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Your examination begins on the next page.

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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) 

ii) 

iii) 

iv) 

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

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**)

\[
\text{F}_3\text{C}=\text{H} > \text{F}_3\text{C}-\text{H} > \text{F}_3\text{C}:\text{H}
\]

A | B | C

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

ii) Identify which of the three has the largest $pK_a$. (0.5 mark) 

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

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

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

Least basic < ________ < ________ < Most basic

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

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

\[
\text{F}_3\text{C}-\text{H} + \text{F}_3\text{C}=\text{H} \rightleftharpoons \text{F}_3\text{C}=\text{H} + \text{F}_3\text{C}:\text{H}
\]

b) Phenol, C\text{\textsubscript{6}}\text{H}_{\text{5}}\text{OH}, 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)
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

---

Least | Most

---

A | B | C

propylcyclopropane | ethylcyclobutane | methylcyclopropane

(1.5 mark)

Rank the following compounds in order of increasing heat of combustion.

A | B | C

propylcyclopropane | ethylcyclobutane | methylcyclopropane

Least | | Most

(1.5 mark)

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

![Chair conformations]

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)
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)

i)  

chiral or achiral? __________________________  
# of chiral centres ________________  

ii)  

chiral or achiral? __________________________  
# of chiral centres ________________  

iii)  

chiral or achiral? __________________________  
# of chiral centres ________________  

iv)  

chiral or achiral? __________________________  
# of chiral centres ________________  

v)  

chiral or achiral? __________________________  
# of chiral centres ________________  

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

i)  

______________________________  

ii)  

______________________________  

iii)  

______________________________  

**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)

\[
\begin{align*}
\text{E1} & \quad \text{E2} & \quad \text{S_N1} & \quad \text{S_N2} \\
\text{H}_2\text{SO}_4 & \quad \text{H}_2\text{O} & \quad & \quad \text{H}^+ \\
\text{CH}_3\text{OH} & \quad & \quad \text{O-CH}_3 & \quad \text{E1} \quad \text{E2} \quad \text{S_N1} \quad \text{S_N2} \\
\text{Br} & \quad & \quad & \quad \text{HBr} \\
& \quad \text{E1} \quad \text{E2} \quad \text{S_N1} \quad \text{S_N2} & \quad \text{H}^+ \quad \text{KCN} & \quad & \quad (\text{only product})
\end{align*}
\]

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

\[
\begin{align*}
\text{A} & \quad \text{B} & \quad \text{C} & \quad \text{D} \\
\text{Least reactive} & \quad < & \quad < & \quad < & \quad \text{Most reactive}
\end{align*}
\]

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.  
   T or F

ii) S_N1 stands for nucleophilic substitution in one step.  
    T or F

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

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

v) S_N1 reactions are stereospecific  
   T or F

vi) Rearrangement is possible  
    T or F
QUESTION 6 [8.5 marks]

a) Answer all questions regarding the reaction shown below:

\[ \text{H}_3\text{C} - \text{OH} \quad \text{HBr} \quad \text{H}_2\text{O} \]

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)

b) Answer all questions regarding the compound given below:

\[ \text{More stable chair conformation (A)} \quad \text{Less stable chair conformation (B)} \]

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

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)
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) LiCl  Diethyl ether

ii) NaOCH₃

iii) H₂O

iv) NaOCH₂CH₃

v) H₃PO₄

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

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 Br$_2$ using CH$_3$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)

\[
\text{compound A}
\]

\[
\begin{align*}
\text{Br}_2 \\
\text{CH}_3\text{OH}
\end{align*}
\]

b) Unsaturated hydrocarbon compound A whose molecular formula is C$_{11}$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 A

Structure of B

Structure of 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)

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) 
\[
\begin{array}{c}
\text{CH}_2 \\
\text{C} \\
\text{H}_2 \\
\text{C} \\
\text{H}_2 \\
\end{array}
\]

ii) 
\[
\begin{array}{c}
\text{radical} \\
\end{array}
\]

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

i) 
\[
\begin{array}{c}
\text{Aromatic} \\
\end{array}
\]

ii) 
\[
\begin{array}{c}
\text{Non-aromatic} \\
\end{array}
\]

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

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

Least reactive Most reactive

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

\[
\begin{array}{c}
\text{HCl} \\
\text{25°C} \\
\end{array}
\]

1 equivalent
QUESTION 11 [6 marks]

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

\[
\begin{align*}
\text{\textbf{(E)-1,4-hexadiene}} & \quad \text{vs} \quad \text{\textbf{(E,E)-2,4-hexadiene}} \\
\end{align*}
\]

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)

\[
\begin{align*}
\text{\textbf{Cl}} & \quad \text{\textbf{AlCl}}_3 \\
\text{\textbf{HCl}} & \quad \text{\textbf{HCl}} \\
\end{align*}
\]
QUESTION 12 [4 marks]

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

i) \( \text{C} \equiv \text{N} \overbrace{\text{FeBr}_3}^{\text{Br}_2} \)

ii) \( \text{HNO}_3 \overbrace{\text{H}_2\text{SO}_4}^{\text{H}_2\text{SO}_4} \)

iii) \( \text{Na}_2\text{Cr}_2\text{O}_7 \overbrace{\text{H}_2\text{O}, \text{H}_2\text{SO}_4, \text{heat}}^{\text{heat}} \)

iv) \( \text{H}_2\text{N} \overbrace{\text{H}_2\text{SO}_4, \text{heat}}^{\text{heat}} \overbrace{\text{F}_3\text{C}}^{\text{H}_2\text{SO}_4} \)
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. [Diagrams]

iv. [Diagrams]

Hint: this problem involves a rearrangement of some sort

• Your proposal for the 1st synthesis problem of your choice (3.5 marks):

• Your proposal for the 2nd synthesis problem of your choice (3.5 marks):