



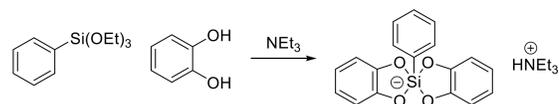
# Synthesis and oxidation of potassium bis(ethyleneglycolato)organo-silicates and organosilatrane

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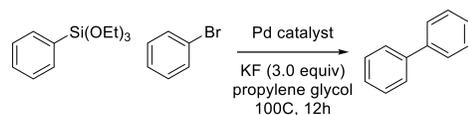
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## Introduction

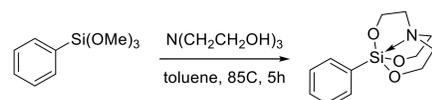
Bis(catechol)silicate salts have enjoyed substantial success over the past several years. This is, in part, due to their easy synthesis, high reactivity, and benchtop stability.<sup>1</sup>



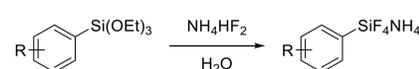
Unfortunately, these silicates suffer from a lack of atom economy and produce a significant amount of waste. However, simpler organosilicates have not yet been developed. There is a single report of a simpler silicate based on propylene glycol that is proposed as an intermediate in a coupling reaction. It was isolated, but its reactivity has not yet been explored.<sup>2</sup>



Another possible formal silicate that could be explored are organosilatrane. The synthesis of these have been reported, but their reactivity has remained largely unexplored as only three reactions with them have been published.<sup>3</sup>



Conversely, the analogous, facile synthesis of organotetrafluorosilicates has recently been developed by our lab.<sup>4</sup> Organofluorosilicates have also been prepared by treating alkoxysilanes with water-free hydrogen fluoride in ether solution<sup>5</sup> or by reacting organotrichlorosilanes with KF.<sup>6</sup> Both of these syntheses rely on starting materials that are not readily synthetically available and require the use of dangerous reagents such as HF. We hope to expand the types of silicates available to us by developing the facile synthesis of bis(ethyleneglycolato)organosilicates.

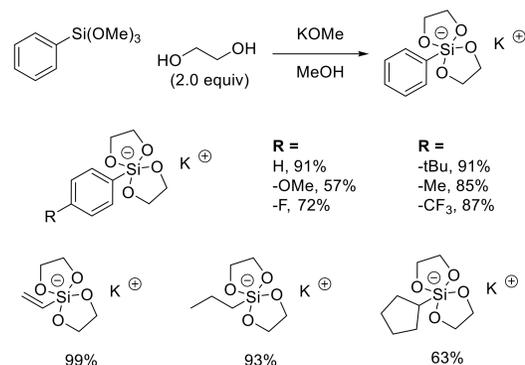


## Hypotheses

1. A bis(ethyleneglycol)organosilicate will form under fluoride-free conditions and with  $\mu\text{W}$  radiation.
2. The resulting bis(ethyleneglycol)organosilicate be able to be oxidized by simple and readily available oxidants.
3. A silatrane will be able to be formed with  $\mu\text{W}$  radiation to reduce reaction times.

## Synthesis of Bis(ethyleneglycol)-organosilicates

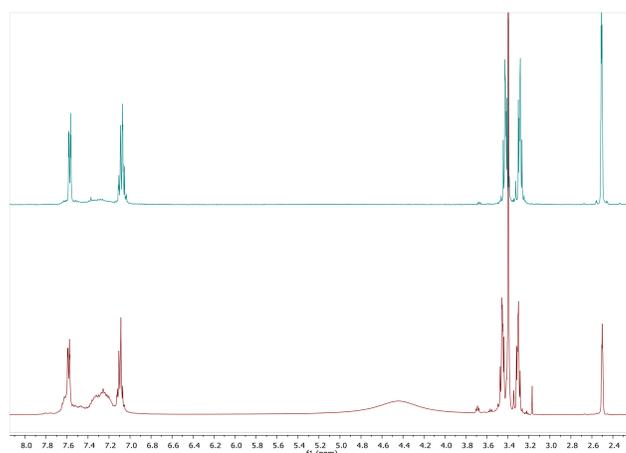
Bis(ethyleneglycol)organosilicates can be easily synthesized by stirring KOMe and ethylene glycol, with or without a solvent, and then adding the silane. The reaction time is quite short at only 15 minutes. It is generally high yielding. Interestingly, NaOMe or longer chain diols, such as 1,3-propanediol, do not work in this reaction and produce a mixture of products. However, use of microwave radiation dramatically reduced the reaction and drying times (30 sec total time!)



The yields for our substrate scope have been good so far. However, base-sensitive or electrophilic functional groups do not seem to be tolerated by the reaction conditions, though this is not surprising. Additionally, the yields for alkyl substrates tend to be highly variable.

## Purification of Silicate Salts

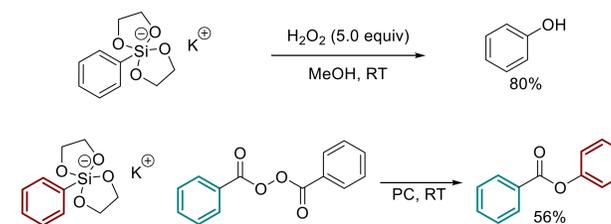
While the crude product was fairly pure, a significant amount of ethylene glycol remained and proved challenging to remove. Eventually, heating overnight at 100°C under a vacuum with a cold finger effectively removed impurities.



## Oxidation of Phenyl Bis(ethyleneglycolato)silicate

Oxidation of silicates is well-known – the Fleming-Tamao oxidation has been in widespread use for several decades. However, it usually uses fluoride to activate the silane and very few reports make a phenol. Notably, this reaction works well as a one pot reaction from phenyltrimethoxysilane.

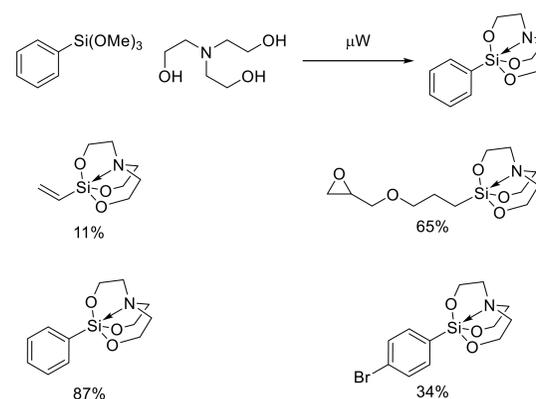
Another potentially interesting oxidation is with benzoyl peroxide to make esters.



Though initial results are promising, this reaction seems to be highly sensitive to the presence of ethylene glycol, making results variable from one reaction to the next. Also, this means that it is not a good candidate for a one-pot reaction.

## Synthesis of Organosilatrane

We have also found that the synthesis of organosilatrane can be carried out neat under  $\mu\text{W}$  radiation in only a few minutes. Current challenges are purifying the silatrane as it is not overly soluble in most solvents and it streaks during column chromatography. Also, triethoxysilanes do not appear to work under solventless reaction conditions as they are too non-polar to be solvated by the triethanolamine.



## Future Directions

1. Continue to expand the substrate scope for silicates and silatrane.
2. Explore the substrate scope for the oxidation of silicates to phenols and esters.
3. Optimize reaction conditions for other oxidations for both silicates and silatrane.
4. Explore nucleophilic additions of silicates and silatrane to various electrophiles.

## Conclusions

We have shown that bis(ethyleneglycolato)organosilicates and organosilatrane can be synthesized with relative ease with microwave irradiation. We have also found that these silicates can be easily oxidized with a variety of different oxidants, and we anticipate that we will be able to oxidize them with even more oxidants. Furthermore, we plan to explore the substrate scope of silicates and silatrane as well as explore other modes reactivity with both silicates and silatrane.

## Acknowledgements

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