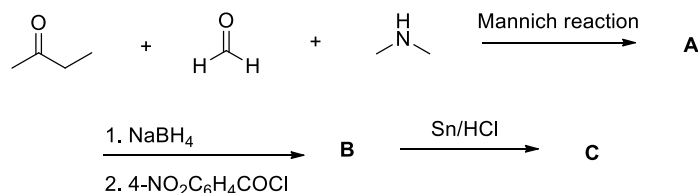


Solutions to problems - Set 10: Carbonyl compounds (Part IV)

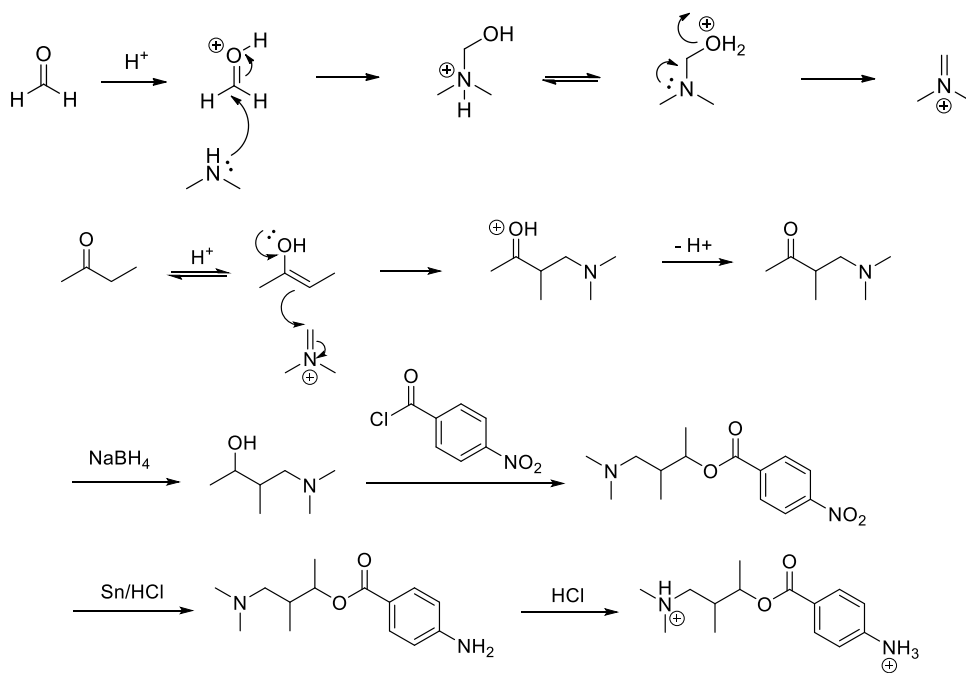
Problem 1

Find the missing compounds to complete the following transformations and give the mechanisms:



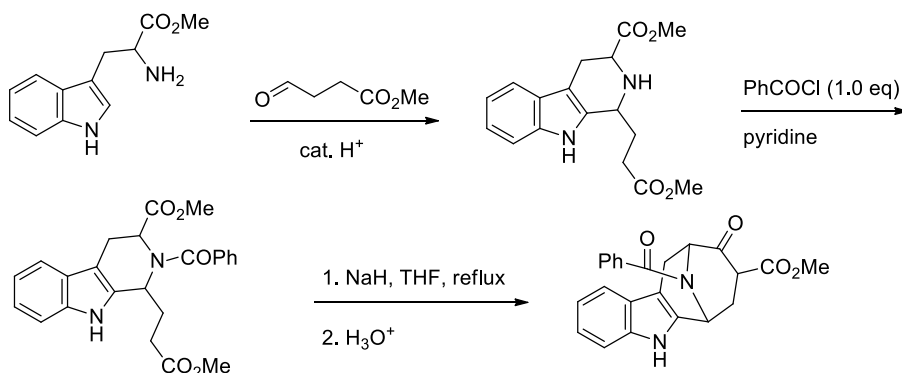
Note: NO_2 groups can be reduced to NH_2 in acidic conditions under the presence of metals such as Zn, Fe, Sn or SnCl_2 , FeCl_2 ...

Solution

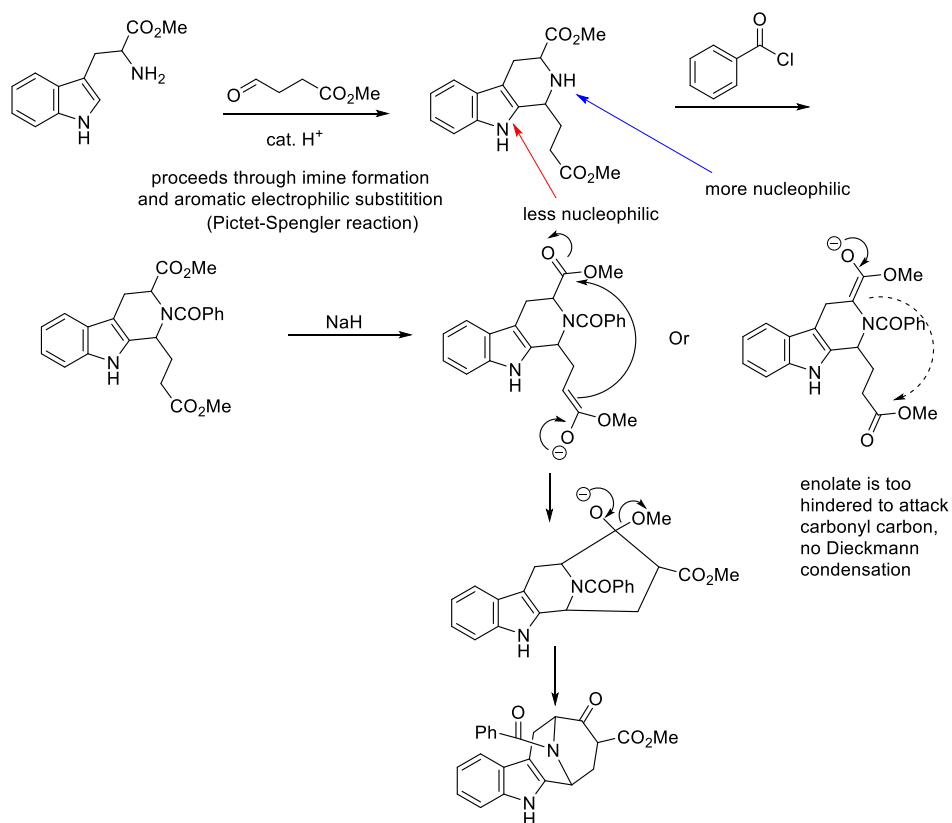


Problem 2

Suggest the mechanisms and try to justify the selectivity issues.

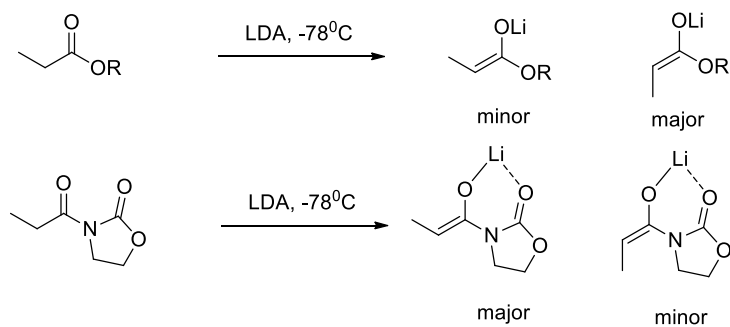


Solution

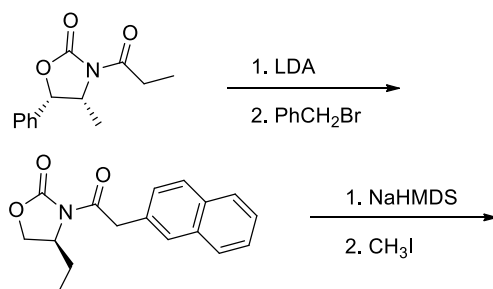


Problem 3

Explain these observations.



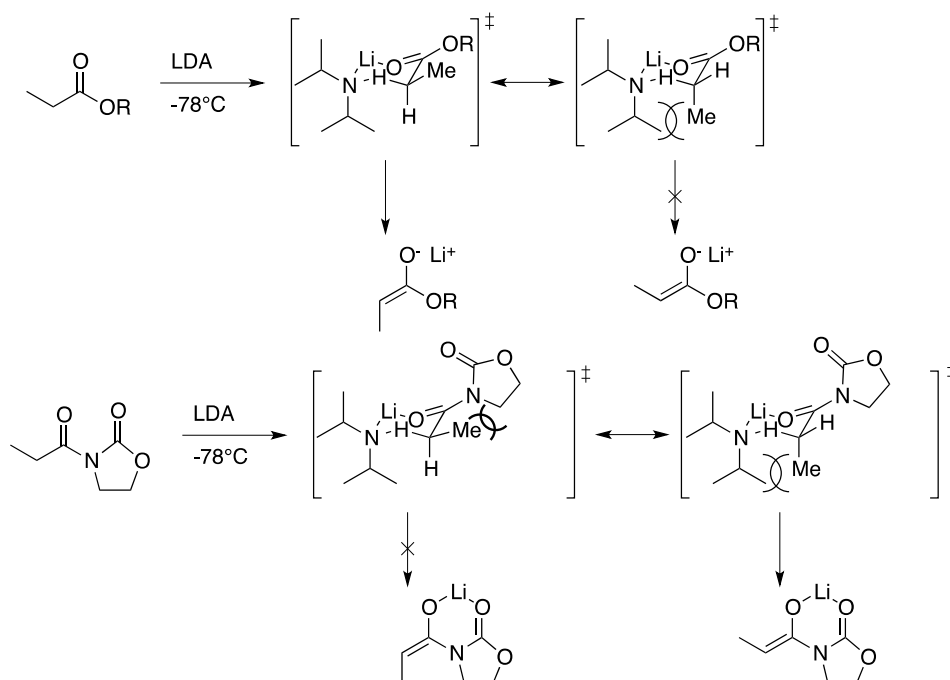
Apply these observations to find the structure of the products (with the absolute configurations!) of following reactions:



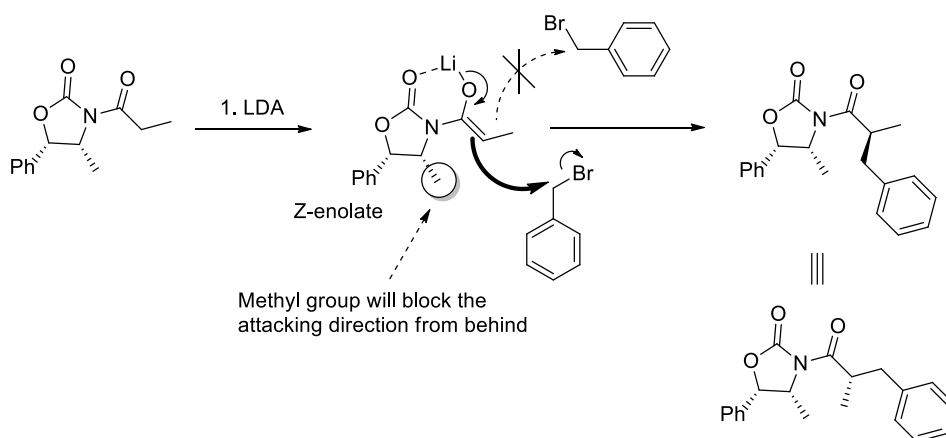
Solution

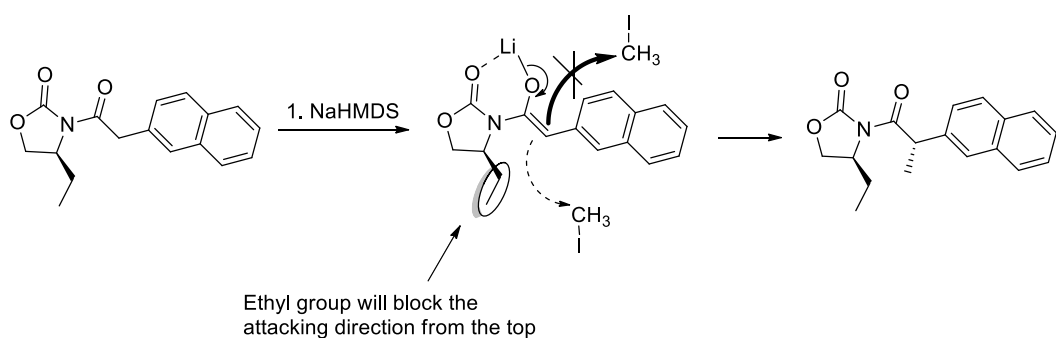
In the ester case, the steric hindrance between the alkyl chain and the LDA is the highest energy difference between the two transition states. The lowest in energy is the one giving the E enolate.

In the case of a carboxylic amide, there is another steric hindrance in the other side of the molecule, between the alkyl chain and the five-membered ring. This hindrance is stronger and disfavor the E enolate. You will obtain selectively the Z enolate.



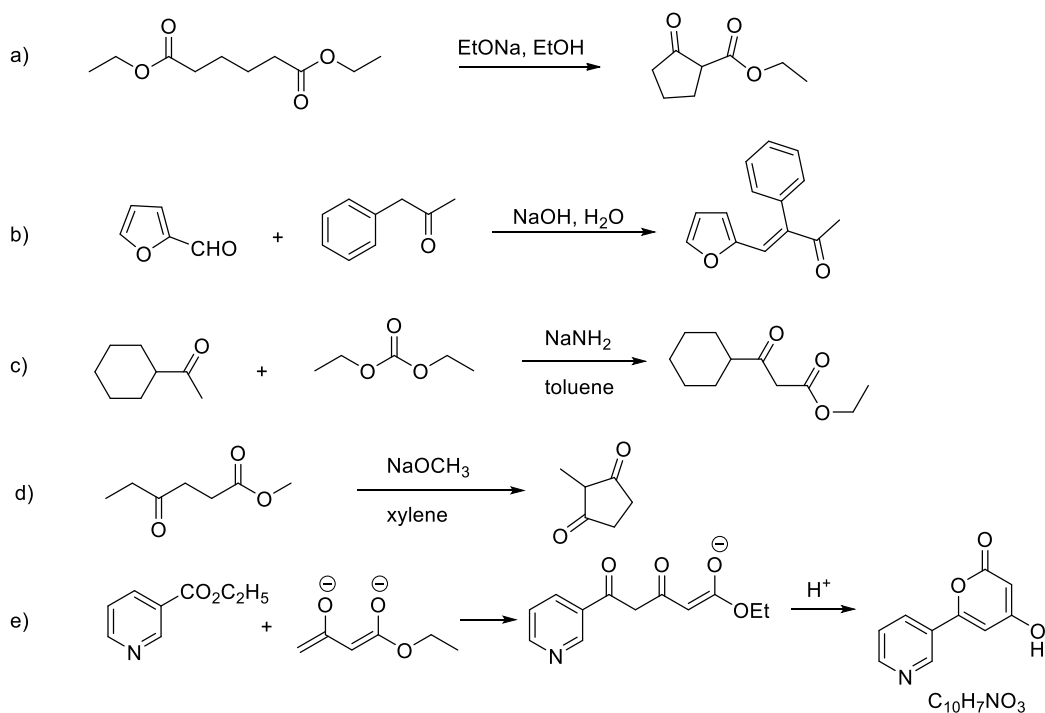
Application



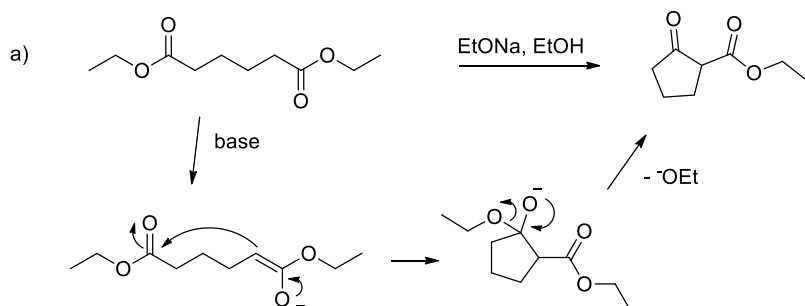


Problem 4

Predict the product formed in each of the following reactions.



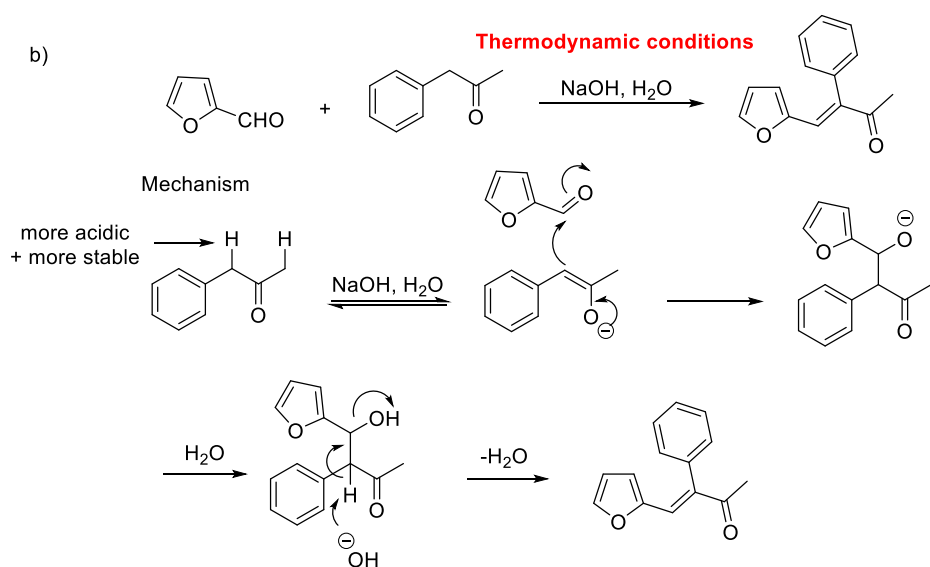
Solution



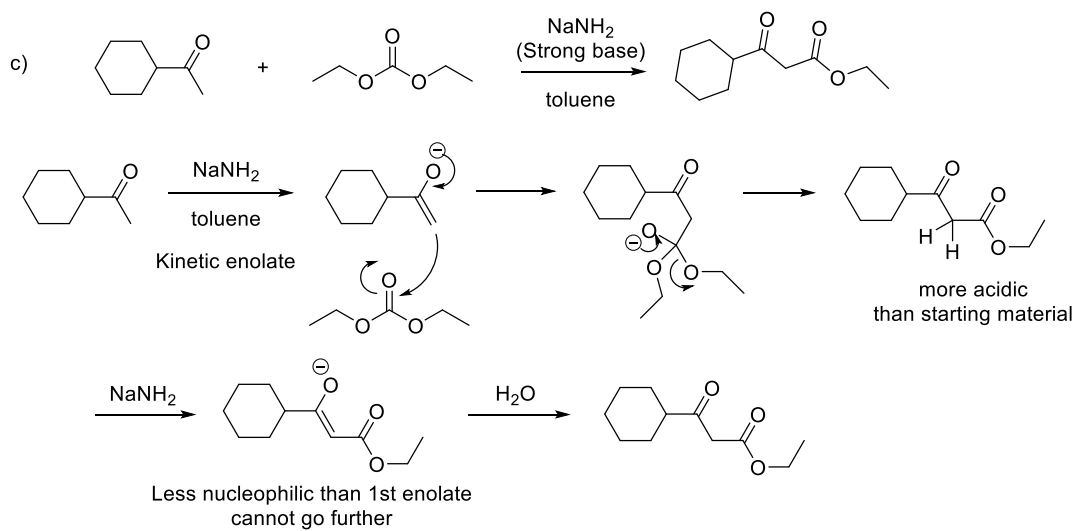
b)

Thermodynamic conditions

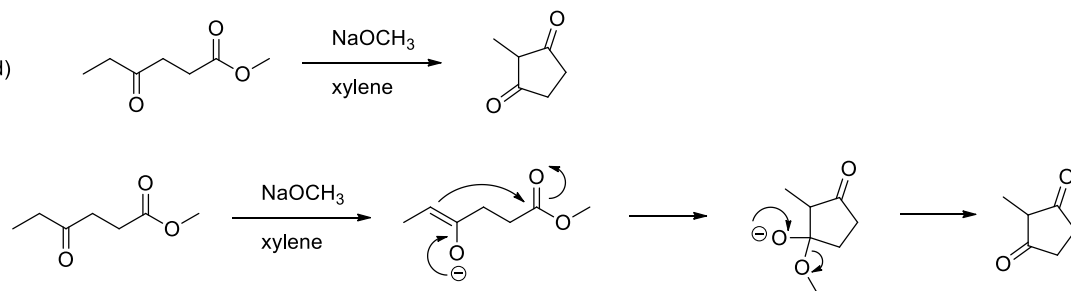
Mechanism

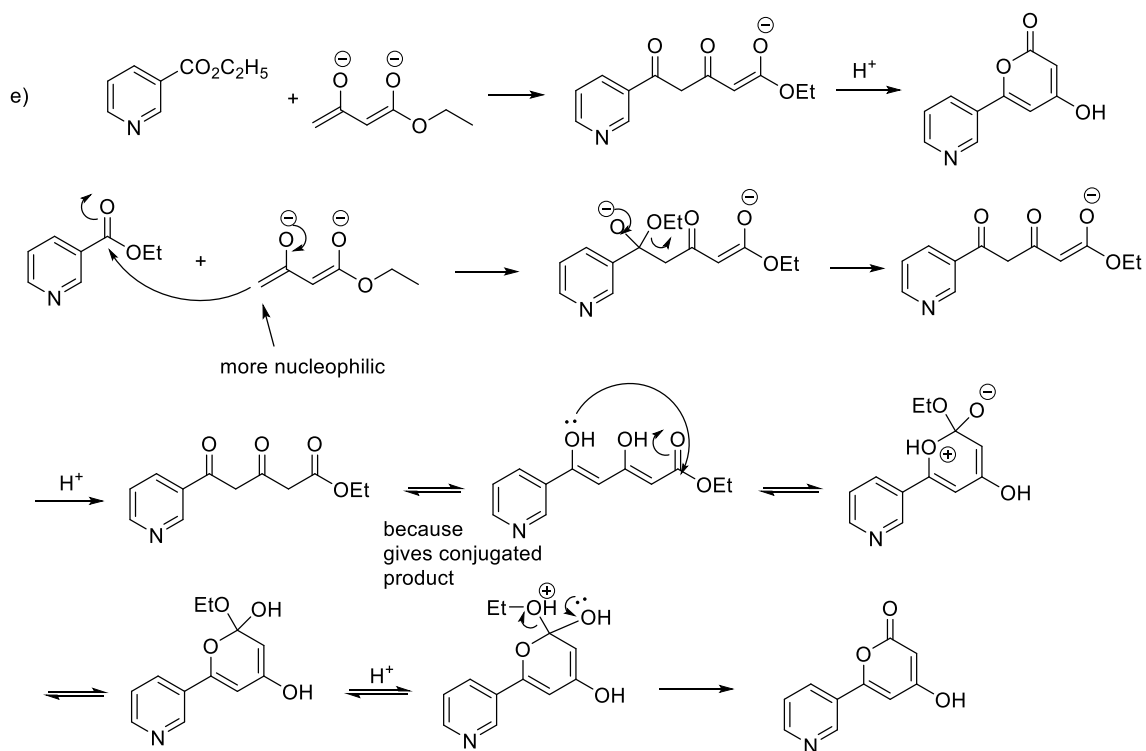
more acidic
+ more stable

c)



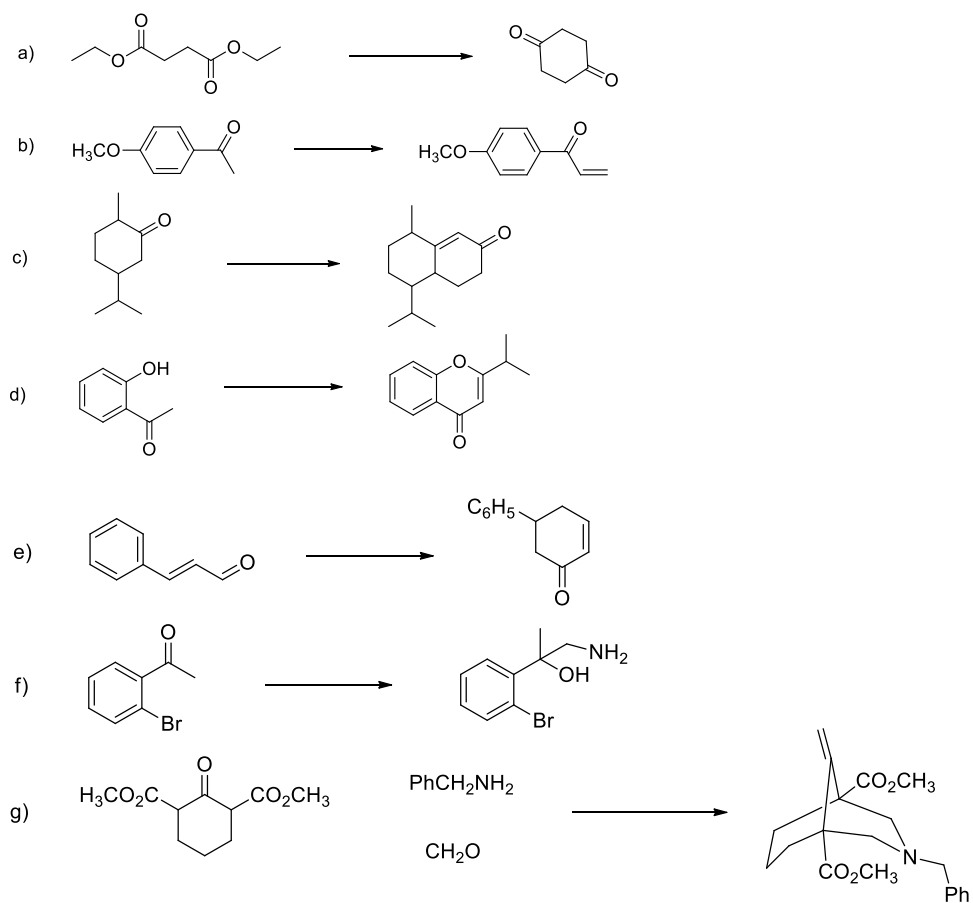
d)



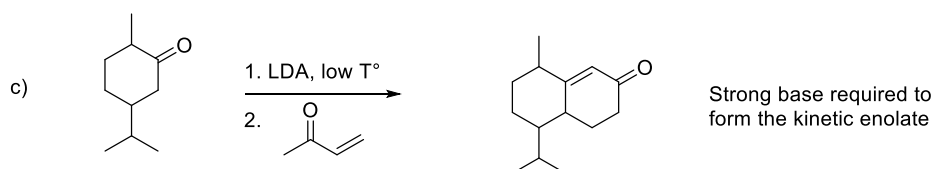
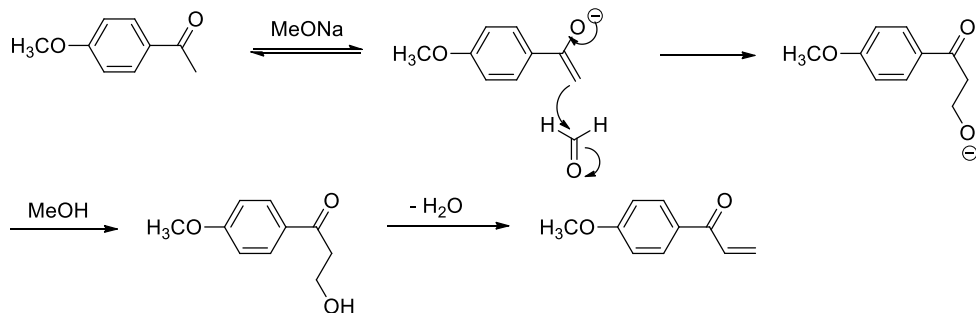
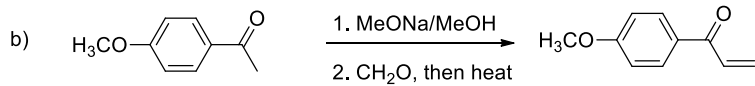
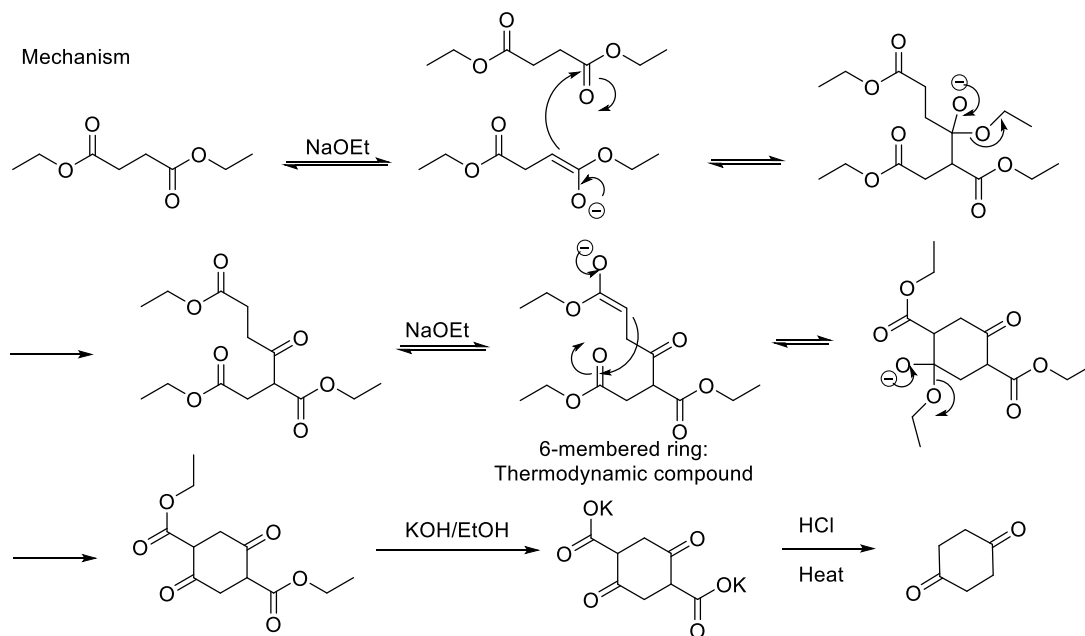
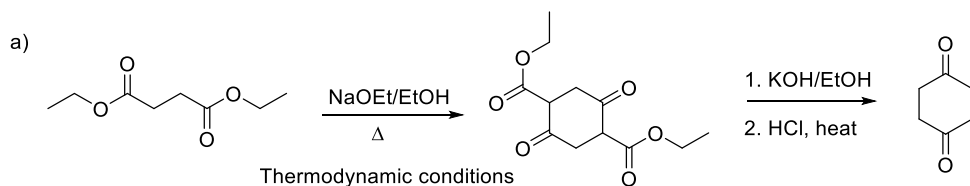


Problem 5

Indicate reaction conditions or a series of reactions that could form the product.



Solution



Mechanism: Robison's annulation

