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One-Step Synthesis of Fluorenyl-Substituted Chlorosilanes: Friedel−Crafts Type Cycloalkylation of Biphenyl with (Dichloroalkyl)silane

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Friedel−Crafts alkylation reactions of biphenyl with (dichloroalkyl)chlorosilanes [$Cl_{3-m}Me_mSi(C_nH_{2n-1}Cl_2)$, $m = 0-2$, $n = 1-3$] at temperatures ranging from 120 to 160 °C in the presence of a Lewis acid catalyst gave cyclized products, fluorenyl-substituted chlorosilanes, in 47−94% yields. In these reactions, the reactivities of (dichloroalkyl)silanes generally increase as the number of methyl groups on the silicon atom and the alkyl chain length increase. However, desilylation of the alkylated products and starting chlorosilanes was observed in the case of (dichloroalkyl)silanes having two or more methyl groups on the silicon. Alkylation with (dichloromethyl)dimethylchlorosilane proceeded at 120 °C but gave fluorene and dimethyldichlorosilane resulting from desilylation of the products. The reactivities of (dichloroalkyl)silanes decrease in the following order: $m = 2 > 1 > 0$; $n = 2 > 1$. The catalytic efficiencies of Lewis acids for the cycloalkylation reactions decrease in the following order: $AlCl_3 > AlBr_3 > HfCl_4 > ZrCl_4 \gg TiCl_4$.

Introduction

Group 4 metal complexes have recently attracted great interest due to their catalytic activities for the stereospecific polymerization of α-olefins.[1−11] Fluorenyl-substituted organosilicon compounds are well known as starting materials for many of these transition metal complexes[1−11] used for olefin polymerizations.[9−11] Generally, organosilicon compounds containing a fluorenyl group such as fluorenyltrialkylsilanes or (fluorenylmethyl)trialkylsilanes are prepared by the coupling reaction of chlorosilanes such as chlorotrialkylsilanes[9] or (chloromethyl)trialkylsilanes[10] with a fluorenyl anion generated by the deprotonation reaction of fluorene with organometallic reagents. However, it is difficult to obtain fluorenylchlorosilanes having reactive chlorine atom(s) on the silicon by this method because of the strong reactivity of organometallic reagents toward the coupling reaction.

We recently reported the Friedel−Crafts alkylations of benzene derivatives[12−15] and ferrocene[16] with organosilicon compounds such as allylchlorosilanes, vinylchlorosilanes, and (ω-chloroalkyl)chlorosilanes in the presence of Lewis acid catalysts to give (phenylalkyl)chlorosilanes with Si−Cl bonds as a functionality.[17] Encouraged by the success of these new organochlorosilane syntheses, we attempted the Friedel−Crafts type cycloalkylation of biphenyl (**1**) with (dichloroalkyl)silanes **2** ($X^1X^2ClSiC_nH_{2n-1}Cl_2$, $n = 1-3$). The cycloalkylation reactions gave fluorenyl-substituted chlorosilanes as the major products along with dialkylation products. One-step synthesis of fluorenyl group-containing chlorosilanes without the need for expensive organometallic reagents or solvents should be attractive to both industry and academia. In this paper, we detail the one-step synthesis of fluorenyl-substituted chlorosilanes by the cycloalkylation of **1** with **2**.

Results and Discussion

Cycloalkylation of Biphenyl (1) with (Dichloroalkyl)chlorosilanes 2a−f. Friedel−Crafts alkylation of **1** with (dichloroalkyl)chlorosilanes **2a**−**f** ($X_1X_2ClSiC_nH_{2n-1}Cl_2$, $n = 1-3$) in the presence of aluminum

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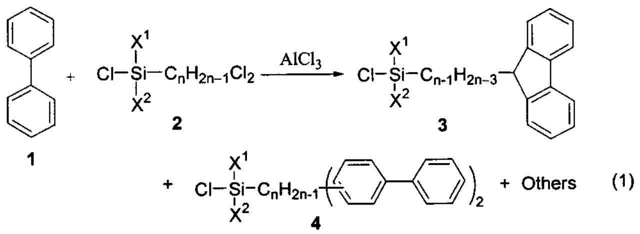
Table 1. Friedel−Crafts Alkylation of 1 with (Dichloroalkyl)chlorosilanes 2a−f ($X^1X^2ClSiC_nH_{2n-1}Cl_2$, $n = 1{-}3$)

silane			reaction conditions[a]		products (%)[b]		
2[c]	X^1, X^2	*n* (position of Cl_2)	temp (°C)	time (h)	**3**	**4**	others
2a (24)	Cl, Cl	1	120	2.5	**3a**, 58	**4a**, 15	2[d]
2a (−)	Cl, Cl	1	160	1.0	**3a**, 91		4[d]
2b (−)	Cl, Me	1	120	2.5	**3b**, 94		4[e]
2c (−)	Me, Me	1	120	2.5	**3c**, −		17[f]
2d (−)	Cl, Cl	2 (1,2-)	120	2.5	**3d**, 35		21[g]
2d (−)	Cl, Cl	2 (1,2-)	160	1.0	**3d**, 47		27[g]
2e (−)	Cl, Me	2 (1,2-)	120	0.5	−		36[h]
2f (−)	Cl, Cl	3 (2,3-)	120	1.5	**3f**, 48		30[i]

[a] 2:1 reaction of **1** and **2** was carried out in the presence of 0.2 equiv of $AlCl_3$ based on **2** used. [b] GLC yield. [c] Unreacted **2** in parentheses. [d] 2-(Trichlorosilylmethyl)-9-(trichlorosilyl)fluorene. [e] 2-[(Methyldichlorosilyl)methyl]-9-(methyldichlorosilyl)fluorene. [f] Fluorene. [g] A 2:3 mixture of *m*- and *p*-[(2-trichlorosilyl)ethyl]biphenyls. [h] 9-Methylfluorene. [i] A 2:3 isomeric mixture of *m*- and *p*-[(3-trichlorosilyl)propyl]biphenyls.

chloride catalyst gave fluorenyl-containing chlorosilanes **3** as major products along with noncyclic byproducts (eq 1). Both *geminal* and *vicinal* (dichloroalkyl)silanes such as (dichloromethyl)silanes and (1,2-dichloroethyl)silanes or (2,3-dichloropropyl)silane were used as starting chlorosilanes. For *geminal* (dichloroalkyl)silanes, only (dichloromethyl)silanes were used because of the difficulties involving in synthesizing and isolating the corresponding longer chain isomers.[18,19]



(1)

The results obtained from the cycloalkylation of **1** with (dichloroalkyl)silanes **2** in the presence of aluminum chloride catalyst are summarized in Table 1.

As shown in Table 1, **1** reacted with *geminal* (dichloromethyl)silanes ($X^1X^2ClSiCHCl_2$, **2a**,**b**) to give the cyclized products of **3a** and **3b** in yields over 90% based on the amount of **2** reacted. The alkylations of **1** with **2a** and **2b** gave fluorenyltrichlorosilane (**3a**, 91%) at 160 °C for 1 h and fluorenyl(methyl)dichlorosilane (**3b**, 94%) at 120 °C for 2.5 h, respectively. When **2a** was reacted for 2.5 h at the lower temperature of 120 °C, **3a** was obtained in relatively low yield (58%) and bis(biphenyl)methyltrichlorosilane (**4a** 15%) was obtained as a byproduct. Reactant **2a** required a slightly higher reaction temperature than **2b**, indicating that the reactivity of **2** increases as the number of methyl groups on the silicon increases. This result suggests that electron-donating groups on the silicon enhance the alkylation ability of silane compounds, which is consistent with the previous reports on the alkylations of benzene derivatives.[12,15] The formation of **4a** can be explained by the double alkylation of **2a** with two moles of **1**. Surprisingly, **4a** is not obtained at the higher reaction temperature, perhaps suggesting its conversion to **3a**. To test the possibility, isolated **4a** was exposed to the same reaction conditions. A 2 h reaction of **4a** with **2a** at 160 °C gave a reaction mixture consisting of **3a** (9%), **1** (48%), 2-(trichlorosilylmethyl)-9-(trichlorosilyl)fluorene (17%), and starting material **4a** (20%), indicating that **4a** could indeed convert to **3a**. Reaction with **2c** gave no alkylation product but instead afforded fluorene and dimethyldichlorosilane, suggesting that the alkylation product, dimethyl(fluorenyl)chlorosilane, underwent a desilylation reaction under the alkylation reaction conditions.[16]

NMR analysis of the residue left from bulb-to-bulb distillation of product mixtures showed peaks due to the fluorenyl group, indicating that fluorene was further alkylated to give high-boiling residues. The decomposition of starting material and multialkylation of desilylated fluorene products likely contributed to the low yield of fluorene.

Since the synthesis of *geminal*-dichlorinated alkylsilanes other than **2a**−**c**[18,19] was difficult, *vicinal*-(dichloroalkyl)silanes were employed for the alkylation. Reaction of **1** with (1,2-dichloroethyl)trichlorosilane (**2d**) at 160 °C for 1 h gave (fluorenylmethyl)trichlorosilane (**3d**, 47%) as a major product along with a mixture of *m*- and *p*-[2-(trichlorosilyl)ethyl]biphenyls but not 9-methyl-9-(trichlorosilyl)fluorene. The reaction of **1** with methyl(1,2-dichloroethyl)dichlorosilane (**2e**) at 120 °C for 0.5 h gave desilylated products, 9-methylfluorene and methyltrichlorosilane, as major products without the formation of any methyl(2-fluorenylmethyl)dichlorosilane (**3e**). The reaction of **1** with (2,3-dichloropropyl)trichlorosilane (**2f**) gave (2-fluorenylethyl)trichlorosilane (**3f**, 48%) as a major product along with a mixture of isomeric [3-(trichlorosilyl)propyl]biphenyls. The consumption rate of (dichloroalkyl)trichlorosilanes decreases in the following order at 120 °C: **2f** > **2d** > **2a**. These results can be rationalized in terms of the stability,[15] ease of 1,2-migration, and electrophilic addition to **1** of the carbocation intermediates, which are generated by the complexation of **2** with aluminum chloride.

On a large scale, the representative reaction of **1** (225.0 mmol) with **2b** (112.5 mmol) in the presence of 20 mol % $AlCl_3$ at 120 °C for 2.5 h gave **3b** and 2-[(methyldichlorosilyl)methyl]-9-(methyldichlorosilyl)fluorene in 77% and 6% isolated yields, respectively, based on the amount of **2b** used.

Optimum Conditions for the Cycloalkylation Reaction of 1 with 2. For the synthesis of **3** by the cycloalkylation reaction of **1** with (dichloroalkyl)silanes **2**, the reaction conditions were optimized by varying the type and amount of Lewis acid, the temperature, and the ratio of reactants. The results obtained from the representative reaction of **1** with **2b** are summarized in Table 2.

As shown in Table 2, aluminum halides such as aluminum chloride and aluminum bromide were found to be good catalysts for the cyclodialkylation of **1** with **2**, while group 4 metal chlorides such as titanium chloride, zirconium chloride, and hafnium chloride were

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Table 2. Reaction Conditions and Alkylation Products in the Reaction of 1 with 2b

Lewis acid (equiv)[a]	mol ratio (**1**/**2b**)	reaction conditions temp (°C)	 time (h)	products (%)[b] **3b**	 **4b**	 other[c]
$TiCl_4$ (0.2)	2	120	2.5	0	0	0
$ZrCl_4$ (0.2)	2	120	2.5	trace	0	0
$HfCl_4$ (0.2)	2	120	2.5	3	0	0
$AlBr_3$ (0.2)	2	120	2.5	84	9	3
$AlCl_3$ (0.2)	2	120	2.5	94	0	4
$AlCl_3$ (0.4)	2	120	1.0	94	0	3
$AlCl_3$ (0.1)	2	120	3.5	91	0	7
$AlCl_3$ (0.2)	2	80	30.0	86	0	7
$AlCl_3$ (0.2)	2	160	1.0	92	0	5

[a] Equiv of Lewis acid is with respect to **2b** used. [b] GLC yields. [c] Dialkyated products.

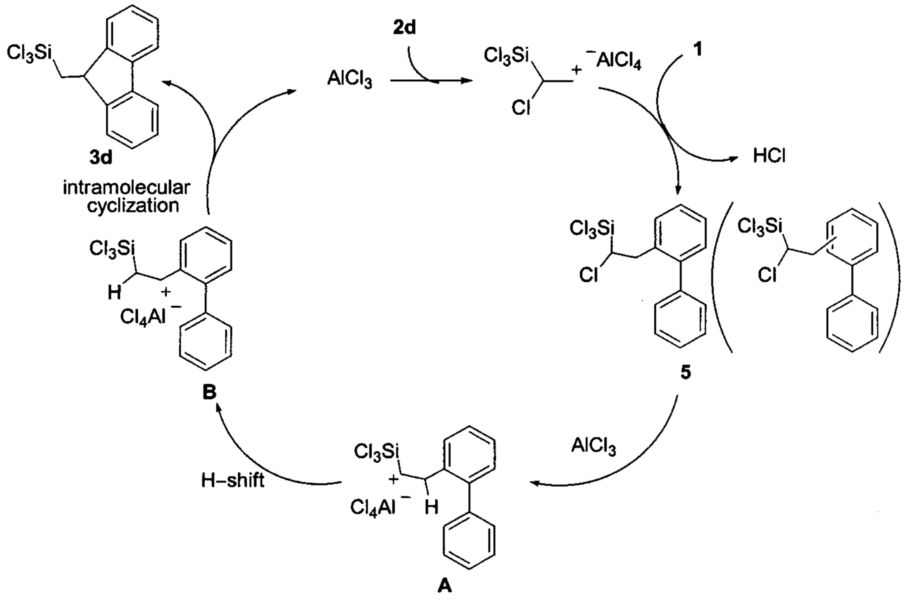
not. Generally, aluminum halides show much higher catalytic activities for alkylation reactions than group 4 transition metal chlorides.[12] Comparing aluminum bromide and chloride, aluminum chloride was slightly better for the synthesis of **3b**. To find the optimal amount of catalyst for the alkylation, reactions were carried out using amounts of aluminum chloride ranging from 10 to 40 mol % with respect to **2b**. Product **3b** was obtained in the highest yield when more than 20 mol % of aluminum chloride was used. Thus, 20 mol % of aluminum chloride was used for later alkylation reactions. As the reaction temperature was increased from 80 to 160 °C, the yield of **3b** increased from 86% to 92% while the reaction time drastically decreased from 30 to 1 h, suggesting that the yields are sensitive to the reaction temperatures.

Mechanism. For the Friedel–Crafts cycloalkylation of **1** with **2** in the presence of aluminum chloride, a mechanism for the formation of **3d** from the representative reaction of **1** with **2d** is outlined in Scheme 1. The β-positioned C–Cl bond of **2d** is first complexed with aluminum chloride to give the polar intermediate species $^{\delta+}C-Cl^{\delta-}$ ($^{\delta+}C-Cl\cdots Al^{\delta-}Cl_3$) or $C^+AlCl_4^-$.[12,16] It is well known that a carbocation β to the silicon is more stable than an α carbocation through $\sigma-\pi$ conjugation between the vacant p orbital of the carbocation and the σ orbital of the C–Si bond.[20] This intermediate then attacks **1** electrophilically to generate a benzenoniom ion, followed by deprotonation to give the monoalkylated product, (2-biphenyl-1-chloroethyl)trichlorosilane, **5**, and the liberation of hydrogen chloride as a gas. Although the alkylation of **1** is reported to give a mixture of *ortho*, *meta*, and *para* isomeric products, the *ortho* isomer is the least favorable product due to steric hindrance.[12] Thus, isomerization must be possible under the reaction conditions.

The *ortho* isomer of (2-biphenyl-1-chloroethyl)trichlorosilanes forms complexes again with aluminum chloride to generate the 2-biphenyl-1-(trichlorosilyl)ethyl cation intermediate **A**, which rearranges to the more stable carbocation, 1-biphenyl-2-trichlorosilylethyl, intermediate **B**. Intermediate **B** then cyclizes through an intramolecular electrophilic substitution on the neighboring phenyl ring to give fluorene **3d**.

In conclusion, (dichloroalkyl)silanes **2** [$Cl_{3-m}Me_mSi(C_nH_{2n-1}Cl_2)$, $m = 0, 1$; $n = 1-3$] undergo double alkylations with **1** in the presence of aluminum chloride at temperatures ranging from 120 to 160 °C to give fluorenyl-substituted chlorosilanes in 47–94% yields. In the alkylation of **1**, the reactivities of (dichloroalkyl)silanes **2** generally increase as the number (m) of methyl groups at the silicon increases and the alkyl chain length increases. Decompositions of starting silanes and alkylation products were observed in the alkylation reactions with chlorosilanes having two or more methyl groups on the silicon. The reaction with (dichloromethyl)dimethylchlorosilane at 120 °C gave no dimethyl(fluorenyl)chlorosilane, but dimethyldichlorosilane and fluorene via decomposition reactions. The reactivities of (dichloroalkyl)silanes decrease in the following order: $m = 2 > 1 > 0$; $n = 2 > 1$. The catalytic efficiencies of Lewis acids for the alkylations decrease in the following order: $AlCl_3 > AlBr_3 > HfCl_4 > ZrCl_4 \gg TiCl_4$.

Scheme 1



Experimental Section

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 (99%) and **1** were purchased from Aldrich Chemical Co., and aluminum chloride was purified by sublimation. (Dichloromethyl)trichlorosilane and (dichloromethyl)methyldichlorosilane were obtained from Gelest, Inc. and used without purification. (1,2-Dichloroethyl)trichlorosilane[21] and (2,3-dichloropropyl)trichlorosilane[22] were prepared by the photochlorination of vinyltrichlorosilane and allyltrichlorosilane with chlorine gas, respectively. 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 in. × 1.5 m) or a capillary column (SE-30, 30 m) with a Varian 3300 gas chromatograph, thermal conductivity detector, and ds chrom 99 program connected to a computer. The progress of the reactions was monitored by GLC. Yields of some products were determined chromatographically with *n*-dodecane as an internal standard, if not described in detail and calibrated with their response factors in TCD. 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 by 1/8 in. stainless steel column packed with 20% OV-101 on 80−100 mesh chromosorb P/AW. NMR spectra were recorded on a Bruker Avance 300 (FT, 300 MHz, ^1H; 75 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 Korea Basic Science Institute, Seoul, Korea. The structures of products **3a**,**b** were confirmed by comparison with samples purchased commercially.

General Procedure for the Reaction of 1 with 2a. A mixture of aluminum chloride (0.2 g, 1.5 mmol), **1** (2.3 g, 15.0 mmol), and **2a** (1.63 g, 7.5 mmol) was stirred and warmed to 160 °C for 20 min and kept at that temperature for 1.0 h. Then, NaCl (0.44 g, 75 mmol) and hexane (30 ml) were added to the reaction mixture, and the mixture was stirred for 2 h at 80 °C. The $NaCl-AlCl_3$ complexed salt was filtered off. The resulting solution was bulb-to-bulb distilled under vacuum to give 2.18 g of crude **3a**[23] containing small amount of 2-(trichlorosilylmethyl)-9-(trichlorosilyl)fluorene, and recrystallization from pentane solution gave 2.05 g of **3a** (91% yield, mp; 108−110 °C). The results obtained from the reaction are summarized in Table 1. In a 2.5 h reaction at 120 °C, **3a** (58%) and **4a** (15%) were observed by GLC with a 76% consumption of **2a**. Data for **3a**: ^1H NMR (300 MHz) δ 4.41 (s, 1H, $CHSi$), 7.51 (t, 2H), 7.57 (t, 2H), 7.92 (d, 2H), 7.98 (d, 2H) (aromatic-*H*); ^{13}C NMR (75 MHz) δ 45.67 ($CHSi$), 120.62, 125.71, 127.17, 127.67, 136.61, 141.66 (aromatic-*carbons*). For 2-(trichlorosilylmethyl)-9-(trichlorosilyl)fluorene: ^1H NMR (300 MHz) δ 3.07 (s, 2H, $SiCH_2$), 4.39 (s, 1H, $SiCH$), 7.33−7.90 (m, 7H, aromatic-*H*); ^{13}C NMR (75 MHz) δ 33.22 ($SiCH_2$), 45.41 ($SiCH$), 120.32, 120.63, 125.56, 126.28, 127.03, 127.74, 128.77, 131.00, 138.63, 139.53, 140.26, 141.30 (aromatic-*carbons*); HRMS (*m*/*e*) calcd for $Si_2C_{14}H_{10}Cl_6$ (M^+), 443.8452; found, 443.8542. For the mixture of three isomers of **4a**: ^1H NMR (300 MHz) δ 4.35, 4.38, 4.41 (s, 1H, $SiCH$), 7.39−7.69 (m, 54H, aromatic-H); ^{13}C NMR (75 MHz) δ 49.75, 50.17, 50.53 ($SiCH$), 126.12, 127.00, 127.18, 127.40, 127.51, 127.58, 128.21, 128.26, 128.36, 128.42, 128.78, 128.82, 129.31, 129.82, 135.54, 135.60, 137.03, 137.09, 140.07, 140.36, 140.73, 141.86 (aromatic-carbons); HRMS (*m*/*e*) calcd for $Si_1C_{25}H_{19}Cl_3$ (M^+) 452.0322; found, 452.0339.

Reactions of 1 with Compounds 2b,d,f. Using the same procedure above, the reactions of **1** (2.3 g, 15.0 mmol) with **2** (7.5 mmol) in the presence of $AlCl_3$ (0.2 g, 1.5 mmol) were carried out at 120 or 160 °C, respectively. The results obtained from the reactions are summarized in Tables 1 and 2. Data for **3b**: ^1H NMR (300 MHz) δ 0.29 (s, 3H, $SiCH_3$), 4.30 (s, 1H, $CHSi$), 7.43 (t, $J = 7.5$ Hz, 1H), 7.44 (t, $J = 7.4$ Hz, 1H), 7.51 (t, $J = 7.4$ Hz, 2H), 7.87 (d, $J = 7.5$ Hz, 2H), 7.94 (d, $J = 7.4$ Hz, 2H) (aromatic-*H*); ^{13}C NMR (75 MHz) δ 1.45 ($SiCH_3$), 44.45 ($CHSi$), 120.20, 125.39, 126.78, 127.01, 140.46, 141.23 (aromatic-*carbons*). Data for 2-[(methyldichlorosilyl)methyl]-9-(methyldichlorosilyl)fluorene: ^1H NMR (300 MHz) δ 0.24 (s, 3H, CH_2SiCH_3), 0.77 (s, 3H, $CHSiCH_3$), 2.82 (s, 2H, CH_2Si), 4.25 (s, 1H, $CHSi$), 7.24−7.89 (m, 7H, aromatic-*H*); ^{13}C NMR (75 MHz) δ 1.49 (CH_2SiCH_3), 4.41 ($CHSiCH_3$), 31.35 ($SiCH_2$), 44.42 ($SiCH$), 120.00, 120.36, 125.47, 125.75, 126.61, 127.09, 127.80, 133.18, 139.22, 140.28, 141.06, 141.26 (aromatic-carbons); HRMS (*m*/*z*) calcd for $Si_2C_{16}H_{16}Cl_4$ (M^+), 403.9545; found, 403.9533. For **3d**: bp 133−135 °C/0.2 mmHg; ^1H NMR (300 MHz) δ 2.31 (d, $J = 5.4$ Hz, 2H, $SiCH_2$), 4.37 (br t, 1H, $SiCH_2CH$), 7.47−7.59 (m, 4H), 7.72 (d, $J = 7.0$ Hz, 2H), 7.88 (d, $J = 7.0$ Hz, 2H) (aromatic-*H*); ^{13}C NMR (75 MHz) δ 28.36 ($SiCH_2$), 41.83 ($SiCH_2CH$), 119.96, 124.58, 127.08, 127.62, 140.55, 146.18 (aromatic-carbons); HRMS (*m*/*z*) calcd for $Si_1C_{14}H_{11}Cl_3$ (M^+), 311.9696; found, 311.9669. Data for a mixture of *m*- and *p*-[2-(tichlorosilyl)ethyl]biphenyls: ^1H NMR (300 MHz) δ 1.90−1.97 (m, 4H, $SiCH_2$), 3.00−3.20 (m, 4H, $SiCH_2CH_2$), 7.40−7.66 (m, 18H, aromatic-*H*); ^{13}C NMR (75 MHz) δ 25.92, 26.02 ($SiCH_2$), 27.78, 28.26 ($SiCH_2CH_2$), 125.29, 126.69, 126.90, 127.14, 127.24, 128.22, 128.72, 129.03, 141.54, 141.70 (aromatic-carbons); HRMS (*m*/*z*) calcd for $Si_1C_{14}H_{13}Cl_3$ (M^+), 313.9852; found, 313.9901. Data for **3f**: bp 140−142 °C/0.2 mmHg; ^1H NMR (300 MHz) δ 0.95 (m, 2H, $SiCH_2$), 2.48 (dt, $J = 4.7$, 12.6 Hz, 2H, $SiCH_2CH_2$), 4.20 (t, $J = 4.7$, 1H, benzylic-C*H*), 7.41−7.47 (m, 4H), 7.56 (d, $J = 7.1$ Hz, 2H), 7.84 (d, $J = 9.2$ Hz, 2H) (aromatic-H); ^{13}C NMR (75 MHz) δ 18.35 ($SiCH_2$), 24.52 ($SiCH_2CH_2$), 47.51 (benzylic-CH_2), 120.02, 124.03, 127.22, 127.44, 141.57, 145.24 (aromatic-carbons); HRMS (*m*/*z*) calcd for $Si_1C_{15}H_{13}Cl_3$ (M^+), 325.9852; found, 325.9823. Data for a mixture of *m*- and *p*-[3-(trichlorosilyl)propyl]biphenyls: ^1H NMR (300 MHz) δ 1.45−1.55 (m, 4H, $SiCH_2$), 1.90−2.10 (m, 4H, $SiCH_2CH_2$), 2.83, 2.86 (t, $J = 7.7$ Hz, 1H, benzylic-C*H*), 7.40−7.66 (m, 18 aromatic-*H*); ^{13}C NMR (75 MHz) δ 23.76, 23.77 ($SiCH_2$), 23.98, 24.06 ($SiCH_2CH_2$), 37.32, 37.80 (benzylic-CH_2), 125.13, 127.16, 127.22, 127.28, 127.34, 127.36, 128.74, 128.88, 128.92, 141.11, 141.25, 141.47 (aromatic-carbons).

Scaled-Up Reaction of 1 with 2b in a Large Scale. Using the same procedure described above, the reaction of **1** (34.7 g, 225.0 mmol) with **2b** (22.05 g, 112.5 mmol) in the presence of $AlCl_3$ (3.0 g, 22.5 mmol) was carried out at 120 °C for 2.5 h. The reaction mixture was distilled under vacuum (118−120 °C/0.2 mmHg) to give **3b** (24.0 g, 77%) and 2-[(methyldichlorosilyl)methyl]-9-(methyldichlorosilyl)fluorene (1.3 g, 6%) based on **2b** used.

Reactions of 1 with Compound 2c. Using the procedure described above, the reaction of **1** (2.3 g, 15.0 mmol) with **2c** (1.33 g, 7.5 mmol) in the presence of $AlCl_3$ (0.2 g, 1.5 mmol) was carried out at 120 °C for 2.5 h. The reaction mixture consisted of fluorene (17%), dimethyldichlorosilane (50%), and polymeric materials.

Reactions of 1 with Compound 2e. Using the procedure described above, the reaction of **1** (2.3 g, 15.0 mmol) with **2e** (1.59 g, 7.5 mmol) in the presence of $AlCl_3$ (0.2 g, 1.5 mmol) was carried out at 120 °C for 0.5 h. The reaction mixture consisted of 9-methylfluorene (36%) and methyltrichlorosilane (46%) by GLC, and polymeric materials.

Conversion Reaction of 4a to 3a. A mixture of three isomeric **4a** (1.04 g, 2.3 mmol) and *n*-dodecane (0.2 g) was stirred in the presence of aluminum chloride (0.06 g, 0.46 mmol) at 160 °C for 2 h. The reaction mixture consisted of **3a**

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(9%), **1** (48%), 2-(trichlorosilylmethyl)-9-(trichlorosilyl)fluorene (17%), and starting material **4a** (20%) by GLC.

Effect of Lewis Acids on the Reaction of 1 with 2b. Using the same procedure described in the reaction of **1** with **2b**, reactions were carried out with various Lewis acids such as $AlCl_3$, $AlBr_3$, $TiCl_4$, $ZrCl_4$, and $HfCl_4$. The results are summarized in Table 2.

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