Russian Chemical Reviews **64** (1) 25–46 (1995) ©1995 Russian Academy of Sciences and Turpion Ltd

UDC 547.345

Silicon-containing alka-1,3-dienes and their functional derivatives in organic synthesis

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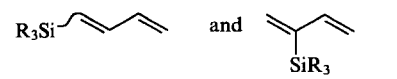
Abstract. Data on the synthesis and chemical reactions of silicon-containing 1,3-dienes are surveyed for the first time in the present review. It is shown that the addition reactions of 1- and 2-triorganosilylalka-1,3-dienes and their derivatives are the most interesting and promising in fine organic synthesis. The application of the trialkylsilyl group as a protecting group and as a new reaction centre, which makes it possible to obtain carbon—carbon or carbon–heteroatom bonds, is examined. It has been found that the double bonds remote from the silicon atom are the most reactive in addition reactions and that regardless of the nature of the reagent the attacking species always binds to the terminal carbon atom of the buta-1,3-diene fragment. The bibliography includes 329 references.

I. Introduction

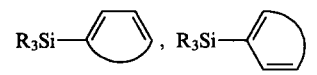
1,3-Diene hydrocarbons and their derivatives have long served as convenient and readily available intermediates in the synthesis of complex aliphatic, carbocyclic, and heterocyclic compounds as well as polymers with useful properties. Silicon-containing derivatives of 1,3-diene hydrocarbons were first obtained in 1954.[1] The authors suggested that the product of the catalytic hydrogenation of 1-trimethylsilylbut-3-en-1-yne is 1-trimethylsilylbuta-1,3-diene. However, it was later established that the product is a mixture of 1-trimethylsilylbut-1-yne and the isomeric 1-trimethylsilylbuta-1,2-diene and 1-trimethylsilylbuta-1,3-diene.[2–4] Judging from gas–liquid chromatographic (GLC) data, the fraction of the 1,3-diene isomer in the mixture does not exceed 36%.[4]

2-Trialkylsilylbuta-1,3-dienes[5] and 1-trialkylsilylbuta-1,3-dienes[6] were first obtained in a pure state as late as 1956 to 1957 by the dehydration of the corresponding alcohols. Subsequently the chemistry of unsaturated organosilicon compounds began to develop in two directions. The first is associated with the development of the methods of synthesis of silicon-containing hydrocarbons—model compounds for the investigation of the relation between structure and reactivity and also of the delocalisation of the π-electrons of the multiple bonds with participation of unoccupied *d* orbitals of silicon ($d_\pi - p_\pi$ interaction); the second direction is associated with the development of methods of synthesis of carbofunctional derivatives of 1,3-diene silicon-containing hydrocarbons and with their application as synthetic units in the synthesis of natural products and their synthetic analogues, including silane analogues.[7,8]

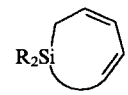
Representatives of virtually all possible types of silylalka-1,3-dienes have now been synthesised, but the present review surveys the results of studies on only 1- and 2-organosilylalka-1,3-dienes containing the fragments



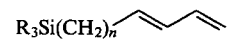
In view of the specificity of the methods of synthesis and of the characteristic features of their structure and reactivity, silylcyclo-1,3-dienes



silacyclo-1,3-dienes



and aliphatic compounds of the type



$n > 0$,

are not analysed in the present review.

Special reviews, including a full analysis of the chemistry of silicon-containing alkadienes and their functional derivatives, are lacking although compilatory[9–13] and narrow-profile[14–23] reviews, as well as certain monographs[24–26] include data also on the chemistry of 1,3-diene organosilicon compounds.

II. Synthesis of 1- and 2-triorganosilylalka-1,3-dienes and their functional derivatives

All the methods of synthesis of silicon-containing 1,3-dienes known at present can be divided into two groups. The first includes all the methods in which the initial compounds already contain the required carbon skeleton and the task of the investigator reduces either to the introduction of the organosilyl group into the organic molecule or to the creation of silyl-substituted 1,3-diene structures as a result of the chemical transformation of the corresponding unsaturated organosilicon compounds. The second group consists of methods involving the

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Received 18 March 1994
Uspekhi Khimii **64** (1) 28–49 (1995); translated by A K Grzybowski

creation of silicon-substituted 1,3-diene structures from simpler synthetic units. The methods include the obligatory formation of new carbon–carbon bonds.

1. Synthesis of silicon-containing 1,3-dienes from the corresponding alkenynes

Catalytic hydrogenation of the available 1,3-enyne silicon-containing hydrocarbons and their derivatives is one of the promising methods of synthesis of the corresponding dienes.[26] According to Petrov et al.,[1] catalytic hydrogenation of 1-trimethylsilylbut-3-en-1-yne in the presence of palladium on barium sulfate actually takes place chemoselectively at the triple bond.

$$Me_3SiC{\equiv}C{-}CH{=}CH_2 + H_2 \xrightarrow{Pd/BaSO_4} Me_3SiCH{=}CH{-}CH{=}CH_2$$

Other workers who investigated the catalytic reduction of silicon-containing vinylethyne ethers[27] and glycols[28] arrived at a similar conclusion.

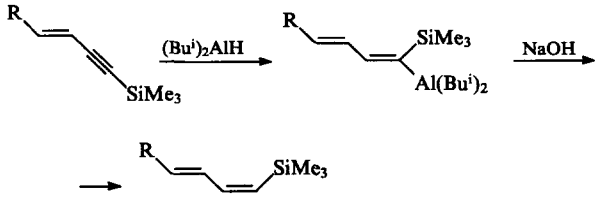
$$Me_3SiC{\equiv}C{-}CH{=}CHOR + H_2 \xrightarrow{Pd+Pt} Me_3SiCH{=}CH{-}CH{=}CHOR$$

$$Me_2C(OH)C{\equiv}C{-}CH{=}\underset{\displaystyle SiEt_3}{C}{-}C(OH)Me_2 \xrightarrow{Pd/BaSO_4} Me_2C(OH)CH{=}CH{-}CH{=}\underset{\displaystyle SiEt_3}{C}{-}C(OH)Me_2$$

It has been noted that the alkenyne ethers are not hydrogenated in the presence of palladium on calcium carbonate or platinum on charcoal, but readily combine with catalytically activated hydrogen when a mixture of these catalysts is employed.

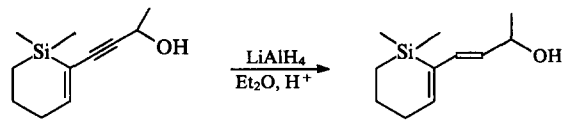
However, it was later shown[2–4] that the hydrogenation of silicon-containing alkenynes is a nonselective process: apart from the corresponding 1,3-diene, silicon-containing hydrocarbons and ethyne and allene products are formed. Since conclusions concerning the mode of hydrogenation were reached in the above investigations[1,27,28] on the basis of spectroscopic data (Raman or IR spectra) and the ability of the hydrogenation products to form cyclic adducts with maleic anhydride (which is possible also when the mixture contains 20%–30% of the 1,3-diene), the authors' conclusion[1,27,28] that catalytically activated hydrogen adds chemoselectively to the triple bond of silicon-containing 1,3-enyne hydrocarbons must be regarded as erroneous.

According to the available data, silicon-containing alk-1-en-3-ynes combine chemospecifically with diisobutylaluminium hydride at the triple bond. The corresponding (*Z*, *E*)-alkadienes were obtained by the protodemetallation of the adduct and the interaction with donors of the electrophilic halogens (chlorosuccinimide, bromocyanogen, and iodine) afforded the corresponding halo-derivatives of silicon-containing dienes.[29–33]

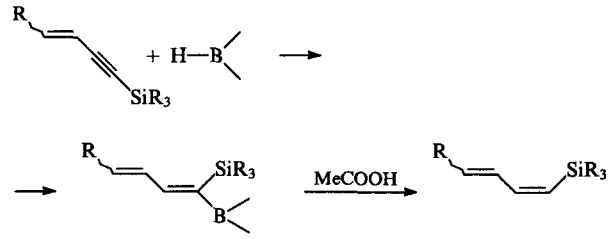


R = C_6H_{13}, C_6H_{11}, Bu^t, Me_3Si.

The reduction of the triple bond by lithium tetrahydroaluminate is known only for the corresponding alkenyne alcohols (a stereo-, regio-, and chemospecific reaction).[7]



The hydroboration of 1-trialkylsilylalk-3-en-1-ynes as well as their hydroalumination proceed chemo-, regio-, and stereo-specifically with formation of (*Z*)-adducts. The configuration of the 3,4-double bond is not altered.[32,34–37] Treatment of the adducts with acetic acid afforded the corresponding (1*Z*)-alkadienes.



The addition of hydrosilanes to 1,3-enyne compounds is nowadays one of the most important methods of synthesis of silicon-containing alka-1,3-dienes despite the fact that in many cases these reactions are characterised by a relatively low chemo- and regioselectivity. A 0.1 N solution of chloroplatinic acid in isopropyl alcohol (the Speier catalyst) is usually employed as the reaction catalyst; platinum on charcoal or other compounds of platinum group metals are more rarely employed.

It has been reported that conjugated alkenynes[38–47] and their functional derivatives[48,49] containing terminal ethyne groups combine with hydrosilanes exclusively at the triple bond with the silyl group becoming attached to the α-carbon atom. The nature of the R^1 and R^2 substituents does not affect the mode of the reaction and the yield of its products. In the interaction of trichlorosilane with vinylethyne, no individual adducts could be isolated.[43]

$$CH{\equiv}C{-}CR^1{=}CHR^2 + Cl_nR_{3-n}SiH \longrightarrow Cl_nR_{3-n}SiCH{=}CH{-}CR^1{=}CHR^2$$

R^1 = H, Me; R^2 = H, Me, OMe, NEt_2.

Judging from the yields, the reactivity of haloalkylhydrosilanes decreases in the sequence $Me_2ClSiH > MeCl_2SiH > Cl_3SiH$, which differs from that obtained previously in Greber's study.[45]

However, it was later established[50,51] that alkenynes with a terminal triple bond interact with hydrosilanes chemo- and regio-specifically: apart from 1-trialkylsilylalka-1,3-dienes, the products of the addition of hydrosilanes to the double bond also in the 1,4-positions as well as 2-trialkylsilylalka-1,3-dienes are formed. The yields of these compounds are low and they can be removed by fractionation.

Judging from the available data,[52–56] 1-trialkylsilyl alk-1-en-3-ynes also combine with hydrosilanes preferentially at the triple bond. However, considerable amounts of allene adducts are also formed in these reactions, their fraction in the mixture being determined by the structure of the enyne fragment and the hydrosilane.

$$Me_3SiC{\equiv}C{-}CR^2{=}CHR^3 + R^1_nCl_{3-n}SiH \longrightarrow$$

$$\longrightarrow Me_3SiCH{=}C(SiCl_{3-n}R^1_n){-}CR^2{=}CHR^3$$

$$\xrightarrow{H^+}$$

$$\longrightarrow Me_3SiCH{=}C{=}CR^2{-}CHR^3SiCl_{3-n}R^1_n$$

Trialkylhydrosilanes add to 1-trialkylsilylbut-3-en-1-ynes ($R^2 = R^3 = H$) exclusively in the 1,4-positions, while 3-methyl-1-trimethylsilylbut-3-en-1-yne ($R^2 = Me$) reacts with the same reagents to form almost exclusively the products of addition to the triple bond.

Alkylchlorohydrosilanes react with 1-trialkylsilylalk-3-en-1-ynes almost always at the triple bond regardless of the structure of the enyne fragment. It has been established that allene adducts readily isomerise in an acid medium to 1,3-diene adducts with migration of the trialkylsilyl group. These results enabled the authors [52,55] to postulate that the reactions proceed in all cases as 1,4-addition. The adducts obtained under these conditions isomerise to 1,3-dienes already under the conditions of the addition reaction. Chloroplatinic acid or hydrogen chloride, which is always present in chlorohydrosilanes, function as isomerisation catalysts. The isomerisation most probably proceeds via a quasi-cyclic transition state stage. [53]

It has been shown for the hydrosilylation of 1,2,4-tris-(trimethylsilyl)but-1-en-3-yne that the nature of the catalyst [H_2PtCl_6, $PtCl(PPh_3)_3$, $Pt(PPh)_4$, $PdCl_2(PPh_3)_2$, and $Pd(PPh_3)_4$] and the structure of the hydrosilane ($PhMeSiH_2$, Ph_2SiH_2, and Et_3SiH) affect the yield and structure of the adducts. [55]

The interaction of alkenes with trialkylhydrosilanes in the presence of chloroplatinic acid is optimal for the preparation of 1,3-dienes. [55]

Regardless of the structure of the reactants and the nature of the catalyst (chloroplatinic acid or platinum on charcoal), hydrosilanes add exclusively to the triple bond of vinylethyne alcohols [57-62] and their ethers [63-65] and esters [66] in the hydrosilylation reaction.

$R^1R^2C(OR^3)C{\equiv}C{-}CH{=}CH_2$,

R^3 = H, Me, CH_2CH_2CN, MeCO, $CH_2CH{-}CH_2$ (O).

On the grounds that the adducts did not undergo "β-cleavage" on heating, a type **A** structure was initially attributed to them, but later the structure **B** was proposed on the basis of ^1H NMR spectroscopic data.

$$R^1R^2C(OR^3){-}C(SiR_nCl_{3-n}){=}CH{-}CH{=}CH_2$$

A

$$R^1R^2C(OR^3){-}CH{=}C(SiR_nCl_{3-n}){-}CH{=}CH_2$$

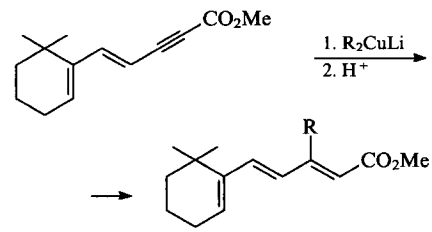
B

Ethyne and allene adducts have also been found in some investigations, [62,64] but the conclusions reached by the authors concerning the structure are open to doubt.

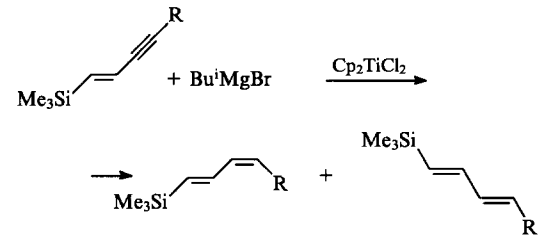
According to the data of Kakhniashvili and coworkers [67-69] and Shikhiev and coworkers, [70] alkenynes of the type *p*-$ROC_6H_4C(Me)_2C{\equiv}C{-}CH{=}CH_2$ give rise to a mixture of the corresponding 1,3-diene regioisomers, with type **B** adducts predominating (80%-90%), on interaction with trialkylhydrosilanes in the presence of chloroplatinic acid.

Analysis of the available data shows that hydrosilanes add to the triple bond of alkenynes with a high degree of selectivity and that in the case of terminal ethynes the silicon-containing group is attached predominantly to the α-carbon atom of the triple bond, while in reactions with internal triple bonds this group is attached to the β-carbon atom.

The addition of organometallic compounds to the double bond and in the 1,4-positions in alkenynes is of no interest as regards the synthesis of silicon-containing dienes with conjugated double bonds. [21] Only the reactions of silicon-containing lithium cuprates are an exception. Judging from the available data, these add chemo-, regio- and stereo-specifically to the triple bond of the methyl ester of the corresponding alkadienynoic acid. [71]

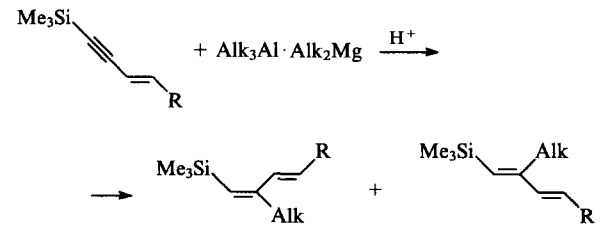


Under the usual conditions, Grignard reagents do not interact with silicon-containing alkenynes, but in the presence of catalytic amounts of dichloro(dicyclopentadienyl)titanium a reaction in which hydrogen and magnesium add to the unsaturated compound takes place. [32]



The overall yield of 1,3-diene silicon-containing hydrocarbons formed on demetallation with water does not exceed 30% and the isomer ratio is $E:Z = 42:58$.

Trialkylaluminium adds to 1-trialkylsilylalk-3-en-1-ynes only on heating. When a complex of trialkylaluminium with dialkylmagnesium is used as the reagent, the reaction takes place under milder conditions (the isomer ratio is $E,E:E,Z = 95:5$). [72,73]



The addition of mixed alkylaluminium chlorides in the presence of Cp_2TiCl_2 takes place similarly (the isomer ratio is $E,E:E,Z = 50:50$). [74]

The dealumination of the adducts formed can be carried out with iodine, whereupon one obtains 1-iodoalkadienes, which are difficult to obtain otherwise.

Judging from the data of Petrov et al., [1] the bromination of 1-trialkylsilylbut-3-en-1-ynes takes place exclusively at the triple bond and can be a convenient preparative method of synthesis of the corresponding 1,3-diene silicon-containing dibromo-derivatives. It was shown later that the 1,2-dibromo-derivatives are obtained as a result of the thermal isomerisation of the 1,4-dibromo-derivatives formed initially. [75]

$$R_3SiC{\equiv}C{-}CH{=}CH_2 + Br_2 \longrightarrow$$

$$\longrightarrow R_3SiCBr{=}C{=}CHCH_2Br \xrightarrow{\Delta}$$

$$\longrightarrow R_3SiCBr{=}CBr{-}CH{=}CH_2$$

The functional derivatives of the silylalkenynes $Me_3SiC{\equiv}C-CH{=}CRX$ (X = CN, COR, CO_2R) combine with bromine at the double and triple bonds. The ratio of the dibromo-derivatives formed is ~1:1.[76] The introduction of a methyl group in the α-position relative to the functional-group substituent promotes the formation of dibromo-1,3-dienes.[76]

In contrast to the halogens, sulfinic acid halides, and other electrophiles[21] which add to silicon-containing alkenes at the double bond and in the 1,4-positions, sulfenic acid chlorides and bromides and their selenium-containing analogues react exclusively[77] or preferentially[78-82] at the triple bond.

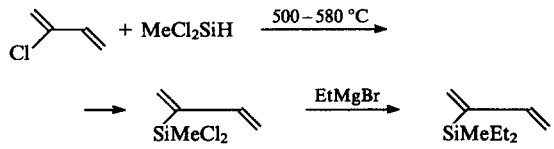
$$Me_3SiC{\equiv}C-CR^1{=}CHR^2 + R^3XY \longrightarrow$$
$$\longrightarrow Me_3SiC(XR^3){=}CY-CR^1{=}CHR^2$$
$$+ Me_3SiC{\equiv}C-CR^1YCHR^2XR^3$$

X = S, Se; Y = Cl, Br.

Other reagents (secondary amines[83] and thiols) add to the double bond and in the 1,4-positions under the conditions of free-radical initiation,[84,85] the content of 1,3-diene adducts not exceeding 5%. Therefore these reactions are of no interest as methods of synthesis of polyfunctional derivatives of silicon-containing 1,3-diene hydrocarbons.

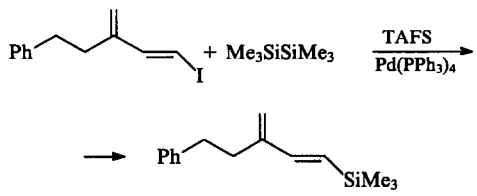
2. Silylation of derivatives of alka-1,3-dienes

Only two examples of the direct silylation of haloalkadienes, leading to the synthesis of the corresponding silicon-containing alka-1,3-dienes, are known. Thus 2-triorganosilylbuta-1,3-diene has been obtained in a low yield by the high-temperature (500–580 °C) condensation of dichloromethylsilane and chloroprene.[86]



Under milder conditions in the presence of a palladium catalyst and tris(diethylamino)sulfonium difluorotrimethylsilicate (TAFS), hexamethyldisilane interacts stereospecifically with 1-iodoalkadienes (Scheme 1).[87]

Scheme 1



The use of potassium or caesium fluoride as the fluoride anion donor is ineffective.[87]

Silicon-containing 1,3-diene ethers are formed readily and in satisfactory yields on condensation of lithium alkoxydienides with triorganosilanes.[14,88-92]

$$R^1OCH{=}CH-CH{=}CHR^2 \xrightarrow{BuLi}$$
$$\longrightarrow [R^1OC{=}CH-CH{=}CHR^2]^-Li^+ \xrightarrow{Me_3SiCl}$$
$$\longrightarrow R^1OC(SiMe_3){=}CH-CH{=}CHR^2$$

R^1 = Me, Et, $MeOCH_2$, $Me_3SiOCH_2CH_2CH_2$;

R^2 = H, Me, Pr^i.

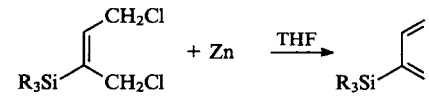
The lithium or sodium alkadienides interacting with Me_3SiCl can be obtained by metallating the corresponding halogen compounds[93] or as a result of the opening of the ring in furan derivatives[94] and cyclic acetals,[91] by transmetallation,[95,96] and by other procedures.[97-103]



TBS = Bu^tMe_2Si.

3. 1,2- and 1,4-Elimination reactions

Judging from the available data,[18,104-106] 1,4-dechlorination is the easiest method of synthesis of 2-triorganosilylbuta-1,3-dienes.



The initial 1,4-dichloro-2-triorganosilylbut-2-enes are obtained by hydrosilylating 1,4-dichlorobut-2-yne.

1,2-Dechlorination[107] can also be recommended as a convenient preparative method of synthesis of the corresponding derivatives of silicon-containing 1,3-dienes.

$$CF_2ClCFCl-CH{=}CHSiMe_3 + Zn \longrightarrow$$
$$\longrightarrow CF_2{=}CF-CH{=}CHSiMe_3$$

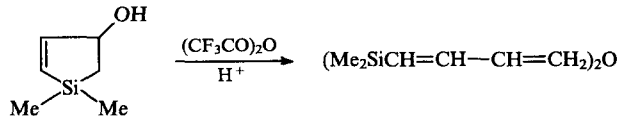
Another method of synthesis of 2-triorganosilylalka-1,3-dienes involves the 1,2- and 1,4-elimination of water from silicon-containing ethene alcohols. However, owing to the relatively low hydrolytic stability of the silicon–carbon bond towards strong inorganic acids and bases, the reaction must be carried out in the presence of acid potassium sulfate. It has been shown that tertiary and secondary alcohols are dehydrated under these conditions.[5,6,108-110]

$$R_3SiCH_2\underset{OH}{C}H-CH{=}CHR^1 \xrightarrow{KHSO_4}$$
$$R^1 = H \rightarrow R_3SiCH{=}CH-CH{=}CHR^1$$
$$R^1 = Me \rightarrow R_3SiOSiR_3 + CH_2{=}CH-CH{=}CHR^1$$
$$Me_2\underset{HO}{C}-\underset{SiR_3}{C}{=}CH_2 \xrightarrow{KHSO_4} CH_2{=}\underset{Me}{C}-\underset{SiR_3}{C}{=}CH_2$$

In all the cases investigated, tertiary alcohols are dehydrated under milder conditions than secondary alcohols. The dehydration of 1-trimethylsilylpent-3-en-2-ol takes place with almost complete desilylation. Heating the dihydric alcohols $R_2Si[CH_2CR^1(OH)-CH{=}CH_2]_2$ with $KHSO_4$ affords the corresponding bisbutadienylsilanes in low (~20%) yields.

Toluene-*p*-sulfonic acid began to be used later for the dehydration of secondary[111,112] and tertiary[113-116] silicon-containing alcohols.

The dehydration of 1,1-dimethyl-1-silacyclopent-2-en-4-ol by trifluoroacetic acid anhydride takes place with the opening of the ring and the formation of the corresponding siloxane.[117]

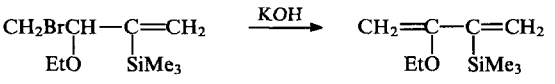


Examples of the dehydration of secondary silicon-containing alcohols on treatment with 1,8-diazabicyclo[5.4.0]undecane (DBU) are also known.[118]

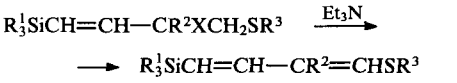


Thus, by varying the structure of the silicon-containing ethene alcohols and dehydrating agents synthesised by traditional methods, it is possible to obtain any silicon-containing conjugated alkadienes.

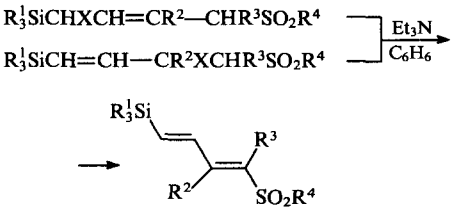
The 1,2- and 1,4-elimination of hydrogen halides and other acids proceeds as a rule only in a highly alkaline medium at high temperatures. This is apparently the reason why there are no data on the synthesis of silicon-containing 1,3-dienes by this procedure. However, it is known that, when carbonyl derivatives of silicon-containing ethene hydrocarbons contain a halogen and electron-accepting substituents, they readily split off hydrogen halides, the rate of reaction depending on the nature of the halogen (I > Br > Cl). Thus, according to the data of Shchukovskaya and coworkers,[119] β-bromoethers are dehydrobrominated by solid alkali at 90–120 °C.



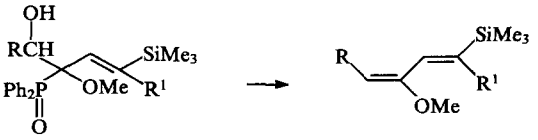
It was shown at the same time that silylchloro- and silylbromoalkyl sulfides containing a halogen in the allyl position readily split off the corresponding halogen halides even on treatment with triethylamine.[120] DBU was later used for similar purposes.[121–123]



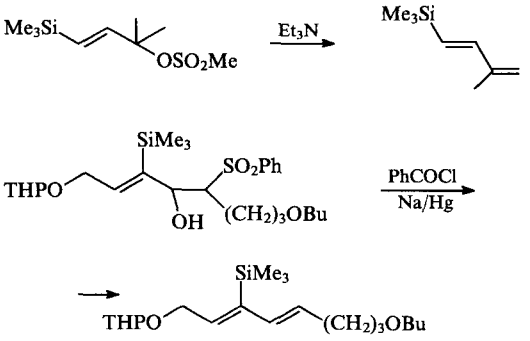
On treatment with triethylamine, the 1,2- and 1,4-dehydrohalogenation of unsaturated silicon-containing sulfones takes place at room temperature.[124–127] The 1,3-dienyl sulfones obtained under these conditions have the (*E*, *E*)-configuration.[128]



The 1,2-elimination of diphenylphosphonic acid takes place readily on treatment with butyllithium, lithium diisopropylamide,[129,130] or sodium hydride.[131]

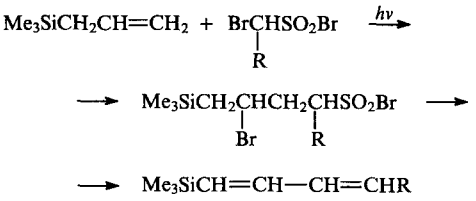


Examples of the synthesis of silicon-containing dienes as a result of the elimination of organic sulfonic acid from the corresponding esters[112] or sulfones[132] are known.



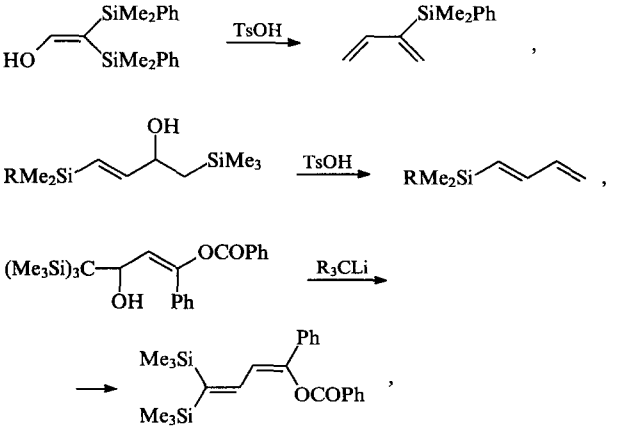
THP = 2–tetrahydropyranyl.

Block[133,134] proposed a novel method of synthesis of silicon-containing 1,3-diene hydrocarbons from readily available allylsilanes, which includes a stage in which hydrogen bromide and a sulfonic acid are eliminated.

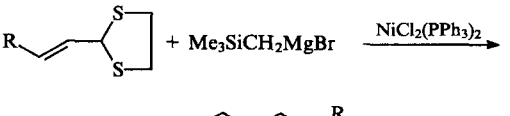


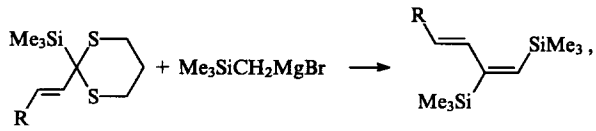
The replacement of triethylamine by 1,5-diazabicyclo [4.3.0]nonene does not affect the yields and the stereochemical result of the reaction. The employment of lithium or caesium *tert*-butoxide lowers somewhat the stereoselectivity of the reaction.[134]

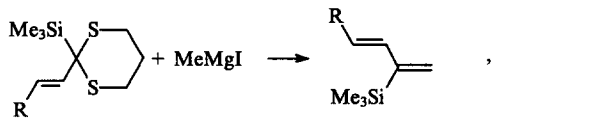
The synthesis of silicon-containing dienes as a result of the 1,2- or 1,4-elimination of silanols (on treatment with toluene-*p*-sulfonic acid[19,111,112,135] or bases[136])

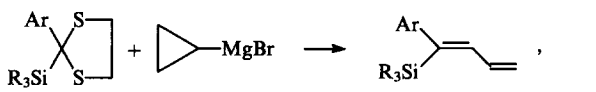


or of thiols from the products of the interaction of organomagnesium compounds with unsaturated dithioacetals[136,137]





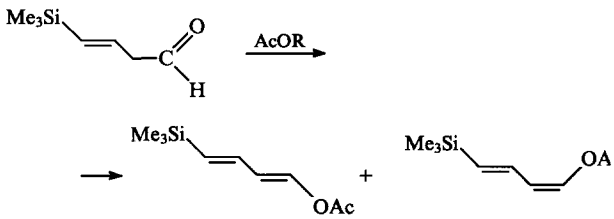




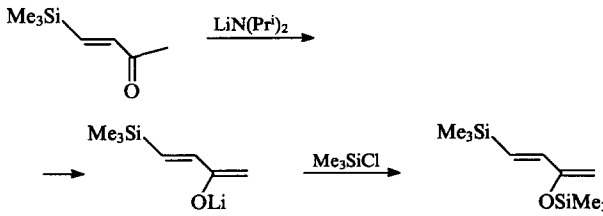
formally also belongs to the group of methods considered.

4. Isomerisation and ring opening

The keto – enol tautomerisation of silicon-containing aldehydes [138] and ketones [139,140] with subsequent fixation of the enol structure in the form of the corresponding ene-ethers has been widely used in the synthesis of acyloxy- and siloxy-buta-1,3-dienes. [112,138–141] Esters or anhydrides of the corresponding carboxylic acids may be used as the fixation reagents.

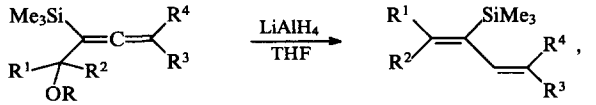


Siloxy-derivatives with a similar structure are obtained by treating an enolate (synthesised from a α,β-unsaturated ketone and lithium diisopropylamide [112] or dimethyllithium cuprate [142]) with chlorotrimethylsilane. [112]

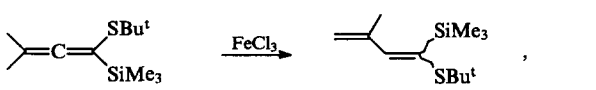


An instance of the photoinitiated isomerisation of non-conjugated unsaturated trialkylsilyl ketones to the conjugated ketones has also been described. [143]

The base-catalysed reactions of allene alcohols [144] and ethers, [145] i.e.

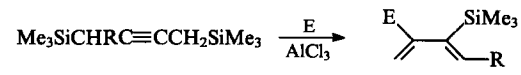


as well as the isomerisation of silicon-containing allenyl sulfides under the influence of $FeCl_3$, [146] i.e.

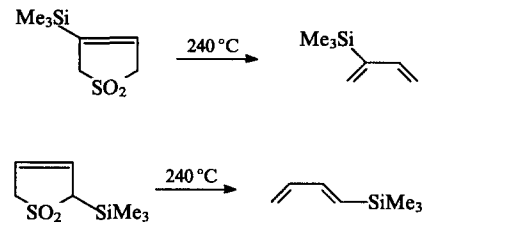


lead to the corresponding derivatives of silicon-containing 1,3-diene hydrocarbons. In certain cases, the base-catalysed isomerisation is combined with subsequent silylation. [144]

A novel method of synthesis of 2-trialkylsilylalka-1,3-dienes from the corresponding 1,4-bis(trialkylsilyl)alk-2-ynes is used in the treatment of an ethyne substrate by an electrophile (E = acetone, isobutyraldehyde, or trifluoroacetic acid) in the presence of anhydrous aluminium chloride. [147] The reaction involves a stage with a 1,2-shift of the trimethylsilyl group.

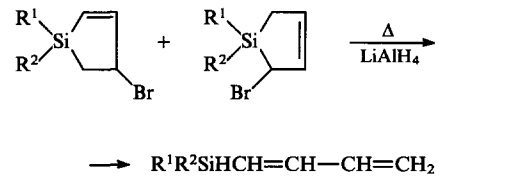


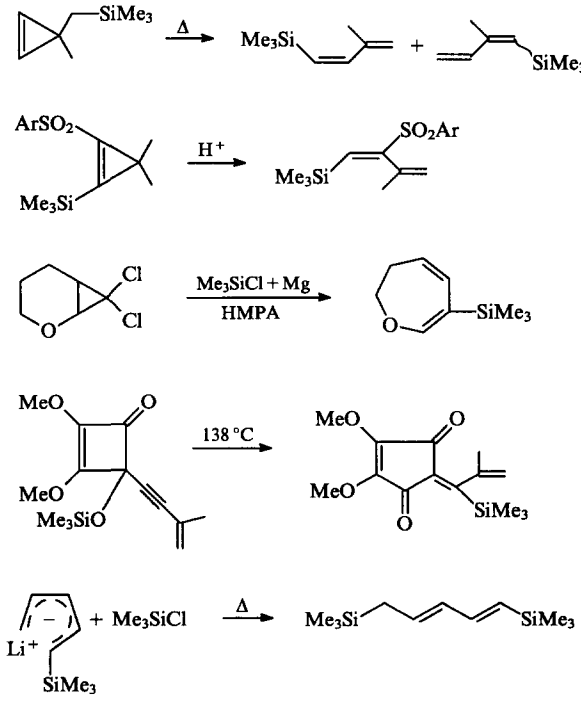
Pyrolysis of silicon-containing sulfolenes can also be included in the group of methods involving the isomerisation of the starting materials. This entails the cleavage of the heterocycle with formation of 1- or 2-trialkylsilylbuta-1,3-dienes, depending on the position of the trialkylsilyl group. [148–150]



Mono- and di-alkyl-substituted silicon-containing sulfolenes afford mixtures of isomeric dienes under these conditions. [151]

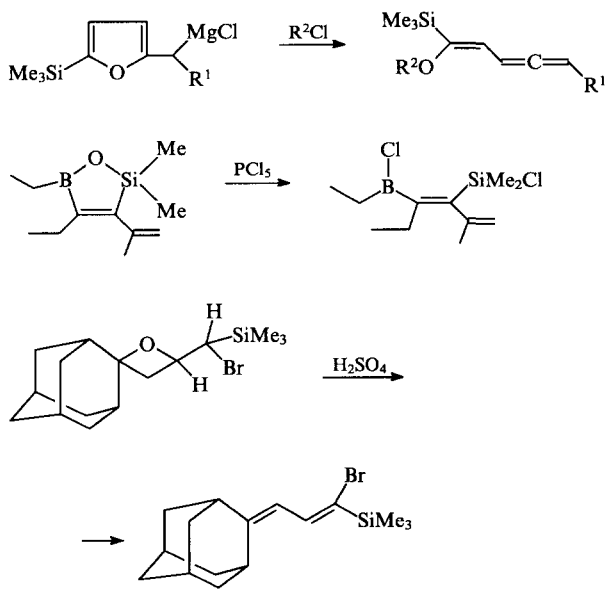
Pyrolysis of silacyclopentenes and silacyclopentadienes ultimately also leads to silicon-containing alka-1,3-dienes. [152–156]





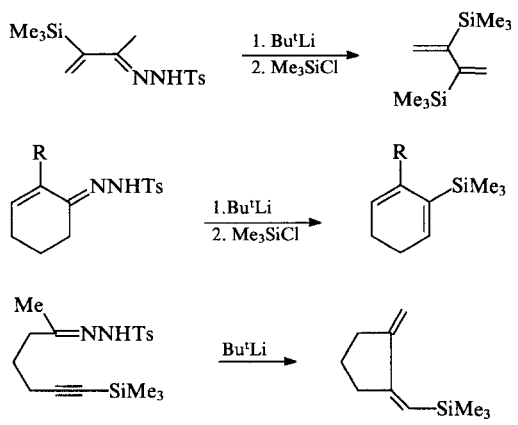
The methods of photochemical synthesis of silicon-containing 1,3-diene hydrocarbons and their derivatives are of interest.[162-165]

The opening of oxygen-containing heterocycles has been investigated only for isolated examples and has nowadays hardly any preparative interest.[166-169]

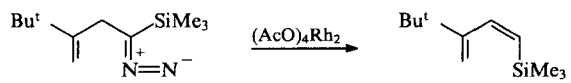


5. Synthesis of silicon-containing 1,3-diene hydrocarbons by the decomposition of tosylhydrazones or diazo-compounds

On treatment with lithium alkyls, tosylhydrazones decompose even at low temperatures with formation of the corresponding organolithium compounds, which give rise to the corresponding silicon-containing 1,3-diene hydrocarbon on interaction with trialkylchlorosilanes.[170-172]

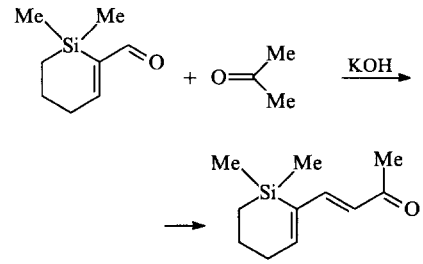


A stereoselective synthesis of (1*Z*)-isomers has been developed on the basis of the decomposition of the available aliphatic diazo-compounds by dirhodium-tetraacetate.[173]

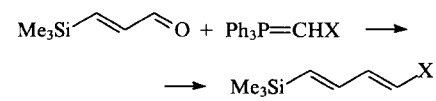


6. Methods for the construction of 1,3-diene fragments

In the synthesis of 1,3-diene fragments, the most important methods are those which presuppose their construction from simpler synthetic units. The corresponding reactions can occur as the condensation of two vinyl fragments, including silicon-containing fragments, or as the interaction of two fragments with the simultaneous formation of one or two double bonds. Owing to the low availability and the characteristic features of the spectra of α,β-unsaturated silicon-containing aldehydes and ketones, the latter are hardly used in the synthesis of silicon-containing 1,3-diene hydrocarbons and their derivatives. However, an example of the preparation of a ketone by the reaction of the corresponding aldehyde with acetone is known.[8] It was subsequently used in the synthesis of a sila-analogue of retinol.



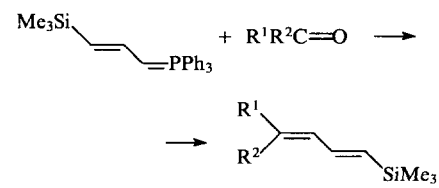
The Wittig reaction and its phosphonate (the Horner–Emmons reaction) and silyl (the Peterson reaction) modifications constitute nowadays a well developed method of synthesis of silicon-containing 1,3-dienes and their derivatives. The Wittig method was first applied in the synthesis of carbofunctional derivatives of silicon-containing 1,3-diene hydrocarbons in 1971 in the reaction of silicon-containing α,β-ethene aldehydes with phosphoranes.[174]



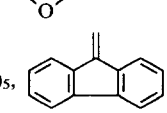
X = COMe, COOMe, CN.

It was later shown that the replacement of ether or THF, in which the Wittig reaction was usually carried out, by hexane simplifies significantly the purification and tends to increase the yield of the target products. (*Z*)- and (*E*)-aldehydes were introduced into the reaction.[175] The ethene fragment formed as a result of the condensation has predominantly or exclusively the (*E*)-configuration.[174-178] The introduction of a chlorine atom into the α-position relative to the silicon atom of the carbonyl component does not affect the yield and stereochemical result of the synthesis.[179]

An alternative version of the Wittig reaction, involving the interaction of a silicon-containing allylphosphorane with aldehydes and ketones, can also be used to obtain 1-trialkylsilylalka-1,3-dienes and their derivatives.[180,181]

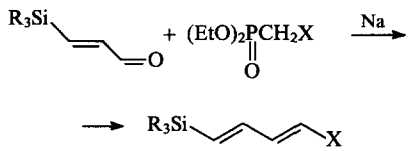


R^1 = H; R^2 = C_6H_{13}, PhCH=CH, 4-$NO_2C_6H_4$, 4-MeC_6H_4, ;

R^1 = R^2 = Me, Ph; R^1 = R^2 = $(CH_2)_5$, .

In such cases, the configuration of the 1,2-double bond does not change and the configuration of the newly formed ethene fragment depends in a complex manner on the structure of the carbonyl component and consists to the extent of 50% – 100% of the (*E*)-isomer.[181] The yields of the target products are 70% – 90%.

Judging from the available data, the phosphonate modification of the phosphorane synthesis (the Horner – Emmons reaction) also gives rise to satisfactory results in the synthesis of silicon-containing 1,3-diene compounds.[175,182-184]

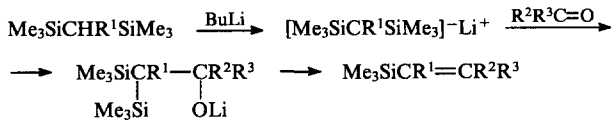


X = COOMe, COMe, CN.

The configuration of the double bond at the silicon atom does not change, as in the Wittig reaction, while the newly formed bond has predominantly the (*E*)-configuration. In the synthesis of ketones, the stereoselectivity of the reaction is higher when the Wittig method is used, while that of the reaction in the synthesis of nitriles is higher when the Horner – Emmons method is employed.[175]

The silyl modification of the Wittig reaction (the Peterson reaction) can be achieved in two ways: (1) by the reaction of the carbanions obtained from bis(trialkylsilyl)methanes with α,β-ethene aldehydes[11,136,185-188] and (2) by the reaction of the mesomeric carbanion of 1,3-bis(trialkylsilyl)prop-1-ene with carbonyl compounds (Scheme 2).[189-192]

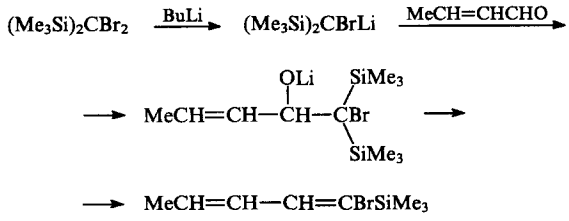
Scheme 2



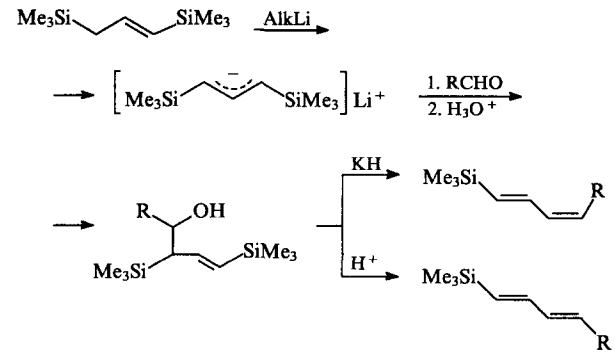
R^2 or R^3 = CH =CHX.

The carbanions needed in this reaction may be obtained also by the addition of lithium alkyls to 1,1-bis(trimethylsilyl)alk-1-enes.[185]

The interaction of dibromobis(trimethylsilyl)methane in succession with butyllithium and crotonaldehyde leads to a satisfactory yield of 1-bromo-1-trimethyl-silylpenta-1,3-diene [a mixture of the (1*E*)- and (1*Z*)-isomers in proportions of 2:1].[193]



A second version of the Peterson reaction in the synthesis of silicon-containing 1,3-diene hydrocarbons and their derivatives also includes a stage with formation of a carbanion and its condensation with the carbonyl compound.[118,189-192,194,195]



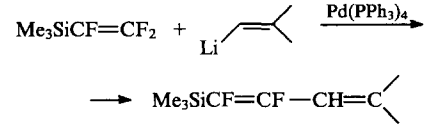
The stereochemical result of the reaction is determined by the nature of the silanol reagent split off.[189,192] In the presence of potassium hydride, the ethene fragment formed has predominantly the (*Z*)-configuration (60% – 90%) and in an acid medium the (*E*)-configuration (90%). The addition of magnesium bromide or trimethoxyboron to the reaction mixture reduces the stereoselectivity of the condensation and the isomer ratio *E,E*: *E,Z* is (60 – 70) : (40 – 30).[192] In the presence of silicates, (1*E*,3*E*)-trialkylsilylalka-1,3-dienes [R = H, Me, Bu^i, iso-C_5H_{11}, C_6H_{13}, Ph, $Ph(CH_2)_3$, $(CH_2)_nCH=CH_2$, n = 3,4] are formed exclusively;[190] in the presence of dicyclopentadienyltitanium chloride, the stereochemical result depends on the nature of the reagent promoting the elimination of trialkylsilanol. In an acid medium (sulfuric acid in THF), the (1*E*,3*E*)-isomers are formed exclusively, while on treatment with KF in THF the exclusive products are the (1*E*,3*Z*)-isomers.[191]

The data presented show that, in the synthesis of the (1*E*,3*E*)-isomers, preference should be given to the methods involving the Wittig or the Horner – Emmons reaction, while in the synthesis of the (1*E*,3*Z*)- or (1*Z*,3*Z*)-isomers the second version of the Peterson reaction is preferable.

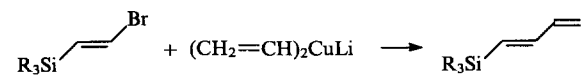
7. Organometallic synthesis

All the known methods including a stage in which a new carbon – carbon bond is formed with participation of classical organometallic compounds containing metal – carbon σ-bonds and the methods of synthesis of 1,3-diene structures as a result of the reacitons of unsaturated (including silicon-containing) compounds in the presence of metal complex catalysts are combined in this group. These reactions presuppose the formation of organometallic compounds of transition metals with classical or donor – acceptor carbon – metal bonds as an obligatory stage.

Organolithium α,β-ethene compounds do not alkenylate β-halovinylsilanes under the usual conditions. However, it is known that, in the presence of a palladium catalyst, trimethylperfluorovinylsilane reacts with vinyllithium to form the corresponding 1,3-dienes.[196-199]



Lithium vinylcuprates react similarly with β-bromovinylsilanes.[200]

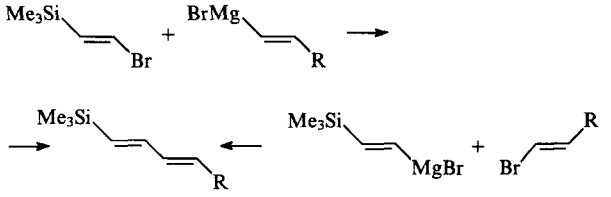


The interaction of vinylcuprates with halovinylsilanes afforded not only the corresponding silicon-containing 1,3-diene hydrocarbons but also their halo-[201] and amino-derivatives.[202]

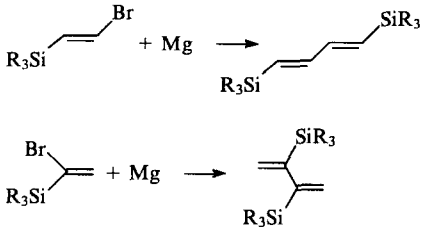
Mixed organomagnesium α,β-ethene compounds (the Norman reagent) interact with the corresponding vinyl halides also only in the presence of nickel and palladium complexes — $Ni(dppm)_2Cl_2$,[203,204] $Ni(dppe)_3Cl_2$, $Ni(dppp)_2Cl_2$,[205,206] $Ni(acac)_2AlMe_3$,[207] $NiCl_2(PPh_3)_2$,[136] and $PdCl_2(PPh_3)_2$,[203,204] where dppm = $Ph_2PCH_2PPh_2$, dppe = $Ph_2PCH_2CH_2PPh_2$, and dppp = $Ph_2PCH_2CH_2CH_2PPh_2$.

Both possible combinations have now been tested: organosilicon bromide–vinyl-magnesium halide and silicon-containing organomagnesium compounds–vinyl halide.

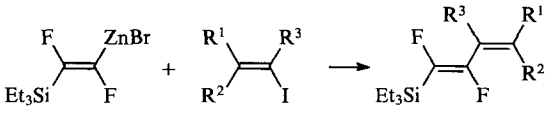
The stereoselectivity of the reaction in the synthesis of the (*E*, *E*)-isomers is about 90%[204] and in the synthesis of the (*E*, *Z*)-isomers it is somewhat lower (in the range 70%–80%).[203]



The 1,4- and 2,3-bis(trimethylsilyl)buta-1,3-dienes have been synthesised from the corresponding bromovinylsilanes and metallic magnesium without the preliminary preparation of the corresponding organomagnesium compounds.[208]



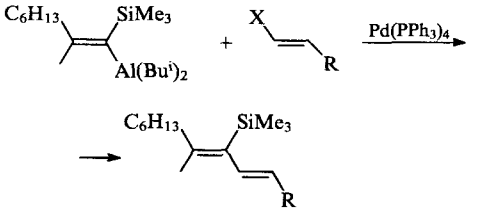
Mixed α,β-unsaturated organozinc compounds stereoselectively alkenylate vinyl halides in the presence of a palladium catalyst [$Pd(PPh_3)_4$[209,210] or $PdCl_2(PPh_3)_2$[211–213]].



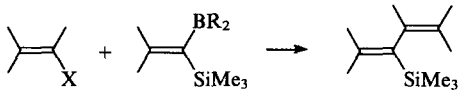
The target silicon-containing 1,3-diene hydrocarbons are obtained in satisfactory yields (80%–90%).

α,β-Unsaturated or organoaluminium compounds also react readily and stereospecifically with vinyl halides. The reaction is catalysed by the palladium complex $Pd(PPh_3)_4$.[199,214]

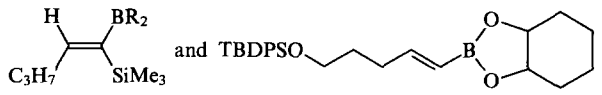
It has been shown in relation to 2-bromo-1-trimethylsilylethenes[214] that the (*E*)-isomer is more reactive than the (*Z*)-isomer.



In the presence of tetrakis(triphenylphosphine) palladium, α,β-unsaturated boranes interact with vinyl halides [CH_2=$CH(CH_2)_2$.CH(OBz)CH=CBr($SiMe_3$), Me_2C=$CHBr$, CH_2=$CHCH_2CH$(OBz)CH=CI($SiMe_3$)] to form the corresponding silicon-containing conjugated dienes.[215–217]

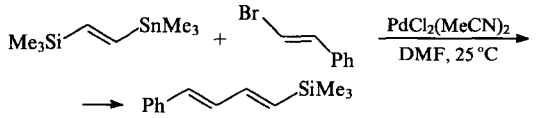


The boron-containing reagents investigated were

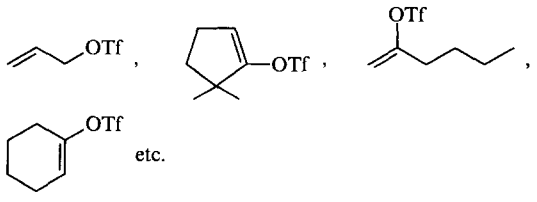


TBDPS = *tert*-butyl diphosphite-silane.

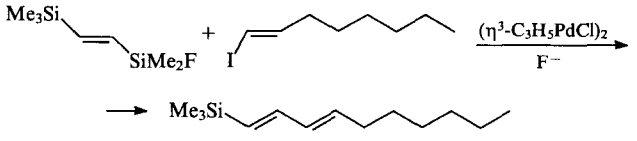
α,β-Unsaturated stannanes alkenylate vinyl halides under the conditions of the Stille reaction.[218]



The advantage of this method is manifested in the interaction of unsaturated stannanes with functional derivatives of vinyl halides containing as substituents groups which are reactive in relation to organolithium, organomagnesium, or organoaluminium compounds. Triflates can be used instead of halides.[219–223]



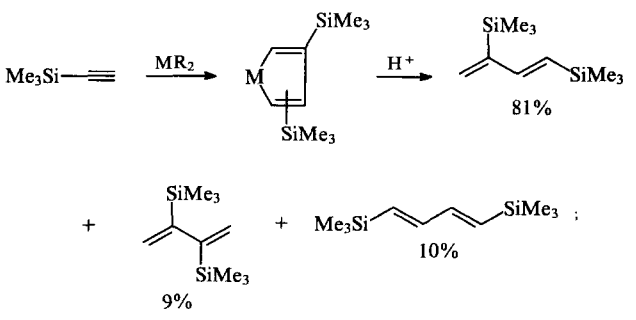
The ability of vinylsilanes to function as alkenylating agents in the synthesis of the corresponding silicon-containing 1,3-diene hydrocarbons has been recently discovered.[224]



The successful occurrence of this reaction requires fluoride anion donors [in the study quoted, the donor employed was tris(diethylamine)sulfenyl difluorotrimethylsilicate (TASF)]. Bis(trimethylsilyl)ethene does not react with vinyl iodides.

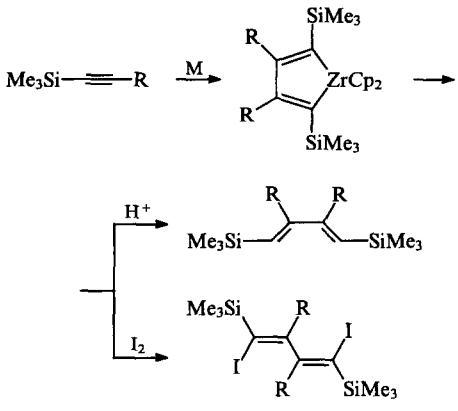
8. Dimerisation of ethynes and their codimerisation with ethenes catalysed by transition metal complexes

On interaction with zirconium complexes [Cp_2ZrPh_2, $Cp_2Zr.(CH_2$=$CH)_2$,[225] $Zr(C_5Me_5)_2MeB(4\text{-}FC_6H_4)_4$[226]], trialkylsilylethynes afford 1,3-diene complexes of zirconium, the proto-demetallation of which gives rise to the corresponding silicon-containing 1,3-diene hydrocarbons, for example:



M = Cp_2Zr.

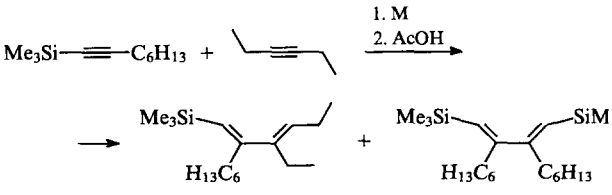
Disubstituted silylethynes behave similarly in this reaction.[227-229]



M = Cp_2ZrCl_2.

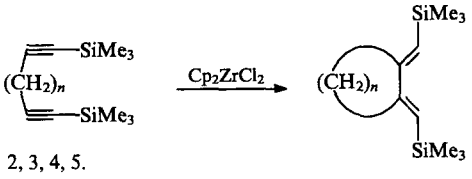
Zirconium compounds have been used as catalysts: Cp_2Zr(4-Me_2NPy).Z (Z = THF or CH_2=CHEt), Cp_2ZrCl_2,[229] and Cp_2ZrHCl,[227] while the demetallating agents were organic acids or iodine.

The codimerisation of disubstituted silylalkynes and dialkylethynes[227,228] leads to a cross-dimer and a dimer of the silicon-containing alkyne in proportions of 1:1.



It is striking that the 'head to head' principle operates in all cases in the dimers.

Nonconjugated silicon-containing alkenynes behave in this reaction as disubstituted ethynes,[230] while nonconjugated diethynes give rise to the corresponding cycloalkanes with conjugated endocyclic double bonds.[231-233]

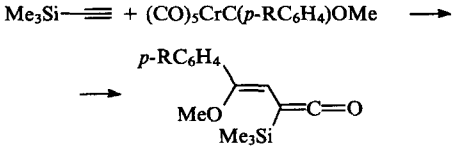


n = 2, 3, 4, 5.

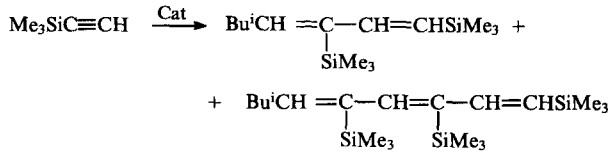
Nonconjugated diynes react similarly also in the presence of the palladium complexes $Pd_2(DBA)_3$[234] and $PdCl_2Py$.[235]

The codimerisation of nonconjugated alkenynes with bis-(trimethylsilyl)ethyne in the presence of a cobalt catalyst leads to silicon-containing cyclohexadienes.[236]

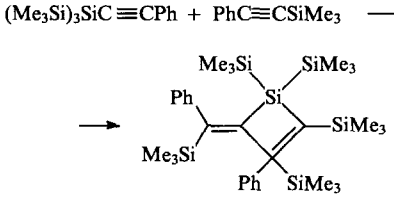
The interaction of trialkylsilylethynes with the pentacarbonyl[aryl(methoxy)carbene]chromium complexes $(CO)_5CrC.(p\text{-}RC_6H_4)OMe$ (R = H, Me, OMe, CF_3) proceeds in a more complex manner. The silylketenes formed indicate the involvement of the ligands forming part of the complex in the construction of the reaction product.[237,238]



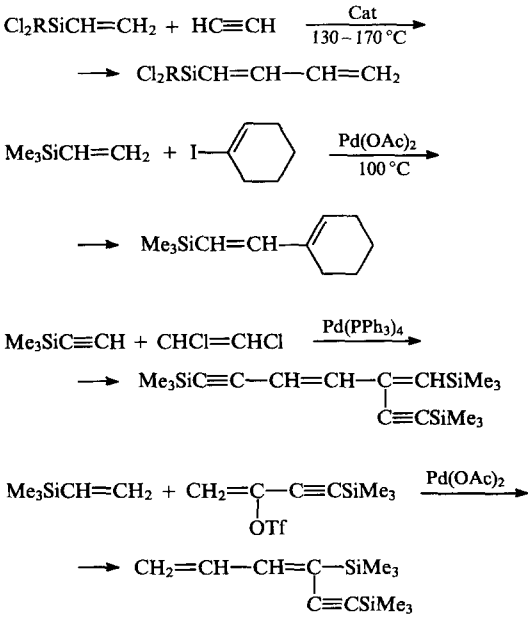
The use of trialkylaluminium complexes[72,239] or the complexes of these compounds with metal chlorides [$Bu^i_3Al.MX_n$, where MX_n = $TiCl_4$, $VOCl_3$, $VO(acac)_2$, VCl_3, $NbCl_5$, $CrCl_3$, $MoCl_3$[240]] as catalysts of the dimerisation of silylethynes leads to the formation of a mixture of the corresponding dimers and trimers, the proportions of which are determined by the nature of the catalyst.



The codimerisation of silylethynes in the presence of $Ni(PEt_3)_4$ gives rise to conjugated dienes, one of the double bonds of which is in the silacyclobutene ring.[241]



The codimerisation of vinylsilanes with ethyne (catalysts — Pd/Al_2O_3, $Pd/CaCO_3$, Pd/C, or Pt/Al_2O_3[242,243]), haloalkenes,[244,245] or triflates[244] [catalysts — $Pd(OAc)_2$ or $Pd(PPh_3)_4$] leads to 1- or 2-silylalka-1,3-dienes.



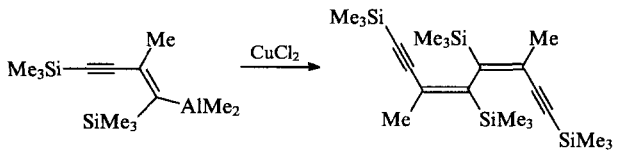
The reactions proceed as a rule under relatively severe conditions and the yields of the target products are low.

9. Other methods

A convenient preparative method of synthesis of disilylated alka-1,3-dienes involves the cleavage of the silylalkenyl derivatives of mercury,[246] silicon,[247] or aluminium[248] catalysed by transition metal compounds.

$$(Me_3SiCH{=}CH)_2Hg \xrightarrow{Pd(PPh_3)_4} Me_3SiCH{=}CH{-}CH{=}CHSiMe_3$$

$$K(Me_3SiCH{=}CHSiF_2) \xrightarrow{Ag\ or\ Cu} Me_3SiCH{=}CH{-}CH{=}CHSiMe_3$$



The catalytic reduction of ethynes with participation of hydrosilanes,[249-251] boranes,[252] or hydrogen[253] also leads to the formation of the corresponding alka-1,3-dienes, for example:

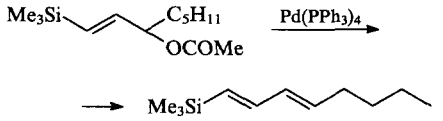
$$PrC{\equiv}CH + R_3SiH \xrightarrow{Cat} CH_2{=}CPr{-}CPr{=}CHSiR_3,$$

Cat = $Ni(acac)_2 \cdot AlEt_3$, $Ni(acac)_2 \cdot LiAlH_4$.

$$Me_3SiC{\equiv}CH + H_2 \xrightarrow{Cat} Me_3SiCH{=}CH{-}CH{=}CHSiMe_3,$$

Cat = $[(PPh_3)FeHX_2]BPy_4$.

Several examples of the synthesis of silicon-containing diene hydrocarbons and their aliphatic[254] and alicyclic[255,256] derivatives as a result of the [2+4]-cycloaddition reactions and subsequent isomerisation of the cyclic adducts as well as the β-elimination of carboxylic acids from the corresponding silicon-containing esters under the influence of a palladium catalyst[257,258] have been described.



Finally a comparatively interesting method of synthesis of 1-trialkylsilylalka-1,3-dienes has been developed by Japanese workers on the basis of the chromium(II) chloride-catalysed interaction of dibromomethyltrimethylsilane with cinnamaldehyde and its analogues.[259]

$$RCH{=}CH{-}CH{=}O + Me_3SiCHBr_2 \xrightarrow{CrCl_2} RCH{=}CH{-}CH{=}CHSiMe_3$$

The reaction takes place at room temperature and the yields of the dienes are ~80%.

III. Chemical properties of 1- and 2-triorganosilylalka-1,3-dienes and their derivatives

The chemical reactions of 1- and 2-triorganosilylalka-1,3-dienes and their carbofunctional derivatives known at the present time may be divided into three groups: (1) reactions with participation of multiple bonds — addition, polymerisation, and complex formation reactions; (2) reactions with participation of silicon–carbon bonds; (3) reactions with participation of functional groups.

The mode and selectivity of the addition of reagents of different nature are known to depend in a complex manner on the structure of the 1,3-dienes, their polarity, and their polarisability.[260] The study of the characteristic features of the variation of their reduction half-wave potentials,[56,208] the parameters of Raman and IR spectra,[175,261,262] as well as the bond lengths[263] and the enthalpies of formation of the bonds[264] on passing from 1,3-diene hydrocarbons and their derivatives to silicon-containing compounds with a similar structure permitted the conclusion that silicon-containing substituents at the double bond are weaker electron-donating agents than the analogous hydrocarbon groups. The measured molecular refractions indicate the high polarisability of the conjugated π-bonds in 1-trialkylsilylalka-1,3-dienes.[56,265]

Similar conclusions concerning the nature of the redistribution of electron density in silicon-containing dienes have been reached from the analysis of the ^1H and ^{13}C NMR spectra[125,175,266,267] and their dipole moments.[128,175,268]

In conformity with the existing tradition, the observed features of the electronic structure of the silicon-containing dienes have been explained by the delocalisation of the π-electron density of the multiple bonds to the unoccupied *d* orbitals of silicon ($d_\pi - p_\pi$ conjugation).

1. Addition of electrophiles

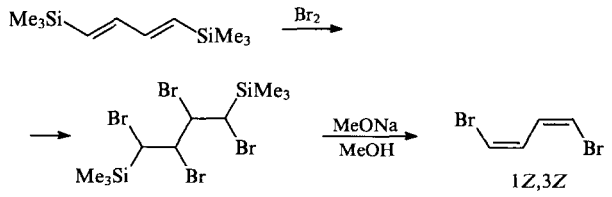
The interaction of silicon-containing 1,3-diene hydrocarbons and their derivatives with the halogens has been investigated only for reactions with bromine. Regardless of the structure of the substrates, it proceeds nonselectively in all cases. 1-Trialkylsilylalka-1,3-dienes combine with bromine at the double bond remote from the silicon atom and in the 1,4-positions,[50] the ratio of the dibromo-derivatives formed being ~1:1. On heating, the 1,4-dibromo-derivatives rearrange with migration of the double bond to the α,β-position relative to the silicon atom.

$$Me_3SiCHBrCH{=}CHCH_2Br \rightleftharpoons Me_3SiCH{=}CHCHBrCH_2Br$$

It is appropriate to recall that the allyl rearrangement of dibromo-derivatives obtained on bromination of 1,3-diene hydrocarbons is directed towards the formation of 1,4-dibromo-derivatives.[260] Silicon-containing dienes are brominated more slowly than hydrocarbons with a similar structure and the rate of reaction is described by a third-order kinetic equation.[269] The increase in the kinetic order of reaction to three is caused, according to the authors,[269] by the relative stability of the complexes $A_\pi \cdot Br_2$, where A_π is an alkene–bromine complex.

Ethyl 5-trimethylsilylpenta-2,4-dienoate also combines with bromine nonselectively at both double bonds. The 1,4-adducts were not detected.[175]

Exhaustive bromination of 1,4-bis(trimethylsilyl)buta-1,3-diene leads to the corresponding tetrabromo-derivative. On treatment with sodium methoxide in methanol, the latter affords 1,4-dibromobuta-1,3-diene in a satisfactory preparative yield.[270]



Judging from the available data,[271] the addition of the elements of hypohalites to silicon-containing 1,3-diene hydrocarbons proceeds chemo- and regio-specifically at the double bond remote from the silicon atom.

$$R^1_3SiCH{=}CH{-}CR^2{=}CHR^3 + \text{>N–X} \xrightarrow{R^4OH} R^1_3SiCH{=}CH{-}CR^2(OR^4)CHR^3X$$

X = Cl, Br.

The 1,3-diene was treated with the haloamide in an alcoholic medium.[271]

Alkyl hypohalites add to 3-*tert*-butyl-4-methyl-1-triethylsilylpenta-1,3-diene, containing a double bond subjected to a considerable steric hindrance, also only at the remote double bond.[272] This observation shows that the addition of alkyl hypochlorites and alkyl hypobromites to the double bond remote from the organosilicon substituents, which is unexpected from the standpoint of Ingold's classical ideas,[260] is due to nonsteric factors.

Organosulfenyl and organoselenyl halides also react at the double bond remote from the silicon atom with attachment of the electrophilic species to the terminal carbon atom of the 1,3-diene fragment.[120,273]

$$R^1_3SiCH{=}CH{-}CR^2{=}CHR^3 + R^4YX \longrightarrow$$
$$\longrightarrow R^1_3SiCH{=}CH{-}CR^2XCHR^3YR^4$$

X = Cl, Br; Y = S, Se.

The adducts containing mobile halogen atoms in the allylic position readily isomerise to 1,4-adducts, while on treatment with triethylamine they split off the hydrogen halide.[120,273]

On distillation, selenium-containing adducts are partly dehydrohalogenated, which hinders their isolation in a pure state.[273]

The addition of C-electrophiles has been investigated in relation to the interaction of 1-trialkylsilylbuta-1,3-dienes with chloromethyl ethers[118,274] or sulfides[142] catalysed by aprotic Lewis acids ($ZnCl_2$,[274] $ZnBr_2$,[142] $TiCl_4$[118]).

According to the data of Shikhmamedbekova and Khudieva, in the presence of zinc(II) chloride chloromethyl ether adds both in the 1,4-positions and to the double bond remote from the silicon atom in silicon-containing 1,3-diene hydrocarbons (the ratio of the adducts formed is 1:3:3).[274]

$$Me_3SiCH{=}CH{-}CH{=}CH_2 + ClCH_2OMe \xrightarrow{ZnCl_2}$$
$$\longrightarrow Me_3SiCHClCH{=}CHCH_2CH_2OMe$$
$$\longrightarrow Me_3SiCH{=}CH{-}CHClCH_2CH_2OMe$$

In the presence of titanium(IV) chloride, the interaction of dichloromethyl ether with 1-trialkylsilylalka-1,3-dienes leads to the corresponding silicon-free 1,3-diene aldehydes.[118]

$$R\!\!\sim\!\!\sim\!\!SiMe_3 + Cl_2CHOMe \xrightarrow{TiCl_4}$$
$$\longrightarrow R\!\!\sim\!\!\sim\!\!CHO$$

The possible paths in this interesting reaction are not discussed.

The reaction of 3-trimethylsiloxy-1-trimethylsilylbuta-1,3-diene with α-chlorosulfides results in the formation of the corresponding unsaturated carbonyl compounds, which presupposes the addition of the sulfide to the terminal double bond.[142]

$$Me_3Si\!\!\sim\!\!\sim\!\!OSiMe_3 + ClCHRSPh \xrightarrow{ZnBr_2}$$
$$\longrightarrow Me_3Si\!\!\sim\!\!\sim\!\!C(=O)\!\!\sim\!\!\sim\!\!R$$

R = H, Pr.

2. Addition of nucleophiles

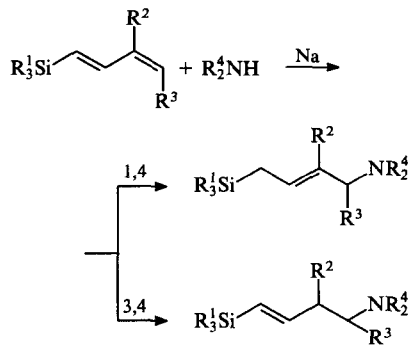
The interaction of 1-trialkylsilylalka-1,3-dienes with thiols in the presence of sodium thiolate had been described.[275] It has been shown that the reaction takes place only under severe conditions (100 °C, 70 h). The overall yield of the adducts does not exceed 20%. Chromatographic and spectroscopic analysis of the products showed that the thiol added to the 1,4-, 3,4-, and 4,1-positions (the yields of the corresponding products were 41%, 57%, and 2%).

The reactions of unsaturated organosilicon compounds with ammonia and amines are also nucleophilic addition processes, although their mechanism has not been investigated.

The attempts to add ammonia to 1-trialkylsilylbuta-1,3-dienes have not been successful: in the presence of metallic sodium, hydrogen undergoes 1,4-addition with formation of trialkylbut-2-enylsilane.[276]

Under the same conditions, secondary amines react with silicon-containing 1,3-dihydrocarbons, giving rise to mixtures of 1,4- and 3,4-adducts (~2:3) (Scheme 3).[277]

Scheme 3



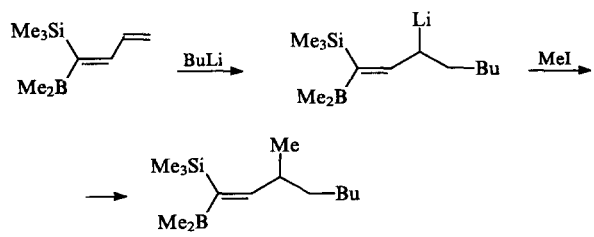
The methyl group in the 3-position promotes addition in the 1,4-positions. The same group at the C(4) atom hinders the addition, but hardly affects the ratio of the isomeric products.[277]

The interaction with organometallic compounds was first achieved by Sadykh-Zade[278] in relation to the reaction of 1-trimethylsilylbuta-1,3-diene with butyllithium.

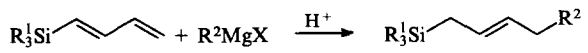
According to the author, the silicon-containing hydrocarbon obtained after demetallating the adduct with water had the structure of *trans*-1-trimethylsilyloct-2-ene. It was established somewhat later that silicon-containing alka-1,3-dienes are formed after the demetallation of a mixture of alk-1-enes and alk-2-enes.[279] The ratio of the isomers formed hardly depends on the structure of the 1,3-diene fragment. It is not possible to isolate the adducts in the reactions of 1-trialkylsilyl-3-methylbuta-1,3-diene with lithium alkyls: regardless of the structure of the organolithium compounds and the experimental conditions, the diene polymerises.[279]

It is also noteworthy that the decrease in temperature and the replacement of the ether employed as the solvent by THF in the reactions of 1-trialkylsilylbuta-1,3-diene and 1-trialkylsilylpenta-1,3-diene promotes the formation of 1,4-adducts. In hydrocarbon solvents, the dienes polymerise.

Judging from the available data, 1-dimethylboryl-1-trimethylsilylbuta-1,3-diene combines with butyllithium at the double bond remote from the silicon atom. The adducts formed are readily alkylated.[37]



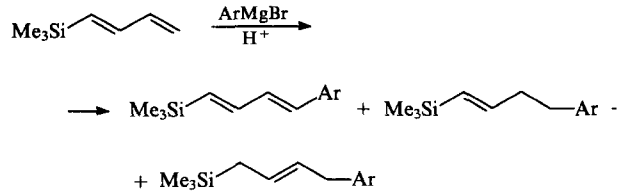
Mixed organomagnesium compounds add to 1-trialkylsilylbuta-1,3-dienes exclusively in the 1,4-positions.[280]



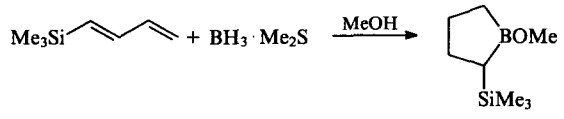
R^1 = Me, Et; R^2 = Et, Pr.

A change in temperature from −25 to 35 °C and of the solvent (Et_2O, glyme, THF) did not affect the mode of the reaction and the yield of its products.

On interaction with 1-trimethylsilylbuta-1,3-diene in the presence of transition metal complexes, arylmagnesium halides give rise to a mixture of products of substitutional arylation of the products of addition to the double bond and in the 1,4-positions.[281]



On interaction with 1-trimethylsilylbuta-1,3-diene, borane stabilised by trimethylsulfide gives rise to a cyclic adduct. The latter affords a satisfactory yield of (±)-1-methoxy-2-trimethylsilylborolane on treatment with methanol.[282]

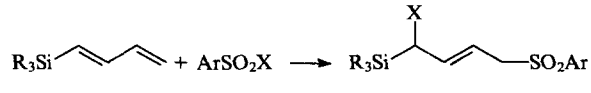


3. Free-radical addition

The free-radical addition of thiols has been investigated only in relation to the interaction of 1-triethylsilylbuta-1,3-diene with ethanethiol. *tert*-Butyl peroxide was used as the initiator.[275] As in nucleophilic addition reactions, a mixture of 1,4-, 4,1-, and 3,4-adducts is formed in this process in proportions of 65 : 10 : 25.[275]

The interaction of organic sulfonic acids with acid halides, initiated by copper(I) halides (the Asher – Vovsi reaction) or thermally, is also included among the free-radical addition reactions.

It has been shown in relation to the reactions of 1-methyldiethylsilylbuta-1,3-diene that benzenesulfonic acid chloride adds to the above 1,3-diene on heating in the presence of the Asher – Vovsi catalyst — copper(I), triethylamine, and acetonitrile — exclusively in the 1,4-positions;[126] the reaction with the acid bromide proceeds also without a catalyst. The addition of the latter does not alter the mode of reaction. The acid iodide adds spontaneously and exothermically even at room temperature and also only in the 1,4-positions.



R_3Si = Me_3Si, $MeEt_2Si$, Et_3Si;

Ar = Ph, *p*-MeC_6H_4, *p*-$NO_2C_6H_4$; X = Cl, Br, I.

Toluene-*p*-sulfonic and *p*-nitrobenzenesulfonic acids behave similarly in this reaction.[124] The chlorides of methane- and ethane-sulfonic acids react with 1-trialkylsilylbuta-1,3-diene under more severe conditions to form a mixture of 1,4- and 3,4-adducts.[124,125] It is of interest that 5,5-dimethylhexa-1,3-diene, a hydrocarbon with a similar structure, combines with the chlorides of alkane- and arene-sulfonic acids under milder conditions exclusively in the 1,4-positions.[124] Specially formulated experiments established that the 1,4-adducts do not isomerise to the 3,4-adducts on heating in the presence of the Asher – Vovsi catalyst.[124]

Within the limits of the accuracy of the method of competing reactions, the rate of addition is almost independent of the nature of the aromatic group (phenyl, *p*-tolyl, and *p*-nitrophenyl) attached to sulfur.[124] Variation of the alkyl groups at the silicon atom (R_3Si = Me_3Si, $MeEt_2Si$, Et_3Si) also does not affect the rate and mode of the reaction.[125]

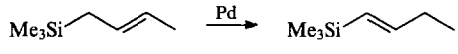
1-Methyldiethylsilyl-3-methylbuta-1,3-diene reacts with the chlorides of alkane- and arene-sulfonic acids with much more difficulty than dienes without substituents in the 1,3-diene fragment.[127] A mixture of the 1,4- and 3,4-adducts and of the product of substitutional sulfonylation — 4-alkanesulfenyl-1-methyl diethylsilyl-3-methylbuta-1,3-diene (~10%) — has been obtained in an overall yield not exceeding 25%. Attempts to carry out the reaction of this silicon-containing diene with the chlorides or bromides of arenesulfonic acids were unsuccessful: the initial reactants which failed to react are recovered at low temperatures while at high temperatures charring takes place.

1-Trialkylsilylpenta-1,3-diene behaves similarly in the reaction with arene-sulfonyl halides.[127]

The above data combined with those obtained in the study of the influence of the nature of the catalyst components (metal, ligands) and the solvent (benzene, toluene, acetone, dibutyl ether, carbon tetrachloride, acetonitrile, chloroform, pyridine, methanol, dimethyl sulfoxide, hexamethylphosphoramide)[283] enabled the author to conclude that the thermally initiated addition of the bromides and iodides of sulfonic acids proceeds as a classical free-radical chain process.[282] The addition of the acid chlorides and bromides with participation of copper salts is a redox-initiated intracomplex reaction of the ligands in which the 1,3-diene participates as a bidentate ligand. In those cases where the interaction requires relatively high temperatures, the reagent – metal – diene complex decomposes and the reaction proceeds as the usual redox-initiated free-radical addition with formation of a mixture of the 1,4- and 3,4-adducts.[283]

4. Reduction and oxidation of 1- and 2-triorganosilylalka-1,3-dienes

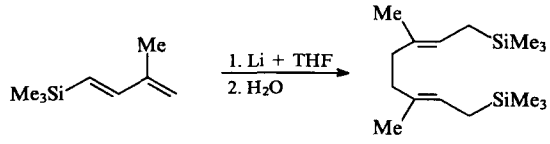
The catalytic hydrogenation of 1-trialkylsilylalka-1,3-dienes in the presence of platinum or palladium catalysts proceeds at room temperature and at atmospheric pressure with formation of a mixture of 1-triorganosilylalk-1-enes and 1-triorganosilylalk-2-enes.[41,42,284] The study of the composition of the hydrogenation products as a function of time has shown that 1-trialkylsilylalk-2-enes predominate in the mixture in the first stage, while 1-trialkylsilylalk-1-enes predominate in the concluding stage.[284] These results indicate that the alk-2-enes isomerise in the course of time with migration of the double bond towards the silicon-containing substituent.



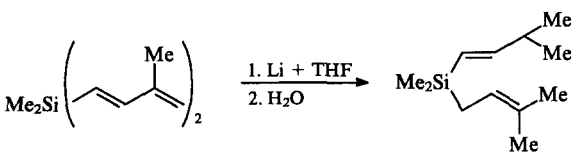
Under the same conditions in the presence of a palladium catalyst, 1,2-bis(trialkylsilyl)alka-1,3-dienes also combine with hydrogen in the 1,4-positions with formation of 1,2-bis-(trialkylsilyl)but-2-enes, which are not apparently hydrogenated further owing to steric factors.[52,53]

Exhaustive hydrogenation of 1-trialkylsilylalka-1,3-dienes and their functional derivatives in the presence of $Pd/CaCO_3$ or Pt/C afforded the corresponding saturated organosilicon compounds.[41,42,242,274]

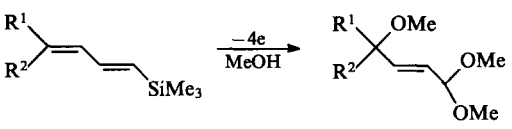
The interaction of 1-trimethylsilyl-3-methylbuta-1,3-diene with lithium in an aprotic medium results in the formation of hydrodimerisation products.[285]



Under the same conditions, dimethylbis(3-methylbuta-1,3-dienyl)silane is hydrogenated in the 1,4- and 3,4-positions.[285]



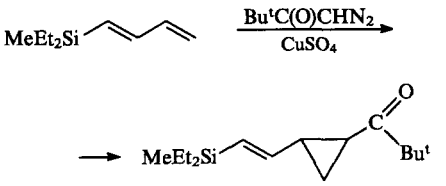
There is only one communication which describes results of the electrochemical oxidation of 1-trialkylsilylalka-1,3-dienes in methanol.[194]

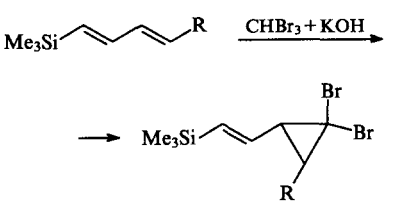


The reaction proceeds as the addition of methoxyl radicals accompanied by the substitution of the silyl group.

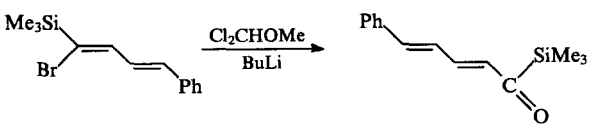
5. Cycloaddition reactions

The interaction with carbenes — [1+2]-cycloaddition — has been used as a method of synthesis of the corresponding alkenylcyclopropanes also in relation to silicon-containing dienes. Thus it is known that pivaloylcarbene[286] and dibromocarbene[22] add chemoselectively to the double bond of 1-trialkylsilylbuta-1,3-dienes remote from the silicon atom.





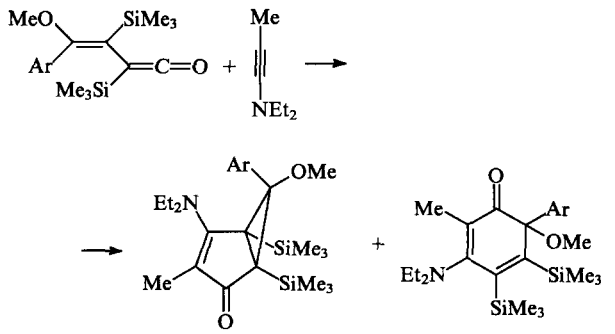
However, in the interaction of 1-bromo-4-phenyl-1-trimethylsilylbuta-1,3-diene with methoxymethylenecarbene a silicon-containing ketone was obtained instead of the expected cyclic adduct.[287]



The [2+2]-cycloaddition in the interaction of disilylated ketenes with 1-diethylaminoprop-1-yne takes place nonselectively (Scheme 4).[254]

Diene synthesis {[2+4]-cycloaddition} — the interaction of conjugated silicon-containing dienes with dienophiles — is one of the most thoroughly investigated reactions of 1- and 2-trialkylsilylalka-1,3-dienes and their derivatives. A considerable proportion of the studies in this field have been carried out in order to demonstrate the 1,3-diene structure of the silicon-containing

Scheme 4



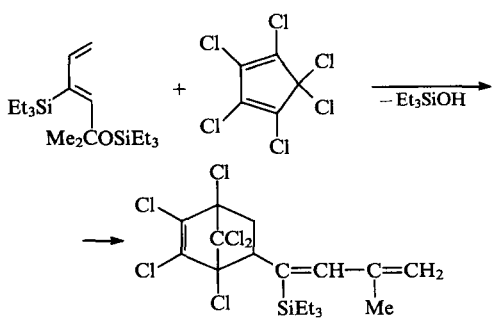
compounds (see, for examples, Refs 6, 27, 52, 109, 129, 175, 208, 249, 274, etc.). However, the studies of the influence of the structure of the diene and the dienophile on the relative rates and the regio- and stereo-selectivity of the ring formation are of greater interest.[18,170,177,288-290] Diene synthesis is also a key stage in the multistage synthesis of compounds such as (±)-daunomycin, (±)-isodaunomycin[139,140,289,291,292] the aglucone of chlorotricin,[216] the agilactones A and F,[293] and other complex polycyclic biologically active substances.[20,93,216,217,289,294,295]

The importance of this aspect increased sharply after the development of methods for the protodesilylation (the removal of the silyl protecting group) of the cyclic adducts by potassium fluoride[20,160,209,296,297] and especially for the replacement of the triorganosilyl group by hydroxy-groups on treatment of silicon-containing compounds with lead(IV) tetraacetate[170,291,298] or perfluorotetraacetate.[140]

Diene synthesis with participation of organosilicon 1,3-diene compounds was first carried out in 1954 by heating a mixture of the products of the hydrogenation of 1-trimethylsilylbut-3-en-1-yne with maleic anhydride.[1] Maleic anhydride,[1,6,27,42,52,53,104,105,109,111,112,130,138,170,175,177,201,208,274,299-303] methylmaleic anhydride,[138,304] maleimides,[130,170,201,300] acrolein,[177] methylacrolein,[104,304] acrylonitrile,[177] methyl acrylate,[138,288,304] ethyl acrylate,[18,104,112] dimethyl maleate,[104,177,205] diethyl maleate,[177] 1,4-benzoquinone,[104,170,201] 2-methylbenzoquinone,[304] 3-methylbenzoquinone,[304] 2,6-dimethylbenzoquinone,[112] 2,3-dimethoxybenzoquinone,[290] 1,4-naphthoquinone,[100,130,138,300] quinizarinquinone and its derivatives,[139-141,290,291] tetracyanoethene,[180,184,249,301] and other compounds containing a dienophile group[100,112,205,298,300] were used later as dienophiles.

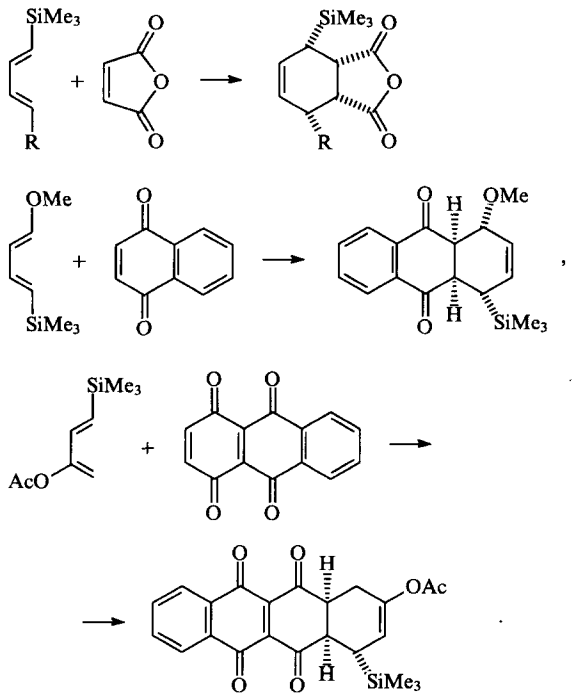
Examples of the cyclodimerisation of silicon-containing 1,3-dienes via the [2+4]-mechanism in which the diene itself plays the role of the dienophile are known.[305] The reaction is chemo- and regio-selective, but the preferred path involves condensation via the unsubstituted vinyl group of the 1,3-diene dienophile.

Hexachlorocyclopentadiene (diene) undergoes also an unusual condensation with the triethylsilyl ether of 2-methyl-4-triethylsilylhexa-3,5-dien-2-ol (dienophile):[116] the adduct formed splits off triethylsilanol under the conditions of the isolation process.

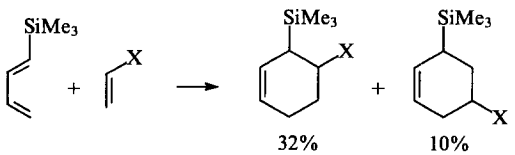


Compounds with activated triple bonds can also act as dienophiles: propiolic and methylpropiolic acids,[138,292,304] the nitrile[294] and ester[288,300,304] of propiolic acid, ethynedicarboxylic acid and its dimethyl ester,[100,104,170,300] and bis(trifluoro-methyl)ethyne.[35]

It has been noted that, in reactions with symmetrical dienophiles such as maleic anhydride, maleimide, etc., silicon-containing dienes condense with somewhat greater difficulty than silicon-free hydrocarbons.[112,305,306] Other conditions being equal, 2-silyldienes are more reactive than the isomeric compounds containing the organosilicon group at the first or fourth carbon atom of the conjugated fragment. The introduction of other substituents in the 1- and/or 4-position also hinders the cycloaddition. For example, 1,4-disubstituted dienes of the type $Me_3Si(CH{=}CH)_2X$ (X =COMe, COOMe) interact with the maleic anhydride only in the (*E*,*E*)-configuration on heating in a sealed tube.[112,175] As a rule, the reactions with symmetrical dienophiles are stereoselective: in relation to the plane of the ring, all the substituents are in the *cis*-positions, for example:



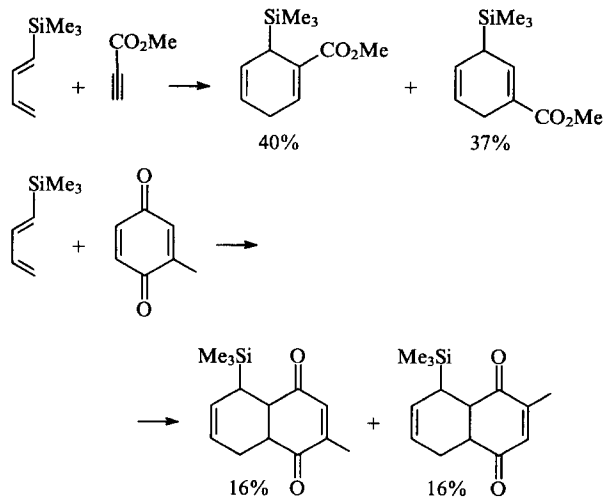
The acrylic dienophiles $CH_2{=}CHX$ (X = CHO, CN, COOR, etc.) can react with 1-trialkylsilylalka-1,3-dienes to form two regioisomers. The available data show that the reaction proceeds non-regioselectively, but 1,2-disubstituted cyclohexenes are formed in somewhat greater amounts (the *ortho*-effect).[112,304]



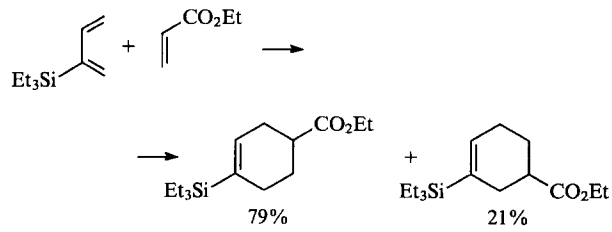
This difference virtually disappears in the reactions of silicon-containing dienes with methyl propiolate and methylbenzoquinone (Scheme 5).[304]

The isomeric 1,3- and 1,4-disubstituted cyclohexenes are formed in proportions of 1:3.3 in the interaction of ethyl acrylate with 2-triethylsilylbuta-1,3-diene. The use of catalysts (usually aprotic Lewis acids) promotes the formation of 1,4-isomers and increases the yield of cyclic adducts (Scheme 6).[18,104]

Scheme 5



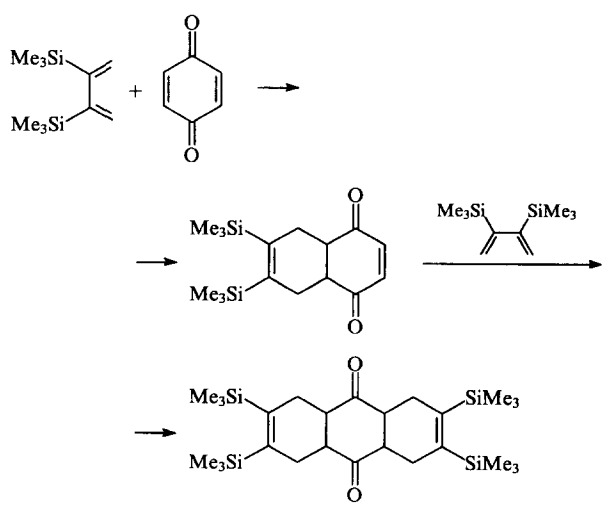
Scheme 6



In the presence of boron trifluoride etherate, the ratio changes to 1:7.3.[104]

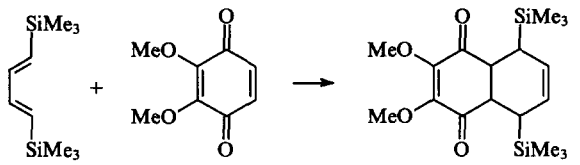
A comparative study of the regioselectivity of the cycloaddition of the diene $Me_3Si{-}CH{=}CH{-}CR^1{=}CHR^2$ (R^1 =H, R^2 = Me; R^1 =Me, R^2 =H, Me_3SiO) to various dienophiles by Fleming showed that it is controlled to a larger extent by the nature of the substituents R^1 and R^2 than by the trialkylsilyl fragment at C(1).[288]

The formation of adducts with both multiple bonds is also possible in the reactions of silicon-containing dienes with benzoquinones, naphthoquinones, and quinizarinquinones. In most of the instances investigated, only one of the monoadducts is formed:[201,290,304] The possibility of obtaining the second isomer has not been discussed, although there are indications that it is absent.[201] The formation of an adduct via both double bonds of benzoquinone has been specially emphasised only in the study of Garrat and Tsotins.[170]

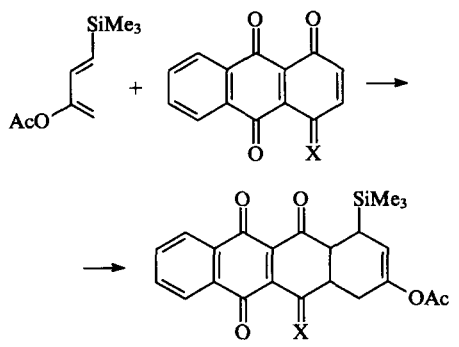


It is also appropriate to note that methyl-1,4-benzoquinone [304] and 2,3-dimethoxy-1,4-benzoquinone [290] combine with silicon-containing dienes only via the unsubstituted double bond (Schemes 5 and 7).

Scheme 7



Naphthoquinones, [130] quinizarinquinones, [139,140,289,291] and ketiminequinizarinquinones [289] form cyclic adducts exclusively via the 'external' double bond.



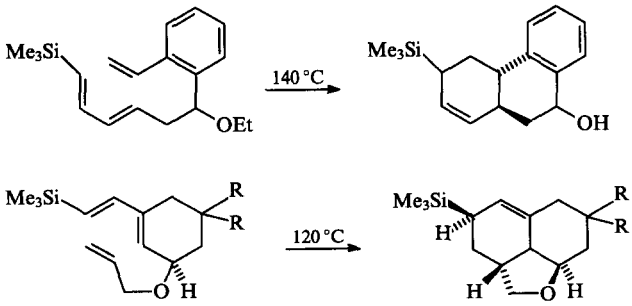
X = O, TsN.

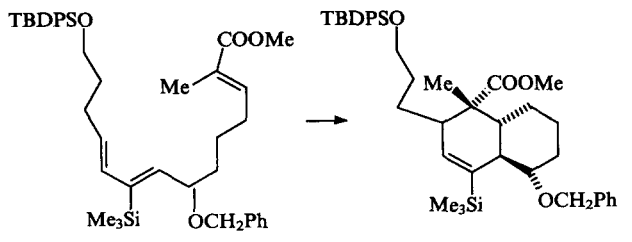
The high regio- and stereo-selectivity of the cycloaddition can be explained in terms of the perturbation of the frontier orbitals [306] of the electron-donating diene and the electron-accepting dienophile.

Examples of diene synthesis employing the dienes formed on pyrolysis of silicon-containing sulfolenes have been described. [148,151]

Intramolecular diene synthesis occupies a special place in the stereospecific synthesis of cyclic natural products.

1,3-Diene and dienophile fragments can be components of aliphatic [216,217] or alicyclic [20,105,131,293,295] compounds.





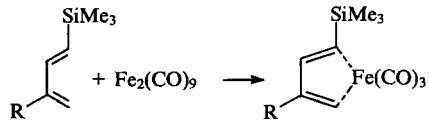
TBFDPS = *tert*-butyl diphosphite-silane.

This reaction is distinguished by a high stereoselectivity.

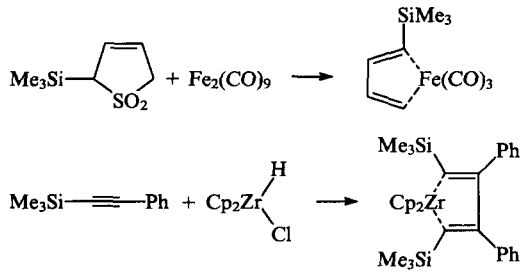
6. Synthesis of complexes with silicon-containing 1,3-diene ligands

Numerous iron, [96,106,167,190,307–310] cobalt, [311,312] zirconium, [313–315] and other transition metal [190,316] complexes of acyclic silicon-containing 1,3-dienes have now been obtained. In all cases, the 1,3-dienes behave as bidentate ligands.

The synthesis of the complex may include both the interactions of silicon-containing 1,3-diene structures already formed with metal complexes (ligand exchange), i.e.



and the interaction of metal complexes with organic precursors of 1,3-dienes. [307,310,315] The method presupposes the synthesis of silicon-containing 1,3-diene compounds in the course of the formation of the complex.



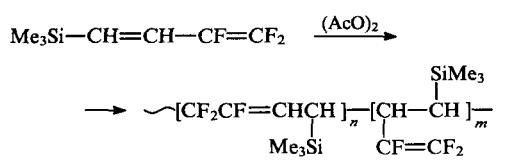
In the vast majority of cases, the structure of the silicon-containing complexes has been demonstrated by X-ray diffraction.

The reactions of silicon-containing complexes with carboxylic acids, [226–229] their halides, [106,308,309] and ketones, [314] as well as photochemical isomerisation reactions [316] have been described.

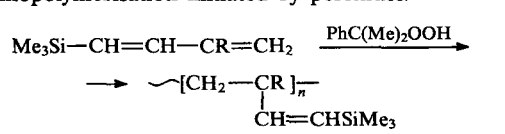
7. Polymerisation and copolymerisation of silicon-containing alka-1,3-dienes

The polymerisation of silicon-containing 1,3-dienes was first reported in 1956. According to the data of Shchukovskaya et al., [5] 3-methyl-2-triethylsilylbuta-1,3-diene gives rise to a viscous oil with a molecular mass of 9 000 on heating with *tert*-butyl peroxide. The structure and physicochemical properties of the polymer obtained were not investigated.

Somewhat later, Haszeldine and coworkers [107] showed that 3,4,4-trifluoro-1-trimethylsilylbuta-1,3-diene polymerises nonregioselectively under the influence of acetyl peroxide.



In contrast to fluorinated monomers, 1-trialkylsilylbuta-1,3-dienes and 3-methyl-1-trialkylsilylbuta-1,3-dienes give rise to high-molecular-mass compounds containing only 3,4-units on homopolymerisation initiated by peroxides. [317–319]

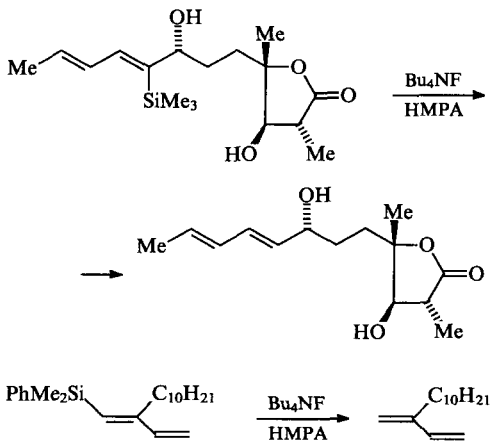


The copolymerisation of silicon-containing 1,3-diene hydrocarbons with vinyl monomers has also been investigated. [320,321] and the copolymerisation constants and activity factors have

been determined for 1-triethylsilylbuta-1,3-diene and styrene.[320,322,323] Similar high-molecular-mass compounds have been obtained by the copolymerisation of 1-triethylsilylbuta-1,3-diene with styrene on a cathode.[324] Copolymers having effective mechanical characteristics have been synthesised from arylvinyl monomers and 2-trimethoxysilylbuta-1,3-diene.[321]

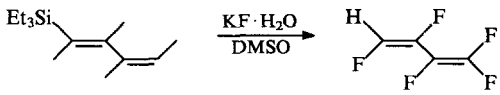
8. Reactions with participation of silicon–carbon bonds

The protodesilylation of 1- and 2-triorganosilylalka-1,3-dienes takes place with much greater difficulty than that of structurally similar 1-trialkylsilylalk-3-en-1-ynes.[26] This method has come to be fairly widely used only when the possibility of removing the silyl group from silicon-containing dienes by means of the fluoride anions had been demonstrated. Tetrabutylammonium fluoride[20,160,296,297] or potassium fluoride[168,169] are usually employed as fluoride anion donors. Both silicon-containing 1,3-diene hydrocarbons[296] and their derivatives[169,209,297] have been desilylated.



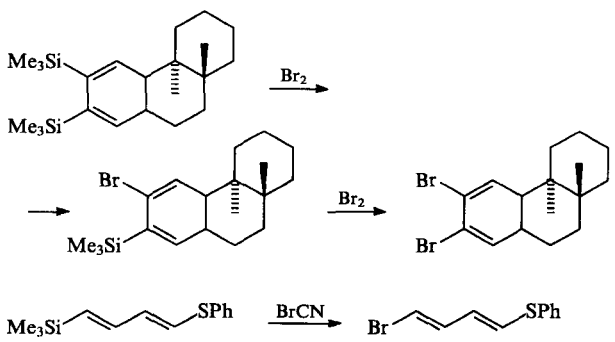
HMPA = hexamethylphosphoramide.

The protodesilylation by tetrabutylammonium fluoride is as a rule carried out in hexamethylphosphoramide or tetrahydrofuran[296,297] and that by potassium fluoride is performed in dimethyl sulfoxide.[209]



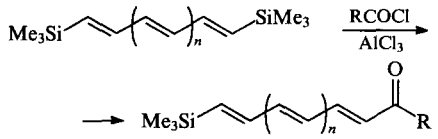
The use of alkalis or alkoxides as the nucleophile is relatively effective in the removal of the silyl protecting group, although it is known that dehydrohalogenation and desilylation take place on treatment of 1,2,3,4-tetrabromo-1,4-bis(trimethylsilyl)butane with sodium methoxide. (1*E*,4*E*)-dibromobuta-1,3-diene was first obtained by this method.[270]

Examples of the replacement of triorganosilyl groups by halogen on interaction of the corresponding 1,3-dienes with bromine[256] or bromocyanogen[204] are known.



The attempt to introduce iodine instead of the trimethylsilyl group by treating 1-trimethylsilylnona-1,3-diene with iodine was unsuccessful.[31]

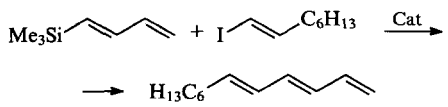
The reaction involving the replacement of the trialkylsilyl group by an acyl group in the presence of anhydrous aluminium chloride may be recommended as a convenient preparative method of synthesis of 1,3-diene ketones.[32,325,326]



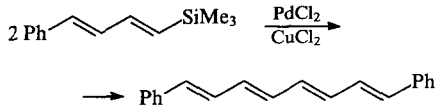
The use of dibasic acid dichloride in this reaction leads to the corresponding polyenepolyones.[325]

A similar acylation reaction is also known for complexes of 1-trialkylsilylalka-1,3-dienes with iron carbonyl.[106]

The alkenylation[327] and arylation[328] of silicon-containing 1,3-dienes by the corresponding halides occurs only in the presence of palladium catalysts — $Pd(OAc)_2.P(OEt)_3$, $PdCl(\eta^3\text{-}C_3H_7)$, etc.

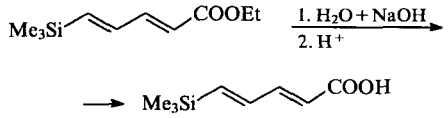


Naso[204] described a very interesting 'dimerisation' reaction of 1-trialkyl silylalka-1,3-dienes on treatment with copper and palladium chlorides accompanied by desilylation.

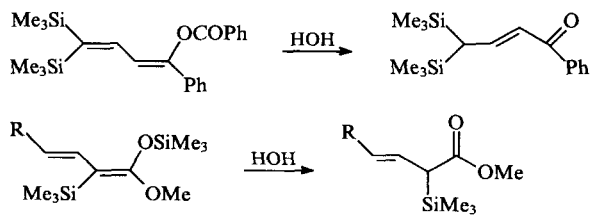


9. Reactions with participation of functional groups

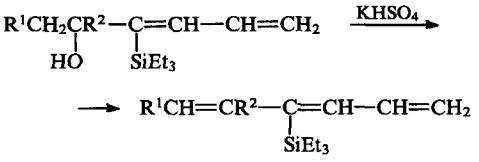
Reactions of this type of derivatives of silicon-containing 1,3-diene hydrocarbons have been least investigated. It has been reported that ethyl (5*E*,*E*)-trimethylsilylpenta-2,4-dienoate is hydrolysed by an aqueous alcoholic solution of sodium hydroxide without the cleavage of the silicon–carbon bond and a change in configuration.[175]



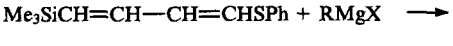
Hydrolysis of alkoxy-1,3-dienes,[14,131] acyloxy-1,3-dienes,[136] and mixed acetals[101] in an acid medium leads to unsaturated ketones or esters respectively.



Primary silicon-containing 1,3-diene alcohols give rise to the corresponding aldehydes in satisfactory yields on oxidation with pyridinium chlorochromate.[329] Tertiary silicon-containing alcohols are dehydrated on heating with acid potassium sulfate, but there is no elimination of the corresponding trialkylsilanols.[61,62]

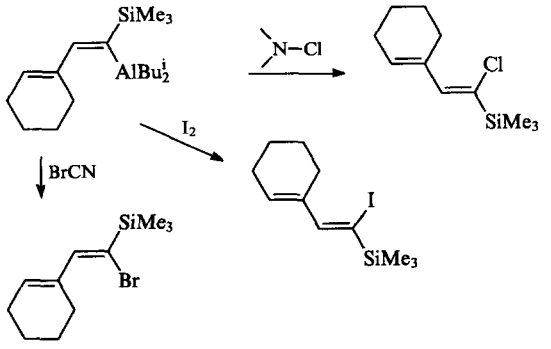


Silicon-containing 1,3-dienyl sulfides are alkylated by organomagnesium compounds in the presence of palladium or nickel complexes.[204]



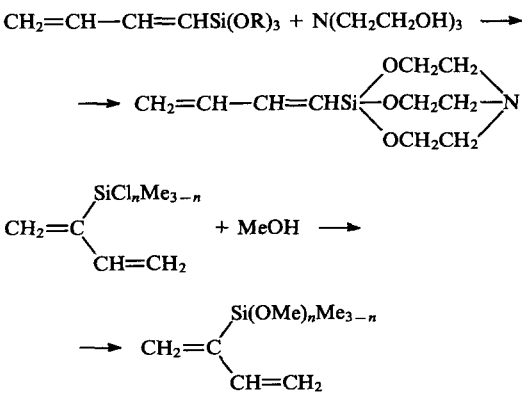
Derivatives of silicon-containing 1,3-diene hydrocarbons containing the BX_2 (X = Cl, Br, OAlk) group at the double bond lose boron on treatment with carboxylic acids[35] and are alkylated by mixed organozinc compounds or α-haloalkenes in the presence of palladium complexes.[210,211,213] On oxidation, these hydrocarbons give rise to silicon-containing ketones,[34] whilst their interaction with carbon monoxide in an alcoholic medium affords the esters of silicon-containing 1,3-dienoic acids.[212]

Organoaluminium derivatives of silicon-containing alka-1,3-dienes give rise to the corresponding halides on treatment with donors of the electrophilic halogens.[33]



Alka-1,3-dienes containing halogens or alkoxy-groups at the silicon atom enter into alcoholysis[105] or transalkylation (Scheme 8)[301] reactions.

Scheme 8



Analysis of the data examined in this review permits the following generalisations.

(1) The methods based on the Wittig, Horner–Emmons, Peterson, and dehydration reactions of silicon-containing alcohols make it possible to obtain any silicon-containing 1,3-diene hydrocarbons and their carbofunctional derivatives with a specified structure in a satisfactory preparative yield. In the synthesis of (1*E*,3*E*)-isomers, preference should be given to the methods based on the Wittig, Horner–Emmons, or dehydration reactions, whereas in the synthesis of (1*E*,3*Z*)- or (1*Z*,3*Z*)-isomers the second version of the Peterson reaction is preferred.

(2) Regardless of the structure of the substrate and the nature of the reagent, in the reactions of conjugated silicon-containing dienes the attacking species is almost always attached to the C(4) atom of the 1,3-diene fragment remote from the silicon atom. The occurrence of this reaction path in the addition reactions cannot be accounted for by the steric influence of the triorganosilyl group and is probably due to the stabilisation of the allyl intermediates containing the organosilyl group (formal analogy with 1-phenylbuta-1,3-diene).

(3) In terms of the overall electron-donating effect, the trialkylsilyl group occupy an intermediate position: $R_3C > R_3Si > H$.

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