

Chemistry 235, Winter 2006

Mid-quarter exam 2 (Chapters 9, 10 and 11)

You may take as long as you like on the exam, but please do the exam in one sitting (you may take short breaks). Recommended time is 50 minutes; there are 55 points possible, but the exam is scored out of 50 (consider the extra five points to be "extra credit"). Please record the time of when you began the exam and when you finished the exam below so that I can get an idea of how long it took the class as a whole. The exam is closed books (textbooks and other books) and websites, open notes, class handouts, lab notebooks, homework and exercises. There is to be no collaboration. This exam is due in class at **6 p.m., February 22.**

Name:

Please sign the following statement:

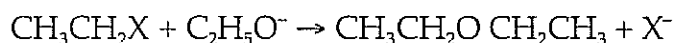
"I have abided by the conditions of the exam."

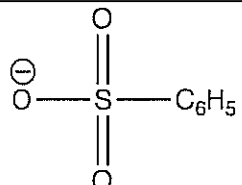
Signature:

Time of exam start:

Time of exam finish:

1. a. (6 points) Explain the following trend for S_N2 reactions:



X =		Br	Cl	NH ₂
Relative rate (Br = 1.0)	76.3	1.0	0.0131	10 ⁻¹¹

This is a leaving group problem; for the rate to be high, X must be a good leaving group, and thus should be stable as an ion. Clearly the ~~benzenesulfonate~~ benzenesulfonate (SO₂C₆H₅⁻) ion has plenty of resonance contributors & thus is stable; NH₂⁻ does not & so is unstable. For single atoms, the larger the size, the more stable the ion — the negative charge is diffused over a larger volume which is more energetically stable than a concentrated charge.

b. (4 points) What relative rate would you expect if X = I?

Following the trend above, I should fall between SO₂C₆H₅⁻ & Br⁻

c. (6 points) The solvation energies for the halide ions are given below:

- F⁻ (g) → F⁻ (aq) ΔH° = -489.5 kcal/mol
- Cl⁻ (g) → Cl⁻ (aq) ΔH° = -355.6 kcal/mol
- Br⁻ (g) → Br⁻ (aq) ΔH° = -326.3 kcal/mol
- I⁻ (g) → I⁻ (aq) ΔH° = -284.5 kcal/mol

solvation energies

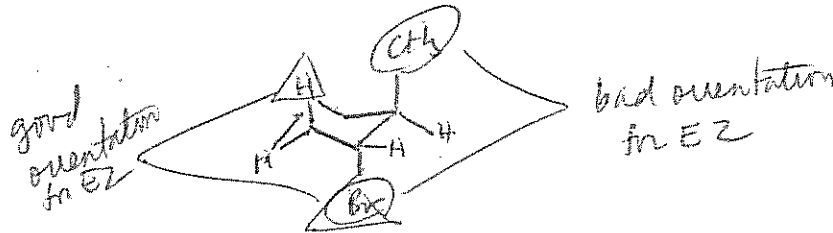
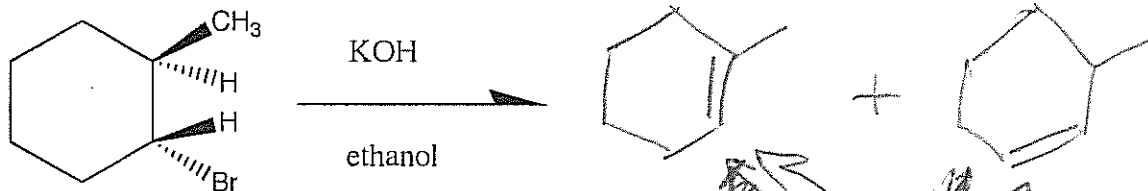
Use this information above to justify the halogen relative rate of S_N2 reaction trend. Hint: But there's no gas phase in an S_N2 reaction! Wait, what does a nucleophile have to do with the solvent molecules just before the reaction takes place?

for the rxn
 $\text{CH}_3\text{CH}_2\text{X} + \text{HPO}_4^- \rightarrow \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 + \text{X}^-$
 fastest for X = I
 slowest for X = F

The point of the g → aq trend is to show that fluorine ions ~~are~~ have a hard time getting rid of solvating water molecules. They must do that in order to react with the other reactant molecule.

Thus, because the de-solvation is energetically unfavorable, the rxn is slow for F⁻ & fast for I⁻

2. Consider the following reaction:



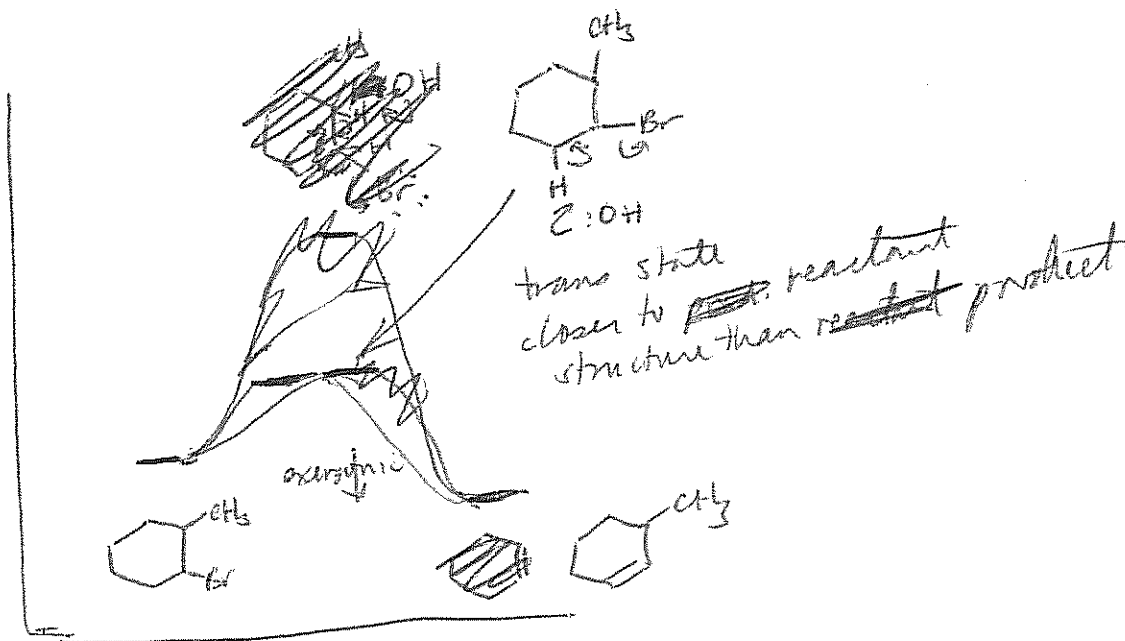
a. (6 points) Write the two possible structures resulting from elimination of HBr from the reactant.

b. (2 points) Which is the major product under E2 conditions?

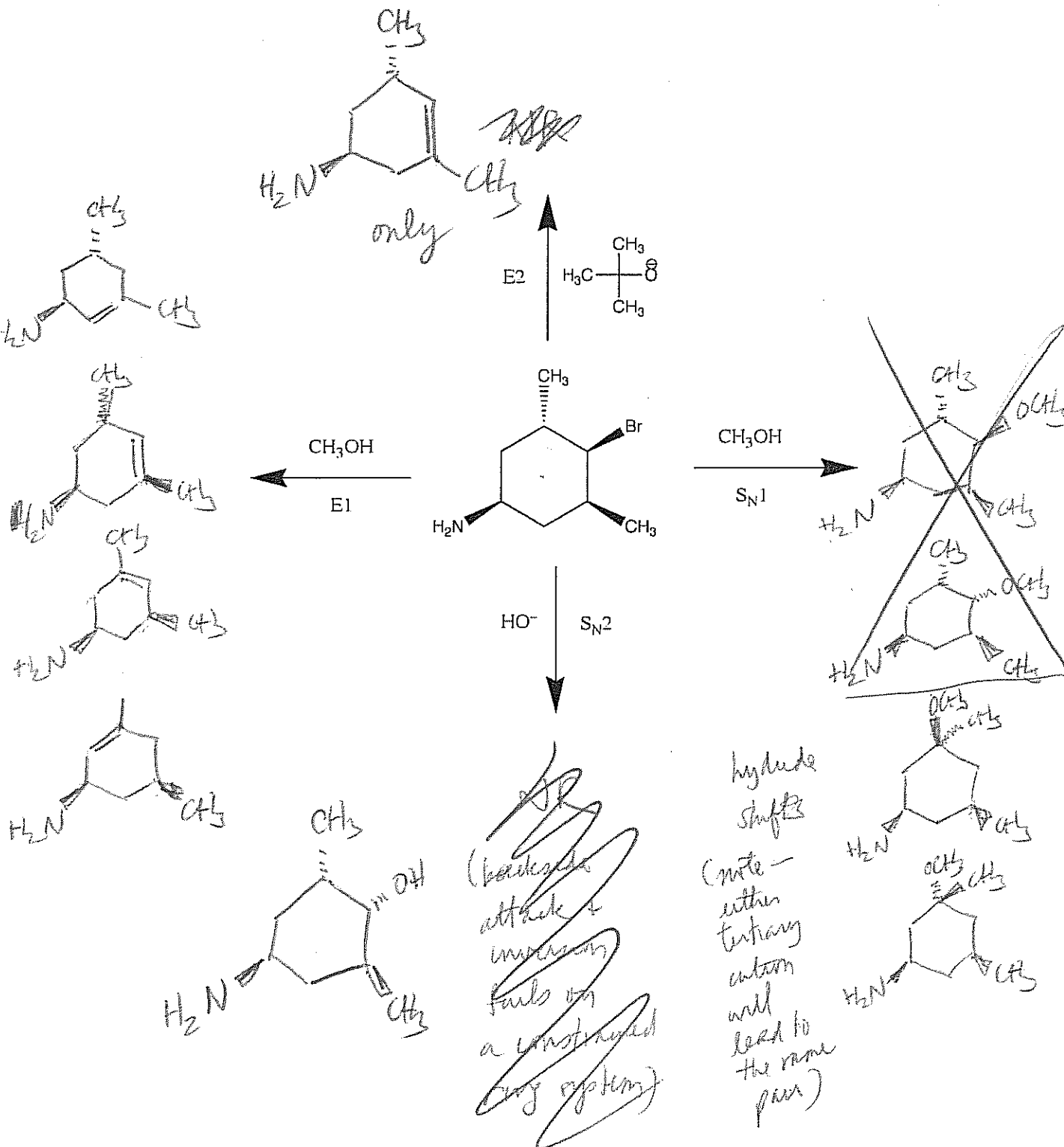
c. (2 points) Which is the major product under E1 conditions?

d. (5 points) Draw an energy diagram that demonstrates energy changes during the E2 reaction. Points to include: exergonic or endergonic? transition state structure (write it)? energy level path during the reaction? Hammond postulate consistency?

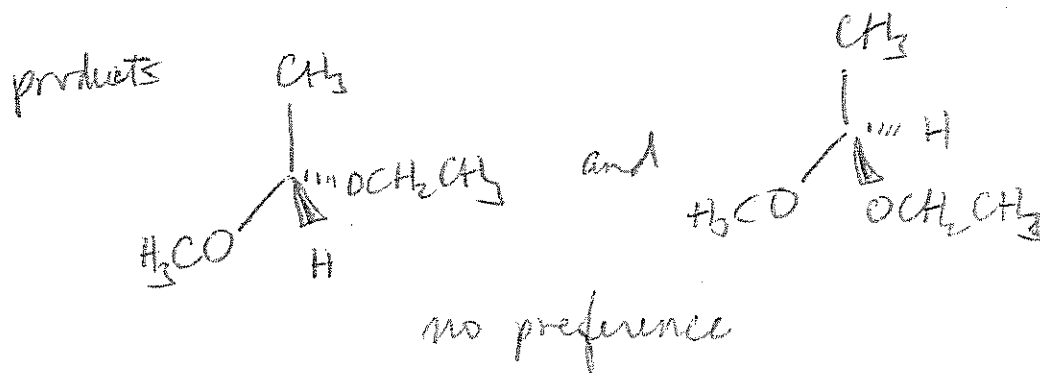
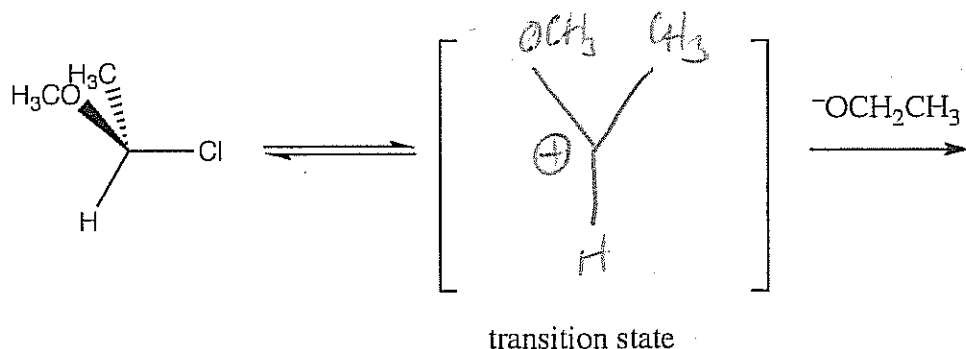
trans product more favored due to less steric hindrance
(most stable carbon)



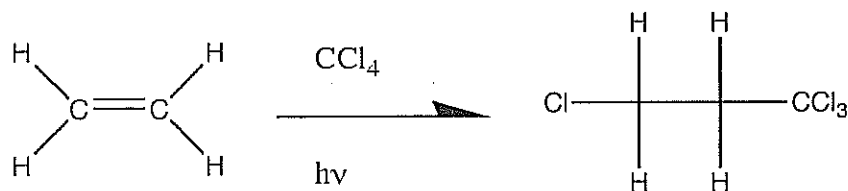
3. (8 points) Draw the products for the following reactions (the mechanism is given for each reaction). Be sure to show the stereochemistry of the products. Use "NR" to indicate no reaction, if needed.



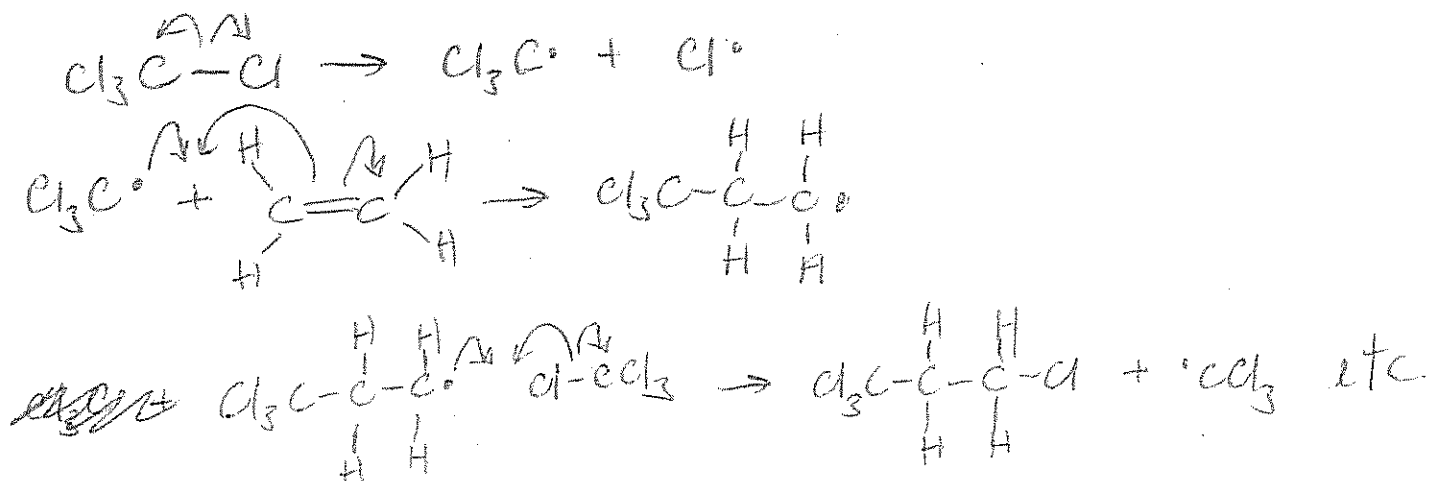
4. (6 points) Draw the transition state and final product(s) for the following S_N1 reaction. Be sure to show pertinent stereochemistry. If there is more than one product, indicate the preferred product. Give a justification why the preferred product is preferred, if relevant.



5. (10 points) Write the mechanism for the following reaction:



Hint: there is more than one step.



Chemistry 235, Winter 2006

Key

Final (all chapters)

You may take as long as you like on the exam, but please do the exam in one sitting (you may take short breaks). Recommended time is 120 minutes; there are 105 points possible, but the exam is scored out of 100 (consider the extra five points to be "extra credit"). Please record the time of when you began the exam and when you finished the exam below so that I can get an idea of how long it took the class as a whole. The exam is closed books (textbooks and other books) and websites, open notes, class handouts, lab notebooks, homework and exercises. There is to be no collaboration. This exam is due in class at **6 p.m., March 22.**

Name:

Please sign the following statement:

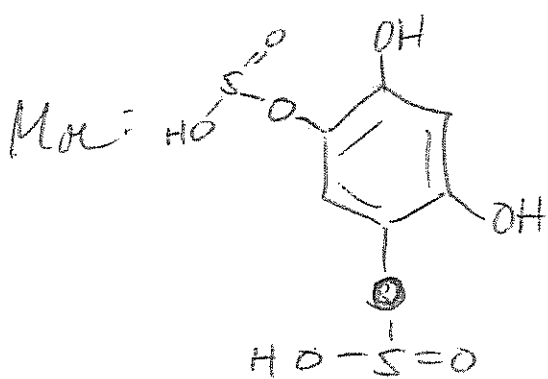
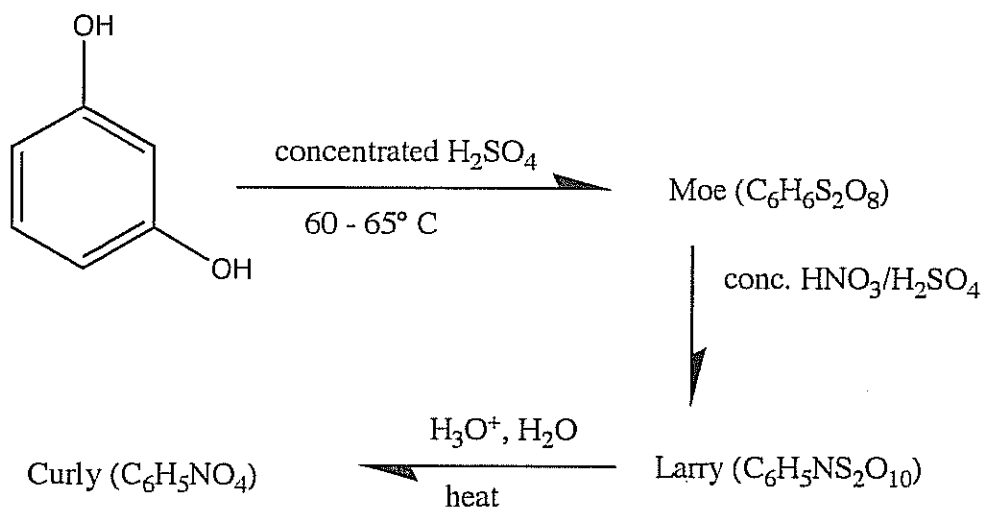
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Signature:

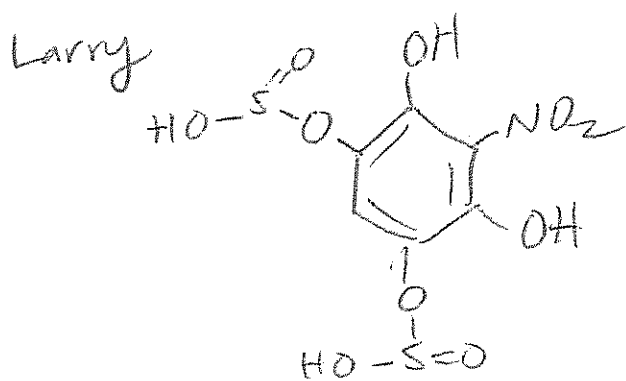
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Time of exam finish:

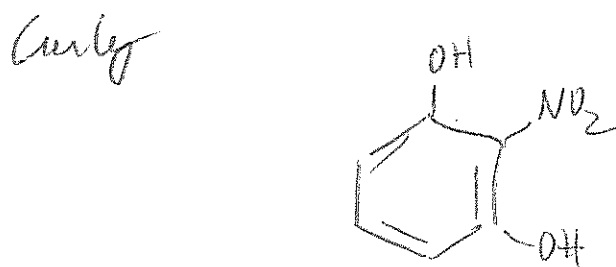
2. (15 points) Propose structures for the molecules called Moe, Larry and Curly below:



-OH is ortho/para directing
both sites are both ortho to one OH & para to the other OH

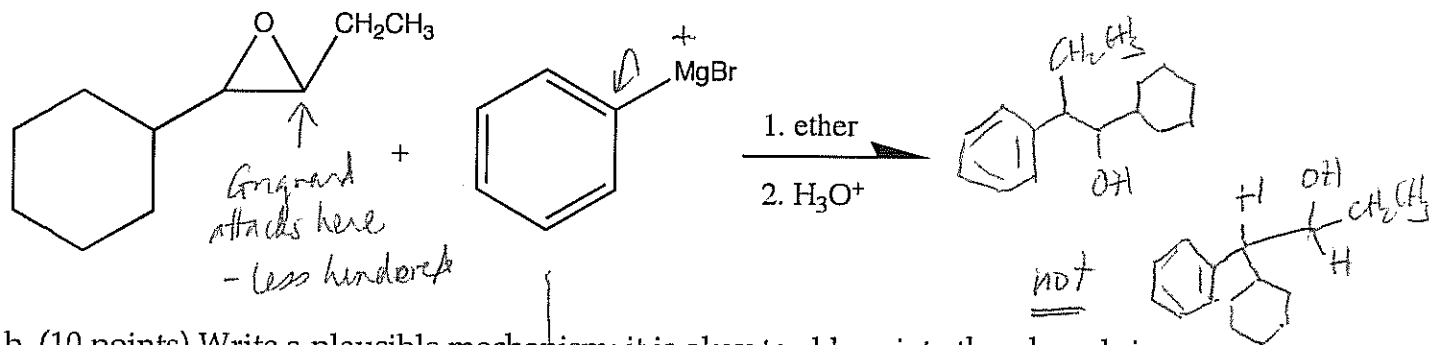


-OH is ortho/para directing
-SO₃H is meta directing

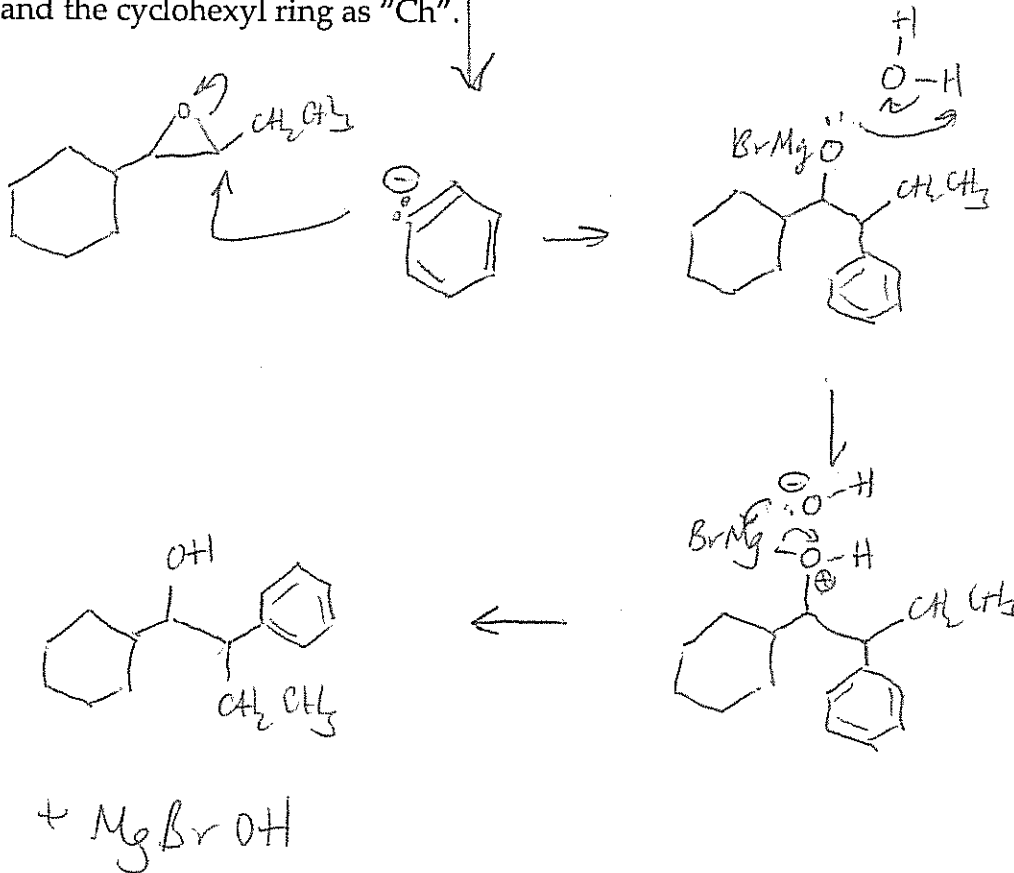


-SO₃H₂ is a good leaving group!

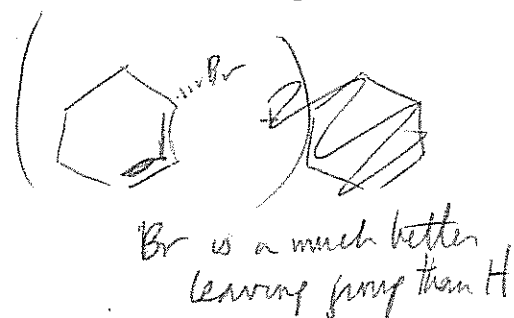
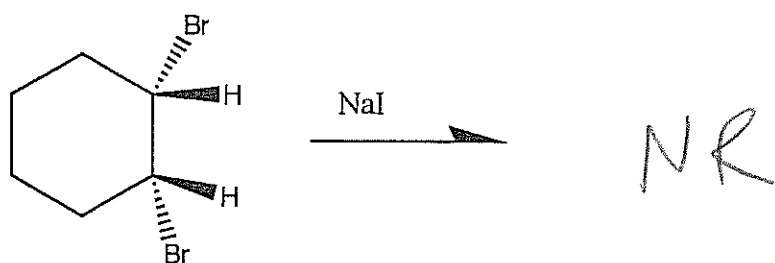
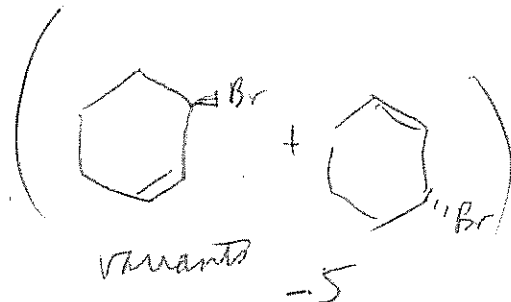
3. a. (5 points) Predict the product:



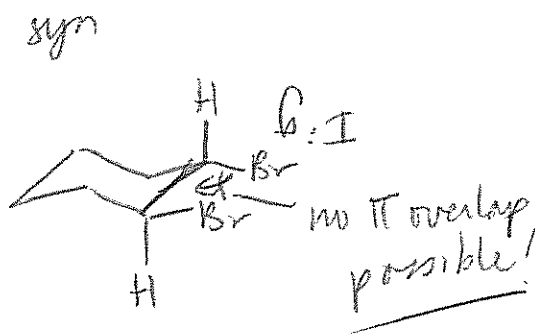
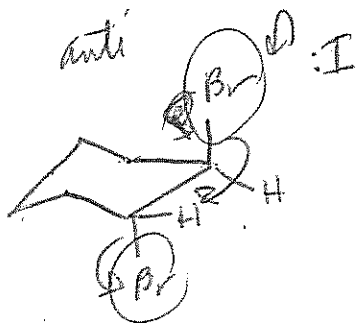
b. (10 points) Write a plausible mechanism; it is okay to abbreviate the phenyl ring as "Ph" and the cyclohexyl ring as "Ch".



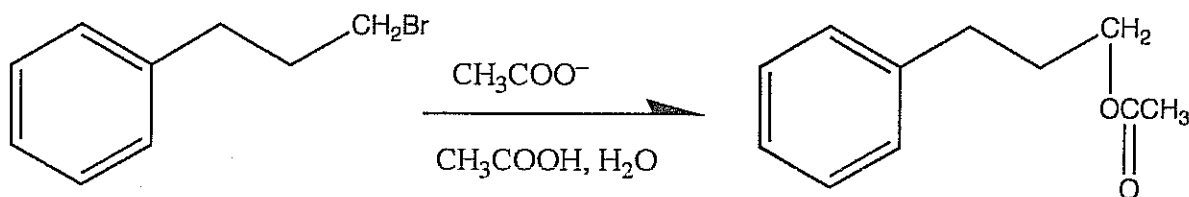
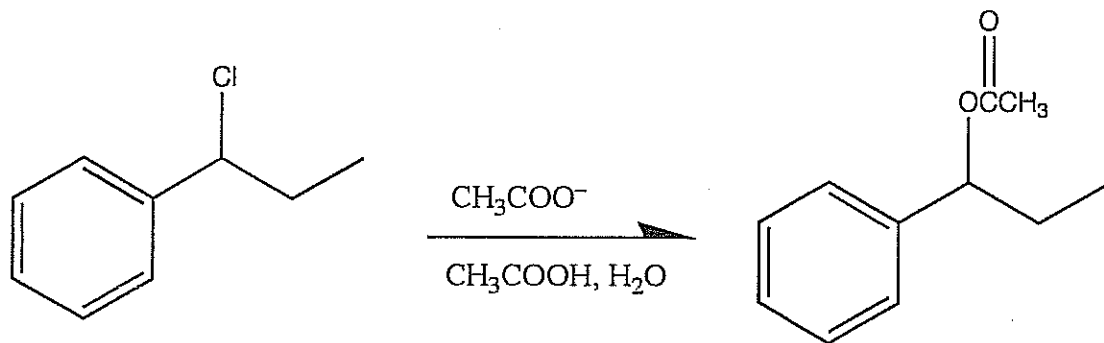
4. (10 points) Under E2 conditions, are the products the same or different in the following two reactions? Justify your answer by citing a mechanism, or at least a portion of a mechanism!



different because the bromines must be anti- to each other

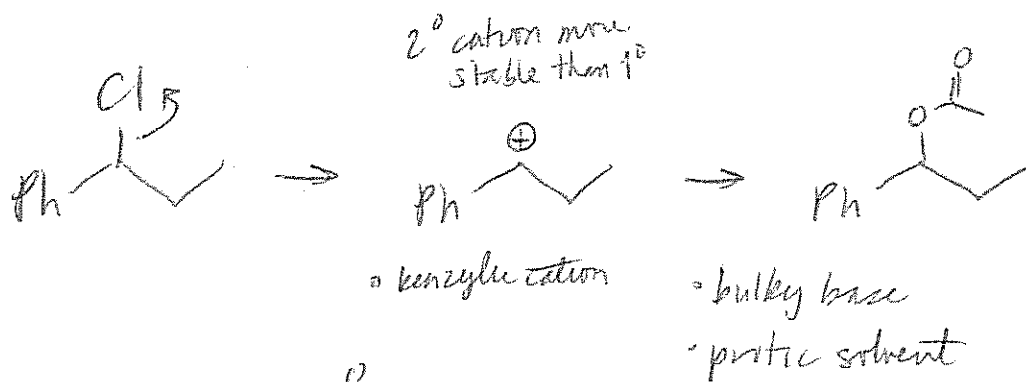


5. (10 points) Predict whether each of the following substitution reactions is likely to be S_N1 or S_N2 :

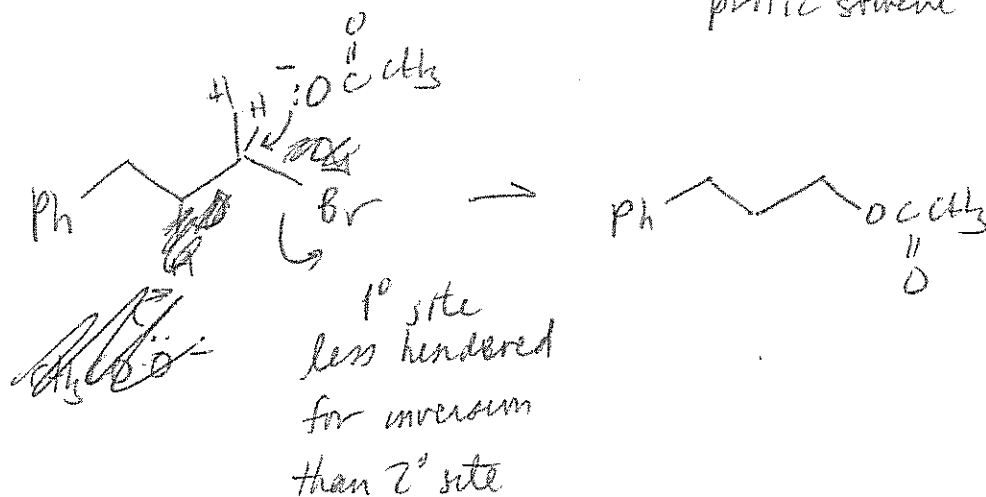


Please justify your choices.

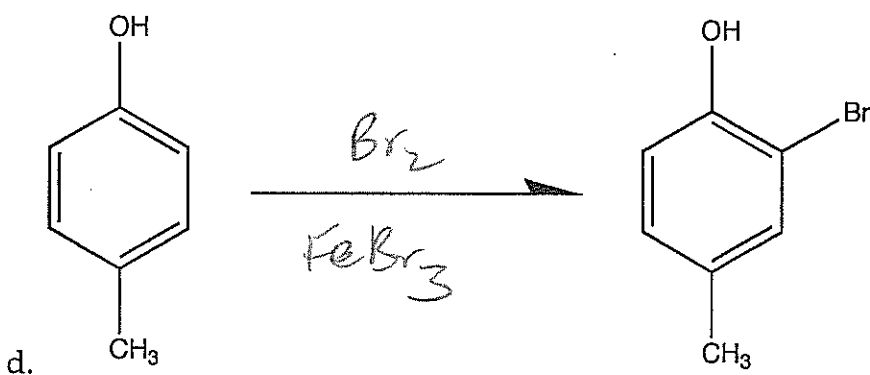
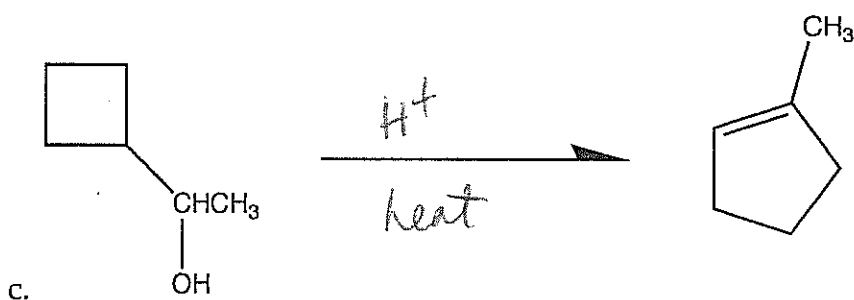
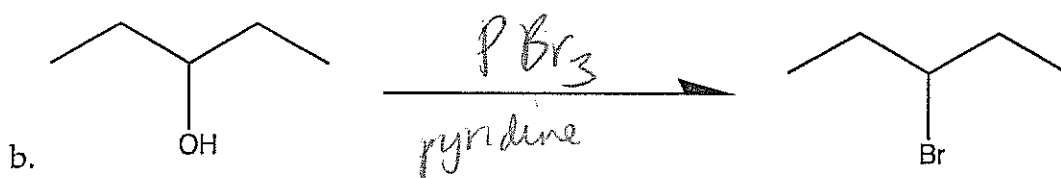
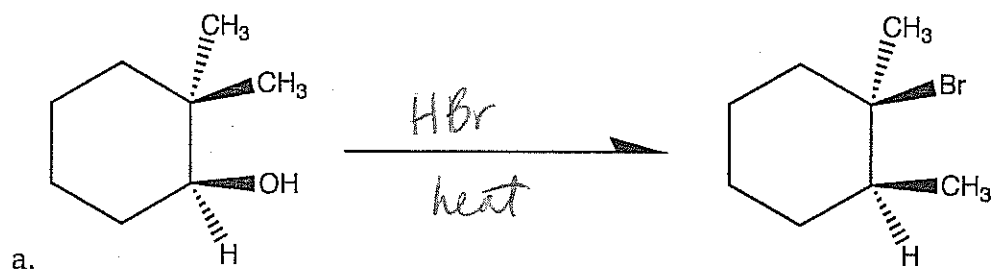
S_N1



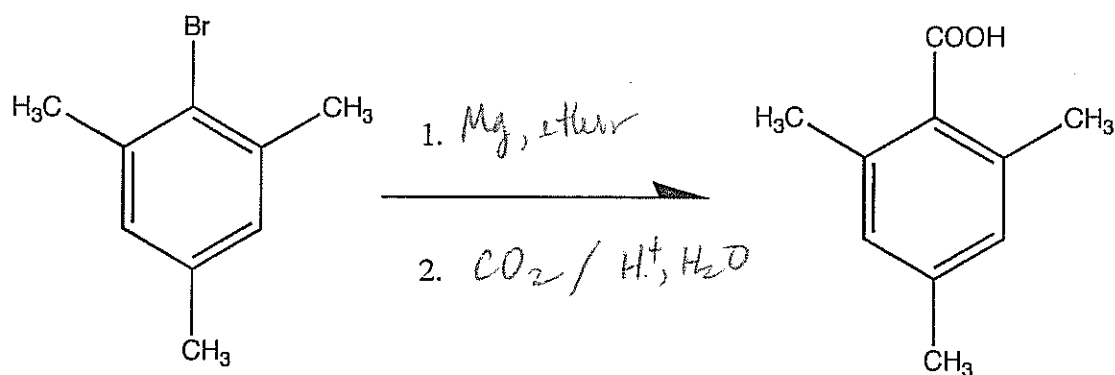
S_N2



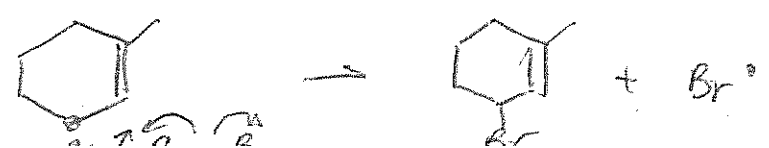
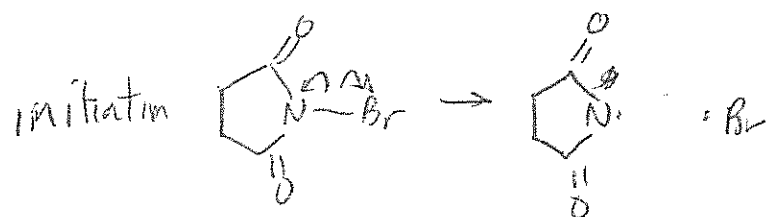
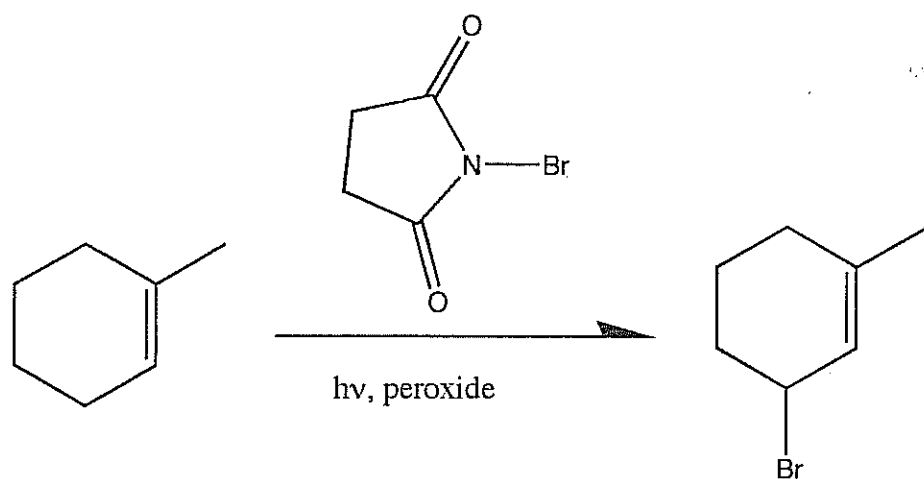
6. (15 points) Give the other reactants and any appropriate conditions for the following reactions:



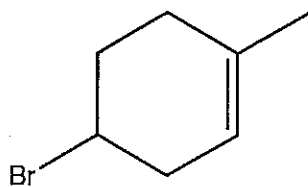
e. (note that there are two steps required)



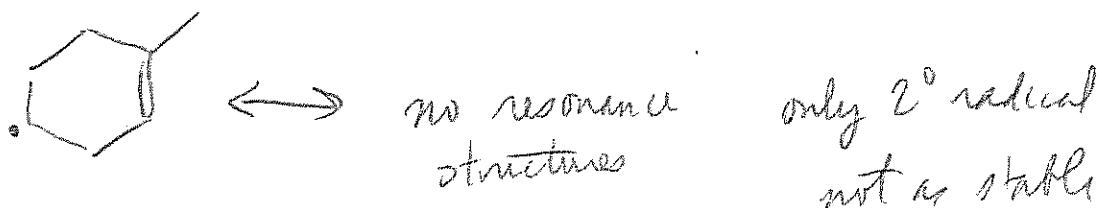
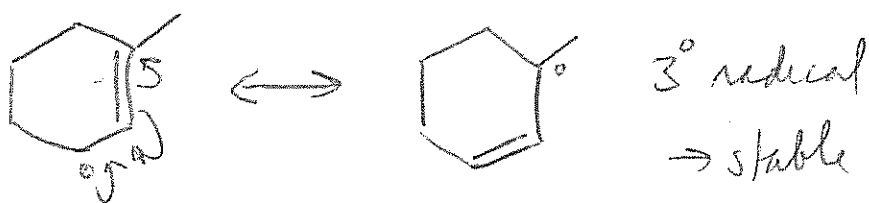
7. a. (10 points) Did you really think you could get through this exam without a radical question? (That was not really a question). Write the mechanism for the following reaction:



b. (10 points) In the reaction on the previous page, why is the product the one given and not:



Hint: resonance of the intermediate...



Extra credit — (5 points) Recall from Chemistry 231 that sodium metal could be used to generate a radical anion when reacted with a sp or sp^2 hybridized carbon atom. Also recall that hydrogenating a benzene molecule to yield 1,4-cyclohexadiene is a slow process, even with a nickel catalyst because benzene has resonance stability. Show a mechanism by which two equivalents of Na metal and two equivalents of H^+ will accomplish the same reaction. It turns out that this reduction of benzene occurs under much less harsh conditions than the traditional hydrogenation route. Hint: Resonance structures will be needed to explain the 1,4- part.

