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Halogen Derivatives of Alkyl(or aryl)halogenosilanes and Tetrasubstituted Silanes

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In recent years there have been many investigations in the field of organosilicon compounds containing halogen-substituted organic groups. These investigations offer prospects of the use of these compounds in the synthesis of polyorganosiloxanes. The extensive data on methods of synthesis of halogen derivatives of alkyl(or aryl)halogenosilanes and tetrasubstituted silanes, their properties, and use are scattered in many periodicals. Monographs and review articles have so far examined only isolated aspects of the chemistry of organosilicon compounds[1-4]. This has stimulated us to survey the accumulated experimental results, the analysis of which even now allows definite regularities to be found in the occurrence of certain reactions and processes in the synthesis and conversions of halogen derivatives of organosilicon compounds. There is a bibliography of 677 references.

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I. METHODS OF SYNTHESIS

1. Halogenation of Alkyl(or aryl)halogenosilanes and Tetrasubstituted Silanes

When halogens act on organosilicon compounds two reactions are possible: (1) detachment of an alkyl or aryl group from a silicon atom, for example, in the bromination of tetraphenylsilane[5,6]:

$$(C_6H_5)_4Si + Br_2 \rightarrow (C_6H_5)_3SiBr + C_6H_5Br,$$

or in the halogenation of a trialkylhalogenosilane[7]:

$$R_3SiX + X'_2 \rightarrow R_2SiXX' + RX',$$

where R = alkyl, and X and X′ are halogens.

Depending on the halogen attached to the silicon in the alkylhalogenosilane(X), the rate of this reaction increases in the order Br < Cl < F < I. (2) Halogenation of the alkyl and aryl groups of the organosilicon compound, for example, in the chlorination of triethylphenylsilane[8]:

$$(C_2H_5)_3Si-C_6H_4 + Cl_2 \rightarrow (C_2H_5)_3Si-C_6H_4-Cl + HCl$$

In practice both reactions usually occur simultaneously. The predominating direction of the reaction depends on the conditions under which the process is carried out, and also the catalyst type.

a. Halogenation of alkylhalogenosilanes and tetra-alkylsilanes. The first studies of the chlorination of alkylchlorosilanes and tetrasubstituted alkylsilanes date back to 1945[9].

The chlorination of alkylchlorosilanes and tetra-alkylsilanes can be brought about by the action of chlorine in the liquid or the gaseous phase or by the action of sulphuryl chloride. The photochemical chlorination of methylchlorosilanes, depending on their structure, takes place at different rates, and leads to the formation of chloro(chloromethyl)silanes with different degrees of substitution[10-12].

In liquid-phase chlorination of chlorotrimethylsilane in the presence of azobisisobutyronitrile the composition of the reaction products depends mainly on the ratio of $(CH_3)_3SiCl$ to Cl_2. With increase in this ratio the proportion of polychloro-substituted derivatives diminishes and the yield of $CH_2ClSi(CH_3)_2Cl$ increases[13]. When $(CH_3)_3SiCl : Cl_2 = 1 : 4.15$ the chlorination proceeds with the formation of appreciable quantities of $CH_3.SiCl.(CH_2Cl)_2$ [14] and also of tri- and tetra-substituted derivatives[15]. Further chlorination in CCl_4 leads to the formation of chlorotris(trichloromethyl)silane in 50% yield.

Dichlorodimethylsilane and trichloro(methyl)silane are chlorinated with greater difficulty than chlorotrimethylsilane. It was found[14-19] that the replacement of one methyl radical in chlorotrimethylsilane by a chlorine atom reduces the rate of chlorination by a factor of nine. Unlike chlorotrimethylsilane, in the chlorination of dichlorodimethylsilane by chlorine the hydrogen atoms of a single methyl group are replaced successively[14,16]. Increasing the reaction temperature from 0° to 24.4°C increases the rate of the process three times, but the ratio between the rates of chlorination of $CH_2ClSiCl_3$ and CH_3SiCl_3 is retained. In chlorination by gaseous chlorine at 60°C in the presence of azobisisobutyronitrile, dichlorobis(trichloromethyl)silane is formed in 40–50% yield[17]. The reaction is accompanied by the formation of CCl_4 and CCl_3SiCl_3 as side-products[18]. The chlorination of $CH_3(CCl_3)SiCl_2$ under analogous conditions leads to the formation of $(CCl_3)_2SiCl_2$ in ~ 60% yield. In the liquid-phase photochemical chlorination of trichloro(methyl)silane CCl_3SiCl_3 is formed predominantly[20-23].

The considerable difference in the rates of chlorination of the methyl and chloromethyl groups connected with a silicon atom hinders the production of trichloro(chloromethyl)silane, which is usually obtained by carrying out the reaction with a great excess of trichloro(methyl)silane[24] or by continuously removing the trichloro(chloromethyl)-silane from the reaction zone[25-33]. The chlorination by this method of trichloro(methyl)silane, dichlorodimethylsilane, chlorotrimethylsilane, and tetramethylsilane gives the corresponding monochloro-derivatives in good yields[16,28,34,35].

The use of azobisisobutyronitrile as initiator in the chlorination of chlorotrimethylsilane, unlike the initiation by ultraviolet light, allows $CH_2ClSiCl_3$ to be obtained even in conditions which do not provide for the removal of the chlorination product from the reaction zone[36], which shows

that the nature of the initiator has a significant effect on the chlorination.

In the liquid-phase chlorination of trichloro(methyl)silane and of dichlorodimethylsilane, acetylcyclohexylsulphonyl peroxide is a better initiator for the process than azobisisobutyronitrile[37] but the use of the former helps to increase the yield of polychloro-derivatives.

Tetramethylsilane is readily chlorinated in liquid-phase chlorination[38], just as is neopentane[7]. Here, as for chlorotrimethylsilane, the introduction of a second chlorine atom into the molecule leads to the formation of $(CH_3)_2Si(CH_2Cl)_2$.[39] In the photochemical chlorination of trichloro(methoxy)silane[40,41], a mixture of $CH_2ClOSiCl_3$ and CCl_3OSiCl_3 is formed[42].

With fluorine as the initiator, the chlorination of chloro(methyl)silanes takes place in the dark[43,44]. $CH_2Cl.SiCl_2.CH_3$ was obtained in 50.2% yield from dichlorodimethylsilane by this method, and $(CH_3)_2SiCl.CH_2Cl$ (40.9%) and $(CH_3)_2SiCl.CHCl_2$ (3.8%) from the chlorination of chlorotrimethylsilane. The chlorination of trichloro(methyl)silane under the action of γ-radiation takes place at a high rate[45,46]. The chlorination of poly(dimethylsiloxane) rubber at 0°C under the action of γ-radiation (^{60}Co source) proceeds readily up to the introduction of an average of two chlorine atoms in the polymer unit, after which the rate of the process drops sharply[47]. The chlorination of poly(dimethylsiloxane) rubber by elemental chlorine in CCl_4 in the presence of azobisisobutyronitrile is slow and accompanied by decomposition with formation of difficultly soluble polymers[48].

$(CH_3)_3Si.SiCl.(CH_3)_2$ (25%) and $[CH_2Cl(CH_3)_2Si]_2$ (5.0%) are obtained in the chlorination of hexamethyldisilane[49].

Under the action of chlorine, especially on prolonged chlorination, methylsiloxanes decompose with rupture of the siloxane bond[30,50-55], owing to the hydrogen chloride which is formed.

When the reaction is carried out under mild conditions and the chlorination products are removed continuously from the sphere of the reaction, breaking of the Si–O–Si bonds can be avoided. For example, in the chlorination of octamethylcyclotetrasiloxane[30,56-58] chloromethylheptamethylcyclotetrasiloxane is obtained; more extensive chlorination in the presence of azobisisobutyronitrile leads to the formation of a difficultly separable mixture of chloro-substituted derivatives[59].

On initiation with ultraviolet light tetraethylsilane is chlorinated with the formation of monochloro- and dichloro-derivatives; the reaction is accelerated by phosphorus(V) chloride[60-62].

The photochemical chlorination of chloro(ethyl)silanes with removal of the chlorination products from the reaction zone allows the trichloro-(1-chloroethyl)- and trichloro-(2)-chloroethyl)-silanes to be obtained in 1 : 1.6 ratio[63-68]. The vapour-phase chlorination of trichloro(ethyl)silane at 350°C leads to the formation of 1- and 2-chloroethyl derivatives[69] in the ratio 1 : 1.08. In the chlorination of dichloro(ethyl)methylsilane under ultraviolet irradiation dichloro(chloromethyl)ethylsilane is formed predominantly[70]. When the reaction is carried out with illumination from a 150 W electric lamp (16–21°C) dichloro-(1-chloroethyl) methylsilane can be obtained in 38% yield on the dichloro(ethyl)methylsilane which has reacted. $CF_2HCF_2SiCl_3$ is chlorinated at 150–200°C with the formation of $CF_2ClCF_2SiCl_3$.[71]

The chlorination of trichloro(propyl)silane leads to the formation of α-, β-, and γ-chloro-derivatives in the ratio 0.7 : 1 : 1.[31] Trichloro-(isopropyl)silane is chlorinated with preferential formation of trichloro-(2-chloro-1-methylethyl)silane[72]. A necessary condition for obtaining the monochloro-derivatives in the chlorination of the trichloro-(propyl)silanes is the removal of the chlorination products from the reaction zone[73-76].

In the chlorination of $CF_3CH_2CH_2SiCl_3$ under the action of ultraviolet radiation[77] the C–H bond in the α-position is 6.2 times more susceptible to attack by chlorine than that in β-position. At the ratio $Cl_2 : CF_3CH_2CH_2SiCl_3 = 1.5$ and 25–100°C, 80% $CF_3CH_2CHClSiCl_3$ and 20% $CF_3CHClCH_2SiCl_3$; $CF_3CH_2CCl_2SiCl_3$ is formed as an impurity. The predominant formation of the α-chloro-derivatives also occurs in the chlorination of $CF_3CH_2CH_2Si(CH_3)Cl_2$.[78] Consequently the CF_3 group acts more strongly than the dichloro(methyl)-silyl and trichlorosilyl groups as β-orienting agents.

Trichloro(vinyl)silane is chlorinated differently depending on the temperature: at 200–350°C substitution occurs with the formation of $CH_2=CClSiCl_3$; at 160–200°C chlorine adds at the double bond with the formation of $CH_2ClCHClSiCl_3$.[79] Trichloro(methylallyl)silane is chlorinated with replacement of hydrogen in the methyl group even at room temperature[80,81]:

$$Cl_3SiCH_2C(CH_3)=CH_2 \xrightarrow{Cl_2} Cl_3SiCH_2C(CH_2Cl)=CH_2 .$$

Substitutional chlorination also takes place with trichloro(isocrotyl)silane[82]; however, the addition of chlorine in the chlorination of alkenyl- and (alkenyl)alkylchlorosilanes is the main reaction[21,23,74,79,83-86].

A series of studies was devoted to the chlorination of hexachlorodisilylmethane[31,37], hexachlorodisilylethane[31,88], and other compounds of this type[39,89,90]. In the photochlorination of 1,1,3,3,5,5,7,7-octachloro-1,3,5,7-tetrasilacyclo-octane[91] 1,1,2,2,3,3,4,5,5,6,7,7,8-tridecachloro-1,3,5,7-tetrasilacyclo-octane is formed.

Chlorocyanoalkyl-substituted silanes of the general formula

$$[NC(CH_{2-a}Cl_a)_b]_n SiR_mX_{4-m-n}$$

where $a = 1$ or 2, $b = 2$–12, $n = 1$–3, $m = 0$–2, and X = Cl or F, are obtained by chlorination with elemental chlorine at 20–80°C and ultraviolet irradiation of the corresponding cyanoalkyl-substituted halogenosilanes[92].

Chlorination of alkylchlorosilanes and alkyl-substituted esters of orthosilicic acid by sulphuryl chloride takes place on heating in the presence of benzoyl peroxide[93-95].

Sulphuryl chloride is a less active chlorinating agent, therefore it is recommended for the chlorination of chloro(methyl)silanes when the formation of polychloro-derivatives must be avoided[96].

In the chlorination by sulphuryl chloride of chlorotrimethylsilane in the presence of peroxide in chlorobenzene as medium chloro(chloromethyl)dimethylsilane is formed[97,98]. Trichloro(methyl)silane in a medium of *o*-dichlorobenzene at 80°C is chlorinated by sulphuryl chloride to trichloro(chloromethyl)silane, but its yield is only ~ 2.6%[23].

Under ultraviolet irradiation dichlorodimethylsilane reacts with sulphuryl chloride with great difficulty, giving a small quantity of dichloro(chloromethyl)methylsilane[99].

Owing to their higher boiling points chloro(ethyl)silanes are readily chlorinated by sulphuryl chloride in the absence of solvents; 1- and 2-chloroethylchlorosilanes are formed as a result[21,93,100]. The ethyl group is chlorinated more easily than the methyl group. Thus in the chlorination by sulphuryl chloride of dichloro(ethyl)methyl silane the main products are dichloro-(1-chloroethyl)methylsilane and dichloro-(2-chloroethyl)methylsilane[101]. Tetraethylsilane forms 1-chloroethyl derivatives[28,63,102,103]; in the chlorination of trichloro(ethyl)silane, dichlorodiethylsilane, and

chlorotriethylsilane, mixtures of chloro-(1- and 2-chloroethyl)silanes are formed[93,100,104]. The yield of the 2-isomers increases with the increase in the number of chlorine atoms at the silicon[64].

Chlorination of trichloro(propyl)silane by sulphuryl chloride leads to the formation of the 1-, 2-, and 3-isomers[108] in the ratio 1 : 3.5 : 3.1; trichloro(isopropyl)silanes give a mixture of the 1- and 2- isomers[106] in the ratio 1 : 3.5. Trichloro-(t-butyl)silane forms $CH_2Cl(CH_3)_2C.SiCl_3$ on chlorination[107]. Hexamethyldisilane is chlorinated by sulphuryl chloride to chloromethylpentamethyldisilane[108].

Organosilicon alcohols, can be easily converted into the corresponding halogen derivatives with hydrogen halides[109-111,113], thionyl chloride[112-115], phosphorus(III) bromide[116-119], etc.

Sulphuryl chloride readily chlorinates bis(trichlorosilyl)-methane and bistrichlorosilylethane[31] and also cyclocarbosilanes containing chlorine atoms[120,121] and methyl groups[122] at the silicon.

t-Butyl hypochlorite is also used as a chlorinating agent in the chlorination of alkyl-substituted organosilicon compounds[123,124].

Tetrasubstituted silanes are brominated directly by bromine[125-127] and by bromosuccinimide[128-130]. In the bromination of tetraethylsilane $(C_2H_5)_3SiCHBrCH_3$ and $(C_2H_5)_3SiCBr_2CH_3$[25,28-33] are formed[134]. Chloro(methyl)-silanes and tetramethylsilanes have been brominated by ultraviolet irradiation and the simultaneous passage of bromine and chlorine[135]. Bromination of chloro(ethyl)silanes in this way gives a mixture of 1- and 2-bromoethylsilanes[136,137]. Under these conditions hexamethyldisiloxane forms bromomethylpentamethyldisiloxane[138]. Trichloro-(2-cyanoethyl)silane is brominated with formation of bromocyanoethyltrichlorosilane[139]. The bromination of 1,1,2-triphenyl-1-silacyclobutane with *N*-bromosuccinimide leads to the formation of 2-bromo-1,1,2-triphenyl-1-silacyclobutane[140].

When bromine acts on unsaturated alkenylchlorosilanes and alkenylalkylsilanes addition of bromine at a multiple bond takes place[71,141-143].

b. Halogenation of arylhalogenosilanes, arylalkylhalogenosilanes, and tetra-aryl (or arylalkyl)-substituted silanes. Ladenburg carried out the direct chlorination of triethoxy(phenyl)-silane[144] but an intensive study of this process began in the 1940's after the appearance of a patent[145] on the chlorination of dichlorodiphenylsilane and dichloro(methyl)phenylsilane.

The chlorination of the aromatic nuclei of organosilicon compounds takes place in the presence of catalysts: metallic iron, iodine, phosphorus(V) chloride, antimony(III) chloride, or aluminium chloride, and is initiated by ultraviolet light[146].

There have been many studies of the chlorination of trichloro(phenyl)silane[147-159]; in these investigations the production of trichlorochlorophenylsilanes of all degrees of substitution of chlorine for hydrogen in the phenyl group under various conditions was investigated using radical catalysts.

The chlorination of chloro(phenyl)silanes in the presence of iodine and phosphorus(V) chloride takes place at 110–140°C without splitting of the chlorination products, but the catalytic activity of these substances is low. They can therefore be used for obtaining monochloro-derivatives of trichloro(phenyl)silane and dichlorodiphenylsilane. ICl and ICl_3 react with trichloro(phenyl)silane at low temperature (–40°C) with the formation of $C_6H_5 - nCl_nSiCl_3$ ($n = 1$ or 2), the main reaction product being trichloro-(*m*-chlorophenyl)silane[160]. The reaction of $Cl_2C_6H_3SiCl_3$ with ICl_3 at 20°C leads to $Cl_3C_6H_2SiCl_3$. Photochemical chlorination of trichloro(phenyl)silane in the presence of iodine at 20°C leads to the formation of a product of incompletely additive chlorination[161] $C_6H_5Cl_4SiCl_3$.

The splitting of the Si–C bond in the presence of catalysts increases with the chlorination temperature; it can be reduced to a minimum by carrying out the reaction under milder conditions (for example, at 20–30°C in a medium of carbon tetrachloride or some other solvent which is inert in relation to chlorine). When aluminium chloride or iron(III) chloride is used as catalyst splitting of the reaction products takes place even at 30°C—at the very start of chlorination. In the presence of antimony(III) chloride this process is observed in more extensive chlorination and at higher temperatures[162].

In the chlorination of dichlorodiphenylsilane at 70–80°C in the presence of antimony(V) chloride the process takes place with considerable evolution of heat; the main product of the reaction is dichlorobistrichlorophenylsilane. Dichlorobispentachlorophenylsilane can be obtained by further chlorination at 120°C but then the splitting of the Si–C bond can be considerably intensified.

Chlorination at 100°C and over without catalysts or chlorination with irradiation of the reaction mixture with ultraviolet light at 70°C does not bring about splitting of the Si–C bond in trichloro(phenyl)silane or dichlorodiphenylsilane.

Temperature has a considerable influence on the nature of the chlorination of trichloro(phenyl)silane in light (there is no reaction in the dark) and in ultraviolet radiation[158,161,163]. At 0–2°C addition of chlorine occurs, at 95–100°C as well as the addition there is replacement of hydrogen atoms of the phenyl group by chlorine; at 125–150°C the reaction is more vigorous than in the presence of azobisisobutyronitrile.

Depending on the chlorination conditions, the $SiCl_3$ group exhibits a different orienting effect. In chlorinating trichloro(phenyl)silane in the presence of iron a mixture of *m*-, *p*-, and *o*-chlorophenyltrichlorosilanes in the ratio 74 : 2 : 24 is formed[150], but in the chlorination of trifluoro-(phenyl)silane the ratio is 82 : 0 : 18[164]. This shows that the trichlorosilyl and trifluorosilyl groups orient the replacement of hydrogen of the benzene nucleus by chlorine, mainly in the *meta*-position. Chlorination of trimethyl-(phenyl)silane gives a mixture of the *o*-, *p*-, and *m*-chlorophenyltrimethylsilanes in the ratio 24 : 25 : 51[164].

In the electrophilic chlorination of trichloro(phenyl)-silane in the presence of $FeCl_3$ and $AlCl_3$ and $SiCl_3$ group is also a *meta*-orientant; 28% of the *ortho*-isomer is formed[159].

In the photochemical chlorination of trichloro(phenyl)-silane at 120–150°C in the presence of azobisisobutyronitrile 43% *o*-$ClC_6H_4SiCl_3$ is formed. When iodine is used as catalyst (whether with illumination or in the dark) at 20°C 67% trichloro-*o*-chlorophenylsilane and $C_6H_5Cl_4SiCl_3$ is formed.

The polymers which contain phenyl groups at silicon atoms are converted during chlorination into the corresponding polymers with chlorophenyl groups[165].

It should be noted that the distribution of chlorine between the phenyl groups in the fractions is irregular: the degree of chlorination increases with decrease in the molecular weight of the fraction.

The chlorination of *p*-chlorophenyltrichlorosilane, trifluoro(phenyl)silane[164] and tetraphenylsilane[166] is effected

in the presence of $FeCl_3$ and $SbCl_5$ as catalysts in CCl_4 medium to decrease cleavage of the Si–C bond.

When there are alkyl substituents at the phenyl group they are the first to be chlorinated. In the chlorination of trichloro-*p*-tolylsilane, trichloro-*p*-trichloromethylphenylsilane is obtained[167,168]; when the process is carried out with ultraviolet irradiation trichloro-*p*-trichloromethylphenylsilane can be obtained in 92% yield. Trichloro-*o*-tolylsilane under these conditions is not chlorinated, owing to steric hindrance by the $SiCl_3$ group[168], whereas trifluoro-*o*-tolylsilane is chlorinated readily.

The chlorination of trichloro(ethyl)phenylsilanes lead to the production of $C_2H_5 - {}_nCl_nC_6H_4SiCl_3$ [169] and p-$CH_2ClCH_2 . C_6H_5SiCl_3$ [170,171]. Trichloro(p-ethylphenyl)silane is readily chlorinated on illumination with two luminescent lamps; the p-$C_2H_4ClC_6H_4SiCl_3$ which is formed is used to obtain p-$CH_2{=}CHC_6H_4SiCl_3$.[170,172–174].

Compounds in which the phenyl groups are connected with silicon by methylene links are readily chlorinated by sulphuryl chloride[175]:

$$C_6H_5CH_2SiCl_3 \xrightarrow{SOCl_2} C_6H_5CH_{2-n}Cl_nSiCl_3.$$

A series of compounds of this type was obtained by this reaction, for example, $C_6H_5CHClSi(CH_3)_3$, and $(C_6H_5)_2 . CClSi(CH_3)_3$ [93,176–178] and also chloro-substituted benzyltrichlorosilane and trichloro-(-p-xylenyl)silane[176].

The direction of the chlorination of dichloro(methyl)phenylsilane is determined by the conditions. The use as catalysts of $FeCl_3$ and $SbCl_5$,[180] $SbCl_3$ at 10–15 °C, and also iodine (the reaction being carried out in CCl_4 or without a solvent)[181] leads to substitution of chlorine for hydrogen atoms in the phenyl groups; chlorination of the methyl groups does not take place under these conditions, but the reaction is accompanied by splitting of the Si–C_{aryl} bond, the splitting proceeding more readily than with dichlorodiphenylsilane. The CH_3SiCl_2 group, like the $SiCl_3$ group, orients the replacement of hydrogen in the benzene nucleus by chlorine mainly into the *meta*-position.

In the presence of azobisisobutyronitrile the chlorination of dichloro(methyl)phenylsilane takes place with the chlorine replacing hydrogen atoms in the methyl group; the product of exhaustive chlorination at 110–115 °C is $C_6H_5(CCl_3)SiCl_2$.[182,183]

In the photochemical chlorination of dichloro(methyl)phenylsilane at 20–25 °C in addition to the substitution of chlorine for the hydrogen atoms in the methyl groups[163] addition of chlorine to the phenyl group takes place[184].

The chlorination of dichloro(methyl)phenylsilane in diffuse daylight proceeds in different directions depending on the temperature of the reaction. At 0–5 °C the only reaction is addition of chlorine to the phenyl group with the formation of dichloro(methyl)(hexachlorocyclohexyl)silane in 78.4% yield[185]; raising the temperature of the reaction to 20–25 °C leads to a decrease in the yield of $C_6H_5Cl_6(CH_3) . SiCl_2$ to 46% owing to the formation of dichloro(dichlorophenyl)methylsilane (19.6%)[163,186]. With a further rise in the chlorination temperature the substitution reaction rate increases and at 50–55 °C replacement of hydrogen by chlorine in the phenyl group takes place exclusively[187], with the formation of $C_6H_5 - {}_nCl_n(CH_3)SiCl_2$ (n = 2 or 3); the CH_3SiCl_2 group is a *meta*-orientant here.

Unlike dichloro(methyl)phenylsilane, dichloro(phenyl)(trichloromethyl)silane does not react with chlorine in diffuse daylight at 110–115 °C in the absence of initiating and catalysing additions[188]. On raising the temperature to 150 °C the Si–C_{aryl} bond is broken. In the presence of $SbCl_3$ or iodine, $C_6H_5 - {}_nCl_n(CCl_3)SiCl_2$ is formed (n = 1–3). Like $SiCl_3$, the CCl_3SiCl_2 group directs the chlorine atom entering the phenyl nucleus mainly into the *meta*-position.

$C_6H_4Cl_6(CCl_3)SiCl_2$ is formed in the photochemical chlorination of $C_6H_5(CCl_3)SiCl_2$ at 20–25 °C. Analogous results are given by azobisisobutyronitrile as initiator. The increased stability of $C_6H_5(CCl_3)SiCl_2$ in comparison with $C_6H_5(CH_3)SiCl_2$ in electrophilic and radical chlorinations is explained by the increaee in the electrophilic nature of the silicon atom in $C_6H_5(CCl_3)SiCl_2$ owing to replacement of the electron-donating methyl group by the electron-accepting trichloromethyl group.

In the chlorination of (p-$CH_3C_6H_4$)CH_3SiCl_2 in the presence of azobisisobutyronitrile at 110–115 °C by chlorine the hydrogen in the methyl group of the aromatic nucleus is replaced first[189]. Trichloromethyltriphenylsilane is formed in the chlorination of methyltriphenylsilane[190].

The chlorination of dichloro(methyl)phenylsilane with the aid of sulphuryl chloride in the presence of radical catalysts takes place with substitution of chlorine for the hydrogen atoms in the methyl groups[191]; the main product of the reaction when the process is carried out in the presence of azobisisobutyronitrile is $C_6H_5(CHCl_2)SiCl_2$.

The chlorination of dichloro(methyl)phenylsilane under the action of radiation (^{60}Co) leads to the formation of $C_6H_2Cl_3(CCl_3)SiCl_2$.[47] In the chlorination of polyphenylmethylsiloxanes under these conditions, in addition to substitution additive chlorination in the phenyl nucleus also takes place under these conditions[47,192].

The production of bromoarylchlorosilanes by the direct bromination of aryltrichlorosilanes and diaryldichlorosilanes is accompanied by cleavage of the Si–C bond. This reaction is especially prominent in the synthesis of the polybromophenylchlorosilanes.

Bromophenyltrichlorosilane was obtained in 40% yield by the simultaneous action of bromine and chlorine on trichloro(phenyl)silane with irradiation by ultraviolet light[135,193]. The bromination of trifluoro(phenyl)silane in the presence of iron gives pronounced splitting of the Si–C bond; the yield of bromophenyltrifluorosilane is only 3.5%.

Of the other aromatic chlorosilanes there have been studies of the bromination of benzyltrichlorosilane[194], trichloro-(p-tolyl)silane[195], and tetra-(p-tolyl)silane[196]. It was found that the $-(CH_2)_nSiCl_mR_{3-n-m}$ groups are strong *ortho*- and *para*-orienting agents and activate the benzene ring in electrophilic substitutions[197].

Benzyltrimethylsilane is brominated more readily than benzyltrichlorosilane[198]; on boiling a solution of it in CCl_4 with N-bromosuccinimide $C_6H_5CHBrSi(CH_3)_3$ and $C_6H_5CBr_2Si(CH_3)_3$ are formed[177]. In the bromination of $R_3SiCH(C_6H_5)_2$, $R_3SiC(C_6H_5)_2Br$ is obtained in yields up to 96%.[199] p-$CH_2BrC_6H_4Si(C_6H_5)_3$ is obtained by an analogous method[128]. o-$CH_2BrC_6H_4Si(C_6H_5)_2Br$ was obtained by the action of N-bromosuccinimide on o-$CH_3C_6H_4Si(C_6H_5)_2H$.[200] N-Bromosuccinimide readily brominates 2:3-benz-1-silacycloalkanes[201] to form 4-bromo-substituted derivatives.

The formation of p-bromobenzyltrifluorosilane in the bromination of benzyltrifluorosilane takes place without cleavage of the Si–C bond[164].

The bromination of dichloro(methyl)phenylsilane in the absence of a catalyst at 0°–25 °C leads to the production of $C_6H_5 - {}_nBr_n(CH_3)SiCl_2$ and is not accompanied by Si–C bond cleavage[202]. With catalysts (iodine, $SbCl_3$) at 10–15 °C the formation of these products is accompanied by Si–C_{aryl} bond cleavage. In both instances the CH_3SiCl_2 group is a *meta*-orientant.

In the bromination of $BrC_6H_4Si(CH_3)_3$ 92.5% trimethylbromosilane and 92.7% dibromobenzene are formed.

The bromination of arylsilanes containing acetamido-[203], dimethylamino-[204], and hydroxyl[205] groups in the phenyl

group and of 9-fluorenyltrimethylsilane[206] has also been studied.

2. Addition of a Triorgano(halogeno)silyl Group to Unsaturated Halogenohydrocarbons

The addition of a triorgano(halogeno)silyl group to unsaturated halogenohydrocarbons was first effected at the start of the 1950's[207,208].

The addition of silanes to halogeno-substituted ethylenes takes place with greater difficulty than to ethylene. Depending on the type and number of halogen atoms in the molecule, the halogen-substituted ethylenes can be arranged in the following series of decreasing reactivity in the presence of platinum catalysts[209-213]: $CH_2=CH_2 > CH_2=CF_2 > CF_2=CFCl > CF_2=CF_2$.

Dichloro(alkyl)silanes add with difficulty to tetrafluoroethylene in the presence of platinum or palladium on carriers[211,214,215], $H_2PtCl_6.6H_2O$,[211,213] and under the action of γ-radiation[216]. Better results are obtained on initiation with ozone[217-219]; the maximal yield of addition products occurs on initiation of the reaction with ultraviolet light[220-223]. Under these conditions SiH_4 adds to $CF_2=CF_2$ with the formation of tetrafluoroethylsilanes of all degrees of substitution[224].

Trichlorosilane adds more readily to halogenoethylenes, the initiation of the reaction with ultraviolet light also being most effective[225,226].

Radiochemical synthesis with γ-radiation can be effected only when the rate of polymerisation of the halogenoalkene is lower than that for the addition. The maximal yield of addition products occurs when the initial mixture of reagents contains 1 mole alkene per hydrogen atom of silane[216].

Alkenes of the general formula $RR'C=CR''R'''$ add silanes of the formula $SiH_{4-m-n}X_nZ_m$ (where X is halogen, Z alkyl, $n = 2$ or 3, $m = 0$ or 1, and R, R', R'', and R''' are H, alkyl or aryl, at least one group being electronegative) in the presence of catalytic amounts of tertiary amines[227]. The reaction takes place at 25–130°C and pressures of 3.5–17.5 atm.

The order of addition depends on the nature of the compounds reacting and the type of catalyst. In the presence of platinum catalysts silanes add to 1,1-difluoroethylene in such a way that the silyl group will be at the carbon atom of the methyl group:

$$CF_2=CH_2 + HSi\lessdot \rightarrow CF_2H-CH_2Si\lessdot .$$

The addition of trichlorosilane to chloroethylene in the presence of benzoyl peroxide proceeds in two directions[224]:

$$CH_2=CHCl + HSiCl_3 \xrightarrow{(C_6H_5COO)_2} \begin{cases} \rightarrow ClCH_2CH_2SiCl_3 \\ \rightarrow CH_3CHClSiCl_3. \end{cases}$$

The order of addition of trichlorosilane to chlorotrifluoroethylene has not been established: some investigators[214,215,228] think that the silyl group adds to the CFCl group; others[225,226], to the CF_2 group.

Silanes react more difficultly with perfluoropropene than with perfluoroethylene[226]. When the double bond is not screened by fluorine atoms the addition proceeds much more readily, although with somewhat greater difficulty than with propene. For example, silanes add to trifluoropropene under the influence of ultraviolet radiation[226,229-231], peroxides[226], platinum on carbon[228,232,233], and $H_2PtCl_6.6H_2O$.[234-236].

In the presence of hydrogen hexachloroplatinate(IV) $HSiCl_3$ adds to $(CF_3)_2C=CH_2$:[237]

$$(CF_3)_2C=CH_2 + HSiCl_3 \rightarrow (CF_3)_2CHCH_2SiCl_3.$$

In the presence of radical initiators dichlorosilane adds to fluorinated alkenes with the formation of compounds of the general formula:

$$(RCF_2CHR'CH_2)_2SiCl_2,$$

where R = H, F or a perfluoroalkyl group, R' = H, CH_3, CF_3, C_2H_5, or C_3F_7.[238]

Difluoropropene $CHF_2CH=CH_2$ adds to organohydrochlorosilanes more readily than $CF_3CH=CH_2$.[239]

$CF_3CF_2CH=CH_2$ [230,240-242] and $CF_3CF_2CF_2CH=CH_2$ [228,229,232,240] react readily with silanes; $CF_3CF_2CF=CH_2$ [226] reacts with greater difficulty. In the presence of hydrogen hexachloroplatinate(IV) compounds of the formulae $HSiCl_3$, $RSiHCl_2$, and R_3SiH add to 3,4-dichlorobut-1-ene exclusively according to Farmer's rule; addition to 1,4-dichlorobut-2-ene is accompanied by the formation of anomalous reaction products[243].

The addition of silanes to allyl chloride proceeds readily under the action of ultraviolet light and peroxides[244], platinum on carriers[245], and complexes of $PtCl_2$.[246] As well as the additions, reduction of the allyl chloride by the silane occurs[247]:

$$CH_2=CHCH_2Cl + HSi\lessdot \rightarrow \gtrdot SiCl + CH_3=CHCH_3.$$

Dichloro(methyl)silane reacts with allyl bromide in the presence of hydrogen hexachloroplatinate(VI) to form $BrCH_2CH_2CH_2Si(CH_3)Cl_2$;[248,249] the reaction is more difficult than that with allyl chloride.

The addition of silanes to methylallylchloride in the presence of platinum on carriers[214,250,251] or $H_2PtCl_6.6H_2O$ [248-252] proceeds with higher yields than for allyl chloride.

The removal of electronegative groups or atoms from the double bond favours an increase in the reactivity of halogenoalkenes in additions[214].

Trichlorosilane adds to *m*- and *p*-$ClC_6H_4CH_2CH_2CH=CH_2$ with the formation of $ClC_6H_4[CH_2]_4SiCl_3$ with $ClC_6H_4CH.(SiCl_3)[CH_2]_3CH_3$ as impurity; the *o*-chloro-substituted addition of trichlorosilane with the formation of only $ClC_6H_4[CH_2]_4SiCl_3$.[253]

The addition of trichlorosilane and dichloro(methyl)-silane to the chlorobutenes in the presence of platinum is accompanied by allyl rearrangement, loss of chlorine in the allyl position, and migration of a double bond[254].

Compounds with a triple bond react with silanes to form alkenylhalogenosilanes. Trichloro-(1,2-dichlorovinyl)silane was obtained in this way[255,256]:

$$ClC \equiv CCl + HSiCl_3 \rightarrow CHCl = CClSiCl_3.$$

This reaction is accelerated in the presence of peroxides, on irradiation with ultraviolet light, or on heating to a temperature close to the decomposition temperature of dichloroacetylene.

In the presence of $H_2PtCl_6.6H_2O$, $RSiHCl_2$ (R = Cl or CH_3) adds vigorously to $CH_2ClC\equiv CH$ with the formation of various amounts of $RCl_2SiCH=CHCH_2Cl$ and $RCl_2SiC(=CH_2)CH_2.Cl$.[257] The reaction with $HC\equiv CCH_2Br$ takes place in a similar manner[258]. 1,4-Dichlorobutyne reacts with $HSiR_xCl_{3-x}$ according to the scheme[243]:

$$CH_2ClC\equiv CCH_2Cl + HSi\lessdot \rightarrow \gtrdot SiC(CH_2Cl)=CHCH_2Cl.$$

Triorganosilanes add to $CX_3CH(OH)OC(CH_3)(CR_3)C{\equiv}CH$ according to the Farmer rule with the formation of

$$CX_3CH(OH)OC(CH_3)(CR_3)CH{=}CHSiR'_3,$$

where R = H or CH_3, X = Cl or Br, R = CH_3, C_2H_5, or C_3H_7.[259]

In reaction with 1,1,2,2-tetrafluoroethylallyl ether[210, 212, 260-262] in the presence of platinum catalysts the alkylhalogenosilanes can be arranged in order of decreasing activity:

$$R_3SiH > R_2SiHCl > RSiHCl_2 > HSiCl_3.$$

Aryldichlorosilanes add most easily to this ether[263].

The addition of R_nSiHX_{3-n} (R = CH_3, C_2H_5; $n \neq 0, 1, 3$; X = halogen) to vinyl ethers of the $R'OCH{=}CH_2$ type (R' = p-ClC_6H_4, 2,4-$Cl_2C_6H_3$), leading to the formation of $R'OCH_2CH_2SiR_nX_{3-n}$, which is accompanied by β-decomposition, which leads to the production of $R'OSiR_nX_{3-n}$.[264]

The direction of the addition of silanes to unsaturated halogenohydrins depends on the position of the double bond relative to the halogen-bound carbon atom[265,266].

In the presence of hydrogen hexachloroplatinate(IV), $HSiCl_3$, CH_3SiHCl_2, and $HSi(OC_2H_5)_3$ adds to 2-chloromethylbicyclo[2,2,1]hept-5-ene,[267]

3. Addition of Halogens to Multiple Bonds of Alkenylsilanes

The addition of halogens proceeds readily to almost any organosilicon compound containing a multiple bond. When the organosilicon compound has at the silicon atom a vinyl group or another group with a double bond in the α-position, then $\alpha\beta$-alkyldihalogenosilanes are formed, which are rather stable thermally:

$$R_3SiCH{=}CH_2 + X_2 \rightarrow R_3SiCHXCH_2X,$$

where X = halogen. When the double bond is in the β-position to the silicon atom then $\beta\gamma$-dihalogenoalkylsilanes are formed in the reaction with the halogens; these are thermally unstable and undergo the so-called β-decomposition[268]:

$$R_3SiCH_2CH{=}CH_2 + X_2 \rightarrow R_3SiCH_2CHXCH_2X \rightarrow R_3SiX + CH_2XCH{=}CH_2.$$

$\beta\beta$-Difluoroalkyl-substituted organosilicon compounds readily decompose at low temperatures, as do $\alpha\alpha\beta\beta$-tetrafluoroethyl-substituted compounds[269]. Compounds with γ- and more distant positions of the double bond relative to the silicon atom readily add on halogens to form stable dihalogenoalkylsilanes. For example, the pyrolysis of trifluoropropyl-substituted organosilicon compounds is observed only at temperatures above 550°C.[269] The thermal stability of the dihalogenoalkylsilanes depends considerably on the nature of the remaining substituents at the silicon atom. The presence of a trichlorosilyl group sharply increases the thermal stability of even $\beta\gamma$-dichloroalkylsilanes.

There have been many studies of the addition of halogens to various alkenosilanes[81,143,268,270-279]. These papers describe the synthesis and properties of a large number of halogenoalkylsilanes. There have been several recent studies of this problem[280-282]. It was found that the replacement of three hydrogen atoms by fluorine considerably decreases the activity of a double bond in the addition of halogens, hydrogen halides, and polyhalogenomethanes[280].

Organosilicon compounds containing silacycloalkenic structures readily add halogens. For example, 1,1-dichlorosilacyclopent-2-ene adds bromine in CCl_4 at 0°C with the formation of 1,1-dichloro-2,3-dibromosilacyclopentene[283]. The reaction of 1,1,3,3-tetramethyl-1,3-disilacyclopentene with bromine and chlorine takes place analogously[284].

In a gas chromatographic investigation of the pyrolysis products of $Si(CH_3)_4$, $(CH_3)_2Si{=}CHSi(CH_3)_3$ was isolated, which vigorously reacts with bromine[285]:

$$(CH_3)_3Si{=}CHSi(CH_3)_3 + Br_2 \rightarrow (CH_3)_3BrSiCHBrSi(CH_3)_3.$$

$(CH_3)_3SiCH{=}C{=}O$, which is formed in the thermal (120–130°C) decomposition of $(CH_3)_3SiC{=}COC_2H_5$, adds on bromine with the formation of $(CH_3)_3SiCHBrCOBr$.[286]

The reaction of 1,1-bis(trimethylsilyl)ethylene with chlorine and bromine leads to the loss of one trimethylsilyl group[287]:

$$[(CH_3)_3Si]_2C{=}CH_2 + X_2 \rightarrow (CH_3)_3SiX + (CH_3)_3SiCX{=}CH_2.$$

The addition of bromine to silyl-substituted acetylenes leads to the formation of vinyl derivatives[141,288-290].

Hydrogen halides add to alkenylsilanes less vigorously than halogens. The presence of chlorine atoms at the silicon atom strongly retards and the presence of three alkyl groups accelerates the addition of hydrogen halides. On transferring the multiple bond from the α and β position the rate of addition increases, but further in the γ position, it falls. The rate of addition of hydrogen halides to alkenylsilanes increases in the order: HCl < HBr < HI. The addition of hydrogen halides, with the exception of hydrogen bromide, to allyl- and methylallyl-alkylsilanes takes place according to Markovnikov's rule independently of the nature of the alkyl groups connected to the silicon[291-295].

The reaction of vinyl-containing organosilicon compounds with hydrogen halides was first effected by the scheme[296]:

$$(CH_3)_3SiCH{=}CH_2 + HI \rightarrow (CH_3)_3SiCH_2CH_2I.$$

Subsequent investigations[275,292,297-300] showed that the addition of hydrogen halides to vinylsilanes takes place contrary to the Markovnikov rule. Just as for halogens, $CF_2{=}CFSi(C_2H_5)_3$ adds hydrogen halides worse then $CH_2{=}CHSi(C_2H_5)_3$.[280] HBr can add to $(CH_3)_3SiCH_2CH_2CH{=}CH_2$ both according to and contrary to the Markovnikov rule[116,204].

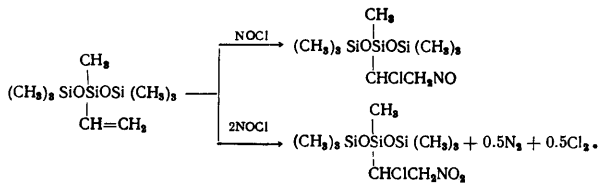
The addition of HBr and HCl to isopropenyltrimethylsilane[82,275,301] and isocrotyltrimethylsilane[82,300,302] obeys the Markovnikov rule, whereas HBr adds to $\alpha\beta$-dimethylvinyltrimethylsilane and $\gamma\gamma$-dimethylallyltrimethylsilane contrary to the Markovnikov rule[82].

Hydrogen halides add to silacyclopentenes with the formation of the corresponding halogeno-substituted silacyclopentanes[283,284].

As already noted, the β-halogenosilanes formed on addition of hydrogen halides to $\alpha\beta$-unsaturated silanes are extremely unstable compounds, which readily undergo β-decomposition with various reagents[173,303] or on raising the temperature[304-306]. The kinetics of the thermal decomposition of trichloro-2-chloroethylsilane[305] and 2,2-difluoroethyltrifluorosilane[307] in the gas phase follow a first-order equation.

Depending on the type of trimethylsilylalka-1,5-diyne, the addition to it of halogens and hydrogen halides proceeds differently[308]: (a) bromine adds to trimethylsilyldipropargyl at both triple bonds; (b) it adds to 1-trimethylsilylocta-1,5-diyne predominantly at the triple bond unsubstituted by silicon. HBr adds to 1-trimethylsilylhexa-1,5-diyne at the disubstituted triple bond with partial splitting of the adduct along the C–Si bond.

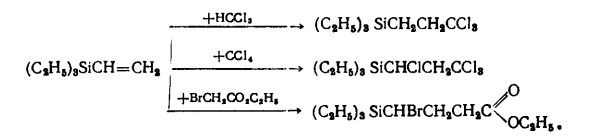
The nitrosochlorination of the vinyl-containing organosilicon compounds takes place in two directions[309]:



$ClNO_3$ adds to vinyltrichlorosilane according to the reaction[310]:

$$Cl_3SiCH{=}CH_2 + ClNO_3 \rightarrow Cl_3SiCHClCH_2NO_3.$$

The addition of polyhalogenomethanes and other halogenated hydrocarbons to vinylsilanes takes place with high yields, according to the reactions[280,311-316]:

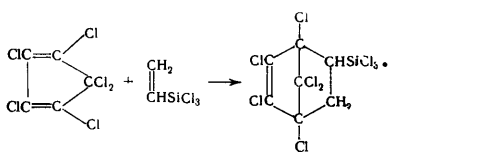


Polyhalogenohydrocarbons containing fluorine also add to vinyl-containing compounds[313,314,316,318].

When $CHCl_3$ and t-C_4H_9OK react with vinyl- and allyl-containing organosilicon compounds, products with dichlorocyclopropane groups are formed[319-322]:

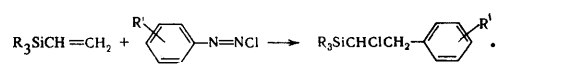
$$\equiv Si[CH_2]_nCH{=}CH_2 + CCl_2 \rightarrow \equiv Si[CH_2]_n\overline{CHCH_2CCl_2}.$$

Trichloro(vinyl)silane readily undergoes a diene condensation with cyclopentadiene and hexachlorocyclopentadiene[323-327]:

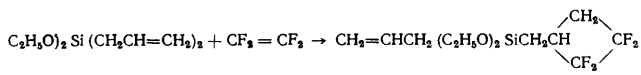


Allyldichloro(methyl)silane and 5,5-difluorotetrachlorocyclopentadiene[328,329] also undergo an analogous reaction[328,329], the latter reacting more readily than hexachlorocyclopentadiene. Alkenylsilanes containing hydrogen at the silicon undergo diene condensation with these compounds particularly readily.

Vinyl-containing organosilicon compounds undergo a Meerwein condensation with aryldiazonium halides[315]:



The reaction of alkenylsilanes with halogenoalkenes is also used for the preparation of halogeno-derivatives of organosilicon compounds[317,330]:



Organosilicon compounds with halogenated sulphur-containing organic groups are obtained by the reaction[331]:

$$p\text{-}ClC_6H_4SH + CH_2{=}CHSi(CH_3)(OC_2H_5)_2 \rightarrow p\text{-}ClC_6H_4SCH_2CH_2Si(CH_3)(OC_2H_5)_2.$$

The reaction takes place at 60°C under ultraviolet irradiation.

4. Organometallic Synthesis

Organometallic synthesis is widely used as a preparative method for obtaining various halogen-substituted organosilicon compounds with the halogen in a known position in the organic group bound to silicon.

The reaction of *p*-chlorophenylmagnesium bromide with silicon tetrachloride gives trichloro-*p*-chlorophenylsilane[332]. The reaction of *p*-chlorophenylmagnesium iodide with trichloro(methyl)silane gives dichloro-(*p*-chlorophenyl)methylsilane[333], that with chlorotrimethylsilane, *p*-chlorophenyltrimethylsilane[334]; that with trichlorosilane, dichloro-*p*-chlorophenylsilane[335]; that with trichloro(vinyl)-silane, dichloro-*p*-chlorophenylvinylsilane; and that with allyltrichlorosilane, allyldichloro-*p*-chlorophenylsilane[336]. *p*-Chlorophenylmagnesium bromide reacts analogously[154,333,336,337-341], but *o*-chlorophenylmagnesium bromide does not undergo these reactions[153]. A phenyl group with halogen in the *ortho*-position can be introduced in the reaction of *o*-halogenophenylmagnesium iodide with organohalogenosilanes[342]:

$$o\text{-}XC_6H_4MgI + (CH_3)_3SiCl \rightarrow o\text{-}XC_6H_4Si(CH_3)_3 + MgClI,$$

where X = Cl or F.

3-(*o*-Chlorophenyl)propylmagnesium bromide reacts with chlorotriphenylsilane by the reaction[343]:

$$o\text{-}ClC_6H_4[CH_2]_3MgBr + (C_6H_5)_3SiCl \rightarrow o\text{-}ClC_6H_4[CH_2]_3Si(C_6H_5)_3 + MgClBr.$$

Chlorobenzyl-substituted compounds are obtained in the reaction of organochlorosilanes with *o*- and *p*-chlorobenzylmagnesium chloride and *m*-chlorobenzylmagnesium bromide[344,345].

Polychlorophenylalkylchlorosilanes $C_6H_5 - {}_nCl_n(C_2H_5).SiCl_2$ [154,155] are obtained with the aid of an organomagnesium synthesis. Hexachlorobenzene, magnesium, and the corresponding halogenosilanes in tetrahydrofuran solution yielded perchlorophenyltrichlorosilane and alkylperchlorophenyldichlorosilanes[346].

p-Chlorophenylmagnesium bromide reacts with diethoxydiphenylsilane according to the reaction[347]

$$p\text{-}ClC_6H_4MgBr + (C_6H_5)_2Si(OC_2H_5)_2 \rightarrow p\text{-}ClC_6H_4(C_6H_5)_2SiOC_2H_5 + Mg(OC_2H_5)Br.$$

Fluorophenylmagnesium bromide reacts with silicon tetrachloride and alkylchlorosilanes to form trichloro-(fluorophenyl)silane[348] and alkyldichloro(fluorophenyl)silanes[349]. *p*-Fluorophenylmagnesium bromide reacts with trichloro(methyl)silane slowly, dichloro-(*p*-fluorophenyl)-methylsilane being formed. The reaction with difluorophenylmagnesium bromide is still more difficult, and as a result 2,4- and 3,5-$F_2C_6H_3(CH_3)SiCl_2$ are obtained. The reaction with dichlorodimethylsilane takes place more readily than that with trichloro(methyl)silane; triethoxy-(methyl)silane reacts even better with fluorophenylmagnesium bromides[350].

The production of fluoroaryl-substituted silanes by Grignard reaction has also been described[338,351,352]. Perfluorophenyl-substituted silanes[353], tetrakis-*m*-fluorobenzylsilane[354], and *m*-trifluoromethylphenyl-substituted silanes[328,348,354-358] were also obtained by this method.

Bromo-derivatives of aromatic and aliphatic-aromatic compounds with a known position of the bromine in the nucleus were obtained in an analogous manner[332,337,338,351,359-370].

Using organomagnesium compounds *p*-chlorophenyl- and *p*-bromophenylpentamethyldisilanes were obtained from pentamethyldisilane[49]. Mono- and di-substituted trifluoropropylchlorosilanes were obtained from $CF_3CH_2CH_2MgCl$ and $HSiCl_3$;[234] $(CF_3CH_2CH_2)_3SiH$ was obtained by the reaction of $HSiCl_3$ and $CF_3CH_2CH_2MgI$.[235]

Fully and partly fluorinated silanes[371-376], ω-chloroalkylsilanes[377,378] and halogen-containing acetylenic silanes[379] are obtained in an analogous manner.

Organolithium compounds are also widely used for obtaining halogenoaryl-substituted organosilicon compounds[190,380-382]. This method is especially effective for obtaining compounds containing rather large groups at the silicon atom. The reaction of *p*-bromophenyl-lithium with chlorotriphenylsilane gives *p*-bromophenyltriphenylsilane in 75% yield[383]. 3,5-Dibromophenyl-lithium reacts with silicon tetrachloride, trichloro(methyl)silane, and dichlorodimethylsilane[384] to form the corresponding dibromodiphenyl derivatives. Pentafluorophenyl-lithium and silicon tetrachloride gave tetrakisperfluorophenylsilane[385]; *m*-fluorophenyl-lithium and chloro(phenyl)silanes gave compounds of the formula $(m\text{-}FC_6H_4)_nSi(C_6H_5)_{4-n}$, where $n = 1-4$.[386]

Trimethyltribromomethylsilane was obtained from tribromomethyl-lithium and trimethylsilane[387]. *p*-Bromo and *p*-chloro-phenylethynyl-lithium react with silicon tetrachloride to form $(p\text{-}XC_6H_4C{\equiv}C)_4Si$, where X = Cl or Br.[388]

Organosodium synthesis was used for the introduction of chlorophenyl groups into bis(organochlorosilyl)-substituted benzenes[389]: the reaction of bromochlorobenzene with bis(phenyldichlorosilyl)benzene in the presence of sodium gave

$$[(ClC_6H_4)_2(C_6H_5)Si]_2C_6H_4;$$

$[(ClC_6H_4)_3Si]_2C_6H_4$ was obtained analogously from $(Cl_3Si)_2C_6H_4$.

5. Other Methods of Synthesis

Of the other methods for obtaining halogeno-derivatives of alkyl(or aryl)halogenosilanes and tetrasubstituted silanes, that of high-temperature condensation of alkyl and aryl halides with chlorosilanes is interesting. This reaction was first described in 1949[390,391] as applicable to the synthesis of alkyl- and alkenyl-silanes:

$$RX + HSiR'_3 \rightarrow RSiR'_3 + HX,$$

where R = alkyl or alkenyl group, and X = halogen. Subsequently it was used successfully for the synthesis of halogenoaryl substituted silanes.

The reaction can be effected in the liquid phase under pressure or in the gas phase at atmospheric pressure and 300–700°C. The reaction temperature can be greatly reduced by use of catalysts and initiators. These include halides of aluminium and of boron[392-394], aluminium oxide[390,395], palladium[396], benzoyl peroxide and ultraviolet light[226,397].

The reaction of dichlorobenzene and trichlorobenzene with trichlorosilane and dichloro(methyl)silane at 525°C in the vapour phase over palladium leads to the synthesis of the corresponding chloro- and dichloro-phenylchlorosilanes[396,398]. *p*-Dichlorobenzene reacts with chloro(methyl)phenylsilane[399] to form *p*-chlorophenylmethylphenylchlorosilane, and with chlorodimethylsilane[400] to form *p*-chlorophenyldimethylchlorosilane.

Hexafluorobenzene reacts with trichlorosilane to form dichlorofluoropentafluorophenylsilane and a mixture of isomers of bis(dichlorofluorosilyl)benzene[401].

The chloro-derivatives of thiophen (like thiophen itself) exhibit a much greater reactivity than benzene and its chloro-derivatives in condensation with silanes[402]. The condensation of silanes with 2,5-dichlorothiophen in the vapour phase at 570–580°C yielded 2-chloro-5-trichlorosilylthiophen and 2-chloro-5-dichloro(methyl)silylthiophen.

This method allowed the corresponding chloro(chlorovinyl)silanes to be obtained easily from dichloroethylene[85,210,400,403,404], trichloroethylene[85,210,398,405], and trichlorosilane, methyl- and ethyl-dichlorosilanes, chlorodimethylsilane, dichlorosilane, and chloro(methyl)silane.

The condensation of 1,3-dichlorobut-2-ene with dichlorosilane and trichlorosilane[406] gave respectively:

$$CH_3CCl{=}CHCH_2SiHCl_2 \text{ and } CH_3CCl{=}CHCH_2SiCl_3.$$

The reaction of silicon difluoride with hexafluorobenzene[407] gave trifluoro(pentafluorophenyl)silane $C_6F_5SiF_3$ and a mixture of the isomers of bis(trifluorosilyl)benzene.

The chloromethylation of benzylchlorodimethylsilane with CH_2O in fuming hydrochloric acid without a catalyst leads to the production of $ClCH_2C_6H_4CH_2Si(CH_3)_2Cl$; in the presence of $ZnCl_2$ chloromethylation is accompanied by side-processes[408]. The chloromethylation of the trialkyl(benzyl)silanes $R_3SiCH_2C_6H_5$ with 37% aqueous formalin solution and also with paraformaldehyde in CCl_4 and CH_3COOH leads to the formation of $CH_2ClC_6H_4CH_2SiR_3$.[409,410] With increase in the size of R the reaction becomes more difficult. Depending on the reaction conditions, different quantities of *p*-chloromethyl derivatives are formed; chloromethylation in water leads to the formation of > 90% of the *para*-isomer.

α-Methyltrimethylene oxide reacts with the chloroorganosilanes to form chloroalkoxy-derivatives[411]. The reaction of ethylene oxide with chloro(chloromethyl)methylphenylsilane, trichlorochlorophenylsilane, and chlorodichloromethyldimethylsilane gave the corresponding 2-chloroethoxysilanes[412].

The reaction of phosphorus(V) chloride with allyltrimethylsilane is interesting[413]:

$$(CH_3)_3SiCH_2CH{=}CH_2 + \overset{+}{P}Cl_4 \cdot \bar{P}Cl_6 \rightarrow (CH_3)_3SiCH_2CHClCH_2\overset{+}{P}Cl_3 \cdot \bar{P}Cl_6 \rightarrow \xrightarrow{SO_2} (CH_3)_3SiCH_2CHClCH_2P(O)Cl_2.$$

Tetrakis-(2,4,6-trichlorophenoxy)silane and tetrakis-(pentachlorophenoxy)silane are obtained from the corresponding phenoxides and silicon tetrachloride[414]. The reaction of chlorotriorganosilanes with $CH_2FCOONa$ and of triorganoethoxysilanes with $CH_2FCOONa$ gave halogen-substituted derivatives of the general formula $R_3SiOCOCH_2X$ (X = F or Br)[415].

On treating the carbinols $R_3SiC{\equiv}CR'R''OH$ with concentrated hydrochloric acid or sulphuryl chloride[416-418] the corresponding compounds with a chlorine atom in the organic group $R_3SiC{\equiv}CR'R''Cl$ are obtained.

An analogous reaction occurs between *p*-(2-hydroxyethyl)phenyltrimethylsilane and sulphuryl chloride in the presence of $CaCO_3$.[112]

On reacting with sulphuryl chloride, silicon-containing carboxylic acids are converted into the corresponding acid chlorides[419].

Chloromethyl-substituted organosilicon compounds can be obtained by the reaction[420]:

$$(C_2H_5OCH_2)_2Si(CH_3)R + 2 \cdot CH_3COCl \rightarrow (ClCH_2)_2Si(CH_3)R + 2 \cdot CH_3COOC_2H_5,$$

where R = CH_3 or C_3H_7.

Trichloro(phenyl)silane reacts with diazomethane[421] to form dichloro(chloromethyl)phenylsilane. Compounds of the general formula $(C_6H_5)_nSiCl_{4-n}$, where $n > 1$, do not undergo this reaction.

Triphenylsilyl-lithium reacts with halogenomethanes thus[422]:

$$(C_6H_5)_3SiLi + CH_nX_{4-n} \rightarrow CH_nX_{3-n}Si(C_6H_5)_3 + LiX,$$

where X = Cl, Br, or I, and $n = 0$, 1, or 2.

II. PROPERTIES

1. Reactions with Participation of the Halogen in the Organic Group

A halogen atom in the organic groups of organosilicon compounds is capable of taking part in nucleophilic substitutions [423-427].

α-Halogenoalkyl-substituted organosilanes are exceptionally inert towards electrophilic agents, but are considerably more reactive towards nucleophiles than the corresponding halogenohydrocarbons.

α-Chloro-derivatives are more reactive than γ-derivatives in most reactions. The reactivity of chlorine in compounds of the type $R_n(CH_3)_{3-n}SiCH_2Cl$ (R = C_6H_5, *p*-ClC_6H_4, $n = 1-3$) is considerably affected by the number of phenyl groups at the silicon atom; with increase in their number there is a sharp drop in the rate of substitution, owing to the steric effect of the phenyl groups [428].

Trialkyl-α-halogenosilanes are readily converted into the corresponding nitriles. Compounds of the general formula $R_nSi([CH_2]_xBr)_{4-n}$ react quantitatively in alcohol with NaCN and KCN to form $R_nSi([CH_2]_xCN)_{4-n}$; [429,430] with chloromethyl derivatives side reactions are observed (splitting). Cyanoalkyl-substituted organofluorosilanes are obtained by the same method [431]. By replacing bromine by the nitrile group in bromophenyl-substituted organoalkoxysilanes, cyanophenylorganoalkoxysilanes are obtained [432,433]. The replacement of bromine in the alkyl substituent in the aromatic ring takes place analogously [112]:

$$p\text{-}BrCH_2C_6H_4Si(CH_3)_3 + NaCN \rightarrow p\text{-}NCCH_2C_6H_4Si(CH_3)_3.$$

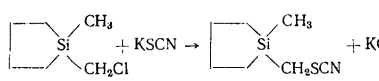
p-Bromophenyltrimethylsilane reacts with CuCn in the presence of pyridine [434]:

$$(CH_3)_3SiC_6H_4Br\text{-}p + CuCN \xrightarrow{C_5H_5N} (CH_3)_3SiC_6H_4CN\text{-}p.$$

$(NC)_2CHCH_2Si(CH_3)(OC_2H_5)_2$ was made from $CH_2I(CH_3)Si(OC_2H_5)_2$ and $NaCH(CN)_2$. [435] $CH_3(NC)_2CCH_2Si(CH_3)(OC_2H_5)_2$, which is more stable, was obtained in an analogous manner.

The nitriles obtained in this way can be easily converted into the corresponding amines, alcohols, and acids.

The halogen in an alkyl group can also be substituted by a thiocyanato-group, for example [436]:

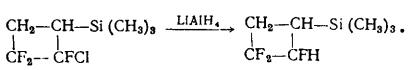


The chlorine atom in organic groups can be readily replaced by iodine [436-440]:

$$(CH_3)_3SiCH_2Cl + NaI \rightarrow (CH_3)_3SiCH_2I + NaCl.$$

In the reaction with KI the steric factor of the groups connected with the silicon plays an important part: $C_6H_5(CH_3)_2SiCH_2Cl$ and $(CH_3)_3SiOSi(CH_3)_2CH_2Cl$ react at only half the rate for $(CH_3)_3SiCH_2Cl$, [118,437] whereas $(C_6H_5)_3SiCH_2Cl$ does not react at all. [119] α-Halogenoalkylsilanes react with KI 3-5 times more rapidly than γ-halogenoalkyl-substituted silanes [423]. In the reaction with alkali metal halides chloroalkyl-substituted disilanes can be used successfully, for example, $ClCH_2(CH_3)_2SiSi(CH_3)_2CH_2Cl$ and $(CH_3)_3SiSi(CH_3)_2CH_2Cl$. [108]

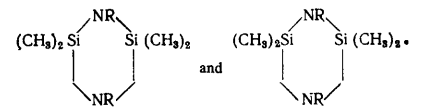
Under the action of $LiAlH_4$ halogen derivatives of tetrasubstituted silanes are hydrided [317]:



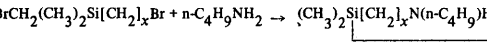
On treating halogenoalkylsilanes with $AgNO_2$ nitroso-derivatives are obtained, but on treatment with $NaNO_2$ nitro-derivatives—for γ-iodopropyltriethoxysilane $ONOCH_2CH_2CH_2Si(OC_2H_5)_3$ and $O_2NCH_2CH_2CH_2Si(OC_2H_5)_3$ respectively [441].

On heating $R_3SiCH_2C_6H_4CH_2Cl$ with $CaCO_3$ a chlorine atom is replaced by a hydroxyl group with the formation of $R_3SiCH_2C_6H_4CH_2OH$. [410]

The reaction of compounds of the type $R_3Si[CH_2]_nCl$ (n = 1 or 3) with ammonia or amines, organosilicon amines are formed [32,176,440,442-446]. A mixture of 2,6- and 2,5-disilapiperazines is formed in the reaction of bromomethylchlorodimethylsilane with primary amines or NH_3: [447]

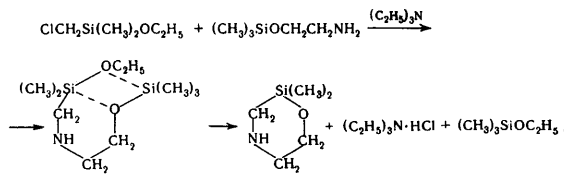


γ-Bromopropyl- and δ-bromobutyldimethyl(bromomethyl)silanes react with primary amines to form 3-sila-1-azacycloalkanes [448,449]:

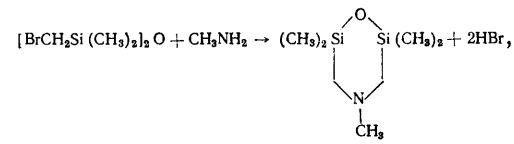


where x = 3 or 4.

α-Chloroalkylalkoxysilanes react with 2-(trimethylsiloxy)ethylamine [450]:



The reaction of 1,3-di(chloromethyl)-1,1,3,3-tetramethyldisiloxane with 2-aminoethoxytrimethylsilane yields 2,2,6,6-tetramethyl-4-(2-trimethylsiloxyethyl)-1-oxa-2,5-disila-4-azacyclohexane [451,452]. 1,3-Di(bromomethyl)-tetramethyldisiloxane reacts with methylamine to form 2,2,4,6,6-pentamethyl-2,6-disilamorpholine [447]:



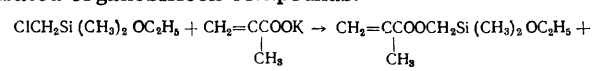
where X = halogen, R = alkyl.

Silylamines are obtained by treating halogenoalkyltrialkylsilanes with sodium acylamides [453,454]:

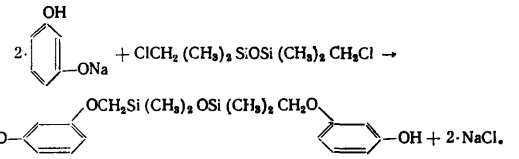
$$CH_3(R_2)SiCH_2X + CH_3CON(Na)C_2H_5 \rightarrow CH_3(R_2)SiCH_2N(C_2H_5)COCH_3 + NaX,$$

where X = halogen, R = alkyl.

In the reactions described above a halogen in the α-position to the silicon atom is more active than one in the γ-position. The reverse occurs in reactions with potassium acetate: greater activity is then exhibited by a halogen in the γ-position [455]. The synthesis of silicon-containing esters by this method has been studied often [420,436,456-459]. There is special interest in the reaction of halogenoalkyl-substituted silanes with salts of unsaturated acids, in particular methylacrylic acid, as a synthetic method for unsaturated organosilicon compounds:



In connection with this reaction mention must also be made of the reaction of chloromethylsiloxanes with monosodium and disodium salts of dihydric phenols[460]:



Silicon-containing esters are also obtained in the reaction of halogenoalkyl-substituted silanes with sodiomalonic and sodioacetoacetic esters[461-468] and also of chloromethylmethylalkoxysilanes with various acids in the presence of triethylamine[469].

Silicon-containing esters are used for obtaining organosilicon alcohols[57]:

$$R_3Si[CH_2)_nOCOCH_3 \xrightarrow[H_2SO_4]{CH_3OH} R_3Si[CH_2]_nOH.$$

γ-Chloroalkyltrialkylsilanes are more reactive than α-derivatives of also in reactions with the exchange of chlorine for an alkoxy-group under the action of sodium alkoxides on chloroalkyltrialkoxysilanes[470] and chloroalkyltrialkylsilanes[471]. Cellulose ethers are also obtained by this reaction—triethylsilylmethyl cellulose and trimethylsilyl methyl cellulose

$$[C_6H_7O_2(OH)_{3-x}(OCH_2SiR_3)_x]_n,$$

where R = CH_3 or C_2H_5.[472]

In these reactions, in addition to the replacement of chlorine by an ester group there is splitting of the Si–C bond[9,10], which increases with increase in the length of the radical in the sodium alkoxide[473].

A study of the reaction of halogenoalkylchlorosilanes with aromatic hydrocarbons in the presence of Friedel–Crafts catalysts[31,474-479] showed that β- and γ-chloroalkylchlorosilanes are more reactive than α-chloro-substituted ones. The reactivity increases with replacement of chlorine at a silicon atom by alkyl groups. These reactions are used for obtaining various aliphatic-aromatic chlorosilanes. The mechanism of this reaction for the α-chloroalkyl-substituted silanes can be represented as follows[475]:

$$Cl_2(C_2H_5)SiCHClCH_3 \xrightarrow{AlCl_3} Cl_2(C_2H_5)\overset{+}{S}iCHCH_3 + [AlCl_4]^- \rightarrow$$

$$\rightarrow Cl_2(C_2H_5)SiCH_3\overset{+}{C}H_2 + [AlCl_4]^- \xrightarrow{C_6H_6} Cl_2(C_2H_5)SiCH_2CH_2C_6H_5 + AlCl_3 + HCl.$$

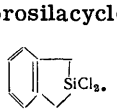
γ-Chloroalkyl-substituted derivatives react according to the scheme[478]:

$$Cl_3SiCH_2CH_2CH_2Cl \xrightarrow[C_6H_6]{AlCl_3} Cl_3SiCH_2\underset{CH_3}{CHC_6H_5} + Cl_3Si(CH_2)_3C_6H_5.$$

Compounds with halogenoacyl group can be used as acylating agents[480]:

$$(CH_3)_3SiC_6H_5COCl + C_6H_5CH_3 \rightarrow (CH_3)_3SiC_6H_5COC_6H_5CH_3\text{-}p + HCl.$$

The action of $AlCl_3$ on chloromethylbenzyldichlorosilane gives 3 : 4 benz-1,1-dichlorosilacyclopentane[481]:



The silylalkylation of aromatic hydrocarbons by dichloromethylchlorosilanes proceeds normally, but for $\alpha\alpha$-, $\beta\beta$-, and $\alpha\beta$-dichloroalkyl-substituted compounds is complicated by the reduction of one C–Cl bond by hydrogen.

Attention has recently been attracted to the high-temperature condensation of (chloroaryl)chlorosilanes with organochlorosilanes, leading to the formation of bis(organochlorosilyl)-substituted benzenes[399,482-484]:

$$Cl_{3-n}R_nSiC_6H_4Cl + HSiR'_mCl_{3-m} \rightarrow Cl_{3-n}R_nSiC_6H_4SiR'_mCl_{3-m}.$$

The condensation can proceed both in the liquid and in the vapour phase and is accompanied by several side-reactions. For example, in the reaction of chlorophenylalkylchlorosilanes with alkylchlorohydrosilanes the main reaction is accompanied by the following reactions[485]:

$$Cl_{3-n}R_nSiC_6H_4Cl + HSiR_mCl_{3-m} \rightarrow Cl_{3-n}R_nSiC_6H_5 + SiR_mCl_{4-m},$$

$$HSiR_mCl_{3-m} + HCl \rightarrow SiR_mCl_{4-m} + H_2,$$

$$Cl_{3-n}R_nSiC_6H_4SiR_mCl_{3-m} + HCl \rightarrow Cl_{3-n}R_nSiC_6H_5 + SiR_mCl_{4-m}.$$

Halogenosilanes other than chlorosilanes are also used in condensation, for example, chlorophenyltrifluorosilane[486].

In the gas-phase condensation of trichlorosilane and dichloro(methyl)silane with $ClC_{10}H_6SiCl_3$ (mixture of isomers), bis(organochlorosilyl)naphthalenes are formed[487].

In the action of nucleophilic and electrophilic reagents on halogenoalkylchlorosilanes, as well as cleavage of the Si–C bond, loss of hydrogen halide also takes place leading to the formation of halogenosilanes with alkenyl radicals.

A systematic study of this reaction[61,82,83,86,101,102,170,171,248,274,298,488-508] led to the finding and formulation of the principal regularities[509] and to the determination of the boundary of applicability of the various dehydrohalogenating agents in this reaction.

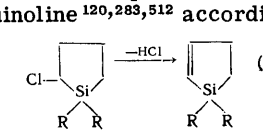
The ease of loss of HCl from the monochloroalkylchlorosilanes depends on the position of chlorine relative to the silyl group and decrease in the order $\beta > \alpha > \gamma$. The HCl is removed from secondary α- and β-chloroalkyl groups more readily than from primary groups. HBr is lost more readily than HCl. In the stepwise replacement of alkyl groups for chlorine the β-decomposition of the compounds of the type $R_3SiCH_2CH_2Cl$ gives way to dehydrochlorination.

Quinoline, isoquinoline, and piperidine dehydrochlorinate compounds with any silyl groups, but with quinoline the removal of HCl takes place successfully only from β-chloroalkyl groups, whereas catalytic amounts of piperidine are capable of bringing about the loss of HCl also from γ-chloroalkyl and chloroacyl groups. In the dehydrochlorination of $\beta\gamma$-dichloropropyltrichlorosilane under the action of $AlCl_3$ γ-chloroallyltrichlorosilane is formed; in the dehydrochlorination by quinoline $Cl_3SiCH{=}CHCH_2Cl$ and $Cl_3SiCH_2CH{=}CHCl$ are formed in approximately equal amounts[510].

In the dehydrochlorination of 1-phenyl-2-trichlorosilyl-1,2-dichloroethane and 1-phenyl-1-trichlorosilyl-1,2-dichloroethane in the presence of $AlCl_3$, 1-phenyl-2-chlorovinyltrichlorosilane is formed[511].

Chloropolychloroalkylsilanes are dehydrochlorinated by quinoline much more readily than the monochloro-derivatives.

Silacycloalkanes are dehydrochlorinated on heating and also in the presence of quinoline and *N*-methyl-1,2,3,4-tetrahydroquinoline[120,283,512] according to the reaction:



Unlike the 2-chloro-substituted, 1,1,3-trichlorosilacyclopentane is converted under analogous conditions into 3-butenyltrichlorosilane. The dehydrobromination of 2-bromo-1,1,2-triphenyl-1-silacyclobutane leads to the formation of 1,1,2-triphenyl-1-silacyclobut-2-ene[140].

The dehydrobromination of 2-cyanobromoethyltrichlorosilane by quinoline gives β-cyanovinyltrichlorosilane [139]. The dehydrochlorination of $R_3SiCH_2SCHClCH_3$ gives $R_3SiCH_2SCH{=}CH_2$. [513]

A reaction very similar to the dehydrohalogenation considered above is dehalogenation, leading to the formation of silyl-substituted compounds of the ethylene and acetylene type [514]. For example:

$$(Cl_3SiCCl_2)_2 \xrightarrow{-Cl_2} Cl_3SiCCl{=}CClSiCl_3.$$

On further dehalogenation, $Cl_3SiC{\equiv}CSiCl_3$ is formed. The reaction occurs at a temperature above 100°C in the presence of copper.

Metallic zinc can also be used as a dehydrochlorinating and dehalogenating agent. The ease of removal of halogens then decreases in the order: I > Cl > Br [229,317,515]; fluorine is not lost. For example [229]:

$$CF_2ClCFClCH_2CHISi(CH_3)_3 \xrightarrow[(C_2H_5)_2O]{Zn} CF_2{=}CFCH{=}CHSi(CH_3)_3.$$

Di-(iodomethyl)dimethylsilane is reduced to tetramethylsilane [38]:

$$(CH_3)_2Si(CH_2I)_2 \xrightarrow[C_2H_5OH]{Zn} (CH_3)_4Si.$$

$AlCl_3$ can be used for the dehydrochlorination only of compounds with trichlorosilyl groups; in other instances there is either decomposition or rearrangement of the organosilicon compounds. The rearrangement consists of the migration of an alkyl group from a silicon to a carbon atom [265]. For example [516]:

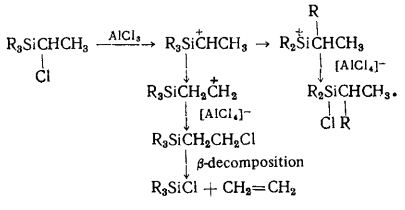
$$(CH_3)_3SiCH_2Cl \xrightarrow{AlCl_3} C_2H_5(CH_3)_2SiCl.$$

The mechanism of this reaction can be represented as follows:

$$(CH_3)_3SiCH_2Cl \xrightarrow{AlCl_3} (CH_3)_3\overset{+}{S}iCH_2 + [AlCl_4]^- \rightarrow$$

$$\rightarrow (CH_3)_2\overset{+}{S}iCH_2CH_3 + [AlCl_4]^- \rightarrow C_2H_5(CH_3)_2SiCl + AlCl_3.$$

For α-chloroethyltriorganosilane the reaction proceeds in two directions [103]:



For dichloromethyltrimethylsilane α-chloroethyldimethylchlorosilane is formed in the first stage, and then rearranges according to the scheme given above:

$$(CH_3)_3SiCHCl_2 \xrightarrow{AlCl_3} \underset{\displaystyle Cl\ Cl}{(CH_3)_2SiCHCH_3} \rightarrow (CH_3)_2SiCl_2 + CH_2{=}CH_2.$$

$AlCl_3$ also catalyses the migration of trimethylsilyl and dimethylchlorosilyl groups [87,517]:

$$\underset{\displaystyle (CH_3)_2SiCH_2Cl}{(CH_3)_nSiCl_{3-n}} \xrightarrow{AlCl_3} (CH_3)_2\overset{\displaystyle Cl}{\underset{|}{S}}iCH_2Si(CH_3)_nCl_{3-n}.$$

Chloromethylpentamethyldisilane undergoes an analogous rearrangement in the presence of sodium ethoxide [108] with the formation of $(CH_3)_3SiCH_2Si(CH_3)_2OC_2H_5$.

Di(chloromethyl)tetramethyldisilane rearranges under the action of $AlCl_3$ into $(CH_3)_3SiCHClSi(CH_3)_2Cl$ or $\{Cl(CH_3)_2Si\}_2CHCH_3$, depending on the conditions [108].

1-Chloromethyl-1-methylsilacyclopentane rearranges into 1-chloromethyl-1-methylsilacyclohexane under the action of $AlCl_3$. [436]

Chloro- and bromo-alkyltriorganosilanes (with the exception of β-halogeno-derivatives) readily form the corresponding organo-magnesium and -lithium compounds, which are capable of all the reactions peculiar to Grignard reagents [205,518,519]. There is a report [520] of the preparation of organomagnesium compounds of the type $R_3SiO[CH_2]_nMgCl$ (where R is alkyl or phenyl; $n = 4$ or 5). Organomagnesium compounds can also be obtained from halogenomethyl-substituted organocyclosiloxanes [521] and disilanes [108].

Organosilicon compounds which contain a halogen in the aromatic nucleus directly connected with silicon directly or through alkyl groups form organo-magnesium and -lithium compounds in high yields [351,368,382,387,410,480,522-528].

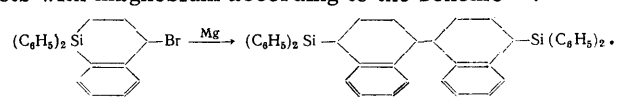
The formation of organolithium compounds is greatly influenced by the steric effect of organic groups bound to the silicon atom. Chloromethyltrimethylsilane readily forms trimethylsilylmethyl-lithium [529,530]:

$$ClCH_2Si(CH_3)_3 + 2Li \rightarrow LiCH_2Si(CH_3)_3 + LiCl.$$

However, organolithium compounds could not be obtained from chloromethyldimethylphenylsilane [531]. γ-(*o*-chlorophenylpropyltriphenylsilane also does not react with lithium. However, all these compounds readily form organomagnesium derivatives.

p-Chlorophenyldimethylsilane forms organo-lithium and -magnesium compounds [532]; $p\text{-}LiC_6H_4Si(CH_3)_2H$ readily condenses with the formation of oligomers with phenylenesilyl units.

4-Bromo-2,3-benz-1,1-diphenyl-1-silacyclobutane reacts with magnesium according to the scheme [201]:



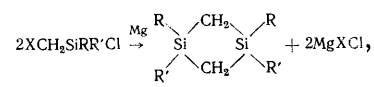
With mercury(II) chloride, organomagnesium compounds can be readily converted into organomercury compounds [92,108,471,531,533]:

$$ClMgCH_2Si(CH_3)_2R + HgCl_2 \rightarrow (CH_3)_2Si(R)CH_2HgCl.$$

Halogenoalkyl(or aryl)silanes which contain reactive atoms or groups (halogen, OR) do not form Grignard reagents. Reactions between γ-chloroalkylchlorosilanes and magnesium lead to the formation of silacyclobutanes [214,534,535]:

$$ClCH_2CH_2CH_2SiRCl_2 \xrightarrow{Mg} \overline{CH_2CH_2CH_2SiRCl}$$

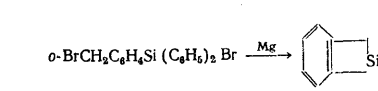
Halogenomethyldialkylchlorosilanes react with magnesium in ether or tetrahydrofuran with the formation of disilacyclobutanes [536-540]:



where X = Cl or Br; R and R′ = CH_3 or C_6H_5.

Under the same conditions $BrR_2SiCH_2SiR_2CH_2SiR_2CH_2Cl$ is converted into 1,3,5-trisilacyclohexane [541].

o-Bromomethylphenyldiphenylbromosilane reacts under the same conditions with magnesium with the formation of 2:3-benz-1,1-diphenyl-1-silacyclobut-2-ene [200]:



Halogenomethyltriorganosilanes react with sodium to form 1,2-triorganosilyl-substituted ethanes[542,543]:

$$2\cdot(CH_3)_3SiCH_2Br \xrightarrow{Na} (CH_3)_3SiCH_2CH_2Si(CH_3)_3.$$

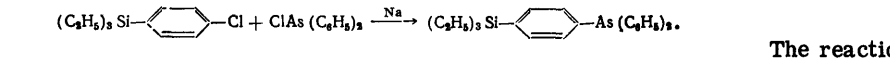
When there is common condensation of halogenoalkyl-substituted silanes and triorganohalogenosilanes with sodium the reaction is[544]:

$$(CH_3)_3SiCCl{=}CH_2 + ClSi(CH_3)_3 \xrightarrow{Na} [(CH_3)_3Si]_2C{=}CH_2.$$

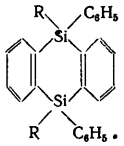
Several disila-alkenes were obtained by this method[545]. The use of bifunctional compounds in this reaction leads to the formation of silacycloalkanes. For example, $Br(CH_3)_2SiCH_2Si(CH_3)_2CH_2Si(CH_3)_2Br$ and $(CH_3)_2Si(CH_2Cl)_2$ react with sodium to form a ring of composition $[Si(CH_3)_2CH_2]_4$.[531]

Silacyclopropane, which is formed in the reaction of $RR'Si(CH_2Cl)_2$ with sodium–potassium alloy (at 260–280°C in a stream of helium) is unstable and readily rearranges into $R'RSiH(CH{=}CH_2)$.[546] When chloro(chloromethyl)dimethylsilane and dichlorodimethylsilane react with magnesium, zinc or alkali metals, ωω′-dichloropoly(dimethylmethylenes) are formed[519]; *m*- and *p*-halogenophenyldiorganochlorosilanes react with finely divided sodium or magnesium to form silylphenylene polymers of linear structure[547].

Condensation with sodium can be used for the replacement of halogens in an organic group, for example, by arsenic[337]:

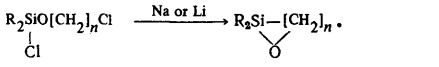


Reaction of ω-(*o*-chlorophenyl)alkyldiorganosilanes with sodium leads to the formation of 2:3-benz-1-silacycloalkanes[548]. o-$ClC_6H_4Si(R)(C_6H_5)H$ reacts with sodium[549] with the formation of *cis*- and *trans*-isomers:



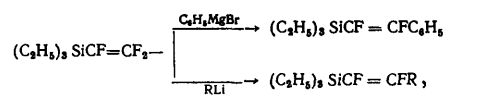
γ-(*o*-Chlorophenyl)propyltriphenylsilane reacts with sodium with loss of a phenyl group and formation of 2:3-benz-1,1-diphenylsilacyclohex-2-ene[343]. This reaction does not take place with lithium, but the same results can be obtained by the reaction of γ-(*o*-chlorophenyl)propyldiphenylsilane with lithium.

Halogenoalkoxy-substituted organochlorosilanes are converted into cyclic compounds under the action of sodium or lithium, according to the reaction[550]:



α- and β-chloroalkyltrichlorosilanes react with organomagnesium compounds differently: $CH_3CHClSiCl_3$ and CH_3MgBr form the corresponding trimethyl derivative, but $ClCH_2CH_2SiCl_3$ undergoes β-decomposition with formation of tetramethylsilane and ethylene only[173]. There are no side reactions in alkylation by Grignard reagents of α-, γ-, and δ-chloroalkylchlorosilanes. It was subsequently established[551] that the reaction of $ClCH_2CH_2SiCl_3$ with a Grignard reagent takes place through trialkylchlorosilanes which are formed as a result of β-decomposition; the latter, by reacting with the Grignard reagent, form the tetraalkylsilanes. There is simultaneous reaction at the C–Cl bond, hence the β-halogenoalkyltrichlorosilanes are capable of undergoing the usual Grignard–Wurtz reaction[292,293], the yield of products thus obtained depends on the nature of both reagents. This reaction enabled the chlorine in the trichlorosilyl group to be partially replaced by organic groups[552].

Perfluorovinyltriorganosilanes react readily with organo-magnesium and -lithium compounds with replacement of the fluorine in the β-position by organic groups[553]:

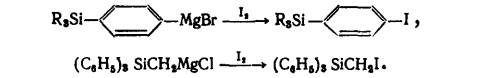


where R = C_6H_5, $CH_2{=}CH$, $CH_2{=}CH{-}CH_2$, or C_4H_9.

Halogenomethyl-substituted organohalogenosilanes react with organomagnesium compounds with replacement of the halogen in the methyl group[119,554]:

$$CH_3Si(Cl_2)CH_2Cl + 2RMgI \rightarrow R_2(CH_3)SiCH_2I + MgCl_2 + MgClI,$$

Similar results are obtained in the reaction with organomagnesium halides of compounds obtained on the basis of halogenoalkyl(or aryl)-substituted silanes[555]:



$$(C_6H_5)_3SiCH_2MgCl \xrightarrow{I_2} (C_6H_5)_3SiCH_2I.$$

The introduction of a halogen into an ethynyl group is based on the same method[556]:

$$R_3SiC{\equiv}CH \xrightarrow{R'MgBr} R_3SiC{\equiv}CMgBr \xrightarrow{Br_2} R_3SiC{\equiv}CBr.$$

The reaction of trichloromethyltrimethylsilane with methylmagnesium bromide proceeds with loss of the trichloromethyl group[557].

Chloro-substituted silacyclopentanes react with CH_3MgI differently depending on the position of the chlorine in the ring[283]: 1,1,2-trichlorosilacyclopentane reacts with replacement of the chlorine atoms at the silicon atom by methyl groups with the formation of 1,1-dimethyl-2-chlorosilacyclopentane, whereas 1,1,3-trichlorosilacyclopentane undergoes rearrangement under the action of CH_3MgI with the formation of 3-butenyltrichlorosilane, which is methylated by methylmagnesium iodide, being converted into $CH_2{=}CHCH_2CH_2Si(CH_3)_3$.

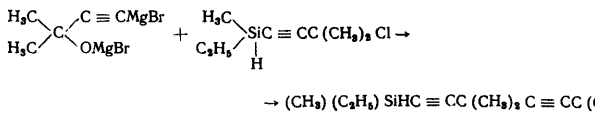
In the reaction of halogen derivatives of organohalogenosilanes with Iotsich reagent, first there is replacement of halogen connected with silicon atoms[558]; for example, $(CH_3)_2(CH_2Cl)SiCl$ and $HOC(R)(R')C{\equiv}CMgX$ give:

$$HOC(R)(R')C{\equiv}CSi(CH_3)_2CH_2Cl.$$

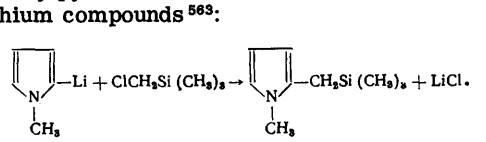
Halogen derivatives of tetrasubstituted silanes react at the halogen atom with entry into the organic group[418]:

$$R_3SiC{\equiv}CC(CH_3)_2Cl + XMgC{\equiv}CC(CH_3)_2OH \rightarrow$$
$$\rightarrow R_3SiC{\equiv}CC(CH_3)_2C{\equiv}CC(CH_3)_2OH + MgClX.$$

This reaction is widely used for obtaining organosilicon alcohols of the diacetylene series[559–562]. For example,



Silylmethylpyrroles have been obtained with the aid of organolithium compounds[563]:

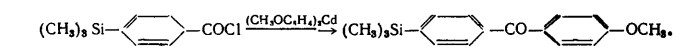


It has been reported[564] that in the reaction of chloromethyltrimethylsilane with butyl-lithium trimethylsilylcarbene $(CH_3)_3SiCH$ is formed, which on recombination gives

$$(CH_3)_2SiCH = CHSi(CH_3)_3.$$

Organosilicon acyl halides react with organocadmium compounds to form the corresponding ketones[110,480]:

$$(CH_3)_3SiCH_2CH_2COCl \xrightarrow{(C_6H_5)_2Cd} (CH_3)_3SiCH_2CH_2COC_6H_5$$



Halogenoalkyl-substituted silanes react with organic derivatives of phosphoric and phosphinic acids.

The Arbuzov rearrangement of $P(OC_2H_5)_3$ [565] and $C_6H_5P(OC_2H_5)_2$ [566] with $R_n(R'O)_{3-n}Si[CH_2]_xCl$ was used to synthesise compounds of the general formula

$$R_n(R'O)_{3-n}Si[CH_2]_xP\cdot(O)(R'')OC_2H_5.$$

where R and R′ are alkyl groups and R″ is C_6H_5 or OC_2H_5.

Chloromethyltrialkylsilanes react with R_3P [567,568] to form phosphonium salts:

$$R'_3SiCH_2Cl + R_3P \longrightarrow (R'_3SiCH_2PR_3)^+Cl^-$$

which on pyrolysis are converted into $R'_3SiCH{=}PR_3$.

Trialkylsilyl-substituted alkylphosphinic acids are obtained by the reactions[569,570]:

$$R_3Si[CH_2]_nCl + (R'O)_3P \xrightarrow{(t\text{-}C_4H_9O)_2} R_3Si[CH_2]_nP(O)(OR')_2 + R'Cl,$$

where R and R′ are alkyl groups and $n = 1$ or 3. The reaction with $(C_6H_5)_2POC_2H_5$ takes place analogously[570,571].

Dialkyl(triorganosilylmethoxymethyl) phosphinates are obtained in the reaction of dialkyl(sodioxymethyl) phosphinates with chloromethyltriorganosilanes[572,573]:

$$R_2P(O)-CH_2ONa + ClCH_2SiR'_3 \longrightarrow R_2P(O)-CH_2OCH_2SiR'_3 + NaCl.$$

Compounds of the formula $(RO)_2P(O)CH_2ONa$, [574] phosphine oxides, and their alkali metal salts[575] can be used in this reaction.

The chlorine in the chloromethyl group can also be replaced by residues of dialkyl(or aryl)dithiophosphonic (or dithiophosphinic) acids[576]. Chloropropylmethyldiethoxysilane is used for the production of γ-mercaptopropylmethyldiethoxysilane[577].

Bromomethyl-γ-bromopropyldimethylsilane reacts with Na_2S to form 3-sila-1-thiocyclohexane[448]:

$$BrCH_2Si(CH_3)_2CH_2CH_2CH_2Br + Na_2S \rightarrow (CH_3)_2\overline{SiCH_2CH_2CH_2SCH_2} + 2\,NaBr.$$

3-Sila-1-thiocycloheptane is obtained analogously from the δ-bromobutyl-derivative of silane[449].

Heterocycles containing silicon and sulphur are also obtained by the reaction[578]:

$$[ClCH_2(CH_3)_2Si]_2NH + 2H_2S \xrightarrow{(C_2H_5)_3N}$$

$$\rightarrow (CH_3)_2\overline{SiSSi(CH_3)_2CH_2SCH_2} + NH_4Cl + (C_2H_5)_3N\cdot HCl.$$

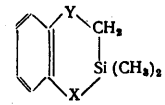
1,3-Bis(chloromethyl)tetramethyldisiloxane reacts with KSH to form 2,2,6,6-tetramethyl-1-oxa-4-thio-2,6-disilacyclohexane[579].

Chloromethyldimethylchlorosilane reacts with thiols[580]:

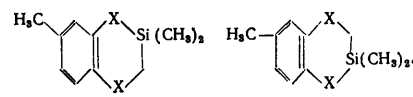
$$ClCH_2(CH_3)_2SiCl + HS[CH_2]_nSH \rightarrow (CH_3)_2\overline{SiS[CH_2]_nSCH_2} + 2HCl,$$

where $n = 2$ or 3.

Chloro(chloromethyl)dimethylsilane in the presence of triethylamine reacts with compounds of the general formula $o\text{-}HXC_6H_4YH$ (where X = O or NH and Y = O, NH, or S)[581] to form



The reaction of chloro(chloromethyl)dimethylsilane with $3,4\text{-}(HX)_2C_6H_3CH_3$ (where X = O or S)[582] in an analogous manner to form a mixture of compounds corresponding to the formulae:



Chloromethyl-containing organosilicon alcohols undergo intramolecular condensation on heating[448,449]:

$$ClCH_2(CH_3)_2Si[CH_2]_nOH \rightarrow (CH_3)_2\overline{Si[CH_2]_nOCH_2} + HCl,$$

where $n = 3$ or 4.

2. Reactions which Do Not Involve a Halogen in an Organic Group

Halogen-substituted organohalogenosilanes, according to the reactivity of the halogens connected with silicon, in reactions with nucleophilic reagents surpass the analogous compounds which do not contain a halogen in an organic group. The Si–Cl bond is more reactive than the C–Cl bond, therefore the action of nucleophilic reagents is directed towards it first[583]. The reactivity of the halogen connected with silicon is also greatly affected by the type and number of the organic groups at the silicon. Chloro(chloromethyl)methylsilanes can be arranged in the following series according to reactivity[584]:

$$CHCl_2Si(CH_3)_2Cl < CH_2ClSi(CH_3)_2Cl < CH_2ClSi(CH_3)Cl_2.$$

In the esterification of halogenoalkyl(or aryl)halogenosilanes the corresponding halogenoalkyl(or aryl)alkoxyderivatives are formed, for example, halogenoalkylethoxysilanes[17,18,184,377], halogenoarylethoxysilanes[180,187], and halogenocycloalkylethoxysilanes[184,186]. In partial esterification under mild conditions (in the presence of hydrogen chloride at reduced temperature) halogenoalkylalkoxychlorosilanes can be isolated, for example, chloromethylmethylethoxychlorosilane[539], γγγ-trifluoropropylmethylethylethoxychlorosilane[585]. The basicity of trimethylethoxysilane decreases regularly as the methyl groups are replaced by γγγ-trifluoropropyl groups[586,587].

In the hydrolysis of trifluoropropylchlorosilanes $(CF_3CH_2CH_2)_nSiCl_{4-n}$ the products obtained[231,235] are $(R_3Si)_2O$ ($n = 3$), $(R_2SiO)_x$ ($n = 2$), and $(RSiO_{1.5})_x$ ($n = 1$), where $R = CF_3CH_2CH_2$. The hydrolysis of γγγ-trifluoro-α-chloropropylmethyldichlorosilane and γγγ-trifluoro-β-chloropropylmethyldichlorosilane leads to the formation of linear and cyclic siloxanes of composition[77]:

$$[CF_3CH_2CHClSi(CH_3)O]_n \text{ and } [CF_3CHClCH_2Si(CH_3)O]_n.$$

Disiloxanes are obtained by hydrolysis of bromophenylmethylvinylchlorosilane[588] and trifluoropropylmethylchlorosilanes of formula[585]:

$$(CF_3CH_2CH_2)_n(CH_3)_{3-n}SiCl,$$

and also acyloxy-derivatives[589,590] of formula

$$(p\text{-}XC_6H_4)_3SiOCOR,$$

where X = halogen.

In the hydrolysis of γγγ-trifluoropropylmethyldichlorosilane and the subsequent catalytic destruction of the moist hydrolysate in a vacuum in the presence of catalytic amounts of alkali[580,591,592], two stereoisomers of 1,3,5-tris-(γγγ-trifluoropropyl)-1,3,5-trimethylcyclotrisiloxane are isolated.

Under the same conditions, cyclic trimer and cyclic tetramer were isolated[239] from a hydrolysate of general formula

$$[CHF_2CH_2CH_2(CH_3)_n \times SiO_{\frac{3-n}{2}}]_x$$

and cyclic tri-, tetra-, and penta-siloxanes were isolated from a mixture of $(CH_3)_2SiCl_2$ and $CF_3CH_2CH_2(CH_3)SiCl_2$.[593] On heating bis-(γγγ-trifluoropropyl)diethoxysilane with dilute HCl, $[(CF_3CH_2CH_2)_2SiO]_4$ was obtained, which on heating in the presence of a little KOH rearranges into a cyclic trimer[594].

Chloromethylmethylcyclosiloxanes with three and four siloxane units were obtained by the hydrolysis of ωω′-dichloro(chloromethyl)methylpolysiloxanes ($n = 1-5$).[595]

On treatment of $ClCH_2(CH_3)SiCl_2$ and $BrCH_2(CH_3)SiCl_2$ with a mixture of ether, acetone, aniline, and water, chloro- and bromo-methylethyldihydroxysilanes are obtained[596]; chloromethyldimethylhydroxysilane is obtained by hydrolysis of 1,3-dichloromethyltetramethyldisilazane[597]. In the hydrolysis of an ethereal solution of $C_6H_3Cl_2Si(OCOCH_3)_3$ with water[598] the monomer $C_6H_3Cl_2Si(OH)_3$ is isolated. Under analogous conditions $(p\text{-}ClC_6H_4)_2Si(OH)_2$ and $(p\text{-}BrC_6H_4)_2.Si(OH)_2$[599,600] are obtained, and also a compound of the formula

$$R_{n-3}(p\text{-}XC_6H_4)Si(OH)_n,$$

where R = CH_3 or C_6H_5; X = Cl or Br and $n = 1$ or 2[601].

In the hydrolysis of m- and p-$XC_6H_4Si(CH_3)_2Y_2$ (where X = Cl or Br and Y = Cl or OCH_3)[602] the corresponding m- and p-$XC_6H_4Si(CH_3)(OH)_2$ are obtained.

$(p\text{-}XC_6H_4)_2Si(OH)_2$, where X = Cl or F, were obtained by hydrolysis of the corresponding organochlorosilanes in the presence of $(NH_4)_2CO_3$ at 0°C.[603,604]

ωω-Dihydroxy(chloromethyl)methylpolysiloxane oligomers with two, three, and four siloxane units were obtained by the hydrolysis of the corresponding ωω-dichloro-containing compounds[595].

The nature of the substituent at the silicon atom has a considerable effect on the acid properties of organohydroxysilanes: the introduction of halogen into alkyl[605] and aryl[604] groups increases the acidity.

The rate of polycondensation of halogenomethylmethyldihydroxysilanes is considerably less than that for dimethylhydroxysilane[606]; in particular, chloromethylmethyldihydroxysilane is condensed at less than one-thirtieth the rate of dimethyldihydroxysilane[607].

Chloromethyldimethylhydroxysilane reacts with dimethyldichlorosilane in the presence of triethylamine to form 1,5-bis(chloromethyl)hexamethyltrisiloxane[608].

In the reactions of halogenated organohalogenosilanes with organometallic compounds, first of all the halogen at the silicon atom is replaced by organic groups[77,202,465,609]. Halogenoaryl silanes react with organolithium compounds with replacement of a hydrogen atom by an organic group[343]:

$$o\text{-}ClC_6H_4[CH_2]_3Si(C_6H_5)_2H + C_6H_5Li \rightarrow o\text{-}ClC_6H_4[CH_2]_3Si(C_6H_5)_3 + LiH.$$

Chloromethylorganodichlorosilanes react with organomagnesium compounds from ωω-dibromoalkanes, forming silacycloalkanes[438,610]:

$$CH_2Cl(CH_3)SiCl_2 + BrMg[CH_2]_4MgBr \rightarrow \text{} + 2MgClBr.$$

In the hydrogenation of chloromethylchlorosilanes of the type

$$CH_{3-n}Cl_nSiCl_3[611] \quad \text{or} \quad CH_3ClSiR_{3-n}Cl_n[448],$$

the corresponding silicon hydrides are formed. In the hydrogenation of organochlorosilanes with trifluoropropyl groups[235,237], compounds of the formula $(CF_3CH_2CH_2)_n.SiH_4 - n$ are obtained. The action of $LiAlH_4$, on $Cl_3SiCCl_2.SiCl_3$ yielded $H_3SiCCl_2SiH_3$,[87] which explodes when heated in a vacuum.

Chloromethyldimethylchlorosilane reacts with ammonia to form a silazane[578]:

$$ClCH_2(CH_3)_2SiCl + NH_3 \rightarrow [ClCH_2(CH_3)_2Si]_2NH + HCl.$$

The main products of the ammonolysis of $CF_3CHFCH_2Si.(CH_3)Cl_2$ are

$$[CF_3CHFCF_2(CH_3)(NH_2)Si]_2NH$$

and cyclosilazanes[612].

In the reaction of chloroalkylorganochlorosilanes with KHF_2 fluorine replaces chlorine attached to silicon[245]:

$$ClCH_2CH_2CH_2Si(C_2H_5)Cl_2 + KHF_2 \rightarrow ClCH_2CH_2CH_2Si(C_2H_5)F_2.$$

Halogeno-organochlorosilanes react with anhydrides and salts of organic acids[613,614] and with salts of difluorophosphoric acid[615] according to the reactions:

$$R_3SiCl + (R'CO)_2O \rightarrow R_3SiOCOR' + R'COCl,$$

$$R_3SiCl + HCOONa \rightarrow R_3SiOCOH,$$

$$RR'_2SiCl + NH_4OP(O)F_2 \rightarrow RR'_2SiOP(O)F_2 + NH_4Cl,$$

where R = p-XC_6H_4 (X = Cl, Br, F), R′ = H, CH_2, C_2H_5, $CH_3 - nCl_n$.

Halogenoalkyl(or aryl)silanes react with alcohols in the presence of sodium alkoxides[616,617] or H_2PtCl_6[249] with the formation of alkoxysilanes; they are readily halogenated at the Si–H bond by the action of halides[613,614,617-620] or phosphorus(V) chloride[200].

The presence of electrophilic halogenoalkyl substituents in silane is responsible for the considerable retardation of the halogenation (in comparison with organosilanes, which do not contain halogen atoms in the organic groups)[620]. The reactivity of $ClC_6H_4SiH_3$ in reactions with RCOOH is greater than that of $C_6H_5SiH_3$.[621] The condensation of tri-p-chlorophenylsilane with alkyl chlorides, alkenyl chlorides, chlorobenzene, and p-dichlorobenzene proceeds with higher yields than for triphenylsilane[367,622].

The introduction of chloroalkyl groups into organosilicon compounds sharply activates them in telomerisation with hexamethylcyclotrisiloxane[623]; the activity depends on the position of chlorine in the alkyl group relative to the silicon atom and decreases in the order: $\beta > \alpha > \gamma$.

Halogenoalkyl-substituted hydrido- and alkenyl-silanes can be used in additions. γ-Trifluoropropylalkenylchlorosilanes add to methylhydrochlorosilanes with the formation of

$$CF_3CH_2CH_2Si(Cl_2)(CH_2)_nSi(R)(CH_3)Cl$$

where R = Cl or CH_3 and $n = 2$ or 3.[624] Chloromethyldimethylsilane adds to

$$CH_2{=}CHCH(R)OSi(CH_3)_3$$

in the presence of Pt/C with the formation[488] of:

$$ClCH_2Si(CH_3)_2CH_2CH_2CH(R)OSi(CH_3)_3.$$

As the methyl groups in hexamethyldisiloxane are replaced by $\gamma\gamma\gamma$-trifluoropropyl groups the splitting of the siloxane bond by nucleophilic reagents is facilitated, but electrophilic reagents are hindered[586,587,625]. Silicon halides break the siloxane bond in $[R(CH_3)_2Si]_2O$, where R is $CF_3C(CH_3)_2$ or $Cl_2C_6H_3$, with formation of the corresponding halogenoalkyl(or aryl)dimethylhalogenosilanes[626].

Halogenoalkyl(or aryl)-containing organoacetoxysilanes undergo condensation with metal alkoxides. Compounds of the general formula $R_nR'_{3-n}SiOAl(OPr^{iso})_2$, where R = $CF_3CH_2CH_2$ or m-$CF_3C_6H_4$ and n = 1–3 have been obtained by the reaction of $R_nR'_{3-n}SiOCOCH_3$ with $Al(OPr^{iso})_3$.[627]

3. Reactions Accompanied by the Loss of a Halogen-Containing Group from Silicon

When aqueous NaOH acts on hexachlorocyclohexylmethyldichlorosilane the loss of $C_6H_6Cl_6$ is accompanied by dehydrochlorination and by the formation of 1,2,4-trichlorobenzene with 86.6% yield; hexachlorocyclohexylchloromethyldichlorosilane decomposes with the formation of chloromethane in addition to trichlorobenzene[184,186]. In the reaction of NaOH with chlorinated dimethyldichlorosilane and bis(trichloromethyl)diethoxysilane[18] the yields of $CHCl_3$ are 94.3 and 89.6% respectively. In 1-chloromethyl-1-methylsilacyclopentane the chloromethyl group is lost even on boiling with quinoline[512]; on boiling in the presence of water *sym*-dimethylbis(cyclotetramethylene)disiloxane is formed. In chloromethyl trichlorosilanes the mono- and di-chloro-substituted groups are completely stable even on boiling with anhydrous $FeCl_3$, and trichloromethyltrichlorosilane decomposes even in the absence of a catalyst with the formation of $SiCl_4$ and C_2H_4.[628]

In polyorganosiloxanes the stability of the halogenoalkyl groups is just the same as for the monomeric compounds, depends on the position of the halogen relative to the silicon atom. In $(CHF_2CF_2SiO_{1.5})_n$ and $(CHF_2CH_2SiO_{1.5})_n$ the Si–C bond is broken on shaking with 10% NaOH solution at 20°C; under these conditions $(CF_3CH_2CH_2SiO_{1.5})_n$ is completely stable[629].

The breaking of the Si–C bond also occurs with sodium, for example, on chloromethyltrimethylsilane[630] and also in the reaction of tetrakis(pentafluorophenyl)silane with lithium[385]:

$$(C_6F_5)_4Si + 2Li \rightarrow (C_6F_5)_3SiLi + C_6F_5Li\ .$$

The pentafluorophenyl group is lost under the action of bromine[385]:

$$(C_6F_5)_4Si + Br_2 \rightarrow (C_6F_5)_3SiBr + C_6H_5Br\ .$$

The presence of a halogenomethyl substituent greatly accelerates the solvolysis of organosilanes in alcohol–water medium[631,632], which here proceeds in two directions:

$$CH_2ClSi(CH_3)_2H + H_2O + OH^- \rightarrow CH_2ClSi(CH_3)_2OH + H_2 + OH^-\ , \quad (1)$$

$$CH_2ClSi(CH_3)_2H + H_2O + OH^- \rightarrow (CH_3)_3SiOH + H_2O + Cl^-\ . \quad (2)$$

The relative contribution of reaction (2) in this process depends on the nature of the halogenoalkyl radical and increases in the order: $CHCl_2 < CH_2Cl < CH_2I < CH_2Br$.

The hydrolysis of $(CH_3)_3SiSi(CH_3)_2CH_2Cl$ gives $[(CH_3)_3SiSi(CH_3)_2]_2O$.[49]

4. Physical Properties

There have been comparatively few studies of the physical properties of the halogenoalkyl(or aryl)-substituted organosilicon compounds.

The infrared[48,78,104,165,201,242,308,361,422,436,596,618,633–637], ultraviolet[253,635,638], Raman[49,267,350,637], electron absorption[281], NMR[77,78,120,140,201,253,308,639], nuclear quadrupole resonance[640–643], and proton magnetic resonance[644] spectra, polarographic behaviour[645], and electron microscopic examination of polyorganosiloxanes[646] have been described.

III. APPLICATIONS

Organosilicon compounds containing halogenated alkyl and aryl groups find application in various fields of technology[647,648].

For example, the use of organochlorosilanes with $\gamma\gamma\gamma$-trifluoropropyl[239] and α-(trichloromethyl)propyl[649] groups for the hydrophobisation of ceramic and other materials is known; halogenoalkyl-containing compounds are converted into nitro- and nitrito-derivatives for use in the pharmaceutical industry[446]. The replacement of alkyl and aryl groups in molecules of polyorganosiloxane liquids by halogenoalkyl and halogenoaryl groups markedly changes their properties, in particular, it increases the activation energy for viscous flow[634], increases chemical stability, and leads to a deterioration in their lubricating properties[650].

One of the most widely used types of liquid for these purposes are the $\gamma\gamma\gamma$-trifluoropropylmethylsiloxanes. They exhibit good lubricating properties on all metals[651]. In distinction from other organosilicon liquids polytrifluoropropylmethylsiloxanes are used successfully as lubricants for steel–steel couples[652].

Consistent lubricants based on these liquids[653,654] exhibit high stability to the action of water and solvents.

Liquids with other halogenoalkyl groups are used under the same designation, for example, $\alpha\alpha\gamma$-tribromopropyl, $\gamma\gamma\gamma$-trichloropropyl[316], β-(perfluoroalkyl)ethyl[655], ω-chloroalkyl[377], trifluorovinyl[419], and also bromophenyl[656], chlorophenyl[657], and chlorocyanoalkyl[92,658] groups. Liquid polyorganosiloxanes with molecules of formula p-$ClC_6H_4SCH_2CH_2Si(CH_3)O$ as elementary units of the chain exhibit good lubricating properties[331].

Linear polidimethylsiloxanes with $-[CH_2]_nCOOR$ terminal groups, where $R = CH_xF_{3-x}[CH_yF_{2-y}]_nCH_2-$ (x = 0–2, y = 0–2, n = 0–10),[659] $CHF_2[CF_2]_nCH_2-$ or $CClF_2.[CF_2CFCl]_nCH_2-$[660] are synthetic liquids which combine the best properties of organosilicon, fluorohydrocarbon, and ester oils. These liquids exhibit good viscosity characteristics over a wide range of temperatures, and a low freezing point; they are suitable for work under conditions of high temperature (205–260°C) and pressure. Analogous properties are exhibited by liquids with elementary unit of the chain molecule $OSi(CH_3)[CH_2]_4COOR$, where R = $C_3H_7CH_2$, $H[CF_2]_4CH_2$, or hexachlorobicycloheptenylmethyl[661].

Liquids which contain fluorinated organic groups are of great interest as dielectrics[239,644,662]. For example, a liquid of composition $[CF_3C_6H_4Si(CH_3)O]_n$ has ϵ = 6.5–9.5 in the range of temperatures from –20° to +100°C and frequencies of 100–100 000 Hz and is used as insulating impregnants of condensers.

Liquids containing hexafluoroisobutyl groups and active hydrogen are used for conferring oil-resistance on articles made of glass, metal, wood, leather, textiles, etc.[237]. Liquids with fluoroalkyl groups are used as fire-extinguishing materials[663], hydraulic liquids, and plasticisers[654].

Rubbers with β-(perfluoroalkyl)ethyl groups [664], in particular with trifluoropropylsiloxane units [238,654,665] and β-trifluoromethylpropyl [649] units are stable in air to 200°C and in a vacuum to 250°C. Polytrifluoropropylmethylsiloxane rubbers exhibit reduced residual deformation [666] and better technological properties [667] in comparison with polydimethylsiloxanes.

Unfilled arylenesiloxane vulcanisates with trifluoropropyl groups [663] have a tensile strength of 30 kgf cm^{-2} and when reinforced 90–105 kgf cm^{-2} at a relative elongation of 300–400%. Resins based on these rubbers retain their elasticity after radiation doses which considerably (more then 15 times) exceed that critical for polydimethylsiloxanes.

Rubbers with chloromethyl groups at silicon atoms are used [669,670]. The use of polyorganosiloxanes with halogenated alkyl groups in the composition with polytetrafluoroethylene is well known [671].

To obtain polymers with halogenophenyl groups, the method of catalytic polymerisation is widely employed. The introduction of halogenophenyl groups instead of phenyl groups greatly retards polymerisation [672,673]; depending on the number of chlorine atoms in the phenyl groups their effect on the retardation of the polymerisation process increases in the order [674]:

$$C_6H_5<ClC_6H_4<Cl_3C_6H_2<Cl_2C_6H_3<Cl_4C_6H.$$

The thermal stability of the polymers decreases with increase in the number of chlorine atoms in the phenyl group [675]. Polymers with halogenophenyl groups are used as non-inflammable adhesives for plastics, enamels, and glues in electrical insulating technology [676,677]. They also modify organic resins and lakes for conferring fire-resistance.

Polymers with halogenoalkyl ($CF_3CH_2CH_2$, [239] $Cl[CH_2]_n$, [377] $CHFClCF_2$, and $CHCl_2CCl_2$ [227]) and chlorocyanoalkyl [92] groups are used for obtaining plastics, decorative coatings, and other purposes.

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