Synthesis of Novel Silicon-Containing Compounds via Lewis Acid-Catalyzed Reactions

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I

INTRODUCTION

This review will describe Lewis acid-catalyzed reactions such as allylsilylation, intramolecular allyl-migration, Friedel–Crafts alkylation, and hydrosilylation reactions commonly used in organosilicon chemistry. The carbenium and silylenium ion intermediates are generated by the interactions of organosilicon compounds such as allyltriorganosilanes,[1a,2] alkenylchlorosilanes,[1b,3] (chloroalkyl)silanes,[1b,4] and triorganohydrosilanes[5] with Lewis acid catalysts, which then react with simple unsaturated electrophilic organic compounds.[1] The isolation and properties of silylenium ions is discussed by Müller in this volume (p. 155). This review will particularly focus on the Lewis acid-catalyzed reactions with unsaturated hydrocarbon compounds. It is well recognized that the reactivity of such electrophiles varies depending upon the electronic nature of substituents and the cation position in the organosilicon compounds.[1b,3,4]

It is useful to compare the reactivity and reaction patterns of various cationic organosilicon species in the Lewis acid-catalyzed reactions with those of their organic analogs. Positive charges on the carbon β to silicon are stabilized by the electron-donating silyl group through σ–π conjugation, commonly known as β-stabilization.[6–8] The reactivity and reaction modes of allylsilanes are different from one another, depending on the number (n) of chlorine substituent on the silicon atom of allylchlorosilanes ($CH_2{=}CHCH_2SiMe_{3-n}Cl_n$). Allylsilanes containing two

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or more chlorine substituents on silicon react readily with aromatic compounds to give alkylation products, 2-aryl-1-silylpropanes [Eq. (1)].[3] However, allyl-trimethylsilane, having three methyl groups on the silicon (**1a**), in benzene solvent is dimerized to give the allylsilylation product 5-(trimethylsilyl)-4-(trimethylsilyl-methyl)-1-pentene without any alkylation products [Eq. (2)].[2]

$$
\text{(1)}
$$

$$
\text{(2)}
$$
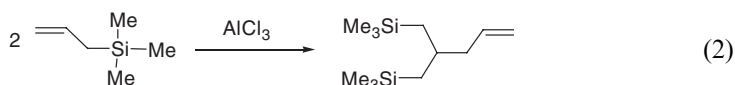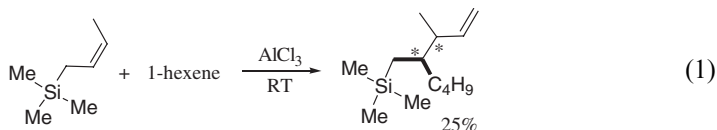
In aluminum chloride-catalyzed reactions, a small amount of hydrogen chloride, resulting from the reaction of anhydrous aluminum chloride with moisture inevitably present in the reactants, initiates the reaction.[9] The proton from the hydrogen chloride interacts with the π-bond of allylsilanes to give a carbenium ion on the carbon β to silicon, because the secondary silylpropyl cation can be stabilized by the electron-donating silyl group through β-stabilization as described above.[1b,3] The stabilization effects can be more significant for allyltrimethylsilane than for allyl-chlorosilanes because of the electron-donating effects from the methyl groups on silicon.[1b,2] This facilitates the protodesilylation[1a,2,10] of allyltrimethylsilane by hydrogen chloride in the presence of aluminum chloride, which gives propene and a Me_3SiCl–$AlCl_3$ complex. Me_3SiCl has been reported to be an excellent promoter of allylsilylation reactions.[1a,11–13] In contrast, the collapse of the β-silyl cation intermediates of allylchlorosilanes is largely retarded, primarily due to less effective σ–π conjugation brought on by the presence of the electronegative chlorine atom(s) on silicon.[1b,3] The cation intermediates undergo alkylation reactions with electron-rich aromatic systems faster than protodesilylation.[1b,3]

II

ALLYLSILYLATION REACTIONS WITH ALLYLTRIORGANOSILANES

A. *Allylsilylation of Alkenes*

Allylsilylation is an addition reaction of allylorganosilanes to carbon–carbon multiple bonds of unsaturated hydrocarbons in the presence of Lewis acids.[1a] Common examples of unsaturated hydrocarbons for allylsilylations include alkenes,[2] cycloalkenes,[1a,2] allyltriorganosilanes,[1a,2,11–13] 5-(trimethylsilyl)-1-pentenes,[13] diallylsilanes,[12,16] conjugated dienes,[13] and alkynes.[19–21]

1. Allylsilylation of Linear Alkenes

The addition reaction of allyltriorganosilanes to 1-alkenes in the presence of anhydrous aluminum chloride as catalyst at room temperature gives regiospecific allylsilylated products, in which the silyl group adds to the terminal carbon and the allyl group adds to the inner carbon of the double bond [Eq. (3)].[2] Compared with the starting alkenes, the products of the allylsilylation reaction possess two additional carbon atoms in addition to a (triorganosilyl)methyl branch at the carbon β to the double bond.
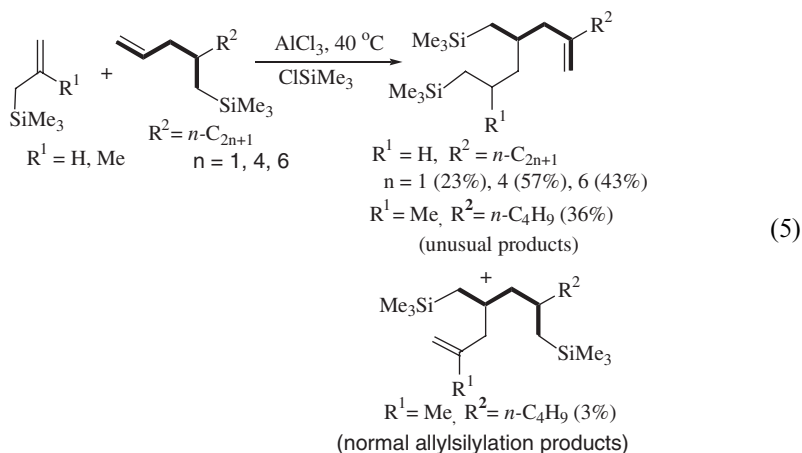

$$R^1=Me, R^2=CH_3 \ (61\%)$$
$$R^1=Me, R^2=C_4H_9 \ (78\%)$$
$$R^1=Me, R^2=C_6H_{13} \ (60\%)$$
$$R^1=Ph, R^2=C_4H_9 \ (42\%)$$
$$R^1=CH_2Ph, R^2=C_4H_9 \ (47\%)$$

(3)
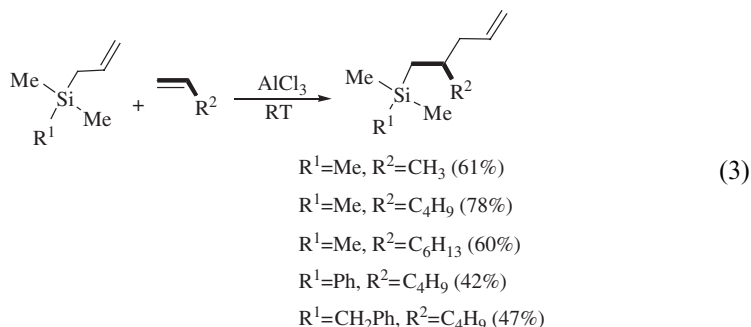
The stereohomogeneous (Z)-crotyltrimethylsilane reacts with 1-hexene to give 3-methyl-4-(trimethylsilyl)methyl-1-octene as a mixture of two diastereomers in 25% yield [Eq. (4)].[2] The diastereomeric products possess a methyl group at the carbon α to the double bond, indicating that an allylic inversion occurs during the allylsilylation.[13,17]


(4)
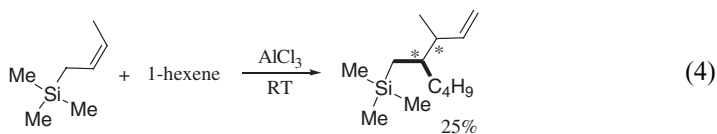
2. Allylsilylation of 4-(Trimethylsilylmethyl)-1-Alkenes

As described above, the allylsilylation of terminal alkenes with **1a** affords 4-(silylmethyl)-1-alkenes. Since these products possess a vinyl group at the terminal position, they can be allylsilylated again with **1a**. Additional reaction in the presence of anhydrous aluminum chloride and trimethylchlorosilane activator[11,12] in organic solvents or neat at ~40 °C gives the double allylsilylation products, 2-alkyl-8,8-dimethyl-4-(trimethylsilylmethyl)-8-silanon-1-enes[13] as the major products. These products are unusual and different from the previously reported normal allylsilylation products,[2,11,12] because they have a double bond on the carbon with the R² group but not on the carbon with R¹ [Eq. (5)]. These results suggest that isomerization of the normal allylsilylation products to the unusual products occurs through a 1,5-hydride shift. Polymeric materials are also obtained due to additional allylsilylations.

$$
\text{(5)}
$$

R^1 = H, R^2 = n-C$_{2n+1}$
n = 1 (23%), 4 (57%), 6 (43%)
R^1 = Me, R^2 = n-C$_4$H$_9$ (36%)
(unusual products)

R^1 = Me, R^2 = n-C$_4$H$_9$ (3%)
(normal allylsilylation products)

3. Allylsilylation of Cycloalkenes

Allyltrimethylsilane (**1a**) reacts with cycloalkenes such as cyclohexene and cyclo-pentene at room temperature to give stereospecifically *trans*-1-trimethylsilyl-2-al-lylcycloalkanes.[1a,2] These products are formed through *trans* addition and an allylic inversion.

$$
\text{(6)}
$$

n = 0 (22%), 1 (39%)
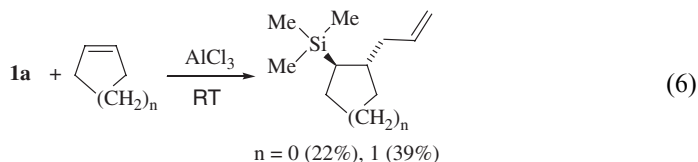
On the basis of the above results, a possible mechanism for the allylsilylation of cyclohexene with **1a** has been proposed as illustrated in Scheme 1. A silyl cation or a complex intermediate **I** is directly formed at the beginning stages of the reaction
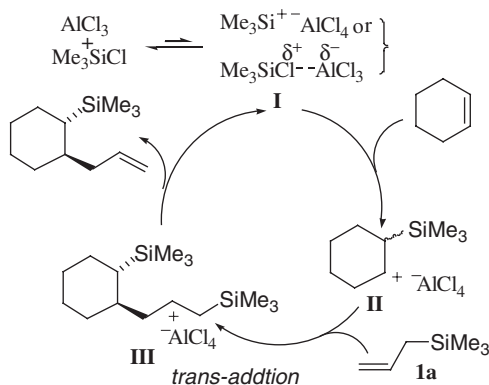
SCHEME 1. Catalytic cycle of allylsilylation.

from aluminum chloride and trimethylchlorosilane,[1a,2,11–13] or from the protodesilylation of **1a** by acids resulting from the reaction of anhydrous aluminum chloride with adventitious water in the reaction mixture.[2,18,19] Intermediate **I** interacts with the carbon–carbon double bond of cyclohexene to generate the secondary carbenium ion intermediate **II**, which is stabilized by the silyl group β-stabilization effect.[11–13,20–22] Intermediate **II** then interacts with the double bond of **1a** in *trans*-fashion to avoid steric interactions between the bulky trimethylsilyl group and incoming **1a**. A new carbon–carbon bond is formed and a carbenium ion at the carbon β to silicon is generated, leading to **III**, which undergoes a desilylation reaction to give *trans*-allylsilylated products and to regenerate intermediate **I**.
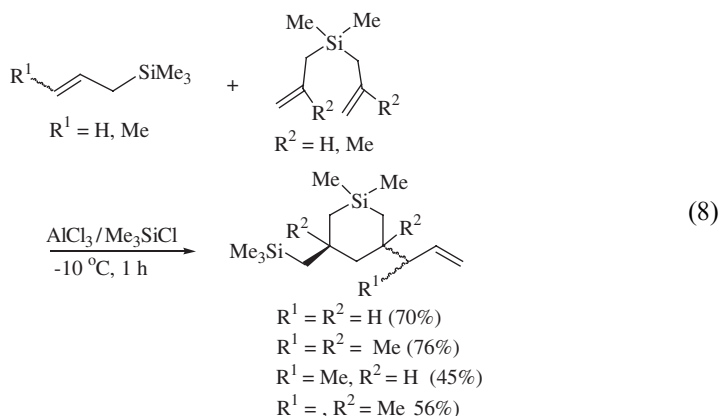
4. Allylsilylation of 1-Allyl-2-(Trimethylsilyl)Cycloalkenes

Trans-1-allyl-2-(trimethylsilyl)cyclopentane and *trans*-1-allyl-2-(trimethylsilyl)-cyclohexane are formed from the reaction of **1a** with cyclopentene and cyclohexene, respectively. A second allylsilylation reaction of these compounds with **1a** also gives unusual allylsilylation products, 7-cyclopent-1-enyl-2,2-dimethyl-4-(trimethylsilyl-methyl)-2-silaheptane (30%) and 4-((cyclohex-1-enyl)methyl)-2,2,8,8-tetramethyl-2,8-disilanonane (39%). As observed in the allylsilylation of 4-(trimethylsilyl-methyl)-1-alkenes, these products are likely formed *via* intramolecular silyl rearrangements. In this case, the results strongly suggest that a 1,5-silyl shift and 1,5-hydride shift have occurred. Under the same reaction conditions, *trans*-1-allyl-2-(trimethylsilyl)cycloalkenes are isomerized to 3-[3-(trimethylsilyl)propyl]-cycloalkenes. Thus, both starting *trans*-1-allyl-2-(trimethylsilyl)cyclopentene and -hexene are isomerized to 3-(3-(trimethylsilyl)propyl)cyclopentene (24%) and 3-(3-(trimethylsilyl)propyl)cyclohexene (15%), respectively [Eq. (7)]. It seems reasonable that the first step in the isomerization is the addition of a silyl cation to the carbon–carbon double bond of the *trans*-1-allyl-2-(trimethylsilyl)cycloalkanes followed by a 1,5-hydride shift to give a carbocation on a ring carbon β to the silyl group. This is followed by regeneration of a silyl cation from the ring to form a double bond.[11,12]

(7)

n = 1 (30%), 2 (39%)   n = 1 (24%), 2 (15%)
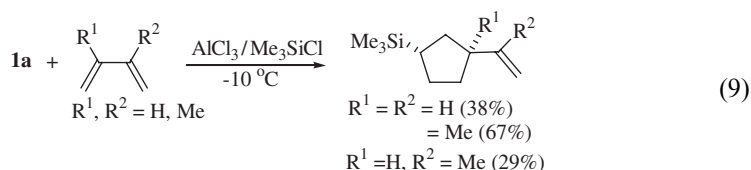(unusual allylsilylation products)
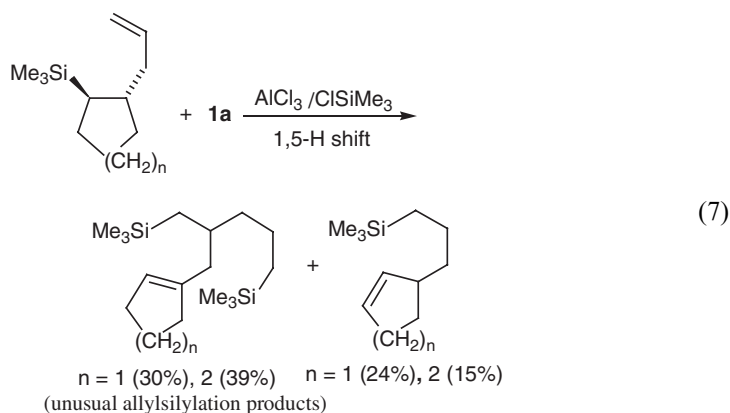
5. Allylsilylation of Diallylsilanes

Diallyldimethylsilanes undergo intramolecular allylsilylation to give cyclic polymer products in the presence of aluminum chloride.[12] When **1a** is used as a chain-terminating reagent, the formation of polymers is reduced and intramolecularly cyclized allylsilylation products are produced. Thus, a 1:3 reaction of diallylsilanes and monoallylsilanes at −10 °C gives the monomeric cyclized allylsilylation products, isomeric *trans-* and *cis-*3-allyl-1,1-dimethyl-5-trialkylsilylmethyl-1-silacyclohexanes, in 45–76% yields [Eq. (8)]. In this reaction, trimethylchlorosilane is a good activator[12,16] for the aluminum chloride-catalyzed allylsilylation reaction.
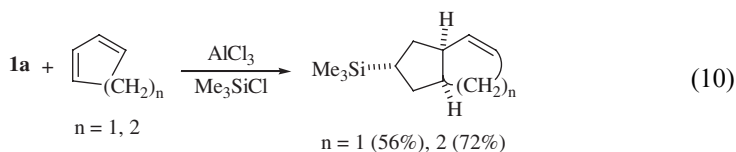
$$R^1 \diagup\!\!\!\diagdown\, SiMe_3 \quad + \quad \text{(diallylsilane, } R^2 = H, Me)$$

$R^1 = H, Me$

$R^2 = H, Me$

$$\xrightarrow[-10\ ^{\circ}C,\ 1\ h]{AlCl_3/Me_3SiCl} \quad Me_3Si\text{—(silacyclohexane product)}$$

$R^1 = R^2 = H\ (70\%)$
$R^1 = R^2 = Me\ (76\%)$
$R^1 = Me, R^2 = H\ (45\%)$
$R^1 = , R^2 = Me\ 56\%)$

$$(8)$$

6. Allylsilylation of Conjugated Dienes

Reaction of linear conjugated dienes with **1a** at −10 °C in hydrocarbon solvent in the presence of $Me_3SiCl/AlCl_3$ affords stereospecific *trans*-1-silyl-3-vinyl-cyclopentanes, indicating a [3 + 2] cycloaddition of the allyl group of **1a** with a carbon–carbon double bond of the diene [Eq. (9)].[13] In the [3 + 2] annulation reaction, of greater significance is the *trans* conformation of the trimethylsilyl group and vinyl groups.

$$\textbf{1a} \ + \ \text{(diene, } R^1, R^2 = H, Me) \xrightarrow[-10\ ^{\circ}C]{AlCl_3/Me_3SiCl} \ Me_3Si\text{—(cyclopentane product)}$$

$R^1, R^2 = H, Me$

$R^1 = R^2 = H\ (38\%)$
$= Me\ (67\%)$
$R^1 = H, R^2 = Me\ (29\%)$

$$(9)$$

The reaction of cyclic conjugated dienes with **1a** in hydrocarbon solvent also gives stereospecific *trans*-1-silyl-3-vinylcyclopentanes as the major products.

$$1a \; + \; \underset{n = 1, 2}{\underset{(CH_2)_n}{\boxed{}}} \; \xrightarrow[\text{Me}_3\text{SiCl}]{\text{AlCl}_3} \; \underset{n = 1 \, (56\%), \, 2 \, (72\%)}{Me_3Si \text{''''} \boxed{} (CH_2)_n} \qquad (10)$$

The reaction of 1,3-cyclohexadiene with **1a** at a temperature of $-50\,^{\circ}\text{C}$ gives a 97:3 mixture of 1,4-allylsilylated product, *trans*-3-allyl-6-(trimethylsilyl)cyclohexene and 1,2-allylsilylated product, *trans*-3-allyl-4-(trimethylsilyl)cyclohexene, in quantitative yield. At the same temperature, the [3 + 2] cycloaddition product is detected only in trace amounts after 1 h. As the reaction mixture is warmed to $-10\,^{\circ}\text{C}$, the allylsilylated compounds are converted to the [3 + 2] cycloaddition product (72%). When purified *trans*-3-allyl-6-(trimethylsilyl)cyclohexene and *trans*-3-allyl-4-(tri-methylsilyl)cyclohexene are treated separately under the same reaction conditions, the former compound is converted to the [3 + 2] cycloaddition product (major) and 3-(trimethylsilyl)propylbenzene [Eq. (11)], while the latter compound is converted to polymeric materials without giving any [3 + 2] cycloaddition product. The reaction rates of allylsilylation and [3 + 2] annulation are also accelerated by the addition of trimethylchlorosilane to aluminum chloride, as observed in other allylsilylation reactions.[14,15]

$$\xrightarrow[\text{Me}_3\text{SiCl}]{\text{AlCl}_3, \, -10\,^{\circ}\text{C}} \qquad (11)$$

(major)   (minor)
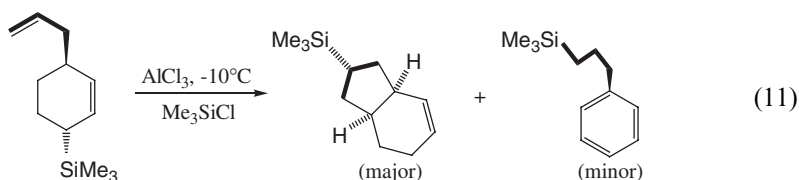
(2-Methyl-2-propenyl)trimethylsilane reacts with cyclohexene at $-10\,^{\circ}\text{C}$ for 25 min to give *trans*-allylsilylated products, *trans*-3-(2-methyl-2-propenyl)-6-trimethylsilylcyclohexene (15%), and *trans*-3-(2-methyl-2-propenyl)-4-trimethylsilylcyclohexene (3%), but no [3 + 2] cycloaddition product. This result suggests that a methyl substituent on the middle carbon of the allyl group prevents the [3 + 2] cycloaddition reaction.

The probable mechanism for the allylsilylation and [3 + 2] cycloaddition is illustrated in Scheme 2, using the reaction of butadiene with **1a** as a representative example. Intermediate **I**, generated as described in Scheme 1, adds to a terminal carbon of butadiene to generate a new intermediate **IV**. This intermediate then interacts with the double bond of **1a** to give **V**, containing a new carbon–carbon bond. In the allylic cationic intermediate **IV**, 1,2-allylsilylation is not favored because of steric repulsion between the bulky trimethylsilyl group of intermediate **IV** and incoming **1a**. Intermediate **V** can undergo a 1,2-silyl shift[17,18] to intermediate **VI** at higher reaction temperatures, even though this is thermodynamically less favorable. Finally, the [3 + 2] cycloaddition product is formed by the cyclization of **VI** to give a five-membered ring through the intramolecular nucleophilic attack by the carbon–carbon double bond on the carbocation of **VI**, followed by the elimination of a silyl cation.

$$Me_3SiCl + AlCl_3$$
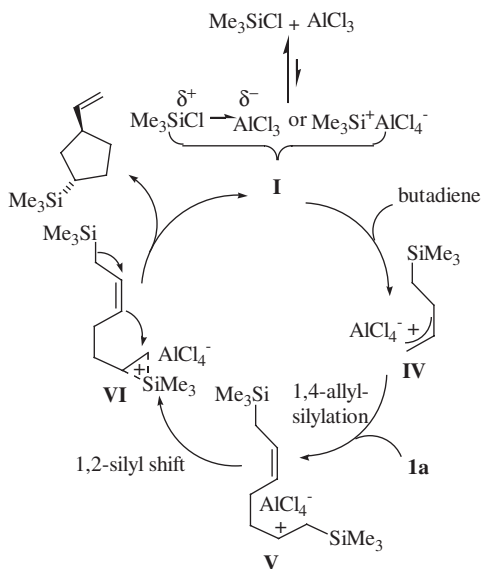
Scheme 2.

B. *Allylsilylation of Alkynes*

The reaction of terminal alkynes with **1a** in the presence of Lewis acid catalyst at room temperature gives regio- and stereospecific *trans*-allylsilylation products (26–66%) from the addition of silyl and allyl groups to the terminal and inner carbon atoms, respectively, of the carbon–carbon triple bond [Eq. (12)].[19,20] The yields of these products are much improved by using trimethylchlorosilane as an activator.[28] In allylsilylations of 1-hexyne, the catalytic activity of Lewis acids decreases in the following order: $HfCl_4 > AlBr_3 > AlCl_3 > EtAlCl_2$.[21] Stereohomogeneous *Z*-crotyltrimethylsilane reacts with alkyne to afford the expected regiospecific allylsilylation product with allylic inversion.[1a,2,11–13] This implies that allylsilylation is not a concerted reaction but occurs stepwise, as observed in the allylsilylation of alkenes.[1a,2,11–13]


$$(12)$$
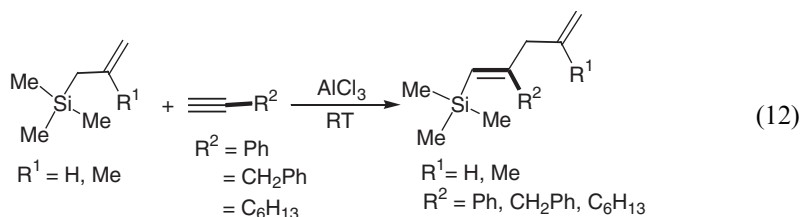
In the presence of hafnium tetrachloride/trimethylchlorosilane catalyst, alkynyl allylsilane compounds undergo an intramolecular allylsilylation reaction to give cyclic alkenylsilanes in good yields.[22]

III

INTRAMOLECULAR ALKENYL-MIGRATION REACTION OF ALKENYLCHLOROSILANES

The chemistry of alkenyl(ω-chloroalkyl)silanes containing both reactive chloroalkyl and alkenyl groups bonded to silicon, in the presence of Lewis acid catalysts is of interest. Simple alkenyl(chloromethyl)silanes $[\omega\text{-}(C_nRH_{2n-2})(ClCH_2)SiMe_2$, $n = 2, 3]$ undergo intramolecular alkenyl-migration in the presence of Lewis acid catalyst to give C_1-increased alkenylchlorosilanes.[23,24] Thus, the reaction of (2-alkylvinyl)(chloromethyl)dimethylsilanes in the presence of aluminum chloride catalyst gives (3-alkylallyl)(dimethyl)chlorosilanes as the major products and (2-alkylcyclopropanyl)chlorosilanes as minor products [Eq. (13)].[23] In this reaction, the yield of vinyl-migration product decreases as the bulk of the alkyl substituent in the (2-alkylvinyl)silanes increases. The reaction of (1-hexylvinyl)(chloromethyl)-dimethylsilane gives only (2-hexylcyclopropyl)dimethylsilane.

$$R = {}^nBu, {}^tBu, hexyl, \tag{13}$$
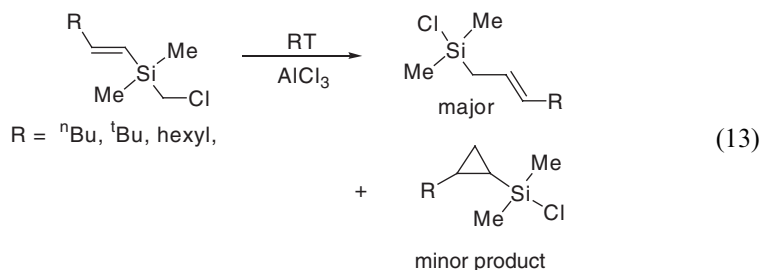
Allyl(chloromethyl)silanes also undergo intramolecular allyl-migration reactions analogous to that observed for (2-alkylvinyl)(chloromethyl)dimethylsilanes. When **1a** is used as a trapping agent, the carbocation formed at the carbon of the chloromethyl group interacts with the allyl group to form an intramolecularly cyclized silacyclopentanyl cation. The silacyclopentanyl cation is then trapped by **1a** to give the intramolecularly cyclized allylsilylation product [Eq. (14)].[24] The reaction of allyl(chloromethyl)dimethylsilane with **1a** in the presence of aluminum chloride catalyst at room temperature affords an isomeric mixture of 2-(2-allyl-4,4-dimethyl-4-silapentyl)-1,1-dimethylsilanes as trapped products in 40% yield and 3-butenyldimethylchlorosilanes as the allyl migration products in 18% yield [Eq. (14)]. However, the same reaction using allyl(chloromethyl)organochlorosilanes or allyl(chloromethyl)dichlorosilanes in the presence of aluminum chloride does not proceed, indicating that the reactions are sensitive to the electronic nature of the substituents on silicon. Generally, the chloromethyl group of allyl(chloromethyl) silanes is activated by alkyl groups bonded to silicon, while deactivated by chloro group(s) due to the decreased stabilizing ability of α-carbocations by the silyl group.[4] Allyl(chloromethyl)diorganosilanes $(CH_2{=}CH{-}CH_2SiR^1R^2CH_2Cl$; $R^1,R^2 = Me$ or Ph) undergo intramolecular allyl-migration reactions in the presence of aluminum chloride to give 3-butenyldiorganochlorosilanes $(CH_2{=}CH{-}CH_2{-}CH_2SiClR^1R^2)$ in 40–75% yields.

$$(14)$$
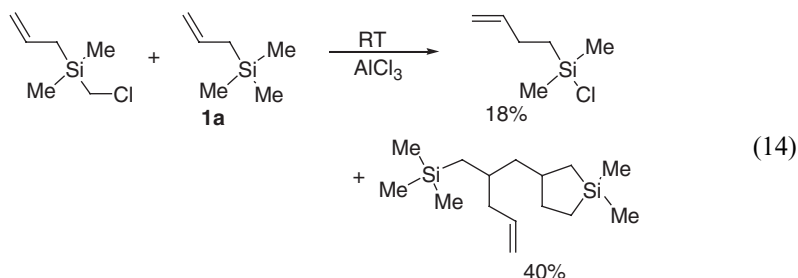
IV

FRIEDEL–CRAFTS ALKYLATION REACTION WITH ORGANOSILICON COMPOUNDS

Organosilicon compounds such as alkenylchlorosilanes and (chloroalkyl)chloro-silanes (alkyl = methyl, ethyl, propyl)[1b,4,14] react with aromatic compounds in the presence of Lewis acid catalysts to give Friedel–Crafts alkylation products. Common examples of alkenylchlorosilanes for the alkylations of aromatic compounds include vinylchlorosilanes and allylchlorosilanes.[1b,3] Aluminum chloride is a very effective catalyst for the reaction. In alkylation reactions with alkenylchlorosilanes, the reactivity of allylchlorosilanes is higher than that of vinylchlorosilanes. Tri-organoalkenylsilanes such as vinyltrimethylsilane and allyltrimethylsilane do not react with benzene to give alkylated products.[2] In the aluminum chloride-catalyzed alkylation reactions, allylchlorosilanes or vinylchlorosilanes should have one or more chlorine atoms bonded to silicon.

A. Alkylation with Allylchlorosilanes

Allylchlorosilanes undergo Friedel–Crafts alkylation with aromatic compounds such as benzene derivatives[3] and ferrocene[25] to give [β-(chlorosilyl)alkyl]arene compounds in the presence of Lewis acid catalyst.[1b] Allylsilanes containing two or more chlorine atoms on silicon react smoothly with benzene under mild conditions to give alkylation products in good yields [Eq. (15)]. In alkylations of benzene, the reactivity of the allylsilanes increases as the number of chlorine atoms on the silicon increases, but decreases as the number of methyl groups increases. Because the reactivity of allylsilanes is sensitive to the electronic nature of the substituents on the silicon atom, allylsilane selection is an important factor for alkylation reactions.

$$(15)$$
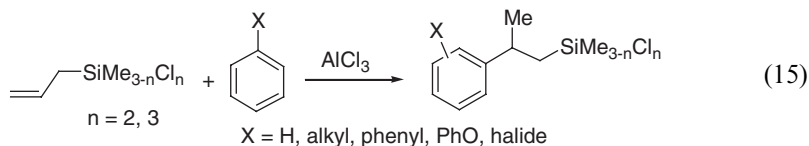
In the Friedel–Crafts alkylation of benzene derivatives (Ph–R: R = Me, Et, i-Pr, Ph, OPh, F, Cl, Br) with allyldichlorosilane (**1b**) in the presence of aluminum chloride catalyst,[3] monoalkylation products, 3-aryl-1,1-dichloro-1-silabutanes, are obtained in 60–83% isolated yields along with small amounts of dialkylation products. The *ortho-*, *meta-*, and *para*-isomeric monoalkylation products can all be formed, but the amount of *ortho*-isomer produced decreases as the steric bulk of the substituent on the benzene ring increases. For example, no *ortho*-alkylation product is found in the case of *i*-propylbenzene. The yield of *meta*-isomer increases as the reaction time increases or at higher temperatures, indicating that it is the thermodynamic product. The alkylation of halogen-substituted benzenes (R = F, Cl, Br) with **1b** gives *ortho-* and *para*-adducts predominantly (91–98%), indicating that halogen atoms are *ortho-* and *para*-directing groups in this reaction.

The effects of ring constituents in the alkylation of benzene derivatives (Ph–R) with **1a** are summarized in Table I.

According to Table I, the reactivity of substituted benzenes (Ph–R) decreases in the following order: R = Ph > PhO > *i*-Pr > Et > Me > H > F > Cl > Br.[3] The alkylation of alkylbenzenes is faster than that of halogen-substituted benzenes. Among the halogen-substituted benzenes, the fastest rate is observed for fluorobenzene and the slowest for bromobenzene, an observation which is not consistent with their relative electronegativities.[26–28] These results indicate that the resonance effect of halogen substituents upon the benzene ring should be considered in addition to electronic effects in order to explain the reaction rates.[26] Stronger resonance effects compared to electronic effects are apparently responsible for the *ortho-* and *para*-directing properties of the halogen atoms. The relative reaction rates for the alkylation of substituted benzenes with respect to benzene ($\log k_R/k_H$) can be plotted against substituent coefficients (σ)[26] for alkyl, aryl, and halogen groups. According to the Hammet equation,[29] $\log k_R/k_H = \rho\sigma$, where σ is a Hammet constant, ρ is found to be 3.1 from the relationship between the substituent coefficients (σ) and

TABLE I

RELATIVE ALKYLATION RATES[a] AND SUBSTITUENT CONSTANTS[42] (S) FOR SUBSTITUTED BENZENES (Ph–R)

Ph–R	Relative rates		Substituent constants		
	(k_R/k_H)	($\log k_R/k_H$)	σ_R	σ_I	σ
H	1.00	0.00	0.00	0.00	0.00
F	0.081	−1.04	0.74	−0.60	0.14
Cl	0.016	−1.44	0.72	−0.24	0.48
Br	0.011	−1.96	0.72	−2.52	0.54
Me	3.89	0.59	−0.01	−0.41	−0.42
Et	4.10	0.61	−0.02	−0.44	−0.46
i-Pr	5.65	0.72	–	–	–
Ph	10.27	1.01	0.25	−0.37	−0.12
PhO	9.42	0.97	0.76	−1.29	−0.53

Definitions: σ_R, resonance constant; σ_I, field constant; $\sigma = \sigma_R + \sigma_I$.
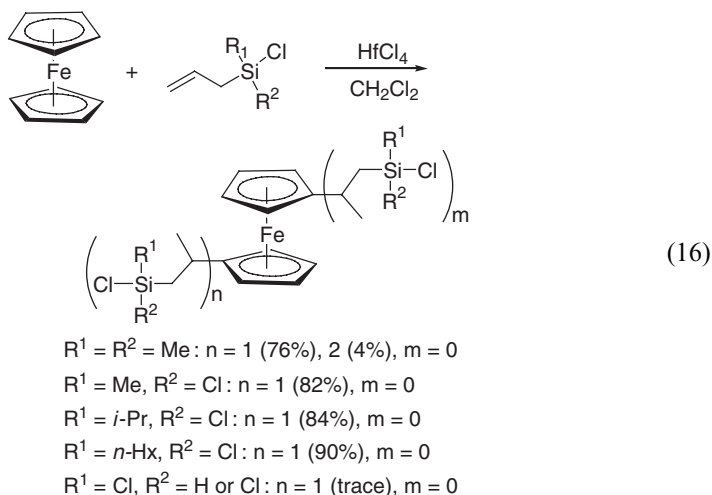[a]Reaction mole ratio of **1b**/Ph–R/aluminum chloride = 1:20:0.1.

the relative reaction rates for the alkylation of substituted benzenes with respect to benzene ($\log k_R/k_H$).[3]

Allylchlorosilanes also react with naphthalene to give isomeric mixtures of poly-alkylated products. However, it is difficult to isolate and purify the products for characterization because the products possess similar boiling points. The alkylation of anthracene with allylchlorosilanes or vinylchlorosilanes is not possible because of the deactivation of aluminum chloride catalyst by complex formation with anthracene.

In the polyalkylation reaction of benzene with allylchlorosilanes, trialkylated compounds are the most substituted products obtained in appreciable amount due to increased steric interactions with additional allyltrichlorosilane. This is the case even when more than a four-fold excess of allyltrichlorosilane is used. In addition, multi-step alkylation reactions give the trialkylated products in higher yields than the one-step reaction.

In the reaction with ferrocene,[30] allyldimethylchlorosilane reacts at $0\,^{\circ}$C, allyl-(methyl)dichlorosilane reacts at the reflux temperature of methylene chloride, but allylsilanes containing two or more chlorine substituents at the silicon do not give alkylation products. In alkylations of ferrocene, allyldimethylchlorosilane shows the highest activity, allyl(methyl)dichlorosilane is less reactive, and allylsilanes containing two or more chlorine-substituents at the silicon have no activity.[25] Allyl-trimethylsilane reacts with both benzene and ferrocene to give allylsilylation products but no alkylation product.[1b,2,25]

The reaction of ferrocene with allylchlorosilanes in the presence of Lewis acid in methylene chloride solvent affords alkylated ferrocenes bearing chlorosilyl groups at the carbon β to the ferrocene ring [Eq. (16)].[25]

$$\text{(16)}$$

$R^1 = R^2 = $ Me : $n = 1$ (76%), 2 (4%), $m = 0$

$R^1 = $ Me, $R^2 = $ Cl : $n = 1$ (82%), $m = 0$

$R^1 = i$-Pr, $R^2 = $ Cl : $n = 1$ (84%), $m = 0$

$R^1 = n$-Hx, $R^2 = $ Cl : $n = 1$ (90%), $m = 0$

$R^1 = $ Cl, $R^2 = $ H or Cl : $n = 1$ (trace), $m = 0$

The reactivity of allylchlorosilanes for the alkylation of ferrocene varies depending upon the substituents on the silicon atom. Generally, the reactivity increases as the number of alkyl groups on the silicon of allylsilanes increases.[4] Allyl(dialkyl)-chlorosilanes react with ferrocene in the presence of HfCl$_4$ under mild reaction
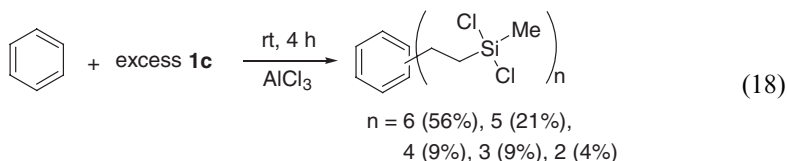
conditions to give alkylated products, (2-silyl-1-methylethyl)ferrocenes, in good yields, while allyl(alkyl)dichlorosilanes give alkylated products at slightly higher temperatures. Allylsilanes fully substituted with alkyl groups on silicon undergo decomposition reactions rather than alkylation in the presence of hafnium chloride catalyst, while allyltrichlorosilane and allyldichlorosilane exhibit little reactivity. The reactivity of allylsilanes for the alkylation of ferrocene decreases in the following order: allyldialkylchlorosilane > allyl(alkyl)dichlorosilane ≫ allyldichlorosilane ≈ allyltrichlorosilane.[25] The catalytic efficiency of Lewis acids for the alkylation decreases in the following order: hafnium chloride > zirconium chloride > aluminum chloride > aluminum bromide.[25] Titanium(IV) chloride shows no catalytic activity for the alkylation of ferrocene. In the alkylation of ferrocene, the catalytic activity of aluminum chloride decreases, accompanied with a coloration to green-blue as the reaction proceeds. Eventually the alkylation reaction stops, with a deep-blue color present when high reaction temperatures are used. Complex formation of aluminum chloride with ferrocene is responsible for the deactivation of catalytic activity.[30] Generally, the abilities of Lewis acids to form complexes with ferrocene increase as the acidity of the Lewis acid increases. It is well documented that ferrocene can be oxidized and converted by most common electrophiles into a ferrocenium cation, which is reluctant to undergo electrophilic substitution.[31] These results indicate that both Friedel–Crafts alkylation with allylchlorosilanes and complexation with Lewis acids are competing reactions in the aluminum chloride-catalyzed alkylation of ferrocene.[31]

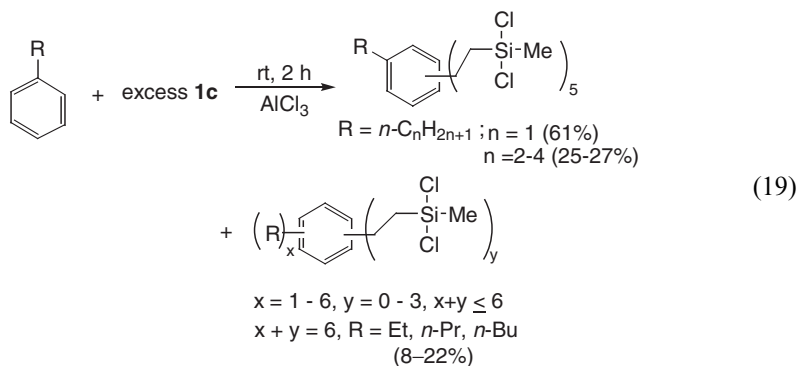## B. *Alkylation with Vinylchlorosilanes*

Vinylchlorosilanes undergo Friedel–Crafts alkylation with aromatic compounds in the presence of Lewis acids to give 2-(chlorosilyl)ethylarenes [Eq. (17)].[1b,32,33] The reactivity of vinylchlorosilanes for the alkylation of aromatic compounds is slightly lower than that of allylchlorosilanes.[1b,3,32] The reactivity of vinylsilanes for alkylation depends on the substituents on the silicon of the vinylsilane. The reactivity of vinylchlorosilanes decreases in the following order: dichloro(methyl)vinylsilane > trichlorovinylsilane > chloro(dimethyl)vinylsilane. The alkylation of monosubstituted benzenes such as toluene, chlorobenzene, and biphenyl with dichloro(methyl)vinylsilane (**1c**) at 75–80 °C for 2 h affords alkylated products in 50–63% yields.[32]

$$R = Cl, Me, Ph, etc.$$
$$X_3 = Cl_3, MeCl_2, Me_2Cl$$

(17)
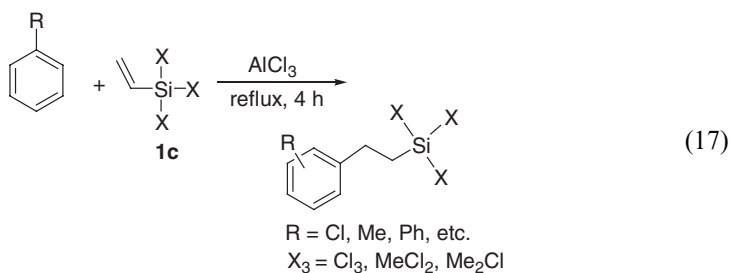
When benzene reacts with a six-fold excess of **1c** in the presence of aluminum chloride at room temperature, the peralkylated product,[34] hexakis[2-(di-chloromethylsilyl)ethyl]benzene is obtained as the major component along with other lower polyalkylated products: pentakis-, tetrakis-, tris-, and bis[2-(di-chloromethylsilyl)ethyl]benzene.

$$\text{benzene} + \text{excess } \textbf{1c} \xrightarrow[\text{AlCl}_3]{\text{rt, 4 h}} \text{product} \left(\overset{Cl}{\underset{Cl}{Si}} \text{-Me} \right)_n \tag{18}$$

n = 6 (56%), 5 (21%),
4 (9%), 3 (9%), 2 (4%)

In the peralkylation of alkylbenzenes with **1c** in the presence of aluminum chloride catalyst,[35] both polyalkylation and transalkylation reactions occur in competition. Peralkylation product yields decrease as the chain length of the alkyl substituent on the benzene ring increases. Toluene reacts with five equivalents of **1c** in the presence of aluminum chloride at room temperature for 2 h to give pentakis[2-(dichloromethylsilyl)ethyl]toluene as the major product in addition to less alkylated products: tetrakis-, tris-, bis-, and mono[2-(dichloromethylsilyl)ethyl]toluene. The peralkylation of alkylbenzenes having longer alkyl groups such as ethyl, n-propyl, and n-butyl, with **1c** gives the peralkylated products in low yields (about 25%) in addition to transalkylation products.

$$\tag{19}$$

R = n-C$_n$H$_{2n+1}$; n = 1 (61%)
n = 2-4 (25-27%)

x = 1 - 6, y = 0 - 3, x+y $\leq$ 6
x + y = 6, R = Et, n-Pr, n-Bu
(8–22%)

The reaction of ethylbenzene with five equivalents of **1c** under the same alkylation conditions used for toluene, gives pentakis- (25%), tetrakis- (9%), tris- (4%), and bis[2-(dichloromethylsilyl)ethyl]ethylbenzene (1%) as well as a mixture of many transalkylated products (44%). It is of interest that longer alkyl-substituted benzenes exhibited different behavior in peralkylations with **1c**. The transalkylation of ethylbenzene is responsible for the significantly low yield (25%) of peralkylation product in comparison with yields obtained from the alkylation of benzene[34] or toluene. Peralkylation of n-propylbenzene and n-butylbenzene gives similar results to those of ethylbenzene.

The reaction of o-, m-, or p-xylene with four equivalents of **1c** affords an isomeric mixture of peralkylated xylenes consisting of tetrakis[(dichloromethylsilyl)ethyl]-xylenes and isomeric transalkylation products. With longer reaction times and

higher temperatures, the formation of tetrakis[(dichloromethylsilyl)ethyl]-*p*-xylene is favored due to less steric hindrance between the substituents on benzene.

Peralkylation of mesitylene with **1c** gives only rearranged products without transalkylated products. The undesirable isomerization of 2,4,6-tris(di-chloromethylsilylethyl)mesitylene to the 3,5,6- or 4,5,6-isomers can be avoided by carrying out the reaction in hexane at room temperature. In this case, the peralky-lated product, 2,4,6-tris[2-(dichloromethylsilyl)ethyl]mesitylene, is obtained in 38% yield along with mono- and bis-alkylated mesitylenes in 7% and 37% yields, re-spectively. No rearranged products are formed.

Friedel–Crafts-type polyalkylations of alkyl-substituted benzenes with **1c** become less difficult as the number of electron-donating methyl groups on the benzene ring increases. This is consistent with the fact that the alkylation occurs via an electro-philic substitution. The tendency of starting methylbenzenes to form rearranged products also increases in the same order from toluene to mesitylene.
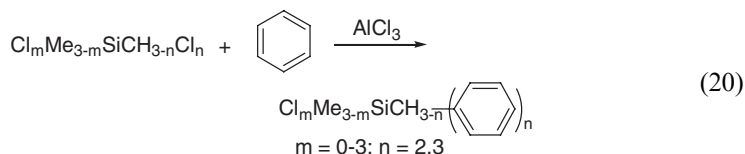
The alkylation of substituted benzenes possessing electron-withdrawing groups, such as chlorobenzene and anisole, with **1c** gives only mono-, bis-, and tris-alkylated compounds. No peralkylated products are obtained even when heating the reaction mixtures for long periods. These results can be explained by the de-activation effects of the electron-withdrawing substituents and the complexation between $AlCl_3$ catalyst and the lone pairs of electrons of the substituents.

C. *Alkylation with (ω-Chloroalkyl)chlorosilanes*

The Friedel–Crafts alkylation of benzene with (ω-chloroalkyl)chlorosilanes ($Cl_mMe_{3-m}Si(CH_2)_n$-Cl, $m = 0$–3; $n = 1$–3) in the presence of aluminum chloride gives ω-(chlorosilyl)alkylbenzenes.[1b,4] The reactivities of (chloroalkyl)silanes de-pends on the substituents on silicon and the alkyl chain length between C–Cl and silicon. In the case of (chloromethyl)silanes ($Cl_mMe_{3-m}SiCH_2Cl$), the reactivity decreases as the number (m) of chlorine substituent(s) on the silicon atom increases. (Chloromethyl)trichlorosilane ($m = 3$) requires a reaction temperature of 200 °C for the alkylation of benzene in a sealed tube. Alkylation with (chloromethyl)methyl-dichlorosilane ($m = 2$) or (chloromethyl)dimethylchlorosilane ($m = 1$) at 80 °C af-fords benzyl(methyl)dichlorosilane in 71% yield and a 1:1 mixture of benzyl(methyl)dichlorosilane (demethylation product) and benzyldimethylchloro-silane in 41% yield. In the case of (chloromethyl)trimethylsilane ($m = 0$), reaction proceeds at room temperature to give trimethylchlorosilane and toluene, derived from the protodesilylation of the benzyltrimethylsilane product by hydrogen chlo-ride.[4] Generally, electron-withdrawing chlorine substituent on the silicon atom of (chloromethyl)silanes deactivate the alkylation, while methyl groups facilitate the alkylation[3,4] and the subsequent decomposition of products. In the alkylation of benzene with (ω-chloroalkyl)trichlorosilanes in the presence of aluminum chloride, the spacer length between C–Cl and the silyl group plays an important role. Al-kylation proceeds under milder conditions as the spacer length increases. Thus, reaction temperatures decrease from 200 °C for (chloromethyl)silane to room tem-perature for (β-chloroethyl)silane and (γ-chloropropyl)silane.[4]
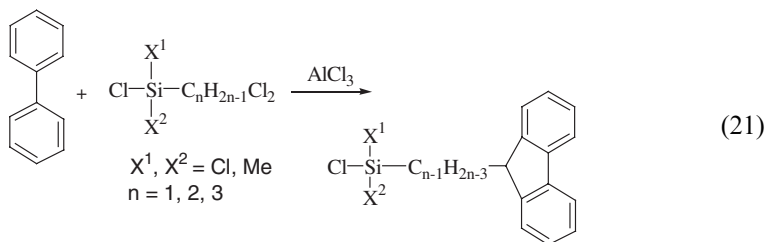
D. Alkylation with (Polychloroalkyl)chlorosilanes

(Polychloromethyl)silanes ($Cl_mMe_{3-m}SiCH_{3-n}Cl_n$, $m = 0$–3; $n = 2, 3$) react with excess benzene in the presence of aluminum chloride to give (polyphenylmethyl)-silanes [Eq. (20)].[14] Such reactions occur at temperatures ranging from room temperature ($m = 0, 1$; $n = 2$) to 80 °C ($m = 2, 3$; $n = 2, 3$), indicating that the reactivity increases as the number (m) of electron-donating chlorine groups on silicon decreases. In particular, (dichloromethyl)silanes having two or three methyl groups at the silicon ($m = 0$ or 1; $n = 2$) undergo alkylation and decomposition reactions of their products at room temperature. Alkylation with (dichloromethyl)trimethyl-silane ($m = 0$) occurs immediately at room temperature to give diphenylmethane and trimethylchlorosilane, but not (diphenylmethyl)trimethylsilane due to decomposition of the alkylation product. (Trichloromethyl)silanes ($m = 2, 3$; $n = 3$) react with excess benzene to give (triphenylmethyl)silanes as major products and the unexpected (diphenylmethyl)silanes as minor products. The (diphenylmethyl)silanes are formed by the decomposition of (triphenylmethyl)silanes under the reaction conditions. In the alkylation of benzene, the reactivity of (polychloromethyl)silanes ($Cl_mMe_{3m}SiCH_{3n}Cl_n$: $m = 0$–3; $n = 2, 3$) decreases in the following order: $m = 0 > 1 > 2 > 3$; $n = 3 > 2$.[14]

$$Cl_mMe_{3-m}SiCH_{3-n}Cl_n \ + \ \ \bigcirc \ \ \xrightarrow{AlCl_3}$$

$$Cl_mMe_{3-m}SiCH_{3-\overline{n}}\left(\!\!\left\langle\!\!\bigcirc\!\!\right\rangle\!\!\right)_n \tag{20}$$

$$m = 0\text{-}3;\ n = 2,3$$

Friedel–Crafts alkylation reactions of biphenyl with (dichloroalkyl)chlorosilanes [$Cl_mMe_{3-m}Si(C_nH_{2n-1}Cl_2)$, $m = 0$–3, $n = 2, 3$] at temperatures ranging from 120 to 160 °C in the presence of Lewis acid catalyst give cyclized products, fluorenyl-substituted chlorosilanes, in 47–94% yields [Eq. (21)].[36] When (dichloro-methyl)trichlorosilane reacts with a two-fold excess of biphenyl in the presence of aluminum chloride catalyst at 160 °C for 1 h, 9-(trichlorosilyl)fluorene is obtained in 91% yield. Reaction with (dichloromethyl)trichlorosilane at 120 °C for 1 h gives the cycloalkylation product in 94% yield. Under similar reaction conditions, (1,2-di-chloroethyl)chlorosilanes afford 9-(chlorosilylmethyl)fluorenes in 35–47% yields and (2,3-dichloropropyl)dichlorosilane gives 9-(2-(trichlorosilyl)ethyl)fluorene in 48% yield. These results can be rationalized in terms of the stability,[4] ease of 1,2-migration, and electrophilic addition to biphenyl of the carbocation intermediates generated by the complexation of (dichloroalkyl)chlorosilanes (alkyl = ethyl and propyl) with aluminum chloride. In these reactions, the reactivities of (di-chloroalkyl)silanes generally increase as the number of methyl groups on the silicon atom and the alkyl chain lengths increase. However, desilylation of the alkylated products and starting chlorosilanes is observed in the case of (dichloroalkyl)silanes having two or more methyl groups on silicon. Alkylation with (dichloromethyl)dimethylchlorosilane proceeds at 120 °C but gives fluorene and dimethyldichlorosilane, resulting from desilylation of the products. The reactivities of (dichloroalkyl)silanes decrease in the following order: $m = 0 > 1 > 2$; $n = 2 > 1$.

The catalytic efficiencies of Lewis acids for the cycloalkylation reactions decrease in the following order: $AlCl_3 > AlBr_3 > HfCl_4 > ZrCl_4 \gg TiCl_4$.[36]


$$(21)$$

Known alkylation reactions of aromatic compounds with organosilicon compounds have been summarized in this review. A variety of chlorosilanes containing alkenyl and chloroalkyl groups can be used for the alkylation of aromatic compounds to afford the corresponding chlorosilyl-containing aromatic compounds. Such organosilicon compounds containing Si–Cl functionality are useful starting materials for the silicone industry.

V

HYDROSILYLATION REACTION WITH TRIORGANOSILANES

Triorganosilanes (R_3SiH) undergo hydrosilylation with unsaturated hydrocarbons in the presence of Lewis acids. The $AlCl_3$-catalyzed reaction[37,38] has received relatively little attention due to the strong catalytic activity of $AlCl_3$ for the polymerization of unsaturated hydrocarbons.[39,40] Hydrosilylations of alkenes and alkynes with chlorodialkylsilanes in the presence of $AlCl_3$ were first reported by Finke and Moretto[37a] in 1979, and later by Oertle and Wetter.[37b] In 1990, Yamamoto and Takemae studied the reaction of 1-methylcyclohexene with chlorodimethylsilane in the presence of $AlCl_3$ catalyst and found that hydrosilylation proceeded stereoselectively in a *trans*-addition manner.[38] Voronkov and co-workers[41] reported the hydrosilylation of alkynes and olefins with triethylsilane in the presence of a mixed catalytic system consisting of H_2PtCl_6 and $AlCl_3$.

The hydrosilylation of alkenes with trialkylsilanes in the presence of Lewis acid catalysts under mild conditions gives the corresponding (trialkylsilyl)alkanes [Eq. (22)]. Reaction with terminal alkenes such as 1-hexene and 1-dodecene at room temperature gives hydrosilylation products in 57 and 58% yields, respectively. Reactions with activated styrene derivatives such as styrene, *p*-chlorostyrene, and α-methylstyrene at −20 °C afford hydrosilylated products in 55–61% yields.[36]

$$(22)$$
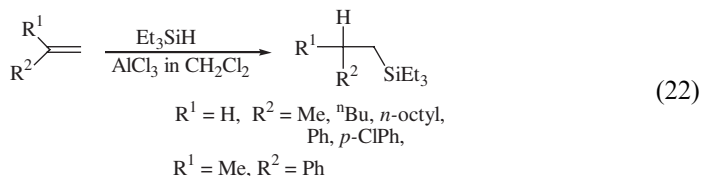
Cycloalkenes such as cyclohexene, 1-methylcyclohexene, cyclopentene, and nor-bornene are hydrosilylated with triethylsilane in the presence of aluminum chloride catalyst in methylene chloride at 0 °C or below to afford the corresponding hydro-silylated (triethylsilyl)cycloalkanes in 65–82% yields [Eq. (23)]. The reaction of 1-methylcyclohexene with triethylsilane at −20 °C occurs regio- and stereoselectively to give *cis*-1-triethylsilyl-2-methylcyclohexane *via* a *trans*-hydrosilylation pathway. Cycloalkenes having an alkyl group at the double-bonded carbon are more reactive than non-substituted compounds in Lewis acid-catalyzed hydrosilylations.[36]

$$ \text{(23)} $$
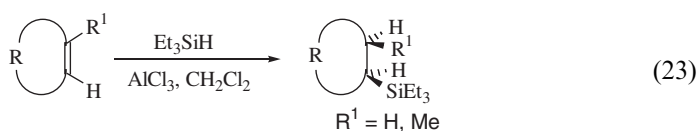
In these hydrosilylation reactions, the reactivity and product yields decrease as the bulk of the triorganosilane increases. The catalytic reactivity of Lewis acids decreases in the following order: $AlBr_3 > AlCl_3 > HfCl_4 > EtAlCl_2 > ZrCl_4 > TiCl_4$.[36] When triorganochlorosilane is used as an activator in the aluminum chloride-catalyzed reaction, the hydrosilylation rate drastically increases. The results are consistent with a stepwise reaction proceeding *via* the formation of a tri-alkylsilylenium ion intermediate.

Other Lewis acid-catalyzed hydrosilylations of alkenes and alkynes on hydride-terminated silicon surfaces result in a surface modified with alkyl and alkenyl functionalities.[42]

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