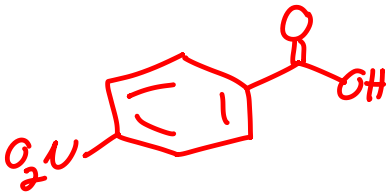
JASPERSE CHEM 350 TEST 4 VERSION 3
Conjugation, Aromaticity, Electrophilic Aromatic Substitution

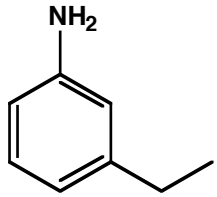
1. Provide Either the Name or the Structure for the Following Chemicals. (6 points) (3 minutes)

a. Furan

b. p-nitrobenzoic acid



c.

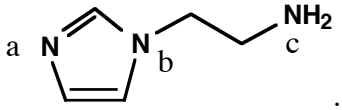


3-ethylaniline
Or m-ethylaniline
Or meta-ethylaniline

2. For the following substituents, classify each as 1) electron-donating or electron-withdrawing ["D" or "W"], 2) as activating or deactivating ["Act" or "Deact"], and as 3) ortho-para directing or meta directing ["o/p" or "m"]. (6 points) (2 minutes)

	-OCH_3	-CCH_2CH_3 (O)	-CH_3	-Cl
1. D or W	D	W	D	W
2. Act or Deact	Act	Deact	Act	Deact
3. o/p or m	o/p	m	o/p	o/p

3. The molecule below has 3 different nitrogens. For each of the nitrogens, classify the hybridization of the nitrogen atom, the hybridization of the nitrogen's lone pair, and whether the basicity of the nitrogen is "normal" or "low". (6 points, 2 min)



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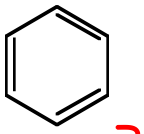
	Lone-Pair Hybridization	
N^a	sp^2	Double bonded
N^b	p	Conjugated
N^c	sp^3	Isolated

4. Rank the reactivity (rates!) of the following sets of molecules toward the reagents shown, 1 being most reactive, 2 being middle, and 3 being least reactive. (10 points) (6 minutes)

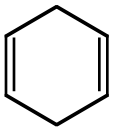
Reagent — Molecules Being Compared

a. H_2, Pt



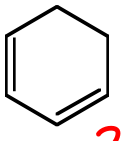
3

Aromatic, most stable



1

Isolated, least stable

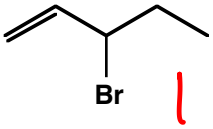


2

Conjugated

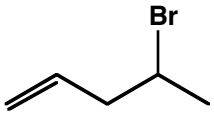
b. H^+, H_2O (S_N1/E1)

Carbocation is key



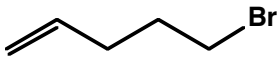
1

Allylic cation best



2

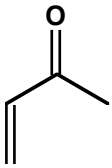
2° cation

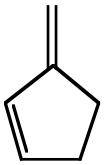


3

1° cation worst

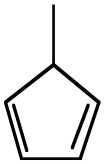
c.





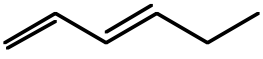
3

Never s-cis



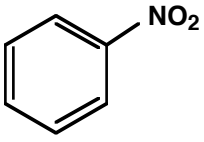
1

Always s-cis



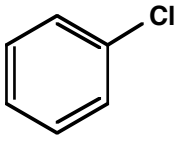
2

d. HNO_3, H_2SO_4

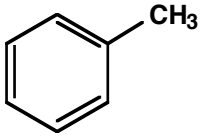


3

deactivator



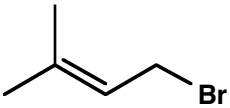
2



1

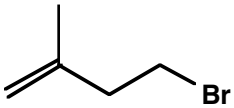
Activator

f. NaOMe
(S_N2 reactivity)

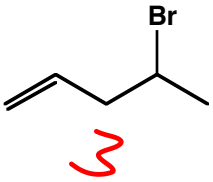


1

Allylic, fast



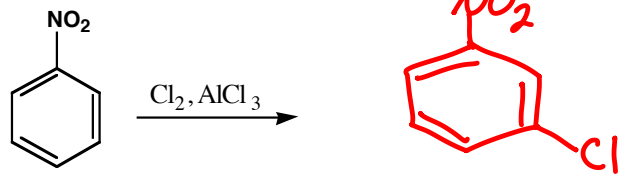
2

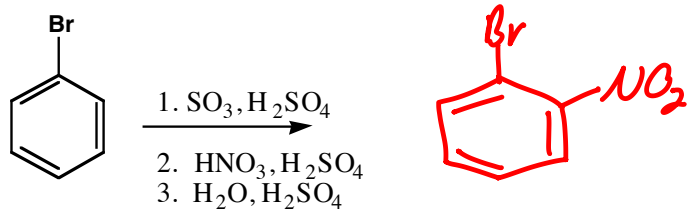


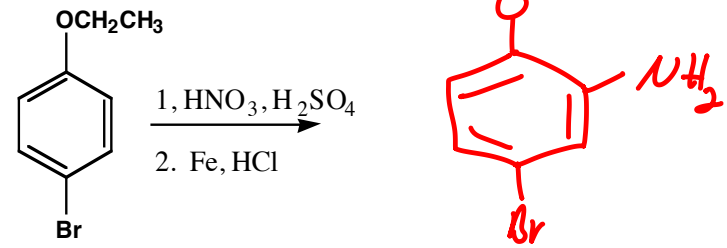
3

1° > 2° for SN2

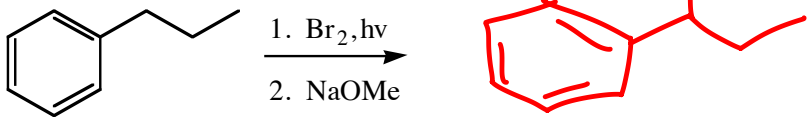
5. Draw the major product for each of the following reactions. (3 points each, 21 total, 7 minutes)

a. 

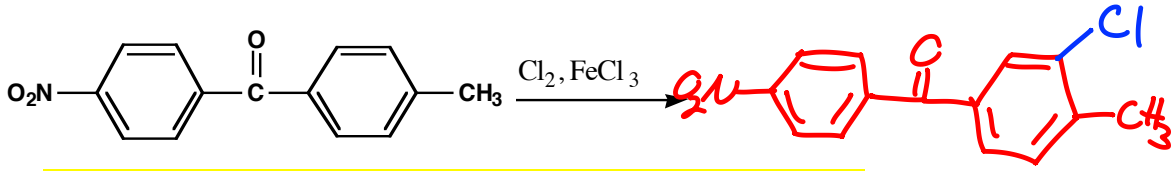
b. 

c. 

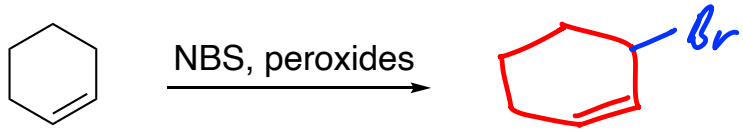
While both substituents are o/p directors, the oxygen group is much strong activator and dictates position.

d. 

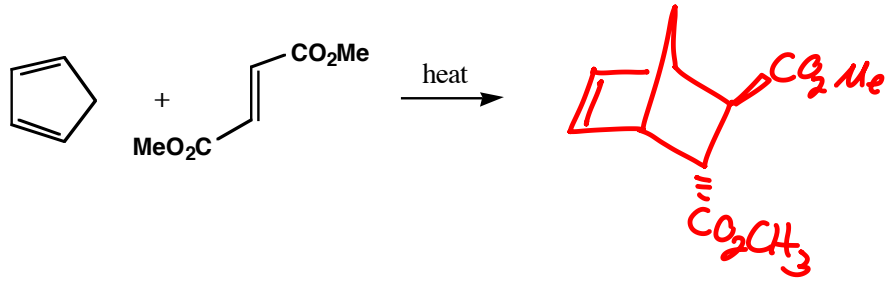
Br2 with Lewis acid adds to the ring. But under radical conditions, radical bromination occurs on the benzylic site. SN2 beats E2 because being allylic/ benzylic greatly activates SN2, plus methoxide is pretty small.

e. 

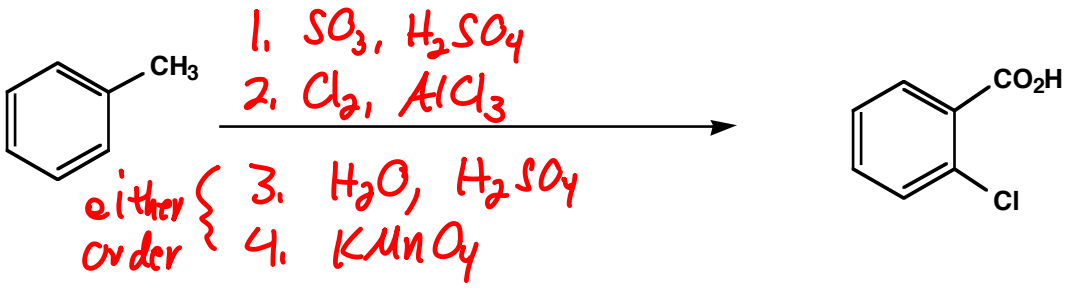
Nitro deactivates the left ring, so the methyl-activated right ring wins.

f. 

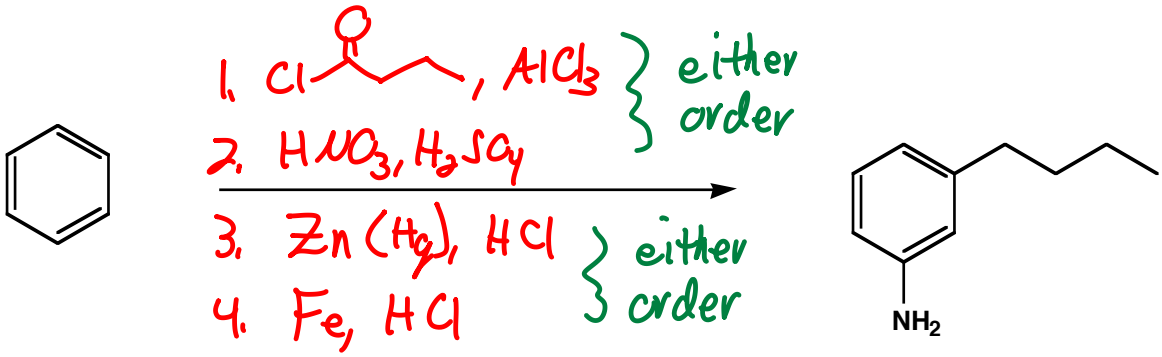
Many allylic brominations give isomers. In this case, both allylic positions are symmetry equivalent, and the allylic radical is also symmetric.

g. 

6. Provide reagents for the following transformations. (5 points each, 10 total, 6 minutes)

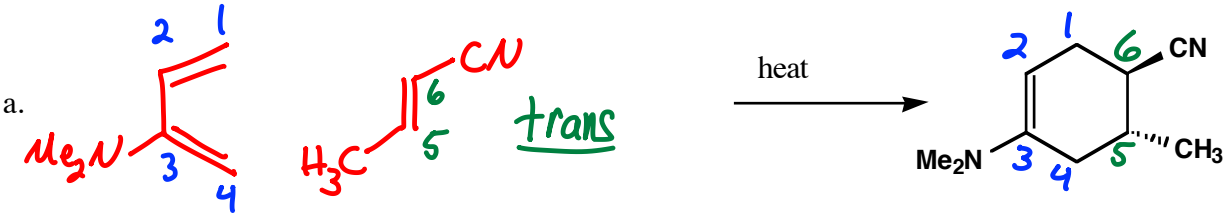
a. 

Note: Methyl is an o/p director, carboxylic acid is a meta director. So, you wanted to install the Cl ortho prior to converting the methyl to carboxyl.
But direct chlorination would have come in predominantly para, *IF* the para position was not blocked. Thus the use of sulfonation to block the para position.

b. 

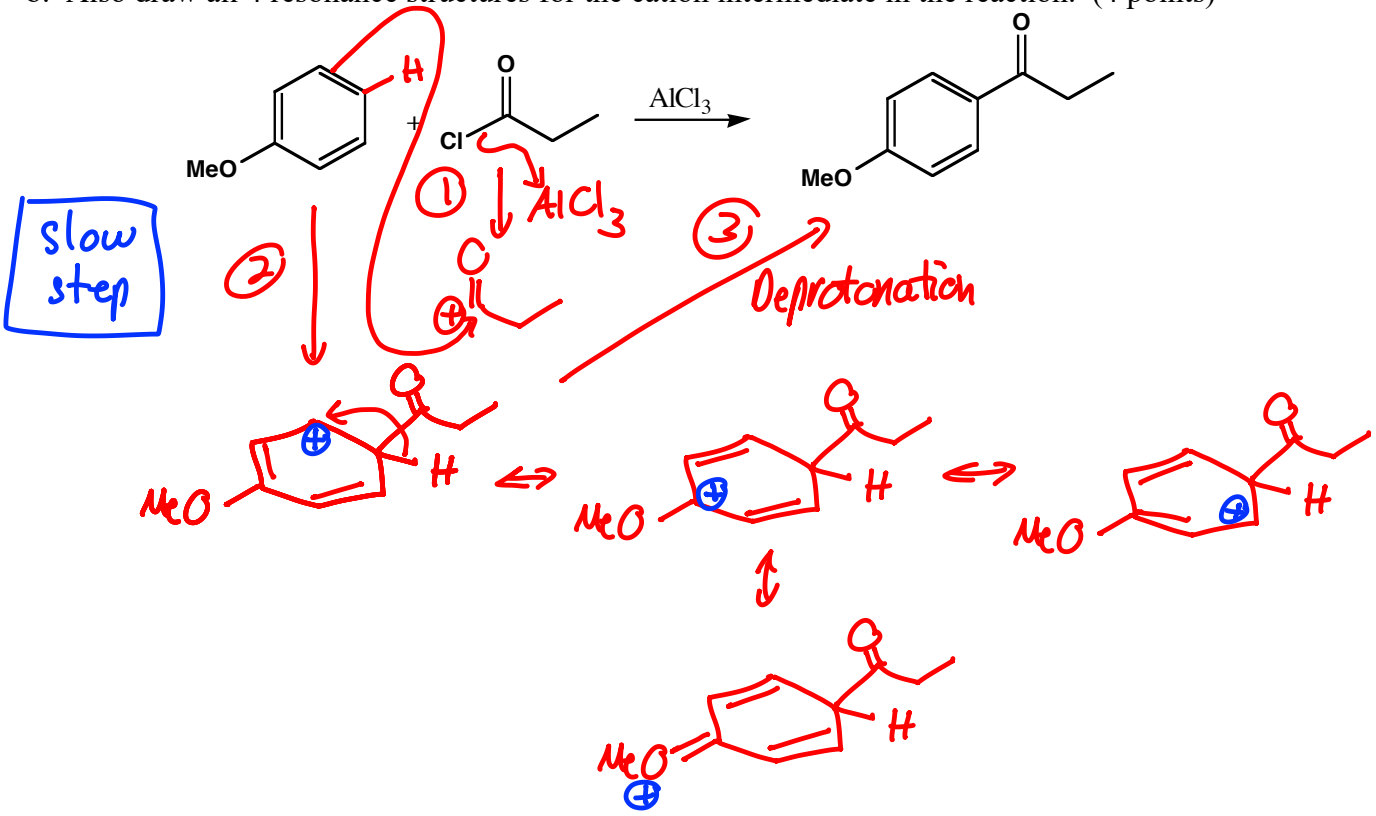
Notes: Direct install of 1° alkyl is problem, due to both instability of 1° carbocations and carbocation rearrangement. So, you need to install the carbon as the carbonyl, and convert it later. When the second group gets added, the first must be a meta director. Nitro could have gone in first.

7. Daw the diene and dienophile from which the following Diels-Alder products would have come. (3 points each, 6 total, 2 minutes)

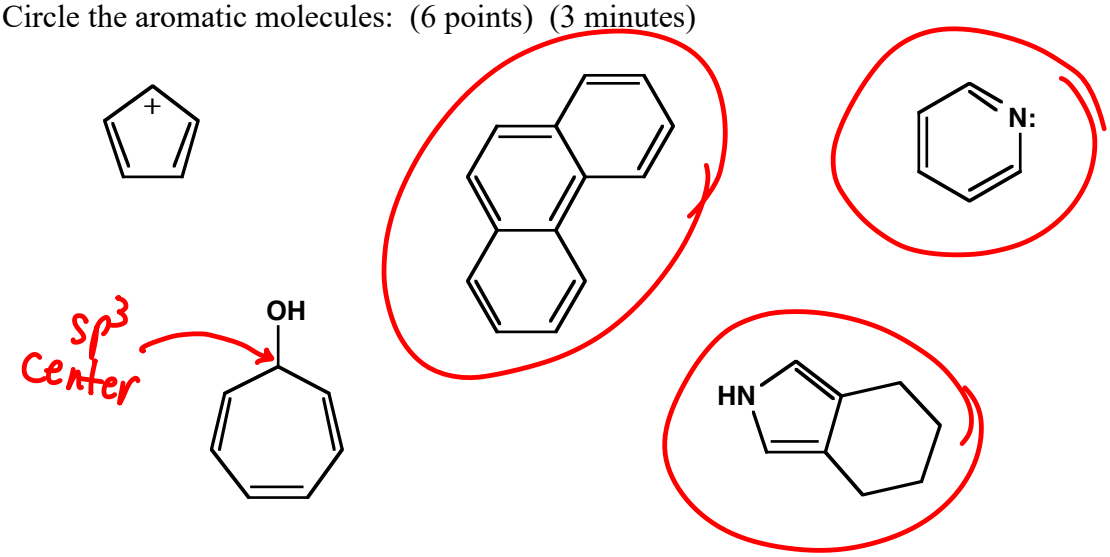
a. 

b. 

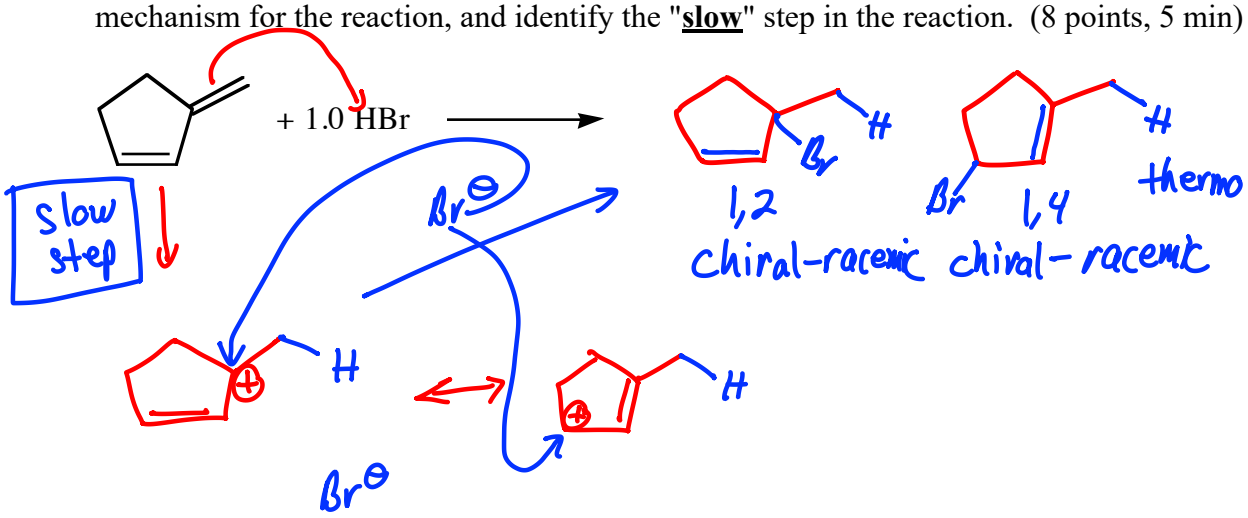
8. a. Draw the mechanism for the formation of the major product shown, and identify the "**slow**" step in the reaction. (6 points, 5 minutes).
b. Also draw all 4 resonance structures for the cation intermediate in the reaction. (4 points)



10. Circle the aromatic molecules: (6 points) (3 minutes)



9. Draw the major product or products that would result from the following reaction, and write either "**chiral**" or "**achiral**" and "**optically active**" or "**racemic**" by each product. Draw a mechanism for the reaction, and identify the "**slow**" step in the reaction. (8 points, 5 min)



9. Provide a synthesis for the following molecule, starting from benzene and anything else you like. (7 points, 5 min)