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New silatranes possessing urea functionality: Synthesis, characterization and their structural aspects

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1-(3-silatranylpropyl)-3-phenylurea
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ABSTRACT

The present work aims at the synthesis of various novel silatranes bearing substituted urea functionality. Nucleophilic addition of various amines (morpholine, aniline, ethylenediamine and 3-aminopropyltriethoxysilane) to 3-isocyanatopropyltriethoxysilane resulted in the four triethoxysilanes; N-[3-(triethoxysilyl)propyl]morpholine-4-carboxylic acid amide (**1**), 1-[3-(triethoxysilyl)propyl]-3-phenylurea (**2**), 1,2-bis{*N*′-[3-(triethoxysilyl)propyl]ureido}-ethane (**3**) and N-[3-(triethoxysilyl)propyl]-N′-[3-(triethoxysilyl)propyl]urea (**4**), respectively. In the presence of a base the resulting silanes undergo transesterification reaction with triethanolamine, thus forming the corresponding silatranes, N-(3-silatranylpropyl)morpholine-4-carboxylic acid amide (**5**), 1-(3-silatranylpropyl)-3-phenylurea (**6**), 1,2-Bis[*N*′-(3-silatranylpropyl)ureido]-ethane (**7**) and N-(3-silatranylpropyl)-N′-(3-silatranylpropyl)urea (**8**), respectively. Among these are four novel compounds (**5**–**8**), which were characterized by elemental analysis, IR, multinuclear (^{1}H, ^{13}C and ^{29}Si) NMR and mass spectroscopy. Structures of compounds **5** and **6** were deduced by X-ray crystallography. Single crystal X-ray studies revealed distorted trigonal bipyramidal coordination about Si in **5** and **6** with Si–N bond distance of 2.121(1) Å and 2.189(2) Å, respectively.

1. Introduction

Research on substituted ureas is a continuously growing field in chemistry due to the importance of urea functional group in a wide range of biological compounds such as enzyme inhibitors [1] and pseudopeptides [2]. Substituted ureas are widely applied in chemical industry, especially pesticides [3] and pharmaceuticals [4]. During the past decade, a considerable amount of academic- and industrial-based research has been carried out with the aim of developing new trialkoxysilanes with substituted urea moiety. Such silanes have been used to prepare new xerogels [5], hybrid materials [6–12] and functionalized mesoporous silicas [13]. Some sol–gel procedures for preparing xerogels containing arch fixed urea functional groups in the surface layer have also been reported [14]. Urea functional groups are efficient in recovery and separation of rare-earth metal ions [15], in preparation of membranes [16] and wear-resistant protective coatings on the surface of lenses made of organic polymers [17]. Urea based ligands can act as anion receptors due to their potential to bind transition metal ions with simultaneous formation of hydrogen bonds with anions. These are good candidates for metal chelation because in these bitopical ligands, urea group can act as hydrogen bond donor and/or acceptor [18].

A large number of silatranes with different groups present at axial position are known. Apparently, crystal structures of silatranes having urea-functionalized substituents in the axial position have not been reported yet. In previous studies, it was shown that urea moieties could also act as mono- or bidentate ligands in the coordination sphere of silicon [19–21]. We have now shown that urea-functionalized triethoxysilanes can be transformed into silatranes despite the presence of this potential competitor.

In continuation of our work on hypervalent silicon chemistry [22,23], we have devoted our considerable attention to the use of 3-isocyanatopropyltriethoxysilane as a precursor for the synthesis of some new silatranes. Herein, we synthesized a series of substituted triethoxysilanes (**1**–**4**) by reacting 3-isocyanatopropyltriethoxysilane with different amines (morpholine, aniline, ethylenediamine and 3-aminopropyltriethoxysilane), respectively. These were further reacted with triethanolamine in the presence of different catalysts to form corresponding silatranes (**5**–**8**). All the compounds were

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analyzed by using elemental analysis, IR, NMR and Mass spectrometry. Furthermore, the molecular structures of **5** and **6** were deduced by using X-ray crystallography. A detailed description of fragmentation pattern of silatranes **5**–**8** is also provided.

2. Results and discussion

2.1. Synthesis

A typical procedure for the synthesis of substituted ureas involves treatment of alkyl isocyanates with primary or secondary amines in organic solvent [24]. In the presence of transition metal catalysts, selenium [25] or sulfur [26] compounds, symmetrical, unsymmetrical and even cyclo-ureas can be prepared by reacting primary amines or ammonia with carbon monoxide.

It is known that carbofunctional organosilicon isocyanates readily react with amines or diamines in a highly exothermic manner. Therefore, to prepare trifunctional silanes containing a urea functional group > NC(=O)N<, reaction of primary and secondary amines with 3-isocyanatopropyltriethoxysilane has been carried out. It is known that 3-isocyanatopropylsilanes are more reactive than isocyanatomethylsilanes.

Herein, a known N-(3-(triethoxysilyl)propyl)morpholine-4-carboxylic acid amide (**1**) [27] was prepared by a new method, whereas the other triethoxysilanes (**2**–**4**) were synthesized according to a method published earlier (Scheme 1). The method of preparation is found to be advantageous because of high yields of desired products as well as no need of further purification [28,29].

In the present work, silatranes (**6**–**8**) were synthesized by transesterification reaction of the corresponding triethoxysilane with triethanolamine in the presence of KOH. By contrast, silatrane **5** was obtained in the presence of sodium ethoxide catalyst, as this reaction was not successful in the presence of KOH (Scheme 2). Therefore, a strong base was used to obtain the product. Silanes **3** and **4** contain two triethoxysilyl groups; therefore, the corresponding silatranes (**7** and **8**) contain two silatranyl moieties, whereas, **5** and **6** contain one silatranyl moiety. All of these compounds are very stable in air and highly soluble in common organic solvents.

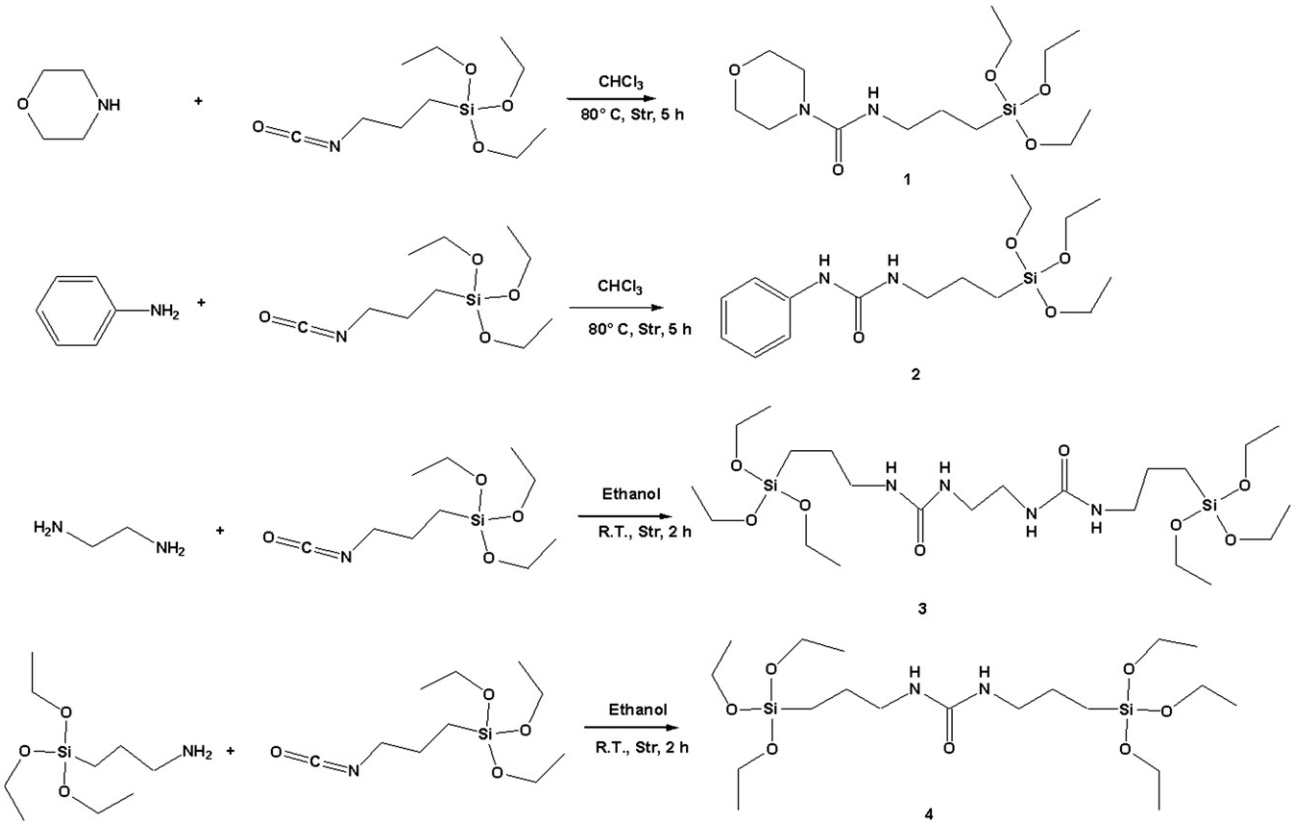
2.2. Spectroscopic studies

2.2.1. IR spectroscopy

IR spectra exhibit absorption bands characteristic of both >NC(=O)N< and silatranyl moiety. These bands are assigned by comparing with the spectra of starting materials [29]. Bands observed in the region of 3400-3000 cm^{-1} are assigned to asymmetric and symmetric NH stretching modes, whereas C–H stretching vibrations of methylene and methyl groups are observed in the region 3000–2800 cm^{-1}. The >C=O stretching vibrations are observed at 1650–1619 cm^{-1}, relatively low values, which are reasoned by C=O bond weakening due to the resonance involved in NHC(=O)NH moiety. Strong bands present in the regions 1550–1150 cm^{-1} are assigned to asymmetric and symmetric deformations of NH and CH_2 group. Si–O stretching vibration is assigned to the bands present in 1100–1080 cm^{-1} region. In addition, symmetric deformational vibration of the silatranyl skeleton with a predominant contribution from the Si–N bond is observed in the region 590–579 cm^{-1}. All bands observed for silatranyl moiety are consistent with previous literature reports [23].

2.2.2. NMR spectroscopy

Multinuclear (^1H, ^{13}C and ^{29}Si) NMR spectra of **2**–**4** are consistent with the literature [28,29]. It is noteworthy that ^1H NMR spectra of compounds **5**–**8** at room temperature are quite different



Scheme 1. Reaction pathway for the synthesis of triethoxysilanes (**1**–**4**).