn. 635) A vinylogous system was also studied to give the diene nitriles. (Eqn. 636)

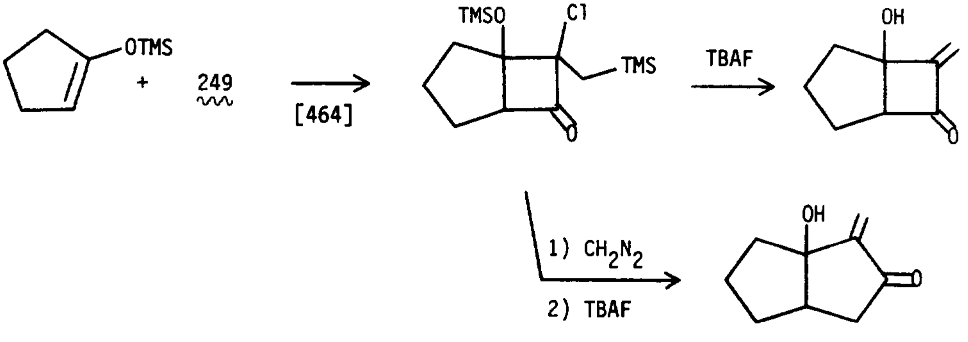


(620)



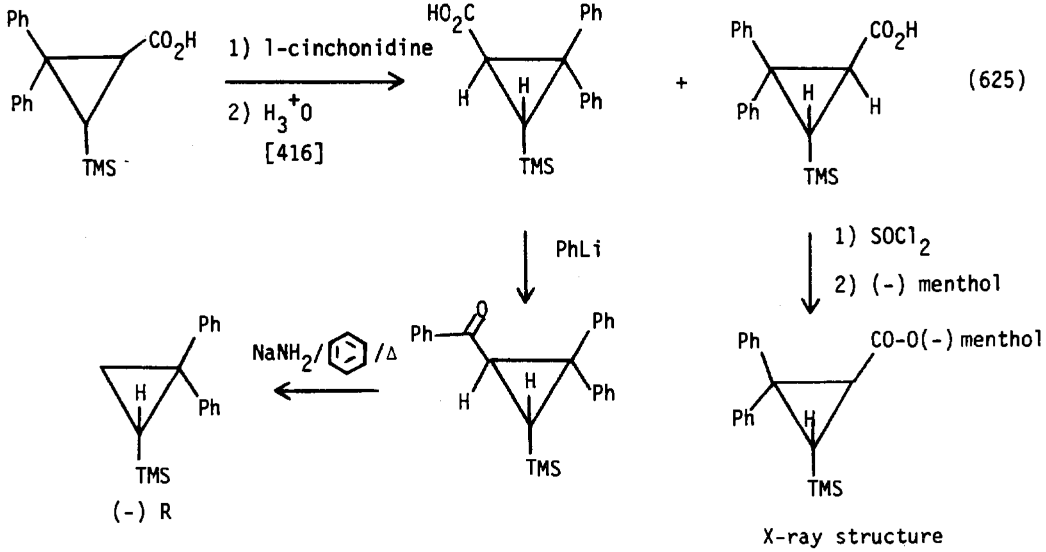
(621)

(622)



(623)

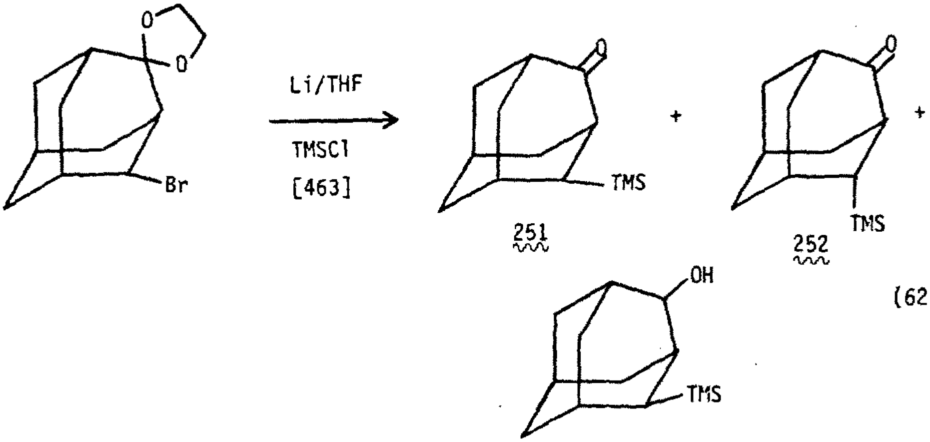
(624)



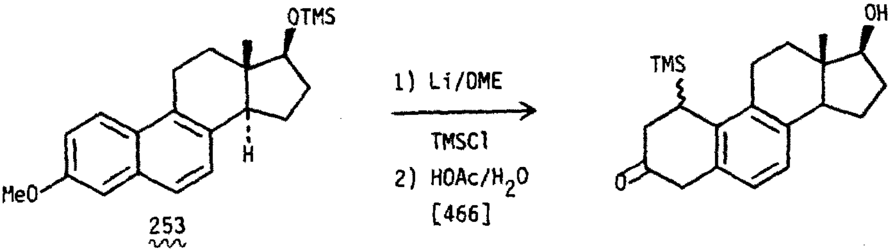
(625)

$$\mathrm{Me_2RSiCH_2CH_2CO_2H} \xrightarrow[\text{[465]}]{95\%/\mathrm{H_2SO_4}} \mathrm{CH_4} + \mathrm{RH} \qquad (626)$$

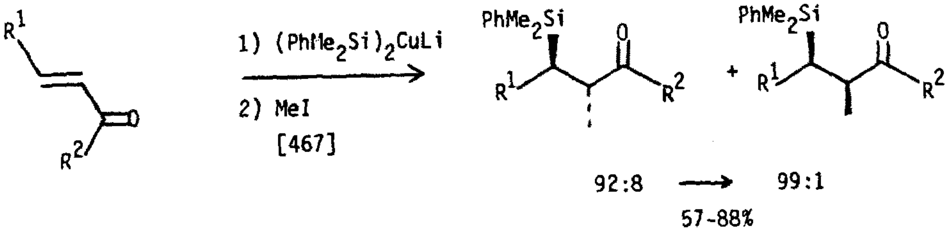
R = Me, Et, Pr, Bu, C_5H_{11}, C_6H_{13}



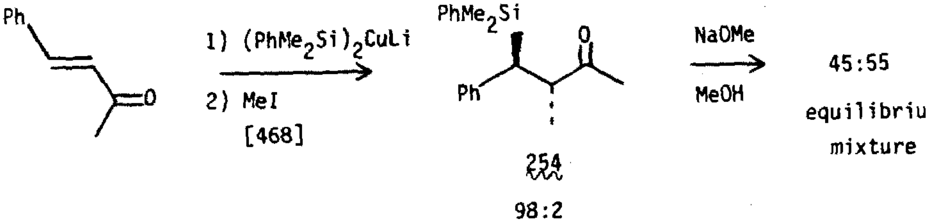
(627)



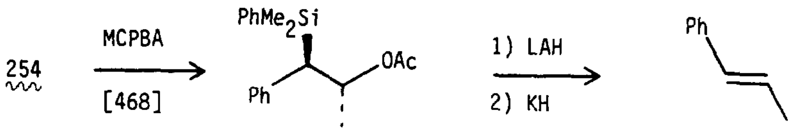
(628)



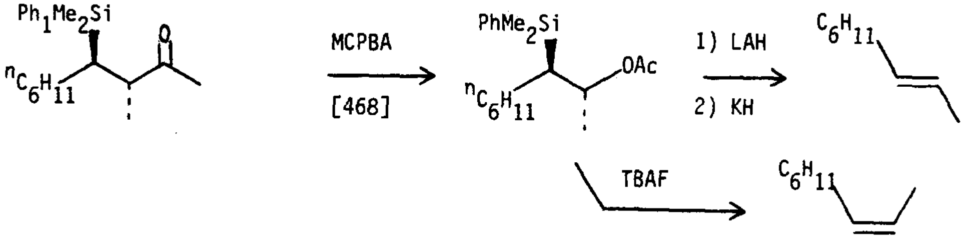
(629)



(630)

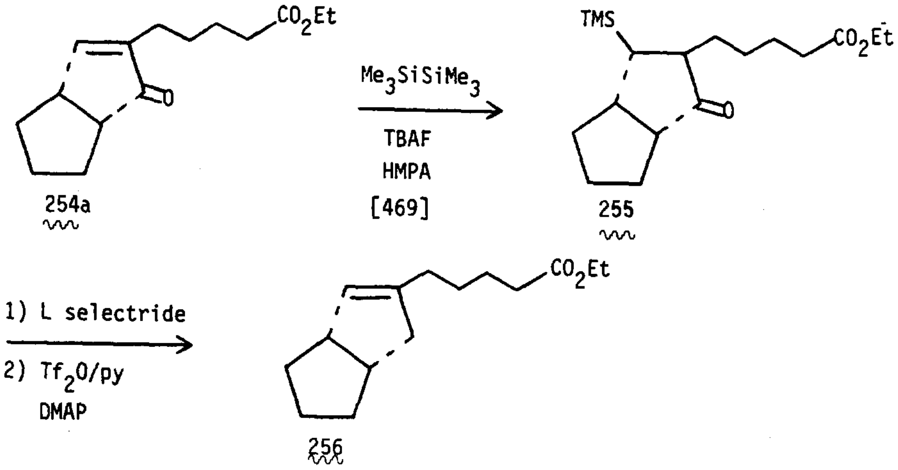


(631)



(632)

(633)

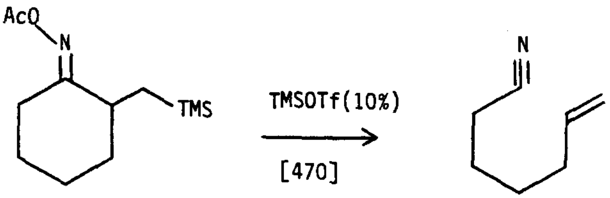


254a

255

256

(634)



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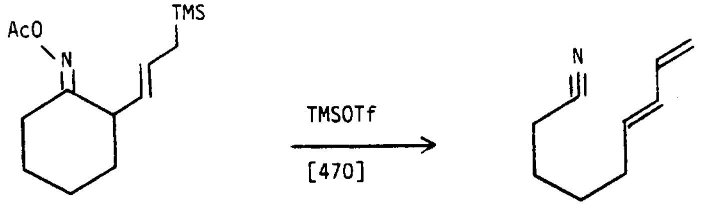
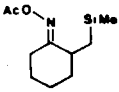
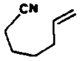
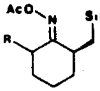
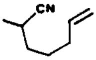
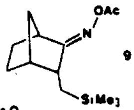
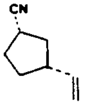
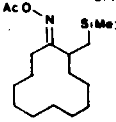
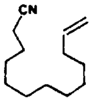
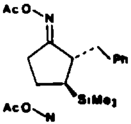
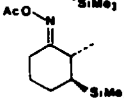
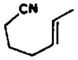
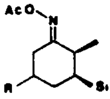
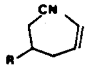


(636)

Table XXX: Beckman Fragmentation According to Eqn. 636.

Entry	β-Trimethylsilylketoxime Acetate		Product		Yield (%)
1		5		3	89
2		6 R = —Me		7	95
3		8 R = ---Me			82
4		9		10	94
5		11		12	81
6		13		14	93
7		15		4	94
8		16 R = H		17 R = H	90
9		18 R = 		19 R = 	94

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[a] To a solution of the oxime acetate (ca. 0.5-1.0 mmol) in anhydrous CH_2Cl_2 (2-4 mL) was added dropwise TMSOTf (10 mol%) at 0°C. The mixture was stirred for 1-4 hr (monitored by TLC), was treated with triethylamine (0.1 mL) and aqueous sodium bicarbonate, and was quickly extracted with ether (10 mL). The extract was concentrated, and the residual oil was purified by silica gel column chromatography to give the corresponding nitrile. Satisfactory ^1H and ^{13}C NMR, IR, and mass spectra were obtained for the products.

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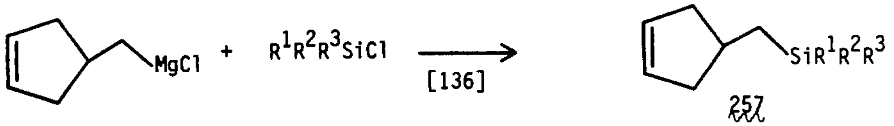
The preparation and some reactions of unsaturated organosilanes are shown in Eqns. 637-640. The cyclopentenes **257**, precursors to 1-silabicycloheptanes (see Eqn. 90), were prepared according to Eqn. 637. Unsaturated silanes were reacted photochemically with hydrogen sulfide to give the corresponding thioethers. (Eqn. 638) 4-Trimethylsilyl-1-butene reacts with the acid chloride of cyclopropane carboxylic acid to give cyclopropyl-(cyclopropylmethyl)ketone. (Eqn. 639) Trisallylborane adds to 4-trimethylsilyl-1-butyne to give **258**, which thermally rearranges to **259**. (Eqn. 640)



257

4 examples

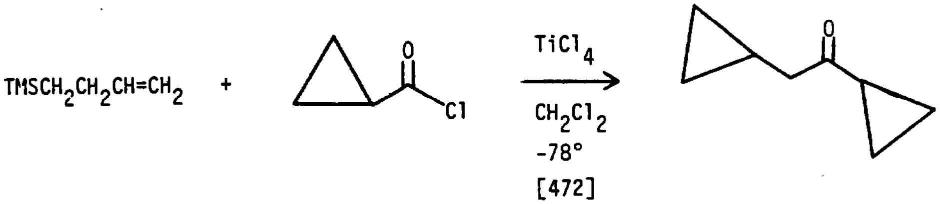
62-98%

(637)

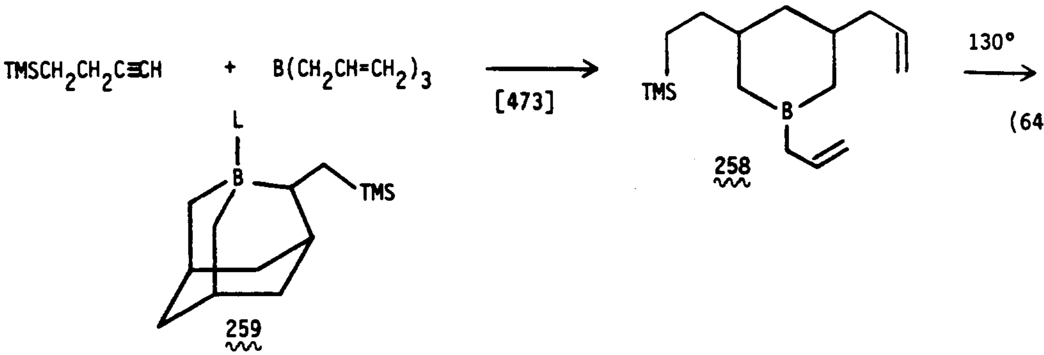
$$R_3Si(CH_2)_nCH{=}CH_2 \xrightarrow[\text{[471]}]{H_2S/h\nu} (R_3Si(CH_2)_nCH_2CH_2)_2S \qquad (638)$$

R = Et, EtO, MeO

17-30.5%



(639)



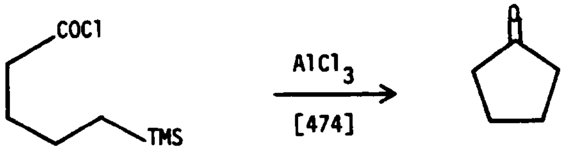
258

259

L = THF, pyridine

(640)

Carboxylic acid chlorides containing a γ-trimethylsilyl group have been shown to give cyclopentanones upon treatment with aluminum chloride. (Eqn. 641, 642)

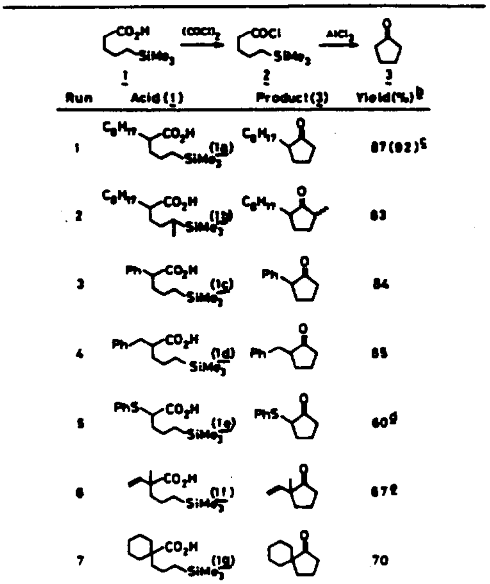


7 examples

60-87%

(641)

Table XXXI: Intramolecular Acylation According to Eqn. 641.



Run	Acid (1)	Product (3)	Yield(%)[b]
1	(1a)		87(92)[c]
2	(1b)		83
3	(1c)		84
4	(1d)		85
5	(1e)		60[d]
6	(1f)		67[e]
7	(1g)		70

[a] Reactions are carried out in 0.2–0.3-mmol scale with the reactant ratio 1/(COCl)$_2$/AlCl$_3$ = 1:2:1. [b] Overall yield from 1. Products are isolated by chromatography. [c] Reaction in 3.5-mmol scale and the product was isolated by Kugelrohr distillation. [d] Reactant ratio: 1/(COCl)$_2$/AlCl$_3$ = 1:1.5:0.75. [e] Relatively low yield may reflect the volatility of the product.

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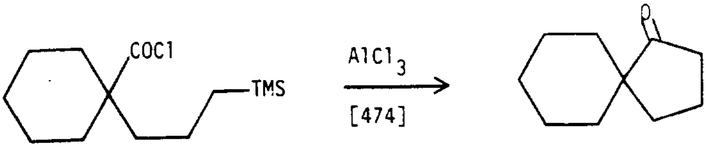


(642)

The protonation energies of **260** and **261** were discussed. [475] The pharmacological properties of **262** were tested. [476] The structure of **263** was determined. [477] The crystal is built of infinite chains of hydrogen bonds between the OH and the nitrogen.

$H_3M(CH_2)_nOH$

260

M = Si, C

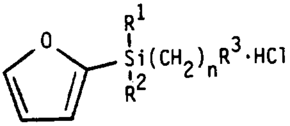
n = 1, 2

$H_3M(CH_2)_nNH_2$

261

M = Si, C

n = 1, 2

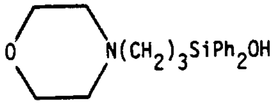


262

R^1 = alkyl, 2-furyl

R^2 = alkyl

R^3 = piperazinyl, morpholino, pyrrolidinyl, among other



263

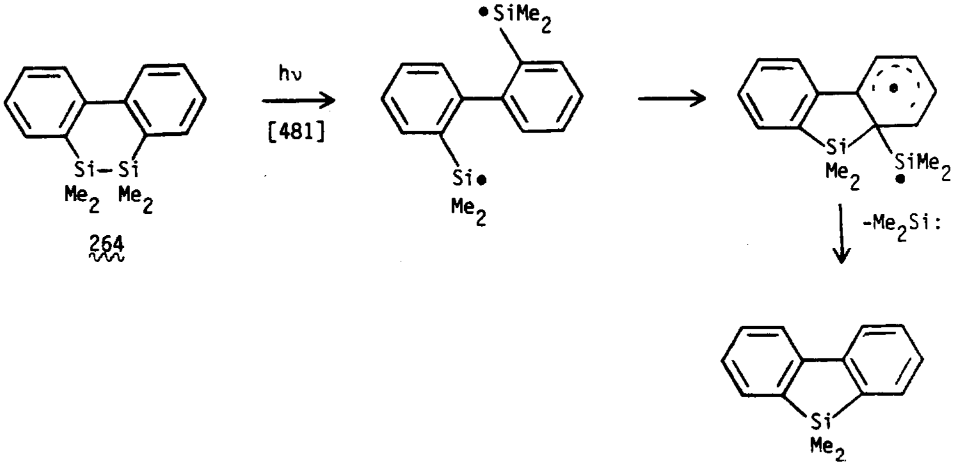
XV. REACTIVE SPECIES

A. Radicals

A theoretical study of the trimethylsilyl radical shows it to have a pyramidal structure with a barrier to inversion of 13.3 kcal/mole via the planar structure. This compares to a barrier of 1.23 kcal/mole for the tert-butyl radical. Substitution of methyl or fluorine ligands for H in SiH_3 increases the inversion barrier. [478] An electron spin resonance study of the triphenylsilyl radical showed hyperfine splitting constants of 2.62, 2.18 and 0.87 Gauss. [479]

Hexamesityldisilane was shown to be in equilibrium with the trimesitylsilyl radical at low temperature. The dissociation enthalpy was measured to be 19.0 (±2) kcal/mole. [480] The radicals will react irreversibly to abstract protons or attack an aromatic ring.

Silyl radicals have been proposed in the mechanism for the extrusion of dimethylsilylene from **264**. (Eqn. 243) Silyl radicals add to allylsilanes to give β, β-bissilyl radicals. (Eqn. 644) The silicon groups eclipse the p orbital of the radicals, but lie anti to one another. (Eqn. 646) Based on the cyclic products of several silyl radicals containing unsaturated ligands it was concluded that the Baldwin-Beckwith rules do not apply to silicon radicals. Some examples are shown in Eqns. 645-647.



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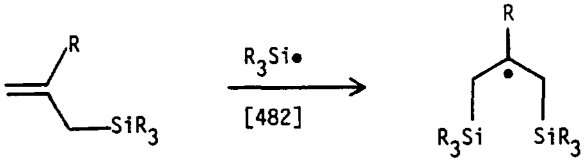
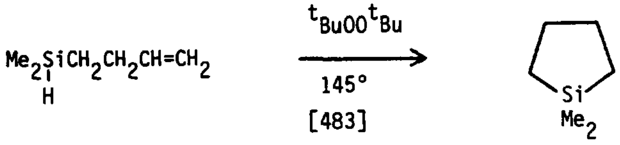


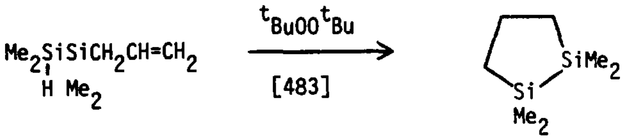
(R = H, Me, OTMS)

(644)



major volatile product

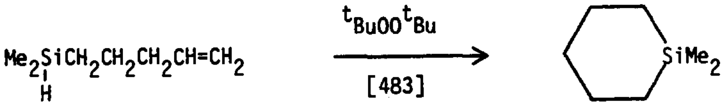
(645)



13%

only volatile product

(646)

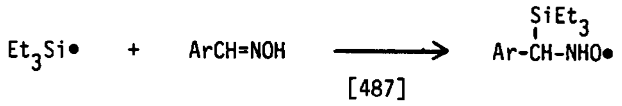


19%

(647)

A variety of traps were used to study silyl radicals in the gas phase. These included tert-nitrosobutane, 2,6-di-tert-butylquinone and $PhCH{=}N(O)^tBu$. [484] These traps are better for carbon radicals than for silyl radicals.

The kinetics of the reaction of triethylsilyl radical with tert-nitrosobutane [485] and with 2,4,6-tri-tert-butylnitroso benzene [486] was measured. The addition of triethylsilyl radical to aromatic aldoximes was studied. (Eqn. 648)



$$Et_3Si\bullet + ArCH{=}NOH \xrightarrow[{[487]}]{} Ar\text{-}\overset{SiEt_3}{CH}\text{-}NHO\bullet \qquad (648)$$

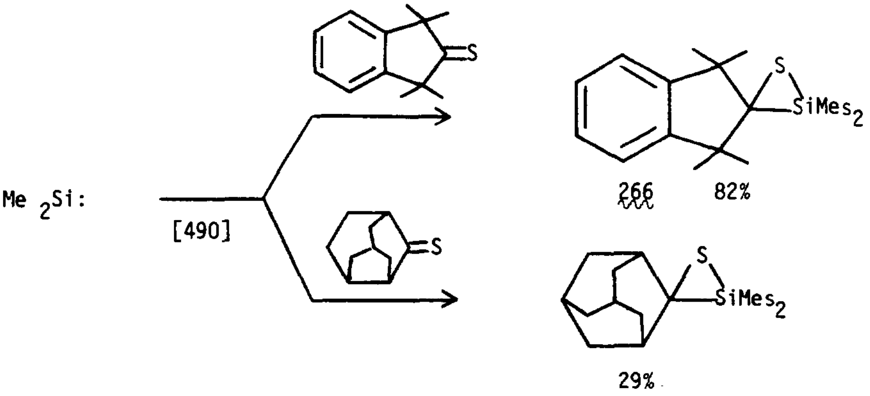
Triphenyldeuteriosilane was used as a donor to determine the rate of hydrogen donation to benzyl radicals. [488] Tetramethylsilane was used to probe the sensitivity of CH_3. and CD_3. [489]

B. Silylenes

Dimesitylsilylene has been generated by photolysis of **265**. (Eqn. 649) It reacts with thioketones to give thiasilacyclopropanes. (Eqns. 650, 651) The structure of **266** was determined by x-ray diffraction. The oxasilacyclopropane **267** generates dimesitylsilylene upon photolysis. In the absence of a trap insertion into an ortho methyl is seen. (Eqn. 652) The 7-silanorbornadiene **268** was shown to be a source of dimethylsilylene. (Eqn. 653) The dimethylsilylene thus generated was trapped with the usual reagents. Silylenes are produced by photolysis or thermolysis of 1, 2, 3-trisilacyclopentenes **269**. Thermally only the central silicon is extruded but photochemically either the central or terminal silicons are extruded depending on the substituents on the central silicon atom. (Eqns. 654, 655) The pyrolysis of 1,1-dichloro and 1,1-difluoro-1-sila-3-cyclopentenes has been shown to proceed via a retro-Diels-Alder extrusion of the silylene. (Eqns. 656, 657)

The hexasilacyclododecatriyne **270** was prepared (Eqn. 658) and thermolyzed to extrude dimethylsilylene. (Eqn. 659) Thermolysis in the presence of pyridine gave adduct **271**. (Eqn. 660)

$$\underset{\textbf{265}}{(TMS)_2SiMes_2} \xrightarrow[\text{[490]}]{h\nu} Me_2Si: \qquad (649)$$

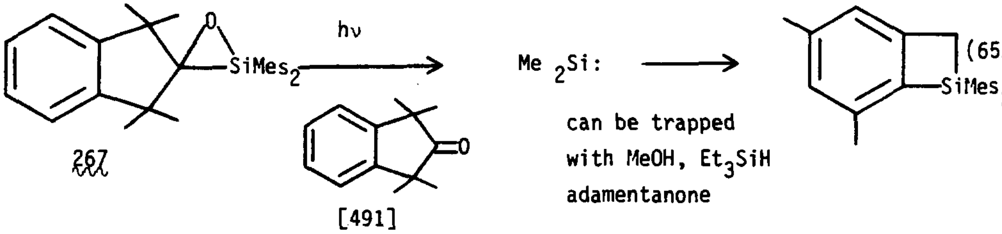


266 82%

29%

(650)

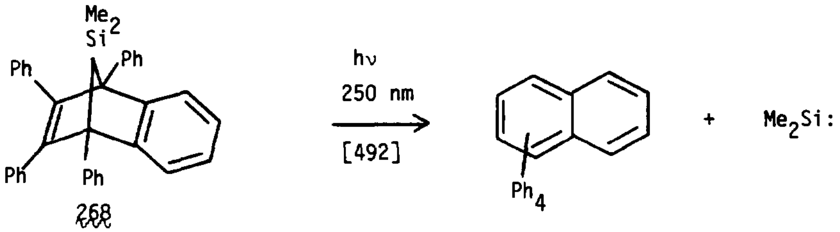
(651)



267

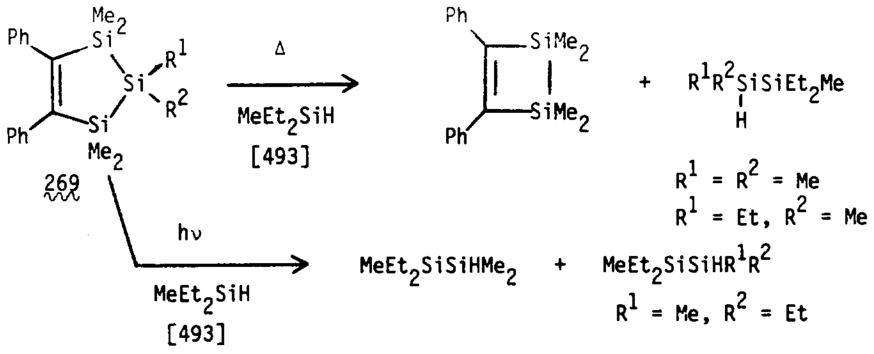
can be trapped with MeOH, Et_3SiH adamentanone

(652)



268

(653)



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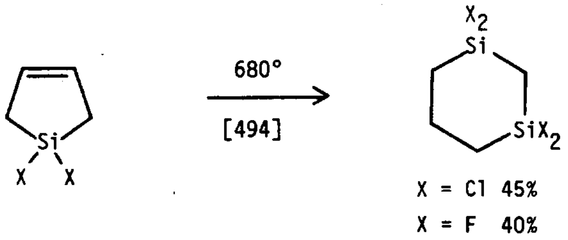

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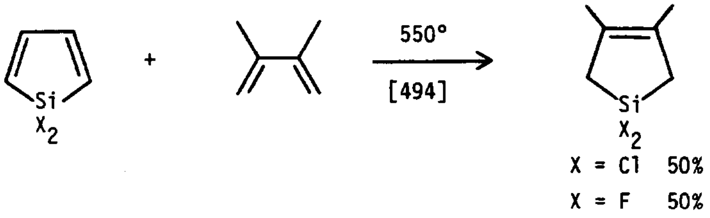

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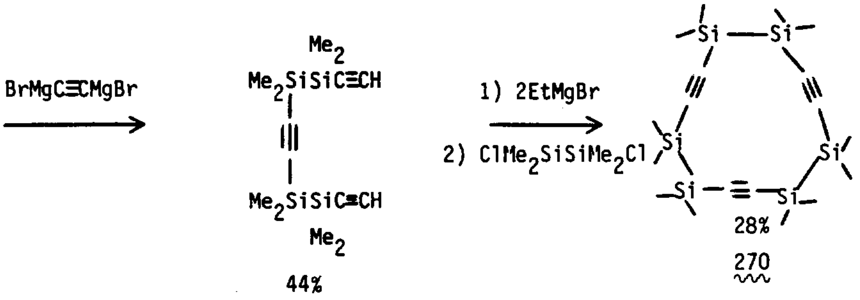

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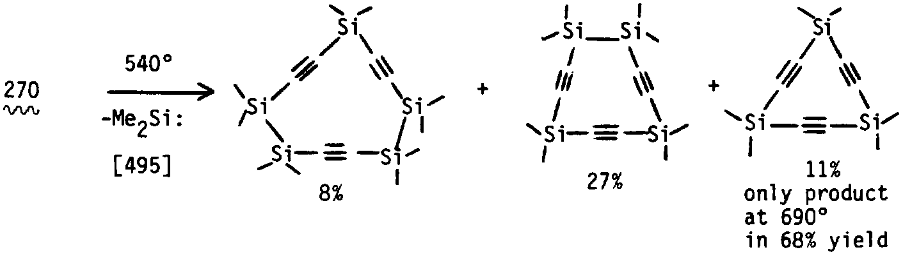

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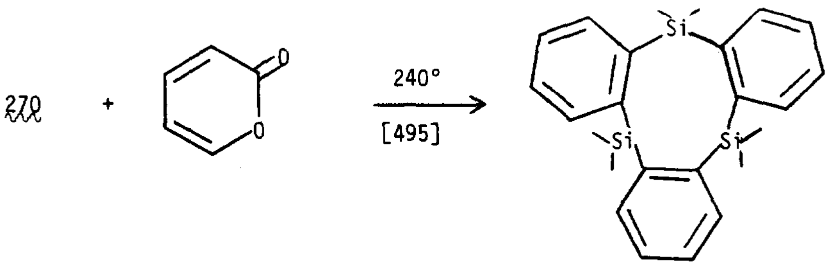
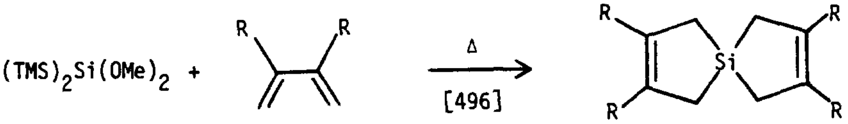


(660)

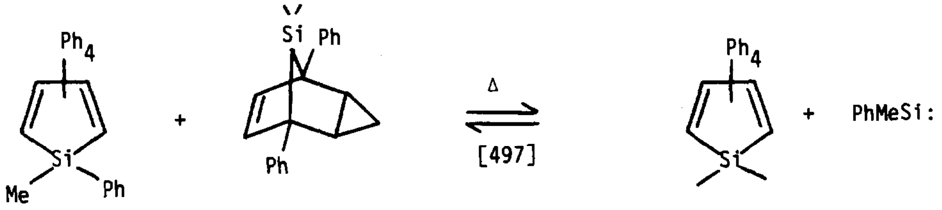
55% 271
X-ray structure

The copyrolysis of 2,2-dimethoxyhexamethyltrisilane in the presence of 1,3-butadienes gives 5-silaspiro[4.4]nona-2,7-dienes via sequential formation reaction of silylenes. (Eqn. 661) A silylene-silylene exchange reaction was reported. (Eqn. 662)



R = H, Me

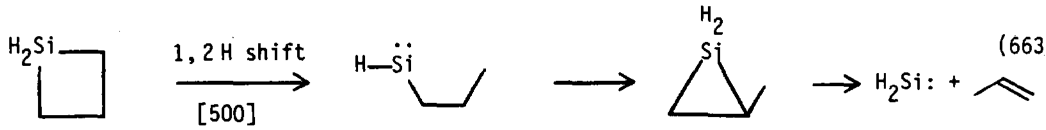
(661)



(662)

The optical absorption spectrum of dimethylsilylene was recorded. A transient absorption at 350 nm due to NO$_2$Si was observed. [498] The rates of reaction of dimethylsilylene with triethylsilane (k=2.0 x 10^{6}M^{-1}S^{-1} at 298^{o}k) were obtained. [499]

The thermolysis of silacyclobutane proceeds via a silylene intermediate arrived at by a 1,2 hydrogen shift from silicon to carbon and not as a homolysis of the Si-C band. (Eqn. 663)



(663)

The mechanism of the shock-tube decomposition of vinylsilane was studied. In the absence of silylene traps some induced decomposition occurs due to a silylene chain sequence. In the presence of silylene traps (butadiene, acetylene) three primary processes were observed, 1,1-H_2 elimination (Eqn. 664), 1,2 H_2 elimination (Eqn. 665) and ethylene elimination (666).

$$\mathrm{ClMe_2SiSiMe_2Cl} \;+\; \mathrm{HC{\equiv}CMgBr} \;\xrightarrow[{[495]}]{}\; \underset{54\%}{\mathrm{ClMe_2SiSiMe_2C{\equiv}CH}}$$

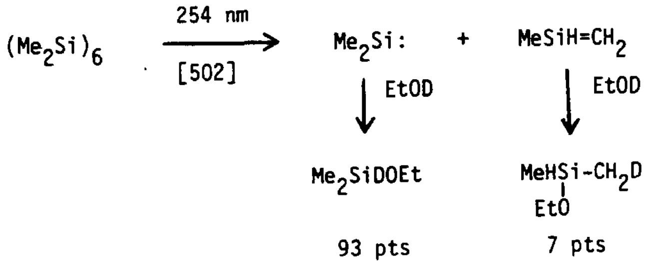
$$\mathrm{H_3SiCH{=}CH_2} \;\xrightarrow[\sim 3100\ \mathrm{Torr}]{1085\text{-}1275°\mathrm{K}}\; \mathrm{H\ddot{S}iCH{=}CH_2} \qquad (664)$$

$$\mathrm{H_3SiCH{=}CH_2} \;\xrightarrow[{[501]}]{}\; \mathrm{H_3SiC{\equiv}CH} \;+\; \mathrm{H_2} \qquad (665)$$

$$\mathrm{H_3SiCH{=}CH_2} \;\xrightarrow[{[501]}]{}\; \mathrm{H_2Si:} \;+\; \mathrm{H_2C{=}CH_2} \qquad (666)$$

The photolysis of dodecamethylcyclohexasilane was shown by spectroscopic and trapping experiments to produce both dimethylsilylene and 1-methylsilene. (Eqn. 667) Photochemically generated dimethylsilylene in an Argon matrix was itself photolyzed at 450 nm to give 1-methylsilene. Detailed assignments of the IR spectra of both systems were made. The Si=C stretch falls at 988 cm^{-1}. [503] The rates of several reactions of dimethylsilylene were estimated and several published reactions as well as much published data on the reactions of this system was brought together in an effort to reconcile some apparent conflicts in the literature and draw attention to mechanistic features heretofore unnoticed. [504]

The reaction of dimethylsilylene with butadienes appears to proceed via a 1,2 addition followed by nonconcerted rearrangements via diradicals. (Eqn. 668)



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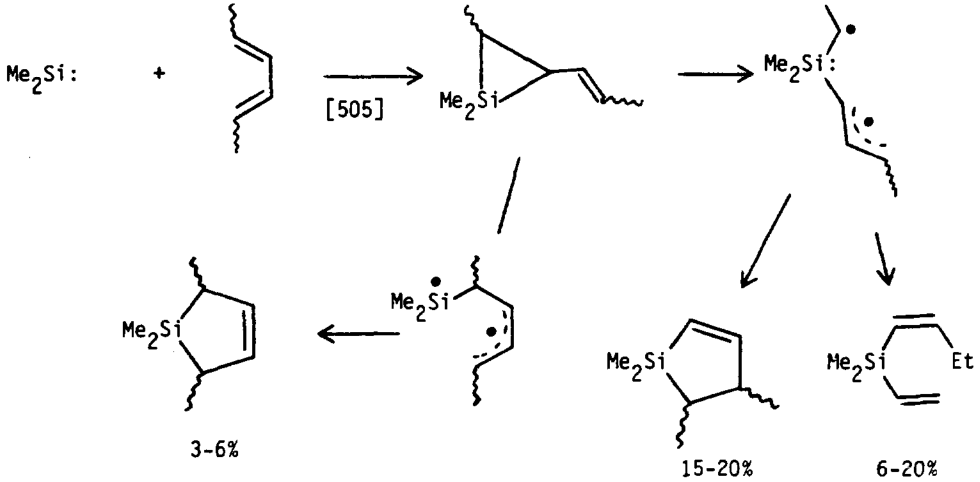
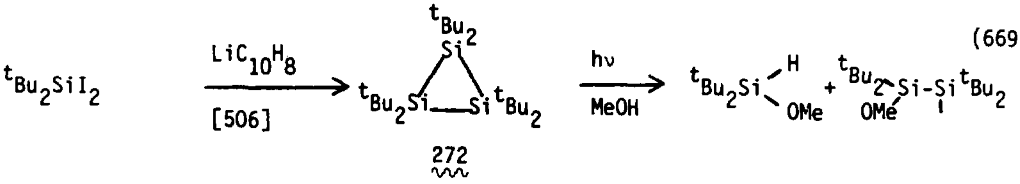


(668)

Treatment of di-tert-butyldiiodosilane with lithium naphthalenide gives hexa-tert-butylcyclopropasilane, **272**, whose structure was determined by x-ray. Photolysis of **272** gives di-tert-butylsilylene. (Eqn. 669)



(669)

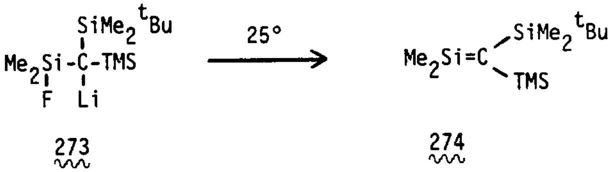
The π-bond energy of disilene was calculated to be 93.8 KJ/mole and a lower limit of 69.11 kJ/mole was found experimentally. (507)

An ab initio calculation of the insertion of silylene into ethylene has been made. [508] As similar study on the insertion of methylene and silylene into methane, silane and hydrogen has been made. [509] Theoretical studies on the ralative stabilities of silylsilylenes and disilenes indicates that the disilenes are more stable except for HCl_2Si-SiCl, which is 1.6 kJ/mole more stable than Cl_2Si=SiHCl. [510] A similar conclusion was reached by other investigators. [511]

C. Silenes

Dechlorination of (chloromethyl)dimethylchlorosilane with metal vapors in the presence and absence of 1,3-butadiene gives products indicative of the intermediacy of 1,1-dimethylsilene. [512] Compound **273** produced silene **274** at room temperature. (Eqn. 670) The silene **274** was reacted with a variety of reagents (Eqns. 671-675) and decomposed at 100°.

The reaction of dimethylfluorovinylsilanes with butyllithium reagents was studied. In addition to displacement of fluoride and of the vinyl group from silicon, addition to the double bond followed by loss of lithium fluoride to give the silene was observed. (Eqn. 676) More attack at silicon was observed with n-butyl and s-butyllithium than with t-butyllithium. The best generation of silene, as seen by dimer (**275**) formation, was with t-butyllithium in hexane.



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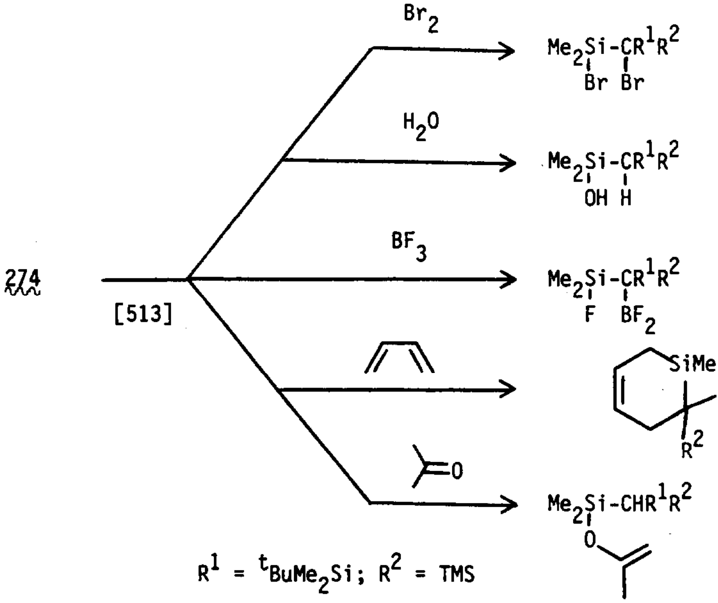


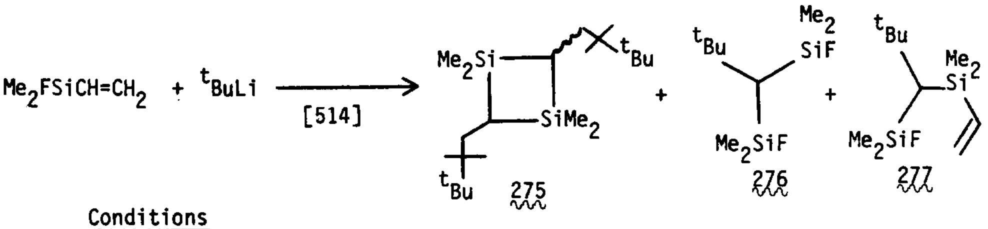
(671)

(672)

(673)

(674)

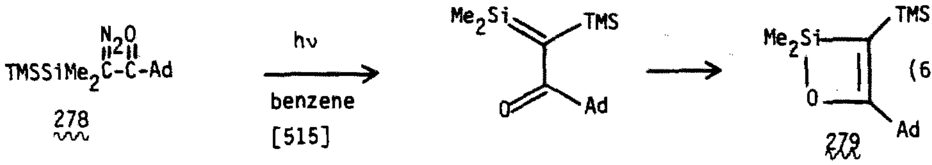
(675)



(676)

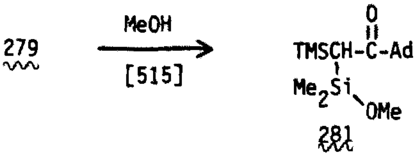
Conditions	275	276	277
1:1 ratio /THF/-78°	44	1	16
2:1 ratio /THF/-78°	8	1	56
1:2 ratio /hexane/-78°	57	trace	trace
1:1 ratio /hexane/25°	50	trace	trace

Photolysis of keto-α-diazodisilane **278** was proposed to produce silaoxetane **279** at low temperature (Eqn. 677) Warming to room temperature gave the acetylene **280** and D_4. (Eqn. 678) The addition of methanol at low temperature gave **281**. (Eqn. 679)



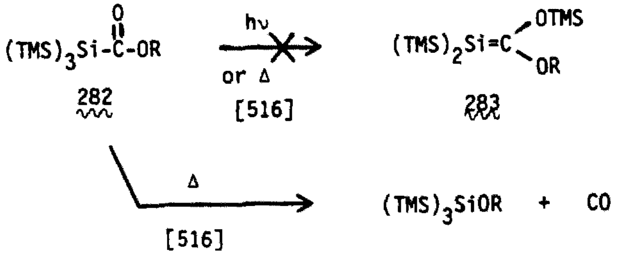
(677)

$$\underset{\mathbf{279}}{} \xrightarrow[\text{[515]}]{25^\circ} \underset{\mathbf{280}}{TMSC{\equiv}CAd} + (Me_2SiO)_4 \qquad (678)$$



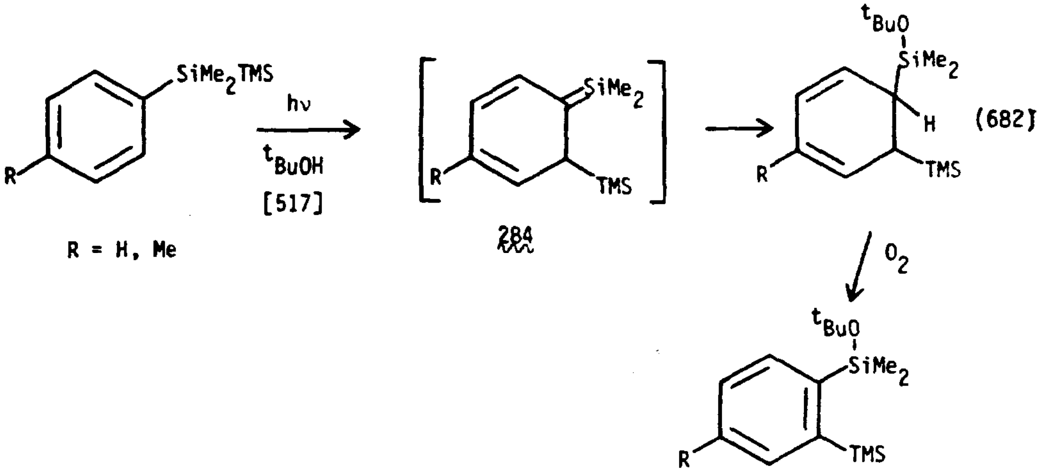
$$\mathbf{279} \xrightarrow[\text{[515]}]{MeOH} \underset{\mathbf{281}}{TMSCH(SiMe_2OMe)\text{-}C(=O)\text{-}Ad} \qquad (679)$$

Attempts to generate **283** from **282** in an analogous fashion to the ketones failed (Eqn. 680) producing only decarbonylation instead. (Eqn. 681) Arylpentamethyldisilanes were shown to rearrange upon photolysis to the silenes **284**. (Eqn. 682) Some ring opening occurs. (Eqn. 683) The debenzosilole **285** gave the intermediate silene **286**, which polymerized. (Eqn 684)

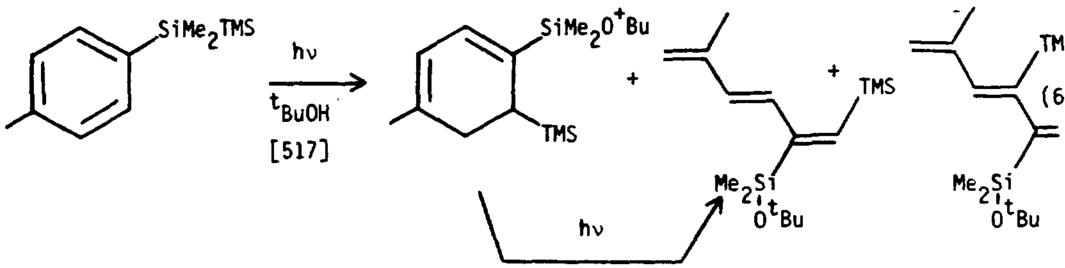


$$(TMS)_3Si\text{-}C(=O)\text{-}OR \;\; (\mathbf{282}) \xrightarrow[\text{or }\Delta\ [516]]{h\nu} (TMS)_2Si{=}C(OTMS)(OR) \;\; (\mathbf{283}) \qquad (680)$$

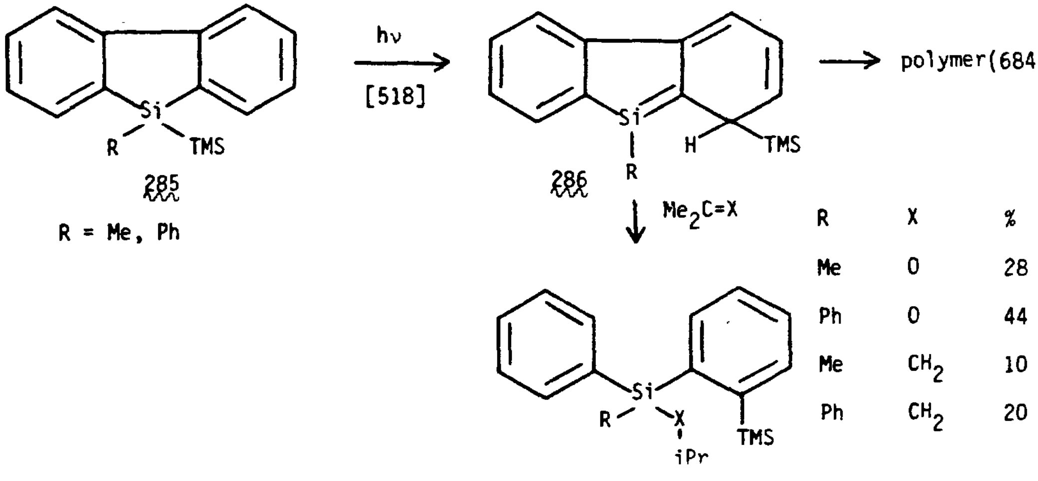
$$\mathbf{282} \xrightarrow[\text{[516]}]{\Delta} (TMS)_3SiOR + CO \qquad (681)$$



(682)



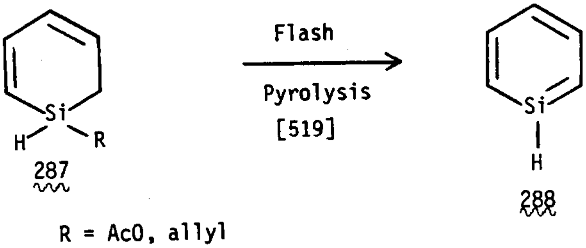
(683)



(684)

R	X	%
Me	O	28
Ph	O	44
Me	CH$_2$	10
Ph	CH$_2$	20

Flash pyrolysis of acetoxy- or allylsilacyclohexadienes **287** give silabenzene, which was isolated in an argon matrix. (Eqn. 685) Photolysis of silabenzene placed it in equilibrium with Dewar silabenzene. (Eqn. 686)



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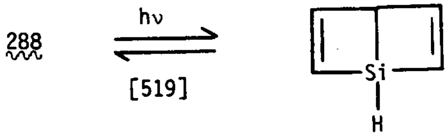
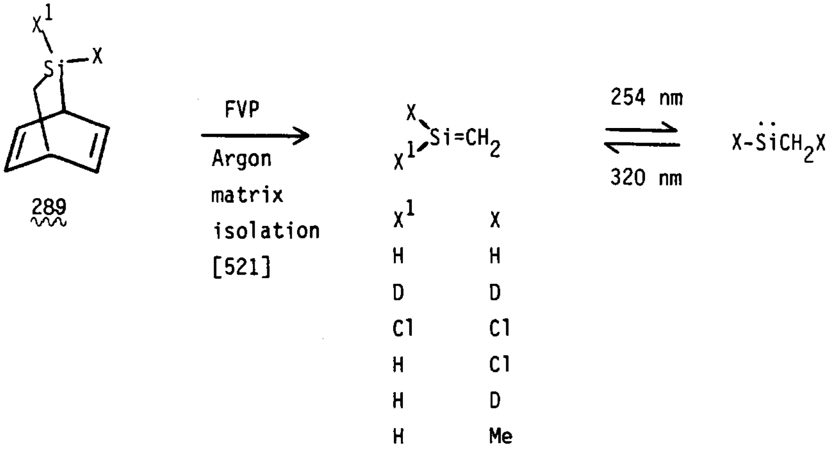


(686)

Thermally generated dimethylsilylene is in equilibrium with 1-methylsilene in the absence of traps. The reaction kinetics have been discussed. [520]

Flash vacuum pyrolysis of bicyclosilacyclooctadienes **289** was used to produce silenes in argon matrices. (Eqn. 687) These matrices were employed in a study of the silene-silylene interconversion. Thermally 1-chlorosilenes prefer the silylene structure, (Eqn. 688) whereas 1-methylsilenes prefer the silene structure. (Eqn. 689). Trapping studies with butadiene and trimethylsilane provided more evidence for the silene-silylene interconversion of methylsilene. (Eqns. 690-692)



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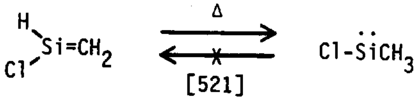

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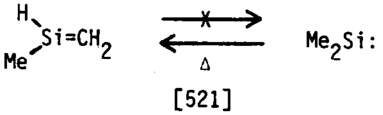

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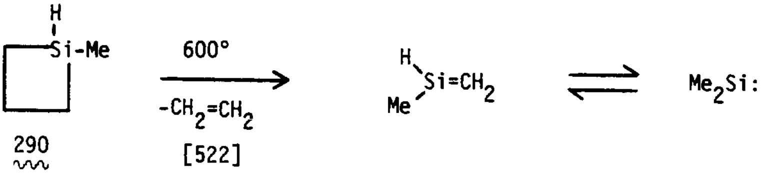

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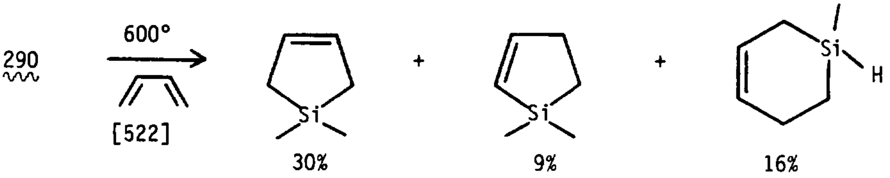

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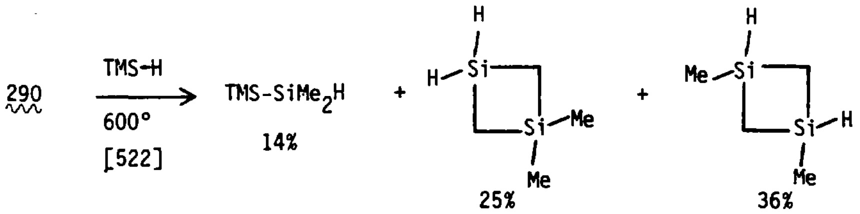


(692)

The pyrolysis of allyltrimethylsilane was shown to go through two processes, a retroene route giving 1,1-dimethylsilene and a homolysis route to give trimethylsilyl and allyl radicals. (Eqns. 693, 694)

Pyrolysis of 3,3-dimethyl-3-thietane produces 1,1-dimethylsilene and thioformaldehyde, which combine to give 2,2-dimethyl-2-silathietane. This then loses ethylene to give thiasilanone, which dimerizes in the expected manner. (Eqn. 695)

$$\mathrm{TMSCH_2CH{=}CH_2} \xrightarrow[\text{[523]}]{} \mathrm{Me_2Si{=}CH_2} + \mathrm{CH_3CH{=}CH_2} \qquad (693)$$

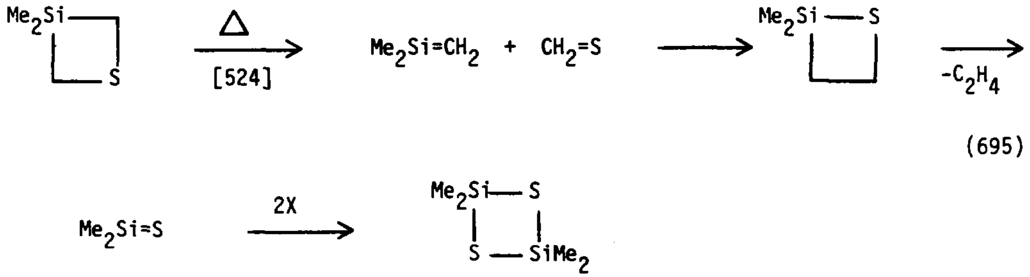
$$E = 55\ 12\ \text{kcal/mole}$$

$$k_1 = 1.84\ \ 10^{-2}\ \ 5^{-1}$$

$$\xrightarrow[\text{[523]}]{} \mathrm{TMS}\bullet + \mathrm{CH_2\text{-}CH\text{-}CH_2} \qquad (694)$$

$$E = 73 \pm 2\ \text{kcal/mole}$$

$$k_2 = 7.5 \times 10^{-3}\ \ 5^{-1}$$



(695)

A direct spectroscopic study of 1,1-dimethylsilenes **291** and **292** was performed. It was concluded that the Si=C stretch corresponds to two bands at 895.1 and 1117.5 cm^{-1} for **292**. [525] The IR, and UV spectra of a variety of silenes **293** were recorded. [526] The photoelectron spectrum of silabenzene was recorded to obtain all valence ionizations up to 21 eV. [527] The radical cation states were assigned by ab initio calculations and compared to those of benzene. The structure of **294** was determined by x-ray diffraction. [528]

Ab initio calculations showed that silene and methylsilylene are thermonuclear with a high (cm. 40 kcal/mole) barrier. [529] Calculations indicate that the relative stabilities of the isomeric silenes **295** and **296** depends on the bond energies. The reverse polarity of the Si=C bond (i.e. C=Si) is the single most important electronic factor in the stability of the bond. [530] Ab initio calculations indicate that germene is much more stable than methylgermylene, but resembles silene in stability. [531]

$Me_2Si{=}CD_2$

291

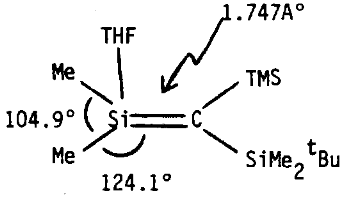
$(CD_3)_2Si{=}CD_2$

292

$XX^1Si{=}CH_2$

293

XX^1 = H, H; D, D; Cl, Cl; H, Cl; H, D; H, Me



(planar)

294

$H_2C{=}SiHR$

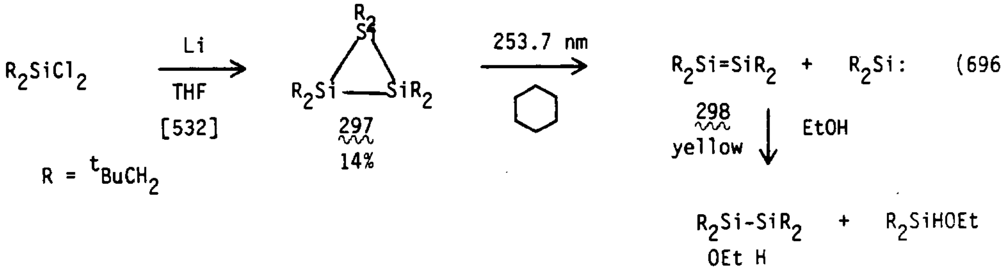
295

$RCH{=}SiH_2$

296

D. Disilenes

Dineopentyldichlorosilane was reacted with lithium in THF to give hexaneopentylcyclotrisilane **297**, which upon photolysis produces disilene **298**. (Eqn. 696) Treatment of **299** with lithium naphthalenide produced cyclopropasilane **300**, which photochemically produced the corresponding disilene. (Eqn. 697) Symmetrical tetra-tert-butyldihalodisilanes were precursors to tetra-tert-butyldisilene. (Eqns. 698) Photolysis of **301** gave tetraisopropyldisilene, which undewent the expected reaction. (Eqn. 699) The cis/trans isomerization of disilenes **302** and **303** was studied under photochemical and thermal conditions. (Eqn. 700)



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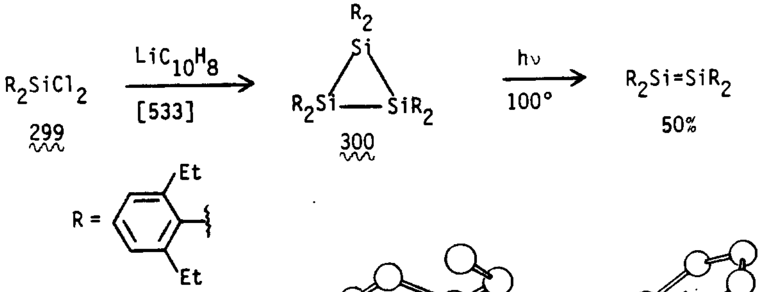

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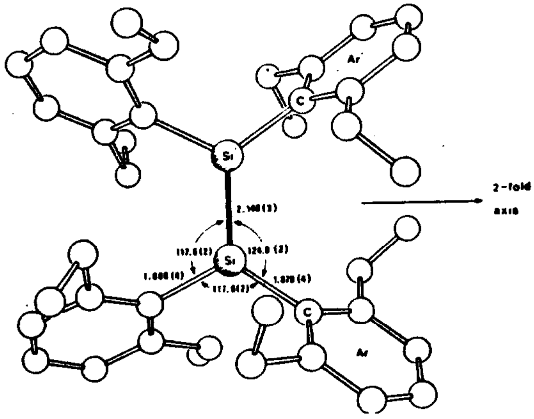

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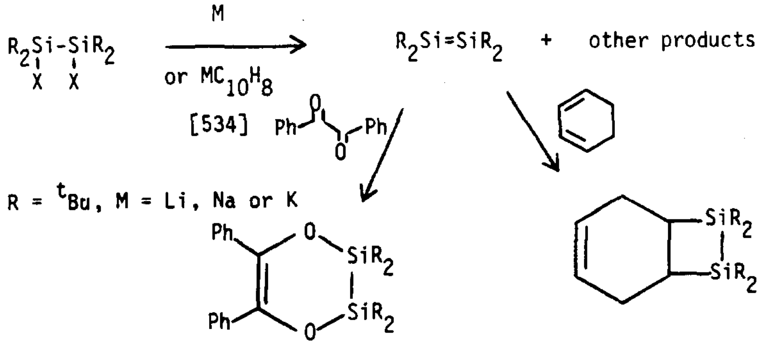
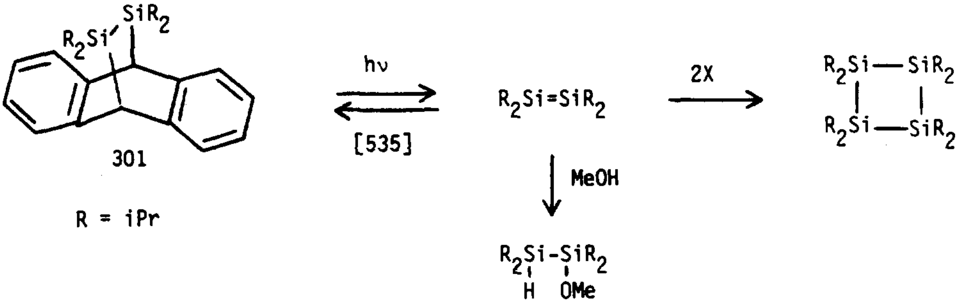


$R = {}^tBu$, M = Li, Na or K

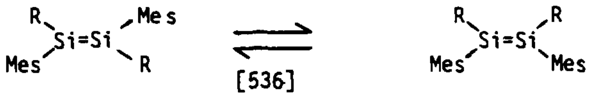
(698)



301

R = iPr

(699)



(700)

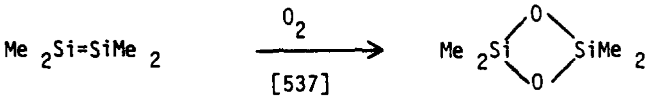
$R = {}^tBu$ 302

$R = (TMS)_2N$ 303

$R = {}^tBu$ c/t = 37:63 at 350 nm

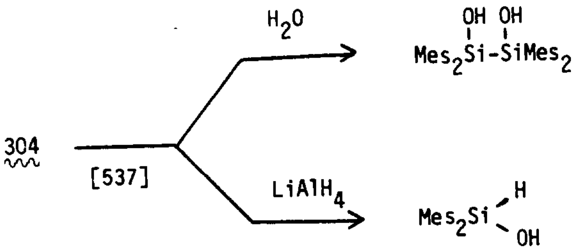
$R = {}^tBu$ c/t = 2:98 at 25°

Tetramesityldisilene reacts with oxygen to give the disiladioxepane 304. (Eqn. 701) The x-ray structure shows it to have a rather short (231 pm) Si-Si distance and a rather long (247 pm) O-O distance. [537] The material reacts with water and lithium aluminum hydride. (Eqns. 702, 703)



(701)

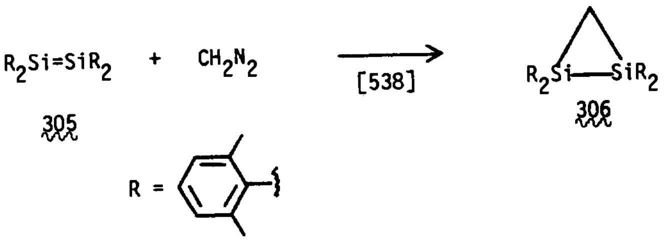
304



(702)

(703)

Disilene **305** reacted with diazomethane to give disilacyclopropane **306**. (eqn. 704) Compound **306** thermally rearranges (Eqn. 705) and photochemically extrudes the silylene (Eqn. 706).



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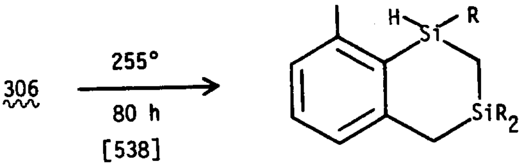

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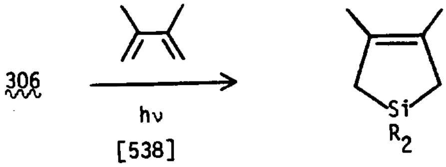
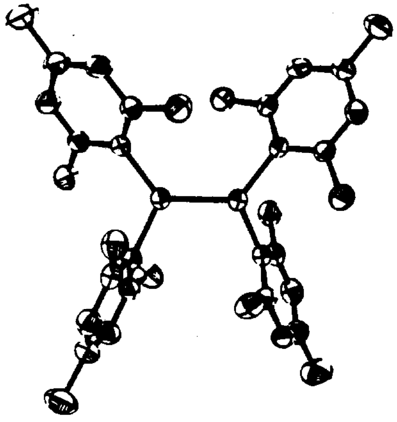
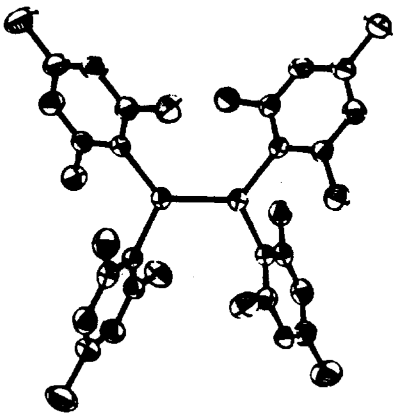


(706)

The x-ray crystal structures of tetramesityldisilene and trans-di-tert-butyl dimesityldisilene were determined. They are shown in the figures below. [539] The x-ray crystal structure of **307** was determined. [533] Molecular orbital calculations on $H_2NHSi{=}SiHNH_2$ indicates it to be a linear 6 election 4-center system. [540]



307



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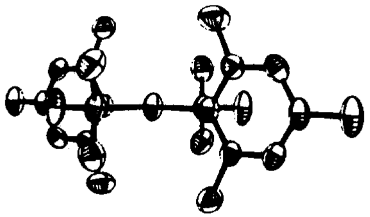

308

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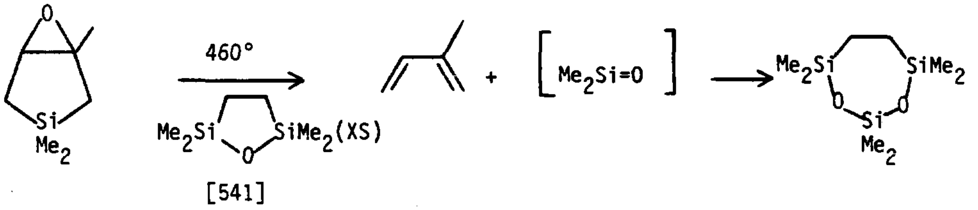
E. Other Double Bonded Silicon Species

Dimethylsilanone is a product of the thermolysis of 6-oxa-3-silabicyclo-[3.1.0]hexanes. (Eqn. 707) The spiro system **308a** is a source of O=Si=O. (Eqn. 708) The photolysis of azido silacycloalkanes provided silaimines which were trapped. (Eqns. 709, 710) Dimethylsilanethione was generated by very low pressure pyrolysis of 312. (Eqn. 711) Pyrolysis of dimethylsilacyclobutane in the presence of 312 also gave dimethylsilanethione. (Eqn. 712)



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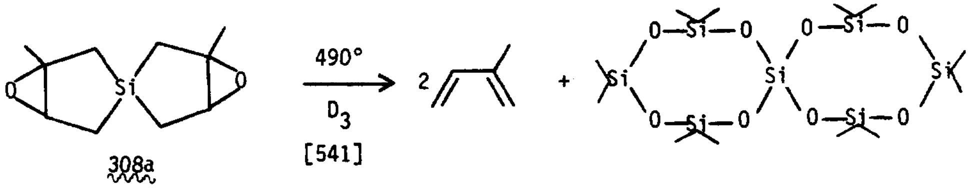

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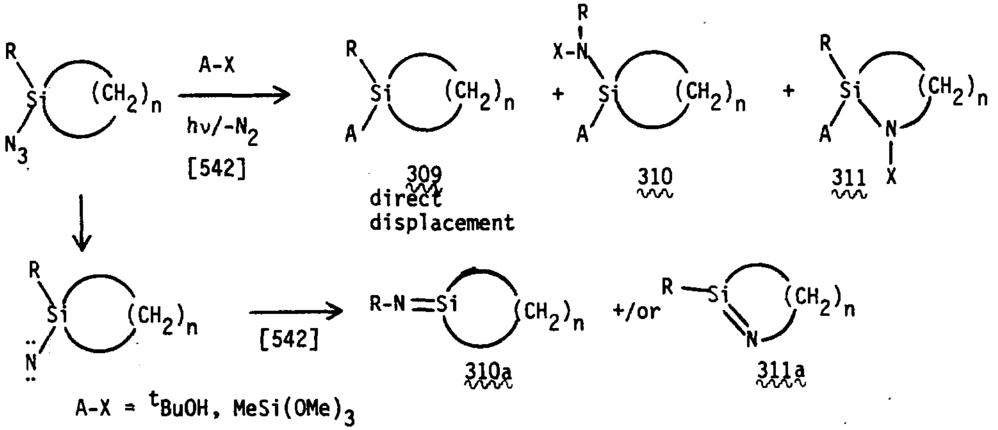

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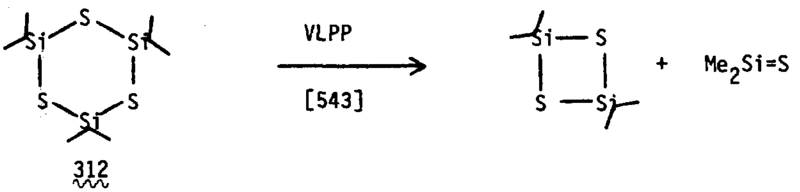
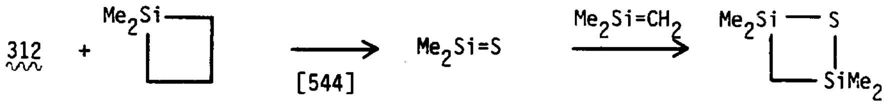
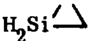


(711)



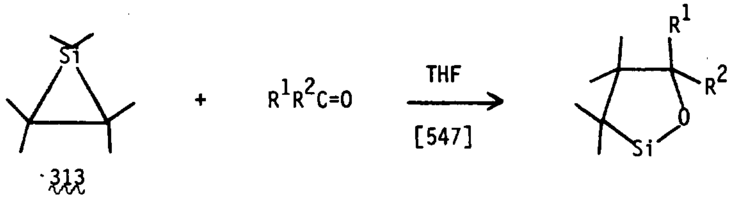
(712)

A theoretical study of dimethylsilanone and five of its isomers showed the silanone structure to be the most stable. The relative energies (kcal/mole) are: $Me_2Si=O$ (0), MeSiCH (7.4), H_3SiCHO(19.0), H(HO)$Si=CH_2$(21.2), H_2Si (25.3), $H_2Si=CHOH$(56.3). [544] These results led to the conclusion that the metathesis reaction of silanone and ethylene would give formaldehyde and silene. (Eqn. 713) Molecular orbital calculations indicate that $Me_2Si=S$ is more reactive than $Me_2Si=CH_2$ in 2+2 cycloadditions. [546]

$$CH_2=CH_2 + H_2Si=O \xrightarrow[{[545]}]{} H_2Si=CH_2 + H_2C=O \qquad (713)$$

F. Silacyclopropanes

Hexamethylsiliranes react with activated ketones and aldehydes at room temperature (Eqn. 714), with aliphatic systems upon photolysis (Eqn. 715), with imines (Eqn. 716) and diazenes (Eqn. 717) This same species reacts with organolithium reagents to cleave the silicon bond. The resulting tertiary carbanion rearranges to the more stable silylmethyl carbanion. (Eqns. 718, 719) The silacyclopropene **314** was reacted with a series of multiple bonded species. (Eqns. 720-725)



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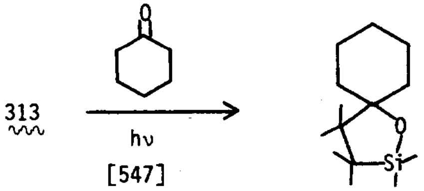

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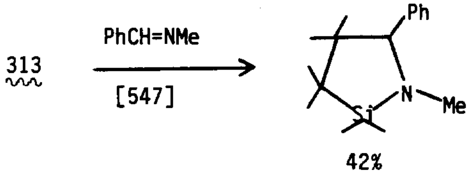

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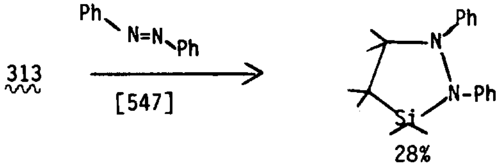
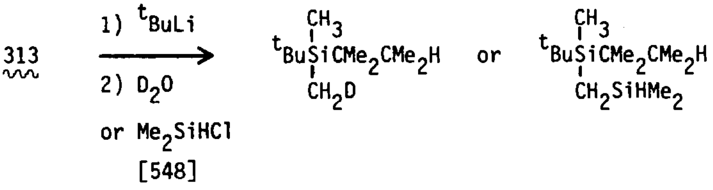


(717)

$$\underset{\sim\sim}{313} \xrightarrow[\text{2) } H_2O]{\text{1) RLi}} RMe_2SiCMe_2CMe_2H \qquad (718)$$

[548]

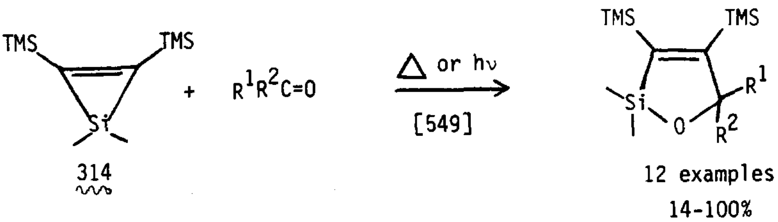
(R = Me, Bu, ^{t}Bu)



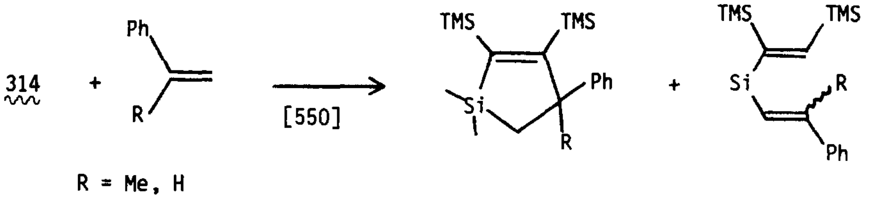
$$\underset{\sim\sim}{313} \xrightarrow[\text{2) } D_2O \text{ or } Me_2SiHCl]{\text{1) } {}^tBuLi} {}^tBu\overset{CH_3}{\underset{CH_2D}{Si}}CMe_2CMe_2H \text{ or } {}^tBu\overset{CH_3}{\underset{CH_2SiHMe_2}{Si}}CMe_2CMe_2H$$

[548]

(719)



(720)



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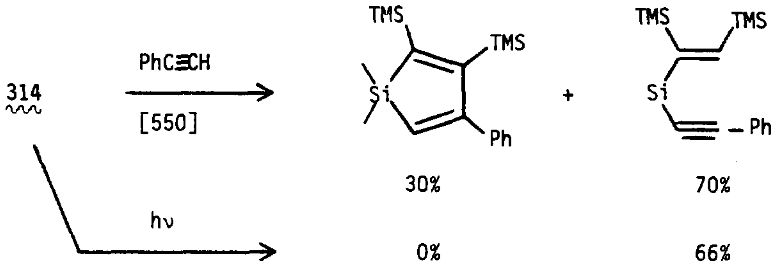

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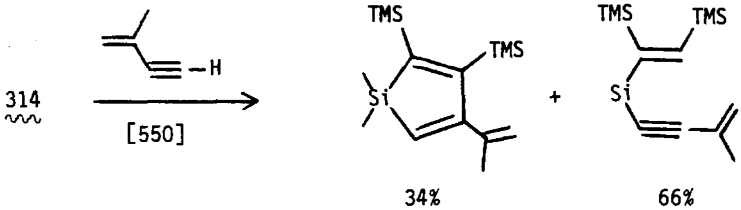

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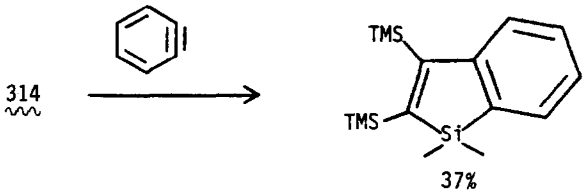

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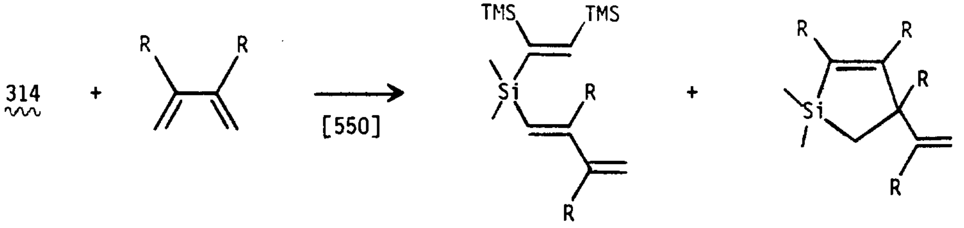


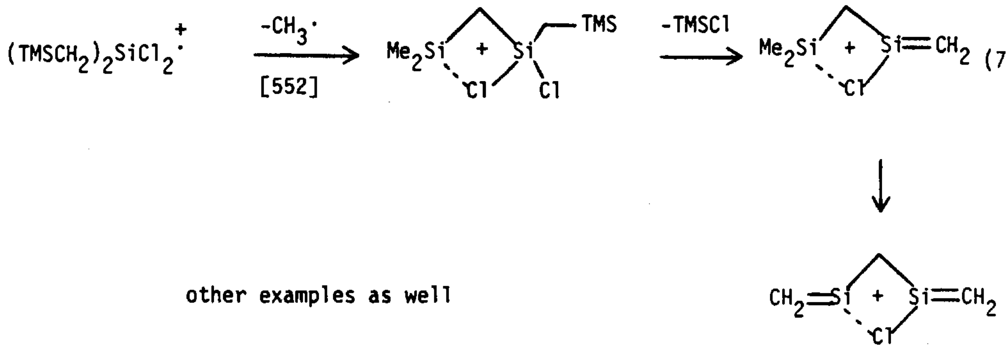
(725)

R = H	20%	45%
R = Me	13%	36%

G. Cations and Anions

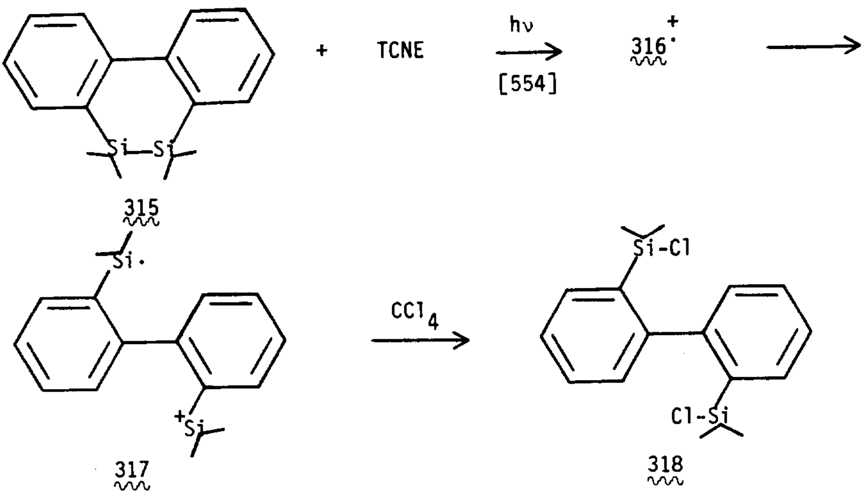
A theoretical study of the effect of electron withdrawing substituents of silicenium ions and silyl anions has been carried out. The silyl anions are pyramidal at silicon. The CHO and CN groups destabilize the cations and stabilize the anions whereas the ethynyl group stabilizes both by approximately 11 kcal/mole. [551]

The electron-induced decomposition of trimethylsilylmethylchlorosilanes produces silicenium ions. (Eqn. 726) Photoelectron spectroscopy was used to investigate the unimolecular decomposition of $Me_6Si_2^+$ in order to obtain the heats of formation of various silicon species. [553] The results obtained are ΔH_f Me_3Si (-49 kJ/mole), Me_4Si (-226.2 kJ/mole), Me_3Si^+ (629.7 kJ/mole), $Me_2Si_2^+$ (423 kJ/mole).



(726)

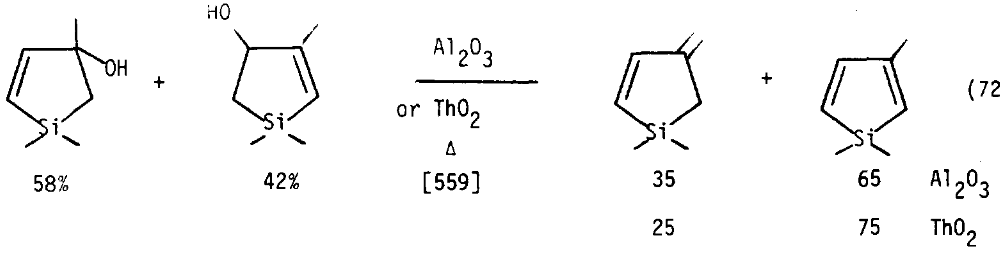
The photolysis of **315** gives the cation radical **316** which is proposed to produce the silyl cation radical **317**. In the presence of carbon tetrachloride this gives the chlorosilene **318**. (Eqn. 727) The appearance potentials of 1-silaphenalenes were obtained and it was concluded that no delocalization of the positve charge ocurred. [555] Similar results were obtained for the corresponding silyl anions. [555] Ab initio studies indicate that vinyl substituents will stabilize H_3Si^+ more than CH_3^+. [556] The flowing afterglow technique was used to study the chemistry of several anionic species. [557] The cation radicals of some silylbenzenes were prepared by treatment with ^{60}Co x-rays. SOMO calculations indicate the maximum spin density to be on the ipso carbon. [558]



(727)

G. Miscellaneous Reactive Species

Siloles were generated according to Eqns. 728 and 729. Some reactions of the siloles **319** and **320** were reported. (Eqns. 730-733) The enolate of dimethylsilanone was generated by collision-induced dissociation from TMSO . [562]



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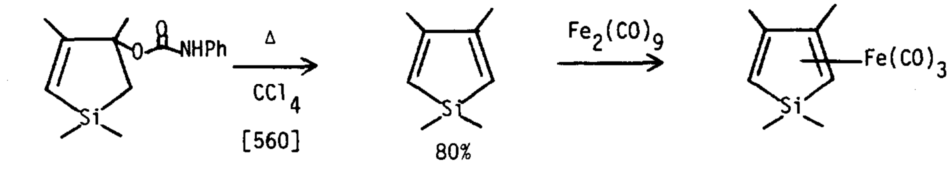

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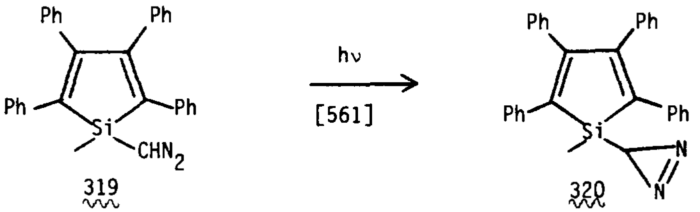

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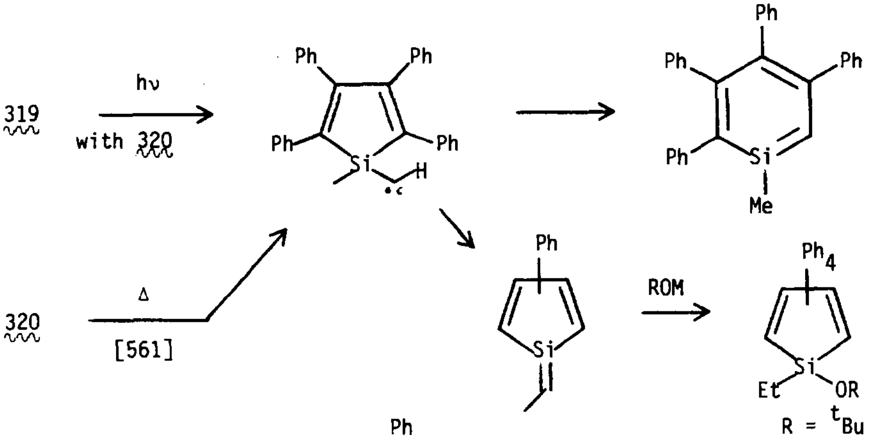
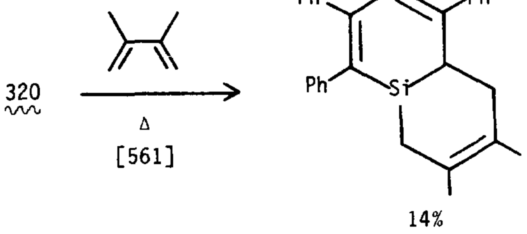


(731)

(732)



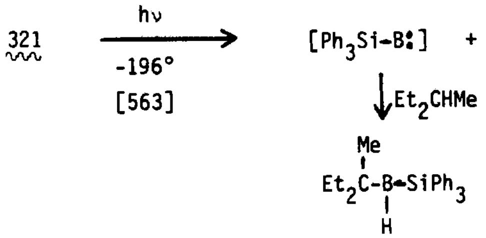
(733)

Triphenylsilyllithium was reacted with bromoboranes to give trigonal boron with triphenylsilyl ligands. These showed interesting photochemistry. (Eqns. 734-738)

Trimethylsilyldiazomethane was prepared from trimethylsilyltriflate. (Eqn. 739)

$$RBBr_2 + 2Ph_3SiLi \xrightarrow[\substack{\text{heptane} \\ -10° \\ [563]}]{\text{THF}} \underset{\substack{\underset{\sim\sim}{321} \\ R\,=\,Me,\ mesityl}}{RB(SiPh_3)_2} \qquad (734)$$

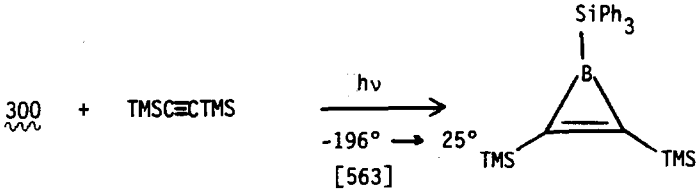
$$BBr_3 + 3Ph_3SiLi \xrightarrow[{[563]}]{} \underset{\underset{\sim\sim}{322}}{B(SiPh_3)_3} \qquad (735)$$



$$\underset{\sim\sim}{321} \xrightarrow[\substack{-196° \\ [563]}]{h\nu} [Ph_3Si-B\colon] + RSiPh_3 \qquad (736)$$

$$\downarrow Et_2CHMe$$

$$Et_2\overset{\overset{Me}{|}}{C}-\underset{\underset{H}{|}}{B}-SiPh_3$$



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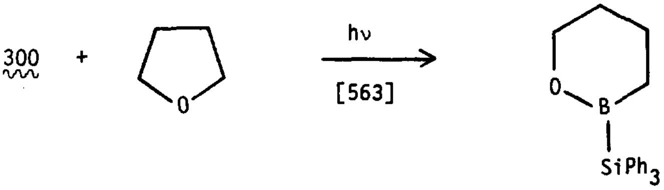

(738)

$$\mathrm{TMSOTf} \quad + \quad \mathrm{CH_2N_2} \xrightarrow[\text{[564]}]{\mathrm{iPr_2NEt}} \mathrm{TMSCHN_2} \qquad (739)$$

ACKNOWLEDGEMENTS I wish to thank Ms. Sara Nieves and Ms. Myrna Roman for their help in the typing and logistics of putting this chapter together. I also wish to thank Dr. John A. Soderquist and Ms. Luz E. Torres for proofreading of the final version and for their suggestions.

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