Chemistry 342-75
Spring 2015
Exam 2
Dr. Richter

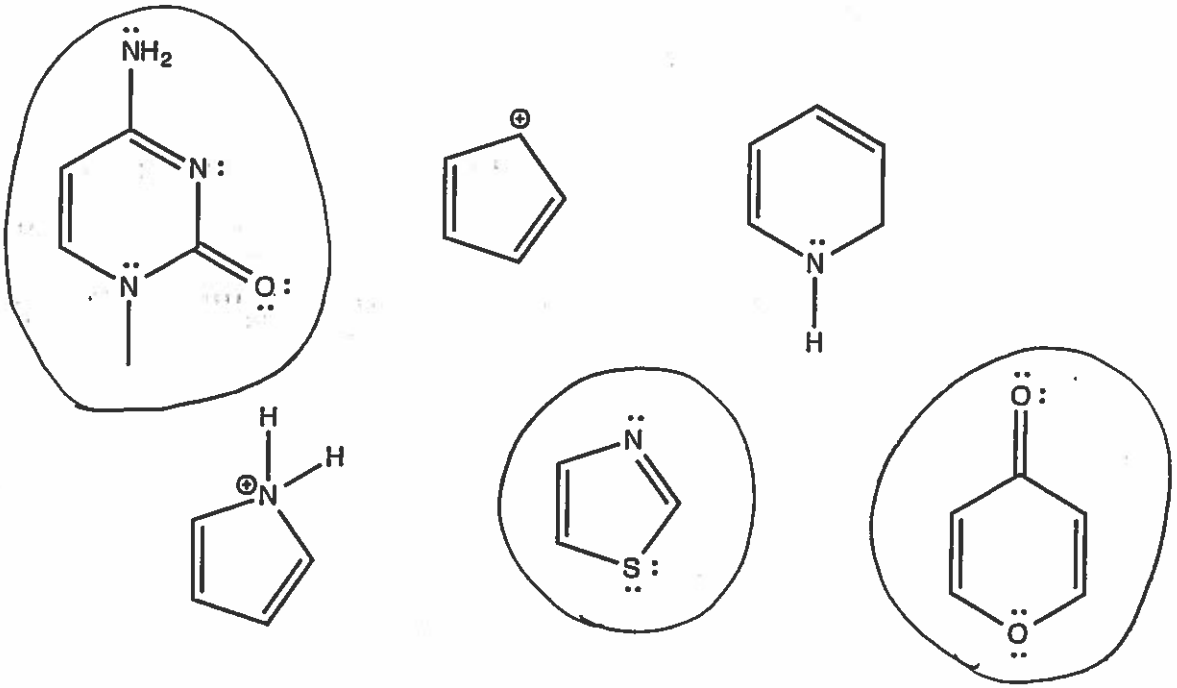
Name KEY

Signature _____

You are required to answer all question sets. Please note that some of the question sets offer you a choice of questions - do only the number of questions asked for. Please write legibly and draw clearly. Points will be deducted for illegible and unclear answers. The point total for this exam is 100 and the value of each question set is shown in parenthesis beside that set. ***READ ALL QUESTIONS CAREFULLY AND APPORTION YOUR TIME ACCORDINGLY***.

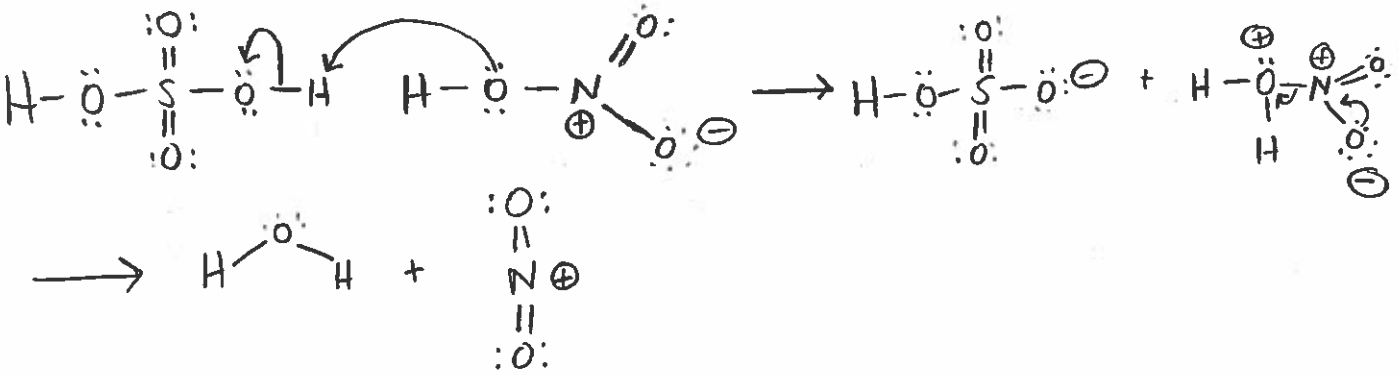
PART ONE: STRUCTURE, MECHANISM, AND REACTIVITY – For each of the sets below, circle the answer(s) as indicated.

1. Consider the structures below. Circle all that are **aromatic**. You may assume planarity in all cases. **(12)**

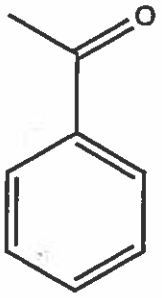


2. **a.** Draw the stepwise mechanism of the reaction below using mechanistic arrows to show electron movement. For full credit your mechanism must account for the formation of all products. **(3)**

$$HNO_3 + H_2SO_4 \longrightarrow NO_2^+ + HSO_4^- + H_2O$$

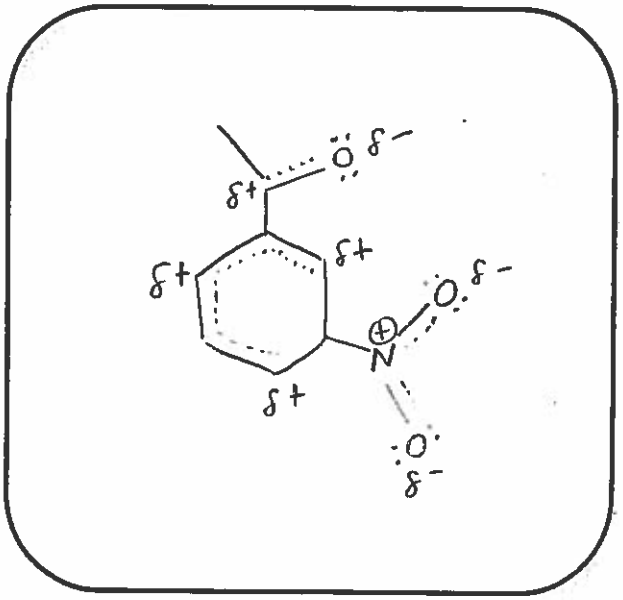


b. Draw the ***resonance hybrid*** of the arenium ion formed during the EAS reaction below. *Place your answer in the box provided.* Remember to show the resonance of the "NO_2" group and the carbonyl in your hybrid. **(6)**

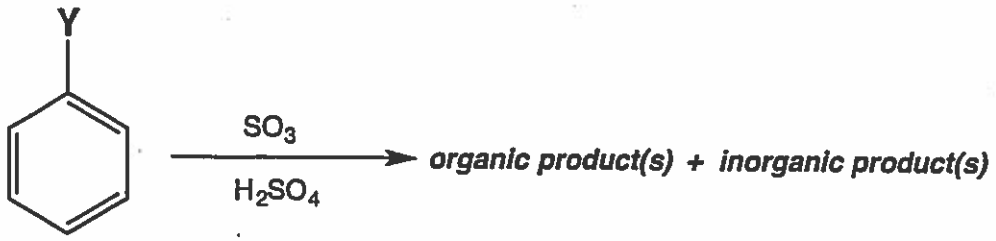


+ NO_2^+ ⟶ ***product(s)***

Answer



3. Consider the following reaction:



Which of the following statements (A-E) regarding the above reaction is TRUE? *Circle **all possible** answers.* **(6)**

(A.) The product of the reaction will be less activated toward electrophilic aromatic substitution than the starting material. (SO_3H deactivating)

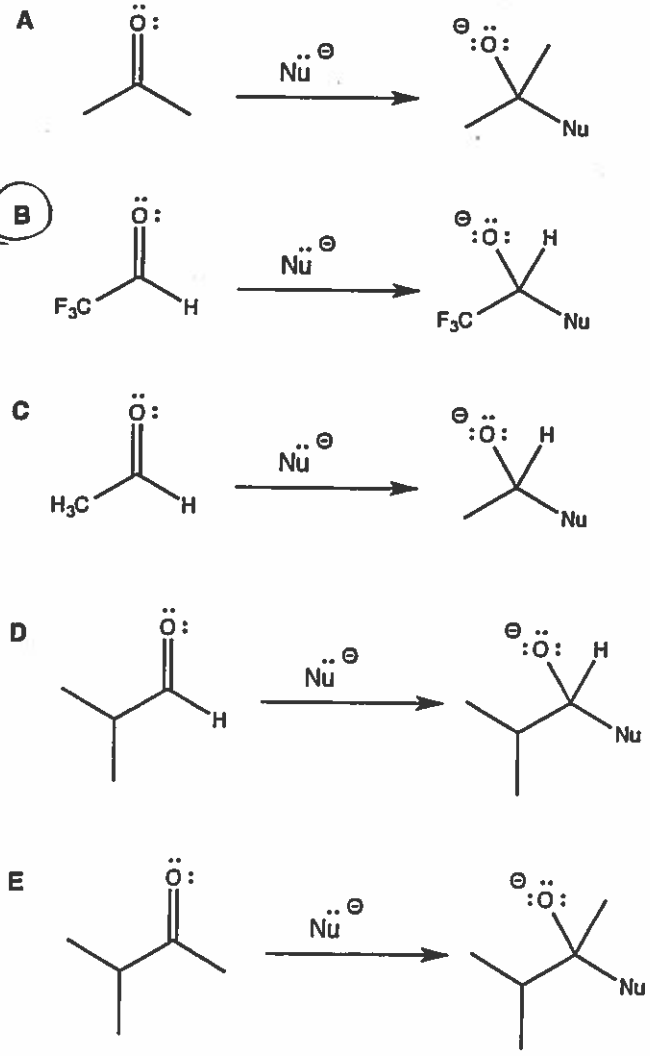
B. Water is a by-product of this reaction.

C. The reaction rate will be faster if Y = Br than if Y = CH_3.

(D.) If Y = OCH_3, an isomeric mixture of organic products will result. (ortho + para)

(E.) The slow step of the reaction involves the formation of a non-aromatic ion. (arenium ion is not aromatic)

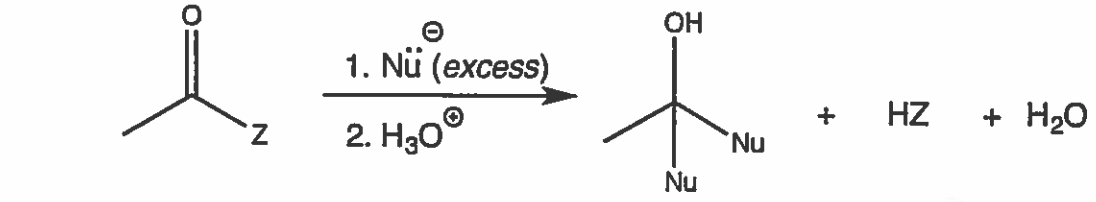
4. Circle which of the reactions (A-E) below would be the most favorable. **(4)**

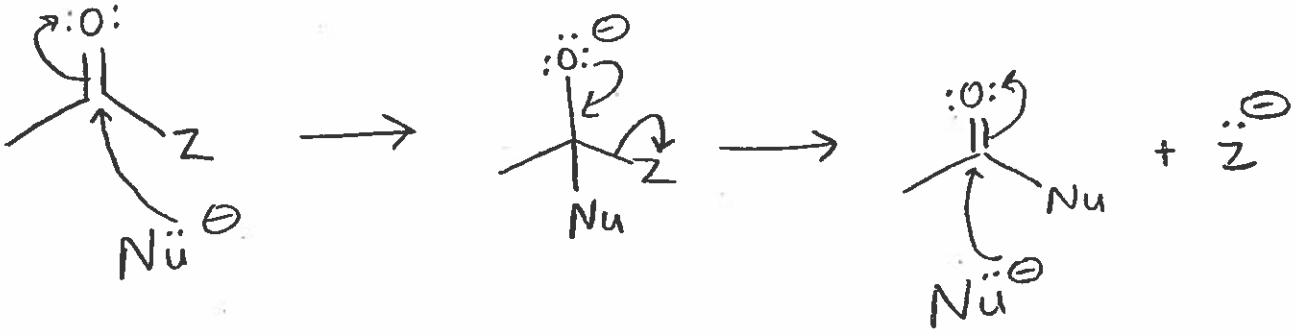


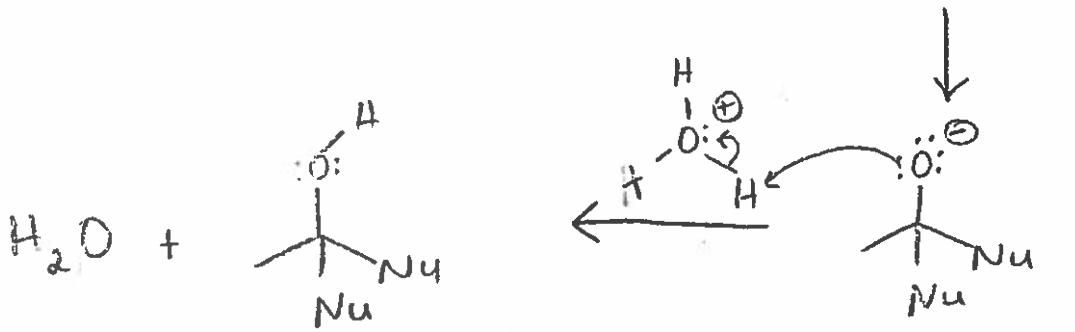
most electrophilic C

5.

a. Draw the stepwise mechanism of the following reaction using mechanistic arrows to indicate electron movement. **(6)**







b. Consider the reaction in part a. For each of the following pairs (A-C), circle which would lead to the more favorable reaction. **(3)**

A. (Z = Cl) **or** $Z = OCH_3$

B. (Z = OCOR) **or** $Z = NHCH_3$

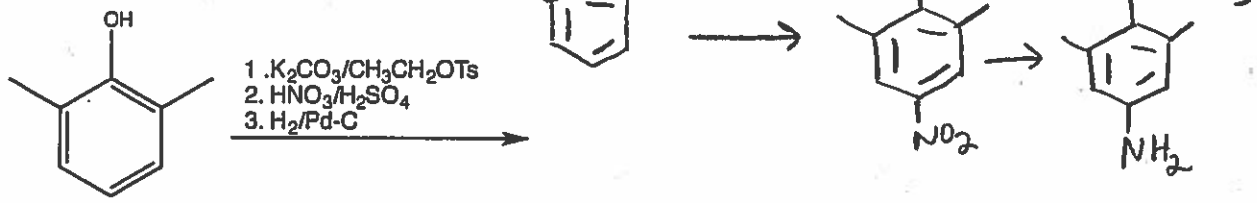
C. $Z = NH_2$ **or** (Z = OH)

PART TWO: PREDICT THE PRODUCT

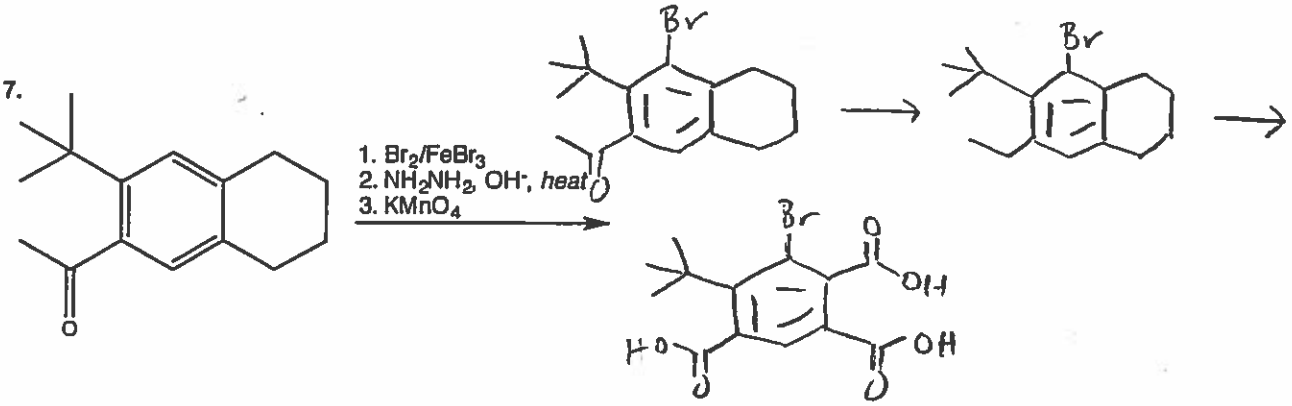
For *five* (5) of the following reactions **6-12** predict the major organic product(s) showing stereochemistry where appropriate. **(30)**

*Check the corresponding boxes for the FIVE answers that you want graded, otherwise **6-10 will be graded automatically.***

☐ 6.



☐ 7.



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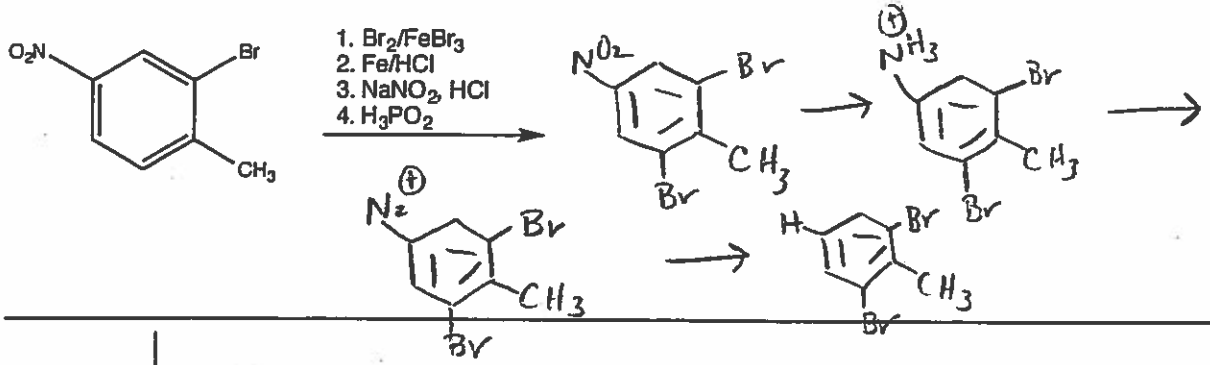
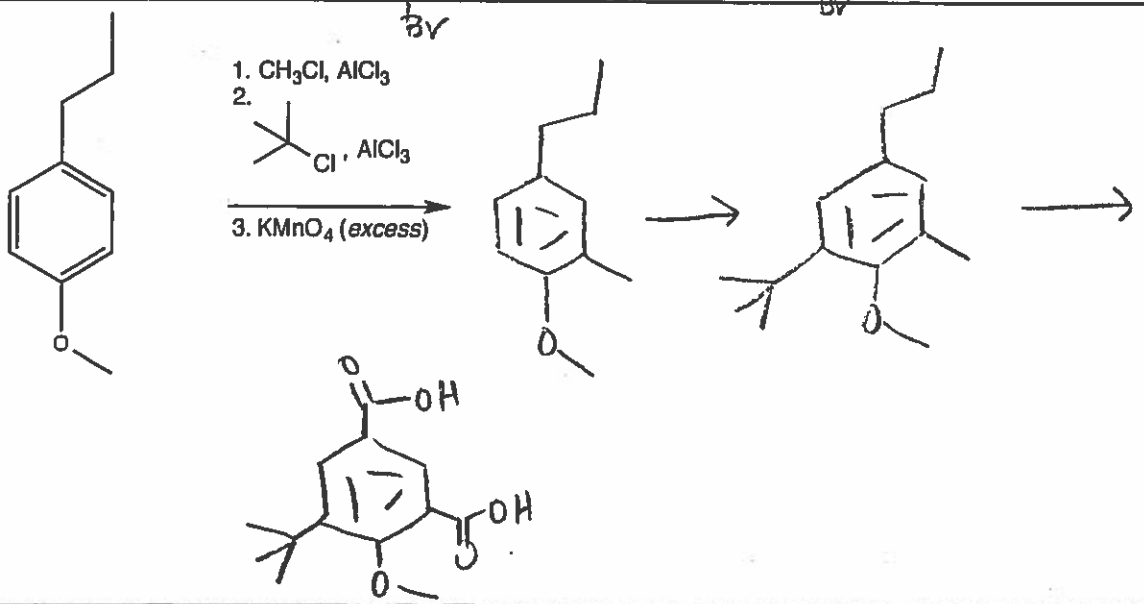
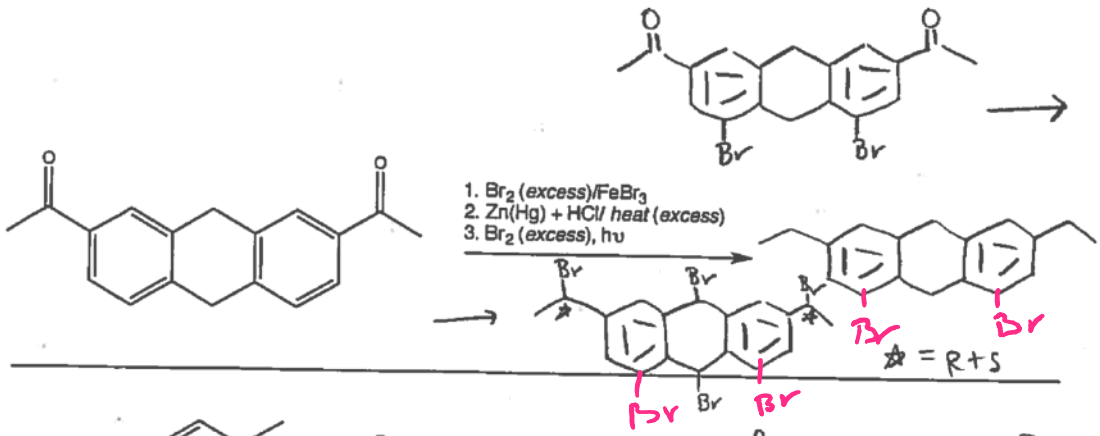


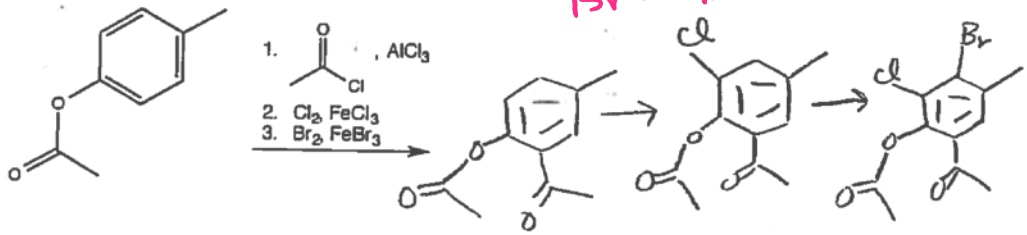
☐ 9.



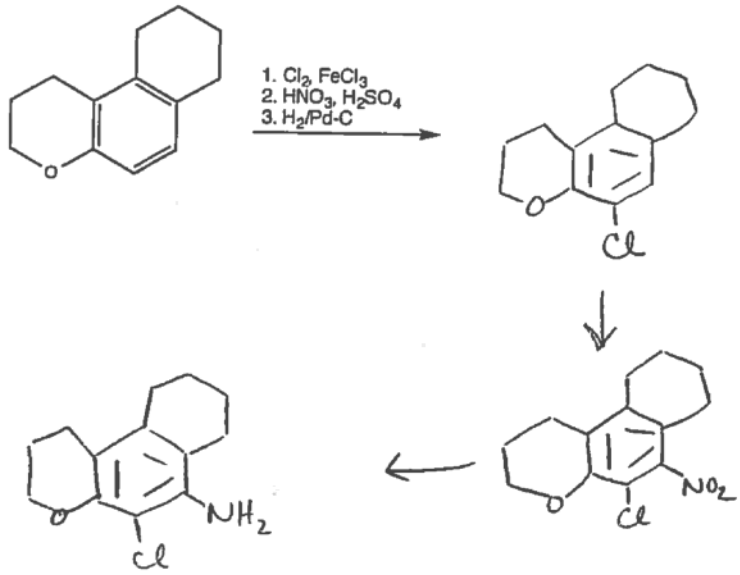
10.


1. Br_2 (excess)/$FeBr_3$
2. Zn(Hg) + HCl/ heat (excess)
3. Br_2 (excess), hυ
Br
Br
Br
Br
Br
Br
Br
Br
☆ = R+S

11.

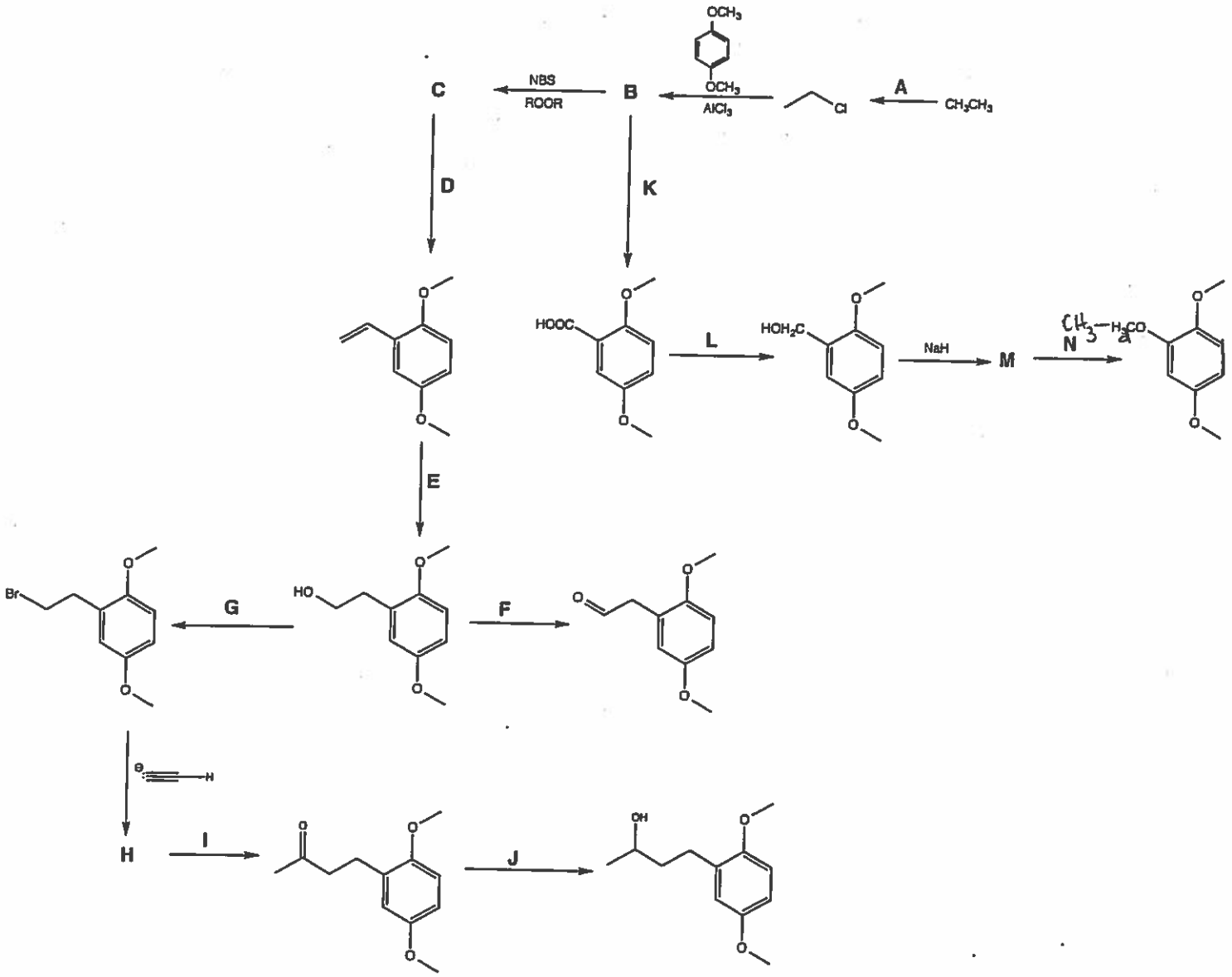

1.
, $AlCl_3$
2. Cl_2, $FeCl_3$
3. Br_2, $FeBr_3$
O
Cl
Cl
Br
Cl

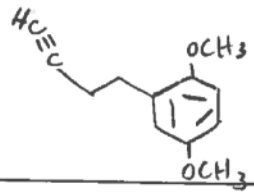
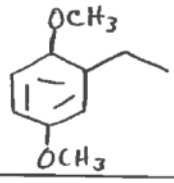
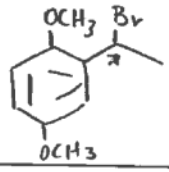
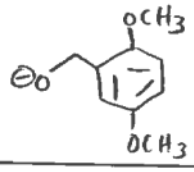
12.


1. Cl_2, $FeCl_3$
2. HNO_3, H_2SO_4
3. H_2/Pd-C
Cl
NO_2
Cl
NH_2
Cl

PART THREE: SYNTHESIS

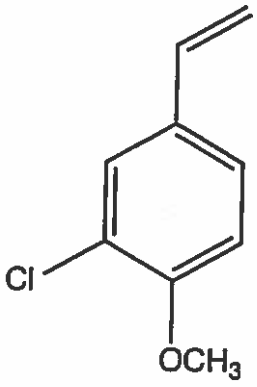
A. Fill in the missing reagents and/or products in the synthetic scheme outlined below. **Place your answers in the table provided on the next page.** **(14)**



Letter	Missing Reagent/Product	Letter	Missing Reagent/Product
A	Cl_2 / $h\nu$	H	
B		I	H_2O / H_2SO_4 or H_2O / TsOH
C		J	1. $LiAlH_4$ 2. H_2O or $NaBH_4$ / CH_3OH or H_2 / Pd-C
D	$^tBuO^-$ / heat or DBU/heat or DBN/heat	K	$KMnO_4$
E	1. BH_3 2. H_2O_2 / OH^-	L	1. $LiAlH_4$ 2. H_2O
F	PCC	M	
G	PBr_3 or HBr	N	CH_3X or CH_3OTs

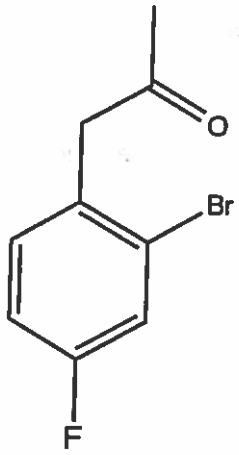
B. Propose a reasonable synthesis for **one** (1) of the two structures below **A** or **B**. You must start from the indicated organic substrates, but you may use any inorganic reagents you need. *You may also use any necessary organic acids, bases, oxidizing, or reducing agents.* **(16)**

You may use the blank page following the questions to write your answers.



A

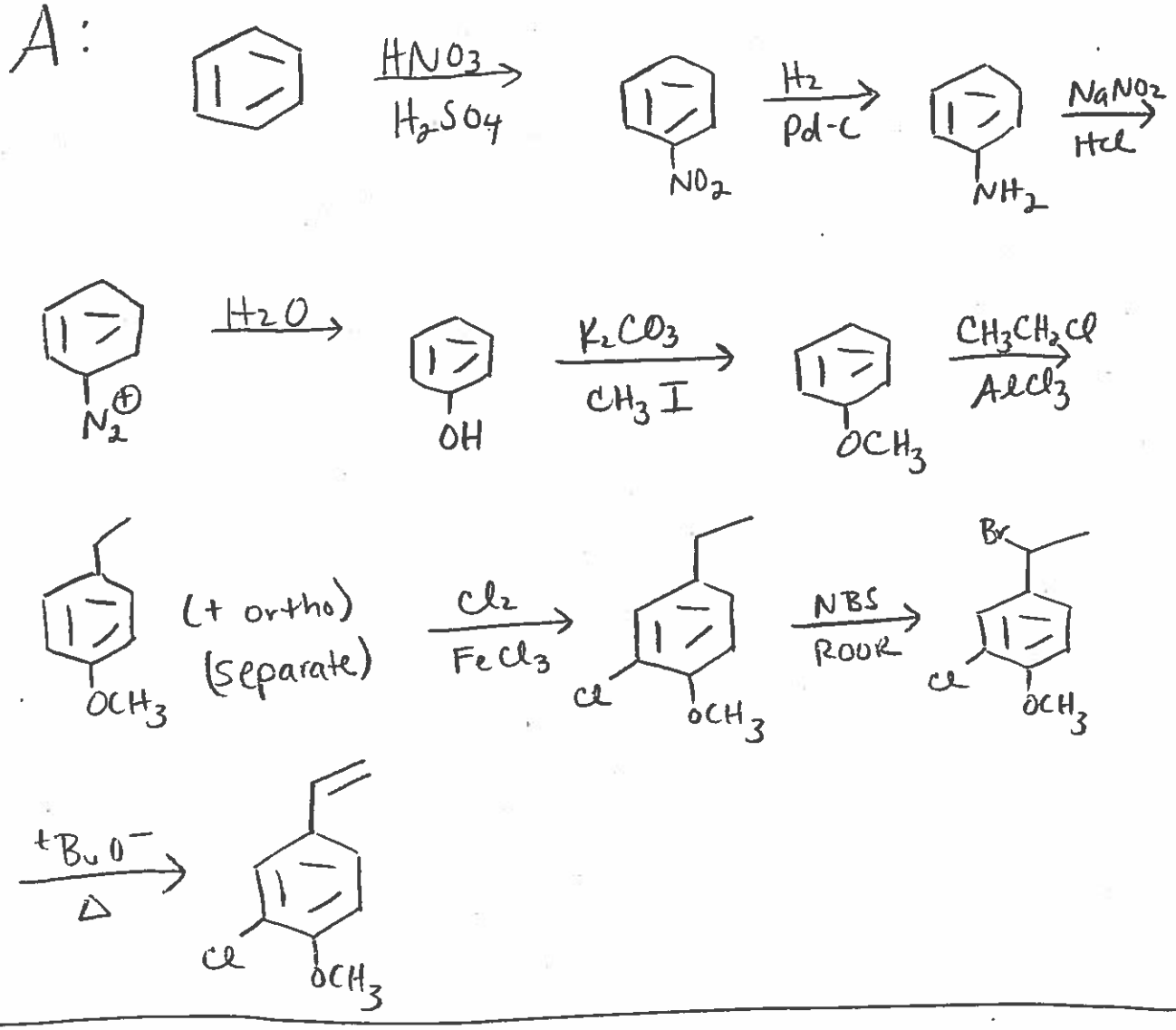
or



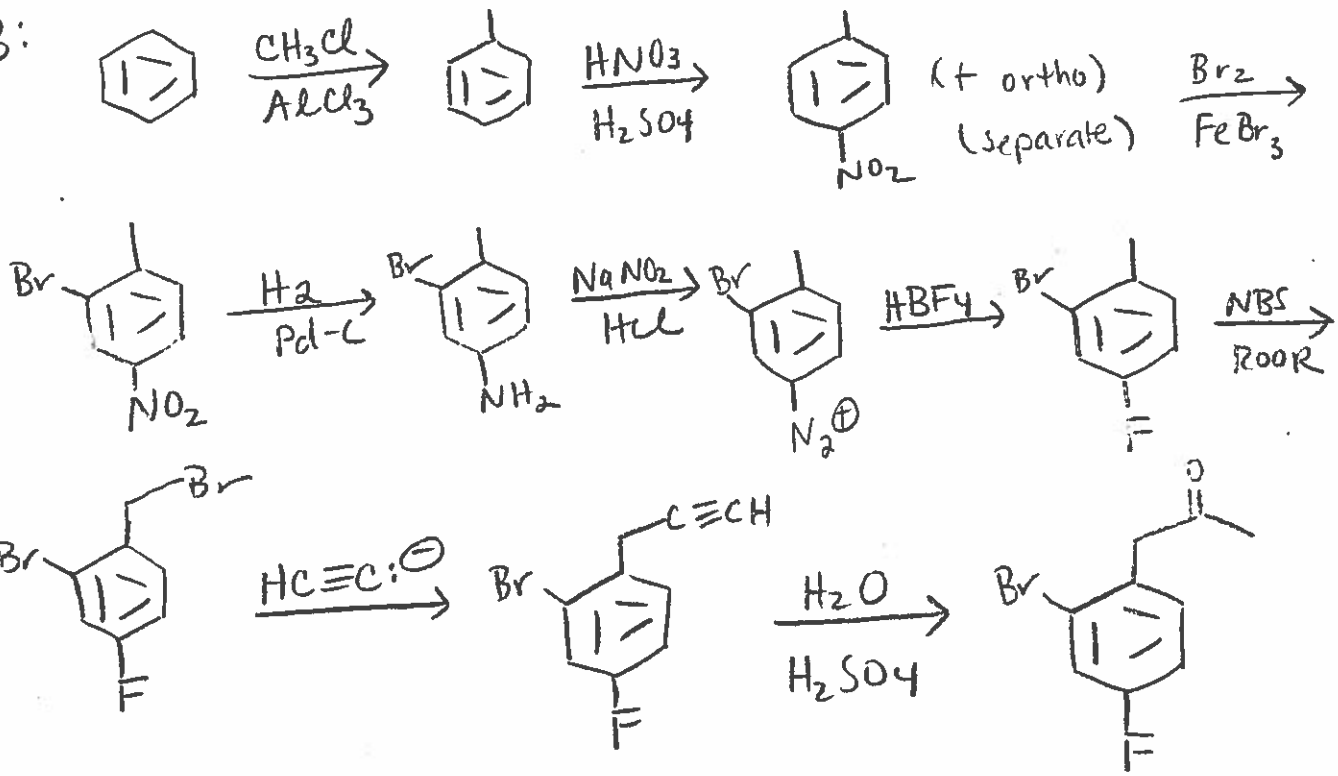
B

from benzene and organic substrates of 2 carbons or less

A:


HNO3
H2SO4
H2
Pd-C
NaNO2
HCl
NO2
NH2
H2O
K2CO3
CH3I
CH3CH2Cl
AlCl3
N2⊕
OH
OCH3
(+ ortho)
(separate)
Cl2
FeCl3
NBS
ROOR
Br
Cl
t-Bu O⁻
Δ

B:


CH3Cl
AlCl3
HNO3
H2SO4
NO2
(+ ortho)
(separate)
Br2
FeBr3
Br
H2
Pd-C
NH2
NaNO2
HCl
N2⊕
HBF4
F
NBS
ROOR
HC≡C:⊖
C≡CH
H2O
H2SO4
O