

Synthesis and Characterization of Novel 1-Methanesulfonato Silatranes

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ABSTRACT: $\text{CH}_3(\text{O})_2\text{SOSi}(\text{OC}_6\text{H}_2\text{Me}_2\text{CH}_2)_3\text{N}$ (**1**), $\text{CH}_3\text{OSi}(\text{OC}_6\text{H}_2\text{Me}_2\text{CH}_2)_3\text{N}$ (**2**) and $\text{CH}_3(\text{O})_2\text{SO}\cdot\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$ (**3**) have been synthesized in high yield by the reaction of 1-isothiocyanato- silatranes with dimethyl sulfite and methyl methanesulfonate. These novel silatranes have been characterized by elemental analysis, infrared spectroscopy, ^1H , ^{13}C , ^{29}Si NMR spectroscopy and mass spectrometry. Semi-empirical quantum mechanical calculations were done to study the N→Si transannular bond length.

KEY WORDS: Six membered silatrane, Methane sulfonato silatrane, Pentacoordinated silicon, Hypervalent compound, Five membered silatranes

I. INTRODUCTION

Silatranes containing six-membered ring were synthesized as reported in literature [1-2]. It was shown that the silatrane systems with the larger rings allowed substituent effects associated with the axial position of the resulting trigonal bipyramidal structures (tbp) to be reflected in dramatically altering the Si-N bond interactions as well as in changes of the ^{29}Si chemical shifts [3-7]. The use of dimethyl sulfite and methyl methanesulfonate as alkylating, alkoxyating and acetylating reagent in synthesis is well known in literature [8,9]. To my knowledge these are the first of type of silatrane containing 1-methane sulfonato as exocyclic group to silicon in silatranes. In order to understand the reactivity of 1-Isothiocyanatosilatranes with dimethyl sulfite & methyl methane sulfonate, a detailed study of this reaction was undertaken.

II. EXPERIMENTAL

All operations were carried out under dry nitrogen atmosphere. Solvents were freshly distilled under an inert atmosphere from sodium and sodium benzophenone (hexane), (tetrahydrofuran, diethylether) and phosphorus pentoxide (acetonitrile and dichloromethane) before use. Bases such as triethanol amine (Aldrich) were refluxed over potassium hydroxide pellets and distilled under dry nitrogen atmosphere before use. Other starting materials such as silicon(IV) chloride (Aldrich AR grade), absolute alcohol (Bengal chemicals), 2,4-dimethyl phenol (E-Merck), hexamethylene tetramine (Aldrich) and potassium thiocyanate (E-Merck) were used as supplied. Tris-(2-hydroxy-3,5-dimethyl benzyl)amine [2], dimethyl sulfite [8], methyl methanesulfonate [9], triethoxyisothiocyanatosilane [7], 1-isothiocyanato six membered ring silatrane [1] and 1-isothiocyanato five membered ring silatrane [10] were synthesized according to procedure reported earlier. Solvents were purified according to standard procedures [11]. IR spectra were obtained as thin films or nujol mulls on Perkin-Elmer RX-1 FTIR spectrophotometer. ^1H (300.4 MHz), ^{13}C (75.45 MHz), ^{29}Si NMR (59.60 MHz) spectra were obtained on JEOL AL 300 instrument. Chemical shifts were reported with respect to TMS as external standard. Mass spectral measurements (EI, 70ev) were carried out with VG Analytical (70-S) spectrometer. The elemental analysis were performed using PERKIN-ELMER (model 2400) C, H, N analyzer. The content of sulfur and silicon was determined by standard gravimetric methods.

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III. SYNTHESIS

Reaction of 1-Isothiocyanato six-membered silatrane with dimethyl sulfite

The reaction of equimolar quantities of 1-isothiocyanato six-membered ring silatrane (1.67 g 3.33 mmol) and dimethyl sulfite (4.00 ml 47.00 mmol) has been carried out at 110 °C by refluxing for 4 h. Dimethyl sulfite was taken slightly in excess. The solid was filtered under the dry nitrogen atmosphere, washed with hexane (2 mL), and dried under vacuum to give a mixture of compounds **1** and **2**. Yield: 86%. M.P: 211-218 °C Anal. calcd. for C₅₆H₆₆O₁₀N₂Si₂S (Mol mass 1014): C:66.27; H:6.51; N:2.76; S:3.15; Si:5.52%. Found C, 66.01; H, 6.59; N, 2.71; S, 3.09; Si, 5.50%. IR (Nujol, KBr, cm⁻¹): ν = 1070 [Si-O(S)], 1145 (Si-OCH₃), 1020, 1040, 1145 (SO₃), 958, 915, 677 (skeleton mode of silatrane). ¹H NMR (CDCl₃): δ = 2.17, 2.19 (s, 9H, aryl-Me), 2.20, 2.24 (s, 9H, aryl Me), 4.21, 4.25 (s, 6H, NCH₂), 6.89, 6.90 (s, 3H, Aryl), 6.91, 6.93 (s, 3H, Aryl), 3.42 (s, 3H, OCH₃), 2.78 (s, 3H, SCH₃). ¹³C NMR (CDCl₃): δ = 16.11, 16.13 (Aryl-CH₃), 19.21, 19.23 (Aryl-CH₃), 54.91, 54.95 (NCH₂), 49.91 (OCH₃), 39.24 (SCH₃), 116.47-150.96 (Aryl carbons). ²⁹Si NMR (CDCl₃): δ = -123.13 (1-methoxy silatrane); δ = -129.27 (1-methanesulfonato silatrane).

Reaction of 1-Isothiocyanato six-membered silatrane with methyl methanesulfite

In a round-bottomed flask a solution of 1-isothiocyanato six membered ring silatrane (0.69 g, 1.37 mmol) and methyl methanesulfite (4.00 ml, 47.00 mmol) were stirred for 4 h at 125 °C. The contents were allowed to retain room temperature. To this viscous liquid anhydrous hexane was added, when a white solid was formed. The solid was filtered under the dry nitrogen atmosphere, washed with hexane (2 mL), and dried under vacuum to give **1**. Yield: 94%. M.P: 215 °C. Anal. calcd. for C₂₈H₃₃NO₆.SiS (Mol mass 539): C: 62.33; H: 6.12; N: 2.60; S: 5.94; Si: 5.20%. Found: C: 62.29; H: 6.09; N: 2.57; S: 5.96; Si: 5.18%. IR (Nujol, KBr, cm⁻¹): ν = 1070 (Si-OCS), 1022, 1108 (SO₃) 960, 925 and 635 (skeleton mode). ¹H NMR (CDCl₃) δ = 2.13, 2.30 (s, 9H, Ar-CH₃), 4.07 (s, 6H, NCH₂), 6.67, 6.86 (s, 3H, Ar-H), 2.94 OS(O)₂CH₃. ¹³C NMR (CDCl₃) δ = 16.14, 20.23 (Ar-CH₃), 56.80 (NCH₂), 41.23 OS(O)₂CH₃, 116.76, 126.10, 128.73, 129.12, 133.80 and 151.85 (aromatic carbons). ²⁹Si NMR (CDCl₃): δ = -115.67.

Reaction of 1-Isothiocyanato five-membered silatrane with methyl methanesulfite

In a round-bottomed flask a solution of 1-isothiocyanato five membered ring silatrane (0.50 g, 1.56 mmol) and methyl methanesulfite (4.00 ml, 47.0 mmol) was stirred for 4 h at 125 °C. The contents were allowed to retain room temperature and diethyl ether (2 mL) was added, and a white solid formed. The solid was filtered under the dry nitrogen atmosphere, washed with diethyl ether (2 mL), and dried under vacuum to give **3**. Yield: 91%. M.P.: 209 °C. Anal. calcd. for C₇H₁₅O₆NSiS (mol mass 269): C: 31.23; H: 5.58; N: 5.21; S: 11.90; Si: 10.41%. Found: C: 31.23; H: 5.62; N: 5.19; S: 11.46; Si: 10.39%. IR (Nujol, KBr, cm⁻¹): ν = 1020, 1040, 1145 (SO₃), 1070 (Si-OCS) 940, 910, 617 (skeleton mode). ¹H NMR (CDCl₃): δ = 3.95 (s, 6H, OCH₂), 2.91 (s, 6H, NCH₂) 2.81 (s, 3H, SCH₃). ¹³C NMR (CDCl₃): δ = 57.85 ppm (OCH₃), 50.19 (NCH₂), 39.21 (SCH₃). ²⁹Si NMR (CDCl₃): δ = -93.71.

IV. RESULTS AND DISCUSSION

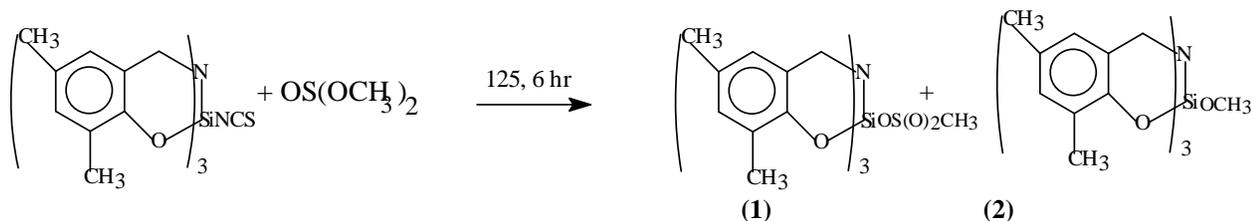
The use of dimethyl sulfite as alkylating, alkoxyating and acetyating reagent in organic synthesis is well known in literature [8,9]. However, this reagent has not been fully exploited in the area of main group element chemistry.

Reaction of 1-isothiocyanato six membered silatrane with dimethyl sulphite in excess at 125 °C for 3 h results in a clear solution. Subsequent heating of reaction mixture for 3 h followed by the addition of dry diethyl ether yields a white solid. This white solid was filtered & washed with diethyl ether in the dry nitrogen atmosphere and dried under vacuum. Elemental analyses of white solid confirmed the formation of 1-methanesulfonato silatrane **1** and 1-methoxy silatrane **2** in equimolar mixture. The reaction may be represented as below (Scheme 1):

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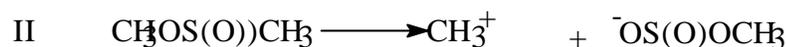
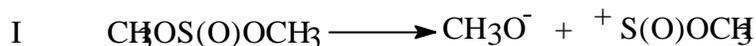
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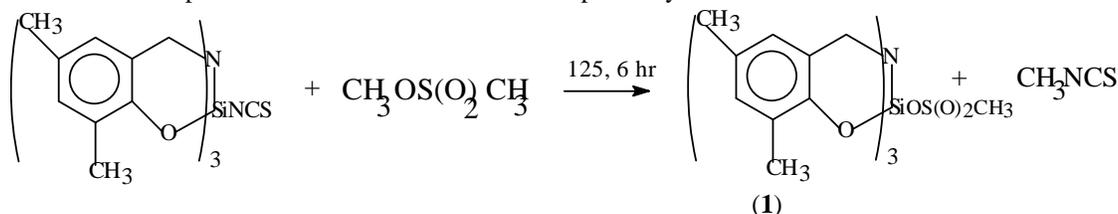


Scheme 1. Reaction of 1-isothiocyanato six-membered silatrane with dimethyl sulfite.

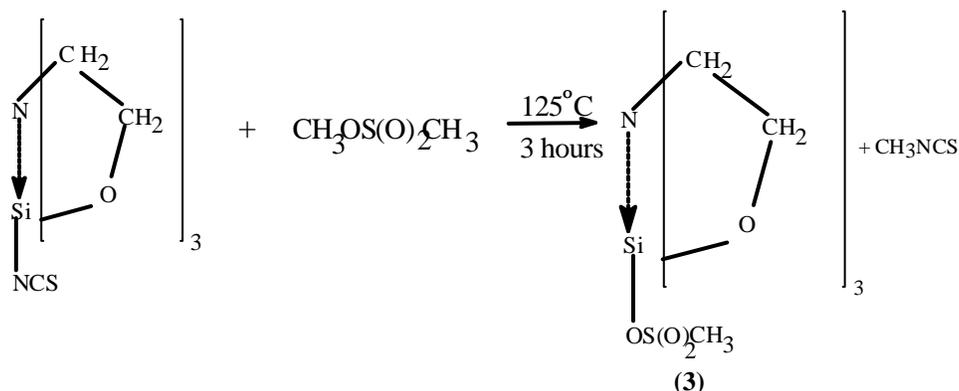
The identities of these compounds have been established by infrared, multinuclei (^1H , ^{13}C , ^{29}Si) spectral studies. In presence of dimethyl sulfite, Si-NCS bond in the title silatrane undergoes cleavage at 125 °C with the formation of two different products which may be justified from the dissociation pathways I & II that dimethyl sulfite may follow under the appropriate reaction conditions [4].



The formation of 1-methoxy silatrane **2** may be visualized by the nucleophilic attack of OCH_3^- on the silicon atom of the parent silatrane, while the nucleophilic attack of the OS(O)OCH_3^- followed by Arbuzov rearrangement may be visualized to explain the formation of methane sulfonato silatrane. All the physical and chemical methods to separate the two silatranes failed, keeping in view the donor ability of methanesulfonato group, the formation of an adduct between the two silatrane derivatives may not be completely ruled out. To obtain methane sulfonato silatrane the reaction of 1-isothiocyanato six membered silatrane and 1-isothiocyanato five membered silatrane with methylmethane sulphonate were carried out as depicted in Scheme 2 and Scheme 3 respectively.



Scheme 2. Reaction of 1-isothiocyanato six-membered silatrane with methyl methanesulfite.



Scheme 3. Reaction of 1-isothiocyanato five-membered silatrane with methyl methanesulfite.

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To supplement our experimental work, we have also performed some semi-empirical quantum mechanical computations using AM1, PM3, MNDO & MNDO/d methods (Table 1 & 2).

Table 1: Semi-empirical quantum mechanical computations of 1-methanesulfonato six membered ring silatrane (1)

Sil-OSOCH ₃	ΔH_f of (Kcal/mol)	$\mu(D)$	N→Si (A)	Si-O-S(O) ₂ CH ₃
AM1	-284.08	5.49	2.61	1.72
PM-3	-337.95	4.82	2.68	1.86
MNDO	-153.31	4.78	2.91	1.65
MNDO/d	-269.97	6.57	2.95	1.74

Table 2: Semi-empirical quantum mechanical computations of 1-methanesulfonato five membered ring silatrane (3)

Sil-OSOCH ₃	ΔH_f of (Kcal/mol)	$\mu(D)$	N→Si (A)	Si-O-S(O) ₂ CH ₃
AM1	-344.57	8.92	2.48	1.71
PM-3	-337.95	7.23	2.46	1.67
MNDO	-208.84	6.68	2.51	1.68
MNDO/d	-328.93	9.05	2.65	1.72

Isosurface plot of total electron density of 1-methane sulfonato six membered ring silatrane 1 have been depicted in Fig.1 and Fig. 2. The different semi-empirical quantum mechanical calculations predict that transannular Si-N bond distance in five-membered ring silatrane ring is found to be considerably reduced as compared to the six-membered ring silatrane. We found from our previous results of ΔH_f of values 1-isothiocyanato six membered ring silatrane that the present methane sulfonato is more stable. The same conclusion is reached for five-membered ring silatrane. This is partially due to ring enlargement and also due to the increased interaction in the transannular Si-N bond. The high negative value of ΔH_f indicates the high thermal stability of the synthesized silatranes. These calculations also predict high dipole moment for these silatranes.

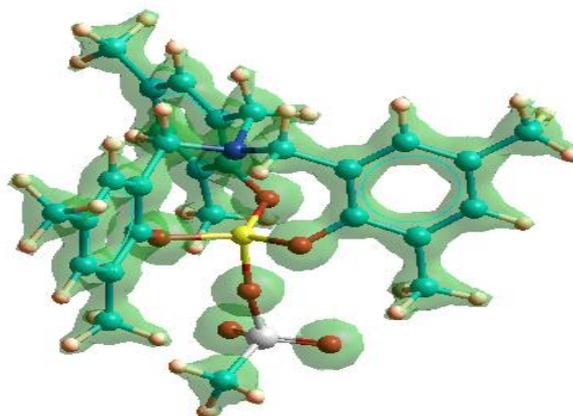


Fig. 1. Isosurface plot of total electron density of 1-methane sulfonato six membered ring silatrane

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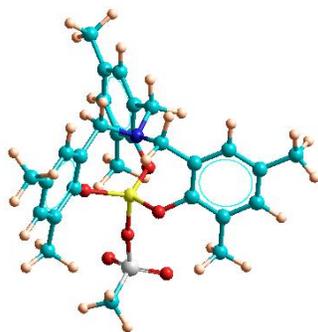


Fig. 2. Isosurface plot of 1-methane sulfonato six membered ring silatrane.

V. CONCLUSIONS

$\text{CH}_3(\text{O})_2\text{SOSi}(\text{OC}_6\text{H}_2\text{Me}_2\text{CH}_2)_3\text{N}$ (**1**), $\text{CH}_3\text{OSi}(\text{OC}_6\text{H}_2\text{Me}_2\text{CH}_2)_3\text{N}$ (**2**) and $\text{CH}_3(\text{O})_2\text{SO.Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$ (**3**) have been reported in good yield. These novel silatranes are valuable from coordination chemistry, biological application and material science point of view. Semi-empirical quantum mechanical calculations predict the dependence of the N→Si transannular bond length on atrane ring and exocyclic substituents.

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