

Enaminone Chemistry for Functionalized, Crosslinked, and Easily Assayed Polymers

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The reaction between amines and diones to make enaminones is a high-yielding, atom-economizing reaction that forms new covalent bonds with clear spectroscopic signatures. (1,2) The Anderson group has recently developed a particularly environmentally friendly medium in which this reaction can be performed. While the small-molecule chemistry of enaminones is well developed, the functionality has never been applied to polymers in a directed way. The high yield and functional group tolerance of the reaction allows for either pre- or post-polymerization modification of functional groups for the attachment of electronically active substituents (such as electron donors, electron acceptors, or alignable dipoles for dielectrics, ferroelectrics, and nonlinear optics) or biochemically relevant substituents, such as antibodies for chemical sensing. Most generally of all, the dione functional group, when attached to polymer chains, offer a new and simple way to crosslink polymers using polyamine additives, for processable and patternable dielectric and biocompatible films. This crosslinking would occur under environmentally benign conditions with water as sole byproduct. Finally, any post-polymerization modification, namely functional group attachment or crosslinking, can be monitored by observing increased ultraviolet absorbance at 300 nm, occurring between the higher energy peaks of simple benzene rings and lower energy peaks of extensively conjugated organics, as well as a relatively isolated infrared peak at 1685 cm^{-1} . Thus, degree of functional group attachment (as opposed to mixing) and degree of crosslinking can be directly measured.

An important synthesis goal for the project is preparation of reactive diones **1-5** (Figure 1) that can be attached to polymerizable monomers, or to polymers themselves. Anderson has extensive experience in dione and enaminone synthetic chemistry and will perform the syntheses of the hydroxy dione monomers, and provide conditions for their coupling to amines following incorporation into polymers.

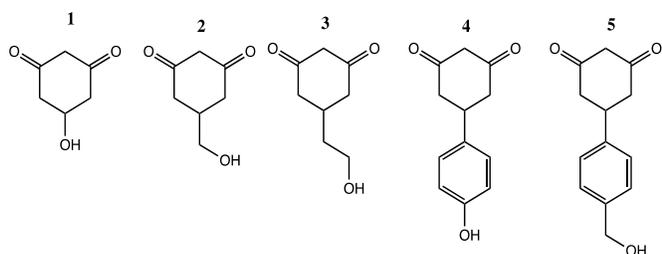


Figure 1: Targeted Hydroxy Diones

Hydroxy-substituted diones are attractive because they can be made into methacrylate esters by reaction with methacryloyl chloride or an activated COOH in a polymethacrylate; or attached to polystyrenes via the benzyl chloride group of readily available poly(chloromethylstyrene). Katz will perform the polymerizations and provide amine-bearing functional molecules and crosslinking agents for

coupling them into the polymers. He will explore optoelectronic and biosensing applications, on which he has extensive experience. The enamine coupling chemistry will be performed by Anderson on small molecules, including monomers if fully functionalized enaminones are to be polymerized, and by Katz when enaminone formation is to be performed post-polymerization.

Initially, we will develop efficient synthetic routes to 1,3-cyclohexadione alcohol compounds **1-5**. This particular work will be carried out in the Anderson Research Group at Bowie State University which possess an exceptional set of analytical instrumentation and provides for a stimulating scientific environment.

The following routes to diones **1-3** have been proposed (Figure 1), using hydrogen at high pressure aromatic compounds **4-6** in the presence of Pt, Rd or Ni catalysts, will be reduced to give diones **1-3**,

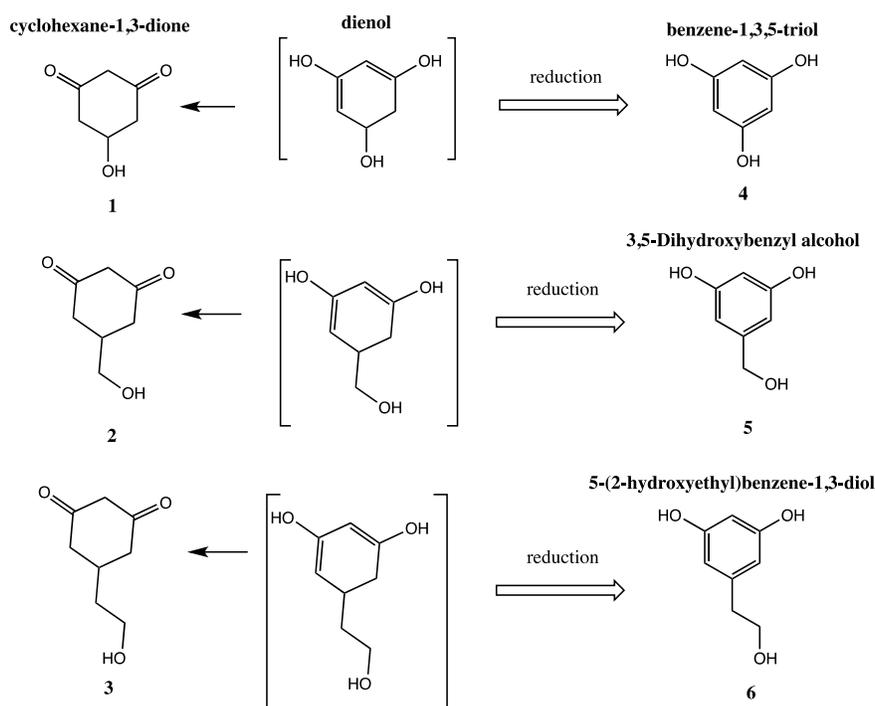


Figure 2: Proposed routes for synthesis of diones 1, 2 and 3

respectively, resulting from the fast ketonization of intermediate dienols. Diones **1** and **2** will be synthesized from commercially available aryl alcohols **5** and **6** respectively employing known methods from the literature. (3-5) We will develop novel methodology to synthesize Compound **6**, a novel compound, (Scheme 1) starting from a styrene intermediate **7**(6-9). Catalytic hydrogenation of **6** will afford dione **3**, a novel compound. Novel methodology will be developed to synthesize Compound **3**, a novel compound, via a three-step reaction sequence starting from a styrene intermediate **7**.

The following routes to **4** and **5**, have been proposed (Figure 3) via cyclization of Compounds **9** and **10** respectively with **DEM** under basic conditions. Compound **4** will be synthesized by known methodology in good yield in which the key reaction (Scheme 3) involves cyclization reaction

Compound **9** and **diethyl malonate (DEM)** with sodium ethoxide; followed by deprotection to give Compound **4**. (10) Rather than use highly reactive sodium metal needed for sodium ethoxide, we propose using sodium hydride or K_2CO_3 in the presence of a cyclic polyether or a tetraalkylammonium salt such as TMac, Tricaprylyl Methyl Ammonium Chloride to affect the cyclization of Compound **9** and Compound **10**. The targeted aryl cyclohexanedione **5** is a novel compound and requires new methodology. We propose a five-step reaction sequence to synthesize the novel Compound **10**; followed by cyclization with **DCM** will afford Compound **5**.

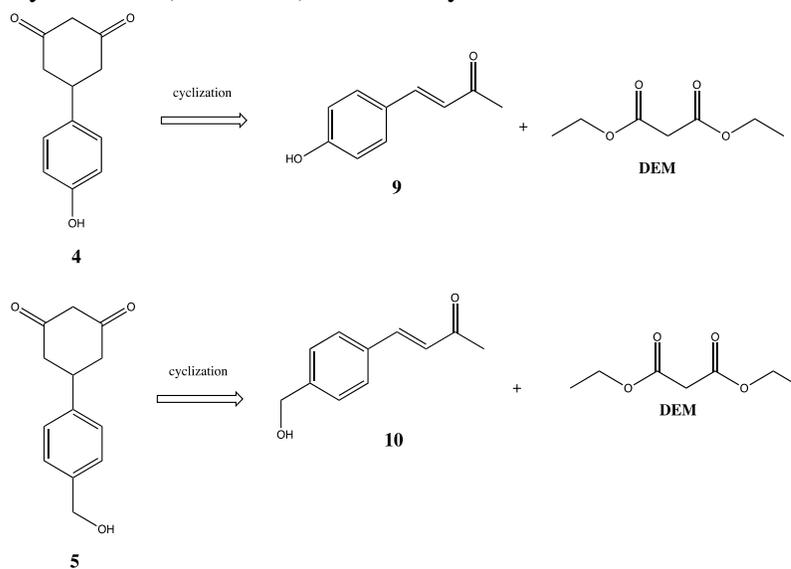


Figure 3: Proposed Synthesis of Compounds 4 and 5

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