Synthesis of a Novel Phospholanium Cation

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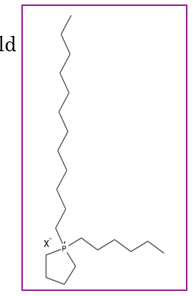
Introduction

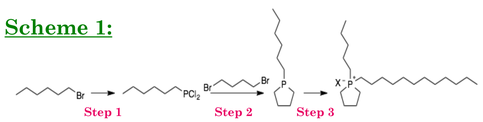
Ionic liquids are commonly used for carbon dioxide capture. Interestingly, an ionic liquid containing a heterocyclic sulfur cation does not react with carbon dioxide as expected. Two factors could explain this. First, the sulfur atom may reduce the reactivity of the ionic liquid, or the ring could be preventing the ionic liquid from reacting with carbon dioxide. To test the first hypothesis, I worked on synthesizing a heterocyclic phosphonium ionic liquid that could then be tested for reactivity with carbon dioxide.



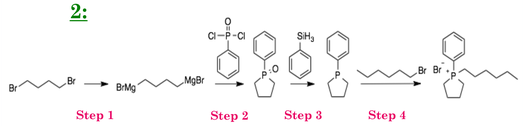
Synthesis Reactions

I tried four different approaches to synthesizing the phospholanium cation:

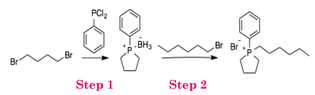
Scheme 1:



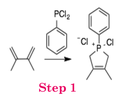
Scheme 2:



Scheme 3:



Scheme 4:



Results

Scheme 1:

The phosphorus-31 NMR taken after Step 2 of Scheme 1 (see Fig. 1) is essentially the same as the P-31 NMR taken after Step 3 (Fig. 2). The proton NMR (Fig. 3) also does not correspond to the desired product of Step 3.

Fig. 1

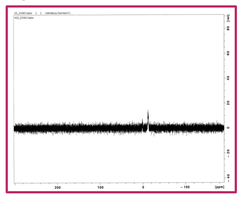


Fig. 2

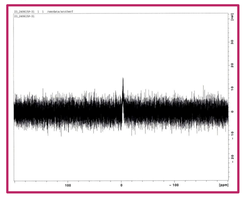
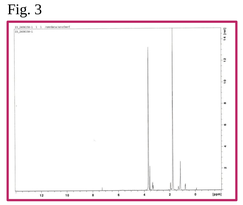


Fig. 3



Scheme 3:

The proton and P-31 NMRs taken after Step 2 of Scheme 3 (Figs. 6 and 7) both show a very close match to the literature values.

Fig. 6

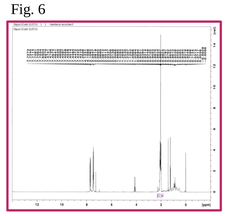
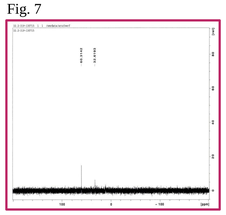


Fig. 7



Scheme 2:

The P-31 NMR taken after Step 2 of Scheme 2 (Fig. 4) and the proton NMR (Fig. 5) are both excellent matches for the product of Step 2.

Fig. 4

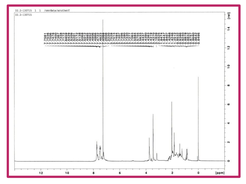
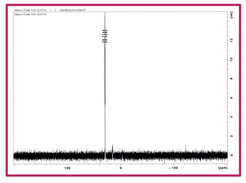


Fig. 5



Scheme 4:

The proton and P-31 NMRs taken of the results of Scheme 4 (Figs 8 and 9) both correspond to the spectra for the starting materials.

Fig. 8

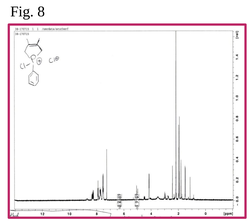
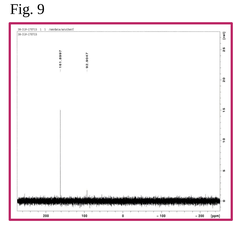


Fig. 9



Conclusions

I started with Scheme 1 because it was the most straightforward approach. As indicated by the NMRs the phosphorus ring did not form when I carried out Step 3. After a literature search, I found a better procedure for activating the dibromobutane and forming the phosphorus ring (Step 1, Scheme 2). Unfortunately, the product of Step 3 reacts quickly with oxygen and is difficult to work with. In Scheme 3, the addition of boron helps prevent oxidation of phosphine. In Step 2, removal of the boron group is followed by immediate addition of the six carbon chain to limit oxygen exposure and decrease the chance of oxidation. The boron-containing product of Step 1 forms with a high yield and is easy to work with, which makes Scheme 3 the best synthetic route.The main disadvantage to Scheme 4 is the time required to form the product. According to the literature, the reaction must run for two weeks. I tried to speed up the reaction with moderate heating, but that had little effect.

Literature cited

Hanaya, T. , Kawase, S. , Yamamoto, H. , & PERGAMON-ELSEVIER SCIENCE, L. (2005). Synthesis of phospholane 1-oxide having oxygen functional groups from a 4-bromobutylphoshinate derivative.*Heterocycles*, *66*, 251-261.

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Acknowledgments

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Curriculum Project:

Types of Reactions

This project is part of the unit on Chemical Equations. We will already have analyzed the parts of a chemical equation and reviewed balancing chemical equations.

Day 1

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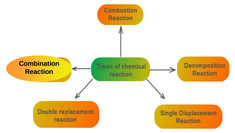
NAME	DEFINITION	GENERAL FORMULA	EXAMPLES

Day 2



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Day 3

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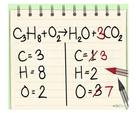

Day 4

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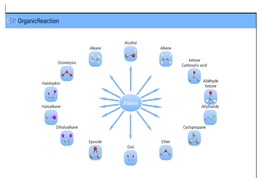
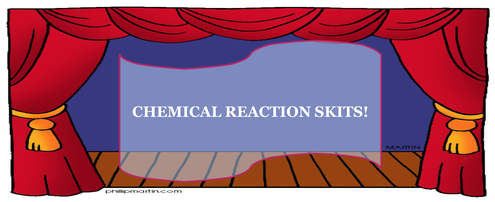
Day 5



Day 6 & 7



The chapter continues with Solubility Rules, and an exploration of the changes in energy that always accompany changes of matter.