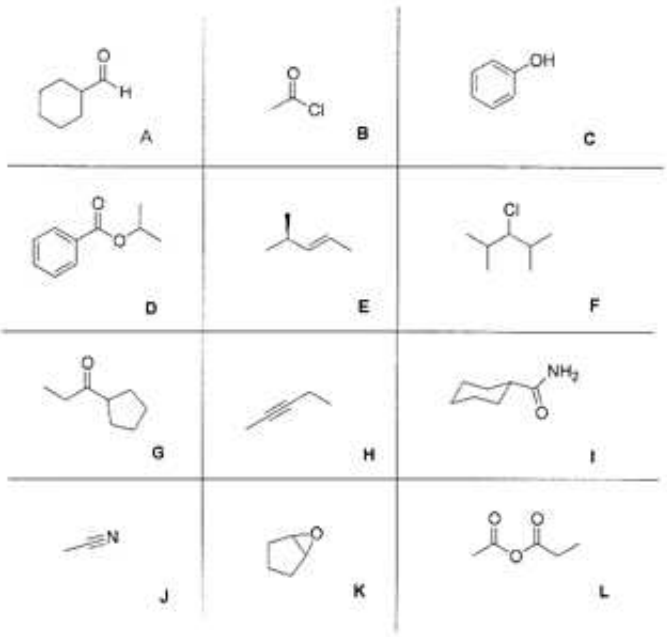
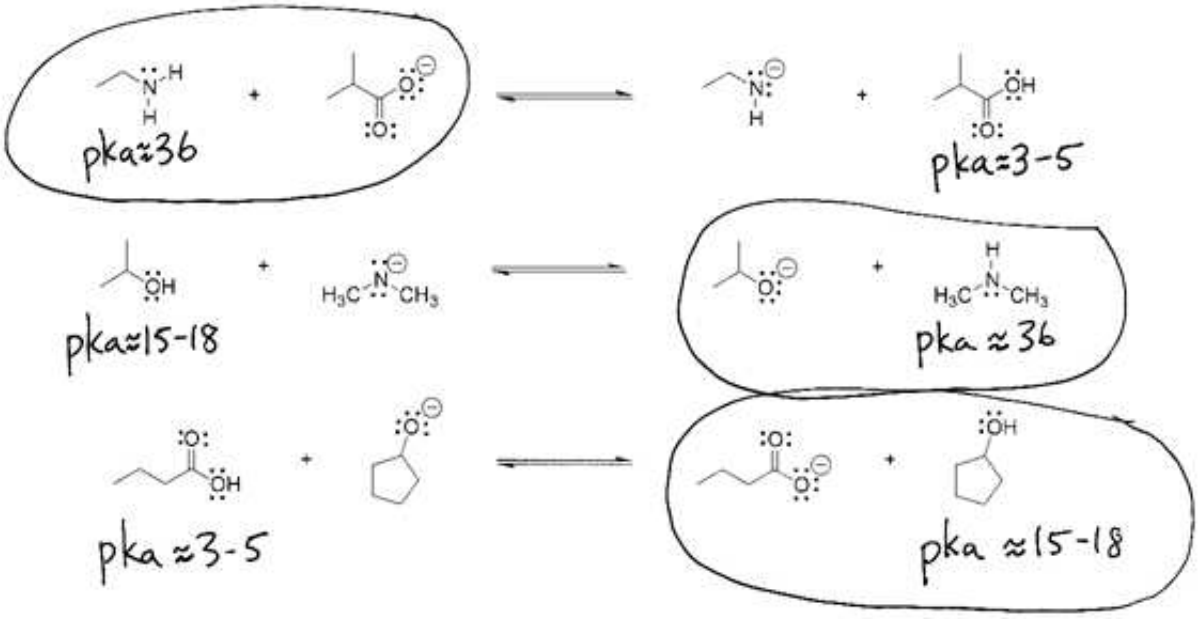
1a) In the column at the left, for each functional group name write the letter of the compound in the grid that contains the functional group (10 pts).

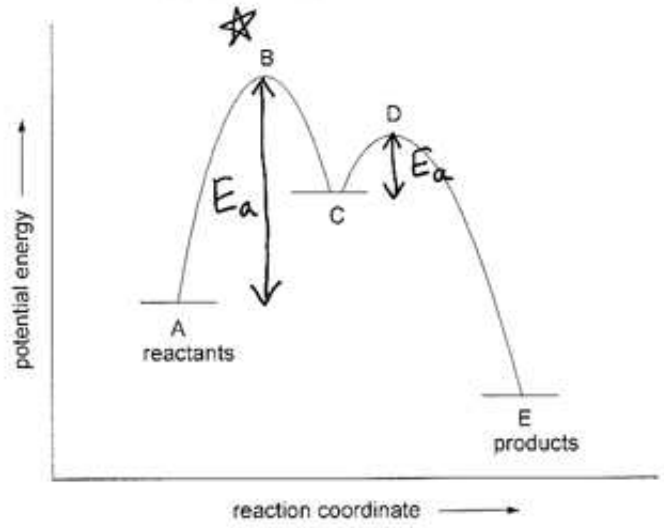
D ester
G ketone
L anhydride
I amide
K epoxide
F alkyl halide
A aldehyde
B acid halide
H alkyne
E alkene



1b) For each of the following acid-base equilibria, circle the side of the reaction that is favored at equilibrium. All lone pairs and formal charges are shown (6 pts).



2. Consider the following diagram of potential energy vs. reaction (8 pts):



2a) Label the activation energies, E_a, for the first and second steps.

2b) What is the sign of ΔH for the overall reaction, + or - ? Circle it: + (−)

2c) How many transition states are in this reaction? B, D 2

2d) How many intermediates are in this reaction? C 1

2e) Circle the step that has the larger rate constant, *k*:

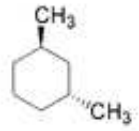
A → C (C → E) (Smaller E_a)

2f) Put a star * on the transition state of the rate-determining step.

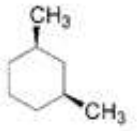
2g) Which of these does the structure of the transition state * most resemble? Circle it.

Reactants **Products** (**An intermediate**)

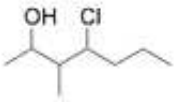
3a) For each of the following pairs of molecules, state whether they are resonance structures, constitutional isomers, conformers, stereoisomers, or identical (6 pts).



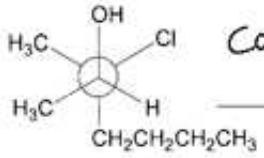
and



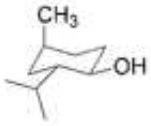
Stereoisomers



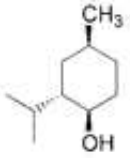
and



Constitutional isomers



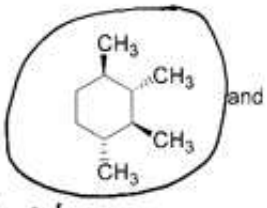
and



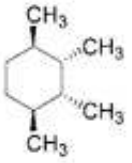
identical

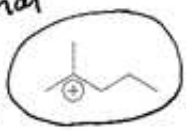
3b) Circle the more stable molecule in each pair (8 pts).

most stable conformer has all groups equatorial



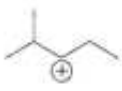
and



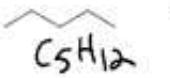


3°

and



2°

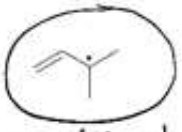


C_5H_{12}

and

C_5H_{12}

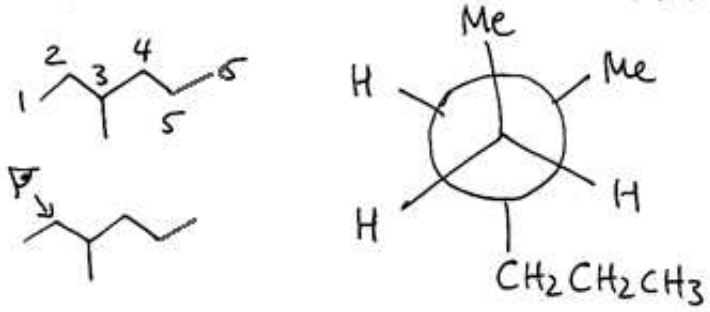
more branched isomer



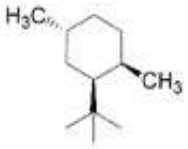
and

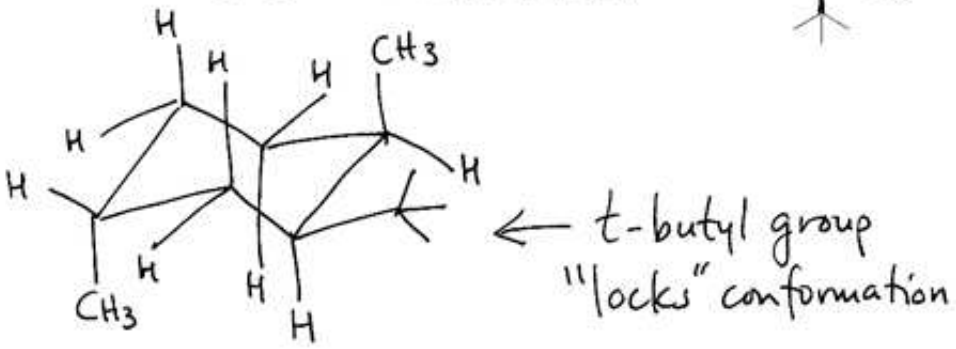
3°, stabilized by resonance

4a) Draw a Newman projection of the most stable conformation of 3-methylhexane looking down the C2-C3 bond. Make C-2 the front carbon (3 pts).

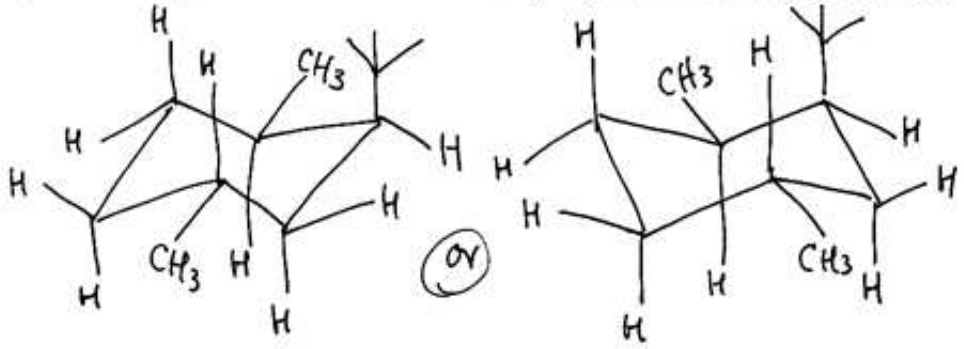


4b) Draw the most stable chair conformation of the molecule shown at right. Draw your chair neatly and following the guidelines in class and text. Draw every hydrogen on the cyclohexane ring. You do not have to draw the hydrogens on the methyl groups (5 pts).

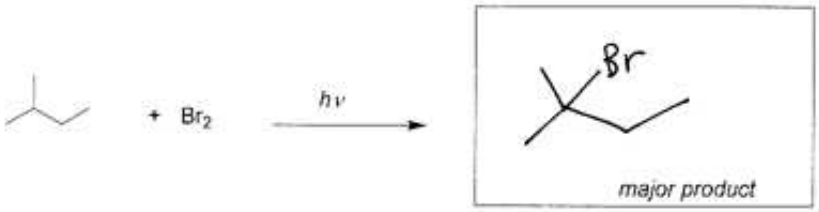




4c) Draw the chair flip of the structure you drew in your answer to 4b. Draw your chair neatly and following the guidelines in class and text. Draw every hydrogen on the cyclohexane ring. You do not have to draw the hydrogens on the methyl groups (5 pts).

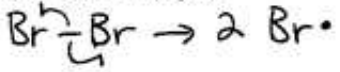


5. Consider the following reaction:



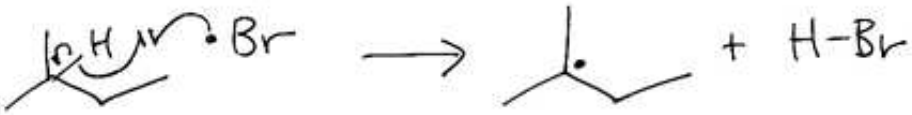
5a) Predict the *major* product of this reaction and draw it in the box above (3 pts).

5b) Is the initiation step for this reaction endothermic or exothermic? Circle it (2 pts):

Endothermic **Exothermic** 

5c) Draw the mechanisms for the two propagation steps for this reaction. Show all bonds, electrons and arrows clearly to receive full credit. Show all reactants and products for each step (10 pts).

First propagation step:



Second propagation step:

5d) Calculate ΔH for the overall reaction in kcal/mole using the following table of bond dissociation energies, all reported in kcal/mol. (5 pts).

✓ H-Br	88
✓ Br-Br	46
CH_3-H	104
1° C-H	98
2° C-H	95
✓ 3° C-H	91
CH_3-Br	70
2° C-Br	68
✓ 3° C-Br	63

bonds broken (+)

3°C-H +91
Br-Br +46
+137

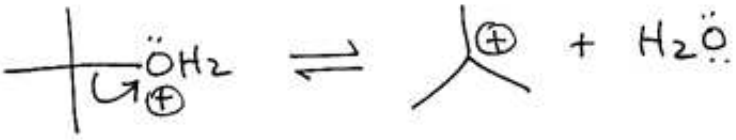
bonds formed (-)

H-Br -88
3°C-Br -63
-151

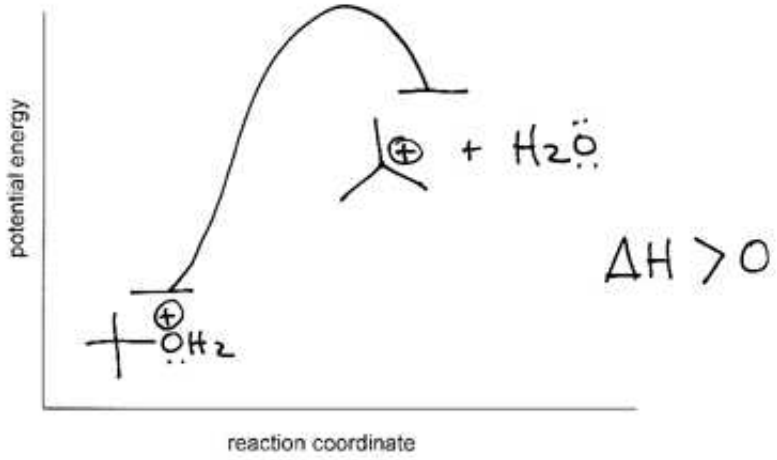
ΔH for the reaction = −14 kcal/mole

6. Consider the reaction of *tert*-butyl alcohol with hydrogen bromide:

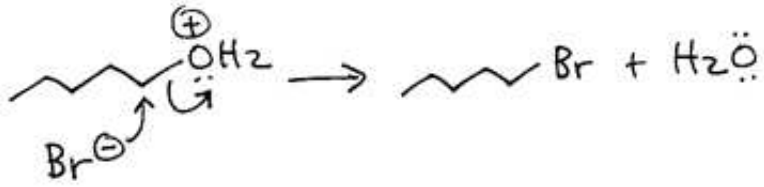
6a) Draw a mechanism for the *rate determining step only* in the above reaction. Show all bonds, electrons, non-zero formal charges and arrows clearly to receive full credit. Show all reactants and products (5 pts).



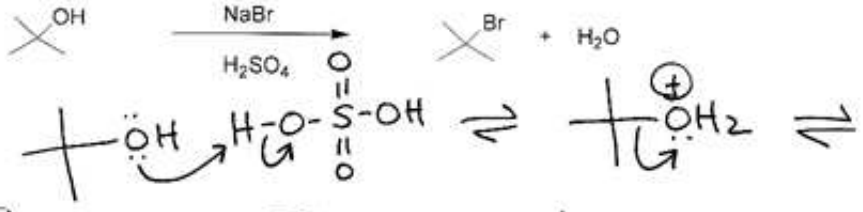
6b) Draw a potential energy vs. reaction coordinate diagram for the *rate determining step only* in the above reaction. Draw the structures and show the relative energies of the starting material(s) and the product(s) for this step (5 pts).

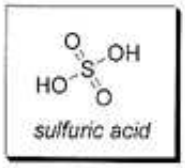


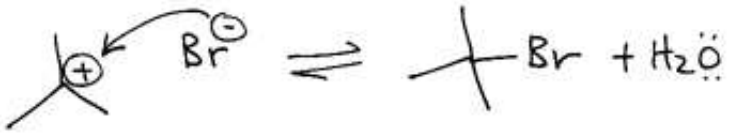
6c) Now consider the reaction of 1-pentanol with hydrogen bromide, shown below. Write a mechanism for the *rate determining step only* for this reaction. Show all bonds, electrons, non-zero formal charges and arrows clearly to receive full credit. Show all reactants and products (5 pts).



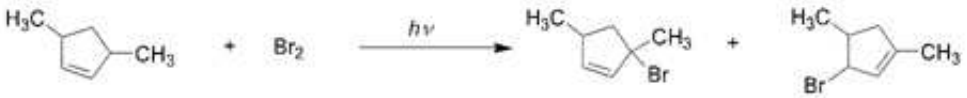
7a) Combining *tert*-butyl alcohol with sodium bromide and sulfuric acid produces *tert*-butyl bromide and water. Propose a mechanism to explain this observation. Show all bonds, electrons, non-zero formal charges and arrows clearly to receive full credit. (7 pts).







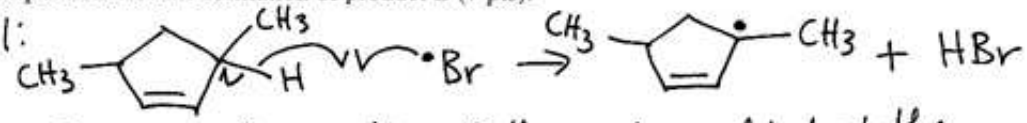
7b) In the presence of molecular bromine (Br_2), the following light-promoted reaction has been observed:



A B

Propose a mechanism for the two propagation steps involved in the formation of product **B**. Show all bonds, electrons, non-zero formal charges and arrows clearly to receive full credit. Show all reactants and products for each step, and any other structures that will help rationalize the formation of product **B** (7 pts).

Step 1:



Step 2: (To show the reaction of the carbon radical at the correct carbon, you must draw the other resonance structure.)