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Short Communication

Synthesis And Characterization of New Organotriethoxysilanes Via Aza-Michael Addition Of τ -Aminopropylsilanes To Substituted N-Phenylmaleimides

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ABSTRACT

An efficient method for C-N bond formation via aza-Michael addition of γ-aminopropylsilanes to substituted N-phenylmaleimides under mild conditions has been described. The five organotriethoxysilanes enclosing maleimide moiety have been synthesized without using any catalyst. All the compounds have been characterized by elemental analysis and spectroscopic techniques [IR and NMR (^{1}H,^{13}C].

Keywords: Aza-Michael addition reaction, N-phenylmaleimides, organotriethoxysilanes.

INTRODUCTION

Silicon is an element which has received well deserved consideration of researchers due to its notable reactivity as well as numerable bonding possibilities [1,2]. Silanes are used as versatile building blocks in organosilicon chemistry [3-6]. Silanes and their derivatives are centre of attraction for research due to their synthetic utility and applications [7]. With the increasing demand for organosilicon compounds in organic chemistry and organic–inorganic hybrid materials having potential applications such as biosensors and supported catalysts, the development of new methodologies that offer the preparation of a variety of novel silanes is eagerly desired [8-10]. Various review articles have been published which throw light on synthesis, reactivity and application of silanes [11-13].

The aza-Michael addition reaction involving conjugate addition of nitrogen containing nucleophiles to α,β-unsaturated compounds for the generation of C-N bond within the Michael product is used for the synthesis of organosilanes. This reaction has a myriad paradigm of achievements in the synthesis of β-amino carbonyl derivatives which are valuable building blocks for the formation of various nitrogen containing biologically active compounds, antibiotics and drugs etc [14-16]. Herein, we have employed substituted N-phenylmaleimide as starting material and its condensation with γ-aminopropyl trimethoxysilane via aza-Michael reaction to synthesize substituted N-phenylsuccinimide possessing silanes.

MATERIALS AND METHODS

All the syntheses were carried out under nitrogen atmosphere using Schlenk technique. Toluene and hexane were distilled over sodium pieces and chloroform was dried over phosphorus pentoxide. γ-Aminopropyltriethoxysilane (Aldich), aniline (Aldich), p-chloroaniline (Aldich), p-hydroxyaniline (Aldich), p-methylaniline (Aldich), p-methoxyaniline (Aldich), maleic anhydride (SDFCL) and acetic anhydride (SDFCL) were used as supplied without any purification. N-(phenyl)maleimide, N-(p-chlorophenyl)maleimide, N-(p-methylphenyl)maleimide, N-(p-methoxyphenyl)maleimide [17] and N-(p-hydroxyyphenyl)maleimide [18] were prepared according to methods reported in literature.

Infrared spectra were obtained with a Thermo Nicolet Nexus 670 spectrometer. C, H and N analyses of samples were performed on a FLASH-2000 organic element analyzer while Cl and Si contents were estimated gravimetrically. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution using 400 MHz (Bruker Avance AL 400) and 300 MHz (JEOL AL 300) FT NMR instrument. Chemical shifts for the protons were reported using tetramethylsilane (TMS) as an internal reference. Mass spectral measurements (ESI source with capillary voltage, 2500 V) were carried out on a VG Analytical (70-S) spectrometer.

General procedure for synthesis: In 100 mL two necked round-bottom flask, substituted N-(phenyl)maleimide (1 equivalent) was dissolved in 50 ml of chloroform under nitrogen atmosphere. To this, γ-aminopropyltrimethoxysilane (1 equivalent) was added drop-wise mixture was stirred for 4 h at room temperature. The excess solvent was evaporated under reduced pressure and highly viscous functionalized silanes were obtained with good yields and high purity.

1-Phenyl-3-(3-(triethoxysilyl)propylamino)pyrrolidine-2,5-dione (1): 3-Aminoropyltriethoxysilane (1 mL, 4.52 mmol) and N-(phenyl)maleimide (0.78 g, 4.52 mmol) were used for the synthesis of silane **1**. Yield: 81%. IR (cm^{-1}) = 1076 s (ν Si-O), 1389 (ν C-N-C), 1710 (νC=O), 2869, 2924 s (ν CH_2), 3282 (ν NH). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 0.39 (t, 2H, *J* = 8.2 Hz, $SiCH_2$), 1.14 (t, 9H, *J* = 5.7 Hz, CH_3), 1.71 (m, 2H, CCH_2C), 2.30 (s, 1H, NH), 2.71 (q, 2H, *J* = 6.6 Hz, CCH_2N), 3.03, 3.09 (dd, 2H, *J* = 8.3 Hz, CH_2CO), 3.71 (t, 6H, *J* = 5.7 Hz, OCH_2), 3.89 (q, 1H, *J* = 5.2 Hz, CHN), 7.31-7.56 (m, 5H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 8.92 ($SiCH_2$), 14.32 (CH_3), 24.21 ($C\boldsymbol{C}H_2C$), 36.21 ($\boldsymbol{C}H_2CO$), 51.31 ($C\boldsymbol{C}H_2N$), 55.72 (CHN), 59.25 (OCH_2), 124.12-133.60 (Ar-C), 173.61, 176.82 (C=O).

1-(4-Chlorophenyl)-3-(3-(triethoxysilyl)propylamino)pyrrolidine-2,5-dione(2):3-Aminoropyl triethoxy silane (1 mL, 4.52 mmol) and N-(p-chlorophenyl)maleimide (0.93 g, 4.52 mmol) were used for the synthesis of silane **2**. Yield: 88%. IR (cm^{-1}) = 1074 s (ν Si-O), 1392 (ν C-N-C), 1709 (νC=O), 2862, 2939 s (ν CH_2), 32827 (ν NH). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 0.42 (t, 2H, *J* = 8.2 Hz, $SiCH_2$), 1.16 (t, 9H, *J* = 5.7 Hz, CH_3), 1.69 (m, 2H, CCH_2C), 2.27 (s, 1H, NH), 2.68 (q, 2H, *J* = 6.6 Hz, CCH_2N), 3.01, 3.05 (dd, 2H, *J* = 8.3 Hz, CH_2CO), 3.65 (t, 6H, *J* = 5.7 Hz, OCH_2), 3.91 (q, 1H, *J* = 5.2 Hz, CHN), 7.42-8.34 (m, 4H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 9.21 ($SiCH_2$), 14.66 (CH_3), 24.79 ($C\boldsymbol{C}H_2C$), 36.42 ($\boldsymbol{C}H_2CO$), 51.69 ($C\boldsymbol{C}H_2N$), 54.95 (CHN), 59.52 (OCH_2), 127.16-135.45 (Ar-C), 174.25, 177.23 (C=O).

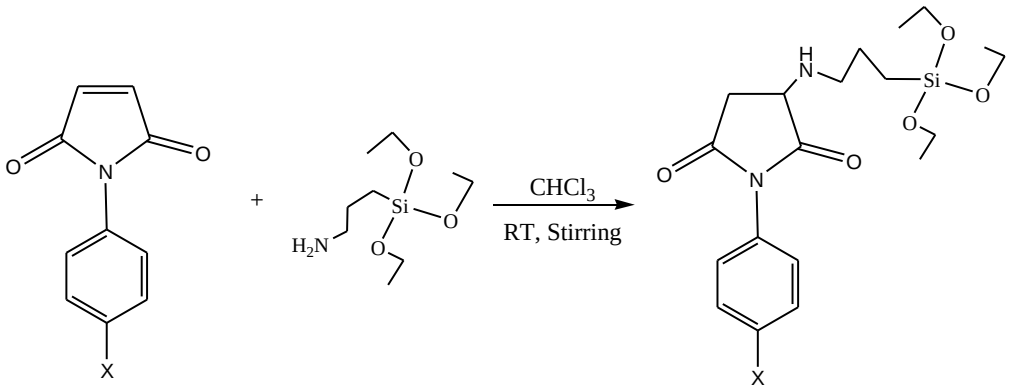
1-(4-Methylphenyl)-3-(3-(triethoxysilyl)propylamino)pyrrolidine-2,5-dione(3):3-Aminoropyltriethoxy silane (1 mL, 4.52 mmol) and N-(p-methylphenyl)maleimide (0.84 g, 4.52 mmol) were used for the synthesis of silane **3**. Yield: 78%. IR (cm^{-1}) = 1076 s (ν Si-O), 1389 (ν C-N-C), 1710 (ν C=O), 2859, 2941 s (ν CH_2), 3286 (ν NH). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 0.44 (t, 2H, *J* = 8.2 Hz, $SiCH_2$), 1.15 (t, 9H, *J* = 5.7 Hz, CH_3), 1.67 (m, 2H, CCH_2C), 2.28 (s, 1H, NH), 2.17 (s, 3H, Ar-CH_3), 2.62 (q, 2H, *J* = 6.6 Hz, CCH_2N), 3.03, 3.08 (dd, 2H, *J* = 8.3 Hz, CH_2CO), 3.69 (t, 6H, *J* = 5.7 Hz, OCH_2), 3.87 (q, 1H, *J* = 5.2 Hz, CHN), 7.38-7.92 (m, 4H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 8.36 ($SiCH_2$), 15.32 (CH_3), 24.57 ($C\boldsymbol{C}H_2C$), 26.50 (Ar-$\boldsymbol{C}H_3$), 36.74 ($\boldsymbol{C}H_2CO$), 51.81 ($C\boldsymbol{C}H_2N$), 54.68 (CHN), 59.70 (OCH_2), 126.13-136.90 (Ar-C), 175.46, 177.56 (C=O).

1-(4-Methoxyphenyl)-3-(3-(triethoxysilyl)propylamino)pyrrolidine-2,5-dione(4):3-Aminoropyl triethoxy silane (1 mL, 4.52 mmol) and N-(p-methoxyphenyl)maleimide (0.91 g, 4.52 mmol) were used for the synthesis of silane **4**. Yield: 87%. IR (cm^{-1}) = 1079 s (ν Si-O), 1384 (ν C-N-C), 1710 (ν C=O), 2848, 2952 s (ν CH_2), 3291 (ν NH). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 0.40 (t, 2H, *J* = 8.2 Hz, $SiCH_2$), 1.17 (t, 9H, *J* = 5.7 Hz, CH_3), 1.63 (m, 2H, CCH_2C), 2.23 (s, 1H, NH), 2.69 (q, 2H, *J* = 6.6 Hz, CCH_2N), 3.01, 3.06 (dd, 2H, *J* = 8.3 Hz, CH_2CO), 3.20 (s, 3H, OCH_3), 3.72 (t, 6H, *J* = 5.7 Hz, OCH_2), 3.89 (q, 1H, *J* = 5.2 Hz, CHN), 7.13-7.86 (m, 5H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 7.92 ($SiCH_2$), 14.79 (CH_3), 24.69 (C***C***H_2C), 32. 01 (OCH_3), 36.59 (***C***H_2CO), 51.78 (C***C***H_2N), 54.64 (CHN), 59.82 (OCH_2), 122.92-133.72 (Ar-C), 175.71, 177.70 (C=O).

1-(4-Hydroxyphenyl)-3-(3-(triethoxysilyl)propylamino)pyrrolidine-2,5-dione(5):3-Aminoropyl triethoxy silane (1 mL, 4.52 mmol) and N-(p-hydroxyphenyl)maleimide (0.85 g, 4.52 mmol) were used for the synthesis of silane **5**. Yield: 87%. IR (cm^{-1}) = 1081 s (ν Si-O), 1391 (ν C-N-C), 1709 (ν C=O), 2838, 2947 s (ν CH_2), 3294 (ν NH), 3381 (ν OH). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 0.38 (t, 2H, *J* = 8.2 Hz, $SiCH_2$), 1.13 (t, 9H, *J* = 5.7 Hz, CH_3), 1.70 (m, 2H, CCH_2C), 2.23 (s, 1H, NH), 2.64 (q, 2H, *J* = 6.6 Hz, CCH_2N), 3.03, 3.08 (dd, 2H, *J* = 8.3 Hz, CH_2CO), 3.75 (t, 6H, *J* = 5.7 Hz, OCH_2), 3.91 (q, 1H, *J* = 5.2 Hz, CHN), 7.24-8.03 (m, 4H, Ar-H), 10.62 (s, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 8.30 ($SiCH_2$), 14.46 (CH_3), 24.34 (C***C***H_2C), 36.71 (***C***H_2CO), 51.56 (C***C***H_2N), 54.87 (CHN), 59.60 (OCH_2), 124.57-135.39(Ar-C), 175.68, 177.81 (C=O).

RESULTS AND DISCUSSION

Synthesis: As depicted in Scheme 1, Michael donors and acceptor reacts via Aza-Michael addition reaction under mild conditions which led to the synthesis of substituted phenylaminosuccinimide silanes **1-6**. In this reaction, aminopropyltrimethoxysilane possessing NH_2 moiety as nucleophilic group behave as Michael donors and substituted phenylmaleimides act as Michael acceptor. Since aminopropylsilane itself can act both as nucleophile and base, no additional base is typically required in this reaction. The standard condition for the aza-Michael addition reaction is stirring at room temperature without any catalyst. Following this methodology, the prepared silanes are obtained with good yields and purity.



X= H, Cl, Me, OMe, OH

Scheme 1. Synthesis of phenylsuccinimide substited aminopropyltriethoxysilanes

Spectroscopic studies: The spectroscopic data [IR and NMR (^{1}H, ^{13}C)] assist to study basic structure analysis. The IR spectra of all compounds were recorded as neat spectra in the range of 4000-400 cm^{-1}. In IR spectra, the decisive absorption bands are Si-O (1100-1082 cm^{-1}) and NH (3300-3287 cm^{-1}) which are found to be in accordance with the proposed structures. In ^{1}H NMR spectra, the aza-Michael addition reaction is confirmed by disappearance of olefinic protons, resulting in silanes possessing substituted

phenyl succinimide. The NH proton of secondary amine adjacent to propyl group is observed as singlet at 2.12-2.21 ppm. The significant signals in succinimide group are due to CH_2 protons of succinimide group as two doublets in the region 3.06-3.13 ppm and CH proton adjacent to NH as quartet at 3.98-4.11 ppm. In ^{13}C NMR, the aza Micheal reaction is confirmed by appearance of upfield methylene carbon of succinimide at 36.64-36.66 ppm for all compounds.

APPLICATIONS

1. **Coupling agents:** Organofunctionalalkoxysilanes are employed to couple organic polymers to inorganic materials [19]. Organofunctionalsilane applications include boats, shoe soles, auto bodies, plastic pipes, satellite dishes, silica-filled molding compounds, silicon-carbide grinding wheels and clay-filled wire and cable.
2. **Crosslinking Agents:** Silanes can react with organic polymers to attach the trialkoxysilyl group on to the polymer backbone. In first step, silane reacts with moisture to crosslink the silane into a stable three-dimensional siloxane structure. This mechanism can be used to crosslink polyethylene and organic resins like urethanes and acrylics to impart durability for water and heat resistance [20].
3. **Adhesion Promoters:** Silanes are efficient adhesion promoters for paints, inks, adhesives, coatings and sealants [21]. Silanes will often maintain adhesion even if subjected to severe environmental conditions.
4. **Moisture Scavenger:** Due to moisture, three alkoxy groups on silanes will hydrolyze and covert water molecules to alcohol molecules. Because of this property, silanes are used in sealants and other moisture-sensitive formulations as water scavengers [22].
5. **Synthetic Organic Chemistry:** Silylating agents are used to protect alcohols and phenols only [23]. The steric and electronic characteristics of the protecting groups can be adjusted by varying the substituents attached to silicon. N,N-Diethyl-1,1,1-trimethylsilylamine is used as strong silylating agents because of good leaving group [24]. Organotrialkoxysilanes have been successfully used as coupling agents with halides and triflates [25].
6. **Building Block:** Organohalo- and alkoxysilanes are key reagents as the building units for a variety of organosilicon compounds [26]. It led to the path for the synthesis of various organosilicon compounds by derivatization of compounds by reaction with a silylating agent.

CONCLUSIONS

Aminosuucinimide substituted silanes are synthesized in good yield. This aza-Michael reaction for the synthesis of silanes would pave path for their application in biological system and polymer industry dye to presence heterocyclic succinimide moiety.

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