

CH 254, Spring 2008

Name KGY

Exam #2, 14 March 2008

(PRINT CLEARLY PLEASE!)

Question #

Points Possible

Points Received

1

20

2

8

3

15

4

12

5

9

6

5

7

16

8

15

Subtotal

100

Extra Credit

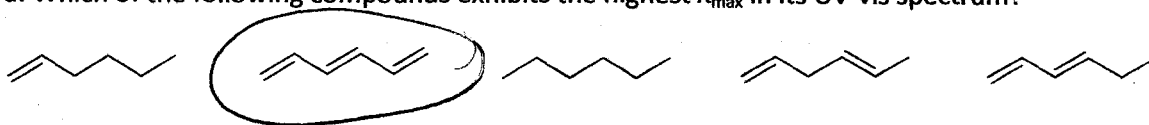
6

Total

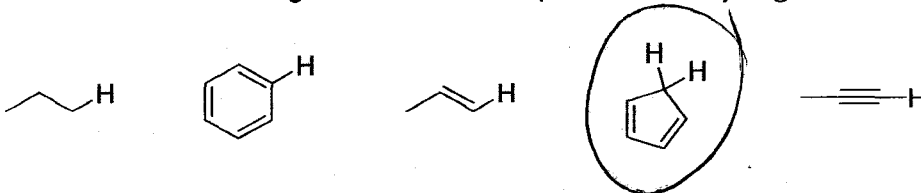
106

1. (20 points) Multiple Choice. For each question, circle ONE answer.

a. Which of the following compounds exhibits the highest λ_{max} in its UV-vis spectrum?



b. Which of the following is the most acidic? (Focus on the hydrogen indicated.)



c. Which of the following is not a correct statement about the electrophilic aromatic substitution mechanism?

- 1) Benzene functions as a nucleophile.
- 2) Formation of a carbocation intermediate is the rate-determining step.
- 3) The carbocation intermediate contains an sp^3 hybridized carbon in the ring.
- 4) The addition product is a frequent minor product.
- 5) Aromaticity is regained by loss of H^+ .

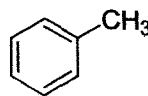
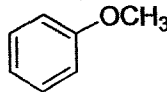
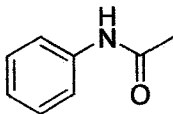
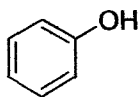
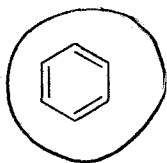
d. Which of the following is not a correct statement concerning the Friedel-Crafts acylation of benzene?

- 1) An alkyl group substitutes for a hydrogen.
- 2) The benzene ring attacks an acylium ion.
- 3) The acylium ion is resonance stabilized.
- 4) The acylium ion is most often produced from an acid chloride.
- 5) More than one equivalent of Lewis acid must be used.

e. The name 2,4,6-tribromobenzene is incorrect. Which of the following is the correct name?

- 1) tribromobenzene
- 2) *m,m*-dibromobromobenzene
- 3) 3,5-dibromobromobenzene
- 4) 1,3,5-tribromobenzene
- 5) *m,m,m*-tribromobenzene

f. Which of the following compounds reacts most slowly during nitration?



g. Which of the following substituents acts as a moderate activator and ortho/para director?

- 1) -Br
- 2) -SO₃H
- 3) -CO₂H
- 4) -NHCOR
- 5) CHO

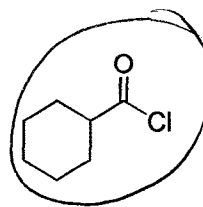
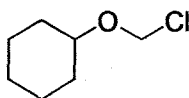
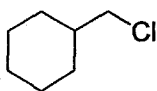
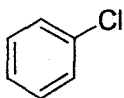
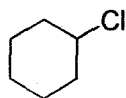
h. Which of the following does not form benzoic acid when heated in the presence of acidic Na₂Cr₂O₇?

- 1) 1-phenylethanol
- 2) 2-phenylethanol
- 3) 2-phenylheptane
- 4) 2-methyl-2-phenylheptane
- 5) 1-phenylheptanol

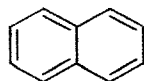
i. In electrophilic aromatic substitution reactions, a chlorine substituent:

- 1) is a deactivator and a *m*-director
- 2) is a deactivator and an *o,p*-director
- 3) is an activator and a *m*-director
- 4) is an activator and an *o,p*-director
- 5) prevents any further reaction

j. Which of the following compounds is an acyl chloride?

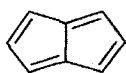


2. (8 points) Hückel's Rule applies only to compounds with a single ring, such as benzene and cyclobutadiene. However, it can be used with polycyclic compounds if the resonance structure with all of the double bonds on the periphery of the ring is considered. For example, using such a structure for naphthalene shows 10 electrons along the periphery, so it is predicted to be aromatic.

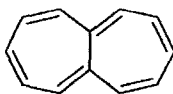


naphthalene

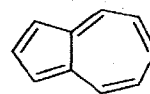
Use this information to explain why two of the following compounds are very reactive, while the third is quite stable.



8 e'



12 e'



10 e'

outer
ring



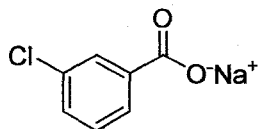
anti aromatic
v. reactive
(4n)

aromatic
v. stable
(4n+2)

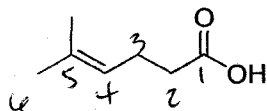
3. (15 points) Name each of the following molecules using proper IUPAC nomenclature. Don't forget to indicate stereochemistry as appropriate.



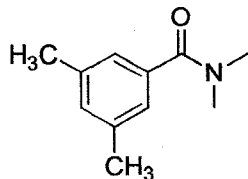
pyridine



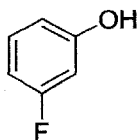
sodium 3-chlorobenzoate
sodium m-chlorobenzoate



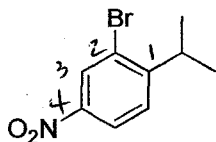
5-methyl-4-hexenoic acid



N,N-dimethyl-3,5-dimethylbenzamide



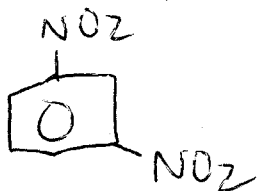
3-fluorophenol
m-fluorophenol



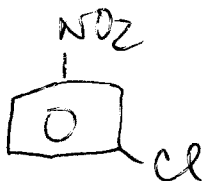
2-bromo-1-isopropyl-4-nitrobenzene

4. (12 points) Show the major product of the reaction of nitrobenzene with each of the following sets of reagents:

a) $\text{HNO}_3, \text{H}_2\text{SO}_4$



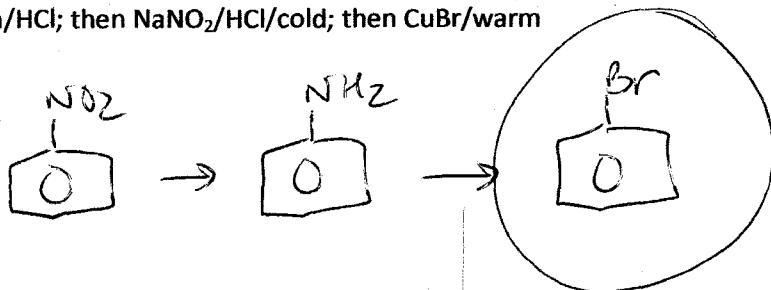
b) $\text{Cl}_2, \text{FeCl}_3$



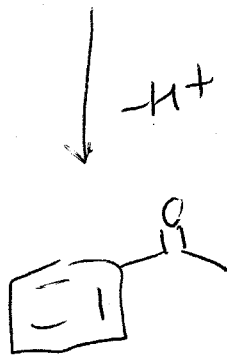
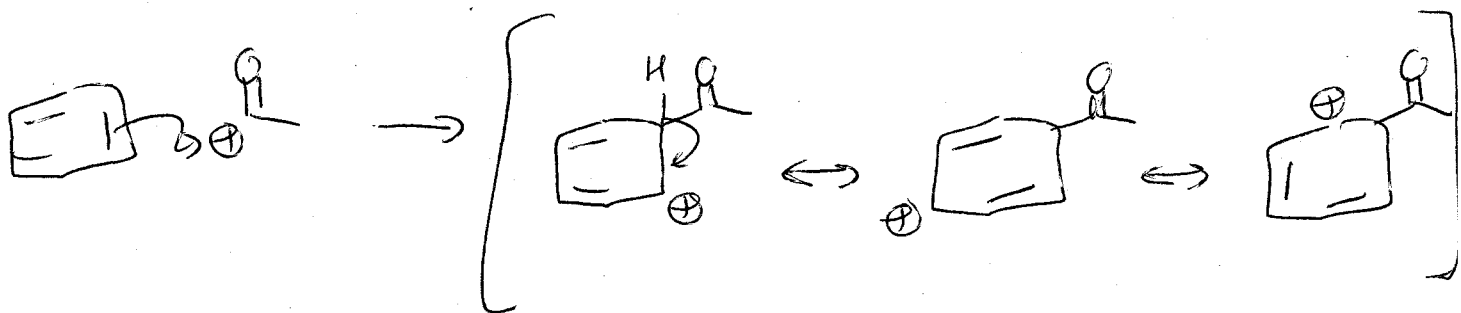
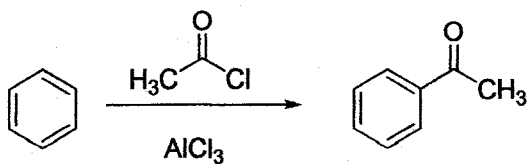
c) $\text{CH}_3\text{COCl}, \text{AlCl}_3$

NRX

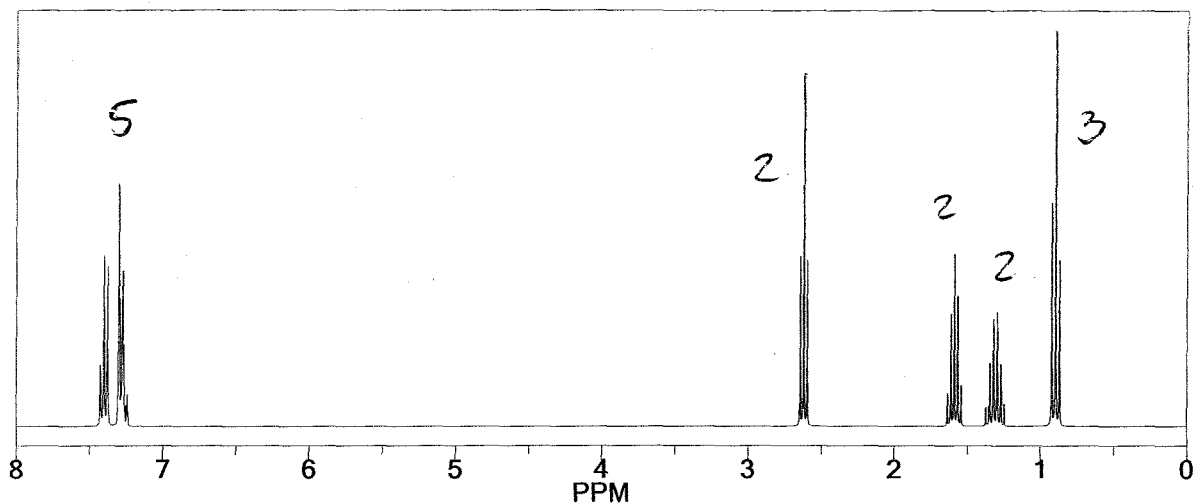
d) Sn/HCl ; then $\text{NaNO}_2/\text{HCl}/\text{cold}$; then CuBr/warm



5. (9 points) Provide a complete mechanism for the following transformation. Include all important resonance structures.



6. (5 points) Benzene underwent a Friedel-Crafts acylation followed by a Clemmensen reduction. The product gave the following ^1H NMR spectrum (integrals, from left to right, 5H; 2H; 2H; 2H; 3H):



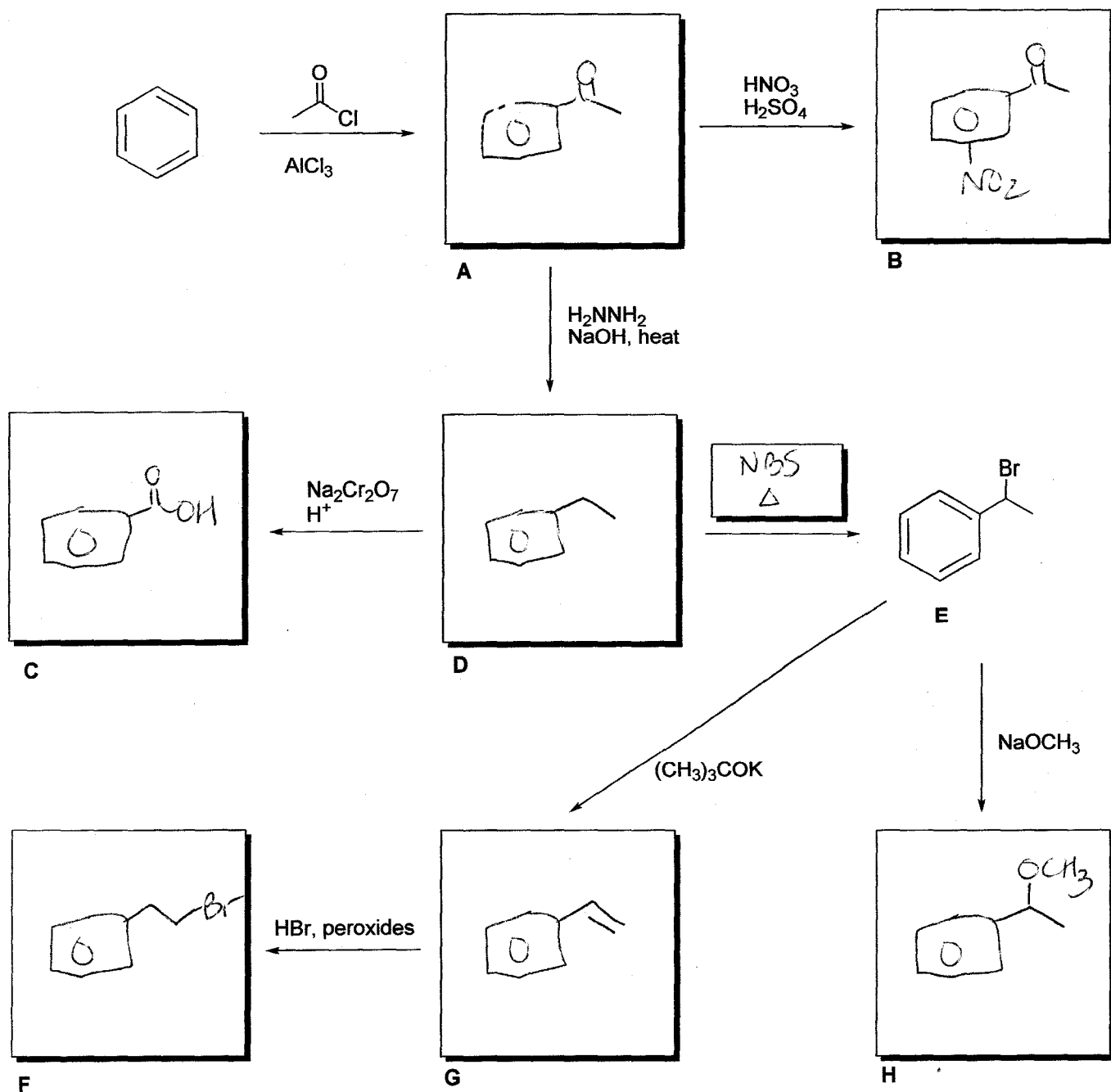
What is the structure of the acyl chloride that was used in the first step?

NMR IS

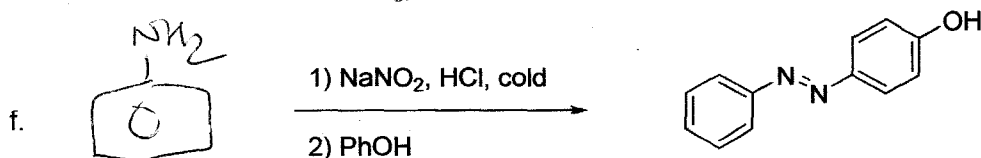
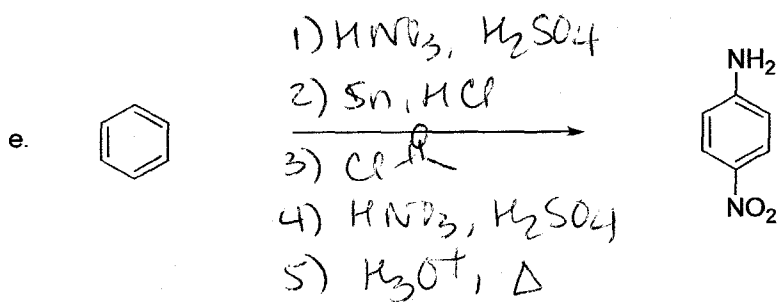
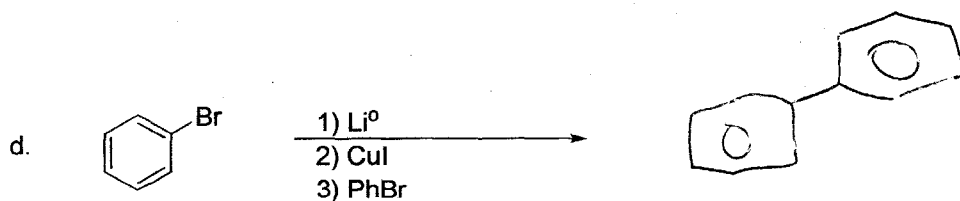
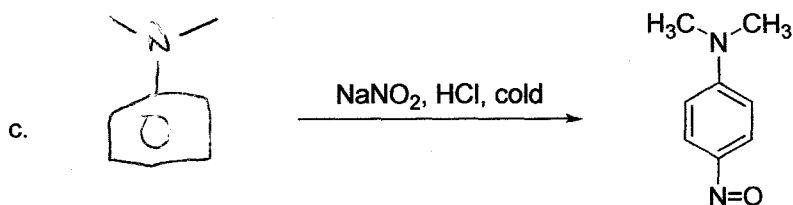
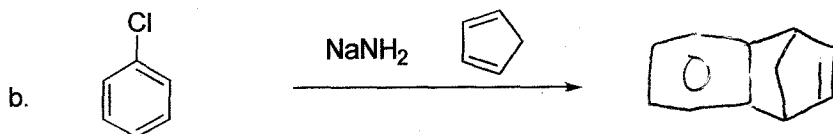
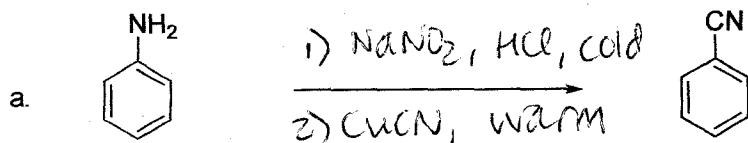


acyl chloride was

7. (16 points) Box problem! Fill in the blanks. ☺



8. (15 points) Each of the following reactions is missing either the reactant(s), the reagent(s), or the product(s). Fill in the missing information so as to successfully complete the equation; keep in mind that "NRX" is always a viable product. Your best five of the six reactions given will be counted.



EXTRA CREDIT

1. Give the "name" of the following:

- a. Problem 5 Friedel-Crafts acylation
- b. Problem 7, conversion of A to D Wolff-Kishner
- c. Problem 8b Diels-Alder
- d. Problem 8d Gilman

2. Who was the founder of the Boy Scouts?

Baden Powell