SILICON - THE SILICON-CARBON BOND: ANNUAL SURVEY FOR THE YEAR 1987*

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I. INTRODUCTION

This section of the annual survey of organosilicon chemistry covers material appearing in volumes 106 and 107 of Chemical Abstracts. It is the intent of the author to be as thorough as possible in covering the silicon-carbon bond and carbofunctional silanes. Liberal use of common abbreviations is employed. An honest attempt has been made to arrange the subject matter into fixed categories, but due to the multiple nature of some of the chemistry the reader will find it useful to peruse all sections.

II. REVIEWS

Two books were published. One of these deals with organophosphorus and organosilicon chemistry [1] and the other is a general treatise of organosilicon chemistry [2].

Thirty eight review articles were related to organosilicon chemistry. These are given here with the number of references to be found in each given in parentheses. Two reviews on hydrosilylation, one dealing with the hydrosilylation of alkenes and alkynes (39) [3] and the other with rhodium catalysis in various reactions including hydrosilylation (14) appeared [4]. Several reviews deal with the reactivity of organosilanes, these include reactions of carbenes with hydrosilanes [5], reactions of acetals and ortho esters with halosilanes (57) [6], the chemistry of fluorosilanes (85) [7], the acceleration of reactions of halo-silanes with ultrasound (62) [8], hypervalent organoiodine compounds in reactions of organosilanes and organostannanes (42) [9], and the gas-phase negative ion chemistry of organosilanes (42) [10].

Several reviews deal with silicon in organic synthesis. A primer on organosilicon chemistry written by a synthetic organic chemist was published (13) [11], others include new silylating reagents (233) [12], silicon-based protective groups (66) [13], silyl ketene acetals in synthesis (147) [14] and in group transfer reactions in natural product synthesis (50) [15], silyl peroxides as selective oxidizing agents (4) [16], fluorine synthons, some of which contain silicon (10) [17], the reaction of organosilanes with aldehydes (47) [18], the cyclization of allyl- and vinylsilanes (30) [19], new synthetic methods for the preparation of five-membered rings by use of 1,2-bis(trimethylsiloxy)-1-cyclobutene (11) [20], and the synthesis and synthetic applications of 1-metallo-1-silylcyclopropanes (235) [21].

Reviews dealing with highly reactive silicon species include those dealing with properties of silylenes (126) [22], silabenzene along with other highly reactive species (50) [23], doubly-bonded silicon species (42) [24], silenes (133) [25], reactive silicon species as building blocks for synthesis (120) [26], and theoretical studies of multiple bonding to silicon (101) [27].

Reviews on other organosilicon topics looked at the role of d-orbitals in organosilanes (11) [28], photochemistry of di-9-anthryl- and benzyl-substituted silanes (19) [29], cyclotrisilanes and related compounds (45) [30], di- oligo- and cyclosilanes (35) [31], an overview on the present state of cyclosilanes (64)

[32], developments in the chemistry of carbosilanes (16) [33], some highly sterically hindered organosilanes (28) [34], the use of bulky trimethylsilyl-substituted ligands (41) [35], sila-substituted natural and active substances (32) [36], organosilicon derivatives of dihydro- and tetrahydrofuran (53 and 42) [37 and 38], heterocyclic organosilicon compounds (30) [39], and silylated phosphines and phosphoranimines (0) [40].

III. DISSERTATIONS

Twenty five doctoral dissertations related to this survey were published. These are available from Dissertation Abstracts, Ann Arbor, Michigan. Those related to the use of organosilanes in organic synthesis are oxidative desilylation and substituent effects in Diels-Alder reactions [41], applications of hydrosilylation in synthesis [42], cerium modification of the Peterson olefination reaction [43], iminium and acyliminium ion initiated cyclizations of vinylsilanes [44], study of β-silylallylic alcohols and iodination of aryltrimethylsilanes [45], protodesilylation of γ-hydroxysilanes [46] ring openings of trimethylsilyloxycyclopropanes [47], deprotonation of hexacarbonyl(trimethylsilylethyne)dicobalt towards the synthesis of (+)-6a-carbaprostaglandin I_2 [48], use of organosilanes in regiocontrolled aromatic electrophilic substitutions [49], and some studies of organolithium and organosilicon chemistry [50]. Those that deal with mechanistic and reactivity aspects of organosilicon chemistry include rearrangements of α-halosilanes [51], conformational analysis of silanes [49], rearrangement-displacement of aryl(chloromethyl)diphenylsilanes with nucleophiles [52], the rearrangement of α-acyloxy silicon-centered radicals [53], reactivity and stereochemistry of silacyclohexanes and their derivatives [54], preparation and characterization of silyl perchlorates in solution [55], kinetic studies of α-silyl radicals [56], fluorescent alkoxysilanes [57], and selective fluorination of organosilicon compounds [58]. Those relating to reactive species of silicon are the photochemical and structural studies of azidosilanes: formation of silanediimines and silanimines [59], the generation and characterization of novel organosilicon reactive intermediates: 1,4-disilabenzenes, di-tert-butylsilylene and N,N'-di-tert-butylsilanediimine [60], gas-phase thermal interconversion of silacyclobutanes, alkylsilylenes,.. and silacyclopropanes [61], silenes and silenoids in the chemistry of cyclopentadienylsilanes [62], and the generation and kinetic study of 1,1-dimethyl-3,4-diphenylsilole [63]. The two dealing with theoretical considerations are ab initio calculations on carbene and silylene insertion reactions [64] and applications of semiempirical SCF-MO theory to aspects of organosilicon chemistry [65]. In addition there is the structural characterization of APTS-modified silica using solid state NMR [66].

IV. ALKYLSILANES

A. Preparation

The preparation of alkylsilanes can also be found in the hydrosilylation section of this survey. The reaction of Grignard reagents with mixed alkoxychlorosilanes gives rise to trialkylalkoxysilanes, useful in the preparation of high molecular weight disiloxanes used as lubricants. (Eqn. 1) A catalytic process utilizing alkylmagnesium halides and a copper (Eqn. 2) or a silver catalyst (Eqn. 3) provides high molecular weight tetraalkylsilanes, also useful as lubricants.

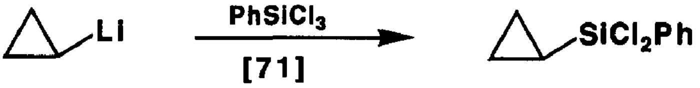
$$R^1_nSi(OR^2)Cl_{3-n} + R^3MgX \xrightarrow[\text{[67]}]{Et_2O} R^1_nSi(OR^2)R^3_{3-n} \qquad (1)$$

$$MeSiCl_3 + ({}^nC_8H_{17})_2Mg \xrightarrow[\text{[68]}]{CuCN} \underset{96\%}{MeSi({}^nC_8H_{17})_3} \qquad (2)$$

$$MeSiCl_3 + R_2Mg \xrightarrow[\text{THF [69]}]{AgSCN} \underset{79\%\ R = {}^nC_8H_{17}}{MeSiR_3} \qquad (3)$$

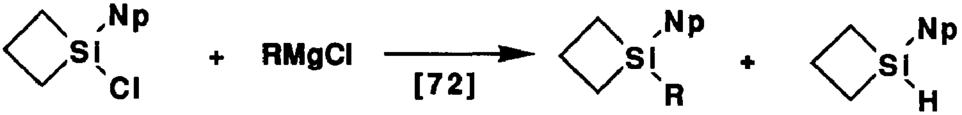
The reaction of tert-butylmagnesium chloride with methyldiethoxysilane provides tert-butylmethylethoxysilane in good yield. (Eqn. 4) Cyclopropyllithium was reacted with phenyltrichlorosilane to give cyclopropylphenyldichlorosilane. (Eqn. 5)

$$\mathrm{MeSiH(OEt)_2} \;+\; {}^{t}\mathrm{BuMgCl} \;\xrightarrow[\text{[70]}]{60^{\circ}}\; \underset{74\%}{{}^{t}\mathrm{BuMeSiHOEt}} \qquad (4)$$



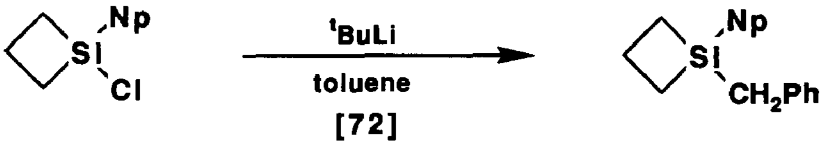
(5)

1-Naphthyl-1-chloro-1-silacyclobutane reacts with cyclohexylmagnesium chloride or tert-butylmagnesium chloride to give a mixture of the substituted and reduced products. Its reaction with tert-butyllithium in toluene, however, gives the benzyl derivative as a result of metal-hydrogen exchange between the tert-butyllithium and toluene. (Eqns. 6 and 7)



(6)

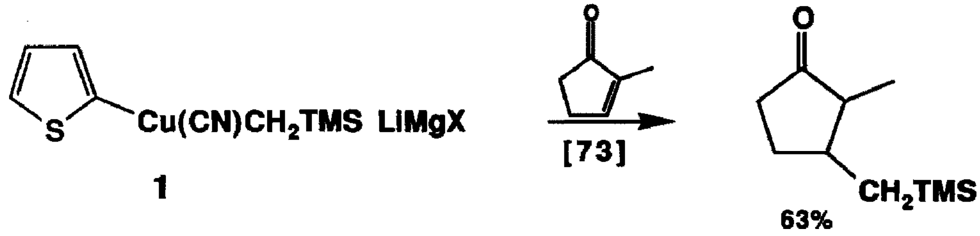
R = cyclohexyl, tert-butyl



(7)

Mixed, higher-order lithiomagnesioorganocuprates containing the trimethylsilylmethyl ligand, such as **1**, are useful in preparing organosilanes. (Eqns. 8 and 9)

(8)



(9)

Dialkylsilanes have been prepared from silane itself or from alkylsilanes and metal tetraalkylaluminates. (Eqns. 10 and 11) Methylalkyldimethoxysilanes have also been prepared *via* the reaction of sodium tetraalkylaluminates and methyltrimethoxysilane. (Eqn. 12)

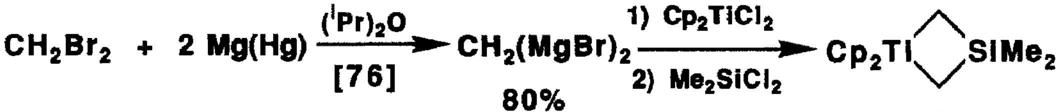
$$R^1SiH_3 + MAlR^2_4 \xrightarrow[{[74]}]{} R^1R^2SiH_2 + R^1R^2_2SiH \qquad (10)$$

M = alkali metal

$$SiH_4 + NaAl(^nC_8H_{17})_4 \xrightarrow[\substack{LiCl\\ {[74]}}]{190°C} H_2Si(^nC_8H_{17})_2 + (^nC_8H_{17})_3SiH \qquad (11)$$

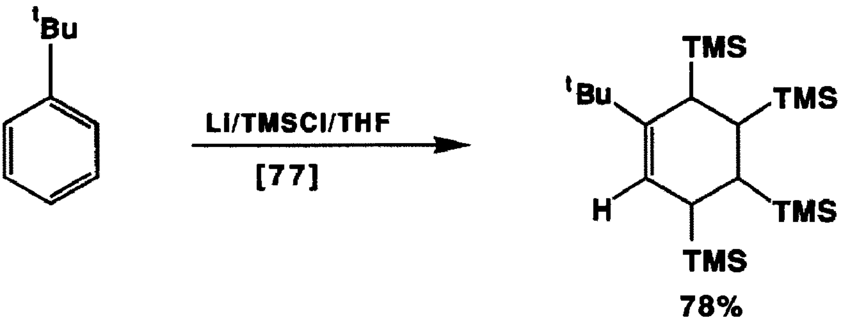
$$MeSi(OMe)_3 + NaAl(^nC_{10}H_{21})_4 \xrightarrow[{[75]}]{} \underset{78.6\%}{MeSi(^nC_{10}H_{21})(OMe)_2} \qquad (12)$$

The di-Grignard reagent of dibromomethane was prepared and first reacted with dicyclopentadienyltitanium dichloride and then with dimethyldichlorosilane to give **2**. (Eqn. 13)



2 (13)

Tert-butylbenzene and trimethylsilylbenzene react with lithium and trimethylchlorosilane in THF solvent to give tert-butyltetrakis(trimethylsilyl)cyclohexene and pentakis(trimethylsilyl)cyclohexene, respectively. (Eqns. 14 and 15) o-Dichlorobenzene reacts under these conditions to give hexakis(trimethylsilyl)benzene (Eqn. 16), whereas, with magnesium and trimethylchlorosilane in HMPA solvent it gives o-bis-(trimethylsilyl)benzene (Eqn. 17), which in turn reacts with lithium and trimethylchlorosilane in THF to give the hexakis(trimethylsilyl)cyclohexene.



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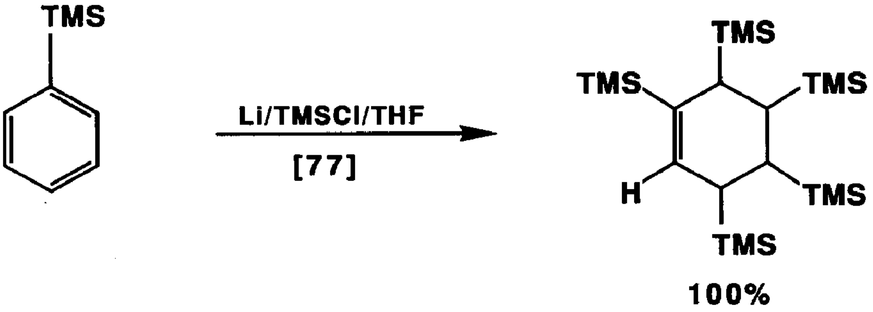

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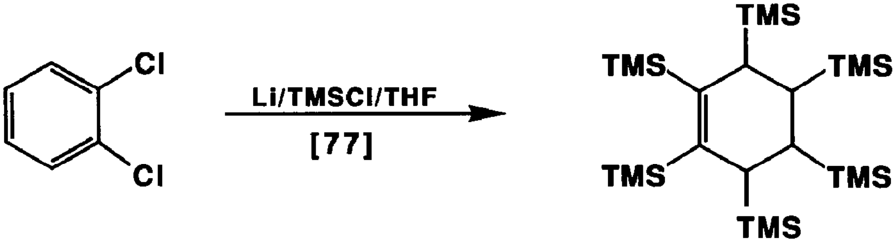

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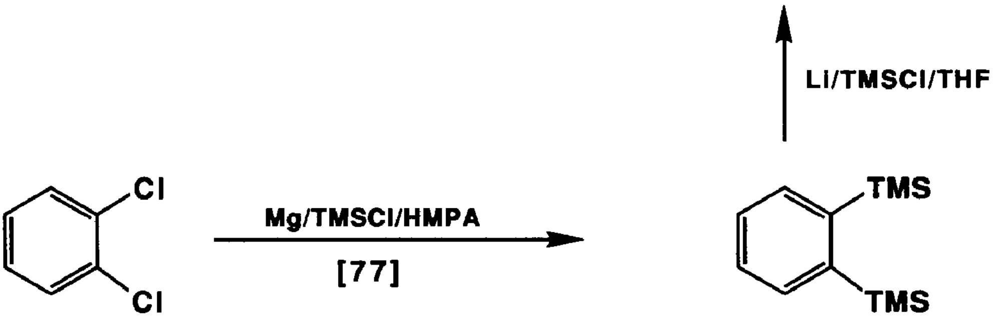
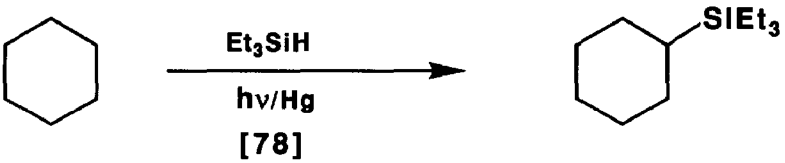


(17)

Mercury-sensitized photolysis of cyclohexane in the presence of triethylsilane gives cyclohexyltriethylsilane in 30 percent yield along with dimers of cyclohexane and triethylsilane. (Eqn. 18) Treatment of 1,3-dimethyladamantane with chloro- and ethoxyvinylsilanes in the presence of tert-butylperoxide leads to silylethylation of the adamantane group in the 5-position. (Eqn. 19) This reaction also works well for ethylsilanes and allylsilanes.



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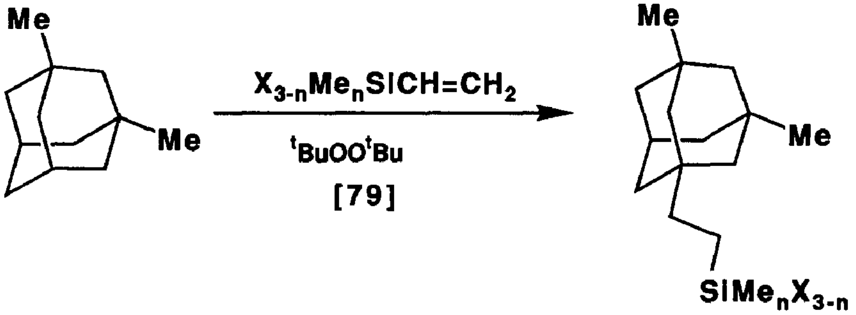


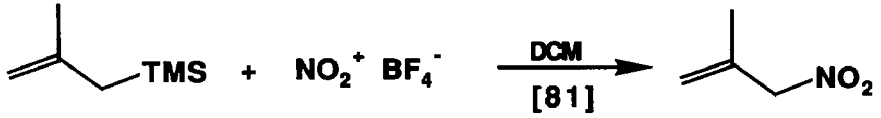
(19)

B. Alkylsilanes-Reactions

The pyrolysis of some methylchlorosilanes was studied. These pyrolyses proceed mainly *via* radical chain mechanisms with little involvement of silylenes or silenes. [80] Tetramethylsilane reacts with nitronium tetrafluoroborate to give nitromethane, boron trifluoride, and trimethylfluorosilane. (Eqn. 20) At 140°C a second methyl group can be cleaved from the silicon. (Eqn. 21) Allylsilanes give allyl nitrates. (Eq. 22)

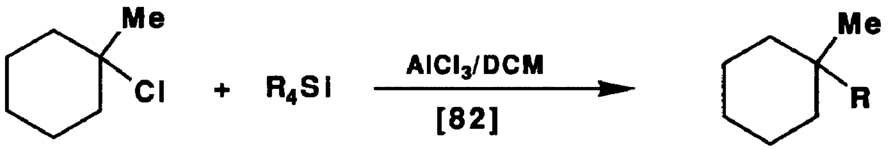
$$Me_4Si \; + \; NO_2^+ \, BF_4^- \xrightarrow[\text{[81]}]{\text{25-80°C}} MeNO_2 \; + \; Me_3SiF \qquad (20)$$

$$Me_3SiF \; + \; NO_2^+ \, BF_4^- \xrightarrow[\text{[81]}]{140°} MeNO_2 \; + \; Me_2SiF_2 \qquad (21)$$



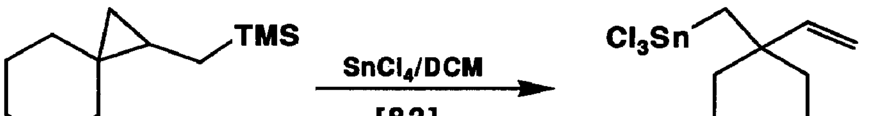
(22)

Tertiary alkyl chlorides and bromides react with tetraalkylsilanes in the presence of aluminum chloride to give alkylation to the corresponding quaternary carbon. (Eqn. 23) Trimethylsilylmethylcyclopropanes react with tin tetrachloride to give ring opening and 4-butenyltrichlorotin systems. (Eqn. 24) The isomerization of 1,2-dimethylsilacyclopentanes on a copper surface has been studied. (Eqn. 25)



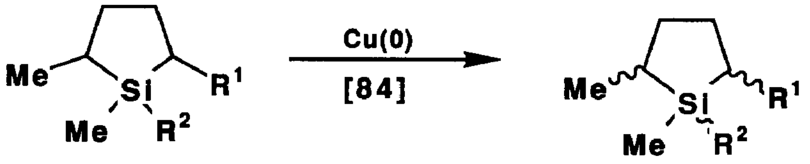
(23)

R = Et, ${}^nPr$, ${}^nBu$, ${}^nC_5H_{11}$; X = Cl, Br



(24)

other examples also



(25)

Several alkylsilanes were subjected to electrophilic cleavage of the alkyl-silicon bond with iodine chloride and chlorosulfonic acid. Some examples are shown in Eqns. 26 - 28. Not surprisingly, the reaction of chlorosulfonic acid with chloromethyldimethylchlorosilane reacts at the silicon-chlorine bond. (Eqn. 29) Ethyl trimethylsilyl acetate reacts readily with the above reagents to give the corresponding α-iodo- or α-sulfonyl ester. (Eqns. 30 and 31)

$$\mathrm{Me_3SiBu} \xrightarrow[\text{[85]}]{\mathrm{ICl}} \mathrm{ClMe_2SiBu} + \mathrm{MeI} \qquad (26)$$

$$\mathrm{Me_3SiCH_2Cl} + 2\,\mathrm{ICl} \xrightarrow[\substack{\mathrm{CCl_4} \\ \text{[85]}}]{0\text{-}25^\circ} \mathrm{ClMe_2SiCH_2Cl} + \mathrm{MeCl} + \mathrm{I_2} \qquad (27)$$

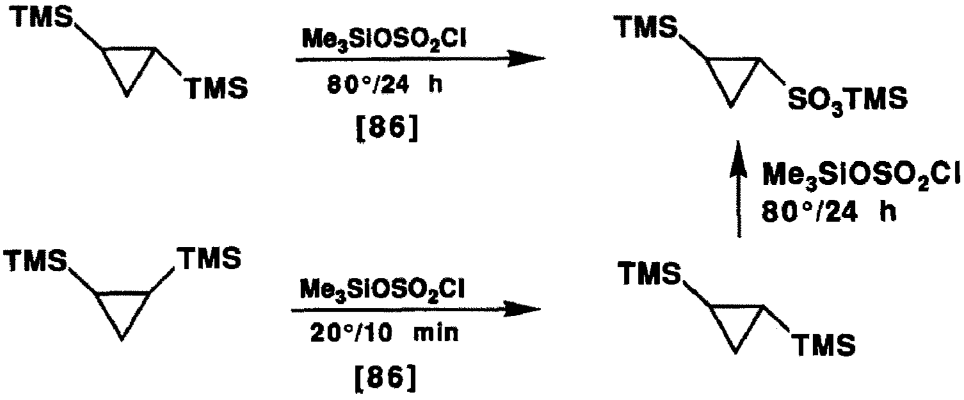
$$\mathrm{Me_3SiCH_2Cl} + \mathrm{ClSO_3H} \xrightarrow[\text{[85]}]{50\text{-}80^\circ} \begin{array}{l} \mathrm{SO_2(OSiMe_2CH_2Cl)_2} + \\ \mathrm{ClMe_2SiCH_2Cl} + \mathrm{CH_4} \end{array} \qquad (28)$$

$$\mathrm{ClMe_2SiCH_2Cl} + \mathrm{ClSO_3H} \xrightarrow[\text{[85]}]{20\text{-}25^\circ} \mathrm{ClSO_3SiMe_2CH_2Cl} + \mathrm{HCl} \qquad (29)$$

$$\mathrm{TMSCH_2CO_2Et} \xrightarrow[\text{[85]}]{\mathrm{ICl}} \mathrm{ICH_2CO_2Et} + \mathrm{TMSCl} \qquad (30)$$

$$\mathrm{TMSCH_2CO_2Et} \xrightarrow[\text{[85]}]{\mathrm{ClSO_3H}} \mathrm{TMSO_3SCH_2CO_2Et} \qquad (31)$$

Some trimethylsilylcyclopropanes were subjected to electrophilic cleavage with chlorotrimethylsilyl sulfonate (Eqns. 32 and 33) and acyl chloride (Eqns. 34 and 35).



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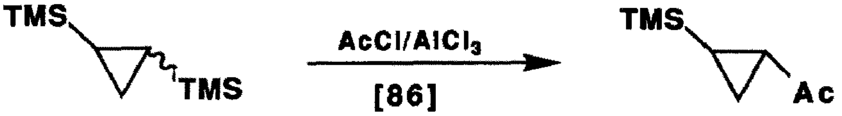

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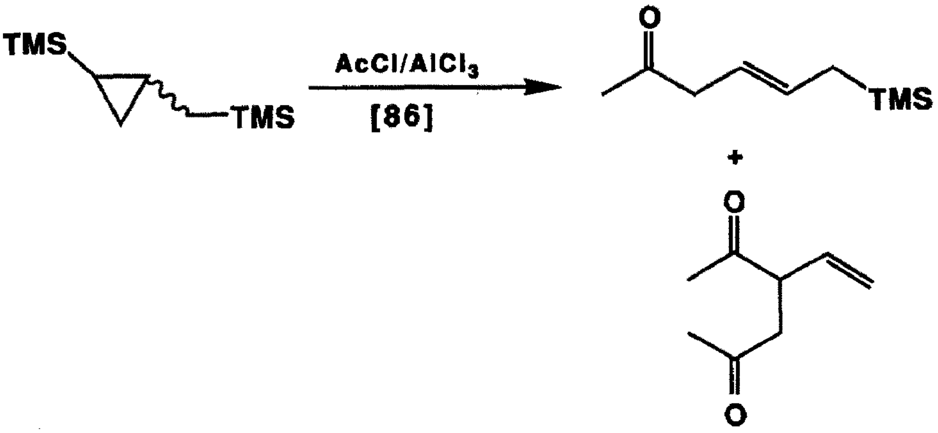
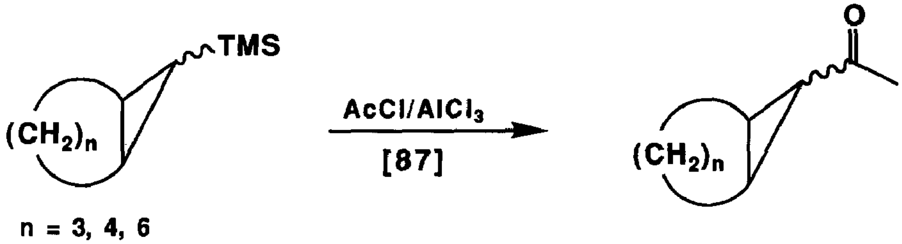


(35)

The acetylation of some trimethylsilyl[n.1.0]alkanes was studied. The reaction pathway depends on the structure of the bicylic alkane and the stereochemical position of the trimethylsilyl group. The results are summarized in Eqns. 36-39.



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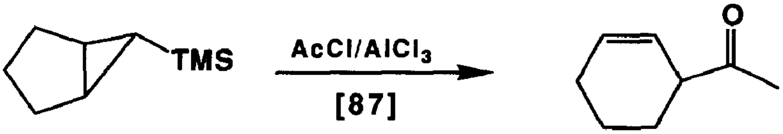

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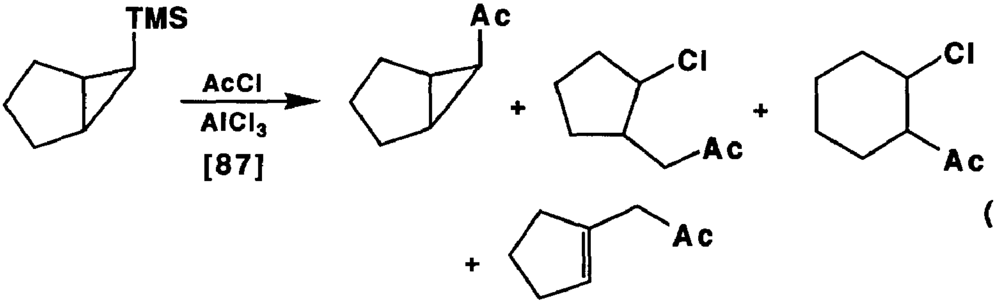

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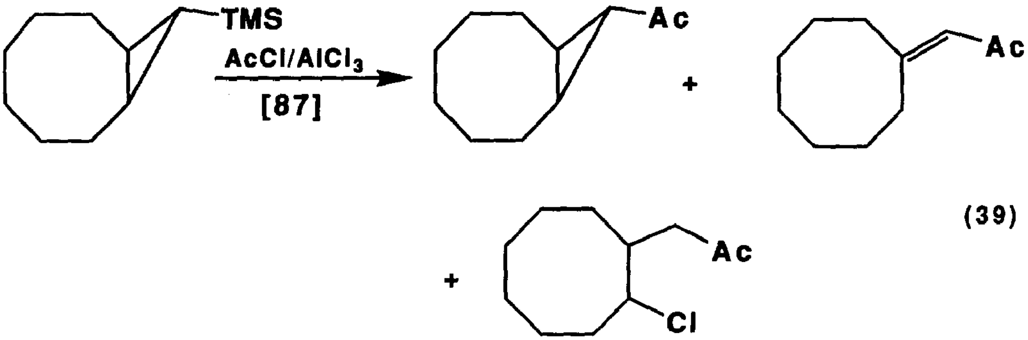


(39)

C. Alkylsilanes-Other Studies

The molecular structure of 1,1-dichloro-1-silacyclobutane was reinvestigated by gas electron diffraction. The tetrahedral bonding of the silicon atom is distorted in such a way that both the C-Si-C and Cl-Si-Cl bond angles are less than the tetrahedral values. [88] The r_s structures of ethylfluorosilane and ethylmethyl sulfide were determined and compared with that of 1-fluoropropane. [89] The molecular structure of cyclopropylsilane was determined by gas phase electron diffraction. The C_1-C_2 bond distance is 1.528 Å, the C_2-C_3 bond is 1.490 Å and the C-Si bond is 1.840 Å. The angle between the ring plane and the silyl group is 55.9°. The role of d-orbitals in the interpretation of the structure is discussed. [90]

A ^{13}C NMR comparison of cyclobutanes and silacyclobutanes has been done. [91] The deuterium isotope effect on the ^{29}Si NMR spectra of several organosilanes and siloxanes were determined. The one bond effects are about -0.2 ppm/deuterium and follow an additivity whereas the 2-bond effect is small. [92]

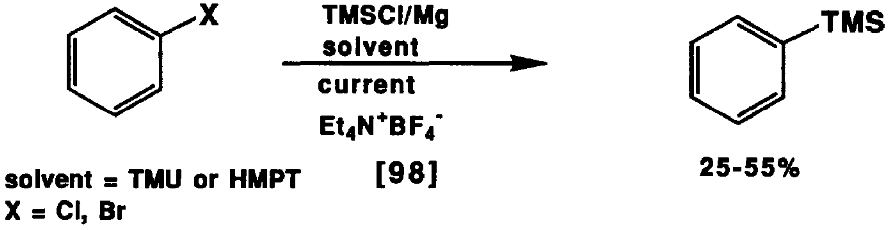
An IR method was employed to demonstrate a very high inductive effect of the silatranyl group with σ^* being -3.49 for the silatranyl group itself and -2.24, -1.48, and -0.32 for the silatranylmethyl-, ethyl- and propyl groups, respectively. [93] Inductive and resonance sigma constants for substituents attached to silicon were determined via the ^{1}H, ^{13}C, and ^{29}Si chemical shifts and the ^{1}H-^{13}C coupling constants of systems Me_3SiR, where R = Me, Cl, Br, CH_2Cl, $CHCl_2$, CH_2OH, Ph, OMe, OPh, SMe, OAc, NMe_2, and CN. [94]

The heats of formation and of combustion of several organosilanes and silatranes were determined. [95] AM1 calculations, which overcome the shortcomings of MNDO, have been applied to silicon compounds and their reactions. [96] Two empirically-modified first order molecular connectivity indexes, which reflect either the larger covalent radius of silicon or the longer silicon-carbon bond length, were calculated for 115 alkylsilanes. The correlation of molar refraction with these empirically derived values is excellent. [97]

V. ARYLSILANES

A. Preparation

Arylsilanes were prepared by the electrochemical reaction of aryl chlorides or bromides with trimethylchlorosilane in a single-compartment cell equipped with a sacrificial magnesium anode in a polar, aprotic solvent. (Eqn. 40)

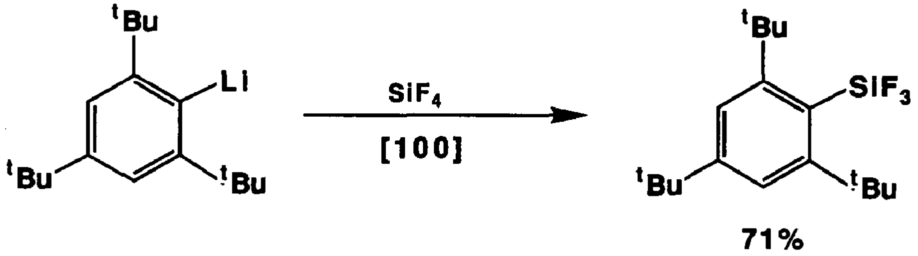


(40)

The reaction of 1,1,2-trichlorotrimethyldisilane with phenyllithium or phenylmagnesium bromide in the presence of cobalt(II) chloride was used to prepare 1,2-dichlorotrimethylphenyldisilane. (Eqn. 41)

$$\mathrm{ClMe_2SiSiMeCl_2} + \mathrm{PhLi\ (or\ PhMgX)} \xrightarrow[\text{[99]}]{\mathrm{CoCl_2\ cat.}} \mathrm{ClMe_2SiSiClMePh} \qquad (41)$$

Arylsilanes containing a very hindered aryl group, a class of compounds that has attracted much attention lately due to their ability to lend stability to otherwise highly unstable systems, were prepared from the corresponding aryllithium reagent and tetrafluorosilane. This takes advantage of the reactivity of the silicon-fluorine bond towards substitution. Both the aryltrifluorosilane (Eqn. 42) and the diaryldifluorosilane (Eqn. 43) can be prepared. This approach was used in the synthesis of mixed disubstituted difluorosilanes as well. (Eqn. 44)



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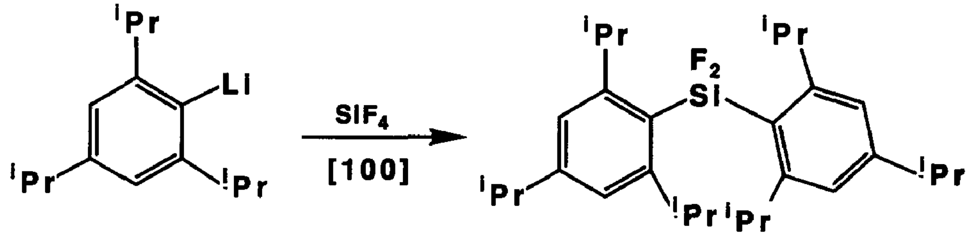

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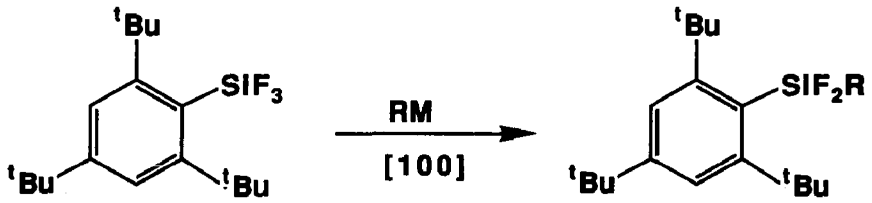
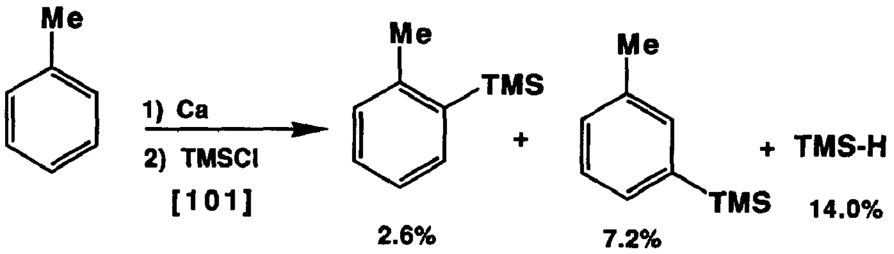


(44)

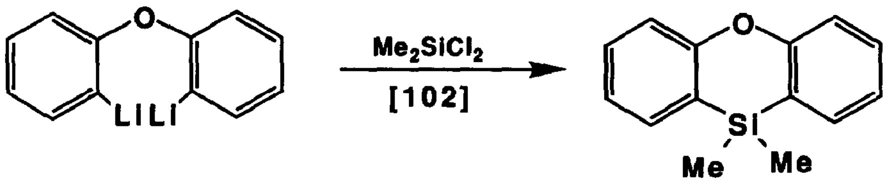
RM = MeLi, EtMgBr, ^{i}PrLi, MesLi, ^{t}BuLi, Arylcalcium hydrides, formed by the direct reaction of the aromatic hydrocarbon and calcium atoms, were reacted with trimethylchlorosilane to provide aryltrimethylsilanes. (Eqns. 45 and 46) These reactions are not of synthetic utility, but of interest from the standpoint of the reaction of calcium atoms with the aryl-hydrogen bond.

$$\text{Ar-H} \xrightarrow[\text{[101]}]{\text{Ca(atoms)}} \text{ArCaH} \xrightarrow{\text{TMSCl}} \text{ArTMS} + \text{TMS-H} \qquad (45)$$

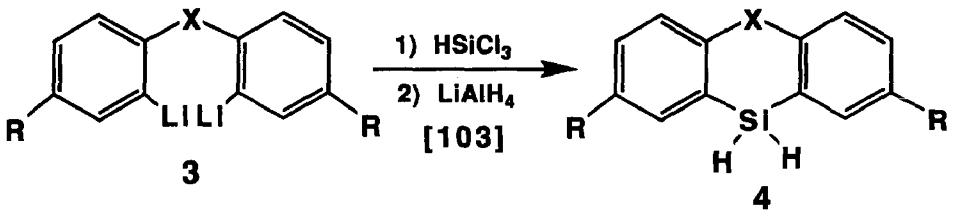


(46)

The synthesis of phenoxasilins was accomplished as illustrated in Eqn. 47. The reaction of dilithium reagent **3** with trichlorosilane followed by lithium aluminum hydride reduction was found to circumvent the problems encountered with the direct reaction of **3** with dichlorosilane for the preparation of silacycles of the general structure **4**.

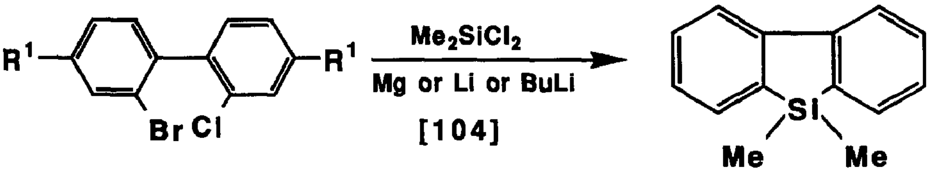


(47)



(48)

Treatment of o, o'-dihalobiphenyls with magnesium, lithium, or butyllithium and dimethyldichlorosilane leads to silafluorenes. (Eqn. 49) A similar approach was used to prepare the 9,10-disila-9,10-dihydroanthracenes as a mixture of cis and trans isomers. (Eqn. 50) These isomers were separated by selective reaction of the cis-dimethoxy derivative with catechol or, cis-1,4-dihydroxy-2-butene, separation of the bridged alkoxysilane, and reduction with lithium aluminum hydride. (Eqn. 51)



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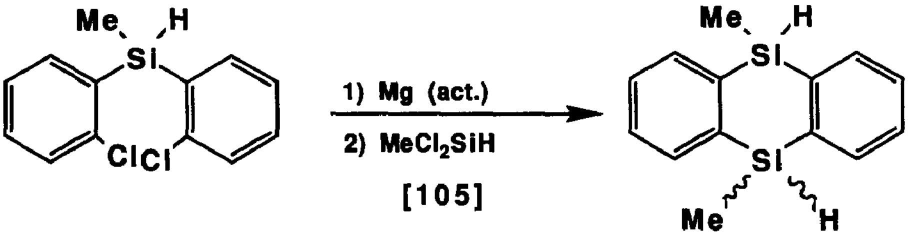

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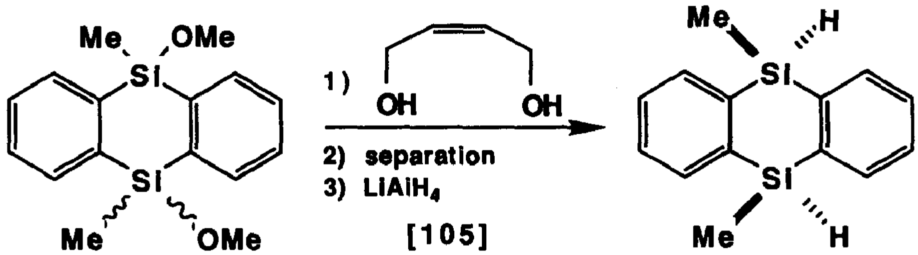
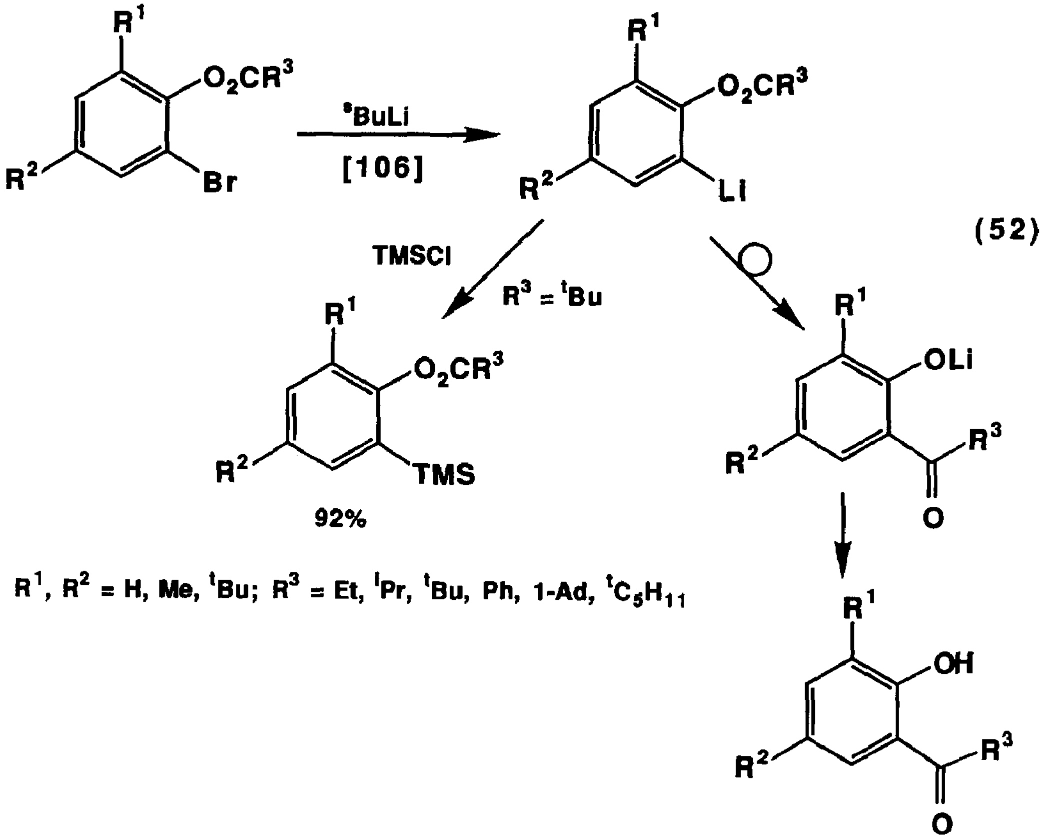


(51)

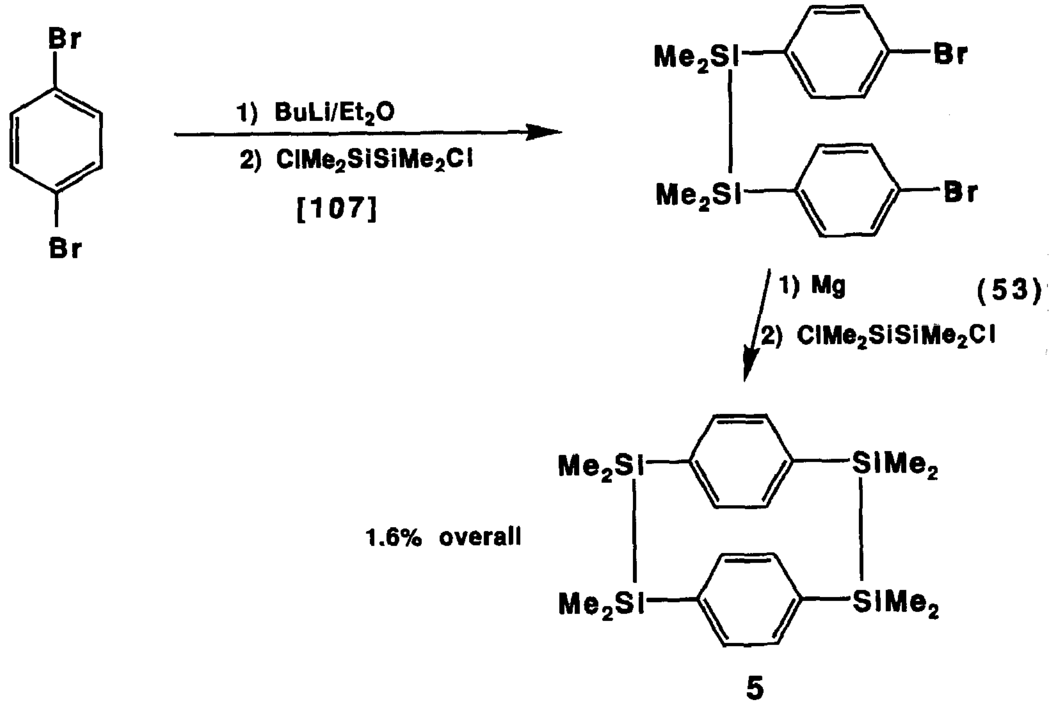
The proposed intermediate o-lithiophenyl esters was trapped with trimethylchlorosilane prior to its rearrangement to the lithium o-phenoxyacetophenone, thus showing that this intermediate has a finite lifetime. (Eqn. 52)



(52)

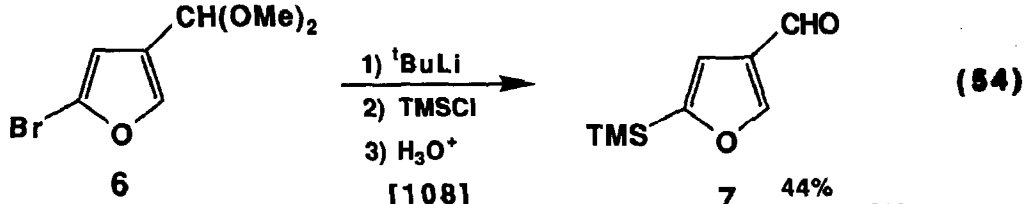
$R^1, R^2 = H, Me, {}^tBu; R^3 = Et, {}^iPr, {}^tBu, Ph, 1\text{-}Ad, {}^tC_5H_{11}$

The sequential reaction of 1,4-dibromobenzene with butyllithium in ether and then sym-dichlorotetramethyldisilane provides sym-bis(p-bromophenyl)tetramethyldisilane, which upon treatment with magnesium in THF and sym-dichlorotetramethyldisilane gives the tetrasilacyclophane **5** in an overall 1.6% yield. The Si-Si bond length was found to be 3.376 Å compared with the normal length of 3.34 Å.



(53)

Bromofuran **6** was lithiated and then trimethylsilylated to give **7**, which was used in a key step for the synthesis of manoalide. (Eqns. 54 and 55)



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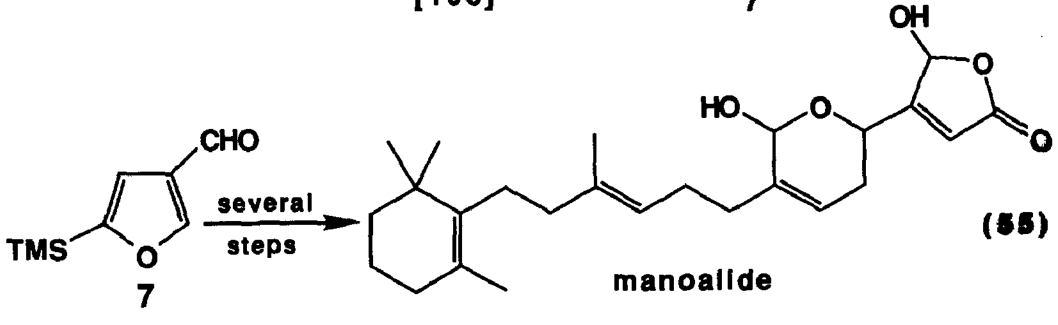
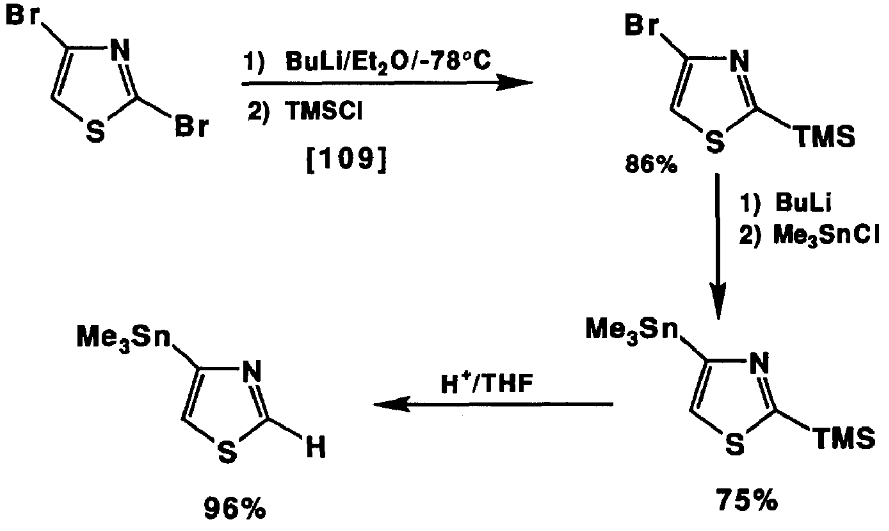
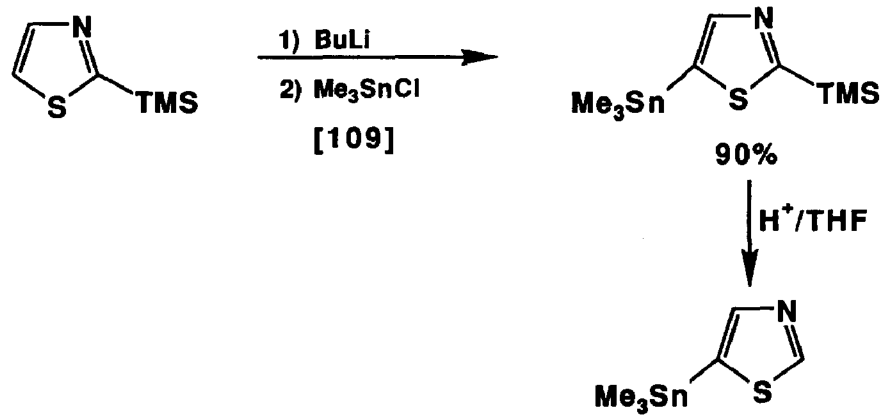


(55)

Mixed trimethylsilyl, trimethylstannylthiazoles were prepared via the lithiation-trimethylsilylation and trimethylstannylation of bromothiazoles. (Eqn. 56) The metal-hydrogen exchange of 2-trimethylsilylthiazole followed by trimethylstannylation leads to 2-trimethylsilyl-4-trimethylstannylthiazole. (Eqn. 57) These materials can be selectively protodesilylated with acid. The reaction of these materials with iodine and bromine are shown. (Eqns. 58, 59 and 60)



(56)



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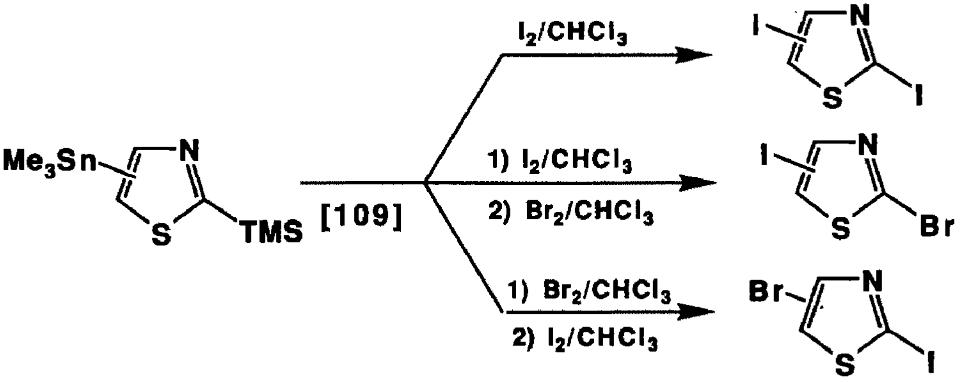
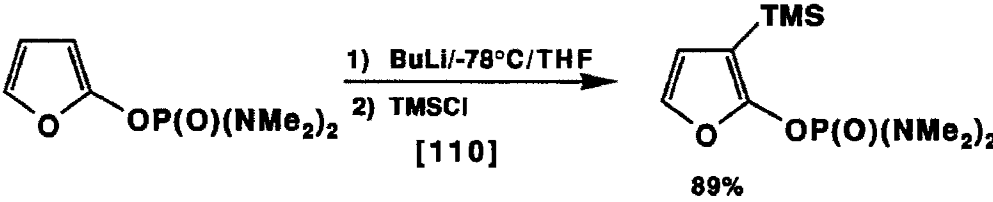


(58)

(59)

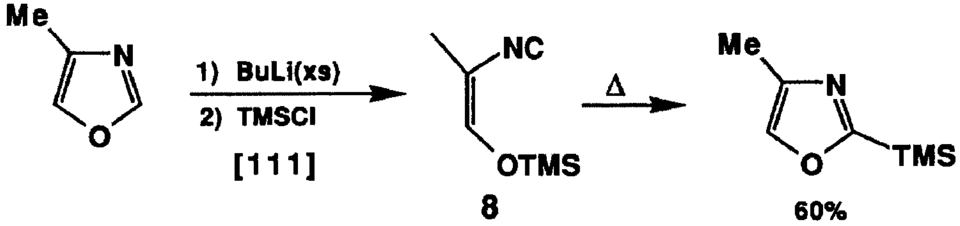
(60)

The bis(dimethylamino)phosphate group is able to direct the lithiation of furan to the β-position as evidenced by the formation of the β-trimethylsilyl derivative. (Eqn. 61)

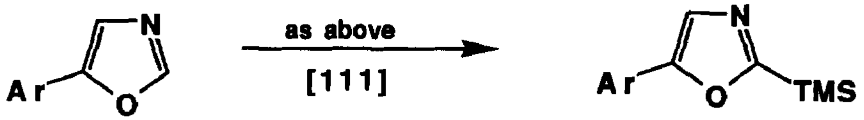


(61)

The lithiation-trimethylsilylation of 4-methyloxazole gives the enol ether **8**, which upon heating gives 2-trimethylsilyl-5-methyloxazole. (Eqn. 62) A series of aryl substituted systems was also prepared. (Eqn. 63)



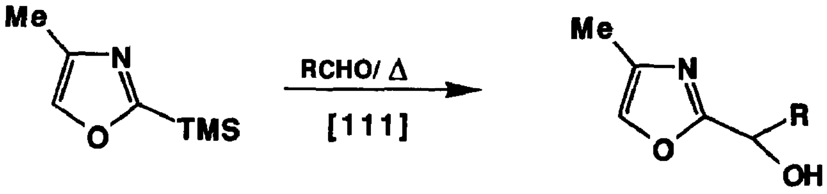
(62)



(63)

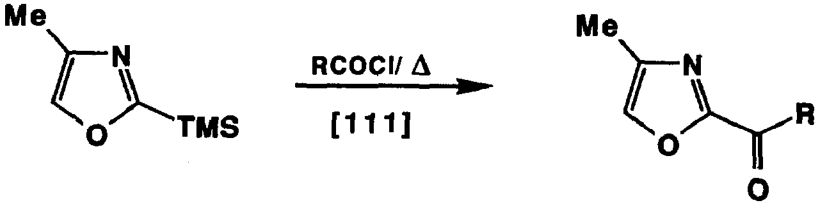
Ar = Ph, p-ClC$_6$H$_4$, p-MeOC$_6$H$_4$, 2-thienyl, 2-pyridyl

These systems can be used to condense with aldehydes and acid chlorides. (Eqns. 64 and 65)



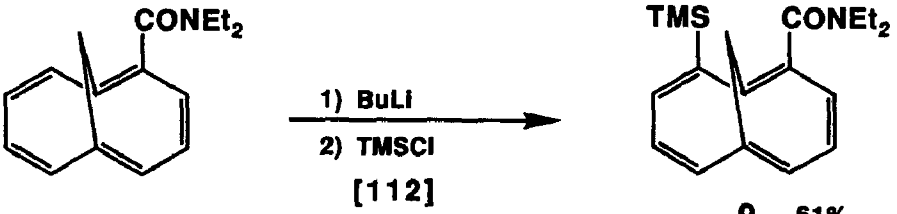
(64)

4 examples; 41-74%



(65)

The methano[10]annulene carboxamide can be lithiated and trimethylsilylated to give **9**. Other electrophiles react similarly. The regiochemistry is attributed to the directive effect of the diethylcarboxamide group during the lithiation step. (Eqn. 66)

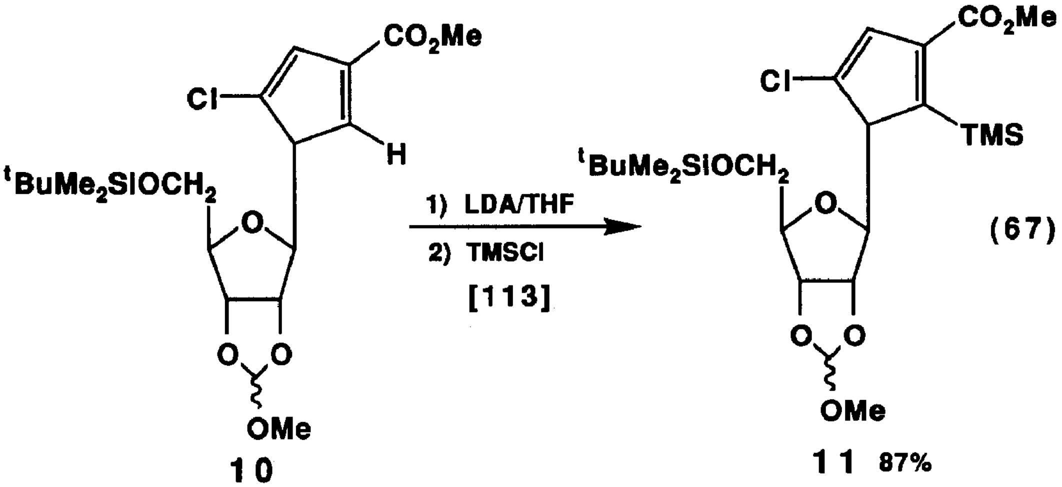


8

9 61%

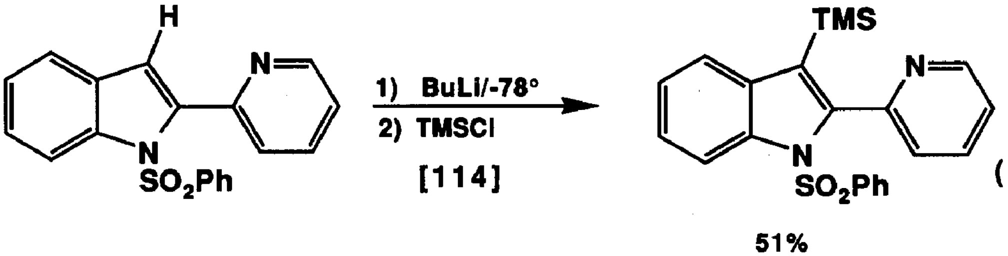
(66)

The lithiation of **10** with lithium diisopropylamide followed by trimethylsilylation provides the arylsilane 11. (Eqn. 67)

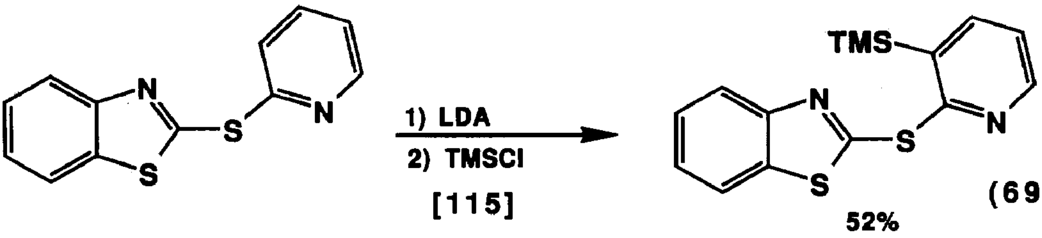


(67)

The directed β-lithiation of indoles was accomplished as shown in Eqn. 68. A similar reaction is seen in Eqn. 69.

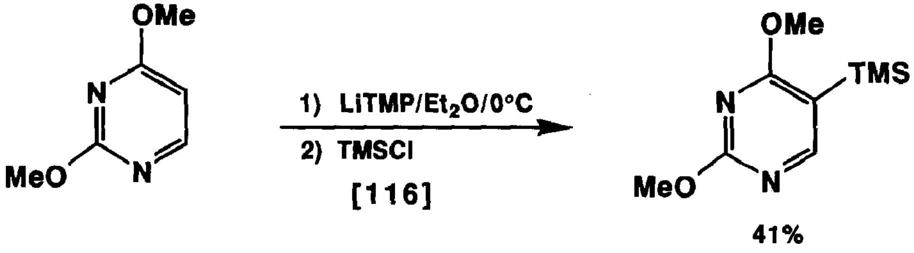


(68)

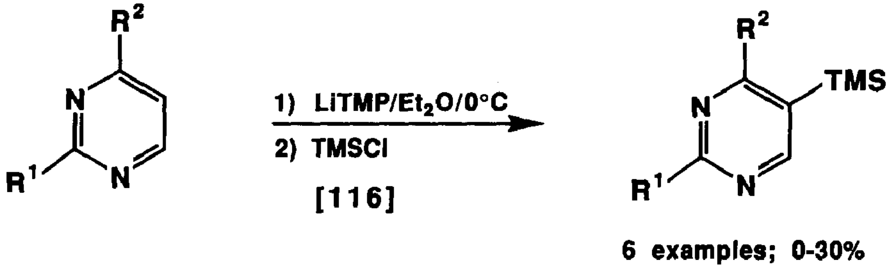


(69)

The preparation of 5-trimethylsilylpyrimidines was accomplished *via* lithiation and trimethylsilylation. (Eqns. 70 and 71) Other 5-substituted pyrmidines are prepared by the reaction of the lithium reagent with an assortment of electrophiles.



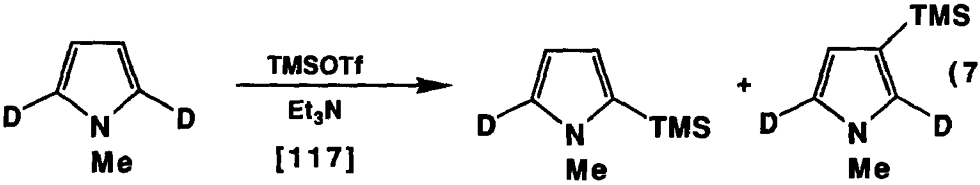
(70)



(71)

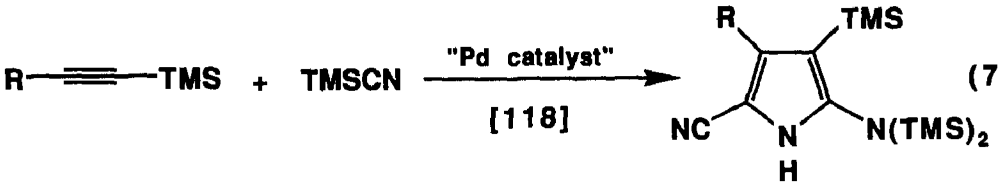
R^1,R^2 = OCH$_2$CH$_2$OMe, OCH$_2$CH$_2$OMe; Cl, OCH$_2$CH$_2$OMe; Cl, OMe; H, OCH$_2$CH$_2$OMe; H, OMe; H, NHCO^{t}Bu

The reaction of N-alkyl pyrroles with trimethylsilyl trifluoromethanesulfonate to give both the α- and β-trimethylsilylpyrroles (Eqn. 72) was subjected to calculations.



(72)

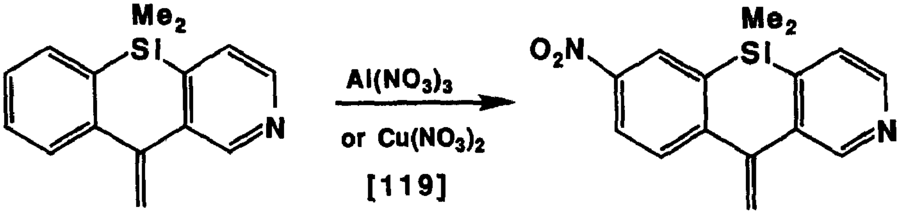
Trimethylsilylacetylenes can be reacted with trimethylsilylnitrile with palladium catalysis to give the 3-trimethylsilylated pyrroles **12** with high regioselectivity. (Eqn. 73)



12

(73)

Nitration of 10,10-dimethyl-10-sila-2-azaanthrones employing aluminum nitrate and copper(II) nitrate in acetic anhydride as the nitrating agents was studied. These reactions lead to 5-, 7-, and 8-nitroderivatives. (Eqns. 74 and 75)



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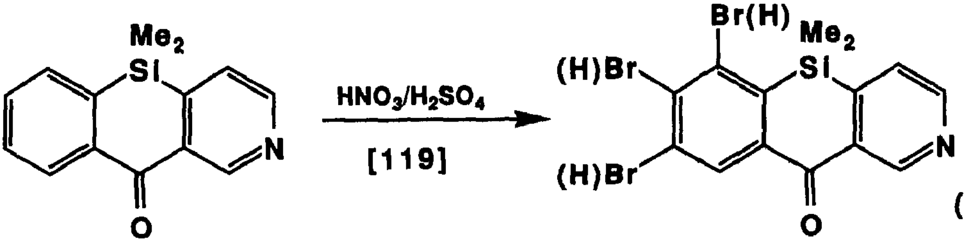
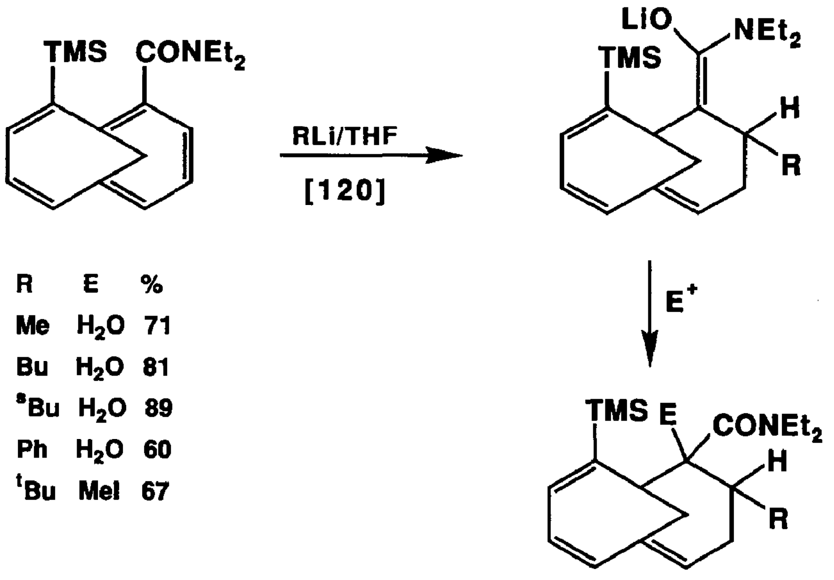


(75)

The reaction of 10-(trimethylsilyl)-1,6-methano-2-carboxamides, formed according to Eqn. 66 with a lithium reagent followed by treatment with an electrophile results in the preparation of the systems depicted by **13**. (Eqn. 76)



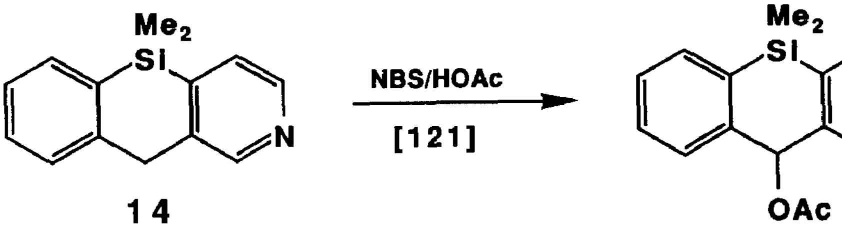
R	E	%
Me	H_2O	71
Bu	H_2O	81
^{s}Bu	H_2O	89
Ph	H_2O	60
^{t}Bu	MeI	67

13

(76)

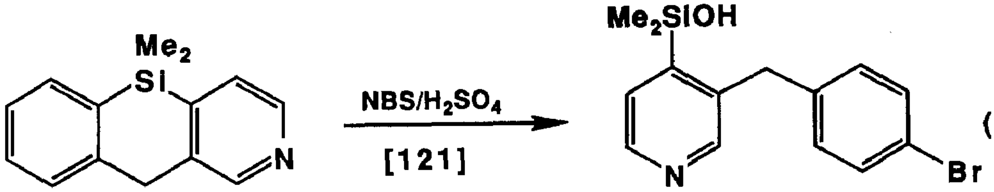
B. Arylsilanes-Reactions

The reaction of **14** with N-bromosuccinimide in acetic acid gives the 9-acetoxy derivative. (Eqn. 77) The reaction with NBS in sulfuric acid, however, gives cleavage of the silicon-carbon bond. (Eqn. 78) On the other hand the reaction of NBS in acetic acid with the ketone **15** gives bromination of the pyridine ring. The regioselectivity depends on the solvent system. (Eqns. 79 and 80)

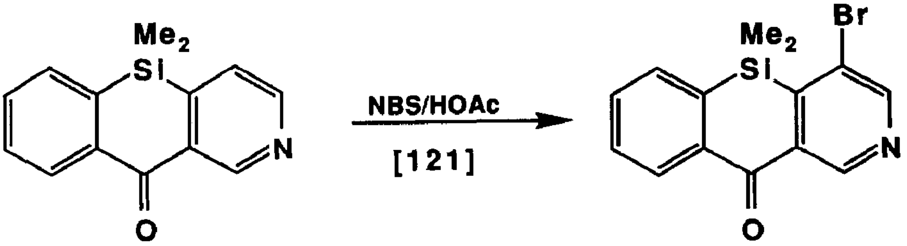


14

(77)

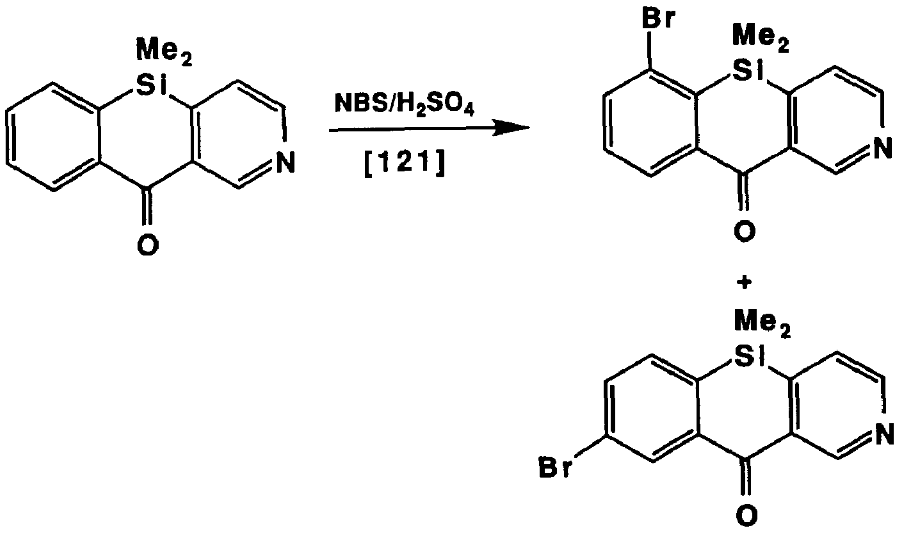


(78)



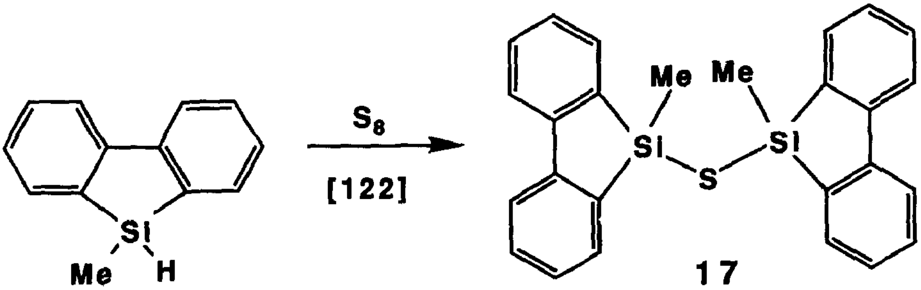
15

(79)



(80)

The reaction of **16** with elemental sulfur gives the product of insertion into the silicon-hydrogen bond. This, however, reacts to give the bis-silyl sulfide **17** in 90 percent yield. (Eqn. 81) An X-ray structure of **17** was determined.



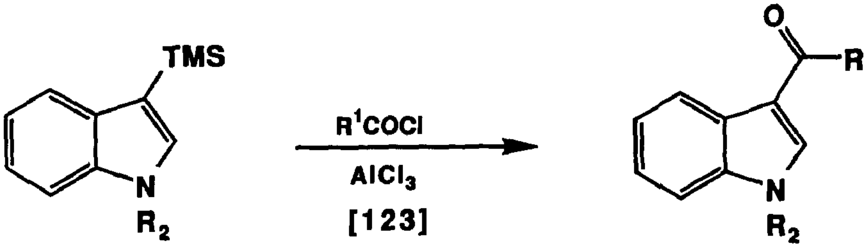
16

17

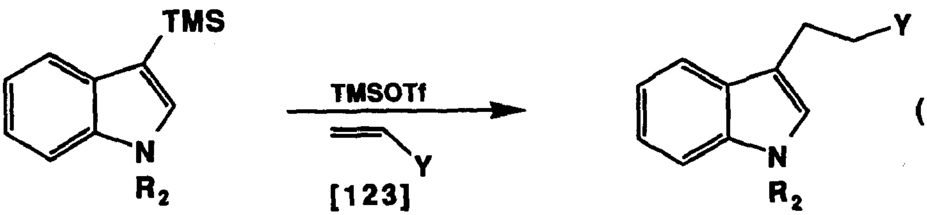
90% X-ray structure determined

(81)

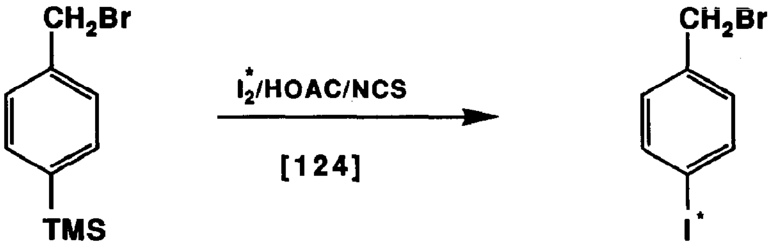
The electrophilic substitution of 3-trimethylsilylindoles with acyl chlorides, acrylo-nitrile and enones was reported. These are illustrated in Eqns. 82 and 83. The electrophilic substitution of p-trimethylsilylbenzyl bromide with radioactive iodine was shown as a route to selective positioning of the radiolabel on the aryl ring. (Eqn. 84)



(82)

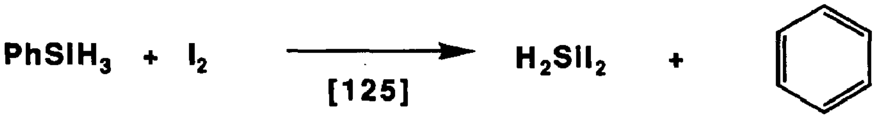


(83)



(84)

The reaction of phenylsilane with iodine gives diiodosilane *via* cleavage of one of the hydrides to form initially phenyliodosilane and HI. The phenyliodosilane and the HI then react to give the observed diiodosilane. (Eqn. 85) The diiodosilane was found to be useful in the cleavage of dialkyl ethers to alkyl iodides and the conversion of alcohols to alkyl iodides, showing selectivity for secondary alcohols. (Eqn. 86)



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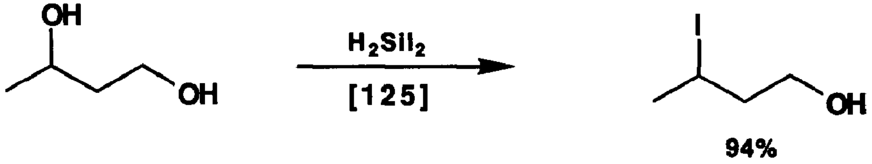
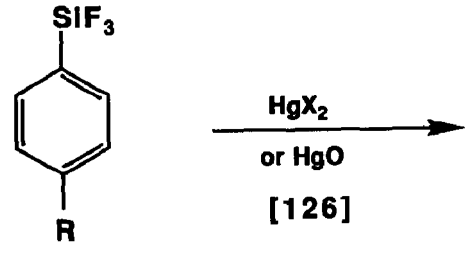


(86)

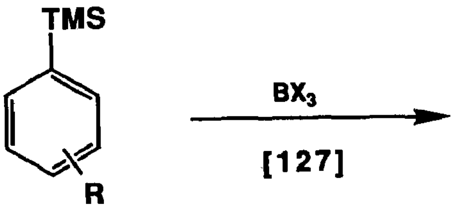
The reaction aryltrifluorosilanes with mercury(II) salts was shown to give the corresponding aryl mercury salt. (Eqn. 87)



(87)

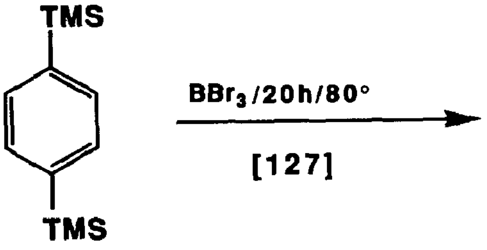
R = H, Me, Cl, Br, NO_2
X = Cl, Br, I, CN, OAc,

Several arylsilanes were reacted with boron trihalides to give arylboron dihalides with loss of a silyl halide. Some examples of these transformations are given below. (Eqns. 88 - 92)



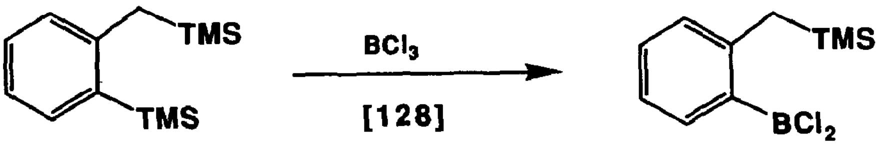
(88)

R = H, Me, Cl, TMS, Mesityl
X = Cl, Br

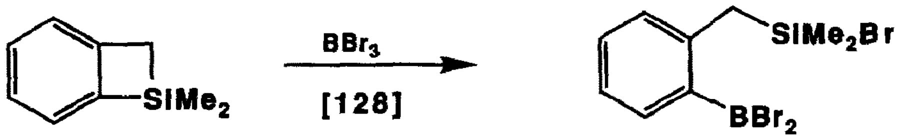


80%

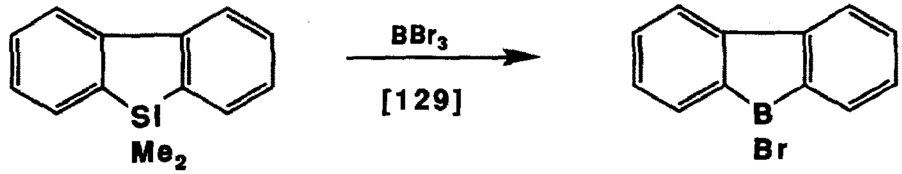
(89)



(90)

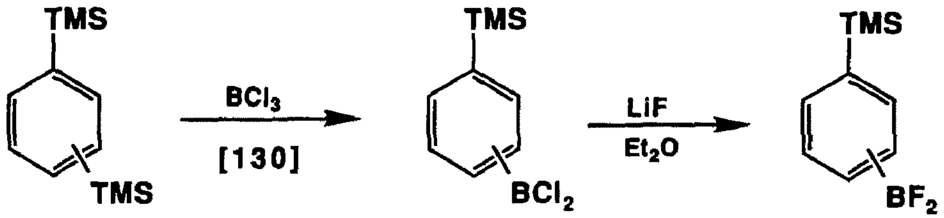


(91)

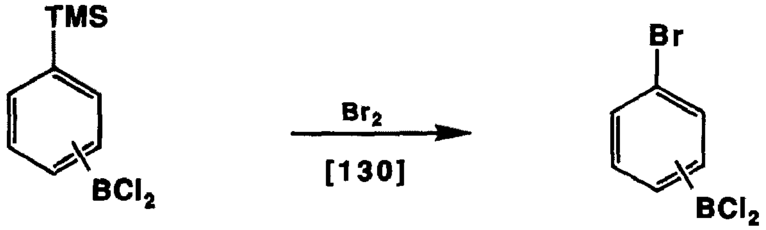


(92)

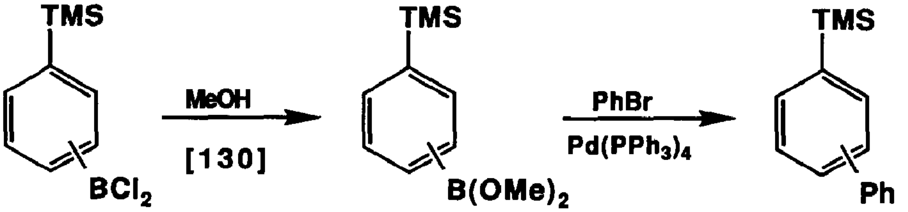
It proved possible to convert the aryldichloro- or dibromoboranes to the difluoro derivatives with lithium fluoride without cleavage of an aryl-silicon bond elsewhere in the molecule. (Eqn. 93) At the same time it is possible to bromodesilylate an aryl-silicon bond in the presence of an aryl-boron bond. (Eqn. 94) The aryl-boron bond will enter into palladium catalyzed coupling reactions leaving the aryl-silicon bond intact. (Eqn. 95)



(93)



(94)



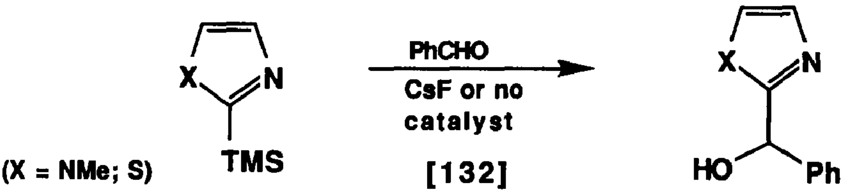
(95)

Reaction of the arylsilane **18** with fluoride ion gave a complex which NMR data indicated to be a bridged species with the fluoride ion complexed to both the silicon and boron atoms. Other examples of this type of complexation were presented. (Eqn. 96)

18

(96)

The addition of the imidazole or thiazole ring system to aldehydes *via* their 2-trimethylsilyl derivatives in the presence or absence of a nucleophilic catalyst was reported. (Eqn. 97) The stereoselectivity of this reaction with 2-substituted aldehydes was studied. (Eqn. 98) Advantage was taken of the fact that the thiazole moiety can be converted to an aldehyde to carry out an iterative diastereoselective homologation of 2,3-O-isopropylidene-D-glyceraldehyde. (Eqn. 99)



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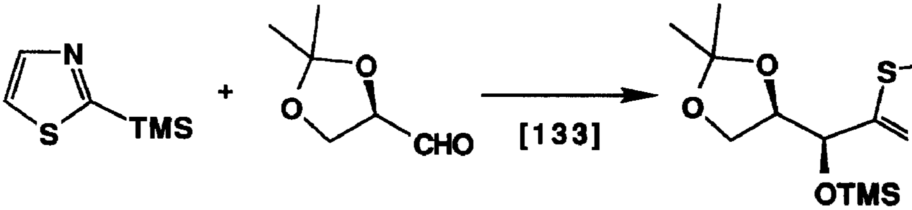

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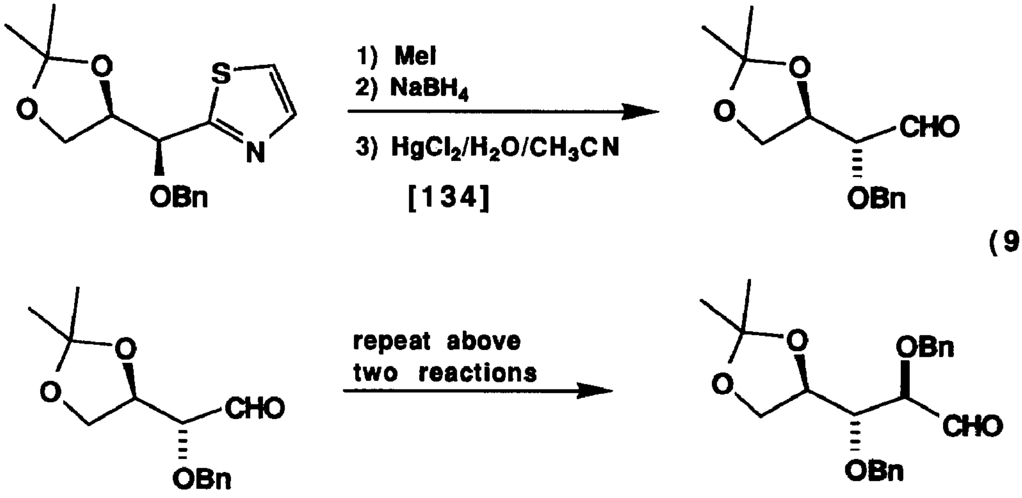
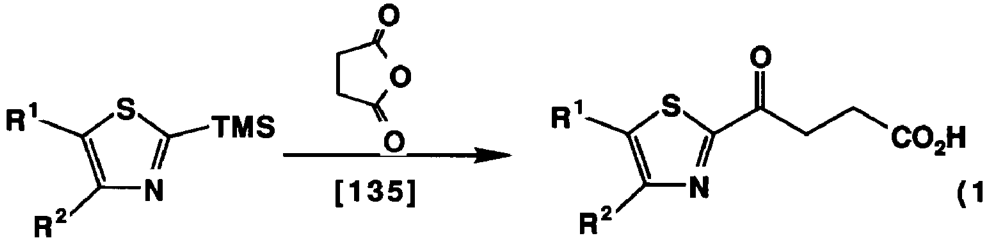


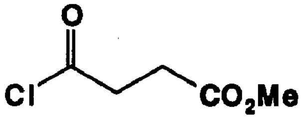
(99)

It was further shown that the silylated thiazoles will react with succinic anhydride. (Eqn. 100)



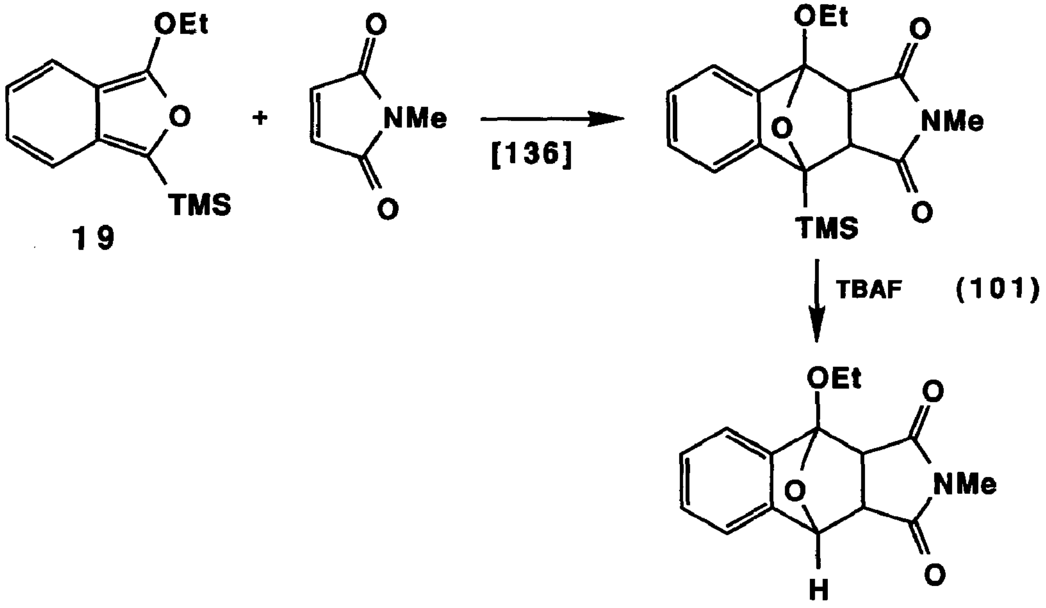
(100)

Also reacted with



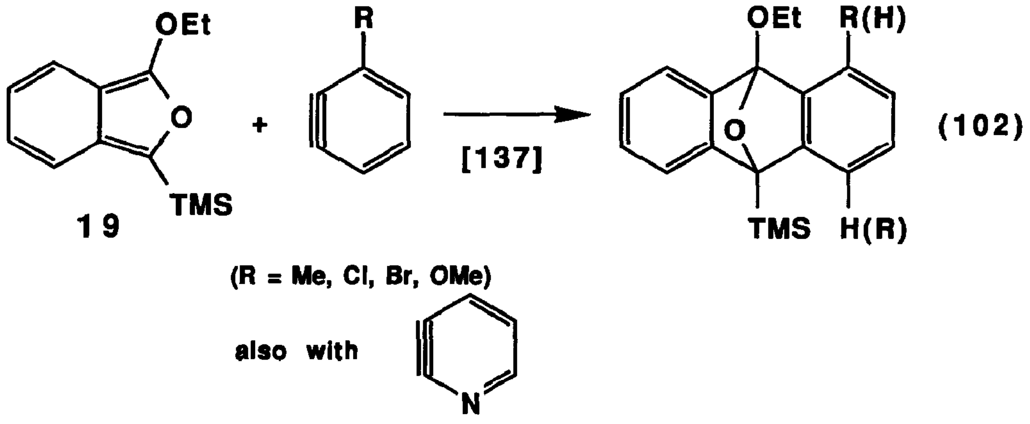
R^1,R^2 = H, H; H, Me; Cl, H; H, Cl; H, TMS

Reports on the cyclization of 2-trimethylsilylated benzofurans with dienophiles continued. Thus, benzofuran **19** was added to N-methyl maleimide. The trimethylsilyl group can be protodesilylated with fluoride ion. (Eqn. 101) The reaction of this same material with arynes was also successful. (Eqn. 102)



19

(101)

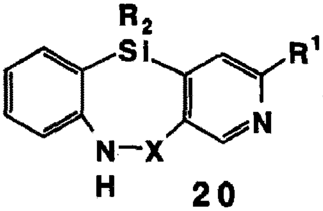


19

(102)

C. Arylsilanes-Other Studies

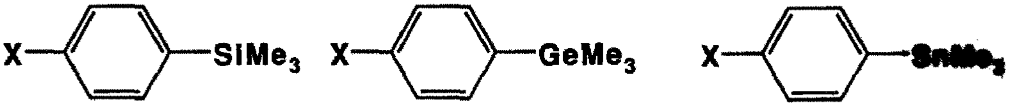
The mass spectra of compounds of the general structure **20** were obtained. The main fragmentation comes from the open form of the molecular ion. [138] NMR techniques were applied to the structure determination of several bromo-, nitro-, and amino derivatives of 10,10-dimethyl-10-sila-2-azaanthrones. [139]



20

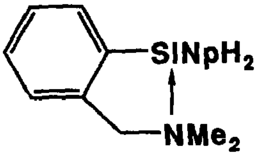
(R = Me, Ph; R^1 = H, Me; X = CH_2, CO)

A method for estimating the pπ-dπ interaction in vinylsilanes and 2-silylfurans using CNDO/2 calculations was reported. [140, 141] The infrared spectra of ten para-substituted aryltrimethylsilanes were studied as were those of the germanium and tin analogs. [142]



(X = NO_2, Br, H, F, Me, OMe, OH, TMS, OTMS)

The variable temperature ^1H NMR spectra of **21 - 24** show that the barrier to pseudorotation is very low. [143] It was shown that the tendency for pseudorotation in the complexed silanes with two or three substitutents is much larger than that for the monofunctional derivatives. [144]



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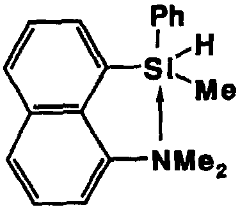

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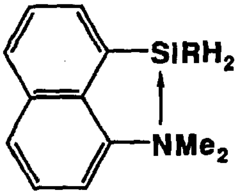

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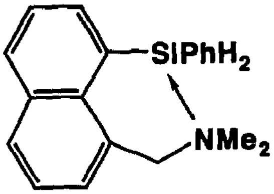
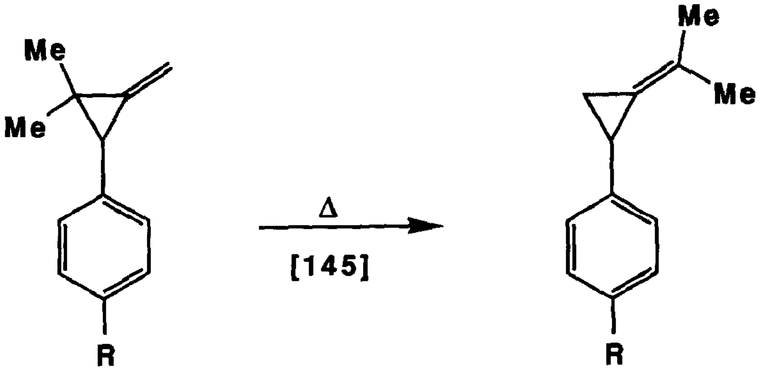


24

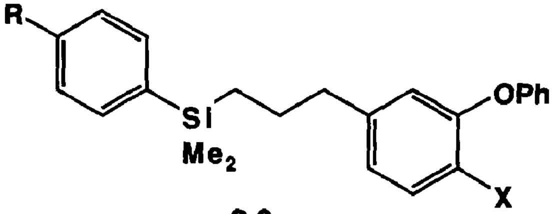
The trimethylsilyl and the trimethylsilylmethyl groups were both found to be rate enhancing in the thermal rearrangement of the methylenecyclopropane **25**. (Eqn. 103) The presence of 2- and 5-trimethylsilyl groups on benzofuran slow its rate of reaction with N-methylmaleimide. [146]



25

(103)

Organosilane **26** has been shown to demonstrate high insecticidal activity. [147, 148]



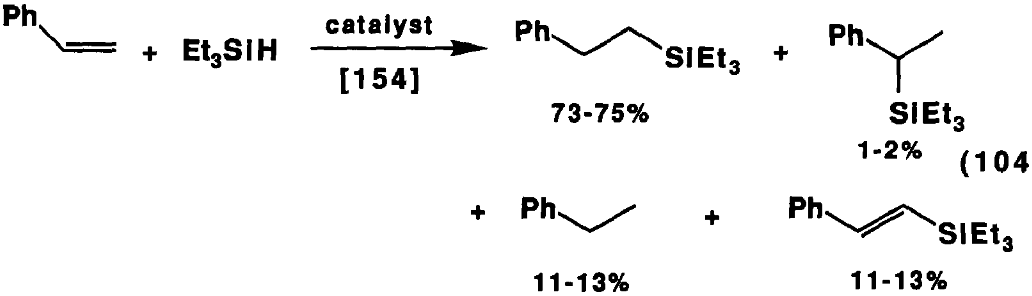
26

VI. HYDROSILATION

A. New Developments

It was found that the hydrosilation of olefins with chloroplatinic acid (CPA) was activated by a small amount of oxygen. Treatment of the used catalyst with oxygen restored its catalytic activity. This technique was applied to hydrosilations of relatively unreactive alkenes with trialkylsilanes, dialkylsilanes and alkylsilanes. [149] In the same paper Wilkinson's catalyst was employed in the hydrosilation of unreactive alkenes with tri-and dialkylsilanes, although this catalyst did not work for alkylsilanes in the preparation of tetralkylsilanes. [149] Quaternary ammonium, phosphonium, and arsonium salts of chloroplatinic acid were found to be effective hydrosilation catalysts. [150] Chloroplatinic acid with added Lewis acids such as aluminum chloride, germanium tetrachloride, cerium trichloride, and others were found to be effective catalysts for the hydrosilation of acetylenes to vinylsilanes. [151] It was reported that the addition of a second silane increases the efficiency of the hydrosilation. [152] The addition of benzothiazole to chloroplatinic acid gives a catalyst capable of the highly efficient hydrosilation of olefins with methyldichlorosilane. [153]

Cis-bis(styryl)platinum dichloride, which exists in several isomeric forms, was utilized in the hydrosilation of styrene with triethylsilane. This gave a mixture of products as shown in Eqn. 104.



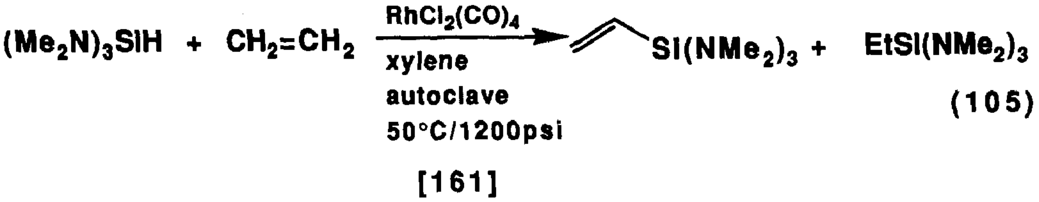
(104)

The hydrosilation of olefins can be catalyzed by dimanganesedecacarbonyl [155] or by dirheniumdecacarbonyl [156]. The effect of ligands on the catalytic activity of nickel complexes in the hydrosilation reaction has been studied. [157] The hydrosilation of olefins with bis(cyclooctadiene)iridium halide catalysts in the presence of various ligands was investigated. [158]

Wilkinson's catalyst anchored to a phosphino-organosiloxane and grafted onto chrysotile asbestos gave good conversion of methyldichlorosilane and acetylene to vinylmethyldichlorosilane and trichlorosilane/acetylene to vinyltrichlorosilane in a flow reactor. [159] Diphenylphosphinoethyltrimethoxysilane was bound to silica and a platinum oxalate complexed to the phosphorous group to give a silica supported hydrosilation catalyst. A high turnover of the catalyst was observed. [160]

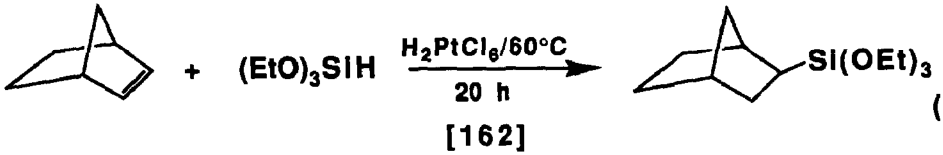
B. Hydrosilylation of Alkenes

Tetracarbonylrhodium dichloride was used to catalyze the hydrosilation of olefins with tris(dimethylamino)silane as illustrated in Eqn. 105.

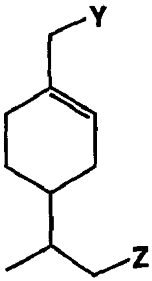


(105)

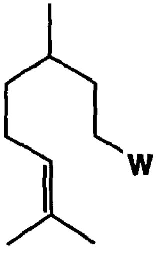
The hydrosilation of norbornene with triethoxysilane and chloroplatinic acid gives a 61 percent yield of the adduct shown, which was found to be compatible with certain rubbers. (Eqn. 106) Terpenes were the starting materials for silanes of the general structures **27** and **28**. The products were used to give hydrophobicity to concrete surfaces. [163]



(106)

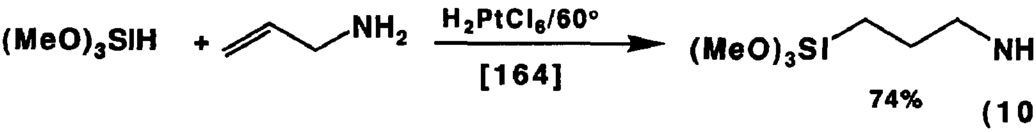


27

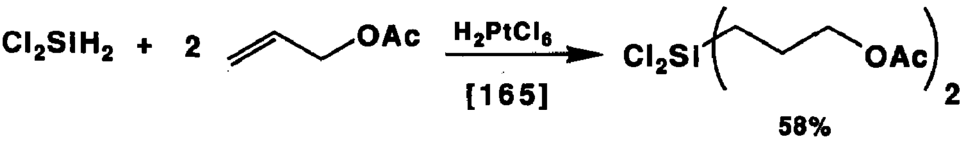


28

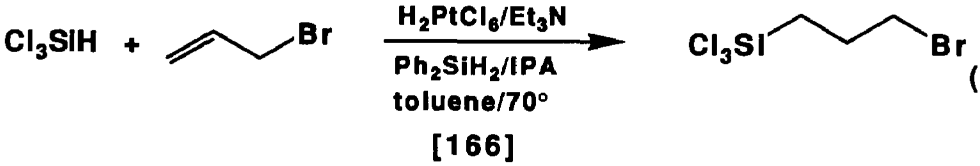
The hydrosilation of several allyl derivatives was reported. The hydrosilation of allylamine, without protection of the amino functionality, with trimethoxysilane was accomplished in good yield using chloroplatinic acid as catalyst. (Eqn. 107) Bis-(acetoxypropyl)dichlorosilane was prepared by the hydrosilation of allyl acetate with dichlorosilane, again using chloroplatinic acid as catalyst. (Eqn. 108) Allyl bromide, which can be difficult to hydrosilate due to a tendency towards reduction, was hydrosilated with trichlorosilane in the presence of chloroplatinic acid/triethylamine with diphenylsilane added. (Eqn. 109)



(107)

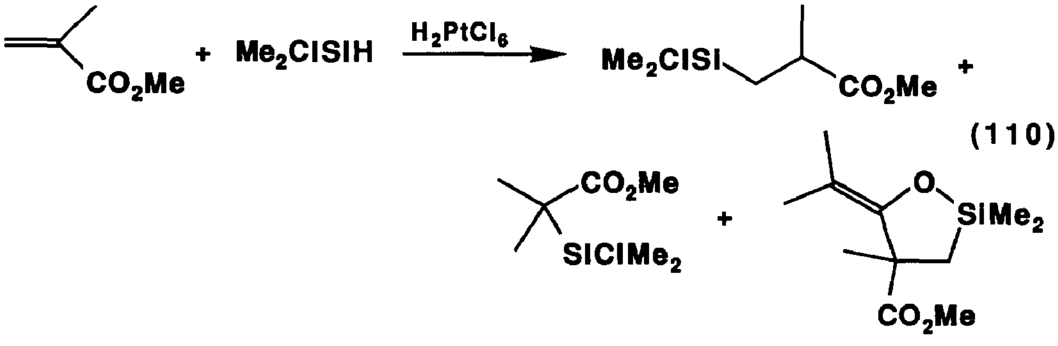


(108)



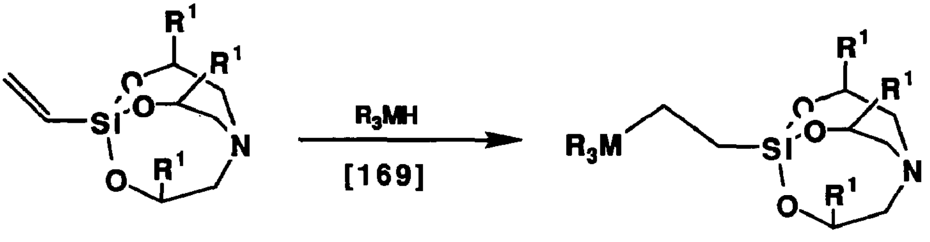
(109)

The hydrosilation of methyl methacrylate with dimethylchlorosilane and chloroplatinic acid catalysis was studied. The products are shown in Eqn. 110. The determination of the structures of the products of the hydrosilation of various acrylates with methyldichlorosilane was investigated by NMR spectroscopy. [168]



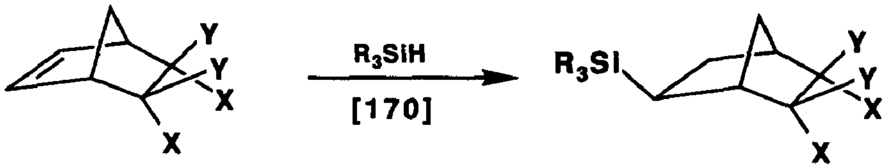
(110)

The hydrosilation of vinyl- and allylsilatrane was carried out, as was the hydrogermylation and hydrostannation. (Eqn. 111)



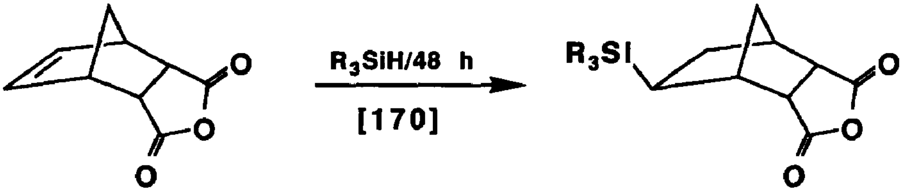
(111)

The effects of proximate polar groups on the rates of hydrosilation were studied via a series of substituted norbornene derivatives. (Eqn. 112) In general electron withdrawing groups in the exo-positions decrease the rate of hydrosilation and in the endo-positions increase the rate. For the endo-acid anhydride the yields depended very much on the silane used. (Eqn. 113)



(112)

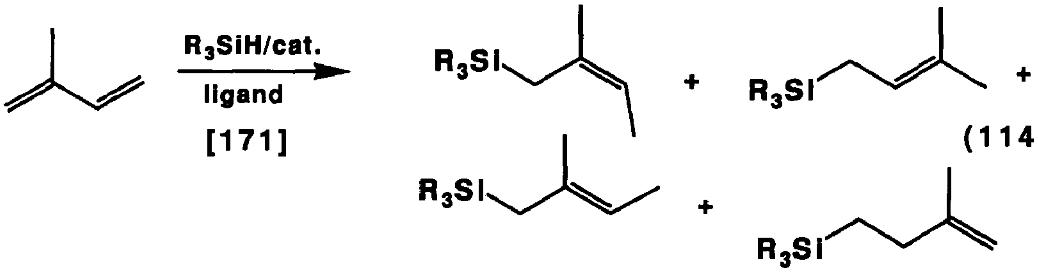
X,X	Y,Y	% Yield	Rel Rate
$(CO)_2O$	H,H	95	0.01
H,H	$(CO)_2O$	99	2.4
$(CO)_2NPh$	H,H	0	- -
H,H	$(CO)_2NPh$	99	5.6
CO_2Me, CO_2Me	H,H	99	0.54
H,CO_2Me	H,CO_2Me	99	1.00
H,H	CO_2Me,CO_2Me	99	1.50
CH_2OCH_2	H,H	99	2.00
H,H	H,H	99	2.50



(113)

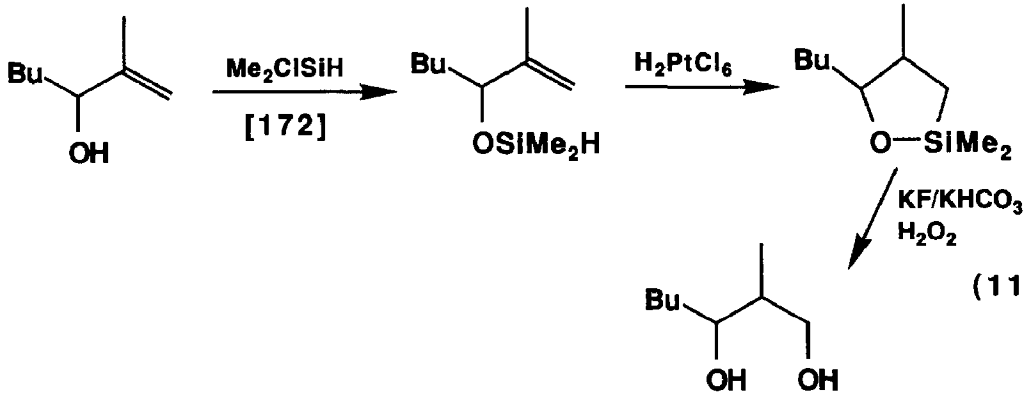
(Et_3SiH (0%); Me_2ClSiH (95%); Me_2PhSiH (95%); $MeCl_2SiH$ (62%); Cl_3SiH (0%))

The regio- and stereoselective hydrosilation of isoprene with rhodium(I) and rhenium(II) complexes was reported. (Eqn. 114)

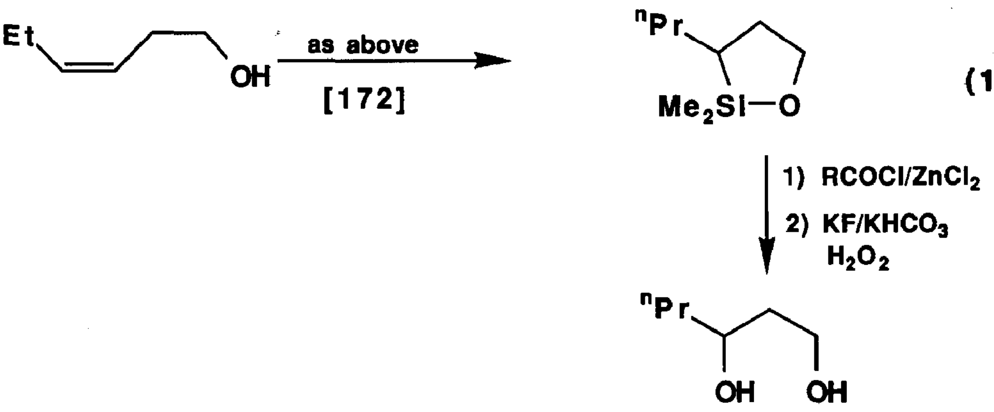


(114)

Intramolecular hydrosilation followed by oxidation of the silicon-carbon bond was used as a method to stereoselectively introduce the hydroxyl group. In one such study, an allyl alcohol and a homoallyl alcohol were studied. (Eqns. 115 and 116)

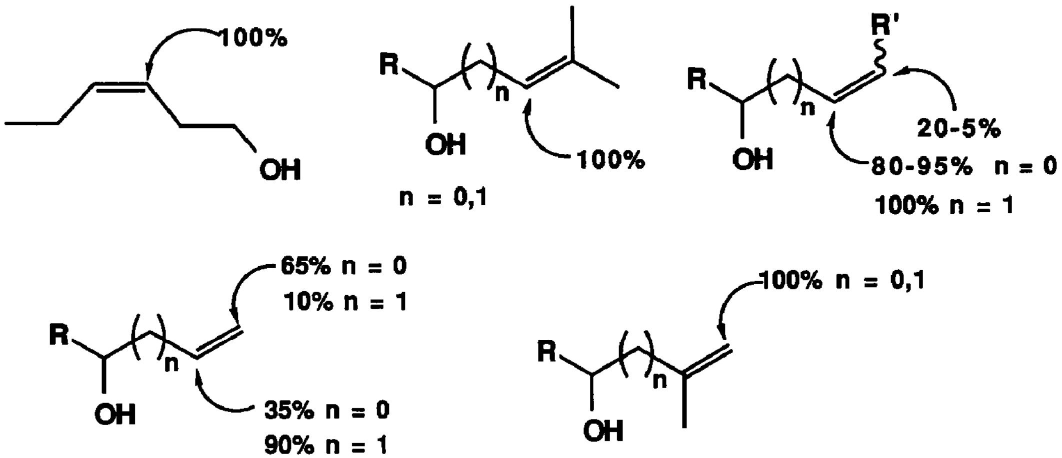


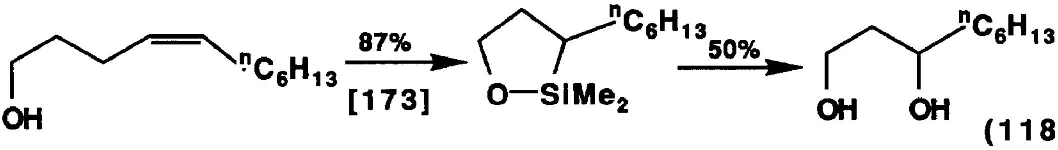
(116)



(117)

In another study involving the intramolecular hydrosilation-oxidation reaction a variety of homoallylic alcohols was employed to study the effects of groups on the regioselectivity of the hydrosilation. The position of the silicon group and hence the new hydroxyl group is as indicated in the structures below. [173] Some olefin isomerization occurs in order to accomodate the intramolecular nature of the reaction (Eqn. 118)

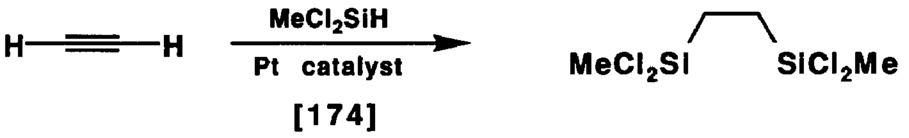




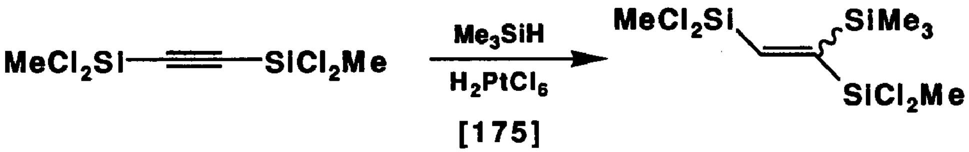
(118)

C. Hydrosilylation of Acetylenes

The hydrosilation of acetylene itself with methyldichlorosilane using a platinum catalyst supported on a sulfur-containing silica surface gives 1,2-bis(methyldichlorosilyl)ethane. (Eqn. 119) The hydrosilation of bis(methyldichlorosilyl)acetylene with trimethylsilane and other silanes with chloroplatinic acid was reported. (Eqn. 120)

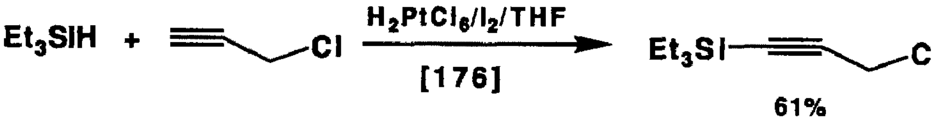


(119)

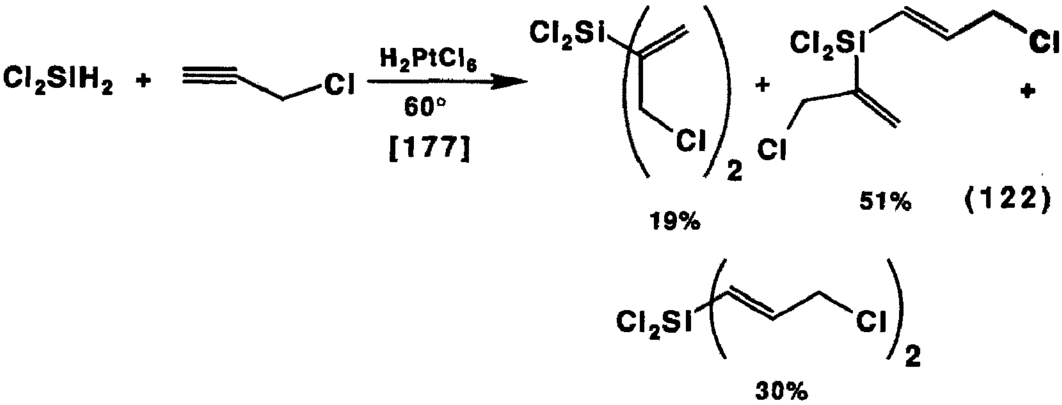


(120)

The hydrosilation of propargyl chloride was carried out with triethylsilane (Eqn. 121) and with dichlorosilane. (Eqn. 122) In the former case a catalyst of chloroplatininc acid and iodine was used and the product was the result of substitution and not addition. In the second case a mixture of bis adducts was obtained.

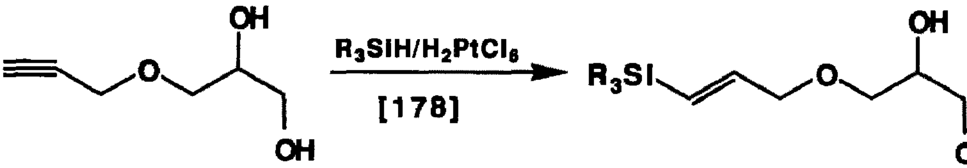


(121)

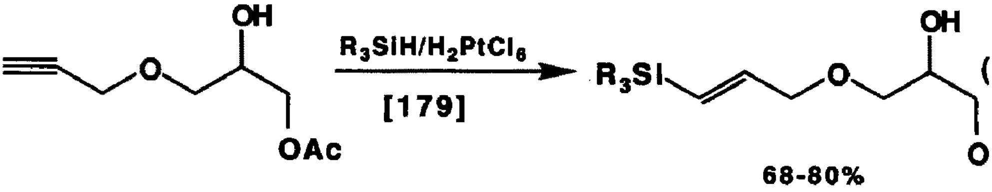


(122)

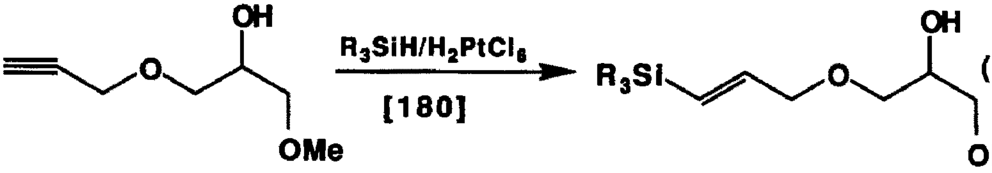
Several derivatives of ring-opened propargyl glycidyl ethers were hydrosilated to the corresponding vinylsilane containing polar functional groups. These are shown in Eqns. 123-126.



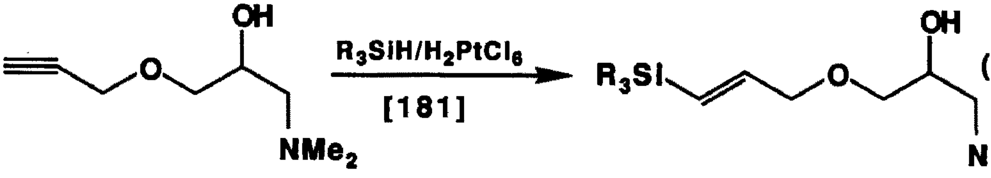
(123)



(124)

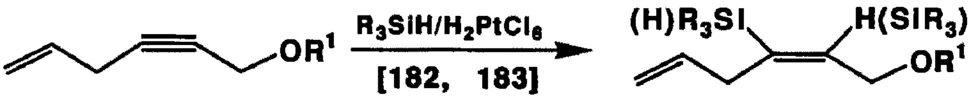


(125)



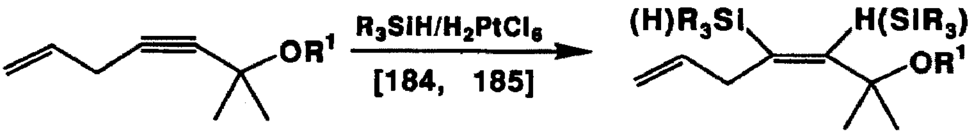
(126)

In a related study several 1-ene-4-ynes were subjected to hydrosilation. In all cases the triple bond, although it is internal, is the site of hydrosilation. The regioselectivity is low, however. Examples of this reaction are given in Eqns. 127 and 128.



(127)

R = oxiranylethyl, cyanopropyl

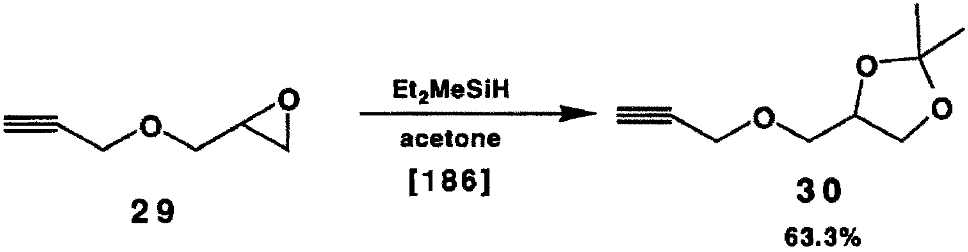


(128)

R = oxiranylethyl

D. Hydrosilylation-Reductions

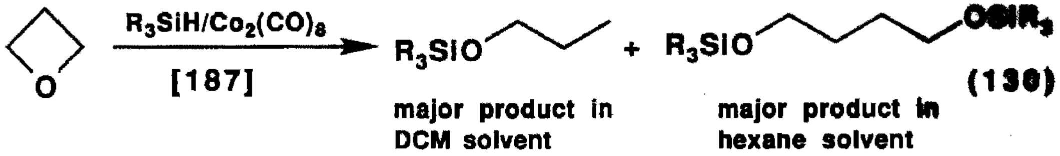
Treatment of alkyne **29** with methyldiethylsilane in acetone results in the formation of the isopropylidene derivative **30**. (Eqn. 129)



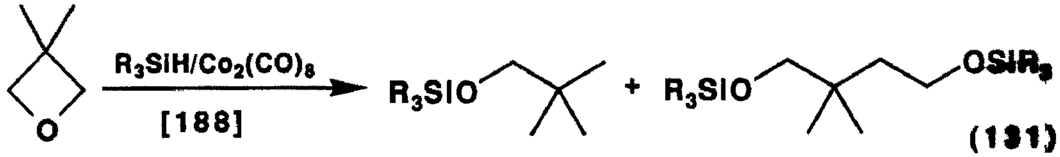
29 **30**

(129)

Oxetanes can be opened with carbon monoxide incorporation under the influence of hydrosilanes and dicobalt octacarbonyl. (Eqns. 130 and 131)



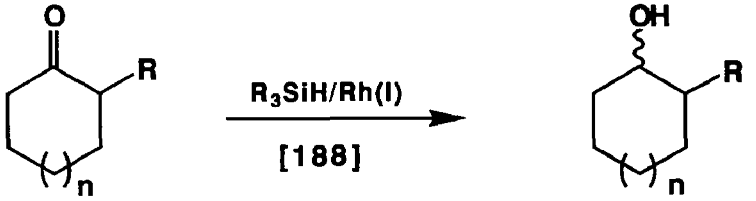
(130)



(131)

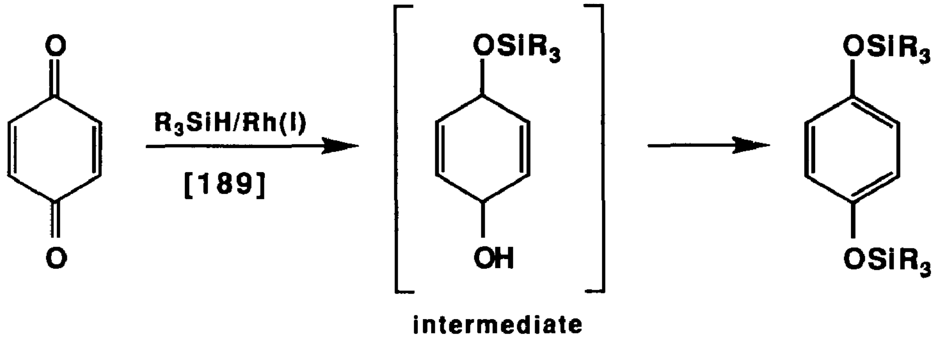
R$_3$Si = Et$_2$MeSi/DCM	68%	12%
R$_3$Si = Me$_3$Si/hexane	trace	67%

The stereoselectivity of the hydrosilation of 2-substituted cyclohexanones was investigated. An increase in the amount of the thermodynamically less stable cis isomer is observed as the steric hinderance of the substituent increases. (Eqn. 132)



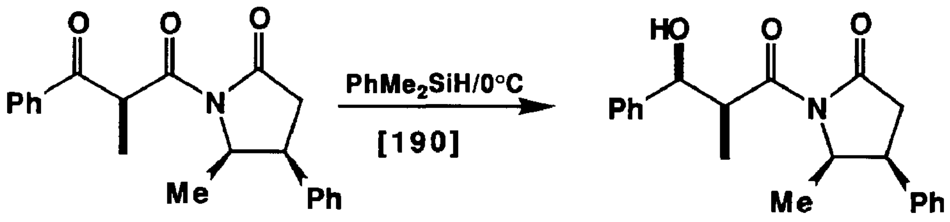
(132)

Quinones react with silanes in the presence of Wilkinson's catalyst to give silylated hydroquinones. (Eqn. 133)



(133)

The highly stereoselective reduction of β-acylcarboxamides was accomplished with phenyldimethylsilane. (Eqn. 134) The asymmetric hydrosilation of acetophenone was done with diphenylsilane and rhodium catalysts with optically active Schiff bases as added ligands. [191a] A similar study using ephedrinium complexes of hexachloroplatinum(IV), bromotrichlororhodium(III) and dibromodichlorozinc(II) and diphenylsilane was done. The optical yields were up to 53.5%. [191b]



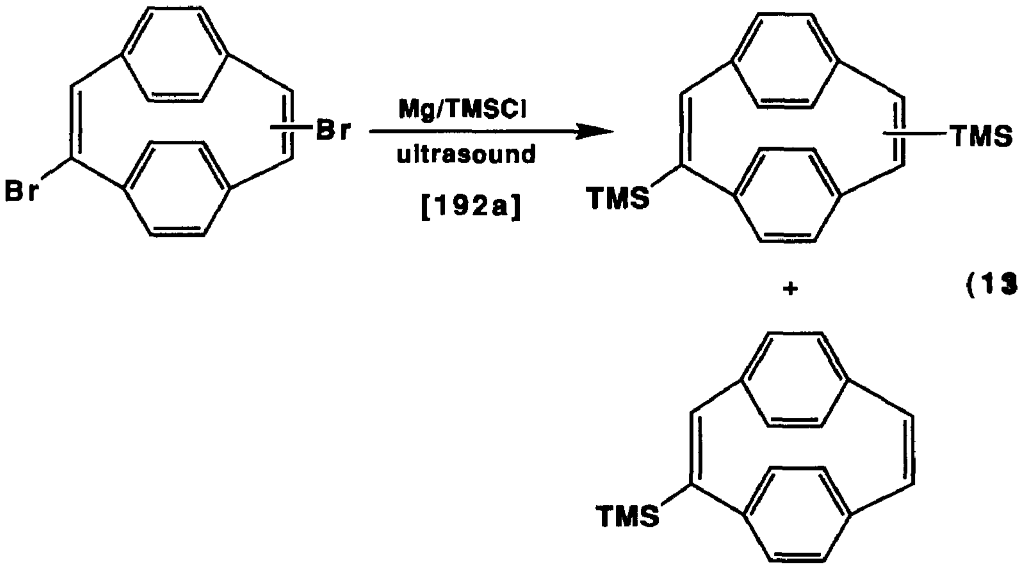
(134)

> 99:1 diastereomeric ratio

VII. VINYLSILANES

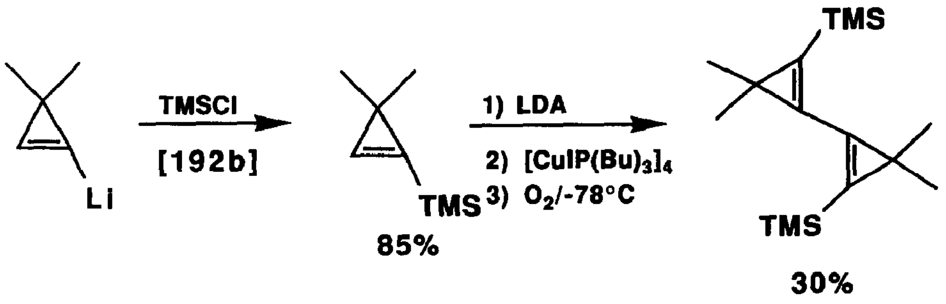
A. Preparation

The formation of trimethylsilylated [2.2]paracyclophane-1,9-dienes was accomplished *via* the Grignard reagent. (Eqn. 135)

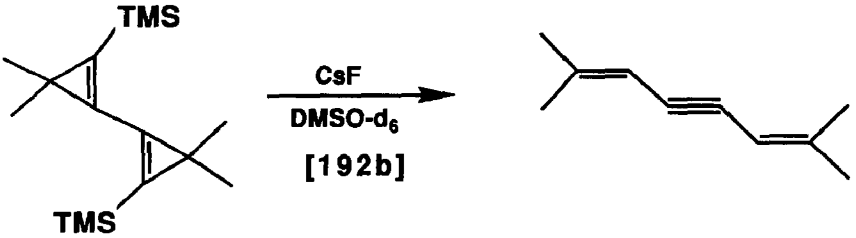


(135)

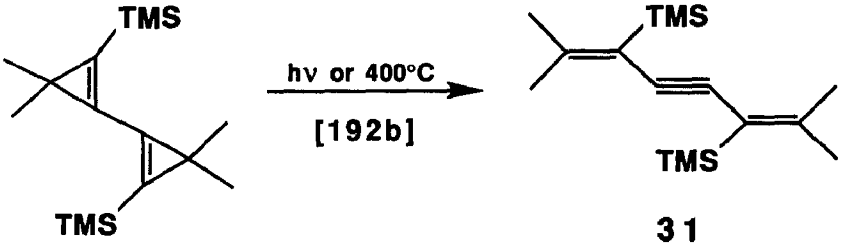
1-Lithio-3,3-dimethylcyclopropene was reacted with trimethylchlorosilane to give the 1-trimethylsilyl derivative, which itself could be deprotonated with LDA and the resulting lithium reagent coupled with copper(I) and oxygen. (Eqn. 136) Treatment of the silylated dimer with cesium fluoride gives a silicon free divinyl acetylene. (Eqn. 137) Thermal or photochemical treatment gives a divinyl acetylene 31 with the trimethylsilyl groups attached. (Eqn. 138)



(136)



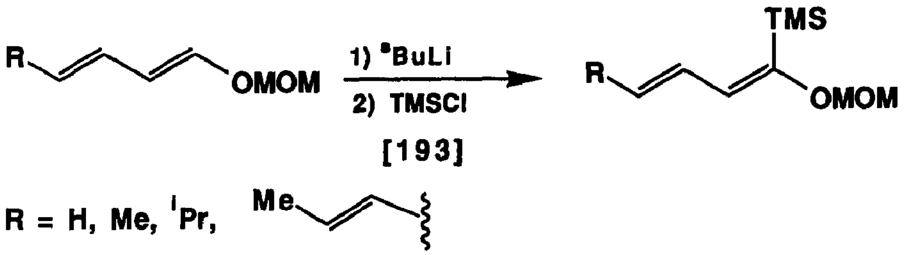
(137)



31

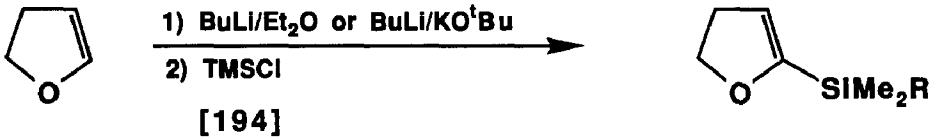
(138)

The α-lithiation-trimethylsilylation of α-alkoxy polyenes gives the expected 1-trimethylsilyl-1-alkoxy polyenes. (Eqn. 139)

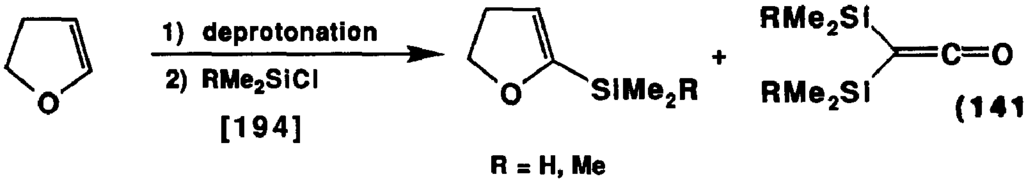


(139)

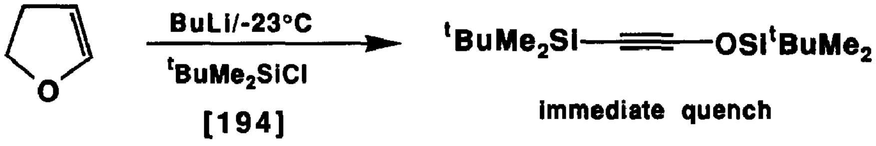
It was demonstrated that the direct lithiation of 2,3-dihydrofurans with butyllithium followed by trimethylsilylation in ether gives the 5-trimethylsilylfuran. (Eqn. 140) When the lithiated dihydrofuran is allowed to stand at 25°C for 24 h and and then quenched with either trimethylchlorosilane or dimethylchlorosilane, both the silylated dihydrofuran and the bis(silyl)ketene are formed. (Eqn. 141) Quenching the lithium reagent formed at low temperature with tert-butyldimethylchlorosilane gave the silylated alkynoate. (Eqn. 142) When the lithium reagent was allowed to stand at 25°C for 8 h and then quenched with tert-butyldimethylchlorosilane only the bis(tert-butyldimethylsilyl)ketene was formed. (Eqn. 143)



(140)



(141)



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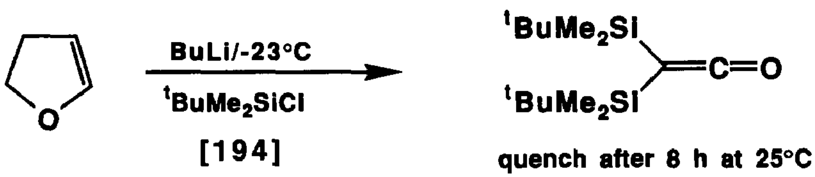
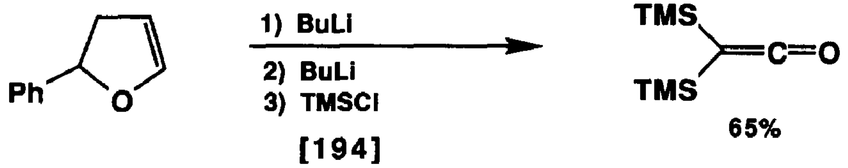


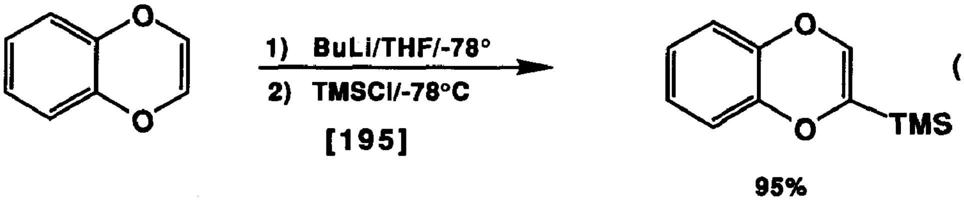
(143)

2-Phenyl-2,3-dihydrofuran, when treated sequentially with 2 equivalents of butyl lithium and then trimethylchlorosilane, gives only bis(trimethylsilyl)ketene and polystyrene. (Eqn. 144)

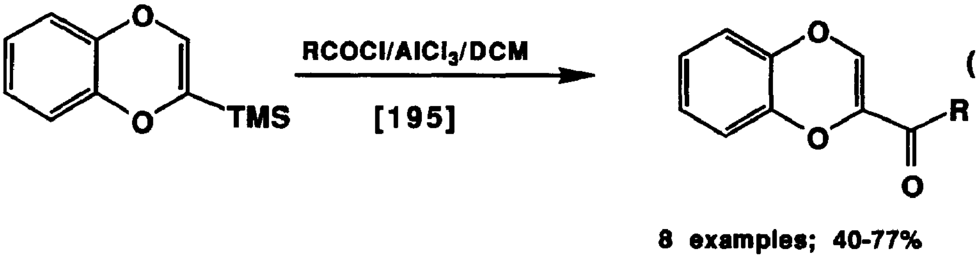


(144)

The lithiation-trimethylsilylation of benzodioxin was carried out without complications. (Eqn. 145) The trimethylsilylated benzodioxin was acylated to give 2-acyl-1,4-benzodioxins. (Eqn. 146)

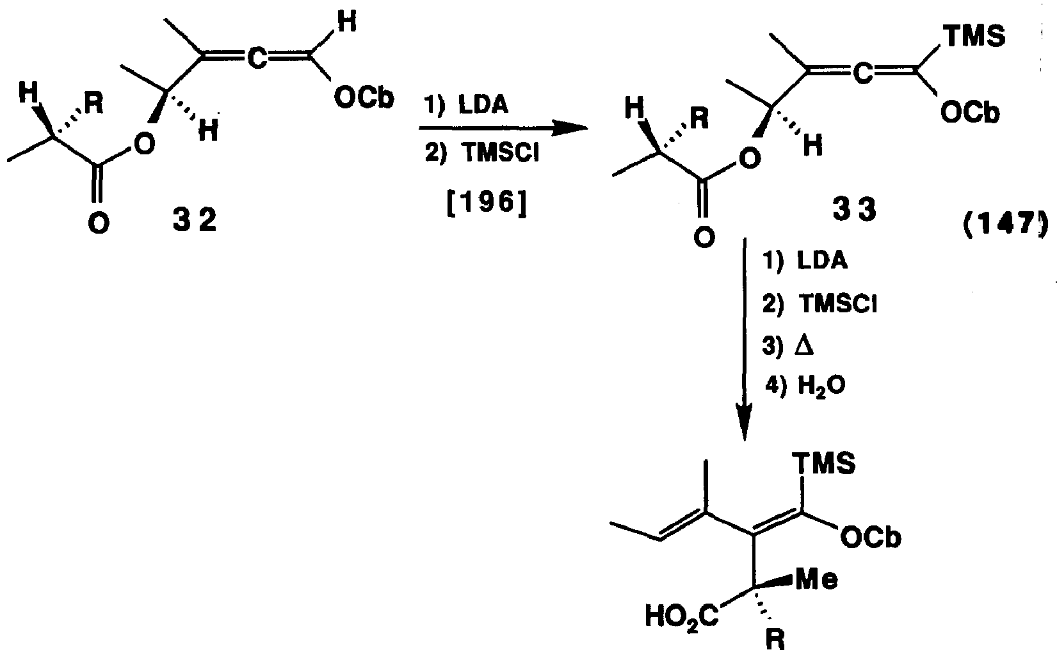


(145)

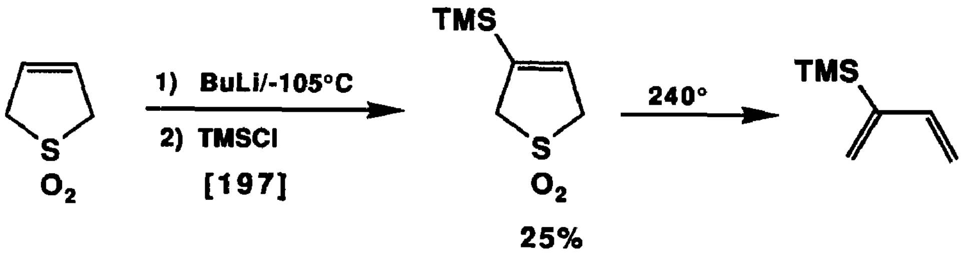


(146)

Lithiation-trimethylsilylation of allene **32** gives **33**, which was subjected to the Ireland-Claisen rearrangement to give highly substituted 1,3-butadienes. (Eqn. 147)



Treatment of 3-sulfolene with butyllithium and then trimethylchlorosilane gives 3-trimethylsilyl-3-sulfolene. (Eqn. 148) This gives 2-trimethylsilyl-1,3-butadiene upon thermolysis. Lithiation with butyllithium in the presence of lithium iodide and then trimethylsilylation gives 2-trimethylsilyl-3-sulfolene, which upon thermolysis gives 1-trimethylsilyl-1,3-butadiene. (Eqn. 149) This concept of SO_2 extrusion route to silylated dienes from sulfolenes was used to prepare silylated cyclohexadienes. (Eqns. 150 and 151) Methylation of 3-trimethylsilyl-3-sulfolene followed by thermolysis leads to trans-2-trimethylsilyl-1,3-pentadiene. (Eqn. 152)



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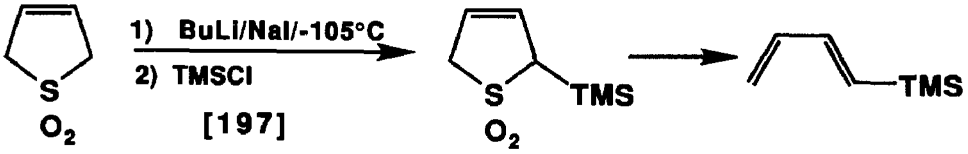

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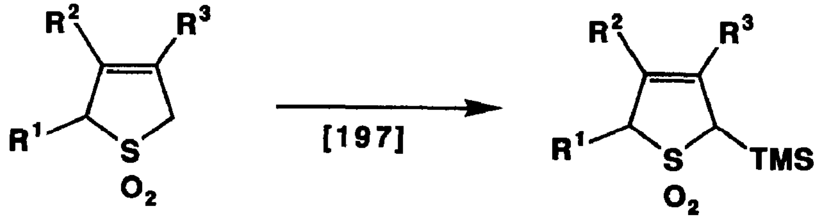
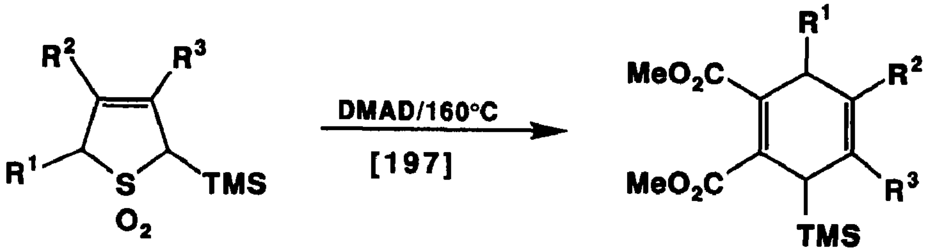
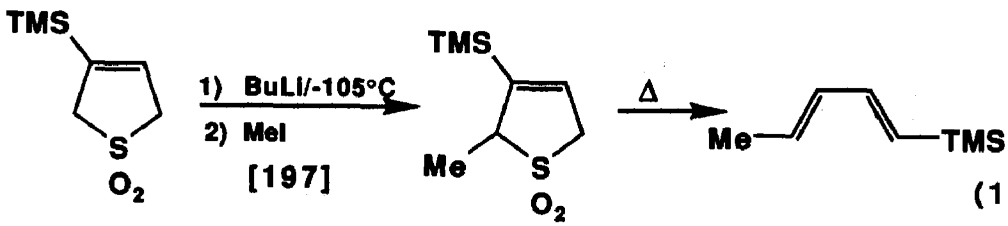


(150)

R^1	R^2	R^3
Me	H	H
H	H	Me
H	Me	Me

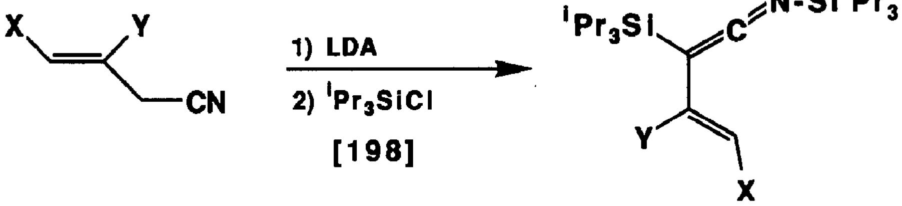


(151)



(152)

Lithiation-triisopropylsilylation of β,γ-unsaturated nitriles provides the **N,C-bis-silylated** vinyl ketene imines. (Eqn. 153) These react with dienophiles to give the corresponding cycloadducts. (Eqn. 154 and 155) These can be converted to other products. (Eqns. 156 and 157)



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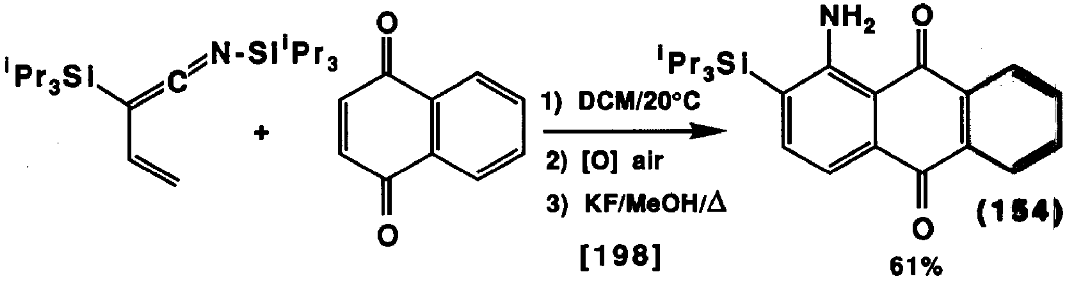

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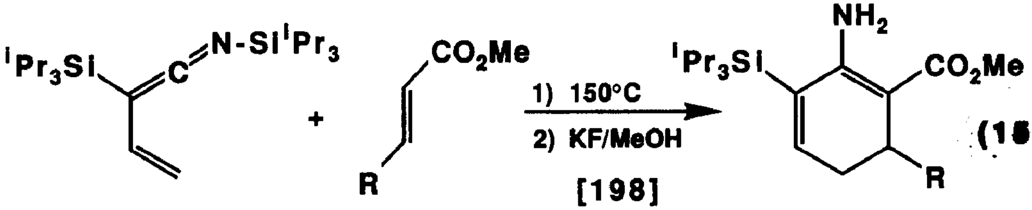

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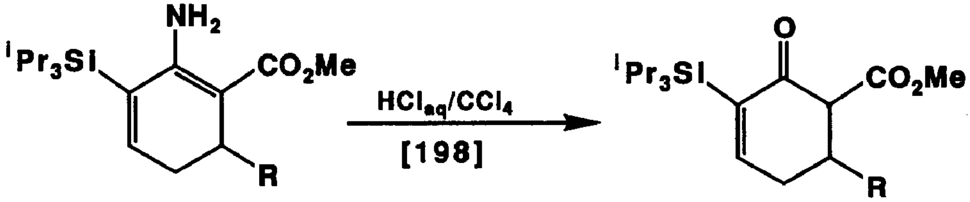
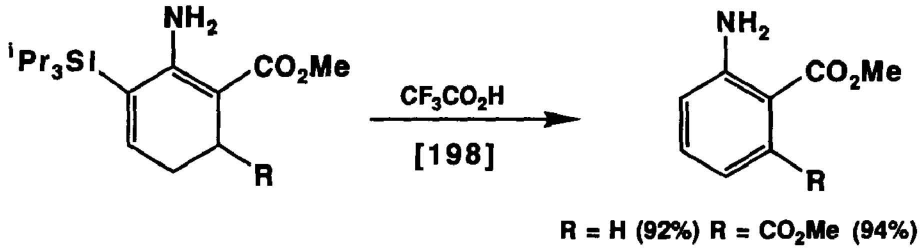


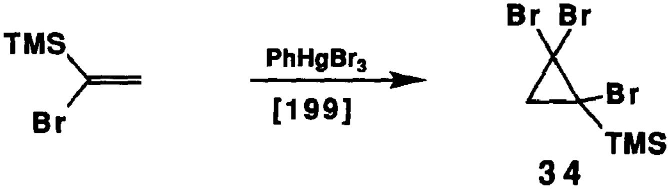
(156)

R = H (70%), R = Me (52%)

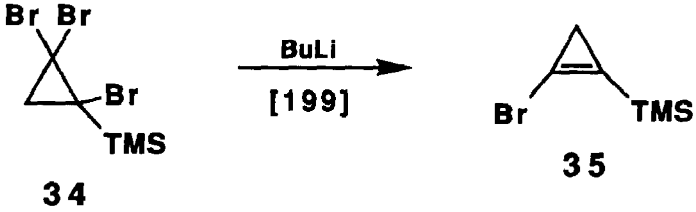


(157)

Reaction of 1-bromovinyltrimethylsilane with dibromocarbene, generated from tribromomethylphenyl mercury, gives **34**, which upon treatment with fluoride ion gives 1,2-dibromocyclopropene. (Eqn. 158) Treatment of **34** with butyllithium, on the other hand, leads to 1-bromo-2-trimethylsilylcyclopropene **35** (Eqn. 159), which can be lithiated and silylated. (Eqn. 160) Compound **35** reacts with dienes. (Eqns. 161 and 162)



(158)



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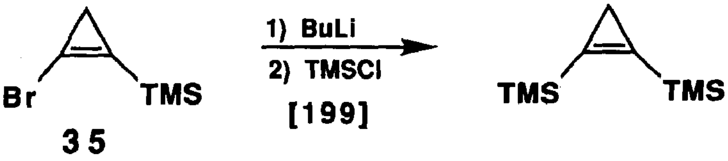

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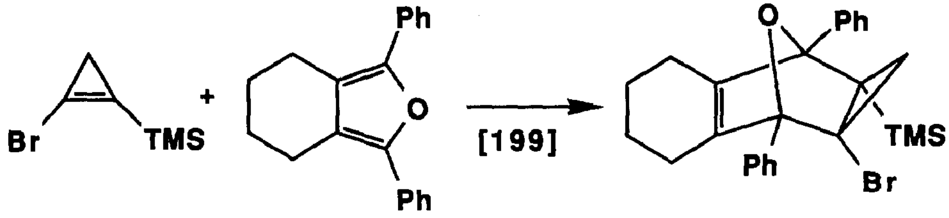

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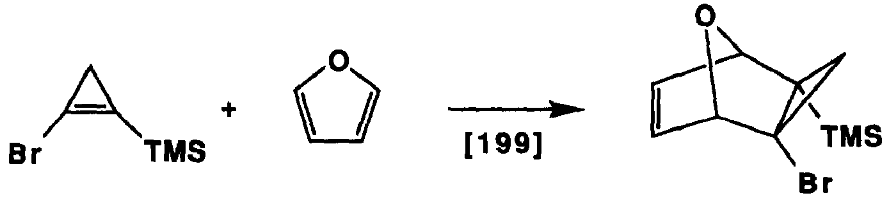
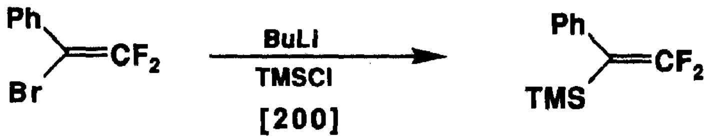


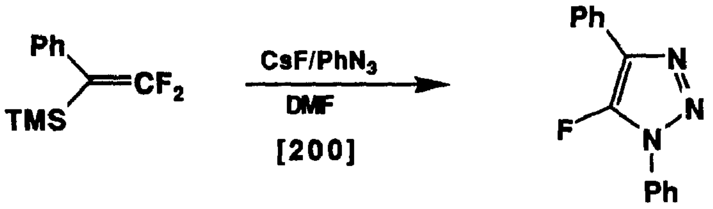
4:3 exo:endo ratio

(162)

1-Bromo-2,2-difluorostyrene can be subjected to lithium-bromine exchange and the resulting lithium reagent silylated. (Eqn. 163) This material reacts with cesium fluoride to give oligomers. It reacts with cesium fluoride in the presence of phenylazide, however, to give the cycloadduct of phenylfluoroacetylene, generated 'in situ'. (Eqn. 164)

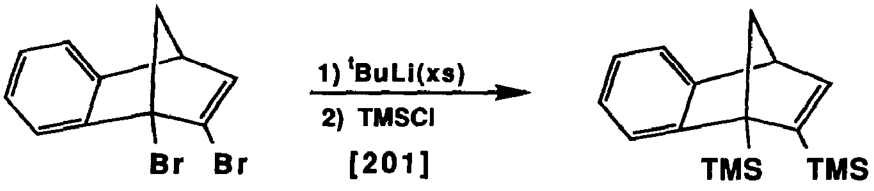


(163)



(164)

Reaction of dibromide **36** with an excess of tert-butyllithium followed by trimethylsilylation gives 60 percent of monosilylated and 40 percent of the disilylated product. (Eqn. 165)

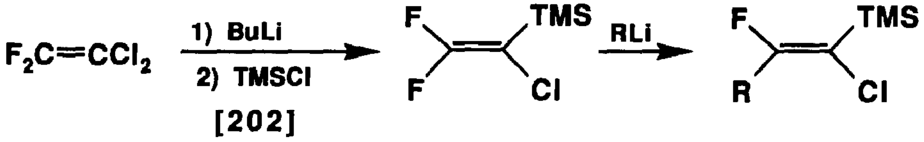


36

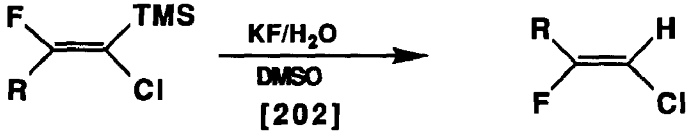
40% isolated plus 60% monosilylated product

(165)

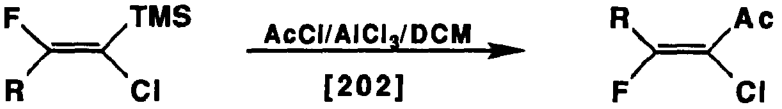
1,1-Difluorodichloroethylene reacts with butyllithium and trimethylchlorosilane to give 1,1-difluorochlorotrimethylsilylethylene. Reaction of this material with lithium reagents gives substitution of one of the fluorines. (Eqn. 166) Its reaction with fluoride ion in wet DMSO gives protodesilylation. (Eqn. 167) Acylation gives α-chloro-β-fluoro-α,β-unsaturated ketones. (Eqn. 168)



(166)

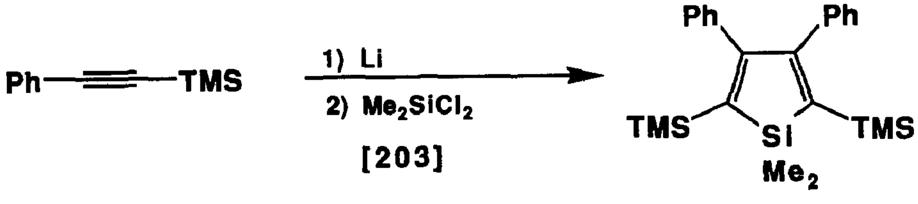


(167)



(168)

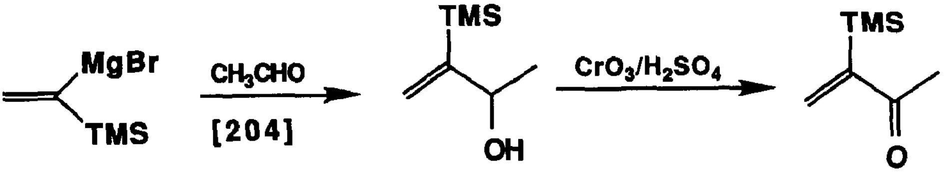
Reaction of phenyltrimethylsilylacetylene with lithium metal and then dimethyldichlorosilane provides silacyclopentadiene **37**. (Eqn. 169)



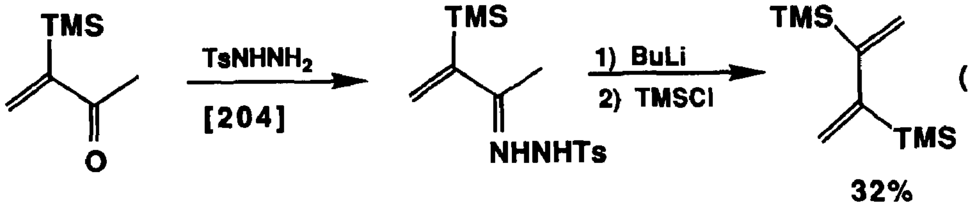
37

(169)

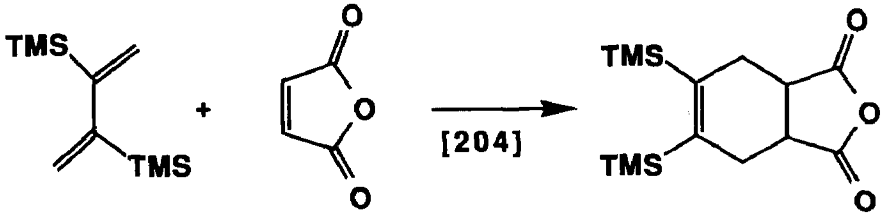
2,3-Bis(trimethylsilyl)-1,3-butadiene was prepared as outlined in Eqns. 170 and 171. It reacts with dienophiles. (Eqn. 172)



(170)



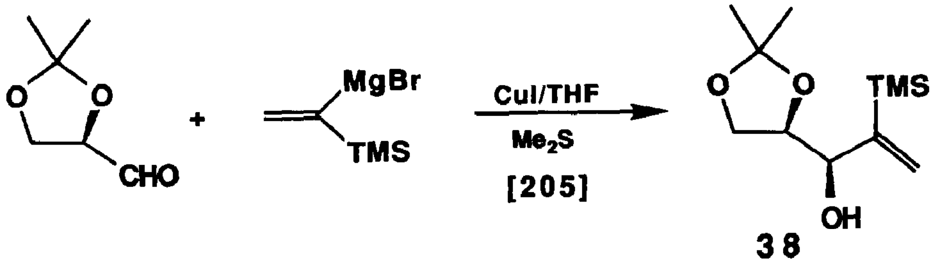
(171)



others also 75-85%

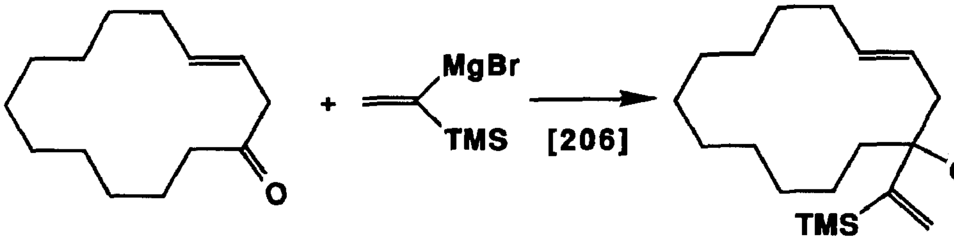
(172)

The chiral silylated syn-glycerol derivative **38** was prepared as shown. (Eqn. 173)



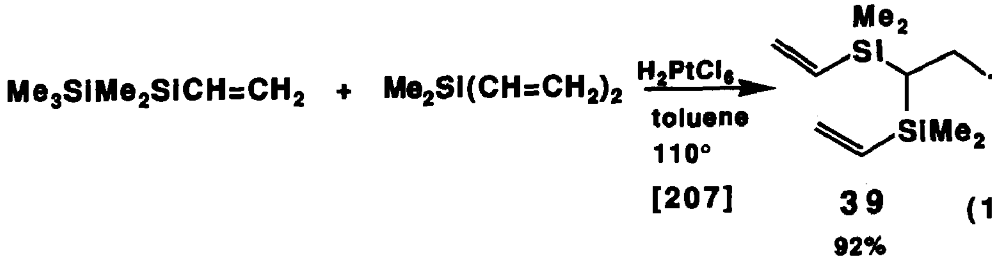
(173)

The reaction of 1-trimethylsilylvinylmagnesium bromide with cyclododec-3-en-1-one was used in a synthesis of muscone. (Eqn 174)



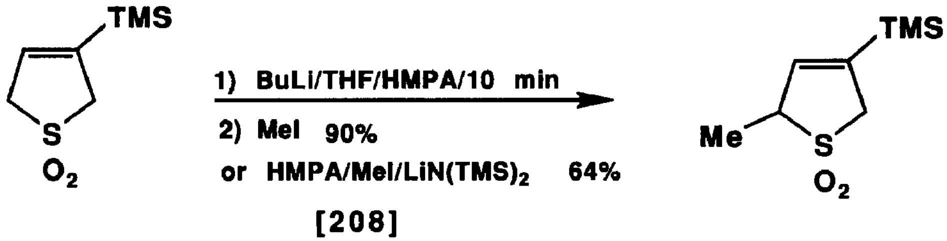
(174)

The reaction of vinylpentamethyldisilane and dimethyldivinylsilane in the presence of chloroplatinic acid gives **39**, a trisilylethane, in excellent yield. (Eqn. 175)

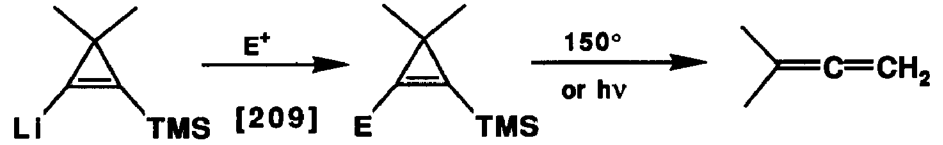


(175)

Vinylsilanes were used as precursors to other vinylsilanes in several instances. 3-Trimethylsilyl-3-sulfolene is deprotonated and methylated to give the 5-methyl derivative by either of two methods. (Eqn. 176) 1-Trimethylsilyl-2-lithio-3,3-dimethylcylopropene was reacted with tert-butylchloroformate and dimethyldisulfide to give the corresponding substituted cyclopropenes, which were used to prepare 1,1-dimethylallene. (Eqn. 177)



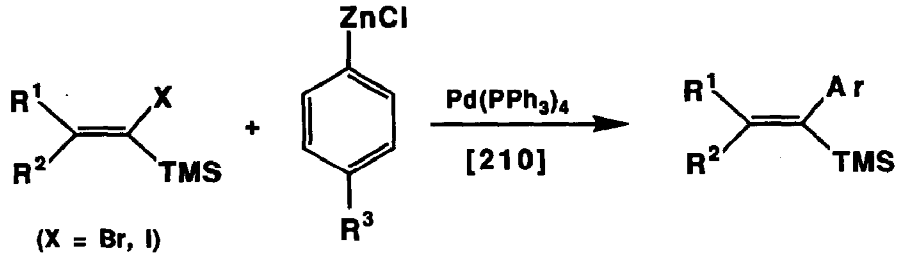
(176)



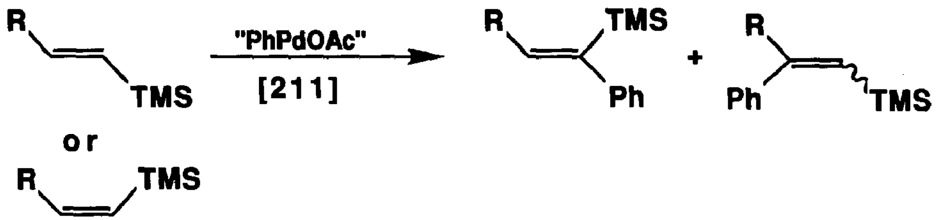
(177)

(E$^+$ = MeSSMe, ClCO$_2{}^t$Bu)

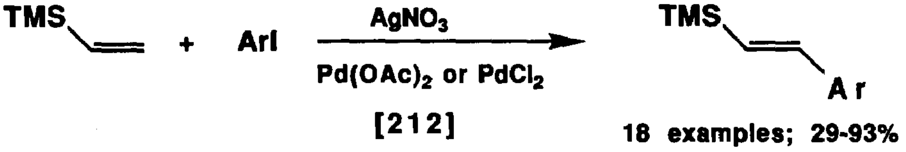
The coupling of vinylsilanes with various aryl systems provides products resulting from arylation of the vinyl group and new vinylsilanes. 1-Halovinylsilanes react with arylzinc chlorides in the presence of tetrakis(triphenylphosphine)-palladium (0) to give 1-arylvinylsilanes. (Eqn. 178) (E) and (Z) vinylsilanes react with phenylpalladium acetate, generated 'in situ' to give a mixture of (E) and (Z) 1- and 2-arylvinylsilanes. (Eqn. 179) Aryl iodides were shown to react with vinylsilanes in the presence of a palladium(II) catalyst and silver nitrate. (Eqns. 180 and 181)



(178)



(17 9)



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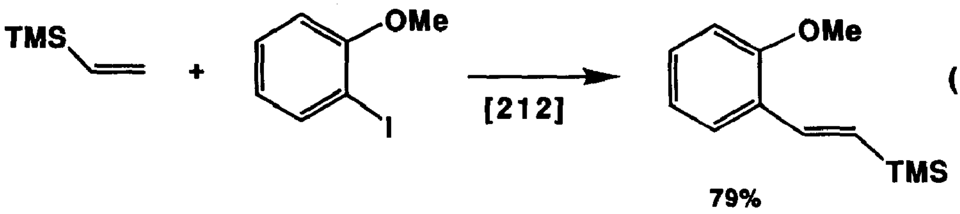
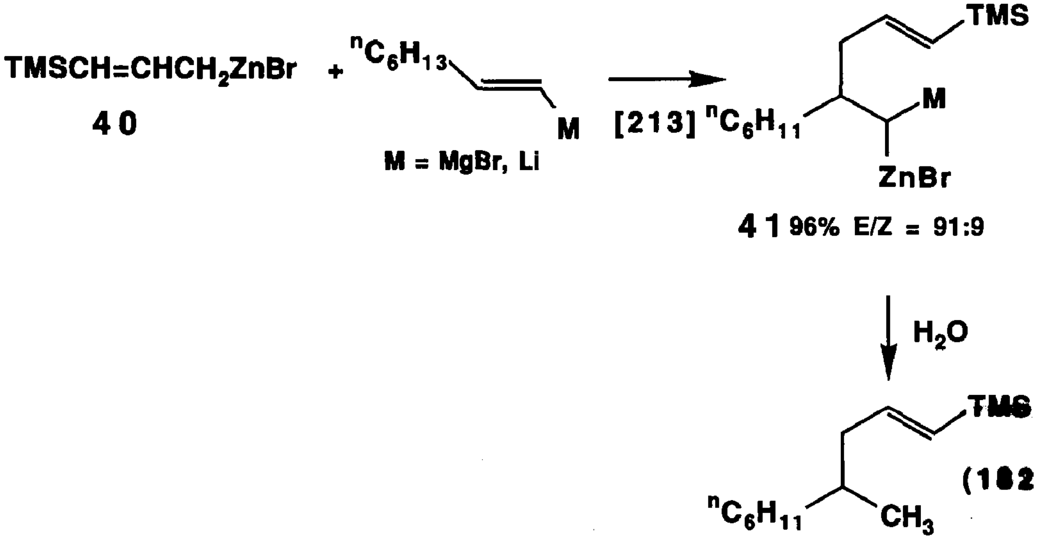


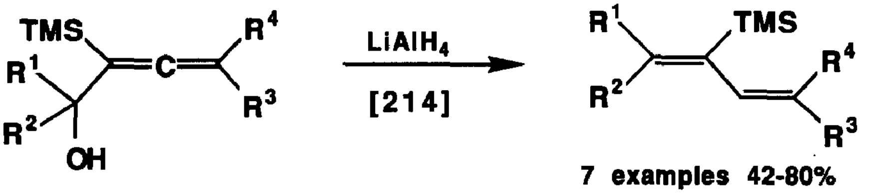
(181)

Allylzinc bromide **40** was reacted with vinyllithium or vinylhalomagnesium reagents to give primarily the vinylsilane **41**. (Eqn. 182)

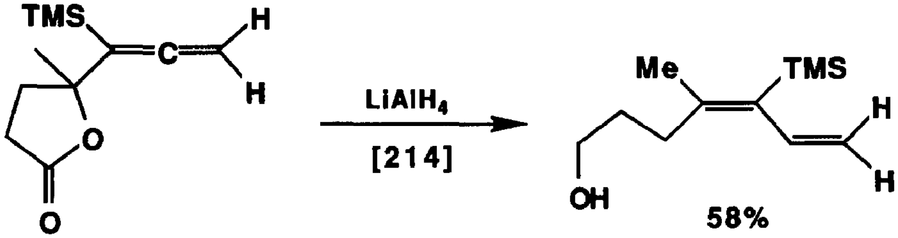


(182)

The synthesis of 2-trimethylsilyl-1,3-butadienes was accomplished by the lithium aluminum hydride reduction of (α-trimethylsilylallenyl)methanols. (Eqns. 183 and 184)

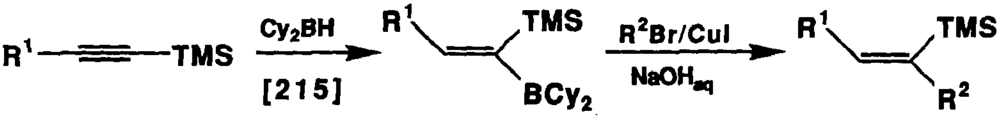


(183)



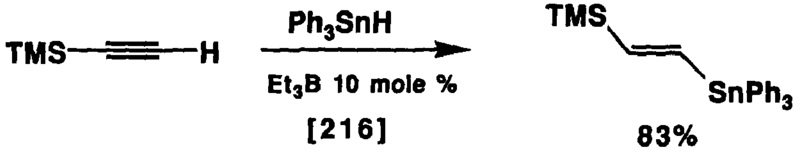
(184)

The addition of organometallic reagents to ethynylsilanes formed the basis for the preparation of vinylsilanes. Hydroboration of ethynylsilanes with dicyclohexylborane gives the 1-borylvinylsilane. These were alkylated with alkyl bromides in the presence of copper(I). (Eqn. 185)

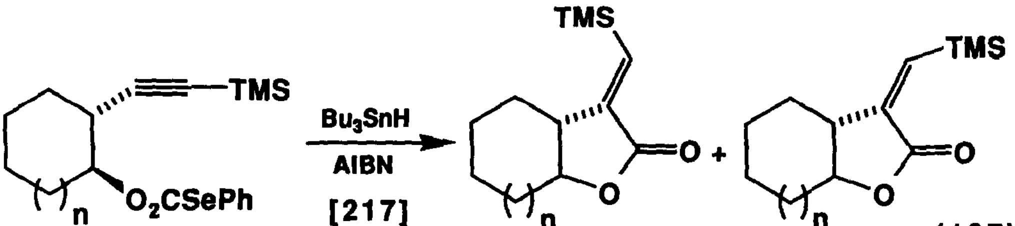


(186)

Trimethylsilylacetylene was reacted with triphenyltin hydride in the presence of 10 mole percent triethylboron to give (E) 2-triphenylstannylvinylsilane. (Eqn. 186) Ethynylsilanes **42a** and **42b** react with tributyltin hydride to give cyclic β-trimethylsilyl-α-methylenebutyrolactones **43a** and **43b**. (Eqn. 187)



(186)

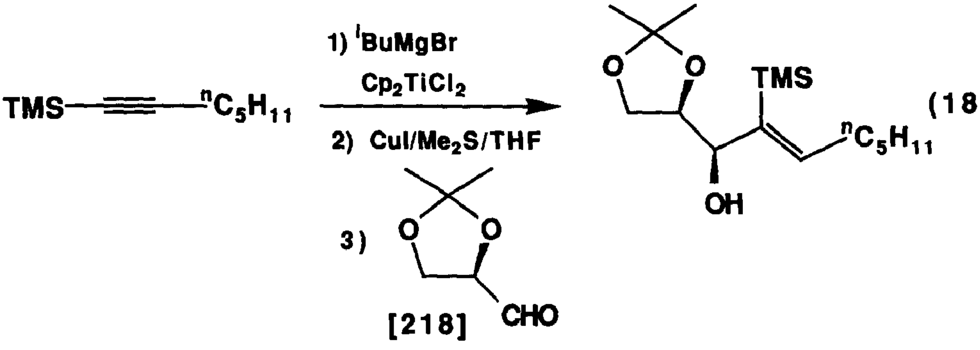


(187)

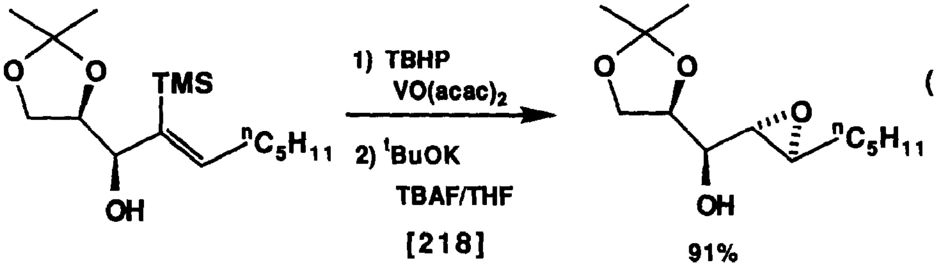
42a n = 1
42b n = 2

	43a	**43b**
n = 1 (80%)	1pt	12 pts
n = 2 (92%)	1pt	10 pts

The addition of the "hydridomagnesium bromide", generated from isobutylmagnesium bromide and dicyclopentadienyltitanium dichloride, across the triple bond of ethynylsilanes was used as a method of preparing multigram quantities of (+)-methyl-5(S),6(R)-epoxy-6-formylhexanoate (Eqns. 188 and 189) and 2(R),3(S)-epoxyoctanal, useful intermediates in the synthesis of leukotrienes.

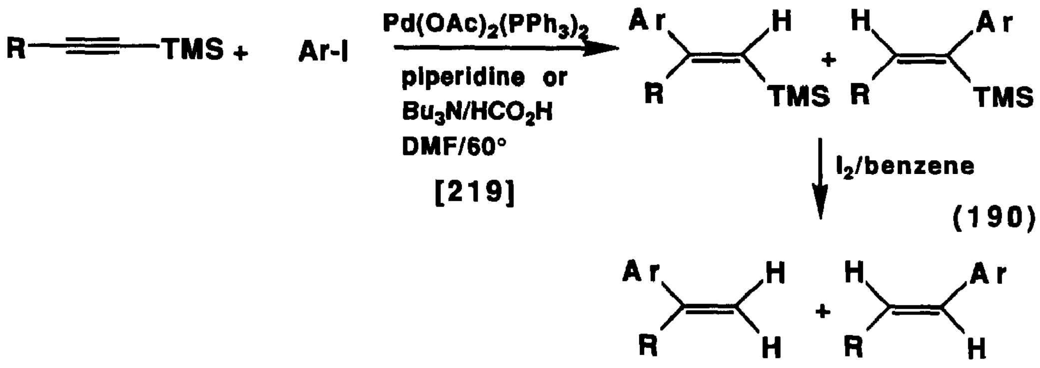


(188)



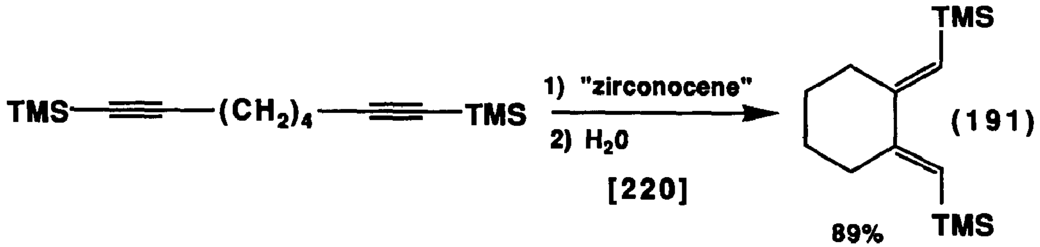
(189)

Aryl iodides can be reacted with ethynylsilanes with palladium(II) catalysis to give a mixture of α- and β-arylvinylsilanes. (Eqn. 190) Treatment of these vinylsilanes with iodine gives the desilylated styrene.



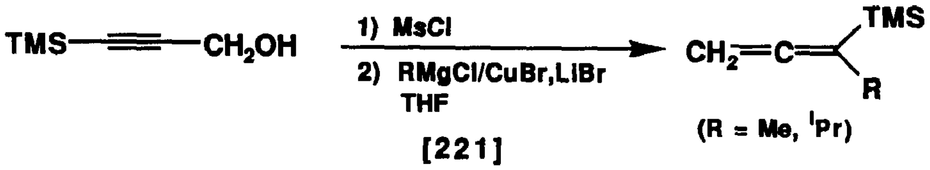
(190)

Bis(trimethylsilyl)-1,7-octadiyne was reacted with 'in situ' generated zirconocene to give **44**. (Eqn. 191)

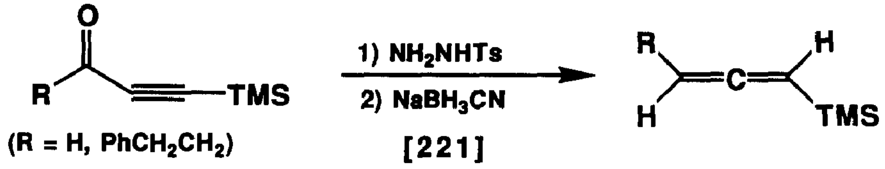


(191)

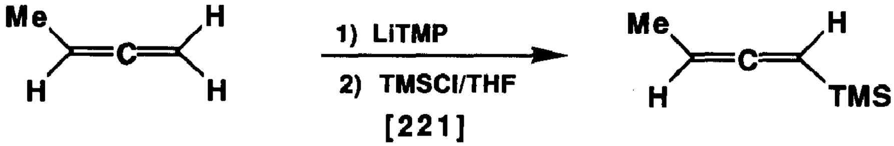
1-Trimethylsilylpropargyl alcohol served as the starting material for 1-substituted trimethylsilylallenes as shown in Eqn. 192. Trimethylsilylethynyl ketones were used to prepare 3-substituted trimethylsilylallenes. (Eqn. 193) Direct lithiation-trimethylsilylation of 1,2-butadiene provides 1-trimethylsilyl-1,2-butadiene. (Eqn. 194)



(192)

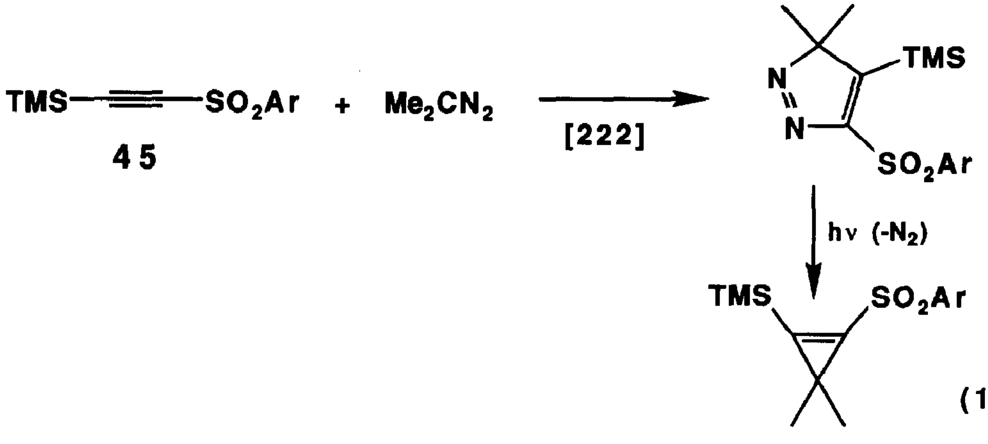


(193)



(194)

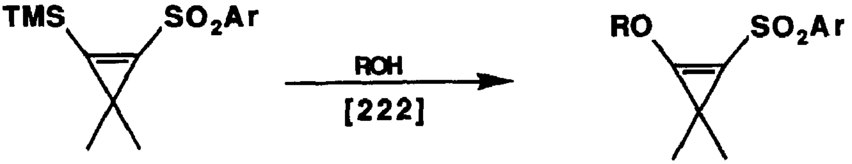
Arylsulfonylethynylsilanes **45**, prepared *via* sulfonylation of bis(trimethylsilyl)-acetylene, were reacted with dimethyldiazomethane to give the cycloadduct, which upon photolysis gives the trimethylsilylcyclopropene **46**. (Eqn. 195) The parent cyclopropenes can be easily prepared by protodesilylation. Compound **46** was shown to react with alcohols and/or alcoholates to give the alkoxycyclopropene. (Eqn. 196) Reaction of **46** with toluenesulfonic acid in benzene gives ring opening. (Eqn. 197)



45

46

(195)



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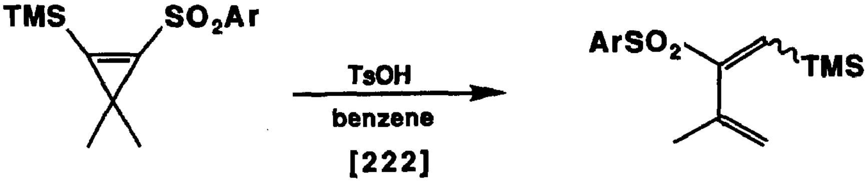
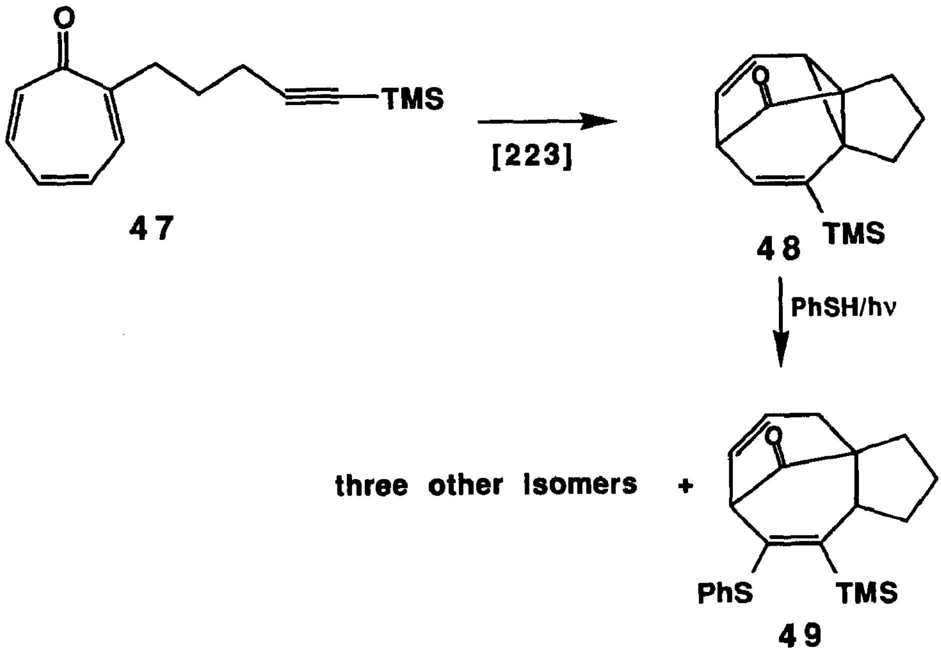


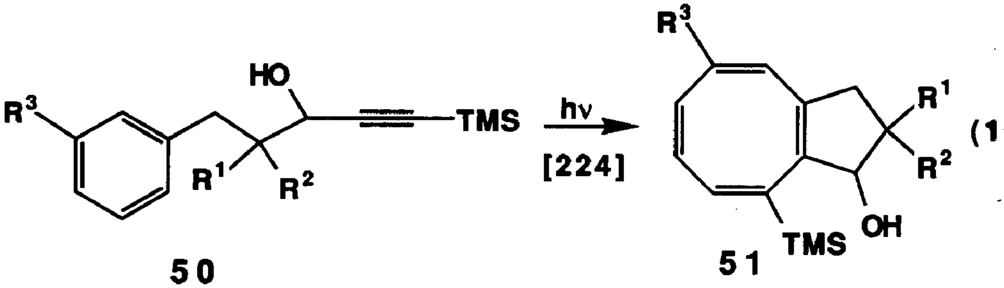
(197)

The ethynylsilane **47** undergoes photolysis in methanol to give **48**, which was reacted with thiophenol to give adduct **49**. (Eqn. 198)



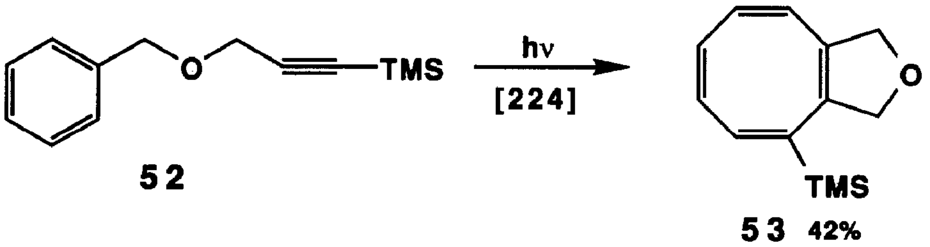
(198)

Photolysis of ethynylsilane **50** provides the bicyclooctatetraene **51** (Eqn. 199), while **52** gives **53**. (Eqn. 200)



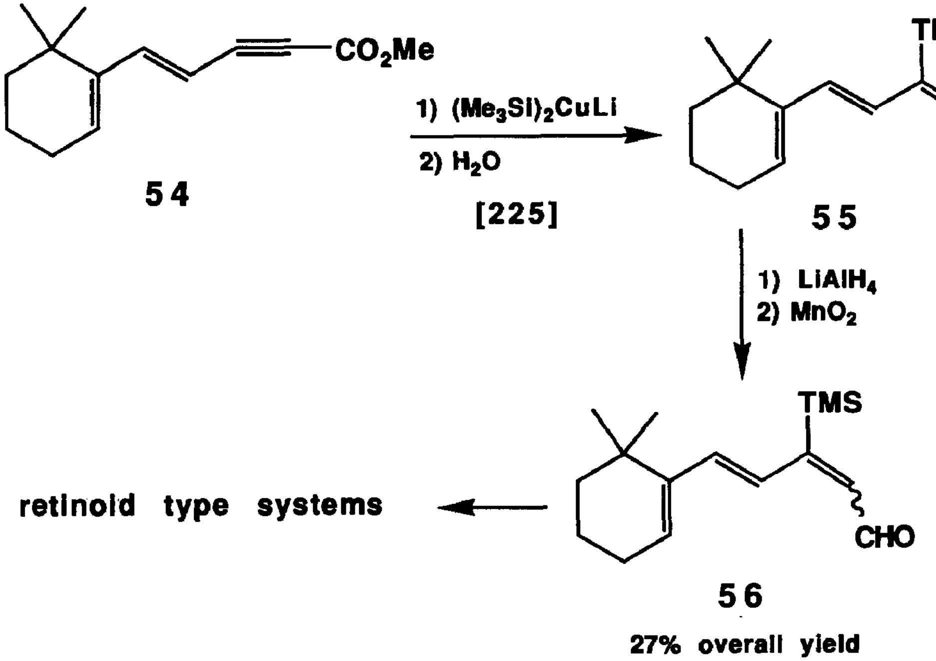
(199)

$R^1 = R^2 = R^3 = H$ (46%)
$R^1 = R^2$, $R^3 = Me$ (38%)
$R^1 = R^2 = Me$, $R^3 = H$ (31%)

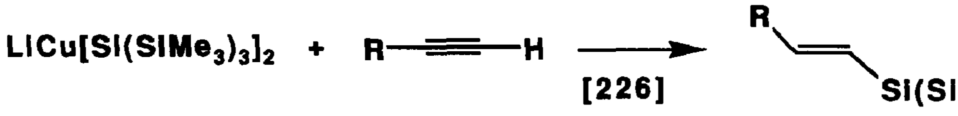


(200)

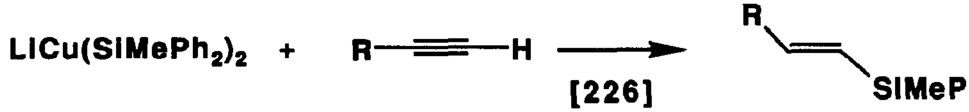
The addition of silylorganometallic reagents to carbon-carbon triple bonds provided convenient entries into several vinylsilanes. The dienynyl ester **54** was reacted with lithium bis(trimethylsilyl)cuprate to produce the β-trimethylsilyl ester **55**, which was not isolated, but converted directly to the aldehyde **56**. (Eqn. 201) This system was used to prepare retinoids. Tris(trimethylsilyl)silyllithium, converted to an organocopper reagent in a ratio of 1:1 or 2:1, reacts with acetylenes to give cis addition and the silicon at the least hindered carbon. (Eqn. 202) This is also true of the reagents similarly prepared from diphenylmethylsilyllithium. (Eqn. 203) The use of phenyldimethylsilyllithium, however, gives a mixture of regioisomers from the reagent prepared in a 1:1 ratio; the silicon positioned exclusively at the least hindered carbon from the reagent prepared with a 2:1 ratio. (Eqn. 204)



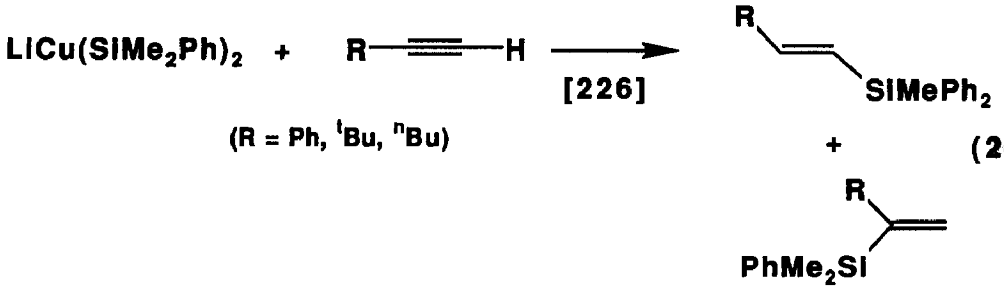
(201)



(202)



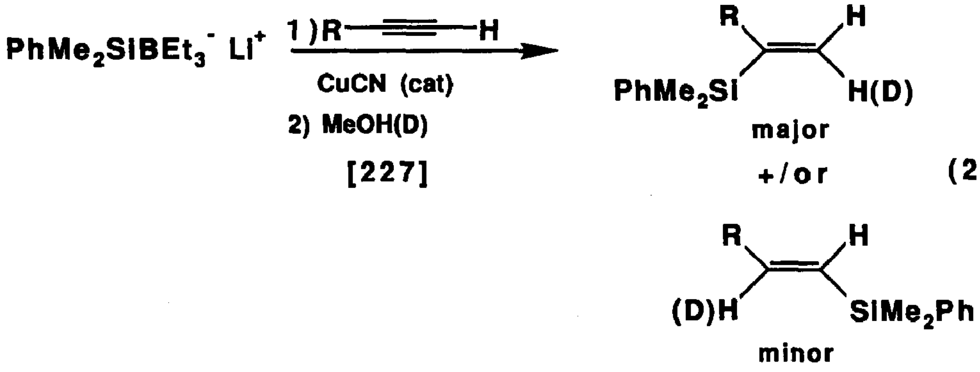
(203)



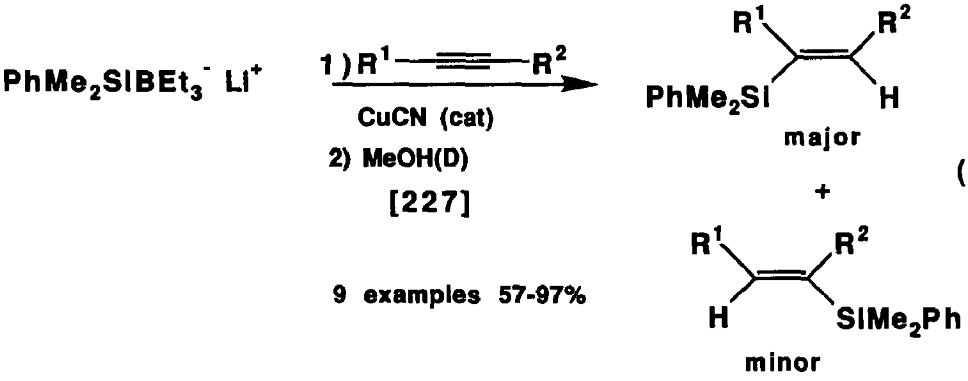
(204)

Phenyldimethylsilyllithium was reacted with triethylboron and the resulting complex (Eqn. 205) added to terminal acetylenes with cuprous cyanide catalysis to give vinylsilanes with the silicon preferrentially at the more substituted internal carbon. (Eqn. 206 and 207) Trimethylsilyltrimethyltin and trimethylsilyltributyltin add acetylenes to give β-stannylvinylsilanes in good yields. (Eqns. 208 and 209) It is possible to utilize the vinyltin group in a metal-metal exchange process to obtain the vinyllithium reagent, which is then reacted with electrophiles. (Eqn. 210) Interestingly, but not surprisingly, treatment with NBS, bromine or iodine results in loss of the tin and not the silicon moiety. (Eqn. 211) Cross coupling of the vinyltin unit with aryl halides provides the β-silylated styrenes. (Eqn. 212) Cross coupling with allyl bromides was also reported in this work.

$$PhMe_2SiLi + Et_3B \xrightarrow[{[227]}]{\qquad\qquad} PhMe_2SiBEt_3^{-}\,Li^{+} \qquad (205)$$

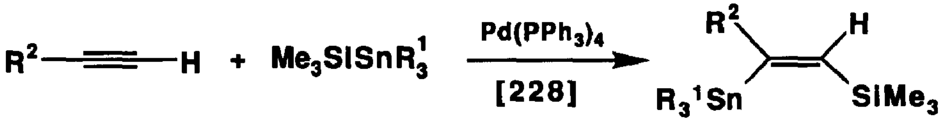


(206)

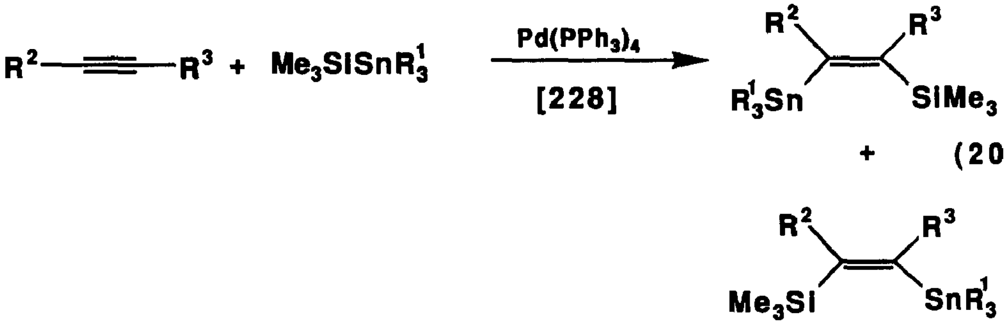


9 examples 57-97%

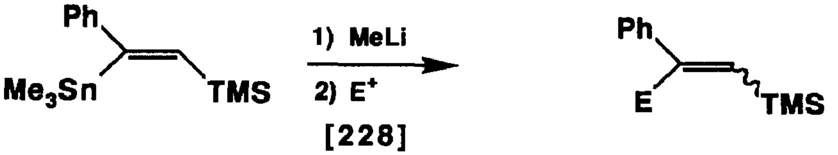
(207)



(208)



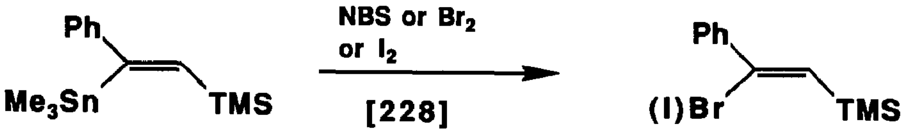
(209)



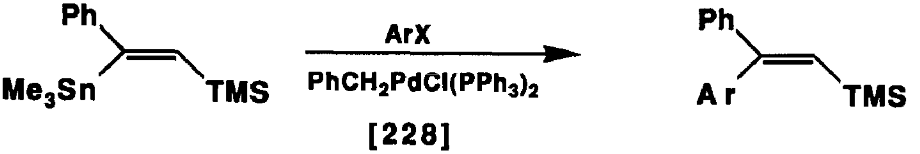
(210)

9 examples; 29-68%

(E$^+$ = H_2O, Me_2SO_4, EtBr, acetone, EtCHO, DMF, TMSCl, Me_3GeCl, Me_3PbCl)

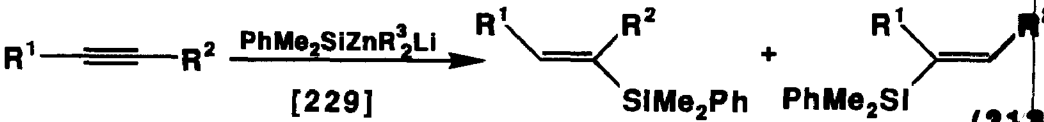


(211)



(212)

Lithium (phenyldimethylsilyl)dialkylzincates add to acetylenes in the presence of transition metal catalysts to produce vinylsilanes. (Eqn. 213)

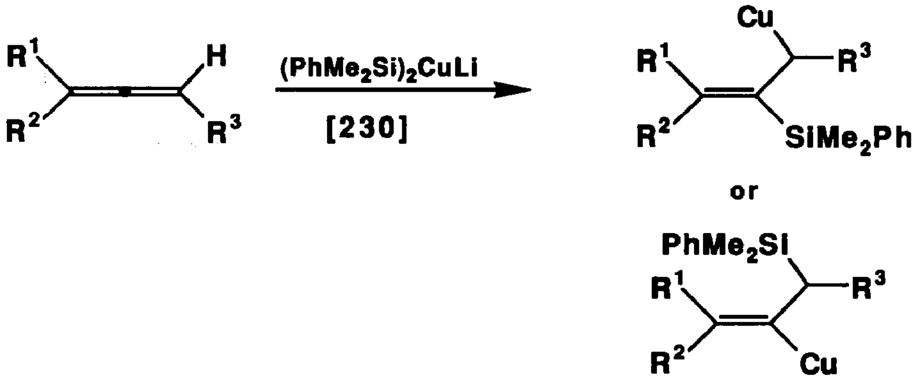


(213)

11 examples; 62-98%

(CuI, $Pd(PPh_3)_4$, $CoCl_2(PPh_3)_2$, CuCN used as catalysts; CuCN best)

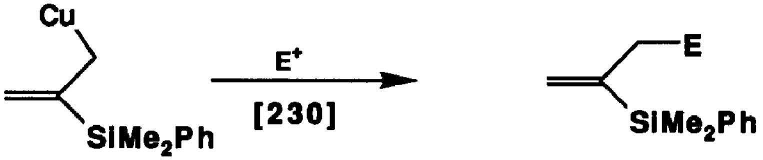
Lithium bis(phenyldimethylsilyl)cuprate adds to allenes to give either vinylsilanes or allylsilanes, depending on the nature of the allene. (Eqn. 214) The vinylsilanes can be reacted with electrophiles (Eqn. 215) as can the allylsilanes (Eqn. 216).



(214)

allylsilane formed when $R^1 = R^2 = R^3 = H$; $R^1 = Ph$, $R^2 = R^3 = H$;
$R^1 = Me$, $R^2 = H$, $R^3 = Ph$; $R^1 = R^2 = Me$, $R^3 = Ph$

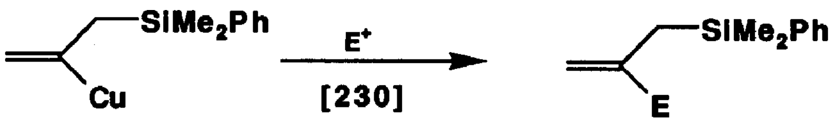
vinylsilane formed when $R^1 = R^2 = H$, $R^3 = Bu$; $R^1 = R^3 = Me$, $R^2 = H$;
$R^1 = R^2 = Me$, $R^3 = H$; $R^1 = R^2 = R^3 = Me$.



(215)

E+ = MeI, AcCl, cyclohexenone (1,2 addition)

73-83%

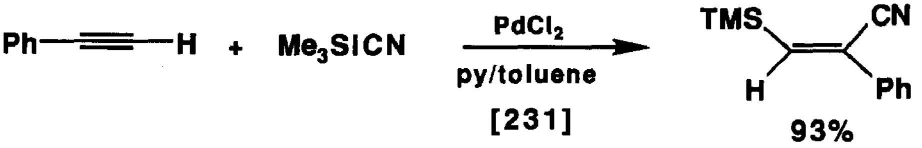


(216)

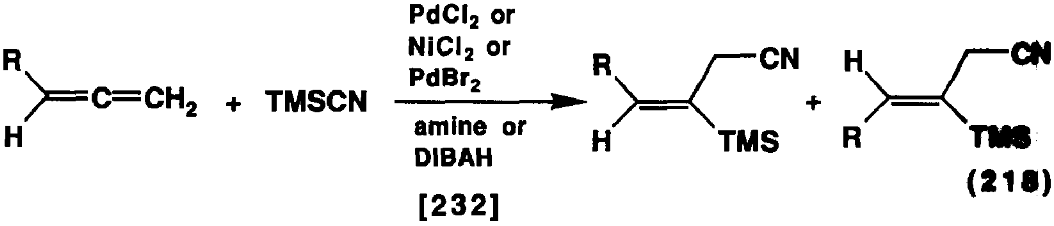
E+ = MeI, AcCl, cyclohexenone (1,4 addition)

52-92%

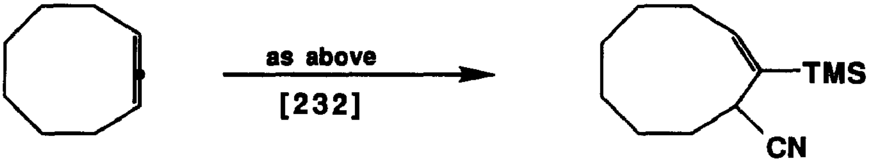
Trimethylsilylnitrile was added to phenylacetylene with palladium(II) catalysis. (Eqn. 217) Under similar conditions trimethylsilylnitrile was added to allenes. (Eqns. 218 and 219) The E isomer was favored over the Z isomer.



(217)

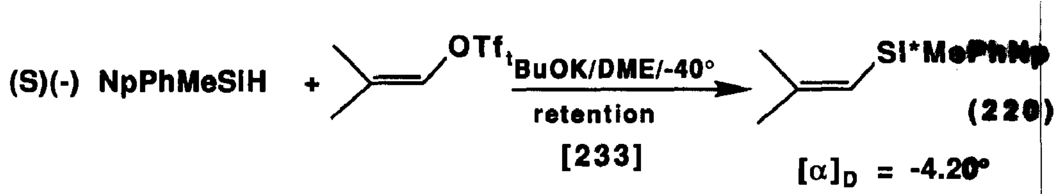


(218)



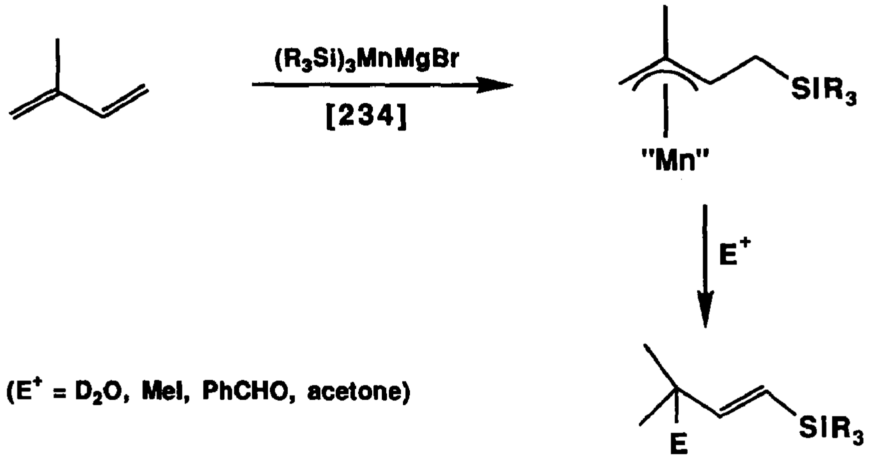
(219)

The insertion of vinylcarbenes into the Si-H bond was studied according to Eqn. 220. Retention of configuration at silicon was observed consistent with other carbene insertions into the Si-H bond.



(220)

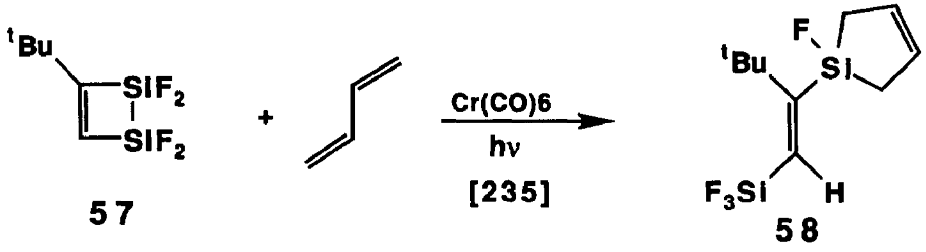
Tris(trimethylsilyl)manganesiomagnesium bromide, prepared from the (silyl)-methylmagnesium and manganese dichloride, was reacted with 1,3-butadienes and then an electrophile to provide 3-substituted vinylsilanes. (Eqn. 221) It is felt that an intermediate π-allyl manganese complex is involved.



(E^+ = D_2O, MeI, PhCHO, acetone)

(221)

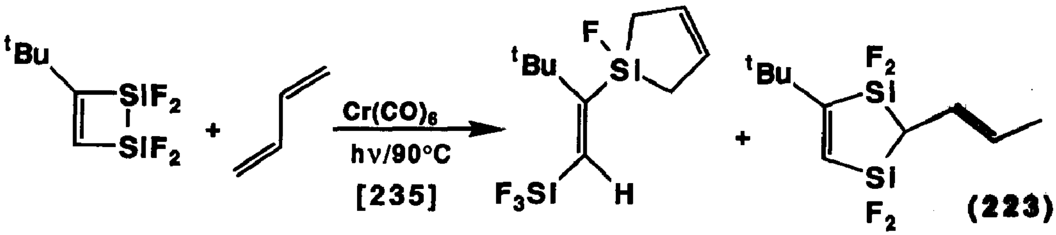
Photolysis of disilacyclobutene **57** with 1,3-butadiene in the presence of chromium hexacarbonyl gives vinylsilane **58**. (Eqn. 222) Similar reaction of the same material in the presence of molybdenum hexacarbonyl gives **59**. (Eqn. 223)



57

58

(222)

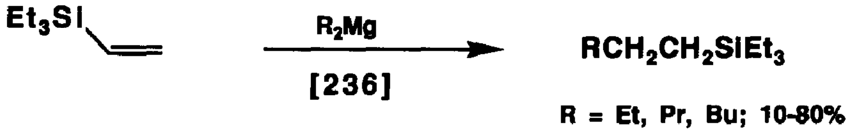


59

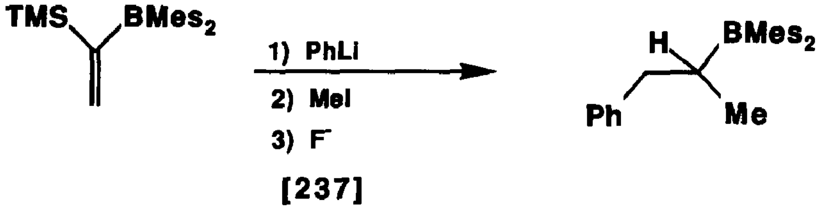
(223)

B. Vinylsilanes-Reactions

Dialkylmagnesium reagents were reacted with vinyltriethylsilane. (Eqn. 224) Organolithium and organomagnesium reagents were added to 1-(dimesitylboryl)-vinyltrimethylsilane. (Eqn. 225)

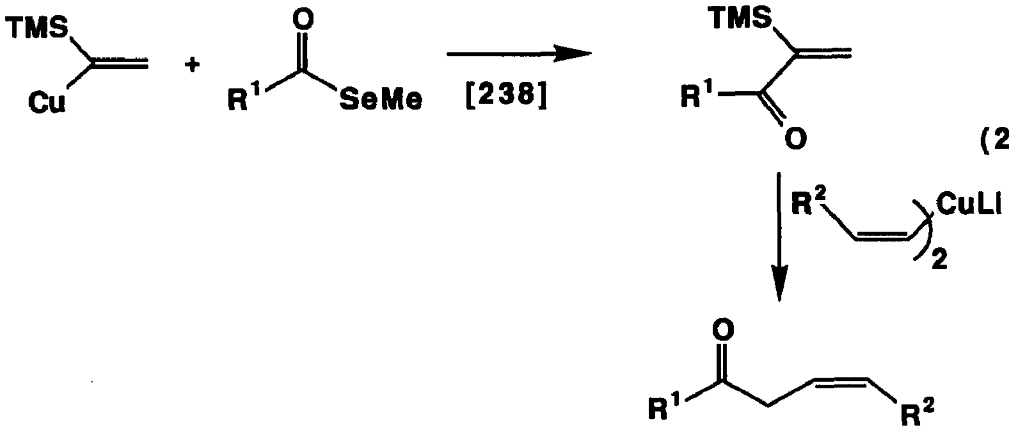


(224)

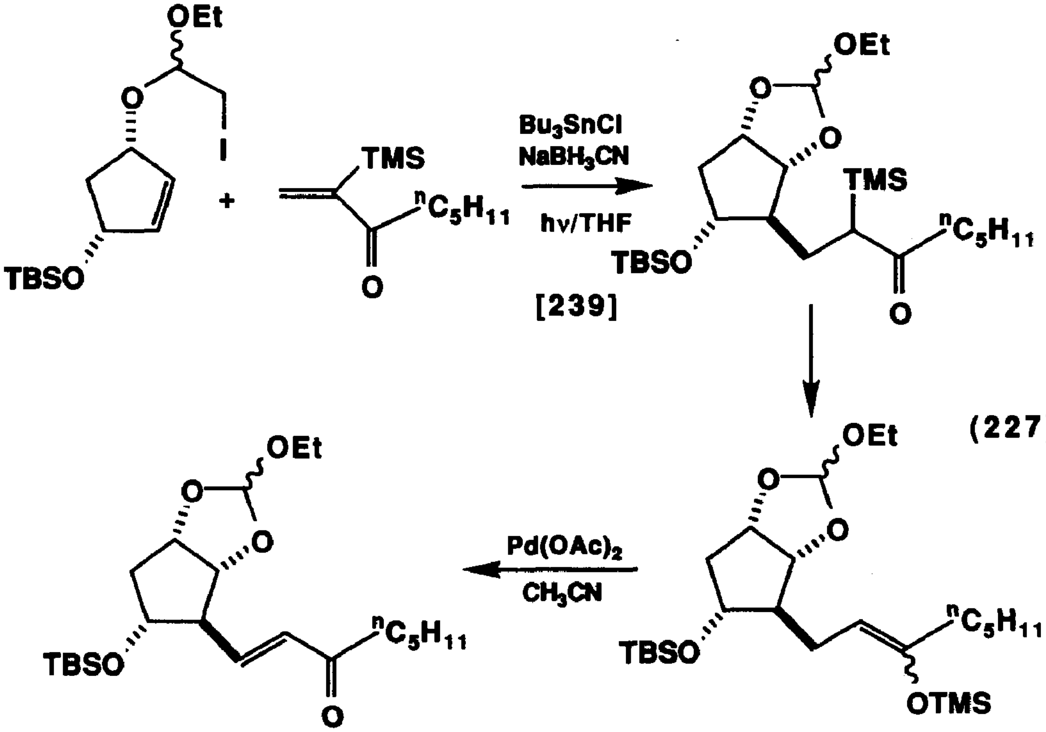


(225)

α-Trimethylsilyl-α,β-unsaturated ketones were employed as acceptors for the conjugate addition of organocuprates (Eqn. 226) and for radicals (Eqn. 227) The latter of these two examples employed the resulting β-ketosilane to regiospecifically prepare an enol silyl ether that was used to introduce the C_{13}-C_{14} double bond of prostaglandins.

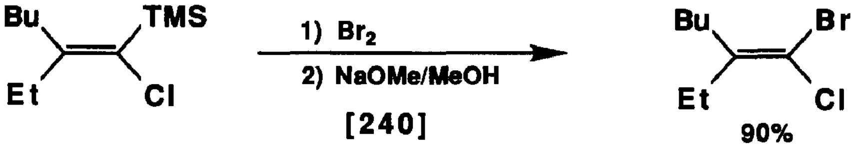

TMS
Cu
+
O
R1
SeMe
[238]
TMS
R1
O
R2
CuLi
2
O
R1
R2

(226)

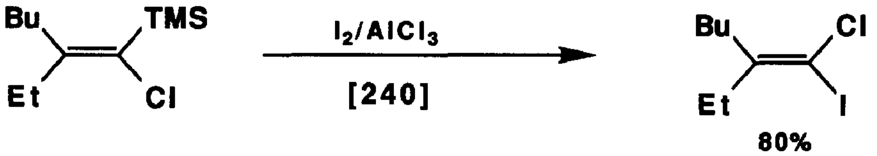

OEt
O
I
TBSO
+
TMS
nC5H11
O
Bu3SnCl
NaBH3CN
hν/THF
[239]
OEt
O
O
TMS
TBSO
nC5H11
O
OEt
O
O
TBSO
nC5H11
OTMS
Pd(OAc)2
CH3CN
OEt
O
O
TBSO
nC5H11
O

(227)

α-Chlorovinyltrimethylsilanes were reacted with bromine followed by treatment with base (Eqn. 228) or with iodine in the presence of aluminum chloride (Eqn. 229) to give α-chlorovinyl bromides and α-chlorovinyl iodides, respectively.

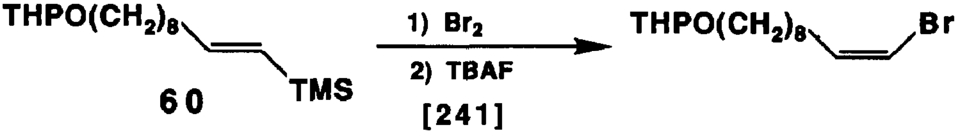


(228)

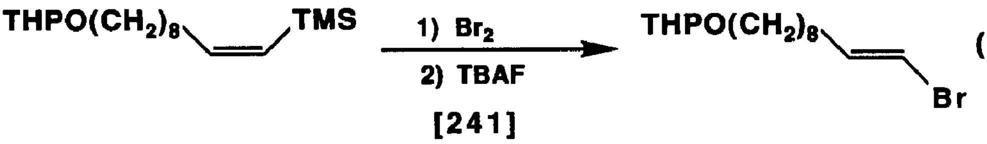


(229)

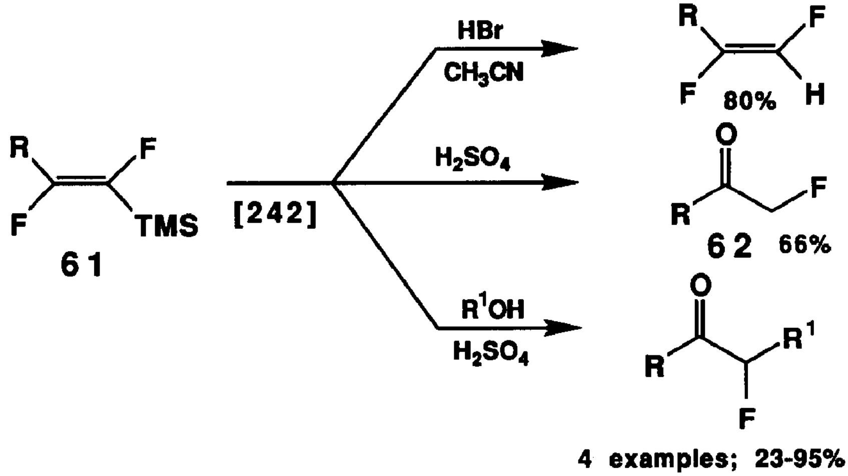
Reaction of trans vinylsilane **60** with bromine and then fluoride ion gives the cis vinyl bromide cleanly. (Eqn. 230) Accordingly, the cis vinylsilane gives the trans vinyl bromide. (Eqn. 231) The addition of HBr to vinylsilane **61** in acetonitrile leads to protodesilylation with retention of geometry. (Eqn. 232) Reaction of **61** with sulfuric acid gives fluoroketone **62** (Eqn. 233) and reaction with alcohols in the presence of sulfuric acid gives substituted α-fluoroketones. (Eqn. 234)



(230)



(231)

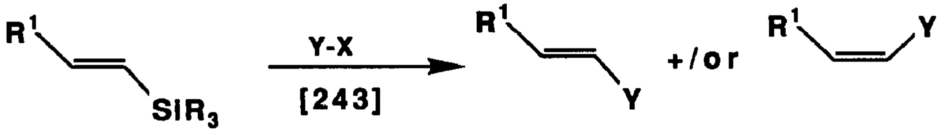


(232)

(233)

(234)

A full acount of the halogenloysis of vinylsilanes was reported. (Eqn. 235) It was found that the reaction proceeds with inversion of the double bond when the silyl group is trimethyl or triethoxy and when iodine monochloride or bromine are used. (Eqn. 235) When the silyl group is the pentafluorosilicate unit the reaction occurs with retention of geometry with the above reagents and with N-bromosuccinimide. (Eqn. 236) It is thus possible, as is shown in Eqns. 237 and 238, to use the same intermediate vinylsilane to prepare both E and Z vinyl bromides.



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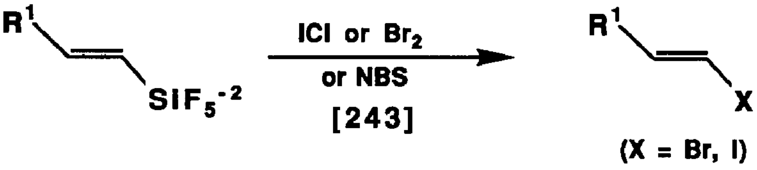

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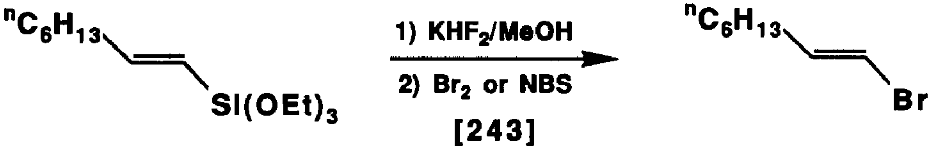

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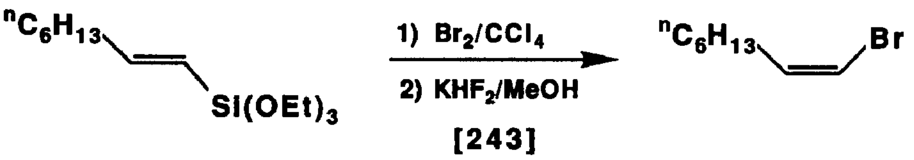
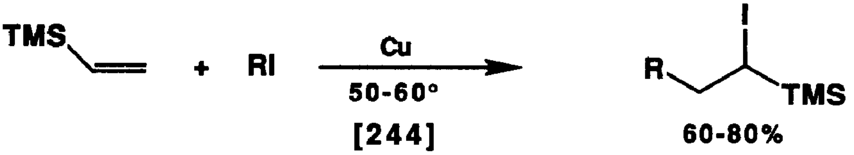


(238)

Several perfluoroalkyl iodides were added to vinyltrimethylsilane in the presence of copper metal. (Eqn. 239) The addition of 1,1,2,2-tetrahydrotrifluorooctyl mercaptan to vinylsilanes was reported. (Eqn. 240)

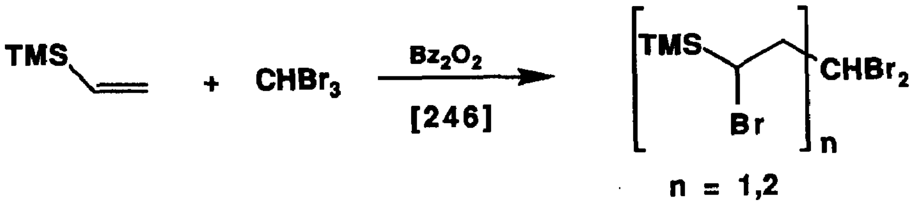


(239)

(R = $Cl(CF_2)n$, n = 2, 4, 6; $CF_3(CF_2)_5$; $H(CF_2)_4$; $FO_2S(CF_2)_2O(CF_2)_4$

(240)

The free radical addition of bromoform to vinyltrimethylsilane was studied and shown to give principally a monomer and a dimer. (Eqn. 241) The addition of sodium bisulfite to vinyltrimethylsilane provides the precursor to trimethylsilylethylsulfonyl chloride (Eqn. 242), which can be used to protect amines (Eqn. 243). It has the advantage that it can be selectively removed by fluoride ion. The addition of N,N-dichloroarylsulfamides to vinyltrimethylsilane was accomplished photolytically. (Eqn. 244) The reaction of vinyltrimethylsilane with ethoxycarbonylnitrene leads to aziridines. (Eqn. 245)



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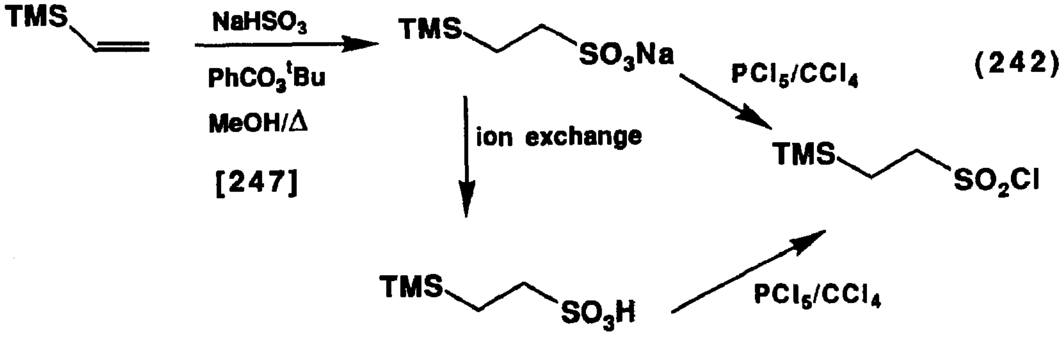

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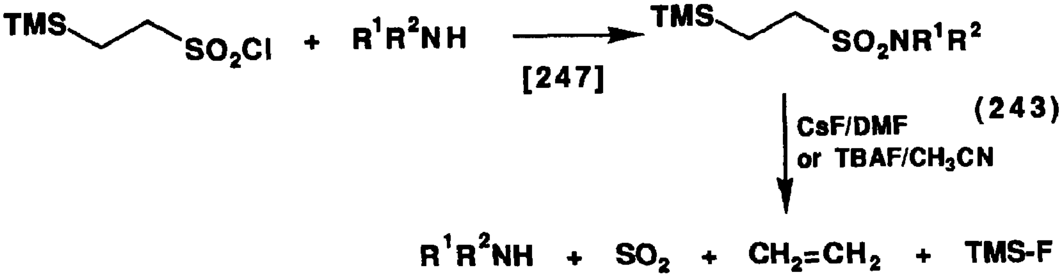
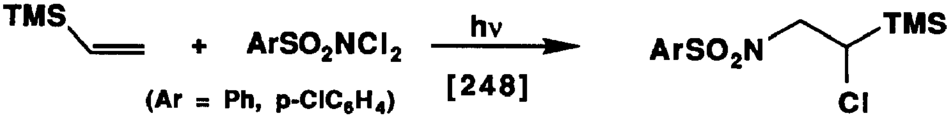


(243)



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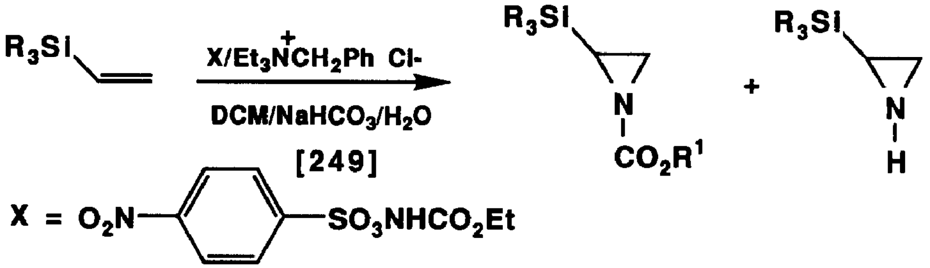
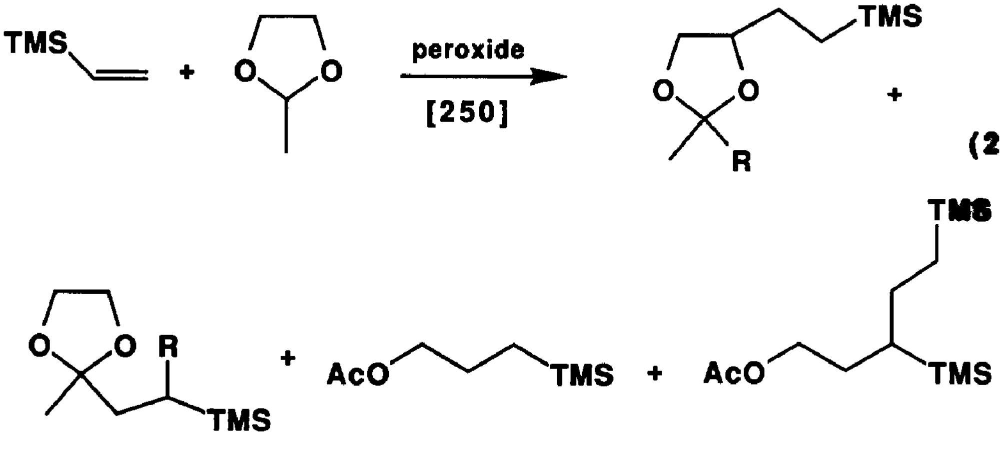


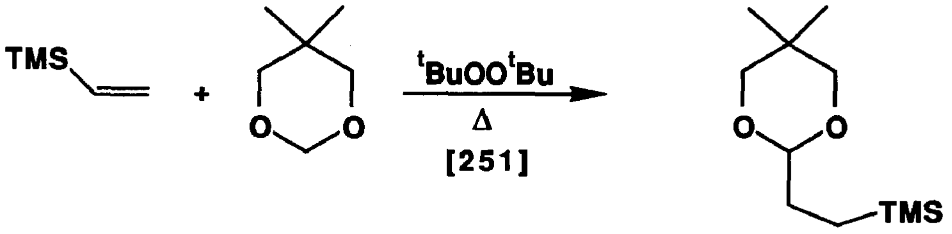
(245)

The free radical initiated reaction of 1,3-dioxolanes and 1,3-dioxanes with vinyltrimethylsilane was reported in two papers. The results are shown in Eqns. 246 and 247. Another reaction involving the 1,3-dioxolane unit was the addition of 2-(trichloromethyl)-1,3-dioxolane to vinyltrimethylsilane. (Eqn. 248)

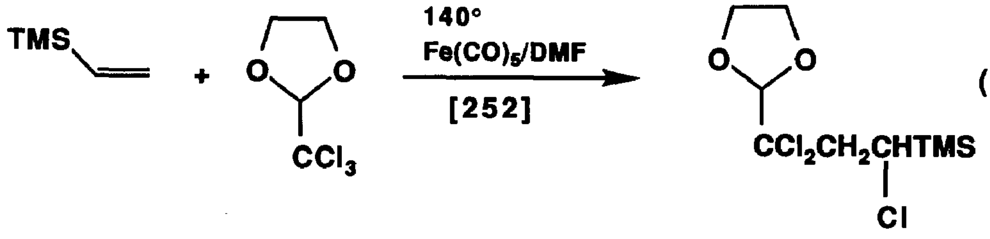


(246)

(R = H, $-CH_2CH_2TMS$)

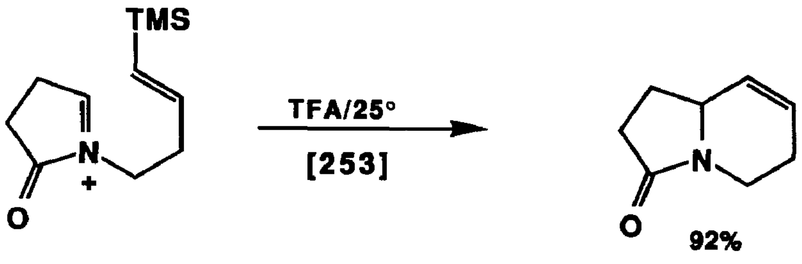


(247)

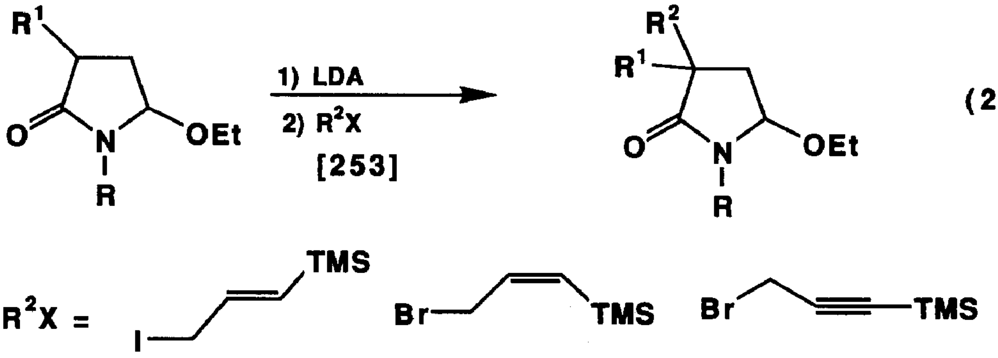


(248)

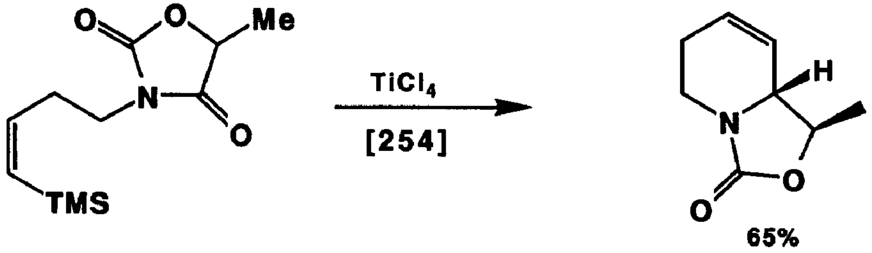
A number of examples of the intramolecular reaction of a vinylsilane with an iminium ion appeared adding to this very attractive entry into nitrogen heterocycles. This approach was used in the preparation of 6-azabicyclo[4.3.0]oct-2-ene-7-one as shown in Eqn. 249. The preparation of the starting materials is illustrated in Eqn. 250. An oxacarbamoyliminium ion vinylsilane cyclization lead ultimately to the synthesis of threo-2-(α-hydroxyalkyl)piperidines. (Eqn. 251) A key part of a synthesis of streptazolin was the intramolecular cyclization of **63**. (Eqn. 252)



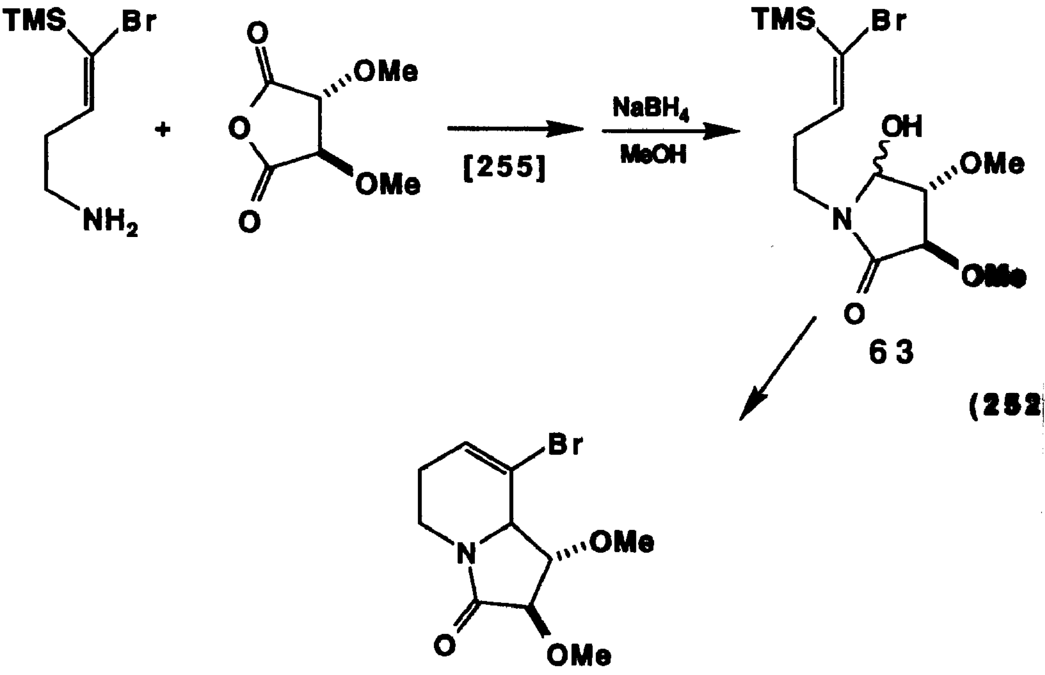
(249)


R^1
O
N
R
OEt
1) LDA
2) R^{2}X
[253]
R^2
R^1
O
N
R
OEt
R^{2}X =
I
TMS
Br
TMS
Br
TMS

(250)

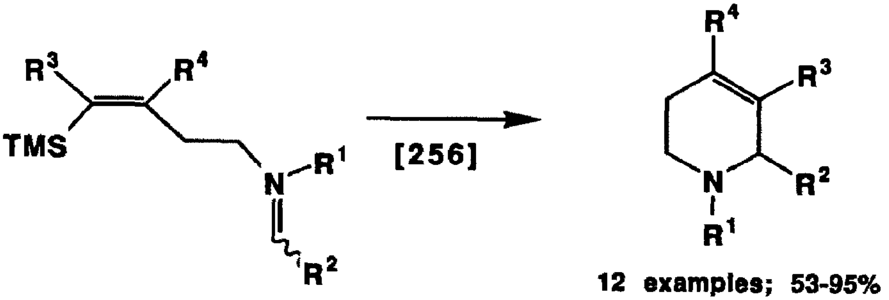

O
O
Me
N
O
TMS
TiCl$_4$
[254]
H
N
O
O
65%

(251)

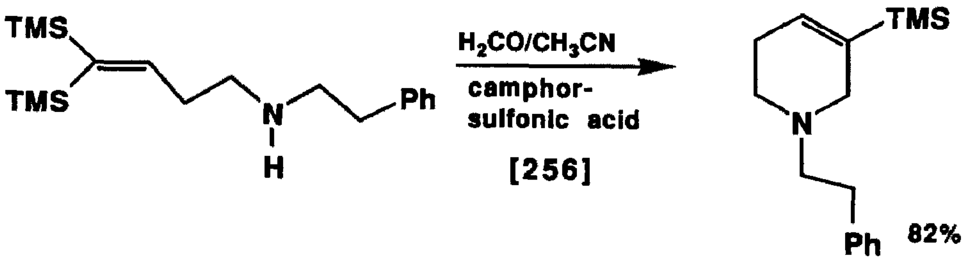

TMS
Br
NH$_2$
+
O
O
OMe
OMe
O
[255]
NaBH$_4$
MeOH
TMS
Br
OH
OMe
N
OMe
O
6 3
Br
N
OMe
O
OMe

(252)

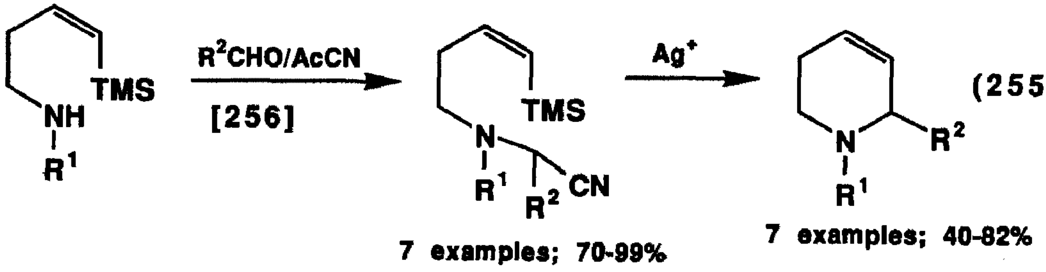
The intramolecular reaction of vinylsilanes with iminium and acyliminium ions provided routes to tetrahydropyridines and related heterocycles. (Eqns. 253-256)



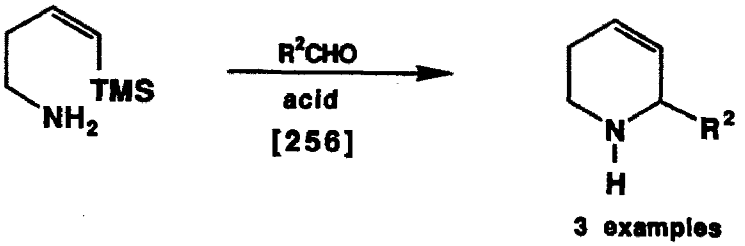
(253)



(254)

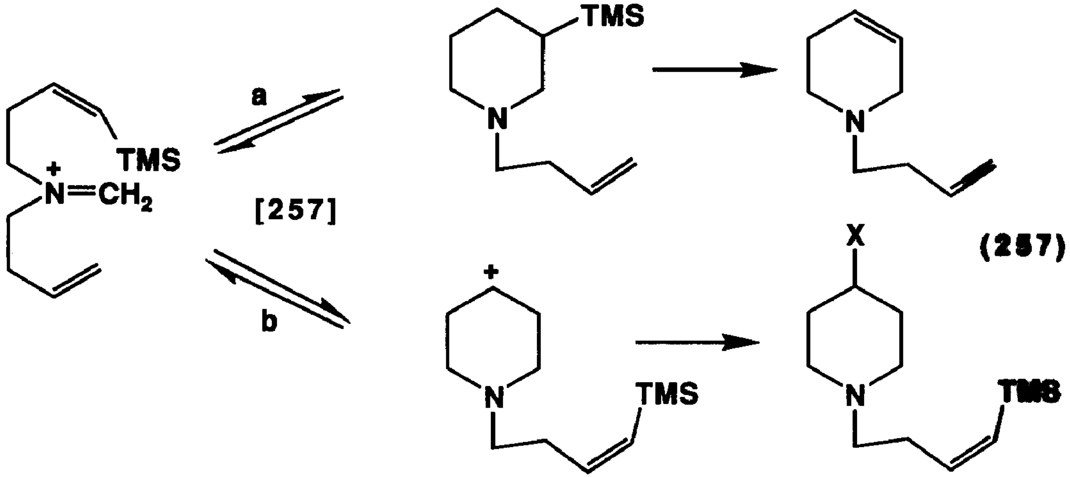


(255)



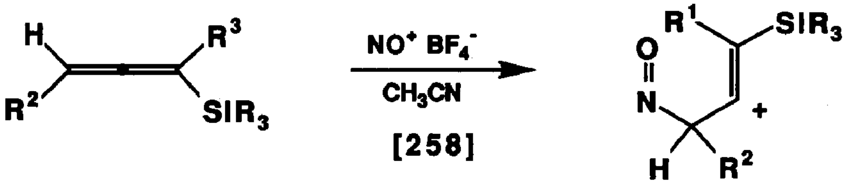
(256)

The effect of the medium and the nature of the rate-determining step in the vinylsilane-iminium salt cyclizations was studied. It was found that the cyclizations with non-silylated olefins depended on the medium, whereas the cyclizations with the vinylsilane group was independent of the medium. The mechanism shown in Eqn. 257 was proposed.



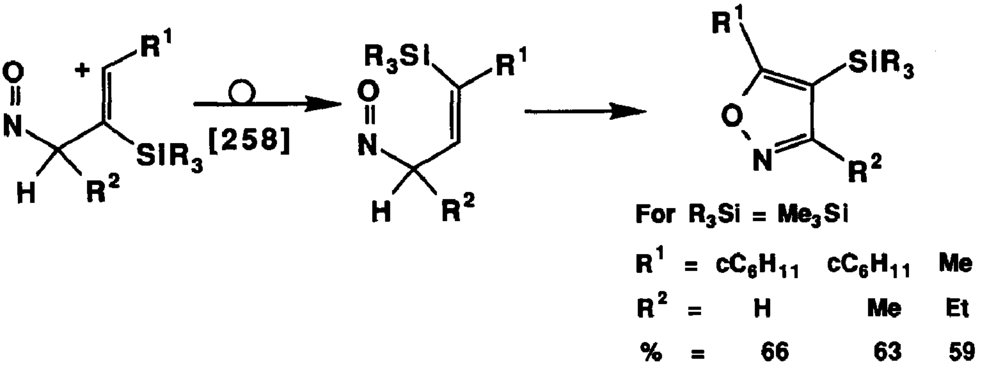
(257)

Allenylsilanes were reacted with nitrosyl tetrafluoroborate to give the interesting 4-trialkylsilylisoxazoles. (Eqn. 258) These systems will undergo protodesilylation in hot water to give the parent isoxazole. Bromodesilylation can also be carried out. (Eqn. 259)



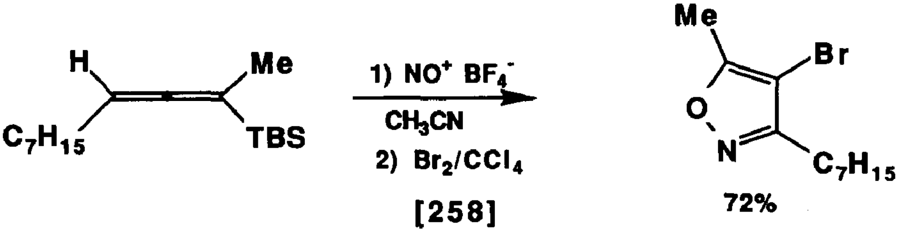
(258)

(continued on next page)



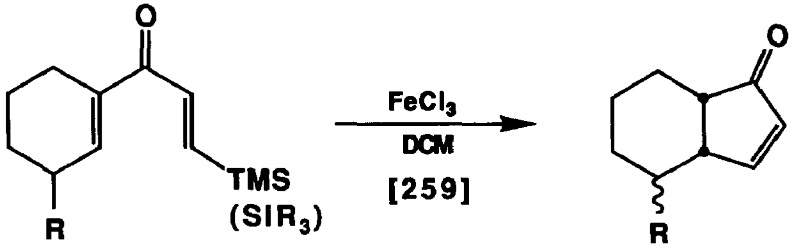
For $R_3Si = Me_3Si$

R^1	=	cC_6H_{11}	cC_6H_{11}	Me
R^2	=	H	Me	Et
%	=	66	63	59

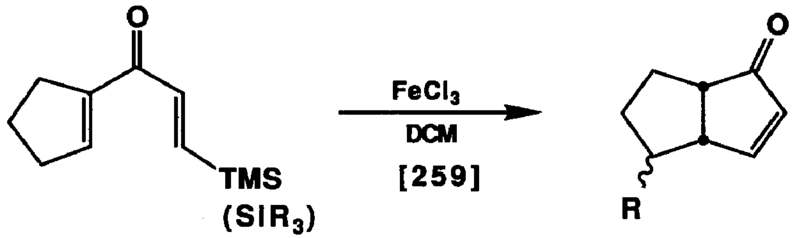


(259)

A full account of the silicon-directed Nazarov cyclization was presented. (Eqns. 260 and 261) The effect of increasing the steric bulk of the silyl group on the stereoselectivity proved beneficial for the six-membered ring, but not as good in the case of the five-membered ring.

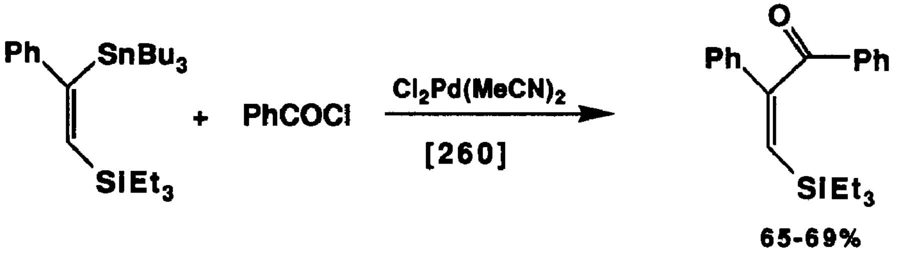


(260)

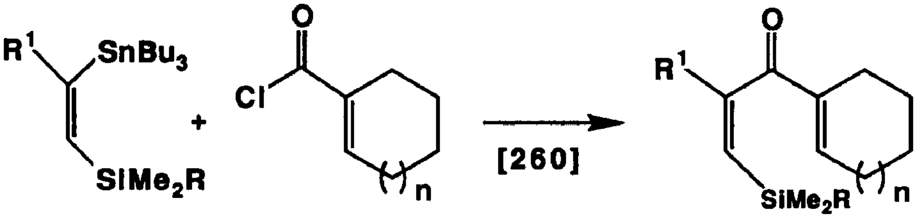


(261)

In related work advantage was taken of the β-stannylvinylsilanes produced by addition of the silicon-tin bond to acetylenes, which then react with acyl chlorides at tin bond. (Eqn. 262) This approach was used to produce the precursors to the silicon-directed Nazarov cyclization. (Eqn. 263) When the silicon group is large the Nazarov reaction occurs without the silicon directive effect and with retention of the silyl group. (Eqn. 264 and 265)



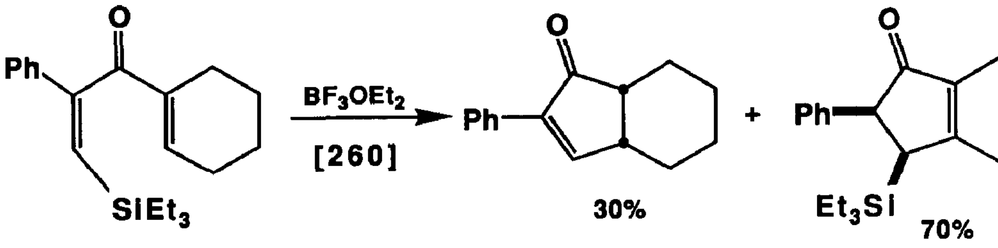
(262)



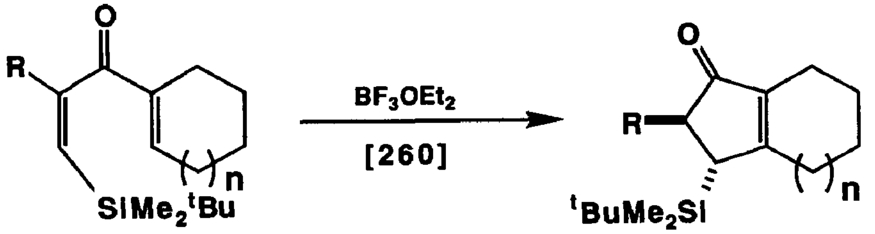
(263)

R^1 = Bu, Cl(CH$_2$)$_3$; R = ^{t}Bu, ^{n}Bu; n = 0, 1

58-87%



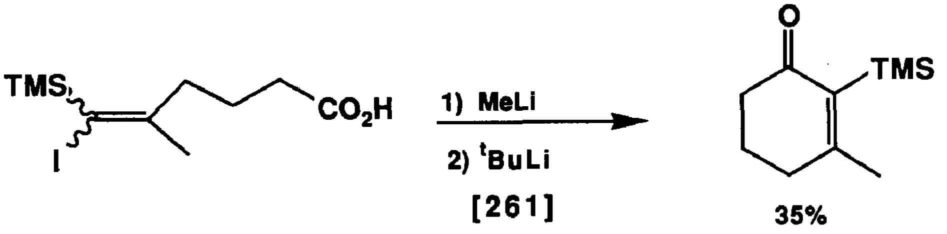
(264)



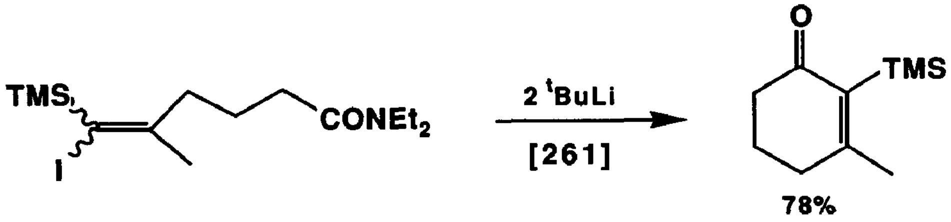
(265)

R = Bu; n = 0 gives 69%
R = $Cl(CH_2)_3$; n = 1 gives 80%

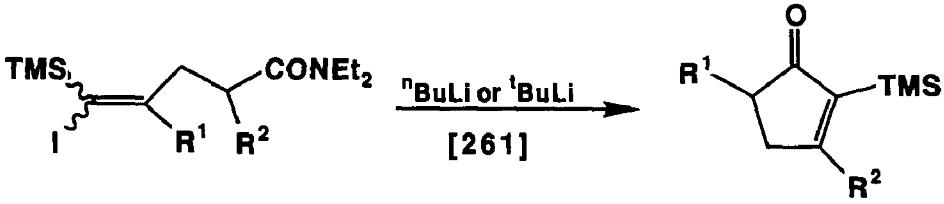
The cycliacylation of α-lithiovinyltrimethylsilanes of unsaturated acids (Eqn. 266) or amides (Eqns. 267 and 268) result in the formation of α-trimethylsilylcyclohexenones or cyclopentenones.



(266)



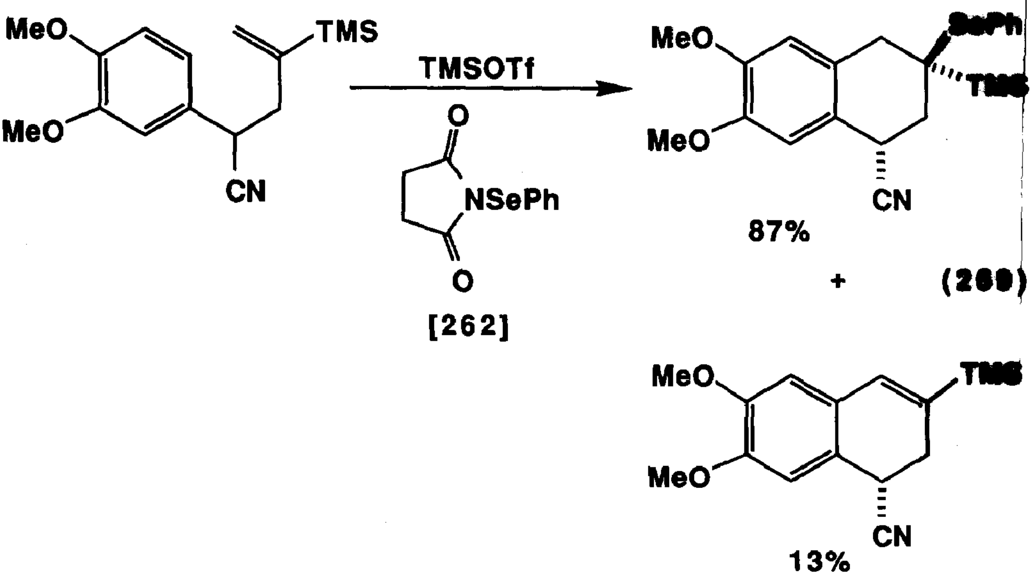
(267)



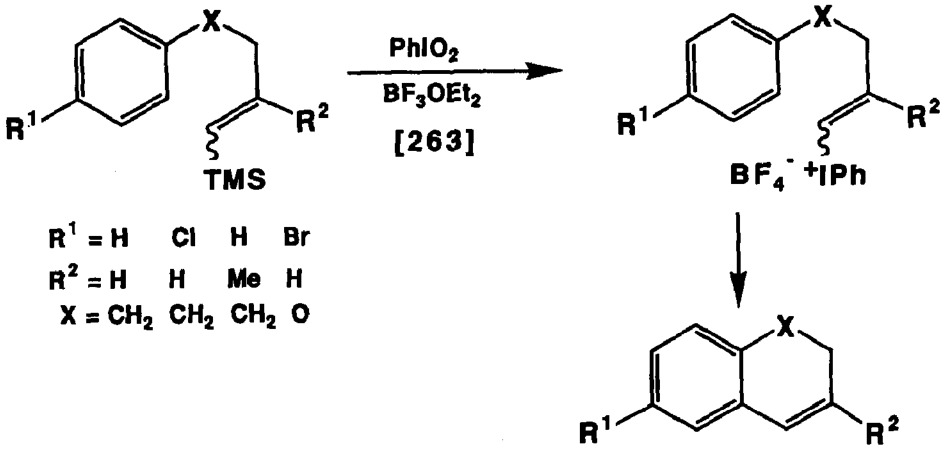
(268)

(R^1 = H, Ph, Me; R^2 = H: R^1 = H, R^2 = Ph; 53-83%

The formation of episelenonium ions of aryl substituted vinylsilanes can result in cyclizations. (Eqn. 269) The same sort of reaction can occur with phenyliodonium dioxide and boron trifluoride etherate, which occurs *via* the phenyliodonium tetrafluoroborate. (Eqn. 270)



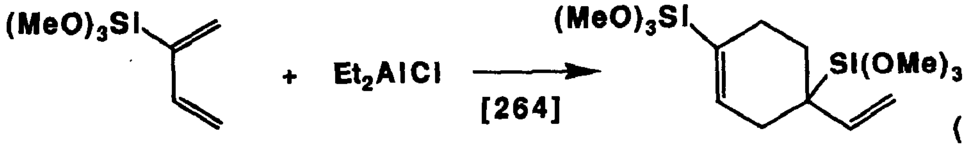
(269)



R^1 =	H	Cl	H	Br
R^2 =	H	H	Me	H
X =	CH_2	CH_2	CH_2	O

(270)

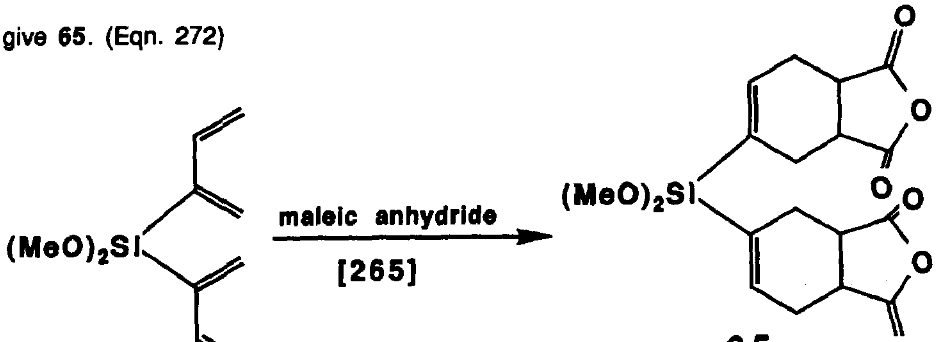
The Diels-Alder cyclization of 2-trimethoxysilyl-1,3-butadiene, catalyzed by diethylaluminum chloride, gives **64**. (Eqn. 271) These systems are useful crosslinking agents.



64

(271)

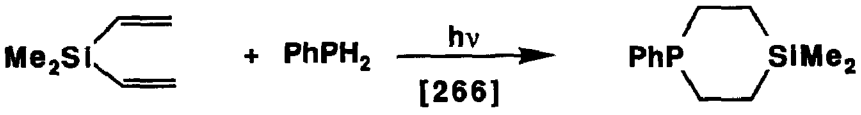
Bis[2-(1,3-butadienyl)]dimethoxysilane was reacted with maleic anhydride to give **65**. (Eqn. 272)



65

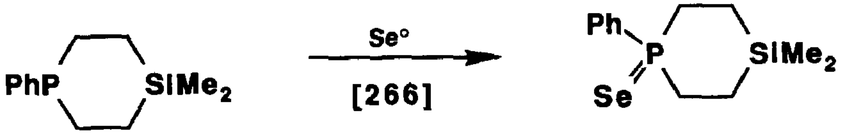
(272)

The reaction of divinyldimethylsilane with phenylphosphine and light produces the 4-phospha-1-silacyclohexane **66**. (Eqn. 273) This material reacts with elemental selenium to give the phosphine selenide. (Eqn. 274)



66 10.6%

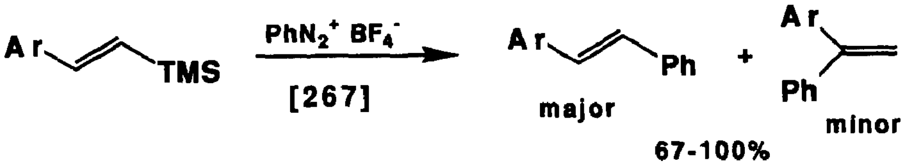
(273)



100%

(274)

Arenediazonium salts will bring about the aryldesilylation of vinylsilanes resulting in the formation of styrenes from vinylsilanes. (Eqns. 275 and 276)



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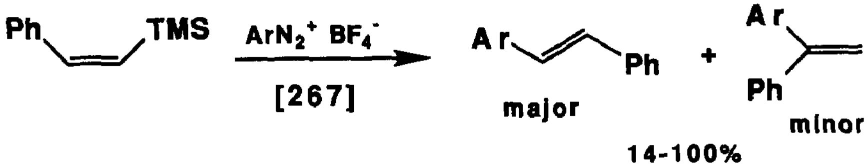
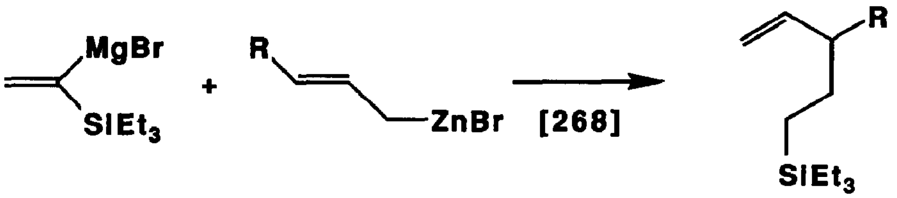


(276)

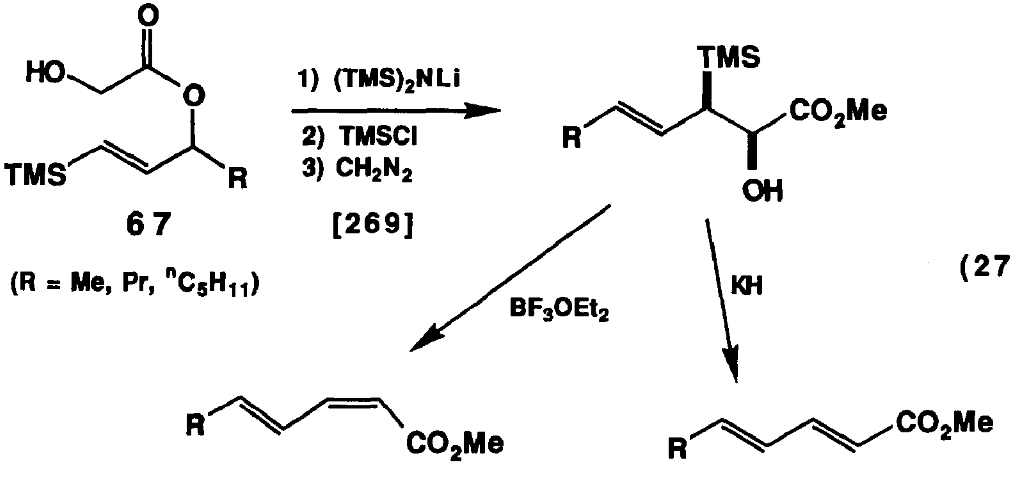
α-Triethylsilylvinylmagnesium bromide reacts with allylzinc bromides to give 3-substituted-5-pentenylsilanes. (Eqn. 277)



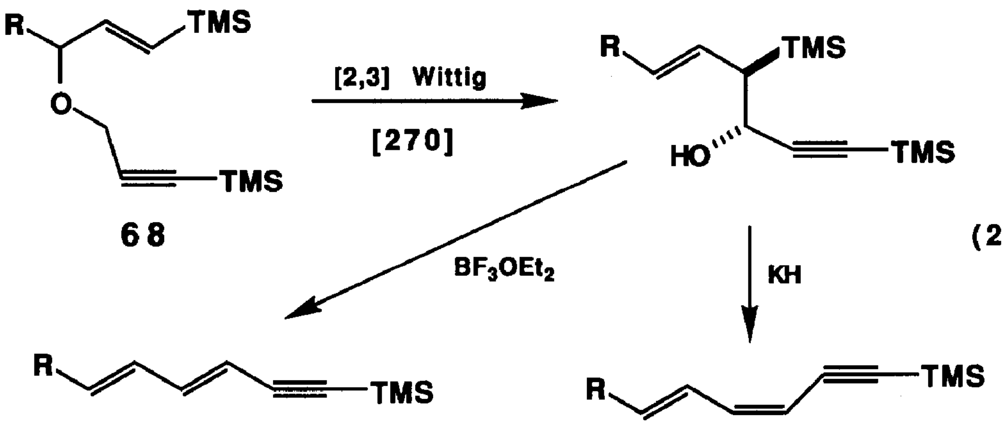
(277)

R = H (90%)
R = Me (83%)

The vinylsilane **67** was employed in the (2E,4E) and (2Z,4E) 2,4-alkyldienoates *via* the ester Claisen rearrangement. (Eqn. 278) A [2,3] Wittig rearrangement-Peterson olefination sequence was employed to produce (3E,5E) and (3Z,5E) dienynes from the same intermediate β-hydroxysilane. (Eqn. 279) Since the erythro:threo ratio varied depending on the R group of the starting material **68** the same elimination conditions did not give the same dienyne in all cases.



(278)

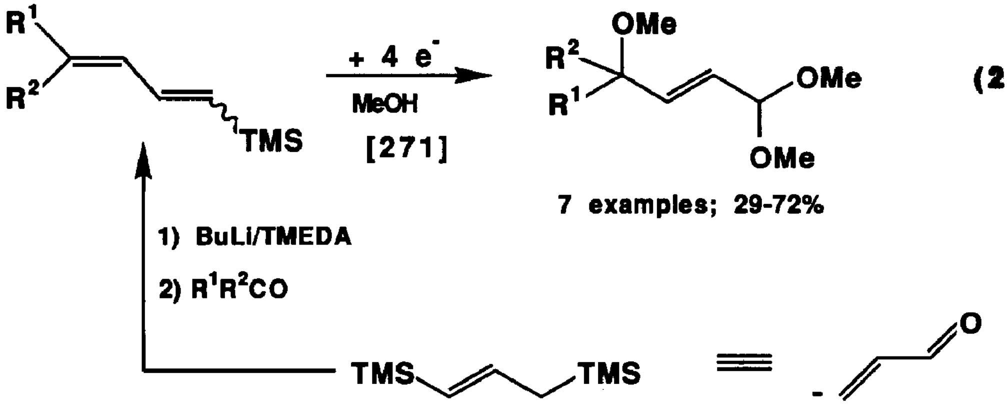


(279)

R	erythro	threo
H	97	3
Me	4	96
Et	3	97
Bu	11	89

(stereochemistry of β-hydroxysilane)

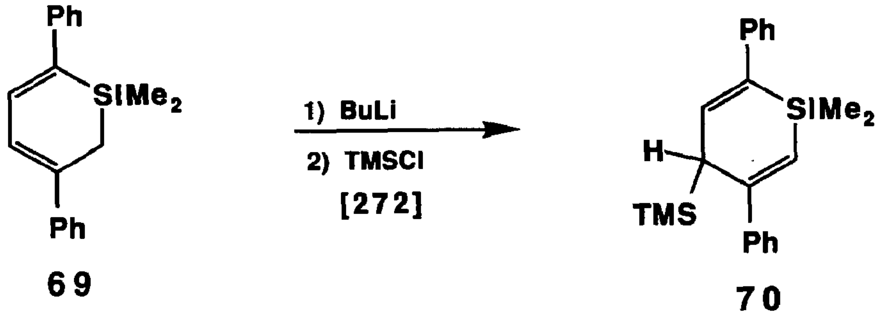
The electrochemical oxidation of 1-trimethylsilyl-1,3-dienes in methanol gives γ-methoxy-α,β-unsaturated dimethylacetals in good yields. (Eqn. 280) Because the starting silylated dienes come from 1,3-bis(trimethylsilyl)propene, the authors propose this reagent to be the synthetic equivalent of a β-acrolyl anion.



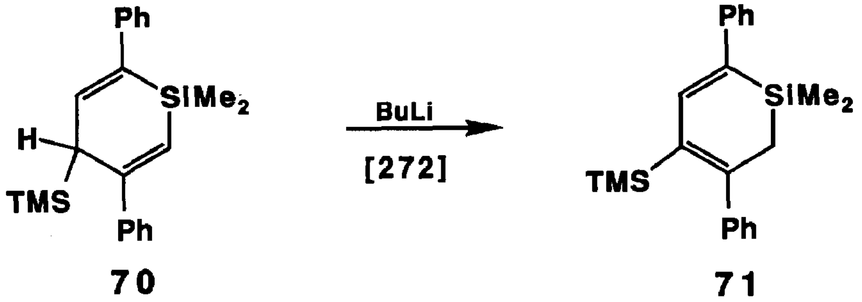
(280)

7 examples; 29-72%

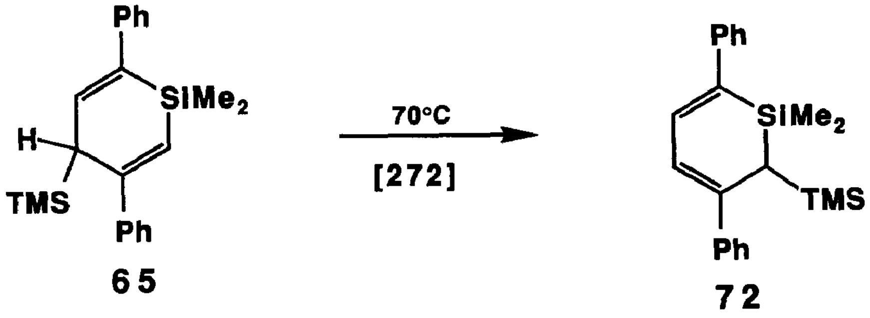
Lithiation-trimethylsilylation of **69** gives **70**. (Eqn. 281) Lithiation of **70** leads to double bond isomerization producing the conjugated diene **71** (Eqn. 282). Thermolysis of **70**, on the other hand, leads to migration of the trimethylsilyl group and **72**. (Eqn. 283) Some of the iron complexes of the conjugated dienes were studied.



(281)

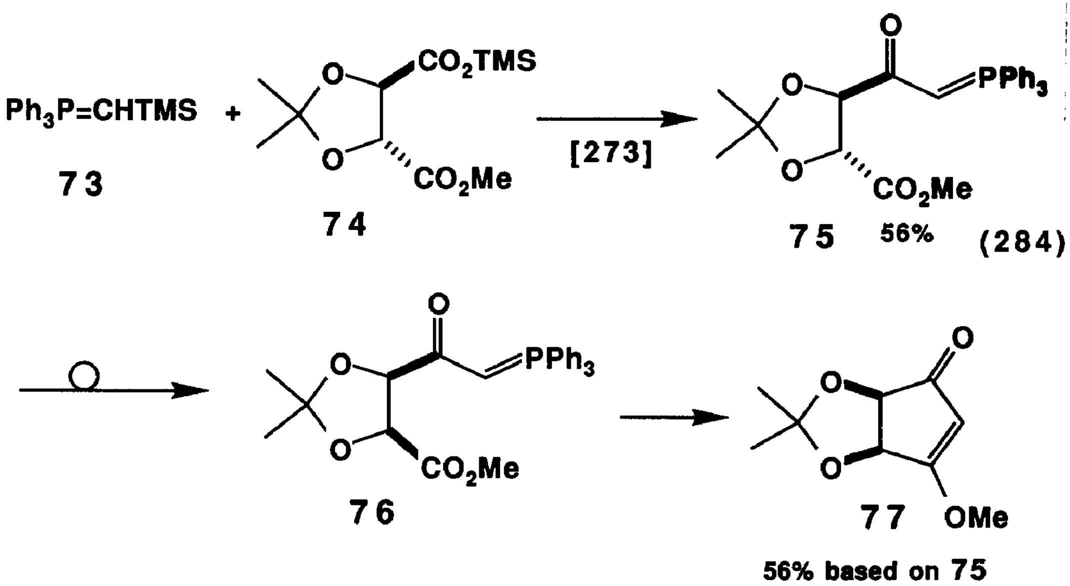


(282)



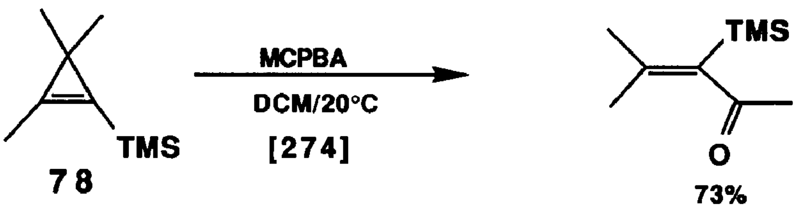
(283)

In an interesting reaction, the Wittig reagent **73** was reacted with the trimethylsilylated acid **74** to give the stabilized Wittig reagent **75**, which rearranges to the cis isomer **76** and ultimately gives cyclopentenone **77**. (Eqn. 284)

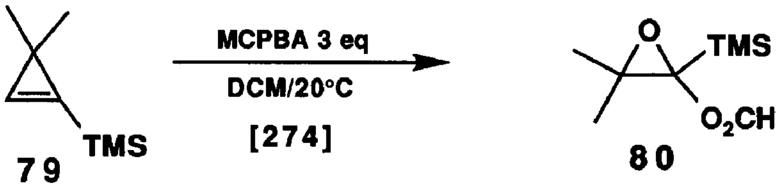


(284)

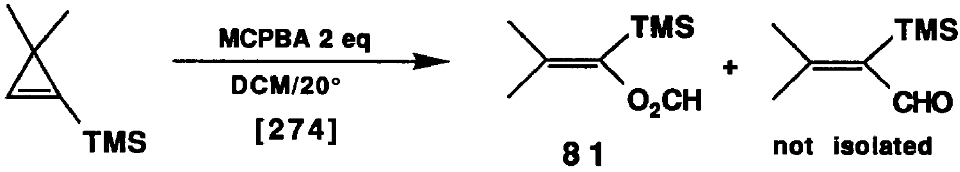
Oxidation of the 1-trimethylsilylcyclopropene **78** produces α-trimethylsilyl mesityl oxide. (Eqn. 285) Oxidation of **79** with 3 equivalents of meta-chloroperbenzoic acid gives epoxy formate **80**, whereas with 2 equivalents of the oxidizing agent vinyl formate **81** is formed. (Eqns. 286 and 287)



(285)

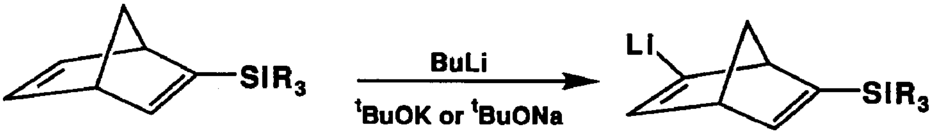


(286)



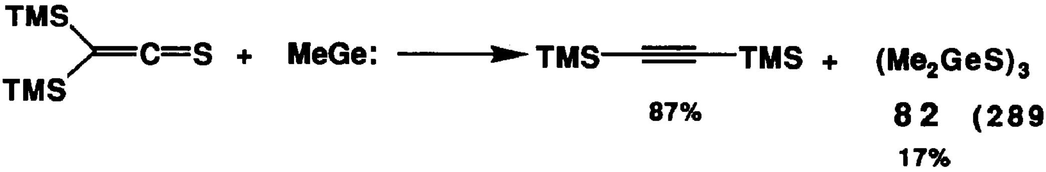
(287)

Lithiation of 2-(trimethylsilyl)norbornadiene occurs to place the lithium at the 5 position. (Eqn. 288)



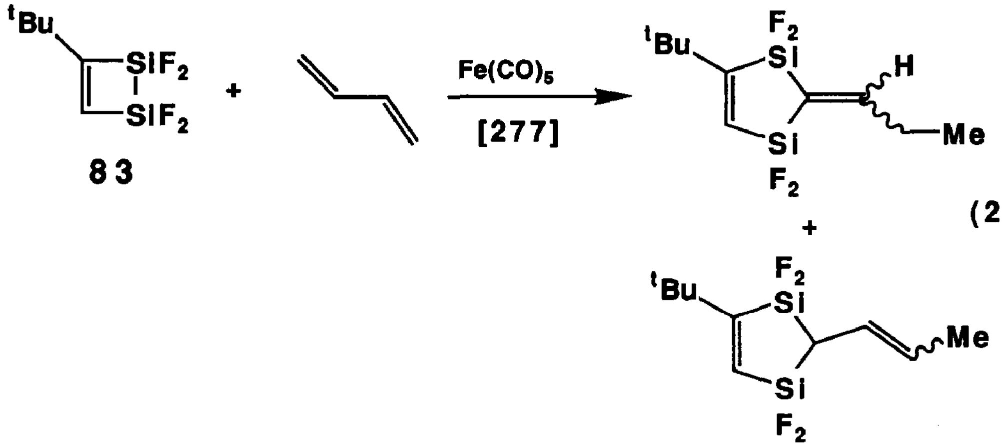
(288)

Bis(trimethylsilyl)thioketene was shown to react with dimethylgermylene to give bis(trimethylsilyl)acetylene and **82**. (Eqn. 289)



(289)

The reactions of 1-tert-butyl-3,3,4,4-tetrafluoro-3,4-disilacylobutene **83** with 1,3-butadienes was reported. Examples are shown in Eqns. 290 and 291. Disilacyclohexadiene **84** reacts with iron pentacarbonyl and light to give reduction of the external vinyl group. (Eqn. 292) Treatment of **85** with iron pentacarbonyl gives **86**. (Eqn. 293)



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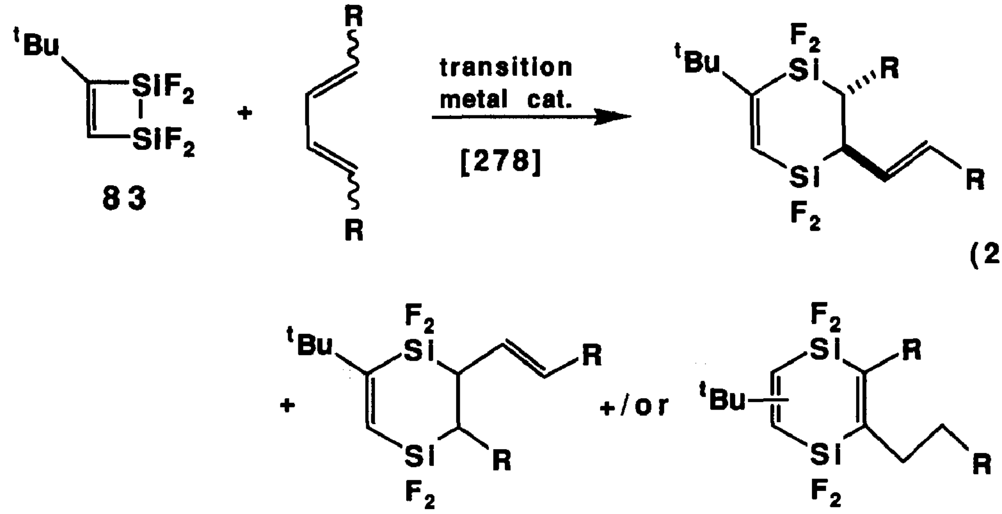
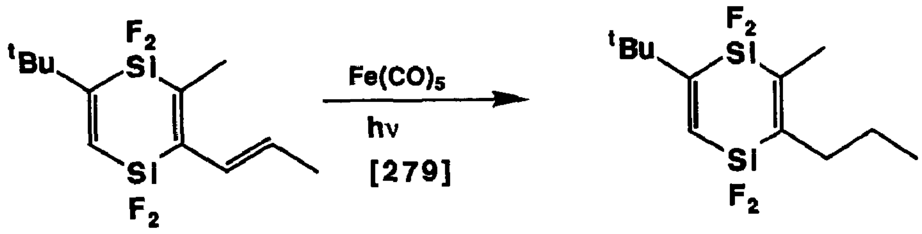
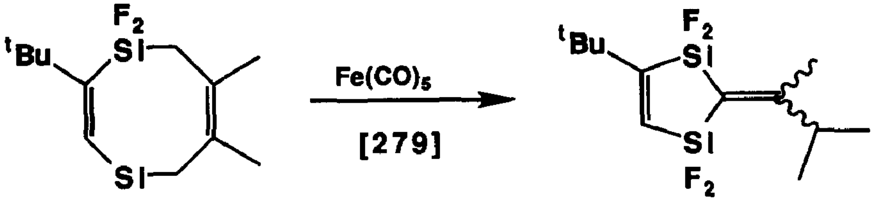


(291)



84

(292)



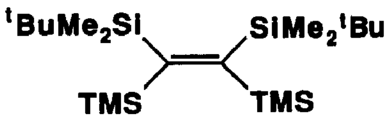
85

86

(293)

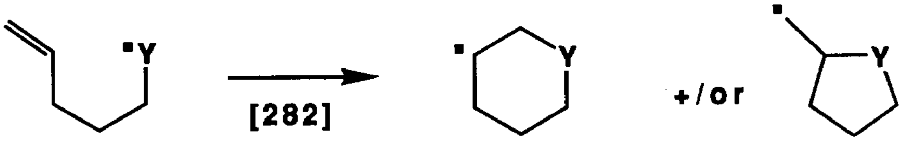
C. Vinylsilanes--Other Studies

The infrared spectra of divinylsilane, ethynylsilane and their fluorinated derivatives were studied. [280] The bis(trimethylsilyl)-bis(tert-butyldimethylsilyl)-ethylene **87** was prepared and its structure determined by x-ray crystallography. It shows a large twist angle of 50.2° between the two tert-butyldimethylsilyl groups and a dihedral angle of 47.1° between the tert-butyldimethylsilyl and trimethylsilyl groups. The C=C length is 1.369 Å and the C-Si(Me$_2$tBu) length is 1.930 Å. It showed no isomerization thermally nor photolytically. [281]



87

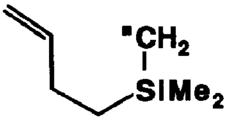
The radical **89** was part of a general study of the cyclization mode of radicals of the general structure **88**. (Eqn. 294)



(294)

88

Y = CH_2, Me_2Si



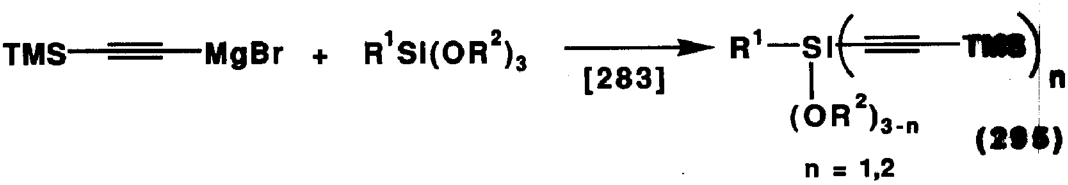
also studied

89

VIII. ETHYNYLSILANES

A. Preparation

Alkyltrialkoxysilanes were reacted with trimethylsilylethynylmagnesium bromide to give mixtures of alkylalkoxyethynylsilanes. (Eqn. 295)



$$\text{TMS}{-}{\equiv}{-}\text{MgBr} + R^1Si(OR^2)_3 \xrightarrow[\text{[283]}]{} R^1{-}Si\left({\equiv}{-}\text{TMS}\right)_n(OR^2)_{3-n} \qquad n = 1,2$$

(295)

Dimetalated acetylene was reacted with dimethyldichlorosilane to give oligomers. (Eqn. 296) The reaction with dimethylchlorosilane gives the expected disilyl acetylene (Eqn. 297), which upon treatment with carbon tetrachloride under free radical conditions gave the bis(dimethylchlorosilyl)acetylene (Eqn. 298) and the mixed chlorohydridosilyl acetylene. (Eqn. 299) These were converted to the dimethoxy derivative. (Eqn. 300) These acetylenic silanes were reacted in Diels-Alder cyclizations. (Eqn. 301)

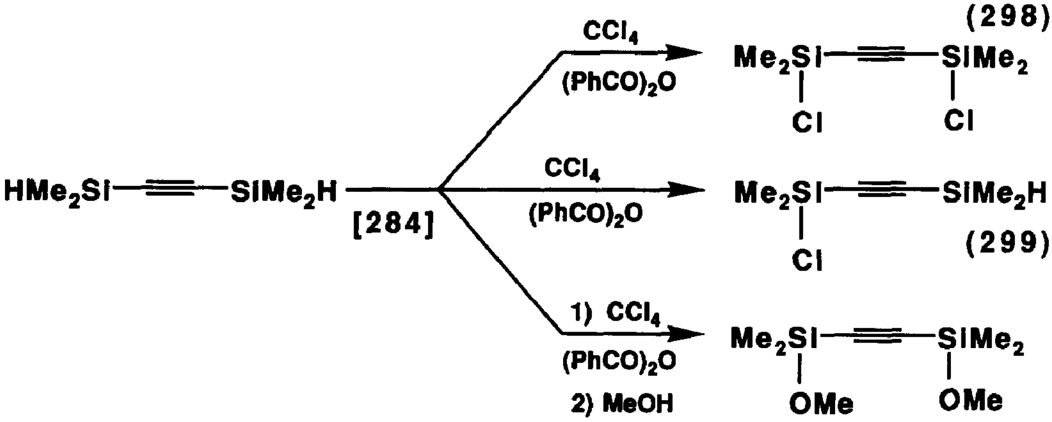
$$\mathrm{M{-}C{\equiv}C{-}M} \xrightarrow[\text{[284]}]{\mathrm{Me_2SiCl_2}} \text{oligomers} \qquad (296)$$

(M = Li, MgBr)

$$\mathrm{M{-}C{\equiv}C{-}M} \xrightarrow[\text{[284]}]{\mathrm{Me_2SiHCl}} \mathrm{HMe_2Si{-}C{\equiv}C{-}SiMe_2H} \qquad (297)$$

(M = Li, MgBr)

(298)



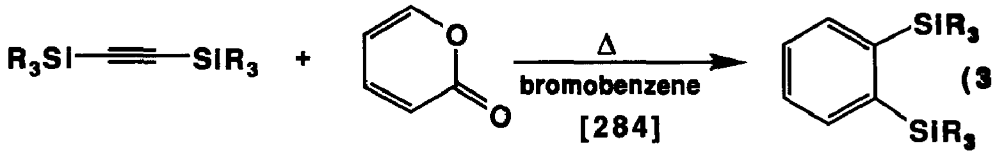
$$\mathrm{HMe_2Si{-}C{\equiv}C{-}SiMe_2H} \xrightarrow[\text{[284]}]{\mathrm{CCl_4},\ (PhCO)_2O} \mathrm{Me_2Si(Cl){-}C{\equiv}C{-}SiMe_2(Cl)}$$

$$\mathrm{HMe_2Si{-}C{\equiv}C{-}SiMe_2H} \xrightarrow[\text{[284]}]{\mathrm{CCl_4},\ (PhCO)_2O} \mathrm{Me_2Si(Cl){-}C{\equiv}C{-}SiMe_2H}$$

(299)

$$\mathrm{HMe_2Si{-}C{\equiv}C{-}SiMe_2H} \xrightarrow[\text{[284]}]{\text{1) } \mathrm{CCl_4},\ (PhCO)_2O\text{; 2) MeOH}} \mathrm{Me_2Si(OMe){-}C{\equiv}C{-}SiMe_2(OMe)}$$

(300)



(301)

3,3,3-Trifluoro-1-propynyllithium was prepared and trimethylsilylated to give the corresponding ethynylsilane in good yield according to Eqn. 302.

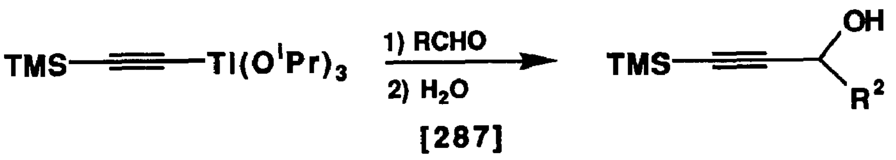
(302)

Bis(trimethylsilyl)butadiyne was reacted with alkyllithium reagents, which brings about a metal-metal exchange. Methylation then gives the trimethylsilyl-1,3-pentadiyne. Other examples were reported as well. (Eqn. 303)

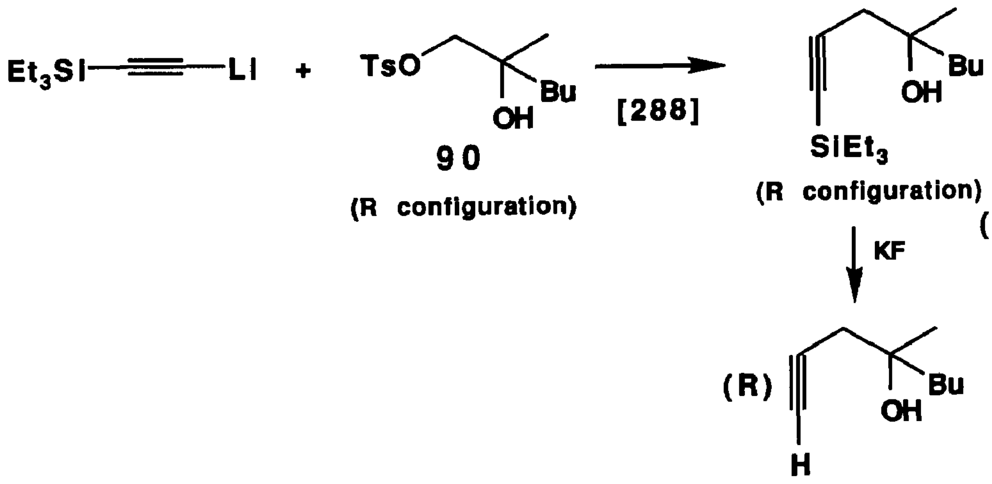
$$\mathrm{TMS}-\!\equiv\!-\!\equiv\!-\mathrm{R}^1 \xrightarrow[\text{2) MeI}]{\text{1) }\mathrm{R}^2\mathrm{Li}} \mathrm{Me}-\!\equiv\!-\!\equiv\!-\mathrm{R}^1 \qquad (303)$$

[286] R^1 = Ph, 1-Np, TMS)

Lithiation of trimethylsilylacetylene followed by conversion of the ethynyllithium reagent to an ethynyltitanium reagent allows for the reaction with aldehydes in an improved manner to give the silylated propargyl alcohols. (Eqn. 304) Lithiotriethylsilylacetylene reacts with the monotosylate **90** to give substitution. The triethylsilyl group can be protodesilylated readily. (Eqn. 305)



(304)



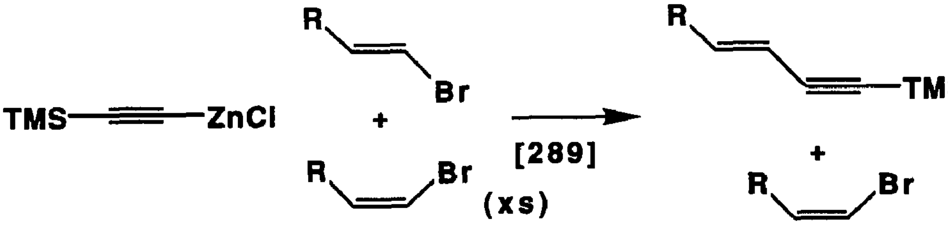
9 0

(R configuration)

(R configuration)

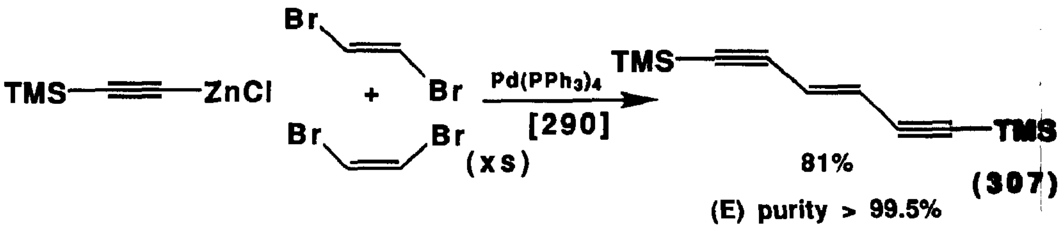
(305)

(E) Vinylbromides selectively react with trimethylsilylethynylzinc chloride to give the trimethylsilylated enyne in good yield. Due to the selectivity of the reaction for the (E) isomer, mixtures of (E) and (Z) vinylbromides can be employed. The isomeric purity of the (E) enyne is high. (Eqn. 306) This approach was used to prepare bis-(trimethylsilyl)endiynes according to Eqn. 307.



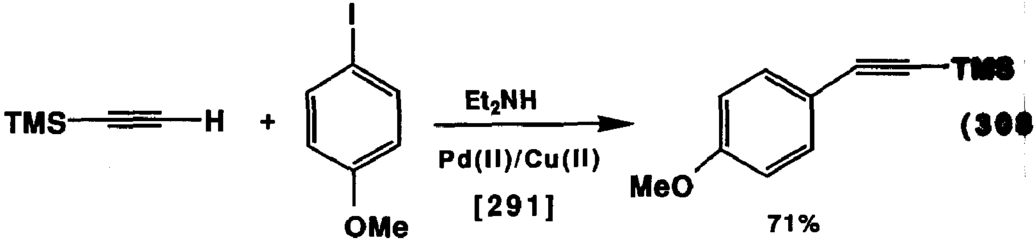
(306)

3 examples; 75-80.9%
(E) purity > 95.5%

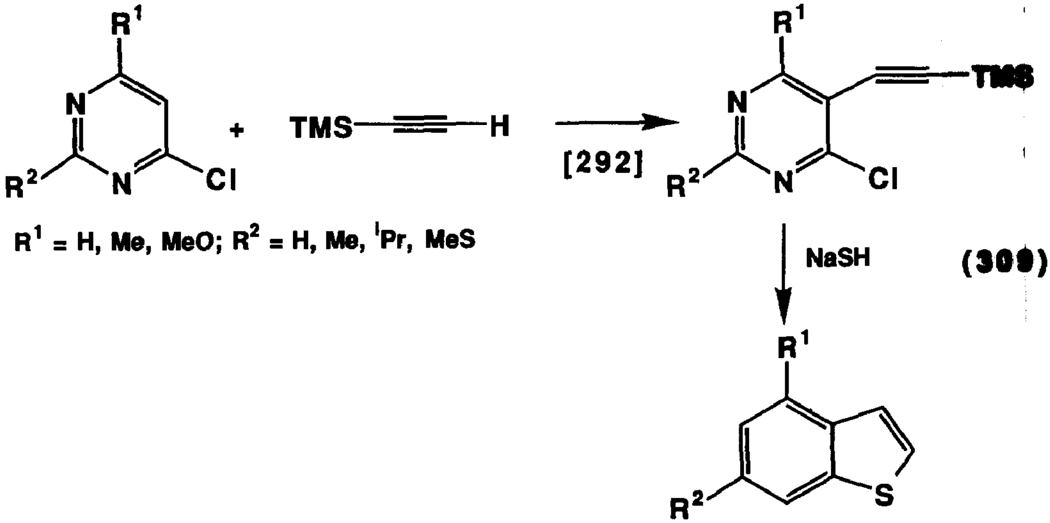


(307)

The cross coupling of aryl iodides with trimethylsilylacetylene results in aryl-trimethylsilyl acetylenes. (Eqn. 308) A second example of this was elaborated to prepare thienopyridines. (Eqn. 309)

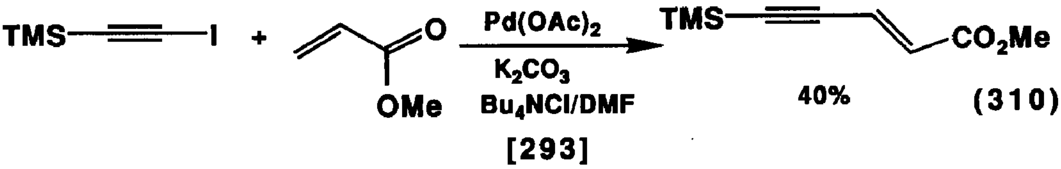


(308)



(309)

Methyl acrylate can be reacted with trimethylsilyliodoacetylene with palladium(II) catalysis to give the trimethylsilylated enynyl ester. (Eqn. 310)

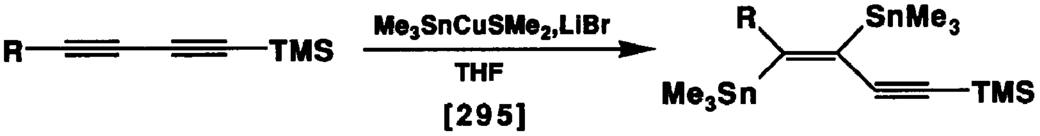


(310)

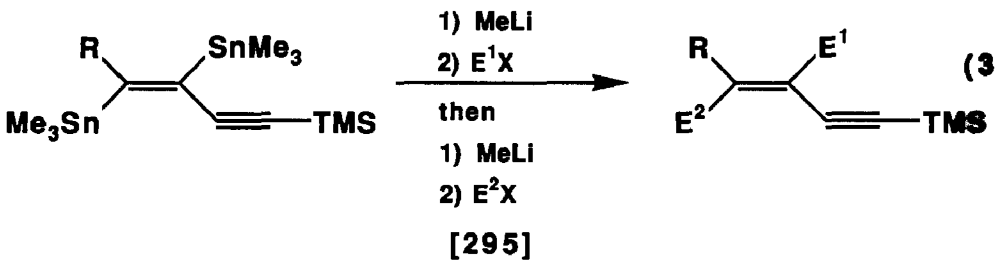
Trimethylsilylacetylene reacts with diethylacetoxychlorotin to give direct stannylation of the ethynyl group. (Eqn. 314)

$$\mathrm{TMS{-}{\equiv}{-}H} + \mathrm{Et_2Sn(OAc)Cl} \xrightarrow[{[294]}]{} \mathrm{TMS{-}{\equiv}{-}SnOAcEt_2} \qquad (311)$$

Trimethylsilyl-1,3-alkadiynes react with trimethylstannylcopper(I) species to give bis trimethylstannylation of the non-silylated triple bond. (Eqn. 312) These interesting materials can be subjected to tin-lithium exchange and the resulting lithium reagent reacted with electrophiles to give highly substituted enynes. (Eqn. 313)



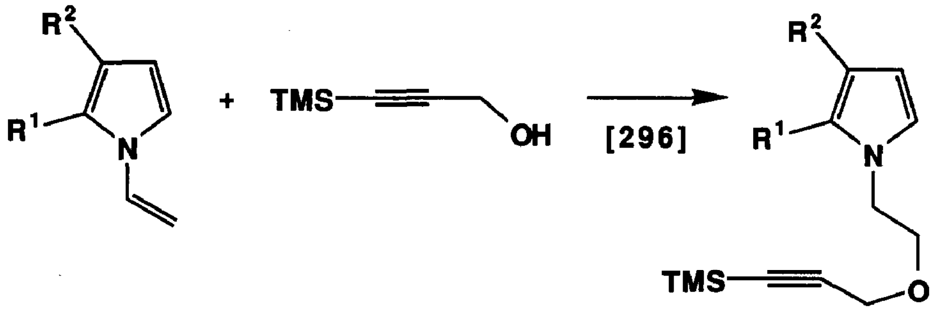
(312)



(313)

E^{1}X	MeI	EtI	C_3H_5Br	MeOH	MeOH	MeI	BuI	MeI
E^{2}X	MeOH	MeOH	MeOH	MeI	MeI	MeI	MeI	BuI
%	94	87	92	93	90	90	88	81

Trimethylsilylpropargyl alcohol was reacted with vinylpyrroles to give **91**. (Eqn. 314)

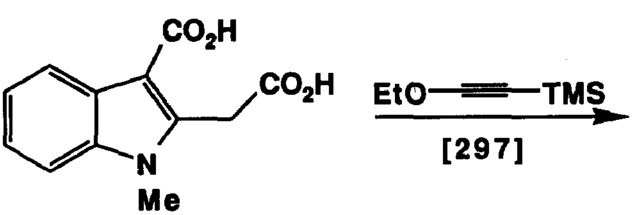


(314)

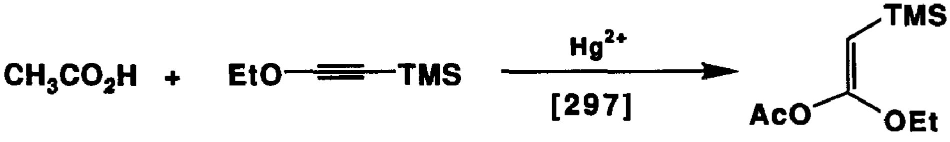
91

B. Ethynylsilanes-Reactions

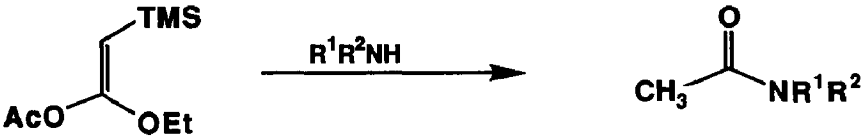
Ethoxytrimethylsilylacetylene was shown to be an excellent dehydration reagent in the formation of acid anhydrides, esters, amides, lactones, and lactams. The silicon product is ethyl trimethylsilylacetate. (Eqns. 315, 316, and 317)



(315)

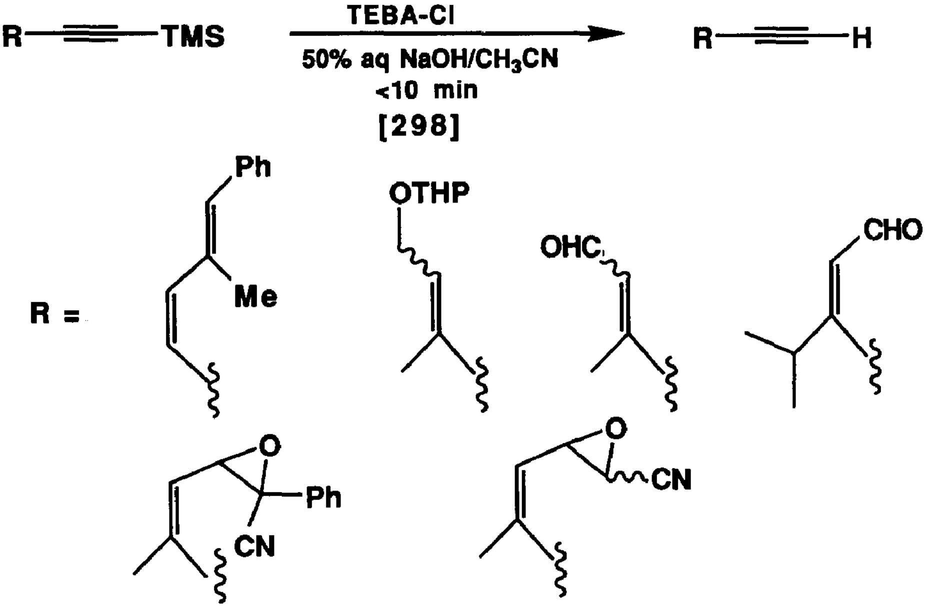


(316)



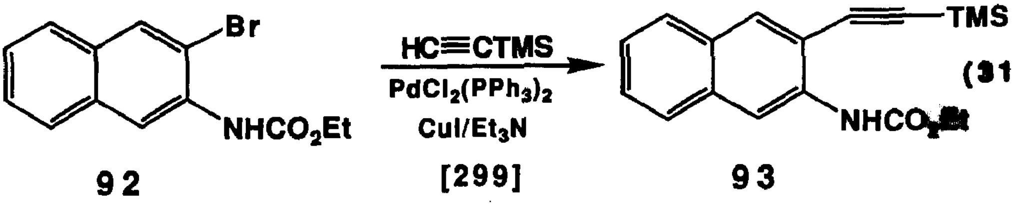
(317)

1-Trimethylsilylacetylenes were shown to be conveniently converted to the parent acetylene with triethylbenzylammonium chloride in aqueous base. (Eqn. 318)

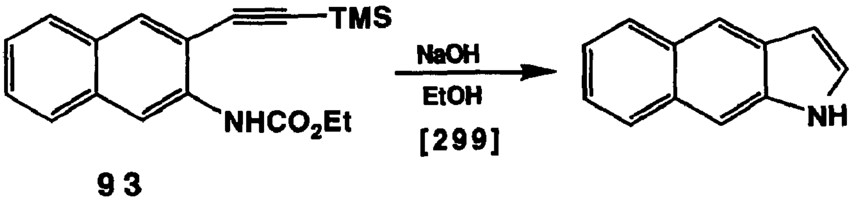


(318)

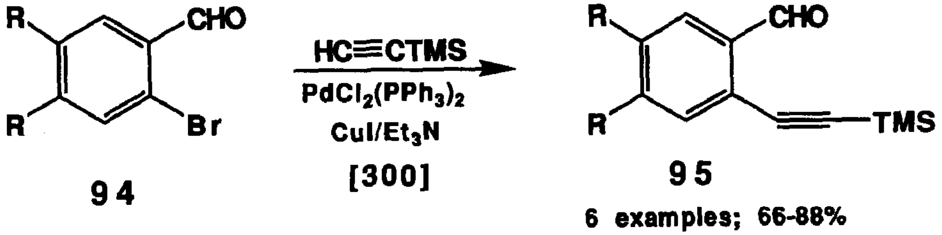
Trimethylsilylacetylene was coupled with bromide **92** to give **93**, which was protodesilylated. (Eqns. 319 and 320) In a similar vein **94** was converted to **95**. (Eqns. 321 and 322)



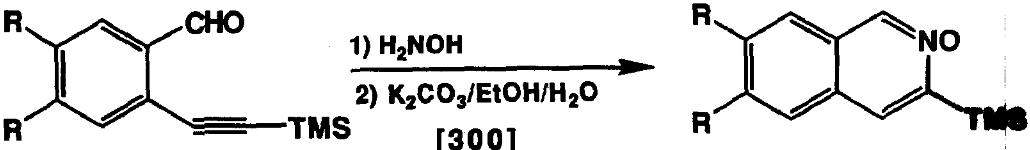
(319)



(320)



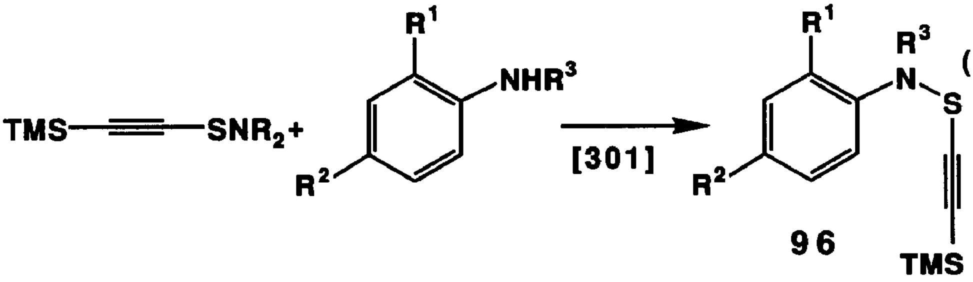
(321)



(322)

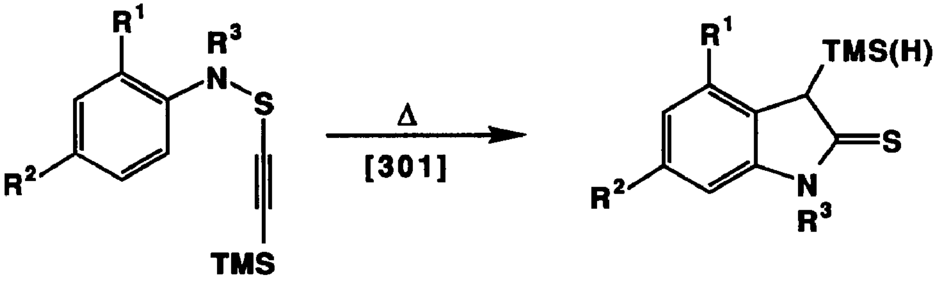
The reaction of trimethylsilylethynyllithium (or magnesium bromide) with diethylaminosulfur chloride leads to alkynylsulfenamides. (Eqn. 323) These are reacted with substituted anilines to give **96**, which thermally rearrange to indoine-2-thiones. (Eqns. 324 and 325)

$$\mathrm{TMS{-}{\equiv}{-}Li(MgX)} + \mathrm{R_2NSCl} \xrightarrow[\text{[301]}]{} \mathrm{TMS{-}{\equiv}{-}SNR_2} \qquad (323)$$



96

(324)

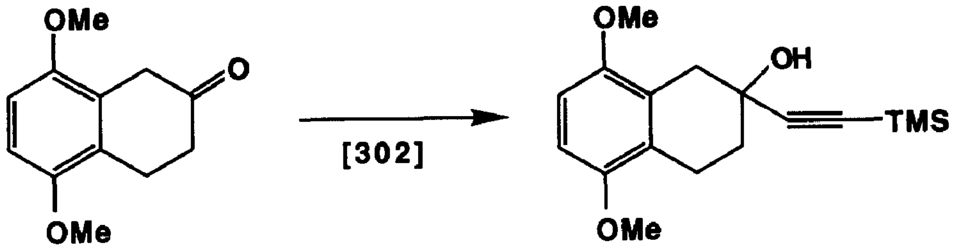


(325)

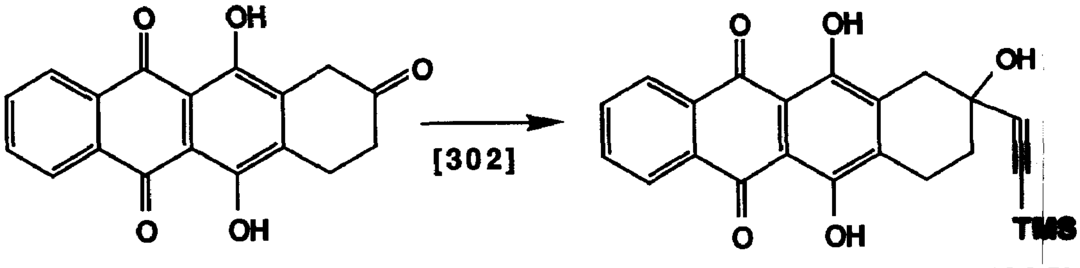
Trimethylsilylethynyl cerium reagents **97** and **98** were shown to add nicely to carbonyls of systems that ordinarily undergo facile enolization. (Eqns. 326 and 327)

$$\mathrm{TMS{-}{\equiv}{-}CeCl_2} \qquad \mathrm{(TMS{-}{\equiv}{-})_3Ce}$$

97 **98**

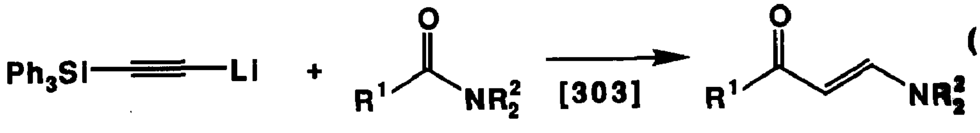


(326)



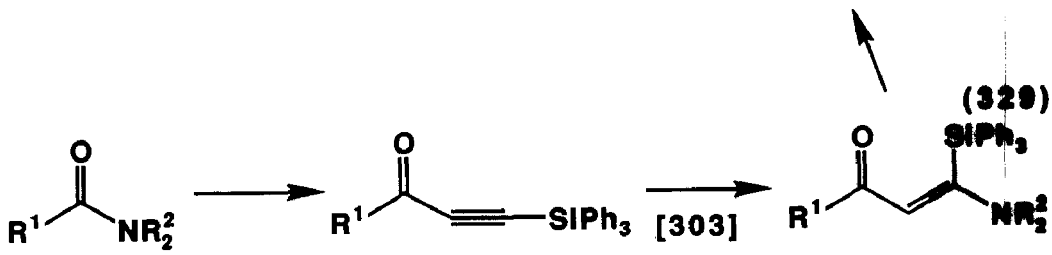
(327)

Triphenylsilylethynyllithium reacts with tertiary amides leading eventually to β-amino-α,β-unsaturated enones. (Eqn. 328) The reaction apparently occurs *via* displacement of the amide followed by addition of the displaced amine to the ethynyl ketone and protodesilylation. (Eqns. 329 and 330)

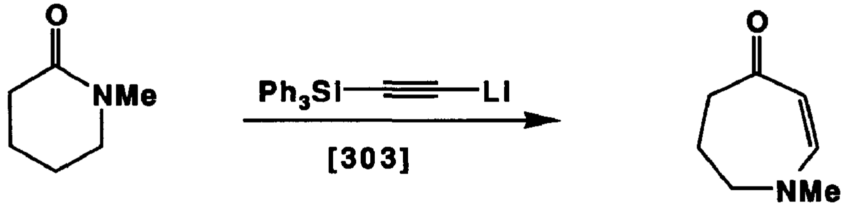


(328)

8 examples; 28-82%



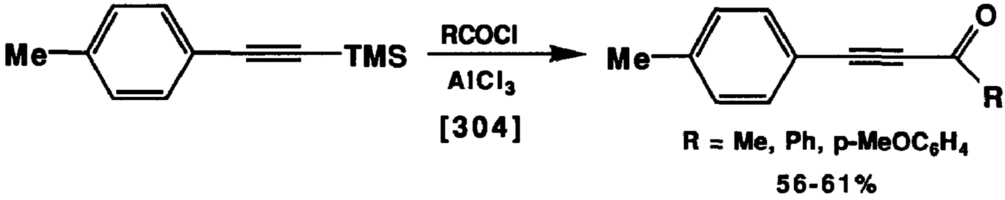
(329)

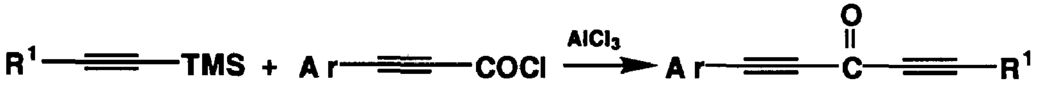


(330)

The reaction of ethynylsilanes with electrophiles, which results in the electrophilic replacement of the silyl group, was a popular synthetic transformation. The acylation of ethynylsilanes was reported by yet another group. (Eqn. 331) This was applied nicely to the ethynylation of ethynyl ketones to form diethynyl ketones. (Eqn. 332) The trimethylsilylated diethynyl ketones can be prepared according to Eqn. 333.

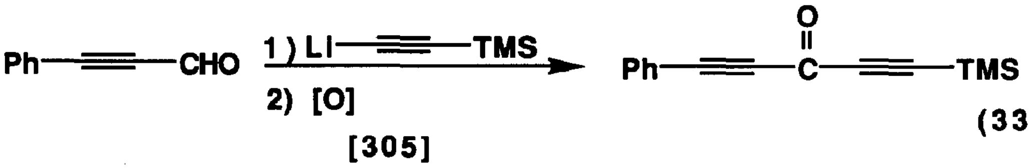
(331)





$$R^1—\equiv—TMS + Ar—\equiv—COCl \xrightarrow[{[305]}]{AlCl_3} Ar—\equiv—\overset{O}{\overset{\|}{C}}—\equiv—R^1$$

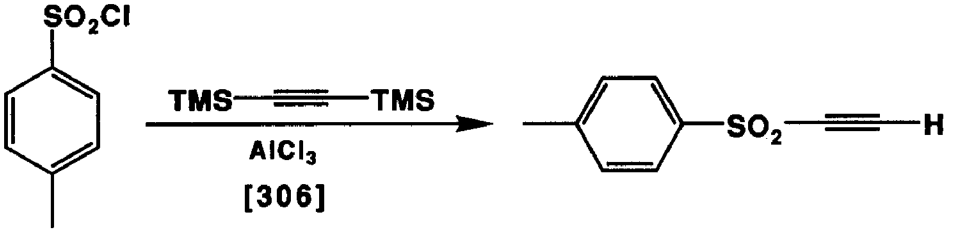
(332)



$$Ph—\equiv—CHO \xrightarrow[\text{2) [O]}\ [305]]{\text{1) Li—}\equiv\text{—TMS}} Ph—\equiv—\overset{O}{\overset{\|}{C}}—\equiv—TMS$$

(333)

Ethynylsulfones can be prepared by the reaction of ethynylsilanes with sulfonyl chlorides. (Eqn. 334) The nitration of ethynylsilanes is also possible. The trimethylsilyl group is selectively substituted in this reaction. (Eqns. 335 and 336)



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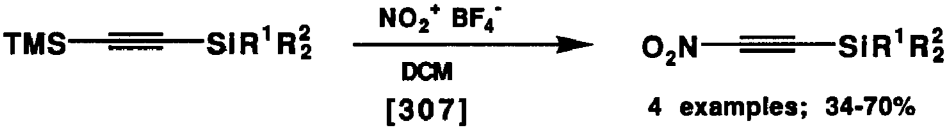
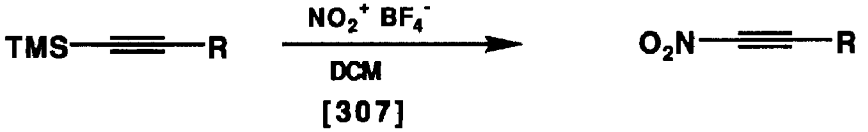
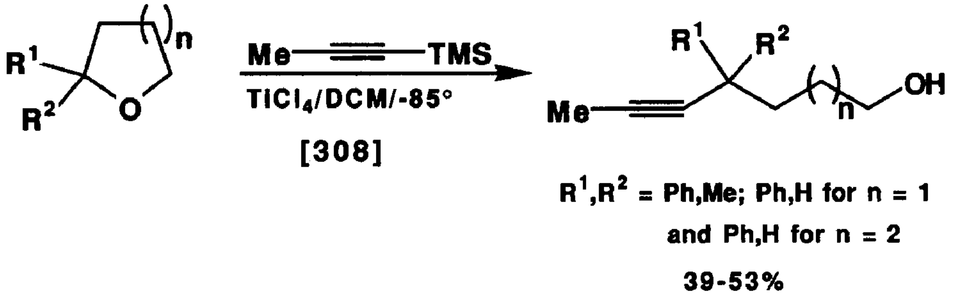


(335)



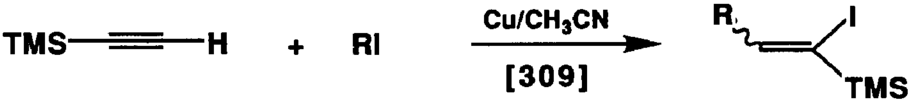
(336)

Tetrahydrofurans and tetrahydropyrans were reacted with 1-trimethylsilylpropyne to give ring cleavage. (Eqn. 337)



(337)

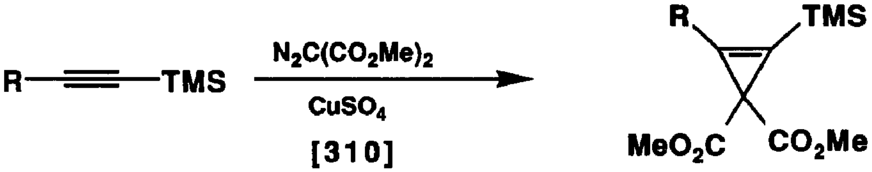
The addition of alkyl iodides to ethynylsilanes under the influence of copper(0) to give α-iodovinylsilanes was reported. (Eqn. 338)



(338)

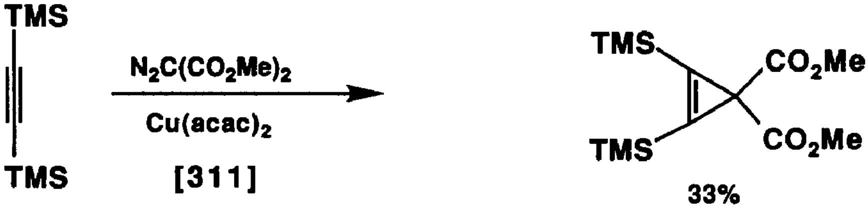
(R = $CF_3(CF_2)_5$, $Cl(CF_2)_6$, $Cl(CF_2)_4$, $ClCF_2CF_2$, $CF_3CF_2CF_2$, $H(CF_2)_4$, $(CF_2)_4O(CF_2)_4$, FSO_2

The reaction of ethynylsilanes with diazomalonates gives silylated cyclopropenes. (Eqns. 339 and 340) Protodesilylation gives the parent cyclopropene. (Eqn. 341) The reaction of methyl diazoacetate with 3-silylpropynal gives heterocycle **99**. (Eqn. 342)

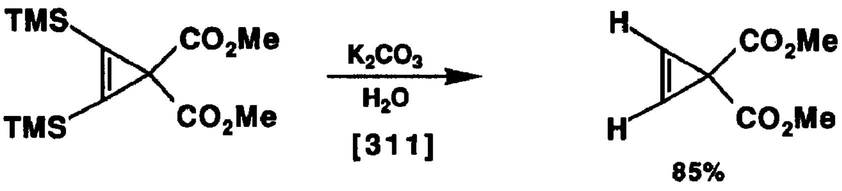


(339)

(R = Bu, Pr, TMS)



(340)



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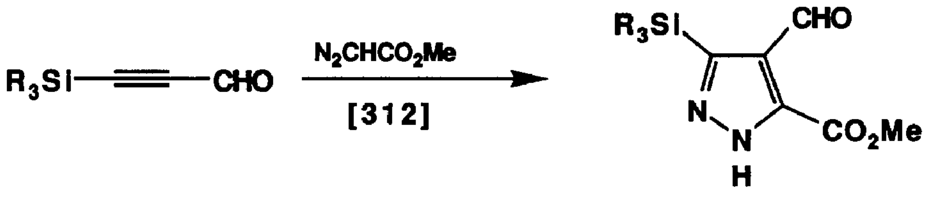
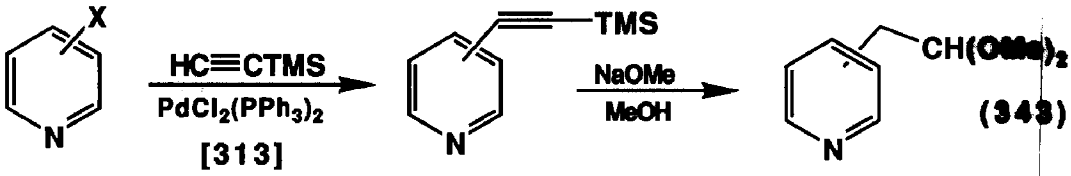


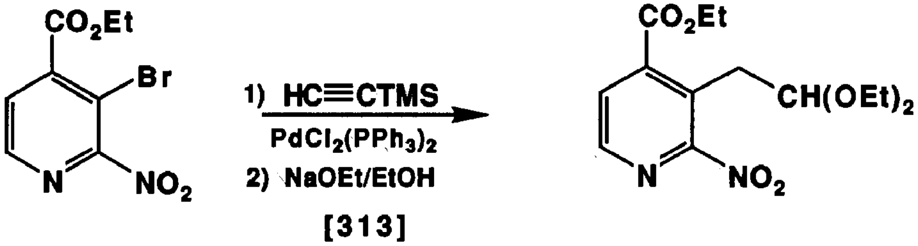
99

(342)

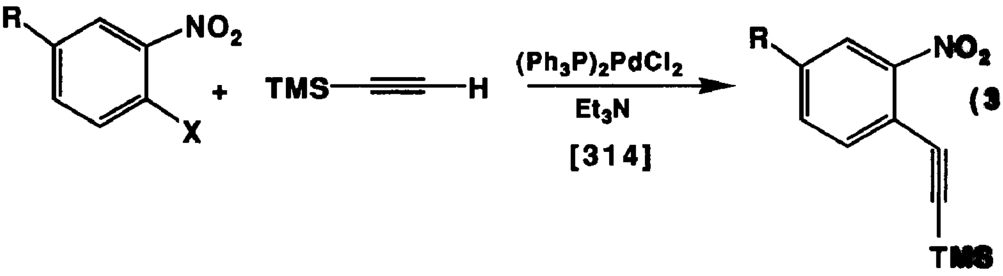
It was shown that it is possible to directly convert ethynylsilanes to dimethyl or diethyl acetals. This procedure was combined with the cross coupling of trimethylsilylacetylene with aryl halides followed by transformation of the arylethynylsilane to the acetal. (Eqns. 343, 344, 345 and 346)



(343)



(344)



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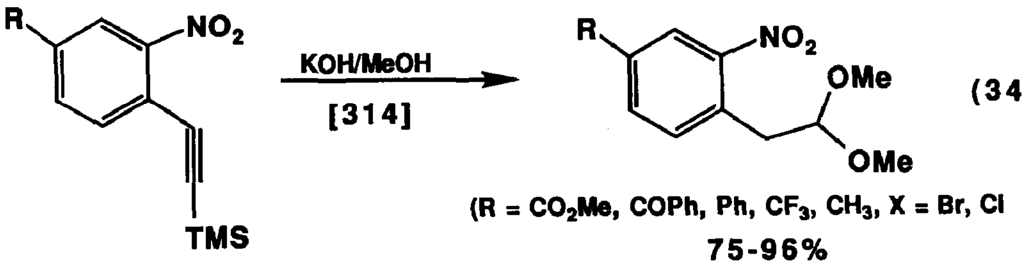
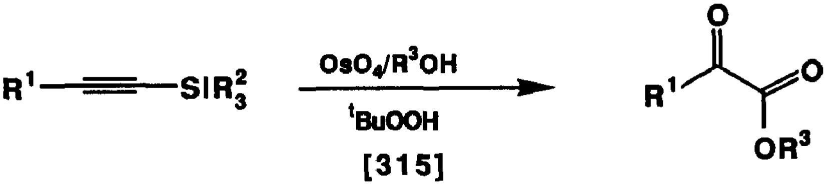


(R = CO_2Me, COPh, Ph, CF_3, CH_3, X = Br, Cl
75-96%

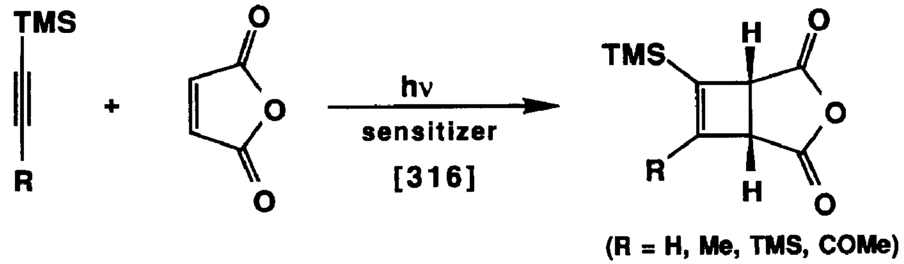
(346)

The osmium tetroxide oxidation of ethynylsilanes gives α-keto esters in moderate yields. (Eqn. 347)



(347)

Ethynylsilanes were involved in several cyclization procedures resulting in some useful organosilanes. Trimethylsilylacetylenes were reacted with maleic anhydride to give silylated cyclobutenes. (Eqns. 348, 349 and 350) 1-Trimethylsilylpropargyl alcohol was reacted with dimethylacetylene dicarboxylate and a palladium catalyst to give the [2+4] cycloadduct. (Eqn. 351) Trimethylsilylacetylene itself was coupled to 5-hydroxyuracil triflates. (Eqn. 352) The reaction of alkoxy silylacetylenes with α-ketoketenes was reported. (Eqn. 353)



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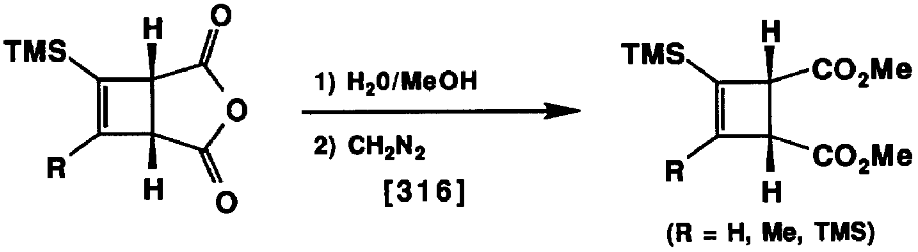

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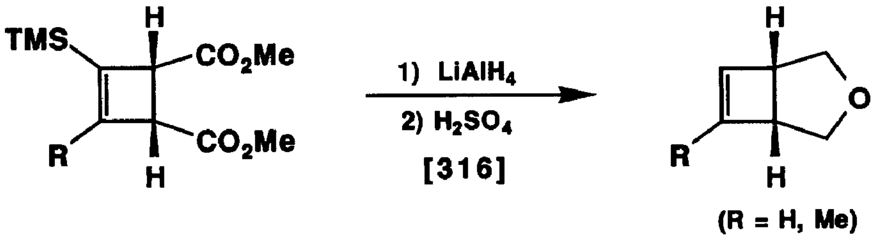

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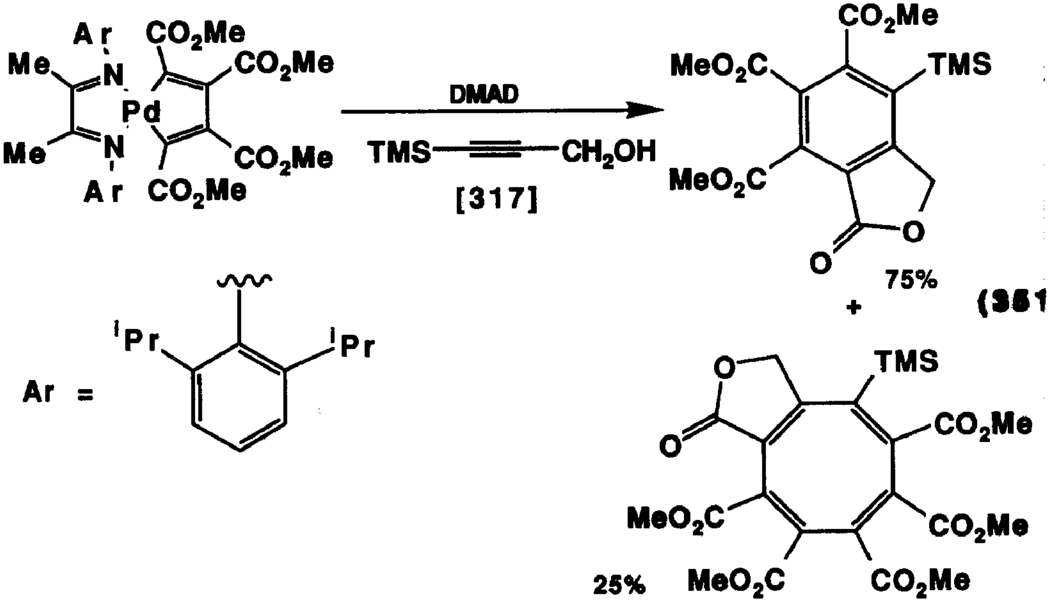

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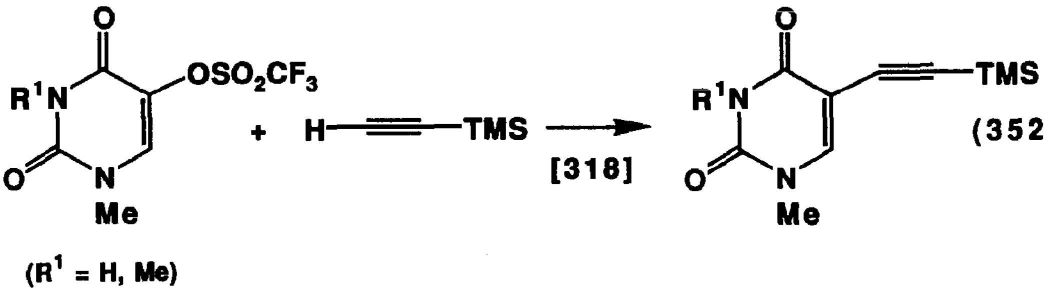

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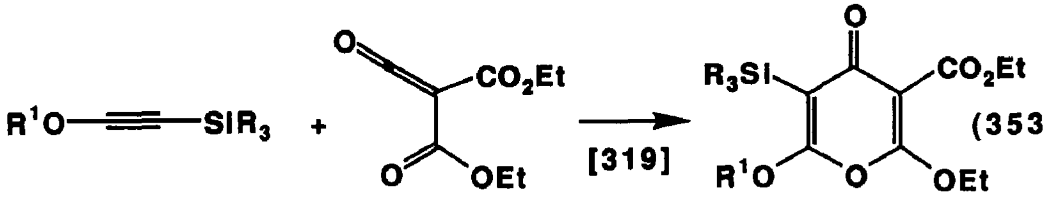
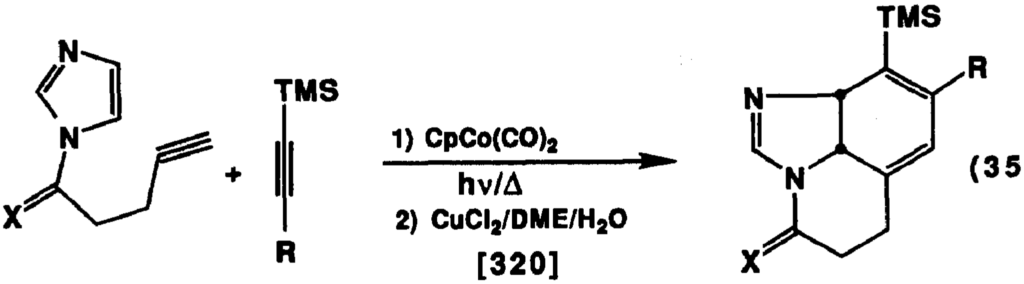


(353)

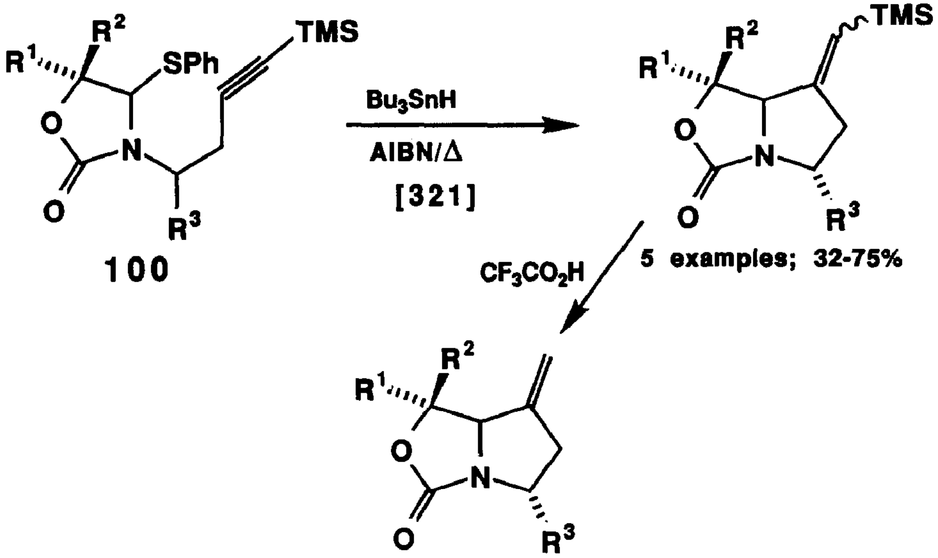
The cobalt-mediated [2+2+2] cycloaddition of trimethylsilylacetylenes was employed in the synthesis of 3a,7a-dihydrobenzimidazoles. (Eqn. 354)



(354)

(X = O, H$_2$; R = TMS, Et, OMe, CO$_2$Me)

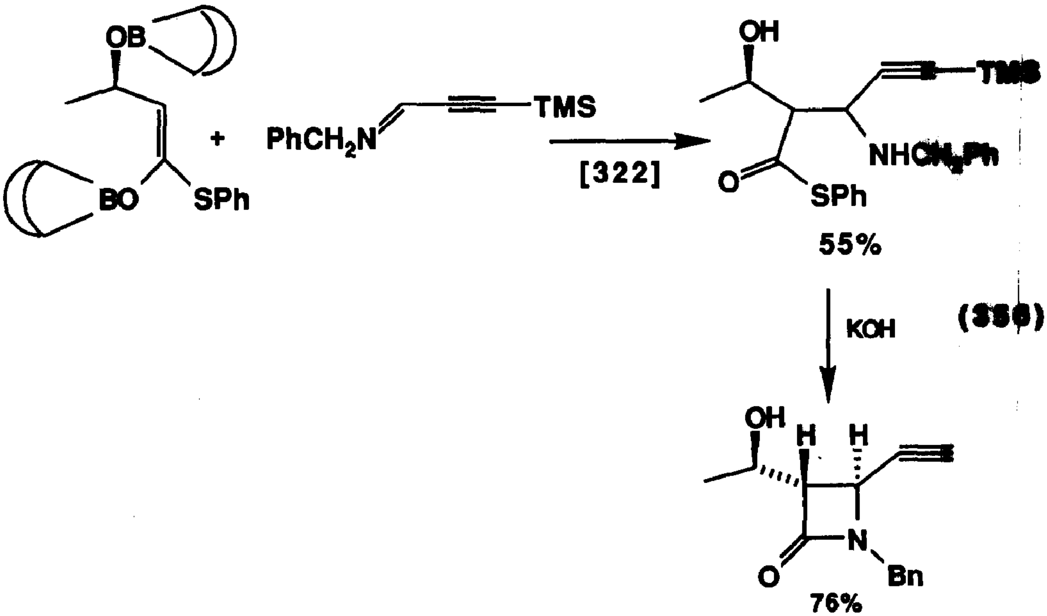
Ethynylsilane **100** was subjected to intramolecular cyclization *via* radicals initiation (Eqn. 355) The resulting vinylsilane can be protodesilylated.



100

(355)

The reaction of enaminoethynylsilanes with vinylboronates of thioesters was reported. This reaction gives β-amino thioesters, which can be cyclized to β-lactams. (Eqns. 356 and 357)



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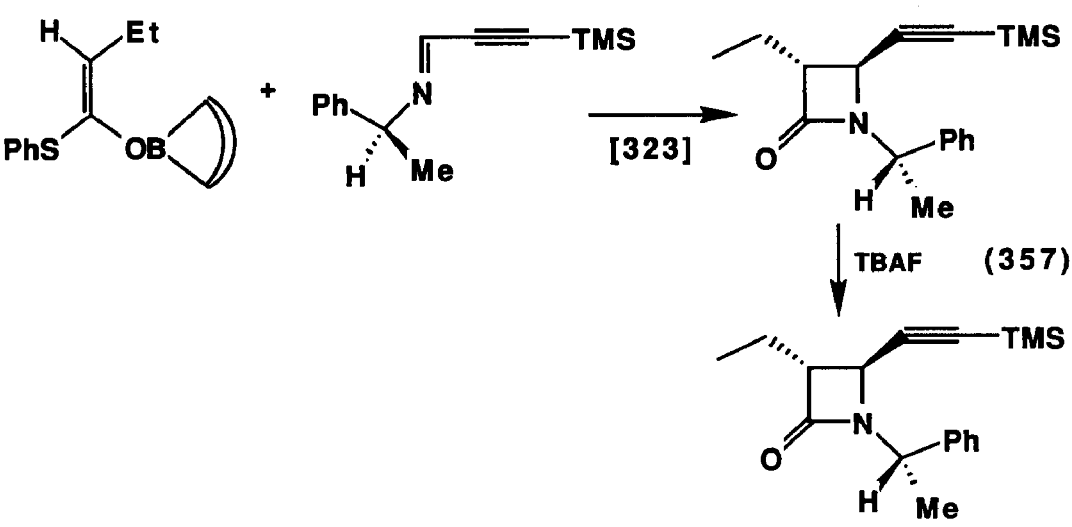
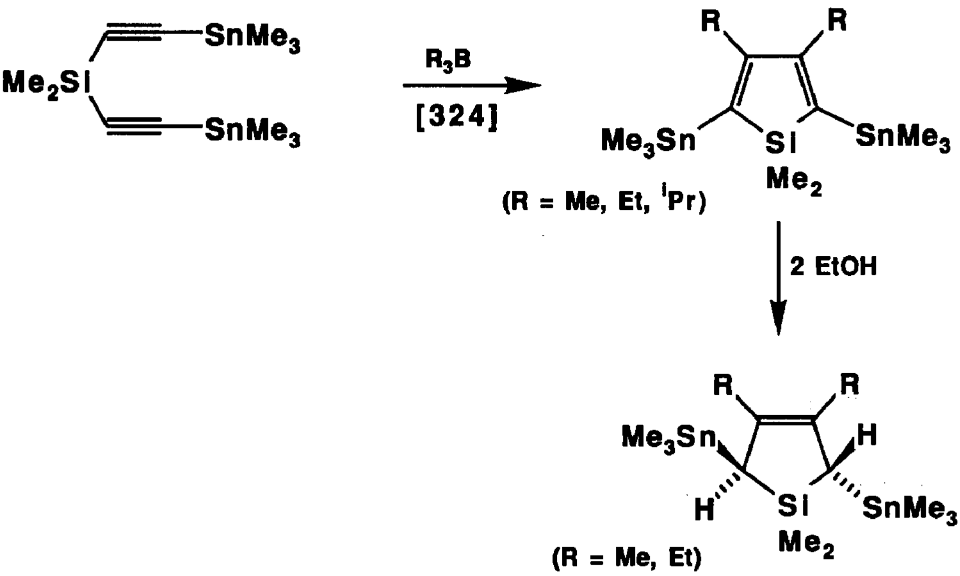


(357)

The reaction of trialkylboranes with the ethynyl-tin bond of mixed silyl stannyl acetylenes results in siloles (Eqn. 358) and silaborapins (Eqn. 359).



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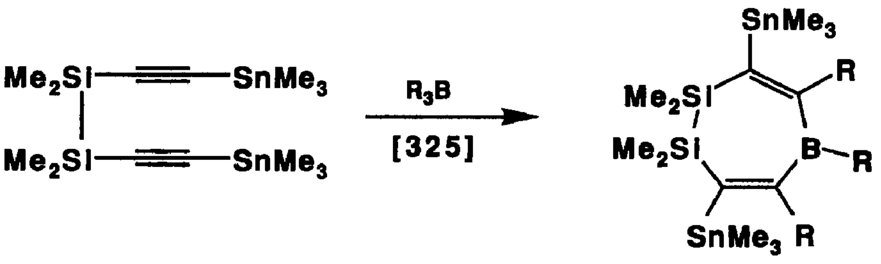


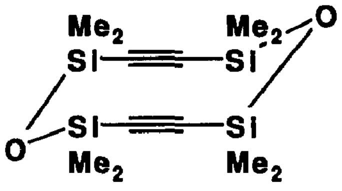
(R = Me, Et, ^{i}Pr)

(359)

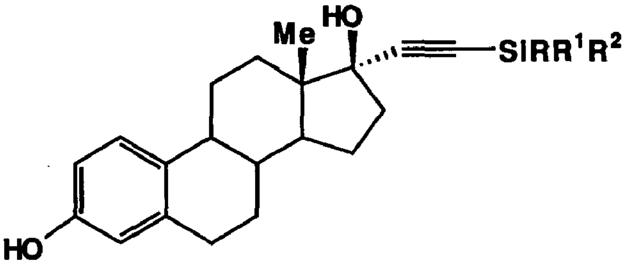
C. Ethynylsilanes-Other Studies

An infrared spectroscopic study of a series of substituted propynals was carried out in order to look at the basicity of the aldehydic oxygen. The triethylgermyl, triethylsilyl, and trimethylsilyl substituted propynals were less basic than the alkyl substituted ones. [326] Infrared and Raman studies of trimethylsilylpropiol amides were done; the basicity of the oxygen atom is higher in systems substituted with alkyl groups. [327] The carbon-carbon and carbon-chalcogen coupling constants have been determined for a number of ethynyl derivatives including trimethylsilyl methoxyacetylene and trimethylsilyl thiomethoxyacetylene. [328] The ^{13}C, ^{29}Si, and ^{199}Hg NMR spectra of ethynyltrimethylsilyl mercurials were determined. [329]

The crystal structure of **101** was determined. The Si-C-C-Si array is not quite linear with the mean Si-C-C angle being 175.5° in order to allow more distance between silicon atoms in the ring. [330] The steroidal silicon side chain analog **102** shows potential as antifertility agents. [331]



101

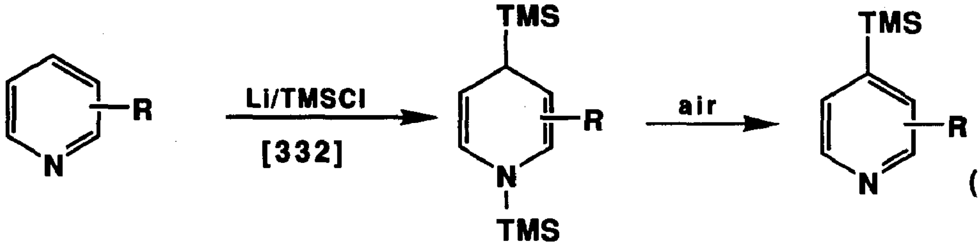


102

IX. ALLYLSILANES

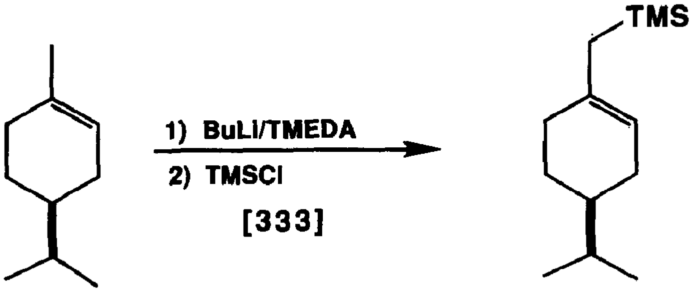
A. Preparation

The reaction of pyridyl systems with lithium metal in the presence of trimethylchlorosilane gives the trimethylsilylated versions of the Birch products, allylsilanes. Upon oxidation in air these are converted to the pyridyltrimethylsilanes. (Eqn. 360)



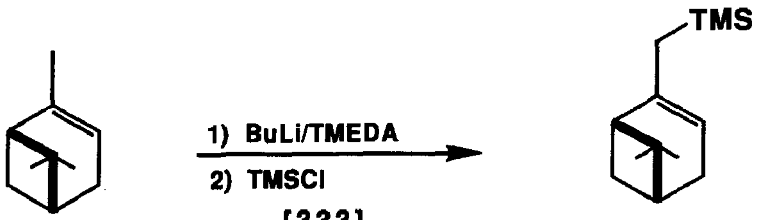
(360)

The direct metalation of olefins followed by trimethylsilylation gives allylsilanes. This was used to prepare some allylsilanes from terpenes. (Eqns. 361 and 362) It was also used to prepare allylsilane **103**, which was employed in the synthesis of racemic fredericamycin A. (Eqn. 363)



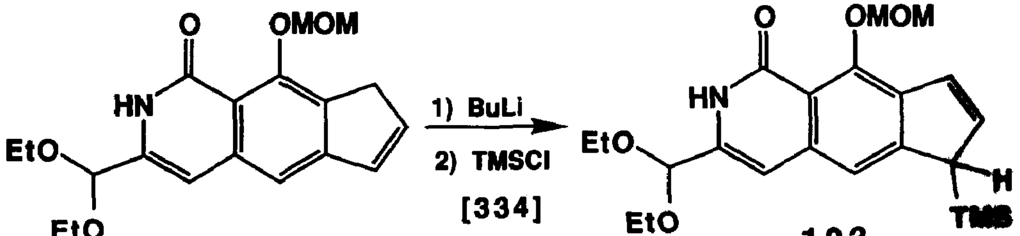
30%

(361)



54%

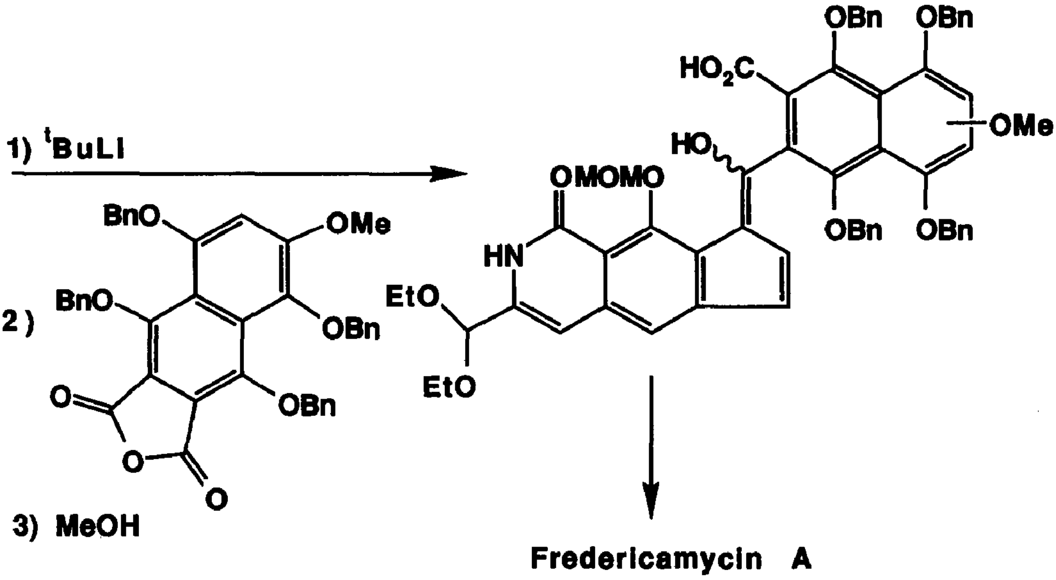
(362)



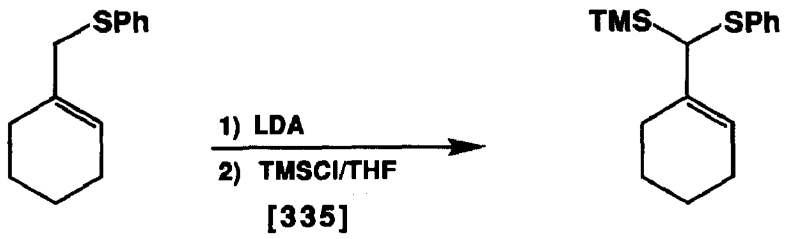
103

(363)

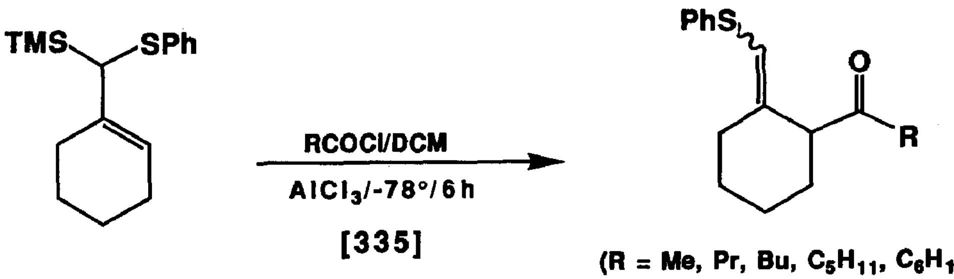
Eqn. 336 continued



The metalation-silylation of functional olefins provided routes to functional allylsilanes useful in synthetic transformations. Allyl sulfides were lithiated with lithium diisopropylamide and trimethylsilylated in the α-position. (Eqn. 364) These allylsilanes proved useful in acylation reactions with no interference from the sulfide group. (Eqn. 365) The lithiation of α-alkoxyallylphosphonates followed by tri-methylsilylation results in the formation of γ-silylation to give allylsilane **104**. (Eqn. 366) The lithiation of α,β-unsaturated acids gives the dianion, which upon tri-methylsilylation produces the product of γ-attack. (Eqn. 367)



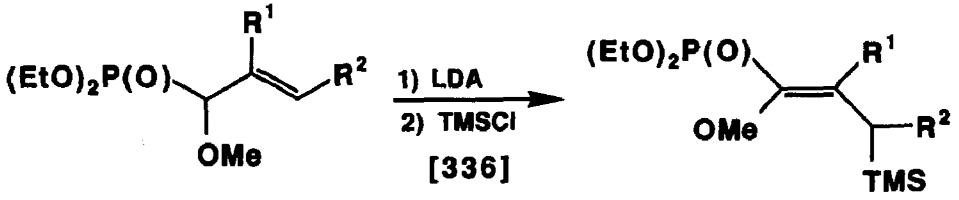
(364)



(365)

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

Yields 26-81%; E:Z approx. 3:2



104

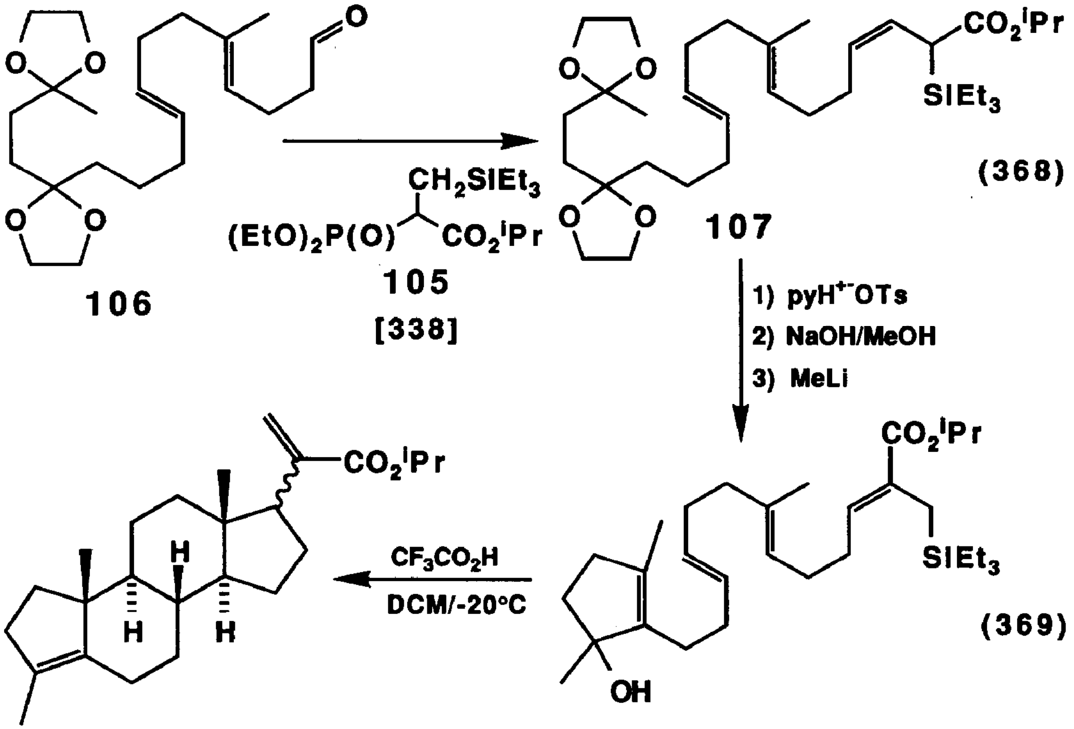
(366)

3 examples; 82-88%

65-85%

(367)

The β-triethylsilylphosphonate **105** was deprotonated and reacted with aldehyde **106** to give allylsilane **107**. This allylsilane was used in an acid catalyzed polyene cyclization. (Eqns. 368 and 369)



106

105

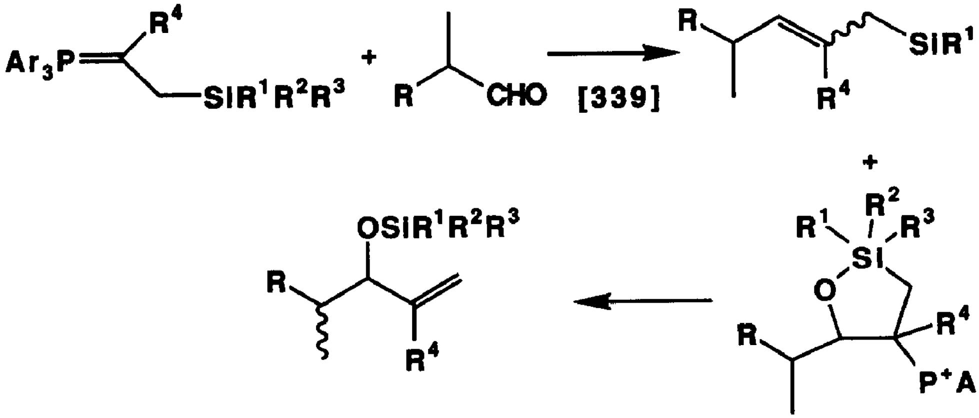
[338]

107

(368)

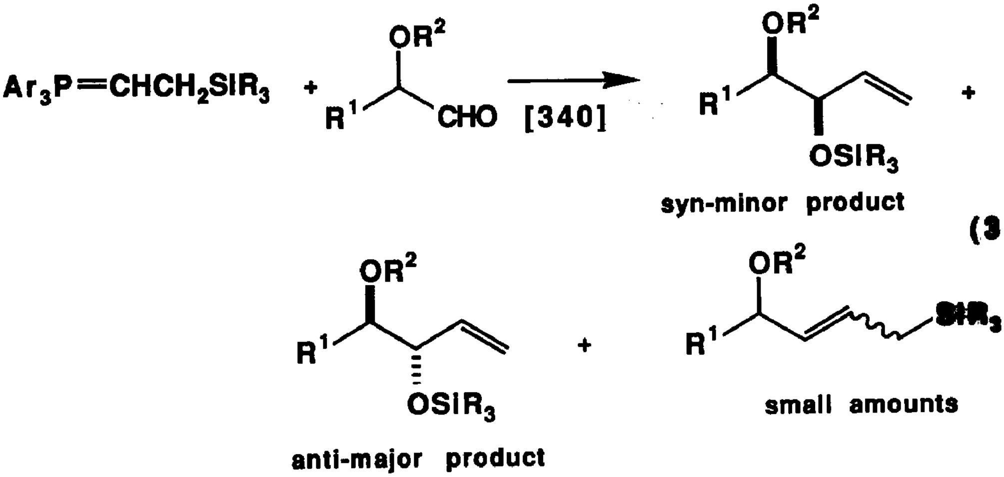
(369)

It was found that by modifying both the aryl group of the triarylphosphine portion and the ligands on silicon in the β-silyl Wittig reagent (Seyferth Wittig reagent) that alkenylation rather than allylsilane formation occurs. (Eqn. 370) The stereoselectivity of reaction was studied in the reaction with α-alkoxy aldehydes. (Eqn. 371)

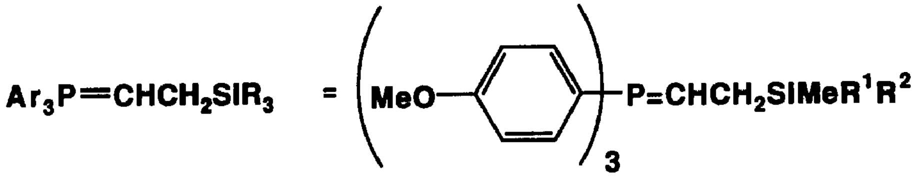


(370)

(R = Ph, c-C_6H_{11}; R^1 = Me; R^2 = Me, Ph, O^{i}Pr;
R^3 = Me, Ph, O^{i}Pr; R^4 = H. Me; Ar = Ph, p-$MeOC_6H_4$)

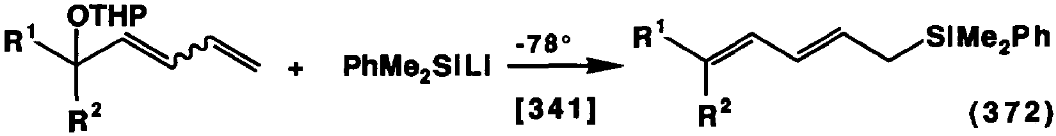


(371)



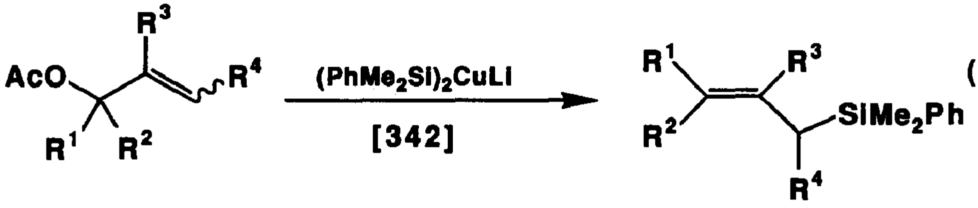
where R^1,R^2 = Me, Me; Me, O^{i}Pr; Ph, Ph)

Silylmetallic species were employed in the synthesis of allylsilanes. Allylic tetrahydropyranyl ethers of 1,3-dienes were reacted with phenyldimethylsilyllithium to give allylsilanes. (Eqn. 372) Lithium bis(phenyldimethylsilyl)cuprate was reacted with allyl acetates to provide allylsilanes. (Eqn. 373) This approach was used to prepare optically active allylsilanes. Thus, reaction of lithium bis(phenyldimethylsilyl)cuprate with allylbenzoate **108** gives allylsilane **109** and the allyl carbamate **110** yields the opposite diastereomeric allylsilane **111**. Equations 374 through 377 nicely illustrate the potential of these reactions.

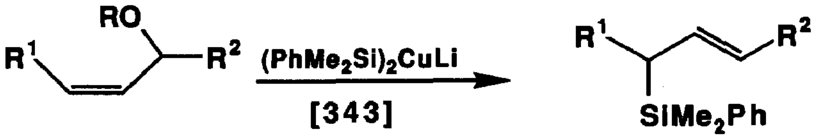


(372)

R^1	R^2	% Yield
^iPr	H	85
C_7H_{15}	H	81
Me	Me	90
$-(CH_2)_5-$		78

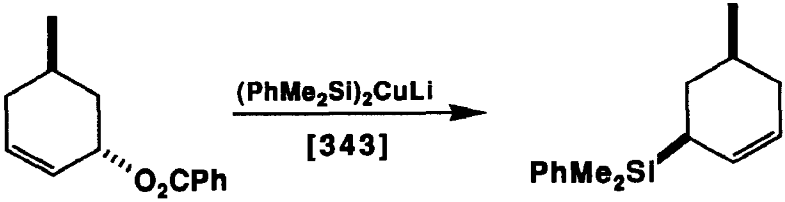


(373)



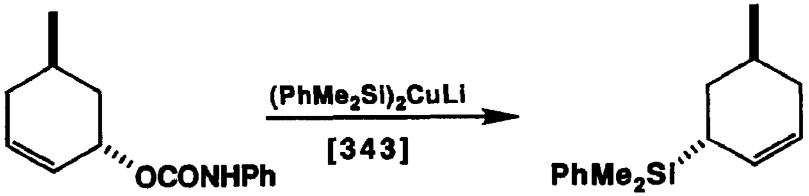
(374)

anti addition for R = Ac, PhCO
syn addition for R = CONHPh



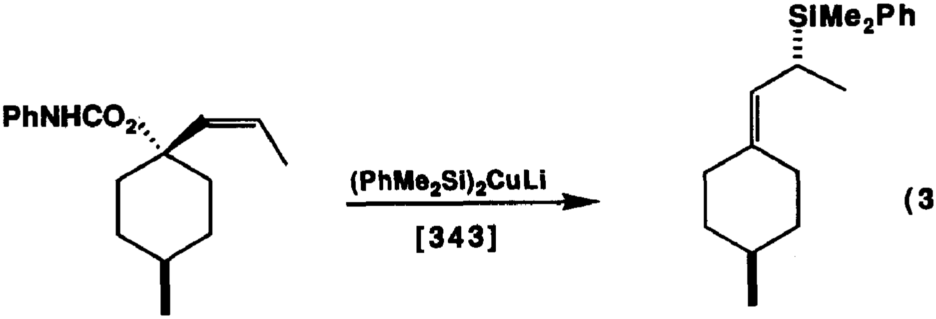
(375)

108 **109** 86%



(376)

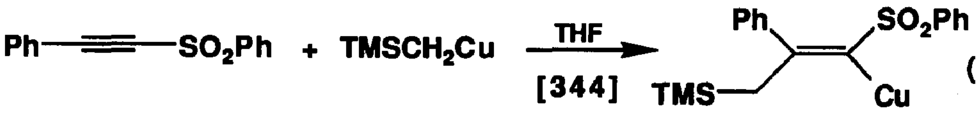
110 **111** 74%



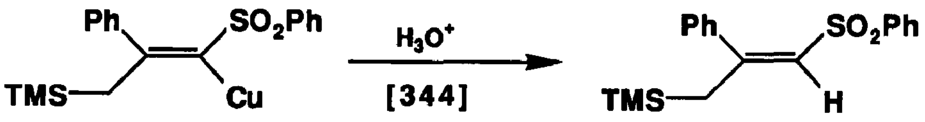
(377)

92%

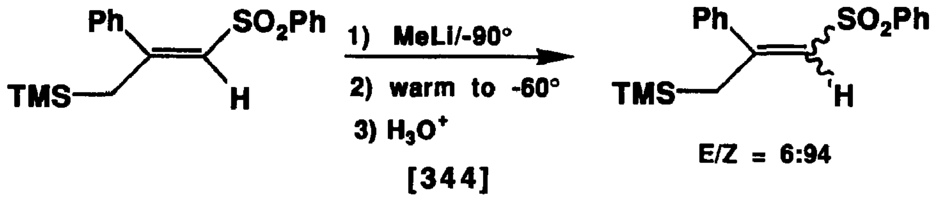
Trimethylsilylmethylcopper was reacted with ethynylsulfones to give addition across the triple bond. The resulting vinyl copper species was then protonated to give the allylsilane. (Eqns. 378 and 379) It was shown in these studies that whereas the α-sulfonyl-vinyl copper species is configurationally stable, the corresponding lithium reagent, prepared from the parent vinylsulfone, is not. (Eqn. 380)



(378)

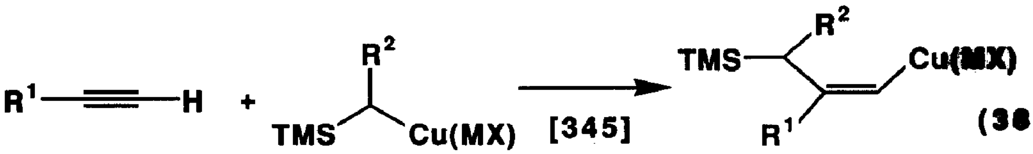


(379)



(380)

The reaction of α-silyl organocopper reagents with acetylenes gives rise to allylsilanes, which are at the same time vinylcopper reagents. (Eqn. 381) These intriguing reagents can be coupled to give 1,6-bis(trimethylsilyl)-2,4-hexadienes. (Eqn. 382) Reaction with iodine gives the corresponding vinyliodide. (Eqn. 383) Alkylation is also possible, (Eqn. 384) as is acylation, (Eqn. 385) and carboxylation (Eqn. 386). Interestingly, the reaction of trimethylsilylmethylcopper with acetyl chloride in the presence of palladium(0) gives rise to the trimethylsilyl enol ether of acetone. (Eq. 387)



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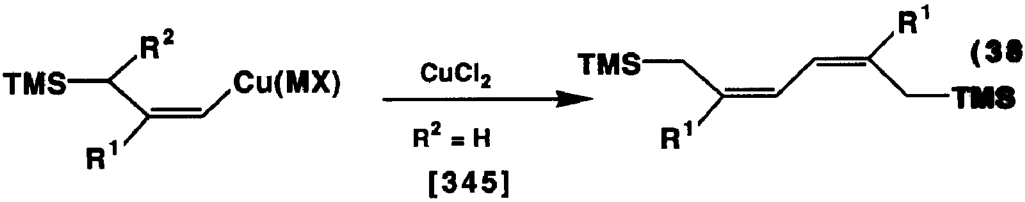
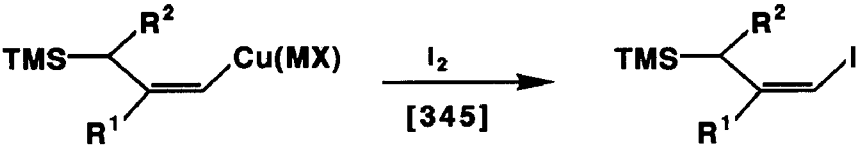


(382)



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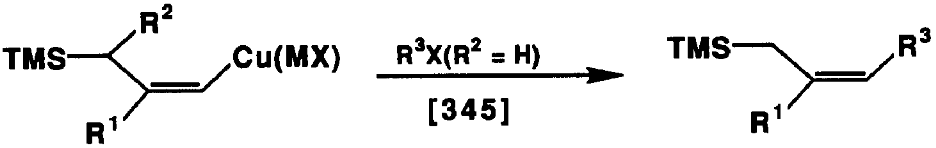

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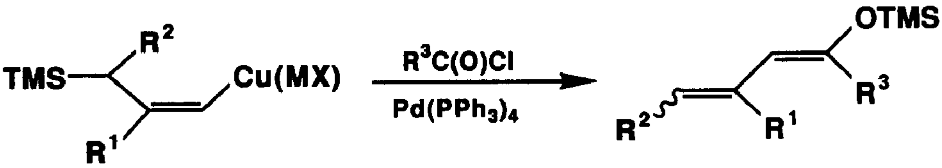

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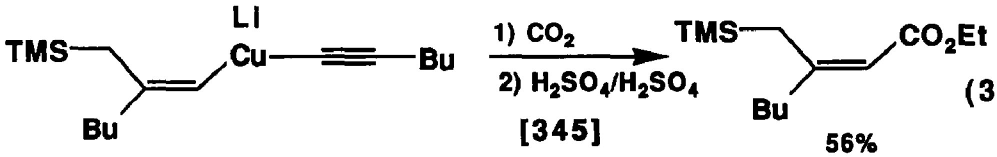

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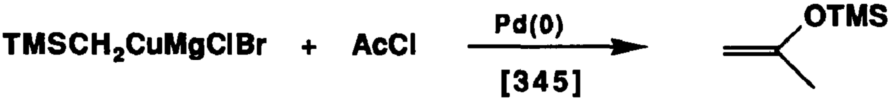
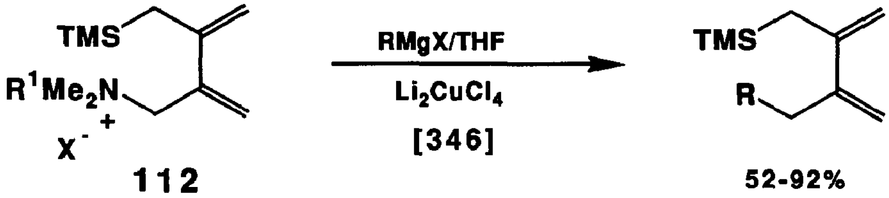


(387)

3-Substituted isoprenylsilanes were prepared *via* the reaction of Grignard reagents on **112** in the presence of dilithium tetrachlorocuprate. (Eqn. 388)

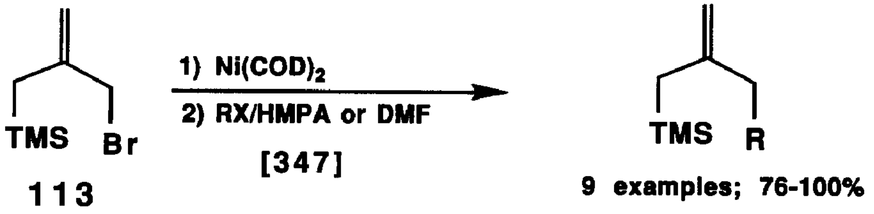


112

(388)

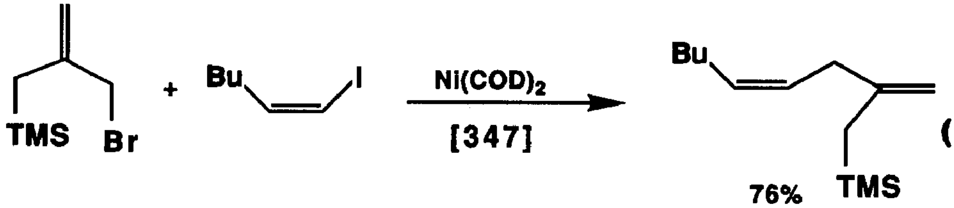
(R^2 = Me, Bu, $PhCH_2$; X = I, Cl
R^1 = Bu, $PhCH_2$)

The reaction of **113** with bis(cyclooctadiene)nickel(0) and then alkyl halides affords 1-substituted allylsilanes in excellent yields. (Eqn. 389) Vinyl halides are also employable in this sequence. (Eqns. 390 and 391) This reaction is stereospecific with respect to the starting vinyl halide.

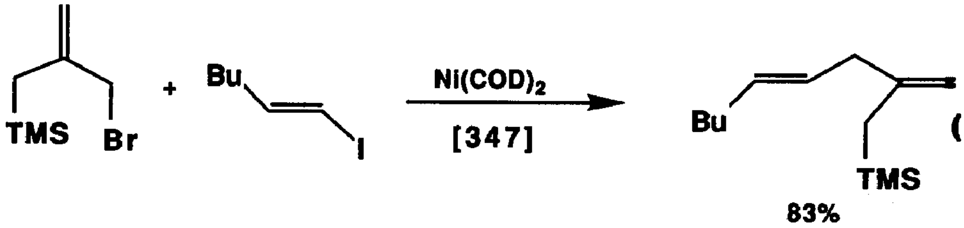


113

(389)

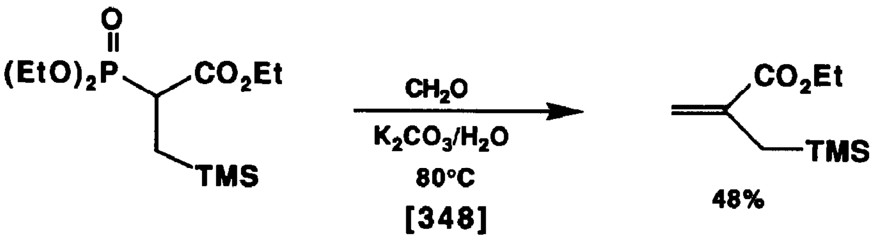


(390)



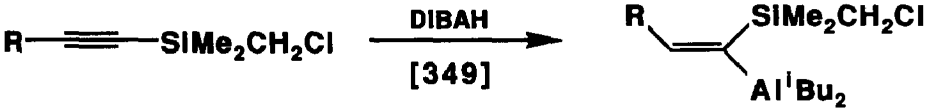
(391)

Methyl α-trimethylsilylmethylacrylate was prepared as shown in Eqn. 392.



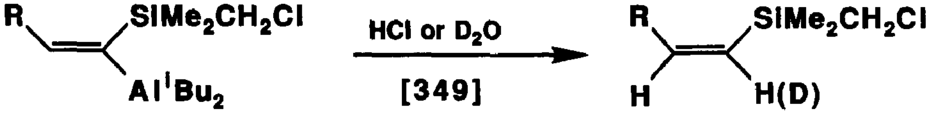
(392)

Chloromethyl(ethynyl)silanes proved to be precursors to allylsilanes *via* hydroalumination of the ethynyl group (Eqn. 393) and subsequent transformations of the resulting vinylalane. Thus intermediate **114** can be simply protonated to give the vinylsilane (Eqn. 394), treated with methyllithium and protonated to give *via* rearrangement (E) allylsilanes (Eqn. 395) or treated with a trialkylalane to give a mixture of (E) and (Z) allylsilanes by way of the Lewis acid catalyzed rearrangement (Eqn. 396).

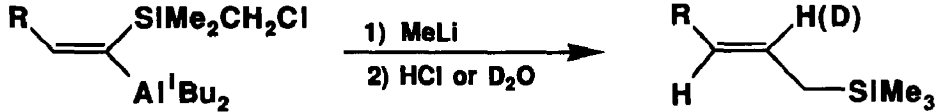


114

(393)



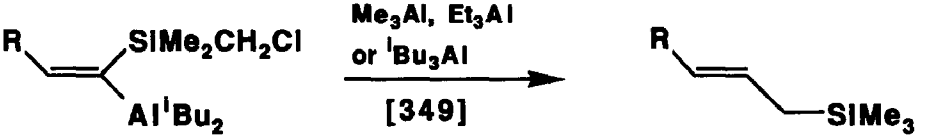
(394)



(395)

3 examples; 73-90%

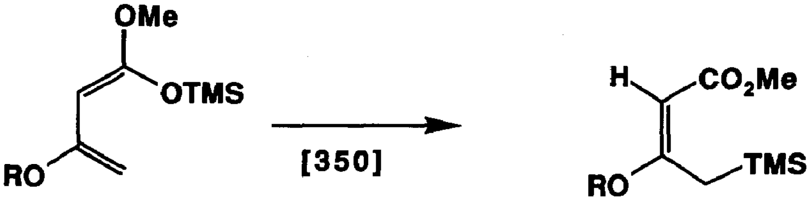
>99% E



(396)

R = C_6H_{13}; E/Z = 30/70
3 examples; 70-85%

Silyl ketene acetals **115**, available from the enol ethers of β-keto esters, thermally rearrange to give allylsilanes **116**. (Eqn. 397)



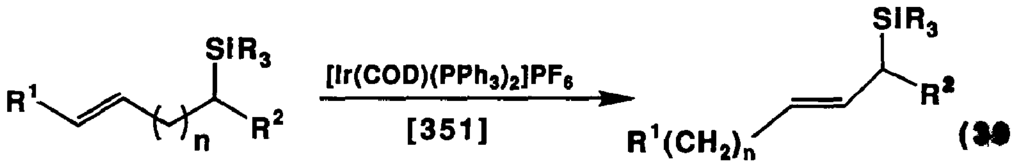
(R = Me, TMS)

115

116

(397)

The rhodium(I) or iridium(I) catalyzed isomerization of olefinic silanes gives allylsilanes in excellent yields. (Eqn. 398)



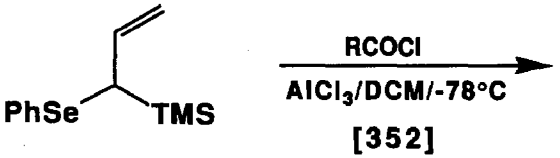
(R_3Si = Me_3Si; $PhMe_2Si$)

6 examples; 85-97%

(398)

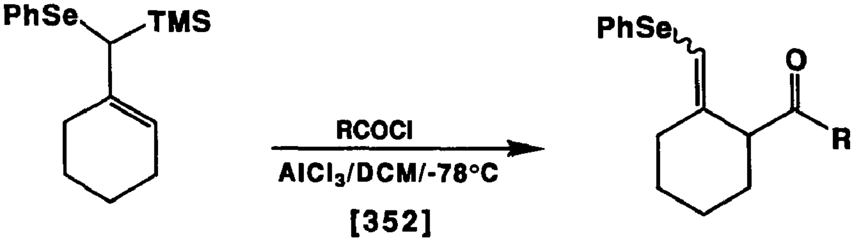
B. Allylsilanes-Reactions

The reaction of allylsilanes with electrophiles continues to be an excellent allylation procedure. It was shown that α-phenylselenyl allylsilane **117** undergoes reaction with acyl chlorides to give the allylation reaction with double bond transposition and without reaction of the phenylselenyl group. (Eqn. 399) Eqn. 400 shows another example. In a like manner α-thiophenoxyallylsilanes, prepared according to Eqn. 401, can be acylated. (Eqn. 402) Another example is seen in Eqn. 403. This reaction, however, can lead to other products as well. (Eqn. 404)



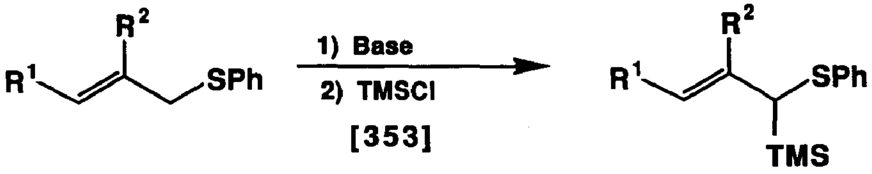
117

(399)

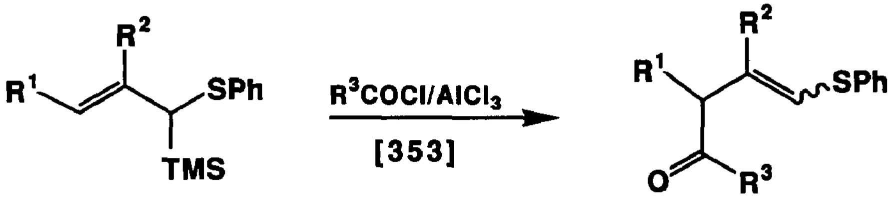


4 examples; 56-61%

(400)

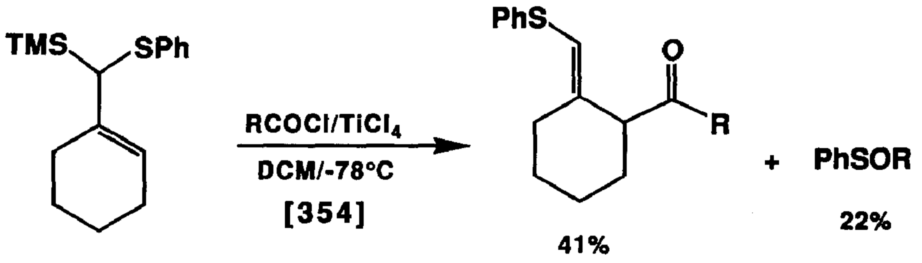


(401)

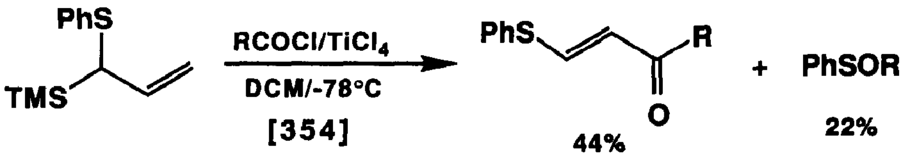


(402)

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



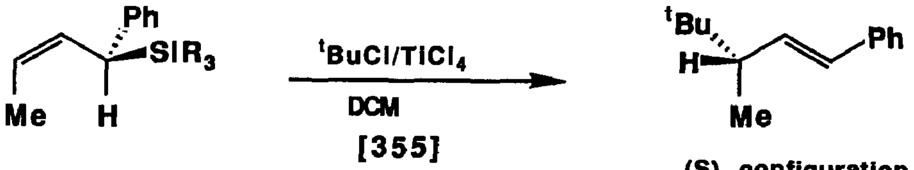
(403)



(404)

The asymmetric hydrosilation of 1-phenyl-1,3-butadiene provides optically active allylsilanes, which were employed in the acylation and alkylation reactions to determine the stereochemistry of these transformations. The stereochemistry of both the acylation and alkylation of allylsilanes was shown to be predominantly anti with less anti attack occurring with more fluorine ligands on silicon. (Eqns. 405 and 406)

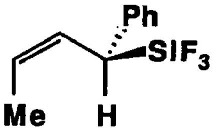
(405)



(406)

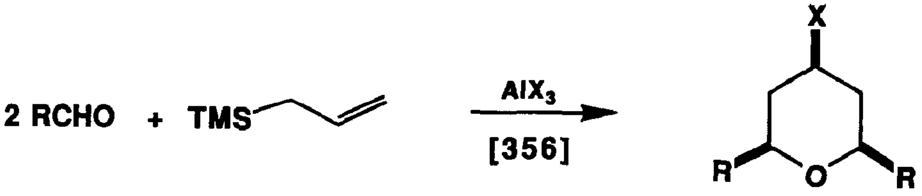
(S) configuration

(SiR$_3$ = Me$_3$Si, Me$_2$FSi, MeF$_2$Si)



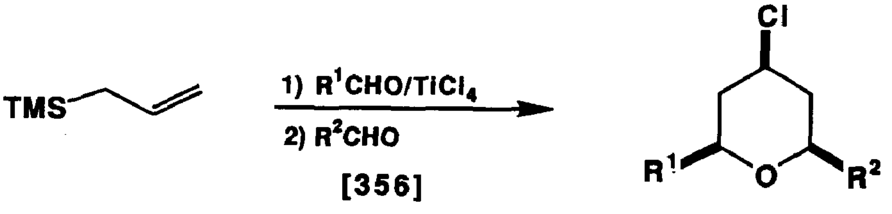
gives slow reaction and racemic product.

The allylation of aldehydes with allylsilanes continues to be studied and applied. It was found that under certain conditions the reaction of aldehydes with allyltrimethylsilane in the presence of a Lewis acid results in the formation of 4-halotetrahydropyrans. (Eqn. 407) The reaction was also carried out with two different aldehydes. (Eqn. 408)



(407)

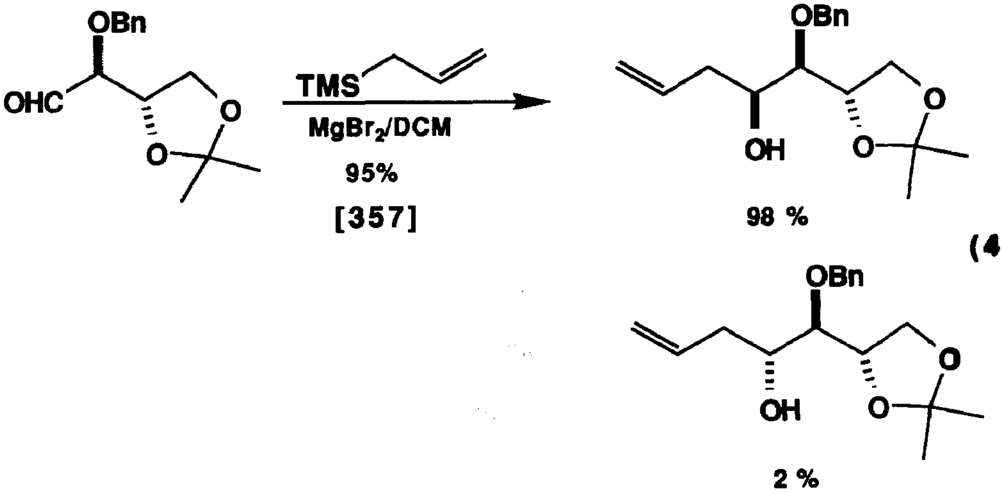
5 examples; 43-86%



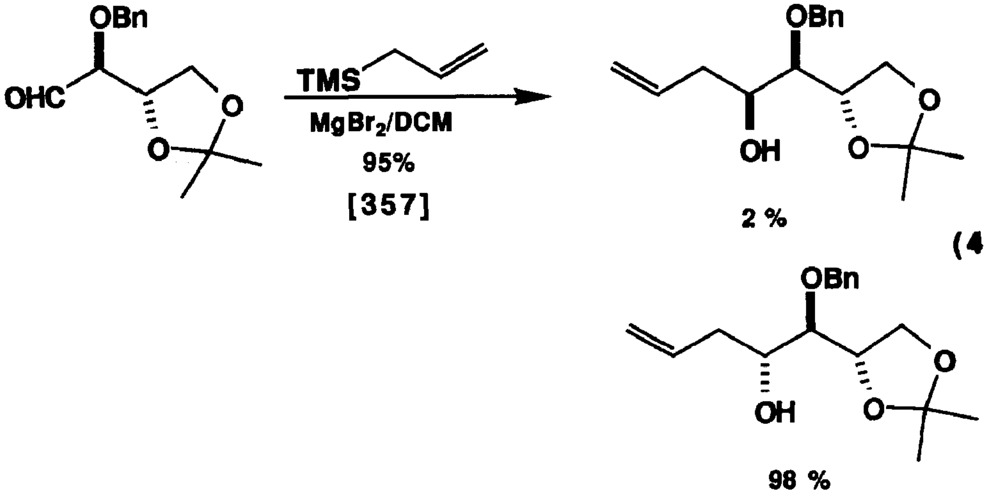
(408)

5 examples; 41-62%

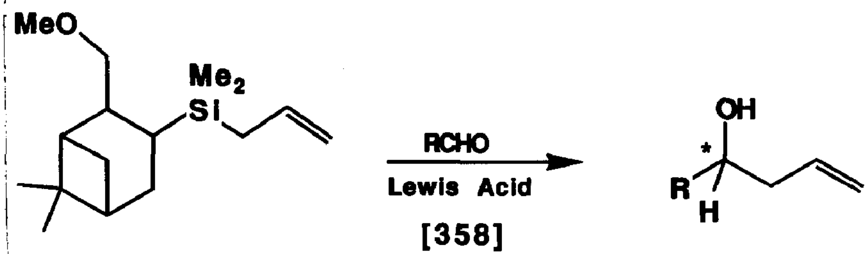
The allylation of 2,3-dialkoxy aldehydes with allyltrimethylsilane was reported. The reaction is highly stereoselective. (Eqns. 409 and 410) The optically active allylsilane **118** was employed in the allylation of aldehydes. Both the yields and the enantiomeric excesses are moderate. (Eqn. 411)



(409)



(410)

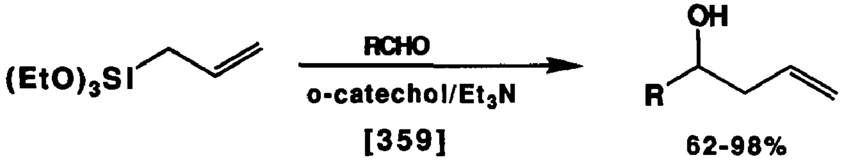


118

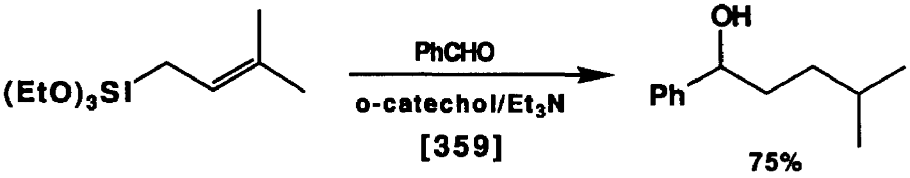
(411)

R	% Yield	ee
nPr	58	46
Me	61	40
Ph	40	21

The allylation of aldehydes with allyltrialkoxysilanes using catechol and triethylamine as the catalyst was accomplished. (Eqns. 412 and 413)

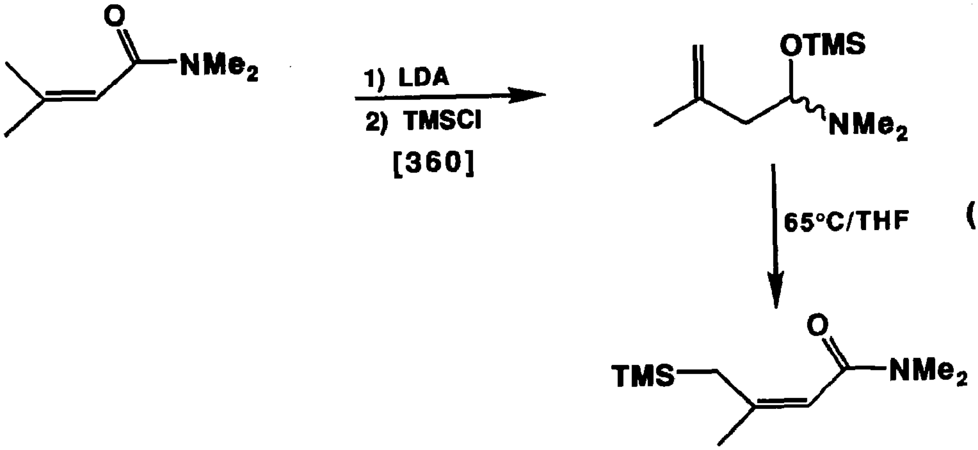


(412)



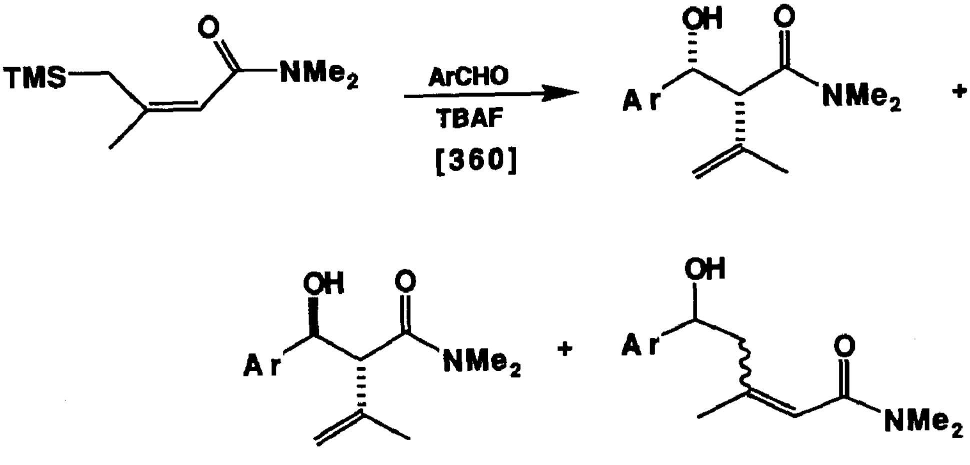
(413)

The allylsilane **119**, prepared by the thermal rearrangement of the corresponding trimethylsilyl ketene aminal, was reacted with aldehydes to provide α-vinyl-β-hydroxy amides. (Eqns. 414 , 415 and 416)



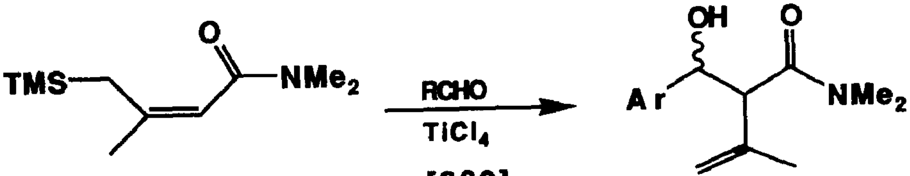
119

(414)



(415)

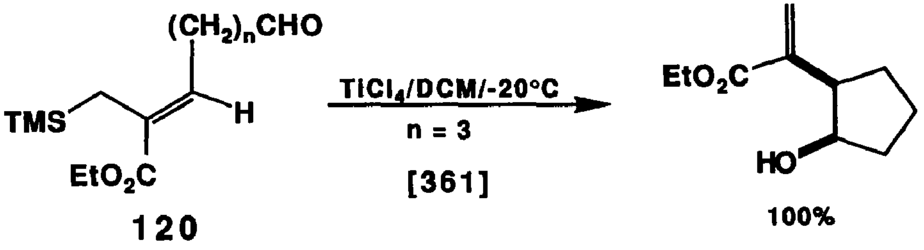
4 examples; 58-85%



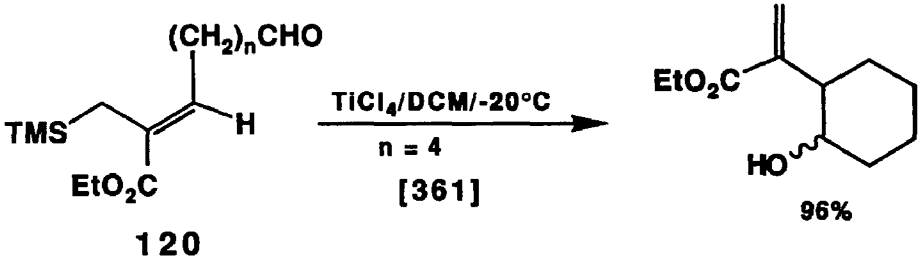
(416)

6 examples; 25-74%
syn:anti 59-99:41-1

Examples of the intramolecular reaction of allylsilanes with aldehydes appeared. The allylsilanes **120** were cyclized as shown. The resulting unsaturated hydroxy esters were further cyclized to fused α-methylene butyrolactones. (Eqns. 417 and 418)

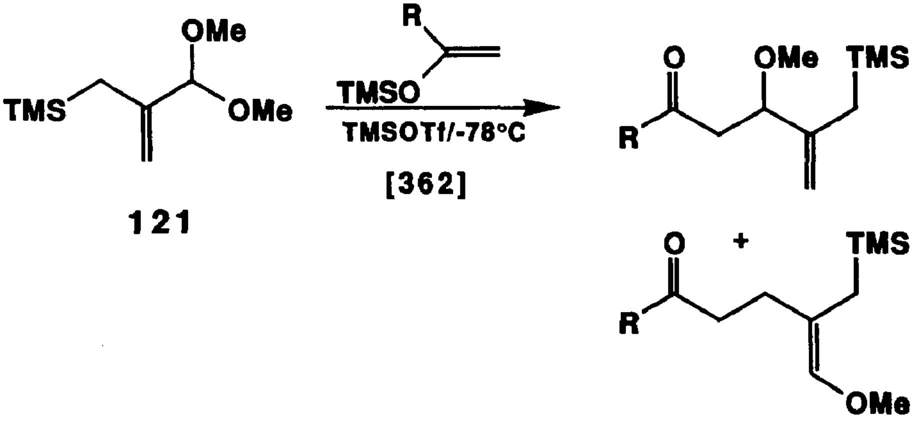


(417)

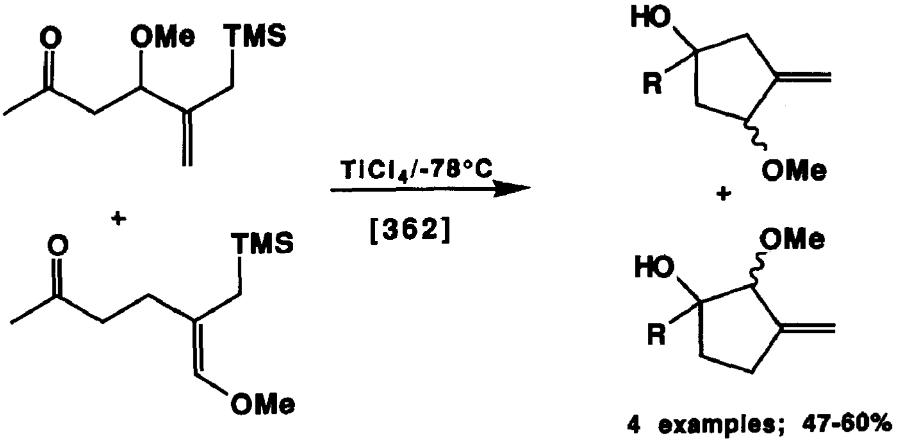


(418)

Allylsilane **121** was first reacted as the acetal with trimethylsilyl enol ethers and then the resulting ketone from this reaction subjected to Lewis acid catalyzed cyclization to the exo-methylene cyclopentanols. (Eqns. 419 and 420)



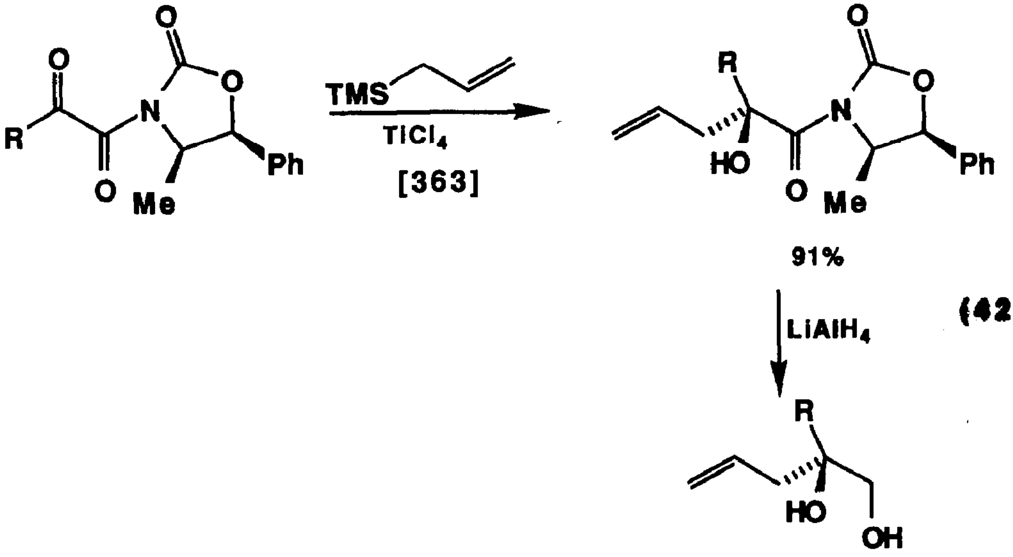
(419)



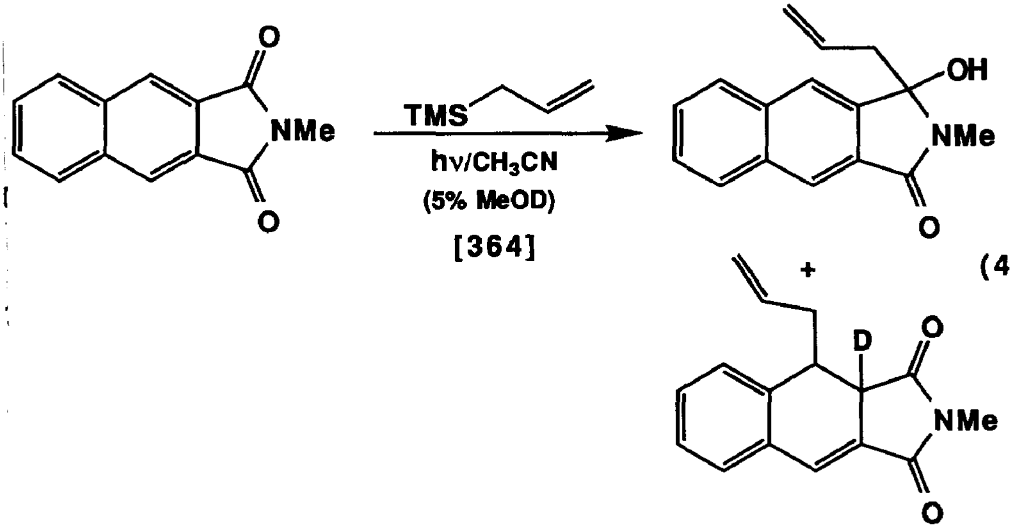
4 examples; 47-60% overall yields

(420)

The allylation of chiral α-keto imides was reported. Reduction of the product gives chiral homoallylic alcohols and diols. (Eqn. 421) The allylation of N-methyl-arenedicarboxylimides was also reported. (Eqn. 422)

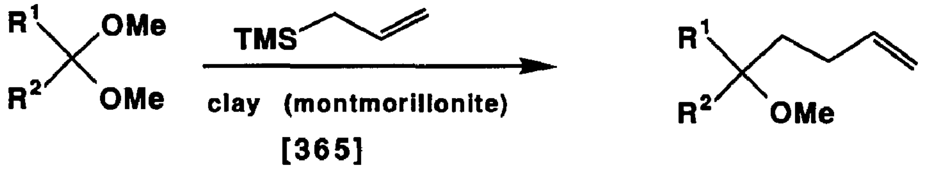


(421)

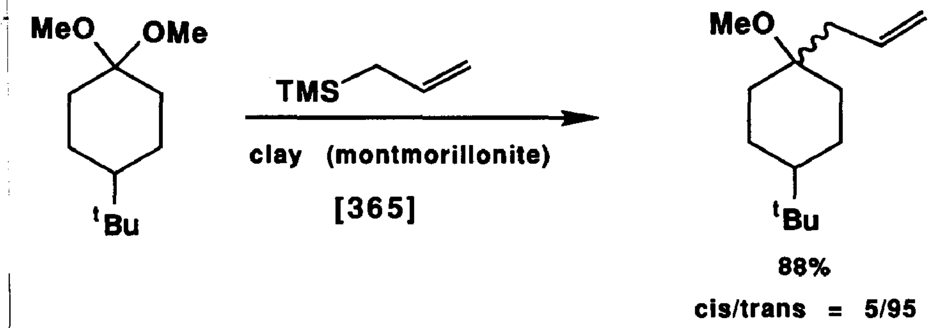


(422)

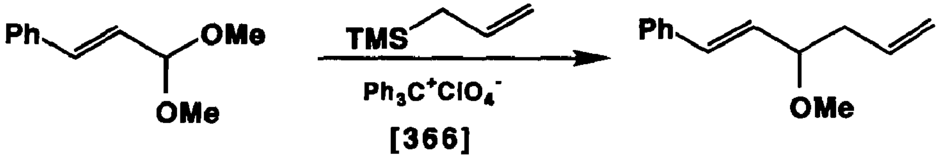
New methods for the allylation of acetals with allylsilanes continue to appear. The allylation of dimethyl acetals with montmorillonite, a solid acid catalyst, was reported. (Eqns. 423 and 424) Trityl perchlorate was emloyed as a catalyst for the allylation of the dimethyl acetals of α,β-unsaturated aldehydes. (Eqn. 425)



(423)

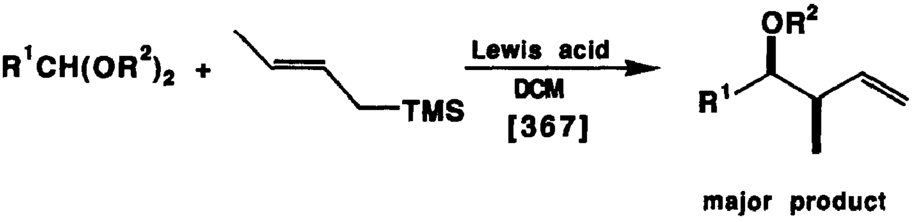


(424)

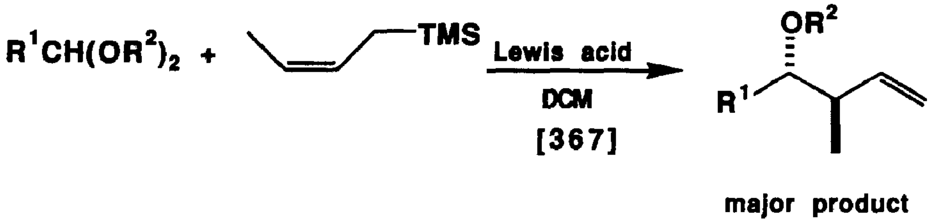


(425)

The allylation of acetals with crotylsilanes was investigated as to the stereoselectivity of the reaction. (Eqns. 426 and 427)

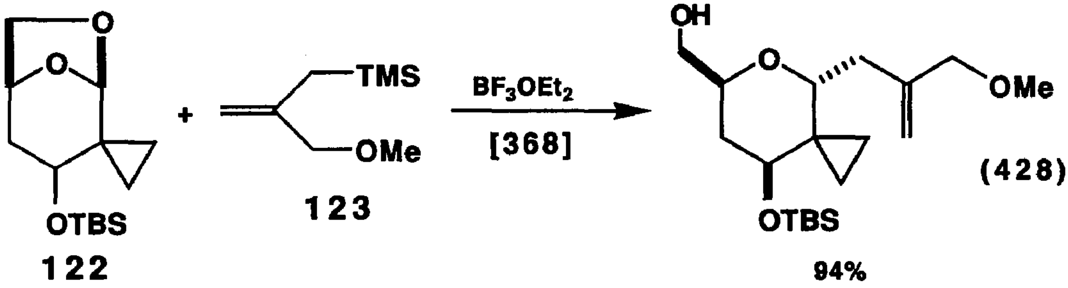


(426)

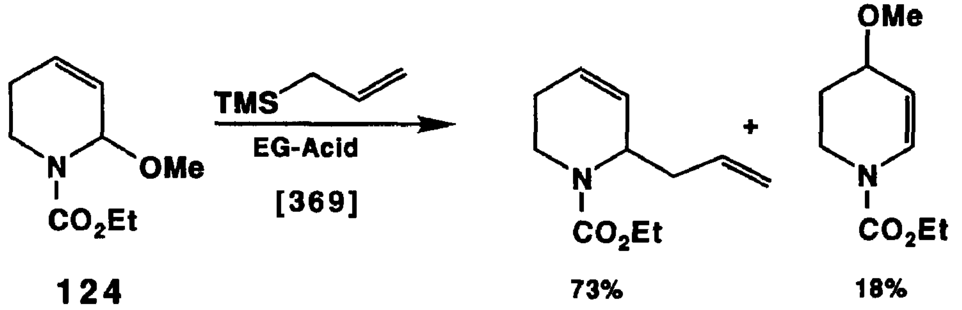


(427)

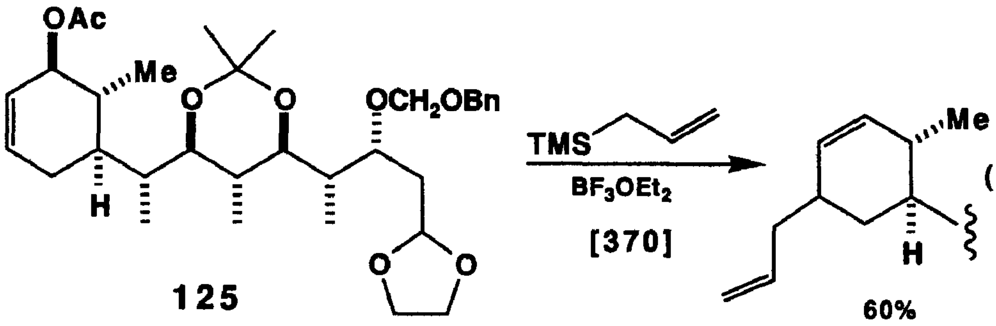
The ketal **122** was reacted with allylsilane **123** as shown in Eqn. 428. The allylation of a vinylogous acyl iminium ion generated from **124** occurs at the α-position. (Eqn. 429) The allylation of **125** with allyltrimethylsilane was used in the synthesis of zincophorin. (Eqn. 430)



(428)

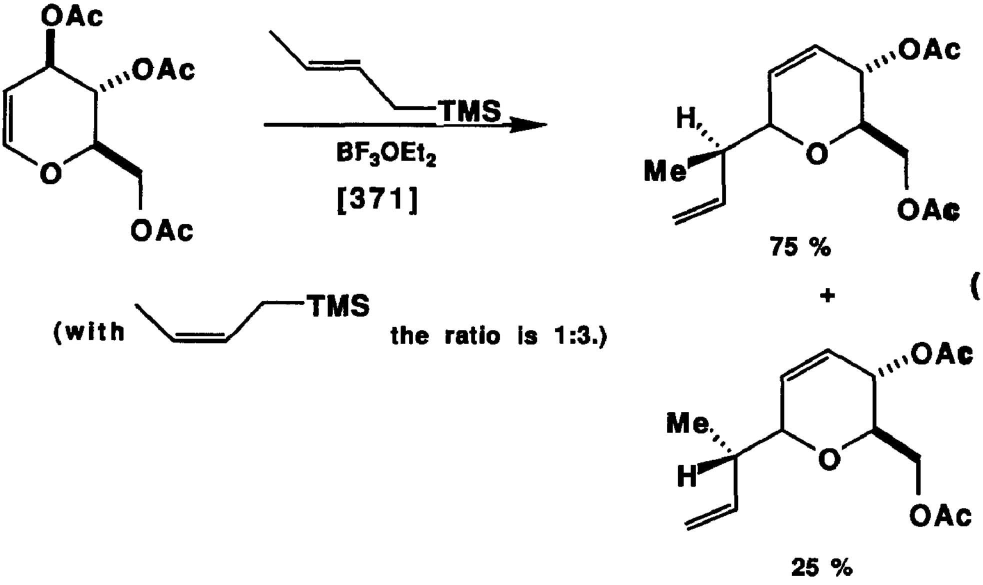


(429)



(430)

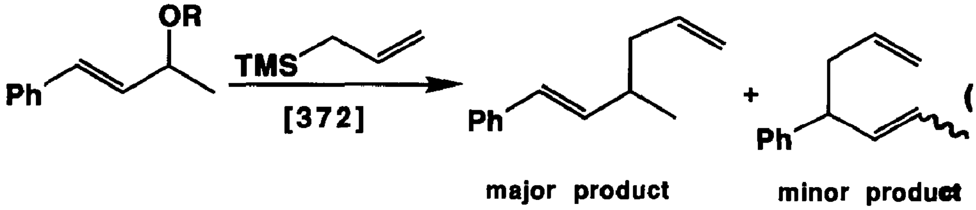
The stereochemistry of the allylation of activated glycol derivatives with (Z) and (E) crotylsilanes was studied. (Eqn. 431) Several other examples were looked at in this study.



(with [cis-crotyl-TMS] the ratio is 1:3.)

(431)

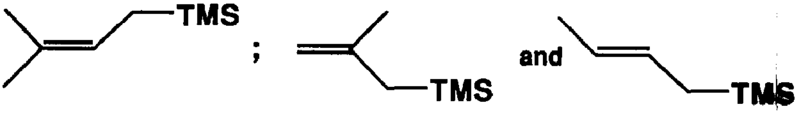
A ready synthesis of 1,5-dienes from allylsilanes and allyl ethers under the catalysis of trityl perchlorate was shown. (Eqn. 432)



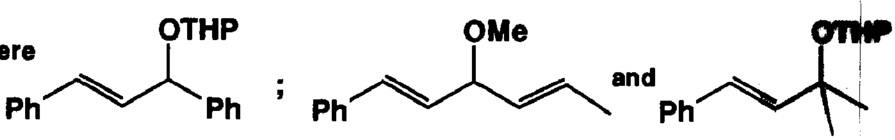
(432)

(R = Me, MeOCH$_2$, THP; 43-99%)

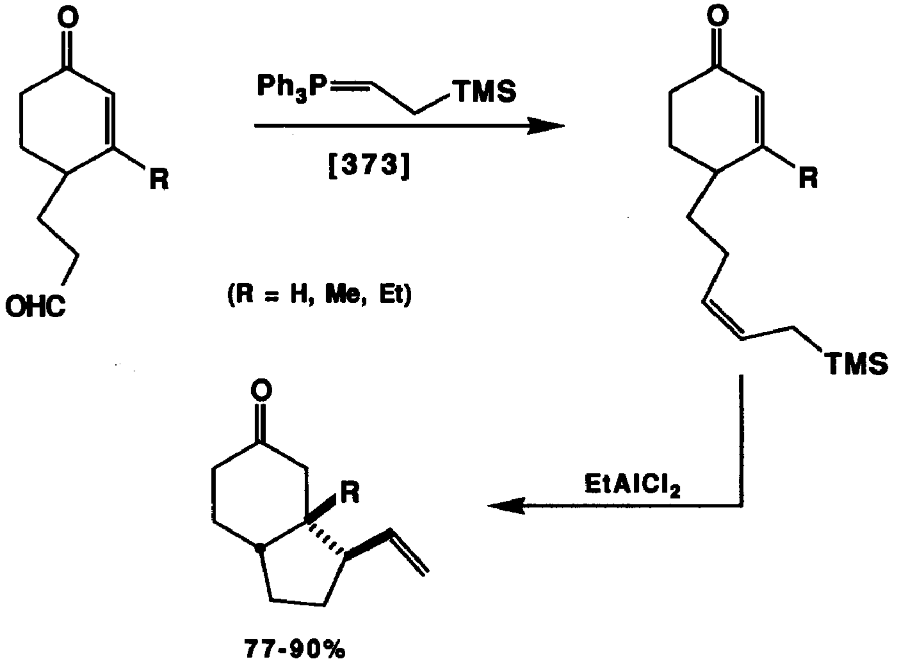
silanes also employed were



ethers also employed were

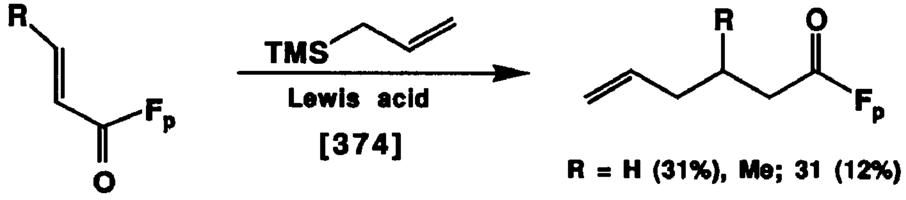


The intramolecular cyclization of an allylsilane and an enone was reported. (Eqn. 433)



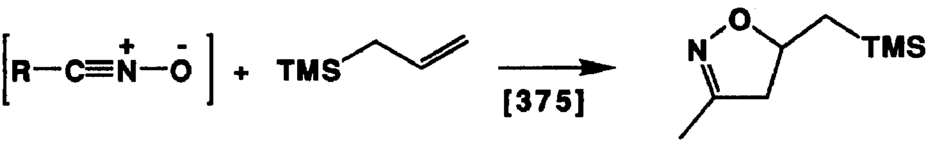
(433)

The reaction of allylstannanes and allylsilanes with unsaturated acyliron complexes was reported. The allylsilane reaction is shown in Eqn. 434.

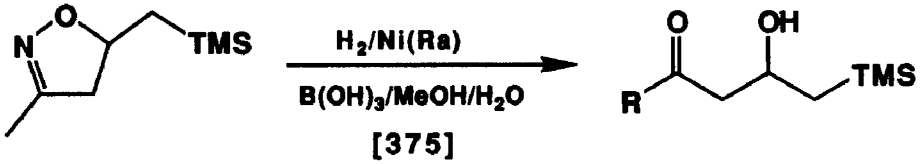


(434)

Allylsilanes react with nitrile oxides, generated 'in situ', to produce 4,5-dihydro-1,2-oxazoles. (Eqn. 435) These β-functional silanes were reduced and eliminated to provide β,γ-unsaturated ketones. (Eqns. 436 and 437) In similar chemistry α-chloro-oximes were reacted with allyltrimethylsilane to produce the dihydro-1,2-oxazine (Eqn. 438), which can be treated with acid to give γ,δ-unsaturated ketones (Eqn. 439), or reduced and eliminated to give 5-amino olefins (Eqn. 440).



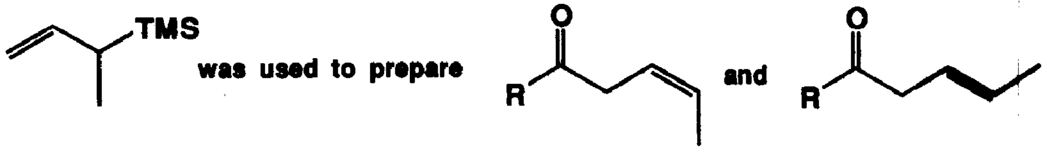
(435)

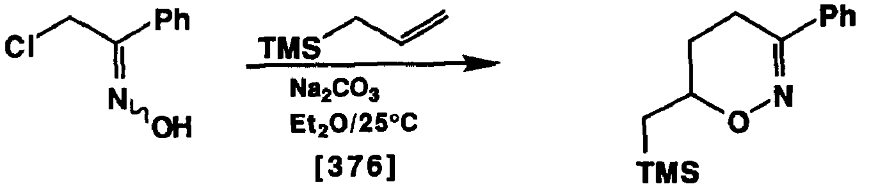


(436)

(437)

R = Ph, (100%); R = ^{t}Bu (77%)





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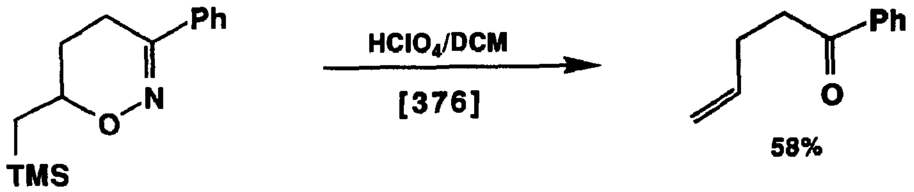
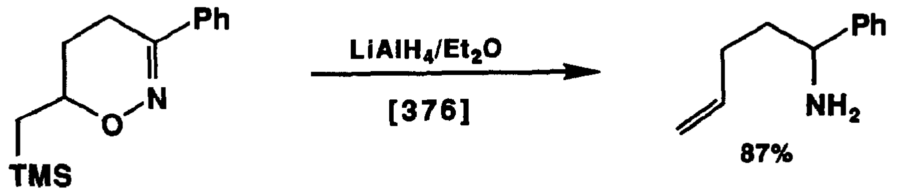
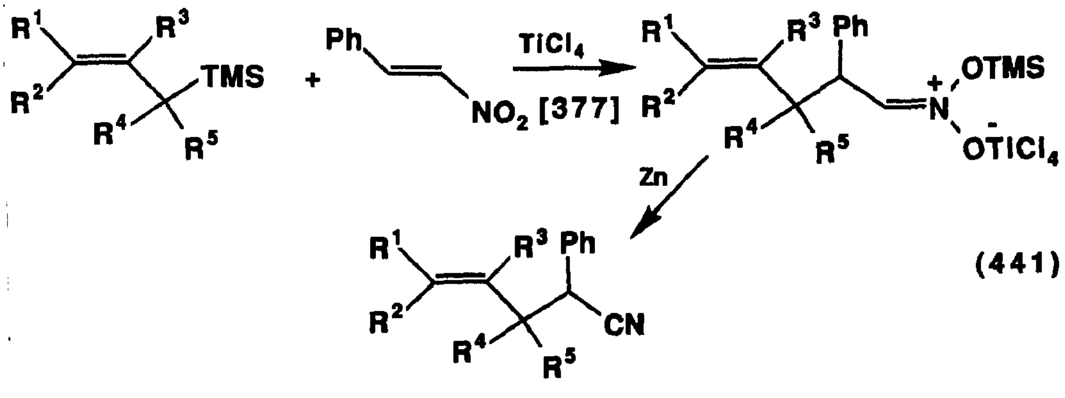


(439)



(440)

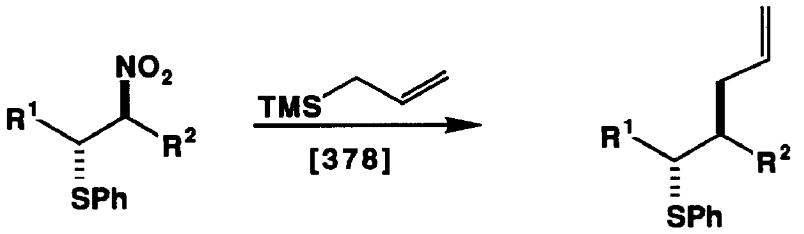
The reaction of allylsilanes with β-nitrostyrene in the presence of titanium tetrachloride followed by reduction with zinc metal provides α-phenylhomoallyl nitriles. (Eqn. 441)



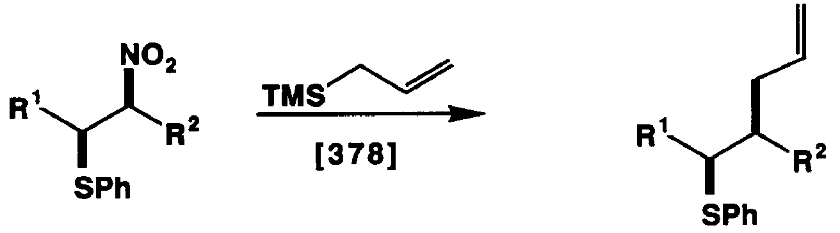
(441)

9 examples; 0-69%

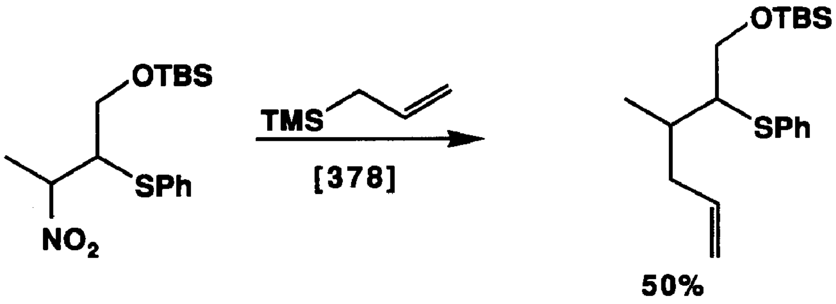
The direct allylation of β-nitro sulfides with allylsilanes occurs *via* the episulfonium ion to replace the nitro group. (Eqns. 442, 443 and 444)



(442)

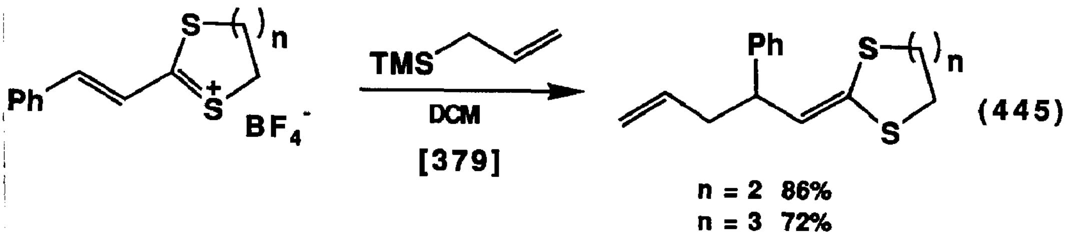


(443)

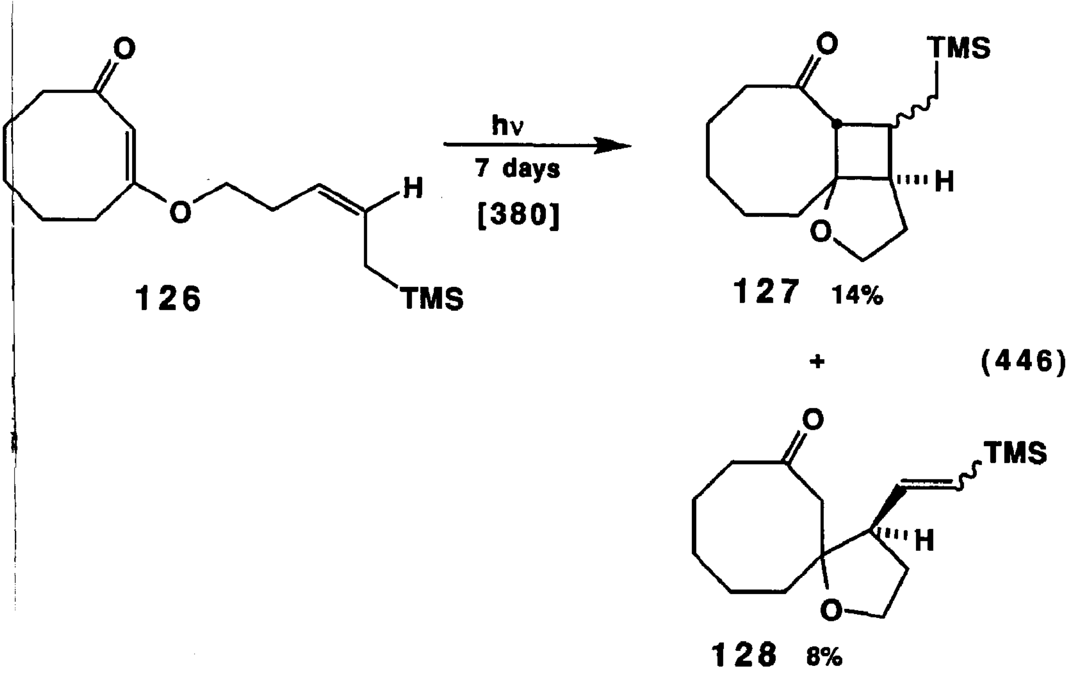


(444)

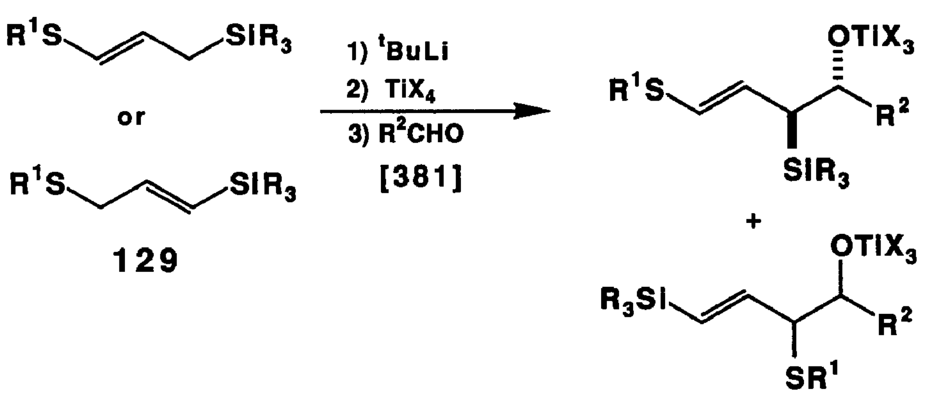
Ketene dithioacetals react with allylsilanes in the presence of trityl tetrafluoroborate to give allylation. (Eqn. 445) This reaction works with enol silyl ethers as well as with allylsilanes.



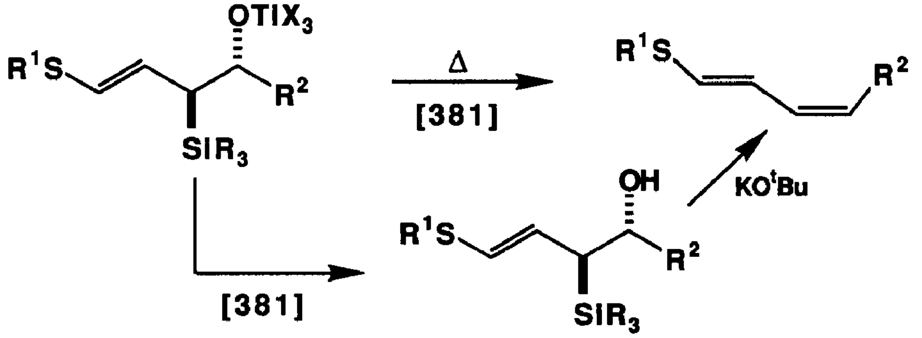
The allylsilane **126** was subjected to photochemical cyclization to produce **127** and **128**. (Eqn. 446)



Lithiation of **129** followed by treatment of the lithium reagent with titanium tetrachloride and then reaction of the titanium reagent with aldehydes leads to β-alkoxysilanes, which can be converted to (Z) or (E) dienyl sulfides. (Eqns. 447, 448 and 449)



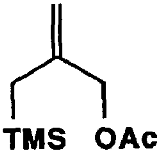
(447)



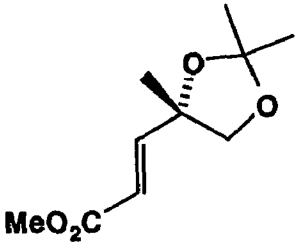
(448)

(449)

The reaction of allylsilanes of the type **130**, which react with palladium(0) to form a palladium complex of trimethylenemethane, were utilized in a number of cyclizations wherein the allylsilane provides a three carbon unit in these cyclizations. The mechanism of the cycloaddition reactions was studied and it was found that the reactivities paralleled those of the Diels-Alder reaction with the same substrates, namely structures **131** and **132**. The reaction of the trimethylenemethane palladium complex with aldehydes was reported. This gives methylene tetrahydrofurans in good yield. (Eqns. 450 and 451) The reaction with oxocyclohexenones provides methylene-oxobicyclononanones. (Eqn. 452) The reaction with activated norbornadienes followed by flash vacuum pyrolysis gives exo-methylenecyclopentenes. (Eqn. 453)



130



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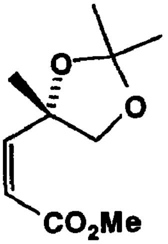

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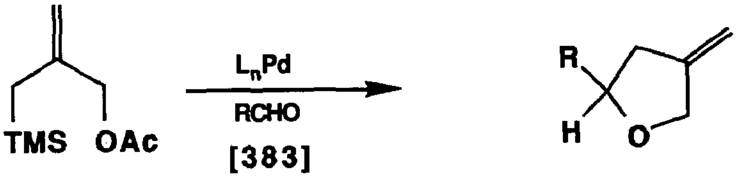
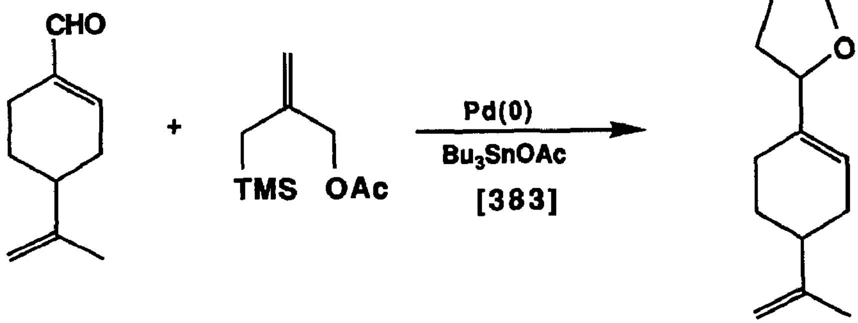
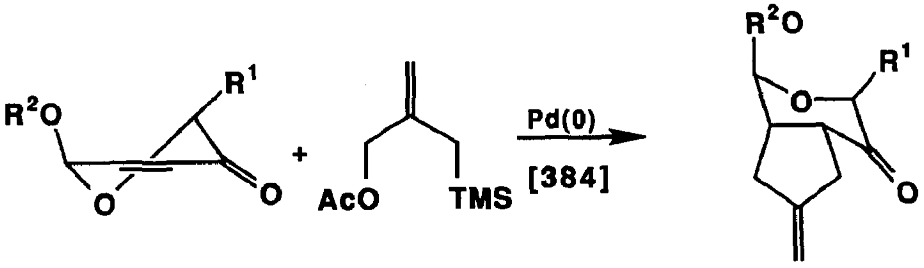


(450)

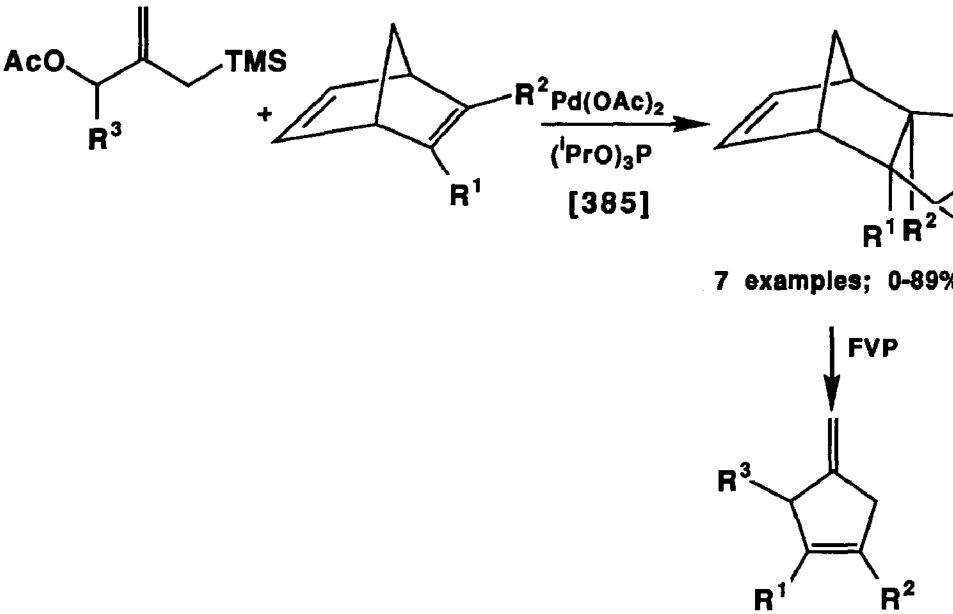


(451)



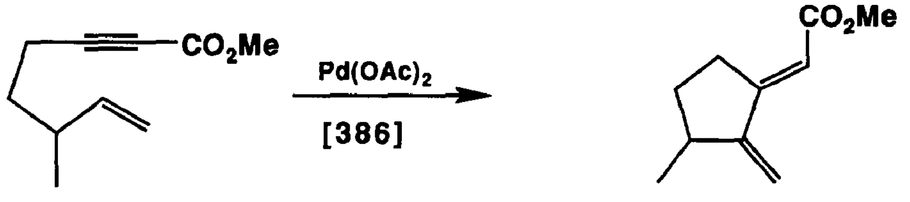
(452)

R^1 = H, R^2 = Et; 25%
R^1 = ^{i}Pr, R^2 = TBS; 94%



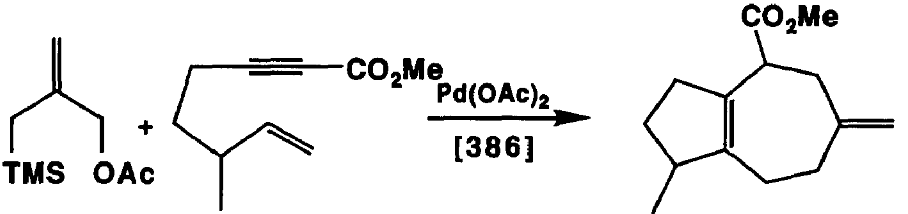
(453)

The reaction of 1,6-enynes with palladium(II) results in the cyclization to dialkylidenecyclopentanes. (Eqn. 454) This same reaction in the presence of allyl[illegible] 130, however, gives fused polyhydroazulenes. (Eqn. 455)



83%

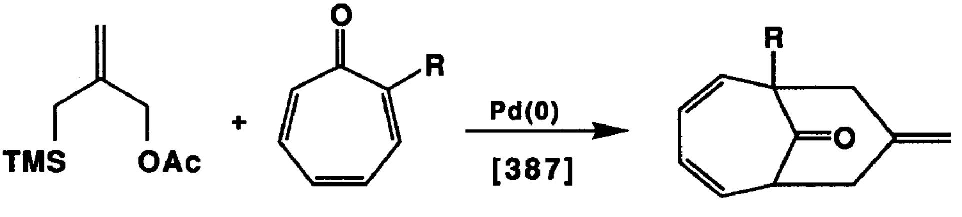
(454)



130

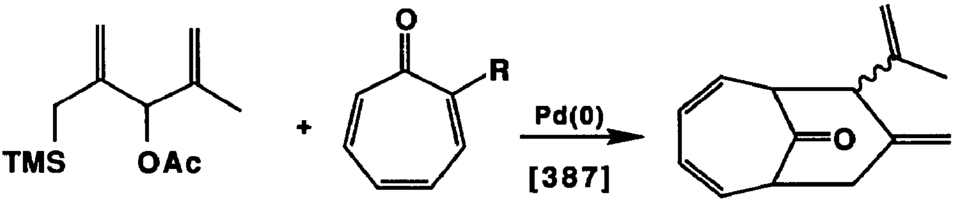
(455)

The reagent **130** was employed along with palladium(0) in a [6+3] cycloaddition reaction with cycloheptatrienones. (Eqn. 456) An extension of this cycloaddition is shown in Eqn. 457.



(456)

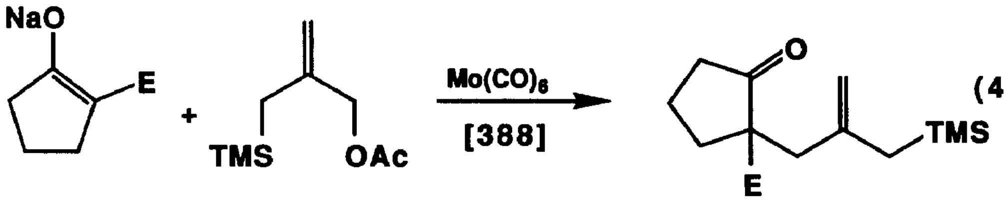
R = H (68%), Me (74%), OMe (41%)



(457)

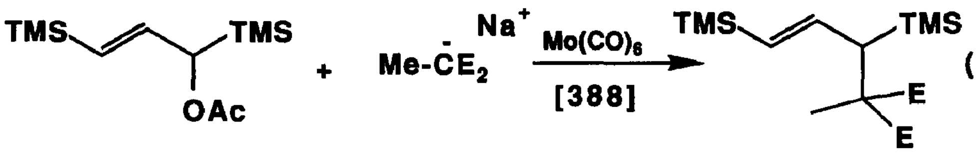
81%

The reaction of **130** with sodium enolates of 1,3-dicarbonyl systems with molybdenumhexacarbonyl catalysis results in the direct substitution of the acetate group without protodesilylation as is seen with palladium. (Eqns. 458 and 459)



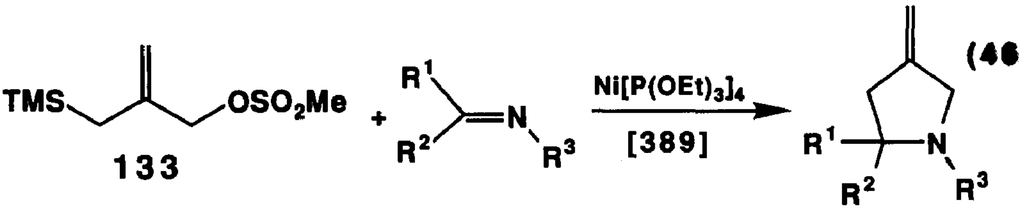
(458)

130



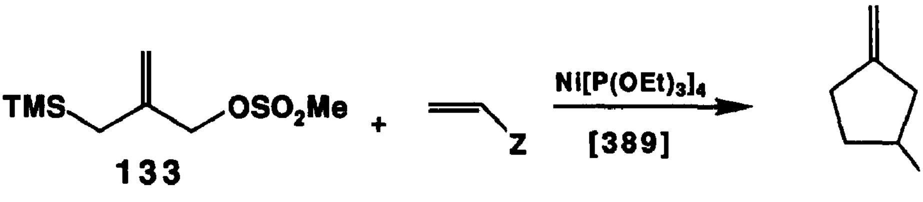
(459)

A nickel catalyzed [3+2] cycloaddition of allylsilane **133** with imines was reported. (Eqns. 460 and 461)



(460)

10 examples; 19-77%

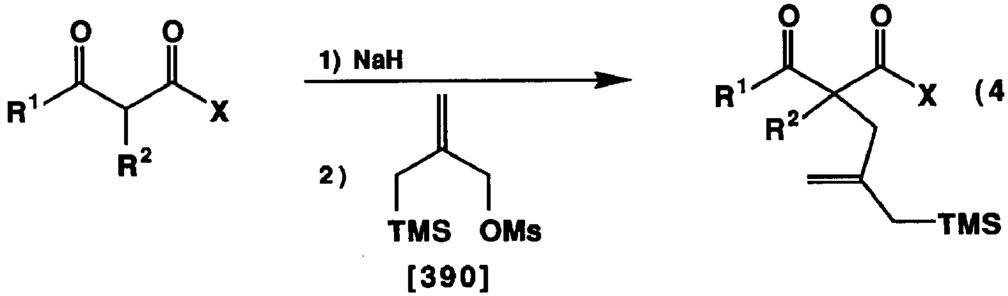


(461)

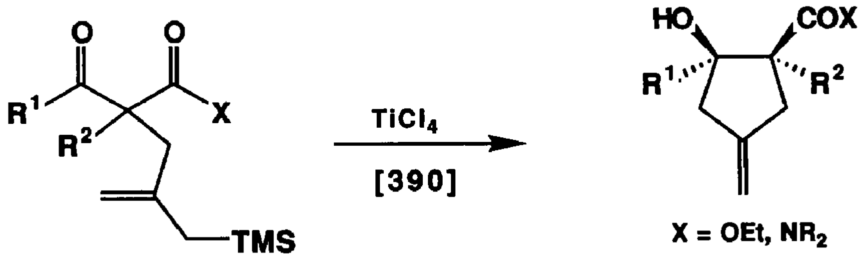
Z = electron witdrawing group

4 examples; 50-87%

This same reagent was employed in the reaction with sodium enolates of 1,3-dicarbonyl systems and the resulting substitution product cyclized with titanium chloride. (Eqs. 462 and 463)



(462)

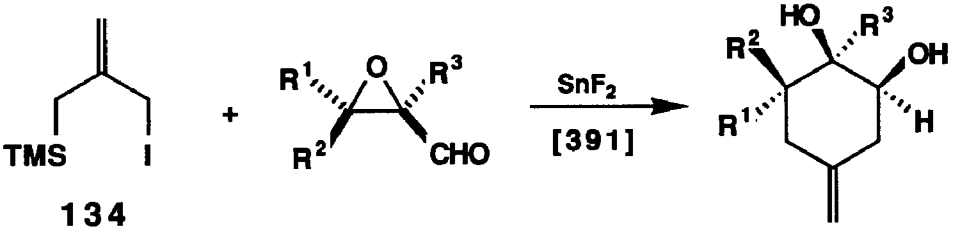


(463)

X = OEt, NR$_2$

X = OEt (8 examples; 65-88%)
X = NR$_2$ (R = Et or Me 5 examples; 56-100%)

Allylsilane **134** was shown to undergo [3+3] cycloadditions with α,β-epoxy aldehydes under the catalytic influence of tin difluoride. (Eqn. 464) The reaction of this same reagent under the same general conditions with 1,4-diketones, dialdehydes, or keto aldehydes produces the products of a [4+3] cycloaddition. (Eqn. 465)

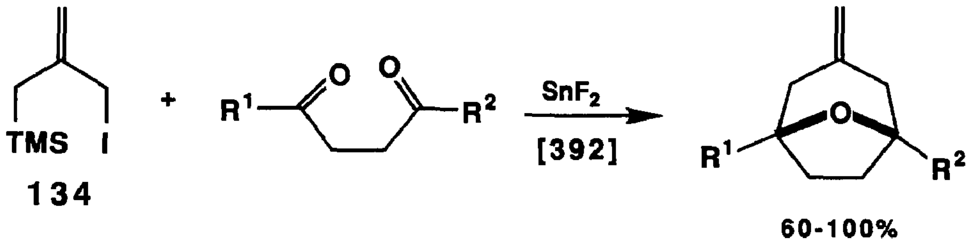


134

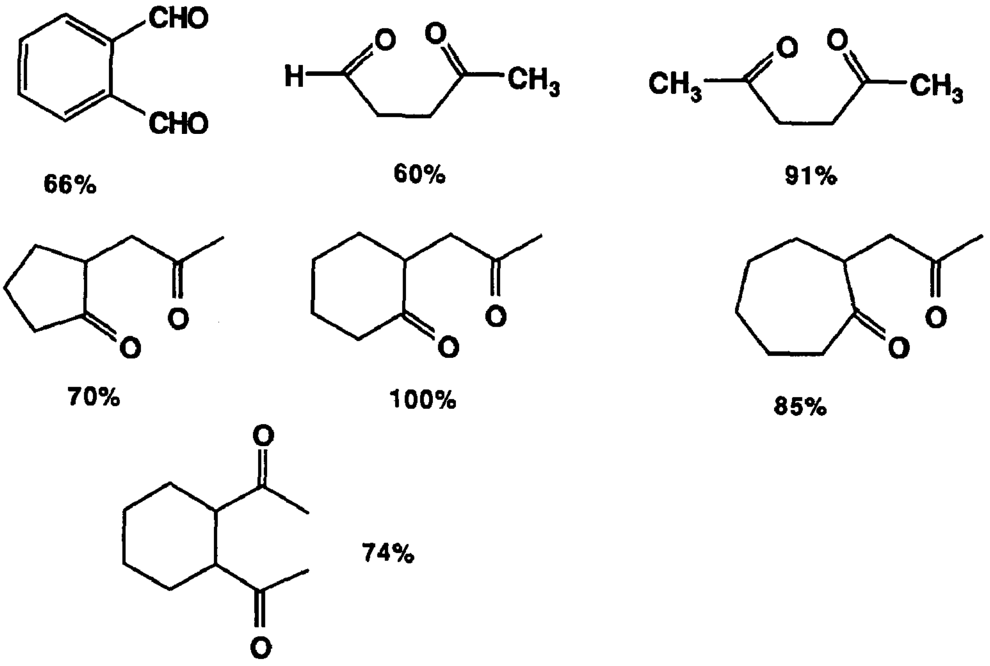
(464)

major diastereomer

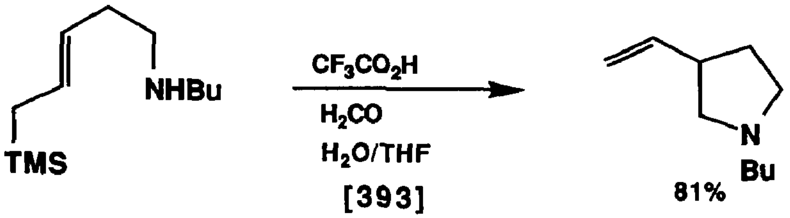
8 examples; 0-67%
diastereomeric ratio 4:1 to 50:1



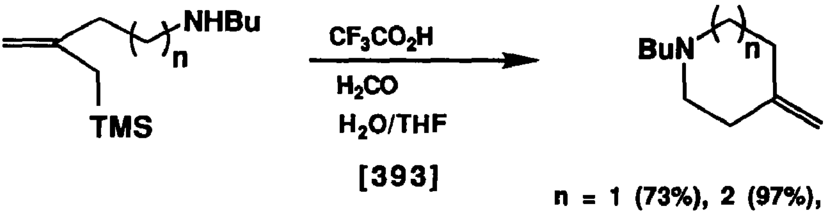
(465)



The acid catalyzed cyclization of amino allylsilanes to vinylated azacycles was reported. The yields are good. (Eqns. 466 and 467)



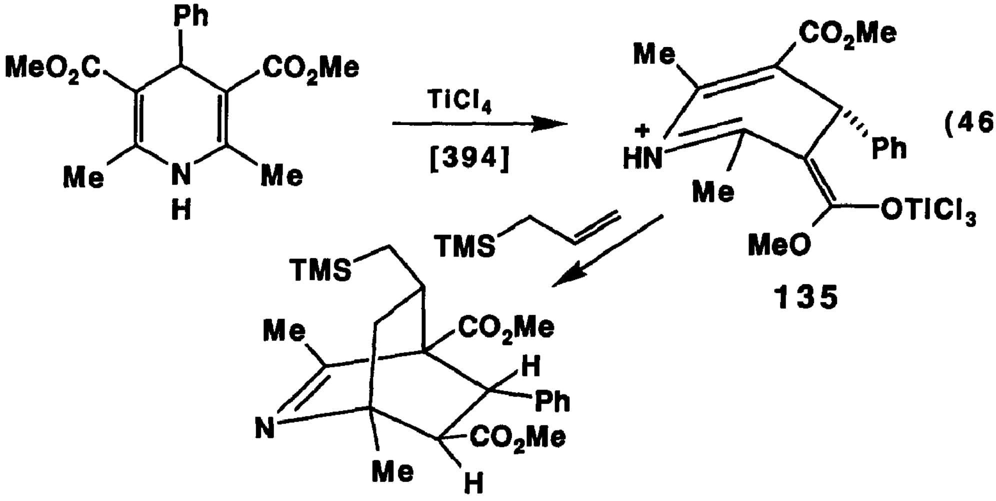
(466)



n = 1 (73%), 2 (97%), 3 (64%)

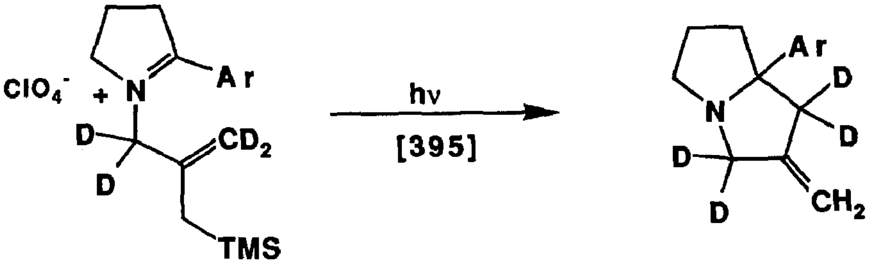
(467)

The reaction of iminium ions with allylsilanes continues to be studied. Treatment of dimethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate with allyltrimethylsilane in the presence of titanium tetrachloride or boron trifluoride etherate proceeds *via* the intermediate **135** and without loss of the silyl group. (Eqn. 468) The mechanism of the photochemical intramolecular cyclization between allylsilanes and iminium ions was studied. (Eqn. 469) The reaction appears to proceed through a duality of mechanisms which differ in the timing of the cleavage of the silicon-carbon bond. As part of a study involving reactions of allenylsilanes and propargylsilanes with iminium ions, 2-methylcrotyltrimethylsilane was reacted with 2-phenyliminium perchlorate. (Eqn. 470)

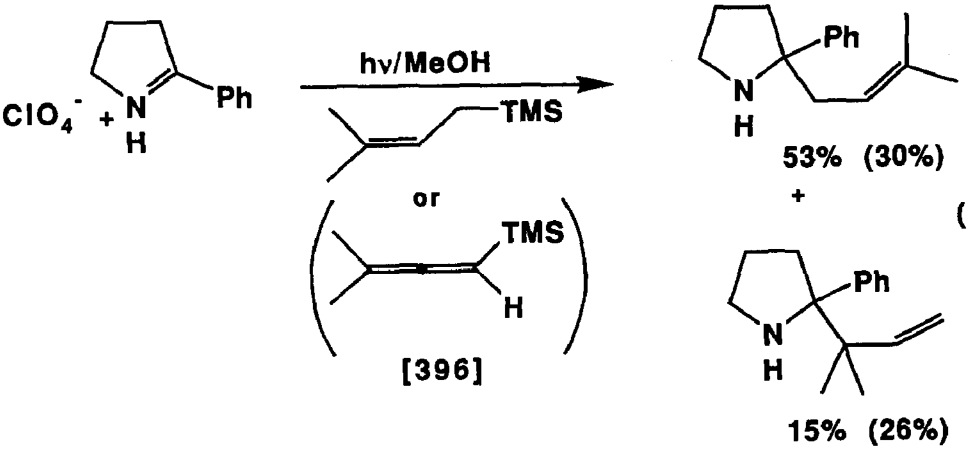


135

(468)

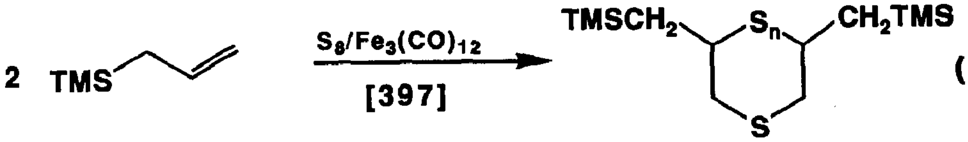


(469)



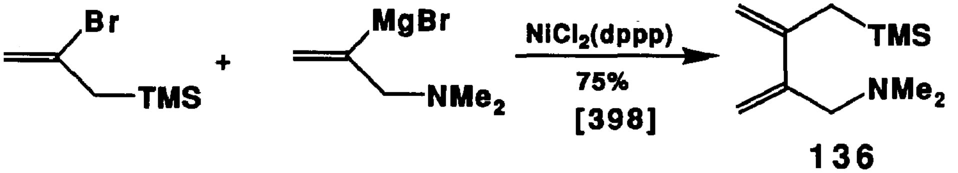
(470)

The reaction of allyltrimethylsilane with elemental sulfur in the presence of triirondodecacarbonyl is shown in Eqn. 471.



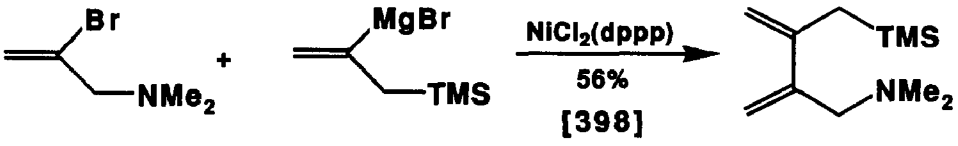
(471)

2-Bromoallyltrimethylsilane was coupled with the Grignard reagent of (2-bromoallyl)dimethylamine to give diene **136**. (Eqn. 472) This material was also prepared in the reverse manner. (Eqn. 473) The resulting diene was cycloadded to various dienophiles giving rise to allylsilanes of the type **137**, which were further employed as precursors to dienes for cycloadditions. (Eqns. 474 and 475)



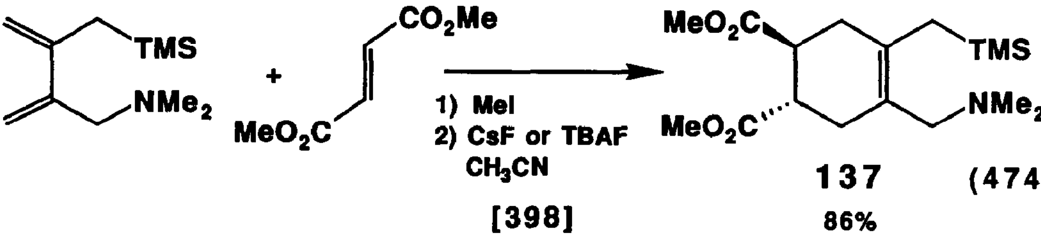
136

(472)

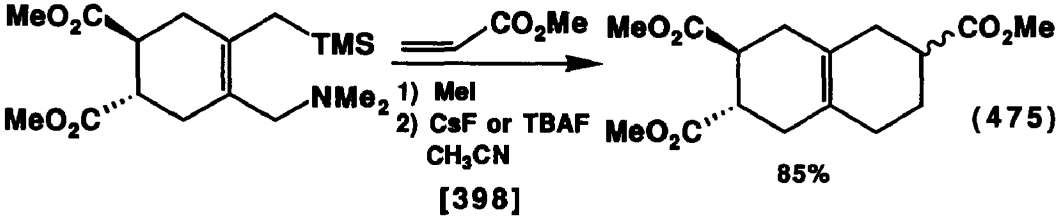


136

(473)

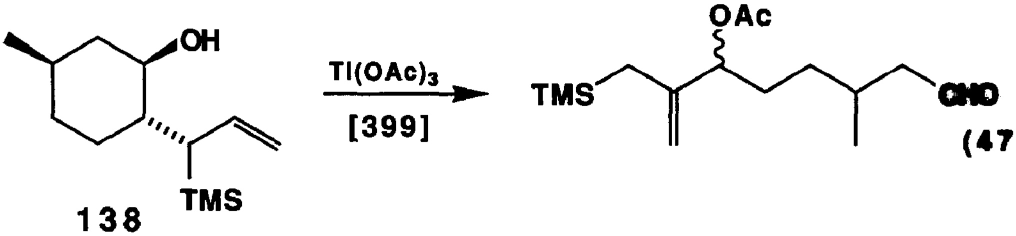


(474)



(475)

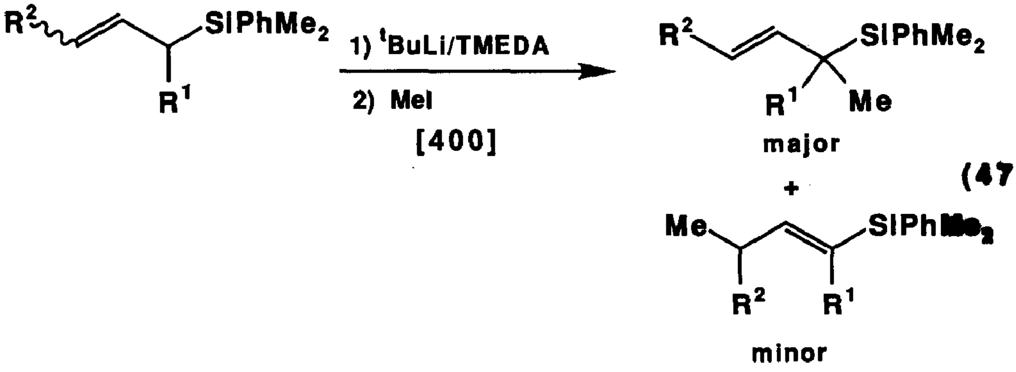
Reaction of allylsilane **138**, derived from isopulegol, with thallium triacetate results in oxidative ring opening with no loss of the trimethylsilyl group. (Eqn. **476**)



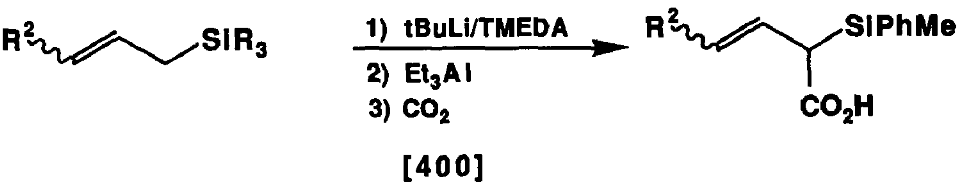
138

(476)

The deprotonation-alkylation of allylphenyldimethylsilanes was reported. The major product is the allylsilane from alkylation at the α-position. (Eqn. 477) The reaction of the initial lithium reagent with triethylaluminum and then carbon dioxide gives the (E) allylsilane. (Eqn. 478) Deprotonation of allyldimethyl(diisopropylamino)-silane with butyllithium followed by treatment with zinc chloride and then an aldehyde and oxidation gives allylic diols in good yields. (Eqns. 479 and 480) Another example of deprotonation of allylsilanes was shown previously in Eqns. 447 through 449.

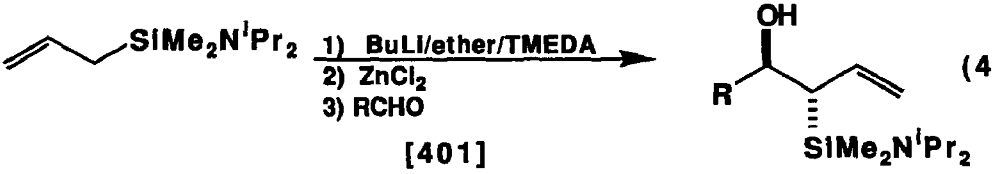


(477)



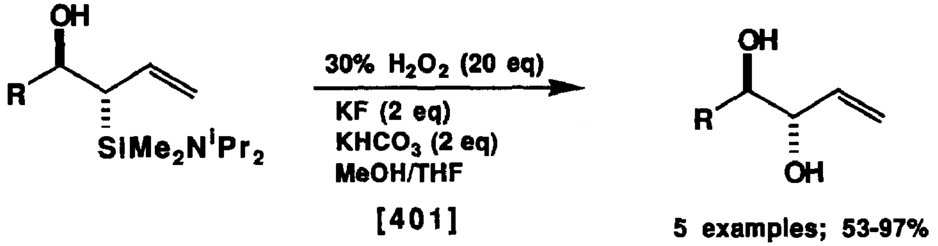
(478)

R_3Si = TMS, Ph_3Si, $PhMe_2Si$, Ph_2MeSi, $ViMe_2Si$, p-$C_6H_4Me_2Si$, $^tBuMe_2Si$)



(479)

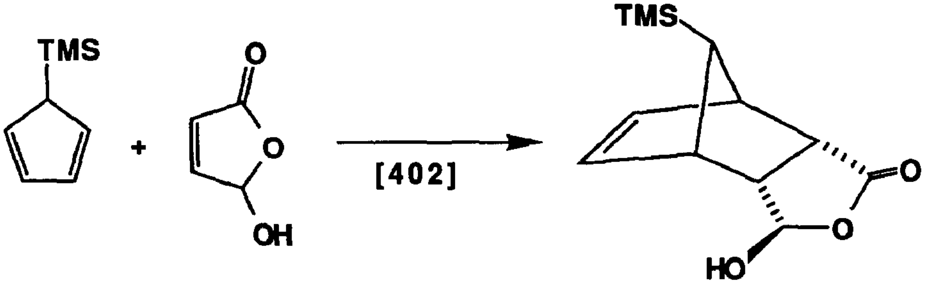
5 examples; 61-93%



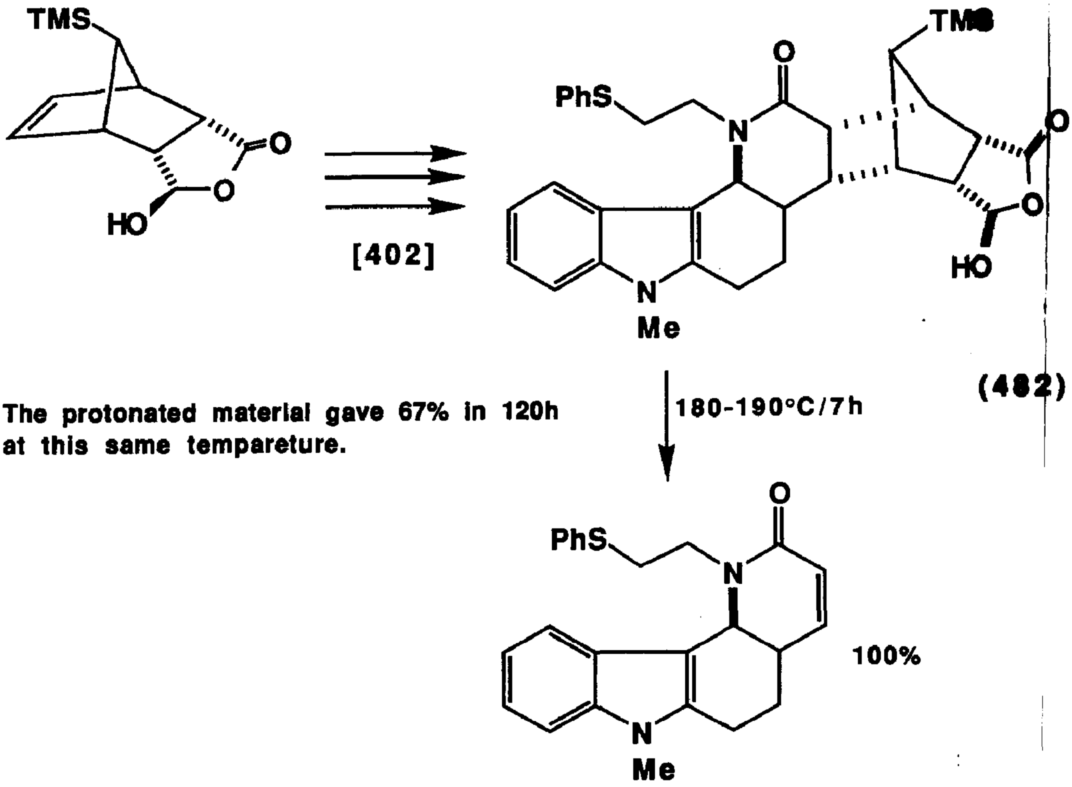
(480)

5 examples; 53-97%

Trimethylsilylcyclopentadiene was reacted with maleic anhydride and the cycloadduct shown to be more reactive in a retro-Diels-Alder reaction due to the β-effect of the trimethylsilyl group. (Eqns. 481 and 482)



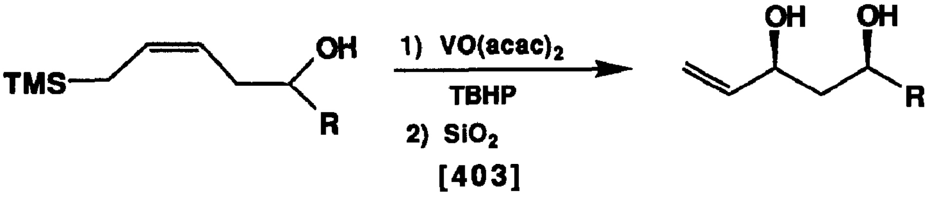
(481)



(482)

The protonated material gave 67% in 120h at this same tempareture.

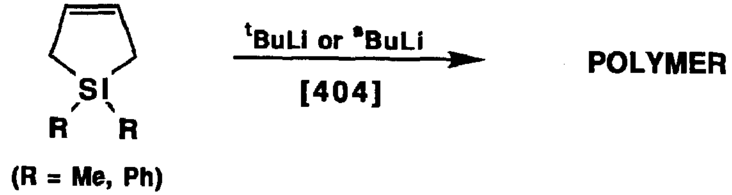
The epoxidation of homoallylic allylsilanes followed by treatement with silica gel to eliminatively open the β,γ-epoxysilane gives rise to vinylated 1,3-diols in a stereoselective manner. (Eqn. 483)



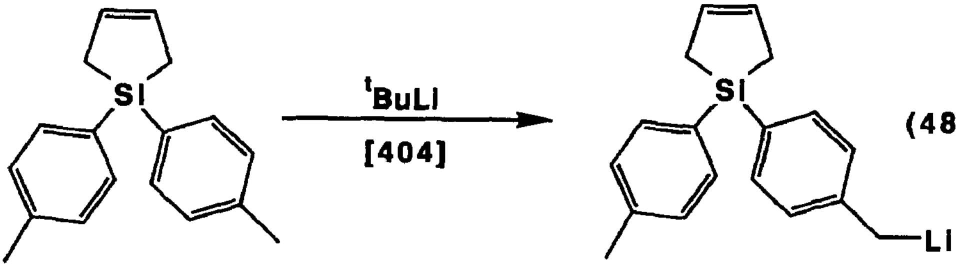
(483)

(R = Me, CH_2CH_2OBn, CH_2CH_2OAc, CH_2CO_2Bn)
erythro:threo = 83:17 to 97:3

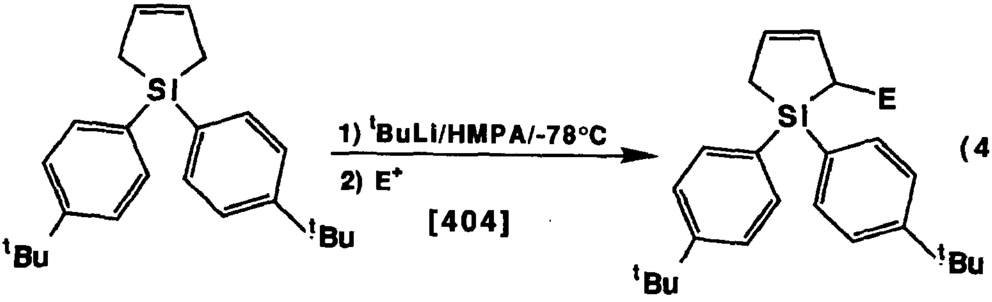
Deprotonation of 1,1-dimethyl-1-silacyclopent-3-ene leads to polymer. (Eqn. 484) On the other hand the di-p-tolyl derivative undergoes deprotonation on the aryl methyl group. (Eqn. 485) The di-p-tert-butylphenyl derivative undergoes deprotonation at the allylic position without polymerization. A number of electrophiles were reacted with this interesting lithium reagent. (Eqn. 486)



(484)



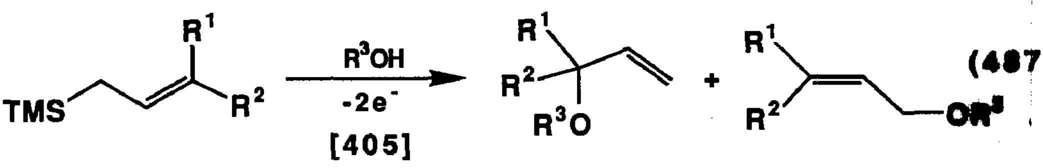
(485)



(486)

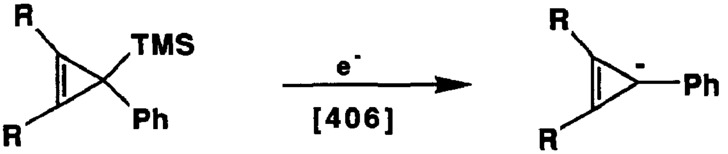
24 examples; 42-77%: for example,
E = Me_3Si (71%), Et_3Si (57%), Pr_3Si (59%),
$^iPr_3Si$ (71%)

The reaction of allyltrimethylsilanes with alcohols under electrolytic oxidation gives allyl ethers, although with low regioselectivity. (Eqn. 487)



(487)

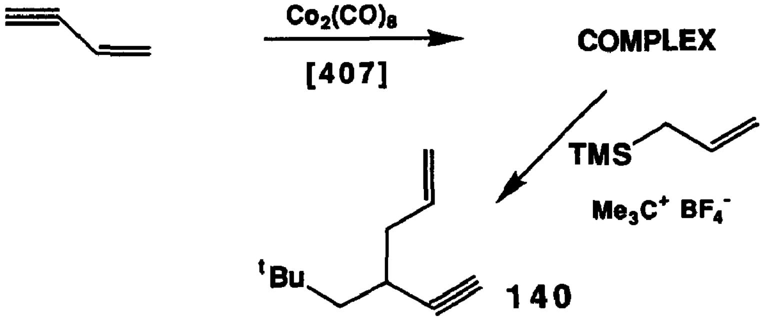
The gas phase acidity of triphenylcyclopropene was measured by generating the anion from allylsilane 139. (Eqn. 488)



139

(488)

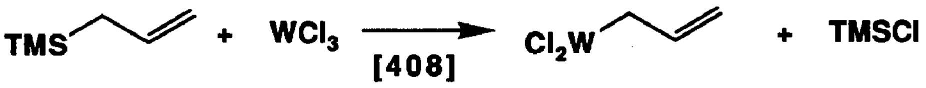
Allyltrimethylsilane was reacted with the complex formed between dicobalt octacarbonyl and vinylacetylene in the presence of tert-butyl tetrafluoroborate as catalyst to give neopentyl enyne 140. (Eqn. 489)



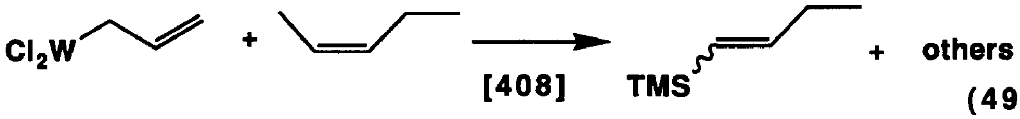
140

(489)

Allyltrimethylsilane reacts with tungsten trichloride to give trimethylchlorosilane and an allyltungsten intermediate, which was reacted with olefins to give other allylsilanes. (Eqns. 490 and 491) This sequence amounts to a metathesis of allylsilanes. The reactions proceed better with an added cocatalyst such as aluminum trichloride or tetramethyltin.

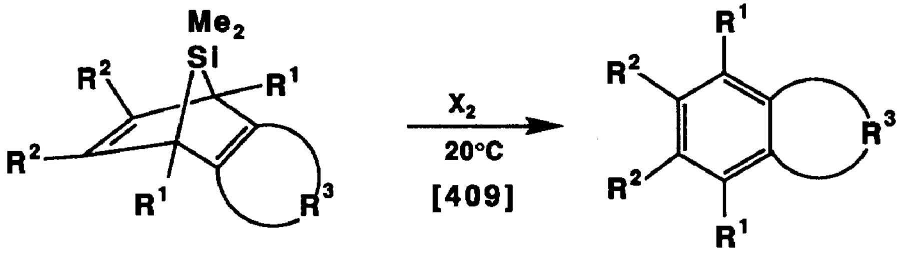


(490)

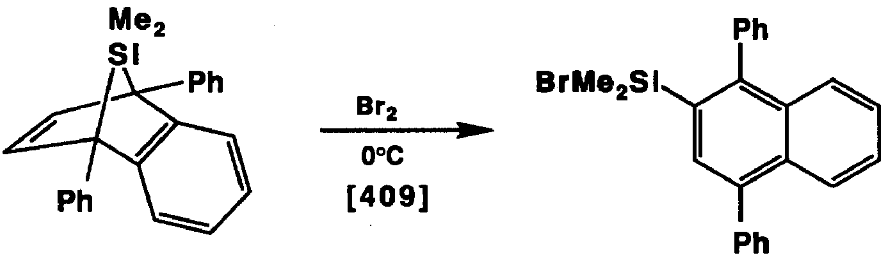


(491)

The reaction of 7-silanorbornadienes produces aromatic systems *via* an addition elimination process. (Eqns. 492 and 493)



(492)

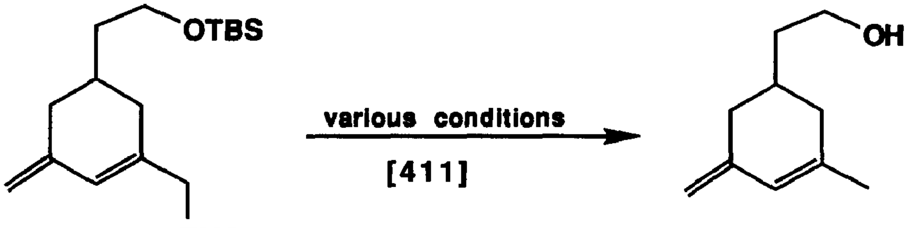


(493)

C. Allylsilanes-Other Studies

The relative rates of reaction towards diphenylmethyl carbocation and di-(p-tolyl)methyl carbocation were measured. Allyltrimethylsilane proved to be some 30,000 times more reactive than propene and even more reactive than a 1,1-disubstituted olefin, but less reactive than trisubstituted olefins. The data is shown below. [410] It was found that a variety of reaction conditions employed to deprotect the tert-butyldimethylsilyl group in **141** resulted in the loss of the trimethylsilyl group from the pentdienylsilane unit. The diphenylmethylsilyl group, however, was much more stable. (Eqn. 494)

Ph_2CH^+	1.00	4.45	89.9	1.45×10^{-4}
$p\text{-}Tol_2CH^+$	1.00	5.56	81.7	

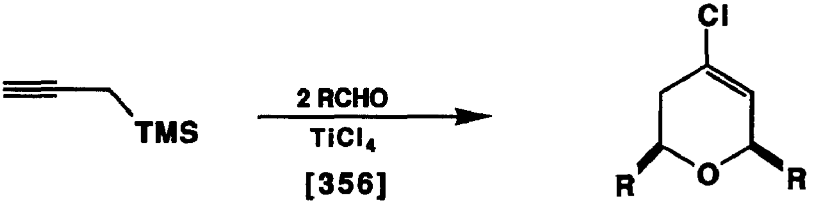


141

(494)

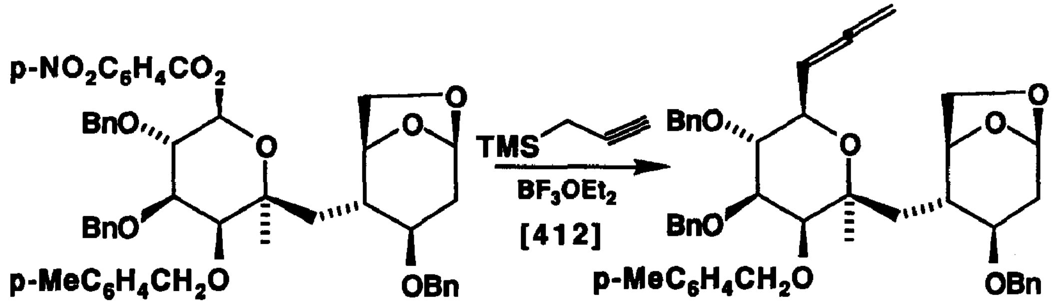
X. Propargylsilanes

Propargyltrimethylsilane was reacted with aldehydes in the presence of titanium tetrachloride as catalyst to give 4-chlorodihydropyrans. (Eqn. 495)

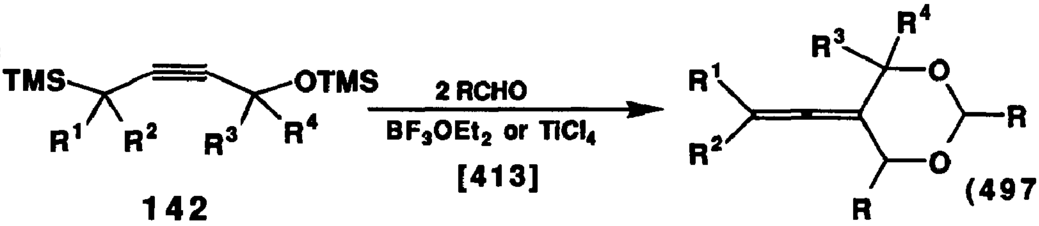


(495)

Propargyltrimethylsilanes were reacted with glycosides to give the allenyl substituted glycosides. (Eqn. 496) The bis trimethylsilylated butynols 142 were reacted with two equivalents of an aldehyde to produce 5-vinylidene-1,3-dioxanes. (Eqn. 497)

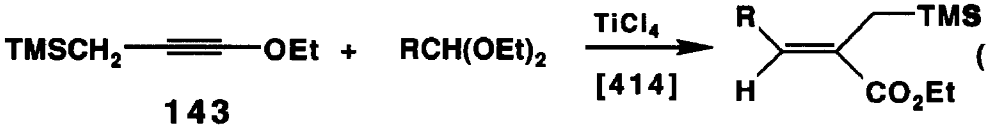


(496)



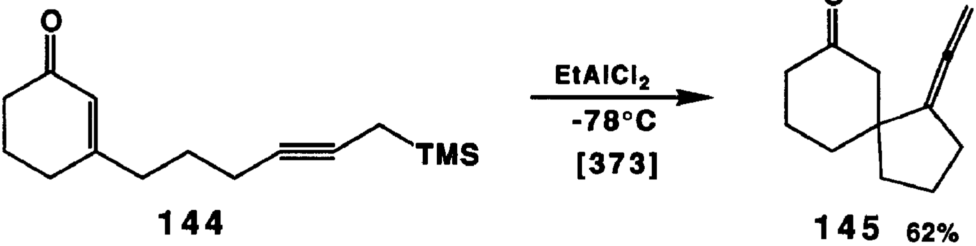
(497)

1-Ethoxypropargylsilane **143** reacts with acetals under Lewis acid catalysis to give α-trimethylsilylmethyl-α,β-unsaturated esters. (Eqn. 498) This reagent was also reacted with aldehydes, ketones and ketals.



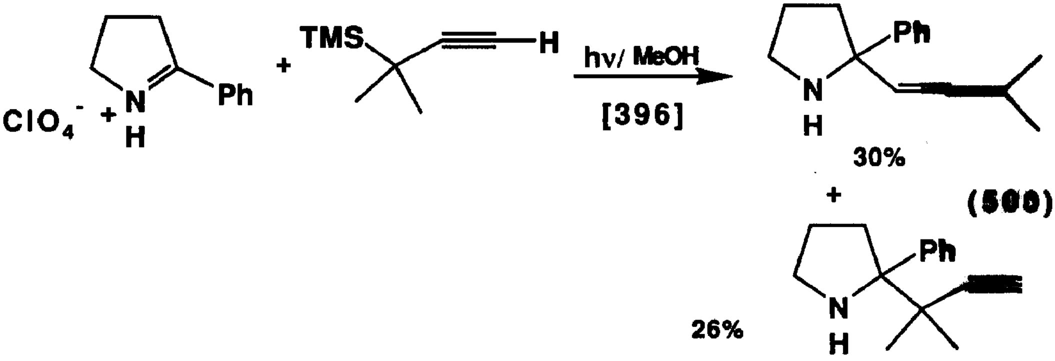
(498)

The propargylsilane **144** reacts intramolecularly to form spiro ketone **145**. (Eqn. 499)

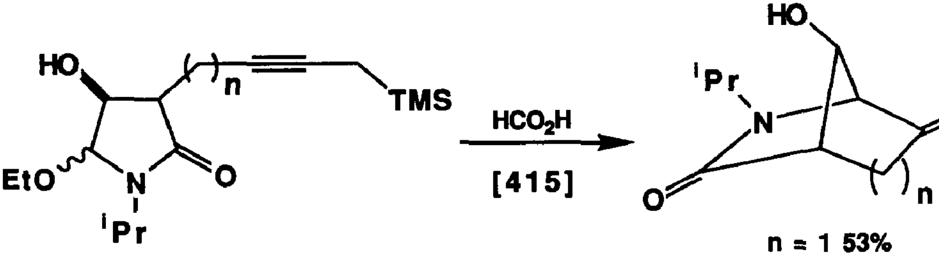


(499)

The photochemical reaction of propargyltrimethylsilane with 2-phenylpyrrole iminium perchlorate, gives a mixture of the propargyl and allenyl products. (Eqn. 500) The acid catalyzed cyclization of propargylsilanes **146** via an 'in situ' generated iminium ion was reported. (Eqn. 501)



(500)

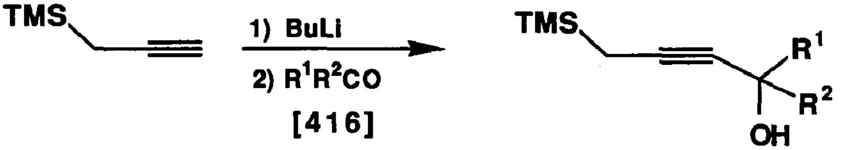


146

(501)

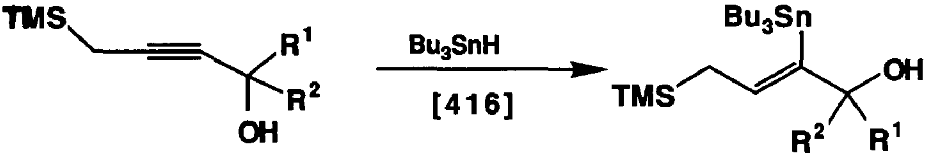
n = 1 53%
n = 2 87%
n = 3 53%

Propargyltrimethylsilane was converted to 1-trimethylsilylated propargyl alcohols. (Eqn. 502) These were in turn hydrostannylated to give β-hydroxyvinyltin systems **147** (Eqn. 503), which were acetylated and then treated with fluoride ion to provide 2-stannyl-1,3-butadienes (Eqn. 504).



(502)

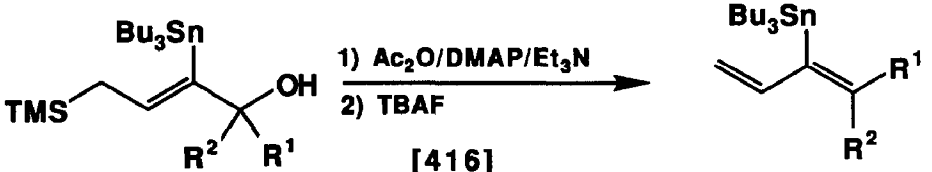
8 examples; 62-89%



147

(503)

8 examples; 59-75%

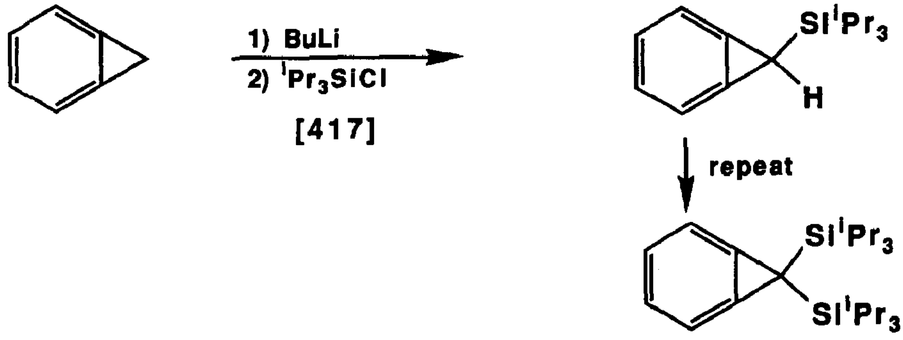


(504)

4 examples; 41-65%

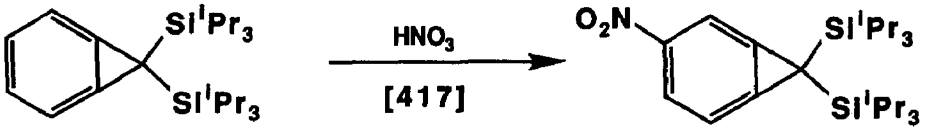
XI. BENZYLSILANES

The bis(triisopropylsilyl)cyclopropabenzene **148** was prepared as shown. (Eqn. 505) This material was nitrated to give **149**; (Eqn. 506) reduction of the nitro system with lithium aluminum hydride gave the diazo system **150**. (Eqn. 507) Reduction with zinc in base gives the correspnding aniline.



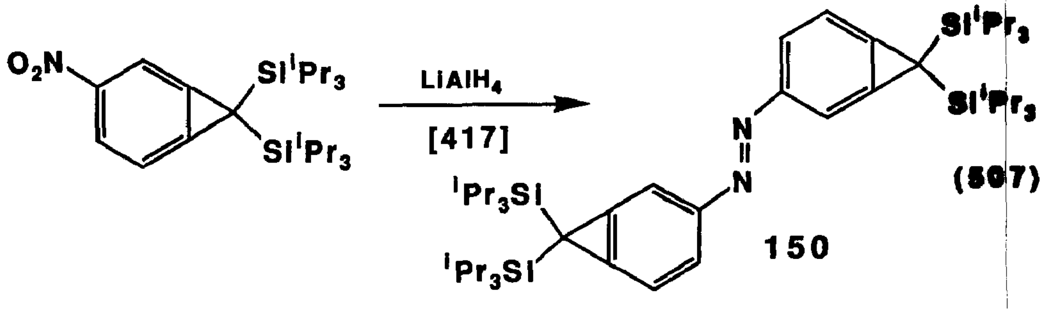
148

(505)



(506)

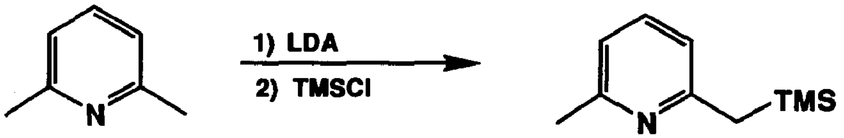
149 58%



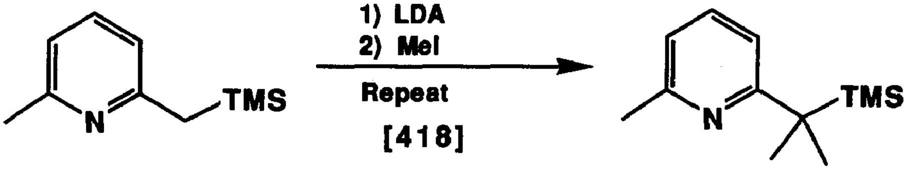
150

(507)

The deprotonation silylation of 2,6-dimethylpyridine gives the corresponding benzylsilane (Eqn. 508), which is selectively deprotonated on the carbon containing the methylsilyl group; methylation of the anion gives **151** in an overall 52 percent yield. (Eqn. 509) This material was rearranged and then reduced to **152**. Compound **152** was converted to the pheromone of the Comstock mealybug. (Eqn. 510)

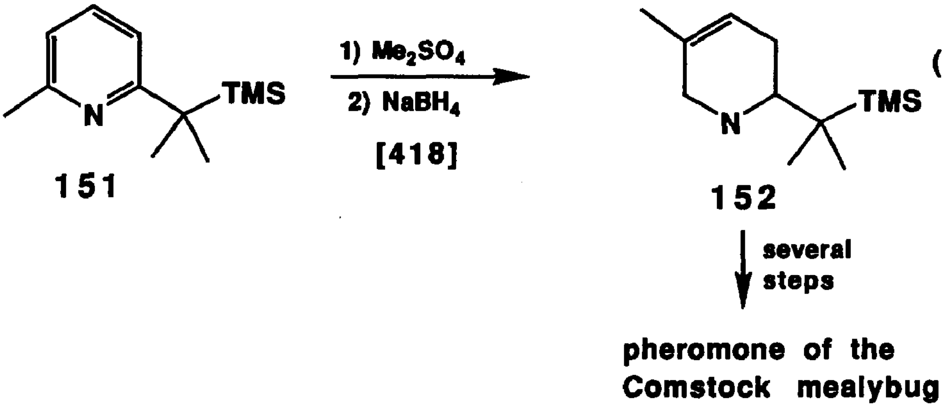


(508)



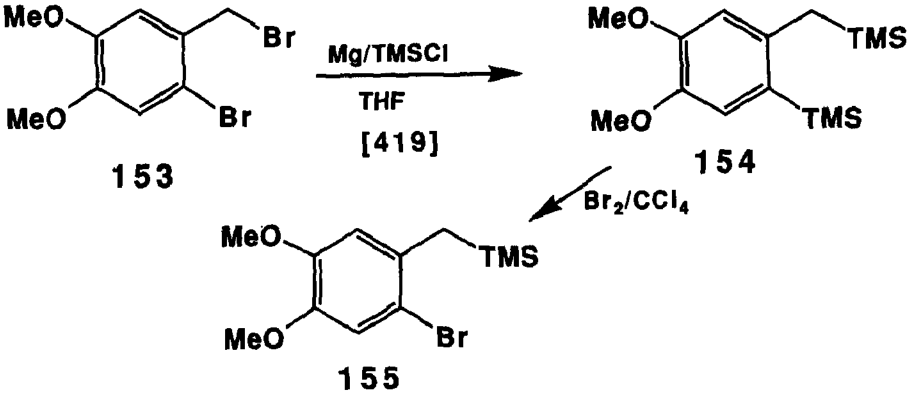
151 52%

(509)

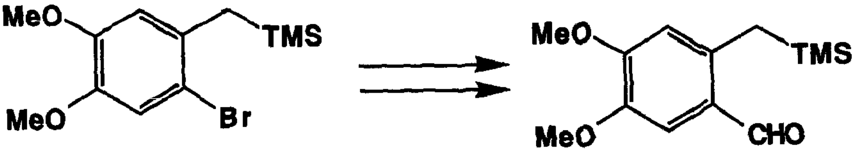


(510)

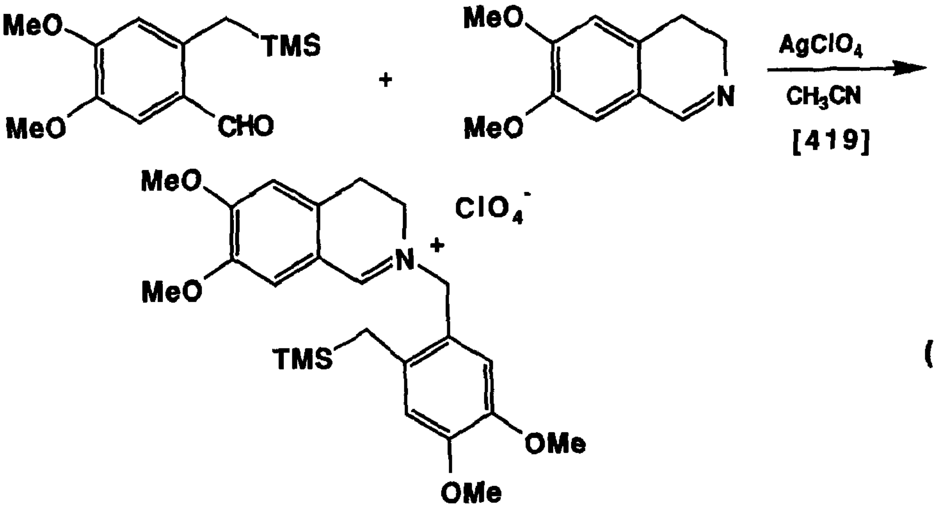
Dibromide **153** was converted to benzylsilane **154** bromodesilylation of which gives o-bromobenzylsilane **155**. (Eqn. 511) This was converted to the aldehyde (Eqn. 512), which was condensed with a cyclic imine and subsequently cyclized to give **156**. (Eqns. 513 and 514).



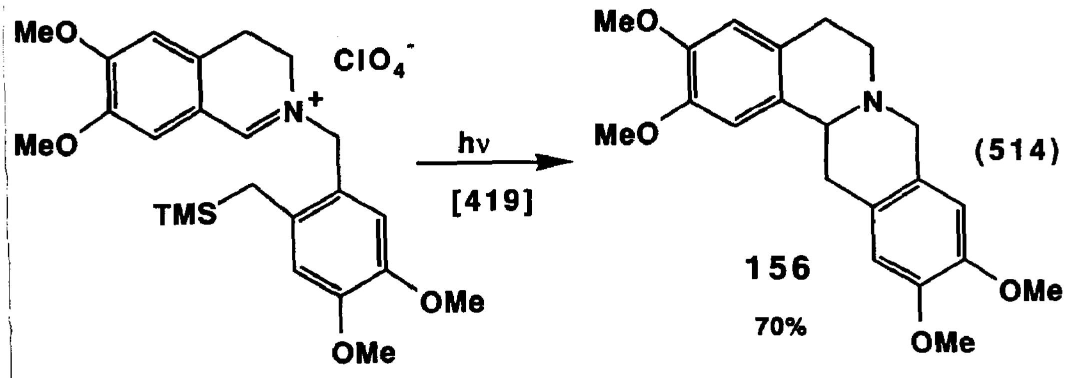
(511)



(512)



(513)

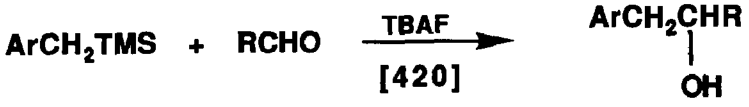


156

70%

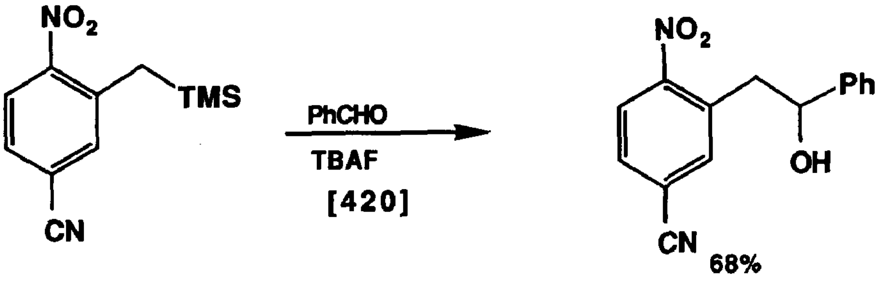
(514)

Benzylsilanes of nitrobenzenes were employed in the arylmethylation of aldehydes in the presence of fluoride ion. (Eqns. 515 and 516) This proves to be an excellent method of generating "benzyl anion" chemistry of sensitive systems such as the nitro functionalized ones.



$$ArCH_2TMS + RCHO \xrightarrow[[420]]{TBAF} ArCH_2\underset{\displaystyle OH}{\underset{|}{C}}HR \qquad (515)$$

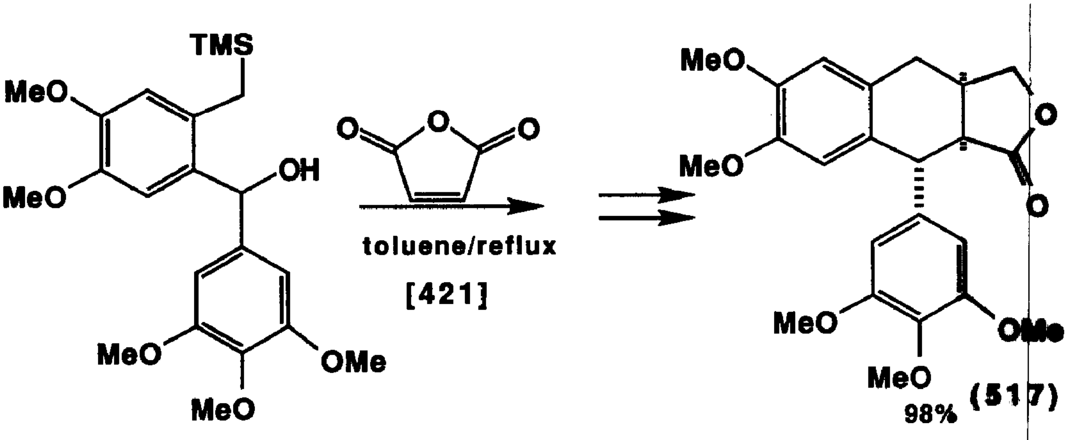
16 examples; 60-98%



68%

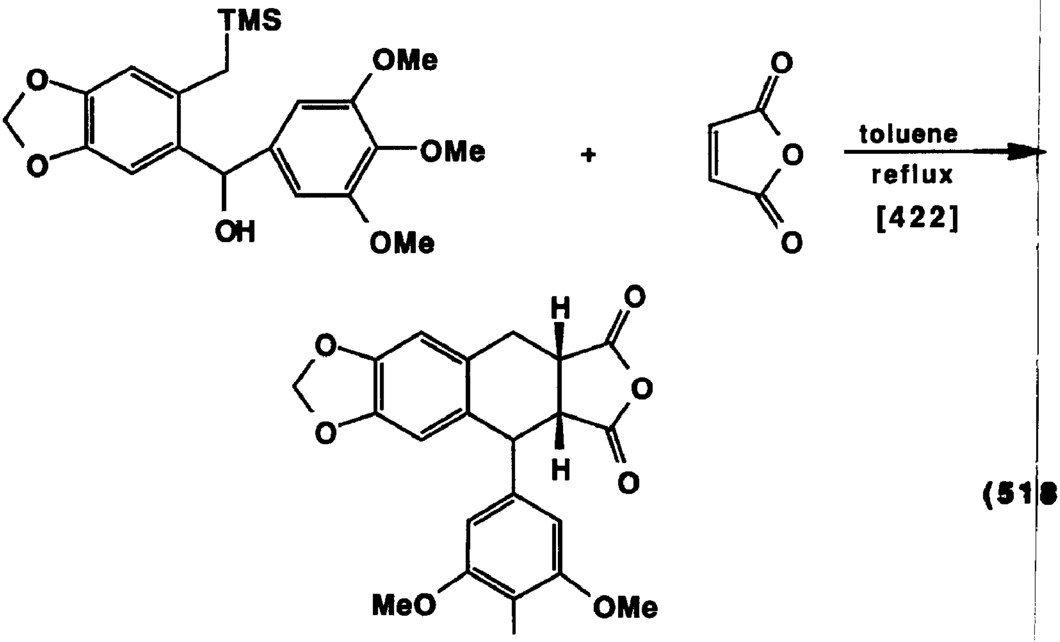
(516)

o-Trimethylsilylmethylbenzyl alcohol **157** was reacted with maleic anhydride *via* the o-xylylene generated thermally from **157**. (Eqn. 517) A similar reaction is shown in Eqn. 518 and a preparation of the vital precursor in Eqns. 519 and 520.

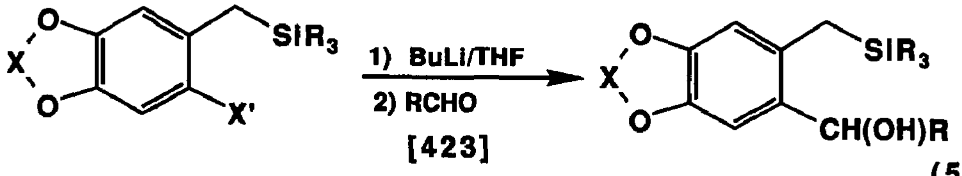


157

(517)

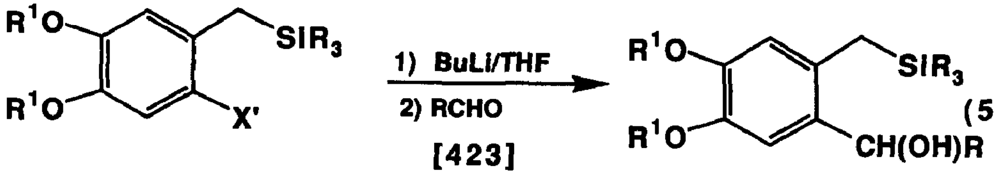


(518)



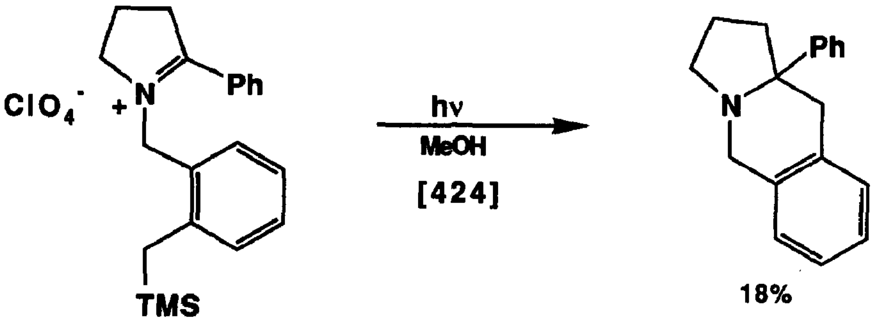
(X = CH$_2$, CH$_2$CH$_2$, X' = Br)

(519)



(520)

The mechanism of the photocyclization of arene iminium ions was studied. Among those studied was the benzylsilane **158**. (Eqn. 521)

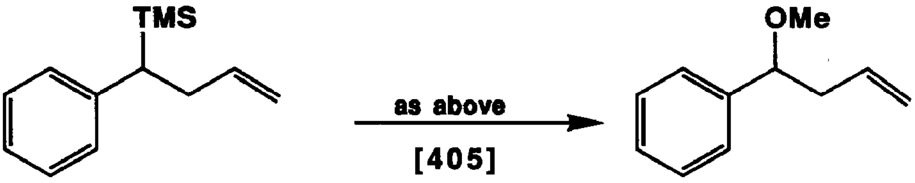


158

(521)

Benzyltrimethylsilanes were directly converted electrolytically to methyl ethers. (Eqns. 522 and 523)

$$\mathrm{ArCH_2TMS} \xrightarrow[\mathrm{Et_4NOTs/\ MeOH} \\ {[405]}]{-2e^-} \mathrm{ArCH_2OMe} \qquad (522)$$



(523)

XII. α-FUNCTIONAL ORGANOSILANES

A. Preparation

The successful monochlorination of methyltrichlorosilane was accomplished with N_2-laser irradiation (Eqn. 524) and with a barrier discharge (Eqn. 525).

$$CH_3SiCl_3 + Cl_2 \xrightarrow[\substack{h\nu \\ [425]}]{N_2\text{-laser}} \underset{70\%}{ClCH_2SiCl_3} \qquad (524)$$

$$CH_3SiCl_3 \xrightarrow[[426]]{Cl_2} \underset{65.7\%}{ClCH_2SiCl_3} + \text{others in small amounts} \qquad (525)$$

The reaction of chlorosilanes with tris(diethylamino)bromophosphonium trifluoromethide results in the formation of trifluoromethylsilanes. Trifluoromethyltrichlorosilane reacts to form a complex with pyridine. The Si-Cl bond reacts preferentially to the Si-N bond with this reagent. (Eqns. 526, 527 and 528)

$$P(NEt_2)_3Br^+\ CF_3^- \underset{[427]}{\xrightarrow[\text{DCM}]{\text{SiCl}_4}} \underset{\substack{50\% \\ \text{mixed with DCM}}}{F_3CSiCl_3} \qquad (526)$$

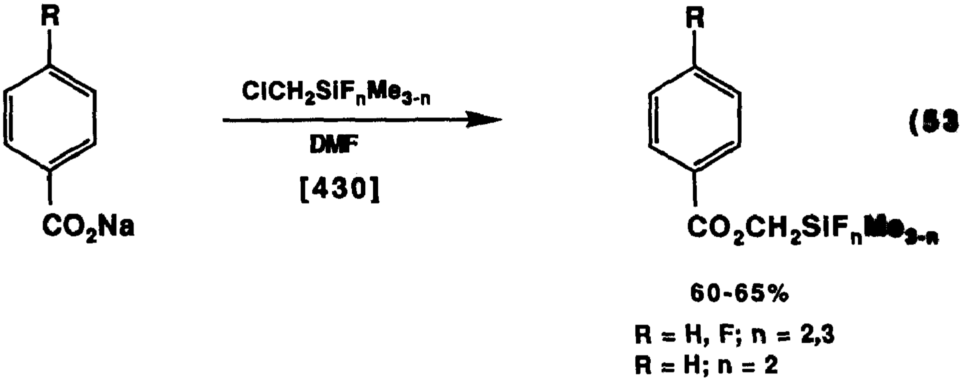
$$\begin{tikzcd}
F_3CSiCl_3 \arrow[r, "\text{pyridine}"] & F_3CSiCl_3\ 2py \arrow[r, "\text{HCl}"] & F_3CSiCl_3 \quad (527) \\
P(NEt_2)_3Br^+\ CF_3^- \arrow[r, "\text{HClSi(NMe}_2)_2"] & CF_3SiH(NMe_2)_2 \arrow[ur, "\text{HCl}"'] & (528)
\end{tikzcd}$$

The reaction of chloromethylsilanes with sodium alkylselenides gives the α-selenylsilane. (Eqn. 529) The reaction of chloromethylsilanes with formamide produces the trimethylsilyl formamide. This was treated with phosphorus oxychloride and diisopropylamine to give trimethylsilylmethyl isocyanide. (Eqn. 530)

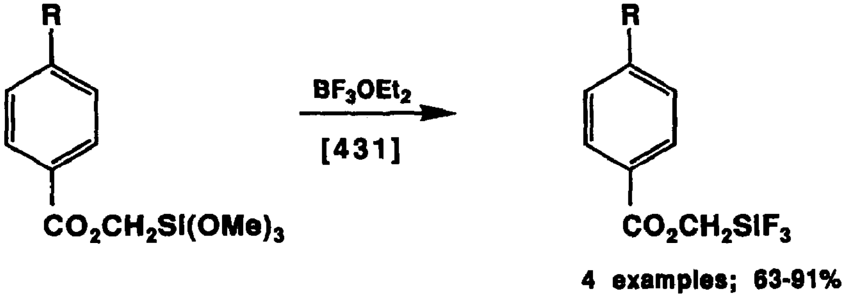
$$ClCH_2Si(OMe)_3 + RSeNa \xrightarrow[{[428]}]{} \underset{\substack{(R = Et,\ Pr,\ Ph) \\ 65\text{-}80\%}}{RSeCH_2Si(OMe)_3} \qquad (529)$$

$$TMSCH_2Cl + H_2NCHO \underset{[429]}{\xrightarrow[\text{DMF/120°C}]{\text{NaH}}} TMSCH_2NHCHO \xrightarrow[\substack{{}^iPr_2NH \\ \text{DCM/-20°}}]{\text{POCl}_3} TMSCH_2N{\equiv}C \qquad (530)$$

Chloromethylfluorosilanes were reacted with sodium benzoates to give the corresponding silylmethyl benzoates. (Eqn. 531) Another route to these materials is to react a chloromethylalkoxysilane with the sodium benzoate and then convert the alkoxy groups to fluorides. (Eqn. 532)

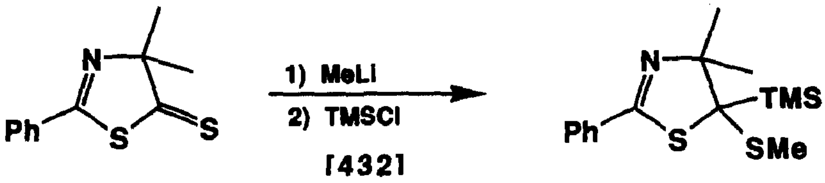


(531)



(532)

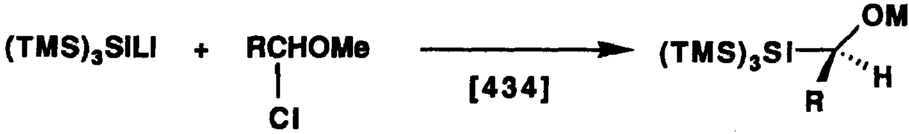
The reaction of 1,3-thiazole-5(4H)-thiones with Grignard or organolithium reagents and then trimethylchlorosilane gives the α-thiosilane. (Eqn. 533)



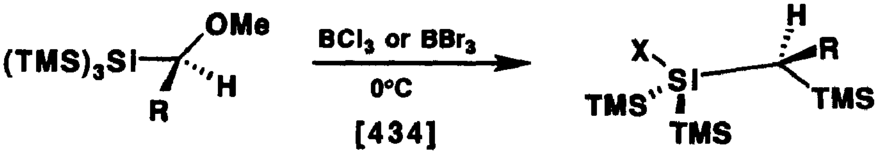
(533)

Tris(trimethylsilyl)methyllithium was reacted with methyl borate and the product of this reaction then hydrolyzed to the boronic acid and oxidized to produce tris(trimethylsilyl)methanol. (Eqn. 534) Tris(trimethylsilyl)silyllithium was reacted with α-chloromethyl ethers to give the α-methoxysilane. (Eqn. 535) This upon treatment with boron trichloride (or bromide) suffers a migration of one of the trimethylsilyl groups and loss of the methoxy group. (Eqn. 536) Other examples of this process are given in Eqns. 537, 538 and 539.

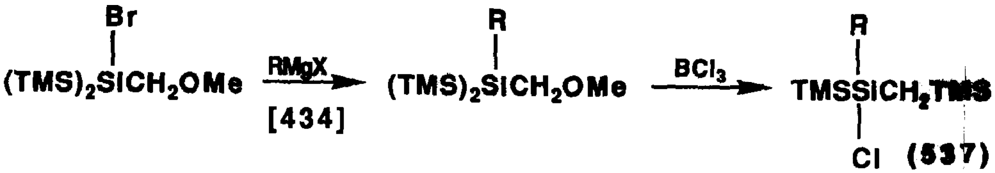
$$\mathrm{(TMS)_3CLi + B(OMe)_3 \xrightarrow[{[433]}]{} (TMS)_3CB(OMe)_2 \xrightarrow{1)\ H_2O\quad 2)\ H_2O_2/NaOAc} \underset{30\%}{(TMS)_3COH} + (TMS)_3CH} \qquad (534)$$


(535)

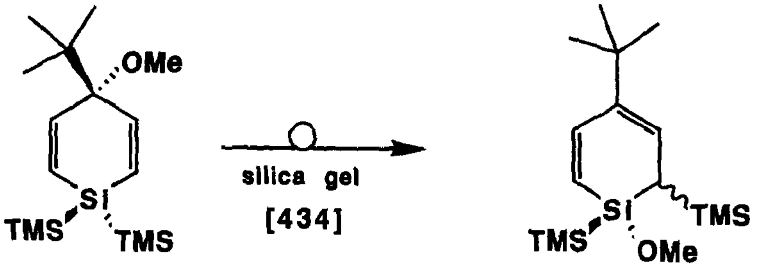
R = H (82%), ^{t}Bu (81%), Ph (81%), Mes (60%)


(536)

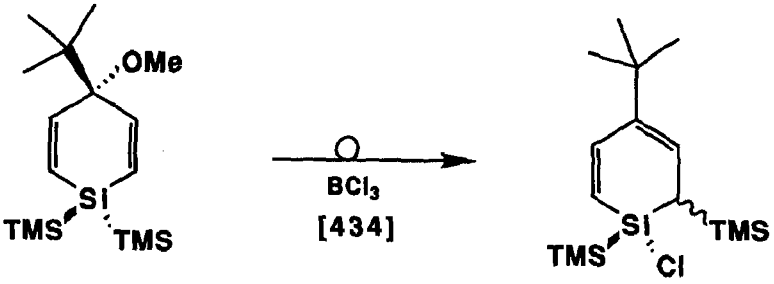
X = Cl, R = H (99%), ^{t}Bu (95%), Ph (97%), Mes (87%)
X = Br, R = H (92%), ^{t}Bu (79%), Ph (96%)



(537)

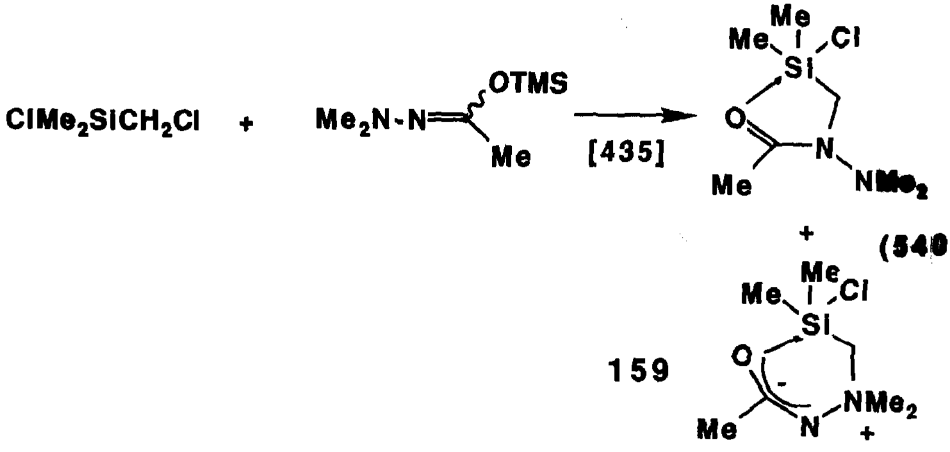


(538)



(539)

Chloromethyldimethylchlorosilane was reacted with trimethylsilylated dimethylacetylhydrazine to give **159**. (Eqn. 540)



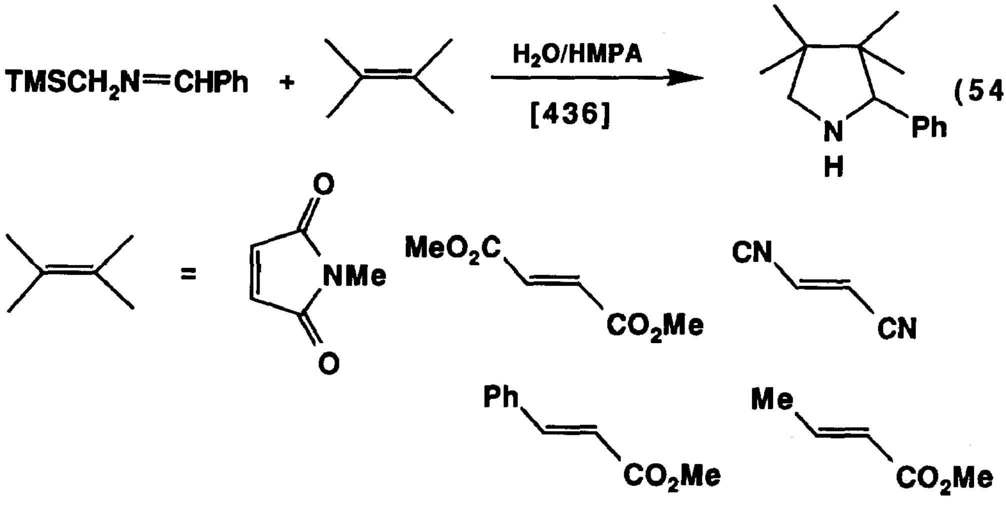
(540)

Trimethylsilylmethylamine, prepared from trimethylsilylmethylazide (Eqn. 541), was reacted with aldehydes and ketones to give the imines (Eqns. 542 and 543). These imines can be reacted with water in HMPA and the resulting N-protonated azomethine ylide undergo stereospecific and regioselective cycloadditions with electron poor olefins. (Eqn. 544)

$$\mathrm{TMSCH_2N_3} \underset{[436]}{\xrightarrow[\text{2) } \mathrm{H_2O}]{\text{1) } \mathrm{Ph_3P}}} \mathrm{TMSCH_2NH_2} \qquad (541)$$

$$\mathrm{TMSCH_2NH_2} \xrightarrow[{[436]}]{\mathrm{RCHO}} \mathrm{TMSCH_2N{=}CHR} \qquad (542)$$

$$\mathrm{TMSCH_2NH_2} \underset{[436]}{\xrightarrow[\mathrm{Et_3Al}]{\mathrm{Ph_2CO}}} \mathrm{TMSCH_2N{=}CPh_2} \qquad (543)$$



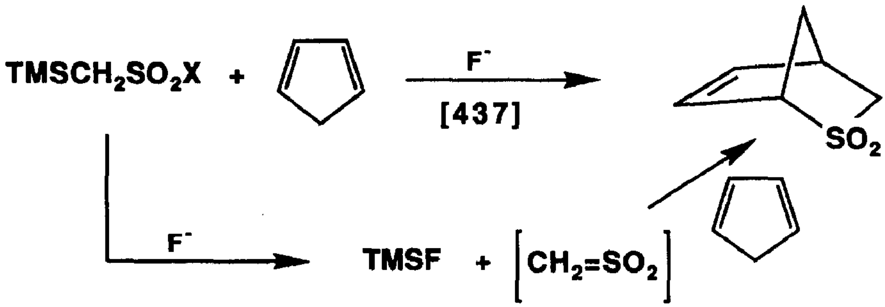
(544)

Z isomers were also reacted

Trimethylsilylmethylsulfonyl chloride, prepared from chloromethyltrimethylsilane and thiourea followed by chlorination in water (Eqn. 545), was used to generate sulfenes in the presence of dienes. (Eqn. 546) The anhydride can also be used in this reaction. (Eqns. 547 and 548) Sulfines can be generated in a similar manner as shown in Eqns. 549, 550 and 551.

$$\mathrm{TMSCH_2Cl} \xrightarrow[\text{2) } \mathrm{Cl_2/H_2O}]{\text{1) } \mathrm{(NH_2)_2C{=}S}} \mathrm{TMSCH_2SO_2Cl} \qquad (545)$$

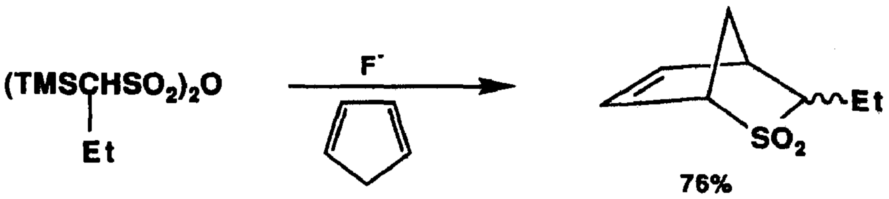
[437]



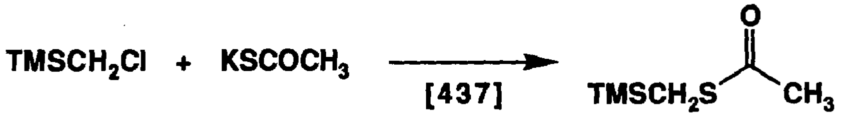
(546)

$$\mathrm{TMSCH_2SH} \xrightarrow[\text{2) } \mathrm{PCl_5}]{\text{1) } \mathrm{CH_3CO_3H}} \mathrm{(TMSCH_2SO_2)_2O} \qquad (547)$$

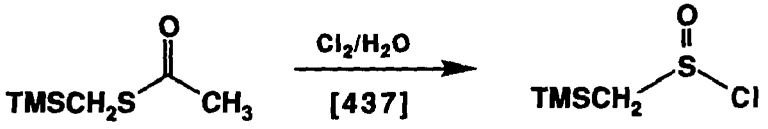
[437]



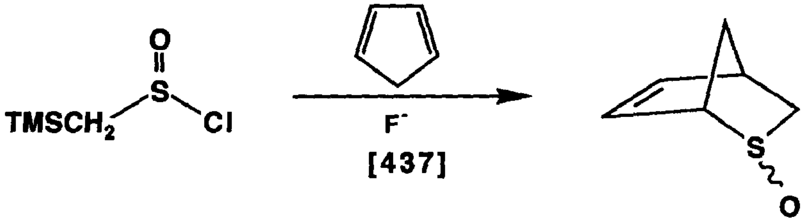
(548)



(549)



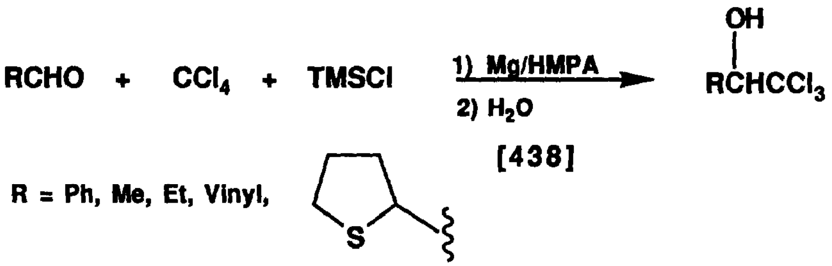
(550)



(551)

B. α-Functional Organosilanes-Reactions

The reaction of an aldehyde with carbon tetrachloride and trimethylchlorosilane with magnesium in HMPA followed by hydrolysis results in the formation of α-trichloromethyl alcohols. (Eqn. 552) The reaction is proposed to proceed via trichloromethyltrimethylsilane.



(552)

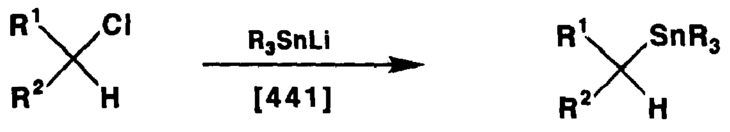
Thermolysis of methoxydibromomethyltriphenylsilane results in the loss of carbon monoxide and methyl bromide and the formation of bromotriphenylsilane. (Eqn. 553) The reaction is assumed to go through the intermediacy of methoxybromocarbene.

$$\mathrm{Ph_3SiCBr_2OMe} \xrightarrow[\text{[439]}]{110^\circ\mathrm{C}} \mathrm{Ph_3SiBr} + \mathrm{CO} + \mathrm{CH_3Br} \qquad (553)$$

(S) (+) Naphthylphenylmethyl(dibromomethyl)silane reacts with potassium alkoxides in alcohol to displace the dibromomethyl group with inversion of configuration at silicon. (Eqn. 554)

$$\text{(R) }\mathrm{NpPhMeSiCHBr_2} + \mathrm{ROK} \xrightarrow[\text{[440]}]{\mathrm{ROH}} \underset{\text{inversion}}{\text{(S) }\mathrm{NpPhMeSiOR}} \qquad (554)$$

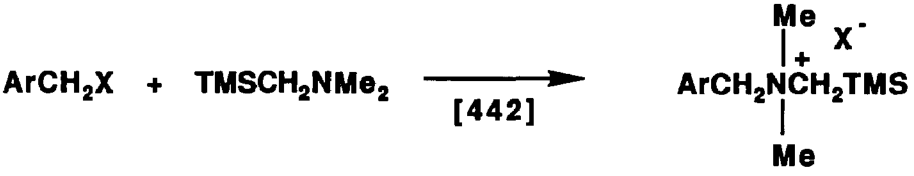
It was reported that in the substitution of alkyl chlorides with trialkylstannyllithium reagents that trimethylsilylmethyl chloride is less reactive than trimethylstannylmethyl chloride, benzyl chloride, and allyl chloride, but more reactive than n-butylchloride. (Eqn. 555)



(555)

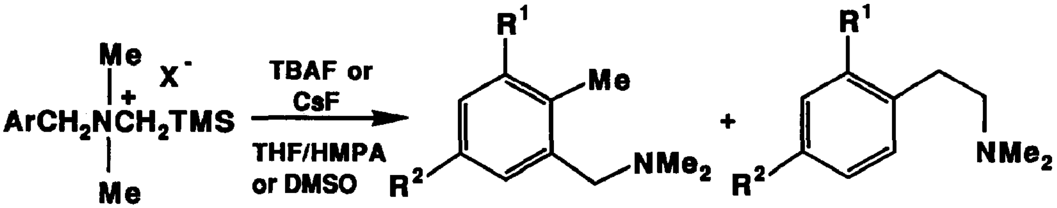
R^1 and R^2 = various alkyl, aryl trimethylsilyl and trimethylstannyl groups

Trimethylsilylmethyldimethyl amine was reacted with benzyl chlorides and the resulting benzyl ammonium salt, when treated with fluoride ion, undergoes a Sommelet-Hauser rearrangement with very little of the competing Stevens rearrangement. (Eqns. 556 and 557) This is a consequence of the trimethylsilyl group directing the reaction since the protonated version give considerable amounts of the Stevens product.



$$ArCH_2X + TMSCH_2NMe_2 \xrightarrow[\text{[442]}]{} ArCH_2\overset{+}{N}(Me)_2CH_2TMS\ X^- \quad (556)$$

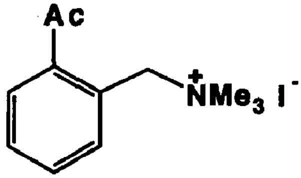
12 examples; 80-93%



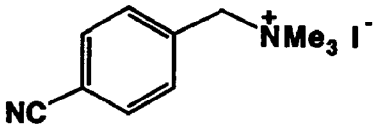
(557)

12 examples; 80-93%

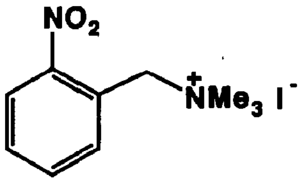
Sommelet-Hauser:Stevens = 94-99:1-6



S-H:S = 42:58



S-H:S = 81:19



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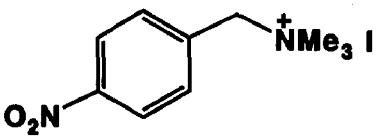
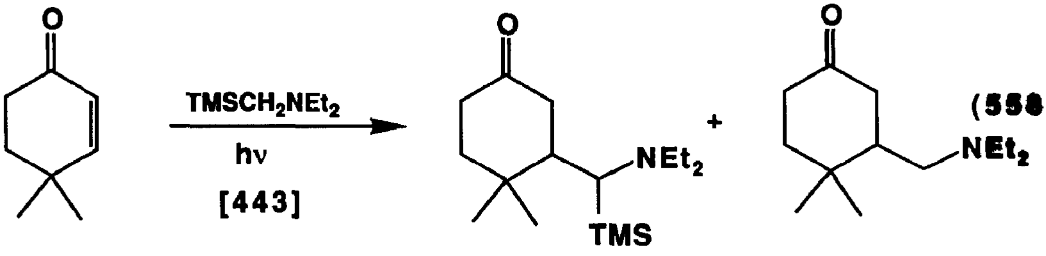


S-H:S = 12:>88

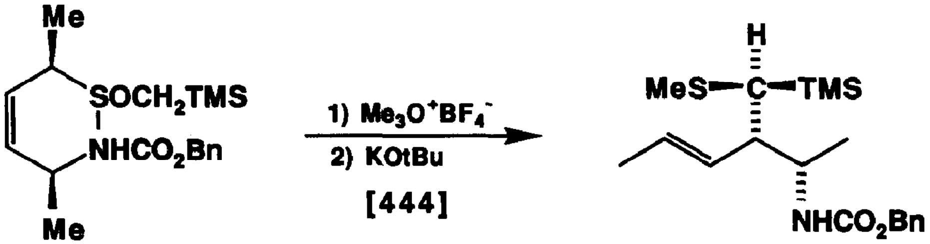
The photoinduced reaction of trimethylsilylmethyldiethylamine with cyclohexenones was reported. (Eqn. 558) Increasing the polarity and ionic strength of the reaction medium leads to more desilylation. The mechanism is discussed.



(558)

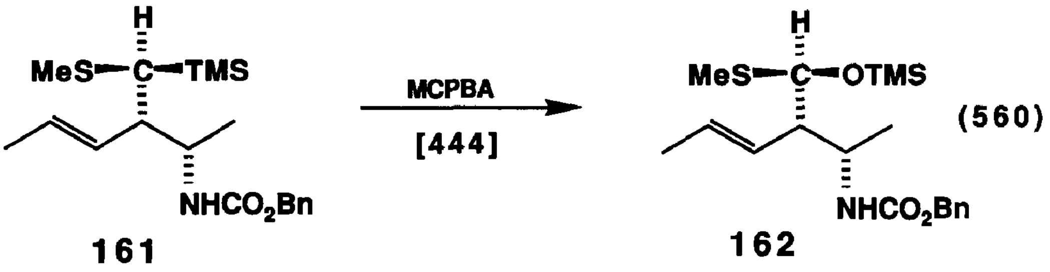
CH_3CN	70%	5%
MeOH	30%	60%

A diastereoselective synthesis of functionalized homoallylic amines was accomplished starting with **160**. Treatment of **160** with trimethyloxonium tetrafluoroborate and then t-butoxide gives α-thiomethoxysilane **161**. (Eqn. 559) This can be oxidized to **162**, which can be converted to the hydroxymethyl or aldehyde. (Eqn. 560) Another example is shown in Eqn. 561.

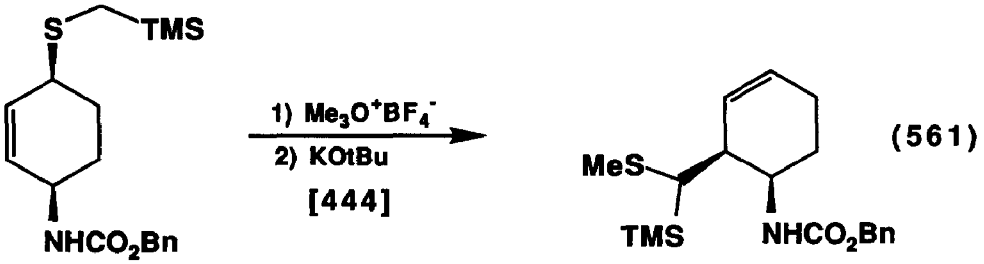


160 **161**

(559)

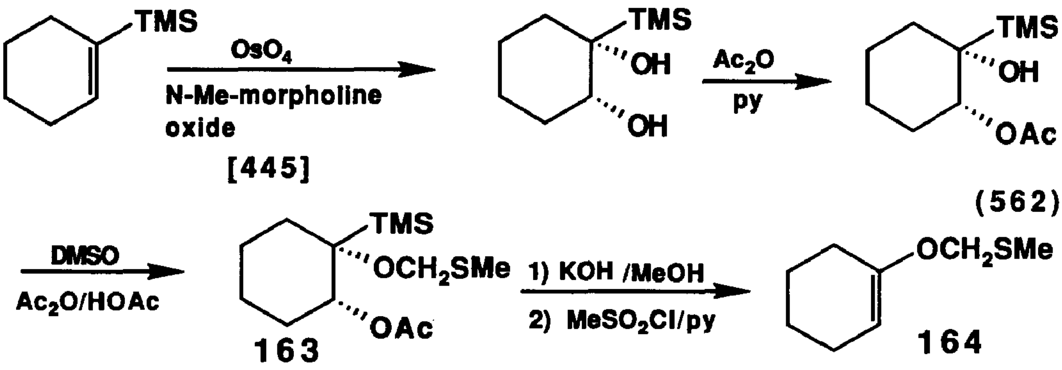


161 **162** (560)

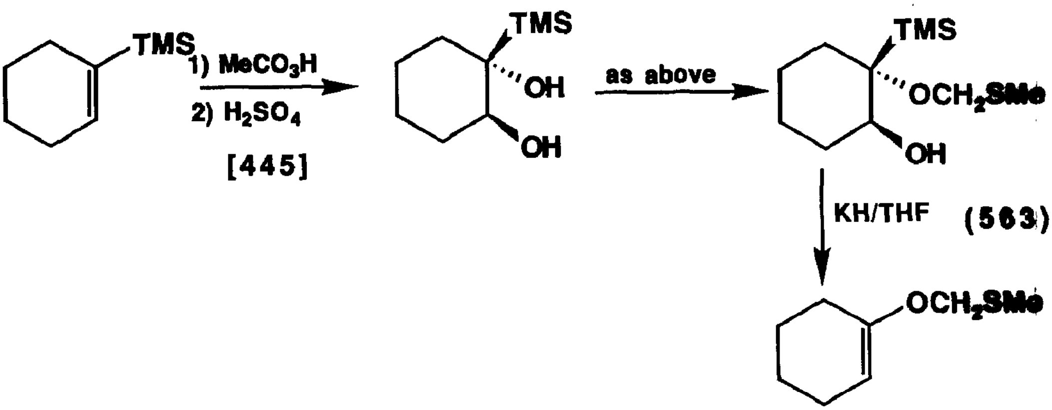


(561)

The oxidation of 1-trimethylsilylcyclohexene with osmium tetroxide produces the cis diol, which was sequentially acetylated and reacted with dimethyl sulfoxide and acetic anhydride to give **163**. This was then deacetylated and the alcohol converted to the mesylate; elimination then gives the enol ether **164**. (Eqn. 562) The trans diol, prepared *via* the epoxide, is also a viable precursor to this enol ether. (Eqn. 563)



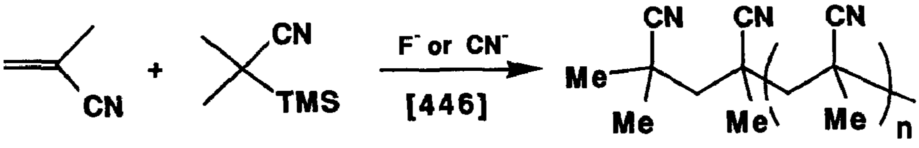
163 **164** (562)



(563)

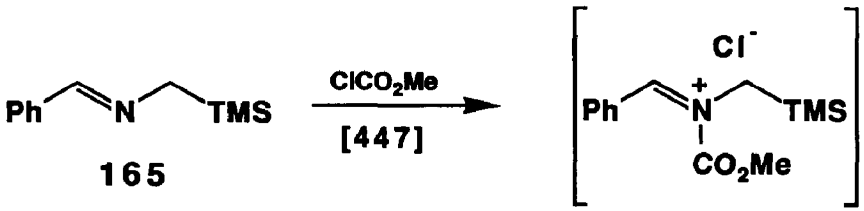
164

Group transfer polymerization of methacrylonitrile was initiated with α-trimethylsilyl-α-methylpropionitrile. (Eqn. 564)

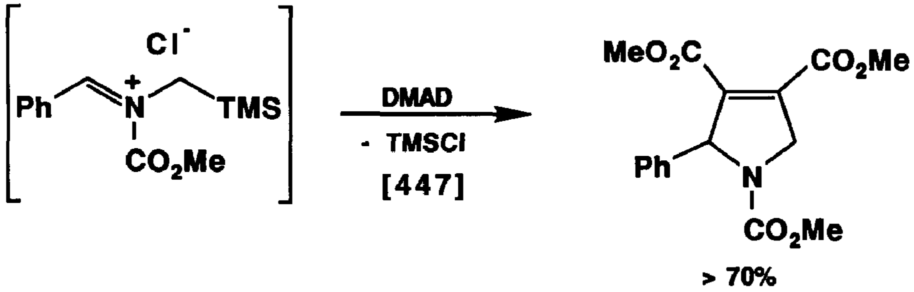


(564)

α-Aminosilanes were used in the 'in situ' generation of azomethine ylides. This very highly useful methodology for the generation of an unstable reactive intermediate in the presence of dipolarophiles continues to show considerable application. α-Iminosilane **165** reacts with methyl chloroformate to first give the adduct, which suffers attack at silicon by the chloride ion giving the azomethine ylide. This cyclizes with dimethylacetylene dicarboxylate. (Eqns. 565 and 566)

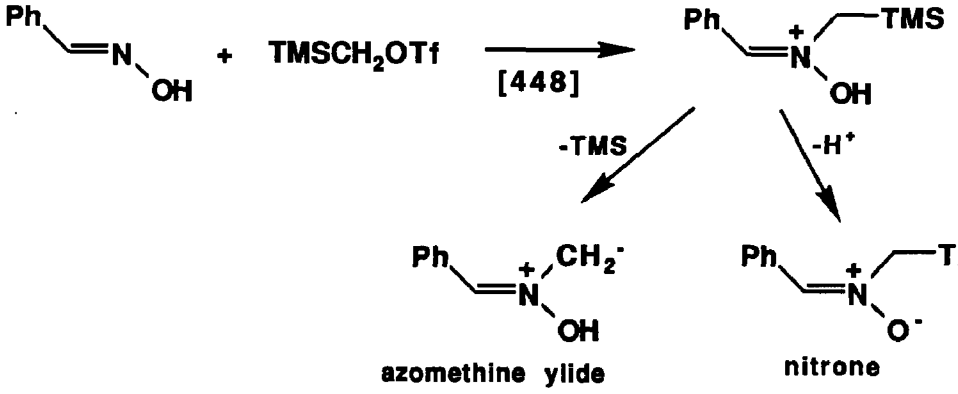


(565)

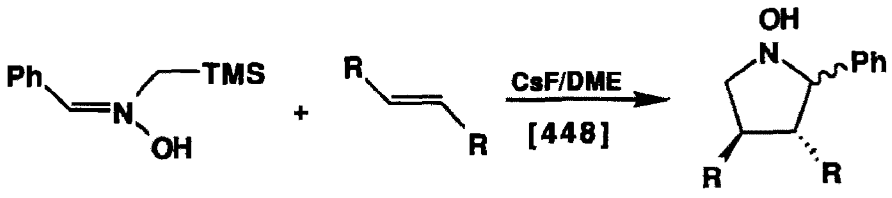


(566)

Treatment of benzaldehyde oxime with trimethylsilylmethyl triflate gives the hydroxyl iminium salt, which can either lose a proton to form the ntirone or the trimethylsilyl group to form the azomethine ylide. (Eqn. 567) When treated with fluoride ion the azomethine ylide is formed due to the high silicophilicity of the fluoride ion. Generation of the azomethine ylides in this manner in the presence of dipolarophiles results in the cycloadducts. (Eqn. 568) The reaction with benzaldehyde was also investigated. (Eqn. 569)

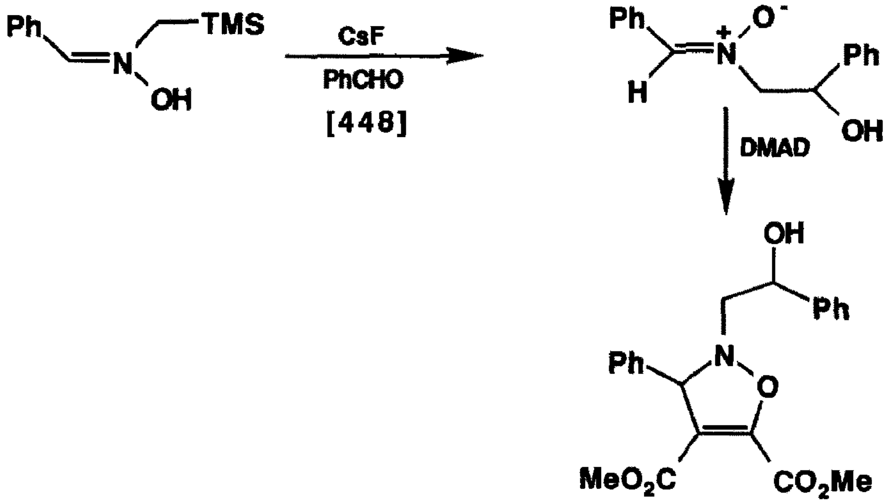


(567)



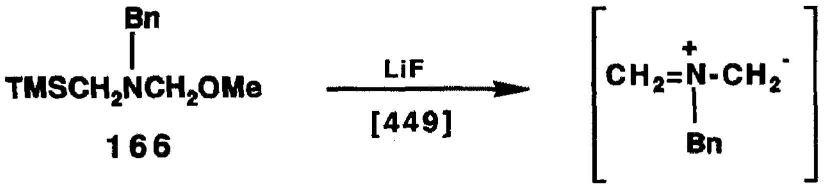
(568)

(R = CO_2Me, CN, dimethylmaleate also reacted)

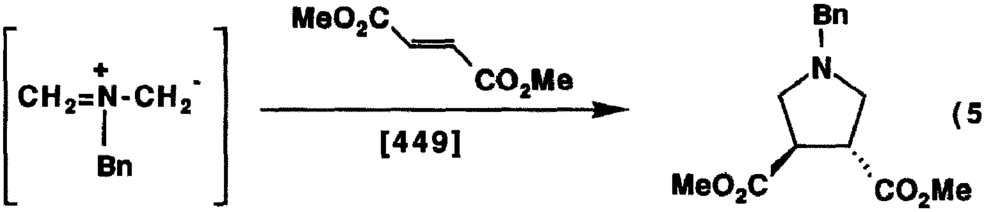


(569)

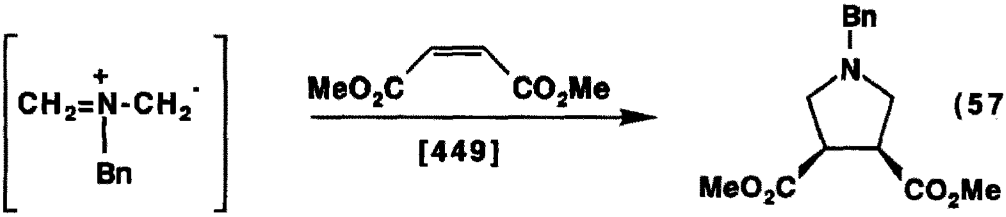
The reaction of **166** with lithium fluoride was used to generate the azomethine ylide, which was reacted stereospecifically with dimethyl fumarate and dimethyl maleate. (Eqns. 570, 571 and 572)



(570)



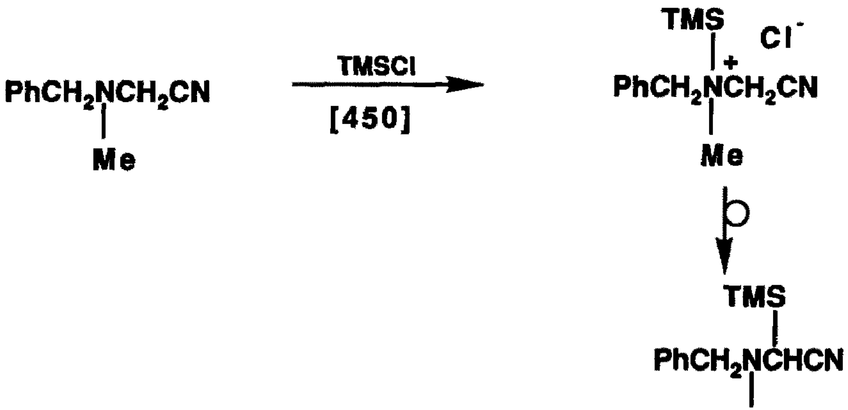
(571)



(572)

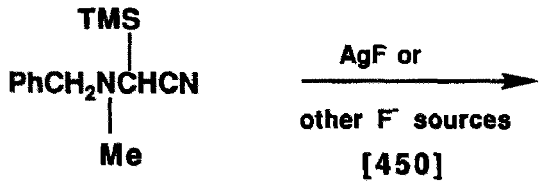
(other dipolarophiles also used)

The α-cyano-α-aminosilane **167**, a potential precursor to azomethine ylides, was prepared (Eqn. 573), but only gave protodesilylation upon treatment with fluoride ion (Eqn. 574). On the other hand, system **168** reacts with silver fluoride in the presence dipolarophiles to give the cycloadducts. (Eqn. 575)

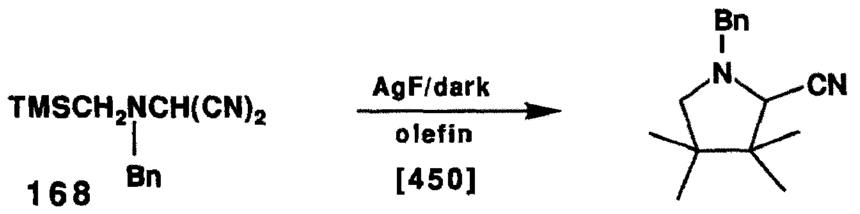


quantitative **167**

(573)



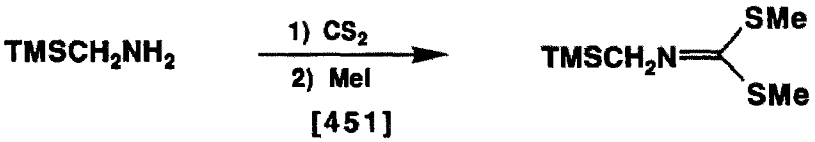
(574)



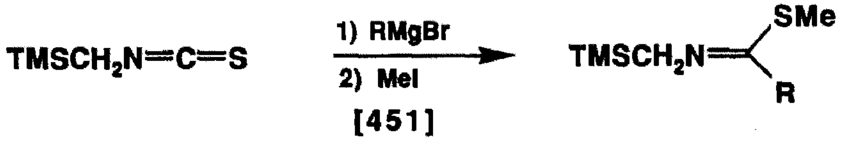
168

(575)

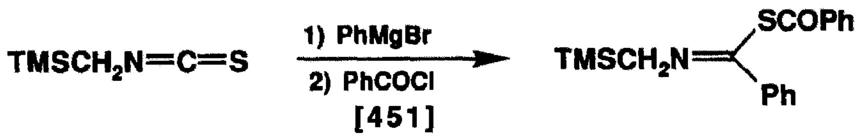
N-(trimethylsilylmethyl)thioimidates, prepared according to Eqn. 576, were reacted with a Grignard reagent and then methyl iodide or benzoyl chloride to provide substituted trimethylsilylmethylimines. (Eqns. 577, 578 and 579) These upon reaction with fluoride ion or even water produce the azomethine ylide via loss of the trimethylsilyl group. (Eqns. 580). The reaction of **169** with dipolarophiles in the presence of tetra-butylammonium fluoride gives both α-attack and γ-attack, with only the γ-attack leading to cyclization. (Eqn. 581)



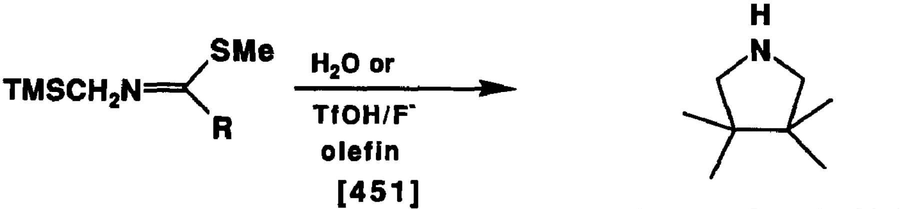
(576)



(577)

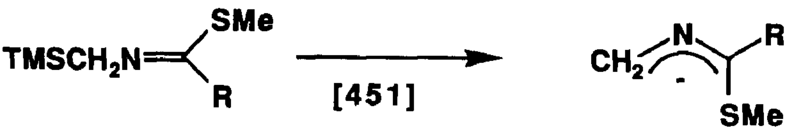


(578)

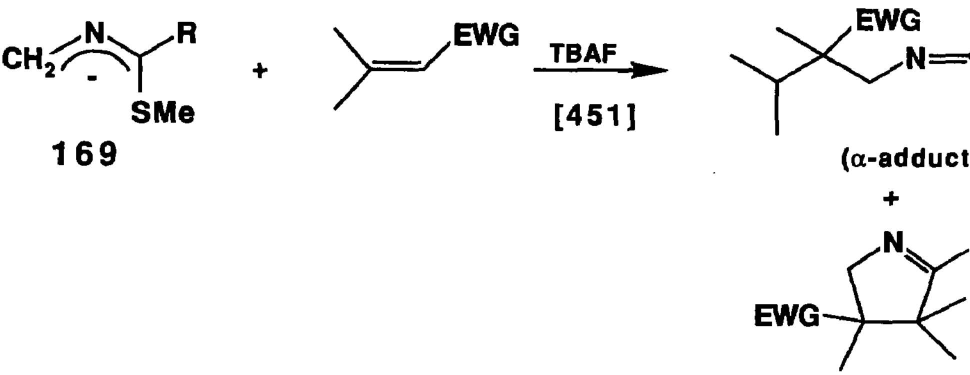


15 examples; 23-98%

(579)



(580)

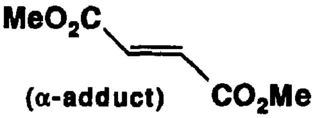


169

(581)

(γ-adduct)

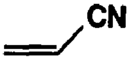
(α-adduct)



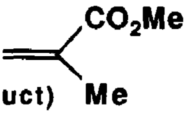
(α-adduct)

(γ-adduct)

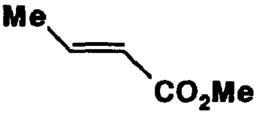
(γ-adduct)



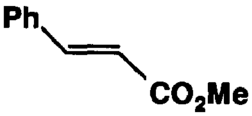
(γ-adduct)



(γ-adduct)



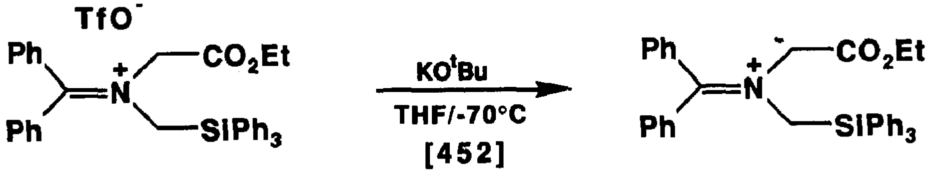
(α and γ-adduct)



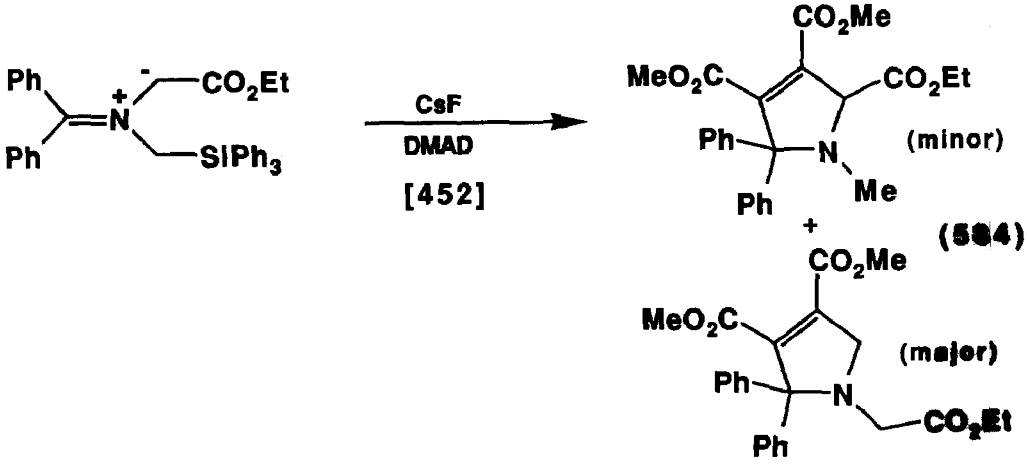
(α and γ-adduct)

The triphenylsilylmethylimine of benzophenone was treated with the triflate of ethyl hydroxyacetate and the resulting imino ester reacted with potassium tert-butoxide to form a red anion. (Eqn. 582) This, when warmed to -20°C, gives the aziridine in the absence of a dipolarophile. (Eqn. 583) In the presence of a dipolarophile and fluoride ion cycloadducts are formed. (Eqn. 584)

(582)

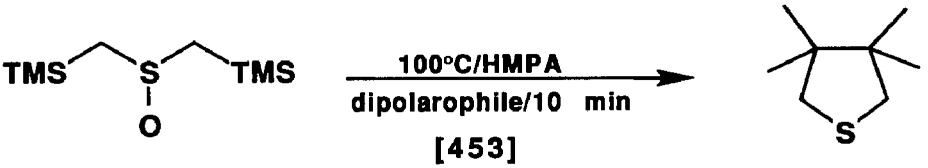


(583)



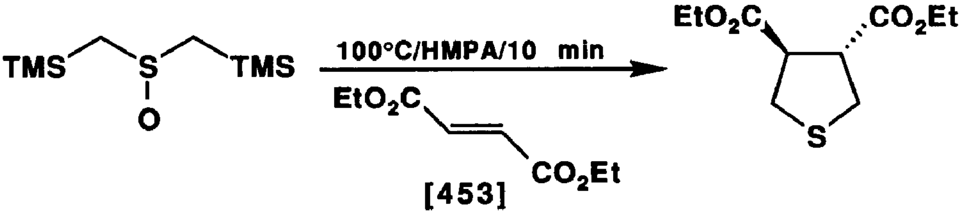
(584)

Thiocarbonyl ylides were generated from organosilane precursors and cycloadded to various dipolarophiles. As with organosilicon synthons for azomethine ylides, these reactions can be carried out in the presence of the dipolarophile, greatly enhancing their utility. Thermally, 1,3-bis(trimethylsilyl)dimethyl sulfoxide eliminated hexamethyldisiloxane and produces the thiocarbonyl ylide, which cycloadds to olefins. (Eqns. 585 and 586)



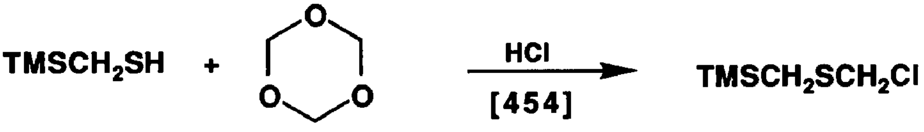
(585)

8 examples; 50-81%

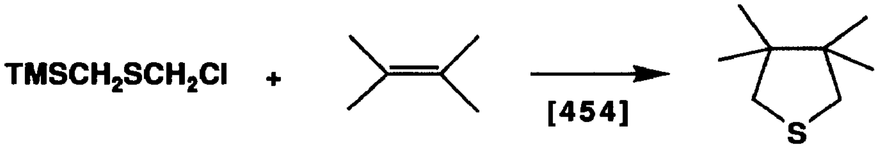


(586)

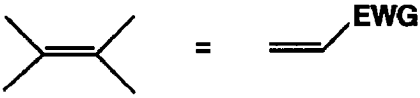
The reaction of mercaptomethyltrimethylsilane with paraformaldehyde and HCl gives chloromethyltrimethylsilylmethyl sulfide. This when treated with cesium fluoride liberates thiocarbonyl ylide, which was cycloadded to several electron poor olefins. (Eqns. 587 and 588)



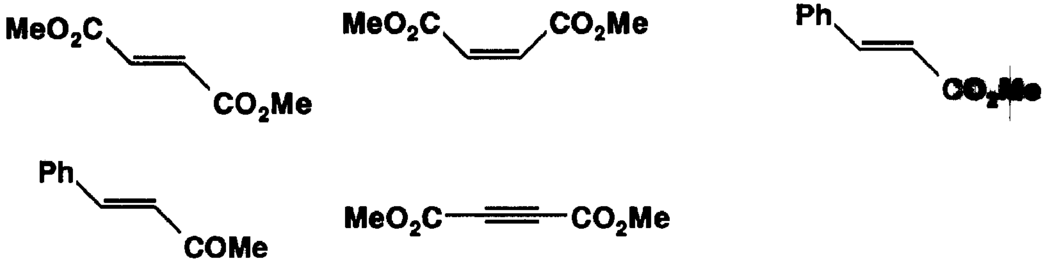
(587)



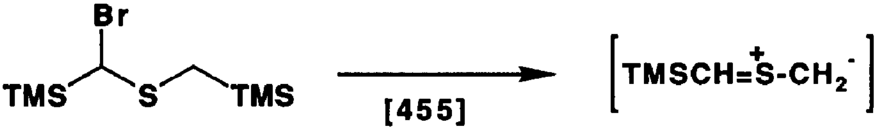
(588)



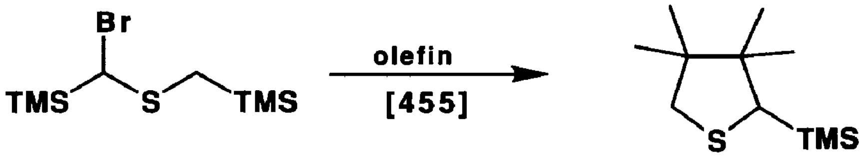
(EWG = CO_2Me, CO_2TBS, CO_2menthyl, CO_2bornyl, acyl)



The effect of the trimethylsilyl group on the regio- and stereoselectivity of the [2+3] dipolar addition reaction of a trimethylsilyl substituted thiocarbonyl ylide, generated according to Eqn. 589, was investigated. It was found that a mixture of regio- and stereoisomers was obtained. (Eqn. 590) A new synthetic route to 3,4-disubstituted tetrahydrothiophenes was reported. This route employs the desilylation of 2-trimethylsilyl tetrahydrothiophenes with cesium fluoride. (Eqns. 591 and 592)

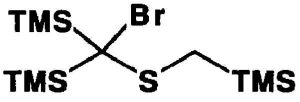


(589)

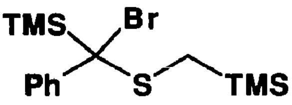


(590))

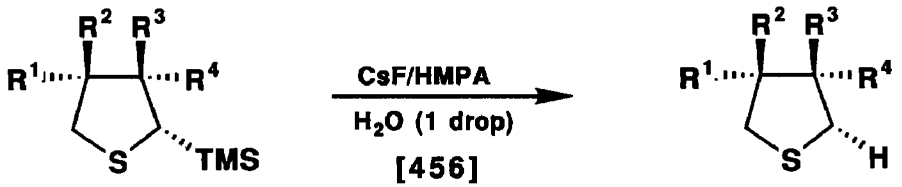
olefin = methyl acrylate, acrylonitrile, dimethyl fumarate



and

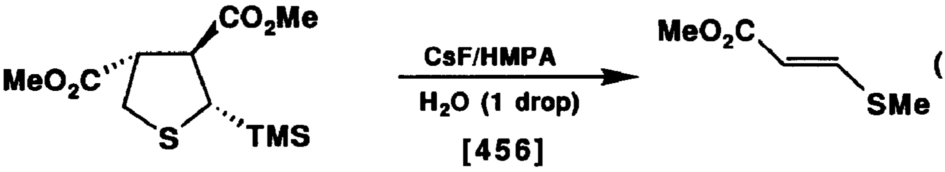


were also investigated.



(591)

5 examples



(592)

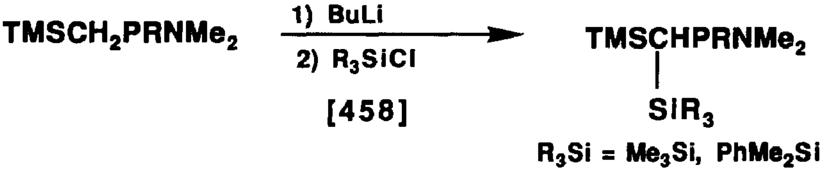
C. α-Silyl Organometallic Reagents

Trimethylsilylmethyllithium was reacted with erbium trichloride and the product treated with deuterium oxide. (Eqn. 593) Trimethylsilylmethylmagnesium chloride was reacted with alkyl(dimethylamino)chlorophosphines to give trimethylsilylmethyl phosphines *via* displacement of the chloride. (Eqn. 594) These silylmethyl phosphines were alkylated via the α-lithio derivative. (Eqn. 595)

$$\mathrm{TMSCH_2Li} + \mathrm{ErCl_3} \xrightarrow[\text{[457]}]{} \text{INTERMEDIATE} \xrightarrow{\mathrm{D_2O}} \mathrm{TMSCH_2D} \quad (593)$$

$$\mathrm{TMSCH_2Cl} \xrightarrow[\text{2) } \mathrm{Me_2NRPCl}]{\text{1) Mg}} \mathrm{TMSCH_2PRNMe_2} \quad (594)$$

[458]

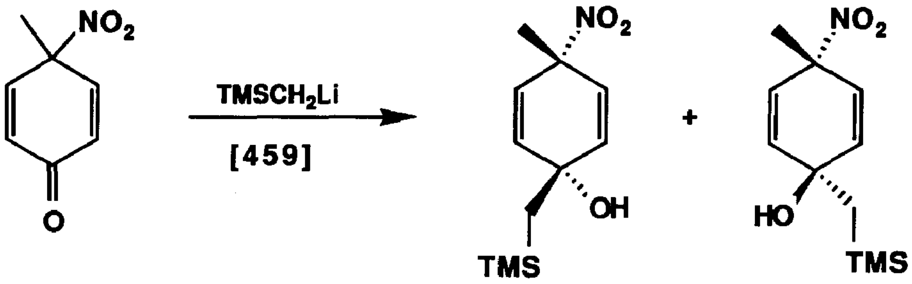


$$\mathrm{TMSCH_2PRNMe_2} \xrightarrow[\text{2) } \mathrm{R_3SiCl}]{\text{1) BuLi}} \underset{\displaystyle \mathrm{SiR_3}}{\mathrm{TMSCHPRNMe_2}} \quad (595)$$

[458]

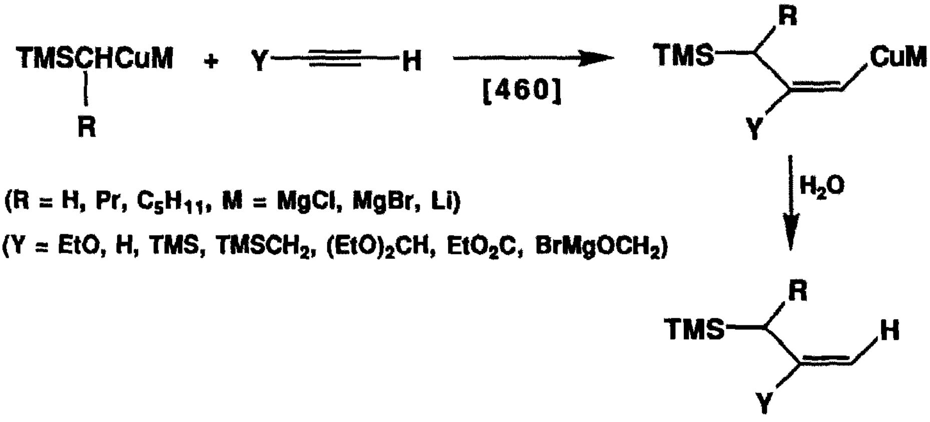
$\mathrm{R_3Si = Me_3Si, PhMe_2Si}$

Trimethylsilylmethyllithium was reacted with 4-methyl-4-nitrocyclohexadienone at the carbonyl to give a mixture of diastereomers. (Eqn. 596)



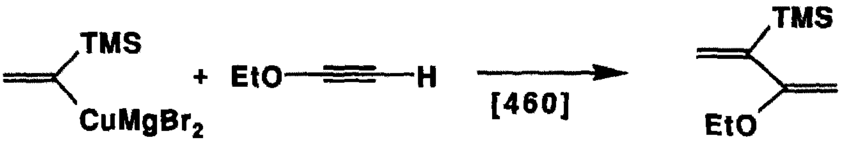
(596)

α-Trimethylsilyl organocuprates were added to acetylenes to give 3-trimethylsilylvinyl copper species. (Eqn. 597) 1-Trimethylsilylvinyl copper(I) was added to ethoxyacetylene and protonated (Eqn. 598), as were two α-trimethylsilylmethyl copper(I) systems (Eqn. 599). The 3-trimethylsilylvinyl copper derivatives were subjected to alkylation (Eqn. 600), iodination (Eqn. 601), coupling (Eqn. 602), acylation (Eqn. 603) and carboxylation (Eqn. 604).

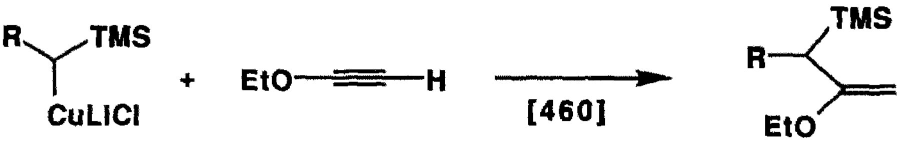


(R = H, Pr, C_5H_{11}, M = MgCl, MgBr, Li)
(Y = EtO, H, TMS, $TMSCH_2$, $(EtO)_2CH$, EtO_2C, $BrMgOCH_2$)

(597)

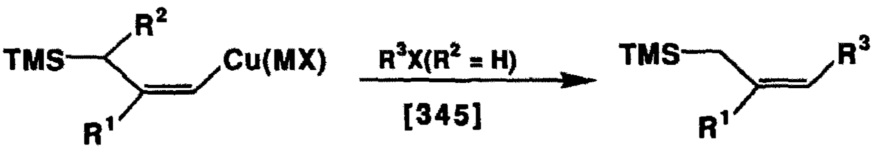


(598)

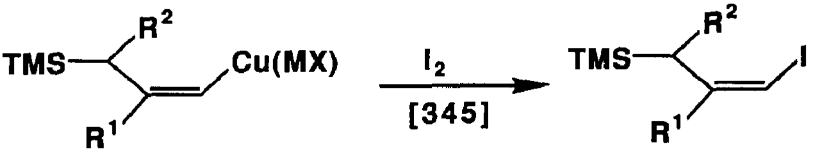


56-62%

(599)



(600)



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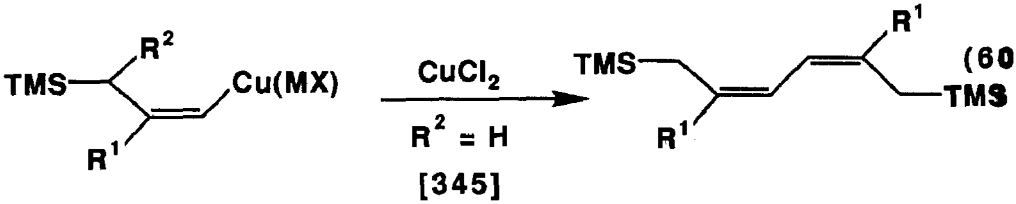
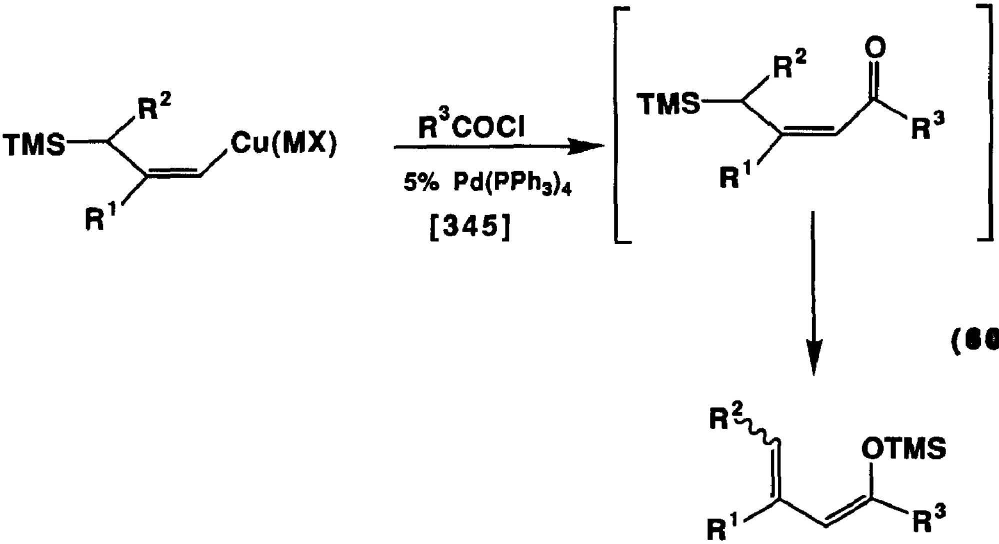


(602)



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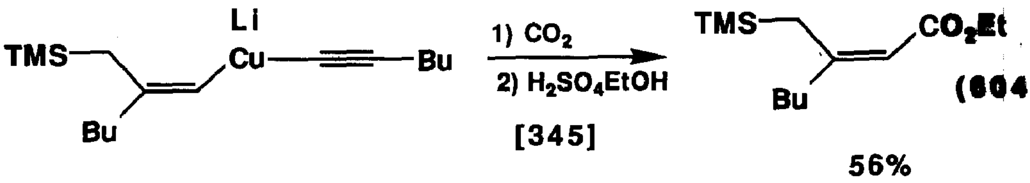
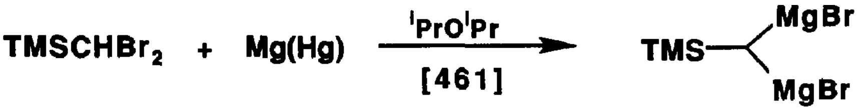


(604)

Dibromomethyltrimethylsilane reacts with magnesium amalgam in diisopropyl ether to form bis(bromomagnesio)trimethylsilylmethane. (Eqn. 605) This was derivatized with trimethyltin chloride (Eqn. 606), benzophenone (Eqn. 607) and cyclohexanone (Eqn. 608).



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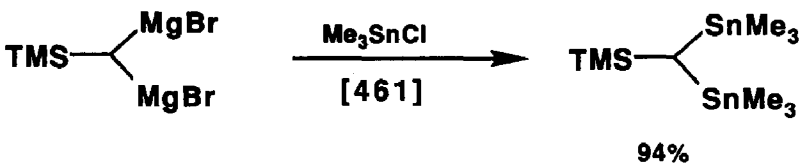

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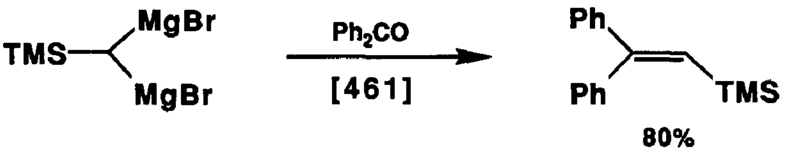

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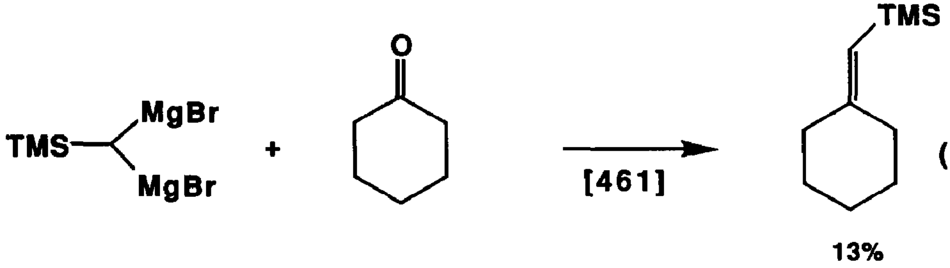
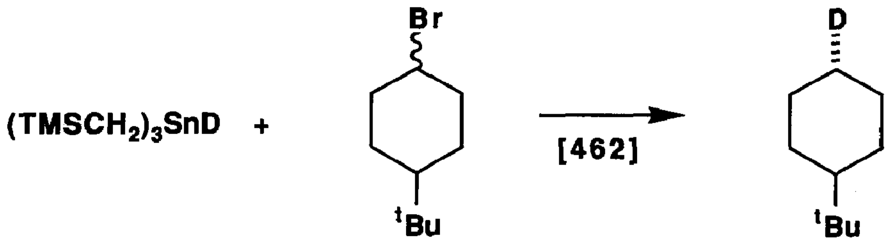


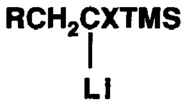
(608)

Tris(trimethylsilylmethyl)stannyl deuteride was reacted with either cis or trans 4-bromo-tert-butylcyclohexane to give predominantly the trans 4-deuterio-tert-butyl-cyclohexane. (Eqn. 609) It is argued that the stereoselectivity is a result of torsional strain in the transition state.



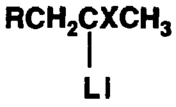
(609)

The stabilities of α-trimethylsilyl-α-halomethyllithium reagents was studied. It was found that these materials were stable to about -50°C, whereas α-bromomethyllithium was totally unstable, and secondary α-haloalkyllithium reagents were stable to -110°C, and primary ones to -105°C. [463] Lithiation of 1,1-dibromononyltrimethylsilane followed by chromatography gave (E) and (Z) 1-trimethylsilyl-1-nonene. (Eqn. 610)

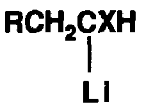


$RCH_2\underset{Li}{C}XTMS$ **Stable to -50°C**

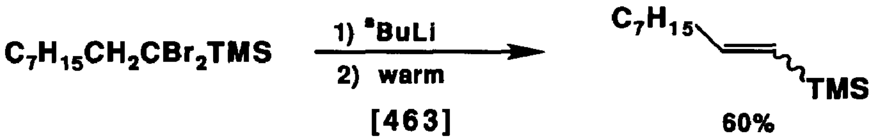
CH_2BrLi Totally unstable at all temperatures



$RCH_2\underset{Li}{C}XCH_3$ **Stable below -110°C**

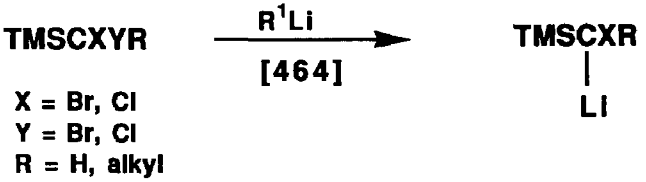


$RCH_2\underset{Li}{C}XH$ **Stable below -105°C**



(610)

Metal-halogen exchange was used to prepare α-halo-α-trimethylsilylalkyllithium reagents. (Eqn. 611) These were alkylated (Eqn. 612) and protonated (Eqn. 613); when elimination is possible this is a serious side reaction. (Eqn. 614)

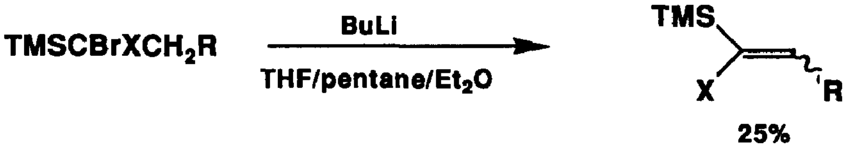


$$\mathrm{TMSCXYR} \xrightarrow[\text{[464]}]{\mathrm{R^1Li}} \mathrm{TMS}\underset{\substack{|\\ \mathrm{Li}}}{\mathrm{C}}\mathrm{XR} \qquad (611)$$

X = Br, Cl
Y = Br, Cl
R = H, alkyl

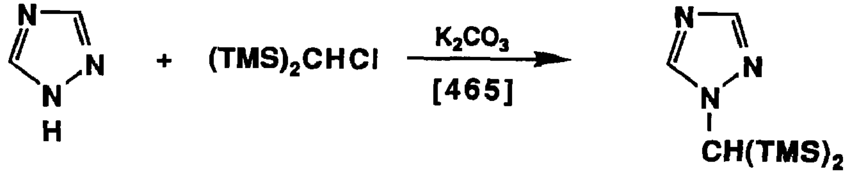
$$\mathrm{TMSCBrClH} \xrightarrow[\text{2) BuI}\ \ \text{[464]}]{\text{1) }{}^{s}\text{BuLi/-115°C}} \underset{71.5\%}{\mathrm{TMSCHClBu}} \qquad (612)$$

$$\mathrm{TMSCBr_2C_8H_{17}} \xrightarrow[\text{2) }\mathrm{H_2O}\ \ \text{[464]}]{\text{1) }{}^{s}\text{BuLi/-115°C}} \underset{81\%}{\mathrm{TMSCHBrC_8H_{17}}} \qquad (613)$$

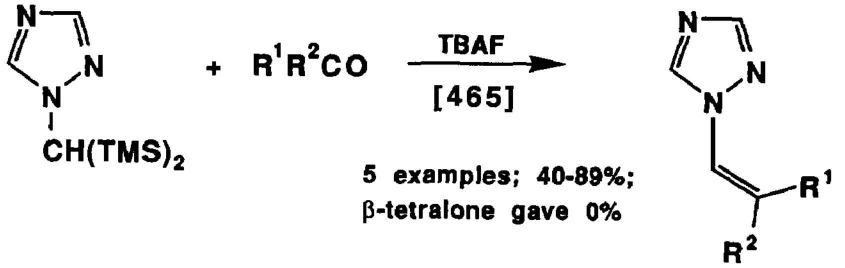


(614)

A novel route to 1-vinyl-1,2,4-triazoles via a fluoride induced Peterson olefination of 1-bis(trimethylsilyl)methyl-1,2,4-triazole, prepared according to Eqn. 615, with ketones and aldehydes was develpoed. (Eqn. 616)



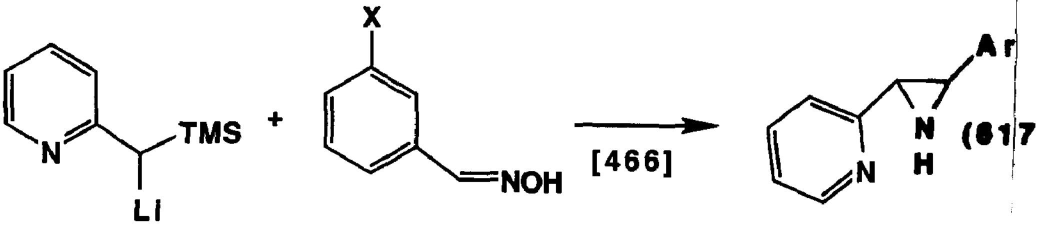
(615)



5 examples; 40-89%;
β-tetralone gave 0%

(616)

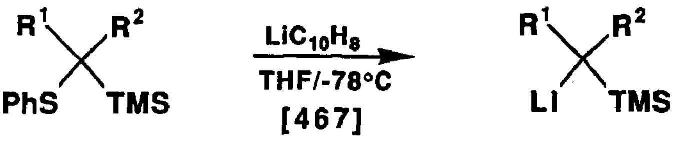
2-Trimethylsilylmethylpyridine was deprotonated and reacted with oximes of benzaldehydes to give 2-pyridylaziridines. (Eqn. 617)



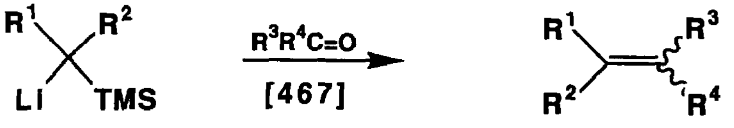
(617)

X = H, Cl, Me, OMe, NMe$_2$
60-85%

α-Thiophenoxysilanes were reacted with lithium naphthalenide converting the thiophenoxy group to a lithio group. (Eqn. 618) The resulting α-trimethylsilyl lithium reagent was utilized in Peterson olefinations of aldehydes and ketones. (Eqn. 619) α-Thiophenoxytrimethylsilylmethyllithium reagents and their applications was a popular topic. These useful reagents were reacted with aldehydes and ketones to give vinylsulfides (Eqn. 620), and added to activated olefins (Eqn. 621). The products of this addition were converted to trimethylsilyl cyclopropanes (Eqn. 622) and esters (623). The lithium reagent of thiophenoxymethyltrimethylsilane was reacted with epoxide **170** and then converted to the aldehyde **171**. (Eqns. 624 and 625) In related chemistry α-phenylsulfonylalkyltrimethylsilanes were lithiated and reacted with aldehydes and ketones to provide vinyl sulfones. (Eqn. 626)

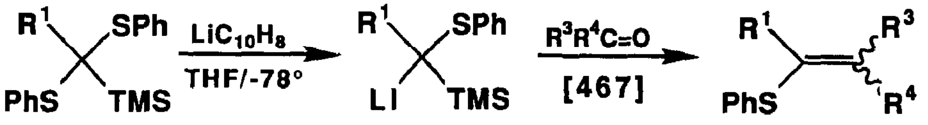


(618)



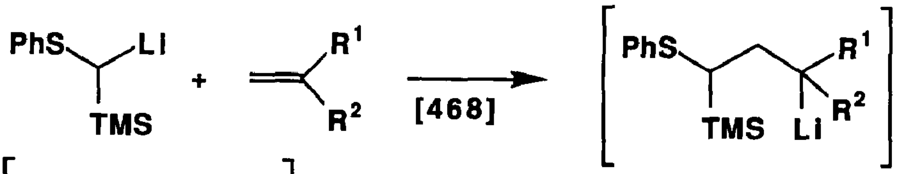
(619)

44 examples; 0-85%

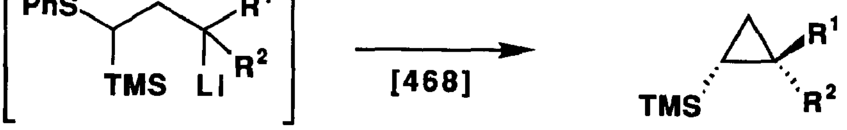


(620)

38 examples; 38-82%



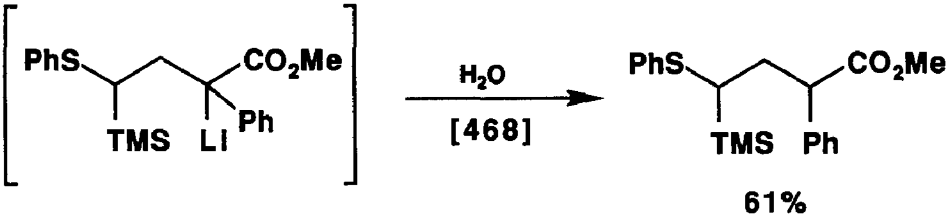
(621)



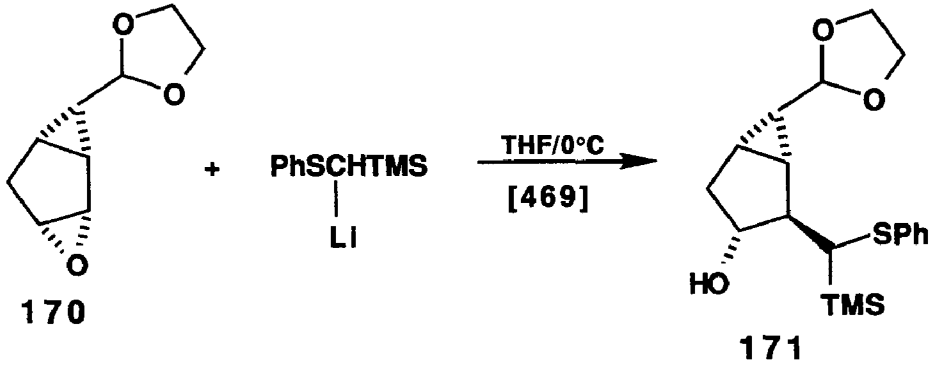
(622)

30-75%

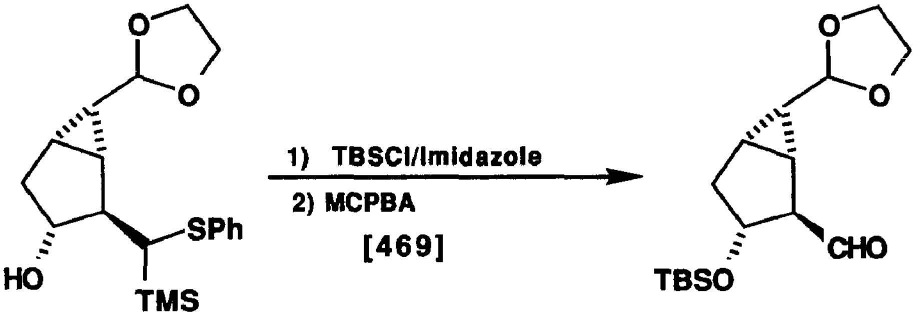
(R^1,R^2 = Ph, Ph; SMe, SMe; $S(CH_2)_3S$; SPh, SMe; SPh, SPh; TMS, Ph; CO_2Me, Ph)



(623)



(624)



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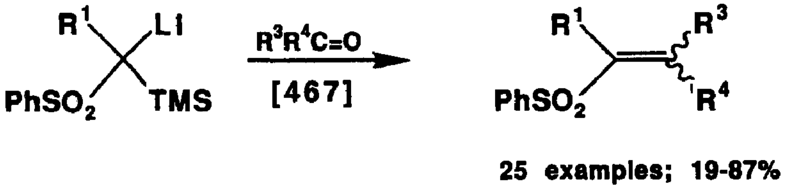
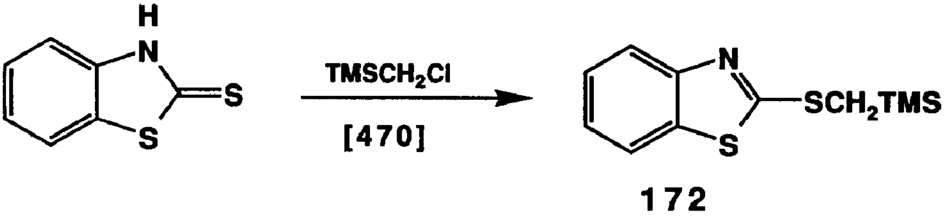


(626)

A general methodology for α-mercaptoalkylation was developed around the reagent **173** available *via* lithiation of **172**. (Eqns. 627 and 628) Thus, **173** was alkylated (Eqn. 629) and the alkylation product reacted with tert-butyllithium to give α-mercaptosilanes (Eqn. 630) or with aldehydes and ketones, the product of which was treated with tert-butyllithium to give β-mercapto alcohols. (Eqn. 631) Reaction of **173** with aldehydes and ketones gives the expected Peterson olefination product. (Eqn. 632) The reaction with enones results in conjugate addition. (Eqn. 633)



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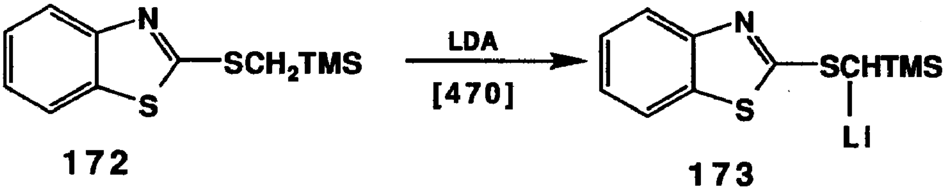
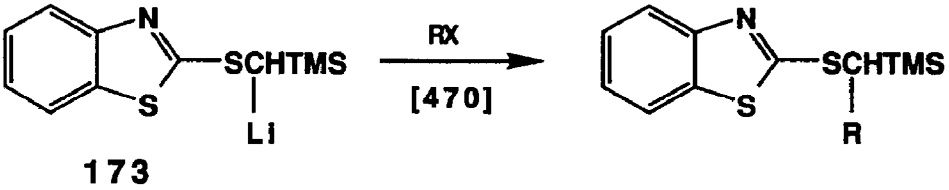
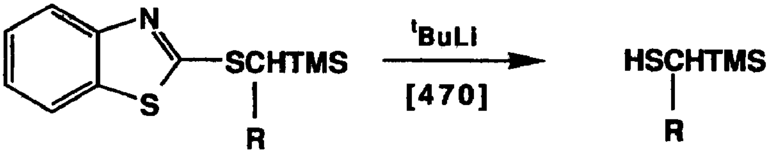


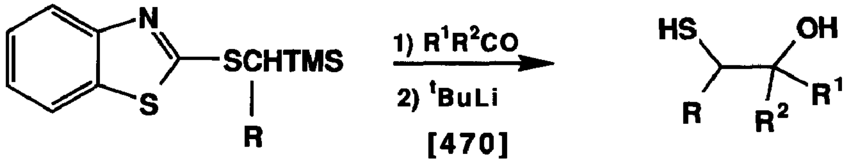
(628)



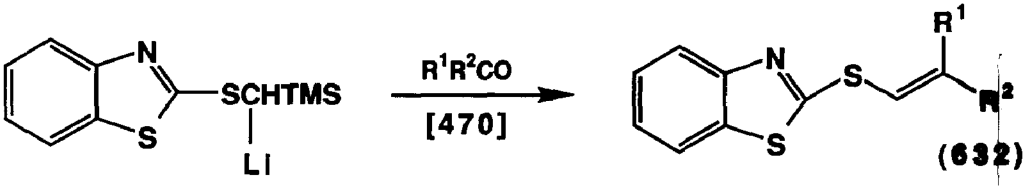
(629)



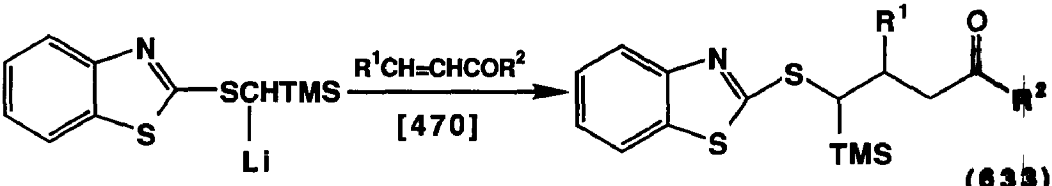
(630)



(631)



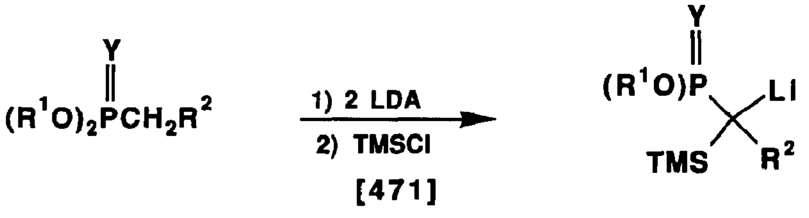
(632)



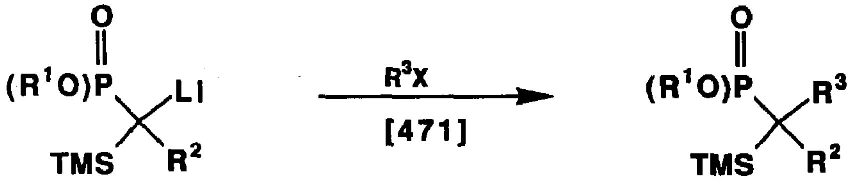
173

(633)

Dialkyl-1-(trimethylsilyl)alkanephosphonates were prepared and deprotonated in a single operation. (Eqn. 634) The α-trimethylsilyllithium reagents were alkylated (Eqn. 635), reacted with aldehydes to give vinylphosphonates (Eqn. 636), and protonated. (Eqn. 637)

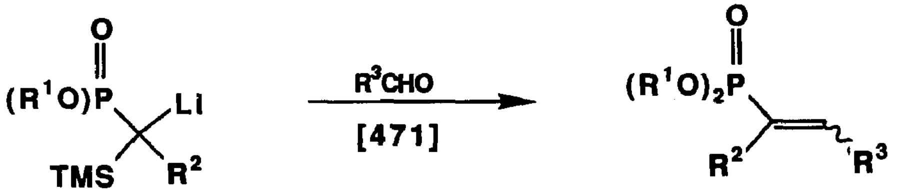


(634)



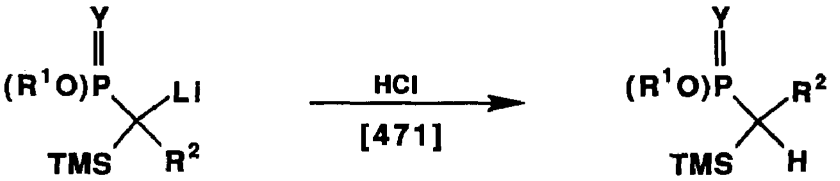
5 examples; 77-90%

(635)



7 examples; 64-78%

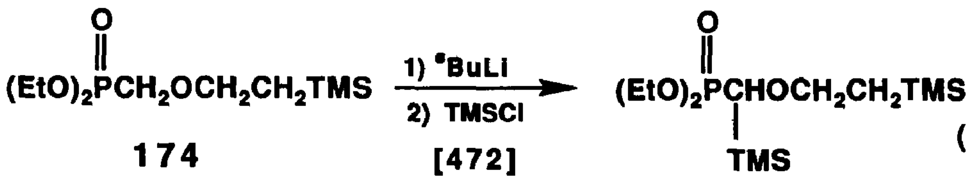
(636)



(637)

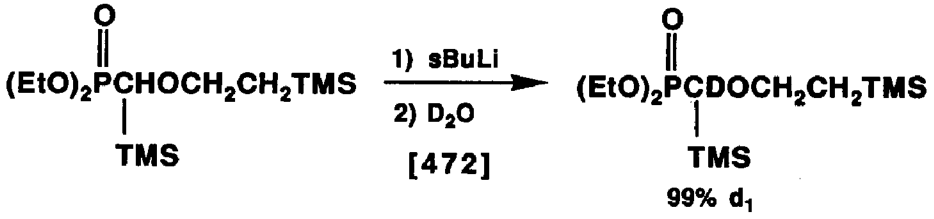
(Y = O, 9 examples; Y = S R^2 = H (sole example) ; 65-90%)

Trimethylsilylethoxymethylphosphonate **174** was deprotonated and trimethylsilylated (Eqn. 638) and the resulting phosphonate deprotonated and deuterated (Eqn. 639) Reactions with aldehydes and ketones gave the Peterson olefination product. (Eqn. 640)

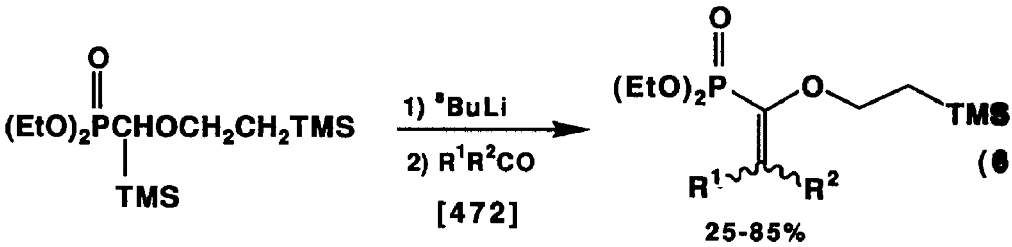


70%

(638)

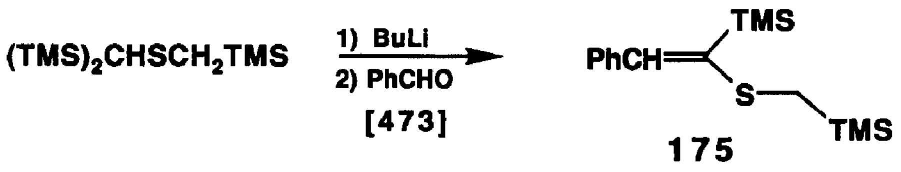


(639)



(640)

1,1,3-Tris(trimethylsilyl)dimethylsulfide was deprotonated and reacted with benzaldehyde to give **175**. (Eqn. 641) This was oxidized (Eqn. 642) and the sulfoxide used to thermally generate thiocarbonyl ylides in the presence of dipolarophiles. (Eqn. 643)



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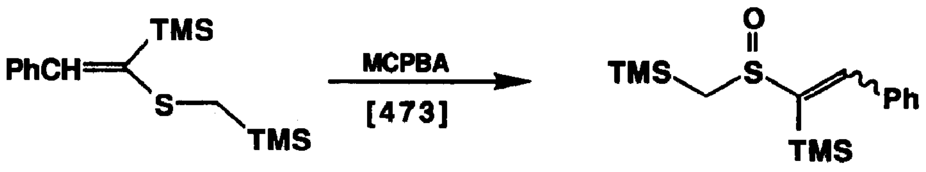

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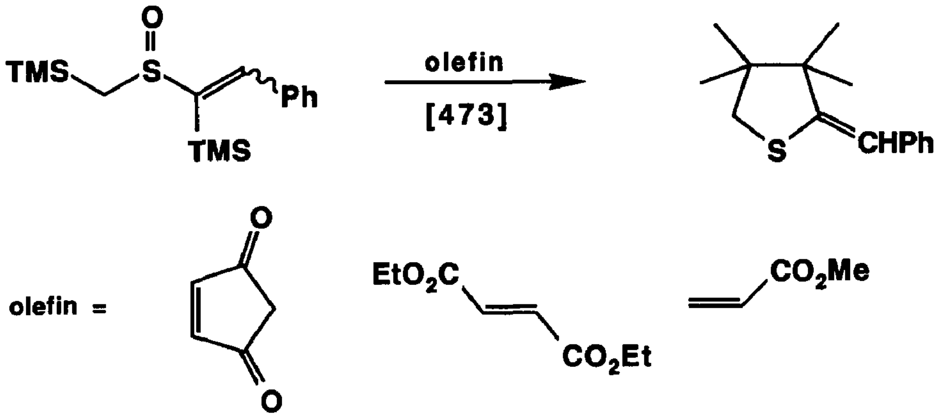
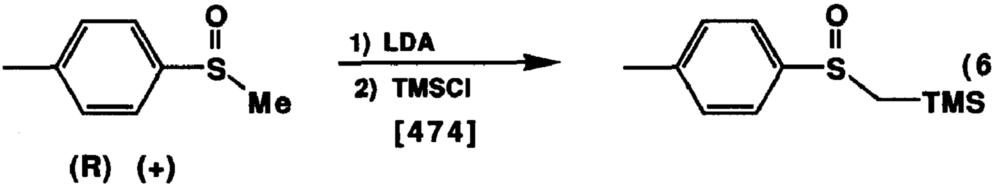
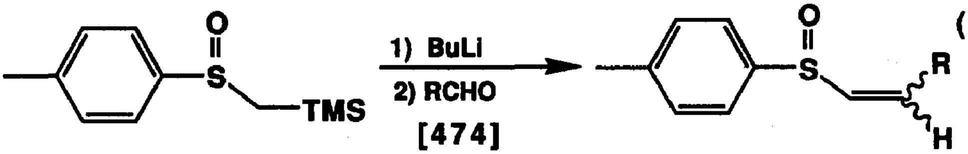


(643)

Enantiomerically pure vinyl sulfoxides were prepared from (R) (+) methyl p-tolylsulfoxide via trimethylsilylation (Eqn. 644) followed by lithiation and reaction with aldehydes and ketones (Eqn. 645).



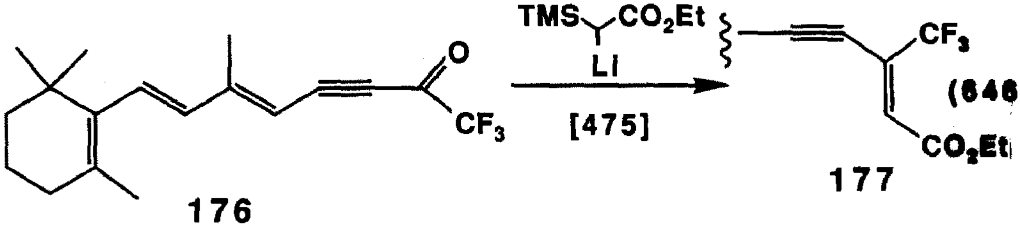
(644)



(645)

6 examples; 50-65%
acetone gave 15% yield

Trifluoromethyl ethynyl ketone **176** was reacted with ethyl lithiotrimethylsilylacetate to give **177**. (Eqn. 646)

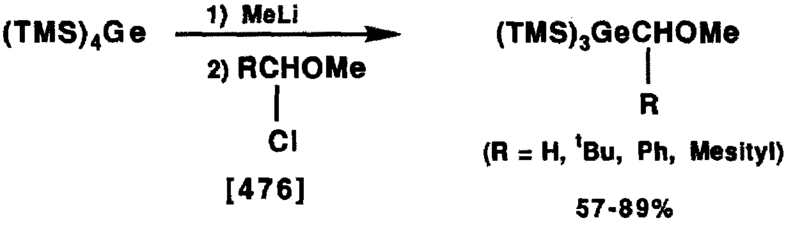


176

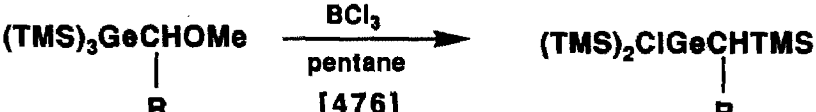
177

(646)

Tetrakis(trimethylsilyl)germanium was reacted with methyllithium to liberate tetramethylsilane and the resulting germyllithium reagent was reacted with α-chloro ethers. (Eqn. 647) These ethers, when reacted with boron trichloride gave migration of a trimethylsilyl group and the α-germylsilanes **178** and **179**. (Eqns. 648 and 649)

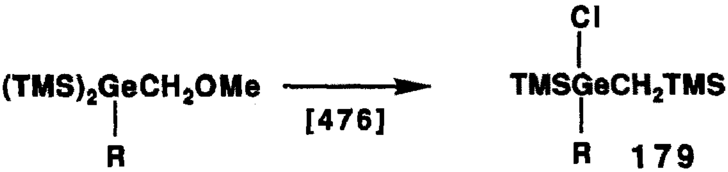


$$(TMS)_4Ge \xrightarrow[\substack{2)\ \underset{\textstyle Cl}{\underset{|}{RCHOMe}} \\ [476]}]{1)\ MeLi} \underset{\textstyle R}{\underset{|}{(TMS)_3GeCHOMe}} \quad (R = H, {}^tBu, Ph, Mesityl) \quad 57\text{-}89\% \qquad (647)$$



$$\underset{\textstyle R}{\underset{|}{(TMS)_3GeCHOMe}} \xrightarrow[\substack{pentane \\ [476]}]{BCl_3} \underset{\textstyle R}{\underset{|}{(TMS)_2ClGeCHTMS}} \qquad (648)$$

178

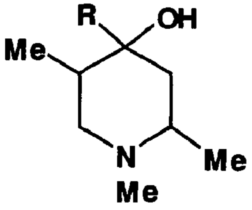


$$\underset{\textstyle R}{\underset{|}{(TMS)_2GeCH_2OMe}} \xrightarrow[[476]]{} \underset{\textstyle R}{\underset{|}{\overset{\textstyle Cl}{\overset{|}{TMSGeCH_2TMS}}}} \qquad (649)$$

179

D. α-Functional Organosilanes-Other Studies

MM2 calculations were carried out on $H_2Si(CX_3)_2$ systems where X = Cl and Br. The stable conformation is predicted to be of C_2 symmetry. [477] Frontier MO theory was used to explain the regioselectivity in the 1,3-dipolar cycloadditions of thiocarbonyl ylides generated from [bromo[[(trimethylsilyl)methyl]thio]methyl]trimethylsilane and related compounds. [478] MM2 calculations were carried out on $Si(CH_2X)_4$ molecules where X = F, Cl, Br. They were compared to the values for the carbon analogs. [479] The conformational analysis of the halogenated molecules $Me_2C(CH_2X)_2$ and $Me_2Si(CH_2X)_2$ were looked at with molecular mechanics. [480] The most stable conformation of **180** was determined to be an equilibrium between chair and skewed boat forms. [481]



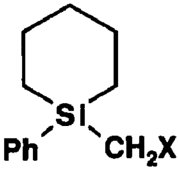
(R = Ph, Ph_3Si, Ph_2MeSi, $PhMe_2Si$)

180

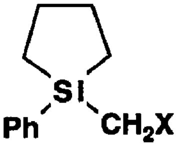
The x-ray crystal structure of trimethylsilylmethyllithium was determined. The compound is in hexameric units with two distinct Li-Li distances. [482] The IR analysis of intramolecular coordination in **181** was accomplished. [483]

181

The ^{13}C NMR assignments for **182** and **183** were made. [484] The photoelectron spectrum of 3,3-dimethyl-3-silathietane was obtained. It shows that this molecule prefers a planar arrangment. [485]



182



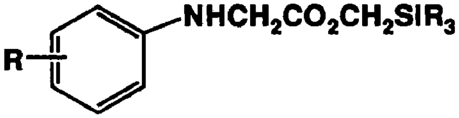
183

The electronic absorption spectra of charge-transfer complexes based on ferrocene complexes with halogenated alkanes including α-bromosilane **184** was studied. [486] The charge-transfer complexes of chloranil with trimethylsilylmethyl esters of α-phenylbutyric acid and N-substituted aminoacetic acids **185** were studied by electronic spectroscopy. The results indicate that the trialkylsilylmethyl acetates are electron donating groups. [487]

Br_3CCH_2CHBrR

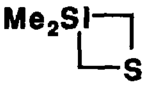
$Br_3CCH_2CHBrTMS$

184



185

The electron donating ability of sulfur in thiasilacycloalkanes **186-189** was studied. [488] The donating ability of aryloxysilanes was also determined with compounds of the structures **190** and **191**. [489]



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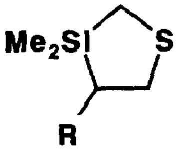

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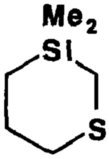

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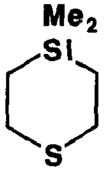

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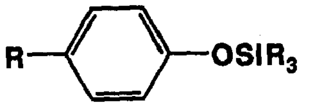

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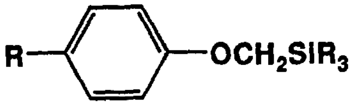
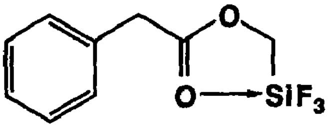


191

Pentacoordination of the silicon atom in compounds of the structure **192** was investigated. [490]



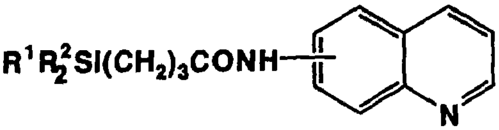
192

Compounds of the structure **193** were found to have pesticidal activity [491] and those of structure **194** to have antiviral activity [492].

$R^1R^2R^3SiCH_2ZCHR^4R^5$

($Z = CH_2, O, NR^8$)

193



R^1,R^2 = Me, Me; Et, Et; Me, Pr

194

XIII. β-FUNCTIONAL ORGANOSILANES.

A. Preparation

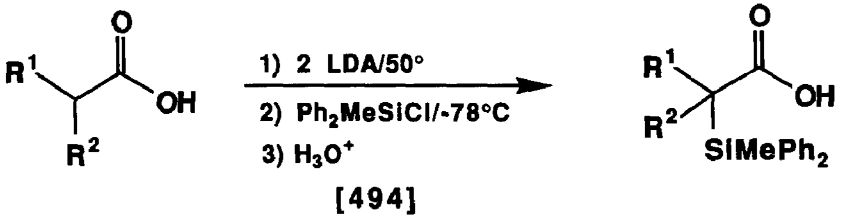
Several syntheses of α-silyl carbonyl systems were reported. Silyl acetic acids optically active at silicon, were prepared from the appropriate silylmethylmagnesium chloride and carbon dioxide. (Eqn. 650) These were used in the determination of the optical purity of chiral amines, alcohols, and acids.

$$\mathrm{PhMeRSiCH_2Cl} \xrightarrow[\text{2) } \mathrm{CO_2}]{\text{1) Mg}} \mathrm{PhMeRSiCH_2CO_2H} \qquad (650)$$

[493]

$(\mathrm{R} = \mathrm{PhCH_2}, \mathrm{Et}, \text{o-tolyl})$

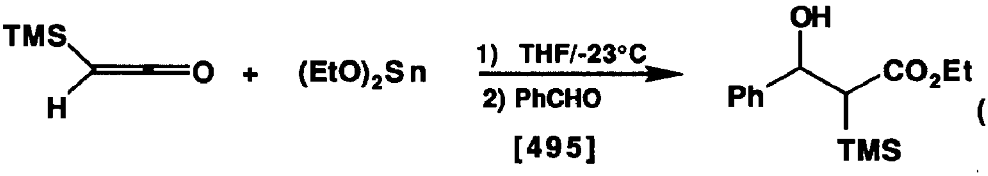
The deprotonation-diphenylmethylsilylation of acids results in the formation of the α-silyl acid. (Eqn. 651)



(651)

$\mathrm{R^1,R^2}$ = Me, H; $\mathrm{PhCH_2}$, H; $\mathrm{(CH_2)_3}$; $\mathrm{(CH_2)_4}$, $\mathrm{(CH_2)_5}$; $\mathrm{(CH_2)_6}$

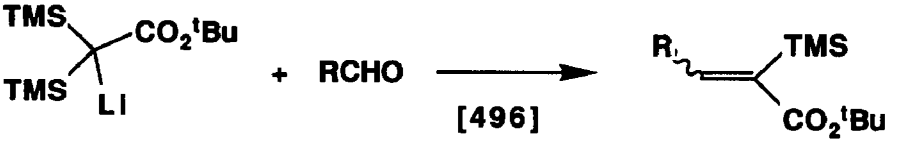
The β-hydroxy-α-trimethylsilyl esters **195** were prepared from trimethylsilylketene as shown in Eqn. 652.



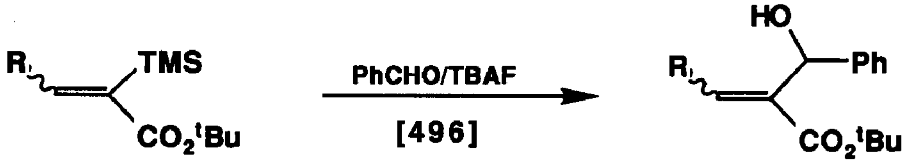
195

(652)

tert-Butyl bis(trimethylsilyl)lithioacetate was reacted with aldehydes to give the α-trimethylsilyl-α,β-unsaturated esters. (Eqn. 653) These were directly reacted with aldehydes in the presence of fluoride ion to give the condensation product. (Eqn. 654)



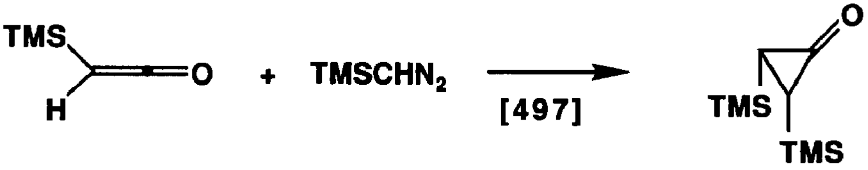
(653)



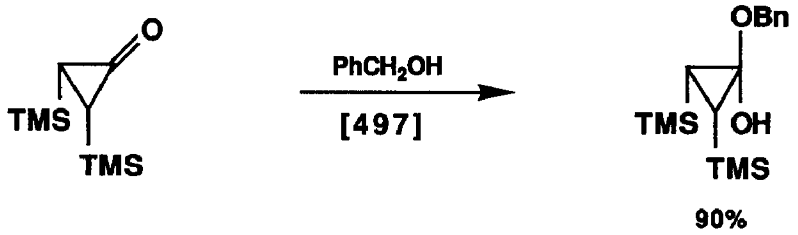
($R = CF_3$)

(654)

Trimethylsilylketene was reacted with trimethylsilyldiazomethane to give 2,3-bis(trimethylsilyl)cyclopropanone. (Eqn. 655) This was reacted with benzyl alcohol to give the hemiketal in excellent yield. (Eqn. 656)

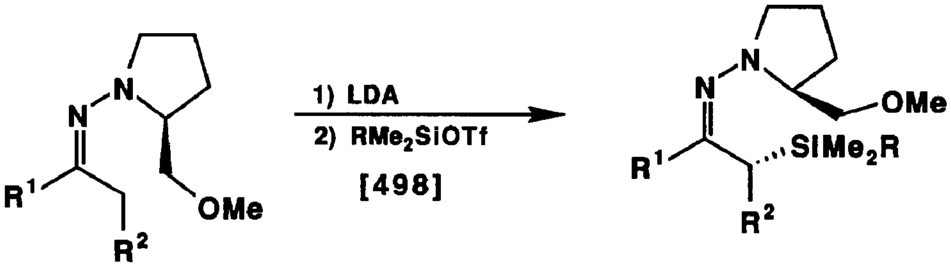


(655)



(656)

A clever synthesis of α-silyl ketones, optically active at the α-carbon containing the silyl group, was reported starting from optically active hydrazones. (Eqns. 657 and 658)



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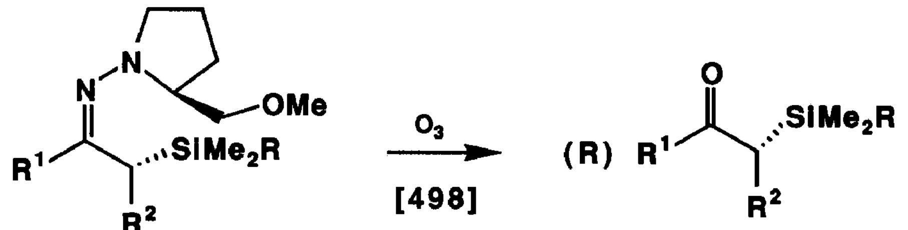
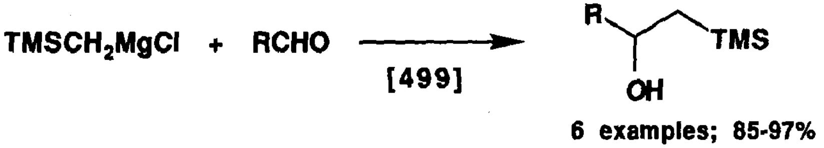


(658)

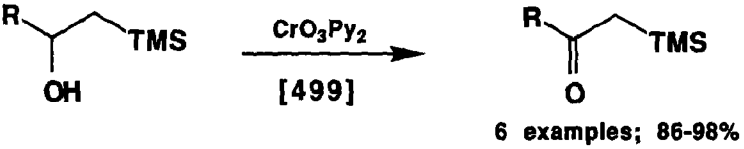
7 examples; 22-79%; ee >96%

R = ᵗBu, thexyl

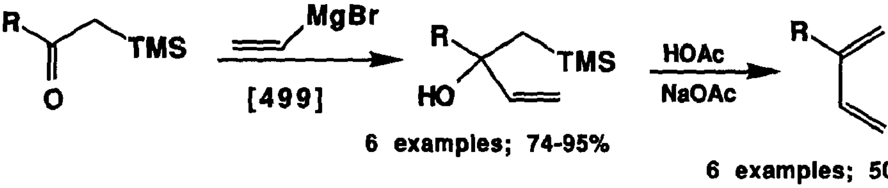
α-Trimethylsilyl ketones were synthesized by oxidation of β-hydroxysilanes, prepared from trimethylsilylmethylmagnesium chloride and aldehydes. (Eqns. 659 and 660) The α-trimethylsilyl ketones were used in a 1,3-diene synthesis. (Eqn. 661)



(659)

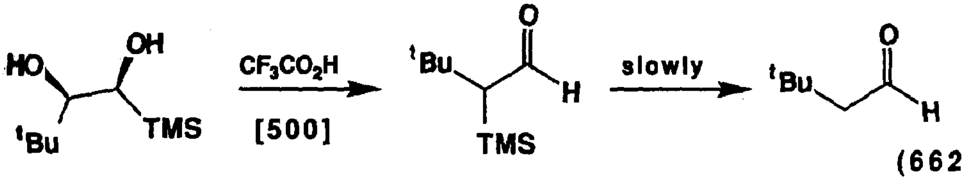


(660)

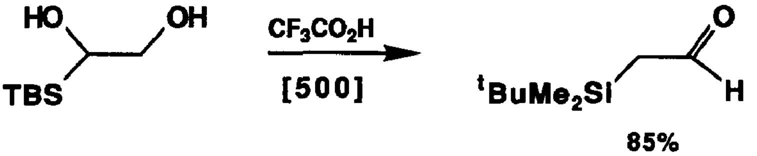


(661)

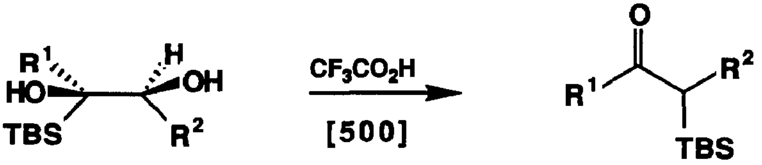
α-Silyl aldehydes were prepared *via* the acid catalyzed rearrangement of α,β-dihydroxysilanes. (Eqns. 662 and 663) α-Silyl ketones can be prepared in this manner as well. (Eqn. 664)



(662)



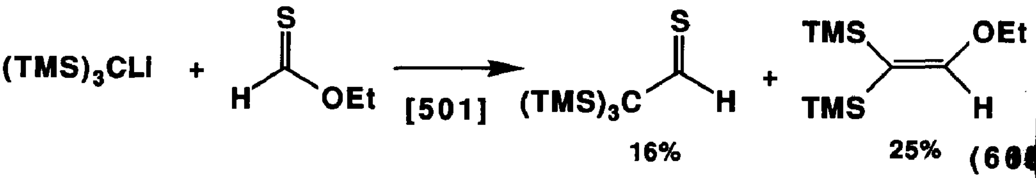
(663)



R^1 = H, R^2 = C_6H_{11} 86%
R^1 = Ph, R^2 = H 99%
R^1 = Pr, R^2 = Pr 90%

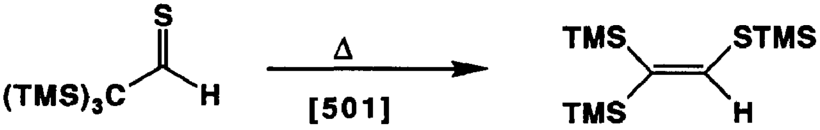
(664)

Tris(trimethylsilyl)methyllithium was reacted with O-ethyl thioformate to give the ethyl enol ether of bis(trimethylsilyl)acetaldehyde and the interesting tris(trimethylsilyl)ethanethial **196**. (Eqn. 665) The thial **196** thermally provides thioenol ether (Eqn. 666) and photolytically gives tris(trimethylsilyl)ethene (Eqn. 667).

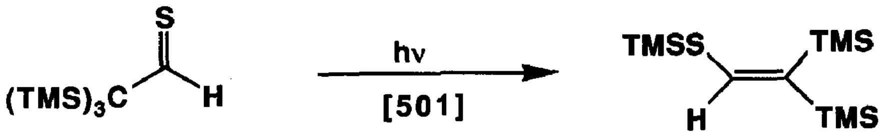


196

(66[illegible])



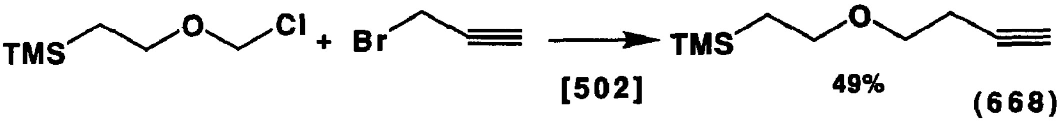
(66[illegible])



196

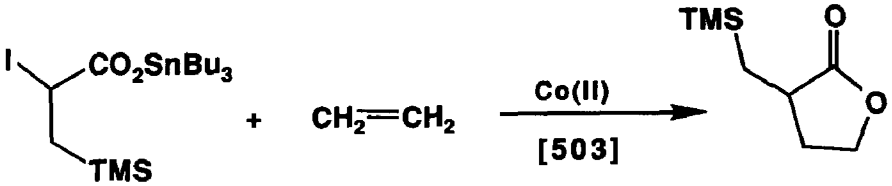
(667)

The homopropargyl ether of trimethylsilylethanol was prepared as shown in Eqn. 668.



(668)

The cyclization of **197** with ethylene and other olefins gives the silylated lactone, for example, **198**. (Eqn. 669)

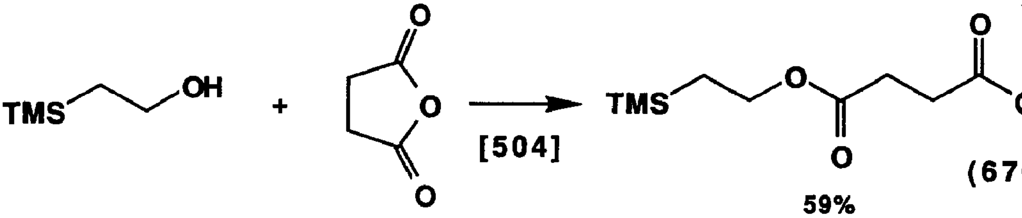


197

198

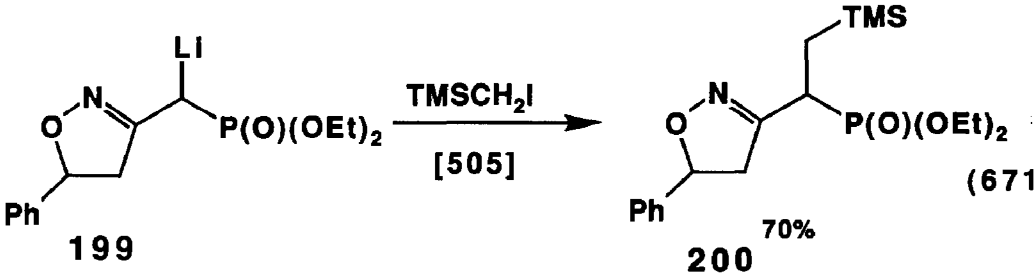
(669)

Trimethylsilylethanol was reacted with succinic anhydride to give the half ester. (Eqn. 670)



(670)

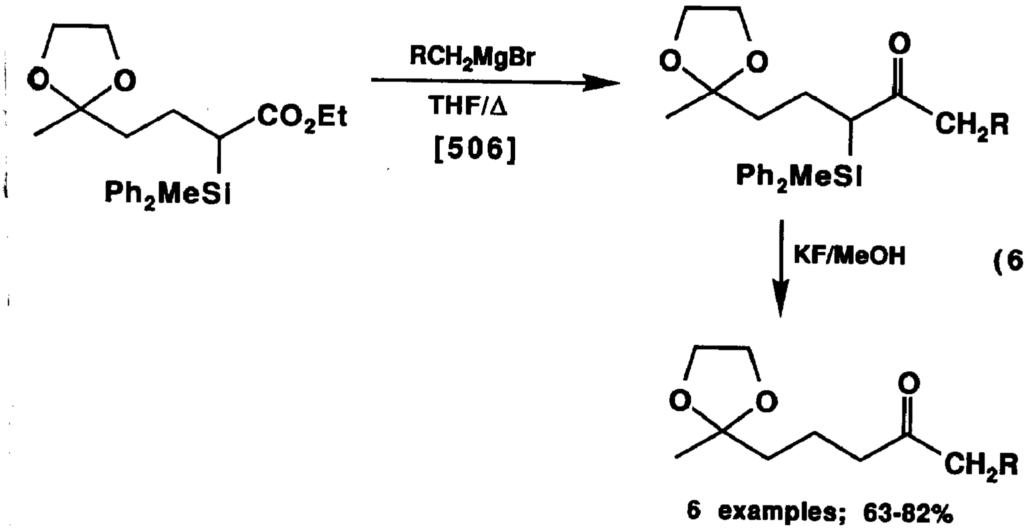
Lithium reagent **199** followed by alkylation with iodomethyltrimethylsilane gives the β-functional silane **200**. (Eqn. 671)



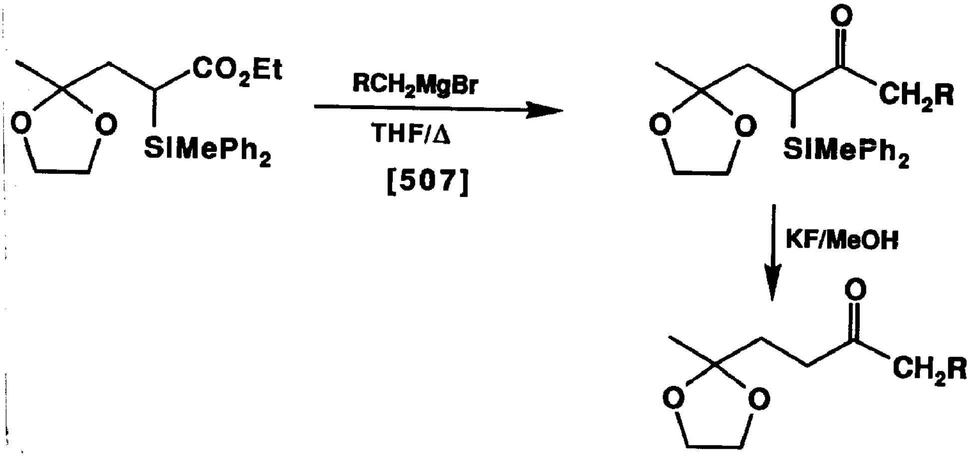
(671)

B. β-Functional Organosilanes-Reactions

Synthetically useful reactions of α-silyl esters were reported. A facile synthesis of the monoprotected 2,2-ethylenedioxy-6-ketones was reported starting from ethyl 5,5-ethylenedioxyhexanoate *via* diphenylmethylsilylation as reported earlier and then treatment of the α-silyl ester with a Grignard reagent and desilylation. (Eqn. 672) A identical approach was used to prepare 2,2-ethylenedioxy-5-ketones. (Eqn. 673)

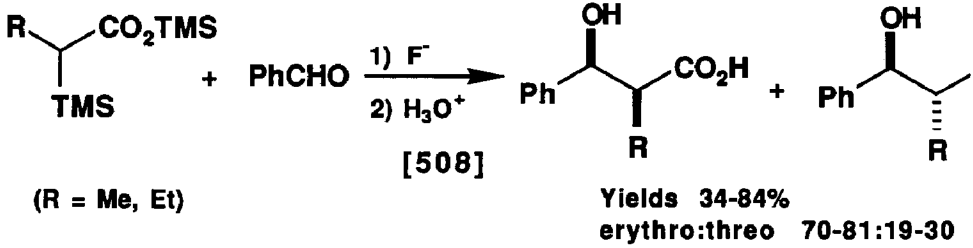


(672)



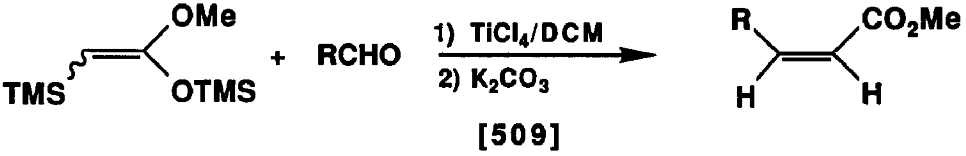
(673)

α-(Trimethylsilyl)trimethylsilyl carboxylates undergo fluoride-induced condensations with aldehydes. (Eqn. 674)

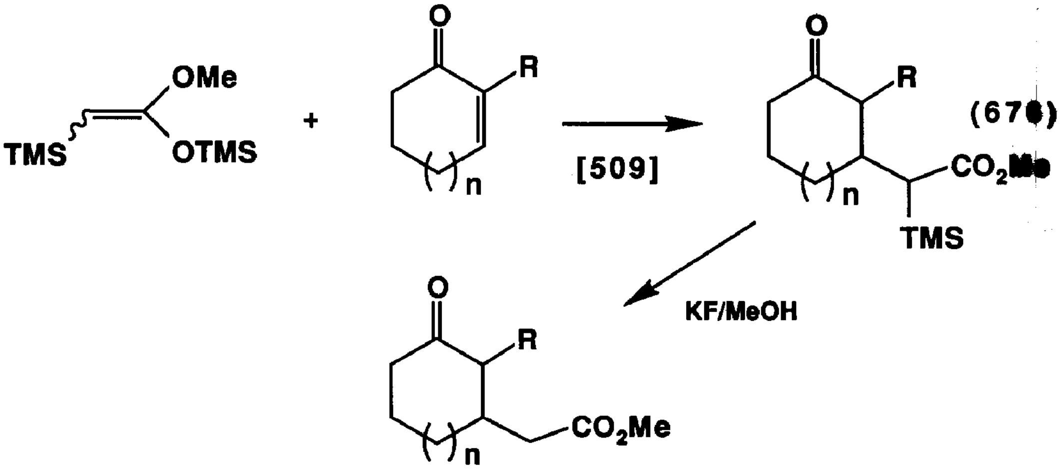


(674)

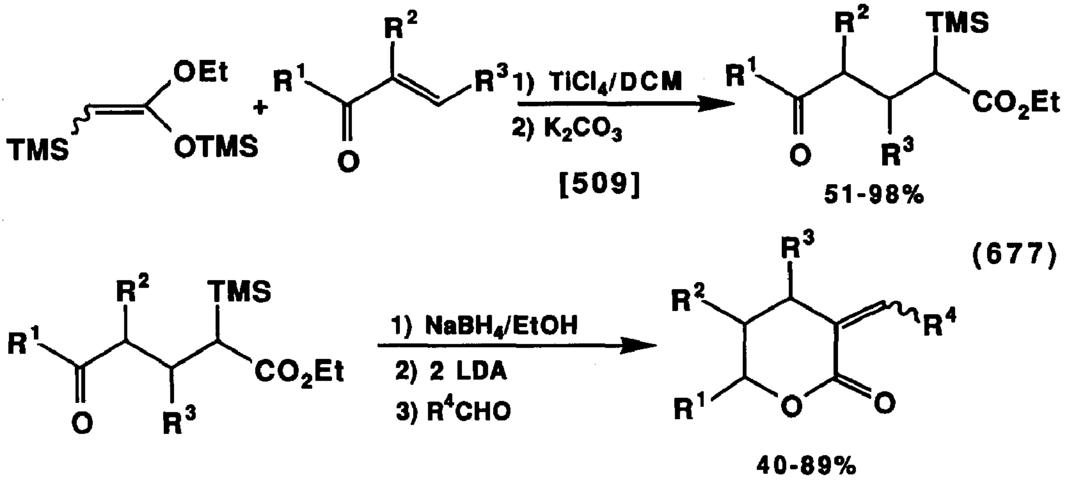
The trimethylsilyl ketene acetal of methyl trimethylsilylacetate was used in the preparation of α,β-unsaturated esters *via* a condensation-Peterson olefination sequence. (Eqn. 675) The reaction of this reagent with cycloalkenones gives the β-carboxymethyl cycloalkanone. (Eqn. 676) The reaction of the trimethylsilyl ketene acetal of ethyl trimethylsilylacetate with enones produces 5-keto-2-trimethylsilylpentanoates, which were converted to exo-methylenevalerolactones. (Eqn. 677)



(675)

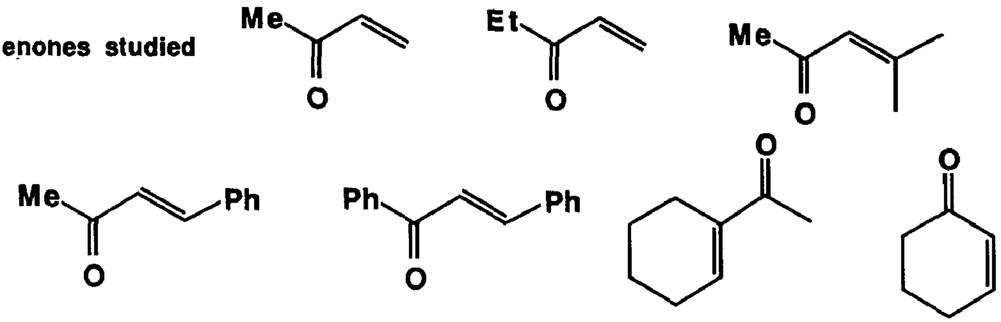


(676)

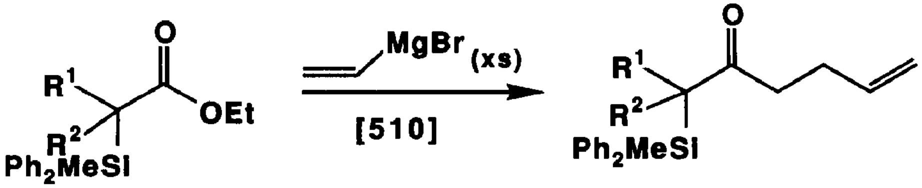


(677)

enones studied



α-Diphenylmethylsilyl esters were reacted with vinylmagnesium bromide, the first equivalent providing an unsaturated ketone, which then undergoes addition of a second equivalent of the Grignard reagent in a Michael fashion. (Eqn. 678) The resulting α-silyl ketone can be quantitatively thermally rearranged to the silyl enol ether. (Eqn. 679) Treatment of the silyl enol ether with palladium(II) acetate in acetonitrile gives 6-endo-trig cyclization products. (Eqn. 680)



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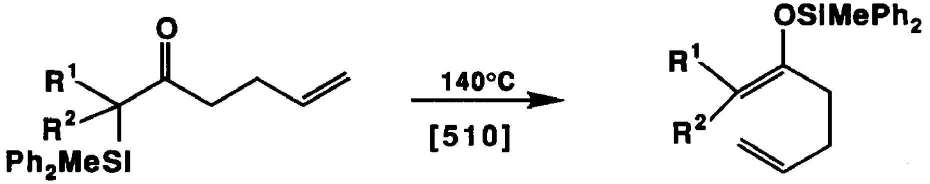

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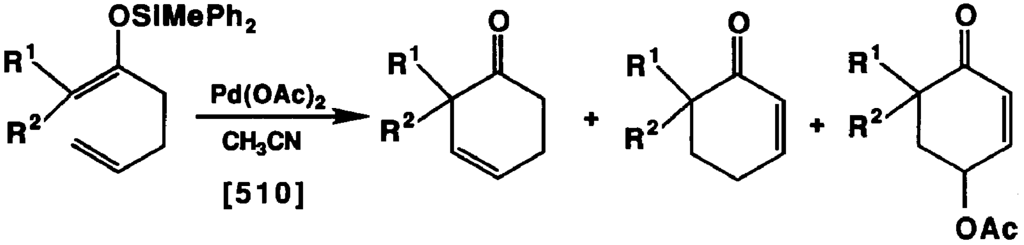
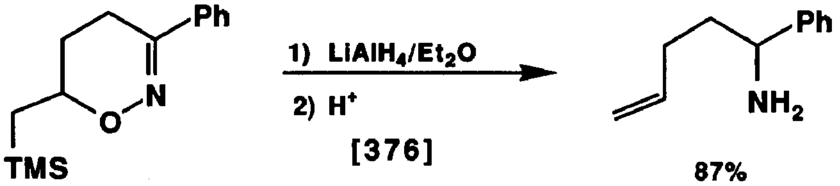


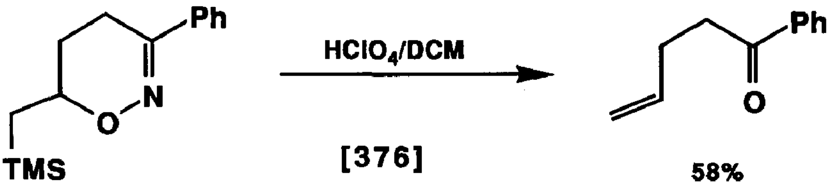
(680)

The β-trimethylsilyl-1,2-oxazines **201** were reduced and eliminated to give unsaturated amines (Eqn. 681) or hydroyzed with concomitant elimination to give γ,δ-unsaturated ketones (Eqn. 682).



201

(681)



201

(682)

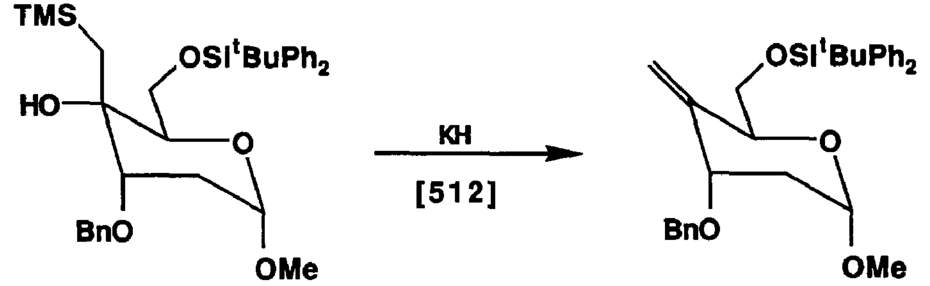
The silane **202** was pyrolyzed to provide a sample of P-cyanophosphaethene for microwave spectroscopy. (Eqn. 683)

$$\underset{\textbf{202}}{\mathrm{TMSCH_2PClCN}} \xrightarrow[\text{[511]}]{\Delta} \mathrm{CH_2{=}PCN} \qquad (683)$$

The reaction of trimethylsilylmethylmagnesium chloride with ketone **203** was a key step in an approach to the Prelog-Djerassi lactone. (Eqn. 684) It was found that treatment of the axial trimethylsilylmethyl isomer with potassium hydride gave the desired exo-methylene cyclohexane (Eqn. 685), but similar treatment of the equatorial trimethylsilylmethyl isomer gave a complex mixture of products. (Eqn. 686)

203

(684)



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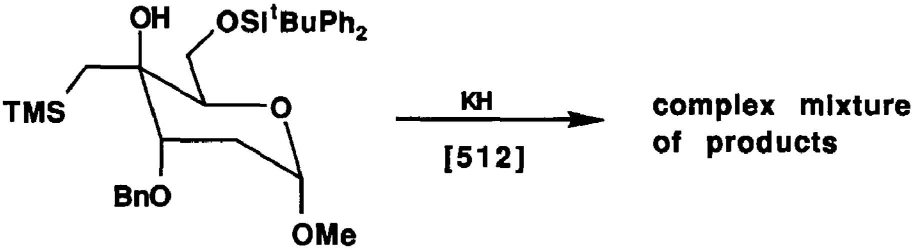
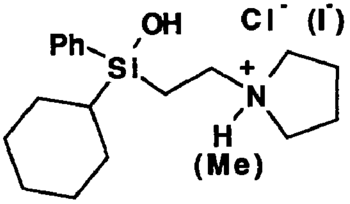


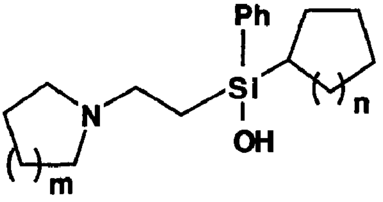
(686)

C. β-Functional Organosilanes-Other Studies

The structure of several gaseous ω-(acyloxy)alkyltrihalosilanes, including the β-substituted ones, were studied by mass spectral techniques. [513] The pyrrolidinoethylsilane **204** was prepared in optically active form. It demonstrates antimuscarinic activity. [514] The sila-procyclidine **205** was studied for its peripheral and central anticholinergic activity. [515]



204

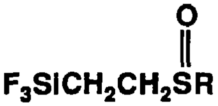


205

$R^1CO_2(CH_2)_nSiR_3$ where (R^1 = Me, Ph, R = Cl, F; n = 2, 3)

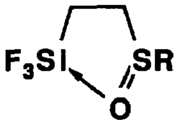
$PhCH_2SCH_2CH_2SiF_3$

Benzylmethylphenylsilyl acetic acid has been put forth as a reagent for determining the optical purity of chiral amines [516] as has been ethylmethylphenylsilyl acetic acid [517]. The IR, UV and mass spectra of **206** indicate an O-Si interaction as in **207**. [518]



$F_3SiCH_2CH_2\overset{O}{\overset{\|}{C}}SR$

206

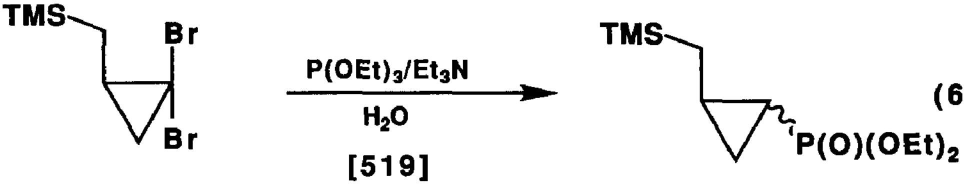


207

XIV. MISCELLANEOUS FUNCTIONAL ORGANOSILANES.

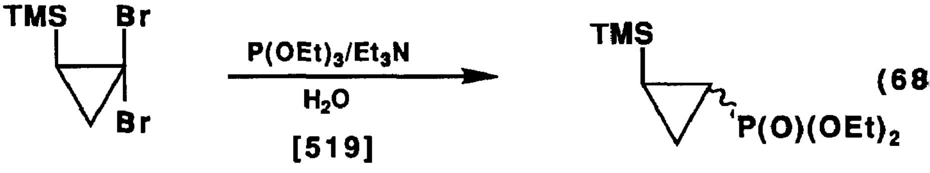
A. γ-Functional Organosilanes

The reaction of triethylphosphite with 1,1-dibromotrimethylsilylmethylcyclopropane gives the phosphonate **208**. (Eqn. 687) A similar reaction leads to the β-functional system **209**. (Eqn. 688)



(687)

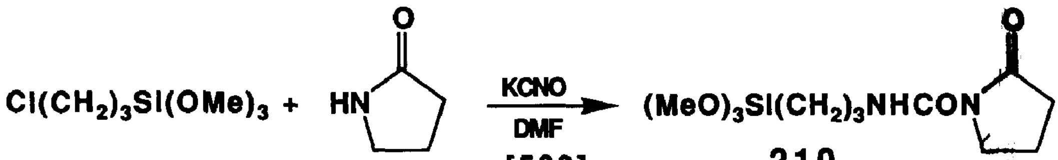
208 39%



(688)

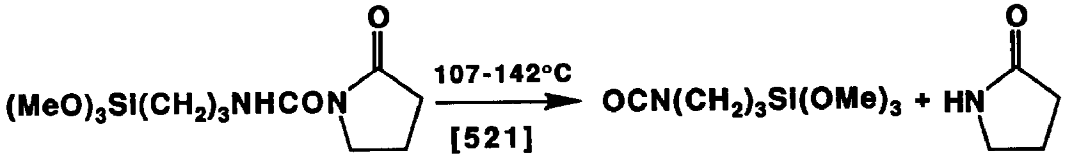
209

The reaction of chloropropyltrimethoxysilane with potassium isocyanate and pyrrolidinone gives **210**, (Eqn. 689) heating of which leads to the isocyanatopropyltrimethoxysilane. (Eqn. 690) The N-(3-trimethoxysilylpropyl)acrylamide **211** was reacted with proline to give **212**, which was used to treat silica gel for HPLC applications. (Eqn. 691) Bis-(chloropropyl)dimethoxysilane was reacted with potassium methacrylate to give bis-(methacryloxypropyl)dimethoxysilane. (Eqn. 692) Chloropropyl- and chloromethyltriethoxysilane were reacted with sodium cyclopentadienide to give the corresponding cyclopentadienylpropyl (or methyl) triethoxysilane. (Eqn. 693)



210

(689)



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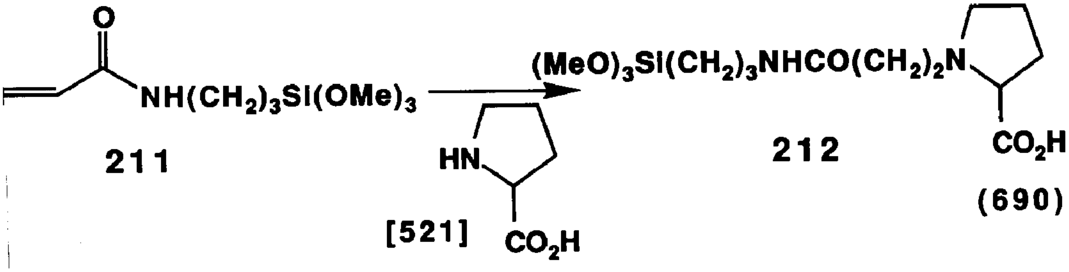

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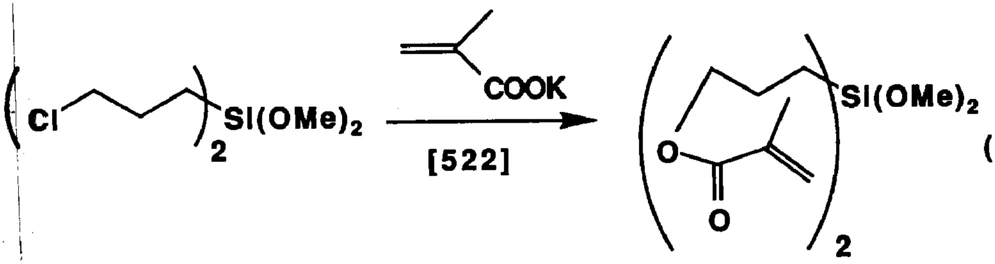

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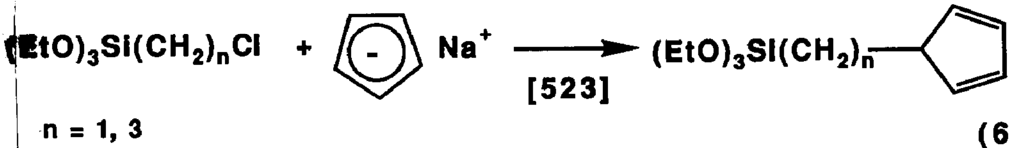
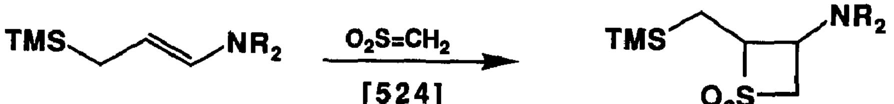


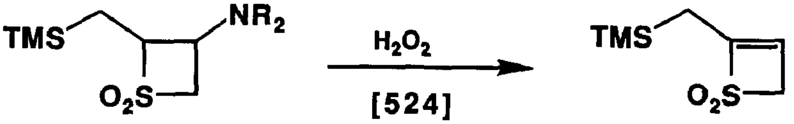
(693)

The γ-amino allylsilane **213** was reacted with a variety of substrates to give silylated heterocycles. Some examples are given in Eqns. 694-699.



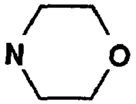
213

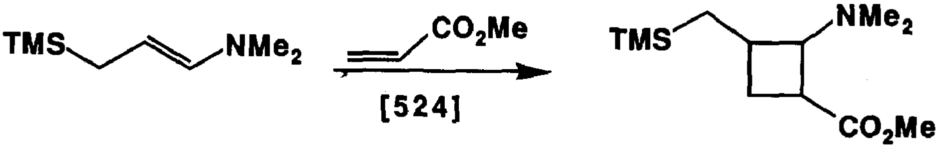
(694)



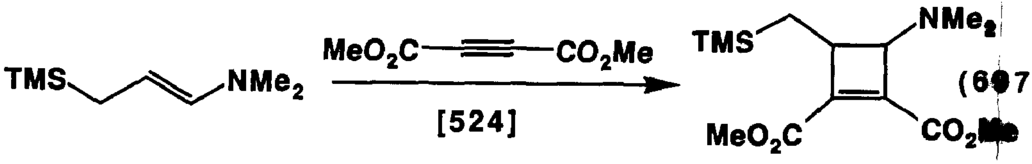
(695)

R_2N = Me_2N, Et_2N and

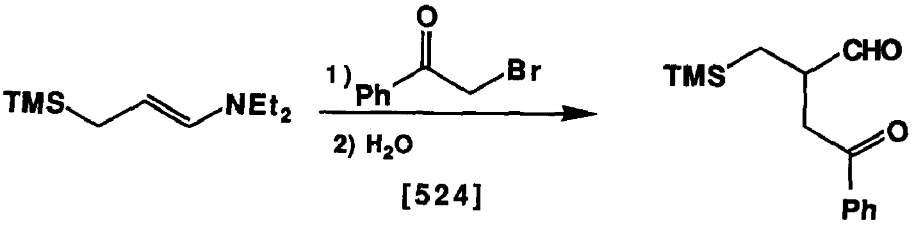




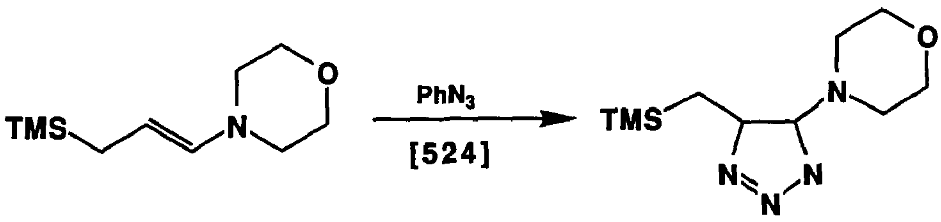
(6[illegible]6)



(6[illegible]7)

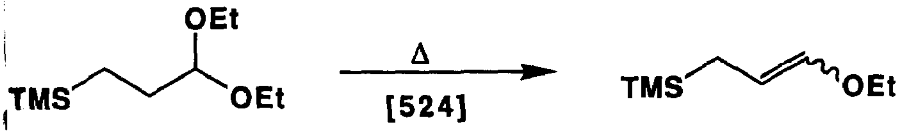


(6[illegible]8)

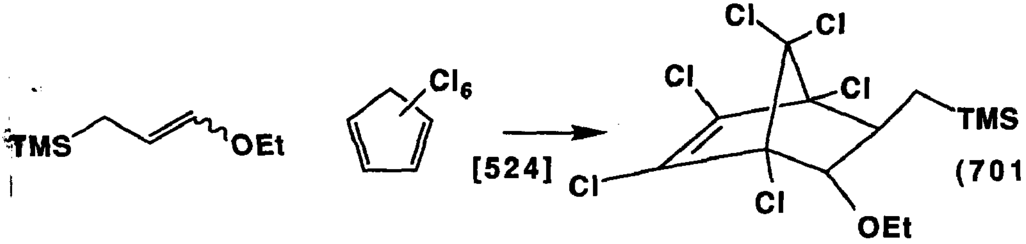


(699)

In related chemistry a γ-ethoxy allylsilane was formed (Eqn. 700) and cycloadded to hexachlorocyclopentadiene (Eqn. 701).

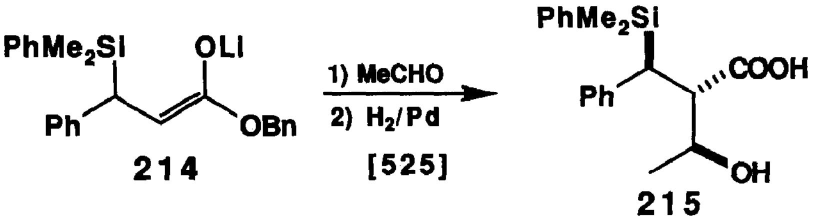


(700)

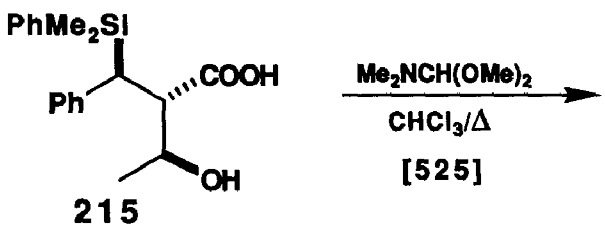


(701)

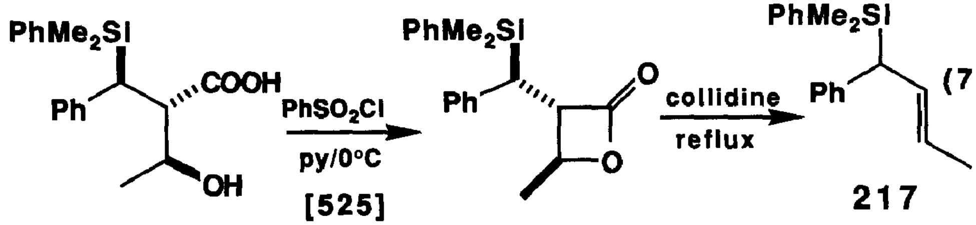
The diastereoselectivity of the aldol reactions of β-silyl enolates was studied. Thus, **214** was condensed with acetaldehyde to give **215** (Eqn. 702). Compound **215** was decarboxylated and dehydrated to allylsilane **216** (Eqn. 703) or converted to the β-lactone and then allylsilane **217** (Eqn. 704). Other examples of these approaches to stereodefined allylsilanes were reported.



(702)

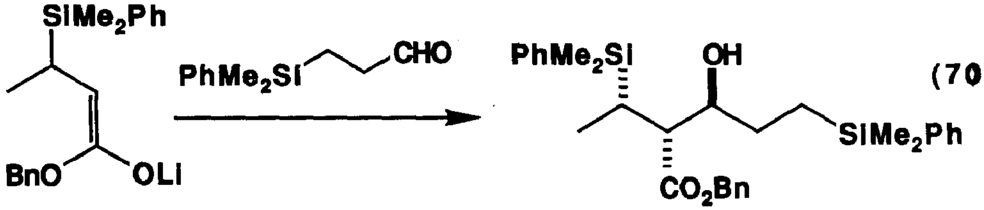


(703)

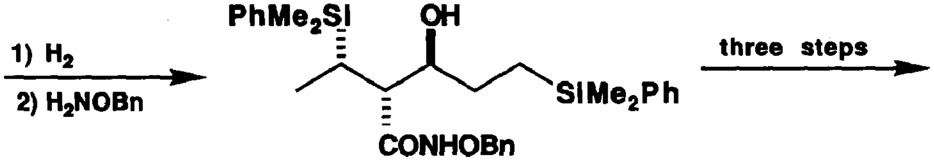


(704)

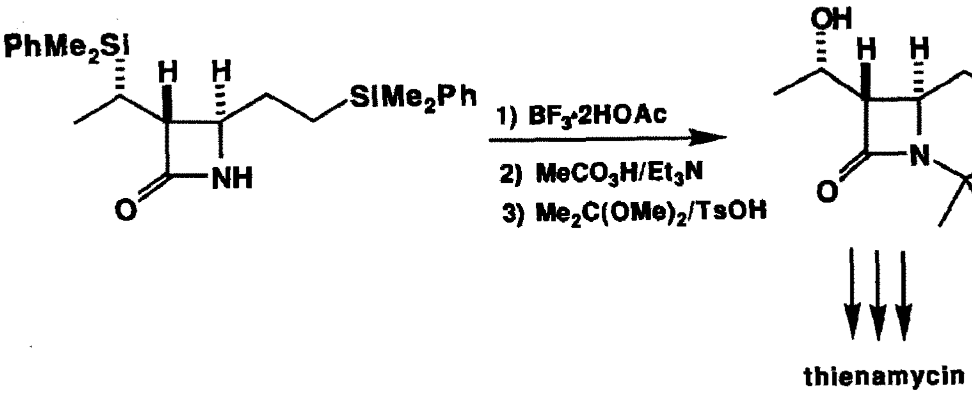
This diastereoselectivity was applied to the formal synthesis of thienamycin as illustrated in Eqns. 704-706.



(704)

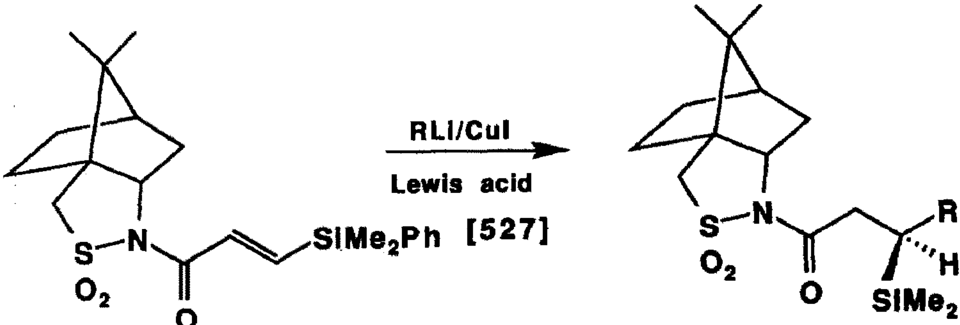


(705)



(706)

Enantiomerically pure β-silyl esters were prepared from the optically active sultam **218**. (Eqns. 707 and 708)

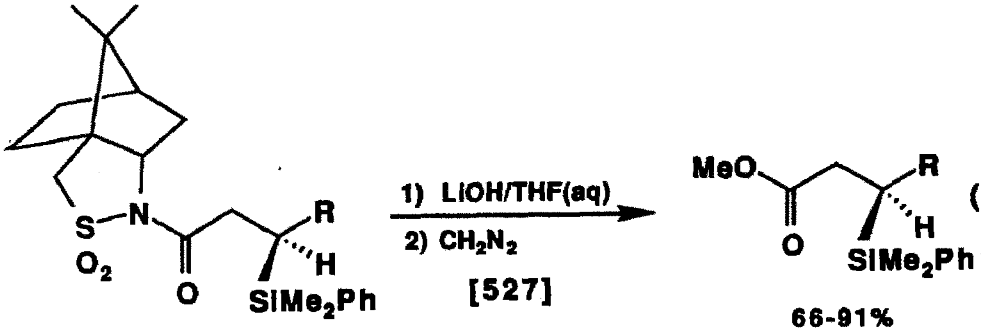


218

(707)

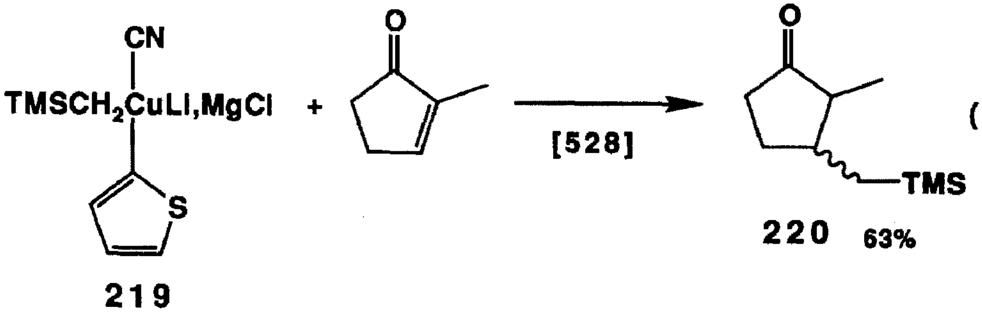
Lewis acid = BF$_3$OEt$_2$, Et$_2$AlCl; R = vinyl, 1-propenyl, Me, Et, Pr, iPr, Bu, Ph, PhMe$_2$Si

Yields 43-86%; ee high



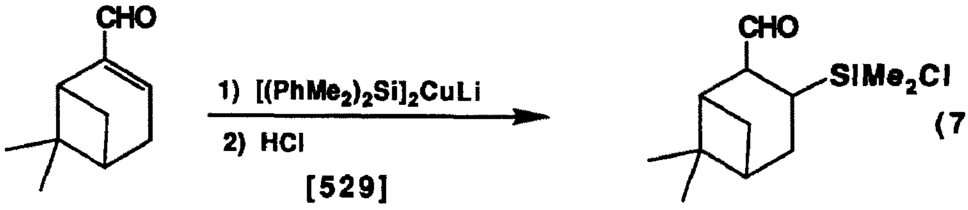
(708)

The trimethylsilylmethylcuprate **219** was added to 2-methylcyclopentenone with boron trifluoride etherate catalysis to give ketosilane **220**. (Eqn. 709)

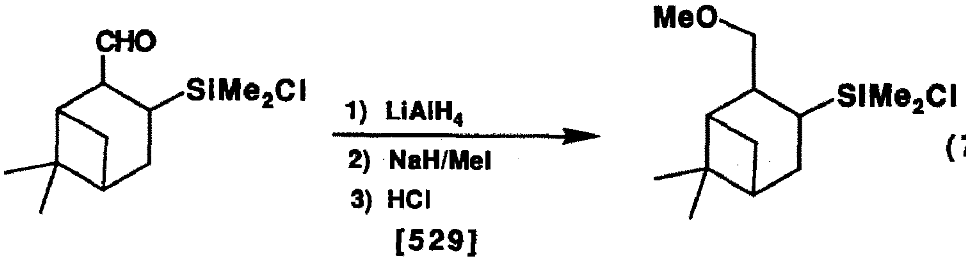


(709)

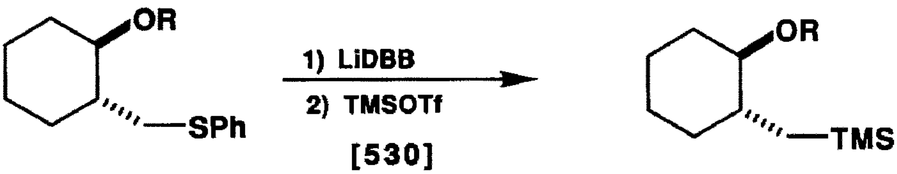
(1R) (-) Myrtenal was converted to the γ-methoxysilane optically active at carbon. (Eqns. 710 and 711) Another route to γ-alkoxysilanes is from the γ-alkoxyalkylsulfide. (Eqn. 712)



(710)



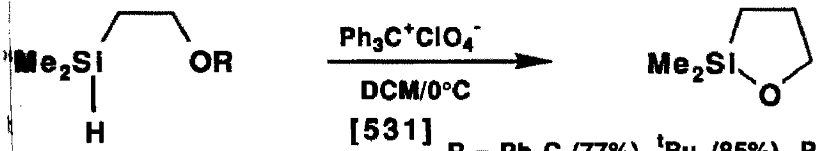
(711)



(712)

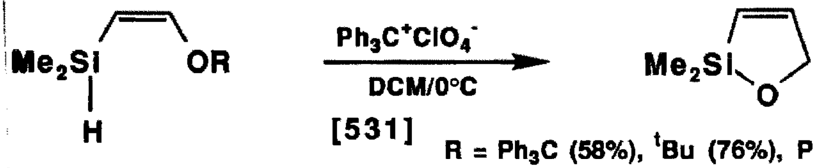
(LiDBB = lithium di-tert-butylbiphenyl)

Various alkoxyalkyldimethylsilanes were treated with trityl perchlorate resulting in cyclization to the alkoxysilane. Examples of this process are given in Eqns. 713-716.



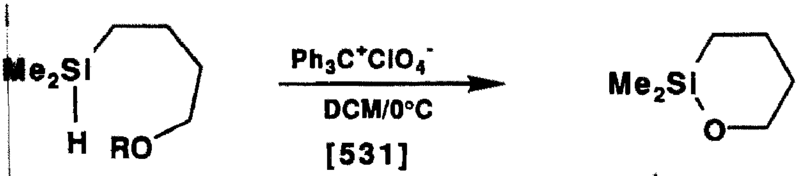
(713)

R = Ph_3C (77%), ^tBu (85%), $PhCH_2$ (16%)



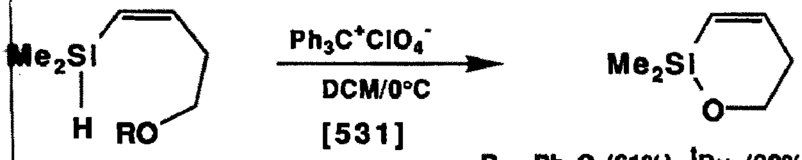
(714)

R = Ph_3C (58%), ^tBu (76%), $PhCH_2$ (48%)



(715)

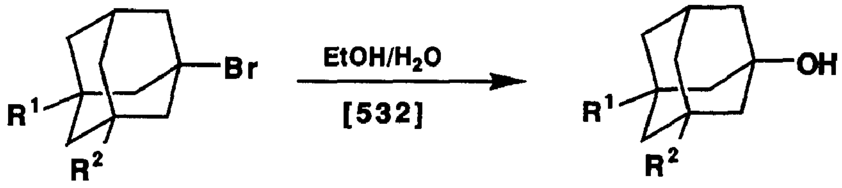
R = Ph_3C (86%), ^tBu (79%), $PhCH_2$ (49%)



(716)

R = Ph_3C (61%), ^tBu (82%), $PhCH_2$ (18%)

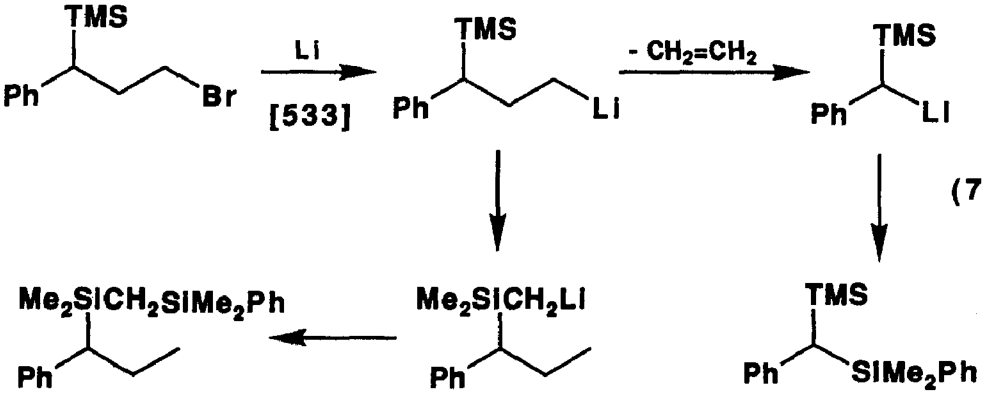
The effect of γ-trimethylsilyl groups on the solvolysis of 1-bromoadamantane was studied. It was found that one trimethylsilyl group enhanced the rate by a factor of 8.6 and two trimethylsilyl groups by a factor of 33. (Eqn. 717)



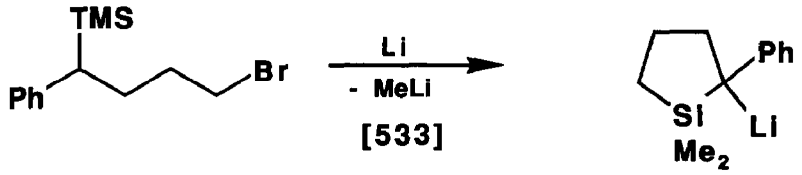
(717)

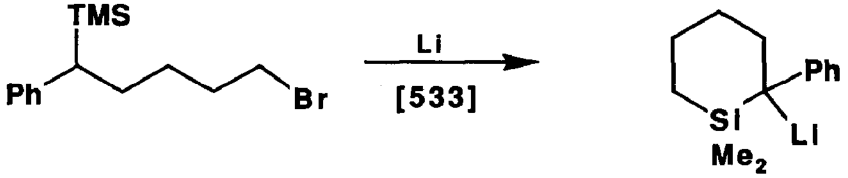
(R^1,R^2 = H, H; H, TMS; TMS, TMS)

The carbanion reactions of several lithioalkylbenzylsilanes were investigated. Four possible reactions were seen depending on the chain length. These were transmetalation of a methyl group on silicon, an intramolecular shift of the benzyl proton, a trimethylsiyl shift, and an elimination process. Some examples are shown in Eqns. 718, 719, and 720.

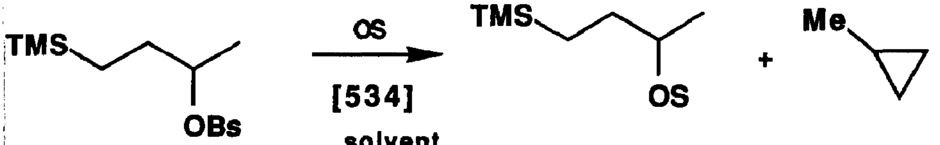


(718)


(719)

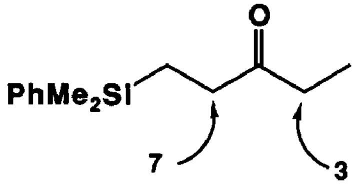

(720)

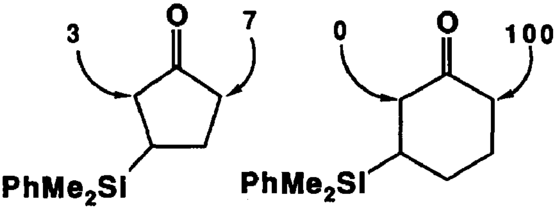
The stabilization of a carbocation by a trimethylsilyl group in the γ-position was demonstrated by the solvolysis of 4-(trimethylsilyl)-2-butyl p-bromobenzenesulfonates. (Eqn. 721) The rate of solvolysis was observed to be much faster than that of the tert-butyl analog.

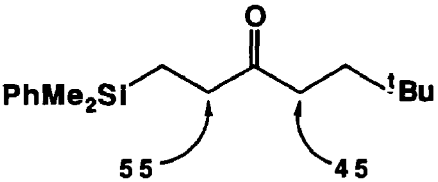

(721)

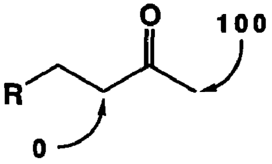
solvent		
60% EtOH	80	20
80% EtOH	85	15
90% EtOH	88	12
97% CF_3CH_2OH	73	27

The effect of a β-silyl group on the regioselectivity of ketone enolization with lithium diisopropylamide was studied. The results are summarized in the structures below. [535]





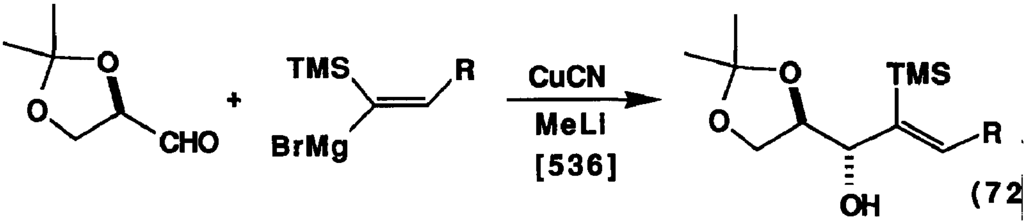




R = TMS, $PhMe_2Si$, ^tBu

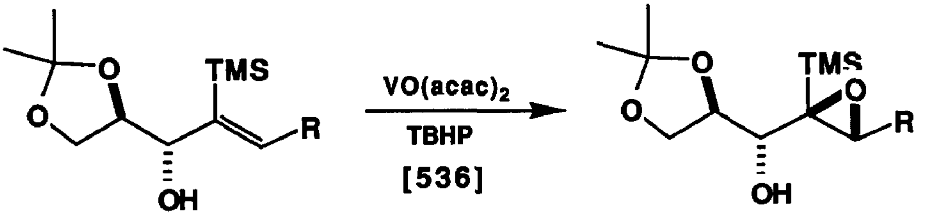
B. Epoxysilanes

Glyceraldehyde was converted to all four diastereomeric β,γ-epoxy glycerols as shown for two of them in Eqns. 722-725.

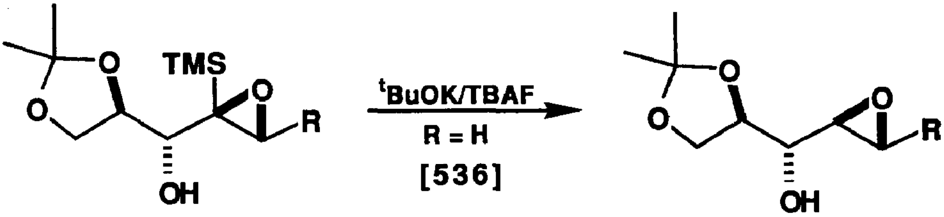


(722)

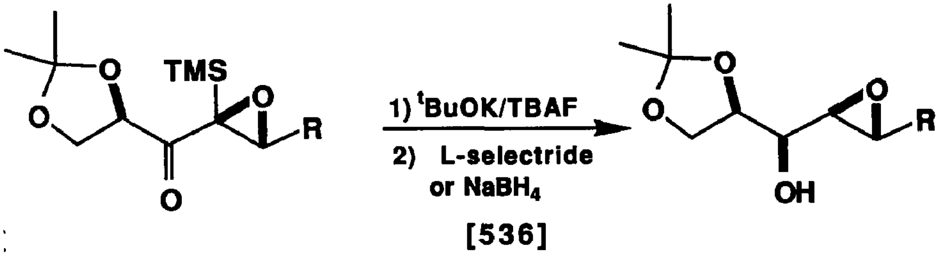
95% with 5% other diastereomer
CuCl catalyst gives other diastereomer



(723)

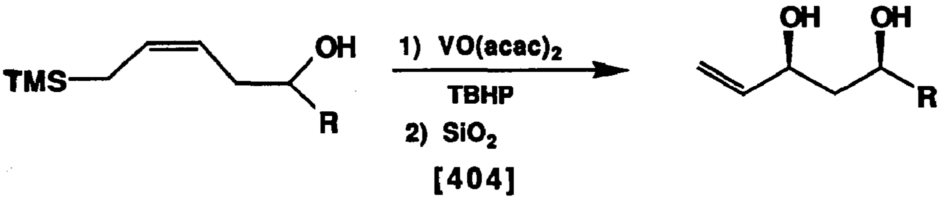


(724)



(725)

A stereoselective synthesis of unsaturated erythro 1,3-diols *via* the epoxidation of an allylsilane was reported. (Eqn. 726)

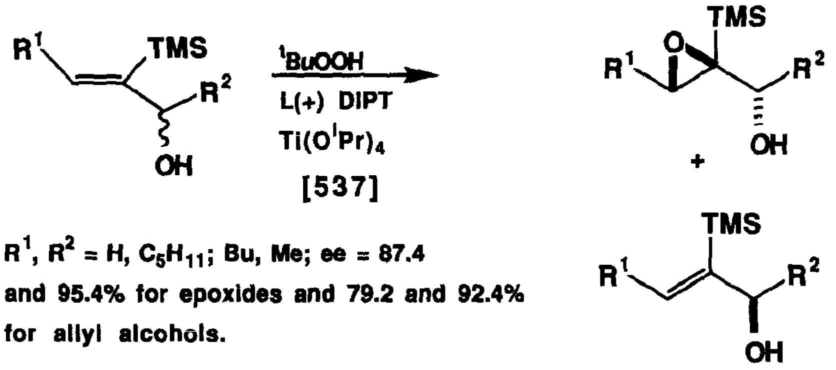


(726)

(R = Me, CH_2CH_2OBn, CH_2CH_2OAc, CH_2CO_2Bn)

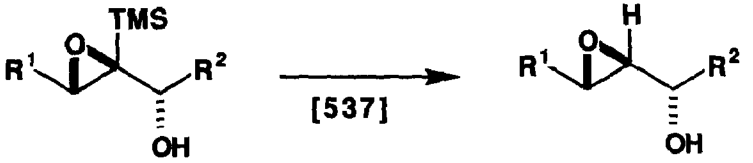
erythro:threo = 83:17 to 97:3

The separation of optically active erythro-epoxy secondary alcohols employing kinetic resolution with the Sharpless oxidation on β-trimethylsilyl secondary allylic alcohols was successful. (Eqns. 727, 728, and 729) This same procedure was also successful with the α-isomers. It was also used to prepare optically active allyl alcohols. (Eqns. 730, 731, and 732)

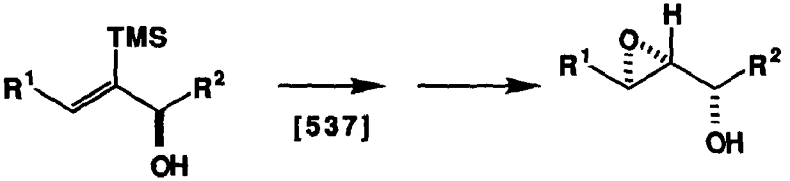


$R^1, R^2 = H, C_5H_{11}$; Bu, Me; ee = 87.4 and 95.4% for epoxides and 79.2 and 92.4% for allyl alcohols.

(727)



(728)



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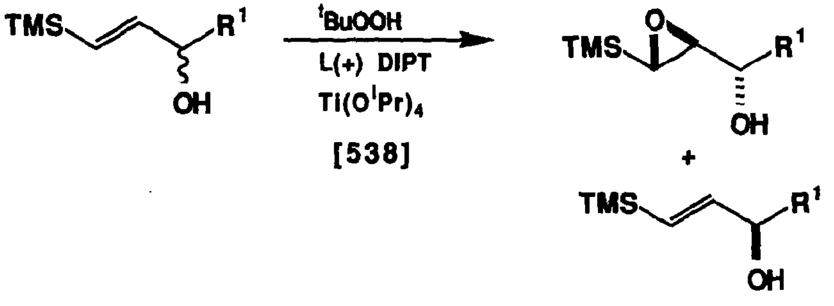
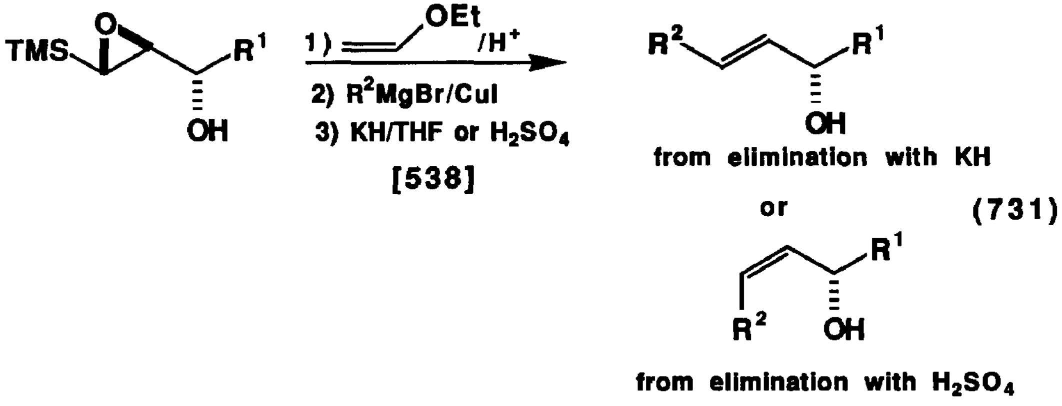
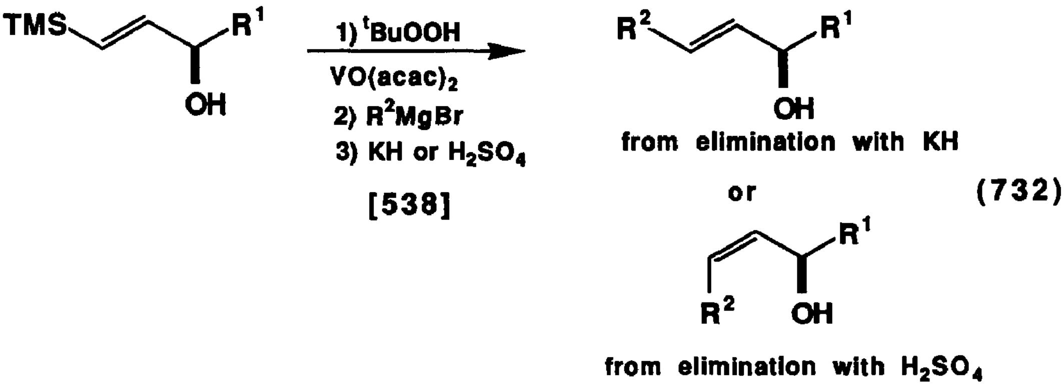


$R^1 = C_5H_{11}$ ee = 97.6%

(730)

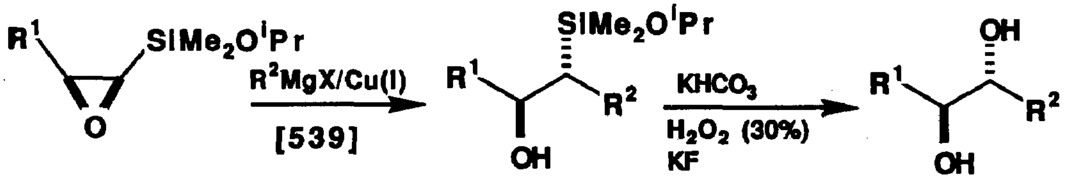


(731)



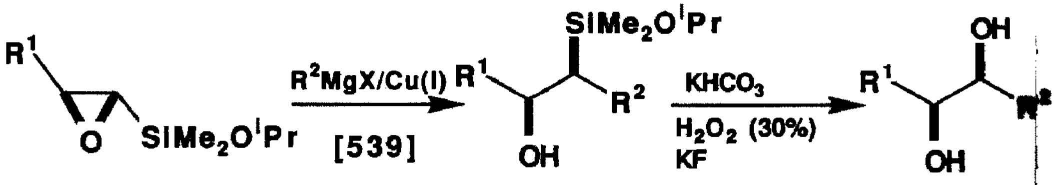
(732)

α,β-Epoxydimethylisopropoxysilanes were converted to erythro and threo 1,2-diols *via* reaction with a Grignard reagent followed by oxidation of the silicon-carbon bond. (Eqns. 733 and 734)



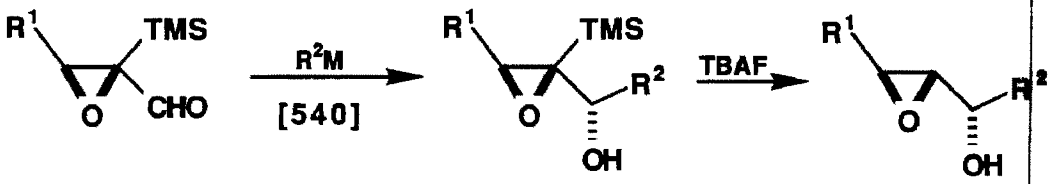
$R^1 = C_6H_{13}$; R^2 = Et, allyl, Ph, 2-thienyl

(733)

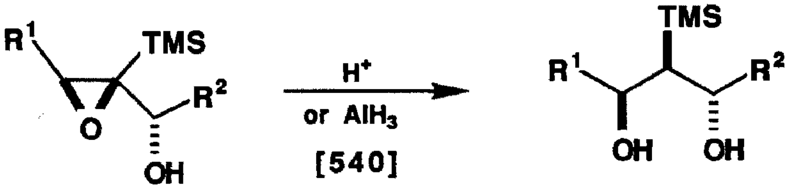


$R^1 = C_6H_{13}$; R^2 = Et, Bu, Ph, 2-thienyl (734)

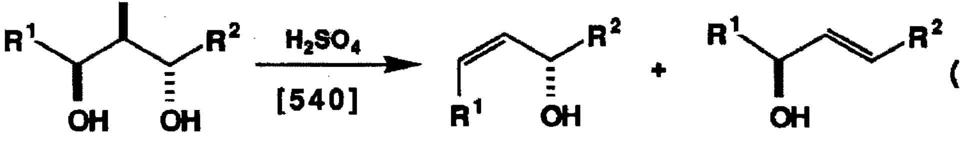
The synthesis of optically active β,γ-epoxy alcohols and secondary allylic alcohols was accomplished by the addition of organometallic reagents to α-(trimethylsilyl)-α,β-epoxy aldehydes. Some examples are shown in Eqns. 735-740.



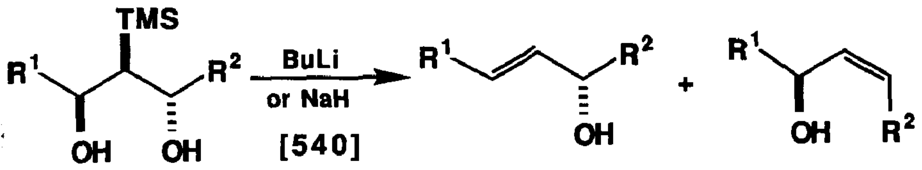
7 examples; 81-97%
erythro:threo = 5.4:1-26:1 (735)



(736)



(737)



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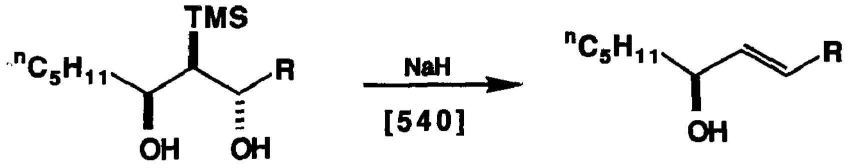
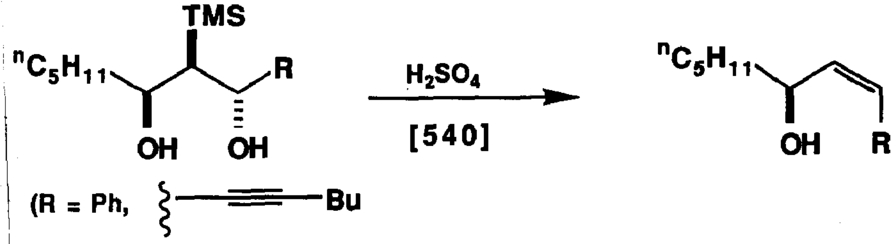
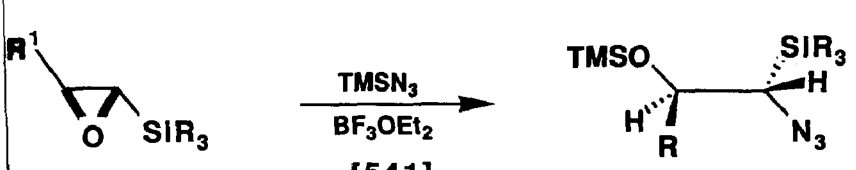


(739)



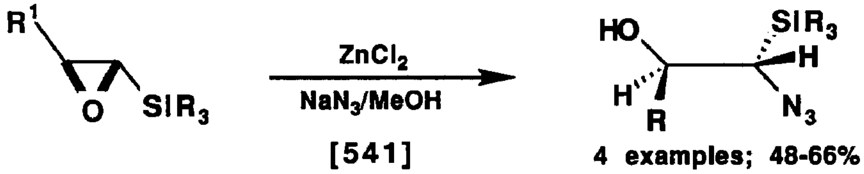
(740)

α,β-Epoxysilanes were reacted with trimethylsilyl azide in the presence of boron trifluoride etherate (Eqn. 741) or with zinc chloride and sodium azide. (Eqn. 742) The resulting β-hydroxysilanes were reduced to the amine, condensed with benzaldehyde, and then eliminated to give N-vinyl imines. (Eqn. 743)

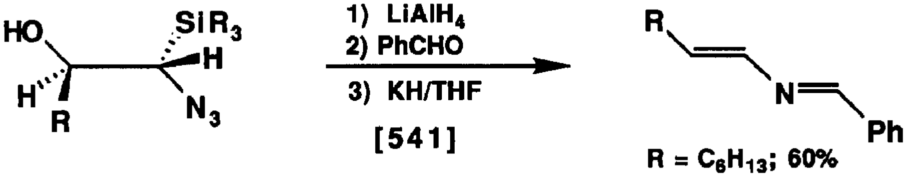


2 examples; 74 and 86%

(741)

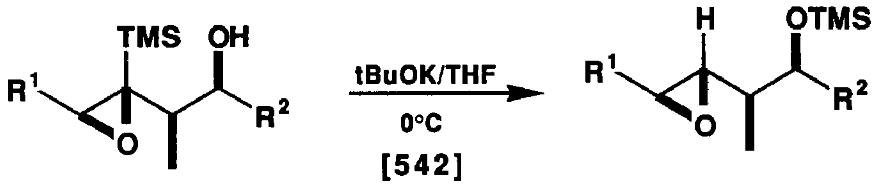


(742)

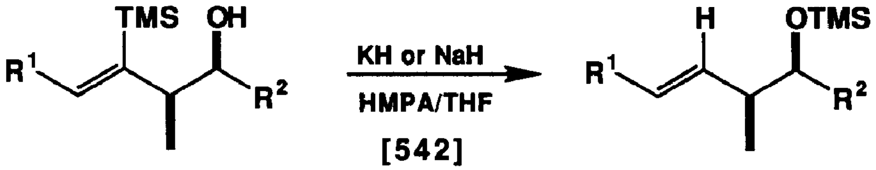


(743)

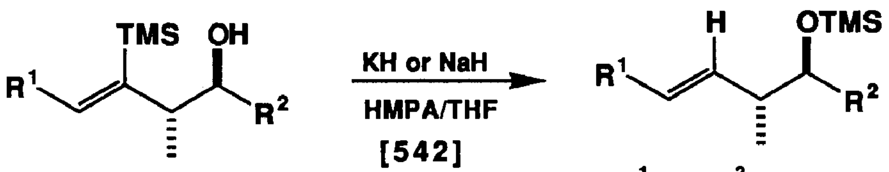
γ-Hydroxy epoxysilanes were shown to rearrange to the silyloxy epoxides under the influence of strong base. (Eqn. 744) This was also found for the corresponding vinylsilanes (Eqns. 745 and 746)



(744)



(745)

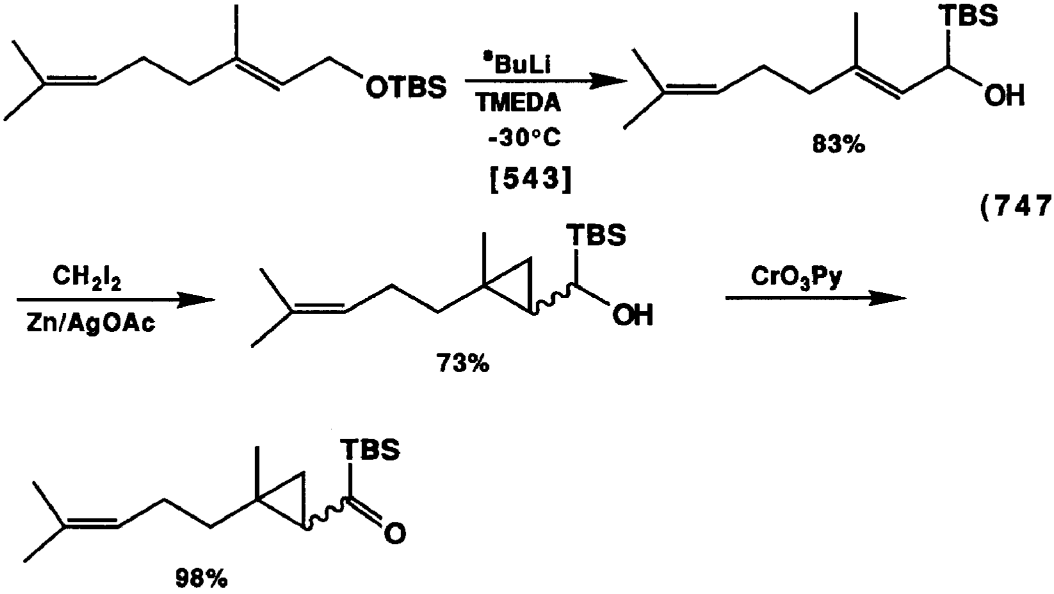


(746)

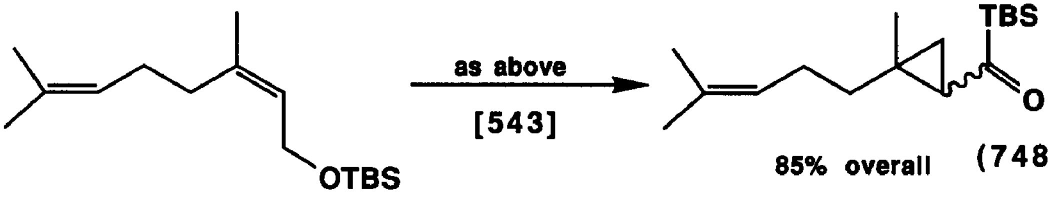
R^1 = H, R^2 = Et, Ph
R^1 = Bu, R^2 = Me

C. Acylsilanes

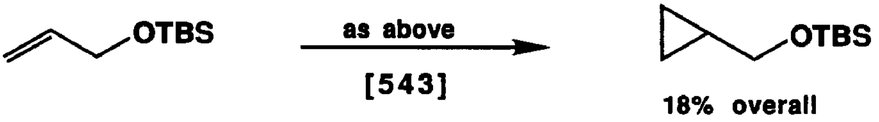
Cyclopropylacylsilanes were prepared by a Brook rearrangement on a silylated allyl alcohol followed by oxidation and cyclopropanation. (Eqns. 747, 748, and 749) The tert-butyldimethylsilyl group showed more stability.



(747)

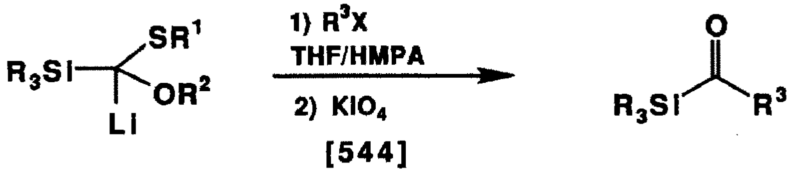


(748)



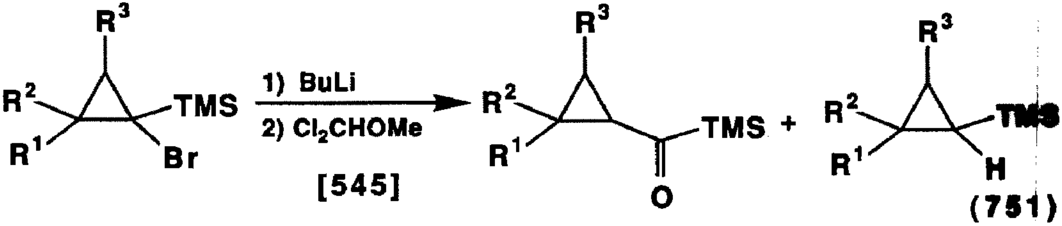
(749)

Acylsilanes were prepared from a silylated acyl anion equivalent as reported in a patent. (Eqn. 750)



(750)

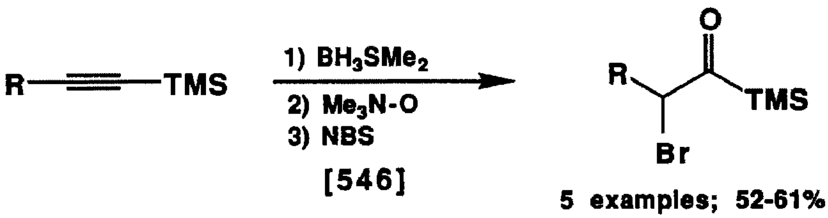
α-Bromocyclopropyltrimethylsilanes can be converted to their lithium reagent and this reacted with dichloromethylmethyl ether to give cyclopropylacylsilanes. (Eqn. 751)



(751)

R^1	$-(CH_2)_4-$	H	Me	H	Me	H	H
R^2		Ph	H	Me	Me	H	Bu
R^3	H	H	Me	H	H	H	H
%	50	46	39	16	35	30	35

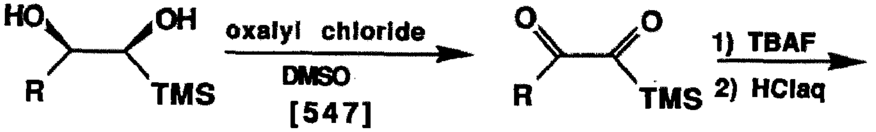
α-Bromoacylsilanes were prepared by the hydroboration-oxidation of ethynylsilanes followed by reaction with N-bromosuccinimide. (Eqn. 752)



5 examples; 52-61%

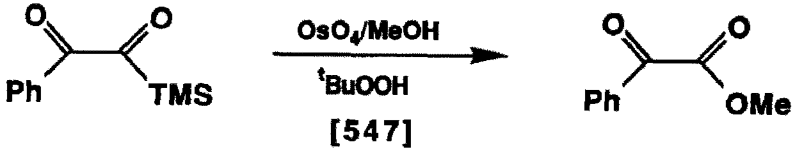
(752)

A general preparation of α-ketoacylsilanes was reported. (Eqn. 753) Oxidation of these acylsilanes gives the α-ketoesters (Eqn. 754) and reduction gives the silylated acyloins (Eqn. 755).

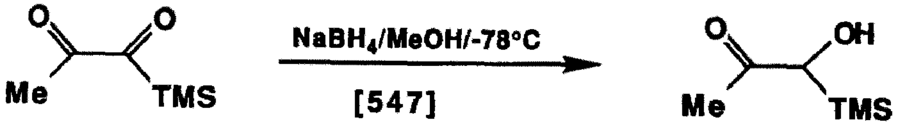


(R = Ph (55%), ^{n}C$_5$H$_{11}$ (39%), ^{n}Bu (41%))

(753)

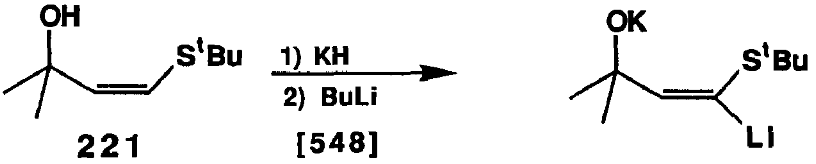


(754)



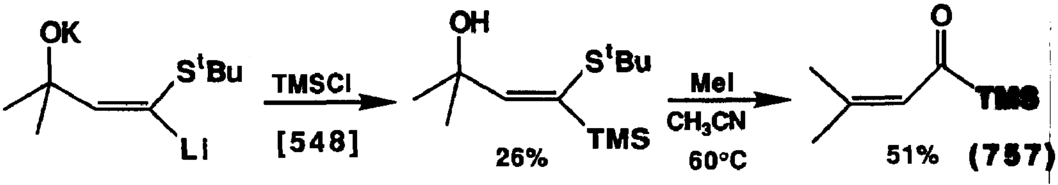
(755)

Double deprotonation-trimethylsilylation of **221** gives **222**, treatment of which with methyl iodide in acetonitrile gives the α,β-unsaturated acylsilane **223**. (Eqns. 756 and 757)



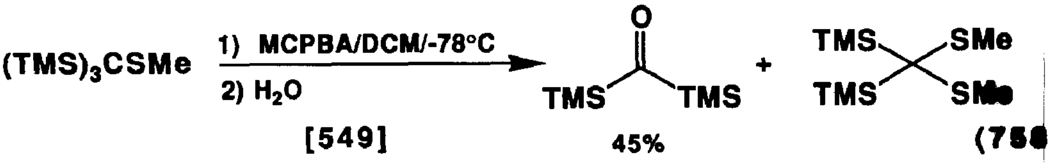
221

(756)

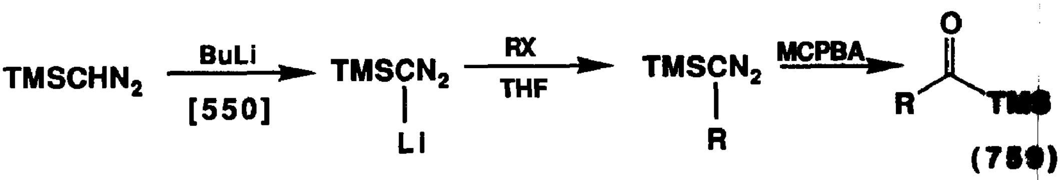


222 223 (757)

[Tris(trimethylsilyl)methyl]methylsulfide can be oxidized to bis(trimethylsilyl)-ketone. (Eqn. 758) Trimethylsilyldiazomethane when lithiated and then reacted with alkyl halides gives α-diazoalkylsilanes, oxidation of which leads to acylsilanes in good yields. (Eqns. 759 and 760)



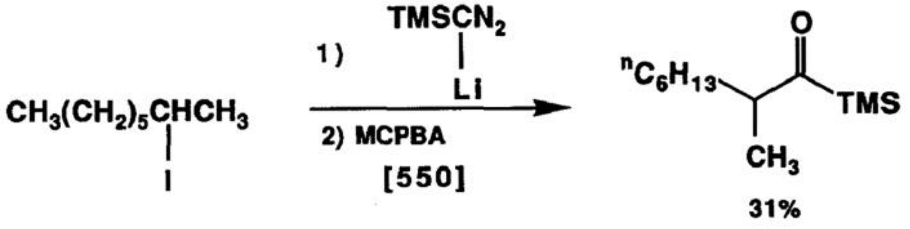
(758)



(759)

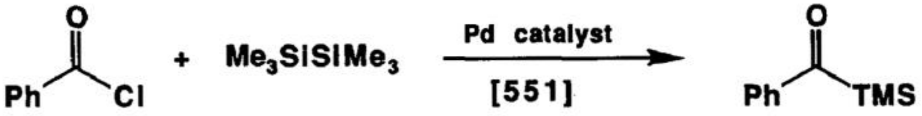
(Best with R = primary and X = I, Br)

6 examples; 56-71%



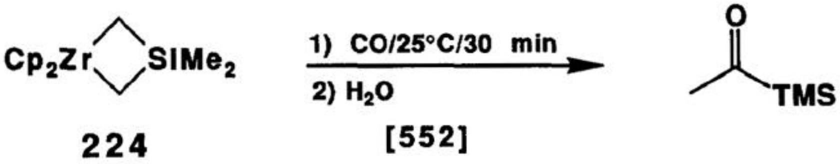
(760)

A full account of the formation of acylsilanes from the reaction of hexamethyldisilane with acyl chlorides and a palladium catalyst has appeared. (Eqn. 761) The best catalyst was shown to be π-allylpalldium chloride dimer with triethylphosphite.

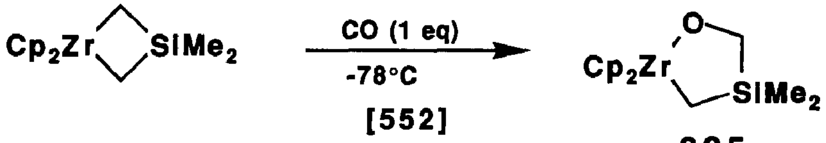


(761)

The 1-sila-3-zirconacyclobutane **224** was carbonylated to give acyltrimethylsilane. (Eqn. 762) The reaction proceeds *via* the insertion product **225**. (Eqn. 763) Two equivalents of carbon monoxide leads to **226**. (Eqn. 764)

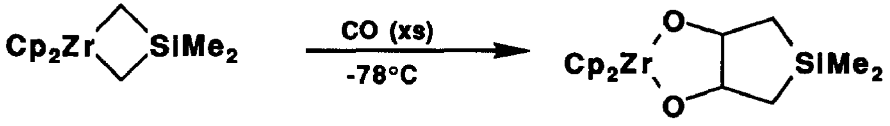


(762)



225

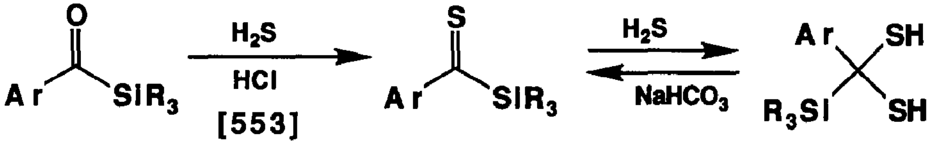
(763)



226

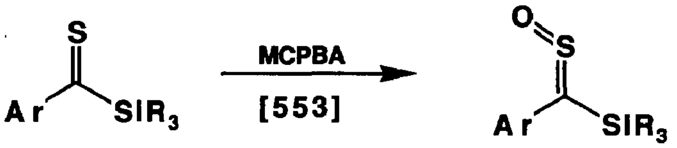
(764)

Aryl acylsilanes were shown to react with hydrogen sulfide to give thioacylsilanes. (Eqn. 765) Oxidation of these with m-chloroperbenzoic acid gives the (E) S-oxide. (Eqn. 766) Reaction with diphenyldiazomethane gives the silylated thiirane, which when treated with fluoride ion gives elimination to the olefin. (Eqn. 767) Reaction with an alkyllithium reagent gives attack at the sulfur atom and the α-thioalkylsilane. (Eqn. 768)

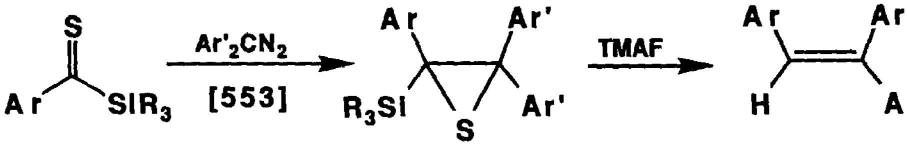


(765)

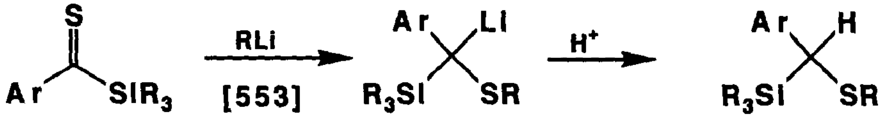
Ar = Ph, p-MeC$_6$H$_4$; R$_3$Si = Me$_3$Si
Ar = Ph, R$_3$Si = Ph$_3$Si



(766)

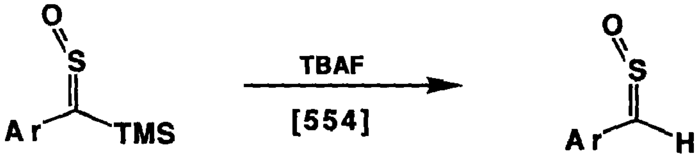


(767)



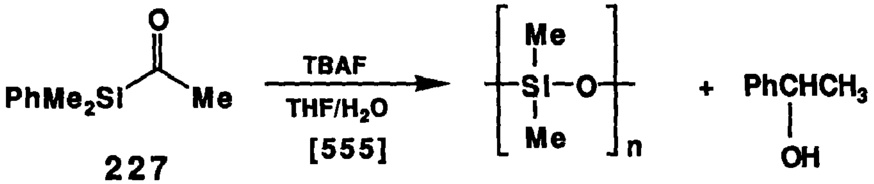
(768)

A second report on the oxidation of aryl thioacylsilanes further showed that the resulting S-oxides can be protodesilylated with fluoride ion. (Eqn. 769)



(769)

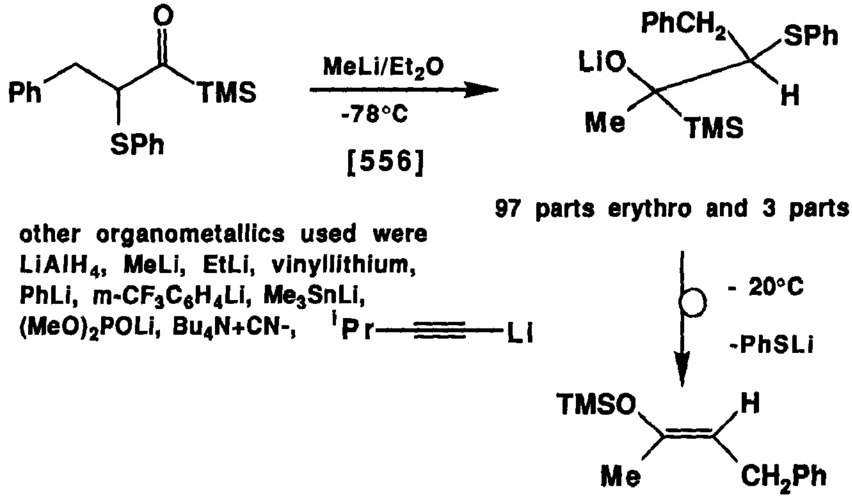
Treatment of phenyldimethylacylsilane **227** with fluoride ion gives 1-phenylethanol and polydimethylsiloxane. (Eqn. 770) A mechanism involving a pentcoordinate silicone and a migration of the phenyl group is proposed.



227

(770)

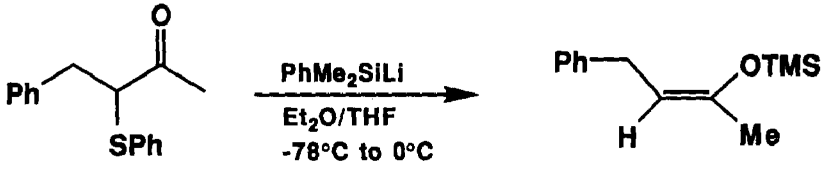
A regio- and stereospecific synthesis of enol silyl ethers from α-phenylthiosilyl ketones was reported. The reaction involves addition of an organolithium reagent to the carbonyl followed by a Brook rearrangement of the α-alkoxysilane and elimination of lithium thiophenoxide. (Eqns. 771 and 772)



97 parts erythro and 3 parts threo

other organometallics used were LiAlH$_4$, MeLi, EtLi, vinyllithium, PhLi, m-CF$_3$C$_6$H$_4$Li, Me$_3$SnLi, (MeO)$_2$POLi, Bu$_4$N+CN-, ^{i}Pr—≡—Li

(771)

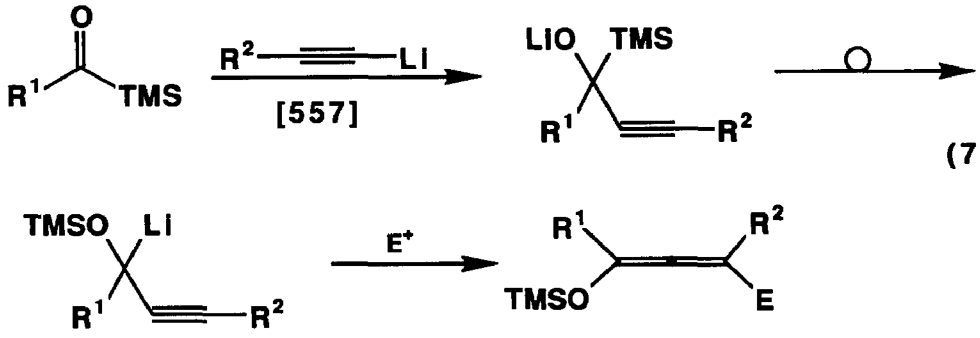


[556]

> 99 parts and < 1 part E isomer

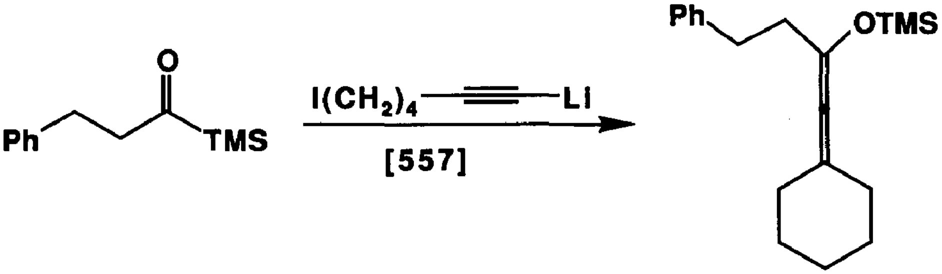
(772)

Silyl allenol ethers were prepared from acylsilanes *via* reaction of the acylsilane with an ethynyllithium reagent, a Brook rearrangement and trapping of the resulting allenyllithium intermediate with an electrophile. (Eqns. 773 and 774)



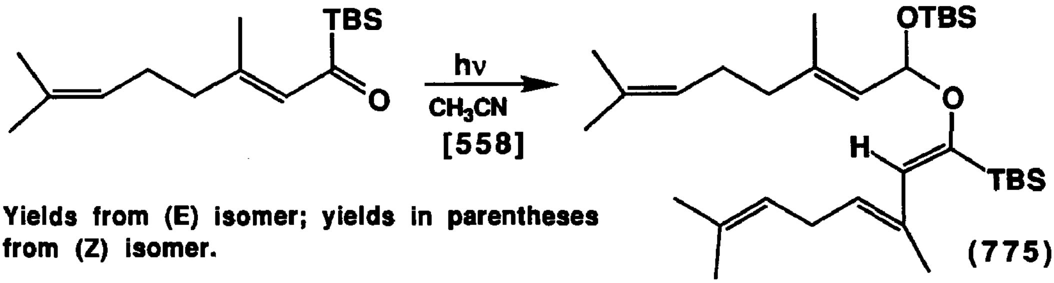
several examples; 36-92%

(773)



(774)

The photolysis and thermolysis of α,β-unsaturated acylsilanes was studied. The results of these studies are given in Eqns. 775-778. The products can be explained by abstraction of a γ-hydrogen and silyloxycarbenes.

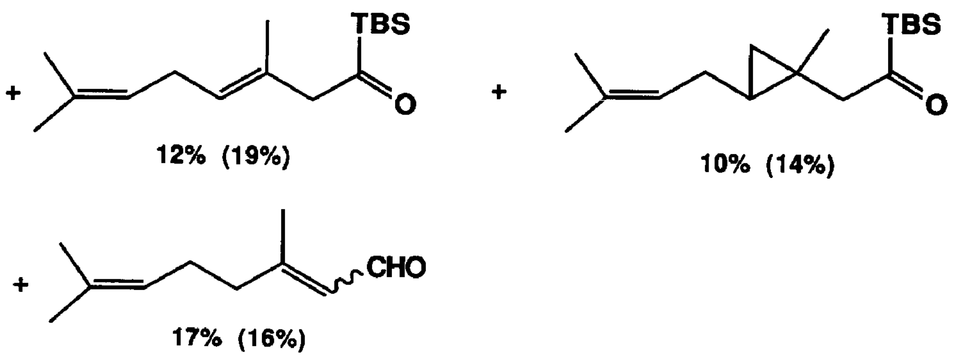


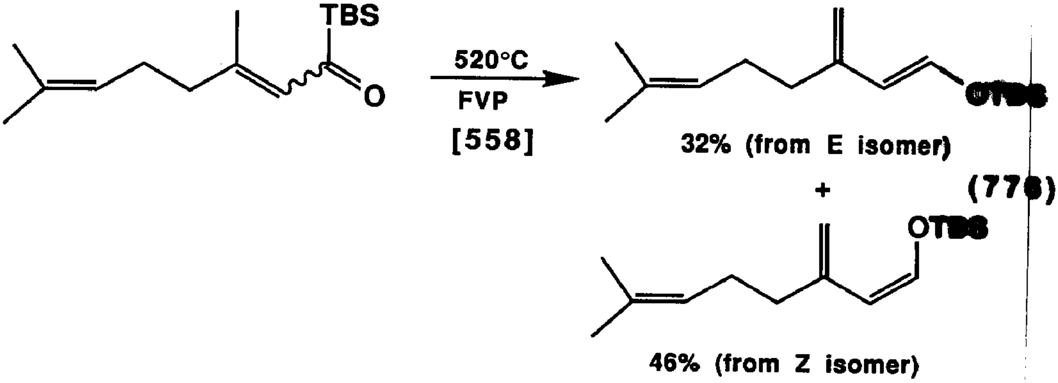
Yields from (E) isomer; yields in parentheses from (Z) isomer.

22% (24%)

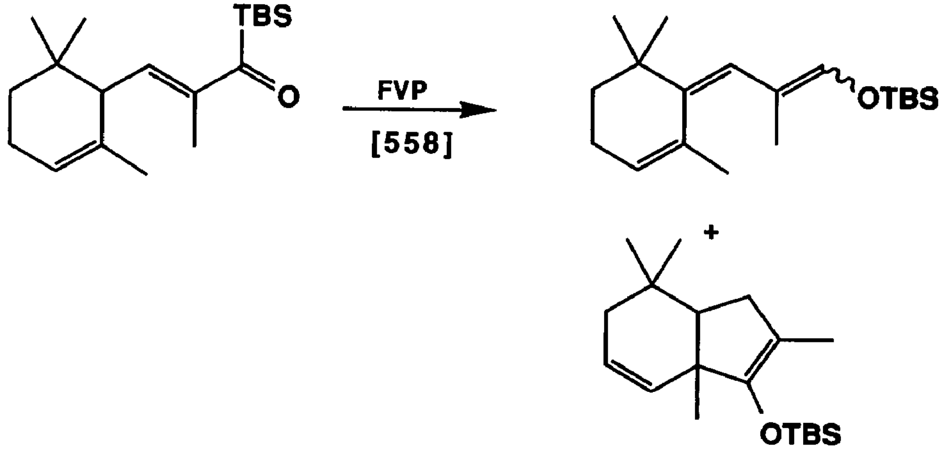
(775)

Eqn. 774 continued.





(776)



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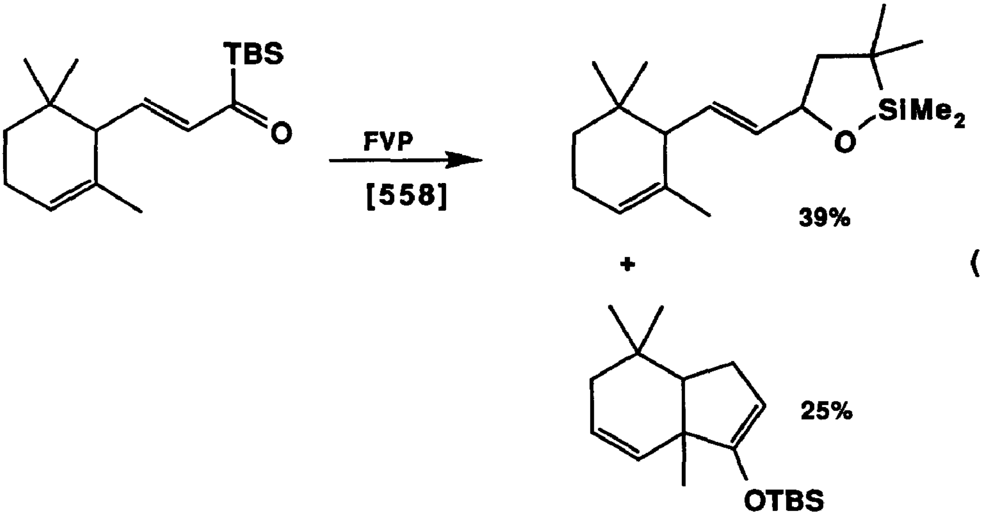


(778)

A ^{13}C NMR and theoretical study of acylsilanes was reported. The 25 to 103 ppm downfield shift of the carbonyl carbon in the ^{13}C NMR spectrum was explained by the theoretical results, which indicates that the silyl group acts as a σ donor and a π acceptor. [559] The UV spectra of several aryl acyl silanes were obtained. A straight line was obtained when the Hammett σ value of the substituents on the aryl ring against the wavelength of the n-π^* transition. The plot of the dual substituent paramters gives σ_R^{*}/σ_I of 2.5 indicating more resonance than inductive effect at work. [560]

XV. REACTIVE ORGANOSILYL SPECIES.

A. Silyl Radicals

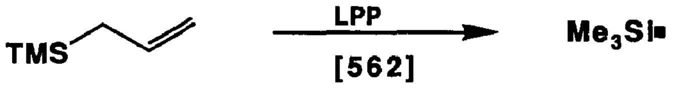
An experiment was designed to test the hypothesis of pentamethyldisilyl radical being the precursor to dimethylsilylene. The radical, generated as shown in Eqn. 778, was shown not to lead to dimethylsiylane.

$$Me_3SiSiMe_2H + {}^tBuO\bullet \xrightarrow[{[561]}]{} {}^tBuOH + Me_3\underset{\bullet}{Si}SiMe_2 \qquad (779)$$

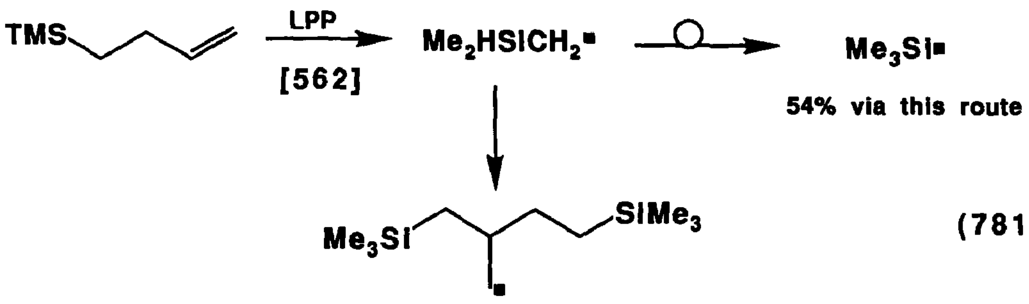
$$Me_3\underset{\bullet}{Si}SiMe_2 \longrightarrow Me_3SiSiHMe_2 + Me_3SiMe_2SiMe_2SiSiMe_3$$

no evidence for Me_2HSiO^tBu from Me_2Si:
or $Me_3SiMe_2SiSiMe_2H$ from insertion

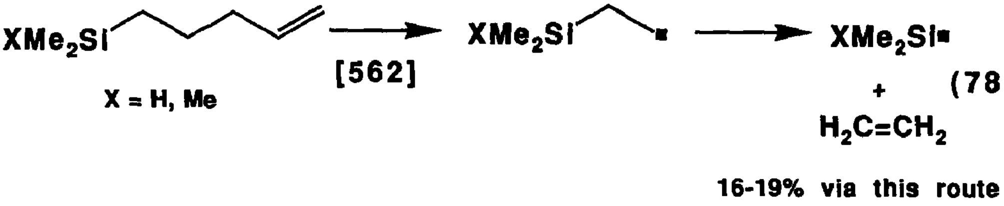
The kinetics of the radical formation from homolysis of alkenylsilanes and tert-butylsilanes was studied. The results indicate that the α- and β-silylalkyl radicals generated by pyrolytic cleavage are stabilized by about 2.6 kcal mol^{-1}. The tert-butyl systems were similar in stability. Some of the results are shown in Eqns. 780-783.



(780)

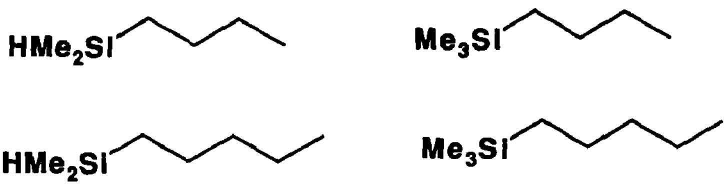


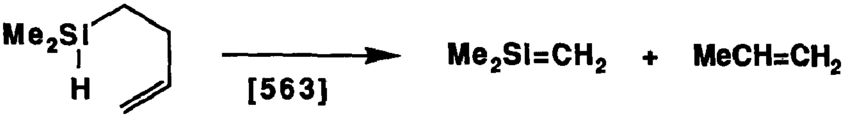
(781)



(782)

$RMe_2Si(CH_2)_nCH{=}CH_2$ R = H, Me; n = 2, 3



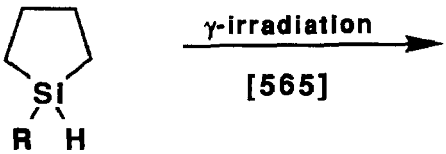


(783)

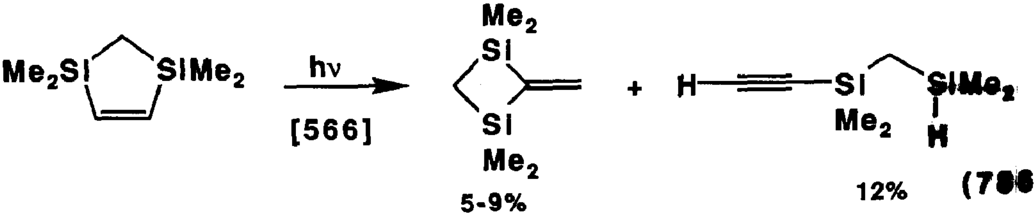
Chloromethyldimethylsilane was reacted on a silicon mirror to give trimethylchlorosilane *via* a radical mechanism. (Eqn. 784)

$$ClCH_2SiHMe_2 \xrightarrow[\text{Catalysis}\ [564]]{\text{Silicon Mirror}} Me_3SiCl \qquad (784)$$

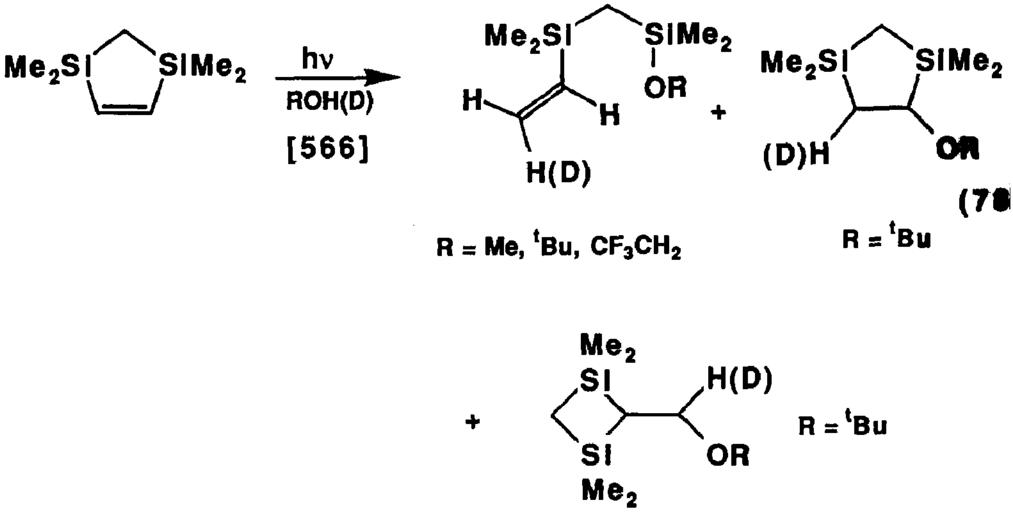
The electron spin resonance spectra of the radicals generated from silacyclopentanes were reported. (Eqn. 785) Silicon radicals are the intermediates in the far-UV photolysis of unsaturated silanes. (Eqns. 786, 787 and 788)



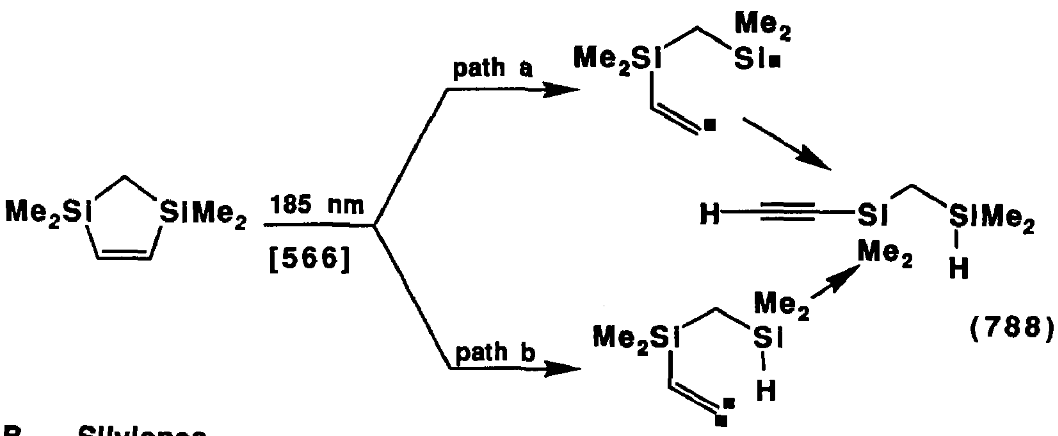
(785)



(786)



(787)

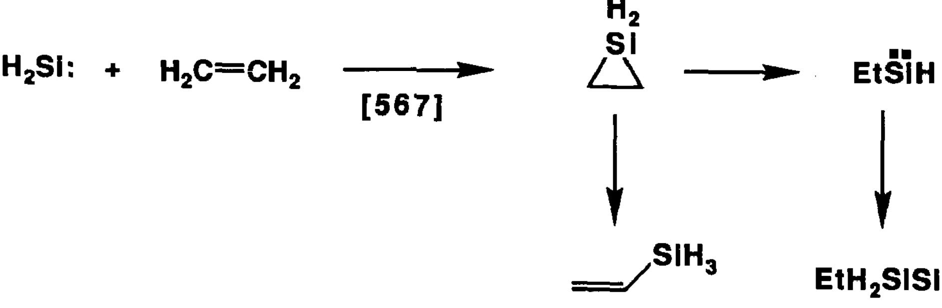


(788)

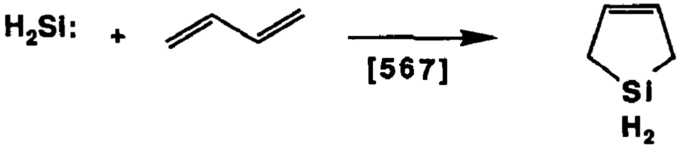
B. Silylenes

The pyrolysis of disilane generates silylene, which was added to ethylene and 1,3-butadiene. The reaction with ethylene goes through the intermediacy of silacyclopropane leading to ethylsilylene and ethyldisilane in the presence of silane or to vinylsilane. (Eqns. 789 and 790) With butadiene the silacyclopentane is formed. (Eqn. 791)

$$H_3SiSiH_3 \xrightarrow[{[567]}]{\text{pyrolysis}} H_2Si: \qquad (789)$$

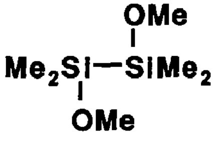


(790)



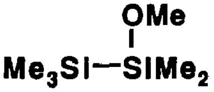
(791)

The kinetics of the formation of silylenes from the four disilanes **228-231** were measured. The results were discussed in terms of substituent effects on the bond dissociation energies, the energies of the silylene insertion reactions, and the reactions of silylenes.



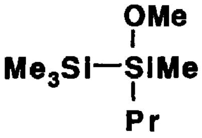
$\underset{OMe}{\overset{OMe}{Me_2Si}}-SiMe_2$

228



$Me_3Si-\overset{OMe}{SiMe_2}$

229



$Me_3Si-\underset{Pr}{\overset{OMe}{SiMe}}$

230

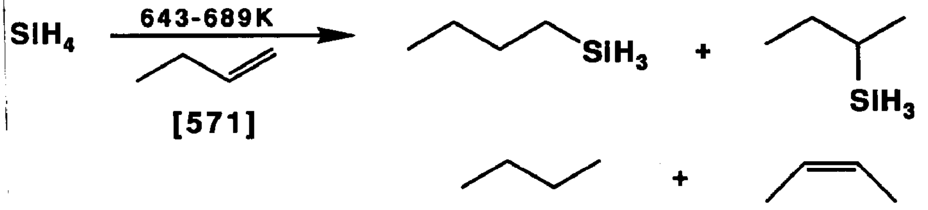
$H_2MeSiSiMe_2H$

231

Evidence for the silylsilylene to disilene rearrangement was presented. The evidence comes from the observance of the adducts of both silylsilylene and disilene to butadiene in addition to the previously reported products from the reactions of recoiling silicon atoms in gaseous mixtures of phosphine, butadiene and silane. (Eqn. 792)

(792)

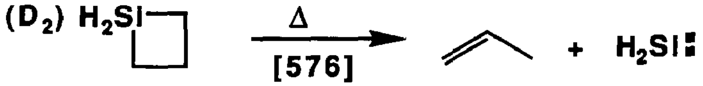
The mechanism of the gas-phase thermolysis of monomethylsilane was shown to involve methylsilylene in addition to some methylsilyl radical and hydrogen radicals. [570] Silylene, generated from silane, was reacted with 1-butene to give addition and olefin isomerization. (Eqn. 793)



(793)

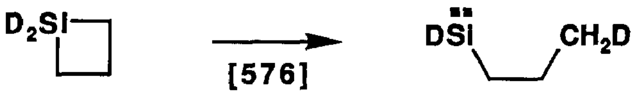
The relative rate constants for the reactions of methylphenylsilylene with various substrates were determined. The results conflict with those of a flash photolysis study of this species. The relative rates found were $k_{EtOH}/k_{Et3SiH} = 4.8$; $k_{diene}/k_{Et3SiH} = 3.0$. [572] Time-resolved studies of the reactions of dimethylsilylene with silane, methylsilane, dimethylsilane trimethylsilane and pentamethyldisilane were carried out. The rate constants, on a per Si-H basis, increase with an increase in the number of methyl groups. [573] The absolute rate constants for silylene reactions with hydrocarbons were determined. This study showed that silylene is unreactive towards alkanes and reacts rapidly and unselectively with unsaturated hydrocarbons. [574] The decomposition mechanism and kinetics of n-butylsilane was shown to proceed through silylene and radical intermediates. [575]

The mechanism of the decomposition of silacyclobutane to silylene and propene was studied. It was determined, *via* deuterium labelling experiments, that the reaction proceeds through a 1,2-migration of hydrogen (or deuterium) from silicon to produce propylsilylene, which reversibly forms a silacyclopropane before decomposing to silylene and propene. (Eqns. 794 and 795)



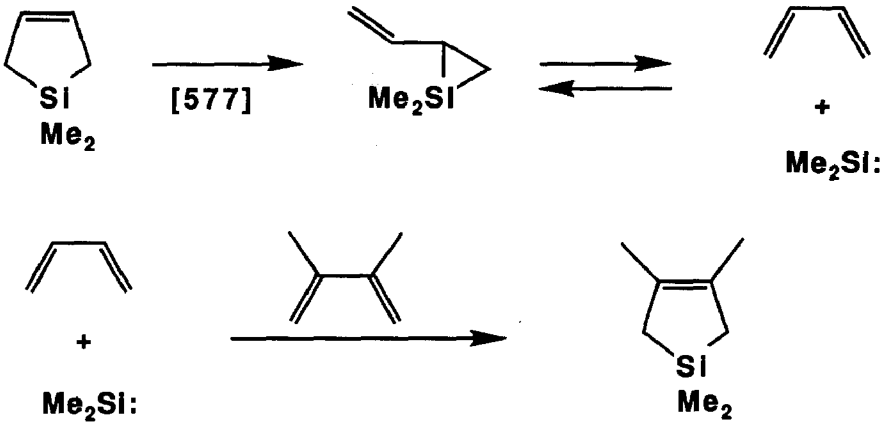
(794)

d_0, d_1, d_2 with deuterium found on all positions



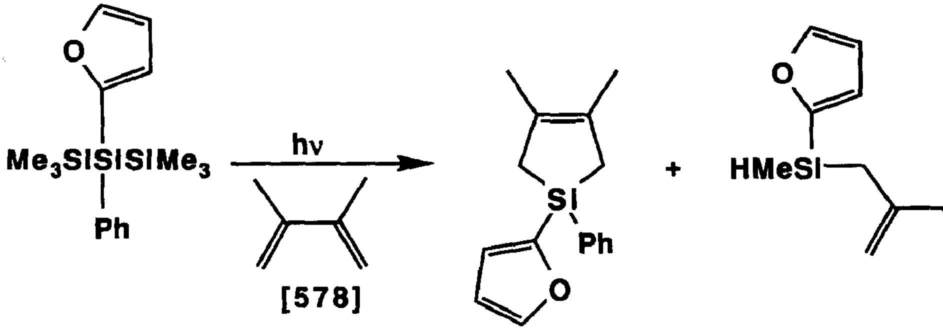
(795)

The kinetics and mechanism of the pyrolysis of 1,1-dimethylsilacyclopent-3-ene. The results are consistent with a nonconcerted mechanism involving vinylsilacyclopropane intermediates. (Eqn. 796)

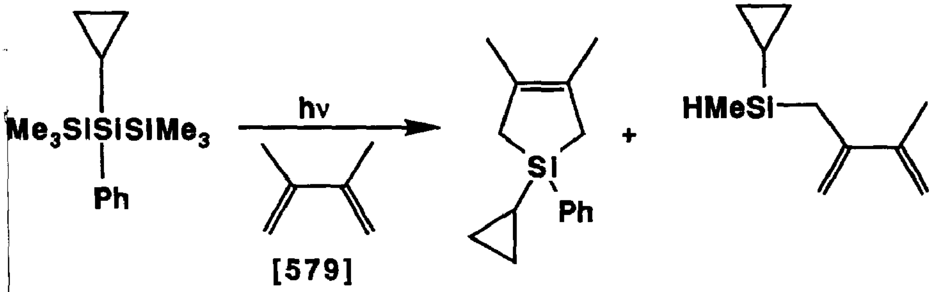


(796)

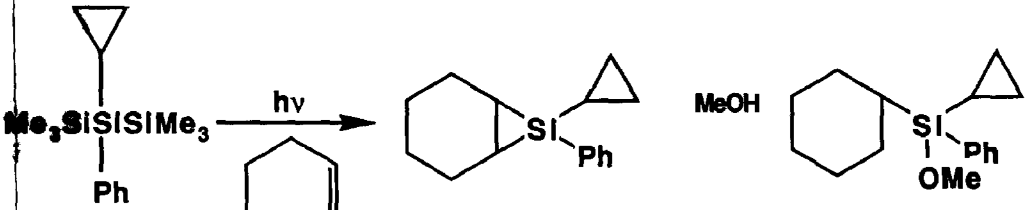
Furylphenylsilylene was generated and its reaction with 2,3-dimethyl-1,3-butadiene studied. (Eqn. 797) Cyclopropylphenylsilylene was generated photochemically and its reactions with 2,3-dimethyl-1,3-butadiene and cyclohexene studied. (Eqns. 798 and 799)



(797)



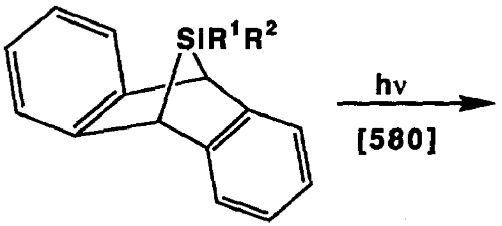
(798)



(799)

[579]

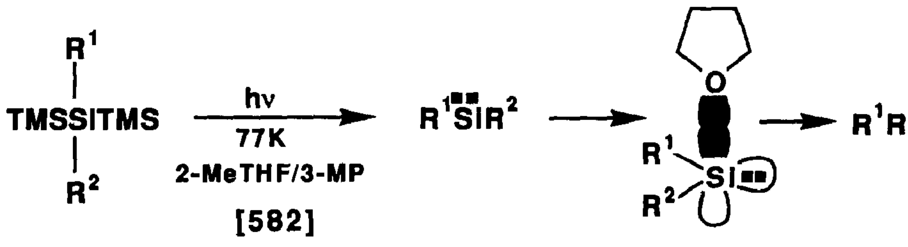
Several dibenzo-7-silanorbornadiene derivatives were prepared and studied as precursors to silylenes. The silylenes, thusly generated, formed disilenes in the absence of traps and were trapped with 2,3-dimethyl-1,3-butadiene and with adamantanone. (Eqn. 800)



$R^1R^2Si{=}SiR^1R^2$ (800)

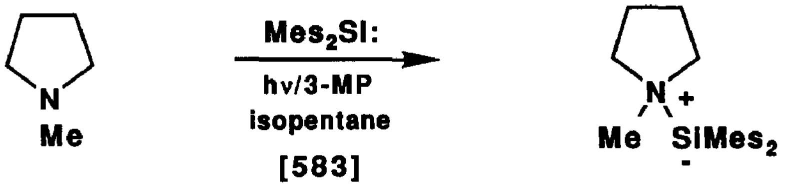
the silylene can also be trapped with anthracen and 2,3-dimethylbutadiene

Twenty two different silylenes were generated and isolated in 3-methylpentane glass. The wavelengths of the principal electronic transitions were obtained. These a range from 368 to 577 nm. Upon annealing of the glass the silylene absorption is lost and new bands appear, which are assigned to disilenes. [581] Spectroscopic evidence of the product of the reaction of hindered silylenes with 2-methyltetrahydrofuran was obtained. (Eqn. 801) The first spectroscopic detection of silaylides from the reaction of dimesitylsilylene with phosphorus, sulfur and nitrogen-containing substrates was reported. (Eqn. 802)

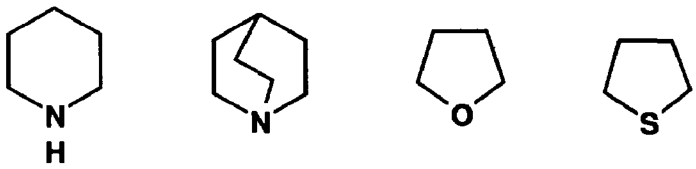


(801)

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



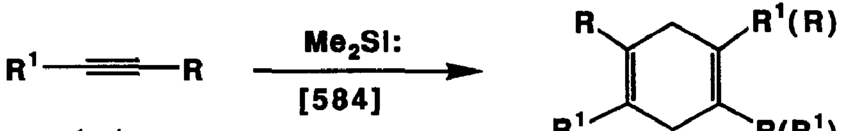
(802)



$^{n}Bu_3P$

also reacted with dimesitylsilylene

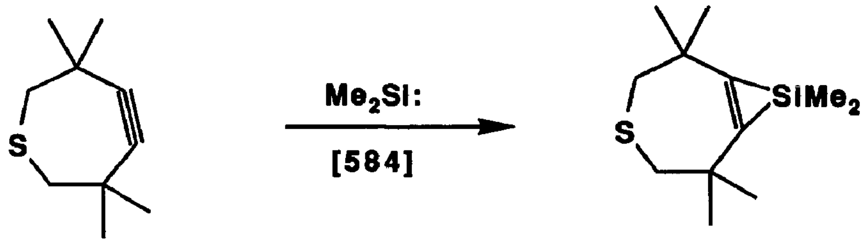
Thermally generated dimethylsilylene was reacted with alkynes to give disilacyclohexadienes. (Eqn. 803) The reaction with a cyclic alkyne gave the silacyclopropene. (Eqn. 804) The reaction with trans, trans-1,4-diphenyl-1,3-butadiene gives addition to one of the olefinic groups as the primary reaction course. (Eqn. 805)



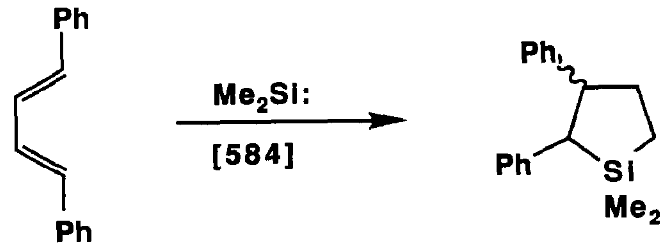
(803)

R = R^1 = ^{t}Bu or TMS no reaction

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

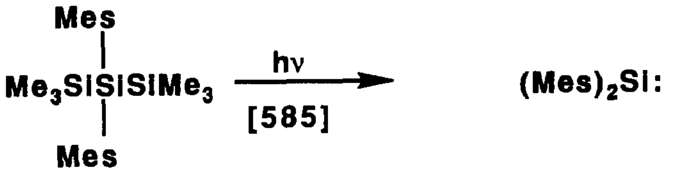


(804)

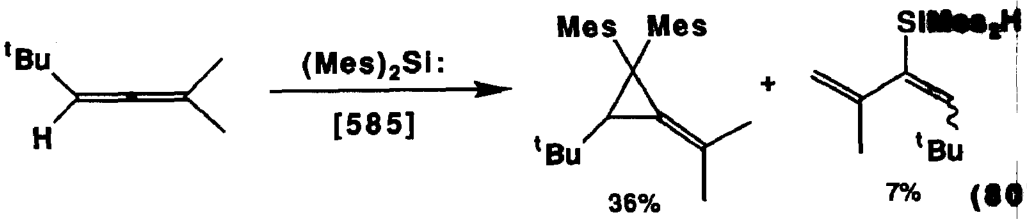


(805)

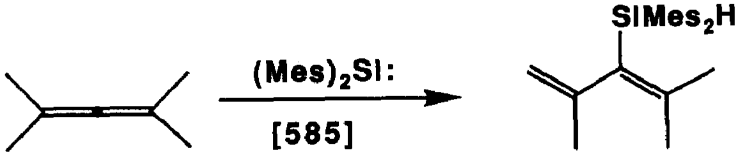
Dimesitylsilylene was reacted with allenes to give, as the major product, the alkylidenesilacyclopropane and/or a 3-silyl-1,3-butadiene. (Eqns. 806-809)



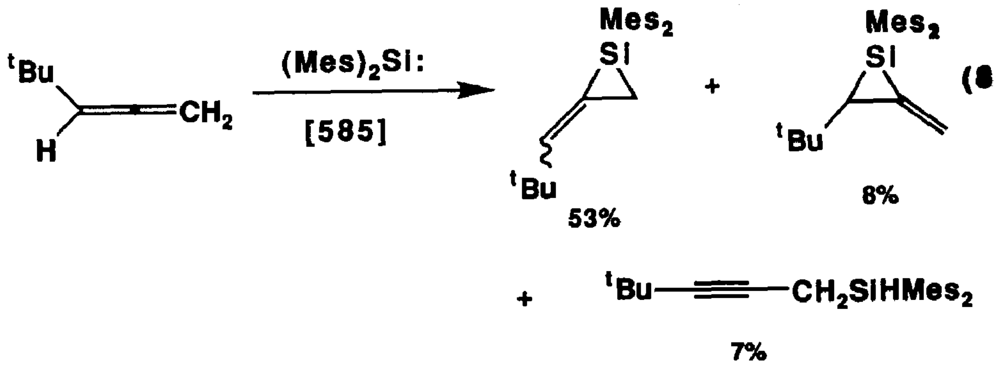
(806)



(807)

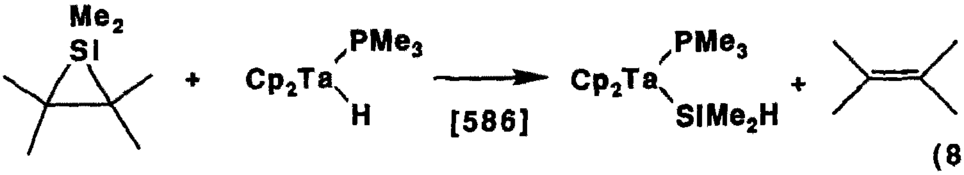


(808)

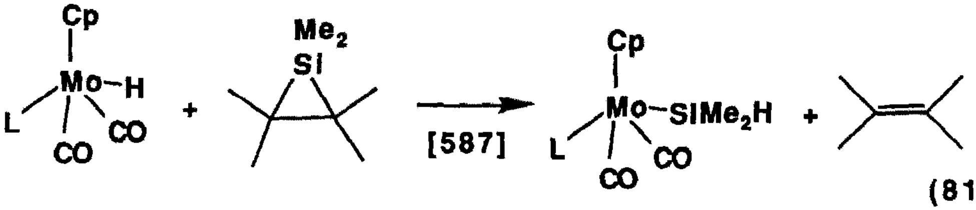


(809)

Dimethylsilylene, generated from hexamethylsilacyclopropane, was reacted with a tantalum hydride to give insertion into the tantalum-hydrogen bond. (Eqn. 810) A similar reaction was observed with a molybdenum-hydrogen bond. (Eqn. 811)

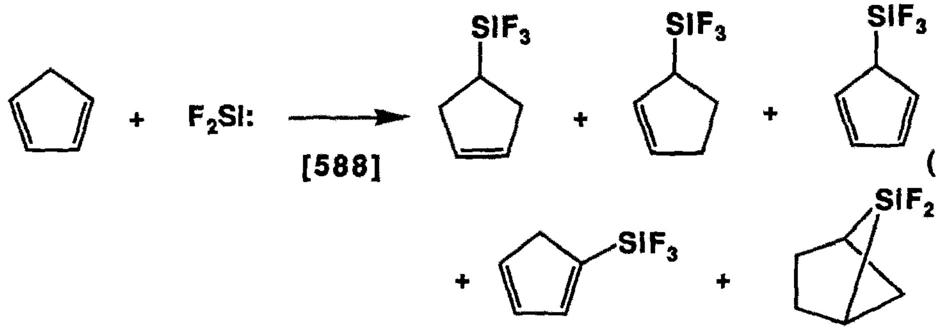


(810)



(811)

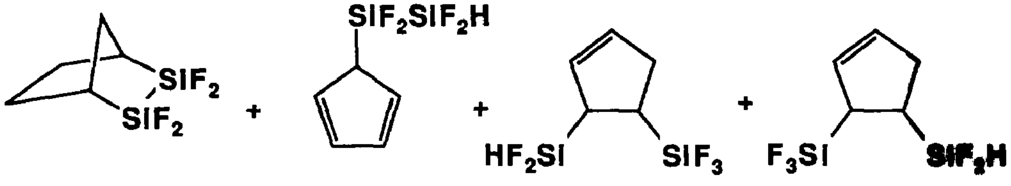
Difluorosilylene was reacted with cyclopentadiene according to Eqn. 812. Difluorosilylene, generated from hexafluorodisilane in a flow pyrolysis apparatus, was very reactive, reacting with butadiene to give the silacyclopentene and disilacyclohexene. (Eqn. 813)

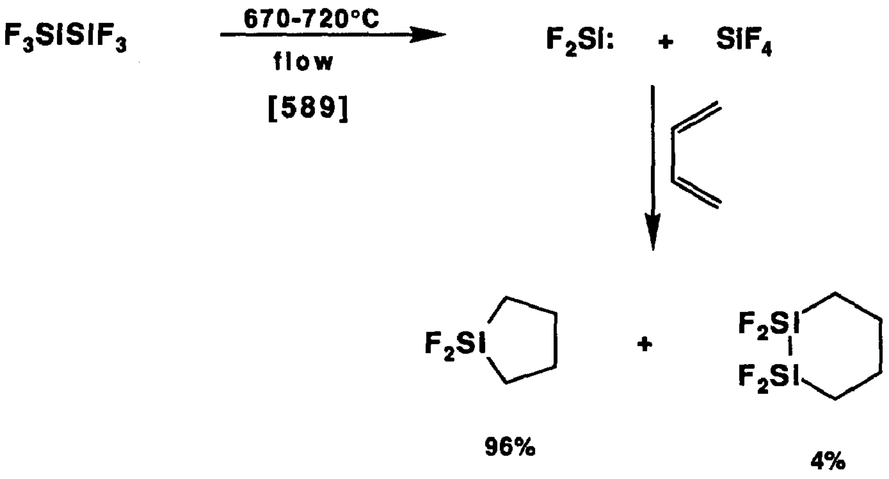


(812)

Eqn. 811 continued.

When reacted in the condensed phase the above products are obtained along with those shown below.



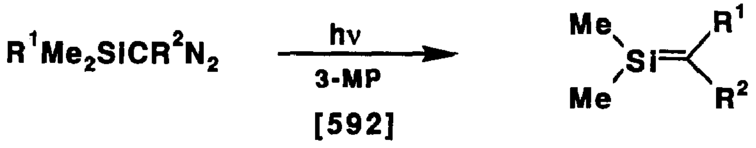


(813)

A thoeretical investigation for the silanone to silylene isomerization was conducted. The barrier for the 1,2-shift in trisilylsilanone to silyloxysilylene was calulated to be about 22.7 kcal mol^{-1}, consistent with the experimental evidence. [509] The atomic properties of carbenes and silylenes were calculated. [591]

C. Silenes

Photolysis of α-diazosilanes leads to silenes in such a manner that they are isolable in frozen matrices. Several silenes were thus generated. (Eqn. 814) The ultraviolet spectra of these silenes were studied.

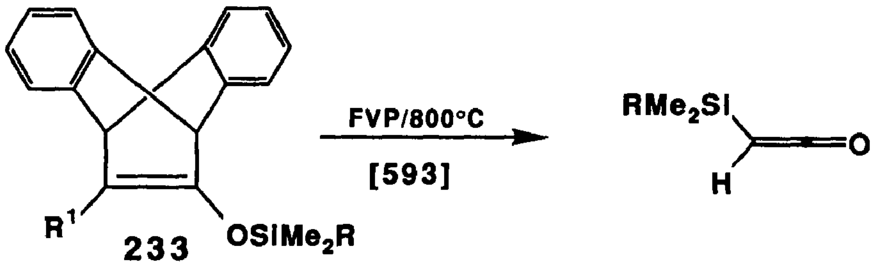


(814)

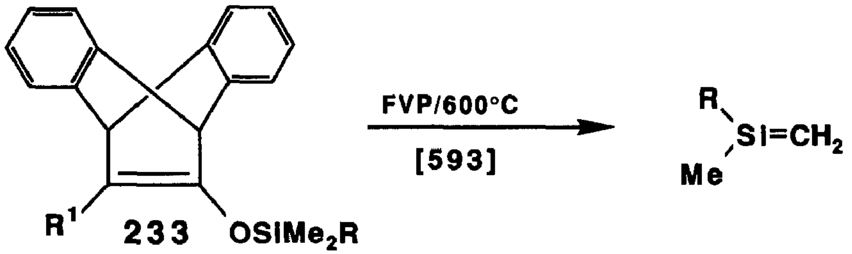
Me_3SiCHN_2 $Me_3SiSiMe_2SiCHN_2$ $Me_3SiSiMe_2CN_2SiMe_3$

$PhMe_2SiCN_2CO_2Me$ $Me_3SiMe_2SiCN_2COAd$

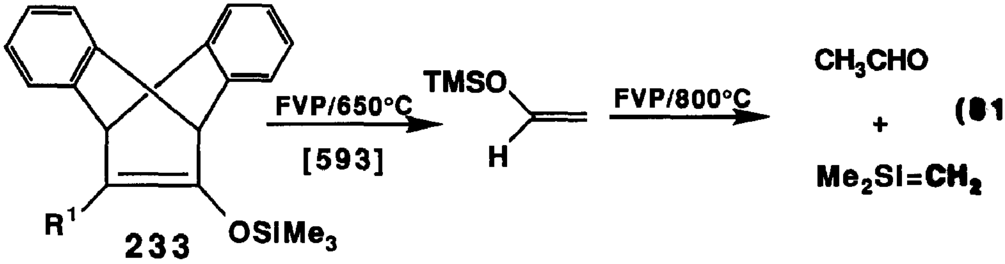
The enol silyl ethers **233** undergo a retro-Diels-Alder reaction upon flash pyrolysis at 800°C to give a silyl ketene (Eqn. 815), but at 600°C to give a silene (Eqn. 816 Vinyloxytrimethylsilane gives acetaldehyde and 1,1-dimethylsilene at 650°C. (Eqn. 817)



(815)

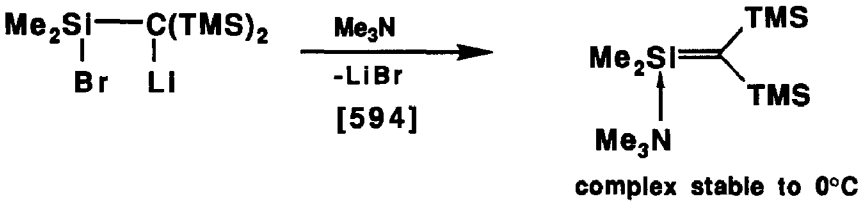


(816)

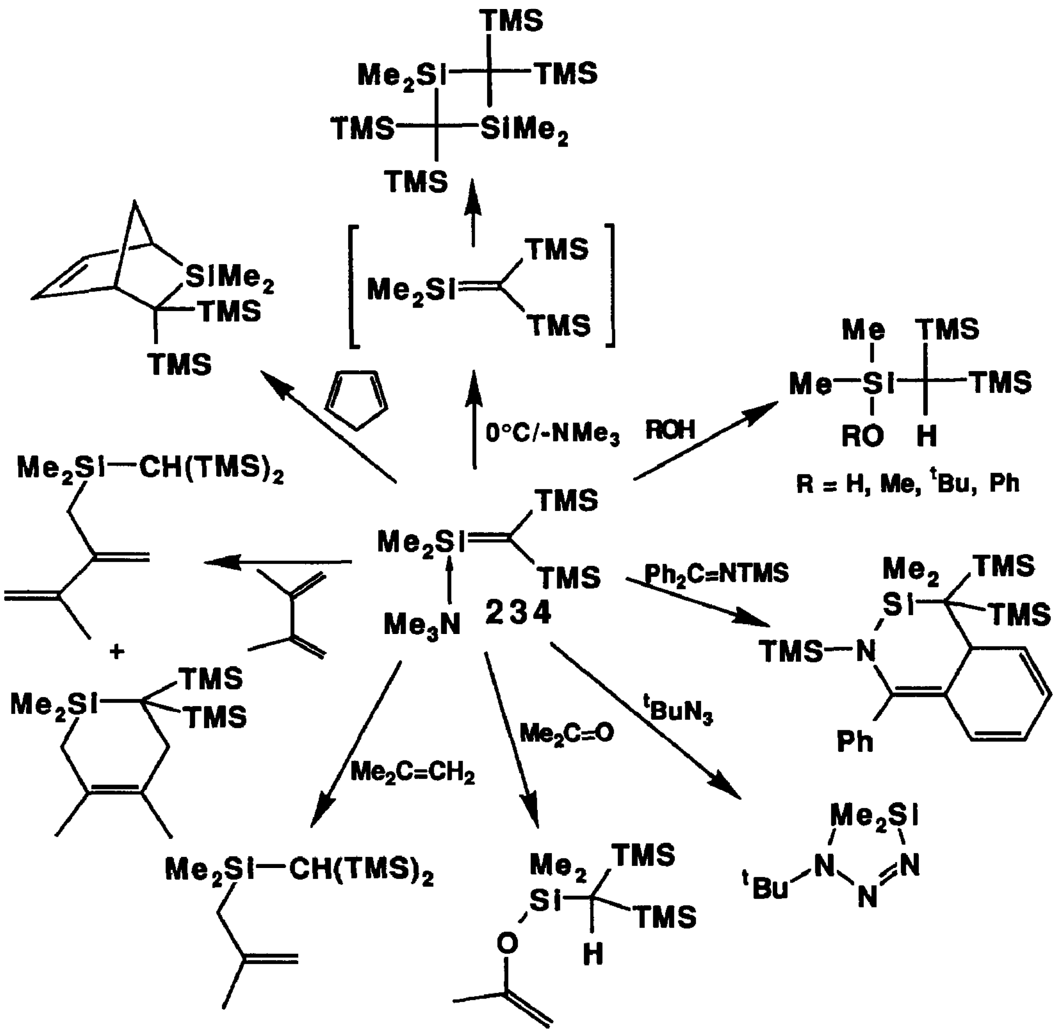


(817)

The elimination of lithium bromide again served as a method to prepare silenes. The silene **234** was shown to form a complex with trimethylamine. (Eqn. 818) The silene 234 undergoes the classic reactions of silenes. (Scheme I)

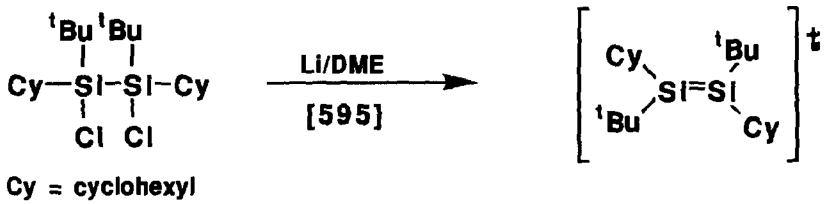


(818)

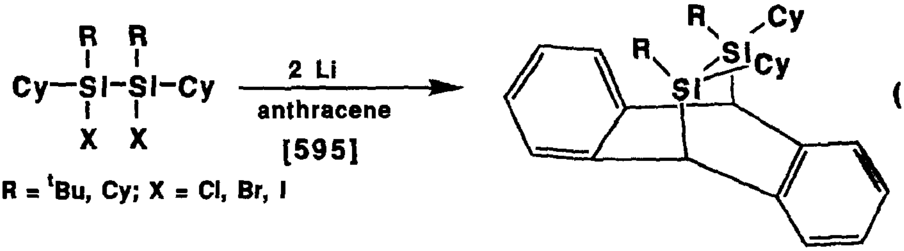


Scheme I

1,2-Dichlorodisilanes containing the tert-butyl and cyclohexyl groups react with lithium metal to give, in the absence of an acceptor, the anion radical of the corresponding disilene. (Eqn. 819) In the presence of anthracene the disilene is trapped. (Eqn. 820)

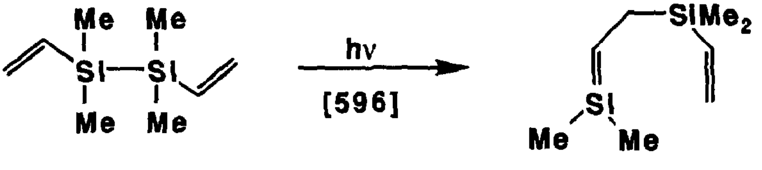


(819)



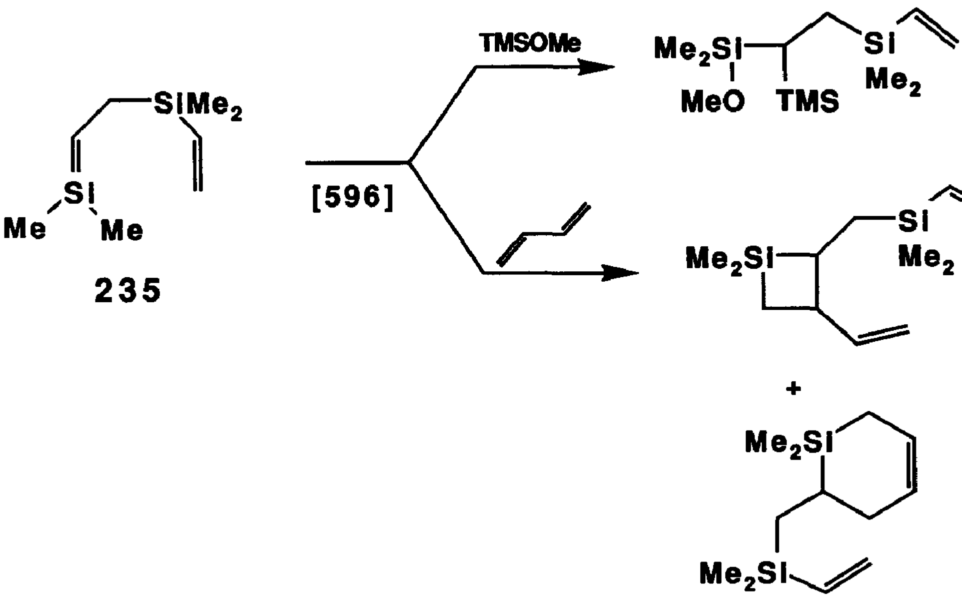
(820)

1,2-Divinyltetramethyldisilane photochemically gives silene **235** (Eqn. 821), which can be trapped with trimethylmethoxysilane (Eqn. 822) and butadiene (Eqn. 823). Thermolysis of the silacyclobutane **236** was carried out in this study as well. (Eqn. 824)



235

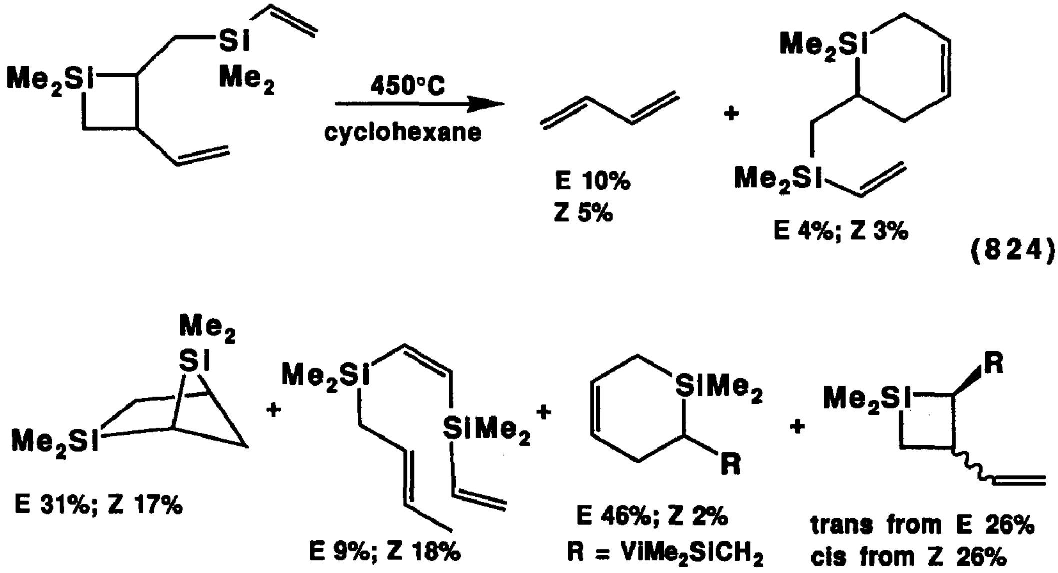
(821)



235

(822)

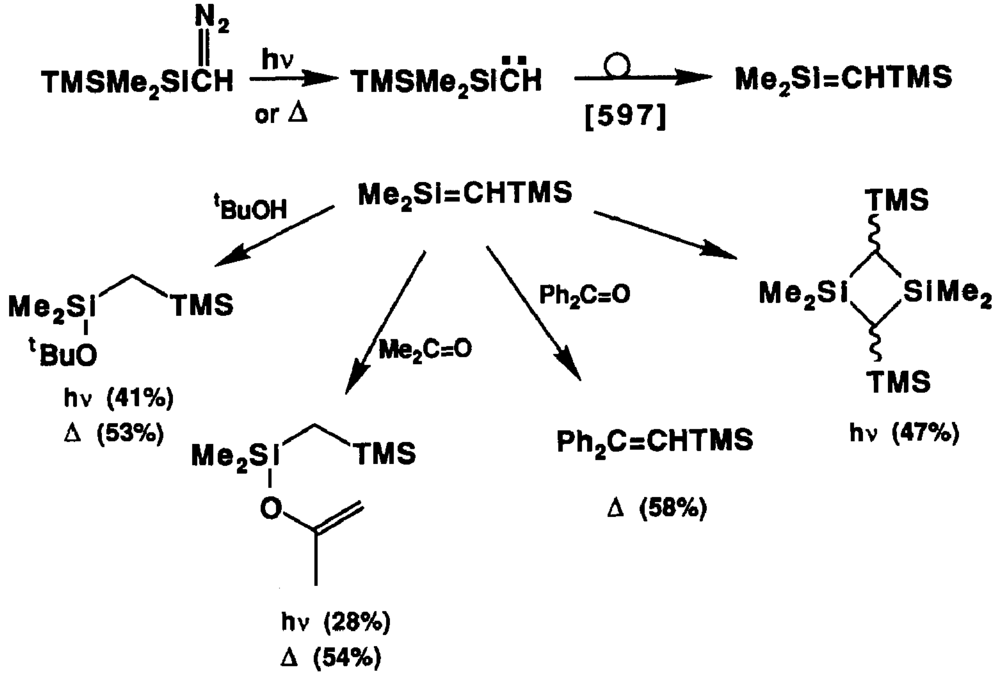
(823)



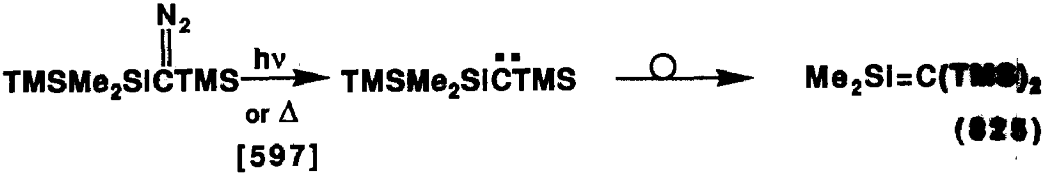
(824)

Precentages indicate yield from the (E) or (Z) starting material.

In another study silenes were again generated from α-diazosilanes, but this time the silenes were trapped with various reagents. (Scheme II) The interesting silylated silenes were prepared in a similar manner. (Eqns. 825 and 826)



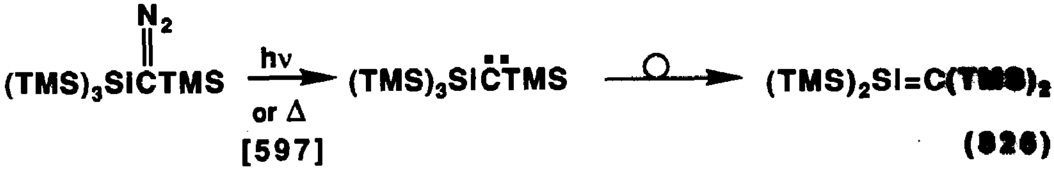
Scheme II



$$\text{TMSMe}_2\text{Si}\overset{N_2}{\overset{\|}{C}}\text{TMS} \xrightarrow[\text{or }\Delta]{h\nu} \text{TMSMe}_2\text{Si}\ddot{C}\text{TMS} \xrightarrow{\bigcirc} \text{Me}_2\text{Si=C(TMS)}_2$$

[597]

(825)

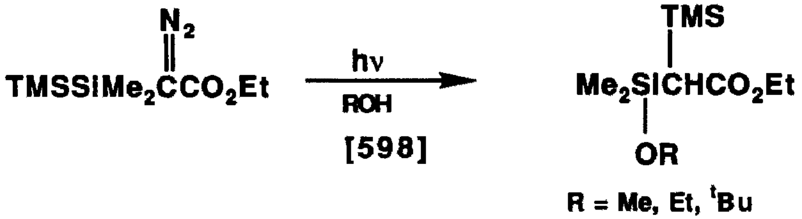


$$(\text{TMS})_3\text{Si}\overset{N_2}{\overset{\|}{C}}\text{TMS} \xrightarrow[\text{or }\Delta]{h\nu} (\text{TMS})_3\text{Si}\ddot{C}\text{TMS} \xrightarrow{\bigcirc} (\text{TMS})_2\text{Si=C(TMS)}_2$$

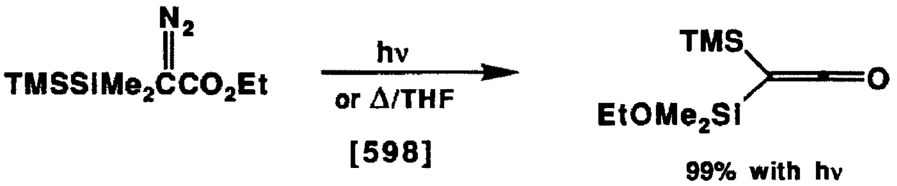
[597]

(826)

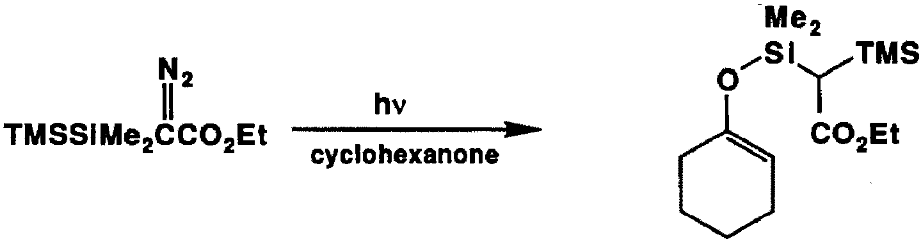
The photolysis of α-pentamethyldisilyldiazo esters leads to α,α-bis(silyl) esters and bis(silyl) ketenes. Thermolysis also gives the ketene. (Eqns. 827 and 828) Trapping experiments with cyclohexanone (and also benzophenone) indicates the intermediacy of silene **237**. (Eqn. 829)



(827)

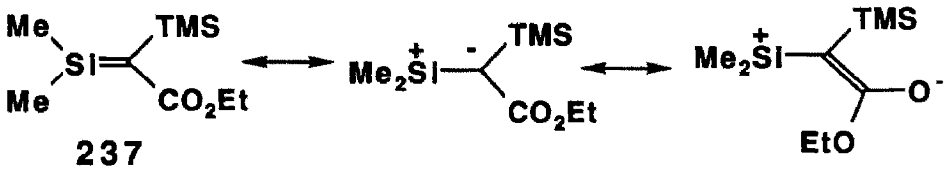


(828)

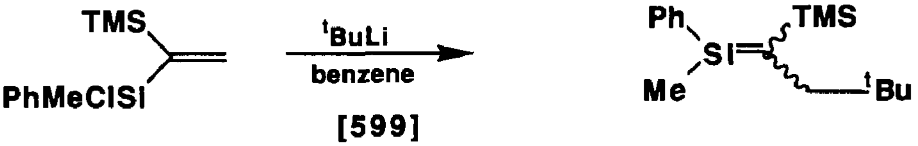


(829)

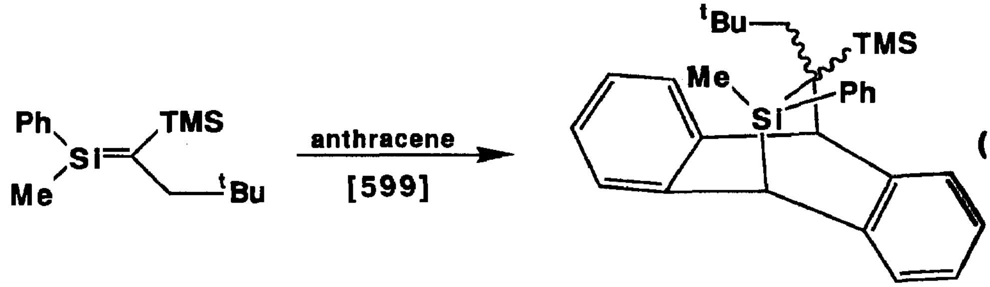
proposed route



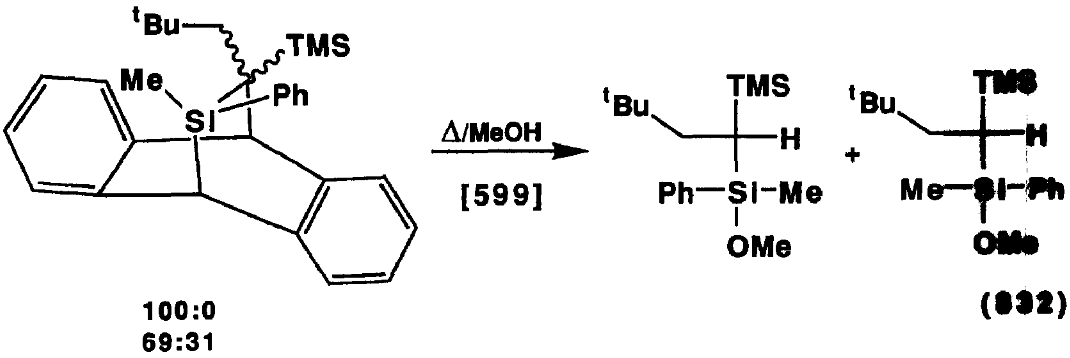
The stereochemistry of the addition of methanol to silenes was determined. The reactio was shown to be stereospecific and is believed to occur *via* a cis addition. (Eqns. 830, 831, and 832) The activation energy for a silene isomerization was determined to be 43 kcal mol^{-1} for 1-phenyl-1-methyl-1-sila-4,4-dimethylpentane. [600]



(830)



(831)



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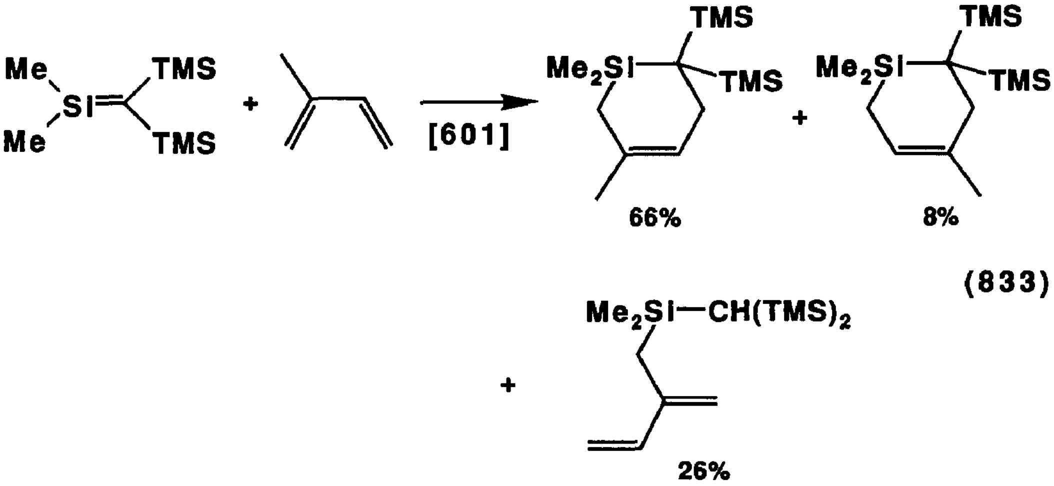
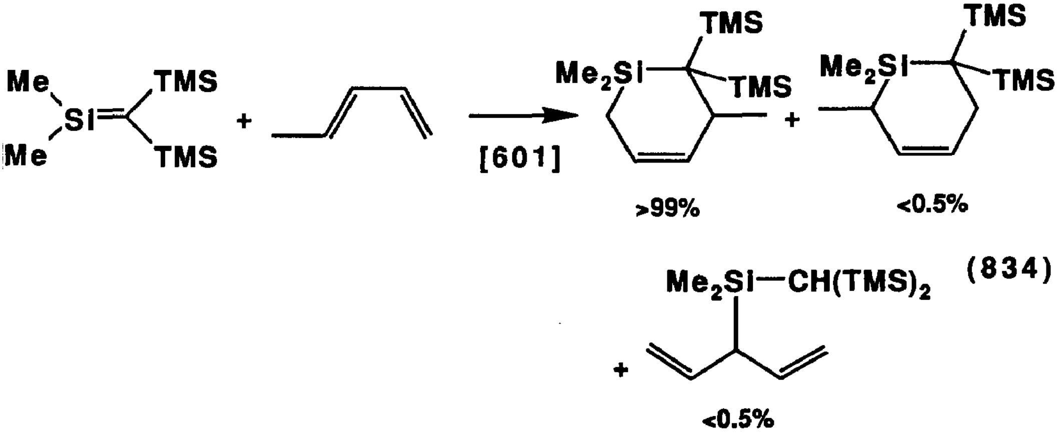
69:31

(832)

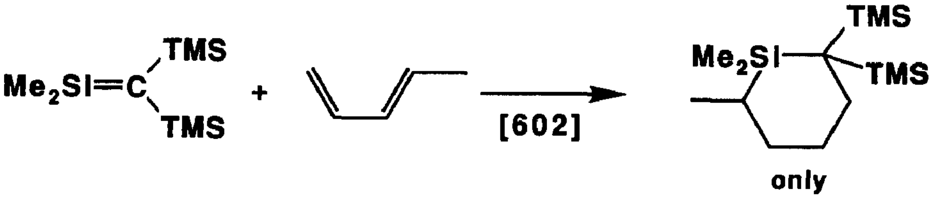
The regiospecificity of the cycloaddition of 1,1-dimethylbis(trimethylsilyl)silene with isoprene and piperylene was studied. The results are given in Eqns. 833 and 834; the regiospecificity of the reaction is high. The conformational effects of the reaction with trans- and cis-piperylene were also studied. (Eqns. 835 and 836)



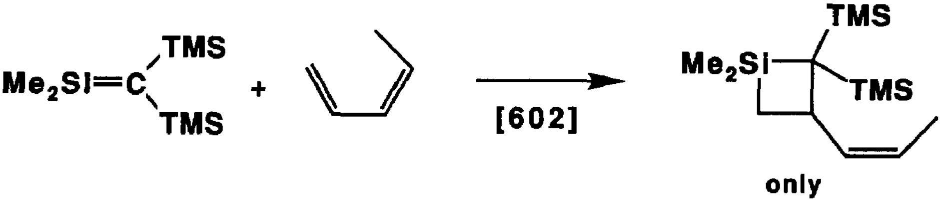
(833)



(834)

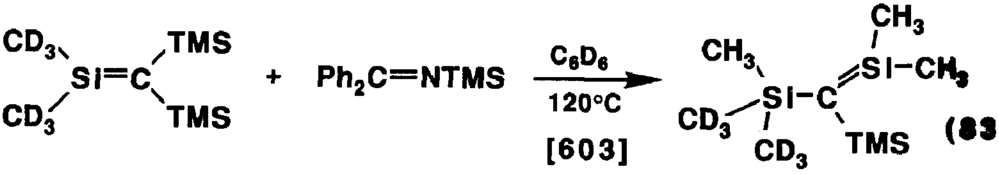


(835)



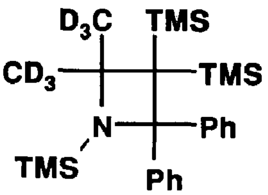
(836)

The fluxional behavior of silenes was demonstrated with deuterium labelling experiments. It was shown that the methyl groups of the silene migrate with a rapid shift of the Si=C douible bond from one silicon atom to another in **238**. (Eqn. 837)

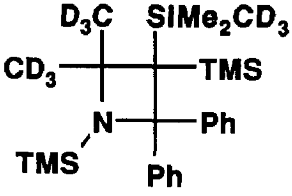


(837)

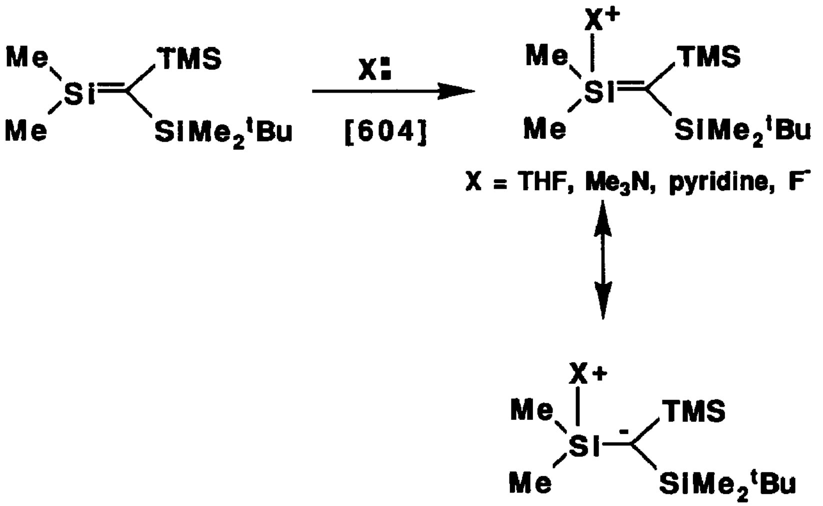
Trapped as the adducts:



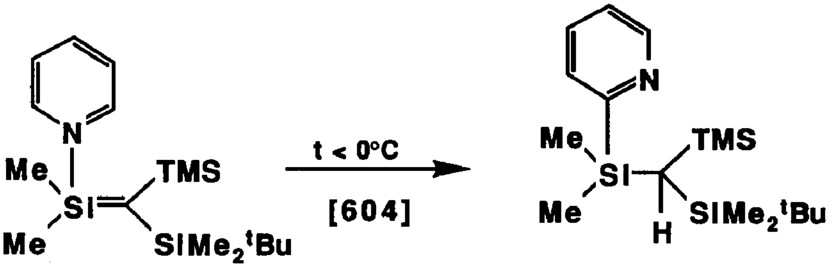
and



Donor adducts of silenes with tetrahydrofuran, trimethylamine, pyridine, and fluoride ion were reported. (Eqns. 838 and 839)

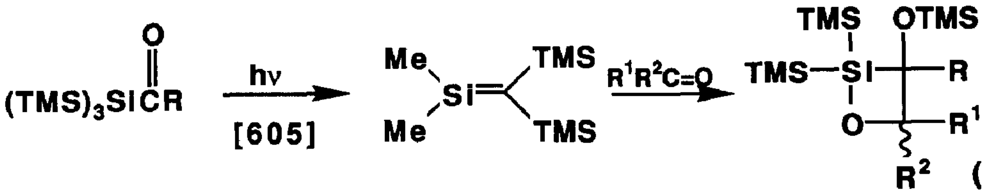


(838)



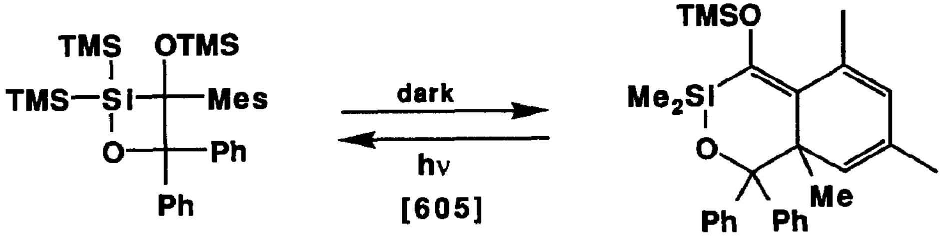
(839)

Several relatively stable silenes were generated and trapped with ketones to give 1,2-siloxetanes. (Eqn. 840) These 1,2-siloxetanes undergo some interesting thermal chemistry of their own. (Eqns. 841, 842 and 843)

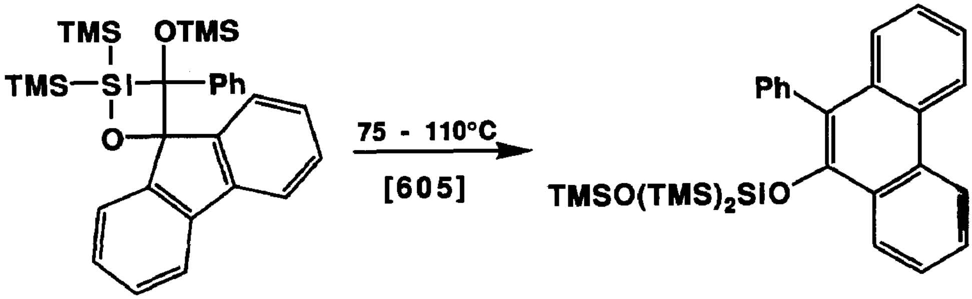


(840)

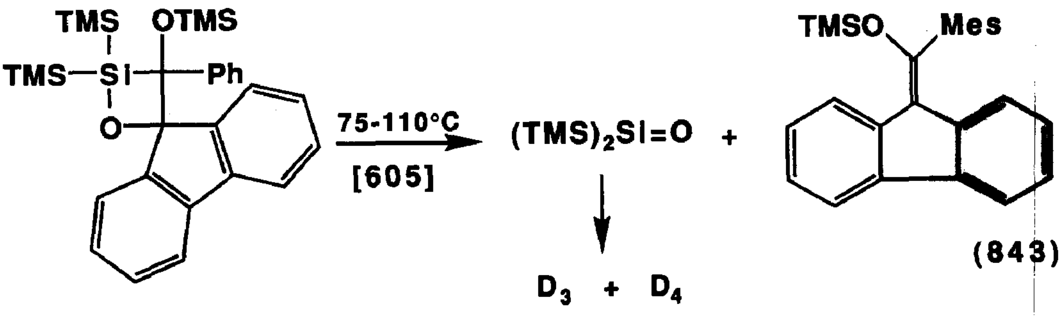
R = Ph, Mes, ^{t}Bu, Adamantyl;
R^1 = R^2 = Ph, fluorenyl, p-tol;
R^1 = ^{t}Bu, R^2 = H, R^1 = Ph, R^2 = H



(841)

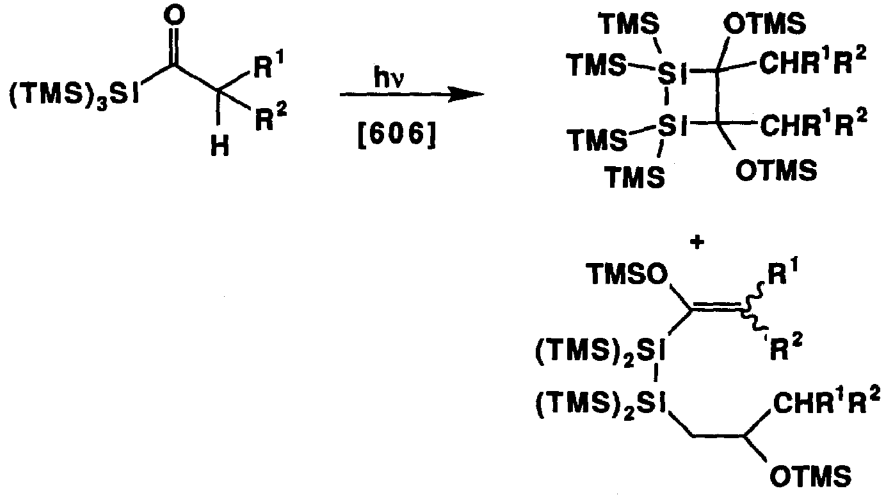


(842)



(843)

The photolysis of tris(trimethylsilyl)acylsilanes containing α-hydrogens leads to cyclic and linear head to head dimers. (Eqn. 844)

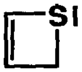


(844)

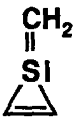
Restricted Hartree-Fock ab initio calculations on the isomers of C_3SiH_4 were done. The order of stability of these isomers is shown below. [607]

most stable

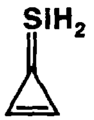
+ 27 kcal/mol



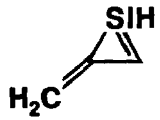
+12 kcal/mol



+43.6 kcal/mol



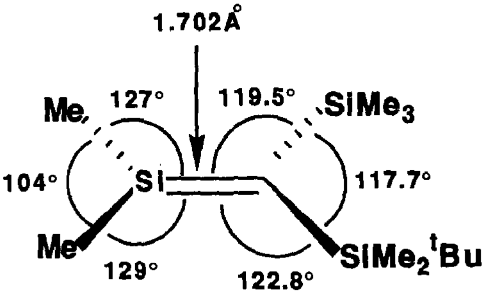
+59 kcal/mol



+66.9 kcal/mol

Ab initio calculations were directed towards the question as to why π bonds to phosphorus are more stable than those of silicon towards addition reactions. It was essentially shown that the π bonds to silicon are weaker in π character and stronger in σ character whereas those of phosphorus are the other way around. [608]

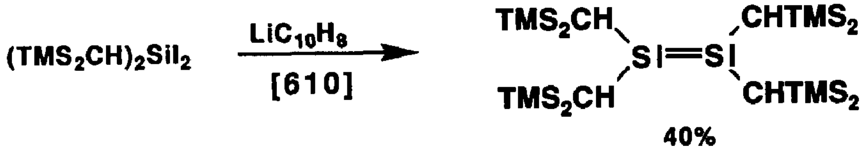
gThe crystal structure of **239** was done. The results are as shown. [609]



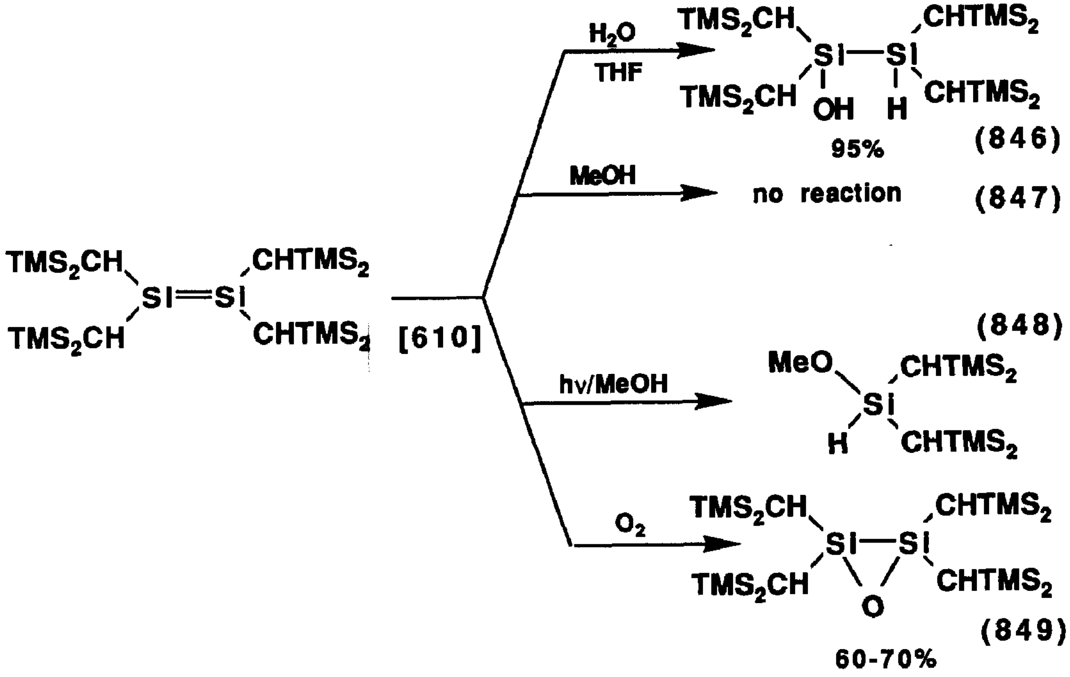
239

D. Disilenes

Tetrakis[bis(trimethylsilyl)methyl]disilene was synthesized and characterized. Thus, treatment of di[bis(trimethylsilylmethyl)]diiodosilane with lithium naphthalenide gives rise to the disilene. (Eqn. 845) Some of its reactions are given in Eqns. 846-849.



(845)



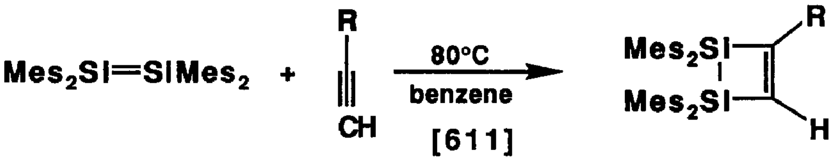
(846)

(847)

(848)

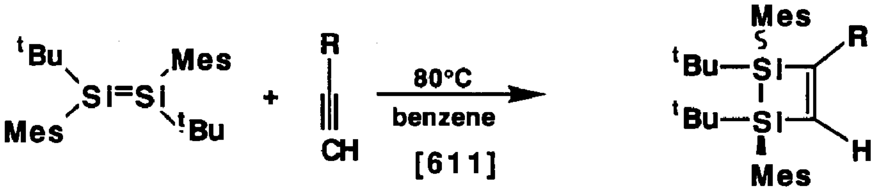
(849)

Tetramesityldisilene and trans-1,2-di-tert-butyl-1,2-dimesityldisilene were reacted with terminal acetylenes to provide 1,2-disilacyclobutenes. (Eqn. 850) These materials were found to be air stable. The obtention of both possible stereoisomers as shown in Eqn. 851 is consistent with a stepwise mechanism.



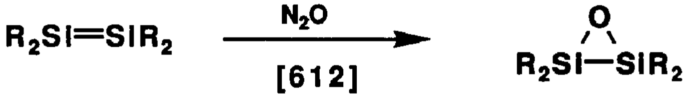
(850)

R = Ph, TMS, MeO$_2$C, EtO;
no reaction with R = Bu, Me, H or
with PhC$_2$TMS, Ph$_2$C$_2$, DMAD



(851)

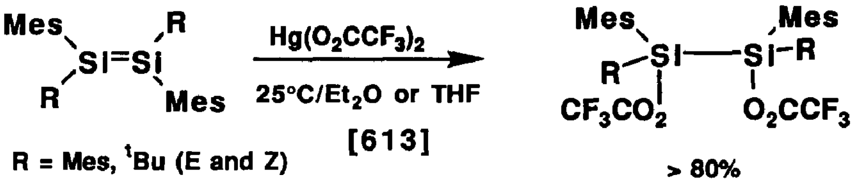
Hindered disilenes were reacted with nitrous oxide to give disilaoxiranes. An x-ray structure of one of these shows that there is considerable Si=Si character in these species. (Eqn. 852)



(852)

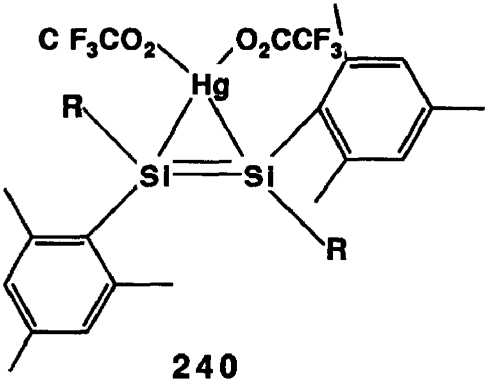
(R = Mes, 2,6-dimethylphenyl, 2,6-dimethyl-4-tert-butylphenyl)

Evidence was provided for possible π-complex intermediates, such as **240**, in the reaction of disilenes with mercury(II) trifluoroacetate. (Eqn. 853)



(853)

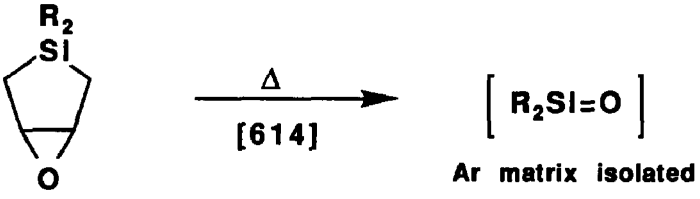
(Pure E gives a single diastereomer whereas a 65:35 mixture gives a 65:35 mixture of diastereoemers)



240

E. Silanones

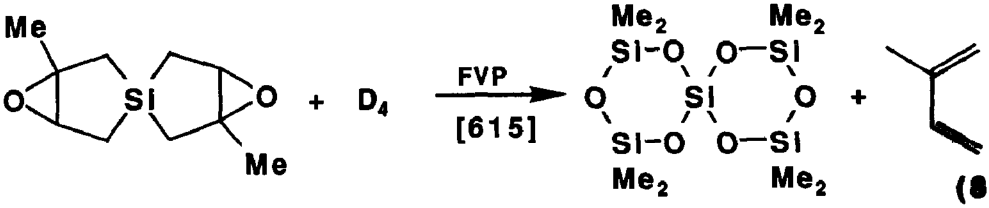
The low temperature generation of dimethylsilanone and its perdeuterated version from epoxysilacyclopentane **241** allowed for the matrix isolation of these materials in argon. (Eqn. 854)



241

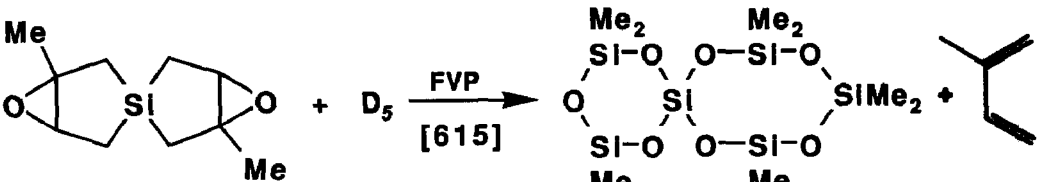
(854)

Flash vacuum pyrolysis of silaspirocycle **242** leads to spirocyclosiloxanes *via* the intermediacy of silanones. (Eqns. 855 and 856)



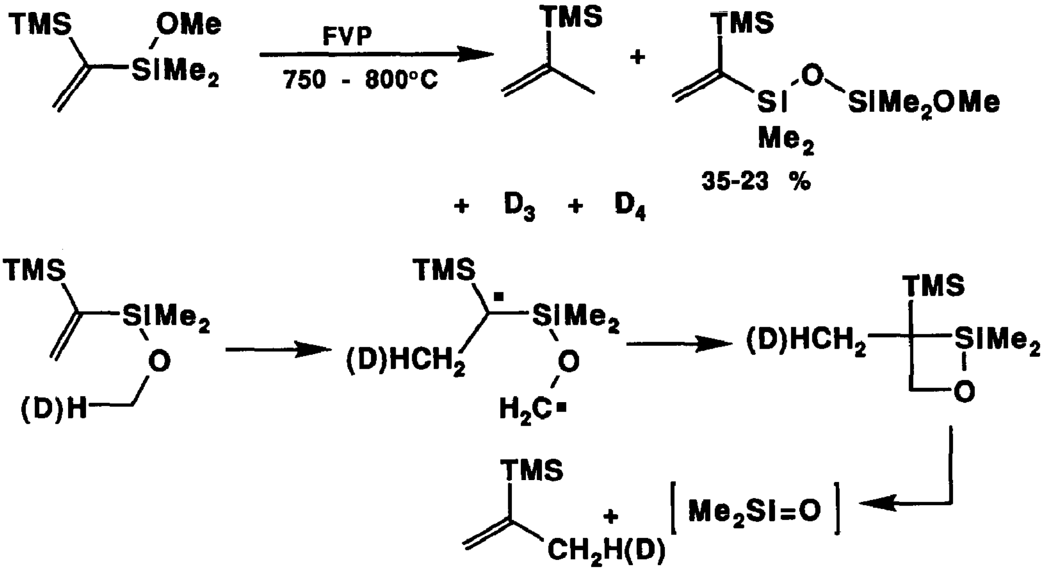
242

(855)



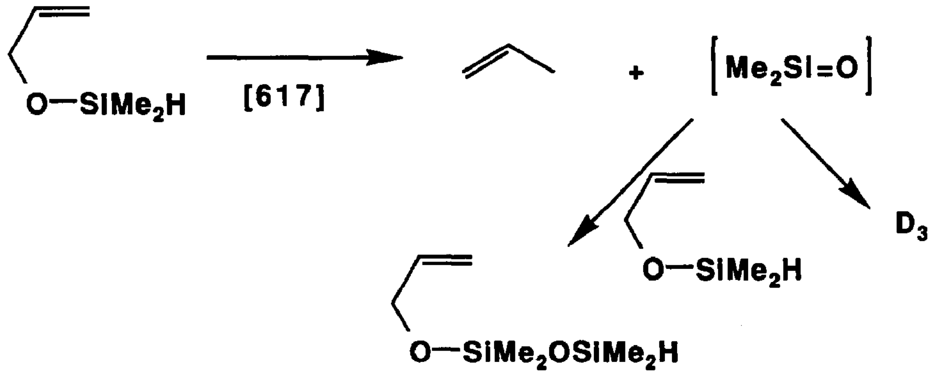
(856)

The mechanism of extrusion of silanone from alkoxyvinylsilanes was studied. No evidence for a silaallene was found, but the extrusion of silanone was seen. Labelling experiments indicate that the reaction starts with a 1,5-shift of a hydrogen of the methoxy group to give a 1,4-diradical, which closes and extrudes dimethylsilanone. (Scheme III)

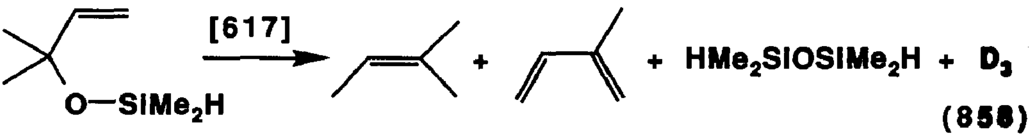


Scheme III

Dimethylsilanone was generated *via* a retroene reaction of allyloxysilanes. Substitution of the ether linked carbon with methyl groups brought about competition between C-O bond homolysis and retroene decomposition. (Eqns. 857 and 858)

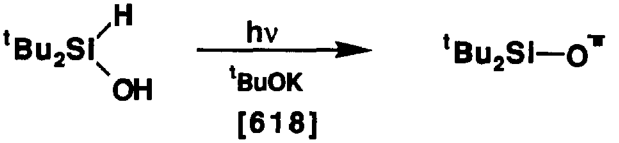


(857)

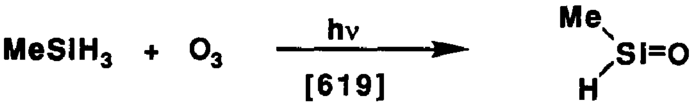


(858)

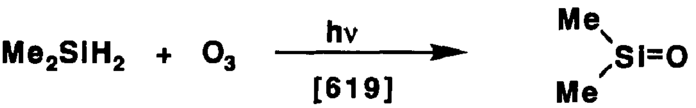
The photolysis of di-tert-butylsilanol in the presence of potassium tert-butoxide leads to the anion radical of di-tert-butylsilanone. (Eqn. 859) The photochemical reaction of methylsilane and dimethylsilane with ozone provides methylsilanone and dimethylsilanone, respectively. (Eqns. 860 and 861) The IR spectra of dimethylsilanone with ^{16}O showed an absorbance at 1209.6 cm^{-1} and with ^{18}O at 1174.4 cm^{-1}.



$${}^{t}Bu_2Si(H)(OH) \xrightarrow[{}^{t}BuOK \ [618]]{h\nu} {}^{t}Bu_2Si{-}O^{\bullet-} \qquad (859)$$

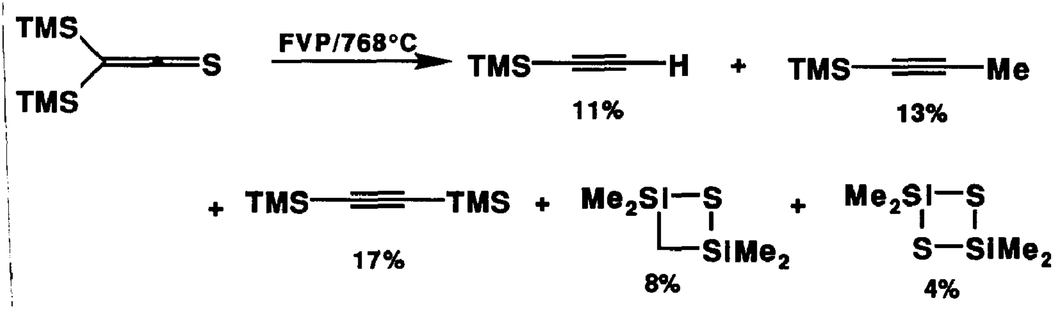


$$MeSiH_3 + O_3 \xrightarrow[[619]]{h\nu} (Me)(H)Si{=}O \qquad (860)$$

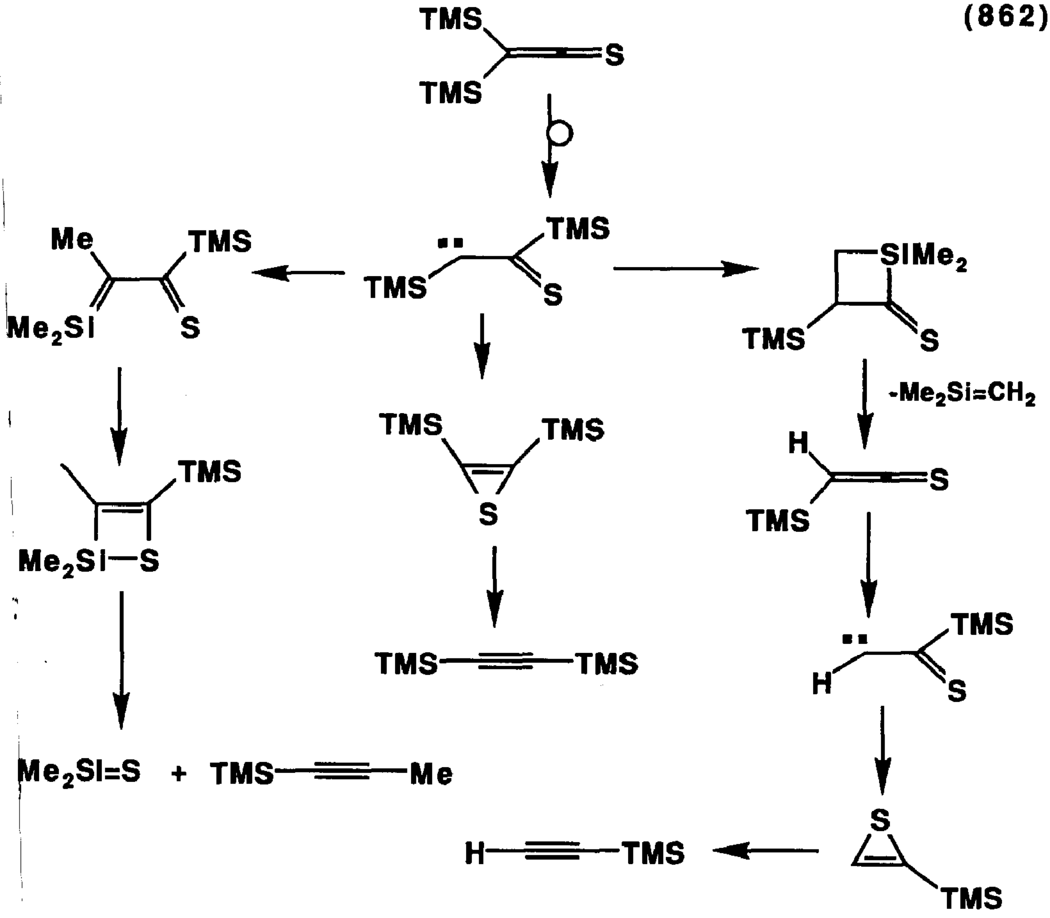


$$Me_2SiH_2 + O_3 \xrightarrow[[619]]{h\nu} (Me)(Me)Si{=}O \qquad (861)$$

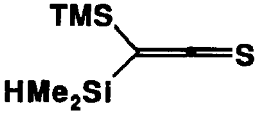
Flash vacuum pyrolysis of bis(trimethylsilyl)thioketene extrudes dimethylsilthione and forms trimethylsilylacetylene. (Eqn. 862) A mechanism was proposed. (Scheme IV)



(862)

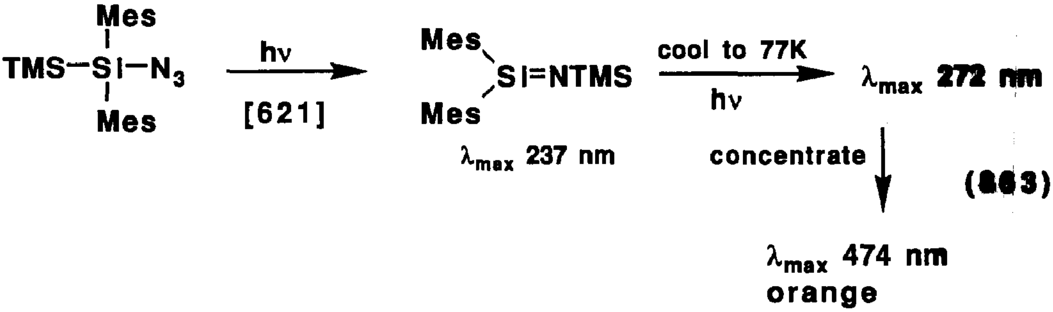


Scheme IV

 was used to aid in the mechanistic studies.

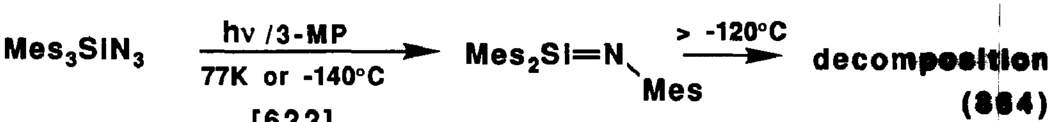
F. Silaimines

The photolysis of trimethylsilyldimesitylsilyl azide extrudes nitrogen and gives N-trimethylsilyldimesitylsilaimine, which was matrix isolated. (Eqn. 863) This material shows a λ_{max} of 272 nm, but when it is concentrated it shows a λ_{max} of 474 nm. These are attributed to a π–π^* and n-π^* transitions, respectively.

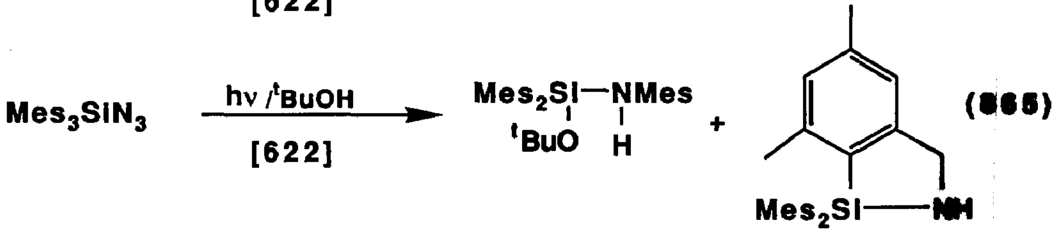


(863)

Trimesitylsilyl azide was photolyzed and the resulting silaimine matrix isolated. It adds tert-butanol and inserts into an ortho methyl group of one of the mesityl ligands. It shows λ_{max} at 296 and 444 nm. (Eqns. 864 and 865)

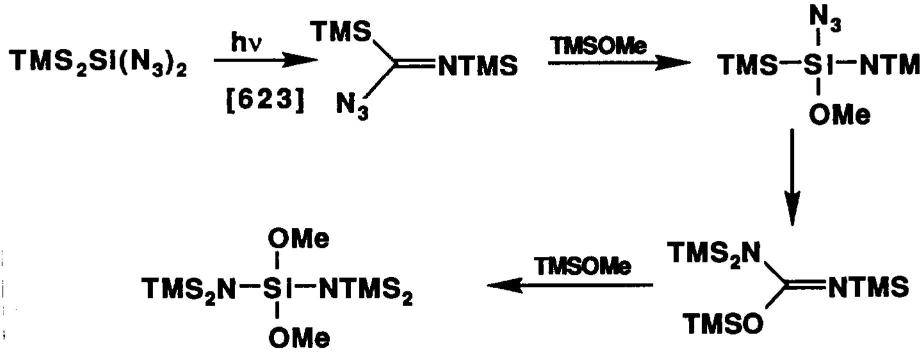


(864)

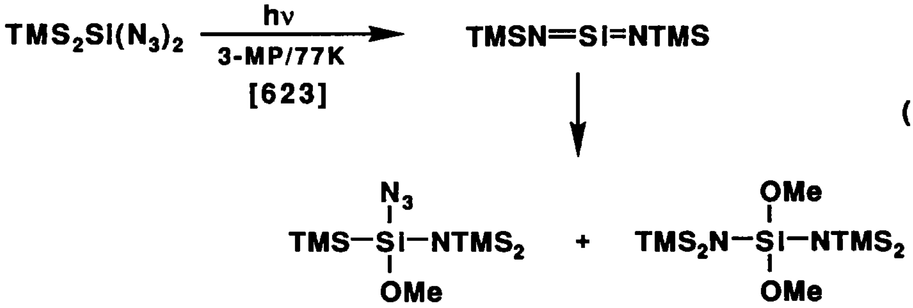


(865)

Bis(trimethylsilyl)silyldiazide upon photolysis gives N-trimethylsilyl(trimethylsilyl)azidosilaimine. This can be trapped with trimethylmethoxysilane and a new silaimine generated, which in turn can be trapped. (Eqn. 866) Carrying out the photolysis in 3-methylpentane at low temperature and then trapping with trimethylmethoxysilane gives the adduct of both the azidosilaimine and N,N'-bis(trimethylsilyl)siladiimine. (Eqn. 867)

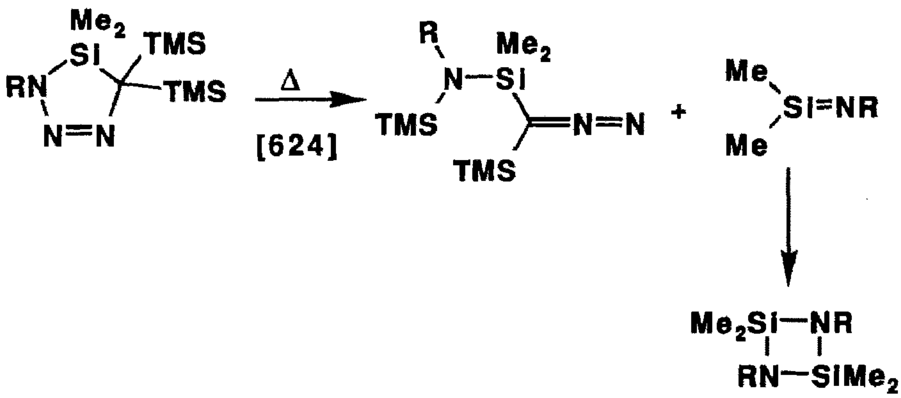


(866)

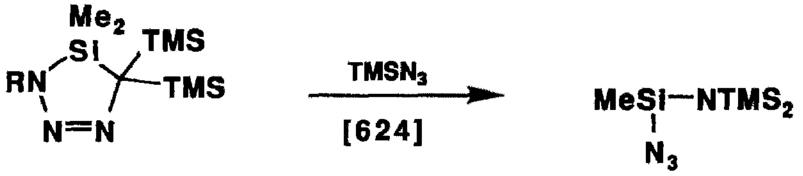


(867)

Thermolysis of sila-1,2,3-triazoles gives silaimines, which, in the absence of a trap, produce the head-to-tail cyclic dimers. (Eqn. 868) Trapping of the silaimine with azides was accomplished. (Eqn. 869)

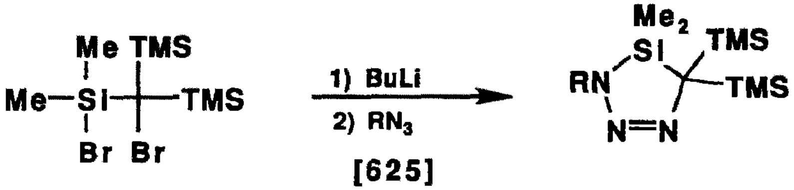


(868)

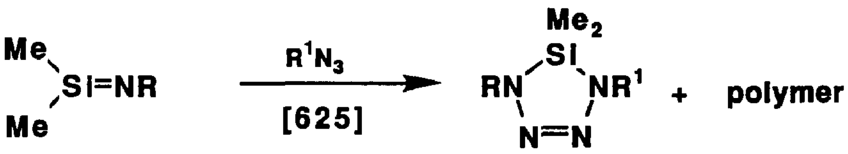


(869)

In a similar study sila-1,2,3-triazoles, prepared from dibromide **243**, (Eqn. 870) were thermolyzed in the presence of alkyl azides to give silatetrazoles *via* silaimines. (Eqn. 870)

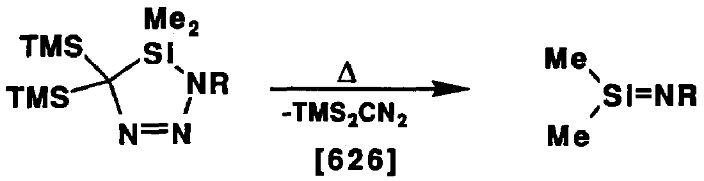


(870)



(871)

5,5-Bis(trimethylsilyl)-4-sila-1,2,3-triazole thermally extrudes bis(trimethylsilyl)diazomethane and produces silaimines. (Eqn. 872)

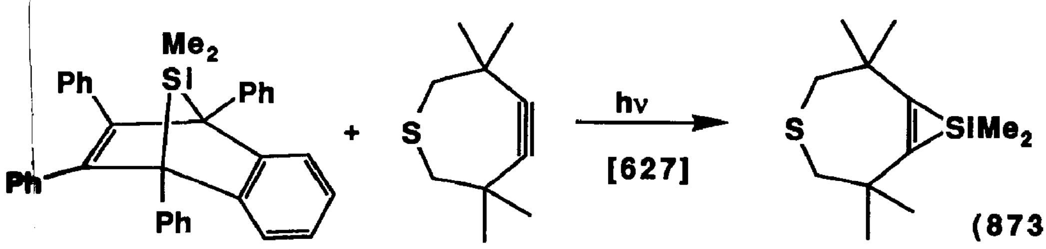


(872)

R = TMS, TBS, $^tBu_2MeSi$, TMS_2NMe_2Si, p-tol

G. Miscellaneous Reactive Organosilane Species

Photoreaction of 245 with silanorbornadiene 244 gives silirene 246. The x-ray structure was determined and argued to be consistent with pseudoaromaticity. (Eqn. 873) The contrasting ring energies of small ring carbon and silicon rings were studied. In the silicon rings angle deformations dominate. [628]



644 **645** **646**

(873)

A high pressure mass spectrometric study of the binding of the trimethylsilicenium cation to various bases was studied. [629] The first demonstration of the solvolytic generation of a silicenium ion was reported. It occurs *via* the 1,2-migration of methyl group from silicon. [630] The formation of heptamethyldisilyl cation and the methyl exchange reactions that it undergoes were reported. [631]

Acknowledgements

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