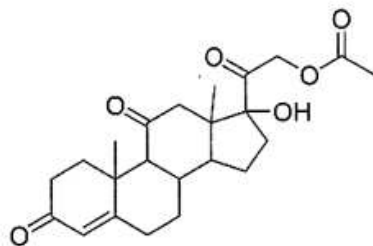


1. Provide the best answer for each question in the space provided (22 pts).

D

1a. Which functional groups are present in cortisone acetate?

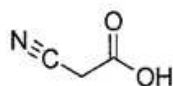


cortisone acetate

- a) alkene, alcohol and ketone
- b) ester, alkyne, alcohol and ketone
- c) alkene, aldehyde, alcohol and ether
- d) alcohol, ketone, ester and alkene

B

1b. From left to right, the hybridization of the **carbon atoms** in cyanoacetic acid are:

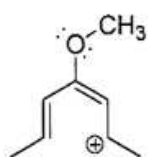
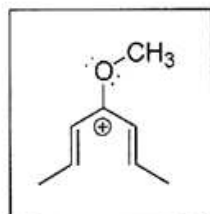


cyanoacetic acid

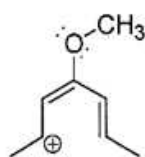
- a) sp , sp^2 , sp^3
- b) sp , sp^3 , sp^2
- c) sp^2 , sp^3 , sp^2
- d) sp^2 , sp , sp^2

C

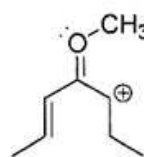
1c. Which of the following is NOT a valid resonance contributor for the ion shown in the box?



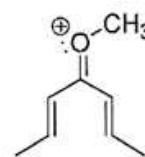
A



B

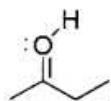


C



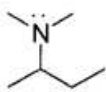
D

- 1d. Indicate the formal charge on the indicated atoms in each structure below. All lone pairs are shown.



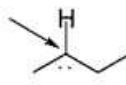
Oxygen

+1



Nitrogen

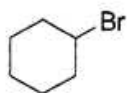
0



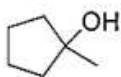
Carbon (indicated with arrow)

-1

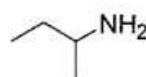
- 1e. Label each of the alcohols, alkyl halides and amines shown below as primary (1°), secondary (2°), or tertiary (3°).



2°

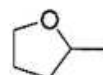
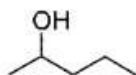
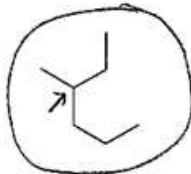
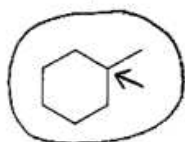


3°

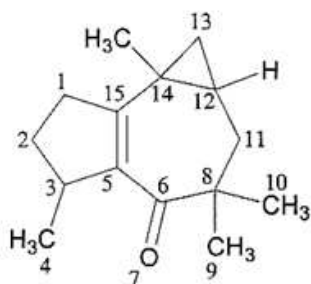


1°

- 1f. Circle any of the structures shown below that contain at least one tertiary carbon.



2a. Africanone is an oil isolated from the leaves of *Lippia integrifolia*, a plant used in Argentinian folk medicine to treat gastrointestinal disorders. Use the numbering system shown on the drawing of africanone to answer the following questions. Not all lone pairs are shown. All formal charges are zero (18 pts).



The hybridization of C-13 is sp^3 .

The hybridization of O-7 is sp^2 .

The sigma bond between C-6 and O-7 is formed by the overlap of a/n sp^2 orbital on C-6 and a/n sp^2 orbital on O-7.

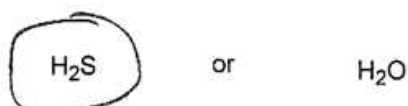
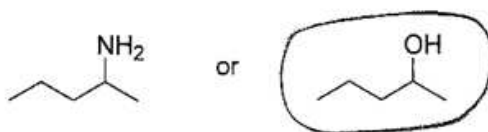
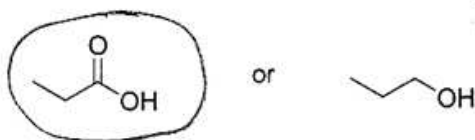
The pi bond between C-6 and O-7 is formed by the overlap of a/n p orbital on C-6 and a/n p orbital on O-7.

The functional group containing the C-6/O-7 carbonyl is a/an ketone.

Is O-7 a Bronsted-Lowry acid or base (circle it)? **Acid** **(Base)**

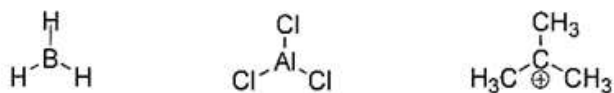
How many π (pi) bonds are there in africanone? 2

3. Circle the *more acidic* molecule in each of the following pairs (9 pts).



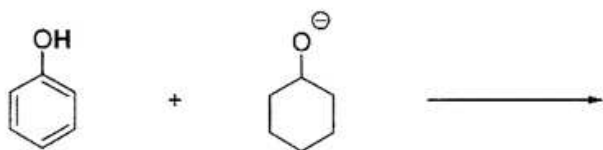
4. For each of the following statements, circle "T" if the statement is true or "F" if the statement is false (8 pts).

- T F In the MO diagram for a carbon-carbon π bond, there are two nodes in the π^* anti-bonding orbital.
- T F Not all Lewis acids are Bronsted acids.
- T F Hydroxide ion can deprotonate (remove a proton from) any Bronsted acid whose pK_a is less than 15.7.
- T F The three structures shown here are all Lewis acids. (Lone pairs are omitted on the chlorine atoms for clarity.)



All have empty p orbitals

5. When phenol ($pK_a = 10$) is combined with the conjugate base of cyclohexanol (pK_a of cyclohexanol = 16) as shown in this equation, a Bronsted-Lowry acid-base reaction occurs. Because of the difference in pK_a values, the reaction goes to completion. Lone pairs are omitted for clarity. The acidic proton on phenol is shown in bold:



5a. Draw an arrow-pushing mechanism for the reaction of phenol with the conjugate base of cyclohexanol. Draw the products of this reaction, showing all lone pairs and non-zero formal charges (8 pts).



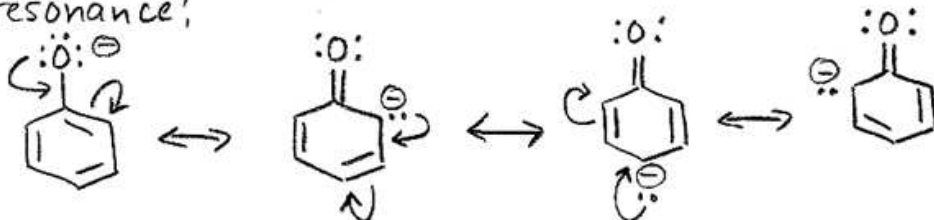
5b. Phenol is about 10^6 times more acidic than cyclohexanol. Explain this observation using appropriate chemical structures to support your argument (7 pts).

Comparing conjugate bases:

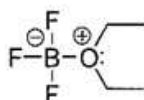
Conjugate base of cyclohexanol has localized charge:



Conjugate base of phenol ("phenoxide") is stabilized by resonance:

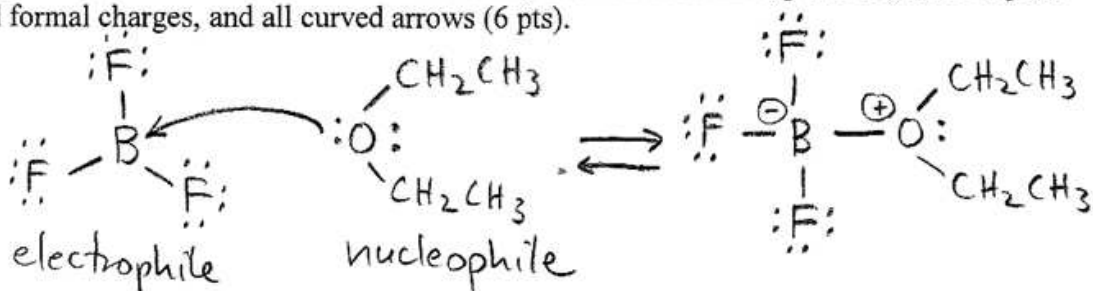


6. Boron trifluoride etherate ("BF₃ etherate") is a Lewis adduct commonly used in the organic laboratory:



It is formed by the reaction of boron trifluoride (BF₃) and diethyl ether (CH₃CH₂OCH₂CH₃).

6a. Draw an arrow-pushing mechanism showing the formation of boron trifluoride etherate from the two reactants. For full credit, show the reactants, products, all lone pairs and formal charges, and all curved arrows (6 pts).



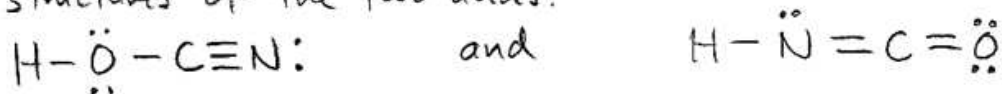
6b. In your mechanism in 6a, label the nucleophile and the electrophile (6 pts)

6c. Identify the frontier orbitals in this reaction. Circle the correct choice for each (6 pts):

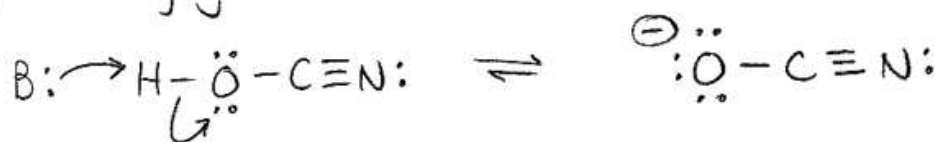
HOMO:	C-O σ	C-O σ^*	B non-bonding (sp^3)	B-O σ
	B 2s	B 2p	<u>O non-bonding (sp^3)</u>	B-O σ^*
	B-F σ	B-F σ^*	C non-bonding (sp^3)	C-O π
LUMO:	C-O σ	C-O σ^*	B non-bonding (sp^3)	B-O σ
	B 2s	<u>B 2p</u>	O non-bonding (sp^3)	B-O σ^*
	B-F σ	B-F σ^*	C non-bonding (sp^3)	C-O π

7. Cyanic acid, HOCN, and isocyanic acid, HNCO, have the same pK_a ; that is, they are equally acidic. Explain why these two structurally different acids have the same acidity. The molecular formulas given show the atomic connectivity in each molecule. Use carefully drawn chemical structures to support your answer. Include all lone pairs and formal charges where necessary (10 pts).

Lewis structures of the two acids:



Compare conjugate bases:



The conjugate bases are both contributors to the same resonance hybrid; thus, the acids are equally acidic.

