

Synthesis and Characterization of Organosilicon Substituted Fluorenyl Derivatives

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Summary: Friedel-Crafts cycloalkylation of biphenyl with 2,3-dichlorobutyltrichlorosilane ($\text{Cl}_3\text{Si-CH}_2\text{CHClCHClCH}_3$) at a temperature of 100 °C in the presence of anhydrous aluminum chloride catalyst gave cyclized product, 9-methyl-9-(2-trichlorosilylethyl)fluorene **1a**, in 33% yield. Methylation of **1a** with nucleophilic reagent such as methyl magnesium chloride, gave 9-Methyl-9-(2-trimethylsilylethyl)fluorene **2** while bromination of **2** with excess amount of bromine in DMF resulted in 2,7-dibromo-9-methyl-9-(2-trimethylsilylethyl)fluorene **3** in good yield. All the compounds were structurally identified by GC/MS, ^1H and ^{13}C -NMR spectroscopy.

Introduction

Fluorenyl-substituted organosilicon compounds are well known as starting materials for many of group 4 transition metal complexes [1-11] used for olefin polymerizations [9-11]. Generally, organosilicon compounds containing a fluorenyl group such as fluorenyltrialkylsilanes or (fluorenyl-methyl)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 towards the coupling reaction.

Friedel-Crafts cycloalkylations of biphenyl with (dichloroalkyl)chlorosilanes [$\text{Cl}_{3-m}\text{Me}_m\text{Si}(\text{C}_n\text{H}_{2n-1}\text{Cl}_2)$, $m=0-2$, $n=1-3$] in the presence of Lewis acid catalysts to give fluorenyl-substituted chlorosilanes as the major products along with dialkylation products, have been reported earlier [12]. In this paper, I wish to report a convenient one-step synthesis of 9-methyl-9-(2-trichlorosilylethyl) fluorene **1a**, 9-Methyl-9-(2-trimethylsilylethyl) luorene **2** and 2,7-dibromo-9-methyl-9-(2-trimethyl-silylethyl) fluorene **3** via cyclization of biphenyl with dichlorobutyltrichlorosilane followed by methylation and bromination reactions. It is anticipated that the resulted dibromo derivative should be attractive precursor for the synthesis of blue-light-emitting polyfluorenes via reductive polymerization.

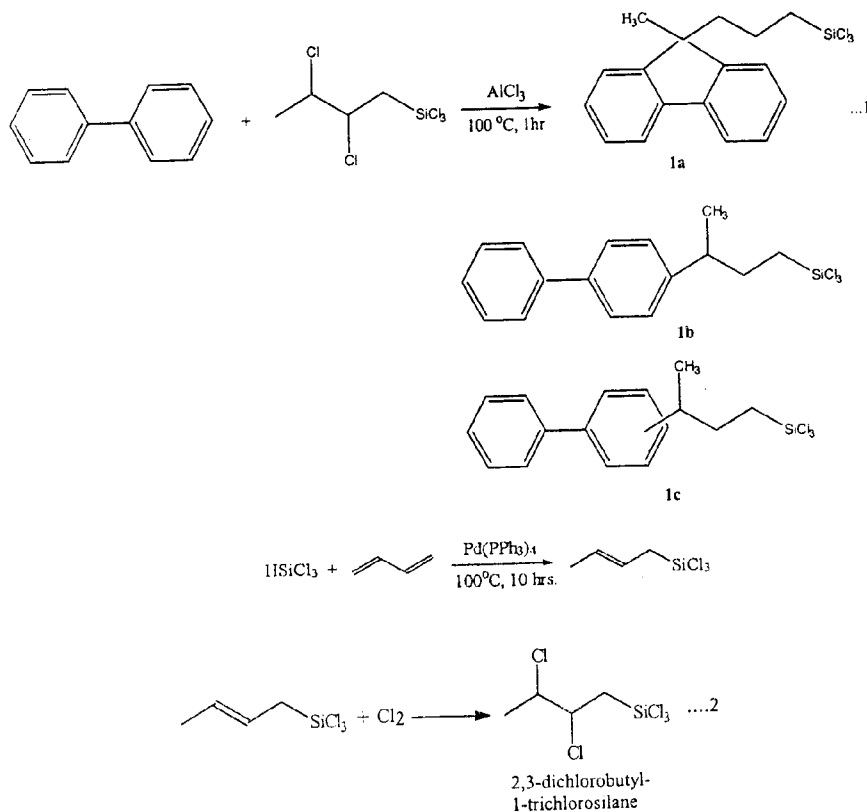
Results and Discussion

Cyclization of biphenyl with 2,3-dichlorobutyl-1-trichlorosilane:

Friedel-Crafts alkylation of biphenyl with dichlorobutyltrichlorosilane in the presence of anhydrous aluminum chloride catalyst gave fluorenyl-containing chlorosilane **1a** as the major product along with noncyclic by-products (eq. 1). Dichlorobutyltrichlorosilane was prepared according to the published procedure [13], 1,3-butadiene was hydrosylated with trichlorosilane to get 1-trichlorosilyl-2-butene which was later on converted to 2,3-dichlorobutyl-1-trichlorosilane through chlorination reaction (eq. 2)

Mechanism

For the Friedel-Crafts cycloalkylation of biphenyl with 2,3-dichlorobutyl-1-trichlorosilane in the presence of anhydrous aluminum chloride, a mechanism for the formation of 9-methyl-9-(2-trichlorosilylethyl)fluorene is outlined in the Scheme. The γ -positioned C-Cl bond of 2,3-dichlorobutyl-1-trichlorosilane is first complexed with aluminum chloride to give the polar intermediate species $\delta^+\text{C}-\text{Cl}^{\delta-}$ ($\delta^+\text{C}-\text{Cl} \text{ Al } \delta^-\text{Cl}_3$) or $\text{C}^+\text{AlCl}_4^-$ [14-18]. It is well known that a carbocation γ to the silicon is more stable than β and α carbocations through σ - π conjugation between the vacant p orbital of the carbocation and the σ orbital of the C-Si bond [19]. This intermediate then attacks biphenyl electro-philically to generate a benzenonium ion, followed by deprotonation to give the monoalkylated product,



(3-biphenyl-3-methyl-2-chloropropyl) trichlorosilane **A**, and the liberation of hydrogen chloride gas. Although the alkylation of biphenyl 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 [14]. Thus, isomerization must be possible under the reaction conditions.

The ortho isomer of (3-biphenyl-3-methyl-2-chloropropyl)trichlorosilane forms a complex again with aluminum chloride to generate the 3-biphenyl-3-methyl-1-trichlorosilylpropyl cation intermediate **B**, which rearranges to the more stable carbocation, 1-biphenyl-1-methyl-3-trichlorosilylpropyl intermediate **C**. Intermediate **C** then cyclizes through an intramolecular electrophilic substitution on the neighboring phenyl ring to give fluorenyl trichlorosilane **1a**.

Methylation of **1a**

Chlorosilyl-containing organosilanes can easily react with organometallic reagents, alcohols

and amines to afford useful new organosilicon compounds in which Si-C, Si-O and Si-N bonds are present.²⁰⁻²² In order to synthesize 9-methyl-9-(2-trimethylsilylethyl)fluorene derivative, **1a** was treated with methylmagnesium chloride in THF to give the desired compound **2** in 96% yield which was later on characterized by GC/MS and NMR spectroscopy.

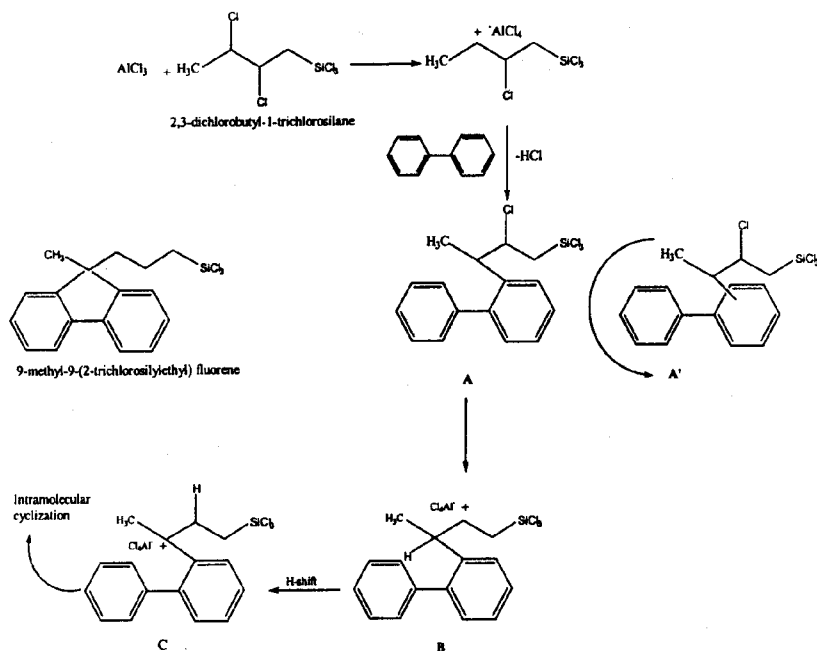
Bromination of **2**

Bromination of **2** with excess amount of bromine in DMF was completed at 22°C within 10 min. The product was purified by preparative gas chromatography to get 2,7-dibromo-9-methyl-9-(2-trimethylsilylethyl)fluorene **3** in 70% yield (eq 3 & 4).

Experimental

General Notes

All reactions were carried out under nitrogen atmosphere. Glassware was flame-dried before use. Dried solvents were employed in all reactions. Aluminum chloride, biphenyl, trichlorosilane and



1,3-butadiene were purchased from Aldrich Chemical Co. 2,3-dichlorobutyl-trichlorosilane was prepared by the published procedure [13]. 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. X 1.5 m.) or a capillary column (SE-30, 30m) 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. 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 . Mass spectra were obtained using a Hewlett-Packard 6890 GC/MS.

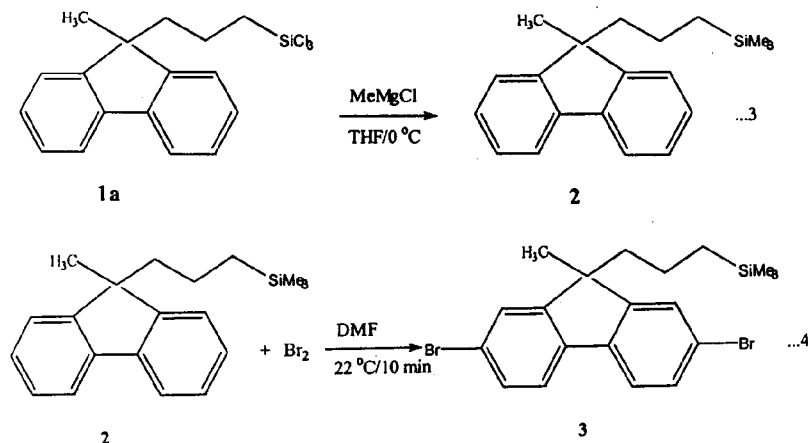
Synthesis of 9-methyl-9-(2-trichlorosilylethyl) fluorene 1a

A mixture of aluminum chloride (0.33g, 2.475 mmol), biphenyl (8g, 51.88 mmol) and 2, 3-dichlorobutyltrichlorosilane (3.38g, 12.97 mmol) was

stirred and warmed to 100°C for 1h. Then POCl_3 (0.46g, 2.97 mmol) and hexane 30 ml. were added to the reaction mixture and the mixture was stirred for 2h at 80°C . The $\text{POCl}_3\text{-AlCl}_3$ complexed salt was filtered-off. The resulting solution was bulb-to-bulb distilled at atmospheric pressure, while high boilers were distilled at reduced pressure. Yellow oily distillate was obtained at a temperature of $140\text{--}145^\circ\text{C}/0.2$ torr which contained a mixture of 3 isomers. The yield of the major product i.e 9-methyl-9-(2-trichlorosilylethyl)fluorene was 33% as determined by GLC analysis. Preparative G.C. was performed to separate all the three isomers and were fully characterized by GC/MS, ^1H and ^{13}C NMR spectroscopy. The other two isomers were characterized as substituted biphenyls as represented by structures 1b and 1c.

$^1\text{H-NMR}$, 300MHz(1a): δ 0.60-0.66 (m, 2H, SiCH_2), 1.54 (s, 3H, CH_3 at 9th position of fluorene ring), 2.24-2.30 (m, 2H, SiCH_2CH_2), 7.36-7.77 (m, 8H, aromatic-H).

$^{13}\text{C-NMR}$, 75MHz(1a): δ 19.05 (SiCH_2), 26.48 (CH_3 at 9th position of fluorene ring), 32.56 (SiCH_2CH_2), 51.0 (9th carbon of fluorene ring), 120.13, 122.61, 127.52, 127.64, 141.74, 150.41 (aromatic carbon).



GC/MS (*m/z*)(1a): Calcd. for $\text{C}_{16}\text{H}_{15}\text{SiCl}_3$ (M^+) 340, found 340.

$^1\text{H-NMR}$, 300MHz (1b & 1c): δ 1.34-1.36[(d, 3H, CH_3) (t, 2H, SiCH_2)], 1.87-1.95 (q, 2H, SiCH_2CH_2), 2.78-2.85 (h, 1H, benzylic CH), 7.27-7.62 (m, 9H, aromatic-H).

$^{13}\text{C-NMR}$, 75MHz (1b & 1c): δ 21.03 (CH_3), 21.92 (SiCH_2), 30.41 (SiCH_2CH_2), 41.33 (benzylic CH), 126.78, 126.89, 127.03, 127.16, 139.14, 144.21 (aromatic carbon).

GC/MS (*m/z*) (1b & 1c): Calcd. for $\text{C}_{19}\text{H}_{17}\text{SiCl}_3$ (M^+) 342, found 342.

Synthesis of 9-methyl-9-(2-trimethylsilylethyl) fluorene 2:

To a solution of 0.19 g (0.57 mmol) of 9-methyl-9-(2-trichlorosilylethyl) fluorene 1a (which also contained small amount of isomers 1b & 1c) in 30 ml THF was added 2.8 ml(8.40 mmol) of 3M methylmagnesium chloride in THF dropwise with stirring. A slight exothermic reaction was observed. After the addition was complete, the mixture was stirred at room temperature for 2h. Subsequently it was poured into a saturated aqueous solution of NH_4Cl . The aqueous layer was extracted with diethyl ether and the combined organic layers were washed twice with 50 ml. Of water and 20 ml. Of saturated NaCl and were dried over anhydrous MgSO_4 . Rotary evaporation of the volatiles left 2.16 g (96%) of 2.

$^1\text{H-NMR}$, 300 MHz: δ -0.45-0.20 (s, m, 11H, SiMe_3 , CH_2), 1.49 (s, 3H, methyl at 9th carbon of

fluorene ring), 1.49-2.0 (m, 2H, fluorene-coordinated CH_2), 6.83-7.91 (m, 8H, aromatic-H).

$^{13}\text{C-NMR}$, 75MHz: δ -1.99 (SiMe_3), 10.62 (silicon-coordinated CH_2) 25.89(methyl at 9th carbon of fluorene ring), 34.77 (fluorene-coordinated CH_2), 52.67 (9th carbon of fluorene ring), 120.13, 122.61, 127.52, 127.64, 141.74, 150.41 (aromatic carbon).

GC/MS (*m/z*): Calcd. for $\text{C}_{19}\text{H}_{24}\text{Si}$ (M^+), 280, found 280.

Synthesis of 2,7-dibromo-9-methyl-9-(2-trimethylsilylethyl)fluorene 3:

To a solution of 7.45 g (26.75 mmol) of 2 in 20 ml DMF was added 6.97 g (43.82 mmol) of bromine, and the reaction mixture was stirred for 1h at room temperature. After completion of the reaction, the solvent along with excess bromine were removed under vacuum, leaving an oily product with some polymeric solid. The oily product was extracted with dry n-hexane to give product 3 in 70% yield which was fully characterized by GC/MS, ^1H and ^{13}C NMR after purified by preparative gas Chromatography.

$^1\text{H-NMR}$, 300MHz: δ (-0.12)-(-0.11) (s, m, 11H, SiMe_3 , SiCH_2), 1.45 (s, 3H, CH_3 at 9th position of the fluorene ring), 1.88-1.94 (m, 2H, SiCH_2CH_2), 7.47-7.53 (m, 6H, aromatic-H).

$^{13}\text{C-NMR}$, 75MHz: δ -1.99 (SiMe_3), 10.62 (SiCH_2), 25.89 (CH_3 at 9th position of the fluorene ring), 34.77 (SiCH_2CH_2), 52.67 (carbon at 9th

position of fluorene ring), 121.26, 121.30, 121.52, 130.21, 138.50, 159.77 (aromatic carbon).

GC/MS (m/z): Calcd. for C₁₉H₂₂Br₂Si (M⁺), 438, found 438.

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