

CHEMISTRY 164 / 261 - Section A2

MIDTERM - October 18, 2007 - Dr. John C. Vederas

150 Points - 80 Minutes

Part	Points		PRINT LAST NAME:
I	60		KEY
II	40		
III	27		ID NUMBER (If Known):
IV	23		SIGNATURE:
Total	150		

Before you begin be sure that your exam has **11** consecutively numbered pages including this cover sheet. **Do not begin until told to do so.** When you begin, please **print** your name **on each page** of this exam in the upper right hand corner. Loose pages without names will be discarded. Illegible answers will be marked as incorrect. No books, notes, or unauthorized communications are permitted. If you have any questions or problems, please raise your hand. Do not leave your seat without permission. **Models are permitted but may not be handed to another and NO CALCULATORS or other electronic devices are to be used.** Slide rules are permitted.

GOOD LUCK

"Nothing is so firmly believed as that which is least known - a persuasion of certainty is a manifest testimony of foolishness." Michael Eyquem, Sieur de Montaigne 1533 -1592

"The reason why we have two ears and only one mouth is that we may hear more and talk less." Zeno of Citium (Cyprus) ca 350 - 260 BC

It must not be assumed that atoms of every sort can be linked in every variety of combination.

-from On the Nature of the Universe by Titus Lucretius Carus (100-55 BC)

I. Structure and Nomenclature - 60 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. methylene chloride



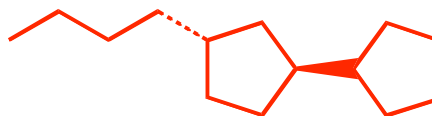
2. vinyl iodide



3. allyl fluoride

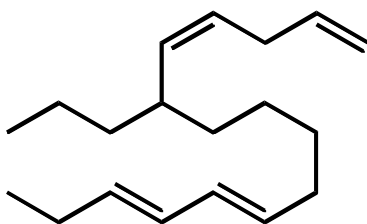


*** 4. trans-1-cyclopentyl-3-butylcyclopentane



- 2 pts wrong or no stereochemistry

*** 5.



6-propyl-1,4(Z),11(E),13(E)-hexadecatetraene

- 1 pt each error up to 4; Z and E can be listed separately

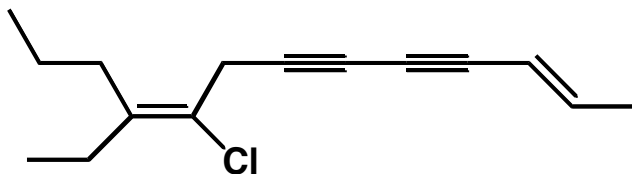
*** 6.



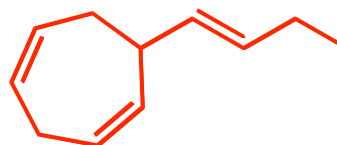
trans-1-butyl-4-ethylcyclohexane

- 2 pts wrong or no stereochemistry, will accept trans-1-ethyl-4-butylcyclohexane

*** 7.

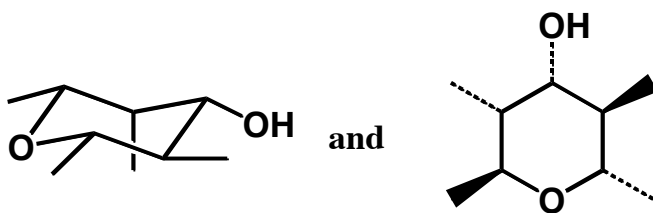
**9-chloro-10-ethyl-2(E),9(E)-tridecadien-4,6-diyne** -1 pt each error

*** 8. 6-(trans-1-butenyl)cyclohepta-1,4-diene



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

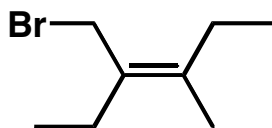
1.



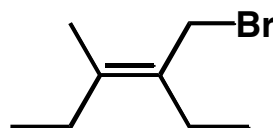
and

Stereoisomers

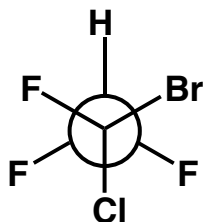
2.



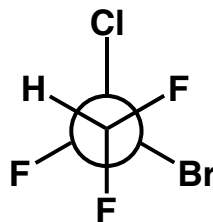
and

**Stereoisomers**

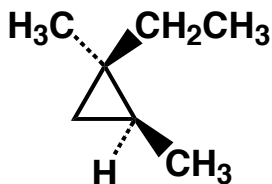
3.



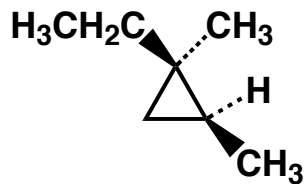
and

**Identical**

4.

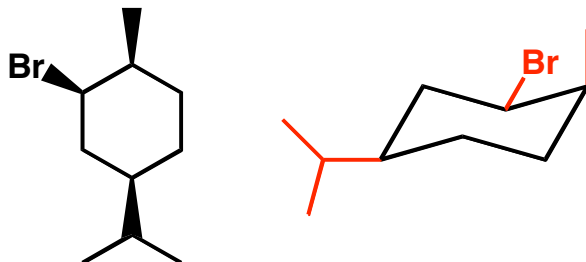


and

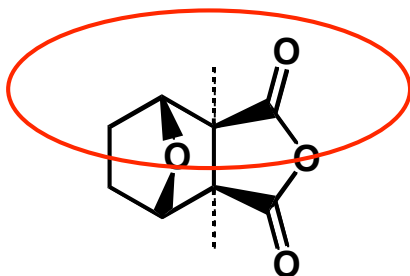
**Identical**

C. Conformation and Structural Features

1. 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)



2. Cantharidin shown below was isolated from the “Spanish fly,” *Cantharis vesicatoria*, and is a highly irritating toxin that has been used as an aphrodisiac and to promote breeding in cattle. It is an isoprenoid. Examine its structure below and answer the questions that follow.



- Provide the molecular formula of cantharidin : **C10 H12 O4** 2 pts
- How many degrees of unsaturation does cantharidin have ? **Five** 2 pts
- Circle one of the isoprene units in the structure of cantharidin above. 2 pts
- What kind of a terpene is cantharidin ? **Monoterpene** 2 pt
- Name the two oxygen containing functional groups in cantharidin. **Anhydride, Ether** 2 pts

II. Quantitative Analysis and Definitions - 40 points

A. Briefly define (10 words or less) each of the following concepts - (2 points each)

1. electronegativity

desire of an atom for electrons (negative charge)

2. Lewis acid

a substance that can accept a pair of electrons

3. Transition state

point of highest energy in a reaction when bonds are partially made and broken

B. Mescaline is the most active hallucinogenic compound in a cactus called “peyotyl” by the Aztecs. Mescaline contains carbon, hydrogen, nitrogen and oxygen. Quantitative analysis gave: C 62.54 %; H 8.05 %; N 6.63 %

1. Show how to calculate the empirical formula and obtain the correct result. **(12 pts)**
2. If the molecular weight is 211, what is the molecular formula? **(2 pts)**
3. Suppose you completely burned 211 mg of mescaline to CO₂, H₂O and nitrogen oxides. Show how to calculate the volume of CO₂ produced at standard pressure and temperature. **(4 pts)**
4. Show how to calculate the volume the CO₂ in part 3 would occupy if the temperature were lowered to -50 °C, but the pressure was kept constant. **(6 pts)** *(Page 11 has extra space for calculations)*

Question 1: Obtain % Oxygen: $100\% - 62.54\% - 8.05\% - 6.63\% = 22.78\%$ Oxygen

Calculate Crude ratios Divide Each Crude Ratio by Smallest Multiply by Integer for Whole No.

C: $62.54 / 12 = 5.21$	$5.21 / 0.474 = 11$	One (1) works as Integer to give whole numbers
N: $6.63 / 14 = 0.47$	$0.474 / 0.474 = 1$	
H: $8.05 / 1.0 = 8.05$	$8.05 / 0.474 = 17$	Empirical Formula is: C₁₁H₁₇NO₃
O: $22.78 / 16 = 1.42$	$1.42 / 0.474 = 3$	

Question 2: Determine empirical weight and compare to molecular weight

$(11 \times 12) + (17 \times 1) + (1 \times 14) + (3 \times 16) = 211$ empirical weight same as molecular weight
 Molecular Formula is same as empirical formula : **Molecular Formula is: C₁₁H₁₇NO₃**

Question 3: $(211 \text{ mg}) \times (1 \text{ mmol} / 211 \text{ mg}) = 1 \text{ mmol burned} \rightarrow$ since 11 carbons, get 11 mmols CO₂

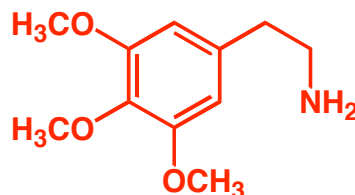
$22.4 \text{ mL} / \text{mmol (at STP)} \times (11 \text{ mmol CO}_2) = \mathbf{246 \text{ mL CO}_2 \text{ at STP}}$

Question 4: Gas Law $PV=nRT$ tells us that if n (number of moles) and pressure (P) stay constant, the volume V will decrease as we lower the temperature (i.e. directly proportional). Temperature must be converted to degrees Kelvin

STP is 0 °C or 273 °K; -50 °C is 223 °K

$(246 \text{ mL CO}_2) \times (223 \text{ °K} / 273 \text{ °K}) = \mathbf{201 \text{ mL as volume at -50 °C}}$

Mescaline Structure (can not be determined from information given) is:



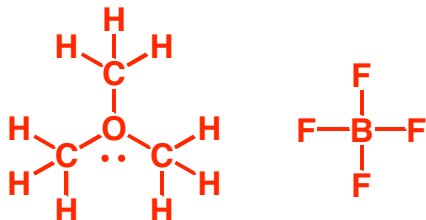
C. Circle the appropriate letter to indicate whether each of the following statements is true (T) or false (F). No penalty for guessing. (Similar to previous exams but be cautious) (1 point each - total 10 points)

- | | | |
|---|----------|----------|
| 1. ΔG is negative for an endothermic reaction | T | F |
| 2. Resonance forms are rapidly interconverting molecules | T | F |
| 3. About 15 to 20 kcal/mole of energy are available at room temperature | T | F |
| 4. The net dipole of chloroform is not aligned with any carbon-chlorine bond | T | F |
| 5. A completely pure organic compound may have different physical properties depending on whether it was made by chemists or isolated from Nature | T | F |
| 6. Bronsted-Lowry acids are also Lewis acids | T | F |
| 7. A radical intermediate in a reaction is correctly described as a transition state | T | F |
| 8. The pK_a of pure water is about 7 | T | F |
| 9. The structure of a molecule determines all of its physical and biological properties | T | F |
| 10. Overlap of two sp orbitals in a triple bond generates a sigma molecular orbital | T | F |

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

A. Trimethyloxonium fluoroborate [$(\text{CH}_3)_3\text{O}^+ \text{BF}_4^-$] is a salt which is a very powerful methyl donor.

1. Based on your understanding of 1st and 2nd row elements in the periodic table, draw its molecular structure. Be sure to show all bonds and any lone pairs of electrons that may be present. (2 points)



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

$$\begin{aligned}
 &+ 8 \text{ protons} - 2 (1s \text{ electrons}) - 2 (\text{unshared electrons}) - 3 (\text{half of } 6 \text{ electrons shared}) \\
 &= + 1 \text{ is formal charge on oxygen}
 \end{aligned}$$

3. Calculate the formal charge on a boron. Use any method, but show calculations. (2 points)

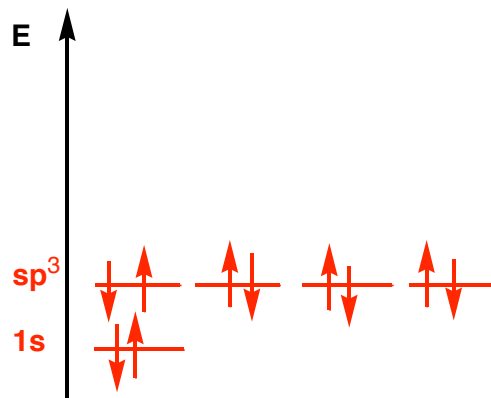
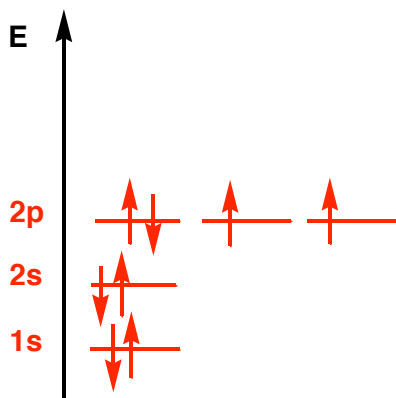
$$\begin{aligned}
 &+ 5 \text{ protons} - 2 (1s \text{ electrons}) - 4 (\text{half of } 8 \text{ electrons shared}) \\
 &= - 1 \text{ is formal charge on boron}
 \end{aligned}$$

4. What is the hybridization of boron in tetrafluoroborate anion [BF_4^-] and what are the bond angles ? (2 points)

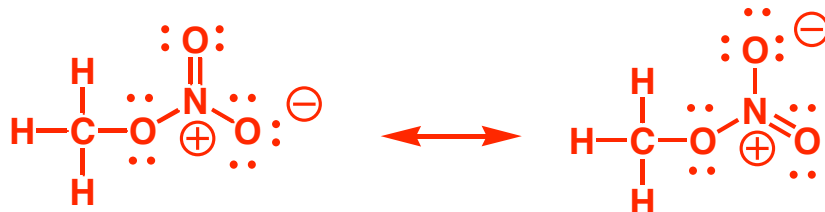
hybridization on boron is sp^3

F-B-F bond angles are 109 degrees

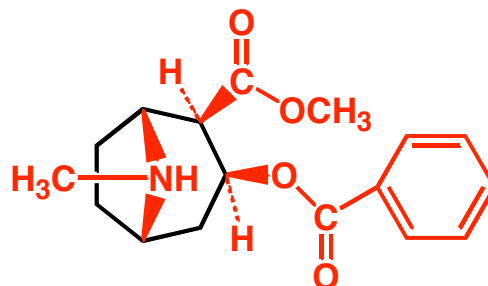
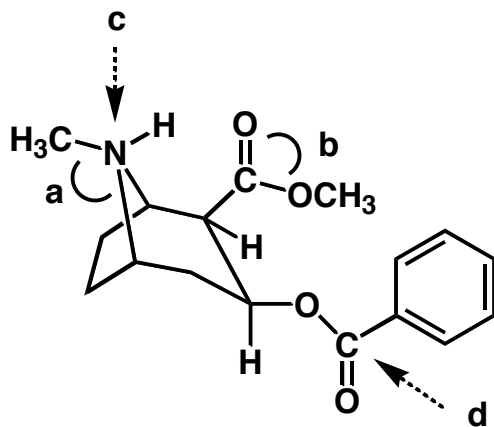
5. Draw two energy diagrams: one depicting all of the atomic orbitals of an oxygen atom by itself and another indicating the electronic structure of oxygen in [$(\text{CH}_3)_3\text{O}^+ \text{BF}_4^-$]. Be sure to label each orbital. (6 pts – 3 pts each)



B. Methyl nitrate is a rocket fuel that explodes spontaneously at 65 °C. Its molecular formula (and linear structure) is CH_3ONO_2 . Draw the structure in full to show all bonds, lone pairs and formal charges that are not zero. Then draw an equally good resonance form. (4 points)



C. Cocaine from *Erythroxylon coca* bushes grown in the Amazon basin is a stimulant which acts on the nervous system. It has been taken for more than 2000 years to obtain a euphoric effect (e.g. as hydrochloride), but recent 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.

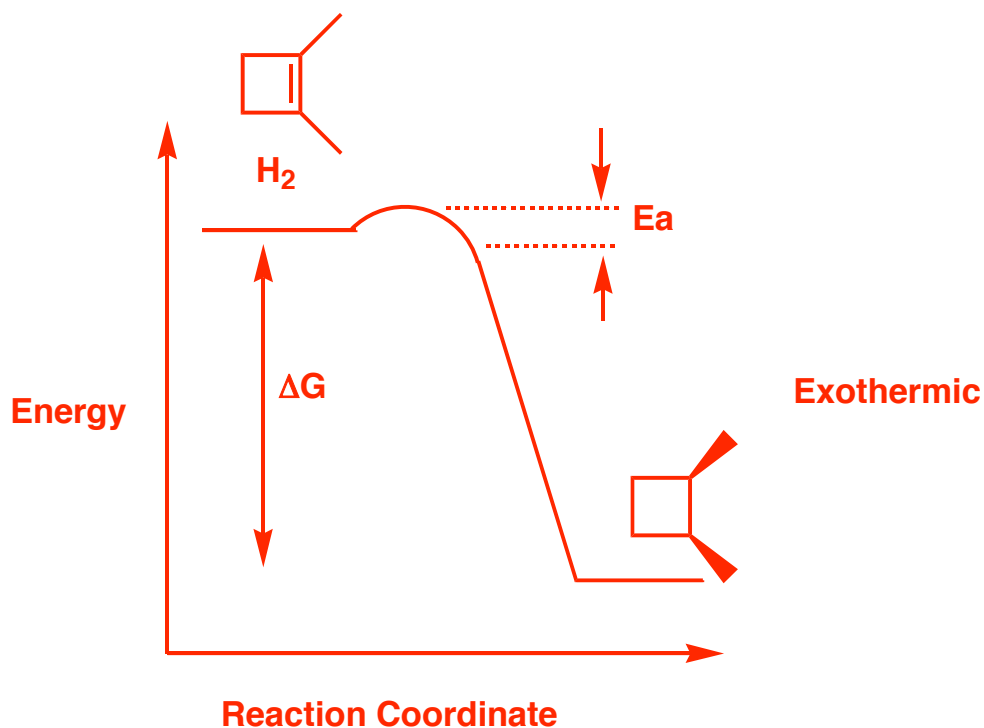
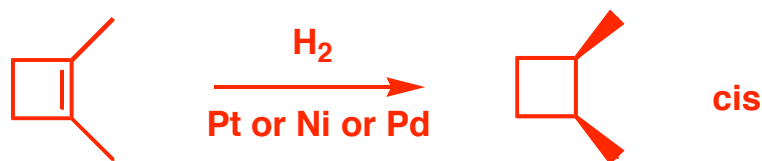


1. What is the angle labeled **a** ? (1 pt) **109 degrees**
2. What is the angle labeled **b** ? (1 pt) **120 degrees**
3. What is the functional group labeled **c** ? (1 pt) **amine (or amine salt or ammonium salt)**
4. What is the functional group labeled **d** ? (1 pt) **ester**
5. Examine the perspective drawing of cocaine and redraw this molecule in flat projection using the seven-member ring provided above 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. (5 pts)

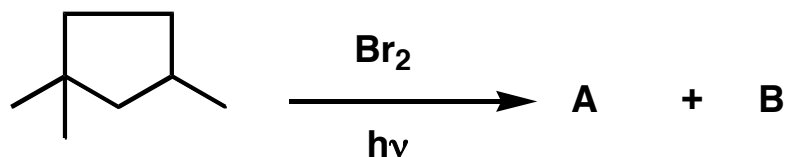
IV. Reactions and Mechanism - (23 points)

A. Write a balanced equation for complete reaction of 1,2-dimethylcyclobutene with hydrogen in the presence of a catalyst. Provide a catalyst and show the product with correct stereochemistry (3 points). Draw a simple energy diagram for this process (no intermediates). 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.

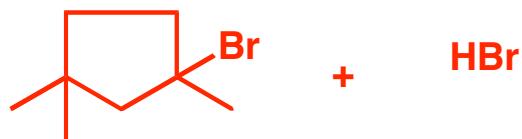
(10 points)



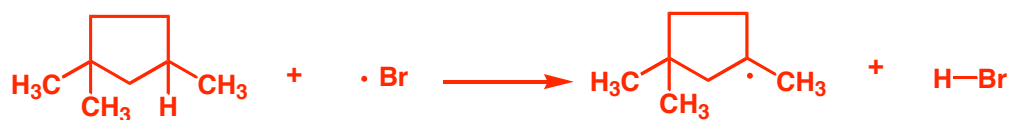
B. Examine the overall reaction shown below and answer the questions that follow.



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. (3 points)

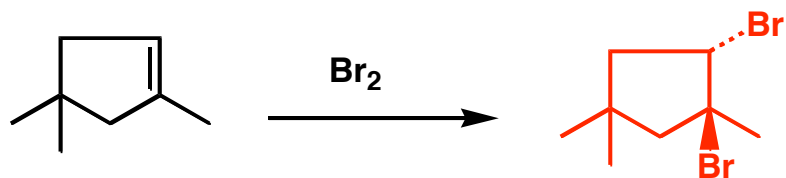


2. Write the first propagation step for the reaction. (4 pts)

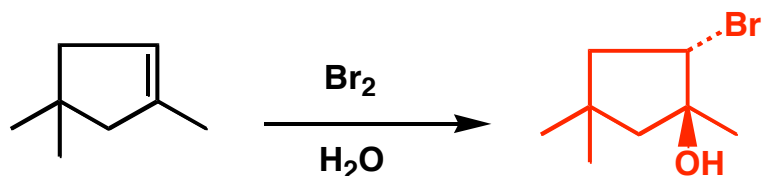


C. Show the products of the following reactions with correct stereochemistry (6 pts - 3 pts each)

1.



2.



Extra Credit (3 points): Name one person who won the Nobel Prize in Chemistry or Medicine this month ?

No partial credit here

Last name of one of the following:

Medicine: Mario Capecchi , Martin Evans, Oliver Smithies

Chemistry: Gerhard Ertl