DEPARTMENT OF CHEMISTRY AND CHEMICAL TECHNOLOGY 202-BZF-05 ORGANIC CHEMISTRY I

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SOLUTIONS TO FINAL EXAMINATION

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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

or its enantiomer
iii) 2,4,6-tribromoaniline

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

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)

A

B

C
i) Identify which of $\mathrm{A}, \mathrm{B}$ and/or C has the largest $\mathrm{K}_{\mathrm{a}}$ ( 0.5 mark)

A
C
ii) Identify which of the three has the largest $\mathrm{pK}_{\mathrm{a}}$. ( 0.5 mark)
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 $\mathrm{A}, \mathrm{B}$ and C undergo acid-dissociation. (1.5 mark)

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)


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 acidbase reaction favours the side with weaker acid and base.
b) Phenol, $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OH}$, is an aromatic alcohol. It has a $\mathrm{pK}_{\mathrm{a}}$ of 9.9 , which is considerably lower than typical $\mathrm{pK}_{\mathrm{a}}$ ranges of alcohols $\left(\mathrm{pK}_{\mathrm{a}}=16-20\right)$. Why? (2 mark)


QUESTION 3 [8 marks]
a) For each of the following pairs, circle the compound that would display a higher boiling point.
i)

$$
\begin{array}{|l|}
\hline \text { pentane } \\
\hline
\end{array}
$$

Or
Or
2-methylbutane
ii) propane
2-chloropropane
iii)
butane
Or
1-propanol
b) Provide the most and the least stable Newman projections of 2-bromo-3-methylbutane along its $\mathrm{C}_{2}-\mathrm{C}_{3}$ bond.
(2 marks)

Most stable

Least stable
c) Rank the following compounds in order of increasing heat of combustion.

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

most 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.

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)
chiral or achiral?

Chiral

Achiral
iii)

iv)



Achiral

Chiral
i)

ii)


Achiral
v)

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

and


Constitutional Isomers
ii)

and
 Identical
iii)



QUESTION 5 [9 marks]
a) Which mechanism ( $E 1, E 2, S_{N} 1$ or $S_{N} 2$ ) 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)


Two possible answers
b) Rank the following molecules in order of their expected $\mathrm{S}_{\mathrm{N}} 1$ reactivity (from least to most reactive).
(2 marks)

c) Determine if the following statements in reference to $\mathrm{S}_{\mathrm{N}} 1$ mechanism are TRUE ( T ) or FALSE ( F ) by circling the appropriate letter: (3 marks)
i) Tertiary alkyl halides predominantly undergo substitution reactions $\mathbf{I}$ via $\mathrm{S}_{\mathrm{N}} 1$ mechanism.
ii) $\quad \mathrm{S}_{\mathrm{N}} 1$ stands for nucleophilic substitution in one step.
iii) The rate of a $S_{N} 1$ reaction is independent of nucleophile $\mathbf{I}$ concentration.
iv) Polar aprotic solvents promote faster rates for $\mathrm{S}_{\mathrm{N}} 1$ reactions than $\mathrm{S}_{\mathrm{N}} 2$ reactions
v) $S_{N} 1$ reactions are stereospecific

QUESTION 6 [8.5 marks]
a) Answer all questions regarding the reaction shown below:

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)


1: 1: mixture of enantiomers (Racemic mixture)



The use of a non-polar solvent would lower the reaction rate of the $S_{N} 1$ mechanism by minimizing the solvation of the carbocation, hence de-stabilizing the rate determining step.
b) Answer all questions regarding the compound given below:

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 E2 reaction using potassium methoxide as base? (1 mark)
iii) If an E1 mechanism was instead involved in part ii), what would be the structure of the expected final product? (1 mark)
$\qquad$
B


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)




Diethyl ether
ii)

iii)

iv)

v)

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?


Circle your choice
(1 mark)
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 $\mathrm{Br}_{2}$ using $\mathrm{CH}_{3} \mathrm{OH}$ as solvent. Show the formation of the final product(s) with the correct stereochemical outcome by providing a plausible reaction mechanism. (3.5 marks)
 $?$


b) Unsaturated hydrocarbon compound $A$ whose molecular formula is $\mathrm{C}_{11} \mathrm{H}_{18}$ was subject to several reactions as shown below. Provide the bond-line structures of compounds $A, B$ and $C$. ( 3 marks)




Structure of $\mathbf{C}$


QUESTION 9 [11 marks]
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)
Initiation

Propagation
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)

ii)

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


## Non-aromatic

ii)


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

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


must involve this alkene, not the other

## QUESTION 11 [6 marks]

a) Which of the following compounds has the higher heat of hydrogenation? Explain. (2 marks)

vs

(E)-1,4-hexadiene
(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 $\sigma$-complex/cyclohexadienyl) intermediates, for the formation of the given product. (4 marks)



## QUESTION 12 [4 marks]

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

ii)

iii)

iv)


## QUESTION 13 [7 marks]

Four synthesis questions are given below. Select TWO questions of your choice by putting $\sqrt{ }$ 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.



iv.



Hint : this problem involves a rearrangement of some sort

## Synthesis 1



## Synthesis 2



## Synthesis 3





## Synthesis 4




