Optimization of Azobenzene Molecular Switch in Organic Synthesis

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Background

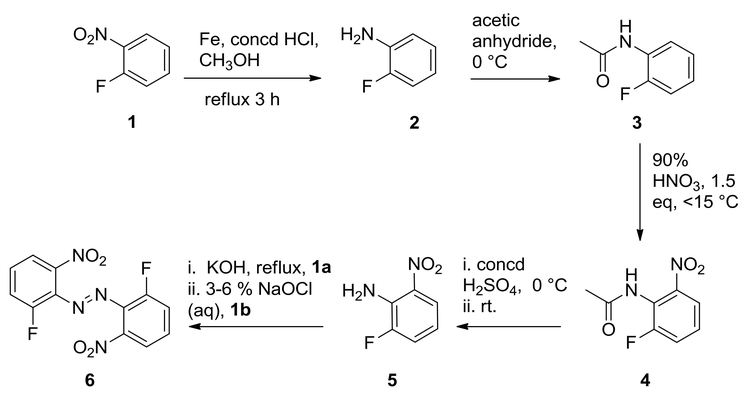
- Photosensitive azobenzene molecules are potential molecular switches for a nanoscale optoelectronic device due to their properties that are based on fast, light-driven processes.[1]
- An azobenzene conductor has the ability to transform from trans to cis configuration when light with a certain wavelength is absorbed, thus converting the electromagnetic radiation to mechanical work by contraction and retraction on an atomic force microscope tip.[1,2]
- The transformation is reversible,[1,2] which means the mechanism can be restarted without renewing the molecular switch.
- Previous synthetic method of 6,6'-difluoro-2,2'-dinitroazobenzene, **6**, from 2-fluoro-6-nitroaniline, **5**, was 40% with unreacted **5** as the only contaminant.[3] This suggested that the reaction from **5** to **6** did not go to completion.

Objective

- To optimize the synthesis of **6** by studying the effects of several reaction conditions, including heat, solvents, and concentration of oxidizing agent.

Methods

Scheme 1. [3,4]



Preliminary Results

Entry	1a solvent	1b equivalence (v/w)[a] , temperature	% yield[b]
1	Methanol	1, < 0 °C	40[c]
2	Methanol	1, rt	31
3	Methanol	1.5, rt	41
4	Methanol	1.5, heat	42
5	Ethanol	1, rt	20
6	Ethanol	1.5, rt	31

[a] commercial base bleach was assumed to be 3-6% (w/w).

[b] base on proton NMR.

[c] by Paul Erdman[3]

Table 1. Reagents and conditions for reaction of **5** to **6**.

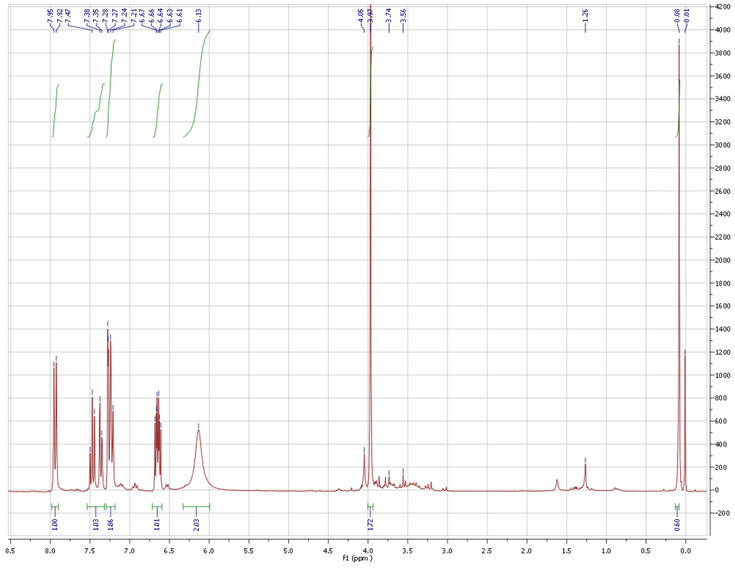


Figure 1. Proton NMR for mixture of **5** and **6**.

Discussion

- The replacement of ethanol as solvent did not improve the yield. Instead, it diminished it.
- Temperature difference s did not have much influence in product yield.
- There was a significant increase in yield of **6** through the increase in stoichiometric amount of sodium hypochlorite.
- This demonstrated that temperature has minute role in the reaction and the amount of sodium hypochlorite added was not enough to fully oxidize all intermediates of **5** to **6**.

Conclusion

- The use of ethanol as solvent did not accommodate the synthesis of **6** as well as methanol. However, ethanol is less toxic than methanol and hence still worth further research.
- Stoichiometric equal amount of sodium hypochlorite is needed for oxidization process of **5** to **6**.
- The synthesis of **5** to **6** was less thermodynamically regulated.

Future Research

- To continue the investigation of the equivalence of sodium hypochlorite (% mol) on the synthesis of **6**.
- To synthesize other azobenzene derivatives with a different fluoronitrobenzene isomer as a starting material, possibly with para-fluoro substitution instead of at the ortho position.
- If successful, the new derivative can be tested for its candidacy in making a molecular switch. This would indicate the difference is stereo and electronic effects of a fluorine substituent in a different position.

References

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(4) Gullickson G. C. M.S. Thesis, University of Minnesota, Minneapolis, MN, 2010, 27.

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