

Synthesis of Naphthalene and Biphenylene Tetraimides

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Research Progress

In the reporting period, we tackled both of the synthetic methods proposed initially for the synthesis of naphthalene and biphenylene tetraimides, namely the “all-at-once” and “stepwise” approaches. To date, we have successfully synthesized the key polymethyl precursors required for the “all-at-once” approach to the proposed compounds (Figure 1). We have now begun initial synthetic trials for the polyoxidation process required to form the requisite arenepolycarboxylic acids. Initial mass spectrometric analyses suggest the formation of mixtures of oxidation products, including the desired fully oxidized form. However, further optimization is required to improve the conversion of polymethylnaphthalene into the fully oxidized product. Currently, we are exploring the use of large excesses of KMnO_4 and long reaction times to achieve oxidation (Figure 2), in addition to altering the solvent system.

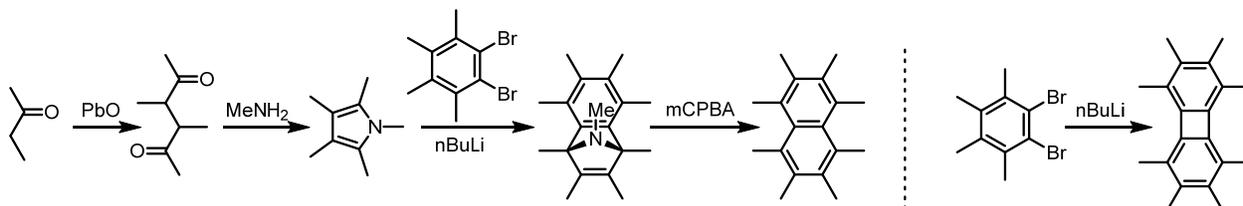


Figure 1. Completed syntheses of octamethylnaphthalene and octamethylbiphenylene.

In the course of oxidation optimization, we have also explored the possibility of utilizing the catalytic conditions found in the so-called AMOCO process in which molecular O_2 serves as oxidant (Figure 2). However, our initial attempts reveal that high pressures of O_2 (~20 atm) may be required to achieve polyoxidation reactivity. We currently do not have the capability of safely performing reactions under more than 8 atm of O_2 , but we are pursuing collaborative options, in addition to seeking funding necessary to obtain high pressure equipment.

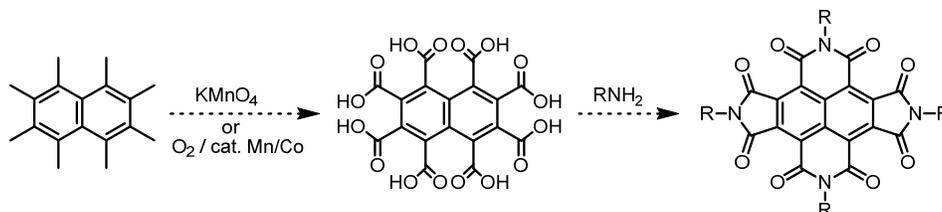
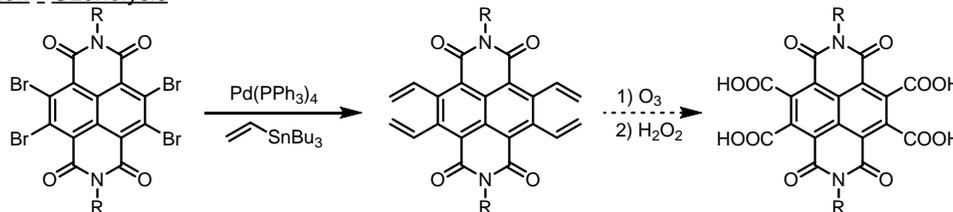
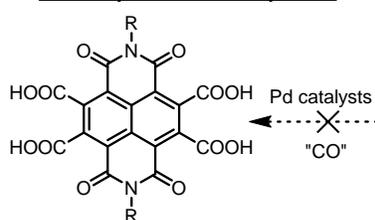


Figure 2. Remaining synthetic steps for the “all-at-once” approach of synthesizing naphthalene tetraimide.

Vinylation - Ozonolysis



Carbonylation/Carboxylation



Methylation

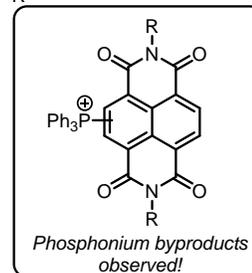
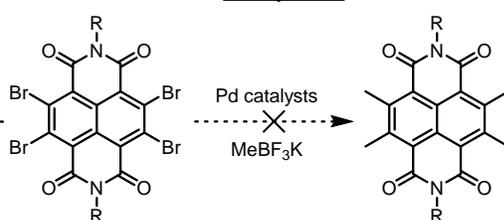


Figure 3. Approaches attempted for “stepwise” installation carboxylic acids onto the naphthalene diimide core.

At the same time, we also pursued the “stepwise” approach to installing imides onto the naphthalene core (Figure 3). This method entails the conversion of the known tetrabrominated naphthalene diimide into the analogous core-carboxylated derivative, either through direct aryl halide carbonylation or sequential alkylation followed by oxidation. We have had the most success pursuing a vinylation strategy that sets the stage for oxidative cleavage by O₃ to form the carboxylic acids (Figure 3, top). The tetravinylation reaction is effective and proceeds in high yields under mild conditions. In our carbonylation and methylation attempts, however, reactivity proved to be minimal at low temperatures and we began to see competing phosphonium formation processes take place when heat is applied. This result can be rationalized by observing that the highly electron-poor nature of the naphthalene core should make it more susceptible to nucleophilic aromatic substitution reactions and/or metal-catalyzed phosphonium formation processes.

The observation of phosphonium formation, however, inspired us to initiate a deeper investigation into cationic aromatic diimides. We have been able to successfully synthesize and characterize both pyridinium- and phosphonium-functionalized pyromellitic diimides, which have a single benzene ring core instead of a naphthalene one (Figure 4). The bispyridinium compounds exhibit significantly stabilized reduced states (greater than +0.5 V redox shifts) with minimal perturbations in electronic structure and photophysical properties. Our findings regarding the pyridinium derivatives was published recently (*ACS Omega* **2018**, 3, 240) (Figure 4, right). In the case of phosphine nucleophiles, an interesting reaction is observed in which a highly stabilized ylide is formed, presumably because of substitution reactivity with adventitious H₂O (Figure 4, left). We are now engaged in an in-depth investigation into the properties of this stabilized ylide and other phosphonium aromatic diimides.

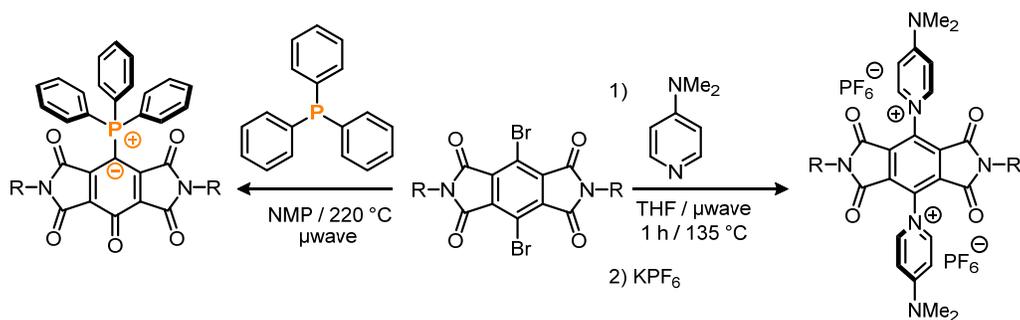


Figure 4. The reaction between phosphine or pyridine nucleophiles and brominated pyromellitic diimides under microwave conditions leads to the formation of cationic aromatic diimides.

Career Impact

This research enabled by funding from the PRF has been instrumental in launching my independent career. My first independent publication (Figure 4) arose directly from observations made while pursuing the synthesis of the naphthalene tetraimides. Beyond the immediate career impacts of publishing an article, these PRF-funded results also served as the foundational preliminary evidence for two grant proposals that I submitted in July 2018. In my submission to the National Science Foundation CAREER Award program, I proposed a holistic study on the chemistry of core-substituted pyromellitic diimides while for the Research Corporation Cottrell Scholars Award, I proposed expanding the study of cationic systems to both naphthalene and perylene diimide scaffolds, in order to investigate tetracationic systems. Moreover, this PRF funding and the resultant publication of an article have served as crucial evidence of scholarly commitment for my mid-tenure review process. I was recently reappointed and am currently on a mid-tenure sabbatical for the 2018–2019 academic year, during which my research students and I will be focusing on the ongoing work described here.

Student Outcomes

The Macalester undergraduate students who assisted in this research work have all benefited greatly from PRF support. Two of the student co-authors of the *ACS Omega* article recently began their pursuit of PhDs; Qifan Xiao is at University of Texas at Austin and Andrew Greenlee is at University of Illinois Urbana-Champaign. The other student co-authors have also found success and are now all gainfully employed at companies such as Sherwin-Williams and United Health. All the first-year students who contributed to the synthetic work for this research, particularly that which is described in Figures 1–3, were able to land prestigious REUs in the summer after their second year of college.