ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 605 (2000) 239–245

Journal of Organometallic Chemistry

Effect of the substituents at the silicon of (ω-chloroalkyl)silanes on the alkylation to benzene

Bok Ryul Yoo [a],*, Jeong Hyun Kim [a], Ho-Jin Lee [b], Kang-Bong Lee [b], Il Nam Jung [a]

[a] *Organometallic Chemistry Laboratory, Korea Institute of Science and Technology, PO Box 131, Cheongryang, Seoul 130-650, South Korea*
[b] *Advanced Analysis Center, Korea Institute of Science and Technology, PO Box 131, Cheongryang, Seoul 130-650, South Korea*

Received 29 February 2000; received in revised form 17 April 2000; accepted 25 April 2000

Abstract

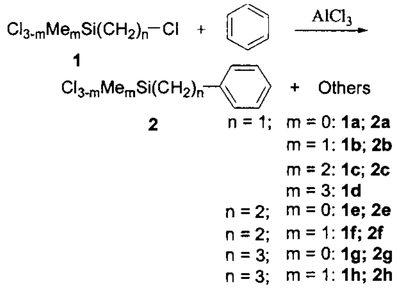
(ω-Chloroalkyl)silanes [$Cl_{3-m}Me_mSi(CH_2)_n$–Cl: $m = 0$–3, $n = 1$–3] underwent Friedel–Crafts alkylation with benzene in the presence of aluminum chloride to give alkylated products. Such alkylation reactions took place at temperatures ranging from room temperature ($m = 0$–1, $n = 2$, 3; $m = 3$, $n = 1$) to 80 ($m = 1$, 2; $n = 1$) and 200°C ($m = 0$; $n = 1$), depending on the substituent(s) of the silicon and the alkylene-chain spacer between the silicon and C–Cl bond of (ω-chloroalkyl)silanes. In the alkylation to benzene, the reactivities of (ω-chloroalkyl)silanes increase as the number (m) of methyl-group(s) at the silicon and the alkylene length between the silicon and C–Cl bond increases. While decomposition of alkylation products was observed at two more methyl groups substituted at silicon in the cases of (chloromethyl)silanes such as (chloromethyl)dimethylchlorosilane and (chloromethyl)trimethylsilane. The reaction with (chloromethyl)trimethylsilane occurred at room temperature to give trimethylchlorosilane, toluene and xylene via a decomposition reaction of the products. No (trimethylsilylmethyl)benzene was formed. In the alkylation to benzene, the reactivity of (ω-chloroalkyl)silanes decreases in the following order: $m = 3 > 2 > 1 > 0$; $n = 3 > 2 \gg 1$. The results are consistent with the stability of the carbocation generated by the complexation of (ω-chloroalkyl)silanes with aluminum chloride.

Keywords: Alkylation; Friedel–Crafts alkylation; Alkylation to benzene; (ω-Chloroalkyl)silanes; Lewis acid; Aluminum chloride

---

1. Introduction

Friedel–Crafts alkylations catalyzed by Lewis acid have for a long time [1,2] been widely used and are an established route for the introducing of alkyl substituent to aromatic rings both in the laboratory and in the petrochemical industry. While the alkylations with silicon compounds [3] such as alkenylchlorosilanes [4–7] and (chloroalkyl)chlorosilanes [8–11] attracted relatively little attention in this field because of the limits of the syntheses and separation of alkenylchlorosilanes [12,13] and (chloroalkyl)chlorosilanes [14,15], even though organylchlorosilanes such as methylchlorosilanes, vinylchlorosilanes, phenylchlorosilanes, etc. are used as starting materials in the silicone industry. Some benzene derivatives containing the Si–Cl functionality synthesized by alkylation with the limited (chloroalkyl)chlorosilanes such as (ω-chloroalkyl)methyldichlorosilanes and (ω-chloroalkyl)trichlorosilanes were reported [8–11], but the details of the alkylations have not been reported. We have studied the Friedel–Crafts alkylation of benzene with alkenylsilanes such as allylchlorosilanes [16] and vinylchlorosilanes [17,18] in the presence of aluminum chloride and have



Scheme 1.

---

* Corresponding author. Tel.: +82-2-9585087; fax: +82-2-9585089.
E-mail address: bryoo@kist.re.kr (B.R. Yoo).

0022-328X/00/$ - see front matter
PII: S0022-328X(00)00319-3

Table 1
Reaction conditions of benzene with (ω-chloromethyl)silanes (**1a**–**d**) and alkylation products

Silane 1 (unreacted)		Reaction conditions [a]		Alkylation products (%)	
		Temperature (°C)	Time (h)	**2**	di-
1a	55	200	20	**2a**, 31	
	99	80	20		
1b	10	80	16	**2b**, 71	13
1c [b]		80	3	**2b**, 18	1
				2c, 22	
1d		r.t.	4	Other products [c]	

[a] The reaction was carried out in the presence of 20 mol% aluminum chloride catalyst.

[b] Decomposition products, **2c** (22%), dimethyldichlorosilane (25%), and toluene (15%), also were obtained.

[c] Toluene and trimethylchlorosilane as major products were obtained along with a small amount of xylene.

extended the alkylations of (ω-chloroalkyl)chlorosilanes to aromatic compounds, eventually making multifunctionalized compounds with Si–Cl bonds as shown in the polyalkylation with vinylsilanes [17,18]. As basic research for a systematic study on the alkylation with (ω-chloroalkyl)silanes, simple benzene, as a representative among aromatic compounds, reacted with various (ω-chloroalkyl)silanes ($Cl_{3-m}Me_mSi(CH_2)_n$–Cl: $m = 0$–3; $n = 1$–3) in the presence of aluminum chloride catalyst. In this paper, we wish to report in detail the activation effect of the C–Cl bond of (ω-chloroalkyl)silanes by $AlCl_3$ catalyst on the substituents at the silicon and on the alkylene-chain spacer between C–Cl and the silicon in this alkylation to benzene.

2. Results and discussion

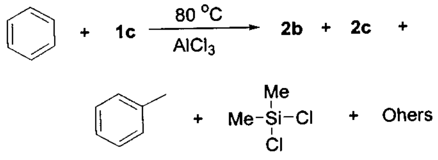
(Chloroalkyl)chlorosilanes ($Cl_{3-m}Me_mSi(CH_2)_n$–Cl: $m = 0$–2; $n = 1$–3) undergo the Friedel–Crafts alkylation with benzene in the presence of aluminum chloride catalyst to give (ω-silylalkyl)benzenes containing an Si–Cl bond as a useful functionality (Scheme 1). In these reactions, the alkylation reactivities of (ω-chloroalkyl)benzenes depend on the substituents at silicon and the alkyl-chain length between C–Cl and silicon. Both effects were estimated by experimental and simple computer calculation studies.

2.1. Effect of substituents at silicon on the alkylation of (chloromethyl)silanes to benzene

To study the effect of substituents at the silicon of (ω-chloroalkyl)silanes on the Friedel–Crafts alkylation, the alkylation to benzene was carried out by varying the substituents at the silicon of simple (chloromethyl)silanes ($Cl_{3-m}Me_mSiCH_2Cl$ (**1a**), $m = 0$; **1b**, $m = 1$; **1c**, $m = 2$; **1d**, $m = 3$) in the presence of aluminum chloride. In this reaction, a 10-fold excess of benzene with respect to **1** was used in each experiment to reduce the formation of dialkylated compounds. These results are summarized in Table 1.

As shown in Table 1, the alkylation reactivity of (chloromethyl)silanes ($Cl_{3-m}Me_mSiCH_2Cl$) to benzene increases as the number of methyl-substituent(s) at the silicon of (chloromethyl)silanes increase, depending on the substitutents at the silicon atom. In particular, **1a** substituted with all chloro-groups at the silicon reacted with benzene under drastic conditions, the high temperature of 200°C in a sealed stainless steel tube, to afford the alkylated product. After a 20 h reaction period, only 49% of **1a** was consumed to give **2a** in 31% yield. But the alkylation reaction with **1a** was not observed at an 80°C reaction temperature described in the literature [9]. The alkylation reactions with **1b** and **1c** occurred at 80°C to afford **2b** in 71% yield and a 1:1 mixture of **2b** and **2c** in 61% yield, respectively. In the case of **1d**, the reaction occurred at room temperature to give trimethylchlorosilane, toluene, and xylene (trace) which would be expected to be formed by the decomposition of (trimethylsilylmethyl)benzene, and (trimethylsilylmethyl)toluene. These results indicate that the electron-withdrawing chloro group(s) at the silicon of (chloromethyl)silanes deactivate the alkylation, while the electron-donating methyl group(s) facilitate it [16,19] and also the decomposition reaction. The effect of the substituents at the silicon of (chloromethyl)silanes on the alkylation to benzene can be rationalized in terms of the stability of the carbocation intermediate [20], generated by the reaction of (chloromethyl)silanes with aluminum chloride, attacking benzene electrophilically.

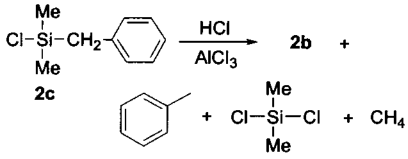
In the alkylation with (chloromethyl)silanes, **1c** and **1d**, substituted with two more methyl-groups at silicon, unexpected products, toluene, xylene, and chlorosilanes, were obtained. In the case of the reaction with **1c**, both alkylation products of normal **2c** and unexpected **2b** were obtained along with decomposed products, dimethyldichlorosilane, toluene, xylene, etc. (Scheme 2).



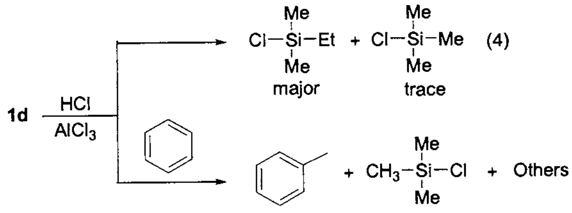
Scheme 2.

Reaction pathway to these unusual products whether coming from the decomposition of an alkylation product or starting material was investigated. In detail, the reaction of benzene with **1b** in the presence of 20 mol% aluminum chloride at 80°C was monitored at various reaction times using GLC. In this reaction, the distributions of both alkylation products, **2b** and **2c**, were summarized along with those of the decomposed products, dimethyldichlorosilane and toluene in Table 2.

As shown in Table 2, when the reactant **1c** consumed from 57% in 1 h reaction to 100% in 3 h reaction, unexpected product **2b** increases from 8 to 18%, while normal alkylation product **2c** decreases from 24 to 22%. In this reaction, the decomposed products, dimethyldichlorosilane and toluene, increase from 11 and 9 to 22 and 18%, respectively. The results suggest that the alkylation product **2c** is initially formed by the reaction of benzene with **1c** and is consumed to give an unexpected **2b**, toluene, dimethyldichlorosilane, etc. To clarify the formation pathway of **2b** in this reaction, reactant **1c** and product **2c** in the presence of aluminum chloride catalyst at room temperature were stirred in the presence and the absence of HCl gas, respectively. In these reactions, the reactant **1c** remained without decomposition after 1 h in both cases and compound **2c** was decomposed to give **2b**, toluene, and dimethyldichlorosilane in the presence of HCl gas, but also to give trace amounts of those in the absence of HCl (Scheme 3). These results suggest that compound **2c** reacted with HCl in the presence of aluminum chloride to give **2b**, toluene, and dimethyldichlorosilane involving the cleavage reaction of Si–C bonds between both benzyl and methyl groups at silicon by HCl attack in competition.



Scheme 3.



Scheme 4.

In the case of the reaction with **1d**, the decomposed products, trimethylchlorosilane and toluene, were observed predominantly along with a trace of xylene without an expected alkylation product, benzyltrimethylsilane (**2d**). To investigate the reaction pathway for the formation of decomposed products compounds **1d** and **2d** were stirred in the presence and the absence of HCl at room temperature in the presence of aluminum chloride catalyst, respectively. In these reactions, **1d** was converted to ethyl(dimethyl)chlorosilane (major) [21] and trimethylchlorosilane (trace) in the absence and the presence of HCl (Scheme 4) and **2d** in the presence of HCl was decomposed to give toluene, trimethylchlorosilane, and **2c** (small amount). It is suggested that such decomposed products were obtained from the cleavage of benzylic carbon–silicon and methyl carbon–silicon bonds at the alkylation products by the attack of HCl formed in the presence of aluminum chloride. For preparation of the expected alkylation compounds, (chloromethyl)silanes are required to have at least two chlorine groups at silicon, indicating that the substituents at the silicon of (chloromethyl)silanes play a key role in the synthesis of (silylmethyl)benzenes using the Friedel–Crafts alkylation method.

Table 2
Product distribution in the reaction of benzene with **1c** [a]

Reaction time (h)	Reactant	Products			
	1c	**2b**	**2c**	Me_2SiCl_2 [b]	Others
1	43	9	29	13	
2	11	20	32	26	
3	0	23	28	30	Trace [c]

[a] The reaction was carried out at 80°C in the presence of 20 mol% aluminum chloride.

[b] Toluene was obtained as a major product in 75–82 mol% with respect to Me_2SiCl_2 among decomposition products in three cases.

[c] Dialkylated products were observed in GLC–MS analysis.

2.2. Effect on alkylene-chain length between the C–Cl bond and silicon in the alkylation of (ω-chloroalkyl)silanes to benzene

To study the effect of the alkylation reactivity on the alkylene-chain length between the C–Cl bond and the silicon at (chloroalkyl)silanes, (ω-chloroalkyl)silanes such as (chloromethyl)silanes, (chloroethyl)silanes, and (chloromethyl)silanes were tested. In this study, (ω-chloroalkyl)silanes substituted with two or more chloro-groups at the silicon [$Cl_{3-m}Me_mSi(CH_2)_nCl$: $m=0$, $n=2$ (**1e**); $m=1$, $n=2$ (**1f**); $m=0$, $n=3$ (**1g**); $m=1$, $n=3$ (**1h**)] as representative were used restrictively because of the unexpected decomposition of alkylation compounds formed by the reaction with (chloromethyl)silanes containing one or no chloro-group at the silicon above and compared with (chloromethyl)silanes **1a**,b. (ω-Chloroalkyl)chlorosilanes **1e**–**h** reacted with 10-fold excess of benzene in the presence of aluminum chloride catalyst. The results obtained from the reaction with **1e**–**h** are summarized in Table 3.

As shown in Table 3, the alkylation of benzene with (ω-chloroalkyl)trichlorosilanes, **1e** and **1g**, containing methylene or ethylene as a spacer between C–Cl and the silicon, respectively, occurred at much lower temperature (room temperature) than at 200°C for that with **1a** in a series of (ω-chloroalkyl)trichlorosilanes. In a series of (ω-chloroalkyl)trichlorosilanes such as **1a**, **1e**, and **1g**, the alkylation reactivity of **1e** is slightly less than that of **1g**, but is much higher than that of **1a**, indicating that (ω-chloroalkyl)silanes such as (2-chloroethyl) (**1e**) and (3-chloropropyl)silane (**1g**) are affected little by the electronic nature of the silyl-group in their reactivity to alkylation. The alkylation reaction with (2-chloroethyl)chlorosilanes **1e** and **1f** under mild conditions afforded (2-silylethyl)benzenes **2e** and **2f** in 88 and 91% yields, respectively. In the case of both 3-chloropropylchlorosilanes **1g** and **1h**, the normal alkylation products, [3-(silyl)propyl]benzenes **2g** and **2h**, were obtained in 89 and 80% yields along with [1-methyl-2-(silyl)ethyl]benzenes (**2g**′ and **2h**′) as minor products in 2 and 13% yields, respectively. The formation of [1-methyl-2-(silyl)ethyl]benzenes as minor products from the reactions with **1g** and **1h** can be rationalized in terms of the stability of carbocation intermediates which a primary carbocation generated from the complexation of (3-chloropropyl)silanes with aluminum chloride is rearranged to a more stable secondary carbocation at β-carbon to the silicon [10]. In the alkylation reaction of both (3-chloropropyl)silanes **1g** and **1h** to benzene, **1g** substituted all chloro-groups to the silicon was shown to be more selective than **1h** for the formation of (3-silylpropyl)benzene, implying that the production of isomeric compounds can be affected by the substituents on the silicon of (3-chloropropyl)silanes. It seems likely that the methyl-substituent at the silicon of **1h** facilitates the rearrangement of the primary carbocation to the secondary carbocation in the $AlCl_3$-catalyzed reaction compared with **1g** facilitated by the σ–π interaction between the Si–C bond and the secondary-carbocation as observed in other alkylation [3,16,22] and allylsilylation reactions with allylsilanes [23,24].

Table 3
Reaction conditions of benzene with **1e–h** and alkylation products

Silane	Reaction conditions [a]		Alkylation products (%)	
	Temperature (°C)	Time (h)	**2**	Others
1e	r.t.	1.5	**2e** (88)	–
1f	r.t.	1	**2f** (91)	**2** [b]
1g	r.t.	1	**2g** (89)	**2g**′ (2) [c]
1h	r.t.	1	**2h** (80)	**2h**′(13) [d]

[a] The reaction was carried out in the presence of 20 mol% aluminum chloride catalyst.

[b] Bis[(methyldichlorosilyl)methyl]benzenes.

[c] **2g**′ is [2-(methyldichlorosilyl)ethyl]benzene an isomeric product.

[d] **2h**′ is [1-methyl-2-(methyldichlorosilyl)ethyl]benzene as an isomeric product.

2.3. Approximate calculation of the substituent effect at the silicon of (chloroalkyl)silane for the activation energy of the C–Cl bond catalyzed by $AlCl_3$

To estimate the activation effect of the C–Cl bond on the substituents at the silicon of (ω-chloroalkyl)silanes in the alkylation to benzene, the following four-step reaction pathway from the starting material **1** to the product is considered. First, the C–Cl bond of (chloroalkyl)silane **1** interacts with the aluminum chloride catalyst to afford a **1**–$AlCl_3$ complex which is generated to give a carbocation intermediate ($C^{+}\cdots{}^{-}ClAlCl_3$) as an ionic pair [25]. This carbocation intermediate electrophilically attacks the benzene ring to generate a benzenonium ion intermediate, which eventually gives alkylated benzene through deprotonation by the aluminum tetrachloride anion. Finally the hydrogen aluminum tetrachloride complex affords aluminum chloride and hydrogen chloride. In this mechanism, the carbocation intermediate generation step is considered to simplify the calculation even though it should not be ruled out that the **1**–$AlCl_3$ complex generated in the first step may interact directly with benzene to give the benzenonium ion intermediate [1,26]. In such an assumption, the stability of the carbocation intermediate generated affected by the substituents at the silicon of (chloroalkyl)silanes. The activation energy of the C–Cl bond by $AlCl_3$ at the variation of methyl- and chloro-substituent(s) at the silicon of (ω-chloroalkyl)silanes was estimated by

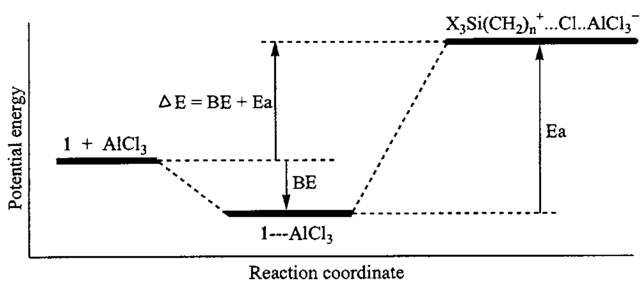


Fig. 1. Potential energy diagram for the activation of **1** by $AlCl_3$.

Table 4
The binding energy (BE) [a] and the reaction activation energy (E_a) [b] of (ω-chloroalkyl)silane with $AlCl_3$ and the energy sum (ΔE) [c] of BE and E_a at the HF/6-31G* level of theory [d]

1	BE (kcal mol^{-1})	E_a (kcal mol^{-1})	ΔE (kcal mol^{-1})
H_3SiCH_2–Cl	−9.2	34.9	25.6
1a	−5.6	44.6	39.0
1b	−7.0	36.2	29.2
1c	−8.5	30.5	22.0
1d	−11.3	30.6	19.3
1e	−7.5	26.3	18.7

[a] BE is an energy difference between the sum of the reactant **1** and $AlCl_3$ and the **1**–$AlCl_3$ complex.

[b] E_a is an energy difference between the **1**–$AlCl_3$ complex and the carbocation intermediate.

[c] ΔE is an energy sum of the sum of the reactant **1** and $AlCl_3$ and the carbocation intermediate.

[d] All calculations included the zero-point energy scaled by 0.9315.

means of ab initio MO SCF calculation using GAUSSIAN-94 software [27]. All possible geometries of (ω-chloroalkyl)silane, $AlCl_3$ and their reactant interaction complexes, and carbocation intermediates [28] were examined at the HF/3-21G level [29] and the stable conformers were selected. The selected conformers were reoptimized at the HF/6-31G* level [30]. The potential energies of the reactants **1a**–**e**, $AlCl_3$ catalyst, the interaction complexes of **1a**–**e** with $AlCl_3$, and the formations of carbocation intermediates were calculated and compared to the substituent contribution to C–Cl bond activation at **1a**–**e** in Fig. 1. The data of calculated energies for the reactants **1a**–**e**, catalyst $AlCl_3$, the complexes of **1a**–**e** with $AlCl_3$, and the formation of the carbocation intermediate are summarized in Table 4.

As shown in Table 4, the energy difference (BE) between the complex **1**–$AlCl_3$ and the sum of **1** and $AlCl_3$ and the energy difference (E_a) between the complex **1**–$AlCl_3$ and the ionic pair intermediate decrease as the number of methyl-group(s) at the silicon among **1a**–**d** increases indicating that the methyl-group as electron donor facilitate the C–Cl bond activation by $AlCl_3$. The activation of the C–Cl bond of **1a** is required for the highest energy in the $AlCl_3$-catalyzed alkylation among **1a**–**e**. The activation of the C–Cl bond of **1e**, which contains the methylene spacer between the C–Cl bond and the silicon, is the lowest in energy even though the silicon of **1e** is substituted with three chloro-groups, reflecting that the electron withdrawing effect of the trichlorosilyl-group through the methylene σ-bond on the activation of the C–Cl bond is negligible. In this calculation, the energy sum (ΔE) of the reactant **1** and $AlCl_3$, and the ionic pair intermediate decreases in the following order: **1a** > **1b** > **1c** > **1d** > **1e**. The data of these simple calculations coincides with experimental values in the trend of alkylation reactivity of **1a**–**e** to benzene.

In conclusion, the Friedel–Crafts alkylation of (ω-chloroalkyl)silanes to benzene in the presence of aluminum chloride catalyst was generally affected on both factors of the electronic nature of the substituents at the silicon atom and the alkylene-chain length between the C–Cl and the silicon of (ω-chloroalkyl)silanes. Firstly, in the electronic nature of substituents at the silicon atom of (ω-chloroalkyl)silanes, as the number of electron-donating methyl substituent(s) at the silicon of (chloromethyl)silans increases, the reativity for the allylation increases as follows: **1a** < **1b** < **1c** < **1d**. The decomposition of alkylation products obtained in the reaction with **1c** and **1d** occurred in the presence of HCl: in particular, the alkylation with **1d** only gives the decomposed products, toluene, xylene, and trimethylchlorosilane, etc. as major products without the normal alkylation product **2d**. Secondly, as the alkylene-chain spacer between the C–Cl and silicon increases from **1a** to **1e** and **1f**, the reactivity of the silanes increases. It is consistent with that the generation of carbocation intermediate is affected by the inductive effect of silyl group as the electronic nature of the substituents at the silicon, reflecting that the reactivities on the alkylation of **1** and the decomposition of products decrease with increasing the number of chloro-groups at the silicon. In the alkylation to benzene, the reactivity of (ω-chloroalkyl)silanes [$Cl_{3-m}Me_mSi(CH_2)_n$–Cl: $m = 0$–3, $n = 1$–3] decreases in the following order: $m = 3 > 2 > 1 > 0$; $n = 3 > 2 \gg 1$. The alkylations are required for at least two chlorine groups at the silicon of (ω-chloroalkyl)chlorosilanes in an synthetic approach to benzene derivatives bearing Si–Cl functionality which may be useful as starting materials in silicone industry.

3. Experimental

3.1. General comments

All reactions and manipulations were carried out under prepurified dinitrogen using Schlenk techniques. Glassware was flame-dried before use. Dried solvents were employed in all reactions. Aluminum chloride and benzene were purchased from Aldrich Chemical and all (ω-chloroalkyl)silanes from Gelest. Reagents were used without purification except for benzene. Benzene was dried by distillation from sodium benzophenone ketyl prior to use. The reaction products were analyzed by GLC using a packed column (10% SE-30 or SE-54 on 80–100 mesh Chromosorb W/AW, 1/8″ × 1.5 m) or a capillary column (SE-30, 30 m) with a Varian 3300 gas chromatograph, thermal conductivity detector, and Hitachi D-2500 integrator. Product yields were determined chromatographically with *n*-dodecane as an internal standard, unless otherwise stated. Samples for characterization were purified by a preparative GLC using a Donam system series DS 6200 gas chromatograph with a thermal conductivity detector and a 4 m × 1/8″ stainless steel column packed with 20% OV-101 on 80–100 mesh Chromosorb P/AW. NMR spectra were recorded on a Varian Unity Plus 600 (FT, 600 MHz, ^{1}H; 150 MHz, ^{13}C) spectrometer in $CDCl_3$ solvent. Mass spectra were obtained using a Hewlett–Packard 6890 GC–MS. HRMS (high-resolution mass (70 eV, EI) spectra) were performed by the Korea Basic Science Institute, Seoul, Korea. Elemental analyses were performed by the chemical analysis laboratory of the Korea Institute of Science and Technology. The structures of products **2a**–**f** were confirmed by comparison with purchased samples.

3.2. Reaction of benzene with **1a**

To a 25 ml stainless steel bomb was charged aluminum chloride (0.29 g, 2.2 mmol), **1a** (2.0 g, 10.9 mmol), benzene (8.5 g, 109.0 mmol), and dodecane (0.5 ml, 0.38 g). The reactions were carried out at 80 and 200°C for 20 h, respectively. The progresses of the reactions were monitored by GLC. Product **2a** (31%) was observed with a 45% consumption of **1a** in a 20 h reaction at 200°C, but not in a 20 h reaction at 80°C.

3.3. General procedure for the reaction of benzene with compounds **1b**–**g**

To a suspension of $AlCl_3$ (0.4 g, 3.0 mmol) under nitrogen atmosphere at 0°C was charged a mixture of **1** (15.0 mmol) and benzene (150 mmol). The reaction mixtures were stirred at 0 or 80°C. The progresses of the reactions were monitored by GLC. After **1** was consumed, trichlorophosphine oxide was added. The complex of aluminum chloride and phosphine oxide was filtered off. The filtrate was distilled to give reaction products. The reaction products are summarized in Tables 1 and 3. Data for **2g**: ^{1}H-NMR (600 MHz): δ 1.58–1.63 (m, 2H, SiCH_2), 2.11–2.16 (m, 2H, CH_2), 2.71 (t, $J = 7$ Hz, 2H, benzylic-CH_2), 7.38 (d, $J = 7$ Hz, 2H), 7.42 (t, 7 Hz, 1H), 7.51 (t, 7 Hz, 2H) (phenyl-*H*). ^{13}C-NMR (150 MHz): δ 23.63, 23.95 (CH_2), 37.65 (benzylic-CH_2), 126.22, 128.41, 128.50, 140.64 (*ipso-C*) (phenyl-carbons). Data for **2g′**: ^{1}H-NMR (600 MHz): δ 1.53 (d, $J = 7$ Hz, 3H, CH_3), 1.88 (dd, $J = 7$, 15 Hz) 1.96 (dd, $J = 7$, 15 Hz) (1H, SiCH_2), 3.32 (sex, $J = 7$ Hz, 1H, benzylic-C*H*), 7.27–7.42 (m, 5H, phenyl-*H*). ^{13}C-NMR (150 MHz): δ 25.65 (SiCH_2), 33.92 (CH_3), 35.20 (benzylic-*C*H), 126.63, 126.68, 128.65, 146.43 (*ipso-C*) (phenyl-carbons). Anal. Calc. for $C_9H_{11}Cl_3Si$: C, 42.62; H, 4.37. Found for an 89:2 mixture of **2g** and **2g′**: C, 42.59; H, 4.38%. Data for **2h**: ^{1}H-NMR (600 MHz): δ 0.76 (s, 3H, SiCH_3), 1.15 (t, 2H, SiCH_2), 1.86 (sex, $J = 8$ Hz, 2H, CH_2), 2.71 (t, $J = 8$ Hz, 2H, benzylic-CH_2), 7.18–7.31(m, 5H, phenyl-*H*). ^{13}C-NMR (150 MHz): δ 5.18 (CH_3), 21.21 (SiCH_2), 24.24 (CH_2), 38.34 (benzylic-CH_2), 126.06, 128.44, 128.50, 141.39 (*ipso-C*) (phenyl-carbons). Data for **2h′**: ^{1}H-NMR (600 MHz): δ 0.50 (s, 3H, SiCH_3), 1.47 (d, $J = 7$ Hz, 3H, CH_3), 1.65 (m, 2H, SiCH_2), 3.23 (t, $J = 7$ Hz, 1H, benzylic-C*H*), 7.27–7.39 (m, 5H, phenyl-*H*). ^{13}C-NMR (150 MHz): δ 5.80 (CH_3), 25.46 (SiCH_2), 31.80 (CH_3), 35.34 (benzylic-*C*H), 126.53, 126.65, 128.62, 147.10 (*ipso-C*) (phenyl-carbons). Anal. Calc. for $C_{10}H_{14}Cl_2Si$: C, 51.50; H, 6.05. Found for an 80:13 mixture of **2h** and **2h′**: C, 51.49; H, 6.07%.

3.4. Reaction of **2** with hydrogen chloride in the presence of aluminum chloride

Into a 100 ml flask were charged **2c** (2.03 g, 11.0 mmol), aluminum chloride (0.29 g, 2.2 mmol), and *n*-dodecane (0.4 g) as an internal standard. Gaseous HCl was bubbled to the stirred reaction solution at room temperature for 10 min. The reaction mixture was then analyzed by GLC. Compound **2b** (12%), toluene (23%), and dimethyldichlorosilane (23%) were observed along with 62% of unreacted **2c**.

Using the same procedure described for **2c** with HCl, compound **2d** reacted with bubbling gaseous HCl in the presence of aluminum chloride for 10 min. The decomposed products, toluene (62%), trimethylchlorosilane (62%), and **2c** (12%) were observed along with 8% of unreacted **2d** by GLC.

3.5. Aluminum chloride-catalyzed reaction of **1d**

Using the procedure described for **2c** with HCl, **1d** (1 g, 8.2 mmol) was stirred with and without bubbling gaseous HCl in the presence of $AlCl_3$ (0.2 g, 1.5 mmol) at room temperature for 30 min. With the 36% consumption of **1d** in the absence of gaseous HCl, ethyldimethylchlorosilane (34%) was observed predominantly along with a trace of trimethylchlorosilane by GLC analysis. The reaction of **1d** in the presence of gaseous HCl gave the similarity to the results from the reaction in the absence of HCl.

3.6. Computational details

GAUSSIAN-94 software [27] was employed for ab initio MO SCF calculation on a Cray T3E supercomputer. All possible geometries of (ω-chloroalkyl)silane, $AlCl_3$ and their reactant complexes were examined at the HF/3-21G level [29], and the stable conformers were selected. The selected conformers were reoptimized at the HF/6-31G* level [30]. The cleavage state of the C–Cl bond at (ω-chloroalkyl)silane by $AlCl_3$ as a transition state was characterized on their respective potential energy surfaces by performing frequency calculations at the same level of theory. The zero-point energies (ZPE) were scaled by 0.9135 [31].

Acknowledgements

This research was supported financially by the Ministry of Science and Technology.

References

[1] (a) R.M. Roberts, A.A. Khalaf, Friedel–Crafts Alkylation Chemistry, Marcel Dekker, New York, 1984. (b) G.A. Olah, Friedel–Crafts and Related Reactions, vol. I–IV, Wiley-Interscience, New York, 1963.

[2] M. Huellmann, H. Mayr, R. Becker, Ger. Offen. DE 4 008 694, 1991; Chem. Abstr. 116 (1991) 6262x.

[3] I.N. Jung, B.R. Yoo, in: F.G.A. Stone, R. West (Eds.), Advances in Organometallic Chemistry, Academic, New York, in press.

[4] G.H. Wager, D.L. Bailey, A.N. Pines, M.L. Dunham, D.B. Mcintire, Ind. Eng. Chem. 45 (1953) 367.

[5] K.A. Andrianov, A.A. Zhdanov, V.A. Odinnets, Zh. Obshch. Khim. 31 (1961) 4033; Chem. Abstr. 57 (1962) 9874a: 32 (1962) 1126; Chem. Abstr. 58 (1963) 1484a.

[6] N.S. Nametkin, V.M. Vdovin, E.S. Findel-Shtein, V.D. Oppengeim, N.A. Chekalina, Isv. Akad. Nauk. SSSR. Ser. Khim. 11 (1966) 1998.

[7] M.G. Voronkov, V.M. Kovrigin, V.I. Lavrent'ev, V.M. Moralev, Dokl. Akad. Nauk. SSSR. 281 (6) (1985) 1374.

[8] A.D. Petrov, V.F. Mironov, V.A. Ponomarenko, E.A. Chernyshev, Dokl. Akad. Nauk SSSR. 97 (1954) 687; Chem. Abstr. 51 (1955) 10166g.

[9] A.D. Petrov, E.A. Chernyshev, M.E. Dolgaya, Zh. Obshch. Khim. 25 (1955) 2469; Chem. Abstr. 50 (1956) 9319a.

[10] E.A. Chernyshev, M.E. Dolgaya, Yu.P. Egorov, Zh. Obshch. Khim. 27 (1957) 267; Chem. Abstr. 52 (1958) 7187b: 28 (1958) 2829; Chem. Abstr. 53 (1959) 9110c.

[11] E.A. Chernyshev, M.E. Dolgaya, Zh. Obshch. Khim. 27 (1957) 48; Chem. Abstr. 51 (1957) 12045g, 29 (1959) 1850; Chem. Abstr. 54 (1960) 8604d.

[12] D.T. Hurd, J. Am. Chem. Soc. 67 (1945) 1813.

[13] V.F. Mironkov, D.N. Zelinskii, Izv. Akad. Nauk SSSR, Ser. Khim. (1957) 383.

[14] R.H. Krieble, J.R. Elliott, J. Am. Chem. Soc. 67 (1947) 1810.

[15] F. Runge, W. Zimmermann, Chem. Ber. 87 (1954) 282; Chem. Abstr. 49 (1955) 6088a.

[16] B.W. Lee, B.R. Yoo, S.-I. Kim, I.N. Jung, Organometallics 13 (1994) 1312.

[17] E.J. Cho, V. Lee, B.R. Yoo, I.N. Jung, H. Sohn, D.R. Powell, R. West, Organometallics 16 (1997) 4200.

[18] E.J. Cho, V. Lee, B.R. Yoo, I.N. Jung, J. Organomet. Chem. 548 (1997) 237.

[19] C.G. Swain, S.H. Unger, N.R. Rosenquist, M.S. Swain, J. Am. Chem. Soc. 105 (1983) 492.

[20] F.A. Houle, J.L. Beauchamp, J. Am. Chem. Soc. 101 (1979) 4067.

[21] F.C. Whitmore, L.H. Sommer, J. Gold, J. Am. Chem. Soc. 69 (1947) 1976.

[22] (a) S.G. Wierschke, J. Chandrasekhar, W.L. Jorgensen, J. Am. Chem. Soc. 107 (1985) 1496. (b) A.J. Kresge, J.B. Tobin, Angew. Chem. Int. Ed. Engl. 32 (1993) 721.

[23] S.H. Yeon, B.W. Lee, B.R. Yoo, M.-Y. Suk, I.N. Jung, Organometallics 14 (1995) 2361.

[24] I.N. Jung, B.R. Yoo, Synlett (1999) 519.

[25] C.C. Price, Chem. Rev. 29 (1941) 37.

[26] H.C. Brown, M. Grayson, J. Am. Chem. Soc. 75 (1953) 6285.

[27] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, GAUSSIAN-94, Revision E.1, Gaussian, Pittsburgh, PA, 1995.

[28] G. Frenking, S. Fau, C.M. Marchand, H. Grützmacher, J. Am. Chem. Soc. 119 (1997) 6648.

[29] J.S. Binkley, J.A. Pople, W.J. Hehre, J. Am. Chem. Soc. 102 (1980) 939.

[30] G.A. Petersson, A. Bennett, T.G. Tensfeldt, M.A. Al-Laham, W.A. Shirley, J. Mantzaris, J. Chem. Phys. 89 (1988) 2193.

[31] J.A. Pople, A.P. Scott, M.W. Wong, L. Radom, Isr. J. Chem. 33 (1993) 345.