JASPERSE CHEM 341 TEST 4 VERSION 1 Conjugation, Diels-Alder, Aromaticity, Aromatic Reactions

1. Provide the Name or Structure for the Following (7 points)



m-nitroaniline



## 2. Circle the aromatic molecules (6 points)



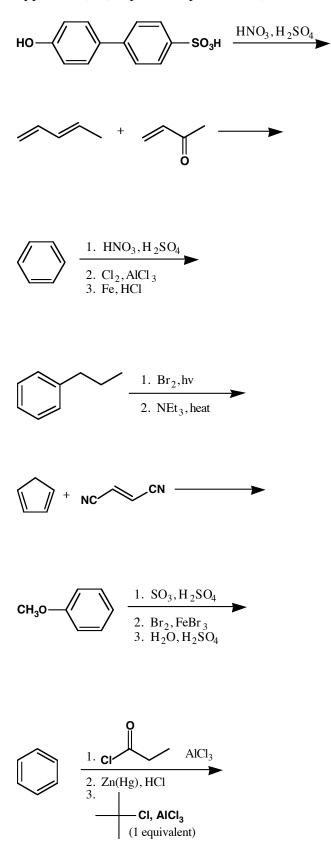
3. Outline the energies of the  $\pi$ -molecular orbitals for benzene, and draw electrons into the orbitals that are occupied. (5 points)

Nonbonding line -----

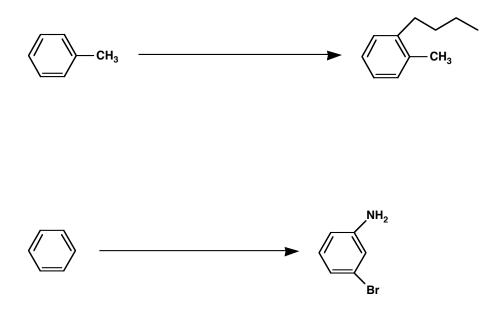
4. Bromide **B** has normal reactivity (for a 2° bromide) toward  $S_N 1$  substitution, but **A** has much higher reactivity and **C** has much lower reactivity. a) Why is **A** more reactive toward  $S_N 1$ ? b) Why is **C** much less reactive toward  $S_N 1$ ? (4 points)

$$\overbrace{A}^{\mathbf{Br}} \gg \overbrace{B}^{\mathbf{Br}} \gg \overbrace{C}^{\mathbf{Br}} = \operatorname{Kinetic reactivity toward}_{S_{N}1 \text{ reactivity } (H_{2}O, H^{+})}$$

5. Synthesis Reactions. Draw the feature product of the following reactions (need not show any byproducts). (21 points, 3 points each)



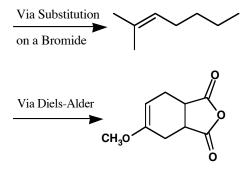
6. Design sequences for the designated conversions. (5 points each)



7. Design a synthesis for the following molecule beginning with toluene. (6 points)  $\mathbf{O}_2 \mathbf{N}$ 

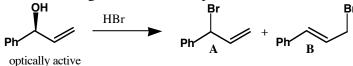
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8. Draw the Reactants for the Following (6 points)



9. a) Draw the major product for the following reaction, and b) draw the mechanism for its formation. c) Identify the slow step. d) Draw all the resonance structures for the cation intermediate and e) circle the most important contributor. (7 points)

10. (9 points total) a) Draw the mechanism for the following reaction, in which a common intermediate gives rise to both products.



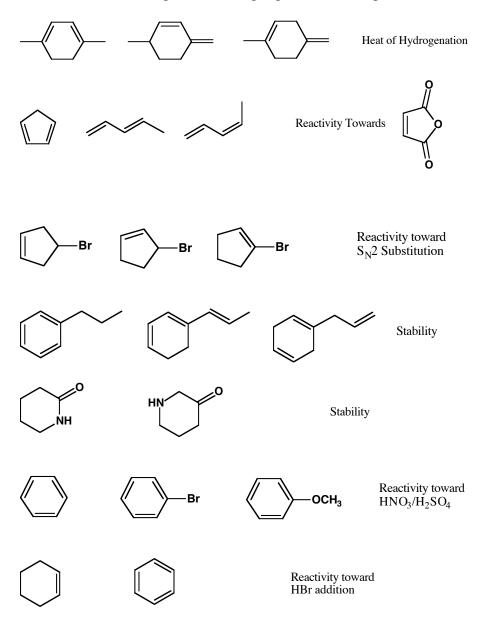
b) In the above reaction, is product **A** chiral or achiral?

c) Product **A** is formed preferentially at low temperature, but **B** is major when the reaction is conducted at high temperature such that product equilibration occurs. Which is the "thermodynamic" product (more stable, so it builds up under equilibrating conditions) and which is the "kinetic" product (less stable but forms preferentially under non-equilibrating conditions.)

Thermodynamic Control Product: Kinetic Product:

d) Draw the 2 relavant resonance structures for the key intermediate (or mark them if you already drew both in your mechanism). Circle the one that would make the greater contribution to the resonance hybrid. Why is the "kinetic" product formed preferentially under irreversible conditions?

11. Rank the following, with 1 being highest/most. (2 points each)



12. For each nitrogen in the molecule, classify the hybridization of the nitrogen atom, the hybridization of the nitrogen lone pair, and classify whether the basicity of the nitrogen is "normal" or "low". (5 points)

	Nitrogen Hybridization	Lone-Pair Hybridization	Nitrogen Basicity	
$N_{a}$				
$N_{b}$				H H
N <sub>c</sub>				$a $ $N $ $C $ $NH_2$ $d$
$N_{d}$				H Ö U