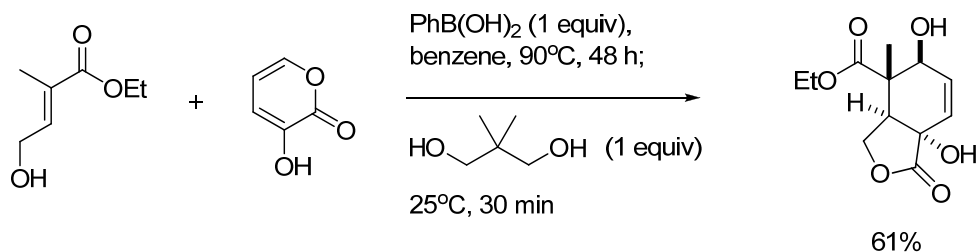


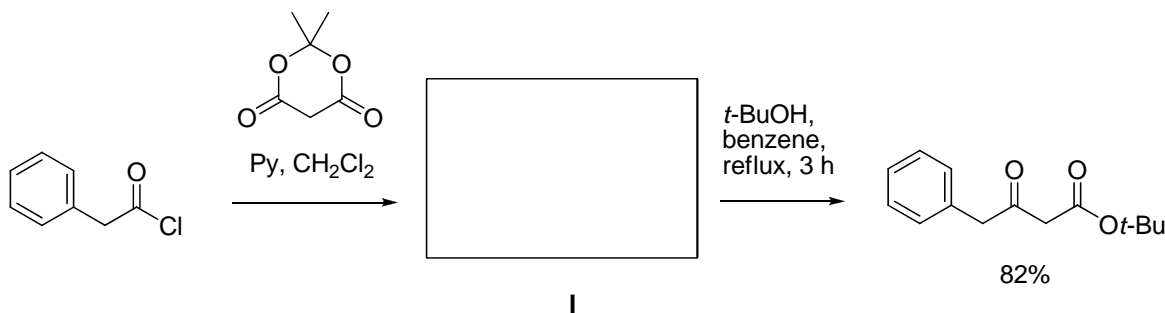
VanNieuwenhze Group Problem Set

December 15, 2009

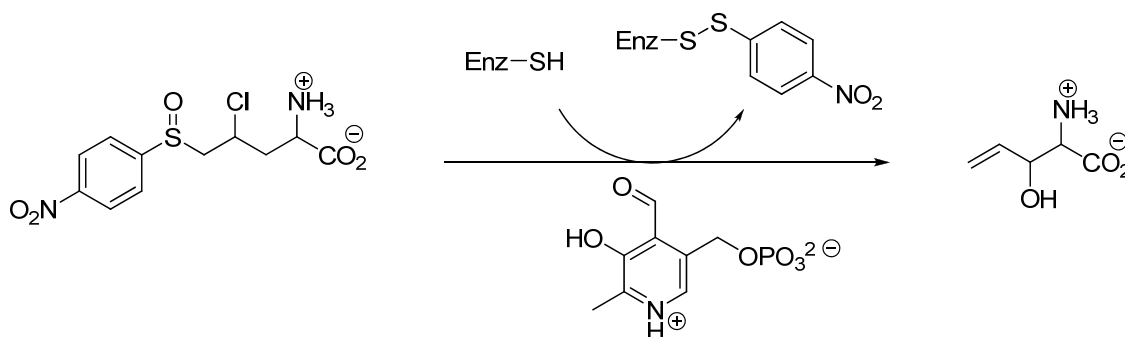
1. Propose a mechanism for the following transformation. Include a realistically drawn transition structure that accounts for the regio- and stereochemical outcome of the key C-C bond-forming step.



2. Depicted below is a procedure for elaborating acyl chlorides into β -ketoesters using Meldrum's acid. (A) Identify intermediate **I**. Does **I** exist predominantly in the keto or enol form? Give at least two reasons for your answer. (B) Provide a mechanism for the overall reaction.



3. The sulfoxide shown below is an irreversible inhibitor of cystathionine γ -synthetase and methionine γ -lyase. Propose a mechanism for the inactivation that involves blocking of a Cys side chain to give the products represented below via pyridoxal phosphate (PLP) catalysis.



4. Suggest a mechanism for the following transformation. (Hints: Work both forward and backward and don't be afraid of zwitterions.)

