

Key

Exam #1

Chemistry 220B (01) Kaszynski

February 2, 2006

Student Name: _____ (please print)

Honor Pledge: _____ (signature)

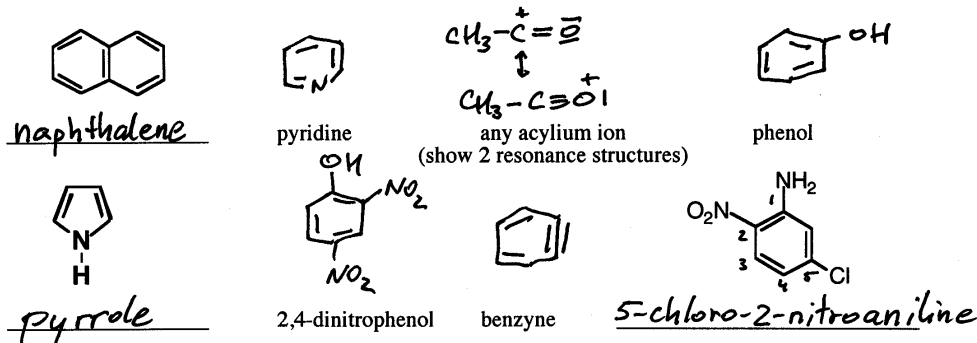
You have 50 minutes to complete this exam. Exams are due promptly at 10:50. Partial credit will be given for partially correct answers in most cases, so be sure to show your work.

I. General Knowledge (27 pts)

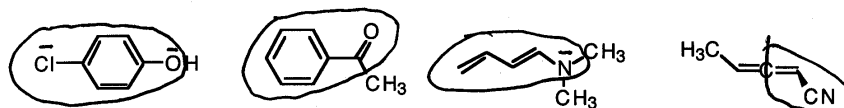
1. (3 pts) π -Aromaticity is a fundamental concept in chemistry that involves some of the following terms (circle all that are necessary):

π -conjugation (circular array) florist shop ($4n+2 e^-$) filled orbitals (p-orbitals)

2. (8 pts) Give the structures of the molecules written below and provide the names of any structures shown.



3. (4 pts) Circle the complete sets of any π conjugated atoms (of length ≥ 3 atoms) in the molecules below.



4. (2 pts) Attaching π electron withdrawing groups to an aromatic ring (circle one) activates (deactivates) the ring toward electrophilic aromatic substitution and directs the substitution reaction to (circle all that apply) the ortho (meta) para position(s).

5. (4 pts) True or False (Circle T or F)

i. The two Kekulé resonance forms of benzene are in equilibrium with each other. T (F)

ii. Electron-withdrawing groups activate aryl halides toward nucleophilic aromatic substitution. (T) F

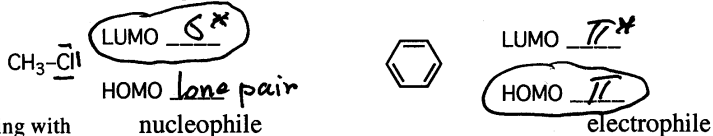
6. (6 pts) Circle the π electron donating groups listed below and box-in the π electron withdrawing groups.



problem	points
I. general knowledge	_____ (27 pts)
II. MO's and UV-vis	_____ (25 pts)
III. reactions	_____ (23 pts)
IV. mechanisms	_____ (20 pts)
V. synthesis	_____ (10 pts)
TOTAL	_____ 105 pts (5 pts extra credit)

II. MO's, Aromaticity, Spectroscopy, and Reactivity (25 pts)

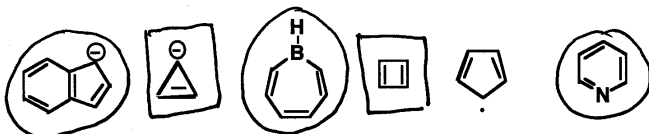
1. (6 pts) Give HOMO and LUMO orbital types for these molecules (σ , π , π^* , σ^* , or nonbonding):



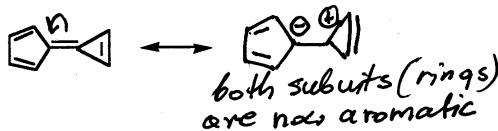
circle the orbital interacting with

nucleophile

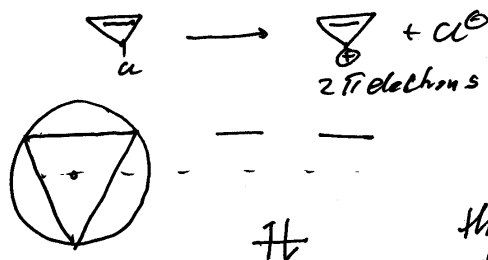
2. (6 pts) Of the following, circle the aromatic molecules, box-in the anti-aromatic species, and do not disturb molecules which are neither aromatic nor anti-aromatic.



3. (3 pts) A hydrocarbon (shown on the right) displays an unusually high dipole moment. Using resonance structures account for the polar character of the molecule and explain its origin.



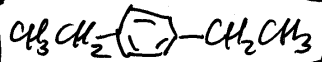
4. (5 pts) 3-Chlorocyclopropene relatively easily dissociates into ions. Using the "circle trick" construct the π MO energies of the cyclopropenyl cation and explain this abnormal reactivity of the compound.



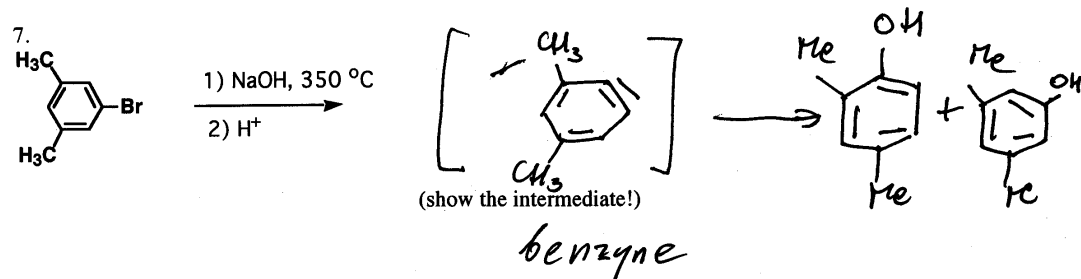
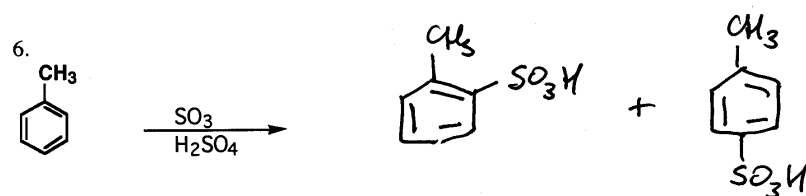
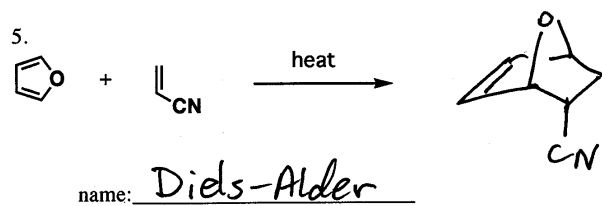
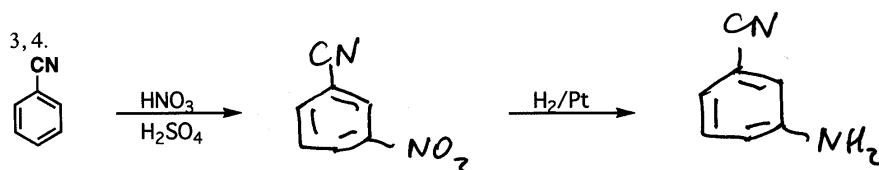
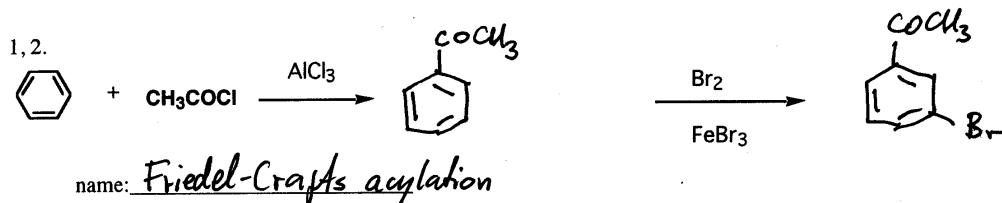
the cation is aromatic
 $(4n+2 e^- n=0)$
 therefore there is high tendency to form it.

5. (5 pts) A hydrocarbon $\text{C}_{10}\text{H}_{14}$ shows the following spectral characteristics: $^1\text{H NMR}$ δ 1.20 (t, 6H), 2.70 (q, 4H), 7.18 (s, 4H); The $^{13}\text{C NMR}$ spectrum shows only four signals: two aliphatic and two aromatic. Identify the compound (hint: s = singlet, t = triplet, q = quartet).

absorption at 1.20 and 2.70 ppm indicates an ethyl group; two distinct aromatic carbons + a siglet at 7.18 ppm (4H) suggests p-subst. benzene.



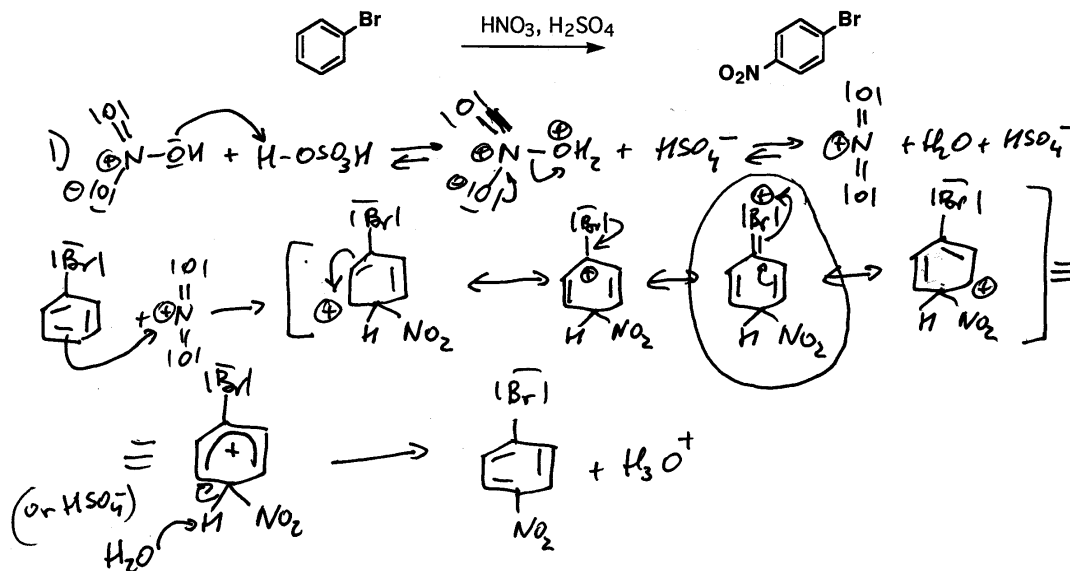
III. Reactions (23 pts; 3 pts each rxn, 2 pts for the name) Draw structures of the expected organic products (some of these reactions may give you more than one product) formed under the following reaction conditions and provide the name of the reaction where requested. If no reaction takes place, write "no reaction".



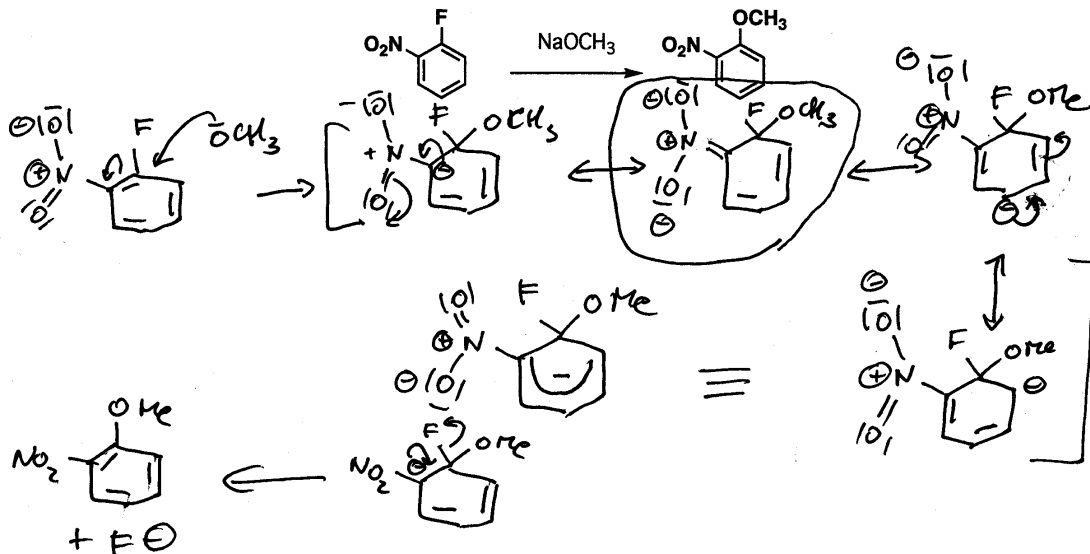
IV. Mechanism (20 pts) Provide detailed mechanisms for the transformations given below, showing each step in the process clearly. Use **electron pushing arrows** to show the flow of electrons.

(a) (10 pts) *Show the formation of the electrophile!

*Show **all** resonance structures for the intermediates and box-in the most important resonance structure.

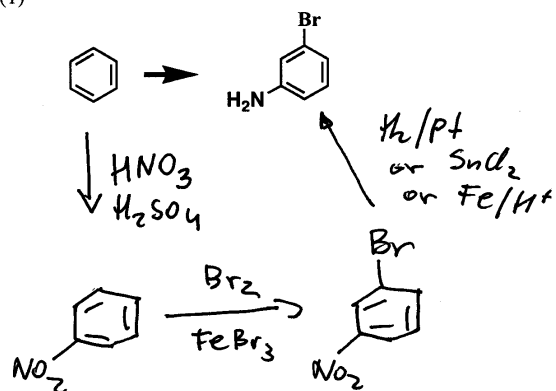


(b) (10 pts) Show **all** resonance structures for the intermediates and box-in the most important resonance structure.



V. Synthesis (10 pts) Provide a reaction sequence to accomplish *one of the two* following conversions (left to right) using any reagents you need. 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.

(1)



(2)

