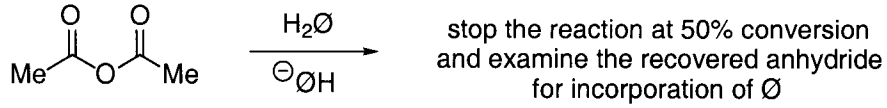
Massachusetts Institute of Technology

5.13: Organic Chemistry II *Spring 2003*

Problem Set 7: Carboxylic Acids and Derivatives; Enols and Enolates
Due: Wednesday, April 16, by noon

(1) Consider the experiment outlined below:

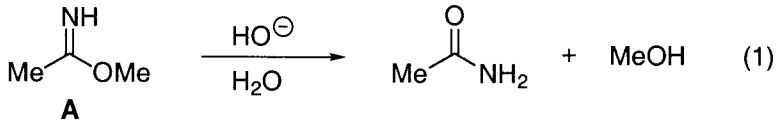


Ø = isotopically labeled oxygen

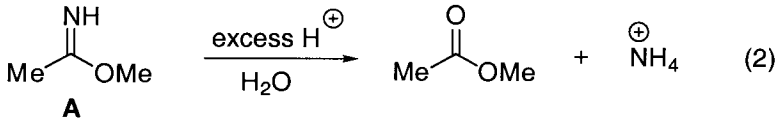
In analogy with the discussion in class regarding the labeling studies of acid chloride, amides, etc., carefully explain what level ("high" or "low") of Ø incorporation you expect to observe in the recovered anhydride. Your explanation should include the mechanism for this hydrolysis reaction.

(2) Methyl acetimidate (**A**) is hydrolyzed in aqueous sodium hydroxide to (initially) give mainly acetamide and methanol (eq 1). In aqueous acid, **A** hydrolyzes to (initially) give primarily methyl acetate and the ammonium ion (eq 2).

(a) Write a detailed mechanism for the illustrated process. Please show all arrow pushing.

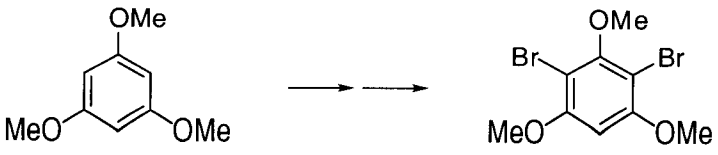


(b) Write a detailed mechanism for the illustrated process. Please show all arrow pushing.



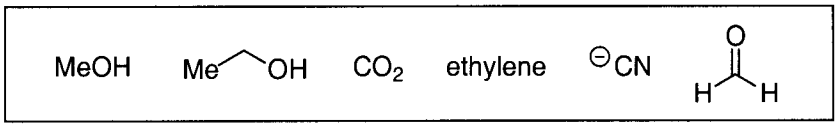
(c) Briefly explain why the two reactions provide different products.

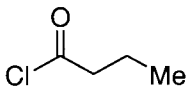
(3) Provide a synthesis that will **selectively** convert A to B. Show all of the key intermediates and furnish all of the important reagents.

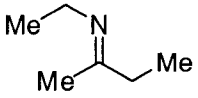


(4) Synthesize the indicated compounds from the allowed starting materials shown below. All of the carbons of the target compounds should be derived from the allowed starting materials.

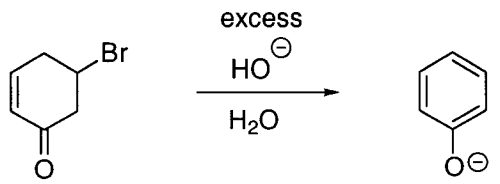
Allowed starting materials



(a) 

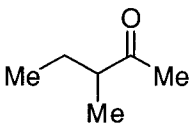
(b) 

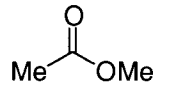
(5) Provide the best mechanism. Please show all arrow pushing.



(6) Synthesize the illustrated ketone. ALL carbons of the ketone must be derived from molecules of methyl acetate, which has three carbons. You may not use lithium diisopropylamide in your synthesis.

Target:





methyl acetate

(7) Provide the best mechanism for the illustrated transformation. Please show all arrow pushing.