1. (25 pts) Quick answers: True/False questions @ 5 pts each, 3 for the T/F answer, 2 for a counterexample (if the statement is False) or other scratch work for your analysis.

   a. A compound in which a carbon has four different substituents must be chiral
      T F

   b. If a substrate can do an E1 it can always do an S_N1 reaction
      T F

   c. All stable isomers of C_3H_6O must be polar
      T F

   d. Removing electrons always weakens a molecule’s bonds
      T F

   e. Aromatic species are always highly volatile
      T F
2. (25 pts) Consider the six compounds shown below.

Among species A-F, find...

(a) (4 pts) An acyclic tetraene _____.

(b) (4 pts) Two conformations of the same compound: _____ and _____.

(c) (4 pts) The one compound of a different molecular formula _____.

(d) (4 pts) Two aromatic compounds that are structural isomers? _____ and _____

(e) (4 pts) The compound with the highest $\Delta H_f$ value _____.

(f) (5 pts) A compound that can undergo Diels-Alder addition with 1,1,1,4,4,4-hexafluoro-2-butyne to form a product with a bicyclo[2.2.2]octa-2,5-diene framework ______.
3. (25 pts) Consider the three brominated benzenes below.

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

Names: __________________  __________________  __________________

a. (3 pts) In the spaces given, name these compounds, using ortho, meta, para terms.

b. (3 pts) All three have similar mass spectra (see next page). The molecular ion portion is blown up above. Write the integer value (no decimal places) of the main (\(= 100\%\)) ion mass “M” for these compounds (Hint: see the attached table of isotopes):

\[
\text{Mass } M = \underline{\quad}\n\]

c. (5 pts) It turns out that the main molecular ion peak(s) actually show up as a triplet with approximately 1:2:1 peak intensities. Assign integer masses to the peaks drawn above (i.e. label them) and explain the 1:2:1 intensity pattern and mass spacing by identifying the ion formulas, including isotopes, that give the three main mass peaks.

d. (5 pts) One mass unit above each of the big peaks, there are little ones, also roughly in 1:2:1 proportions, but only about 6\% as large as the big ones. Explain where these come from (i.e. give formulas including isotopes), and how they confirm that it’s a six-carbon compound we’re analyzing.

e. (3 pts) The mass spectra don’t help a lot to distinguish among our compounds, so we resort to \(^1\text{H} \text{NMR spectroscopy}. \textit{On the next page}, add the second Br and the four H’s to each of the bromobenzene structures at left. Then label the H’s A,B,C, etc. to correspond to the labels in the spectra.

f. (6 pts) For the one dibromobenzene that shows a \(^1\text{H} \text{resonance split into a triplet, show which compound and } ^1\text{H} \text{site it is, what the splitting intensity pattern is, and why (in terms of the number and magnetic character of the splitting nuclei).}
EXAMPLE:
p-bromo-toluene

Add Br & H's to complete

Add Br & H's to complete

Add Br & H's to complete

Add Br & H's to complete
4. (25 pts) The triphenylmethyl radical, discovered by Moses Gomberg at the University of Michigan (groan), was the first free radical ever directly observed. Here’s its synthesis (Ag = silver):

a. (5 pts) Use resonance (just show for one phenyl ring) to explain why this radical is stable enough to be observed (as a yellow color in solution). How many resonance forms contribute in total: __________

b. (5 pts) Though it is all sp² C’s, the triphenylmethyl radical isn’t flat! In fact, as shown by the dark wedges, the rings are twisted about 45° out of the central carbon’s plane like propeller blades. Why? It certainly hinders π delocalization. (hint: geometry)

c. (5 pts) Surprisingly, when triphenylmethyl does dimerize, it forms this dimer which equilibrates with radical on gentle warming. Why doesn’t the more obvious hexaphenylethane form, and why is the dimer bond easy to break.

d. (5 pts) When triphenylmethyl radical reacts with O₂ (air) it connects up “normally” in forming the peroxide. Explain why this process is OK despite what we saw in (c).

e. (5 pts) Write the mechanism for radical reaction with O₂ to form the peroxide.
5. (25 pts; Student-supplied questions) Circle whether the following processes in a halogenation reaction are initiation, propagation, or termination steps (3 pts each):

a. (3 pts)

\[
\begin{array}{ccc}
\text{Initiation} & \text{Propagation} & \text{Termination} \\
\cdot \text{Cl} & \text{Cl} \cdot & \text{Cl}_2
\end{array}
\]

b. (3 pts)

\[
\begin{array}{ccc}
\text{Initiation} & \text{Propagation} & \text{Termination} \\
\text{H}_3\text{C} - \text{C} \cdot \text{Cl} & \text{Cl} - \text{Cl} & \text{H}_3\text{C} - \text{C} \cdot \text{Cl} \cdot \text{Cl}
\end{array}
\]

c. (3 pts)

\[
\begin{array}{ccc}
\text{Initiation} & \text{Propagation} & \text{Termination} \\
\text{Cl} & \text{Cl} & 2 \cdot \text{Cl}
\end{array}
\]

d. (3 pts)

\[
\begin{array}{ccc}
\text{Initiation} & \text{Propagation} & \text{Termination} \\
\text{H}_3\text{C} - \text{C} \cdot \text{H} & \text{Cl} & \text{H}_3\text{C} - \text{C} \cdot \text{H} \cdot \text{Cl}
\end{array}
\]

e. (3 pts)

\[
\begin{array}{ccc}
\text{Initiation} & \text{Propagation} & \text{Termination} \\
\text{H}_3\text{C} - \text{C} \cdot \text{H} & \text{Cl} & \text{H}_3\text{C} - \text{C} \cdot \text{Cl}
\end{array}
\]

f. (10 pts) Hydrogen sulfide (H\textsubscript{2}S) adds to conjugated systems in the presence of peroxides via a free radical process. Write a reasonable mechanism for the following reaction showing the appropriate initiation and propagation steps (hint--think of radical addition of HBr).

\[
\begin{array}{c}
\text{Initiation} \\
\text{ROOR} \Delta \text{ (heat)} \\
\text{H}_2\text{S}
\end{array}
\]
6. (25 pts; student-supplied questions)

a. (3 pts) One of the species in part (b) is missing a charge. Please fix it on the drawing.

b. (18 pts) Circle whether the following species are aromatic, antiaromatic, or nonaromatic.

\[
\begin{array}{cccc}
\text{i} & \text{Cl} & \text{ii} & \text{Cl}^- \\
i. & \text{Aromatic} & \text{Antiaromatic} & \text{Nonaromatic} \\
ii. & \text{Aromatic} & \text{Antiaromatic} & \text{Nonaromatic} \\
iii. & \text{Aromatic} & \text{Antiaromatic} & \text{Nonaromatic} \\
iv. & \text{Aromatic} & \text{Antiaromatic} & \text{Nonaromatic} \\
v. & \text{Aromatic} & \text{Antiaromatic} & \text{Nonaromatic} \\
vi. & \text{Aromatic} & \text{Antiaromatic} & \text{Nonaromatic} \\
\end{array}
\]

c. (4 pts) Styrene, also known as vinylbenzene, is a compound with 8 π electrons, a 4n number. And yet, it’s not antiaromatic; we consider it to be just as aromatic as benzene itself. Explain.

\[
\text{Styrene}
\]
7. (25 pts) Stereochemistry and naming

a. (12 pts) Provide full IUPAC names to represent the following structures. Be sure to pay attention to stereochemistry.

<table>
<thead>
<tr>
<th>Structures</th>
<th>Names</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i)</td>
<td></td>
</tr>
<tr>
<td>(ii)</td>
<td></td>
</tr>
<tr>
<td>(iii)</td>
<td></td>
</tr>
<tr>
<td>(iv)</td>
<td></td>
</tr>
</tbody>
</table>

b. (4 pts) Which of the compounds in (a) is achiral? Please circle your answer

(i)  (ii)  (iii)  (iv)

c. (9 pts) The compound in (i) has three other stereoisomers; draw them below:

<table>
<thead>
<tr>
<th>Cl-Cl</th>
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8. (25 pts) We’ve analyzed substituent effects on benzene reactivity in electrophilic aromatic substitution in terms of resonance structures of the intermediates formed by electrophilic attack. Now let us look at their effects on other aspects of aromatic systems.

a. (6 pts) Trimethylamine (TMA), like ammonia, is a respectable base (many natural amines are called alkaloids because they act as bases--alkali). As shown above, its protonated form has pK_a = 10.8, but replace a methyl (Me) with a phenyl (Ph) group and the basicity drops; protonated dimethylaniline’s pK_a = 5.2, more acidic by >5 pK_a units than H-TMA+. Why this shift in pK_a? (Hint: basicity has to do with N lone pair availability/localization; how freely it can be shared with a proton?).

b. (6 pts) Pyridine, with the N in the ring, is also a base; its protonated form happens to have the same pK_a as protonated dimethylaniline. Noting the different environments for the pyridine and the trimethylamine N’s, please explain their pK_a difference.

c. (7 pts) Now let’s see how putting dimethylamino (Me_2N-) on pyridine to form DMAP affects the pyridine pK_a. DMAP’s Me_2N group doesn’t protonate at all—why? (Hint: If it’s pK_a 5.2 with phenyl, how is its pK_a changed with pyridine in place of phenyl?).

d. (6 pts) Finally, why is the pK_a of DMAP-H+ (protonated on the ring N) so much higher (4 pK_a units) than that for unsubstituted pyridine. (Hint: Look back at your reasoning in (a) and (c) to see how this is a natural result of the parts interacting.)
9. (25 pts) 1,3-Butadiene reacts with HCl to give two products: 3-chloro-1-butene (C) and 1-chloro-2-butene (B). The reaction involves a common carbocation intermediate (A). On the basis of the energy diagram shown below, answer the following questions:

(a) (3 pts) Assign the labels A, B, and C to the structures in the diagram below.

(b) (7 pts) Write the reaction step that forms A from 1,3-butadiene and HCl.

(c) (5 pts) Which product, B or C, is the kinetic product—i.e. will form faster? Explain.

(d) (5 pts) Which product, B or C, is the thermodynamic product—i.e. is more stable? Explain.

(e) (5 pts) Intermediate A is a resonance hybrid. Only one of the resonance forms is shown. Draw the other major resonance form at right.
10. (25 pts) The anisidines encompass the three possible isomers of aminoanisole (benzene with a methoxy and an amino group on it).
   a. (3 pts) Draw and label each of the three possible isomers below.
   b. (12 pts) A synthesis of two of the anisidine isomers is provided below, starting from phenol. Fill in intermediates, names and formulas en route, and identify products.
      ![Synthesis diagram]
   c. (10 pts) Shown below are 5 structural isomers of the anisidines. Match each isomer with its $^1$H NMR spectrum by filling in the letters A-E in the blanks below.
      ![NMR spectra]