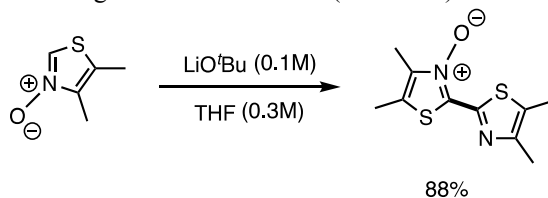


Dehydration Polymerization for Poly(hetero)arene Conjugated Polymers

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Interest in synthesis of organic conjugated molecules has grown over the years due to their potential uses in applications such as plastic light emitting diodes, photovoltaics and transistors. Discovering new synthetic routes allows us to synthesize new and unique conjugated molecules with unique set of properties that were previously not accessible. A dehydration type reaction was discovered by the Schipper group, in which thiazole *N*-oxide dimerizes in the presence of a base eliminating a molecule of water (Scheme 1).



Scheme 1: Dehydration reaction of 4,5-dimethylthiazole 3-oxide.

This dehydration reaction occurs in 5 minutes (0°C-RT), requiring minimal workup and is typically high yielding. The first focus of this research was to optimize reaction conditions as well as test the scope and limitations of the dehydration reaction. Various small conjugated molecules were synthesized with yields obtained ranging from 25%-98%. The reaction was able to tolerate various substituents such as electron donating and electron withdrawing groups.

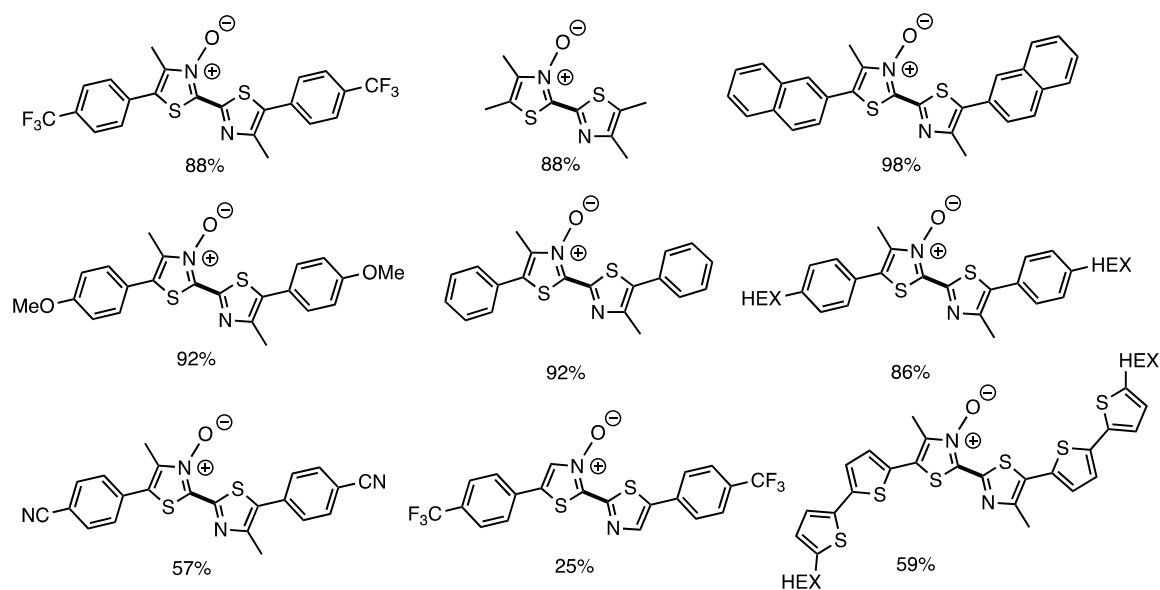
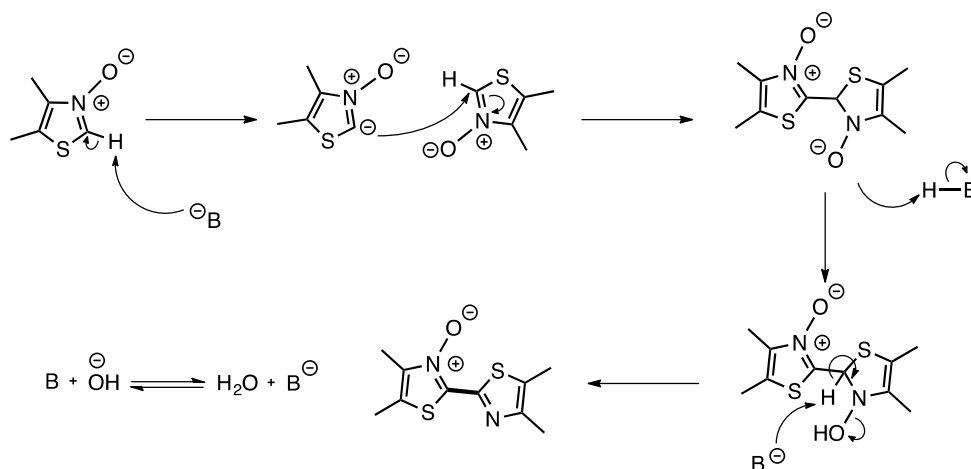


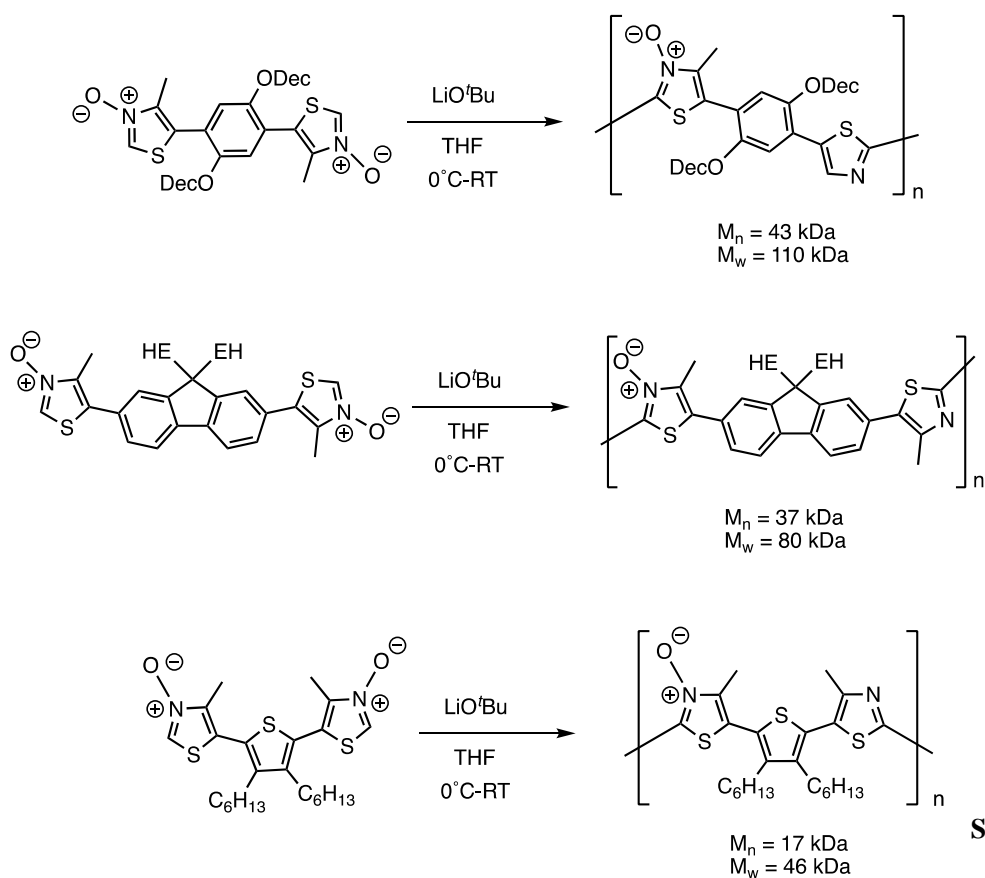
Figure 1: Dehydration products of various *N*-oxides.

Mechanistic studies have not yet been carried out on this reaction however, a proposed mechanism is shown in Scheme 2. The mechanism starts off with a base deprotonating the most acidic proton (2-position) of the *N*-oxide forming a carbanion. The carbanion then acts as nucleophile attacking the C2 position of another equivalent of *N*-oxide resulting in loss of aromaticity. Through an elimination reaction aromaticity is regained affording the thiazole dimer while eliminating a molecule of water.



Scheme 2: Proposed dehydration reaction mechanism.

The second focus of this research was to extend the scope of this reaction to synthesis of conjugated polymers. By incorporating thiazole molecules with various π -spacers, we were able to synthesize di-*N*-oxides allowing synthesis of conjugated polymers. The reaction is quick, as polymer can be seen as soon as the first couple drops of base were added. Respectable molecular weights were obtained for three different dehydration polymerization reaction.



reactions.

Scheme 3:
Dehydration
polymerization