

Evaluation Exam in Organic Chemistry

Code _____

1. _____ (50)

2. _____ (28)

3. _____ (20)

4. _____ (14)

5. _____ (45)

6. _____ (14)

7. _____ (16)

8. _____ (20)

9. _____ (28)

10. _____ (32)

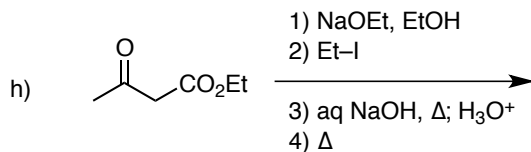
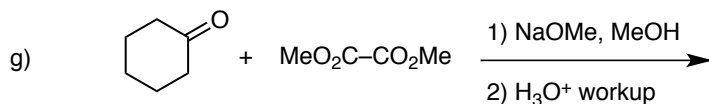
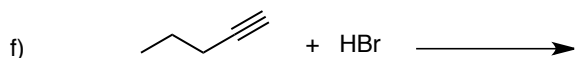
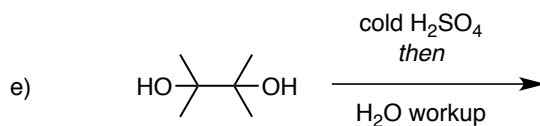
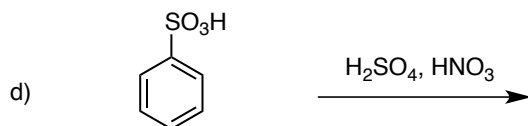
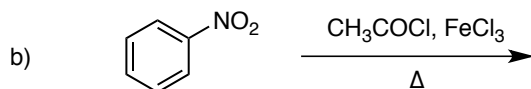
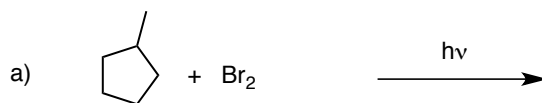
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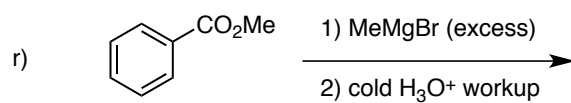
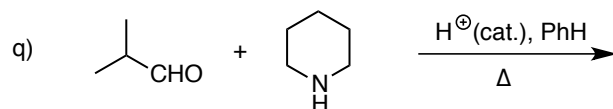
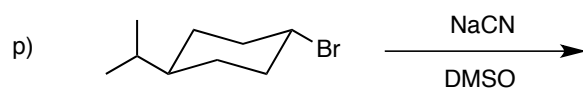
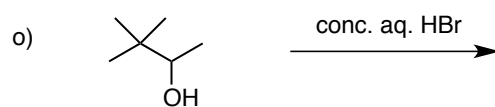
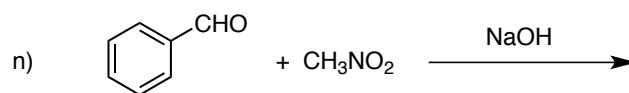
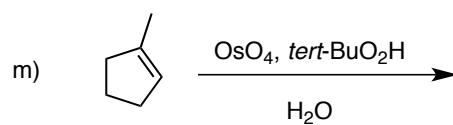
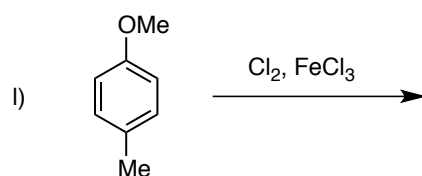
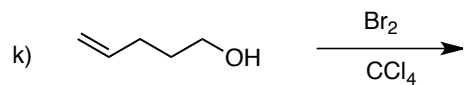
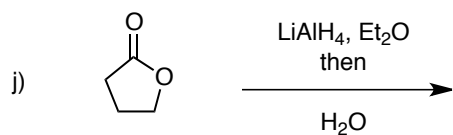
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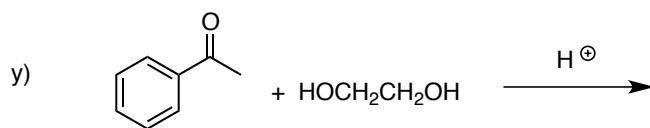
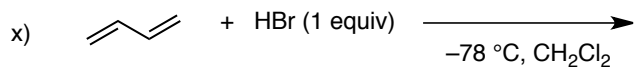
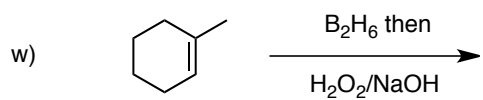
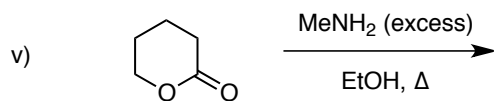
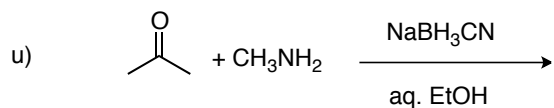
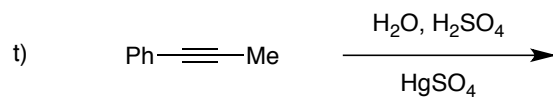
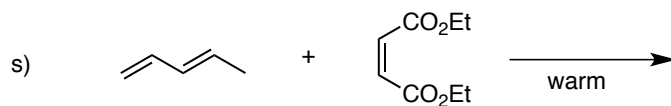
Total _____ (300)

1. Write answers to as many questions as you can.
If you write on both sides of a page, be sure to indicate by writing : See on back
2. Print your code (A, B, C, etc) on each page.
3. Follow the directions for each question carefully.

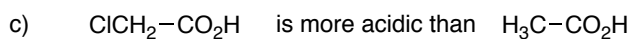
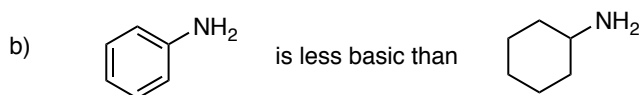
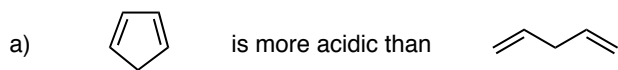
1. (50 pts) Write the structure(s) of the major organic product(s) formed from each of the following reactions. If more than one product is expected, circle the one you believe will be the major product. Indicate relative stereochemistry where appropriate using bold and hatched lines or wedges. If there is no reaction, write NR.



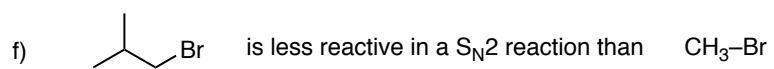
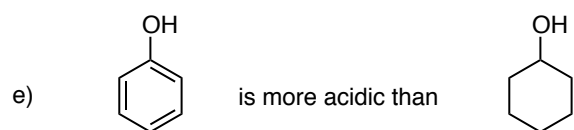
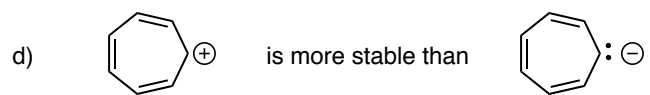




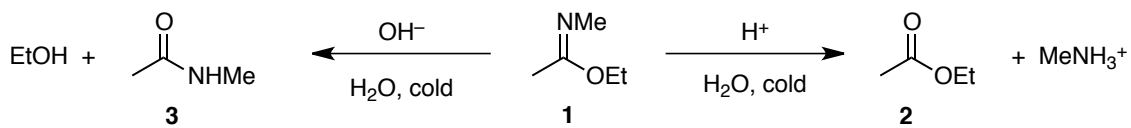
- 2) (28 pts) Provide a rationale for the following observations. You should use *as needed* concepts of resonance theory, aromaticity, conformational analysis, electronegativity, induction, polarizability, steric effects, and/or any other principles you deem relevant. You should be complete, but concise. As needed you should draw key structures to support and illustrate your answers.



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- 3) (20 pts) The product obtained upon hydrolysis of the imidate ester **1** varies depending upon the conditions for the hydrolysis as shown.

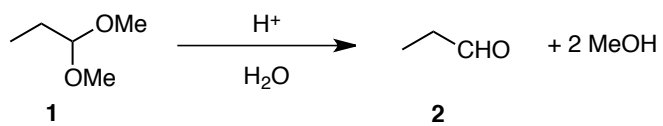


- a) Write the mechanism for the hydrolysis of **1** to give **2** showing all proton transfer steps and symbolizing the flow of electrons with curved arrows.

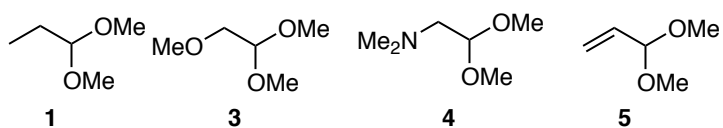
- b) Write the mechanism for the hydrolysis of **1** to give **3** showing all proton transfer steps and symbolizing the flow of electrons with curved arrows.

- c) Based upon the mechanisms you formulated in parts a) and b), propose a rationale for the observed difference in product formed based upon reaction conditions.

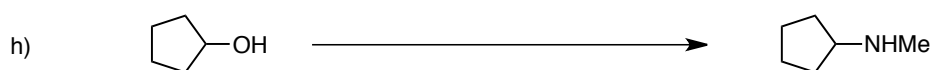
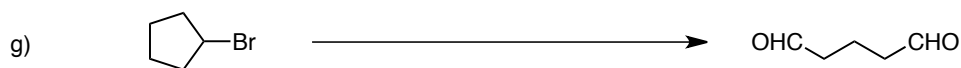
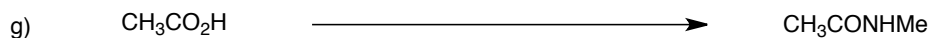
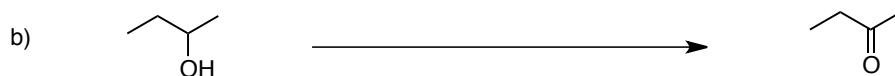
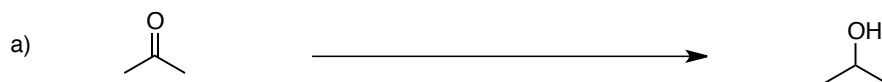
4. (14 pts) a) Write the mechanism for the hydrolysis of **1** to give **2** showing all proton transfer steps and symbolizing the flow of electrons with curved arrows.



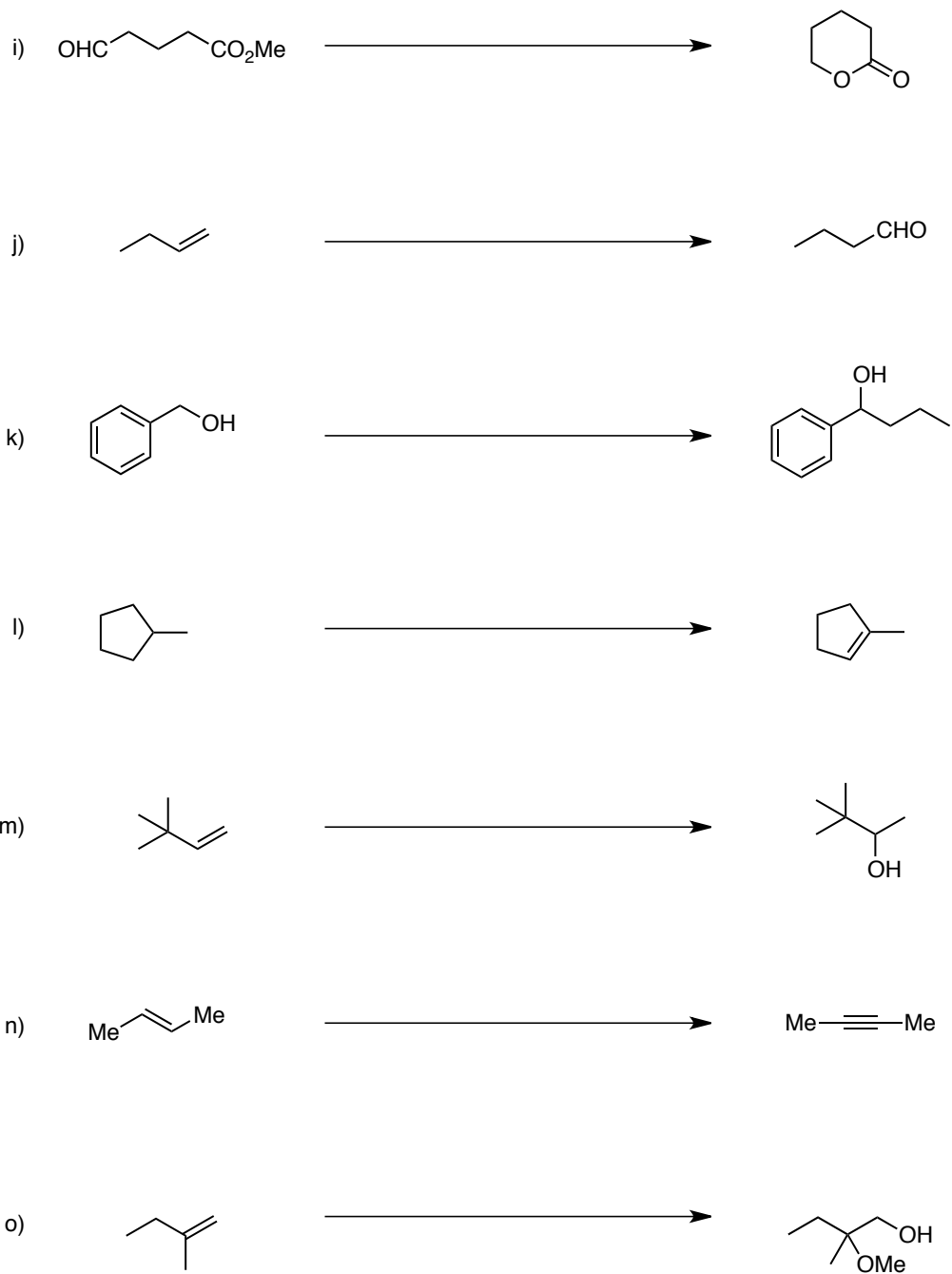
- b) The acetals **1** and **3–5** undergo acid-catalyzed hydrolysis at different rates. Predict the relative rates of hydrolysis and provide a mechanistic rationale to justify your answer.



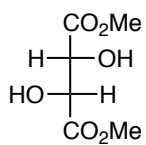
5. (45 pts) Write the reagent(s) over the arrow that will convert the starting material shown into the product indicated. For those transformations requiring more than one step, you need not draw intermediates, but you must number the individual steps over/under the arrow and the reagent for each step.



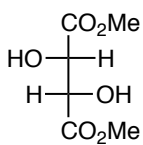
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6. (14 pts) Indicate whether each of the following pairs of compounds are identical, enantiomers, diastereomers, constitutional isomers, conformational isomers, or none of these.



and





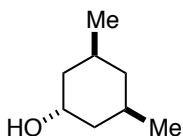
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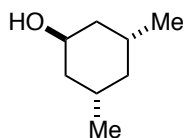


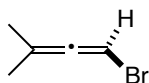
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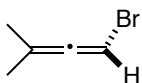


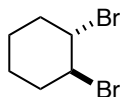
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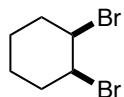


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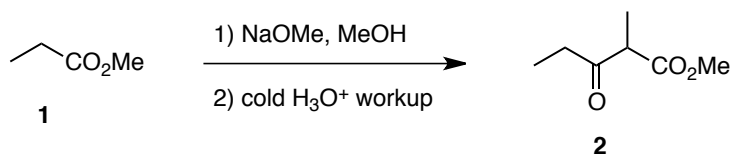




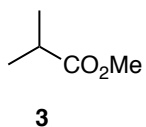
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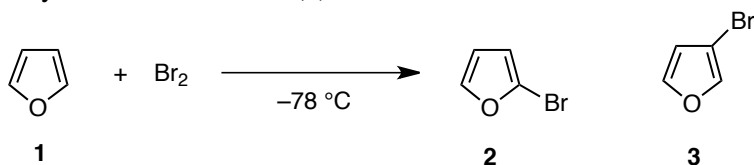
7. (16 pts) a) Write the mechanism for the Claisen condensation of **1** to give **2** showing all proton transfer steps and symbolizing the flow of electrons with curved arrows.



- b) When the ester **3** is subjected to the same reaction conditions for the Claisen condensation as **1**, it was recovered nearly quantitatively. Based upon the mechanism you provided for part a), suggest a rationale for this observation.



8. (20 pts) Furan (**1**) undergoes rapid bromination to give 2-bromofuran (**2**) as the major product as shown.; very little 3-bromofuran (**3**) is formed.

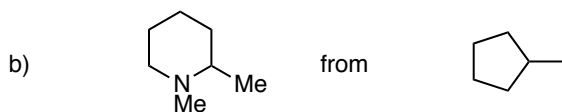
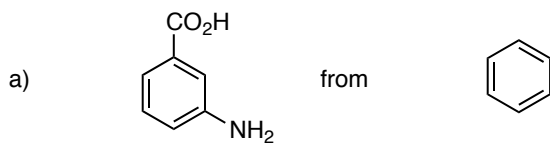


a) Write the mechanism for the bromination of **1** to give **2** showing all proton transfer steps and symbolizing the flow of electrons with curved arrows. Draw the important contributing resonance structures for the intermediate that is formed in the rate determining step of the reaction.

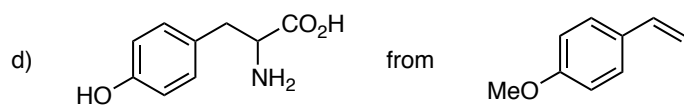
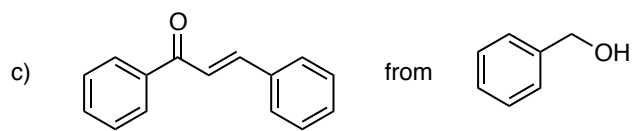
b) Write the mechanism for the bromination of **1** to give **3** showing all proton transfer steps and symbolizing the flow of electrons with curved arrows. Draw the important contributing resonance structures for the intermediate that is formed in the rate determining step of the reaction.

c) Based upon mechanistic considerations provide a complete rationale for the preferential formation of **2** in the reaction. You must be specific and explain why.

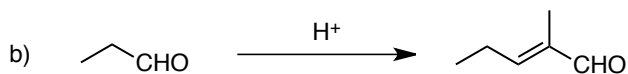
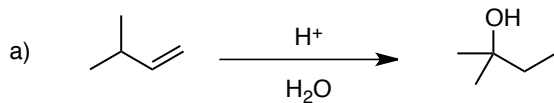
9. (28 pts) Outline a synthesis for each of the following compounds from the indicated organic starting materials together with any other organic reagents having four carbon atoms or less and any inorganic reagents you need. Show the isolable product of each of your synthetic steps.



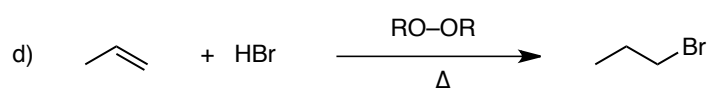
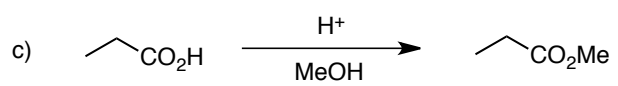
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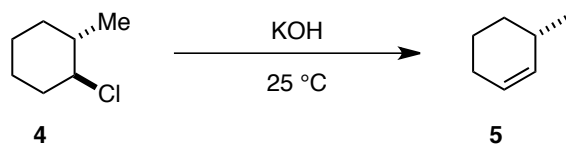
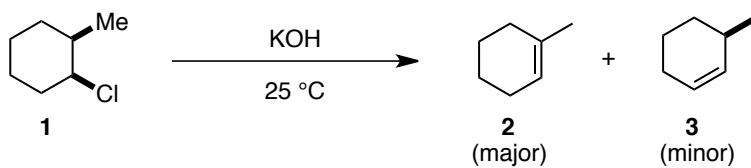
- 10) (32 pts) Write mechanisms for the transformations shown below showing all proton transfer steps and symbolizing the flow of electrons with curved arrows. Use double headed arrows for ionic reactions and single-headed (fish hook) arrows for radical reactions.



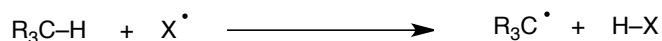
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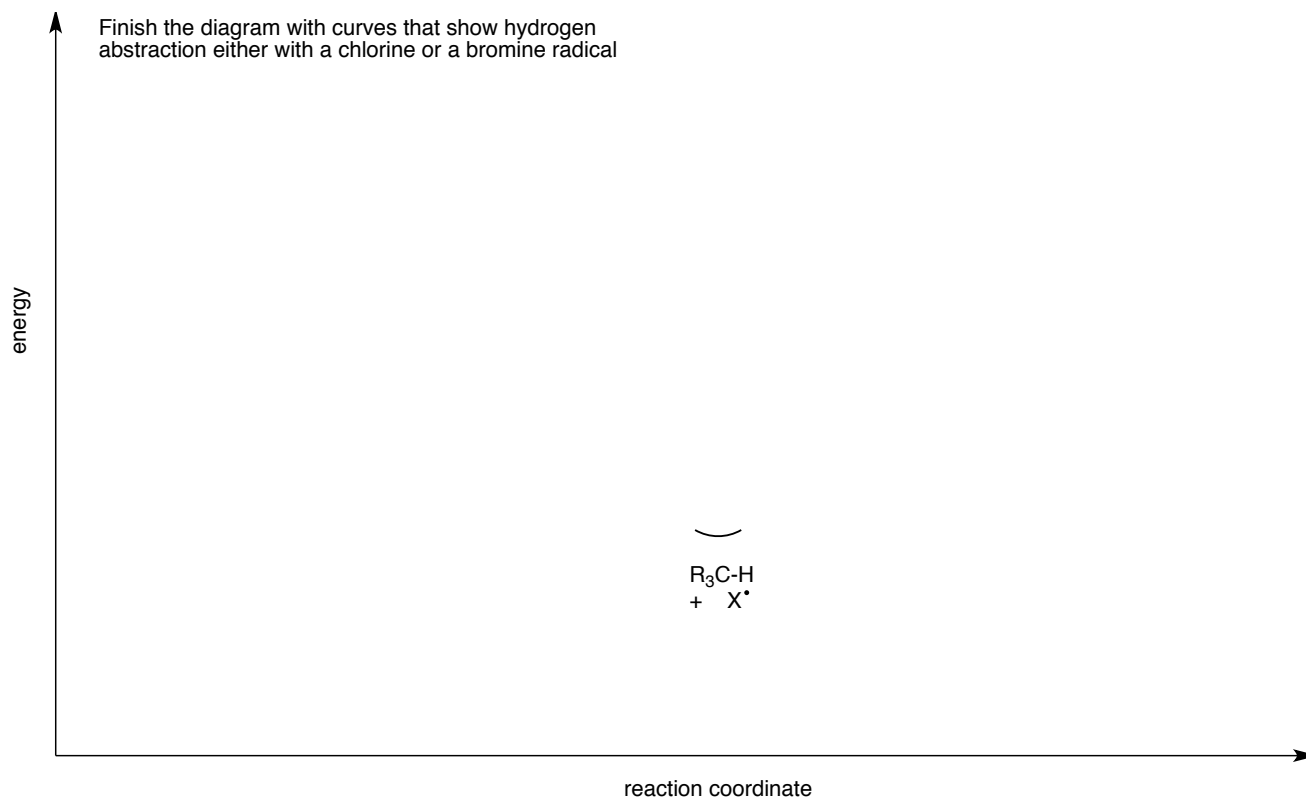
11. (19 pts) The dehydrochlorination of **1** occurs readily at room temperature to give **2** as the major olefinic product and small amounts of **3**, whereas dehydrochlorination of **4** requires heating and gives **5** as the only olefinic product. Based upon stereochemical features associated with the E2 reaction and using chair-like representations for the appropriate reactive conformations of **1** and **4**, provide a rationale for these observations. Be sure to include an explanation of why dehydrochlorination of **1** is easier than of **4** and why **2** is formed as the major product from **1**.



12. (14 pts) Free radical halogenation of alkanes using Cl_2 or Br_2 (X_2) with light is a radical chain reaction, and the regiochemistry of this process is set in the propagation step shown below.



- a) Bond dissociation energies of H-Cl and H-Br are 103 and 88 kcal/mol, respectively, and the average value of the bond dissociation energy of C-H is 98 kcal/mol. Given these values, plot the coordinate diagrams for the reactions of an alkane with a chlorine and a bromine atom; superimpose both reactions on the same plot below. Clearly show the relative energies of the two transition states and the two sets of products on the y-axis, as well as the relative positions of the transition states along the x-axis. Show structures of the products and the transition state species.



- b) When tertiary, secondary, or primary carbon atoms are in the alkane, the relative reactivity of the respective hydrogens in chlorination is 5, 4 to 1, respectively, whereas the same trend for bromination is 1600, 80, to 1. Referring to your energy diagram and focusing on relative transition state structures and energies, explain why free radical bromination is much more selective than free radical chlorination.