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Progress in the Halogenation of Organic Silicon Compounds

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The Review deals mainly with the direct halogenation of organic silicon compounds by halogens and halogenated compounds as among the most important methods for the preparation of organosilicon compounds containing halogen in the organic radicals. With respect to preparative possibilities, experimental simplicity, and in individual cases the yields obtained, the direct chlorination and bromination of organic silicon compounds has no equal. The preparation of halogenated alkyl (and aryl) silanes by various methods has been partly covered in previous monographs and reviews[1-8], but the direct halogenation of organic halogenosilanes has not yet been adequately reported in the review literature. The present paper makes an attempt to fill this gap. It gives a detailed discussion of the conditions and the mechanisms of radical halogenation (mainly with chlorination as example) under the influence of various initiators (ultraviolet radiation, peroxides, azo-compounds, γ-rays), and also electrophilic substitution and cleavage of the silicon-carbon bond in aryl- and alkylaryl-chlorosilanes. Besides substitutive halogenation, involving replacement of hydrogen in organic radicals by halogen atoms, the addition of halogen at double bonds present in these radicals is also surveyed. A list of 335 references is included.

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I. INTRODUCTION

Typical polysiloxane materials, despite their valuable technical properties, are no longer able at present to satisfy completely the increasing demands of modern technology, especially with respect to stability to heat and thermal oxidation, resistance to oils and fuels, lubricating and adhesive properties, etc.

A promising method for the controlled modification of the properties of polyorganosiloxanes is to introduce functional groups into the organic radicals framing the siloxane chains. The presence of a polar substituent in a hydrocarbon radical attached to a silicon atom increases the polarity of the polymer molecule and therefore improves the adhesion, mechanical strength, and other properties of practical importance.

The production of modified organosilicon polymers of this type demands appropriate monomers with functional groups, primarily halogeno-derivatives (especially chloro-derivatives) of various alkyl- and aryl-chlorosilanes. These are convenient initial compounds for obtaining other carbon functions of silicon—amines, nitriles, alcohols, acids, thiols, thiocyanates, etc. This is probably the reason for the rapid development of research on the halogenation of various organosilicon compounds.

Before examining the halogenation of organic silicon compounds we must consider certain specific properties of silicon, distinguishing it from carbon and resulting from the intermediate position which it occupies between this typical non-metal and the Group IV metals (germanium, tin, lead). This is important for a correct understanding of the influence of these characteristics on the reactivity of silicon–carbon and silicon–halogen bonds (compared with carbon–carbon and carbon–halogen bonds), which must be taken into account in order to accomplish the halogenation of organosilicon compounds.

II. SOME SPECIFIC FEATURES OF THE SILICON ATOM INFLUENCING THE REACTIVITY OF ITS ORGANIC COMPOUNDS

While occupying a position between carbon and germanium in the Periodic System, silicon is closer to the latter in most of its properties[4,6] (see Table).

Physical properties of the elements—carbon, silicon, and germanium—and their bonds with carbon and chlorine.

Element	Nuclear charge	Electronic structure	Covalent radius	Electronegativity (Ref.9)	Coordination No.	Energy of bond, kcal mole^{-1}, with		Ionic character of bond with Cl, %
						carbon	chlorine	
Carbon	6	$1s^2 2s^2 2p^2$	0.77	2.5	4	84.9	77.9	6
Silicon	14	$1s^2 2s^2 2p^6 3s^2 3p^2$	1.17	1.8	6	75.0	90.3	30
Germanium	32	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$	1.22	1.7	6			

By readily donating its valency electrons, the silicon atom is more liable to be attacked by various reagents than is the carbon atom in compounds of similar structure.

The comparatively high energy of the silicon–chlorine bond in chlorosilanes is explained by the considerably lower electronegativity of the silicon atom compared with carbon, which, combined with the great polarisability of the electron sheath of the silicon atom, ensures that the silicon–chlorine bond shall be highly reactive. The lower energy of the silicon–carbon bond than of the carbon–carbon bond promotes greater lability of the former, especially in electrophilic substitutions[4]. Silicon is able to form additional bonds by filling vacant 3*d*-orbitals. In most of its compounds silicon is electronically unsaturated[10,11], because its capacity for coordination is not completely utilised in these compounds.

The above specific structural features of the silicon atom and the bonds it forms with carbon and halogens have a definite effect on the reactivity of organosilicon compounds towards halogens.

III. STABILITY OF THE SILICON–CARBON BOND UNDER CONDITIONS OF HALOGENATION

The halogenation of alkylhalogenosilanes at various temperatures involves not only the compounds undergoing halogenation, an elementary halogen, and a catalyst (usually a metal chloride) but also the hydrogen halide which is liberated. All these factors (halogen, hydrogen halide, catalyst, and temperature), either individually or in combination, are able under certain conditions to cleave the silicon–carbon bond. Before considering the halogenation of organosilicon compounds, therefore, it is advisable to discuss the stability of this bond to the above reagents.

The greater polarity of the silicon–carbon bond and the shielding effect of the silicon atom make this bond thermally more stable than is the carbon–carbon bond.

When halogens act on aliphatic compounds of silicon, the hydrogen atoms of the alkyl group undergo radical replacement by halogen. The rate of cleavage of the silicon–carbon bond by bromine or iodine depends on the structure of the initial silane[12], and is greatly increased in the presence of a catalyst of the aprotic acid type. Thus boiling tetraethylsilane with iodine in the presence of aluminium iodide splits off two ethyl groups with the formation of diethyldi-iodosilane[13]. The action of aluminium chloride on tetraethylsilane in chloroform splits off all four ethyl radicals even under ordinary conditions. Iron(III) chloride, bismuth chloride, and mercury(II) chloride also detach aliphatic radicals from the silicon atom under considerably more severe conditions[14]. Tetra-alkylsilanes undergo fission in the presence of aluminium chloride[15].

The introduction of halogen atoms into the alkyl group of an organosilicon compound facilitates its detachment from the silicon atom, the stability of the silicon–carbon bond depending on the position of the halogen relative to the silicon atom[6,8]. α-Halogenoalkylsilanes are relatively stable, with the exception of chloromethyltrialkylsilanes. The introduction of a halogen atom into an aliphatic radical in the β-position with respect to silicon produces a sharp decrease in the stability of the silicon–carbon bond. A γ-halogen atom weakens the bond to a lesser extent than does a β-halogen.

Mono- and di-chloromethyl derivatives of silanes are stable towards acids[16], but in the presence of alkalis quantitative elimination of α-chlorinated alkyl groups takes place. As was to be expected, the polarity and hence the sensitivity of the silicon–carbon bond to nucleophilic reagents falls in the sequence $CCl_3 > CHCl_2 > CH_2Cl$.[17–19] The stability of the silicon–carbon bond improves with increase in the length of the aliphatic chain containing halogen in the α-position to the silicon atom[20], but when a β-halogen atom is present these compounds, on treatment with acids and alkalis, also readily undergo the so called β-decomposition with formation of an alkene[21–25]. The tendency of the molecule to β-decomposition increases markedly with increase in the number of alkyl radicals attached to the silicon atom, and completely substituted derivatives, e. g. $(C_2H_5)_3SiCH_2CH_2Cl$, decompose even on distillation (at 80°C). γ-Decomposition, with the formation of cyclopropane (or propene) and its derivatives, takes place similarly to β-decomposition, but less vigorously.

Halogens and hydrogen halides are able to detach aryl radicals from the silicon atom with the formation of a silicon–halogen bond. Thus the phenyl groups in tetraphenylsilane are eliminated by the action of bromine[26–28]. The removal of an aromatic group by bromine and iodine becomes easier with the accumulation of alkyl radicals on the silicon atom[29,30]. Under more severe conditions (270–300°C) dry chlorine is also able to split off phenyl radicals[31,32]. The stability of the $Si-C_{Ar}$ bond is greatly affected by the nature of other atoms and groups attached to the silicon. Electronegative substituents make cleavage of the bond more difficult, as is shown especially clearly by phenyltrichlorosilane, which can be chlorinated normally by an electrophilic mechanism[32]. Depending on the nature of the substituents the stability of aromatic silicon compounds towards the action of bromine in solvent solution[33] diminishes in the sequence

$$o\text{-}NO_2C_6H_4Si(CH_3)_3 > p\text{-}NO_2C_6H_4Si(CH_3)_3 > m\text{-}NO_2C_6H_4Si(CH_3)_3 > C_6H_5Si(CH_3)_3$$

The products of this reaction indicate that the usual electrophilic replacement of the trimethylsilyl group by bromine has taken place[34]:

$$C_6H_5Si(CH_3)_3 + Br_2 \rightarrow C_6H_5Br + (CH_3)_3SiBr$$

Hydrogen halides act similarly to halogens on the $Si-C_{Ar}$ bond. Comparison of the stability of the aromatic silanes to acid reagents[16–18,35–79] has provided quantitative estimates, based on the Hammett constants δ, of the influence of nuclear substituents on the stability of $Si-C_{Ar}$ bond. It was found that the strength of the bond increases with increase in δ. Nuclear substituents having $\delta > +0.4$ (*m*-CN, *p*-CN, *m*-NO_2, *p*-COOH, *p*-CH_3CO) so strengthen the bond that it is not cleaved by electrophilic reagents[37].

Among the strongest electrophilic reagents are aluminium chloride, iron(III) chloride, and other metal chlorides normally employed as catalysts in the halogenation of aromatic silicon compounds. Aluminium chloride vigorously cleaves the $Si-C_{Ar}$ bond in diphenyldichlorosilane[53], tetraphenylsilane[54], phenyltriethylsilane[55], phenyltrichlorosilane[56–58], and also several other phenyl- and halogenophenyl-silanes[54,56,57,59]. The action of aluminium chloride is especially clearly developed in certain solvents: e.g. in chloroform aluminium chloride cleaves not only the $Si-C_{Ar}$ bond but also the Si–Si, Si–O–Si, and $Si-CH_2C_6H_5$ bonds[53]. It was assumed originally[53–58] that reaction between aromatic silanes and aluminium chloride involves the intermediate formation of phenylaluminium dichloride. Later investigations have shown[60,61] that the true cleaving agent is the acid $HAlCl_4$, formed from aluminium chloride and hydrogen chloride, the latter resulting from the hydrolysis of chlorosilane and aluminium chloride by moist air. In the absence of moisture (or hydrogen chloride) aluminium chloride is unable to effect the cleavage

of phenylchlorosilanes. Yet fission of the $Si-C_{Ar}$ bond in the presence of aluminium chloride is appreciably accelerated by passing hydrogen chloride through the reaction mass[62]. Chlorides of other metals, e.g. iron and antimony, have a more moderate effect on the $Si-C_{Ar}$ bond[58,63-65]. Phosphorus pentachloride is a strong electrophilic reagent, rupturing the silicon–carbon bond in aliphatic and aromatic silanes[27,46].

In contrast to alkylchlorosilanes the introduction of a halogen atom into a phenyl radical produces only a slight increase in polarity of the $Si-C_{Ar}$ bond. In this case the bond is stabilised, as is confirmed by the resistance to alkaline hydrolysis of chlorophenyltrichlorosilane and ethylchlorophenyldichlorosilane[80]. Increasing the number of chlorine atoms in the phenyl group has hardly any effect on the $Si-C_{Ar}$ bond.

IV. RADICAL HALOGENATION (CHLORINATION, BROMINATION) OF SILICON-CONTAINING ALIPHATIC COMPOUNDS

1. Preparation of Chloroalkyl Compounds of Silicon

Chlorination of alkylchlorosilanes in liquid and vapour phases takes place by a radical–chain mechanism. Chlorine and sulphuryl chloride are usually employed as chlorinating agents. Chlorination is initiated by ultraviolet radiation, ionising radiations, peroxides, and other chemical initiators.

(*a*) Chlorination by chlorine

Systematic investigation of the chlorination of aliphatic organosilicon compounds began in 1945, when the photochemical liquid-phase chlorination of several methylchlorosilanes was first achieved[16], after which study of this reaction was continued on a wide scale[17,18,67-76]. Several regularities were found in the chlorination of these compounds. The rate of chlorination of methylchlorosilanes decreases in the sequence

$$(CH_3)_4Si > (CH_3)_3SiCl > (CH_3)_2SiCl_2 > CH_3SiCl_3$$

When one chlorine atom in dimethyldichlorosilane is replaced by a methyl group, the rate of chlorination is increased ninefold[67], which is probably explained by the difference between the induction effects of chlorine atoms and of methyl groups.

In the chlorination of methylchlorosilanes the chlorine exhibits a tendency to replace successively hydrogen atoms in the same methyl group, which indicates that the chloromethyl group is more rapidly chlorinated than is an unsubstituted methyl group. As a consequence, only trichloromethyltrichlorosilane can be obtained by the photochemical liquid-phase chlorination of methyltrichlorosilane[17,68,69,77]. Increase in the number of methyl groups attached to silicon increases the possibility that a second chlorine atom will enter an adjacent methyl group. Thus the chlorination of dimethyldichlorosilane involves the successive replacement by chlorine of the hydrogen atoms only in one methyl group; trimethylchlorosilane yields an appreciable quantity of methylbischloromethylchlorosilane; and the main product of the chlorination of chloromethyltrimethylsilane is bischloromethyldimethylsilane[97,78]. Thus chlorosilyl groups possess a well developed orienting effect[67,73].

It is interesting to compare the chlorination behaviour of methylchlorosilanes and their carbon analogues[67]. Neopentane and tetramethylsilane react readily with chlorine on ultraviolet irradiation[11] to form analogous products, as is evident from the ratios

$$\frac{(CH_3)_3SiCHCl_2}{(CH_3)_2Si(CH_2Cl)_2}=0.66 \qquad \frac{(CH_3)_3CCHCl_2}{(CH_3)_2C(CH_2Cl)_2}=0.67$$

No such analogy is found in the chlorination of trimethylchlorosilane and t-butyl chloride. In an equimolar mixture of these compounds the former is chlorinated more slowly and with preferential substitution by chlorine of hydrogen atoms in the same methyl group, as is evident from the proportions of the chlorination products

$$\frac{(CH_3)_2(CHCl_2)SiCl}{CH_3(CH_2Cl)_2SiCl}=4.9 \qquad \frac{(CH_3)_2(CHCl_2)CCl}{CH_3(CH_2Cl)_2CCl}=0.67$$

These results show that differences in the direction of chlorination are determined primarily by the nature of the central atom.

The marked difference in rates of chlorination between methyl and chloromethyl groups attached to a silicon atom makes it difficult to obtain monochloro-derivatives of methylchlorosilanes, especially chloromethyltrichlorosilane. To obtain an appreciable yield of these compounds the chlorination of methylchlorosilanes is usually conducted at very low degrees of conversion of the initial silane[79]. A high yield of monochloro-derivatives can be achieved by continuous removal of the products from the reaction zone[73,81-89]. This principle has been used in the liquid-phase photochlorination of methylchlorosilanes[90,91] and in obtaining poly(monochloromethyl)silanes[92].

Elementary fluorine has been used[93,94] as initiator for the chlorination of methylchlorosilanes. The mechanism assumed for the reaction is

$$(CH_3)_2SiCl_2 + F_2 \rightarrow CH_3(\dot{C}H_2)SiCl_2 + HF + F\cdot$$
$$(CH_3)_2SiCl_2 + F\cdot \rightarrow CH_3(\dot{C}H_2)SiCl_2 + HF$$
$$CH_3(\dot{C}H_2)SiCl_2 + Cl_2 \rightarrow CH_3(CH_2Cl)SiCl_2 + Cl\cdot, \text{ etc.}$$

Azoisobutyronitrile, which readily generates free radicals when heated above 60°C, has recently become widely used as an initiator for the practical chlorination of organic compounds. Chlorination can be effected with 0.05–0.1% of this initiator in the dark at 70–90°C. Under these conditions the initiator dissociates into $\cdot C(CH_3)_2CN$ radicals, which react easily with chlorine. It is important to note that this compound is widely used in industry at the present time for processes taking place by a radical–chain mechanism. Its use has eliminated the defects inherent in photochemical chlorination (difficulty of producing powerful reaction vessels, danger of fire and explosions, etc.).

The initiated chlorination of organosilicon compounds by elementary chlorine in the presence of azoisobutyronitrile was first proposed in 1956, [95] and has now found practical application for the production of monochloro-derivatives of methylchlorosilanes. This is conducted in the liquid phase at 55–70°C, the content of the initiator in the original silane being initially not more than 0.1%. Subsequently the initiator is added periodically to the reaction mixture, or it is introduced continuously into the latter as a solution in the initial silane.

Chlorination of methylchlorosilanes in the presence of azoisobutyronitrile proceeds in conformity with the usual scheme for a chain reaction:

$$NC(CH_3)_2CN{=}NC(CH_3)_2CN \xrightarrow{\Delta} 2(CH_3)_2\dot{C}CN + N_2$$
$$(CH_3)_2\dot{C}CN + Cl_2 \rightarrow Cl\cdot + (CH_3)_2C(Cl)CN$$
$$CH_3(CH_3)_{3-n}SiCl_n + Cl\cdot \rightarrow \dot{C}H_2(CH_3)_{3-n}SiCl_n + HCl \quad (n=1-3)$$
$$\dot{C}H_2(CH_3)_{3-n}SiCl_n + Cl_2 \rightarrow CH_2Cl(CH_3)_{3-n}SiCl_n + Cl\cdot$$

Depending on the molar proportions of the reactants—the silane and chlorine—it is possible in this way to obtain a wide range of derivatives of methyltrichlorosilane, dimethyldichlorosilane, and trimethylchlorosilane containing chlorine atoms in the methyl groups[96-100]. The main rules of the substitution of hydrogen by chlorine atoms in methylchlorosilanes when chlorinated in the presence of azoisobutyronitrile proved to be the same as for photochemical chlorination. Figs. 1–3 illustrate the dependence of the composition of the chlorination products on the molar ratio of the reactants. The results show the detailed effect of the chlorosilyl group on the direction of the chlorination of methylchlorosilanes, and enable optimum conditions to be selected for obtaining their monochloro-derivatives. It is interesting that the content of monochloro-derivatives in the reaction mixture remains almost constant (at 9–10% for chloromethyltrichlorosilane, and 26–30% for methylchloromethyldichlorosilane and chloromethyldimethylchlorosilane) within a certain range (1 : 0.2–1.0) of molar ratios of silane to chlorine.

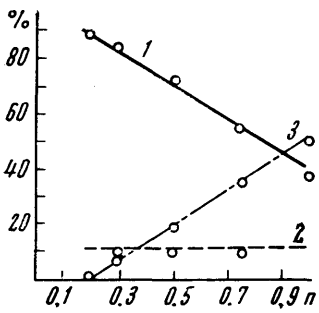


Figure 1. Dependence of composition of chlorination products of methyltrichlorosilane on number n of moles of chlorine per mole of the silane: 1) methyltrichlorosilane; 2) chloromethyltrichlorosilane; 3) dichloromethyltrichlorosilane.

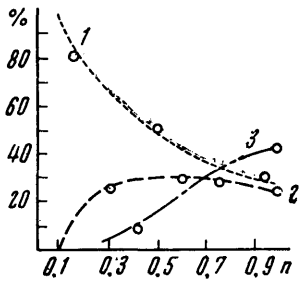


Figure 2. Dependence of composition of chlorination products of dimethyldichlorosilane on number n of moles of chlorine per mole of the silane: 1) dimethyldichlorosilane; 2) methylchloromethyldichlorosilane; 3) dichloro-derivative.

A detailed investigation of the chlorination of methyltrichlorosilane and dimethyldichlorosilane has shown that the composition of the reaction products depends not only

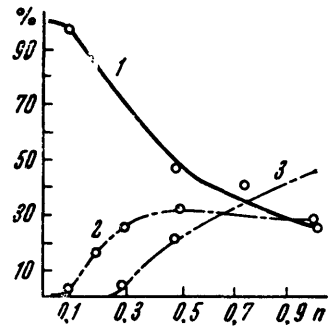


Figure 3. Dependence of composition of products of the chlorination of trimethylchlorosilane on number n of moles of chlorine per mole of the silane: 1) trimethylchlorosilane; 2) chloromethyldimethylchlorosilane; 3) dichloro-derivative.

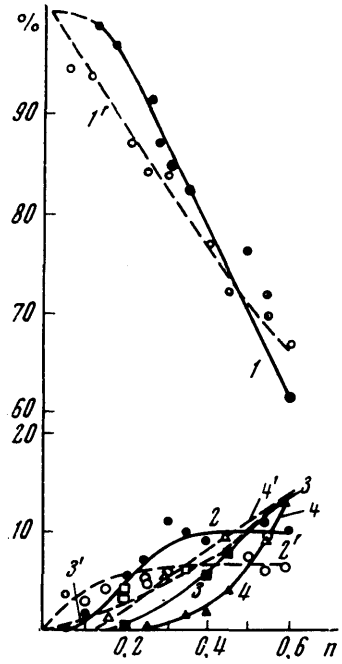


Figure 4. Dependence of composition of products of the chlorination of methyltrichlorosilane on number n of moles of chlorine per mole of the silane for chlorination in the dark in the presence of azoisobutyronitrile (full lines) and during exposure to ultraviolet radiation (broken lines): 1), 1′) methyltrichlorosilane; 2), 2′) chloromethyltrichlorosilane; 3), 3′) dichloromethyltrichlorosilane; 4), 4′) trichloromethyltrichlorosilane.

on the molar proportions of the reactants but also on the nature of the initiator[101] (Figs. 4 and 5). With azoisobutyronitrile as initiator the content of monochloro-derivative in the reaction mixture is 40–70% higher than in photochemical chlorination. It is interesting that, whereas in photochemical chlorination polychloro-derivatives of methyltrichlorosilane are formed at the molar

ratio $CH_3SiCl_3 : Cl_2 = 1 : 0.05$, this occurs with azoisobutyronitrile at a corresponding ratio of 1 : 0.15–0.2. The composition of the polychloro-derivatives is also different in the two cases: whereas in photochemical chlorination trichloromethyltrichlorosilane is formed (1–2%) at the molar ratio $CH_3SiCl_3 : Cl_2 = 1 : 0.15$, when azoisobutyronitrile is used the trichloro-derivative appears in the reaction mixture only at a molar ratio of the reactants of 1 : 0.25, and in only one-sixth of the quantity (0.2%) obtained with photochemical chlorination. Even with the same degree of conversion of the initial silane the quantity of polychloro-derivatives formed per unit weight of the monochloride in the presence of azoisobutyronitrile is 40–70% of the amount obtained in photochemical chlorination (Figs. 6 and 7). Thus the photochemical chlorination of methylchlorosilanes by elementary chlorine is a less selective process than chlorination initiated by azoisobutyronitrile.

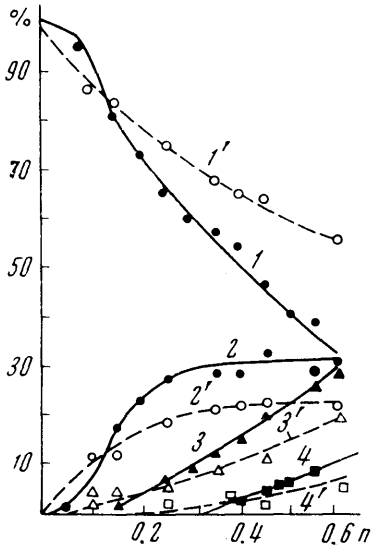


Figure 5. Dependence of composition of products of the chlorination of dimethyldichlorosilane on number *n* of moles of chlorine per mole of the silane for chlorination in the dark in the presence of azoisobutyronitrile (full lines) and during ultraviolet exposure (broken lines): 1), 1′) dimethyldichlorosilane; 2), 2′) methylchloromethyldichlorosilane; 3), 3′) dichloro-derivative; 4), 4′) trichloro-derivative.

The continuous chlorination of methylchlorosilanes in the presence of azoisobutyronitrile has been described[98]. In order to obtain an equivalent yield of the monochloro-derivative the process must be conducted at a lower degree of conversion of the initial silane than in the batch process (e.g. for methyltrichlorosilane 3–4% instead of 10%). The degree of conversion can be increased appreciably by the continuous chlorination of the residue of the initial silane directly in a fractionating column packed with Raschig rings[102]. Methylchlorosilane containing 2–2.5% of the initiator is fed to the upper part of the column, and chlorine gas enters the middle portion. The chlorination products are led from the reaction zone into the lower part of the column, where they are separated from unchanged methylchlorosilane. The latter returns to the reaction zone, where it mixes with the initiator solution supplied to this point. The products collect in the still. This procedure is possible only when a chemical initiator, e.g. azoisobutyronitrile, is used, but cannot be applied to photochemical initiation, since the packing would cut off the action of the light. Under these conditions the conversion of methyltrichlorosilane and dimethyldichlorosilane reaches 70–80% with a yield of monochloro-derivatives of 70–75% (based on the silane used).

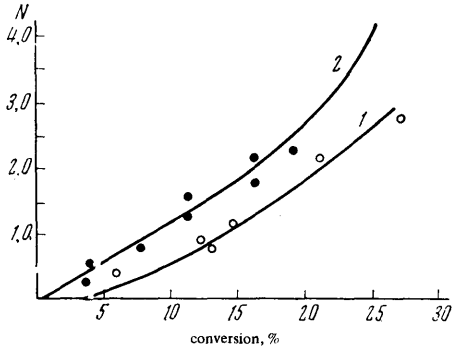


Figure 6. Dependence of quantity *N* of polychlorinated derivatives of methyltrichlorosilane formed per unit weight of the monochloro-derivative on degree of conversion of initial silane for chlorination: 1) in the presence of azoisobutyronitrile in the dark; 2) on ultraviolet exposure.

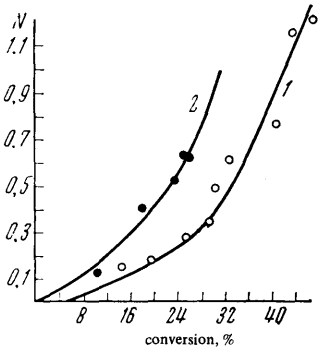


Figure 7. Dependence of quantity *N* of polychlorinated derivatives formed per unit weight of the monochloro-derivative on degree of conversion of dimethyldichlorosilane during chlorination: 1) in the presence of azoisobutyronitrile in the dark; 2) during exposure to ultraviolet radiation.

Another chemical initiator which merits attention is acetyl cyclohexanesulphonyl peroxide[103], which easily decomposes at 30–70°C to form free radicals:

$$C_6H_{11}SO_2OOCOCH_3 \rightarrow C_6H_{11}SO_2O^{\cdot} + CH_3COO^{\cdot}$$

With the chlorination of methyltrichlorosilane and dimethyldichlorosilane as examples this peroxide has been shown to be a more active initiator than is azoisobutyronitrile[104].

Considerably less work has been done on the preparation of polychlorinated methylchlorosilanes and methylpolysiloxanes.

Trichloromethyltrichlorosilane is easily formed by the photochemical chlorination of methyltrichlorosilane in the absence of a solvent at high temperatures[17] or in chloroform under ordinary conditions[68]. The photochemical chlorination of dimethyldichlorosilane extends[68] to the substitution of only five hydrogen atoms, but in the chlorination of trimethylchlorosilane up to eight hydrogen atoms are replaced. Later investigations have confirmed[105,106] that the chlorination of dimethyldichlorosilane in the presence of azoisobutyronitrile proceeds easily to the trichloro-derivative, after which the process is abruptly retarded. Pentachlorodimethyldichlorosilane is formed with great difficulty, requiring the prolonged action of excess of chlorine at 105–110°C. Under these conditions the main process is accompanied by secondary cleavage of the chlorination products at the silicon–carbon bond with the formation of carbon tetrachloride and trichloromethyltrichlorosilane, so that bistrichloromethyldichlorosilane cannot be obtained in this way. Cleavage is greatly diminished by conducting the chlorination of dimethyldichlorosilane under milder conditions—in a solvent (carbon tetrachloride) at 20–25°C (ultraviolet irradiation)—when yields of up to 60% of bistrichloromethyldichlorosilane have been obtained[105,106].

The polychlorination of trimethylchlorosilane is still more difficult[107]. Tristrichloromethylchlorosilane has been obtained in 50% yield only by the prolonged action on trimethylchlorosilane of a large excess of chlorine (molar ratio 19:1) in the presence of azoisobutyronitrile and a small amount of carbon tetrachloride at 53–65°C.

Most polychlorinated methylchlorosilanes are white crystalline substances, sensitive to atmospheric moisture and to heat. Since it is difficult to separate mixtures of these chlorides by distillation, they are converted into alkoxy-derivatives, which can be separated by normal fractional distillation. The following compounds—$CCl_3Si.(OC_2H_5)_3$, $CH_3Si(CCl_3)(OC_2H_5)_2$, $(CCl_3)_2Si(OC_2H_5)_2$, and $(CCl_3)_3SiOC_2H_5$—and also several intermediate chloromethylethoxysilanes—$CH_3Si(CHCl_2)(OC_2H_5)_2$, $CCl_3Si(CH_2Cl).(OC_2H_5)_2$, and $CCl_3Si(CHCl_2)(OC_2H_5)_2$—have been isolated in this way[105,107].

Ethoxytrichloromethylchlorosilanes decompose violently when heated rapidly. Thus trichloromethyltrichlorosilane, in contrast to mono- and di-chloromethyltrichlorosilanes, decomposes readily at 160–175°C:[108]

$$2CCl_3SiCl_3 \rightarrow 2SiCl_4 + C_2Cl_4$$

Tristrichloromethylchlorosilane and ethoxytristrichloromethylsilane are stable when heated, but replacement of a chlorine atom by hydrogen even in only one trichloromethyl group sharply lowers the stability of such a molecule[109]. The exhaustive chlorination of polychloromethylchlorosilanes in a fluidised bed of catalyst (activated carbon) at 300°C results in high yields of carbon tetrachloride and silicon tetrachloride[110].

The polychlorination of linear and cyclic methylsiloxanes exposed to ultraviolet radiation[16,109,111–113] is accompanied by cleavage of Si–O–Si bonds, with the formation of compounds of low molecular weight containing Si–Cl as well as Si–O bonds.

The chlorination of a dimethylsiloxane elastomer as a 5% solution in carbon tetrachloride in the presence of azoisobutyronitrile at 50°C proceeds slowly to the formation of a polymer of mean composition $[(C_2H_2Cl_4)SiO]_n$ and is accompanied by degradation of the molecule[114]. On storage the chlorinated polymer gradually decomposes. Analysis shows that the elastomer chain contains all possible chloromethyl groups—CH_2Cl, $CHCl_2$, and CCl_3—which indicates that it is impossible to obtain a perchlorodimethylsiloxane polymer whose macromolecules are built up solely of $(CCl_3)_2SiO$ units.

In contrast to the dimethylsiloxane elastomer, octamethylcyclotetrasiloxane is chlorinated in the presence of azoisobutyronitrile (at 60°C) without cleavage of Si–O–Si bonds[115], a complicated mixture of chlorides of various degrees of substitution being formed. Chloromethylheptamethylcyclotetrasiloxane has been isolated from the products of the photochemical chlorination of octamethylcyclotetrasiloxane[70,116]. The chlorination of hexamethyldisiloxane is not accompanied by fission of the siloxane bond when the products are able to escape from the reaction zone, so that the yield of monochloro-derivative is quite high[86,117]. Under analogous conditions methoxytrichlorosilane gives $ClCH_2OSiCl_3$, exhaustive chlorination of which yields CCl_3OSiCl_3.[119,120] The products of the photochemical chlorination of methylchlorodisilanes

$$(CH_3)_n Cl_{3-n} SiSiCl_{3-m} (CH_3)_m \; (n\,m = 0, 1, 2;\; n + m > 1)$$

at 0–100°C are $(ClCH_2)(CH_3)_{n-1}Si_2Cl_{6-n}$.[121]

Perchlorinated methylchlorosilanes and methylsiloxanes may decompose spontaneously and explosively[109].

The chlorination of the higher alkylchlorosilanes exhibits special features due to the nature of the alkyl radicals.

Ethyl derivatives of silicon react readily with chlorine. Tetraethylsilane is chlorinated under normal conditions in the absence of initiators with the formation of mono- and di-chloro-derivatives[122,123], the reaction being accelerated appreciably by the addition of phosphorus pentachloride[20,22,124]. Study of the photochemical chlorination of ethylchlorosilanes[73,125–129] has established certain rules for the direction of chlorination. In effect only hydrogen attached to an α-carbon atom in tetraethylsilane is replaced by chlorine. The activity of hydrogen atoms attached to a β-carbon atom increases appreciably with the accumulation of chlorine atoms attached to silicon in ethylchlorosilanes; thus the monochloro-derivative formed by the chlorination of ethyltrichlorosilane contains a considerable quantity of the β-chloride ($CH_3CHClSiCl_3 : ClCH_2CH_2SiCl_3 = 1 : 1.6–1.8$). The chlorination of ethylchlorosilanes in the presence of azoisobutyronitrile[130] maintains essentially the same effects of silyl groups on the rate and the direction of chlorination as in the photochemical process. The yields of monochloro-derivatives of ethylchlorosilanes are equivalent in the two cases, but the simplicity of the apparatus required indicates that preference should be given to chlorination initiated by azoisobutyronitrile.

The polychlorination of ethyltrichlorosilane and diethyldichlorosilane in the presence of azoisobutyronitrile (at 80°C), and also on ultraviolet irradiation[130–133], in contrast to the corresponding chlorination of methylchlorosilanes, does not involve fission of the silicon–carbon bond and leads to the formation of the perchloroethyl derivatives [$C_2Cl_5SiCl_3$ and $(C_2Cl_5)_2SiCl_2$]. Under these conditions tetrachloroethyltrichlorosilane has been isolated from the products of the polychlorination of ethyltrichlorosilane. The hydrolysis of polychloroethylchlorosilanes with water and aqueous alkalis is accompanied by β-decomposition with the formation of tetra- and tri-chloroethyl-

enes. The dehydrochlorination of tetrachloroethyltrichlorosilane under the influence of high temperatures and also of quinoline[131] involves β-decomposition; the main product of dehydrochlorination under the influence of aluminium chloride is trichlorovinyltrichlorosilane. This compound is formed also by the dechlorination of perchloroethyltrichlorosilane in the presence of copper powder[131].

A β-orienting effect is still more strongly developed with ethylfluorosilanes ($CH_3CHClSiF_3$: $ClCH_2CH_2SiF_3$ = 1 : 4.4),[134] which is explained by the considerably greater electronegativity of the fluorine than of the chlorine atom. It is interesting that, when ethylmethyldichlorosilane undergoes chlorination, the chlorine enters mainly the ethyl radical[135]. Attempts have been made[126,136] to explain the rules of the chlorination of ethylchlorosilanes by the electronic structure of these compounds.

The orienting effect of the trichlorosilyl group is apparent also in the photochemical chlorination of propyltrichlorosilane[87], as is indicated by the relative proportions of 1-, 2-, and 3-chloropropyltrichlorosilanes formed (0.7 : 1 : 1). As with ethyltrichlorosilane, 70% more of the β-chloro-derivative than of the α-chloro-derivative is formed from isopropyltrichlorosilane[137]. These and other papers[138,139] refer to the need to remove monochloro-derivatives from the reaction zone. This method has been used also for the chlorination of bistrichlorosilylmethane[87], 1,2-bistrichlorosilylethane[23,87,140], and several other chloroalkylchlorosilanes[78,92,139,141]. The photochemical chlorination of $CF_3CH_2CH_2SiCl_3$ and $CF_3CH_2CH_2SiCl_2CH_3$ leads to the formation of monochloro-derivatives containing the chlorine atom in the CF_3CH_2CHCl radical mainly in the α-position relative to the silicon atom[142,143]. With $CF_3CH_2CH_2SiCl(CH_3)_2$ and $CF_3CH_2CH_2SiCl_2C_2H_5$ the direction of chlorination is determined not only by the trifluoromethyl group but also by the nature of the chlorosilyl group[144].

The liquid-phase photochemical chlorination of more complicated organosilicon compounds has been described[19,145-149], and also the preparation of polychloro-derivatives of several other alkylchlorosilanes[150-153].

Cobalt-60 γ-radiation has been used to initiate the chlorination of alkylchlorosilanes, in particular trimethylchlorosilane[153,154]. The chlorination of methylchlorosilanes under the influence of radiation[155-158] conforms mainly to the same rules as their chlorination under the influence of ultraviolet radiation and in the presence of chemical initiators. The composition of the products, determined by the molar proportions of the reactants (silane and chlorine), is independent of the dosage rate. The radiation chlorination of a dimethylsiloxane elastomer has been reported[159,160]. The radiation chlorination of ethyltrichlorosilane[157,158] leads to the formation of α- and β-chloro-derivatives in the proportions 1 : 1.7, in agreement with results for the chlorination of ethylchlorosilane on exposure to ultraviolet radiation[73] and in the presence of azoisobutyronitrile[130].

A new method for obtaining chlorinated polyorganosiloxanes proposed recently is based on the combined hydrolytic polycondensation and chlorination of silicon-containing compounds by the hydrolysis of alkylchlorosilanes containing no chlorine atom in the hydrocarbon radicals, with simultaneous introduction of oxidants such as hydrogen peroxide, manganese dioxide, etc. into the reaction[161]. These convert the hydrogen chloride, formed by hydrolysis, into chlorine, which chlorinates the organic radical attached to the silicon. In this case three reactions—hydrolysis, condensation, and chlorination—take place in a single stage, but the apparent simplification in fact does not yield a polymer of high quality, and the technology is greatly complicated by the additional stage of purifying the final product from oxidants. In contrast to known processes of the oxidative chlorination of hydrocarbons, therefore, the above reaction is of no practical interest.

Little information has been published on the vapour-phase chlorination of alkylchlorosilanes at elevated temperatures (in the absence of ultraviolet radiation). Ethylchlorosilane at 350°C yields α- and β-monochloro-derivatives in the ratio 1 : 1.08.[141] When vinyltrichlorosilane is chlorinated under these conditions the main product is CH_2 : $CClSiCl_3$;[162] at a lower temperature (100–200°C) the reaction shifts towards formation of $ClCH_2CHClSiCl_3$. The chlorination of $F_2CHCF_2SiCl_3$ (at 150–200°C) yields $ClCF_2CF_2SiCl_3$.[163]

Unsaturated organosilicon compounds are chlorinated extremely readily by elementary chlorine to form predominantly addition products[69,77,162-169]. In contrast to vinyltrichlorosilane, however, trichlorovinyltrichlorosilane does not add chlorine at the double bond in the absence of illumination at 0–100°C.[170,171] The presence of lithium chloride under these conditions accelerates the addition of chlorine. Ultraviolet irradiation produces an especially marked acceleration of the reaction, its mechanism changing from heterolytic to a chain (homolytic) mechanism. The presence of an electron-donor trimethylsilyl group in the vicinity of the double bond in the trichlorovinyl radical facilitates the addition of chlorine to the double bond: thus trimethyltrichlorovinylsilane readily adds chlorine at the double bond in the absence of irradiation at 20°C.

(*b*) Chlorination by sulphuryl chloride

Chlorination by sulphuryl chloride is usually accomplished in the presence of the free-radical type of initiators. With methylchlorosilanes this method of chlorination initially gave negative results[21,172,173]. Subsequently the use of chlorobenzene as medium enabled the temperature of the reaction to be raised and this accelerated the decomposition of benzoyl peroxide into the free radicals necessary for the occurrence of chlorination. In this way sulphuryl chloride can be used to chlorinate trimethylchlorosilane[173] and other methylchlorosilanes[69,174]. Under these conditions it is comparatively easy to chlorinate also bistrichlorosilylmethane and 1,2-bistrichlorosilylethane in spite of the presence of two trichlorosilyl groups[87]. In bistrimethylsilylmethane the methyl groups are the first to be chlorinated[175]. There are references to the chlorination with sulphuryl chloride of other silicon compounds containing a methyl group and a methylene group[21,176-179]. The chlorination of alkylchlorosilanes with sulphuryl chloride during exposure to ultraviolet radiation[180,181] enables individual chloro-derivatives of different degrees of substitution to be obtained depending on the molar ratio of the reactants. Such selectivity is not observed when chlorine is used.

The chlorination of methylchlorosilanes with sulphuryl chloride can be initiated by azoisobutyronitrile[182], which decomposes into free radicals at a lower temperature than is observed with benzoyl peroxide.

Ethylchlorosilanes are readily chlorinated by sulphuryl chloride in the absence of solvents, when 1- and 2-chloroethylchlorosilanes are formed[21,82,183]. Chlorine enters ethylmethyldichlorosilane predominantly in the ethyl group[184]. The chlorination of tetraethylsilane yields only

the α-isomer[22,73,94,185]. With decrease in the number of ethyl radicals attached to the silicon atom the β-orienting effect of the trichlorosilyl group is more strongly developed when sulphuryl chloride is used than on chlorination with chlorine[21,77,125,183,186]. For example, the proportions of 1- and 2-chloroethyltrichlorosilanes obtained with sulphuryl chloride are 1:2.5, compared with the 1:1.6–1.8 with chlorine.

The directional effect of a chlorosilyl group is evident also in the chlorination of higher alkylchlorosilanes by means of sulphuryl chloride[24,188,189]. Several cyclic organosilicon compounds react effectively with sulphuryl chloride[190–193]. The above regularities are observed also in the chlorination of alkylchlorosilanes containing chlorine atoms in the alkyl group, although the orienting effect of the trichlorosilyl group is then more complicated. Thus 2-chloroethyltrichlorosilane yields only the 2,2-derivative, whereas 1-chloroethyltrichlorosilane forms equal proportions of 1,1- and 1,2-dichloroethyltrichlorosilanes.

(*c*) Chlorination by *t*-butyl hypochlorite

t-Butyl hypochlorite can be used to chlorinate alkylchlorosilanes and alkylpolysiloxanes, the reaction being initiated with peroxides and ultraviolet radiation. Compounds of the types $(R_3Si)_2O$ (R = CH_3), $(R_2SiO)_4$, $C_6H_5SiR_3$, R_3SiCH_2Cl, R_4Si, and $(R_3Si)_2$ can be chlorinated by means of this agent[194,195]. However, this method is of no practical interest because of the difficulties of manipulations with t-butyl hypochlorite, resulting from the violent decomposition of the latter under the influence of light, heat, or contact with rubber.

2. Preparation of Bromoalkyl Compounds of Silicon

In contrast to chlorine, bromine does not always react with alkylchlorosilanes. It reacts extraordinarily easily with hydrocarbon derivatives of silicon[196–201], especially with the higher tetra-alkylsilanes[196,197]. As with chlorination, bromine first enters an α-position in tetraethylsilane[143,196–199]. A similar situation is found in the bromination of $(iso\text{-}C_3H_7SiO_{1.5})_8$ by means of *N*-bromosuccinimide[202].

Bromination of methyl- and ethyl-chlorosilanes has proved possible only by the combined action of bromine, chlorine, and ultraviolet radiation[179,183,203–206]. Sulphuryl chloride can be used instead of chlorine[207].

The photochemical bromination of linear and cyclic methylsiloxanes with a mixture of bromine and chlorine leads to the formation of mono- and poly-brominated derivatives[200,203,208,209]. Incompletely methylated polysiloxanes have been selectively brominated with bromine in the presence of a stoichiometric quantity of pyridine[210].

Bromine is easily added at the double bonds in unsaturated organosilicon compounds[167,211,212]; under certain conditions substitutive bromination is possible[213]. The bromination of allyltriethylsilane[25] and allyltrimethylsilane[214] is accompanied by β-decomposition of the reaction products. Allyldiethylsilane, naphthyltriallylsilane, and vinyltriethylsilane add bromine without cleavage of the silicon–carbon bond[25]. Trichlorovinyltrichlorosilane, unlike vinyltrichlorosilane, does not add bromine at 20–80°C.[171] Nor does trichlorovinyltrimethylsilane react with bromine at 20°C, although it readily adds chlorine under these conditions, as mentioned above. When the temperature of the reaction is raised to 80–85°C products resulting from cleavage at the silicon–carbon bond—bromotrichloroethylene and trimethylbromosilane—are formed exclusively[171].

V. ELECTROPHILIC HALOGENATION (CHLORINATION, BROMINATION) OF SILICON-CONTAINING AROMATIC AND ALIPHATIC–AROMATIC COMPOUNDS

Systematic study of the direct halogenation of aromatic and aliphatic–aromatic compounds of silicon began in 1948 with the catalytic chlorination of phenylchlorosilanes. Earlier work had been concerned mainly with the preparation of monohalogeno-derivatives of certain aromatic silanes by the organomagnesium method[215,216]. The direct halogenation of aromatic compounds of silicon is an electrophilic substitution catalysed by metal halides. This reaction easily leads to the substitution by halogen of the hydrogen atoms in the aromatic ring.

1. Preparation of Chloroaryl Compounds of Silicon

The first mention of the direct chlorination of phenyltriethylsilane appeared in 1874.[217,218] In 1941 the patent literature reported the possibility of obtaining polychlorophenylchlorosilanes by chlorinating diphenyldichlorosilane and methylphenyldichlorosilane with chlorine in the presence of iron and antimony halides as catalysts at 70 to 120°C.[219] Later investigations of the electrophilic chlorination of aromatic silanes established that, in the presence of iron, iron(III) chloride[220], antimony(III) chloride[25,222], aluminium chloride[221], iodine, or phosphorus pentachloride[222], different numbers of chlorine atoms can be introduced into the phenyltrichlorosilane[223–225] and diphenyldichlorosilane[224] molecules depending on the molar ratio of the reactants and the temperature. In the absence of a catalyst this reaction does not take place even at high temperatures (150–200°C). The electrophilic chlorination of phenyltrichlorosilane and diphenyldichlorosilane has been described also in several other publications[80,226–233].

Depending on the conditions—the presence of a catalyst and its nature, the duration of the action of chlorine, and the temperature—the substitutive chlorination of phenylchlorosilanes is accompanied by the parallel cleavage of the $Si-C_{Ar}$ bond[32,224,234]. This side-reaction occurs only in the presence of catalysts—metal halides—which form the sequence $AlCl_3 > FeCl_3 \gg SbCl_5$ according to their dearylating activity, in conformity with which this reaction occurs more or less intensely[57,58]. Cleavage of the $Si-C_{Ar}$ bond can be diminished by conducting chlorination at a lower temperature and in a solvent[235]. As already stated above, hydrogen chloride must be present in the reaction mixture for phenylchlorosilanes to be cleaved by metal halides (e.g. aluminium chloride)[60,61]. The chlorination of phenylchlorosilanes in the presence of iodine is not accompanied by rupture of the $Si-C_{Ar}$ bond.

The reactivity of arylchlorosilanes in electrophilic halogenation is determined by the nature of the atoms and groups attached to the silicon atom. In recent years various aromatic compounds containing a silyl group in the benzene ring or in a side-chain have been subjected to electrophilic halogenation. The results have provided a more exact idea of the orienting influence of the silyl group and have revealed the reactivity of several arylsilanes and alkylarylsilanes towards electrophilic substitution as a function of the nature of the atoms and groups attached to silicon.

The *meta*-orienting nature of the trichlorosilyl group, which is a consequence of its electron-acceptor properties, is clearly evident in the fact that the benzene ring in phenyltrichlorosilane is so deactivated that it does not react with either chlorine[224] or bromine[236] at 150–200°C, in contrast to benzene itself, which with bromine is able to give phenyl bromide in the absence of catalysts even at 60°C.[237] This *meta*-orienting power is distinctly shown also in the electrophilic chlorination of phenyltrichlorosilane, which gives a mixture of the *meta*-, *ortho*-, and *para*-isomers in the proportions 75 : 21 : 4 [238] and 74 : 24 : 2.[226] The trifluorosilyl group had a still stronger *meta*-orienting effect under these conditions (82 : 18 : 0).[239] Further investigations have shown[240] that on electrophilic chlorination phenyltrifluorosilane is more subject than phenyltrichlorosilane to cleavage at the silicon–carbon bond, so that only mono- and di-chloro-derivatives of phenyltrifluorosilane can be isolated from the reaction products.

It must be emphasised that, despite the deactivation of the aromatic ring in phenyltrichlorosilane, it can be chlorinated with chlorine in the presence of ionic catalysts even below 0°C with the formation solely of substitution products, in which the *meta*-isomer predominates[241]. A similar effect of the trichlorosilyl group is evident in the chlorination of phenyltrichlorosilane by means of iodine trichloride[242]. As a consequence of the presence of strongly polarised chlorine in this latter agent, the reaction takes place readily even at −40°C with the formation of a mixture of mono- and di-chloro-derivatives. Rise in temperature to −20°C appreciably accelerates the reaction, and under these conditions chlorination is accompanied by partial iodination of the aromatic ring. At 20°C the reaction occurs violently with the evolution of elementary iodine and the formation of substituted mono-, di-, and tri-chloro-derivatives. Unlike iodine trichloride the monochloride does not react with phenyltrichlorosilane at 20°C.[242]

With rise in temperature to 200°C the *meta*-orienting effect of the trichlorosilyl group on the chlorination of phenyltrichlorosilane becomes weaker (*meta* : *para* : *ortho* = 60 : 15 : 25).[243] At 350–400°C the trichlorosilyl group loses its *meta*-orienting power (39 : 39 : 22).[244]

The chlorination of phenyltrichlorosilane by means of sulphuryl chloride exposed to ultraviolet radiation[181] is extremely sluggish and is accompanied by cleavage of the $Si-C_{Ar}$ bond.

The introduction of an *ortho*–*para*-orienting substituent (methyl) into the phenyltrichlorosilane molecule results in some activation of the aromatic ring, so that *p*-tolyltrichlorosilane, in contrast to phenyltrichlorosilane, reacts with chlorine in the absence of a catalyst at only 95–100°C.[245] In the presence of metal halides [iron(III) chloride, antimony trichloride] *p*-tolyltrichlorosilane is easily chlorinated as far as the replacement of three hydrogen atoms in the aromatic ring. When an attempt is made to obtain the tetrachloro-derivative, cleavage of the $Si-C_{Ar}$ bond takes place. The results obtained for the interaction of a halogen with *p*-tolyltrichlorosilane indicate that the latter behaves normally in electrophilic substitutions: the entering halogen atom is directed by both existing substituents (1-methyl and 4-trichlorosilyl), in conformity with their nature, to position 2.

The introduction, into the aromatic ring of phenyltrichlorosilane, of a second kind of orienting group (trichloromethyl), which is a *meta*-orienting substituent, results in strong deactivation of the benzene ring. In fact, *p*-trichloromethylphenyltrichlorosilane is difficult to chlorinate at 100–110°C even in the presence of catalysts[245], mono- and dichloro-derivatives being formed; further chlorination of this compound results in cleavage of the $Si-C_{Ar}$ bond. A chlorine atom entering the aromatic ring of *p*-trichloromethylphenyltrichlorosilane is directed by both substituents (1-trichloromethyl and 4-trichlorosilyl) to positions 2 and 3.

The trifluoromethyl group has a still stronger deactivating effect on an aromatic ring, so that *p*-trifluoromethylphenyltrichlorosilane and *p*-trifluoromethylphenyltrifluorosilane, in contrast to *p*-trichloromethylphenyltrichlorosilane, do not react with chlorine at 120°C even in the presence of iron(III) chloride[246].

A similar effect is observed when two trichlorosilyl groups are present in the aromatic ring. Electrophilic chlorination of bistrichlorosilylbenzene takes place with great difficulty, and leads to the substitution of only one hydrogen atom in the aromatic ring. Further chlorination results in cleavage of the $Si-C_{Ar}$ bond[247].

The methylene bridge separating the trichlorosilyl group from the aromatic ring in benzyltrichlorosilane produces marked changes in the orienting influence and the deactivating effect of the trichlorosilyl group[248]. Unlike phenyltrichlorosilane, benzyltrichlorosilane reacts with chlorine even at ordinary temperatures to form *p*-chlorobenzyltrichlorosilane. In the presence of catalysts the whole possible range of chloro-derivatives containing 1–5 nuclear chlorine atoms is formed: the first chlorine atom enters the ring only in the *para*-position, and the next two chlorine atoms *ortho* to the trichlorosilylmethyl group[248,249]. In contrast to phenyltrichlorosilane, these reactions are not accompanied by cleavage of the silicon–carbon bond. Similar results have been obtained for the electrophilic chlorination of benzylmethyldichlorosilane: methylpentachlorobenzyldichlorosilane $C_6Cl_5CH_2SiCl_2CH_3$ has been isolated from the products of the reaction[250].

It is interesting that the trichlorosilyldichloromethyl group, in contrast to the trichlorosilylmethyl group, is *meta*-orienting towards a chlorine atom entering the aromatic ring. Thus the electrophilic chlorination [in the presence of iron, iron(III) chloride, antimony(V) chloride] of $\alpha\alpha$-dichlorobenzyltrichlorosilane yields *m*-chlorophenyldichloromethyltrichlorosilane[242]. Further chlorination gives the trichloro-derivative. The compound containing five chlorine atoms in the ring cannot be obtained because of cleavage of the silicon–carbon bond.

The replacement of halogen atoms attached to silicon by the less electronegative alkyl groups leads to a change in the orienting effect of the silyl group. A detailed study of this phenomenon has been made on the electrophilic halogenation of methylphenyldichlorosilane[251–253] and phenyltrimethylsilane[239,254].

The chlorination of phenylmethyldichlorosilane in the absence of catalysts at 50–115°C results in nuclear substitution (to give mono-, di-, and tri-chloro-derivatives) and is accompanied by appreciable cleavage of the $Si-C_{Ar}$ bond. At 145–150°C compounds of the type $C_6H_{5-n}Cl_n \cdot SiCl_2CCl_3$ appear, which under these conditions readily decompose at the $Si-C_{Alk}$ bond to form carbon tetrachloride and $C_6H_{5-n}Cl_nSiCl_3$.[254] The chlorination of phenylmethyldichlorosilane in the presence of antimony trichloride[252,253] leads to the formation merely of the dichloro-derivative and is accompanied by considerable cleavage of the $Si-C_{Ar}$ bond. On chlorination in the presence of iodine[253,256], especially under mild conditions (in carbon tetrachloride at 10–12°C),[253] degradation is greatly diminished, so that trichlorophenylmethyldichlorosilane can be obtained. The yield of polychloro-derivatives is increased by chlorinating in the presence of iodine

the monochloro-derivative, chlorophenylmethyldichlorosilane[257]. The rate of chlorination of the aromatic ring and the rate of cleavage of the $Si-C_{Ar}$ bond increase in the sequence $C_6H_5SiCl_2CH_3 < C_6H_5SiCl(CH_3)_2 < (C_6H_5)_2SiClCH_3$.[256] Phenylmethyldichlorosilane does not react with sulphuryl chloride in the presence of ionic catalysts.

During electrophilic chlorination phenyltrimethylsilane undergoes considerable cleavage at the $Si-C_{Ar}$ bond, so that the yield of the monochloro-derivative does not exceed 50%.[254]

Phenylmethyldichlorosilane yields ~60% of the *m*-chloro-isomer, but chlorination of phenyltrimethylsilane gives mainly the other two isomers (*para* + *ortho* : *meta* = 78 : 22).[239,254] Thus the replacement of chlorine atoms attached to silicon by electropositive methyl radicals changes the *meta*-orienting power of the silyl group into an *ortho*–*para*-orientation effect.

It is interesting that the presence of the trichloromethyl group attached to silicon in phenyltrichloromethyldichlorosilane results in considerable deactivation of the aromatic ring and strengthening of its bond with silicon. In its behaviour towards electrophilic chlorination this compound resembles phenyltrichlorosilane, the trichloromethyldichlorosilyl group, like the trichlorosilyl group, having a *meta*-orienting effect[258]. Phenyltrichloromethyldichlorosilane behaves similarly on electrophilic bromination[259].

The chlorination of 1-naphthyltrichlorosilane[260] in the presence of the usual catalysts for the halogenation of aromatic compounds [iron(III) chloride, antimony trichloride] at 55–100°C yields various chloro-derivatives (from mono- to tetra-chloronaphthyltrichlorosilanes) in yields of 60–90%. Cleavage of the silicon–carbon bond does not occur and, in spite of the prolonged action of excess of chlorine (molar proportions of $1\text{-}C_{10}H_7SiCl_3 : Cl_2 = 1 : 25$), the reaction terminates at the formation merely of the tetrachloro-substituted derivative. Attempts to obtain more highly chlorinated products by raising the temperature (to 150°C and above) have been unsuccessful, since cleavage of the silicon–carbon bond occurs under these conditions.

Several publications have appeared on the ionic chlorination of certain other aromatic silanes—biphenyl-4-yltrichlorosilane[261], *p*-xylyltrichlorosilane[262], and tetraphenylsilane[263]. Polychloro-derivatives of aromatic silanes have been obtained by chlorinating the latter in the presence of a mixed catalyst ($FeCl_3 + SbCl_5$),[229] and also in the presence of aluminium chloride and iron(III) chloride in an organic solvent[238,263]. Chlorination of polytitanophenylsiloxanes[264] and polyaluminophenylsiloxanes[265] in the presence of a catalyst (phosphorus pentachloride) in carbon-tetrachloride solution gives the corresponding polymers having chlorine atoms in the phenyl groups, which possess improved thermal stability in comparison with the original compounds.

2. Preparation of Bromoaryl Compounds of Silicon

With rare exceptions the direct bromination of arylsilanes is accompanied by cleavage of the $Si-C_{Ar}$ bond[27-29,33,215,239]. The tendency for the aromatic ring to become detached from the silicon atom diminishes as chlorine atoms accumulate on the silicon. Thus the bromination of phenyltrichlorosilane in the presence of iron(III) chloride gives a quite high yield of mono- and di-bromo-derivatives[203,224,226,236]. It is interesting that most (69%) of the bromophenyltrichlorosilane formed comprises a mixture of the *p*- and *o*-bromo-isomers (38% and 31%). These results indicate that the trichlorosilyl group exhibits an anomalous *ortho*–*para*-orienting effect during bromination.

Extraordinary ease of detachment is exhibited by the trifluorylsilyl group when phenyltrifluorosilane is brominated in the presence of iron[239]. Under mild conditions of bromination it is possible to obtain monobromophenyltrifluorosilane (in 52% yield)[240], which is a mixture of isomers (*meta* : *para* + *ortho* ≃ 60 : 40).

Phenylmethyldichlorosilane reacts readily with bromine in the absence of catalysts at 0–25°C to form mono- and di-bromophenylmethyldichlorosilanes[266]. Further increase in the extent of bromination under these conditions, as well as bromination in the presence of ionic catalysts, leads to considerable cleavage of the reaction products at the $Si-C_{Ar}$ bond. The first bromine atom to enter the aromatic ring of phenylmethyldichlorosilane occupies predominantly the *ortho* and *para* positions (*meta* : *ortho* : *para* = 25 : 35 : 40).

Phenyltrimethylsilane is cleaved quantitatively by bromine at the $Si-C_{Ar}$ bond, even under mild conditions.

Publication of a series of papers on the direct bromination of phenyltrichlorosilane[236], benzyltrichlorosilane[248], *p*-tolyltrichlorosilane[254], and phenylmethyldichlorosilane[266] has been followed by other investigations in this field. Study of the electrophilic bromination of compounds of the type $C_6H_5[CH_2]_nSiCl_mR_{3-m}$ ($n = 1, 2$; $m = 0-3$; and $R = CH_3$, C_2H_5) showed that in all cases the $[CH_2]_nSiCl_m$. R_{3-m} groups are strongly *ortho*–*para*-orienting[249,267]. The high reactivity of benzyltrimethylsilane compared with benzyltrichlorosilane is explained by conjugation of the silicon–carbon bond with the aromatic ring[267]. The bromination of benzyltrifluorosilane, in contrast to that of phenyltrifluorosilane, is not accompanied by cleavage of the silicon–carbon bond, the sole product being the *p*-bromo-isomer[239].

3. Mechanism of Electrophilic Substitution and Cleavage of the $Si-C_{Ar}$ Bond in Aryl- and Alkylaryl-chlorosilanes

The characteristic features of the substitutive chlorination of aryl- and alkylaryl-chlorosilanes agree well with the generally accepted mechanism of electrophilic substitution in the aromatic series:

$$Cl_2 + MCl_3 \rightleftarrows \overset{\delta+}{Cl} \ldots Cl \ldots \overset{\delta-}{MCl_3} \rightleftarrows \overset{+}{Cl}\,[MCl_4]^-$$

(M = Fe, Al, Sb)

$$C_6H_5SiCl_3 + \overset{+}{Cl}\,[MCl_4]^- \rightarrow \left[\text{C}_6\text{H}_5(\text{SiCl}_3)(\text{Cl})\right]^+ [MCl_4]^- \rightarrow C_6H_4ClSiCl_3 + HCl + MCl_3$$

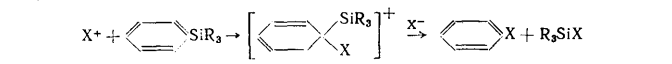
Phenylchlorosilanes react by a similar mechanism with iodine trichloride, which acts here as a reactive electrophilic form of the halogen[242]:

$$ICl_3 \rightleftarrows \overset{+}{Cl}\,[ICl_2]^-$$

$$C_6H_5SiCl_3 + \overset{+}{Cl}\,[ICl_2]^- \rightarrow \left[\text{C}_6\text{H}_5(\text{SiCl}_3)(\text{Cl})\right]^+ [ICl_2]^- \rightarrow C_6H_4ClSiCl_3 + HCl + ICl$$

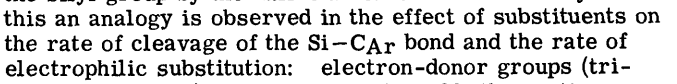
As already noted above, a characteristic feature of the electrophilic halogenation of arylsilanes and alkylarylsilanes is the accompanying secondary degradative halogenation involving cleavage of starting materials and products at the $Si-C_{Ar}$ bond with the formation of halogenated aromatic derivatives not containing silicon. A definite relation exists between such cleavage and electrophilic substitution in aryl- and alkylaryl-chlorosilanes[37-52,69,268-273].

Thus trialkylsilyl groups are detached from an aromatic ring by a mechanism of electrophilic substitution[33,44-51]:



In this case electrophilic attack on the aromatic ring by the halogen cations, leading to formation of an intermediate addition product, is accompanied by nucleophilic attack on the silyl group by the halide anions. In conformity with this an analogy is observed in the effect of substituents on the rate of cleavage of the $Si-C_{Ar}$ bond and the rate of electrophilic substitution: electron-donor groups (trimethylsilyl, etc.) increase the rates of both reactions; electron-acceptor groups (trichlorosilyl) decrease the rates. The tendency of the $Si-C_{Ar}$ bond to undergo cleavage by the halogen falls rapidly in the sequence $C_6H_5Si(CH_3)_3 > C_6H_5SiCl(CH_3)_2 > C_6H_5SiCl_2CH_3 > C_6H_5SiCl_3$. The rate of cleavage is determined not only by the nature of the silyl group but also significantly by induction and steric effects, the nature of the halogen, the catalyst, and other factors.

Cleavage of the $Si-C_{Ar}$ bond by the hydrogen halide formed during halogenation in the presence of ionic catalysts takes place by an analogous mechanism of electrophilic substitution[60-62,239,274]:



where R = Alk, Cl, F; X = Cl, Br; and M = Fe, Al, Sb.

The sequence of increasing stability of aromatic silanes to cleavage by the $HX.MX_3$ complex under conditions of halogenation is

$$R_3'SiR < RR'SiCl_2 < R_2SiCl_2 < RSiF_3 < p\text{-}R'C_6H_4SiCl_3 < p\text{-}CCl_3C_6H_4SiCl_3 < RSiCl_3,\ RSiCl_2(CCl_3),$$

where $R = C_6H_5$ and $R' = CH_3$.

Fluorine atoms, in spite of their greater electronegativity, are for steric reasons incapable of resisting nucleophilic attack on the silicon atom, so that cleavage of the $Si-C_{Ar}$ bond takes place more easily in phenyltrifluorosilane than in phenyltrichlorosilane.

VI. RADICAL HALOGENATION (CHLORINATION, BROMINATION) OF SILICON-CONTAINING ALIPHATIC–AROMATIC AND AROMATIC COMPOUNDS

1. Substitutive Halogenation with Replacement of Alkyl Hydrogen Atoms by Chlorine and Bromine

The photochemical chlorination of alkylarylchlorosilanes yields substitution products containing chlorine in the alkyl radical or in the aliphatic portion of an aralkyl group[179,275-280]. It is interesting that *o*-tolyltrichlorosilane, in contrast to *p*-tolyltrichlorosilane, is not chlorinated, probably because of the steric effect of the trichlorosilyl group[155,277], for the less bulky trifluorosilyl group does not exert such hindrance. Benzyltrichlorosilane can be chlorinated with sulphuryl chloride in the presence of benzoyl peroxide[173].

Tolyl and benzyl groups in hydrocarbon derivatives of silicon are easily brominated by *N*-bromosuccinimide, usually without cleavage of the $Si-C_{Ar}$ bond[179,281,282]. Tetra-*p*-tolylsilane and certain other hydrocarbon derivatives of silicon are exceptions[179,283]. When benzylsilane is brominated in weak daylight (at 8°C), α-bromobenzyltribromosilane is formed. Heating a mixture of benzylsilane and bromine in sunlight yields αα-dibromobenzyltribromosilane[284].

The radical chlorination of aliphatic–aromatic chlorosilanes has been studied in the greatest detail on *p*-tolyl- and benzyl-trichlorosilanes, and also on phenyl- and *p*-tolyl-methyldichlorosilanes, in the presence of azoisobutyronitrile as initiator.

Chlorination of *p*-tolyl- and benzyl-trichlorosilanes in the presence of this initiator[95,97,285] takes place without cleavage of the reaction products at the silicon–carbon bond. The process can easily be controlled with the formation of compounds of a desired degree of substitution. A distinguishing feature of these reactions is the formation of the monochloro-derivatives in high yields with complete conversion of the initial silane (in contrast to aliphatic chlorosilanes). Among polychloro-derivatives *p*-trichloromethylphenyltrichlorosilane is of practical interest as the starting material for the preparation of *p*-trifluoromethylphenyltrifluorosilane. α*H*-Hexachlorobenzyltrichlorosilane $C_6Cl_5CHClSiCl_3$ has been isolated from the products of the photochemical chlorination of pentachlorobenzyltrichlorosilane[286]; the product of the exhaustive chlorination of benzyltrichlorosilane cannot be obtained.

The chlorination of phenylmethyldichlorosilane can occur selectively—either in the methyl group or in the aromatic ring—depending on the nature of the catalyst. Initiation with azoisobutyronitrile leads to the formation of all possible products in which the methyl group is substituted[287,288]. The ability of the chloromethyl group to be chlorinated more easily than the unsubstituted methyl group is clearly evident in phenylmethyldichlorosilane, just as in the methylchlorosilanes, which is indicated by the ~10% content of the dichloro-derivative in the reaction mixture on conversion of the initial silane. Under otherwise similar conditions the content of polychloro-derivatives in the reaction mixture is appreciably higher in the continuous chlorination of phenylmethyldichlorosilane[289] than with a batch method of chlorination: i.e. the situation is the same as in the chlorination of methylchlorosilanes. The exhaustive chlorination of phenylmethyldichlorosilane in the presence of azoisobutyronitrile at 110–115°C is not accompanied by side-reactions and gives a 90% yield of phenyltrichloromethyldichlorosilane. When the temperature is lowered to 45–50°C, the reaction mixture contains partly chlorinated products; and raising the temperature to 145–150°C lowers appreciably the yield of phenyltrichloromethyldichlorosilane owing to degradation of the chlorination products at the silicon–carbon bond. Because of the high selectivity of the reaction it is desirable to obtain this product by a continuous counterflow scheme[290]. The chlorination of benzylmethyldichlorosilane in the presence of azoisobutyronitrile (at 110°C) results in the formation of αα-dichlorobenzyltrichloromethyldichlorosilane[250]. This compound is obtained also by photochemical chlorination, but then a nuclear addition product, hexachlorocyclohexylmethylmethyldichlorosilane, is also formed[250].

The rate of chlorination of the methyl group in compounds of the type $C_6H_{5-n}Cl_nSiCl_2CH_3$ decreases with increase in n.[291] When $n = 1$ the *p*-chloro-isomer is chlorinated considerably more easily than is the *meta*-isomer, although chlorination of *p*-chlorophenylmethyldichlorosilane is slower than that of unsubstituted phenylmethyldichlorosilane.

Sulphuryl chloride proved to be a milder chlorinating agent for phenylmethyldichlorosilane, and was more selective, so that a high yield of phenyldichloromethyldichlorosilane could be obtained[292].

The chlorination of *p*-tolylmethyldichlorosilane in the presence of azoisobutyronitrile at 110–115°C (molar ratio

silane : chlorine = 1 : 3) leads initially to replacement of the nuclear methyl hydrogen atoms. With a large excess of chlorine (1 : 10) *p*-trichloromethylphenyltrichloromethyldichlorosilane is formed in 80% yield[293]. The fact that the aromatic ring of *p*-tolylmethyldichlorosilane contains a substituent of the first kind [*sic*—presumably means +*I* group (Ed. of Translation)] (a methyl group) *para* to the silicon atom weakens the $Si-C_{Ar}$ bond, as is indicated by the greater ease of cleavage of this compound than of phenylmethyldichlorosilane.

2. Addition of Chlorine at Double Bonds and Replacement of Nuclear Hydrogen Atoms by Chlorine

Phenyltrichlorosilane readily undergoes photochemical chlorination at ordinary temperatures (20°C) to form a product—hexachlorocyclohexyltrichlorosilane $C_6H_5Cl_6.SiCl_3$—in which chlorine atoms have added to the aromatic ring[294-296]. The yield decreases with rise in temperature, and at 120°C the photochemical chlorination of phenyltrichlorosilane proceeds solely as a substitution reaction (Fig. 8).

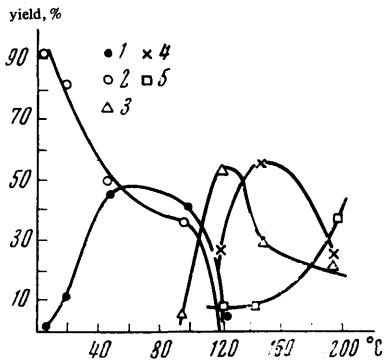


Figure 8. Temperature dependence of yield of products of the photochemical chlorination of phenyltrichlorosilane (for molar ratio $Cl_2 : C_6H_5SiCl_3 = 10 : 1$):
1) $C_6H_5SiCl_3$; 2) $C_6H_5Cl_6SiCl_3$; 3) $C_6H_4ClSiCl_3$; 4) $C_6H_3Cl_2SiCl_3$; 5) $C_6H_2Cl_3SiCl_3$.

The additive chlorination of phenyltrichlorosilane is a chain reaction initiated by free chlorine atoms according to the usual scheme:

$$Cl_2 \xrightarrow{h\nu} Cl^{\cdot} + Cl^{\cdot} \quad (1)$$

$$C_6H_5SiCl_3 + Cl^{\cdot} \rightarrow C_6H_5ClSiCl_3^{\cdot} \quad (2)$$

$$C_6H_5ClSiCl_3^{\cdot} + Cl_2 \rightarrow C_6H_5Cl_2SiCl_3 + Cl^{\cdot}, \text{etc.} \quad (3)$$

A free-radical mechanism is indicated by the fact that additive chlorination can be conducted in the presence of azoisobutyronitrile in the dark[297]. The overall rate of addition is limited by stage (2). Subsequent stages take place at very high rates, so that intermediate addition products—dichlorocyclohexadienyltrichlorosilane and tetrachlorocyclohexenyltrichlorosilane—cannot be detected in the products of the photochlorination of phenyltrichlorosilane: two components—phenyltrichlorosilane and hexachlorocyclohexyltrichlorosilane—are present in the reaction mixture, independently of the molar ratio of the reactants (silane and chlorine) (Fig. 9). The linear dependence of the logarithm of the phenyltrichlorosilane concentration on the duration of chlorination (Fig. 10) indicates that the reaction is of the first order with respect to the silane. The stepwise addition of chlorine to the aromatic ring is proved by the fact that the chain can be terminated by means of iodine, and tetrachlorocyclohexenyltrichlorosilane $C_6H_5Cl_4SiCl_3$ isolated[297].

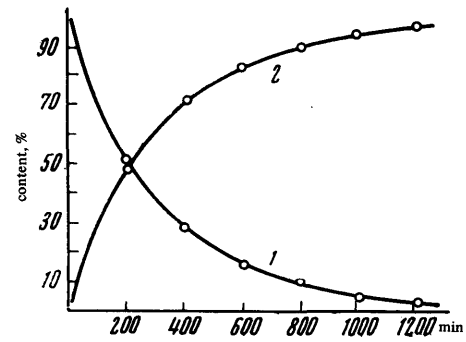


Figure 9. Dependence of composition of reaction mixture on extent of chlorination (at +5°C):
1) $C_6H_5SiCl_3$; 2) $C_6H_5Cl_6SiCl_3$.

The course of the radiation chlorination of phenyltrichlorosilane, initiated by cobalt-60 γ-radiation[18,148], is analogous to the photochemical process.

Hexachlorocyclohexyltrichlorosilane is a mixture of stereoisomers[101]. Its structure is confirmed by the infrared spectrum, which contains no absorption bands characteristic of an aromatic ring. Aqueous alkali hydrolyses this compound with detachment of the hexachlorocyclohexyl radical from the silicon atom. The hexachlorocyclohexane formed as an intermediate is dehydrochlorinated under these conditions and converted into trichlorobenzene. With absolute alcohols hexachlorocyclohexyltrichlorosilane forms the corresponding hexachlorocyclohexylalkoxysilanes. It is inert towards chlorine at 150°C and on exposure to ultraviolet radiation, and also at 75–100°C in the presence of iron(III) chloride. When heated to 550–580°C it splits off hydrogen chloride and is converted into trichlorophenyltrichlorosilane. The product of partial additive chlorination, tetrachlorocyclohexenyltrichlorosilane, is able to eliminate hydrogen chloride at 250°C with the formation of dichlorophenyltrichlorosilane.

Phenyltrifluorosilane forms an addition product, hexachlorocyclohexyltrifluorosilane, more easily than does phenyltrichlorosilane[295].

If the silane contains alkyl radicals as well as the phenyl group, the rate of addition of chlorine to the aromatic ring drops sharply. Thus the photochemical chlorination of phenyltrimethylsilane and *p*-tolyltrichlorosilane involves mainly substitution of the methyl hydrogen atoms, the yield of addition products not exceeding 10–12%.[295] The introduction of halogen atoms and trichloromethyl, trifluoromethyl, and trichlorosilyl groups into the aromatic ring of

phenyltrichlorosilane results in almost complete inhibition of additive chlorination.

Benzyltrichlorosilane gives a high yield of the nuclear addition product hexachlorocyclohexylmethyltrichlorosilane, which is formed on photochemical chlorination together with products in which the methylene hydrogen atoms have been replaced by chlorine[101,285,294].

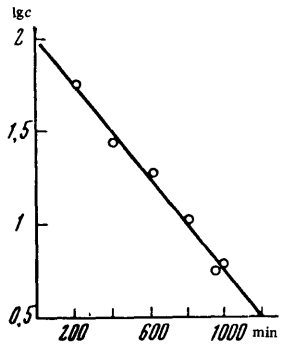


Figure 10. Dependence of logarithm of concentration of phenyltrichlorosilane on duration of chlorination.

Under the same conditions the additive chlorination of diphenyldichlorosilane proceeds relatively easily, but chlorine adds to only one aromatic ring to form hexachlorocyclohexylphenyldichlorosilane $C_6H_5Cl_6SiCl_2C_6H_5$.[295]

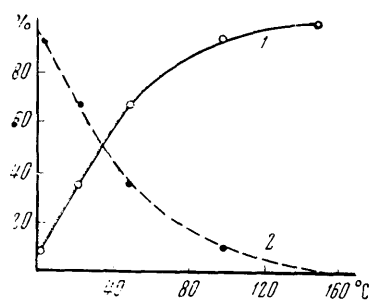


Figure 11. Temperature dependence of composition of products of the photochemical chlorination of phenylmethyldichlorosilane ($Cl_2 : C_6H_5SiCl_2CH_3 = 3.5 : 1$): 1) nuclear addition products; 2) products of substitution in the methyl group.

Addition of chlorine to 1-naphthyltrichlorosilane occurs especially easily with ultraviolet irradiation and a low temperature (0–5°C), but in spite of the prolonged action of excess of chlorine (molar ratio 1-$C_{10}H_7SiCl_3 : Cl_2$ = 1 : 12) the product is 1-$C_{10}H_7Cl_4SiCl_3$.[259,294] This indicates that the addition of chlorine to double bonds probably occurs only in one six-membered ring of 1-naphthyltrichlorosilane. At high temperatures, and also under the influence of iron(III) chloride, the compound 1-$C_{10}H_7Cl_4SiCl_3$ eliminates hydrogen chloride and is converted into dichloro-1-naphthyltrichlorosilane[260].

The action of chlorine on phenylmethyldichlorosilane in daylight at temperatures not above 5°C yields only the nuclear addition product hexachlorocyclohexylmethyldichlorosilane[294,298,299]. Raising the temperature to 20–25°C accelerates substitutive chlorination; at 50°C and above the main product is chlorophenylmethyldichlorosilane. The photochemical chlorination of phenylmethyldichlorosilane at 0°C gives an addition product[299,300]. With rise in temperature substitution in the methyl radical becomes predominant, and is the only process at 95–100°C (Fig. 11). The radical mechanism of formation of hexachlorocyclohexylmethyldichlorosilane is confirmed by the occurrence of additive chlorination in the presence of azoisobutyronitrile at 45–50°C.

The radiation chlorination of phenylmethyldichlorosilane by means of cobalt-60 γ-rays differs from its photochemical chlorination only in that rise in temperature leads to substitution of hydrogen atoms not in the methyl group but chiefly in the aromatic ring[157,169] (Fig. 12). With radiation chlorination the highest yield of chloromethyl products is observed at 20–30°C. Similar results have been obtained for the radiation chlorination of a phenylmethylpolysiloxane polymer[159].

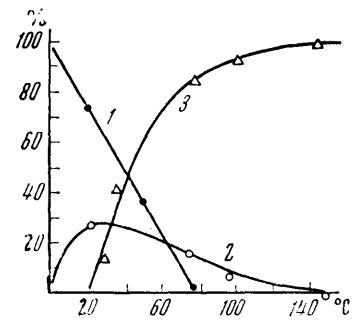


Figure 12. Temperature dependence of composition of products of the radiation chlorination of phenylmethyldichlorosilane: 1) nuclear addition products; 2) products of substitution in the methyl group; 3) nuclear substitution products.

It is interesting that no compounds containing both a hexachlorocyclohexyl radical and di- and tri-chloromethyl groups attached to silicon have been found among the products of the photochemical and radiation chlorination of phenylmethyldichlorosilane. This indicates considerable deactivation of the aromatic ring in phenyltrichloromethyldichlorosilane owing to the presence of the trichloromethyl group. This is confirmed by the exceptional inertness of this compound not only towards thermal and ionic chlorination but also towards additive chlorination[258].

Analysis of the data indicates a definite correlation among the electrophilic character of the substituent, the rate of additive chlorination of substituted aromatic com-

pounds of silicon, and steric hindrance. The sequence of increasing capacity for additive nuclear chlorination in aryl- and alkylaryl-silanes is

$$p\text{-}CF_3C_6H_4SiF_3,\ p\text{-}CCl_3C_6H_4SiCl_3,\ C_6H_4(SiCl_3)_2 < C_6H_4Cl_2SiCl_3 < < C_6H_4ClSiCl_3 < C_6H_5(CCl_3)SiCl_2 < (C_6H_5)_2SiCl_2,$$
$$\alpha\text{-}C_{10}H_7SiCl_3 < C_6H_5SiCl_3 < C_6H_5SiF_3 < C_6H_5(CH_3)SiCl_2,\ C_6H_5CH_2SiCl_3.$$

VII. CHLORINATION OF PHENYLTRICHLOROSILANE IN THE PRESENCE OF IODINE AND ON γ-IRRADIATION

The chlorination of phenyltrichlorosilane is distinguished by interesting features. Depending on the conditions chlorine either adds to the aromatic ring or replaces hydrogen atoms[101]. Photochemical chlorination at 0–50°C involves solely addition of chlorine. With rise in temperature the rate of substitutive chlorination increases with formation mainly of the *o*-chloro-isomer (43%). A similar reaction is observed in the chlorination of phenyltrichlorosilane in the presence of azoisobutyronitrile at 120–125°C. A still stronger shift towards predominant formation of the *o*-chloro-isomer (67%) occurs in the presence of iodine as catalyst[101,241,301]. Thus under the above conditions the trichlorosilyl group loses its inherent *meta*-orienting power.

An interesting property of iodine as catalyst is that it is able to activate equally the nuclear addition of chlorine and its nuclear substitution[101]. Both in the chlorination of benzene in the presence of iodine[302–304] and in that of phenyltrichlorosilane under similar conditions[101] there is simultaneous formation of substitution products (chlorophenyltrichlorosilane) and products of partial additive chlorination (tetrachlorocyclohexenyltrichlorosilane).

The addition of chlorine to an aromatic ring usually takes place by a radical mechanism. Since the formation of atoms and radicals is excluded in chlorination in the presence of iodine, the most probable mode of addition under these conditions must be assumed to be heterolytic, in which the iodine polarises the chlorine and promotes its addition:

$$Cl{-}Cl + I_2 \rightleftarrows \overset{\delta+}{Cl} \ldots \overset{\delta-}{ClI_2}$$

$$C_6H_5SiCl_3 + Cl^+ \rightarrow \left[\text{C}_6\text{H}_5(\text{SiCl}_3)\text{Cl}^+\right] \xrightarrow{+Cl^-} C_6H_4Cl_2SiCl_3 \quad \text{(I)}$$

$$C_6H_4Cl_2SiCl_3 + Cl^+ \rightarrow \left[C_6H_4Cl_3(SiCl_3)Cl^+\right] \xrightarrow{+Cl^-} C_6H_3Cl_4SiCl_3 \quad \text{(II)}$$

The cyclohexadiene system in (I) is highly reactive, and therefore the intermediate dichlorocyclohexadienyltrichlorosilane (I) cannot be isolated from the reaction products. Formation of the dichloro-derivative (I) is confirmed by the appearance among the chlorination products, together with tetrachlorocyclohexenyltrichlorosilane (II), of a considerable quantity of *o*-chlorophenyltrichlorosilane, obviously resulting from dehydrochlorination of (I):

$$\left[C_6H_5(SiCl_3)Cl_2\right] \xrightarrow{-HCl} C_6H_4Cl(SiCl_3)$$

This change in the usual electrophilic mechanism of substitutive chlorination probably explains the loss of the *meta*-orienting power of the trichlorosilyl group in the chlorination of phenyltrichlorosilane in the presence of iodine.

The radiation chlorination of phenyltrichlorosilane, initiated by cobalt-60 γ-rays[157] at 0–20°C, involves predominantly nuclear addition of chlorine to form hexachlorocyclohexyltrichlorosilane, and in this respect resembles photochemical chlorination. With rise in temperature nuclear substitution begins, and at 100°C the chlorination of phenyltrichlorosilane already consists solely in substitution. The isomeric composition of the monochlorophenyltrichlorosilane obtained under these conditions shows that in radiation chlorination the chlorosilyl group exerts its normal *meta*-orienting effect (*meta* : *ortho* : *para* = 75 : 20 : 5).

Substitutive chlorination of the phenyl group under the influence of γ-radiation is not inhibited by either oxygen or air. This suggests that the replacement of hydrogen atoms in the aromatic ring of phenyltrichlorosilane during radiation chlorination occurs by an ionic mechanism involving chlorine cations[157,305] formed by the radiolysis of chlorine:

$$Cl_2 \rightsquigarrow \begin{cases} Cl_2^+ + e^- \\ Cl^+ + Cl^- + e^- \end{cases}$$

The radiolysis of silanes is accompanied by the appearance in the reaction mass of excited molecular and splinter ions, which are able to react with a chlorine molecule:

$$[Ion]^+ + Cl_2 \rightarrow [ion]\,Cl + Cl^+$$

The primary Cl^+ ions can then react with a molecule of the initial silane:

$$C_6H_5SiCl_3 + Cl^+ \rightarrow C_6H_4ClSiCl_3 + H^+$$

The proton, on reacting with molecular chlorine, may liberate fresh chlorine ions:

$$H^+ + Cl_2 \rightarrow HCl + Cl^+ + 2.5\ eV$$

Regeneration of Cl^+ ions by these reactions will probably continue until either H^+ or Cl^+ combines with a negative ion, which will correspond to the stage of chain termination.

The only argument against an ionic mechanism for the radiation chlorination of phenyltrichlorosilane is the relatively high temperature of the reaction, since the lifetime of positive ions is too short under these conditions. It increases as the temperature becomes lower, and also in the presence of substances having a high electron affinity and a considerable capture cross-section for thermal electrons. In the present case chlorine and also phenyltrichlorosilane itself may fill this role. Hence there may be factors which promote reaction by an ionic mechanism at high temperatures.

VIII. PREPARATION OF ORGANOSILICON COMPOUNDS CONTAINING FLUORINE (IODINE) IN THE ORGANIC RADICALS

It is not possible to fluorinate organic radicals attached to a silicon atom directly by means of fluorine, because of the accompanying degradation of the molecule to be fluorinated. However, the valuable properties of fluorinated organosilicon polymers have stimulated research aimed at finding other methods for preparation of the corresponding monomers. The principal methods known at present will be described briefly below.

1. Organoelementary Method

The first organosilicon compound containing a fluorine atom in the organic radical was obtained[306] from *p*-fluorophenylmagnesium bromide and trimethylchlorosilane. A large number of diverse compounds of this type have since been obtained by Soviet[307-310] and foreign[311-313] workers. By means of Grignard reagents it is relatively easy to obtain various derivatives from silicon tetrachloride, silicochloroform, tetraethyl orthosilicate, and other compounds. Aromatic and aliphatic fluorine-containing compounds can be used to prepare the Grignard reagent. Compounds based on unsaturated polyfluorides, e.g. tetrakistrifluorovinylsilane[314], can be obtained by the organomagnesium method.

The reactions can be conducted under milder conditions if organolithium compounds are used[315-317], and the yield of the fluorinated organosilicon compounds is higher. In comparison with the use of magnesium that of lithium has not found sufficiently wide application.

Sufficient experimental data have now been published to derive the main principles of the organoelementary synthesis of fluorinated organosilicon compounds.

2. The Swarts Reaction

The Swarts reaction can be used to exchange halogens in an organic radical for fluorine atoms[318]. Halogen atoms attached to silicon are replaced at the same time. To diminish the consumption of antimony trifluoride and antimony pentachloride use is made e.g. of the following scheme[246,319]

$$CH_3C_6H_4SiCl_3 \xrightarrow{HF} CH_3C_6H_4SiF_3 \xrightarrow{+Cl_2} CCl_3C_6H_4SiF_3 \xrightarrow{SbF_3+SbCl_5} CF_3C_6H_4SiF_3$$

Various aryl- and alkyl-fluorosilanes can be obtained by means of the Swarts reaction. Exchange for fluorine depends on the position of the halogen in the organic radical: in 1-bromo-3,3,3-trichlorpropylmethyldichlorosilane and 1,3,3,4,4,4-hexabromobutylphenyldichlorosilane, for example, the 1-bromine atom cannot be replaced by fluorine[320,321].

Several difficulties in conducting the reaction and the limited choice of compounds diminish the possibilities of the Swarts method for introducing fluorine atoms into the organic radicals of alkylsilanes and arylsilanes.

3. Addition at a Silicon–Hydrogen Bond

Many investigations have been undertaken with the aim of obtaining fluorinated organosilanes by the addition of unsaturated fluorine-containing compounds at a silicon–hydrogen bond. This reaction was first accomplished[322,323] in 1954 with the addition of silicochloroform to 1,1-difluoroethylene and tetrafluoroethylene. During many subsequent researches various catalysts and initiators have been found and a large number of diverse compounds have been prepared. Addition is initiated by ultraviolet radiation[324], cobalt-60 γ-rays[325,326], and various compounds such as peroxides[327]. It takes place by a radical–chain mechanism:

$$HSiCl_3 \xleftarrow{h\nu} Cl_3Si^{\cdot} + H^{\cdot} \quad Cl_3Si^{\cdot} + CF_2{=}CF_2 \rightarrow Cl_3SiCF_2CF_2^{\cdot}$$
$$Cl_3SiCF_2CF_2^{\cdot} + HSiCl_3 \rightarrow Cl_3SiCF_2CF_2H + {}^{\cdot}SiCl_3$$

Good results have been obtained by using platinised carbon and especially chloroplatinic acid as catalyst[328,329]. The action of platinum is explained in the literature as involving both heterogeneous and homogeneous catalysis.

Individual examples have been reported of the addition of fluoroalkenes at a silicon–hydrogen bond in the presence of boric acid in an autoclave at high temperatures[330], etc., but they have not interested investigators.

Among all the known methods, addition at a silicon–hydrogen bond is in several cases of the greatest practical interest for the industrial production of fluorinated organosilicon compounds.

4. Other Reactions

In contrast to the well known industrial processes for the direct synthesis of alkyl- and aryl-chlorosilanes, only the simplest halogenated fluorocarbons react directly with a silicon–copper alloy[331], and the yield is low.

Several compounds have been obtained by the Diels–Alder method[332], and by the addition of compounds of the type RCF_2Br or RCF_2I (where R = F or a radical) at the double bonds of alkenylsilanes in the presence of radical initiators[333]. Fluorinated esters[334] and ethers[335] have also been obtained. However, these methods for preparing fluorinated organosilanes have no practical interest.

The literature contains no serious investigations on the preparation of organosilicon compounds containing iodine in the organic radical. Individual publications in which preparations of iodinated organosilanes are encountered are of no theoretical interest and still less of practical interest.

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