**Infrared Correlation Chart**

- **C–H** ~3000
- **C=O** broad ~3000
- **O–H** ~3000

**NMR Correlation Chart**

- **Aromatic** Ar–H mainly 8–6.5
- **Alkyl** C=CH
- **Alkyl** 3′ > 2′ > 1′
- **Aromatic** C=CR
- **Aromatic** C–NR

**Interaction Energies, kcal/mol**

<table>
<thead>
<tr>
<th>Eclipsing</th>
<th>Gauche</th>
</tr>
</thead>
<tbody>
<tr>
<td>H/H</td>
<td>~1.0</td>
</tr>
<tr>
<td>H/Me</td>
<td>~1.4</td>
</tr>
<tr>
<td>Me/Me</td>
<td>~2.6</td>
</tr>
<tr>
<td>Me/Et</td>
<td>~0.9</td>
</tr>
</tbody>
</table>

**Approximate Coupling Constants, J (Hz), for \(^1\)H NMR Spectra**

- **H/H** ~7
- **H/C** ~10
- **H/C** ~8
- **H/C** ~2
- **H/C** ~15

**Chemical Elements**

Question 1. Give the IUPAC name for the following. Specify stereochemistry as appropriate.

a)

b)

Question 2. On the following structures and for the orbitals indicated, roughly sketch the shape of the wavefunctions ON TOP OF THE STRUCTURES, taking care to make the locations of any nodes clear, and to explicitly state the A.O.'s used to make any M.O.'s.

the C-Br s* anti-bonding orbital (where the electrons "go to", THE LUMO in an S_N2 reaction)

one of the C–H s-bonding orbitals (i.e., where the electrons are that determine the shapes of alkanes)

Question 3. Draw all reasonable resonance contributors, identify the major contributor and draw the "actual" structure (use the δ symbol rather than trying to calculate accurate fractional charges)

the tosylate anion (−OTs)
Question 4. For the following two reactions A and B, give the full curved arrow-pushing mechanisms, indicate the Lewis acid/base and Bronsted acid/base at each step as appropriate and state which reaction would be faster and explain using a reaction energy diagram that has BOTH reactions on the SAME diagram.

A
\[ \text{HBr} \xrightarrow{\text{CCl}_4} \text{Br} \]

B
\[ \text{HBr} \xrightarrow{\text{CCl}_4} \text{Br} \]

The rate determining step is the initial protonation. Protonation of both alkenes give the same cationic intermediate. The alkene in B is disubstituted and thus “starts” higher in energy than the tetrasubstituted alkene in A. \( E_a(B) \) is thus smaller than \( E_a(A) \).

FASTER

SLOWER

Question 5. In WORDS, describe the differences and similarities between a nucleophile and a Lewis base. Give one example of a strong base that is NOT a strong nucleophile.

All nucleophiles are Lewis bases, both provide the electrons to make a new bond in a reaction with a Lewis acid/electrophile. The definition of basicity is thermodynamic, stronger bases undergo more exothermic reactions. The definition of nucleophilicity is kinetic, stronger nucleophiles undergo faster reactions. The tertiary butoxide anion (t-BuO–) is a strong base but a weak nucleophile for steric reasons.
Question 6. Classify the two alkenes shown as enantiomers, diastereomers or the same structure drawn a different way. Classify the provided reactions as addition, substitution, elimination or rearrangement. Which reaction is more exothermic? Give a BRIEF explanation.

A

\[
\begin{align*}
A & \xrightarrow{\text{H}_2/\text{Pd/C}} \quad \text{H}_2 \\
\end{align*}
\]

B

\[
\begin{align*}
B & \xrightarrow{\text{H}_2/\text{Pd/C}} \quad \text{H}_2 \\
\end{align*}
\]

Question 7. Assign absolute configurations to all asymmetric centers in the following two structures and determine whether they are enantiomers, diastereomers or the same structure drawn differently. Identify any meso compounds.
Question 8. For the following reactions:

a) Give the missing major ORGANIC PRODUCT

b) Properly describe all stereoisomeric products if any and identify any MESO compounds

c) Explain whether a solution of the product(s) would be optically active and why or why not

d) Assign each reaction to addition, elimination, rearrangement or substitution

a) \[
\begin{array}{c}
\text{Ph} \\
\text{Ph} \\
\text{Ph}
\end{array}
\begin{array}{c}
\text{Br}_2 \\
\text{CCl}_4
\end{array}
\]

b) \[
\begin{array}{c}
\text{Cyclic}
\end{array}
\begin{array}{c}
\text{H}_2 \\
Pd/C
\end{array}
\]

c) \[
\begin{array}{c}
\text{Cyclic}
\end{array}
\begin{array}{c}
\text{Br} \\
\text{(CH}_3\text{)}_3\text{O}^- \cdot \text{Na} \\
\text{acetonitrile}
\end{array}
\]

d) \[
\begin{array}{c}
\text{Cyclic}
\end{array}
\begin{array}{c}
\text{Br} \\
\text{CH}_3
\end{array}
\begin{array}{c}
\text{Na}^+ \\
\text{CN} \\
\text{acetonitrile}
\end{array}
\]

e) \[
\begin{array}{c}
\text{Cyclic}
\end{array}
\begin{array}{c}
\text{Br}_2 \\
\text{H}_2\text{O}
\end{array}
\]

f) \[
\begin{array}{c}
\text{Cyclic}
\end{array}
\begin{array}{c}
1. \text{Hg(OAc)}_2 / \text{H}_2\text{O} \\
2. \text{NaBH}_4
\end{array}
\]

g) \[
\begin{array}{c}
\text{Ph} \\
\text{Ph}
\end{array}
\begin{array}{c}
1. \text{Hg(OAc)}_2 / \text{H}_2\text{O} \\
2. \text{NaBH}_4
\end{array}
\]
Question 9. Draw a reaction energy diagram for both reactions A and B ON THE SAME DIAGRAM with properly labelled axes (normalize your energy diagrams at the transition states), include a drawing of the transition state for the rate determining step (it is the same for both reactions). Indicate the activation energy for both reactions and indicate which is faster (A or B) and give a brief explanation for your choice. CLASSIFY EACH REACTION as addition, elimination, substitution or rearrangement.

Question 10. Draw minor resonance contributors that show which of the carbon atoms A or B will have the SMALLEST chemical shift in a carbon NMR spectrum, include curved arrow pushing and resonance arrows and brackets. Give a brief explanation.
Question 11 (22 pts.) For the following Bronsted acid/base equilibrium
a) Draw the curved-arrows that describes the bond making and breaking in BOTH directions
b) Label the STRONGER acid/base and the WEAKER acid/base on EACH side
c) Indicate which reaction would be faster, left to right or right to left
d) Indicate on which side the equilibrium will lie
e) Indicate which acid has the smaller and which the larger pKa
f) Give a BRIEF explanation for your choice of stronger/weaker Bronsted acids/bases that includes drawings of ALL relevant resonance contributors

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{N} & \quad \text{N} \\
\text{O} & \quad \text{O} \\
\text{H} & \quad \text{H}
\end{align*}
\]

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{N} & \quad \text{N} \\
\text{O} & \quad \text{O} \\
\text{H} & \quad \text{H}
\end{align*}
\]

g) Draw a reaction energy diagram and include the activation energy is BOTH directions and a drawing of the transition state
Question 12.

a) Give a full curved-arrow pushing mechanism for the provided reaction, indicate the Lewis and Bronsted acids/bases as appropriate and indicate the rate determining step.

\[
\begin{align*}
\text{H}_2\text{O} & \quad \text{HCl (cat.)} \\
\text{H} & \quad \text{O} \\
\end{align*}
\]

b) For your mechanism:

give the number of sets of intermediates ____________
give the number of transition states ____________

c) Briefly describe your reasoning for your choice of rate determining step in your mechanism

d) Draw a properly labelled reaction energy diagram that corresponds to the mechanism that you drew. On the diagram, clearly indicate the activation energy for the rate determining step, and the overall reaction exo- or endothermicity. Indicate the positions of the transition states but do not draw them
Question 13. For BOTH reactions A and B
a) Give the products AND THE mechanisms for ELIMINATION of HCl for the provided reagents/conditions, indicate the Lewis and Bronsted acids/bases at each BIMOLECULAR step as appropriate
b) For each mechanism, give the number of sets of intermediates and transition states for each

number of sets of intermediates ____________
number of transition states ____________

c) Draw a reaction energy diagram ON THE SAME DIAGRAM for each mechanism, clearly indicate which reaction refers to which diagram, indicate the rate determining steps for each reaction (you do not need to indicate or draw transition states)

d) Which reaction, A or B, would be faster? Give a BRIEF explanation.
Question 14  Provided are spectra for a compound with molecular formula $C_9H_{10}O$

a) Give the degrees of unsaturation ________________

b) On the infrared spectrum, indicate the peaks that identify the functional groups in the molecule (including C(sp$^3$)-H). Indicate BOTH the functional group, and where appropriate, the specific BOND in the functional that corresponds to the peak.

[Infrared spectrum image]

- 3412
- 3392
- 3051
- 3044
- 2991
- 2826
- 2981
- 2730
- 1681
- 1598
- 1198
- 1376
- 1529
- 220
- 180
- 160
- 140
- 120
- 100
- 80
- 60
- 40
- 20
- 0

ppm

- 2H doublet
- 2H doublet
- 1H singlet
- 3H triplet
- 2H quartet

ppm

10 9 8 7 6 5 4 3 2 1 0

H

sp2

O

CH2

CH3

O

H

sp2

O

H

sp3

2981

1376

1110

817

776

C(sp$^3$)-H

1H

singlet

3H

triplet

2H

doublet

2H

doublet

2H

quartet

1

2

3

4

5

6

7

8

9

10

1529

1376

1110

817

776


c) draw the structure and clearly indicate which hydrogens correspond to which signals in the proton nmr spectrum (only)

[Proton nmr spectrum image]
Question 1. Give the IUPAC name for the following. Specify stereochemistry as appropriate.

a) \[
\begin{align*}
\text{CH}_3 & \text{C} = \text{C} \text{H} \\
\text{H}_3\text{C} & \text{H} = \text{C} \text{CH}_3 \\
\text{H}_3\text{CH}_2\text{CH}_2\text{C} & \text{H} \\
\end{align*}
\]

4,5-dimethyl-(2Z,4E)-octadiene

b) 

1-chloro-1-cyclohexyl-(2S,4)-dimethyl-(3Z)-heptene

Question 2.

a) Rank the following in order of increasing basicity in a polar APROTIC solvent. Give a BRIEF explanation.

\[
\begin{align*}
\text{Cl}^- & \quad \text{F}^- & \quad \text{Br}^- & \quad \text{I}^- \\
\text{A} & \quad \text{B} & \quad \text{C} & \quad \text{D} \\
\end{align*}
\]

weakest _____ < _____ < _____ < _____ strongest

b) How would nucleophilicity vary for the same anions in a polar APROTIC solvent? Give a VERY brief explanation.

c) How would nucleophilicity vary for the same anions in a polar PROTIC solvent? Give a VERY brief explanation.
Question 3) Give a curved arrow mechanism and a reaction energy diagram for the following reaction. Indicate LB, LA, BB, BA as usual and state the number of sets of intermediates and transition states. Indicate the positions of the transition states on the diagram but do not draw them. This mechanism is NOT IN THE NOTES, you need to figure it out using what you know about Lewis/Bronsted acid base and other reactions that you have learned. The first step is given for you.

```
O Et

H Cl

EtOH

 energy

reaction coordinate

‡ ‡ ‡

Et

H Cl

LA/BA

LB/BB

LB

LA

LB/BB

LA/BA

2 sets of intermediates and 3 transition states
```

Question 4) Below is an intermediate in an electrophilic aromatic substitution reaction we will study next semester that gives a minor product. Draw all reasonable resonance contributors for this ion and also an "actual" structure (use the δ notation for partial charge, do not attempt to assign absolute fractional charges). Indicate the major resonance contributor, if any, and give a brief explanation.

```
Br

H

OH

δ δ

"actual"
```
Question 4)

a) Give a full curved-arrow pushing mechanism for the provided reaction, indicate the Lewis and Bronsted acids/bases as appropriate and indicate the rate determining step.

b) Draw a properly labelled reaction energy diagram that corresponds to the mechanism that you drew. On the diagram, clearly indicate the activation energy for the rate determining step, and the overall reaction exo- or endothermicity. Indicate the positions of the transition states but do not draw them. INDICATE THE POSITIONS OF THE VARIOUS SETS OF INTERMEDIATES ON YOUR DIAGRAM.

c) For your mechanism:
   give the number of sets of intermediates _____________
   give the number of transition states ______________

   d) Briefly describe your reasoning for your choice of rate determining step in your mechanism
Question 5. For the following reactions:

a) Give the missing major ORGANIC PRODUCT

b) Properly describe all stereoisomeric products if any and identify any MESO compounds

c) Explain whether a solution of the product(s) would be optically active and why or why not

d) Assign each reaction to addition, elimination, rearrangement or substitution

a) \[ \text{cyclohexene} \xrightarrow{\text{H}_2\text{SO}_4/\text{H}_2\text{O/heat}} \]

c) \[ \text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_3 \xrightarrow{\text{CH}_3\text{S}^-+\text{Na}} \text{acetone} \]

d) \[ \text{Br} \xrightarrow{\text{Br}_2/\text{CCl}_4} \]

e) \[ \text{Br} \xrightarrow{\text{Na}^+ -\text{OH}/\text{DMF}} \]

f) \[ 1. \text{Hg(OAc)}_2/\text{H}_2\text{O} \xrightarrow{2. \text{NaBH}_4} \]

g) \[ \text{H}_2/\text{Pd/C} \]
Question 6) For (2R,3S)-dibromobutane (meso-1,2-dibromobutane)

a) Draw a 3-D structure using wedged/dashed bonds showing the stereochemistry at the two asymmetric centers, IN THE REACTIVE CONFORMATION FOR AN E2 ELIMINATION

b) Draw a Newman projection for the reactive conformation for E2 elimination, looking FROM carbon #2 TO carbon #3.

c) Give the product of E2 elimination to give the Sayetzeff (Zaitsev) alkene product

Question 7) For the two SN2 reactions shown, A and B

a) Give the curved arrow pushing and indicate the Lewis acid and base (LA/LB) and ALSO the nucleophile (Nuc) and electrophile (Elec)

b) Draw reaction energy diagrams on the SAME DIAGRAM (normalize at the reactants), indicate the activation energy for both reactions and indicate the positions of the transition states

c) Indicate the faster reaction and give a brief explanation that includes Hammond Postulate

A \[ \text{Na}^{+} \cdot \text{NH}_2^- \quad \text{CH}_3\text{CN} \rightarrow \quad \text{NH}_2^- \quad + \quad \text{Br}^- \quad \]

B \[ \text{Na}^{+} \cdot \text{OH}^- \quad \text{CH}_3\text{CN} \rightarrow \quad \text{OH}^- \quad + \quad \text{Br}^- \quad \]
Question 7) Draw the conjugate base anion that results from deprotonation of the N-H bond in A, B and C below. Include ALL resonance contributors where appropriate. AND, rank A B and C in order of increasing Brønsted acidity. Give a BRIEF explanation.

A \[\begin{array}{c}
\text{N} \\
\text{H}
\end{array}\]  \hspace{1cm} B \[\begin{array}{c}
\text{N} \\
\text{H}
\end{array}\]  \hspace{1cm} C \[\begin{array}{c}
\text{N} \\
\text{O}
\end{array}\]

weakest < \hspace{1cm} < \hspace{1cm} strongest

Question 8) On the following structures and for the orbitals indicated, roughly sketch the shape of the wavefunctions ON TOP OF THE STRUCTURES, taking care to make the locations of any nodes clear, and to explicitly state the A.O.'s used to make any M.O.'s.

\[\begin{array}{c}
\text{H}_3\text{C} \\
\text{C} \\
\text{O}
\end{array}\]  \hspace{1cm} \text{the C–O } \pi^* \text{ antibonding orbital (i.e., where the electrons will "go", THE LUMO, when a C=O acts as an electrophile in second semester)}

\[\begin{array}{c}
\text{H} \\
\text{H} \\
\text{O}
\end{array}\]  \hspace{1cm} \text{the H-O } \sigma^* \text{ antibonding orbital (i.e., where the electrons are "given to", THE LUMO, when H}_3\text{O}^+ \text{ reacts with a base)}
Question 9) For the following acid/base reaction, show the curved-arrow pushing, identify the Lewis acid/base and whether they are also Brønsted acids/bases, draw a reaction energy diagram and the structure of the transition state. Indicate the activation energy and the reaction exothermicity or endothermicity as appropriate. Briefly explain why you think the reaction is endo- or exothermic.

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{Li}^+ \\
\text{H}_2\text{C}-\text{CH}_2 & \quad \rightarrow \\
\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2 & \quad \text{Li}^+
\end{align*}
\]

Question 10) For (2R)-bromo-2,(3R)-diphenylbutane
a) Draw a 3-D structure in the reactive conformation for an E2 elimination using wedged/dashed bonds to indicate stereochemistry

b) Draw a Newman projection in the reactive conformation for E2 elimination

c) Give the alkene product obtained upon E2 elimination using a non-bulky base
Question 11) Give a full curved arrow mechanism for the following reaction, indicate LB/AL/BB/BA as appropriate, and give a reaction energy diagram. State the number of sets of intermediates and transition states, do not draw transition state structures but indicate the positions of the transition states on the diagram and how these positions correspond to the mechanism that you drew. Include all reasonable resonance contributors as appropriate.

\[
\begin{align*}
\text{Br} & \text{MeOH} \quad \text{MeO} \\
\text{heat} & \quad \text{MeO} \\
\end{align*}
\]

Question 12) For each of the following reactions, give the major organic product and assign the mechanism as E1, E2, SN1 or SN2 and briefly explain the reasoning for your choice. Identify all stereoisomeric products as appropriate.

\[
\begin{align*}
a) & \quad \text{Na}^+ \text{OH} \\
& \quad \text{DMF} \\
& \quad \text{MeO} \\
\end{align*}
\]

\[
\begin{align*}
b) & \quad \text{CH}_3\text{OH} \\
& \quad \text{heat} \\
\end{align*}
\]
Question 14  Provided are spectra for a compound with molecular formula $\text{C}_{10}\text{H}_{14}$

a) Give the degrees of unsaturation __________________

b) On the infrared spectrum, indicate the peaks that identify the functional groups in the molecule (including C(sp$^3$)-H). Indicate BOTH the functional group, and where appropriate, the specific BOND in the functional that corresponds to the peak.

(c) draw the structure and clearly indicate which hydrogens correspond to which signals in the proton nmr spectrum ONLY
Question 1. Give the IUPAC name for the following. Specify stereochemistry as appropriate.

a) \[
\begin{array}{c}
\text{Br} \\
\text{Ph}
\end{array}
\]

because all other things are equal, and ONLY because all other things are equal, number alphabetically to give the carbon with the Br #1 in these structures

(1S)-bromo-(2R)-phenylcyclohexane

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

1,6-dibromo-(3R)-methylhexane

compared to l) switched the position of 2 substituents at the chiral center (Me and H), thus simply the enantiomer

Question 2. Glucose exists mainly in the two cyclic forms shown below (the non-bonding electrons are omitted for clarity).

a) For each structure, identify ALL chiral/asymmetric carbons using the symbol *

b) Assign the absolute configuration of the carbon indicated as C1 in each structure

c) Assign the two structures as enantiomers, diastereomers and give a reason for your choice

\[
\begin{array}{c}
\text{HO} \\
\text{HO} \\
\text{OH} \\
\text{OH}
\end{array}
\]

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

α-D-glucopyranose

β-D-glucopyranose

The structures are stereoisomers, but do not have opposite configuration at all asymmetric centers, therefore they are DIASTEREOMERS

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

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

the \( \Psi \) for the \( \pi \)-bonding M.O. that is the HOMO when an alkene reacts with any electrophile, e.g. HBr, etc. (take the effect of the electronegative elements into account)

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

the \( \Psi^2 \) for the C–O \( \sigma \) bonding orbital (i.e. where the electrons are that don’t get involved in reactions!!)
Question 4) Give a curved arrow mechanism for the following reaction. Indicate LB, LA, BB, BA as usual and state the number of sets of intermediates and transition states. This mechanism is NOT IN THE NOTES, you need to figure it out using what you know about Lewis/Bronsted acid base and other reactions that you have learned. The first step is given for you. INCLUDE A DRAWING OF ALL OF THE TRANSITION STATES

Question 4) For (1S)-t-butyl-(2S)-methyl-cyclohexane, draw both chair conformations and determine the energy difference using the tables on the front page of this test. Indicate the lower energy chair and give the energy difference.
Question 5) Here is a reaction we will not do until the end of second semester organic. It is a Hofmann E2 type elimination. It is unusual in that the NON-Sayetzeff product as the major one. Indicate which reaction (A and B) is which in the provided reaction energy diagram, give a BRIEF explanation. Draw the transition state for reaction A only. The reactions are slightly exothermic. Indicate which reaction you would expect to be less exothermic and why.

![Reaction Diagram](image)

Question 6) For the following Bronsted acid/base equilibrium, add the curved arrow-pushing that describes the bond making/breaking in both directions, identify the acids and the bases and decide which acid/base pair is the stronger and give a BRIEF explanation. You will need to add the important hydrogen atoms that are missing from the line-angle structures to do the proper curved arrow-pushing. Draw all reasonable resonance contributors for any species that is involved in the reaction as appropriate. Which reaction is faster and why?

![Bronsted Equilibrium Diagram](image)
Question 5. For the following reactions:

a) Give the missing major ORGANIC PRODUCT or reagents/conditions
b) Properly describe all stereoisomeric products if any and identify any MESO compounds
c) Explain whether a solution of the product(s) would be optically active and why or why not
d) Assign each reaction to addition, elimination, rearrangement or substitution

\[
\begin{align*}
a) & \quad \begin{array}{c}
\text{CH}_3\text{OH} \\
\text{Cl}
\end{array} \\
& \quad \text{(CH}_3\text{O}^- \text{K} \\
& \quad \text{(CH}_3\text{O} \text{OH)}
\end{align*}
\]
Question 6) For the following two reactions
a) Add the curved arrow-pushing showing bond making/breaking, assign them both as addition, elimination, substitution or rearrangement
b) Draw a reaction energy diagram for both reactions ON THE SAME DIAGRAM, normalize your diagrams at the transition states and show BOTH activation energies
c) Indicate which reaction would be faster and give a brief explanation

\[ \text{Ea}_A < \text{Ea}_B \]

Question 7) Draw the base anions that results from deprotonation of the most acidic proton in A B and C, include ALL resonance contributors as appropriate, rank A B and C in order of increasing Brønsted acidity. Give a BRIEF explanation.

\[ A \quad \text{weakest} \quad < \quad B \quad < \quad C \quad \text{strongest} \]

To answer this question, you FIRST need to identify WHICH is the most acidic proton on each structure.
Question 8) Write a curved arrow mechanism for the following reaction. Indicate LB, LA, BB, BA as usual and state the number of sets of intermediates and transition states. At each step in the mechanism, properly identify the relative stereochemistry of the substituents using wedged/dashed bonds, and also indicate the presence of any racemic mixtures in the intermediates using the (±) notation and identify any meso structures, even if they are intermediates.

\[
\begin{array}{c}
\text{Br} & \text{Br} \\
\text{EtOH} \\
\hline
\text{Br} & \text{O} & \text{H} \\
\end{array}
\]

\[
\begin{array}{c}
\text{Br} & \text{O} & \text{H} \\
\text{Et} & \text{O} & \text{Et} \\
\end{array}
\]

(±)

Question 9) Below is the structure of (+)-xylose. Identify all of the chiral/asymmetric centers and indicate with the * symbol, and assign the absolute configuration in each case (non-bonding electrons omitted for clarity). Draw a structure for (-)-xylose.

\[
\begin{array}{c}
\text{H} \\
\text{OHC} \\
\text{OH} \\
\text{OH} \\
\text{OH} \\
\end{array}
\]

\[
\begin{array}{c}
\text{H} \\
\text{*} \\
\text{(* R)} \\
\text{S} \\
\end{array}
\]

\[
\begin{array}{c}
\text{H} \\
\text{OHC} \\
\text{OH} \\
\text{OH} \\
\text{OH} \\
\end{array}
\]

\[
\begin{array}{c}
\text{H} \\
\text{*} \\
\text{(* S)} \\
\text{R} \\
\end{array}
\]
Question 10) Give a curved-arrow pushing mechanism for the following reaction, indicate the Lewis acid and base at each step and whether they are also Bronsted acids/bases. Assign the reaction as addition, elimination, substitution or rearrangement.

\[
\text{Cyclohexene} + \text{HCl cat.} \rightarrow \text{Product}
\]

Question 11) Rank the following in order of increasing rate of solvolysis in methanol. Give a BRIEF explanation that includes drawings of the primary intermediate cations for each structure (you do not need to draw ALL resonance contributors).

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

Solvolysis is an SN1 reaction. The rate determining step involves heterolytic cleavage of the C-Cl bond to form an intermediate cation. The cations from A and B are resonance stabilized, that from C is not. That from B has an extra resonance form compared to that from A, and thus formation of cation from B will be fastest.
Question 11) For the acid/base reaction shown below
a) add the curved arrow pushing that shows bond making/breaking IN BOTH DIRECTIONS
b) identify the stronger and weaker acids and stronger and weaker bases, and give a brief explanation for your choice
c) state which reaction would have the larger rate constant (be faster) left to right or right to left
d) identify on which side the equilibrium would lie
e) draw a reaction energy diagram that includes a drawing of the transition state
   if your explanation uses resonance arguments, draw all important resonance contributors

\[
\begin{align*}
\text{NH} & \quad \text{O} \\
\text{H} & \quad \text{C} \quad \text{C} \\
\text{H} & \quad \text{H}
\end{align*}
\begin{align*}
\text{H} & \quad \text{C} \quad \text{C} \\
\text{H} & \quad \text{H}
\end{align*}
\begin{align*}
\text{H} & \quad \text{C} \quad \text{C} \\
\text{H} & \quad \text{H}
\end{align*}
\begin{align*}
\text{H} & \quad \text{C} \quad \text{C} \\
\text{H} & \quad \text{H}
\end{align*}
\begin{align*}
\text{H} & \quad \text{C} \quad \text{C} \\
\text{H} & \quad \text{H}
\end{align*}
\begin{align*}
\text{H} & \quad \text{C} \quad \text{C} \\
\text{H} & \quad \text{H}
\end{align*}
\]

Question 12) Rank the following in order of increasing acidity. Give a brief explanation, illustrated using resonance contributors (ignore keto-isomers and also intramolecular hydrogen-bonding)

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

least ____ < ____ < ____ most
Question 14  Provided are spectra for a compound with molecular formula $\text{C}_5\text{H}_{11}\text{Br}$

a) Give the degrees of unsaturation ________________

b) On the infrared spectrum, indicate the peaks that identify the functional groups in the molecule (including $\text{C}(\text{sp}^3)-\text{H}$). Indicate BOTH the functional group, and where appropriate, the specific BOND in the functional that corresponds to the peak.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{infrared_spectrum.png}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{nmr_spectrum.png}
\end{figure}

c) draw the structure and clearly indicate which hydrogens correspond to which signals in the proton nmr spectrum ONLY

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{structure.png}
\end{figure}
Question 1. Give the IUPAC name for the following. Specify stereochemistry as appropriate.

a) \[
\begin{tikzpicture}
\draw (0,0) circle (1cm);
\draw (0,0) -- (0,-1);
\draw (0,0) -- (1,0);
\draw (0,0) -- (1,1);
\draw (0,0) -- (-1,0);
\draw (0,0) -- (-1,1);
\draw (0,0) -- (0,1);
\draw (0,0) -- (0,-1);
\draw (0,0) -- (1,0);
\draw (0,0) -- (-1,0);
\draw (0,0) -- (0,1);
\draw (0,0) -- (0,-1);
\draw (0,0) -- (1,0);
\draw (0,0) -- (-1,0);
\draw (0,0) -- (0,1);
\draw (0,0) -- (0,-1);
\draw (0,0) -- (1,0);
\draw (0,0) -- (-1,0);
\draw (0,0) -- (0,1);
\draw (0,0) -- (0,-1);
\draw (0,0) -- (1,0);
\draw (0,0) -- (-1,0);
\draw (0,0) -- (0,1);
\draw (0,0) -- (0,-1);
\draw (0,0) -- (1,0);
\draw (0,0) -- (-1,0);
\draw (0,0) -- (0,1);
\draw (0,0) -- (0,-1);
\end{tikzpicture}
\]

\[
\text{trans-1,4-dibromocyclohexane}
\]

b) \[
\begin{tikzpicture}
\draw (0,0) -- (0,-1);
\draw (0,0) -- (1,0);
\draw (0,0) -- (1,1);
\draw (0,0) -- (-1,0);
\draw (0,0) -- (-1,1);
\draw (0,0) -- (0,1);
\draw (0,0) -- (0,-1);
\draw (0,0) -- (1,0);
\draw (0,0) -- (-1,0);
\draw (0,0) -- (0,1);
\draw (0,0) -- (0,-1);
\draw (0,0) -- (1,0);
\draw (0,0) -- (-1,0);
\draw (0,0) -- (0,1);
\draw (0,0) -- (0,-1);
\draw (0,0) -- (1,0);
\draw (0,0) -- (-1,0);
\draw (0,0) -- (0,1);
\draw (0,0) -- (0,-1);
\end{tikzpicture}
\]

\[
\text{(6R)-chloro-(3,4S)-methyl-(2E)-heptene}
\]

Question 2. For the following reactions

a) Given the provided curved arrows, give the major products, include all important resonance contributors as appropriate.

b) Indicate the Lewis acid/base and whether they are also Brønsted acids/bases.

c) Indicate whether the reaction is endothermic or exothermic and justify your answer with a BRIEF 1 sentence explanation.

a) \[
\begin{tikzpicture}
\draw (0,0) -- (0,-1);
\draw (0,0) -- (1,0);
\draw (0,0) -- (1,1);
\draw (0,0) -- (-1,0);
\draw (0,0) -- (-1,1);
\draw (0,0) -- (0,1);
\draw (0,0) -- (0,-1);
\draw (0,0) -- (1,0);
\draw (0,0) -- (-1,0);
\draw (0,0) -- (0,1);
\draw (0,0) -- (0,-1);
\draw (0,0) -- (1,0);
\draw (0,0) -- (-1,0);
\draw (0,0) -- (0,1);
\draw (0,0) -- (0,-1);
\draw (0,0) -- (1,0);
\draw (0,0) -- (-1,0);
\draw (0,0) -- (0,1);
\draw (0,0) -- (0,-1);
\end{tikzpicture}
\]

\[
\text{endothermic, breaks 2 bonds only makes one bond}
\]

b) \[
\begin{tikzpicture}
\draw (0,0) -- (0,-1);
\draw (0,0) -- (1,0);
\draw (0,0) -- (1,1);
\draw (0,0) -- (-1,0);
\draw (0,0) -- (-1,1);
\draw (0,0) -- (0,1);
\draw (0,0) -- (0,-1);
\draw (0,0) -- (1,0);
\draw (0,0) -- (-1,0);
\draw (0,0) -- (0,1);
\draw (0,0) -- (0,-1);
\draw (0,0) -- (1,0);
\draw (0,0) -- (-1,0);
\draw (0,0) -- (0,1);
\draw (0,0) -- (0,-1);
\draw (0,0) -- (1,0);
\draw (0,0) -- (-1,0);
\draw (0,0) -- (0,1);
\draw (0,0) -- (0,-1);
\end{tikzpicture}
\]

\[
\text{Lewis acid/base: Na, Lewis acid/base: Na}
\]

\[
\text{Brønsted acids/bases: Na, Brønsted acids/bases: Na}
\]

\[
\text{endothermic, makes resonance stabilized anion}
\]

d) \[
\begin{tikzpicture}
\draw (0,0) -- (0,-1);
\draw (0,0) -- (1,0);
\draw (0,0) -- (1,1);
\draw (0,0) -- (-1,0);
\draw (0,0) -- (-1,1);
\draw (0,0) -- (0,1);
\draw (0,0) -- (0,-1);
\draw (0,0) -- (1,0);
\draw (0,0) -- (-1,0);
\draw (0,0) -- (0,1);
\draw (0,0) -- (0,-1);
\draw (0,0) -- (1,0);
\draw (0,0) -- (-1,0);
\draw (0,0) -- (0,1);
\draw (0,0) -- (0,-1);
\draw (0,0) -- (1,0);
\draw (0,0) -- (-1,0);
\draw (0,0) -- (0,1);
\draw (0,0) -- (0,-1);
\end{tikzpicture}
\]

\[
\text{exothermic, puts electron pair in an sp}^2 \text{ hybrid orbital instead of an sp}^3 \text{ orbital, lowers energy of electrons}
\]
Question 3) For the following compound, rank the pairs of electrons indicated as A, B, C and D, in order of INCREASING energy. Give a BRIEF explanation.

\[
\begin{align*}
\text{A (nonbonding electrons)} & \\
\text{(electrons in C–C } \sigma \text{ bond) C} & \\
\text{(electrons in C–C } \sigma \text{ bond) D} &
\end{align*}
\]

\[
\text{lowest} < \text{ } < \text{ } < \text{ } < \text{ highest}
\]

Question 4). For each pair of electrons indicated, draw the wavefunction on TOP OF THE STRUCTURE, and INDICATE THE ATOMIC ORBITALS THAT ARE USED TO BUILD THE MOLECULAR ORBITALS AS APPROPRIATE

\[
\begin{align*}
\text{Ψ for N-H } \sigma \text{-bonding orbital} & \\
\text{Ψ for C-N } \pi \text{-antibonding orbital} &
\end{align*}
\]

Question 5) Rank in order of increasing rate of E1 elimination in hot methanol. Give a BRIEF explanation.

\[
\begin{align*}
\text{slowest} & < \text{ } < \text{ } < \text{ fastest}
\end{align*}
\]
Question 3) Give a curved arrow mechanism and a reaction energy diagram for the following reaction. Indicate LB, LA, BB, BA as usual and state the number of sets of intermediates and transition states. Indicate the positions of the transition states on the diagram but do not draw them. Indicate the rate determining step on the mechanism and the activation energy for the rate determining step on the diagram. Briefly justify your choice of rate determining step.

![Reaction Mechanism and Energy Diagram]

Question 4) Explain which of the following two reactions will be faster. Include in your explanation an indication of the reaction mechanism and also a discussion of exactly how the presence of Br or F influences the reaction rate (i.e. not just "Reaction X is faster because it is Y as a substituent...")

![Reaction Mechanism A and B]
Question 5. For the following reactions:

a) Give the missing major ORGANIC PRODUCT or reagents/conditions

b) Properly describe all stereoisomeric products if any and identify any MESO compounds

c) Explain whether a solution of the product(s) would be optically active and why or why not

d) Assign each reaction to addition, elimination, rearrangement or substitution

---

a) \[
\begin{align*}
&\text{1. BH}_3 \cdot \text{THF} \\
&\text{2. } -\text{OH, H}_2\text{O}_2
\end{align*}
\]

b) \[
\begin{align*}
&\text{Excess HBr} \\
&\text{ROOR}
\end{align*}
\]

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Question 8  For each of the following reactions
a) give the major organic product
b) state whether the mechanism is SN1, SN2, E1 or E2 and give a brief justification for your choice
c) state whether a solution of the product would be optically active and give a brief explanation

a)  
\[
\begin{align*}
\text{Me} & \quad \text{Br} \\
\text{t-Bu} & \quad \text{Me}
\end{align*}
\]
\[\text{t-BuO}^- + \text{K} \quad \text{DMF} \]

b)  
\[
\begin{align*}
\text{OTs} & \quad \text{CH}_3\text{OH} \\
\text{heat} & \quad \text{(substitution product only)}
\end{align*}
\]

c)  
\[
\begin{align*}
\text{Na}^+ & \quad \text{N:C} \\
\text{acetonitrile} & \quad \text{Br} \\
\end{align*}
\]

Question 9  For (1S,2S)-1-bromo-1,2-diphenylpropane, draw
a) a 3D structure showing stereochemistry in terms of wedged and dashed bonds
b) a Newman projection of BOTH the lowest energy conformer for rotation around the C1-C2 bond, AND a Newman projection of the conformer that would undergo an E2 elimination
c) the alkene product of an E2 elimination

3D structure  
lowest energy conformer  
E2 conformer  
alkene product
Question 10) For the following two reactions

\[ \text{Br} \quad \text{Br} \quad \text{Na}^+ - \text{OCH}_3 \quad \text{DMF} \quad \text{A} \]

\[ \text{Br} \quad \text{Br} \quad \text{Na}^+ - \text{OCH}_3 \quad \text{DMF} \quad \text{B} \]

a) draw the transition states for both reactions, clearly indicate which is which

b) draw a reaction energy diagram for BOTH reactions on the SAME diagram (same axes) clearly indicate BOTH activation energies, and BOTH exothermicities on the diagram

c) Indicate which reaction would be faster, A or B, and give an explanation
Question 10) For each reaction give a full curved-arrow pushing mechanism, indicate the Lewis and Bronsted acids/bases for each bimolecular step and give the number of transition states and sets of intermediates.

a) 

b)
Question 12)

a) Draw a structure (using wedged and dashed bonds) of (2S)-chloro-(3S)-methylpentane.

b) Draw a structure (using wedged and dashed bonds) of the product of the substitution reaction of (2S)-chloro-(3S)-methylpentane shown below. Assign the absolute configurations of all asymmetric centers.

\[
\text{(2S)-chloro-(3S)-methylpentane} \quad \xrightarrow{\text{H–S; } \text{Na}} \quad \text{DMF} \]

c) Draw a 3-D structure of a diastereomer of the product of the reaction you gave above. Assign the absolute configurations of all asymmetric centers.

Question 13) Provide detailed (arrow pushing) mechanism for the following reaction, provide a reaction energy diagram, indicate the positions of any intermediates, where appropriate label the Lewis/Bronsted Acids/bases.

\[
\text{Cl}_2 \quad \xrightarrow{\text{CCl}_4} \quad \text{(±)}
\]
Question 14  Provided are spectra for a compound with molecular formula C_8H_10O_2

a) Give the degrees of unsaturation ________________

b) On the infrared spectrum, indicate the peaks that identify the functional groups in the molecule (including C(sp^3)-H). Indicate **BOTH the functional group**, and where appropriate, **the specific bond** in the functional that corresponds to the peak.

![Infrared Spectrum](image)

C) draw the structure and clearly indicate which hydrogens correspond to which signals in the proton nmr spectrum ONLY

![Proton NMR Spectrum](image)