

FORMATION OF CARBON-SILICON BOND AND EFFECT OF SILICON ON ORGANIC REACTIONS

Ashis K. Sarker*

Department of Chemistry, Mawlana Bhashani Science and Technology University, Tangail-1902, Bangladesh

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ABSTRACT

In this work, we report carbon-silicon bond formation in thiophene, assisted with alkylated silylchloride. The formylation reaction of silylated thiophene has been discussed and achieved 61% overall yield of reactions. The compounds obtained are characterized quantitatively and qualitatively by using elemental analysis, FT-IR spectroscopy, UV/Visible spectroscopy, and proton NMR spectroscopy. This research work will boost chemists to make the carbon-silicon bond and utilize them in various applications.

Keywords: Silicon; Thiophene; Formylation; Vilsmeier reaction; Orbital overlapping

1. INTRODUCTION

Organosilicon compounds are discovered in pharmaceuticals and in many other products, including agricultural chemicals, paints semiconductors, and computer and TV screens (Kan *et al.*, 2016). At present, these products are manufactured synthetically, since the silicon-carbon bonds are not available in nature (Kan *et al.*, 2016). Scientists are trying to get the new strategy that can be used to make these carbon-silicon bonds in ways that are more environmentally friendly and potentially much less expensive. In chemistry, carbon and silicon are chemically different atoms. However, both can make bonds to several atoms simultaneously, making them well appropriate to make the long chains of molecules (Visco *et al.*, 2016).

The chemistry of carbon and silicon compounds has many pronounced differences. These differences are the best reflected in a comparison of C/Si atoms replaced by alkyl chain (CR₃/SiR₃) (Estevez *et al.*, 2000; Lauvergnat *et al.*, 1996). The smaller electronegativity, the larger atomic radius and different electronic configuration of silicon were comparable to carbon which are clearly associated with all that phenomena. Pertinent theoretical treatments have focused on d-orbital participation and should be complemented by a consideration of π/σ^* interactions (Hillier *et al.*, 1970). From spectroscopic studies of alkylsilyl-substituted heterocycles, the intramolecular interactions between the heteroatom donor center and the substituents may improve the electronic and structural properties (Pater, *et al.*, 2005; Miyazawa *et al.*, 2000). Introduction of silyl functional group onto organic molecules can ensue electronic perturbations and thus represent an effective means to change the electronic properties of the molecules. Therefore, silyl groups on a π -conjugated system can be established to interrelate with the π -system through σ - π and σ^* - π^* conjugation (Richeter *et al.*, 2002; Mathew *et al.*, 2011). Silylation of aromatic hydrocarbons generally rises to alterations of the optical and electronic properties of the parent aromatic hydrocarbons such as enhanced fluorescent quantum yields, therefore it should be extensively investigated (Kato *et al.*, 2015). In spite of their potential, there are no reports on silylated thiophene aldehyde, because of the lack of appropriate synthetic procedures to introduce a silyl group and further reactions.

In this work, carbon-silicon bond has been prepared in thiophene moiety. Using organolithium reagents, thiophene was metalated to give lithiothiophene, which were treated with a chlorotrialkylsilane to give the trialkylsilylthiophene. For the formylation reaction, a method is developed to produce highly reactive Tributyl (thiophen-2yl) silane-5-carbaldehyde reagent which can be effortlessly applicable for the synthesis of numerous imperative materials.

2. EXPERIMENTAL SECTION

2.1 Materials

All reactions were performed under an atmosphere of dry nitrogen. The following reagents were obtained from commercial sources and used without further purification. Thiophene, *n*-Butyllithium (*n*-BuLi), (hexane solution, 2.5 M), Tetrahydrofuran, anhydrous (THF), Tributylsilylchloride (TBS), N, N-dimethylformamide (DMF), Phosphorus (V) oxychloride (POCl₃) were purchased from Aldrich.

2.2 Methods

Column chromatography was performed using silica gel 230-300 mesh (purchased from Aldrich) as the solid support. All NMR spectra were recorded on a Bruker Advance DPX 400 MHz spectrometer at 25 °C in CDCl₃.

* Corresponding Author: ashischemru@gmail.com

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¹H NMR chemical shifts are reported in δ units, part per million (ppm) relative to the chemical shift of residual solvent. Deuterated solvents were used as received from Aldrich. Reference peaks for chloroform in ¹H NMR spectra were set at 7.18 ppm. The absorption spectra were measured on a SHIMADZU/UV-2550 model UV-visible spectrophotometer. Infrared spectra were recorded using FT-IR Spectrophotometer (Nicolet). For elemental analysis, all three samples (3 mg per analysis) were thoroughly dried prior to elemental analysis and stored under an inert atmosphere. Elemental analysis was performed as C/H/S analyses on an EA 1108 CHNS-O (Carlo Erba Instruments, CE Elantech, Inc.) elemental analyzer.

2.3 Synthesis

2.3.1 Thiophene (1)

Physical state: colorless liquid (bp = 84 °C). ¹H-NMR (400 MHz, CDCl₃), δ (ppm): 7.40 (d, 2H), 7.19 (d, 2H). C₄H₄S (84.00): Calcd C 57.10, H 4.79, S 38.11: found C 56.74, H 4.91, S 38.61. FT-IR (ν_{\max} , cm⁻¹): 3108, 1408, 1252, 1080, 832 and 708.

2.3.2 Tributyl(thiophen-2-yl) Silane (2)

n-BuLi (40 mL, 2.5M in hexane, 100 mmol) was added slowly to a solution of thiophene (8.4 g, 100 mmol) in THF (100 mL) at -78 °C under nitrogen protection. The reaction mixture was stirred for 1 h at the same temperature and then the mixture was warming slowly to room temperature. To the reaction mixture, chlorotripropylsilane (19.2 g, 100 mmol) was added and stirred overnight. Diethyl ether was used to extract product from the reaction mixture and washed with water and brine solution. To obtain pure tributyl (thiophen-2-yl) silane, column chromatography was carried out. Hexane was used as eluent (R_f = 0.85, bp = 200~201 °C) (24 g, 94% yield). Physical state: light oily liquid. ¹H-NMR (400 MHz, CDCl₃), δ (ppm): 7.62 (d, 1H), 7.28 (d, 1H), 7.22 (t, 1H), 1.4 (m, 12H), 0.95 (m, 9H), 0.85 (m, 6H). C₁₆H₃₀SSi (282.18): calcd. C 68.01, H 10.70, S 11.35, Si 9.94: found C 67.82, H 9.63, S 11.48, Si 10.28. FT-IR (ν_{\max} , cm⁻¹): 2920, 1460, 1212, 1080, 984, 704 and 488.

2.3.3 Tributyl (thiophen-2-yl) silane-5-carbaldehyde (3)

DMF (2 mL) was added into the round bottom flask which was kept under an iced bath. POCl₃ (3 mL) was added dropwise and the solution color turned into red. The mixture was stirred for another 0.5 h. Then, tributyl (thiophen-2-yl) silane (2.0 g, 7.0 mmol) was added and the temperature was increased to 90 °C. The reaction mixture was stirred for another 4h at 90 °C. Then temperature was reduced to room temperature and water (50 mL) was added to the mixture and the reaction mixture was hydrolyzed. Chloroform was used to extract the product from the reaction mixture and washed with water and KOH solution (0.0 g, 0.0% yield). Starting material was found and confirmed by TLC, proton NMR, FT-IR spectroscopy, and boiling point (bp = 200~201 °C). Physical state: light oily liquid. ¹H-NMR (400 MHz, CDCl₃), δ (ppm): 7.62 (d, 1H), 7.28 (d, 1H), 7.22 (t, 1H), 1.4 (m, 12H), 0.95 (m, 9H), 0.85 (m, 6H). FT-IR (ν_{\max} , cm⁻¹): 2920, 1460, 1212, 1080, 984, 704 and 488.

2.3.4 Tributyl (thiophen-2-yl) silane-5-carbaldehyde (3)

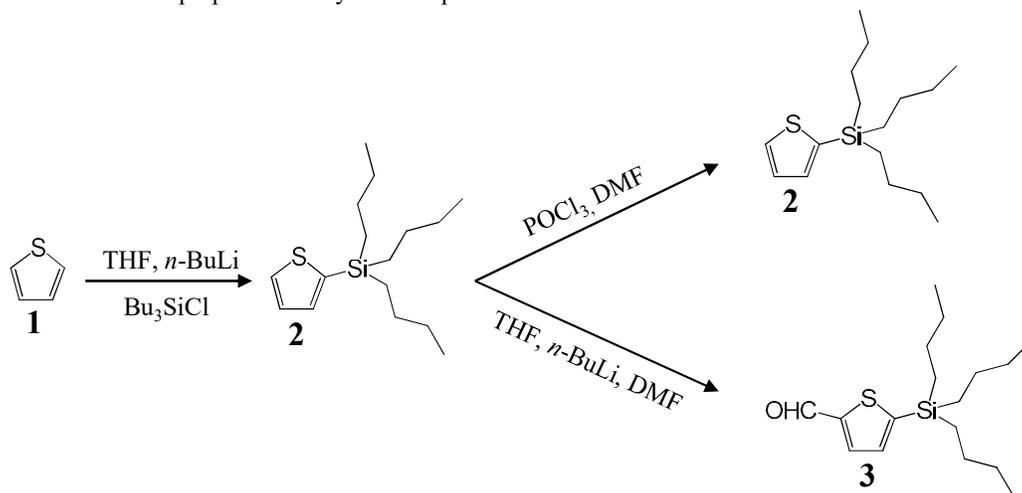
n-BuLi (11.3 mL, 2.5 M in hexane, 28.31mmol) was added slowly to a solution of tributyl(thiophen-2-yl)silane (8.0 g, 28.0 mmol) in THF (100 mL) at -78 °C under nitrogen protection. The reaction mixture was stirred for 1 h at the same temperature and then the mixture was warming slowly to room temperature. After 1 h, DMF (4.14 g, 4.36 mL, 56.62 mmol) was added and stirred overnight. Chloroform was used to extract product from the reaction mixture and washed with water and brine solution. To obtain pure tributyl (thiophen-2-yl) silane-5-carbaldehyde, column chromatography was carried out. Hexane and ethylacetate mixture were used as eluent (R_f = 0.62, bp = 361~363 °C) (5.3 g, 61% yield). Physical state: deep oily dense liquid. ¹H-NMR (400 MHz, CDCl₃), δ (ppm): 9.98 (s, 1H), 7.83 (d, 1H), 7.32 (d, 1H), 1.4 (m, 12H), 0.95 (m, 9H), 0.85 (m, 6H). C₁₇H₃₀OSSi (310.18): calcd. C 65.74, H 9.74, O 5.15, S 10.32, Si 9.04: found C 64.54, H 9.70, O 5.25, S 10.23, Si 9.83. FT-IR (ν_{\max} , cm⁻¹): 2920, 1676, 1512, 1460, 1296, 1200, 1060, 984, 884, 760 and 500. (GC-mass): m/z 310.18 [M⁺]; C₁₇H₃₀OSSi (310.51).

3. RESULTS AND DISCUSSION

Tributyl(thiophen-2-yl)silane has been synthesized which involve reaction of thiophene and tributylsilylchloride assisting by *n*-BuLi (Scheme 1). 2-H of thiophene has been substituted by strong nucleophile Li ion at low (-78 °C) temperature. This Li ion is highly stable with deprotonated thiophene negative anion because of the π

electrons of thiophene (aromaticity) and lone pair of heteroatom sulfur. After adding tributylsilylchloride, Li ion was substituted by Si and new C-Si covalent bond was formed (Scheme 1, compound 2).

If the molecular orbital theory has been considered, the C-Si bond has higher HOMO compared to C-H bond. Si is raised the HOMO level of this molecule (Pater *et al.*, 2005). Therefore, C-Si will be better donor than C-H as well as band gap of this silylated thiophene will be lower. Therefore, silyl groups on a π -conjugated system can be established to cooperate with the π -system through σ - π and σ^* - π^* conjugation (Richeter *et al.*, 2002; Mathew *et al.*, 2011). Silylation of aromatic hydrocarbons gave rise to alterations of the optical and electronic properties of the parent aromatic hydrocarbons. π electron from thiophene conjugation and vacant d orbital of Si can be overlap with each other which may increase the conjugation length of the molecule. This overlapping can be occurred by hyperconjugation with p orbital and vacant d orbital. This is the main reason for the modification of optical and electronic properties of silylated thiophene.



Scheme 1: Synthetic route to Tributyl (thiophen-2-yl) silane-5-carbaldehyde.

For formylation of thiophene, Vilsmeier reaction is well known for the formulation of thiophene (Vogt *et al.*, 2012; Su *et al.*, 2010). Vilsmeier reaction has been performed which form comparatively weak electrophile (Scheme 1). The Vilsmeier-Haack reaction is an organic reaction utilized to alter an electron rich aromatic ring to an aryl aldehyde by DMF, an acid chloride, and aqueous work-up. The mechanism starts with the reaction of DMF through the acid chloride to produce an iminium salt acknowledged as the Vilsmeier reagent. The electron rich aromatic ring then charges the iminium ion with loss of aromaticity. A deprotonation step reimposes aromaticity, which is accompanied by the release of a chloride ion to produce another iminium intermediate. Aqueous work-up then escorts to the aryl aldehyde final product. DMF with POCl_3 produce this electrophile where positive charge can be delocalized with nitrogen atom. However, efforts to carry out a reduction of these intermediates by means of POCl_3 were not successful. We concluded that silyl moiety of this thiophene made the difficulties to complete the reaction by sharing electron with thiophene conjugation. Having the empty d orbital in silicon decreases the concentration of electron density in the 5 position of thiophene by accepting electron from thiophene π conjugation. The nucleophile moves through the π conjugation of thiophene to the empty d orbital of silicon by delocalization. Therefore, the nucleophilicity of thiophene has decreased and unable to perform reaction with weak electrophile. Now the only solution is to use strong electrophile to react with weak nucleophile silylated thiophene. As a strong electrophile $n\text{-BuLi}$ has been selected, that can be participated in the substitution reaction with silylated thiophene. These were metalated by organolithium reagents to produce lithiothiophene, which were treated with DMF to provide aldehyde functional group by formylation reaction after hydrolysis. At first, DMF was added at -78°C and the yield was found only 10%, the reason being low temperature has been used to react with DMF. Then the temperature has been increased until 0°C to add DMF to the reaction mixture and yield was increased up to 36%, which encouraged us to use room temperature to add DMF to the reaction mixture and the yield was 61%, which is the highest yield ever in silylated thiophene formylation reaction (Table 1). Usually, in formylation reaction low temperature (-78°C) was used and reaction proceed appropriately (Su *et al.*, 2010). High temperature is required here because of weak nucleophilicity of silylated thiophene. We optimize the formylation reaction of silyl thiophene and successfully synthesize tributyl (thiophen-2-yl) silane-5-carbaldehyde (Table 1). The structures were confirmed by the proton NMR and FT-IR spectroscopy.

Usually thiophene has four protons and in the NMR spectra two peaks have been shown in the aromatic region because of symmetry of the thiophene moiety. After silylation, the aromatic peaks showed at δ 7.62, 7.28 and

7.22 which confirm that one proton was substituted by other functional group and three protons were attached with thiophene group. After analyzing the aliphatic protons, the addition of R_3Si - group has been confirmed.

In the final molecule, two protons have been found in aromatic portion and the peaks showed at δ 7.83, 7.32 and both aromatic peaks become doublet which indicate the two aromatic protons in thiophene group and proton at 5 position substituted by another functional group. The peak at δ 9.99 indicates the addition of aldehyde group with thiophene at 5 position.

Table 1: Conditions for the synthesis of tributyl(thiophen-2-yl)silane-5-carbaldehyde

Reactant	Time (h)	Temp ($^{\circ}C$)	Yield (%)	Product
2	12	-78	10	3
2	12	0	36	3
2	12	25	61	3
2	12	50	46	3

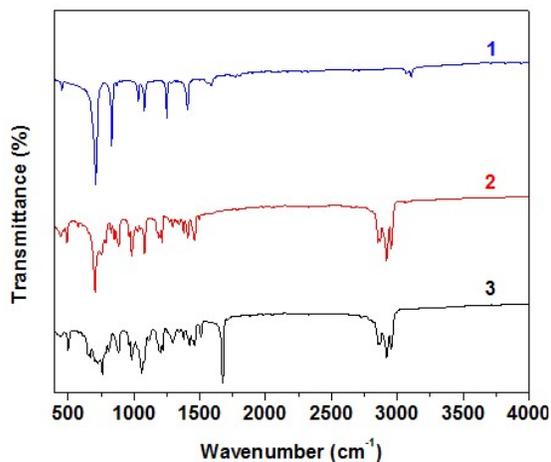


Figure 1: Infrared spectra of thiophene (1), Tributyl (thiophen-2-yl) silane (2) and Tributyl (thiophen-2-yl) silane-5-carbaldehyde (3)

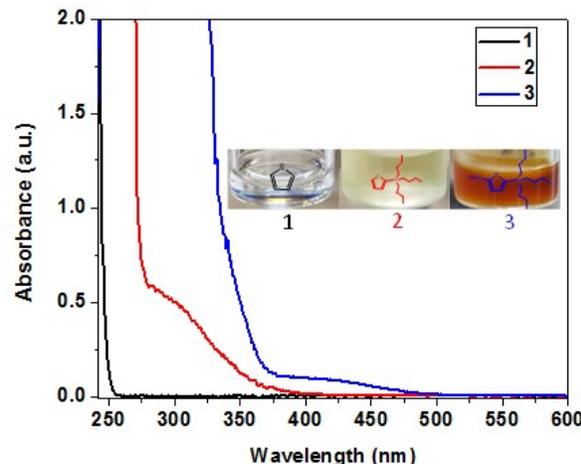


Figure 2: UV/Visible absorption spectra of thiophene (1), Tributyl (thiophen-2-yl) silane (2) and Tributyl (thiophen-2-yl) silane-5-carbaldehyde (3)

The structures of the molecules 1, 2 and 3 were confirmed by FT-IR spectroscopy. In the FT-IR spectra of thiophene (1), the bands at $2872\text{-}2965\text{ cm}^{-1}$ and 1676 cm^{-1} region were absent (Figure 1). The FT-IR spectra of 2 showed the presence of a characteristic band for the sp^3 C-H stretching with the $2872\text{-}2965\text{ cm}^{-1}$ region which indicated the formation of C-Si bond with thiophene moiety. The FT-IR spectra of 3 showed the presence of a characteristic band for the sp^3 C-H stretching within the $2872\text{-}2965\text{ cm}^{-1}$ region and appearance of band at 1676 cm^{-1} for the compound 3 was attributed to the formation of carbonyl groups which confirmed the aldehyde group present in the silylated thiophene (Figure 1). From the above discussion, the formation of C-Si bond and the attachment of aldehyde function group to the thiophene moiety have been confirmed.

Table 2: UV/Visible absorption data of compounds 1, 2 and 3 in chloroform. The concentration was 10^{-4} M.

Compound	Band λ_{ab} (nm) ($\log \epsilon$)	Onset λ_{ab} (nm)
1	244 (2.10)	256
2	249 (3.48)	400
3	300 (1.23)	500

Thiophene is an aromatic moiety which absorbs in the range of 200-265 nm, and it may act as electron rich compound. The UV/Visible spectra of all thiophene and substituted thiophenes were recorded in chloroform and data presented in Table 2. A comparison of UV/Visible spectra of thiophene, Tributyl (thiophen-2-yl) silane and Tributyl (thiophen-2-yl) silane-5-carbaldehyde are shown in Figure 2. Thiophene showed onset band at 256 nm and after carbon silicon bond formation the band of Tributyl(thiophen-2-yl)silane were significantly red shifted by 144 nm with respect to the parent thiophene; this suggest better communication between the thiophene and silicon because of vacant d orbital of silicon. Similarly, Tributyl(thiophen-2-yl)silane-5-carbaldehyde showed the highest onset absorption band at 500 nm and after adding aldehyde with silyl thiophene the band were significantly red shifted by 100 nm with respect to the compound Tributyl(thiophen-2-yl)Silane. This observation reflects that the carbon silicon bond can make conjugation by σ - π or σ^* - π^* interactions.

This highly reactive tributyl(thiophen-2-yl)silane-5-carbaldehyde can be used as precursor for numerous number of syntheses and silicon moiety could be incorporated in the various important molecules to tune the electronic properties. The chemical structures can be steadily modified to understand effect of structural tuning on opto-electronic and photovoltaic properties.

4. CONCLUSIONS

In summary, we developed a method to prepare highly reactive Tributyl(thiophen-2-yl)silane-5-carbaldehyde reagent which can be effortlessly applicable for the synthesis of various important molecules. R₃Si-group plays an important role to the formylation reaction of thiophene. Silylated thiophene gives the larger red shift in the UV/Vis absorption spectrum because of the more efficient σ - π conjugation between the silyl group and thiophene π system and the electronic perturbation by the silyl group is very effective. We are currently investigating the use of this methodology for the preparation of other organic conjugated molecules in our laboratory. The results will be reported in due course.

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