SILICON - REACTION MECHANISMS

ANNUAL SURVEY COVERING THE YEAR 1974

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CONTENTS

INTRODUCTION

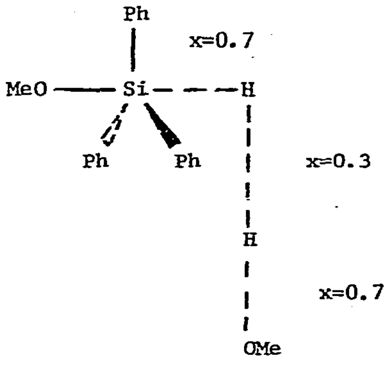
This survey brings together the information published in 1974 which relates to organosilicon reaction mechanisms. Also included are references to a number of papers published in 1973, mainly from Russian journals, which were received too late for inclusion in the annual survey covering the year 1973.[1] On grouping reactions by type, some overlapping is bound to occur; therefore, it may be necessary to consult more than one section for information concerning a specific reaction.

Silicon - Reaction mechanisms; Annual Survey covering the year 1973 see J. Organometal. Chem., 83 (1974) 265-308.

A monograph entitled, "Organometallic Reaction Mechanisms of the Nontransition Elements", which includes information on organosilicon compounds, has been published.[2] A review article entitled, "The Siliconium Ion Question", collates the published data on the role of the siliconium ion in organosilicon reaction mechanisms.[3]

SUBSTITUTION

A number of mechanistic studies on the solvolysis of organosilicon compounds have been reported. The solvent isotope effect for the base-catalyzed alcoholysis of a series of triorganosilanes has been found to increase with the increasing reactivity of the silicon hydride.[4] The authors conclude that proton transfer occurs in the rate-determining step and propose a non-linear transition state involving the pentacoordinate silicon intermediate (1), where x is the bond order. Both homogeneous and heterogeneous catalysis have been observed for the methanolysis of trimethoxysilane in methanol medium containing mono-, di- and tribasic sodium phosphates.[5] The heterogeneous solvolysis of trimethoxysilane is interpreted as involving the formation of a surface complex, which acts as a reaction intermediate.



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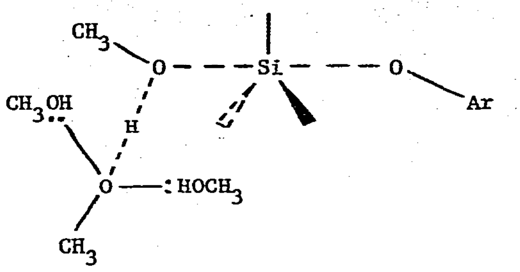
A hidden isotope effect has been observed for the methoxide-catalyzed methanolysis of p-chlorophenoxytriphenylsilane and p-methoxyphenoxytriphenylsilane.[6] The authors propose a transition state of structure 2 based on an analysis of the kinetic data in CH_3OH-CH_3OD mixtures in terms of isotope fractionation factors. Two different views have been presented on the mechanism of hydrolysis of triethylethoxysilane at a silica-carbon tetrachloride interface.[7,8] Steric effects play an important role in the reaction of chlorodimesitylsilane with alcohols and phenols.[9]



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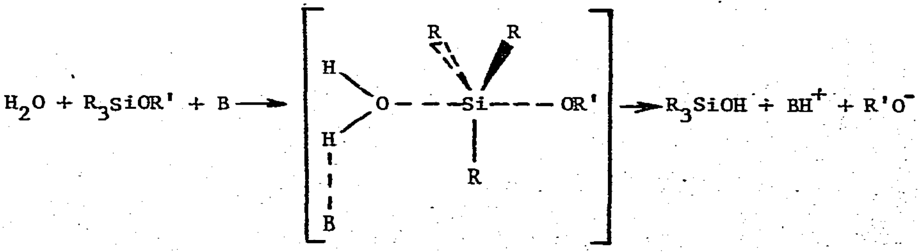
The kinetics of the acid- and base-catalyzed hydrolysis[10,11] and the base-catalyzed methanolysis[11] of aryloxytriorganosilanes have been reported. Studies of the acid-catalyzed hydrolysis in aqueous organic solvents suggest the concerted process, eq. 1, and indicate that one or more water molecules are involved in the transition state.[10] The base-catalyzed hydrolysis of aryloxytriphenylsilanes is second order in hydroxide ion at low base concentrations. This behavior is consistent with a process in which a pentacoordinate silicon intermediate reacts with OH^- in the rate-determining step, eq. 2[11]



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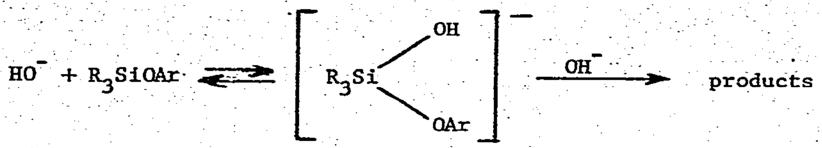


(2)

$$HO^{-} + R_3SiOAr \rightleftharpoons \left[R_3Si \begin{matrix} OH \\ OAr \end{matrix} \right]^{-} \xrightarrow{OH^{-}} \text{products} \qquad (2)$$

In contrast, the base-catalyzed methanolysis can best be interpreted as a concerted process.[11] The rapid rate of hydrolysis of phenoxytrimethylsilane in 96% ethanol at ambient temperatures renders this solvent unsuitable for UV absorption studies.[12] The first-order rate constant for the hydrolysis of methyl 2-(trimethylsiloxy)benzoate in dioxane-water varies with pH reaching a minimum value at pH 4.[13] The stability of the Si-O bond in di(alkynehydroxy)-diorganosilanes toward acid-catalyzed hydrolysis is explained in terms of the inductive effects of the organic groups.[14]

The substituent effects on the rate of isopropanolysis of a series of ring-substituted (benzoyloxy)trialkylsilanes indicate that cleavage of the Si-O bond occurs in the rate-determining step and that an even distribution of charge between the Si and O atoms occurs in the transition state.[15]

The hydrolysis of octamethylcyclotetrasiloxane has been investigated by GLC and PMR methods in aqueous solutions of hydrochloric, sulfuric and phosphoric acids under heterogeneous conditions.[16] Evidence is presented in favor of an S_N2 process in which a water molecule enters into the rate-determining step.

Mechanisms for the acid- and base-catalyzed solvolysis[17,18] and the uncatalyzed ethanolysis[19] of the Si-N bond in triorganosilyl derivatives of amines have been proposed. Hammett correlations for the acid- and base-catalyzed ethanolysis of aryldimethylsilylpyrroles suggest that for the acid-catalyzed process the slow step involves nucleophilic attack at silicon by the solvent on the protonated amine with considerable Si-N bond breaking occurring in the transition state, and for the base-catalyzed process a pentacoördinate silicon intermediate is involved.[17] Kinetic studies on the base-catalyzed solvolysis of N-(triorganosilyl)anilines suggest that in the transition state of the rate-determining step, the Si-O bond is fully formed, the Si-N bond is partially broken (20-50%), and the nitrogen atom is partially solvated (10-30%).[18] Kinetic data on the uncatalyzed ethanolysis of N-(aryldimethylsilyl)-N-methylanilines suggest the mechanism given in eq. 3 and 4, where the transition state lies close to the reactants, with the Si-O bond little formed.[19]

$$ArMe_2SiNMePh + EtOH \rightleftharpoons ArMe_2\overset{+}{N}HMePh + EtO^- \qquad (3)$$

$$ArMe_2\overset{+}{Si}NHMePh + EtO^- \rightleftharpoons ArMe_2SiOEt + NHMePh \qquad (4)$$

The basic hydrolysis of the hexafluorosilicate ion proceeds by two parallel reactions, one of which is catalyzed by Li^+.[20] An intermediate complex (ion-pair) is proposed for the Li^+-catalyzed process.

The rates of hydrolysis of a series of trimethylsilyl(arylthio)-silanes have been determined and are compared to the corresponding Ge, Sn and Pb compounds.[21] Substituent and solvent isotope effects indicate some differences in the cleavage mechanism of these compounds. The relative hydrolytic stabilities of trialkoxysilanethiols,[22] and alkoxyorganosilanethiols and -silthianes[23] have been reported.

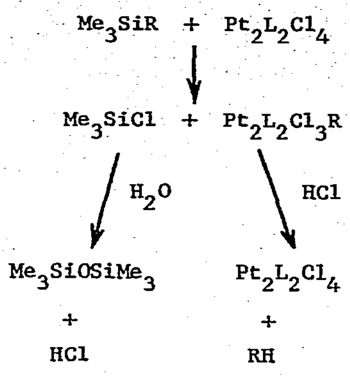
A number of studies have been reported on the base-catalyzed cleavage of the Si-C bond. Kinetics of the solvolysis of Me_3SiX (where $X = CHCl_2$, $CHBr_2$, CHI_2 and CCl_3) have been determined in an NH_3-NH_4Cl buffered, n-propanol-water medium.[24] The results indicate two parallel cleavage routes involving nucleophilic substitution at silicon by the conjugate base of the solvent and by ammonia. Reactivity increases with increasing ability of the departing carbanion to stabilize a negative charge. Rates of cleavage of benzyl- and benzofuryl-silicon bonds in aqueous methanolic alkali and the latter in water-DMSO containing borax indicate similar reactivities and similar sensitivities to substituent group effects.[25] A mechanism in which the rate-determining step is cleavage of the Si-C bond within a pentacovalent silicon intermediate is suggested. Solvent isotope effects for the cleavage of benzyltrimethylsilanes have been determined in methanol containing sodium methoxide and compared with similar data for the corresponding tin derivatives.[26] These studies indicate that the rate-determining step involves proton transfer from the solvent to the carbon atom of the leaving group with the MeO-Si bond fully or almost fully formed.

The order of reactivity toward cleavage of the Si-C_{ar} bond of aryltrimethylsilanes in H_2O-DMSO containing potassium hydroxide is pyrenyl > 9-phenanthryl > 2-naphthyl > 1-naphthyl > phenyl.[27] The stability of the departing aryl carbanion seems to be the dominant factor in determining the above order. The Mills-Nixon effect has been investigated by studying the base-catalyzed cleavage of trimethylsilylveratrole, -1,3-benzodioxole and -1,4-benzodioxane derivatives in H_2O-DMSO medium.[28] The enhanced reactivity of the benzodioxole derivative is explained by hybridization changes enforced on the ring-junction carbons by the strained dioxole ring.

The Si-C bonds in $(h^6\text{-ArSiMe}_3)\text{Cr(CO)}_3$ and $(h^6\text{-PhCH}_2\text{SiMe}_3)\text{Cr(CO)}_3$ are much more readily cleaved by aqueous methanolic alkali than in the corresponding uncomplexed compounds.[29] The $Cr(CO)_3$ group facilitates these reactions by a powerful electron-withdrawing effect.

Group VIII metals and metal compounds {$[\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{Me}_3\text{C}_5\text{H}_2\text{N})]$,[30] $[\text{Pt}_2\text{Cl}_4(\text{C}_2\text{H}_4)_2]$,[31] $PdCl_2$,H_2PtCl_6, H_2PtCl_6-$SnCl_2$, $Pt(PPh_3)_3$, $Pt(PPh_3)_4$, Pt/C and Pd[32]} catalyze the cleavage of Si-C bonds yielding siloxanes with one less organic group on silicon. These reactions proceed by an exchange of organic groups between silicon and the group VIII atoms as illustrated by Scheme I.[31]

The stereochemistry of substitution at silicon continues to be an active area of study. Bifunctional optically active phenyl-α-naphthyl-(-)-menthoxysilanes [Ph-α-Np(-)MenOSiX; where X = H, Cl, OMe, OEt] have been synthesized.[33] Their absolute configuration has been deduced by chemical correla-



Scheme I

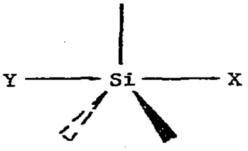
tion with (R)-phenyl-α-naphthylmethylsilane, by NMR studies of diastereoisomers and by X-ray diffraction studies. The stereochemistry of substitution by organometallic reagents (RM; where M = Li, Mg) on the bifunctional system has been determined, eq. 5, 6 and 7.[34] For the bifunctional derivatives,

$$R_2Si^{*}OMen(-)H \xrightarrow[\text{(retention)}]{R'M} R_2Si^{*}HR' \qquad (5)$$

$$R_2Si^{*}OMen(-)OMe \xrightarrow[\text{(retention)}]{R'M} R_2Si^{*}OMen(-)R' \qquad (6)$$

$$R_2Si^{*}OMen(-)Cl \xrightarrow[\text{(inversion)}]{R'M} R_2Si^{*}OMen(-)R' \qquad (7)$$

$R_2Si^{*}OBornOMe$ and $R_2Si^{*}OHexOMe$, reaction with aromatic and saturated organomagnesium compounds in ether solvent substitutes only the methoxy group with retention of configuration, while allylic and benzylic organomagnesium compounds substitute the bulky alkoxy group with inversion of configuration.[35] In THF and DMF only the methoxy group is substituted with retention of configuration. The reaction of allylic crotylic and benzylic lithium and magnesium compounds with R_2Si^{*}-OMenX (where X = H, Cl, OMe) leads to both retention and inversion of configuration depending on the bifunctional silane, organometallic reagent and solvent.[36] These results reinforce the stereochemical conclusions reached with the system, Ph-α-NpMeSi*X. A general discussion of the mechanism of substitution by organometallic reagents on chiral bifunctional silanes has been published.[37] The differences in the stereochemistry of substitution at the chiral mono- and difunctional silanes are minor. Two possible modes of attack are suggested: axial entry which leads to inversion of configuration (3); equatorial entry which leads to retention (4).



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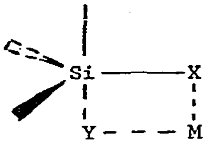

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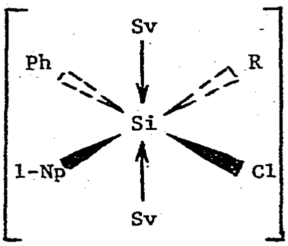
Kinetic studies of coupling of Grignard reagents with optically active, monofunctional silanes, R_3Si^*X (where X = F, OMe), show the follow order of reactivity with respect to solvent: dimethoxyethane > THF > ether.[38] Retention of configuration at silicon is observed in all of these solvents. Electrophilic assistance as a substitution reaction driving force is ruled out. A mechanism involving slow nucleophilic attack leading to formation of a pentacovalent silicon intermediate is proposed.

The reduction of optically active monofunctional silanes, R_3Si^*Y (where Y = OR", Cl, F), by R'MgX-Cp_2TiCl_2 in ether is highly stereoselective, eq. 8.[39] Optically active α-ferrocenylsilanes have been prepared.[40] A high stereospecificity has been observed for the reactions of these compounds.

$$R_3Si^*Y \xrightarrow[\text{ether}]{\text{R'MgX-}Cp_2TiCl_2} R_3Si^*H \qquad (8)$$

In contrast to previous studies which indicate that hydrogen exchange of R_3Si^*H proceeds with retention of configuration, in LiAlH$_4$-THF, R_3Si^*H racemizes rapidly.[41] An addition-elimination mechanism is proposed involving an expanded-octet intermediate. The kinetics for the solvent-induced racemization of chloro- and bromotriorganosilanes indicate two solvent molecules are involved in the transition state.[42,43] Either the hexacoordinated octahedral intermediate (5) or the pentacoordinate bipyramidal siliconium ion intermediate (6) is consistent with the kinetic data.



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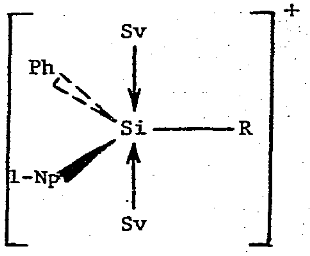

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In contrast to earlier studies, the $LiAlH_4$ reduction of 1,2-dimethyl-1-chloro-1-silacyclobutane has been found to proceed with a stereospecificity of >95%.[44] Based on NMR studies, a retentive substitution process is assigned.

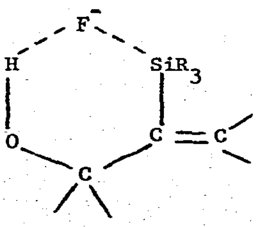
Substitution at silicon by a number of organometallic reagents has been reported. Crotyllithium, prepared from both cis- and trans-crotyltrimethyltin, and alkyllithium reagents, couples with trimethylchlorosilane to yield a 3/2 mixture of cis- and trans-crotyltrimethylsilane.[45] gem-Dichloroallyllithium, prepared from 3,3,3-trichloropropene and n-butyllithium, is seemingly an ambident nucleophile, since it reacts with Me_3SiCl to yield $Me_3SiCCl_2CH{=}CH_2$ and with Me_3SnBr to yield $Me_3SnCH_2CH{=}CCl_2$, while with Me_3GeCl a mixture of the two isomers is obtained.[46] The reactivity of $Ph_{3-n}Cl_nMM'$ [where n = 1-3; M = Si, Ge, Sn; M' = $Mn(CO)_5$, $Fe(CO)_2Cp$] toward C_6F_5Li to form $Ph_{3-n}(C_6F_5)_nMM'$ has been determined.[47]

Bis(perhaloaryl)methylsilanes and tris(perhaloaryl)silanes are cleaved by alkyllithium and Grignard reagents to yield perhaloarylmetallic species.[48,49] n-Butyl substituted polysilanes are produced by the reaction of n-butyllithium with trisilane, n-tetrasilane and n-pentasilane.[50] The unusual product distribution obtained when methyl Grignard is reacted with α,ω-dichloropermethylpolysilanes is attributed to the transmission of substituent effects through the silicon chain via molecular orbitals.[50a] Metal-hydrogen exchange occurs when silylpotassium is added to disilane and trisilane in monoglyme.[51]

The mechanisms of substitution of triorganosilanes and reductions of chloro- and alkoxytriorganosilanes by Grignard reagents in the presence of nickel complexes have been studied.[52] Ni(O) complexes are proposed as intermediates. The authors suggest that substitution occurs by oxidative addition of the silane to the nickel complex while reduction takes place by direct attack of a nickel hydride on the silane.

The system, $Me_3SiCl/Mg/HMPA$, has been used to polysilylate *gem*-polychlorinated compounds,[53] N-acetyl- and N-propionylimidazoles[54] and N-phenylpivalimidoyl chloride.[55] Vinyltrimethylsilane is polysilylated by the above system when $FeCl_3$ and $TiCl_4$ are added.[56] Mechanisms involving radical intermediates are proposed.[53,56]

Nucleophilic cleavage of the silicon-vinyl carbon bond in silanes of the type $R_3Si[R'R''C(OH)C{=}CH_2]$ by fluoride ion dissolved in DMSO or acetonitrile has been observed.[57] The six-membered ring intermediate (**7**) is proposed. Intramolecular nucleophilic substitution at silicon by oxygen, *cf.* **8**, is proposed for cyclization of γ-hydroxysilicon hydrides.[58] A mechanism involving nucleophilic attack by oxygen at silicon is suggested for the reaction of oximes



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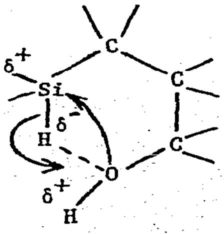

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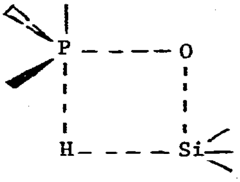
with triorganosilyldiorganoamines.[59] A bimolecular nucleophilic substitution mechanism is proposed for the reaction of triorganosilanes with chlorobenzene in the presence of colloidal nickel to yield phenyltriorganosilanes.[60] Cyclic intermediates involving nucleophilic attack at silicon by oxygen with $ZnCl_2$ acting as an electrophile have been suggested for the reversible cleavage of acetoxysilanes to siloxanes and acetanhydride based on rates of cleavage and IR studies.[61] The cyclic activated complex (9) is proposed to explain the stereospecific reduction of phosphine oxides to phosphines by phenylsilane with retention of configuration.[62]



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Studies on the electrophilic cleavage of Si-C bonds have been reported. Vinyl groups are cleaved from silicon by $CH_3COCl/AlCl_3$.[63] Reaction of 1,1,4-trimethylsilyl-3-methylbutadiene-1,2, an allenylsilane, with electrophilic reagents ($MeSO_3H$, Br_2, $ClSO_3SiMe_3$, t-BuCOCl/$AlCl_3$) results in cleavage of a trimethylsilyl group followed by rearrangement to an acetylenic trimethylsilane.[64] Thallium(III) trifluoroacetate cleaves the $Si\text{-}C_{ar}$ bond in aryltrimethylsilanes yielding arylthallium(III) bistrifluoroacetates.[65] This reaction is probably mechanistically similar to other electrophilic desilylation reactions. Large solvent isotope effects, 6.0-6.5, have been observed for the desilylation of aryltrimethylsilanes by trifluoroacetic acid.[66] The authors suggest that the data indicate that the proton transfer to form the Wheland intermediate is rather more than half-complete in the activated complex. Evidence has been obtained that the protodesilylation of trimethylsilylferrocene by H_2SO_4 in H_2O-EtOH solvent does not involve any appreciable iron participation.[67] Direct attack of the electrophilic reagent on the ring is proposed.

Second-order rate constants and thermodynamic activation parameters have been determined for the cleavage of 1,2-diphenyltetramethyldisilane by bromine.[68] The mode of reaction of cyanogen chloride with trisubstituted silanes in the presence of triethylamine has been determined and related to the complexing ability of the silane with triethylamine.[69] The rates of reaction of silyl derivatives of organic alcohols with phosgene, leading to formation of chlorosilanes and chloroformates, have been determined.[70] The rate increases with size, degree of unsaturation and degree of branching of the organic group.

Cleavage reactions of silyl-transition metal complexes by electrophilic reagents have been described: Si-M bonds (where M = Cr, Mn, Co, Mo, W)[71,72] and Si-C bonds.[73,74]

The reactions of a number of reagents containing organosilyl groups have been reported. Rate data have been obtained by the stopped-flow method for the reaction of triorganosilyllithium and -sodium reagents with fluorene in THF and dimethoxyethane.[75] These data indicate that on changing from Na^+ to Li^+ the increase in solvation of the initial state is more important than in the transition state. The reagent, bis(trimethylsilyl)mercury, has been used to form $Pt\text{-}SiMe_3$ and $Pt\text{-}HgSiMe_3$ bonds.[76] The reaction of $(Me_3Si)_2CBrLi$ with Me_2SnCl_2 at low temperatures (-115°) yields 1,1,3,3-tetramethyl-2,2,4,4-tetrakis(trimethylsilyl)-1,3-distannacyclobutane.[77] Reactions involving the reagents $(Me_3SiCH_2)_3SnLi$[78] and $(Me_3Si)_2NCu$[79] have been reported.

Electrophilic attack by silicon at oxygen is proposed for the reactions of Cl_nSiMe_{4-n} (where n = 1-3) with cobalt carbonyl species[80] and dimethylaminotrimethylsilane with bicyclic ketones.[81] Two triphenylsilyl-substituted acetylenes displace three carbonyl groups in $CpNb(CO)_4$ under UV irradiation.[82]

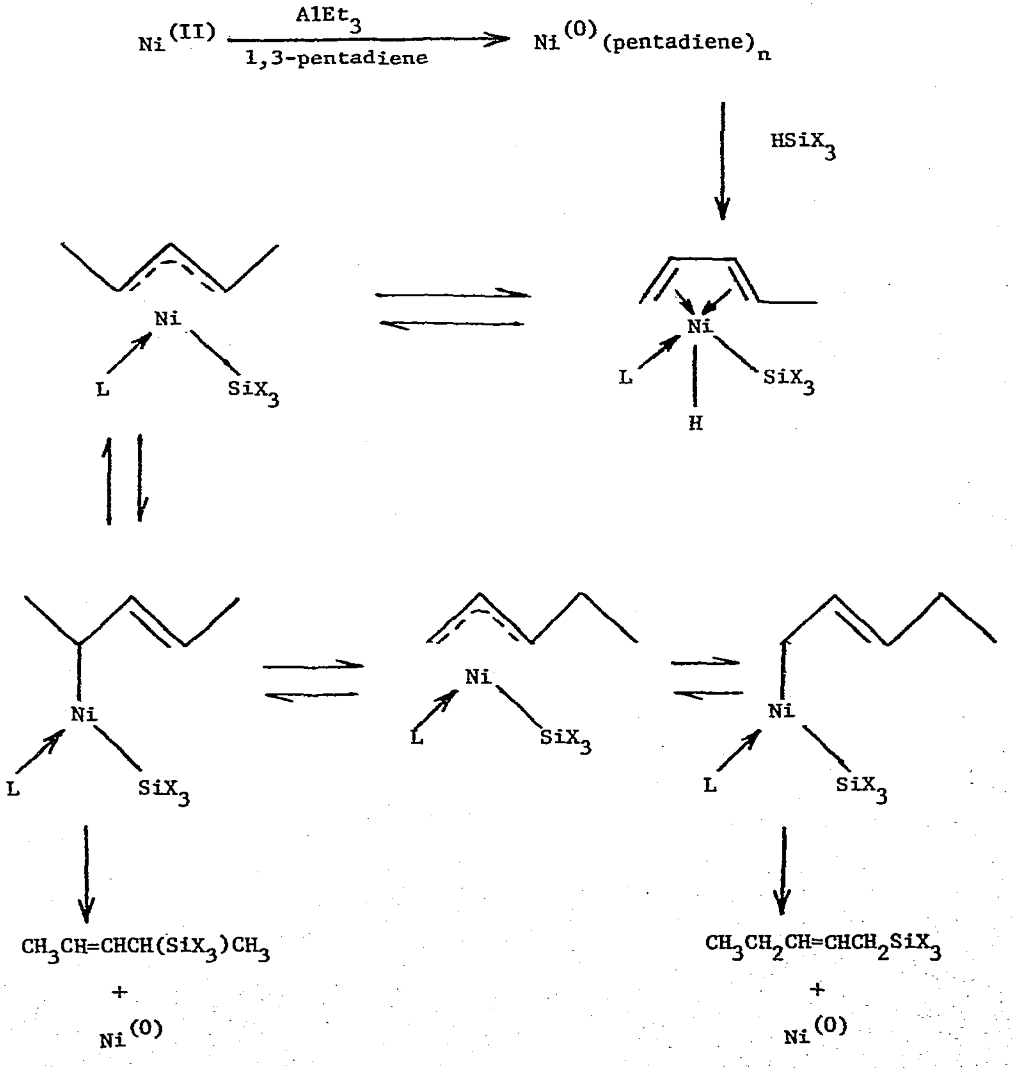
Substitution reactions at atoms other than silicon in organosilicon compounds have been studied. The rate constants for the acid- and base-catalyzed hydrolysis of the esters, $MeCO_2(CH_2)_nSiMe_3$ (where n = 1-6), were determined and compared with their carbon and germanium analogs.[83,84] These data are discussed in terms of steric and inductive effects. Second-order rate constants and activation parameters were determined for the hydrolysis of $R_3Si[(CH_2)_nOCH{=}CH_2]$ (where R = Me, Et, Me_2CH, Ph; n = 1-3).[85] A two-stage mechanism has been proposed for the reaction of $O(SiMe_2CH_2Cl)_2$ and $O[SiMeEt(CH_2)_3Cl]_2$ with KCNO in DMF medium.[86] The rate factors for detritiation of *o*- and *p*-$Me_3Si(CH_2)_nC_6H_4{}^3H$ (where n = 1-4) in trifluoroacetic acid have been determined.[87] These factors are related to the ease of and cleavage of $ArSiMe_3$ compounds with reference to the importance of hyperconjugative electron-release from $Me_3Si{-}CH_2$ bonds. Substitution at oxygen in trimethylsilyl peroxides has been studied.[88,89]

ADDITION-ELIMINATION

The factors which affect the addition of silicon hydrides to unsaturated compounds continue to be studied extensively. Kinetics of the homogeneous hydrosilylation of styrene with alkylchlorosilanes in the presence of dinuclear platinum-olefin complexes have been reported.[90] The coordination of the solvent and reactants with the platinum atoms of the catalytic complex has a substantial effect on the addition process. The effectiveness of these platinum catalysts as a function of the nature of the ligands also has been investigated.[91] The reaction of silicon hydrides with the alkylnickel complexes, $Ni(bipy)R_2$ and $Ni(h^5{-}C_5H_5)(PPh_3)Et$, to yield silicon-nickel compounds probably proceeds by an oxidative-addition process followed by a reductive-elimination process.[92] These silicon-nickel compounds may act as intermediates in the phosphine-nickel-catalyzed hydrosilylation of olefins. Similarly, oxidative addition of Si-H and Si-Cl compounds to low valent Fe, Co, and Ni complexes stabilized by phosphine ligands yields silyl-transition metal complexes.[93] New rhodium(III) complexes, $(R_3P)RhH(SiR'_3)Cl$, which are presumed to be involved as intermediates in the hydrosilylation of olefins, have been synthesized and their stability toward dissociation studied.[94] The rate of addition of triethylsilane to hex-1-ene catalyzed by the complexes, $(R_3P)_3RhCl$, has been studied as a function of the phosphine ligand. The complex, $(Ph_3P)_3RuCl_2$, reacts with silicon hydrides to form compounds containing Ru-H and Ru-Si bonds.[95] The inactivity of these ruthenium compounds as catalyst for the hydrosilylation of olefins may be related to their stability. The hydrosilylation of styrene with trichlorosilane and methyldichlorosilane catalyzed by $Ni(CO)_4$ and H_2PtCl_6 in the presence of Lewis base cocatalysts has been studied as a function of the mode of addition to the olefinic bond.[96] Palladium compounds and metallic palladium combine with triorganophosphines to form catalysts which selectively catalyze the hydrosilylation of terminal olefins.[97] The activity of the catalysts as a function of the type of phosphine has been determined. Heterogeneous catalysts consisting of Rh, Pd and Pt complexes on inorganic supports[98] and Rh complexes on polymer supports[99] have been evaluated as hydrosilylation catalysts. The mecnanistic implications of these studies for the hydrosilylation of olefins are discussed.

The addition of organosilicon hydrides to 1,3-dienes has been described. Ziegler-type systems [$M(acac)_n$-AEt_3; where M = Fe, Co, Ni] have been found to catalyze the hydrosilylation of 1,3-dienes yielding 1,4-adducts as the major products.[100] The proposed mechanism of the nickel-catalyzed hydrosilylation of 1,3-pentadiene is given in Scheme II, where L represents all other ligands. Other studies on the hydrosilylation of 1,3-dienes, indicating isomeric composition of the products, have been reported using the following catalytic systems: metallic palladium and palladium compounds with phosphines,[97] halobis(benzonitrile)palladium complexes,[101] metal-bis(8-hydroxy 5-chinolyl)methane polymers (Ni, Rh, Pd, Pt),[102] chromium carbonyl (photo-catalyzed).[103] IR techniques have been developed for determining the composition of mixtures obtained by the hydrosilylation of 1,3-dienes.[104] The hydrosilylation of acrylonitrile by trichlorosilane and methyldichlorosilane with the binary catalyst system, a copper compound [Cu_2O, CuCl or $Cu(acac)_2$] and an isocyanide (t-butyl or cyclohexyl isocyanide), yields exclusively the 2-cyanoethyl derivatives.[105]

Ring formation by intramolecular hydrosilylation (H_2PtCl_6 catalyst) of $CH_2{=}CH(CH_2)_nSiMe_2H$ (where n = 0-6) has been studied as a function of n.[106]

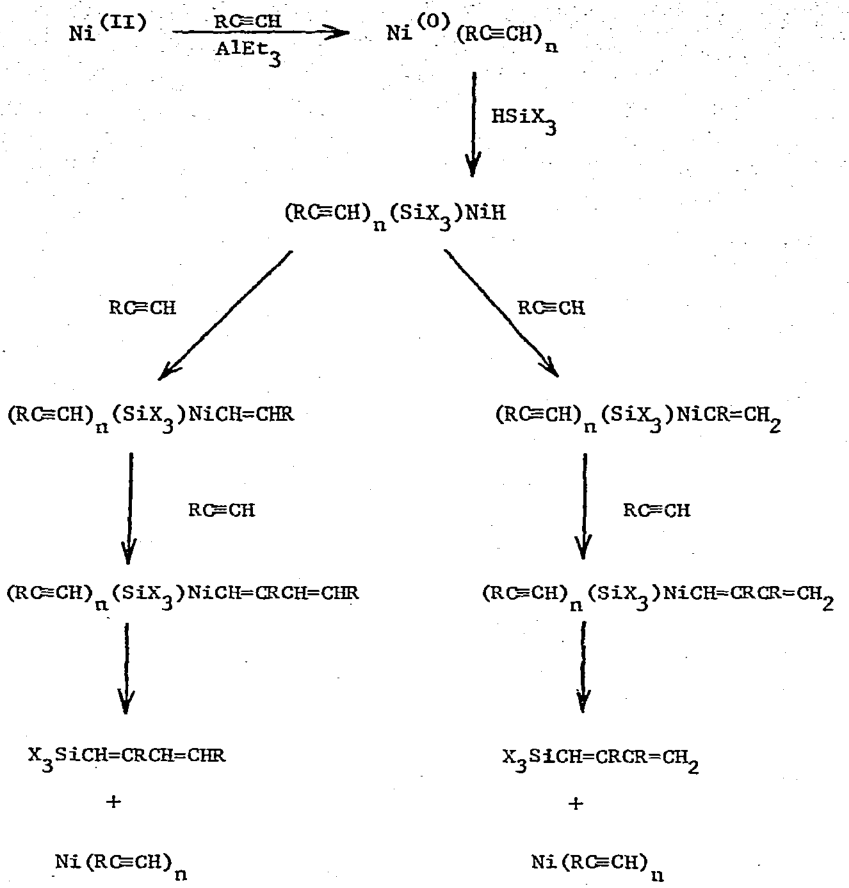


Scheme II

The product distribution is explained in terms of a mechanism involving cyclic intermediates containing Si-Pt bonds.

The kinetics of the addition of trichlorosilane to acetylene catalyzed by chloroplatinic acid on polymers (styrene-divinylbenzene copolymer with cyanomethyl and dimethylaminomethyl groups) have been studied.[107,108] A study of the changes that occur in solutions of $H_2PtCl_6 \cdot 6H_2O$ in i-PrOH and THF on standing and during hydrosilylation reactions of acetylenic hydrocarbons has been reported.[109] In the above processes, Pt(IV) is reduced to Pt(II) and partially to Pt(0). Ziegler systems [$M(acac)_n$-$AlEt_3$; where M = Fe, Co, Ni] have been found to catalyze the hydrosilylation of terminal acetylenes to yield products in which linear dimerization accompanies the hydrosilylation.[100] The proposed mechanism is given in Scheme III. Stereoselective trans addition has been observed for the $(Ph_3P)_3RhCl$-catalyzed addition of triorganosilanes to alkylacetylenes.[110] The stereochemistry of the addition of dichlorosilane to substituted acetylenes has been reported.[111] The platinum-catalyzed addition yields trans adducts while the peroxide-catalyzed addition yields predominently cis adducts.

The hydrostannylation of ethynylsilanes is reported to proceed stereospecifically yielding trans-substituted ethylenes.[112] The hydroalumination of vinylsilanes yields 1- and 2-alumino adducts, the mode of addition depending on electronic and steric factors.[113] Similarly, the stereochemistry of the hydroboration of trimethylsilyl-substituted 3,3-dimethylcyclohexenes depends on electronic and steric factors.[114] The hydroboration-oxidation of a variety of trimethylsilyl enol ethers has been investigated.[115] The trimethylsiloxy group exerts a strong directive effect on the hydroboration reaction yielding predominently the β-boryl derivatives.



Scheme III

The asymmetric hydrosilylation of ketones catalyzed by chiral rhodium complexes has been used to synthesize optically active silanes and alcohols: $R_2CHOSi^*HR'R''$,[116] $RR'C^*HOSi^*HR''R'''$,[117] $RR'C^*HOSiR''_3$.[118,119] Mechanisms are proposed for the above asymmetric hydrosilylations involving chiral Si-Rh compounds formed by the oxidative addition of silanes to the rhodium complexes. Similarly, the asymmetric hydrosilylation of α-keto esters can be used to prepare optically active α-hydroxy esters, $RC^*H(OH)COOR'$.[120] The mechanism of the fluoride ion-catalyzed hydrosilylation of aryl carbonyl compounds is proposed to proceed through the intermediate, R_3SiHF^-, which adds to the carbonyl group.[121]

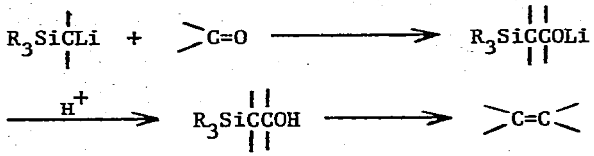
Chiral rhodium complexes have been used to catalyze the hydrosilylation of imines to yield optically active silylamines, $RR'HC^*NR''SiHPh_2$, which can be hydrolyzed to optically active secondary amines.[122] The hydrosilylation of carbodiimides to yield N-silylformamidines has been reported.[123]

The reduction of aldehydes and ketones to alcohols and alcohol derivatives by alkylsilanes in acidic media is proposed to proceed via oxonium ion intermediates.[124] Triethylsilane and trifluoroacetic acid in THF reduce $RCOCCo_3(CO)_9$ to $RCH_2CCo_3(CO)_9$.[125] The asymmetric hydrogenation of silyl enol ethers catalyzed by chiral phosphine-rhodium complexes has been reported.[126]

The system, trimethylchlorosilane/magnesium/hexamethylphosphoramide, has been used to add trimethylsilyl groups to unsaturated systems: α-ethylenic esters; [127] α-acetylenic ketones,[128] and N-phenylpivalimidoyl chloride.[55] Similarly, the system, trimethylchlorosilane/lithium/tetrahydrofuran, has been used to add trimethylsilyl groups to unsaturated systems: tetralin;[129] α-ethylenic ketones;[130] α-ethylenic aldehydes;[131] α-ethylenic esters.[132] Radical-anion and/or diradical intermediates are proposed. The stereochemistry of the disilylation of acetylenes by disilylbipyridylnickel(II) has been determined.[133] The formation of the 1-silacyclopent-3-ene system directly from chlorosilanes and 1,3-dienes in the presence of magnesium has been observed.[134,135]

The addition of silylmetallic reagents to unsaturated systems has been reported. Mechanisms have been suggested for the intramolecular cyclization of dimethyl(1-pent-4-enyl)silyllithium,[136] the addition of t-butyl(trimethylsilyl)mercury to benzylidenemalonodinitrile,[137] and the addition of ethylbis(triphenylsilyl)aluminum to diphenylacetylene.[138]

The addition of α-silyllithium reagents to carbonyl compounds yields β-hydroxy organosilicon compounds which undergo a β-elimination reaction to yield olefins (<u>cf.</u> Scheme IV).[139-144] The addition of alkyllithium



Scheme IV

reagents to α-chlorovinyltrimethylsilane yielding β-(alkylvinyl)trimethylsilanes has been reported.[145] Dehydrochlorination and displacement products in addition to addition products are observed for phenyllithium and alkyllithium reagents when TMEDA is added.

The conjugate addition of 3-trimethylsilylpropynylcopper derivatives to ethyl trans-2,4-pentadienoates yields 1,6-addition products.[146] Similarly, conjugate addition occurs when α- and β-trimethylsilylvinylcopper derivatives are added to substituted 3-cyclohexen-1-ones.[147] The methylation and phenylation of olefins by methyl- and phenylsilanes in the presence of palladium metal and compounds probably proceed via addition of methyl- and phenylpalladium intermediates to the olefins followed by elimination of palladium hydride.[32]

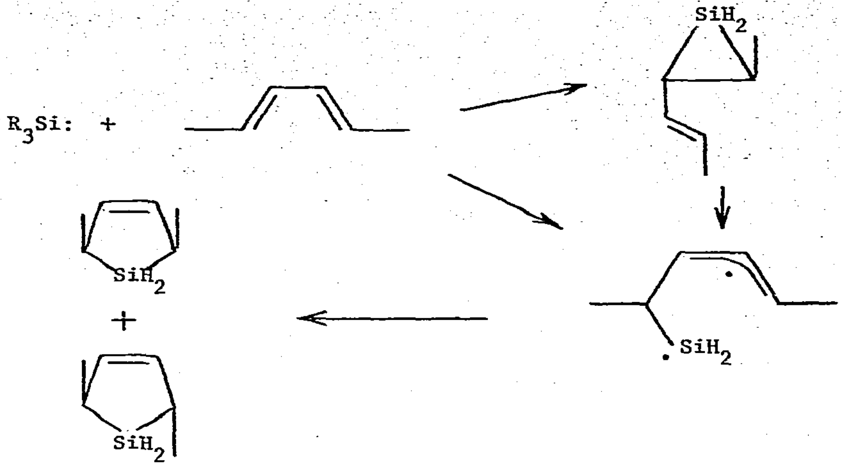
Vinyltrichlorosilane is a good enophile and readily adds to 1-alkenes, cyclohexene and allylsilanes.[148] Bis(trimethylsilyl)acetylene adds to 3,6-bis(carbomethoxy)-1,2,4,5-tetrazine to yield an unstable Diels-Alder type product, which on loss of nitrogen gives 3,6-bis(carbomethoxy)-4,5-bis(trimethylsilyl)pyridazine.[149]

Cross-aldol addition products are obtained by the reaction of silyl enol ethers with aldehydes and ketones in the presence of titanium tetrachloride under mild conditions.[150] Lewis acids ($AlCl_3$, $GaCl_3$) catalyze the addition of silylated hydrocarbons having an activated Si-C bond (allyl-, ethynyl-, and phenylsilanes) to chloral and chloroacetone.[151] The addition of silicon pseudohalides to carbonyl compounds in the presence of anionic catalysts has been observed.[152] The authors propose that the intermediate, RR'CXO$^-$ (where X is the anion of the catalyst), is involved. Base on structure, reactivity studies, the addition of trimethylsilyl phosphite to carbonyl compounds is proposed to proceed by a mechanism involving nucleophilic attack by phosphorus at the carbonyl carbon.[153] Trimethylsilylketone undergoes addition reactions with hindered amines and alcohols, and phosphorus and sulfur ylides.[154]

Addition-elimination processes are involved in the reaction of mono-, di- and trisilylated hydroxylamines with imines to yield silylated oximes.[155] Addition-elimination reactions of the Wittig type occur when phenyl isocyanate, phenyl isothiocyanate or carbon disulfide is added to $Ph_2MeP{=}NSiMe_3$.[156] The addition of $RR'NCH_2SiMe_3$ to benzyme yields N-alkyl-N-(1-trimethylsilylalkyl)anilines.[157] However, (piperidinomethyl)trimethylsilane gives an anomalous addition product, 1-(α-trimethylsilylbenzyl)piperidine. Trimethylhalosilanes add to tris(trimethylsilyl) phosphate to give tetrakis(trimethylsiloxy)·phosphonium halides.[158]

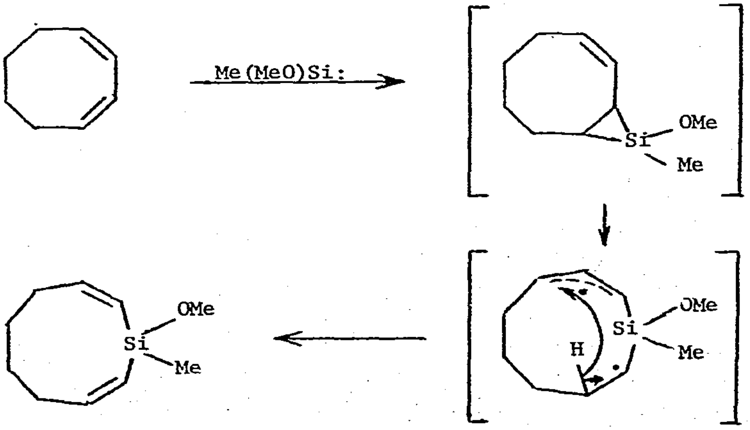
The stereospecific synthesis of vinyl halides using vinylsilanes as the synthetic precursors has been reported.[159] Addition reactions followed by stereoselective elimination reactions are described. The halogenation of silyl enol ethers yields α-haloaldehydes and -ketones.[160] A mechanism involving addition of the halogen to the double bond followed by elimination of the silyl halide is suggested. A similar mechanism is proposed for the addition of nitrosyl chloride to silyl enol ethers.[161] Anti-Markownikoff addition of hydrogen bromide to $\pi\text{-}C_5H_5(CO)_2FeSiCl_2CH{=}CH_2$ has been observed.[73] Substitution at the double bond of 3-buten-1-ynylsilanes increases the difficulty of the addition of alkane- and arenesulfonyl halides.[162]

The mechanism and stereochemistry of the addition of silylenes to unsaturated compounds have been studied. The gas phase addition of silylene to _trans_-2-_trans_-4-hexadiene yields equal quantities of the _cis_ and _trans_ isomers of 2,5-dimethyl-1-silacyclopent-3-ene.[163] The authors favor a diradical pathway for the reaction, _cf._ Scheme V. Silylene-^{31}Si adds to 1,3-butadiene



Scheme V

to give 1-silacyclopent-3-ene-^{31}Si.[164-165] These studies indicate that the ground electronic state of silylene is singlet and the reacting silylene is present as 80% triplet and 20% singlet.[164] The reaction of methoxymethylsilylene with 1,3-cyclooctadiene yields 1-methoxy-1-methyl-1-sila-2,8-cyclononadiene.[166] The authors propose the mechanism presented in Scheme VI.



Scheme VI

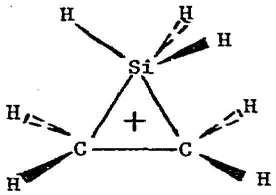
Evidence has been obtained that the addition of diorganosilylenes to disubstituted acetylenes may proceed via a 1,4-disila-1,3-butadiene intermediate which undergoes a Diels-Alder condensation with a second molecule of the acetylene to yield 1,4-disilacyclohexadienes.[167] Photochemically generated silylenes add to cyclohexene to yield silacyclopropane derivatives which can be stored unchanged in cyclohexane and ether solutions.[168]

The addition of trimethylsilylcarbene, generated by photolysis of diazomethyltrimethylsilane, to olefins yields trimethylsilylcyclopropanes.[169] The addition to <u>trans</u>-but-2-ene is stereospecific. Dihalocarbenes add to the olefinic bond in 1-silacyclopent-3-enes,[170] and 1-allyl-1-cycloalkanols and their trimethylsilyl ethers.[171]

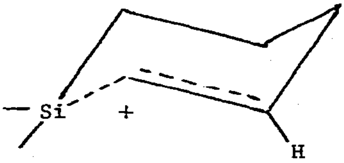
The cycloaddition reaction of tropone with 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene follow the same stereo- and regioselectivity as reported for the cycloaddition of tropone to cyclopentadiene.[172] The 1,3-cycloaddition of a variety of silyldiazoalkanes to several alkenes has been studied.[173] The data are consistent with initial formation of Δ^1-pyrazolines which undergo a thermal 1,3-rearrangement of the silyl group from carbon to nitrogen. Cycloaddition reactions are reported for the following: triphenylsilyl cyanide with aryl isocyanates;[174] bis(trimethylsilyl) hydrogen phosphate with 1,1- and 1,2-divinyloxyalkanes;[175] and trialkylsilylketenes with ketene dialkyl acetals.[176]

Addition reactions involving ring opening have been studied for silacyclobutanes.[177-178] Both nucleophilic and electrophilic reagents cleavage the Si-C bond in silacyclobutanes. N-Trimethylsilyloxazinone derivatives are obtained when $Ph_2C{=}NSiMe_3$ is heated with diketene.[179]

The solvolysis of RMe_2SiCMe_2Br in aqueous ethanol results in elimination of hydrogen bromide to produce isopropenylsilanes in high yields.[180] Effects of solvent, added salts, and variations of R on the rate of solvolysis are rationalized in terms of a transition state in which the carbon adjacent to silicon has developed considerable carbonium ion character. _Ab-initio_ SCFMO calculations indicate that the bridged β-silylethyl cation (<u>10</u>) is more stable than the open classical structure by 0.5 eV.[181] Calculations on carbonium ion stability indicate that the relative rates of S_N1 solvolysis of trimethylsilylalkyl halides largely are determined by the relative stabilities of the carbonium ion intermediates. Studies suggest that a 1-silaethylene intermediate may be formed by a β-elimination process when $(RMe_2SiOSiMe_2-CH_2)_3B$ is reacted with NaOEt in EtOH.[182] The enhanced reactivity of 1,1-dimethyl-1-silacyclohexane over tetraethylsilane toward dehydrosilylation by trityl fluoroborate is attributable to σ - π conjugation, <u>11</u>.[183] The α-triethylsilyl derivatives of acrolein and acrylic acid, and β-triethylsilylallyl alcohol are more stable than the saturated systems toward the β-elimination process.[184]



<u>10</u>



<u>11</u>

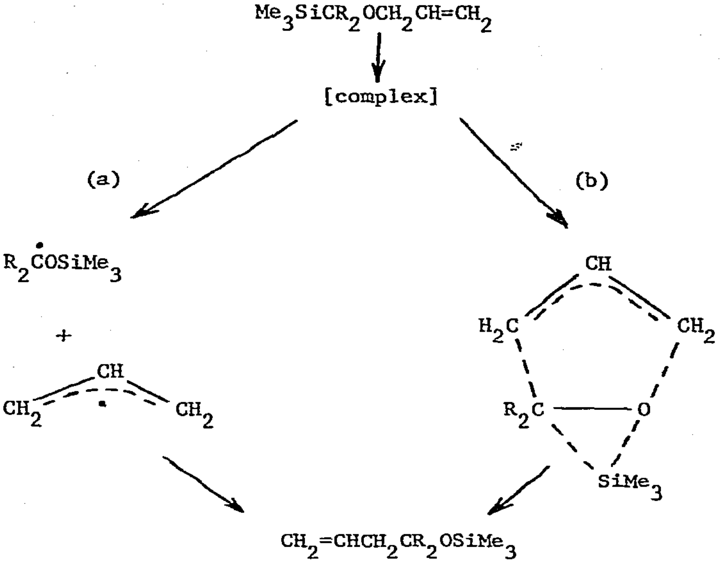
REARRANGEMENT

Molecular rearrangements involving interactions between silicon and oxygen are discussed in a recent publication.[185]

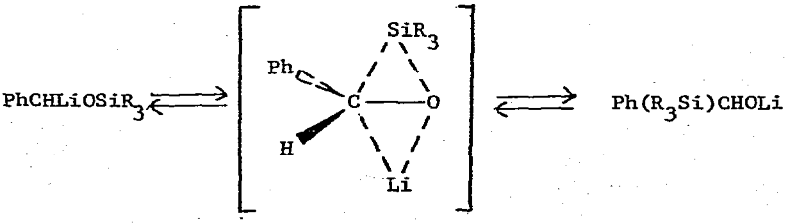
The facile migration of silyl groups from C→C in silyl-olefinic ring systems (fluxional behavior) continues to receive attention. A review article has been published on the implications for orbital symmetry rules in explaining the direction of molecular rearrangements of fluxional group IV organometallic compounds.[186] A potential curve close to the reaction coordinate has been calculated for the symmetry-allowed 1,5-rearrangement channel of cyclopentadienylsilane.[187] CNDO/2 calculations of the ground state geometry and the transition state geometry for SiH_3 migration have been reported.[188] Ab initio molecular orbital calculations and photoelectron spectroscopy data have been used to interpret in detail the differences in fluxional behavior of a variety of cyclopentadiene derivatives of the representative elements.[189] The ^1H and ^{13}C NMR spectra of the fluxional molecules, $C_9H_7MMe_3$ (when M = Si, Ge, Sn), have been determined over a wide temperature range in order to determine the relative migratory ability of the cyclopentadienyl and indenyl ligands.[190-191] Similarly, the ^1H and ^{13}C NMR spectra have been used to study silicon migration in N-(trimethylsilyl)-3,5-dimethylazoles.[192] An intermolecular exchange of the trimethylsilyl groups between the two nitrogen atoms is proposed to explain the NMR data. 5,8-Bis(trimethylsilyl)-1,3,6-cyclooctatriene does not appear to undergo facile trimethylsilyl migration.[193]

The C→O migration of a triorganosilyl group is common in organosilicon chemistry due to the large Si-O bond energy. Based on kinetic and isotope studies, the thermal rearrangement of (trimethylsilyl)methyl allyl ethers is proposed to proceed by rate-determining formation of a short-lived complex in which the silyl moiety coordinates with oxygen followed by a rapid rearrangement by pathway (a) or (b) as shown in Scheme VII.[194] Stereochemical and kinetic studies show that both C→O and O→C migrations of silyl groups occur with retention of configuration at silicon on the thermal rearrangement of $Me_3SiCR_2OSiMe_2Ph$.[195] Kinetics of the thermal rearrangements of $[p\text{-}XC_6H_4Me_2SiO]_2$ (when X = MeO, Me, H, Br) which yield products consistent with an intramolecular migration of silicon from carbon to oxygen have been studied.[196]

In some reactive intermediates, O→C and S→C migrations of triorganosilyl groups have been reported. 1,2-Rearrangements of the above type have been observed for the benzylic anions of benzyloxyorganosilanes[197,198] and benzylthiotrimethylsilane.[199] Stereochemical studies indicate that the O→C anionic rearrangement is reversible and proceeds with inversion of configuration at the benzylic carbon (cf. Scheme VIII). 1,2-Triorganosilyl shifts from



Scheme VII



Scheme VIII

carbon to oxygen or sulfur are proposed for unstable silyloxonium and silylsulfonium ylides.[200]

O→O, 1,4-trimethylsilyl shifts occur during the m-chloroperbenzoic acid oxidation of silyl enol ethers.[201,202] Angle strain at silicon in 1-acetylacetonato-1-methyl-1-silacyclobutane enhances the 1,5-silyl migration between the two oxygen centers.[203] At slightly elevated temperatures, a facile irreversible rearrangement via ring opening occurs to yield 1,3,5-trimethyl-2,9-dioxa-1-silabicyclo[3.3.1]non-3-ene.

C→N migration of triorganosilyl groups, a 1,2-anionic rearrangement, has been observed when aminomethylsilanes are treated with small amount of n-butyllithium.[204] The reverse process, N→C migration, has been observed when N-trimethylsilyldibenzylamine is treated with t-butyllithium or n-butyllithium-TMEDA. The thermal rearrangement of 3-trimethylsilyl-Δ^1-pyrazolines to 1-trimethylsilyl-Δ^2-pyrazolines may proceed by a C→N, 1,3-silyl migration.[173] Similarly, a C→N, 1,3-silyl migration is observed when α-silylated aldimines are allowed to stand in the presence of bromotrimethylsilane.[205]

NMR techniques have been used to study the facile O→N, 1,3-silyl migration in bis(trimethylsilyl)amides.[206] Silyl derivatives of nitramines undergo a similar O↔N migration at room temperature.[207] Increasing temperature and bulky substituent groups on silicon favor the O-derivative.

The rearrangement of organosilicon-transition metal compounds has been reported. Both silicon- and iron-containing groups are proposed to undergo 1,2-migrations in the thermal rearrangement of $Me_3SiSiMe_2CH_2Fe(CO)_2Cp$ resulting in the following change in the bonding sequence, SiSiCFe → SiCSiFe.[208] An intramolecular migration of a trimethylsilyl group from Rh→C is suggested in order to explain the silylation of the cycloheptatriene ring, eq. 9.[209] Both iron and chlorine undergo 1,2 migrations between

$$Ru(SiMe_3)_2(CO)_4 + C_7H_8 \longrightarrow Ru(SiMe_3)(CO)_2(C_7H_8SiMe_3) \qquad (9)$$

silicon and carbon in the compounds, $CpFe(CO)_2(SiMe_{3-n}Cl_n)CH_2Cl$, on heating.[210]

Other types of rearrangements of organosilicon compounds have been reported. A free radical mechanism is proposed for the 1,4-aryl-group migration in $ArSiMe_2CH_2CH_2CH_2X$ (where X = Cl, Br) on reduction with n-Bu_3SnH-DTBP.[211] Aryl and alkyl groups rearrange between silicon and aluminum when dimethyl(triphenylsiloxy)aluminum is heated to 250°.[212] The trimethylsiloxycyclopropane derivatives obtained from silyl cycloalkenyl ethers by the Simons-Smith reaction, can be isomerized in situ to silyl ethers of 2-methylenecycloalkanols by changing the amount of solvent.[213] A high stereoselectivity has been observed for the rearrangement of allyl siloxyvinyl ethers to β, γ-unsaturated acids.[214] A chair cyclohexane-like transition state has been proposed. Polar solvents catalyze the allylic rearrangement given in eq. 10.[144]

$$RR'CCl(Ph_3Si)C{=}CH_2 \longrightarrow RR'C{=}C(SiR_3)CH_2Cl \qquad (10)$$

(Dialkylaminomethyl)triphenylsilanes are formed when dialkylmethyl(2-triphenylsilylethyl)ammonium halides are allowed to react with n-butyllithium.[215] Rearrangement of the unstable ylide intermediate by a cyclic process is proposed. Isomerization by ring expansion from a four- to a six-membered ring system has been observed for silylated phosphorus ylides.[216]

The thermal rearrangement of cis- and trans-1-trimethylsiloxy-1-vinylcyclodec-3-ene, a siloxy-Cope rearrangement, has been studied to evaluate ring-strain effects.[217] The thermal rearrangement of 3,4-bis(trimethylsiloxy)-endo-tricyclo[4.2.1.$0^{2,5}$]nona-3,7-diene has been reported.[218] Kinetic studies of the gas-phase isomerization of hexamethyldisilane to trimethylsilyl(dimethylsilyl)methane indicate that the isomerization proceeds by a radical chain reaction.[219] The photochemical isomerization of 1-sila-2,4-cyclohexadienes,[220] 1,2-disila-3,5-cyclohexadienes[221] and some silyl-1,3-butadienes[222] has been reported.

REDISTRIBUTION

The products resulting from the exchange of hydrogen and chlorine between $EtHSiCl_2$ and Me_2SiCl_2 catalyzed by $AlCl_3$ and $AlBr_3$ have been determined.[223] Equilibrium distributions have been investigated by NMR methods for scrambling of fluorine vs. chlorine between silicon-based central moieties[224] and between the following centers: Me_2C, Me_2Si, Me_3Si, Me_2Ge, Me_3Ge, MeP(O), Me_2As.[225] The former study indicates a definite preference of fluorine for the silicon atom which bears the lesser number of alkyl groups, and the latter study allows predictions to be made for the following order of preferential affinities for fluorine vs. chlorine: $MeSi > MeP(O) > P(O) > Me_2Si > Me_2P(O) > MeP(S) > Me_3Si \approx MeP(Se) > MeP$. The exchange reaction of Me_3SiMMe_2 (where M = N, P, As) with $(CF_3)_2M'H$ (where M' = P, As) has been studied as a means of preparing compounds of the type $Me_3SiM'(CF_3)_2$.[226] The transsilylation of various methyl- and chloro-substituted disilazanes by Cl_nSiMe_{4-n} (where n = 2-4) has been investigated using NMR techniques.[227] The order of reactivity, $Me_2SiCl_2 < MeSiCl_3 > SiCl_4$, has been observed for the transsilylating agent. The transsilylation reactions of benzothiazol-2-ylsilanes with various chlorosilanes have been found to be sensitive to small differences in the ligands of both components.[228]

The conditions for the symmetrization reactions of $RHgSiR_3'$ have been investigated and discussed.[229] The exchange reactions between trimethylsilyl-VIB transition metal complexes and heterosiloxanes can be used for a qualitative estimate of relative metal-metalloid bond reactivity.[230] Symmetrical species are favored in the equilibrium between the dimeric species of tris(trialkylsiloxy)iron(III), tris(trialkylsiloxy)aluminum and the unsymmetrical iron-aluminum complex.[231]

FREE RADICAL

A review article has been published on organometal peroxides of the group IVB elements in which the homolytic cleavage of silyl peroxides is discussed.[232]

Organosilyl free radicals are important intermediates in many reactions of organosilicon compounds. A relatively stable silyl radical, $[(Me_3Si)_2CH]_3Si$, has been prepared by the reaction of $(Me_3Si)_2CHLi$ with Si_2Cl_6 followed by photolysis.[233] The ESR spectrum of this radical has been determined, $t_{\frac{1}{2}} \approx 10$ min. The thermolysis of bis(trimethylsilyl)dimine has been found to give rise to five main products.[234-236] ESR studies indicate that some of the products are formed via radical chain reactions involving trimethylsilyl radicals.[236] Similarly, ESR studies indicate that the thermal and photochemical decompositions of phenylazotriphenylsilane proceed by homolytic fission of the Si-N and N-C bonds.[237] The thermolysis and photolysis of $R_3CHgSiR'_3$ involve homolytic bond cleavage yielding free radical intermediates.[229] Kinetics of the reduction of methyltrichlorosilane by hydrogen are consistent with a mechanism in which the initial reaction is homolytic fission of the C-Si bond.[238] The reaction of deuterium atoms with silane has been studied by ESR methods.[239] Hydrogen-deuterium isotope effects have been calculated for the reaction of hydrogen atoms with disilane.[240] The following reactions which probably involve silyl-radical intermediates have been studied: the photolysis of H_2S in Me_2SiH_2;[241] the photochemical reduction of lactones with $HSiCl_3$;[242] the halogenation of transition metal-substituted silicon hydrides;[243] the direct silylation of non-conjugated olefins in the system, $Me_3SiCl/Mg/HMPA$, at > 170°.[244] Chemically induced dynamic nuclear polarization has been used to study the mechanism of photolysis of acylsilanes in CCl_4 solution.[245] The results call into question the accepted mechanism for acylsilane photolysis in CCl_4 and suggest caution in interpreting the chemical and stereochemical behavior of silyl radicals generated under these conditions.

The reactions of silyl radicals with unsaturated systems have been studied. A flash photolysis-ESR kinetic study of the addition of trimethylsilyl radicals to ethylene has been reported.[246] The results indicate ethylene is an efficient scavenger for trimethylsilyl radicals under steady illumination, photochemical reaction conditions. The addition of silyl radicals to other unsaturated systems has been reported: 1,1-di[bis(trifluoromethyl)amino]-ethylene;[247] tetrafluoropropyne and 3,3,3-trifluoropropyne;[248] 2-chloro- and 2-bromo-1,1-difluoroethylene;[249] diphenyldiazomethane;[250] nitrothiophenes, nitrothienothiophenes and nitrobenzene;[251] phenyl t-butyl nitrone;[252] methyl acetate.[253]

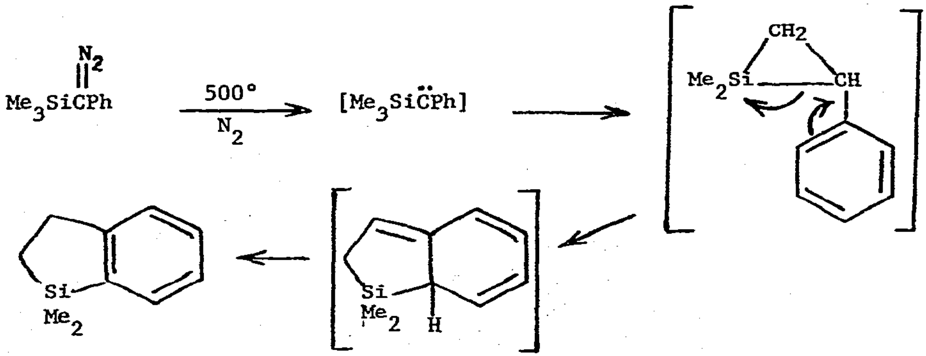
The reactions of silicon compounds with free radicals have been studied. Kinetics have been reported for the abstraction of hydrogen atoms from tetramethylsilane by $CF_3\cdot$ and $CD_3\cdot$[254] and from cyclic and noncyclic silicon hydrocarbons by 2,2,6,6-tetramethyl-4-hydroxypiperidino-1-oxyl.[255] ESR studies have shown that silyl-substituted phenoxyl radicals are intermediates in the reaction of hindered silicon-containing phenols with phenylmercury(II) hydroxide.[256,257] The photochemical chlorination of alkyltrichlorosilanes has been studied.[258,259] The relative reactivities of hydrogen atoms have been determined, and an activating β-mesomeric effect from $SiCl_3$ has been proposed. Free radical mechanisms have been proposed for the addition of hydrogen bromide to 1-trimethylsilyl-1-alkynes[260] and for the photolytic addition of hydrogen sulfide to dimethyldiallylsilane.[261] ESR techniques have shown that free radicals are involved in the Cu(II)-catalyzed oxidation of triorganosilanes.[262]

The anion radicals formed in an ether solution by electron transfer from an alkali metal to 1,4-bis(trimethylsilyl)buta-1,3-diyne,[263] 1-phenyl-2-trimethylsilylacetylene,[264] and bis(trimethylsilyl)diimine[265] have been studied. The electrochemical reduction of aryltrimethylsilanes in methylamine solvent is proposed to involve anion-radical intermediates.[266]

INSERTION

The products obtained from the reaction of magnesium or sodium with chlorohydrogenosilanes in THF, 1,2-dihydrogenodisilanes, can be explained in terms of insertion of silylene intermediates into Si-Cl and Si-H bonds.[267] 1-Oxa-2-silacyclohexanes are produced in the magnesium halide-catalyzed reaction of magnesium with diorganodichlorosilanes in THF.[268] The mechanism of formation of the insertion-type products is discussed.

A number of reactions have been reported for the insertion of carbenes into C-X and Si-X bonds of organosilicon compounds; trimethylsilylcarbene into Si-H and C-H bonds;[169] carbomethoxycarbene into the Si-H bond;[269] carboalkoxycarbenes into α-C-H, β-C-H, and Si-C bonds;[270] carboethoxy(trimethylsilyl)carbene into the C-S bond;[271] dichlorocarbene into the Si-Br bond;[272] 1,2,2-trifluoroethylidine into Si-H, Si-Cl and Si-Br bonds;[273] n-alkylvinylidine carbenes into Si-H and C-H bonds.[274-275] Based on Hammett correlations for the reaction of aryldimethylsilanes with carbomethoxycarbene, the authors suggest that the insertion of the free carbene into the Si-H bond involves a slightly ionic transition state.[269] The pyrolysis of phenyl(trimethylsilyl)diazomethane yields 1,1-dimethyl-2,3-benzo-1-silacyclopent-2-ene which probably is formed by an intramolecular insertion in the intermediate phenyl(trimethylsilyl)carbene, *cf.* Scheme IX.[276]



Scheme IX

Photolysis of phenyl(trimethylsilyl)diazomethane in alcoholic media results in an O-H insertion product.

(Trimethylsilylmethylene)dimethylphenylphosphorane reacts with phenyl isocyanate to form a 2:1 insertion product, which results from insertion of phenyl isocyanate into both the C-Si and C-H bonds.[277] The reaction of benzoyl-t-butylcarbodiimide with Me_3SiNMe_2 and $(Me_3Si)_2NMe$ yields products in which the diimide inserts in the Si-N bond.[278] Oxygen insertion into the Si-H bond occurs on ozonolysis of silanes[279] and into the Si-Si bond on the peracid oxidation of 1,2-disilacycloalkanes.[280] In the ozonolysis study, the effect of substituent groups on silicon on the rate of reaction are reported; for the peracid oxidation, a rate-charge transfer energy relationship has been found. The insertion of carbon dioxide in the Si-N bonds of 1,4-diaza-2,5-disilacyclohexane derivatives yields products with an expanded ring system.[281]

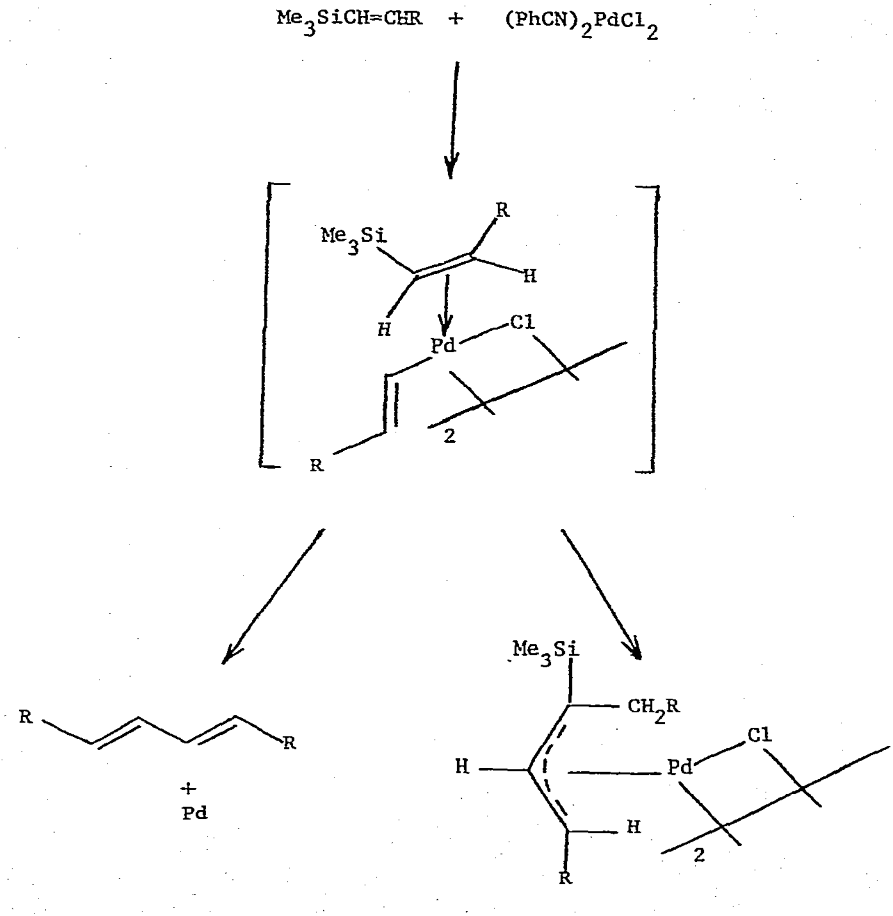
Insertion reactions of various metallic species of low coordination number have been reported: $[(Me_3Si)_2CH]_2Sn$ into M-H, M-C, M-Cl and M-M bonds (where M is a transition metal);[282] $SnCl_2$ into the C-Cl bond of chloromethylsilanes;[283] $Fe(CO)_4$ into the Si-Hg bond;[284] $Ni(CO)_4$ into the Si-Si bond of 1-t-butyl-3,3,4,4-tetrafluoro-3,4-disilacyclobut-1-ene.[285]

The reaction of vinyltrimethylsilanes with dichlorobis(benzonitrile)-palladium(II) is proposed to proceed by an addition-elimination-insertion process as shown in Scheme X.[286]

DECOMPOSITION

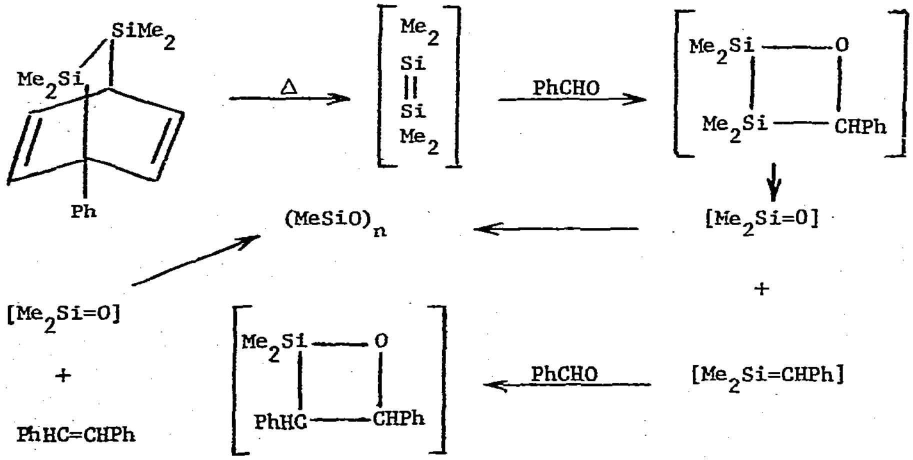
The mechanisms of decomposition reactions may be complex involving a variety of processes: ionization, free radical, elimination, rearrangement, etc. For this reason, some decomposition processes may have been placed in one of the above sections if it was deemed more appropriate.

Considerable attention has been focused on decomposition reactions involving unstable silicon analogs of unsaturated compounds as intermediates. A review article has been published in this area.[287] CNDO/2 and EHMO calculations have been performed on molecules containing C=Si and Si=Si bonds.[288-289] The results indicate that the C=Si bond is exceedingly polar and extremely reactive while the Si=Si bond is expected to be much less reactive and compounds containing this linkage may be amenable to isolation. The factors influencing cyclodimerization vs. polymerization of $R_2Si=CH_2$ have been



Scheme X

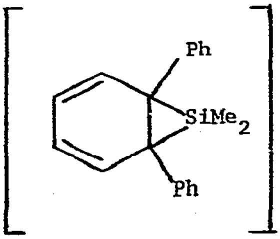
studied.[290] The pyrolysis of 1,1-dimethyl-2-phenyl-1-silacyclobutane yields products which indicate that the silacyclobutane ring can fragment in two different ways forming the intermediates, $Me_2Si{=}CH_2$ and $Me_2Si{=}CPhH$.[291] The reactions of $R_2Si{=}CH_2$ have been outlined in a paper on the chemistry of silacyclobutanes.[177] Two major pathways have been observed for the reaction of $R_2Si{=}CH_2$ with aldehydes and ketones: (a) olefin formation, postulated to occur via a pseudo-Wittig reaction; (b) silyl enol ether formation.[292] The order of reactivity and selectivity of $Me_2Si{=}CH_2$ toward a variety of substrates has been determined: $Ph_2C{=}O > ROH > ArOH \gg$ m-$ClPhNH_2 > CH_3CN$.[293] The dipolar character in reactions of $Me_2Si{=}CH_2$ with various halosilanes has been emphasized.[294] Evidence has been presented which indicates that silicon-nitrogen, double-bonded intermediates, $R_2Si{=}NPh$, are formed on thermolysis of silacyclobutanes in presence of the imines, $R'_2C{=}NPh$.[295] Studies suggest that the copyrolysis of 7,8-disilabicyclo[2.2.2]octa-2,5-dienes with benzaldehyde yields the intermediates, $Me_2Si{=}SiMe_2$, $Me_2Si{=}O$ and $Me_2Si{=}CPh$ (cf. Scheme XI).[296]



Scheme XI

The photochemical decomposition of the 1,2,3-trisilacycloheptane system to yield 1,2-disilacyclohexanes and silylenes has been shown to proceed stereospecifically.[297] The results are interpreted in terms of a concerted mechanism in which singlet silylene is eliminated. The application of Woodward-Hoffmann selection rules to the above photolysis requires that the process proceed through a σ^* excited state.[298] The photochemical fragmentations of 1,1-dimethyl-2-phenyl-1-silacyclobutane in methanol,[291] and 3-(trimethylsilyl)propyl and 2-(trimethylsilyl)ethyl thioacetates[299] have been studied.

The structure of the carbosilanes formed on pyrolysis of tetramethylsilane have been investigated.[300] Evidence has been obtained for a hydrogen atom chain sequence during the pyrolysis of trimethylsilane.[301] A mathematical model based on a homogeneous chain reaction with degenerate branching has been developed to interpret the experimental data on the pyrolysis of disilane.[301a] The pyrolysis of 1,1-dimethyl-2,7-diphenyl-1-silacyclohepta-2,4,6-triene yields dimethylsilylene and o-terphenyl. The intermediacy of 12 is proposed.[302] The products of the thermal degradation of phenyl(tolyloxy)-silanes have been determined.



12

α-Elimination processes are observed on the thermolysis of α-(halomethyl)trihalosilanes yielding carbene intermediates.[304-305] Kinetics of the thermal decomposition of β-(trifluoroethyl)silanes and the hot molecule kinetics of β-(trifluoroethyl)trifluorosilane have been studied.[306] The thermal stabilities of 6,6-dihalo-3-silatricyclo[3.1.0]hexanes toward rearrangement to cyclic and linear dienes have been reported.[170] Cyclization occurs when dichloro(o-chlorophenyl)-1-naphthylsilane and dichloro-1-naphthyl-o-tolylsilane are pyrolyzed.[307] Oxasilaphenanthrenes and oxasilanaphthalenes are obtained on pyrolysis of o-anisylphenylsilanes.[308]

On pyrolysis, N-silyl-N-(silylalkyl)carbamic esters undergo transsilylation with formation of cyclic carbamic esters as well as β-elimination of alkoxysilanes.[309] The electronic and structural effects of substituent groups were studied, and the mechanistic aspects are discussed. Kinetics of the thermal transformations of N-(trimethylsilyl)carboxamides have been determined and mechanisms are proposed.[310] The kinetics and stereochemistry of the thermolysis of trimethylsilylated sulfonyl carbonates yielding sulfonyl isocyanates and alkoxysilanes have been studied.[311] α-Deoxysilylation occurs when N-(trimethylsilyl)-substituted derivatives of hydroxylamines, $Me_3SiNROR'$, are pyrolyzed yielding nitrene intermediates.[312] A three-centered concerted mechanism is suggested for the unimolecular fragmentation.

The modes of thermal decomposition of various types of organopolysiloxanes have been studied: crosslinked polyorganosiloxanes;[313] oligo(methylphenylsiloxanes);[314] poly(metallophenylsiloxanes);[315,316] polyorganocarbosiloxanes;[317] urethanes with silarylene chain units.[318]

The factors which lead to the unusually high thermal stability of triorganosilylmethyl derivatives of metals continue to be investigated. The importance of the bulky nature of the bis(trimethylsilyl)methyl ligand has been emphasized in preparing trigonal and distorted trigonal d^0 to d^3 complexes, MR_3, (M = Y, Ti, V or Cr).[319] He(I) photoelectron spectra of Me_3SiCH_2- and Me_3CCH_2- derivatives of group IVA and IVB elements indicate that the observed stability trends are not related to ground state electronic effects.[320] The enhanced stability of trimethylsilylmethylthallium(III) compounds in comparison with the simple alkyl derivatives is attributed to steric effects.[321] Trimethylsilylmethyl derivatives of Zn, Al, Nb and Ta have been described.[322]

A review article has been published on the mass spectra of organometallic compounds of group IVB.[323] A number of studies have been reported on the fragmentation of organosilicon compounds: t-alkylsilanes;[324] vinylsilanes;[325] substituted phenyldimethylsilanes;[326-327] phenyl- and pentafluorophenylsilicon derivatives of pentacarbonylmanganese;[328] hexamethyldisiloxane;[329] methylphenyldisiloxanes and hexaphenyldisiloxane;[330] methylphenylcyclopolysiloxanes;[331] methylphenylspirosiloxanes;[332] 2,2-diorgano-1,3,2-dioxabenzo[d]silanes;[333] bis(trimethylsiloxy)naphthalenes;[334] substituted dimethylalkoxysilanes;[335] dimethyl- and trimethylalkoxysilanes;[336] products from the silylalkylation of adamantane;[337] 4-silaspiro[3,3]heptane, -octane and -nonane;[338] 1-silacyclohexa-2,4-diene and its 1,1-dimethyl and 1,1-dichloro derivatives;[339] 2,2-diorganosilicon-substituted oxazolidones;[340] trimethylsilyl derivatives of barbituates,[341] silylpyrazoles;[342] substituted 1,3-diaza-2-silacyclopentanes and -hexanes;[343] silyl derivatives of _o_-, _m_- and _p_-carboranes;[344] 1-silalactones;[345] trimethylsilyl derivatives of alkyl and aminoalkyl phosphonates;[346] ω-(trimethylsilyl)alkyl methyl sulfides and sulfones;[347] S-alkyl thioacetates.[299]

A number of studies have been reported on ion-molecular reactions. The kinematics of hydride-ion transfer reactions of monosilane and disilane and of hydrogen-atom transfer reactions of monosilane have been investigated.[348,349] Reactions involving hydride-ion transfer are proposed to proceed by a direct, stripping-type process and by a complex-formation mechanism. Ion-molecular reactions in monosilane-ethylene mixtures,[350] monosilane-acetylene mixtures,[351] disilane,[352] methylsilane,[353] and methylfluorosilanes[354] also have been investigated.

POLYMERIZATION

The polymerization reactions of four-membered silicon-carbon heterocycles have been reviewed.[177] Mono- and disilacyclobutanes with Ti, Zr and V halides are effective catalyst systems for the polymerization of olefins and can be used in place of Ziegler-Natta systems.[355] The mechanism of the anionic polymerization of trimethylvinylsilane using n-butyllithium has been investigated.[356] The anionic copolymerization of trimethylvinylsilane or phenyldimethylvinylsilane with acrylonitrile in the presence of n-butyllithium does not give a random copolymer, but yields a block copolymer with terminal polyacrylonitrile units.[357] The polymerization of cyclopentadienyltrimethylsilane in the presence of $SnCl_4$ and Cl_3CCO_2H has been found to be both first and second order with respect to monomer.[358] Carbonium ion intermediates are proposed on the basic of spectroscopic data. Mechanistic studies have been carried out on the polymerization of N,N'-(methylvinylsilylene)di-ε-caprolactam and N,N'-(methylvinylsilylene)di-γ-pyrrolidinone and their copolymerization with methyl methacrylate and styrene in the presence of dicumyl peroxide.[359]

The kinetics of the condensation of tetramethyl-1,3-disiloxanediol catalyzed by dibutyltin acetate and tin(II) 2-ethylhexanoate have been studied, and mechanisms for the catalytic condensation reactions have been suggested.[360] Evidence has been obtained which indicates that the electron acceptor property of silicon is gradually reduced during the dehydration of polysilicic acid.[361] Kinetic parameters have been determined for the condensation of polyfunctional organosiloxanes.[362] Experimental data indicate that the orders of the polycondensation reactions of polyfunctional compounds depend on the mean functionality of the system. Data on the cationic polymerization of siloxanes have been rationalized in terms of three possible reaction mechanisms.[363] The effect of the counter-ions on the anionic polymerization of 1,3,5-trimethyl-1,3,5-(trifluoropropyl)cyclotrisiloxane has been studied: $Na^+ > Li^+ > K^+ \gg n\text{-}Bu_2NH_2^+ > C_5H_{10}NH_2^+ > Et_3NH^+$.[364] Rate constants and activation energies have been determined for the anionic polymerization of (perfluoroalkylaryl)pentamethylcyclotrisiloxanes.[365] The anionic polymerization of methyl- and phenyl-substituted spirbicyclosiloxanes has been studied.[366]

For the $FeCl_3$—catalyzed bulk copolymerization of 1,7-di(methoxysilyl)-1,7-dicarba-closo-dodecaborane(12) and a dichlorosilane, a three-stage process has been observed: (a) low temperature polymerization; (b) high temperature polymerization; (c) foaming.[367] Polymerization and crosslinking mechanisms of the poly(m-carboanylene-siloxane)s are discussed. The mechanism of the catalytic influence of $FeCl_3$ on the heterofunctional condensation of m-carboranesilanes and -siloxanes has been investigated by UV spectroscopy.[368] Siliconium ion and $FeCl_4^-$-intermediates are proposed. The second-order rate constants for the copolymerization of substituted phenylmethylbis-(dimethylamino)silanes with 1,4-bis(hydroxydimethylsilyl)benzene have been determined and correlated by the Hammett equation.[369] The displacement at silicon is discussed in terms of a bimolecular mechanism involving a four-centered transition state. The electron density at nitrogen is more important than ring size effects in the copolymerization of disilaazacycloalkanes with aromatic and organosilicon diols.[370] Second-order rate constants and energies of activation have been determined for the polycondensation of (hydroxyalkyl)-arylsiloxanes with chlorocyclophosphazenes.[371]

DIRECT PROCESS

A review article has been published on the reactions of silicon and germanium with halogens, hydrogen halides and organic halides.[372] This review article includes a discussion on reaction mechanisms. Schemes have been proposed for the interaction of methyl chloride with the surface of chlorinated silicon in the synthesis of dimethyldichlorosilane[373] and methyltrichlorosilane.[374] Analysis of the experimental data suggests that intermediate surface molecules are formed in which the silicon atoms are in a five-valent state. Kinetic studies of the direct synthesis of methylchlorosilanes (Si-Cu alloy, $ZnCl_2$ promoter) indicate that the reaction is pseudo first order in methyl chloride.[375] The direct participation of surface $SiCl_n$ compounds in the formation of methylchlorosilanes by the direct process has been confirmed experimentally.[376] The formation, reaction and regeneration of surface compounds resemble a chain process. The effect of partical size of the Si-Cu catalyst on the direct synthesis of methylchlorosilanes has been studied.[377] The effect of added H_2 and HCl, temperature, and promoters on the reaction of chlorobenzene with Si-Cu alloys has been investigated.[378]

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