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Silicon-containing 1,3-alkenynes and more unsaturated compounds

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ABSTRACT. The methods of synthesis and characteristic features of the reactivity of silicon-containing alkenynes are treated systematically and surveyed for the first time. It is shown that the carbon–carbon double bonds are reactive in the reactions of silahydrocarbons and their functional derivatives containing the $\equiv Si-C\equiv C-C<$ fragments. Only aluminium, boron, and tin hydrides as well as certain weak electrophiles add preferentially or exclusively to the triple bond. The absence of a dependence of the mode of addition on the polarity of the unsaturated compound and the other reactant indicates orbital control in the reactions investigated.

Studies of the dependence of the mode of reaction (addition, desilylation, reactions of functional groups) on the structure of the silicon-containing alkenynes, the nature of the other reactant, and the experimental conditions served as a basis of the development of methods for the introduction of functional groups into the alkenynes and of a silyl protecting group method in the chemistry of acetylenic compounds and have demonstrated the extensive possibilities of the application of these procedures in the stereocontrolled synthesis of natural products and their synthetic analogues.

The bibliography includes 346 references.

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I. Introduction

The highly unsaturated compounds containing a conjugated double and triple bond and an organosilyl group attached to a multiply bound carbon atom exist in the form of three isomers differing in the position of the silicon-containing substituent:

$R^1_3Si-C\equiv C-CR^2=CR^3R^4$ (A)

$R^1_3Si-CR^2=CR^3-C\equiv CR^4$ (B)

$R^2R^3C=C(SiR_3)-C\equiv C-R^4$ (C)

Representatives of all these types have now been synthesised, but compounds of type (A) are historically the first and have been most thoroughly investigated. Hundreds of original articles have been devoted to the methods of their synthesis and chemical properties, but there are no reviews on the problem.

Compounds of types (B) and (C) have not been studied systematically. The communications published on this problem were devoted to the development of the methods of their synthesis and are as a rule non-systematic in character.

In the first stage, the chemistry of 1-triorganosilylalk-3-en-1-ynes (A) was indissolubly linked to the study of fundamental problems of theoretical organic chemistries such as conjugation, including $d_\pi-p_\pi$ conjugation, the relation between reactivity and structure, and the redistribution of the π-electron density of conjugated multiple bonds under the influence of the organosilicon substituent. A considerable proportion of studies in the first stage were therefore devoted mainly to the synthesis of 1-trialkylsilylalk-3-en-1-ynes and to the study of their properties. Such investigations (UV,[1] IR,[2–8] and photoelectron spectra,[9] molecular refraction,[10,11] quantum-chemical calculations,[12,13] ^1H[14] and ^{13}C[13,15–17] NMR spectra, dipole moments,[18–20] and mass spectra[21]) yield direct or indirect information about the magnitude and sign of the induction and mesomeric constants of the silicon-containing groups. The results have demonstrated unambiguously that the triorganosilyl groups attached to the triple bond exhibit an overall electron-donating effect, which is somewhat smaller than that of the hydrocarbon groups with the corresponding structures, while the basic (π-donor) properties of the triple bond in the 1,3-enyne silahydrocarbons are weaker than those of the hydrocarbons having similar structures. The spectroscopic parameters (IR, ^1H NMR, and mass spectra) have been recommended for analytical purposes in the determination of the structures of highly unsaturated organosilicon compounds.

Interest in the chemistry of enyne organosilicon compounds of type (A) increased appreciably after the development of mild desilylation methods (the removal of the triorganosilyl substituent stabilising the triple bond) as well as methods for the stereocontrolled synthesis of functional derivatives of 1-triorganosilylalk-3-en-1-ynes and the possibility of using them as synthetic units in fine organic synthesis was demonstrated.

II. Synthesis of 1-triorganosilylalk-3-en-1-ynes

The methods of synthesis of 1-triorganosilylalk-3-en-1-ynes and their carbofunctional derivatives known at present include procedures such as silylation of complete 1,3-enyne hydrocarbons and their derivatives, the creation of enyne structures as a result of β-elimination reactions of the derivatives of the corresponding acetylenic silylhydrocarbons or reactions involving the addition of silicon-containing diynes, the isomerisation (including reactions with ring opening) of unsaturated organosilicon compounds, as well as the creation of alkenyne structures as a result of the cross-coupling of silicon-containing acetylenes with the corresponding alkenes or

their precursors. As a rule, these fundamental approaches to the synthesis of a specific compound are intertwined and may involve simultaneously the formation of a double bond and the construction of the carbon skeleton and silylation.

1. Silylation of alkenynes

The most important methods for the laboratory synthesis of silicon-containing alkenynes and their derivatives is organometallic synthesis involving the interaction of the corresponding Iotsich complex with trialkylchlorosilane. 3-Methyl-1-triethylsilylpent-3-en-1-yne, the first representative of silicon-containing vinylacetylenes, was synthesised by this method in 1946:[1]

$$Et_3Si{-}Cl + CH_3CH{=}\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}{-}C{\equiv}CMgBr \longrightarrow$$

$$\longrightarrow Et_3Si{-}C{\equiv}C{-}\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}{=}CHCH_3.$$

The Iotsich reagents derived from the simplest vinylacetylenic (vinyl-,[22–24] isoalkenyl-,[25–29] alkenyl-,[25–30] and cycloalkenyl-acetylenes[25,27,28]) and more unsaturated hydrocarbons[31–34] were initially made to react with trialkylchloro- and dialkyldichloro-silanes. Trialkyl-, dialkylaryl-, and alkyldiaryl-chloro-silanes, entered into this reaction. With increase in the number of aryl groups at the silicon atom, the yield of the condensation products fell.[23,24] The attempts obtain 1-triphenylsilylbut-3-en-1-yne by the reaction of chlorotriphenylsilane and vinylethynylmagnesium bromide was unsuccessful.[23] The corresponding silylhydrocarbon was synthesised only by the reaction of the Iotsich complex with fluorotriphenyl-silane.[24] However, tri-*p*-chlorophenylsilylvinylacetylene was obtained by the reaction of the corresponding chlorosilane with the Iotsich complex, but it was necessary to heat the reaction system to a high temperature—the temperature of boiling dibutyl ether.[24]

The vinylacetylenic hydrosilanes $R_2HSi{-}C{\equiv}C{-}CH{=}CH_2$ and $RHSi(C{\equiv}C{-}CH{=}CH_2)_2$ were synthesised by the reaction of chlorohydrosilanes with vinylethynylmagnesium bromide.[23]

There are data showing the trialkyliodosilanes give rise to the corresponding vinylacetylenic silylhydrocarbons in higher yields than trialkylchlorosilanes.[25]

Alkoxysilanes, siloxanes, alkoxychlorosilanes, and triflates can be used as the silicon-containing component:

$$R^1_{4-n}(R^2O)_nSi + CH_2{=}CH{-}CMgBr \rightarrow R^1_{4-n}Si(C{\equiv}C{-}CH{=}CH_2)_n$$

(Refs. 23, 35, 36),

$$(R^1R^2SiO)_x + CH_2{=}CH{-}C{\equiv}CMgBr \rightarrow HO(R^1R^2)SiC{\equiv}C{-}CH{=}$$

$$={=}CH_2 \quad \text{(Refs. 37, 38)},$$

$$(RO)_3SiCl + CH_2{=}CH{-}C{\equiv}CMgBr \rightarrow (RI)_3SiC{\equiv}C{-}CH{=}CH_2$$

(Refs. 39, 40),

$$R_3SiCTf + CH_2{=}CH{-}C{\equiv}CMgBR \rightarrow R_3SiC{\equiv}CH{=}CH_2 \text{ (Ref.41)}.$$

A method based on the reaction of a mixture of the enyne hydrocarbon and chlorotrimethylsilane with butyllithium in hexane, presupposing the formation of lithium vinylacetylide, was developed for the synthesis of alkenyl-1-trimethylsilyl-, isoalkenyl-1-trimethyl-silyl-, and cycloalkenyl-1-trimethylsilyl-acetylenes:[30,42–44]

$$R^2CH{=}CR^1{-}C{\equiv}CH \xrightarrow[2.\ Me_3SiCl]{1.\ LiBu} Me_3SiC{\equiv}C{-}CR^1{=}CHR^2.$$

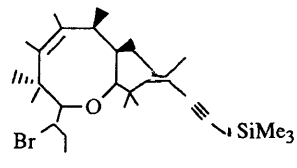
When isopropenylacetylene is treated with a mixture of butyllithium and potassium t-butoxide, the corresponding organo-potassium compound reacts with the chlorosilane:[43]

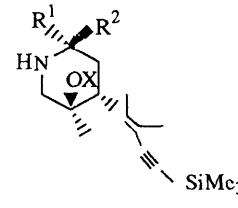
$$\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH_2{=}C{-}C{\equiv}CH}} \xrightarrow{BuLi;\ t\text{-}BuOK} \underset{\displaystyle CH_2K}{\overset{\displaystyle |}{CH_2{=}C{-}C{\equiv}CK}} \xrightarrow{Me_3SiCl} \underset{\displaystyle CH_2SiMe_3}{\overset{\displaystyle |}{CH_2C{-}C{\equiv}}}$$

$$\equiv CSiMe_3.$$

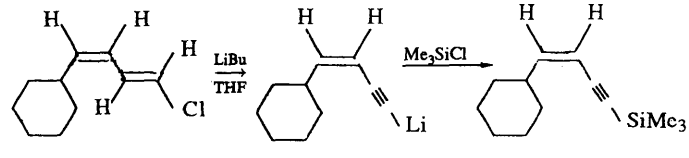
Subsequently the method of synthesis of lithium acetylides was simplified and reduced to the single-stage interaction of metallic lithium with vinylacetylene in tetrahydrofuran (THF).[45,46] Sodium vinylacetylide was obtained similarly.[47] The use of lithium and sodium acetylides makes it possible to increase the yield of the target products by 30–40% compared with the reactions of Iotsich complexes having analogous structures.[45–47]

The organolithium, organosodium, and organomagnesium syntheses of silicon-containing alkenynes can be used also for the preparation of functional derivatives of hydrocarbons subject to the condition that the functional group does not interact with the organometallic compound. Silicon-containing vinylacetylenic alcohols,[48–51] ethers,[52–54] sulphides,[55] acetals,[56,57] ketals,[41] tertiary amines,[30,42,58–60] and more complex organic compounds[61,63] were obtained in this way, for example:





An unusual version of this method involves a procedure employed in the synthesis of (*Z*)-4-cyclohexyl-1-trimethylsilylbut-3-en-1-yne:[64]



and 3-ethoxy-1-trimethylsilylbut-3-en-1-yne:[65]

$$CH{\equiv}CF + CH_2{=}C(Li)OEt \longrightarrow \underset{\displaystyle OEt}{\overset{\displaystyle |}{CH_2{=}C}}{-}C{\equiv}CLi \xrightarrow{Me_3SiCl}$$

$$\longrightarrow \underset{\displaystyle OEt}{\overset{\displaystyle |}{CH_2{=}C}}{-}C{\equiv}CSiMe_3.$$

The method involving the direct silylation of vinylacetylene with iodosilatrane was developed by Voronkov et al.:[66]

$$CH_2{=}\,CH{-}C{\equiv}CH + ISi(OCH_2CH_2)_3N \longrightarrow$$

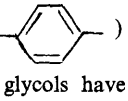
$$\longrightarrow CH_2{=}\,CH{-}C{\equiv}CSi(OCH_2CH_2)_3N.$$

The same vinylethynylsilatrane was obtained by the transalkylation of triethoxyvinylethnylylsilane with triethanolamine.[67]

2. β-Elimination reactions

(a) Dehydration of silicon-containing acetylenic alcohols

This method was successfully used for the first time in the synthesis of silicon-containing alkenynes in 1957. Distillation of dimethyl(trimethylsilylethynyl)carbinol in the presence of catalytic amounts of potassium hydrogen sulphate afforded 3-methyl-1-trimethylsilylbut-1-yne in a satisfactory yield.[68] Phosphorus pentoxide,[69,70] adipic acid,[71,72] boric acid,[72] toluene-*p*-sulphonic acid,[70–75] and phosphoryl chloride[76] began to be used later as dehydrating agents.

The method yields positive results not only in the synthesis of the corresponding silylhydrocarbons[68–78] but also of their derivatives,[70,74,76] as well as bisalkenylsilanes. In the latter case, the corresponding glycols of the type $Me_2Si[C{\equiv}C{-}C(CH_3)_2OH]_2$ and $[HO(CH_3)_2C{-}C{\equiv}C{-}SiR_2]_2A$ (A = $-CH_2CH_2-$ or ) were dehydrated.[79–83]

Oxygen-containing tertiary acetylenic alcohols and glycols have also been dehydrated. The attempts to dehydrate a secondary alcohol with potassium hydrogen sulphate failed to give positive results.[84]

One should evidently note the unusual dehydration, contrary to Zaitsev's rule, of a diacetylenic ketoalcohol, which led to the formation of a "stable" enol:[74]

$$Me_3SiC{\equiv}C{-}\,C(OH)CH_3CH_2COC{\equiv}\,CSiMe_3 \xrightarrow[-H_2O]{H^+}$$

$$\longrightarrow Me_3SiC{\equiv}C-\underset{\underset{CH_2}{\|}}{C}-CH=\underset{\underset{OH}{|}}{C}-C{\equiv}\,CSiMe_3.$$

The stereochemistry of the dehydration has not been studied in most cases but there are indications that water is split off stereospecifically.[85,86]

(b) Base-catalysed elimination of hydrogen halides and other acids

The dehydrohalogenation method, widely used in the chemistry of alkenes, has been scarcely employed in the synthesis of silylhydrocarbons owing to the low hydrolytic stability of the silicon–carbon bond: the elimination of hydrogen halides is as a rule accompanied by desilylation. For example, treatment of 1,4-dibromo(bromochloro)-1-trimethylsilylbuta-1,2-diene with an alcoholic solution of alkali involves dehydrohalogenation and desilylation even in the cold with formation of the corresponding α-halovinylacetylenes:

$$Me_3SiCX{=}C{=}CHCH_2Br \xrightarrow[EtOH]{KOH} XC{\equiv}C{-}CH{=}CH_2;$$

X = Cl (Ref.87), Br (Ref.25).

The data on the dehydrobromination of silicon-containing acetylenic bromoethers are contradictory; whereas according to the data of Komarov and co-workers dehydrobromination without the cleavage of the silicon–carbon bond occurs only when triethylamine is used as the base and dehydrosilylation takes place in the presence of alkali,[88] according to Shchukovskaya and Kapustyanskaya[89] the dehydrobromination of bromoethers can be carried out also in the presence of solid potassium hydroxide:

$$R_3SiC{\equiv}C{-}\underset{\underset{OR'}{|}}{CH}CH_2Br \begin{cases} \xrightarrow[EtOH]{KOH} CH{\equiv}\,C-C(OR'){=}CH_2\ ; \\ \xrightarrow[\text{or KOH}]{Et_3N} R_3SiC{\equiv}C-C(OR'){=}CH_2\ . \end{cases}$$

Dehydrohalogenation without appreciable cleavage of the silicon–carbon bond has been used successfully in the synthesis of 1-trimethylsilylalk-3-ene-1,5-diynes[90] and 1,8-bis(trimethylsilyl)octa-3,5-diene-1,7-diyne.[33]

The dehyodrohalogenation (X = Cl, Br, I) of silicon-containing acetylenic and alka-1,2-diene sulphones by tertiary amines takes place particularly readily and with virtually quantitative yields (the reactions occurs at room temperature):[91–94]

$$R_3SiC{\equiv}\,C{-}CR'XCHR''SO_2Ar \xrightarrow[C_6H_6]{Et_3N} R_3SiC{\equiv}\,C-CR'{=}\,CR''SO_2Ar.$$

The study of the IR and ^1H NMR spectra as well as the dipole moments of the sulphones formed indicates their exclusive *trans*-structure.[20,91–93]

It has been shown in relation to the dehydroiodination of silicon-containing iodonitroacetylenes that mercury [lead?] acetate may be used as a weak base which does not cleave the silcon–carbon bond:[95]

$$R_3SiC{\equiv}\,CCHICH_2NO_2 \xrightarrow[AcOH,\ 30-40^{\circ}C]{Pb(OAc)_2} R_3SiC{\equiv}\,C-CH{=}CHNO_2.$$

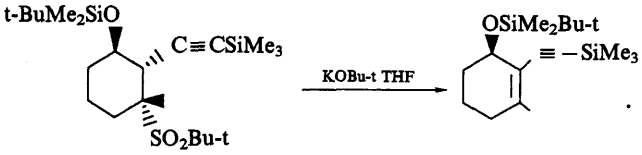
The reaction takes place stereospecifically with formation of compounds having the *trans*-configuration.

The data presented permit the claim that the base-catalysed dehydrohalogenation can serve as a convenient preparative method of synthesis of 1,3-enyne silylhydrocarbons and their derivatives but in each specific instance the solvent and base must be selected empirically. The method involving the base-catalysed (pyridine, diazabicycloundecyne) β-elimination of toluene-*p*-sulphonic acid proved to be successful in the synthesis of 1,3-enyne silylhydrocarbons and their derivatives.[85,86] Tosylates have been obtained from the corresponding secondary silicon-containing acetylenic alcohols and glycols. 4-Trialkylsilylbuta-2,3-diene-1-yl tosylate gives rise to a satisfactory yield of 1-trimethylsilylbut-2,3-en-1-yne on treatment with triphenylphosphine or the palladium complex $Pd(PPh_3)_4$:[96]

$$Me_3Si\diagdown\!=\!\cdot\!=\!\diagup OH \xrightarrow[2.Pd(PPh_3)_4]{1.\ TsCl} Me_3Si-{\equiv}-\diagdown\ .$$

The base-catalysed cleavage of acetylenic sulphones, sulphoxides, selenoxides, and other reagents with elimination of H–X, where X = PhSO,[97] PhSeO,[98] t-$BuSO_2$,[99] and $(EtO)_2P(O)O$ [100] respectively, can also be included in this group of methods. It is of interest that

the elimination of 2,2-dimethylethanesulphonic acid on treatment with potassium t-butoxide in the example below is not accompanied by the cleavage of the silicon–carbon bond:[99]



3. Synthesis from 1-trialkylsilylalka-1,3-diynes

The 1,3-diyne silicon-containing compounds, which are available under laboratory conditions, are convenient "starters" for the synthesis of two types of the corresponding silylalkenynes containing a silicon atom attached to the triple or double bond: $R_3SiC{\equiv}C{-}CX{=}CYR'$ and $R_3SiCX{=}CY{-}C{\equiv}CR'$, which can be obtained by adding the reagent XY to one of the triple bonds of the diyne.

(a) Reduction of 1,3-diynes

The catalytic reduction of silicon-containing diacetylenic hydrocarbons was first achieved in 1964.[101] It was established that the reaction proceeds with a high chemoselectivity in relation to the triple bond remote from the silicon atom:

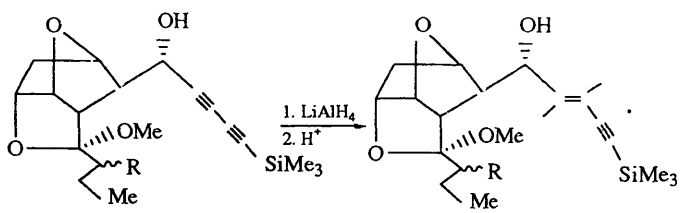
$$R_3SiC{\equiv}C-C{\equiv}C-R' + H_2 \xrightarrow{Pd/CaCO_3} R_3SiC{\equiv}C-CH{=}CHR'.$$

The stereochemistry of the process was not investigated.

The protecting effect of the trialkyl(aryl)silyl groups was used later by other investigators for the selective catalytic hydrogenation of triple bonds "unprotected" by silicon-containing groups in the synthesis of 1,3-enyne silicon-containing hydrocarbons. These studies served as the experimental basis of the method involving the "silyl protection" of the triple α,β-bond in catalytic reduction reactions, the method being widely used in organic synthesis.[102] It has been established that, regardless of the nature of the catalyst (palladium on calcium carbonate or sulphate,[32,101,103] Lindlar's platinum[104,105]) the reaction is chemoselective and stereospecific: the 1-trialkylsilylalk-3-en-1-ynes formed have the (*Z*)-configuration.

The reduction of silylalkadiynes with metallic zinc in ethanol proceeds similarly, i.e. it involves the bond remote from the heteroatom, with the preferential formation of (*Z*)-enynes.[106] The reaction takes place when zinc is activated with lithium dibromocuprate and 1,2-dibromoethane or with 1,2-dibromoethane alone.

(*Z*)-Alkenynes have been obtained exclusively also in the reduction of bis(trimethylsilyl)buta-1,3-diyne with lithium tetrahydroaluminate in THF.[107] On the other hand, the reduction of diacetylenic alcohols with lithium tetrahydroaluminate takes place stereo-specifically in the *trans*-position:[108–110]

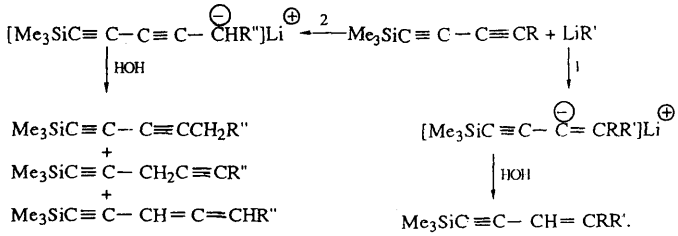


Enyne silicon-containing hydrocarbons with the exclusive (*E*)-configuration are formed in high yields (more than 90%) when lithium trialkylaluminates are used as the reducing agents:[111,112]

$$Me_3SiC{\equiv}C-C{\equiv}CR + Li[AlH(iso\text{-}Bu)_2Bu] \xrightarrow{E} Me_3SiC{\equiv}C-\underset{\displaystyle E}{\underset{|}{C}}{=}C-R.$$
$$\qquad\qquad\qquad

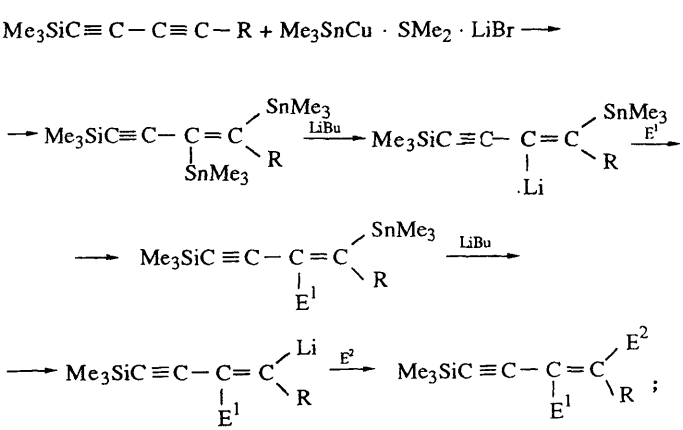
(c) Interaction with organometallic compounds

Organolithium compounds add to the triple bond of 1-trialkylsilylalka-1,3-diynes remote from the silicon atom. After the demetallation of the lithium-containing adducts with water, the corresponding vinylacetylenic silyl-substituted hydrocarbons were obtained in satisfactory yields:[119,120]



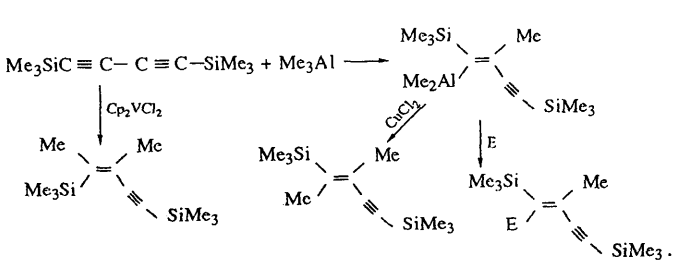
The addition reaction is accompanied by the isomerisation of the initial diacetylenes (pathway 2). Appreciable amounts of the isomerisation products were obtained in reactions of 1-trialkylsilylpenta-1,3-diyne with lithium alkyls.

The silicon-containing alkenynes $Me_3SiC{\equiv}CE^1C{=}CE^2R$ are obtained from the corresponding diacetylenic silicon-containing hydrocarbons by the successive treatment of the diyne with trimetylstannyl cuprate and the corresponding electrophile E in accordance with the scheme[121]



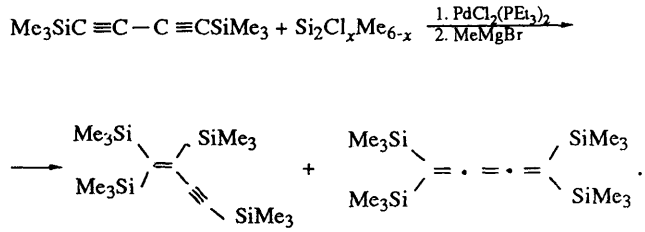
E^1 and E^2 = AlkBr.

The addition of trialkylaluminium and subsequent treatment of the alumnium-containing adducts with an electrophile E can also be recommended as a preparative method of synthesis of silicon-containing alkenynes:[122,123]



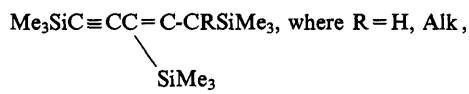
The reaction is regio- and stereo-specific and takes place only in the presence of catalysts. In the series Cp_2ZrCl_2, Cp_2TiCl_2, and Cp_2VCl_2, the best yields were obtained with the zirconium catalyst.

An interesting method of synthesis of persilylated butenynes is based on the catalytic silylation of bis(trimethylsilyl)buta-1,3-diyne with alkylchlorodisilanes[124]



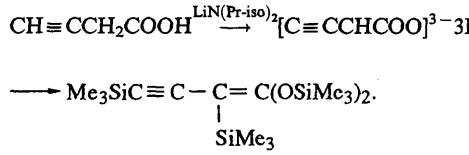
The yield and the rate of the isomeric 1,2- and 1,4-adducts are determined by the structure of the disilane as well as the temperature and duration of the experiment.

Mono- and poly-silylated alkadienynes of the type



where R = H or alkyl, are formed in the reaction of the anions or polyanions obtained from alka-1,2-diynes with chlorotrimethylsilane.[125–128]

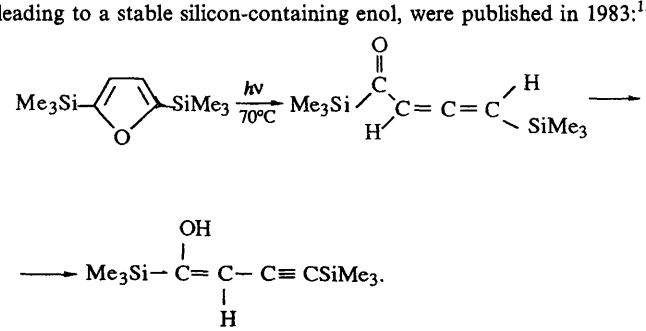
Polysilylated alkenynes have also been obtained by treating the trianion of but-3-ynoic acid with chlorotrimethylsilane:[129]



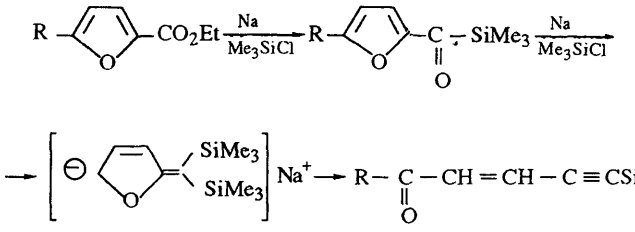
The reaction involving the addition[130–134] or cycloaddition (the Diels–Alder reaction)[135] of the corresponding reagents (bromine,[133,134] thiols,[130,131] hydrazine,[132] hydroxylamine[132]) to one of the triple bond of 1-trialkylsilylalka-1,3-diyne may be recommended as a method of synthesis of halogen-, sulphur-, and nitrogen-containing derivatives of silylalkenynes.

(4) Isomerisation reactions

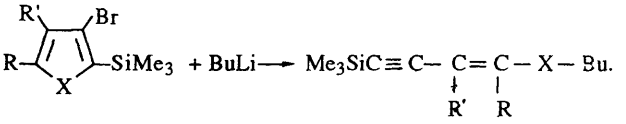
Oxygen containing functional derivatives of 1-trialkylsilylalk-3-en-1-ynes can be obtained as a result of the specific cleavage reaction of silylated furans and their sulphur and selenium analogues. Thus the results of an unusual photoinitiated opening of the furan ring, leading to a stable silicon-containing enol, were published in 1983:[136]



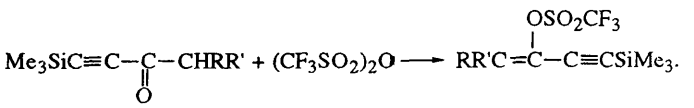
Ethyl furoates[137] and thioketals of the furan series[138] are converted into vinylacetylenic silicon-containing ketones on treatment with metallic sodium:



Silylated 3-bromothiophenes and 3-bromoselenophenes give rise to silicon containing alkenyne thio- and seleno-ethers with a (*Z*)-configuration in satisfactory yields on reaction with butyl-lithium:[139]



Silicon-containing triflates with alkenyne fragments are readily obtained from acetylenic ketones and the anhydride of trifluoromethanesulphonic [triflic] acid:[140–143]



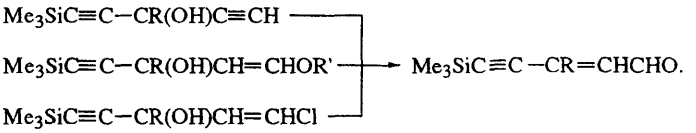
The kinetics of this reaction were investigated.[141]

Carbofunctional derivatives of 1-trialkylsilylalk-3-en-1-ynes (alcohols, aldehydes, ethers, esters, amides, etc.) are formed in satisfactory yields as a result of the acid-catalysed isomerisation of the corresponding non-conjugated vinylethynyl and diethynyl alcohols (the Claisen rearrangement). The nature of the functional group and the configuration of the substances obtained under these conditions are determined by the nature of the donor of the anion introduced into the reaction mass:[144–148]

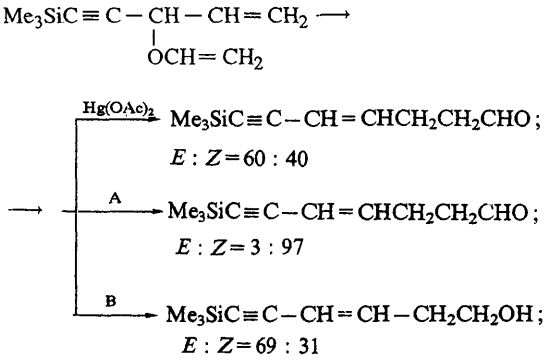
The availability of the initial vinylethynyl alcohols and the high preparative yields of the target products make this reaction one of the promising and stereocontrolled processes in the synthesis of derivatives of 1,3-enyne silicon-containing hydrocarbons.

The isomerisation of secondary alcohols proceeds stereospecifically and the reactions of tertiary alcohols afford mixtures of the (*E*) and (*Z*)-isomers, the isomers in which the substituent R is in the *trans*-position relative to the functional group predominating under these conditions.[144]

The isomerisation of diacetylenic alcohols[145] and alcohols containing substituted vinyl groups[146,149] leads to the formation of the corresponding aldehydes:

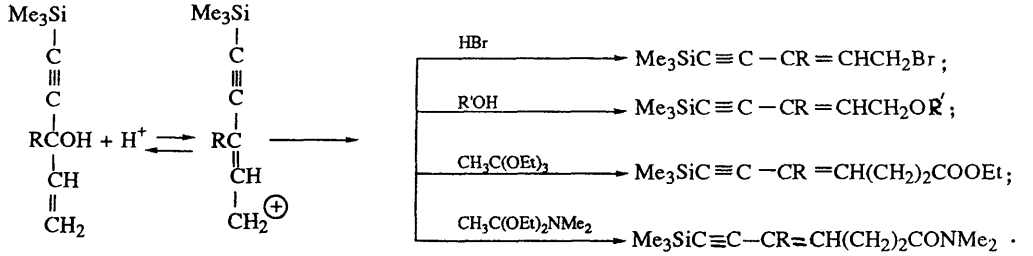


The rearrangement of the vinyl ethers (the Cope–Claisen rearrangement) also leads to the corresponding vinylacetylenic alcohols or ethers. The nature of the functional group and the configuration of the substances obtained are determined by the nature of the catalyst:[150,151]

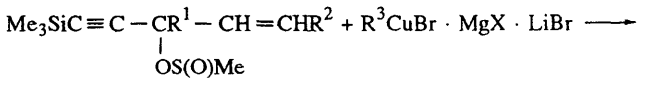


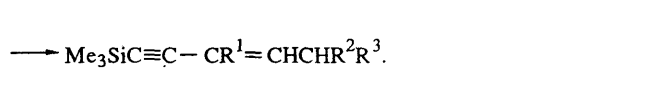
A = [2,6-(t-Bu)$_2$–4-BrC$_6$H$_2$]$_2$MeAl; B = [2,4-Ph$_2$-C$_6$H$_3$]$_2$MeAl.

Similar reactions occur also when the sulphinate of a silicon-containing vinylethynylcarbinol is treated with alkyl or aryl cuprates [the ratio of the (*E*) and (*Z*)-isomers is (4–10) : (96–89)]:[152]

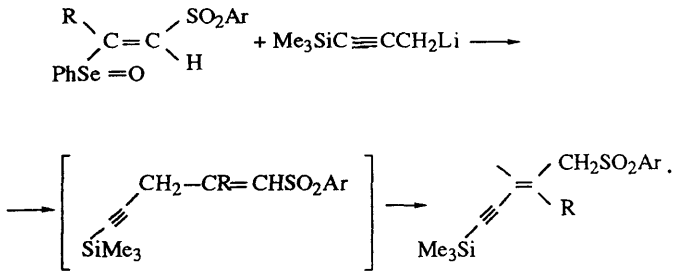


R' = H, Me, Et, Ac.

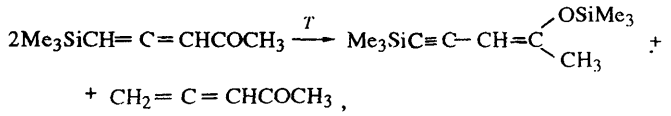




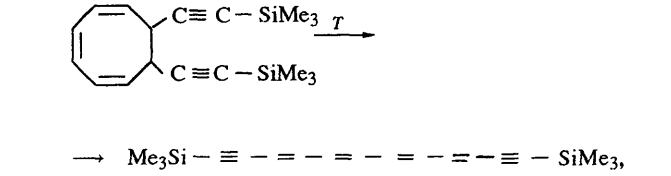
A protropic isomerisation apparently also takes place in the synthesis of vinylacetylenic sulphones by the condensation of a selenoxide with trimethylsilylpropargyllithium:[153]



The method of synthesis of silicon-containing enyne enols by the thermal disproportionation of silicon-containing allenyl ketones,[154] i.e.



and of bis(trimethylsilyl)cyclooctatetraene,[155] i.e.



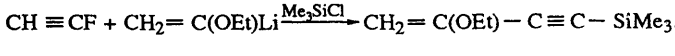
can be formally assigned to the same group of reactions (isomerisation).

5. Construction of enyne structures from block-synthons

In the construction of enyne structures from block-synthons, use is made of methods based on the transition metal complex-catalysed reactions of organometallic compounds, condensations of the type of the Knoevenagel reaction, and the Wittig reaction and its phosphonate (the Horner–Emmons reaction) and silyl (the Petersen reaction) modifications. An obligatory feature of these methods is the formation of new single or multiple carbon–carbon bonds.

(a) Organometallic synthesis

The possibilities in the synthesis of silicon-containing alkenynes from organolithium compounds have been demonstrated solely in relation to the condensation of fluoroacetylene with α-ethoxyvinyllithium:[65]

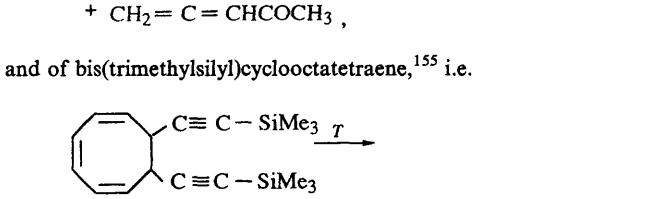


Trimethylsilylethynylmagnesium bromide condenses with *trans*-1,2-dichloroethylene only in the presence of the nickel catalyst $NiCl_2.Ph_2P(CH_2)_3PPh_2$:[156]

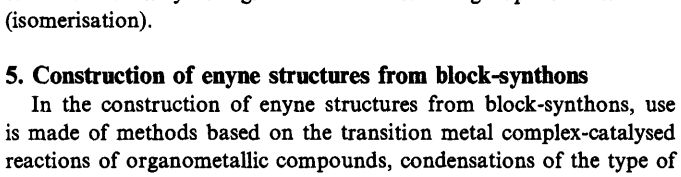
The best results were obtained in the reaction of haloalkenes with acetylenic organozinc compounds. The reactions take place only when palladium complexes are used as the catalyst.[157–162] It has been noted that *cis*- and *trans*-haloalkenes give rise to only alkenynes in these reactions:

However, it has been reported[163] that the interaction of trimethylsilylethynylzinc bromide with *cis*- and *trans*-1-iodoalkenes afforded individual *cis*- and *trans*-1-trimethylsilyldec-3-en-1-ynes respectively in 74 and 75% yields.

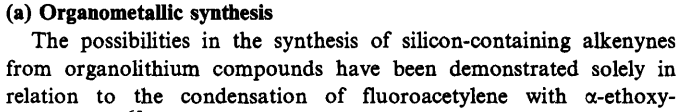
Alkenyne structures were formed somewhat unexpectedly in the reaction of trimethylsilylethynylzinc chloride with tertiary chlorides of the propargyl type.[164,165] The reaction is described by the following scheme:



The reaction of zinc acetylides with acetylenic epoxides proceeds similarly under the condition of catalysis by palladium:[166,167]



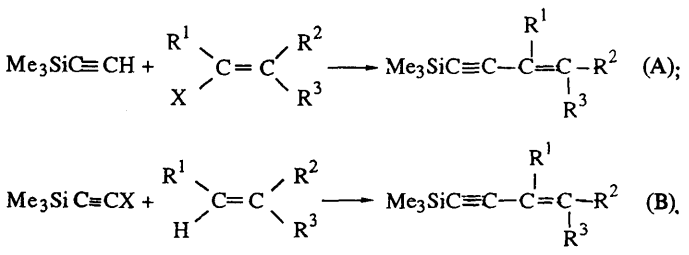
Alkenyne silicon-containing structures can be obtained by condensing silicon-containing halides (bromides, iodides) with alkenyl cuprate:[166,168–171]



where X = Br or I and R^2 and R^1 are alkyl and alkenyl groups, including groups with functional substitutents.

The cross-coupling of organic halides with an unsaturated hydrocarbon, catalysed by compounds of platinum group metals, occupies a special place in the synthesis of organosilicon alkenynes.

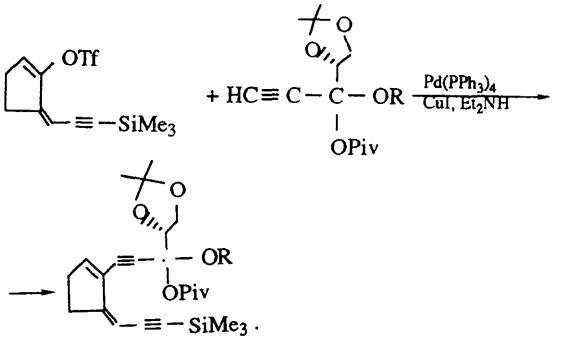
It can be achieved in two ways:



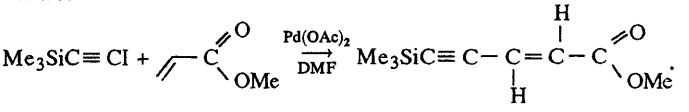
The availability of the starting compounds and the higher stereoselectivity of the processes make it possible to use method (A) on a wide scale in fine organic synthesis, including the synthesis of complex natural products and their synthetic analogues.[36,149,172–190]

$Pd(PPh_3)_4$ [149,175,176,178–180,182,186,187,189–191] or $PdCl_2(PPh_3)_2$ [36,174,175,177,183–185,188] are used as catalysts. It has been noted that *trans*-1,2-dichloro(dibromo)alkenes are much less reactive in this reaction than their *cis*-isomers.[175]

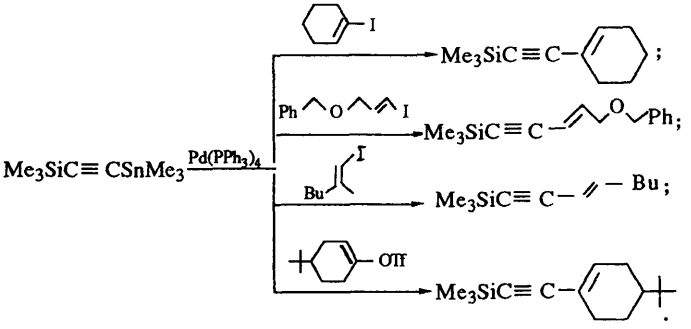
Cases are known where the corresponding triflate is made to enter into the palladium-catalysed cross-coupling reaction instead of the vinyl halide:[192–194]



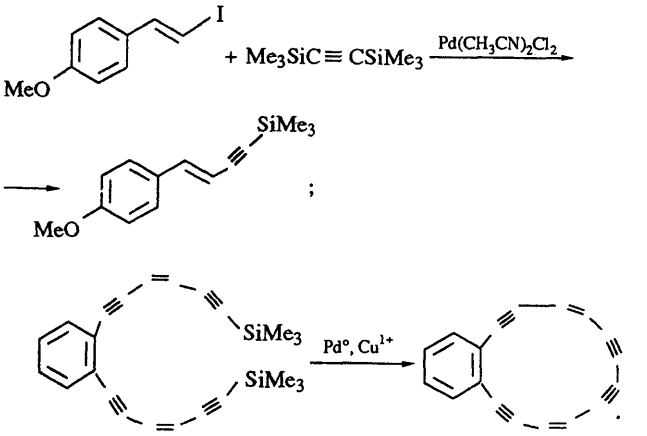
There have been only isolated instances where scheme (B) was realised:[195]



The method of synthesis of silicon-containing alkenynes by the stereospecific alkynylation of alkenyl halides[196,197] or triflates[198–200] with trialkylstannylacetylenes catalysed by a palladium complex was developed significantly during the last decade.



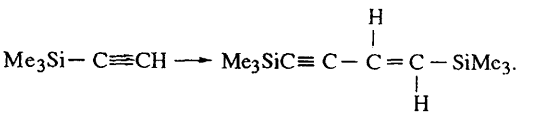
Silicon-containing acetylenes can also serve as alkynylating agents:[184,201]



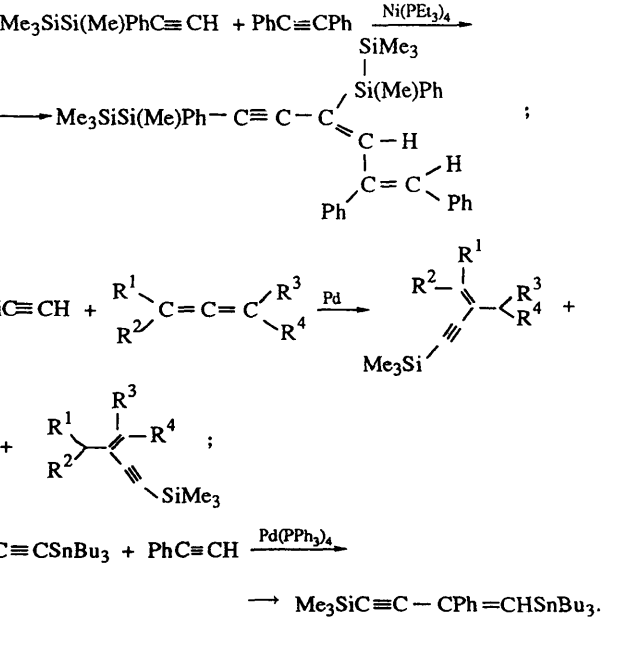
The silicon–carbon bonds are dissociated in these reactions.

(b) Dimerisation of silylacetylenes catalysed by transition metal complexes

Under the influence of the nickel complexes $Ni(acac)_2PPh_3$ [202,203] and $Ni(PEt_3)_4$,[204] the palladium complex $Pd(PPh_3)_4$,[205] the rhodium complex $RhCl(PPh_3)_3$,[206] or the titanium complex $(\eta^5\text{-}C_5H_5)TiCl_2.RMgX$ [207] as catalysts, silylacetylenes are readily dimerised with formation of the corresponding bissilylated alkenynes. The satisfactory yields (up to 90%) and controlled stereochemistry make it possible to recommend these reactions as convenient preparative methods of synthesis of alkenynes:



Under the conditions of metal complex catalysis, it is possible to carry out the codimerisation reactions of trialkylsilylacetylenes with other acetylenes or allenes:[204,208,209]



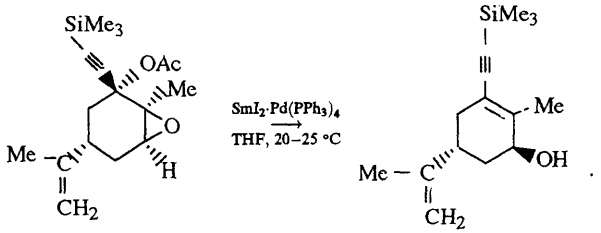
An unusual reaction involving alkynylation with silylacetylenes was described in 1978 by Japanese investigators,[210] who established that alkynylamines add to electron-deficient acetylenes with formation of silylated alkenynes containing a silicon atom attached to the double bond:

$$\begin{matrix}R^1\\R^2\end{matrix}\!\!>\!N-C\equiv C-SiR_3 + YC\equiv C-COOMe \longrightarrow$$

$$\longrightarrow \begin{matrix}R^1\\R^2\end{matrix}\!\!>\!N-C\equiv C-\underset{\displaystyle SiR_3}{\overset{\displaystyle Y}{\underset{|}{\overset{|}{C}}}}=C-COOMe\ ;$$

Y = H or COOMe.

(3*S*, 5*R*)-3-Hydroxy-5-isopropenyl-2-methyl-1-(2-trimethylsilylethynyl)-1-cyclohexene — a key compound in the synthesis of $\Delta^{9(11)}$-unsaturated vitamin D — was obtained from the corresponding epoxide using a palladium catalyst:[211]



(c) The Wittig reaction and its modifications

Silicon-containing alkenynes can be synthesised in two ways using phosphoranes: (1) by the reaction of a silicon-containing acetylenic phosphorane with a carbonyl compound:

$$Me_3SiC\equiv C-CH=PPh_3 + O=C\begin{matrix}H(R^2)\\R^1\end{matrix} \longrightarrow$$

$$\longrightarrow Me_3Si-\equiv-\underset{\displaystyle H}{\overset{\displaystyle H(R^2)}{\underset{|}{\overset{|}{C}}}}-R^1\ ; \qquad (1)$$

(2) by the reaction of a silicon-containing acetylenic aldehyde with the corresponding phosphorane:

$$Me_3SiC\equiv C-CH=O + Ph_3P=CHR^1 \longrightarrow$$

$$\longrightarrow Me_3Si-\equiv-\underset{|}{\overset{|}{C}}-R^1 \qquad (2)$$

The silicon-containing acetylenic phosphorane $Me_3SiC\equiv C-CH=PPh_3$ was first obtained by Belyaev, Stadnichuk, and Petrov in 1972.[212,213] By condensing it with cyclohexanone or benzaldehyde, it was shown that it can be used in the synthesis of silicon-containing alkenynes.[212]

Somewhat later Corey et al.[64] and then Eiter et al.[214] again described the silicon-containing propargyl-substituted phosphorane and confirmed the possibility of using it in the synthesis of the simplest vinylacetylenic hydrocarbons[64] and more complex compounds.[215] The silicon-containing propargyl-substituted phosphorane $Me_3SiC\equiv C-CH=PPh_3$ has come to be widely used in studies by other investigators.[216–223] In all these investigations, complex polyfunctional organic compounds containing the aldehyde group were employed as the carbonyl component. The condensation was stereospecific or highly stereoselective with formation of the corresponding (*E*)-alkenynes containing the trimethylsilyl protecting group at the triple bond.

The silicon-containing alkenyne-substituted phosphorane $Me_3SiC\equiv C-CH=CH-CH=PPh_3$ is frequently used in the synthesis of more unsaturated compounds, for example lipoxin[49,50] and leukotriene antagonists.[224]

The synthesis of 1-trialkylsilylalk-3-en-1-ynes and their derivatives using the second variant of the Wittig reaction was first achieved by Belyaev, Stadnichuk, and co-workers:[213,225]

$$Me_3SiC\equiv C-CH=O + Ph_3P=CHX \longrightarrow Me_3SiC\equiv C-CH=CHX;$$

X = $COOCH_3$, $COCH_3$, CN.

The stereoselectivity of the reaction depends on the structure of the phosphorane and the nature of the solvent.[225,226] The replacement of ether or THF by hexane not only increases the yield of the target products but also promotes the formation of the (*E*)-isomer in the mixture.

The phosphonate modification of the Wittig reaction (the Horner–Emmons reaction) is as a rule characterised by a greater *trans*-stereoselectivity in the synthesis of alkenes. The available data on the use of the phosphonate methods in the synthesis of silicon-containing alkenynes[49,227] agree on the whole with this claim:

$$Me_3SiC\equiv C-CH=O + (EtO)_2\,P\,(O)\,CH_2X \xrightarrow{Na}$$

$$\longrightarrow Me_3SiC\equiv C-CH=CHX\ ;$$

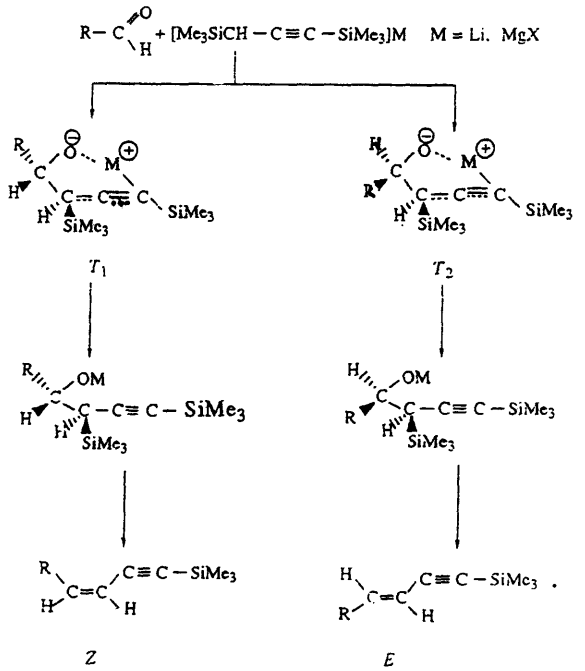
X = COOR, CN.

It is interesting that the synthesis of vinylacetylenic nitriles by the Horner–Emmons reaction produces better results (yield, stereoselectivity) than the Wittig reaction, while in the synthesis of carbonyl compounds the Wittig reaction is preferable.[213,225–227]

The conversion into silylalkenes or alkenes by the Peterson method is frequently regarded as one of the variants of the Wittig method. This procedure presupposes attack by the silicon-containing anions on the carbonyl carbon atom of the substrate. The reaction is distinguished by a high stereoselectivity. An advantage of the method (compared with the Wittig and Horner–Emmons reactions) is the fact that the hexamethyldisiloxane produced as a result of the reaction is volatile (T_b = 100 °C) and can be readily removed.

The Peterson reaction was first applied in the synthesis of silylalkenyls by a group of Japanese workers[228] in 1981 in relation to the interaction of certain aldehydes and ketones with the allene

carbanion obtained by treating 1,3-bis(trimethylsilyl)propyne with organolithium or organomagnesium compounds:



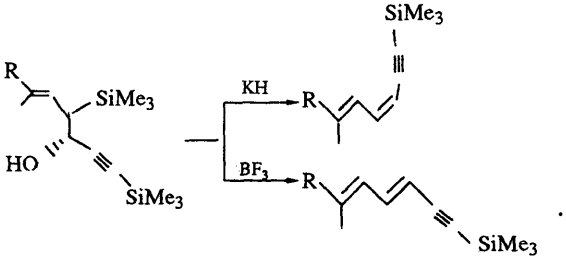
In conformity with the proposed scheme of the possible interaction pathways, the reactions of the bis(trimethylsilyl)propargyl anion with aldehydes give rise to mixtures of the (*E*)- and (*Z*)-isomers, with the latter predominating.[228–230] Judging from the yields (80–90%) and the ratio of the (*E*)- and (*Z*)-isomers, this reaction should be regarded as a convenient preparative method of synthesis of (*Z*)-alkenynes.

It follows from the available data[228–230] that the fraction of the (*Z*)-isomer increases with increase in the bulk of the SiR_3 group and also when lithium is replaced by magnesium. The replacement of magnesium by titanium[229,230] hardly affects the stereochemical result of the reaction. The authors are inclined to explain this by the steric destabilisation of the transition state T_2 compared with T_1 with increase in the bulk of the SiR_3 group.

The low level of stereoselectivity in the reactions with benzaldehyde[228,230] canot be explained. As regards the role of the counterion, the principal idea used in its explanation reduces to the fact that the ability of the cation to form the transition state T_1, possibly with the allene structure, increases in the series Li < Mg < T_1. In this transition state, the steric repulsion increases to a maximum (T_1 is more favourable on energy grounds than T_2). Therefore the allene carbanion attacks the carbonyl carbon atom preferentially, which leads to the formation of the energetically more favourable transition state T_1.[229,230]

In 1982 Corey and Ruecker[231] repeated the experiments of the Japanese workers and also showed that the reaction of lithiated 1,3-bis(trimethylsilyl)propyne with cyclohexanecarbaldehyde and trimethylacetaldehyde in THF results in the formation of the corresponding alkenynes in a satisfactory yield and with the ratio *E*:*Z* = 20:1 (as in the study of Yamakado et al.[228]). However, when the reaction is carried out in a THF–hexamethylphosphoramide (HMPA) mixture, the corresponding alkenynes are formed in proportion of 1:2.[231] The preferential formation of the (*E*)-isomer (*E*:*Z* = 7:1) when the reaction is carried out in a THF–HMPA mixture has also been observed by other workers.[232] The lithium derivative of 1-triisopropylsilyl-3-trimethylsilyl-1-propyne does not react with aldehydes under these conditions.[231] It has been suggested that the lithium derivative of bis(triisopropylsilyl)propyne exists in THF in the form of an allene, to which corresponds the energetically most favourable cyclic transition state T_1. This promotes the formation of the (*Z*)-isomer. In a more polar solvent (a mixture of THF and HMPA), an acyclic transition state is formed, promoting the formation of the (*E*)-isomers.[231]

The stereoselectivity of the elimination of trimethylsilanols also depends on the nature of the catalyst (KH or BF_3):[233]



Judging from the available data, the Peterson rection constitutes a convenient preparative method of synthesis of silicon-containing alkenynes with the (*Z*)-configuration.[234–237]

Trialkylsilylpropynals react with C–H acids (the Knoevenagel reaction) to form the corresponding derivatives of silicon-containing alkenyne hydrocarbons:[238]

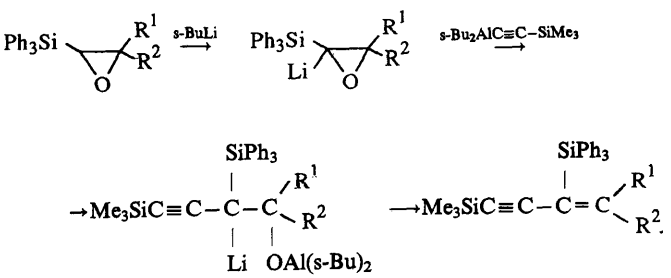
$$Me_3SiC{\equiv}C{-}CHO + CH_2XY \longrightarrow Me_3SiC{\equiv}C{-}CH{=}CXY;$$

X = Y = CN, CO_2Et; X = Ac, Y = CO_2Et; X = NO_2, Y = H.

5-Trimethylsilylbut-2-en-4-ynoic acid was obtained on hydrolysis of the diester and heating the resulting acids:

$$Me_3SiC{\equiv}C{-}CH{=}C(CO_2Et)_2 \xrightarrow[H^+]{HOH} Me_3SiC{\equiv}C{-}CH{=}C(CO_2H)_2 \xrightarrow{T} Me_3SiC{\equiv}C{-}CH{=}CHCOOH.$$

The method involving the elimination of lithium aluminate in the concluding stage, described recently,[239] can be also included formally in this group of methods:



III. Chemical properties of silicon-containing alk-3-en-1-ynes

Among the chemical reactions of silicon-containing alkenynes, three large groups can be distinguished.

1. Reactions occurring with participation of multiple bonds. They lead as a rule to the synthesis of new types of functional derivatives of alkynes or alka-1,3-dienes and alka-1,2-dienes.

2. Reactions in which the trialkylsilyl group is replaced by a proton (removal of the silyl group protecting the triple bond) or another atom or radical (halogen, acyl, etc.)—desilylation reactions.

3. Reactions with participation of the functional groups of derivatives of silicon-containing alkenynes.

1. Addition reactions

The addition of reagents of different nature of 1-trialkylsilylalk-3-en-1-ynes and their carbofunctional derivatives constitutes the most thoroughly investigated type of reactions of compounds of this class. However, their rigorous classification in terms of reaction mechanisms is impossible, since in most cases such mechanisms have not been investigated. The known types of reactions have therefore been classified in this review in terms of the type of reagent. Despite the fact that the same reagent adds via different mechanisms depending on the experimental conditions and the proposed classification principle cannot therefore be maintained throughout, this approach appears to be most acceptable at the present stage.

(a) Interaction with electrophiles

The study of the addition of electrophiles to compounds with multiple carbon–carbon bonds traditionally with the analysis of data on their reactions with hydrogen halides. Unfortunately, it is merely stated in the literature that 1-trimethylsilylbut-3-en-1-yne combines with two moles of hydrogen chloride. The structure of the reaction products was not demonstrated. The reaction could not be stopped at the stage involving the formation of monoadducts.[23]

Bromination of 1-trialkylsilylalk-3-en-1-ynes and their derivatives. Whilst describing the simplest reactions of vinylacetylenic silicon-containing hydrocarbons, Petrov, Sadykh-zade, and Egorov[22,23] noted that the addition of the first mole of bromine to 1-trimethylsilylbut-3-en-1-ynes takes place exclusively at the triple bond. However, it was later established that the bromination of silicon-containing alkenynes takes place non-chemoselectively, while the relative amounts of the dibromo-derivative formed are determined by the structure of the initial silicon-containing hydrocarbons and the conditions in the isolation and purification of the dibromo-derivatives. In the reactions of silylalkenynes in which the alkenyne fragment has the normal structure, the main products are 1,4-dibromo-derivatives, while bromination of compounds with a branched structure affords acetylenic dibromo-derivatives. Dibromo-derivatives of 1,3-dienes are either not formed at all or are present only in trace amounts.[26]

On heating, the 1,4-dibromo-derivatives readily isomerise to the bromo-derivatives of 1,3-dienes. Alkenyldimethylsilylbut-3-en-1-ynes are also brominated non-selectively,[31] the main product formed in the case of 1-dimethylvinylsilylbut-3-en-1-yne being dibromoallene. 1-Allyldimethylsilylbut-3-en-1-yne combines with the first molecule of bromine preferentially at the double bond which is not conjugated with the triple bond.

Bromine adds essentially only to the double bond also in the bromination of 1,6-bis(trimethylsilyl)oct-4-ene-1,7-diyne.[33] These data[25,26,31,33] agree well with the rule according to which bromine adds to double bonds at a rate approximately an order of magnitude higher than that of its addtion to the triple bond.[240]

The study of the dependence of the rate of bromination on the structure of the silicon-containing alkenyne[241] and the polarity of the solvent[242] and also data on the way in which 1-trimethylsilylbut-3-en-1-yne reacts with bromine in a saturated solution of lithium chloride in acetic acid[87] enabled the authors to claim that bromination, whose rate is described by a second order equation, is a two-step electrophilic process. The bromine molecule and (or) the complex Br_3^- functions as the electrophile.[242]

The functional derivatives of vinylacetylenic silicon-containing hydrocarbons $Me_3SiC{\equiv}C-CH=CH-X$, where X = NMe_2, $COCH_3$, $COOCH_3$,CN, or NO_2,[59,95,243] combines with bromine exclusively[59,95] or preferentially[243] at the triple bond regardless of the donor–acceptor properties of the substituents X. 1,4-Adducts were never detected.

The bromination of nitroalkenynes takes place only in highly polar solvents in the presence of lithium bromide and most probably via a nucleophilic mechanism.[241,244] One cannot rule out the possibility that the isotypical mode of addition of bromine to alkenynes containing the electron-donating dimethylamino-group and the electron-accepting carbonyl, carboxy-, cyano-, and nitro-groups is determined by the fact that the corresponding complexes of the reagents with bromine of the type

$$[R_3SiC{\equiv}C{-}CH{=}CHNMe_2{\cdot}Br]^+Br^-$$

enter into the bromine reaction.[245]

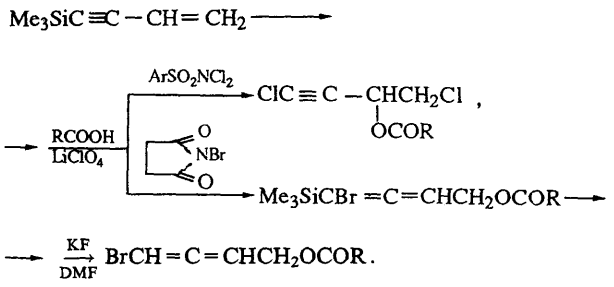
Hydroxy-, alkoxy-, and acyloxy-halogenation. The coupled hypohalogenation of silylalkenynes, where the nucleophilic solvent (water, alcohols, carboxylic acids) is involved in the concluding stage of the reaction, has not been studied systematically. It has only been stated that, when 1-trimethylsilylbut-3-en-1-yne was treated with the dichloroamide of *p*-chlorobenzenesulphonic acid or *N*-bromosuccinimide in methanol, a mixture of positional isomers of the corresponding dihalo-derivatives containing chloro- or bromo-ethers was obtained in low yields (5–10%).[246] 3-Methyl-1-trimethylsilylbut-1-yne reacts with the dichloroamide of *p*-chlorobenzenesulphonic acid and 85% formic acid to form the corresponding chlorohydrin in a satisfactory yield:[247]

$$Me_3SiC{\equiv}CC(CH_3){=}CH_2 + ArSO_2NCl_2 \xrightarrow[LiClO_4]{H_2O\ +\ HCOOH} Me_3SiC{\equiv}CC(CH_3)CH_2Cl \quad (OH)$$

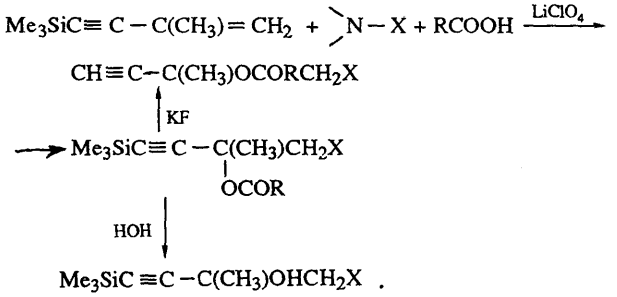
The reaction with bromosuccinimide affords under these conditions bromohydrin and the corresponding formate.[247]

The interaction of silicon-containing alkenynes with haloamides in carboxylic acids (formic, acetic, and propionic acids) has been studied in greater detail.[247] The reaction proceeds only in the presence of an equimolar amount of lithium perchlorate. The mode of reaction is determined by the structure of the alkenyne silicon-containing hydrocarbon and the nature of the halogen. The

interaction of 1-trimethylsilylbut-3-en-1-yne with a dichloroamide in formic and acetic acid takes place with desilylation:

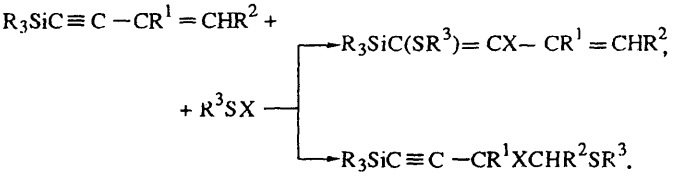


1-Trimethylsilylbut-3-en-1-yne reacts with *N*-bromosuccinimide in both acetic and formic acid to form the products of coupled 1,4-addition, uncharacteristic of the given type of reactions, with the electrophilic bromine being attached to the α-carbon atom of the triple bond. 3-Methyl-1-trimethylsilylbut-3-en-1-yne reacts with chloro- and bromo-amides to form only the products of acyloxyhalogenation at the double bond:



There is no acceptable explanation of the inversion of the electrophilic attack (at the triple bond in 1-trimethylsilylbut-3-en-1-yne in reactions with chloro- and bromo-amides and at the double bond in the reactions of an isopropenylacetylenic compound).

Interaction with the acid halides of sulphenic acids and their selenium containing analogues. The halides of sulphenic acids RSX are known to add to multiple carbon–carbon bonds via an electrophilic mechanism. These reagents belong to the category of weak electrophiles and their electrophilicity can be varied by altering the nature of the organic group. In conformity with the rule that, in reactions with electrophiles, the double bond is more reactive approximately by an order of magnitude than the triple bond, vinylacetylene[248] combines with methanesulphenyl chloride via the double (90%) and triple (10%) bonds, while its homologue 5,5-dimethylhex-1-en-3-yne combines with the above reagent exclusively via the double bond.[249,250] In contrast to hydrocarbons, their silicon-containing analogues $R_3SiC{\equiv}CCR^1{=}CHR^2$ combine with the halides of alkane- and arene-sulphenic acids exclusively or preferentially via the triple bond:[249–251]



The mode of reaction is independent of the nature of the solvent (CH_2Cl_2, $CHCl_3$, CH_3COOH, and the $CH_3COOH-LiClO_4$ mixture) and is determined by the structure of the reactants. The fraction of the minor acetylenic adduct increases with increase in the bulk of R and R^3, on passing from acid chlorides to bromides, and on passing from compounds with R^1 = H to compounds with R^1 = CH_3, and also as the electron-accepting properties of R^3 are enhanced. It has been established in relation to derivatives of vinylacetylenic silicon-containing hydrocarbons with nitro-,[252] acetyl, ethoxycarbonyl, and cyano-groups[253] in the alkenyne fragments that the introduction of electron-accepting groups increases sharply the chemoselectivity of the addition of the halides of sulphenic acids to the triple bond.

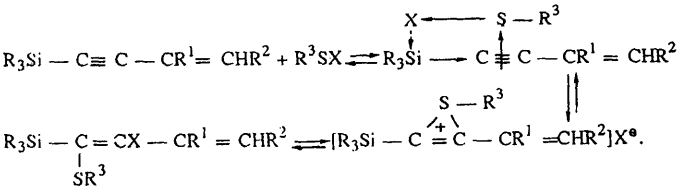
The study of the kinetics of the addition of methanesulphenyl chloride to derivatives of vinylacetylenic silicon-containing hydrocarbons[254] shows that the rate of addition to hydrocarbon and silylhydrocarbon derivatives with similar structures decreases as the electron-accepting properties of the group R^2 weaken in the sequence COR > COOR > CN, which agrees with an electrophilic mechanism of the addition reaction. This conclusion is supported also by the formation of a certain amount of solvoadducts when arenesulphenyl chlorides add to acetic acid in the presence of lithium perchlorate.[249]

However, silicon-containing alkenynes are more reactive in this reaction than the hydrocarbon derivatives of similar structure.[254] It is appropriate to recall here that hydrocarbons are more reactive approximately by an order of magnitude in electrophilic bromination reactions than their silicon-containing analogues: owing to the $d_\pi-p_\pi$ interaction, organosilicon substituents have weaker electron-donating properties than the hydrocarbon groups of similar structure.[255]

In the presence of anhydrous aluminium chloride, methanesulphenyl chloride adds to 1-trimethylsilylbut-3-en-1-yne preferentially at the double bond.[256]

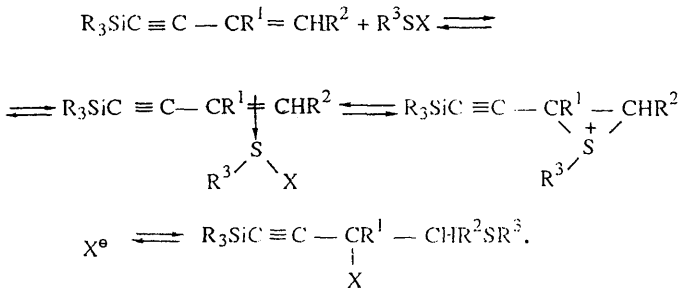
The results of the studies of the reactions of alkane(arene)sulphenyl halides with 1,3-alkenynes, their silicon-containing analogues, and their functional derivatives, examined above, made it possible to conclude that the unusual mode of reaction is due to the characteristic features of the donor–acceptor reagent–substrate interaction, in which the silicon atom with its unoccupied orbitals (a soft acid as defind by Pearson) interacts with the electron-donating end of the polar molecule of the sulphenyl halide:[249–254,256,257]

Scheme 1



This reaction should compete with the donor–acceptor interaction leading to the formation of a π-complex, which is characteristic of electrophilic addition:

Scheme 2



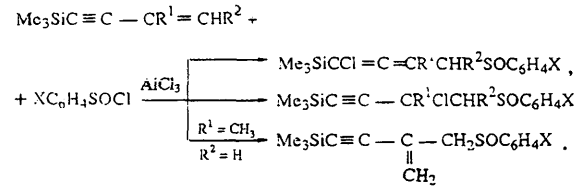
Evidently a greater bulk of R and X (the *d* orbitals are less accessible), a lower effective electronegativity of the alkenyne fragment (a smaller partial positive charge on the heteroatom), and more pronounced electron-accepting properties of R^3 (a low basicity of X) entail a greater difficulty of the realisation of Scheme 1, which presupposes the specific solvation of the substrate by the reagent, and a smaller probability of the addition of the reagent to the triple bond. The formation of molecular associated species with participation of the unoccupied *d* orbitals of silicon should facilitate the addition of the electrophile to the triple bond.[254]

The addition to 1-trialkylsilylalk-3-en-1-ynes and areneselenyl chlorides takes place similarly, i.e. preferentially to the double bond, and apparently for the same reason.[257–259] Data on the addition of sulphenyl and selenyl halides to vinylacetylenic germyl-[250,257] and stannyl-hydrocarbons[260] are satisfactorily consistent with the proposed scheme, which involves the reagent–substrate intermolecular association stage as one determining the chemoselectivity of the addition. The availability of the *d* orbitals of the heteroatoms increases in the series of silicon, germanium, and tin compounds, which is the reason for the increase in the fraction of the products of the addition to the triple bond almost to 100%.[250,257,260] It is of interest that 1-dimethylvinylsilylbut-3-en-1-yne (one of the double bonds and the triple bond are in the α,β-positions relative to the silicon atom) combines with methanesulphenyl chloride via the vinyl group non-conjugated with the triple bond:

$$CH_2{=}CH(CH_3)_2SiC{\equiv}C-CH{=}CH_2 + CH_3SCl \longrightarrow$$
$$\longrightarrow CH_3SCH_2CHCl(CH_3)_2SiC{\equiv}C-CH{=}CH_2.$$

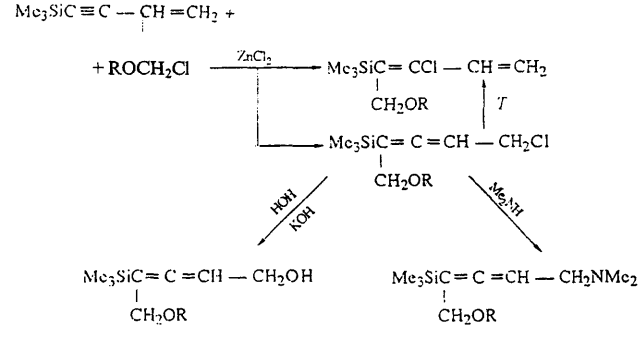
Under identical conditions, the double bond is more reactive in reactions with an electrophile.

Interaction with the halides of sulphinic acids. It has been established in relation to the interaction of the chlorides of arenesulphinic acids with 1-trialkylsilylbut-3-en-1-ynes that, in the absence of catalysts and also in the presence of zinc chloride, the reaction does not occur. In the presence of anhydrous aluminium chloride, the mode of reaction is determined by the structure of the silicon-containing alkenyne: compounds with an unbranched structure of the alkenyne fragment give rise to a mixture of the products of the addition to the double bond and in the 1,4-positions, while alkenynes having the iso-structure give rise to the products of substitutional sulphinylation:[261,262]



The corresponding vinylacetylenic hydrocarbons behave similarly in reactions with sulphinyl chlorides.[262] The chlorides of arenesulphonic acids containing electron-accepting substituents (chloro- and nitro-groups) in the aromatic ring do not react. Chlorine-containing adducts are not dehydrochlorinated when they are treated with triethylamine.[262]

Interaction with α-haloethers. There exists only one communication devoted to this problem. According to the data of Vartanyan and Tosunyan,[263] chloromethyl methyl, chloromethyl ethyl, and chloromethyl isopropyl ethers add to 1-trimethylsilylbut-3-en-1-yne at the triple bond and in the 1,4-positions in the presence of zinc(II) chloride:



It is also striking that in such cases the electrophile attacks the α-carbon atom of the triple bond, which is not characteristic of alkenynes.

(b) Interaction with radical reagents

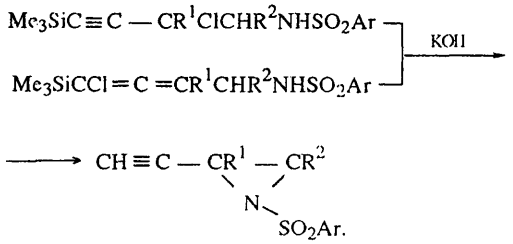
Interaction with triphenylmethyl radicals. This was investigated in relation to their addition to 1-trimethylsilylbut-3-en-1-yne and its closest homologues — 1-trimethylsilylpent-3-en-1-yne and 3-methyl-1-trimethylsilylbut-3-en-1-yne. It was established that the introduction of the methyl group into the alkenyne fragment not only hinders the addition reaction but also alters its mode: 1-trimethylsilylbut-3-en-1-yne combines with triphenylmethyl radicals at the double bond, 3-methyl-1-trimethylsilylbut-3-en-1-yne combines with them in the 1,4-positions, and 1-trimethylsilylpent-3-en-1-yne combines with them at the triple bond.[264]

Interaction with thiols. The tertiary butyl peroxide-initiated addition of alkanethiols to 1,3-alkenyne silicon-containing hydrocarbons $R_3SiC{\equiv}C-CR^1{=}CHR^2$ (R = Me, Et: R^1 and R^2 = H or CH_3) via a free-radical mechanism involves preferentially the double bond (80–90%), the thiyl radical being attached to the α-carbon atom of the double bond and the content of allene adducts in the mixture not exceeding 15%. 1,3-Diene adducts were not

detected in the reactions of silicon-containing alkenynes. The sharp decrease in the reactivity of the alkenynes after the introduction of methyl groups at the α- and β-carbon atom of the double bond is striking.

Interaction with *N,N*-dichloroamides of arenesulphonic acids. It was noted above that treatment of silicon alkenynes with haloamides in hydroxylated solvents leads to the formation of the products of coupled halogenation. In aprotic solvents (chloroform, methylene chloride, etc.), arenesulphonic acid dichloroamides add to the double bond and in the 1,4-positions in trialkylsilylbutenynes,[246,268] which affords the compounds $Me_3SiC{\equiv}C-CR^1ClCHR^2NClSO_2Ar$ and $Me_3SiCCl=C=CR^1CHR^2NClSO_2Ar$.

On treatment with bisulphite, the adducts form the corresponding amides which are readily converted into *N*-arenesulphenylaziridines;



In all cases, the addition of the dihalo-derivative to the multiple bonds of the silicon-containing alkenynes is accompanied by side reactions involving chlorination.[246,268]

Oxidation. The oxidation of 1,3-alkenyne silicon-containing hydrocarbons and their derivatives can involve the multiple bonds or the functional groups.

The oxidation of silylalkenynes with peracids (they are usually obtained by treating the anhydrides of the corresponding carboxylic acids with concentrated hydrogen peroxide or with urea peroxide in the presence of a base) takes place chemoselectively at the double bond with formation of the corresponding acetylenic oxirans $R^1_3SiC{\equiv}C-CR^2-CHR^3$.[27-29,269-273] Examples of the stereo-

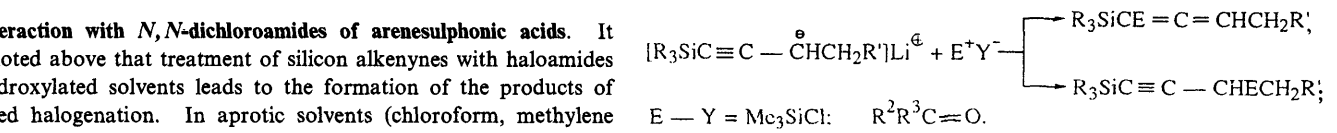


oxidation of *cis*- and *trans*-1-trimethylsilyldec-3-en-1-ynes have been described.[163] The oxidation of silicon-containing alkenynes with participation of functional groups was examined in subsection 2.

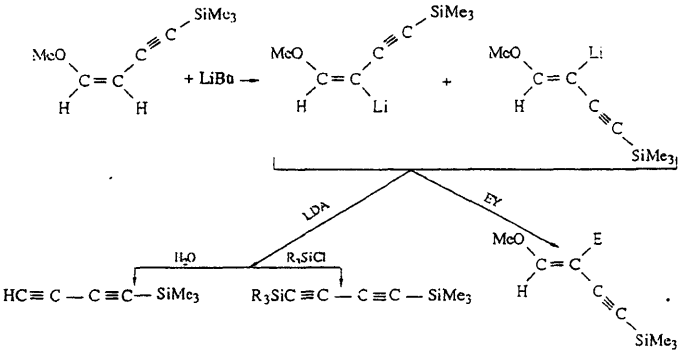
(c) Reactions with nucleophiles

Interaction with organolithium compounds. The interaction of organolithium compounds with trialkylsilylalkenynes was first mentioned by Petrov et al.[23] According to their data, methyllithium and butyllithium add to 1-trialkylsilylbut-3-en-1-ynes exclusively at the double bond with formation, after demetallation with water, of the corresponding acetylenic silylhydrocarbons. It was later shown[274,275] that trialkylsilylalkenynes combine with organolithium compounds non-selectively at the double bond and in the 1,4-positions. The introduction of methyl groups at the α- and β-carbon atoms of the double bond hinders the addition reaction and lowers the yield of the products. It is noteworthy that 1,4-disubstituted alkenynes isomerise under these conditions with migration of the triple bond to the end of the chain.[276]

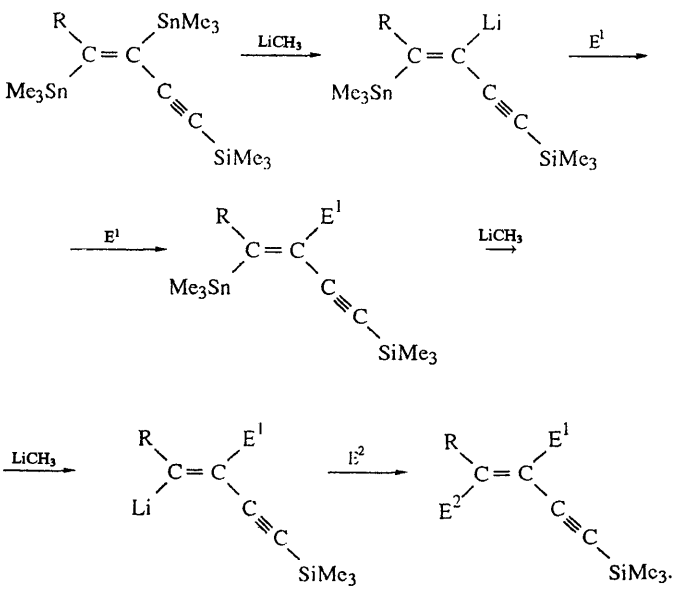
The ratio of the isomeric acetylenic and allene silylhydrocarbons depends little on the structure of the starting materials. A change in the structure of the demetallating agents also hardly affects the ratio of the isomeric reaction products: when lithium-containing adducts are treated with chlorotrimethylsilane, aldehydes, or ketones, the corresponding allene and acetylene derivatives are formed in proportions of approximately 1 : 1:



1-Methoxy-4-trialkylsilylbut-1-en-3-ynes are metallated on treatment with lithium alkyls, a mixture of the *cis*- and *trans*-lithiated silylalkenynes being formed from the *cis*-ether.[53] On interaction with electrophiles, the lithiated silylalkenynes form the corresponding derivatives with the *trans*-configuration,[53] while their interaction with nucleophiles[54] affords the lithiated derivatives of 1-trialkylsilylbutadiyne:



3,4-Bis(trialkylstannyl)-1-trimethylsilylalk-3-en-1-ynes are trans-metallated on interaction with organolithium compounds. The organolithium compounds formed on treatment with the corresponding electrophiles afford derivatives of silicon-containing alkenynes in satisfactory yields:[121]



Judging from the structure of the reaction products after demetallation with water, the methyl ester of 5-trimethylsilylpent-2-en-4-ynoic acid combines with triphenyl lithiotrithioformate exclusively at the double bond (most probably via the 1,4-addition to the $-C=C-C=O$ fragment):[48]

$$Me_3SiC\equiv C-CH=CH-\underset{\displaystyle OMe}{\underset{|}{C}}=O + LiC(SPh)_3 \xrightarrow{HOH}$$

$$\longrightarrow Me_3SiC\equiv C-\underset{\displaystyle C(SPh)_3}{\underset{|}{CHCH_2COOMe}}$$

The interaction of the silicon-containing vinylacetylenic ketone with metallic sodium in chlorotrimethylsilane apparently proceeds as 1,4-addition of trimethylsilylsodium:[138]

$$Me_3SiC\equiv C-CH=CH-\underset{\displaystyle Me}{\underset{|}{C}}=O \xrightarrow[2.\ HOH]{1.\ Na + Me_3SiCl}$$

$$\longrightarrow Me_3SiC\equiv C-\underset{\displaystyle SiMe_3}{\underset{|}{CHCH_2}}-\underset{\displaystyle Me}{\underset{|}{C}}=O\ .$$

Treatment of an alkenynyl chloride with a mixture of metallic lithium and chlorotrimethylsilane followed by the demetallation of the reaction products with water afforded a vinylallene. Its formation presupposes the 1,4-addition of trimethylsilyllithium to the conjugated system of multiple bonds and dehydrochlorination:[46]

$$Me_3SiC\equiv C-\overset{CH_3}{\overset{|}{C}}=CHCH_2Cl \xrightarrow[2.\ HOH]{1.\ Li + Me_3SiCl}$$

$$\longrightarrow \begin{matrix} Me_3Si \\ \diagdown \\ \quad C=C=C \\ \diagup \\ Me_3Si \end{matrix} \begin{matrix} \diagup CH_3 \\ \quad \\ \diagdown CH=CH_2 \end{matrix}\ .$$

In the absence of chlorotrimethylsilane, treatment of 1-trialkylsilylbut-3-en-1-yne with lithium and then water leads to a mixture of diacetylene and diallene hydrodimerisation products. Cross-coupling products (the corresponding allenylacetylenes) were not detected.[277]

Interaction with organomagnesium, organocalcium, and organobarium compounds. Organomagnesium compounds (Grignard reagents) are less reactive: silicon-containing alkenynes do not react with the Grignard reagent obtained beforehand under standard conditions.[278,279] However, at the instant of their formation, such reagents add fairly vigorously to 1-trimethyl- and 1-triethyl-silylbut-3-en-1-ynes,[278–280] affording, after demetallation with water, mixtures of the corresponding acetylene and allene silylhydrocarbons in proportions of 10 : 1 (yield about 10–15%) and oligomers.

Tris(trimethylsilyl)allene is apparently formed via the same mechanism in the reaction of 1-trimethylsilylbut-3-en-1-yne with a mixture of metallic magnesium and chlorotrimethylsilane.[46,281]

It has been shown for the reactions with phenylmagnesium bromide that silicon-containing alkenynes combine with organomagnesium compounds at the double bond in the presence of nickel(II) halides. The yield of the corresponding acetylenic hydrocarbons is 30–35%.[282] It can be increased by using other catalysts—$Fe[CH(COMe)_2]_3$, $Ni[CH(COR)_2]_2$; R = Me, Ph.[283]

Organocalcium and organobarium compounds RMI (M = Ca, Ba) add to silicon-containing alkenynes also in the absence of catalysts and, as in the reactions with organolithium compounds, mixtures of allene and acetylene silylhydrocarbons are formed after the demetallation of the adducts with water. Whereas in the reactions with organocalcium compounds the ratio of the isomers formed is 70 : 30,[284] in those with organobarium compounds the ratio is approximately 1 : 1.[285,286] Organozinc compounds (investigated in relation to the interaction of allylzinc bromide with 3-methyl-1-trimethylsilylbut-3-en-1-yne[287]) add chemo- and regio-selectively (95% *trans*) to the triple bond.

Interaction with organoaluminium compounds. Trialkylaluminium interacts with 1-trialkylsilylalk-3-en-1-ynes only under severe conditions. The reaction takes place chemoselectively at the triple bond with formation of a mixture of (*E*,*E*)- and (*E*,*Z*)-2-alkyl-1-trialkylsilylalka-1,3-dienes. The addition of bimetallic complexes of trialkylaluminium and dialkylmagnesium also takes place chemoselectively to the triple bond but much more readily:[288,289]

$$Me_3SiC\equiv C-CH=CH-C_6H_{13} + Alk_3Al\cdot Bu_2Mg \xrightarrow{H^+}$$

$$\longrightarrow \begin{matrix} Me_3Si \\ \diagdown \\ \quad C=C \\ \diagup \\ H \end{matrix} \begin{matrix} \diagup Alk \\ \quad \\ \diagdown H \end{matrix} \begin{matrix} \diagup H \\ \quad \\ \diagdown C_6H_{13} \end{matrix} +$$

$$+ \begin{matrix} H \\ \diagdown \\ \quad C=C \\ \diagup \\ Me_3Si \end{matrix} \begin{matrix} \diagup C_6H_{13} \\ \quad \\ \diagdown H \end{matrix} \begin{matrix} \diagup H \\ \quad \\ \diagdown Alk \end{matrix}\ .$$

The isomer ratio is $(E,E):(E,Z) \simeq 95:5$.

Silicon-containing (*E*,*E*)- and (*E*,*Z*)-alka-1,3-dienes are desilylated stereospecifically with iodine. The reaction can be recommended as an easy preparative method of synthesis of the corresponding *cis*- or *trans*-1-iodoalkadienes.

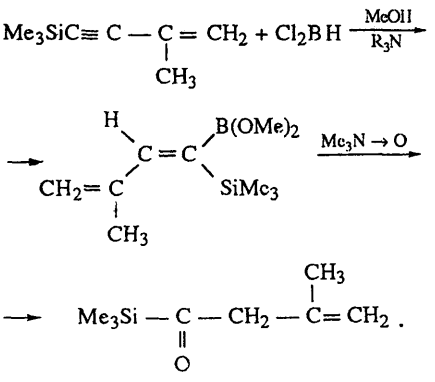
It was shown in relation to cyclohexenyltrimethylsilylacetylene that alkylating Ziegler–Natta reagents (complex of bis-η^5-cyclopentadienyltitanium and alkylaluminium chloride–$EtAlCl_2$ or Et_2AlCl) also alkylate the triple bond regiospecifically and stereospecifically ($E:Z \simeq 1:1$).[290] In the case of hydroorganoaluminium compounds, the Al–H bonds are more reactive in reactions with unsaturated compounds. In all the known cases,[44,111,121,291] the hydroaluminium compound adds chemo-, regio-, and *trans*-stereo-specifically to the triple bond of the alkenyne. In the presence of tertiary amines, stereospecific *cis*-addition takes place:[291]

$$Me_3SiC\equiv C-C=C + iso\text{-}Bu_2AlH \rightarrow \begin{matrix} Me_3Si \\ \diagdown \\ \quad C=C \\ \diagup \\ iso\text{-}Bu_2Al \end{matrix} \begin{matrix} \diagup C=C \\ \quad \\ \diagdown H \end{matrix}$$

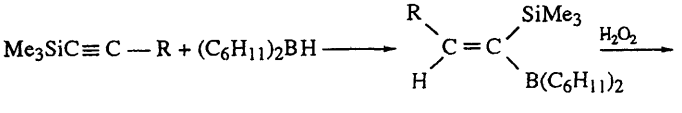
$$\xrightarrow{N-Br} \begin{matrix} Me_3Si \\ \diagdown \\ \quad C=C \\ \diagup \\ Br \end{matrix} \begin{matrix} \diagup H \\ \quad \\ \diagdown C=C \end{matrix} \qquad \xrightarrow{I_2} \begin{matrix} Me_3Si \\ \diagdown \\ \quad C=C \\ \diagup \\ I \end{matrix} \begin{matrix} \diagup H \\ \quad \\ \diagdown C=C \end{matrix} \qquad \xrightarrow{H} \begin{matrix} Me_3Si \\ \diagdown \\ \quad C=C \\ \diagup \\ H \end{matrix} \begin{matrix} \diagup H \\ \quad \\ \diagdown C=C \end{matrix}$$

On interaction with electrophiles, the adducts formed corresponding silylhydrocarbons or their derivatives.

Hydroboration of unsaturated compounds. This most probably proceeds via a molecular quasi-cyclic mechanism. However, it is formally analogous to hydroalumination. The first studies on the hydroboration of alkenynes were undertaken in order to develop an effective method of synthesis of silicon-containing ketones by oxidising the corresponding boron-containing adducts. It was found that the hydroboration of silylalkenynes proceeds chemo-, regio-, and *cis*-stereo-specifically at the triple bond.[292–294] The adducts formed isomerise to the *trans*-isomer on irradiation. Oxidation of the adduct with *N*-oxides leads to the formation of unsaturated silicon-containing ketones in good yields:

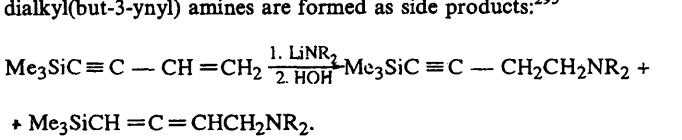


Dicyclohexylborane also adds stereo- and regio-selectively to the triple bond in silylalkenynes.[294] The adducts formed are oxidised in an alkaline medium with hydrogen peroxide to the corresponding unsaturated acids:



This method was subsequently used successfully in the synthesis of *cis*- and *trans*-6-phenyl-3-hexenoic and 5-amino-6-(4-t-butoxyphenyl)-3-hexenoic acid—key compounds in the synthesis of enkephalin analogues.[218,219]

Interaction with amines and amides. In the absence of a basic catalyst, primary and secondary amines do not interact with silylalkenynes. However, lithium dialkylamides, obtained beforehand, add under mild conditions to 1-trimethylsilylbut-3-en-1-yne with formation of a mixture of silicon-containing alkynyl- and allenyl-amines after demetallation with water. Silicon-free dialkyl(but-3-ynyl) amines are formed as side products:[295]

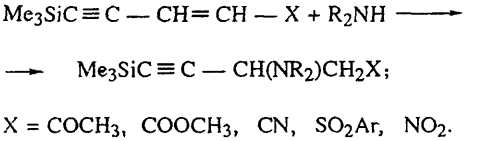


Desilylation most probably proceeds mainly at the stage involving the decomposition of the metal-containing adduct.[295] The fraction of the silicon-free alkynylamines depends on the structure of the amine: in the reaction with dimethylacetamide, they were detected only spectroscopically, while in the reaction with piperidine the yield of *N*-butynylpiperidine is 21%.

The same mixtures of silicon-containing amines derived from acetylenes and allenes are formed when an ethereal solution of the amine and 1-trimethylsilylbut-3-en-1-yne is heated to boiling in the presence of catalytic amounts of metallic sodium.[296] Desilylation products were not detected under these conditions.

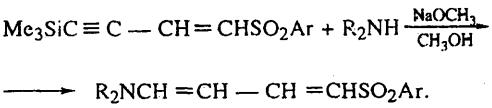
According to the results of Perveev and Afonina,[297] the silicon-containing nitriles $R_3SiC{\equiv}C-C(CH_3)=CH-CN$ are desilylated on interaction with primary and secondary amines. The nitrile of the alkenynoic acid formed combines with amines at the triple bond under these conditions. However, it was noted that, in experiments with methylamine and the nitrile of 3-methyl-1-trimethylsilylpent-3-en-4-ynoic acid, it was also possible to isolate small amounts of the product of the addition of the amine to the double bond.

Systematic study of the characteristic features of the addition of secondary amines to silyl derivatives of vinylacetylenes containing electron-accepting substituents X at the double bond showed that vinylacetylene nitriles, esters, ketones, and sulphones combine with secondary amines chemo- and regio-selectively at the double bond:[95,298–300]



In aprotic solvents (dimethyl ether of ethylene glycol), the addition takes place only after prolonged heating of the reactants at temperatures of the order of 100 °C.[298,299] In the absence of a solvent with an excess of the amine the reaction proceeds under appreciably milder conditions, ketones and ethers combining with amines even at room temperature. A decrease in temperature and reaction time in the interaction of amines with nitriles can be achieved only in proton-donating solvents (120 °C and 12 h without a solvent or 25 °C and 12 h in methanol[299]). The observed dependence of the relative reactivities of the alkenynes investigated in relation to amines has been explained by autocatalysis caused by the acid–base reagent–substrate interaction.

Silicon-containing vinylacetylenic sulphones do not combine with secondary amines in the presence of alcohols. Nor were any of the reactions of the reactants observed when their mixtures in methanol were allowed to stand in the presence of sodium methoxide at room temperature. However, on heating in the presence of methoxide, desilylation and the addition of the amine to the terminal bond take place:[300]



Reactions with thiols and thiolates. As already mentioned,[265–267] the free-radical addition of thiols to 1-trialkylsilylalk-3-en-1-ynes initiated by peroxides proceeds non-regioselectively. The attempts to add alkanethiols to silylalkenynes under the conditions of base catalysis did not yield positive results. In the interaction of 1-trimethylsilylbut-3-en-1-yne with ethanethiolate in methanol, an exothermic reaction takes place, as soon as the reactants are mixed and leads to the formation of sulphides with and without silicon in

proportions of 1 : 5.[301] The silicon-containing sulphides are products of 1,4-, 3,4-, and 1,2-addition in proportions of 4 : 1 : 2, while the sulphides without silicon constitute a mixture of 4-ethylthiobut-1-yne (12%), 1-ethylthiobuta-1,3-diene (34%) and 4-ethylthiobuta-1,2-diene (54%). Since the thiolate-catalysed addition of ethanethiol to vinylacetylene in an alcoholic solution results in the formation of only 1-ethylthiobuta-1,3-diene,[302] the formation of a mixture of silicon-free sulphides in the reaction analysed is most probably due to the desilylation of free-containing adducts.

As was to be expected, the introduction of electron-accepting groups ($COCH_3$, $COOCH_3$, CN, NO_2, SO_2Ar) into the alkenyne fragment increases significantly the rate of addition of thiols. However, when the reaction is carried out in methanol, only silicon-free products are formed from silylalkenyne derivatives even at −10 to −50 °C in the presence of thiolate:[301,303–305]

$$Me_3SiC{\equiv}C-CH=CHX + RSH \xrightarrow[CH_3OH]{RSNa} RSCH=CH-CH=CHX.$$

It has been established empirically that the silylalkenynes investigated can be made to undergo an addition reaction without appreciable cleavage of the silicon–carbon bond, provided that it is carried out in benzene or a 3 : 1 benzene–methanol mixture. Ethanethiol adds to the alkenyne both in benzene and in its mixture with methanol, while the less nucleophilic thiophenol adds only in the mixed solvent:[304]

$$Me_3SiC{\equiv}C-CH=CHX+RSH \xrightarrow[C_6H_6+CH_3OH]{RSNa} Me_3SiC{\equiv}C-CH(SR)CH_2X;$$

$R = C_2H_5$, C_6H_5.

The reaction is chemo- and regio-specific.

The silyl derivatives of vinylacetylenes investigated combine with alkane- and arene-thiols under very mild conditions, which agrees well with the nucleophilic mechanism proposed for these reactions. However, attention has been drawn to the fact[300,304,305] that the corresponding ketones react most readily, while the nitriles and sulphones react with the greatest difficulty. The antiparallel variation of the reactivity with the electron-accepting properties of the substituents X can be explained, according to the authors, by the fact that autocatalysis due to the acid–base reagent–substrate interaction plays a significant role in the reactions:

$$Me_3SiC{\equiv}C-CH=CH-\underset{\displaystyle R'}{\underset{|}{C}}=O + RSH \rightleftharpoons$$

$$\longrightarrow Me_3SiC{\equiv}C-CH=CH-\underset{\displaystyle R'}{\underset{|}{C}}=O\ldots H-SR.$$

Such interaction intensifies the polarisation of the multiple bonds and promotes the addition of the reagent to the double bond with attachment of the alkyl(aryl)thio-group to the β-carbon atom of the double bond. Aprotic solvents decompose such associated species and hinder the addition reaction, whilst proton-donating solvents themselves form associated species with the substrate and promote the addition reaction. This mechanism explains satisfactorily the decrease in the rate of addition on passing from thiophenol to ethanethiol and also the finding that in the presence of an excess of the reagent thiophenol adds to vinylacetylenic esters and ketones (X = $COOCH_3$ and $COCH_3$) at room temperature with 100% conversion in 10–15 min in the absence of a base.[305]

Interaction with arenesulphinates. This has been investigated only in relation to the reaction of 1-nitro-4-trimethylsilylbut-1-en-3-yne with sodium toluene-*p*-sulphinate. According to the available data, the addition proceeds chemo- and regio-selectively but only in the presence of an equivalent amount of acetic acid:[306]

$$Me_3SiC{\equiv}C-CH=CHNO_2 + p\text{-}CH_3C_6H_4SO_2Na \xrightarrow[CH_3OH]{CH_3COOH}$$

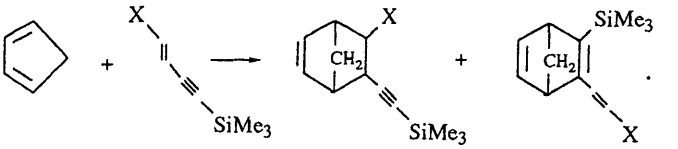
$$\rightarrow Me_3SiC{\equiv}C-\underset{\displaystyle SO_2C_6H_4CH_3\text{-}p}{\underset{|}{CH}}CH_2NO_2.$$

The silicon-containing vinylacetylenic sulphones, containing groups with weaker electron-accepting properties do not combine with sulphinates under these conditions.[307]

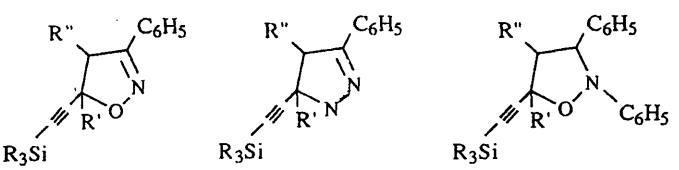
(d) Cycloaddition and cyclisation reactions

This section deals with reactions completed by the formation of carbocyclic and heterocyclic compounds as a result of intermolecular or intramolecular addition regardless of their mechanism. Shostakovskii et al.[308] showed for the first time that 1-triethylbut-3-en-1-yne is an active dienophile in condensation with hexachloropentadiene.

It has also been shown that interaction of cyclopentadiene with functional silyl-substituted derivatives of vinylacetylenes also involves the formation of a mixture of *endo,endo*, and *exo,exo*-isomers. Significant amounts of products of addition to the triple bond have been detected only in the reactions of cyclopentadiene with 1-cyano–4-trimethylsilylbut-1-en-3-yne:[309,310]

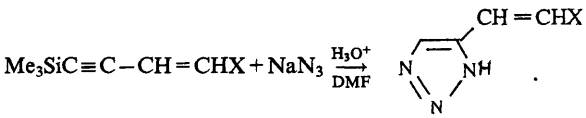


The reactions of 1,3-dipolar reagents (benzonitrile *N*-oxide, diphenylnitrile imine, α,*N*-diphenylnitrone, *C*-ethoxycarbonyl-*N*-phenylnitrile imine, 3-phenylsydnone, and sodium azide) with 1-trialkylsilylalk-3-en-1-ynes and some of their functional derivatives proceed in different ways depending on the structure of the alkenyne and the dipolar compound. Silicon-containing hydrocarbons combined in all cases with Huisgen's 1,3-dipoles at the double bond with formation of the corresponding trialkylsilylethynyl-substituted isoxazolines (I), pyrazolines (II), and isoxazolidines (III):



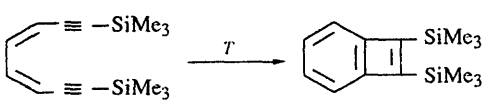
It was shown by the method of competing reactions that silylhydrocarbons are more reactive in their reactions with 1,3-dipoles than silicon-free hydrocarbons with similar structures.[311]

Sodium azide does not react with 1-trialkylsilylalk-3-en-1-ynes. However, their derivatives containing electron-accepting groups at the double bond combine with sodium azide at the triple bond on heating in dimethylformamide (DMF) at 90–95 °C. Demetallation of the adducts with water involves desilylation with formation of substituted triazoles:[312,313]

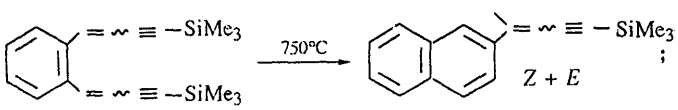


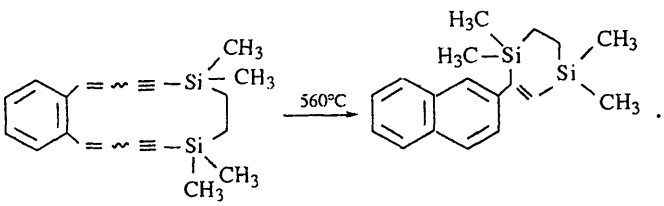
The attempts to add aryl- and trialkyl-silyl azides to silylalkenynes and their derivatives failed.[313]

The first reports concerning the intramolecular cyclisation of organosilicon compounds containing a conjugated double and triple bond appeared recently. It was shown that pyrolysis of 1,8-bis(trimethylsilyl)octa-3,5-diene-1,7-diyne *in vacuo* affords [8]annulene, which is very sensitive to atmospheric oxygen:[314]

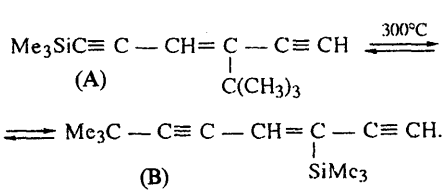


It has been established[315] that the structural analogues of 1,8-bis(trimethylsilyl)octa-3,5-diene-1,7-diyne form the corresponding naphthalene derivatives:

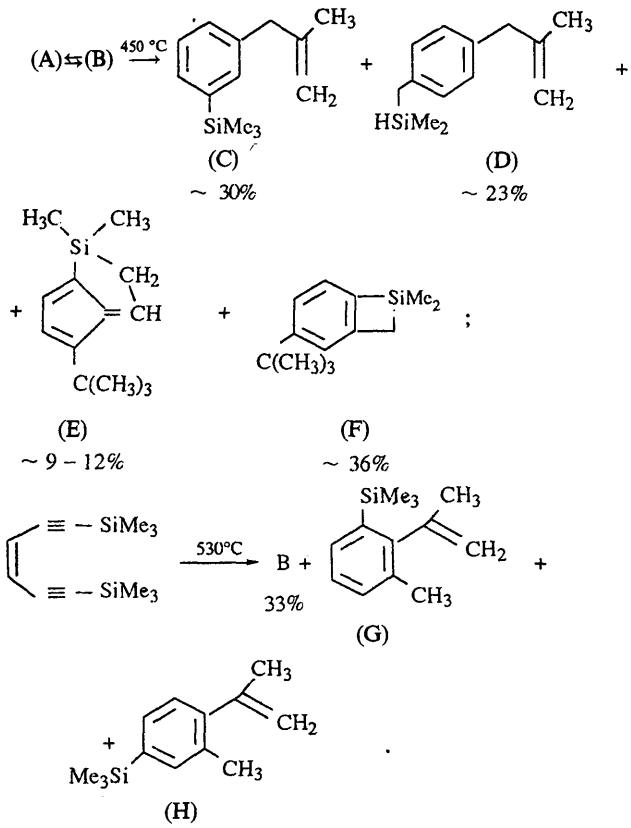




t-Butyltrimethylsilylpent-3-ene-1,4-diynes isomerise to a mixture of isomers containing only 1% of the structure (B):[90]



When a mixture of compounds (A) and (B) or each isomer separately is heated, four isomeric silyhydrocarbons are formed in an overall yield in excess of 90% regardless of the configuration (*E* or *Z*):

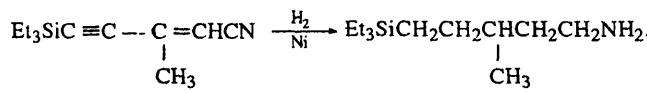


It is difficult to cyclise the disilylated alkenediyne containing the bulky trimethylsilyl groups in the 1,6-positions. The reaction takes place at an appreciable rate only at 530 °C with formation of compounds (C), (G), and (H).

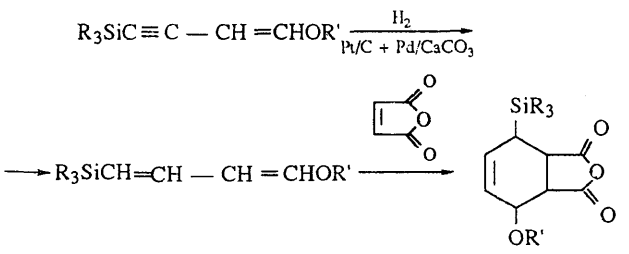
(e) Metal-catalysed homogeneous and heterogeneous reactions

Homogeneous and heterogeneous catalysis by transition metal compounds is one of the most important procedures for the activation of multiple bonds. Their characteristic feature, regardless of the mechanisms of the particular reactions occurring, is the involvement of the unsaturated ligand in intracomplex reactions of the ligands, which is as a rule the reason for a particular stereochemical result.

Catalytic hydrogenation. The catalytic hydrogenation of silicon-containing alkenynes up to complete saturation has been usually carried out in the presence of the Raney nickel catalyst,[70,78,79] the aim being to synthesise the corresponding saturated silylhydrocarbons and their derivatives. It has been noted that the nitrile of the acid derived from vinylacetylene is reduced under these conditions to the corresponding amine:[70]



Incomplete hydrogenation with the aim of determining the relative reactivities of the double and triple bonds of 1-trialkylsilylalk-3-en-1-ynes in relation to catalytically activated hydrogen was carried out by Petrov and co-workers[22,23] in the presence of a palladium catalyst. Since bands characteristic of the double bond were found in the Raman spectrum of the products obtained after hydrogenation and by analogy with data on the catalytic hydrogenation of vinylacetylene and its homologues (see, for example, Bal'yan et al.[316]), it was concluded that the first molecule of hydrogen adds to the triple bond of 1-trialkylsilylalk-3-en-1-ynes. Shostakovskii et al.,[52] who studied the hydrogenation of 4-ethoxy-1-trialkylsilylbut-3-en-1-ynes, arrived at the same conclusion:



The yield of the corresponding cyclic adduct with maleic anhydride reached only 25%. It has also been noted[52] that silicon-containing alkenyl ethers were not hydrogenated in the presence of only platinum on charcoal or palladium on calcium carbonate.

A more thorough investigation of the catalytic hydrogenation of silicon-containing alkenynes[26,244,317] showed that, in contrast to the alkenynes themselves, their silicon-containing analogues are hydrogenated non-selectively. In all cases the reaction products were mixtures of the initial silylhydrocarbon and the products of its hydrogenation in proportions of 1 : 1 (~90%) and the products of more extensive hydrogenation (5%). The products of the addition of the first molecule of hydrogen consisted of a mixture of alkyne, 1,3-diene, and allene isomers $R_3SiC{\equiv}C-CHR'CH_2R''$, $R_3SiCH=CH-CR'=CHR''$, and $R_3SiCH=C=CR'CH_2R''$ in proportions of approximately 60 : 35 : 5.[244]

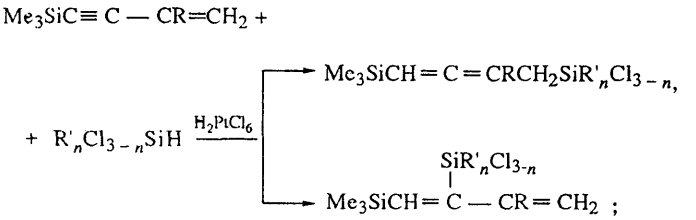
The ratio of the isomeric silylhydrocarbons varies within fairly wide limits depending on the nature of the substituents at the double bond and the silicon atom. The formation in all cases of appreciable amounts of silylallenes is striking. Their maximum amount is observed in the hydrogenation of 3-t-butyl-1-trimethylsilylbut-3-en-1-yne.[26] The addition of hydrogen in the 1,4-positions was not observed in th catalytic hydrogenation of vinylacetylenes.

It is also noteworthy that the rate of catalytic hydrogenation of silicon-containing alkenynes depends greatly on the bulk of the substituents at the silicon atom and in the alkenyne fragment.

Judging from the available data[31] allyldimethylsilylbut-3-en-1-yne is also hydrogenated in the vinylacetylene fragment, the ratio of the isomeric hydrogenation products being approximately the same as in the hydrogenation of 1-trialkylsilylbut-3-en-1-ynes.[244,317]

The data examined show that the trialkyl(aryl)silyl group at the α-carbon atom of the triple bond of the alkenyne hinders the addition of the first molecule of hydrogen to the triple bond and renders the process non-chemoselective.

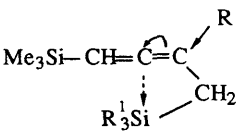
Hydrosilylation of 1-trialkylsilylalk-3-en-1-ynes. This was investigated solely in relation to the interaction of trialkyl- and alkylchloro-hydrosilanes with 1-trimethylsilylbut-3-en-1-ynes[318,319] and 3-methyl-1-trimethylsilylbut-3-en-1-yne[320] in the presence of Speier's catalyst. Chlorosilanes are more reactive in this process than trialkylsilanes and the mode of reaction depends on the structure of the alkenyne and the hydrosilane. 1-Trimethylsilylbut-3-en-1-yne combines with trimethyl- and triethyl-silanes preferentially in the 1,4-positions, while the chlorosilanes CH_3Cl_2SiH, $C_2H_5Cl_2SiH$, and Cl_3SiH combine with the above alkenyne at the triple bond:



n = 0, 1, 3; R = H, CH_3; R' = CH_3, C_2H_5.

On heating in the presence of a catalyst of the addition reaction or copper(I) chloride in an acid medium, the allene adducts isomerise almost wholly to the 1,3-diene adducts.

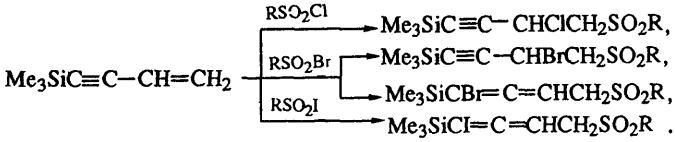
Regardless of the nature of the hydrosilane, 3-methyl-1-trimethylsilylbut-3-en-1-yne forms predominantly 1,3-diene adducts.[320] The authors suggest that the addition takes place in all cases in the 1,4-positions as an intramolecular reaction of the ligands. The ability of silicon-containing alkenynes to form "allene" complexes with platinum group metals has been demonstrated experimentally.[321,322] The allene adduct formed isomerises via a quasi-cyclic complex to the 1,3-diene adduct with migration of the trialkylsilyl group R^1_3Si:[320]



By inducing a partial positive charge on the silicon atom, the electron-accepting substituents R^1 (in the given instance chlorine) should promote the same type of isomerisation as that promoted by the introduction of a methyl group in the 3-position (R = CH_3), which increases the electron density on the C^2 carbon atom. The electron-donating substituents R^1 should hinder isomerisation. The observed dependence of the structure of the reaction products on the nature of the substituents at the silicon atom[318,320] as well as the data obtained for the hydrosilylation of 1,2,3-tris(trimethylsilyl)but-1-en-yne[117] are explained satisfactorily by the proposed mechanism. The hydrosilylation of alkenynes by trialkylsilanes is regarded[117] as a new effective preparative method of synthesis of allenes.

Intereaction with sulphonic acid halides. The relative reactivities of organic sulphonic acid halides in reactions with 1-trialkylsilylalk-3-en-1-ynes depend on the halogen; whereas acid iodides add exothermically merely on mixing the reactants, the bromides react on heating or in the presence of a catalyst, while the chlorides react only in the presence of the Asscher–Vofsi catalyst [a mixture of copper(I) halide, triethylamine hydrochloride, and acetonitrile[323]]. There are no literature data for the addition of these reagents to 1,3-alkenynes in the presence of aprotic Lewis acids.

The addition of the chlorides of alkane- and arene-sulphonic acids catalysed by copper(I) halides proceedes chemoselectively at the double bond:[91,92,94]



Regardless of the conditions (catalytic or thermal addition), the acid bromides add regioselectively to the alkenynes investigated with formation of a mixture of acetylene and allene adducts in proportions of approximately 1 : 1. In the absence of a catalyst, the acid iodides add exclusively in the 1,4-positions. The addition of the Asscher–Vofsi catalyst does not affect the mode of reaction.[93] It is of interest that t-butylvinylacetylene combines under these conditions with the acid chlorides, bromides, and iodides only at the double bond.[91,95] The introduction of a methyl group in the 3- or 4-position greatly hinders the reaction and impairs its selectivity. The chlorine-containing adducts formed in these reactions in low yields (20–30%) are mixtures of products of the addition to the double bond and in the 1,4-positions.[92]

It is also noteworthy that finely dispersed copper can be used instead of copper(I) chloride (bromide). Copper(II) hydroxide and copper oxide are inactive in the reaction.[324] It has been suggested that the reactions of the acid chlorides and bromides in the presence of copper salts proceed as intracomplex redox-initiated interaction of the ligands.[325]

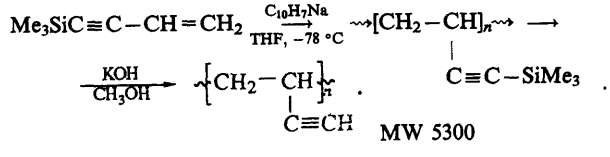
Chlorine-, bromine-, and iodine-containing products obtained in the reactions are readily dehydrohalogenated with triethylamine to form the corresponding *trans*-ethynylvinyl sulphones $R^1_3SiC{\equiv}CCR^2{=}CHR^3SO_2R^4$ in almost quantitative yields.[20]

(f) Polymerisation and copolymerisation

Trialkylsilylbut-3-en-1-ynes are known to polymerise spontaneously even at room temperature with formation of brittle vitreous masses.[23] On heating in the presence of benzene peroxides, the process proceeds at a much higher rate.[23,326] The relatively high rate of the peroxide-initiated polymerisation of dialkylhydroxysilylbut-3-en-1-yne has been pointed out.[38] There are data on the copolymerisation of 1-dimethylphenylsilylbut-3-en-1-yne with methyl methacrylate and certain physicochemical properties of the copolymers have been published.[326] The data on the structure of the polymers and copolymers obtained have not been discussed.[38,326]

In the presence of azobisisobutyronitrile, bisvinylethynylsilanes polymerise even at room temperature. The homopolymer formed under these conditions (most probably with a three-dimensional structure) is stable on heating to 400 °C.[327] The copolymerisation of bisvinylethynylsilanes with methyl methacrylate takes place at 60 °C. The influence of the ratio of the monomers on the yields, dielectric constants, and solubilities of the copolymers has been studied.

Japanese workers[328,329] have patented an effective method of synthesis of the vinylacetylene homopolymers by the naphthylsodium-initiated polymerisation of 1-trimethylsilylbut-3-en-1-yne and subsequent disilylation of the polymer with alkali:



Similar results were obtained using naphthyl- or butyl-lithium as polymerisation initiators.[329]

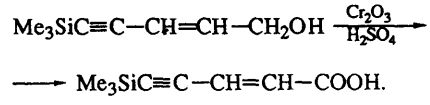
Two stages have been found in the polymerisation of 1-trimethylsilylbut-3-en-1-yne under the influence of γ-radiation: the formation of a linear polymer and the formation of three-dimensional structures in the polymer.[330] It was established that the replacement of the acetylene hydrogen by the trimethylsilyl group promotes the first stage and hinders the second.

A method has been patented for the preparation of materials for gas-permeable contact lenses from substances obtained by the polymerisation and copolymerisation of organosilicon vinylacetylene monomers of the type $CH_2{=}CR^1C{\equiv}CSiR^2R^3OSiR^4R^5R^6$ [331] or $CH_2{=}CR^1C{\equiv}CSiR^2R^3R^4$ and $[CH_2{=}CMeC{\equiv}C]_2SiMe_2$.[332]

2. Reactions with participation of functional groups

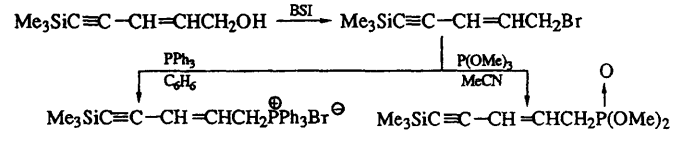
This type of chemical reaction of functional derivatives of silicon-containing alkenynes has been least investigated. However, it is known that the oxidation of silicon-containiing alkenynes with active manganese dioxide[145,186] or nickel peroxide[51] leads to the formation of the corresponding aldehydes in satisfactory yields. It has been noted that the oxidation of the (*Z*)-isomer proceeds without change in the configuration. Dimethyl sulphoxide can also be used as the oxidant.[179]

The oxidation of silicon-containing (*E*)- and (*Z*)-vinylacetylen alcohols with the Jones reagent leads to the corresponding acids, which have been converted, without purification, into methyl esters by treatment with diazomethane[48] or methanol in the presence of concentrated sulphuric acid[51]

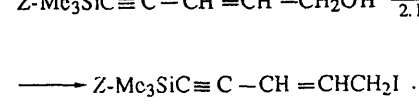


When the (*Z*)-carbinol is treated with the chlorides of acetic and (*E*)- or (*Z*)-2-methylbut-2-enoic acids,[51] the corresponding esters are produced. The configuration of the alkenyl fragments does not change under these conditions.

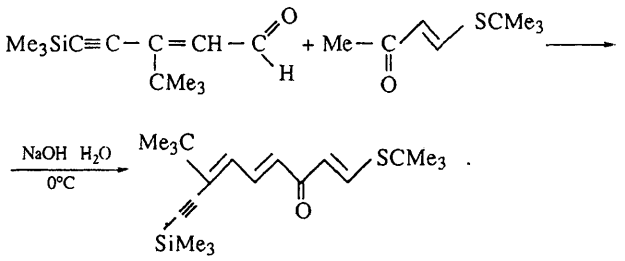
The interaction of 5-trimethylsilylpent-2-en-4-yn-1-ol with bromosuccinimide (BSI) afforded the corresponding bromide, which is readily converted into phosphoranes or phosphonates—key compounds in the synthesis of lipoxin A,[49,50,333,334,335] numerous dehydroannulenes (see Nakagawa[336] and the references quoted therein and Nakagawa and co-workers[337,338]) as well as other natural products and their synthetic analogues:[186,220,339]



A method has been developed for the synthesis of (*Z*)-1-iodo-5-trimethylsilylhex-2-en-4-yne which is used in the total synthesis of (±)-penacene:

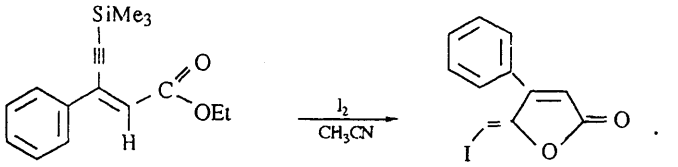


It has been shown for 3-t-butyl-5-trimethylsilylpent-2-en-4-yn-1-al[140,340] that silicon-containing aldehydes of the alkenyne series enter into aldol and crotonic condensations without the cleavage of the silicon–carbon bond:

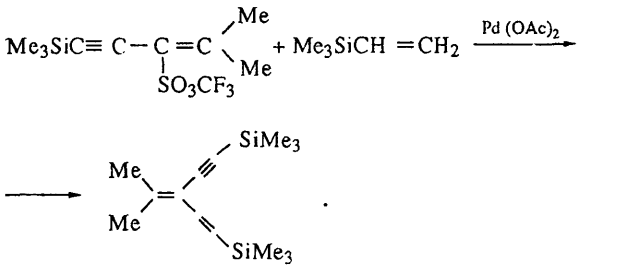


They also interact with organometallic compounds, affording the corresponding alcohols.[336,341,342]

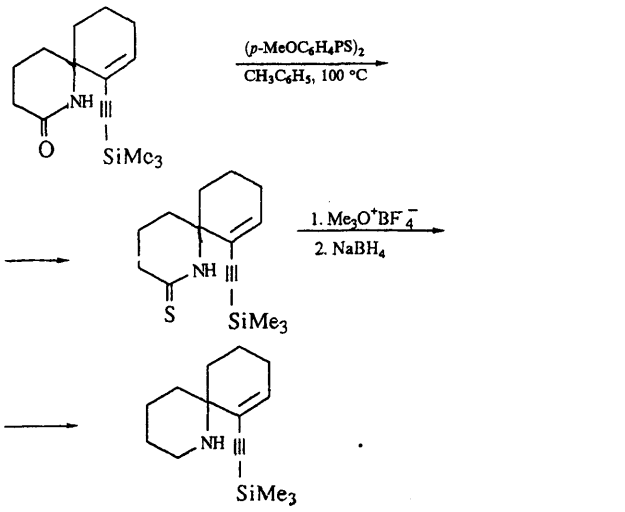
Iodolactonisation also takes place with participation of functional groups:[85]



It has been shown that 1,3-alkenyne silicon-containing triflates are capable of undergoing the palladium-catalysed cross-coupling reaction. The trimethylsilyl group is not then involved:[343,344]

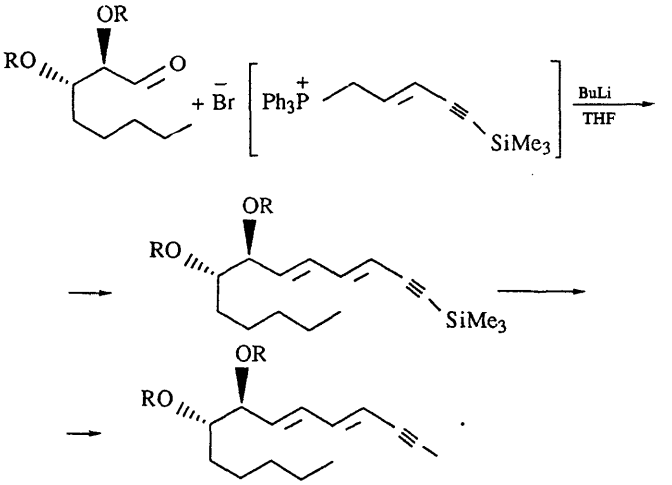


The reactions of an organosilicon lactam, described by Bultin et al.,[178] proceed with participation of functional groups:



3. Reactions with participation of the silicon–carbon bond

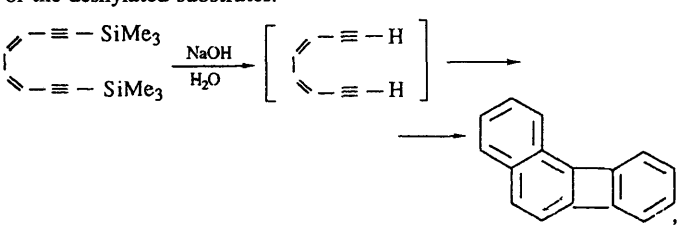
The introduction of a trialkyl(aryl)silyl group at the terminal carbon atom of the triple bond is known to increase significantly the stability of alkynes, alkenynes, and more unsaturated derivatives. The silyl protecting group is therefore used widely in the synthesis of natural products containing conjugated alkenyl fragments. As an example, one may quote the scheme for the preparation of the synthetic block (A)—the key compound in the synthesis of the four possible isomers of lipoxin B:[333,334]



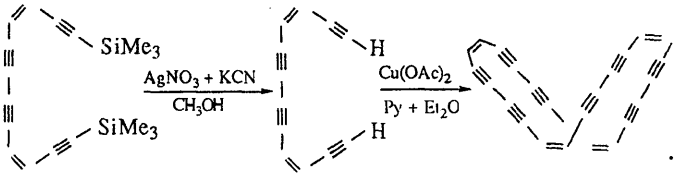
(A)

The triorganosilyl (most often trimethylsilyl) group is usually removed by the reaction of the corresponding silicon-containing acetylene with an alcoholic solution of an alkoxide,[169,170,206] an aqueous[33,85,120,155] or alcoholic[73,76,166,169,344] solutions of alkali, an aqueous solution of sodium carbonate[178] or potassium carbonate,[183] an alcoholic or aqueous alcoholic solution of a mixture of silver nitrate and potassium cyanide,[32,34,50,97,105,145,174,216,234,344] or the same reagents in a 1:1:1 ethanol–tetrahydrofuran (THF)–water mixture.[49,187,333] Desilylation takes place also when silylacetylenes are treated with methyllithium.[36,206,345] The fluorides of potassium,[30,112,141,158,159,172,201,215,224,235] sodium,[62] and tetrabutylammonium[103,104,113,173,176,182,232] have become particularly popular desilylating agents in recent years. Tetrahydrofuran, alcohol, and dimethylformamide are used as solvents in such cases. The reactions proceed as a rule at room temperature or with slight heating. The yields of the desilylation products are nearly quantitative. A method has been developed for the desilylation of silylalkenynes using phase transfer catalysts.[346] For example, the method helps to cleave the silicon–carbon bond under mild conditions without affecting the oxiran ring.

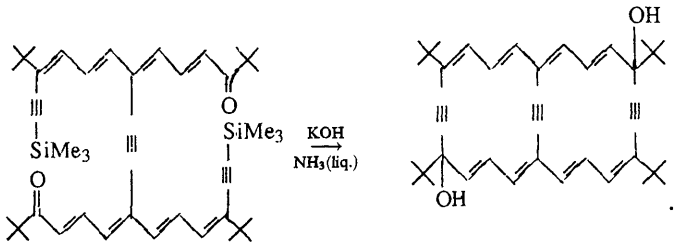
Reactions in which the removal of the silyl protecting group is completed with the formation of a new carbon–carbon bond are extremely interesting. Such processes may be due to the low stability of the desilylated substrates:[33]



or they can take place on treatment with new reagents:[34]



Japanese workers[340] developed a single-stage desilylation-alkynylation method involving the reaction of 1-trialkylsilylalk-1-ynepolyene aldehydes and ketones with alkalies in liquid ammonia. The method presupposes intramolecular or intermolecular nucleophilic attack on the carbonyl carbon atom by the acetylide anion formed on heterolysis of the silicon–carbon bond:



Subsequently this method was used widely in the synthesis of dehydroannulenes with a wide variety of structures (see, for example, Nagakawa[336] and the references quoted therein as well as Yoshikawa et al.[342]).

The reactions involving the acylation of silicon-containing alkenynes catalysed by aprotic acids,[73,107] i.e.

$$R-C(=O)Cl + Me_3SiC\equiv C-CR'=CHR'' \xrightarrow{MCl_x}$$

$$\longrightarrow R-C(=O)-C\equiv C-CR'=CHR'',$$

$$M = Al^{3+}, Ti^{4+}, Zn^{2+},$$

or by zerovalent palladium compounds are especially interesting as a method for the formation of a new carbon–carbon bond. The best yields of the corresponding ketones have been obtained using titanium chloride as the catalyst.[107] Judging from the available data,[73] the formation of ketones derived from acetylenes, which possess fungicidal activity, is also possible in the absence of a catalyst.

The heterolysis of a silicon–carbon bond can be carried out also in the presence of protic acids (perchloric, hydriodic[122]).

Desilylation of acetylenes with an aqueous alcoholic solution of silver nitrate followed by iodination leads to the synthesis of iodoacetylene:[51]

$$Z\text{-}Me_3SiC\equiv C-CH=CH-CH_2OR \xrightarrow[H_2O+EtOH]{AgNO_3+I_2}$$

$$\longrightarrow Z\text{-}IC\equiv C-CH=CH-CH_2OR.$$

Analysis of the data presented in this review permits the following conclusions:

1. The development of numerous methods for the stereospecific synthesis of readily desilylated organosilicon compounds containing the $\equiv Si-C\equiv C-C=C<$ fragments makes silicon-containing alkenynes unique synthons in the fine organic synthesis of natural products and their synthetic analogues, including sila-analogues.

2. Detailed study of the reactions involving the introduction of functional groups into 1-trialkylsilylalk-3-en-1-ynes has shown that the chemo-, regio-, and stereo-selectivities of the reactions are independent of the polarity of the reagents and substrates in all the cases investigated. The results indicate orbital control in the test reactions and to a first approximation may be generalised within the framework of the model of acid–base interaction.

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