

**Short Communication****Benzotriazole Derived Triethoxysilanes: Synthesis and Characterization****Gurjaspreet Singh**Assistant Professor, Department of Chemistry, Panjab University, Chandigarh, **INDIA**Email: gjpsingh@pu.ac.inAccepted on 11th September 2014**ABSTRACT**

1- and 2-(trimethoxysilylmethyl)benzotriazoles, 1 and 2 were synthesized by reaction of 3-chloropropyltriethoxysilane and benzotriazole. Both the isomers have been separated into the individual isomers. The structures of the compounds prepared were investigated using IR, and multinuclear NMR spectroscopy.

Keywords: Benzotriazole, 3-chloropropyltriethoxysilane, sodium hydride.

INTRODUCTION

Silanes are used as versatile building blocks in organosilicon chemistry [1,2]. The exploration of silanes in synthetic organic chemistry is continuously growing and their most important applications are as silyl protecting and derivatisation reagents, reducing agents, reagents in cross-coupling reactions and to stabilize α -carbanions and β -carbocations [3-8]. Various review articles have been published which shows the importance of synthesis, reactivity and applications of silanes [9-11]. The extension of the functional group versatility in organotriethoxysilanes has made it a flexible building block in organic synthesis [12-15]. Organosilane derivatives of nitrogen-containing heterocyclic compounds attracted the attention of many investigators [15-20]. These studies made a valuable contribution to synthetic, theoretical, medicinal and applied chemistry. Some of these compounds have already found practical application as synthons in organic synthesis, biologically active substances, sorbents, etc [21].

MATERIALS AND METHODS

All the syntheses were carried out under nitrogen atmosphere using Schlenk technique. THF and ether were distilled over sodium pieces. 3-Chloropropyltriethoxysilane (Aldich), benzotriazole (CDH) and sodium hydride (SDFCL) were used as supplied without any purification.

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. ¹H and ¹³C NMR spectra were recorded in CDCl₃ solution using 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.

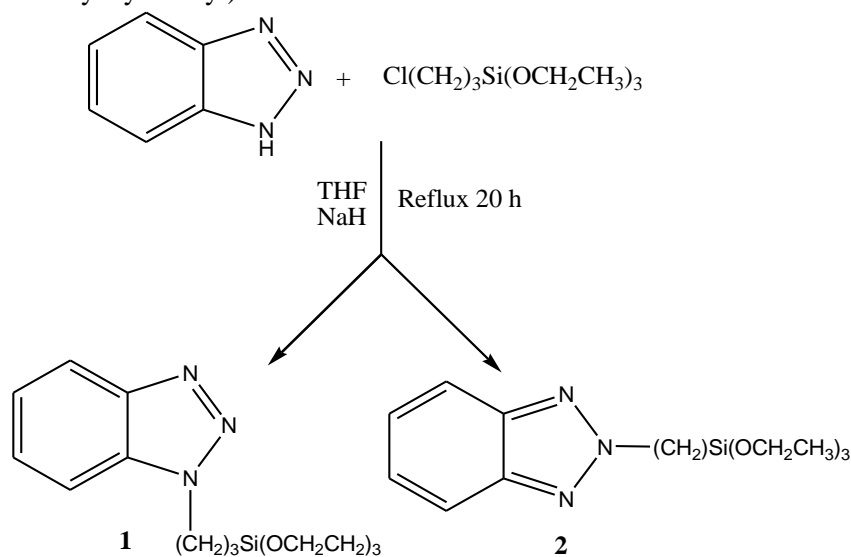
Synthesis of silanes: To a suspension of NaH (0.30 g, 12.50 mmol) in anhydrous THF (35 mL) at 0 °C, 1-H benzotriazole (0.74 g, 6.25 mmol) was added and 3-chloropropyltriethoxysilane (1.50 mL, 6.25 mmol) was added slowly with stirring. Then the reaction mixture was allowed to stir for 30 min. The reaction was allowed to warm to room temperature and stirred under reflux for a further 20 h. The reaction was cooled to room temperature, filtered and washed with ether. On keeping the reaction mixture at room temperature, white color precipitates were appeared. This white solid was filtered off and dried under vacuum. The remaining yellowish oil corresponding to 2-isomer was further purified by distillation under vacuum.

Silane 1: M.p.: 69-72 °C. Yield: 60%. IR (cm^{-1}) = 1078 s (ν Si-O), 1140 vs (ν C-N), 2832, 2939 s (ν , CH_2). ^1H NMR (300 MHz, CDCl_3): δ (ppm) = 0.63 (t, 2H, $J = 8.2$ Hz, SiCH_2), 1.17 (t, 9H, $J = 5.7$ Hz, CH_3), 1.78 (m, 2H, CCH_2C), 3.37 (t, 2H, $J = 6.4$ Hz, CCH_2N), 3.65 (q, 6H, $J = 5.7$ Hz, OCH_2), 6.81-7.50 (m, 4H, Ar-H). ^{13}C NMR (75 MHz, CDCl_3): δ (ppm) = 7.92 (SiCH_2), 18.09 (CH_3), 26.43 (CCH_2C), 47.24 (CCH_2N), 58.28 (OCH_2), 116.99-132.03 (Ar-C).

Silane 2: Bp.: 132-135°C. Yield: 1.40 mL (93%). IR (cm^{-1}) = 1075 s (ν Si-O), 1143 vs (ν C-N), 2831, 2939 s (ν , CH_2). ^1H NMR (300 MHz, CDCl_3): δ (ppm) = 0.59 (t, 2H, $J = 8.2$ Hz, SiCH_2), 1.13 (t, 9H, $J = 5.7$ Hz, CH_3), 1.74 (m, 2H, CCH_2C), 3.41 (t, 2H, $J = 6.4$ Hz, CCH_2N), 3.72 (q, 6H, $J = 5.7$ Hz, OCH_2), 6.72-7.21 (m, 4H, Ar-H). ^{13}C NMR (75 MHz, CDCl_3): δ (ppm) = 8.10 (SiCH_2), 18.33 (CH_3), 26.61 (CCH_2C), 47.40 (CCH_2N), 58.45 (OCH_2), 118.71-133.91 (Ar-C).

RESULTS AND DISCUSSION

1- and 2-(triethoxysilylmethyl)benzotriazoles were synthesized by the treatment of N-H heterocycle, benzotriazole with sodium hydride in tetrahydrofuran generating the corresponding anions. The abstraction of proton from N-H heterocycle was found to be a clean reaction due to the stabilization of the resulting anion by resonance, which upon reaction with 3-chloropropyltriethoxysilane afforded the desired triethoxysilane. 1-(triethoxysilylmethyl)benzotriazoles isomer is precipitated as white solid and separated by filtration. 2-(triethoxysilylmethyl)benzotriazoles is distilled under vacuum.



Scheme 1. Synthesis of 1- and 2-(triethoxysilylmethyl)benzotriazoles.

IR Spectroscopy: IR Spectra exhibit characteristic absorption bands of silatranyl moiety and are assigned on the basis of previous literature reports. The Si-O stretching vibration is assigned to the bands present in 1097-1075 cm^{-1} . The methylene absorption bands are appeared in the range of 3000-2800 cm^{-1} . The absence of NH absorption band depicts the synthesis of desired compound.

NMR Spectroscopy: The NMR spectroscopy (^1H and ^{13}C) data recorded for all compounds at room temperature are founded in agreement with the synthesized products. In ^1H NMR spectra, an upfield triplet appears for the methylene group attached to the silicon atom i.e. SiCH_2 of all silatranes, which clearly point out the increase in the electron density on the silicon due to the presence of silatranyl skeleton. Noteworthy, CCH_2C proton resonances split up into a multiplet due to coupling with adjacent methylene protons and appeared in region of $\delta \approx 1.45\text{-}1.60$ ppm. The CCH_2N protons are confirmed by triplet splitting which depends upon exocyclic group attached. The ethoxy group is confirmed by triplet and quartet in region of 1.70-1.75 ppm and 3.58-3.80 ppm respectively.

In ^{13}C NMR spectra, the methylene carbon of propyl chain attached to silicon atom appeared as the most shielded carbon atom which is observed around $\delta \approx 7.90\text{-}8.10$ ppm for all silatranes. Other peak due to CCH_2C is observed in region $\delta \approx 26.40\text{-}26.70$ ppm. The peak for CCH_2N revealed large variation in region $\delta \approx 47.50\text{-}47.90$ ppm depending upon the exocyclic moiety.

APPLICATIONS

- Silanes and its derivatives find applications as bactericides and fungicides as anticancer and antitumour agents and are also useful for immobilizations of DNA [22].
- Silicon is a bioactive element associated with beneficial effects on mechanical and physiological properties of plants. Several studies have suggested that hypervalent silicon compounds activate plant defence mechanisms against pathogenic fungi [23].
- Hypervalent silicon compounds have been suggested to play a role in silica biomineralization a process that controls silicon fluxes in the oceans, and thus, global silicon cycling [24].
- Recently, a high-quality cubic MCM-48 (one of the members of ordered mesoporous molecular sieves) has been synthesized using silanes and CTAB (cetyltrimethyl-ammonium bromide) as the structure directing agents via *sol-gel* process [25].
- Silanes has been shown to be a good reducing agent for some organic compounds for instance, 1-Hydrosilatranes containing Si—H bond can reduce benzyl bromide, benzoyl chloride, azoxybenzene, and some carbonyl compounds [26].

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