CARBON-FUNCTIONAL SILICONES

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I. INTRODUCTION

A. SCOPE OF THE REVIEW

Carbon-functional silicones[2] are organosilicon compounds which contain functional groups in the organic substituents attached to silicon. Representative members of the class are $ClCH_2Si(CH_3)Cl_2$, $CH_2{=}CHSiCl_3$, $CH_3SO_2CH_2Si(CH_3)_3$, and $[NH_2CH_2Si(CH_3)_2]_2O$. These compounds contain at least one heteroatom or non-benzenoid unsaturated linkage attached to silicon through carbon. This definition was selected because (*a*) it is based on structure rather than on a variable concept such as reactivity, (*b*) it includes all the commonly accepted functional groups, and (*c*) it unequivocally arbitrates borderline cases. The generic name "carbon-functional" was selected because (*a*) it parallels standard organic nomenclature, (*b*) it is abbreviated readily by the use of the symbol for carbon, and (*c*) it fits well with the companion term "silicon-functional," which refers to functional groups attached directly to silicon.

Over twelve hundred such compounds have appeared in more than five hundred references. Over ninety per cent of this material has been published since 1947,

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[2] The term "silicone" has had various meanings since Wöhler coined it in 1857; usage is making "silicone" fill the need for a handy term to replace "organosilicon compound."

in which year the review by Burkhard, Rochow, Booth, and Hart (92a) appeared. Some of these compounds were mentioned by Rochow (381a) in the second edition of his book. The present review covers the literature through January 1, 1955.

B. NOMENCLATURE

Carbon-functional silicones may be named either as functional organic derivatives of parent silicon compounds or as silicon derivatives of parent functional organic compounds. According to the first system $NH_2CH_2Si(CH_3)_2OSi(CH_3)_3$ becomes aminomethylpentamethyldisiloxane, and according to the second system it becomes pentamethyldisiloxanylmethylamine.

The Fifteenth Conference of the International Union of Pure and Applied Chemistry favored naming carbon-functional silicones according to the second system, i.e., as silicon derivatives of functional organic compounds, wherever feasible. This system works well with very simple compounds. *Chemical Abstracts* uses it to some extent but relies more on the first system, which regards carbon-functional silicones as functional organic derivatives of parent silicon compounds. Both systems are used in this review. Usually, compounds are designated by line formulas because they are shorter and clearer.

C. FORMAT OF TABLES OF COMPOUNDS

The tables containing the compounds are designed as a complete key to the scientific and patent literature on monomeric and polymeric carbon-functional silicones. The data tabulated for each compound are (*a*) its structural formula, (*b*) selected physical properties, and (*c*) references. The structural formulas present the carbon-functional groups first and the silicon-functional groups last, with the silicon and hydrocarbon groups in between. The references for each substance include all articles in which it is mentioned; one or two major references are set in italics. Within the tables the compounds are arranged in order of increasing complexity. Subdivisions are small enough so that the reader will find it easier to scan for desired compounds than to learn classification rules in an effort to pin-point their proper location.

For those who wish to make more extensive use of the tables the following rules are given: The major divisions into tables are outlined in the contents. Within these tables the compounds are first grouped according to the kind of carbon-functional group: e.g., all $ClCH_2$— in one, all Cl_2CH— in another, etc. Where there is more than one kind of carbon-functional group, cross references are provided. Where different substituents occur in the same organic group the compound is listed according to the substituent nearest the silicon, frequently with cross references to the others. Each of the major groups is then subdivided into monosilanes, polysilmethylenes, and polysiloxanes. Further subdivision is on the basis of increasing number of carbon-functional groups of a given kind per silicon atom. The arrangement within these groups is based on increasing organic substitution for the monosilanes and polysilmethylenes and on increasing functionality for the polysiloxanes. Compounds of indefinite structure follow their known isomers.

II. TYPICAL SYNTHETIC METHODS

Syntheses of carbon-functional silicones fall into three major categories: direct methods, in which a silicon–carbon bond is formed; substitution methods, in which a functional group is introduced into an unsubstituted organosilicon compound; and replacement methods, in which functional groups already present are replaced with other functional groups.

Direct and substitution methods are more attractive industrially. Replacement methods are simpler for laboratory use, and by far the most carbon-functional silicones have been made in this way.

Many examples of the above three basic types of synthesis are illustrated below by means of equations. The reactions depicted are treated in greater detail and with specific references in succeeding sections.

A. DIRECT SYNTHESES

1. Direct reaction with silicon

$$CH_2{=}CHCH_2Cl + Si \xrightarrow[Cu]{heat} (CH_2{=}CHCH_2)_2SiCl_2$$

2. Addition of Si—H *to unsaturates*

$$CH_3CH_2CH_2C{\equiv}CH + HSiCl_3 \xrightarrow[(C_6H_5CO)_2O_2]{heat} CH_3CH_2CH_2CH{=}CHSiCl_3$$

$$ClCH_2CH{=}CH_2 + HSiCl_3 \xrightarrow{Pt} ClCH_2CH_2CH_2SiCl_3$$

3. Coupling of Si—Cl *with functional organometallics*

$$(C_2H_5)_2SiCl_2 + CF_3CF_2CF_2Li \xrightarrow{-50°C.} (CF_3CF_2CF_2)_2Si(C_2H_5)_2$$

$$SiCl_4 + ClC_6H_4MgBr \rightarrow ClC_6H_4SiCl_3$$

$$(CH_3)_3SiOC_6H_4Cl \xrightarrow[(CH_3)_3SiCl]{Na} (CH_3)_3SiOC_6H_4Si(CH_3)_3 \xrightarrow{H_2O} HOC_6H_4Si(CH_3)_3 + (CH_3)_3SiOH$$

$$HSiCl_3 + (CH_3)_2NC_6H_4Li \rightarrow [(CH_3)_2NC_6H_4]_3SiH$$

4. Other direct syntheses

$$C_6H_5SiK + CO_2 \xrightarrow{H_2O} (C_6H_5)_3SiCOOH$$

$$SiCl_4 + CH_2N_2 \rightarrow ClCH_2SiCl_3 + N_2$$

B. SUBSTITUTION REACTIONS

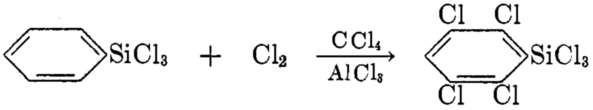
1. Free-radical substitutions

$$(CH_3)_2SiCl_2 + Cl_2 \xrightarrow{light} (ClCH_2)(CH_3)SiCl_2$$

$$(CH_3)_3SiCl + Br_2 + Cl_2 \xrightarrow{light} (BrCH_2)(CH_3)_2SiCl + HCl$$

$$(CH_3)_4Si + PCl_3 + O_2 \rightarrow (CH_3)_3SiCH_2POCl_2$$

2. *Silyl aromatic substitutions*



$$C_6H_5Si(CH_3)_3 + \text{fuming } HNO_3 \rightarrow 2\text{-}NO_2C_6H_4Si(CH_3)_3 + 3\text{-}NO_2C_6H_4Si(CH_3)_3 + 4\text{-}NO_2C_6H_4Si(CH_3)_3$$

C. REPLACEMENT REACTIONS

1. *Ionic displacement on silyl organic halides*

$$\underline{OSi(CH_3)_2OSi(CH_3)_2OSi(CH_3)_2OSi}(CH_3)CH_2Cl \xrightarrow[(CH_3)_2CO]{NaI} \underline{OSi(CH_3)_2OSi(CH_3)_2OSi(CH_3)_2OSi}(CH_3)CH_2I$$

$$(CH_3)_3SiCH_2Cl + CH_3COOK \xrightarrow{CH_3COOH} (CH_3)_3SiCH_2OCOCH_3$$

$$(CH_3)_3SiOSi(CH_3)_2CH_2Cl + NH_3 \rightarrow (CH_3)_3SiOSi(CH_3)_2CH_2NH_2$$

$$(CH_3)_3SiCH_2Cl + CH_2(COOC_2H_5)_2 \xrightarrow{NaOC_2H_5} (CH_3)_3SiCH_2CH(COOC_2H_5)_2$$

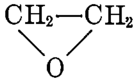
$$(CH_3)_3SiCH_2Cl + NaOC_2H_5 \xrightarrow{C_2H_5OH} (CH_3)_3SiCH_2OC_2H_5$$

$$\underline{OSi(CH_3)_2OSi(CH_3)_2OSi(CH_3)_2OSi}(CH_3)CH_2Cl \xrightarrow[C_2H_5OH]{NaSH} \underline{OSi(CH_3)_2OSi(CH_3)_2OSi(CH_3)_2OSi}CH_3CH_2SH$$

2. *Silcarbanion displacements*

$$(CH_3)_3SiCH_2MgCl + ClCOOC_2H_5 \rightarrow (CH_3)_3SiCH_2COOC_2H_5$$

$(CH_3)_3SiCH_2CH_2CH_2MgBr$ +



$\rightarrow (CH_3)_3SiCH_2CH_2CH_2CH_2CH_2OH$

$$BrCH_2CH_2CH_2Si(CH_3)_2Cl + Mg \rightarrow \underline{CH_2CH_2CH_2Si}(CH_3)_2$$

3. *Silylalkene addition reactions*

$$(CH_3)_3SiCH_2CH{=}CH_2 + CO + H_2 \xrightarrow[Co]{heat} (CH_3)_3SiCH_2CH(CHO)CH_3$$

$$(CH_3)_3SiCH{=}CH_2 + HSCH_2COOH \xrightarrow{O_2} (CH_3)_3SiCH_2CH_2SCH_2COOH$$

$$(CH_2{=}CHCH_2)_2Si(OC_2H_5)_2 + CF_2{=}CF_2 \xrightarrow{heat}$$

$$(\underbrace{CF_2CF_2CH_2CH}CH_2)_2Si(OC_2H_5)_2$$

$$(CH_3)_3SiCH{=}CH_2 + CH_3CH_2CHO \xrightarrow{(CH_3CO)_2O_2} (CH_3)_3SiCH_2CH_2COCH_2CH_3$$

$$CH_2{=}CHSiCl_3 + Cl_2 \rightarrow ClCH_2CHClSiCl_3$$

4. Other syntheses

$$CH_2ClCH_2SiCl_3 \xrightarrow{AlCl_3} CH_2{=}CHSiCl_3$$

$$(CH_3)_3SiOSi(CH_3)_2CH_2SCH_3 \xrightarrow{CH_3CO_3H} (CH_3)_3SiOSi(CH_3)_2CH_2SO_2CH_3$$

III. TYPICAL REACTIONS

Basically there are three types of carbon-functional silicone reactions: (*a*) those of the carbon-functional substituents; (*b*) those involving silicon–carbon cleavages; (*c*) those of the silicon-functional substituents.

A. CARBON-FUNCTIONAL SUBSTITUENTS

The reactions of the carbon-functional substituents are very similar to those encountered in analogous purely organic compounds. Representative examples have been given in the preceding section. This type of reaction is important both in synthesis and in elucidating the electronic influences of silicon and is treated extensively in succeeding sections.

B. SILICON–CARBON CLEAVAGES

Silicon–carbon cleavage reactions may involve either substituted or unsubstituted groups in carbon-functional silicones. Such reactions are frequently the bane of the synthetic chemist, but they have their constructive uses too: for example, in determining structure, in providing facile curing mechanisms for polymers, and in elucidating mechanisms of substitution at a silicon atom.

Examples of silicon–carbon cleavage reactions are given below in equation form. They are treated in greater detail and with specific references in succeeding sections. Factors which influence silicon–carbon cleavage include: (*a*) the nature of the functional group and of the attacking reagent; (*b*) the location of the functional group along an aliphatic chain or in an aromatic nucleus; (*c*) the influence of the other substituents on the silicon.

1. Cleavage of substituted groups

$$\mathrm{CH_2{=}CHCH_2Si(CH_3)_3 + Br_2 \rightarrow CH_2{=}CHCH_2Br + (CH_3)_3SiBr}$$

$$\mathrm{Cl_3CSiCl_3 + H_2O \rightarrow CHCl_3 + silicic\ acid + HCl}$$

$$\mathrm{ClCH_2CH_2SiCl_3 + H_2O \rightarrow CH_2{=}CH_2 + silicic\ acid + HCl}$$

$$\mathrm{(CF_3CF_2CF_2)_2Si(C_2H_5)_2 \xrightarrow[NaOCH_3,\ CH_3OH]{75°C.} CF_3CF_2CF_2H + [(C_2H_5)_2SiO]_{\mathit{x}}}$$

$$\mathrm{(CH_3)_3SiCH_2COOC_2H_5 + C_2H_5OH \xrightarrow{heat} (CH_3)_3SiOC_2H_5 + CH_3COOC_2H_5}$$

$$\mathrm{4\text{-}NO_2C_6H_4Si(CH_3)_3 + Br_2 \xrightarrow[H_2O]{heat} 4\text{-}NO_2C_6H_4Br + (CH_3)_3SiOSi(CH_3)_3}$$

$$\mathrm{4\text{-}HOC_6H_4Si(CH_3)_3 \xrightarrow{heat} C_6H_5OSi(CH_3)_3}$$

2. Cleavage of unsubstituted groups

$$\mathrm{(CH_3)_3SiCH_2Cl \xrightarrow{AlCl_3} (CH_3)_2C_2H_5SiCl}$$

$$\mathrm{(C_6H_5CH_2)(C_3H_7)(C_2H_5)SiCH_3 \xrightarrow{concd.\ H_2SO_4} \xrightarrow{H_2O} [(4\text{-}HSO_3C_6H_4CH_2)(C_3H_7)(C_2H_5)Si]_2O + CH_4}$$

$$\mathrm{ClCH_2Si(CH_3)_3 \xrightarrow[concd.\ H_2SO_4]{heat} \xrightarrow{H_2O} [ClCH_2(CH_3)_2Si]_2O + CH_4}$$

$$\mathrm{(CH_3)_3SiCH_2CH_2COOH \xrightarrow[concd.\ H_2SO_4]{heat} \xrightarrow{H_2O} O[Si(CH_3)_2CH_2CH_2COOH]_2 + CH_4}$$

$$\mathrm{CH_2{=}C(CH_3)Si(CH_3)_3 \xrightarrow{concd.\ H_2SO_4} \xrightarrow{H_2O} [(CH_3)_3CSi(CH_3)_2]_2O}$$

C. SILICON-FUNCTIONAL REACTIONS

The silicon-functional reactions of carbon-functional silicones exhibit no unusual features, although they are undoubtedly influenced by nearby substituents on carbon. They are important as an indirect means for obtaining monomeric and polymeric derivatives which are not easily prepared directly. Examples of silicon-functional reactions are given below and are discussed in greater detail in succeeding sections.

$$\mathrm{ClCH_2Si(CH_3)_2Cl + H_2O \rightarrow ClCH_2Si(CH_3)_2OSi(CH_3)_2CH_2Cl}$$

$$\mathrm{CH_2{=}CHSiCl_3 + RMgX \rightarrow CH_2{=}CHSiR_3}$$

$$\mathrm{\underline{OSi(CH_3)_2CH_2CH_2CO} + H_2O \rightarrow O[Si(CH_3)_2CH_2CH_2COOH]_2}$$

IV. OLEFINS AND ACETYLENES (SEE TABLE 1)

A. SYNTHESES OF OLEFINS

1. Direct syntheses

Vinylchlorosilanes consisting mostly of $CH_2{=}CHSiCl_3$ are produced by the action of vinyl chloride with silicon in the presence of copper at about 300°C. (253, 254). The yields are low, but they may be improved with a tin promoter (487). Allylchlorosilanes constitute about 60 per cent of the product obtained from the reaction of allyl chloride with silicon–copper at 230–300°C.; $CH_2{=}CHCH_2SiCl_3$ is the major product (253, 254). This complex heterogeneous

$$CH_2{=}CHCH_2Cl \quad + \quad Si \quad \xrightarrow[Cu]{heat}$$

$$CH_2{=}CHCH_2SiCl_3 \quad + \quad (CH_2{=}CHCH_2)_2SiCl_2 \quad + \quad CH_2{=}CHCH_2SiHCl_2$$

catalytic process has been investigated to only a limited extent and is probably capable of significant improvement.

2. Dehydrohalogenation

Dehydrohalogenation has been used very extensively in synthesizing alkenyl silicon compounds. The reaction has been described in detail for $CH_2{=}CHSiCl_3$, which is obtained in an overall yield of 60 per cent (253, 255). Of the common dehydrohalogenation reagents, quinoline can be used most generally.

$$CH_3CH_2SiCl_3 \xrightarrow[(C_6H_5COO)_2]{SO_2Cl_2} \left\{\begin{array}{c} CH_2ClCH_2SiCl_3 \\ + \\ CH_3CHClSiCl_3 \end{array}\right. \xrightarrow{quinoline} CH_2{=}CHSiCl_3$$

Aluminum chloride is very effective in dehydrohalogenating chloroalkyltrichlorosilanes (9, 526), but where alkyl groups are attached to silicon extensive silicon–carbon cleavage occurs (526).

$$CH_2ClCH_2Si(C_2H_5)_2Cl \xrightarrow{AlCl_3} CH_2{=}CH_2 \quad + \quad (C_2H_5)_2SiCl_2$$

Dehydrohalogenation of the α-, β-, and γ-chloropropyltrichlorosilanes with aluminum chloride gives good yields of $CH_2{=}CHCH_2SiCl_3$ and $CH_3CH{=}CH_2SiCl_3$ (9). In each case the latter predominates. The reaction must be carried out below

$$CH_3CHClCH_2SiCl_3 \xrightarrow{AlCl_3} CH_2{=}CHCH_2SiCl_3 \quad + \quad CH_3CH{=}CHSiCl_3$$

165°C. to minimize silicon–carbon cleavage, and the products must be continuously removed by distillation to avoid their polymerization.

Strong bases such as potassium hydroxide have also been used as dehydrohalogenating agents (350, 519), but they are less satisfactory because they cannot be used with compounds containing hydrolyzable silicon-functional groups. Moreover, they produce silicon–carbon cleavage, particularly with β-halogeno compounds.

TABLE 1

Silicon-containing olefins and acetylenes

Compound	Melting Point	Boiling Point	n_D	d	References*
	°C.	*°C.*			
Vinyls:					
$CH_2=CHSiCl_3$		90	1.436 (20°)	1.28 (20°)	(1, 4, 5, 26, 48, 49, 50, 51, 90, 91, 97, 98, 161, *253*, 254, 255, 256, 257, 265, 266, 295, 333, 334, 335, 410, 425, 487, 502, 517, 525, 526, 530)
Ozonide					(526)
$CH_2=CHSi(OCOCH_3)_3$		127/25 mm.			(161)
$CH_2=CHSi(OCH_3)_3$		123/760 mm.	1.3910 (25°)	0.9669 (25°)	(*336*, 517)
$CH_2=CHSi(OC_2H_5)_3$		158 63/20 mm.	1.3960 (25°)	0.9027 (25°)	(117,265, 266, *336*, 485, 486, 525, 526, 543)
$CH_2=CHSi(OC_3H_7)_3$		103/20 mm.	1.4088 (25°)	0.8903 (25°)	(336)
$CH_2=CHSi(OC_3H_7\text{-}i)_3$		78/20 mm.	1.3961 (25°)	0.8627 (25°)	(336)
$CH_2=CHSi(OC_4H_9)_3$		142/20 mm.	1.4181 (25°)	0.8820 (25°)	(336)
$CH_2=CHSi(OC_4H_9\text{-}i)_3$		111/7 mm.	1 4130 (25°)	0.8718 (25°)	(336)
$CH_2=CHSi[OCH(CH_3)C_2H_5]_3$		101/8 mm.	1.4155 (25°)	0.8767 (25°)	(336)
$CH_2=CHSi(OC_5H_{11})_3$		159/9 mm.	1.4265 (25°)	0.8797 (25°)	(336)
$CH_2=CHSi(OC_5H_{11}\text{-}i)_3$		137/6 mm.	1.4232 (25°)	0.8738 (25°)	(335)
$CH_2=CHSi(OC_6H_{13})_3$		178/8 mm.	1.4311 (25°)	0.8719 (25°)	(335)
$CH_2=CHSi(OC_5H_{11})_3$		193/8 mm.	1.4378 (25°)	0.9956 (25°)	(335)
$CH_2=CHSi(OC_6H_5)_3$		210/7 mm.	1.5617 (25°)	1.1300 (25°)	(335)
$CH_2=CHSi(OC_7H_{15})_3$		202/6 mm.	1.4335 (25°)	0.8706 (25°)	(335)
$CH_2=CHSi(OC_8H_{17})_3$		225/8 mm.	1.4390 (25°)	0.8639 (25°)	(335)
$CH_2=CHSi(OCH_2CH=CH_2)_3$		90/8 mm.	1.4380 (25°)	0.9435 (25°)	(335)
$CH_2=CHSi(OCH_2CH_2OCH_3)_3$		136/6 mm.	1.4271 (25°)	1.0336 (25°)	(335)
$CH_2=CHSi(OCH_2CH_2Cl)_3$		153/7 mm.	1.4631 (25°)	1.2462 (25°)	(335)
$CH_2=CHSiCl_3$-glycol condensates					(518)
$CH_2=CHSiHCl_2$		67			(487)
$CH_2=CHSiH_3$					
α-form	−179.08	−22.8			(269, 504, *505*, 537)
β-form	−171.61				
$CH_2=CHSi(CH_3)Cl_2$		93		1.085 (25°/27°)	(26, 161, *253*, 254, 255, 256, 257, 320)
$CH_2=CHSi(CH_3)(OCOCH_3)_2$		85/24 mm.			(161)
$CH_2=CHSi(CH_3)(OC_2H_5)_2$		133–134	1.4000 (20°)	0.858 (20°)	(117)
$CH_2=CHSi(C_2H_5)Cl_2$		122/750 mm.	1.4405 (20°)	1.058 (25°)	(51, 231, 253, 265, 266, *525*)

* See the first paragraph of Section I,C.

$(CH_2{=}CH)(CH_2{=}CHCH_2)SiCl_2$		69/57 mm.	1.4602 (25°)	1.098 (25°)	(392)
		34/10 mm.			
$CH_2{=}CHSi(C_6H_5)Cl_2$		121/36 mm.	1.5335 (25°)	1.196 (25°)	(51, 160, *392*)
$CH_2{=}CHSi(C_6H_5)(OCOCH_3)_2$		86–88/0.2 mm.			(160, *161*)
$CH_2{=}CHSi(CH_2C_6H_5)Cl_2$		71/1 mm.	1.5312 (25°)	1.232 (25°)	(392)
$CH_2{=}CHSi(CH_2C_5H_5)(OH)_2$	83				(161)
$CH_2{=}CHSi(CH_2C_6H_6)(OCOCH_3)_2$		121/2.0 mm.			(161)
$(CH_2{=}CH)(4\text{-}ClC_6H_4)SiCl_2$		86/2 mm.	1.5462 (25°)	1.291 (25°)	(160, *392*)
$(CH_2{=}CH)(4\text{-}ClC_6H_4)Si(OCOCH_3)_2$		132/0.4 mm.			(160, *161*)
$(CH_2{=}CH)(H_3SiCH_2CH_2)SiH_2$					(537)
$CH_2{=}CHSiH_2SiH_2C_2H_5$					(537)
$CH_2{=}CHSi(CH_3)_2OC_2H_5$		99	1.3983 (20°)	0.790 (20°)	(117)
$CH_2{=}CHSi(CH_3)_3$		55/739 mm.	1.3902 (20°)	0.6903 (20°)	(65, 90, 91, 99, 255, *334*, 410, 425)
		54	1.3880 (25°)	0.6865 (25°)	
Ozonide					(425)
$CH_2{=}CHSi(CH_3)_2C_2H_5$		88/737 mm.	1.4089 (20°)	0.7242 (20°)	(425)
$CH_2{=}CHSi(CH_3)(C_2H_5)_2$		118/734 mm.	1.4230 (20°)	0.7503 (20°)	(425)
$CH_2{=}CHSi(C_2H_5)_2Cl$		138/738 mm.	1.4392 (20°)	0.9061 (20°)	(425)
$CH_2{=}CHSi(C_2H_5)_3$		146	1.4330 (20°)	0.7767 (20°)	(305, 306, 308, 334, 360, 519, 554)
		144	1.4340 (25°)	0.7674 (25°)	
$CH_2{=}CHSi(C_2H_5)_2C_6H_5$		123/29 mm.	1.5117 (20°)	0.9023 (20°)	(425)
$CH_2{=}CHSi(C_3H_7)_3$		73/5 mm.	1.4432 (25°)	0.8310 (25°)	(334)
$(CH_2{=}CH)(CH_2{=}CHCH_2)_3Si$		70/6 mm.	1.4790 (25°)	0.8313 (25°)	(334)
$CH_2{=}CHSi(C_4H_9)_3$		99/7 mm.	1.4479 (25°)	0.8261 (25°)	(334)
$CH_2{=}CHSi(C_5H_{11})_3$		145/8 mm.	1.4480 (25°)	0.8078 (25°)	(334)
$CH_2{=}CHSi(C_6H_5)_3$	65				(98, 99, 187. 334)
	59				
$CH_2{=}CHSi(CH_2C_6H_5)_3$	77				(334)
$C_6H_5CH{=}CHSi(CH_3)_3$		98/10.5 mm.	1.5270 (20°)	0.888 (20°)	(425)
$C_6H_5CH{=}CHSi(C_6H_5)_3$	147				(198)
$(CH_2{=}CH)_2SiCl_2$		119		1.088 (27°/27°)	(51, *253*, 254, 255, 257, 320, 487)
$(CH_2{=}CH)_2(CH{\equiv}C)SiH$		0/13.3 mm.			(537)
		31.6/62.0 mm.			
$(CH_2{=}CH)_4Si$		66/1 mm.			(371)
$[CH_2{=}CHSi(OCH_3)_2]_2O$		121/46 mm.	1.4172 (25°)	1.0627 (25°)	(336)
$[CH_2{=}CHSi(OC_2H_5)_2]_2O$		119/19 mm.	1.4100 (25°)	0.9618 (25°)	(336)
$[CH_2{=}CHSi(OC_5H_{11})_2]_2O$		199/7 mm.	1.4308 (25°)	0.9150 (25°)	(336)
$[CH_2{=}CHSi(CH_3)OH]_2O$					(161)
$[CH_2{=}CHSi(C_6H_5)OH]_2O$	107				(160, *161*)
$[(CH_2{=}CH)(4\text{-}ClC_6H_4)SiOH]_2O$	122				(160, *161*)
Vinyl addition polymers					(256, 371, 526)

TABLE 1—*Continued*

Compound	Melting Point	Boiling Point	n_D	d	References
	°C.	*°C.*			
Vinylsiloxanes					(49, 255. 256, 257, 260, 382, 526)
Sodium vinylpolysiloxanolate					(47)
Halogenovinyls:					
$CH_2{=}CClSiCl_3$		124/724 mm.	1.4638 (20°)	1.43 (28°)	(*4*, 51, 403, 425, *526*)
		124.5	1.4608 (20°)	1.428 (25°)	
$CHCl{=}CHSiCl_3$		134/738 mm.	1.4735 (20°)	1.45 (22°)	(*4*, 51, 397)
$ClC_2H_2SiCl_3$		124			(3, 231, *502*)
$CH_2{=}CClSi(OC_2H_5)_3$					(485)
$ClC_2H_2Si(OC_2H_5)_3$		176	1.4126 (25°)	1.0122 (25°)	(502)
$CH_2{=}CClSi(C_6H_5)Cl_2$		~85/2 mm.			(403)
$CH_2{=}CClSi(CH_3)_3$		150/729 mm.	1.4299 (20°)	0.8875 (20°)	(403, *425*)
$CHCl{=}CHSiCl_3$		135/735 mm.			(425)
$CHCl{=}CClSiCl_3$		164/750 mm.	1.4958 (20°)	1.56 (20°)	(2, 4, 333, *527*)
$CCl_2{=}CHSiCl_3$		163/750 mm.	1.4942 (20°)	1.54 (20°)	(2, 3, 4, 333, 525, 527)
$CCl_2{=}CHSi(OCH_3)_3$		105/50 mm.	1.4421 (20°)		(2, 3, 4, 527)
$CCl_2{=}CHSi(OC_4H_9)_3$		164/10 mm.	1.4434 (20°)		(2, 3, 4, 527)
$CCl_2{=}CHSi(C_2H_5)_3$		99/14 mm.	1.4780 (20°)		(2, 3, 4, 527)
$CH_2{=}CBrSiCl_3$		147/722 mm.	1.4920 (25°)		(5)
		60/36 mm.			
$CH_2{=}CBrSi(OC_2H_5)_3$		79/6 mm.	1.4321 (25°)	1.1951 (25°)	(502)
$BrC_2H_2SiCl_3$		147–165	1.4897 (20°)	1.8 (22°)	(5)
$CH_2{=}CBrSi(OC_2H_5)_2OCH_3$		74/6 mm.	1.4330 (25°)	1.2219 (25°)	(335)
$CH_2{=}CBrSi(OC_2H_5)_3$		78/6 mm.	1.4325 (25°)	1.1990 (25°)	(335)
$BrC_2H_2Si(C_2H_5)_3$		67/5 mm.		1.1200 (25°)	(334)
$CHBr{=}CBrSiCl_3$		212/735 mm.	1.5458 (20°)	2.1 (22°)	(5)
		90/11 mm.			
$(CH_3)_3SiCBr{=}CBrSi(CH_3)_3$	41–42	167–168/77 mm.			(*167*, 168)
Halogenovinylsiloxanes					(2, 4, 260, 527)
$CH_2{=}CClSiCl_3$ polymer					(425)
$CH_2{=}CClSi(CH_3)_3$ polymer					(425)
Allyls:					
$CH_2{=}CHCH_2SiCl_3$		118		1.211 (27°/27°)	(*9*, 26, 80, 92, 161, *253*, 254, 257, 265, 266, 297, 299, 362, 392, 446, 530)
		116–118	1.4449 (20°)	2.215 (25°)	
Ozonide					(9)
$CH_2{=}CHCH_2Si(OCOCH_3)_3$					(317)

$CH_2{=}CHCH_2Si(OC_2H_5)_2$		176	1.4063 (25°)	0.9032 (25°)	(6, 7, 8, *80*, 265, 310, 354, 449, *496*, 498, 499, 543)
		100/50 mm.	1.4073 (20°)	0.9030 (20°)	
$CH_2{=}CHCH_2Si(OCOCH_3)_3$		136/28 mm.			(*161*, 316)
$CH_2{=}CHCH_2Si(OC_5H_{11})_3$		181/23 mm.	1.4421 (20°)		(354)
$CH_2{=}CHCH_2SiHCl_2$		98		1.086 (27°/27°)	(*253*, 254, 257)
$CH_2{=}CHCH_2Si(CH_3)Cl_2$		120		1.057 (27°/27°)	(91, 161, *253*, 254, 257)
$CH_2{=}CHCH_2Si(CH_3)(OC_2H_5)_3$		155/736 mm.	1.4097 (25°)	0.8597 (25°)	(498)
$CH_2{=}CHCH_2Si(CH_3)(OCOCH_3)_2$		97/26 mm.			(161)
$(CH_2{=}CHCH_2)(CH_2{=}CH)SiCl_2$		69/57 mm.	1.4602 (25°)	1.098 (25°)	(392)
		34/10 mm.			
$(CH_2{=}CHCH_2)[CH_2{=}C(CH_3)CH_2]Si(OC_2H_5)_3$		78/13 mm.	1.4370 (20°)	0.8865 (20°/20°)	(73)
$(CH_2{=}CHCH_2)[CH_2{=}CHCH_2CH(CH_3)CH_2]SiH(CH_3)$		184/751 mm.	1.4482 (20°)	0.7881 (20°)	(360)
$(CH_2{=}CHCH_2)[CH_2{=}CHCH_2CH(CH_3)CH_2]Si(CH_3)_2$		201/747 mm.	1.4500 (20°)	0.8021 (20°)	(360)
$(CH_2{=}CHCH_2)(C_5H_5F_4)Si(OC_2H_5)_2$		103/10 mm.		1.096 (25°)	(174)
$CH_2{=}CHCH_2Si(C_6H_5)Cl_2$		101/8 mm.	1.5351 (25°)	1.168 (25°)	(160, *392*)
$CH_2{=}CHCH_2Si(C_5H_5)(OH)_2$					(161)
$CH_2{=}CHCH_2Si(C_6H_5)(OC_2H_5)_2$		118/10 mm.	1.4822 (25°)	0.9610 (25°)	(499)
$CH_2{=}CHCH_2Si(C_6H_5)(OCOCH_3)_2$		134/1.3 mm.			(160, *161*)
$(CH_2{=}CHCH_2)(4\text{-}ClC_6H_4)SiCl_2$		112/45 mm.	1.5442 (25°)	1.261 (25°)	(392)
$CH_2{=}CHCH_2Si(CH_2C_6H_5)Cl_2$		85/1 mm.	1.597 (25°)	1.141 (25°)	(392)
$CH_2{=}CHCH_2Si(CH_2C_6H_5)(OH)_2$					(161)
$CH_2{=}CHCH_2Si(CH_3)_2Cl$		112		0.922 (27°/27°)	(80, 161, *253*, 257)
$CH_2{=}CHCH_2Si(CH_3)_2OC_2H_5$		123/73 mm.	1.4100 (25°)	0.7972 (25°)	(498)
$CH_2{=}CHCH_2Si(CH_3)_3$		85/737 mm.	1.4036 (25°)	0.7158 (25°)	(32, 65, 71, 80, 90, 91, 290, 359, *446*, *498*, 554)
			1.4074 (20°)	0.7193 (20°)	
$CH_2{=}CHCH_2Si(CH_3)_2C_6H_5$		213.6/751 mm.	1.5090 (20°)	0.8911 (20°)	(*359*, 554)
$CH_2{=}CHCH_2Si(CH_3)(C_6H_5)_2$		310–311/740 mm.	1.5660 (20°)	0.9876 (20°)	(359)
$CH_2{=}CHCH_2Si(C_2H_5)_3$		171/735 mm.	1.4445 (20°)	0.7873 (20°)	(71, 358, 360, 554)
$CH_2{=}CHCH_2Si(C_3H_7)_3$		217.0/748 mm.	1.4490 (20°)	0.7950 (20°)	(71, *359*, 554)
$CH_2{=}CHCH_2Si(C_4H_9)_3$		252.3/750 mm.	1.4534 (20°)	0.8031 (20°)	(*359*, *364*, 554)
		145/12 mm.	1.4515 (20°)		
$CH_2{=}CHCH_2SiR_3$					(99)
$CH_2{=}CHCH_2Si$ compounds					(30)
$(CH_2{=}CHCH_2)_2SiF_2$		46.5/20 mm.			(396)
$(CH_2{=}CHCH_2)_2SiCl_2$		166			(80, *253*, 254, 257, 297, 349, 392, 517)
		84/50 mm.			
$(CH_2{=}CHCH_2)_2Si(OH)_2$	81			1.105 (10°)	(349)
$(CH_2{=}CHCH_2)_2Si(OCH_3)_2$					(517)
$(CH_2{=}CHCH_2)_2Si(OC_2H_5)_2$		190/741 mm.	1.4316 (25°)	0.8787 (25°)	(47, 174, 310, 394, 484, *496*, 498, 499)
$(CH_2{=}CHCH_2)_2Si(OC_4H_9\text{-}i)_2$					(385)
$(CH_2{=}CHCH_2)_2Si(CH_3)H$		123	1.4430 (20°)	0.7630 (20°)	(71, 360, 522, 554)
		122.5/745 mm.	1.4662 (20°)	0.8055 (20°)	

TABLE 1—*Continued*

Compound	Melting Point	Boiling Point	n_D	d	References
	°C.	°C.			
$(CH_2{=}CHCH_2)_2Si(CH_3)_2$		137	1.4420 (20°)	0.7679 (20°)	(32, *80*, 88, 321, *360*)
		68/50 mm.	1.4409 (20°)	0.7651 (20°)	
$(CH_2{=}CHCH_2)_2Si(C_2H_5)_2$		92/34 mm.	1.4594 (20°)	0.8076 (20°)	(78, *544*)
$(CH_2{=}CHCH_2)_3SiF$		67/20 mm.			(396)
$(CH_2{=}CHCH_2)_3SiCl$		98/30 mm.	1.4779 (25°)	0.941 (25°)	(297, *392*)
$(CH_2{=}CHCH_2)_3SiOC_2H_5$		82/23 mm.	1.4541 (25°)	0.855 (25°)	(310, *392*, 496, 498, 499)
$(CH_2{=}CHCH_2)_3SiH$		163	1.4678 (25°)	0.8705 (25°)	(267)
$(CH_2{=}CHCH_2)_3SiCH_3$		180.3/745 mm.	1.4662 (20°)	0.8055 (20°)	(32, 71, *360*, 371)
$(CH_2{=}CHCH_2)_3SiC_2H_5$		105–106/34 mm.	1.4723 (20°)	0.8337 (20°)	(71, *546*)
$(CH_2{=}CHCH_2)_3SiC_3H_7$		218.3/750 mm.	1.4705 (20°)	0.8178 (20°)	(359)
$(CH_2{=}CHCH_2)_3SiC_4H_9$		108/11 mm.	1.4722 (20°)	0.8200 (20°)	(364)
$(CH_2{=}CHCH_2)_3SiC_6H_5$		274.8/751 mm.	1.5300 (20°)	0.9174 (20°)	(359)
$(CH_2{=}CHCH_2)_3Si\underbrace{CH(CH_2)_4CH_2}$		127–129/13 mm.	1.4790 (20°)	0.8659 (20°)	(364)
$(CH_2{=}CHCH_2)_3SiCH{=}CH_2$		70/6 mm.	1.4790 (25°)	0.8313 (25°)	(334)
$(CH_2{=}CHCH_2)_3Si(1\text{-}C_{10}H_7)$		194–195/10 mm.	1.5872 (20°)	0.9928 (20°)	(364)
$(CH_2{=}CHCH_2)_4Si$		207/750 mm.	1.4864 (20°)	0.8353 (20°)	(32, *296*, 314, *315*, 364, 371, 381)
		103/15 mm.			
$CH_2{=}CHCH_2Si(C_3H_7)_3$		208			(350)
$CH_2{=}CHCH_2Si(CH_3)_2OSi(CH_3)_3$		142	1.4061 (20°)	0.7948 (20°)	(65, *80*)
$[CH_2{=}CHCH_2Si(CH_3)_2]_2O$		180/758 mm.	1.4280 (20°)	0.8208 (20°)	(*80*, 88, 321)
$[CH_2{=}CHCH_2Si(CH_3)OH]_2O$					(161)
$[CH_2{=}CHCH_2Si(C_6H_5)OH]_2O$					(160, *161*)
$[(CH_2{=}CHCH_2)_2SiO]_x$					(31, 78, 257, 496)
Allyl addition polymers					(257, 315, 371, 484)
Allylsiloxanes					(87, 257, 315, 317, 484)
Sodium allylpolysiloxanolate					(47)
Higher olefins:					
$CH_3CH{=}CHSiCl_3$		126.5	1.4513 (20°)	1.214 (25°)	(9)
$CH_3CH{=}CHSi(OC_2H_5)_3$		177–179		0.90 (25°)	(9)
$CH_2{=}C(CH_3)SiCl_3$		113/736 mm.			(432)
$CH_2{=}C(CH_3)Si(CH_3)_3$		82/730 mm.	1.4061 (20°)	0.7168 (20°)	(425, *432*)
$CH_2{=}CHCH_2CH_2Si(CH_3)_3$		113	1.4102 (27°)	0.7294 (27°)	(71, *240*, *361*)
		111.5–112.5	1.4148 (20°)	0.7358 (20°)	
$CH_2{=}CHCH_2CH(C_5H_5)Si(CH_3)_3$		92/5 mm.	1.5028 (25°)	0.8805 (26°)	(240)
$CH_2CH{=}CHCH_2SiCl_3$		143	1.4548 (20°)	1.19 (25°)	(*9*, 525)
Ozonide					(9)

$CH_3CH{=}CHCH_2Si(OC_2H_5)_3$		193–195		0.89 (25°)	(9)
$(CH_3CH{=}CHCH_2)_2Si(OC_2H_5)_2$		217–221		0.87 (25°)	(9)
n-$C_4H_7SiCl_3$		64/40 mm.			(22)
$(CH_2{=}CHSiCl_3)_2$		60–70/1 mm.			(526)
$(CH_2{=}CHSiH_3)_x$					(537)
$(CH_2{=}C(CH_3)CH_2SiCl_3$		141	1.4504 (20°)	1.1784 (20°)	(360, 369)
$CH_2{=}C(CH_3)CH_2Si(OC_2H_5)_3$		102/40 mm.	1.4122 (25°)	0.8999 (25°)	(*73*, 238, *497*)
		86/19 mm.	1.4140 (20°)	0.9065 (20°/20°)	
$[CH_2{=}C(CH_3)CH_2](CH_2{=}CHCH_2)Si(OC_2H_5)_2$		78/13 mm.	1.4370 (20°)	0.8865 (20°/20°)	(73)
$CH_2{=}C(CH_3)CH_2Si(C_4H_9)(OC_2H_5)_2$		96–98/16 mm.	1.4270 (20°)	0.8731 (20°/20°)	(73)
$CH_2{=}C(CH_3)CH_2SiC_5H_9(OC_2H_5)_2$		123–126/21 mm.	1.4460 (20°)	0.9205 (20°/20°)	(73)
$CH_2{=}C(CH_3)CH_2Si(C_6H_{11})(OC_2H_5)_2$		133/20 mm.	1.4560 (20°)	0.9245 (20°/20°)	(73)
$CH_2{=}C(CH_3)CH_2Si(C_6H_{10}C_6H_9)(OC_2H_5)_2$		157–162/5 mm.	1.4639 (20°)	0.9195 (20°/20°)	(73)
$CH_2{=}C(CH_3)CH_2Si(C_6H_5)(OC_2H_5)_2$		142–144/21 mm.	1.4840 (20°)		(73)
$CH_2{=}C(CH_3)CH_2Si(CH_2C_6H_5)(OC_2H_6)_2$		106/4 mm.	1.4973 (20°)	0.9626 (20°/20°)	(73)
$CH_2{=}C(CH_3)CH_2Si(C_4H_9)_2OC_2H_5$		118–119/13 mm.	1.4410 (20°)	0.8394 (20°/20°)	(73)
$CH_2{=}C(CH_3)CH_2Si(C_6H_5)_2OC_2H_5$		180–185/17 mm.	1.5259 (20°)		(73)
$CH_2{=}C(CH_3)CH_2(CH_2C_6H_5)_2OC_2H_5$		140–150/3 mm.			(73)
$CH_2{=}C(CH_3)CH_2Si(C_2H_6)_3$		189	1.4505 (20°)	0.7994 (20°)	(71, *360*, 522)
$[CH_2{=}C(CH_3)CH_2]_2SiCl_2$					(258)
$[CH_2{=}C(CH_3)CH_2]_2Si(OC_2H_5)_2$		122/40 mm.	1.4387 (25°)	0.8828 (25°)	(*73*, 238, *497*)
		102/18 mm.	1.4410 (20°)	0.8905 (20°/20°)	
$[CH_2{=}C(CH_3)CH_2]_2Si(CH_3)H$		61–63/17 mm.	1.4450 (20°)	0.7885 (20°)	(361)
$[CH_2{=}C(CH_3)CH_2]_2Si(CH_3)_2$		178–178.5/atm.	1.4515 (20°)	0.8012 (20°)	(361)
$[[CH_2{=}C(CH_3)CH_2]_2SiO]_x$					(497)
$[CH_2{=}C(CH_3)CH_2]_3SiOC_2H_5$		110–112/12 mm.	1.4675 (20°)	0.8795 (20°/20°)	(73)
$[CH_2{=}C(CH_3)CH_2]_3SiCH_3$		231.9–232.1/atm.	1.4772(20°)	0.8338 (20°)	(361)
$[CH_2{=}C(CH_3)CH_2]_4Si$		269.5–270.5/atm.	1.4950 (20°)	0.8609 (20°)	(361)
$CH_2{=}C(CH_3)CH_2Si$–maleic anhydride adducts		130–133/11 atm.			(73)
$CH_2{=}C(CH_3)CH_2Si$–maleic ester adducts					(73)
$CH_2{=}C(CH_3)CH_2Si$–fumaric ester adducts					(73, 237)
$C_4H_7SiCl_3$					(231)
$CH_3(CH_2)_2CH{=}CHSiCl_3$		85/80 mm.			(*81*, 318)
$CH_3(CH_2)_2CH{=}CHSi(CH_3)_3$		133–135	1.4200 (28°)	0.734 (28°)	(*167*, 171)
$CH_2{=}CH(CH_2)_3Si(C_2H_5)_3$		207	1.4460 (20°)	0.7971 (20°)	(360)
$CH_2CH_2CH_2CH{=}CHSiCl_2$					(242)
$CH_3CH_2CH_2CH_2CH{=}CHSiCl_3$		65/3 mm.			(318)
$(C_2H_5OCO)_2C(CH_2CH{=}CH_2)CH_2Si(CH_3)_3$		89/2 mm.	1.4472 (20°)		(433)
$[CH_2{=}CHCH_2CH(CH_3)CH_2](CH_2{=}CHCH_2)Si(CH_3)H$		184	1.4482 (20°)	0.7881 (20°)	(360)
$CH_2{=}CHCH_2CH(CH_3)CH_2Si(CH_3)_3$		151.3/750 mm.	1.4264 (20°)	0.7575 (20°)	(*359*, 554)
$CH_2{=}CHCH_2CH(CH_3)CH_2Si(C_2H_5)_3$		219/758 mm.	1.4515 (20°)	0.8073 (20°)	(*358*, 359, 360, 554)
$CH_2{=}CHCH_2CH(CH_3)CH_2Si(C_3H_7)_3$		255-256/760 mm.	1.4545 (20°)	0.8098 (20°)	(359)

TABLE 1—*Continued*

Compound	Melting Point	Boiling Point	n_D	*d*	References
	°C.	°C.			
$CH_2{=}CHCH_2CH(CH_3)CH_2Si(C_4H_9)_3$		288–289/745 mm.	1.4568 (20°)	0.8122 (20°)	(359)
$[CH_2{=}CHCH_2CH(CH_3)CH_2](CH_2{=}CHCH_2)Si(CH_3)_3$		201	1.4500 (20°)	0.8021 (20°)	(360)
$CH_2{=}CHCH_2CH(CH_3)CHSi(CH_3)_2C_6H_5$		256–258/743 mm.	1.4990 (20°)	0.8859 (20°)	(359)
$[CH_2{=}CHCH_2CH(CH_3)CH_2]_2Si(CH_3)H$		233	1.4560 (20°)	0.8150 (20°)	(360)
$CH_2{=}C(CH_3)CH_2CH_2CH_2Si(C_2H_5)_3$					(71)
$CH_2{=}C(CH_3)CH_2CH_2CH_2Si(CH_3)_2C_6H_5$					(71)
n-$C_6H_{11}SiCl_3$		105/50 mm. 71/10 mm.			(22, *23*, 29)
$CH_2{=}CHCH_2C(CH_3)_2CH_2Si(C_2H_5)_3$		236	1.4590 (20°)	0.8208 (20°)	(360)
$CH_2{=}CH(CH_2)_9Si(CH_3)_2Cl$		98/1 mm.			(77)
$CH_2{=}CH(CH_2)_9Si(CH_3)_2C_4H_9$		128/2 mm.	1.4460 (27°)		(77)
$CH_2{=}CH(CH_2)_9Si(CH_3)_2C_5H_{11}$		143/2 mm.	1.4467 (27°)		(77)
$CH_2{=}CH(CH_2)_9Si(CH_3)_2CH_2CH_2C_6H_5$		178/2 mm.	1.4850 (27°)		(77)
$CH_2CH_2CH{=}CHCH_2CHSiCl_3$		87–88/16 mm.	1.4905 (20°)	1.25 (25°)	(69, 70, 231, *526*)
Cyclo-$C_6H_9SiCl_3$					(70, 266)
$CH{=}CHCH_2CH_2CH_2C(CH_3)SiCl_3$					(70)
$CH{=}CHCH(CH_3)CH_2CH_2CHSiCl_3$					(70)
Cyclo-$C_6H_9CH_2CH_2SiCl_3$					(69, 70)
$CH{=}CHCHCH_2CHCH_2CHSiCl_3$		116–117/49 mm.		1.27 (25°)	(526)
$CH{=}CHCHCH_2CHCH_2CHSi(OC_2H_5)_2$		115–117/12 mm.		0.98 (25°)	(526)
4-$CH_2{=}CHC_6H_4SiCl_3$		103/8 mm.			(76)
4-$CH_2{=}CHC_6H_4Si(CH_3)_3$					(542)
4-$CH_2{=}CHC_6H_4Si(CH_3)_3$ polymer					(542)
$CH_2{=}CHC_6H_4CH_2CH_2SiCl_3$		170/3 mm.			(234)
$(CHO)[Si(CH_3)_3]C_2H_2{=}CHC_2H_4Si(CH_3)_3$		194–209	1.4549 (20°)		(*90*, 91)
$(CHO)[CH_2CH_2Si(CH_3)_3]C{=}CH(CH_2)_3Si(CH_3)_3$		152/15 mm.	1.4550 (20°)	0.8910 (20°)	(*90*, 91)
2,4-Dinitrophenylhydrazone	153				
$CH{=}CHCH{=}CHCHSi(CH_3)_3$		138–140/atm.	1.4622 (20°)	0.8208 (20°)	(159, *361*)
Maleic anhydride adduct	102–102.5				(159, *361*)
$(CH{=}CHCH{=}CHCH)_2Si(CH_3)_2$		73/25 mm.			(159)

Polyolefin-silicon hydride adducts					(15, 19, 23 204, 238, 311)
$COC[CH_2Si(CH_3)_3]{=}C(CH_3)CH_2CH_2$	58–58.5	118/21 mm.	1.4827 (20°)		(443)
Oxime	108–108.5				(443)
Indenes:					
$1\text{-}C_6H_4C_3H_3Si(CH_3)Cl_2$		92/3 mm.		1.201 (20°)	(438)
$1\text{-}C_6H_4C_3H_3Si(CH_3)(OC_4H_9)_2$		130/1.5 mm.	1.5015 (20°)	0.976 (20°)	(438)
$1\text{-}C_6H_4C_3H_3Si(CH_3)_2Cl$		92/3 mm.	1.5530 (20°)	1.074 (20°)	(438)
$1\text{-}C_6H_4C_3H_3Si(CH_3)_2OC_4H_9$		113/3 mm.	1.5165 (20°)	0.964 (20°)	(438)
$1\text{-}C_6H_4C_3H_3Si(CH_3)_3$		87/4 mm.	1.5425 (20°)	0.945 (20°)	(438)
$1\text{-}C_6H_4C_3H_3Si(C_2H_6)_3$		113/2 mm.	1.5416 (20°)	0.950 (20°)	(438)
$1\text{-}C_6H_4C_3H_3Si(C_6H_5)_3$	136				(*185*, 186)
$1,1\text{-}C_6H_4C_3H_2[Si(CH_3)_3]_2$		104/3 mm.	1.5304 (20°)	0.930 (20°)	(438)
$1,1\text{-}C_6H_4C_3H_2[Si(C_2H_5)_3]_2$		170/3 mm.	1.5333 (20°)	0.940 (20°)	(438)
$1,1\text{-}C_6H_4C_3H_2[Si(C_6H_5)_3]_2$	206				(*185*, 186)
$(1\text{-}C_6H_4C_3H_3)_2Si(CH_3)Cl$		179/2 mm.		1.131 (20°)	(438)
$(1\text{-}C_6H_4C_3H_3)_2Si(CH_3)_2$		155/4 mm.	1.6110 (20°)	1.060 (20°)	(438)
Acetylenes:					
$CH{\equiv}CSiCl_3$					(5, 252)
$CH{\equiv}CSi(OC_2H_5)_3$		163	1.3982 (20°)		(56)
		91/52 mm.			
$(CH{\equiv}C)(CH_2{=}CH)_2SiH$		0/13.3 mm.			(537)
		31.6/62.0 mm.			
$CH{\equiv}CSi(C_2H_5)_3$		59–61/43 mm.	1.4347 (20°)	0.7918 (20°)	(365, *366*)
$CH{\equiv}CSi(C_4H_9)_3$					(365)
$BrC{\equiv}CSiCl_3$		78/11 mm.	1.5240 (25°)		(3, 5)
$(CH{\equiv}C)_2Si(OC_2H_5)_2$		32/1 mm.			(56)
$(CH{\equiv}C)_3SiOC_2H_5$		40/1 mm.			(56)
$(C_2H_5O)_3SiC{\equiv}CSi(OC_2H_5)_3$		106/101 mm.			(56, 252)
$Cl(CH_3)_2SiC{\equiv}CSi(CH_3)_2Cl$		113/65 mm.			(*167*, 169)
$HO(CH_3)_2SiC{\equiv}CSi(CH_3)_2OH$					(167, 169)
$(CH_3)_3SiC{\equiv}CSi(CH_3)_3$		134–136	1.4260 (20°)	0.7703 (20°)	(*167*, 168, *365*)
		133–135	1.4259 (25°)	0.763 (25°)	
$(C_2H_5)_3SiC{\equiv}CSi(C_2H_5)_3$		132–134/25 mm.	1.4268 (20°)	0.8174 (20°)	(365)
$(C_4H_9)_3SiC{\equiv}CSi(C_4H_9)_3$		215–218/22 mm.	1.4568 (20°)	0.8339 (20°)	(365)
$(C_2H_5O)_2(CH{\equiv}C)SiC{\equiv}CSi(C{\equiv}CH)(OC_2H_5)_2$		100/1 mm.			(56)
$CH_3(CH_2)_2C{\equiv}CSi(CH_3)Cl_2$		168–169			(*167*, 170)
$CH_3(CH_2)_2C{\equiv}CSi(CH_3)(OCOCH_3)_2$		96–102/0.3 mm.			(*167*, 170)
$CH_3(CH_2)_2C{\equiv}CSi(CH_3)_3$		134	1.4272 (25°)	0.765 (25°)	(*167*, 171)
$[CH_3(CH_2)_2C{\equiv}CSi(CH_3)OH]_2O$					(*167*, 170)
$CH_3C{\equiv}CSi(CH_3)_3$		99–100/760 mm.	1.4091 (20°)	0.7581 (20°)	(366)
$CH_3C{\equiv}CSi(C_2H_5)_3$		169.5–170.5	1.4485 (20°)	0.8029 (20°)	(366)

TABLE 1—*Concluded*

Compound	Melting Point	Boiling Point	n_D	d	References
	°*C.*	°*C.*			
$[CH_3C\equiv CSi(C_2H_5)_3]_2$					(366)
$CH_3(CH_2)_3C\equiv CSi(CH_3)Cl_2$		187–188			(167, 170)
$CH_3(CH_2)_3C\equiv CSi(CH_3)(OCOCH_3)_2$		102–106/0.3 mm.			(167)
$CH_3(CH_2)_2C\equiv CSi(CH_3)_3$		155	1.4318 (25°)	0.768 (25°)	(*167*, 171)
$[CH_3(CH_2)_3C\equiv C]_2Si(CH_3)Cl$					(167)
$[CH_3(CH_2)_3C\equiv CSi(CH_3)OH]_2O$					(167, 170)
$[CH_3(CH_2)_3C\equiv CSi(CH_3)O-]_4$		167/0.5 mm.			(*167*, 170)
$(CH_3CH_2CH_2CH_2C\equiv C)_2Si(CH_3)Cl$		148–150/8 mm.			(170)
$C_6H_5C\equiv CSi(OC_2H_5)_3$		142/6 mm.	1.4898 (21°)	0.986 (22°/22°)	(523)
$C_6H_5C\equiv CSi(CH_3)_3$		87.5/9 mm.	1.5284 (20°)	0.8961 (20°)	(366)
$C_5H_5C\equiv CSi(C_2H_5)_3$		132–133.5/10 mm.	1.5259 (20°)	0.8984 (20°)	(366)
$C_6H_5C\equiv CSi(C_6H_5)_3$	101				(185, 186, *190*, 192, 198)
$(C_6H_5C\equiv C)_2Si(OC_2H_5)_2$		185/12 mm.	1.529 (9°)	1.0001 (9°)	(523)
Polyunsaturates:					
$CH_2{=}CHCH{=}CHSi(C_2H_5)_3$		74–75/19 mm.	1.4584 (20°)	0.7988 (20°)	(363)
Maleic anhydride adduct	132				(363)
$CH_2{=}CHC\equiv CSi(CH_3)_3$		52–53/80 mm.	1.4510 (20°)	0.7714 (20°)	(363)
$CH_2{=}CHC\equiv CSi(C_2H_5)_3$		74–76/20 mm.	1.4695 (20°)	0.8145 (20°)	(363)
$CH_2{=}CHC\equiv CSi(C_3H_7)_3$		87–89/7 mm.	1.4700 (20°)	0.8173 (20°)	(363)
$CH_2{=}CHC\equiv CSi(C_4H_9)_3$		108–110/8 mm.	1.4700 (20°)	0.8201 (20°)	(363)
$(CH_2{=}CHC\equiv C)_2Si(CH_3)_2$		67–68/9 mm.	1.5108 (20°)	0.8495 (20°)	(363)
$(CH_2{=}CHC\equiv C)_2Si(C_2H_5)_2$		84–86/8 mm.	1.5140 (20°)	0.8556 (20°)	(363)
$(CH_2{=}CHC\equiv C)_2Si(C_3H_7)_3$		84–86/5 mm.	1.5145 (20°)	0.8561 (20°)	(363)
$CH_3CH{=}C(CH_3)C\equiv CSi(C_2H_5)_3$		115–116/20 mm.			(57)

In the dehydrohalogenation of α,β-dichloroethyl silicon compounds the beta chlorine atom is removed preferentially. Thus, addition of chlorine to alkenyl

$$CH_2ClCHClSiCl_3 \xrightarrow{\text{quinoline}} CH_2{=}CClSiCl_3$$

compounds followed by dehydrohalogenation provides a very satisfactory procedure for making α-halogenovinyl compounds (4, 5, 334, 335, 425).

The thermal elimination of hydrogen halide from halogenoalkylsilanes has also been carried out, but this method is often accompanied by side reactions (4, 5, 76, 231). In contrast to the directed dehydrohalogenation of CH_2Cl-$CHClSiCl_3$ by quinoline, the thermal reaction at 600°C. produces both $CH_2{=}CClSiCl_3$ and $CHCl{=}CHSiCl_3$ (4, 5).

3. Silicon hydride additions

The addition of silicon hydrides, especially trichlorosilane, to unsaturated organic compounds has received considerable attention. When applied to acetylenes and to polyolefins, this reaction gives alkenyl silicon compounds. The addition is catalyzed by peroxides, azodinitriles, ultraviolet light, and platinum and may also be carried out thermally.

The addition of trichlorosilane to acetylene at moderate temperature in the presence of a platinum-on-charcoal catalyst gives a good yield of vinyltrichlorosilane (525). The concentration of platinum required is very low. Higher pres-

$$HC{\equiv}CH + HSiCl_3 \xrightarrow[\text{Pt}]{\text{heat}} CH_2{=}CHSiCl_3$$

sures of acetylene favor the yield of $CH_2{=}CHSiCl_3$, since the latter can undergo further addition of trichlorosilane. Triethoxysilane and ethyldiethoxysilane also add to acetylene in the presence of platinum (525). The peroxide-catalyzed addition of trichlorosilane to acetylene produces some $CH_2{=}CHSiCl_3$ (92). One mole of trichlorosilane adds satisfactorily to 1-pentyne in the presence of peroxides or ultraviolet light to give $CH_3CH_2CH_2CH{=}CHSiCl_3$ (81, 318). Thermal addition of silane to acetylene produces some vinyl silicon compounds (537).

The addition of trichlorosilane to polyolefins also produces alkenyl silicon compounds. Thus, addition to dipentene (204) and to butadiene (9, 22, 311, 525) gives products containing a double bond.

$$HSiCl_3 + CH_2{=}CHCH{=}CH_2 \xrightarrow[\text{Pt}]{\text{heat}} CH_3CH{=}CHCH_2SiCl_3$$

Trichlorosilane has been added thermally to polymeric polyolefins such as rubber and butadiene–styrene copolymers (15, 19).

The thermal or platinum-catalyzed reaction of trichlorosilane with chlorinated olefins produces chlorovinyl silicon compounds (2, 4, 525, 527).

$$HSiCl_3 + CCl_2{=}CHCl \xrightarrow{500°\text{C.}} CCl_2{=}CHSiCl_3$$

Since the thermal reaction does not involve conventional free-radical addition followed by dehydrohalogenation of the adduct, the following mechanism has been suggested (4).

$$HSiCl_3 \rightarrow H\cdot + \cdot SiCl_3$$

$$\cdot SiCl_3 + CHCl{=}CCl_2 \rightarrow Cl_3SiCHClCCl_2\cdot$$

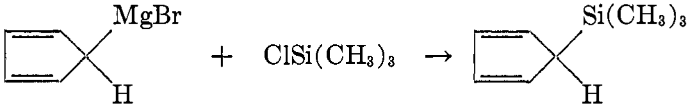
$$Cl_3SiCHClCCl_2\cdot \rightarrow Cl\cdot + Cl_3SiCH{=}CCl_2$$

$$Cl\cdot + HSiCl_3 \rightarrow HCl + \cdot SiCl_3$$

The thermal reaction has also been applied to the dichloroethylenes (4).

4. Unsaturated organometallic reagents

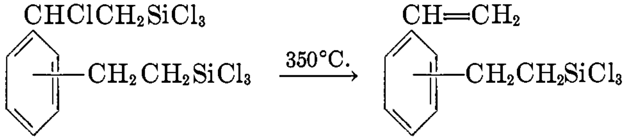
The coupling of unsaturated organometallic reagents with chlorosilanes or with ethoxysilanes provides a convenient synthetic route to alkenyl silicon compounds. Tetravinylsilane is prepared by reacting vinyl bromide with magnesium and silicon tetrachloride (371). The most widely used method for preparing allyl silicon compounds involves coupling allylmagnesium halides with chlorosilanes or ethoxysilanes (30, 80, 267, 310, 334, 371, 392, 446, 496, 544, 545). Mixtures are often encountered where polysubstitution is possible. A variation of the method involves reacting the allyl halide with magnesium in the presence of the silicon compound without prior formation of the Grignard reagent (7, 8, 297, 358, 359, 360). Fair yields are obtained by either method. The analogous syntheses may be carried out with methallyl halides (73, 237, 310, 361, 497). Cyclopentadienyl silicon compounds have been prepared via the Grignard route (159). Indenylsilanes have been obtained in fair yield by treating chlorosilanes with indenylsodium or indenyllithium (185, 438), and styrylsilanes have been prepared from styryllithium and from styrylmagnesium halide (198, 425).



Other Grignard coupling reactions may be used for the synthesis of alkenyl silicon compounds. Thus, $(CH_3)_3SiCH_2MgCl$ couples with allyl chloride to produce $(CH_3)_3SiCH_2CH_2CH{=}CH_2$ (240, 361). Also, low yields of alkenylsilanes are obtained by coupling allyl Grignard reagents with β-bromoalkyl silicon compounds in spite of their tendency toward beta elimination (358, 359).

5. Other syntheses

The addition of silicon tetrachloride to acetylene has been claimed (397), but no further publications have appeared concerning this potentially valuable reaction. Vinyl- and allylchlorosilanes are obtained from the pyrolysis of higher alkylchlorosilanes (26). $CH_2{=}C(CH_3)CH_2SiCl_3$ is formed upon heating trichlorosilane with low polymers of isobutylene (369). Styrene with a $(CH_3)_3Si$— group in the para position is formed upon dehydrohalogenation of $4\text{-}(CH_3)_3Si\text{-}C_6H_4CH_2CH_2Br$ (542). An interesting example of olefin formation involves the thermal elimination of silicon tetrachloride (234).



B. PROPERTIES OF OLEFINS

Olefinic silicon compounds exhibit many of the typical reactions of double bonds. Free-radical reactions generally proceed smoothly. Many ionic reactions can also be carried out, but difficulty may be encountered because of silicon–carbon bond cleavage, particularly with allyl compounds. In all reactions the thermal or hydrolytic instability of the adducts may pose additional difficulties.

1. Addition reactions

Hydrogenation of alkenyl silicon compounds has received little attention because the saturated compounds are prepared by more direct methods. Allyltrimethylsilane (446), stryryltrimethylsilane (425), and indenyltrimethylsilane (438) undergo hydrogenation smoothly with the Raney nickel catalyst.

Chlorine and bromine add to a variety of vinyl silicon compounds in good yield (4, 5, 9, 334, 335, 425, 502, 526). Bromine adds more rapidly to vinyltriethoxysilane than to vinyltrichlorosilane (526). Chlorine adds to $CH_2{=}CHCH_2SiCl_3$ and $CH_2{=}CHCH_2Si(CH_3)_3$, but bromine causes silicon–carbon cleavage in these compounds (9, 446), as well as in crotyltrichlorosilane (9) and indenyltrimethylsilane (438). High-temperature chlorination of $CH_2{=}CHSiCl_3$ results mainly in substitution (526). This reaction takes place via direct replacement of

$$CH_2{=}CHSiCl_3 + Cl_2 \xrightarrow{300^\circ C.} CH_2{=}CClSiCl_3$$

hydrogen rather than via addition followed by dehydrohalogenation, because the adduct $CH_2ClCHClSiCl_3$ is stable under the reaction conditions.

Hydrogen halides add to olefinic silicon compounds to produce halogenoalkylsilanes. With aluminum chloride as catalyst hydrogen chloride adds to $CH_2{=}CHSiCl_3$ and to $CH_3CH{=}CHSiCl_3$; the reaction is reversible (9, 526). Hydrogen bromide and hydrogen iodide add to $CH_2{=}CHSi(CH_3)_3$, but the former requires a peroxide catalyst (425). These hydrogen halides, as well as hydrogen chloride, have been added to $CH_2{=}CHCH_2Si(CH_3)_3$ (359, 360, 446), but hydrogen chloride gives only silicon–carbon cleavage products with $CH_2{=}CHCH_2SiCl_3$ and with $CH_3CH{=}CHCH_2SiCl_3$ (9).

The direction of addition for hydrogen halides is usually in agreement with Markownikoff's rule, but exceptions have been noted in the addition of hydrogen chloride and hydrogen iodide to vinyl compounds (425, 526). The results are surprising, since neither of these two hydrogen halides is subject to the

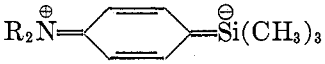
$$CH_2{=}CHSiCl_3 + HCl \xrightarrow{AlCl_3} CH_2ClCH_2SiCl_3$$

$$CH_2{=}CHSi(CH_3)_3 + HI \rightarrow CH_2ICH_2Si(CH_3)_3$$

peroxide effect which would give rise to the observed orientation. The first result may be due to the inductive effect of electron-attracting chlorine, and similar orientation has been observed with vinyl compounds having electron-attracting groups. The other result is unusual because the $(CH_3)_3Si$— group is considered electron-releasing. A possible explanation may be that silicon can expand its octet with the double bond acting as an electron source, so that a contributing resonance form would be

$$\overset{\oplus}{C}H_2CH{=}\overset{\ominus}{Si}(CH_3)_3$$

This type of resonance has been proposed in aromatic systems where an electron donor is present,



in order to explain anomalous dipole moment data and acid-base strengths (38, 400). An alternate explanation is that the α-iodo compound forms first and then rearranges in the presence of hydrogen iodide to the beta isomer.

Ozone adds to alkenyl silicon compounds, but the ozonides from vinyl and allyl derivatives undergo silicon–carbon cleavage upon decomposition by hydrolysis.

$$CH_2{=}CHSi(CH_3)_3 \xrightarrow{O_3} \text{ozonide} \xrightarrow{H_2O} HCHO + (CH_3)_3SiOH$$

This is probably due to the hydrolytic instability of the $Si{-}C{=}O$ and $SiCH_2C{=}O$ structures in the hydrolysis products. Silicon–carbon cleavage has been observed with the ozonides from $CH_2{=}CHSi(CH_3)_3$ (425), $CH_2{=}CHSiCl_3$ (9, 526), $CH_3CH{=}CHSiCl_3$ (9), and $CH_2{=}CHCH_2SiCl_3$ (9).

Some of the less common radical-type additions have also been carried out with alkenyl silicon compounds. Trichlorosilane adds to vinyl- and allylsilanes with a peroxide (92, 238) or platinum (525) catalyst.

$$HSiCl_3 + CH_2{=}CHSiCl_3 \xrightarrow{(CH_3COO)_2} Cl_3SiCH_2CH_2SiCl_3$$

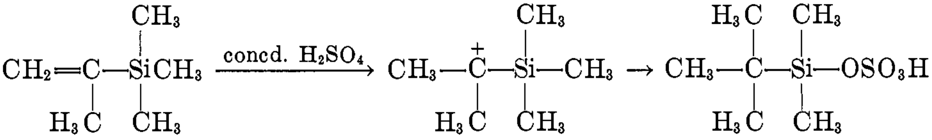
Silane adds photochemically to $CH_2{=}CHSiH_3$ (537). Various thiols, such as $HSCH_2COOH$, $HSCH_2COOC_2H_5$, and 4-$CH_3C_6H_4SH$, add to vinyl and allyl silicon compounds, frequently without added catalyst (78, 80, 87, 187, 306). Dithiols and diallyl silicon compounds give polymers (80, 321). Butyraldehyde adds to $CH_2{=}CHSi(CH_3)_3$ in the presence of peroxides (425).

Other additions to alkenyl silicon compounds are known. Under oxo reaction conditions carbon monoxide adds to vinyl- and allylsilanes to produce aldehydes and their aldols (90, 91). Organolithium reagents add to $CH_2{=}CHSi(C_6H_5)_3$ in

$$CH_2{=}CHSi(C_6H_5)_3 + RLi \rightarrow [RCH_2CH(Li)Si(C_6H_5)_3] \xrightarrow{H_2O} RCH_2CH_2Si(C_6H_5)_3$$

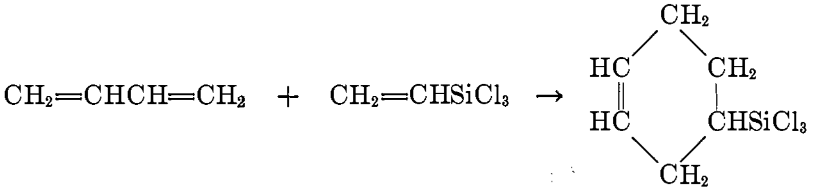
a rare example of such addition to a simple double bond (98, 99). Thiocyanogen also adds to alkenyl silicon compounds (71).

An interesting transformation is the following example of a Wagner–Meerwein type of rearrangement. The reaction is believed to proceed through an alpha carbonium ion (432).



$$CH_2{=}\underset{H_3C}{\underset{|}{C}}-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{Si}}}}CH_3 \xrightarrow{\text{concd. } H_2SO_4} CH_3-\overset{+}{\underset{H_3C}{\underset{|}{C}}}-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{Si}}}}-CH_3 \rightarrow CH_3-\overset{H_3C}{\overset{|}{\underset{H_3C}{\underset{|}{C}}}}-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{Si}}}}-OSO_3H$$

Several examples of the codimerization of unsaturated organic compounds and alkenyl silicon compounds are available. Butadiene and cyclopentadiene undergo Diels–Alder addition with $CH_2{=}CHSiCl_3$ and $CH_2{=}CHSi(OC_2H_5)_3$ (526).



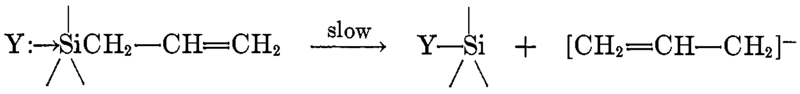
Similarly, fluorinated olefins codimerize with allylsilanes to produce such compounds as $(\underline{CF_2CF_2CH_2CH}CH_2)_2Si(OC_2H_5)_2$ (174). Double-bond polymerizations and copolymerizations of alkenyl silicon compounds are considered in a later section.

In the presence of aluminum chloride, benzene adds to $CH_2{=}CHSiCl_3$ to form $C_6H_5CH_2CH_2SiCl_3$ (526).

2. Cleavage reactions

Olefinic groups can be cleaved from silicon by either nucleophilic or electrophilic reagents. The ease of the reaction depends upon the strength of the attacking base or acid, the type of olefinic group, and the nature of the other groups attached to silicon.

A number of nucleophilic cleavages are known. Ethylene is formed almost quantitatively when $CH_2{=}CHSiH_3$ is heated with 30 per cent aqueous sodium hydroxide at 170°C. for 15 hr.; under similar conditions $CH_3CH_2SiH_3$ gives no ethane (505). Propylene is formed in 70 per cent yield when $CH_2{=}CHCH_2Si(CH_3)_3$ is refluxed with 50 per cent methanolic potassium hydroxide for 24 hr. (446). The process can be formulated as a typical nucleophilic attack on silicon



$$Y{:}\rightarrow \overset{|}{\underset{/\ \backslash}{Si}}CH_2{-}CH{=}CH_2 \xrightarrow{slow} Y{-}\overset{|}{\underset{/\ \backslash}{Si}} + [CH_2{=}CH{-}CH_2]^-$$

$$[CH_2{=}CH{-}CH_2]^- + YH \xrightarrow{fast} CH_2{=}CHCH_3 + Y{:}$$

or as a concerted mechanism. Refluxing strong aqueous alkali attacks the silicon–carbon bond in $CH_2{=}CHCHSiCl_3$ extensively, that in $CH_3CH{=}CHCH_2SiCl_3$ less readily, and that in $CH_3CH{=}CHSiCl_3$ not at all (9).

Halogenovinyl groups are readily cleaved from silicon by alcoholic alkali with formation of halogenated olefins. This degradation has been used in establishing structure (4, 5, 527). The beta halogen on a vinyl group does not show the facile beta elimination of a beta halogen on an ethyl group (2, 425). This behavior is in accord with the greater stability of vinyl halogen in displacement reactions compared to saturated alkyl halides.

Indenyl groups are readily cleaved by base, and the mechanism is probably similar to that given previously (438). The basic cleavage of indenyl and other groups has been examined qualitatively and related to the acidity of the hydrocarbon formed (186). The greater the acidity of the hydrocarbon, the greater the cleavage by nucleophilic reagents. This may be related to the resonance stabilization of the anion which is formed in the first step of the cleavage.

Electrophilic reagents such as hydrogen chloride, bromine, and sulfuric acid can also cleave alkenyl groups, particularly allyl groups, from silicon (446). Similar to the examples below is the cleavage of allyl, indenyl, and styryl groups

$$CH_2{=}CHCH_2Si(CH_3)_3 + HCl \rightarrow CH_2{=}CHCH_3 + (CH_3)_3SiCl$$

$$CH_2{=}CHCH_2Si(CH_3)_3 + Br_2 \rightarrow CH_2{=}CHCH_2Br + (CH_3)_3SiBr$$

by sulfuric acid (80, 198, 425, 438). In the hydrolysis and alcoholysis of $CH_2{=}CHCH_2SiCl_3$ it is advisable to use a weak base as acid acceptor in order to prevent silicon–carbon cleavage; this is not necessary with $CH_3CH{=}CHCH_2SiCl_3$ and $CH_3CH{=}CHSiCl_3$ (9).

In electrophilic cleavages the first step is probably addition of the positive fragment to form a beta carbonium ion (A), followed by reaction at the carbon to give addition (B) or by reaction at the silicon to give cleavage (C). The cleavage reaction can occur because of the electropositive nature of silicon and its

$$(CH_3)_3SiCH_2CH{=}CH_2 + X^+Y^- \rightarrow (CH_3)_3SiCH_2\overset{\oplus}{C}HCH_2X + Y^- \qquad (A)$$

$$\begin{tikzcd}
 & (CH_3)_3SiCH_2CHYCH_2X & (B) \\
(CH_3)_3SiCH_2\overset{\oplus}{C}HCH_2X \arrow[ur, "addition"] \arrow[dr, "cleavage"'] & & \\
 & (CH_3)_3SiY + CH_2{=}CHCH_2X & (C)
\end{tikzcd}$$

ability to release a pair of electrons to carbon (446). Another factor may be the ability of silicon to coordinate with the incoming negative fragment.

3. *Polymerization*

This section deals with the polymerization and copolymerization of alkenyl silicon compounds via the double bonds. Dimerizations and codimerizations are considered in an earlier section. Polymer formation through silicon-functional groups is dealt with in a later section.

The picture on the addition polymerization behavior of olefinic silicon compounds is incomplete because few comprehensive studies have been reported and most of the available observations are qualitative in nature. Most of the polymerization work deals with vinyl and allyl compounds. Free-radical catalysts are generally more satisfactory than ionic catalysts. Copolymerization appears to proceed best with vinyl monomers containing strong electron-attracting groups.

Vinyl silicon compounds polymerize with varying ease. Vinyltriethylsilane does not polymerize with benzoyl peroxide or sulfuric acid (519). Vinyltrichlorosilane polymerizes thermally at 250–350°C. or with acidic catalysts to very low-molecular-weight polymers (526). The polymerization of this olefin by benzoyl peroxide has been claimed but not substantiated (517, 526). Vinyltriethoxysilane and vinylpolysiloxanes polymerize with peroxides (257, 526); the former gives viscous liquids of 5000–8000 molecular weight with di-*t*-butyl peroxide. Vinylsilane polymerizes to a white solid upon irradiation with ultraviolet light (537).

Allyl silicon compounds can also be polymerized. Thus, while $CH_2{=}CHCH_2Si(CH_3)_3$ does not polymerize with benzoyl peroxide, it does form low polymers with aluminum chloride (446). Allyltriethoxysilane polymerizes with peroxides (496, 498), as do also diallylsilanes and allylpolysiloxanes (257, 496, 498, 499, 517, 544). Diallylpolysiloxanes behave like drying oils (257).

Other alkenyl silicon compounds which have been polymerized include $CH_2{=}CClSi(CH_3)_3$ with ultraviolet light (425) and nuclear silicon-substituted styrenes with benzoyl peroxide (76, 542).

Vinyl silicon compounds copolymerize with various vinyl monomers. Thus, $CH_2{=}CHSiCl_3$ copolymerizes to a limited extent with hydrocarbon olefins such as styrene and isobutylene in the presence of an acid catalyst and with vinyl monomers such as vinyl acetate, methyl acrylate, and acrylonitrile in the presence of peroxide catalysts (526). In contrast, $CH_2{=}CHSi(OC_2H_5)_3$ copolymerizes extensively with ethyl maleate and maleic anhydride, forming hard brittle resins with molecular weights up to 3000 (526). Methyl(vinyl)polysiloxanes copolymerize with many vinyl monomers (257).

Allyl silicon compounds also form copolymers. Thus, $CH_2{=}CHCH_2Si(OC_2H_5)_3$ copolymerizes readily with maleic and fumaric esters (73, 310) as well as with fluorinated olefins (174) and alkyd resins (449). Methallyl compounds behave similarly (73). Polyallylsilanes have been used to cross-link vinyl monomers (174, 314, 371). Allylpolysiloxanes copolymerize with many unsaturated materials (257, 296, 496, 530).

4. *Silicon-functional reactions*

Silicon-functional groups in alkenyl silicon compounds show typical reactions. The chloro- and ethoxysilanes have been hydrolyzed and cohydrolyzed to polysiloxanes (6, 9, 137, 256, 257, 297, 320, 496, 498, 499, 526, 530). The chlorosilanes have also been alcoholyzed to alkoxysilanes (9, 335, 336, 502). In both the hydrolysis and the alcoholysis of alkenylchlorosilanes, particularly allyl compounds, an acid acceptor is sometimes used to prevent silicon–carbon cleavage (9, 336). Many unsaturated chloro- and ethoxysilanes couple satisfactorily with Grignard reagents (2, 117, 160, 267, 392, 403, 472, 498, 499). Allyltriethoxysilane undergoes alcohol exchange with amyl alcohol in the presence of silicon tetrachloride as catalyst (354). Unsaturated acetoxysilanes have been hydrolyzed to silanediols and disiloxanediols (161) and have also been converted to siloxanes by thermally splitting out acetic anhydride and by heating with butoxysilanes to form butyl acetate (317). An unusual silicon-functional reaction is the disproportionation of $CH_2{=}CHCH_2Si(OC_2H_5)_3$ and $CH_3CH{=}CHCH_2Si(OC_2H_5)_3$ in the presence of sodium ethoxide to give ethyl silicate and the corresponding dialkenyldiethoxysilanes (9).

5. *Other properties*

The infrared absorption spectra of $CH_2{=}CHSiH_3$ (269), $CH_2{=}CHCH_2Si(CH_3)_3$ (290), $CH_2{=}CHCH_2SiCl_3$ (9), $CH_3CH{=}CHCH_2SiCl_3$ (9), and of other vinyl and allyl silicon compounds (161) have been determined. Raman spectra have been reported for $CH_2{=}CHSiCl_3$, $CCl_2{=}CHSiCl_3$ (cited as $CHCl{=}CClSiCl_3$), and $CH_2{=}C(CH_3)CH_2Si(C_2H_5)_3$ (333, 522). The dipole moment of $CH_2{=}CH Si(C_2H_5)_3$ is close to zero (305). The vapor pressure, heat of vaporization, heat of combustion, heat of formation, and silicon–carbon bond energy of $CH_2{=}CHSiH_3$ have been determined (504, 505). The toxicity of $CH_2{=}CHSiCl_3$ toward rats is similar to that of other alkyltrichlorosilanes (97).

Vinyltrichlorosilane and its derivatives are used to treat glass cloth for making polyester laminates (49, 50, 51, 543). When made with untreated glass cloth, such laminates lose a great deal of their flexural strength on exposure to moisture. However, glass cloth which has been treated with the vinyl silicon compound produces laminates which retain 90 per cent of their flexural strength even after being boiled in water for 3 hr. Allyl silicon compounds are also of value in treating glass cloth for polyester laminates (484).

Vinyl silicon compounds are also used in silicone rubbers. Such materials have improved compression set and greater hardness (257, 320). In addition, vinyl-containing silicone rubbers may be covulcanized with hydrocarbon elastomers such as natural rubber, Perbunan, GR-S, or Butyl. Some of the latter covulcanizates have good low-temperature properties (349a).

Vinyl, allyl, and methallyl silicon compounds have been used in rapid-curing silicone resins (257, 496, 497, 498, 499, 526). Copolymerizing vinylsiloxanes with methyl methacrylate improves its thermal stability (382). Copolymerizing allyl and methallyl silicon compounds with alkyd resins improves their resistance to alkali and weathering (237, 449).

C. SYNTHESES OF ACETYLENES

Acetylenic silicon compounds are synthesized most conveniently by reacting organometallic ethynyl derivatives with chlorosilanes. Grignard reagents, which are used most commonly, give fair yields (167, 363, 365, 523). Cuprous chloride is

$$(CH_3)_3SiCl + BrMgC{\equiv}CMgBr \rightarrow (CH_3)_3SiC{\equiv}CSi(CH_3)_3$$

sometimes used to catalyze the reaction (167). Sodium and lithium acetylides also couple satisfactorily with chlorosilanes (56, 185).

Other reactions which produce acetylenic silicon compounds are the dehydrohalogenation of chlorovinyl silanes (5) and the reaction of acetylene with silane at 500°C. (537).

D. PROPERTIES OF ACETYLENES

A few addition reactions of acetylenic silicon compounds are known. Bromine reacts with $(CH_3)_3SiC{\equiv}CSi(CH_3)_3$, but the addition stops at the olefin stage

$$(CH_3)_3SiC{\equiv}CSi(CH_3)_3 + Br_2 \rightarrow (CH_3)_3SiCBr{=}CBrSi(CH_3)_3$$

(167). One mole of hydrogen adds to $(CH_3)_3SiC{\equiv}CSi(CH_3)_3$ with a palladium catalyst (167, 363), and 2 moles of hydrogen add with the Raney nickel catalyst (363).

A number of silicon–carbon cleavages have been observed in acetylenic silicon compounds. Attempted hydration of the triple bond results in cleavage (363, 365). Alkali also causes cleavage (56, 186), and the formation of acetylene (56) demonstrates that the cleavage actually occurs in the starting material and not in its hydration product. Hydrogen chloride in refluxing glacial acetic acid also cleaves the ethynyl group (198). Acetylenic silicon compounds are reasonably stable in neutral solution (363) and the acetoxy derivatives can be hydrolyzed to siloxanediols without silicon–carbon cleavage (167).

The ultraviolet absorption spectra of $CH(CH_3){=}C(CH_3)C{\equiv}CSi(C_2H_5)_3$ and of $CH(CH_3){=}C(CH_3)C{\equiv}CH$ have been compared, and a small auxochromic effect has been attributed to the triethylsilyl group (57).

V. FLUORO COMPOUNDS (SEE TABLE 2)

A. PERFLUOROALKYL DERIVATIVES

Perfluoroalkyl silicon compounds have long been sought because of the notion that they might inherit superstability from their silicone and fluorocarbon parentage. Perfluoromethyl silicon halides are said to be obtainable from coupling trifluoromethylmagnesium iodide with silicon tetrachloride (230), from heating trifluoromethyl bromide and other alkyl halides with silicon–copper at 300–500°C. (351, 399) and from reacting a mixture of fluorine and silicon tetrafluoride with calcium carbide at 300°C. (399). However, yields, analyses, and physical properties are unavailable. Trifluoromethyl chloride gives no perfluoromethyl silicon compounds on reaction with silicon or silicon–copper; below 400°C. no reaction occurs, and at 500–1000°C. an exothermic reaction gives only fluorochlorosilanes

TABLE 2

Silicon-containing fluoro compounds

Compound	Melting Point	Boiling Point	n_D	d	References
	°C.	*°C.*			
Aliphatics:					
CF_3SiF_2		−42			(399)
CF_3SiF_2Br		12–13			(399)
$(CF_3)_3SiCl_2$					(230, 263)
$CHF_2CH_2SiCl_3$		104–105.5	1.4050	1.43 (25°)	(525)
$CF_3CF_2CF_2Si(C_2H_5)_2Cl$		119/743 mm. 80/2 mm.	1.3538 (20°)		(368)
$(CF_3CF_2CF_2)_2Si(C_2H_5)_2$		148 79/12 mm.	1.3380 (20°)		(368)
$C_4F_9SiF_3$					(399)
$CF_3CF_2CF_2CH_2CH_2Si(OC_2H_5)_3$		92.5–93/25 mm.			(367)
$(CF_3CF_2CF_2CH_2CH_2)_2Si(OC_2H_5)_2$		117.5–118/25 mm.			(367)
$(CF_3CF_2CF_2CH_2CH_2)_2Si(OH)_2$	64.5–65				(367)
$(CF_3CF_2CF_2CH_2CH_2)_3SiCl$	34–35	133–134/15 mm.			(367)
$(CF_3CF_2CF_2CH_2CH_2)_2SiOH$		151–153/25 mm.	1.3378 (20°)		(367)
$(CF_3CF_2CF_2CH_2CH_2)_4Si$		71–72/25 mm.			(367)
$[(CF_3CF_2CF_2CH_2CH_2)_3Si]_2O$	66.5–67				(367)
$(C_6H_6F_4)Si(CH_3)(OC_2H_5)_2$		201		1.096 (25°)	(174)
$(C_5H_5F_4)(CH_2{=}CHCH_2)Si(OC_2H_5)_2$		103/10 mm.		1.096 (25°)	(174)
$(C_5H_5F_4)Si(CH_3)_2OC_2H_5$		176		1.092 (25°)	(174)
$(C_5H_6F_4)_2Si(OC_2H_5)_2$		117/3 mm.		1.259 (25°)	(174)
$[(C_5H_5F_4)_2SiO]_x$					(174)
$(C_5H_5Cl_2F_2)Si(CH_3)_2OC_2H_5$		220		1.159 (25°)	(174)
$[(C_5H_5Cl_2F_2)Si(CH_3)_2]_2O$	4	142/2 mm.		1.273 (25°)	(174)
$CF_2{=}CF_2$–$(CH_2{=}CHCH_2)_2Si(OC_2H_5)_2$ copolymer					(174)
Fluoroalkylsilanes					(263)
Perfluoroalkylsilicon halides					(351)
$CF_2{=}CFCl$ --- $(C_2H_5O)_4Si$ telomer					(331)
Aromatics:					
$4\text{-}FC_6H_4SiCl_3$		194.5–196.5			(102)
$4\text{-}FC_6H_4Si(CH_3)(OC_2H_5)_2$		87.5–88/4–5 mm.	1.4558 (25°)	1.0149 (25°)	(536)
$4\text{-}FC_6H_4Si(CH_3)_2OC_2H_5$		69/6 mm.	1.3639 (25°)	0.9846 (28°)	(536)
$4\text{-}FC_6H_4Si(CH_3)_3$		93/60 mm. 170–171/745 mm.	1.4711 (25°) 1.4751 (20°)	0.9452 (25°) 0.9656 (20°)	(102, 374)
$(4\text{-}FC_6H_4)_2SiCl_2$		293–294/738 mm.			(102)

$(4\text{-}FC_6H_4)_2Si(CH_3)_2$		184–185/60 mm.	1.5331 (20°)	1.1121 (20°)	(102)
$(FC_6H_4)_2SiCl_2$					(377)
$(FC_6H_4)_2Si(OH)_2$					(377)
$[4\text{-}FC_6H_4Si(CH_3)_2]_2O$		96–98/1–2 mm.	1.4950 (25°)	1.0653 (23°)	(536)
Fluorophenylsiloxanes					(102, 177, 377, 536)
$3\text{-}CF_3C_6H_4SiF_3$	−34	118.2	1.3783 (25°)	1.3985 (25°)	(175)
$CF_3C_6H_4SiF_3$					(286, *287*)
$3\text{-}CF_3C_5H_4SiCl_3$		108/47 mm.	1.4678 (25°)		(*175*, 286, *287*)
$3\text{-}CF_3C_6H_4Si(OC_2H_5)_3$		86.5–87.5/4 mm.			(175)
$4\text{-}CF_3C_6H_4SiCl_3$	−4 to −3	118.7	1.3783 (25°)	1.399 (25°)	(175)
$3\text{-}CF_3C_6H_4Si(CH_3)Cl_2$		115.5/50 mm.	1.4639 (25°)	1.3436 (25°)	(285, 287)
$(CF_3C_6H_4)(CH_2Cl)SiCl_2$		86/4 mm.	1.4839 (25°)	1.4663 (25°)	(284)
$2\text{-}CF_3C_5H_4Si(CH_3)_2Cl$		78/12 mm.			(175)
$(CF_3C_6H_4)(ClCH_2)Si(CH_3)Cl$		131/25 mm.	1.4796 (25°)	1.3411 (25°)	(284)
$3\text{-}CF_3C_5H_4Si(C_6H_5)_3$	101				(*185*, 186)
$(3\text{-}CF_3C_6H_4)_2SiCl_2$		125/3 mm.	1.4884 (25°)	1.4274 (25°)	(*175*, 286, *287*)
$(3\text{-}CF_3C_6H_4)_2Si(OC_2H_5)_2$	20	104–115/1 mm.			(175)
$(CF_3C_6H_4)_2SiCl_2$		195–198/65 mm.			(63, 259)
$(CF_3C_6H_4)_2Si(OH)_2$					(*286*, 287)
$(3\text{-}CF_3C_6H_4)_2Si(CH_3)Cl$		123/4 mm.	1.4841 (25°)	1.3535 (25°)	(285, 287)
$(CF_3C_6H_4)_2(ClCH_2)SiCl$		152/4 mm.	1.4987 (25°)	1.4407 (25°)	(284)
$(CF_3C_6H_4)_2(ClCH_2)SiCH_3$		131/2 mm.	1.4925 (25°)	1.3434 (25°)	(284)
$(3\text{-}CF_3C_6H_4)_3SiCl$		154.2/0.7 mm.	1.5018 (25°)		(286, *287*)
$(4\text{-}CF_3C_6H_4)_3SiH$	83				(43)
$(3\text{-}CF_3C_6H_4)_3SiF$		168/1 mm.	1.4859 (25°)	1.4008 (25°)	(500)
$(CF_3C_6H_4)_3SiOH$					(*286*, 287)
$(4\text{-}CF_3C_5H_4)_3SiCH_3$	107				(43)
$(3\text{-}CF_3C_6H_4)_4Si$	103	197/2 mm.			(132, *500*)
$[CF_3C_6H_4Si(CH_3)O]_3$			1.4698 (25°)	1.318 (25°)	(285)
$[CF_3C_6H_4Si(CH_3)O]_4$			1.4701 (25°)	1.319 (25°)	(285)
$(CF_3C_6H_4)_3SiOSi(CF_3C_5H_4)_2OSi(CF_3C_6H_4)_3$		550			(*286*, 287)
		240/1 mm.	1.4948 (25°)	1.4084 (26°)	
$2,4\text{-}(CF_3)_2C_5H_3SiCl_3$		55–57.2/1.7 mm.	1.4322 (30°)	1.532 (30°)	(286, *287*)
$2,5\text{-}(CF_3)_2C_6H_3SiCl_3$		~80/25 mm.			(286, *287*)
$3,5\text{-}(CF_3)_2C_6H_3SiCl_3$		57/2 mm.	1.4322 (30°)	1.532 (30°)	(287)
$(CF_3)_2C_5H_3SiCl_3$		120/50 mm.	1.442 (25°)	1.5872 (25°)	(132)
$(CF_3)_2C_6H_3Si(CH_3)Cl_2$		101/24 mm.			(132, *285*)
$[(CF_3)_2C_5H_3](ClCH_2)SiCl_2$					(284)
$[(CF_3)_2C_6H_3](ClCH_2)Si(CH_3)Cl$					(284)
$(CF_3)_2C_6H_3Si(CH_3)_3$		179.4/740 mm.	1.4222 (25°)	1.2205 (25°)	(132)
$[2,4\text{-}(CF_3)_2C_6H_3]_2SiCl_2$		116.6/214 mm.	1.4424 (30°)	1.567 (30°)	(286, *287*)
$[2,5\text{-}(CF_3)_2C_5H_3]_2SiCl_2$		110/3 mm.	1.4248 (30°)		(286, *287*)

TABLE 2—*Concluded*

Compound	Melting Point	Boiling Point	n_D	d	References
	°C.	*°C.*			
$[3,5\text{-}(CF_3)_2C_6H_3]_2SiCl_2$		117/2 mm.	1.4424 (30°)	1.567 (30°)	(287)
$[(CF_3)_2C_5H_3]_2SiCl_2$		169–171/20 mm.			(*63*, 132)
$[(CF_3)_2C_6H_3]_2(ClCH_2)SiCl$					(284)
$[(CF_3)_2C_5H_3]_2(ClCH_2)SiCH_3$					(284)
$[2,4\text{-}(CF_3)_2C_6H_3]_3SiCl$		156/1.8–2.3 mm.	1.4445 (30°)	1.552 (30°)	(286, *287*)
$[2,5\text{-}(CF_3)_2C_6H_3]_3SiCl$		155–160/3 mm.	1.4549 (30°)		(286, *287*)
$[3,5\text{-}(CF_3)_2C_6H_3]_3SiCl$		156/2 mm.	1.4445 (30°)	1.552 (30°)	(287)
$[(CF_3)_2C_6H_3]_3SiCl$		186–188/20 mm.			(63)
$[2,4\text{-}(CF_3)_2C_6H_3]_2Si(OH)_2$	220				(*286*, 287)
$[2,4\text{-}(CF_3)_2C_6H_3]_3SiOH$					(*286*, 287)
$2,4\text{-}(CF_3)_2C_6H_3Si$ siloxane					(*286*, 287)
$[(CF_3)_2C_5H_3Si(CH_3)O]_3$		169/0.4 mm.	1.4380 (25°)	1.483 (25°)	(285)
$\{[(CF_3)_2C_6H_3]_2SiO\}_x$					(63)
$\{[(CF_3)_2C_6H_3]_3Si\}_2O$		378–382/750 mm.			(63)
Trifluoromethylphenylsiloxanes					(63, 135, 175, 177, 259, 260, 286, 287)

—the degradation is so complete that it is suggested for analyzing volatile chlorofluorocarbons (263). The only definite perfluoroalkyl derivative is $(C_3F_7)_2Si(C_2H_5)_2$, obtained in 30 per cent yield from C_3F_7Li and $(C_2H_5)_2SiCl_2$ at $-50°C$. (368).

Few reactions of perfluoroalkylsilanes are known. $(C_3F_7)_2Si(C_2H_5)_2$ is stable to 3 *N* sulfuric acid at 100°C., but it forms heptafluoropropane with methanolic sodium hydroxide above 75°C. (368). It is said that $—CHF_2$ and $—CF_3$ groups are cleaved from silicon with cold water (381a). There are no reports on the thermal stability of perfluoroalkylsiloxanes.

B. PARTIALLY FLUORINATED ALKYL DERIVATIVES

A number of these derivatives have been prepared and some show reasonable chemical and thermal stability. Compounds like $(CF_3CF_2CF_2CH_2CH_2)_3SiCl$ and $(CF_3CF_2CF_2CH_2CH_2)_2Si(OC_2H_5)_2$ are made through typical Grignard couplings (367). Partially fluorinated materials are also obtained as adducts of allylsilanes with fluoroölefins or chlorofluoroölefins. For example, $(CH_2{=}CHCH_2)_2Si(OC_2H_5)_2$ with $CF_2{=}CF_2$ at 150°C. for 15 hr. gives a 30 per cent yield of $(\underbrace{CF_2CF_2CH_2C}HCH_2)(CH_2{=}CHCH_2)Si(OC_2H_5)_2$, a 10 per cent yield of $(\underbrace{CF_2CF_2CH_2C}HCH_2)_2Si(OC_2H_5)_2$, and polymeric adducts (174). In another synthetic method $CF_2{=}CH_2$ and $HSiCl_3$ give a 20 per cent yield of $CHF_2CH_2SiCl_3$ at 150°C. under pressure for 2 hr. with a platinum-on-charcoal catalyst (525). $FCH_2Si—$ derivatives are not obtained from silicon tetrafluoride with diazomethane (see $ClCH_2Si$ derivatives); the products are nitrogen and polymethylene (546, 547).

The chemical properties of partially fluorinated alkyl silicon compounds are not very well known. $(CF_3CF_2CF_2CH_2CH_2)_3SiCl$ gives a 42 per cent yield of silanol on being boiled with water for 7 hr. (367). The silanol is converted to the disiloxane in 33 per cent yield on being heated with hydrochloric acid in methanol and then in acetic acid (367). Hydrolysis of $(CF_3CF_2CF_2CH_2CH_2)_2Si(OC_2H_5)_2$ in aqueous methanol gives a 65 per cent yield of the diol (367). The adducts of fluoroölefins and chlorofluoroölefins with allyl silicon compounds can be hydrolyzed to liquid siloxanes having good lubricating and dielectric properties and to resinous siloxanes having good thermal stability (174).

C. SIDE-CHAIN FLUORINATED AROMATIC DERIVATIVES

Trifluoromethylphenyl silicon compounds are readily obtained via trifluoromethylphenyl Grignard and organolithium reagents (43, 175, 287, 500). Another method of making such compounds involves fluorination of trichloromethylphenyl silicon compounds with a mixture of antimony trifluoride and antimony pentachloride (175).

Hydrolysis of the various trifluoromethylphenyl silicon halides and ethoxides gives polysiloxanes having high stability toward heat and acid reagents (175, 285); some are said to be unaffected by boiling fuming sulfuric acid or fuming nitric acid (285). The silanols from compounds containing two $—CF_3$ substituents are very resistant toward dehydration; $[(CF_3)_2C_6H_3]_2Si(OH)_2$ melts at

220°C. without decomposition, and $[(CF_3)_2C_6H_3]_3SiOH$ is unaffected by "toluene chlorosulfonic acid" at its evaporation temperature (286). This inertness toward dehydration poses some problems in converting such compounds to polymeric siloxanes, especially copolymeric materials. One method of converting them to polysiloxanes involves heating the appropriate silicon chloride mixtures with lead monoxide and a little cupric chloride in acetonitrile (259). Another method of making polymers containing these groups is through silmethylene linkages from the sodium condensation of compounds such as $(ClCH_2)(CF_3C_6H_4)SiCl_2$ and their hydrolyzates (284). The electronic effect of the substituents in $(4\text{-}CF_3C_6H_4)_3SiH$ is not enough to alter the reaction with methyllithium to give the silyllithium derivative; $(4\text{-}CF_3C_6H_4)SiCH_3$ is obtained in good yield (43).

Although $—CF_3$ substituents strongly deactivate the phenyl–silicon bond towards acid reagents, they have the opposite effect with basic reagents. In $3\text{-}CF_3C_6H_4Si(C_6H_5)_3$ (185) the trifluoromethylphenyl group, rather than the phenyl groups, is cleaved with potassium hydroxide in aqueous ethanol–dioxane; thus at 85°C. for 24 hr. a 0.7 *M* solution gives a 51 per cent yield of $C_6H_5CF_3$ and a 48 per cent yield of $(C_6H_5)_3SiOH$ (186).

D. NUCLEARLY FLUORINATED AROMATIC DERIVATIVES

Few nuclearly substituted compounds are known. They are prepared from 4-fluorobromobenzene via the Grignard reaction (374, 553). The 4-fluorophenyl group is cleaved from silicon about as easily as the 4-chlorophenyl group with 71 per cent nitric acid in refluxing acetic anhydride (102, 553). The dipole moment of $4\text{-}FC_6H_4Si(CH_3)_3$ has been compared with those of analogous compounds (374).

VI. Chloro Compounds (See Table 3)

A. SYNTHESES OF CHLOROMETHYL DERIVATIVES

1. Photochemical chlorination

Chloromethyl silicon compounds are made principally by the photochemical chlorination of methyl silicon compounds. The reaction has been extensively investigated, because the starting materials are readily available and the products are very versatile synthetic intermediates.

Photochemical chlorination of $(CH_3)_3SiCl$ with one molar equivalent of chlorine gives $ClCH_2Si(CH_3)_2Cl$, $Cl_2CHSi(CH_3)_2Cl$, and $(ClCH_2)_2Si(CH_3)Cl$ in 62 per cent, 23 per cent, and 9 per cent yields, respectively, based on 81 per cent unrecovered starting material (293). Similar chlorination of $(CH_3)_2SiCl_2$ gives $ClCH_2Si(CH_3)Cl_2$, $Cl_2CHSi(CH_3)Cl_2$, and $Cl_3CSi(CH_3)Cl_2$ in 37 per cent, 38 per cent, and 7 per cent yields, respectively, together with 26 per cent recovered $(CH_3)_2SiCl_2$ (293). The photochemical chlorination of $(CH_3)_4Si$ also proceeds satisfactorily with the formation of $ClCH_2Si(CH_3)_3$ (538) and higher chlorination products (459). Exhaustive photochemical chlorination of CH_3SiCl_3 gives a 55 per cent yield of CCl_3SiCl_3 (182); other studies (456, 459) suggest that the lower chlorination products are more readily chlorinated than the starting material.

That chlorinated methyl groups are more readily chlorinated than methyl groups in compounds derived from $(CH_3)_2SiCl_2$ and $(CH_3)_3SiCl$ is clearly indicated by the relative amounts of the products obtained (293). Confirmation and extension of these results are available in an investigation involving photochemical chlorination of $(CH_3)_3SiCl$, $ClCH_2Si(CH_3)_3$, and a mixture of $(CH_3)_3SiCl$ with $(CH_3)_2SiCl_2$ (459). With $ClCH_2Si(CH_3)_3$ no unusual orientation effects are encountered; the tendency toward exhaustive chlorination of a single carbon atom is largely subdued, since $Cl_2CHSi(CH_3)_3$ and $(ClCH_2)_2Si(CH_3)_2$ are obtained in 31 per cent and 48 per cent yields, respectively (459). This product distribution is typical of hydrocarbon chlorinations and demonstrates that silicon alone is not responsible for the anomalous distribution of chlorination products obtained with methylchlorosilanes; the presence of chlorine or some other negative substituent on silicon appears necessary for this phenomenon (459).

In the competitive chlorination of $(CH_3)_3SiCl$ and $(CH_3)_2SiCl_2$, the former is chlorinated about nine times faster; thus the presence of chlorine on silicon strongly deactivates neighboring methyl groups toward chlorination (459). Competitive and comparative chlorinations of $(CH_3)_3SiCl$ and $(CH_3)_3CCl$ have also been carried out (459). Despite the different orientation effects of the central silicon and carbon atoms, the rates for the substitution of the first chlorine are about the same. The introduction of the first chlorine in $(CH_3)_3CCl$ results in considerable deactivation toward further chlorination, but this is not observed with the analogous silicon compound. On the other hand, the exhaustive chlorination of one methyl group in $(CH_3)_3SiCl$ is much more pronounced than in the carbon analog (459). In a different type of competition involving reaction of a mixture of chlorine and bromine with a methyl silicon compound, it is interesting to note that the products are bromo derivatives almost exclusively (460); only small amounts of chloro derivatives are found (240).

The tendency of entering chlorine atoms to exhaustively chlorinate one methyl group in the methylchlorosilanes poses a problem. The yields of $ClCH_2$— derivatives are lowered, and these are the products most frequently sought. Higher yields of monochlorinated methylchlorosilanes may be obtained from a continuous recycle operation in which the starting material is maintained in large excess; for example, with CH_3SiCl_3 such a process gives about a 40 per cent yield of $ClCH_2SiCl_3$ (456).

Chlorinated methylpolysiloxanes may be obtained by direct chlorination. Thus $[—Si(CH_3)_2O—]_4$ with a limited amount of chlorine under illumination gives a 70 per cent yield of the monochloro derivative (294).

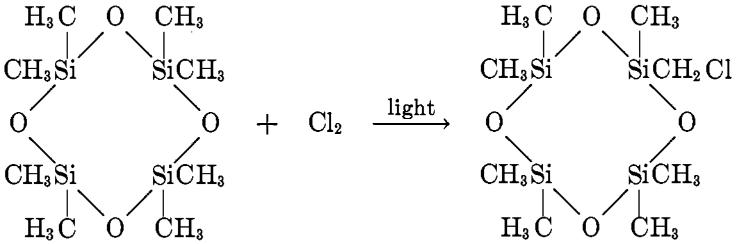


TABLE 3

Silicon-containing chloro compounds

Compound	Melting Point	Boiling Point	n_D	*d*	References
	°C.	*°C.*			
$ClCH_2$ *monosilanes:*					
$ClCH_2SiCl_3$		116.5/750 mm.		1.4776 (20°/20°)	(284, 456, 503, *546*, *547*)
$ClCH_2Si(OC_2H_5)_3$		91/25 mm.			(134)
$ClCH_2Si(CH_3)Cl_2$		122		1.2778 (20°/20°)	(144, 183, 284, *293*, 326, 453, 456, 458, 466, 467, *546*, *547*)
$ClCH_2Si(CH_3)(OC_2H_5)_2$					(106, 134, 210, 213)
$(ClCH_2)(CF_3C_6H_4)SiCl_2$		86/4 mm.	1.4839 (25°)	1.4663 (25°)	(284)
$(ClCH_2)[(CF_3)_2C_6H_3]SiCl_2$					(284)
$ClCH_2Si(CH_3)_2Cl$		115	1.4360 (20°)	1.0865 (20°)	(133, 144, 152, 155, 181, 205, 211, 216, 218, 219, 221, 222, *293*, 294, 322, 326, 426, 435, 453, 456, *459*, 479)
$ClCH_2Si(CH_3)_2OH$		89/40 mm.			(294)
$ClCH_2Si(CH_3)_2OC_2H_5$		132/741 mm.	1.4124 (25°)	0.9438 (25°)	(134, 155, 205, 206, 211, 218, 219, 222)
$ClCH_2Si(CH_3)(C_4H_9)Cl$					(205)
$ClCH_2Si(CH_3)(C_4H_9)OC_2H_5$					(206, 211)
$ClCH_2Si(CH_3)(C_5H_5)Cl$		136/24 mm.			(205, 218, 219, 457, 458, *461*)
$ClCH_2Si(CH_3)(C_5H_5)OC_2H_5$					(206, 211)
$ClCH_2(Cl_2CH)Si(CH_3)Cl$					(133)
$ClCH_2(CF_3C_6H_4)Si(CH_3)Cl$		131/25 mm.	1.4796 (25°)	1.3411 (25°)	(284)
$ClCH_2[(CF_2)_2C_6H_3]Si(CH_3)Cl$					(284)
$ClCH_2(CF_3C_6H_3)_2SiCl$		152/4 mm.	1.4987 (25°)	1.4407 (25°)	(284)
$ClCH_2[(CF_3)_2C_5H_3]_2SiCl$					(284)
$ClCH_2Si(CH_3)_3$		97/734 mm. 97	1.4180 (20°) 1.4148 (25°)	0.8791 (20°) 0.8764 (25°)	(119, 120, 121, 122, 133, 134, *153*, 181, 212, 217, 221, 223, 229, 240, 361, 373, 383, 406, 407, 412, 413, 417, 429, 433, 435, 436, 440, 441, 445, 451, 459, 463, 466, 467, 482, *538*, 539, 540)
$ClCH_2Si(CH_3)_2C_6H_5$		135/48 mm. 121/24 mm.	1.5218 (20°) 1.5186 (25°)	1.031 (20°) 1.024 (25°)	(134, *154*, 206, 216, 217, 412, 413, 433, 436)
$(ClCH_2)(Cl_2CH)Si(CH_3)_2$		184	1.4753 (25°)	1.209 (25°)	(459)
$ClCH_2Si(CH_3)(C_6H_5)_2$		198/23 mm.	1.5785 (25°)	1.101 (25°)	(457, 458, *461*)
$ClCH_2(4\text{-}ClC_6H_4)SiCH_3$		168/<1 mm.	1.6062 (20°)	1.349 (20°)	(196)

$\mathrm{(ClCH_2)(CF_3C_6H_4)_2SiCH_3}$		131/2 mm.	1.4925 (25°)	1.3434 (25°)	(284)
$\mathrm{ClCH_2[(CF_3)_2C_6H_3]_2SiCH_3}$					(284)
$\mathrm{(ClCH_2)_2SiCl_2}$		100/155 mm. 59/16 mm.		1.4624 (20°/20°)	(293, 546, 547)
$\mathrm{(ClCH_2)_2Si(CH_3)Cl}$		172			(133,143, 152, *293*, 481)
$\mathrm{(ClCH_2)_2Si(CH_3)_2}$		160/724 mm.	1.4579 (25°)	1.075 (25°)	(131, 133, 154, 221, 373, 459 466, 467, *481*)
$\mathrm{(ClCH_2)_2Si(CH_3)C_4H_9}$					(131)
$\mathrm{(ClCH_2)_2Si(CH_3)C_6H_5}$					(131)
$\mathrm{(ClCH_2)_3SiCl}$		70/4 mm.		1.4377 (20°/20°)	(546, 547)
$\mathrm{(ClCH_2)_3SiCH_3}$		205	1.4857 (25°)	1.24 (25°)	(459)
$\mathrm{ClCH_2}$ *disilmethylenes:*					
$\mathrm{ClCH_2[Si(CH_3)_2CH_2]_1Si(CH_3)_3}$		186/760 mm. 141/200 mm.	1.4480 (20°)	0.8950 (20°)	(433, 435, *440*)
$\mathrm{ClCH_2[Si(CH_3)_2CH_2]_2Si(CH_3)_3}$		246/760 mm. 197/200 mm.	1.4630 (20°)	0.9000 (20°)	(440)
$\mathrm{ClCH_2[Si(CH_3)_2CH_2]_3Si(CH_3)_3}$		297/760 mm. 242/200 mm.	1.4706 (20°)	0.9029 (20°)	(440)
$\mathrm{ClCH_2}$ *polysiloxanes:*					
$\mathrm{ClCH_2Si(CH_3)_2OSi(CH_3)_3}$		152	1.4106 (20°)	0.9105 (20°)	(52, 53, 119, 120, 121, 122, 142, 144, 181, *293*, 294, 383, 388, 436, 452, 455, 483)
$\mathrm{[ClCH_2Si(CH_3)_2]_2O}$		205	1.4390 (20°)	1.045 (20°)	(144, 155, *293*, 341, 407, 417, 429, 483)
$\mathrm{[ClCH_2Si(CH_3)(C_5H_5)]_2O}$		237/24 mm.	1.5466 (25°)	1.161 (25°)	(457, *458*, 461)
$\mathrm{[(ClCH_2)_2Si(CH_3)]_2O}$					(143)
$\mathrm{ClCH_2Si(CH_3)_2O[Si(CH_3)_2O]_1Si(CH_3)_2CH_2Cl}$	−79	142/40 mm.	1.4283 (25°)	1.020 (25°)	(326, *453*)
$\mathrm{ClCH_2Si(CH_3)_2O[Si(CH_3)_2O]_2Si(CH_3)_2CH_2Cl}$	−94	168/40 mm.	1.4231 (25°)	1.008 (25°)	(326, *453*)
$\mathrm{ClCH_2Si(CH_3)_2O[Si(CH_3)_2O]_3Si(CH_3)_2CH_2Cl}$	−85	190/40 mm.	1.4200 (25°)	1.002 (25°)	(326, *453*)
$\mathrm{ClCH_2Si(CH_3)_2O[Si(CH_3)_2O]_4Si(CH_3)_2CH_2Cl}$	−77	223/40 mm.	1.4173 (25°)	0.996 (25°)	(326, *453*)
$\mathrm{ClCH_2Si(CH_3)_2O[Si(ClCH_2)(CH_3)O]_1Si(CH_3)_2CH_2Cl}$		176/40 mm.	1.4465 (25°)	1.112 (25°)	(326, *453*)
$\mathrm{ClCH_2Si(CH_3)_2O[Si(ClCH_2)(CH_3)O]_2Si(CH_3)_2CH_2Cl}$		167/5 mm.	1.4520 (25°)	1.157 (25°)	(326, *453*)
$\mathrm{ClCH_2Si(CH_3)_2O[Si(ClCH_2)(CH_3)O]_3Si(CH_3)_2CH_2Cl}$		210/5 mm.	1.4553 (25°)	1.182 (25°)	(326, *453*)
$\mathrm{(CH_3)_3SiO[Si(ClCH_2)(CH_3)O]_1Si(CH_3)_3}$	−85	102/40 mm.	1.4058 (25°)	0.918 (25°)	(326, *453*)
$\mathrm{(CH_3)_3SiO[Si(ClCH_2)(CH_3)O]_2Si(CH_3)_3}$	−77	162/40 mm.	1.4212 (25°)	1.006 (25°)	(326, *453*)
$\mathrm{(CH_3)_3SiO[Si(ClCH_2)(CH_3)O]_3Si(CH_3)_3}$	−85	210/40 mm.	1.4311 (25°)	1.063 (25°)	(326, *453*)
$\mathrm{(CH_3)_3SiO[Si(ClCH_2)(CH_3)O]_4Si(CH_3)_3}$	−77	251/40 mm.	1.4375 (25°)	1.100 (25°)	(326, *453*)
$\mathrm{ClCH_2}\underline{\mathrm{Si(CH_3)OSi(CH_3)_2OSi(CH_3)_2OSi(CH_3)_2O}}$	−1	214 127/50 mm.	1.4158 (20°)	1.0444 (20°)	(119,120, 121, 122, 143, 144, 181, 209, *294*)
Chloromethylsiloxanes					(144, 325, 327, 341, 348, 383)
Dichloromethyls:					
$\mathrm{Cl_2CHSi(CH_3)Cl_2}$		108/225 mm.			(183, *293*)
$\mathrm{Cl_2CHSi(CH_3)_2Cl}$		149			(133, 143, *293*, 426, 459, 481)

TABLE 3—*Continued*

Compound	Melting Point	Boiling Point	n_D	d	References
	°C.	°C.			
$Cl_2CHSi(CH_3)_2OH$		89/40 mm.			(294)
$(Cl_2CH)(ClCH_2)Si(CH_3)Cl$					(133)
$Cl_2CHSi(CH_3)_3$		133/730 mm.	1.4430 (25°)	1.0395 (25°)	(133, 153, 373, 426, 459, *481*)
$(Cl_2CH)(ClCH_2)Si(CH_3)_2$		184	1.4753 (25°)	1.209 (25°)	(459)
$(Cl_2CH)_2Si(CH_3)Cl$					(459)
$[(Cl_2CHSi(CH_3)_2]_2O$		150/40 mm.	1.4660 (20°)	1.2213 (20°)	(143, *294*)
Chlorinated methylsiloxanes					(327, 348)
Trichloromethyls:					
Cl_3CSiCl_3	116	156			(*182*, 183, 503)
$Cl_3CSi(OC_2H_5)_3$		81/3 mm.	1.4320 (25°)	1.1860 (25°)	(503)
$Cl_3CSi(CH_3)Cl$	99	109/150 mm.			(143, 183, *293*)
$Cl_3CSi(CH_3)_2Cl$	96	161/739 mm.			(133, *459*)
$Cl_3CSi(CH_3)_3$	60–66	146–156			(459)
$Cl_3CSi(C_6H_5)_3$	194				(186, *196*)
$Cl_3CSi(C_6H_4Cl\text{-}4)_3$	161				(196)
Chlorinated methylsiloxanes					(143, 327, 348)
1-Chloroethyls:					
$CH_3CHClSiCl_3$		138 66/75 mm.		1.3919 (20°/20°)	(4, 58, 61, 72, 74, 232, 236, 239, 255, 261, 425, 431, *448*, 526, *546*, *547*)
$CH_3CHClSi(OC_3H_7)_2Cl$		89/7 mm.	1.4264 (25°)	1.0550 (25°)	(58)
$CH_3CHClSi(OC_3H_7\text{-}i)_2Cl$		49/1 mm.	1.4178 (25°)	1.0403 (25°)	(58)
$CH_3CHClSi(OCH_3)_3$		164	1.4095 (25°)	1.0908 (25°)	(*58*, 59, 61)
$CH_3CHClSi(OC_2H_5)_3$		194/747 mm.	1.4087 (25°)	0.9991 (25°)	(*58*, 59, 61)
$CH_3CHClSi(OC_3H_7)_3$		98/4 mm.	1.4180 (25°)	0.9680 (25°)	(*58*, 59)
$CH_3CHClSi(OC_3H_7\text{-}i)_3$		74/4 mm.	1.4079 (25°)	0.9451 (25°)	(58)
$CH_3CHClSi(OC_4H_9)_3$		129/4 mm.	1.4262 (25°)	0.9486 (25°)	(*58*, 59)
$CH_3CHClSi(OC_4H_9\text{-}i)_3$		113/4 mm.	1.4190 (25°)	0.9335 (25°)	(58)
$CH_3CHClSi[OCH(C_2H_5)(CH_3)]_3$		110/4 mm.	1.4243 (25°)	0.9450 (25°)	(58)
$CH_3CHClSi(OC_5H_{11})_3$		157/4 mm.	1.4315 (25°)	0.9344 (25°)	(*58*, 59)
$CH_3CHClSi(CH_3)Cl_2$		136			(253)
$CH_3CHClSi(C_2H_5)Cl_2$		160/731 mm. 76/43 mm.			(231, 232, 236, 239, 425)
$CH_3CHClSi(C_2H_5)_2F$		152/760 mm. 107/200 mm.	1.4208 (20°)	0.9955 (20°)	(10, *427*)
$CH_3CHClSi(C_2H_5)_2Cl$		182/760 mm. 134/200 mm.	1.4561 (20°)	1.0401 (20°)	(10, 304, 425, 426, *427*)

$CH_3CHClSi(C_2H_5)_2Br$		195 106/46 mm.	1.4784 (20°)	1.2661 (20°)	(10)
$CH_3CHClSi(C_2H_5)_2NH_2$		93/38 mm.	1.4570 (20°)	0.9604 (20°)	(10)
$CH_3CHClSi(C_2H_5)_2OH$		195/760 mm. 150/200 mm.	1.4607 (20°)	1.0238 (20°)	(427)
$CH_3CHClSi(CH_3)_3$		118/735 mm.	1.4242 (20°)	0.8768 (20°)	(425, 426, *448*)
$CH_2CHClSi(CH_3)(C_2H_5)_2$		172/760 mm. 125/200 mm.	1.4452 (20°)	0.9036 (20°)	(425, *427*)
$CH_3CHClSi(C_2H_5)_3$		195 112/58 mm.	1.4564 (20°) 1.4540 (20°)	0.9122 (20°) 0.9086 (20°)	(304, 305, 360, *426*, *428*, 519)
$CH_3CHClSi(C_2H_5)_3C_6H_5$		274/760 mm. 219/200 mm.	1.5229 (20°)	1.0109 (20°)	(427)
$CH_3CHClSi(C_6H_5)_3$	130				(198)
$[CH_3CHClSi(OCH_3)_2]_2O$		105/2 mm.	1.4284 (25°)	1.176 (25°)	(61)
$[CH_3CHClSi(OC_2H_5)_2]_2O$		133/6 mm.	1.4243 (25°)	1.080 (25°)	(61)
$(CH_3CHClSiO_{1.5})_x$					(58)
$CH_2BrCClBrSiCl_3$		108/14 mm.	1.5492 (20°)	2.07 (27°)	(4)
2-Chloroethyls:					
$ClCH_2CH_2SiCl_3$		152/734 mm.	1.4622 (20°)	1.42 (25°)	(4, 58, 61, 72, 232, 235, 236, 239, 255, 261, 332. 397, 425, 434, *448*. *526*)
$ClCH_2CH_2Si(OCH_3)_3$		114/106 mm.	1.4157 (25°)	1.1078 (25°)	(*58*, 60, 61)
$ClCH_2CH_2Si(OCH_3)_2OC_3H_7$		102/18 mm.	1.4176 (25°)	1.047 (25°)	(61)
$ClCH_2CH_2Si(OCH_3)_2OC_4H_9$		104/10 mm.	1.4206 (25°)	1.033 (25°)	(61)
$ClCH_2CH_2Si(OCH_3)_2OC_5H_{11}$		129/21 mm.	1.4245 (25°)	1.029 (25°)	(61)
$ClCH_2CH_2Si(OCH_3)(OC_3H_7)_2$		122/18 mm.	1.4196 (25°)	1.006 (25°)	(61)
$ClCH_2CH_2Si(OCH_3)(OC_4H_9)_2$		131/10 mm.	1.4244 (25°)	0.9821 (25°)	(61)
$ClCH_2CH_2Si(OC_2H_5)_3$		90/9 mm.	1.4130 (25°)	1.0090 (25°)	(*58*, 60, 61)
$ClCH_2CH_2Si(OC_2H_5)_2OC_4H_9$		116/11 mm.	1.4193 (25°)	0.9828 (25°)	(61)
$ClCH_2CH_2Si(OC_2H_5)(OC_4H_9)_2$		137/11 mm.	1.4251 (25°)	0.9672 (25°)	(61)
$ClCH_2CH_2Si(OC_3H_7)_3$		108/4 mm.	1.4218 (25°)	0.9742 (25°)	(*58*, 60, 61)
$ClCH_2CH_2Si(OC_3H_7\text{-}i)_3$		86/4 mm.	1.4098 (25°)	0.9500 (25°)	(58)
$ClCH_2CH_2Si(OC_4H_9)_3$		139/4 mm.	1.4296 (25°)	0.9548 (25°)	(*58*, 60, 61)
$ClCH_2CH_2Si(OC_4H_9\text{-}i)_3$		122/4 mm.	1.4235 (25°)	0.9432 (25°)	(58)
$ClCH_2CH_2Si[OCH(C_2H_5)CH_3]_3$		118/4 mm.	1.4266 (25°)	0.9503 (25°)	(58)
$ClCH_2CH_2Si(OC_5H_{11})_3$		165/4 mm.	1.4344 (25°)	0.9392 (25°)	(*58*, 60, 61)
$ClCH_2CH_2Si(OCOCH_3)(OCH_3)_2$		97/9 mm.	1.4211 (25°)	1.161 (25°)	(60)
$ClCH_2CH_2Si(OCOCH_3)(OC_2H_5)_2$		118/20 mm.	1.4184 (25°)	1.079 (25°)	(60)
$ClCH_2CH_2Si(OCOCH_3)(OC_3H_7)_2$		123/7 mm.	1.4228 (25°)	1.052 (25°)	(60)
$ClCH_2CH_2Si(OCOCH_3)(OC_4H_9)_2$		144/8 mm.	1.4265 (25°)	1.018 (25°)	(60)
$ClCH_2CH_2Si(OCOCH_3)(OC_5H_{11})_2$		156/5 mm.	1.4311 (25°)	1.000 (25°)	(60)
$ClCH_2CH_2Si(OCOCH_3)_2OCH_3$		115/8 mm.	1.4216 (25°)	1.190 (25°)	(60)
$ClCH_2CH_2Si(OCOCH_3)_2OC_2H_5$		120/8 mm.	1.4243 (25°)	1.157 (25°)	(60)

TABLE 3—*Continued*

Compound	Melting Point	Boiling Point	n_D	*d*	References
	°*C.*	°*C.*			
$ClCH_2CH_2Si(OCOCH_3)_2OC_3H_7$		115/3 mm.	1.4241 (25°)	1.129 (25°)	(60)
$ClCH_2CH_2Si(OCOC_2H_5)(OCH_3)_2$		99/7 mm.	1.4206 (25°)	1.124 (25°)	(60)
$ClCH_2CH_2Si(OCOC_2H_5)(OC_2H_5)_2$		119/11 mm.	1.4206 (25°)	1.068 (25°)	(60)
$ClCH_2CH_2Si(OCOC_2H_5)(OC_3H_7)_2$		139/10 mm.	1.4252 (25°)	1.035 (25°)	(60)
$ClCH_2CH_2Si(CH_3)Cl_2$		157			(253)
$ClCH_2CH_2Si(C_2H_5)Cl_2$		178/737 mm.			(231, 232, 236, 239, 425)
		89/42 mm.			
$ClCH_2CH_2Si(C_2H_5)_2F$		171/760 mm.	1.4277 (20°)	1.0100 (20°)	(*427*, 428)
$ClCH_2CH_2Si(C_2H_5)_2Cl$		201/760 mm.	1.4636 (20°)	1.0552 (20°)	(*427*, 428)
		153/200 mm.			
$ClCH_2CH_2Si(C_2H_5)_2NH_2$		65/7 mm.	1.4624 (20°)	0.9769 (20°)	(428)
$ClCH_2CH_2Si(C_2H_5)_3$		208			(304, 426, 428, 519)
		80/9 mm.	1.4562 (17°)	0.9158 (17°)	
$ClCH_2CH_2Si(C_6H_5)_3$	125				(198)
$[ClCH_2CH_2Si(OCH_3)_2]_2O$		133/3 mm.	1.4333 (25°)	1.189 (25°)	(61)
$[ClCH_2CH_2Si(OC_2H_5)_2]_2O$		135/1 mm.	1.4280 (25°)	1.091 (25°)	(61)
$[ClCH_2CH_2Si(OC_3H_7)_2]_2O$		181/7 mm.	1.4330 (25°)	1.045 (25°)	(61)
$ClCH_2CH_2Si(C_2H_5)_2OSi(C_2H_5)_3$		140/7 mm.			(236)
$(ClCH_2CH_2SiO_{1.5})_x$					(434)
$CHBrClCHBrSiCl_3$		132/10 mm.			(4)
x-Chloroethyls:					
$ClC_2H_4SiCl_3$					(253, 254)
$ClC_2H_4SiH_3$(?)		92			(172)
$ClC_2H_4Si(CH_3)Cl_2$					(253, 254)
$ClC_2H_4Si(C_2H_5)Cl_2$					(253)
$ClC_2H_4Si(C_2H_5)_3$					(156, 157, 158, 342)
$(ClC_2H_4)_2SiCl_2$					(254)
Polychloroethyls:					
$CH_3CCl_2SiCl_3$	112–114	152/734 mm.			(231, 239, *425*)
$CH_2ClCHClSiCl_3$		179	1.4876 (20°)	1.53 (27°)	(*4*, 231, 232, 236, 239, 265, 410, 425, *502*, 526)
		64/13 mm.			
$CH_2ClCHClSi(OC_2H_5)_3$		120/9 mm.	1.4308 (25°)	1.1130 (25°)	(502)
$CH_2ClCHClSi(CH_3)_3$	−15	61/14 mm.	1.4617 (20°)	1.0573 (20°)	(410, *425*)
$CHCl_2CH_2SiCl_3$		172/739 mm.			(425)
$Cl_2C_2H_3Si(C_2H_5)_3$					(158)
$CCl_2BrCHBrSiCl_3$		119/10 mm.	1.5595 (25°)		(2, 4, 527)
$Cl_3SiCCl_2CH_2SiCl_3$		101/4 mm.	1.5158 (20°)		(2, 4, 527)
$(CH_3O)_3SiCCl_2CH_2Si(OCH_3)_3$		121/1 mm.	1.4406 (22°)		(2, 4, 527)
$CH_2ClCCl_2SiCl_3$	56	79/10 mm.			(4)
$CHCl_2CCl_2SiCl_3$		104–106/17 mm.	1.5149 (27°)		(3)

$CCl_3CHClSiCl_3$		105/17 mm.	1.5149 (27°)		(2, 4, 527)
Unsaturated chloroethyls: see table 1					
Other chloro aliphatics:					
$CH_3CH_2CHClSiCl_3$		157/739 mm.			(9, 239, *431*)
$CH_3CHClCH_2SiCl_3$		162/729 mm.			(9, 72, 232, 236, 239, *431*, 434)
$CH_3CHClCH_2Si(CH_3)_3$		43–46/25 mm.	1.4280 (20°)	0.8738 (20°)	(359)
$CH_3CHClCH_2Si(C_2H_5)_3$					(360)
$Cl(CH_2)_3SiCl_3$		179/732 mm.			(9, 236, 239, 265, 318, *431*, 525)
$Cl(CH_2)_3Si(C_2H_5)Cl_2$					(525)
$Cl(CH_2)_3Si(CH_3)_3$					(401)
$CH_3CHClCHClSiCl_3$		84.5–86.5/17 mm.	1.45 (25°)		(9)
$CH_2ClCHClCH_2SiCl_3$		36/0.15 mm.	1.47 (25°)		(9)
$CH_2ClCHClCH_2Si(CH_3)_3$		36/4 mm.	1.4581 (20°)	1.030 (20°)	(446)
$(CH_3)_2CClSiCl_3$	109–110	151/atm.			(432)
$(CH_3)_2CClSi(CH_3)_3$	95–97				(425)
$ClCH_2CH(CH_3)SiCl_2$		164/atm.			(432)
$CH_2ClCHClCH_2Cl\text{–}RSi(OR')Cl$ (zinc coupled)					(128)
$CH_3CH_2CHClCH_2SiCl_3$					(232, 236)
$CH_3CHClCH_2CH_2SiCl_3$					(232, 236)
n-$C_4H_8ClSiCl_3$		104/25 mm.			(231)
$CH_3CHClCHClCH_2SiCl_3$		76–77/5 mm.	1.41 (28°)		(9)
$(CH_3)_2CClCH_2SiCl_3$					(236)
$(CH_3)_2CClCH_2Si(C_2H_5)_3$					(360)
$ClCH_2C(CH_3)_2SiCl_3$	47	180/739 mm.			(516)
$CH_2ClCH(SiCl_3)CH_2CHClSiCl_3$		120/2 mm.		1.57 (25°)	(526)
$o\text{-}\underbrace{CHClC_6H_4CHClSi}Cl_2$					(242)
$(CH_3)_2CClCH_2CH_2Si(CH_3)_3$		90/55 mm.	1.4338 (20°)	0.869 (20°)	(437)
$(C_5H_5Cl_2F_2)Si(CH_3)_2OC_2H_5$		220		1.159 (25°)	(174)
$[(C_5H_5Cl_2F_2)Si(CH_3)_2]_2O$	4	142/2 mm.		1.273 (25°)	(174)
$\underbrace{CH_2CH_2CH_2CHClCHClSi}Cl_2$					(242)
Cyclo-$C_6H_{10}ClSiCl_3$		110/6 mm.			(75, 231, 232, *236*, 239)
$C_6H_5CHClSiCl_3$		243/735 mm. 162/75 mm.			(448)
$C_6H_5CHClSi(CH_3)_3$		101/6 mm.	1.5132 (25°)	0.9980 (25°)	(240)
$(C_6H_5)_2CClSi(CH_3)_3$		151/3 mm.	1.5816 (20°)	1.0940 (20°)	(240)
$C_6H_5CHClCH_2SiCl_3$		134/2 mm.			(72)
$CH_2ClCH(ClC_6H_4)SiCl_3$					(72)
$CH_3CCl(ClC_5H_4)SiCl_3$					(72)
$CH_3CCl(Cl_2C_6H_3)CH_2SiCl_3$					(72)
$(Cl_2C_6H_3)CClCH_2SiCl_3$					(72)
$Cl_3SiCH_2CH_2C_6H_4CHClCH_2SiCl_3$					(234)
4-$CCl_3C_5H_4SiCl_3$	67.5–68				(175)
4-$ClC_2H_4C_6H_4SiCl_3$		127/7 mm.			(76)
$CH_2{=}CH_2$ --- $SiCl_4$ telomer					(393)

TABLE 3—*Continued*

Compound	Melting Point	Boiling Point	n_D	*d*	References
	°C.	*°C.*			
Monochlorophenyls:					
$2\text{-}ClC_6H_4SiCl_3$					(27)
$4\text{-}ClC_6H_4SiCl_3$		240.5-205.5/744 mm. 105/15 mm.			(102, 225, 549, 550, 551, 552)
$ClC_6H_4SiCl_3$		152/47 mm.		1.443 (26°)	(14, 21, 150, *328*)
$4\text{-}ClC_6H_4SiHCl_2$		106/20 mm.	1.5431 (20°)		(*12*, 18)
$3\text{-}ClC_6H_4Si(CH_3)Cl_2$		150/61 mm.			(*85*, 89)
$4\text{-}ClC_6H_4Si(CH_3)Cl_2$		62-63/1 mm.	1.5332 (25°)	1.2998 (26°)	(85, 89, *536*)
$ClC_6H_4Si(CH_3)Cl_2$		129/30 mm.			(*14*, 108, 127, 151, 328)
$ClC_6H_4Si(CH_3)(OC_2H_5)_2$					(108)
$ClC_6H_4Si(C_6H_5)Cl_2$		208–213.5/30 mm.			(*21*, 549, 550, 551)
$(4\text{-}ClC_6H_4)(CH_2{=}CH)SiCl_2$		86/1.7 mm.	1.5462 (25°)	1.201 (25°)	(160, *392*)
$(4\text{-}ClC_6H_4)(CH_2{=}CH)Si(OCOCH_3)_2$		132/0.4 mm.			(160, *161*)
$4\text{-}ClC_6H_4Si(i\text{-}C_3H_7)HCl$		135/30 mm.	1.5239 (20°)	1.115 (20°)	(13)
$(4\text{-}ClC_6H_4)(CH_2{=}CHCH_2)SiCl_2$		112/45 mm.	1.5442 (25°)	1.261 (25°)	(392)
$ClC_6H_4Si(C_6H_5)Cl_2$					(14)
$4\text{-}ClC_6H_4Si(CH_3)_2OC_2H_5$		61.5/1 mm.	1.4950 (25°)		(536)
$4\text{-}ClC_6H_4Si(C_6H_5)_2Cl$		150/0.3 mm.			(189)
$4\text{-}ClC_6H_4Si(C_6H_5)_2H$		162/1 mm.			(189)
$2\text{-}ClC_6H_4Si(CH_3)_3$		208/740 mm.	1.512 (25°)	1.0266 (25°)	(115, *116*)
$3\text{-}ClC_6H_4Si(CH_3)_3$	−43	207/740 mm. 105/24.5 mm.	1.5070 (25°)	0.9992 (25°)	(38, 115, *116*, *154*, *374*)
$4\text{-}ClC_6H_4Si(CH_3)_3$	0.5	207/740 mm. 120/50 mm.	1.5067 (25°) 1.5128 (20°)	0.9959 (25°) 1.0282 (20°)	(39, 40, *79*, 83, 102, 115, *116*, 193, 374)
$ClC_6H_4Si(CH_3)_3$					(103, 104, 115)
$4\text{-}ClC_6H_4Si(C_2H_5)_3$		262 137/15 mm.	1.5219 (9.6°)	1.0056 (9.6°) 0.9971 (18.5°)	(126, *225*)
$ClC_6H_4Si(C_2H_5)_3$		263		1.1085 (0°/0°)	(300)
$4\text{-}ClC_6H_4Si(C_3H_7)_3$		160/14 mm.	1.5123 (9°)	0.9708 (9°) 0.9663 (14°)	(225)
$4\text{-}ClC_6H_4Si(C_6H_5)_3$	157				(186, *196*)
$ClC_6H_3(SiCl_3)_2$		180.5–184/30 mm.			(21)
$ClC_6H_3[Si(CH_3)Cl_2]_2$					(14)
ClC_6H_4Si compounds					(30)
$(4\text{-}ClC_6H_4)_2SiCl_2$	71.2	364.5–367.5/744 mm. 234/36 mm.			(102, 552)

$(ClC_6H_4)_2SiCl_2$		224–227/30 mm.			(21)
$(4\text{-}ClC_6H_4)_2Si(CH_3)Cl$		187/5 mm.			(85)
$(4\text{-}ClC_6H_4)_2Si(CH_3)OH$					(185)
$(4\text{-}ClC_6H_4)_2Si(CH_3)_2$	47	334–336/740 mm. 168/0.5 mm.			(83, 102, 196)
$(4\text{-}ClC_6H_4)_2(ClCH_2)SiCH_3$		168/<1 mm.	1.6062 (20°)	1.349 (20°)	(196)
$(4\text{-}ClC_6H_4)_2Si(C_6H_5)_2$	131				(196)
$(4\text{-}ClC_5H_4)_3SiOH$	121				(*196*, 197)
$(4\text{-}ClC_6H_4)_3SiOC_2H_5$	128				(*196*, 197)
$(4\text{-}ClC_6H_4)_3SiH$	81				(*43*, 125)
$(4\text{-}ClC_6H_4)_3SiCH_3$	86	210/0.2 mm.			(43, *196*)
$(4\text{-}ClC_6H_4)_3SiCCl_3$	161				(196)
$(4\text{-}ClC_6H_4)_3SiC_6H_5$	134				(196)
$(4\text{-}ClC_6H_4)_3SiC_{12}H_{25}$			1.5679 (22°)	1.106 (22°)	(196)
$(4\text{-}ClC_6H_4)_4Si$	181				(196)
$[4\text{-}ClC_6H_4Si(CH_2)_2]_2O$		153/4 mm.	1.5327 (25°)	1.1175 (26°)	(536)
$[(4\text{-}ClC_5H_4)(CH_2{=}CH)SiOH]_2O$	122				(160, *161*, 255)
$[-Si(4\text{-}ClC_6H_4)(CH_3)O-]_3$	126				(85)
$[(4\text{-}ClC_6H_4)_2Si(CH_3)]_2O$	68–69	174–185/0.1 mm.			(185)
$[(4\text{-}ClC_6H_4)_2Si]_2O$	210				(196)
Chlorophenylsiloxanes					(18, 89, 102, 123, 124, 151, 177, 225, 251, 398, 536, 552)
Polychlorophenyls:					
$2,4\text{-}Cl_2C_6H_3SiCl_3$					(550)
$3,4\text{-}Cl_2C_6H_3Si(CH_3)Cl_2$		127–133/10 mm.			(89)
$(3,4\text{-}Cl_2C_6H_3)_2Si(CH_3)Cl$		249–250/10 mm.			(89)
$Cl_2C_6H_3SiCl_3$		155/27 mm.		1.537 (26°)	(21, 150, 328)
$Cl_2C_6H_3Si(CH_3)Cl_2$		150–160/29 mm.		1.410 (26°)	(14, *328*)
Dichlorophenylsiloxanes					(89, 151, 177, 251, 260, 536)
$Cl_3C_6H_2SiCl_3$	69–71	113/1 mm.			(150)
$(1,3,5\text{-}Cl_3C_6H_2)_2SiCl_2$					(264)
$(1,3,5\text{-}Cl_3C_6H_2)_2Si(OCH_2CH_2Cl)_2$					(264)
$1,3,5\text{-}Cl_3C_6H_2)_2Si(OCH_2CH_2Py\cdot Cl)_2$					(264)
$(Cl_3C_6H_2)_2SiCl_2$					(377)
$(Cl_3C_6H_2)_2Si(OH)_2$					(377)
$[-Si(Cl_3C_6H_2)_2O-]_x$					(377)
$Cl_4C_6HSi(CH_3)Cl_2$					(377)
$Cl_4C_6HSi(CH_3)(OH)_2$					(377)
$[-Si(Cl_4C_6H)(CH_3)O-]_x$					(377)

TABLE 3—*Concluded*

Compound	Melting Point	Boiling Point	n_D	d	References
	°C.	°C.			
Chlorophenylalkyls:					
2-$ClC_6H_4CH_2Si(CH_3)_3$		222–223/atm.	1.5128 (20°)		(140)
3-$ClC_6H_4CH_2Si(CH_3)_3$		228–229/atm.	1.5108 (20°)		(140)
4-$ClC_6H_4CH_2Si(CH_3)_3$		231–232/atm.	1.5154 (12°)		(140)
$CH_3CH(ClC_6H_4)SiCl_3$		127/2 mm.			(72, 232, 236)
$CH_3CH(Cl_2C_6H_3)SiCl_3$		150–155/1 mm.			(74)
$CH_3CCl(ClC_6H_4)SiCl_3$					(72)
$CH_2ClCH(ClC_6H_4)SiCl_3$					(72)
$CH_3CCl(Cl_2C_5H_3)CH_2SiCl_3$					(72)
$(ClC_5H_4)CH_2CH_2SiCl_3$		119/1 mm.			(232, *236*)
$(Cl_2C_6H_3)CH_2CH_2SiCl_3$		137/2 mm.			(72)
$(Cl_2C_6H_3)CClCH_2SiCl_3$					(72)
$CH_2(C_6H_4Cl)CH(C_6H_4Cl)SiCl_3$		200/1 mm.			(232, 236)
$(Cl_3C_6H_2)C_2H_4SiCl_3$		167/2 mm.			(236)
$CH_3CH(Cl_2C_6H_3)CH_2SiCl_2$		144/1 mm.			(72, 232, 236)
$(Cl_2C_6H_3)CH_2CH_2CH_2SiCl_3$		137/2 mm.			(232, 236)
$(Cl_3SiCH_2CH_2)_2C_5H_3Cl$		194/1 mm.			(232, 235)
Chlorobiphenyls:					
$ClC_{12}H_8SiCl_3$					(21)
$ClC_{12}H_8Si(CH_3)Cl_2$					(14)
$Cl_4C_{12}H_5SiCl_3$					(*149*, 150)
$Cl_5C_{12}H_3SiCl_3$					(*149*, 150)
$Cl_7C_{12}H_2SiCl_3$					(*149*, 150, 151)

The photochemical chlorination of $(CH_3)_3SiOSi(CH_3)_3$ soon results in the separation of a saturated aqueous hydrogen chloride phase because of cleavage of siloxane bonds with by-product hydrogen chloride (294); nevertheless, when the chlorination is continued and the product is thoroughly washed, a 58 per cent yield of $ClCH_2Si(CH_3)_2OSi(CH_3)_3$ is obtained (52). This product is formed in somewhat higher yield with a continuous recycle process (455).

Photochemical chlorination of compounds containing both methyl and phenyl groups gives only products of methyl group chlorination. $CCl_3Si(C_6H_4Cl\text{-}4)_3$ is obtained in 22 per cent yield from $CH_3Si(C_6H_4Cl\text{-}4)_3$, and $CCl_3Si(C_6H_5)_3$ is similarly prepared (196). The photochemical chlorination of $4\text{-}CH_3C_6H_4SiCl_3$ gives $4\text{-}CCl_3C_6H_4SiCl_3$ (175).

2. Other syntheses

Chlorination with sulfuryl chloride in the presence of benzoyl peroxide is applicable to methyl silicon compounds only with difficulty. Refluxing $(CH_3)_3SiCl$ with this reagent gives no reaction in several hours; however, adding sulfuryl chloride to $(CH_3)_3SiCl$ and benzoyl peroxide in refluxing chlorobenzene gives a 52 per cent yield of $ClCH_2Si(CH_3)_2Cl$ and 59 per cent of unreacted starting material (322). With CH_3SiCl_3 even a higher boiling solvent such as *o*-dichlorobenzene is of little avail, and only a 3 per cent yield of $ClCH_2SiCl_3$ is obtained (503). In contrast with the foregoing results $C_6H_5CH_2SiCl_3$, $C_6H_5CH_2Si(CH_3)_3$, and $(C_6H_5)_2CHSi(CH_3)_3$ react quite satisfactorily with refluxing sulfuryl chloride in the presence of benzoyl peroxide to give $C_6H_5CHClSiCl_3$ (448), $ClCH(C_6H_5)Si(CH_3)_3$ (240), and $ClC(C_6H_5)_2Si(CH_3)_3$ (240) in good yield.

The reaction of diazomethane with silicon halides under certain conditions is a very interesting method of synthesis because it gives $ClCH_2$-substituted derivatives exclusively.

$$CH_2N_2 \quad + \quad SiCl_4 \quad \xrightarrow{-50^\circ C.} \quad ClCH_2SiCl_3 \quad + \quad N_2$$

The vigorous reaction of diazomethane with silicon tetrachloride at room temperature gives only polymethylene. However at −50°C. in ether, 40–80 per cent yields of chloromethyl silicon compounds are obtained. CH_3SiCl_3 and $(CH_3)_2SiCl_2$ react more slowly than silicon tetrachloride and the chloromethyl silicon halides. Copper bronze and anhydrous copper sulfate, which catalyze the decomposition of diazomethane at low temperatures, accelerate the rate of formation of halomethyl silicon halides ten to fifteen times. Among the compounds prepared by this reaction are $ClCH_2SiCl_3$, $(ClCH_2)_2SiCl_2$, $(ClCH_2)_3SiCl$, and $ClCH_2Si(CH_3)Cl_2$. Diazoethane gives $CH_3CHClSiCl_3$ (546, 547).

Another reaction from which chloromethyl silicon compounds are obtained involves the irradiation of ferric chloride in methylpolysiloxane solution. This is of interest less from the synthetic point of view than from the bearing that it

$$(CH_3)_3SiOSi(CH_3)_3 \quad + \quad FeCl_3 \quad \xrightarrow{\text{light}} \quad ClCH_2Si(CH_3)_2OSi(CH_3)_3 \quad + \quad HCl \quad + \quad FeCl_2$$

might have on the ferric chloride polymerization of methylpolysiloxanes. A solution of anhydrous ferric chloride in hexamethyldisiloxane gives no reaction in the dark, but under ultraviolet irradiation the yellow color is discharged with formation of a white precipitate, presumably ferrous chloride, together with $ClCH_2Si(CH_3)_2OSi(CH_3)_3$, $(CH_3)_3SiCl$, and HCl. These products apparently arise through chlorination of a methyl group with formation of hydrogen chloride, which cleaves siloxane bonds to form $(CH_3)_3SiCl$ (142).

B. PROPERTIES OF CHLOROMETHYL DERIVATIVES

1. *Halogen replacement reactions*

Halogen replacement reactions are by far the most important ones which chloromethyl silicon compounds undergo. Such reactions are frequently in competition with chloromethyl group cleavages, about which more will be said later. But in the main it is carbon–halogen replacements which prevail and which make the haloalkyl derivatives very versatile intermediates for making other carbon-functional compounds.

Chloromethyl silicon compounds readily form Grignard and organolithium derivatives. These undergo the normal reactions of such compounds and therefore expand manyfold the synthetic potentialities of the parent halides. Under the usual conditions $ClCH_2Si(CH_3)_3$ forms good yields of $ClMgCH_2Si(CH_3)_3$ (538) and of $LiCH_2Si(CH_3)_3$ (441). $ClCH(C_6H_5)Si(CH_3)_3$ also readily forms a Grignard reagent, but $ClC(C_6H_5)_2Si(CH_3)_3$ does not (240). Even $ClCH_2Si(CH_3)_2OSi(CH_3)_3$ (383) and $ClCH_2\underline{Si(CH_3)[OSi(CH_3)_2]_3O}$ (370b) give the corresponding Grignard reagents without difficulty.

Sodium derivatives of chloromethyl silicon compounds are probably involved in the sodium coupling of such compounds with silicon halides to give derivatives having silicon atoms bridged by methylene groups. A wide variety of such silmethylene compounds, both monomeric and polymeric, have been prepared in this way. In a typical reaction 2 moles each of $(CH_3)_3SiCl$ and $ClCH_2Si(CH_3)_2OC_2H_5$ are added to 4 moles of molten sodium in refluxing toluene with vigorous stirring, and a 79 per cent yield of $(CH_3)_3SiCH_2Si(CH_3)_2OC_2H_5$ is obtained. The self-condensation of $ClCH_2Si(CH_3)_2Cl$ type compounds with molten sodium takes place very readily, so that the use of ethoxy derivatives is an important control measure in getting the types of compounds desired. Chloromethyl silicon compounds can be made to couple with ethoxysilanes by means of molten sodium, but the reaction is much more sluggish than with chlorosilanes (222).

Dehalogenations of $(ClCH_2)_2Si(CH_3)_2$ with metals do not produce a silacyclopropane derivative. Thus, heating $(ClCH_2)_2Si(CH_3)_2$ with magnesium in xylene and in butyl ether gives no ring closure (373). Refluxing $(ClCH_2)_2Si(CH_3)_2$ with zinc in ethanol in the presence of sodium carbonate and sodium iodide results only in reduction to $ClCH_2Si(CH_3)_3$ in 55 per cent yield (373).

Chloromethylsilicon compounds undergo the Williamson reaction with sodium alkoxides in refluxing alcohols. $ClCH_2Si(CH_3)_3$ gives the corresponding methyl,

ethyl, and *n*-butyl ethers:

$$ClCH_2Si(CH_3)_3 + NaOC_2H_5\text{–}C_2H_5OH \rightarrow C_2H_5OCH_2Si(CH_3)_3$$

the yields decrease from over 70 per cent to about 30 per cent as the alkyl group becomes larger, presumably because of increased silicon–carbon cleavage possibly arising from the higher reflux temperatures (451). $ClCH_2Si(CH_3)_2OSi(CH_3)_3$ with refluxing 2 *M* sodium ethoxide in ethanol for 2 hr. gives 91 per cent reaction, while $ClCH_2Si(CH_3)_3$ gives only 36 per cent reaction; however, the former includes 32 per cent silicon–carbon cleavage, while the latter includes less than 2 per cent (383). With the same reagent for 4 hr. $ClCH_2Si(CH_3)_3$ gives 67 per cent reaction, including less than 8 per cent cleavage, and $C_2H_5OCH_2Si(CH_3)_3$ is isolated (383). In a comparison of the reactivities of $ClCH_2Si(CH_3)_3$ and *n*-hexyl chloride with sodium ethoxide in ethanol, the former reacts to the extent of 40 per cent while the latter reacts completely in 4 hr. or less (538).

$ClCH_2Si(CH_3)_3$, $ClCH_2Si(CH_3)_2OSi(CH_3)_3$, and $ClCH_2Si(CH_3)[OSi(CH_3)_2]_3O$ give the corresponding mercaptans with sodium hydrosulfide in refluxing ethanol (119). This normal reaction contrasts with the extensive silicon–carbon cleavage observed with potassium hydroxide in aqueous alcohols (294). Other reactions in which little silicon–carbon cleavage is observed with the three chlorides above are their conversion to sulfides with sodium mercaptides (121) and their conversion to thiocyanates with sodium thiocyanate in refluxing ethanol (120).

$$(CH_3)_3SiOSi(CH_3)_2CH_2Cl + NaSH \rightarrow (CH_3)_3SiOSi(CH_3)_2CH_2SH$$

With potassium acetate in refluxing glacial acetic acid chloromethyl silicon compounds readily undergo chlorine replacement to form the corresponding acetoxy derivatives. The reaction usually goes essentially without silicon–carbon cleavage; however, in the case of siloxanes rearrangement of the siloxane bonds does occur. $CH_3COOCH_2Si(CH_3)_3$ (482) and $(CH_3COOCH_2)_2Si(CH_3)_2$ (481) are obtained from the corresponding chlorides in 80–90 per cent yields with potassium acetate in glacial acetic acid at 150–190°C.; $Cl_2CHSi(CH_3)_3$ also reacts at 200°C., but the product gives formaldehyde on being washed with water (481). Under similar conditions siloxane rearrangement occurs with $ClCH_2Si(CH_3)_2OSi(CH_3)_3$, so that both $CH_3COOCH_2Si(CH_3)_2OSi(CH_3)_3$ and $[CH_3COOCH_2Si(CH_3)_2]_2O$ are obtained; likewise, $ClCH_2\underline{Si(CH_3)[OSi(CH_3]_3O}$ gives polymeric acetoxymethyl methylpolysiloxanes (461, 483). With refluxing 1 *M* potassium acetate in glacial acetic acid for about 2 hr., $ClCH_2Si(CH_3)_3$ gives only 2 per cent reaction while $ClCH_2Si(CH_3)_2OSi(CH_3)_3$ gives 76 per cent reaction; no silicon–carbon cleavage occurs, but the latter compound may undergo siloxane rearrangement (383). With refluxing potassium acetate in glacial acetic acid for 4 hr. $ClCH_2Si(CH_3)_3$ and *n*-hexyl chloride react to the extent of 26 per cent and 32 per cent, respectively (538).

$$ClCH_2Si(CH_3)_3 + CH_3COOK\text{–}CH_3COOH \rightarrow CH_3COOCH_2Si(CH_3)_3$$

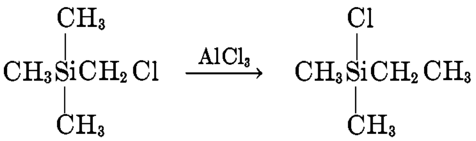
The most clean-cut reaction exhibited by chloromethyl silicon compounds is their conversion to iodides with sodium iodide in refluxing acetone. High yields of the iodides are obtained from $ClCH_2Si(CH_3)_3$ (538), $(ClCH_2)_2Si(CH_3)_2$ (373), $ClCH_2Si(CH_3)_2CH_2Si(CH_3)_3$ (433), and $ClCH_2Si(CH_3)_2OSi(CH_3)_3$ (383). Because this reaction brings about replacement of chlorine by iodine without silicon–carbon cleavage or siloxane rearrangement it is well suited for detailed kinetic study (122). Second-order rate constants for the reaction of potassium iodide in acetone with $ClCH_2Si(CH_3)_3$, $ClCH_2Si(CH_3)_2OSi(CH_3)_3$, $ClCH_2\underbrace{Si(CH_3)[OSi(CH_3)_2]_3O}$, and *n*-butyl chloride at 20°, 30°, and 40°C. have been determined, and energies and entropies of reaction have been calculated. The silicon atom strongly activates the adjacent carbon in this reaction; $ClCH_2Si(CH_3)_3$ reacts twenty to thirty times faster than *n*-butyl chloride. The replacement of methyl groups attached to silicon by oxygen causes a slight decrease in the rate of reaction; thus $ClCH_2Si(CH_3)_2OSi(CH_3)_3$ reacts 50 per cent more slowly and $ClCH_2\underbrace{Si(CH_3)[OSi(CH_3)_2]_3O}$ another 50 per cent more slowly than $ClCH_2Si(CH_3)_3$ (122).

Chloromethyl silicon compounds behave very satisfactorily in malonic ester syntheses. $ClCH_2Si(CH_3)_3$ and $ClCH_2Si(CH_3)_2C_6H_5$ react smoothly with ethyl sodiomalonate; the 60–70 per cent yields of substituted malonates compare favorably with those from alkyl halides and suggest that no significant amount of silicon–carbon cleavage occurs (433). $ClCH_2Si(CH_3)_2OSi(CH_3)_3$ in the malonic ester synthesis gives a low yield of $[HOOCCH_2CH_2Si(CH_3)_2]_2O$ without isolation of the intermediate malonate (407).

Another chlorine replacement shown by chloromethyl silicon compounds is found in their reaction with anhydrous ammonia and organic amines. Thus, $ClCH_2Si(CH_3)_3$, $ClCH_2Si(CH_3)_2OC_2H_5$, $ClCH_2Si(CH_3)(OC_2H_5)_2$, and $ClCH_2Si(OC_2H_5)_3$ give the corresponding amines in good yield (344). Under proper conditions $ClCH_2Si(CH_3)_2OSi(CH_3)_3$ and $ClCH_2\underbrace{Si(CH_3)[OSi(CH_3)_2]_3O}$ are also converted to the corresponding aminomethyl silicon compounds with little difficulty from silicon–carbon cleavage and siloxane rearrangement (181). In a related reaction $ClCH_2Si(CH_3)_3$ couples satisfactorily with potassium phthalimide (445).

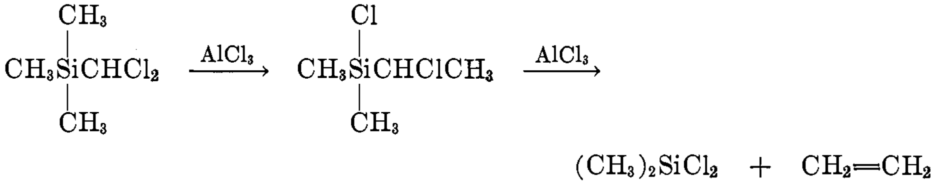
The chlorine replacement reactions thus far considered have involved nucleophilic reagents. Now let us turn to electrophilic reagents. Reactions with silver nitrate in ethanol fall into this category; they have been studied only on a qualitative basis, and no effort to isolate organic products has been made. $ClCH_2Si(CH_3)_3$ is inert toward this reagent, while *n*-hexyl chloride is attacked (538). It will be recalled that with nucleophilic reagents the reverse is true, since $ClCH_2Si(CH_3)_3$ is more reactive than its carbon analog toward sodium ethoxide in ethanol, potassium acetate in glacial acetic acid, and sodium iodide in acetone (538). $ClCH(C_6H_5)Si(CH_3)_3$ and $ClC(C_6H_5)_2Si(CH_3)_3$ give immediate precipitates with silver nitrate in ethanol at room temperature (240). Like $ClCH_2Si(CH_3)_3$, $ClCH_2Si(CH_3)_2OSi(CH_3)_3$ is inert toward silver nitrate in boiling ethanol for 5 min. (383).

While $ClCH_2Si(CH_3)_3$ is inert toward alcoholic silver nitrate, with another electrophilic reagent, anhydrous aluminum chloride, it undergoes a profound change formally analogous to the well-known neopentyl rearrangement. When $ClCH_2Si(CH_3)_3$ is warmed with a little anhydrous aluminum chloride a vigorous reaction takes place with formation of $(CH_3)_2(C_2H_5)SiCl$ by intramolecular rearrangement (539).



$$\mathrm{CH_3\overset{CH_3}{\underset{CH_3}{Si}}CH_2Cl \xrightarrow{AlCl_3} CH_3\overset{Cl}{\underset{CH_3}{Si}}CH_2CH_3}$$

$ClCH_2Si(CH_3)_2Cl$ and $Cl_2CHSi(CH_3)_2Cl$ are unaffected by refluxing for several hours with anhydrous aluminum chloride (426). Under similar conditions $ClCH(C_6H_5)Si(CH_3)_3$ reacts vigorously, with the formation of carbonized products (240). When $Cl_2CHSi(CH_3)_3$ is added to a little anhydrous aluminum chloride, a violent reaction gives rise to a 76 per cent yield of ethylene and an 88 per cent yield of $(CH_3)_2SiCl_2$ (426). Apparently the starting material rearranges intramolecularly to $CH_3CHClSi(CH_3)_2Cl$, which then undergoes hydrogen migration and elimination of ethylene to form $(CH_3)_2SiCl_2$.



$$\mathrm{CH_3\overset{CH_3}{\underset{CH_3}{Si}}CHCl_2 \xrightarrow{AlCl_3} CH_3\overset{Cl}{\underset{CH_3}{Si}}CHClCH_3 \xrightarrow{AlCl_3} (CH_3)_2SiCl_2 + CH_2{=}CH_2}$$

Indeed, such a reaction has been demonstrated with $CH_3CHClSi(CH_3)_2Cl$ and with $CH_3CHClSi(C_2H_5)_2Cl$ (426). Other α-chloroethyl compounds also undergo the cleavage reaction, but some also give rearrangement products. For example, $CH_3CHClSi(CH_3)_3$ gives a 15 per cent yield of $(CH_3)_2CHSi(CH_3)_2Cl$ together with 55 per cent yields of ethylene and $(CH_3)_3SiCl$ (426). Similarly, $CH_3CHClSi(C_2H_5)_3$ gives a 42 per cent yield of $CH_3(C_2H_5)CHSi(C_2H_5)_2Cl$, together with 20–35 per cent yields of cleavage products (426). A rearrangement analogous to those above is found in the conversion of $CH_2{=}C(CH_3)Si(CH_3)_3$ to $(CH_3)_3CSi(CH_3)_2OH$ with concentrated sulfuric acid (432).

2. Chloromethyl group cleavage reactions

The chlorine replacement reactions previously discussed compete with chloromethyl group cleavage, a side reaction involving removal of the carbon-functional group through scission of the silicon–carbon bond. It is important to know more about this type of reaction, because it imposes serious limitations on the chlorine replacements which can be carried out. In this section will be considered reactions in which cleavage of the chlorinated methyl groups is essentially complete.

In general, cleavage is favored with strong bases, particularly those with small anions such as OH^- and NH_2^-. Cleavage is also favored by an increasing number of chlorine atoms on the carbon and by an increasing number of negative substituents on the silicon. The picture is obscured in many cases by the fact that it is unknown whether the cleavage occurs in the chloromethyl silicon compound starting material or in a replacement product.

All chlorinated methyl silicones undergo silicon–carbon cleavage to form chloromethanes and siloxanes with boiling aqueous alcoholic caustic (294); the reaction is of considerable value in distinguishing polychlorinated isomers

$$(ClCH_2)_2Si(CH_3)_2 \ + \ \text{alc. KOH} \xrightarrow{\text{heat}} CH_3Cl \ + \ [(CH_3)_2SiO]_x$$

$$Cl_2CHSi(CH_3)_3 \ + \ \text{alc. KOH} \xrightarrow{\text{heat}} CH_2Cl_2 \ + \ [(CH_3)_3Si]_2O$$

(293). When $ClCH_2Si(CH_3)_3$ and $ClCH_2Si(CH_3)_2OSi(CH_3)_3$ are refluxed with potassium hydroxide in moist butanol, both give about 80 per cent reaction; however, the latter gives a great deal more silicon–carbon cleavage than the former (383). Some materials require no caustic; CCl_3SiCl_3 gives chloroform with distilled water and with 6 *N* hydrochloric acid (182). While CCl_3SiCl_3 with boiling absolute ethanol in benzene gives a good yield of $CCl_3Si(OC_2H_5)_3$, this compound is cleaved to ethyl silicate and ethyl orthoformate with sodium ethoxide in ethanol (503). $CCl_3Si(C_6H_4Cl\text{-}4)_3$ is unaffected by 15 min. boiling in water and in 30 per cent hydrochloric acid; however, it undergoes silicon–carbon cleavage with formation of $[(4\text{-}ClC_6H_4)_3Si]_2O$ upon being warmed for 10 min. in 50 per cent aqueous sodium hydroxide (196).

Silicon–carbon cleavage in chloromethyl silicon compounds is observed with a number of other reagents. With refluxing aqueous ethanolic sodium cyanide $ClCH_2\underline{Si(CH_3)[OSi(CH_3)_2]_3O}$ gives a cross-linked polymer (294). With sodium amide in liquid ammonia only silicon–carbon cleavage products are obtained from $ClCH_2Si(CH_3)_3$ (344) and from $ClCH(C_6H_5)Si(CH_3)_3$ (240). With sodium ethoxide in ethanol $Cl_2CHSi(CH_3)_3$ gives a 70 per cent yield of methylene chloride (481); this result provides an interesting contrast with that from $ClCH_2Si(CH_3)_3$, which gives a 70 per cent yield of $C_2H_5OCH_2Si(CH_3)_3$ (451). With both butyllithium and phenyllithium in ether $CCl_3Si(C_6H_5)_3$ gives only low yields of the silicon–carbon cleavage products, $C_4H_9Si(C_6H_5)_3$ and $(C_6H_5)_4Si$ (186). $ClCH_2Si(CH_3)_3$ and $ClCH(C_6H_5)Si(CH_3)_3$ do not react with silver cyanide in refluxing ether (240).

3. Silicon-functional reactions

The silicon-functional reactions of chloromethyl silicon compounds include the coupling of silicon chlorides with organometallic reagents, the hydrolysis and alcoholysis of silicon chlorides, the rearrangement of chloromethylsiloxanes, and silicon–methyl cleavage in $ClCH_2Si(CH_3)_3$.

In couplings with organometallic compounds chloromethyl silicon chlorides behave very much like unsubstituted organosilicon chlorides. Thus, $ClCH_2Si(CH_3)_2Cl$ (539) as well as $Cl_2CHSi(CH_3)_2Cl$ and $(ClCH_2)_2Si(CH_3)Cl$ (481) couple smoothly with methylmagnesium bromide, giving $ClCH_2Si(CH_3)_3$,

$Cl_2CHSi(CH_3)_3$, and $(ClCH_2)_2Si(CH_3)_2$, respectively. The chloromethyl silicon chlorides also react satisfactorily with phenylmagnesium bromide (433) and with trifluoromethylmagnesium bromide (284).

The alcoholysis of halomethyl silicon chlorides gives the corresponding silicon alkoxides in a straightforward manner. Even CCl_3SiCl_3 gives a 64 per cent yield of $CCl_3Si(OC_2H_5)_3$ upon being refluxed with ethanol in benzene (503). Chloromethylethoxysilanes are of value because the ethoxy group, though hydrolyzable, is comparatively inert toward reagents with which the corresponding silicon chloride is quite reactive. Examples of the use of ethoxy groups as a control measure during carbon-functional reactions may be found in the sodium condensation of $ClCH_2Si(CH_3)_2OC_2H_5$ with $(CH_3)_3SiCl$ to form $(CH_3)_3SiCH_2Si(CH_3)_2OC_2H_5$ (222) and in the amination of $ClCH_2Si(CH_3)(OC_2H_5)_2$ to $NH_2CH_2Si(CH_3)(OC_2H_5)_2$ (344).

Hydrolysis of chloromethyl silicon chlorides is an important reaction because it leads to chloromethylpolysiloxanes. The reaction may be carried out with $ClCH_2$— and Cl_2CH— derivatives, but CCl_3SiCl_3 gives chloroform (182). It is difficult to generalize regarding the cleavage of such groups, because scission is dependent on the other substituents attached to silicon and complete data are unavailable. Hydrolysis of $ClCH_2Si(CH_3)_2Cl$ gives $[ClCH_2Si(CH_3)_2]_2O$, while its cohydrolysis with $(CH_3)_3SiCl$ gives $ClCH_2Si(CH_3)_2OSi(CH_3)_3$ (293). Hydrolysis of $Cl_2CHSi(CH_3)_2Cl$ with ice water gives $Cl_2CHSi(CH_3)_2OH$ and $[Cl_2CHSi(CH_3)_2]_2O$ without appreciable silicon–carbon cleavage; the silanol is thought to be unusually stable toward intermolecular dehydration (294).

The polymerization of chloromethylpolysiloxanes through siloxane rearrangement has been studied only with materials containing monochloromethyl substituents; these exhibit no unusual behavior. Polymerization is carried out with ferric chloride and with concentrated sulfuric acid (144). With the latter the equilibration of $ClCH_2Si(CH_3)_2OSi(CH_3)_3$ and methyl polysiloxanes occurs at room temperature without silicon–carbon cleavage (383). Members of the series

$$ClCH_2Si(CH_3)_2O[\text{—}Si(CH_3)_2O\text{—}]_xSi(CH_3)_2CH_2Cl$$

$$(CH_3)_3SiO[\text{—}Si(CH_3)CH_2ClO\text{—}]_xSi(CH_3)_3$$

and

$$ClCH_2Si(CH_3)_2O[\text{—}Si(CH_3)CH_2ClO\text{—}]_xSi(CH_3)_2CH_2Cl$$

are obtained upon refluxing appropriate chlorosilanes in aqueous ethanol (453).

The final type of reaction in which chloromethyl compounds participate without direct involvement of the carbon-functional group is the selective cleavage of a methyl group with warm concentrated sulfuric acid to form methane. Only one instance with a chloromethyl compound is known. $ClCH_2Si(CH_3)_3$

$$ClCH_2Si(CH_3)_3 \xrightarrow[\text{heat}]{H_2SO_4} CH_4 + ClCH_2Si(CH_3)_2OSO_3H \xrightarrow{H_2O} [ClCH_2Si(CH_3)_2]_2O$$

is completely unaffected by concentrated sulfuric acid at room temperature (383), but upon warming to 70–100°C. the organic material goes into solution with formation of 1 mole of methane. Dilution of the sulfuric acid solution gives an 80 per cent yield of $[ClCH_2Si(CH_3)_2]_2O$ (429).

4. *Other properties*

Dipole moments have been determined for $ClCH_2Si(CH_3)_3$ and $Cl_2CHSi(CH_3)_3$ (153), for $ClCH_2Si(CH_3)_2C_6H_5$ and $(ClCH_2)_2Si(CH_3)_2$ (154), and for $ClCH_2Si(CH_3)_2OC_2H_5$ (155). An electron diffraction study of $ClCH_2Si(CH_3)_3$ has been reported (229). The surface and lubricating properties of

$$ClCH_2Si(CH_3)_2O[\text{—}Si(CH_3)_2O\text{—}]_xSi(CH_3)_2CH_2Cl$$

have been studied (341).

C. SYNTHESES OF HIGHER CHLOROALKYL COMPOUNDS

1. *Direct chlorination*

Since the first carbon-functional silicon compound was a chloroethyl derivative made by direct chlorination, this subject will be approached historically. Soon after they synthesized the first organosilicon compound, tetraethylsilane, Friedel and Crafts undertook a study of its chlorination, which they first reported in 1865. They were gratified to find (156, 157) that tetraethylsilane formed chlorine substitution products instead of undergoing cleavage of organic groups, as has been reported for certain organometallic compounds. The concern of these earliest workers for the possibility of silicon–carbon cleavage showed a prophetic understanding of the most formidable problem that was to tax the ingenuity of chemists working with carbon-functional silicones.

Friedel and Crafts isolated from their chlorination product a monochloro compound (apparently the alpha isomer), which was converted to the acetate and thence to the alcohol (157, 158); this work was successfully repeated (342). Friedel and Crafts also isolated a dichloro derivative of tetraethylsilane. They demonstrated that both chlorines were in the same ethyl group, because heating with potassium acetate in glacial acetic acid gave hexaethyldisiloxane and unsaturated gases (158). This is the first example of cleavage of a carbon-functional group. The degree to which the Friedel and Crafts papers nearly a century ago anticipated the broad outlines of carbon-functional silicone chemistry to come is indeed remarkable.

The chlorination of tetraethylsilane was reinvestigated by Ushakov and Itenberg, who carried out the reaction in the presence of phosphorus pentachloride (519). They obtained two monochloro derivatives boiling about 10° apart at 9 mm. pressure. The lower boiling of these was unreactive toward boiling alcoholic sodium hydroxide, while the other isomer reacted completely at room temperature in less than an hour. The lower boiling isomer gave $CH_2{=}CH\text{-}Si(C_2H_5)_3$ with alcoholic sodium hydroxide at 145°C. Ushakov and Itenberg correctly postulated (for reasons that do not now seem valid) that the lower boiling isomer was the alpha isomer and the other the beta isomer. This work was repeated and the yield of the higher boiling isomer was 19 per cent (428).

As will subsequently be seen, many other chloroethyl silicon compounds were later prepared, and the assignment of isomeric configuration was made on plausible (but not unequivocal) grounds, as for example in reference 448. It was not until recently that indisputable confirmation of the assigned structures was reported by Larsson. Reaction of the lower boiling chloroethyltriethylsilane with alkaline aqueous $HSCH_2COOH$, followed by acidification, gave $HOOCCH_2SC_2H_4Si(C_2H_5)_3$. Partial resolution of the alkaloid salts of this acid into optically active isomers established that it contained an asymmetric carbon atom and that it was therefore the alpha isomer (304). The structure of the supposed $CH_3CHClSi(C_2H_5)_2Cl$ (427) was also confirmed by conversion to $CH_3CHClSi(C_2H_5)_3$, which was then carried through the above reaction sequence (304).

In spite of the early interest in direct chlorination it has been very little used with aliphatic silicon compounds (except for the methyl derivatives), because a more convenient laboratory method is available (448); this is discussed below. Direct chlorination has, however, been used for substitution in the aliphatic side-chains of aromatic groups bound to silicon. By photochemical chlorination $C_2H_5C_6H_4SiCl_3$ is converted to chloroethyl derivatives (76) and 4-$CH_3C_6H_4SiCl_3$ is converted to 4-$CCl_3C_6H_4SiCl_3$ in good yield (175).

2. Chlorination with sulfuryl chloride

A convenient method for the chlorination of aliphatic compounds in general involves refluxing them with sulfuryl chloride in the presence of benzoyl peroxide. This method is applicable to aliphatic silicon compounds (448). It is of limited utility with methyl derivatives (322, 503), but it goes satisfactorily with benzyl compounds. Its most extensive use has been with ethyl and higher alkyl silicon compounds. Refluxing $C_2H_5SiCl_3$ with sulfuryl chloride in the presence of benzoyl peroxide gives a 90 per cent yield of monochlorinated products containing 2.5

$$CH_3CH_2SiCl_3 + SO_2Cl_2 \xrightarrow{(C_6H_5CO)_2O_2} ClCH_2CH_2SiCl_3 + CH_3CHClSiCl_3 + SO_2 + HCl$$

moles of $ClCH_2CH_2SiCl_3$ for each mole of $CH_3CHClSiCl_3$ (448). The deactivation of the alpha carbon is due to the silicon–chlorine bonds and not to silicon alone, because in $(C_2H_5)_4Si$ alpha chlorination predominates (304, 428). The decrease in the deactivation of the alpha carbon parallels the replacement of chlorine atoms with ethyl groups. $(C_2H_5)_2SiCl_2$ gives a 40 per cent yield of monochlorinated product containing 40 per cent alpha isomer and 60 per cent beta isomer (425). Both $(C_2H_5)_3SiCl$ and $(C_2H_5)_3SiF$ give about 60 per cent yields of monochlorinated products containing about equal amounts of the alpha and beta isomers (427).

In the sulfuryl chloride chlorination of higher alkyl groups the deactivation of the alpha carbon is also observed. $C_3H_7SiCl_3$ gives a 90 per cent yield of monochlorinated product in which the alpha, beta, and gamma isomers are found in the ratio 1:3.5:3.1 (431). $(CH_3)_2CHSiCl_3$ gives a 9 per cent yield of the alpha and a 32 per cent yield of the beta monochloro isomers (432). $(CH_3)_3CSiCl_3$ gives a 40 per cent yield of the only possible monochloro derivative (516).

The dichlorination products obtained with sulfuryl chloride in the presence of benzoyl peroxide have been studied to only a limited extent. $ClCH_2CH_2SiCl_3$ gives a 70 per cent yield of $CHCl_2CH_2SiCl_3$, while $CH_3CHClSiCl_3$ gives 30 per cent yields of $CH_3CCl_2SiCl_3$ and $CH_2ClCHClSiCl_3$ (425).

The difference in the rates of chlorination of methyl and ethyl groups by sulfuryl chloride can apparently be used to attain a selective chlorination of the ethyl group. It has been stated that refluxing $(CH_3)(C_2H_5)SiCl_2$ with sulfuryl chloride in the presence of benzoyl peroxide gives monochlorides of the ethyl group without chlorination of the methyl group (253).

3. Other syntheses

The reaction of chlorine with vinyl silicon compounds is useful for preparing vicinal dichloroalkyl derivatives and is of special interest because of the commercial availability of vinyltrichlorosilane. Bubbling chlorine into $CH_2{=}CHSiCl_3$ in the cold either with or without sunlight gives a 65–75 per cent yield of $CH_2ClCHClSiCl_3$ (4, 502). Liquid-phase chlorination of $CH_2{=}CHSiCl_3$ at reflux temperature also gives the adduct in good yield, but considerable bis(trichlorosilyl)dichlorobutane is also formed; this can be suppressed by using silicon tetrachloride as a diluent (526). Vapor-phase chlorination of $CH_2{=}CHSiCl_3$ at 100–250°C. also gives the adduct, but at 200–350°C. it gives $CH_2{=}CClSiCl_3$, apparently by substitution because $CH_2ClCHClSiCl_3$ is not dehydrohalogenated even at 400°C. (526). Chlorination of $CH_2{=}CHSi(CH_3)_3$ at -80°C. gives a 55 per cent yield of $CH_2ClCHClSi(CH_3)_3$; considerable substitution may also occur because hydrogen chloride is evolved as the crude reaction product is warmed to room temperature (425, 446). Chlorination of $CH_2{=}CClSiCl_3$ in sunlight gives a 73 per cent yield of $CH_2ClCCl_2SiCl_3$ (4). Chlorine also adds to $CCl_2{=}CHSiCl_3$ in sunlight (2).

Another synthesis for higher chloroalkyl silicon compounds involves the addition of $HSiCl_3$ to chlorinated olefins. This method differs from all the others in that it involves the formation of a silicon–carbon bond and is therefore a one-step synthesis. $HSiCl_3$ adds to $CH_2{=}CHCH_2Cl$ to give a 50 per cent yield of $ClCH_2CH_2CH_2SiCl_3$ at 150°C. over a platinum-on-carbon catalyst under pressure

$$ClCH_2CH{=}CH_2 \quad + \quad HSiCl_3 \quad \xrightarrow[Pt]{heat} \quad ClCH_2CH_2CH_2SiCl_3$$

(525). With $CCl_2{=}CHCl$ the reaction takes a somewhat different course and gives $CCl_2{=}CHSiCl_3$ (525). The same product is obtained at 600°C. and atmospheric pressure without a catalyst (2). In this case the product was for some time thought to be $CHCl{=}CClSiCl_3$ (2), but it is now agreed that it is $CCl_2{=}CHSiCl_3$ (4, 527), even though the former structure is favored on the basis of its Raman spectrum (333). $HSiCl_3$ with $CHCl{=}CHCl$ at 600°C. gives a good yield of

$CHCl{=}CHSiCl_3$ (4), but with $CHCl_2CHCl_2$ at 500°C. it gives only a low yield of dichlorovinyltrichlorosilanes (2), and with $CH_2{=}CCl_2$ at 550°C. it gives only a little chlorovinyltrichlorosilane (4). $HSiCl_3$ adds to $ClC{\equiv}CCl$ to give $CHCl{=}CClSiCl_3$ (3). $HSiCl_3$ with $CCl_2{=}CHSiCl_3$ also gives an adduct, probably $Cl_3SiCCl_2CH_2SiCl_3$ (2).

Other methods for synthesizing higher chloroalkyl silicon compounds have thus far been of limited utility. Stirring $CH_2{=}C(CH_3)Si(CH_3)_3$ with concentrated hydrochloric acid gives a 35 per cent yield of $(CH_3)_2CClSi(CH_3)_3$ (425). However, bubbling hydrogen chloride into refluxing $CH_2{=}CHCH_2Si(CH_3)_3$ gives only the silicon–carbon cleavage products trimethylchlorosilane and propylene (446). With concentrated hydrochloric acid $(CH_3)_2C(OH)CH_2CH_2Si(CH_3)_3$ gives the corresponding chloride in 48 per cent yield. $CH_3CHClSiCl_3$ is obtained from the low-temperature reaction of diazoethane with silicon tetrachloride; this type of reaction has been much more extensively applied to the synthesis of chloromethyl silicon compounds (546, 547). The catalyzed addition of silicon tetrachloride to ethylene under heat and pressure to give $ClCH_2CH_2SiCl_3$ (397) and $Cl(CH_2CH_2)_nSiCl_3$ (393) has been disclosed with little elaboration.

D. PROPERTIES OF HIGHER CHLOROALKYL COMPOUNDS

The reactions of the higher chloroalkyls depend remarkably on the position of the halogen relative to silicon. Alpha chlorine atoms usually undergo displacement without disturbing the silicon–carbon bond; many such transformations are already familiar from the chemistry of the chloromethyls. Beta chlorine atoms usually give rise to eliminations involving silicon–carbon cleavage with expulsion of the organic group as an olefin. The behavior of chlorines further removed than the beta carbon is largely unexplored; however, gamma bromine atoms show both displacement reactions and elimination reactions involving silicon.

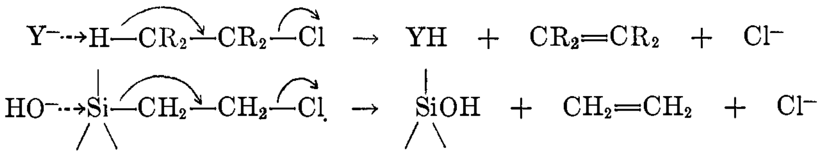
1. *Alkaline reagents*

The α- and β-chloroethyl silicon compounds differ markedly in their behavior toward alkaline reagents. The beta isomers react much faster than the alpha isomers and faster than any alkyl halide. Ushakov and Itenberg first demonstrated this when they found that $ClCH_2CH_2Si(C_2H_5)_3$ gives a quantitative yield of chloride ion on standing in alcoholic sodium hydroxide for about an hour at room temperature (519). In marked contrast, $CH_3CHClSi(C_2H_5)_3$ is unaffected even on refluxing, and it is not until the temperature is raised to 145°C. in a sealed tube that $CH_2{=}CHSi(C_2H_5)_3$ is formed (519).

So reactive is $ClCH_2CH_2SiCl_3$ that the chlorine on carbon is titrated completely with 0.5 *N* alkali in water at room temperature; with $CH_3CHClSiCl_3$ only the chlorine atoms bound to silicon are titrated (448). In general, other α- and β-monochloro isomers behave in the same contrasting fashion, though in some cases alcohol is needed to provide a homogeneous medium for quantitative results. The β-monochloro isomers of $(C_2H_5)_3SiCl$ and $(C_2H_5)_3SiF$ are titrated completely, while the alpha isomers are titrated only for the silicon–halogen bonds (427, 428). Titration of one carbon–chlorine bond also takes place in

$ClCH_2CH_2Si(C_2H_5)_3$ (428), $CH_2ClCHClSiCl_3$ (4), $CH_2ClCCl_2SiCl_3$ (4), $CCl_3CHClSiCl_3$ (2), and $Cl_3SiCCl_2CH_2SiCl_3$ (2). Among the monochloro derivatives of propyltrichlorosilane, the beta chlorine is titrated, but the alpha and the gamma are not (431). In $CH_2ClCHClCH_2SiCl_3$ (9, 446), $CH_3CHClCHClSiCl_3$ (9), and $CH_3CHClCHClCH_2SiCl_3$ (9) one carbon–chlorine titrates. Both $ClCH_2CH(CH_3)SiCl_3$ (432) and $ClCH_2C(CH_3)_2SiCl_3$ (516) titrate for all four chlorines, while a tertiary halide like $ClC(CH_3)_2Si(CH_3)_3$ is inert (425). Also inert toward alkali is the carbon–chlorine in $C_6H_5CHClSiCl_3$ (448). In a compound like $CBrCl_2CHBrSiCl_3$ the beta carbon–bromine appears to be the principal carbon–halogen bond that is titrated (2). The beta halogens in $CHCl{=}CHSiCl_3$ (4, 425) and $CCl_2{=}CHSiCl_3$ (2) are not titrated like those in the saturated compounds.

The product which forms when a β-haloalkyl silicon compound is treated with aqueous or alcoholic caustic has been demonstrated repeatedly to be an olefin arising from carbon–chlorine displacement and silicon–carbon cleavage. That this reaction is at least formally analogous to elimination reactions in alkyl halides has been recognized (434).



$$Y^- \dashrightarrow H{-}CR_2{-}CR_2{-}Cl \rightarrow YH + CR_2{=}CR_2 + Cl^-$$

$$HO^- \dashrightarrow \overset{|}{\underset{/\ \backslash}{Si}}{-}CH_2{-}CH_2{-}Cl \rightarrow \overset{|}{\underset{/\ \backslash}{Si}}OH + CH_2{=}CH_2 + Cl^-$$

Ethylene is evolved in high yield from $ClCH_2CH_2SiCl_3$ and $(ClCH_2CH_2SiO_{1.5})_x$ (434) as well as from $ClCH_2CH_2Si(C_2H_5)_2Cl$ (428). Propylene arises from $CH_3CHClCH_2SiCl_3$ (431) and isobutylene from $ClCH_2C(CH_3)_2SiCl_3$ (516). Chloroethylenes form from polychloroethyl derivatives containing at least one beta chlorine; for example, vinyl chloride forms in 68 per cent yield from $CH_2ClCHClSi(CH_3)_3$ (425), vinylidene chloride from $CH_2ClCCl_2SiCl_3$ (4), and trichloroethylene from $CCl_3CHClSiCl_3$ (2). The chloroölefins from the alkali cleavage of $CH_3CHClCHClSiCl_3$ and $CH_3CHClCHClCH_2SiCl_3$ have also been isolated (9). Chlorobromoethylenes arise from eliminations by alkali in $CH_2BrCBrClSiCl_3$ (4) and $CBrCl_2CHBrSiCl_3$ (2).

The contrasting behavior of alpha and beta isomers is also found with sodium alkoxides in alcohols. $CH_3CHClSi(OR)_3$ compounds are converted to $CH_3CH(OR')Si(OR)_3$ derivatives in 35–60 per cent yields (59). But $CH_2ClCHClSi(OC_2H_5)_3$ gives vinyl chloride and ethyl orthosilicate with sodium ethoxide in ethanol (502).

β-Chloro compounds such as $CCl_2{=}CHSiCl_3$ and $CHCl{=}CClSiCl_3$ do not undergo the facile beta-elimination reaction, but with hot concentrated alcoholic caustic they do undergo a silicon–carbon cleavage analogous to that which occurs with chloromethyl compounds. Thus $CCl_2{=}CHSiCl_3$ gives vinylidene chloride (4, 527), and $CHCl{=}CClSiCl_3$ gives 1,2-dichloroethylene (527). A similar reaction occurs with $CH_2{=}CClSiCl_3$, which gives vinyl chloride (4).

Other reagents also give elimination with β-chloro compounds. An aqueous alkali solution of $HSCH_2COOH$ cleaves $ClCH_2CH_2Si(C_2H_5)_3$, but it reacts smoothly with the alpha isomer to form $HOOCCH_2SCH(CH_3)Si(C_2H_5)_3$ (304). Although the malonic ester synthesis works well with α- and γ-haloalkylsilanes, it is said to be inapplicable to beta compounds because of the elimination reaction (433). Refluxing $ClCH_2CH_2Si(C_2H_5)_2Cl$ and $ClCH_2CH_2Si(C_2H_5)_2F$ with 1.25 *N* potassium acetate in glacial acetic acid for 5 min. gives 30–50 per cent yields of ethylene (428). In this connection it is interesting to note that conversion of $CH_3CHClSi(C_2H_5)_3$, an alpha isomer, to the corresponding acetate is the first instance of a carbon-functional silicone reaction (158, 342).

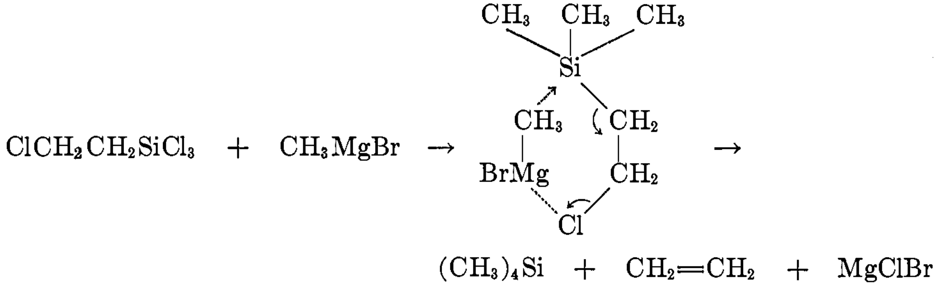
In view of the extreme reactivity of beta chlorine substituents toward alkaline reagents it is of some interest to consider the reactivity of alpha and gamma chlorine atoms in comparison with alkyl halides. $CH_3CHClSi(CH_3)_3$, $CH_3CHClSi(C_2H_5)_2CH_3$, and $CH_3CHClSi(C_2H_5)_2C_6H_5$ are less reactive than secondary butyl chloride toward reagents such as $NaOC_2H_5$–C_2H_5OH, CH_3COOK–CH_3COOH, and KOH–C_2H_5OH, but $CH_3CHClSi(C_2H_5)_2OH$ is more reactive (427). $ClCH_2CH_2CH_2SiCl_3$ gives 100 per cent reaction with KOH–C_2H_5OH for 1 hr. at room temperature, while $CH_3CH_2CHClSiCl_3$, $CH_3CHClSiCl_3$, and *n*-hexyl chloride give no reaction; at reflux temperature for 2 hr. $CH_3CH_2CHClSiCl_3$ and $CH_3CHClSiCl_3$ give 99 per cent reaction, while *n*-hexyl chloride gives only 56 per cent reaction (431).

2. Grignard reagents

In their reaction with Grignard reagents α- and β-chloroalkylsilanes exhibit the same dual behavior that they show with alkaline reagents. The alpha isomers react normally and the beta isomers give elimination reactions.

Grignard reagents couple satisfactorily with α-chloroalkyl silicon chlorides to replace only the chlorine atoms bound to silicon. With methylmagnesium bromide $CH_3CHClSiCl_3$ (448), $CH_3CHClSi(C_2H_5)_2Cl$ (427), and $CH_2{=}CClSiCl_3$ (425) give good yields of the trimethylsilyl derivatives; with phenylmagnesium bromide $CH_3CHClSi(C_2H_5)_2Cl$ gives a good yield of $CH_3CHClSi(C_2H_5)_2C_6H_5$ (427).

On the other hand, Grignard reagents give extensive silicon–carbon cleavage of β-chloroethyl silicon compounds to ethylene and tetraalkylsilanes. The reaction has been pictured (434) as a cyclic process in which the beta carbon–chlorine bond permits the formation of a Grignard coordination complex in which the alkyl group of the Grignard reagent and the silicon atom are brought into the 1,6-position, thereby permitting the electron displacements indicated to take place. With methylmagnesium bromide the β-chloro compounds $ClCH_2$-



CH_2SiCl_3 (434), $ClCH_2CH_2Si(C_2H_5)_3$ (428), and $ClCH_2CH_2Si(C_2H_5)_2F$ (428) give large amounts of ethylene together with $(CH_3)_4Si$, $CH_3Si(C_2H_5)_3$, and $(CH_3)_2Si(C_2H_5)_2$, respectively. Similarly, ethylmagnesium bromide with $ClCH_2CH_2SiCl_3$ gives ethylene and $(C_2H_5)_4Si$ (434). In the case of $ClCH_2CH_2SiCl_3$ the cleavage takes place principally after the three silicon–chlorine bonds have reacted, because stepwise addition of methylmagnesium bromide gives ethylene only upon introduction of the fourth equivalent (434).

Although silicon–carbon cleavage is the major reaction with the above β-chloroethyl compounds, this is not the case for all β-haloalkyls. Various 2-bromoalkyl derivatives give some carbon–bromine coupling products with many Grignard reagents (359). Although the reaction has been studied extensively, the significance of the work with respect to the mechanism of silicon–carbon cleavage by Grignard reagents is obscure because of the crude starting materials and the incomplete experimental details (359). The beta chlorine atoms of $CCl_2{=}CHSiCl_3$ are undisturbed by ethylmagnesium bromide; $CCl_2{=}CHSi(C_2H_5)_3$ is obtained with this reagent (2).

Phenyllithium with $CH_3CHClSiCl_3$ and $ClCH_2CH_2SiCl_3$ gives only 15 per cent and 5 per cent yields, respectively, of the corresponding triphenylsilyl derivatives (198). Organolithium compounds are superior to Grignard reagents in coupling with 2-bromoalkylsilanes (246).

3. *Quinoline*

Both α- and β-chloroalkylsilanes are smoothly dehydrohalogenated to olefinic compounds with quinoline. The reactants are simply heated so that the product distills. A 60 per cent overall yield of $CH_2{=}CHSiCl_3$ can thus be obtained from the mixed monochlorides obtained on chlorinating ethyltrichlorosilane (255). The individual isomers too have been subjected to this reaction (4, 428). In a

$$CH_3CHClSiCl_3 \quad \text{or} \quad ClCH_2CH_2SiCl_3 \xrightarrow[\text{quinoline}]{\text{heat}} CH_2{=}CHSiCl_3$$

similar manner $CH_2{=}CHSi(CH_3)Cl_2$ is obtained in 35 per cent overall yield from the mixed monochlorides obtained by heating $(CH_3)(C_2H_5)SiCl_2$ with sulfuryl chloride in the presence of benzoyl peroxide (255). Quinoline dehydrohalogenation of $ClCH_2CH(CH_3)SiCl_3$ gives a 76 per cent yield of $CH_2{=}C(CH_3)SiCl_3$ (432).

Dichloroethylsilanes can also be converted to olefins by this reaction. Heating $CH_3CCl_2SiCl_3$ with quinoline gives a 58 per cent yield of $CH_2{=}CClSiCl_3$; similarly, $CHCl_2CH_2SiCl_3$ gives a 50 per cent yield of $CHCl{=}CHSiCl_3$ (425). The product obtained from $CH_2ClCHClSiCl_3$ in 80 per cent yield is $CH_2{=}CClSiCl_3$ (5, 502); $CH_2ClCHClSi(OC_2H_5)_3$ gives only an 18 per cent yield of $CH_2{=}CClSi(OC_2H_5)_3$ (502). Complex products are obtained on heating $CH_2ClCCl_2SiCl_3$ with quinoline (4).

4. *Aluminum chloride*

Dehydrochlorination of $ClCH_2CH_2SiCl_3$ to $CH_2{=}CHSiCl_3$ occurs in good yield on heating with 1 per cent aluminum chloride; the reaction is reversible and must be carried out in a still so that the product can be removed as it is formed (526). The three chloropropyltrichlorosilanes behave similarly, giving $CH_2{=}CHCH_2SiCl_3$ and $CH_3CH{=}CHSiCl_3$ (9).

Silicon–carbon cleavage is another reaction that aluminum chloride brings about in β-chloroethyl compounds. When $ClCH_2CH_2Si(C_2H_5)_2Cl$ is heated with aluminum chloride in pentane, ethylene is evolved and a 77 per cent yield of $(C_2H_5)_2SiCl_2$ is obtained; with $ClCH_2CH_2Si(C_2H_5)_2F$ a 71 per cent yield of $(C_2H_5)_2SiCl_2$ is obtained instead of $(C_2H_5)_2SiFCl$ (428). $ClCH_2CH_2Si(C_2H_5)_3$ gives ethylene and $(C_2H_5)_3SiCl$ (428).

Friedel–Crafts coupling occurs when chloroethyltrichlorosilanes are heated with a little aluminum chloride in benzene. In the case of the beta isomer the isomeric composition of the product has not been established (232, 236). $CH_3CHClSiCl_3$ gives about equal parts of α- and β-phenylethyltrichlorosilanes (526).

5. *Pyrolysis*

Dehydrohalogenation occurs when chloroethyltrichlorosilanes are pyrolyzed. At 600°C. $CH_3CHClSiCl_3$ gives a good yield of $CH_2{=}CHSiCl_3$, together with considerable ethylene and silicon tetrachloride; $ClCH_2CH_2SiCl_3$ gives about the same amount of $CH_2{=}CHSiCl_3$, together with much more ethylene and silicon tetrachloride (4). Other data on the pyrolytic dehydrohalogenation of these compounds have been presented (231). At 400°C. $CH_2ClCHClSiCl_3$ is unaffected (526), but at 600°C. it gives gaseous products and a complex mixture containing chlorovinylsilanes (4). At 600°C. $CH_2ClCCl_2SiCl_3$ gives complex products (4). Pyrolysis of the mixed side-chain monochlorides of $C_2H_5C_6H_4SiCl_3$ gives $CH_2{=}CHC_6H_4SiCl_3$ (76).

Silicon–carbon cleavage predominates when other chloroalkyl compounds are heated at relatively low temperatures. Refluxing $ClCH_2CH_2Si(C_2H_5)_3$ for 3 hr. gives ethylene and a 64 per cent yield of $(C_2H_5)_3SiCl$ (428). Under similar conditions $CH_2ClCHClCH_2Si(CH_3)_3$ gives 87 per cent allyl chloride and 81 per cent $(CH_3)_3SiCl$ (446).

6. *Other carbon-functional reactions*

The reactions of various chloroalkyl silicon compounds with alcoholic silver nitrate have been studied principally for a comparison of their reactivities with those of alkyl halides. $CH_3CHClSi(CH_3)_3$ does not react with ethanolic silver nitrate on refluxing for 1 hr. (448). In contrast, all secondary alkyl chlorides, including pinacolyl chloride, give a precipitate. Even on refluxing for 4 hr. with ethanolic silver nitrate $CH_3CHClSi(CH_3)_3$, $CH_3CHClSi(C_2H_5)_2CH_3$, and $CH_3CHClSi(C_2H_5)_2C_6H_5$ give no reaction (427). Contrasting with the inertness of the α-chloroethyl compounds is the reactivity of the beta derivatives. Refluxing $ClCH_2CH_2Si(C_2H_5)_3$ and $ClCH_2CH_2Si(C_2H_5)_2Cl$ with methanolic silver nitrate for 10 min. gives a 95 per cent yield of silver chloride; $ClCH_2CH_2Si(C_2H_5)_2F$ gives a 45 per cent yield in 30 min. (428).

$CH_3CHClSi(CH_3)_3$ readily forms a Grignard reagent (448). With sodium iodide in acetone $CH_3CHClSi(CH_3)_3$ gives a very good yield of the iodide (425). Similar reactions have not been reported for analogous beta compounds.

7. *Silicon-functional reactions*

Both α- and β-chloroethylsilanes can undergo hydrolysis, alcoholysis, and ammonolysis of their silicon-functional groups without disturbance of carbon–chlorine bonds.

Hydrolysis of $ClCH_2CH_2SiCl_3$ with distilled water gives an 80 per cent yield of the trifunctional β-chloroethylpolysiloxane (448). The silanol obtained by hydrolysis of $CH_3CHClSi(C_2H_5)_2Cl$ with distilled water appears unusually stable toward intermolecular dehydration (427). Hydrolysis of $CCl_2{=}CHSiCl_3$ gives the corresponding polysiloxane, which is degraded on being heated at 110°C. (2).

Alcoholysis of both $CH_3CHClSiCl_3$ and $ClCH_2CH_2SiCl_3$ at reflux temperature gives satisfactory yields of the corresponding trialkoxy compounds (58); with moist alcohols 10–30 per cent yields of the corresponding tetraalkoxydisiloxanes are obtained (61). Normal alcoholysis also occurs with $CH_2ClCHClSi(OC_2H_5)_3$ (502) and with $CCl_2{=}CHSiCl_3$ (2). Methanolysis of $Cl_3SiCCl_2CH_2SiCl_3$ is accompanied by carbon–chlorine attack, but this can be suppressed with pyridine as an acid acceptor (2). The $ClCH_2CH_2Si(OR)_3$ compounds can be converted to the mixed acyloxy alkoxy derivatives with acid anhydrides (60).

Ammonolysis of $CH_3CHClSi(C_2H_5)_2Cl$ with liquid ammonia at low temperature gives an 88 per cent yield of $CH_3CHClSi(C_2H_5)_2NH_2$ (428). This silylamine is converted smoothly to the corresponding silyl halide with cold concentrated hydrochloric acid or hydrogen chloride in ether, with cold concentrated hydrofluoric acid, and with cold concentrated hydrobromic and sulfuric acids (10). The ammonolysis of $ClCH_2CH_2Si(C_2H_5)_2Cl$ at −80°C. gives a 60 per cent yield of $ClCH_2CH_2Si(C_2H_5)_2NH_2$, which slowly decomposes to ammonium chloride, ethylene, and other products on standing (428).

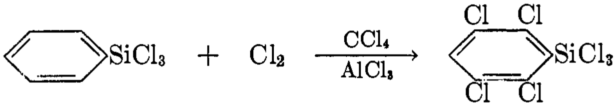
8. *Other properties*

The dipole moment of $CH_3CHClSi(C_2H_5)_3$ has been determined. Electron diffraction studies have been made on $CH_3CHClSiCl_3$ and $ClCH_2CH_2SiCl_3$ (261). The Raman spectrum of $ClCH_2CH_2SiCl_3$ has been discussed (332).

E. CHLORINATED ARYL COMPOUNDS

1. *Syntheses*

The direct chlorination of aromatic silicon compounds dates back to Ladenburg's synthesis of $ClC_6H_4Si(C_2H_5)_3$ by chlorinating $C_6H_5Si(C_2H_5)_3$ in 1874 (300). Brief descriptions of the chlorination of phenyltrichlorosilane (116, 150) and xenyltrichlorosilane (149) are available. The only detailed study is concerned with the polychlorination of $C_6H_5SiCl_3$ (301a). A 60 per cent yield of tetrachlorophenyltrichlorosilanes is obtained by chlorinating $C_6H_5SiCl_3$ in carbon tetrachloride with aluminum chloride as catalyst. Without the carbon tetrachloride



considerable silicon–carbon cleavage occurs; the solvent exerts its beneficial effect supposedly through its poor solubility for by-product hydrogen chloride, which is presumed to be responsible for dephenylation. Ferric chloride and iodine are unsatisfactory as catalysts for producing the higher chlorination products. The order of positions taken by the entering chlorines on stepwise substitution is 2, 5, 3, 6. No pentachlorophenyltrichlorosilane is obtained. Other studies of the chlorination of $C_6H_5SiCl_3$ and $(C_6H_5)_2SiCl_2$ have been reported (550).

Another synthetic route involves coupling chlorinated aryl organometallic reagents with silicon halides. This method is very versatile and offers the advantage of giving definite isomers. 4-ClC_6H_4MgBr couples satisfactorily with silicon tetrachloride (553), $(CH_3)_3SiCl$ (79), $HSiCl_3$ (12), $CH_2{=}CHSiCl_3$, and $CH_2{=}CHCH_2SiCl_3$ (392). 3-ClC_6H_4MgI gives the coupled product with $(CH_3)_3SiCl$ (116, 154), but 2-ClC_6H_4MgI does not (116). More highly chlorinated aromatic silicon compounds are also obtained by Grignard couplings (85). 4-ClC_6H_4Li couples satisfactorily with chlorosilanes and ethoxysilanes (196). Dichlorobenzene and silicon tetrachloride are not coupled by sodium in ether (30).

Chlorinated aromatic silicon compounds may also be obtained by reacting chlorobenzenes with silicon hydrides and with polysilanes. Thus, chlorobenzene and $HSiCl_3$ at 300°C. with boron trichloride as catalyst give both $ClC_6H_4SiCl_3$ and C_6H_5 $SiCl_3$ (21). A similar reaction occurs with CH_3SiHCl_2 (14). Dichlorobenzene and $HSiCl_3$ at 500°C. give $ClC_6H_4SiCl_3$ (328). Dichlorobenzene cleaves Si_2Cl_6 to form $ClC_6H_4SiCl_3$ at 325°C. (27).

Compounds in which the chlorinated aromatic group is attached to silicon through an aliphatic side-chain may also be obtained. Reacting the three ClC_6H_4-CH_2MgX isomers with $(CH_3)_3SiCl$ gives the corresponding $ClC_6H_4CH_2Si(CH_3)_3$ derivatives (140). Friedel–Crafts coupling of chlorobenzenes with chloroethyltrichlorosilanes gives various chlorophenylethyltrichlorosilanes (236).

2. Chemical properties

The only known carbon-functional reactions of the chlorinated aromatic silicon compounds involve formation of organometallic derivatives. 4-$LiC_6H_4Si(CH_3)_3$ is conventionally formed from the chloro compound (40), as are also the three $LiC_6H_4CH_2Si(CH_3)_3$ derivatives (140). The sodium coupling of the three $ClC_6H_4Si(CH_3)_3$ compounds with $(CH_3)_3SiCl$ gives the corresponding $(CH_3)_3SiC_6H_4Si(CH_3)_3$ derivatives (116).

Chlorophenyl silicon compounds are ordinarily quite stable, but they do undergo cleavage with certain reagents. Hydrogen chloride in boiling glacial acetic acid cleaves various aryl groups in aryltrimethylsilanes. The 4-ClC_6H_4— group is less readily cleaved than C_6H_5— and 4-$(CH_3)_2NC_6H_4$— groups and more readily cleaved than $C_6H_5CH_2$— and $C_6H_5CH_2CH_2$— groups (193). With the same reagent the 3-ClC_6H_4— group is less readily cleaved than the 4-ClC_6H_4— group in the corresponding aryltrimethylsilanes (39). With molar amounts of aluminum chloride, phosphorus trichloride, and antimony pentachloride 4-ClC_6H_4— groups are cleaved from silicon, for example as 4-$ClC_6H_4AlCl_2$; in 4-$ClC_6H_4Si(C_6H_5)Cl_2$ cleavage of the chlorinated aryl group predominates (549, 551, 552). On the other hand, the chlorophenyl groups in [—$Si(CH_3)$(4-ClC_6H_4)-

O—]$_x$ and [—Si(CH$_3$)(3-ClC$_6$H$_4$)O—]$_x$ suffer negligible cleavage on equilibration with concentrated sulfuric acid at room temperature, whereas phenyl groups are extensively cleaved (85). With 71 per cent nitric acid in refluxing acetic anhydride for several hours 4-ClC$_6$H$_4$— groups are readily cleaved (102, 553). With dilute potassium hydroxide in aqueous ethanol–dioxane at 85°C. for 24 hr. 4-ClC$_6$H$_4$Si(C$_6$H$_5$)$_3$ gives only a little chlorobenzene and a 26 per cent recovery of starting material; under similar conditions the 3-CF$_3$C$_6$H$_4$— group is much more extensively cleaved (186).

In their silicon-functional reactions chlorophenyl silicon compounds behave quite straightforwardly. The silicon chlorides may be hydrolyzed (18, 85, 161, 377) and cohydrolyzed (151). They may be alcoholyzed (108), coupled with Grignard reagents (116), and reduced with lithium aluminum hydride (189). The silicon ethoxides are readily converted to the corresponding silanols and siloxanes (196). Like analogous silanols, (4-ClC$_6$H$_4$)$_3$SiOH is titrated quantitatively with the Karl Fischer reagent (197). Chlorophenylsiloxanes are satisfactorily equilibrated by means of concentrated sulfuric acid at room temperature (85). The rates of hydrolysis of various monosubstituted triphenylsilanes, including 4-ClC$_6$H$_4$Si(C$_6$H$_5$)$_2$H, with wet piperidine are in agreement with those predicted from Hammett's sigma constants (189). The electronic effect of the substituents in (4-ClC$_6$H$_4$)$_3$SiH is not enough to alter the reaction with methyllithium to give the silyllithium derivative; (4-ClC$_6$H$_4$)$_3$SiCH$_3$ is obtained in good yield (43). A kinetic study of the reaction of (4-ClC$_6$H$_4$)$_3$SiH with iodine has been made (125).

3. Other properties

The dipole moment of 3-ClC$_6$H$_4$Si(CH$_3$)$_3$ is known (152). Comparison of the dipole moments of 4-ClC$_6$H$_4$Si(CH$_3$)$_3$ and 4-FC$_6$H$_4$Si(CH$_3$)$_3$ with that of C$_6$H$_5$Si(CH$_3$)$_3$ suggests that the (CH$_3$)$_3$Si— group is slightly electron-releasing (374).

Chlorinated aryl groups improve the lubricity of methylsiloxanes without seriously affecting other valuable properties such as thermal stability. The groups may be introduced in the form of additives such as (ClC$_6$H$_4$)$_2$Si(CH$_3$)$_2$ (83) or as integral parts of the siloxane molecules (85, 151, 177). The improved lubricating characteristics may be enhanced by adding certain metal carboxylates (123) or chlorinated biphenyls with various sulfur compounds (251). Chlorinated aryl groups also improve the flame resistance of siloxane resins (377).

VII. BROMO COMPOUNDS (SEE TABLE 4)

A. BROMOALKYL DERIVATIVES

1. Syntheses

Syntheses of bromoalkyl silicon compounds resemble those of their chloro analogs. Direct bromination occurs simply upon refluxing tetraethylsilane (307) and tetra-*n*-propylsilane (350) with bromine. The former yields a monobrominated derivative and a dibrominated derivative (307). The monobromo compound gives CH$_2$=CHSi(C$_2$H$_5$)$_3$ with hot alcoholic potassium hydroxide (308). With NaSCH$_2$COONa and NaSCH$_2$CH$_2$COONa it also gives bromine displacement products whose alkaloid salts can be partially resolved into optically active isomers. The monobromo compound is therefore the alpha isomer (302, 303). The dibromo derivative of tetraethylsilane is identical with the monobromination product of $CH_3CHBrSi(C_2H_5)_3$ and is different from

$$(C_2H_5)_3SiCHBrCH_3 + NaSCH_2COONa \rightarrow (C_2H_5)_3SiCH(CH_3)\text{-}SCH_2COONa$$

$CH_2BrCHBrSi(C_2H_5)_3$, obtained as the bromine adduct of $CH_2{=}CHSi(C_2H_5)_3$. The dibromo derivative is therefore $CH_3CBr_2Si(C_2H_5)_3$ (308). Another direct bromination is the photobromination of methylsiloxane films on glass surfaces with radiobromine vapor (520).

Bromination does not occur when $(CH_3)_3SiCl$, $(CH_3)_2SiCl_2$, and $(CH_3)_3SiOSi(CH_3)_3$ are refluxed with bromine (460). However, when chlorine is bubbled through the mixture under illumination, immediate evolution of hydrogen chloride occurs with the formation of brominated derivatives (460) and only small amounts of chlorinated derivatives (240). The reaction involving bromine

$$(CH_3)_2SiCl_2 + Br_2 + Cl_2 \rightarrow BrCH_2Si(CH_3)Cl_2 + HCl$$

and chlorine may also be carried out in the vapor phase (479). Bromination of $(CH_3)_3SiCl$ in the liquid phase by alternate incremental additions of liquid bromine and gaseous chlorine under illumination gives a 62 per cent yield of $BrCH_2Si(CH_3)_2Cl$. Under similar conditions $(CH_3)_2SiCl_2$ gives a 34 per cent yield of $BrCH_2Si(CH_3)Cl_2$ and a 25 per cent yield of $Br_2CHSi(CH_3)Cl_2$ (460). Hexamethyldisiloxane gives a 25 per cent yield of monobrominated derivative and lachrymatory polybrominated materials (460). Tetramethylsilane is satisfactorily converted to $BrCH_2Si(CH_3)_3$ with a mixture of bromine and chlorine (240, 479). Diethyldichlorosilane gives two monobromo isomers (479). It is interesting that a bromine and chlorine mixture converts $CH_2{=}CHSiCl_3$ to $CH_2ClCHClSiCl_3$ and $CH_2BrCHBrSiCl_3$ and not to the mixed chlorobromo adduct (502).

Another method of bromination applicable to organosilicon compounds involves refluxing them with *N*-bromosuccinimide in carbon tetrachloride. With this method $C_6H_5CH_2Si(CH_3)_3$ gives a 60 per cent yield of $C_6H_5CHBrSi(CH_3)_3$ and a 21 per cent yield of $C_6H_5CBr_2Si(CH_3)_3$, whereas on direct bromination it gives only a 34 per cent yield of somewhat impure monobromo derivative (240). Both $C_6H_5CH_2Si(C_6H_5)_3$ (240) and $4\text{-}CH_3C_6H_4Si(C_6H_5)_3$ (62) are readily brominated in the aliphatic group with *N*-bromosuccinimide; direct bromination of such compounds might prove very unsatisfactory because phenyl groups are frequently cleaved from silicon by bromine. Even *N*-bromosuccinimide can cause silicon–carbon cleavage; thus with $(CH_3)_3SiCH(C_6H_5)CH(C_6H_5)Si(CH_3)_3$ it gives $C_6H_5CHBrCHBrC_6H_5$ (240).

Bromoalkylsilanes may also be obtained by adding hydrogen bromide to unsaturated alkysilanes. Thus the reaction of $CH_2{=}CHSi(CH_3)_3$ with hydrogen bromide in the presence of benzoyl peroxide gives a 79 per cent yield of $BrCH_2CH_2Si(CH_3)_3$; without the peroxide no reaction occurs in a reasonable time (425). Treating $CH_2{=}CHCH_2Si(CH_3)_3$ with hydrogen bromide at −80°C. gives a 70

TABLE 4

Silicon-containing bromo compounds

Compound	Melting Point	Boiling Point	n_D	d	References
	°C.	°C.			
Bromomethyls:					
$BrCH_2SiBr_3$		70/6 mm.		2.5730 (20°/20°)	(546, 547)
$BrCH_2Si(CH_3)Cl_2$		141/740 mm.	1.4750 (25°)	1.57 (25°)	(*460*, 479)
$BrCH_2Si(CH_3)_2Cl$		130/740 mm.	1.4630 (25°)	1.375 (25°)	(*460*, 479)
$BrCH_2Si(CH_3)(C_6H_5)Br$					(152)
$BrCH_2Si(CH_3)_3$		116/740 mm.	1.4423 (25°)	1.170 (25°)	(134, 240, 346, 347, *460*, 479)
$(BrCH_2)_2SiBr_2$		107/9 mm.		2.4614 (20°/20°)	(152, *546*, *547*)
$(BrCH_2)_2Si(C_6H_5)Br$					(152)
$(BrCH_2)_3SiBr$		123/5 mm.		2.3440 (20°/20°)	(546, 547)
$BrCH_2Si(CH_3)_2OSi(CH_3)_3$		83/49 mm.	1.4279 (25°)	1.097 (25°)	(460)
$[BrCH_2Si(CH_3)_2]_2O$		234/734 mm.	1.4719 (25°)	1.3918 (25°)	(460, 546)
$Br_2C_5H_{15}Si_2O$		72–104/16 mm.			(460)
$[(BrCH_2)_3Si]_2O$	69.5–70				(546, 547)
$Br_2CHSi(CH_3)Cl_2$		89/25 mm.	1.5185 (25°)		(*460*, 479)
Bromomethylsiloxanes					(520)
Bromoethyls:					
$CH_3CHBrSi(C_2H_5)Cl_2$		110/95 mm.	1.4772 (25°)	1.41 (25°)	(479)
$CH_3CHBrSi(CH_3)_3$		134/736 mm.	1.4509 (20°)	1.1440 (20°)	(357, *425*)
$CH_3CHBrSi(C_2H_5)_3$		88/15 mm.			(302, 303, 305, *307*, 308)
$BrCH_2CH_2Si(C_2H_5)Cl_2$		128/95 mm.	1.4908 (25°)	1.45 (25°)	(479)
$CH_2BrCH_2Si(CH_3)_3$		64–65/39 mm.	1.4575 (20°)	1.1499 (20°)	(425)
$BrCH_2CH_2Si(C_2H_5)_3$					(360)
$(CH_2BrCH_2)_2SiCl_2$					(228, 541)
$CH_3CBr_2Si(C_2H_5)_3$		114/15 mm.			(305, *307*, 308)
$CH_2BrCHBrSiCl_3$		215/735 mm.			(5, 502)
		91/11 mm.	1.5370 (20°)	2.05 (21°)	
$CH_2BrCHBrSi(OC_2H_5)_3$		113/2 mm.	1.4600 (25°)	1.4430 (25°)	(502)
$CH_2BrCHBrSi(CH_3)_3$	−9 to −11	74–75/8 mm.	1.5095 (20°)	1.5497 (20°)	(425)
$CH_2BrCHBrSi(C_2H_5)_3$		137/15 mm.		1.421 (20°)	(305, *308*)
$CH_2BrCClBrSiCl_3$		108/14 mm.	1.5492 (20°)	2.07 (27°)	(4)
$CHBrClCHBrSiCl_3$		132/10 mm.			(4)
$CCl_2BrCHBrSiCl_3$		119/10 mm.	1.5595 (25°)		(2, 4, 527)
$CH_2BrCBr_2SiCl_3$	65–70	107/6 mm.			(5)

$Br_3C_2H_2SiCl_3$		122/3 mm.	1.566 (20°)	2.2 (22°)	(5)
$CHBr_2CHBrSi(OC_2H_5)_3$		143/7 mm.	1.4905 (25°)	1.6637 (25°)	(335)
Unsaturated bromoethyls: see table 1					
Higher bromo aliphatics:					
$CH_3CHBrCH_2Si(CH_3)_3$		31/6 mm.	1.4580 (20°)	1.113 (20°)	(357, 359, *446*)
$CH_3CHBrCH_2Si(CH_3)_2C_6H_5$					(359)
$CH_3CHBrCH_2Si(CH_3)(C_6H_5)_2$					(359)
$CH_3CHBrCH_2Si(C_2H_5)_3$					(357, 358, 360)
$CH_3CHBrCH_2Si(C_3H_7)_3$					(359)
$CH_3CHBrCH_2Si(C_4H_9)_3$					(357, 359)
$(CH_3CHBrCH_2)_2Si(CH_3)_2$					(360)
$Br(CH_2)_3Si(CH_3)_2Cl$					(430)
$Br(CH_2)_3Si(CH_3)_3$		70/25 mm.	1.4541 (20°)	1.1173 (20°)	(401, 404, 406, 407, 412, 413, 417, 430, 433, 444, *447*)
$[Br(CH_2)_3Si(CH_3)_2]_2O$					(430)
$(n\text{-}C_3H_6Br)Si(C_3H_7)_3$		138/60 mm.			(350)
$CH_3CHBrCH_2CH_2Si(CH_3)_3$		64/15 mm.	1.4542 (20°)	1.0894 (20°)	(361)
$Br(CH_2)_5Si(CH_3)_3$		113/23 mm.	1.4570 (20°)		(406, 433, *447*)
$CH_3CHBrCH_2CH(CH_3)CH_2Si(CH_3)_3$		92–93/18 mm.	1.4590 (20°)	1.0628 (20°)	(359)
$CH_3CHBrCH_2CH(CH_3)CH_2Si(C_2H_5)_3$		124/8 mm.	1.4745 (20°)	1.0517 (20°)	(359)
$Br(CH_2)_{11}Si(CH_3)_2C_4H_9$		174/4 mm.			(77)
$Br(CH_2)_{11}Si(CH_3)_2C_5H_{11}$		174/2 mm.			(77)
$Br(CH_2)_{11}Si(CH_3)_2CH_2CH_2C_6H_5$					(77)
$(C_6H_5)_2CBrSi(CH_3)_3$		167/4 mm.	1.5986 (20°)	1.2437 (20°)	(240)
$C_6H_5CBr_2Si(CH_3)_3$		128/4 mm.	1.5778 (20°)	1.5074 (20°)	(240)
$C_6H_5CHBrSi(CH_3)_3$		99/4 mm.	1.5389 (20°)	1.2112 (20°)	(240)
$C_6H_5CHBrSi(C_5H_5)_3$	145				(240)
$4\text{-}BrC_2H_4C_6H_4SiCl_3$					(76)
Bromoaryls:					
$4\text{-}BrC_6H_4SiCl_3$		264.5–265.5/744 mm. 106–108/6 mm.		1.6771 (20°)	(102, 225, *548*, 549, 550, 551, 553)
$BrC_6H_4SiCl_3$		127/23 mm.			(150, 460)
$4\text{-}BrC_6H_4Si(OCH_3)_3$		136/14 mm.		1.3493 (20°)	(224)
$4\text{-}BrC_6H_4Si(OC_2H_5)_3$		150/12 mm.		1.2244 (20°)	(224)
$4\text{-}BrC_6H_4Si(OC_3H_7)_3$		176/14 mm.		1.1553 (20°)	(224)
$4\text{-}BrC_6H_4Si(OC_4H_9\text{-}i)_3$		191/14 mm.		1.0923 (20°)	(224)
$4\text{-}BrC_5H_4Si(CH_3)(OC_2H_5)_2$		87–88/2–3 mm.	1.4980 (25°)	1.219 (25.7°)	(536)
$4\text{-}BrC_6H_4Si(C_6H_5)(OC_2H_5)_2$		201/17 mm.		1.2488 (20°)	(224)
$4\text{-}BrC_6H_4Si(CH_3)_2Cl$		136/18 mm.	1.5438 (25°)	1.3904 (25°)	(*309*, 536)
$4\text{-}BrC_6H_4Si(CH_3)_2(OC_2H_5)$		148/34 mm.	1.5131 (25°)	1.2212 (25°)	(309)

TABLE 4—*Concluded*

Compound	Melting Point	Boiling Point	n_D	d	References
	°*C.*	°*C.*			
3-$BrC_5H_4Si(CH_3)_3$		96–97/5 mm.	1.5290 (20°)		(40)
4-$BrC_6H_4Si(CH_3)_3$		230/752 mm.	1.5302 (20°)	1.2197 (20°)	(40, *79*, 83, 102, 162, 163, 164, 165, 195, 400, 542)
4-$BrC_6H_4Si(C_2H_5)_3$		150/14 mm.	1.5332 (20°)	1.1652 (20°)	(126, *225*)
4-$BrC_6H_4Si(C_6H_5)(C_2H_5)_2$		203/14 mm.		1.2153 (20°)	(224)
4-$BrC_6H_4Si(C_6H_5)_3$	168				(194)
$(4\text{-}BrC_6H_4)_2SiCl_2$	87–88	389–397/739.4 mm.			(*102*, 225)
		239/21 mm.			
$(4\text{-}BrC_6H_4)_2Si(CH_3)_2$	74	363.5–367.5/739.4 mm.			(*102*, 450, 514)
BrC_6H_4Si compounds					(370)
$[4\text{-}BrC_5H_4Si(CH_3)_2]_2O$		120/<1 mm.	1.5550 (25°)	1.3641 (25°)	(25, *309*, *536*)
		150–151/1.5 mm.	1.5501 (25°)	1.2176 (24°)	
$[4\text{-}BrC_6H_4Si(C_6H_5)(OC_2H_5)]_2O$		318/20 mm.		1.3369 (20°)	(224)
Bromophenylsiloxanes					(123, 151, 177, 225, 536)
$(2\text{-}CH_3O\text{-}4\text{-}BrC_6H_3)SiCl_3$		130–140/13 mm.			(148)
2,4-$Br_2C_5H_3SiCl_3$		144–146/6 mm.		1.9502 (20°)	(*548*, 550)
3,5-$Br_2C_6H_3Si(CH_3)Cl_2$	44–45	65/0.1 mm.			(330)
$(3,5\text{-}Br_2C_5H_3)_2Si(CH_3)Cl$	109–110				(330)
$(3,5\text{-}Br_2C_6H_3)_2Si(CH_3)_2$	113–114				(330)
$(3,5\text{-}Br_2C_5H_3)_3SiCH_3$	214–215				(330)
$(3,5\text{-}Br_2C_6H_3)_4Si$	298–302				(330)
$(Br_2C_6H_3SiO_{1.5})_x$					(251)
$Br_3C_5H_2SiCl_3$		157–192/3 mm.			(150)
$(Br_3C_6H_2SiO_{1.5})_x$					(151)
4-$BrCH_2C_6H_4Si(C_5H_5)_3$	175–176				(62)
4-$Br_2CHC_6H_4Si(C_6H_5)_3$	184–184.5				(62)

per cent yield of $CH_3CHBrCH_2Si(CH_3)_3$; benzoyl peroxide does not reverse the addition (446). Adding hydrogen bromide to $CH_2{=}CHCH_2CH_2Si(CH_3)_3$ (361) and $CH_2{=}CH(CH_2)_9SiR_3$ (77) also proceeds satisfactorily.

Adding bromine to the unsaturated linkage of alkenylsilanes provides another way of making bromoalkylsilanes. Vinyltrichlorosilane with bromine under illumination gives a 91 per cent yield of $CH_2BrCHBrSiCl_3$ (5). Similar results are obtained with $CH_2{=}CHSi(OC_2H_5)_3$ (335) and with $CH_2{=}CHSi(CH_3)_3$ (425). However, even at $-80°C$. $CH_2{=}CHCH_2Si(CH_3)_3$ gives only silicon–carbon cleavage and no $CH_2BrCHBrCH_2Si(CH_3)_3$ (446). $CH_2{=}CBrSiCl_3$ with bromine gives $CH_2BrCBr_2SiCl_3$ (5). $CH_2{=}CHClSiCl_3$ with bromine in sunlight gives an 84 per cent yield of $CH_2BrCClBrSiCl_3$ (4); $CCl_2{=}CClSiCl_3$ behaves similarly (2).

Bromoalkyl silicon compounds are obtained in other ways too. Bromination of $CH_3CH(MgCl)Si(CH_3)_3$ gives $CH_3CHBrSi(CH_3)_3$ (425). The three possible monobromomethyl silicon bromides are obtained from the reaction of diazomethane with silicon tetrabromide under conditions analogous to those for the chloro analogs (546, 547). $HO(CH_2)_3Si(CH_3)_3$ and $HO(CH_2)_5Si(CH_3)_3$ with phosphorus tribromide give the corresponding bromides in excellent yield (447). The synthesis of $(BrCH_2CH_2)_2SiCl_2$ from the sodium coupling of $BrCH_2CH_2Br$ with silicon tetrachloride (228) has been disputed (541).

2. Properties

The reactions of bromoalkyl silicon compounds closely parallel those of their chloro analogs. Bromine displacements will be considered first. $BrCH_2Si(CH_3)_3$ and $C_6H_5CHBrSi(CH_3)_3$ readily form Grignard reagents, but $(C_6H_5)_2CBrSi(CH_3)_3$ does not (240). With sodium in amyl ether at 105°C. $BrCH_2Si(CH_3)_3$ gives a 40 per cent yield of the coupled product, $(CH_3)_3SiCH_2CH_2Si(CH)_3$, and about 10 per cent of $(CH_3)_4Si$ (346). With sodium mercaptides in ethanol $BrCH_2Si(CH_3)_3$ gives 35–90 per cent yields of $RSCH_2Si(CH_3)_3$ compounds (347). It also reacts with thiourea to give the thiuronium bromide (347). With potassium acetate in glacial acetic acid $BrCH_2Si(CH_3)_3$ and $C_6H_5CHBrSi(CH_3)_3$ give the corresponding acetates in 37 per cent and 84 per cent yields, respectively, but $(C_6H_5)_2CBrSi(CH_3)_3$ gives only $(C_6H_5)_2CHOCOCH_3$ from silicon-carbon cleavage during the reaction or subsequent washing (240).

Some of the bromine displacement reactions of higher bromoalkyl silicon compounds have already been considered in connection with the identification of the bromination products of tetraethylsilane. Other examples of displacement reactions are considered in this paragraph. Dehydrohalogenation of $CH_2BrCHBrSi(OC_2H_5)_3$ to $CH_2{=}CBrSi(OC_2H_5)_3$ occurs with quinoline (502) and with diethylamine (335). $CH_2{=}CBrSiCl_3$ can be obtained similarly (5). $BrCH_2CH_2CH_2Si(CH_3)_3$ behaves like an ordinary alkyl bromide in the malonic ester synthesis (433). With magnesium in ether $BrCH_2CH_2CH_2Si(CH_3)_2Cl$ is cyclized to a silacyclobutane, $\underline{CH_2CH_2CH_2Si}(CH_3)_2$ (430).

Silicon–carbon cleavage reactions of bromoalkyl silicon compounds parallel very closely those of their chloro analogs. $Br_2CHSi(CH_3)Cl_2$ gives dibromomethane on steam distillation with alkali (460). With potassium cyanide in methanol $BrCH_2Si(CH_3)_3$ and $C_6H_5CHBrSi(CH_3)_3$ give only cleavage products such as $(CH_3)_3SiOCH_3$ and $C_6H_5CH_2CN$; it has been suggested that these products arise from intermediate silylmethyl nitriles (240). β-Bromoethyl derivatives exhibit with alkalies the familiar enhanced reactivity due to olefin elimination. The bromine of $BrCH_2CH_2SiCl_3$ titrates completely with dilute alkali, while that of the alpha isomer is untouched (425). Similarly, $CH_3CHBrCH_2Si(CH_3)_3$ titrates completely with dilute alkali (446). In $CH_2BrCHBrSiCl_3$, which contains both an alpha and a beta carbon–bromine bond, only one carbon–bromine bond titrates with dilute alkali, and vinyl bromide is obtained with concentrated aqueous caustic (5). $CH_2BrCHBrSi(CH_3)_3$ also gives titration of only one carbon–bromine (425). $CH_2BrCBr_2SiCl_3$ with aqueous caustic gives vinylidene bromide (5). Silicon–carbon cleavage with olefin elimination also occurs simply on heating β-bromoalkyl silicon compounds; at reflux temperature $CH_3CHBrCH_2Si(CH_3)_3$ gives a 73 per cent yield of propylene and an 88 per cent yield of $(CH_3)_3SiBr$ (446). Under drastic conditions silicon–carbon cleavage can also occur in α-bromoethyl compounds; thus with hot alcoholic caustic $CH_3CBr_2Si(C_2H_5)_3$ gives $CH_2{=}CHBr$, $HC{\equiv}CH$, and $(C_2H_5)_3SiOH$ (308). An unusual cleavage reaction is found in the formation of cyclopropane on warming $Br(CH_2)_3Si(CH_3)_3$ with a

$$(CH_3)_3SiCH_2CH_2CH_2Br \xrightarrow{AlCl_3} (CH_3)_3SiBr + \underline{CH_2CH_2CH_2}$$

little aluminum chloride; the cyclic alkane is formed in 92 per cent yield together with 82 per cent of $(CH_3)_3SiBr$ (447). Under the same conditions $Br(CH_2)_5Si(CH_3)_3$ gives no cyclopentane; only a 17 per cent yield of impure 1-pentene and a 67 per cent recovery of $(CH_3)_3Si$— groups are obtained (447). $Br(CH_2)_3Si(CH_3)_3$ gives no cyclopropane with aqueous ethanolic potassium hydroxide, but complete loss of halogen occurs through metathesis or dehydrohalogenation (447).

Few silicon-functional reactions of bromoalkyl silicon compounds have been carried out. Hydrolysis of $BrCH_2Si(CH_3)_2Cl$ gives $[BrCH_2Si(CH_3)_2]_2O$ in good yield (460). With ethanol $CH_2BrCHBrSiCl_3$ is satisfactorily converted to $CH_2BrCHBrSi(OC_2H_5)_3$ (502). The reaction of $BrCH_2Si(CH_3)_2Cl$ with methylmagnesium bromide gives a high yield of $BrCH_2Si(CH_3)_3$ (460).

The dipole moments of $CH_3CHBrSi(C_2H_5)_3$, $CH_3CBr_2Si(C_2H_5)_3$, and $CH_2BrCHBrSi(C_2H_5)_3$ have been determined (305).

B. BROMOARYL DERIVATIVES

The direct bromination of some aromatic silicon compounds can be accomplished, but in many cases serious complications with silicon–carbon cleavage occur. Bromine cleaves $(C_6H_5)_4Si$ to bromobenzene and complex silicon-containing products (370). Bromine in the presence of iron cleaves 4-$(C_2H_5)_3SiC_6H_4Si(C_2H_5)_3$ to 1,4-dibromobenzene and $(C_2H_5)_3SiBr$ (224). Heating $C_6H_5Si(CH_3)_3$ with bromine gives a good yield of $(CH_3)_3SiBr$ (370a).

The aliphatic side-chains of aromatic silicon compounds can be brominated with *N*-bromosuccinimide without cleavage (62). $C_6H_5SiCl_3$ may be brominated in the presence of iron to $4\text{-}BrC_6H_4SiCl_3$ and $2,4\text{-}Br_2C_6H_3SiCl_3$ in good yield; higher bromination products are not obtained with excess bromine (548). Other studies of the bromination of $C_6H_5SiCl_3$ and $(C_6H_5)_2SiCl_2$ have been reported (550).

A versatile synthetic route to brominated aryl silicon compounds that gives isomers of known structure is organometallic couplings. $4\text{-}BrC_6H_4MgBr$ couples satisfactorily with silicon tetrachloride (225, 553), $C_6H_5SiCl_3$ (224), $(CH_3)_3SiCl$ (79), $(CH_3)_2SiCl_2$, and $(CH_3)_2Si(OC_2H_5)_2$ (309). $4\text{-}BrC_6H_4Li$ gives a 78 per cent yield of $4\text{-}BrC_6H_4Si(C_6H_5)_3$ with $(C_6H_5)_3SiCl$ (194), and $3,5\text{-}Br_2C_6H_3Li$ gives various coupled products with $SiCl_4$, CH_3SiCl_3, and $(CH_3)_2SiCl_2$ (330).

Few carbon-functional reactions of bromoaryl silicon compounds are known. The $4\text{-}BrC_6H_4SiR_3$ type readily form Grignard reagents (224). Both $(4\text{-}BrC_6H_4)_2\text{-}Si(CH_3)_2$ (514) and $[4\text{-}BrC_6H_4Si(CH_3)_2]_2O$ (25) form di-Grignard reagents. These two compounds are also converted to the dinitriles in the usual way (309, 450). $4\text{-}BrC_6H_4Si(CH_3)_3$ and $4\text{-}BrC_6H_4Si(C_6H_5)_3$ with lithium dimethylformamide in ether give $3\text{-}(CH_3)_2NC_6H_4Si(CH_3)_3$ and $3\text{-}(CH_3)_2NC_6H_4Si(C_6H_5)_3$; this meta rearrangement is also observed with other organic compounds (194, 195).

Bromophenyl silicon compounds undergo silicon–carbon cleavage with reagents that are known to give the same reaction with unsubstituted phenyl groups. With bromine water at 150°C. $4\text{-}BrC_6H_4SiCl_3$ and $2,4\text{-}Br_2C_6H_3SiCl_3$ give 1,4-dibromobenzene and 1,2,4-tribromobenzene, respectively (548). With 71 per cent nitric acid in refluxing acetic anhydride $4\text{-}BrC_6H_4\text{—}$ groups are readily cleaved (102, 553). With molar amounts of aluminum chloride and of phosphorus pentachloride $4\text{-}BrC_6H_4\text{—}$ groups are also readily cleaved (549, 551).

The few silicon-functional reactions of bromophenyl silicon compounds that are known resemble those of the chlorophenyls. $4\text{-}BrC_6H_4SiCl_3$ can be completely alkylated with Grignard reagents (225), and it can be alcoholyzed to alkoxides (224). $4\text{-}BrC_6H_4Si(CH_3)_2OC_2H_5$ gives a 92 per cent yield of disiloxane on being stirred 3 hr. in benzene solution mixed with 75 per cent sulfuric acid (309).

The dipole moment of $4\text{-}BrC_6H_4Si(CH_3)_3$ is known (400).

VIII. IODO COMPOUNDS (SEE TABLE 5)

The principal method for making iodoalkyl silicon compounds is the reaction of chloroalkyl silicon compounds with sodium iodide in refluxing anhydrous acetone; 70–90 per cent yields of $ICH_2Si(CH_3)_3$ (538), $ICH_2Si(CH_3)_2OSi(CH_3)_3$ (383), $ICH_2Si(CH_3)_2CH_2Si(CH_3)_3$ (433), and $CH_3CHISi(CH_3)_3$ (425) are obtained. A detailed kinetic study of this reaction made with $ClCH_2Si(CH_3)_3$, $ClCH_2Si(CH_3)_2OSi(CH_3)_3$, and $ClCH_2\underbrace{Si(CH_3)[OSi(CH_3)_2]_3O}$ (122) has been discussed with the chemistry of these compounds.

Another method of making iodoalkyl silicon compounds involves adding gaseous hydrogen iodide to unsaturated alkyls. $CH_2{=}CHSi(CH_3)_3$ gives $ICH_2\text{-}$

TABLE 5

Silicon-containing iodo compounds

Compound	Boiling Point	n_D	d	References
	°C.			
$ICH_2Si(CH_3)_3$	140/744 mm.	1.4917 (20°)	1.4431 (20°)	(122, 406, 416, 436, 437, 445, *538*)
$ICH_2Si(CH_3)_2C_6H_5$	131/14 mm.	1.5749 (20°)	1.453 (20°)	(416, 437)
$(ICH_2)_2Si(CH_3)_2$	115/15 mm.	1.5941 (20°)	2.072 (20°)	(373)
$ICH_2Si(CH_3)_2CH_2Si(CH_3)_3$	98/15 mm.	1.4945 (20°)	1.257 (20°)	(406, *433*)
$ICH_2Si(CH_3)_2OSi(CH_3)_3$	187/757 mm. 77/20 mm.	1.4575 (20°)		(122, *383*)
$ICH_2\underline{Si(CH_3)[OSi(CH_3)_2]_3O}$				(122)
$CH_3CHISi(CH_3)_3$	156/729 mm.	1.4941 (20°)	1.3862 (20°)	(425)
$CH_2ICH_2Si(CH_3)_3$	76–76.5/27 mm.	1.5008 (20°)	1.3862 (20°)	(425)
$CH_3CHICH_2Si(CH_3)_3$	57/6 mm.	1.496 (20°)		(446)
$(IC_6H_4)_2SiCl_2$				(377)
$4\text{-}IC_6H_4Si(C_2H_5)_3$	165/13 mm.	1.5623 (20°)	1.3304 (20°)	(225)
$[\text{—}Si(IC_6H_4)_2O\text{—}]_x$				(377)

$CH_2Si(CH_3)_3$ in 65 per cent yield (425), and $CH_2{=}CHCH_2Si(CH_3)_3$ gives $CH_3CHICH_2Si(CH_3)_3$ in 50 per cent yield (446).

The few known displacement reactions of the iodoalkyl silicon compounds are very much like those of their chloro analogs. $ICH_2Si(CH_3)_2OSi(CH_3)_3$ easily forms a Grignard reagent (383). $ICH_2Si(CH_3)_3$ condenses with ethyl sodioacetoacetate like an ordinary alkyl halide (437). Amination of $ICH_2Si(CH_3)_3$ gives $NH[CH_2Si(CH_3)_3]_2$ (445). $ICH_2Si(CH_3)_2CH_2Si(CH_3)_3$ reacts smoothly with ethyl sodiomalonate (433). Metallic dehalogenation of $(ICH_2)_2Si(CH_3)_2$ gives no silacyclopropane. With magnesium in refluxing ether it gives polymeric products probably containing silethylene bridges (373). With zinc in refluxing ethanol it is reduced to $(CH_3)_4Si$ in 87 per cent yield (373). $ICH_2Si(CH_3)_3$ is inert to boiling alcoholic silver nitrate for 5 min.; this is unusual in view of the known reactivity of all alkyl iodides, even neopentyl iodide, with this reagent (383, 538). $ICH_2Si(CH_3)_2OSi(CH_3)_3$ gives a precipitate with alcoholic silver nitrate in a few minutes at room temperature (383).

The silicon–carbon cleavage reactions of iodoalkyl silicon compounds are similar to those of their chloro analogs. The iodine in $ICH_2CH_2Si(CH_3)_3$ titrates completely with dilute alkali at room temperature, while that in $CH_3CHISi(CH_3)_3$ is inert (425). $ICH_2CH_2Si(CH_3)_3$ is quite unstable; on standing it gives iodine as one decomposition product (425). $CH_3CHICH_2Si(CH_3)_3$ fumes in air and readily decomposes on heating above 75°C. or on treatment with dilute alkali or aluminum chloride; on being heated at 80°C. for 30 min. it gives a 55 per cent yield of propylene and a 46 per cent yield of $(CH_3)_3SiI$ (446).

The only known iodo aromatic derivative is $4\text{-}IC_6H_4Si(C_2H_5)_3$, which is obtained in 82 per cent yield by the iodination of $BrMgC_6H_4Si(C_2H_5)_3$ (225). Refluxing $C_6H_5Si(CH_3)_3$ with iodine gives iodobenzene and $(CH_3)_3SiI$ (370a). The iodination of other aromatic silicon compounds is briefly described (377).

IX. HYDROXY COMPOUNDS (SEE TABLE 6)

A. ALCOHOLS

1. *Syntheses*

Hydroxyalkyl silicon compounds are obtained principally by three methods: (*1*) hydrolysis of esters; (*2*) reaction of silicon-containing Grignard reagents with oxygenated compounds; (*3*) hydrolysis of siloxyalkylsilanes.

One of the oldest carbon-functional silicon compounds is an alcohol prepared by hydrolysis of an acetate ester. In 1866 Friedel and Crafts carried out the following reaction sequence (157, 158):

$$(C_2H_5)_4Si \xrightarrow{Cl_2} (C_2H_5)_3SiC_2H_4Cl \xrightarrow{CH_3COOK}$$

$$(C_2H_5)_3SiC_2H_4OCOCH_3 \xrightarrow{\text{alc. KOH}} (C_2H_5)_3SiC_2H_4OH$$

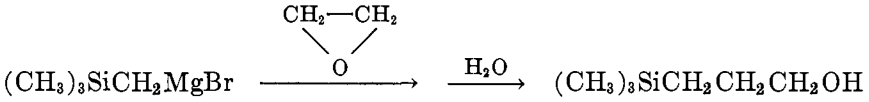
seventy-four years later these experiments were repeated and confirmed (342).

The hydroxymethyl silicon compounds are still prepared via ester hydrolysis, since direct hydrolysis of the halomethyl compounds has not been fruitful (240). Good yields of acetates are obtained from the chloro compounds, but with siloxanes the potassium acetate–acetic acid reagent also produces a rearrangement of the siloxane linkages. Generally the acetates are converted to alcohols by a slow hydrolysis at room temperature with a trace of acid (461, 466, 467, 481, 482, 483). Polymeric hydroxymethylsiloxanes and a series of α,ω-alcohols are also obtained via this route (341, 457, 458, 481).

$$(CH_3)_2Si(CH_2Cl)_2 \xrightarrow[CH_3COOH]{CH_3COOK} (CH_3)_2Si(CH_2OCOCH_3)_2 \xrightarrow[H^+ \text{ (trace)}]{CH_3OH}$$

$$(CH_3)_2Si(CH_2OH)_2$$

Silicon-containing Grignard reagents add to various oxygenated compounds, producing simple aliphatic alcohol and benzyl alcohol derivatives (224, 240, 413, 447, 540, 542). These reactions are straightforward and the yields are usually good. When organometallic compounds in which the metal is attached directly to silicon react with carbonyl compounds, Si—O—C bonds rather than Si—C bonds are formed. Thus $(C_6H_5)_3SiK$ reacts with benzophenone to form $(C_6H_5)_3SiOCH(C_6H_5)_2$ (203).



$$(CH_3)_3SiCH_2MgBr \xrightarrow{\text{CH}_2\text{—CH}_2\text{(O)}} \xrightarrow{H_2O} (CH_3)_3SiCH_2CH_2CH_2OH$$

Hydrolysis of siloxyalkylsilanes provides a very convenient synthetic route to silicon-containing alcohols in which the hydroxyl group is further removed than the beta carbon atom from silicon (465, 478). The key to this method of pre-

$$Cl(CH_2)_3OH \xrightarrow{(CH_3)_3SiCl} Cl(CH_2)_3OSi(CH_3)_3 \xrightarrow[(CH_3)_3SiCl]{Na}$$

$$(CH_3)_3Si(CH_2)_3OSi(CH_3)_3 \xrightarrow{H_2O} (CH_3)_3Si(CH_2)_3OH$$

TABLE 6

Silicon-containing hydroxy compounds

Compound	Melting Point	Boiling Point	n_D	d	References
	°C.	°C.			
Alcohols:					
$HOCH_2Si(CH_3)_3$		122/751 mm.	1.4169 (25°)	0.8261 (25°)	(423, 467, *482*)
Phenylurethan					
3,5-Dinitrobenzoate	70				
Aluminum and sodium salts					
$(HOCH_2)_2Si(CH_3)_2$		130/27 mm.	1.4611 (25°)	0.993 (115°)	(467, *481*, 515)
Polyurethans					(457)
$HOCH_2Si(CH_3)_2OSi(CH_3)_2$					(458)
$[HOCH_2Si(CH_3)_2]_2O$	−5		1.4358 (25°)	0.979 (25°)	(457, 458, *483*)
Bis-3,5-dinitrobenzoate	118.5–119				(483)
Polyurethans					(457)
Hydroxymethylsiloxanes					(341, 458, 467)
$HOC(C_6H_5)_2Si(C_5H_5)_3$					(203)
$[HO(CH_2)_2SiO_{1.5}]_x$					(141)
$HOC_2H_4Si(C_2H_5)_3$		190			(157, 158, *342*)
$HO(CH_2)_3Si(CH_3)_3$		83/27 mm.	1.4290 (20°)	0.8316 (20°)	(404, 407, 412, 413, 417, *447*, *465*, 478)
		82/24 mm.	1.4250 (25°)	0.822 (25°)	
Adipic ester		101/25 mm.	1.4370 (25°)	0.839 (25°)	
Chloromagnesium salt					
$HO(CH_2)_3Si(C_2H_5)(CH_3)_2$		101/25 mm.	1.4370 (25°)	0.839 (25°)	(*465*, 478)
$CH_3CHOHCH_2Si(CH_3)_3$		48/10 mm.	1.4281 (20°)	0.8309 (20°)	(540)
$[HO(CH_2)_3]_2Si(CH_3)_2$		176/24 mm.	1.4649 (25°)	0.940 (25°)	(*465*, 478)
$HO(CH_2)_4Si(CH_3)_3$		96/25 mm.	1.4315 (25°)	0.830 (25°)	(*465*, 478)
$(CH_3)_2COHCH_2Si(CH_3)_3$		92/98 mm.	1.4984 (27°)	0.9380 (27°)	(240)
$(CH_3)_2COHCH_2Si(CH_3)_2C_6H_5$	10	118/3 mm.	1.5058 (20°)	0.9457 (20°)	(437)
$HO(CH_2)_5Si(CH_3)_3$	4	85/8 mm.	1.4371 (20°)	0.8358 (20°)	(*447*, *465*, 478)
		110/25 mm.	1.4358 (25°)	0.841 (25°)	
$HO(CH_2)_5Si(C_2H_5)(CH_3)_2$		124/4 mm.	1.4421 (25°)	0.838 (25°)	(*465*, 478)
$(CH_3)_2COH(CH_2)_2Si(CH_3)_3$	13	48/4 mm.	1.4315 (20°)	0.8255 (20°)	(437)
$C_6H_5CHOHCH_2Si(CH_3)_3$		104	1.4984 (27°)	0.9380 (27°)	(240)
$4\text{-}HOC_6H_{10}Si(CH_3)_3$	58				(*465*, 476, 477)
	77				
$HOCH_2CH_2CH(CH_3)CH_2CHCH(CH_3)CH_2Si(CH_3)_3$		120–125/5 mm.	1.4480 (20°)	0.8315 (20°)	(359)
$4\text{-}HOCH_2C_6H_4Si(C_6H_5)_3$	54–55				(62)
$C_5H_5COH[C_6H_4Si(C_6H_5)_{3-4}]_2$	290				(185)
Acyloxyalkyl derivatives: see table 13					

Hydroxyalkylaryls:					
$(HOCH_2C_6H_4)_2Si(OC_2H_5)_2$		200–210/15 mm.			(148)
4-$CH_3CHOHC_6H_4Si(CH_3)_3$					(542)
4-$CH_3CHOHC_6H_4Si(C_2H_5)_3$		174/15 mm.		0.9596 (20°)	(224)
4-$CH_3CH_2CHOHC_6H_4Si(C_2H_5)_3$		185/17 mm.		0.9575 (20°)	(224)
4-$CH_3(CH_2)_2CHOHC_6H_4Si(C_2H_5)_3$		200/21 mm.		0.9491 (20°)	(224)
4-$(CH_3)_2CHCHOHC_6H_4Si(C_2H_5)_3$		191/18 mm.		0.9512 (20°)	(224)
Hydroxyalkoxyaryls: see table 7					
Phenols:					
2-$HOC_5H_4Si(CH_3)_3$	9	113/26 mm.	1.515 (25°)	0.966 (25°)	(198, *465*, 470, 480)
3,5-Dinitrobenzoate	124				
3-$HOC_6H_4Si(CH_3)_3$		70/1 mm.	1.5190 (20°)	0.977 (20°)	(38)
4-$HOC_6H_4Si(CH_3)_3$	74				(38, 164, 198, *465*, 470, 480)
3,5-Dinitrobenzoate	143				
1-Naphthylurethan	155				
4-$HOC_6H_4Si(C_2H_5)(CH_3)_2$	33	148/24 mm.			(*465*, 470, 480)
(4-$HOC_6H_4)_2Si(CH_3)_2$	171				(*465*, 469, 470, 480)
4-HO-2-$CH_3C_6H_4Si(CH_3)_2$	51				(*465*, 470, 480)
4-Nitrobenzoate	129				
(4-HO-3-$CH_3C_6H_3)_2Si(CH_3)_2$	209				(*465*, 470, 480)
(4-HO-2-$CH_3C_6H_3)_2Si(CH_3)_2$	209				(*469*, 473)
4-HO-3-$C_5H_6C_6H_3Si(CH_3)_3$		198/25 mm.			(470, 480)
Silylphenol–formaldehyde copolymer					(470, 480)
2-HO-1-$C_{10}H_6Si(CH_3)_3$		127/0.5 mm.	1.5569 (20°)	1.002 (20°)	(*489*, 490)
2-HO-6-$C_{10}H_5Si(CH_3)_3$	108				(*489*, 490, 491)
Azo derivatives					(490, 491)
2-HO-6-$C_{10}H_6Si(C_6H_5)_2$	140				(*489*, 490, 491)
Azo derivatives					(490, 491)

paration lies in protecting the hydroxyl group during the organometallic coupling required to establish the silicon–carbon bond and, once this bond is formed, hydrolyzing the protecting group to regenerate the alcohol. A related preparation of silicon-containing alcohols is found in an interesting rearrangement reaction which occurs when certain chloroalkoxysilanes are treated with active metals (465).

$$(CH_3)_3SiO(CH_2)_4Cl \xrightarrow{Li} \xrightarrow{H_2O} (CH_3)_3Si(CH_2)_4OH$$

Among other methods that have been used for making silicon-containing alcohols are: the reaction of a silicon-containing ester with a Grignard reagent (437); the reaction of a bromoaryl alcohol with 2 moles of a lithium alkyl, followed by coupling with a chlorosilane and hydrolysis (185); the addition of silicon tetrachloride to ethylene, followed by hydrolysis (141).

2. Chemical properties

Hydroxyalkyl silicon compounds exhibit many of the reactions of their purely organic alcohol counterparts, particularly in those reactions involving the oxygen–hydrogen bond. Esters and urethans may be prepared (465, 482), and halides are readily obtained from higher alcohols with hydrochloric acid or phosphorus tribromide (185, 413, 437, 447). With phenyl isocyanate $HOCH_2Si(CH_3)_3$ reacts three times faster than methanol and six times faster than neopentyl alcohol; this result has been attributed to the greater electronegativity of the $—CH_2Si(CH_3)_3$ group (482). Cyanoethylation of $HOCH_2Si(CH_3)_3$ proceeds normally (423).

A number of silicon–carbon cleavage reactions have been observed in silicon-containing alcohols. Thus, while $HOCH_2Si(CH_3)_3$ can be recovered from basic solution or after heating with ethanol, the presence of oxygen substituents on the silicon promotes cleavage of the hydroxymethyl group (482, 483). Extensive silicon–carbon cleavage is observed in compounds which can form a beta carbonium ion (450). Alcohols in which the hydroxyl group is further removed from

$$(CH_3)_3SiCH_2CHOHCH_3 \xrightarrow[H_2SO_4]{10\%\ \text{warm}} (CH_3)_3SiOSi(CH_3)_3 + CH_2{=}CHCH_3$$

silicon do not readily undergo cleavage with acid reagents.

3. Other properties

The surface properties of some short-chain α,ω-hydroxymethylsiloxanes have been examined (341). Force area measurements of these silicone films on water show that at low pressures the molecule lies flat on the water surface, but at pressures of 10 dynes cm.$^{-1}$ the siloxane lifts out of the water, the molecule being anchored by the alcohol groups. Because of the small lateral adhesion the molecules do not undergo close packing, even at pressures of 25 dynes cm.$^{-1}$ These alcohols have lower coefficients of friction than the corresponding dimethylsiloxanes.

Trimethylsilylmethanol exhibits antiseptic properties (467). Hydroxymethylsiloxanes possess antifoam properties (467), form tough resilient coatings when heated (467), and also form polyurethans with isocyanates (457, 458). The diacetate esters of difunctional silicon-containing alcohols form polyesters with dibasic acids (464).

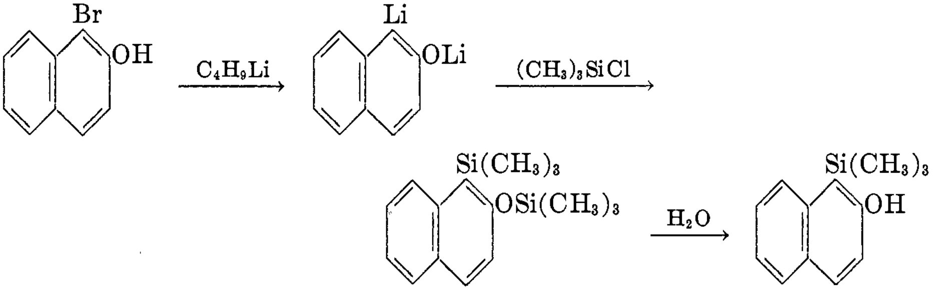
B. PHENOLS

Silicon-substituted phenols are prepared by the hydrolysis of siloxyphenylsilanes with a trace of acid or base (38, 164, 465, 469).

$$ClC_6H_4OH \xrightarrow{(CH_3)_3SiCl} ClC_6H_4OSi(CH_3)_3 \xrightarrow[(CH_3)_3SiCl]{Na}$$

$$(CH_3)_3SiC_6H_4OSi(CH_3)_3 \xrightarrow{H_2O} (CH_3)_3SiC_6H_4OH$$

As in the previously described alcohol synthesis, the main features of the method are the protection of the phenolic group during the Wurtz coupling and the subsequent easy removal of the protecting group by hydrolysis. This procedure is not satisfactory for preparing hydroxyphenylsiloxanes (465). Silicon-substituted naphthols (489), but not phenols (198), are obtained by the following reaction sequence.



Hydroxyaryl silicon compounds show a number of typical phenol reactions—formation of urethan and ester derivatives (465), condensation with formaldehyde (470, 480), coupling with diazonium salts (489, 490), and formation of methyl ethers (489). Certain silicon-containing naphthols do not give a ferric chloride test (489).

The hydroxyphenyl group is cleaved from silicon by hot acids and bases (465, 489). However, $4\text{-}HOC_6H_4Si(CH_3)_3$ remains unchanged on standing six months in basic solution at room temperature (465). An interesting rearrangement takes place when $4\text{-}HOC_6H_4Si(CH_3)_3$ is heated above 150°C.; this reaction does not occur with analogous alcohols (465).

$$4\text{-}HOC_6H_4Si(CH_3)_3 \xrightarrow{\text{heat}} (CH_3)_3SiOC_6H_5$$

The apparent ionization constants of $3\text{-}HOC_6H_4Si(CH_3)_3$ and $4\text{-}HOC_6H_4Si(CH_3)_3$ are 11.01 and 10.64, respectively, compared to 10.85 for phenol itself (38). Hammett σ constants for the $(CH_3)_3Si—$ group are -0.08 in the meta isomer and $+0.07$ in the para isomer. These data point to slight electron release by the

$(CH_3)_3Si$— group in the meta position and weak electron attraction by the same group in the para position. The findings are consistent with the concept that silicon can expand its octet when an electron donor is present, i.e.,

$$HOC_6H_4Si(CH_3)_3 \leftrightarrow H\overset{+}{O}{=}C_6H_4{=}\overset{-}{Si}(CH_3)_3$$

a form of resonance which cannot occur in the meta compound (38).

Silicon-containing phenol–formaldehyde resins have been reported (470, 480). Some of the bisphenols are active bactericides (469). Dyes have been obtained from some of the naphthols (489, 490).

X. ETHERS (SEE TABLE 7)

Carbon-functional silicon compounds containing ether linkages of the type C—O—C or Si—O—C are considered in this section.

A. SYNTHESES

The two principal methods for preparing C—O—C ethers involve (*1*) application of the Williamson synthesis to silicon-containing alkyl halides or (*2*) coupling organometallic derivatives of organic ethers with chlorosilanes or other silicon-functional compounds.

The Williamson synthesis has been used most extensively with chloromethyl silicon compounds and good yields are obtained with the lower alcohols (451,

$$(CH_3)_3SiCH_2Cl \xrightarrow[CH_3OH]{NaOCH_3} (CH_3)_3SiCH_2OCH_3$$

463). This method is less satisfactory with siloxanes because of the greater susceptibility of the chloromethyl group toward silicon–carbon cleavage in these compounds. However, this procedure can be used satisfactorily with (chloromethyl)alkoxysilanes; the best yields are obtained when the alcohol of the alkoxy group and of the sodium alkoxide are the same (59).

$$(C_2H_5O)_3SiCHClCH_3 \xrightarrow[C_2H_5OH]{NaOC_2H_5} (C_2H_5O)_3SiCH(OC_2H_5)CH_3$$

In the other principal method for synthesizing C—O—C silicon-containing ethers the lithium, magnesium, and sodium derivatives of purely organic ethers are coupled with various silicon-functional compounds, particularly chlorosilanes. Thus the sodium coupling of CH_3OCH_2Cl with $(CH_3)_3SiCl$ produces $CH_3OCH_2Si(CH_3)_3$ (463). The easy preparation of lithium and Grignard reagents from alkoxyaryl compounds, such as anisole, has resulted in their extensive use and good yields can be obtained (38, 43, 144, 148, 164, 184, 189, 193, 198, 201, 252, 324, 378, 489, 534). When organolithium compounds are used, silicon hydrides

$$(C_2H_5)_3SiCl + 4\text{-}LiC_6H_4OCH_3 \rightarrow (C_2H_5)_3SiC_6H_4OCH_3$$

or alkoxides may be employed instead of the more reactive chlorosilanes (201). In connection with the study of steric effects on the preparation of tetraarylsilanes by organometallic couplings, it is interesting to note that *o*-methoxyphenylsilanes are formed with surprising ease compared to the corresponding *o*-tolyl compounds (201).

An isolated example of a different type of synthesis for C—O—C silicon-containing ethers is the cyanoethylation of $HOCH_2Si(CH_3)_3$ under standard conditions to form $CNCH_2CH_2OCH_2Si(CH_3)_3$ (423).

The principal method for the synthesis of Si—O—C carbon-functional ethers involves the sodium coupling of chlorosilanes with siloxy-substituted alkyl halides (465, 472, 473, 474, 478). With aliphatic compounds the reaction is successful when the chlorine and the siloxy group are separated by more than two carbon atoms (465). With aromatic compounds good yields are obtained

$$(CH_3)_3SiO(CH_2)_3Cl + ClSi(CH_3)_3 \xrightarrow{Na} (CH_3)_3SiO(CH_2)_3Si(CH_3)_3$$

when the alkyl substituents of the chlorosilane and the siloxy group are the same (465). However, when these groups are different, complications arise be-

$$(CH_3)_3SiCl + 4\text{-}ClC_6H_4OSi(CH_3)_3 \rightarrow 4\text{-}(CH_3)_3SiC_6H_4OSi(CH_3)_3$$

cause of rearrangement, which is sometimes complete (465).

$$(C_2H_5)(CH_3)_2SiCl + 2\text{-}ClC_6H_4OSi(CH_3)_3 \rightarrow 2\text{-}(C_2H_5)(CH_3)_2SiOC_6H_4Si(CH_3)_3$$

Another synthesis of Si—O—C carbon-functional ethers is found in the formation of $(CH_3)_3SiOCH_2Si(CH_3)_3$ in excellent yield from the reaction of $(CH_3)_3SiCl$ with $HOCH_2Si(CH_3)_3$ in the presence of quinoline (482).

B. PROPERTIES

Few typical ether reactions of carbon-functional silicon ethers are known. Among the C—O—C compounds methoxyarylsilanes do not cleave to phenols with sodium in pyridine (198), but they do undergo metalation with the usual reagents (184). The ready hydrolyzability of the Si—O—C ethers provides the basis for their use in the preparation of silicon-containing alcohols and phenols (465). The siloxyaryl ethers also undergo reduction of the aromatic ring (465, 476).

The influence of the C—O—C group on silicon–carbon bond stability is shown by a number of observations. That the aliphatic compounds $ROCH_2Si(CH_3)_3$ are stable toward basic reagents is indicated by their preparation in strongly alkaline solution (451). Considerable acid stability as well is indicated by the hydrolysis of $CNCH_2CH_2OCH_2Si(CH_3)_3$ to $HOOCCH_2CH_2OCH_2Si(CH_3)_3$ with concentrated hydrochloric acid in glacial acetic acid (423).

More detailed information is available on silicon–carbon bond stability in aromatic C—O—C ethers. Those of the type $CH_3OC_6H_4Si\equiv$ appear to be fairly stable in base (186), but the methoxyl group accelerates silicon–phenyl cleavage by acid (39, 193). This cleavage has been studied kinetically (139). The reaction is first order in silane, and for a given solvent the rate is governed by the acidity function of the system. This indicates the rapid formation of a protonated intermediate (step 1). The variation in the rate constant with water

TABLE 7

Silicon-containing ethers

Compound	Melting Point	Boiling Point	n_D	*d*	References
	°C.	*°C.*			
Alkoxyalkyls:					
$CH_3OCH_2Si(CH_3)_3$		83/740 mm.	1.3878 (25°)	0.7576 (25°)	(*451*, 463)
$C_3H_5OCH_2Si(CH_3)_3$		102/739 mm.	1.3915 (25°)	0.761 (25°)	(*383*, *451*, 463)
			1.3940 (20°)		
$C_3H_7OCH_2Si(CH_3)_3$		124	1.3957 (25°)	0.764 (25°)	(463)
$C_4H_9OCH_2Si(CH_3)_3$		150/738 mm.	1.4038 (25°)	0.774 (25°)	(*451*, 463)
$HOOCCH_2CH_2OCH_2Si(CH_3)_3$		116–117/8 mm.	1.4300 (20°)		(423)
$CNCH_2CH_2OCH_2Si(CH_3)_3$		98/20 mm.	1.4245 (20°)		(423)
$CH_3CH(OCH_3)Si(OCH_3)_3$		157	1.3952 (25°)	0.9936 (25°)	(59)
$CH_3CH(OCH_3)Si(OC_2H_5)_2OCH_3$		178	1.3979 (25°)	0.9543 (25°)	(59)
$CH_3CH(OCH_3)Si(OC_3H_7)_3$		86/1 mm.	1.4084 (25°)	0.9124 (25°)	(59)
$CH_3CH(OCH_3)Si(OC_4H_9)_2OCH_3$		84/1 mm.	1.4131 (25°)	0.9253 (25°)	(59)
$CH_3CH(OCH_3)Si(OC_4H_9)_3$		114/2 mm.	1.4178 (25°)	0.9051 (25°)	(59)
$CH_3CH(OC_2H_5)Si(OC_2H_5)_3$		129/94 mm.	1.4000 (25°)	0.9237 (25°)	(59)
$CH_3CH(OC_2H_5)Si(OC_5H_{11})_3$		123/1 mm.	1.4219 (25°)	0.8863 (25°)	(59)
$CH_3CH(OC_3H_7)Si(OC_3H_7)_3$		123/10 mm.	1.4112 (25°)	0.8975 (25°)	(59)
$(C_2H_5O)_2CHCH_2CH_2Si$ compounds					(30)
$CH_2{=}CH_2$- - -$(C_2H_5O)_4Si$ telomer					(227)
Siloxyalkyls:					
$(CH_3)_3SiOCH_2Si(CH_3)_3$		130/738 mm.	1.3971 (25°)	0.7781 (25°)	(482)
$(CH_3)_3SiO(CH_2)_3Si(CH_3)_3$		81/25 mm.	1.4120 (25°)	0.796 (25°)	(465)
$C_2H_5(CH_3)_2SiO(CH_2)_3Si(C_2H_5)(CH_3)_2$		115/25 mm.	1.4251 (25°)	0.817 (25°)	(*465*, 478)
$(CH_3)_3SiO(CH_2)_4Si(CH_3)_3$		94/24 mm.	1.4166 (25°)	0.802 (25°)	(465)
$(CH_3)_3SiO(CH_2)_5(CH_3)_3$		112/24 mm.	1.4200 (25°)	0.804 (25°)	(465)
$C_2H_5(CH_3)SiO(CH_2)_5Si(C_2H_5)(CH_3)_2$		140/24 mm.	1.4328 (25°)	0.826 (25°)	(*465*, 478)
4-$(CH_3)_3SiOC_6H_{10}Si(CH_3)_3$		115/23 mm.	1.4409 (25°)	0.854 (25°)	(*465*, 476)
		120/23 mm.	1.4427 (25°)	0.857 (25°)	(465, 476)
Alkoxyaryls:					
4-$CH_3OC_5H_4SiCl_3$		129/13 mm.		1.46 (20°)	(252)
4-$CH_3OC_6H_4SiBr_3$	21–22	147/1 mm.	1.5958 (25°)	1.9089 (25°)	(*324*, 372)
4-$CH_3OC_5H_4Si(C_6H_5)_2Cl$		191/1 mm.			(189)
4-$CH_3OC_6H_4Si(C_6H_5)_2H$		184/1.5 mm.			(189)
2-$CH_3OC_5H_4Si(CH_3)_3$		206/733 mm.	1.5055 (20°)	0.9587 (20°)	(198)
		92/15 mm.			
3-$CH_3OC_5H_4Si(CH_3)_3$		216/751 mm.	1.5020 (20°)	0.9383 (20°)	(39)
4-$CH_3OC_6H_4Si(CH_3)_3$		220/740 mm.	1.5014 (20°)	0.9398 (20°)	(*39*, 139, *198*)

$4-CH_3OC_5H_4Si(C_2H_5)_3$		103/0.2 mm.	1.5130 (20°)	0.9487 (20°)	(184)
$3-HOOC-4-CH_3OC_5H_3Si(C_2H_5)_3$	52–56				(184)
$4-CH_3OC_6H_4Si(CH_2C_6H_5)_3$	85				(186, *193*)
$4-CH_3OC_5H_4Si(C_5H_4CH_3-2)_2$	180				(201)
$2-CH_3O-4-BrC_6H_3SiCl_3$		135/13 mm.			(148)
$(4-CH_3OC_6H_4)_2SiH_2$	57–58.5				(534)
$(2-CH_3OC_5H_4)_3SiCl$	203				(201)
$(4-CH_3OC_6H_4)_3SiH$	76				(43)
$(2-CH_3OC_6H_4)_3SiOC_2H_5$	103				(201)
$(4-CH_3OC_6H_4)_3SiCH_3$	134				(43)
$(2-CH_3OC_6H_4)_3SiC_6H_4CH_3-2$	194				(201)
$(2-CH_3OC_6H_4)_4Si$	224				(201)
$(2-CH_3OC_6H_4)_3SiC_5H_4OCH_2-4$	179				(201)
Methoxyphenylsiloxanes					(177)
$4-C_2H_5OC_6H_4SiCl_3$		138/13 mm.		1.36 (20°)	(252)
$1-CH_3O-2-[(CH_3)_3Si]C_{10}H_6$		100/0.4 mm.	1.5802 (20°)	1.034 (20°)	(489)
$1-CH_3O-2-[(C_6H_5)_3Si]C_{10}H_6$	177				(489)
$2-CH_3O-1-[(CH_3)_3Si]C_{10}H_6$		109/0.4 mm.	1.5802 (20°)	1.030 (20°)	(489)
$2-CH_3O-3-[(CH_3)_3Si]C_{10}H_6$	59				(489)
$2-CH_3O-6-[(CH_3)_3Si]C_{10}H_6$	78				(489)
$2-CH_3O-1-[(C_6H_5)_3Si]C_{10}H_6$	166				(489)
$2-CH_3O-3-[(C_6H_6)_3Si]C_{10}H_6$	132				(489)
$2-CH_3O-6-[(C_6H_5)_3Si]C_{10}H_6$	168				(489)
Siloxyaryls:					
$2-[(CH_4)_4SiO]C_6H_4Si(CH_3)_2OC_2H_5$		142/24 mm.	1.4764 (20°)	0.946 (20°)	(465)
$4-[(CH_3)_3SiO]C_6H_4Si(CH_3)_2OC_2H_5$		152/25 mm.			(465, 474)
$2-[(CH_3)_3SiO]C_6H_4Si(CH_3)_3$		128/25 mm.	1.4830 (20°)	0.910 (20°)	(*465*, 470, 472, 474, 480)
$3-[(CH_3)_3SiO]C_6H_4Si(CH_3)_3$		60/2 mm.	1.4770 (20°)		(38)
$4-[(CH_3)_3SiO]C_6H_4Si(CH_3)_3$		132/25 mm.	1.4794 (20°)	0.900 (20°)	(164, 465, 470, 472, 476, 480)
$4-[(CH_3)_3SiO]C_6H_4Si(C_2H_5)(CH_3)_2$		144/23 mm.	1.4806	0.902	(465, *472*)
$(CH_3)_3SiOC_6H_3[Si(CH_3)_3]_2-2,4$		162/24 mm.	1.4843 (20°)	0.899 (20°)	(*465*, 472)
$2,4-[(CH_3)_3SiO]_2C_6H_3Si(CH_3)_3$		169/19 mm.	1.4772 (20°)	0.947 (20°)	(*465*, 472)
$[4-(CH_3)_3SiOC_6H_4]_2Si(CH_3)_2$		206/1.5 mm.	1.5139 (20°)	0.974 (20°)	(*465*, 470, *473*, 480)
$[2-(CH_3)_3SiOC_6H_4]_2Si(C_2H_5)_2$		241/24 mm.			(473)
$4-C_2H_6O(CH_3)_2SiOC_6H_4Si(CH_3)_2OC_2H_5$		168/25 mm.	1.4634 (20°)	0.957 (20°)	(*465*, 474, 476)
$4-C_2H_5O(CH_3)_2SiOC_5H_4Si(CH_3)_3$					(465)
$2-C_2H_5(CH_3)_2SiOC_6H_4Si(CH_3)_3$		144/23 mm.	1.4873 (20°)	0.9136 (20°)	(*465*, 472)
$4-C_2H_5(CH_3)_2SiOC_6H_4Si(C_2H_5)(CH_3)_2$		164/25 mm.	1.4841 (20°)	0.906 (20°)	(*465*, 470, 472, 480)
$4-(CH_3)_3SiO-2-CH_3C_6H_3Si(CH_3)_2OC_2H_5$					(474)
$4-(CH_3)_3SiO-2-CH_3C_5H_3Si(CH_3)_3$		148/24 mm.	1.4892 (20°)	0.916 (20°)	(*465*, 470, 472, 480)

TABLE 7—*Concluded*

Compound	Melting Point	Boiling Point	n_D	d	References
	°*C.*	°*C.*			
$[4\text{-}(CH_3)_3SiO\text{-}2\text{-}CH_3C_6H_3]_2Si(CH_3)_2$		252–276/1 mm.			(473)
$[4\text{-}(CH_3)_3SiO\text{-}3\text{-}CH_3C_6H_3]_2Si(CH_3)_2$					(*465*, 470, 480)
$2\text{-}(CH_3)_3SiO\text{-}3\text{-}C_5H_5C_6H_3Si(CH_3)_3$	62.9	200/24 mm.			(*465*, 472)
	71.6	200/24 mm.			(*465*, 472)
$4\text{-}(CH_3)_3SiO\text{-}3\text{-}C_6H_5C_6H_3Si(CH_3)_2OC_2H_5$					(474)
$4\text{-}(CH_3)_3SiO\text{-}3\text{-}C_6H_5C_5H_3Si(CH_3)_3$		195/21 mm.	1.5329 (20°)	0.974 (20°)	(*465*, 470, 472, 480)
$[4\text{-}(CH_3)_3SiO\text{-}3\text{-}C_6H_5C_6H_3]_2Si(CH_3)_2$					(473)
$R_3SiOC_5H_4SiR_3$					(471)
Hydroxyalkoxyaryls:					
$2\text{-}HO(CH_2)_2OC_5H_4Si(CH_3)_3$		106/1 mm.	1.5157 (25°)	1.01 (25°)	(*465*, 468)
$4\text{-}HO(CH_2)_2OC_6H_4Si(CH_3)_3$		130/1 mm.	1.514 (25°)	1.01 (25°)	(*465*, 468)
$4\text{-}CH_3CHOHCH_2OC_5H_4Si(CH_3)_3$	63	283/747 mm.			(*465*, 468)
Siloxyalkoxyaryls:					
$2\text{-}(CH_3)_3SiOCH_2CH_2OC_6H_4Si(CH_3)_3$		166/24 mm.	1.4818 (25°)	0.945 (25°)	(*465*, 468)
$4\text{-}(CH_3)_3SiOCH_2CH_2OC_6H_4Si(CH_3)_3$		172/24 mm.	1.4827 (25°)	0.935 (25°)	(*465*, 468)
$4\text{-}(CH_3)_3SiOCH(CH_3)CH_2OC_6H_4Si(CH_3)_3$		179/24 mm.	1.4770 (25°)	0.922 (25°)	(*465*, 468)
Phenoxyphenyls:					
$4\text{-}C_6H_5OC_6H_4Si(C_5H_5)_3$	125				(198)
$(C_5H_5OC_5H_4)_2SiCl_2$					(378)
Phenoxyphenylsiloxanes					(177, 378)
$[4\text{-}C_6H_5(CH_3)_2SiC_6H_4]_2O$	−8	249/2.5 mm.			(115)

content of the solvent suggests that nucleophilic attack by water is the rate-determining step (step 2).

$$(CH_3)_3SiC_6H_4OCH_3 + H^+ \underset{\text{step 1}}{\overset{\text{fast}}{\rightleftarrows}} (CH_3)_3Si\overset{+}{C}_6H_5{=}OCH_3$$

$$(CH_3)_3Si\overset{+}{C}_6H_5{=}OCH_3 + HOH \xrightarrow[\text{step 2}]{\text{slow}} (CH_3)_3SiOH_2^+ + C_6H_5OCH_3$$

$$(CH_3)_3SiOH_2^+ \rightarrow (CH_3)_3SiOSi(CH_3)_3 + HOH + H^+$$

Introducing a single *p*-methoxy group into triphenylsilane reduces by one-fourth its rate of reaction with moist piperidine (189). This is consistent with an S_N2 reaction in which substituents which increase the electron density at silicon decrease the rate of attack by negative ions.

Aliphatic ethers of the type $ROCH_2Si(CH_3)_3$ show a typical infrared absorption band at 1100 cm.$^{-1}$ (451). The infrared spectra of some methoxyarylsilanes have been reported (534). The large dipole moment of $4\text{-}CH_3OC_6H_4SiBr_3$ has been interpreted as revealing resonance interaction between the methoxyl group and the tribromosilyl group (372).

XI. AMINES (SEE TABLE 8)

A. ALIPHATIC DERIVATIVES

1. Syntheses

Aminomethyl silicon compounds are the most widely known members of this class. They are readily obtained by the reaction of chloromethyl silicon compounds with anhydrous amines in a manner that parallels the amination of alkyl halides. This synthesis is applicable not only to simple compounds, such as $ClCH_2Si(CH_3)_3$ (345), but also to more complex materials, such as $ClCH_2\text{-}Si(OC_2H_5)_3$ (345) as well as $ClCH_2Si(CH_3)_2OSi(CH_3)_3$ and

$$ClCH_2Si\underline{(CH_3)[OSi(CH_3)_2]_3O}$$

(181). In the latter cases the Si—O—C and Si—O—Si bonds are not disturbed, and compounds exemplified by $NH_2CH_2Si(OC_2H_5)_3$, $NH_2CH_2Si(CH_3)_2OSi(CH_3)_3$,

$$ClCH_2Si(OC_2H_5)_3 + NH_3 \rightarrow NH_2CH_2Si(OC_2H_5)_3$$

and $C_6H_5NHCH_2\underline{Si(CH_3)[OSi(CH_3)_2]_3O}$ are readily obtained in excellent yield. Symmetrical aminoalkyldisiloxanes may also be obtained indirectly by sulfuric acid cleavage of a methyl group from aminoalkyltrimethylsilanes (345, 444).

$$NH_2CH_2CH_2Si(CH_3)_3 \xrightarrow[H_2SO_4]{\text{concd.}} \xrightarrow{\text{NaOH}} [NH_2CH_2CH_2Si(CH_3)_2]_2O + CH_4$$

Other well-known amine syntheses may also be applied in preparing aminomethyl silicon compounds and higher aminoalkyl silicon compounds as well. These preparative methods are limited, however, to tetraorganosilanes, since

TABLE 8

Silicon-containing amines

Compound	Melting Point	Boiling Point	n_D	*d*	References
	°C.	*°C.*			
Aminomethyls:					
$NH_2CH_2Si(OC_2H_5)_3$		93/26 mm.	1.4080 (25°)	0.955 (25°)	(134, 344, *345*)
$NH[CH_2Si(OC_2H_5)_3]_2$		117/0.4 mm.	1.4132 (25°)	0.973 (25°)	(134, *345*)
$NH_2CH_2Si(CH_3)(OC_2H_5)_2$		68/24 mm.	1.4123 (25°)	0.915 (25°)	(134, 344, *345*)
$NH[CH_2Si(CH_3)_2OC_2H_5]_2$		160–170/24 mm.	1.433 (25°)	0.892 (25°)	(134, *345*)
$NH_2CH_2Si(CH_3)_2OC_2H_5$		132/740 mm.	1.411 (25°)	0.849 (25°)	(134, 344, *345*)
Hydrochloride	182–187				(134)
Cyclo-$C_6H_{11}NHCH_2Si(CH_3)_2OC_2H_5$		162/99 mm.	1.4488 (25°)	0.889 (25°)	(134, *345*)
$NH_2CH_2Si(CH_3)_3$		93/737 mm.	1.4139 (25°)	0.7646 (25°)	(134, 181, 344, *345*,
			1.4168 (20°)		*445*)
Water azeotrope		83/750 mm.	1.4161 (25°)	0.815 (25°)	(345)
Hydrochloride	243				(134, 345, 445)
Bicarbonate					(345)
Sulfate	216 (d.)				(134, *345*)
Phthalimide	23	117/2 mm.	1.5427 (20°)		(445)
Urea	78				(445)
p-Nitrobenzamide					(134)
Adipamide					(134)
$NH[CH_2Si(CH_3)_3]_2$		171/737 mm.	1.4267 (20°)	0.7864 (20°)	(134, 181, 344, *345*,
		90/57 mm.	1.4217 (25°)	0.773 (25°)	*445*)
Hydrochloride	159				(345)
	176				
$CH_3NHCH_2Si(CH_3)_3$		102/735 mm.	1.4094 (25°)	0.754 (25°)	(134, *345*)
Water azeotrope		83/735 mm.	1.4132 (25°)		(345)
Hydrochloride	198				(345)
$(CH_3)_2CHNHCH_2Si(CH_3)_3$		130/737 mm.	1.4141 (25°)	0.758 (25°)	(134, 344, *345*)
Hydrochloride	137				(345)
$C_4H_9NHCH_2Si(CH_3)_3$		165/atm.	1.4238 (20°)		(181)
		90/62 mm.			
$C_6H_5NHCH_2Si(CH_3)_3$		242/741 mm.	1.5213 (25°)	0.918 (25°)	(134, *181*, 344, *345*)
		119/12 mm.	1.5241 (20°)		
Hydrochloride	119–120				(134)
4-Nitrophenylazo derivative	89				(134)
Cyclo-$C_6H_{11}NHCH_2Si(CH_3)_3$		211/737 mm.	1.4519 (25°)	0.839 (25°)	(134, 344, *345*)
Hydrochloride	235–239				
Phenylthiourea	137				

$n\text{-}\mathrm{C_{18}H_{37}NHCH_2Si(CH_3)_3}$	26–32	194/2 mm.	1.4507 (26°)	0.815 (26°)	(134, *345*)
Hydrochloride	102				
$\mathrm{(CH_3)_2NCH_2Si(CH_3)_3}$		110/746 mm.	1.4102 (25°)	0.746 (25°)	(134, *345*)
Hydrochloride	186				
Methyl bromide	262				
Methyl iodide	242				
$\mathrm{(C_2H_5)_2NCH_2Si(CH_3)_3}$		145–150/atm.	1.4231 (20°)		(181)
$\mathrm{(CH_2)_5NCH_2Si(CH_3)_3}$		59/9 mm.	1.4519 (20°)		(181)
$\mathrm{NH_2CH_2Si(CH_3)_2C_6H_5}$		227/744 mm.	1.5202 (25°)	0.940 (25°)	(134, 344, *345*)
Hydrochloride	200				
$\mathrm{NH[CH_2Si(CH_3)_2C_6H_5]_2}$		215/23 mm.	1.5332 (25°)	0.958 (25°)	(134, *345*)
Hydrochloride	121–126				
$\mathrm{HOCH_2CH_2NHCH_2Si(CH_3)_3}$		101/24 mm.	1.4461 (25°)	0.883 (25°)	(134)
Hydrochloride	114–116				(134)
$\mathrm{NH_2CH_2Si(CH_3)_2OSi(CH_3)_3}$	−71	52/21 mm.	1.4105 (20°)	0.846 (20°)	(181)
$\mathrm{NH[CH_2Si(CH_3)_2OSi(CH_3)_3]_2}$		127/18 mm.	1.4143 (20°)	0.852 (20°)	(181)
$\mathrm{[NH_2CH_2Si(CH_3)_2]_2O}$					(344, *345*)
Dihydrochloride	249				
$\mathrm{[(CH_3)_2CHNHCH_2Si(CH_3)_2]_2O}$		245/737 mm.	1.4278 (25°)	0.850 (25°)	(344, *345*)
Dihydrochloride	180				
$\mathrm{[Cyclo\text{-}C_6H_{11}NHCH_2Si(CH_3)_2]_2O}$			1.4679 (25°)	0.922 (25°)	(344, *345*)
Dihydrochloride	228–232				
$\mathrm{—Si(CH_3)_2CH_2NHCH_2Si(CH_3)_2O—]_2}$	45–49	152/23 mm.			(*345*, 462)
$\mathrm{[—Si(CH_3)_2CH_2NHCH_2Si(CH_3)_2O—]_{\mathit{x}}}$			1.4488 (25°)	0.946 (25°)	(*345*, 462)
$\mathrm{[—Si(CH_3)(C_6H_5)CH_2NHCH_2Si(C_6H_5)(CH_3)O—]_{\mathit{x}}}$					(462)
$\mathrm{(CH_3)_2CHN[CH_2Si(CH_3)_2]_2O}$		188/737 mm. 117/95 mm.	1.4328 (25°)	0.875 (25°) 0.785 (25°)	(344, *345*, *462*)
$\mathrm{C_4H_9N[CH_2Si(CH_3)_2]_2O}$		98/11 mm.	1.4360 (20°)		(181)
$\mathrm{(CH_3)_2NCH_2}\underbracket{\mathrm{Si(CH_3)[OSi(CH_3)_2]_3O}}$		92–94/9 mm.			(181)
$\mathrm{(C_2H_5)_2NCH_2}\underbracket{\mathrm{Si(CH_3)[OSi(CH_3)_2]_3O}}$		80–87/1.5 mm.			(181)
$\mathrm{C_4H_9NHCH_2}\underbracket{\mathrm{Si(CH_3)[OSi(CH_3)_2]_3O}}$		75–94/0.5 mm.			(181)
$\mathrm{C_5H_5NHCH_2}\underbracket{\mathrm{Si(CH_3)[OSi(CH_3)_2]_3O}}$		122–127/0.5 mm.	1.4710 (20°)	1.042 (20°)	(181)
$\mathrm{C_6H_6(CH_3)NCH_2}\underbracket{\mathrm{Si(CH_3)[OSi(CH_3)_2]_3O}}$		126–136/1 mm.			(181)
Higher aminoalkyls:					
$\mathrm{NH_2(CH_2)_2Si(CH_3)_3}$		121/735 mm.	1.4244 (20°)		(404, 405, 411, 439, 444, *445*)
Hydrochloride	300				
$\mathrm{NH_2(CH_2)_2SiC_6H_5(CH_3)_2}$					(404)
Hydrochloride					

TABLE 8—*Continued*

Compound	Melting Point	Boiling Point	n_D	d	References
	°*C.*	°*C.*			
$[NH_2CH_2CH_2Si(CH_3)_2]_2O$		115/13 mm.	1.4473 (20°)	0.9075 (20°)	(344, 405, 439, *444*)
Dihydrochloride	267–268				
"$NH_2C_2H_5\cdot Si(C_6H_5)_3$"	45				(*44*, 288)
$NH_2(CH_2)_3Si(CH_3)_3$		145/726 mm.	1.4301 (20°)	0.7866 (20°)	(404, *445*)
Hydrochloride	184				
$(CH_3)_3SiCH_2CH_2CHNH_2CH_2CH_2Si(CH_3)_3$		115/15 mm.	1.4438 (20°)	0.8123 (20°)	(*415*, 418, 444)
Hydrochloride	131–131.5				(*415*, 418, 444)
$NH_2CH[CH_2CH_2Si(CH_3)_2OSi(CH_3)_3]_2$		98/2 mm.	1.4282 (20°)	0.8654 (20°)	(418, 444)
$[-Si(CH_3)_2(CH_2)_2CHNH_2(CH_2)_2Si(CH_3)_2O-]_x$					(418)
Aminoaryls:					
$4\text{-}H_2NC_6H_4Si(OC_2H_5)_3$		148/14 mm.			(148)
$4\text{-}(CH_3)_2NC_6H_4Si(OC_2H_5)_3$		145/2 mm.	1.5012 (25°)	1.012 (25°)	(148, *201*, 268)
Azo derivative					(268)
$3\text{-}(CH_3)_2NC_6H_4Si(C_6H_5)_2Cl$		185/0.2 mm.			(189)
$3\text{-}(CH_3)_2NC_6H_4Si(C_6H_5)_2H$		177/0.1 mm.			(189)
$4\text{-}(CH_3)_2NC_6H_4Si(C_6H_5)_2Cl$		228/2.5 mm.			(189)
$4\text{-}(CH_3)_2NC_6H_4Si(C_6H_5)_2OH$	66				(188, *200*)
$4\text{-}(CH_3)_2NC_6H_4Si(C_6H_5)_2H$		187/0.2 mm.			(189)
$2\text{-}H_2NC_6H_4Si(CH_3)_3$		101/10 mm.	1.5388 (20°)	0.952 (20°)	(34, *35*)
Acetyl derivative	131				
$3\text{-}H_2NC_6H_4Si(CH_3)_3$		111/10 mm.	1.5362 (20°)	0.947 (20°)	(*35*, 38, 488)
Acetyl derivative	115				
Diazonium chloride					
Azo-β-naphthol	95				
$4\text{-}H_2NC_6H_4Si(CH_3)_3$		113/10 mm.	1.5393 (20°)	0.947 (20°)	(*35*, 38, 400)
Acetyl derivative	170				
Diazonium chloride					
Azo-β-naphthol	95				
$2\text{-}(CH_3)_2NC_6H_4Si(CH_3)_3$		65/1 mm.	1.5080 (20°)	0.9324 (20°)	(490)
$3\text{-}(CH_3)_2NC_5H_4Si(CH_3)_3$		87/1 mm.	1.5257 (20°)	0.9124 (20°)	(38, 39, *195*, *490*, 491)
		59–60/0.4 mm.	1.5312 (25°)	0.9484 (20°)	
Azo derivatives					
Methyl iodide salt	195				(39)
$4\text{-}(CH_3)_2NC_6H_4Si(CH_3)_3$		136/20 mm.	1.5338 (20°)	0.9249 (20°)	(*38*, *39*, *193*, 195, 400, 490)
$3\text{-}(HOCH_2CH_2)_2NC_6H_4Si(CH_3)_3$	67–68				(*492*, 493)
Azo derivatives					

$H_2NC_5H_4Si(C_2H_5)_2$		285			(129)
Azo compound	78				
Hydrazo compound	121				
$3\text{-}H_2NC_6H_4Si(C_6H_5)_3$	248–251				(488)
$2\text{-}(CH_3)_2NC_6H_4Si(C_6H_5)_3$	96				(490)
$3\text{-}(CH_3)_2NC_6H_4Si(C_6H_5)_2$	96				(*194*, 490, 491)
Hydrochloride	211				
Picrate	204				
Azo derivatives					(*490*, 491)
$4\text{-}(CH_3)_2NC_6H_4Si(C_6H_5)_3$	146				(*200*, 490)
Hydrochloride	229				
$[4\text{-}(CH_3)_2NC_6H_4]_2Si(OH)_2$	174				(200)
$3\text{-}(HOCH_2CH_2)_2NC_6H_4Si(C_6H_5)_3$	127				(*492*, 493)
Azo derivatives					
$[4\text{-}(CH_3)_2NC_6H_4]_2Si(OC_2H_5)_2$	126	230/3 mm.	1.5765 (25°)	1.102 (25°)	(200, 201)
$(3\text{-}H_2NC_6H_4)_2Si(C_2H_5)_2$	90				(280)
Acetyl derivative	164				
$[4\text{-}(CH_3)_2NC_5H_4]_2Si(C_5H_5)_2$	181				(200)
$[4\text{-}(CH_3)_2NC_6H_4]_3SiCl$	213				(200)
$[4\text{-}(CH_3)_2NC_6H_4]_3SiOH$	184	278/12 mm.			(118, *148*, 188, 191, 197, *200*)
$[4\text{-}(CH_3)_2NC_5H_4]_3SiH$	157				(118, 197, *200*)
$[4\text{-}(CH_3)_2NC_6H_4]_3SiN(C_4H_9)_2$	63				(191)
$[4\text{-}(CH_3)_2NC_6H_4]_3SiC_5H_5$	173				(200)
$(3\text{-}H_2NC_6H_4)_4Si$	380 (d.)				(279)
Acetyl derivative	301				
$[4\text{-}(CH_3)_2NC_6H_4]_4Si$	235				(118, *200*)
$4\text{-}[\underline{C(CH_3)=CHCH=C(CH_3)N}]C_5H_4Si(C_6H_5)_3$					(192)
$4\text{-}H_2N\text{-}3\text{-}CH_3C_6H_3Si(C_2H_5)_3$		126–130	1.5382–1.5385 (20°)	0.944 (20°)	(42)
Acetyl derivative	66–67				(42)
$2\text{-}CH_3\text{-}5\text{-}H_2NC_6H_3Si(C_2H_5)_3$		123/2.5 mm.	1.5430 (20°)	0.9570 (20°)	(42)
Acetyl derivative	105				(42)
$3\text{-}H_2N\text{-}4\text{-}CH_3C_6H_3Si(C_2H_5)_3$		109/0.5 mm.	1.5350 (20°)	0.944 (20°)	(42)
Acetyl derivative	65–66				(42)
$H_2N\text{-}3\text{-}CH_3C_6H_3Si(C_2H_5)_2$		110–126	1.5362–1.5383 (20°)		(42)
$2\text{-}H_2N\text{-}5\text{-}CH_3C_6H_3Si(C_2H_5)_3$					(42)
Acetyl derivative	124–125				(42)
$(4\text{-}NH_2CH_2C_6H_4)_2Si(CH_3)_2$	45–47	180–190/0.5 mm.			(450)
$(4\text{-}HOOCC_5H_4)_2Si(CH_3)_2$ salt	240–245				(450)
$[(4\text{-}HOOCC_6H_4Si(CH_3)_2]_2O$ salt	140–145				(450)
$[(4\text{-}HOOCC_6H_4Si(C_5H_5)_2OSi(CH_3)_2O]_2$ salt	210–215				(450)

TABLE 8—*Concluded*

Compound	Melting Point	Boiling Point	n_D	d	References
	°C.	°C.			
$[3\text{-}(CH_3)_2CHNHC_6H_4]_4Si$	135				(279)
Aminophenylalkyls:					
$2\text{-}H_2NC_6H_4CH_2Si(CH_3)_3$		114/10 mm.	1.5345 (20°) 1.5234 (22°)	0.939 (20°) 0.9385 (25°)	(*35*, 400)
Acetyl derivative	117				
Diazonium chloride					
Azo-β-naphthol	98				
$4\text{-}H_2NC_6H_4CH_2Si(CH_3)_3$	34	119/10 mm.			(*35*, 400)
Acetyl derivative	133				
Diazonium chloride					
Azo-β-naphthol	127				
$4\text{-}(CH_3)_2NC_6H_4CH_2CH_2Si(C_6H_5)_3$					(99)
Hydrochloride	153–154				
$4\text{-}(CH_3)_2NC_6H_4CH_2CH(Li)Si(C_6H_5)_3$					(99)

the conditions necessarily involved would probably attack Si—O—C and Si—O—Si bonds. The Gabriel synthesis with $ClCH_2Si(CH_3)_3$ in dimethylformamide solution provides a route to $NH_2CH_2Si(CH_3)_3$ (445). The Hofmann degradation of $NH_2COCH_2CH_2Si(CH_3)_3$ gives $NH_2CH_2CH_2Si(CH_3)_3$ (445). The lithium aluminum hydride reduction of $CNCH_2CH_2Si(CH_3)_3$ gives $NH_2CH_2CH_2CH_2Si(CH_3)_3$ (445), while that of $HONCH[CH_2CH_2Si(CH_3)_3]_2$ gives $NH_2CH_2[CH_2CH_2Si(CH_3)_3]_2$ (444). Heating $(CH_3)_3SiCH_2CH_2COOH$ with sulfuric acid and sodium azide affords $O[Si(CH_3)_2CH_2CH_2NH_2]_2$ (344).

2. Properties

Probably the most interesting chemical property of aminoalkyl silicon compounds is base strength. In general, the effect of the trimethylsilyl group is to increase base strength (344, 445). This is in keeping with the electropositive character of silicon relative to carbon. The inductive effect of the trimethylsilyl group of course drops off as the length of the carbon chain between silicon and nitrogen increases. Thus $NH_2CH_2Si(CH_3)_3$ and $NH_2CH_2CH_2Si(CH_3)_3$ have basic dissociation constants almost twice those of methylamine and ethylamine, while $NH_2CH_2CH_2CH_2Si(CH_3)_3$ has a basic dissociation constant only slightly greater than that of propylamine (445). Even though $NH_2CH_2Si(CH_3)_3$ is about a five times stronger base than $NH_2CH_2C(CH_3)_3$, the former is anomalously only about one-twentieth as soluble in water on a molar basis (445).

Although trimethylsilyl substituents increase the base strengths of aliphatic amines, other silyl groups, such as phenyl- or oxygen-substituted ones, decrease base strength, as may be seen from table 9. The results are in keeping with the fact that electronegative substituents such as phenyl or oxygen usually decrease the base strengths of amines. Strangely, the weakening effect of $Si—C_6H_5$ or Si—O on the basic dissociation of silylalkylamines does not show

TABLE 9

Base strength of silylalkylamines

Compound	$K_B \times 10^4$	
	Reference 445	Reference 344
$(CH_3)_3SiCH_2NH_2$	9.1	9.6
$(CH_3)_3Si(CH_2)_2NH_2$	9.7	
$(CH_3)_3Si(CH_2)_3NH_2$	5.6	
$(CH_3)_3SiCH_2NHCH(CH_3)_2$		12
$(CH_3)_3SiCH_2NHC_5H_{11}$		17
$[(CH_3)_3SiCH_2]_2NH$	25.0	14
$(CH_3)_3SiCH_2NHC_6H_5$		<1
$C_6H_5(CH_3)_2SiCH_2NH_2$		2.8
$O[Si(CH_3)_2CH_2NH_2]_2$		2.0
$O[Si(CH_3)_2CH_2CH_2NH_2]_2$		5.5
CH_3NH_2		5.1
$C_3H_7NH_2$	4.9	
$(CH_3)_2CHNH_2$		4.3
$(CH_3)_3CCH_2NH_2$	1.6	

up as a strengthening effect in silyl-substituted carboxylic acids. The acid strengths of $(CH_3)_3SiCH_2COOH$, $C_6H_5(CH_3)_2SiCH_2COOH$, and $(CH_3)_3SiOSi(CH_3)_2CH_2COOH$ are about the same (436).

That the base strength of the $(CH_3)_3Si$-substituted propylamine, $(CH_3)_3SiCH_2CH_2CH_2NH_2$, is somewhat greater than that of propylamine itself has been advanced (445) as an indication that in this compound silicon shows no tendency to expand its valence shell and coordinate the extra electron pair of the nitrogen. Were such a coordination to occur it might be expected to lower materially the base strength of the amine. That the effect of such coordination should be of considerable magnitude is suggested by comparison of the basic dissociation constants of trimethylamine and trimethylamine oxide, which are about 10^{-4} and 10^{-10}, respectively. In $(CH_3)_3Si$-substituted carboxylic acids, too, is found a similar indication that silicon shows no tendency to expand its valence shell beyond the normal covalency of four. Substitution of a trimethylsilyl group at the beta position in propionic acid does not increase the acid strength, as might be expected if the carbonyl were to coordinate on the silicon (445). No information is available on what influence, if any, ring strain might have in suppressing any tendency toward internal coordination through octet expansion in the above compounds.

Few reactions of aminoalkyl silicon compounds are known. Their principal carbon-functional reaction is formation of salts (345, 445). With concentrated sulfuric acid (trimethylsilyl)alkylamines undergo loss of one methyl group with formation of silyl sulfates whose hydrolysis gives rise to symmetrical aminoalkyldisiloxanes (345, 444). A silicon-functional reaction exhibited by amine-substituted dimethylsiloxanes is ready siloxane rearrangement at room temperature without added catalyst, which occurs with various alkylamine-substituted derivatives but not with $C_6H_5NHCH_2\underbrace{Si(CH_3)[OSi(CH_3)_2]_3O}$ (181).

B. AROMATIC AND RELATED DERIVATIVES

1. Synthesis

Aminoaryl silicon compounds are obtained principally either by reducing the corresponding nitroaryl derivatives or by coupling aminoaryl alkali metal derivatives with chlorosilanes. Both these methods date from the turn of the century.

Reducing nitroaryl silicon compounds to aminoaryl derivatives is best done by catalytic hydrogenation. Reductions in aqueous media are not very satisfactory because they usually require acid conditions and these are conducive to cleavage of aminoaryl groups, particularly with ortho and para isomers. Thus, 3-nitrophenylsilanes can be reduced to amines with zinc in hydrochloric acid, but 4-nitrophenylsilanes give only aniline through silicon–carbon cleavage (279, 280).

Hydrogenation in the presence of Raney nickel has been applied to $NO_2C_6H_4Si(C_2H_5)_3$ (129), but it has been more extensively studied with nitrophenyl- and nitrobenzyltrimethylsilanes (35). In both cases all three isomers are smoothly

$$2\text{-}NO_2C_6H_4Si(CH_3)_3 + H_2 \xrightarrow{Ni} 2\text{-}NH_2C_6H_4Si(CH_3)_3$$

reduced at low pressure to the corresponding amines. Nitrotolyltriethylsilanes are similarly reduced (42).

Synthesizing aminoaryl silicon compounds by organometallic coupling reactions is confined to tertiary amines. Thus the sodium coupling of $4\text{-}(CH_3)_2NC_6H_4Br$ with silicon tetrachloride and with $HSiCl_3$ gives $[4\text{-}(CH_3)_2NC_6H_4]_4Si$ and $[4\text{-}(CH_3)_2NC_6H_4]_3SiH$ (118). Organolithium reagents have been more extensively applied. Coupling of $4\text{-}(CH_3)_2NC_6H_4Li$ occurs with ethyl silicate (148, 200) and with chlorosilanes (200), though much more slowly than do C_6H_5Li and $4\text{-}CH_3C_6H_4Li$. Nevertheless, satisfactory yields of such compounds as $[4\text{-}(CH_3)_2NC_6H_4]_4Si$, $[4\text{-}(CH_3)_2NC_6H_4]_3SiH$, and $[4\text{-}(CH_3)_2NC_6H_4]_2Si(C_6H_5)_2$ are readily obtained. The ortho and meta isomers of $(CH_3)_2NC_6H_4Li$ also couple satisfactorily with chlorosilanes (194, 490), as also does the organolithium derivative of $3\text{-}(HOCH_2CH_2)_2NC_6H_4Br$ (492).

Other methods are known for synthesizing aminoaryl and related silicon compounds. Lithium dimethylamide produces $3\text{-}(CH_3)_2NC_6H_4Si(CH_3)_3$ and $3\text{-}(CH_3)_2NC_6H_4Si(C_6H_5)_3$ from $4\text{-}BrC_6H_4Si(CH_3)_3$ and $4\text{-}BrC_6H_4Si(C_6H_5)_3$ in an interesting example of a meta rearrangement (194, 195). Hydrogenation of $(4\text{-}CNCH_2C_6H_4)_2Si(CH_3)_2$ with Raney nickel in liquid ammonia produces $(4\text{-}NH_2CH_2C_6H_4)_2Si(CH_3)_2$ (450). Addition of $4\text{-}(CH_3)_2NC_6H_4Li$ to $CH_2{=}CH\text{-}Si(C_6H_5)_3$, followed by hydrolysis, gives $4\text{-}(CH_3)_2NC_6H_4CH_2CH_2Si(C_6H_5)_3$ (99).

2. Chemical properties

The known carbon-functional group reactions of aminoaryl silicon compounds are limited to salt formation, acetylation, diazotization, and coupling with diazonium salts. The hydrochloride salts are the most widely known (35, 118) and exhibit no unusual features. $(4\text{-}NH_2CH_2C_6H_4)_2Si(CH_3)_2$ forms salts with various dicarboxylic acids, including silicon-containing ones, and these salts can be converted to polyamides in the usual way (21). Acetylation and diazotization under the usual conditions can be carried out with aminophenyltrimethylsilanes and aminobenzyltrimethylsilanes (35). The reactions of aminoarylsilanes with diazonium salts are discussed under the synthesis of azo dyes; in some cases $R_3Si—$ substituents are eliminated (490).

The base strengths of aminoaryl silicon compounds are of considerable theoretical import. The effect of substituting a $p\text{-}(CH_3)_3Si—$ group in aniline and dimethylaniline is to decrease their base strengths somewhat (38). The $p\text{-}(CH_3)_3Si—$ group behaves similarly in increasing the acid strength of phenol (38). In these cases then, the $p\text{-}(CH_3)_3Si—$ group exhibits an electron-withdrawing effect. This suggests (38) that the $p\text{-}(CH_3)_3Si—$ group is capable of conjugation to at least a limited extent. This conclusion is consistent also with dipole moment studies which indicate that silicon may act as an electron acceptor if some strong electron-releasing group is present (400). The electron-withdrawing effect of the $p\text{-}(CH_3)_3Si—$ group apparently arises through expansion of the silicon valence shell to ten electrons in resonance structures such as

$$H_2\overset{+}{N}{=}C_6H_4{=}\overset{-}{Si}(CH_3)_3$$

A m-$(CH_3)_3Si$ substituent affects the ionization constants of aniline and dimethylaniline only slightly (38).

Cleavage of aminoaryl groups from silicon occurs with hydrogen halides and with halogens. Susceptibility to cleavage by the former has long been known to vary with the position of the functional group on the ring. Thus, aminophenyl silicon compounds have been made by reducing *m*-nitro derivatives with zinc in hydrochloric acid, but only aniline has been obtained upon so reducing analogous *p*-nitro silicon compounds (279, 280). *m*-Aminoaryl groups too can be cleaved if desired; for example, those in $2\text{-}CH_3\text{-}5\text{-}NH_2C_6H_3Si(C_2H_5)_3$ and $4\text{-}CH_3\text{-}3\text{-}NH_2C_6H_3Si(C_2H_5)_3$ are cleaved with alcoholic hydrogen chloride (42).

A broader picture of the cleavability of aminoaryl groups may be obtained from recent studies. Hydrogen chloride cleaves the aryl group from an aryltrimethylsilane in refluxing glacial acetic acid. In this reaction the $4\text{-}(CH_3)_2NC_6H_4$ group cleaves more readily than $4\text{-}CH_3C_6H_4$—, C_6H_5—, and $4\text{-}ClC_6H_4$— groups

$$4\text{-}(CH_3)_2NC_6H_4Si(CH_3)_3 + HCl \xrightarrow{CH_3COOH} 4\text{-}(CH_3)_2NC_6H_5 + ClSi(CH_3)_3$$

(193). The $3\text{-}(CH_3)_2NC_6H_4$— group not only cleaves less readily than the para isomer but also less readily than C_6H_5—, $3\text{-}CH_3C_6H_4$—, $4\text{-}CH_3C_6H_4$—, and $4\text{-}ClC_6H_4$— groups; the $3\text{-}(CH_3)_2NC_6H_4$— group is comparable to the $3\text{-}ClC_6H_4$— group in resistance to acid cleavage (39). To account for the great difference in cleavability between the $3\text{-}(CH_3)_2NC_6H_4$— and $4\text{-}(CH_3)_2NC_6H_4$— groups it has been suggested (40) that the equilibria between salt and free base are such that the meta isomer reacts as the salt and the para isomer reacts as the free base.

A number of halogen cleavages of aminoaryl groups are known. They serve principally for isomer identification. Thus, $2\text{-}NH_2C_6H_4Si(CH_3)_3$ is cleaved much more readily with bromine water at 200°C. than is $2\text{-}NO_2C_6H_4Si(CH_3)_3$; hence

$$2\text{-}NH_2C_6H_4Si(CH_3)_3 + Br_2 + H_2O \rightarrow 2\text{-}NH_2C_6H_4Br + [(CH_3)_3Si]_2O$$

identifying the latter is facilitated by first reducing it to the amine (34). Cleavage with iodine has been used to identify $3\text{-}CH_3\text{-}4\text{-}NH_2C_6H_3Si(C_2H_5)_3$ (42).

Silicon-functional reactions are known only for dimethylaminophenyl silicon compounds. Such chlorosilanes and ethoxysilanes may be hydrolyzed to the corresponding silanols and silanediols (200). The chlorosilanes may also be reduced to silicon hydrides (200), which in turn may be converted to silanols (118). Like many other triarylsilanols, $[4\text{-}(CH_3)_2NC_6H_4]_3SiOH$ can be titrated quantitatively with the Karl Fischer reagent (197). This silanol also reacts almost quantitatively with $(C_4H_9)_2NH$ to give $[4\text{-}(CH_3)_2NC_6H_4]_3SiN(C_4H_9)_2$, even though unsubstituted triphenylsilanol does not undergo this reaction at all (191).

A silicon-functional reaction of dimethylaminophenyl silicon compounds that has been studied in some detail is the hydrolysis of triarylsilanes with wet piperidine. The relative rates of $3\text{-}(CH_3)_2NC_6H_4Si(C_6H_5)_2H$ and $4\text{-}(CH_3)_2N$-

$C_6H_4Si(C_6H_5)_2H$ are in agreement with those predicted from Hammett's σ constants (189).

3. Other properties

The ultraviolet absorption spectra of $4\text{-}(CH_3)_2NC_6H_4Si(C_6H_5)_2OH$ and $[4\text{-}(CH_3)_2NC_6H_4]_3SiOH$ in anhydrous alcoholic hydrogen chloride solution have been compared with those of their carbon analogs (188). The strong bathochromic shift of absorption maxima into the visible shown by the carbinols does not occur with the silanols. This observation is taken (188) as indicating the difficulty of forming siliconium ions analogous to the $[4\text{-}(CH_3)_2NC_6H_4]_3C^+$ carbonium ion, which with its resonance forms is thought to be responsible for the bathochromic shift shown by such carbinols in acid solution. This difficulty of forming siliconium ions, coupled with the known ability of silicon to expand its octet, is offered (188) as a reason for favoring pentacovalent silicon intermediates over siliconium-ion intermediates in reactions of silicon compounds. Two factors advanced (188) as contributing to the difficulty of forming triarylsiliconium ions involve lowered steric strain and decreased resonance stabilization.

The dipole moments of 4-amino- and 4-dimethylaminophenyltrimethylsilanes indicate that these and other electron-supplying groups para to the $(CH_3)_3Si—$ group produce a marked decrease in the algebraic value of the moment of this group. This decrease seems to be proportional to the ease with which the para groups give up electrons to the ring. A structure which may be postulated to account for this decrease is $H_2\overset{+}{N}{=}C_6H_4{=}\overset{-}{Si}(CH_3)_3$ (400).

XII. ALDEHYDES AND KETONES (SEE TABLE 10)

A. ALDEHYDES

Silicon-containing aldehydes have received scant attention and little is known about them. They have been obtained by application of the oxo reaction to alkenyltrimethylsilanes (90, 91). This type of synthesis also produces aldol

$$(CH_3)_3SiCH_2CH{=}CH_2 \xrightarrow[Co(CO)_4]{H_2,\ CO} (CH_3)_3SiCH_2CH(CHO)CH_3$$

condensation products and substances arising from silicon–carbon cleavage. Aromatic aldehydes may be prepared via the Grignard synthesis (164, 165) and by the hydrolysis of silicon-containing benzal dihalides (62).

$$4\text{-}(CH_3)_3SiC_6H_4MgBr \xrightarrow{HC(OC_2H_5)_3} \xrightarrow[H_2O]{H^+} 4\text{-}(CH_3)_3SiC_6H_4CHO$$

The few known silicon-containing aldehydes react normally with 2,4-dinitrophenylhydrazine (90, 164). It is noteworthy that during its preparation $4\text{-}(CH_3)_3SiC_6H_4CHO$ is steam-distilled from an acid solution without silicon–phenyl cleavage (164, 165).

TABLE 10

Silicon-containing aldehydes and ketones

Compound	Melting Point	Boiling Point	n_D	d	References
	°C.	*°C.*			
Aldehydes:					
$CHOC_2H_4Si(CH_3)_3$		63/25 mm.	1.4238 (20°)	0.8347 (20°)	(*90*, 91)
2,4-Dinitrophenylhydrazone	132				
$CHOC_2H_4Si(CH_3)_3$		64/10 mm.	1.4252 (20°)	0.8365 (20°)	(*90*, 91)
2,4-Dinitrophenylhydrazone	130				
$CHO[Si(CH_3)_3]C_2H_2{=}CHC_2H_4Si(CH_3)_3$		194–209	1.4549 (20°)		(*90*, 91)
$CHO(CH_2)_5Si(CH_3)_3$					(91)
$CHOCH(CH_3)CH_2Si(CH_3)_3$		74/22 mm.	1.4239 (20°)	0.8459 (20°)	(*90*, 91)
2,4-Dinitrophenylhydrazone	109				
$CHO(CH_2CH_2Si(CH_3)_3]C{=}CH(CH_2)_3Si(CH_3)_3$		152/15 mm.	1.4550 (20°)	0.8910 (20°)	(*90*, 91)
2,4-Dinitrophenylhydrazone	153				
$4\text{-}CHOC_6H_4Si(CH_3)_3$	109–110	119/15 mm.			(164, 165)
2,4-Dinitrophenylhydrazone	209				(164, 165)
Ethyl acetal					
$4\text{-}CHOC_6H_4Si(C_6H_5)_3$	110–111				(62)
Oxime	194–195				(62)
Thiosemicarbazone	234–235				(62)
Ketones:					
$CH_3CO(CH_2)_2Si(CH_3)_3$		84/65 mm.	1.4228 (20°)	0.833 (20°)	(409, 414, 416, *437*, 439, 443, 444)
$CH_3COCH_2Si(CH_3)_3$		74/96 mm.	1.4188 (26°)	0.8275 (26°)	(240, 540)
$CH_3CO(CH_2)_2Si(CH_3)_2C_6H_5$		109/4 mm.	1.5065 (20°)	0.963 (20°)	(416, *437*)
$CH_3COCH(CH_3)CH_2Si(CH_2)_3$		83/40 mm.	1.4280 (20°)	0.836 (20°)	(409, 416, *437*)
$[CH_3CO(CH_2)_2Si(CH_3)_2]_2O$		142/6 mm.	1.4390 (20°)	0.943 (20°)	(409, 439, 444)
$C_6H_5CO(CH_2)_2Si(CH_3)_3$		115/4 mm.	1.5085 (20°)	0.955 (20°)	(409, 416, *437*)
$CH_3COCH(C_2H_5)CH_2Si(CH_3)_3$		88/30 mm.	1.4295 (20°)	0.843 (20°)	(409, 416, *437*)
$[CH_3COCH(CH_3)CH_2Si(CH_3)_2]_2O$					(409)
$[CH_3COCH(C_2H_5)CH_2Si(CH_3)_2]_2O$					(409)
$[C_6H_5CO(CH_2)_2Si(CH_3)_2]_2O$					(409)
"$[(CH_3CO)_2CH]_3SiCl \cdot HCl$"	98 (d.)				(384)
$C_6H_6CH(COCH_3)Si(CH_3)_3$		102/5 mm.	1.5242 (21°)		(240)
2,4-Dinitrophenylhydrazone	143				
$RCOC_6H_4Si(C_2H_5)_3$		53/4 mm.	1.4204 (20°)		(130)
$CH_3CH_2CH_2COCH_2CH_2Si(CH_3)_3$					(425)
Semicarbazone	72–73				(425)

$CO[CH_2CH_2Si(CH_3)_3]_2$		103/7 mm.	1.4414 (20°)	0.8424 (20°)	(419, 420, 421, *444*)
Oxime	76–76.5				(415, 420, *444*)
$CO[CH_2CH_2Si(CH_3)_2OSi(CH_3)_3]_2$		95/2 mm.	1.4262 (20°)	0.8857 (20°)	(419, *444*)
2,4-Dinitrophenylhydrazone	245–247				(*419*, 444)
$[-Si(CH_3)_2CH_2CH_2COCH_2CH_2Si(CH_3)_2O-]_2$	129–130				(419, 444)
$[-Si(CH_3)_2(CH_2)_2CO(CH_2)_2Si(CH_3)_2O-]_x$					(419)
$C_2H_5OCOCH[COCH_2CH_2Si(CH_3)_3]CH_2Si(CH_3)_3$		141/8 mm.	1.4472 (20°)	0.9196 (20°)	(444)
$2\text{-}CH_3COC_6H_4Si(CH_3)_3$		116–117/14 mm.	1.5200 (20°)	0.9627 (20°)	(395)
2,4-Dinitrophenylhydrazone	135–137				(395)
$3\text{-}CH_3COC_6H_4Si(CH_3)_3$		132/17 mm.	1.5120 (20°)	0.9554 (20°)	(395)
Semicarbazone	166–168				(395)
2,4-Dinitrophenylhydrazone	160–163				(395)
$4\text{-}CH_3COC_6H_4Si(CH_3)_3$		136/17 mm.	1.5170 (20°)	0.9648 (20°)	(395)
Semicarbazone	198–200				(395)
2,4-Dinitrophenylhydrazone	203–207				(395)
$CH_3COC_6H_4Si(CH_3)_3$	40–41	80–100/3 mm.			(501)
2,4-Dinitrophenylhydrazone	194–195				(501)
$C_6H_5COC_5H_4Si(CH_3)_3$	64				(501)
2,4-Dinitrophenylhydrazone	211–213				(501)
$2\text{-}(4'\text{-}CH_3C_5H_4CO)C_6H_4Si(CH_3)_3$	76–76.5				(40)
$2\text{-}(4'\text{-}CH_3OC_6H_4CO)C_6H_4Si(CH_3)_3$	70–70.5				(40)
$3\text{-}(4'\text{-}CH_3C_6H_4CO)C_6H_4Si(CH_3)_3$	43–44				(40)
Semicarbazone	184–185				(40)
$4\text{-}(4'\text{-}CH_3C_6H_4CO)C_6H_4Si(CH_3)_3$	44–44.5	159–162/0.5 mm.			(40)
Phenylhydrazone	137–138				(40)
	128.5–120				
$4\text{-}(4'\text{-}CH_3OC_6H_4CO)C_6H_4Si(CH_3)_3$	53.5–54	168–170/0.8 mm.			(40)
Phenylhydrazone	145.6–146				(40)
$\underline{COC[CH_2Si(CH_3)_3]{=}C(CH_3)CH_2CH_2}$	58–58.5	118/21 mm.	1.4827 (20°)		(443)
Oxime	108–108.5				(443)
β-Keto esters: see table 13					
$CH_3COCH_2COCH_2CH_2Si(CH_3)_3$		105/15 mm.	1.4623 (20°)	0.9155 (20°)	(414, *443*)
Copper chelate	101–102				(414, *443*, 521)
Other chelates					(521)
$CH_2[COCH_2CH_2Si(CH_3)_3]_2$		148/8 mm.	1.4668 (20°)	0.8961 (20°)	(414, *443*)
Copper chelate	123.5–124.5				(414, *443*, 521)
Other chelates					(521)
$CH_3CO(CH_2)_3CO(CH_2)_2Si(CH_3)_3$	49.5–50				(443)
Disemicarbazone					(443)

B. KETONES

1. Synthesis

Aliphatic silicon-containing ketones have been prepared in various ways. The reaction of $BrMgCH_2Si(CH_3)_3$ with acetic anhydride at $-70°C.$ produces $CH_3COCH_2Si(CH_3)_3$, providing the hydrolysis step is carried out very carefully with aqueous ammonium chloride (240). Another type of synthesis is exemplified by the coupling of $C_6H_5(CH_3)_2SiCH_2CH_2COCl$ with dimethylcadmium (416, 437) or with methylmagnesium halide in the presence of ferric chloride at low temperature (443) to give $C_6H_5(CH_3)_2SiCH_2CH_2COCH_3$. The peroxide-catalyzed addition of butyraldehyde to $CH_2{=}CHSi(CH_3)_3$ in acetic anhydride produces $C_3H_7COCH_2CH_2Si(CH_3)_3$ (425). The well-known ketone cleavage of acetoacetic esters readily gives rise to aliphatic silicon-containing ketones (416, 421, 437, 444).

$$(CH_3)_3SiCH_2CH_2COCH[CH_2Si(CH_3)_3]COOC_2H_5 \xrightarrow[CH_3COOH]{H_2SO_4} [(CH_3)_3SiCH_2CH_2]_2CO$$

The simple ketones prepared by the above methods may be used as starting points for more complex ketones. Thus Claisen condensations lead to β-diketones (414, 443), and a more complex series of condensations and cyclizations leads to unsaturated cyclic ketones (443). The sulfuric acid demetholation of trimethylsilyl-substituted ketones produces the corresponding disoloxane diketones (409, 419, 439, 444). An interesting example of this reaction involves polymer formation by the loss of two methyl groups from the same molecule (444). The polymer

$$[(CH_3)_3SiCH_2CH_2]CO \xrightarrow{\text{concd. } H_2SO_4} \xrightarrow{H_2O} [\text{—}Si(CH_3)_2CH_2CH_2COCH_2CH_2Si(CH_3)_2O\text{—}]_x$$

can be equilibrated with hexamethyldisiloxane to give $[(CH_3)_3SiOSi(CH_3)_2CH_2CH_2]_2CO$, and the polymer can also be cracked at elevated temperature to produce the unusual sixteen-membered ring diketone, $[\text{—}Si(CH_3)_2CH_2CH_2COCH_2CH_2Si(CH_3)_2O\text{—}]_2$.

For preparing aromatic silicon-containing ketones the Friedel–Crafts coupling of acyl halides with aromatic silicon compounds is of limited utility because of the susceptibility of silicon-aromatic bonds toward cleavage by acid reagents (40, 130). Nevertheless some examples of this type of synthesis are known. The acylation of silicon-substituted thiophenes and furans in the presence of iodine produces low yields of ketones (36). The *m*- and *p*-trimethylsilylbenzoyl chlorides acylate toluene smoothly in the presence of aluminum chloride, but the ortho isomer does not (40). Acetyl fluoride acylates silicon-substituted phenyl compounds satisfactorily in the presence of boron fluoride (501).

The majority of aromatic silicon-containing ketones have been synthesized by other synthetic routes. These include the coupling of silicon-containing acid halides with cadmium reagents (40), the Oppenauer oxidation of silicon-substituted benzyl alcohols (96a), and the chromic acid oxidation of silicon-substituted phenylethanes (395).

2. Properties

Many silicon-containing ketones show typical carbonyl group reactions—formation of phenylhydrazones (40, 240, 425), semicarbazones (425), and oximes (444), as well as sodium hypobromite oxidation (437) and reaction with Grignard reagents to form tertiary alcohols (437). In aromatic ketones an *o*-trimethylsilyl substituent prevents phenylhydrazone formation (40). Silicon-containing β-diketones form characteristic chelate compounds (414, 443, 521)·

The silicon–carbon cleavages encountered in the ketones are similar to those found in analogous compounds containing other electron-attracting groups, such as esters. The α-substituted ketone, $CH_3COCH_2Si(CH_3)_3$, may be prepared through very careful control of conditions (240, 540), but silicon–carbon cleavage takes place when an attempt is made to prepare its 2,4-dinitrophenylhydrazone. β-Substituted ketones, such as $CH_3COCH_2CH_2Si(CH_3)_3$, undergo reactions in acidic or basic media without apparent difficulty from silicon–carbon cleavage (437, 443, 444).

A number of other properties have been reported for silicon-substituted ketones. The β-diketones are weaker acids than their unsubstituted analogs. This is in accord with the concept of electron release by the trimethylsilyl group (443), but it is surprising that one trimethylsilyl group produces a greater effect than two such groups. The formation constants of metal chelates from β-diketones have been measured (521). Ultraviolet absorption spectra have been reported for unsaturated cyclic ketones (443). The aromatic ketone 4-[2-$(CH_3)_3SiC_6H_4CO]C_6H_4CH_3$ exhibits the interesting property of reversible photocoloration; it turns pink in ultraviolet light and colorless in the dark (40).

XIII. CARBOXYLIC ACIDS (SEE TABLE 11)

A. SYNTHESES

Silicon-substituted aliphatic carboxylic acids are obtained principally by the carbonation of silicon-containing organometallic reagents and by the hydrolysis of silicon-substituted acetoacetic and malonic esters. Thus the carbonation of $(C_6H_5)_3SiK$ produces $(C_6H_5)_3SiCOOH$ (45, 66, 68) and that of $(CH_3)_3SiCH_2MgCl$ gives $(CH_3)_3SiCH_2COOH$ (436). Other acids, including $(C_6H_5)_3SiCH(COOH)C_5H_{11}$ (99) and $(CH_3)_3Si(CH_2)_3COOH$ (406, 413) have been obtained analogously.

Hydrolysis of silicon-containing acetoacetic and malonic esters provides a very satisfactory method for producing acids in which the carboxyl group is

$$(CH_3)_3SiCH_2Cl + CH_2(COOC_2H_5)_2 \xrightarrow[C_2H_5OH]{Na}$$

$$(CH_3)_3SiCH_2CH(COOC_2H_5)_2 \xrightarrow{KOH} \xrightarrow{HCl} (CH_3)_3SiCH_2CH_2COOH$$

TABLE 11

Silicon-containing carboxylic acids

Compound	Melting Point	Boiling Point	n_D	d	References
	°*C.*	°*C.*			
$HOOCSi(C_5H_5)_3$	169				(*45*, 66, 68)
$HOOCCH_2Si(CH_3)_3$	40				(436, 540)
$HOOCCH_2Si(CH_3)_2C_6H_5$	90				(*436*, 439)
$HOOCCH_2Si(CH_3)_2OSi(CH_3)_3$	17		1.4149 (20°)		(436)
$HOOCCH(C_5H_{11})Si(C_6H_6)_3$	138–139				(99)
$LiOCOCH(C_6H_5)Si(C_5H_5)_3$					(190)
Carboxymethylsiloxane					(341)
$HOOC(CH_2)_2Si(CH_3)_2OSO_3H$					(407)
$HOOC(CH_2)_2Si(CH_3)_3$	22	147/65 mm.	1.4279 (20°)	0.9196 (20°)	(55, 404, 406, 412, 413, 416, 417, 429, *433*, *436*, *437*, 439, 444, 445)
$HOOC(CH_2)_2Si(CH_3)_2C_6H_5$	27	116/1 mm.	1.5148 (20°)	1.037 (20°)	(408, 412, 413, 416, *433*, *437*)
$HOOC(CH_2)_2Si(CH_3)_2CH_2Si(CH_3)_3$	~ -2	123/4 mm.	1.4521 (20°)	0.9165 (20°)	(406, *433*)
$[HOOCCH_2CH_2Si(CH_3)_2]_2O$	55				(136, 407, 408, 417, 424, *439*, 442, 444)
$HOOCCH(CH_3)CH_2Si(CH_3)_3$		92/4 mm. 118/13 mm.	1.4310 (20°) 1.4312 (20°)	0.9121 (20°) 0.9102 (20°)	(406, *433*, *437*)
$HOOC(CH_2)_3Si(CH_3)_2OSO_3H$					(407)
$HOOC(CH_2)_3Si(CH_3)_3$	4	91/5 mm.	1.4325 (20°)	0.9098 (20°)	(404, *406*, 407, 412, 413, 417, 444)
$[HOOC(CH_2)_3Si(CH_3)_2]_2O$	49/49.5				(407, 417, *444*)
$HOOC(CH_2)_4Si(CH_3)_3$	0	134/14 mm.	1.4358 (20°)	0.9047 (20°)	(*406*, 433)
$HOOC(CH_2)_5Si(CH_3)_3$	−7	260/738 mm. 80/0.1 mm.	1.4390 (20°)	0.8923 (20°)	(*406*, 433)
$HOOC(CH_2)_{10}Si(C_2H_5)_3$		180–181/15 mm.	1.4636 (20°)	0.9041 (20°)	(95)
$[HOOC(CH_2)_{10}Si(C_2H_5)_2]_2O$		280–282/1 mm.	1.4701 (20°)	0.9566 (20°)	(96)
$HOOCC_{10}H_{20}Si(C_6H_5)_3$	59	260/<1 mm.			(176)
$HOOC(CH_2)_{11}Si(CH_3)_2C_4H_9$		195/2 mm.	1.4545 (25°)		(77)
$HOOC(CH_2)_{11}Si(CH_3)_2C_5H_{11}$		201/2 mm.	1.4553 (25°)		(77)
$HOOC(CH_2)_{11}Si(CH_3)_2CH_2CH_2C_6H_5$			1.4893 (25°)		(77)
$HOOCCH_2CH[Si(CH_3)_3]CH_2CH_2COOH$	87				(465)
9-(9-HOOC)$C_{13}H_9Si(CH_3)_3$					(184)
Diels–Alder adducts: see table 1					
$HOOCCH_2CH_2OSi(CH_3)_3$		116–117/8 mm.	1.4300 (20°)		(423)

2-$HOOCC_6H_4Si(CH_2)_3$	98–98.5				(*40*, 395)
3-$HOOCC_6H_4Si(CH_2)_2$	113–114				(38, 40, 374, 375, 395)
4-$HOOCC_5H_4Si(CH_3)_3$	117–118				(38, 40, 164, 166, 186, *374*, 375, 395, 400)
4-$HOOCC_6H_4Si(C_6H_5)_3$	213–214				(62)
(4-$HOOCC_6H_4)_2Si(CH_3)_2$	283–287				(450)
$NH_2(CH_2)_6NH_2$ salt	215–220				(450)
$NH_2(CH_2)_{10}NH_2$ salt	216–220				(450)
(4-$H_2NCH_2C_6H_4)_2Si(CH_3)_2$ salt	240–245				(450)
(4-$HOOCC_5H_4)_2Si(C_6H_6)_2$	250–257				(450)
[(4-$HOOCC_6H_4Si(CH_3)_2]_2O$	242				(24, 25, *309*, 450)
NH_4, Na, Cu, and Fe salts					(25)
$NH_2(CH_2)_6NH_2$ salt	225–230				(450)
(4-$NH_2CH_2C_6H_4)_2Si(CH_3)_2$ salt	140–145				(450)
[4-$HOOCC_5H_4Si(C_5H_5)_2OSi(CH_3)_2]_2O$	150–152				(450)
$NH_2(CH_2)_6NH_2$ salt	205–210				(450)
(4-$NH_2CH_2C_5H_4)_2Si(CH_3)_2$ salt	210–215				(450)
$(HOOCC_6H_4SiO_{1.5})_x$					(25)
Carboxyphenyl silicone polymers and copolymers					(25)
(4-$HOOCC_6H_4)_2Si(CH_3)_2$	288 (d.)				(514)
$(HOOCC_5H_4)_2Si(CH_3)_2$					(515)
3-HOOC-4-$CH_3OC_6H_3Si(C_2H_6)_3$	52–56				(184)
(2-$HOOCCH_2C_6H_4)_3SiH$	222				(43)
2-$HOOCC_6H_4CH_2Si(CH_3)_3$	77.5				(140)
Anilide	113				(140)
Sodium salt					(140)
3-$HOOCC_6H_4CH_2Si(CH_3)_3$	96.5				(140)
Anilide	111.4				(140)
Sodium salt					(140)
4-$HOOCC_6H_4CH_2Si(CH_3)_3$	179				(140)
Anilide	137.4				(140)
Sodium salt					(140)
$HOOCCH_2CH_2CH[Si(CH_3)_3]CH_2COOH$	85–86.5				(477)
$HOOCCH_2CH_2CH(COOH)CH_2Si(CH_3)_3$	63–64				(422, *433*)
Anhydride		142/5 mm.	1.4712 (20°)		(422, *433*)
$[HOOCCH_2CH_2CH(COOH)CH_2Si(CH_3)_2]_2O$	85–86				(422, *433*)
Carboxyalkylthioalkyls: see table 15					

beyond the alpha carbon, because such compounds are not susceptible to silicon–carbon cleavage under the vigorous hydrolysis conditions required (77, 406, 413, 433, 436, 437, 445). One limitation imposed on this type of synthesis is the instability of β-chloroethyl silicon compounds under the strong alkaline conditions required in making the esters (433).

Other methods which have been used in making silicon-containing monocarboxylic acids include the sodium hypobromite oxidation of $CH_3COCH_2CH_2Si(CH_3)_3$ to $HOOCCH_2CH_2Si(CH_3)_3$ (437) and the addition of silicon hydrides to unsaturated carboxylic acids (176).

$$(C_6H_5)_3SiH \;+\; CH_2{=}CH(CH_2)_8COOH \xrightarrow{(C_6H_5CO)_2O_2} (C_6H_5)_3Si(CH_2)_{10}COOH$$

Silicon-substituted polycarboxylic acids include two types. One is exemplified by trimethylsilyladipic and trimethylsilylglutaric acids. These are made respectively by the nitric acid oxidation of trimethylsilylcyclohexanol (465, 477) and by the hydrolysis of the cyanoethylation product of $(CH_3)_3SiCH_2CH(COOC_2H_5)_2$ (433).

$$(CH_3)_3SiCH_2C(COOC_2H_5)_2CH_2CH_2CN \xrightarrow{HCl,\ CH_3COOH} (CH_3)_3SiCH_2CH(COOH)CH_2CH_2COOH$$

The other type of polycarboxylic acid bears the carboxyl groups on more than one silicon atom, as in $O[Si(CH_3)_2CH_2CH_2COOH]_2$. This compound may be prepared by application of the malonic ester synthesis to $O[Si(CH_3)_2CH_2Cl]_2$ (407). Another method involves the selective cleavage of one methyl group from trimethylsilylcarboxylic acids with concentrated sulfuric acid (407, 408, 433, 439, 444). The selective demethylation of trimethylsilylglutaric acid produces a disiloxanetetracarboxylic acid (433).

$$(CH_3)_3SiCH_2CH_2COOH \xrightarrow[H_2SO_4]{\text{concd.}} HOSO_3Si(CH_3)_2CH_2CH_2COOH \;+\; CH_4 \xrightarrow{H_2O} O[Si(CH_3)_2CH_2CH_2COOH]_2$$

Silicon-substituted aromatic carboxylic acids are obtained in various conventional ways. The oxidation of tolyl silicon compounds with chromic anhydride or potassium permanganate produces the corresponding carboxyphenyl derivatives (25, 40, 309, 450). Similar results are obtained upon oxidation of the three $(CH_3)_3SiC_6H_4C_2H_5$ isomers (395). The carbonation of silylaromatic organometallic reagents also gives the corresponding aromatic acids (38, 40, 140, 184, 374, 514). A silyl-substituted thiophenecarboxylic acid has been prepared in this way (184). The alkali hydrolysis of silylaromatic nitriles constitutes another method for preparing the corresponding aromatic acids (309, 450).

B. PROPERTIES

The acid strengths of silicon-substituted carboxylic acids are of great interest because of the bearing they have on the electronic influence of silicon. From the acid strengths given in table 12 it is apparent that compared to alkyl and hydrogen the $(CH_3)_3Si$— group exerts an inductive effect of electron release which drops sharply with increasing chain length (433, 436). It is of interest that replacing a methyl group in $(CH_3)_3SiCH_2COOH$ with a trimethylsiloxy group has no influence on acid strength, whereas a similar substitution in trimethylsilylalkylamines produces a large change in base strength (344). The acid strengths of 3-$(CH_3)_3SiC_6H_4COOH$ and 4-$(CH_3)_3SiC_6H_4COOH$ are slightly lower than that of benzoic acid; hence the $(CH_3)_3Si$— group is weakly electron-releasing in these compounds (38, 374, 375). A stronger electropositive effect is observed when the acid strengths of the three isomeric forms of $(CH_3)_3SiCH_2C_6H_4COOH$ are compared with those of the corresponding toluic acids (140). Since the $(CH_3)_3Si$— group acts as an electron donor in carboxylic acids and aliphatic amines and as an electron acceptor in anilines and phenols, the influence of this group is apparently variable depending upon the electronic demands of other portions of the molecule.

The reactions of silicon-substituted aliphatic carboxylic acids depend upon the position of the carboxyl group relative to silicon. In compounds having the carboxyl group beyond the alpha carbon, the usual carboxylic acid reactions prevail. Thus such compounds are smoothly converted to acid halides (437) and to anhydrides (433). Another reflection of the stability of such compounds is found in their preparation in strongly acidic and basic media.

When the carboxyl group is closer to silicon, greater susceptibility to silicon–carbon cleavage is encountered. Thus $(CH_3)_3SiCH_2COOH$ exhibits some hydrolytic instability (436, 540), which is increased when phenyl or indenyl groups are on the alpha carbon (184, 190). Slightly impure $(C_6H_5)_3SiCOOH$ decomposes merely upon being heated or upon being dissolved in alcohol or acetone (45), but the pure acid is more stable (67).

$$(C_6H_5)_3SiCOOH \rightarrow (C_6H_5)_3SiOH + CO$$

It is not always true that the silicon-containing acids in which the carboxyl is furthest removed from silicon are the most stable toward silicon–carbon cleavage. Thus in concentrated sulfuric acid $(CH_3)_3SiCH_2CH_2COOH$ undergoes silicon–methyl cleavage exclusively, while $(CH_3)_3SiCH_2CH_2CH_2COOH$ gives not only

TABLE 12

Acid strengths of silicon-substituted carboxylic acids

Acid	$K \times 10^5$	Acid	$K \times 10^5$
$(CH_3)_3SiCH_2COOH$	0.60	CH_3CH_2COOH	1.32
CH_3COOH	1.75	$(CH_3)_3SiCH_2CH_2CH_2COOH$	1.30
$(CH_3)_3CCH_2COOH$	1.00	$(CH_3)_3SiOSi(CH_3)_2CH_2COOH$	0.60
$(CH_3)_3SiCH_2CH_2COOH$	1.24	$C_6H_5(CH_3)_2SiCH_2COOH$	0.54

methane but also a small yield of butyric acid from cleavage of the carboxypropyl group (444).

A kinetic study of the demethylation of $(CH_3)_3SiCH_2CH_2COOH$ by concentrated sulfuric acid shows that it is first order in unionized sulfuric acid and first order in the silicon compound (429). These results are consistent with two mechanisms. The first, which involves electrophilic attack on carbon followed by a

$$(CH_3)_3SiCH_2CH_2COOH + H_2SO_4 \xrightarrow{\text{slow}} CH_4 + \overset{+}{Si}(CH_3)_2CH_2CH_2COOH + HSO_4^- \quad (A)$$

$$\overset{+}{Si}(CH_3)_2CH_2CH_2COOH + HSO_4^- \xrightarrow{\text{fast}} HOSO_3Si(CH_3)_2CH_2CH_2COOH$$

$$(CH_3)_3SiCH_2CH_2COOH + H_2SO_4 \rightarrow CH_4 + HOSO_3Si(CH_3)_2CH_2CH_2COOH \quad (B)$$

fast reaction of the siliconium ion, is preferred by the investigators. Mechanism B involves electrophilic attack on carbon and nucleophilic attack on silicon by the same molecule of sulfuric acid. Another mechanism is favored in a very recent study (396a).

The properties of silicon-containing aromatic acids include the following in addition to the acid strengths already mentioned. Because of the electron-attracting carboxyl group, silylaromatic acids are more stable toward silicon–phenyl cleavage by acidic reagents (39). They can be converted to acid halides by thionyl chloride without special precautions to minimize cleavage by hydrogen chloride (39, 40). It is noteworthy that $4\text{-}(CH_3)_3SiC_6H_4COOH$ is stable toward silicon–phenyl cleavage by base even though electron-attracting groups ordinarily enhance such cleavage; this is probably due to the existence of the acid group as the carboxylate ion, which has a lower electron attraction (186). Rates of esterification of silylaromatic acids give Hammett σ constants indicating electron release by the $(CH_3)_3Si$— group (375). The dipole moments of these compounds lead to the same conclusion (374, 400).

XIV. Carboxylic Esters (See Table 13)

A. SYNTHESES

Aliphatic carboxylic esters substituted with silyl groups have been made in various ways. The reaction of $(CH_3)_3SiCH_2MgCl$ with $ClCOOC_2H_5$ gives a good yield of $(CH_3)_3SiCH_2COOC_2H_5$ providing mild hydrolysis conditions are used (223). Similar compounds are produced by coupling chlorosilanes with sodio derivatives of simple aliphatic esters (226). The reaction of triethylchlorosilane with sodioacetoacetic ester has also been carried out, but whether carbon or oxygen silico-alkylation occurred is unknown (540).

$$CH_3COOC_2H_5 + (C_6H_5)_3CNa \rightarrow NaCH_2COOC_2H_5 \xrightarrow{(CH_3)_3SiCl} (CH_3)_3SiCH_2COOC_2H_5$$

Thus with $(CH_3)_3SiCH_2I$ the acetoacetic ester synthesis produces good yields of simple silyl-substituted carboxylic esters or of silyl-substituted acetoacetic esters depending upon conditions (433, 437). The iodo compound cannot be replaced by its chloro analog. The tendency to form the simple ester directly is even

$$(CH_3)_3SiCH_2I + CH_3COCH_2COOC_2H_5 \xrightarrow[\text{in excess}]{NaOC_2H_5} (CH_3)_3SiCH_2CH_2COOC_2H_5$$

$$(CH_3)_3SiCH_2I + CH_3COCH_2COOC_2H_5 \xrightarrow[\text{excess ester}]{NaOC_2H_5} CH_3COCH[CH_2Si(CH_3)_3]COOC_2H_5$$

more pronounced with $C_6H_5(CH_3)_2SiCH_2I$. Silylalkyl chlorides readily undergo the malonic ester synthesis with formation of a variety of silyl-substituted malonic esters (433, 445). β-Silylalkyl halides are considered unsuitable for these condensations because of their instability in basic media (433).

Other syntheses of silicon-containing aliphatic esters include the addition of silicon hydrides to the unsaturated linkage of methyl undecylenate (95, 96, 175) and the acid-catalyzed esterification of $O[Si(CH_3)_2CH_2CH_2COOH]_2$ to $O[Si(CH_3)_2CH_2CH_2COOC_2H_5]_2$, which can be equilibrated with other siloxanes (442, 450).

Silicon-substituted aromatic esters such as $3\text{-}(CH_3)_3SiC_6H_4COOR$ and $4\text{-}(CH_3)_3SiC_6H_4COOR$ are obtained from the reaction of silver carboxylates with alkyl iodides or from the reaction of carboxylic acids with diphenyldiazomethane (375). Silicon-containing aromatic polyesters are formed by the reaction of silicon-substituted aromatic carboxylic acids (515) or esters (450) with polyalcohols.

B. PROPERTIES

Study of the reactions of silicon-containing esters has largely been confined to aliphatic compounds in which the silicon atom is alpha or beta to the ester group. In the former silicon–carbon cleavage reactions predominate, while in the latter normal carboxylic ester reactions prevail.

Basic hydrolysis of $(CH_3)_3SiCH_2CH_2COOC_2H_5$ gives the corresponding carboxylic acid in good yield (433, 437, 445). This ester readily forms the tertiary alcohol with methyl Grignard reagent (437), and it also undergoes Claisen condensations to form β-diketones and acetoacetic esters (414, 443, 444).

More complex β-trimethylsilyl-substituted esters also exhibit normal ester reactions. Thus the acetoacetic and malonic esters can be further alkylated, though not with another $(CH_3)_3SiCH_2$— group (433, 437). The acetoacetic esters are satisfactorily cleaved to ketones with concentrated hydrochloric acid or with 10 per cent sodium hydroxide (416, 437). The malonic esters undergo a Michael condensation with acrylonitrile and may be condensed with urea to yield barbituric acids (433). The complex ester $(CH_3)_3SiCH_2CH_2COCH(COOC_2H_5)CH_2$-

TABLE 13

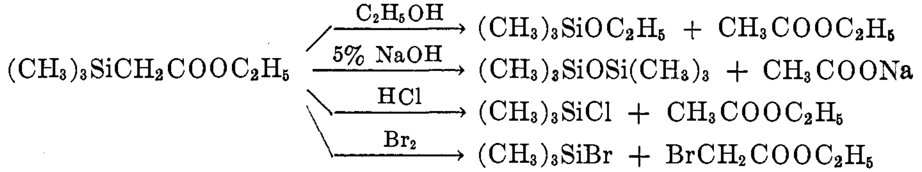
Silicon-containing carboxylic esters

Compound	Melting Point	Boiling Point	n_D	*d*	References
	°*C.*	°*C.*			
Carbalkoxyalkyls and aryls:					
$C_2H_5OCOCH_2Si(CH_3)_3$		157/730 mm. 76/42 mm.	1.4149 (20°)	0.8762 (20°)	(*223*, 226)
$C_2H_5OCO(CH_2)_2Si(CH_3)_3$		93/40 mm.	1.4198 (20°)	0.8763 (20°)	(406, 414, 416, 421, *437*, 443, 444, 445)
$C_2H_5OCO(CH_2)_2Si(CH_3)_2C_6H_5$		106/2 mm.	1.4972 (20°)	0.9856 (20°)	(437)
$[C_2H_5OCOCH_2CH_2Si(CH_3)_2]_2O$		94/1 mm.	1.4341 (20°)	0.9788 (20°)	(136, 408, 424, *442*)
$C_2H_5OCOCH_2CH_2Si(CH_3)_2O[Si(CH_3)_2O]_1Si(CH_3)_2CH_2CH_2COOC_2H_5$		174/7 mm.	1.4288 (20°)	0.9787 (20°)	(136, 424, *442*)
$C_2H_5OCOCH_2CH_2Si(CH_2)_2O[Si(CH_3)_2O]_2Si(CH_3)_2CH_2CH_2COOC_2H_5$		186/7 mm.	1.4257 (20°)	0.9797 (20°)	(136, 424, *442*)
$C_2H_5OCOCH_2CH_2Si(CH_3)_2[Si(CH_3)_2O]_3Si(CH_3)_2CH_2CH_2COOC_2H_5$		190/4 mm.	1.4255 (20°)	0.9807 (20°)	(136, 424, *442*)
$C_2H_5OCOCH(CH_3)CH_2Si(CH_3)_3$		50/9 mm.	1.4168 (20°)	0.8553 (20°)	(226)
$C_2H_5OCOCH[COCH_2Si(CH_3)_3]CH_2Si(CH_3)_3$		141/8 mm.	1.4472 (20°)	0.9196 (20°)	(444)
$CH_3OCO(CH_2)_{10}SiCl_3$		193/15 mm.	1.4622 (15°)	1.1231 (15°)	(95)
$CH_3OCO(CH_2)_{10}Si(OC_2H_5)_3$		164–165/2 mm.	1.4340 (20°)	0.9529 (20°)	(95)
$CH_3OCO(CH_2)_{10}Si(C_2H_5)Cl_2$		150–151/0.7 mm.	1.4611 (20°)	1.0429 (20°)	(96)
$CH_3OCO(CH_2)_{10}Si(C_2H_5)_2Cl$		155–156/1 mm.	1.485 (20°)	0.9666 (20°)	(96)
$CH_3OCO(CH_2)_{10}Si(C_2H_6)OH$		159/1 mm.	1.4580 (20°)	0.9399 (20°)	(96)
$[CH_3OCO(CH_2)_{10}Si(C_2H_5)_2]_2O$		258–260/1 mm.	1.4592 (20°)	0.9373 (20°)	(96)
$C_2H_5OCOC_{10}H_{20}Si(C_6H_5)_3$	49	270/<1 mm.			(176)
Diels–Alder adducts: see table 1					
Carbethoxyalkylthiaalkyls: see table 15					
$(2\text{-}C_2H_6OCOCH_2C_6H_4)_3SiH$	107				(43)
$3\text{-}C_2H_5OCOC_6H_4Si(CH_3)_3$		90–91/1.5 mm.			(375)
$4\text{-}C_2H_5OCOC_6H_4Si(CH_3)_3$		105–106/2.7 mm.			(375)
$[4\text{-}CH_3OCOC_6H_4Si(CH_3)_2]_2O$	57–61				(450)
$[4\text{-}CH_3OCOC_5H_4Si(C_6H_5)_2OSi(CH_3)_2O]_2$	134–136				(450)
$C_2H_5OCOC_6H_4Si$ compounds					(30)
$(4\text{-}CH_3OCOC_6H_4)_2Si(CH_3)_2$	83–84				(450)
$(4\text{-}C_6H_5OCOC_6H_4)_2Si(CH_3)_2$	107–108				(450)
$(4\text{-}CH_3OCOC_6H_5)_2Si(C_5H_5)_2$	169–170				(450)
$[C_2H_5OCOCH_2CH_2(COOC_2H_5)CH_2Si(CH_3)_2]_2O$		205/2 mm.	1.4500 (20°)		(433)
$C_2H_5OCOCH_2CH_2CH[CH_2Si(CH_3)_3]COOC_2H_5$		122/4.5 mm.	1.4598 (20°)		(433)
$(4\text{-}HOOCC_5H_4)_2Si(CH_3)_2$ – – – $HOCH_2CH_2OH$ polyester					(450)
$(4\text{-}HOOCC_6H_4)_2Si(C_6H_5)_2$ – – – $HOCH_2CH_2OH$ polyester					(450)

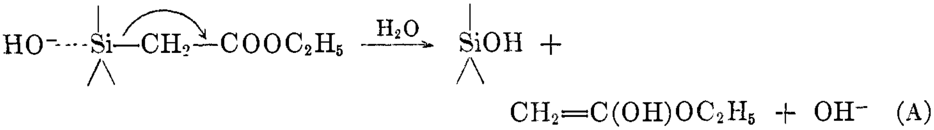
$[4\text{-}HOOCC_6H_4Si(CH_3)_2]_2O$ – – – $HOCH_2CH_2OH$ polyester					(450)
Carboxyphenylsiloxane–glycerol polyesters					(25)
$OC[CH_2CH_2Si(CH_3)_3]{=}C(COOC_2H_5)CH{=}CCH_3$		90/2 mm.	1.4695 (20°)		(443)
β-Keto esters:					
$CH_3COCH[CH_2Si(CH_3)_3]COOC_2H_5$		126/50 mm.	1.4405 (20°)	0.949 (20°)	(406, 416, *437*, 443)
$CH_3COC(CH_3)[CH_2Si(CH_3)_3]COOC_2H_5$		87/5 mm.	1.4420 (20°)	0.9512 (20°)	(416, *437*)
$CH_3COC(C_2H_5)[CH_2Si(CH_3)_3]COOC_2H_5$		92/3 mm.	1.4453 (20°)	0.9509 (20°)	(416, *437*)
$C_2H_5OCOCH_2COCH_2CH_2Si(CH_3)_3$		126/14 mm.	1.4392 (20°)	0.9465 (20°)	(443)
$(CH_3)_3SiCH_2CH(COOC_2H_5)COCH_2CH_2Si(CH_3)_3$		161/8 mm.	1.4473 (20°)		(421)
$CH_3COCH_2CH(COOC_2H_5)COCH_2CH_2Si(CH_3)_3$					(443)
Malonic esters:					
$(C_2H_5OCO)_2CHCH_2Si(CH_3)_3$		119/13 mm.	1.4312 (20°)	0.9680 (20°)	(406, 422, *433*)
$(C_2H_5OCO)_2CHCH_2Si(CH_3)_2C_6H_5$		132/1 mm.	1.4900 (20°)	1.042 (20°)	(406, 408, *433*)
$(C_2H_5OCO)_2CHCH_2Si(CH_3)_2CH_2Si(CH_3)_3$		88/1 mm.	1.4460 (20°)	0.9516 (20°)	(406, 425)
$[(C_2H_5OCO)_2CHCH_2Si(CH_3)_2]_2O$		81–86/1 mm.	1.4299 (20°)		(417)
$(C_2H_5OCO)_2C(CH_3)CH_2Si(CH_3)_3$		122/15 mm.	1.4351 (20°)	0.9663 (20°)	(406, *433*)
$(C_2H_5OCO)_2CH(CH_2)_3Si(CH_3)_3$		114/2 mm.	1.4330 (20°)	0.9472 (20°)	(406, 433)
$(C_2H_5OCO)_2C(CH_2CH{=}CH_2)CH_2Si(CH_3)_3$		89/2 mm.	1.4472 (20°)		(433)
$(C_6H_6OCO)_2C(CH_2CH_2CN)CH_2Si(CH_3)_3$		138/1.2 mm.	1.4519 (20°)		(422, *433*)
Acyloxyalkyls and aryls:					
$CH_3COOCH_2Si(CH_3)_3$		137/748 mm.	1.4060 (25°)	0.8667 (25°)	(240, 466, 467, *482*)
$C_6H_5CH(OCOCH_3)Si(CH_3)_3$		107/6 mm.	1.4917 (25°)	0.9780 (25°)	(240)
$3,5\text{-}(NO_2)_2C_6H_3COOCH_2Si(CH_3)_3$	70				(482)
$(CH_3COOCH_2)_2Si(CH_3)_2$		223/739 mm. 124/27 mm.	1.4310 (25°)	1.0135 (25°) 1.1035 (25°)	(466, 467, *481*)
$CH_3COOCH_2Si(CH_3)_2OSi(CH_3)_3$		180/735 mm.	1.4040 (25°)	0.902 (25°)	(458, 461, *483*)
$[CH_3COOCH_2Si(CH_3)_2]_2O$		250/760 mm.	1.4215 (25°)	0.993 (25°)	(457, 458, 461, 464, *483*)
Dibasic acid polyesters					(464)
$[CH_3COOCH_2Si(CH_3)C_6H_5]_2O$		210/1 mm.	1.5118 (25°)	1.092 (25°)	(457, 458, *461*)
Acetoxymethylsiloxanes					(341, 458, 461, 466, 467)
$CH_3COOC_2H_4Si(C_2H_5)_3$		211			(157, 158, *342*)
$(C_6H_5COOCH_2Si(CH_3)_2]_2O$					(461)
$[(CH_3)_3Si(CH_2)_3OCOCH_2CH_2]_2$		101/25 mm.	1.4370 (25°)	0.839 (25°)	(465)
$4\text{-}(4\text{-}NO_2C_6H_4COO)\text{-}2\text{-}CH_3C_6H_3Si(CH_3)_3$	120				(465)
$2\text{-}[3,5\text{-}(NO_2)_2C_6H_3COO]C_6H_4Si(CH_3)_3$					(465)
$4\text{-}[3,5\text{-}(NO_2)_2C_6H_3COO]C_6H_4Si(CH_3)_3$	143				(465)

$COCH_3$ behaves normally with strong acid and base, giving the corresponding furan and cyclopentenone, respectively (443).

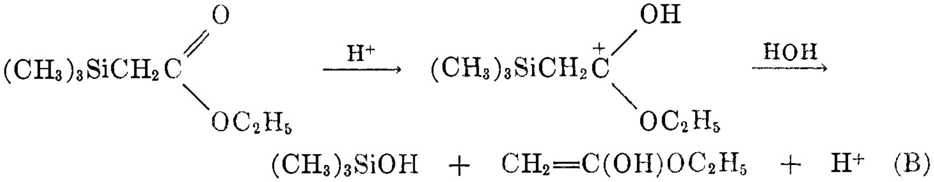
The susceptibility of alpha-substituted silylalkyl esters to silicon–carbon cleavage is very amply demonstrated by the behavior of $(CH_3)_3SiCH_2COOC_2H_5$ toward both nucleophilic and electrophilic reagents (223). The mechanisms of these reactions have been pictured (223) as involving nucleophilic attack on silicon (A) or electrophilic attack on the carbonyl group (B).



$$(CH_3)_3SiCH_2COOC_2H_5 \xrightarrow{C_2H_5OH} (CH_3)_3SiOC_2H_5 + CH_3COOC_2H_5$$
$$(CH_3)_3SiCH_2COOC_2H_5 \xrightarrow{5\%\ NaOH} (CH_3)_3SiOSi(CH_3)_3 + CH_3COONa$$
$$(CH_3)_3SiCH_2COOC_2H_5 \xrightarrow{HCl} (CH_3)_3SiCl + CH_3COOC_2H_5$$
$$(CH_3)_3SiCH_2COOC_2H_5 \xrightarrow{Br_2} (CH_3)_3SiBr + BrCH_2COOC_2H_5$$



$$HO^- \cdots Si{-}CH_2{-}COOC_2H_5 \xrightarrow{H_2O} SiOH + CH_2{=}C(OH)OC_2H_5 + OH^- \quad (A)$$



$$(CH_3)_3SiCH_2C(=O)OC_2H_5 \xrightarrow{H^+} (CH_3)_3SiCH_2\overset{+}{C}(OH)OC_2H_5 \xrightarrow{HOH} (CH_3)_3SiOH + CH_2{=}C(OH)OC_2H_5 + H^+ \quad (B)$$

A silicon-functional reaction that is readily carried out with $O[Si(CH_3)_2CH_2CH_2COOC_2H_5]_2$ is its equilibration with $[{-}Si(CH_3)_2O{-}]_4$ in the presence of a little concentrated sulfuric acid to form a series of linear α,ω-esters of the type $C_2H_5OOCCH_2CH_2Si(CH_3)_2O[Si(CH_3)_2O]_xSi(CH_3)_2CH_2CH_2COOC_2H_5$ (442). The lower members of this series have activation energies for viscous flow that are higher than those of the parent siloxanes and that are therefore indicative of increased intermolecular forces.

Few properties of silicon-substituted aromatic esters have been studied. The rates of hydrolysis of simple esters like $(CH_3)_3SiC_6H_4COOC_2H_5$ have been determined in connection with elucidating the electron-donating influence of the $(CH_3)_3Si{-}$ group (375). Silylaryl esters have been alcoholyzed with ethylene glycol (450). Polyesters prepared in this way and also from analogous carboxylic acids and polyalcohols have exhibited no outstanding properties (450).

Esters of the acyloxyalkylsilyl type, i.e., those in which the silicon is part of the alcohol group rather than the ester group, are considered in the section on hydroxy compounds.

XV. Other Carbonyl and Related Compounds (See Table 14)

A. ACID HALIDES

The formation of $Cl_3SiCOCl$ by catalytic addition of silicon tetrachloride to carbon monoxide has been claimed, but with little substantiation (397). Aliphatic acid halides with silicon in the beta and gamma positions, e.g., $(CH_3)_3SiCH_2CH_2COCl$, are obtained without difficulty by treating the corresponding acids with thionyl chloride or phosphorus tribromide (413, 437, 445). Silyl aromatic acid halides are similarly prepared; here it is noteworthy that electron attraction by —COOH and —COCl groups minimizes silicon–phenyl cleavage (38, 39, 40).

The reactions of silicon-containing acid halides include the formation of amides with amines (38, 164, 411, 437) and the formation of ketones with organometallic reagents (40, 437). The *m*- and *p*-silyl aromatic acid halides also readily undergo Friedel–Crafts coupling with toluene and anisole (40); the fact that the silicon–phenyl bond is not cleaved, as it frequently is by acidic reagents,

$$4\text{-}(CH_3)_3SiC_6H_4COCl + C_6H_5CH_3 \xrightarrow{AlCl_3} 4\text{-}[4'\text{-}(CH_3)_3SiC_6H_4CO]C_6H_4CH_3$$

demonstrates the stabilizing effect of the electron-attracting carbonyl group.

B. AMIDES

Aliphatic amides containing silyl groups beyond the alpha carbon, e.g., $(CH_3)_3SiCH_2CH_3CONH_2$, are readily obtained from reaction of the corresponding acid halides with amines (38, 164, 411, 412, 445). Related polyamides are formed by heating together dicarboxylic acids and diamines either or both of which contain silicon (450).

The reactions of silicon-substituted amides include the dehydration and Hofmann degradation of $(CH_3)_3SiCH_2CH_2CONH_2$ (445) and the sulfuric acid demethylation of $(CH_3)_3SiCH_2CH_2CONHCH_2CH_2Si(CH_3)_3$ to $[—Si(CH_3)_2CH_2CH_2CONHCH_2CH_2Si(CH_3)_2O]_x$(411). The known silicon-containing polyamides show no unusual fiber properties (450).

C. NITRILES

The preparation of H_3SiCN by the reaction of silyl bromide with silver cyanide has been reported (145), but later work suggests that actually the isonitrile is obtained (138, 323). Cyanomethyl silicon compounds are obtained in fair yield by the reaction of cyanogen with appropriate Grignard reagents (370b). Similar compounds are not isolated from the reaction of chloromethyl silicon derivatives

$$(CH_3)_3SiOSi(CH_3)_2CH_2MgCl + (CN)_2 \rightarrow (CH_3)_3SiOSi(CH_3)_2CH_2CN$$

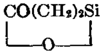
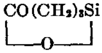
with alcoholic sodium cyanide, probably because the cyanomethyl group readily undergoes hydrolytic silicon–carbon cleavage (240, 294). The reaction of $(CH_3)_3SiCH_2Cl$ and sodium cyanide without solvent produces $(CH_3)SiCH_2CN$ in low yield (370b). The next higher homolog, $(CH_3)_3SiCH_2CH_2CN$, is obtained by the dehydration of $(CH_3)_3SiCH_2CH_2CONH_2$ with phosphorus pentoxide (445). Aromatic silicon-containing nitriles are prepared by the Rosenmund–von Braun reaction (309, 450).

$$(CH_3)_2Si(C_6H_4Br)_2 \xrightarrow[C_5H_5N]{Cu(CN)_2} (CH_3)_2Si(C_6H_4CN)_2$$

TABLE 14

Other carbonyl (and related) compounds containing silicon

Compound	Melting Point	Boiling Point	n_D	d	References
	°C.	*°C.*			
Nitriles:					
$CNSiH_3$	34				(145, 323)
$CN(CH_2)_2Si(CH_3)_3$		94/49 mm.	1.4240 (20°)	0.8270 (20°)	(404, *445*)
$(C_2H_5OCO)_2C(CH_2CH_2CN)CH_2Si(CH_2)_3$		138/1.2 mm.	1.4519 (20°)		(422, *433*)
$CNCH(C_6H_5)Si(CH_3)_3$					(240)
$CNCH_2CH_2OCH_2Si(CH_3)_3$		98/20 mm.	1.4245 (20°)		(423)
$[4\text{-}CNC_6H_4Si(CH_3)_2]_2O$		200/2 mm.	1.5351 (25°)	1.0460 (25°)	(309)
$(4\text{-}CNC_6H_4)_2Si(CH_3)_2$	100–101				(450)
Cyanophenylsiloxanes					(177)
Acid halides:					
$COClSiCl_3$					(397)
$COCl(CH_2)_2Si(CH_3)_3$		92/65 mm.	1.4375 (20°)	0.9609 (20°)	(404, 411, 412, 413, 416, *437*, 439, 443, 445)
$COCl(CH_2)_2Si(CH_3)_2C_6H_5$		114/3 mm.	1.5188 (20°)	1.0664 (20°)	(412, 413, 416, 437)
$COCl(CH_2)_3Si(CH_3)_3$		105/57 mm.	1.4381 (20°)	0.9464 (20°)	(404, 412, 413)
$2\text{-}COClC_6H_4Si(CH_3)_3$		66–67/0.5 mm.	1.5360 (20°)		(40)
$3\text{-}COClC_5H_4Si(CH_3)_3$		70/0.5 mm.	1.5252 (20°)		(38, 40)
$4\text{-}COClC_6H_4Si(CH_3)_3$		75–76/1 mm.	1.5315 (20°)		(*39*, 40, 164, 166)
Amides:					
$CONH_2(CH_2)_2Si(CH_3)_3$	96				(404, 412, 439, *445*)
$CONH_2(CH_2)_2Si(CH_3)_2C_6H_5$					(412)
$CONH(CH_3)(CH_2)_2Si(CH_3)_3$		108/12 mm.	1.4410 (20°)		(404, *445*)
$CONH[(CH_2)_2Si(CH_3)_3](CH_2)_2Si(CH_3)_3$		132/2 mm.			(411)
$CONH[(CH_2)_2Si(CH_3)_2C_5H_5](CH_2)_2Si(CH_3)C_6H_5$					(411)
$[\text{—}Si(CH_3)_2(CH_2)_2CONH(CH_2)_2Si(CH_3)_2O\text{—}]_x$					(411)
$CONH_2(CH_2)_3Si(CH_3)_3$	67				(404, 412)
$2\text{-}CONH_2C_6H_4Si(CH_3)_3$	124.5–125				(*40*, 395)
$2\text{-}CONH(C_6H_5)C_6H_4Si(CH_3)_3$	120.5–130				(40)
$3\text{-}CONH_2C_6H_4Si(CH_3)_3$	129.5–130				(*38*, 395)
$3\text{-}CONH(C_6H_5)C_6H_4Si(CH_3)_3$	127–127.5				(40)
$4\text{-}CONH_2C_5H_4Si(CH_3)_3$	155				(*39*, 164, 166, 395)
$4\text{-}CONH(C_6H_5)C_6H_4Si(CH_3)_3$	142–142.5				(40)
$(4\text{-}HOOCC_6H_4)_2Si(CH_3)_2$ – – – $NH_2(CH_2)_6NH_2$ polyamide					(450)
$(4\text{-}HOOCC_6H_4)_2Si(CH_3)_2$ – – – $NH_2(CH_2)_{10}NH_2$ polyamide					(450)
$(4\text{-}HOOCC_6H_4)_2Si(CH_2)_2$ – – – $(4\text{-}NH_2CH_2C_6H_4)_2Si(CH_3)_2$ polyamide					(450)

$[(4\text{-}HOOCC_6H_4Si(CH_3)_2]_2O$ --- $NH_2(CH_2)_6NH_2$ polyamide					(450)
$[4\text{-}HOOCC_6H_4Si(CH_3)_2]_2O$ --- $(4\text{-}H_2NCH_2C_6H_4)_2Si(CH_3)_2$ polyamide					(450)
$[4\text{-}HOOCC_6H_4Si(C_6H_5)_2OSi(CH_3)_2]_2O$ --- $NH_2(CH_2)_6NH_2$ polyamide					(450)
$[4\text{-}HOOCC_6H_4Si(C_6H_5)_2OSi(CH_2)_2]_2O$ --- $(4\text{-}NH_3CH_2C_6H_4)_2Si(CH_3)_2$ polyamide					(450)
Amidoalkylthiaalkyls: see table 15					
Acylaminomethyls: see table 8					
Acylaminophenyls: see table 8					
Lactones and urethans:					
 $CO(CH_2)_2Si(CH_3)_2$ (ring closed by O)		96/4 mm.			(407, 408, *417*, 433)
 $CO(CH_2)_3Si(CH_3)_2$ (ring closed by O)		115/14 mm.	1.4560 (20°)		(407, 417)
$C_6H_5NHCOOCH_2Si(CH_3)_3$					(482)
$4\text{-}(1\text{-}C_{10}H_7NHCOO)C_6H_4Si(CH_3)_3$	155				(465)
$[-Si(CH_3)_2CH_2OCONH(CH_2)_5NHCOOCH_2-]_x$					(457)
$[-Si(CH_3)_2CH_2OCONH(2,4\text{-}C_6H_3)NHCOOCH_2-]_x$					(457)

Cyanomethyl silicon compounds are hydrolytically unstable like many other alpha-substituted silicon derivatives. The cyanomethylsiloxanes can be equilibrated with other siloxanes by means of sulfuric acid, but this reaction is accompanied by some cleavage of cyanomethyl groups. Activation energies for viscous flow, dielectric constants, dipole moments, and other properties indicative of enhanced intermolecular forces have been reported for cyanomethyl silicon compounds (370b). Other properties of higher silicon-containing nitriles include reduction to amines and hydrolysis to acids (309, 445, 450).

D. URETHANS

The Hofmann reaction with $(CH_3)SiCH_2CH_2CONH_2$ produces a good yield of the urethan, $(CH_3)_3SiCH_2CH_2NHCOOCH_3$, whose hydrolysis gives the amine and an unexpected by-product alkyl urea, $[(CH_3)_3SiCH_2CH_2NH]_2CO$ (445).

E. LACTONES

The lactone $\underbracket{OSi(CH_3)_2CH_2CH_2CO}$ has been isolated from the reaction of $(CH_3)_3SiCH_2CH_2COOH$ with sulfuric acid and from the thermal degradation of $O[Si(CH_3)_2CH_2CH_2COOH]_2$. The lactone is readily hydrolyzed to the disiloxanedicarboxylic acid (407, 408, 417).

XVI. SULFUR COMPOUNDS (SEE TABLE 15)

A. MERCAPTANS

Mercaptomethyl silicon compounds are readily obtained by the reaction of chloromethyl silicon derivatives with sodium hydrosulfide in alcohol (120). A less direct route, which has been applied only to making $HSCH_2Si(CH_3)_3$,

$$(CH_3)_3SiOSi(CH_3)_2CH_2Cl \xrightarrow[C_2H_5OH]{NaSH} (CH_3)_3SiOSi(CH_3)_2CH_2SH$$

involves the alkaline decomposition of the isothiuronium salt (347). Another method for preparing silicon-containing thiols proceeds through the addition of thioacetic acid to unsaturated silicon compounds, followed by hydrolysis of the resulting thiol ester (321).

$$(CH_3)_2Si(CH_2CH{=}CH_2)_2 + CH_3COSH \rightarrow$$

$$(CH_3)_2Si(CH_2CH_2CH_2SCOCH_3)_2 \xrightarrow{NaOH} (CH_3)_2Si(CH_2CH_2CH_2SH)_2$$

Only limited studies of the reactions of silyl-substituted mercaptans have been made. The isolation of mercaptomethyl silicon compounds from alkaline solution suggests that an alpha-thiol group produces no profound decrease in silicon–carbon stability. Silicon-containing bisthiols have been emulsion copolymerized with various dienes (321).

B. THIO ETHERS

Silyl-substituted thio ethers are readily prepared by the reaction of chloromethyl silicon compounds with sodium mercaptides in alcohol (121, 347). A similar type of reaction has been used in establishing unequivocally the structures of isomers produced in the chlorination and bromination of ethyl silicon compounds (302, 303, 304). Another method for making silyl-substituted thio ethers involves coupling metalated thio ethers with chlorosilanes or alkoxysilanes (187). An excellent synthesis for many silicon-containing thio ethers is through the free-radical addition of various thiols to unsaturated silicon compounds (78, 80, 82, 84, 86, 87, 187, 306, 321).

$$\underline{OSi(CH_3)_2OSi(CH_3)_2OSi(CH_3)_2OSi}(CH_3)CH_2Cl \xrightarrow[C_2H_5OH]{NaSCH_3} \underline{OSi(CH_3)_2OSi(CH_3)_2OSi(CH_3)_2OSi}(CH_3)CH_2SCH_3$$

$$C_6H_5SCH_3 \xrightarrow{C_4H_9Li} C_6H_5SCH_2Li \xrightarrow{Si(OC_2H_5)_4} (C_6H_5SCH_2)_4Si$$

$$(CH_3)_3SiCH_2CH{=}CH_2 + HSCH_2COOH \rightarrow (CH_3)_3SiCH_2CH_2CH_2SCH_2COOH$$

Few reactions of silyl-substituted thio ethers have been studied. They may be oxidized to sulfones, methylated to sulfonium iodides, and equilibrated with other siloxanes by means of sulfuric acid as catalyst (121, 187).

C. SULFONES

Silicon-containing sulfones are prepared principally by the oxidation of the corresponding thio ethers with such reagents as hydrogen peroxide, peracetic acid, and monoperphthalic acid (121, 187). Another method involves coupling metalated organic sulfones with chlorosilanes (187).

$$(CH_3)_3SiOSi(CH_3)_2CH_2SCH_3 \xrightarrow{1,2\text{-}C_6H_4(COOH)(CO_3H)} (CH_3)_3SiOSi(CH_3)_2CH_2SO_2CH_3$$

Little is known about the reactions of silicon-containing sulfones. The α-silyl-substituted compounds readily undergo silicon–carbon cleavage by base, in accord with other observations on the effect of strong electron-attracting groups in the alpha position. These compounds are less susceptible to acid cleavage, and some observations on their equilibration with other siloxanes are available (121).

D. THIOCYANATES

Thiocyanatomethyl silicon compounds are readily prepared by the reaction of the corresponding chloromethyl derivatives with sodium thiocyanate (119).

$$(CH_3)_3SiOSi(CH_3)_2CH_2Cl + NaSCN \rightarrow (CH_3)_3SiOSi(CH_3)_2CH_2SCN$$

TABLE 15

Silicon-containing sulfur compounds

Compound	Melting Point	Boiling Point	n_D	d	References
	°C.	°C.			
Mercaptans and thio ethers:					
$HSCH_2Si(CH_3)_3$		115	1.4468 (25°)	0.8320 (25°)	(347)
		55/93 mm.	1.4502 (20°)	0.8430 (20°)	
$S[CH_2Si(CH_3)_3]_2$		129/95 mm.	1.4570 (20°)	0.8000 (20°)	(121)
$CH_3SCH_2Si(CH_3)_3$		70/93 mm.	1.4505 (20°)	0.8399 (20°)	(121)
Methyl iodide salt	106				(121)
$Cl(NH_2)_2CSCH_2Si(CH_3)_3$	141.5–143				(120)
$Br(NH_2)_2CSCH_2Si(CH_3)_3$	173				(347)
$C_2H_5SCH_2Si(CH_3)_3$		44/9 mm.	1.4512 (25°)	0.8402 (25°)	(347)
$C_3H_7SCH_2Si(CH_3)_3$		60/9 mm.	1.4518 (25°)	0.8377 (25°)	(347)
$(CH_3)_2CHSCH_2Si(CH_3)_6$		53/9 mm.	1.4494 (25°)	0.8321 (25°)	(347)
$C_4H_9SCH_2Si(CH_3)_3$		75/9 mm.	1.4530 (25°)	0.8352 (25°)	(347)
$(CH_3)_2CHCH_2SCH_2Si(CH_3)_3$		66/9 mm.	1.4502 (25°)	0.8314 (25°)	(347)
$(CH_3)_3CSCH_2Si(CH_3)_3$		56/9 mm.	1.4496 (25°)	0.8270 (25°)	(347)
$C_5H_{11}SCH_2Si(CH_3)_3$		89/9 mm.	1.4542 (25°)	0.8374 (25°)	(347)
$(CH_3)_2CHCH_2CH_2SCH_2Si(CH_3)_3$		86/9 mm.	1.4530 (25°)	0.8347 (25°)	(347)
$C_6H_5SCH_2Si(CH_3)_3$		158.5/52 mm.	1.5380 (20°)	0.9671 (20°)	(121)
$(C_5H_5SCH_2)_4Si$	67–69				(*187*, 192)
$4\text{-}CH_3C_5H_4SCH_2Si(CH_3)_3$		83–85/1 mm.	1.5356 (20°)	0.9545 (20°/20°)	(187)
$4\text{-}CH_3C_5H_4SCH_2Si(C_6H_5)_3$	148–149				(187)
$(4\text{-}CH_3C_6H_4SCH_2)_4Si$	70				(187)
$C_6H_5CH_2SCH_2Si(CH_3)_3$		124/8 mm.	1.5242 (25°)	0.9507 (25°)	(347)
$HSCH_2Si(CH_3)_2OSi(CH_3)_3$		99/88 mm.	1.4308 (20°)	0.8909 (20°)	(120)
$HSCH_2\underline{Si(CH_3)[OSi(CH_3)_2]_3O}$		98.5/10 mm.	1.4280 (20°)	1.0310 (20°)	(120)
$CH_3SCH_2Si(CH_3)_2OSi(CH_3)_3$		114/96 mm.	1.4342 (20°)		(121)
$[CH_3SCH_2Si(CH_3)_2]_2O$		87/2 mm.	1.4742 (20°)		(121)
$CH_3SCH_2\underline{Si(CH_3)[OSi(CH_3)_2]_3O}$		110/11 mm.	1.4318 (20°)	1.0203 (20°)	(121)
Methyl iodide	129–130				(121)
Methylthiomethylsiloxanes					(121)
$C_6H_5SCH_2Si(CH_3)_2OSi(CH_3)_3$		170.5/37 mm.	1.5014 (20°)	0.9705 (20°)	(121)
$C_6H_5SCH_2\underline{Si(CH_3)[OSi(CH_6)_2]_3O}$		178/12 mm.	1.4807 (20°)	1.0664 (20°)	(121)
$C_6H_5SCH_2CH_2Si(C_6H_5)_3$	99–100				(187)

4-$CH_2C_5H_4SCH_2CH_2Si(C_5H_5)_3$	97–99				(187)
$C_6H_5CH_2SCH_2CH_2Si(C_6H_5)_2$	72–73				(187)
$(HSCH_2CH_2CH_2)_2Si(CH_3)_2$		66–67/1 mm.			(321)
$(CH_3COSCH_2CH_2CH_2)_2Si(CH_3)_2$		127.5–129.5/0.35 mm.	1.5068 (20°)		(321)
$[(HSCH_2CH_2CH_2Si(CH_3)_2]_2O$		87–89/0.25 mm.	1.4739 (20°)		(321)
$[(CH_3COSCH_2CH_2CH_2Si(CH_3)_2]_2O$		125–127/0.15 mm.	1.4816 (20°)		(321)
4-$CH_3C_6H_4S(CH_2)_3Si(CH_3)_3$		208/46 mm.	1.5267 (20°)	0.9408 (20°)	(*80*, 82)
$HOOCCH_2SCH(CH_3)Si(C_2H_5)_2$					(302, 303, 304)
$HOOC(CH_2)_2SCH(CH_3)Si(C_2H_5)_3$					(303)
$HOOCCH_2S(CH_2)_2Si(CH_3)_3$		144/7 mm.	1.4811 (20°)	1.0139 (20°)	(65, *80*, 86)
Sodium salt					
$HOOCCH_2SCH_2CH_2Si(C_2H_5)_3$		184–186/12 mm.			(306)
$C_2H_5OCOCH_2S(CH_2)_3Si(OC_2H_5)_3$		201/50 mm.	1.4479 (20°)	1.0301 (20°)	(*80*, 84)
$HOOCCH_2S(CH_2)_3Si(CH_3)_3$		165/9 mm.	1.4790 (20°)	1.0009 (20°)	(65, *80*, 86)
4-Toluide	73				
Sodium salt					
$C_2H_5OCOCH_2S(CH_2)_3Si(CH_3)_3$		263 149/24 mm.	1.4630 (20°)	0.9493 (20°)	(65, *80*)
$HOOCCH_2S(CH_2)_3Si(CH_3)_2OSi(CH_2)_3$		150/2 mm.	1.4588 (20°)	0.9902 (20°)	(65, *80*, 86)
Sodium salt					
Lithium salt					
$[C_2H_5OCOCH_2S(CH_2)_3]_2Si(C_2H_5)_2$					(78)
$NH_2(CH_2)_6NH_2$ polymer					(78)
$(HSCH_2COOCH_2)_2$ - - - $(CH_2{=}CHCH_2)_2Si(CH_3)_2$ adduct					(88)
$(HSCH_2COOCH_2)_2$ - - - $[CH_2{=}CHCH_2Si(CH_3)_2]_2O$ adduct					(88)
$HSCH_2COOH$ - - - allylsiloxane adduct					(87)
$HS(CH_2)_6SH$ - - - $(CH_2{=}CHCH_2)_2Si(CH_3)_2$ adduct					(321)
$(HSCH_2CH_2CH_2)_2Si(CH_3)_2$ - - - $(CH_2{=}CHCH_2)_2Si(CH_3)_2$ adduct					(321)
$(HSCH_2CH_2CH_2)_2Si(CH_3)_2$ - - - $[CH_2{=}C(CH_3)CH_2]_2$ adduct					(321)
$(HSCH_2CH_2CH_2)_2Si(CH_3)_2$ - - - 2,6-$(CH_2{=}CHCH_2)_2C_6H_3OCOCH_3$ adduct					(321)
$(HSCH_2CH_2CH_2)_2Si(CH_3)_2$ - - - 2,6-$(CH_2CH{=}CH_2)_2C_6H_3OH$ adduct					(321)
$(HSCH_2CH_2CH_2)_2Si(CH_3)_2$ - - - $(CH_2{=}CHCH_2)_2CHOH$ adduct					(321)
$(HSCH_2CH_2CH_2)_2Si(CH_3)_2$ - - - $(CH_2{=}CHCH_2)_2$ adduct					(321)
$[HSCH_2CH_2CH_2Si(CH_3)_2]_2O$ - - - $(CH_2{=}CHCH_2)_2$ adduct					(321)
$[HSCH_2CH_2CH_2Si(CH_3)_2]_2O$ - - - $[CH_2{=}C(CH_3)CH_2]$ adduct					(321)
$[HSCH_2CH_2CH_2Si(CH_3)_2]_2O$ - - - $(CH_2{=}CHCH_2)_2Si(CH_3)_2$ adduct					(321)
Thiocyanates:					
$NCSCH_2Si(CH_3)_3$		196–197/atm.	1.4676 (20°)	0.9426 (20°)	(119)
$NCSCH_2Si(CH_3)_2OSi(CH_3)_3$		135/42 mm.	1.4443 (20°)	0.9518 (20°)	(119)
$NCSCH_2Si(CH_3)[OSi(CH_3)_2]_3O$		168/47 mm.	1.4370 (20°)	0.0645 (20°)	(119)
$NCSCH_2$ siloxane					(119)
Thiocyanogen–olefin adducts					(71)

TABLE 15—*Concluded*

Compound	Melting Point	Boiling Point	n_D	d	References
	°C.	*°C.*			
Sulfones:					
$CH_3SO_2CH_2Si(CH_3)_3$	78–79				(121)
$SO_2[CH_2Si(CH_3)_3]_2$	47–48				(121)
$C_5H_5SO_2CH_2Si(CH_3)_2$		160/6 mm.	1.5250 (20°)		(121)
$4\text{-}CH_3C_6H_4SO_2CH_2Si(C_6H_5)_3$	175				(187)
$CH_3SO_2CH_2Si(CH_3)_2OSi(CH_3)_3$		91/1 mm.	1.4432 (20°)		(121)
$[CH_3SO_2CH_2Si(CH_3)_2]_2O$	71–72				(121)
$CH_3SO_2CH_2\underbrace{Si(CH_3)[OSi(CH_3)_2]_3O}$	61–62.5				(121)
$C_6H_5SO_2CH_2CH_2Si(C_6H_5)_3$	155				(187)
$4\text{-}CH_3C_6H_4SO_2CH_2CH_2Si(C_5H_5)_3$	152				(187)
$C_6H_5CH_2SO_2CH_2CH_2Si(C_6H_5)_3$	153–154				(187)
Dibenzothiophene sulfones: see dibenzothiophenes (table 19)					
Sulfonic acids and derivatives:					
$(HSO_3C_6H_4)_3SiOH$					(126, 283, 301)
$[(HSO_3)(NO_2)C_8H_3]_3SiOH$					(283, 301)
$HSO_3C_6H_4CH_2Si(C_2H_5)(C_3H_7)OH$					(270, 272)
$4\text{-}HSO_3C_6H_4CH_2Si(CH_3)_3$					(94)
Monohydrate	116				
Amine salts					
dl-$HSO_3C_8H_4CH_2Si(C_2H_5)(CH_3)(C_3H_7)$					(272, 274)
Metal and amine salts					
$HSO_3C_6H_4CH_2Si(C_2H_5)(C_2H_7)_2$					(319)
Amine salts					
dl-$HSO_3C_5H_4CH_2Si(C_2H_5)(C_2H_7)(i\text{-}C_4H_9)$					(281)
Amine salts					
dl-$HSO_3C_5H_4CH_2Si(C_2H_5)(C_3H_7)(CH_2C_6H_5)$					(101)
Metal and amine salts					
dl-$[HSO_3C_6H_4CH_2Si(C_2H_5)(C_3H_7)]_2O$					(271, 272, 273, 275, 277, 319)
Amine salts					
d-$[HSO_3C_6H_4CH_2Si(C_2H_5)(C_3H_7)]_2O$					(275, 276)
Amine salts					
l-$[HSO_3C_6H_4CH_2Si(C_2H_6)(C_3H_7)]_2O$					(275, 276)
Amine salts					

dl-$[HSO_3C_6H_4CH_2Si(C_2H_5)(i\text{-}C_4H_9)]_2O$					(312)
Amine salts					
d-$[HSO_3C_6H_4CH_2Si(C_2H_5)(i\text{-}C_4H_9)]_2O$					(313)
Amine salts					
l-$[HSO_3C_6H_4CH_2Si(C_2H_5)(i\text{-}C_4H_9)]_2O$					(313)
Amine salts					
$[\text{—}Si(HSO_3C_6H_4CH_2)(C_2H_5)O\text{—}]_3$					(376)
dl-$(HSO_3C_8H_4CH_2)_2Si(C_2H_5)(C_3H_7)$					(101)
Metal and amine salts					
4-$SO_2ClC_6H_4CH_2Si(CH_3)_3$	46				(94)
4-$SO_2BrC_6H_4CH_2Si(CH_3)_3$	61				(94)
4-$SO_2NH_2C_6H_4CH_2Si(CH_3)_3$	82				(94)
4-$CH_3NHSO_2C_6H_4CH_2Si(CH_3)_3$	77				(94)
4-$C_5H_6NHSO_2C_6H_4CH_2Si(CH_3)_3$	125				(94, 555)
4-$[(2\text{-}CH_3C_6H_4)NHSO_2]C_6H_4CH_2Si(CH_3)_3$	153				(94)
4-$[(4\text{-}CH_3C_6H_4)NHSO_2C_6H_4CH_2Si(CH_3)_3$	98				(94)
4-$(C_6H_5NHSO_2)C_5H_4CH_2Si(CH_3)_3$	131				(94)
4-$[(CH_3)(C_6H_5)NSO_2]C_6H_4CH_2Si(CH_3)_3$	72				(94)

Another method of preparation, which gives 1,2-dithiocyanates, involves the addition of thiocyanogen to unsaturated alkyl silicon compounds (71).

The thiocyanatomethyl group is readily cleaved from silicon by base, but it is more stable toward acid. Methylpolysiloxanes containing thiocyanatomethyl groups exhibit an enhanced energy of activation for viscous flow, and they show infrared absorption characteristic of the thiocyanate group (119).

E. SULFONIC ACIDS AND DERIVATIVES

Sulfonated benzyl silicon compounds, which figured prominently in Kipping's classic resolution of organosilicon enantiomorphs, are readily obtained by sulfonating benzyl-substituted silanes, siloxanes, and disilanes in the para position with concentrated sulfuric acid or preferably chlorosulfonic acid (94, 101, 270, 271, 272, 273, 274, 275, 276, 277, 281, 312, 313, 319, 376).

A side reaction observed during the above studies foreshadowed a synthetic method later to prove of considerable utility. Kipping found (271, 274) that a methyl group was cleaved by concentrated sulfuric acid, and others later showed (439, 444) this reaction to be applicable to the synthesis of many symmetrical carbon-functional disiloxanes.

$$CH_3Si(C_2H_5)(C_3H_7)(CH_2C_6H_5) \xrightarrow[H_2SO_4]{\text{concd.}} \xrightarrow{H_2O} O[Si(C_2H_5)(C_3H_7)(CH_2C_6H_4SO_3H)]_2 + CH_4$$

$$(CH_3)_3SiCH_2CH_2COCH_3 \xrightarrow[H_2SO_4]{\text{concd.}} \xrightarrow{H_2O} O[Si(CH_3)_2CH_2CH_2COCH_3]_2 + CH_4$$

Sulfonated benzyl silicon compounds form salts with ease, and those with optically active bases have received considerable attention in connection with the resolution of compounds containing an asymmetric silicon atom (273, 275, 281, 312, 313). With phosphorus pentachloride silicon-containing sulfonic acids form the corresponding sulfonyl chlorides, which are readily converted to amide derivatives (94). The crystallographic properties of $(CH_3)_3SiCH_2C_6H_4SO_2$-NHC_6H_5 have been described (555).

The sulfonation of phenyl silicon compounds does not produce the corresponding sulfonic acids as claimed (301); silicon–phenyl cleavage products are obtained instead (271, 273, 283).

XVII. Nitro Compounds (See Table 16)

A. SYNTHESES

Among nitro carbon-functional silicon compounds only those with the substituent on an aromatic ring are known. They are obtained solely by the nitration of aromatic silicon compounds, a reaction whose study dates from the early days of silicon chemistry (370). The nitration of $(C_6H_5)_4Si$ gives a complex mixture from which the only pure compound thus far isolated is $(3\text{-}NO_2C_6H_4)_4Si$ in about 10 per cent yield (278, 279). The nitration of $(C_6H_5)_3SiC_2H_5$, $(C_6H_5)_2Si(C_2H_5)_2$,

TABLE 16

Silicon-containing nitro compounds

Compound	Melting Point	Boiling Point	n_D	d	References
	°*C.*	°*C.*			
2-$NO_2C_6H_4Si(CH_3)_3$		117/10 mm. 149/40 mm.	1.5321 (20°) 1.5290 (25°)	1.073 (20°)	(*34*, 46, 400, 475)
3-$NO_2C_5H_4Si(CH_3)_3$		126/10 mm. 161/40 mm.	1.5329 (20°) 1.5229 (25°)	1.055 (20°) 1.051 (25°)	(*34*, 46, *154*, 475)
4-$NO_2C_6H_4Si(CH_3)_3$	39	129/10 mm.	1.5238 (25°)		(*34*, 46, 400, *475*)
$NO_2C_6H_4Si(C_2H_5)_3$		307 175/20 mm.			(129, 280)
$NO_2C_6H_4Si$ compounds					(30)
(3-$NO_2C_6H_4)_2Si(C_2H_5)_2$	103				(280)
$[NO_2(BaSO_3)C_6H_3]_3SiOH$					(283, 301)
(3-$NO_2C_6H_4)_4Si$	256				(*278*, 279, 282, 524)
$(NO_2C_6H_4)_4Si$	93-105				(278, 279, 282, *370*, 524)
2-$NO_2C_6H_4CH_2Si(CH_3)_3$		125/10 mm.	1.5276 (20°)	1.045 (20°)	(34)
2-CH_3-5-$NO_2C_6H_3Si(C_2H_6)_3$	40–41	129-142/3 mm.			(42)
NO_2-3-$CH_3C_6H_3Si(C_2H_5)_3$		135-136/1 mm.	1.5299-1.5307 (20°)	1.029 (20°)	(42)
3-NO_2-4-$CH_3C_5H_3Si(C_2H_5)_3$		140/1 mm.	1.5268 (20°)	1.0277 (20°)	(42)
4-$NO_2C_6H_4CH_2Si(CH_3)_3$		147/10 mm.	1.5423 (20°) 1.5386 (22°)	1.069 (20°) 1.0510 (25°)	(34, 400)

and $C_6H_5Si(C_2H_5)_3$ also gives complex mixtures whose composition is known only through their silicon–carbon cleavage products obtained upon heating them with bromine water (280).

More recent nitration studies have centered about $C_6H_5Si(CH_3)_3$. The most clean-cut results are obtained by reaction with 90 per cent fuming nitric acid in acetic anhydride (475). At 0–10°C. the starting material reacts completely, giving only mononitro derivatives and 7 per cent of nitrobenzene through silicon–carbon cleavage. At 25–70°C. the reaction behaves similarly, except that about twice as much nitrobenzene is formed. Nitration of $C_6H_5Si(CH_3)_3$ may also be carried out with cupric nitrate trihydrate in acetic anhydride (34, 475). At 30–40°C. most of the starting material reacts, giving a 60 per cent yield of mononitro derivatives and a 25 per cent yield of nitrobenzene through silicon–carbon cleavage. The ratios ortho:meta:para nitrophenyltrimethylsilanes under these three sets of conditions are 27:42:32, 33:35:33, and 30:40:30, respectively, compared with the statistically expected isomer distribution ratio 40:40:20, or 30:47:23 if one allows for a 10 per cent decrease in ortho isomer because of steric factors. The isomer distribution ratios obtained indicate that the trimethylsilyl group is a very weak ortho–para director (34, 475). Parallel with this is a slight activation of the aromatic nucleus by the trimethylsilyl group; this is demonstrated by competitive nitration of $C_6H_5Si(CH_3)_3$ and benzene (475).

The nitration of other simple aromatic silicon compounds has also been studied. With copper nitrate in acetic anhydride the *o*-, *m*-, and *p*-tolyltriethylsilanes give respectively 50 per cent, 74 per cent, and 60 per cent yields of mononitro derivatives. The structure of pure isomers isolated in only small amounts suggests that the methyl group is dominant over the triethylsilyl group in determining the orientation (42). Benzyltrimethylsilane can also be nitrated with copper nitrate in acetic anhydride. There is obtained about a 5 per cent yield of nitrobenzene cleavage product and a 66 per cent yield of mononitro isomers containing 80 per cent ortho and 20 per cent para (34).

B. PROPERTIES

Not many reactions of nitro aromatic silicon compounds are known. Their reduction to amine, azo, and hydrazo derivatives will be discussed in connection with the synthesis of these compounds. The only other reaction that has received any considerable study is cleavage of the nitro aromatic group with bromine and water at elevated temperature. The silicon is displaced by bromine with formation of bromonitrobenzenes whose identity is of value in deducing the structures of nitroaryl silicon compounds (280).

$$NO_2C_6H_4Si(CH_3)_3 + Br_2 \xrightarrow[H_2O]{heat} NO_2C_6H_4Br + (CH_3)_3SiOSi(CH_3)_3$$

The ortho isomer of $NO_2C_6H_4Si(CH_3)_3$ undergoes cleavage with bromine and water at 200°C. with much greater difficulty than the other two isomers. Greater stability of an ortho isomer is also found in the superior resistance of $2\text{-}NO_2C_6H_4CH_2Si(CH_3)_3$ to alkali as compared with $4\text{-}NO_2C_6H_4CH_2Si(CH_3)_3$. The lowered reactivity of the ortho isomers may be attributed to steric factors or to chelation of a nitro oxygen with silicon by expansion of the latter's valence shell (34). In another study of the cleavage of silicon–aryl bonds with bromine it is shown that the reaction goes much more readily in nitrobenzene than in carbon tetrachloride and that the cleavage of $C_6H_5Si(CH_3)_3$ gives overall third-order kinetics (second order in bromine). The relative rates of cleavage of aryltrimethylsilanes are $C_6H_5 > 3\text{-}NO_2C_6H_4 > 4\text{-}NO_2C_6H_4 > 2\text{-}NO_2C_6H_4$, and this is the order expected for electrophilic substitution. The similarity between removal of a trimethylsilyl group by bromine and replacement of hydrogen in aromatic bromination has been pointed out (46).

The dipole moments of $2\text{-}NO_2C_6H_4Si(CH_3)_3$ (400), $3\text{-}NO_2C_6H_4Si(CH_3)_3$ (153), and $4\text{-}NO_2C_6H_4Si(CH_3)_3$ (400) have been determined.

XVIII. Azo Compounds (See Table 17)

A. SYNTHESES

Many azo compounds containing silyl substituents have been prepared, mainly in order to study their dyeing and carcinogenic properties. They can be obtained from the reduction of trialkylsilyl-substituted nitrobenzenes and from the diazotization of trialkylsilyl-substituted anilines. However, for the most part they are prepared by coupling diazonium salts with trialkylsilyl-substituted anilines and naphthols. A side reaction that occurs in some cases is the displacement of the trialkylsilyl group by the diazonium cation.

The only instance of the reduction of a trialkylsilyl-substituted nitrobenzene

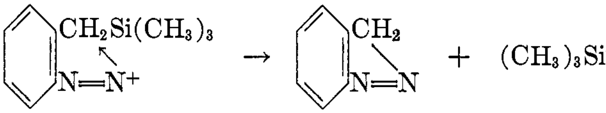
TABLE 17

Silicon-containing azo compounds

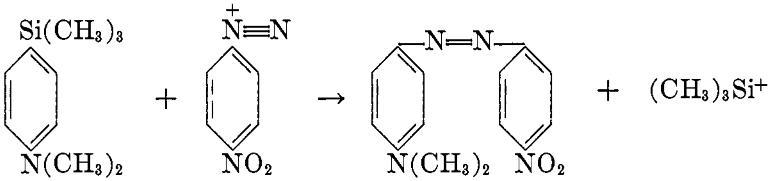
Compound	Melting Point	References
	°C.	
Azoarylsilanes:		
Diazonium halides: see table 8		
$[NC_6H_4Si(C_2H_5)_3]_2$	78	(129)
$[NHC_6H_4Si(C_2H_5)_3]_2$	121	(129)
$(2\text{-}HO\text{-}1\text{-}C_{10}H_6)[3\text{-}N_2C_5H_4Si(CH_3)_3]$	95	(35)
$(2\text{-}HO\text{-}1\text{-}C_{10}H_6)[4\text{-}N_2C_6H_4Si(CH_3)_3]$	95	(35)
$(2\text{-}HO\text{-}1\text{-}C_{10}H_6)[2\text{-}N_2C_6H_4CH_2Si(CH_3)_3]$	98	(35)
$(2\text{-}HO\text{-}1\text{-}C_{10}H_6)[4\text{-}N_2C_6H_4CH_2Si(CH_3)_3]$	127	(35)
Azodiorganoaminophenylsilanes:		
$(C_6H_5N_2)\text{-}4\text{-}(CH_3)_2NC_6H_3Si(OC_2H_5)_3$ hydrolysate		(268)
$(C_6H_5N_2)\text{-}5\text{-}(CH_3)_2NC_6H_3Si(CH_3)_3$	110	(490, 491)
$2\text{-}(4\text{-}NO_2C_6H_4N_2)\text{-}5\text{-}(CH_3)_2NC_6H_3Si(CH_3)_3$	192	(490, 491)
$[2,4\text{-}(NO_2)_2C_6H_3N_2]\text{-}5\text{-}(CH_3)_2NC_6H_3Si(CH_3)_3$	240	(490, 491)
$(2\text{-}Cl\text{-}4\text{-}NO_2C_6H_3N_2)\text{-}5\text{-}(CH_3)_2NC_6H_6Si(CH_2)_3$	206	(490, 491)
$(2,6\text{-}Cl_2\text{-}4\text{-}NO_2C_5H_2N_2)\text{-}5\text{-}(CH_3)_2NC_6H_3Si(CH_3)_3$	146	(490, 491)
$[2,4\text{-}(NO_2)_2\text{-}6\text{-}ClC_6H_2N_2]\text{-}5\text{-}(CH_3)_2NC_6H_3Si(CH_3)_3$	158	(490, 491)
$(2\text{-}CF_3\text{-}4\text{-}NO_2C_6H_3N_2)\text{-}5\text{-}(CH_3)_2NC_6H_3Si(CH_3)_3$	224	(490, 491)
$[2\text{-}CH_3SO_2\text{-}4\text{-}NO_2C_6H_3N_2]\text{-}5\text{-}(CH_3)_2NC_6H_3Si(CH_3)_3$	244	(490, 491)
$[2,4\text{-}(CH_3SO_2)_2C_6H_3N_2]\text{-}5\text{-}(CH_3)_2NC_6H_3Si(CH_3)_3$	218	(490, 491)
$(3\text{-}HSO_3C_6H_4N_2)\text{-}5\text{-}(CH_3)_2NC_6H_3Si(CH_5)_3$	241	(490, 491)
$(4\text{-}HSO_3C_6H_4N_2)\text{-}5\text{-}(CH_6)_2NC_6H_3Si(CH_3)_3$	251	(490, 491)
$(4\text{-}NH_2SO_2C_6H_4N_2)\text{-}5\text{-}(CH_3)_2NC_6H_3Si(CH_3)_3$	213	(490, 491)
$(2\text{-}HOOCC_3H_4N_2)\text{-}5\text{-}(CH_3)_2NC_6H_3Si(CH_6)_3$	242	(490, 491)
$(4\text{-}HOOCC_6H_4N_2)\text{-}5\text{-}(CH_3)_2NC_6H_3Si(CH_3)_3$	241	(490, 491)
$[2\text{-}HO\text{-}4\text{-}NO_2C_6H_6N_2]\text{-}5\text{-}(CH_3)_2NC_3H_3Si(CH_3)_3$	226	(490, 491)
$(C_6H_5N_2)\text{-}5\text{-}(CH_3)_2NC_6H_3Si(C_6H_5)_3$	194	(490, 491)
$(4\text{-}NO_2C_6H_4N_2)\text{-}5\text{-}(CH_3)_2NC_6H_3Si(C_6H_5)_3$	206	(490, 491)
$(2\text{-}Cl\text{-}4\text{-}NO_2C_6H_3N_2)\text{-}5\text{-}(CH_3)_2NC_6H_3Si(C_6H_5)_3$	234	(490, 491)
$(2,6\text{-}Cl_2\text{-}4\text{-}NO_2C_6H_2N_2)\text{-}5\text{-}(CH_3)_2NC_6H_3Si(C_6H_5)_3$	231	(490, 491)
$(2\text{-}CH_3SO_2\text{-}4\text{-}NO_2C_6H_3N_2)\text{-}5\text{-}(CH_3)_2NC_6H_3Si(C_6H_5)_3$	263	(490, 491)
$[2,4\text{-}(CH_3SO_2)_2C_6H_3N_2]\text{-}5\text{-}(CH_3)_2NC_6H_3Si(C_6H_5)_3$	236	(490, 491)
$(4\text{-}HSO_3C_6H_4N_2)\text{-}5\text{-}(CH_3)_2NC_6H_3Si(C_6H_5)_3$	254	(490, 491)
$(3\text{-}HSO_3C_6H_4N_2)\text{-}5\text{-}(CH_3)_2NC_6H_3Si(C_6H_5)_3$	260	(490, 491)
$(4\text{-}NH_2SO_2C_6H_4N_2)\text{-}5\text{-}(CH_3)_2NC_6H_3Si(C_6H_5)_3$	224	(490, 491)
$(2\text{-}HOOCC_6H_4N_2)\text{-}5\text{-}(CH_3)_2NC_6H_3Si(C_6H_5)_3$	255	(490, 491)
$(4\text{-}HOOCC_6H_4N_2)\text{-}5\text{-}(CH_6)_2NC_6H_3Si(C_6H_5)_3$	275	(490, 491)
$2\text{-}(4\text{-}NO_2C_6H_4N_2)\text{-}4\text{-}(HOCH_2CH_2)_2NC_6H_3Si(CH_3)_3$	165–167	(*492*, 493)
$2\text{-}(2\text{-}Cl\text{-}4\text{-}NO_2C_6H_3N_2)\text{-}4\text{-}(HOCH_2CH_2)_2NC_6H_3Si(CH_3)_3$	158–159	(*492*, 493)
$2\text{-}(2,6\text{-}Cl_2\text{-}4\text{-}NO_2C_6H_2N_2)\text{-}4\text{-}(HOCH_2CH_2)_2NC_6H_3Si(CH_3)_3$	163–164	(*492*, 493)
$2\text{-}(2\text{-}CF_6\text{-}4\text{-}NO_2C_6H_3N_2)\text{-}4\text{-}(HOCH_2CH_2)_2NC_6H_3Si(CH_3)_3$	158–159	(*492*, 493)
$2\text{-}(2\text{-}CH_3SO_2\text{-}4\text{-}NO_2C_6H_3N_2)\text{-}4\text{-}(HOCH_2CH_2)_2NC_6H_3Si(CH_3)_3$	195–197	(*492*, 493)
$2\text{-}[2,4\text{-}(CH_3SO_2)_2C_6H_3N_2]\text{-}4\text{-}(HOCH_2CH_2)_2NC_6H_3Si(CH_3)_3$	164–165	(*492*, 493)
$2\text{-}(4\text{-}NO_2C_6H_4N_2)\text{-}4\text{-}(HOCH_2CH_2)_2NC_6H_3Si(C_6H_5)_3$	178–179	(*492*, 493)
$2\text{-}(2\text{-}Cl\text{-}4\text{-}NO_2C_6H_3N_2)\text{-}4\text{-}(HOCH_2CH_2)_2NC_6H_3Si(C_6H_5)_3$	189–190	(*492*, 493)
$2\text{-}(2,6\text{-}Cl_2\text{-}4\text{-}NO_2C_6H_2N_2)\text{-}4\text{-}(HOCH_2CH_2)_2NC_6H_3Si(C_6H_5)_3$	169–170	(*492*, 493)
	218 (d.)	
$2\text{-}(2\text{-}CH_3SO_2Cl\text{-}4\text{-}NO_2C_6H_3N_2)\text{-}4\text{-}(HOCH_2CH_2)_2NC_6H_3Si(C_6H_5)_3$	209–210	(*492*, 493)
$2\text{-}[2,4\text{-}(CH_3SO_2Cl)_2C_6H_3N_2]\text{-}4\text{-}(HOCH_2CH_2)_2NC_6H_3Si(C_6H_5)_3$	211–212	(*492*, 493)
Azohydroxynaphthylsilanes:		
$[3,3'\text{-}(CH_3O)_2(C_6H_3N_2)_2]\text{-}[2\text{-}HO\text{-}6\text{-}Si(CH_3)_3C_{10}H_5]_2$	202	(490, 491)
$1\text{-}(4\text{-}NO_2C_6H_4N_2)\text{-}[2\text{-}HO\text{-}6\text{-}Si(CH_3)_3C_{10}H_5]$	235	(490, 491)
$[(C_5H_4N_2)_2][2\text{-}HO\text{-}6\text{-}Si(CH_3)_3C_{10}H_5]_2$	315	(490, 491)
$[(C_6H_4N_2)_2][2\text{-}HO\text{-}6\text{-}Si(C_6H_5)_3C_{10}H_5]_2$	360	(490, 491)
$(4\text{-}NH_2SO_2C_6H_4N_2)\text{-}[2\text{-}HO\text{-}6\text{-}Si(C_6H_5)_3C_{10}H_5]$	313	(490, 491)
$(4\text{-}NO_2C_6H_4N_2)\text{-}[2\text{-}HO\text{-}6\text{-}Si(C_6H_5)_3C_{10}H_5]$	317	(490, 491)
$[3,3'\text{-}(CH_3O)_2(C_6H_3N_2)_2]\text{-}[2\text{-}HO\text{-}6\text{-}Si(C_6H_5)_3C_{10}H_5]_2$	340	(490, 491)

to azo derivatives is the reduction of $4\text{-NO}_2C_6H_4Si(C_2H_5)_3$ to $4\text{-}[4'\text{-}(C_2H_5)_3SiC_6H_4N{=}N]C_6H_4Si(C_2H_5)_3$ and $4\text{-}[4'\text{-}(C_2H_5)_3C_6H_4NHNH)C_6H_4Si(C_2H_5)_3$ (129) by zinc and alkali.

The diazotization of the isomers of $NH_2C_6H_4Si(CH_3)_3$ and $NH_2C_6H_4CH_2Si(CH_3)_3$ gives unstable diazonium salts which couple satisfactorily with 2-naphthol to form orange to red azo derivatives. In the case of $2\text{-NH}_2C_6H_4CH_2Si(CH_3)_3$ a 16 per cent yield of indazole is also obtained, presumably through intramolecular displacement of a trimethylsilyl group (35).

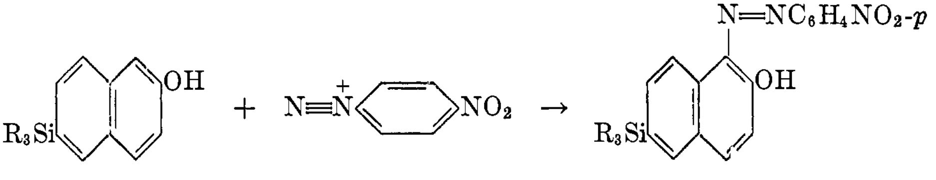


The first instance of the coupling of a silyl-substituted dimethylaniline with a diazonium salt is the reaction of hydrolyzed $(CH_3)_2NC_6H_4Si(OC_2H_5)_3$ on glass fibers with benzenediazonium chloride to give a yellow color (268). Many other examples are known and have been worked out in greater detail. There are notable differences in the reactions of the various isomers of $(CH_3)_2NC_6H_4SiR_3$ with diazonium salts. The ortho isomers do not couple at all and in this respect are like many other ortho-substituted dimethylanilines. The para isomers of $(CH_3)_2NC_6H_4SiR_3$ undergo displacement of the trialkylsilyl group by the diazonium cation. Competitive reaction shows that the 4-nitrobenzene diazonium cation displaces a proton from $(CH_3)_2NC_6H_5$ in preference to the triphenylsilyl group in $4\text{-}(CH_3)_2NC_6H_4Si(C_6H_5)_3$. The meta isomers of $(CH_3)_2NC_6H_4SiR_3$ couple normally with many diazonium salts; the trimethylsilyl compound couples more readily than the triphenylsilyl compound, perhaps because of steric effects in the latter (490).



The meta isomers of $(HOCH_2CH_2)_2NC_6H_4SiR_3$ also couple satisfactorily with diazonium salts, forming a wide variety of azo dyes (492).

Silicon-containing azo compounds are also obtained by coupling trialkylsilyl-substituted naphthols with diazonium salts. Here, too, the course of the reaction is greatly dependent on the isomer involved. Thus 6-trimethylsilyl- and 6-triphenylsilyl-2-naphthols couple satisfactorily with 4-nitrobenzenediazonium salt. However, 1-trimethylsilyl-2-naphthol undergoes displacement of the trimethylsilyl group (490).



B. REACTIONS

Little is known of the reactions of silicon-containing azo compounds. A limited study of the hydrogen chloride cleavage of triorganosilyl groups from these materials in boiling glacial acetic acid is available (490). The substantivity, lightfastness, and pH range of triorganosilyl-substituted azo dyes have been studied (491, 493).

Some reactions of silicon-containing diazonium salts have already been mentioned in connection with their synthesis.

XIX. ORGANOMETALLIC COMPOUNDS (SEE TABLE 18)

Many compounds containing a metallic atom and a silicon atom bound by some organic group are known. Examples of these are $(CH_3)_3SiCH_2MgCl$ and $4\text{-}(C_2H_5)_3SiC_6H_4As(C_2H_5)_2$. Few silicon-containing organometallic compounds have actually been isolated. Most of them are of interest principally as synthetic intermediates, and their presence is manifested by the products to which they give rise.

A. GRIGNARD REAGENTS

Silicon-containing Grignard reagents are as easily made and as synthetically versatile as their organic counterparts, and they therefore play a prominent role in the synthesis of carbon-functional silicon compounds. The first instance of an organosilicon Grignard reagent is $4\text{-}(C_2H_5)_3SiC_6H_4MgBr$ (225). Aliphatic compounds such as $ICH_2Si(CH_3)_3$ (538), $CH_3CHClSi(CH_3)_3$ (448), $Br(CH_2)_3Si(CH_3)_3$ (447), and $Br(CH_2)_5Si(CH_3)_3$ (433) also readily form Grignard reagents in good yield. Even siloxanes such as $ClCH_2Si(CH_3)_2OSi(CH_3)_3$ (383), $ClCH_2\underline{Si(CH_3)[OSi(CH_3)_2]_3O}$ (370b), and $[4\text{-}BrC_6H_4Si(CH_3)_2]_2O$ (25) easily form organomagnesium derivatives straightforwardly.

Only in the reaction of β-haloalkyl silicon compounds with magnesium is anything unusual encountered. Organomagnesium derivatives of β-haloalkyl silicon compounds are unknown. $CH_3CHBrCH_2Si(CH_3)_3$ is said to react readily with magnesium in ether at 10–15°C.; however, upon hydrolysis of the reaction mixture and treatment of the product with concentrated sulfuric acid only small amounts of $(CH_3)_3SiC_3H_7$ and the coupled product are found, together with much hexamethyldisiloxane (359).

The reactions of silicon-containing Grignard reagents are quite normal; however, this fact is sometimes obscured by silicon–carbon cleavage occurring in the products during the hydrolysis step (240, 540). The known straightforward reactions of organosilicon Grignard reagents involve the synthesis of many carbon-functional silicon compounds and are discussed therewith. Detailed references listed according to the organometallic reagent may be found in table 18.

B. ORGANOALKALI COMPOUNDS

Silicon-containing organolithium reagents are obtained straightforwardly either from the reaction of silicon-containing organic halides with metallic lithium or from the reaction of appropriate organosilicon compounds with

TABLE 1—*Concluded*

Compound	Melting Point	Boiling Point	n_D	d	References
	°C.	*°C.*			
$[CH_3C{\equiv}CSi(C_2H_5)_3]_2$					(366)
$CH_3(CH_2)_3C{\equiv}CSi(CH_3)Cl_2$		187–188			(167, 170)
$CH_3(CH_2)_3C{\equiv}CSi(CH_3)(OCOCH_3)_2$		102–106/0.3 mm.			(167)
$CH_3(CH_2)_2C{\equiv}CSi(CH_3)_3$		155	1.4318 (25°)	0.768 (25°)	(*167*, 171)
$[CH_3(CH_2)_3C{\equiv}C]_2Si(CH_3)Cl$					(167)
$[CH_3(CH_2)_3C{\equiv}CSi(CH_3)OH]_2O$					(167, 170)
$[CH_3(CH_2)_3C{\equiv}CSi(CH_3)O-]_4$		167/0.5 mm.			(*167*, 170)
$(CH_3CH_2CH_2CH_2C{\equiv}C)_2Si(CH_3)Cl$		148–150/8 mm.			(170)
$C_6H_5C{\equiv}CSi(OC_2H_6)_3$		142/6 mm.	1.4898 (21°)	0.986 (22°/22°)	(523)
$C_6H_6C{\equiv}CSi(CH_3)_3$		87.5/9 mm.	1.5284 (20°)	0.8961 (20°)	(366)
$C_6H_5C{\equiv}CSi(C_2H_6)_3$		132–133.5/10 mm.	1.5259 (20°)	0.8984 (20°)	(366)
$C_6H_5C{\equiv}CSi(C_6H_5)_3$	101				(185, 186, *190*, 192, 198)
$(C_6H_5C{\equiv}C)_2Si(OC_2H_5)_2$		185/12 mm.	1.529 (9°)	1.0001 (9°)	(523)
Polyunsaturates:					
$CH_2{=}CHCH{=}CHSi(C_2H_5)_3$		74–75/19 mm.	1.4584 (20°)	0.7988 (20°)	(363)
Maleic anhydride adduct	132				(363)
$CH_2{=}CHC{\equiv}CSi(CH_3)_3$		52–53/80 mm.	1.4510 (20°)	0.7714 (20°)	(363)
$CH_2{=}CHC{\equiv}CSi(C_2H_5)_3$		74–76/20 mm.	1.4695 (20°)	0.8145 (20°)	(363)
$CH_2{=}CHC{\equiv}CSi(C_3H_7)_3$		87–89/7 mm.	1.4700 (20°)	0.8173 (20°)	(363)
$CH_2{=}CHC{\equiv}CSi(C_4H_9)_3$		108–110/8 mm.	1.4700 (20°)	0.8201 (20°)	(363)
$(CH_2{=}CHC{\equiv}C)_2Si(CH_3)_2$		67–68/9 mm.	1.5108 (20°)	0.8495 (20°)	(363)
$(CH_2{=}CHC{\equiv}C)_2Si(C_2H_5)_2$		84–86/8 mm.	1.5140 (20°)	0.8556 (20°)	(363)
$(CH_2{=}CHC{\equiv}C)_2Si(C_3H_7)_3$		84–86/5 mm.	1.5145 (20°)	0.8561 (20°)	(363)
$CH_3CH{=}C(CH_3)C{\equiv}CSi(C_2H_5)_3$		115–116/20 mm.			(57)

organolithium reagents. Among the chlorides that readily form organolithium reagents in good yield with metallic lithium are such compounds as $ClCH_2$-[—$Si(CH_3)_2CH_2$—$]_3Si(CH_3)_3$ (440) and 2-$ClC_6H_4Si(CH_3)_3$ (140). Among the silicon compounds reactive toward organolithium reagents are $C_6H_5CH_2Si(C_6H_5)_3$ (190), $CH_2{=}CHSi(C_6H_5)_3$, and $CH_2{=}CHSi(CH_3)_3$ (99, 225), 9-fluorenyltrimethylsilane (184), 2-furyltrimethylsilane, and 2-thienyltrimethylsilane (36). In these cases the products of subsequent reactions indicate the intermediate formation of such compounds as $C_6H_5CH(Li)Si(C_6H_5)_3$, $C_4H_9CH_2CH(Li)Si(C_6H_5)_3$, and 9-lithio-9-trimethylsilylfluorene.

The reactions of silicon-containing organolithium reagents are quite normal. They frequently involve the synthesis of other carbon-functional derivatives and are discussed therewith. Like their organic counterparts the silicon-containing organolithium compounds are more versatile than Grignard reagents in couplings with silicon chlorides. For example, while $(CH_3)_3SiCH_2MgCl$ readily forms $(CH_3)_3SiCH_2SiCl_3$ with silicon tetrachloride, $(CH_3)_3SiCH_2Li$ is required to substitute the remaining three chlorine atoms (441).

Little is known about other organoalkali compounds. Sodium derivatives of halomethyl silicon compounds are probably involved in the sodium coupling of such compounds with silicon halides to give derivatives having silicon atoms bridged by methylene groups (222). A potassium derivative, $(C_6H_5)_3SiCH(C_6H_5)CH(C_6H_5)K$, is formed in the reaction of $(C_6H_5)_3SiK$ with $C_6H_5CH{=}CHC_6H_5$ (202).

C. ORGANOMERCURY COMPOUNDS

Silicon-containing organomercury compounds such as $(CH_3)_3SiCH_2HgCl$ and $(CH_3)_3SiCH_2HgR$ are readily obtained via conventional Grignard couplings (538). The principal interest in such compounds stems from their use in determining the position of the $(CH_3)_3SiCH_2$— group in a scale of relative electronegativities of organic groups. The method involves cleavage of unsymmetrical diorganomercury compounds with alcoholic hydrogen chloride. The group which

$$RHgR' + HCl \rightarrow RHgCl + R'H$$

takes the proton and forms the hydrocarbon is considered the more electronegative group, i.e., R′ above, where electronegativity is defined as the affinity of a group for electrons in a stable molecule. With the above criterion the $(CH_3)_3SiCH_2$— group is found more electron-attracting than methyl and *n*-hexyl and less electron-attracting than phenyl. On this scale the electronegativity of the $(CH_3)_3SiCH_2$— group is higher than that of any alkyl group; those measured range from methyl, as the highest, through ethyl, *n*-hexyl, and *sec*-butyl to *t*-butyl and neopentyl as the lowest.

This high electronegativity, or electron attraction, of the $(CH_3)_3SiCH_2$— group has been interpreted on the basis that silicon is coordinatively unsaturated and thus behaves as an electron sink relative to carbon, inasmuch as silicon has a maximum covalency of six and carbon only four (538). While this concept that silicon can expand its octet may be useful in other areas of silicon chemistry, it has no bearing here, since no attack on silicon is involved. A simpler explanation consistent with the known facts of silicon chemistry has been advanced (294): electropositive silicon, in its role of an electron source, makes its alpha carbon atom more negative than the corresponding carbon atom of the other group and hence more susceptible to electrophilic attack by hydrogen chloride.

The high electronegativity, or electron attraction, of the $(CH_3)_3SiCH_2$— group on the basis of the above criterion has been used to explain (538) the inertness of $ClCH_2Si(CH_3)_3$ and $ICH_2Si(CH_3)_3$ toward silver nitrate in ethanol. That other factors must be involved is suggested by the fact that $ClCH_2Si(CH_3)_3$ and $ClCH_2C(CH_3)_3$, which are at opposite ends of this electronegativity scale, are both inert toward silver nitrate in ethanol, which acts by electrophilic attack on chlorine and is relatively unaffected by steric considerations.

D. OTHER ORGANOMETALLIC REAGENTS

The few other organometallic silicon compounds known include lead, tin, and arsenic derivatives (225). Although they represent the first silicon-containing organometallic compounds, little is known about them. The reaction of 4-$(C_2H_5)_3SiC_6H_4MgBr$ with the appropriate lead and tin halides gives 4-$(C_2H_5)_3SiC_6H_4Pb(CH_3)_3$ and 4-$(C_2H_5)_3SiC_6H_4Si(C_2H_5)_3$. A similar compound, 4-$(C_2H_5)SiC_6H_4As(C_2H_5)_2$, is obtained by the sodium coupling of 4-$(C_2H_5)_3SiC_6H_4Br$ with $(C_2H_5)_2AsCl$.

The reaction of 4-$(C_2H_5)_3SiC_6H_4Pb(CH_3)_3$ with bromine at −75°C. results in preferential cleavage of the carbon–lead bond with formation of 4-$(C_2H_5)_3SiC_6H_4Br$ and $(CH_3)_3PbBr$.

XX. HETEROCYCLIC COMPOUNDS (SEE TABLE 19)

A. FURANS

Only a few furyl silicon compounds have been made, and little is known about them. 2-Furyltrimethylsilane is prepared by coupling 2-furyllithium with $(CH_3)_3SiCl$ (36). A more complex furyl silicon derivative, 2-trimethylsilylethyl-3-carbethoxy-5-methylfuran, has been made by refluxing a trimethylsilyl-substituted acyl levulinate, $(CH_3)_3SiCH_2CH_2COCH(COOC_2H_5)CH_2COCH_3$, with 50 per cent aqueous sulfuric acid in acetic acid (443).

Acetylation of 2-furyltrimethylsilane with acetic anhydride in the presence of iodine gives 2-trimethylsilyl-5-acetylfuran (36). The latter is oxidized to 5-trimethylsilyl-2-furoic acid with alkaline sodium hypoiodite (36). Milder oxidation with selenium dioxide gives 5-trimethylsilyl-2-furylgloxal, which forms a quinoxaline with *o*-phenylenediamine (41).

Only one silicon–carbon cleavage reaction has been reported for furyl silicon compounds. Refluxing 5-trimethylsilyl-2-furoic acid with bromine in carbon tetrachloride gives 5-bromo-2-furoic acid (36).

B. THIOPHENES

Thienyl-substituted silicon compounds are readily obtained by coupling organometallic thiophene derivatives with chlorosilanes. Thus, excess 2-thienylmagnesium halide with silicon tetrachloride gives tetra-2-thienylsilane (289); the intermediate 2-thienylchlorosilanes can also be isolated (180), as can also 2-thienylchlorosilane derivatives of methylchlorosilanes and phenylchlorosilanes (179). Other Grignard syntheses include the preparation of thienylethoxysilanes from ethyl silicate (180) and of 5-bromo-2-thienyltrimethylsilane from 5-bromo-2-thienylmagnesium bromide with $(CH_3)_3SiCl$ (46). Thienyllithium also couples with chlorosilanes to form 2-thienyltrimethylsilane (36) and 2-thienyltriphenylsilane (199). A synthesis of thienyl silicon compounds which does not involve organometallic reagents is the reaction of 2-chlorothiophene with $HSiCl_3$ and CH_3SiHCl_2 at 500°C. to give $(2\text{-}C_4H_3S)SiCl_3$ and $(2\text{-}C_4H_3S)Si(CH_3)Cl_2$ (328).

Thienyl silicon compounds exhibit a number of carbon-functional reactions. They can be metalated with organolithium reagents. Thus, with butyllithium 2-thienyltriphenylsilane is converted to an organometallic derivative which gives 5-triphenylsilyl-2-thiophenecarboxylic acid with carbon dioxide and also undergoes anil additions with quinolines, giving, for example, [5-(2′-quinolyl)-2-thienyl]triphenylsilane (199). 2-Thienyltrimethylsilane similarly undergoes metalation with butyllithium; the resulting 5-lithio derivative can be carbonated to give the acid (36) and can be added to quinoxaline to give the coupled product (41). An organometallic compound analogous to the above lithium derivatives is obtained by converting 5-bromo-2-thienyltrimethylsilane to a Grignard reagent; this too can be carbonated to the acid (46).

Another carbon-functional reaction of thienyl silicon compounds is the acetylation of 2-thienyltrimethylsilane with acetic anhydride in the presence of iodine (36). The 5-acetyl derivative thus formed can be oxidized to a carboxyl substituent through the iodoform reaction (36). Milder oxidation with selenium dioxide gives the glyoxal, which may be converted to a quinoxaline with *o*-phenylenediamine (41).

Cleavage of the thienyl group from silicon occurs both with hydrogen chloride and with bromine. Bubbling hydrogen chloride into a refluxing benzene solution of 5-trimethylsilyl-2-thiophenecarboxylic acid gives 2-thiophenecarboxylic acid (36). Bromine in carbon tetrachloride cleaves 5-bromo-2-thienyltrimethylsilane twenty to thirty times faster than phenyltrimethylsilane.

The only silicon-functional reaction of thienyl silicon compounds is the hydrolysis of chlorosilanes and ethoxysilanes to polysiloxanes. Thermally stable oils and resins are obtained without loss of the thienyl groups (178).

Closely related to thienyl silicon compounds are silyl-substituted dibenzothiophenes. These are readily obtained by coupling organometallic derivatives of dibenzothiophene with $(CH_3)_3SiCl$ and $(C_6H_5)_3SiCl$. Both 4-trimethylsilyl- and 4-triphenylsilyldibenzothiophenes are oxidized to the corresponding 5-dioxides with hydrogen peroxide in glacial acetic acid. Silicon–carbon cleavage readily occurs when hydrogen chloride is bubbled through a refluxing glacial acetic acid solution of 4-trimethylsilyldibenzothiophene. However, neither the corresponding 5-dioxide nor 4-triphenylsilyldibenzothiophene undergoes cleavage with this reagent. The stability of the former toward acid cleavage is further demonstrated by its formation of a mononitro derivative with fuming nitric acid (198). The 2-trimethylsilyl- and 3-trimethylsilyldibenzothiophenes undergo

TABLE 19

Silicon-containing heterocyclic compounds

Compound	Melting Point	Boiling Point	n_D	d	References
	°C.	°C.			
Furans:					
$(2\text{-}C_4H_3O)Si(CH_3)_3$		125/750 mm.	1.4470 (20°)	0.880 (20°)	(36)
$[2\text{-}(5\text{-}CH_3CO)C_4H_2O]Si(CH_3)_3$		79/3 mm.	1.4925 (20°)	0.978 (20°)	(*36*, 41)
Semicarbazone	201				
$[2\text{-}(5\text{-}HOOC)C_4H_2O]Si(CH_3)_3$	111				(36)
$[2\text{-}(5\text{-}COCHO)C_4H_2O]Si(CH_3)_3$		71/0.6 mm.			(41)
Monohydrate	108–114				
$[2\text{-}[5\text{-}(2'\text{-}C_6H_4C_2HN_2)]C_4H_2O\}Si(CH_3)_3$	64				(41)
$COCH{=}C[CH_2CH_2Si(CH_3)_3]CH_2CH_2CH_2$		125/6 mm.	1.4888 (20°)		(443)
Semicarbazone	204–207				(443)
$OC[CH_2CH_2Si(CH_3)_3]{=}C(COOC_2H_5)CH{=}CCH_3$		90/2 mm.	1.4695 (20°)		(443)
$(2\text{-}C_6H_3OC_6H_4)Si(C_6H_5)_3$	124–125				(198)
Thiophenes:					
$(2\text{-}C_4H_3S)SiCl_3$		196–197		1.41 (25°)	(178, 180, *328*)
		108/45 mm.		1.427 (26°)	
$(2\text{-}C_4H_3S)Si(OC_2H_5)_3$		150/50 mm.	1.4659 (20°)	1.050 (20°)	(178, 180)
$(2\text{-}C_4H_3S)Si(CH_3)Cl_2$		199–200			(178, *179*, *328*)
		101/34 mm.		1.313 (28°)	
$(2\text{-}C_4H_3S)Si(C_6H_5)Cl_2$		144–160/2–3 mm.			(179)
$(2\text{-}C_4H_3S)Si(CH_3)_2Cl$		98/40 mm.			(178, 179)
$(2\text{-}C_4H_3S)Si(CH_3)_3$		160/748 mm.	1.4966 (20°)	0.945 (20°)	(*36*, 41)
$(2\text{-}C_4H_3S)Si(C_6H_5)_3$	198				(184)
$(2\text{-}C_4H_3S)Si(C_6H_5)_3$					(199)
5-Li derivative					
$(2\text{-}C_4H_3S)_2SiCl_2$		305–308			(178, 180)
		188/22 mm.			
$(2\text{-}C_4H_3S)_2Si(OC_2H_5)_2$		209/50 mm.	1.5401 (20°)		(180)
$(2\text{-}C_4H_3S)_2Si(CH_3)Cl$		301–307			(178, 179)
		138–148/3 mm.			
$(2\text{-}C_4H_3S)_3SiCl$		190–205/1 mm.			(178, 180)
$(2\text{-}C_4H_3S)_4Si$	136				(289)
$[(2\text{-}C_4H_3S)Si(CH_3)_2]_2O$		117–121/1 mm.			(178)
$[(2\text{-}C_4H_3S)_2SiO]_x$	327–328				(178)
Thienylsiloxanes					(178)

2-Br-5-$(CH_3)_3SiC_4H_2S$		218-218.5	1.5315 (20°)	1.298 (20°/20°)	(46)
$[2\text{-}(5\text{-}CH_3CO)C_4H_2S]Si(CH_3)_3$		104/4 mm.	1.5289 (20°)	1.028 (20°)	(*36*, 41)
Semicarbazone	220				
$[2\text{-}(5\text{-}HOOC)C_4H_2S]Si(CH_3)_3$	134.5-135				(*36*, 46)
$[2\text{-}(5\text{-}HOOC)C_4H_2S]Si(C_6H_5)_3$	190				(184)
$[2\text{-}(5\text{-}COCHO)C_4H_2S]Si(CH_3)_3$		90/0.6 mm.			(41)
Monohydrate	102-109				
Monosemicarbazone	224				
$[2\text{-}[5\text{-}(2'\text{-}C_6H_4C_2HN_2)]C_4H_2S]Si(CH_3)_2$	100				(41)
$[2\text{-}[5\text{-}(2'\text{-}C_6H_4C_3H_2N)]C_4H_2S\}Si(C_6H_6)_3$	169				(199)
$[2\text{-}[5\text{-}(6'\text{-}CH_3O\text{-}2'\text{-}C_6H_3C_3H_2N)]C_4H_2S\}Si(C_5H_5)_3$	228				(199)
$[2\text{-}[5\text{-}(4',7'\text{-}Cl_2\text{-}2'\text{-}C_6H_3C_3HN)]C_4H_2S\}Si(C_6H_5)_2$	202				(199)
Dibenzothiophenes:					
$(2\text{-}C_6H_3SC_6H_4)Si(CH_3)_3$	48				(198, 262)
$(3\text{-}C_6H_3SC_6H_4)Si(CH_3)_3$	104				(262)
$(4\text{-}C_6H_3SC_6H_4)Si(CH_3)_3$		216/20 mm.	1.6354 (20°)	1.112 (20°)	(198)
$(5\text{-}O_2\text{-}2\text{-}C_6H_3SC_6H_4)Si(CH_3)_3$	165				(192, *262*)
$(5\text{-}O_2\text{-}3\text{-}C_6H_3SC_5H_4)Si(CH_3)_3$	172				(192. *262*)
$(5\text{-}O_2\text{-}4\text{-}C_6H_3SC_6H_4)Si(CH_3)_3$	147				(192, *198*)
$(5\text{-}O_2\text{-}x\text{-}NO_2\text{-}4\text{-}C_6H_2SC_6H_4)Si(CH_3)_3$	147				(192, *198*)
$(4\text{-}C_6H_3SC_6H_4)Si(C_6H_5)_3$	194				(198)
$(5\text{-}O_2\text{-}4\text{-}C_6H_3SC_6H_4)Si(C_6H_6)_3$	213				(198)
Pyridines and others:					
$(2\text{-}C_5H_4N)Si(CH_3)_3$		88-90/38 mm.	1.4918 (20°)		(64)
$(2\text{-}C_5H_4N)_2SiCl_2$					(55)
$\underbrace{COCH_2C[CH_2CH_2Si(CH_3)_3]{=}NNH}$	203-204				(443)
$\underbrace{COCH[CH_2Si(CH_3)_3]C(CH_3){=}NNH}$	247-248				(443)
$\underbrace{NHCONHCOCH[CH_2Si(CH_3)_3]CO}$	240-241 (d.)				(406, *433*)
$\underbrace{NHCONHCOC(CH_3)[CH_2Si(CH_3)_3]CO}$	180-181				(433)
$\underbrace{NHCONHCOC(CH_2CH{=}CH_2)[CH_2Si(CH_3)_3]CO}$	116-118				(433)
Cyclopolymethylenesilanes: see table 20					

silicon–carbon cleavage about as easily as the 4-trimethylsilyl isomer with hydrogen chloride in refluxing glacial acetic acid; similarly, their 5-dioxides are stable toward this reagent (262).

C. PYRIDINES

The synthesis of 2-pyridyltrimethylsilane (64) and of bis(2-pyridyl)dichlorosilane (55) by conventional methods is described briefly in the patent literature. Other compounds involving nitrogen-containing rings attached to silicon include pyrazolones (443) and barbiturates (433).

XXI. Carbon-bridged Polysilicon Compounds (See Table 20)

A. POLYSILMETHYLENES

Polysilmethylenes are compounds containing at least one —$SiCH_2Si$— group. A great many such compounds are known. Interest in them stems from their stability and from their structural analogy to siloxanes. The latter consist of chains of silicon atoms bridged by oxygens, while the silmethylenes consist of silicon atoms bridged by methylenes. The siloxane linkage is quite reactive under the influence of appropriate reagents, while the silmethylene linkage approaches the silicon–methyl linkage in stability.

The silmethylenes themselves are obtainable at present principally as relatively short-chain materials, and they therefore do not now offer the diversity of useful physical forms that has contributed so greatly to the widespread use of siloxanes. Moreover, the silmethylenes do not exhibit the unusual physical characteristics for which methylpolysiloxanes are well known and widely sought. Nevertheless the silmethylenes are of considerable interest because they offer a stable linkage that can be introduced into siloxanes to modify their properties.

The nomenclature of the silmethylenes is patterned after that of the siloxanes. For example, $(CH_3)_3SiCH_2Si(CH_3)_3$ is hexamethyldisilmethylene just as $(CH_3)_3SiOSi(CH_3)_3$ is hexamethyldisiloxane. Likewise $CH_3[—Si(CH_3)_2CH_2—]_4Si(CH_3)_3$ becomes dodecamethylpentasilmethylene, and $(—SiCl_2CH_2—)_3$ is hexachlorocyclotrisilmethylene. In mixed compounds of the type $(CH_3)_3SiCH_2Si(CH_3)_2OSi(CH_3)_3$ any but the simpler ones are best named by the "oxa-aza" system, in which this compound would become 2,2,4,4,6,6-hexamethyl-2,4,6-trisila-3-oxaheptane.

1. *Syntheses*

The principal method for making silmethylenes involves the coupling of chloromethyl silicon compounds with silicon chlorides by means of magnesium, lithium, or sodium. This is of course a conventional way of establishing silicon–carbon bonds, the only difference being that a silicon-containing organic halide is used instead of an ordinary organic halide. $(CH_3)_3SiCH_2MgCl$ (435, 441) and $(CH_3)_3SiOSi(CH_3)CH_2MgCl$ (52) couple satisfactorily with chlorosilanes to form disilmethylenes and trisilmethylenes, but the yields drop off with the latter. Organolithium reagents give good yields of the higher members. $(CH_3)_3SiCH_2Li$

gives $[(CH_3)_3SiCH_2]_2SiCl_2$, $[(CH_3)_3SiCH_2]_3SiCl$, and even $[(CH_3)_3SiCH_2]_4Si$ if the reaction mixture is heated at 150°C. (441). Coupling $(CH_3)_3SiCH_2Li$ with $ClCH_2Si(CH_3)_2Cl$ offers a means of progressively lengthening a silmethylene chain, because the resulting $ClCH_2Si(CH_3)_2CH_2Si(CH_3)_3$ can itself be coupled with more $ClCH_2Si(CH_3)_2Cl$ and the cycle can be repeated with good yields at least until the tetrasilmethylene derivative is reached (440). The lithium reagents from these $ClCH_2[—Si(CH_3)_2CH_2—]_xSi(CH_3)_3$ compounds couple with $(CH_3)_3SiCl$ and $(CH_3)_2SiCl_2$ to give good yields of $CH_3[—Si(CH_3)_2CH_2—]_xSi(CH_3)_3$ derivatives, at least up to the pentasilmethylene (440).

Sodium coupling of chloromethyl silicon compounds with chlorosilanes is the method by far most extensively used for making silmethylenes and has been extended to diverse types ranging from simple monomers to resinous silmethylene-siloxanes. The method is described only briefly in the scientific literature and specific references may be found in the tables. In a typical reaction 2 moles each of $(CH_3)_3SiCl$ and $ClCH_2Si(CH_3)_2OC_2H_5$ are added to 4 moles of molten sodium in refluxing toluene with vigorous stirring, and a 79 per cent yield of $(CH_3)_3SiCH_2Si(CH_3)_2OC_2H_5$ is obtained. The use of ethoxy derivatives is an important control measure in getting materials convertible to polysiloxanes. The self-condensation of $ClCH_2Si(CH_3)_2Cl$ type compounds to produce $[—Si(CH_3)_2CH_2—]_x$ derivatives takes place very readily. Chloromethyl silicon compounds can be made to couple with ethoxysilanes by means of molten sodium, but the reaction is much more sluggish than with chlorosilanes.

Silmethylene compounds are obtained from a number of other reactions too. The first instance of their preparation is the reaction of methylene chloride with silicon–copper at 300°C. to give products such as $Cl_3SiCH_2SiCl_3$, $Cl_3SiCH_2SiHCl_2$, and $(—SiCl_2CH_2—)_3$ (352). Silmethylenes are obtained as by-products in the redistribution of methylchlorosilanes at 400°C. with aluminum chloride (391). Less well defined is their formation from the reaction of $(CH_3)_3SiCl$ with the product from the action of methylene chloride on aluminum–copper (107). A small amount of $(CH_3)_3SiCH_2Si(CH_3)_3$ is obtained from the lithium coupling of $(CH_3)_3SiCl$ with methylene chloride (535). $Cl_3SiCH(CH_3)SiCl_3$ occurs as a by-product in the reaction of benzene with $SiHCl_3$ in the presence of boron chloride (20).

2. Properties

The reactions of silmethylene compounds are quite similar to those of organo-substituted monosilanes and polysiloxanes. As far as carbon-functional reactions are concerned, no functional groups have been introduced directly into the methylene group, and the behavior of such derivatives as $ClCH_2Si(CH_3)_2CH_2Si(CH_3)_3$ is discussed in the section on chloromethyl compounds. The silicon-functional reactions of the silmethylenes proceed without disturbance of the carbon bridge. Thus, compounds like $(CH_3)_3SiCH_2SiCl_3$ can, for example, be coupled with Grignard reagents, alcoholyzed to alkoxides, hydrolyzed to siloxanes, and reduced to hydrides with lithium aluminum hydride or lithium hydride. Certain silmethylene compounds exhibit the effect of some steric

TABLE 20

Carbon-bridged polysilicon compounds

Compound	Melting Point	Boiling Point	n_D	d	References
	°*C.*	°*C.*			
Disilmethylenes:					
$Cl_3SiCH_2SiCl_3$		185/756 mm. 64/10 mm.	1.471 (22°)	1.545 (17°)	(112, *147*, 243, 244, 246, 248, 261, 299, 338, 340, 343, *352*, 353, 362, 390, 391, 507, 508, 511, 513)
$(CH_3O)_3SiCH_2Si(OCH_3)_3$		212–213 92–93/5 mm.	1.4071 (20°)	1.0873 (20°)	(*243*, 249, 299, *340*)
$(C_2H_5O)_3SiCH_2Si(OC_2H_5)_3$		114–115/3.5 mm.	1.4098 (20°)	0.9741 (20°)	(244, 249, 299, *340*)
$(C_3H_7O)_3SiCH_2Si(OC_3H_7)_3$		146–147/1.5 mm.	1.4210 (20°)	0.9427 (20°)	(249, *508*)
$(i\text{-}C_3H_7O)_3SiCH_2Si(OC_3H_7\text{-}i)_3$		144.5/1 mm.	1.4098 (20°)	0.9207 (20°)	(508)
$(C_4H_9O)_3SiCH_2Si(OC_4H_9)_2$		204/2.5 mm.	1.4287 (20°)	0.9218 (20°)	(249, *508*)
$(i\text{-}C_4H_9O)_3SiCH_2Si(OC_4H_9\text{-}i)_3$		180–182/1.5 mm.	1.4240 (20°)	0.9116 (20°)	(340)
$(C_5H_{11}O)_3SiCH_2Si(OC_5H_{11})_3$		206–207/1 mm.			(249)
$(i\text{-}C_5H_{11}O)_3SiCH_2Si(OC_5H_{11}\text{-}i)_3$		193.5/0.4 mm.	1.4320 (20°)	0.9061 (20°)	(508)
$(C_6H_{11}O)_3SiCH_2Si(OC_6H_{11})_2$		284–287/1.5 mm.	1.4772 (50°)	1.0205 (50°)	(513)
$(C_6H_{13}O)_3SiCH_2Si(OC_5H_{13})_2$		242–244/0.4 mm.	1.4403 (20°)	0.9038 (20°)	(338)
$(C_7H_{15}O)_3SiCH_2Si(OC_7H_{15})_3$		261–262/0.4 mm.	1.4435 (20°)	0.8954 (20°)	(338)
$(C_8H_{17}O)_3SiCH_2Si(OC_8H_{17})_3$		299–302/1 mm.	1.4476 (20°)	0.8907 (20°)	(338)
$(C_9H_{19}O)_3SiCH_2Si(OC_9H_{19})_3$		314–317/1 mm.	1.4499 (20°)	0.8851 (20°)	(338)
$(C_6H_5CH_2O)_3SiCH_2Si(OCH_2C_6H_5)_3$		324–328/2 mm.	1.5643 (20°)	1.1505 (20°)	(513)
$(C_6H_5O)_3SiCH_2Si(OC_5H_5)_3$	70	297–299/2 mm.			(513)
$(4\text{-}CH_3C_6H_4O)_3SiCH_2(C_6H_4CH_3\text{-}4)_3$		308–309/2 mm.	1.5688 (20°)	1.1342 (20°)	(513)
$Cl_3SiCH_2SiHCl_2$		167–168 52/10 mm.		1.464 (27.5°)	(*147*, 248, 337, 352, *353*)
$Cl_2HSiCH_2SiHCl_2$		57–58/10 mm.			(510)
$Cl_4H_2Si_2CH_2$		151–152.5/772 mm.			(337)
$H_3SiCH_2SiH_3$		26 14.7/754.3 mm.	 1.4115 (4°)	0.754 (20°) 0.6979 (4°)	(146, *147*, 362)
$Cl_2(CH_3)SiCH_2SiCl_3$					(106, 110, 112, 216, 250)
$Cl_2(C_6H_{13})SiCH_2SiCl_3$		265/747 mm. 124–124.5/3 mm.			(337)
$(i\text{-}C_4H_9O)_3SiCH_2Si(C_6H_{13})(OC_4H_9\text{-}i)_2$		201.7–202/2 mm.	1.4313 (20°)	0.8976 (20°)	(337)
$Cl_4H(C_6H_{13})Si_2CH_2$		113.5–114.0/2 mm.			(337)
$Cl_3SiCH_2Si(C_7H_{16})Cl_2$		280.5/753 mm. 136.3–137.0/3 mm.			(337)

$Cl(CH_3)_2SiCH_2SiCl_3$					(106, 112, 390)
$Cl_2(CH_3)SiCH_2Si(CH_3)Cl_2$		192		1.288 (25°)	(105, 106, *110*, *112*, 210, 216)
$(C_2H_5O)_2(CH_3)SiCH_2Si(CH_3)(OC_2H_5)_2$		112/25 mm.	1.4148 (25°)	0.8914 (25°)	(*106*, 113)
$(C_2H_5O)_2(CH_3)SiCH_2Si(CH_3)Cl_2$					(113)
$Cl_2(CH_3)SiCH_2Si(C_5H_5)Cl_2$		149/13 mm.	1.5290 (25°)	1.313 (25°)	(105, 106, *110*)
$Cl_2(C_2H_5)SiCH_2Si(C_2H_5)Cl_2$		231–233			(243)
$Cl_3SiCH_2Si(C_2H_5)_2Cl$		221–223			(*243*, 247)
$Cl_2(C_6H_{13})SiCH_2Si(C_6H_{13})Cl_2$		200–205/5 mm.			(510)
$Cl_4(C_6H_{13})_2Si_2CH_2$		175.5–180/2 mm.			(337)
$Cl_4(C_7H_{15})_2Si_2CH_2$		186–188/2 mm.			(337)
$Cl_2(C_6H_5)SiCH_2Si(C_6H_5)Cl_2$					(105)
$Cl(CH_3)_2SiCH_2Si(CH_3)Cl_2$		186		1.160 (25°)	(*106*, 111, *112*, 216)
$(C_2H_5O)(CH_3)_2SiCH_2Si(CH_3)(OC_2H_5)_2$		112/25 mm.			(113)
$(C_2H_5O)_2(CH_3)SiCH_2Si(CH_3)(C_6H_5)Cl$					(113)
$(CH_3)_3SiCH_2SiCl_3$		166	1.4448 (25°)	1.1234 (25°)	(*208*, 216, *217*, 441)
$(CH_3)_2(C_6H_5)SiCH_2SiCl_3$		146/20 mm.	1.5174 (25°)	1.187 (25°)	(208, 217)
$Cl(CH_3)(C_6H_5)SiCH_2Si(CH_3)Cl_2$					(106)
$Cl(CH_3)(C_6H_5)SiCH_2Si(C_6H_5)Cl_2$					(106)
$F(CH_3)_2SiCH_2Si(CH_3)_2F$		115	1.3780 (20°)	0.920 (20°)	(*52*, 54, 299, 388)
$F(CH_3)_2SiCH_2Si(CH_3)_2Cl$		72/50 mm.			(52)
$Cl(CH_3)_2SiCH_2Si(CH_3)_2Cl$		177/754 mm. 96/50 mm.	1.4480 (20°)	1.016 (20°)	(*52*, 111, 112, 131, 216, 221, 243, 387, *388*, 389, 390, 391)
$CH_3O(CH_3)_2SiCH_2Si(CH_3)_2OCH_3$		184 167.5			(243, 209)
$C_2H_5O(CH_3)_2SiCH_2Si(CH_3)_2OC_2H_5$		80/20 mm.			(218, 219, 243, 299)
$HO(CH_3)_2SiCH_2Si(CH_3)OH$	86				(*52*, 299, 388)
$(CH_3)_3SiCH_2Si(CH_3)Cl_2$		163/742 mm.	1.4400 (25°)	0.9942 (25°)	(*210*, 214, 441)
$(CH_3)_3SiCH_2Si(CH_3)Cl(OC_2H_5)$		175/740 mm.	1.4245 (25°)	0.9146 (25°)	(210)
$(CH_3)_3SiCH_2Si(CH_3)(OC_2H_5)_2$		181/740 mm.	1.4113 (25°)	0.8505 (25°)	(*210*, 214, 216)
$(CH_3)_2(C_5H_5)SiCH_2Si(CH_2)(OC_2H_5)_2$		160/25 mm.	1.4750 (25°)	0.9435 (25°)	(*210*, 214)
$(CH_3)_3SiCH_2Si(CH_3)_2Cl$		155/740 mm.	1.4277 (25°)	0.8662 (25°)	(*206*, 210, 247)
$(CH_3)_3SiCH_2Si(CH_3)_2OCH_3$					(245)
$(CH_3)_3SiCH_2Si(CH_3)_2OC_2H_5$		161/740 mm.	1.4148 (25°)	0.8060 (25°)	(*206*, 216, 222)
$(CH_3)_3SiCH_2Si(CH_3)_2OC_4H_9$		199/740 mm.	1.4211 (25°)	0.812 (25°)	(*206*, 211)
$(CH_3)_3SiCH_2Si(CH_3)_2OSi(CH_3)_3$		179–181			(245)
$(CH_3)_3SiCH_2Si(CH_3)_2OSi(C_2H_5)_3$					(245)
$(CH_3)_2(C_6H_5)SiCH_2Si(CH_3)_2OC_2H_5$		144/24 mm.	1.4839 (25°)	0.9152 (25°)	(*206*, 211)
$(CH_3)_2(C_6H_5)SiCH_2Si(C_4H_9)(CH_3)OC_2H_5$		184/25 mm.	1.4948 (25°)	0.9177 (25°)	(211)
$(CH_3)_2(C_6H_5)SiCH_2Si(CH_3)(C_6H_5)OC_2H_5$		207/24 mm.	1.5314 (25°)	0.984 (25°)	(206, *211*)
$(C_2H_5)_3SiCH_2Si(C_2H_5)_2OCH_3$					(245)
$(C_2H_5)_3SiCH_2Si(C_2H_5)_2OSi(CH_3)_3$					(245)

TABLE 20—*Continued*

Compound	Melting Point	Boiling Point	n_D	d	References
	°C.	*°C.*			
$(CH_3)_3SiCH_2Si(CH_3)_3$		134/760 mm.	1.4172 (20°)	0.7520 (20°)	(100, *206*, 207, 212, 244, 299, 435, *440*, 507, 535)
		91/200 mm.	1.4154 (25°)	0.7504 (25°)	
$(CH_3)_3SiCH_2Si(CH_3)_2C_2H_3$		157–159	1.4272 (20°)	0.7713 (20°)	(244)
$(CH_3)_3SiCH_2Si(CH_3)_2C_6H_5$		125/26 mm.	1.4940 (25°)	0.8763 (25°)	(*216*, *244*, 247)
		118–120/20 mm.	1.4790 (20°)	0.8711 (20°)	
$(CH_3)_2(C_6H_5)SiCH_2Si(CH_3)_2C_6H_5$	−73	143/0.3 mm.	1.5426 (25°)	0.9615 (25°)	(216)
$(CH_3)_3SiCH_2Si(CH_3)(C_5H_5)_2$	−63	149/3 mm.	1.5391 (25°)	0.9643 (25°)	(216)
$(CH_3)_2(C_5H_5)SiCH_2Si(CH_3)(C_6H_5)_2$	−50	165/0.2 mm.	1.5800 (25°)	1.0214 (25°)	(216)
$(CH_3)_3SiCH_2Si(C_6H_5)_3$	63	151/0.05 mm.			(216)
$CH_3(C_6H_5)_2SiCH_2Si(C_6H_5)_2CH_3$	78	199/0.2 mm.			(216)
$(CH_3)_2(C_6H_5)SiCH_2Si(C_6H_5)_3$	−26	195/0.5 mm.	1.5917 (25°)	1.0505 (25°)	(216)
$CH_3(C_6H_5)_2SiCH_2Si(C_6H_5)_3$		245/0.4 mm.	1.6148 (25°)	1.091 (25°)	(216)
$(SiCH_2Si)(CH_3)_2(C_2H_5)_4(?)$		160			(172)
$(C_2H_6)_3SiCH_2Si(C_2H_5)_3$		243–245	1.4578 (20°)	0.8218 (20°)	(244, *507*)
$(C_6H_5)_3SiCH_2Si(C_6H_6)(C_2H_5)_2$					(247)
$(C_3H_7)_2SiCH_2Si(C_3H_7)_3$		145–153/3 mm.			(244)
$ClCH_2(CH_3)_2SiCH_2Si(CH_3)_3$		186/760 mm.	1.4480 (20°)	0.8950 (20°)	(435, *440*)
		141/200 mm.			
$ICH_2Si(CH_3)_2CH_2Si(CH_3)_3$		98/15 mm.	1.4945 (20°)	1.257 (20°)	(406)
$CH_2[Si(CH_3)_2C_6H_4Si(CH_3)_3]_2$	−54	171/1 mm.	1.5113 (25°)	0.923 (25°)	(103)
$Cl_3SiCH(CH_3)SiCl_3$		191		1.454 (27.5°)	(20, 137, 147)
		182		1.479 (20°/20°)	
$H_3SiCH(CH_3)SiH_3$	−50	57			(146, 147)
$(CH_3)_3SiCH(CH_3)Si(CH_3)_3$					(20)
$Cl(CH_3)_2SiCH(CH_3)Si(CH_3)_2Cl$					(20)
$[-Si(CH_3)_2CH(CH_3)Si(CH_3)_2O-]_x$					(20)
$(1,1\text{-}C_6H_4C_3H_4)[Si(CH_3)_3]_2$		94/2 mm.	1.5135 (20°)	0.920 (20°)	(438)
$(1,1\text{-}C_5H_4C_3H_4)[Si(C_2H_5)_3]_2$		155/2 mm.	1.5270 (20°)	0.941 (20°)	(438)
$(1,1\text{-}C_6H_4C_3H_2)[Si(CH_3)]_2$		104/3 mm.	1.5304 (20°)	0.930 (20°)	(438)
$1,1\text{-}C_6H_4C_3H_2[Si(C_2H_5)_3]_2$		170/3 mm.	1.5333 (20°)	0.940 (20°)	(438)
$1,1\text{-}C_6H_4C_3H_2[Si(C_5H_5)_3]_2$	206				(*185*, 186)
Disilmethylenesiloxanes:					
$(CH_3)_3SiOSi(CH_3)_2CH_2Si(CH_3)_3$		179/760 mm.	1.4137 (20°)	0.8081 (20°)	(*52*, 53, 452)
		97/51 mm.			
$[(CH_3)_3SiCH_2Si(CH_3)_2]_2O$	−115	126/20 mm.	1.4319 (25°)	0.8311 (25°)	(206, *211*)
$[(CH_3)_2(C_6H_5)SiCH_2Si(CH_3)_2]_2O$		198/2 mm.	1.5107 (25°)	0.9548 (25°)	(206, *211*)

$[(CH_3)_2(C_6H_5)SiCH_2Si(C_4H_9)(CH_3)]_2O$					(206, 211)
$[(CH_3)_2(C_5H_5)SiCH_2Si(CH_3)(C_5H_5)]_2O$					(206, 211)
$[(C_2H_5)_3SiCH_2Si(C_2H_5)_2]_2O$		190–196/10 mm.			(244)
$(CH_3)_3SiOSi(CH_3)_2CH_2Si(CH_3)_2OH$					(53)
$CH_2[Si(CH_3)_2OSi(CH_3)_3]_2$		131/54 mm.	1.4121 (20°)	0.8447 (20°)	(*52*, 53)
$[—Si(CH_3)_2CH_2Si(CH_3)_2O—]_2$	~30	214	1.4341 (20°)	0.9039 (20°)	(*52*, 215, *219*, 222, 299, *389*, 391)
		104/20 mm.	1.4328 (25°)	0.9042 (25°)	
$[(CH_3)_3SiOSi(CH_3)_2CH_2Si(CH_3)_2]_2O$		185/35 mm.	1.4243 (20°)	0.8725 (20°)	(*52*, 53, 54, 388)
$\{—Si[CH_2Si(CH_3)_3]CH_3O—\}[—Si(CH_3)_2O—]_3$		121/25 mm.	1.4137 (25°)	0.9475 (25°)	(209)
$C_2H_5O\{[—SiCH_2Si(CH_3)_3]CH_3O—\}_3C_2H_5$		223/24 mm.			(214)
cis-trans-$[—Si[CH_2Si(CH_3)_3]CH_3O—\}_3$		181/24 mm.	1.4391 (25°)	0.9151 (25°)	(209, *214*, 529)
$\{—Si[CH_2Si(CH_3)_3]CH_3O—\}_3$		183/25 mm.	1.4395 (25°)	0.9180 (25°)	(*214*, 220)
$[—Si[CH_2Si(CH_3)_3]CH_3O—\}_3$		177/25 mm.	1.4355 (25°)	0.9111 (25°)	(*214*, 220)
$[—Si[CH_2Si(CH_3)_3]CH_3O—\}_4$		223/24 mm.	1.4452 (25°)	0.9390 (25°)	(214)
$[—Si[CH_2Si(CH_3)_3]CH_3O—\}_5$		270/25 mm.	1.4493 (25°)	0.9303 (25°)	(214)
$\{—Si[CH_2Si(CH_3)_2(C_5H_5)]CH_3O—\}_x$					(209, 214)
$[CH_2(SiCH_3O)_2]_3$	199				(105)
Bisdisilmethylenes:					
$(SiCH_2SiCH_2Si)(CH_3)_3Cl_5$					(112)
$[CH_2Si(CH_3)(OC_2H_5)_2]_2[Si(CH_3)_2]$		159/25 mm.	1.4282 (25°)	0.9229 (25°)	(213)
$[CH_2Si(CH_3)Cl_2]_2[Si(CH_3)_2]$					(213)
$(CH_3)_3SiCH_2Si(CH_3)_2CH_2Si(CH_3)(OC_2H_5)_2$		132/25 mm.	1.4314 (25°)	0.8700 (25°)	(*210*, 214)
$[F(CH_3)_2SiCH_2]_2Si(CH_3)_2$		188	1.4150 (20°)	0.926 (20°)	(52)
		102/44 mm.			
$C_2H_5O(CH_3)_2SiCH_2Si(CH_3)_2CH_2Si(CH_3)_2OC_2H_5$		128/20 mm.			(218, *219*)
$[(CH_3)_3SiCH_2]_2SiCl_3$		92/9 mm.			(441)
$[(CH_3)_3SiCH_2]_2Si(OH)_2$					(441)
$(CH_3)_3SiCH_2Si(CH_3)_2CH_2Si(CH_3)_2Cl$		227/740 mm.	1.4502 (25°)	0.8888 (25°)	(*206*, 211)
$(CH_3)_3SiCH_2Si(CH_3)_2CH_2Si(CH_3)_2OC_2H_5$		226/740 mm.	1.4360 (25°)	0.8348 (25°)	(*206*, 211, 212)
		135/50 mm.			
$[(CH_3)_3SiCH_2]_2Si(CH_3)Cl$		110/20 mm.			(441)
$(CH_3)_3SiCH_2Si(CH_3)_2CH_2Si(CH_3)_3$	−64	206/760 mm.	1.4420 (20°)	0.7987 (20°)	(107, *206*, *212*, 435, *440*)
		159/200 mm.	1.4403 (25°)	0.7990 (25°)	
$(CH_3)_2(C_6H_5)SiCH_2Si(C_6H_5)_2CH_2Si(CH_3)_2C_6H_5$	20	182–203/0.3 mm.	1.5724 (25°)		(216)
$(CH_3)_2(C_6H_5)SiCH_2Si(CH_3)(C_6H_5)CH_2Si(CH_3)_2C_6H_5$	−44	180/0.2 mm.	1.5632 (25°)	0.9985 (25°)	(216)
$ClCH_2[Si(CH_3)_2CH_2]_2Si(CH_3)_3$		246/760 mm.	1.4630 (20°)	0.9000 (20°)	(440)
		197/200 mm.			
$[—Si(CH_3)_2Si(CH_3)_2CH_2—]_2$	42	85/3 mm.			(111)
$\{(CH_3)_3Si[CH_2Si(CH_3)_2]_2\}_2O$	−115	200/19 mm.	1.4542 (20°)	0.8601 (20°)	(206, *211*, *440*)
			1.4528 (25°)	0.8580 (25°)	
$(CH_3)_2Si[CH_2Si(CH_3)_2]_2O$					(222)
$[(CH_3)_3OSi(CH_3)_2CH_2]_2Si(CH_3)_2$		176/55 mm.	1.4276 (20°)	0.855 (20°)	(*52*, 53)
$[(CH_3)_3SiO[Si(CH_3)_2CH_2]_2Si(CH_3)_2\}_2O$					(53)

TABLE 20—*Continued*

Compound	Melting Point	Boiling Point	n_D	d	References
	°*C.*	°*C.*			
$[-Si(CH_3)_2[CH_2Si(CH_3)_2]_2O-\}_2$		77/27 mm.	1.4371 (25°)	0.872 (25°)	(219)
$[-Si[CH_2Si(CH_2)_2CH_2Si(CH_3)_3](CH_3)O-\}_3$		252/25 mm.	1.4598 (25°)	0.9208 (25°)	(214)
$[(CH_3)_3SiCH_2]_2$ siloxanes					(441)
$[CH_3)_3SiCH_2]_2Si$ silazanes					(441)
Trisdisilmethylenes:					
$(SiCH_2SiCH_2SiCH_2Si)(CH_3)_8Cl_7$					(112)
$(Cl_2SiCH_2)_3$	82				(*352*, 353, 362)
$(CH_2SiH_2)_3$	10	134.9/769 mm.	1.5059 (20°)	0.9001 (20°)	(362)
$C_2H_5OSi(CH_3)_2[CH_2Si(CH_3)_2]_3OC_2H_5$		153/20 mm.			(218, *219*)
$(CH_3)_3Si[CH_2Si(CH_3)_2]_3Cl$					(211)
$(CH_3)_3Si[CH_2Si(CH_3)_2]_3OC_2H_5$		260/740 mm.			(206, 211, 212)
		159/23 mm.	1.4501 (25°)	0.8521 (25°)	
$[(CH_3)_3SiCH_2]_3SiCl$	13–14	112/4 mm.	1.4600 (20°)	0.8900 (20°)	(402)
$[CH_2Si(CH_3)_2]_3$		201/745 mm.	1.4606 (25°)	0.846 (25°)	(131, 221)
$CH_3[(CH_3)_2SiCH_2]_3Si(CH_3)_3$	−110	259/760 mm.	1.4552 (20°)	0.8245 (20°)	(107 206, *212*, *440*)
		208/200 mm.		0.8210 (25°)	
$\{CH_2[Si(C_6H_5)_2][Si(CH_3)_2]\}[CH_2Si(CH_3)_2C_6H_5]_2$					(216)
$ClCH_2[Si(CH_3)_2CH_2]_3Si(CH_3)_3$		297/760 mm.	1.4706 (20°)	0.9029 (20°)	(440)
		242/200 mm.			
$[(CH_3)_3Si[CH_2Si(CH_3)_2]_3]_2O$	−115	280/26 mm.	1.4645 (25°)	0.8705 (25°)	(206, *211*)
Higher disilmethylenes:					
$[-SiCH_2-]_4(CH_3)_2Cl_5$					(221)
$C_2H_5OSi(CH_3)_2[CH_2Si(CH_3)_2]_4OC_2H_5$		180/20 mm.			(218, 219)
$(CH_3)_3Si[CH_2Si(CH_3)_2]_4Cl$					(212)
$CH_3[(CH_3)_2SiCH_2]_4Si(CH_3)_3$	−95	309/760 mm.	1.4640 (20°)	0.8408 (20°)	(212, 440)
		254/200 mm.		0.8386 (25°)	
$[(CH_3)_3SiCH_2]_4Si$	29	150/23 mm.			(*402*, 441)
$[CH_2Si(CH_3)_2]_4$		75/1 mm.	1.4690 (25°)	0.8674 (25°)	(221)
$(SiCH_2)_4(CH_3)_2(C_6H_5)_6$					(221)
$\{(CH_3)_3Si[CH_2Si(CH_3)_2]_4\}_2O$					(211)
$[(CH_3)_3Si[CH_2Si(CH_3)_2]_5\}_2O$					(211)
$(Cl_2SiCH_2)_x$					(352, 353)
$Cl(CH_3)_2Si[CH_2Si(CH_3)_2]_xCl$					(222)
$C_2H_5O(CH_3)_2Si[CH_2Si(CH_3)_2]_xCl$					(222)
$C_2H_5O(CH_3)_2Si[CH_2Si(CH_3)_2]_xOC_2H_5$					(222)
$(CH_3)_3Si[CH_2Si(CH_3)_2]_xCl$					(222)
$(CH_3)_3Si[CH_2Si(CH_3)_2]_xOC_2H_5$					(222)
$C_6H_5(CH_3)_2Si[CH_2Si(C_6H_5)CH_3]_xOC_2H_5$					(206)
$(CH_3)_3Si[CH_2Si(CH_3)_2]_xCH_3$					(107, 222)

$[CH_2Si(CH_3)_2]_x$					(205)
$[-CH_2Si(CH_3)_2CH_2Si(C_4H_9)(CH_3)-]_x$					(131)
$[CH_2Si(CH_3)_2]_x$					(221)
$[CH_2Si(C_4H_9)CH_3]_x$					(205)
$[CH_2Si(C_6H_5)CH_3]_x$					(205)
$[-CH_2Si(CH_3)_2CH_2Si(C_6H_5)(CH_3)-]_x$					(131)
$(-SiR_2CH_2-)_x(-CH_2\underset{\vert}{Si}RCH_2-)_y$					(152)
$[-Si(CH_3)_2Si(CH_3)_2CH_2-]_2$	42	85/3 mm.			(111)
$[-Si(CH_3)_2Si(CH_3)_2CH_2-]_x$					(111)
$[-Si(CH_3)_2Si(CH_3)(C_5H_5)CH_2-]_x$					(111)
Cyclic silpolymethylenes:					
$CH_2(CH_2)_2SiCl_2$					(228, 541)
$CH_2(CH_2)_2Si(CH_3)_2$		81/730 mm.	1.4270 (20°)	0.7746 (20°)	(430)
$CH_2(CH_2)_3SiCl_2$		141 143	1.4651 (20°) 1.463 (25°)	1.1505 (20°) 1.173 (25°)	(298, 531)
$CH_2(CH_2)_3Si(OCH_3)_2$		150 148.5	1.4269 (20°) 1.433 (25°)	0.9623 (20°) 0.960 (25°)	(298, 531)
$CH_2(CH_2)_3Si(OC_2H_5)_2$		74/38 mm.	1.4300 (20°)	0.9468 (20°)	(298)
$CH_2(CH_2)_3SiH_2$		71/atm.	1.444 (25°)	0.80 (25°)	(531, 532)
$CH_2(CH_2)_3Si(CH_3)Cl$		132/atm.	1.453 (25°)	0.981 (25°)	(531)
$CH_2(CH_2)_3Si(CH_3)H$		91.5/atm.	1.4390 (25°)	0.798 (25°)	(531)
$CH_2(CH_2)_3Si(CH_3)_2$		105 107	1.5330 (20°) 1.4335 (25°)	0.7931 (20°) 0.780 (25°)	(298, 531)
$CH_2(CH_2)_3Si(C_2H_5)_2$		160	1.4471 (20°)	0.8256 (20°)	(298)
$[CH_2(CH_2)_3SiCH_3]_2O$		221/atm.	1.457 (25°)	0.933 (25°)	(241, 531)
$[CH_2(CH_2)_3SiOC_2H_5]_2O$					(241)
$[CH_2(CH_2)_3SiO]_x$					(241)
$CH_2(CH_2)_3Si(CH_2)_3CH_2$	<−70	178.5/atm.	1.4860 (25°)	0.899 (25°)	(531)
$CH_2(CH_2)_4Si(CH_2)_3CH_2$	−35	203/atm.	1.4860 (25°)	0.899 (25°)	(531, 533)
$CH_2(CH_2)_4Si(CH_2)_4CH_2$	−18	227/atm.	1.4869 (25°)	0.900 (25°)	(531, 533)
o-$CH_2C_6H_4CH_2SiCl_2$					(242)

TABLE 20—*Continued*

Compound	Melting Point	Boiling Point	n_D	d	References
	°C.	°C.			
$o\text{-}\underline{CHClC_6H_4CHClSi}Cl_2$					(242)
$\underline{CH_2(CH_2)_4Si}Cl_2$		170	1.4697 (20°)	1.1560 (20°)	(*93*, 241, 531, 533)
$\underline{CH_2(CH_2)_4Si}(OCH_3)_2$		171/atm.	1.4309 (25°)	0.958 (25°)	(531)
$\underline{CH_2(CH_2)_4Si}HCl$		143/atm.	1.467 (25°)	1.018 (25°)	(531)
$\underline{CH_2(CH_2)_4Si}H_2$		102	1.4533 (25°)	0.818 (25°)	(531, 532)
$\underline{CH_2(CH_2)_4Si}(OH)_2$	130–132				(531)
$\underline{CH_2(CH_2)_4Si}(CH_3)Cl$		167/atm.	1.466 (25°)	1.01 (25°)	(531)
$\underline{CH_2(CH_2)_4Si}(CH_3)H$		118	1.4462 (25°)	0.809 (25°)	(531)
$\underline{CH_2(CH_2)_4Si}(CH_3)_2$		133/atm.	1.4380 (25°)	0.798 (25°)	(531)
$(CH_2)_5Si(C_2H_5)_2$		184–194			(93)
$[\underline{CH_2(CH_2)_4Si}(CH_3)]_2O$		253/atm.	1.4640 (25°)	0.927 (25°)	(531)
$[(CH_2)_5SiO]_x$					(241)
$\underline{CH_2CH_2CH_2CH{=}CHSi}Cl_2$					(242)
$\underline{CH_2CH_2CH_2CHClCHClSi}Cl_2$					(242)
$(\underline{CH_2CH_2CH_2CHClCHClSi}O)_x$					(242)
$\underline{CH_2(CH_2)_5Si}Cl_2$		201/atm.	1.452 (25°)	1.065 (25°)	(531)
$\underline{CH_2(CH_2)_5Si}H_2$		135/atm.	1.459 (25°)	0.80 (25°)	(531)
$\underline{CH_2(CH_2)_5Si}(CH_3)H$		144/atm.	1.423 (25°)		(531, 532)
$\underline{CH_2(CH_2)_5Si}(CH_3)_2$		161/atm.	1.4335 (25°)	0.780 (25°)	(531)
$[o\text{-}\underline{CHClC_6H_4CHClSi}O]_x$					(242)

Disilpolymethylenes:					
$Cl_3Si(CH_2)_2SiCl_3$	28	203		1.467 (28°)	(11, 20, 92, 137, *147*, 201, *292*, 299, 332, 339, 340, *352*, 362, 365, 507, 509. 512, 525, 537)
		93/25 mm.			
$(Cl_3Si)_2C_2H_4$		44–57/1 mm.		1.48 (25°)	(265, 526)
$[(C_2H_5O)_3Si]_2C_2H_4$		256			(525)
$(CH_3O)_3SiCH_2CH_2Si(OCH_3)_2$		103–104/5 mm.	1.4091 (20°)	1.0687 (20°)	(340)
$(C_2H_5O)_3SiCH_2CH_2Si(OC_2H_5)_3$		122–123/1.5 mm.	1.4120 (20°)	0.9660 (20°)	(209, 340)
$(C_3H_7O)_3SiCH_2CH_2Si(OC_3H_7)_3$		163–164/2.3 mm.	1.4228 (20°)	0.9398 (20°)	(509)
$(i\text{-}C_3H_7O)_3SiCH_2CH_2Si(OC_3H_7\text{-}i)_3$		122–123/0.9 mm.	1.4105 (20°)	0.9112 (20°)	(509)
$(C_4H_9O)_3SiCH_2CH_2Si(OC_4H_9)_3$		201–202/0.6 mm.	1.4300 (20°)	0.9228 (20°)	(509)
$(i\text{-}C_4H_9O)_3SiCH_2CH_2Si(OC_4H_9\text{-}i)_3$		193–194/3 mm.	1.4242 (20°)	0.9068 (20°)	(509)
$(i\text{-}C_5H_{11}O)_3SiCH_2CH_2Si(OC_5H_{11}\text{-}i)_3$		224–225/2.5 mm.	1.4331 (20°)	0.9039 (20°)	(509)
$(C_6H_{13}O)_3Si(CH_2)_2Si(OC_6H_{13})_3$		267–268/1.2 mm.	1.4406 (20°)	0.9007 (20°)	(512)
$(C_7H_{15}O)_3Si(CH_2)_2Si(OC_7H_{15})_3$		271–272/0.4 mm.	1.4444 (20°)	0.8982 (20°)	(512)
$(C_8H_{17}O)_3Si(CH_2)_2Si(OC_8H_{17})_3$		307–309/1 mm.	1.4480 (20°)	0.8893 (20°)	(512)
$(C_9H_{19}O)_3Si(CH_2)_2Si(OC_9H_{19})_3$		307–309/0.4 mm.	1.4500 (20°)	0.8858 (20°)	(512)
$(C_6H_{11}O)_3SiCH_2CH_2Si(OC_6H_{11})_3$		209–302/2.2 mm.	1.4863 (20°)	1.0292 (20°)	(339)
$(C_6H_5CH_2O)_3Si(CH_2)_2Si(OCH_2C_6H_5)_3$		335–336/1.5 mm.	1.5679 (20°)	1.5522 (20°)	(339)
$(C_6H_5O)_3Si(CH_2)_2Si(OC_6H_5)_3$	96	310–313/1.2 mm.			(339)
$(3\text{-}CH_3C_6H_4O)_3Si(CH_2)_2Si(OC_6H_4CH_3\text{-}3)_3$	78–79	316–318/1 mm.			(339)
$H_3Si(CH_2)_2SiH_3$	−14	67–68.5	1.4140 (20°)	0.6987 (20°)	(146, *147*, 362, 537)
		46/746.6 mm.			
$H_3SiCH_2Si(CH_2{=}CH)H_2$					(537)
$Cl_2(CH_3)Si(CH_2)_2Si(CH_3)Cl_2$					(292)
$[Cl_2(C_2H_5)Si]_2C_2H_4$		248/750 mm.	1.4742 (20°)	1.192 (25°)	(525)
		94/4 mm.			
$C_2H_5O(CH_3)_2CH_2CH_2Si(CH_3)_2OC_2H_5$		92–94/21 mm.			(209)
$HO(CH_3)_2SiCH_2CH_2Si(CH_3)_2OH$	86–87				(299)
$(CH_3)_3Si(CH_2)_2Si(CH_3)_3$		150–151	1.4204 (20°)	0.7536 (20°)	(299, *346*, *507*)
		151/750 mm.	1.4170 (25°)	0.7457 (25°)	
$(C_2H_5)_3SiCH_2CH_2Si(C_2H_5)_3$		265–267	1.4582 (20°)	0.8222 (20°)	(365, *507*)
$Cl_3SiCH_2CH(CH_2)SiCl_3$		175–180/80 mm.			(147)
$H_3SiCH(CH_3)CH_2SiH_3$		94–96			(146, 147)
$Cl_3SiCCl_2CH_2SiCl_3$		101/4 mm.	1.5158 (20°)		(2, 4, 527)
$(CH_3)_3SiCH(C_6H_5)CH(C_5H_5)Si(CH_3)_3$	152				(240)
$(CH_3O)_3SiCCl_2CH_2Si(OCH_3)_3$		121/1 mm.	1.4406 (22°)		(2, 4, 527)
$(CH_3)_3SiCBr{=}CBrSi(CH_3)_3$	41–42	167–168/77 mm.			(*167*, 168)
$(C_2H_5O)_3SiC{=}CSi(OC_2H_5)_3$					(56)
$Cl(CH_3)_2SiC{\equiv}CSi(CH_3)_2Cl$		113/65 mm.			(*167*, 169)
$HO(CH_3)_2SiC{\equiv}CSi(CH_3)_2OH$					(167, 169)

TABLE 20—*Continued*

Compound	Melting Point	Boiling Point	n_D	d	References
	°C.	*°C.*			
$(CH_3)_3SiC{\equiv}CSi(CH_3)_3$		134–136	1.4260 (20°)	0.7703 (20°)	(*167*, 168, *365*)
		133–135	1.4259 (25°)	0.763 (25°)	
$(C_2H_5)_3SiC{\equiv}CSi(C_2H_5)_3$		132–134/25 mm.	1.4268 (20°)	0.8174 (20°)	(365)
$(C_4H_9)_3SiC{\equiv}CSi(C_4H_9)_6$		215–218/22 mm.	1.4568 (20°)	0.8339 (20°)	(365)
$Cl_3Si(CH_2)_3SiCl_3$		222/760 mm.			(92, *291*, 209, 362)
		111/20 mm.			
$(CH_3O)_3Si(CH_2)_3Si(OCH_3)_3$		155–156/34 mm.			(299)
$H_3SiCH_2CH_2CH_2SiH_3$		77.9/757 mm.	1.4235 (20°)	0.7276 (20°)	(362)
$F(CH_3)_2Si(CH_2)_3Si(CH_3)_2F$		160.5			(299)
$CH_3O(CH_3)_2Si(CH_2)_3Si(CH_3)_2OCH_3$		96/23 mm.			(299)
$\underline{Si(CH_3)_2(CH_2)_3}Si(CH_3)_2O$		146			(299)
		48/19 mm.			
$(CH_3)_3Si(CH_2)_3Si(CH_3)_3$		172–173			(299)
$Cl_3SiCH_2CH_2CH(CH_3)SiCl_3$		250	1.4776 (20°)	1.37 (20°)	(9)
$(CH_2{=}CHSiCl_3)_2$		60–70/1 mm.			(526)
$(C_6H_4SiC_5H_{10})_x$					(379, 380)
$CH_2ClCH(SiCl_3)CH_2CHClSiCl_3$		120/2 mm.		1.57 (25°)	(526)
$Cl_3SiCH(CH_3)CH_2CH_2SiCl_3$		250/750 mm.			(525)
		102–104/4 mm.			
$Cl_3SiCH_2CH(CH_3)CH_2Si(OC_2H_5)_3$		115–122/4 mm.			(238)
$SiCH_2CH(CH_3)CH_2Si$ siloxanes					(238)
$Cl_3Si(CH_2)_4SiCl_3$		97–99/5 mm.			(147)
$H_3Si(CH_2)_4SiH_3$		0/8 mm.			(537)
		20/22 mm.			
$(CH_3)_3Si(CH_2)_4Si(CH_3)_3$		199/748 mm.	1.4244 (25°)	0.763. (25°)	(299, *535*)
$(CH_3)_3Si(CH_2)_5Si(CH_3)_3$		216/760 mm.	1.4278 (25°)	0.768 (25°)	(299, *535*)
$CO[CH_2CH_2Si(CH_3)_3]_2$		103/7 mm.	1.4414 (20°)	0.8424 (20°)	(444)
Oxime	76–76.5				(415, 444)
$CO[CH_2CH_2Si(CH_3)_2OSi(CH_3)_3]_2$		95/2 mm.	1.4262 (20°)	0.8857 (20°)	(444)
$[-Si(CH_3)_2CH_2CH_2COCH_2CH_2Si(CH_3)_2O-]_2$	129–130				(444)
$H_2NCH[CH_2CH_2Si(CH_3)_3]_2$		115/15 mm.	1.4438 (20°)	0.8123 (20°)	(*415*, 418)
Hydrochloride	131–131.5				(*415*, 418)
$(CH_3)_3SiOSi(CH_3)_2(CH_2)_2CHNH_2(CH_2)_2Si(CH_3)_2OSi(CH_3)_3$		98/2 mm.	1.4282 (20°)	0.8654 (20°)	(418)
$[-Si(CH_3)_2(CH_2)_2CHNH_2(CH_2)_2Si(CH_3)_2O-]_x$					(418)
$C_2H_5OCO[COCH_2CH_2Si(CH_3)_3]CH_2Si(CH_3)_3$		141/8 mm.	1.4472 (20°)	0.9196 (20°)	(444)
$(CH_3)_3SiCH_2CH(CH_3)CH(CH_3)CH_2Si(CH_3)_3$		220–220.3/730 mm.	1.4400 (20°)	0.7922 (20°)	(357, *359*)
$(C_2H_5)_3SiCH_2CH(CH_3)CH(CH_3)Si(C_2H_5)_3$		314–317	1.4672 (20°)	0.8376 (20°)	(357)
$Cl(CH_3)_2Si(CH_2)_6Si(CH_3)_2Cl$		110/2 mm.			(494)

$HO(CH_3)_2Si(CH_2)_6Si(CH_3)_2OH$					(494)
$(CH_3)_2Si(CH_2)_5Si(CH_3)_3$		109.5/16 mm.	1.4298 (25°)	0.772 (25°)	(535)
$Cl_3SiC_6H_{12}SiCl_3$		151/10 mm.			(22, 23, 20)
$(C_2H_5)_3SiCH_2CH(CH_3)CH_2CH(CH_3)CH(CH_3)CH_2CH(CH_3)$-$CH_2Si(C_2H_5)_3$		380	1.4687 (20°)	0.8443 (20°)	(359)
$Cl_3SiC_5H_8SiCl_3$		169–175/55 mm.			(238)
$(Cl_3SiC_6H_4)(Cl_3Si)(CH_3)_3C_5H_5$					(233)
$(Cl_3SiC_2H_4)(Cl_3Si)C_6H_{10}$		161/6 mm.			(22, 233, 238)
$SiC_2H_4C_6H_{10}Si$ siloxanes					(238)
1,6-$(SiCl_3)_2$-2,5-$(CH_3)_2C_6H_8$		165/10–15 mm.			(238)
$(Cl_2SiC_3H_5)(Cl_3Si)(CH_3)_2C_6H_8$					(233)
$(Cl_3SiC_4H_8)(Cl_3Si)(C_2H_5)C_6H_9$					(233)
$(Cl_3SiC_5H_{10})(Cl_3Si)(CH_3)_2C_6H_8$					(233)
$(Cl_3SiCH_2CH_2)_2C_6H_4$		135–137/0.5 mm.		1.38 (25°)	(232, 234, 235, 526)
$Cl_2Si(CH_2)_2C_6H_4CHClCH_2SiCl_3$					(234, 235)
$(Cl_3SiCH_2CH_2)_2C_6H_3Cl$		194/1 mm.			(232, 235)
Polyolefin–silicon hydride adducts					(15,19, 23, 29, 204, 238)
Naphthylethylenetrichlorosilane polymer					(236)
Polysilarylenes:					
1,3-$C_6H_4(SiCl_3)_2$		160/30 mm.		1.497 (20°)	(16)
1,4-$C_6H_4(SiCl_3)_2$		168/30 mm.			(16, 114, 127)
$C_5H_4(SiCl_3)_2$		160/30 mm.		1.497 (20°)	(*20*, 127)
$C_6H_4(SiCl_3)_2$	Solid	168/30 mm.			(20)
$C_6H_4(SiCl_3)[Si(C_6H_5)Cl_2]$		226/30 mm.		1.386 (20°)	(*16*, 20, 109, 114)
$Cl_3SiC_6H_4SiHCl_2$					(386)
$Cl_2(CH_3)SiC_6H_4SiHCl_2$					(386)
$Cl_2(C_4H_9)SiC_6H_4SiHCl_2$					(386)
Cl_2(cyclo-C_6H_{11})$SiC_6H_4SiHCl_2$					(386)
$Cl_2(C_6H_5)SiC_6H_4SiHCl_2$					(386)
$Cl_2(C_6H_5)SiC_6H_4Si(C_2H_5)Cl_2$					(386)
$Cl_2(C_6H_5)SiC_6H_4Si(C_5H_{11})Cl_2$					(386)
$Cl_2(C_6H_5)SiC_6H_4$(cyclo-C_6H_{11})Cl_2					(386)
[1,4-$C_5H_4[Si(CH_3)Cl_2]_2$		169/30 mm.			(127)
$C_6H_4[Si(CH_3)Cl_2]_2$		165/30 mm.			(17, *127*)
$C_6H_4[Si(C_6H_5)Cl_2]_2$		213/3 mm.			(17, *109*)
4-$(Cl_3Si)C_6H_4Si(C_2H_5)_3$		175/14 mm.			(224)
1,4-$C_6H_4[Si(CH_3)_2Cl]_2$	87	110/1.5 mm.			(494)
1,4-$C_6H_4[Si(CH_3)_2OH]_2$	135				(494)
1,4-$C_6H_4[Si(C_6H_5)_2Cl]_2$					(495)
1,2-$[(CH_3)_3Si]_2C_6H_4$	−72	135/20 mm.	1.5110 (25°)	0.8985 (25°)	(115, *116*)
1,3-$[(CH_3)_3Si]_2C_6H_4$	−26	112/26 mm.	1.4867 (25°)	0.8685 (25°)	(115, *116*)
1,4-$[(CH_3)_3Si]_2C_6H_4$	88	143/43 mm.			(115, *116*, 186)
4-$(CH_3)_3SiC_6H_4Si(C_5H_5)_3$	162.5				(115)
$(CH_2)_3SiC_6H_4Si(C_6H_5)_3$		205–215			(115)

TABLE 20—*Concluded*

Compound	Melting Point	Boiling Point	n_D	d	References
	°C.	°C.			
2,4-$[(CH_3)_3Si]_2C_6H_3OSi(CH_3)_3$		162	1.4843 (20°)	0.899 (20°)	(465)
$[-Si(CH_3)_2(1,4\text{-}C_6H_4)Si(CH_3)_2O-]_x$					(495)
$[-Si(C_6H_5)_2(1,4\text{-}C_6H_4)Si(C_5H_5)_2O-]_x$					(495)
$(Cl_3SiC_6H_4)_2SiCl_2$		212/5 mm.		1.490 (20°)	(16)
$[(CH_3)_3SiC_8H_4]_2Si(CH_3)_2$		142/25 mm.			(104)
$[(CH_3)_3SiC_6H_4]_2Si(CH_3)C_6H_5$	−4	198/0.5 mm.	1.5604 (25°)		(104)
$[(CH_3)_3SiC_5H_4]_2Si(C_6H_5)_2$		210/0.3 mm.			(104)
$CH_2[Si(CH_3)_2C_6H_4Si(CH_3)_3]_2$	−54	171/1 mm.	1.5113 (25°)	0.923 (25°)	(103)
$(C_6H_4SiCl_2)_x$					(379, 380)
$[C_6H_4Si(CH_3)Cl]_x$					(379, 380)
$[C_5H_4Si(CH_3)OH]_x$					(379, 380)
$[C_5H_4Si(CH_3)_2]_x$					(379, 380)
$(C_6H_4SiC_5H_{10})_x$					(379, 380)
$Cl_2(C_6H_5)Si(C_6H_4SiCl_2)_xCl$					(109)
$Cl_2(C_6H_5)Si(C_6H_4SiCl_2)_xC_6H_5$					(109)
$Cl_2(C_6H_5)Si[C_6H_4Si(C_6H_5)Cl]_xC_6H_5$					(109)
$Cl(C_6H_5)_2Si[C_5H_4Si(C_6H_5)Cl]_xC_6H_5$					(109)
$C_6H_3(CH_3)(SiCl_3)_2$		166/30 mm.			(20)
$C_6H_3(CH_3)[Si(CH_3)Cl_2]_2$					(17)
$Cl_2(CH_3)SiC_5H_3(CH_3)Si(C_6H_4CH_3)(CH_3)Cl$					(17)
$C_6H_3Cl(SiCl_3)_2$		180.5–184.0/30 mm.			(21)
$C_6H_3Cl[Si(CH_3)Cl_2]_2$					(14)
(1,2-$C_6H_4)_2Si$					(228, 541)
$[Cl_2(CH_3)SiC_6H_4]_2$					(17)
[4-$(CH_3)_3SiC_6H_4]_2$	79	150/1 mm.			(*115*, 192)
[4-$C_5H_5(CH_3)_2SiC_6H_4]_2$	75	241/1 mm.			(115)
CHC_6H_5[4-$C_6H_4Si(C_5H_5)_3]_2$	315				(185)
$C_6H_5C(OH)$[4-$(C_5H_5)_3SiC_6H_4]_2$	290				(185)
1,4-H_2-1,4-$[(C_4H_9)_3Si]_2C_6H_3C_6H_5$		218–220	1.4771 (20°)	0.8692 (20°)	(356)
1,4-H_2-1,4-$(CH_3)_3SiC_{10}H_6$	−30	152–155/20 mm.	1.5329 (20°)	0.9444 (20°)	(356)
1,4-H_2-1,4-$(C_2H_5)_3SiC_{10}H_6$	−37	320–328/atm. 157–160/3 mm.	1.5163 (20°)	0.9319 (20°)	(356)
1,4-H_2-1,4-$(C_4H_9)_3SiC_{16}H_6$	−42	250–253/12 mm.	1.5096 (20°)	0.9057 (20°)	(356)
$C_{10}H_{10}(SiCl_3)_2$		220–233/30 mm.			(28)
$C_{10}H_6(SiCl_3)_2$					(127)
9,10-H_2-9,10-$[(CH_3)_3Si]_2C_{14}H_8$	168–170				(355)
9,10-H_2-9-$(CH_3)_3Si$-10-$(C_2H_5)_3SiC_{14}H_8$		140–150/10–14 mm.	1.5725 (20°)	1.0011 (20°)	(356)
9,10-H_2-9,10-$[(C_2H_5)_3Si]_2C_{14}H_8$	80	234/3 mm.			(355)
9,10-H_2-9-$(C_2H_5)_3Si$-10-$(C_4H_9)_3SiC_{14}H_8$		150–160/10–14 mm.	1.5521 (20°)	0.9748 (20°)	(355, 356)

hindrance in their silicon-functional reactions (441). Thus $[(CH_3)_3SiCH_2]_2Si(OH)_2$ is somewhat more stable than di-*n*-alkylsilanediols but not as stable as $[(CH_3)_3C]_2Si(OH)_2$. $[(CH_3)_3SiCH_2]_2SiCl_2$ gives silazanes rather than stable diamines, as does $[(CH_3)_3C]_2SiCl_2$. $[(CH_3)_3SiCH_2]_3SiCl$ shows the effect of steric hindrance in that it survives being stirred with cracked ice and with aqueous silver nitrate, although it reacts with the alcoholic reagent. The silmethylenesiloxanes behave pretty much like other organopolysiloxanes. $(CH_3)_3SiOSi(CH_3)_2CH_2Si(CH_3)_2OSi(CH_3)_3$ in concentrated sulfuric acid solution can be cleaved with hydrogen fluoride to $FSi(CH_3)_2CH_2Si(CH_3)_2F$; the carbon bridge is also undisturbed by refluxing for 3 hr. with 15 per cent aqueous potassium hydroxide because a good yield of $[-Si(CH_3)_2CH_2Si(CH_3)_2O-]_x$ is obtained (52).

The physical properties of compounds such as $CH_3[-Si(CH_3)_2CH_2-]_xSi(CH_3)_3$ are of special interest in determining the origin of the unusual physical properties exhibited by the linear methylpolysiloxanes $CH_3[-Si(CH_3)_2O-]_xSi(CH_3)_3$ (440). The two series are quite analogous in that they have the same degree of branching. Their principal difference lies in the replacement of oxygen by methylene. Since the physical properties of the silmethylene compounds are quite normal, the unusual physical properties of the siloxanes must be due largely to their siloxane linkages rather than to their extensive branching.

B. SILPOLYMETHYLENES

Silpolymethylenes embrace those compounds in which silicon atoms are bridged by a chain of two or more carbons. Examples are $Cl_3SiCH_2CH_2SiCl_3$ and $Cl(CH_3)_2Si(CH_2)_6Si(CH_3)_2Cl$.

Such compounds are usually obtained by the application of conventional silicon–carbon syntheses to polyfunctional starting materials. Thus α,ω-polymethylene chlorides react with silicon–copper at 300°C. to give low yields of $Cl_3Si(CH_2)_xSiCl_3$ derivatives (147, 512). Alkyldilithium compounds couple with $(CH_3)_3SiCl$ to form $(CH_3)_3Si(CH_2)_4Si(CH_3)_3$, $(CH_3)_3Si(CH_2)_5Si(CH_3)_3$, and $(CH_3)_3Si(CH_2)_6Si(CH_3)_3$ in good yield; however, the dimethylene and trimethylene derivatives are not obtained from this reaction (535). An analogous synthesis is the reaction of $ClMg(CH_2)_6MgCl$ with $(CH_3)_2SiCl_2$ to form $Cl(CH_3)_2Si(CH_2)_6Si(CH_3)_2Cl$ (494); similarly, $BrMgC{\equiv}CMgBr$ with methylchlorosilanes gives $(CH_3)_3SiC{\equiv}CSi(CH_3)_3$ and $Cl(CH_3)_2SiC{\equiv}CSi(CH_3)_2Cl$ (167). Related organometallic syntheses are the sodium coupling of $BrCH_2Si(CH_3)_3$ to form $(CH_3)_3SiCH_2CH_2Si(CH_3)_3$ (346) and the magnesium coupling of $C_6H_5CHBrSi(CH_3)_3$ to form $(CH_3)_3SiCH(C_6H_5)CH(C_6H_5)Si(CH_3)_3$ (240).

Silpolymethylenes are readily obtained by the addition of silicon hydrides to acetylenes, polyolefins, and unsaturated alkylsilanes. Thus 2 moles of $HSiCl_3$ readily add to acetylene in the presence either of peroxide (92) or of platinum (525) to give $Cl_3SiCH_2CH_2SiCl_3$. $HSiCl_3$ adds to $CH_2{=}CHSiCl_3$ and $CH_2{=}CHCH_2SiCl_3$ (92) and to $CCl_2{=}CHSiCl_3$ (2, 4) with formation of carbon-bridged products. The reaction of $HSiCl_3$ with diolefins produces similar products (9, 22, 204, 233). Silicon hydride adds to $CH_2{=}CH_2$ and to $CH_2{=}CHSiH_3$ upon photochemical activation to give silpolymethylenes (537). An interesting by-product formation of $Cl_3SiCH_2CH_2SiCl_3$ is found in the reaction of $HSiCl_3$ with benzene in the presence of boron chloride (20).

Complex carbon-bridged materials are obtained from the reaction of $HSiCl_3$ with natural and synthetic rubber and from the reaction of $CH_2{=}CHSiCl_3$ with benzene and other unsaturated materials. While such complex products are beyond the scope of this discussion, detailed references to them may be found in the tables.

Related to the silpolymethylenes are carbon-bridged compounds typified by $(Cl_3SiCH_2CH_2)_2C_6H_4$. These are obtained, for example, by coupling $ClCH_2CH_2SiCl_3$ with benzene in the presence of a Friedel–Crafts catalyst (234, 235).

Silpolymethylenes exhibit no unusual carbon-functional or silicon-functional reactions. Carbon-bridged compounds of the type $[(CH_3)_3SiCH_2CH_2]_2CO$ and $[(CH_3)_3SiCH_2CH_2]_2CHNH_2$ are known, and they are discussed under the particular functional group involved. The Raman spectrum of $Cl_3SiCH_2CH_2SiCl_3$ is known (332).

C. CYCLIC SILPOLYMETHYLENES

This section deals with compounds in which silicon is a member of saturated aliphatic rings. The five- and six-membered cyclics exhibit no unusual features, but the four-membered rings clearly show the effect of strain.

Six-membered heterocyclic compounds of the type $\underline{CH_2(CH_2)_4Si}Cl_2$ are numbered among the earlier known organosilicon derivatives. They are obtained conventionally through the coupling of di-Grignard reagents with silicon halides (93, 531), as are also five-membered ring compounds such as $\underline{CH_2(CH_2)_3Si}(CH_3)_2$ (298, 531) and seven-membered ring compounds such as $\underline{CH_2(CH_2)_5Si}(CH_3)_2$ (531). Spiranes in which silicon is simultaneously a member of two saturated rings are not obtained by the reaction of excess di-Grignard reagent with silicon tetrachloride (533). However, $\underline{CH_2(CH_2)_3Si}Cl_2$ and $\underline{CH_2(CH_2)_4Si}Cl_2$ couple satisfactorily with dilithium reagents to form $\underline{CH_2(CH_2)_3\overline{Si}}\overline{(CH_2)_3CH_2}$, $\underline{CH_2(CH_2)_3\overline{Si}}\overline{(CH_2)_4CH_2}$, and $\underline{CH_2(CH_2)_4\overline{Si}}\overline{(CH_2)_4CH_2}$ (531, 533).

Only one compound is known in which silicon is part of a ring of less than five members. This is $\underline{CH_2(CH_2)_2Si}(CH_3)_2$, 1,1-dimethylsilacyclobutane, which has only recently been obtained. It arises in good yield from the intramolecular coupling of $BrCH_2CH_2CH_2Si(CH_3)_2Cl$ by means of magnesium in ether (430). An earlier claim that $\underline{CH_2(CH_2)_2Si}Cl_2$ is formed through the sodium coupling of $Br(CH_2)_3Br$ with silicon tetrachloride is not very well supported (228) and has been disputed (93, 541). No cyclic derivatives are obtained by the dehalogenation of $(ClCH_2)_2Si(CH_3)_2$ or $(ICH_2)_2Si(CH_3)_2$ (373).

No unusual reactions of the five-, six-, and seven-membered ring compounds are known. The silicon chlorides may be hydrolyzed to siloxanes, alcoholyzed in the presence of pyridine, coupled with Grignard reagents, and reduced with lithium aluminum hydride (93, 298, 531). The effect of ring size on rate of alkali-catalyzed hydrolysis of silicon–hydrogen bonds has been studied (532). $\underline{CH_2(CH_2)_4}\overline{Si(CH_2)_4CH_2}$ resembles tetraalkylsilanes in that it is unchanged by boiling with dilute acids and bases and is only slowly affected by molten sodium (533).

The effects of strain are quite apparent in the reactions of the four-membered ring compound $\underline{CH_2(CH_2)_2Si}(CH_3)_2$. It reacts exothermally with dilute alcoholic potassium hydroxide and violently with concentrated sulfuric acid. No gas is formed in either reaction. Ring opening occurs in concentrated sulfuric acid at 0°C., for the product isolated on dilution with water is $[C_3H_7(CH_3)_2Si]_2O$ (430).

D. POLYSILARYLENES

The most widely investigated polysilarylenes are those containing the silphenylene grouping, SiC_6H_4Si. These are of interest because they are similar to phenyl silicones in high thermal stability and because they occur as by-products in certain of the industrial processes for making phenylchlorosilanes. The disilphenylenes can have a functionality greater than three and are of interest as high cross-linking centers in resinous compositions.

The methods for synthesizing silphenylenes are simple extensions of those for making phenyl silicon compounds. The first instance of a silphenylene synthesis is the formation of $(C_2H_5)_3SiC_6H_4SiCl_3$ by coupling $(C_2H_5)_3SiC_6H_4MgBr$ with silicon tetrachloride (224). In a slightly modified Grignard reaction 1,4-dibromobenzene couples with $(CH_3)_2SiCl_2$ to form $Cl(CH_3)_2SiC_6H_4Si(CH_3)_2Cl$ (494). The sodium coupling of aromatic halides with chlorosilanes also provides a satisfactory route to disilphenylenes. Thus all three $[(CH_3)_3Si]_2C_6H_4$ compounds are obtained by the sodium coupling of $(CH_3)_3SiCl$ with the appropriate $ClC_6H_4Si(CH_3)_3$ derivatives (116). On the other hand, the sodium coupling of $(CH_3)_3SiCl$ with 1,2-$Cl_2C_6H_4$ and 1,4-$Cl_2C_6H_4$ fails to give disilphenylenes even at 200°C. (116).

Silarylenes occur as by-products in the production of aromatic chlorosilanes; for example, by the reaction of $HSiCl_3$ or CH_3SiHCl_2 with aromatic compounds at elevated temperature and pressure in the presence of Friedel–Crafts catalysts. Presumably the by-products can be made to be the main products by suitably proportioning the starting materials. The reaction of benzene with $HSiCl_3$ (20) or CH_3SiHCl_2 (17) at 300°C. in the presence of boron trichloride produces by-product $(Cl_3Si)_2C_6H_4$ or $[Cl_2(CH_3)Si]_2C_6H_4$. The same by-products appear when chlorobenzene is used (14, 21). These compounds are also produced by the reaction of $C_6H_5SiCl_3$ with $HSiCl_3$ or CH_3SiHCl_2 at 300°C. in the presence of boron chloride (16). Silphenylenes are also formed in the reaction of dichlorobenzene with $HSiCl_3$ or CH_3SiHCl_2 at 400°C. without a catalyst (127). Another by-product formation of silphenylenes occurs during the preparation of $C_6H_5SiCl_3$

from the reaction of benzene with $Cl_3SiSiCl_3$ at 300°C. in the presence of aluminum chloride (114). A reaction which may have some bearing on the by-product formations of silphenylenes above is the dephenylation of $(C_6H_5)_2SiCl_2$ with aluminum chloride at 200–250°C. to form benzene and $Cl_2(C_6H_5)SiC_6H_4$-$Si(C_6H_5)Cl_2$ (109).

The reactions of silphenylenes are very much like those of phenyl silicon compounds. Thus with a Grignard reagent 4-$(C_2H_5)_3SiC_6H_4SiCl_3$ gives a good yield of 4-$(C_2H_5)_3SiC_6H_4Si(C_2H_5)_3$ (224). The latter undergoes silicon–carbon cleavage with bromine in the presence of iron to form 1,4-$Br_2C_6H_4$ and $(C_2H_5)_3$-SiBr (224). On the other hand, 4-$(CH_3)_3SiC_6H_4Si(CH_3)_3$ is unaffected by boiling for 16 hr. with 10 per cent potassium hydroxide in 1:1 aqueous acetone (186). A very interesting aspect of silphenylenes is the formation of a linear orientable polymeric siloxane, $[—Si(CH_3)_2C_6H_4Si(CH_3)_2O—]_x$, upon dehydration of 4-$HO(CH_3)_2SiC_6H_4Si(CH_3)_2OH$ with a few hundredths per cent alkali at 100–250°C. under nitrogen (495).

The infrared spectra of the three $[(CH_3)_3Si]_2C_6H_4$ compounds are known and are discussed (116).

XXII. OTHER COMPOUNDS

A few additional silicon-containing compounds are listed in table 21.

TABLE 21

Other silicon-containing compounds

Compound	Melting Point	Boiling Point	References
	°C.	*°C.*	
$C_6H_5NC[(CH_3)_3SiCH_2]OMgCl$			(481)
4-$HOOCCH_2SeC_6H_4Si(CH_6)_3$		172/4 mm.	(33)
$[4\text{-}(CH_3)_3SiC_6H_4]_2PCl$		72/43 mm.	(*162*, 163)
$[4\text{-}(CH_3)_3SiC_6H_4]_2P(OH)O$	213–214.5		(*162*, 163)
$[4\text{-}(CH_3)_3SiC_6H_4]_3PO$	259		(*162*, 163)
$[4\text{-}(CH_6)_3SiC_6H_4]_3P$	95–96	112–117/31 mm.	(*162*, 163)
$(C_6H_5)_3SiC_{10}H_9Fe$	142–143		(37)
$[(C_3H_5)_3Si]_2C_{10}H_8Fe$	253–254		(37)

Acetals, chelates, hydrazones, oximes, semicarbazones, and thiosemicarbazones may be found under aldehydes and ketones in table 10, Diels–Alder adducts and ozonides under olefins and acetylenes in table 1, and alkoxides in table 6. The table on amines (table 8) includes amine salts, phenylthioureas, phthalimides, picrates, quaternary ammonium halides, and ureas. Anhydrides and carboxylate salts are in table 11, acylthioalkyls, sulfonium salts, and thiuronium salts are listed in table 15, and barbiturates and pyrazolones are mentioned under heterocyclic compounds in table 19.

XXIII. REFERENCES

(1) ABRAHAMSON, E. A., JR., AND REYNOLDS, C. A.: Anal. Chem. **24**, 1827–9 (1952).

(2) AGRE, C. L.: J. Am. Chem. Soc. **71**, 300–4 (1949).

(3) AGRE, C. L.: U.S. patent 2,682,512 (1954).

(4) AGRE, C. L., AND HILLING, W.: J. Am. Chem. Soc. **74**, 3895–9 (1952); *cf.* references 332 and 333.

(5) Agre, C. L., and Hilling, W.: J. Am. Chem. Soc. **74**, 3899–902 (1952).

(6) Andrianov, D. A.: J. Gen. Chem. (U.S.S.R.) **16**, 639–46 (1946); Chem. Abstracts **41**, 1206 (1947).

(7) Andrianov, K., and Gribanova, O.: J. Gen. Chem. (U.S.S.R.) **8**, 558–62 (1938).

(8) Andrianov, K., and Kamenskaya, M.: J. Gen. Chem. (U.S.S.R.) **8**, 969–71 (1938); Chem. Abstracts **33**, 1266 (1939).

(9) Bailey, D. L., and Pines, A. N.: Ind. Eng. Chem. **46**, 2363–7 (1954).

(10) Bailey, D. L., Sommer, L. H., and Whitmore, F. C.: J. Am. Chem. Soc. **70**, 435–6 (1948).

(11) Bailey, D. L., and Wagner, G. H.: U.S. patent 2,532,387 (1950).

(12) Barry, A. J.: British patent 618,403 (1949); Chem. Abstracts **43**, 5801 (1949).

(13) Barry, A. J.: British patent 622,970 (1949); Chem. Abstracts **44**, 658 (1950).

(14) Barry, A. J.: U.S. patent 2,499,561 (1950).

(15) Barry, A. J.: U.S. patent 2,557,778 (1951).

(16) Barry, A. J.: U.S. patent 2,557,931 (1951). Dow Corning, Ltd.: British patent 682,835 (1952).

(17) Barry, A. J.: U.S. patent 2,572,302 (1951). Dow Corning Corporation: British patent 646,629 (1950); Chem. Abstracts **45**, 5184 (1951).

(18) Barry, A. J.: U.S. patent 2,590,812 (1952). Dow Corning Corporation: British patent 654,054 (1951); Chem. Abstracts **46**, 292 (1952).

(19) Barry, A. J.: British patent 671,747 (1952); Chem. Abstracts **46**, 9338 (1952).

(20) Barry, A. J.: U.S. patent 2,626,266 (1953).

(21) Barry, A. J.: U.S. patent 2,626,269 (1953). British patent 671,710 (1952); Chem. Abstracts **47**, 4909 (1953).

(22) Barry, A. J., DePree, L., Gilkey, J. W., and Hook, D. E.: J. Am. Chem. Soc. **69**, 2916 (1947).

(23) Barry, A. J., DePree, L., and Hook, D. E.: British patent 633,732 (1949); Chem. Abstracts **45**, 3409 (1951).

(24) Barry, A. J., and Gilkey, J. W.: U.S. patent 2,570,090 (1951). British patent 669,791 (1952); Chem. Abstracts **46**, 7823 (1952).

(25) Barry, A. J., and Gilkey, J. W.: U.S. patent 2,601,237 (1952). British patent 669,790 (1952); Chem. Abstracts **46**, 10681 (1952).

(26) Barry, A. J., and Gilkey, J. W.: U.S. patent 2,628,243 (1953). Dow Corning Ltd.: British patent 677,464 (1952); Chem. Abstracts **47**, 5959 (1953).

(27) Barry, A. J., Gilkey, J. W., and DePree, L.: U.S. patent 2,474,087 (1949).

(28) Barry, A. J., Hook, D. E., and DePree, L.: U.S. patent 2,556,462 (1951).

(29) Barry, A. J., Hook, D. E., and DePree, L.: U.S. patent 2,626,271 (1953).

(30) Bassett, E. A., Emblem, H. G., Frankel, M., and Ridge, D.: J. Soc. Chem. Ind. **67**, 177–9 (1948).

(31) deBataafsche Petroleum Maatschappij, N. V.: Dutch patent 68,393 (1951); Chem. Abstracts **46**, 6436 (1952).

(32) Bazhulin, P. A., Yegorov, Y. P., and Mironov, V. F.: Doklady Akad. Nauk S.S.S.R. **92**, 515–17 (1953).

(33) Behrens, O. K., Corse, J., Huff, D. E., Jones, R. G., Soper, Q. F., and Whitehead, C. W.: J. Biol. Chem. **175**, 771–92 (1948).

(34) Benkeser, R. A., and Brumfield, P. E.: J. Am. Chem. Soc. **73**, 4770–3 (1951).

(35) Benkeser, R. A., and Brumfield, P. E.: J. Am. Chem. Soc. **74**, 253–4 (1952).

(36) Benkeser, R. A., and Currie, R. B.: J. Am. Chem. Soc. **70**, 1780–2 (1948).

(37) Benkeser, R. A., Goggin, D., and Schroll, G.: J. Am. Chem. Soc. **76**, 4025–6 (1954).

(38) Benkeser, R. A., and Krysiak, H. R.: J. Am. Chem. Soc. **75**, 2421–4 (1953).

(39) Benkeser, R. A., and Krysiak, H. R.: J. Am. Chem. Soc. **75**, 4528–31 (1953).

(40) Benkeser, R. A., and Krysiak, H. R.: J. Am. Chem. Soc. **76**, 599–603 (1954).

(41) Benkeser, R. A., and Landesman, H.: J. Am. Chem. Soc. **71**, 2493–4 (1949).

(42) Benkeser, R. A., and Landesman, H.: J. Am. Chem. Soc. **76**, 904–5 (1954).

(43) Benkeser, R. A., and Riel, F. J.: J. Am. Chem. Soc. **73,** 3472–4 (1951).
(44) Benkeser, R. A., Robinson, R. E., and Landesman, H.: J. Am. Chem. Soc. **74,** 5699–701 (1952).
(45) Benkeser, R. A., and Severson, R. G.: J. Am. Chem. Soc. **73,** 1424–7 (1951).
(46) Benkeser, R. A., and Torkelson, A.: J. Am. Chem. Soc. **76,** 1252–3 (1954).
(47) Biefield, L. P.: U.S. patent 2,683,097 (1954).
(48) Biefield, L. P., and Philipps, T. E.: Am. Dyestuff Reptr. **41,** 501–6 (1952); Chem. Abstracts **47,** 2536 (1953).
(49) Biefield, L. P., and Philipps, T. E.: Ind. Eng. Chem. **45,** 1281–6 (1953).
(50) Bjorksten, J., and Yaeger, L. L.: Modern Plastics **30,** 124–5 (1952). See also Clark, G. A.: Modern Plastics **30,** 142–4, 218–19 (1952).
(51) Bjorksten, J., Yaeger, L. L. and Henning, J. E.: Ind. Eng. Chem. **46,** 1632–4 (1954).
(52) Bluestein, B. A.: J. Am. Chem. Soc. **70,** 3068–71 (1948).
(53) Bluestein, B. A.: U. S. patent 2,452,895 (1948). British Thomson-Houston Co., Ltd.: British patent 696,572 (1953).
(54) Bluestein, B. A.: U.S. patent 2,519,879 (1950). British Thomson-Houston Co., Ltd.: British patent 657,152 (1951); Chem. Abstracts **46,** 4855 (1952).
(55) Bluestein, B. A.: U. S. patent 2,584,665 (1952). British Thomson-Houston Co., Ltd.: British patent 685,187 (1952).
(56) Boldebuck, E. M.: U. S. patent 2,551,924 (1951).
(57) Bowden, K., Braude, E. A., and Jones, E. R. H.: J. Chem. Soc. **1946,** 948–52.
(58) Boye, F. C., and Post, H. W.: J. Org. Chem. **16,** 391–4 (1951).
(59) Boye, F. C., and Post, H. W.: J. Org. Chem. **17,** 344–6 (1952).
(60) Boye, F. C., and Post, H. W.: J. Org. Chem. **17,** 1386–8 (1952).
(61) Boye, F. C., and Post, H. W.: J. Org. Chem. **17,** 1389–92 (1952).
(62) Brannen, C. G.: Iowa State Coll. J. Sci. **26,** 170–2 (1952); Chem. Abstracts **48,** 624 (1954).
(63) British Thomson-Houston Co., Ltd.: British patent 659,439 (1951); Chem. Abstracts **46,** 4855 (1952).
(64) British Thomson-Houston Co., Ltd.: British patent 685,186 (1952).
(65) British Thomson-Houston Co., Ltd.: British patent 688,408 (1953).
(66) Brook, A. G., and Gilman, H.: J. Am. Chem. Soc. **76,** 2338–42 (1954).
(67) Brook, A. G., and Gilman, H.: J. Am. Chem. Soc. **77,** 2322 (1955).
(68) Brook, A. G., Gilman, H., and Miller, L. S.: J. Am. Chem. Soc. **75,** 4759–65 (1953).
(69) Brooks, M. C., and Ewart, R. E.: U. S. patent 2,680,124 (1954).
(70) Brooks, M. C., and Ladd, E. C.: U. S. patent 2,665,264 (1954).
(71) Bugorkova, A. A., Petrova, L. N., and Rodionov, V. M.: Zhur. Obshcheĭ Khim. **23,** 1808–13 (1953).
(72) Bunnell, R. H.: U. S. patent 2,584,544 (1952).
(73) Bunnell, R. H.: U. S. patent 2,632,755 (1953). Libbey-Owens-Ford Glass Co.: British patent 663,770 (1951); Chem. Abstracts **46,** 11228 (1952).
(74) Bunnell, R. H.: U. S. patent 2,679,495 (1954).
(75) Bunnell, R. H.: U. S. patent 2,679,496 (1954).
(76) Bunnell, R. H., and Hatcher, D. B.: U. S. patent 2,469,154 (1949).
(77) Bunnell, R. H., and Shirley, D. A.: J. Org. Chem. **17,** 1545–50 (1952).
(78) Burke, W. J., and Hoffman, W. A.: U. S. patent 2,515,857 (1950).
(79) Burkhard, C. A.: J. Am. Chem. Soc. **68,** 2103 (1946).
(80) Burkhard, C. A.: J. Am. Chem. Soc. **72,** 1078–80 (1950).
(81) Burkhard, C. A.: J. Am. Chem. Soc. **72,** 1402 (1950).
(82) Burkhard, C. A.: U. S. patent 2,544,296 (1951). British Thomson-Houston Co., Ltd.: British patent 671,879 (1952).
(83) Burkhard, C. A.: U. S. patent 2,561,178 (1951). British Thomson-Houston Co., Ltd.: British patent 626,515 (1949); Chem. Abstracts **44,** 2555 (1950).

(84) Burkhard, C. A.: U.S. patent 2,563,516 (1951). British Thomson-Houston Co., Ltd.: British patent 684,999 (1952).

(85) Burkhard, C. A.: J. Am. Chem. Soc. **74,** 6275–6 (1952).

(86) Burkhard, C. A.: U. S. patent 2,583,322 (1952). British Thomson-Houston Co., Ltd.: British patent 688,407 (1949).

(87) Burkhard, C. A.: U. S. patent 2,604,486 (1952).

(88) Burkhard, C. A.: U.S. patent 2,604,487 (1952).

(89) Burkhard, C. A.: U.S. patent 2,689,859 (1954). British Thomson-Houston Co., Ltd.: British patent 709,920 (1954).

(90) Burkhard, C. A., and Hurd, D. T.: J. Org. Chem. **17,** 1107–9 (1952).

(91) Burkhard, C. A., and Hurd, D. T.: U.S. patent 2,588,083 (1952). British Thomson-Houston Co., Ltd.: British patent 702,933 (1954).

(92) Burkhard, C. A., and Krieble, R. H.: J. Am. Chem. Soc. **69,** 2687–9 (1947).

(92a) Burkhard, C. A., Rochow, E. G., Booth, H. S., and Hart, J.: Chem. Revs. **41,** 97–149 (1947).

(93) Bygden, A.: Ber. **48B,** 1236–42 (1915).

(94) Bygden, A.: J. prakt. Chem. **96,** 86–104 (1917).

(95) Calas, R., and Duffaut, N.: Oléagineux **8,** 21–3 (1953); Chem. Abstracts **47,** 12223 (1953).

(96) Calas, R., and Duffaut, N.: Bull. mens. inform. ITERG. **7,** 438–40 (1953); Chem. Abstracts **48,** 11303 (1954).

(97) Carpenter, C. P., Smyth, H. F., Jr., and Pozzani, U. C.: J. Ind. Hyg. Toxicol. **31,** 343–6 (1949).

(98) Cason, L. F., and Brooks, H. G.: J. Am. Chem. Soc. **74,** 4582–3 (1952).

(99) Cason, L. F., and Brooks, H. G.: J. Org. Chem. **19,** 1278–82 (1954).

(100) Cerato, C. C., Lauer, J. L., and Beachell, H. C.: J. Chem. Phys. **22,** 1–5 (1954).

(101) Challenger, F., and Kipping, F. S.: J. Chem. Soc. **97,** 142–54 (1910).

(102) Chvalovsky, V., and Bazant, V.: Chem. Listy **46,** 158–63 (1952); Chem. Abstracts **47,** 8030 (1953); Collection Czechoslov. Chem. Communs. **16,** 580–90 (1951); Chem. Abstracts **48,** 10642 (1954).

(103) Clark, H. A.: U.S. patent 2,507,514 (1950); Reissue 23,270. British patent 669,178 (1952); Chem. Abstracts **46,** 8894 (1952).

(104) Clark, H. A.: U.S. patent 2,507,515. Clark, H. A. (to Dow Corning Ltd.): British patent 669,179 (1952); Chem. Abstracts **46,** 8894 (1952).

(105) Clark, H. A.: U.S. patent 2,507,516 (1950). Dow Corning Ltd.: British patent 675,041 (1952).

(106) Clark, H. A.: U.S. patent 2,507,517 (1950); British patent 672,825 (1952).

(107) Clark, H. A.: U.S. patent 2,507,521 (1950).

(108) Clark, H. A.: U.S. patent 2,553,845 (1951); British patent 670,859 (1952).

(109) Clark, H. A.: U.S. patent 2,557,782 (1951).

(110) Clark, H. A.: U.S. patent 2,557,942 (1951). Clark, H. A. (to Dow Corning Ltd.): British patent 672,824 (1952); Chem. Abstracts **46,** 9120 (1952).

(111) Clark, H. A.: U.S. patent 2,563,004 (1951); British patent 671,773 (1952).

(112) Clark, H. A.: U.S. patent 2,590,937 (1952).

(113) Clark, H. A.: British patent 672,825 (1952); Chem. Abstracts **47,** 3869 (1953).

(114) Clark, H. A.: British patent 674,591 (1952); Chem. Abstracts **47,** 3875 (1953).

(115) Clark, H. A.: U.S. patent 2,628,242 (1953); British patent 671,553 (1952).

(116) Clark, H. A., Gordon, A. F., Young, C. W., and Hunter, M. J.: J. Am. Chem. Soc. **73,** 3798–3803 (1951).

(117) Cohen, M., and Ladd, J. R.: J. Am. Chem. Soc. **75,** 988 (1953).

(118) Combes, C.: Compt. rend. **122,** 622–4 (1896).

(119) Cooper, G. D.: J. Am. Chem. Soc. **76,** 2499–2500 (1954).

(120) Cooper, G. D.: J. Am. Chem. Soc. **76,** 2500 (1954).

(121) Cooper, G. D.: J. Am. Chem. Soc. **76,** 3713–16 (1954).

(122) COOPER, G. D., AND PROBER, M.: J. Am. Chem. Soc. **76**, 3943–5 (1954).

(123) CURRIE, C. C.: U.S. patent 2,642,395 (1953).

(124) DAUDT, W. H., AND TYLER, L. J.: U. S. patent 2,676,182 (1954).

(125) DEANS, D. R., AND EABORN, C.: J. Chem. Soc. **1954**, 3169–73.

(126) DENISON, G. H., JR., AND CONDIT, P. C.: U.S. patent 2,346,155 (1944).

(127) DEPREE, L., BARRY, A. J., AND HOOK, D. E.: U.S. patent 2,580,159 (1951). DOW CORNING CORPORATION, BARRY, A. J., DEPREE, L., AND HOOK, D. E.: British patent 635,645 (1950); Chem. Abstracts **44**, 6882 (1950).

(128) DEREICH, J. E.: U.S. patent 2,648,654 (1953). Diamond Alkali Co.: British patent 691,395 (1953).

(129) DOLGOV, N., AND PANINA, O. K.: Zhur. Obshcheĭ Khim. (J. Gen. Chem.) **18**, 1129–32 (1948); Chem. Abstracts **43**, 1737 (1949).

(130) DOLGOV, N., AND PANINA, O. K.: Zhur. Obshcheĭ Khim. (J. Gen. Chem.) **18**, 1293–6 (1948); Chem. Abstracts **43**, 2177 (1949).

(131) DOW CORNING LTD.: British patent 667,435 (1952); Chem. Abstracts **46**, 6429 (1952).

(132) DOW CORNING LTD.: British patent 679,418 (1952).

(133) DOW CORNING LTD.: British patent 681,527 (1952); Chem. Abstracts **47**, 4128 (1953).

(134) DOW CORNING LTD.: British patent 686,068 (1953).

(135) DOW CORNING LTD.: British patent 699,759 (1953).

(136) DOW CORNING LTD.: British patent 706,290 (1954); Chem. Abstracts **49**, 6300 (1955).

(137) DUANE, J. J.: U.S. patent 2,646,441 (1953). Linde Air Products Co.: British patent 683,182 (1952).

(138) EABORN, C.: J. Chem. Soc. **1949**, 2757.

(139) EABORN, C.: J. Chem. Soc. **1953**, 3148–53.

(140) EABORN, C., AND PARKER, S. H.: J. Chem. Soc. **1954**, 939–41.

(141) ELLINGBOE, E. K.: U.S. patent 2,443,898 (1948).

(142) ELLIOTT, J. R., AND BOLDEBUCK, E. M.: J. Am. Chem. Soc. **74**, 1853–4 (1952).

(143) ELLIOTT, J. R., AND KRIEBLE, R. H.: U.S. patent 2,457,539 (1948).

(144) ELLIOTT, J. R., AND KRIEBLE, R. H.: U.S. patent 2,513,924 (1950).

(145) EMELIUS, H. J., MADDOCK, A. G., AND REID, C.: J. Chem. Soc. **1941**, 353–8; *cf.* references 138 and 323.

(146) ENGLISH, W. D.: J. Am. Chem. Soc. **74**, 2927–8 (1952).

(147) ENGLISH, W. D., TAURIUS, A., AND NICHOLLS, R. V. V.: Can. J. Chem. **30**, 646–52 (1952); Chem. Abstracts **47**, 9258 (1953).

(148) FLEMING, P. F., JR.: U. S. patent 2,386,452 (1945).

(149) FLETCHER, H. J., AND DINGMAN, H. D.: U.S. patent 2,528,355 (1950). Dow Corning Ltd.: British patent 672,496 (1952); Chem. Abstracts **46**, 10681 (1952).

(150) FLETCHER, H. J., AND DINGMAN, H. D.: British patent 673,322 (1952); Chem. Abstracts **46**, 11670 (1952).

(151) FLETCHER, H. J., AND HUNTER, M. J.: U.S. patent 2,599,984 (1952).

(152) FRANCIS, J. D.: U.S. patent 2,573,426 (1951). Dow Corning Ltd.: British patent 688,799 (1953).

(153) FREISER, H., CHARLES, R., SPEIER, J., AND EAGLE, MARY: J. Am. Chem. Soc. **73**, 5229–30 (1951).

(154) FREISER, H., EAGLE, M. V., AND SPEIER, J. L.: J. Am. Chem. Soc. **75**, 2821–4 (1953).

(155) FREISER, H., EAGLE, M. V., AND SPEIER, J. L.: J. Am. Chem. Soc. **75**, 2824–7 (1953).

(156) FRIEDEL, C., AND CRAFTS, J. M.: Compt. rend. **61**, 792–6 (1865).

(157) FRIEDEL, C., AND CRAFTS, J. M.: Ann. **138**, 19–24 (1866).

(158) FRIEDEL, C., AND CRAFTS, J. M.: Ann. chim. **259**, 334–67 (1870).

(159) FRISCH, K. C.: J. Am. Chem. Soc. **75**, 6050–1 (1953).

(160) FRISCH, K. C., AND GOODWIN, P. A.: U.S. patent 2,678,938 (1954).

(161) FRISCH, K. C., GOODWIN, P. A., AND SCOTT, R. E.: J. Am. Chem. Soc. **74**, 4584–5 (1952).

(162) Frisch, K. C., and Lyons, H.: J. Am. Chem. Soc. **75**, 4078–9 (1953).
(163) Frisch, K. C., and Lyons, H.: U.S. patent 2,673,210 (1954).
(164) Frisch, K. C., and Shroff, P. D.: J. Am. Chem. Soc. **75**, 1249–50 (1953).
(165) Frisch, K. C., and Shroff, P. D.: U.S. patent 2,641,605 (1953); Chem. Abstracts **47**, 9055 (1953).
(166) Frisch, K. C., and Shroff, P. D.: U.S. patent 2,647,137 (1953).
(167) Frisch, K. C., and Young, R. B.: J. Am. Chem. Soc. **74**, 4853–6 (1952).
(168) Frisch, K. C., and Young, R. B.: U.S. patent 2,671,099 (1954).
(169) Frisch, K. C., and Young, R. B.: U.S. patent 2,671,100 (1954).
(170) Frisch, K. C., and Young, R. B.: U.S. patent 2,671,101 (1954).
(171) Frisch, K. C., and Young, R. B.: U.S. patent 2,671,795 (1954).
(172) Fritz, G.: Z. Naturforsch. **6b**, 47–8 (1951); Chem. Abstracts **45**, 8971 (1951).
(173) Fritz, G., and Kautsky, H.: Z. Naturforsch **5b**, 395–6 (1950); Chem. Abstracts **45**, 2003 (1951).
(174) Frost, L. W.: U.S. patent 2,596,967 (1952).
(175) Frost, L. W.: U.S. patent 2,636,896 (1953).
(176) Gadsby, G. N.: Research (London) **3**, 338–9 (1950).
(177) Gainer, G. C.: Ind. Eng. Chem. **46**, 2355–62 (1954).
(178) George, P. D.: U.S. patent 2,640,818 (1953). British Thomson-Houston Co., Ltd.: British patent 695,462 (1953).
(179) George, P. D.: U.S. patent 2,640,833 (1953).
(180) George, P. D.: U.S. patent 2,645,644 (1953). British Thomson-Houston Co., Ltd.: British patent 694,440 (1953).
(181) George, P. D., and Elliott, J. R.: J. Am. Chem. Soc. **77**, 3493–8 (1955).
(182) George, P. D., Sommer, L. H., and Whitmore, F. C.: J. Am. Chem. Soc. **70**, 3512–13 (1948).
(183) Gilliam, W. F.: U.S. patent 2,474,578 (1949).
(184) Gilman, H., Benkeser, R. A., and Dunn, G. E.: J. Am. Chem. Soc. **72**, 1689–91 (1950).
(185) Gilman, H., Brook, A. G., and Miller, L. S.: J. Am. Chem. Soc. **75**, 3757–9 (1953).
(186) Gilman, H., Brook, A. G., and Miller, L. S.: J. Am. Chem. Soc. **75**, 4531–4 (1953).
(187) Gilman, H., Cason, L. F., and Brooks, H. G., Jr.: J. Am. Chem. Soc. **75**, 3760–2 (1953).
(188) Gilman, H., and Dunn, G. E.: J. Am. Chem. Soc. **72**, 2178–80 (1950).
(189) Gilman, H., and Dunn, G. E.: J. Am. Chem. Soc. **73**, 3404–7 (1951).
(190) Gilman, H., and Harzfeld, H.: J. Am. Chem. Soc. **73**, 5878–9 (1951).
(191) Gilman, H., Hofferth, B., Melvin, H. W., and Dunn, G. E.: J. Am. Chem. Soc. **72**, 5767–8 (1951).
(192) Gilman, H., Ingham, R. K., and Gorsich, R. D.: J. Am. Chem. Soc. **76**, 918–9 (1954).
(193) Gilman, H., and Marshall, F. J.: J. Am. Chem. Soc. **71**, 2066–9 (1949).
(194) Gilman, H., and Melvin, H. W., Jr.: J. Am. Chem. Soc. **72**, 995–6 (1950).
(195) Gilman, H., Melvin, H. W., and Goodman, J. J.: J. Am. Chem. Soc. **76**, 3219–20 (1954).
(196) Gilman, H., and Miller, L. S.: J. Am. Chem. Soc. **73**, 968–70 (1951). See also Richardson, C. H., and DuChanois, F. R.: J. Econ. Entomol. **44**, 997–8 (1951).
(197) Gilman, H., and Miller, L. S.: J. Am. Chem. Soc. **73**, 2367–8 (1951).
(198) Gilman, H., and Nobis, J. F.: J. Am. Chem. Soc. **72**, 2629–32 (1950).
(199) Gilman, H., and Plunkett, M. A.: J. Am. Chem. Soc. **71**, 1117 (1949).
(200) Gilman, H., Plunkett, M. A., and Dunn, G. E.: J. Am. Chem. Soc. **73**, 1686–8 (1951).
(201) Gilman, H., and Smart, G. N. R.: J. Org. Chem. **15**, 720–40 (1950).
(202) Gilman, H., and Wu, T. C.: J. Am. Chem. Soc. **75**, 234 (1953).
(203) Gilman, H., and Wu, T. C.: J. Am. Chem. Soc. **75**, 2935–6 (1953).
(204) Goldblatt, L. A., and Oldroyd, D. M.: U.S. patent 2,533,240 (1950).
(205) Goodwin, J. T., Jr.: U.S. patent 2,483,972 (1949).

(206) Goodwin, J. T., Jr.: U.S. patent 2,507,512 (1940). Dow Corning Corporation and Goodwin, J. T., Jr.: British patent 631,619 (1949); Chem. Abstracts **44,** 4491 (1950).
(207) Goodwin, J. T., Jr.: U.S. patent 2,507,513 (1950). Dow Corning Corporation and Goodwin, J. T., Jr.: British patent 627,809 (1949); Chem. Abstracts **44,** 3518 (1950).
(208) Goodwin, J. T., Jr.: U.S. patent 2,507,518 (1950); British patent 668,903 (1952).
(209) Goodwin, J. T., Jr.: U.S. patent 2,507,519 (1950); British patent 671,140 (1952).
(210) Goodwin, J. T., Jr.: U.S. patent 2,507,520 (1950).
(211) Goodwin, J. T., Jr.: U.S. patent 2,511,056 (1950). Dow Corning Corporation and Goodwin, J. T., Jr.: British patent 632,563 (1949); Chem. Abstracts **44,** 6425 (1950).
(212) Goodwin, J. T., Jr.: U.S. patent 2,511,812 (1950).
(213) Goodwin, J. T., Jr.: U.S. patent 2,527,805 (1950); British patents 684,102 and 684,149 (1952).
(214) Goodwin, J. T., Jr.: U.S. patent 2,527,808 (1950). Dow Corning Ltd.: British patent 667,436 (1952); Chem. Abstracts **46,** 6141 (1952).
(215) Goodwin, J. T., Jr.: U.S. patent 2,527,809 (1950). British patent 671,722 (1952); Chem. Abstracts **46,** 10694 (1952).
(216) Goodwin, J. T., Jr.: U.S. patent 2,544,079 (1951).
(217) Goodwin, J.T., Jr.: U.S. patent 2,590,957 (1952).
(218) Goodwin, J. T., Jr.: U.S. patent 2,592,681 (1952). Dow Corning Corporation and Goodwin, J. T., Jr.: British patent 624,551 (1949); Chem. Abstracts **44,** 4924 (1950).
(219) Goodwin, J. T., Jr.: U.S. patent 2,592,682 (1952). Dow Corning Corporation: British patent 624,551 (1949); Chem. Abstracts **44,** 2010 (1950).
(220) Goodwin, J. T., Jr., British patent 671,140 (1952).
(221) Goodwin, J. T., Jr.: U.S. patent 2,607,791 (1952); Chem. Abstracts **48,** 13732 (1954).
(222) Goodwin, J. T., Jr., Baldwin, W. E., and McGregor, R. R.: J. Am. Chem. Soc. **69,** 2247 (1947).
(223) Gould, J. R., Sommer, L. H., and Whitmore, F. C.: J. Am. Chem. Soc. **70,** 2874–6 (1948).
(224) Gruttner, G., and Cauer, M.: Ber. **51,** 1283–92 (1918).
(225) Gruttner, G., and Krause, E.: Ber. **50,** 1559–68 (1917).
(226) Hance, C. R., and Hauser, C. R.: J. Am. Chem. Soc. **75,** 994–5 (1953).
(227) Hanford, W. E., and Joyce, R. M.: U.S. patent 2,478,390 (1949).
(228) Hart, W. B.: Brit. Assoc. Advancement Sci. Rept. **57,** 661–5 (1887).
(229) Hastings, J. M., and Bauer, S. H.: J. Chem. Phys. **18,** 13–26 (1950).
(230) Haszeldine, R. N.: Nature **168,** 1028–31 (1951).
(231) Hatcher, D. B.: U.S. patent 2,574,390 (1951).
(232) Hatcher, D. B.: U.S. patent 2,618,647 (1952).
(233) Hatcher, D. B., and Bunnell, R. H.: U.S. patent 2,545,780 (1951).
(234) Hatcher, D. B., and Bunnell, R. H.: U.S. patent 2,570,551 (1951).
(235) Hatcher, D. B., and Bunnell, R. H.: U.S. patent 2,612,510 (1952).
(236) Hatcher, D. B., and Bunnell, R. H.: U.S. patent 2,618,646 (1952).
(237) Hatcher, D. B., and Bunnell, R. H.: U.S. patent 2,624,720 (1953).
(238) Hatcher, D. B., and Bunnell, R. H.: U.S. patent 2,624,721 (1953).
(239) Hatcher, D. B., and Bunnell, R. H.: U.S. Patent 2,684,974 (1954).
(240) Hauser, C. R., and Hance, C. R.: J. Am. Chem. Soc. **74,** 5091–6 (1952).
(241) Hersh, J. M.: U.S. patent 2,464,231 (1949).
(242) Hersh, J. M.: U.S. patent 2,615,033 (1952).
(243) Hizawa, K., and Nojimoto, E.: Japanese patent 3418 (1952); Chem. Abstracts **48,** 3992 (1954).
(244) Hizawa, K., and Nojimoto, E.: Japanese patent 3767 (1952); Chem. Abstracts **48,** 3992 (1954).
(245) Hizawa, K., and Nojimoto, E.: Japanese patent 330 (1953); Chem. Abstracts **48,** 11481 (1954).

(246) Hizawa, K., and Nojimoto, E.: Japanese patent 988 (1953); Chem. Abstracts **48,** 2084 (1954).
(247) Hizawa, K., and Nojimoto, E.: Japanese patent 1281 (1953); Chem. Abstracts **48,** 12801 (1954).
(248) Hizawa, K., and Nojimoto, E.: Japanese patent 4792 (1953); Chem. Abstracts **48,** 11109 (1954).
(249) Hizawa, K., and Nojimoto, E.: Japanese patent 4794 (1953); Chem. Abstracts **48,** 11082 (1954).
(250) Hizawa, K., and Nojimoto, E.: Japanese patent 4940 (1953); Chem. Abstracts **48,** 11109 (1954).
(251) Hommel, M. C.: U.S. patent 2,599,917 (1952).
(252) Hurd, C. D., and Yarnell, W. A.: J. Am. Chem. Soc. **71,** 755 (1949).
(253) Hurd, D. T.: J. Am. Chem. Soc. **67,** 1813–14 (1945).
(254) Hurd, D. T.: U.S. patent 2,420,912 (1950).
(255) Hurd, D. T.: *Inorganic Syntheses*, Vol. III, pp. 58–61. McGraw-Hill Book Company, Inc., New York (1950).
(256) Hurd, D. T.: U.S. patent 2,645,628 (1953).
(257) Hurd, D. T., and Roedel, G. F.: Ind. Eng. Chem. **40,** 2078–81 (1948).
(258) Hyde, J. F.: U.S. patent 2,480,822 (1949).
(259) Hyde, J. F.: U.S. patent 2,629,725 (1953); Chem. Abstracts **47,** 5720 (1953). Dow Corning Ltd.: British patent 699,658 (1953).
(260) Hyde, J. F.: U.S. patent 2,692,844 (1954).
(261) Iida, C., Yokoi, M., and Yamasaki, K.: J. Chem. Soc. Japan, Pure Chem. Sect. **73,** 882–5 (1952); Chem. Abstracts **47,** 6200 (1953).
(262) Illuminati, G., Nobis, I. F., and Gilman, H.: J. Am. Chem. Soc. **73,** 3887–8 (1951).
(263) Izard, E. F., and Kwolek, S. L.: J. Am. Chem. Soc. **73,** 1156–8 (1951).
(264) Janes, J. R.: U.S. patent 2,637,623 (1953).
(265) Jenkins, A. C., and Chambers, G. F.: Ind. Eng. Chem. **46,** 2367–9 (1954).
(266) Jenkins, A. C., and Reid, A. J.: Ind. Eng. Chem. **46,** 2566–7 (1954).
(267) Jenkins, J. W., Lavery, N. L., Guenther, P. R., and Post, H. W.: J. Org. Chem. **13,** 862–6 (1948).
(268) Johannson, O. K.: U.S. patent 2,436,304 (1948).
(269) Kaye, S., and Tannebaum, S.: J. Org. Chem. **18,** 1750–4 (1953).
(270) Kipping, F. S.: Proc. Chem. Soc. **21,** 65–6 (1905).
(271) Kipping, F. S.: Proc. Chem. Soc. **23,** 9 (1907).
(272) Kipping, F. S.: Proc. Chem. Soc. **23,** 83 (1907).
(273) Kipping, F. S.: J. Chem. Soc. **91,** 209–40 (1907).
(274) Kipping, F. S.: J. Chem. Soc. **91,** 717–47 (1907).
(276) Kipping, F. S.: J. Chem. Soc. **95,** 408–16 (1909).
(277) Kipping, F. S.: J. Chem. Soc. **119,** 647–53 (1921).
(278) Kipping, F. S., and Blackburn, J. C.: J. Chem. Soc. **1932,** 2200–5.
(279) Kipping, F. S., and Blackburn, J. C.: J. Chem. Soc. **1935,** 1085–91.
(280) Kipping, F. S., and Cusa, N. W.: J. Chem. Soc. **1935,** 1088–91.
(281) Kipping, F. S., and Davies, H.: J. Chem. Soc. **95,** 69–80 (1909).
(282) Kipping, F. S., and Lloyd, L. I.: J. Chem. Soc. **79,** 449–59 (1901).
(283) Kipping, F. S., and Martin, G.: J. Chem. Soc. **95,** 489–94 (1909).
(284) Kohl, C. F., Jr.: U.S. patent 2,530,202 (1950). Dow Corning Ltd.: British patent 678,541 (1952).
(285) Kohl, C. F., Jr.: U.S. patent 2,571,090 (1951).
(286) Kohl, C. F., Jr.: U.S. patent 2,640,063 (1953).
(287) Kohl, C. F., Jr.: U.S. patent 2,640,066 (1953); British patent 655,105 (1951); Chem. Abstracts **46,** 11239 (1952).
(288) Kraus, C. A., and Eatough, H.: J. Am. Chem. Soc. **55,** 5008–14 (1933).
(289) Krause, E., and Renwanz, G.: Ber. **62,** 1710–16 (1929).

(290) Kreshkov, A. P., Mikhailenko, Yu. Ya., and Yakimovich, G. F.: Zhur. Fiz. Khim. **28**, 537–51 (1954); Chem. Abstracts **48**, 13427 (1854); Zhur. Anal. Khim. **9**, 208–16 (1954); Chem. Abstracts **48**, 13542 (1954).

(291) Krieble, R. H.: U. S. patent 2,479,374 (1949). British Thomson-Houston Co., Ltd.: British patent 661,094 (1951); Chem. Abstracts **46**, 5365 (1952).

(292) Krieble, R. H.: U.S. patent 2,510,642 (1950). British Thomson-Houston Co., Ltd.: British patent 663,740 (1951); Chem. Abstracts **46**, 11228 (1952).

(293) Krieble, R. H., and Elliott, J. R.: J. Am. Chem. Soc. **67**, 1810–12 (1945).

(294) Krieble, R. H., and Elliott, J. R.: J. Am. Chem. Soc. **68**, 2291–4 (1946): *cf.* reference 506.

(295) Kronstein, M.: Paint Varnish Production Mgr. **31**, 5, 17–21 (1951); Chem. Abstracts **45**, 7363 (1951).

(296) Kropa, E. L.: U.S. patent 2,388,161 (1945).

(297) Kropa, E. L.: U.S. patent 2,465,731 (1949).

(298) Kumada, M.: J. Inst. Polytech., Osaka City Univ., Ser. C, **2**, No. 1, 11–18 (1951); Chem. Abstracts **46**, 6082 (1952).

(299) Kumada, M., and Habuchi, A.: Inst. Polytech., Osaka City Univ., Ser. C, **3**, 65–76 (1952); Chem. Abstracts **48**, 9907 (1954).

(300) Ladenburg, A.: Ann. **173**, 143–66 (1847).

(301) Ladenburg, A.: Ber. **40**, 2274–9 (1907).

(301a) Lamoreaux, H. F., and Holdstock, N. G.: Abstracts of Papers Presented at the 125th Meeting of the American Chemical Society, Kansas City, Missouri, April, 1954.

(302) Larsson, E.: Svensk Kem. Tid. **60**, 178–80 (1948); Chem. Abstracts **43**, 5003 (1949).

(303) Larsson, E.: Trans. Chalmers Univ. Technol. Gothenburg **79**, 13–15 (1948); Chem. Abstracts **43**, 2929 (1949).

(304) Larsson, E.: Trans. Chalmers Univ. Technol. Gothenburg **79**, 17–22 (1948); Chem. Abstracts **43**, 2929 (1949).

(305) Larsson, E.: Trans. Chalmers Univ. Technol. Gothenburg **115**, 15–19 (1951); Chem. Abstracts **47**, 3639 (1953).

(306) Larsson, E.: Trans. Chalmers Univ. Technol. Gothenburg **115**, 21–3 (1951); Chem. Abstracts **47**, 11124 (1953).

(307) Larsson, E., and Knopp, L. O.: Acta Chem. Scand. **1**, 268 (1947); Chem. Abstracts **42**, 5416 (1948).

(308) Larsson, E., and Knopp, L. O.: Trans. Chalmers Univ. Technol. Gothenburg **79**, 7–11 (1948); Chem. Abstracts **43**, 2929 (1949).

(309) Lewis, D. W., and Gainer, G. C.: J. Am. Chem. Soc. **74**, 2931–2 (1952).

(310) Libbey-Owens-Ford Glass Co.: British patent 663,770 (1951); Chem. Abstracts **46**, 11228 (1952).

(311) Lipscomb, R. D.: U. S. patent 2,570,462 (1951).

(312) Luff, B. D. W., and Kipping, F. S.: J. Chem. Soc. **93**, 2004–16 (1908).

(313) Luff, B. D. W., and Kipping, F. S.: J. Chem. Soc. **93**, 2090 (1908).

(314) MacKenzie, C. A., and Rust, J. B.: U.S. patent 2,438,612 (1948).

(315) MacKenzie, C. A., and Rust, J. B.: U.S. patent 2,628,246 (1953).

(316) MacKenzie, C. A., and Schoffman, M.: U.S. patent 2,537,073 (1951).

(317) MacKenzie, C. A., and Schoffman, M.: U.S. patent 2,623,832 (1952).

(318) MacKenzie, C. A., Spialter, L., and Schoffman, M.: British patent 684,579 (1952).

(319) Marsden, H., and Kipping, F. S.: J. Chem. Soc. **93**, 198–210 (1908).

(320) Marsden, J.: U.S. patent 2,445,794 (1948).

(321) Marvel, C. S., and Cripps, H. N.: J. Polymer Sci. **9**, 53–60 (1952).

(322) McBride, J. J., Jr., and Beachell, H. C.: J. Am. Chem. Soc. **70**, 2532–3 (1948).

(323) McBride, J. J., Jr., and Beachell, H. C.: J. Am. Chem. Soc. **74**, 5247–50 (1952).

(324) McCusker, P. A., and Reilly, E. L.: J. Am. Chem. Soc. **75**, 1583–5 (1953).

(325) McGregor, R. R., and Warrick, E. L.: U.S. patent 2,435,148 (1948).

(326) McGregor, R. R., and Warrick, E. L.: U.S. patent 2,507,316 (1950). Dow Corning Ltd.: British patent 671,586 (1952).

(327) McGregor, R. R., and Warrick, E. L.: U.S. patent 2,522,053 (1950).

(328) Mohler, D., and Sellers, J. E.: U.S. patent 2,598,436 (1952).

(329) Moody, L. S.: J. Am. Chem. Soc. **72,** 5754 (1950).

(330) Morgan, C. R., Hoffman, H. A., and Granchelli, F. E.: J. Am. Chem. Soc. **75,** 4602–4 (1953).

(331) Moschel, W., and Muller, W.: U.S. patent 2,690,423 (1954).

(332) Murata, H.: J. Chem. Soc. Japan, Pure Chem. Sect. **72,** 471–3 (1951); Chem. Abstracts **46,** 1869 (1952).

(333) Murata, H.: J. Chem. Phys. **21,** 181–2 (1953).

(334) Nagel, R., and Post, H. W.: J. Org. Chem. **17,** 1379–81 (1952).

(335) Nagel, R., and Post, H. W.: J. Org. Chem. **17,** 1382–5 (1952).

(336) Nagel, R., Tamborski, C., and Post, H. W.: J. Org. Chem. **16,** 1768–71 (1951).

(337) Nametkin, N. S., Topchiev, A. V., and Solovova, O. P.: Doklady Akad. Nauk S.S.S.R. **93,** 285–8 (1953); Chem. Abstracts **48,** 12671 (1954).

(338) Nametkin, N. S., Topchiev, A. V., and Zetkin, V. I.: Doklady Akad. Nauk S.S.S.R. **84,** 513–14 (1952); Chem. Abstracts **47,** 5352 (1953).

(339) Nametkin, N. S., Topchiev, A. V., and Zetkin, V. I.: Doklady Akad. Nauk S.S.S.R. **87,** 59–60 (1952); Chem. Abstracts **48,** 114 (1954).

(340) Nametkin, N. S., Topchiev, A. V., and Zetkin, V. I.: Doklady Akad. Nauk S.S.S.R. **87,** 601–3 (1952); Chem. Abstracts **48,** 113 (1954).

(341) Newing, M. J.: Trans. Faraday Soc. **46,** 755–62 (1950).

(342) Niedzielski, E. L.: J. Am. Chem. Soc. **62,** 3519 (1940).

(343) Nojimoto, E.: Japanese patent 3968 (1952); Chem. Abstracts **48,** 5207 (1954).

(344) Noll, J. E., Daubert, B. F., and Speier, J. L.: J. Am. Chem. Soc. **73,** 3781–3 (1951).

(345) Noll, J. E., Speier, J. L., and Daubert, B. F.: J. Am. Chem. Soc. **73,** 3867–71 (1951).

(346) Noller, D. C., and Post, H. W.: J. Am. Chem. Soc. **74,** 1361 (1952).

(347) Noller, D. C., and Post, H. W.: J. Org. Chem. **17,** 1393–6 (1952).

(348) Nordlander, B. W.: U.S. patent 2,439,669 (1948).

(349) Okawara, R., Hashitani, K., and Watase, T.: Bull. Chem. Soc. Japan **26,** 279–80 (1953); Chem. Abstracts **48,** 5081 (1954).

(350) Pape, C.: Ann. **222,** 354–74 (1884).

(351) Passino, H. J., and Rubbin, L. C.: U.S. patent 2,686,194 (1954).

(352) Patnode, W. I., and Schiessler, R. W.: U.S. patent 2,381,000 (1945).

(353) Patnode, W. I., and Schiessler, R. W.: U.S. patent 2,381,002 (1945).

(354) Peppard, D. F., Brown, W. G., and Johnson, W. C.: J. Am. Chem. Soc. **68,** 73–5 (1946).

(355) Petrov, A. D., and Chernysheva, T. I.: Doklady Akad. Nauk S.S.S.R. **84,** 515–18 (1952); Chem. Abstracts **47,** 3288 (1953).

(356) Petrov, A. D., and Chernysheva, T. L.: Doklady Akad. Nauk S.S.S.R. **89,** 73–6 (1953); Chem. Abstracts **48,** 3916 (1954).

(357) Petrov, A. D., and Lavrishchev, V. P.: Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk, **1952,** 1125–7; Chem. Abstracts **48,** 1248, 5078 (1954).

(358) Petrov, A. D., and Mironov, V. F.: Doklady Akad. Nauk S.S.S.R. **75,** 707–10 (1950); Chem. Abstracts **45,** 7003 (1951).

(359) Petrov, A. D., and Mironov, V. F.: Izvest. Akad. Nauk S.S.S.R. **1952,** 635–45; Chem. Abstracts **47,** 10471 (1953); **48,** 4462, 5078 (1954).

(360) Petrov, A.D., and Miranov, V. F.: Doklady Akad. Nauk S.S.S.R. **80,** 761–4 (1951); Chem. Abstracts **46,** 11102 (1952).

(361) Petrov, A. D., and Nikishin, G. I.: Izvest. Akad. Nauk S.S.S.R. **1952,** 1128–30; Chem. Abstracts **48,** 1247, 5078 (1954).

(362) Petrov, A. D., and Ponmarenko, V. A.: Doklady Akad. Nauk S.S.S.R. **90,** 387–90 (1953); Chem. Abstracts **48,** 5080 (1954).

(363) Petrov, A. D., and Sadykhzade, S. I.: Doklady Akad. Nauk S.S.S.R. **85,** 1297–1300 (1952); Chem. Abstracts **47,** 4285 (1953).

(364) Petrov, A. D., and Shchukovskaya, L. L.: Izvest. Akad. Nauk S.S.S.R. **1952,** 564–5; Chem. Abstracts **47,** 3792 (1953); **48,** 4160 (1954).

(365) Petrov, A. D., and Shchukovskaya, L. L.: Doklady Akad. Nauk S.S.S.R. **86,** 551–3 (1953); Chem. Abstracts **47,** 12225 (1953).

(366) Petrov, A. D., Shchukovskaya, L. L., and Egorov, Yu. P.: Doklady Akad. Nauk S.S.S.R. **93,** 293–6 (1953); Chem. Abstracts **48,** 13616 (1954).

(367) Pierce, O. R., McBee, E. T., and Cline, R. E.: J. Am. Chem. Soc. **75,** 5618–20 (1953).

(368) Pierce, O. R., McBee, E. T., and Judd, G. F.: J. Am. Chem. Soc. **76,** 474–8 (1954).

(369) Plueddemann, E. P.: U.S. patent 2,642,447 (1953).

(370) Polis, A.: Ber. **19,** 1012–24 (1886).

(370a) Pray, B. O., Sommer, L. H., Goldberg, G. M., Kerr, G. T., George, P. D., and Whitmore, F. C.: J. Am. Chem. Soc. **70,** 433 (1948).

(370b) Prober, M.: J. Am. Chem. Soc. **77,** 3224–8 (1955).

(371) Pyle, J. J.: U.S. patent 2,448,391 (1948). British Thomson-Houston Co., Ltd.: British patent 641,268 (1950); Chem. Abstracts **45,** 391 (1951).

(372) Reilly, E. L., Curran, C. and McCusker, P. A.: J. Am. Chem. Soc. **76,** 3311–12 (1954).

(373) Roberts, J. D., and Dev, S.: J. Am. Chem. Soc. **73,** 1879–80 (1951).

(374) Roberts, J. D., McElhill, E. A., and Armstrong, R.: J. Am. Chem. Soc. **71,** 2923–6 (1949).

(375) Roberts, J. D., and Regan, C. M.: J. Am. Chem. Soc. **75,** 4102–3 (1953).

(376) Robison, R., and Kipping, F. S.: J. Chem. Soc. **93,** 439–73 (1908).

(377) Rochow, E. G.: U.S. patent 2,258,219 (1941).

(378) Rochow, E. G.: U.S. patent 2,258,221 (1941).

(379) Rochow, E. G.: U.S. patent 2,352,974 (1944).

(380) Rochow, E. G.: U.S. patent 2,383,817 (1945).

(381) Rochow, E. G.: U.S. patent 2,538,657 (1951).

(381a) Rochow, E. G.: *An Introduction to the Chemistry of the Silicones*, 2nd edition. John Wiley and Sons, Inc., New York (1951).

(382) Roedel, G. F.: U.S. patent 2,420,911 (1947).

(383) Roedel, G. F.: J. Am. Chem. Soc. **71,** 269–72 (1949).

(384) Rosenheim, A., Loewenstamm, W., and Singer, L.: Ber. **36,** 1833–9 (1903).

(385) Rust, J. B.: U.S. patent 2,637,718 (1953).

(386) Rust, J. B.: U.S. patent 2,689,860 (1954).

(387) Sage, C. M.: U.S. patent 2,467,858 (1959).

(388) Sauer, R. O.: U.S. patent 2,491,833 (1949). British Thomson-Houston Co., Ltd.: British patent 656,385 (1951); Chem. Abstracts **46,** 10191 (1952).

(389) Sauer, R. O.: U.S. patent 2,582,799 (1952).

(390) Sauer, R. O.: U.S. patent 2,647,136 (1953).

(391) Sauer, R. O., and Hadsell, E. M.: J. Am. Chem. Soc. **70,** 3590 (1948).

(392) Scott, R. E., and Frisch, K. C.: J. Am. Chem. Soc. **73,** 2599–2600 (1951).

(393) Scott, S. L.: U.S. patent 2,407,181 (1946).

(394) Semmelman, J. O., and Watson, J. E.: U.S. patent 2,611,958 (1952).

(395) Severson, R. G., and Rosscup, R. J.: J. Am. Chem. Soc. **76,** 4552–4 (1954).

(396) Shaw, C., Langrish-Smith, W. E., and Page, A.: British patent 637,739 (1950); Chem. Abstracts **44,** 8362 (1950).

(396a) Shorr, L. M., Freiser, H., and Speier, J. L.: J. Am. Chem. Soc. **77,** 547–51 (1955).

(397) Shtetter, I.: Russian patent 44,934 (1935).

(398) Simon, E., and Thomas, F. W.: U.S. patent 2,575,687 (1951).

(399) Simons, J. H., and Dunlap, R. D.: U.S. patent 2,651,651 (1953). Minnesota Mining and Manufacturing Co.: British patent 714,846 (1954).

(400) SOFFER, H., AND DEVRIES, T.: J. Am. Chem. Soc. **73**, 5817–9 (1951).
(401) SOMMER, L. H.: U.S. patent 2,496,419 (1950).
(402) SOMMER, L. H.: U.S. patent 2,507,551 (1950); British patent 668,234 (1952); Chem. Abstracts **47**, 2766 (1953).
(403) SOMMER, L. H.: U.S. patent 2,512,390 (1950). Dow Corning Ltd.: British patent 675,051 (1952).
(404) SOMMER, L. H.: U.S. patent 2,557,802 (1951). Dow Corning Ltd.; British patent 684,295 (1952).
(405) SOMMER, L. H.: U.S. patent 2,557,803 (1951). Dow Corning Ltd.: British patent 684,296 (1952).
(406) SOMMER, L. H.: U.S. patent 2,589,445 (1952). British patent 685,268, and 684,310 (1952).
(407) SOMMER, L. H.: U.S. patent 2,589,446 (1952). Dow Corning Ltd.: British patent 685,533 (1953).
(408) SOMMER, L. H.: U.S. patent 2,589,447 (1952). Dow Corning Ltd.: British patent 685,533 (1953).
(409) SOMMER, L. H.: U.S. patent 2,591,736 (1952). Dow Corning Ltd.: British patent 688,017 (1953).
(410) SOMMER, L. H.: U.S. patent 2,605,273 (1952). Dow Corning Ltd.: British patent 675,050 (1952).
(411) SOMMER, L. H.: U.S. patent 2,607,793 (1952). Dow Corning Ltd.: British patent 709,157 (1954).
(412) SOMMER, L. H.: U.S. patent 2,610,198 (1952). Dow Corning Ltd.: British patent 684,293 (1952).
(413) SOMMER, L. H.: U.S. patent 2,610,199 (1952). Dow Corning Ltd.: British patent 684,294 (1952).
(414) SOMMER, L. H.: U.S. patent 2,634,282 (1953). Dow Corning Ltd.: British patent 710,249 (1954).
(415) SOMMER, L. H.: U.S. patent 2,634,283 (1953). Dow Corning Ltd.: British patent 709,691 (1954).
(416) SOMMER, L. H.: U.S. patent 2,635,108 (1953).
(417) SOMMER, L. H.: U.S. patent 2,635,109 (1953).
(418) SOMMER, L. H.: U.S. patent 2,662,909 (1953). Dow Corning Ltd.: British patent 716,536 (1954).
(419) SOMMER, L. H.: U.S. patent 2,662,910 (1953). Dow Corning Ltd.: British patent 716,535 (1954).
(420) SOMMER, L. H.: U.S. patent 2,672,473 (1954). Dow Corning Ltd.: British patent 709,690 (1954).
(421) SOMMER, L. H.: U.S. patent 2,672,474 (1954). Dow Corning Ltd.: British patent 709,689 (1954).
(422) SOMMER, L. H.: U.S. patent 2,687,418 (1954).
(423) SOMMER, L. H.: U.S. patent 2,687,424 (1954).
(424) SOMMER, L. H.: U.S. patent 2,691,032 (1954).
(425) SOMMER, L. H., BAILEY, D. L., GOLDBERG, G. M., BUCK, C. E., BYE, T. S., EVANS, F. J., AND WHITMORE, F. C.: J. Am. Chem. Soc. **76**, 1613–18 (1954).
(426) SOMMER, L. H., BAILEY, D. L., GOULD, J. R., AND WHITMORE, F. C.: J. Am. Chem. Soc. **76**, 801–3 (1954).
(427) SOMMER, L. H., BAILEY, D. L., STRONG, W. A., AND WHITMORE, F. C.: J. Am. Chem. Soc. **68**, 1881–3 (1946).
(428) SOMMER, L. H., BAILEY, D. L., AND WHITMORE, F. C.: J. Am. Chem. Soc. **70**, 2869–72 (1948).
(429) SOMMER, L. H., BARIE, W. P., AND GOULD, J. R.: J. Am. Chem. Soc. **75**, 3765–7 (1953). See also DENO, N. C., AND TAFT, R. W., JR.: J. Am. Chem. Soc. **76**, 248 (1954).
(430) SOMMER, L. H., AND BAUM, G. A.: J. Am. Chem. Soc. **76**, 5002 (1954).

(431) Sommer, L. H., Dorfman, E., Goldberg, G. M., and Whitmore, F. C.: J. Am. Chem. Soc. **68**, 488–9 (1946).
(432) Sommer, L. H., and Evans, F. J.: J. Am. Chem. Soc. **76**, 1186–7 (1954).
(433) Sommer, L. H., Goldberg, G. M., Barnes, G. H., and Stone, L. S., Jr.: J. Am. Chem. Soc. **76**, 1609–12 (1954).
(434) Sommer, L. H., Goldberg, G. M., Dorfman, E., and Whitmore, F. C.: J. Am. Chem. Soc. **68**, 1083–5 (1946).
(435) Sommer, L. H., Goldberg, G. M., Gould, J. R., and Whitmore, F. C.: J. Am. Chem. Soc. **69**, 980 (1947).
(436) Sommer, L. H., Gould, J. R., Goldberg, G. M., and Marans, N. S.: J. Am. Chem. Soc. **71**, 1509 (1949).
(437) Sommer, L. H., and Marans, N. S.: J. Am. Chem. Soc. **72**, 1935–9 (1950). See also Gilman, H., and Clark, R. N.: J. Am. Chem. Soc. **69**, 967 (1947).
(438) Sommer, L. H., and Marans, M. S.: J. Am. Chem. Soc. **73**, 5135–8 (1951).
(439) Sommer, L. H., Marans, N. S., Goldberg, G. M., Rockett, J., and Pioch, R. P.: J. Am. Chem. Soc. **73**, 882 (1951).
(440) Sommer, L. H., Mitch, F. A., and Goldberg, G. M.: J. Am. Chem. Soc. **71**, 2746–50 (1949).
(441) Sommer, L. H., Murch, R. M., and Mitch, F. A.: J. Am. Chem. Soc. **76**, 1619 (1954).
(442) Sommer, L. H., and Pioch, R. P.: J. Am. Chem. Soc. **75**, 6337–8 (1953).
(443) Sommer, L. H., and Pioch, R. P.: J. Am. Chem. Soc. **76**, 1606–9 (1954).
(444) Sommer, L. H., Pioch, R. P., Marans, N. S., Goldberg, F. M., Rockett, J., and Kerlin, J.: J. Am. Chem. Soc. **75**, 2932–4 (1953).
(445) Sommer, L. H., and Rockett, J.: J. Am. Chem. Soc. **73**, 5130–4 (1951).
(446) Sommer, L. H., Tuler, L. J., and Whitmore, F. C.: J. Am. Chem. Soc. **70**, 2872–4 (1948).
(447) Sommer, L. H., Van Strien, R. E., and Whitmore, F. C.: J. Am. Chem. Soc. **71**, 3056–60 (1949).
(448) Sommer, L. H., and Whitmore, F. C.: J. Am. Chem. Soc. **68**, 485–7 (1946).
(449) Sowa, F. J.: U.S. patent 2,605,243 (1952).
(450) Speck, S. B.: J. Org. Chem. **18**, 1689–1700 (1953).
(451) Speier, J. L., Jr.: J. Am. Chem. Soc. **70**, 4142–3 (1948).
(452) Speier, J. L., Jr.: U.S. patent 2,444,858 (1948).
(453) Speier, J. L., Jr.: J. Am. Chem. Soc. **71**, 273–4 (1949).
(454) Speier, J. L., Jr.: British patent 629,719 (1949); Chem. Abstracts **44**, 3518 (1950).
(455) Speier, J. L., Jr.: U.S. patent 2,510,148; British patent 629,491 (1949); Chem. Abstracts **44**, 5899 (1950).
(456) Speier, J. L., Jr.: U.S. patent 2,510,149; British patent 629,719 (1949); Chem. Abstracts **44**, 3518 (1950).
(457) Speier, J. L., Jr.: U.S. patent 2,527,590 (1950).
(458) Speier, J. L., Jr.: U.S. patent 2,527,591 (1950). Dow Corning Corporation: British patent 631,049 (1949); Chem. Abstracts **44**, 4491 (1950).
(459) Speier, J. L., Jr.: J. Am. Chem. Soc. **73**, 824–6 (1951).
(460) Speier, J. L., Jr.: J. Am. Chem. Soc. **73**, 326–7 (1951).
(461) Speier, J. L., Jr.: U.S. patent 2,550,205 (1951). Dow Corning Corporation: British patent 635,733 (1950); Chem. Abstracts **44**, 6876 (1950).
(462) Speier, J. L., Jr.: U.S. patent 2,567,131 (1951). Dow Corning Ltd.: British patent 694,605 (1953).
(463) Speier, J. L., Jr.: U.S. patent 2,572,402 (1951).
(464) Speier, J. L., Jr.: U.S. patent 2,576,486 (1951). Dow Corning Ltd.: British patent 659,009 (1951); Chem. Abstracts **46**, 4846 (1952).
(465) Speier, J. L., Jr.: J. Am. Chem. Soc. **74**, 1003–10 (1952); *cf.* reference 329.
(466) Speier, J. L., Jr.: U.S. patent 2,582,568 (1952). Dow Corning Corporation: British patent 630,951 (1949); Chem. Abstracts **44**, 4491 (1950).

(467) Speier, J. L., Jr.: U.S. patent 2,582,569 (1952). Dow Corning Corporation: British patent 630,952 (1949); Chem. Abstracts **44**, 4491 (1950).
(468) Speier, J. L., Jr.: U.S. patent 2,584,751 (1952); British patent 688,817 (1953).
(469) Speier, J. L., Jr.: U.S. patent 2,611,776 (1952). Dow Corning Ltd.: British patent 685,538 (1953).
(470) Speier, J. L., Jr.: U.S. patent 2,611,777 (1952). Dow Corning Ltd.: British patent 685,542 (1953).
(471) Speier, J. L., Jr.: U.S. patent 2,611,778 (1952). Dow Corning Ltd.: British patent 685,539 (1953).
(472) Speier, J. L., Jr.: U.S. patent 2,611,779 (1952). Dow Corning Ltd.: British patent 685,540 (1953).
(473) Speier, J. L., Jr.: U.S. patent 2,611,780 (1952). Dow Corning Ltd.: British patent 685,541 (1953).
(474) Speier, J. L., Jr.: U.S. patent 2,611,781 (1952).
(475) Speier, J. L., Jr.: J. Am. Chem. Soc. **75**, 2930–1 (1953).
(476) Speier, J. L., Jr.: U.S. patent 2,628,244 (1953); Chem. Abstracts **47**, 5720 (1953). Dow Corning Ltd.: British patent 688,177 (1953).
(477) Speier, J. L., Jr.: U.S. patent 2,628,245 (1953); Chem. Abstracts **47**, 5720 (1953). Dow Corning Ltd.: British patent 688,178 (1953).
(478) Speier, J. L., Jr.: U.S. patent 2,629,727 (1953); British patent 692,669 (1953).
(479) Speier, J. L., Jr.: U.S. patent 2,640,064 (1953); British patent 683,460 (1952).
(480) Speier, J. L., Jr.: U.S. patent 2,645,630 (1953).
(481) Speier, J. L., Jr., and Daubert, B. F.: J. Am. Chem. Soc. **70**, 1400–1 (1948).
(482) Speier, J. L., Jr., Daubert, B. F., and McGregor, R. R.: J. Am. Chem. Soc. **70**, 1117–19 (1948).
(483) Speier, J. L., Jr., Daubert, B. F., and McGregor, R. R.: J. Am. Chem. Soc. **71**, 1474–5 (1949).
(484) Steinman, R.: U.S. patent 2,563,288 (1951).
(485) Steinman, R.: U.S. patent 2,688,006 (1954).
(486) Steinman, R.: U.S. patent 2,688,007 (1954).
(487) Strother, C. O.: U.S. patent 2,532,430 (1950).
(488) Summers, L.: Iowa State Coll. J. Sci. **26**, 292–4 (1952); Chem. Abstracts **47**, 8673 (1953).
(489) Sunthankar, S. V., and Gilman, H.: J. Am. Chem. Soc. **72**, 4884–7 (1950).
(490) Sunthankar, S. V., and Gilman, H.: J. Org. Chem. **15**, 1200–10 (1950).
(491) Sunthankar, S. V., and Gilman, H.: Textile Research J. **22**, 574–83 (1952).
(492) Sunthankar, S. V., and Gilman, H.: J. Org. Chem. **18**, 47–54 (1953); Chem. Abstracts **47**, 6141 (1953).
(493) Sunthankar, S. V., and Gilman, H.: Textile Research J. **23**, 53–8 (1953); Chem. Abstracts **47**, 2988 (1953).
(494) Sveda, M.: U.S. patent 2,561,429 (1951).
(495) Sveda, M.: U.S. patent 2,562,000 (1951).
(496) Swiss, J., and Arntzen, C. E.: U.S. patent 2,595,728 (1952). Westinghouse Electric International Co.: British patent 624,362 (1949); Chem. Abstracts **44**, 2287 (1950).
(497) Swiss, J., and Arntzen, C. E.: U.S. patent 2,595,727 (1952). Westinghouse Electric International Co.: British patent 624,361 (1949); Chem. Abstracts **44**, 2287 (1950).
(498) Swiss, J., and Arntzen, C. E.: U.S. patent 2,595,729 (1952). Westinghouse Electric International Co.: British patent 624,363 (1949); Chem. Abstracts **44**, 2287 (1950).
(499) Swiss, J., and Arntzen, C. E.: U.S. patent 2,595,730 (1952). Westinghouse Electric International Co.: British patent 624,364 (1949); Chem. Abstracts **44**, 2287 (1950).
(500) Szmant, H. H., and Anzenberger, J. F.: J. Am. Chem. Soc. **72**, 5346 (1950).
(501) Szmant, H. H., and Skendrovich, S.: J. Am. Chem. Soc. **76**, 2282 (1954).
(502) Tamborski, C., and Post, H. W.: J. Org. Chem. **17**, 1397–9 (1952).
(503) Tamborski, C., and Post, H. W.: J. Org. Chem. **17**, 1400–4 (1952).

(504) Tannenbaum, S.: J. Am. Chem. Soc. **76,** 1027 (1954).
(505) Tannenbaum, S., Kaye, S., and Lewenz, G. F.: J. Am. Chem. Soc. **75,** 3753–7 (1953).
(506) Tatlock, W. S., and Rochow, E. G.: J. Am. Chem. Soc. **72,** 528–30 (1950).
(507) Topchiev, A. V., Nametkin, N. S., and Shcherbokova, A. A.: Doklady Akad. Nauk S.S.S.R. **86,** 559–60 (1952); Chem. Abstracts **47,** 12223 (1953).
(508) Topchiev, A. V., Nametkin, N. S., and Zetkin, V. I.: Doklady Akad. Nauk S.S.S.R. **83,** 423–5 (1952); Chem. Abstracts **47,** 5353 (1953).
(509) Topchiev, A. V., Nametkin, N. S., and Zetkin, V. I.: Doklady Akad. Nauk S.S.S.R. **87,** 431–2 (1952); Chem. Abstracts **47,** 12223 (1953).
(510) Topchiev, A. V., Nametkin, N. S., and Solovova, O. P.: Doklady Akad. Nauk S.S.S.R. **86,** 965–8 (1952); Chem. Abstracts **47,** 10471 (1953).
(511) Topchiev, A. V., Nametkin, N. S., and Zetkin, V. I.: Doklady Akad. Nauk S.S.S.R. **82,** 927–9 (1952); Chem. Abstracts **47,** 4281 (1953).
(512) Topchiev, A. V., Nametkin, N. S., and Zetkin, V. I.: Doklady Akad. Nauk S.S.S.R. **82,** 981–2 (1952); Chem. Abstracts **47,** 3228 (1953).
(513) Topchiev, A. V., Nametkin, N. S., and Zetkin, V. I.: Doklady Akad. Nauk S.S.S.R. **86,** 1133–4 (1952); Chem. Abstracts **47,** 12281 (1953).
(514) Tyler, L. J.: U.S. patent 2,517,146 (1950). Dow Corning Ltd.: British patent 670,923 (1952); Chem. Abstracts **46,** 8894 (1952).
(515) Tyler, L. J.: U.S. patent 2,601,646 (1952). Dow Corning Ltd.: British patent 673,148 (1952); Chem. Abstracts **46,** 10685 (1952).
(516) Tyler, L. J., Sommer, L. H., and Whitmore, F. C.: J. Am. Chem. Soc. **70,** 2876–8 (1948).
(517) Tyran, L. W.: U.S. patent 2,532,583 (1950).
(518) United States Rubber Co.: British patent 710,051 (1954).
(519) Ushakov, S. N., and Itenburg, A. M.: J. Gen. Chem. (U.S.S.R.) **7,** 2495–8 (1937); Chem. Abstracts **32,** 2083 (1938).
(520) Vandervort, G. L., and Willard, J. E.: J. Am. Chem. Soc. **70,** 3148 (1948).
(521) Van Uitert, L. G., Fernelius, W. C., and Douglas, B. E.: J. Am. Chem. Soc. **75,** 457–60 (1953).
(522) Volkenshtein, M. V., and Pokrovskiĭ, E. I.: Izvest. Akad. Nauk S.S.S.R. **1953,** 177; Chem. Abstracts **47,** 6254 (1953); **48,** 12558 (1954).
(523) Volnov, Y. N., and Reutt, A.: J. Gen. Chem. (U.S.S.R.) **10,** 1600–4 (1940).
(524) Vorlander, D.: Ber. **58,** 1893–1914 (1925).
(525) Wagner, G. H.: U.S. patent 2,637,738 (1953).
(526) Wagner, G. H., Bailey, D. L., Pines, A. N., Dunham, M. L., and McIntire, D. B.: Ind. Eng. Chem. **45,** 367–74 (1953).
(527) Wagner, G. H., and Pines, A. N.: J. Am. Chem. Soc. **71,** 3567–8 (1949).
(528) Wagner, G. H., and Strother, C. O.: U.S. patent 2,632,013 (1953). British patent 670,617 (1952); Chem. Abstracts **46,** 8894 (1952).
(529) Warrick, E. L.: U.S. patent 2,541,137 (1951).
(530) Welsh, C. E., and Holdstock, N. G.: U.S. patent 2,661,348 (1953).
(531) West, R.: J. Am. Chem. Soc. **76,** 6012–14 (1954).
(532) West, R.: J. Am. Chem. Soc. **76,** 6015–17 (1954).
(533) West, R., and Rochow, E. G.: Naturwissenschaften **40,** 142 (1953).
(534) West, R., and Rochow, E. G.: J. Org. Chem. **18,** 303–8 (1953).
(535) West, R., and Rochow, E. G.: J. Org. Chem. **18,** 1739–42 (1953).
(536) Westinghouse Electric International Co.: British patent 706,703 (1954).
(537) White, D. G., and Rochow, E. G.: J. Am. Chem. Soc. **76,** 3897–3902 (1954).
(538) Whitmore, F. C., and Sommer, L. H.: J. Am. Chem. Soc. **68,** 481–4 (1946).
(539) Whitmore, F. C., Sommer, L. H., and Gould, J. R.: J. Am. Chem. Soc. **69,** 1976–7 (1947).
(540) Whitmore, F. C., Sommer, L. H., Gould, J. R., and Van Strien, R. E.: J. Am.

Chem. Soc. **69,** 1551 (1947). See also Gilman, H., and Clark, R. H.: J. Am. Chem. Soc. **69,** 967 (1947).

(541) Widdowson, R. R.: J. Chem. Soc. **1926,** 958–9.

(542) Winslow, F. H.: U.S. patent 2,642,415 (1953).

(543) Witt, R. K., Carson, W. G., and Raskin, B. L.: U.S. patent 2,649,396 (1953).

(544) Yakovlev, B. I.: Zhur. Obshcheĭ Khim. (J. Gen. Chem.) **19,** 1969–70 (1949); Chem. Abstracts **44,** 1016, 6385 (1950).

(545) Yakovlev, B. I., and Vinogradova, N. V.: Zhur. Obshcheĭ Khim. (J. Gen. Chem.) **22,** 1464–5 (1952); Chem. Abstracts **47,** 6340 (1953); **48,** 2573 (1954).

(546) Yakubovich, A. Ya., and Ginsburg, V. A.: Zhur. Obshcheĭ Khim. **22,** 1783–7 (1952); Chem. Abstracts **47,** 9256 (1953); **48,** 4435 (1954).

(547) Yakubovich, A. Ya., Makarov, S. P., Ginsburg, V. A., Gavilov, G. I., and Merkulova, E. N.: Doklady Akad. Nauk S.S.S.R. **72,** 69–72 (1950); Chem. Abstracts **45,** 2856 (1951).

(548) Yakubovich, A. Ya., and Motsarev, G. V.: Zhur. Obshcheĭ Khim. **23,** 412–17 (1953); Chem. Abstracts **48,** 3286 (1950); **49,** 3050 (1955).

(549) Yakubovich, A. Ya., and Motsarev, G. V.: Doklady Akad. Nauk S.S.S.R. **88,** 87–9 (1953); Chem. Abstracts **48,** 143 (1954).

(550) Yakubovich, A. Ya., and Motsarev, G. V.: Doklady Akad. Nauk S.S.S.R. **91,** 277–80 (1953); Chem. Abstracts **48,** 8750 (1954).

(551) Yakubovich, A. Ya., and Motsarev, G. V.: Zhur. Obshcheĭ Khim. **23,** 771–6 (1953); Chem. Abstracts **48,** 4462, 12694 (1954).

(552) Yakubovich, A. Ya., and Motsarev, G. V.: Zhur. Obshcheĭ Khim. **23,** 1414–17 (1953); Chem. Abstracts **47,** 12281 (1953).

(553) Yakubovich, A. Ya., and Motsarev, G. V.: Zhur. Obshcheĭ Khim. **23,** 1547–52 (1953); Chem. Abstracts **48,** 10642 (1954).

(554) Yegorov, Y. P., and Bazhulin, P. A.: Doklady Akad. Nauk S.S.S.R. **88,** 647–50 (1953).

(555) Zenzen, N.: Arkiv Kemi, Mineral. Geol. **8** (34), 1–10 (1923).