Person on your LEFT (or Aisle)

- PRINT YOUR NAME ON EACH PAGE!
- READ THE DIRECTIONS CAREFULLY!
- USE BLANK PAGES AS SCRATCH PAPER
  work on blank pages will not be graded...
- WRITE CLEARLY!
- MOLECULAR MODELS ARE ALLOWED
- DO NOT USE RED INK
- DON'T CHEAT, USE COMMON SENSE!

Person on your RIGHT (or Aisle)

1. nomen /12
2. RED /25
3. rxns /32
4. radical /20
5. NMR /20
6. mxn2 /38
7. spectrum /28

Extra Credit /5
Total (incl Extra) /175+5

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Interaction Energies, kcal/mol

<table>
<thead>
<tr>
<th>Eclipsing</th>
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<tbody>
<tr>
<td>H/H</td>
<td>~1.0</td>
</tr>
<tr>
<td>H/Me</td>
<td>~1.4</td>
</tr>
<tr>
<td>Me/Me</td>
<td>~2.6</td>
</tr>
<tr>
<td>Me/Et</td>
<td>~2.9</td>
</tr>
<tr>
<td>i-Pr/Me</td>
<td>~0.95</td>
</tr>
<tr>
<td>t-Bu/Me</td>
<td>~2.7</td>
</tr>
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Infrared Correlation Chart

- C-H 3000–3100
- O-H 3500–3300
- N-H 3000–3100
- O=C 1700–1735

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NMR Correlation Charts

- OCH3
- CH3-X
- H2C-NR2
- Alkyl
- 3° > 2° > 1°
- Aromatic

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

- H-H ~7
- H-C-H ~10
- C-H ~15

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Aromatic

- H2C-NR2
- Alkyl
- 3° > 2° > 1°
Question 1 (12 pts.) Give the IUPAC name for the following structure.

7-bromo-4-methyl-3-phenyl-(3Z)-octene

7-bromo-4-methyl-3-phenyl-3-octene

7-bromo-4-methyl-3-phenyloct-(3Z)-ene

(Z)-7-bromo-4-methyl-3-phenyloct-3-ene

Question 2 (25 pts.) Add the curved arrows to indicate bond making/breaking for the reactions A and B, indicate the Lewis acids/bases (LA/LB) and if they are also Bronsted acids/bases (BA/BB)

A

B

b) Draw a reaction energy diagram with properly labelled axes for BOTH reactions on the SAME diagram, clearly indicating which is A and which is B, indicate the activation energy for both reactions, AND, the reaction exothermicities or endothermicities as appropriate. Indicate the positions of BOTH transition states (but do not draw them).

c) BRIEFLY explain why one of these reactions is more exothermic or more endothermic than the other one, AND, which reaction would be faster, your explanation should include the term "Hammond postulate"

both are endothermic since both break 2 bonds and make only 1 bond, reaction B starts higher in energy because this alkene is less substituted, reaction B is thus less endothermic, according to the Hammond postulate the less endothermic reaction will have the smaller activation energy and thus be faster
Question 3 (32 pts.) Give the missing major organic products OR reagents/conditions as appropriate for each of the following reactions. Classify each reaction as addition, elimination, substitution or elimination, CLEARLY INDICATE STEREOCHEMISTRY IF APPROPRIATE

a) \[ \text{Br}_2 \xrightarrow{\text{hv}} \] substitution

b) \[ 1. \text{BH}_3\cdot\text{THF} \quad 2. \text{-OH/H}_2\text{O}_2 \quad \text{addition} \]

\[ \text{Ph} \]

\[ \text{Ph} \]

\[ \text{Ph} \]

\[ \text{Ph} \]

\[ \text{or...} \]

\[ \text{addition} \]

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

d) \[ \text{H}_2\text{O} \quad \text{HCl (catalytic)} \quad \text{addition} \]

Extra Credit (5pts) Light is used in photobromination and photochlorination reactions. Light was also mentioned in one of the "Real Life" pages to do which of the following?

- make a polymer
- make a hydrocarbon
- make a benzene ring
- make DNA
Question 4 (20 pts.) Give a curved arrow pushing mechanism for the following reaction. Clearly indicate the initiation and propagation steps (but do not include any termination steps), add H atoms to the line angle structures as necessary and include any important resonance contributors for any intermediates.

\[
\text{Br}_2 + \text{H}_2 \xrightarrow{\text{hv}} 2\text{HBr} \quad \text{initiation step}
\]

\[
\text{Br}^{-} \xrightarrow{\text{Br}} \text{Br}^{-} \xrightarrow{\text{Br}} \text{BrH} + \text{Br}^{-} \quad \text{propagation steps}
\]

Question 5 (20 pts.) Assign signals A, B, C and D in the proton nmr spectrum to the appropriate protons on the phenol structure provided. Using drawings of minor resonance contributors, explain why the 2H signal labelled B has a larger chemical shift than the 2H signal labelled A. Your explanation must include the following terms: "electron density", "local magnetic field", "shielding" and "deshielding".

the minor resonance contributors show that there is a partial negative charge on the carbons that carry H_A, these hydrogens see higher ELECTRON DENSITY which results in MORE SHIELDING which results in a SMALLER LOCAL MAGNETIC FIELD which results in less DESHIELDING and thus a smaller chemical shift.
Question 6 (38 pts) For the provide reaction, give a curved arrow-pushing mechanism, indicate the Lewis acid and base (LA, LB) at each step where appropriate, and whether they are also Bronsted acids and bases (BA, BB), CLEARLY indicate the RATE DETERMINING STEP.

b) How many steps are there in your mechanism? ____________
c) How many transition states are associated with your mechanism? ______ depends upon the mxn

d) Draw a reaction energy diagram for your mechanism, indicate the positions of the reactants, products and any intermediates (don't redraw the structures, you can circle the items on the mechanism and use arrows, or use symbols such as I1 for intermediates 1 etc.). Indicate the ACTIVATION ENERGY FOR EACH STEP, the REACTION EXOTHERMICITY and the RATE DETERMINING STEP.

e) Draw below the TRANSITION STATE for the rate determining step (only)
So, as you may have guessed, I completely messed up this question!
I re-wrote the question several times going back and forth between a hydride shift and an alkyl shift, and I eventually settled on making it an alkyl shift, except that I forgot to go back and put into the starting structure the alkyl groups that are needed to do the shift! THIS is what the problem was supposed to be (with the 2 extra methyl groups in blue):

Without the blue methyl groups, a carbocation rearrangement is not even required with the structures given, but if you did the methyl shift you were not marked incorrect because the problem invited you to do so....

The grader was told to allow multiple correct answers to this question, even some that were not technically correct!
Question 7 (28 pts) Provided are spectra for a compound with molecular formula $\text{C}_{10}\text{H}_{12}\text{O}$

a) Give the degrees of unsaturation $\boxed{5 \text{ degrees}}$

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

c) Draw the structure and clearly indicate which hydrogens correspond to which signals in the proton NMR spectrum (only).

- 3 peaks in this region
- 4 peaks in this region

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<thead>
<tr>
<th>Peak</th>
<th>Assignment</th>
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<tbody>
<tr>
<td>A</td>
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</tr>
<tr>
<td>B</td>
<td>2H triplet</td>
</tr>
<tr>
<td>C</td>
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<td>E</td>
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<tr>
<td>F</td>
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