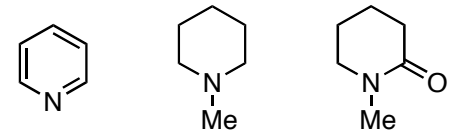
Name: _____

CHEM 633: Advanced Organic Chem: Physical
Problem Set 1: Review & Molecular Orbital Theory
Answers must be in the boxes provided to receive full credit. You may work in groups, but please turn in your own work.

1. Please label the hybridization of the nitrogen atoms in the molecules below.



2. (a) What is the molecular geometry of CH_3^+: trigonal planar or trigonal pyramidal? (Circle your answer.)

trigonal planar trigonal pyramidal

(b) Draw both molecular orbital diagrams to explain your answer to part (a). You may ignore the core electrons and only show the orbitals where the valence electrons reside plus the LUMO (you do not need to show the higher, unoccupied molecular orbitals). Please illustrate the MO's as well as their relative energy levels. A Walsh diagram may be helpful.

(c) Now consider CH_3^-. Rationalize why it is trigonal pyramidal by comparing the appropriate molecular orbital diagrams.

3. (a) Using your "chemical intuition," please name and draw the HOMO and LUMO for the following molecules. Please put your answer in the table below.

i) CN^- ii) $H_2C{=}NH_2^+$ iii) H_3CBr

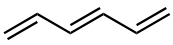
(b) Now, in the table below, construct molecular orbital diagrams for each of the molecules. Clearly label the HOMO and LUMO in each MO diagram. You may ignore the core electrons and only show the orbitals where the valence electrons reside plus the LUMO (you do not need to show the higher, unoccupied molecular orbitals). Please illustrate the MO's as well as their relative energy levels.

CN^-	
Chemical Intuition: HOMO	Chemical Intuition: LUMO
Molecular Orbital Diagram	
$H_2C{=}NH_2^+$	
Chemical Intuition: HOMO	Chemical Intuition: LUMO
Molecular Orbital Diagram	

H_3CBr	
Chemical Intuition: HOMO	Chemical Intuition: LUMO
Molecular Orbital Diagram	

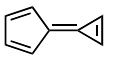
4. Using Huckel MO Theory, please illustrate why the cyclopropenyl cation is stable, yet cyclopentyl cation is unstable.

5. Construct a Huckel MO diagram for hexatriene Label the frontier molecular orbitals. Draw the molecular orbitals. Determine the energy of each MO in terms of α and β. Determine the coefficients of the atomic orbitals in the frontier molecular orbitals.

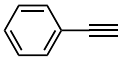


6. (Grossman, Ch 1, #1d,f,g) Explain each of the following observations.

(a) Compound **1** has a much larger dipole moment than its isomer **2**.



1



2

(b) Imidazole (**3**) is considerably more basic than pyridine (**4**).

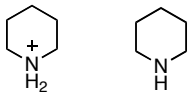
3

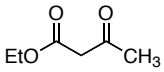
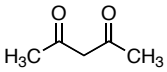
4

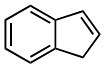
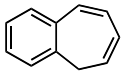
(c) Fulvene (**5**) is electrophilic at the exocyclic C atom.

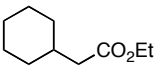
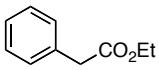
5

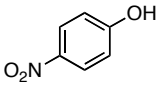
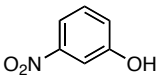
7. (Grossman, Ch 1, #2b,c,d,g,i,j) Please circle which of each pair of compounds is likely to be more acidic and explain why.

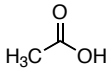
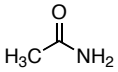
(a) 

(b)  

(c)  

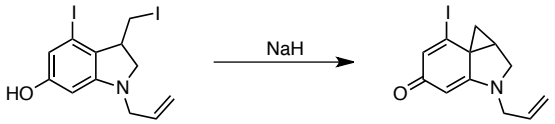
(d)  

(e)  

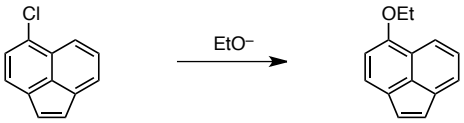
(f)  

8. (Grossman, Ch 2) Draw reasonable arrow-pushing mechanisms for the following reactions.

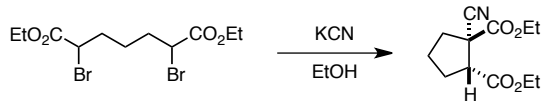
(a)



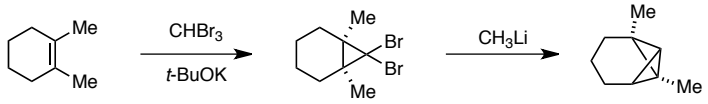
(b)



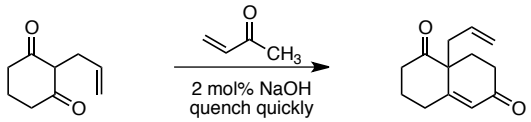
(c)


EtO2C
CO2Et
Br
Br
KCN
EtOH
CN
CO2Et
H
CO2Et

(d)


Me
Me
CHBr3
t-BuOK
Me
Br
Br
Me
CH3Li
Me
Me

(e)



(f)