



Oxidation of organotetrafluorosilicate salts to form new carbon-heteroatom bonds

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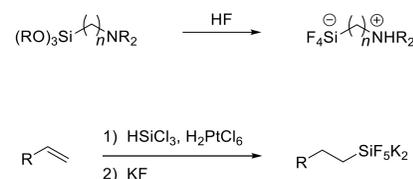
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Introduction

Organotrifluoroborate salts have enjoyed substantial success over the past several years. This is, in part, due to their easy synthesis, high reactivity, and benchtop stability.¹



However, the analogous, facile synthesis of organotetrafluorosilicates has recently been developed by our lab.² Organofluorosilicates have also been prepared by treating alkoxy silanes with water-free hydrogen fluoride in ether solution³ or by reacting organotrichlorosilanes with KF.⁴ Both of these syntheses rely on starting materials that are not readily synthetically available and require the use of dangerous reagents such as HF.



Several research groups have reported on the synthetically useful electrophilic cleavage reactions of the carbon-silicon bond, however, organofluorosilicates have not received much attention in part due to their inaccessibility.^{4,5} Currently, there is one report of using alkoxy silanes to make organofluorosilicates, but they do not report a yield and their procedure has not been reproducible in our hands.⁶

Formation of aromatic-heteroatom bonds remains a significant challenge in modern organic chemistry. Many C-X forming reactions are redox neutral and couple a nucleophile and electrophile such as the Buchwald-Hartwig Coupling and Ullman-type reactions. Another strategy is to couple two nucleophiles together in the presence of an oxidant, which is employed in reactions such as the Chan-Lam Coupling. This strategy is not often utilized since it usually requires somewhat fickle reaction conditions. As such, these types of oxidations have not been studied in as much depth as couplings like the Buchwald-Hartwig Coupling. Furthermore, oxidations of silanes, such as the Fleming-Tamao oxidation, generally perform poorly on aromatic silanes.⁷ We report the oxidation of these salts to form new aromatic carbon-heteroatom bonds. Our efforts towards optimization of reaction conditions and the substrate scope will be discussed.

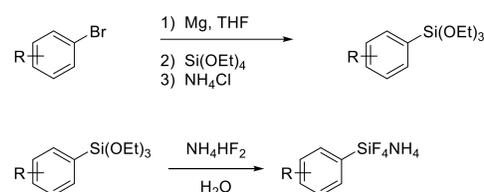
Hypothesis

1. An ammonium organotetrafluorosilicate can be oxidized using a readily available oxidant under mild conditions.
2. Identity of the solvent and the oxidant will be crucial as organotetra-fluorosilicates have limited solubility in several solvents.

Substrate Synthesis

Aryltrialkoxysilanes can be easily synthesized by Grignard attack of tetraethylorthosilicate. Ammonium organotetrafluorosilicates can be readily synthesized with ammonium bifluoride in water.

synthesis of tetrafluorosilicate:



Optimization of Phenol Synthesis Reaction Conditions

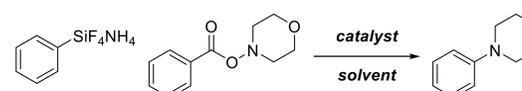
Oxidation of aryltetrafluorosilicates to phenols was undertaken with a variety of different solvents and oxidants. In general, oxidation in propylene carbonate with either ammonium persulfate or hydrogen peroxide worked best.

entry	oxidant	solvent	temp.	yield
1	H ₂ O ₂ (5 equiv)	H ₂ O	50C	2%
2	H ₂ O ₂ (5 equiv)	sulfolane	50C	10%
3	H ₂ O ₂ (5 equiv)	toluene	50C	16%
4	H ₂ O ₂ (5 equiv)	propylene carbonate	50C	58%
5	(NH ₄) ₂ S ₂ O ₈ (2 equiv)	propylene carbonate	50C	42%
6	H ₂ SeO ₃ (2 equiv)	propylene carbonate	50C	0%
7	KBrO ₃ (2 equiv)	propylene carbonate	50C	0%
8	NaOCl (5 equiv)	propylene carbonate	50C	0%
9	H ₂ O ₂ (5 equiv)	propylene carbonate	80C	43%
10	(NH ₄) ₂ S ₂ O ₈ (2 equiv)	propylene carbonate	80C	62%

Yields determined by NMR using mesitylene as an internal standard

Other Attempts to Oxidize Aryltetrafluorosilicate Salts

Since hydrogen peroxide could oxidize aryltetrafluorosilicate salts, other oxidants were attempted. Notably, benzoyl amines are particularly interesting oxidants since they should form an aniline.



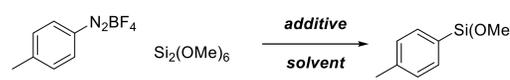
entry	solvent	temp	catalyst	yield
1	methanol	70C	none	trace
2	methanol	70C	Cu(OAc) ₂ ·H ₂ O	trace
3	methanol	100C	none	mixture
4	PC	100C	none	20%
5	toluene	50C	Ni(cod) ₂	0%
6	toluene	50C	Ni(PPh ₃) ₄	0%
7	toluene	50C	Ni[P(OPh) ₃] ₄	trace
8	toluene	50C	Pd(PPh ₃) ₄	0%

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

Overall, the reaction yielded poorly with or without a catalyst. Although, a small amount of product formation is encouraging that this reaction can be further optimized.

Synthesis of Aryltrialkoxysilanes

Another project this summer was exploring the possibility of synthesizing aryltrialkoxysilanes via an alternative synthesis. The current methods tend to have poor yields or use expensive catalysts.



entry	solvent	additive	result
1	acetone/H ₂ O	none	no reaction
2	acetone/H ₂ O	Bz ₂ O ₂	no reaction
3	acetone/H ₂ O	TsOH	no reaction
4	acetone/H ₂ O	ZnCl ₂	no reaction
5	methanol	NaOMe	toluene
6	methanol	K ₂ CO ₃	toluene
7	sulfolane	NaOMe	toluene
8	DMSO	NaOMe	toluene
9	PC	NaOMe	toluene
10	PC	CuO	toluene
11	PC	Me ₄ F	toluene
12	PC	KF	toluene
13	PC	CuF ₂	toluene

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

Future Directions

1. Continue to optimize reaction conditions for the oxidation of aryltetrafluorosilicates to phenols.
2. Once the reaction is fully optimized, establish a substrate scope as well as the functional group tolerance of the transformation.
3. Further explore other sets of conditions that can transform an aryltetrafluorosilicate into an aryl ether or an aniline.

Conclusions

We have shown that an aryltetrafluorosilicate salt can be cleanly oxidized to a phenol. The best reaction conditions use propylene carbonate as the solvent and ammonium persulfate as the oxidant. Other attempts at oxidizing the aryltetrafluorosilicate were not successful. Future work will focus on isolating the product and establishing the substrate scope.

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