

CHEM 3311-200 Fall 2006

Final Exam

Professor R. Hoenigman

Average Score = 145

High Score = 235

Low Score = 27

I pledge to uphold the CU Honor Code:

Signature _____

Name (printed) _____

Last four digits of your student ID number _____

Recitation TA _____

Recitation number, day, and time _____

You have 2 hours and 30 minutes to complete this exam.

No model kits or calculators allowed.

Periodic table and scratch paper are attached.

DO NOT TURN THIS PAGE UNTIL INSTRUCTED TO DO SO.

Recitation Sections:

#	Day	Time	TA
211	Monday	8 am	Noel
251	Monday	2 pm	Carolynn
291	Monday	5 pm	Heather
252	Tuesday	12 pm	Sam
293	Tuesday	5 pm	Carolynn
212	Wednesday	8 am	Noel
253	Wednesday	1 pm	Tom
292	Wednesday	5 pm	Heather
213	Friday	8 am	Heather

Score:

Page 1 _____/16 Page 6 _____/40

Page 2 _____/15 Page 7 _____/40

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Page 4 _____/30 Page 9 _____/45

Page 5 _____/20 Page 10 _____/10

TOTAL _____/250

1. (10 pts) BenzaClin is a topical antibiotic with the structure shown below.

A. Label the configuration of each indicated chirality center in BenzaClin.

(2 pts each)

B. Circle **all** of the terms below that describe one or more structural feature of BenzaClin.

(1 pt each)

Amine

Ketone

Aldehyde

Amide

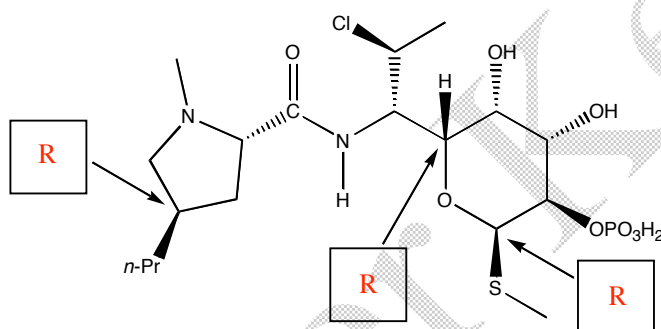
Ester

Sulfide

Nitrile

Ether

Thiol



2. (6 pts) Give the IUPAC name for each of the following compounds.

(2 pts each, -1 for no stereochemistry, -1 for wrong numbers)

A.



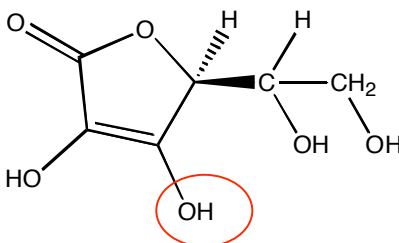
B.



C.

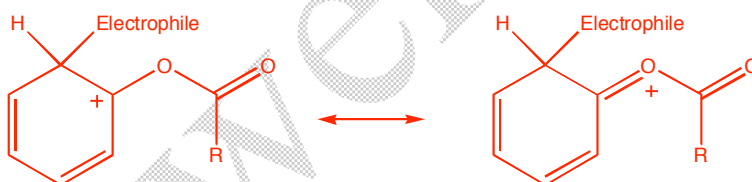


3. (5 pts) Vitamin C, shown below, has a pK_a of 4.1. Circle the most acidic hydrogen in Vitamin C.

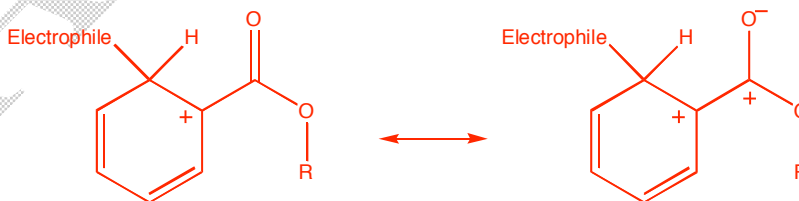


4. (10 pts) Explain why an ester can be both an activating, *ortho/para* director and also a deactivating, *meta* director. Use resonance structures to support your discussion. (4 pts for resonance structures, 6 pts for explanation)

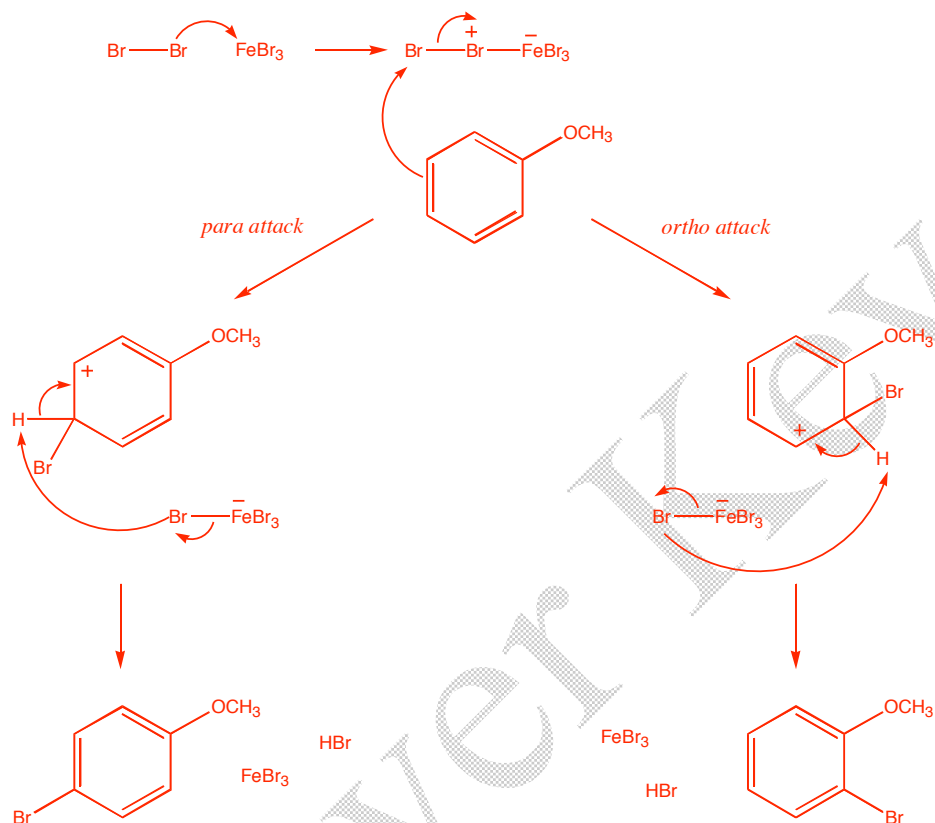
The ester functional group can be attached to a benzene ring in one of two ways. If the ester is attached at the oxygen, a lone pair of electrons can help stabilize the arenium ion towards *ortho/para* attack. The resulting resonance structure is particularly good, since all atoms have an octet of electrons.



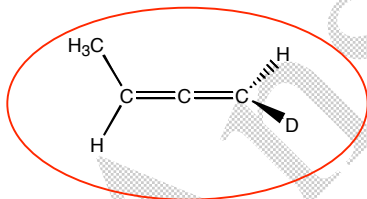
If the ester functional group is attached to the benzene ring at the carbonyl group, the benzene ring becomes less electron-rich and is deactivated. In addition, the adjacent carbonyl group is a *meta* director, since the following resonance structure would be *destabilized* (due to the adjacent positive charges) by *ortho/para* attack.



5. (15 pts) The bromination of anisole produces two isomeric bromoanisoles. Using curved arrows to show the flow of electrons, give a mechanism to account for the formation of these two products.

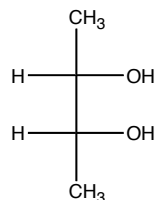
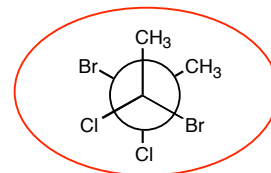


6. (5 pts) Circle the compounds below that are chiral. (1 pt each)

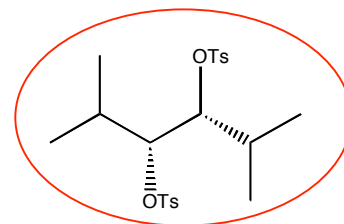
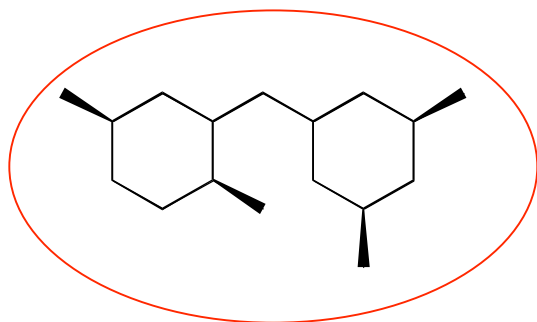


(1*R*,2*S*)-1,2-dimethylcyclopentane

cis-3-methylcyclobutanol

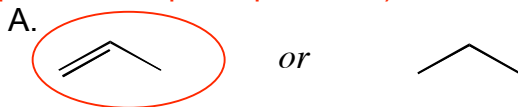


(+)-2-chlorobutane

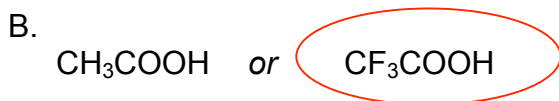


7. (15 pts) Circle the more acidic compound in the following pairs. Give the reason for your choice in the adjacent box.

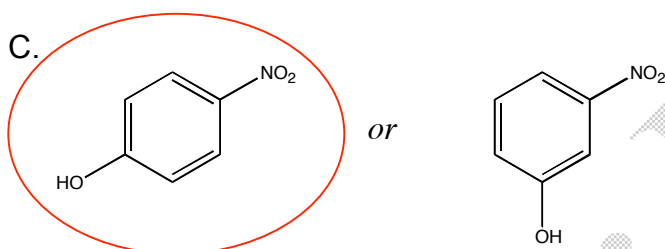
(2 pts circle, 3 pts explanation)



The allylic conjugate base is resonance stabilized



Inductive effect

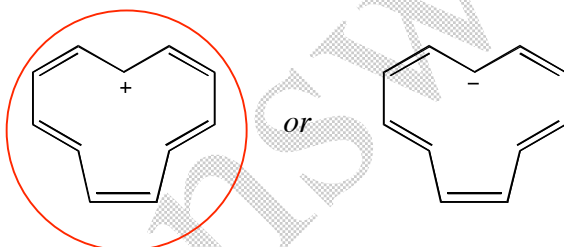


More stable conjugate base (more resonance structures)

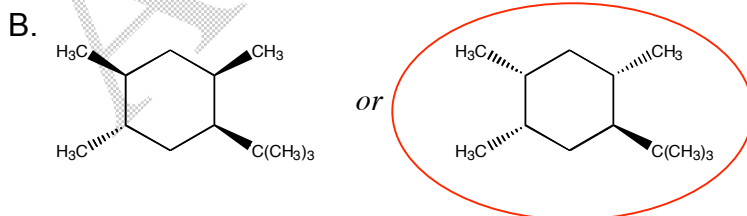
8. (15 pts) Circle the compound that has the *lower* heat of combustion. Give the reason for your choice in the adjacent box.

(2 pts circle, 3 pts explanation)

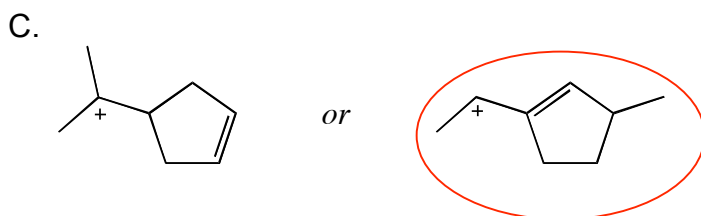
A. Book Problem 11.50c/d



Aromatic cation versus an antiaromatic anion



More substituents are in the equatorial position



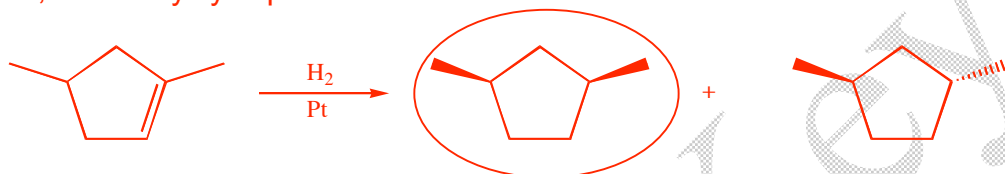
Allylic cation is resonance stabilized

9. (10 pts) Catalytic hydrogenation of 1,4-dimethylcyclopentene yields a mixture of two products. One of these products is formed in a much greater yield than the other (the observed ratio is 10:1). Draw the products of this reaction and circle the major product. Why is there a preference for one of these products?

Book Problem 6.40

(2 pts each product, 1 pt circle, 5 pts explanation)

Hydrogenation is regioselective to the less hindered face of the double bond. Thus, the alkene will attach to the catalyst on the side opposite the C4 methyl group and the hydrogen will add to the opposite side, favoring formation of *cis*-1,3-dimethylcyclopentane.



10. (5 pts) Match the following alkenes with the appropriate ΔH_{H_2} value. Heats of hydrogenation: 151 kJ/mol, 122 kJ/mol, 114 kJ/mol, 111 kJ/mol, 105 kJ/mol

Book Problem 6.29

(1 pt each)

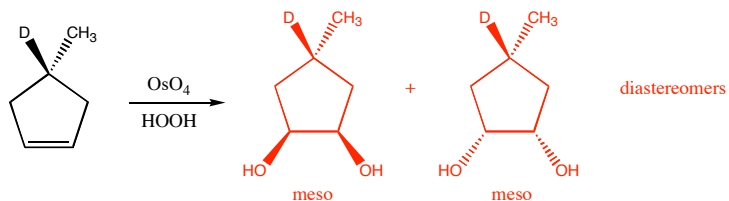
- 122 kJ/mol 1-pentene
- 111 kJ/mol (*E*)-4,4-dimethyl-2-pentene
- 114 kJ/mol (*Z*)-4-methyl-2-pentene
- 151 kJ/mol (*Z*)-2,2,5,5-tetramethyl-3-hexene
- 105 kJ/mol 2,4-dimethyl-2-pentene

11. (5 pts) Explain why 3-pentanol has a higher boiling point than 3-chloropentane.

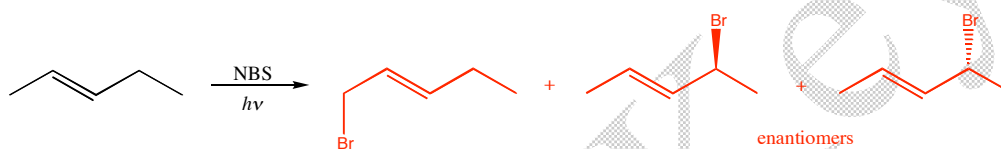
Boiling points are determined by intermolecular forces. 3-pentanol has greater intermolecular forces than 3-chloropentane, since the alcohol can participate in hydrogen bonding. Hydrogen bonds require a lot of energy to break (relatively) and thus, the alcohol has a higher boiling point.

12. (80 pts) Give the major organic product(s) of the following reactions. Be sure to clearly show stereochemistry using dashes and wedges. Write NR if no reaction occurs. **Clearly label any enantiomers, diastereomers, and/or meso compounds.** (Note: some problems have more than one step.)

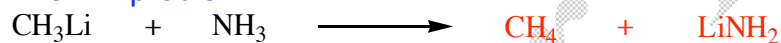
A.



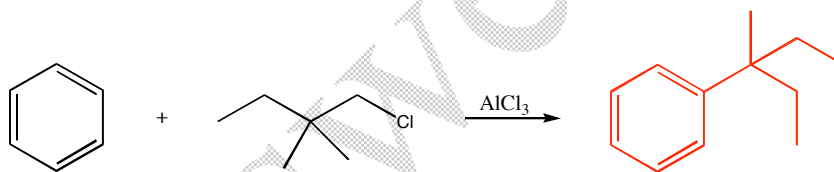
B.



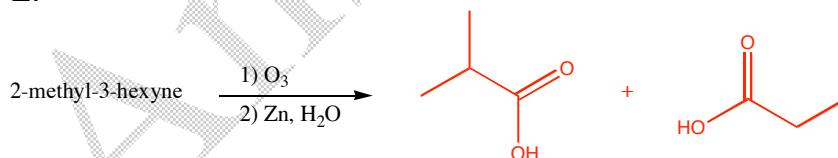
C. Exam 1 problem



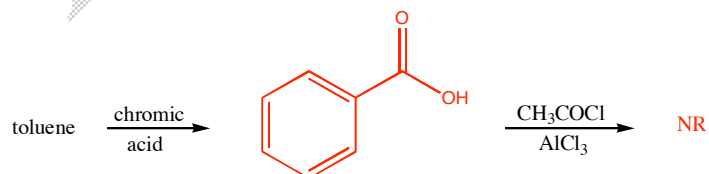
D.



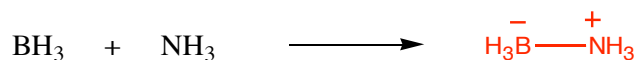
E.



F.

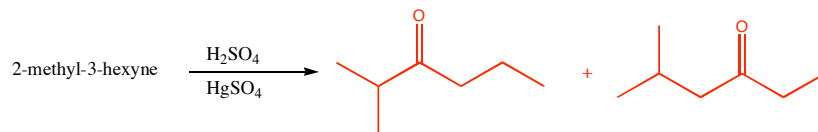
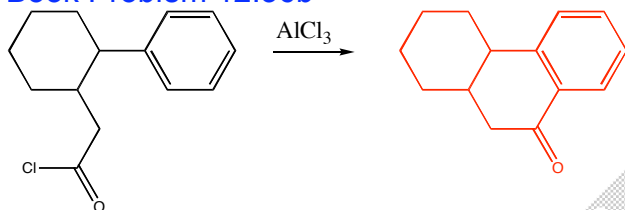


G.

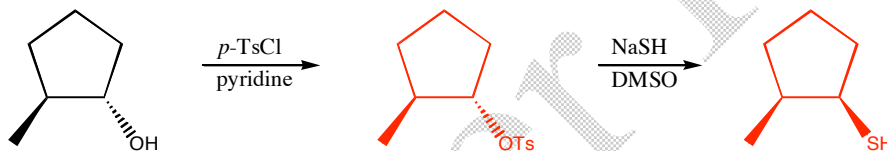


12. continued. [Be sure to clearly show stereochemistry using dashes and wedges. Write NR if no reaction occurs. Clearly label any enantiomers, diastereomers, and/or meso compounds; some problems have more than one step.]

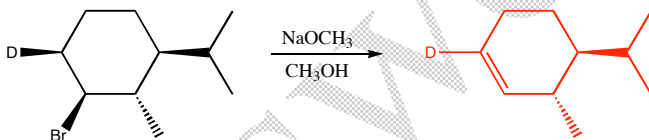
H.

I. **Book Problem 12.36b**

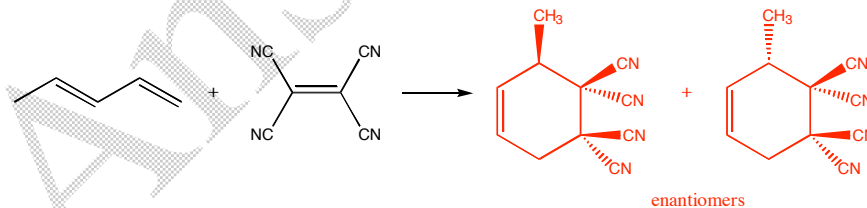
J.



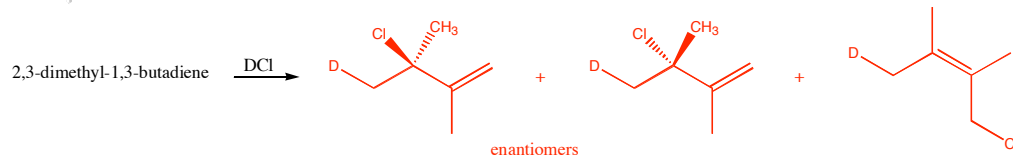
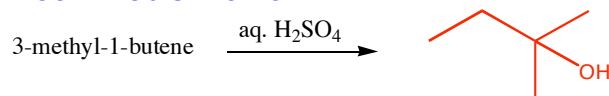
K.



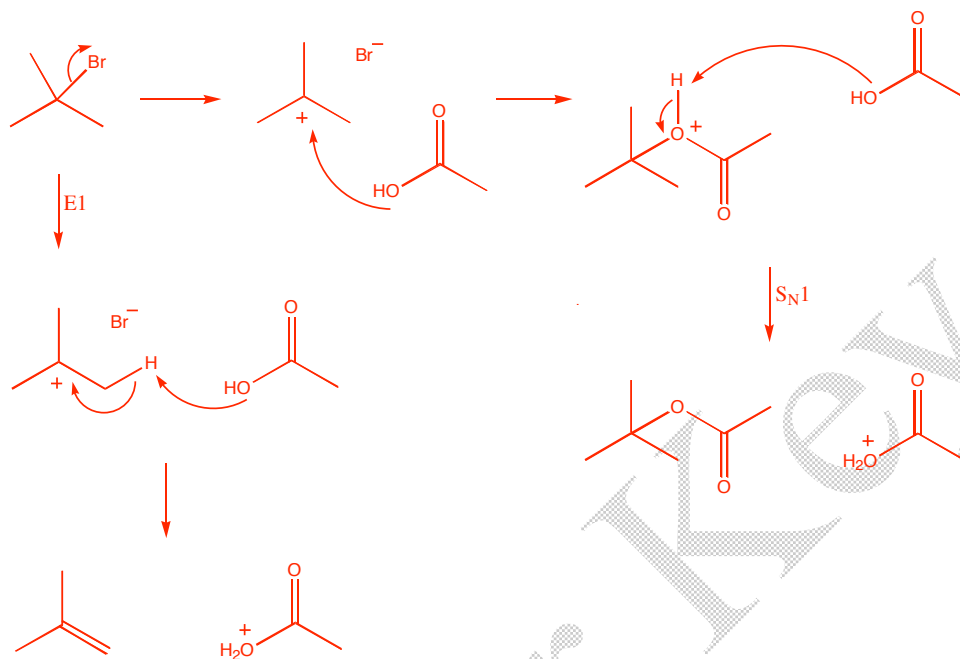
L.



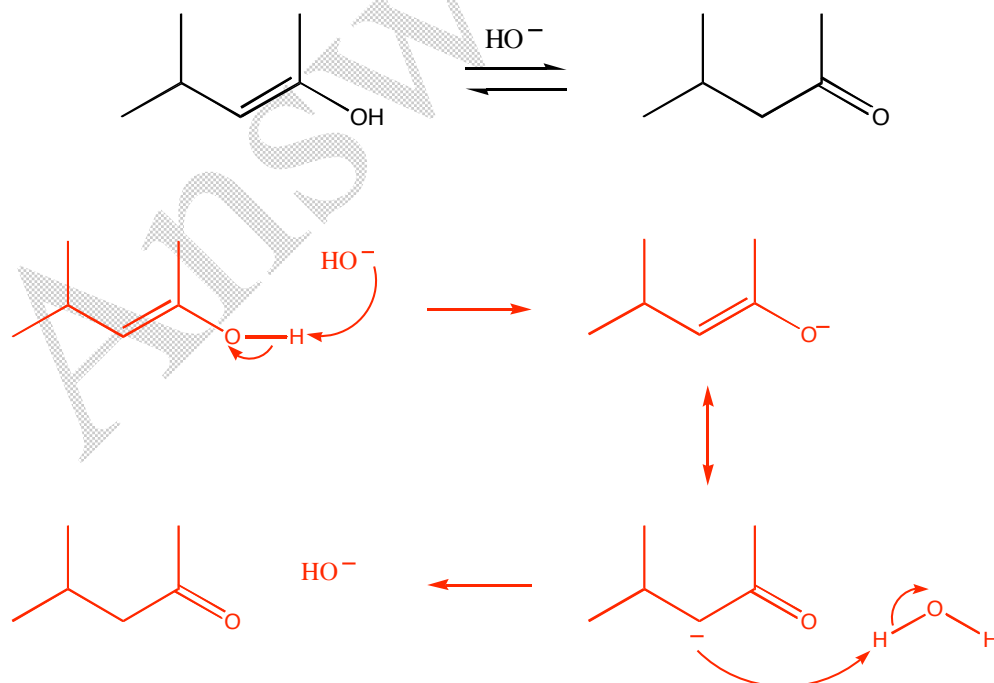
M.

N. **Book Problem 6.46**

13. (12 pts) Using curved arrows to show the flow of electrons, draw a mechanism for the solvolysis of *tert*-butyl bromide in acetic acid.

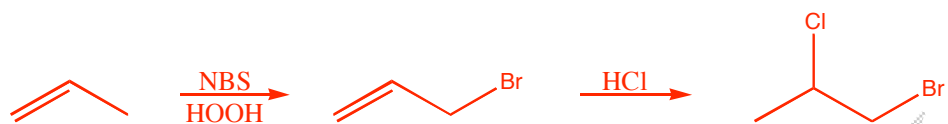


14. (12 pts) Using curved arrows to show the flow of electrons, propose a mechanism for the base catalyzed enol-keto tautomerization shown below.

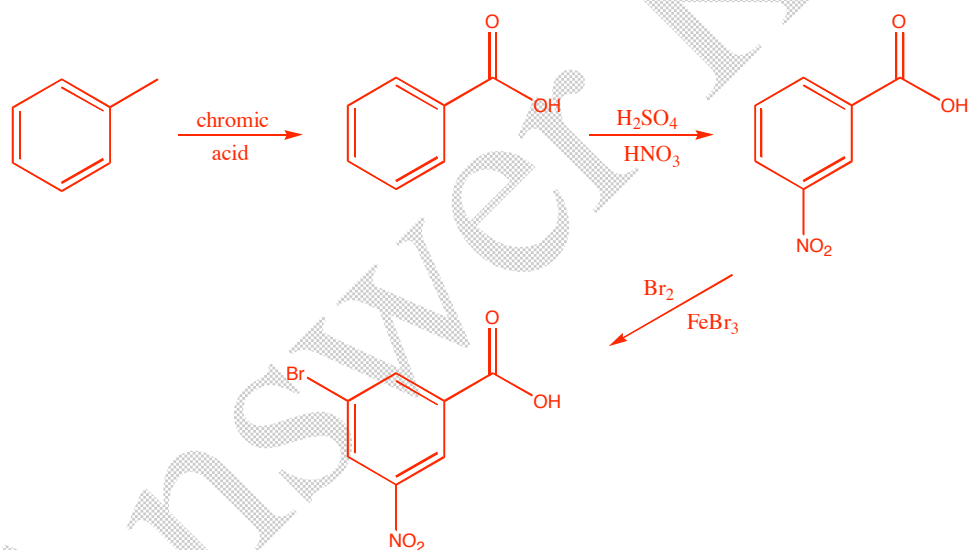


15. (45 pts) Propose an efficient synthesis for the following transformations. You may use any reagents you like. Be sure to show any intermediates. (Do not draw a mechanism.)

A. 1-bromo-2-chloropropane *starting from* propene
Book Problem 10.24d



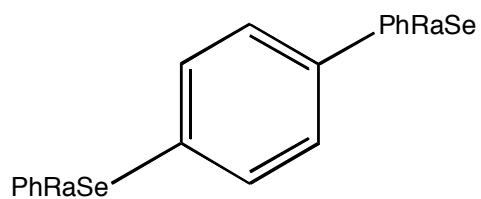
B. 3-bromo-5-nitrobenzoic acid *starting from* toluene
Book Problem 12.27k



C. 2-butyne *starting from* 1-butyne



Extra Credit: (10 pts) Draw a parody of aromatic nomenclature. For example, below is paraphrase.



Answer Key

Scratch Page

Answer Key

Scratch Page

Answer Key