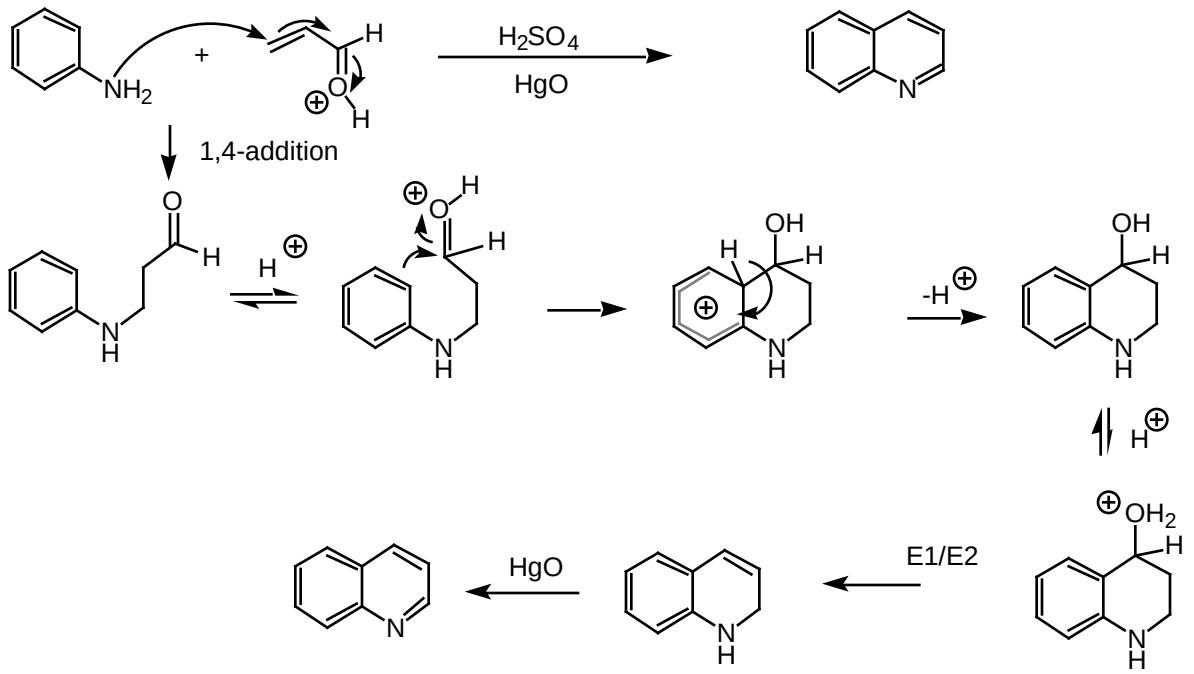
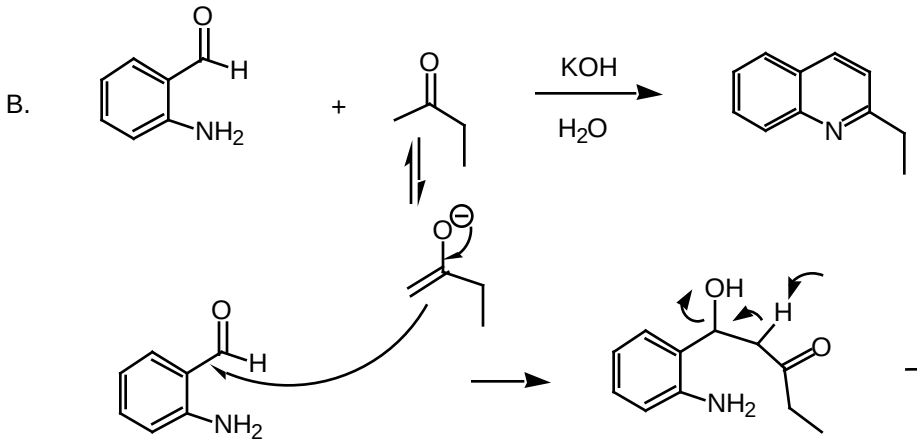
Chemistry 304B **KEY TO** Problem Set 9 [practice]

I. Write the best mechanism to rationalize the following "classic" heterocycle synthesis procedures. Each involves a series of the basic mechanisms we have been studying. The hard part is to find the "best" sequence of steps to rationalize the product. Best means shortest and proceeding through "good" intermediates.

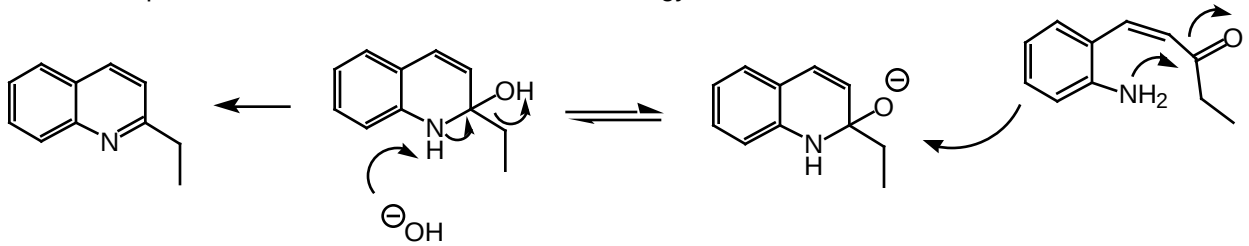
A.



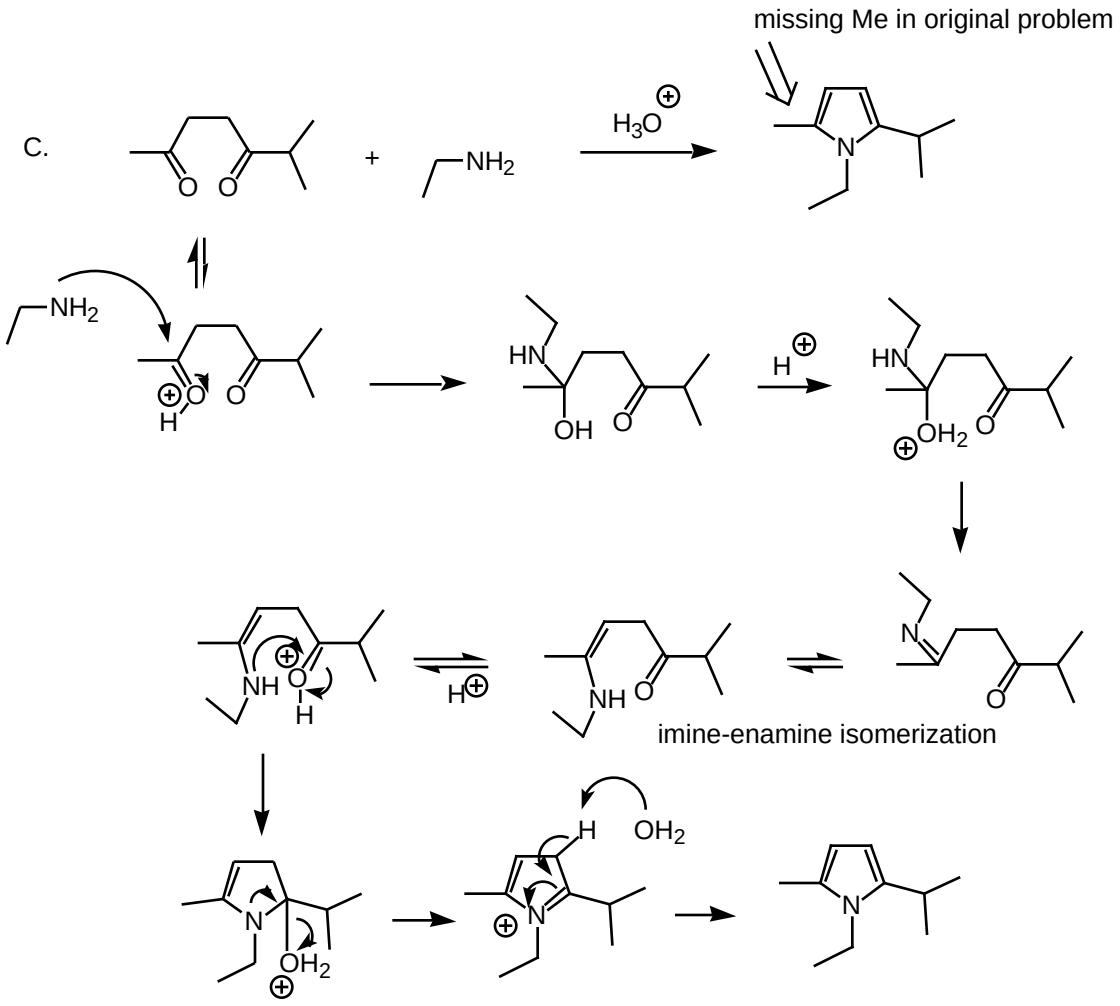
B.



In this step, the less substituted enolate reacts selectively. Is this reasonable? Perhaps (below), but the key point is that under equilibrium, which this surely is, all possible enolates can be sampled and the one leading to the best TS is responsible for the next step. How do you know which one is reponsible for the next step? Look at the product! Without the product structure or some other close analogy, it would be hard to tell.



There is an alternate mechanism. An almost identical problem is in Jones, 25.27a.
Check the Study Guide, p 688



There are alternate steps in some cases. If you have some ideas that are different, that does not mean they are wrong. Ask me or Anatoliy. There are many steps if one writes every proton transfer, etc. When should you do that? Whenever it is important: unless I specify otherwise, on the exams and/or whenever you are having trouble with a mechanism.