Translated from *Uspekhi Khimii*, 55, 1096-1123 (1986) U.D.C. 547.245

The Oxidative Cleavage of the Silicon-Silicon Bond

G.A.Razuvaev, T.N.Brevnova, and V.V.Semenov

Data on the oxidative cleavage of single and double silicon-silicon bonds in inorganic and organic polysilanes with linear and cyclic structures have been summarised. Particular attention has been paid to studies in which the mechanisms of the oxidation are discussed. The nature of the silicon-silicon bond in organopolysilanes and disilenes has been briefly reviewed. The bibliography contains 248 references.

CONTENTS

I.	Introduction	606
II.	The nature of the silicon-silicon bond	606
III.	The oxidation of inorganic compounds containing a silicon-silicon bond	607
IV.	The oxidative cleavage of the silicon-silicon bond in organopolysilanes	608
V.	The oxidative cleavage of the silicon-silicon double bond	616

I. INTRODUCTION

Compounds with silicon–silicon bonds have not yet found such wide application as, for example, organopolysiloxanes, but the chemistry of compounds of this class[1-23] is now being intensively developed. Important recent achievements include the synthesis of stable disilenes, that is compounds with a silicon–silicon double bond.[24,25] The possible use of polysilanes to obtain silicon carbide materials,[26-30] as components of catalytic systems for the polymerisation of ethylene hydrocarbons,[31,32] and as stabilisers of polyvinyl chloride,[33] silylating and reducing reagents,[34] and also semiconductors,[35-36] is being studied.

The aim of the present review is to show how the reactivity of the Si–Si bond with respect to oxidation reactions of different types depends on the type of polysilane, the substituents on the silicon atom and in the organic group, the size of the ring, the length of the $-(-\mathrm{Si}-)_n-$ chain, and various other factors. Of greatest interest in this connection are studies in which the mechanisms of the oxidation reactions are discussed, and also studies from which it is possible to reach definite conclusions about the influence of the structure of the polysilane on its reactivity. Material on the application of reactions of this type in synthesis have not been considered, since this topic has been dealt with in detail in a number of reviews.[1,2,7-9,17,18] The photochemical and thermal reactions of polysilanes, taking place via radical, silylene, and sila-alkene intermediates, are discussed very briefly. The review does not deal with reactions taking place under the influence of catalysts.

Extensive material on the study of the properties of the Si–Si bond by spectroscopic methods has now accumulated. The use of spectroscopic data is extremely fruitful in the examination of the reactivity of polysilanes. For this reason, a separate section deals briefly with the properties of the silicon–silicon bond, based chiefly on ultraviolet spectroscopic data.

II. THE NATURE OF THE SILICON–SILICON BOND

In 1962, the ultraviolet spectrum of hexaphenyldisilane was found to contain a band at 240 nm,[37] not observed for tetraphenylsilane. At first, the authors cited attributed the appearance of this band to strong interactions between the phenyl groups via the 3*d* atomic orbitals (AO) of the two silicon atoms of the disilane bridge. It was subsequently shown,[38-40] however, that the absorption in the region of 240 nm is characteristic of the $-(-\mathrm{SiR_2}-)_n-$ and $\mathrm{Ph}-(-\mathrm{SiR_2}-)_n-$ systems, that is that the chain of silicon atoms itself shows chromophoric properties and also undergoes conjugation with the π-electrons of the aromatic ring. Increase in the length of the polysilicon chain and the pres- of phenyl or vinyl substituents at its ends displace the absorption band maximum to longer wavelengths. The ultraviolet spectra of linear and cyclic organopolysilanes with different substituents on the silicon atoms,[41-57] and compounds containing chains of other group IVb elements (Ge, Sn, Pb),[58,59] have been studied. The photoelectron spectra (PES) and electronic absorption spectra of charge-transfer complexes (CTC) show that the electrons of the silicon–silicon bond have a relatively low first ionisation potential (8.69 eV for hexamethyldisilane), which decrease with increase in the polysilane chain length. These data indicate that the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of polysilanes approach one another with increase in the number of silicon atoms. A similar phenomenon is observed more clearly in conjugated polyenes. In alkanes also, there is a slight displacement of the absorption maximum towards longer wavelengths. It was therefore concluded[55,60] that as in saturated hydrocarbons, in polysilanes there is delocalisation of electrons through the σ_{C-C} or σ_{Si-Si} bonds, the delocalisation being very slight in alkanes, but considerable in polysilanes. Thus the $-(-\mathrm{MR_2}-)_n-$ (M = Si, Ge, Sn) systems as it were occupy an intermediate position between saturated hydrocarbons and polyenes, that is they show signs of "double-bond character".

The unoccupied 3*d* AO of silicon have been used to explain the delocalisation of electrons along the $-(-\mathrm{SiR_2}-)_n-$ chains. For example, the absorption in the region of 240 nm has been attributed[39,41] to transitions of the π or σ_{Si-Si} electrons of the $\mathrm{Ph}-(-\mathrm{SiR_2}-)_n-$ fragment into non-bonding molecular orbitals formed by the combination of unoccupied 3*d* AO of the silicon atoms; the possible partial transfer of the electron density of the σ_{Si-Si} bond into the 3*d* AO and delocalisation through the system of *d* orbitals of silicon in the ground state: $\mathrm{Si-Si} \leftrightarrow \mathrm{Si\overline{\quad\quad}Si}$ have been assumed.[4,5] It has been suggested[61-64] that the π electrons of multiple bonds or

the lone pairs of electrons of the oxygen atoms in alkoxypolysilanes may be partly transferred not only to the first silicon atom (p_π, d_π conjugation) but also to subsequent atoms (p_π, d_π, d_π conjugation). It has been shown,[65] however, that to explain the photoelectron spectra of permethylsilanes it is not necessary to introduce the unoccupied 3*d* AO of silicon. Electron delocalisation can take place through the system of σ_{Si-Si} bonds (σ, σ conjugation).[20-22] For example, in octamethyltrisilane the original level of the σ_{Si-Si} electrons ($\alpha_{Si-Si} = 8.69$ eV) is split into two σ-orbital levels $\alpha_{Si-Si} + \beta$ and $\alpha_{Si-Si} - \beta$. A quantitative expression of the interaction of two σ_{Si-Si} bonds is provided by the magnitude of the resonance integral β_{Si-Si}, which has been estimated as -0.5 eV.[65]

It has been shown[14,15,56,66-73] that a system of σ_{Si-Si} bonds can interact with different π- and *n*-electron systems (phenyl, naphthyl, vinyl, –O–, –S–). Analysis of data obtained from the photoelectron spectra and electronic absorption spectra of CTC shows that significant interaction of a σ_{Si-Si} bond with π- and *n*-electron systems takes place at differences in the levels of the HOMO (ΔE) of the interacting fragments up to 0.5–0.6 eV. At these ΔE values, the σ_{Si-Si}–π or σ_{Si-Si}–*n* interaction is 0.25–0.72 eV. At $\Delta E = 1$ eV or more, the σ_{Si-Si}–π interaction is slight, and amounts to less than 0.1 eV. In the ultraviolet spectrum of a substituted disilane, the long-wave absorption maximum may undergo an appreciable bathochromic shift, as for example in vinylpentamethyldisilane and 1,2-divinyltetramethyldisilane.[73] The displacement of the absorption maximum to longer wavelengths without a significant change in the first ionisation potential of substituted polysilane is attributed to the interaction of the σ^*_{Si-Si} and π^* molecular orbitals.[73]

The high polarisability of the silicon–silicon bond is revealed by the ability of organopolysilanes to form charge-transfer complexes with various electron acceptors, for example tetracyancethylene,[74,75] and by their higher reactivity, compared with aliphatic hydrocarbons. Some similarity in chemical behaviour between Si–Si and C=C bonds can be demonstrated for reactions with such electrophilic reagents as peroxybenzoic acid and bromine. The reaction takes place with cleavage of the Si–Si or C=C bonds via the formation of donor–acceptor complexes, in which electron density is transferred from the σ_{Si-Si} or π_{C-C} bonds to the molecular orbitals of the electrophile.

$$R_3SiSiR_3 + PhCO_3H \rightarrow R_3SiOSiR_3 + PhCOOH$$

$$R_3SiSiR_3 + Br_2 \rightarrow 2R_3SiBr$$

$$RCH{=}CH_2 + PhCO_3H \rightarrow RCH(O)CH_2$$

$$RCH{=}CH_2 + Br_2 \rightarrow RCH(Br)CH_2Br$$

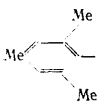
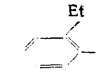
At the same time, organopolysilanes also take part in transformations characteristic of saturated hydrocarbons, for example isomerisation.[11]

$$Me_3SiSiMe_2SiMe_2SiMe_3 \xrightarrow{AlCl_3} (Me_3Si)_3SiMe$$

$$MeCH_2CH_2Me \xrightarrow{AlCl_3} Me_3CH$$

In 1981, West and co-workers reported the synthesis of tetramesityldisilene, the first stable compound with a silicon–silicon double bond.[24,25] This was followed by the preparation of several more representatives of this class of compound, including some with alkyl substituents. The chief factor leading to stabilisation of the Si=Si bond is the presence of bulky substituents on silicon. Some physicochemical characteristics of a number of disilenes are given in the Table.[76-89] The Si=Si bond length is approximately 0.18–0.20 Å shorter than the typical silicon–silicon single bond length.[78,84] The decrease in length due to π-bonding is 8–9% for disilenes, and about 12% for alkenes.[78] The four Si–C bonds in tetramesityldisilene are approximately coplanar.[76,79] From data on the measurement of the anisotropy of the ^{29}Si chemical shift it was concluded that the electronic structures of the Si=Si and C=C bonds are completely analogous.[79] The contribution of the π-component is considerable.

Physicochemical characteristics of disilenes $R_2Si{=}SiR_2$.

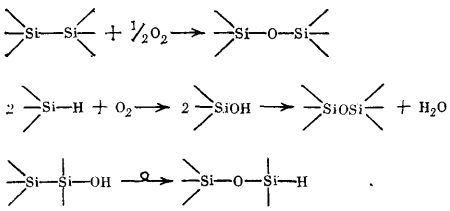
R	$r_{Si=Si}$, Å	λ_{max}, nm	M.p., °C	Refs.
	2.16	420	178	[24,25, 76–79]
	—	422	216–217	[80,82]
	2.14	426	201–204	[84]
Me_3CCH_2–	—	400	—	[85]
Me_3C–	—	433	—	[83,87]
Me_2CH–	—	400	—	[86]
Et_2CH	—	390	—	[81]

All prepared disilenes, in solution or the solid state, are bright yellow. The ultraviolet absorption maximum lies at 400–430 nm, and for aryl derivatives it is displaced to longer wavelengths as a result of the perturbation produced by the π-system of the aryl groups (an exception is tetra-t-butyldisilene, for which an unusually high value of λ_{max} = 433 nm is observed[83]). The absorption band in the range 400–430 nm is evidently due to a π–π^* transition, whose energy is much lower in disilenes than in alkenes. The first ionisation potential (I_1^D) of tetrakis(2,6-dimethylphenyl)-disilene (8.40 eV)[83] is close to the known values for phenyl-substituted disilanes: Me_5Si_2Ph (8.39 eV), $PhMe_2SiSiMe_2Ph$ (8.23 eV).[90]

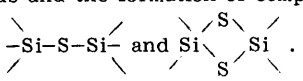
III. THE OXIDATION OF INORGANIC COMPOUNDS CONTAINING A SILICON–SILICON BOND

Among inorganic silicon derivatives, the highest reactivity towards oxidising agents is shown by the hydrides, with linear, branched Si_nH_{2n+2} ($n = 1$–6),[3-5,7] and cyclic $(SiH_2)_n$ ($n = 5,6$) structures.[18,91-93] They are rapidly decomposed by alkalis, and the reaction with oxygen and chlorine takes place with the production of flames or an explosion. The spontaneous flammability of silanes increases in the order $SiH_4 < Si_2H_6 < Si_3H_8$.[3-5] Disilane derivatives such as disilanyl ether $(Si_2H_5)_2O$, bis(disilanyl) sulphide $(Si_2H_5)_2S$, tris(disilanyl)amine $(Si_2H_5)_3N$, and

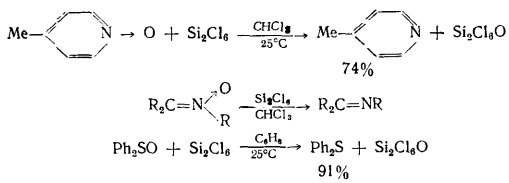
iododisilane Si_2H_5I are also very sensitive to oxygen.[3] The polymeric silicon hydrides $(SiH_m)_n$ ($m = 1-2$), obtained by different methods,[4,5] are also oxidised in air. The rate of oxidation may vary over a wide range, depending on the method of preparation and the Si/H ratio. In the reaction of amorphous polysilane $(SiH)_n$ with oxygen, three types of transformation are assumed:[4,5,94]



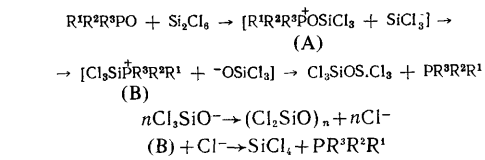
Oxidative cleavage of the Si–Si bond as a result of rearrangement is also possible for polysilanes with alkoxy or thiol groups.[6,16,17,95] In some cases of this kind the reactions are explosive.[16,17] A necessary condition for these rearrangements to take place is the fullest possible replacement of all the remaining valences in the $-(-Si-)_n-$ chain by OH, OR, or SR groups.

Halogenopolysilanes[6,18,19,23,96-99] are much more stable to oxygen than the corresponding silicon hydrides. The perfluorinated compounds are most easily oxidised. Decafluorotetrasilane and the subsequent members of the series, and also the higher fluorides of silicon $(SiF_2)_n$ and $(SiF)_n$ inflame spontaneously in air.[6,100] Perchloropolysilanes react with oxygen much more slowly. For example, the subchloride $(SiCl_2)_n$ inflames in a dry air atmosphere only when heated to 150 °C.[6] The reaction of the subhalides $(SiCl_2)_n$ and $(SiBr_2)_n$ with sulphur[6] takes place at an increased temperature (~170 °C) with cleavage of the Si–Si bonds and the formation of compounds containing the fragments  .

Hexachlorodisilane has been proposed as a reducing agent for the synthesis of organic derivatives of nitrogen, sulphur, and phosphorus.[101-104] The possibilities provided by the method are demonstrated by some examples given below.



The products are obtained in high yields. The reduction takes place rapidly and under mild conditions. This last feature is particularly important for preparing optically active phosphines and their oxides, since racemisation takes place at increased temperatures. The reduction of acyclic phosphine oxides takes place with inversion of the configuration and with a high stereospecificity. The proposed[102] mechanism of reduction includes several successive stages. The reaction begins with nucleophilic attack by the oxygen atom of the oxide on the silicon atom. The trichlorosilyl anion formed reacts with the intermediate (A) to give the trichlorosilylphosphonium cation (B) and a trichlorosiloxy-anion (inversion of the configuration at the phosphorus atom takes place at this stage). The Cl_3SiO^- anion is 70% decomposed to perchloropolysiloxane $(Cl_2SiO)_n$ and Cl^-. The remaining 30% Cl_3SiO^-, and also Cl^-, react with the trichlorosilylphosphonium cation to give hexachlorodisiloxane, silicon tetrachloride, and the optically pure phosphine.



Phosphetane oxides and phosphine sulphides are reduced by hexachlorodisilane with complete preservation of the configuration at the phosphorus atom.[102] Reducing properties are also shown by perchloropolysilanes Si_nCl_{2n+2} ($n > 2$) and by the vat residues from the direct synthesis of methylchlorosilanes.[105] The reactions of oxidative cleavage of the Si–Si bond in chloropolysilanes present in residues from direct synthesis have been reviewed.[106]

IV. THE OXIDATIVE CLEAVAGE OF THE SILICON–SILICON BOND IN ORGANOPOLYSILANES

1. Oxidation of Organopolysilanes with a Linear Structure

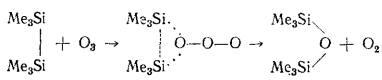
a) Reactions with oxygen and ozone

Peralkylated organopolysilanes with linear and branched structures are stable to atmospheric oxygen even at increased temperatures. Polysilanes containing the substituents OR, $CH{=}CH_2$, H, Cl, Br, and I in addition to alkyl and aryl groups on the silicon atoms also are not oxidised in air at room temperature. Fluoro-derivatives with the general formula $Si_2F_nMe_{6-n}$, containing two or more fluorine atoms, react with oxygen at 20 °C.[107] The reaction of 1,2-difluorotetramethyldisilane gives a mixture of products:

$$FMe_2SiSiMe_2F \xrightarrow{O_2} (FMe_2Si)_2O + (CH_2O)_n + H_2O + \text{polysiloxanes}$$

The isomeric 1,1-difluorotetramethyldisilane is oxidised much more slowly, and the main product is the corresponding disiloxane. 1,1,2-Trifluorotrimethyldisilane and 1,1,2,2-tetrafluorodimethyldisilane react with oxygen by a free-radical mechanism, analogous to that proposed for the oxidation of distannanes.[108]

Hexamethyldisilane reacts exothermally with ozone to give hexamethyldisiloxane in 95% yield. Bis(trimethylsilyl) peroxide was not found in the reaction products. The cleavage of the silicon–silicon bond by ozone takes place more readily than that of the Si–C_{alkyl} bond. The marked difference in the oxidation rates ensures a high yield of hexamethyldisiloxane. It is assumed that the reaction takes place via a three-membered intermediate complex, and that ozone acts as an electrophilic reagent.[109]



The products and kinetics of the reactions of ozone with a number of organic derivatives of group IVb elements R_4E, R_3EX, R_3EER_3 (X = H, Cl, Br, OR; E = Si, Ge, Sn, Pb) in different solvents have been studied.[110-115] The reactions take place by a bimolecular heterolytic mechanism. The reactivity of the hetero-organic compound and ozone is increased by non-specific solvation. The sensitivity of the reaction to non-specific solvation is greater, the greater the reactivity of the hetero-organic compound (HOC) towards ozone. This result agrees with the suggestion that the polarity of the activated "HOC–ozone" complex is greater than that of the original reagents, and confirms that the

ozonolysis of the HOC takes place by a heterolytic mechanism. It has been shown that ozone takes part in the formation of the activated complex in an amphi-ionic form, in which the nucleophilic centre is localised chiefly on one oxygen atom. The values of the rate constants of reactions of E_2Et_6 (E = Si, Ge, Sn, Pb) with O_3 correlate satisfactorily with the values of the effective electronegativity of the heteroatom in these compounds, which increase in the order Pb < Sn < Ge < Si. The reactivity of the compounds decreases on going from Pb to Si.

b) Reactions with metal salts and oxides

Organopolysilanes reduce salts of mercury, nickel, platinum, and copper to the corresponding metals.[116–118]

$$Me_3SiSiPh_3 + Hg(OCOMe)_2 \xrightarrow{200^\circ C} Hg + Me_3SiOCOMe + Ph_3SiOCOMe$$
$$(MeO)_2MeSiSi(OMe)_2Me + CuCl_2 \rightarrow Cu + 2MeSi(OMe)_2Cl$$

Silver nitrate and vanadium(V) oxide oxidise disilanes to disiloxanes at increased temperatures.[116,117] Hexaphenyldisilane is very inert towards various oxidising agents. It begins to react with silver or sodium nitrate only when heated to 198 °C or 360 °C respectively.[119]

The oxidative cleavage of the Si–Si bond in polysilanes under the influence of tungsten and molybdenum chlorides has been studied.[120] The linear polysilanes Si_nMe_{2n+2} (n = 2, 3, 4, 6) and the branched polysilane $Si(SiMe_3)_4$ react exothermally with tungsten hexachloride or molybdenum pentachloride in benzene, chlorobenzene, or CCl_4 to give chlorosilanes and WCl_4 or $(MoCl_3)_x$. In decamethyltetrasilane, the terminal trimethylsilyl groups are removed first.

$$n\text{-}Si_4Me_{10} \xrightarrow{WCl_6} Me_3SiCl + ClMe_2SiSiMe_2SiMe_3$$

The product of the cleavage of octamethyltrisilane–pentamethylchlorodisilane–reacts with WCl_6 ten times more slowly than the original trisilane. A linear correlation was established between the first ionisation potentials of the polysilanes and the logarithms of the relative rate constants of the cleavage of the Si–Si bonds. Decrease in I_1^D is accompanied by an increase in the rate of the reaction of the polysilanes with WCl_6, indicating that the rate-determining stage of the reaction is the transfer of the electrons of the σ_{Si-Si} bond to WCl_6.

c) Reactions with halogens

Organopolysilanes are split by halogens to give halogenosilanes.[121–129]

$$R_3SiSiR_3 + X_2 \rightarrow 2R_3SiX$$
$$X = Cl, Br, I$$

When solutions of Si_2R_6 (R = Me, Et) and halogens (Br_2, I_2) are mixed, the ultraviolet spectrum shows a new strong charge-transfer band due to the donor–acceptor complex (DAC) $Si_2R_6.X_2$, not observed in the spectra of the starting materials and final reaction products.[126] In an excess of hexa-alkyldisilane, the rates of consumption of the DAC and the halogen are equal, indicating that the following equilibrium is rapidly established:

$$Si_2R_6 + X_2 \rightleftarrows Si_2R_6 \cdot X_2 .$$

The reaction is of first order with respect to each reagent, and takes place by a molecular mechanism, probably via the DAC detected, in which transfer of electron density takes place from the σ_{Si-Si} bond to the molecular orbitals of the halogen.[126,129] The energy and entropy of activation for the reaction of 1,2-diphenyltetramethyldisilane with bromine in CCl_4 are 10.5 kcal mole^{-1} and −25.4 e.u. respectively.[128]

The reactivity of the Si–Si bond in polysilanes towards halogens depends markedly on the nature of the substituents on silicon. Hexa-alkyldisilanes react very readily,[123,124] hexa-aryldisilanes react slowly,[123,130] and hexahalogenodisilanes react only at high temperatures.[6,123] The relative reactivity of the halogens decreases in the order $Cl_2 > Br_2 \gg I_2$.[8] In hydrogen-containing disilanes, the Si–H bond reacts first.[123]

$$R_3SiSiR_2H + X_2 \rightarrow R_3SiSiR_2X + HX$$
$$X = Br, I$$

Kinetic studies[122] have shown that the replacement of one methyl group in hexamethyldisilane by a chlorine atom decreases the rate of cleavage by iodine by a factor of approximately ten. The introduction of a second chlorine atom leads to a further decrease in the reaction rate. The silicon–silicon bond in $Cl_2MeSiSiMe_2Cl$ and $Cl_2MeSiSiMeCl_2$ is stable towards halogens.[6,9] On irradiation with light, the methyl groups are chlorinated. The rates of the reactions with halogens are increased by Friedel–Crafts catalysts.[123] In α,ω-dichloropermethylpolysilanes $Cl(Me_2Si)_nCl$ (n = 4–6), the terminal Si–Si bond is less reactive towards chlorine than the inner Si–Si bonds, which are also split by the action of halogen. The relative reactivity of these compounds in chlorination[125] decreases with decrease in n: $6 \geq 5 \geq 4 > 3 \gg 2$. In n-decamethyltetrasilane, contrary to the result expected from the statistical factor, the inner Si–Si bond is split by bromine more rapidly.[123]

$$n\text{-}Si_4Me_{10} + Br_2 \begin{cases} \rightarrow 2Me_3SiSiMe_2Br\ 57\% \\ \rightarrow Me_3SiBr + BrMe_2SiSiMe_2SiMe_3\ 43\% \end{cases}$$

These data are consistent with electrophilic attack by the halogen on the polysilane molecule. There is a qualitative analogy with the electrophilic addition of halogens to a C=C bond.[131] In the reactions of polysilanes, the nucleophilic centre is the σ_{Si-Si} bond. In spite of this, the opposite mechanism has been proposed[127] for the cleavage of aryl-substituted disilanes by bromine, where the silicon atoms of the Si–Si bond act as electrophile centres.

d) Reactions with acids and alkalis

In the reaction of hexamethyldisilane with concentrated sulphuric acid, one or two methyl groups are removed. Subsequent treatment of the reaction mixture with ammonium chloride gives pentamethylchlorodisilane and 1,2-dichlorotetramethyldisilane.[132] In the linear permethylpolysilanes $Me(Me_2Si)_nMe$ (n = 2–4), partial rupture of Si–Si bonds takes place.[8] Gaseous HCl splits the Si–Si bond in permethylpolysilanes[8,9] only at high temperatures.

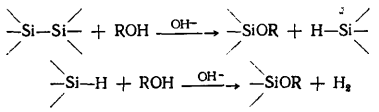
$$Me_3SiSiMe_3 + HCl \xrightarrow{450^\circ C} Me_3SiCl + Me_3SiH$$

Concentrated nitric acid reacts with hexamethyldisilane according to the equation:[8]

$$Me_3SiSiMe_3 + 2HNO_3 \rightarrow Me_3SiOSiMe_3 + 2NO_2 + H_2O$$

The reactivity of organopolysilanes towards aqueous and alcoholic solutions of alkalis[2,9,133] depends on the substituents on the silicon atoms. Electronegative substituents facilitate cleavage of the Si–Si bond. Peralkylated disilanes do not react with aqueous or alcoholic or alkali solutions, and the ethoxy-substituted $Si_2Me_n(OEt)_{6-n}$ react more rapidly, the smaller n; for example, hexa-acetoxydisilane[134] reacts

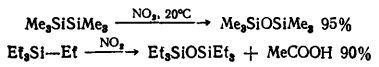
with aqueous NaOH solution with vigorous liberation of hydrogen. The reaction with alcoholic alkali solutions takes place according to the scheme:



The reaction is used for the quantitative determination of Si–Si bonds in various polysilanes. The reactions of alkalis with disilanes containing halogen atoms in the organic group are more complex.[135]

e) Reactions with oxides of nitrogen

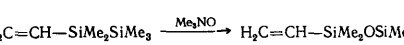
Oxides of nitrogen split not only the Si–Si bonds but also Si–C bonds in alkylsilanes.[136]



The activity of the oxides in these reactions decreases in the order: $NO_2 > NO_3 > NO > N_2O$. Hexaphenyldisilane does not react with oxides of nitrogen in diethyl ether.[130]

f) Reactions with amine N-oxides

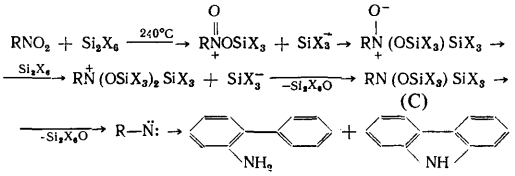
Trimethylamine oxide and pyridine N-oxide behave as nucleophilic reagents towards disilanes. A study of the oxidation of various *meta*- and *para*-substituted phenoxypentamethyldisilanes $Me_5Si_2OC_6H_4X$ by pyridine N-oxide[137] show that the reaction rate increases when electronegative substituents are introduced into the phenyl ring ($\rho = +1.18$). Vinylpentamethyldisilane is oxidised by trimethylamine oxide to vinylpentamethyldisiloxane; the vinyl group is unaffected.[137]



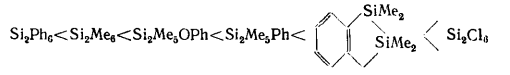
Organodisilanes can be used as reducing agents in the synthesis of various organic compounds.[138,139] Their reducing power is weaker than that of perchloropolysilanes. For example, hexamethyldisilane does not react with phosphine oxides[102] or amine N-oxides[137] at 70 °C. Aryl-substituted disilanes do not react with dimethyl sulphoxide on prolonged heating up to 100 °C.[140] On the other hand, hexachlorodisilane readily reduces these compounds even at room temperature.[102]

g) Reactions with aromatic nitro-compounds

The reducing properties of substituted disilanes with respect to aromatic nitro-compounds have been studied.[139] When a solution of the reagents in *o*-dichlorobenzene is heated to 240 °C, reaction takes place with the intermediate formation of a nitrene. The reaction mechanism proposed by the authors cited is fairly complex, and involves the nucleophilic attack by RNO_2 on silicon with subsequent heterolysis of the Si–Si bond. The nitrene is formed as a result of the removal of the disiloxane from the bis(silyl)hydroxylamine intermediate (C). [With 2-nitrobipherryl the products are as shown in the scheme. Ed.]



The reducing power of the disilanes is determined by their structure, and increases in the order:



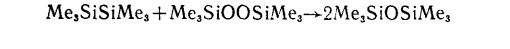
Hexaphenyldisilane does not show reducing properties, probably because of the steric hindrance created by the phenyl groups. In contrast to this, the introduction of a substituent into the molecule of the compound being reduced in the *ortho*-position to the nitro-group has practically no influence on the rate of the reaction with hexamethyldisilane.

h) Reactions with hydrogen peroxide

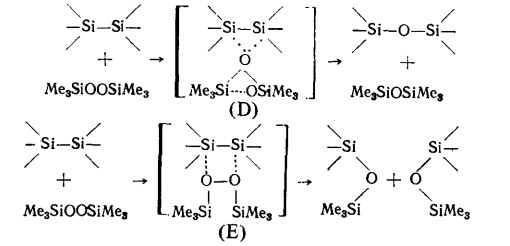
The silicon–silicon bond in permethylpolysilanes is not oxidised by hydrogen and sodium peroxides.[8,9] Hexaphenyldisilane is very inert towards various oxidising agents, and does not react with organic hydroperoxides and 30% H_2O_2 on boiling for 43 h in mixed THF–CCl_4 solvent.[119] Splitting takes place when an oxidising mixture consisting of H_2O_2 and NaOH in THF is used. The chief reaction products are triphenylsilanol and hexaphenyldisiloxane.

i) Reactions with bis(trimethylsilyl) peroxide (BTMSP)

Hexamethyldisilane reacts with BTMSP at 80 °C.[107]



After 42 h in an excess of the peroxide, the extent of the transformation of hexamethyldisilane was 40%. Methylfluorodisilanes $Si_2F_nMe_{6-n}$ ($n = 1-4$) are oxidised by BTMSP even at temperatures from −10 °C ($n = 4$) to +20 °C ($n = 1, 2$).[107] The compounds with $n = 1, 2$ give the corresponding disiloxanes as chief products, whereas the oxidation of tri- and tetrafluorodisilanes ($n = 3, 4$) give in addition Me_3SiF, $Me_3SiOSiMe_2F$, and $Me_3SiOSiMeF_2$. The rate of the oxidation of 1,2-difluorotetramethyldisilane does not decrease when the inhibitor 2,4,6-tri(t-butyl)phenol is added. It is suggested that the reactions take place via the intermediate states (D) and (E). The oxygen atoms of BTMSP act as nucleophilic centres.



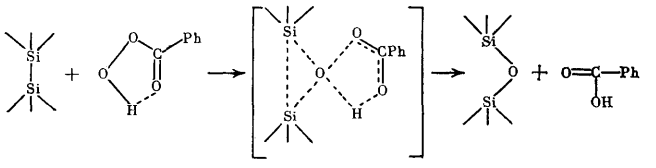
For the tri- and tetrafluorodisilanes, the free-radical direction may make a contribution. Pentamethyldisilane is oxidised by BTMSP more rapidly than hexamethyldisilane, to give a

mixture of products.

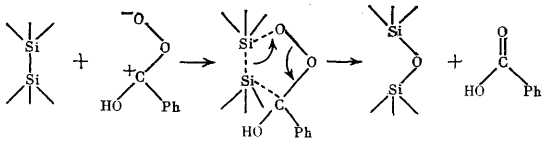
$$Me_5Si_2H + Me_3SiOOSiMe_3 \rightarrow (Me_3SiO)_2SiMe_2 + Me_5Si_2OSiMe_3 + + (Me_5Si_2)_2O + (Me_3SiOSiMe_2)_2O + (Me_3Si)_2O + H_2O$$

j) Reactions with peroxyacids

Hexamethyldisilane, 1,2-diphenyltetramethyldisilane, and the disilanes $XC_6H_4Si_2Me_5$ (X = H, Me, MeO, Cl) are oxidised by peroxybenzoic acid in dichloromethane or benzene to the corresponding siloxanes.[141] The reactions obey a kinetic equation of second order, first order with respect to each reagent. The satisfactory correlation between lg k and σ^+ gives for the reaction constant the value $\rho = -0.29$, which characterises the disilane and the peroxyacid as nucleophilic and electrophilic reagents respectively. The author cited proposed a mechanism analogous to that of the epoxidation of alkenes, including electrophilic attack and the insertion of an oxygen atom of the peroxyacid at the Si–Si bond.



A bipolar 1,3-addition mechanism, analogous to that of the epoxidation of alkenes in strongly polar solvents, has also been proposed.[9]



It might have been expected that disilanes having electronegative substituents (Cl, Br, OR, OCOR) on the silicon atoms would be oxidised by peroxybenzoic acid more slowly than the peralkylated compounds. It was found, however, that these compounds react more rapidly than hexamethyldisilane.[142–144] The reactions are of first order with respect to each reagent, and give as the only products the corresponding disiloxanes and benzoic acid.

$$XMe_2SiSiMe_2Y + PhCO_3H \xrightarrow[\text{hexane}]{20^\circ C} XMe_2SiOSiMe_2Y + PhCOOH$$

X	Y	k, litre mole^{-1}min^{-1}	X	Y	k, litre mole^{-1}min^{-1}
Me	Me	0.008	Me_3Si	Cl	0.42
Me	n-Bu	0.006	Me_3Si	$OSiMe_2Cl$	0.06
Me	Cl	0.28	Cl	Cl	0.15
n-Bu	Cl	0.15	Me	OCOPh	0.20
Ph	Cl	0.09	Me	OEt	0.06

The increased reactivity is evidently due to the existence of n,σ-conjugation in disilanes having n-donor substituents on the silicon atoms. Effects of this kind raise the HOMO of the polysilene,[71] and this should be revealed by an increase in its nucleophilic activity towards soft electrophiles, and in particular towards peroxybenzoic acid. As a result of the combined influence of the Me_3Si group and the n-donor substituent in 1-chloroheptamethyltrisilane, only the Si–Si bond adjacent to the chlorine atom reacts initially. Cleavage of the second bond takes place much more slowly ($k_1/k_2 = 7$).[142]

$$Me_3SiSiMe_2SiMe_2Cl + PhCO_3H \xrightarrow{k_1} Me_3SiSiMe_2OSiMe_2Cl + PhCOOH$$
$$Me_3SiSiMe_2OSiMe_2Cl + PhCO_3H \xrightarrow{k_2} Me_3SiOSiMe_2OSiMe_2Cl + PhCOOH$$

The influence of the dielectric constant and basic strength of the solvent on the rate of the oxidation of pentamethylchlorodisilane by peroxybenzoic acid is extremely slight.[143] This agrees with the low absolute values of the Hammett ($\rho = -0.29$)[141] and Taft ($\rho = -0.56$) reaction constants,[143] which indicate that the intermediate state of the system in the oxidation is weakly polar.

Vinylpentamethyldisilane (I) can be converted quantitatively into the epoxydisiloxane (II) by treating with peroxyacids.[141]

$$\underset{(I)}{Me_5Si_2}\!\!\diagup\!\!\diagdown + 2PhCO_3H \xrightarrow[24\,CH]{CH_2Cl_2,20^\circ C} \underset{(II)}{Me_3SiOSiMe_2}\!\!-\!\!\langle\!\rangle^{O} + 2PhCOOH$$

At an equimolar reagent ratio, the chief product (79%) is the disilanyl epoxide (III).[145]

$$(I) + RCO_3H \rightarrow \underset{(III)}{Me_5Si_2}\!\!-\!\!\langle\!\rangle^{O} + (II) + Me_3SiOSiMe_2\!\!\diagup\!\!\diagdown + RCOOH$$

The reaction takes place in stages, and in the first stage the vinyl group is oxidised preferentially. The relative rates of oxidation of the C=C bond in $Me_3SiOSiMe_2Vin$, Me_3SiVin, and Me_5Si_2Vin are 1.0, 2.1, and 5.6 respectively. Thus the Me_5Si_2 group shows stronger donor properties than the Me_3Si and $Me_3SiOSiMe_2$ fragments. *m*-Chloroperoxybenzoic acid (MCPBA) reacts with allylpentamethyldisilane[145] according to the equation:

$$Me_5Si_2\!\!\diagup\!\!\diagdown \xrightarrow{MCPBA} Me_3SiOSiMe_2\!\!\diagup\!\!\diagdown +$$
$$+ Me_3SiSiMe_2\!\!\diagup\!\!\diagdown^{O} \xrightarrow{H^+} Me_3SiSiMe_2CH_2CH_2C\!\!\diagup\!\!\diagdown^{O}_{H}$$

k) Reactions with benzoyl peroxide and di-t-butyl peroxide

The reactions of hexamethyldisilane,[146,147] hexaethyldisilane,[148] and pentamethylchlorodisilane[149] with di-t-butyl and benzoyl peroxides take place only at the temperatures of the decomposition of the peroxides to free radicals. In the reactions of hexamethyl- and hexaethyldisilanes, the Si–Si bond is not split by the peroxide compounds or the radicals formed by their thermal decomposition. The reaction of pentamethylchlorodisilane with di-t-butyl peroxide is accompanied by the formation of siloxane products, but the latter are obtained as a result of secondary reactions of Me_5Si_2Cl with t-butyl alcohol and not with the peroxide or its radicals. The reaction of pentamethylchlorodisilane with benzoyl peroxide gives a complex mixture of products as a result of radical and exchange reactions.[149]

$$Me_5Si_2Cl \xrightarrow[80-90^\circ C]{(PhCOO)_2} Me_3SiCl + Me_2SiCl_2 + Me_2SiOCOPh + + Me_5Si_2OCOPh + PhCOOH + \text{polymer}$$

The free-radical reactions of organopolysilanes with peroxides have been reviewed,[150] and are used for preparative purposes.[9,17]

l) Reactions with t-butyl hydroperoxide and its derivatives

In Ref.151, an attempt was made to obtain two peroxides with a silicon–silicon bond in the molecule by the reaction of pentamethylchlorodisilane (IV) and 1,2-dichlorotetramethyldisilane (VII) with t-butyl hydroperoxide (TBHP) in the presence of pyridine. Instead of the compounds

expected, the authors cited obtained t-butoxypentamethyldisiloxane (VI) and the siloxane peroxide (X), whose formation was attributed to successive substitution and rearrangement:

$$\underset{(IV)}{Me_3Si_2Cl} + Me_3COOH \xrightarrow[-C_5H_5N\cdot HCl]{C_5H_5N} \underset{(V)}{Me_3SiSiMe_2OOCMe_3} \xrightarrow{O} \underset{(VI)}{Me_3SiOSiMe_2OCMe_3}$$

$$\underset{(VII)}{ClMe_2SiSiMe_2Cl} + Me_3COOH \xrightarrow[-C_5H_5N\cdot HCl]{C_5H_5N} \underset{(VIII)}{ClMe_2SiSiMe_2OOCMe_3} \xrightarrow{O}$$

$$\xrightarrow{O} \underset{(IX)}{ClMe_2SiOSiMe_2OCMe_3} \xrightarrow[-C_5H_5N\cdot HCl]{Me_3COOH/C_5H_5N} \underset{(X)}{Me_3COOMe_2SiOSiMe_2OCMe_3} .$$

It was subsequently established,[152] however, that the reaction of equimolar quantities of compound (IV) and TBHP, in addition to compound (VI), gives t-butylperoxypentamethyldisiloxane (XII) in up to 20% yield, which increases to 65% when a two-fold excess of TBHP is used. When the reaction is carried out not with TBHP but with its lithium salt, the yield of compound (XII) increases to 80%. The reaction begins not with the replacement of the chlorine atom but with the oxidation of the Si–Si bond in compound (IV):

$$\begin{gathered} \underset{(IV)}{Me_3Si_2Cl} + Me_3COOLi \rightarrow \underset{(XI)}{Me_3SiOSiMe_2Cl} + Me_3COLi \\ (XI) + Me_3COOLi \rightarrow \underset{(XII)}{Me_3SiOSiMe_2OOCMe_3} + LiCl \\ (XI) + Me_3COLi \rightarrow \underset{(VI)}{Me_3SiOSiMe_2OCMe_3} + LiCl \quad . \end{gathered}$$

Analogous reactions with Me_3COOLi are undergone by the disilanes $RMe_2SiSiMeR'Cl$, where R and R' = Me, Ph, Bu, Me_3SiO.[153,154] Pentamethylchlorodisilane is not reactive towards nucleophilic reagents, so that the peroxide (V) is not formed.[143,152]

Compound (VII), 1,2-dichlorotetramethyldisilane, has a greater tendency to undergo nucleophilic substitution, compared with pentamethylchlorodisilane,[143,153] so that the reaction of compound (VII) with TBHP and its lithium salt begins with the replacement of one of the chlorine atoms by an Me_3COO group, with subsequent rearrangement of the peroxide (VIII) to 1-chloro-3-t-butoxytetramethyldisiloxane (IX) (see above). The reaction is complicated by the parallel oxidation of the Si–Si bond in compound (VII) and the subsequent transformation of the siloxanes (XIII) and (XIV) formed:

$$\underset{(VII)}{ClMe_2SiSiMe_2Cl} \xrightarrow[-Me_3COLi]{Me_3COOLi} \underset{(XIII)}{ClMe_2SiOSiMe_2Cl} \rightarrow$$

$$\xrightarrow[-LiCl]{Me_3COOLi} \underset{(XIV)}{Me_3COOMe_2SiOSiMe_2Cl} \xrightarrow[-LiCl]{Me_3COOLi} Me_3COOMe_2SiOSiMe_2OOCMe_3 .$$

The driving force of the rearrangement of the disilanyl peroxide (VIII) is evidently the transformation of the unstable structure Si–Si–O–O into the thermodynamically more stable state with three strong Si–O bonds. A calculation based on the bond energies[155] shows that the gain in energy in the rearrangement is 99 kcal mole^{-1}.

The reactions of 1- and 2-chloroheptamethyltrisilanes with Me_3COOLi are multistage successive and parallel processes, beginning with the oxidation of one Si–Si bond.[154] In 1-chloroheptamethyltrisilane (XV), the disilanyl fragment joined to the chlorine atom is oxidised first.

$$\begin{gathered} \underset{(XV)}{Me_3SiSiMe_2SiMe_2Cl} + Me_3COOLi \rightarrow Me_3SiSi\underset{(XVI)}{Me_2OSiMe_2Cl} + Me_3COLi \\ (XVI) + Me_3COOLi \rightarrow Me_3SiSiMe_2OSiMe_2OOCMe_3 + LiCl \\ \underset{(XVII)}{} \\ (XVI) + Me_3COLi \rightarrow Me_3SiSiMe_2OSiMe_2OCMe_3 + LiCl \\ \underset{(XVIII)}{} \\ (XVII) + Me_3COOLi \rightarrow Me_3SiOSiMe_2OSiMe_2OOCMe_3 + Me_3COLi \\ (XVIII) + Me_3COOLi \rightarrow Me_3SiOSiMe_2OSiMe_2OCMe_3 + Me_3COLi \end{gathered}$$

The yield of the peroxide (XVII), containing an Si–Si bond in the molecule, reaches 75% when the reaction is carried out with a three-fold excess of Me_3COOLi.

The reaction of the organochloropolysilanes $RMe_2SiSiMe_2Cl$ (R = Me, n-Bu, Me_3Si) with lithium t-butyl peroxycarbonate[144] takes place in two directions. The first involves the formation of the unstable peroxycarbonate (XIX), which liberates CO_2 to give the disilanyl peroxide (XX); the latter undergoes rearrangement to the t-butoxysiloxane (XXI):

$$RMe_2SiSiMe_2Cl + \underset{\underset{O}{\|}}{Me_3COOCOLi} \longrightarrow \underset{(XIX)}{RMe_2SiSiMe_2OCOOCMe_3} \underset{O}{\|} + LiCl$$

$$(XIX) \xrightarrow{-CO_2} \underset{(XX)}{RMe_2SiSiMe_2OOCMe_3} \xrightarrow{O} \underset{(XXI)}{RMe_2SiOSiMe_2OCMe_3} .$$

The second direction involves the oxidation of the Si–Si bond by the peroxycarbonate and the subsequent transformations of the chlorodisiloxane (XXII) formed.

$$RMe_2SiSiMe_2Cl \xrightarrow[-Me_3COC(O)OLi]{Me_3COOC(O)OLi} \underset{(XXII)}{RMe_2SiOSiMe_2Cl} \rightarrow$$

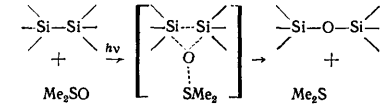
$$\xrightarrow[-LiCl]{Me_3COOC(O)OLi} RMe_2SiOSiMe_2OC(O)OOCMe_3 \xrightarrow[-CO_2]{} RMe_2SiOSiMe_2OOCMe_3$$

m) Photolytic reactions of organopolysilanes in the presence of oxygen-containing reagents

The photolysis of organopolysilanes in the presence of alcohols, ketones, and other organic compounds containing one or several oxygen atoms in the molecule gives products containing the fragments Si–O–Si and Si–O–C.[12,13,140,156–166] Reactions of this type involve several stages, and take place with the initial formation of silylenes, which undergo subsequent transformations to give the final siloxane products. For example, the irradiation of a mixture of dodecamethylcyclohexasilane and dimethyl sulphoxide (DMSO) gives dimethylsilylene, which is then oxidised by DMSO to dimethylsilanone. The latter, in the absence of reagents which act as traps, undergoes oligomerisation.[162]

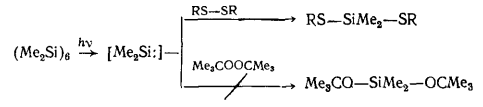
$$(Me_2Si)_6 \xrightarrow{h\nu} [Me_2Si:] \xrightarrow{Me_2SO} [Me_2Si{=}O] \rightarrow (Me_2SiO)_n$$

In the photolysis of pentamethylphenyldisilane, 2-phenylheptamethyltrisilane, and other aryl-substituted polysilanes in the presence of DMSO, one of the directions of the reaction involves the oxidation of the photo-excited Si–Si bond by dimethyl sulphoxide to give the corresponding siloxanes.[140,161,163,164]



Dimethylsilylene is introduced at the S–S bond of the

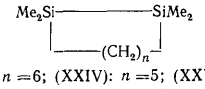
disulphides. The corresponding reaction with di-t-butyl peroxide does not take place.[165]



2. Oxidation of Cyclic Organopolysilanes

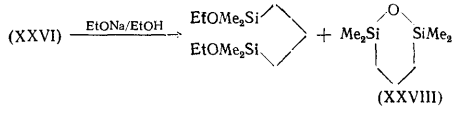
a) The influence of ring size on reactivity

The organopolysilane ring size is one of the important factors determining the reactivity of these compounds in oxidative cleavage. The reactivity of the Si–Si bond is also influenced strongly by the size of the substituents on the silicon atoms and the nature of the heteroatoms in the ring. The increase in reactivity with decrease in ring size can be followed in the series of tetramethyl-1,2-disilacycloalkanes (XXIII)–(XXVII).[167]



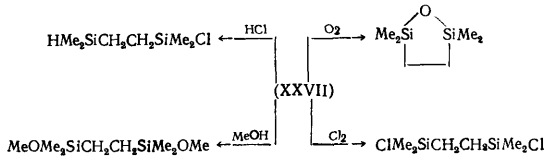
(XXIII): $n=6$; (XXIV): $n=5$; (XXV): $n=4$; (XXVI): $n=3$, (XXVII): $n=2$

In these compounds, the influence of internal angular strain on the reactivity of the Si–Si bond begins to appear in the six-membered ring of compound (XXV). The action of sulphuric acid on disilacyclo-octane (XXIII) and disilacycloheptane (XXIV), as in the case of hexamethyldisilane, does not split the Si–Si bond, and the methyl group is replaced, whereas the reactions of compounds (XXV) and (XXVI) with concentrated sulphuric acid lead to cleavage of the Si–Si bond. The greater angular strain in compound (XXVI), compared with compound (XXV), is revealed in the reactions with oxygen, bis(trimethylsilyl) peroxide,[107] and sodium ethoxide.[157] 1,2-Disilacyclohexane (XXV) does not react with oxygen, whereas 1,2-disilacyclopentane (XXVI) absorbs oxygen exothermally, and is converted into the corresponding siloxane derivative (XXVIII). The reaction of compound (XXV) with BTMSP takes place only on heating to 50 °C, whereas compound (XXVI) reacts readily even at 20 °C. The silicon–silicon bond in compound (XXV) is not split by a solution of sodium ethoxide in ethanol at 90 °C, whereas in compound (XXVI), quantitative cleavage of the Si–Si bond takes place:



(XXVIII)

With further decrease in the ring size there is a sharp increase in the reactivity of the disilacycloalkane. 1,1,2,2-Tetramethyl-1,2-disilacyclobutane (XXVII) is extremely reactive.[168] It can be kept for a long time only at liquid nitrogen temperature. At 20 °C, the polymer $-(-CH_2CH_2.SiMe_2SiMe_2-)_n-$ is formed. The reactions of compound (XXVII) with oxygen, chlorine, hydrogen chloride, and methanol take place very vigorously.



A decrease in the reactivity of the Si–Si bond with increase in ring size was also observed[169] in the reactions of the 1,2-disilacycloalkanes (XXIV)–(XXVI) with *m*-chloroperoxybenzoic acid. The relationship between the kinetic parameters of the oxidation and the energies of charge transfer (E_{ct}) in the disilane–tetracyanoethylene complexes was studied. On going from the linear hexamethyldisilane to 1,2-disilacyclopentane (XXVI), the reaction rate constant increases by a factor of 2000. The entropy of activation remains practically constant, and the enthalpy of activation decreases. With decrease in the ring size, E_{ct} decreases regularly, indicating that the HOMO level of the disilacycloalkane is raised, probably as a result of strain in the ring. The observed linear relationship between the enthalpy of activation and the energy of charge transfer indicated that in the transition state of the reaction, an important role is played by electronic donor–acceptor interaction between the disilane (donor) and the peroxyacid (acceptor).

The data on the oxidative splitting of organocyclopolysilanes, given below, also show that the reactivity of these compounds increases with decrease in the ring size.

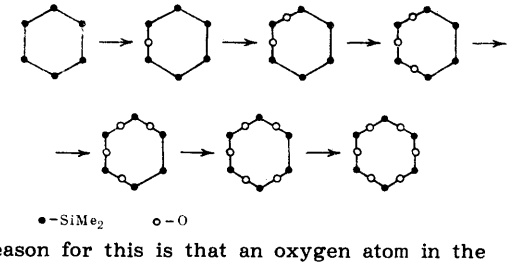
b) The oxidation of six-membered cyclic compounds containing silicon–silicon bonds

A fairly large number of varied six-membered cyclic compounds containing from one to six Si–Si bonds in the molecule are now known. In addition to disilanyl fragments, the ring may contain

$-(CR_2-)_n-$, $-CR=CR-$, $\diagdown C=PR_3$, $-NH-$, $-NR-$ $\diagdown N-NH_2$, $\diagup$

$-O-SO_2-O-$, etc. groups, and also elements such as oxygen and sulphur.[1,2,7,9,17,18,21,22] Most of these compounds are inert towards atmospheric oxygen at room temperature. The instability of some of them[52,170,171] in air may be due to the presence in the ring of a phosphorus-containing ligand such as $\diagdown P-Ph$.
$\diagup$

The six-membered ring $(Me_2Si)_6$ is the most stable thermodynamically. The equilibrium in a mixture of the compounds $(Me_2Si)_n$ (n = 5, 6, 7) in the presence of Na/K alloy is displaced towards the formation of dodecamethylcyclohexasilane.[172] The latter undergoes practically no oxidation by atmospheric oxygen and 30% hydrogen peroxide solution at 80 °C. Chromium oxide, potassium dichromate, and potassium permanganate oxidise dodecamethylcyclohexasilane to a complex mixture of siloxane products.[173] MCPBA splits all six Si–Si bonds in $(Me_2Si)_6$, and each successive oxygen is introduced into the bond adjacent to that already oxidised.[174]



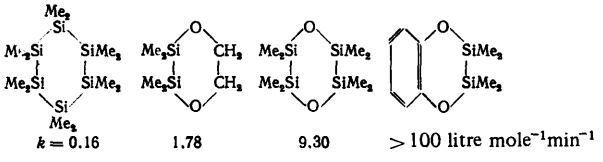
•–$SiMe_2$ o–O

The reason for this is that an oxygen atom in the

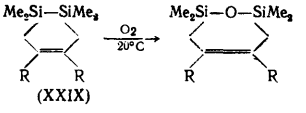
$-(-\overset{|}{\underset{|}{Si}}-)_n-$ chain activates the neighbouring Si–Si bond

towards oxidation by peroxyacids. The first stage is the slowest, so that the intermediate oxygen-containing rings formed do not accumulate to significant concentration in the

reaction mixture. Comparison of the rate constants for the reactions of various six-membered rings with peroxybenzoic acid (benzene, 35 °C)[144] shows the magnitude of the activating influence of oxygen (particularly when combined with the π-system of the benzene ring[159]) on the Si–Si bond being oxidised.

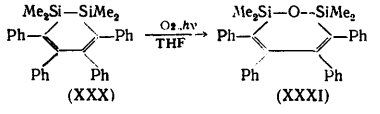


The presence of one multiple bond in the six-membered silicon–carbon ring of compound (XXIX) increases its ability to be oxidised by oxygen, compared with 1,2-disilacyclohexane (XXV).[157–177]



(XXIX)

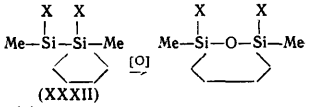
The cyclodisilane (XXX), which contains a diene group, is not oxidised by oxygen in acetone under the influence of light and in the presence of a sensitiser, but the reaction takes place readily in tetrahydrofuran (THF). MCPBA converts compound (XXX) quantitatively into the cyclodisiloxane (XXXI) at 20 °C.



(XXX) (XXXI)

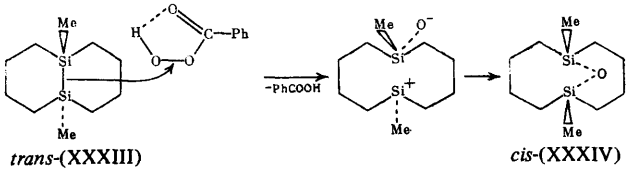
The reactions with di-t-butyl peroxide and t-butyl hydroperoxide take place only at 60–100 °C.[178]

The reactions of the stereoisomeric 1,2-disilacycloalkanes (XXXIIa,b) with peroxybenzoic acid or bis(trimethylsilyl) peroxide take place with preservation of the configuration, indicating that the oxidation takes place by a molecular mechanism.[179,180]



(XXXII)
(a) X=F;
(b) X=Ph.

In the reactions of *trans*-9,10-dimethyl-9,10-disiladecaline (XXXIII) with $PhCO_3H$ and $Me_3SiOOSiMe_3$, inversion of the configuration is observed, due to the fact that the *trans*-isomeric siloxane oxidation product has considerable strain, whereas the *cis*-isomer (XXXIV) is unstrained. In the opinion of the authors cited, the inversion takes place at the moment of electrophilic attack by the peroxide on the Si–Si bond.[181,182]

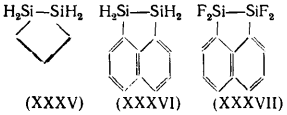


trans-(XXXIII) *cis*-(XXXIV)

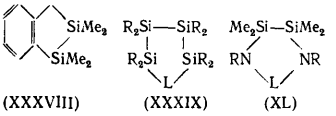
c) The oxidation of five-membered cyclic compounds containing Si–Si bonds

Five-membered silicon or silicon–carbon rings containing Si–Si bonds are more strained than six-membered rings. This is revealed by the slightly higher reactivity of these compounds towards oxygen and other oxidising agents. Dodecamethylcyclohexasilane does not react with atmospheric oxygen, whereas decamethylcyclopentasilane is slowly oxidised in air.[183,184] Compounds with more bulky substituents on the silicon, such as decaphenyl- and decaethylcyclopentasilanes, however, do not react with atmospheric oxygen.[1,185] The cleavage of decamethylcyclopentasilane by chlorine is much more rapid than that of dodecamethylcyclohexasilane.[125] Sulphur or selenium are inserted into the polysilicon ring $(Me_2Si)_5$ at 190 °C.[186] Dodecamethylcyclohexasilane does not react with sulphur and selenium under analogous conditions.

1,2-Disilacyclopentane (XXXV) was found to be extremely reactive towards O_2, probably due to not only the deformation of the Si–Si bond but also the presence in the molecule of easily oxidised Si–H bonds. In contrast to this, the Si–Si and Si–H bonds in 1,2-disila-acenaphthene (XXXVI) are stable to atmospheric oxygen.[187] It was previously noted that fluorodisilanes with a linear or cyclic structure, containing two or more fluorine atoms on silicon, are rapidly oxidised in air.


(XXXV) (XXXVI) (XXXVII)

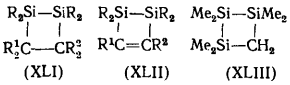
The disila-acenaphthene (XXXVII), however, whose molecule contains four fluorine atoms, was found to be stable to oxygen.[187] 1,1,2,2-Tetramethyl-1,2-disila-4,5-benzocyclopentene (XXXVIII) reacts under mild conditions with MCPBA and oxygen to give the corresponding siloxane. The higher rate of oxidation of this compound compared with pentamethylphenyldisilane has been noted.[188]


(XXXVIII) (XXXIX) (XL)

The introduction of the heteroelement into the ring alters the sensitivity of the product to oxygen. For example, compounds with the general formula (XXXIX) with R = Me, Ph and L = O, NH, NR are stable in air. The boron- and phosphorus-containing heterocycles with L = $BNMe_2$, PPh[52,170,189] were found to be very sensitive to oxygen and moisture. In all known five-membered heterocycles with the general formula (XL),[190,191] the Si–Si bond remains inert to O_2. In the phosphorus-containing heterocycles, the heteroelement is oxidised.[190]

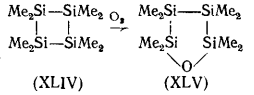
d) The oxidation of four-membered cyclic compounds

The even greater angular strains of the Si–Si, Si–C and C–C bonds in di- and trisilacyclobutanes (XLI), (XLIII), disilacyclobutenes (XLII), and cyclotetrasilanes $(R_2Si)_4$ lead to a further increase in the reactivity of these compounds. The tetrafluorodisilacyclobutenes (XLII) (R = F, R^1 and R^2 = H, Me, Et, Me_3C)[192] and 1,1,2,2,3,3-hexamethyl-1,2,3-trisilacyclobutane (XLIII)[193] are thermally unstable, and rapidly oxidised in air.


(XLI) (XLII) (XLIII)

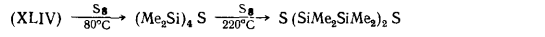
The disilacyclobutanes (XLI) and disilacyclobutenes (XLII) with methyl substituents on the silicon atoms[194,198] are fairly stable to heat, but are very sensitive to oxygen, and are oxidised in solution to the corresponding siloxanes. The aryl-substituted compounds (XLI) (R = phenyl, *m*- or *p*-tolyl) are stable to atmospheric oxygen, but are transformed into siloxanes by the action of MCPBA.[199,200]

Octamethylcyclotetrasilane (XLIV) is very reactive towards oxygen. The formation of small quantities of this compound in the reaction of dimethyldichlorosilane with sodium–potassium alloy in THF has been assumed.[201] In spite of the precautions taken, the authors cited could not isolate this compound from the reaction mixture, because of its rapid oxidation by even traces of oxygen. Kumada and co-workers[202,203] obtained compound (XLIV) by the photolysis of a cyclohexane solution of dodecamethylcyclohexasilane in a nitrogen atmosphere. It was impossible to avoid partial oxidation of compound (XLIV) to the monoxide (XLV) during the reaction and the isolation of the product.

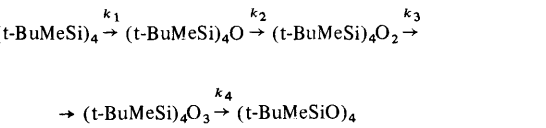


(XLIV) (XLV)

1,2,3,4-Tetraethyltetramethylcyclotetrasilane is also unstable in air.[204] Sulphur or selenium are inserted at the Si–Si bonds of octamethylcyclotetrasilane to give five-membered and symmetrical six-membered rings.[205,206]

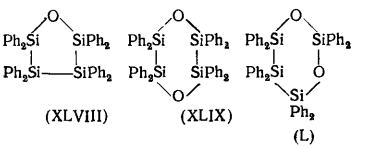


1,2,3,4-Tetra-t-butyltetramethylcyclotetrasilane (XLVI), prepared by West and co-workers,[207] showed a number of unexpected properties, namely the lowest first ionisation potential of all known polysilanes (7.42 eV, PES) and the maximum long-wave ultraviolet absorption (300 nm),[51,208,209] indicating that the energies of the ground and the first excited states differ little. The silicon–silicon bond length (2.377 Å) is greater than the known values for permethylated cyclopolysilanes (2.338 Å for dodecamethylcyclohexasilane). It should be expected that in the strained four-membered ring of compound (XLVI), the strongly deformed silicon–silicon bond with a low value for the first ionisation potential would readily be split by oxidising reagents. It was found, however, that this compound is stable to oxygen and warm concentrated sulphuric acid. The unusual chemical inertness of compound (XLVI) is attributed to the steric effects of the bulky t-butyl groups.[210] All four isomers of $(t\text{-BuMeSi})_4$ are oxidised by MCBPA, but at different rates.[211]



The oxygen atom in the ring is activated towards oxygen by the neighbouring Si–Si bonds, but the ring strain still predominates, so that $k_1 > k_2 > k_3$. The Si–Si bond between the *cis*-substituents is most easily oxidised. The triply-oxidised product $(t\text{-BuMeSi})_4O_3$ does not accumulate in the reaction mixture, but is rapidly oxidised to the tetrasiloxane ($k_4 \gg k_3$).

Perphenylated cyclotetrasilane $(Ph_2Si)_4$ (XLVII), which is thermally stable, is slowly oxidised by atmospheric oxygen to give octaphenoxytetrasilacyclopentane (XLVIII) and a siloxane polymer.[1,2]



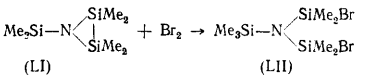
(XLVIII) (XLIX) (L)

Octaphenylcyclotetrasilane is oxidised by atmospheric oxygen in toluene at 100 °C and by ozone in CCl_4 or carbon disulphide. Compounds (XLVIII) and (XLIX) were isolated from the products of these reactions.[1,2] Nitrobenzene reacts with compound (XLVII) to give as main product the 1,3-dioxide (L). Benzaldehyde oxidises compound (XLVII) rapidly, whereas benzyl alcohol, acetophenone, paraldehyde, and pentyl nitrite react slowly. The products of these reactions are the monoxide (XLVIII), the 1,4-dioxide (XLIX), and a polymer.[1,2] The silicon–silicon bond in octaphenylcyclotetrasilane is readily split by halogens, hydrogen halides, mercury halides and acetate, tin(IV) chloride, phosphorus(V) chloride, and various organic halogeno-compounds. Decaphenylcyclopentasilane is more stable to these reagents, and cleavage requires more severe conditions.[1,2,17,212,213]

Thus four-membered cyclic compounds containing from one to four Si–Si bonds in the ring have different thermal stabilities, but practically all are fairly sensitive to oxidising agents, and cleavage of the Si–Si bonds, and not the Si–C, C–C, or C=C bonds, always takes place. Bulky substituents have an appreciable stabilising influence on the cyclosilane molecule.[214,215]

e) The oxidation of three-membered rings

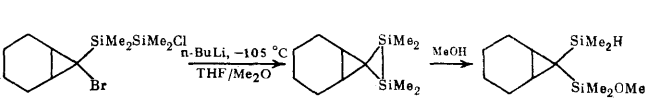
The first three-membered ring with an Si–Si bond in the molecule, namely N-trimethylsilyltetramethylcyclodisilazane (LI), was obtained in 1963;[216] it is thermally stable, and is not oxidised in air. Prolonged boiling of compound (LI) in a solution of alkali in hexanol leads to only partial cleavage of the Si–Si bond. On the other hand, the reaction with bromine in CCl_4 takes place readily to give the dibromo-derivative (LII).



(LI) (LII)

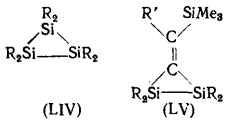
Compound (LI) is slowly hydrolysed by water to give ammonia and siloxanes. Its low reactivity may indicate that there is very little or no deformation of the Si–Si bond.

Disilacyclopropane (LIII), synthesised in 1976, exists only at temperatures below −100 °C. As expected, the most reactive bond in this compound is not the Si–C but the Si–Si bond, which is split by methanol at −105 °C.[217]



(LIII)

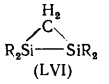
The subsequent search for methods of synthesising silicon-containing rings[80–86,218–221] gave a number of di- and trisilacyclopropane systems (LIV)–(LVI), which were found to be completely stable to heat and fairly inert towards oxygen or moisture.



(LIV) (LV)

R = 2,6-dimethylphenyl (a) (Ref.80), neopentyl (b) (Ref.85), t-butyl (c) (Ref.219), 1-ethylpropyl (d) (Ref.81), isopropyl (e) (Refs.81, 86)

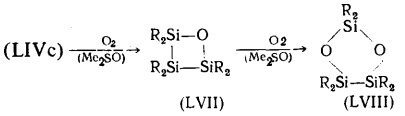
R = mesityl, R′ = trimethylsilyl (a) or phenyl (b) (Ref.218)



(LVI)

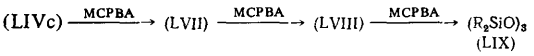
R = 2,6-dimethylphenyl (Ref.82)

An exception is hexaisopropylcyclotrisilane (LIVe), which decomposes slowly when kept, and reacts rapidly with atmospheric oxygen.[81,86] Hexa(2,6-dimethylphenyl)-cyclotrisilane (LIVa) is readily split by chlorine.[80] Hexa-t-butylcyclotrisilane (LIVc) in toluene is oxidised very slowly by atmospheric oxygen to the mono- and dioxa-derivatives (LVII) and (LVIII). The reaction with dimethyl sulphoxide in boiling toluene is similar.



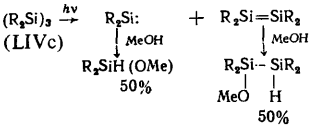
(LVII) (LVIII)

MCPBA successively splits all three silicon–silicon bonds in compound (LIVc) at room temperature, the final product being hexa-t-butylcyclotrisiloxane (LIX).

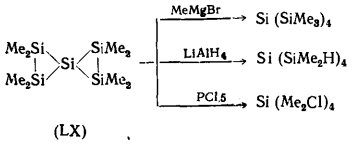


(LIX)

Sulphur and selenium are inserted at the Si–Si bond of hexa-t-butylcyclotrisilane in boiling toluene to give the four-membered rings $(R_2Si)_3Z$ (Z = S, Se).[220] The reaction of compound (LIVc) with methanol with irradiation by ultraviolet light takes place with the intermediate formation of di-t-butylsilylene and tetra-t-butyldisilene.[219]



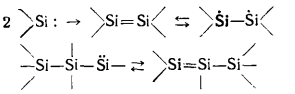
The disilacyclopropanes (LVa, b) do not react with alcohols at room temperature.[218] Compounds (LIVd) and (LVI) are oxidised to the corresponding mono-oxa-derivatives by atmospheric oxygen[81] or MCPBA.[82] The high thermal stability and low chemical activity of the silacyclopropanes (LIVa–d), (LV), and (LVI) is attributed to the steric shielding of the silicon atoms by the bulky substituents. According to Ref.221, unexpected thermal stability is shown by octamethylspiropentasilane (LX), which has practically no stabilising bulky substituents on the silicon atoms. Its chemical activity is fairly high, however.



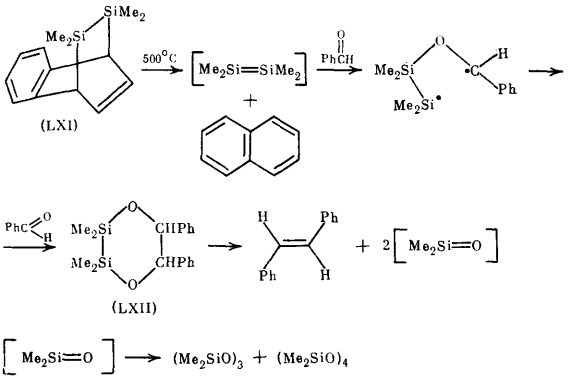
(LX)

V. THE OXIDATIVE CLEAVAGE OF THE SILICON–SILICON DOUBLE BOND

The formation of disilene as a short-lived intermediate compound in the thermal decomposition of benzo-7,8-disilabicyclo[2,2,2]-octa-2,5-dienes, for example compound (LXI), was first postulated in 1972.[222] It was subsequently shown that disilene intermediates[223] may be obtained by the dimerisation[224,225] and rearrangement[226,227] of silylenes.



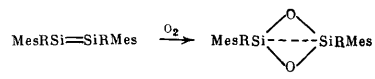
These highly active species behave as disilenes[228] or as biradicals,[229–231] depending on the substituents on silicon and on the reaction conditions. Disilenes undergo cycloaddition with dienes,[232,233] and dimerise to cyclotetrasilanes;[234,235] the reactions with oxygen-containing compounds[233,236] give products with Si–O bonds. For example, tetramethyldisilene, obtained by decomposing compound (LXI), reacts with benzaldehyde to give hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, and trans-stilbene.[236] The proposed scheme includes the formation of radical and silanone intermediates.



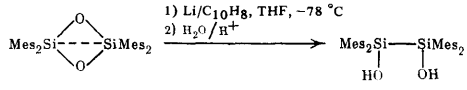
(LXI) (LXII)

Evidence in support of this scheme is provided by the fact that 1,2-disila-3,5-dioxacyclohexane (LXII), obtained by direct synthesis, decomposes at 500 °C to give the same products.

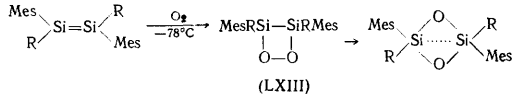
The latest achievements in the synthesis of stable disilenes[24,25,76–88,237–248] have made it possible to investigate their reactivity towards various oxidising reagents under ordinary conditions, that is in solution and at room temperature. The disilenes known at present differ in their thermal stability and reactivity, which are determined by the steric effects of the substituents on the silicon atoms. The mesityl[25,77] 2,6-dimethylphenyl,[80] and 2,6-diethylphenyl[84] groups give fairly stable compounds, which withstand heating for a short time up to the melting points (see Table). Alkyl-substituted disilenes are less stable. Thus the half-decomposition time of tetra-t-butyldisilene at room temperature is 4–10 h;[83,87] tetraisopropyldisilene is even less stable.[86] The disilenes with the highest thermal stability are slightly less active in reactions with oxidising reagents. Overall, the chemical properties of disilenes are similar to those of alkenes, but their activity is appreciably greater. The yellow colour characteristic of disilenes disappears rapidly on contact with air. Oxygen reacts with the powdered disilenes MesRSi=SiRMes [R = Mes (mesityl), Me_3C, $(Me_3Si)_2N$] at 25 °C to give the corresponding cyclodisiloxanes.[237]



X-Ray diffraction[238] has shown that in the cyclodisiloxanes, the silicon atoms are situated at a distance shorter than the length of an ordinary silicon–silicon bond. Thus in tetramesitylcyclodisiloxane the Si–Si distance is 2.31 Å, whereas the length of the silicon–silicon bond in 1,1,2,2-tetramesityldisilane is 2.35 Å. Thus bonding is possible between the silicon atoms in cyclodisiloxanes.[238–243] This is confirmed by the reaction of tetramesitylcyclodisiloxane with naphthalene–lithium, which takes place with preservation of the Si–Si bond and gives 1,1,2,2-tetramesityldisilandiol after hydrolysis.[238]

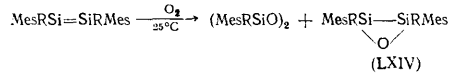


The oxidation of *trans*-dimesityldi-t-butyldisilene by oxygen in solution in pentane or THF at −78 °C gives the disiloxetane (LXIII), which undergoes quantitative rearrangement into *trans*-dimesityl-di-t-butylcyclodisiloxane when the solution is heated to room temperature.[237]



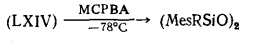
(LXIII)

When the reaction is carried out in pentane at 25 °C, the products are *trans*-dimesityldi-t-butylcyclodisiloxane and the disilanyl epoxide (LXIV).

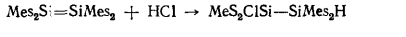


(LXIV)

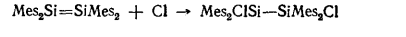
The disilanyl epoxide (LXIV) is stable to oxygen, but it can be converted into the cyclodisiloxane by the action of MCPBA.[237]



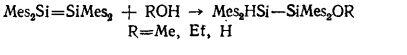
Hydrogen chloride splits the silicon–silicon double bond in tetramesityldisilene to give 1-chloro-2-H-tetramesityldisilane.[25,77]



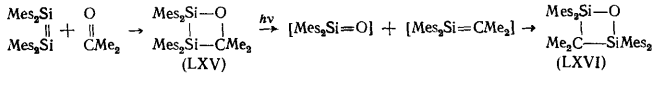
The reaction with chlorine in benzene gives 1,2-dichlorotetramesityldisilane.[77]



If however the reaction is carried out in alkanes, the product is 1-chloro-2-H-tetramesityldisilane, and this was attributed to the radical mechanism.[77] Tetramesityldisilene reacts with alcohols and water at 50 °C,[25,77] and also with carbonyl compounds.[77]

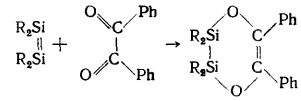


The product of the addition of acetone (LXV) undergoes rearrangement on irradiation to give the 1,3-isomer (LXVI).

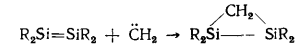


(LXV) (LXVI)

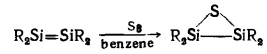
The reactions of tetramesityldisilene[76] and tetra-t-butyldisilene[87] with benzil takes place as [2 + 4]-cyclo-addition.



Carbene is inserted at the silicon–silicon bond to give disilacyclopropane.[82]



The reaction with sulphur gives the episulphide.[237,243]



The reaction of tetra-t-butyldisilene with dienes takes place as [2 + 2]- or [2 + 4]-cyclo-addition.[83,87] Tetramesityldisilene does not react with traditional disilene traps such as anthracene, 2,3-dimethylbutadiene, 1,4-diphenylbutadiene, and phenyl(trimethylsilyl)acetylene, but it undergoes cycloaddition with phenylacetylene.[77]

---o0o---

The oxidative cleavage of the silicon–silicon bond may take place by free-radical, molecular, or heterocyclic mechanisms, depending on the type of polysilane and oxidising agent. The cleavage may be due to rearrangement of the polysilane, in which the R_3Si group migrates from the silicon atom to a more electronegative element. The silicon–silicon bond acts as the nucleophilic centre in reactions with electrophilic reagents such as peroxyacids and halogens. Cleavage by nucleophilic reagents takes place more readily if the silicon atoms are surrounded by electron-acceptor substituents. The influence of ring size and the size of the substituents on the reactivity of the Si–Si bond can be clearly seen. The reactivity of the silicon–silicon double bond is appreciably greater than that of σ_{Si-Si} and π_{C-C} bonds.

REFERENCES

1. H.Gilman and G.L.Schwebke, Adv.Organometal. Chem., 1964, **1**, 89.
2. H.Gilman, W.H.Atwell, and F.K.Cartledge, Adv. Organometal.Chem., 1966, **4**, 1.
3. A.G.MacDiarmid, Adv.Inorg.Chem.Radiochem., 1961, **3**, 207.
4. G.Schott, Z.Chem., 1962, **2**, 194.
5. G.Schott, Fortschr.chem.Forsch., 1967, **9**, 60.
6. M.Schmeisser and P.Voss, Fortschr.chem.Forsch., 1967, **9**, 165.
7. K.M.Mackay and R.Watt, Organometal.Chem.Rev., A, 1969, **4**, 137.
8. M.Kumada, Pure Appl.Chem., 1966, **13**, 167.
9. M.Kumada and K.Tamao, Adv.Organometal.Chem., 1968, **6**, 19.
10. M.Kumada, M.Ishikawa, H.Okinoshima, and K.Yamamoto, Ann.N.Y.Acad.Sci., 1974, **239**, 32.
11. M.Kumada, J.Organometal.Chem., 1975, **100**, 127.
12. M.Ishikawa and M.Kumada, Rev.Silicon, Germanium, Tin, Lead Compounds, 1979, **4**, 7.
13. M.Ishikawa and M.Kumada, Adv.Organometal.Chem., 1981, **9**, 51.
14. H.Sakurai, J.Japan Chem., 1975, **29**, 36.
15. H.Sakurai, J.Organometal.Chem., 1975, **200**, 261.

16. E.Hengge, Fortschr.chem.Forsch., 1967, **9**, 145.
17. E.Hengge, Top.Curr.Chem., 1974, **51**, 1.
18. E.Hengge, J.Organometal.Chem.Libr., 1980, **9**, 261.
19. E.Hengge, Rev.Inorg.Chem., 1980, **1**, 139.
20. R.West, Ann.N.Y.Acad.Sci., 1974, **239**, 262.
21. R.West and E.Carberry, Science, 1975, **189**, 179.
22. R.West, Pure Appl.Chem., 1982, **54**, 1041.
23. G.Urry, Acc.Chem.Res., 1970, **3**, 306.
24. R.C.West and M.J.Fink, VI Intern.Symp.on Organosilicon Chemistry. Abstracts. Budapest, 1981, p.122.
25. R.C.West, M.J.Fink, and J.Michl, Science, 1981, **214**, 1343.
26. "Soedineniya Kremniya dlya Polucheniya Kremniikarbidnykh Materialov" (Silicon Compounds for the Preparation of Silicon Carbide Materials), Izd. NIITEKhIM, Moscow, 1982.
27. S.Yajima, Nature, 1976, **261**, 238, 683; 1978, **273**, 525.
28. S.Yajima, J.Mater.Sci., 1978, **13**, 2569.
29. C.L.Schilling, J.P.Wesson, and T.C.Williams, J.Polym.Sci., Polym.Symp., 1983, **70**, 121.
30. R.H.Baney, J.H.Gaul, and T.K.Hilty, Organometallics, 1983, **2**, 859.
31. M.Mazurek and J.Chojnowski, VI Intern.Symp.on Organosilicon Chemistry. Abstracts. Budapest, 1981, p.148.
32. S.P.Kolesnikov, T.L.Mitenina, A.Ya.Shteinshneider, and O.M.Nefedov, Izv.Akad.Nauk SSSR, Ser.Khim., 1982, 942.
33. L.S.Troitskaya, B.B.Troitskii, A.S.Yakhnov, and M.A.Novikova, "VI Vsesoyuznaya Konferentsiya "Starenie i Stabilisatsiya Polimerov". Tezisy Dokladov" (Summaries of Papers Presented at the Sixth All Union Conference on the Ageing and Stabilisation of Polymers), Ufa, 1983, p.83.
34. W.P.Weber, in "Silicon Reagents for Organic Synthesis". Springer Verlag, Berlin–Heidelberg–New York, 1983, pp.35, 326.
35. R.C.West, L.D.David, P.I.Djurovich, K.L.Stearley, K.S.V.Srinivasan, and H.Yu, J.Amer.Chem.Soc., 1981, **103**, 7352.
36. P.John, J.M.Odeh, and J.Wood, Chem.Communs., 1983, 1496.
37. D.N.Hague and R.H.Prince, Proc.Chem.Soc., 1962, 3862.
38. D.N.Hague and R.H.Prince, Chem.Ind.(London), 1964, 1492.
39. D.N.Hague and R.H.Prince, J.Chem.Soc., 1965, 4690.
40. H.Gilman, W.H.Atwell, and G.L.Schwebke, Chem. Ind.(London), 1964, 1063.
41. H.Gilman, W.H.Atwell, and G.L.Schwebke, J. Organometal.Chem., 1964, **2**, 369.
42. H.Gilman and W.H.Atwell, J.Organometal.Chem., 1965, **4**, 176.
43. H.Gilman and D.R.Chapman, J.Organometal.Chem., 1966, **5**, 392.
44. H.Gilman and P.J.Morris, J.Organometal.Chem., 1966, **6**, 102.
45. H.Sakurai and M.Kumada, Bull.Chem.Soc.Japan, 1964, **37**, 1894.
46. H.Sakurai, H.Yamamori, and M.Kumada, Bull.Chem. Soc.Japan, 1965, **38**, 2024.
47. H.Sakurai, H.Yamamori, and M.Kumada, Chem. Communs., 1968, 198,
48. H.Sakurai, H.Sugiyama, M.Kira, and K.Yamamoto, J.Organometal.Chem., 1982, **225**, 163.
49. E.A.Carberry, R.C.West, and G.E.Glass, J.Amer. Chem.Soc., 1969, **91**, 5446.
50. R.C.West and A.Indriksons, J.Amer.Chem.Soc., 1972, **94**, 6110.
51. M.S.Biernbaum and R.C.West, J.Organometal.Chem., 1977, **131**, 179.
52. T.H.Newman, R.C.West, and R.T.Oakley, J.Organometal.Chem., 1980, **197**, 159.
53. C.G.Pitt, L.L.Jones, and B.G.Ramsey, J.Amer. Chem.Soc., 1967, **89**, 5471.
54. C.G.Pitt, J.Amer.Chem.Soc., 1968, **91**, 6613.
55. P.P.Shorygin, V.A.Petukhov, O.M.Nefedov, S.P.Kolesnikov, and V.I.Shiryaev, Teor.i Eksper. Khim., 1966, **2**, 190.
56. V.A.Petukhov, V.I.Zhun', V.D.Sheludyakov, and V.F.Mironov, Zhur.Obshch.Khim., 1979, **49**, 1054.
57. H.Kelling, Z.Chem., 1967, **7**, 237.
58. W.Drenth, J.G.Noltes, E.J.Bulten, and H.M.J.C.Creemers, J.Organometal.Chem., 1969, **17**, 173.
59. A.Castel, P.Riviere, B.Saint-Roch, J.Satge, and J.P.Malrieu, J.Organometal.Chem., 1983, **247**, 149.
60. N.D.Sokolov, Uspekhi Khim., 1967, **36**(12), 2195 [Russ.Chem.Rev., 1967(12)].
61. H.A.Brune and D.Schulte, Chem.Ber., 1967, **100**, 3438.
62. E.Hengge and H.Grupe, Chem.Ber., 1964, **97**, 1783.
63. H.Kelling, K.Dauber, and E.Popowski, Z.Chem., 1975, **15**, 114.
64. E.A.Chernyshev, N.G.Tolstikova, A.A.Ivashchenko, A.A.Zelenetskaya, and L.A.Leites, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 1963, 660.
65. H.Bock and W.Ensslin, Angew.Chem., 1971, **83**, 435.
66. C.G.Pitt and H.Bock, Chem.Communs., 1972, 28.
67. C.G.Pitt, in "Homoatomic Rings, Chains and Macromolecules of Main-group Elements" (Edited by A.L.Rheingold), Elsevier, Amsterdam–Oxford–New York, 1977, p.203.
68. A.H.Cowley, in "Homoatomic Rings, Chains and Macromolecules of Main-group Elements" (Edited by A.L.Rheingold), Elsevier, Amsterdam–Oxford–New York, 1977, p.59.
69. A.L.Allred, C.A.Ernst, and M.A.Ratner, in "Homoatomic Rings, Chains and Macromolecules of Main-group Elements" (Edited by A.L.Rheingold), Elsevier, Amsterdam–Oxford–New York, 1977, p.307.
70. K.A.Ostoja Starzewski, H.Tom Dieck, and H.Bock, J.Organometal.Chem., 1974, **65**, 311.
71. V.F.Traven', L.Voronina, M.I.German, V.F.Donyagina, V.B.Knyazhevskaya, E.E.Kostyuchenko, T.V.Pyatkina, V.V.Redchenko, B.I.Stepanov, R.C.West, and M.Yu.Eismont, Zhur.Obshch.Khim., 1973, **43**, 442; 1975, **45**, 824; 1978, **48**, 2232; 1980, **50**, 606, 2007.
72. A.N.Egorochkin, Uspekhi Khim., 1984, **53**(5), 772 [Russ.Chem.Rev., 1984(5)].
73. V.I.Khvostenko, B.G.Zykov, V.P.Yur'ev, V.F.Mironov, G.I.Kovel'zon, A.A.Panasenko, V.D.Sheludyakov, and I.A.Galiunas, J.Organometal. Chem., 1981, **218**, 155.
74. V.F.Traven and R.C.West, J.Amer.Chem.Soc., 1973, **95**, 6824.
75. H.Sakurai, M.Kira, and T.Uchida, J.Amer.Chem. Soc., 1973, **95**, 6826.
76. P.R.Boudjouk, B.H.Han, and K.R.Anderson, J.Amer. Chem.Soc., 1982, **104**, 4992.
77. M.J.Fink, D.J.DeYoung, R.C.West, and J.Michl, J.Amer.Chem.Soc., 1983, **105**, 1070.

78. M.J.Fink, M.J.Michalczyk, K.J.Haller, R.C.West, and J.Michl, Chem.Communs, 1983, 1010.
79. K.W.Zilm, D.M.Grant, J.Michl, M.J.Fink, and R.C.West, Organometallics, 1983, 2, 193.
80. S.Masamune, Y.Hanzawa, S.Murakami, T.Bally, and J.F.Blount, J.Amer.Chem.Soc., 1982, **104**, 1150.
81. S.Masamune, H.Tobita, and S.Murakami, J.Amer. Chem.Soc., 1983, **105**, 6524.
82. S.Masamune, S.Murakami, H.Tobita, and D.J.Williams, J.Amer.Chem.Soc., 1983, **105**, 7776.
83. S.Masamune, S.Murakami, and H.Tobita, Organometallics, 1983, **2**, 1464.
84. S.Masamune, S.Murakami, J.T.Snow, H.Tobita, and D.J.Williams, Organometallics, 1984, **3**, 333.
85. H.Watanabe, T.Okawa, M.Kato, and Y.Nagai, Chem. Communs, 1983, 781.
86. H.Watanabe, Y.Kougo, and Y.Nagai, Chem.Communs, 1984, 66.
87. M.Weidenbruch, A.Schaefer, and K.L.Thom, Z.Naturforsch., 1983, **38b**, 1695.
88. R.C.West, M.J.Fink, M.J.Michalczyk, D.J.DeYoung, and J.Michl, VII Intern.Symp.on Organosilicon Chemistry. Abstracts Kyoto, 1984, p.1.
89. M.Yoshino, Kagaku to Kogyo (Chem. and Chem.Ind.), 1982, **35**, 581.
90. V.F.Traven', M.F.Eismont, V.V.Redchenko, and B.I.Stepanov, Zhur.Obshch.Khim., 1980, **50**, 2001.
91. E.Hengge and G.Bauer, Angew.Chem., 1973, **85**, 304.
92. E.Hengge and G.Bauer, Monatsh.Chem., 1975, **106**, 503.
93. E.Hengge and D.Kovar, Z.anorg.allgem.Chem., 1979, **459**, 123.
94. G.Schott and E.Herrmann, Z.anorg.allgem.Chem., 1960, **307**, 97.
95. A.Weiss, G.Beil, and H.Meyer, Z.Naturforsch., 1980, **35b**, 25.
96. E.Hengge and D.Kovar, J.Organometal.Chem., 1977, **125**, C29.
97. E.Hengge and D.Kovar, Z.anorg.allgem.Chem., 1979, **458**, 163.
98. E.Hengge and D.Kovar, Angew.Chem., 1981, **93**, 698.
99. V.F.Kochubei, A.P.Gavrilin, F.B.Moin, and Yu.A.Pazderskii, Kinetika i Kataliz, 1978, **19**, 1320.
100. P.L.Timms, R.A.Kent, T.C.Ehlert, and J.L.Margrave, J.Amer.Chem.Soc., 1965, **87**, 2824.
101. K.Naumann, G.Zon, and K.Mislow, J.Amer.Chem. Soc., 1969, **91**, 2788.
102. K.Naumann et al., J.Amer.Chem.Soc., 1969, **91**, 7012, 7023, 7027.
103. A.G.Hortmann, J.Koo, and C.Yu, J.Org.Chem., 1978, **43**, 2289.
104. D.K.Myers and L.D.Quin, J.Org.Chem., 1971, **36**, 1285.
105. G.Deleris, J.Dunogues, and R.Calas, Bull.Soc.chim. France, 1974, 672.
106. R.Calas, J.Dunogues, G.Deleris, and N.Duffaut, J.Organometal.Chem., 1982, **225**, 117.
107. K.Tamao, M.Kumada, and T.Takahashi, J.Organometal.Chem., 1975, **94**, 367.
108. Yu.A.Aleksandrov, "Zhidkofaznoe Avtookislenie Eoementoorganicheskikh Soedinenii" (The Liquid-Phase Autoxidation of Hetero-organic Compounds), Izd.Nauka, Moscow, 1978, p.115.
109. L.Spialter and J.D.Austin, Inorg.Chem., 1966, **5**, 1975.
110. Yu.A.Aleksandrov, Organometal.Chem.Rev., A, 1970, **6**, 209.
111. Yu.A.Aleksandrov and B.I.Tarunin, Uspekhi Khim., 1977, **46**(10), 1721 [Russ.Chem.Rev., 1977(10)].
112. Yu.A.Aleksandrov and B.I.Tarunin, J.Organometal. Chem., 1982, **238**, 125.
113. Yu.A.Aleksandrov and B.I.Tarunin, Zhur.Obshch. Khim., 1972, **42**, 717.
114. Yu.A.Aleksandrov, B.I.Tarunin, and M.L.Perepletchikov, in collected papers, "Trudy po Khimii i Khimicheskoi Tekhnologii" (Papers on Chemistry and Chemical Technology), No.4, Izd.Gor'kovsk.Univ., Gor'kii, 1974, p.85.
115. B.I.Tarunin, N.N.Seliverstov, and Yu.A.Aleksandrov, Zhur.Obshch.Khim., 1982, **52**, 1404.
116. R.Calas, E.Frainnet, and Y.Dentone, Compt.rend., 1964, **259**, 3777.
117. R.Calas, A.Marchand, E.Frainnet, and P.Gerval, Bull.Soc.chim.France, 1968, 2478.
118. P.Mazerolles, M.Joanney, J.C.Maire, and R.Gassend, J.Organometal.Chem., 1975, **87**, 269.
119. T.T.Tsai, W.L.Lehn, and C.J.Marshall, J.Org.Chem., 1966, **31**, 3047.
120. V.F.Traven', V.N.Karel'skii, V.F.Donyagina, E.D.Babich, V.M.Vdovin, N.S.Nametkin, and B.I.Stepanov, Dokl.Akad.Nauk SSSR, 1975, **224**, 837.
121. M.Kumada, K.Shiina, and M.Yamaguchi, J.Chem. Soc.Japan, Ind.Chem.Sect., 1954, **57**, 230;
122. A.Taketa, M.Kumada, and K.Tarama, J.Chem.Soc. Japan, Pure Chem.Sect., 1957, **78**, 999;
123. U.Stolberg, Chem.Ber., 1963, **96**, 2798.
124. M.Gielen, J.Nasielski, and G.Vandendunghen, Bull. Soc.chim.Belg., 1971, **80**, 165.
125. W.Wojnowski, C.J.Hurt, and R.C.West, J.Organometal.Chem., 1977, **124**, 271.
126. Yu.G.Bundel', S.I.Bobrovskii, V.V.Smirnov, I.A.Novikova, G.B.Sergeev, and O.A.Reutov, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 2129.
127. E.Hengge and F.J.Krysl, Monatsh.Chem., 1981, 112, 731.
128. M.A.Zayed and M.H.Nosseir, Chem.and Petro-Chem.J., 1982, **13**, 25.
129. A.Herman, B.Dreczewski, and W.Wojnowski, J. Organometal.Chem., 1983, **251**, 7.
130. T.C.Wu and H.Gilman, J.Org.Chem., 1958, **23**, 913.
131. P.B.D.De La Mare and R.Bolton, in "Electrophilic Additions to Unsaturated Systems", Elsevier, Amsterdam–Oxford–New York, 1982, chapter 5.
132. M.Kumada, M.Yamaguchi, Y.Yamamato, J.Nakajima, and K.Shiina, J.Org.Chem., 1956, **21**, 1264.
133. G.Schott and W.Langecker, Z.anorg.allgem.Chem., 1968, **358**, 210.
134. H.Kelling, Z.Chem., 1968, **8**, 391.
135. K.Tamao and M.Kumada, J.Organometal.Chem., 1971, **30**, 349.
136. L.Spialter and J.D.Austin, J.Amer.Chem.Soc., 1966, **88**, 1828.
137. H.Sakurai, M.Kira, and M.Kumada, Bull.Chem.Soc. Japan, 1971, **44**, 1167.
138. H.F.Vorbrueggen and K.Krolikiewicz, Tetrahedron Letters, 1983, **24**, 5337.
139. F.P.Tsui, T.M.Vogel, and G.Zon, J.Org.Chem., 1975, **40**, 761.
140. R.E.Swaim and W.P.Weber, J.Amer.Chem.Soc., 1979, **101**, 5703.
141. H.Sakurai, T.Imoto, N.Hayashi, and M.Kumada, J.Amer.Chem.Soc., 1965, **87**, 4001.
142. G.A.Razuvaev, T.N.Brevnova, and V.V.Semenov, Zhur.Obshch.Khim., 1980, **50**, 1806.

143. V.V.Semenov, T.N.Brevnova, and S.Ya.Khorshev, Zhur.Obshch.Khim., 1983, **53**, 2085.
144. G.A.Razuvaev, T.N.Brevnova, and V.V.Semenov, J.Organometal.Chem., 1984, **271**, 261.
145. T.A.Dixon, K.P.Steele, and W.P.Weber, J.Organometal.Chem., 1982, **231**, 299.
146. H.Sakurai, R.Koh, A.Hosomi, and M.Kumada, Bull.Chem.Soc.Japan, 1966, **39**, 2050.
147. H.Sakurai, T.Kishida, A.Hosomi, and M.Kumada, J.Organometal.Chem., 1967, **8**, 65.
148. N.S.Vyazankin, G.A.Razuvaev, and O.A.Kruglaya, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 1962, 2008.
149. T.N.Brevnova, V.V.Semenov, and G.A.Razuvaev, Zhur.Obshch.Khim., 1978, **48**, 1380.
150. J.W.Wilt, in "Reactive Intermediates", Vol.3, (Edited by R.A.Abramovitch), Plenum Publ.Corp., New York, 1983, p.113.
151. K.Kawazumi and B.Murai, Bull.Chem.Soc.Japan, 1966, **39**, 1951.
152. G.A.Razuvaev, T.N.Brevnova, and V.V.Semenov, Zhur.Obshch.Khim., 1977, **47**, 2270.
153. T.N.Brevnova, V.V.Semenov, and G.A.Razuvaev, Zhur.Obshch.Khim., 1981, **51**, 2010.
154. G.A.Razuvaev, T.N.Brevnova, V.V.Semenov, E.I.Sevast'yanova, and S.Ya.Khorshev, Zhur. Obshch.Khim., 1980, **50**, 2267.
155. H.Burger, Fortschr.chem.Forsch., 1967, **9**, 1.
156. P.P.Gaspar, in "Reactive Intermediates", Vol.1 (Edited by M.Jones and R.A.Moss), Wiley-Intersci., New York, 1978, p.229; 1981, Vol.2, p.335.
157. Y.N.Tang, in "Reactive Intermediates", Vol.2 (Edited by R.A.Abramovitch), Plenum Press, New York, 1982, 297.
158. W.Ando and M.Ikeno, Chem.Letters, 1978, 609.
159. W.Ando and M.Ikeno, Chem.Communs, 1979, 655.
160. W.Ando, Y.Hamada, and A.Sekigychi, Tetrahedron Letters, 1982, **23**, 5323.
161. H.Okinoshima and W.P.Weber, J.Organometal.Chem., 1978, **149**, 279.
162. H.S.D.Soysa, H.Okinoshima, and W.P.Weber, J. Organometal.Chem., 1977, **133**, C17.
163. H.S.D.Soysa and W.P.Weber, J.Organometal.Chem., 1979, **173**, 269.
164. H.Okinoshima and W.P.Weber, J.Organometal.Chem., 1978, **155**, 165.
165. A.Chihi and W.P.Weber, J.Organometal.Chem., 1981, **210**, 163.
166. D.Tzeng and W.P.Weber, J.Amer.Chem.Soc., 1980, **102**, 1451.
167. M.Kumada, K.Tamao, T.Takubo, and M.Ishikawa, J.Organometal.Chem., 1967, **9**, 43.
168. L.E.Gusel'nikov, Yu.P.Polyakov, and N.S.Nametkin, Dokl.Akad.Nauk SSSR, 1980, **253**, 1133.
169. H.Sakurai and Y.Kamiyama, J.Amer.Chem.Soc., 1974, **96**, 6192.
170. R.T.Oakley, D.A.Stanislawski, and R.C.West, J.Organometal.Chem., 1978, **157**, 389.
171. T.H.Newman, J.C.Calabrese, R.T.Oakley, D.A.Stanislawski, and R.C.West, J.Organometal. Chem., 1982, **225**, 211.
172. L.F.Brough and R.C.West, J.Organometal.Chem., 1980, **194**, 139.
173. P.K.Sen, T.B.Brennan, and H.Gilman, Indian J. Appl.Chem., 1972, **35**, 121.
174. I.S.Alnaimi and W.P.Weber, Organometallics, 1983, 2, 903.
175. L.Birkofer, V.Foremny, and G.Schmidtberg, J. Organometal.Chem., 1977, **142**, 37.
176. L.Birkofer and W.Weniger, Chem.Ber., 1973, **106**, 3595.
177. P.Mazerolles, M.Joanny, and C.Tourrou, J.Organometal.Chem., 1973, **60**, C3.
178. Y.Nakadaira and H.Sakurai, J.Organometal.Chem., 1973, **47**, 61.
179. K.Tamao, M.Ishikawa, and M.Kumada, Chem. Communs., 1969, 73.
180. K.Tamao, M.Kumada, and M.Ishikawa, J.Organometal.Chem., 1971, **31**, 17.
181. K.Tamao, M.Kumada, and T.Sugimoto, Chem. Communs, 1970, 285.
182. K.Tamao and M.Kumada, J.Organometal.Chem., 1971, **31**, 35.
183. E.Carberry and R.C.West, J.Organometal.Chem., 1966, **6**, 582.
184. E.Hengge, H.G.Schuster, and W.Peter, J.Organometal.Chem., 1980, **186**, C45.
185. C.W.Carlson, K.Matsumura, and R.C.West, J. Organometal.Chem., 1980, **194**, C5.
186. M.Wojnowska, W.Wojnowski, and R.C.West, J. Organometal.Chem., 1980, **194**, C1.
187. E.A.Chernyshev, N.G.Komalenkova, T.A.Klochkova, S.A.Shchepinov, and A.M.Mosin, Zhur.Obshch. Khim., 1971, **41**, 122.
188. F.P.Tsui and G.Zon, J.Organometal.Chem., 1974, **71**, C3.
189. E.Hengge and D.Wolfer, J.Organometal.Chem., 1974, **66**, 413.
190. U.Wannagat, M.Schlingmann, and H.Autzen, Z. Naturforsch., 1976, **31b**, 621.
191. U.Wannagat, R.Seifert, and M.Schlingmann, Z. anorg.allgem.Chem., 1978, **439**, 83.
192. C.S.Liu, J.L.Margrave, J.C.Thompson, and P.L.Timms, Canad.J.Chem., 1972, **50**, 549, 465.
193. G.Fritz and B.Frunert, Z.anorg.allgem.Chem., 1981, **473**, 59.
194. W.H.Atwell and J.G.Uhlmann, J.Organometal.Chem., 1973, **52**, C21.
195. D.Seyferth and S.C.Vick, J.Organometal.Chem., 1977, **125**, C11.
196. D.Seyferth, D.C.Annarelli, and S.C.Vick, J.Organometal.Chem., 1984, **272**, 123.
197. H.Sakurai, T.Kobayashi, and Y.Nakadaira, J.Organometal.Chem., 1978, **162**, C43.
198. M.Ishikawa, H.Sugisawa, M.Kumada, H.Kawakami, and T.Yamabe, Organometallics, 1983, 2, 974.
199. M.Ishikawa, D.Kovar, T.Fuchikami, K.Nishimura, M.Kumada, T.Higuchi, and S.Miyamoto, J.Amer. Chem.Soc., 1981, **103**, 2324.
200. M.Ishikawa, K.Nishimura, H.Ochiai, and M.Kumada, J.Organometal.Chem., 1982, **236**, 7.
201. E.A.Carberry and R.C.West, J.Amer.Chem.Soc., 1969, **91**, 5440.
202. M.Ishikawa and M.Kumada, Chem.Communs, 1970, 612.
203. M.Ishikawa and Z.Kumada, J.Organometal.Chem., 1972, **42**, 325.
204. A.Katti, C.W.Carlson, and R.C.West, J.Organometal. Chem., 1984, **271**, 353.
205. E.Hengge and H.G.Schuster, J.Organometal.Chem., 1982, **231**, C17.
206. E.Hengge and H.G.Schuster, J.Organometal.Chem., 1982, **240**, C65.
207. M.S.Biernbaum and R.C.West, J.Organometal.Chem., 1974, **77**, C13.
208. C.J.Hurt, J.C.Calabrese, and R.C.West, J.Organometal.Chem., 1975, **91**, 273.

209. T.F.Block, M.Biernbaum, and R.C.West, J.Organometal.Chem., 1977, **131**, 199.
210. M.S.Biernbaum and R.C.West, J.Organometal.Chem., 1977, **131**, 189.
211. B.J.Helmer and R.C.West, Organometallics, 1982, **1**, 1463.
212. E.Hengge, H.Reuter, and R.Petzold, Z.Naturforsch., 1963, **18b**, 425.
213. H.Gilman, D.R.Chapman, and G.L.Schwebke, J. Organometal.Chem., 1968, **14**, 267.
214. H.Watanabe, T.Muraoka, M.Kageyama, and Y.Nagai, J.Organometal.Chem., 1981, **216**, C45.
215. H.Watanabe, J.Inose, K.Fukushima, Y.Kougo, and Y.Nagai, Chem.Letters, 1983, 1711.
216. W.Fink, Helv.Chim.Acta, 1963, **46**, 720.
217. D.Seyferth and D.P.Duncan, J.Organometal.Chem., 1976, **111**, C21.
218. M.Ishikawa, H.Sugisawa, M.Kumada, T.Higuchi, K.Matsui, K.Hirotsu, and J.Iyoda, Organometallics, 1983, **2**, 174.
219. A.Schaefer, M.Weidenbruch, K.Peters, and H.Von Schnering, Angew.Chem., 1984, **96**, 311.
220. M.Weidenbruch and A.Schaefer, J.Organometal. Chem., 1984, **269**, 231.
221. P.R.Boudjouk and R.Sooriyakumaran, Chem.Communs, 1984, 777.
222. D.N.Roark and G.J.D.Peddle, J.Amer.Chem.Soc., 1972, **94**, 5837.
223. L.E.Gusel'nikov and N.S.Nametkin, Chem.Rev., 1979, **79**, 529.
224. R.T.Conlin and P.P.Gaspar, J.Amer.Chem.Soc., 1976, **98**, 868.
225. Y.Nakadaira, T.Kobayashi, T.Otsuka, and H.Sakurai, J.Amer.Chem.Soc., 1979, **101**, 486.
226. H.Sakurai, H.Sakaba, and Y.Nakadaira, J.Amer. Chem.Soc., 1982, **104**, 6156.
227. H.Sakurai, Y.Nakadaira, and H.Sakaba, Organometallics, 1983, **2**, 1484.
228. H.Sakurai, Y.Nakadaira, and T.Kobayashi, J.Amer. Chem.Soc., 1979, **101**, 487.
229. J.L.Margrave and D.L.Perry, Inorg.Chem., 1977, **16**, 1820.
230. W.F.Reynolds, J.C.Thompson, and A.P.G.Wright, Canad.J.Chem., 1980, **58**, 419.
231. Y.-M.Pai, C.-K.Chen, and C.-S.Liu, J.Organometal. Chem., 1982, **226**, 21.
232. Y.Nakadaira, T.Otsuka, and H.Sakurai, Tetrahedron Letters, 1981, **22**, 2417.
233. A.Marchand, P.Gerval, F.Duboudin, M.-H.Gaufryan, M.Joanny, and P.Mazerolles, J.Organometal.Chem., 1984, **267**, 93.
234. Y.S.Chen and P.P.Gaspar, Organometallics, 1982, **1**, 1410.
235. H.Matsumoto, T.Arai, H.Watanabe, and Y.Nagai, Chem.Communs, 1984, 724.
236. T.J.Barton and J.A.Kilgour, J.Amer.Chem.Soc., 1976, **98**, 7231.
237. M.J.Michalczyk, R.C.West, and J.Michl, Chem. Communs, 1984, 1525.
238. M.J.Michalczyk, R.C.West, and J.Michl, J.Amer. Chem.Soc., 1984, **106**, 821.
239. M.J.Fink, K.J.Haller, R.C.West, and J.Michl, J.Amer.Chem.Soc., 1984, **106**, 822.
240. M.J.Fink, M.J.Michalczyk, K.J.Haller, R.C.West, and J.Michl, Organometallics, 1984, **3**, 793.
241. R.C.West, Pure Appl.Chem., 1984, **56**, 1, 163.
242. R.C.West, Science, 1984, **225**, 1109.
243. R.C.West, M.J.Fink, M.J.Michalczyk, D.J.De Young, and J.Michl, in "Organosilicon and Bioorganosilicon Chemistry: Structure, Bonding, Reactivity and Synthetic Application" (Edited by H.Sakurai), Wiley, New York, 1985, p.3.
244. S.Murakami, S.Collins, and S.Masamune, Tetrahedron Letters, 1984, **25**, 2131.
245. M.Weidenbruch, K.Kramer, A.Schaefer, and J.K.Blum, Chem.Ber., 1985, **118**, 107.
246. A.Schaefer, M.Weidenbruch, and S.Pohl, J.Organometal.Chem., 1985, **282**, 305.
247. M.Weidenbruch, K.Kramer, K.Peters, and H.Von Schnering, Z.Naturforsch., 1985, **40b**, 601.
248. A.H.Cowley, Polyhedron, 1984, **3**, 389.

Institute of Chemistry,
Academy of Sciences of the
USSR, Gor'kii