



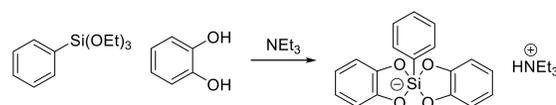
# Synthesis and functionalization of potassium bis(ethyleneglycol)-organosilicates

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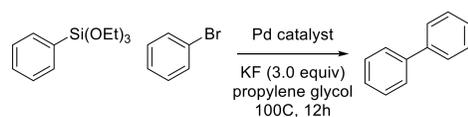
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## Introduction

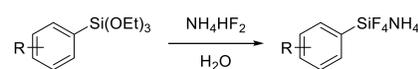
Bis(catechol)silicate salts have enjoyed substantial success over the past several years. This is, in part, due to their easy synthesis, high reactivity, and benchtop stability.<sup>1</sup>



Unfortunately, these silicates suffer 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 ethylene glycol that is proposed as an intermediate in a coupling reaction. It was isolated, but its reactivity has not been explored.<sup>2</sup>



However, the analogous, facile synthesis of organotetrafluorosilicates has recently been developed by our lab.<sup>3</sup> Organofluorosilicates have also been prepared by treating alkoxy silanes with water-free hydrogen fluoride in ether solution<sup>4</sup> or by reacting organotrichlorosilanes with KF.<sup>5</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 synthesis of bis(ethyleneglycol)organosilicates.

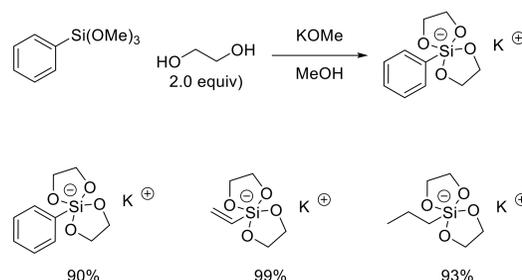


## Hypotheses

1. A bis(ethyleneglycol)organosilicate will form under fluoride-free conditions.
2. The resulting bis(ethyleneglycol)organosilicate be able to be oxidized by simple and readily available oxidants.

## Synthesis of Bis(ethyleneglycol)-organosilicates

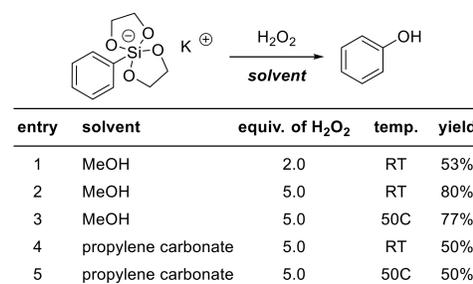
Bis(ethyleneglycol)organosilicates can be easily synthesized by stirring KOMe and ethylene glycol, with or without a solvent, and then adding the silane. The reaction time is quite short at only 15 minutes. It is generally high yielding. Interesting, NaOMe or longer chains such as 1,3-propanediol, do not work in this reaction and produce a mixture of products.



The yields for our substrate scope have been good so far. However, base-sensitive functional groups do not seem to be tolerated by the reaction conditions. This is not surprising.

## Oxidation of Silicate with H<sub>2</sub>O<sub>2</sub>

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.

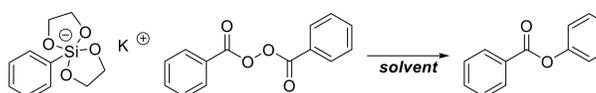


yields determined by using 1,1,1,2-tetrachloroethane or mesitylene as an internal standard

Notably, this reaction also works well in a one-pot fashion, where both the silicate formation and the oxidation occur in the same flask without isolation.

## Oxidation with Benzoyl Peroxide

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

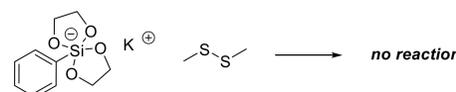
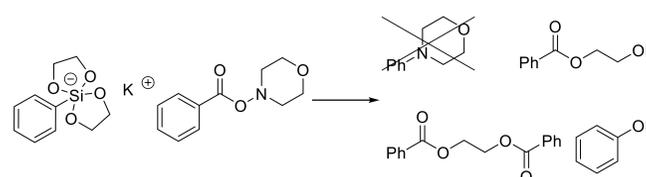


entry	solvent	equiv. of benzoyl peroxide	temp.	yield
1	MeOH	1.0	RT	0%
2	propylene carbonate	1.0	RT	80%
3	sulfolane	1.0	RT	20%
4	propylene carbonate	1.0	80C	39%
5	propylene carbonate	1.2	80C	56%
6	propylene carbonate	1.5	RT	40%
7	propylene carbonate	1.2	RT	35%
8	propylene carbonate	1.2	RT	55%

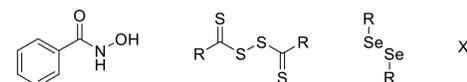
yields determined by using 1,1,1,2-tetrachloroethane or mesitylene as an internal standard

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.

## Other Attempted Oxidations



## Other Potential Oxidants



## Future Directions

1. Continue to expand the substrate scope for silicates.
2. Explore the substrate scope for the oxidation to phenols and esters.
3. Optimize reaction conditions for other oxidations.

## Conclusions

We have shown that bis(ethyleneglycol)organosilicates can be synthesized with relative ease. 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 the silicates as well as the oxidations.

## Acknowledgements

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