CHEM 343 –Principles of Organic Chemistry II – Summer 2014

Instructor: Paul J. Bracher

Exam #1

Tuesday, July 8th, 2014

8:00–9:15 a.m. (in class)

Student Name (Printed)	Solutions
Student Signature	N/A

Instructions & Scoring

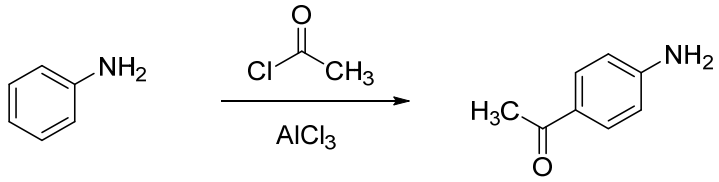
- Please write your answers on the official answer sheet. No answers marked in this booklet will be graded.
- You may use a single sheet of notes and a model kit. You may not collaborate with others.
- Your exam answer sheet may be photocopied.

Problem	Points Earned	Points Available
I		35
II		24
III		21
IV		20
TOTAL		100

Questions, Required Information, Supplementary Information

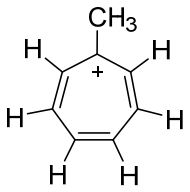
Problem I. Multiple choice (35 points total; +5 points for a correct answer, +2 points for an answer intentionally left blank, and 0 points for an incorrect answer). For each question, select the best answer of the choices given. Write the answer, legibly, in the space provided on the answer sheet.

(1) C The yield of the following reaction will be poor for what reason(s)?



(a) amino groups are *meta* directors, not *ortho*/*para* directors
(b) these conditions are prone to multiple substitutions (overalkylation)
(c) the amino group will form a complex with $AlCl_3$
(d) aniline is a poor nucleophile for electrophilic aromatic substitutions
(e) all of the above

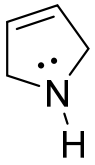
(2) A Which of the following adjectives best describes the electronic structure of the methyltropylium cation (**A**)?



A

(a) aromatic
(b) antiaromatic
(c) nonaromatic
(d) pseudoaromatic
(e) radical

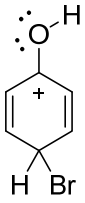
(3) D Which of the following statements about compound **B** is true?



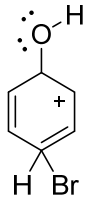
B

(a) the compound is aromatic
(b) the compound is antiaromatic
(c) the nitrogen atom is sp^2 hybridized
(d) the nitrogen atom is sp^3 hybridized
(e) none of the above statements is true

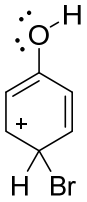
(4) B Which of the following structures is <u>not</u> a valid resonance form to describe the intermediate formed when phenol reacts with Br_2.



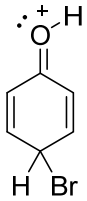
(a)



(b)



(c)

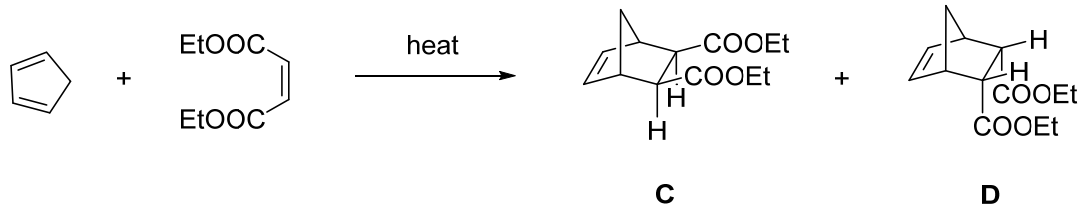


(d)

all four of these structures are valid

(e)

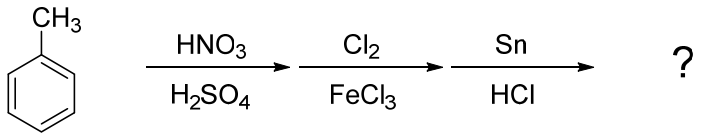
(5) B Which of the following statements about the following reaction is true?

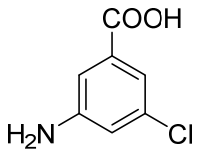


C **D**

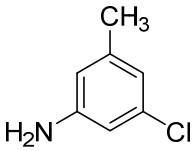
(a) product **C** will be produced in higher yield than **D**
(b) the rate of the reaction would increase if 2-methylcyclopentadiene were used in place of cyclopentadiene
(c) the reaction produces another enantiomer of **C** that is not shown
(d) all of the above
(e) none of the above

(6) C What is the major product expected of the sequence of reactions below?

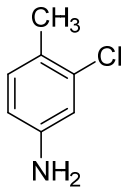




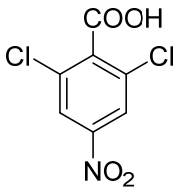
(a)



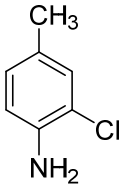
(b)



(c)

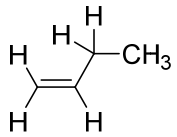


(d)



(e)

(7) D Which of the following statements accurately describes the bonding in 1-butene (**E**)?

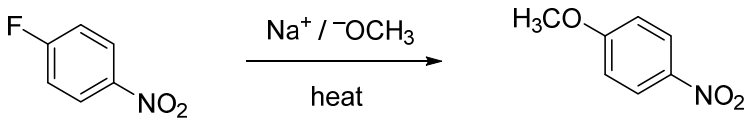


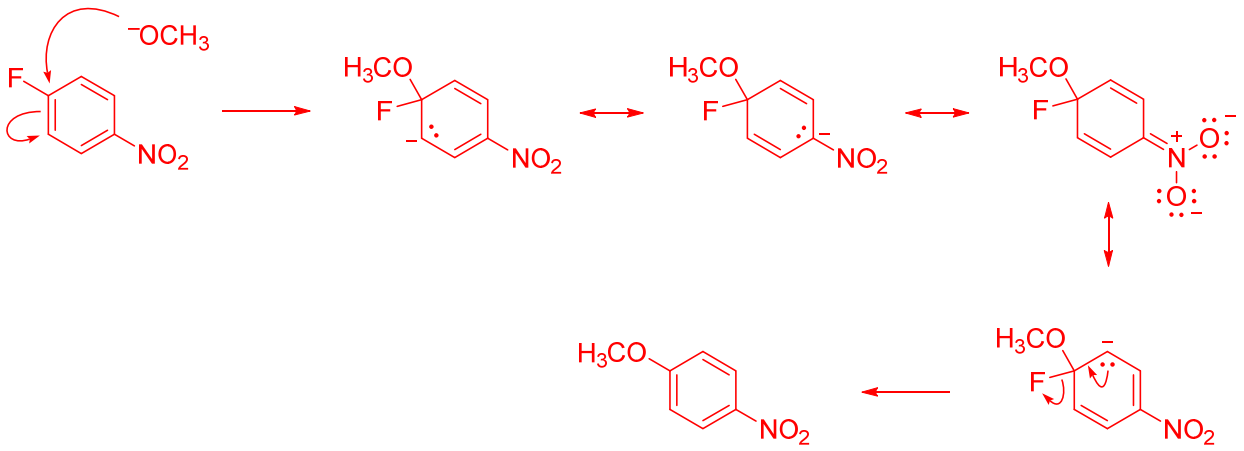
E

(a) the C2–C3 bond is shorter than the C3–C4 bond
(b) the C3 carbon is sp^3-hybridized
(c) the π* molecular orbital of the compound is empty
(d) all of the above
(e) none of the above

Problem II. Mechanism (24 points).

(1) (16 points) Draw a sensible mechanism for the following reaction. Remember to use proper "curved arrow notation" to account for the movement of electrons in the making and breaking of bonds. Show all significant resonance forms that account for the stability of the intermediates in the reaction.



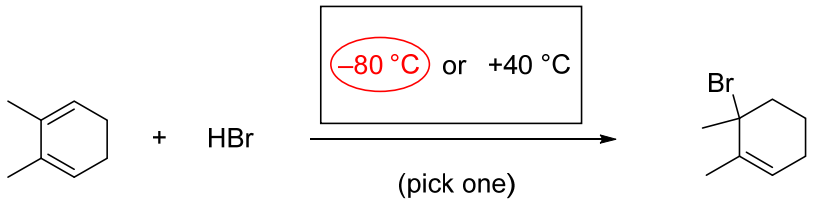


(2) (8 points) Will the reaction above become faster or slower if the fluorine atom is replaced with bromine? Explain why in no more than two sentences.

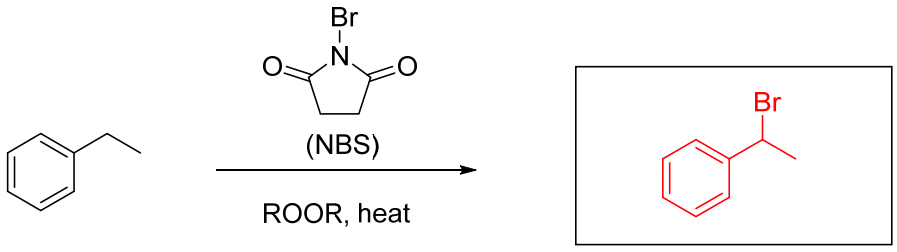
The reaction will be slower with bromine. The rate-determining step of this sort of nucleophilic aromatic substitution reaction is the attack of the methoxide nucleophile, not the step where the fluorine is lost. So, even though fluoride ion (F^-) is a worse leaving group than bromide ion (Br^-), the reaction will proceed faster with the fluoro compound because fluorine is more electronegative, which makes the ring a better electrophile for attack by methoxide in the rate-determining step.

Problem III. Reactions (21 points). The following chemical reactions are missing their starting materials, products, or reagents. Write the missing compounds into the empty boxes below, as appropriate. For missing products, draw the single organic product that you expect to be produced in the highest yield among all of the possibilities. In some cases, there will be more than one correct answer that will merit full credit.

(1) (6 points)

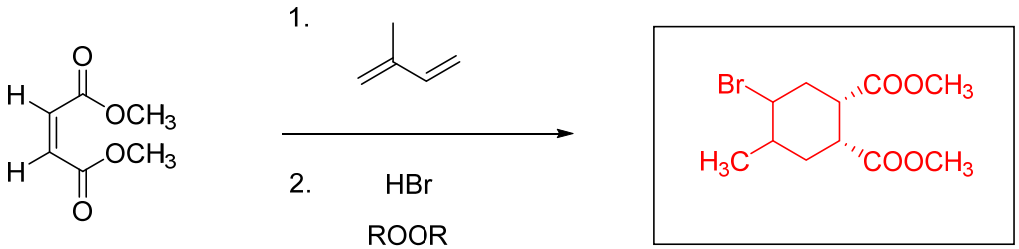


(2) (7 points)



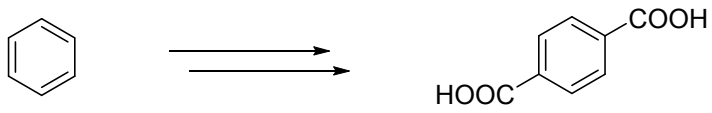
racemic mix of enantiomers

(3) (8 points)

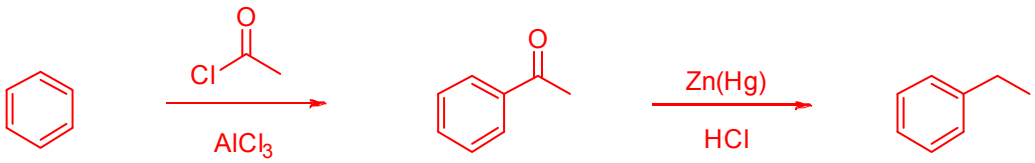


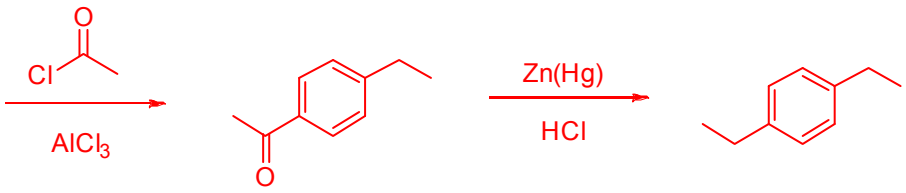
mix of stereoisomers
but esters are *cis*

Problem IV. Synthesis (20 points). Design an efficient synthesis of compound **F** from the indicated starting materials and any other reagents you wish. Assume that your boss has a passionate hatred of overalkylation and insists that under no circumstances are you allowed to use Friedel–Crafts alkylation reactions (but acylations are OK). Note: You can accomplish this synthesis in five steps.



F





Note: Friedel–Crafts alkylation is generally a poor method for the functionalization of aromatic rings due to the likelihood of overalkylation. With that said, you can see that using Friedel–Crafts acylation to avoid Friedel–Crafts alkylation can be quite tedious.