DO NOT OPEN THIS EXAM UNTIL INSTRUCTED TO DO SO

ONLY ANSWERS WRITTEN IN THE BOXES PROVIDED WILL BE GRADED

INTERPRETATION OF THE QUESTIONS IS PART OF THE EXAM – DO NOT ASK FOR THE QUESTIONS TO BE EXPLAINED TO YOU

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"It is possible to store the mind with a million facts and still be entirely uneducated." — Alec Bourne

"An education isn’t how much you have committed to memory, or even how much you know. It’s being able to differentiate between what you do know and what you don’t." — Anatole France
Question 1. Compound A can be converted into either compound B, C, or D, depending upon what reagents are chosen, i.e., E, F, and G, respectively. Using the characterization data (1H-NMR, 13C-NMR, IR spectroscopies and mass spectrometry) shown below for each compound, propose structures for compounds A, B, C, and D, (6 points each) and the appropriate reagents E, F, and G, (2 points each) to achieve the transformation of A into each of B, C, and D, respectively. (30 points)

Cmpd A  
MS: m/z = 69  \( \leftarrow \) contains N
1H-NMR: \( \delta = 1.33 \) (doublet, 6H), 2.72 (septet, 1H)
13C-NMR: \( \delta = 19, 20, 124 \)

Cmpd B  
MS: m/z = 73  \( \leftarrow \) contains N
1H-NMR: \( \delta = 1.28 \) (doublet, 6H), 1.50 (broad singlet, 2H), 2.87 (nonet, 1H), 3.82 (doublet, 2H)
13C-NMR: \( \delta = 20, 32, 50 \)

Cmpd C  
MS: m/z = 88  \( \leftarrow \) no N
1H-NMR: \( \delta = 1.20 \) (doublet, 6H), 2.58 (septet, 1H), 11.88 (broad singlet, 1H)
13C-NMR: \( \delta = 19, 34, 184 \)

Cmpd D  
MS: m/z = 72  \( \leftarrow \) no N
1H-NMR: \( \delta = 1.06 \) (doublet, 6H), 2.39 (septet, 1H), 9.57 (singlet, 1H)
13C-NMR: \( \delta = 15, 41, 205 \)

For ease of comparison, all of the IR spectra are lined up on the next page –
Question 2. Some spectroscopic data for an unknown compound (H) are shown below. Use these data to answer the questions on the following page. (20 points)

Mass Spectrum

IR Spectrum

$^1$H-NMR: $\delta = 2.24$ (singlet, 1H), 3.94 (singlet, 2H) ppm

$^{13}$C-NMR: $\delta = 30, 75, 79$ ppm
(a) What is the molecular formula of compound H? (5 points)

\[ \text{C}_3\text{H}_3\text{Cl} \]

(b) What is the structure of compound H? (10 points)

\[ \text{+Z} \quad \text{X2} \quad \text{C1} \]

(c) What is the exact structure of the species that gives rise to the peak at m/z = 74? (1 point)

\[ \text{H} - \text{C} = \text{C} - \text{O}_2\text{Cl} \quad \text{The charge is not necessary} \]

(d) Suggest the exact structure of one of the species that gives rise to the peak at m/z = 75? (1 point)

\[ \text{H}^{13} - \text{C} = \text{C} - \text{CH}_2\text{Cl} \]

(e) What is the exact structure of the most abundant species that gives the peak at m/z = 76? (1 point)

\[ \text{H} - \text{C} = \text{C} - \text{CH}_2\text{Cl} \]

(f) Suggest the exact structure of a reasonable species that gives rise to the peak at m/z = 77? (1 point)

\[ \text{H}^{13} - \text{C} = \text{C} - \text{CH}_2\text{Cl} \]

(g) What is the structure of the fragment that gives rise to the base peak at m/z = 39? (1 point)

\[ \text{H} - \text{C} = \text{C} - \text{CH}_2\text{C}^{+} \quad \text{H} \quad \text{H} \]
Question 3. Some spectroscopic data for an unknown compound (J) are shown below. Use these data to answer the questions on the following page. (25 points)

Mass Spectrum

IR Spectrum

1H-NMR: $\delta = 0.86$ (triplet, 3H), 1.50 (sextet, 2H), 2.02 (triplet, 2H), 6.96 (broad singlet, 2H) ppm

13C-NMR: $\delta = 14, 19, 38, 176$ ppm
(a) What is the molecular formula of compound J? (5 points)

\[ \text{C}_4\text{H}_9\text{NO} \]

(b) What is the structure of compound J? (10 points)

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

(c) What is the structure of the fragment (K) that gives rise to the base peak at \( m/z = 59 \)? (3 points)

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

(d) What is the name of the rearrangement that results in the formation of fragment K? (2 points)

Mclafferty

(e) Draw the mechanism showing how J fragments to give K? (5 points)
Question 4. The structure of methyl propionate is shown opposite.

(a) Draw the 1H-NMR spectrum of methyl propionate. (10 points)

(b) Draw the 1H-decoupled 13C-NMR spectrum of methyl propionate. (6 points)

(c) Draw the overall 13C-DEPT-NMR spectrum of methyl propionate. (4 points)
(This is also known as the DEPT-135 spectrum – and can have positive and negative peaks)
Question 5. The Wolff-Kishner reduction (shown below) converts a C=O group into a CH₂ group upon treatment with hydrazine (NH₂NH₂) and base (KOH) at elevated temperatures (>200 °C). What is the mechanism for the second step in the reaction, i.e., the decomposition of the hydrazone upon reaction with KOH? (14 points)

I DO NOT want you to write out the mechanism for this step.

What's the mechanism for this step?

NO H⁺ IN MECHANISM!!
Question 6. Predict the number of signals you would expect to see in the 1H-decoupled 13C-NMR spectrum of each of the molecules shown below. (2 points each)
Question 7. Predict the MAJOR product for each of the reactions shown below? (2 points each)

(a) \( \text{Zn} / \text{HCl} \)
\[ \text{H}_2\text{O} \]

(b) \( \text{i) LiAlH}_4 / \text{Et}_2\text{O} \)
\( \text{H}_2\text{O}^+ \)

(c) \( \text{i) NaBD}_4 / \text{MeOH} \)
\( \text{H}_2\text{O}^+ \)

(d) \( \text{i) NaBH}_4 / \text{MeOH} \)
\( \text{H}_2\text{O}^+ \)

(e) \( \text{i) LiAlH}_4 / \text{Et}_2\text{O} \)
\( \text{H}_2\text{O}^+ \)

(f) \( \text{H}_2 \)
\( (\text{Ph}_3\text{P})_3\text{RhCl} \)

(g) \( \text{H}_2 / \text{Pt} \)

(h) \( \text{i) LiAlD}_4 / \text{Et}_2\text{O} \)
\( \text{H}_2\text{O}^+ \)

(i) \( \text{i) NaBH}_4 / \text{MeOH} \)
\( \text{D}_3\text{O}^+ \)
Question 8. For each of the three cyclobutane derivatives shown below, indicate the relationships (HOMOTOPIC, ENANTIOTOPIC, DIASTEREOTOPIC, or CONSTITUTIONALLY HETEROTOPIC) between the pairs of hydrogen atoms listed in each case? (1 point each)

(a)  
\[
\begin{align*}
\text{Br} & \quad \text{Br} \\
\text{Cl} & \quad \text{Cl} \\
\text{H}_a & \quad \text{H}_b \\
\text{H}_c & \quad \text{H}_d
\end{align*}
\]
- \(H_a\) and \(H_b\) = DIASTEREOTOPIC
- \(H_a\) and \(H_c\) = ENANTIOTOPIC
- \(H_a\) and \(H_d\) = DIASTEREOTOPIC

(b)  
\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{Br} & \quad \text{Br} \\
\text{H}_a & \quad \text{H}_b \\
\text{H}_c & \quad \text{H}_d
\end{align*}
\]
- \(H_a\) and \(H_b\) = DIASTEREOTOPIC
- \(H_a\) and \(H_c\) = DIASTEREOTOPIC
- \(H_a\) and \(H_d\) = HOMOTOPIC

(c)  
\[
\begin{align*}
\text{Br} & \quad \text{Br} \\
\text{Cl} & \quad \text{Cl} \\
\text{H}_a & \quad \text{H}_b \\
\text{H}_c & \quad \text{H}_d
\end{align*}
\]
- \(H_a\) and \(H_b\) = ENANTIOTOPIC
- \(H_a\) and \(H_c\) = CONSTITUTIONALLY HETEROTOPIC
- \(H_a\) and \(H_d\) = CONSTITUTIONALLY HETEROTOPIC
Question 9. Propose a reasonable mechanism that accounts for the transformation shown in the box below. (10 points)
Question 10. Each of these reactions produces ONE MAJOR PRODUCT. In each case, draw this product (including appropriate stereochemistry where relevant) in the box provided. For multi-step reactions just give the FINAL product, i.e., no intermediates. (2 points each)

(a) 

(b) 

(c) 

(d) 

(e) 

(f) 

question 10 continues on the next page...
(g) \[
\begin{align*}
\text{Cyclohexanol} & \xrightarrow{H_3PO_4} \text{Cyclopentane} \\
\end{align*}
\]

(h) \[
\begin{align*}
\text{Cyclohexane-1,2-diol} & \xrightarrow{H_2SO_4} \text{Cyclopentanone} \\
\end{align*}
\]

(i) \[
\begin{align*}
\text{Cyclohexanol} & \xrightarrow{(i) \text{NaH}} \text{Cyclohexylmethanol} \\
& \xrightarrow{(ii) \text{CH}_3\text{CH}_2\text{CH}_2\text{OMs}} \text{Cyclopentylmethylmethanesulfonate} \\
\end{align*}
\]

(j) \[
\begin{align*}
\text{2-Chloro-6-nitrophenyl acetate (mCPBA)} & \xrightarrow{} \text{Cyclopentanone} \\
\end{align*}
\]

(k) \[
\begin{align*}
\text{2-Methylpropan-2-yl iodide} & \xrightarrow{(i) \text{H}_2\text{N}^-\text{CH}^-\text{NH}_2} \text{2-Methylpropan-2-ylamine} \\
& \xrightarrow{(ii) \text{NaOH} / \text{H}_2\text{O}} \text{2-Methylpropanethiol} \\
\end{align*}
\]

(l) \[
\begin{align*}
\text{Cyclopentene} & \xrightarrow{\text{CH}_2\text{I}_2 / \text{Cu/Zn}} \text{Cyclopentane} \\
\end{align*}
\]

*question 10 continues on the next page...*
Question 11. (BONUS) Propose a synthesis of 2-butanone using acetaldehyde as your only source of carbon atoms (i.e., all of the C atoms in your product must originate from acetaldehyde). You may use any other reagents of your choosing, however, if the reagents contain carbon and form part of your product you must make these reagents from acetaldehyde!). Show all intermediates and reagents for each transformation. DO NOT SHOW MECHANISMS! (14 points)

\[
\begin{align*}
\text{Acetaldehyde} & \xrightarrow{\text{many steps}} \text{2-butanone} \\
& \quad \downarrow (i) \text{LiAlH}_4 / \text{Et}_2\text{O} \quad (\text{or NaBH}_4 / \text{MeOH}) \\
& \quad \downarrow (ii) \text{H}_3\text{O}^+ \\
\text{CH}_3\text{CH}_2\text{OH} & \quad \downarrow \text{SOCl}_2 \text{ or PCl}_3 \text{ or PBr}_3 \quad \text{(or similar)} \\
& \quad \downarrow \text{Mg} / \text{Et}_2\text{O} \quad \text{(or Li)} \\
\text{CH}_3\text{CH}_2\text{Br} & \quad \downarrow \text{H}_2\text{CrO}_4 \\
\text{CH}_3\text{CH}_2\text{MgBr} & \quad \text{PCC} \\
\end{align*}
\]

MAY BE OTHER VIABLE SYNTHESSES.
**Question 12. (BONUS)** When D-Threitol reacts with formaldehyde, three isomeric products are formed, A, B, and C. Each of these products has the formula C₆H₁₀O₄ and contains two rings. Propose structures for A, B, and C. (3 points each)

![Chemical structures](image)

If the mixture of products A, B, and C above, are heated in the presence of an acid catalyst for an extended amount of time the system converges to one single product (i.e., two of the products are converted into the third). In this case, what is the structure of this exclusive product and explain why it is the sole product under these conditions? (3 points)

![Chemical structure](image)

**Question 13. (BONUS)** Explain why the 1H-NMR spectrum of dimethylformamide contains two methyl singlets at room temperature, but only one at elevated temperatures? (4 points)

![Chemical structures](image)

Dimethylformamide

At rt, rotation is slow, and methyl groups are in different environments - at higher temp, rotation is fast, and exchanges methyl groups making them equivalent.