SILICON - REACTION MECHANISMS
ANNUAL SURVEY COVERING THE YEAR 1973

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CONTENTS

INTRODUCTION

This survey brings together the information published in 1973 which relates to organosilicon reaction mechanisms. All papers which suggest mechanisms based only on reaction products are not included. The survey is divided into sections based on reaction types; in some cases where overlapping occurs, both sections should be consulted. Within each section, papers on related areas are grouped together as much as possible.

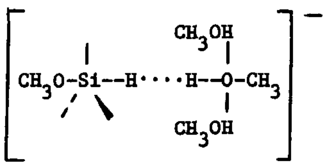
SUBSTITUTION

Ab initio quantum chemical techniques have been employed to study the mode of formation and stability of a Si(V) intermediate.[1] Using the model system

$$SiH_4 + H^- \longrightarrow SiH_5^-$$

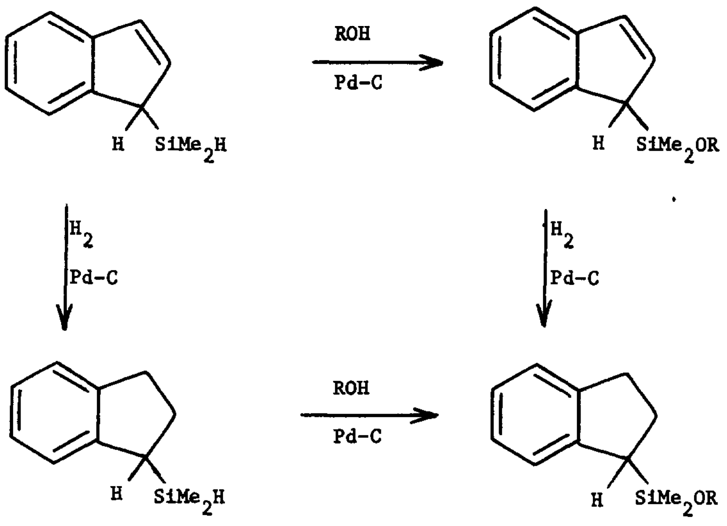
calculations indicate that attack of the hydride ion on a face of the tetrahedron of silane proceeds with an activation energy of 8.6 kcal/mol. forming a trigonal bipyramidal species that is 16.93 kcal/mol. more stable than the reactants. Effects of electronegative substituents on the stability and geometry of the intermediate also are discussed. Positive-ion gas phase reactions in monosilane have been reported.[2,3]

The solvolysis of organosilicon hydrides has been investigated. Solvent isotope effects on the rate and product ratio, HH/HD, for the methoxide-catalyzed methanolysis of triphenylsilane have been reported.[4] These studies suggest the five-coordinate transition state (1) in which the silicon-hydrogen bond remains essentially intact.



(1)

The reductive alcoholysis of dimethylindenylsilane catalyzed by Pd-C has been shown to occur in a stepwise manner.[5]



The alcoholysis of silanes is catalyzed by $(Ph_3P)_3RhCl$.[6] The following relative rates are reported:

$MeOH > EtOH > Me_2CHOH > Me_3SiOH$

$RSiH_3 > R_2SiH_2 > R_3SiH$

The asymmetric alcoholysis of diorganosilanes catalyzed by rhodium complexes has been observed.[7] The asymmetry may be induced by either an optically active alcohol or an optically active rhodium complex.

The reactivities of various mercaptans with organosilicon hydrides catalyzed by $(Ph_3P)_3RhCl$ to yield silyl thioethers are reported.[8] This rhodium complex in the presence of a silyl thioether catalyzes the reaction of triorganosilanes with enolizable ketones to yield triorganosilyl vinyl ethers.[9] The hydrolytic stability of the thiol group in a series of trialkoxysilanethiols has been determined.[10]

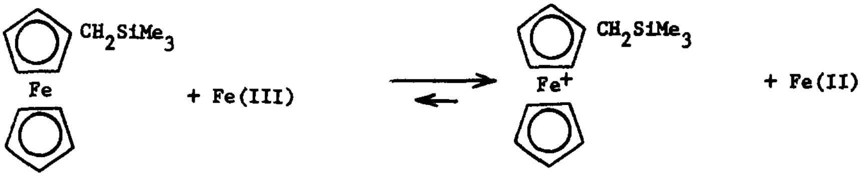
The rates of the acid- and base-catalyzed alcoholysis of $(p\text{-}XC_6H_4)Me_2SiOPh$ (X = F, Cl, Br, H, Me, MeO) in absolute ethanol have been reported.[11] The ρ values of -0.57 for the acid- and +0.19 for the base-catalyzed process are discussed in terms of bimolecular mechanisms. A pentacoordinate silicon intermediate is proposed for the acid-catalyzed reaction while this type of intermediate is considered unimportant for the base-catalyzed reaction.

In the alcoholysis of alkoxytrimethylsilanes,

$$Me_3SiOR + MeOH \rightleftharpoons Me_3SiOMe + ROH$$

the rate of obtainment of equilibrium varies with the nature of R as follows: $PhCH_2 > Ph_2CH > PhMeCH > PhMe_2C$.[12]

The solvolytic cleavage of the silicon-carbon bond has been investigated in ferrocenylmethyl-[13,14] m-carboranyl-[15], and alkynylsilanes.[16] Relative rate and polarographic studies are cited in support of the following mechanism for the iron(III) chloride-catalyzed methanolysis of ferrocenylmethylsilanes.[13]



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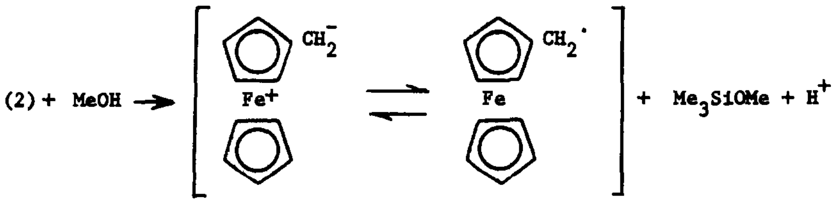

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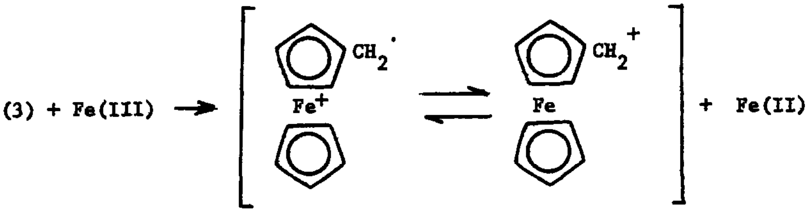

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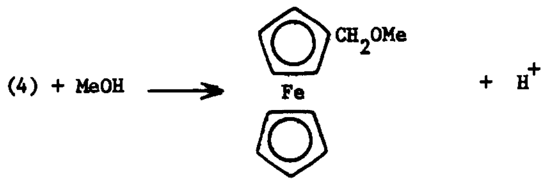
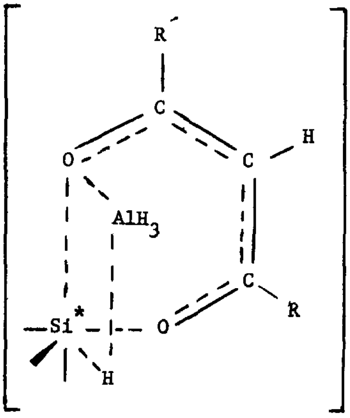
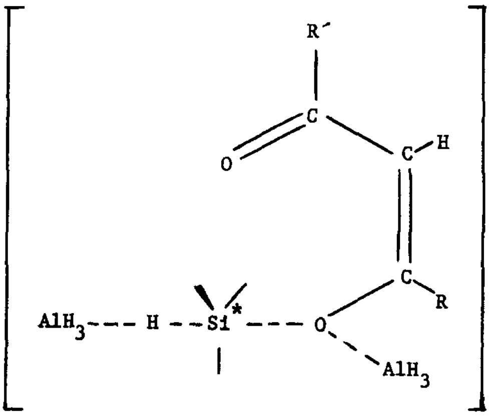


In a second paper,[14] the iron(III) chloride-catalyzed methanolysis of [α-(trimethylsilyl)benzyl]ferrocene and [*p*-methyl-α-(trimethylsilyl)benzyl]ferrocene is reported to proceed as indicated above. However, if insufficient Fe(III) is present and the reaction time is extended or a mixture of the reactant and product is treated with methanolic hydrogen chloride, radical coupling products are observed. These observations are in support of the proposed radical intermediates. On methanolysis of 1,7-bis(dimethylsilyl)-*m*-carborane, palladium-catalyzed, solvolytic cleavage of the $Si-C_{carb}$ bond, in addition to the usual cleavage of the Si-H bond, is observed.[15] The base-catalyzed solvolysis of $Et_3Si(C{\equiv}C)_nSiEt_3$ and $Et_3Si(C{\equiv}C)_nH$ in aqueous methanol has been reported.[16] The rate of cleavage parallels the acidity of the conjugate acid of the learning group. The studies indicate that electron-withdrawal by $H(C{\equiv}C)_n$ groups attenuates rapidly as n increases, reaching a limiting value for n = 8-10.

Further studies have been reported on the stereochemistry of substitution at silicon. Nucleophilic substitution at optically active O-silyl-β-dicarbonyl compounds has been investigated.[17] Solvolysis with water or methanol probably leads to inversion of configuration. While the reaction of the silyl derivatives of ethyl acetoacetate and ethyl butyroacetate with lithium aluminum hydride leads to inversion of configuration, the reaction with the silyl derivatives of acetylacetone, diethyl malonate, ethyl benzoacetate and benzoylacetone leads to retention of configuration. The following intermediates are proposed:

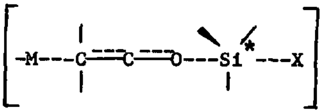


retention



inversion

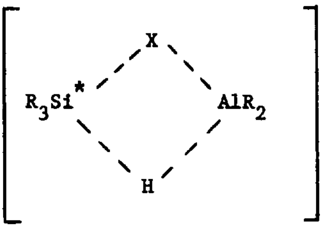
The reaction of optically active halo- and thiosilanes with α-mercurated and α-stannylated carbonyl compounds proceeds with inversion of configuration at silicon.[18] The transition state (5) is proposed to explain the stereochemistry (M = Hg, Sn; X = Cl, Br, SH, $SSiMe_3$).



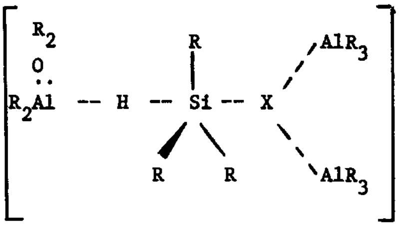
(5)

In a second paper, the stereochemistry of the cleavage of the silicon-oxygen bond in O-silyl-substituted enols, formed by the above reaction, is reported.[19] The alkenyloxy groups are poor leaving groups and in many ways resemble alkoxy groups.

Stereochemical-rate law correlations are given for the reduction of R_3Si^*X compounds with $i\text{-}Bu_2AlH$ in ether and n-hexane.[20] Retention or inversion at silicon is correlated with the number of molecules of the nucleophile involved in the transition state.

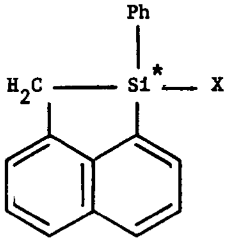


S_Ni-Si

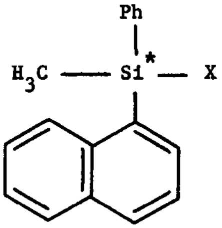


S_N2-Si

A comparison in the stereochemistry of substitution in the following two systems has been reported.[21]



(6)



(7)

While substitution at silicon in (7) may proceed with retention or inversion, in (6) only retention is observed. The results are explained in terms of the effect of angle strain on displacement at silicon.

Kinetic, isotopic and stereochemical studies on the reaction of R_3SiX with organolithium and Grignard reagents in ether or THF solvents are consistent with an S_Ni-Si mechanism in which the Si(V) complex is formed in the rate-determining step.[22]

A highly stereospecific method for reduction of triorganosilyl derivatives with Grignard reagents having β-hydrogens has been developed.[23,24]

$$R_3Si^*X + RMgBr \xrightarrow[\text{ether}]{\text{Ni(II)}} R_3Si^*H$$

X = OMe, F, Cl; R = Et, n-Pr, i-Pr, n-Bu, i-Bu

Retention of configuration at silicon is observed, and the order of reactivity of the Grignard reagents parallels the order observed for the hydrogen-deuterium exchange reaction of the corresponding deuteriosilane.

Other stereochemical studies on the reaction of organometallic reagents with optically active triorganosilyl derivatives are given below:

$$R_3Si^*H + R'MgX \xrightarrow[\text{ether}]{\text{Ni(II)}} R_3Si^*R' \qquad \text{(Ref. 25)}$$

$$R_3Si^*X \xrightarrow[\text{ether}]{Me_2CuLi} R_3Si^*Me \qquad \text{(Ref. 26)}$$

X = H, OMe, F, Cl, O-Menthyl

$$R_3Si^*Li + R_3Si^*Cl \xrightarrow{C_6H_{12}} R_3Si^*Si^*R_3 \qquad \text{(Ref. 27)}$$

An optically active triorganosilylketene has been synthesized.[28]

$$R_3Si^*Cl \xrightarrow[\text{ether}]{EtOC{\equiv}CMgBr} R_3Si^*C{\equiv}COEt \xrightarrow{125\text{-}130^\circ} R_3Si^*CH{=}C{=}O$$

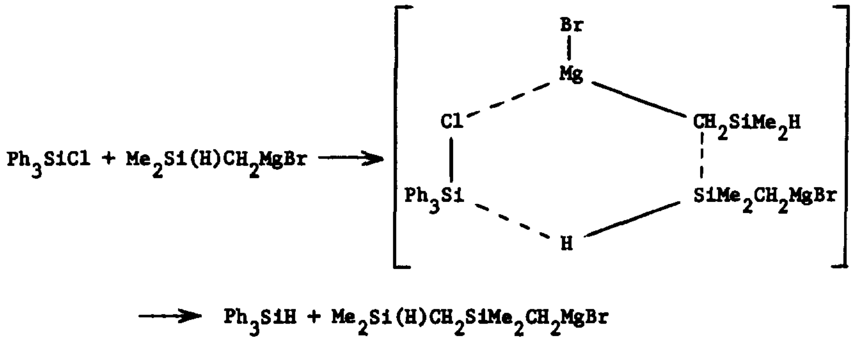
The stereochemistry of the formation and cleavage of silicon-platinum and silicon-mercury bonds has been studied.[29,29a] The complexes $[PtX(Si^*R_3)(PMe_2Ph)_2]$, where X = Cl, Br, I, and $[PtH(Si^*R_3)(PPh_3)_2]$ were used in these studies. The absolute configuration of (+)-<u>trans</u>-$[PtCl\{SiMe(1\text{-}C_{10}H_7)\ Ph\}(PMe_2Ph)_2]$ has been determined by X-ray diffraction which enables the stereochemistry of the following reaction, retention of configuration, to be assigned.[30]

$$R_3Si^*H + \underline{cis}\text{-}PtCl_2(PMe_2Ph)_2 \longrightarrow \underline{trans}\text{-}[PtCl(Si^*R_3)(PMe_2Ph)_2]$$

The work reported on optically-active silylmercurials suggests that the configuration of silicon is predominently retained in the formation and cleavage reactions studied.[29a]

Some new chiral organosilanes have been partially resolved by a kinetic method: phenylethylmethylsilane, benzylphenylmethylsilane, mesitylphenylmethylsilane and phenylisopropylmethylsilane.[31] There are indications that the observed stereochemistry for some reactions with these systems may differ from that reported in the literature. It is suggested that the presence of a naphthyl group at the asymmetric reaction center may lead to a different transition state topology.

The kinetics of the reduction of triorganochlorosilanes with (hydrosilyl)methyl and -ethyl Grignard reagents are reported.[32] The simplest scheme to explain the third-order kinetics, first order in silane and second order in Grignard reagent, is given below:



The reactions of ethyl bis(triphenylsilyl)aluminum with mercury compounds and peroxides have been studied.[33]

The replacement of various ligands, HMPA, DMAA, DMSO, DMFA and TBP, from the complexes $R_nSiCl_{4-n}\cdot mL$, where R = Me and Ph and m = 1 and 2, by pyridine appears to proceed by a dissociative process.[34]

Reactivity studies at bridgehead organosilicon compounds, 1-chloro-1-silabicyclo[2.2.1]heptane and 1-chloro-3,5,7-trimethyl-1,3,5,7-tetrasilaadamantane, with nucleophilic reagents are reported and compared with an acyclic analog, tris(trimethylsilylmethyl)chlorosilane.[35,36] Most of the results for nucleophilic displacement at silicon are best explained in terms of an S_N2-Si mechanism which proceeds with retention of configuration.

Fluoride ion catalyzes the reaction of trialkylsilanes with alcohols in anhydrous acetonitrile.[37] The proposed mechanism emphasizes the basicity of fluoride ion in this solvent.

$$ROH + F^{-} \longrightarrow RO^{-} + HF$$

$$RO^{-} + R'_3SiH + ROH \longrightarrow ROSiR'_3 + H_2 + RO^{-}$$

The reaction of thiols with hexamethyldisilazane is catalyzed by imidazole.[38] Evidence is presented for the formation of the intermediate, 1-(trimethylsilyl)imidazole. The high nucleophilic character of the imino-nitrogen has an important influence on the reaction path in hydrolysis and trans-silylation reactions of 2-imidazolylsilanes[39] and 2-benzothiazolylsilanes.[40] The trimethylsilylation of trinitromethane by N,N-diphenyl-N-trimethylsilylurea and by trimethylchlorosilane and silver or mercury salts of trinitromethane yields trimethylsilyl dinitromethanenitronate.[41]

The kinetics of the reaction of Me_3SiOMe with $SiCl_4$ have been studied by NMR methods.[42] The reaction is catalyzed by MeOH, Et_3SiOH, HCl and H_2O. The initial rate was found to be proportional to the catalyst concentration and inversely proportional to the square of the $SiCl_4$ concentration.

Extensive studies have been reported on the isomer distribution and relative rates of the iodine- and iron-catalyzed bromination of organosilicon compounds of the type $C_6H_5SiMe_{3-n}X_n$, where X = Cl, F; n = 0-3.[43] Bromination in the <u>ortho</u> and <u>para</u> positions is favored. The relative rate constants for bromodesilylation and iododesilylation are reported. Studies on the nitration of trimethylsilyl and dimethylfluorosilyl substituted benzene, indicate the Me_3Si- group is a poor <u>para</u>-director.[44] These results are explained in terms of competing inductive and π-bonding effects. Silacyclopentadiene complexes of cobalt are reported to undergo electrophilic substitution.[45]

The preparation of optically active perfluorophenylsilicon compounds is reported.[46] The cleavage of the α-naphthyl group from α-naphthylperfluorophenylphenylmethylsilane in a BrCl-chloroform solution followed by reduction with lithium aluminum hydride yields an optically active product.

A few studies have been reported on substitution at atoms other than silicon in organosilicon compounds. Steric and electronic effects are discussed for the metal-hydrogen exchange reaction of trimethylsilyl substituted methanes.[47,48] The modes of lithiation of vinyltrimethylsilanes are reported.[49] Nucleophilic substitution at both oxygen and silicon in bis(trimethylsilyl) peroxide has been observed.[50]

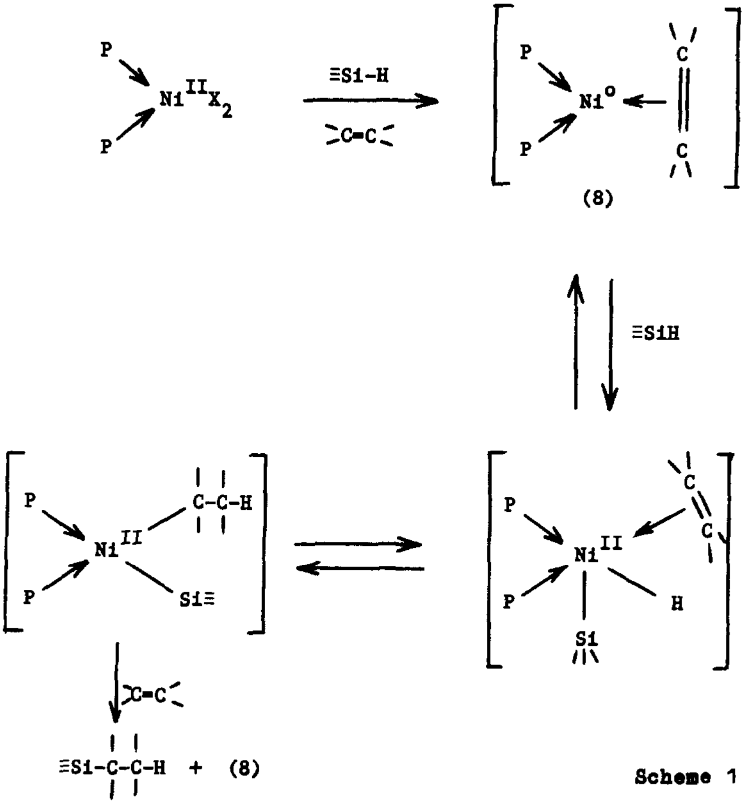
By fast reaction techniques the rates of metalation of 9-methylfluorene were determined: $Ph_3SiCs > Ph_3SiRb > Ph_3SiK > Ph_3SiNa > Ph_3SiLi$.[51] With the exception of Ph_3SiLi, the reactivity is determined by the ion-pair Coulombic binding energy.

ADDITION-ELIMINATION

Probably the most common addition reaction encountered in organosilicon chemistry is the addition of silicon hydrides to unsaturated compounds. The use of phosphine-nickel complexes to catalyze the hydrosilylation of olefins has been extensively studied.[52-54] Based on these **studies, the mechanism of Scheme 1 has been proposed for the hydrosilylation reaction.**

The role of metal-π-allylic intermediates in the palladium- and platinum-catalyzed addition of trimethylsiloxy-substituted silicon hydrides to β-methallyl chloride is discussed.[55] A mechanism involving a platinum-diene-silane complex is proposed to explain the stereochemistry of the addition of methyldichlorosilane to pentadienes.[56]

Kinetic and structure-orientation studies have been conducted on the platinum-catalyzed addition of silicon hydrides to alkenes[57] and alkynes.[58,59] Rate constants and activation energies for the hydrosilylation of 1-nonene and 2-methyl-1-pentene by $MeSiHCl_2$, $EtSiHCl_2$ and Et_2SiHCl (catalyst, H_2PtCl_6) were determined. With alkynes, the reaction (solvent,



Scheme 1

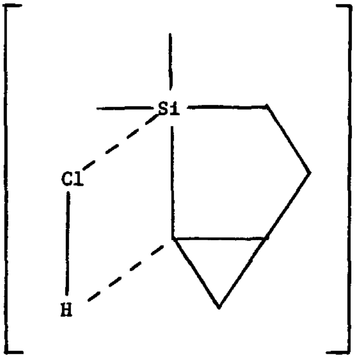
THF; catalyst, $H_2PtCl_6 \cdot 6H_2O$) is approximately second order; the relationship between rate and catalyst concentration is nonreproducible. The rate of hydrosilylation of unsaturated compounds using a platinized ion-exchange resin indicates a multistep process.[60]

Some studies have been reported on the addition of organosilicon hydrides to aldehydes and ketones. The relative effectiveness of ruthenium and rhodium complexes as catalysts for the addition of organosilicon hydrides to aldehydes and ketones is discussed.[61] A chiral cationic rhodium complex has been used to catalyze the asymmetric hydrosilylation of ketones.[62] The inductive effect of silicon in benzoyltrimethylsilane impedes the indium trichloride-catalyzed addition of triethylsilane to the carbonyl group.[63] The catalytic effect of fluoride to add trimethylsilanol to butadiene.[75] Metal-olefin intermediates are proposed to explain the addition-dimerization reaction which yields 1-trimethylsiloxy-2,7-octadiene.

Addition mechanisms are discussed for the reaction of silylphosphines with α-diketones[76] and ketenes,[77] of (trimethylsilylmethylene)-triphenylphosphorane with ketones,[78] and of triorganosilyl azides with perfluoroacyl chlorides.[79] Mechanistic implications are also discussed for the addition of RSO_2Cl,[80] H_2S[81] and $RSeCl$[82] to unsaturated organosilicon compounds.

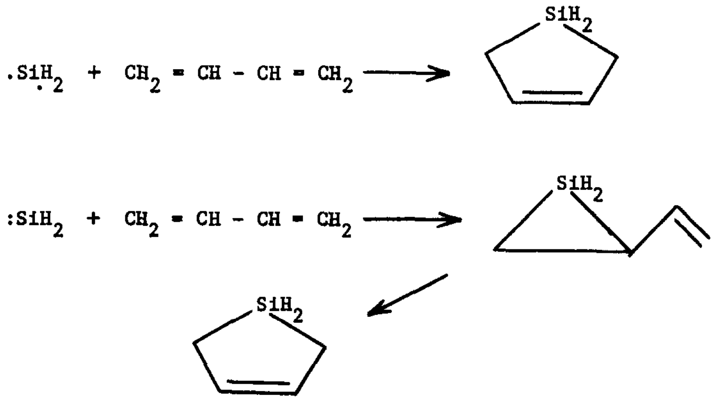
The symmetry allowed $\pi^4S + \pi^2S$ additions of various dienophiles to silacyclopentadienes have been observed.[83] The stereochemistry of the 1:1 adducts has been deduced on the basis of high resolution NMR studies. The reaction of trimethylsilylcyclopentadiene with various 1,3-dienes is reported.[84]

Ring-opening addition reactions for small-ring systems have been studied. The much higher reactivity of the silacyclopropane ring system as compared to the silacyclobutane system toward ring-opening reactions has been demonstrated.[85] The silacyclobutane ring is cleaved by phosphorus ylides.[85] 3,3-Dimethyl-3-silabicyclo[3.1.0]hexane is cleaved by hydrogen chloride under mild conditions in the gas phase to yield β-(chlorodimethylsilyl)ethylcyclopropane.[87] The activated complex (11) is proposed.

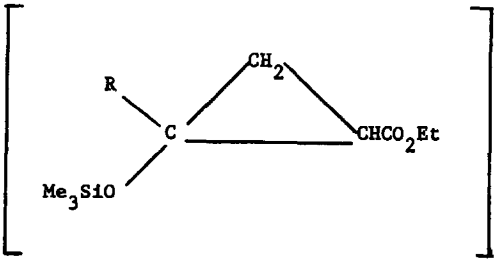


(11)

The addition of silylenes to olefins and carbenes to unsaturated silicon compounds has been studied. The reaction of lithium with 1,2-dichlorodisilane and conjugated dienes in the solvent, THF, yields monosilylcyclopentenes.[88] A silylene intermediate is proposed. The nuclear recoil technique has been used to generate SiH_2 in the presence of buta-1,3-diene.[89] Both singlet and triplet SiH_2 add to butadiene to yield silacyclopent-3-ene.



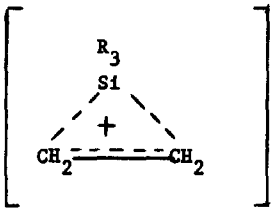
1,1-Dichlorocyclopropane derivatives are obtained in good yields when trichloromethylsilane is thermally decomposed in the presence of olefins.[90] Kinetic evidence is presented for the intermediacy of dichlorocarbene. The addition of $:CHCO_2Et$ to trimethylsiloxyalkenes which yields ν-keto esters probably proceeds through the intermediate (12).[91]



(12)

The reaction of bromine and deuterium chloride with <u>cis</u>- and *trans*-β-trimethylsilylstyrene gives products in which the trimethylsilyl group is replaced by bromine and deuterium with a high degree of stereospecificity.[92,93] For both reactions, addition products can be isolated at low temperatures. Bridging trimethylsilyl-stabilized carbonium ion intermediates are proposed to explain the stereochemistry. A bridging trimethylsilyl-stabilized carbanion is proposed for the dehydrobromination of *trans*-2-bromovinyltrimethylsilane.[94] An addition-elimination mechanism involving a cyclic transition state is proposed for the reaction of acyl chlorides with $CH_2=C(OR)OSiEt_3$.[95,96]

The cleavage of β-substituted alkyl groups from silicon, formally analogous to the β-elimination reaction of alkyl halides, is an important class of reactions of organosilicon compounds. A kinetic study of solvolysis of (2-chloroethyl)aryldimethylsilanes in aqueous ethanol and methanol has been reported.[97] Linear Grunwald-Winstein and Hammett correlations are observed. Two independent solvolytic pathways leading to products are proposed: a solvent assisted process and a process involving the nonclassical carbonium ion (13).



(13)

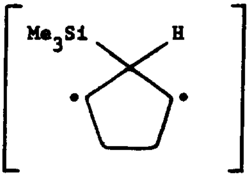
Kinetic studies on the acid- and base-catalyzed hydrolysis and fragmentation of 2-haloethyltrimethoysilanes indicate that the process can proceed by a number of mechanisms.[98] The nature of the substituents on silicon and the leaving group are important factors in determining the mechanistic pathway. A mechanism involving rate-determining formation of a silyl-substituted carbonium ion is proposed for the acid-catalyzed decomposition of (2-hydroxyethyl)aryldimethylsilanes in aqueous methanol.[99] The addition of various reagents to 1-sila-3-cyclopentene gives β-substituted silicon compounds which undergo ring-opening reactions through a β-elimination process.[100]

Elimination reactions also have been reported for the acid-catalyzed cleavage of allylic organosilicon derivatives[70] and the dehalosilylation of (o-halophenyl)trimethylsilanes by potassium t-butoxide or tetramethylammonium fluoride in aprotic solvents.[101] A benzyne intermediate is proposed for the latter process.

The ions formed in the mass spectrometer from 2,2,3,3-tetrafluorocyclobutylsilanes[102] and perfluorocyclobutylsilanes[103] undergo β-elimination reactions yielding olefins; molecular ions are usually absent.

REARRANGEMENT

One of the most common types of rearrangement of organosilicon compounds involves the migration of a silyl group between two or more atoms. The facile migration of silyl groups from C→C in nonrigid silyl-olefin ring systems (fluxional behavior) continues to receive attention. Variable temperature PMR probes of the 5-silylcyclopentadiene and 5-silylmethylcyclopentadiene systems indicate a 1,2 or random shift of the silyl group.[104] PMR studies are also reported on tris- and tetrakis(trimethylsilyl)cyclopentadiene.[105] Rate and equilibrium data are reported for the thermal isomerization of several substituted silylindenes.[106,107] The rate data suggests that the thermal rearrangement of 5-trimethylsilylbicyclo[2.1.0]-pentane to 3-trimethylsilylcyclopentene proceeds through the diradical intermediate (14), followed by migration of the trimethylsilyl group.[108]



(14)

The kinetics and stereochemistry of the silaallylic and silapropynylic rearrangements are reported.[109] Stereochemical studies using optically active compounds and deuterium labeling techniques show that each act of migration is accompanied by inversion of the silicon configuration. Thermolysis of the diazo derivatives of α,β-unsaturated esters gives rise to products which entails the migration of a trimethylsilyl group.[110] 1,2- and 1,4-trimethylsilyl shifts occur when 1,1-bis(trimethylsilyl)-1,2-diphenylethane is lithiated with n-butyllithium-TMEDA in hexane.[111]

O→O migration of silyl groups has been reported for trimethylsilyl esters of nitronic acids[112,113] and triorganosilyl ethers of β-dicarbonyl systems.[114-116] With the carbonyl derivatives, migration of the silyl group occurs with retention of stereochemistry.[114,115] Retention of configuration at silicon is observed for the *cis*-isomer and inversion for the *trans*-isomer.[115]

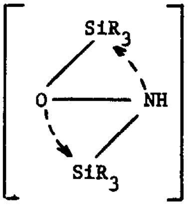
C→O rearrangements are common in organosilicon chemistry due to the large bond energy of the silicon-oxygen bond. First-order kinetics are reported for the thermal rearrangement, Si-C-O-N → N-C-O-Si, of 1-[bis(trifluoromethyl)aminoxyl]alkylsilanes.[117] The thermal decomposition of organosilicon peroxides, a first-order reaction, yields products consistent with an intramolecular migration of silicon from carbon to oxygen.[118-121] 1-Trimethylsilyl-1-(phenylsulfinyl)ethane rearranges to O-trimethylsilyl-S-phenyl throacetal on heating to 80°C.[122]

Several C↔N rearrangements of silyl groups have been reported. 2-Trimethylsilylpyrrole is unstable and slowly converts to the N-isomer.[123] When N-trimethylsilyldibenzylacetamidine (15) is lithiated with n-butylithium, the trimethylsilyl group migrates from nitrogen to carbon yielding N-benzyl-N'-[phenyl(trimethylsilyl)]methylacetamidine (16) on alcoholysis.[124] The process is reversed, (16) → (15), on heating to >95°. Trimethylbromosilane is a catalyst for the rearrangement,

$$\mathrm{Me_2C(SiMe_3)CH{=}NR \longrightarrow Me_2C{=}CHN(SiMe_3)R}$$

where R = Me, Et, n-Pr, i-Bu.[125]

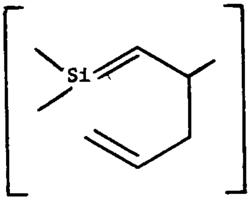
O ↔ N migration of silyl groups has been observed. The anions of organosilylhydroxylamines undergo a 1,2-rearrangement in which an organosilyl group migrates from oxygen to nitrogen.[126] Bis(organosilyl)-nitroxide radicals are formed by hydrogen abstraction and radical rearrangement of N,O-bis(organosilyl)hydroxylamines.[127] The exchange of organosilyl groups in N,O-bis(organosilyl)hydroxylamines is reported, and the intermediate (17) is suggested.[128]



(17)

The migration of a phenyl group from silicon to carbon occurs when (chloromethyl)phenyldimethylsilane and potassium acetate in anhydrous acetic acid are heated to 240-250°.[129]

Two papers report on the Cope rearrangement of organosilicon compounds. The silicon-Cope rearrangement of <u>cis</u>- and <u>trans</u>-propenyl-allyldimethylsilane is proposed to proceed through the double bonded silicon intermediate (18).[130]



(18)

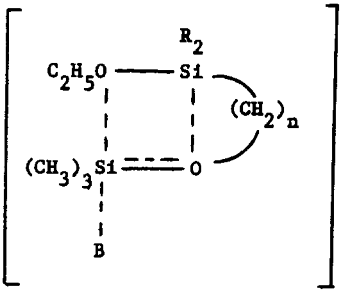
The siloxy-Cope rearrangement of cis-1-trimethylsiloxy-1-vinylcyclooct-3-ene yields predominantly ring contraction products.[131] Diradical intermediates are proposed.

REDISTRIBUTION

Redistribution reactions involving only organosilicon moieties have been studied. A quantitative study of the redistribution equilibria of fluorine vs. methoxy, thiomethyl and dimethylamino groups between methyl-substituted silicon moieties is reported.[132] Based on these and published data, the order of substituent groups with respect to preferential affinity for the least alkylated silicon was determined to be OMe $> NMe_2 \geqslant H > F \geqslant SMe > Cl > Br$. The constants for the equilibration of dimethylchlorosilane with vinyldimethylethoxysilane have been determined by NMR and gas-liquid chromatographic methods.[133]

The thermal disproportionation of diorganoalkoxyfluorosilanes[134] and dialkylfluorosilanes[135] has been observed. During the thermal degradation of phenyl-containing siloxanes in the presence of alkaline catalysts, some disproportionation occurs through migration of the phenyl groups.[136] The dimer and trimer species of phenylmethylcyclosilthianes are thermally interconvertible.[137]

The relative rates of the acid- and base-catalyzed cyclization of (ω-ethoxysilylalkoxy)trimethylsilanes have been determined.[138] Based on the kinetic data, a four-centered mechanism is proposed involving the intermediate (19).



(19)

(Chloromethyl)methylchlorosilanes undergo condensation-disproportionation reactions with trichlorosilane in the presence of tertiary amines.[139] These redistributions may be associated with the occurrence of the "α-effect".

Redistribution reactions between organosilicon and non-silicon moieties also have been studied. Kinetics, stereochemistry, isotope effects and steric effects have been determined for the exchange reactions between organosilicon hydrides and alkoxytin compounds.[140] The results support a S_Ni mechanism in which O-Si bond formation is more important than Sn-H bond formation or a two-step mechanism involving an unstable pentacovalent silicon intermediate. Studies on the oxygen-halogen exchange between organosilicon,-germanium and -tin moieties have been extended.[141] The exchange of organosilylmercury compounds with bis(perfluoroalkyl)-mercury and mercury(II) fluoride favors the unsymmetrical products.[142]

Equilibrium constants have been measured by PMR procedures for the exchange between Me_2SiX_2 and $MePY_2$, $MeP(O)Y_2$, $MeP(S)Y_2$, moieties: where X = Cl, Br, OPh, SMe; Y = Br, OPh, SMe, NMe_2.[143] The equilibrium data and kinetics of exchange of chlorine and bromine between the dimethylsilicon and methylthiophosphonyl moieties are discussed. PMR methods also have been used to study the exchange between and the condensation to oligomers of Me_2SiX_2 and $MeP(O)Y_2$, where X and Y = Cl, OMe.[144]

FREE RADICAL

A review article covering the preparation and chemistry of group IVb free radicals with particular emphasis on silyl radicals has been published.[145]

Mechanistic studies have been reported on the generation of silyl radicals by atom transfer and chemical activation processes. Arrhenius parameters have been measured for the reaction of methyl radicals with silane and methylsilane[146] and for the reaction of higher alkyl radicals with silane.[147] The kinetics of hydrogen atom abstraction from chlorosilane by trifluoromethyl radicals have been determined.[148] Decomposition kinetics of chemically activated dimethylsilane and ethylsilane produced by reaction of singlet methylene with methylsilane are reported.[149] Rate constants for various decomposition paths were deduced from the kinetic data. A free radical process is proposed for the reaction of nitrogen dioxide with trimethylsilane and triethylsilane in which triorganosilyl radicals are formed by hydrogen extraction by nitrogen dioxide and radical intermediates.[150] Data are presented which indicate that branched-chain polysilanyl radicals generated by hydrogen extraction by t-butoxy radicals in benzene solution survive until dimerization occurs.[151] A radical pathway, rather than a four-centered molecular process, is suggested for the thermolysis of ethyltrichlorosilane and ethyltrimethylsilane.[152] The primary process in each case is the dehydrosilylation reaction.

Several studies have been reported on the photolysis of silicon compounds to produce silyl radicals. Mechanistic pathways involving silyl radicals are proposed for the room-temperature mercury $6(^3P_1)$ photosensitization of disilane.[153] Kinetic, isotopic and scavenger studies have established the nature of the initiation step. The trichlorosilyl radical has been prepared in an adamantane matrix by irradiating ethyltrichlorosilane.[154] ESR studies indicate that $(d\text{-}p)\pi$ bonding between silicon and chlorine is important. Mechanistic studies indicate that the trichlorosilyl radical is an intermediate in the photoinduced reductions of methyl acetate and ethyl methyl ether by trichlorosilane.[155] The photolysis of acylsilanes in non-polar solvents yields silyl radicals.[156] In non-halogenated solvents, e.g., cyclohexane, the products result primarily from attack of the silyl radical on the carbonyl oxygen of the acylsilane. Photolysis of bis(trimethylsilylmethyl)mercury yields products resulting from reactions involving the radicals, $Me_3SiCH_2\cdot$, $Me_3Si\cdot$ and $Me\cdot$.[157] Ultraviolet irradiation of an optically active organosilylmercurial, $(R_3Si^*)_2Hg$, in cyclohexane, gives the disilane, $(R_3Si^*)_2$, in high yield.[29a]

A free radical process is suggested in which the R_3Si^* radicals at least partially retain their configuration.

Trimethylsilyl radicals are formed by an electron transfer process when trimethylsilylsodium in HMPA is treated with a substrate such as naphthalene, fluorene or benzophenone.[158]

$$Me_3Si^- + ArH \xrightarrow{HMPA} Me_3Si\cdot + ArH\cdot^-$$

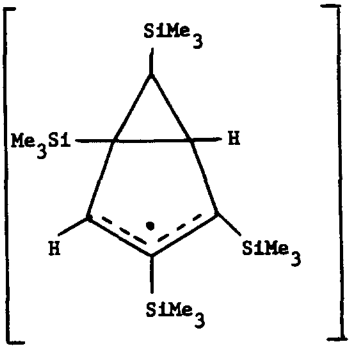
Bond dissociation energies of Si-H and Si-Si have been determined by studying free radical reactions. The relative bond dissociation energies of the Si-H bond in methylsilanes have been estimated from recoil tritium abstraction yields.[159] The kinetics of the gas-phase reaction between iodine and trimethylsilane have been studied, and the data obtained used to calculate the Si-H bond dissociation energy.[160] The values obtained are considerably higher than previous estimates. The kinetics of the thermolysis of hexamethyldisilane have been reinvestigated.[161] The process has been found to be a short-chain, free-radical process, and the kinetic data have been used to calculate the Si-Si bond dissociation energy.

The reactions of silyl radicals with various organic compounds have been reported. The relative rates of chlorine atom extraction from alkyl chlorides by the trimethylsilyl radical have been determined in the gas phase by a competitive technique.[162] A kinetic study of the gas phase photoaddition of trichlorosilane to ethylene in the presence of acetone at 200° indicates that the reaction is reversible.[163] The thermal addition of trichlorosilane to ethylene, and the decomposition of ethyltrichlorosilane also have been studied.[152] The addition of triplet silylene to buta-1,3-diene has been observed (*cf*. Addition-Elimination).[89] Tetrafluorodisilylene, a diradical, undergoes cycloaddition reactions with unsaturated hydrocarbons[164] and trifluoroacetyl chloride.[165] In the olefin cycloaddition reaction, application of the principle of orbital symmetry conservation requires the tetrafluorodisilane unit to approach the acetylene molecule perpendicularly. The ease of addition of silyl radicals to the carbonyl group is related to the nature of the carbonyl compound, diketones > oxaletes > ketones > trifluoroacetates > formates > acetates.[166] The silyl radicals are more reactive than radicals of the other group IVb elements of similar structure, excluding carbon. A radicals mechanism is proposed for the addition of triorganosilicon hydrides to N=N bonds of dialkyl azodicarboxylates and azobenzene.[167]

Homolytic substitution at silicon, S_H2, is proposed for the reaction of trimethylsiloxy radicals with trimethylsilyl t-butyl peroxide to generate t-butylperoxy radicals.[168] The photo-oxidation in THF and peroxide oxidation of 1,1,2,2-tetramethyl-3,4,5,6-tetraphenyl-1,2-disila-3,4-cyclohexadiene to the cyclic disiloxane are proposed to proceed by attack of a peroxy radical at the Si-Si bond.[169] The triphenylsiloxy radical is proposed as an intermediate in the reaction of triphenylsilyl hydroperoxide with phenyl isocyanate.[170]

Other radicals containing trimethylsilyl groups have been reported. Pyrolysis of $Et_3SiCH_2CH_2CO_2O\text{-}t\text{-}Bu$ and $Et_3SiCH_2CO_2OCMe_2Ph$ are reported to form the radicals $Et_3SiCH_2CH_2\cdot$ and $Et_3SiCH_2\cdot$ respectively.[171,172] When 2-bromoalkoxysilanes react with magnesium in diethyl ether solution, elimination, coupling and disproportionation products are obtained.[173] A mechanism is proposed in which the Grignard reagent decomposes forming the radical, $Me_3SiO-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot$. Tris(trimethylsilyl)hydrazyl and tris(t-butyldimethylsilyl)hydrazyl radicals have been obtained by electrolytic oxidation of the lithium salt of the parent hydrazine and by the ultraviolet photolysis of the parent hydrazine.[174] The photolysis of bis[bis(trimethylsilyl)methyl]tin(II) yields the unusually stable free radical, tris[bis(trimethylsilyl)methyl]tin(III).[175] The overall process is viewed as a photochemical disproportionation.

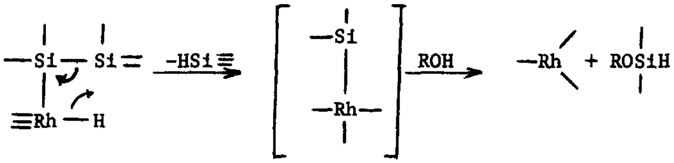
The products of the photolysis of 1,2,4,5-tetrakis(trimethylsilyl)-benzene have been determined.[176] It is proposed that the reaction proceeds <u>via</u> a symmetry allowed concerted process from excited states of 1,2,4,5-tetrakis(trimethylsilyl)benzene and/or <u>via</u> the intermediate (20) which also may be involved in a symmetry forbidden rearomatization.



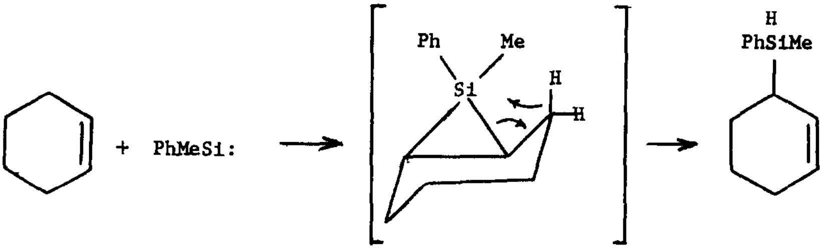
(20)

INSERTION

Insertion reactions are common for silylenes and carbenes. Arrhenius parameters and relative rates of the insertion of silylene, prepared by pyrolysis of disilane, into Si-Si and Si-H bonds are reported.[177] Similarly, silylenes were prepared by pyrolysis of Si_2F_6, FSi_2H_5, $ClSi_2H_5$, 1,1-F_2SiH_4, 1,1-$Cl_2Si_2H_4$ and $(MeSiHCl)_2$.[178] The following order of silylene insertion rates into Si-H bonds was determined: SiH_2 > ClSiH > FSiH >> $SiCl_2$, SiF_2. The relative rates of SiH_2 insertion into several methylsilanes and methylgermanes in competition with disilane can be correlated with steric effects and the hydridic character of the M-H bond.[179,180] Pyrolysis of trisilane yields the diradicals, SiH_2 and Si_2H_4.[179] Insertion of R_2Si species into Si-H bonds can account for the tris(triphenylphosphine)chlororhodium-catalyzed disproportionation of polyhydromonosilanes.[181] It is proposed that a rhodium-"silenoid" intermediate is formed. This rhodium catalyst also is effective for inserting R_2Si species into O-H bonds of alcohols.[182] The following mechanism is proposed for the reaction of hydropolysilanes with alcohols.



The insertion of photochemically generated methylphenylsilylene into the allylic C-H bonds of cyclohexene is proposed to proceed by the following mechanism.[183]



The formation of hexamethyl-1,2-disila-3-cyclobutene by the vapor phase thermolysis of 1,2-dimethoxytetramethyldisilane in the presence of dimethylacetylene is proposed to proceed by a mechanism involving formation of a silacyclopropene intermediate followed by insertion of dimethylsilylene into a C-Si bond.[184]

The photolysis of acylsilanes in polar solvents, *e.g.*, alcohols, acetic acid, hydrogen cyanide, leads to the isomeric siloxycarbenes.[156,185] The siloxycarbenes act as nucleophiles and insert into the polar H-X bond of the solvent. The kinetics and stereochemistry of the photolysis of acylsilanes also are reported.[185]

The insertion of carbenes into Si-H bonds has been studied. Fluorobromocarbene, formed by the thermal decomposition of phenyl(fluorodibromomethyl)mercury, reacts with triethylsilane to yield products which are attributed to insertion of the carbene into the Si-H bond.[186] Carbene compounds of group VI metals, $(CO)_5MC(X)C_6H_4Y$, where M = Cr, Mo, W; X = OMe, NC_nH_{2n} (n = 2,4); Y = *p*-OMe, *p*-Me, H, *p*-Cl, react with triorganosilanes to yield products resulting from insertion of the carbene in the Si-H bond.[187,188] The relative reactivities of these compounds with various group IVb metal hydrides were determined by competition experiments, and kinetic studies on the chromium complex suggest a mechanism in which the silicon hydride attacks an activated carbene-chromium complex.

Dichlorocarbene, generated from the decomposition of phenyl(bromodichloromethyl)mercury reacts with _cis_- and _trans_-1,3-dimethyl-1-n-butyl-1-silacyclobutane to give products resulting from insertion of the carbene into the Si-C(ring) and β-C-H bonds.[189] Kinetic studies indicate that dichlorocarbene is an intermediate in the thermal reaction of trichloromethylsilane derivatives with olefins yielding addition and insertion products.[90] The reaction of dichlorocarbene, generated from thermolysis of phenyl(trichloromethyl)mercury, and methylene, generated from diazomethane (Cu-catalysis), with hexachlorodisilane yields products resulting from insertion of these species into the Si-Cl bond.[190]

Two other reactions which lead to insertion products have been studied. Rate constants have been determined for the ozonolysis of triorganosilanes, and linear free energy correlations were obtained.[191] Trimethylsilyl- and trimethylsiloxyalkynes and trimethylsiloxyallenes yield sulfur trioxide insertion products when treated with sulfonating agents such as, trimethylsilyl chlorosulfonate and dioxane containing sulfur trioxide.[192] With the trimethylsiloxyallenes, rearrangements may occur.

DECOMPOSITION

The mechanisms of decomposition reactions may be complex involving a variety of processes: free radical, ionization, elimination, rearrangement, etc. Decomposition reactions not included in this section may appear in one of the above sections because it was deemed more appropriate.

The kinetics of the thermal decomposition of tetramethylsilane in the presence of ammonia forming silicon nitride, Si_3N_4, and other products have been studied.[193] The rate constants for the thermal decomposition of 7-silanorbornadienes by elimination of silylenes have been measured.[194] Stability toward silylene elimination is increased by bulky groups and electron-withdrawing substituents.

The pyrolysis of carbon-functional silicon compounds, usually leads to elimination products when the functional group is alpha or beta to silicon. The rate of the thermal decomposition of trichloromethyltrichlorosilane in the gas phase in the presence of ethylene has been reported.[195] The unimolecular formation of dichlorocarbene and silicon tetrachloride accounts for about 90% of the decomposition reaction. The rates of the thermal decomposition of 1,1,2,2-tetrafluoroethyltrifluorosilane and -trimethylsilane are kinetically first order.[196,197] The proposed mechanism involves the formation of the intermediate (difluoromethyl)-fluorocarbene in the rate-determining step which, in the absence of other compound, isomerizes quantitatively to trifluoroethylene. A kinetic study of the gas phase pyrolysis of the three isomeric 1-(trimethylsilylphenyl)ethyl acetates has been reported.[198] The trimethylslyl substituent activates in all positions according to the sequence, o > m > p. The thermal stability of β-aminoethylsilanes and their quaternary salts has been studied.[199]

Studies on the thermal decomposition of silicon-functional compounds have been reported. Kinetic studies of the thermal decomposition of bis(trimethylsilyl)mercury in solution indicate a bimolecular reaction occurs either with itself or with the solvent.[200] These reactions may proceed by a four-centered molecular process or via free radical intermediates. Pyrolysis of silylphosphine and germylsilane yields products which can be accounted for in terms of the intermediates, SiH_2, PH, and, SiH_2, GeH_2, respectively.[201] First-order kinetics are observed for the thermal decomposition of N-trimethylsilylamides of carboxylic acids.[202] The kinetic data suggest a mechanism involving N $\longleftrightarrow$ O rearrangements of the triorganosilyl group before decomposition. The simultaneous processes of a siloxane-type degradation leading to elimination of cyclic monomer and a radical-type splitting of the Si-C and C-C bonds in the hydrocarbon segment followed by subsequent reactions are proposed for the pyrolysis of poly[alkylene-bis(dimethylsiloxane)].[203]

A number of decomposition reactions have been reported for which Si=C intermediates are proposed: photolysis of 1,1-diphenylsilacyclobutane,[204] pyrolysis of 1,1-dimethylsilacyclobutane,[205,206] pyrolysis of 4-silaspiro[3,3]heptane,[207] and photolysis of trimethylsilyldiazoacetate.[208] Evidence in support of the proposed Si=C intermediates is based on reactions with alcohols,[204,208] aldehydes and ketones,[205] and acetonitrile and its derivatives.[206]

The unusually high thermal stability of triorganosilylmethyl derivatives of transition metals has been attributed to the absence of β-hydrogens which prevents decomposition via alkene elimination and the large steric requirements of the bulky organic groups hindering access to the vacant coordination sites.[209-212] Thermolysis of the oxido-carbene salts, $(CO)_5CrC(ONR_4)CH_2SiMe_3$, where R = Me, Et, results in fission of the CH_2-C(carbene) bond, yielding tetramethylsilane and the zwitterionic carbene compound, $(CO)_5CrC(O^-)CHR'N^+R_3$.[213]

A number of studies have been reported on the fragmentation of organosilicon compounds in the mass spectrometer: organocyclopolysilanes,[214] linear organopolysilanes,[215] 2,2-difluorocyclopropyl- and 3,3-difluoroallylsilanes,[216] 2,2,3,3-tetrafluorocyclobutylsilanes,[102] perfluorocyclobutylsilanes,[103] silacyclopentanols,[217] silacyclopent-3-enes,[218] phenoxyphenyl- and tolyloxyphenylsilanes,[219] trimethylsiloxy derivatives in tetramethylsilane,[220] and trimethylsiloxy derivatives of steroids.[221,222]

POLYMERIZATION

A kinetic study of the polymerization of monomeric silicic acid in aqueous hydrochloric acid solutions has been carried out, and the simple polymeric species isolated by chromatographic means.[223] The polymerization proceeds *via* the di-, cyclotri-, cyclotetra-, cyclohexa- or double-threering-silicic acid as intermediates. The hydrolytic polycondensation of methyltrichlorosilane in the presence of a hydrogen chloride acceptor proceeds with the formation of soluble polycyclic compounds and is independent of the methyltrichlorosilane concentration when a water soluble solvent is employed.[224] The formation of soluble hydrolytic polycondensation products of methyltrichlorosilane under these conditions is due to the faster rate of the intramolecular condensation reaction which leads to termination of the growing chain. Infrared and ebullioscopic studies on alkali metal silanolates in media of low dielectric constants indicate dimer formation.[225] These results readily explain the observed reaction order of 0.5 for the alkali metal silanolate catalysts in siloxane polymerization reactions.

The effectiveness of metal halides for catalyzing the polymerization of 1,1-dimethylsilacyclobutane and 1,1,3,3-tetramethyl-1,3-disilacyclobutane has been evaluated.[226] The studies reveal that polymerization occurs *via* cleavage of a ring Si-C bond with the formation of a linear polymer. Kinetics studies are reported for the CuCl-catalyzed polymerization. Dilatometric methods have been used to study the kinetics of the n-butyllithium-initiated polymerization of 1,1-dimethyl- and 1-phenyl-1-methyl-1-silocyclobutane.[227] The polymerization reaction was found to be first order in silane and one-half order in n-butyllithium for 5-15% conversion.

DIRECT PROCESS

Several papers have appeared during 1973 which deal with mechanistic aspects of the so-called direct process. A chain process occurring on the surface of the contact mass of silicon-copper powder which proceeds with the participation of initiators is proposed.[228] The initiators of the chain process are proposed to be $SiCl_n$ compounds on the surface of the contact mass formed by reaction with chlorine or chlorine donors (CuCl, HCl). Studies of the direct synthesis of methyltrichlorosilane in the presence of methyldichlorosilane or toluene led the authors to the conclusion that the direct synthesis proceeds by a chemisorption mechanism.[229] Chlorination of the surface of the contact mass before reaction with methyl chloride leads initially to loss in activity of the silicon surface.[230] The reduced activity is explained in terms of consumption of the intermediate products formed on the surface during chlorination.

The decomposition products of ethyl chloride on the silicon-copper and silicon-copper-calcium silicide contact masses have been determined.[231] Addition of calcium silicide enhances the decomposition of ethyl chloride, the adsorption of ethylene on the contact mass, and the formation of ethyldichlorosilane.[231,232] The addition of microamounts of bismuth to the silicon-copper contact mass inhibits the decomposition of ethyl chloride and enhances the yield of diethyldichlorosilane.[233]

Analysis of the data on the direct synthesis of phenylchlorosilanes using chlorobenzene and hydrogen chloride mixtures indicates that a chain mechanism holds with the involvement of an initiator (hydrogen chloride) and surface compounds of the type, $SiCl_n$, as indicated in Ref. 228.[234] An examination of the silicon-copper contact mass before and after reaction with chlorobenzene by x-ray diffraction, electron microscopy and ESR is reported.[235] These studies indicate an intermetallic compound Cu_3Si is formed and broken down during reaction and the catalyst activity can be related to the amount of Cu_3Si. The mechanistic effect of trichlorosilane on the direct synthesis of phenyltrichlorosilanes is discussed in terms of surface catalytic reactions.[236] The effect of hydrogen-hydrogen chloride mixtures on the course of the direct synthesis of phenylchlorosilanes has been determined.[237]

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