

**Answer Key** – *Red are the nominal correct answer expected* – *Blue are further explanation*

*Please read the following before proceeding*

1. Write your roll number at the top of this page and in the box on the last page. If you need to verify your class roll number, you can do this at the front of the room when you turn in your exam paper.

2. The exam is divided into three parts.

Part A is Scantron scored (44 points)

- a. **IMPORTANT** Bubble-in your GTID number correctly.
- b. **IMPORTANT** Bubble-in the TEST FORM, located at the top of the page.

Part B is free response (40 points)

Part C is free response (20 points)

Exam 1 Total (104 points available, includes extra credit)

3. Materials: Turn off cell phones and wireless PDA devices. Place all other materials on the floor. You will only need a pencil. Molecular models are optional.
4. Show your Buzz Card when you turn in your completed exam.
5. You must work alone.
6. This is a closed book exam. Give or take no assistance from other students. Recall the Georgia Tech Honor Code.

*"I have always worked better alone."-- Claude Monet*

"I pledge my honor that I have not violated the Honor Code during this examination."

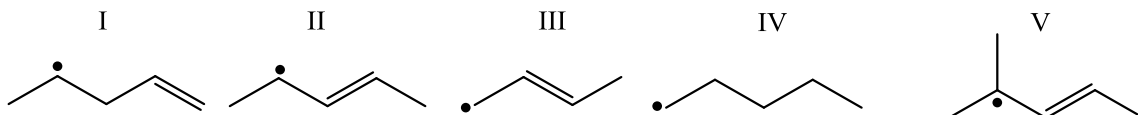
Signed \_\_\_\_\_

Part A (44 points, 4 points each) Circle the correct answer. There is only one correct answer.

1 Which compound contains the oxygen atom with the greatest electron density?

- A)  $\text{CH}_3\text{-O-CH}_3$  (dimethyl ether)
- B)  $\text{H-C(=O)-CH}_3$  (acetaldehyde)
- C)  $\text{CH}_3\text{-C(=O)-CH=CH}_2$  (methyl vinyl ketone)
- D)  $\text{CH}_3\text{-C(=O)-CH}_2\text{CH=CH}_2$  (4-penten-2-one)
- E)  $\text{H-C(=O)-H}$  (formaldehyde)

2. Which free radical would be the lowest energy intermediate?



- A) V
- B) I
- C) II
- D) IV
- E) III

3. The allyl radical has how many electrons in nonbonding molecular orbitals?

- A) 0
- B) 1
- C) 2
- D) 3

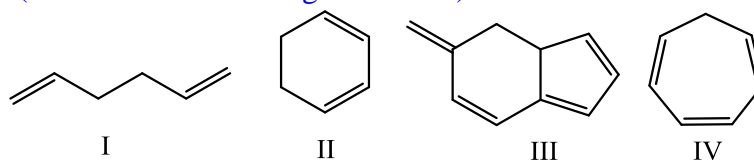
4. Which of the following compounds contains a nitrogen with a lone pair that is not engaged in resonance?

- A)  $\text{C}_6\text{H}_5\text{-NH}_2$
- B)  $\text{CH}_2\text{=CH-NH}_2$
- C)  $\text{CH}_2\text{=CH-CH}_2\text{-NH}_2$
- D) *E* isomer of  $\text{CH}_3\text{-CH=CH-NH}_2$
- E) *Z* isomer of  $\text{CH}_3\text{-CH=CH-NH}_2$

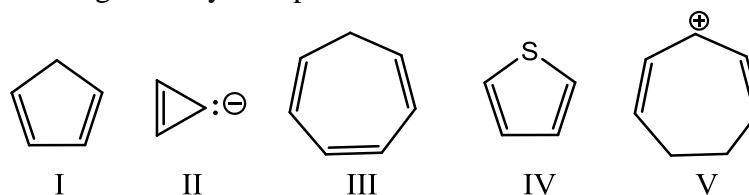
5. How many atoms in the benzyl carbocation,  $\text{C}_6\text{H}_5\text{CH}_2^+$ , share the positive charge?

- A) 1
- B) 3
- C) 4
- D) 7

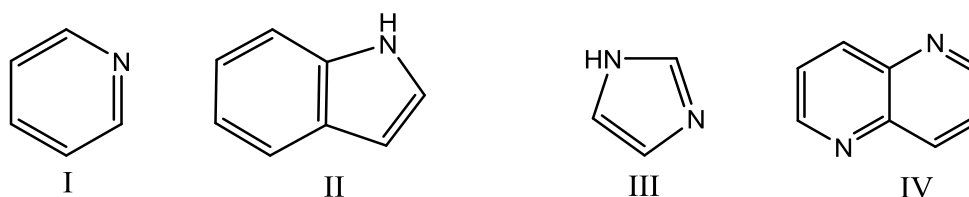
6. What is the order of the following compounds in increasing lambda max ( $\lambda_{\text{max}}$ )? Hint: when lambda max increases the energy of the HOMO to LUMO electronic transition decreases. **Granted credit for any answer. On the exam ">" should have been "<"**. **Correct below. (smallest lambda < largest lambda)**



- A) II < I < III < IV  
 B) IV < III < II < I  
**C) I < II < IV < III (III is the most conjugated)**  
 D) III < II < IV < I
7. Which of the following would you expect to be antiaromatic?

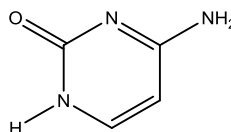


- A) I  
**B) II**  
 C) III  
 D) IV  
 E) V
8. Some heteroarene compounds can be Lewis bases (electron donors) and react with acidic hydrogens. Which of the following is **not** a base?  
 (B = group III, C = group IV and N = group V element)



- A) I  
**B) II**  
 C) III  
 D) IV

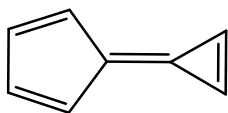
9. Consider the molecular orbital model of cyclopentadienyl anion ( $C_5H_5^{-1}$ ). In the ground state how many  $\pi$  (pi) molecular orbitals are filled with electrons?
- A) 1  
B) 2  
C) 3  
D) 4  
E) 6
10. Which of the following instructions does not lead to a correct resonance structure?
- A) Move lone pair electrons toward a positive charge.  
B) Move a single nonbonding electron toward a pi bond.  
C) Move lone pair electrons towards an  $sp^3$  hybridized atom.  
D) Move pi electrons toward an empty bond.  
E) Move pi electrons toward a positive charge.
11. Cytosine (below) is one of the four main bases found in DNA and RNA. Considering resonance and molecular orbital theory, which term below would best describe cytosine?



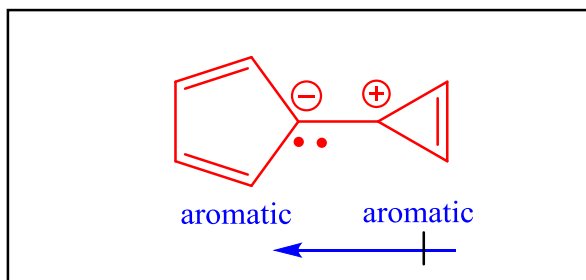
- A) Acyclic  
B) Not aromatic  
C) Anti-aromatic  
D) Aromatic

**Part B** (40 points, 4 points each) Provide the explanation or structure(s) of the major organic products(s), including stereochemistry.

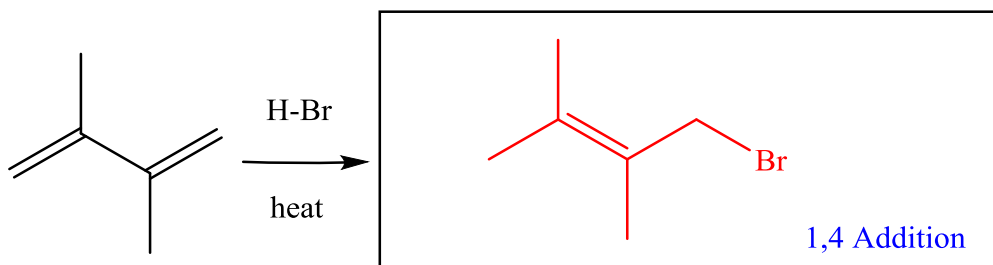
- 12.) A dipole moment can be defined as the product of magnitude of charge and the distance of separation between the charges. The conjugated hydrocarbon calicene is a polar molecule with a calculated dipole moment of 4.3 Debye. How can you explain this polarization of calicene?



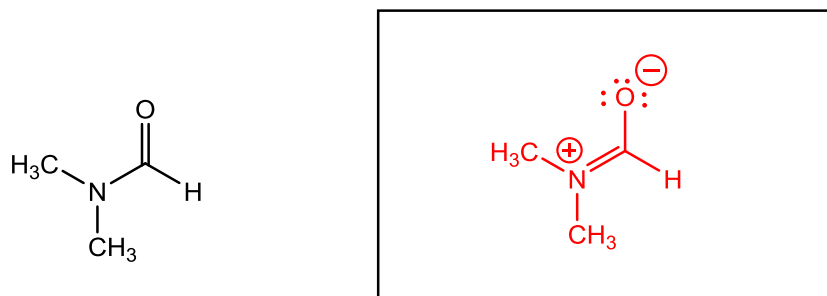
Calicene



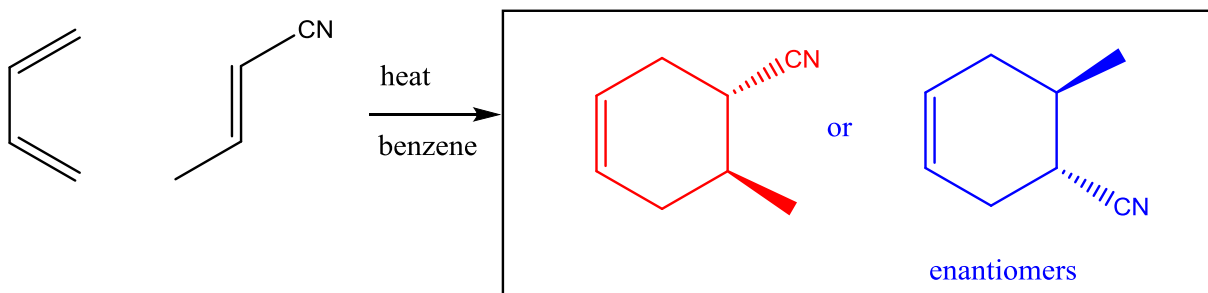
13.) Draw the products for the following reaction



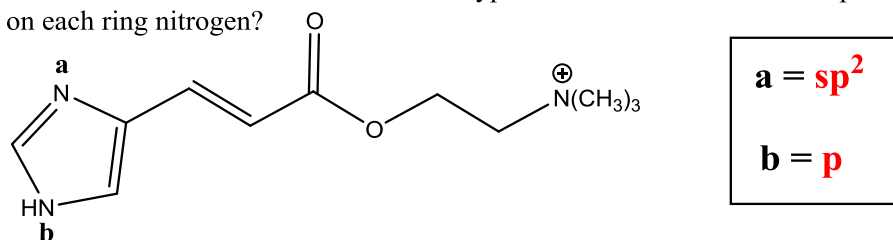
14. Draw a resonance structure for N, N-dimethylformamide (lone pairs not shown). Account for all lone pair electrons and charges.



15.) Draw one of the two enantiomeric products for the following thermal reaction.



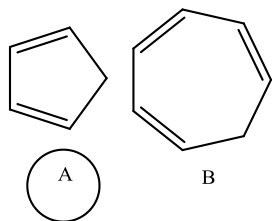
16.) Murexine is a neuromuscular blocker. What type of orbitals contain the lone pairs of electrons on each ring nitrogen?



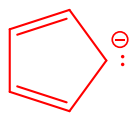
17) Which of the following polyenes would have the smallest (most acidic) pKa value? Explain with a short phrase or drawing

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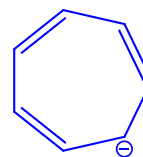
circle: A or B



Explanation

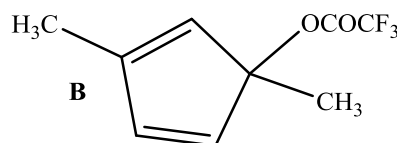
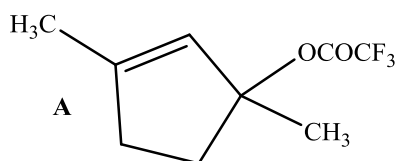


aromatic, more stable  
conjugate base of A

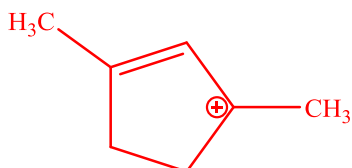


anti-aromatic

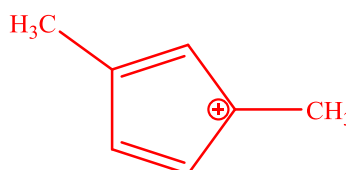
18.) The rate of solvolysis, under  $S_N1$  conditions, of compound A below is about **100 trillion** times faster than compound B. Explain with a phrase or drawing



**A** forms a relatively stable allylic carbocation, while **B** forms an anti-aromatic carbocation

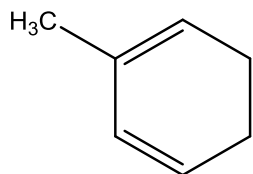


allylic carbocation

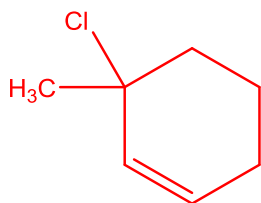


anti-aromatic carbocation

19 and 20.) (8 points) When 2-methyl-1,3-cyclohexadiene is treated with HCl at  $-80^\circ\text{C}$  or  $+40^\circ\text{C}$ , two different major products are obtained. Draw the major product formed under these two conditions.



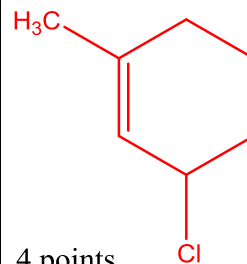
major lower temperature product



4 points

1,2 addition

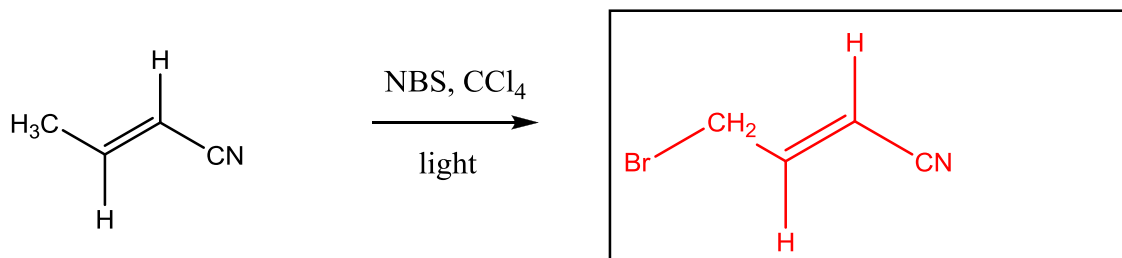
major higher temperature product



4 points

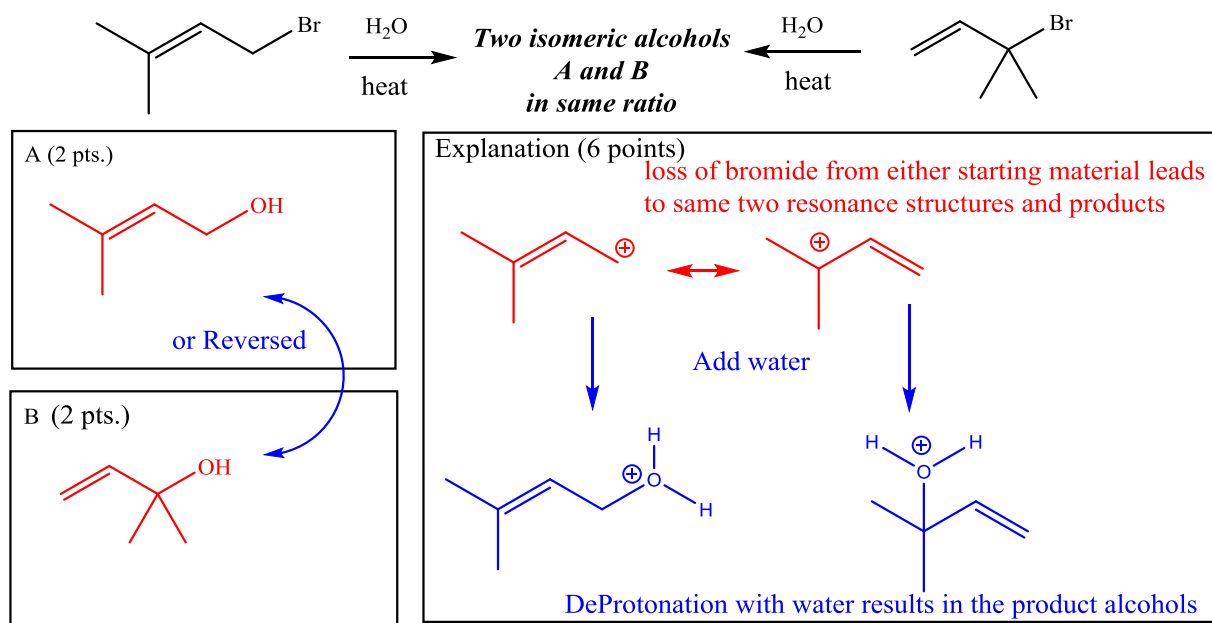
1,4 addition

21. Give the major product of the following reaction.

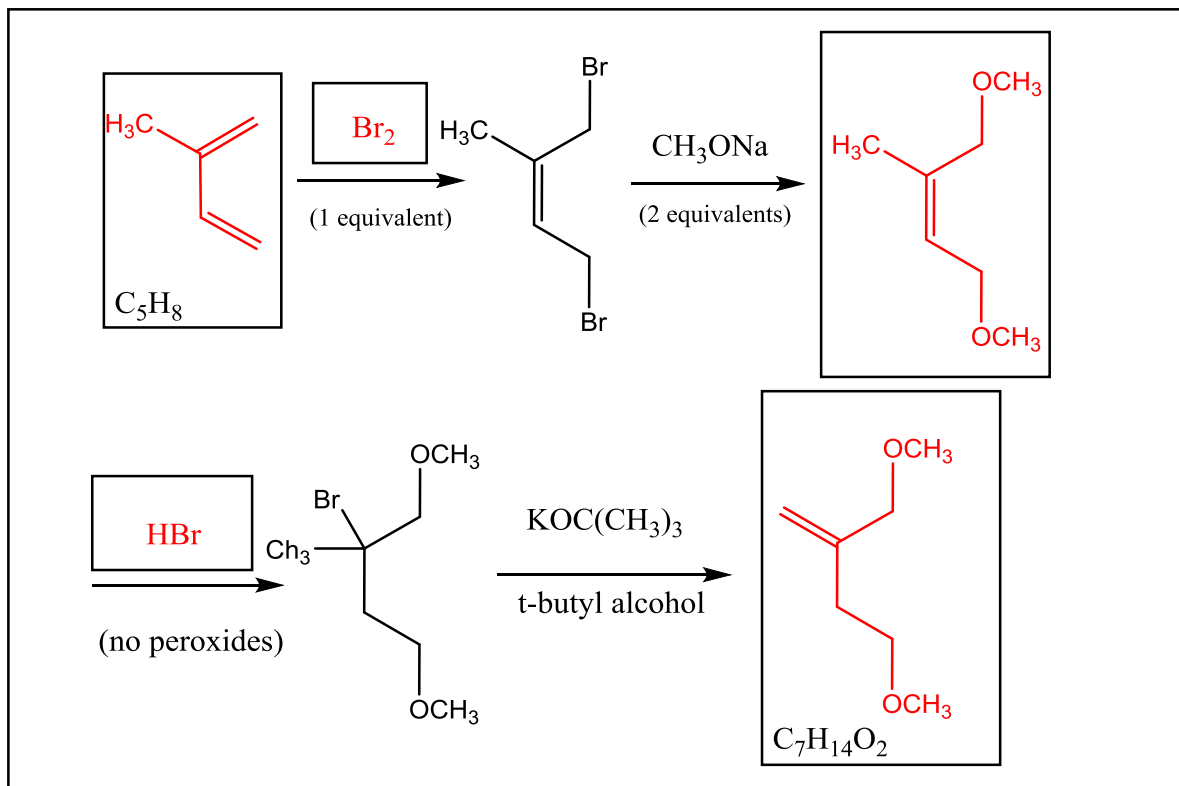


**Part C** (20 points, 10 points each)

22. (10 points) **Mechanism:** When treated under  $S_N1$  conditions, the two bromides below give the same pair of alcohols in the same ratio. Provide structures for **A & B** and explain with drawings or brief phrases why the two bromides lead to the same products.



23. (10 points) Elucidate the missing reagents and structures in the following synthesis



Acid	Approximate $pK_a$	Conjugate Base
$Hsbf_6$	$< -12$	$Sbf_6^-$
$HI$	$-10$	$I^-$
$H_2SO_4$	$-9$	$HSO_4^-$
$HBr$	$-9$	$Br^-$
$HCl$	$-7$	$Cl^-$
$C_6H_5SO_3H$	$-6.5$	$C_6H_5SO_3^-$
$(CH_3)_2OH^+$	$-3.8$	$(CH_3)_2O$
$(CH_3)_2C=OH^+$	$-2.9$	$(CH_3)_2C=O$
$CH_3OH_2^+$	$-2.5$	$CH_3OH$
$H_3O^+$	$-1.74$	$H_2O$
$HNO_3$	$-1.4$	$NO_3^-$
$CF_3CO_2H$	$0.18$	$CF_3CO_2^-$
$HF$	$3.2$	$F^-$
$CH_3CO_2H$	$4.75$	$CH_3CO_2^-$
$H_2CO_3$	$6.35$	$HCO_3^-$
$CH_3COCH_2COCH_3$	$9.0$	$CH_3COCH^--COCH_3$
$NH_4^+$	$9.2$	$NH_3$
$C_6H_5OH$	$9.9$	$C_6H_5O^-$
$HCO_3^-$	$10.2$	$CO_3^{2-}$
$CH_3NH_3^+$	$10.6$	$CH_3NH_2$
$H_2O$	$15.7$	$OH^-$
$CH_3CH_2OH$	$16$	$CH_3CH_2O^-$
$(CH_3)_3COH$	$18$	$(CH_3)_3CO^-$
$CH_3COCH_3$	$19.2$	$^-CH_2COCH_3$
$HC\equiv CH$	$25$	$HC\equiv C^-$
$H_2$	$35$	$H^-$
$NH_3$	$38$	$NH_2^-$
$CH_2=CH_2$	$44$	$CH_2=CH^-$
$CH_3CH_3$	$50$	$CH_3CH_2^-$



**NOTE:** If you need to verify your class roll number, you can do this at the front of the room when you turn in your exam paper.

**READ:**

- ✓ **Write your class roll number on**
  - (a) the top of the first page and
  - (b) in the box to the right.
- ✓ **Verify that you have bubbled in the following on your Scantron card**
  - (a) **Bubbled-In GTID number**
- ✓ **Show your Buzzcard when submitting exam and card**

**Class Roll number** \_\_\_\_\_

**Part A** Scantron scored (44 points)  
and will be posted on T-square

**Part B & C** Free Response

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**Part B & C only** \_\_\_\_\_ (60)