Teachers: E. Cadieux, I. Dionne, D. Montecalvo

Student Name and Number: [blank]

Instructions:

1. This examination package has 10 questions and 17 pages. It is your responsibility to ensure that there are no pages missing.

2. Please write your name and student number before beginning the exam.

3. Answer all questions directly on the exam pages in the spaces provided.

4. Write in ink or you may lose the right to grieve the exam grade.

5. Write clearly. Illegible answers will result in grade deductions.

6. **Do not detach** any of the sheets in this package.

7. Two blank pages are provided at the end of the examination package for your **rough work. Your teacher will not look at any work written on those pages**.

8. **Calculators are not permitted**.

9. Molecular models are permitted but may not be passed to other students.

10. Unless otherwise indicated, structural formulas must be shown with all hydrogen atoms, except in ring structures where bond-line formulas are permitted.

   1. _______ / 16  2. _______ / 8  3. _______ / 15  4. _______ / 6  5. _______ / 10  6. _______ / 2  7. _______ / 7  8. _______ / 6  9. _______ / 25  10. _______ / 10  Total _______ / 105  Total _______ / 40
1. Provide appropriate names or structural formulas for the following: (16 marks)

(a) \[
\begin{array}{c}
\text{benzoic anhydride} \\
\end{array}
\]

(b) \[
\begin{array}{c}
\text{N-ethyl-N-methylpropanamine} \\
\end{array}
\]

(c) 4-oxo-3-chlorobutanoic acid

(d) \[
\begin{array}{c}
\text{3-ethylpentanoyl bromide} \\
\end{array}
\]

(e) benzyl benzoate

(f) \[
\begin{array}{c}
\text{N-(2,4-cyclopentadienyl)-3-chlorobutanamide} \\
\end{array}
\]

(g) ethyl phenyl ether

(h) \[
\begin{array}{c}
m\text{-bromophenol or 3-bromophenol} \\
\text{or 3-bromobenzenol} \\
\end{array}
\]
2. Propose a structure for each of the following compounds based on the $^1$H NMR information. (8 marks)

(a) $C_5H_{10}O$

- 0.95 $\delta$ doublet
- 2.10 $\delta$ singlet
- 2.43 $\delta$ septet

(b) $C_4H_6Cl_2$

- 1.4 $\delta$ pentet (5 peaks)
- 2.1 $\delta$ triplet
3. An unknown chemical, \( X \), whose molar mass is 169, produces the following infrared, \(^1\text{H} \) NMR and \(^{13}\text{C} \) NMR spectra. Hydrolysis of \( X \) produces two products, \( Y \) and \( Z \).

The molar mass of \( Y \) is 72 and the spectra are provided below.

The molar mass of \( Z \) is 115. Infrared peaks: 1715 cm\(^{-1}\) and 3290, 3350 cm\(^{-1}\).

Propose structural formulas for \( X \), \( Y \) and \( Z \). Your grade will be based on the thoroughness of your analysis and not solely on the final answer. Write directly on the spectra themselves.

\( \text{MM is odd: likely one nitrogen} \)
OH stretch of acid

alkene hydrogens only

3 heterotopic complex splitting pattern

molar mass = 72

"Y" is acrylic acid

H₂C=CHCOOH

72 - 45 = 27 for R

R is
Proposed structures:

**Compound X**

\[
\begin{align*}
\text{H}_2\text{C}=&\text{C} \longrightarrow \text{N} \longrightarrow \text{C} \longrightarrow \text{H}_2 \text{C} \longrightarrow \text{CH}_3 \\
\text{predict singlet at 1.2 ppm} \quad &\quad \text{predict singlet at 2.8 ppm}
\end{align*}
\]

**Compound Y**

\[
\text{H}_2\text{C} \longrightarrow \text{CHCOOH}
\]

**Compound Z**

\[
\begin{align*}
\text{H}_2\text{N} \rightarrow \text{C} \rightarrow \text{CH}_2 \rightarrow \text{C} \rightarrow \text{CH}_3 \\
\text{predicted singlet at 1.2 ppm} \quad &\quad \text{predicted singlet at 2.8 ppm}
\end{align*}
\]

"X" 169 likely \( \text{H}_2\text{C} \longrightarrow \text{C} \longrightarrow \text{N} \longrightarrow \text{R} \)

"Z" 115 \( \text{H}_2\text{N} \longrightarrow \text{R} \)

IR - doublet

<table>
<thead>
<tr>
<th>Wavenumber</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3290</td>
<td>mass of &quot;R&quot; is 99 amu</td>
</tr>
<tr>
<td>3350</td>
<td>has C=O (28)</td>
</tr>
</tbody>
</table>

99 - 28 = 71 amu

Fragment \( \text{C}_5\text{H}_{11} \) reasonable
4. (a) Why are NH$_3$ and CH$_3$NH$_2$ no longer nucleophiles in acidic solution? (2 marks)

\[
\text{NH}_3 + H^+ \rightarrow \text{NH}_4^+ \\
\text{CH}_3\text{NH}_2 + H^+ \rightarrow \text{CH}_3\text{NH}_3^+
\]

lone pair on N atom is gone! 
nucleophilicity disappears, charge weakens nucleophile

(b) Why does a Grignard reagent not attack and bond to the carbonyl carbon of a carboxylic acid? (2 marks)

for instance,

\[
\text{R-C-O} + \text{CH}_3\text{MgBr} \rightarrow \text{R-C-O}^- + \text{CH}_4
\]

This is now an anion and resists attack by a nucleophile

(c) Only 15% of 2,4-pentanedione exists as the enol tautomer in water, but 92% exists as the enol tautomer in hexane. Explain why this is so. (2 marks)

**Hexane**

\[
\text{CH}_3\text{C-CH=CH-CH}_3
\]

internal hydrogen bonding strong in hexane

**Water**

\[
\text{CH}_3\text{C-CH}_2\text{C-CH}_3
\]

no need to enolise to form stable H-bonds intramolecurally

The molecule can H-bond to water via C=O groups, making internal H-bond less important and less favorable to enolisation
5. Give a detailed step-by-step mechanism to show how the products of the following reaction are formed. Used the curved arrow convention to show electronic movements.

(a) \[ \text{O} \quad \text{I} \quad \text{I} \quad \text{OH} \quad 2\text{HI} \quad \rightarrow \quad \text{I} \quad \text{I} \quad + \quad \text{H}_2\text{O} \]

(b) \[ \text{C} \quad \text{O} \quad \text{O} \quad \text{CH}_3 \quad + \quad \text{NaOH} \quad \rightarrow \quad \text{C} \quad \text{O} \quad \text{O}^{-} \quad \text{Na}^+ \quad + \quad \text{CH}_3\text{OH} \]
6. Rank the following compounds in order of decreasing solubility in water. 

Do not explain.

\[
\begin{array}{ccc}
\text{CH}_3 & \text{OH} & \text{OH} \\
\text{C}_5 & \text{COOH} & \text{C}_5 \\
1 & 2 & 3
\end{array}
\]

Answer: \( 2 > 3 > 1 \)

7. (a) Indicate the aldehyde or ketone from which the following compound would be formed by an aldol addition

2-ethyl-3-hydroxyhexanal

Product is from butanal, addition with itself

\[
\begin{array}{c}
\text{O} \\
2 \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \\
\rightarrow \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH} = \text{CH} \text{CH} \\
\text{CH}_3 \\
\text{CH}_3
\end{array}
\]

This bond forms during reaction.
(b) What carbonyl compound and what phosphonium ylide are required in the last step of the Wittig synthesis of the following alkene? Provide two routes to achieve this synthesis.

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH} = \text{C} - \text{CH}_3
\]

or

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}^+\text{P} - \text{Ph}_3 \quad \text{and} \quad \text{O} = \text{C} - \text{CH}_3
\]

(c) The Gabriel synthesis is used to make what class of compound (functional group)? (1 mark)

primary amines
8. Provide brief answers to the following questions, concerning your laboratory work. (6 marks)

(a) What technique did you use to separate the clove oil (eugenol) from the ground cloves?
   
   steam distillation

(b) What apparatus was used to remove a volatile solvent from a final nonvolatile product, other than a distillation?

   rotary (flask) evaporator

(c) What color is $\beta$-carotene? Is this compound uv-visible active?

   red-orange

   definitely active in visible range
   (absorbs in blue-green region)

(d) Name 2 techniques, other than spectroscopy (IR, NMR, MS, uv-vis), that can be used to verify the identity of a product.

   thin layer chromatography
   refractive index
   m.p.
   b.p.
   etc.
9. Supply missing major organic products. (25 marks)

(a) \[
2 \text{CH}_3\text{C-H} \rightarrow \text{NaOH} \rightarrow \text{H}_2\text{O} \rightarrow \text{CH}_3\text{C-CH}_2\text{C-OH} \rightarrow \text{heat} \rightarrow \text{CH}_3\text{CH=CH-C-H}
\]

(b) \[
\text{CH}_3\text{CH-CH}_2\text{C-CH}_2\text{C-NH}_2 \rightarrow \text{Br}_2, \text{NaOH} \rightarrow \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH-CH}_2\text{-NH}_2
\]

(c) \[
\text{CH}_3\text{C-CH}_3 + \text{H}_3\text{C-CH-P^+Ph}_3 \rightarrow \text{cis + trans}
\]

(d) \[
\text{C}_6\text{H}_5\text{NH}_2 \rightarrow \text{NaNO}_2, \text{HCl} \rightarrow \text{0°C} \rightarrow \text{H}_2\text{F} \rightarrow \text{heat} \rightarrow \text{C}_6\text{H}_5\text{F}
\]

(e) \[
\text{CH}_3\text{CH}_2\text{MgBr} + \text{C}_6\text{H}_5\text{C-OH} \rightarrow \text{1. ether} \rightarrow \text{2. H}_3\text{O}^+ \rightarrow \text{CH}_3\text{C}_6\text{H}_5\text{-C-H}
\]

(f) \[
\text{CH}_3\text{C-O-C-CH}_3 + \text{NH}_3 \rightarrow \text{CH}_3\text{COOH or anion} + \text{CH}_3\text{-C-NH}_2
\]

(g) \[
\text{CH}_3\text{O-CH}_2\text{CH}_2\text{-C-H} \rightarrow \text{H}_2 / \text{Pt ethanol} \rightarrow \text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_2\text{OH}
\]
(h) \[
\text{CH}_3\text{CH}_2\text{C}≡\text{CH} + 2\text{HBr} \rightarrow \text{CH}_3\text{CH}_2\text{C}–\text{CH}_3 \]

(i) \[
\text{CH}_3\text{C}≡\text{CH} + (\text{CH}_3)_2\text{CuLi} \rightarrow -78°C \text{ ether} \]

(j) \[
\text{CH}_3\text{C}–\text{CH}_2\text{CN} + \text{KOH} \rightarrow \text{H}_2\text{O, heat} \]

(k) \[
\text{CH}_3\text{CH}_2\text{C}–\text{OH} + \text{Cl}_2 \rightarrow \text{P} \]

(l) \[
\text{CH}_3\text{CH}≡\text{CH}_3 + \text{CH}_3\text{C}–\text{O}–\text{OH} \rightarrow \]

(m) \[
\text{CH}_3\text{CH}–\text{CH}^-\text{N}^+(\text{CH}_3)_3^-\text{OH} \rightarrow 160°C \]

\[
\text{CH}_3\text{C}–\text{CH}_2\text{CN} \rightarrow \text{CH}_3\text{C}–\text{CH}_2\text{COOH} + \text{NH}_3
\]

\[
\text{CH}_3\text{CH}_2\text{COOH} \rightarrow 1. \text{excess} -\text{OH, heat} \]

\[
\text{CH}_3\text{CH}_2\text{COOH} \rightarrow 2. \text{H}_2\text{O}^+ \]

\[
\text{CH}_3\text{COOH} \]

\[
\text{CH}_3\text{COOH} \]

\[
\text{CH}_3\text{COOH} \]

\[
\text{CH}_3\text{COOH} \]

\[
\text{CH}_3\text{COOH} \]
(n) \( \text{CH}_3 \) + \( \text{C}_6\text{H}_5 \text{COCl} \) \( \xrightarrow{\text{AlCl}_3, \text{heat}} \) \( \text{C}_6\text{H}_5\text{COCH}_3 \)

(o) \( \text{CH}_3\text{CO-CO-} \) \( \xrightarrow{\text{1. excess LiAlH}_4} \) \( \text{CH}_3\text{C}_2\text{H}_5\text{OH} \) + \( \text{C}_6\text{H}_5\text{OH} \)

(p) \( \text{CH}_2=\text{CH-C-Cl} \) \( \xrightarrow{\text{1. LiAlH(O-Ot-Bu)}, \text{ether, } -78^\circ\text{C}} \) \( \text{CH}_2=\text{CH-C-H} \)

(q) \( \text{C}_3\text{H}_6\text{O} \) + \( \text{HCN} \) \( \xrightarrow{\text{1. LiAlH}_4, \text{2. H}_2\text{O}} \) \( \text{C}_3\text{H}_6\text{OH} \)

(r) \( \text{C}_6\text{H}_5\text{CH}_3 \) \( \xrightarrow{\text{Na}_2\text{Cr}_2\text{O}_7, \text{H}_2\text{SO}_4, \text{heat}} \) \( \text{C}_6\text{H}_5\text{COOH} \)
10. Show how you would carry out the following syntheses. You must begin with the indicated chemical(s) and you may use any necessary inorganic or organic reagents. All your reactions must produce the desired products in good yields and in a reasonably pure state.

(a) \[ \text{trans} \text{cyclohexanol from 1-cyclohexyl-2-bromopropane} \]

\[ \text{Br} \]

\[ \text{CH}_3 \]

\[ \begin{array}{c}
\text{NaOCH}_3 \\
\text{CH}_3\text{OH, heat}
\end{array} \]

\[ \rightarrow \]

\[ \begin{array}{c}
\text{CH}_3 \text{CH}_2 \text{C} \text{C} \\
\text{OH}
\end{array} \]

\[ \begin{array}{c}
1. \text{THF}: \text{BH}_3 \\
2. \text{aq. base, H}_2\text{O}_2
\end{array} \]

via anti-Markovnikov syn-addition

(b) 3-heptanone from 1-propanol

\[ \begin{array}{c}
\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \\
\text{PCC}
\end{array} \]

\[ \rightarrow \]

\[ \begin{array}{c}
\text{CH}_3\text{CH}_2\text{CH}_2\text{C} \text{H} \\
\text{OH}
\end{array} \]

\[ \begin{array}{c}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\text{MgBr}
\end{array} \]

\[ \rightarrow \]

\[ \begin{array}{c}
\text{CH}_3\text{CH}_2\text{C} \text{C} \text{H}_2\text{CH}_2\text{CH}_3
\end{array} \]

\[ \begin{array}{c}
\text{K}_2\text{Cr}_2\text{O}_7 \\
\text{H}_2\text{SO}_4
\end{array} \]

(c) \[ \text{CH}_3\text{C} \text{C} \text{COOH from ethanol} \]

\[ \begin{array}{c}
\text{CH}_3\text{CH}_2\text{OH} \\
\text{PCC}
\end{array} \]

\[ \rightarrow \]

\[ \begin{array}{c}
\text{CH}_3\text{C} \text{C} \text{H} \\
\text{OH}
\end{array} \]

\[ \begin{array}{c}
\text{CH}_3\text{MgBr}
\end{array} \]

\[ \rightarrow \]

\[ \begin{array}{c}
\text{CH}_3\text{CCH}_3
\end{array} \]

\[ \begin{array}{c}
\text{K}_2\text{Cr}_2\text{O}_7 \\
\text{H}_2\text{SO}_4
\end{array} \]
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