<table>
<thead>
<tr>
<th>Problems</th>
<th>Points</th>
<th>Credit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Functional Group Nomenclature (1 large structure)</td>
<td></td>
<td>X</td>
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<tr>
<td>2. Various possibilities: Types of Isomers, Degrees of Unsaturation,</td>
<td></td>
<td>X</td>
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<tr>
<td>common nomenclature, polarity, logic arguments of organic chemistry</td>
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<tr>
<td>3. Cyclohexane Conformations, 2 substituents, Newman Projections</td>
<td></td>
<td>X</td>
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<tr>
<td>5. Stereochemical Analysis</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>6. 3D Structure, Hybridization, Angles, Shapes</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>7. Forces of Interaction and Physical Properties,</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Inductive and Resonance Effects</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8. Acid / Base Chemistry, Explanation, Curved Arrows, Formal Charge</td>
<td></td>
<td>X</td>
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<tr>
<td>9. S_N/E Mechanisms, with all of the details</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>10. Various Reactions, predict the products (20 reactions)</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>11. Fill in all mechanistic details, curved arrows, lone pairs, formal</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>charge, 3 examples in acid or base</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12. SN/E Chemistry, Carbocations</td>
<td></td>
<td>X</td>
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<tr>
<td>13. Free Radical Chemistry</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
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</table>

This is a long exam. It has been designed so that no one question will make or break you. The best strategy is to work steadily, starting with those problems you understand best. Make sure you show all of your work. Draw in any lone pairs of electrons, formal charge and curved arrows to show electron movement where appropriate. Do your best to show me what you know in the time available.
1. Provide an acceptable name for the following molecule. (X pts)

2. Match the arrows with the terms. Some arrows may be associated with more than one term. (X pts)

   1. vinyl
   2. allyl
   3. propargyl
   4. phenyl
   5. benzyl
   6. primary amine
   7. sec-butyl
   8. t-butyl
   9. neopentyl
   10. quartemary
   11. isopropyl
   12. isobutyl
   13. methyl
   14. methylene
   15. methine
   16. primary
   17. secondary
   18. tertiary
   19. quartemary ammonium ion
   20. tertiary amine
   21. secondary amine
3. Draw all possible chair conformations of trans-1-ethynyl-2-phenylcyclohexane. Draw C1 as the left-most carbon and number towards the front. Show all axial and equatorial groups. Which conformation is more stable? Draw it first. Provide a reason for your answer. Draw a Newman projections of the more stable conformation using the C₂→C₁ and C₄→C₅ bonds to sight along. Point out any gauche interactions shown in your Newman projection. If the axial energy of a ethynyl group is 0.5 kcal/mole and 2.9 kcal for a phenyl group and a ethynyl/phenyl gauche interaction is 1.0 kcal/mole, what is the difference in energy between the chair conformations? What is the ratio of the more stable conformation to the less stable conformation? Sketch an energy diagram that shows how the energy changes with the conformational changes. (X pts)

\[
\begin{aligned}
\Delta G &= -2.3RT \\
K &= 10 \\
R &= 2 \text{ cal/mol-K} \\
T &= 300 \text{ K}
\end{aligned}
\]

(15 pts)

a. Newman projection (C₂→C₁ and C₄→C₅) – most stable, point out any gauche interactions with the substituent(s)

b. Energy diagram (lower to higher) and relative percents (K_{eq} = ?) (5 pts)

c. Calculate an approximate ΔH difference between the two conformations. Use that value to estimate a K_{eq}. (Assume R = 2 cal/mol-K and T = 300 K.) Use energy values provided in the box. Show your work. (5 pts)

ΔH ≈

K_{eq} ≈

One axial methyl group = +1.7 kcal/mole,
Two axial methyl groups, on the same side (cis) = +5.5 kcal/mole,
Three axial methyl groups, on the same side = +12.9 kcal/mole and
1,2 gauche methyl groups = 0.8 kcal/mole.
4. Use a Newman projection of the C1→C2 bond of 2-methyl-1-phenylbutane to show the most stable conformation first. Rotate through all of the eclipsed and staggered conformations. Using the energy values provided in the table below, calculate the relative energies of the different conformations. Plot the changes in energy in the graph diagram provided. Hint: Draw a 2D structure first and “bold” the bond viewed in your Newman projection, then decide your line of sight. (X pts)

2D structure

Approximate Eclipsing Energy Values (kcal/mole)
Some were estimated by me.

<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>Me</th>
<th>Et</th>
<th>i-Pr</th>
<th>t-Bu</th>
<th>Ph</th>
<th>Br</th>
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<td>1.4</td>
<td>1.5</td>
<td>1.6</td>
<td>3.0</td>
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<td>23.0</td>
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<tr>
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<td>3.8</td>
<td>8.1</td>
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<tr>
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<td>3.6</td>
<td>9.1</td>
<td>4.2</td>
<td>3.0</td>
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</tbody>
</table>

\[ \Delta G = \Delta H - T \Delta S \]

\[ K_{eq} = 10^{-\frac{\Delta H}{2.3RT}} \]

Approximate Gauche Energy Values (kcal/mole)
Some were estimated by me.

<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>Me</th>
<th>Et</th>
<th>i-Pr</th>
<th>t-Bu</th>
<th>Ph</th>
<th>Br</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0</td>
<td>0</td>
<td>0.1</td>
<td>0.2</td>
<td>0.5</td>
<td>0.2</td>
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<tr>
<td>Me</td>
<td>0</td>
<td>0.8</td>
<td>0.9</td>
<td>1.1</td>
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<tr>
<td>Et</td>
<td>0.1</td>
<td>0.9</td>
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<tr>
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<tr>
<td>Ph</td>
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<td>3.9</td>
<td>2.3</td>
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<tr>
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<td>1.0</td>
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<td>1.6</td>
<td>3.3</td>
<td>1.9</td>
<td>1.1</td>
</tr>
</tbody>
</table>

\[ \Delta H^o = \Delta H^o = \Delta H^o = \Delta H^o = \Delta H^o = \Delta H^o = \]

(4 pts)

K_calculation (4 pts)
5. For the following set of Fischer projections answer each of the questions below by circling the appropriate letter(s) or letter combination(s). Hint: Redraw the Fischer projections with the longest carbon chain in the vertical direction and having similar atoms in the top and bottom portion. Classify all chiral centers in the first structure as R or S absolute configuration. (X pts)

a. Which are optically active? A B C D E
b. Which are meso? A B C D E
c. Which is not an isomer with the others? A B C D E
d. Which pairs are enantiomers? AB AC AD AE BC BD BE CD CE DE
e. Which pairs are identical? AB AC AD AE BC BD BE CD CE DE
f. Which pairs are diastereomers? AB AC AD AE BC BD BE CD CE DE
g. Which pairs, when mixed in equal amounts will not rotate plane polarized light? AB AC AD AE BC BD BE CD CE DE
h. Draw any stereoisomers, which are not shown above, as Fischer projections. If there are none, indicate this.

i. In the most recent Organic Letters, 2018, 20, 28-31, three new sulfur compounds were isolated from welsh onion plant grown in Kyoto, Japan (only Kujounin A₁ is shown). Circle all of the chiral centers. How many stereoisomers are possible? Show work.

Kujounin A₁ has anti-cancer activity.
6. Draw additional 2D resonance structures of the given structure as indicated. Which structure(s) is (are) best and why? Draw a 3D structure for the best resonance structure. Show bonds in front of the page as wedges, bonds in back of the page as dashed lines and bonds in the page as simple lines. Show orbitals for pi bonds and lone pairs along with their electrons. Be able to identify the hybridization, bond angles and descriptive shape for all non-hydrogen atoms. (X pts)

![Resonance Structures](resonance_structures.png)
7. a. The structures of vitamin A and vitamin C are shown below. If they are taken in large daily amounts one is toxic and one is not. Explain why this observation is reasonable? (X pts)

[Diagram of vitamin A and vitamin C structures]

b. The melting points and boiling points for the following two compounds are: -57°C, 101°C, 106°C and 126°C. Match those temperatures with the structures below and provide a possible explanation for the differences. (X pts)

[Structures of two compounds with melting points and boiling points]

Tbp =  
Tmp = 

Tbp =  
Tmp = 

c. Explain what the following dipole moments suggest about inductive effects and resonance effects in organic and biochemistry. You may need to draw additional structures to help your explanation. (X pts)

[Structures with dipole moments]

\[ \mu = 2.68 \]  \[ \mu = 2.91 \text{ D} \]  \[ \mu = 2.02 \]  \[ \mu = 0.95 \]  \[ \mu = 3.71 \]  \[ \mu = 4.56 \]
8. Using arrow-pushing mechanisms, write the expected products from the following reactions and indicate whether the equilibrium lies to the “right” or to the “left”. Also, very briefly explain your reasoning. (X pts)

a. 
\[ \text{H}_2\text{C}^\Theta \text{C}^\Theta \text{O}^\Theta \text{H} + \text{H}_2\text{C}^\Theta \text{C}^\Theta \text{O}^\Theta \text{F}^\Theta \rightarrow \text{H}_2\text{C}^\Theta \text{C}^\Theta \text{O}^\Theta \text{H} \text{H} \] 

b. 
\[ \text{H}_2\text{C} \text{C} \text{H} \text{H} + \text{H}_2\text{C} \text{C} \text{H} \text{H} \rightarrow \text{H}_2\text{C} \text{C} \text{H} \text{H} \text{H} \text{H} \]

The two acids have Ka's of $10^{-50}$ and $10^{-42}$. Calculate an equilibrium constant for this reaction.

c. 
\[ \text{H}_2\text{C} \text{C} \text{Cl} \text{H} + \text{H}_2\text{C} \text{C} \text{F} \text{H} \rightarrow \text{H}_2\text{C} \text{C} \text{Cl} \text{H} \text{H} \]

d. 
\[ \text{H}_2\text{C} \text{C} \text{N}^\Theta \text{H} + \text{N} \text{C} \text{CH}_3 \rightarrow \text{H}_2\text{C} \text{C} \text{N}^\Theta \text{H} \text{H} \]

e. 
\[ \text{H}_2\text{C} \text{C} \text{O} \text{H} \text{H} \text{H} + \text{H}_2\text{C} \text{C} \text{CH}_3 \rightarrow \text{H}_2\text{C} \text{C} \text{O} \text{H} \text{H} \text{H} \text{H} \]

f. 
\[ \text{H}_2\text{C} \text{C} \text{N}^\Theta \text{H} + \text{N} \text{C} \text{CH}_3 \rightarrow \text{H}_2\text{C} \text{C} \text{N}^\Theta \text{H} \text{H} \]
9. Use 4S-bromo-5R-deuteriooctane to provide a simple, arrow-pushing mechanism for each of the following reaction conditions (show curved arrows, lone pairs & formal charge). Fill in the necessary details to clearly indicate any stereochemical features and/or conformational requirements. If reactants are not drawn in the proper orientation to show how the reaction must proceed, then redraw them in a more informative way that shows this. Do not consider carbocation rearrangement possibilities. (40 pts)

a. Draw a 2D structure and then a 3D structure of the reacting molecule. A 3D structure will be provided for the cost of the points of this part. (3 pts)

2D structure

3D structure of (4S,5R)-5-deuterio-4-bromooctane

b. Show a mechanism for each Cβ position and simply draw all other possible E reaction products (what kind?). Indicate if E, Z or neither. You can abbreviate common branch names if they are not part of your mechanism. There may or may not be fewer products than there are numbers. (10 pts)

Mechanism

E/Z configuration

Other possible E products

Mechanism

E/Z configuration

c. Show the SN reaction (what kind?), indicate the absolute configuration(s) of the Cα center in the product. (6 pts)

Mechanism

Cα configuration
d. Show all steps of the $S_N$ reaction (what kind?). You can use one intermediate to show all possible $S_N$ possibilities. Indicate the absolute configuration(s) of the $C_\alpha$ center in the product. You can abbreviate common branch names if they are not part of your mechanism (9 pts)

\[ \text{mechanism} \]

\[ C_\alpha \text{ configuration(s)} \]


e. Show a mechanism for two E products and simply draw all other possible E reaction products (you can use the same intermediate for your two mechanisms). Indicate if E, Z or neither. There may or may not be fewer products than numbers. (12 pts)

\[ \text{mechanism} \]

\[ E \text{ or } Z \]

other possible E products
10. Indicate the major product in the following reactions. Indicate stereochemistry if part of the reaction. Do NOT show mechanisms. (WK = workup = neutralize conditions) (X pts)

a.

\[
\begin{align*}
\text{Br}_2 \quad \text{hv} & \rightarrow \text{Br} \\
\text{1. Mg} & \rightarrow \text{CO}_2 \\
\text{2. CO}_2H & \rightarrow \text{workup} \\
\text{3. workup} & \rightarrow \text{PhBr}_3 \\
\text{NaCN} & \rightarrow \text{1. LiAlH}_4 \\
\text{2. workup} & \rightarrow \text{NH}_2
\end{align*}
\]

b.

\[
\begin{align*}
\text{Br} & \rightarrow \text{1. Mg} \\
\text{2. } & \rightarrow \text{OH} \\
\text{3. workup} & \rightarrow \text{CrO}_3 \quad \text{pyridine} \\
\text{O} & \rightarrow \text{1. } \text{NaOH} \\
\text{H} & \rightarrow \text{2. } \text{Br} \\
\text{Br} & \rightarrow \text{1. } \text{LDA} \\
\text{2. } & \rightarrow \text{CH}_3\text{MgBr} \\
\text{OH} & \rightarrow \text{1. workup} \\
\text{Br} & \rightarrow \text{1. workup} \\
\text{OH} & \rightarrow \text{2. NaBH}_4 \\
\end{align*}
\]

c.

\[
\begin{align*}
\text{HBr, } \text{hv} & \rightarrow \text{ROOR (cat.)} \\
\text{Br} & \rightarrow \text{1. Mg} \\
\text{2. } & \rightarrow \text{OH} \\
\text{3. workup} & \rightarrow \text{1. } \text{TsCl, py.} \\
\text{NaBr} & \rightarrow \text{1. workup} \\
\text{Br} & \rightarrow \text{1. workup} \\
\end{align*}
\]

d.

\[
\begin{align*}
\text{OH} & \rightarrow \text{1. NaOH} \\
\text{CrO}_3 & \rightarrow \text{H}_2\text{O} \\
\text{O} & \rightarrow \text{1. workup} \\
\text{Br} & \rightarrow \text{1. LDA} \\
\text{2. } & \rightarrow \text{Br} \\
\text{HBr} & \rightarrow \text{1. workup} \\
\text{Br} & \rightarrow \text{1. workup} \\
\end{align*}
\]

e.

\[
\begin{align*}
\text{Br} & \rightarrow \text{1. Mg} \\
\text{2. } & \rightarrow \text{OH} \\
\text{3. workup} & \rightarrow \text{1. } \text{TsCl, py.} \\
\text{NaBr} & \rightarrow \text{1. workup} \\
\text{Br} & \rightarrow \text{1. workup} \\
\end{align*}
\]

f.

\[
\begin{align*}
\text{HBr, } \text{hv} & \rightarrow \text{ROOR (cat.)} \\
\text{Br} & \rightarrow \text{1. Mg} \\
\text{2. } & \rightarrow \text{OH} \\
\text{3. workup} & \rightarrow \text{1. TscI, py.} \\
\text{NaBr} & \rightarrow \text{1. workup} \\
\text{Br} & \rightarrow \text{1. workup} \\
\text{OH} & \rightarrow \text{1. workup} \\
\text{H}_2\text{SO}_4 & \rightarrow \text{5}
\end{align*}
\]

g.

\[
\begin{align*}
\text{Br} & \rightarrow \text{1. Mg} \\
\text{2. } & \rightarrow \text{OH} \\
\text{3. workup} & \rightarrow \text{1. } \text{NaSH} \\
\text{HBr, } \text{hv} & \rightarrow \text{ROOR (cat.)} \\
\text{Br} & \rightarrow \text{1. NaSH} \\
\text{2. } & \rightarrow \text{Br} \\
\text{NaOH} & \rightarrow \text{1. workup} \\
\text{Br} & \rightarrow \text{1. workup} \\
\end{align*}
\]

h.

\[
\begin{align*}
\text{Br} & \rightarrow \text{1. Mg} \\
\text{2. } & \rightarrow \text{OH} \\
\text{3. workup} & \rightarrow \text{1. } \text{NaN}_2 \\
\text{Br} & \rightarrow \text{1. workup} \\
\text{Br} & \rightarrow \text{1. workup} \\
\text{Br} & \rightarrow \text{1. workup} \\
\text{Br} & \rightarrow \text{1. workup} \\
\text{Br} & \rightarrow \text{1. workup} \\
\end{align*}
\]

i.

\[
\begin{align*}
\text{Br}_2 & \rightarrow \text{hv} \\
\text{Br} & \rightarrow \text{1. workup} \\
\text{Br} & \rightarrow \text{2 eq. Na NR}_2 \\
\text{2 eq. Br}_2 & \rightarrow \text{hv} \\
\text{Br} & \rightarrow \text{1. 3 eq. Na NR}_2 \\
\text{Br} & \rightarrow \text{Na} \\
\text{Br} & \rightarrow \text{1 eq. Na NR}_2 \\
\text{O} & \rightarrow \text{H} \\
\text{H} & \rightarrow \text{H} \\
\end{align*}
\]
11. Propose syntheses for any of the following molecules from the given starting structures.

Allowed carbon structures for the following target molecules (TM).

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<tr>
<th></th>
<th>CH₄</th>
<th></th>
<th></th>
<th>Br</th>
<th>NaCN</th>
<th>CO₂</th>
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<td>O</td>
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<td>O</td>
<td>O</td>
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<tr>
<td>carboxylic acids</td>
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<td>O</td>
<td>R₁</td>
<td>C</td>
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<td>esters</td>
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<td>Cl</td>
<td>R₁</td>
<td>C</td>
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<tr>
<td>1°,2°,3° amides</td>
<td>N</td>
<td>R₁</td>
<td></td>
<td>N</td>
<td>R₂</td>
<td></td>
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<td>nitriles</td>
<td>H₃C = C ≡ N</td>
<td>Ph</td>
<td>H₃C = C ≡ N</td>
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R = H or C
1. Make carboxylic acids (2 ways for us)
   - Jones oxidation of primary alcohols
   - Grignard reactions with carbon dioxide

2. Make anhydrides (1 way for us)

3. Make esters (many ways for us)

Carbocations are intermediates, so have to be careful of rearrangements.

Ester enolate chemistry

LDA = lithium diisopropyl amide

Sterically bulky, very strong base
4. Make thioesters (1 way for us)

5. Make primary amides (2 ways for us)

6. Make secondary amides (1 way for us)

7. Make tertiary amides (1 way for us)

7. Make nitriles (2 ways for us)
8. Make aldehydes (1 way for us)
   Jones oxidation of primary alcohols

   \[ \text{RCH}_2\text{OH} \rightarrow \text{RCO} \]

9. Make ketones (many ways for us)
   Jones oxidation of primary alcohols

   \[ \text{RCHO} \rightarrow \text{RCO}_\text{R}_2 \]

10. Make alcohols (many ways for us)
    Sn2, Me, 1°, 2°
1. 2 eqs. Mg
2. 
3. workup
3° alcohols

H₂C─OH

throw away

R₁

Br

R₂

R₁

O

O─CH₃

R₂

11. Make thiols (1 way for us)

R

Br

NaSH

(ionic)

S₂N₂

thiols

Me, 1°, 2°
bromoalkanes

R₁

O

R₂

12. Make amines (3 ways for us)

R₁

Br

NaN₃

(ionic)

S₂N₂

azides

Me, 1°, 2°
bromoalkanes

R₁

Br

NaCN

(ionic)

S₂N₂
	nitriles

Me, 1°, 2°
bromoalkanes

R₁

NH₂

1° amides

R₂

pH = 5

(-H₂O)

aldehydes and ketones

R₂

N

H

1° amines

R₂

pH = 5

(-H₂O)

aldehydes and ketones

R₁

N

R₂

imines

1. NaBH₄
2. workup

H

2° amines

R₃

N

R₂

iminium ions

1. NaBH₄
2. workup

H

3° amines

R₂

OH

13. Make ethers (2 ways for us)

R₁

NaH

(ionic)

alkoxides

R₂

S₂N₂

ethers

Me, 1°, 2°
bromoalkanes

R₁

OH

alcohols

R₁

Br

bromoalkanes

R₂

S₂N₁

2°, 3°

ethers

R₂

OH

alcohols
14. Make thioethers / sulfides (1 way for us)

\[ R_1\text{SH} \xrightarrow{\text{NaOH} \text{ (ionic)}} R_1S \xrightarrow{\text{S}_{\text{N}2}} R_1S\text{R}_2 \]

bromoalkanes

15. Make bromohydrocarbons (many ways for us)

\[ R_1\text{OH} \xrightarrow{\text{PBr}_3} R_1\text{Br} \xrightarrow{\text{SN}_{2, 1^o, 2^o}, \text{SN}_{1, 2^o, 3^o}} R_1\text{OH} \]

bromoalkanes

\[ R_1\text{H} \xrightarrow{\text{Br}_2, \text{hv}} R_1\text{Br} \xrightarrow{\text{SN}_{1, 2^o, 3^o}} R_1\text{H} \]

bromoalkanes

16. Make alkenes (2 ways for us)

\[ R_1\text{Br} \xrightarrow{\text{E}2} \text{alkenes (tetra > tri > trans-di > gem-di = cis-di > mono > unsutstituted ethene)} \]

\[ R_1\text{OH} \xrightarrow{\text{HBr, } \text{hv, ROOR (cat.)}} \text{alkenes (tetra > tri > trans-di > gem-di = cis-di > mono > unsutstituted ethene)} \]

use this approach when rearrangement is a problem
17. Make alkynes (many ways for us)

$$\text{Br}_2 \xrightarrow{\text{hv}} \text{Br}$$

2 eqs. Br\(_2\) (ionic)

$$\text{NaNR}_2$$

3 eqs (ionic)

2. workup (H\(_2\)O\(^+\))

3. workup (H\(_2\)O\(^+\))

18. Make epoxides (2 ways for us)

$$\text{Ph} - \text{S} - \text{Ph} \xrightarrow{\text{Br}} \text{Ph} - \text{S} - \text{Ph}$$

1. n-B uLi

2. O

18. Make alkanes (2 ways for us)

Cuprate coupling of two different RBr compounds, one as the cuprate nucleophile and one as the RBr electrophile

$$\text{H}_3\text{C} - \text{Br}$$

NaOH (ionic)

$$\text{H}_3\text{C} - \text{OH}$$

used above

$$\text{Br}$$

NaOH (ionic)

$$\text{Br}$$

used above
19. Make aromatic compounds using Grignard reaction and bromobenzene (several possibilities)

Grignard reagents react as nucleophiles with various electrophiles. Usually there needs to be a final workup step (neutralization)

- Primary (1°) alcohols
- Secondary (2°) alcohols
- Tertiary (3°) alcohols
- Carboxylic acids
12. Provide all missing arrow-pushing mechanistic details (curved arrows, lone pairs and formal charge) to explain the following transformations, one in acid and one in base. Assume all nonhydrogen atoms have full octets unless a positive charge is written by the atom. (Xpts)
a.

[Diagram of chemical reactions showing the transformation of an ester into alcohol and the reverse reaction into a carboxylic acid.]
b.

\[
\begin{align*}
\text{nitrile} & \quad \leftrightarrow & \quad \text{water} \\
\end{align*}
\]

\[
\begin{align*}
\text{1° amide} & \\
\end{align*}
\]

c.

\[
\begin{align*}
\text{ester} & \quad \leftrightarrow & \quad \text{carboxylic acid} \\
\end{align*}
\]

\[
\begin{align*}
\text{2. workup} & \\
\end{align*}
\]

\[
\begin{align*}
\text{carboxylic acid} & \quad \leftrightarrow & \quad \text{carboxylate} \\
\end{align*}
\]

\[
\begin{align*}
\text{alcohol} & \\
\end{align*}
\]
d.

nitrile

\[
\begin{align*}
\text{H} & \text{C} \equiv \text{N} \\
\text{H} & \text{H} \\
\text{H} & \text{H}
\end{align*}
\]

amide

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

e.

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

di-alcohol

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

carbonyl compounds (C=O)
aldehyde or ketone

13. Provide a complete arrow-pushing mechanism for the following transformations. (X pts)

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

Turn it around and do it the opposite direction.

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

ketal

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

hemi-ketal

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

acid catalyst

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

di-alcohol

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

Br
14. Provide all missing arrow-pushing mechanistic details (curved arrows, lone pairs and formal charge) to explain the following transformation. Assume all nonhydrogen atoms have full octets unless a positive charge is written by a carbon atom. (20 pts)

a. 

15. Provide a complete arrow-pushing mechanism for the following transformations (lone pairs, formal charge and curved arrows). (15 pts)
16. a. Show all possible products when 2-methylpentane is brominated with Br₂/hv? Indicate the approximate relative amounts of each product formed if the relative rates of reaction of a bromine atom with an sp³ C-H bond are: primary = 1, secondary = 80 and tertiary = 1600. (X pts)

b. Provide a complete arrow pushing mechanism to explain formation of the major product from the above reaction (show proper curved arrows, lone pairs as two dots and single electrons as one dot). Clearly label each distinct part of the reaction mechanism. Calculate an overall ΔH for each step of your mechanism using the given bond energies. To make a bond is positive energy and to make a bond is negative bond energy. (X pts)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br—Br</td>
<td>46</td>
</tr>
<tr>
<td>H—Br</td>
<td>87</td>
</tr>
<tr>
<td>Me C-H</td>
<td>105</td>
</tr>
<tr>
<td>1° C-H</td>
<td>98</td>
</tr>
<tr>
<td>2° C-H</td>
<td>95</td>
</tr>
<tr>
<td>3° C-H</td>
<td>92</td>
</tr>
<tr>
<td>Me C-Br</td>
<td>70</td>
</tr>
<tr>
<td>1° C-Br</td>
<td>68</td>
</tr>
<tr>
<td>2° C-Br</td>
<td>68</td>
</tr>
<tr>
<td>3° C-Br</td>
<td>67</td>
</tr>
</tbody>
</table>

17. Show all possible products when the following compounds react. Identify what kinds of isomers are present.
17. (possible answer) a. Show all possible products when 2-methylpentane is brominated with Br₂/hv? Indicate the approximate relative amounts of each product formed if the relative rates of reaction of a bromine atom with an sp³ C-H bond are: primary = 1, secondary = 80 and tertiary = 1600. (X pts)

RA = \( (3) \times (1) = 3 \)  
RA = \( (3) \times (1) = 3 \)  
RA = \( (1) \times (1600) = 1600 \)

b. Provide a complete arrow pushing mechanism to explain formation of the major product from the above reaction (show proper curved arrows, lone pairs as two dots and single electrons as one dot). Clearly label each distinct part of the reaction mechanism. Calculate an overall \( \Delta H \) for each step of your mechanism using the given bond energies. To make a bond is positive energy and to make a bond is negative bond energy. (X pts)

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<td>1º C-H</td>
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<td>95</td>
</tr>
<tr>
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</tr>
<tr>
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<td>3º C-Br</td>
<td>67</td>
</tr>
</tbody>
</table>

1. initiation

2a. propagation

2b. propagation

3. termination = combination of 2 radicals to shut down chain reaction
18. Draw a 2D structure that includes the listed functional groups. Write the functional group name by its appearance in your 2D structure. Calculate the degree of unsaturation for the given formula. (25 pts)

alkyne, alkene, 1° amine, ester, alcohol ether, thiol, ketone, acid, 2° amide, nitrile

degree of unsaturation calculation

C\textsubscript{17}H\textsubscript{21}FClBrIN\textsubscript{3}O\textsubscript{8}S

19. a. Haldol is a potent orally active central nervous system tranquilizer used in the treatment of psychoses. Peak plasma levels, when taken orally, are 2-6 hours (in the aqueous blood). Cell membranes, on the other hand, are composed largely of alkane-like fatty acid chains. A decanoate ester prodrug was prepared to increase Haldol’s lifetime in the body. When injected intramuscularly its anti-psychotic activity lasted about 1 month. Provide an explanation for its longer lifetime. (12 pts)

b. Provide an explanation for why NaCl is soluble in water, but not soluble in hexane. Use structures. (8 pts)
20. Use the formula C₅H₁₀FNO to draw examples for each type of isomerism indicated. This will require that you draw at least two structures to show these differences. What is the degree of unsaturation? (25 pts)

\[
C₅H₁₀FNO \quad 2(5) + 2 + 1 = 13 = \text{saturated number} \\
-11 = \text{actual number} \\
\text{unsaturation} = \frac{2}{2} = 1^0 \text{ unsaturation}
\]

![Skeletal Isomers](image1)

![Positional Isomers](image2)

![Functional Group Isomers](image3)

![Conformational Isomers](image4)

![Enantiomers](image5)

![Diastereomers](image6)

21. Indicate all formal charges present in the following structures. Assume all electrons are shown as lines or dots. If other reasonable resonance structures are possible, draw the best other resonance structure using the proper arrow conventions. Indicate which resonance structure is better or if they are equivalent. (18 pts)

![First Structure](image7)

The second resonance structure is better because it has full octets and it quenches formal charge.

![Second Structure](image8)

The second resonance structure is better because it moves the negative charge from nitrogen to the more electronegative oxygen.

![Third Structure](image9)

The second resonance structure is better because it has full octets and it quenches formal charge.
22. Only the reactant acid and base are drawn below. Decide which is which and draw a mechanism to show formation of the conjugate base and acid. The two acids have pK_a's of 15 and 12 (K_a values are $10^{-15}$ and $10^{-12}$). Match the K_a values with the proper acid, write a K_equilibrium expression and calculate a quantitative K_equilibrium value for the reaction. Show your work. Provide an explanation for your value of K_equilibrium. (15 pts)

\[
K_a = 10^{-15} \\
K_a = 10^{-12}
\]

\[
K_{equilibrium} = \frac{K_a (CH_3OH)}{K_a (CH_3OOH)} = \frac{10^{-15}}{10^{-12}} = 10^{-3}
\]

The equilibrium is favored to the left because of the inductive withdrawing effect of the second oxygen atom, which helps to stabilize the negative charge. There is no resonance effect here.

b. Use the above K_a values to estimate a K_a for the following acid. Very briefly explain your reasoning. (5 pts)

\[
K_a = 10^{-15} \\
K_a \approx 10^{-13} \text{ or } 10^{-14}. \\
K_a = 10^{-12}
\]

We can estimate a K_a value between the two given acids. N is inductively electron withdrawing relative to carbon, but not as electronegative as oxygen, so the inductive withdrawing effect of N helps stabilize the anion more than carbon but not as much as oxygen.
23. Using arrow-pushing mechanisms, write the expected products from the following reactions and indicate whether the equilibrium lies to the “right” or to the “left”. Also, very briefly explain your reasoning. (35 pts)

a. The left side is favored because the anion charge is more delocalized on the larger phosphorous than nitrogen (same Zeff).

b. The right side is favored because the cation charge is more delocalized on 3 nitrogen atoms than 2 nitrogen atoms.

c. The left side is favored because the anion charge is more delocalized on two oxygen atoms than one oxygen.

d. The right side is favored because the anion charge is stabilized by the inductive withdrawing effect of the 3 fluorine atoms.

e. The left side is favored because the cation charge is more stable with resonance donation from a nitrogen than from an oxygen.

f. The left side is favored because the anion is more stabilized in a more electronegative sp orbital (50% s) than in an sp² orbital (33% s).

g. The right side is favored because the anion is more stabilized without the inductive donating effect of 3 methyl groups.