THE DIRECT SYNTHESIS OF ORGANOSILICON COMPOUNDS

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I. Introduction

Reviewing forty years of work on organosilicon compounds (*199*), F. S. Kipping in 1937 thought the economic potentialities of these compounds to be slight; yet only a decade later an industry based on the organosiloxane (*silicone*) polymers had come into being. It is the purpose of this review to describe the methods for the synthesis of intermediates for this industry and their extension to organic derivatives of other elements.[1]

The first methods for the preparation of organosilicon compounds utilized the halides. Elemental silicon (which is made by reduction of silica with carbon at 1500°) or ferrosilicon (35% Si) reacts readily with chlorine or chlorides; ferrosilicon and chlorine, for example, yield almost pure silicon tetrachloride at 500°, the intermediate polychlorosilanes formed being destroyed by their thermal instability and susceptibility to further chlorination at this temperature (*39*, *238*). Hydrogen chloride reacts with silicon to yield a variety of products ($SiCl_4$, $SiHCl_3$, SiH_2Cl_2, and higher chlorides); at 170–200°, 30% yields of polychlorosilanes are obtained (*72*, *126*, *399*). Halosilanes may be converted to organosilicon compounds by

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[1] Other reviews of this subject have recently appeared in the Russian language (*375*) with 161 references and in Japanese (*189*) with 18 references.

several routes (see *33, 101*), chief among which are: treatment with zinc, mercury, or aluminum alkyls; the action of an organic halide in the presence of a halogen acceptor such as zinc, sodium, or lithium; the action of organosodium or -lithium compounds; interaction with reactive methylene compounds; treatment with diazomethane; and the Grignard synthesis. Of these the last is probably the most flexible.

In Kipping's classic work the condensation of silanols (obtained by hydrolysis of organosilicon halides) was shown to lead to the formation of high molecular weight substances of empirical formula R_2SiO, named *silicones* because of the expectation that the reactions would lead to the silicon analogs of ketones. These substances were the prototypes of today's polysiloxane fluids, rubbers, and resins, and the term still persists; the interested reader will find information on history, production, and applications in a number of reviews (*3, 18, 20, 28, 114, 118, 173, 224, 247, 249, 267, 294, 311, 334, 349, 354*). The first plants for the production of silicones in the United States were based on the Grignard process, the essential reactions being:

$$\mathrm{CH_3Cl + Mg \xrightarrow{ether} CH_3MgCl}$$

$$\mathrm{2CH_3MgCl + SiCl_4 \longrightarrow (CH_3)_2SiCl_2 + 2MgCl_2} + \text{other products}$$

$$\begin{array}{l} \mathrm{(CH_3)_2SiCl_2 + 2H_2O \longrightarrow (CH_3)_2Si(OH)_2 + 2HCl} \\ \qquad\qquad\qquad\qquad\qquad\quad \big\downarrow \mathrm{-H_2O} \\ \qquad\qquad\qquad\qquad\quad \mathrm{[(CH_3)_2SiO]_{\mathit{x}}} \end{array}$$

Among the disadvantages inherent in this route were: (1) the need to handle large quantities of ether and of reagents highly sensitive to moisture, (2) interference in separation procedures by the magnesium salts which are precipitated, (3) its inapplicability to compounds containing functional groups which react with Grignard reagents, (4) the number of stages, (5) low efficiency, (6) dependence on silicon tetrachloride, which contains only 16% of silicon. Thus there arose an urgent need for a new synthesis of organosilicon compounds which could be applied to the large-scale production of silicone polymers; the outcome was E. G. Rochow's method, which forms the main subject of this article.

II. The Rochow Reaction

A. Reaction of Methyl Chloride with Silicon

1. Products

The problem of the efficient large-scale production of compounds with silicon-carbon bonds was essentially solved by Rochow in 1940. The reaction, involving what is now known as the Direct Synthesis, was discovered independently by Müller (*264*) in 1942 and by James (*190*) in 1944. A point of some interest is that Wöhler (*72*) and Combes (*86*) had narrowly missed making the discovery a century earlier.[2] Rochow's original paper (*336*), published at the end of World War II,[3] describes the reaction of methyl chloride with elemental silicon in presence of copper metal as a catalyst at 285°. A flow system was used. In the over-all process, which is simple in concept but complex in its chemistry, the net changes may be represented by the equation

$$2RX + Si \xrightarrow{\text{catalyst}} R_2SiCl_2$$

The process is, however, better represented by a series of parallel reactions, among which may be the following:

$$\begin{aligned} 2RX + Si &\longrightarrow R_2SiX_2 \\ 3RX + Si &\longrightarrow RSiX_3 + 2R^* \\ 2R^* &\longrightarrow R_2 \\ R^* &\xrightarrow{\text{decomp}} C + H_2 \\ 3RX + Si &\longrightarrow R_3SiX + X_2 \\ 2X_2 + Si &\longrightarrow SiX_4 \\ 4RX + Si &\longrightarrow SiX_4 + R_4Si \\ RX &\longrightarrow HX + \text{olefin} \\ 3HX + Si &\longrightarrow HSiX_3 + H_2 \\ RX + HX + Si &\longrightarrow RX_2SiH \end{aligned}$$

Reference is made in Section IV to the possible role of the catalyst. In practice, as with the classical methods mentioned previously, a mixture of products is always obtained. In the methyl chloride reaction under appropriate conditions the product consists of ca. 65% of dimethyldichlorosilane (b.p. 70.0°), 25% of methyltrichlorosilane (b.p. 65.7°), and 5% of trimethylchlorosilane (b.p. 57.3°). The remaining 5% is a complex mixture which includes silicon tetrachloride, trichlorosilane, methylchlorodisilanes, tetramethylsilane, dimethylchlorosilane, and higher silanes. Table I lists almost thirty compounds isolated by various workers. Unfortunately the

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[2] The technique of reaction of hydrogen chloride with silicon was well-known to both, even to the inclusion of copper powder. Rochow himself believes, "They *did* try it unsuccessfully; he himself spent over a year trying to get methyl chloride to react with silicon under the conditions of Wöhler and Combes, but to no avail. It is not as simple as that" (*350*).

[3] The basic method has since been published and patented many times by various groups (*24, 45, 56, 98, 111, 119, 123, 129, 153, 183, 184, 188, 265, 326, 337, 342, 353, 361, 472*).

TABLE I

Some Compounds of the Reaction of CH_3Cl with Si—Cu

Compound	B.P.	Reference
H_2	−252.8°	(*254, 390, 397*)
CH_4	−161.5°	(*254, 390, 397*)
C_2H_4	−104.9°	(*397*)
C_2H_6	−88.3°	(*397*)
HCl	−83.7°	(*397*)
CH_3Cl	−24.2°	(*254, 390*)
CH_3SiH_2Cl	8.0°	(*397*)
H_2SiCl_2	8.3°	(*228b, 397*)
$(CH_3)_4Si$	26.5°	(*296, 297, 362, 363, 390, 397*)
$HSiCl_3$	31.8°	(*297, 390, 397*)
$(CH_3)_2SiHCl$	36.0°	(*296, 297*)
CH_3SiHCl_2	41.0°	(*228a, 297, 362, 363, 384, 385, 390, 397*)
$(CH_3)_3SiCl$	57.3°	(*336, 397*)
CH_3CHCl_2	57.3°	(*382*)
$ClCH_2CH_2Cl$	57.4°	(*384, 385*)
$SiCl_4$	57.6°	(*336, 382, 397*)
2-Methylpentane	60.4°	(*382*)
3-Methylpentane	63.3°	(*382*)
CH_3SiCl_3	65.7°	(*336, 397*)
$(CH_3)_2SiCl_2$	70.0°	(*336, 397*)
$(CH_3)_2HSiOSiH(CH_3)_2$	70.5°	(*258, 296*)
$CH_3C_6H_{11}$	90.1°	(*384, 385*)
$(CH_3)_3SiOSi(CH_3)_3$	100.5°	(*258*)
$(CH_3)_3SiSi(CH_3)_3$	113°	(*258*)
$Cl_3SiSiCl_2CH_3$	134–135°	(*258, 260*)
$(CH_3)_3SiSi(CH_3)_2Cl$	135.5–137°	(*216, 258, 260*)
$(CH_3)_2ClSiSiCl(CH_3)_2$	146.5–148°	(*219, 258, 260*)
$Cl_3SiSiCl_3$	147.0°	(*258, 260*)
$Cl_2(CH_3)SiSi(CH_3)_2Cl$	154.4–156.8°	(*79, 216, 217, 219, 258, 260*)
$Cl_2(CH_3)SiSi(CH_3)Cl_2$	150–160°	(*79, 217, 219, 260*)
$[(CH_3)_nSiCl_{3-n}]_2$	100–190°	(*79, 217, 219, 220a, 260*)
$[(CH_3)_nSiCl_{3-n}]_2O$		(*218, 219, 220a*)
$[(CH_3)_nSiCl_{3-n}]_2CH_2$		(*218, 219, 220a*)
Other inert hydrocarbons	—	(*32, 385*)
$R_nSiCl_{4-n}(R > CH_3)$	—	(*32*)
$(CH_3)_nCl_{6-n}Si_2O$	—	(*32*)
$(CH_3)_nCl_{6-n}Si_2$	—	(*32, 258, 260*)
$(CH_3)_n(SiCH_2Si)Cl_{6-n}$	—	(*32*)
$(CH_3)_n(SiCH_2CH_2Si)Cl_{6-n}$	—	(*32*)
$(CH_3)_n(SiCH_2SiCH_2Si)Cl_{8-n}$	—	(*32*)
Higher silanes, siloxanes, and silcarbanes	—	(*32*)
$(Cl_3Si)_2CH_2$	178–84°	(*293*)

purity of the methyl chloride used is almost never stated and some of the minor constituents may arise from impurities.[4]

Many of the less volatile compounds listed in Table I have been isolated from stillpot residues collected from the continuous distillation of large quantities of product. The approximate composition of a typical residue after removal of dimethyldichlorosilane is shown in Table II.

TABLE II[a]

HIGH-BOILING RESIDUES AFTER REMOVAL OF $(CH_3)_2SiCl_2$

$R_nSiCl_{4-n}(R > CH_3)$	27%	$(CH_3)_nSi_2Cl_{6-n}$	8.8%
$(CH_3)_n(SiCH_2Si)Cl_{6-n}$	26.9%	$(CH_3)_nSi_2OCl_{6-n}$	6.1%
$(CH_3)_n(SiCH_2CH_2Si)Cl_{6-n}$		$Cl_3SiSiCl_3$	4.4%
$(CH_3)_n(SiCH_2SiCH_2Si)Cl_{6-n}$		$(CH_3)_nSiCl_{4-n}$	4.4%
Inert hydrocarbons	18.3%	Higher silanes, siloxanes, and silcarbanes	4.1%

[a] Reference (*32*).

The high-boiling residues can be passed with (*32*) or without (*260*) hydrogen chloride over hot quartz, or heated with hydrogen chloride at high pressure to convert some of these by-products to simple methylchlorosilanes (*400*).

2. Laboratory Methods

The laboratory synthesis of methylchlorosilanes is described by Rochow in *Inorganic Syntheses* (*348*). Powdered silicon (60-mesh) is mixed with 10% by weight of finely divided metallic copper and suspended loosely on glass wool in a Pyrex tube held in a furnace. The reaction proceeds without a catalyst, but the second metal facilitates the process. An alternative preparation of the contact mass involves mixing the silicon with powdered copper chloride. When the reaction tube is heated, reduction of the copper salt occurs, silicon tetrachloride distills, and the silicon becomes coated with a highly reactive layer of copper. Additional variations on contact mass preparation are described in Subsection B.

For reactants which are gaseous at room temperature, it is convenient to carry the vapor through the system in a stream of inert gas. Liquid charges may be introduced with a large hypodermic syringe. Working on a laboratory scale, the usual arrangements are made for condensing the product and excluding moisture, and the temperature can be recorded with a protected thermocouple.[5] A convenient working temperature is 300° with

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[4] Commercial methyl chloride may contain air, moisture, hydrogen chloride, and vinyl chloride.

[5] For syntheses where poor yields are expected a recycling system may be preferred (*176*).

a methyl chloride flow rate of ca. 7 gm/hr. The reaction is exothermic and, once started, will maintain itself with less heat than is needed for its initiation. In spite of the closeness of the boiling points of the methylchlorosilanes, they may be separated with an efficient distillation assembly where high reflux rates can be maintained.

B. REACTION CONDITIONS

One of the main conditions for the satisfactory operation of the Direct Synthesis is that the temperature be kept as low as possible. About 1000 BTU is evolved per pound of methyl chlorosilanes produced and this must be dissipated as far as possible. At higher temperatures pyrolysis of organic radicals may occur to form hydrocarbons or hydrogen and carbon soot. The latter accumulates on the surface of the contact mass and lowers its activity. Worse still, the pyrolysis reaction is autocatalytic and the presence of carbon causes further decomposition of the organic groups with further decrease in the over-all ratio of organic groups to chlorine per silicon atom in the product. It is clearly desirable to maintain a temperature close to the minimum for effective reaction. The threshold temperature varies with the organic halide and appears to depend on the strength of the carbon-halogen linkage in any homologous series.

1. Contact Mass

Lowering the reaction temperature is one of the functions of the catalyst. Commercial silicon is mainly reported as reacting with methyl chloride only above 400°, though a reaction at 300° has recently been observed for pure methyl chloride and chemically purified silicon (0.07% Al, <0.01% Mg, Ca, and Ti) giving dimethyldichlorosilane in 90% yield (*192*), but activation of this silicon may have occurred during leaching with aqueous hydrogen halides and aqua regia. Methyl chloride itself begins to pyrolyze at 400° (*459*). There is clearly some uncertainty about the exact conditions for the reaction of *pure* silicon with methyl chloride but, in presence of copper, a reaction occurs at as low as 285°. Threshold and operating temperatures, as well as yields of the various products, depend on the method used to incorporate the catalyst in the contact mass,[6] and the effectiveness of various catalyst preparations has been reported in detail (*1b, 10, 44, 45, 47, 63, 90, 94a, 108, 119, 128a, 148, 160, 184, 266, 303, 331, 391a, 392a, 423a, 424, 425a, 439a, 447a,b, 449*).

a. Preparation of Contact Mass. In Rochow's original paper (*336*) he reported three methods for the preparation of silicon-copper contact masses, which are still those preferred (*113*). These are:

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[6] For example, the preparation is important in the production of Si—H compounds (*14, 145, 146, 263, 427*).

(*i*) Fusion of copper and silicon in a reducing medium to form an alloy. Rapid cooling prevents segregation of the copper. The material may be either used as lumps or ground to a powder (*131*).

(*ii*) Heating a mixture of silicon and copper chloride powders packed loosely in a reaction tube at above 265°. Silicon tetrachloride distills leaving an active silicon-copper contact mass. The powders may also be pressed into pellets and fired (*57*).

(*iii*) Sintering a mixture of finely divided silicon and copper powders in a quartz tube in a stream of hydrogen at just below the melting point of copper (1050°C) (*46, 47, 302*). An ideal particle size is said to be 74–105μ for silicon (*131*) and $<44\mu$ for copper (*132*). Copper shavings or chips may be used to loosen the mass and provide better surface contact (*9*).

b. Addition of Active Metals as Hydrogen Chloride Acceptors. This often leads to a higher yield of the more highly alkylated silane $(CH_3)_3SiCl$ from the methyl chloride reaction (*176*). Thus 2–25% aluminum metal incorporated in a 9:1(w/w) contact mass and sintered in hydrogen at 1000° increases the yield of $(CH_3)_3SiCl$ from the usual 3–5% to 10–20% (*55, 393, 394*). Aluminum can be fused with a copper-silicon in a graphite crucible near the eutectic temperature (800–1100°) (*231, 473*). Surprisingly, as little as 0.05–0.01% of aluminum is said to increase the yield of more highly alkylated products (*106, 176, 231*). Other metals such as zinc (*110, 369*) or magnesium (*110, 171*) can also be used.

c. Addition of a Metal Halide. This results in enhanced reactivity with lower threshold temperatures, but there is a corresponding increase in the proportion of more highly halogenated products. For example, ferric chloride (*284, 285, 287*), aluminum chloride (*232a, 284, 391*), tin(II) chloride (*172, 284*), tin(IV) chloride (*284*), sodium chloride (*391*), zinc chloride (*61, 441*), cobalt chloride (*102*), zirconium chloride (*289*), hexachlorozirconates (*289*), metal fluorides (*419*), or mixtures of these (*285*) have all been claimed to increase the proportion of methyltrichlorosilane from the methyl chloride reaction.

d. Oxide Catalysts. Porous yet mechanically strong contact masses with high surface area and quick reactivity with alkyl halides result when various metal salts are combined with powdered silicon and the mixtures sintered in hydrogen at high temperatures (*303*). Cupric hydroxide (*464, 465*) and ammonium formate (*295*) have been used in this way, while the use of cupric nitrate, acetate, or formate is said to plate the silicon with copper after heating to 900° in a closed vessel (*326, 330, 450*). Because of its ready availability, ferrosilicon often finds application in the Direct Synthesis (*9, 102, 142, 147, 326, 367*). It is less satisfactory, however, and prior leaching of the contact mass with acid is sometimes used to remove part of the iron (*248*). Elements of Group V are claimed to activate mixtures of silicon and copper powders (*89*, *90*, *91*, *196*, *286*, *288*), but these elements are known to react with methyl chloride and their use would be expected to complicate further the list of products. The claim that metal oxides act catalytically, or that air-dried or "aged" silicon-copper is effective is curious in light of the probability that oxide films on silicon have to be broken before reaction with halides can take place. Nevertheless, the usefulness of compounds such as cuprous or cupric oxide has been asserted (*360*), as has that of aluminum oxide (*170*). It has been shown by X-ray diffraction that copper normally has a coating of Cu_2O (*185*).

e. Other Metal Catalysts. The same metal catalyst need not be effective for all organic halides and, indeed, it is found that silver is the best catalyst for the reaction of chlorobenzene with silicon (*2*, *359*). Fifty per cent copper-silicon is also effective (*359*). Cobalt, nickel, zinc (*91*, *424*), tin (*172*), and lead (*207*) have all been proposed. Alloys of pure silicon and copper are also found to be less effective than those containing the usual commercial impurities (Fe, Al, Ca, Ti, etc.) (*441*), and lead, antimony, bismuth (*143*), and copper sulfate are said to poison the catalyst. It would be of interest to know the effect of arsenic on the reactivity of silicon here as a test of the correlation between chemical and semiconductor activity.

Much effort has been devoted to finding a good catalyst for the difficult reaction of vinyl chloride in the Direct Synthesis. The original preparation (*174*) involved the use of copper (*54*, *175*) but magnesium (*422*) and tin, formed by the reduction of stannous chloride (*422*), have also been suggested. More recently a careful study of the efficiency of various contact masses for this particular reaction has shown the superiority of 20% nickel-silicon alloys (*404*).

f. Use of Fillers. Fillers in the inert contact mass often have a favorable effect on the over-all yield of alkylated chlorosilanes (*113*). Twenty per cent of powdered glass (*23*) or, better, of Raschig rings (*300*) has been used, while silica, sodium silicate (*440*), or hydrolyzed tetraethoxysilane (*36*) acts as a binding agent and improves the mechanical strength of the pelleted contact mass. Such additions would be expected to give a more favorable distribution of the heat of reaction and reduce the extent of pyrolysis of organic groups.

2. Gaseous Diluents

a. Inert Gases. Addition of an inert gas to the organic halide reduces local overheating in the contact mass and so leads to less of the undesirable pyrolytic reactions (*22*). For example, in the reaction of methyl chloride with a 9:1(w/w) silicon-copper at 300° with nitrogen dilution, $MeCl:N_2$-2:5(v/v), the yield of dimethyldichlorosilane was reported as 86.5%. There were smaller amounts than usual of methyltrichlorosilane, silicon tetrachloride, trichlorosilane, and other components containing silicon-hydrogen bonds, which result from pyrolysis (*49, 416*).

b. Addition of Hydrogen. This provides not only a diluent but also another reactant and leads to an increase in the amount of compounds with silicon-hydrogen bonds. For example, use of an equimolar mixture of hydrogen and methyl chloride at 390° increases the yield of methyldichlorosilane from 1% to 15–17% (*49, 50, 417, 418*). Hydrogen under pressure in static systems has a similar effect (*451, 458*). A possible mechanism is discussed later (see Section IV).

c. Chlorine Addition. Addition of chlorine to the organic halide would be expected to increase the amount of chlorosilanes in the product, but it also produces an extremely high activity in the contact mass. Thus a 5–35% admixture of chlorine with methyl chloride has been found to give a sevenfold increase in the total amount of product with shorter reaction times (*177*). A mixture of chlorine and hydrogen used with methyl chloride gives methyltrichlorosilane as the major product (ca. 70%) (*292*). The addition of chlorine to either methyl or ethyl chloride can also result in *in situ* formation of difunctional organic chlorides, and the organochlorosilanes expected from these reactants are found in the products (*215, 293*). The yield of low-boiling chlorosilanes is said to be raised, however (*55, 163*).

d. Hydrogen Chloride. The use of hydrogen chloride as a diluent leads to more highly chlorinated products, but the yield of silicon tetrachloride increases markedly if more than an equimolar mixture of hydrogen chloride is employed (*29, 30, 31, 228a, 282, 346*). Methyltrichlorosilane has also been used as an activator (*145a*).

C. SEPARATION OF PRODUCTS

When methyl chloride is used in the Direct Synthesis the separation of the products becomes a major problem as may be seen from the boiling points of products shown in Table I. The complexity of the problem is increased by the formation of both binary and ternary azeotropic mixtures, the most difficult of which is that formed between silicon tetrachloride and trimethylchlorosilane (b.p. 54.5°) (*381, 382, 385*). In addition to the construction of high efficiency distillation outfits which take into account the chemical nature of the substances being separated (e.g., their inflammability and violent reaction with moisture to produce polymeric materials and hydrogen chloride in high enough local concentration to corrode most metals), a number of physical and chemical techniques have been developed for breaking the azeotropes formed between the various components (*261*).

The separation of the gaseous by-products of the methyl chloride reaction is relatively easy. Unreacted methyl chloride may be recovered by passing the exit gases over activated charcoal (*474*) or sandy chalk (*290*). Dimethyldichlorosilane and methyltrichlorosilane fortunately form no azeotropes and may be separated by efficient fractionation (*26*, *66*, *78*, *124*, *225*, *235*). After the separation of this intermediate fraction, the problem of removing trimethylchlorosilane (b.p. 57.3°) from the low-boiling liquids must be considered. Five compounds reported as present in the product of a commercial synthesis boil in the range 57.4–63.2°. Table III lists the binary azeotropes which are known to form.

TABLE III
AZEOTROPES FOUND IN THE RANGE 57.4–63.2°

Azeotropic mixture	B.P.
$SiCl_4$, 64.8%; $(CH_3)_3SiCl$, 35.2%	54.7°
$(CH_3)_3SiCl$, 70%; 2-methylpentane, 30%	56.4°
$(CH_3)_3SiCl$, 75%; 3-methylpentane, 25%	57.3°
$SiCl_4$, 63.5%; 1,1-dichloroethane, 36.5%	53.0°

This separation may be handled by the addition of a second azeotroping agent (*381*, *384*). The following are examples:

	B.P. of azeotrope
Acetonitrile (b.p. 82°) + 92.6% $(CH_3)_3SiCl$	56°
+ 90.6% $SiCl_4$	49°
Acrylonitrile (b.p. 79°) + 93% $(CH_3)_3SiCl$	57°
+ 89% $SiCl_4$	51.2°
1,1-Dichloroethane (b.p. 57.4°) + 36.5% $SiCl_4$	56.0°
Nitromethane (b.p. 101.0°) + 46.2% $SiCl_4$	94.0°
Chloroform (b.p. 61.3°) + 44.0% $SiCl_4$	70.0°

In addition, various chemical methods of overcoming the difficulties in the separation processes arising from the formation of azeotropes have been suggested. These include the addition of a complexing agent (*179a*, *281*, *452*) and esterification followed by regeneration (e.g. *52*, *60*, *64*, *71*, *107*, *128*, *150*, *182*, *186*, *221*, *232*, *251a*, *270*, *279*, *304*, *304a*, *377*, *379*, *392*, *402*, *460*). Much of the difficulty is avoided if the conditions of synthesis are regulated so that no silicon tetrachloride is produced, then trimethylchlorosilane can be separated in a single distillation. The entire separation process may in any case be monitored by gas chromatography. Benzophenone (*469*) and nitrobenzene (*447b*) have been recommended for the stationary phase.

D. INDUSTRIAL REACTION TECHNIQUES

A number of special techniques have been proposed for the Direct Synthesis (*65*, *97a*, *109*, *110*, *169*, *181*, *245*, *278*, *332*, *419a*, *426*, *441a*). Thus for example, the use of a fluidized bed of silicon and copper powders provides a high surface area and assures an even temperature distribution. Higher pressures of methyl chloride may also be used (*7, 8, 21, 43, 51, 56, 106a, 144, 227, 228, 251, 262, 333, 395, 420, 439, 442, 475*). Alternatively silicon-copper powders can be suspended in paraffin oil or polysiloxanes, or in the organic reactant if the latter is a liquid such as chlorobenzene (*42*). Suspension in fused metal chlorides (e.g., LiCl–KCl, NaCl–$AlCl_3$) has also been suggested (*388*). No attempt will be made here to discuss in detail the more technical aspects of the processes (see ref. *36a*).

III. Extension of the Direct Synthesis Reaction

A. APPLICATION OF THE DIRECT SYNTHESIS TO OTHER ELEMENTS

1. Carbon

The analog of the Direct Synthesis reaction for carbon is not known. Reaction of alkyl halides with K-graphite is entirely that expected from a potassium dispersion (*140*).

2. Germanium

Rochow first studied the reaction between organic halides and germanium. Methyl chloride reacts with the pure element only at temperatures in excess of 400°,[7] but the inclusion of a copper catalyst leads to reaction at 340° (*338, 339, 341*). Yields of 50–55% of dimethyldichlorogermane based on the Ge taken have been obtained (*389*), though no trimethylchlorogermane was found (*327*). At 550° the mono- and dimethyl compounds are formed in equal amounts (*310*). The copper-catalyzed reaction of ethyl chloride at 356° gave a condensate containing diethyldichlorogermane (*347*), though this conclusion has been questioned (*310*). The analogous reaction with *n*-propyl chloride gave *n*-propyltrichlorogermane at 310–330° (*357*). Chlorobenzene has also been used to prepare diphenyldichlorogermane (*309, 343*). Allyl chloride and 2-methylallyl chloride react to give the corresponding unsaturated alkyltrichlorogermanes, but no reaction was observed with vinyl chloride (*310*). A full description of the methyl chloride reaction can be found in reference (*389*).

3. Tin

The preparation of organotin halides by Direct Synthesis has been known for over 100 years (*117*). Early workers heated alkyl halides with tin in sealed tubes at 130–180° for long periods (*74, 76, 77, 103, 151a, 197,*

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[7] Germanium reacts with chlorine at 130° (*93*) and so is more reactive in this way than silicon.

226). Later Rochow showed that dimethyltin dichloride could be prepared in over 50% yield by passing methyl chloride (1 gm/hr) through molten tin at 300–350° (*352*, *364*, *410*, *457*). Stannous oxide was said to inhibit the synthesis of dimethyltin dichloride by producing dimethyltin which then absorbs methyl chloride to form trimethyltin chloride (*364*, *410*). This is curious in the light of recent investigation of the reaction of methyl chloride with stannous oxide to give dimethyltin dichloride in good yield (*15*).

Ethyl bromide reacts with an alloy of tin, sodium, and zinc to give tetraethyltin (*155*, *444*). This is analogous to the industrial synthesis of tetraethyllead. The standard method for obtaining alkyltin halides is, however, the reaction of alkyl halides (preferably iodides) *in situ* with tin foil and magnesium in the presence of a trace of the corresponding alcohol. Tin halides substituted with the following groups have been obtained in this way: methyl (*182*, *239*, *243*), ethyl (*239*), *n*-propyl (*222*, *241*), isopropyl (*241*), *n*-butyl (*239*, *240*, *244*), isobutyl (*241*), *sec*-butyl (*241*), isoamyl (*241*), *n*-hexyl (*242*), cyclohexyl (*241*), 2-ethylcyclohexyl (*241*), *n*-octyl (*241*), *n*-decyl (*241*), *n*-dodecyl (*241*, *242*), allyl (*445*), *n*-$C_{18}H_{17}$ (*242*), crotyl (*242*), and methyl vinyl carbonyl (*242*). A mixture of methyl and ethyl iodides gives mixed methylethyltin iodides (*241*). Other catalysts, such as mercuric acetate (*222*) or tetrahydrofuran (*242*, *243*), are also effective. The yield of organotin halide decreases with increasing size of the alkyl group because of dehydrohalogenation of the alkyl halide (*443*, but see *137*, *226*).

A novel synthesis of di- and tribenzyltin chlorides has been reported by Japanese workers (*406*). Benzyl chloride reacts with tin powder in a rapidly stirred slurry in water or toluene according to the following equations (*407*):

$$3C_6H_5CH_2Cl + 2Sn \xrightarrow{H_2O} (C_6H_5CH_2)_3SnCl + SnCl_2$$

$$2C_6H_5CH_2Cl + Sn \xrightarrow{\text{toluene}} (C_6H_5CH_2)_2SnCl_2$$

In the toluene reaction a trace of water (*407*), tertiary amine (*408*), mercuric chloride (*408*), or dibutyl ether (*156*, *157*) is needed, while metals are effective catalysts for the water reaction (*94*, *202*). Methyl-substituted benzyl chlorides (*406*), allyl bromide (*408*), methylvinylcarbinyl bromide (*408*), crotyl bromide (*408*), and α-chloromethyl naphthylene (*158*) can also be used, but only the Wurtz condensation takes place with diphenylchloromethane, phenylmethylchloromethane, or benzal chloride (*409*). The synthesis does not work for silicon or arsenic (*407*) but does proceed in a variety of solvents (*469a*).

The application of the fluididized bed technique to the original synthesis is possible if Cu_3Sn or $Cu_{31}Sn_8$ is used: both are solid at the reaction temperature (*68*, *411*, *456*). Use of γ-ray irradiation allows the synthesis of alkyltin bromides and iodides to proceed at room temperature. Neither ultraviolet radiation nor γ-rays promote reaction of alkyl chlorides below 30° (*1*, *1a*).

4. Lead

Neither lead nor thallium reacts directly with organic halides as far as is known (*356*). (The commercially important synthesis of tetraethyllead from ethyl chloride and a lead-sodium alloy will not be considered here.) Direct reaction can, however, be brought about if the metals are formed *in situ* in the presence of the organic reagent, and dimethyllead diiodide (*135*) and trimethylthallium (*134*) have been synthesized by this route.

5. Other Elements

Phenylboron dibromide can be made by the action of bromine and benzene on boron dispersed with a nickel catalyst on kieselguhr (*120*), but the reaction probably proceeds through the intermediate formation of boron tribromide, which is found in the product. Repeated attempts to bring about reaction between methyl chloride and boron itself have failed (*253*).

Methyl chloride reacts with aluminum to form mono- and dimethylaluminum chlorides in good yield (*73*, *75*, *125*, *133*, *150*, *154*, *165*, *328*, *454*, *470*). The method has been applied to the synthesis of methyl and ethyl aluminum chlorides, bromides and iodides, *n*-propyl and isoamyl aluminum iodides, octyl aluminum bromide, phenyl and *p*-tolyl aluminum iodides, and naphthyl aluminum bromides (*229*, *414*). Butyl bromide also reacts with an Al—Mg alloy in ether at 70–100° to give $Bu_3Al{\cdot}2Et_2O$ (*127*).

Trialkylaluminum and dialkylaluminum hydrides may also be made by the reaction of olefins and hydrogen with a clean aluminum surface, produced by grinding the metal under nitrogen (*84*, *471*). Dehydrohalogenation reactions are always a possibility in synthesis with such active metals (*88*). Organohalogen compounds of other active metals such as zinc (*115*), cadmium (*456*), mercury (*116*, *246*), and tellurium (*92*, *236*, *447*) can also be obtained by direct synthesis (*70*).

Although the fifth group elements have been recommended as catalysts or promoters in the Direct Synthesis of organosilanes (*89*, *223*, *286*, *288*), it is only recently that the reaction of alkyl halides with these elements has been at all fully studied. Methyl chloride reacts with an 80-20 phosphorus-copper mixture to form CH_3PCl_2 in 95% yield, together with $(CH_3)_2PCl_2$. Methyl and ethyl bromides also react (*233*). White phosphorus gives derivatives with *m*-tolyl bromide, bromobenzene, benzyl chloride, and *n*-octyl bromide (*324*).

Methyl bromide and chloride also react with arsenic and antimony at 350–370° using a copper catalyst. The methyl iodide reaction begins at 280°, but yields are poor, while vinyl halides react at 450–475°. Silver is a better catalyst for the bromobenzene reaction. Bismuth does not react with methyl chloride, though it does with methyl bromide. The methyl bismuth halide undergoes extensive decomposition at the reaction temperature. For the Group V elements in general, yields are better with methyl bromide than with methyl chloride (*234*).

B. DETAILED CONSIDERATION OF DIRECT SYNTHESIS REACTIONS

The greater part of the foregoing description of the use of Direct Synthesis in preparing organohalides has dealt with the use of the simpler aliphatic halides and especially methyl chloride which, in the case of silicon, is the most important from the point of view of large-scale production. Much has been done with other halides, however, and also with other types of organic compounds; this is reviewed in the following pages.

1. *Aliphatic Halides*

The Direct Synthesis of organosilicon compounds has been examined with a considerable range of aliphatics. As was mentioned in Rochow's original paper (*336*), methylbromosilanes may be made by this route using silicon-copper, and several of the minor products have also been identified (*130, 428, 432*). Rochow suggested that methyl fluoride and iodide reacted similarly (*229, 336, 337, 361*), but methylfluoro- and methyliodosilanes were not actually isolated. Reinvestigation of the reaction of methyl iodide failed to reveal the formation of methyliodosilanes at 280–350° with copper or silver as the catalyst (*194*). These compounds may indeed be thermally unstable at the reaction temperature and their isolation might depend on rapid removal from the hot zone.

Reaction with ethyl chloride is very similar to that with methyl chloride and a variety of products has been isolated (*5, 11, 25, 35, 89, 163, 198, 221a, 248, 336, 440a*). The reaction with ethyl bromide has also been studied (*196, 213, 214, 435, 436*). Saturated aliphatic chlorides or bromides with up to five carbon atoms have been used in the Direct Synthesis (*100, 104, 200, 236, 276, 277, 315, 322, 436*), but there is a tendency for the higher alkyl bromides to decompose at the temperature of the synthesis. β-Chloropropionitrile and β-chlorovaleronitrile have also been studied and give the corresponding trichlorosilanes in 20% yield. The cyanide function does not seem to be affected (*315*). It is also curious that chloroacetonitrile remains unchanged when passed over silicon-copper at 450°, while 1-chloropropylene oxide reacts to give 1-trichlorosilylpropylene oxide. Ring rupture causes polymerization, however, and the pure compound could not be isolated

(*372*). 3-Chloropropyl methyl ether does not react at 450° (*376*). In general there is a decrease in yield of alkylchlorosilanes with the size of the alkyl group and a corresponding increase in the amount of olefins found in the product, probably due to hydrogen halide abstraction under the reaction conditions. Acetyl chloride does not react with silicon-copper (*105*).

2. Aromatic Halides

Rochow and Gilliam first described the reaction of chlorobenzene with silicon containing a silver or copper oxide catalyst (*229a*, *230*, *335*, *359*). It gave a mixture of products which included

	B.P.
$PhSiCl_3$	201.5° (152°/20 mm)
Ph_2SiCl_2	305.2°
Ph_3SiCl	378.0°
$PhSiHCl_2$	184°
$SiCl_4$	57.6°
Ph—Ph	130°/10 mm
Ph—H	80.1°

The reaction requires a temperature about 100° higher than that for alkyl chlorides: without a catalyst it occurs at 530° and with silver or copper oxide the threshold is at 380° with an optimum at 400–420°. With bromobenzene, the composition of the condensate is: Ph_2SiBr_2, 28%; $PhSiBr_3$, 42%; $SiBr_4$, 13%. It is claimed that Ph_2SiBr_2 becomes the main product when a 1:1 copper-silicon alloy is used (*429*, *432*). The yield of phenylchlorosilanes is raised by the addition of hydrogen and that of diphenyl is reduced (*423*). As in the case of the alkyl halide, reaction promoters (e.g., NaCl with Ag or $AlCl_3$ with Al) may be added to the contact mass (*12*, *68*, *106*, *391*, *425*). As would be expected, addition of hydrogen chloride gives more phenyltrichlorosilanes (*346*).

The reactions of polycyclic aromatic halides have been little investigated. α-Chloronaphthalene reacts at 500° with a contact mass which contains copper and silver oxide to give $C_{10}H_7SiCl_3$. This material is reported, however, to consist of a mixture of α- and β-naphthyltrichlorosilanes (*378*). 2-Chloropyridine has also been used to produce bis(2-pyridyl)-dichlorosilane (*40*, *67*).

3. Unsaturated Hydrocarbons

The first report of the preparation of alkylenechlorosilanes (*174*) emphasized the difficulties that arise in this particular type of synthesis. The chlorine atom in vinyl chloride, which is attached to one of the doubly bonded carbon atoms, is known to be relatively unreactive compared with that in alkyl chlorides. In fact, the vinyl halides show a reduced reactivity in the Direct Synthesis rather like that found in chlorobenzene, where reaction takes place only at higher temperatures and with low efficiency. In allyl chloride, on the other hand, chlorine is attached to the carbon atom adjacent to the double bond and reactivity is enhanced. Compounds with the halogen further removed from the double bond lose this special reactivity.

Allyl chloride reacts with silicon-copper at 250°. Reaction is highly exothermic and this may lead to pyrolysis of the starting material unless the heat is dissipated. Special reactions have been designed (*109*) and both dilution with an inert gas and the use of a filler in the contact mass have been employed (*178*, *181*, *211*). With a contact mass containing 10% of copper, the condensate contains some 40% of low-boiling products (e.g. $SiCl_4$ and $SiHCl_3$) and the remainder is a mixture of allylchlorosilane from which the following have been isolated

	B.P.
$CH_2{=}CHCH_2SiHCl_2$	97°
$CH_2{=}CHCH_2SiCl_3$	117.5°
$(CH_2{=}CHCH_2)_2SiCl_2$	82–84°/50 mm

Only insignificant quantities of difunctional allylchlorosilanes are produced (*175*) and there are no saturated products (*54*). Reaction with methyl-substituted allyl chlorides seems to be similar in all respects (*259*, *313*).

In contrast to the above, vinyl chloride reacts only sluggishly: comparatively high temperatures are necessary and yields are low. At least ten products have been isolated (*13*, *43*, *53*, *404*). With a contact mass containing 20% of copper operating at 350–400°, $CH_2{=}CHSiCl_3$ is formed in 20% yield with 9% of $(CH_2{=}CH)_2SiCl_2$ (*402*). Other variants are the use of an alloy with 24% of tin, which is said to favor the production of $CH_2{=}CHSiHCl_2$ (*422*), and more recently the use of alloys of silicon with nickel. This has been shown to be effective in retarding the pyrolysis of vinyl chloride and in promoting the formation of divinyldichlorosilanes. Even so, the best yields of the latter are 10% (*402*, *402a*).

The reaction of 1,3-dichlorobutene-2, a compound with both vinyl and allylic chlorine, resulted in a mixture of (3-chlorobutene-2)trichlorosilane with some $Cl_3SiCH_2CH{=}C(CH_3)SiCl_3$ (*373*). The allylic chlorine appears to react preferentially and, to a major extent at least, to the exclusion of the vinyl chlorine. Chloroprene polymerized at 420–450° over Si—Cu even when diluted with nitrogen, and no compounds with carbon-silicon bonds were identified (*370*). No attempt has yet been made to investigate the synthesis of γ- and δ-alkenyl halosilanes.

4. Polyfunctional Organic Halides

The use of reactants with more than one site for reaction is an obvious extension of the Direct Synthesis that has been fairly widely explored. It opens the possibility of synthesizing new types of organosilicon compounds with one or more carbon atoms interposed between two silicon atoms. The reactivity of methylene chloride, the simplest of the difunctional chlorides, was examined soon after the discovery of the methyl chloride reaction. The copper-catalyzed reaction sets in at about 300° and was studied with nitrogen dilution of the gas stream. The products are shown in Table IV, together with the products from CH_3CHCl_2 at 300° (*281, 314*) and $(CH_3)_2CCl_2$ at 280° (*281, 314*). Recycling was used to improve yields. 1,1-Dichloro-2-methylpropane, $(CH_3)_2CHCHCl_2$, is converted to $(CH_3)_2C{=}CHCl$ under the conditions of the Direct Synthesis and the products are those expected from this substituted vinyl chloride (*314*). *Sym*-dichloroethylene (either *cis* or *trans*) was inert even at 500°C (*257a*).

The products from chloroform (300°) and carbon tetrachloride are also given in Table IV. An early publication reported that no silicon-carbon bonds resulted from the uncatalyzed reaction of carbon tetrachloride with silicon at 300°: hexachlorodisilane and tetrachloroethylene were said to be the only products (*38*). Later work (*48, 306, 359*) showed the formation of $SiCl_4$ in high yield and 1% of tetrachloroethylene. Carbon was deposited (*403*). This confused situation has been resolved to some extent by careful reinvestigation of the reaction with nitrogen as a diluent (*268, 269*). A range of interesting compounds was identified (Table IV). The yield of bis(trichlorosilyl)acetylene increased with temperature while that of *sym*-bis(trichlorosilyl)dichloroethylene decreased. There was clear evidence for the existence of the equilibrium

$$3CCl_4 + 5Si \rightleftarrows Si(SiCl_3)_4 + 3C$$

The reaction of various other tetrachlorides with a sintered silicon-copper alloy has also been examined and the order of decreasing ease of exchange established is: $CCl_4 > SnCl_4 > GeCl_4 > SiCl_4$ (*203, 204*). Titanium tetrachloride was found not to react.

The products from a range of additional dichloro compounds shown in Table IV will not be commented on in detail. The conditions of the synthesis lead to dehydrohalogenation of 1,2-dichloroalkanes, and the products from substituted vinyl chloride are observed (*314*). The reaction of 1,4-dichlorobutane is of special interest because of the formation of the two cyclic compounds shown (*281, 323*). Reference has been made to the

TABLE IV

PRODUCTS FROM POLYFUNCTIONAL ORGANIC CHLORIDES WITH Si

Organic chloride	Products	Reference
CH_2Cl_2		
at 300°	$HSiCl_3$	*(19, 121, 164)*
at 350°	$SiCl_4$	*(19, 121, 164)*
at 400°	CH_3SiCl_3	*(121, 122)*
	$(CH_3)_2SiCl_2$	*(121, 122)*
	$(Cl_3Si)_2CH_2$	*(121, 122, 430)*
	$Cl_3SiCH_2SiHCl_2$	*(122, 307, 434a)*
	$Cl_2HSiCH_2SiHCl_2$	*(431, 434a)*
	$(Cl_2SiCH_2)_3$	*(122, 307, 434, 434a)*
	$(Cl_2SiCH_2)_n$	*(122, 307)*
	$Cl_3SiCH_2SiCl_2CH_2SiCl_3$	*(121)*
	$(Cl_2HSi)_2CH_2$	*(430, 431, 433, 434)*
	Unsaturated hydrocarbons	*(430, 431, 433, 434)*
CH_3CHCl_2		
at 300°	$SiCl_4$	*(281, 316)*
	$H_2C{=}CHSiHCl_2$ (6.4%)	*(281, 316)*
	$H_2C{=}CHSiCl_3$ (16%)	*(281, 316)*
	$Cl_2HSiCH(CH_3)SiHCl_2$ (6.5)%	*(281, 316)*
	$Cl_2HSiCH(CH_3)SiCl_3$ (18.5%)	*(281, 316)*
	$(Cl_3Si)_2CHCH_3$ (18.5%)	*(281, 316)*
$(CH_3)_2CCl_2$		
at 280°	$SiCl_4$	*(281, 316)*
	$H_2C{=}C(CH_3)SiHCl_2$ (7.6%)	*(281, 316)*
	$H_2C{=}C(CH_3)SiCl_3$ (10.1%)	*(281, 316)*
	$(Cl_3Si)_2C(CH_3)_2$ (8.5%)	*(281, 316)*
	$(Cl_2HSi)_2C(CH_3)_2$ (14%)	*(281, 316)*
	$Cl_2HSiC(CH_3)_2SiCl_3$ (11.5%)	*(281, 316)*
$CHCl_3$		
at 300°	C_2Cl_4	*(272)*
	$HSiCl_3$	*(272)*
	$SiCl_4$	*(272)*
	Si_2Cl_6	*(272)*
	$(Cl_3Si)_3CH$	*(272)*
	$Cl_3SiCH(SiHCl_2)_2$	*(272)*
	$(Cl_3Si)_2CHSiHCl_2$	*(272)*
	$(Cl_3Si)_2CH_2$	*(272)*
	$Cl_3SiCH_2SiHCl_2$	*(272)*
CCl_4		
at 260–300°	$SiCl_4$	*(48, 305, 306, 359)*
at 210°, 310°, 410°	$Cl_2C{=}CCl_2$	*(38, 48, 305, 306)*
	Carbon	*(403)*
	Si_2Cl_6	*(38)*
	$(Cl_3Si)_4C$	*(268, 269)*
	$(Cl_3Si)_4Si$	*(268, 269)*

TABLE IV (*Continued*)

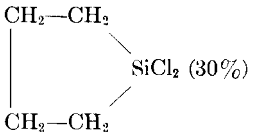
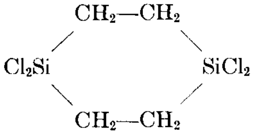
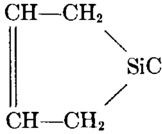
Organic chloride	Products	Reference
	$(Cl_2C=CCl)_4Si$	(*268, 269*)
	$Cl_3SiCCl=CCl_2$	(*268, 269*)
	$Cl_3SiCCl=CClSiCl_3$	(*268, 269*)
	$Cl_3SiC\equiv CSiCl_3$	(*268, 269*)
	$(Cl_3Si)_2C=C(SiCl_3)_2$	(*268, 269*)
Other tetrachlorides	$SiCl_4$	(*203, 204*)
$ClCH_2CH_2Cl$ at 370–380°	$HSiCl_3$	(*305*)
	$SiCl_4$	(*305*)
	$Cl_3SiCH_2CH_2SiCl_3$	(*305, 434a*)
$ClCH_2CHClCH_3$ at 300°	$HSiCl_3$ (24.6%)	(*281, 314*)
	$SiCl_4$ (21.7%)	(*281, 314*)
	$CH_2=CHCH_2SiCl_3$ (7.2%)	(*281, 314*)
	$Cl_3SiCH_2CH(CH_3)SiHCl_2$ (23%)	(*281, 314*)
	$Cl_3SiCH_2CH(CH_3)SiCl_3$ (14%)	(*281, 314*)
$ClCH_2CCl(CH_3)_2$ at 300°	$HSiCl_3$ (8.7%)	(*281, 314*)
	$SiCl_4$ (36%)	(*281, 314*)
	$(CH_3)_2C=CHCl$ (6.8%)	(*281, 314*)
	$Cl_3SiCH_2C(CH_3)_2=CH_2$ (14.7%)	(*281, 314*)
$Cl(CH_2)_4Cl$ at 300°	$HSiCl_3$	(*104, 281, 323*)
	$SiCl_4$	(*104, 281, 323*)
	$ClCH_2CH_2CH=CH_2$	(*281, 323*)
	$Cl_3Si(CH_2)_4SiCl_3$ (6.1%)	(*281, 323*)
	$Cl_3Si(CH_2)_4SiHCl_2$ (5.7%)	(*281, 323*)
	$Cl_2HSiCH_2CH_2CH=CH_2$ (5%)	(*281, 323*)
	 CH_2—CH_2 $SiCl_2$ (30%) CH_2—CH_2	(*281, 323*)
	 CH_2—CH_2 Cl_2Si $SiCl_2$ CH_2—CH_2	(*104*)
$CH_2=CCl_2$ at 450°	$H_2C=C(SiCl_3)_2$	(*314*)
$CH_2=CClCH_2Cl$ at 275–290°	$H_2C=C(SiCl_3)_2$	(*281, 317, 319*)
	$H_2C=C(SiCl_3)SiHCl_2$	(*281, 317, 319*)
	$H_2C=C(Cl)CH_2SiCl_3$	(*281, 317, 319*)

TABLE IV (*Continued*)

Organic chloride	Products	Reference
	$H_2C{=}C(CH_3)SiCl_3$	(*281, 317, 319*)
	$H_2C{=}CHCH_2SiCl_3$	(*281, 317, 319*)
$ClCH{=}CHCH_2Cl$ at 370–380°	$HSiCl_3$	(*281, 317, 319*)
	$SiCl_4$	(*281, 317, 319*)
	$H_2C{=}CHCH_2SiCl_3$	(*281, 317, 319*)
	$CH_3CH{=}CHSiCl_3$	(*281, 317, 319*)
$H_2C{=}CHCH(Cl)CH_2Cl$ at 330°	$ClCH_2CH{=}CHCH_2Cl$	(*281, 312*)
	$Cl_3SiCH_2CH{=}CHCH_2SiCl_3$	(*281, 312*)
at 250°		
at 275–290°	 (15.6%)	(*281, 312*)
$ClCH_2CH{=}C(Cl)CH_3$	$Cl_2HSiCH_2CH{=}C(Cl)CH_3$ (6%)	(*281, 373*)
	$Cl_3SiCH_2CH{=}C(Cl)CH_3$ (9%)	(*281, 373*)
	$Cl_3SiCH_2CH{=}C(SiCl_3)CH_3$ (5.5%)	(*281, 373*)
	$Cl_3SiCH_2CH{=}C(SiHCl_2)CH_3$ (3%)	(*281, 373*)
	$HSiCl_3$	(*281, 373*)
	$SiCl_4$	(*281, 373*)
$(ClCH_2)_2C{=}CH_2$ at 275–290°	$HSiCl_3$ (9.5%)	(*281, 314*)
	$SiCl_4$ (11.3%)	(*281, 314*)
	$(Cl_3SiCH_2)_2C{=}CH_2$ (7.5%)	(*281, 314*)
	$Cl_3SiCH_2C(CH_3){=}CH_2$ (11.5%)	(*281, 314*)
	$Cl_2HSiCH_2C(CH_3){=}CH_2$	(*281, 314*)
$ClCH_2CH{=}CHCH_2Cl$	$HSiCl_3$ (10%)	(*281, 314*)
	$SiCl_4$ (16.7%)	(*281, 314*)
	Si_2Cl_6 (6%)	(*281, 314*)
	$Cl_3SiCH_2CH{=}CHCHSiCl_3$ (7.3%)	(*281, 314*)
	$Cl_2Si(CH_2CH{=}CHCH_2Cl)$ (6%)	(*281, 314*)

behavior of compounds with chlorine atoms belonging to an allylic and a vinylic system. With 1,2-dichlorobutene-3, where both allylic and aliphatic chlorines are present, the reaction conditions are such that the allylic rearrangement occurs:

$$ClCH_2CHClCH{=}CH_2 \rightarrow ClCH_2CH{=}CHCH_2Cl$$

The 1,4-dichlorobutene-2 thus formed reacts at 300° to give 15.6% of the unsaturated silacyclopentene and 9% of the linear $Cl_3SiCH_2CH{=}CHCH_2SiCl_3$ (*311, 373*).

5. *Reactants Containing Silicon*

The use of organosilicon compounds in the Direct Synthesis opens up a number of interesting possibilities. With the series of α-, β-, and γ-chloroalkyltrichlorosilanes the following possibilities are evident:

(a) Reaction to produce the normal product, i.e., replacement of the alkyl chlorine by a trichlorosilane group.
(b) Dehalogenation to give a dimer of the starting material.
(c) Dehydrohalogenation and the formation of alkenyltrichlorosilanes and hydrogen chloride.
(d) Reaction of hydrogen chloride produced in (c) to form $SiHCl_3$.
(e) Reaction of $SiHCl_3$ produced in (d) with the olefin from (c) to give a variety of products.
(f) Rearrangement of the starting material under the conditions of the synthesis.

It is not surprising, therefore, that the products of reactions of this type are complex, as is evident from Table V.

Reasonable yields of the "normal product," where two or more trichlorosilyl groups have been introduced into the alkyl chain, are obtained with α- and β-chlorosubstituted alkylchlorosilanes. Even here, however, many of the possible side reactions mentioned above actually take place and the yields nowhere exceed 50%. Lengthening the alkyl chain increases the yield of compounds formed as a result of dehydrochlorination. In the case of γ-chloroalkyltrichlorosilanes, dehydrochlorination becomes the predominant reaction, and these compounds react more readily with silicon-copper, perhaps because of the activating effect of the hydrogen chloride which is constantly being produced.

Many of the compounds isolated would be difficult to obtain by other means. In addition, with use of ferrosilicon in place of silicon-copper, the reaction provides a good route to alkenylchlorosilanes. For example, β-chloroethyltrichlorosilane reacts with ferrosilicon at 400° in a nitrogen stream to give vinyltrichlorosilane in over 40% yield, along with some $Cl_3SiCH_2CH_2SiCl_3$, formed in all probability by addition of $HSiCl_3$ to $CH_2{=}CHSiCl_3$. The use of α-, β-, and γ-chloropropyltrichlorosilanes is reported to result only in dehydrochlorination with ferrosilicon at 400–500°. It would be interesting in all cases to know the effect of heating with copper metal alone.

6. *Perfluoroalkyl Halides*

Reaction of CF_3Cl, C_2F_5Cl, and C_4F_7Cl with silicon-copper at 500–1000° gave only F_3SiCl and F_2SiCl_2: there was a marked increase in weight

TABLE V
Direct Synthesis with Si-Containing Starting Materials

Type	Halide	%	Products	References
α	Cl_3SiCH_2Cl			
	300–400°	2	$SiCl_4$	*(317, 319, 371)*
		10	$MeSiCl_3$	*(317, 319, 371)*
		30	Starting material	*(317, 319, 371)*
		30	Normal product	*(317, 319, 371)*
		8.5	$Cl_2Si(CH_2SiCl_3)_2$	*(317, 319, 371)*
		—	$HSiCl_3$	*(274)*
		—	$CH_2{=}CHSiCl_3$	*(274)*
α	$Cl_2MeSiCH_2Cl$			
	360–370°	2	$SiCl_4$	*(317, 319, 371)*
		21	Me_2SiCl_2	*(317, 319, 371)*
		17	Starting material	*(317, 319, 371)*
		28.7	Normal product	*(317, 319, 371)*
		16.7	$Cl_2Si(CH_2SiMeCl_2)_2$	*(317, 319, 371)*
α	$Cl_3SiCH(Me)Cl$			
	360–70°	3.3	$SiCl_4$	*(317, 319, 371)*
		28.3	$EtSiCl_3$	*(317, 319, 371)*
			$CH_2{=}CHSiCl_3$	*(317, 319, 371)*
		5	Starting material	*(317, 319, 371)*
		25	Normal product	*(317, 319, 371)*
		5	$Cl_3SiCH(Me)SiHCl_2$	*(317, 319, 371)*
		8.3	$[Cl_3SiCH(Me)]_2$	*(317, 319, 371)*
		6.6	$Cl_2Si[CH(Me)SiCl_3]_2$	*(317, 319, 371)*
	400°	—	$HSiCl_3$	*(273)*
	(Fe—Si)	39.5	$CH_2{=}CHSiCl_3$	*(372)*
	300–	—	HCl	*(271)*
	500°	—	$MeSiCl_3$	*(271)*
	(Fe—Si)	—	C_2H_4	*(271)*
		—	$Cl_3SiCH_2CH_2SiCl_3$	*(271)*
		—	$Cl_2Si(CH_2CH_2SiCl_3)_2$	*(271)*
		—	$(Cl_3SiCH_2CH_2)_2$	*(271)*
α	$EtCl_2SiCH(Me)Cl$			
	370–380°	1	$SiCl_4$	*(374)*
		8	$CH_2{=}CHSiCl_3$	*(374)*
		10	$CH_2{=}CHSiCl_2Et$	*(374)*
		5	$EtSiCl_3$	*(374)*
		15	Et_2SiCl_2	*(374)*
		11	Normal product	*(374)*
		7.5	$EtCl_2SiCH(Me)SiHCl_2$	*(374)*
		7.5	$[EtCl_2SiCH(Me)]_2SiCl_2$	*(374)*
α-di	$Cl_3SiCHCl_2$			
	360–370°	41	$SiCl_4 + MeSiCl_3 + ClCH_2SiCl_3$	*(317, 319)*
		22.4	$CH_2(SiCl_3)_2$	*(317, 319)*
		13	Normal product	*(317, 319)*
α-di	$Cl_2MeSiCHCl_2$			
	360–370°	49	$SiCl_4$	*(317, 319)*
		25.6	$MeSiCl_3$	*(317, 319)*
		4.2	Starting material	*(317, 319)*
		14	Normal product	*(317, 319)*
		10.5	$Cl_2MeSiCH_2SiCl_3$	*(317, 319)*
di-α-di	$(Cl_3Si)_2CCl_2$[a]			
	360–370°	18.2	$SiCl_4$	*(270c, 317, 319)*
		—	Si_2Cl_6	*(270c)*
		—	$(Cl_3Si)_3CH$	*(270c)*
		—	$(Cl_3Si)_3CCl$	*(270c)*
		—	$(Cl_3Si)_4C$	*(270c)*
		11.4	$(Cl_3Si)_2C{=}C(SiCl_3)_2$	*(269, 317, 319)*
		—	$(Cl_3Si)_2C{=}C{=}C(SiCl_3)_2$	*(269, 270c)*

TABLE V (*Continued*)

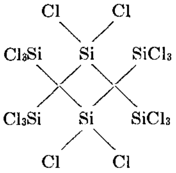
Type	Halide	%	Products	References
di-α	$(Cl_3Si)_2CHCl$			
	360–370°	6.3	$SiCl_4$	(*317, 319*)
		16.7	$CH_2(SiCl_3)_2$	(*317, 319*)
		29.8	Normal product	(*317, 319*)
		10.4	$[(Cl_3Si)_2CH]_2$	(*317, 319*)
tri-α	$(Cl_3Si)_3CCl$		$SiCl_4$	(*270c*)
	400°/5mm		$(Cl_3Si)_3CH$	(*270c*)
			$(Cl_3Si)_4C$	(*270b*)
				(*270c*)
β	$Cl_3SiCH_2CH_2Cl$			
	370–400°	Trace	$HSiCl_3$	(*371*)
		3	$SiCl_4$	(*317, 319*)
		8.3	$EtSiCl_3$	(*317, 319*)
		5	$CH_2=CHSiCl_3$	(*317, 319*)
		43.3	Normal product	(*317, 319*)
		3.3	$Cl_3SiCH_2CH_2SiHCl_2$	(*317, 319*)
		10	$SiCl_2[CH_2CH_2SiCl_3]_2$	(*317, 319*)
		3.3	Starting material	(*317, 319*)
	(Fe—Si) 400°	42.2	$CH_2=CHSiCl_3$	(*273*)
	(Fe—Si) 300–500°	—	$MeSiCl_3$	(*271*)
		—	C_2H_4	(*271*)
		—	$(Cl_3SiCH_2CH_2)_2$	(*271*)
	(Fe—Si) 100 hr	78.5	$Cl_3SiCH=CH_2$	(*275*)
β	$Cl_2MeSiCH_2CH_2Cl$			
	(Fe—Si) 450°	47.6	$CH_2=CHSiMeCl_2$	(*273*)
β	$Cl_2MeSiCH(Me)CH_2Cl$			
		—	$HSiCl_3 + SiCl_4 + MeSiHCl_2 + MeSiCl_3$	(*320*)
		3.2	Normal product	(*320*)
		5.2	$Cl_2MeSiCH(Me)CH_2SiHCl_2$	(*320*)
		58	$Cl_2MeSi(C_3H_7)$ isomers	(*320*)
β	$Cl_3SiCH_2CH(Me)Cl$ 163°			
	(Fe—Si) 150°	—	No normal product	(*274*)
		7.6	$Cl_3SiCH=CH\cdot CH_3$	(*275*)
			$Cl_3SiCH_2CH=CH_2$	(*275*)
		89	$Cl_3SiCH_2CH_2CH_3$	(*275*)
β	$Cl_3SiCH_2CH(CH_2CH_3)Cl$			
	(Fe—Si) 145°	—	$Cl_3SiCH_2CH=CHCH_3$	(*274*)
		—	No normal product	(*274*)
		35.5	Starting material	(*274*)
		7.3	Residue	(*274*)
β	$Cl_3EtSiCH_2CH_2Cl$			
	370–380°	1	$SiCl_4$	(*374*)
		5	$EtSiCl_3$	(*374*)
		6	Et_2SiCl_2	(*374*)
		10	$CH_2=CHSiCl_3$	(*374*)
		17	$CH_2=CHSiEtCl_2$	(*374*)
		13	Normal product	(*374*)
		6	$Cl_2EtSiCH_2CH_2SiHCl_2$	(*374*)
		5	$Cl_2Si[Cl_2EtSiCH_2OH_2]_2$	(*374*)
		37	Losses and unresolved mixtures	(*374*)
β-di	$Cl_3SiCH_2CHCl_2$			
	360–370°	37	$HSiCl_3 + SiCl_4 + CH_2=CHSiCl_3$	(*317, 319*)
		9.1	$Cl_3SiCH=CHCl$	(*317, 319*)

TABLE V (*Continued*)

Type	Halide	%	Products	References
α-tri	Cl_3SiCCl_3			
	210–220°	2.7	$Cl_3SiC(Cl){=}CCl_2$	(*269*)
	$Cl_3SiCH_2CH_2CH_2Cl$			
	(Fe—Si) 400–450°	—	$HSiCl_3$	(*274*)
		—	$SiCl_4$	(*274*)
		—	$Cl_3SiCH_2CH{=}CH_2$	(*274*)
		—	$Cl_3SiCH{=}CHCH_3$	(*274*)
		—	No normal product	(*274*)
		—	Residue	(*274*)
	$Cl_2MeSiCH_2CH_2CH_2Cl$			
	370–380°	—	$SiCl_4 + MeSiHCl_2 + MeSiCl_3$	(*320*)
		—	Dimer	(*321*)
		23.5	$MeCl_2SiCH_2CH{=}CH_2$	(*321*)
			$MeCl_2SiCH{=}CHCH_3$	(*321*)
		14.1	Normal product	(*321*)
		7.1	$MeCl_2SiCH_2CH_2CH_2SiHCl_2$	(*321*)
		3.5	$[MeCl_2Si(CH_2)_3]_2SiCl_2$	(*321*)
	$Cl_2EtSiCH_2CH_2CH_2Cl$			
	370–380°	5.8	$EtSiCl_3$	(*321*)
		25.9	$Cl_2EtSiCH_2CH{=}CH_2$	(*321*)
			$Cl_2EtSiCH{=}CHCH_3$	(*321*)
		17	Normal product	(*321*)
		14.4	$Cl_2EtSiCH_2CH_2CH_2SiHCl_2$	(*321*)
	$Cl_2MeSiCH_2CH(Me)CH_2Cl$			
		1	$HSiCl_3$	(*320*)
		7.6	$MeSiHCl_2$	(*321*)
	270–280°	5.6	$SiCl_4$	(*321*)
	370–380°	6	$MeSiCl_3$	(*321*)
	470–480°	58	$MeCl_2Si(C_4H_7)$ isomers	(*321*)
		5.2	$MeCl_2SiCH_2CH(Me)CH_2SiHCl_2$	(*321*)
		3.2	Normal product	(*321*)
	$Cl_2EtSiCH_2CH(Me)CH_2Cl$			
		3.3	$HSiCl_3$	(*320*)
		1.2	$SiCl_4$	(*320*)
		12	$EtSiCl_3$	(*320*)
		49.4	$EtCl_2Si(C_4H_2)$ isomers	(*320*)
	370–380°	10	Normal product	(*321*)
		9.1	$Cl_2EtSiCH_2CH(Me)CH_2SiHCl_2$	(*321*)
	$Cl_3SiCH(Cl)CH_2CH_3$			
	(Fe—Si) 170°	0.6	$SiCl_4 + SiHCl_3$	(*274*)
		54.5	$Cl_3SiCH{=}CHCH_3$	(*274*)
			$Cl_3SiCH_2CH{=}CH_2$	(*274*)
		22	Starting product	(*274*)
		10.2	Residue	(*274*)
	$Cl_3Si(CH_2)_4Cl$	92	Crotyl trichlorosilane	(*275*)

[a] This starting material rearranges over copper metal alone to form $SiCl_4$, $Cl_3SiC{\equiv}CSiCl_3$, $(Cl_3Si)_2C{=}C(SiCl_3)_2$, and $(Cl_3Si)_2C{=}C{=}C(SiCl_3)_2$ (*270c*).

of the contact mass, attributed to the formation of carbon (*190*). Later, however, patents were filed (*257*, *301*) claiming the production of CF_3SiF_3 from the reaction of CF_3Br with a silicon-copper contact mass at 400°. With more rapid flow, CF_3SiF_2Br was also said to be formed (*405*). These reactions, if confirmed, would be of considerable interest; it is now known that chlorotrifluoroethylene and *unsym*-trichlorotrifluoroethane react with a moving bed of Si—Cu to form compounds containing silicon-carbon linkages (*270a*), and the field is one which could be extended considerably.

C. Reaction of Ethers

The large-scale direct preparation of organoalkoxysilanes by Direct Synthesis with ethers would be an attractive route to the production of silicones, since the alkoxy groups are readily hydrolyzed but without the formation of troublesome hydrogen chloride and much more controllably than with chlorosilanes. This question was examined some time ago (*62*, *345*, *368*) and the conclusion reached that ethers required the admixture of hydrogen halide or an alkyl halide if they were to react with catalyzed silicon. Reaction under such conditions could be explained in terms of a splitting of the ether and subsequent normal reactions of the alkyl halide. It was later claimed that ethers did react without any addition (*463*), but a reinvestigation of the problem (*476*, *477*) has shown that no C—Si bonds are produced up to temperatures at which the ether pyrolyzes.

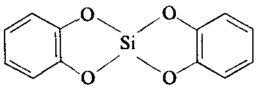
D. Reaction of Alcohols and Phenols

Rochow (*340*) investigated the reaction of methanol with silicon-copper at 250° and obtained fair yields of tetramethyloxysilane, together with hydrogen. Analogous reactions have been observed with ethanol (*51*, *59*, *345*, *352*) and phenol (*210*, *476*, *477*), and magnesium and calcium silicides have also been used (*58*, *152*, *415*).

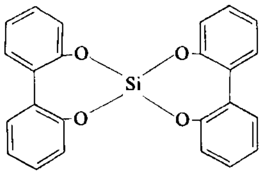
The analogous reactions with methyl mercaptan and thiophenol lead to formation of silicon sulfides in the contact mass. Extraction of the contact mass with benzene, in which the silicon sulfides are insoluble, gave material containing silicon, and it is highly probable that it resulted from thermal breakdown of the desired products (*478*, *479*).

1. Reaction with Difunctional Alcohols and Phenols

These reactions may be studied in an autoclave with a high pressure of hydrogen, using silicon-copper formed by sintering the powders in hydrogen. Catechol reacts under such conditions at 265° to form an almost quantitative yield of the compound I, which can be sublimed from the contact mass *in vacuo* at 236°:



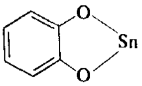
(I)



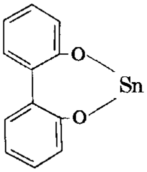
(II)

Reaction with 2,2′-dihydroxydiphenyl occurs at 230° to yield compound II. The usefulness of other polyfunctional aromatic hydroxy compounds in the Direct Synthesis is limited by their thermal stability. An interesting exception to this generalization is β-naphthol which, although thermally stable in the required temperature range, does not react with silicon-copper as phenol does (*478*, *479*). Aliphatic diols (e.g., ethylene glycol) are also thermally unstable at temperatures where they might otherwise be useful in the Direct Synthesis.[8]

Catechol reacts smoothly at 150° with a mixture of tin and copper powders to give a good yield of *o*-phenylenedioxytin(II) (compound III). 2,2′-Dihydroxydiphenyl gives compound IV and hydrogen.[9]



(III)



(IV)

The reaction of catechol with a mixture of lead and copper powders appears to result in a reaction analogous to the above; the product decomposes, however, to lead oxide and benzene on attempted sublimation (*478*, *480*).

IV. Reaction Mechanisms

The Direct Synthesis has, to a very large extent, been studied with the object of preparing new and useful compounds, and it is probably reasonable to question if some of the claims made in the patent literature, which has been extensively quoted in the earlier sections, are in fact scientifically accurate. The whole subject is, indeed, confused when considered from the point of view of possible reaction mechanisms. Nevertheless remarkable progress has been made in elucidating some of the steps by which the simpler reactions proceed.

Hurd and Rochow (*179*) were the first to offer an explanation of the peculiar activity of copper in facilitating the reaction of methyl chloride

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[8] In light of the above, it is curious to find it reported that aromatic silicon ortho esters decompose under heat and hydrogen pressures to give phenol and elementary silicon (*94*). Not only phenol but methyl phenyl ether (which undergoes hydrogenolysis in the presence of finely divided metals to give phenol) produces tetraphenoxysilane from silicon under high hydrogen pressures (*476*, *477*).

[9] These compounds can also be obtained in analogous reaction of stannous oxide (*481*).

with silicon. They found that if a crystal of silicon was imbedded in copper and heated to 350° in a stream of methyl chloride, both silicon and copper were removed from the point at which they were in contact or in close proximity. When copper was heated alone at 250° in a stream of methyl chloride, its surface became coated with a film of copper(I) chloride but, simultaneously, copper metal was transported and deposited downstream. The reaction $2Cu + CH_3Cl \rightarrow CuCH_3 + CuCl$ was proposed, the carry-over of copper being attributed to the breakdown of methyl copper, to liberate the metal and free methyl radicals (*87*, *136*).

This view was supported by a further experiment in which a lead mirror was deposited downstream from a small quantity of finely divided copper at 250°. When methyl chloride was passed the lead mirror gradually disappeared, as it is known to do when attacked by free methyl radicals:

$$CuCH_3 \rightarrow Cu + CH_3$$
$$4CH_3 + Pb \rightarrow (CH_3)_4Pb$$

Hurd and Rochow also established that pure silicon was not attacked at 250–400° by free methyl radicals formed by the pyrolysis of tetramethyllead, nor were $SiCl_4$ and Si_2Cl_6.[10] The reaction scheme proposed as being consistent with these observations is given below.

$$\begin{aligned}
2Cu + CH_3Cl &\rightarrow CuCl + CuCH_3(\rightarrow CH_3)\\
Si + CuCl &\rightarrow Cu + (SiCl) \text{ (active intermediate)}\\
(SiCl) + CH_3 &\rightarrow (CH_3SiCl)\\
\text{or } (SiCl) + CuCH_3 &\rightarrow (CH_3SiCl) + Cu\\
\text{or } (SiCl) + CuCl &\rightarrow (SiCl)_2 + Cu
\end{aligned}$$

These reactions would then continue to give the observed mixture of methylchlorosilanes. The chief function of the metal catalyst is to make the halogen of the organic halide readily available for reaction with the silicon. It also makes the organic group more available by transporting and effectively prolonging the life of the radicals in the form of the metal alkyl. The copper also probably catalyzes the dehydrohalogenation of the alkyl halides (*4*).

The authors suggest that a similar mechanism may be operative when other metals replace copper. For example, in the synthesis of phenylchlorosilanes from chlorobenzene with a silver catalyst (*359*), silver chloride is readily reduced by silicon at the temperature employed and chlorobenzene is known to react with silver at 400° to give AgCl (*138*, *139*, *179*). The silver is thus able to produce the active intermediate SiCl and also phenyl radicals. It seems reasonable to suppose that other metals could also act in this

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[10] The possibility of methyl copper acting on silicon halides in the manner of a Grignard reagent as had been proposed (*16*, *17*) was also ruled out.

way, though it would be very useful, and probably not difficult, to provide additional experimental evidence in support of this view.

An alternative mechanism proposed by Klebanskii and Fikhtengol'ts (*200*) and independently by Trambouze (*437*) rejects Hurd and Rochow's multistage radical scheme in favor of a mechanism involving changes in the Si–Cu system.

X-ray studies have shown the formation of a new Si—Cu intermetallic phase during the reaction of methyl chloride with the contact mass[11] (*6*, *167*, *180*, *209*, *413*, *438*). The new intermetallic phase is depleted as the synthesis continues[12] (Cu lines become stronger). It is postulated that alkyl halides are chemisorbed onto the intermetallic compound and that, as a result, the C—Cl bond is deformed and polarized by the ionic charges in the lattice. This surface phenomenon is said to lower the stability of the C—Cl bond and facilitate transfer of groups to silicon. It is pointed out that reaction of cuprous chloride with silicon occurs only above 260°, while the Direct Synthesis may proceed at temperatures as low as 115°.[13] The transfer of chlorine from copper to silicon must, therefore, take place at the surface of the intermetallic lattice.

Some support for this viewpoint may come from the relationship between the ease of reaction of alkyl halides with Si—Cu and their dipole moments (Table VI).

TABLE VI
DIPOLE MOMENTS AND INITIAL REACTION TEMPERATURES OF ALKYL HALIDES[a]

Halide	Reaction temperature	Dipole moment (D)
MeCl	290°	1.92
EtCl	195°	2.05
i-PrCl	115°	2.15
t-BuCl	122°	2.13

[a] Reference (*200*).

The same sort of relationship is exhibited by methyl chloride, chlorobenzene, and vinyl chloride or by methyl chloride, allyl chloride, and 2,4-dichlorobutene-2. An explanation in these terms is not particularly

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[11] Germanium forms similar compounds with copper (*280*).

[12] The kinetics for the decomposition of this phase with ethyl chloride have been studied, but the rate is closely dependent on the presence of structural imperfections in the alloy (*193*, *194*, *210*, *220*, *228b*).

[13] The reaction of silicon with copper(I) chloride is exothermic and autocatalytic (*205*). It is doubtful that 115° represents an initiation temperature and so would be quite possible to achieve, once the initial passivity of the silicon is overcome.

convincing as one would expect the C—Cl bond energy to be a more significant parameter for such comparisons. It should also be pointed out that the temperature of initial reaction is itself a rather ill-defined criterion since it certainly depends on the extent to which the solid surface is covered with an oxide film. A kinetic study of the oxidation of silicon at high temperatures shows the process to be severely diffusion-controlled by the layer of vitreous oxide (*69*). Just as aluminum is much more susceptible to attack by chlorine and chlorides than by oxygen or oxidizing agents despite the high heat of formation of alumina, so silicon is much more readily attacked by halogens and halides. Such attack probably involves a mechanism much more drastic than diffusion of the halide through the oxide film, reaction with silicon, and outward diffusion of products. These reactions take place at a rate so high as to suggest breaching of the oxide film. In this connection it is interesting to note that silicon itself, when freshly pulverized in presence of the reactant, has an abnormally high reactivity and will react both with chlorine (*208*) and with carbon tetrachloride (*149*) at room temperature.[14]

Other work has helped to clarify the situation. Thus the reaction of *n*-propyl chloride with germanium copper at 310–330° provides evidence for the need of some kind of transport agent (*357*). *n*-Propyl chloride undergoes rearrangement to the isopropyl isomer at 280°, yet the reaction product is *n*-propyltrichlorogermane. It is also known that silicon subchlorides (*161*, *358*) react with methyl chloride at 300° to give the same distribution of products as with elementary silicon (*159*, *291*). Partially chlorinated silicon atoms on the surface of a silicon crystal are also known to retain the halogen very tenaciously, even in a stream of hydrogen. For example, an organic ether, which is normally unreactive to Si—Cu, reacts readily with a silicon-copper contact mass previously treated with hydrogen chloride at 500° and subsequently flushed for long periods with hydrogen at the same temperature. Organochlorosilanes are produced and reaction continues as long as the chlorine lasts (*476*, *477*). Copper metal is transported in flow systems during reaction, and some copper may even be found in the product (*166*, *206*); but although red deposits are observed in the pyrolysis of ethers over silicon-copper, no reaction with silicon takes place presumably because of the absence of an active silicon intermediate (*476*, *477*). The inhibiting effect of nitric oxide on the Direct Synthesis has also been studied (*396*) and is found to rise sharply with temperature. This may be interpreted as meaning that it reacts preferentially with methyl radicals in the gas

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[14] Apparently these are examples of the mechanochemical Russell effect observed when crystals are cleaved to give fresh surfaces (*211*). The method is also effective with aluminum (*207a*).

phase but that, at elevated temperatures, those participating directly in the synthesis are affected.[15]

The above evidence is in no sense conclusively in favor of one or another of the views put forward on the reaction mechanism of the Direct Synthesis, though the elegant experiments made by Hurd and Rochow seem, on the whole, to provide the most satisfying basis for discussion (*4, 17, 34, 37, 143a, 201, 298, 358, 365, 366, 398, 446*). The engaging possibility that the active intermediate these workers describe is actually the silicon analog of dichlorocarbene cannot be ruled out. In addition the novel proposal has been put forward that the process is one of electrochemical corrosion of silicon with cathodic control (and thanks to the small thickness of the layer of adsorbed organic electrolyte and its high resistance—ohmic control as well), based on experiments with pure silicon in a heated electrolytic cell (*298, 448*). Unfortunately this suggestion has not been further pursued (*299*). The fact that the Direct Synthesis may be operated with alcohols and phenols calls for further discussion, since the Hurd and Rochow mechanism is not necessarily valid and there is no clear evidence of the part played by the copper catalyst.

One simple mechanism for the reaction of alcohols and phenols would be to regard them as reacting in the same way as an acid with a metal, hydrogen being set free and the carbon-oxygen bond remaining intact. Indeed, the action of alcohols on active metals is a case in point (*412*). Another lead comes from the observation that, during sintering of a silicon-copper contact mass in hydrogen over long periods, some copper is transported in the gas stream. It is known that unstable volatile copper hydride may form under such conditions (*453*). Silicon is also known to exhibit an abnormal volatility in hydrogen at high temperatures, which is thought to be associated with the formation of an unstable volatile silicon subhydride (*27, 40, 386*). Examination of the infrared spectrum of silicon powder that has been heated in hydrogen at 1000° shows a sharp peak at 2178 cm^{-1}, close to the Si—H stretching frequency at 2187 cm^{-1} observed with monosilane.[16] These observations indicate that reaction of both silicon and copper with hydrogen to form a reactive intermediate may be significant in the synthesis (*478, 479*). The reaction of methanol with monosilane, which is strongly catalyzed by metallic copper, yields tetramethoxysilane and hydrogen and shows an increase in rate after the introduction of the

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[15] Nitric oxide would, of course, also be expected to inhibit Direct Synthesis by the chemisorption mechanism by tying up active sites on the surface (but the steep rise of inhibition with temperature would be difficult to justify by an activation energy argument).

[16] That this absorption may be due to a defect state in the solid cannot be entirely eliminated (*162*).

first methoxy group (*96, 308, 421*). It has been recently shown that trimethoxy- and dimethoxysilane may be isolated from the products of the reaction of methanol with Si—Cu—Zn (*95*). Something of the relative tendency for formation of silicon subhydrides versus silicon subhalides may be judged from the reaction of hydrogen chloride with silicon, where the major product is trichlorosilane, $HSiCl_3$. The following scheme suggests itself:

$$H_2 + Si \rightarrow (SiH) \text{ or } (SiH_2) \text{ (active intermediate)}$$

$$ROH \xrightarrow{Cu} RO\cdot + H\cdot$$

$$RO\cdot + (SiH_2) \rightarrow (ROSiH_2) \xrightarrow{etc.} (RO)_2SiH_2$$

$$ROH + (RO)_2SiH_2 \xrightarrow{Cu} (RO)_3SiH + H_2$$

$$ROH + (RO)_3SiH \xrightarrow{Cu} (RO)_4Si + H_2$$

This mechanism is useful in explaining other observations such as the formation of Si—H components when hydrogen is mixed with methyl chloride passed over silicon-copper, or when methyltrichlorosilane is heated in hydrogen over silicon-copper. Another relevant reaction is that of cyanogen chloride with silicon-copper sintered in hydrogen. This gives hydrogen cyanide, cyanogen, and silicon tetrachloride, whereas only cyanogen and silicon tetrachloride are formed when sintering in hydrogen is omitted (*478*). A silicon subhydride would be destroyed as the result of hydrogen abstraction by organic free radicals formed in the pyrolysis of starting materials. This may account for the fact that 2,2′, 1,1′-dinaphthyl decomposes under the conditions of the synthesis to give β-naphthol in good yield, but the β-naphthol does not then react as do other alcohols and phenols under similar conditions (*478*). Also phenol itself, which has been formed *in situ* during the pyrolysis of anisole at 600° over silicon-copper, does not combine with the silicon, whereas it otherwise reacts normally under the same conditions to give tetraphenoxysilane (*355*). It is also quite possible that copper functions in these reactions by forming a volatile unstable alkoxy compound, though there is no direct evidence of this.

V. Other Direct Syntheses

There are almost certainly other reactions related to that used in making alkyl- and arylchlorosilanes, which remain to be discovered in the future (see e.g., *354*). Foremost among these is the direct reaction of elements such as silicon with hydrocarbons, with or without the addition of hydrogen, to form compounds such as alkyl silicon hydrides (*19, 81, 83, 141, 252, 462*). In fact, it has been claimed that when hydrocarbon gases are passed over silicon carbide at 1500° and the exit gases are rapidly quenched, alkyl silanes are produced (*82*). Such a reaction, if it could be brought about at lower temperatures by a suitable catalyst, would be of the greatest interest. Patents have also been granted for processes involving the dilution of alkyl halides in the Direct Synthesis with methane or benzene. It is said, for example, that addition of methane to ethyl chloride leads to methylethyldichlorosilane, but there appears to be doubts about these reactions as some workers have failed to isolate the products claimed (*143, 188, 260, 464–467*).

The reaction

$$C_2H_2 + Si + 3H_2 \rightarrow (CH_3)_2SiH_2$$

has a high driving force (−78.7 kcal) but hydrogenation of the acetylene occurs preferentially. Hydrocarbons have been used in Direct Synthesis by intermediate formation of organic halides with hydrogen chloride or chlorine. For example, natural gas (presumably containing considerable methane, petroleum gases (containing ethylene) (*237*), or even waste gases from the Direct Synthesis itself (*235, 329*), if passed with chlorine at 400–850° over a silicon-copper contact mass form methylchlorosilanes (*112, 252*). Methane with hydrogen chloride at 350° is reported to give CH_3SiHCl_2 in 38.8% yield along with the usual products (*264*), and organochlorosilanes result if a mixture of olefins with hydrogen chloride is bubbled through a suspension of Si—Cu in paraffin oil (*387*). Aromatic hydrocarbons also find a use here, as in the reaction of hydrogen chloride with benzene over Si—Cu at 600–850°, which gives $PhSiCl_3$ (*254, 462*). When the reaction is carried out in presence of chlorobenzene it can be run at 475–550° (*85*). Aromatic hydrocarbons have also been utilized in Direct Synthesis reactions in the presence of compounds containing silicon-chlorine bonds (e.g., $SiCl_4$, $PhSiCl_3$, $MeSiCl_3$) to produce phenylchlorosilanes (*99*). Here, however, the main reaction is between the silicon-halogen linkages and the aromatic hydrocarbon, and this is catalyzed directly by Lewis acids (*255, 325*). A single-step route to organofluorosilanes utilizes calcium fluoride, coal, sand, sodium chloride, and an organic halide at 800° (*168*).

VI. Conclusion

In his book *Organosilicon Compounds*, (*101*). Professor C. Eaborn states, "The present widespread interest in organosilicon chemistry stems very largely . . . from the commercial importance of silicones, which were first studied as potentially valuable polymers in the late 1930's. . . . The most important single step in these researches was Rochow's discovery, published in 1945, of the Direct Synthesis of organochlorosilanes. . . . Without this process for the all-important methylchlorosilanes, from which the methylsilicones are obtained by hydrolysis, it is certain that the growth of the silicone industry would have been slower [and] the fundamental studies of organosilicon chemistry which it stimulated would also have been delayed."

In the two decades since its discovery, a vast amount of research effort has been concentrated on Rochow's Direct Synthesis method itself. The future possibilities, however, both for the utilization of elemental silicon as a raw material and for the expansion of the usefulness of the Direct Synthesis as a synthetic method are very great indeed.

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