

CHEM 3332 Honors
Homework for Carboxylic Acids

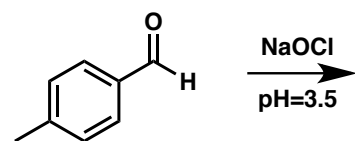
1. Draw a structure for the following:

- A. acetic acid
- B. benzoic acid
- C. sodium butyrate

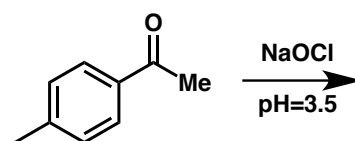
- D. potassium 3-methylpentanoate
- E. 4-cyclohexenyl carboxylic acid
- F. 1,4-butanedioic acid

2. Predict the major product (or products) for these reactions. Don't forget to show the stereochemistry in the products if the reaction is stereoselective.

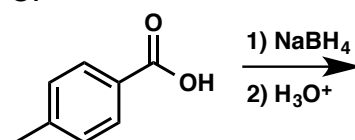
A.



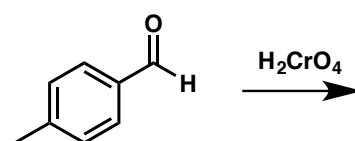
B.



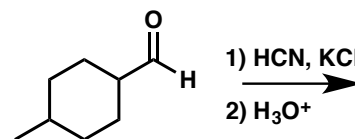
C.



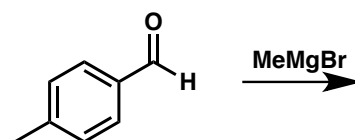
D.



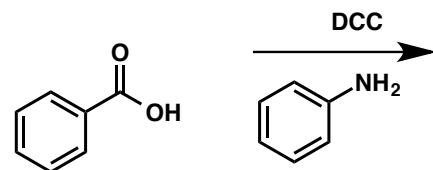
E.



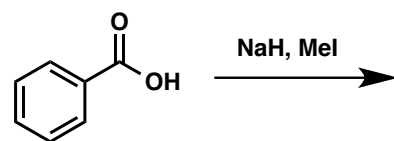
F.

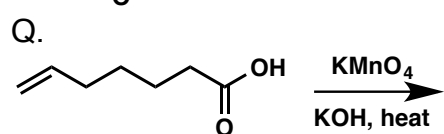
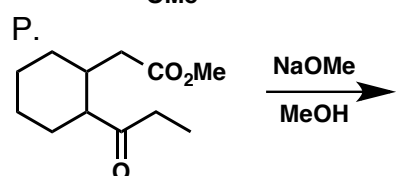
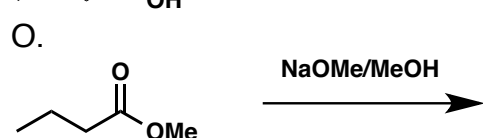
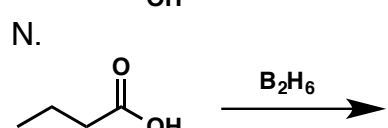
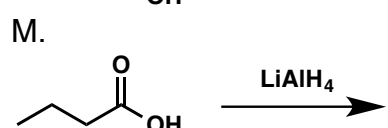
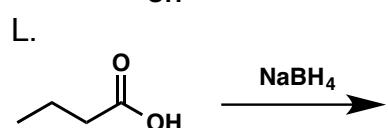
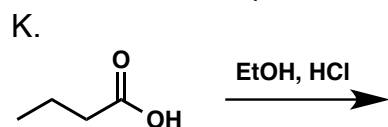
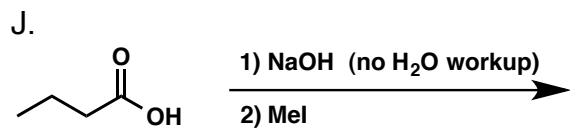
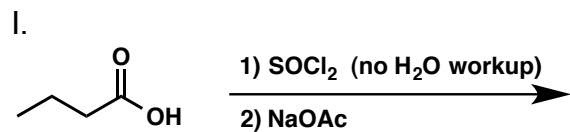


G.

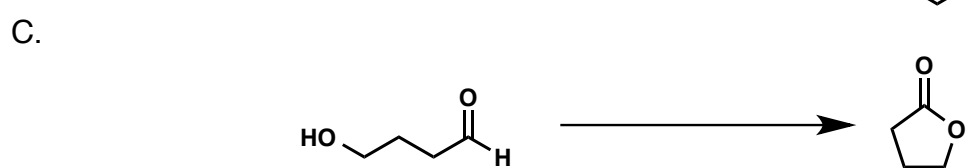
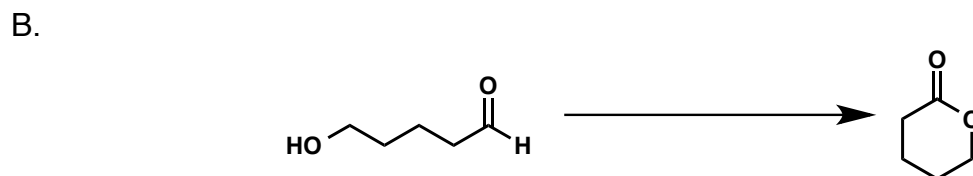
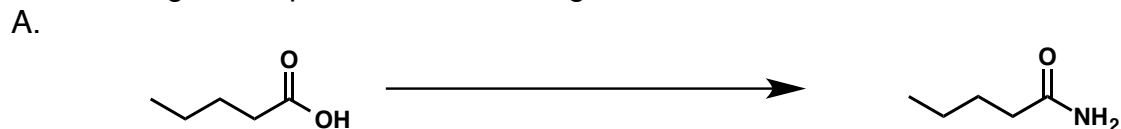


H.



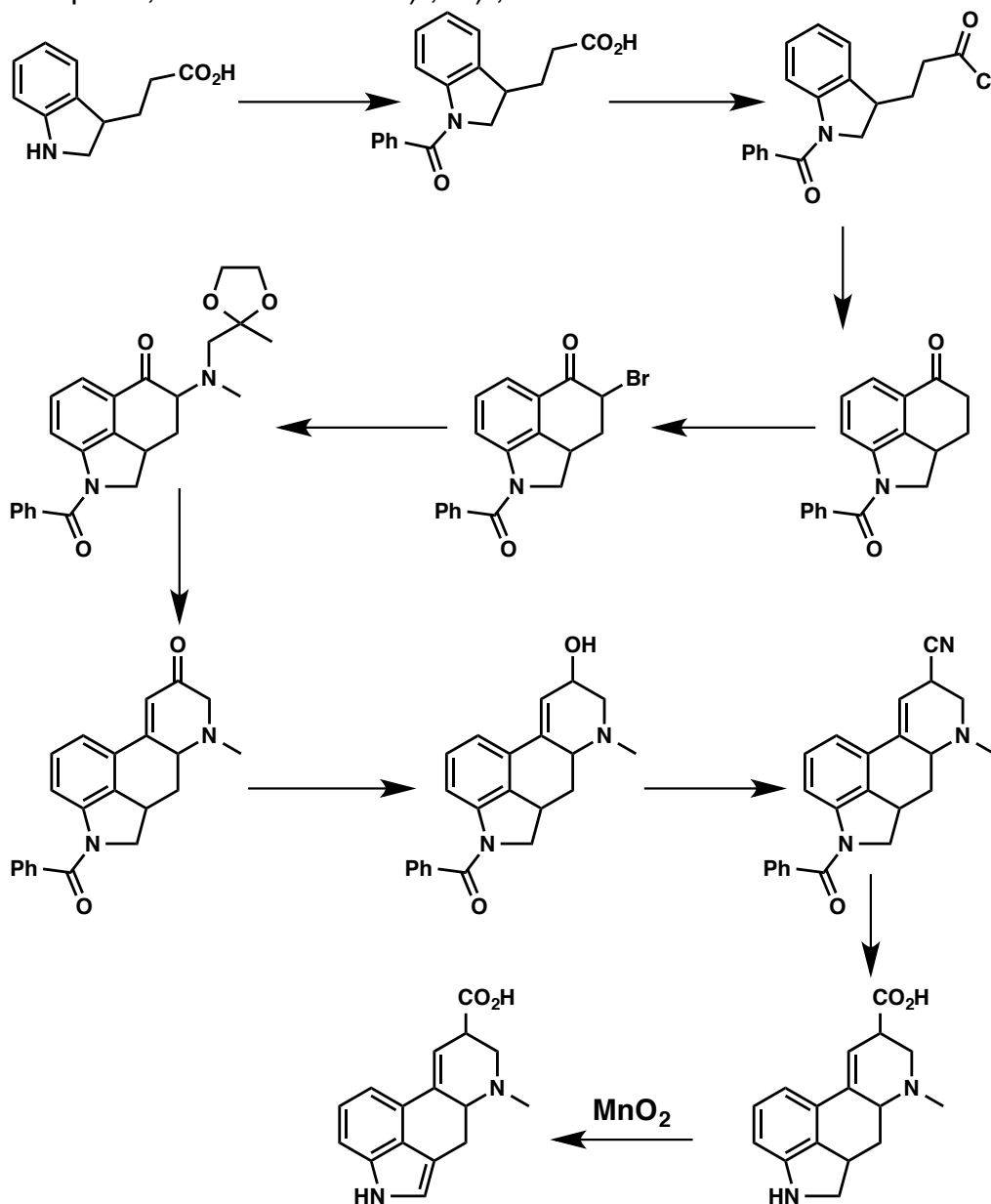


3. Give reagents to perform the following transformations.



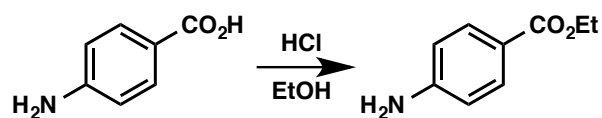
I. "The striking physiological properties of ergot early directed attention to this remarkable product of the growth of the fungus *Claviceps purpurea* on rye grain. Pre-Christian allusions to its effects have been recorded, and it was identified in 1676 as the causative agent of the dreaded medieval gangrenous scourge, St. Anthony's Fire. The therapeutic powers of ergot were likewise recognized during the middle ages. Its capacity to induce uterine contractions was recorded as early as 1582, and crude preparations were introduced into orthodox medicine early in the nineteenth century. However, its present important position in medical practice was made possible only by the extensive researches of the past forty years on the isolation and characterization of the pure active principles. These elegant investigations, in which Arthur Stoll has played a dominant role, have led to the isolation of no less than six related bases all of which have been shown to be amides of the same key substance, lysergic acid."

This is the first paragraph of a 1956 paper by R. B. Woodward, one of the most accomplished and influential synthetic organic chemists ever. In this paper, he described the synthesis of lysergic acid – a feat that you could largely reproduce with your current chemical knowledge. Give reagents for each step in the sequence below without reagents already over the arrow (one of the steps is given already). If multiple steps are required, label them with "1)", "2)", etc.

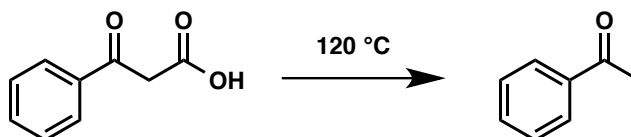


4. Write a full mechanism for the following:

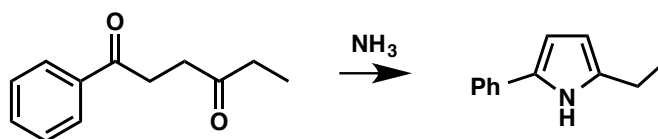
A.



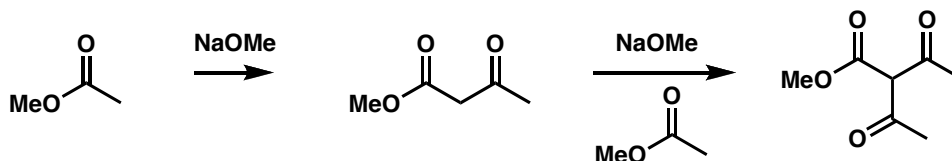
B.



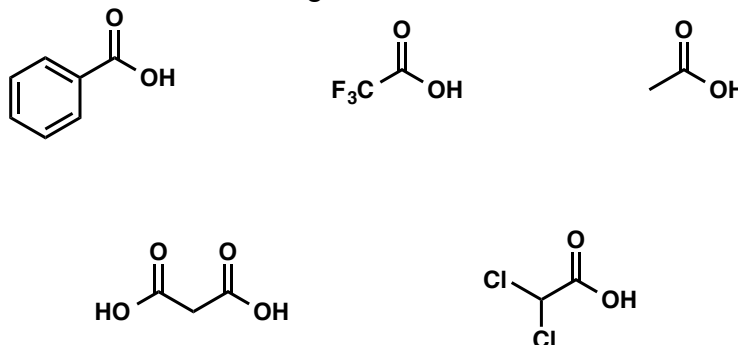
C.



5. In the Claisen condensation, two equivalents of the ester below on the right are converted to the keto-ester in the middle in the presence of base. In theory, this more acidic keto-ester could enolize and react with another equivalent of the methyl acetate to produce the diketo-ester on the right. Why is this product not observed when a Claisen condensation is actually run? In a related matter, how many equivalents of base are needed for complete conversion in a Claisen condensation? (20 points)

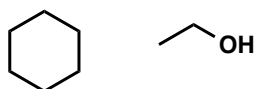


6. Order the acids below from the strongest to the weakest.

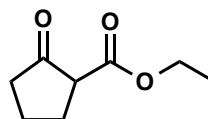


7. Use only the starting materials shown to produce the final product. No additional carbon units are needed.

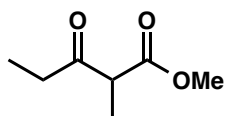
Starting Materials



Product

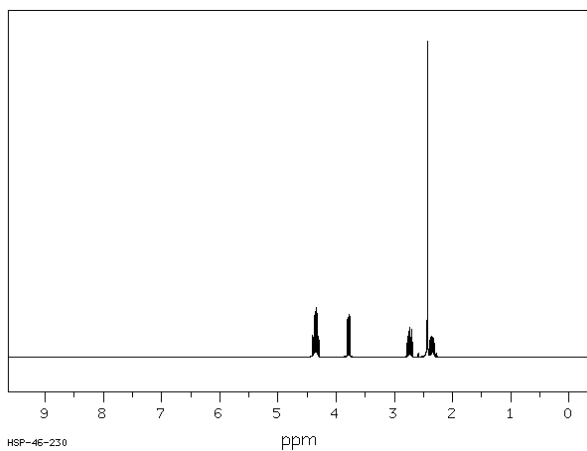


8. Make the following from starting materials and reagents that add 4 carbons or less:



9. Provide the structure for the following:

A. $C_6H_8O_3$



	shift in ppm	integration	multiplicity
A	4.35	2	t
B	3.8	1	m
C	2.5	2	dt
D	2.4	3	s

