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<td>Final Exam Version 1</td>
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<tr>
<td>Final Exam Version 2</td>
<td>101</td>
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</table>
1. Draw the correct Lewis structure of CH$_3$CN. (Needn’t show 3-D geometry) (3pt)

2. Draw the correct Lewis structure for HOCH$_2$CHO. (Needn’t show 3-D geometry). (3pt)

3. Draw a 3-dimensional picture for the atoms in CH$_3$CO$_2$CH$_2$NHCH$_3$, using the hash-wedge convention. (You needn’t specify lone pairs, and orbitals need not be shown). (5pt)

4. For the structure shown, what is the hybridization, electron-pair geometry, and approximate bond angle (90, 109, 120, or 180) relative to: (6pt)

<table>
<thead>
<tr>
<th>Hybridization</th>
<th>Geometry</th>
<th>Angle</th>
<th>Hybridization</th>
<th>Geometry</th>
<th>Angle</th>
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<td>O-1</td>
<td>$sp^3$</td>
<td>Tetrahedral</td>
<td>~109°</td>
<td>C-5</td>
<td>$sp^2$</td>
</tr>
<tr>
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<td>Tetrahedral</td>
<td>109°</td>
<td>N-7</td>
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<td>C-3</td>
<td>$sp^2$</td>
<td>Trig Planar</td>
<td>120°</td>
<td>O-9</td>
<td>$sp^2$</td>
</tr>
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</table>

5. Assign any formal charges to any appropriate atoms for proline, given the structure shown (one of the body’s 20 monomers from which protein and enzyme biopolymers are constructed). (3pt)
6. Rank the acidity of the following, from 1 (most) to 4 (least). (4pt)

Think about lone pairs

3 Acidity Factors:
1. charge (not relevant here)
2. Eneg
3. Resonance

7. Which of the following represent pairs of resonance structures? (4pt)

d. Both a and c

e. a, b, a and c are all resonance structures.

8. Draw arrows to show electron-movement in the following two steps (draw arrows for each step). Draw a circle around the atom that functions as nucleophile in step 1, and a square around the atom that functions as nucleophile in step 2. (5pt)

Explain change in:
1. Bonds
2. Charge
3. Lone Pairs

9. Rank the series on the basis of boiling point, 1 having highest boiling point, 3 having lowest. (3pt)

3 factors:
1. H-bonding
2. London force (# of carbons)
3. Polar vs nonpolar

H-bonding No
Polar Yes
H-bonding No
Non-polar
H-bonding Yes

10. Rank the series on the basis of water solubility, 1 having highest solubility, 3 having lowest. (3pt)

2 factors:
1. H-bonding (raises solubility)
2. London force (# of carbons)
more C's reduces water solubility
11. For each of the following pairs of resonance structures, circle the one that would make a greater contribution to the actual resonance hybrid. (4pt)

\[
\text{HOCH}_3 \quad \text{OCH}_3
\]

\[
\text{extra bond} \quad \text{enol}
\]

2 Factors:
1. More bonds (priority)
2. Electronegativity (if bonds are equal)

12. Cyclopropane is much more “strained” than cyclopentane. Why? (Short!) (3pt)

Angle strain. Bonds are forced to be 60°, far from the ideal ~109° angle.
Note: angle strain only appears in certain rings;
For acyclics, steric and torsional are the only strains available.

13. For the following acid-base reaction,
a. put a box around the weakest base in the reaction
b. put a circle around the weakest acid
c. draw an arrow to show whether the equilibrium goes to the right or left. (4pt)

Base Stability factors:
1. charge
2. eneg
3. resonance
1. Equilibrium favors the more stable base
2. More stable base is "weaker" base
3. "Weaker" acid + base on same side

14. Classify the relationship between the pairs of molecules as either: (8pt)

same compound structural isomers resonance structures geometric isomers not isomers (different molecular formulas)

[Diagrams and structures are presented, including resonance and structural isomers, geometric isomers, and various molecular structures with their respective labels.]
15. Give the name for the following. (7pt)

**cis-1-isopropyl-3-methylcyclohexane**

16. Identify all the functional groups in the following molecules. (Do not include “alkane”, since that isn’t “functional”.) (6pt)

1. **ester**
2. **amine**
3. **alkene**
4. **ketone**
5. **ether**
6. **aldehyde**

17. Which of the following pair will have the larger rotation barrier, relative to the bonds indicated? (3pt)

18. For the following Newman projections, rank them in stability from 1 to 4, 1 being most stable. Identify the “anti” conformation, the “gauche” conformation, and the “totally eclipsed” conformation. (6pt)

19. Draw the Newman projection for the most stable conformation of 1,2-dichloroethane. (3pt)

- **Best**: staggered and "anti"
- **Worst**: Totally eclipsed
20. Draw the two chair conformations of cis-1-ethyl-4-methylcyclohexane. (You don’t have to draw all the hydrogens). (5pt)

21. Which is more stable, cis- or trans-1-t-butyl-2-methylcyclohexane? Draw the best conformation of the more stable isomer. (4pt)

22. Draw as many structural isomers as you can for C₆H₁₄. Be careful not to draw the same isomer twice! I will take off points for duplicating! (6pt)
1. Draw the correct Lewis structure of CH$_3$CO$_2$CH$_2$COCH$_3$.  (Needn’t show 3-D geometry) (3pt)

2. Draw a 3-dimensional picture for the atoms in CH$_3$CH$_2$CHCHCH$_2$NHCH$_2$CHO, using the hash-wedge convention.  (You needn’t specify lone pairs, and orbitals need not be shown). (5pt)

3. For the structure shown, what is the hybridization, electron-pair geometry, and approximate bond angle (90, 109, 120, or 180) relative to: (7pt, 2 points off for each error)

4. Assign any formal charges to any appropriate atoms for the structure shown below. (4pt)
5. Rank the acidity of the following, from 1 (most) to 4 (least). (4pt)

6. For the following pairs, identify as “isomers” (“I”) or “resonance structures” (“R”). (6pt)

7. Draw arrows to show electron movement in the following reactions. (These are reactions, not resonance.) (5pt)

8. Rank the series on the basis of boiling point, 1 having highest boiling point, 3 having lowest. (3pt)

9. Rank the series on the basis of water solubility, 1 having highest solubility, 3 having lowest. (3pt)
10. Circle whichever of the following could fit the formula C₅H₁₀? (3pt)

11. For the following acid-base reaction,
   a. put a box around the weakest base in the reaction
   b. put a circle around the weakest acid
   c. draw an arrow to show whether the equilibrium goes to the right or left. (4pt)

12. Classify the relationship between each pair of molecules as either: (10 pt)
   - same compound
   - structural isomers
   - resonance structures
   - stereoisomers

   Base Stability factors:
   1. charge
   2. eneg
   3. resonance

   1. Equilibrium favors the more stable base
   2. More stable base is "weaker" base
   3. "Weaker" acid + base on same side

   Alkane Acyclic: CₙH₂ₙ₊₂
   Alkane Cyclic: CₙH₂ₙ
   Alkene: CₙH₂ₙ (not expected to remember, but evident if you count)
   Counting H's can always double-check on this!
14. Give the name for the following. (7pt)

trans-1-butyl-3-isopropylcyclopentane

5-ethyl-3-methylcyclooctane

16. Identify and write down the names for each of the functional groups in each of the following molecules. (Do not include “alkane”, since that isn’t “functional”.) For each molecule, try to write the names in order, as they appear from left-to-right in the molecules. (8pt)

17. Circle which of the following pair will have the larger rotation barrier, relative to the bonds indicated? (2pt) Identify which reason explains why: steric strain, torsional strain, or angle strain?

Greater steric strain when totally eclipsed.
(Both will have equal torsional strain when totally eclipsed.)

18. For the following Newman projections: (6pt total)

a. rank them in stability from 1 to 4, 1 being most stable

b. identify the “anti”, “gauche”, and the “totally eclipsed” conformations.

c. Is the energy difference between the gauche and the anti conformation based on steric strain, torsional strain, or angle strain?

d. In the case of ethane (not shown), staggered conformations are better than eclipsed conformations. Is the difference based on steric strain, torsional strain, or angle strain?

19. Draw both the most stable and the least stable Newman projections for 1-bromopropane, BrCH₂CH₃, relative to C₁-C₂ bond. - (3pt)

Best: staggered and "anti"  Worst: Totally eclipsed
20. Which of the following are correct Lewis structures, including formal charges, for nitric acid, HNO₃. (3 pts)

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<td>O:</td>
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<tr>
<td>H-O-N=O:</td>
<td></td>
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<tr>
<td>A</td>
<td></td>
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<td>H-O-N=O:</td>
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<tr>
<td>C</td>
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</table>

21. a. A only  
b. B only  
c. C only  
d. Both A and C  
e. All of the above

1. Do not exceed octet  
2. If formal charges, must sum to net charge  
3. As much "normal bonding" as possible, given the above constraints.

22. Draw the **two chair conformations** of cis-1-isopropyl-4-methylcyclohexane. (You don’t have to draw all the hydrogens). (5pt) (Use “iPr” as abbreviation)

23. Draw the best chair conformation of the more stable isomer. Which is more stable, cis- or trans-1-butyl-2-methylcyclohexane? (4pt)

24. Draw any 6 of the 9 possible structural isomers for **alkanes** with formula C₇H₁₆. When deciding whether to draw cyclic or acyclic alkanes, make sure that you fit the formula! Be careful not to draw the same isomer twice! I will take off points for duplicating! (You can try to show off by getting more than 6, but if you do still be sure you don’t duplicate!) (6pt)

Alkane Acyclic: C₇H₁₆
Alkane Cyclic: C₇H₁₄
Beware of drawing same thing twice!
1. (12 points) Give the relationship between the following pairs of structures. The possible relationships are the following:

- same compound
- structural isomers
- resonance structures
- stereo isomers
- not isomers (different molecular formula)

a. Structural:
   1,2-dibromo vs 1,3-dibromo.

b. Same.
   Bond rotation around single bonds is allowed.

c. Structural:
   CH3CHCHBr vs CH2CHCH2Br

d. Stereo. Trans-cis.
   Double bond can't rotate.

e. Same. Both are 4-methylnonane

f. Resonance. Electrons and charge is repositioned, but no atoms moved.

2. (8 points) Draw line-angle structures and names for 4 of the 5 structural isomers of C6H14.

- Alkane Acyclic: CnH2n+2
- Alkane Cyclic: CnH2n

Beware of drawing same thing twice!
3. (10 Points)
   a. For the above structure, what is the hybridization and approximate bond angles (109, 120, or 180) about:

   C-2 \( \text{sp}^2, \sim 120^\circ \), trig planar
   C-4 \( \text{sp}^2, \sim 120^\circ \)
   C-6 \( \text{sp}^3, \sim 109^\circ \)
   O-8 \( \text{sp}^3, \sim 109^\circ \)

   b. In the above structure, N-1 is actually found to have \( 120^\circ \) bond angles. (This may seem unexpected to you at this point, but we’ll learn why later in the course.) What must be the hybridization of the nitrogen?

4. (2 Points) Bond rotation around C6-C7 in the above structure has a 7 kcal/mol barrier, while rotation around the C4-C5 bond has a 70 kcal/mol barrier. Explain very briefly why it is so much harder to rotate the latter bond?

   Single bond versus double bond.
   A double bond has overlapping p-orbitals.
   To rotate a double bond, the p-p overlap would be lost. The full pi-bond would need to break.
   By contrast, no bonds are broken when you rotate around a single bond.

5. (4 points) For each of the pairs listed, circle the one with the higher boiling point.

   a. \( \text{H-bonding} \)
   b. \( \text{Extra carbons, hydrophobic} \)

6. (6 points) Write a Lewis structure and assign any non-zero formal charges.

   a. \([\text{CH}_3\text{NH}_2]^+\)
   b. \(\text{CH}_3\text{CO}_2\text{Na}^-\)
   c. \(\text{CH}_3\text{CHO}\)
7. (5 points) a) Draw the best resonance structure for anion A, and circle the resonance structure that would make the greater contribution to the resonance hybrid.

b. For the two resonance structures shown below, circle the resonance structure that would make the greater contribution to the resonance hybrid.

8. (6 points) Rank the acidity of the following molecules, 1 being most acidic, 4 being least acidic. Hint: draw the anions!

NH₃, CH₃CH₂OH, CH₃CO₂H, HCl

9. (6 points) Draw a line-angle picture for all of the atoms in the molecule CH₃CH₂COCHClCH₃, including the hydrogens. Use the hash-wedge convention to indicate atoms that are not in the plane of the paper.

10. (5 points) Rank the ring strain in the following, from 1(most) to 3 (least). Explain very briefly the differences in strain.

A: has large angle strain (60° angles, not 109° angles)
B: By taking on chair conformation, there is zero angle strain, and zero torsional (no eclipsing)
C: If it has ideal angles, then some eclipsing and torsional strain destabilizes it.
11. (6 points) Which of the following are capable of cis-trans stereoisorimerism? (Yes/No).

a. 3-ethyl-1,1-dimethylcyclopentane
   - No, no cis/trans distinction

b. 3-pentene (name means a double bond is between carbons 3 and 4)
   - Yes, cis/trans

c. 1,3-dimethylcyclohexane
   - Yes, cis/trans

12. (9 points) Identify the functional groups in the following molecules. (Do not include "alkane", since that is not "functional". And do not specify "cyclic".)

a. H₂N—CO₂H
   - Amine, Carboxylic Acid

b. Testosterone
   - Ketone, Alcohol, Alkene

c. Cocaine
   - Amine, Ester, Arene or aromatic
13. (5 points) Give the IUPAC name for the following compounds.

a. 4-ethyl-3,6-dimethyloctane
b. cis-3-methyl-1-propylcyclobutane

14. (8 points) a. Draw Newman projections for the totally eclipsed, the gauche, and the anti conformations of 2,5-dimethylhexane, relative to the C3-C4 bond. You may abbreviate the isopropyl groups attached to C3 and C4 as "i-Pr" for convenience.
b. Explain very briefly why the rotation barrier around the C3-C4 bond of 2,5-dimethylhexane is greater than the rotation barrier in butane.

15. (8 points) a.) Draw the two chair conformations of cis-3-methyl-1-isopropylcyclohexane. (You don't need to show the H's on carbons other than 1 and 3). For convenience, you may abbreviate methyl as "Me" and isopropyl as "iPr"
b.) Circle the more stable conformation.
c) Would trans-3-methyl-1-isopropylcyclohexane be more stable or less stable than the cis isomer?
1. Order the following according to increasing electron negativity, 1 being highest, 4 lowest. (2pts)

N  3  F  1  O  2  C  4

2. Write Lewis structures and assign any non-zero formal charges. (3pts each)
   a. [CH₃OH]⁺

   b. CH₃CO₂CH₂ONa

   c. CH₃CHCHCONH₂

3. For each of the following, a) draw its resonance structure, and for each pair b) circle the structure that would make the greater contribution to the resonance hybrid. (2 pts each)

   a. 

   b. 

2 Factors:
1. More bonds (priority)
2. Electronegativity (if bonds are equal)

4. Draw line-angle structures for 7 of the 9 structural isomers of C₇H₁₆. (5 pts)

Alkane Acyclic: C₇H₁₆
Alkane Cyclic: C₇H₁₀
Beware of drawing same thing twice!
5. For the following pairs of structures, identify them as either: Resonance Structures, Structural Isomers, Stereoisomers, or Same. (2 pts each)

a. \[ \text{Resonance: No atoms can move!} \]
   \[ \text{Structural: different condensed formula} \]

b. \[ \text{Stereo: same condensed formula} \]

c. \[ \text{Resonance: No atoms move} \]

d. \[ \text{Same} \]

e. \[ \text{Structural} \]

6. Rank the acidity of the following molecules, 1 being most acidic, 4 being least acidic. (3 pts)

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<td>CH(_3)OH</td>
<td>2</td>
<td>HCO(_2)H</td>
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<tr>
<td>CH(_3)CH(_3)</td>
<td>4</td>
<td></td>
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</tbody>
</table>

3 Acidity Factors:
1. charge (not relevant here)
2. Eneg
3. Resonance

7. a) Put a box around the weakest base in the above reaction. (1pt)
   b) Put a circle around the weakest acid in the above reaction. (1pt)
   c) Draw an arrow to show whether at equilibrium the reaction will go left-to-right or right-to-left. (2pt)
8. Draw the line-angle structure for the following condensed structural formula: (CH₃CH₂)₂CO (3pt)

[Diagram of line-angle structure]

9. a. For the above structure, what is the hybridization, electron-pair geometry, and approximate bond angles (109, 120, or 180) about: (6pt)

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<th>Atom</th>
<th>Hybridization</th>
<th>Geometry</th>
<th>Bond Angle</th>
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<tr>
<td>N-1</td>
<td>sp³</td>
<td>tetrahedral</td>
<td>~109</td>
</tr>
<tr>
<td>C-3</td>
<td>sp³</td>
<td>tetrahedral</td>
<td>~109</td>
</tr>
<tr>
<td>C-5</td>
<td>sp²</td>
<td>trigonal planar</td>
<td>~120</td>
</tr>
<tr>
<td>C-8</td>
<td>sp</td>
<td>linear</td>
<td>~180</td>
</tr>
</tbody>
</table>

b. Rank the length of the following bonds, 1 being shortest, 3 being longest. (2pt)

1. C2-C3  
2. C4-C5  
3. C8-C9

10. For each of the pairs listed, circle the one with the higher boiling point. (4pt)

a. O=O  
   OH  
   H-bonding

b.  
   Extra carbons

11. Draw a 3-dimensional picture for all of the atoms (hydrogens included) in the molecule CH₃CHCHCOCH₂CH₂NHCH₃. Your picture should use the hash-wedge convention to illustrate atoms that are not in the plane of the paper, and should reflect approximate bond angles. (5pt)

[Diagram of 3D structure]

Note: N-H hydrogen is NOT in the plane. But it could be drawn hashed or wedged, either is fine.
12. Draw a 3-D picture of CH2O showing the π bond as well as the four atoms. (3pt)

![3D picture of CH2O with π bond highlighted]

p-orbitals used to make the pi-bond are perpendicular to the plane of the atoms. So if we draw the pi-bond in the plane, the attached H's must be out of plane.

13. For the following set, rank the solubility in water, from 1 (most soluble) to 4 (least soluble). (3pt)

- OH
- OH
- non-polar
- OH

14. Identify the functional groups in the following molecules. (8pt)

a. ether alkane ketone

b. carboxylic acid amine alcohol

15. Give the IUPAC name for the following compounds. (6pt)

a. 2,5-di methyl heptane

b. trans-1,4-dimethyl cyclohexane

1. Longest chain
2. Alphabetize substituents
3. Number from end near substituent
4. cis/trans for di-subbed rings
5. Alphabetize substituents
6. Numbering
7. Know isopropyl and t-butyl
16. Draw the Newman projections for the best and worst conformations of butane, and give the names for these conformations. Briefly explain what “strain factors” make the worst conformation worse than the best conformation. (6pt)

Torsional strain: any eclipsed conformation has torsional strain, repulsion between bond-pair electrons.
Steric strain: atoms are unnecessarily close, and repel each other

17. a.) Draw both chair conformations of cis-1-methyl-2-isopropylcyclohexane. Draw the substituents and H-atoms attached to carbons 1 and 2. (You don’t need to show the H’s on the other carbons). (4pt)
  b.) 
    Circle the more stable conformation. (1pt)

18. Draw the best chair conformation for 1,3-diethylcyclohexane, and identify whether it is “cis” or “trans”. (3pt)

19. Use the arrow-pushing convention to show the electron-movement mechanisms for the following two reactions. (5pt)

Good mechanism must explain changes in:
1. Bonds
2. Formal Charges
3. Lone pairs
1. Predict the major organic product for each of the following. (3 points each)

- \( \text{Br}_2, \text{hv} \)

- \( \text{CH}_3\text{SNa} \)

- \( \text{NaOCH}_2\text{CH}_3 \)

2. Show an alkyl bromide and some nucleophile that you could use to make the following by \( \text{S}_\text{N}_2 \). (3 points)

3. For the structure shown, (3 points each)
   a. Draw the major elimination product formed upon treatment with \( \text{H}_2\text{O}/\text{heat} \).
   b. Draw the major elimination product formed upon treatment with \( \text{CH}_3\text{CH}_2\text{ONa} \).
   c. Draw the major substitution product formed upon treatment with \( \text{CH}_3\text{CH}_2\text{ONa} \).
4. Which of the following is true regarding an $S_{N}1$ reaction?
   a. It would be faster at 25˚ than 50˚  
   b. It would be faster in ethanol than in pentane 
   c. Keeping the moles of reactants constant but doubling the quantity of solvent would decrease the rate by a factor of 4.
   d. Stereochemical inversion occurs exclusively

6. Which of the following statements is true?
   a. The rate determining step is always the last step in a reaction mechanism.  
   b. The stability/reactivity principle says that the more stable of two chemicals will be more reactive  
   c. The reactivity/selectivity principle says that the more reactive of two chemicals will be less selective.
   d. The activation barrier for a reaction is the difference in energy between reactants and final products.

7. Which of the following statements is true about the chlorination of methane?
   a. In each propagation step a radical is produced  
   b. $6.02 \times 10^{23}$ initiation events are needed to make one mole of chloromethane 
   c. Most chloromethane is made by combination of a methyl radical with a chlorine radical  
   d. The overall chlorination of methane is strongly endothermic.

8. Which of the following statements is FALSE?
   a. Optically active solutions solutions always contain chiral molecules.
   b. Two diastereomers always have identical melting points 
   c. Optically inactive solutions are either racemic or else contain no chiral chemicals at all 
   d. A solution with 60% optical purity would have an 80/20 mix of enantiomers

9. When the reactants shown undergo substitution, which of the products A-D will form? (3 points)
   a. A only  
   b. B only 
   c. A and B 
   d. A, B, and C 
   e. A, B, C, and D
10. Rank the reactivity of the structures shown toward the reactant(s) indicated on the left (1 being most, etc.) (3 points each)

\[
\begin{align*}
\text{NaOCH}_2\text{CH}_3 & \quad \text{SiMe}_3 \quad \text{E}_2 \\
\text{Br}_2/\text{hv} & \\
\text{CH}_3\text{Br} & \quad \text{NHLi} \quad \text{OLi}
\end{align*}
\]

\[
\begin{align*}
1^\circ & > 2^\circ > 3^\circ \\
I & > Br > Cl
\end{align*}
\]

11. Carbocations often rearrange, as shown below. Draw in the hydrogens on the two carbons involved in the rearrangement, and show formal arrow-pushing to illustrate the transformation. (3 points)

\[
\begin{align*}
\text{H}_2\text{O, heat, catalytic } & \text{H}^+ \\
\text{N} \rightarrow \text{O}^{+} & \quad \text{Stability}
\end{align*}
\]

12. Draw the mechanism for the following reaction, propagation steps only. (4 points)
13. Draw (3R,6R)-6-bromo-3-chloro-2-methyloctane (3 points)

![Draw](image1)

14. Name the following: (3 points)

(optically active)

![Name](image2)

15. Classify each of the chiral carbons in the following structures as R or S (there may be more than one in a molecule). (10 points)

![Classify](image3)

16. a. Classify each pair as diastereomers, enantiomers, or same. (12 points)
b. For the first structure of each pair, circle it if it is not chiral
c. For the first structure of each pair, write “meso” by it if it is meso

![Classify2](image4)

17a. a) Draw all the unique stereoisomers of 2,3-dichlorobutane. Cross out any duplicates.
b) Identify which is meso. c) Identify a pair that are related as diastereomers. (5 points)

![Draw](image5)
18. Draw the mechanisms for the following reactions, using formal arrow pushing. Note: in some case hydrogens that are not illustrated will be involved in bond changes. You would do well to write them in at the beginning. (12 points total, 3/3/6 distribution)
1. Rank the reactivity of the following molecules toward Br$_2$/hv. (1 most, 4 least) (3 points)

\[
\begin{align*}
\text{CH}_3\text{CH}_3 & \quad \text{1} \\
\text{R} & \quad \text{2} \\
\text{CH}_3\text{CH} & \quad \text{3} \\
\text{C}_3\text{H}_5^+ & \quad \text{4}
\end{align*}
\]

2. Rank the reactivity of the following molecules toward ethanol and AgNO$_3$. (1 most, 4 least) (3 points)

\[
\begin{align*}
\text{Br} & \quad \text{1} \\
\text{Cl} & \quad \text{2} \\
\text{Br} & \quad \text{3} \\
\text{Cl} & \quad \text{4}
\end{align*}
\]

3. Rank the reactivity of the following molecules toward NaOCH$_3$. (1 most, 4 least) (3 points)

\[
\begin{align*}
\text{I} & \quad \text{1} \\
\text{Br} & \quad \text{2} \\
\text{Br} & \quad \text{3} \\
\text{Cl} & \quad \text{4}
\end{align*}
\]

4. Rank the reactivity of the following toward 1-iodopropane. (1 most, 4 least) (3 points)

\[
\begin{align*}
\text{CH}_3\text{ONa} & \quad \text{1} \\
\text{CH}_3\text{CO}_2\text{H} & \quad \text{2} \\
\text{CH}_3\text{CO}_2\text{Na} & \quad \text{3} \\
\text{CH}_3\text{SNa} & \quad \text{4}
\end{align*}
\]

5. What is the hybridization of a carbocation? (2 points)

\[\text{SP}^2\]
6. Predict the major organic product (1 major structure is all that is needed in each case) for each of the following reactions. (Minor products or inorganic side products need not be drawn.) (3 points each)

\[
\begin{array}{c}
\text{Br} + CH_3CO_2Na \\
\text{hv} \\
\end{array}
\]

\[
\begin{array}{c}
+ Br_2 \\
\text{hv} \\
\end{array}
\]

\[
\begin{array}{c}
Br + H \\
\text{hv} \\
\end{array}
\]

7. Draw the structures for intermediate A and final product B. (4 points)

\[
\begin{array}{c}
A \\
\text{Br}_2, \text{hv} \\
B \\
\text{NaOCH}_3
\end{array}
\]

8. Draw the product when the following substance undergoes E2 elimination. "D" is deuterium, basically just a labelled hydrogen. If the starting material is optically active, will the product be optically active? (4 points)

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

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

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

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

\[
\begin{array}{c}
\text{trans} \\
\end{array}
\]
9. Show an alkyl bromide and some nucleophile that you could use to make the following by $S_{N2}$. (3 points each)

\[ \text{Br-CH}_3 \rightarrow \text{OCH}_3 \]

10. Draw all possible elimination products that could form from the following reactant. Circle the one that forms in greatest yield. (5 points)

\[ \text{O} \]

11. Which of the following would not increase the rate of an E1 reaction? (3 points)
   a. an increase in temperature
   b. an increase in the "activation energy"
   c. an increase in the concentration of the alkyl halide
   d. an increase in the stability of the carbocation intermediate

12. When comparing the reaction of 2-methylpropane with either Cl$_2$/hv or Br$_2$/hv, which of the following statements is true? (3 points)
   a. bromine is less reactive and more selective
   b. chlorine is less reactive and more selective
   c. bromine is more reactive and more selective
   d. chlorine is more reactive and more selective

13. Which of the following statements is true relative to reactions I-III: (3 points)
   I  CH$_4$ + Br$\bullet$ → CH$_3$• and HBr
   II CH$_3$CH$_3$ + Br$\bullet$ → CH$_3$CH$_2$• + HBr
   III CH$_3$CH$_2$CH$_3$ + Br$\bullet$ → (CH$_3$)$_2$CH• + HBr

   a. I has the smallest energy of activation and the highest energy transition state
   b. II has the smallest energy of activation and I has the lowest energy transition state
   c. III has the largest energy of activation and the highest energy transition state
   d. III has the smallest energy of activation and the lowest energy transition state
14. Classify each of the chiral carbons in the following structures as (R) or (S). (10 points)

15. a. Classify each pair of molecules as diastereomers, enantiomers, or same. (12 points)
b. Circle any molecules that are chiral
c. Write "meso" by any structures that are meso

16. Which of the following statements is true? (3 points)
   a. All solutions with chiral molecules are optically active
   b. All molecules with chiral carbons are chiral
   c. A solution that has 50% optical purity has a 50/50 mixture of enantiomers
   d. Two enantiomers always have identical boiling points

17. Draw (2R,3S)-2-bromo-3-chlorohexane (6 points)

18. Name the following: (3 points)
19. a) Draw all unique stereoisomers of 2,4-dibromopentane. Label each with a letter, A, B, etc.. Cross out any duplicates. (8 points)
b) Identify any that are chiral
c) Identify any that are meso

20. a) Draw the mechanism for the following reaction. (Draw the propagation steps only.) (4 points)
b) Is your product chiral, and if so is it optically active? (1 points)

21. a) Draw the mechanism for the following reaction. (4 points)
b) Identify the slow step. (1 point)
1. List the following radicals in order of increasing stability (from most stable 1 to least stable 4)

\[
\begin{align*}
1 & : \quad \cdot \quad \cdot \quad \cdot \quad \cdot \\
4 & : \quad \cdot \quad \cdot \quad \cdot \quad \cdot \\
3 & : \quad \cdot \quad \cdot \quad \cdot \quad \cdot \\
2 & : \quad \cdot \quad \cdot \quad \cdot \quad \cdot
\end{align*}
\]

2. List the following alkyl halides in order of decreasing reactivity toward S_N1/E1 reactions (from most reactive 1 to least reactive 4).

\[
\begin{align*}
1 & : \quad \text{Br} \\
4 & : \quad \text{Br} \\
3 & : \quad \text{Br} \\
2 & : \quad \text{Br}
\end{align*}
\]

3. List the following alkyl halides in order of decreasing reactivity toward S_N2 reactions (from most reactive 1 to least reactive 4).

\[
\begin{align*}
1 & : \quad \text{Br} \\
4 & : \quad \text{Br} \\
3 & : \quad \text{Br} \\
2 & : \quad \text{Br}
\end{align*}
\]

4. Rank the bond strength of the following (from strongest 1 to weakest 4).

\[
\begin{align*}
1 & : \quad \text{H-Br} \\
2 & : \quad \text{H-Cl} \\
3 & : \quad \text{H-F} \\
4 & : \quad \text{H-I}
\end{align*}
\]

5a. Put a 1 by the reaction for which \( \Delta H^\circ = E_{\text{act}} \).

b. Put a 2 by the reaction for which \( E_{\text{act}} = 0 \).

c. Put a 3 by the reaction for which \( E_{\text{act}} > \Delta H^\circ \).

\[
\begin{align*}
\text{Br-Br} & \rightarrow \text{Br}^\bullet + \text{Br}^\bullet & \text{H}_3\text{C}-\text{H} + \text{Br}^\bullet & \rightarrow \text{H}_3\text{C}^\bullet + \text{H-Br} \\
\text{H}_3\text{C}^\bullet + \bullet\text{CH}_3 & \rightarrow \text{H}_3\text{C-CH}_3
\end{align*}
\]
6. Predict the major organic product for each of the following reactions. (Minor products or inorganic side products need not be drawn.)

\[
\text{\textbf{hv}} + \text{Br}_2 \rightarrow \text{Br} \quad \text{radical}
\]

\[
\text{Br} + \text{NaOH} \rightarrow \text{S N 2}
\]

\[
\text{3° anionic} \quad \text{E 2}
\]

7. Show the Starting Alkyl Bromide which gave the following products.

\[
\text{H}_2\text{O}
\text{heat}
\]

8. Show an alkyl bromide and some nucleophile that you could use to make the following. (I don't care whether you specify a nucleophile just as the anion \(Z^-\) or as \(\text{NaZ}\) with a metal counterion.)

\[
\text{OH}
\text{CN}
\]

9. Optically active \((R)\)-2-bromobutane can be converted to 2-butanol under either conditions A or conditions B. Describe the stereochemistry of the product solutions for the two different conditions.

a. Alcohol is Chiral or Achiral?

b. Optically Active or Not?

c. \((R)\), \((S)\), or both?

d. Reaction occurred by Inversion, Retention, or Racemization?

e. What happens to the rates if you double the concentrations of all reactants?
10. Draw the major product for the following reaction. Then draw the mechanism for its formation. (Draw the propagation steps only.) Is your product chiral? (You may need to add relevant hydrogens.)

\[ \text{H} + \text{Br}_2 \xrightarrow{hv} \text{Br} \]

not chiral

Radical Mech

11. Draw the major product for the following reaction. Then draw the mechanism for its formation. (You may need to add relevant hydrogens.)

\[ \text{H}_2\text{C}_3\text{Br} + \text{NaOH} \xrightarrow{\text{E}_2} \]

13. Draw the mechanism for the following reaction. (Don't worry about designating stereochem.)

\[ \text{H}_3\text{C}_2\text{Br} \xrightarrow{\text{H}_2\text{O}} \text{H}_2\text{C}_3\text{OH} + \text{H-Br} \]
14. Classify each of the chiral carbons in the following structures as (R) or (S).

15. Draw (R)-2-bromopentane

16. Draw meso-1,3-dichlorocyclopentane, and mark the chiral C's as (R) or (S).

17. Draw all of the different isomers of 2,3-dichlorobutane, identify each as either chiral or meso, and classify the relationship between each two as enantiotopic or diastereotopic. (You may use Fischer projections or zig/zag/hash/wedge pictures, as you please. (If two are the same, cross one of them off your list.)

18. Classify the pairs of molecules as diastereomers, enantiomers, or same. For the first molecule in each pair, circle it if it is chiral. For the second molecule in each pair, put a * next to each chiral C.
1. Draw the mechanism for the following reaction, and write “slow” next to the rate-determining step. Be sure to draw all intermediates, and to correctly draw “electron-movement” arrows or half-arrows. (Show the propagation steps only.) (4 points)

\[
\text{H}_2\text{+Br}_2 \xrightarrow{hv} \text{HBr}_2 + \text{H-Br}
\]

2. Draw the mechanism for the following reaction, and write “slow” above the rate-determining step. Be sure to draw all intermediates, and to correctly draw “electron-movement” arrows. (5 points)

\[
\text{Br} + \text{HOCH}_3 \xrightarrow{\text{H}^+ \text{(catalyst)}} \text{OCH}_3 + \text{H-Br}
\]

3. Predict the major products for the following reactions. (4 points each)

a) \[
\text{Br} + \text{NaOCH}_3 \xrightarrow{\text{CH}_3\text{OH (solvent)}} \text{OCH}_3
\]

b) \[
\text{+ Br}_2 \xrightarrow{hv} \text{Radical}
\]
4. Draw the substitution products for the following reactions. (Do not draw the accompanying elimination products). Include stereochemistry in your answer, and if two substitution products are formed draw them both. (4 points each)

a) \[
\begin{align*}
\text{CH}_3\text{C}_2\text{H}_5\text{Cl} + \text{NaOH} & \rightarrow \text{CH}_3\text{C}_2\text{H}_5\text{OH} \\
\end{align*}
\]

b) \[
\begin{align*}
\text{CH}_3\text{CH}_3\text{Cl} + \text{H}_2\text{O} & \rightarrow \text{CH}_3\text{CH}_3\text{OH} \\
\end{align*}
\]

c) \[
\begin{align*}
\text{H}_3\text{C}\text{CH}_2\text{Br} + \text{NaOCH}_3 & \rightarrow \text{H}_3\text{C}\text{CH}=\text{CH}_2 \\
\end{align*}
\]

d) \[
\begin{align*}
\text{C}_6\text{H}_5\text{CH}_2 + \text{Br}_2 & \rightarrow \text{C}_6\text{H}_5\text{CH}=\text{CH}_2 \\
\end{align*}
\]

e) \[
\begin{align*}
\text{H}_3\text{C}\text{CH}_2\text{Br} + \text{CH}_3\text{SNa} & \rightarrow \text{H}_3\text{C}\text{CH}_2\text{SCH}_3 \\
\end{align*}
\]

5. Draw the E2 elimination product(s) [do not draw the substitution product(s)]. (4 points each)

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

b) \[
\begin{align*}
\text{H}_3\text{C}\text{CH}_2\text{Cl} + \text{H}_2\text{O} & \rightarrow \text{H}_3\text{C}\text{CH}=\text{CH}_2 + \text{H}_2\text{O} \\
\end{align*}
\]

6. Of the following alkyl halides, (3 points)

a) Circle the one that would be the most reactive toward S$_n$2 substitution

b) Put a box around the one that would be the least reactive toward S$_n$2 substitution

1°, best leaving group 3°, worst leaving group
7. Of the following alkyl halides, (3 points)
c) Circle the one that would be the most reactive toward $S_{N1}$ substitution
d) Put a box around the one that would be the least reactive toward $S_{N1}$ substitution

8. Rank the stability of the following carbocations, from 1 (most stable) to 4 (least stable) (4 pts)

9. Rank the stability of the following radicals, from 1 (most stable) to 4 (least stable) (4 pts)

10. Classify as R or S (2 pts each)

   a) 

   b) 

   c) achiral, no R or S

   d) S
11. Provide the structure and the IUPAC name for the following (3 pts each)

a) (R)-3-chloro-2-methylheptane

\[
\text{Br} - \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{H} \quad \text{(R)-1-bromo-3-methylpentane}
\]

12. Classify the pairs of molecules as not isomers, structural isomers, diastereomers, enantiomers, or identical, and circle any molecules that are achiral. (2 pts each)

a) H Cl H Br

\[
\text{same (achiral)}
\]

b) H Br H H

\[
enant
\]

c) H Cl H CH$_3$

\[
enant
\]

13. For 1,2-dimethylcyclopentane, (8 pts)

a) How many stereocenters are present

\[
2
\]

b) Draw all the possible stereoisomers, and circle those that are chiral.
Each of the following multiple choice problems is worth 3 points.

14. For the reaction shown below, with bond dissociation energies listed below each key bond, the overall ∆H is:

\[
(CH_3)_3C-H + Cl-Cl \rightarrow (CH_3)_3C-Cl + H-Cl
\]

<table>
<thead>
<tr>
<th>∆H (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>91</td>
</tr>
<tr>
<td>58</td>
</tr>
<tr>
<td>78</td>
</tr>
<tr>
<td>103</td>
</tr>
</tbody>
</table>

a) +58 kcal/mol  
b) -32 kcal/mol  
c) +32 kcal/mol  
d) -57 kcal/mol  
e) +181 kcal/mol

15. Which factor would not increase the rate of an E1 reaction:

a) Use of a more polar solvent  
b) Use of a 3° rather than a 2° alkyl halide  
c) Doubling the concentration of the base  
d) Using iodide rather than bromide as leaving group

16. Consider the S_N2 reaction shown below. Assuming no other changes, what effect on the rate would simultaneously doubling the concentrations of both 1-bromobutane and KOH have?

\[
CH_3CH_2CH_2CH_2Br + KOH \rightarrow CH_3CH_2CH_2CH_2OH + KBr
\]

a) No effect  
b) It would double the rate  
c) It would triple the rate  
d) It would increase the rate by four times  
e) It would increase the rate six times

17. Of the S_N1/S_N2/E1/E2 reactions, rearrangements are likely to occur in:

a) S_N1 reactions only  
b) S_N2 reactions only  
c) E1 reactions only  
d) Both S_N1 and E1 reactions  
e) Both S_N2 and E2 reactions
1. How many elements of unsaturation are in the formula C₆H₄NO₂? (3 points)
   a. 0b. 1  c. 2  d. 3  e. 4  f. 5  g. 6  \((14+1)-q=\text{CH}\)

2. For the three structures shown, which of the statements is true? (3 points)
   - a. A, C, and D are Z; B is E
   - b. A and B are the only Z compounds
   - c. A is the only Z compound; B is the only E compound
   - d. B, C, and D are Z; A is E
   - e. B is the only Z compound; A is the only E compound

3. Rank the reactivity of the following toward H₂SO₄/heat catalyzed dehydration. (3 points)
   - a. A is fastest; C is slowest
   - b. B is fastest; C is slowest
   - c. A is fastest; B is slowest
   - d. C is fastest; B is slowest
   - e. B is fastest; A is slowest
   - f. C is fastest; A is slowest

4. Which of the following reactants would give exactly the same products from both (E)- and (Z)-2-butene? (3 points)
   - a. Br₂
   - b. PhCO₂H
   - c. 1) BH₃-THF 2) NaOH, H₂O₂
   - d. OsO₄, H₂O₂
   - e. D₂, Pt

   If two chiral centers are produced, then diastereomeric products are produced.
   But if only one (or zero) chiral centers are produced, then the two alkenes don't give different products. In this case, with H-OH being added, only the carbon to which OH is added ends up being chiral, so you get the same racemic mix of 2-butanol either way.

5. Draw the alkene that gives the product shown, and specify its stereochemistry. (2 points)
   The normal "E" alkene would have given the wrong product stereochemistry. If the cis/trans sense of the addition and the cis/trans appearance of the product match, then "E" alkene would have worked.
6. Draw the major product for each of the following reactions or reaction sequences. You needn’t bother to show side products or minor products. For chiral molecules that are racemic, you needn’t draw both enantiomers. BE CAREFUL TO SHOW THE CORRECT ORIENTATION, AND THE CORRECT STEREOCHEMISTRY IN CASES WHERE STEREOCHEM IS FACTOR. (3 points each)
7. A single unknown reacts with O₃/Me₂S to give the following three products. What is the structure for the unknown? (3 points)

8. Provide the name or structure for the following. (3 points each)

- Trans 4-allyl-3-chlorocyclohexene
- (Z)-4-butyloct-2-ene (or)
- (Z)-4-butyloct-2-ene

9. Provide a possible structure for a compound with formula C₅H₈, given that it reacts with excess H₂/Pt to give C₅H₁₀. (3 points)

10. Fill in the blanks for the following reaction sequence: (6 points)

11. Consider how the Se-O bond would be polarized and predict the product which would result when CH₃SeOH adds to propene: (Selenium is located two rows directly below oxygen on the periodic table). (3 points)

Markovnikov's rule. Electronegativity/periodic table shows Oxygen more electronegative than selenium, so the oxygen adds to the more substituted end of the alkene.
12. When the following isomeric alkenes are fully burned, rank the amount of heat produced in the combustions, from most heat produced (1) to least heat produced (4). (3 points)

13. Provide structures for starting material A and reactions products B and C, given the formula of starting material A and the stereochemical status of products B and C. (5 points)

With (E)-but-2-ene, Cl2 would give meso and PhCO3H would have given chiral. But-1-ene would have given chiral with both reactions.

14. Draw mechanisms for the following reactions, using formal arrow-pushing. Each intermediate along the mechanism pathway must be shown. (6 points, 3 points, 6 points)
15. Provide reagents for the following transformations. (5 points each)

\[
\begin{align*}
\text{Br} & \quad \rightarrow \quad \text{OH} \\
\text{NET}_3 & \quad \rightarrow \quad \text{vinylic C} \\
1. \text{BH}_3 \cdot \text{THF} & \quad 2. \text{NaOH}, \text{H}_2\text{O}_2
\end{align*}
\]

I may or may not have had time to discuss and require the KMnO$_4$ reaction.

\[
\begin{align*}
\text{OH} & \quad \rightarrow \quad \text{carboxylic acid} \\
\text{H}_2\text{SO}_4 & \quad \rightarrow \quad \text{cyclic C} \\
\text{KMnO}_4 & \quad \rightarrow \quad \text{carboxylic acid} \\
1. \text{O}_3 & \quad 2. \text{Me}_2\text{S} \\
\end{align*}
\]

\[
\begin{align*}
\text{Br} & \quad \rightarrow \quad \text{Br}_2 \\
\text{Br} & \quad \rightarrow \quad \text{alkene} \\
\text{Br} & \quad \rightarrow \quad \text{cyclic C} \\
\text{Br} & \quad \rightarrow \quad \text{cyclic C}
\end{align*}
\]
1. How many elements of unsaturation are in the formula C₅H₉N?
   a. 0
   b. 1
   c. 2
   d. 3
   e. 4
   f. 5

2. Provide the proper IUPAC name for the alkene shown below.

   6-bromo-1-methylcyclohexene

3. Provide the proper IUPAC name for the alkene shown below.

   cis-(Z)-5-chloro-pent-2-ene
   or (Z)-5-chloro-2-pentene
   or cis-(Z)-5-chloro-2-pentene

4. Draw an acceptable structure for 4-phenyl-1-butene.

5. Draw the alkene of formula C₄H₈ which evolves the most heat per mole upon hydrogenation

6. Choose the most stable alkene among the following.
   a. 1-hexene
   b. (E)-2-hexene
   c. (Z)-2-hexene
   d. They are all of equal stability according to Saytzeff's rule.
7. Draw the major product of the following reaction.

8. Draw the major product and the mechanism.

9. Which of the following best describes the geometry about the carbon-carbon double bond in the alkene below?

   a. E
   b. Z
   c. Neither E nor Z

10. Draw 3 examples of molecules with the formula C₄H₆O₂.

11. Draw the major product.

12. Draw the major product.
13. Draw the major product.

\[
\text{CH}_3\text{CH} = \text{CH}_2 \xrightarrow{1. \ BH_3 \cdot THF, 2. \ H_2O_2, -OH} \ \text{H} \ \text{OH}
\]

only one chiral C produced, need not use hash/wedge stereo

14. Draw the major product.

\[
\text{CH}_3\text{CH} = \text{CH}_2 \xrightarrow{\text{Cl}_2, \text{H}_2\text{O}} \ \text{Cl} \ \text{Cl} \ \text{OH} \ \text{or} \ \text{CH}_3 \ \text{Cl} \ \text{Cl} \ \text{OH} \ \text{or} \ \text{CH}_3 \ \text{OH} \ \text{Cl} \ \text{Cl} \ \text{or} \ \text{CH}_3 \ \text{OH} \ \text{Cl} \ \text{Cl}
\]

trans required

15. Draw the major product.

\[
\text{Cyclohexene} \xrightarrow{\text{O}_3\text{O}_4, \text{H}_2\text{O}_2} \ \text{CH}_3 \ \text{C} = \text{C} \ \text{OH}
\]

16. Draw the major product.

\[
\text{Cyclooctatetraene} \xrightarrow{1. \text{O}_3, 2. \text{CH}_3\text{S}_2} \ \text{CH}_3 \ \text{C} = \text{O}
\]

17. Complete the following reaction and provide a detailed, step-by-step mechanism for the process.

\[
\text{H}^+, \text{H}_2\text{O} \xrightarrow{\text{H}_2\text{O}} \ \text{OH} \ \text{CH}_3
\]
18. Suggest a reasonable detailed, step-by-step mechanism for the reaction shown below.

19. Provide the reagents necessary to complete the following transformation. (2 steps minimum).

20. Both (E)- and (Z)-3-hexene can be treated with D₂ in the presence of a platinum catalyst. How are the products from these two reactions related to each other?

   a. The (E)- and (Z)-isomers generate the same products in exactly the same amounts.
   b. The (E)- and (Z)-isomers generate the same products but in differing amounts.
   c. The products of the two isomers are related as diastereomers.
   d. The products of the two isomers are related as enantiomers.
   e. The products of the two isomers are related as structural isomers.

21. Consider how the I-Cl bond is polarized and predict the product which results when this mixed halogen adds to 1-methylcyclohexene.
22. β-Ocimene is a perfume. Suggest a possible structure for β-ocimene that is consistent with the following information.

\[ \text{β-Ocimene (C}_{10}\text{H}_{16}) \xrightarrow{\text{H}_2, \text{Pt}} \text{2,6-dimethyl octane} \]

1. O₃
2. (CH₃)₂S

\[ \text{CH}_2\text{O} + \text{CH}_3\text{COCH}_3 + \text{CH}_3\text{COCHO} + \text{OHCCH}_{2}\text{CHO} \]

\[ \xrightarrow{6 \text{C} = \text{O} \rightarrow 3 \text{ dienes}} \]

23. Fill in the starting reactant.

\[ \text{1. BH}_3\text{-THF} \quad \text{2. NaOH, H}_2\text{O} \]

24. Fill in the blanks for the following reaction sequence.

\[ \text{1. Hg(OAc)}_2, \text{H}_2\text{O} \quad \text{2. NaBH}_4 \]

\[ \text{1. O}_3 \quad \text{2. Me}_2\text{S} \]

25. Provide reagents to carry out the following transformation: (3 steps minimum)

\[ \text{Br}_2, \text{hv} \quad \text{NE}_4\text{+} \quad \text{Cl}_2 \]

or KOC(CH₃)₃
1. Rank the following alkenes in order of stability, 1 being most stable, 4 being least stable. (4)

2. Determine the number of elements of unsaturation for C₅H₇ClO. (3)

3. Give the proper IUPAC name or the structure for the following compounds. (4 points each)

   a. (E)-2-chloro-3-methyl-2-pentene

   b. cis-5-methyl-2-octene

4. Rank the reactivity of the following alcohols towards HBr, 1 being the fastest reactant, 3 being the slowest reactant. (3 points)
5. Predict the **major** product for the following reactions. You needn't bother to show any side products or minor products. Pay careful attention to orientation. (3 points each)

\[ \text{H}_2\text{O}, \text{H}^+ \quad \text{H}_2\text{O}, \text{H}^+ \]

\[ \text{Hg(OAc)}_2, \text{CH}_3\text{OH} \]

1. NaBH_4

6. Predict the **major** product in each of the following reactions. Pay careful attention to stereochemistry! (3 points each)

\[ \text{H}_2, \text{Pt} \quad \text{H}_2, \text{Pt} \]

\[ \text{Br}_2 \quad \text{Br}_2 \]

\[ \text{Cl}_2, \text{H}_2\text{O} \quad \text{Cl}_2, \text{H}_2\text{O} \]

\[ \text{OsO}_4, \text{H}_2\text{O}_2 \quad \text{OsO}_4, \text{H}_2\text{O}_2 \]
7. Fill in the starting reactant. (4 points each)

8. Provide the major product of the following reaction sequences. (4 points each)

9. What is a possible structure for a molecule A given the following: (6 points)
a. has the formula C₆H₁₀
b. it reacts with H₂/Pt to give a product with formula C₆H₁₂
   
   just one alkene

   EU₃

c. upon ozonolysis (O₃; Me₂S) it gives two products, CH₂=O and a product C₅H₈O.
10. Fill in the boxes. (6 points total)

\[ \text{KMnO}_4, \Delta \rightarrow \text{O}_2 \]

1. \( \text{O}_2 \)
2. \( \text{Me}_2\text{S} \)

11. Provide reagents to accomplish the following transformations. (6 points each)

\[ \text{CH}_3\text{CH(OH)}\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{1. \text{H}_2\text{SO}_4, \text{heat}} \xrightarrow{2. \text{HBr}} \text{CH}_3\text{Br} \]

\[ \text{CH}_3\text{CHBrCH}_2\text{CH}_2\text{OH} \xrightarrow{1. \text{NaOH (aq)}} \text{CH}_3\text{CH}(-\text{OH})\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{2. \text{BBr}_3} \text{CH}_3\text{C}(-\text{OH})\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{3. \text{NaOH, H}_2\text{O}_2} \]
12. Draw the mechanisms for the following reactions. Be sure to draw all intermediates, and try to correctly draw "electron-movement" arrows. (8 points for the first, 6 points for the second)

13. Draw as many isomers as you can for alkenes with formula C₅H₁₀. (8 points. 2 points off for each duplicate or each possible isomer not drawn.)
1. Rank the following alkenes in order of stability, 1 being most stable, 4 being least stable. (3 points)

![Alkenes](image)

2. Determine the number of elements of unsaturation for C₅H₈O. (2 points)

3. Give the proper IUPAC name or the structure for the following compounds. (3 points each)

a. 4-vinylcyclopentene

![Structure](image)

b. trans-5-propyl-2-octene

![Structure](image)

4. Rank the reactivity of the following alcohols towards H₂SO₄/Δ catalyzed dehydration, 1 being the fastest reactant, 3 being the slowest reactant. (3 points)

![Alcohols](image)

\[\text{Cation stability} \]
5. Which of the following statements is true for the structures shown: (3 points)

a. A is Z and B is Z
b. A is Z and B is E
c. A is E and B is Z
d. A is E and B is E

6. Predict the major product for the following reactions. You needn't bother to show any side products or minor products. Pay careful attention to orientation, which is important in many of these problems. (3 points each)

a. \[ \text{HBr, no peroxides} \]

b. \[ \text{1. Hg(OAc)}_2, \text{H}_2\text{O} \]
   \[ \text{2. NaBH}_4 \]

c. \[ \text{H}_2, \text{Pt} \]

d. \[ \text{PhCO}_2\text{H} \]

e. \[ \text{Br} \]
   \[ \text{NaOCH}_3 \]
   \[ E2 \]

f. \[ \text{Br} \]
   \[ \text{potassium t-butoxide} \]
   \[ (\text{KOCMe}_3) \]
   \[ \text{bulky base} \Rightarrow E2 \]
7. Predict the major product in each of the following reactions. Pay careful attention to stereochemistry: stereochemistry is involved in each of these problems! (3 points each)

a. \[
\begin{align*}
\text{Br}_2, \text{H}_2\text{O} & \rightarrow \quad \begin{array}{c}
\text{CH}_3 \\
\text{OH} \\
\text{Br}
\end{array} \\
\end{align*}
\]

b. \[
\begin{align*}
\text{OsO}_4 & \rightarrow \quad \begin{array}{c}
\text{OH} \\
\text{OH}
\end{array} \\
\text{H}_2\text{O}_2 & \rightarrow \\
\end{align*}
\]

c. \[
\begin{align*}
\text{BH}_3\cdot\text{THF} & \rightarrow \quad \begin{array}{c}
\text{CH}_3 \\
\text{O}
\end{array} \\
\text{H}_2\text{O}_2, \text{NaOH} & \rightarrow \\
\end{align*}
\]

d. \[
\begin{align*}
\text{CH}_3\text{CO}_2\text{H}, \text{H}_2\text{O} & \rightarrow \quad \begin{array}{c}
\text{OH} \\
\text{OH}
\end{array} \\
\end{align*}
\]

8. Fill in the intermediates in the following transformation. (3 points each)

\[
\begin{align*}
\text{H}_2\text{SO}_4, \Delta & \rightarrow \quad \begin{array}{c}
\text{A} \\
\text{B}
\end{array} \\
\text{HBr, Peroxides} & \rightarrow \quad \begin{array}{c}
\text{C}
\end{array} \\
\text{NEt}_3, \Delta & \rightarrow \\
\text{1. Hg(OAc)}_2, \text{MeOH} & \rightarrow \\
\text{2. NaBH}_4 & \rightarrow
\end{align*}
\]
9. For the following reactions, fill in the missing **starting materials, reagents, or products.** (3 points each)

a. \[
\text{H} = \text{Br}_{2} \\
\text{Br} = \text{H} \\
\text{Br} = \text{H}
\]

b. \[
\text{CH}_{2}=\text{CH}_{2} \quad 1. \text{BH}_3\cdot\text{THF} \\
\quad 2. \text{H}_2\text{O}, \text{NaOH} \quad \rightarrow \quad \text{CH}_{3}\text{CH}_{2}\text{OH}
\]

c. \[
\text{5} \quad 1. \text{O}_3 \\
\quad 2. \text{Me}_2\text{S} \\
\text{KMnO}_4, \Delta \quad \rightarrow \\
\text{4} \quad 3 \quad 2
\]

d. \[
\text{C} = \text{O} \\
\text{C} = \text{O} \\
\text{OH}
\]
10. Provide the major product of the following reaction sequences. (4 points each)

\[
\begin{align*}
\text{CH}_2=\text{CH}_2 & \quad \xrightarrow{1. \text{H}_2\text{O}, \text{H}^+} \quad \text{CH}_3\text{CH}_{2}\text{OH} \quad \xrightarrow{2. \text{H}_2\text{SO}_4, \Delta} \quad \text{CH}_3\text{CH}=\text{CH}_2 \\
\text{CH}_2\text{C}_6\text{H}_5 & \quad \xrightarrow{1. \text{HBr, peroxides}} \quad \text{CH}_2\text{C}_6\text{H}_5\text{Br} \quad \xrightarrow{2. \text{KOCMe}_3} \quad \text{CH}_2\text{C}_6\text{H}_5 \quad \xrightarrow{3. \text{Br}_2} \quad \text{CH}_2\text{C}_6\text{H}_5\text{Br}\text{Br}
\end{align*}
\]

11. Provide reagents to accomplish the following transformations. (4 points each)

\[
\begin{align*}
\text{CH}_2\text{C}_6\text{H}_5\text{Br} & \quad \xrightarrow{1. \text{NEt}_3 \text{ (or any base)}} \quad \text{CH}_2\text{C}_6\text{H}_5 \\
& \quad \xrightarrow{2. \text{H}_2, \text{Pt}} \quad \text{CH}_2\text{C}_6\text{H}_5
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2\text{C}_6\text{H}_5\text{OH} & \quad \xrightarrow{1. \text{H}_2\text{SCy}, \text{H}^+} \quad \text{CH}_2\text{C}_6\text{H}_5\text{COOH} \\
& \quad \xrightarrow{2. \text{OsCy}, \text{H}_2\text{O}} \quad \text{CH}_2\text{C}_6\text{H}_5\text{COOH}
\end{align*}
\]

12. Provide the product for the following reaction. Be sure to show the stereochemistry of the product. (3 points)

\[
\begin{align*}
\text{Br}_2\text{Me} & \quad \xrightarrow{\text{Ph, OMe, NaOH}} \quad \text{CH}_3\text{CH}=\text{CH}_2\text{CH}_3 \\
\text{Ph} & \quad \xrightarrow{\text{H}, \text{Me}} \quad \text{OMe}
\end{align*}
\]
13. Draw the mechanism for the following reaction, and write "slow" next to the rate determining step. Be sure to draw all intermediates, and to correctly draw "electron-movement" arrows or half-arrows. (4 points)

14. Draw the mechanism for the following reaction. Be sure to draw all intermediates, and to correctly draw "electron-movement" arrows or half-arrows. (4 points)

15. Formula: C₄H₈  
Reactivity: reacts with H₂/Pt to give C₄H₁₀ alkene  
DRAW ALL POSSIBLE ISOMERS, INCLUDING STEREOISOMERS. (4 isomers are possible!) (5 points)
1. Provide the Name or Structure for the Following (7 points)

- pyridine
- m-nitroaniline
- o-bromotoluene

2. Circle the aromatic molecules (6 points)

- [Aromatic Molecule 1]
- [Aromatic Molecule 2]
- [Aromatic Molecule 3]
- [Aromatic Molecule 4]

3. Outline the energies of the \( \pi \)-molecular orbitals for benzene, and draw electrons into the orbitals that are occupied. (5 points)

4. Bromide B has normal reactivity (for a 2° bromide) toward \( S_{n}1 \) substitution, but A has much higher reactivity and C has much lower reactivity. a) Why is A more reactive toward \( S_{n}1 \)? b) Why is C much less reactive toward \( S_{n}1 \)? (4 points)

- Kinetic reactivity toward \( S_{n}1 \) reactivity (H\(_2\)O, H\(^+\))

\[ S_{n}1 \rightarrow \text{cation formation} \]

a) A \( \rightarrow \) allylic cation, stabilized

b) C \( \rightarrow \) antiaromatic, destabilized
5. Synthesis Reactions. Draw the feature product of the following reactions (need not show any byproducts). (21 points, 3 points each)

\[
\begin{align*}
\text{HO-} & \begin{array}{c}
\text{HNO}_3, \text{H}_2\text{SO}_4
\end{array} \rightarrow \begin{array}{c}
\text{H} \quad \text{O} \\
\text{O} \\
\text{SO}_3 \text{H}
\end{array} \\
\text{\text{HO-}2} & \begin{array}{c}
\text{Cl}
\end{array} \rightarrow \begin{array}{c}
\text{\text{Cl}}
\end{array} \\
\text{\text{HO-}2} & \begin{array}{c}
\text{NH}_2
\end{array} \\
\end{align*}
\]
6. Design sequences for the designated conversions. (5 points each)

\[ \text{SO}_3 \cdot \text{CH}_2 \text{CO}_3 \]

\[ \text{Cl}_2 \ \text{HCl} \]

\[ \text{H}_2 \text{O}, \text{H}_2 \text{SO}_4 \]

\[ \text{either} \] \[ \text{Zn(H}_2\text{)}, \text{HCl} \]

7. Design a synthesis for the following molecule beginning with toluene. (6 points)

8. Draw the Reactants for the Following (6 points)

\[ \text{ Via Substitution on a Bromide } \]

\[ \text{ Via Diels-Alder } \]
9. a) Draw the major product for the following reaction, and b) draw the mechanism for its formation. c) Identify the slow step. d) Draw all the resonance structures for the cation intermediate and e) circle the most important contributor. (7 points)

\[
\text{H}_2\text{N} - \text{Cl} \xrightarrow{\text{Cl}_2, \text{AlCl}_3} \text{H}_2\text{N} - \text{Cl} \xrightarrow{\text{HCl, AlCl}_3} \text{H}_2\text{N} - \text{Cl} \\
\text{Cl} - \text{Cl} \xrightarrow{\text{AlCl}_3} \text{Cl}^+ + \text{AlCl}_4^- \\
\text{slow step} \]

\[
\text{H}_2\text{N} - \text{Cl} \xrightarrow{\text{HCl, AlCl}_3} \text{H}_2\text{N} - \text{Cl} + \text{HCl} + \text{AlCl}_3 \\
\text{Cl} - \text{AlCl}_3
\]

10. (9 points total) a) Draw the mechanism for the following reaction, in which a common intermediate gives rise to both products.

\[
\text{Ph} - \text{OH} \xrightarrow{\text{HBr}} \text{Ph} - \text{Br} + \text{Ph} - \text{Br} \\
\text{optically active} \xrightarrow{\text{H}_2\text{N} - \text{Cl}} \text{Ph} - \text{Br} + \text{Ph} - \text{Br} \\
\text{resonance delocalized cation} \]

b) In the above reaction, is product A chiral or achiral? \(\text{Chiral} \) (but not \(\text{optically active} \))

c) Product A is formed preferentially at low temperature, but B is major when the reaction is conducted at high temperature such that product equilibration occurs. Which is the "thermodynamic" product (more stable, so it builds up under equilibrating conditions) and which is the "kinetic" product (less stable but forms preferentially under non-equilibrating conditions.)

Thermodynamic Control Product: \(\text{B} \) (more stable). Kinetic Product: \(\text{A} \) (less stable, double bond).

d) Draw the 2 relevant resonance structures for the key intermediate (or mark them if you already drew both in your mechanism). Circle the one that would make the greater contribution to the resonance hybrid. Why is the "kinetic" product formed preferentially under irreversible conditions? A forms faster because the cation form is better.
11. Rank the following, with 1 being highest/most. (2 points each)

- Heat of Hydrogenation

- Reactivity Towards

- Reactivity toward $S_N2$ Substitution

- Stability

- Reactivity toward HNO$_3$/H$_2$SO$_4$

- Reactivity toward HBr addition

12. For each nitrogen in the molecule, classify the hybridization of the nitrogen atom, the hybridization of the nitrogen lone pair, and classify whether the basicity of the nitrogen is “normal” or “low”. (5 points)

<table>
<thead>
<tr>
<th>Nitrogen Hybridization</th>
<th>Lone-Pair Hybridization</th>
<th>Nitrogen Basicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_a$</td>
<td>$sp^2$</td>
<td>$sp^2$</td>
</tr>
<tr>
<td>$N_b$</td>
<td>$sp^2$</td>
<td>$p$</td>
</tr>
<tr>
<td>$N_c$</td>
<td>$sp^2$</td>
<td>$p$</td>
</tr>
<tr>
<td>$N_d$</td>
<td>$sp^3$</td>
<td>$sp^3$</td>
</tr>
</tbody>
</table>
1. Provide the Name of Structure for the following. (7 points)
   
a. 3-nitroaniline

   ![Structure](image)

   b. o-isopropyltoluene

   ![Structure](image)

   c. ![Structure](image)  pyridine

2. Circle the aromatic molecules. (7 points)

   ![Circles](image)

3. The molecule has 3 different nitrogens. For each of them, classify the hybridization of the nitrogen atom, the hybridization of the nitrogen lone pair, and whether the basicity of the nitrogen is "normal" or "low". (6 points)

   ![Structure](image)

<table>
<thead>
<tr>
<th>Nitrogen Hybridization</th>
<th>Lone-Pair Hybridization</th>
<th>Nitrogen Basicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>sp^2</td>
<td>low</td>
</tr>
<tr>
<td>Nb</td>
<td>sp^3</td>
<td>normal</td>
</tr>
<tr>
<td>Nc</td>
<td>sp^2</td>
<td>normal</td>
</tr>
</tbody>
</table>
4. Draw the major products of the following reaction (4 points).

\[ \text{H-Br} \quad \text{(no peroxides)} \]

\[ \text{CH}_3 \quad \text{Br}_2, \text{FeBr}_3 \]

5. Draw the Major Product of the Following Reactions. Note: I want one major product in each case. (3 points each)

\[ \text{CH}_3 \quad \text{Br}_2, \text{hv} \quad \text{NaOH} \]

\[ \text{Cl}_2, \text{AlCl}_3 \quad \text{Fe}, \text{HCl} \]

\[ \text{Br} \quad \text{Cl} \quad \text{Zn(Hg), HCl} \]

\[ \text{Cl} \quad \text{AlCl}_3 \]

\[ \text{heat} \]

\[ \text{1. SO}_3, \text{H}_2\text{SO}_4 \quad \text{3. KMnO}_4 \]

\[ \text{2. HNO}_3, \text{H}_2\text{SO}_4 \quad \text{4. H}_2\text{O}, \text{H}_2\text{SO}_4 \]

\[ \text{(partial credit for E2, } S_N2 \text{ wins with benzylic)} \]
6. Rank the following, with 1 being highest/most. (2 points each)

Reactivity toward \( \text{Br}_2, \text{FeBr}_3 \)

Heat of hydrogenation

Stability

Combined Diels-Alder Reactivity

Cation Stability

Reactivity toward NaOMe

7. Outline the \( \pi \)-molecular orbitals of cyclopentadiene cation (use a Frost diagram), indicate which are occupied by electrons, and indicate whether the species is unusually stable or not. (6 points)
8. Treatment of an alkyl halide with methanolic AgNO₃ often promotes ionization, via the following:

\[ \text{R-X} \xrightarrow{\text{Ag}^+} \text{R}^+ + \text{AgX} \]

When 3-bromo-1-butene undergoes this reaction, two isomeric products A and B are formed. Draw the structure for product B and the detailed mechanism for formation of product B. (7 pts)

9. Draw the product for the following reaction and draw the mechanism for its formation. Identify the slow step. Draw all the resonance structures for the cation intermediate and circle the most important contributor. (7 points)
10. (6 pt) When comparing cyclopentadiene (A) versus 1,3-pentadiene (CH$_2$=CH-CH=CH-CH$_3$, B),

   a. One is much more acidic. Which is it, and why?
      \[ \text{A, C}1 \text{ives aromatic anion} \]

   b. One is a much more reactive diene. Which is it, and why?
      \[ \text{A, Cisoid. B is only cisoid a little bit.} \]

11. Draw the Reactants for the Following Reactions (7 points)

   

12. Provide reagents for the following transformations. (5 points each)

   \[ \text{1, Cl, AlCl}_3 \]
   \[ \text{2, Cl}_2, \text{AlCl}_3 \]
   \[ \text{3, } \text{Zn(C)}_2, \text{HCl} \]
1. Provide Either the Name or the Structure for the Following Chemicals. (6 points) (3 minutes)

   a. Furan

   b. p-nitrobenzoic acid

   c. \( \mu \)-ethylaniline

2. For the following substituents, classify each as 1) electron-donating or electron-withdrawing ("D" or "W"), 2) as activating or deactivating ("Act" or "Deact"), and as 3) ortho-para directing or meta directing ("o/p" or "m"). (6 points) (2 minutes)

   \begin{align*}
   -\text{OCH}_3 & : D & -\text{CH}_3 & : W \\
   \text{O} & : \text{Act} & -\text{Cl} & : \text{Deact} \\
   \text{Act} & : o/p & \text{Deact} & : o/p
   \end{align*}
3. Rank the reactivity (rates!) of the following sets of molecules toward the reagents shown, 1 being most reactive, 2 being middle, and 3 being least reactive. (10 points) (6 minutes)

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Molecules Being Compared</th>
</tr>
</thead>
</table>
a. $H_2$, Pt | ![Cyclohexane molecules] |

| ![Benzene with 3 molecules] |
b. $H^+$, $H_2$O ($S_N$1/E1) | ![Alkenes with 3 molecules] |

| ![Vinyl chloride] |
c. ![Cyclopentene molecules] |

| ![Cyclopentene with 3 molecules] |

d. $HNO_3$, $H_2$SO$_4$ | ![Substituted benzenes] |

| ![Nitrobenzene with 3 molecules] |
f. NaOMe ($S_N$2 reactivity) | ![Substituted alkenes] |
4. Draw the major product for each of the following reactions. (3 points each, 21 total, 7 minutes)

a. \[
\begin{align*}
\text{NO}_2 & \quad \text{Cl}_2, \text{AlCl}_3 \\
& \quad \text{NO}_2 \quad \text{Cl}
\end{align*}
\]

b. \[
\begin{align*}
\text{Br} & \quad 1. \text{SO}_2, \text{H}_2\text{SO}_4 \\
& \quad 2. \text{HNO}_3, \text{H}_2\text{SO}_4 \\
& \quad 3. \text{H}_2\text{O}, \text{H}_2\text{SO}_4
\end{align*}
\]

c. \[
\begin{align*}
\text{OCH}_2\text{CH}_3 & \quad 1. \text{HNO}_3, \text{H}_2\text{SO}_4 \\
& \quad 2. \text{Fe, HCl}
\end{align*}
\]

d. \[
\begin{align*}
& \quad 1. \text{Br}_2, \text{hv} \\
& \quad 2. \text{NaOMe}
\end{align*}
\]

e. \[
\begin{align*}
\text{less active} & \quad \text{more active} \\
\text{O}_2\text{N} & \quad \text{Cl}_2, \text{FeCl}_3
\end{align*}
\]

f. \[
\begin{align*}
\text{Br} & \quad 1. \text{Mg, ether} \\
& \quad 2. \text{Br}
\end{align*}
\]

g. \[
\begin{align*}
& \quad \text{heat}
\end{align*}
\]
5. Provide reagents for the following transformations. (5 points each, 10 total, 6 minutes)

a.  
\[ \text{CH}_3 \text{C}_6 \text{H}_4 \text{CH}_3 \xrightarrow{1. \text{SO}_3, \text{H}_2\text{SCy}} \xrightarrow{2. \text{Cl}_2, \text{FeCl}_3} \text{Cl} \xrightarrow{3. \text{either } \text{H}_2\text{O}, \text{H}_2\text{SCy} \text{ or } \text{K MnO}_4} \text{CO}_2\text{H} \]

b.  
\[ \text{C}_6 \text{H}_6 \xrightarrow{1. \text{either } \text{Cl} \xrightarrow{2. \text{H}_2\text{O}_2, \text{H}_2\text{SCy}} \text{order} \xrightarrow{3. \text{Zn(Cy)}_2, \text{HCl} \text{ or } \text{Fe}, \text{HCl}} \text{NH}_2 \]

6. Draw the diene and dienophile from which the following Diels-Alder products would have come. (3 points each, 6 total, 2 minutes)

a.  
\[ \text{Me}_2\text{C} = \text{C} + \text{Me}_2\text{C} = \text{C} \xrightarrow{\text{heat}} \text{Me}_2\text{N-} \]

b.  
\[ \text{C}_3\text{H}_5 + \text{C}_5\text{H}_5\text{O} \xrightarrow{\text{heat}} \text{MeO} \]
7. a. Draw the mechanism for the formation of the major product shown, and identify the "slow" step in the reaction. (6 points, 5 minutes)

b. Draw all 4 resonance structures for the cation intermediate in the above reaction, and circle the most important contributor. (4 points)
8. Draw the major product or products that would result from the following reaction, and write either "chiral" or "achiral" and "optically active" or "racemic" by each product. Draw a mechanism for the reaction, and identify the "slow" step in the reaction. (8 points, 5 min)

9. Provide a synthesis for the following molecule, using benzene and anything else you like. "Backwards syntheses" are fine, so long as you draw the reagents! (7 points, 5 min)
10. Circle the aromatic molecules: (6 points) (3 minutes).

11. The molecule below has 3 different nitrogens. For each of the nitrogens, classify the hybridization of the nitrogen atom, the hybridization of the nitrogen's lone pair, and whether the basicity of the nitrogen is "normal" or "low". (6 points, 2 min)

<table>
<thead>
<tr>
<th>Nitrogen Hybridization</th>
<th>Lone-Pair Hybridization</th>
<th>Nitrogen Basicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>$sp^2$</td>
<td>normal</td>
</tr>
<tr>
<td>Nb</td>
<td>$sp^2$</td>
<td>low</td>
</tr>
<tr>
<td>Nc</td>
<td>$sp^3$</td>
<td>normal</td>
</tr>
</tbody>
</table>

12. Outline the energies of the $\pi$ molecular orbitals of cyclobutadiene (use a Frost diagram), indicate which are occupied by electrons, and indicate whether the molecule is "unusually stable" or not. (4 points, 1 min)

Not aromatic
(Not aromatic)
1. Provide names or structures for the following. 2 points each. Specify stereochemistry when appropriate!

- trans-4-methyl-1-chlorocyclohexane
- or trans-4-chloro-1-methylcyclohexane
- (R)-2-bromobutane
- m-isopropylphenol
- Z-2-chloro-2-hexene
- m-butylphenol
  - or meta-butylphenol
  - or 2-butylphenol

2. Identify the functional groups in the following molecule. (4 points)
3. Predict the major products for the following reactions. Pay careful attention when orientation is a factor. Draw just one major product in each case. (3 points each)

\[ \text{OCH}_3 \text{CN} + \text{CN} \longrightarrow \text{CN} \text{CN} \]

\[ \text{Br}_2, \text{hv} \]

\[ \text{OCH}_3 \text{CN} \]

\[ \text{Br} \]

\[ \text{Br}_2, \text{FeBr}_3 \]

\[ \text{Zn(Hg), HCl} \]

\[ \text{Br}_2, \text{hv} \]

\[ \text{NaBH}_4 \]

\[ \text{NaOCH}_3 \]

\[ \text{OsO}_4, \text{H}_2\text{O}_2 \]

\[ \text{cis addition} \]

\[ \text{Markownikov} \]

\[ \text{Zaitsev} \]

\[ \text{3°, so E2 not S_n2.} \]

\[ \text{O}_3 \]

\[ \text{Me}_2\text{S} \]

\[ \text{H}_2\text{O}, \text{Hg(OAc)}_2 \]

\[ \text{NaBH}_4 \]
4. Classify the pairs of molecules as totally different, identical, structural isomers, diastereomers, or enantiomers. (2 points each)

- enantiomers

- structural isomers

- identical

5. Classify each chiral carbon as R or S. (2 points each)

- R

- R

6. Classify the hybridization and bond angles (109, 120, or 180) at the labelled atoms. (5 points)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Hybridization</th>
<th>Bond Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-1</td>
<td>sp^2</td>
<td>120</td>
</tr>
<tr>
<td>C-2</td>
<td>sp^3</td>
<td>109</td>
</tr>
<tr>
<td>C-3</td>
<td>sp^2</td>
<td>120</td>
</tr>
<tr>
<td>O-4</td>
<td>sp^3</td>
<td>109</td>
</tr>
</tbody>
</table>
7. Draw the mechanisms for the following reactions. For any radical reactions, draw propagation steps only. 5 points each.

\[
\text{OCH}_3\xrightarrow{\text{Cl}_2, \text{AlCl}_3} \text{OCH}_3
\]

\[
\text{Cl} \xrightarrow{\text{AlCl}_3} \text{Cl} + \text{Cl}^-
\]

Draw the resonance structures for the cation intermediate.
8. Draw the products of the following multi-step sequences. (4 points each)

\[
\begin{align*}
\text{Me} & \quad \text{Br} \\
\text{Ph} & \quad 3^\circ
\end{align*}
\]
\[1. \text{NaOH} \quad \text{E2} \]
\[2. \text{HBr, peroxides} \]
\[3. \text{NaOMe} \]
\[
\text{Ph} \quad \text{Br} \quad \text{anti-Mark} \quad \text{Sn2} \quad \text{Ph} \quad \text{Me} \quad \text{OCH}_3
\]

\[
\begin{align*}
\text{CH}_3 & \\
\text{C} & \quad \text{H}
\end{align*}
\]
\[1. \text{SO}_3, \text{H}_2\text{SO}_4 \]
\[2. \text{2-bromopropane, AlCl}_3 \]
\[3. \text{H}_2\text{O, H}^+ \]

\[
\begin{align*}
\text{OH} & \\
\text{C} & \quad \text{H}
\end{align*}
\]
\[1. \text{H}_2\text{SO}_4 \]
\[2. \text{HBr, Peroxides} \]
\[3. \text{NEt}_3 \quad \text{bulky} \]

9. Draw as many structural isomers as you can for C\textsubscript{6}H\textsubscript{14}. Circle any that are chiral. (Note: be careful! You will lose points for any repeats!) (6 points)

\[\text{C}_6\text{H}_{14} \quad \text{EU} = 0 \quad \text{no rings or alkenes} \]

\[
\begin{align*}
6 & \\
4 & \\
5 & \\
\end{align*}
\]

None are chiral
10. Rank the Following, from most to least. 2 points each.

a. Reactivity toward $S_N2$

\[ \text{I} > \text{Br} > \text{Cl} \]

b. Stability

\[ \text{allylic} > \text{isolated} \]

\[ \text{1}^{\circ} > 2^{\circ} > 3^{\circ} \]

c. Stability

\[ \text{1} > \text{3} > \text{2} \]

\[ \text{1. Equatorial preferred} \\
\text{2. If forces to be axial, worse for big group than for smaller group} \]

d. Acidity

\[ \text{HCl by memory is strong} \\
\text{3. Electronegativity factor} \\
\text{4. Resonance factor} \]

\[ \text{1} > \text{2} > \text{4} \]

e. Stability

\[ \text{1} > \text{3} > \text{2} > \text{4} \]

\[ \text{1. staggered vs eclipsed} \\
\text{2. Anti > gauche} \\
\text{3. Eclipsed > total eclipsed} \]

f. Reactivity toward $\text{H}_2\text{SO}_4$ catalyzed dehydration

\[ \text{Cation stability is key} \]

g. Boiling Point

\[ \text{1. Hydrogen bonding} \\
\text{2. Molecular weight factor} \]
11. Provide reagents for the following transformations. You may use anything you like. Each can be done within ≤3 steps. (4 points each)

1. NBS + peroxides or Br₂, hv

2. Br

12. Provide the appropriate reactant for the following transformation. (3 points)

CH₃CO₂H, H₂O
13. Suggest a structure for X, given the following info: (5 points)

- **Formula:** \( C_8H_{12} \)
- It reacts with excess \( H_2/Pt \) to produce \( C_8H_{16} \)
- When it reacts with \( O_3/Me_2S \), one of the products is \( CH_2=O \).

14. Which of the following are aromatic

![Aromatic structures](image)

15. Draw the products and mechanism for the following reaction:

![Reaction mechanism](image)

16. Rank the following:

<table>
<thead>
<tr>
<th>Diene-wise</th>
<th>Dienophile-wise</th>
<th>Combined S(_N2) Reactivity</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Diene-wise" /></td>
<td><img src="image" alt="Dienophile-wise" /></td>
<td><img src="image" alt="Combined S(_N2) Reactivity" /></td>
</tr>
</tbody>
</table>

Theory = 18
Actual = 12
Eu = 3

Protonation gives asymmetric allylic cation, leading to two isomers. Protonation on left end would have given an inferior allylic cation.
1. Rank the Following, from most to least. 2 points each.

a. Stability

1 2 3 4

b. Stability

allylic > isolate 8 > 2 > 1

1 2 3 4

c. Stability

1 2 3

d. Acidity

CH₃OH PhCO₂H NH₃ CH₃CH₃

2 1 3 4

e. Stability

1 2 3 4
f. Reactivity toward HBr

\[
\begin{align*}
&\text{Reactivity toward } HBr \\
&\text{Stability}
\end{align*}
\]

\[
\begin{align*}
&\text{Reactivity toward } Br_2/hv
\end{align*}
\]

h. Reactivity toward S_N2

\[
\begin{align*}
&\text{Reactivity toward } S_N2
\end{align*}
\]

i. Boiling Point

\[
\begin{align*}
&\text{Boiling Point}
\end{align*}
\]

j. Stability

\[
\begin{align*}
&\text{Stability}
\end{align*}
\]

2. Provide names or structures for the following. 3 points each. Note: don't forget to specify stereochemistry!

a. \[
\begin{align*}
&\text{trans-1,3-dimethylcyclohexane}
\end{align*}
\]

If optically active: \((1S,3S)-1,3\text{-dimethylcyclohexane}\)

b. \[
\begin{align*}
&\text{allylcyclohexane}
\end{align*}
\]

or \(3\text{-cyclohexyl propene}\)
c. \(\text{optically active } S-2\text{-butanol}\)

d. \(E-3\text{-bromo-3-heptene}\)

e. \(5\text{-methyl-2-heptanol} \quad \alpha\text{-heptan-2-ol}\)

f. trans-1-bromo-3-isopropylcyclopentane

3. Classify the pairs of molecules as totally different, identical, structural isomers, diastereomers, or enantiomers. (2 points each)

a. \(\text{Same}\)

b. \(\text{structural isomers}\)

c. \(\text{enantiomers}\)
3. (continued) Classify the pairs of molecules as totally different, identical, structural isomers, diastereomers, or enantiomers. (2 points each)

d. \[\text{diastereomers}\]

e. \[\text{identical}\]

f. \[\text{diastereomers}\]

f. \[\text{enantiomers}\]

4. Draw at least four different isomers for C\text{5}H\text{10}. (There are lots more than four…) (6 points)

5. (a) Draw the appropriate number of lone pairs on the oxygen atom,
(b) Assign a formal charge on oxygen if appropriate,
(c) Draw an additional resonance structure for the following, and
(d) Identify which of the two structures would make the greater contribution to the hybrid. (4 points)
6. Draw resonance structures for each of the following:

\[ \text{\begin{tikzpicture} \draw [-latex] (0,0) -- (2,0); \end{tikzpicture}} \]

\[ \text{\begin{tikzpicture} \draw [-latex] (0,0) -- (2,0); \end{tikzpicture}} \]

7. Identify the functional groups in the following molecule. (4 points)

\[ \text{\begin{tikzpicture} \draw [-latex] (0,0) -- (2,0); \end{tikzpicture}} \]

8. Classify the hybridization and bond angles (109, 120, or 180) at the labelled atoms. (4 points)

\[ \text{\begin{tikzpicture} \draw [-latex] (0,0) -- (2,0); \end{tikzpicture}} \]

9. Draw both chair conformations of trans-1-methyl-3-isopropylcyclohexane, and circle the more stable one. (5 points.)

Note 1: It will simplify things if you abbreviate the isopropyl group as "R".
Note 2: Make sure that your second chair has the same "configuration" as the first, and is not an enantiomer.
10. Classify each chiral carbon as R or S. (Some structures may have more than one chiral carbon!) (2 points each)

a. 
\[
\begin{array}{c}
\text{H} \\
\text{HOH}
\end{array}
\]

b. 
\[
\begin{array}{c}
\text{O} \\
\text{H}
\end{array}
\]

11. Mechanisms Problem. Draw the mechanism for the following reactions, and write "slow" next to the rate-determining step. Be sure to draw all intermediates, and to correctly draw "electron-movement" arrows or half-arrows. For radical reactions, draw propagation steps only. 4 points each.

a. 
\[
\begin{align*}
\text{C}_{\text{6}}\text{H}_{\text{12}} & \xrightarrow{\text{H}_2\text{O}, \text{H}^+} \text{C}_{\text{6}}\text{H}_{\text{13}}\text{O}^- \\
\text{C}_{\text{6}}\text{H}_{\text{13}}\text{O}^- & \xrightarrow{\text{H}_2\text{O}} \text{C}_{\text{6}}\text{H}_{\text{12}}\text{OH}
\end{align*}
\]

b. 
\[
\begin{align*}
\text{C}_{\text{6}}\text{H}_{\text{12}} & \xrightarrow{\text{Br}_2} \text{C}_{\text{6}}\text{H}_{\text{12}}\text{Br} \\
\text{C}_{\text{6}}\text{H}_{\text{12}}\text{Br} & \xrightarrow{\text{Br}_2} \text{C}_{\text{6}}\text{H}_{\text{12}}\text{Br}_2 \\
\text{C}_{\text{6}}\text{H}_{\text{12}}\text{Br}_2 & \xrightarrow{\text{Br}_2} \text{C}_{\text{6}}\text{H}_{\text{12}}\text{Br}_2
\end{align*}
\]
Mechs, continued

c. \[ \text{Br}_2, \text{hv} \]

\[ \begin{align*}
\text{H}^+ & \quad \text{Ph} \quad \text{HBr} \\
\text{H}^+ & \quad \text{Ph} \quad \text{HOH}
\end{align*} \]

\[ \text{H}^+ \quad \text{catalyst} \]

\[ \text{H}_2\text{O} \]

\[ \text{Br}^- \quad \text{H}^- \]

\[ \text{Ph} \quad \text{Ph} \]

\[ + \text{H}-\text{Br} \]
12. Predict the major products for the following reactions. In each case, pay careful attention to orientation and stereochemistry. Draw just one product in each case. (3 points each)

a. \[ \text{HBr} \rightarrow \]

b. \[ \text{H}_2\text{O}, \text{H}^+ \rightarrow \]

c. \[ \text{H}_2\text{ONa} \rightarrow \text{CH}_3\text{CH}_2\text{I} \]

d. \[ \begin{array}{c} \text{a. O}_3 \\ \text{b. Me}_2\text{S} \end{array} \rightarrow \]

e. \[ \text{Br}_2, \text{hv} \rightarrow \]

f. \[ \text{Br} \rightarrow \text{NaOCH}_3 \]

g. \[ \begin{array}{c} \text{1. BH}_3\text{-THF} \\ \text{2. NaOH, H}_2\text{O}_2 \end{array} \rightarrow \]

h. \[ \begin{array}{c} \text{1. NEt}_3 \\ \text{2. Cl}_2 \end{array} \rightarrow \]
13. Draw the substitution products for the following reactions. (Do not draw any accompanying elimination products.) Include stereochemistry in your answer, and if two substitution products are formed, draw them both. Assume the starting material is optically active as drawn. (3 points each)

a. \[ \text{Ph} \quad \text{H} \quad \text{Br} \quad \xrightarrow{\text{NaOMe}} \quad \text{Ph} \quad \text{H} \quad \text{OCH}_3 \quad \text{SN}_2 \quad \text{Inversion, single isomer} \]

b. \[ \text{Me} \quad \text{Br} \quad \xrightarrow{\text{H}_2\text{O, cat. HBr}} \quad \text{Ph} \quad \text{Me OH} + \text{Ph} \quad \text{SN}_1 \quad \text{Racemization both enantiomers} \]

14. Draw the products of the following multi-step sequences. (4 points each)

a. \[ \text{OH} \quad 1. \text{H}_2\text{SO}_4 \quad 2. \text{CH}_3\text{CO}_2\text{H, H}_2\text{O} \quad \text{OH} \quad \text{OH} \]

b. \[ \text{Ph} \quad \text{Me} \quad \xrightarrow{\text{Br}_2, \text{hv}} \quad 1. \text{NEt}_3 \quad 2. \text{CH}_3\text{CO}_2\text{H, H}_2\text{O} \quad \text{Ph} \quad \text{OH} \quad \text{OH} \]


15. Provide reagents for the following transformations. More than one step is needed in each case. (4 points each)

a. \[ \text{Br} \] 

1. \( \text{NE}_3 \) 
2. \( \text{Br}_2 \)

b. \[ \text{OH} \] 

1. \( \text{H}_2 \text{SO}_4 \) 
2. \( \text{MeCO}_3\text{H} \)

16. Provide the appropriate reactant for the following transformation. (3 points)

17. Suggest a structure for A that is consistent with the following information. (There is more than one possible solution, but you only need to provide one.) (5 points)
18. Draw the products for the following reactions:

a. \[
\text{1 H-Br} \quad \rightarrow \quad \text{products}
\]

b. \[
\text{NBS, peroxides}\quad \rightarrow \quad \text{products}
\]

c. \[
\text{products}
\]

d. \[
\text{Draw substitution product(s) only}
\]

e. \[
1. \text{Br}_2, \text{FeBr}_3 \\
2. \text{HNO}_3, \text{H}_2\text{SO}_4
\]

f. \[
1. \text{Br} + \text{AlCl}_3 \\
2. \text{KMnO}_4
\]

g. \[
1. \text{SO}_3, \text{H}_2\text{SO}_4 \\
2. \text{products}
\]

h. \[
1. \text{Br}_2, \text{hv} \\
2. \text{NaOCH}_3
\]

Flawed problem. Not clear which allylic cation you should use. Protonation on the left gives allylic where both carbons are 2°; protonation on the right gives a hybrid of a 3°/1° cation.
19. Which of the following are aromatic

![Aromatic molecules]

20. Classify the lone pair hybridization on the three nitrogen atoms in the following molecule:

![Nitrogen atom hybridization diagram]

21. Draw the major products and mechanism for the following reaction:

![Allylic substitution reaction]

Protonation occurs on the left-most carbon, because that gives by far the best cation. 3° allylic and conjugated to the phenyl as well. The asymmetric allylic cation gives two different products (1,2 and 1,4 addition).

22. Draw the major product and mechanism for the following reaction. Draw all of the resonance structures for the key carbocationic intermediate

![Nitration reaction]

![Resonance structures]

Draw all of the resonance structures for the key carbocationic intermediate.
23. Design a synthesis for the following:

\[
\begin{align*}
\text{C}_6\text{H}_{12} & \xrightarrow{1. \text{Cl}_2\text{CH}_2 + \text{AlCl}_3} \text{C}_6\text{H}_{14} \quad \text{O}_2\text{N} \\
2. \text{Zn(Hg), HCl} & \\
3. \text{HNO}_3, \text{H}_2\text{SO}_4 & \\
\text{C}_6\text{H}_{14} & \xrightarrow{} \text{C}_6\text{H}_{15} \quad \text{O} \\
\end{align*}
\]

24. Explain why A is more acidic than B, but C is less reactive than D towards S_N1 reactivity.

\[
\begin{array}{ccc}
\text{A} & \text{B} & \text{Acidity} \\
\text{C} & \text{D} & \text{S_N1 Reactivity} \\
\end{array}
\]

25. Rank the following:

\[
\begin{align*}
\text{OCH}_3 & \quad \text{Reactivity toward Cl}_2, \text{AlCl}_3 \\
\text{CH}_3 & \quad 2 \\
\text{OCH}_3 & \quad 3 \\
\text{OCH}_3 & \quad 1 \\
\text{alkyl bond} & \\
\end{align*}
\]

\[
\begin{array}{ccc}
\text{I} & \text{Combined Diels-Alder Reactivity} & \text{Extra u good} \\
\text{II} & \text{Stability} \\
\end{array}
\]

1. allylic
2. allylic
3. isolated
4. isolated