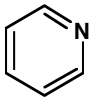
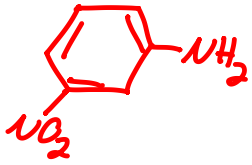
JASPERSE CHEM 350 TEST 4 VERSION 1
Conjugation, Diels-Alder, Aromaticity, Aromatic Reactions

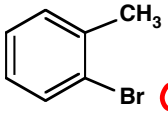
1. Provide the Name or Structure for the Following (7 points)



pyridine

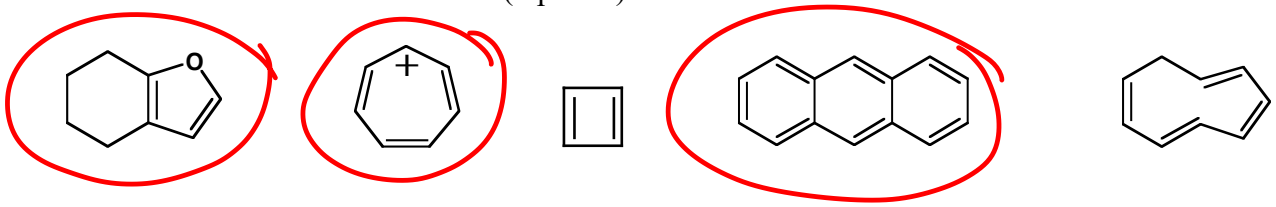
m-nitroaniline





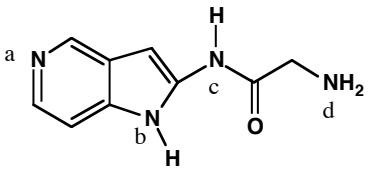
o-bromotoluene or 2- or ortho-

2. Circle the aromatic molecules (6 points)

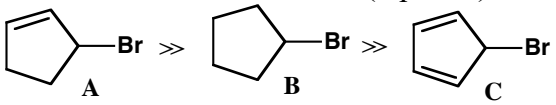


3. For each nitrogen in the molecule, classify the hybridization of the nitrogen atom, the hybridization of the nitrogen lone pair, and classify whether the basicity of the nitrogen is "normal" or "low". (5 points)

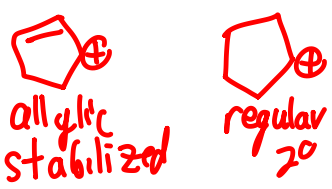
	Nitrogen Hybridization	Lone-Pair Hybridization	Nitrogen Basicity
N_a	sp^2	sp^2	normal
N_b	sp^2	p	low
N_c	sp^2	p	low
N_d	sp^3	sp^3	normal



4. Bromide **B** has normal reactivity (for a 2° bromide) toward S_N1 substitution, but **A** has much higher reactivity and **C** has much lower reactivity. a) Why is **A** more reactive toward S_N1? b) Why is **C** much less reactive toward S_N1? (4 points)



Kinetic reactivity toward S_N1 reactivity (H_2O, H^+)



allylic stabilized

regular 2°

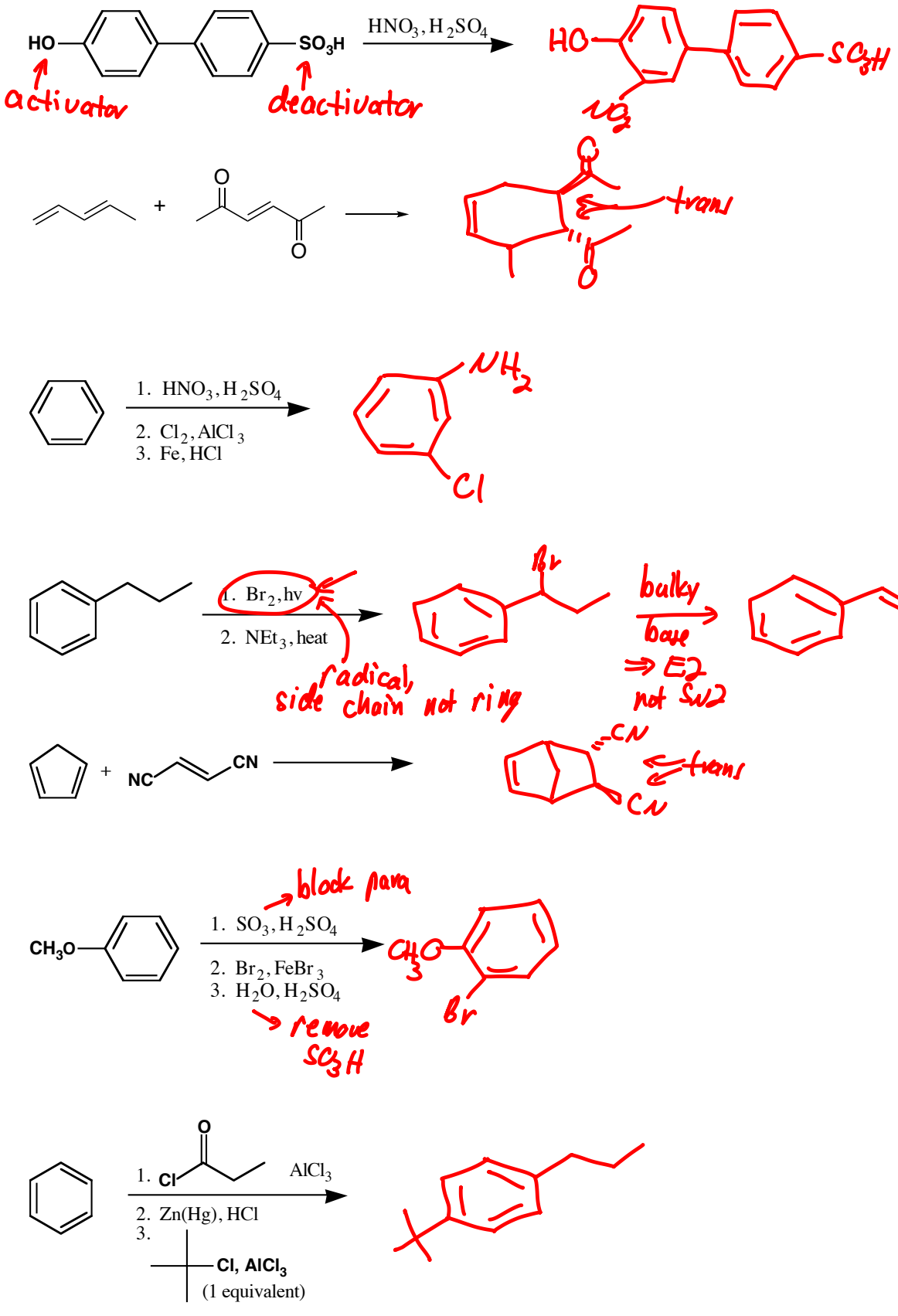
antiaromatic terrible

S_N1 ⇒ cation formation

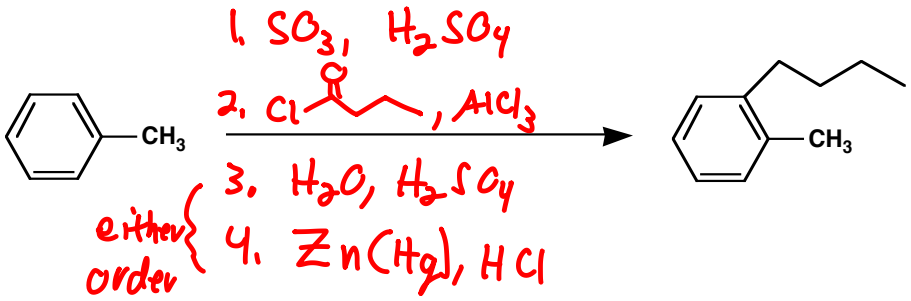
a) A ⇒ allylic stabilized cation

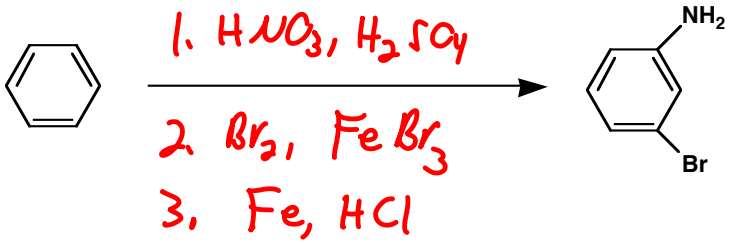
b) C ⇒ antiaromatic cation

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

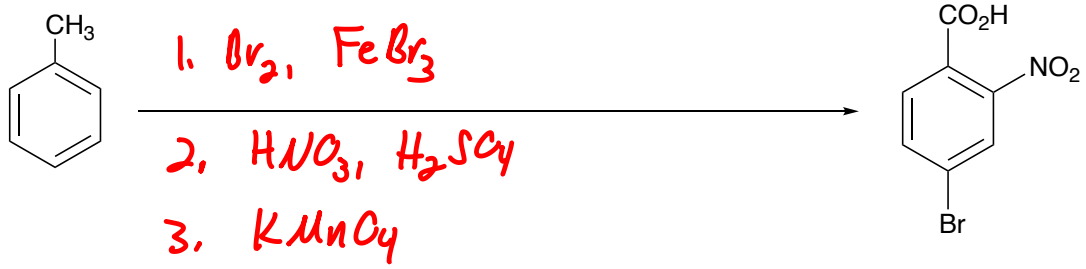


6. Design sequences for the designated conversions. (5 points each)



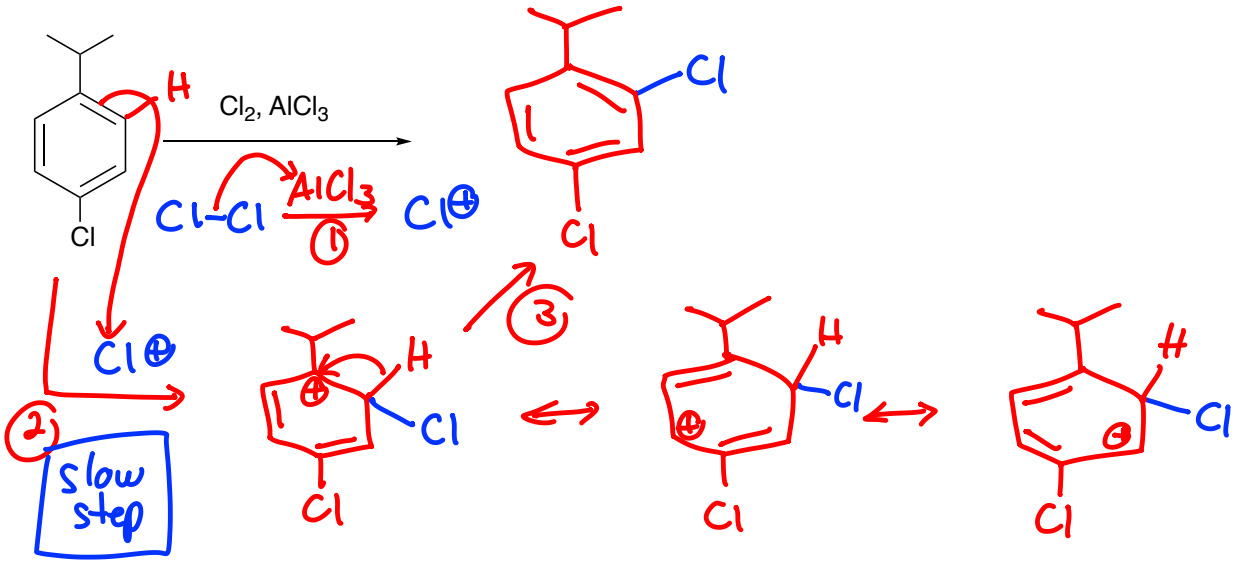


7. Design a synthesis for the following molecule beginning with toluene. (6 points)



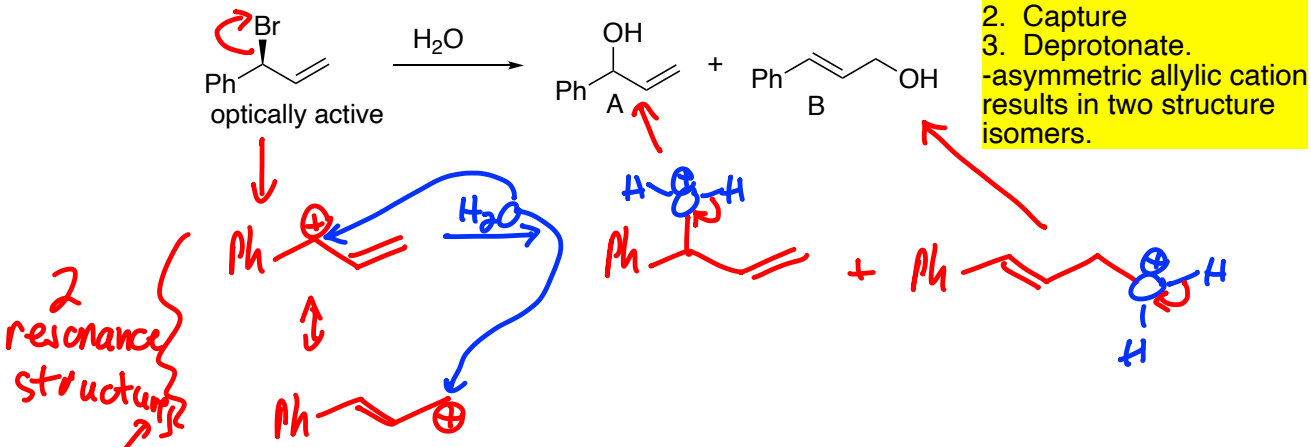
8. Draw the Reactants for the following (3 points)

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. (7 points)



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

SN1 mechanism:
1. Make cation
2. Capture
3. Deprotonate.
-asymmetric allylic cation results in two structure isomers.



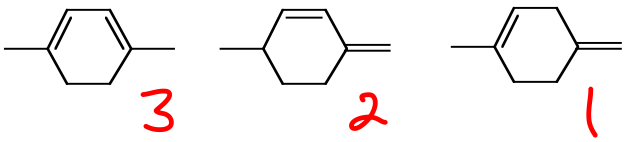
b) In the above reaction, is product **A** chiral or achiral? A is chiral (but would be racemic)

c) Which is the "thermodynamic" product (more stable, which builds up under equilibrating conditions)?

B is the thermodynamic product, due to both higher substitution (di-substituted versus mono-substituted) and also due to conjugation with the phenyl

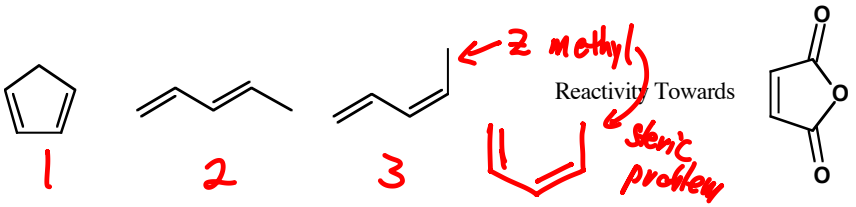
d) You probably already did this, but either re-draw or identify the two key resonance structures for the intermediate in the mechanism above. (You can just circle the two of them, assuming you already sketched them above.).

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



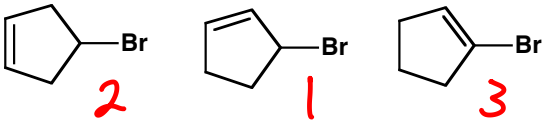
Heat of Hydrogenation

More stable, less heat.
Conjugated more stable than isolated
Higher substitution increases stability.



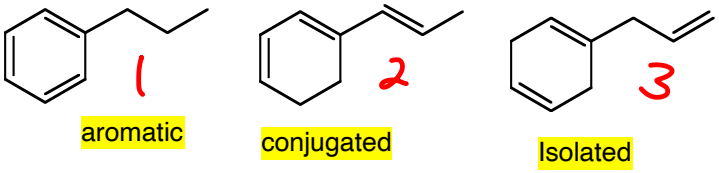
Reactivity Towards

Cyclopentadiene is always "s-cis"
Z-substituent retards reactivity



Reactivity toward S_N2 Substitution

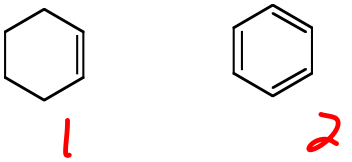
Allylic accelerates SN2
SN2 can't do vinyl/aryl



Stability

Stability

Reactivity toward HNO_3/H_2SO_4



Reactivity toward HBr addition

Aromatic stability makes it less reactive reactant. (Reactant stability/ reactivity principle.