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Forming Carbon-Carbon Bonds Via Photo-oxidation

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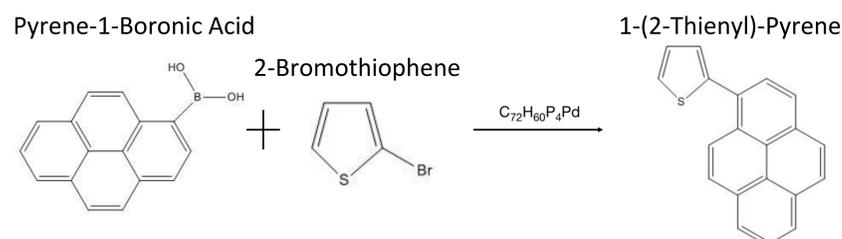
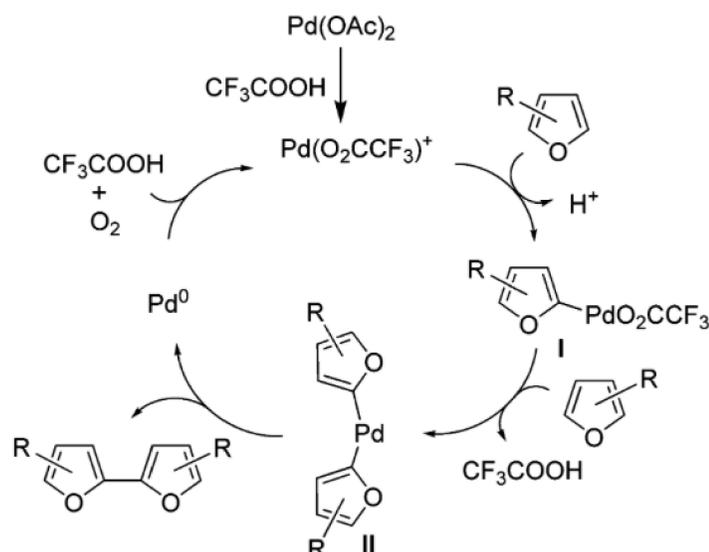
Abstract

1-(2-thienyl)-pyrene has been viewed to form a carbon-carbon bond when oxidized. Scheme 1 illustrates a plausible mechanism for a palladium catalyzed reaction leading to the dimerization of a Furan. However, ostensibly a similar reaction can occur in the absence of palladium but the presence of a photocurrent substantial enough to push an electron to an excited state, leaving a hole in it's previous orbital. After this occurs, this molecule can find another of the same nature and complete the desired carbon-carbon bond. In creating this bond, we will have synthesized a "solar fuel" that can store energy in a stable bond using light.

Introduction

Initially, 1-(2-Thienyl)-Pyrene needed to be synthesized. This reaction is outlined in scheme 2. This molecule, after extensive purification, was placed into dried acetonitrile with a platinum electrode as the working probe and a silver wire as the reference. A counter electrode was placed additionally in dried acetonitrile with a salt bridge connecting the two. This whole apparatus was connected to a potentiostat applying a voltage of 1.2 for 500 seconds at a time. This reaction is outlined in scheme 3. The dimer adhered to the platinum electrode, then was scraped and collected into a scintillation vile also containing a few ml of acetonitrile. After evaporating the solvent from the vile, the dimer residue was dry loaded into a column for column chromatography. UV-vis spectra of every third vile was taken and is illustrated in figure 2. We simultaneously were conducting experiments attempting to replicate the reaction using a light in place of a potentiostat.

Scheme 1. Plausible Mechanism for the Homecoupling



Scheme 2. 1-(2-Thienyl)-Pyrene monomer synthesis

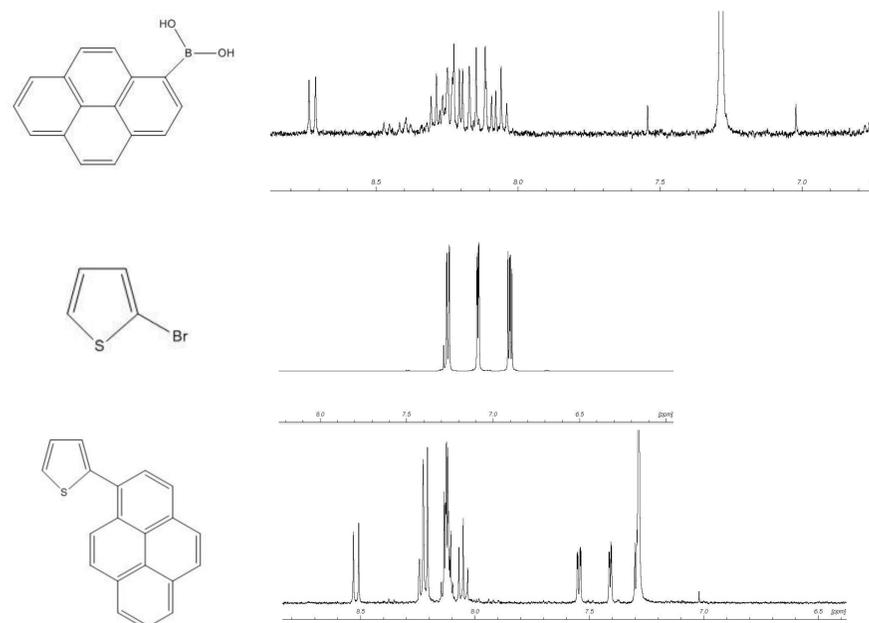
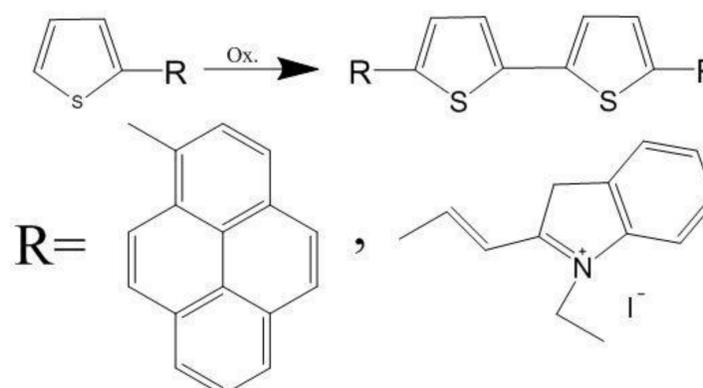


Figure 1. Corresponding NMR Spectra of Products and Reactants



Scheme 3. Theoretical Photocurrent Oxidation Reaction

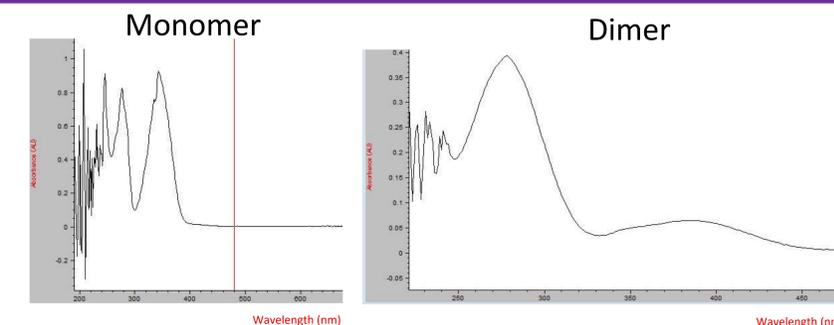


Figure 2. UV-Vis Spectra of 1-(2-Thienyl)-Pyrene Post Bulk Electrolysis and Column Chromatography

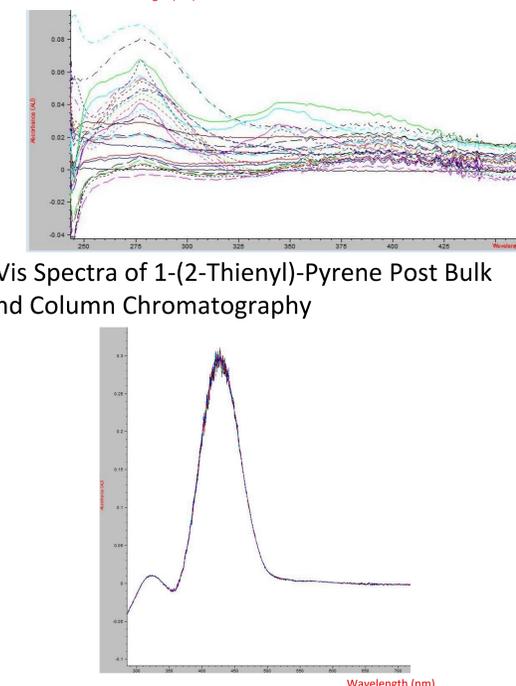


Figure 3. UV-Vis Kinetics Spectra of 1,3,3-Trimethyl-2-(2-Thienyl)Ethenyl]-3H-Indolium BF4 During Cyclic Voltametry

Results

- Successful 1-(2-Thienyl)-Pyrene dimer growth after potentiostat application of 1.2 V
- 1,3,3-trimethyl-2-(2-thienyl)ethenyl]-3H-indolium BF4 did not appear to dimerize to an appreciable amount after voltage application
- Unsuccessful oxidation of 1-(2-Thienyl)-Pyrene using only a controlled light system

Conclusion

Proceeding in research of 1-(2-Thienyl)-Pyrene now extends to manipulating a light source to achieve desired oxidation results. Cyanine type molecule data will be further analyzed on the principle of whether to proceed further in our studies.

Acknowledgments

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References

1. Na-Na Li, Yan-Lei Zhang, Shuai Mao, Ya-Ru Gao, Dong-Dong Guo, and Yong-Qiang Wang *Organic Letters* **2014** 16 (10), 2732-2735
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