

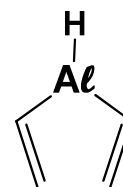
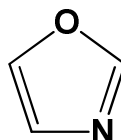
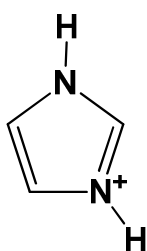
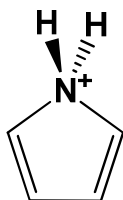
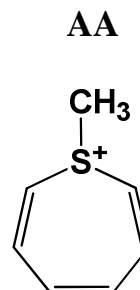
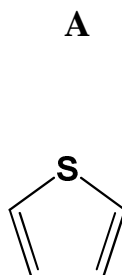
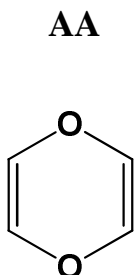
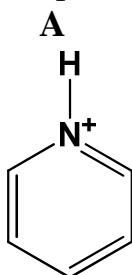
Part A (1-25) True or False. (25 pts)

- 1) F Benzene is catalytically brominated by the Electrophilic Aromatic Addition mechanism.
- 2) T Benzene is catalytically brominated faster than bromobenzene.
- 3) T An antiaromatic compound is less stable than its open chain counterpart.
- 4) T Reaction of cyclooctatetraene with potassium metal generates an aromatic dianion.
- 5) F Pyrrole is a 5 membered heterocycle which, if it could be made, would be anti-aromatic.
- 6) T The mechanism for desulfonation of benzene is identical to the sulfonation mechanism, except in the reverse order.
- 7) F The alkyl group is an **activating** group, and is ortho and para directing through resonance stabilization.
- 8) T Furan has the same number of π electrons as benzene.
- 9) F The plus and minus signs in π molecular orbitals represent the charge. (signs=value of function)
- 10) T Cyclopentadienyl anion is much more stable than its open chain counterpart.
- 11) T A nitrile contains a carbon-nitrogen triple bond.
- 12) T A cyano group contains a carbon-nitrogen triple bond.
- 13) F Aldehydes are usually less reactive than ketones.
- 14) T An imine contains a carbon-nitrogen double bond.

- 15) F An aldehyde is a compound containing a carbonyl group bonded to two alkyl groups and a hydrogen.
- 16) T Aldehydes can be reduced to primary alcohols.
- 17) F The Clemmensen reduction converts phenyl ketones to aldehydes.
- 18) F Cyclopropyl cation is aromatic because it has 2 π electrons in its ring. (Cyclopropenyl cation is.)
- 19) F The enhanced reactivity of carbonyls is due to a resonance structure that makes the C atom a good nucleophile. (electrophile)
- 20) T 1,3-Dithiane can be used in the synthesis of aldehydes or unsymmetrical ketones.
- 21) T The de-activating character of halobenzenes compared to benzene is due to the weak π bonding between a C atom and a halogen atom. (I said in class that the overlap between the C 2p AO and the Br 4p AO is very weak compared to the C 2p and O 2p AOs. The O, N, and halogens are **all** electronegative; the strong, resonance double bonds in C=O and C=N counteract the electronegativity effects but the weak resonance double bonds in C=hal can't counteract them as well.)
- 22) T The methoxy group is so activating that anisole will react with bromine itself, and no catalyst is needed for bromination.
- 23) F The lone pair of electrons on the nitrogen in an amino group causes the -NH₂ substituent to be a powerful **de-activating** group in aromatic substitution reactions.
- 24) T An acyl group is a substituent that contains an alkyl group bonded to a carbonyl group.
- 25) T It is possible for nucleophiles to displace halides ions from aryl halides if there are strong electron withdrawing groups bonded to the ring (and especially if they are located ortho and para to the halide).

Part B

1. Clearly indicate which of the following molecules would be aromatic (**A**), non-aromatic (**NA**) or anti-aromatic (**AA**), assuming that all structures are planar. (8 pts)



NA

A

A

AA

Briefly explain your choice of one of the **anti**-aromatic compounds (2pts)

$4n \pi$ electrons in a conjugated ring

2. a) What is the total number of π electrons in the cyclopentadienyl radical **cation**? 4 (3pt)

b) What is the total number of π MOs in the cyclopentadienyl radical **cation**? 5 (2pt)

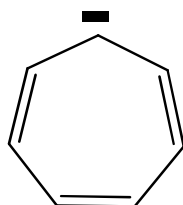
c) What is the total number of π MOs in the cyclopentadienyl radical **anion**? 5 (2pt)

d) How many nodal lines are there in each of the first three π MOs in the cyclopentadienyl radical **anion**? (3pts for getting all correct)

First: 0 Second: 1 Third: 1 (π_2 and π_3 same energy, same nodes)

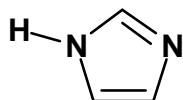
 /20 /45

3. Using the polygon rule, draw out and decide whether the cycloheptatrienyl anion is aromatic, anti-aromatic, or non-aromatic. Assume that the structure is planar. (5pts)



$3 \times 2\pi$ double bond electrons + 2 electrons from lone pair = 8π electrons
Inscribed polygon **must have one apex at the bottom** or else aromatic will be anti-aromatic and *vice versa*; and everything is wrong (-5pts)

4. The compound below displays aromaticity. (10pts total)



For each nitrogen atom, and give its hybridization and whether its lone pair is part of an aromatic π system. (Circle correct answer when given a choice.)

a) The hybrid orbitals for the N atom in N-H are: sp^2 (2pt) (lp in π system)
Does this N atom's lone pair contribute to the aromatic π system? Yes or No(2pt)

b) The hybrid orbitals for the N atom in =N- are: sp^2 (2pt)
Does this N atom's lone pair contribute to the aromatic π system? Yes or No(2pt)

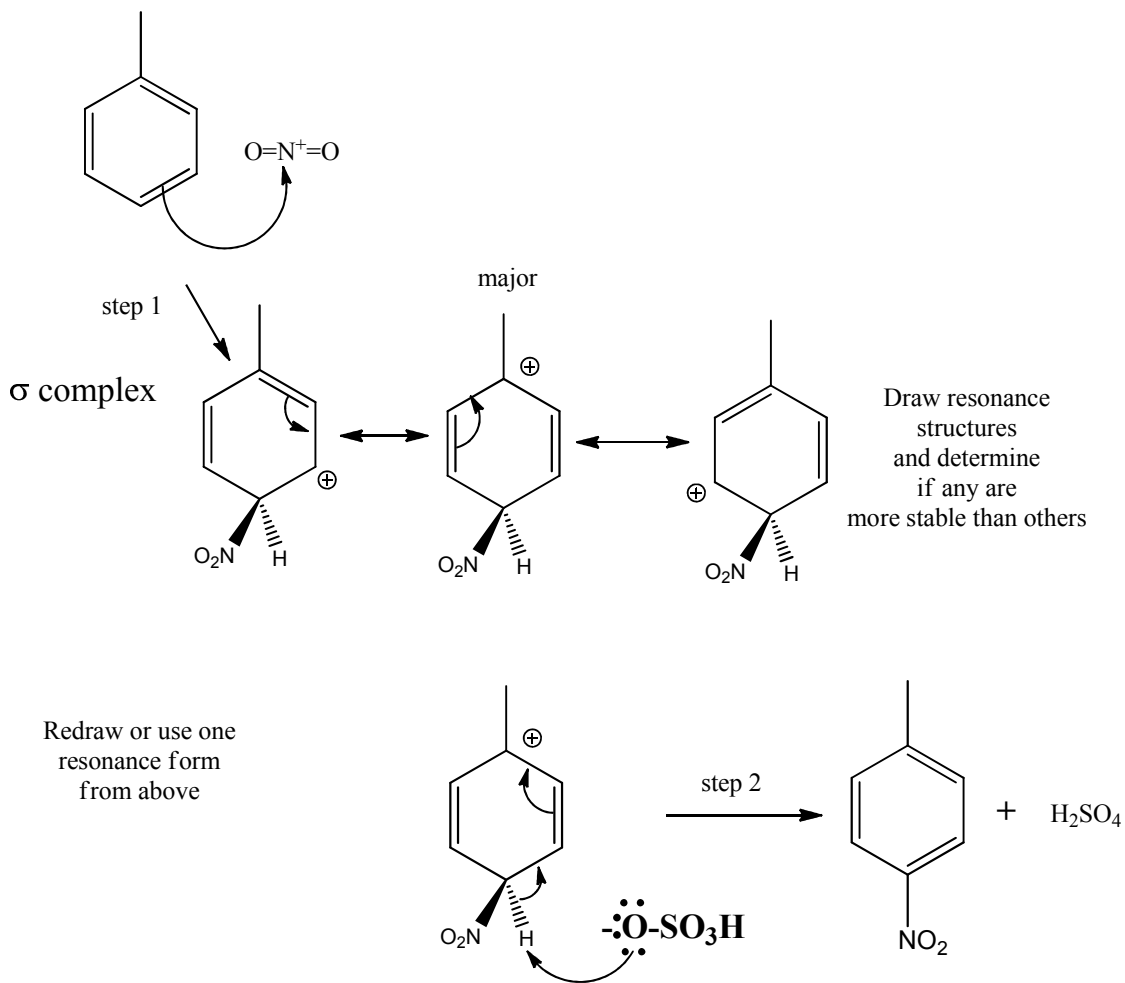
c) Which nitrogen would be protonated first in dilute sulfuric acid?

N-H or =N- (1pt)

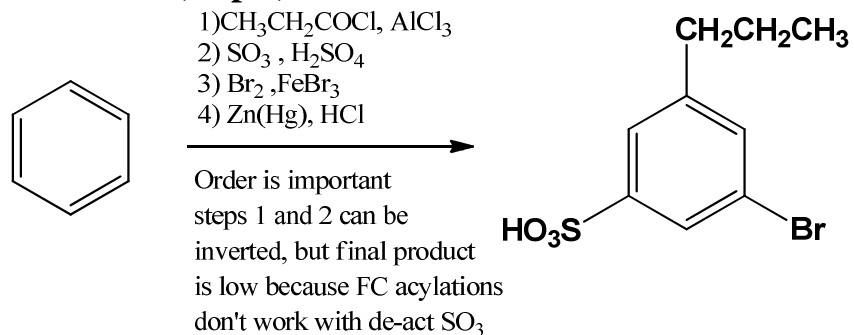
d) Which nitrogen is the more basic? N-H or =N- (1pt)
(Has to be the one protonated first)

_____/15_____/60

5. Draw the mechanism for the Electrophilic Aromatic Substitution of toluene in the para position by the nitronium ion. Include two steps: the formation of the σ -complex, then all the products. Use “curley arrows” in both steps. Mechanistically account for the high proportion of the para substitution in the mixture of products with the use of resonance structures. (12pts)

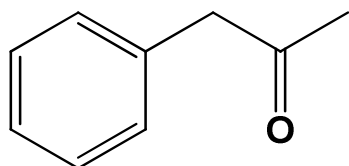


6. Provide reagents in the proper order to achieve the following transformation: (10 pts)

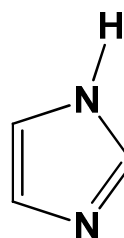


7. Name the following compounds using an IUPAC convention. (8pts)

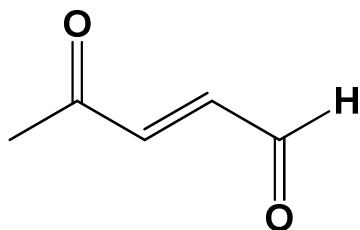
(Don't count the phenyl as C1 or C4.)



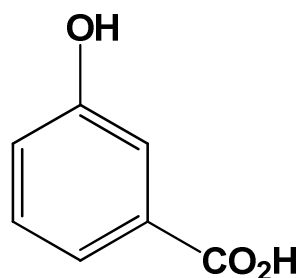
1-phenylpropan-2-one



imidazole



(*E*)-4-oxopent-2-enal



3-hydroxybenzoic acid

____/18____/90

8. Give the reagents and conditions for the following transformations.
(10pts)

