CHEM 161 MIDTERM
October 21, 1999
Dr. John C. Vederas

I. Structure and Nomenclature - 56 Points -

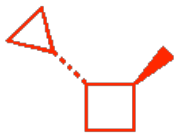
A. Draw structures for which names are given, or name the given structures by any correct (systematic or common) nomenclature. Be sure to give cis or trans (or if appropriate Z or E) or R or S assignment to the isomer where indicated by asterisks (***). **(4 points each)**

1. methylene chloride

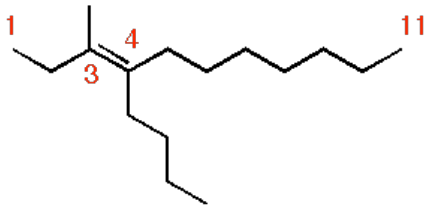
2. isopropyl fluoride

3. neopentane

4. trans-1-cyclopropyl-2-methylcyclobutane



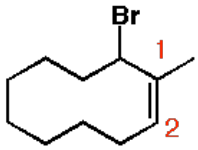
5.



4-butyl-3-methyl-3-undecene

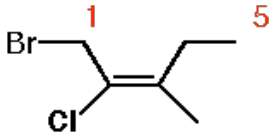
substituents in any order as long as numbers correct as given

6.



10-bromo-1-methyl-1-cyclodecene

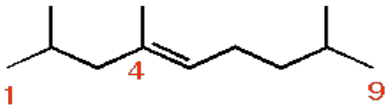
***** 7.**



(E)-1-bromo-2-chloro-3-methyl-2-pentene

will accept trans

***** 8.**

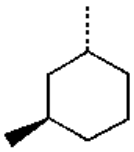


(E)-2,4,8-trimethyl-4-nonene

will accept trans

B. Determine whether the following pairs of structures are identical (i.e. different pictures of the same molecule), structural isomers, or stereoisomers (4 points each).

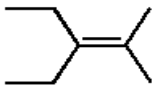
1.



and

stereoisomers

2.



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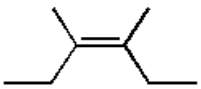
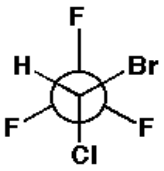
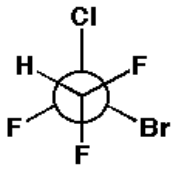


structural isomers

3.

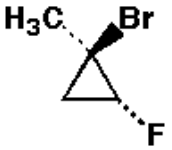


and

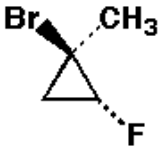


structural isomers

4.



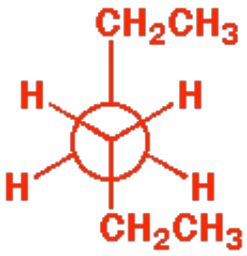
and



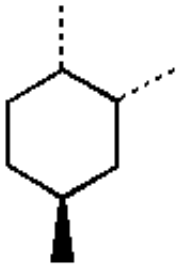
identical

C. Conformational Drawings

1. Draw the most stable conformation of the central bond of hexane using Newman projection (4 points)



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. (4 points)



II. Quantitative Analysis and Definitions - 46 Points

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

1. sigma orbital

A molecular orbital (mathematical function) made of atomic orbitals having an s component - its square gives electron density with cylindrical symmetry

2. Lewis acid

A substance that can accept a pair of electrons

3. London Forces

temporary dipoles that lead to weak intermolecular attraction

B. Adrenalin (also known as epinephrine) is a hormone and neurotransmitter secreted by the adrenal medulla which prepares the body for "fight or flight." It raises blood pressure, increases heart rate, and generally evokes a feeling of anxiety or fear. It was the first hormone to be isolated in crystalline form (1897) and synthesized in the laboratory (1905). It also occurs in banana peels; in the late 1960's this led to widespread smoking of banana peels to try to induce a "high." The results were fruitless. Adrenalin contains only C, H, N, and O.

Quantitative analysis gave: C 59.00 %; H 7.15 %; N, 7.65 %

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

100% - 59.00% - 7.15% - 7.65% = **26.20 % Oxygen**

59.00% C divided by 12 (at wt C) = 4.92 crude ratio

7.15% H divided by 1 (at wt H) = 7.15 crude ratio

7.65% N divided by 14 (at wt N) = 0.546 crude ratio

26.20% O divided by 16 (at wt O) = 1.63 crude ratio

Divide all crude ratios by the smallest to get refined ratios:

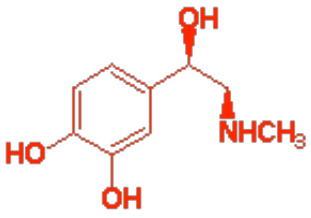
4.92 divided by 0.546 = 9

7.15 divided by 0.546 = 13

0.546 divided by 0.546 = 1

1.63 divided by 0.546 = 3

Therefore the **Empirical Formula is $C_9H_{13}NO_3$**



Adrenalin (epinephrine)

Structure not obtainable from data given

2. If the molecular formula is the same as the empirical formula just calculated, what is the molecular weight? **(2 pts)**

Empirical Formula weight is (12 x 9) + (1 x 13) + (14 x 1) + (16 x 3) = **183**

Empirical Weight is same as molecular weight

3. If adrenalin is burned completely, how many moles of CO_2 are produced for each mole of adrenalin ? **(2 pts)**

Same as number of carbon atoms, i.e. 9 moles

4. Suppose your produce 10 liters of CO_2 at Standard pressure and temperature (STP). Show how to calculate the volume this gas would occupy at a pressure of 1520 mm Hg (2 atm) and a temperature of 25 C. **(9 pts)**

Gas Law is PV=nRT

Hence $P_1V_1 / P_2V_2 = T_1 / T_2$; arbitrariily make V_1 and P_1 and T_1 the final values

then solve equation for V_1 to get: $V_1 = V_2P_2T_1 / T_2P_1$

remember T is in degrees Kelvin: 25 C = 298 K and 0 C = 273 K

Hence V_1 = (10 liters) (1 atm) (293) / (273) (2 atm) = 5.36 liters

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

1. Enthalpy is negative for an endothermic reaction- **False**

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

3. Compounds containing more than 65% halogen usually have a density rho > 1.0 - **True**

4. The atomic number of an atom is the total mass of neutrons and protons in the nucleus - **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 chloroform is not aligned with any carbon-chlorine bond - **True**

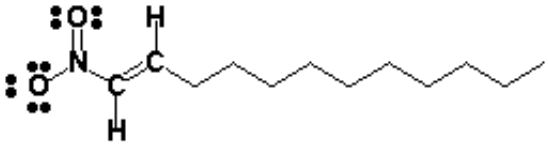
8. Elemental Iodine (I_2) reacts slowly with alkanes to give alkyl iodides- **False**

9. The energy needed to break a carbon-hydrogen single bond is about 15-20 kcal/mole - **False**

10. All Bronsted-Lowry acids are also Lewis acids - **True**

III. Atomic and Molecular Structure - Energy Diagrams - 31 Points

A. The Cuban termite defends itself against enemies by excreting the toxic irritant whose structure is shown below.



1. Determine the formal charge on the oxygen which has three lone pairs of electrons. Use any method, but show calculations. **(3 points)**

For the Oxygen add the following:

2 electrons in 1s shell = -2

6 electrons unshared = -6

one half of 2 electrons shared = -1

Formal Charge on oxygen is therefore -1

2. Determine the formal charge on the nitrogen. Use any method, but show calculations. **(3 points)**

For the Nitrogen add the following:

7 protons = +7

2 electrons in 1s shell = -2

one half of 8 electrons shared = -4

Formal Charge on nitrogen is therefore +1

3. What is the hybridization of the carbon directly attached to nitrogen? **(2 points)**

sp2

8 protons = +8

4. What is the bond angle between nitrogen, the attached carbon and the hydrogen on that carbon ? **(2 points)**

120 degrees

5. What is the hybridization of the 3d carbon from the methyl end of the chain ? **(2 points)**

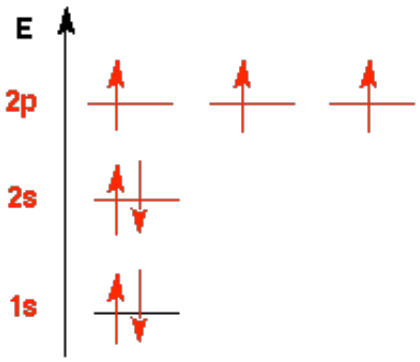
sp3

6. What is the bond angle formed between the 3d carbon from the methyl end of the chain, and its attached hydrogens? **(2 points)**

109 degrees

7. The molecular formula of the above structure is: **C12 H23 N1 O2 (4 points)**

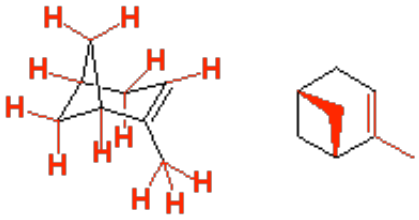
B. Draw an energy diagram depicting all of the atomic orbitals of a neutral nitrogen atom isolated in space and indicate the number of electrons in each. Be sure to label each orbital. **(4 points)**)



atomic number of nitrogen is 7

C. alpha-Pinene is the chief constituent (ca. 58-65%) of oil of turpentine which is obtained from the sap of pine trees. **The true structure of alpha pinene has two additonal methyl groups which are missing in the drawing. This question is graded on the basis of the structure provided. The correct structure of alpha-pinene is:**

1. Examine the perspective drawing of a-pinene depicted below and redraw this molecule in flat projection using the six-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). **(4 points)**

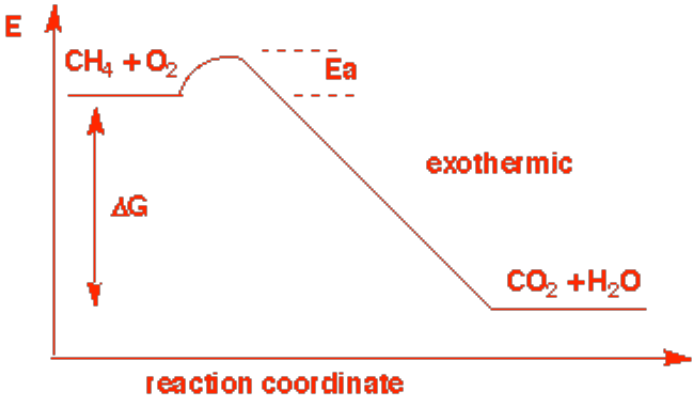


2. Draw in all of the hydrogen atoms on the structure of a-pinene above. **(3 points)**

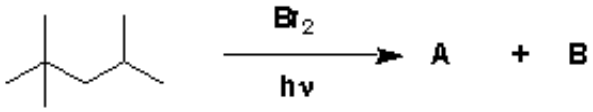
3. How many degrees of unsaturation does a-pinene possess ? **(2 points)** Three

IV. Reactions and Mechanism - (17 points)

A. Draw a simple energy diagram for the combustion (burning) of methane with oxygen. Be sure to label both axes, label the starting materials and products (give their structures) in the correct locations. Also label the deltaG, the activation energy (Ea) and indicate in your drawing whether the reaction is exothermic or endothermic. **(5 points)**



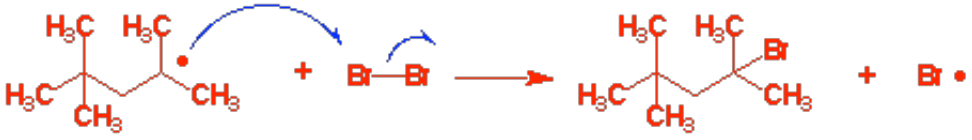
B. Examine the overall reaction shown below and answer the questions that follow.



1. Assuming there is one equivalent of Br2 for each equivalent of alkane, show the structures of the two major products A and B. **(4 points)**

2. Write the initiation step for the reaction. **(2 points)**

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



Extra Credit (2 points): Draw the three dimensional structure of adamantadine, an antiviral agent active against influenza, using the part structure given below as part of your drawing (assigned problem 4.50). If you make a mistake, redraw the part structure carefully and begin again.