Short Communication

Synthesis, Characterization and Reactivity Studies of (trimethylsilyl) propyl triethoxysilane via Grignard Reaction

Gurjaspreet Singh[*], Promila Amandeep Saroa, Shally Girdhar and Mridula Garg

*Department of Chemistry and Center of Advanced Studies in Chemistry, Panjab University, Chandigarh-160014, INDIA

Email: gurjaspreet@gmail.com, gjpsingh@pu.ac.in

ABSTRACT

A new class of silatranes 8-10 were synthesized by the transesterification of (trimethylsilyl)propyl triethoxy silane 4 with triethanolamine 5, trisisopropanolamine 6 and tris(2-aminoethyl)amine 7. Silane 4 was synthesized by the reaction of chloropropyltriethoxysilane with magnesium turnings in tetrahydofuran at 0 to 20 °C to form (triethoxysilyl)propyl magnesium chloride. The structures of all the compounds were established by spectroscopic (IR, ^1H, ^{13}C) techniques and purity of the compounds was confirmed by elemental analyses.

Keywords: Silatrane, triethanolamine, trisisopropanolamine and tris(2-aminoethyl)amine.

INTRODUCTION

In recent years, silatranes have gained increasing popularity due to higher stability than their alkoxy silane analogues and due to ample diversity of their axial substituent [1-5]. The disparity in axial substituents considerably affects the properties of silatranes and enhances their various bio-medical applications [6, 7]. Organyltriethoxysilanes are not only important monomers but are also of interest as precursors for the synthesis of silatranes. Literature reported various routes for the synthesis of trihalogenosilyl and trialkoxysilyl derivatives R-SiX$_3$ (X = Cl, OCH$_3$, OCH$_2$CH$_3$) [8]. Hydrosilylation reactions are the only reactions constitute a general and selective route to trifunctional silanes from olefins. Various routes, often of a less general scope or a lower selectivity, include, silylation with trichlorosilane/Et$_3$N [9], nickel catalysed silylation with SiCl$_4$/disilane [10], palladium catalysed reactions of disilanes [11] or silylation of organometallic intermediates with ClSi(OMe)$_3$. In the present text, we have shown that the Grignard reagent derived from the bulky 3-chloropropyltriethoxysilane are stable and undergoes transesterification reactions with triethanolamine, trisisopropanolamine and tris(2-aminoethyl)amine.

MATERIALS AND METHODS

Syntheses of all the compounds were performed under a dry nitrogen atmosphere using Schlenk technique. The organic solvents used were dried and purified according to standard procedure. 3-chloro propyl

(triethoxy)silane (Aldrich), magnesium turnings (Aldrich), triethanolamine (Merck), trisisopropanolamine (Aldrich), tris(2-aminoethyl)amine (Aldrich). Infrared spectra were obtained as neat on a Thermo Scientific NICOLET IS50 spectrophotometer. Mass spectral measurements (ESI source with capillary voltage, 2500 V) were carried out on a VG Analytical (70-S) spectrometer. CHN analyses were obtained on a FLASH-2000 organic elemental analyzer. The solution NMR spectra were recorded at 25 °C on Bruker Avance FT NMR (AL 400, 300 MHz) spectrometers (^{1}H, ^{13}C) using CDCl$_3$. Chemical shifts in ppm were corrected relative to tetramethylsilane (TMS).

Synthesis of (trimethylsilyl)propyltriethoxy silane: A three-necked, round-bottomed flask is equipped with a mechanical stirrer, a pressure-equalizing dropping funnel, and an efficient reflux condenser mounted with a combined inlet-outlet assembly connected to a nitrogen source and a bubbler. The apparatus was flamed dry while a slow stream of nitrogen was passed through the system. In the cooled flask a solution of (triethoxysilyl)propyl magnesium chloride was prepared from 3-chloropropyltriethoxysilane (1.00g, 4.16 mmol), magnesium turnings (0.10g, 4.16 mmol) in anhydrous tetrahydrofuran (30 mL). Small amount of iodine was added to the reaction mixture to initiate the reaction. The reaction mixture was stirred and heated at reflux for another 30 minutes. The mixture is stirred and cooled in an ice bath and addition of trimethylsilylchloride (0.45 g, 4.16 mmol) was added dropwise requires 15-20 min. Magnesium chloride salt formed was separated by vacuum filtration and the required silane 1-(triethoxysilyl)-3-(trimethylsilyl)propane was obtained by vacuum distillation. Yield: 0.71 g (62%); b.p. 130-135 °C (20 mm Hg); IR (KBr, cm^{-1}): v = 1075 (Si-O), 1266 (C-O); ^{1}H NMR (CDCl$_3$): δ 1.22 (t, 3H, J = 6.9 Hz, OCH$_2$C$\underline{H}_3$), 3.71 (q, 2H, J = 6.9 Hz, OC$\underline{H}_2$CH$_3$), 0.58 (t, 2H, J = 7.8 Hz, CH$_2$Si), 0. 62 (t, 2H, SiCH$_2$), 1.44 (m, 2H, J = 7.9 Hz, C$\underline{H}_2$CH$_2$Si); ^{13}C NMR (75.5 MHz, CDCl$_3$): δ 9.51 (CH$_2$Si), 14.01 (CH$_2$Si), 20.23 (SiCH$_2$), 24.31 (OCH$_2$$\underline{C}H_3$), 58.02 (O$\underline{C}H_2CH_3$)

General Synthetic Procedure for Silatranes 8, 9 and 10: To a dried 100 mL two-neck round-bottomed flask fitted with Dean Stark apparatus, mixture of tripodal ligands **5**, **6** and **7**, silane **4** and a catalytic amount of sodium ethoxide in benzene was refluxed for 4 h at 80° C. Solvent was removed by vacuum evaporation. The addition of hexane to the clear solution resulted in the separation of a solid which was purified from tetrahydrofuran-hexane (3 mL) to yield silatranes **8, 9** and **10.**

1-(3-(trimethylsilyl)propyl)-2,8,9-trioxa-5-aza-1-sila-bicyclo[3.3.3]undecane 8: Compound **8** was obtained by refluxing **5** (0.53 g, 3.59 mmol), silane **4** (1.00 g, 3.59 mmol) and a catalytic amount of sodium ethoxide in benzene. Yield: 0.74 g (72%). m.p.: 267-269 °C (decomp). Anal. Calc. For C$_{12}$H$_{27}$NO$_3$Si$_2$ (289): C, 49.78; H, 9.40; N, 4.84; Si, 19.40%. Found: C, 49.75; H, 9.41; N, 4.83; Si, 19.39%. IR (KBr, cm^{-1}): v = 632 (N→Si), 1012 (Si-O), 1150 (C-O); ^{1}H NMR (300 MHz, DMSO-d$_6$/CDCl$_3$): δ 0.57 (t, 2H, J = 7.9 Hz, CH$_2$Si), 0.62 (t, 2H, J = 7.9 Hz, CH$_2$Si), 1.43 (m, 2H, J = 7.9 Hz, C$\underline{H}_2$CH$_2$Si), 2.77 (t, 3 x 2H, J = 6.0 Hz) NCH$_2$), 3.73 (t, 3 x 2H, J = 6.0 Hz, OCH$_2$); ^{13}C NMR (75.5 MHz, DMSO-d$_6$/CDCl$_3$): δ 0.61 (CH$_3$), 9.5 (CH$_2$CH$_2$Si), 14.01 (CH$_2$Si), 20.21 (SiCH$_2$), 50.9 (NCH$_2$), 57.9 (OCH$_2$).
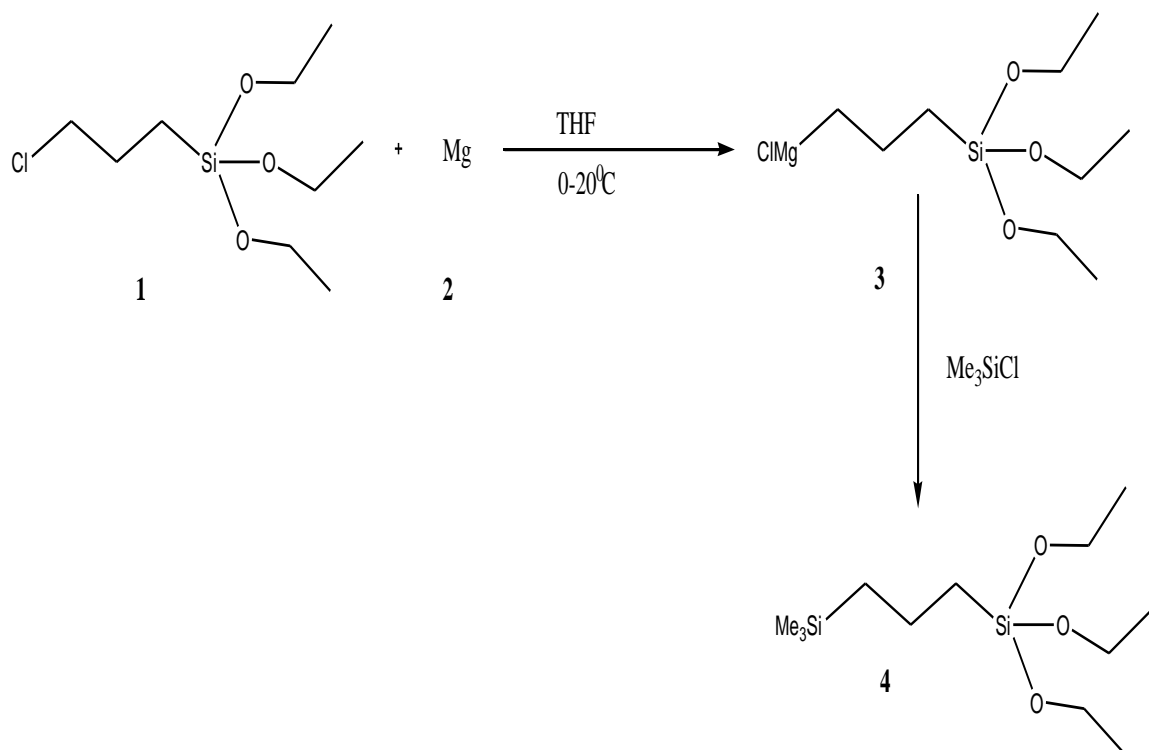
3,7,10-trimethyl-1-(3-(trimethylsilyl)propyl)-2,8,9-trioxa-5-aza-1-sila bicyclo[3.3.3]undecane 9: Compound **9** was obtained by refluxing **6** (0.68 g, 3.59 mmol), silane **4** (1.00 g, 3.59 mmol) and a catalytic amount of sodium ethoxide in benzene. Yield: 0.79 g (67%). m.p.: 256-258 °C. Anal. Calc. For C$_{15}$H$_{33}$NO$_3$Si$_2$ (331): C, 54.33; H, 10.03; N, 4.22; Si, 16.94%. Found: C, 54.32; H, 10.01; N, 4.21; Si, 16.93 %. IR (KBr, cm^{-1}): v = 633 (N→Si), 1015 (Si-O), 1152 (C-O); ^{1}H NMR (300 MHz, DMSO-d$_6$/CDCl$_3$): δ 0.55 (t, 2H, J = 7.9 Hz, CH$_2$Si), 0.64 (t, 2H, J = 7.9 Hz, CH$_2$Si), 1.33 (m, 3 x 3H, C(CH$_3$)), 1.45 (m, 2H, J = 7.9 Hz, C$\underline{H}_2$CH$_2$Si), 2.65 (t, 3 x 2H, J = 6.0 Hz) NCH$_2$), 3.67 (t, 3 x 1H, OCH); ^{13}C NMR (75.5 MHz, DMSO-d$_6$/CDCl$_3$): δ 0.6 (SiCH$_3$), 9.4 (CH$_2$CH$_2$Si), 15.0 (CH$_2$Si), 23.2 (CH$_3$), 59.2 (OCH), 65.0 (NCH$_2$).

1-(3-(trimethylsilyl)propyl)-2,5,8,9-tetraaza-1-sila-bicyclo[3.3.3]undecane 10: Compound **10** was obtained by refluxing **7** (0.52 g, 3.59 mmol), silane **4** (1.00 g, 3.59 mmol) and a catalytic amount of

2203

sodium ethoxide in benzene. Yield 0.77 g (75%); mp 266-268°C. Anal. Calc. For $C_{12}H_{30}N_4Si_2$ (286): C, 50.50; H, 10.55; N, 19.55; Si, 19.60%. Found: C, 50.51; H, 10.52; N, 19.53; Si, 19.58%. IR (KBr, cm^{-1}): ν = 599 (N→Si), 1083 (Si-O), 1388 (C-O); ^{1}H NMR (300 MHz, DMSO-d$_6$/CDCl$_3$): δ 0.65 (t, 2H, J = 7.9 Hz, CH$_2$Si), 1.46 (m, 2H, J = 7.9 Hz, CH$_2$CH$_2$Si), 0.75 (m, 2H, SiCH$_2$), 2.46 (t, 3 x 2H, J = 6.0 Hz, NCH$_2$CH$_2$), 2.68 (t, 3 x 2H, J = 6.0 Hz NCH$_2$CH$_2$), 3.35 (bs, 3 x 1H, NH); ^{13}C NMR (75.5 MHz, DMSO-d$_6$/CDCl$_3$): δ 0.6 (SiCH$_3$), 15.0 (CH$_2$Si), 19.4 (CH$_2$CH$_2$Si), 39.4 NCH$_2$CH$_2$), 55.9 (NCH$_2$CH$_2$).

RESULTS AND DISCUSSION

Syntheses and Spectroscopic studies: The silane **4** was synthesized by the reaction of (triethoxysilyl) propyl magnesium chloride with trimethylsilyl chloride as shown in Scheme 1.

Scheme 1: Synthesis of silane

Silatranes **8, 9 and 10** were obtained by the transesterifications of silane **4** with tripodal ligands **5, 6 and 7** respectively as depicted in Scheme 2.
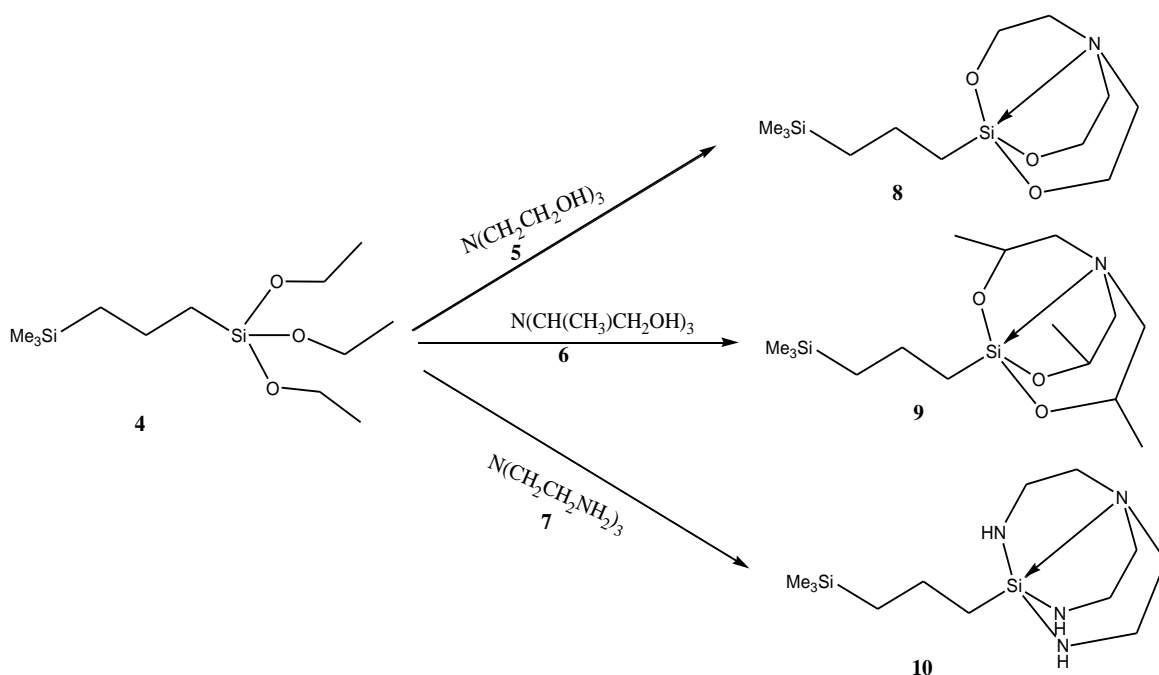
Scheme 2: Synthesis of Silatranes bearing trimethylsilylpropyl functionality as exocyclic group

Yields of all the compounds obtained were appreciable. Structures of the compounds were confirmed on the basis of spectral data (IR and multinuclei NMR).

IR Spectra: The IR spectra of all the compounds were recorded in the range 4000–400 cm^{-1}. The absorption frequencies were in accordance with the structure of the prepared compounds. The absorption bands of interest were those of N→Si, Si-O and C-O bonds. IR spectrum in Nujol/KBr plates showed v N→Si, v Si-O and v C-O absorptions in the ranges 599-633, 1012-1080 and 1150-1388 cm^{-1} respectively for silatranes **8**, **9** and **10**.

NMR Spectra: Multinuclei (^{1}H, ^{13}C and ^{29}Si) NMR spectra were consistent with the structure of the synthesized compounds. In ^{1}H NMR spectra of silane **4**, signals corresponding to -OCH$_2$ and -CH$_3$ of ethoxy groups appeared at 3.71 and 1.22 ppm respectively. In silatrane **8** signals corresponding to -NCH$_2$ and -OCH$_2$ of atrane ring appeared as triplets at 2.72 and 3.73 ppm respectively. Silatrane **9** shows signals of methyl of isopropyl group at 1.33 ppm and at 3.67 ppm due to OCH. In ^{1}H NMR spectra of silatrane **10**, signals corresponding to -NCH$_2$ of atrane ring appeared in the region 2.46-2.68 ppm. All the synthesized silatranes including silanes synthesized according to Scheme 2, displayed a signals corresponding to protons of propyl chain.

In ^{13}C NMR spectra of silane **4**, signals corresponding to -OCH$_2$ and -CH$_3$ of ethoxy groups appeared in the range 58.02 and 24.31 ppm respectively. The silatrane **8** showed signals corresponding to -NCH$_2$ and -OCH$_2$ of atrane ring at 50.9 and 57.9 ppm. The Silatrane **9** shows signals at 59.2 ppm due to OCH, 23.2 ppm due to CH$_3$, and at 65.0 due to NCH$_2$. The silatrane **10** showed signals corresponding to -NCH$_2$ of atrane ring at 39.4 and 55.9 ppm. The ^{13}C NMR spectra of all synthesized compounds displayed signals corresponding to carbon atoms of the propyl chain.

APPLICATIONS

1. Silatranes have been extensively used in manufacturing of silatrane polymers and these silatrane containing polymers are useful as catalyst supports, molding materials and adhesion promoters [12].

2. 1-chloromethylsilatranes in gel and emulsion forms show pilotropic activity which is attributed to the presence of silicon and certain features of the atrane structure. It is manifested by an increase in premeability of connective tissues, blood vessels and skin at the site of drug applications [13].
3. Treatment of plants and seeds with the aqueous solution of commercially available 1-ethylsilatrane (Cherkaz-1) and 1-vinylsilatrane (Cherkaz-2) at development stages can increase crop yields [14].
4. Due to donor-acceptor properties of the Si-N tranannular bond, aminopropylsilatrane has very interesting chemistry in atomic force microscopy [15].
5. Silatranes are adequate precursors for material synthesis by sol-gel route which offers good hydrolysis and condensation control in preparation [16].

CONCLUSIONS

Silatranes from a wide variety of tripodal ligands have been synthesized employing the use of organosilane **4** bearing trimethylsilyl moiety; among these, more facile and commonly used method for their syntheses are sodium ethoxide as catalyst and azeotropic removal of ethanol. Silane 4 synthesized by the Grignard reaction was stable and isolated in high yield. The spectroscopic techniques, *viz.* multinuclear NMR have been successfully applied to determine the wide variety of structural motifs of all the synthesized compounds.

ACKNOWLEDGEMENT

REFERENCES

[1]   Gurjaspreet Singh, Aanchal Arora, Satinderpal Singh Mangat, Jandeep Singh, Sunita Chaudhary, Navneet Kaur, Duane Choquesillo-Lazarte, *J. Molecular Structure*, 2014, http://dx.doi.org/10.1016/j.molstruc.2014.09.042
[2]   G. Singh, S. Girdhar, S. Khullar, S.K. Mandal, *Inorg. Chim. Acta.*, **2014**, 413, 203-207.
[3]   G. Singh, S.S. Mangat, J. Singh, A. Arora, R.K. Sharma, *Tetrahedron Lett.*, **2014**, 55, 903-909.
[4]   G. Singh, M. Garg, Manu, Pooja, J. Singh, *J. Applicab. Chem.*, **2014**, 3, 1031-1035.
[5]   G. Singh, S. Girdhar, Promila, S. Girdhar, M. Garg, B. Singh, *J. Applicab. Chem.*, **2014**, 3, 1042-1049.
[6]   G.K. Min, D. Hernandez, T. Skrydstrup, *Acc. Chem. Res.,* **2013**, 46, 457-470.
[7]   G. Ping, W. Ye-Wu, L. Xin-Tong, Q. Xiao-Lu, H. Le-Ping, P. Zi-Xin, Y. Fa-Qing, *Phosphorus, Sulphur and Silicon Relat. Elem.,* **2014**, 189, 511-518.
[8]   D.S.W. Lim, E.A. Anderson, *Synthesis,* **2012**, 44, 983-1010.
[9]   R.A. Benkeser, J.M. Gaul, W.E. Smith, *J. Am. Chem. Soc.*, **1969**, 91, 3666-3667.
[10]   M. Lefort, C. Simmonet, M. Bimt, G. Deleris, J. Dunogues, R. Calas, *Tetrahedron Lett.*, **1980**, 21, 1857-1860.
[11]   H. Matsumoto, M. Kasaham, I. Matsubara, M. Takabashi, T. Arai, M. Hascgawa, T. Nakano, Y. Nagai, *J. Organomet. Chem.,* **1983**, 250, 99-107.
[12]   W. Huang, *Youjigui Cailiao*, **2005**, 19, 37-43.
[13]   E.V. Bakhareva, M.G. Voronkov, M.K. Vasiltsov, *Bull.Exp. Biol. Med.*., **1983**, 95, 689-695.
[14]   L.E. Makarova, M.G. Sokolova, G.B. Borovskii, A.M. Shigarova, M.G. Voronkov, G.A. Kuznetsova, K.A. Abzaeva, *Agrokhimiya*, **2009**, 151, 26055-26060.
[15]   A.L. Mikheikin, A.Y. Lushnikov, Y.L. Lyubchenko, *Biochemistry*, **2006**, 45, 12998-13006.
[16]   N. Kritchayanon, N. Thanabodeekij, S. Jitkarnka, A. M. Jamieson and S. Wongkasemjit, *Appl. Organomet. Chem.,* **2006**, 20, 155-160.