

CHEM 163 MIDTERM

October 23 , 2001

Dr. John C. Vederas

I. Structure and Nomenclature - 56 Points -

A. Draw structures for which names are given, or name the given structures by any correct (systematic or common) nomenclature. Be sure to give cis or trans (or if appropriate Z or E) assignment to the isomer where indicated by asterisks (**). (4 points each)

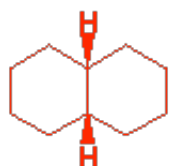
1. chloroform



2. allyl chloride



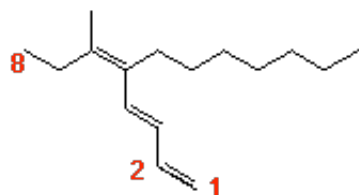
***3. cis-decalin



***4. trans-1-cyclopropyl-2-butylcyclopentane

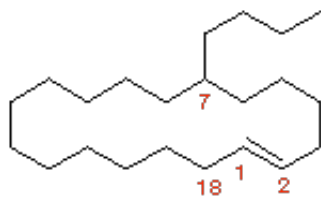


***5.



(5Z,3E) 5-heptyl-6-methyl-1,3,5-octatriene

*** 6.



(E)-7-butylcyclooctadecene

*** 7.



8.



B. Determine whether the following pairs of structures are identical, structural isomers, or stereoisomers. (4 points each)

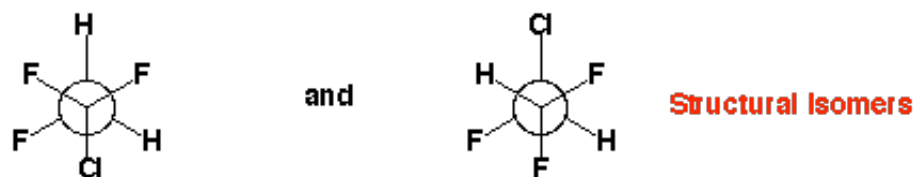
1.



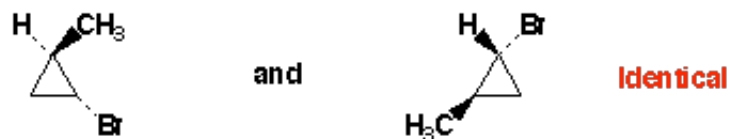
2.



3.

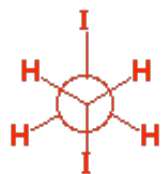


4.

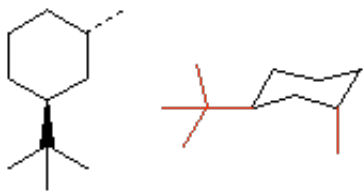


C. Conformation

1. Draw the Newman projection showing the anti conformation of 1,2-diiodoethane. (2 pts)



2. Draw the most stable conformation of the molecule shown below. Use the template provided for your drawing. If you make an error, please redraw the template. (2 pts)



3. For the structure below, provide the molecular formula (C_xH_y) and specify the number of degrees of unsaturation (4 pts)



C_7H_8 4 degrees of unsaturation

II. Quantitative Analysis and Definitions - 44 points

A. Briefly define (15 words or less) each of the following concepts - (3 points each)

1. sigma orbital **molecular wave function (orbital) made by linear combination of atomic orbitals having an s component**
2. enthalpy **bond energy**
3. atomic number **number of protons in nucleus**

B. Acetaminophen (Tylenol) is one of the most widely-used analgesic and antipyretic (lowers body temperature) drugs. Quantitative analysis gave: C 63.56 %; H 6.00%; N 9.27 %. The remainder is oxygen (given on board during exam).

1. Show how to calculate the empirical formula. (14 pts)

$$100\% - 63.56\% - 6.00\% - 9.27\% = 21.17\% \text{ Oxygen}$$

Divide % composition by atomic weights to get crude ratios of atoms

$$63.56\% \text{ C} \div 12 = 5.3$$

$$6.00\% \text{ H} \div 1.0 = 6.00$$

$$9.27\% \text{ N} \div 14 = 0.66$$

$$21.17\% \text{ O} \div 16 = 1.32$$

Divide each crude ratio by smallest crude ratio to get refined ratios (smallest becomes integer)

$$5.3 \div 0.66 = 8 \text{ for carbon}$$

$$6.0 \div 0.66 = 9 \text{ for hydrogen}$$

$$0.66 \div 0.66 = 1 \text{ for nitrogen}$$

$$1.32 \div 0.66 = 2 \text{ for oxygen}$$

As refined ratios are all integers it is not necessary to multiply each refined ratio by integer (1, 2, 3...) to get integral ratios of atoms

Hence, Empirical Formula is $C_8H_9NO_2$

2. If the molecular weight is 151, what is the molecular formula ? Show calculation. (2 pts)

$$\text{Empirical weight} = (8 \times 12) + (9 \times 1) + (1 \times 14) + (2 \times 16) = 151$$

$151 \div 151 = 1$, Hence molecular formula is same as empirical formula

Molecular formula is $C_8H_9NO_2$

3. Suppose burning a certain sample of acetaminophen produces 50 mL of CO_2 gas at 20 oC and 760 mm Hg. Show how to calculate the volume the CO_2 would occupy at standard pressure and temperature. (9 pts)

$$P_1V_1=nRT_1 \text{ divide by } P_2V_2=nRT_2$$

$$\text{get } (P_1V_1)/(P_2V_2) = T_1/T_2$$

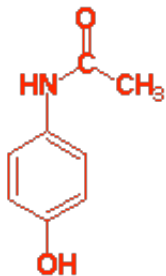
$$\text{Solve for } V_2 = (T_2P_1V_1)/(P_2T_1)$$

STP (standard pressure and temperature) is 760 mm Hg and 273 K

Substituting numbers get

$$V_2 = (273 \text{ K})(760 \text{ mm Hg})(50 \text{ mL})/(760 \text{ mm Hg})(20 + 273 \text{ K}) = 46 \text{ mL}$$

Structure of acetaminophen is shown below (cannot be determined from information given)



C. Circle the appropriate letter to indicate whether each of the following statements is true (T) or false (F). No penalty for guessing. (Similar to previous exams but be cautious) (1 point each - total 10 points)

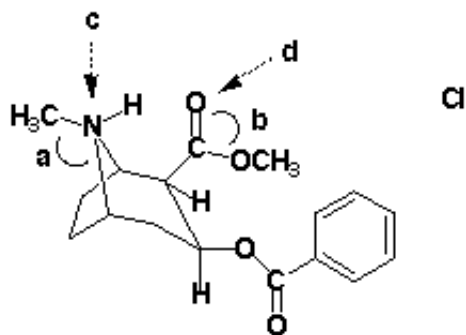
1. Enthalpy is negative for an exothermic reaction **True**

2. Resonance forms are structures of rapidly interconverting molecules **False**

3. Chloroform has a density $r > 1.0$ **True**
4. Elemental iodine reacts slowly with alkanes to give alkyl iodides **False**
5. A completely pure organic compound may have different physical properties depending on whether it was made by chemists or isolated from Nature **False**
6. A radical intermediate in a reaction is accurately described as a transition state **False**
7. The net dipole of methane is zero **True**
8. The pKa of water is about 7.0 **False**
9. The energy available to molecules at room temperature is about 15-20 kcal/mole **True**
10. All Lewis acids accept a pair of electrons **True**

III. Atomic Structure and Molecular Structure - Energy Diagrams - 24 Points

A. Cocaine from *Erythroxylon coca* bushes grown in the Amazon basin is a stimulant which acts on the nervous system. It has been taken orally or nasally for more than 2000 years to obtain a euphoric effect (e.g. as hydrochloride), but recent (15 years) smoking of the corresponding neutral species (free base) in the form of "crack" has enhanced its addictive properties with consequent social problems. Examine its structure and answer the questions.



1. Determine the formal charge on the nitrogen labelled **c**. Use any method, but show calculations. (2 points)

$$7 \text{ protons} = +7$$

$$2 \text{ 1s electrons} = -2$$

$$1/2 \text{ of } 8 \text{ e}^- \text{ shared} = -4$$

$$\text{Total} = \text{Formal Charge} = +1$$

2. Determine the formal charge on the oxygen labelled **d**. Use any method, but show calculations. (2 points)

$$8 \text{ protons} = +8$$

$$2 \text{ 1s electrons} = -2$$

4 lone pair electrons = -4

1/2 of 4 e- shared = -2

Total = Formal Charge = 0

3. What is the hybridization of the nitrogen labelled **c**? (1 point)

sp³

4. What is the bond angle labelled **b**? (1 point)

120 degrees

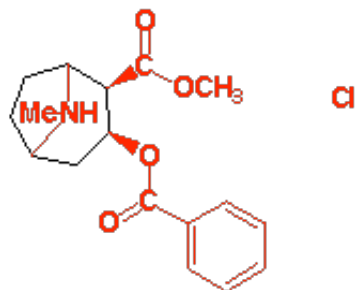
5. What is the bond angle labelled **a**? (1 point)

109 degrees

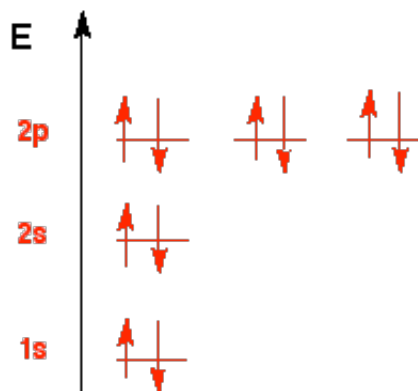
6. The molecular formula of the above structure is: **C17 H22 Cl 1 N 1 O4** (4 points)

(Oxygen was not requested in the question text and is optional)

7. Examine the perspective drawing of cocaine (above) and redraw this molecule in flat projection using the seven-member ring provided below as part of your structure. Be sure to indicate the three dimensional shape with dark and dashed lines. (If you make an error, redraw the ring and start again). Hint: start by making a five-membered ring within the seven-membered ring. (9 points)



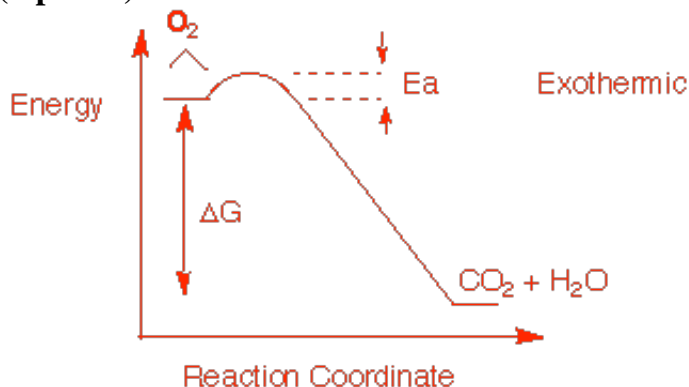
B. Draw an energy diagram depicting all of the atomic orbitals of a fluoride anion and indicate the number of electrons in each. Be sure to label each orbital. (4 points)



IV. Reactions and Mechanism - (26 points)

A. Draw a simple energy diagram for the combustion (burning) of propane with oxygen. Be sure to label both axes, label the starting materials and products (give their structures) in the correct locations. Also label the ΔG , the activation energy (E_a) and indicate in your drawing whether the reaction is exothermic or endothermic.

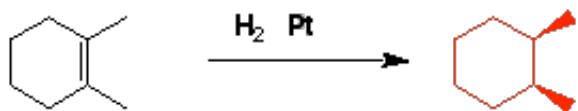
(5 points)



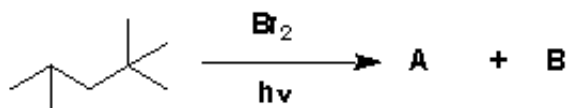
B. Write and balance the chemical equation for the combustion of propane with oxygen. (2 pts)



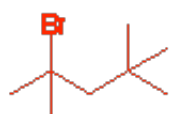
C. Show the product of the following reaction discussed in class. Be sure to show correct stereochemistry. (3 pts)



D. Examine the overall reaction shown below and answer the questions that follow.



1. Assuming there is one equivalent of Br_2 for each equivalent of alkane, show the structures of the two major products A and B. (4 points)



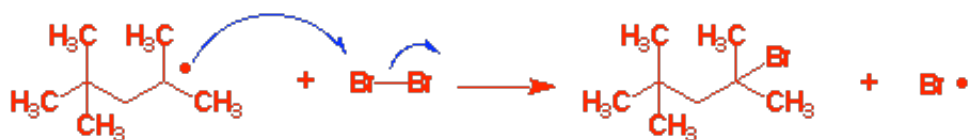
(3 pts)

and



(1 pt)

2. Write the two propagation steps for the reaction. (6 points)



3. Write one possible termination step for the above reaction. (2 points)

Any combination of two possible radicals to yield a stable product

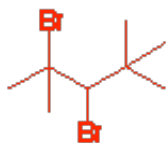
For example:



OR



4. If the major organic product of the reaction depicted above were to be treated with another equivalent of bromine in the presence of light a new organic compound would be formed. Show its structure. (4 points)



Extra Credit (2 points): Provide the last names of at least two of the three scientists who won the Nobel Prize in Chemistry this year (2001). *No partial credit here must have two correct names*

No partial credit here

William KNOWLES

Ryoji NOYORI

K. Barry SHARPLESS