DEPARTMENT OF CHEMISTRY AND CHEMICAL TECHNOLOGY
202-BZF-05 ORGANIC CHEMISTRY I
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SOLUTIONS TO FINAL EXAMINATION

Prepared by

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QUESTION 1 [8 marks]

a) Provide IUPAC names for the following compounds and, where applicable, include R/S or E/Z designation to indicate the stereochemistry. (4 marks)

i) 2,3,7-trimethylnonane

ii) (1S,5R)-5-chlorocyclopent-2-enol

iii) (R,Z)-3-bromohept-4-en-1-yne

iv) 4-tert-butyl-2-nitrotoluene or 4-tert-butyl-1-methyl-2-nitrobenzene

b) Provide the bond-line structures for each of the following names. (4 marks)

i) trans-4-isopropylcyclohexanol

ii) (Z,R)-4-methyl-2-hexene

or its enantiomer

iii) 2,4,6-tribromoaniline

iv) (S)-hepta-3,5-diyn-2-ol
QUESTION 2 [8 marks]

a) Given the following trend in proton acidity among the following hydrocarbon compounds: *(N.B. the acidic proton of each compound is indicated in **bold**)*

\[
\begin{array}{c}
\text{F}_3\text{C} \equiv \text{H} > \text{F}_3\text{C} \equiv \text{H} > \text{F}_3\text{C} \equiv \text{H} \\
\text{A} \quad \text{B} \quad \text{C}
\end{array}
\]

i) Identify which of A, B and/or C has the largest $K_a$. (0.5 mark) **A**

ii) Identify which of the three has the largest p$K_a$. (0.5 mark) **C**

iii) Which one of the three has the acidic proton bonded to the most electronegative carbon? (0.5 mark) **A**

iv) Which one of the three has a C-H bond with the greatest $s$ orbital character? (0.5 mark) **A**

v) Rank the strength of conjugate bases expected when A, B and C undergo acid-dissociation. (1.5 mark)

\[
\begin{array}{c}
\text{A} < \text{B} < \text{C}
\end{array}
\]

Least basic Most basic

vi) Identify which of A, B and/or C has at least one sp2-hybridized carbon. **B** (0.5 mark)

vii) Does the following reaction favour the forward or reverse reaction? Explain. (2 mark)

\[
\begin{align*}
\text{F}_3\text{C} \equiv \text{H} & \quad + \quad \text{F}_3\text{C} \equiv \text{H} \\
& \quad \underset{\text{Forward}}{\longrightarrow} \\
& \quad \underset{\text{Reverse}}{\quad \text{F}_3\text{C} \equiv \text{H} + \text{F}_3\text{C} \equiv \text{H}}
\end{align*}
\]

The reaction will favour the forward reaction because alkane is considerably less acidic than alkene (or alkenyl anion is considerably less basic than alkyl anion). The direction of an acid-base reaction favours the side with weaker acid and base.

b) Phenol, C₆H₅OH, is an aromatic alcohol. It has a $pK_a$ of 9.9, which is considerably lower than typical $pK_a$ ranges of alcohols ($pK_a = 16 - 20$). Why? (2 mark)

\[
\begin{align*}
\text{Phenol} & \quad \text{OH} & \quad \text{Phenol} \quad \text{is} & \quad \text{considerably} & \quad \text{more} & \quad \text{acidic} & \quad \text{than} \\
& \quad \text{charged} & \quad \text{typical} & \quad \text{alcohols} & \quad \text{because} & \quad \text{the} & \quad \text{negative} \\
& \quad \text{charge} & \quad \text{of} & \quad \text{the} & \quad \text{negative} & \quad \text{charge} & \quad \text{of} \\
& \quad \text{anion} & \quad \text{anion} & \quad \text{anion} & \quad \text{anion} & \quad \text{anion} & \quad \text{anion} \\
& \quad \text{phenoxide} & \quad \text{phenoxide} & \quad \text{phenoxide} & \quad \text{phenoxide} & \quad \text{phenoxide} & \quad \text{phenoxide} \\
\text{Charge} & \quad \text{through} & \quad \text{through} & \quad \text{through} & \quad \text{through} & \quad \text{through} & \quad \text{through} \\
\text{stabilization} & \quad \text{benzene} & \quad \text{benzene} & \quad \text{benzene} & \quad \text{benzene} & \quad \text{benzene} & \quad \text{benzene}
\end{align*}
\]
QUESTION 3 [8 marks]
a) For each of the following pairs, circle the compound that would display a higher boiling point. (1.5 marks)
   i) pentane  Or  2-methylbutane
   ii) propane  Or  2-chloropropane
   iii) butane  Or  1-propanol

b) Provide the most and the least stable Newman projections of 2-bromo-3-methylbutane along its C2-C3 bond. (2 marks)

   ![Newman projections]
   Most stable  Least stable

   ![Newman projections]

C

least stable chair conformation of cis-isomer (A)  most stable chair conformation of trans-isomer (B)

ii) Between the two chair conformations (A) and (B), which is more stable? Explain. (1 mark)

Conformation A is more stable. Conformer B displays 1,3-diaxial interaction because of the axial methyl group.

c) Rank the following compounds in order of increasing heat of combustion. (1.5 mark)

   propylcyclopropane  ethylcyclobutane  methylcyclopropane
   A  B  C

   Least  A  B  most

d) i) Draw the most stable chair conformations of cis- and trans-isomers of 1-tert-butyl-3-methylcyclohexane. (2 marks)

   ![Conformations]

   most stable chair conformation of cis-isomer (A)  most stable chair conformation of trans-isomer (B)

   Conformation A is more stable. Conformer B displays 1,3-diaxial interaction because of the axial methyl group.
QUESTION 4 [6.5 marks]

a) Identify whether each of the following compounds is chiral or achiral. For all molecules that are chiral, indicate the number of chiral centres. (3.5 marks)

<table>
<thead>
<tr>
<th></th>
<th>chiral or achiral?</th>
<th># of chiral centres</th>
</tr>
</thead>
<tbody>
<tr>
<td>i)</td>
<td>Chiral</td>
<td>2</td>
</tr>
<tr>
<td>ii)</td>
<td>Achiral</td>
<td></td>
</tr>
<tr>
<td>iii)</td>
<td>Achiral</td>
<td></td>
</tr>
<tr>
<td>iv)</td>
<td>Achiral</td>
<td></td>
</tr>
<tr>
<td>v)</td>
<td>Chiral</td>
<td>1</td>
</tr>
</tbody>
</table>

b) For each of the following pairs, identify their relationships either as identical, constitutional isomers, enantiomers or diastereomers. (3 marks)

i) Constitutional Isomers

ii) Identical

iii) Enantiomers
QUESTION 5 [9 marks]

a) Which mechanism (E1, E2, S_N1 or S_N2) is involved in each reaction of the following alcohol? Circle your answer for each reaction. (N.B. only one choice of mechanism per reaction) (4 marks)

b) Rank the following molecules in order of their expected S_N1 reactivity (from least to most reactive). (2 marks)

b) Rank the following molecules in order of their expected S_N1 reactivity (from least to most reactive). (2 marks)

B < D < A < C
Least reactive Most reactive

Two possible answers

(c) Determine if the following statements in reference to S_N1 mechanism are TRUE (T) or FALSE (F) by circling the appropriate letter: (3 marks)

i) Tertiary alkyl halides predominantly undergo substitution reactions via S_N1 mechanism.

ii) S_N1 stands for nucleophilic substitution in one step.

iii) The rate of a S_N1 reaction is independent of nucleophile concentration.

iv) Polar aprotic solvents promote faster rates for S_N1 reactions than S_N2 reactions

v) S_N1 reactions are stereospecific

vi) Rearrangement is possible

T F T F T
**QUESTION 6 [8.5 marks]**

**a)** Answer all questions regarding the reaction shown below:

\[
\begin{array}{c}
\text{H}_3\text{C} \quad \text{OH} \quad \text{HBr} \\
\text{H}_2\text{O}
\end{array}
\]

i) Write out the reaction mechanism to show the formation and the stereochemistry of the product(s) in this reaction. (3 marks)

ii) Indicate the rate-determining step of the reaction in the mechanism that you deduced in part i). (0.5 mark)

iii) How would the use of a non-polar solvent such as hexane affect the rate of reaction? Explain in no more than two sentences. (1 mark)

The use of a non-polar solvent would **lower** the reaction rate of the S\(_\text{N}^1\) mechanism by minimizing the solvation of the carbocation, hence de-stabilizing the rate determining step.

**b)** Answer all questions regarding the compound given below:

\[
\begin{array}{c}
\text{Br}
\end{array}
\]

i) Provide two chair conformations of this compound as instructed in the boxes below. (2 marks)

More stable chair conformation (A) Less stable chair conformation (B)

ii) Which of the two chair conformations (between A and B) will undergo a faster E\(_2\) reaction using potassium methoxide as base? (1 mark)

iii) If an E\(_1\) mechanism was instead involved in part ii), what would be the structure of the expected final product? (1 mark)
QUESTION 7 [8 marks]

a) Provide the structure of the major product expected in each of the following reactions. Make sure to indicate the stereochemistry of the product, where applicable. (5 marks, 1 mark each)

i) 
\[
\text{Li} \quad \text{Cl} \quad \text{Diethyl ether}
\]

ii) 
\[
\text{Cl} \quad \text{NaOCH}_3 \quad \text{CH}_3\text{OH}
\]

iii) 
\[
\text{Cl} \quad \text{H}_2\text{O} \quad \text{H}_2\text{OH}
\]

iv) 
\[
\text{Br} \quad \text{NaOCH}_2\text{CH}_3 \quad \text{CH}_3\text{CH}_2\text{OH}
\]

v) 
\[
\text{H}_3\text{C}_2\text{OH} \quad \text{H}_3\text{PO}_4 \quad \text{heat}
\]

b) i) Provide the structures of the product(s) formed when the following anion reacts with two different alkyl halides, as specified below. ii) Is the role of the anion in route 2 a base or a nucleophile?

Route 1: 
\[
\text{Br} \quad + \text{Br}^-
\]

(1 mark)

Route 2: 
\[
\text{H} \quad \text{Br}^-
\]

(1 mark)

Circle your choice

The role of the anion in route 2 is Base or Nucleophile (1 mark)
QUESTION 8 [6.5 marks]

a) The following compound shown below was subject to the reaction with Br₂ using CH₃OH as solvent. Show the formation of the final product(s) with the correct stereochemical outcome by providing a plausible reaction mechanism. (3.5 marks)

![Reaction Mechanism Diagram]

b) Unsaturated hydrocarbon compound A whose molecular formula is C₁₁H₁₈ was subject to several reactions as shown below. Provide the bond-line structures of compounds A, B and C. (3 marks)

![Reaction Diagram]

- Structure of A
- Structure of B
- Structure of C
a) Fill in the boxes with the structures of expected product(s) or reagents necessary (for reaction 5) when the following molecule, drawn below, was subject to different reaction conditions. (5 marks)

b) Referring to reaction 1 part a), provide a mechanism to show the formation of the product(s) using appropriate curved-arrows (3 marks)

c) Show a plausible mechanism to account for the following transformation. (3 marks)
QUESTION 10 [9.5 marks]

a) Draw all significant resonance structures for each of the following species using curved-arrows. (3 marks)

i) 

\[ 
\begin{align*}
\text{CH}_2 & \quad \text{CH}_2 \\
\text{CH}_2 & \quad \text{CH}_2 \\
\text{CH}_2 & \quad \text{CH}_2 \\
\end{align*} 
\]

ii) 

\[ 
\begin{align*}
\text{radical} & \quad \text{radical} \\
\end{align*} 
\]

b) Determine if each of the following compounds is aromatic or non-aromatic. (2 marks)

i) Non-aromatic

ii) Aromatic

\[ 
\begin{align*}
\text{Non-aromatic} & \quad \text{Aromatic} \\
\end{align*} 
\]

c) Arrange the following structures in order of increasing rates of electrophilic aromatic substitution with an alkyl cation. (1.5 mark)

\[ 
\begin{align*}
\text{A} & \quad \text{B} & \quad \text{C} \\
\end{align*} 
\]

Least reactive \[ \text{C} < \text{A} < \text{B} \]

Most reactive

\[ 
\begin{align*}
\text{Least reactive} & \quad \text{Most reactive} \\
\end{align*} 
\]

d) Provide a plausible mechanism for the following reaction that leads to the formation of the thermodynamically favoured product. (3 marks)

\[ 
\begin{align*}
\text{HCl} & \quad \text{1 equivalent} \\
\text{25°C} & \\
\end{align*} 
\]

The major addition pathway must involve this alkene, not the other.

\[ 
\begin{align*}
\text{1,4-addition product} & \quad \text{(thermodynamically favoured)} \\
\end{align*} 
\]
a) Which of the following compounds has the higher heat of hydrogenation? Explain. (2 marks)

(E)-1,4-hexadiene vs (E,E)-2,4-hexadiene

(E)-1,4-hexadiene will release a greater amount of heat of hydrogenation since it is an isolated diene which lacks the resonance character observed in a conjugated diene, (E,E)-2,4-hexadiene

b) Provide a mechanism, showing the activation of the alkyl halide by the catalyst and all of resonance stabilized arenium ion (also known as σ-complex/cyclohexadienyl) intermediates, for the formation of the given product. (4 marks)

\[
\begin{align*}
\text{C}_6\text{H}_5 + \text{Cl} & \xrightarrow{\text{AlCl}_3} \text{C}_6\text{H}_6 \quad + \quad \text{HCl} \\
\end{align*}
\]

Arenium ions stabilized by resonance
QUESTION 12 [4 marks]

Draw the major product(s) expected from each of the following reactions.

i) \[
\begin{align*}
\text{C} & \equiv \text{N} \\
\text{Br}_2 & \xrightarrow{\text{FeBr}_3} \\
\text{C} & \equiv \text{N}
\end{align*}
\]

ii) \[
\begin{align*}
\text{HNO}_3 & \xrightarrow{\text{H}_2\text{SO}_4} \\
\text{C} & \equiv \text{N} \text{NO}_2 + \text{C} & \equiv \text{N} \text{O}_2\text{N}
\end{align*}
\]

iii) \[
\begin{align*}
\text{C} & \equiv \text{N} \text{OH} \\
\text{Na}_2\text{Cr}_2\text{O}_7 & \xrightarrow{\text{H}_2\text{O}, \text{H}_2\text{SO}_4, \text{heat}} \\
\text{C} & \equiv \text{N}
\end{align*}
\]

iv) \[
\begin{align*}
\text{H}_2\text{N} & \text{F}_3\text{C} \xrightarrow{\text{H}_2\text{SO}_4, \text{heat}} \\
\text{H}_2\text{N} & \text{F}_3\text{C} \text{SO}_3\text{H} + \text{H}_2\text{N} & \text{F}_3\text{C} \text{SO}_3\text{H}
\end{align*}
\]
QUESTION 13 [7 marks]

Four synthesis questions are given below. Select TWO questions of your choice by putting √ inside the box next to the reaction equation. For each question chosen, devise a synthesis of the final product from the given starting material by using any necessary reagent. Mechanisms are not required.

i. (Z)-pent-2-ene from propene

ii. (E)-hexa-1,3-diene from hex-3-yne

iii. [Chemical equation]

iv. [Chemical equation]

Hint: this problem involves a rearrangement of some sort

Synthesis 1

Synthesis 2