

### Practice Exam #1

#### I. General Knowledge (28 pts)

1. (6 pts)  $\pi$ -Aromaticity is a fundamental concept in chemistry that involves some of the following terms (**circle all that are necessary**):

circular array   
  filled orbitals   
  p-orbitals   
  florist shop   
   $\pi$ -conjugation   
   $4n+2 e^-$

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



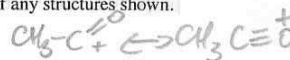
nitronium ion



aniline

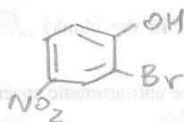


benzyne

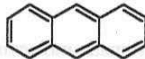


any acylium ion  
(show 2 resonance structures)

structures)



2-bromo-4-nitrophenol



anthracene

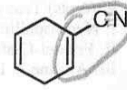
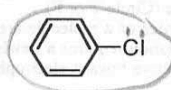
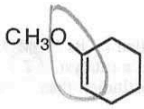
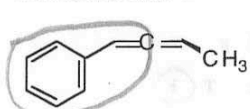


pyridine



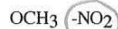
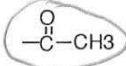
4-nitrotoluene

3. (4 pts) Circle the complete sets of any  $\pi$  conjugated atoms (of length  $\geq 3$  atoms) in the molecules below.



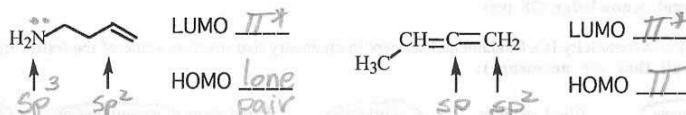
4. (4 pts) Attaching  $\pi$  electron donation groups to an aromatic ring (**circle one**) *activates*/ *deactivates* the ring toward electrophilic aromatic substitution and directs the substitution reaction to (**circle all that apply**) the *ortho*/ *meta*/ *para* position(s).

5. (6 pts) Circle **all** groups that deactivate benzene ring toward electrophilic aromatic substitution.

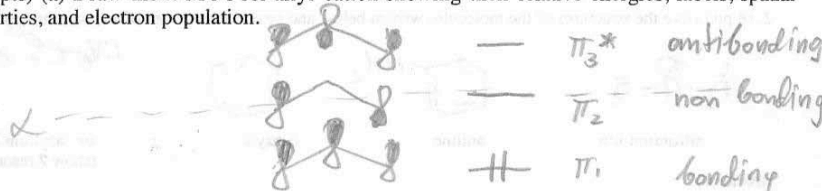


## II. MO's, Aromaticity, and UV-vis Spectroscopy (30 pts)

1. (4 pts) Identify the hybridization level (i.e.  $sp^3$ ,  $sp^2$ ,  $sp$ ) at the indicated atoms in the following molecules and give HOMO and LUMO orbital types for these molecules ( $\sigma$ ,  $\pi$ ,  $\pi^*$ ,  $\sigma^*$ , or nonbonding):

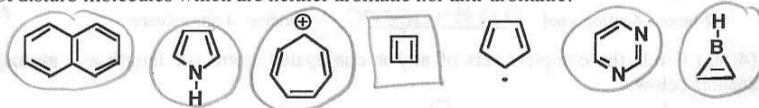


2. (6 pts) (a) Draw the  $\pi$  MO's for allyl cation showing their relative energies, labels, spatial properties, and electron population.



(b) The UV-vis absorption for allyl cation would involve a (fill in the blank)  $\pi_1$  to  $\pi_2$  transition.

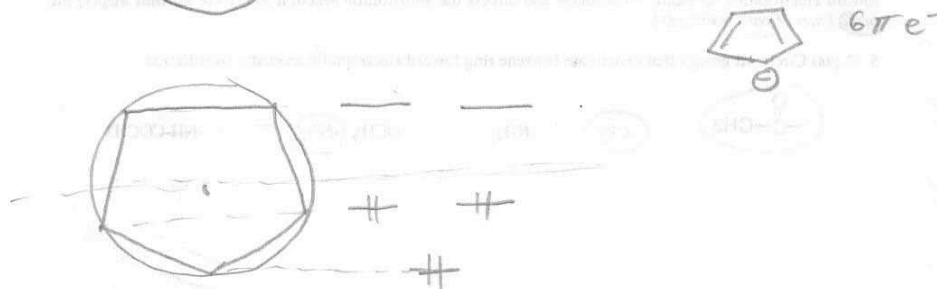
3. (7 pts) Of the following, **circle** the aromatic molecules, **box-in** the anti-aromatic species, and do not disturb molecules which are neither aromatic nor anti-aromatic.



4. (6 pts) True or False (Circle T or F)

- i. Nucleophilic properties of a molecule are controlled by its HOMO.  T  F
- ii. Friedel-Crafts alkylation requires a Lewis acid as a catalyst.  T  F
- iii. Aniline is less reactive toward electrophilic substitution than is benzene.  T  F

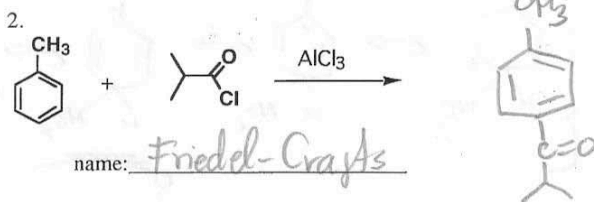
5. (7 pts) Using the "circle trick" construct the  $\pi$  MO energies of cyclopentadienyl anion. Is the molecule aromatic, anti-aromatic or neither (circle one)?



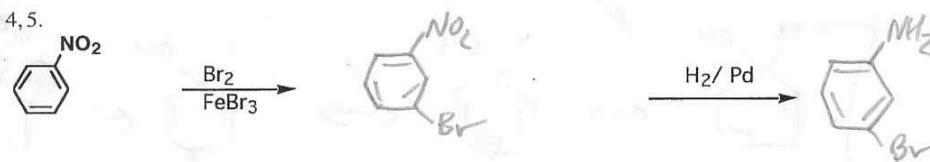
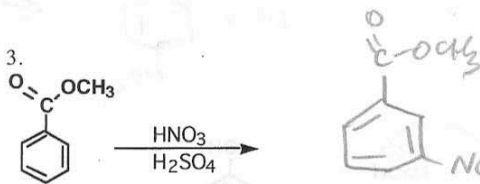
III. Reactions (17 pts; 3 pts each rxn, 1 pts each name) Draw structures of the expected organic products (some of these reactions may give you more than one product) formed under the following reaction conditions and provide the names of the reactions where requested.



name: Diels-Alder

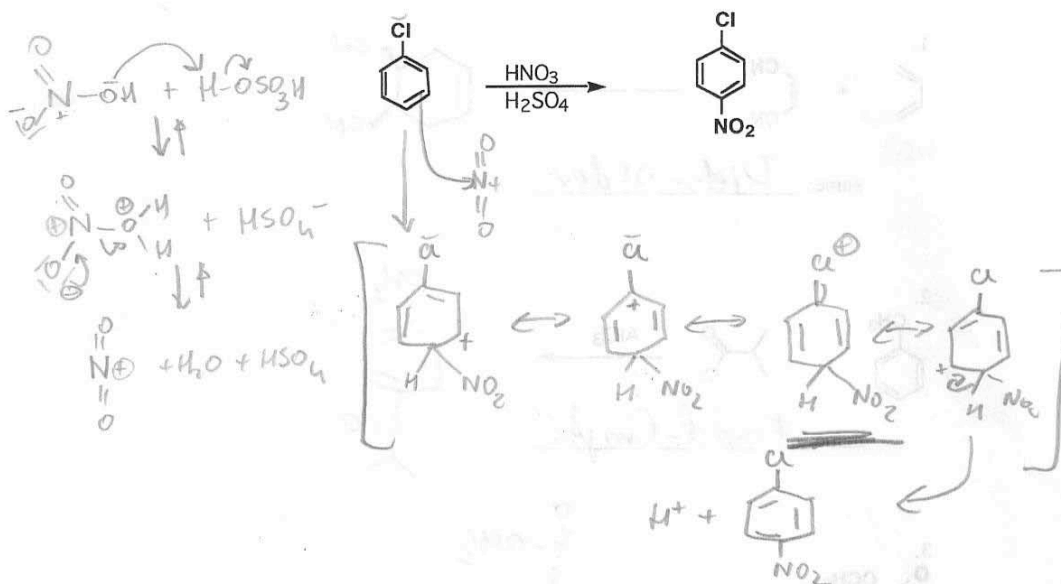


name: Friedel-Crafts

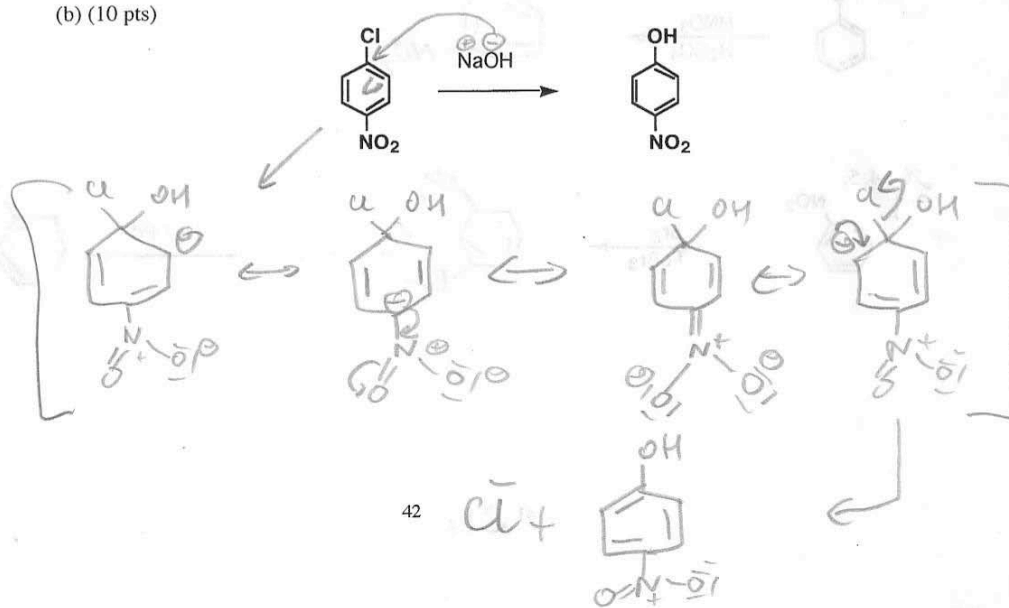


**IV. Mechanism (20 pts)** Provide detailed mechanisms for the transformations given below, showing each step in the process clearly. Show all resonance structures for the intermediates. I recommend that you use electron pushing arrows to show the flow of electrons.

(a) (10 pts)



(b) (10 pts)



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.

