CHEM 161 MIDTERM
October 24 , 2000
Dr. John C. Vederas

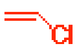
I. Structure and Nomenclature - 56 Points -

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)**

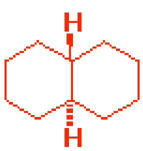
1. chloroform

$CHCl_3$

2. vinyl chloride

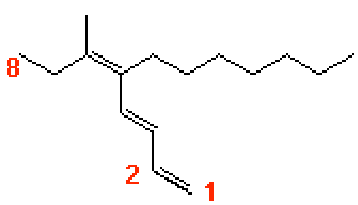


*****3.** trans-decalin



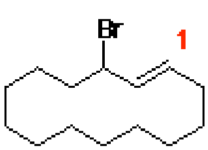
*****4.** cis-1-cyclobutyl-3-ethylcylopentane

*****5.**



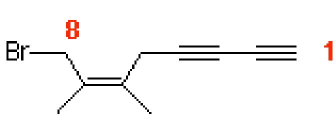
(5Z,3E) 5-heptyl-6-methyl-1,3,5-octatriene

*** **6.**



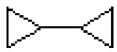
(E)-3-bromocyclotetradec<u>ene</u>

*** **7.**



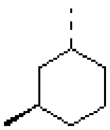
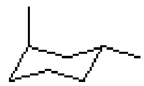
(Z)-8-bromo-6,7-dimethyl-6-octen-1,3-diyne

8.

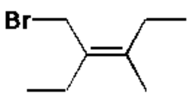
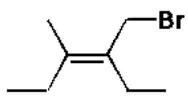
 cyclopropylcyclopropane

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

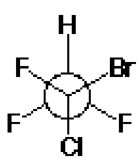
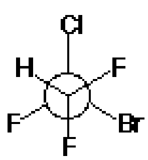
1.

 and  Identical

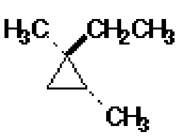
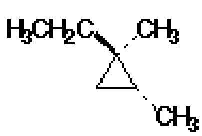
2.

 and  Stereoisomers

3.

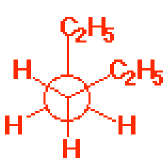
 and  Identical

4.

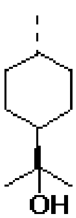
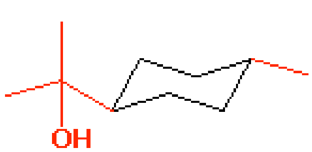
 and  Identical

C. Conformation

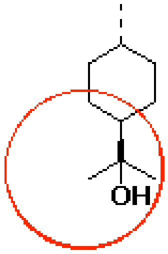
1. Draw the Newman projection showing the gauche conformation of the central bond of hexane. **(4 pts)**



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. In the structure below, circle one of the isoprene units and specify to what type of terpene class this molecule belongs. **(2 pts)**



II. Quantitative Analysis and Definitions - 44 points

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

1. pi orbital **molecular wave function (orbital) made by linear combination of two p atomic orbitals**

2. electronegativity **desire (attraction) of an atom for electrons (negative charge)**

3. London forces **intermolecular attraction due to temporary dipoles**

B. Extracts of the European insect *Cantharis vesicatoria*, also known as Spanish fly, have long been used in folk medicine to stimulate hair growth or cause sexual excitation. The highly irritating and toxic compound in the extract is cantharidin, which contains only C, H and O atoms. Quantitative analysis gave: C 61.21%; H 6.17%.

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

100% - 61.21% - 6.17% = 32.62% Oxygen

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

61.21% C ÷ 12 = 5.10

6.17% H ÷ 1.0 = 6.17

32.62% O ÷ 16 = 2.04

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

5.10 ÷ 2.04 = 2.5 for carbon

6.17 ÷ 2.04 = 3.0 for hydrogen

2.04 ÷ 2.04 = 1.0 for oxygen

Multiply each refined ratio by integer (1, 2, 3...) to get integral ratios of atoms

2.5 x 2 = 5 carbons

3.0 x 2 = 6 hydrogens

1.0 x 2 = 2 oxygens

Hence, Emprical Formula is $C_5H_6O_2$

2. If the molecular weight is 196, what is the molecular formula ? (**2 pts**)

Empirical weight = (5 x 12) + (6 x 1) + (2 x 16) = 98

196 ÷98 = 2, Hence molecular formula is two times empirical formula

Molecular formula is $C_{10}H_{12}O_4$

3. Suppose burning a certain sample of cantharidin produces 100 mL of CO_2 gas at 25 oC and 800 mm Hg. Show how to calculate the volume the CO_2 would occupy at standard pressure and temperature. **(9 pts)**

$P_1V_1=nRT_1$ divide by $P_2V_2=nRT_2$

get $(P_1V_1)/(P_2V_2) = T_1/T_2$

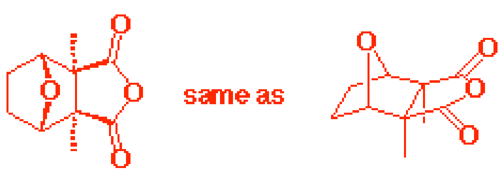
Solve for $V_2 = (T_2P_1V_1)/(P_2T_1)$

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

Substituting numbers get

V_2 = (273 K)(800 mm Hg)(100 mL)/(760 mm Hg)(25 + 273 K) = 96 mL

Structure of cantharidin 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 endothermic reaction **False**

2. Resonance forms are not structures of rapidly interconverting molecules **True**

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

4. Steric effect is caused by mutual repulsion of atoms having inert gas configurations of electrons **True**

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 carbon tetrachloride is zero **True**

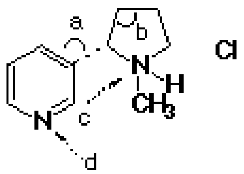
8. Overlap of two sp orbitals in a triple bond generates a sigma molecular orbital **True**

9. The energy needed to break a carbon-hydrogen single bond is about 100 kcal/mole **True**

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

III. Atomic Structure and Molecular Structure - Energy Diagrams - 27 Points

A. Nicotine is a highly toxic and addictive compound in tobacco which acts on the nervous system. It is sold commercially as a 40% solution as the insecticide Black Leaf 40. Examine its structure and answer the questions.



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

7 protons = +7

2 1s electrons = -2

1 lone pair = -2

1/2 of 6 e- shared = -3

Total = Formal Charge = 0

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

7 protons = +7

2 1s electrons = -2

1/2 of 8 e- shared = -4

Total = Formal Charge = +1

3. What is the hybridization of the carbons directly attached to nitrogen in the six-membered ring? **(2 points)**

sp2

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

109 degrees

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

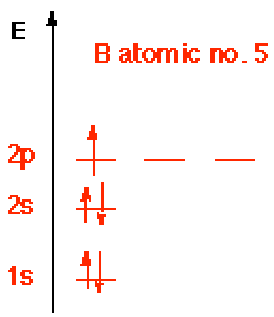
120 degrees

6. What is the charge on the chlorine if the molecular assembly as a whole is stable and uncharged ? **(2 points)**

- 1

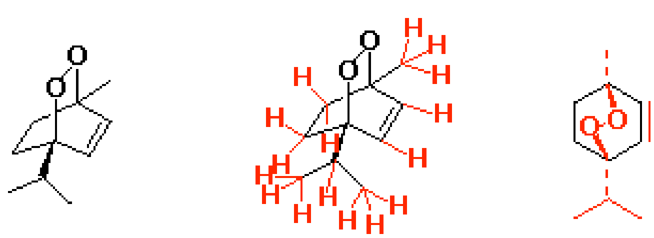
7. The molecular formula of the above structure is: **C10 H15 Cl1 N 2** **(4 points)**

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



C. Ascaridole is an anthelminthic agent which is isolated from chenopodium oil. It is toxic to parasitic worms known as helminths (Greek *ascaris* intestinal worm).

1. Examine the perspective drawing of ascaridole 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)**



ascaridole

2. Draw in all of the hydrogen atoms on the conformational structure (left) of ascaridole above. **(3 points)**

see above - 1 point for each error

3. How many degrees of unsaturation (hydrogen deficiencies) does ascaridole possess ? **(2 points)**

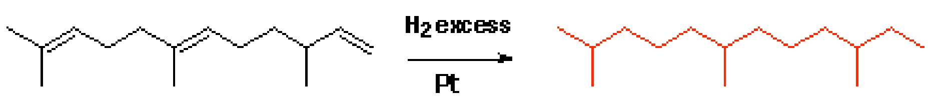
three (no partial credit here)

IV. Reactions, Physical Properties and Mechanism - (23 points)

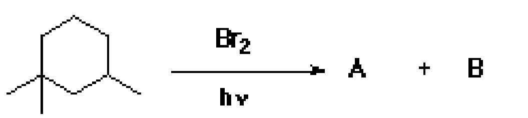
A. Circle those compounds below which have a permanent dipole moment. **(3 pts)**

$CHCl_3$ Br_2 H_2O HBr CBr_4

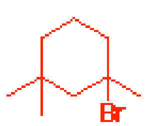
B. Farnesene is a pleasant-smelling compound found in the waxy coating of apples. Show the structure of the product which results when farnesene is treated with excess hydrogen in the presence of platinum (Pt) catalyst. **(3 pts)**



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

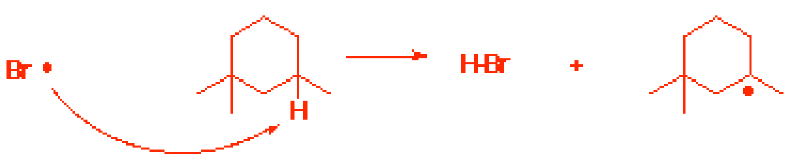


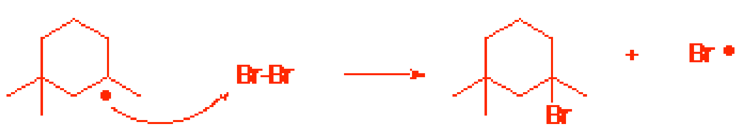
1. Assuming there is one equivalent of Br2 for each equivalent of alkane, show the structures of the two major products A and B. **(4 points)**



(3 pts) HBr (1 pt)

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

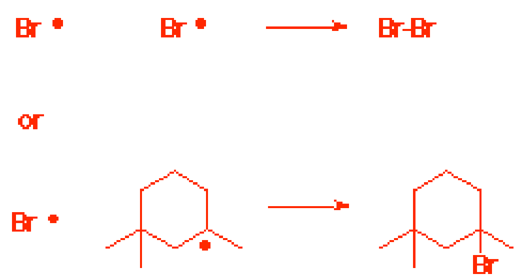




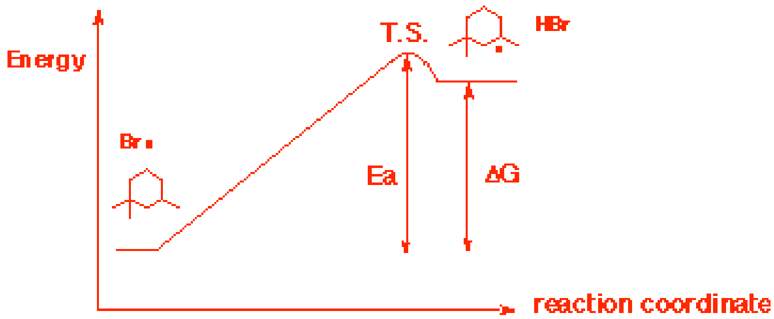
3. Write one possible termination step for the above reaction. **(2 points)**

Any combination of two possible radicals to yield a stable product

For example:

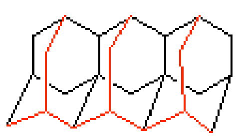


4. One of the propagation steps is endothermic and selective (the first) and the other (second) is strongly exothermic. Draw an energy diagram for the endothermic propagation step. Be sure to label both axes, label the starting materials and products (give their structures) in the correct locations. Also label the DG and the activation energy (Ea). **(5 points)**



Extra Credit (2 points): Draw the three dimensional structure of diamond showing at least three complete carbon ring units (use part structure below) If you make a mistake, redraw the part structure carefully and begin again.

No partial credit here


minimum structure