Memorial University of Newfoundland

Chemistry 2400

Sample

Final Examination	December, 2014	Time: 3 hours
Name:	MUN ID:	
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READ THE FOLLOWING CAREFULLY

- This examination contains 12 pages. Read all questions carefully and use your time wisely.
- The use of molecular models is permitted.
- Answer each question in the space provided. If you need more space you may use the back of pages; however, you should clearly indicate that you have done so.

Do not write in the enclosed area below

Question	Value	Mark
1-10	20	
11	15	
12	15	
13	30	
14	10	
15	10	
Bonus	5	
Total	105	

Part A. Multiple choice questions. [20 pts]

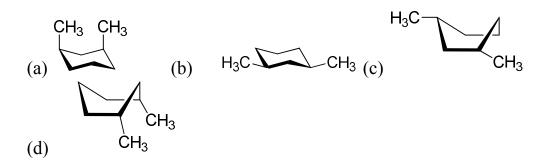
- 1. Which of the following statement is <u>incorrect</u> about benzene? **A**
 - (a) All of the carbon atoms are sp hybridized.
 - (b) It has delocalized electrons.
 - (c) The carbon-hydrogen bond lengths are all the same.
 - (d) All twelve atoms lie in the same plane.
 - (e) Its molecular dipole moment is zero.
- 2. What is the IUPAC name for the following compound?

- (a) 5-Bromo-2-heptyne
- (b) 3-Bromo-5-heptyne
- (c) 2-bromo-2-methyl-4-hexyne
- (d) 5-bromo-5,5-dimethylhexyne
- (e) 5-bromo-5-methyl-2-hexyne
- (f) 5-methyl-2-hexynl bromide
- 3. Which of the following is not a resonance form of the following anion?__C_

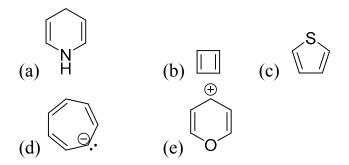
(a)
$$CH_3$$
 CH_3

$$(c) \qquad \stackrel{\bigcirc{CH_3}}{\stackrel{\bigcirc{O}}{\ominus}} \qquad (d) \qquad \stackrel{\bigcirc{CH_3}}{\stackrel{\bigcirc{O}}{\ominus}} \qquad (e) \qquad \stackrel{\bigcirc{O}}{\stackrel{\bigcirc{CH_2}}{\bigcirc}} \qquad (d) \qquad (e) \qquad ($$

4. Which of the following presents the most stable conformation of *cis*-1,3-dimethylcyclohexane?____**B**____



- 5. Which of the following is \underline{not} normally considered to be a nucleophile?____E___
 - (a) NH_3 (b) H_2O (c) CI^- (d) $CH_2=CHCH_3$ (e) CH_3^+
- 6. Which of the following compound will undergo an $S_{\rm N}2$ reaction most readily?____E___
 - (a) $(CH_3)_2CCH_2I$
 - (b) $(CH_3)_3CC1$
 - (c) $(CH_3)_2CHI$
 - (d) (CH₃)₂CHCH₂CH₂CH₂Cl
 - (e) CH₃CH₂CH₂CH₂I
- 7. Which of the following species is the <u>least nucleophilic?______</u>**D**_____
 - (a) $(CH_3)_3CO^-$
 - (b) H₂O
 - (c) $(CH_3)_3N$
 - (d) BF_3
 - (e) CN
- 8. Which of the following structure(s) is (are) aromatic? C, \underline{E}



(a)
$$\stackrel{\mathsf{NH}_2}{(\mathsf{b})}$$
 (c) $\stackrel{\mathsf{N}}{(\mathsf{b})}$ (d) $\stackrel{\mathsf{H}_3\mathsf{C}}{(\mathsf{e})}$

- 10. Which statement below best describes the collection of all the stereoisomers of 1,2-dibromocyclohexane? $\underline{\mathbf{B}}$
 - (a) Two pairs of enantiomers
 - (b) A pair of enantiomers and a meso compound
 - (c) Two diastereomers
 - (d) A meso compound
 - (e) Four diastereomers

Part B. Non-multiple choice questions.

11. Propose reasonable mechanisms for the following reactions. [15 pts]

excess
HBr

Br

H₂O

$$H^+$$
 H^+
 H_2 O

 H^+
 H^+

$$\begin{array}{c} \text{OH} & \text{(i) TsCI, pyridine} \\ \text{H} & \text{(ii) NaCN} \\ \\ \text{H} & \text{CI} \\ \\ \text{H} & \text{NEC} \\ \\ \text{Ts} = \begin{cases} -1 & \text{CH}_3 \\ \text{NC} & \text{CH}_3 \\ \text{NC} & \text{CH}_3 \\ \\ \text{NC}$$

12. Propose reasonable multistep synthesis using the provided starting materials and any necessary reagents. [15 pts]

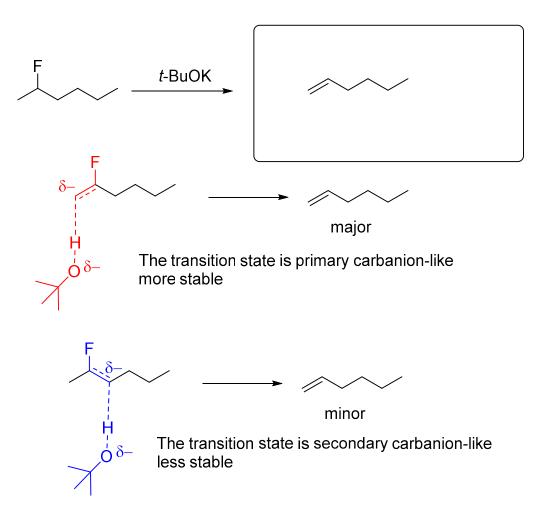
Route 1

Route 2

$$\begin{array}{c} C_2H_5\\ H \longrightarrow OH\\ HO \longrightarrow H\\ C_2H_5 \end{array}$$

Synthesis

13. Provide the major organic products for the following reactions. [30 pts]



OH (i)
$$H_2SO_4$$
, heat (ii) BH_3 : THF (iii) $NaOH$, H_2O_2 , H_2O (ii) H_2SO_4 , heat E1 (ii) BH_3 : THF (iii) $NaOH$, H_2O_2 , H_2O

$$HO$$
 H_2SO_4
heat
 HCI
 CI
 CI
 CH_3I

- 14. Explain each of the following statements. [15 pts]
 - (a) Compound **A** is a weaker base than compound **B**.

$$NH_2$$
 NH_2
 NH_2

$$(\overset{\circ}{N}H_2 \qquad \overset{H}{\overset{\oplus}{N}}H$$

$$\overset{\circ}{N}\overset{\circ}{\to} 0 \ominus \qquad \overset{\ominus}{\to} \overset{\circ}{N}\overset{\circ}{\to} 0 \ominus \ominus$$

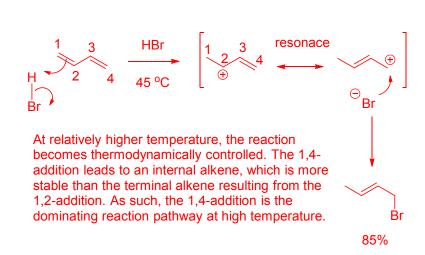
The lone pair electrons on the amino group can be delocalized to the electron-withrawing NO₂ group through resonance effect. As such, the lone pair is deactivated and stablized, which in turn reduces the basicity of the amino group.

The electron-donating methoxy group pushes electrons to the carbon adjacent to the amino group. Through resonance effect, a carbanion character is revealed. The electron pushing activate the lone pair of the amino, making them more readily to donate. As such, the amino becomes a stronger base.

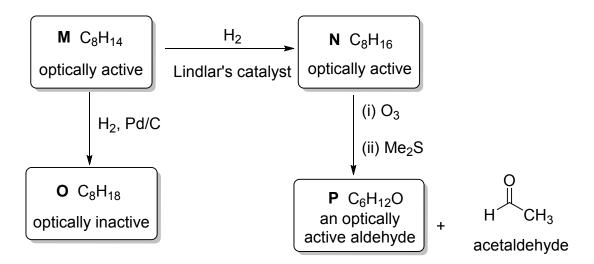
(b) Cyclopentadiene is more acidic than cyclopentane.

The conjugate base of cyclopentadiene is an aromatic anion, which shows remarkable stability. The conjugate base of cyclopentane is a secondary carbanion, which does not gain as much stability as the aromatic cyclopentadiene anion. The considerably stable conjugate base of cyclopentadiene makes cyclopentadiene a relatively stronger acid.

(c) The reaction between HBr and 1,3-butadiene gives 1,2-addition product as the major product at -80 °C. When the reaction temperature is raised to 45 °C, 1,4-addition product becomes the major product.



15. Deduce the structures of compounds **M**–**P**. Draw structures that show stereochemistry where appropriate. [10 pts]



Analysis

(1) $\bf P$ is an optically active aldehyde with six carbons. the formula $C_6H_{12}O$ suggests it has only one degree of unsturation. Therefore, the possible structures that are optically active aldehydes can be enumerated as:

(2) From the ozonolysis, the structure of ${\bf N}$ is deduced to be as two possible alkenes.

(3) From the catalytic hydrogenation using Lindlar's catalyst, it is deduced that compound \mathbf{M} is an alkyne. Therefore, the following two possible structures can be reasoned.

(4) From the hydrogenation reaction, it is reasoned that only **O-1** is an optically inactive hydrogenation product. Therefore, the structures for the above compounds should be **P-1**, **N-1**, **M-1**, and **O-1**.