

Chem 0320
Dennis P. Curran
April 6, 2010
Exam 3

Name: _____

Signature: _____

Answer all questions on this exam. If you need more space than that provided, use the back of any page.

1. _____ (10 points) Names and Structures

2. _____ (30 points) Short Answers

3. _____ (30 points) Reactions

4. _____ (20 points) Mechanisms

5. _____ (10 points) Multi-step Syntheses

TOTAL _____ (100 points)

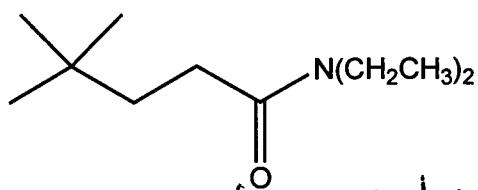
The test has **9** pages (including this cover page) and **5** questions
The exam ends at 12:15 pm sharp.

Good Luck !!!

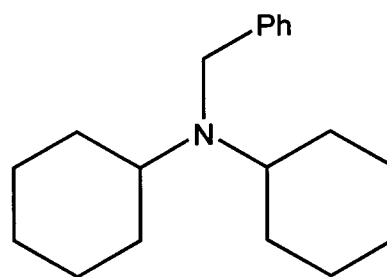
SUGGESTED
ANSWERS

1) Names (10 points)

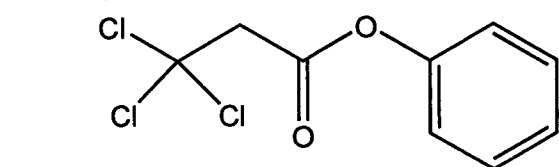
a) Provide acceptable names for the following compounds (don't forget stereochemical descriptors, *R/S*, *E/Z*, *cis/trans*, if needed). (6 points)



N,N-diethyl-4,4-dimethyl
pentanamide



N-benzyl-*N*-cyclohexyl
cyclohexanamine
- or -



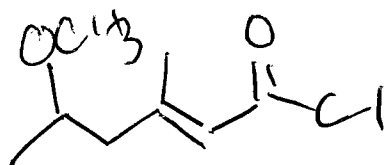
phenyl 3,3,3-trichloropropanoate benzyl dicyclohexyl
amine

b) Draw clear structures of the following compounds. (4 points)

butanoic anhydride



(*E*)-5-methoxy-3-methylhex-2-enoic acid chloride

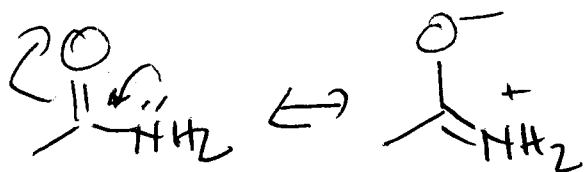


2) Short Answer Questions

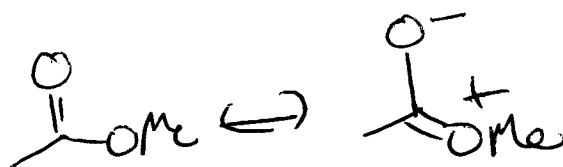
Briefly but clearly answer the following questions (5 x 6 = 30 points).

a) **Amides** and **esters** are both stabilized by resonance. Write resonance forms that show this stabilization for **both** amides and esters. State which functional group is more stabilized by resonance and briefly explain why.

AMIDE resonance



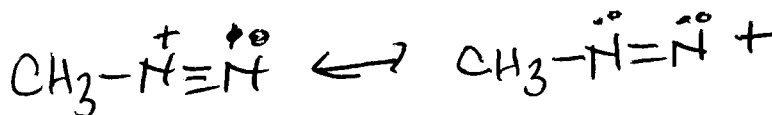
ESTER resonance



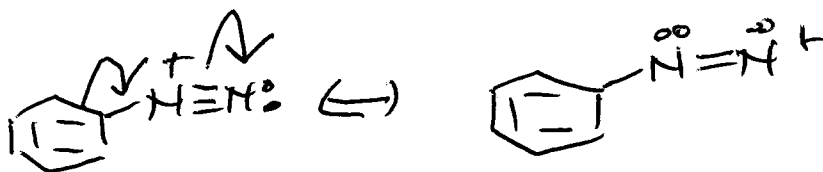
Amide is more stabilized; N is a better donor than O

b) Write resonance forms of the following two diazonium ions and briefly explain why the arene diazonium ion is more stable.

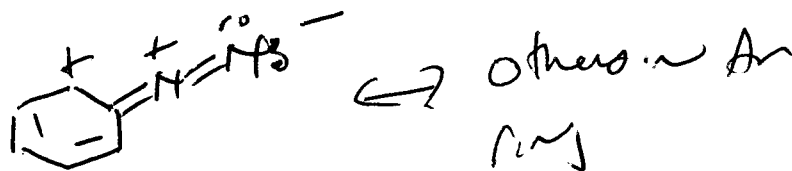
$\text{CH}_3\text{-N}_2^+$
very unstable



$\text{C}_6\text{H}_5\text{-N}_2^+$
stable for days at 0°C

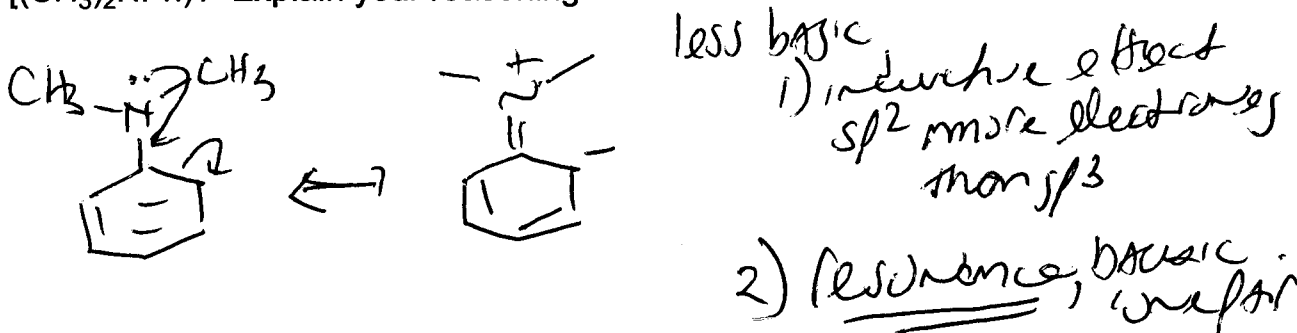


resonance in Ar

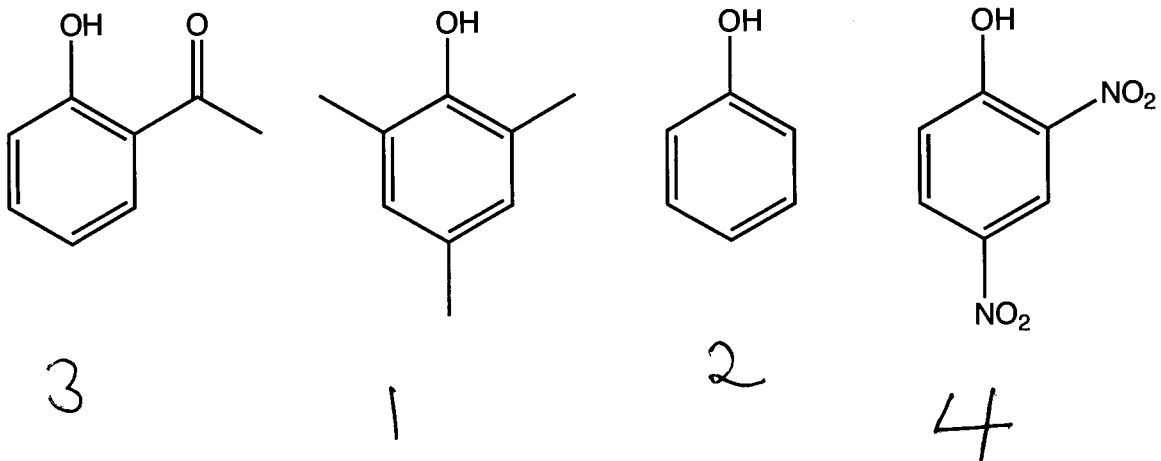


ring 1) delocalizes into Ar ring
2) strengthens C-N bond to Ar ring

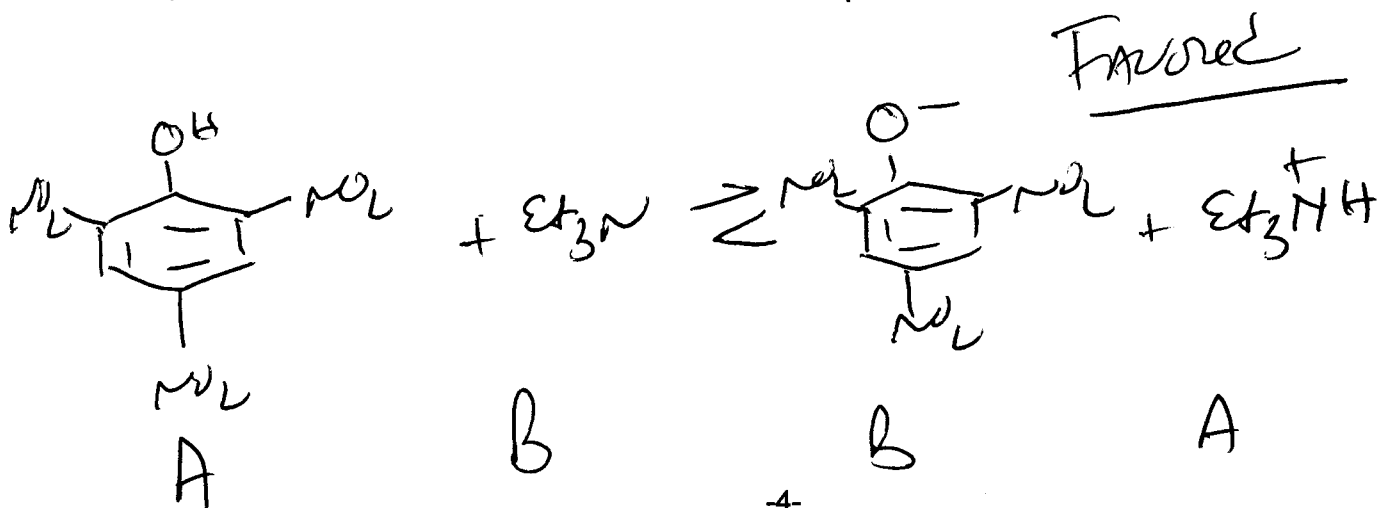
c) Which is the stronger base, trimethylamine $[(CH_3)_3N]$ or *N,N*-dimethylaniline $[(CH_3)_2NPh]$? Explain your reasoning.



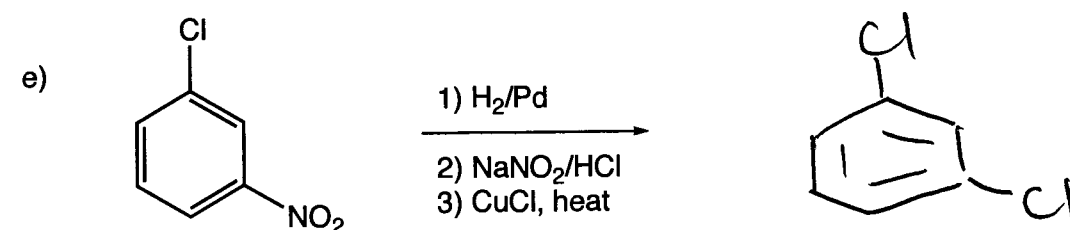
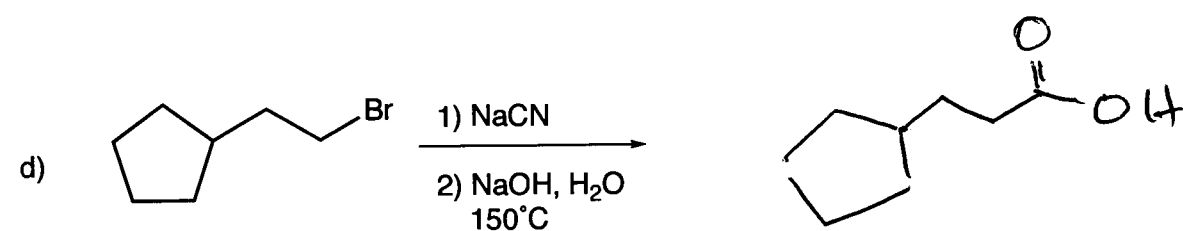
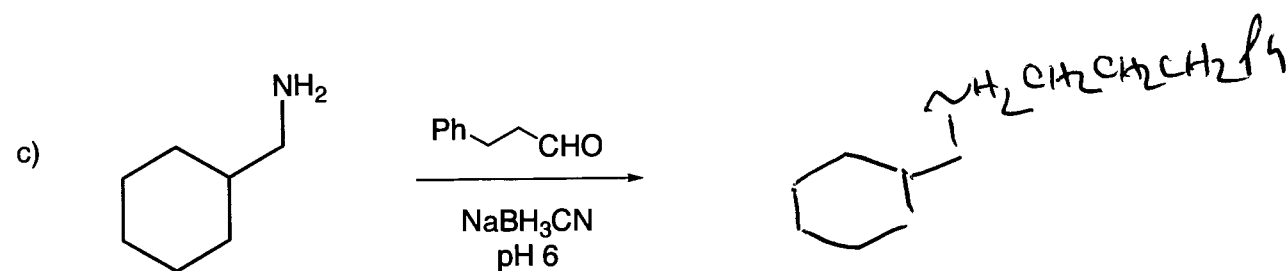
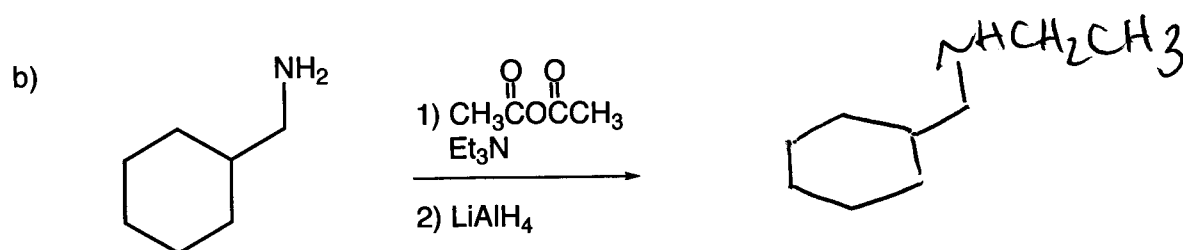
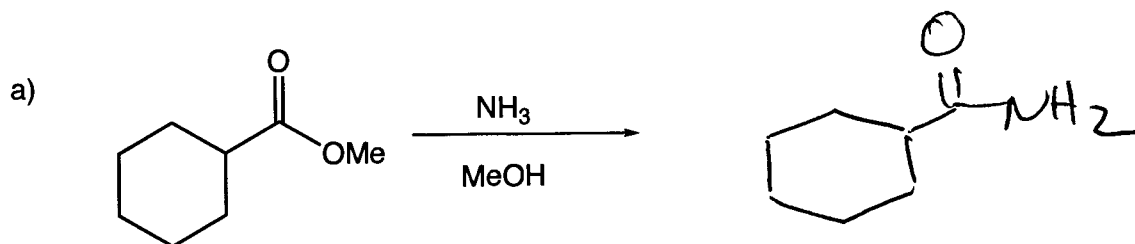
d) Place the following phenols in order of increasing acidity (that is, most acidic last).



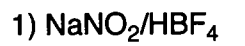
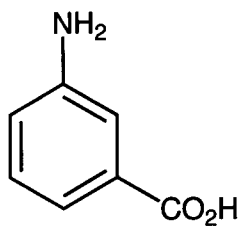
e) Write the equation for the acid/base reaction between picric acid (2,4,6-trinitrophenol) and triethylamine. Label the reactants and products as either acids or bases. Indicate which side is favored at equilibrium.



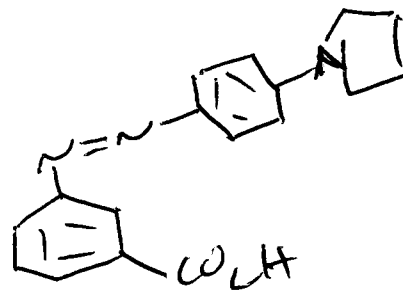
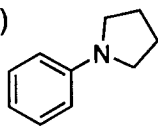
3) Reactions. Show the major product or products of the following reactions. Be sure to indicate stereochemistry, if relevant. (10 x 3 = 30 points) NOTE: "1), 2)" indicates two separate reaction steps with workup in between.



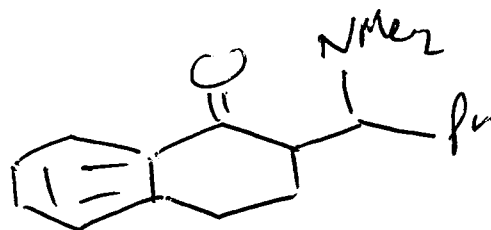
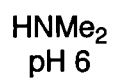
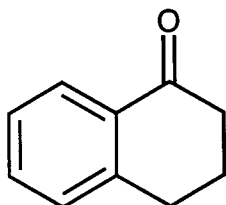
f)



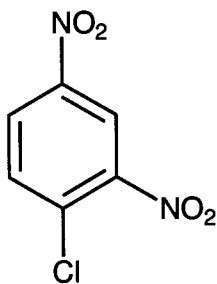
2)



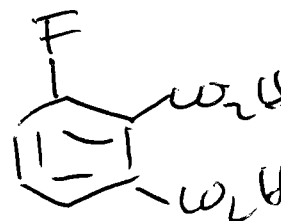
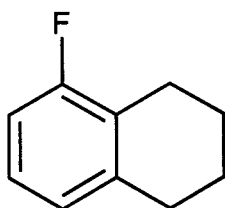
g)



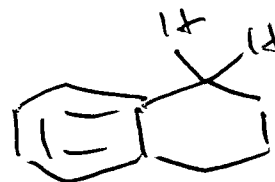
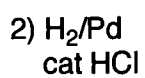
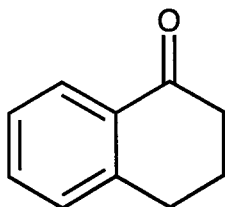
h)



i)

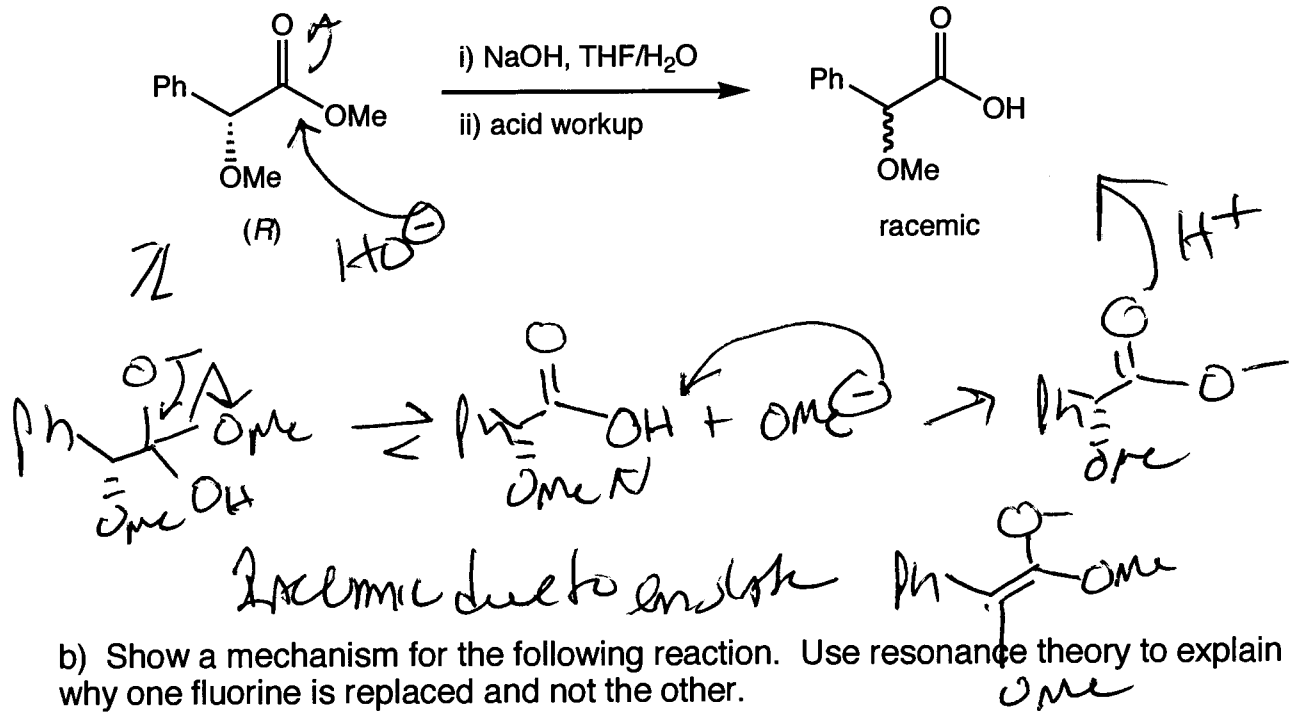


j)

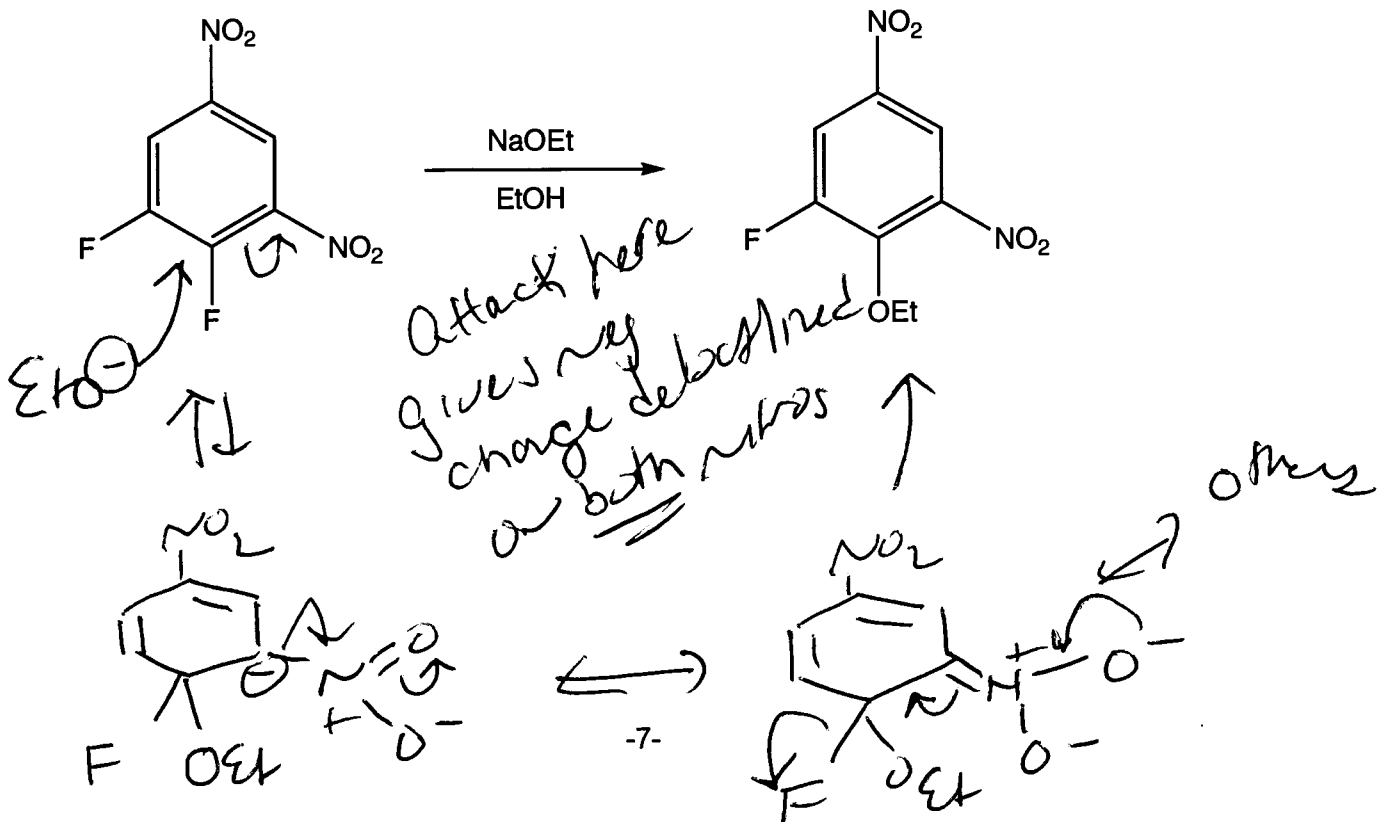


4) Mechanisms. Show clear, step-by-step mechanisms for the following reactions. Use arrows to track electron flow (4 x 5 = 20 points):

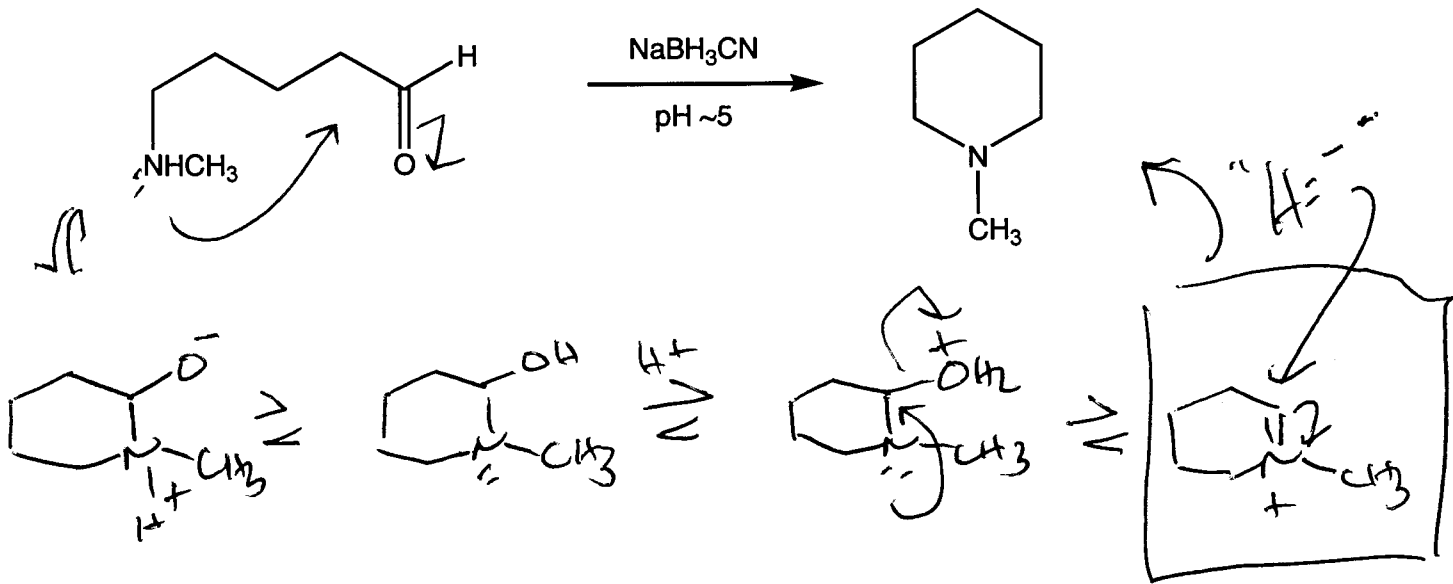
a) Saponification of methyl (*R*)-2-methoxy-2-phenylacetate to the free acid occurs with racemization. Provide a mechanism that shows how the saponification occurs and explain why the product is racemic. (5 points)



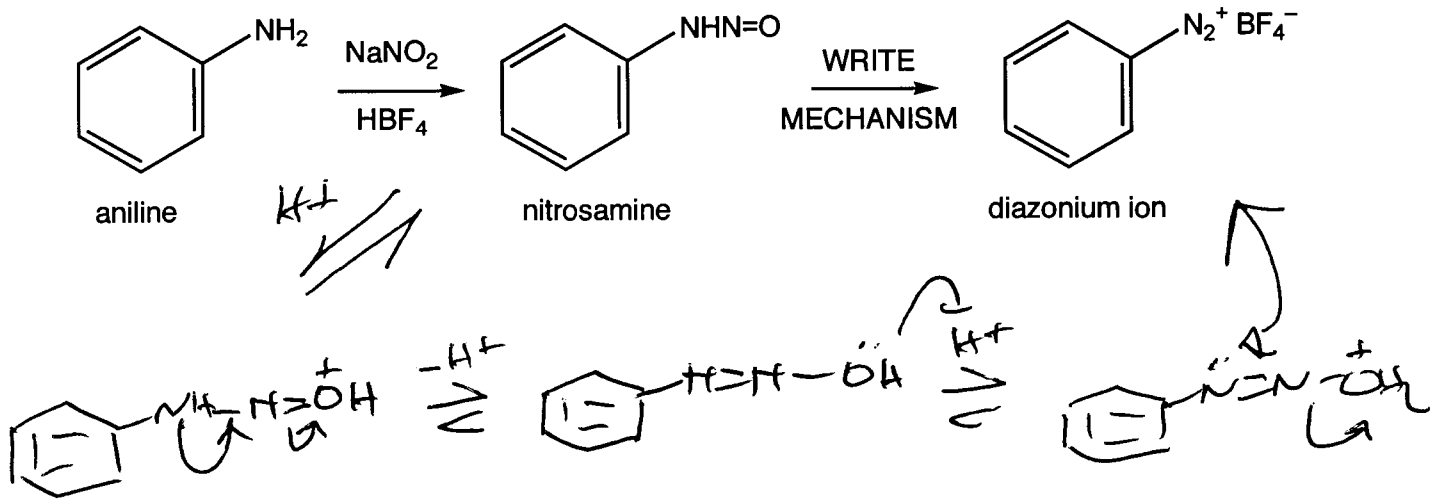
b) Show a mechanism for the following reaction. Use resonance theory to explain why one fluorine is replaced and not the other.



c) Write a mechanism for the following reduction alkylation reaction.

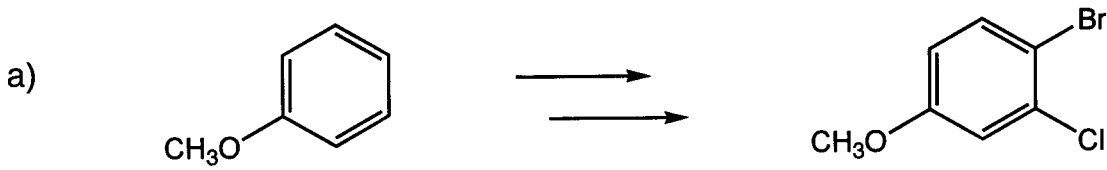


d) One of the key intermediates in the diazotization of aniline with nitrous acid is the nitrosamine shown below. Write the mechanism for the conversion of this nitrosamine to the final diazonium ion.



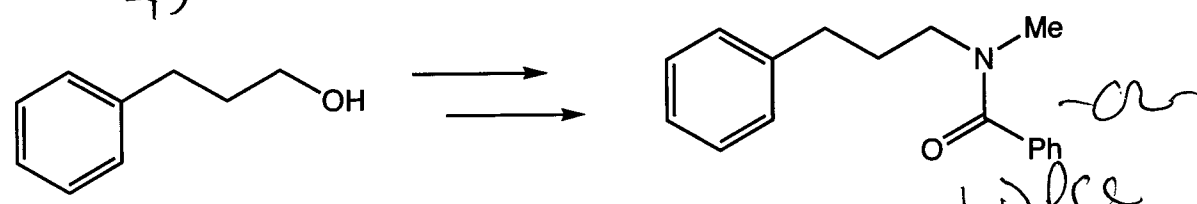
5) Multi-step Synthesis (10 points)

Propose an efficient sequence of reactions for **two of the following three** transformations.

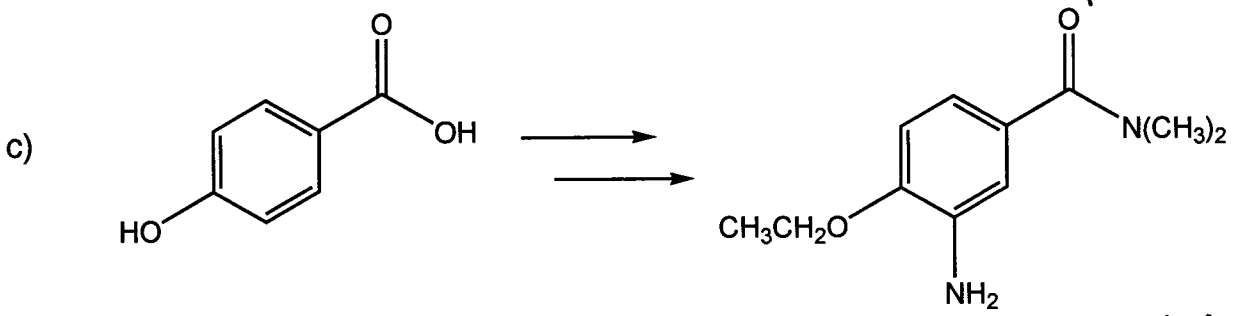


- 1) $\text{HNO}_3 / \text{H}_2\text{SO}_4$
- 2) H_2/Pd
- 3) Cl_2
- 4) $\text{NaNO}_2 / \text{HBr}$, then CuBr

Several ways



- | | | |
|--|--|--|
| <ol style="list-style-type: none"> 1) MsCl 2) azide or Gabriel to NH_2 | <ol style="list-style-type: none"> 3) $\text{H}_2\text{C}=\text{O}, \text{NaCNBH}_3$ 4) $\text{PhCOCl}, \text{Et}_3\text{N}$ | <ol style="list-style-type: none"> 1) PhCOCl 2) $\text{NHMe}, \text{NaCNBH}_3$ 3) PhCOCl |
|--|--|--|



- | | |
|--|--|
| <ol style="list-style-type: none"> 1) $\text{HNO}_3 / \text{H}_2\text{SO}_4$ 2) H_2/Pd 3) Base, $\text{CH}_3\text{CH}_2\text{F}$ | <ol style="list-style-type: none"> 4a) SOCl_2 (make acid chloride) 4b) $(\text{CH}_3)_2\text{NH}$ |
|--|--|
- Steps could be in different order