Columbia University **92CORG11.DOC** **CHEM S3443D** Summer 1992
Professor Grace B. Borowitz Exam No. **1** June 4, 1992

Name: _____ ***Grade:*** ____

Please use a **non-red** pen. Answer questions in the provided space. If you write any answers on the back of the page, indicate this on the **front** of that page. Points appear in parentheses **( )**. ***Good Luck!***

Question		**Max. Pts.**	**Points**
1. **(6 + 6) + (3 + 3)**	=	**18**	
2. **(2 + 2) + (1 + 6) + 2 + 2 + 3**	=	**18**	
3. **4 + (5 + 2) + 1 + 2 + 4**	=	**18**	
4. **2 + 2 + 4 + 3 + 3 + 2**	=	**16**	
5. **(3+3)+2+2+(2+2+2+4+2)+2+2+(2+1+1)**	=	**30**	
Total	=	**100**	

1. **(18)** a. For each of the following molecules or ions, calculate **F**, the **Formal Charge**, on the central atom and indicate its **shape**, including the bond angles.

F **SHAPE/ANGLE**

(1) $(CH_3)_3\mathbf{O}$:

(2) $(CH_3)_3\mathbf{C}$:

(3) $(CH_3)_3\mathbf{B}$

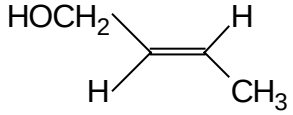
(4) $(CH_3)_4\mathbf{N}$

(5) $(CH_3)_3\mathbf{C}$

(6) $H_2\ddot{\mathbf{N}}$:

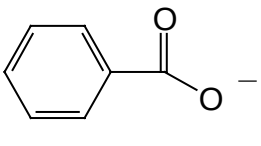
b. (1) Describe in molecular orbital terms the formation of a triple bond.

(2) Draw the molecular orbital structure of the following molecule showing å and ã bonds, atom hybridization, nonbonding electrons, and bond angles.



2. **(18)** a. Draw modified Lewis structures, showing lines for each pair of bonding electron and dots for nonbonding electrons, as well as the major resonance structures, indicating all nonbonding electrons, for the following molecules or ions.

(1) CH_3NO_2

(2) 

b. Write **6** different constitutional isomers for the molecular formula $\mathbf{C_4H_8O}$. In this group be sure to include and label at least one of the following functional groups in each of the five isomers. Calculate the **Index of Hydrogen Deficiency**, **ê**, for $\mathbf{C_4H_8O}$.

(1) an alkene

(2) an ether

(3) an alcohol

(4) an aldehyde

(5) a ketone

(6) a cyclic compound

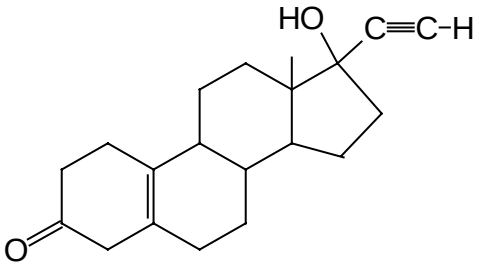
c. Write the structures for a pair of geometric isomers with the formula $\mathbf{C_4H_8O}$, noting which one is ***cis*** and which one is ***trans***.

d. The greatest degree of ionic character is anticipated for the bond between:

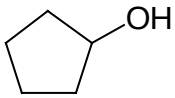
(1) H and C (2) H and Br (3) H and Cl (4) C and Cl (5) Br and Cl

e. Which of the following molecules would have a net dipole moment. You may choose more than one.
(1) CH_2Cl_2 (2) CCl_4 (3) CO_2 (4) $(CH_3)_2C{=}O$ (5) H-CðN:

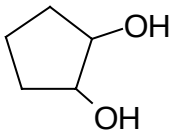
3. **(18)** a. The compound shown below is a synthetic estrogen. It is marketed as an oral contraceptive under the name *Enovid*. In addition to the cycloalkane skeleton, the *Enovid* also contains the following **4** functional groups. Cite them. Be specific if 1º, 2º , and 3º substitution is involved.

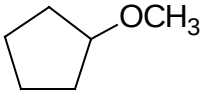


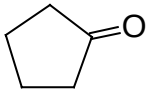
b. Arrange the following molecules in order of increasing boiling point, from lowest to highest. Briefly rationalize your choice.

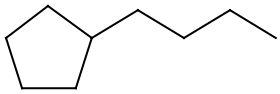
(1) 

(2) 

(3) 

(4) 

(6) 

(7) 

Order:

Why?

c. Overlap of **p**-orbital lobes of opposite signs results in the formation of :

(1) a bonding å molecular orbital.
(2) an antibonding å molecular orbital.
(3) a bonding ã molecular orbital.
(4) an antibonding ã molecular orbital.
(5) a hybrid atomic orbital.
(6) none of the above.

d. The **weakest** of attractive forces are:

(1) hydrogen bonds (2) ion-dipole (3) dipole-dipole
(4) cation-anion (5) van der Waals (6) covalent bonds

e. Draw the structures for all of the unique mono-chloropropenes, $\mathbf{C_3\ H_5\ Cl}$. (constitutional isomers and geometric isomers).

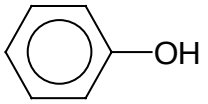
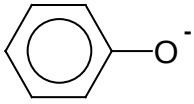
4. **(16)** a. Which acid-base reaction would not take place as written?

(1) $CH_3CH_2CH_2CH_2Li + CH_3CH_2OH \longrightarrow CH_3CH_2CH_2CH_3 + CH_3CH_2OLi$

(2) $H\text{-}C\equiv C:^- Na^+ + H_2O \longrightarrow H\text{-}C\equiv C\text{-}H + NaOH$

(3) $H\text{-}C\equiv C\text{-}H + NaOH \longrightarrow H\text{-}C\equiv C:^- Na^+$

(4) $(CH_3)_2CH\text{-}OH + NaH \longrightarrow (CH_3)_2CH\text{-}O^- Na^+ + H_2$

(5)  + NaOH ⟶  + H_2O

b. Give the definitions of an acid and a base according to Lewis.

(1) Lewis Acid: _____

(2) Lewis Base: _____

c. Complete the reactions and show the mechanism for the following Lewis Acid-Lewis Base (Nucleophile-Electrophile) reactions. Label the appropriate LA-LB species and show the direction of electron flow.

(1) $(CH_3CH_2)_3N: + BF_3$ ÄÄ> **A**

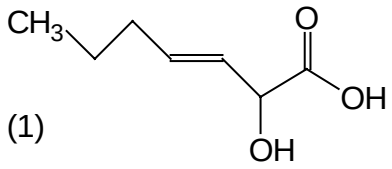
(2) $(CH_3)_3C^+ + {}^-:I$ ÄÄ> **B**

d. The basic species are arranged in decreasing order of basicity (strongest to weakest) in the sequence:
(1) $F^- > CH_3O^- > H_2N^- > CH_3CH_2^-$
(2) $CH_3O^- > CH_3CH_2^- > H_2N^- > F^-$
(3) $CH_3CH_2^- > H_2N^- > CH_3O^- > F^-$
(4) $H_2N^- > CH_3CH_2^- > F^- > CH_3O^-$
(5) $H_2N^- > CH_3O^- > CH_3CH_2^- > F^-$

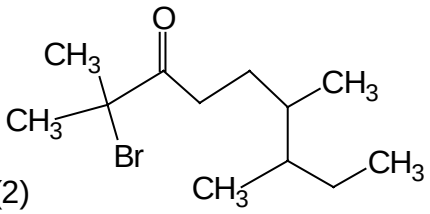
e. Which of the following statements is/are true?
(1) The stronger the acid, the larger is its pK_a.
(2) The conjugate base of a strong acid is a weak base.
(3) Acid-base reactions always favor the formation of the stronger acid and the stronger base.
(4) A proton need not be present in the molecular formula of a Bronsted-Lowry acid.
(5) Strong acids can have negative pK_a.

f. As a consequence of the "leveling effect," the strongest acid which can exist in appreciable concentration in aqueous solution is:
(1) H_3O^+ (2) H_2SO_4 (3) $HClO_4$ (4) HCl (5) HNO_3

5. **(30)** a. Name the following compounds according to *IUPAC* nomenclature. Make sure to note any *cis/trans* designation.



(1)



(2)

(1)_____

(2)_____

b. Arrange the following conformers of cyclohexane in order of decreasing stability, from most stable to least stable.

(1) twisted boat (2) chair (3) boat (4) half-chair

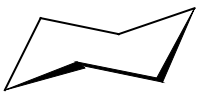
c. From the following list of cycloalkanes in column **A** match the compound with the statement associated with it in column **B.**

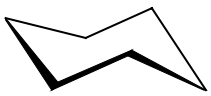
A	**B**
cyclopropane	least angle strain
cyclohexane	butterfly conformation
cyclobutane	least stable - angle strain and torsional strain

d. Draw the following structures in their most stable conformations. In parts (1) and (4), calculate the ä **A** values, DG_{strain}, for each conformer in determining the most stable conformer. Use the following table of **A** values, DG_{strain} in kcal/mole for each axial over equatorial substitution, for the given substituents.

Substituent:	**-OH**	**-CH_3**	**-$C(CH_3)_3$**
A:	**0.7**	**1.7**	**5.4**

(1) *cis*-4-methyl-1-cyclohexanol



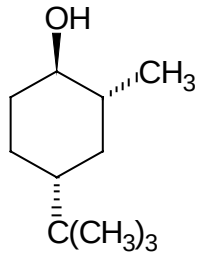


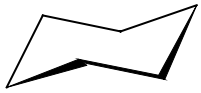
(2) bicyclo[2.2.1]heptane

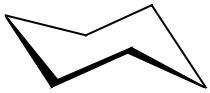
(3) *trans*-bicyclo[4.4.0]decane

5. d. continued

(4)







(5) $(CH_3)_3C\mathbf{C}H_2\text{-}\mathbf{C}H_2\text{-}CH_3$

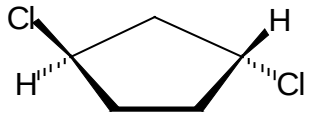
e. The reaction of lithium di-*sec*-butylcuprate, with isopentyl bromide, $(CH_3)_2CH\text{-}CH_2CH_2\text{-}Br$, yields:

(1) 2,5-dimethylheptane (2) 2,6-dimethylheptane (3) 3,5-dimethylheptane
(4) 3,4-dimethylheptane (5) 3,4-dimethylhexane

f. Which of the following yields only one monosubstituted chloroalkane upon chlorinnation.

(1) Isobutane (2) cyclopentane (3) Butane (4) Propane (5) None of these

g. (1) Give the *IUPAC* name for the following compound.



(2) Draw the geometric isomer of this compound.

(3) Draw a constitutional isomer of this compound.

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