Derivatization Reactions of Fluorenyl-Substituted Chlorosilanes

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Summary: Derivatization reactions of 9-methyl-9-(2-trichlorosilylethyl)fluorene [C_6H_5-$C_6H_5(CH_3CCH_2CH_2SiCl_3)$] (1) with nucleophilic reagents such as MeOH, $LiAlH_4$, n-BuLi and Grignard reagents give the corresponding compounds [C_6H_5-$C_6H_5(CH_3CCH_2CH_2SiR_3)$] where 2(R=$CH_3$), 3(R= butyl), 4(R=hexyl), 5(R=OCH_3) and 6(R=H). All the prepared compounds were characterized by GC/MS, ^1H and ^{13}C-NMR spectroscopy.

Introduction

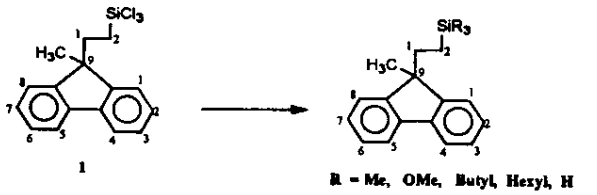
Alkylations of aromatic compounds with alkylhalides or olefins in the presence of Lewis acid catalysts have been reported in many articles since the reaction of benzene with amylchloride to produce amylbenzene was reported by Friedel and Crafts in 1877 [1]. The alkylation of substituted benzenes with alkenyl -silanes has attracted little attention because of the low reactivity of vinylsilanes [2] and the difficulties of allylsilanes syntheses [3]. Nametkin *et al.* first reported that the reaction of substituted benzenes with alkenylsilanes such as allylsilanes and vinylsilanes afforded mono- and bis(silylethyl) benzene derivatives [4,5].

Although, various fluorenylsilanes, i.e. dimethylbis(9-fluorenyl)silane [6,7] and dimethyl (9-fluorenyl)cyclopentadienylsilane [8] are known to be prepared from lithiation reaction of fluorene, the cyclization of biphenyl with alkylhalides containing silyl groups has never been reported.

In our previous paper [9], we reported synthesis of 9-methyl-9-(2-trichlorsilyl ethyl) fluorine(1) and 9-(2-trichlorosilylethyl)fluorene(2) through Friedel-Craf reactions of biphenyl with dichlorobutyl-trichlorosilane and dichloropropyl-trichlorosilane respectively, using anhydrous aluminum chloride as the catalyst. In this study we wish to report a convenient one- step derivatization of (1) with nucleophilic reagents such as MeOH, $LiAlH_4$, n-BuLi and Grignard reagents in order to synthesize precursors for blue-light-emitting polyfluorenes. All the new compounds were characterized by GC/MS, ^1H and ^{13}C NMR Spectroscopy.

Results and Discussion

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 [10-12]. The polyalkylated benzenes having chlorosilyl groups could serve as possible precursors for new silicon-containing materials [13]. To synthesize new silyl-group-containing fluorenyl derivatives, (1) was treated with a variety of reagents such as methyl and hexyl Grignard reagents, methanol, n-BuLi and $LiAlH_4$ to give the corresponding derivatives (Scheme-1). These were obtained in good to excellent yields after purification by fractional distillation. All new derivatives were satisfactorily characterized by GC/MS and NMR spectroscopy.



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R = Me, OMe, Butyl, Hexyl, H

2 5 3 4 6
(96%) (88%) (98%) (98%) (99%)

Using nucleophilic reagents i,e

- MeMgCl(THF/0°C)
- Methanol (pyridine/0°C)
- n-BuLi (THF/20°C)
- HexMgCl (THF/reflux)
- $LiAlH_4$ (THF/0°C)

Scheme-1

Structure Elucidation

The ^1H-NMR spectrum of (2) shows two multiplets each of relative area 2 at δ1.94-2.00 ppm and 6.83-7.91 ppm respectively and attributed to the

protons of the silicon coordinated ethyl group. One singlet (rel area 9) at δ-0.45-0.20 ppm, attributed to silicon coordinated trimethyl group and another singlet of relative area 3 at δ 1.49 ppm is due to the methyl group at the C-9 of the fluorene ring.

In aromatic region two sets of peaks are originating. The multiplets at δ6.83-7.91 ppm are due to the 8 protons of the fluorene ring.

The ^{13}C-NMR spectrum shows five resolved peaks in aliphatic region while six peaks are observed in aromatic region and is in good coincidence with the ^{1}H NMR spectrum.

Similarly, structures for compounds (3-6) were also deduced from the ^{1}H and ^{13}C-NMR data. Figures (1-4) represent ^{1}H and ^{13}C NMR spectra of the parent molecule (1) as well as of the compound (2).

Experimental

General Notes

All reactions were carried out under nitrogen atmosphere. Solvents were purified using standard purification procedure [14]. Anhydrous aluminum chloride, trichlorosilane triphenylphosphine, $PdCl_2$, 1,3-butadiene, and 1,3-cyclohexadiene were purchased from Aldrich Chemical Co. and used without further purification. Biphenyl was purchased from Yakuri Pure Chemical Co. $LiAlH_4$, n-BuLi and MeMgCl were purchased from Aldrich Chemical Co. All air sensitive liquids and dried solvents were transferred by standard syringe or double-tipped needle techniques. Reaction products were analyzed by GLC using a capillary column (SE-30, 30 M) or a packed column (10% OV.101 on 80-100 mesh Chromosorb W/AW, 1/8 in. x 1.5 in.) on a Varian 3300 gas chromatograph equipped with a flame ionization detector or a thermal conductivity detector. The samples for characterization were purified by preparative GLC using a Varian Aerograph Series 1400 gas chromatograph with a thermal conductivity detector and a 2 m by 1/8 in. stainless steel column packed with 20% OV-101 on 80-100 mesh Chromosorb P/AW. Mass spectra were obtained using a Hewlett-Packard 5890 series II gas chromatograph equipped with a 5972 mass selective detector.

NMR spectra were recorded on a Varian spectrometer using $CDCl_3$,^{1}H NMR spectra at 300 MHz and ^{13}CNMR at 75.4 MHz.

9-Methyl-9-(2-trimethylsilylethyl)fluorene (2):

To a solution of 0.19 g (0.57mmol) of 9-methyl-9- (2-trichorosilylethyl)fluorene(**1**) and 30ml

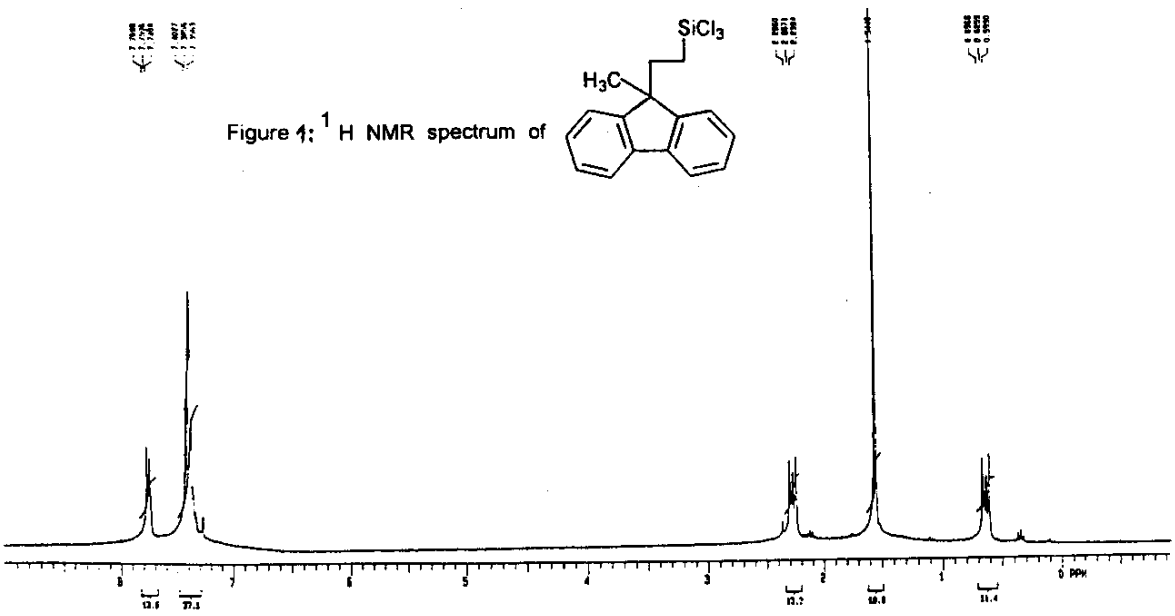

Fig. 1: ^{1}H NMR spectrum of

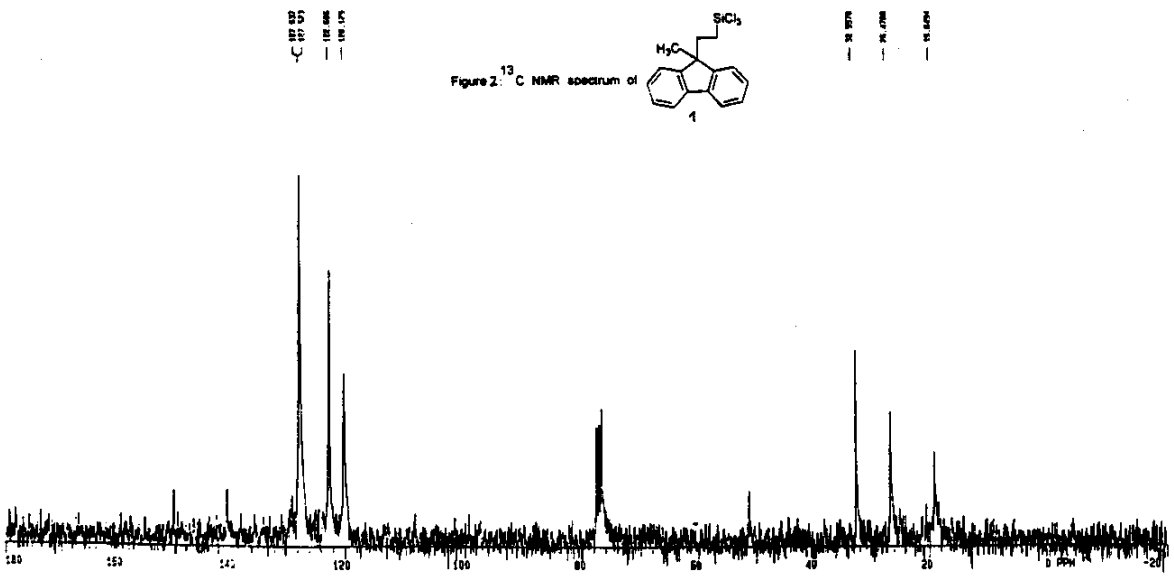

Fig. 2: ^{13}C NMR spectrum of

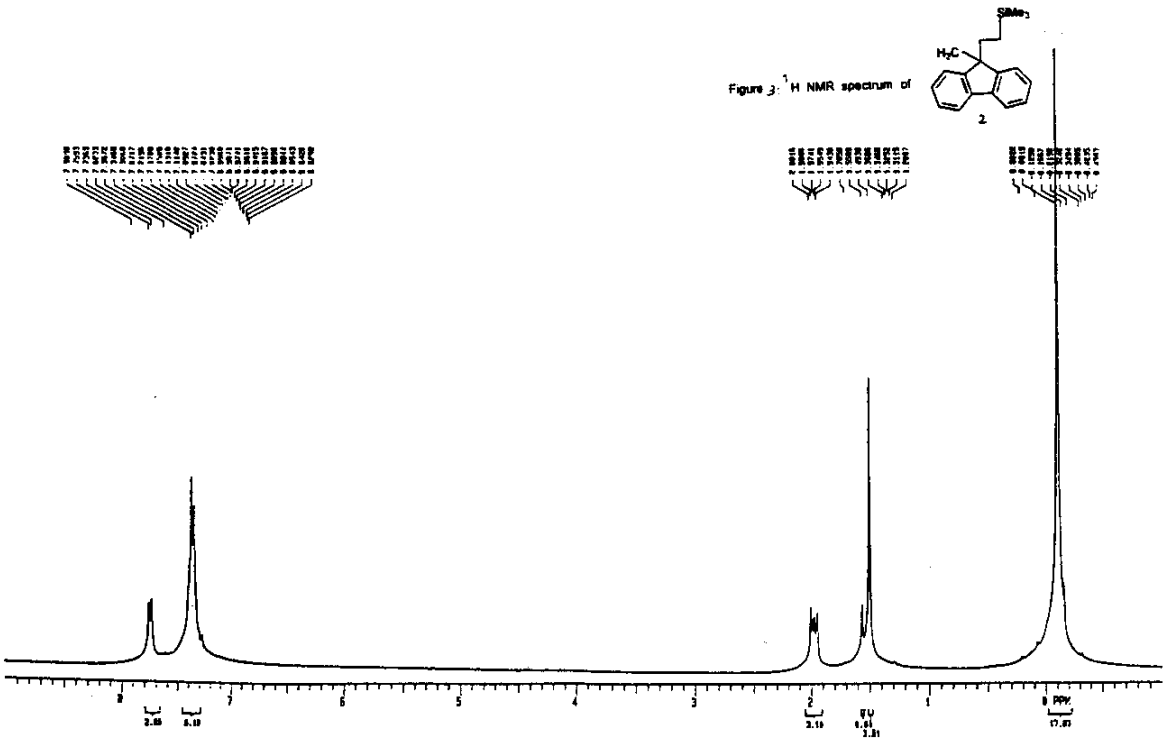

Fig. 3: ^{1}H NMR spectrum of

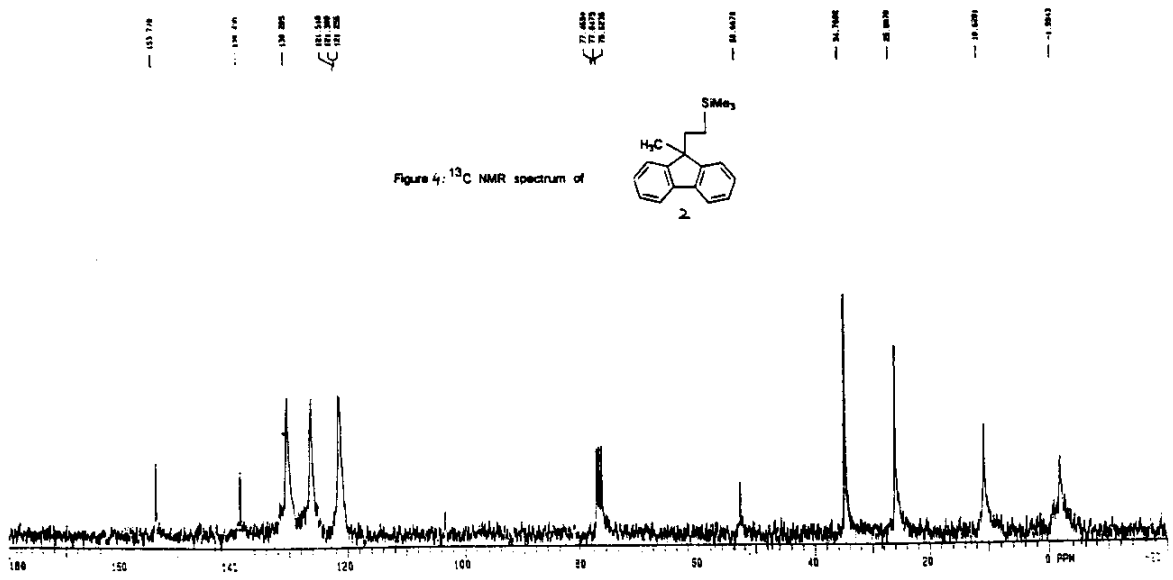

Fig. 4: ^{13}C NMR spectrum of

THF was added 2.8ml of 3M methylmagnesium chloride in THF (8.40mmol) dropwise with stirring. A slightly 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 50ml of water and 20ml of saturated NaCl and were dried over anhydrous $MgSO_4$. Rotary evaporation of the volatiles left 2.16 g (96%) of **(2)**.

^{1}H NMR: δ-0.45-0.20 (s,m, 11H, Si-Me_3, CH_2), 1.49 (s,3H, methyl at C-9), 1.94-2.00 (m, 2H, fluorene-coordinated CH_2), 6-83-7.91 (m, 8H, aromatic).

^{13}C NMR: δ-1.99 ($SiMe_3$), 10.62(silicon-coordinated CH_2), 25.89 (methyl at C-9), 34.77 (fluorene-coordinated CH_2), 52.67 (C-9), 120.13, 122.61, 127.52, 127.64, 141.74, 150.41 (aromatic C). GC/MS(m/z): Calcd. for $C_{19}H_{24}Si(M^+)$, 280, found 280.

9-Methyl-9- (2-tributylsilylethyl)fluorene(3):

2.72g (7.99mmol) of **(1)** was dissolved in dry THF (20cc). 1.54 g of n-BuLi (9.0ml of 2.67M solution in n-hexane) was added dropwise while cooling to -20°C. Color of the reaction mixture changed to red. After addition, the reaction mixture was stirred at room temperature for 1 h, which was then carefully quenched with water. Organic portion was separated. The aqueous layer was extracted with Et_2O. The combined organic portion was dried over $MgSO_4$. Solvent was removed using rotary evaporator to give 3.17 g (97.8%) of (3).

^{1}H NMR: δ(-0.8)-(-0.9) (m,2H, silicon-coordinated CH_2), [0.3-0.45 (m,9H, CH_3), 0.8-0.9 (t, 6H, CH_2), 0.9-1.4 (m, 12H, CH_2) butyl protons], 1.45 (s, 3H, methyl at C-9), 1.9-2.05 (m, 2H, fluorene-coordinated CH_2), 7.20-7.90 (m, 8H, aromatic).

^{13}C NMR: δ 7.12 (silicon-coordinated CH_2), 12.1, 14.0, 26.02, 26.38 (butyl C), 26.81 (methyl at C-9), 34.78 (fluorene-coordinated CH_2), 52.20 (C-9), 119.81, 122.72, 126.83, 127.09, 140.57, 151.88 (aromatic). GC/MS(m/z): Calcd. for $C_{28}H_{42}Si(M^+)$ 406, found 406.

9-Methyl-9-(2-trihexylsilylethyl)fluorene (4):

Reaction of 3.60g (10.6mmol) of **(1)** with 65ml of 2M hexylmagnesium chloride in THF (0.13mmol) using the procedure described for **(2)** gave an oily product of **(4)** in 98% yield.

^{1}H NMR: δ(-0.8)-(-0.9)(m, 2H, (CH_2), 1.45 (s, 3H. methyl at C-9), 1.9-2.05 (m. 2H. CH_2) [0.9-1.2 (t.

9H, (CH_3), 1.35-2.41 (broad single band, 24H, CH_2), 3.50-3.60 (t, 6H, CH_2) hexyl protons], 7.20-7.90 (m, 8H, aromatic).

^{13}C NMR: δ 7.13 (CH_2), 12.0, 12.1, 13.81, 14.0, 26.02, 26.35 (hexyl C), 26.80 (9-methyl), 34.77 (CH_2), 52.21 (C-9), 119.82, 122.70, 126.82, 127.10, 140.57, 151.88 (aromatic). GC/MS (m/z): Calcd. for $C_{30}H_{46}Si(M^+)$434, found 434.

9-Methyl-9-(2-trimethoxysilylethyl)fluorene (5):

To a solution of 0.58 g (18.0mmol) of dried MeOH and 0.71 g (8.96mmol) of dried pyridine surrounded with an ice bath was added 0.25g (0.75mmol) of **(1)** in 10ml of THF solution dropwise with stirring. The resulting mixture was stirred for 30 min, dried hexane was added, and the mixture was transferred to a separating funnel. The organic layer was separated and the solvent was removed under vacuum to give oily product in 88% yield.

^1H NMR: δ(-0.07)-(-0.01)(m, 2H, CH_2), 1.50 (s, 3H, methyl at C-9), 2.07-2.13 (m, 2H, CH_2), 3.44 (s, 9H, $Si(OMe)_3$), 7.30-7.74 (m, 8H, aromatic).

^{13}C NMR: δ 3.97(CH_2), 26.15 (methyl at C-9), 33.37 (CH_2), 50.41 (MeO, C-9), 119.92, 122.7, 127.06, 128.70, 140.53, 151.27 (aromatic). GC/MS(m/z): Calcd. for $C_{19}H_{24}O_3Si$ (M^+) 328, found 328.

9-Methyl-9-(2-silylethyl)fluorene (6):

To a solution of 0.34 g (9.0mmol) of lithium aluminum hydride and 30ml of dried THF was added 0.49g (1.44mmol) of **(1)** in 10 ml of THF solution dropwise with stirring. The resulting mixture was stirred for 30min and hydrolyzed. The organic layer was extracted with diethyl ether and the extracts were washed with water and dried over anhydrous $MgSO_4$. Solvent was removed using rotary evaporator to get **(6)** in 99% yield.

^1H NMR: δ 0.60-0.66 (m, 2H, CH_2), 1.54 (s, 3H, methyl at C-9), 2.24-2.30 (m, 2H, CH_2), 7.36-7.77 (m, 8H aromatic).

^{13}C NMR: δ19.05 (CH_2), 26.48 (CH_3), 32.56 (CH_2), 51.3 (C-9), 120.13, 122.61, 127.52, 127.64, 141.74, 150.41 (aromatic C).

GC/MS(m/z): Calcd. for $C_{16}H_{18}Si$ (M^+) 238, found 238.

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