Exam #3 Chemistry 220B (01) Kaszynski March 23, 2006

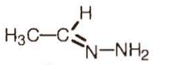
Student Name: Key (please print)

Honor Pledge: ________________________ (signature)

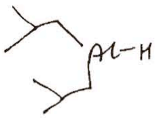
You have 50 minutes to complete this exam. Exams are due promptly at 10:50. Partial credit will be given for partially correct answers in most cases, so be sure to show your work.

I. General Knowledge & Exam 2 review (40 pts)

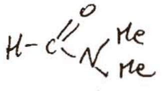
1. (10 pts) Give the structures of the molecules written below and provide the names of any structures shown.


$H_3C-C(H)=N-NH_2$

acetaldehyde hydrazone

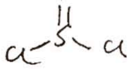


DIBAL-H



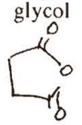
N,N-dimethyl formamide

ethylene glycol

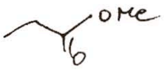


thionyl chloride

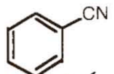
cyclohexanone enol tautomer



Succinic anhydride



methyl propionate



benzonitrile

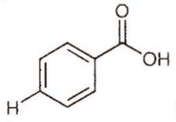
$Ph_3C-COOH$

triphenylacetic acid

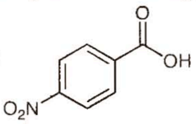
2. (6 pts) True or False. **Read the questions carefully**. (Circle **T** or **F**)

i. $LiAlH_4$ is a less potent reducing reagent than $NaBH_4$. T [✓ F]
ii. More acidic compounds have lower pKa. [✓ T] F
iii. Esters are more reactive toward nucleophiles than are acid anhydrides. T [✓ F]

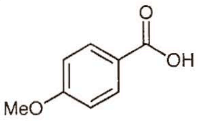
3.(4) Based on activation/deactivation effects of substituents towards aromatic electrophilic substitution, provide order of acidity of the following benzoic acids:



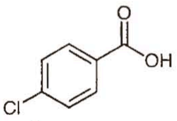
1



2



3



4

Most acidic 2
4
1
Least acidic 3

problem points name:______________________

I. General knowledge (page 1)______ (20 pts)

(page 2) ______ (21 pts)

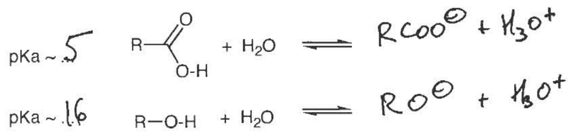
II. Reactions ______ (34 pts)

III. Mechanisms ______ (20 pts)

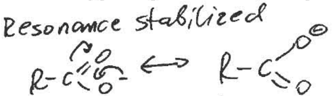
IV. Synthesis ______ (10 pts)

TOTAL ______ (105 pts) (5 pts extra credit)

4. (5 pts) Although heterolytic dissociation of the O–H group is responsible for the acidity of both carboxylic acids and alcohols, the former is far more acidic than the latter. Write the typical pKa values, complete the reactions, and explain the difference in the acidity.

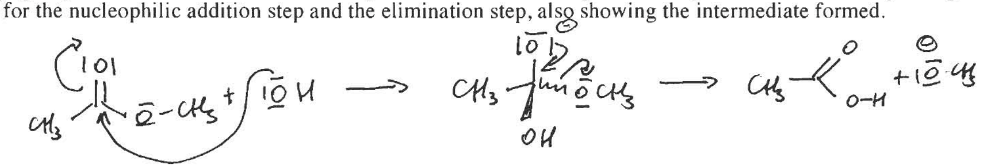


Resonance stabilized

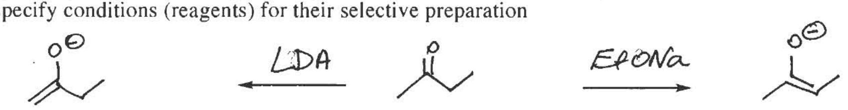


charge distributed onto two electronegative atoms (oxygens)

5. (5 pts) One of the most common reactions of carboxylic acid derivatives is nucleophilic substitution at the carbonyl group. Write this reaction below for **hydroxide anion** reacting with **methyl acetate** and use e- pushing arrows for the nucleophilic addition step and the elimination step, also showing the intermediate formed.



6. (5 pts) Deprotonation of 2-butanone produces the kinetic or thermodynamic **enolates**. Show both enolates and specify conditions (reagents) for their selective preparation



kinetic enolate 2-butanone theromodynamic enolate

7. (6 pts) A compound (C_3H_5N) with an IR absorption at 2235 cm^{-1} was treated with ethylmagnesium bromide and the mixture was decomposed with aqueous acid. The isolated product exhibits the following spectroscopic properties: **IR** strong peak at 1710 cm^{-1}, **^{13}C NMR** (fully decoupled): δ (ppm) 206, 45, 20; **^{1}H NMR**: δ (ppm) 2.4 (q, 2H), 1.1 (t, 3H) [t=triplet, q=quartet]. Write the structures of the reactant and the product. Ascribe observed spectral data to the molecular fragments.

$CH_3-CH_2-CN + EtMgBr \xrightarrow[2.\ H_3O^+]{1.\ Rxn} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$ ← t at 1.1 ppm.

IR ν_{CN} 2235

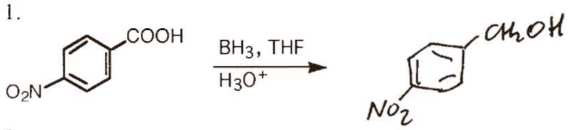
q at 2.4 ppm

^{13}C : 206 ppm

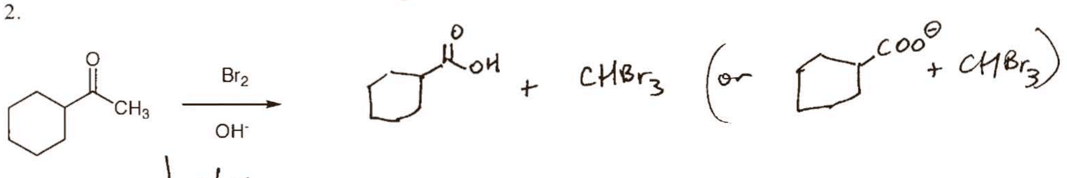
IR: 1710 cm^{-1}

II. Reactions (34 pts total, 3 pts each reaction reaction, + 1 pt for each name) Draw structures (including stereochemistry) of the expected organic products formed under the following reaction conditions and provide the names of the reactions where requested.

1.



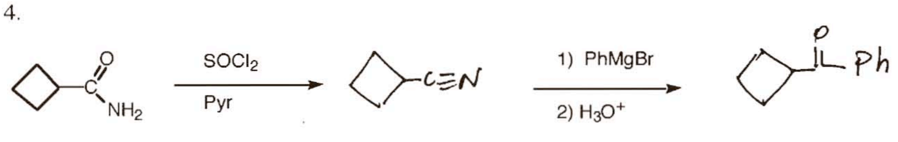
2.



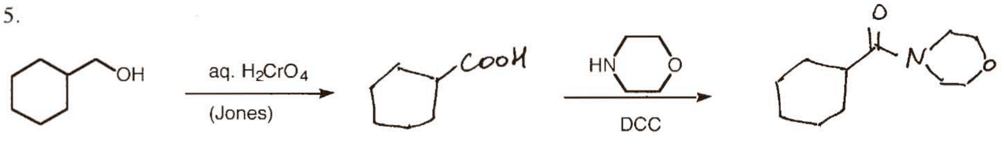
name: haloform

3.

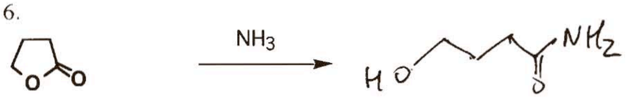
4.



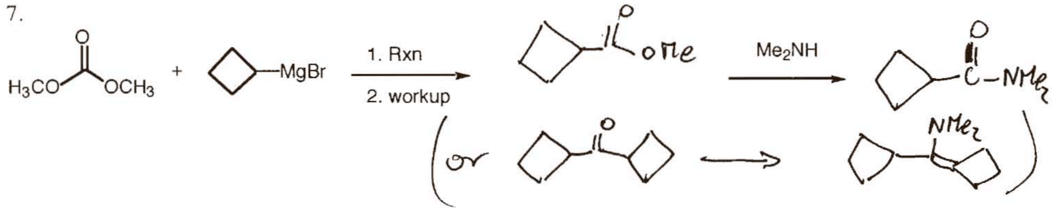
5.



6.

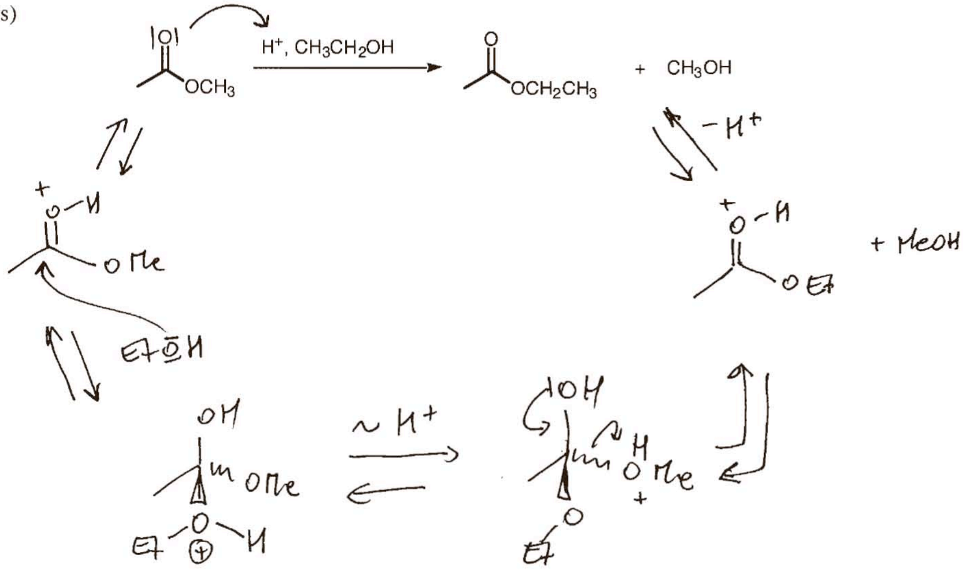


7.

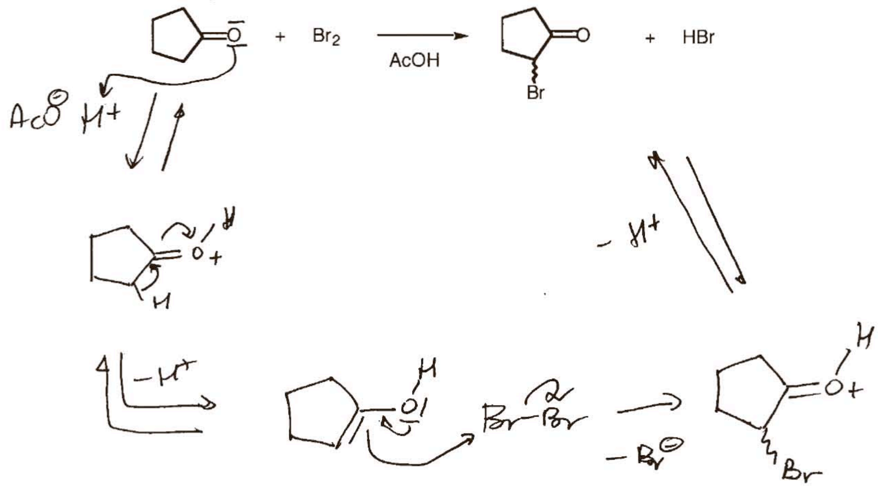


III. Mechanism (20 pts) Provide detailed mechanisms for the transformations given below, showing every step in the process clearly. Use electron pushing arrows.

(a) (10 pts)

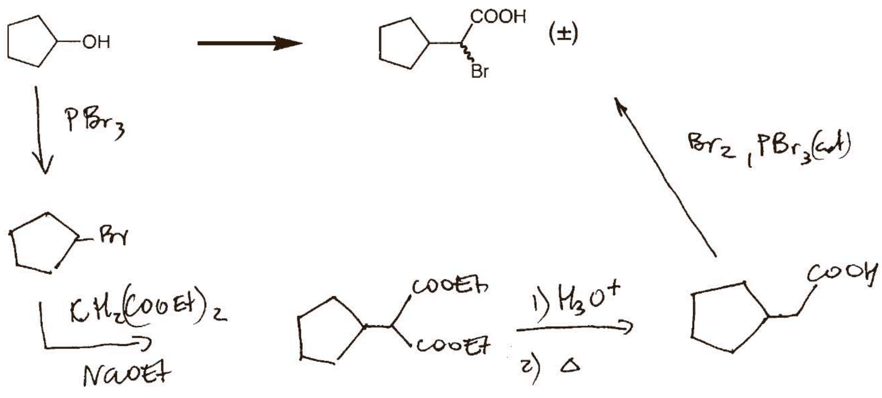


(b) (10 pts)

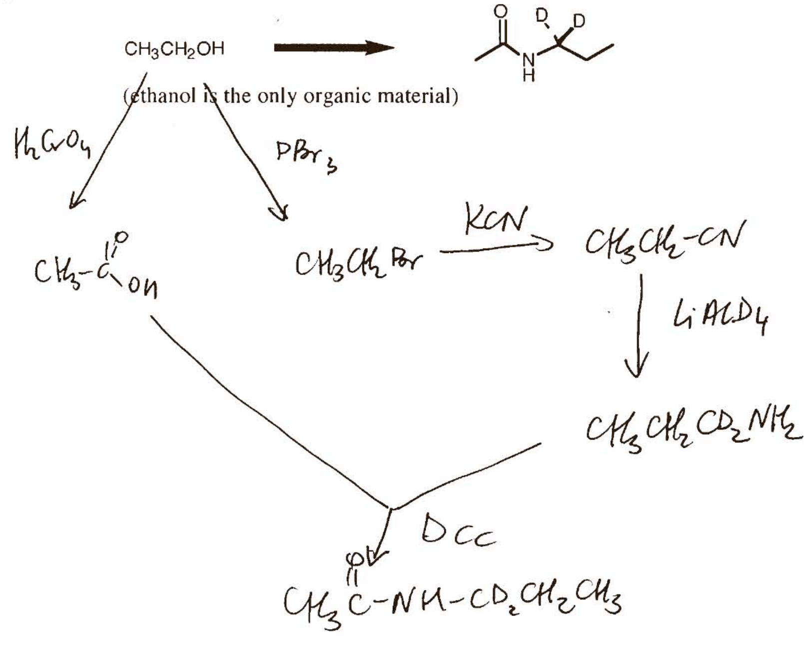


IV. Synthesis (10 pts) Provide a reaction sequence to accomplish *one of the two* following conversions (left to right) using specified organic compounds and any inorganic reagent needed to convert the carbons of the starting material into the product structure. Show reactants, products, and necessary reagents for each step in the sequence, but do not show mechanisms here. Partially correct answers will receive partial credit. Mark clearly the problem that you want us to grade.

(1)



(2)



(ethanol is the only organic material)