Progress towards synthesis of silatrane derivative: 1-ethoxy-4-silatranone

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Introduction

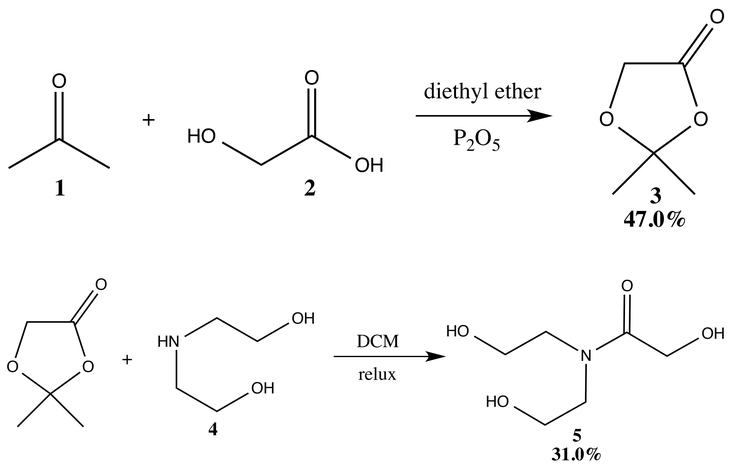
Silatranes are a group of five-membered tricyclic molecules with co-ordinate bonding between nitrogen and a central silicon atom. Silatrane derivatives have applications in many different fields due to their varying properties typically based on the substituent attached to the silicon. Phenylsilatrane is a potent toxin, while others are used to heal wounds, grow back hair and assist in imaging of DNA with atomic force microscopy[1]. The stability of the silatrane is believed to come from the bonding character between the nitrogen and silicon, which leaves the question of how an electron withdrawing group on the nitrogen affects the synthesis and stability of the silatrane.

Figure 1. Structure of general (a) silatrane and (b) silatranone.

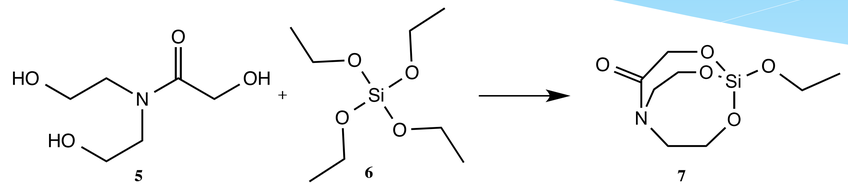
This project aims to synthesize 1-ethoxy-4-silatranone using N-glycolyl-diethanolamine and tetraethoxysilane under varying conditions. The synthesis of 4-silatranone will provide a whole new venue in understanding how the electronic effects of substituents affect the overall stability of the silatrane molecule.

Experimental

To synthesize N-glycolyl-diethanolamine a multistep synthesis was performed starting with mixing acetone and glycolic acid in diethyl ether with phosphorus pentoxide at 0°C to yield crude 2,2-dimethyl-1,3-dioxolan-4-one which was then refluxed overnight in DCM with diethanolamine. The product was purified by column and concentrated to yield a purified product.



Scheme 1. Synthetic pathway to N-glycolyl-diethanolamine



Scheme 2. Proposed pathway to 1-ethoxy,4-silatranone.

Table 1. Summary of reaction conditions used for Scheme 2.

Reaction	Conditions[a]
1	Methanol, st, ref, 12 h
2	Xylene, st, ref, 80°C, 2hr[3]
3	Methanol, xylene, KOH, st, ref, 80°C, 3hr
4	Methanol, NaOMe, st, 0°C, 12 hr

[a]*Conditions:* Solvent, catalyst, stirring (st), refluxing (ref), temperature, time.

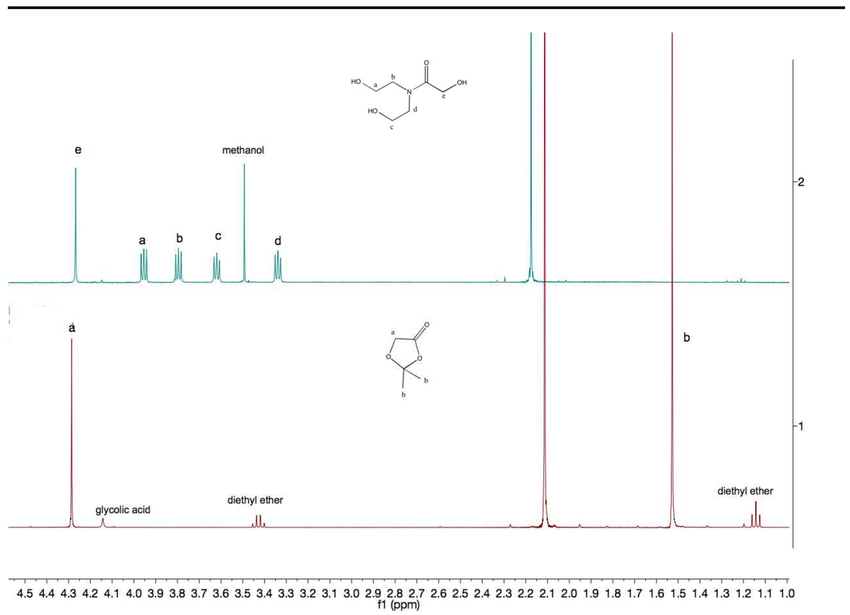


Figure 2. H^1 NMR of (3) and (5).

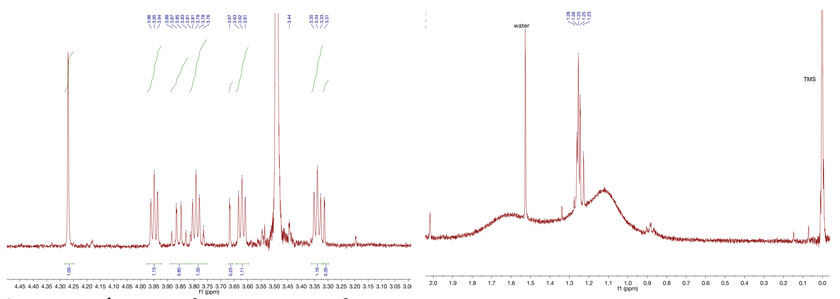


Figure 2. H^1 NMR of Reaction #4 after concentration.

Results and Discussion

Successfully synthesized and purified (3) and (5) with higher yield then reported[2]. Verified with IR and H^1 NMR.

Reaction 1: No product after recrystallization, IR showed unreacted (5).

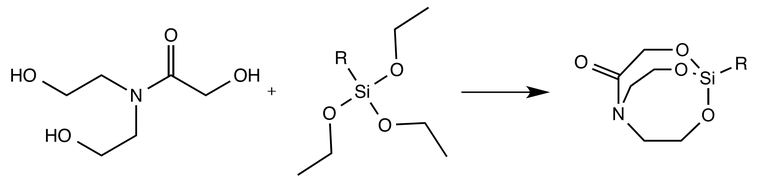
Reaction 2: (5) remained undissolved in the bottom of the flask, no product after recrystallization.

Reaction 3: (6) formed into a sol-gel[4] preventing any reaction to occur with the (5).

Reaction 4: Pale white slurry formed after recrystallization, but showed no indication of silatranone.

Future Work

More reactions will be conducted using different conditions from those performed here. Solvents such as DMF and DMSO have been previously used to assist in synthesis of some silatrane derivatives. Besides changing the reaction conditions, alternative reactants will be considered. Different substituents will be considered to assist in the N-S bonding.



Scheme 3. Conditions proposed for future reactions where X could be $-CF_3$, -F , -Cl.

Conclusions

Silatrane synthesis reactions are typically very easy and can be done in many different conditions. The difficulty in synthesizing 1-ethoxy-4-silatranone is very likely due to the reduced bond character between the nitrogen and silicon. Besides further experimentation, computational chemistry should be done to determine if the desired molecule is theoretically stable.

Acknowledgments

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References

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(4) Buckley, A. M.; Greenblatt, M.; *J. Chem. Ed.* 1994, 71, 599-602.