

## Chemistry 3A – Exam #2

Student Name: \_\_\_\_\_

Student ID Number: \_\_\_\_\_

TA or Section: \_\_\_\_\_

### Point Breakdown

Problem 1 \_\_\_\_\_ / 20

Problem 2 \_\_\_\_\_ / 16

Problem 3 \_\_\_\_\_ / 5

\_\_\_\_\_ / 8

\_\_\_\_\_ / 16

Problem 4 \_\_\_\_\_ / 18

\_\_\_\_\_ / 16

Problem 5 \_\_\_\_\_ / 13

Problem 6 \_\_\_\_\_ / 22

Problem 7 \_\_\_\_\_ / 16

Total _____ / 150
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Check that you have 11 pages.

You will have 140 minutes for this exam.

**REMEMBER:** I am not trying to trick you. If a question looks like it might be super easy, then it probably is. Also, do not leave anything blank. If you are not sure how to get to the end of a question, at least try and start it.

## 1. The Basics. (20 pts)

## 1. A. Fill in the blanks. (6 pts)

"Hammond's Postulate states that the \_\_\_\_\_ of an endothermic reaction will resemble the products."

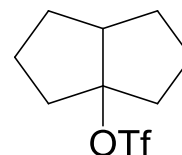
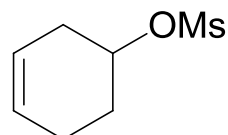
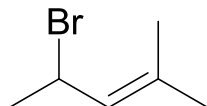
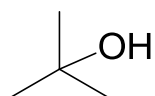
"The kinetic product will come from the reaction pathway with the \_\_\_\_\_ transition state energy."

## 1. B. Select whether these statements are true (T) or false (F). (6 pts)

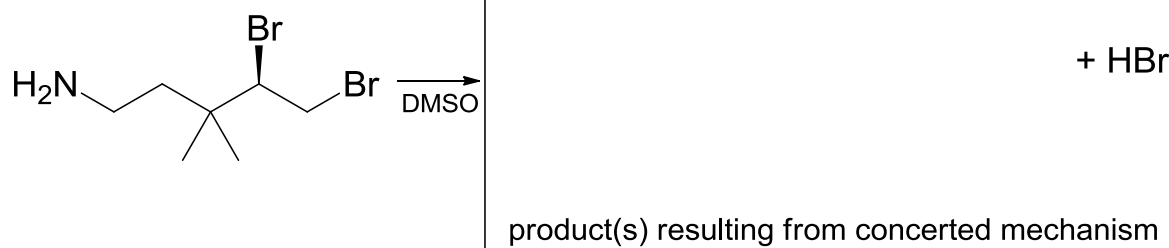
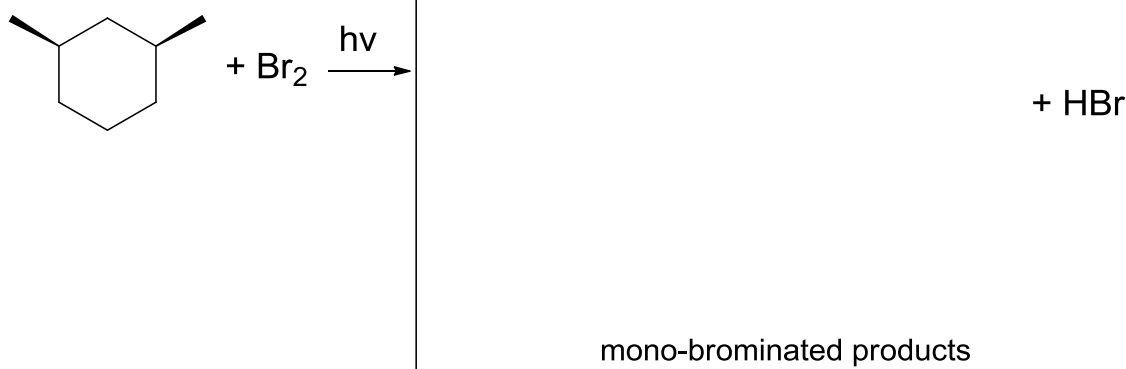
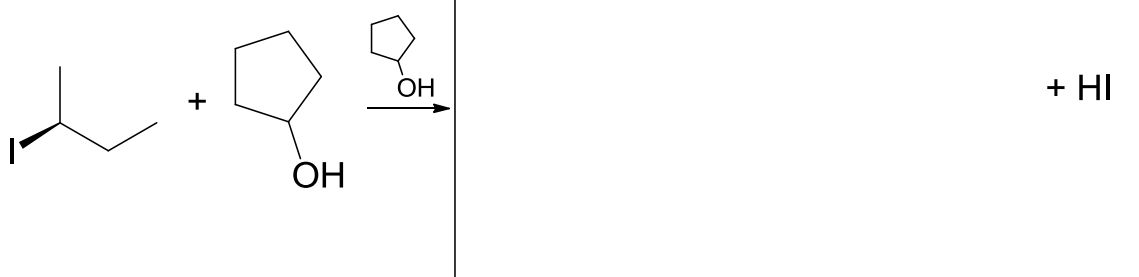
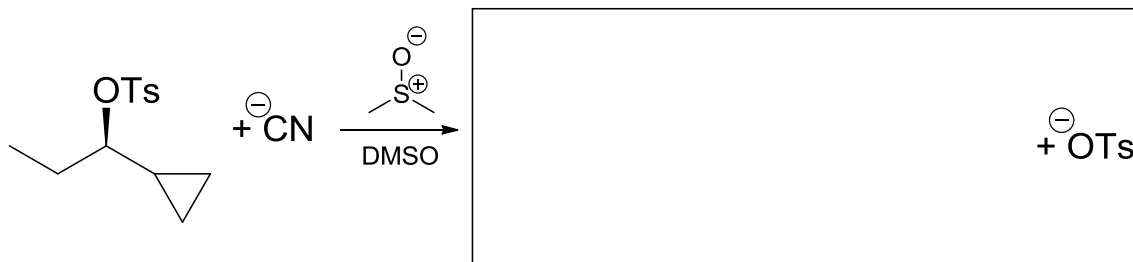
The major product in a radical reaction will always be the thermodynamic product T / F

Enantiomeric transition states have the same energy as each other. T / F

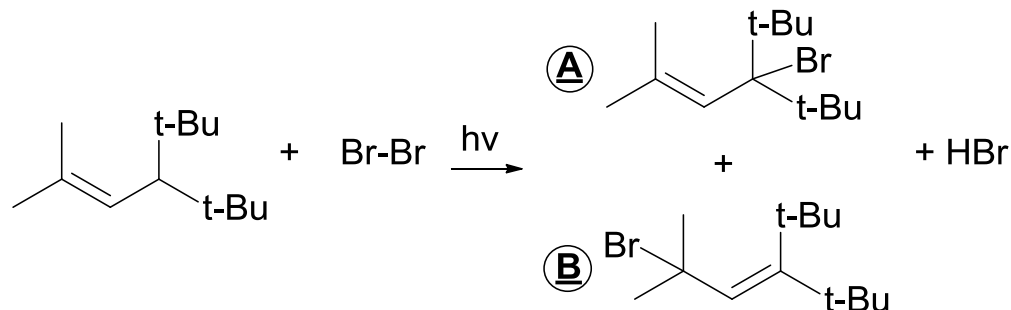
Hyperconjugation has a larger stabilizing effect on radicals than it does on carbocations. T / F

1. C. Circle the best  $S_N1$  electrophile below. (2 pts)1. D. Draw the best  $S_N2$  electrophile with a tosylate (OTs) leaving group. (3 pts)1. E. Draw the orbital interaction responsible for inversion of stereochemistry in an  $S_N2$  reaction. (3 pts)

2. Predict the products of the following reactions. Be sure to show all possible constitutional as well as stereoisomers. Remember that conformational isomers are considered identical molecules. Any repeat answers will cancel out a correct answer. (16 pts)



3. A. Calculate the overall reaction energy for the transformation below using the BDE table at the bottom of the page. Only take formation of **B** into account in your calculations. Show your work. (5 pts)



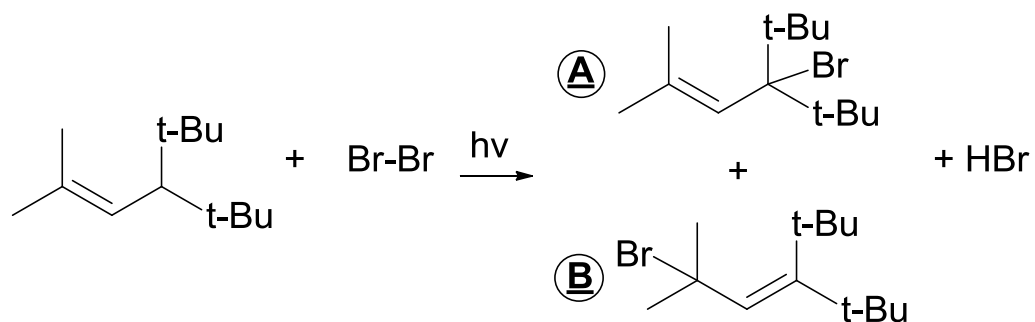
Show work:

Reaction Energy :	$\frac{\text{kcal}}{\text{mol}}$
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**Important Bond Dissociation Energies (rounded)**

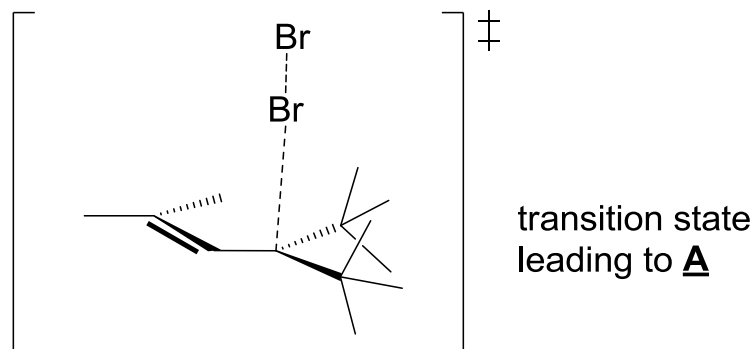
Bond	BDE (kcal/mol)	Bond	BDE (kcal/mol)
Br-Br	45	3° allylic C-H	90
H-Br	90	3° allylic C-Br	60

3. B. Draw the mechanism for the following reaction. Specifically show the initiation step as well as each relevant propagation step. Do NOT SHOW any termination steps. (8 pts)

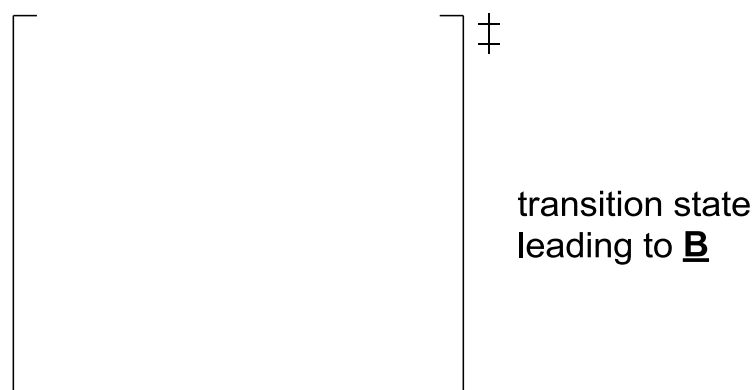


Blank area for drawing the mechanism.

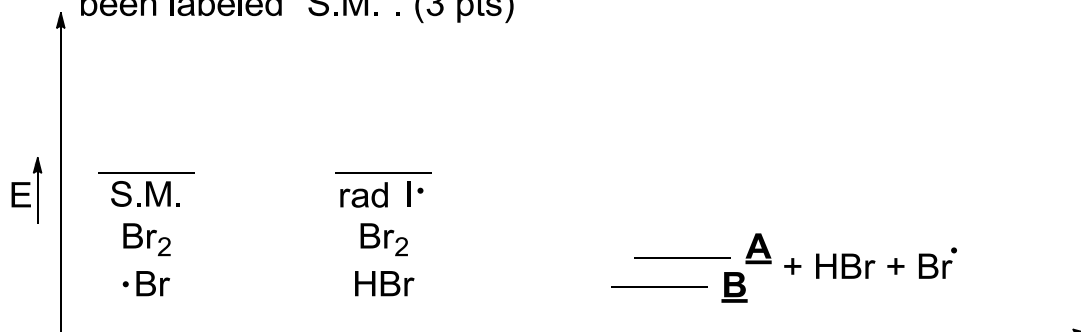
3. C. Below is the transition state leading to product **A**. Use curved lines to indicate any steric interactions between the approaching  $\text{Br}_2$  molecule and the radical intermediate. (3 pts)



3. D. Draw the transition state leading to product **B**. Use curved lines to indicate any steric interactions between the approaching  $\text{Br}_2$  molecule and the radical intermediate. (5 pts)

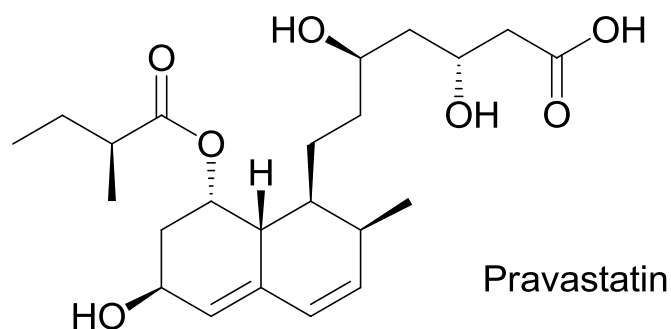


3. E. Complete the reaction coordinate diagram below. The intermediate radical compound has been labeled "rad I" and the starting material has been labeled "S.M.". (3 pts)



3. F. Will compound **A** or **B** be the major product? Explain using 15 or fewer words. (5 pts)

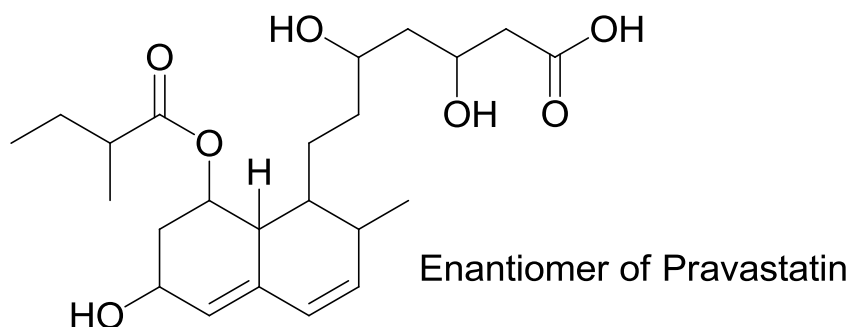
4. Statins are molecules commonly isolated from mushrooms. They have been shown to have cholesterol lowering properties.



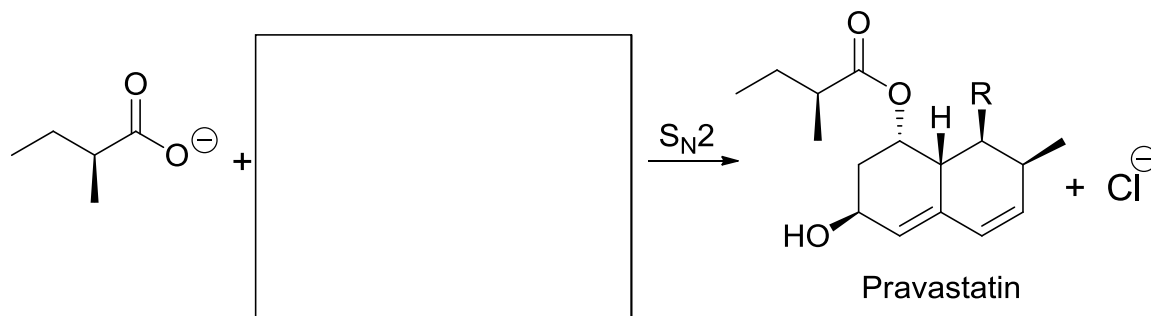
4. A. How many stereocenters does Pravastatin contain? (2 pts)

4. B. Locate each **alcohol functional group** on Pravastatin. Label those stereocenters as R or S on the molecule above. (6 pts)

4. C. Add wedges and dashes to the molecule below to show the enantiomer of Pravastatin. (3 points)

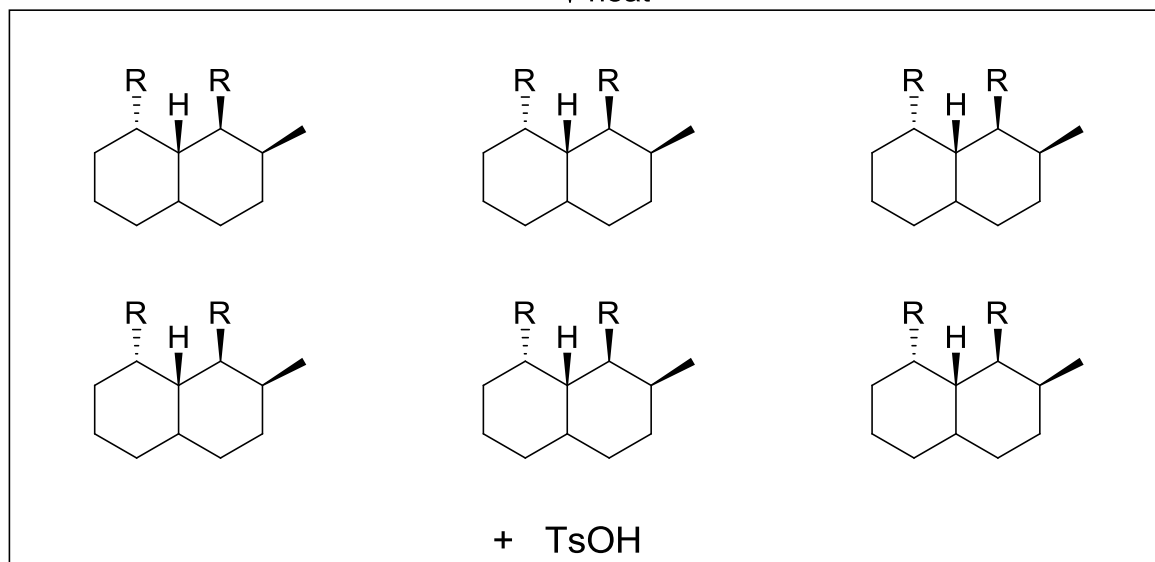
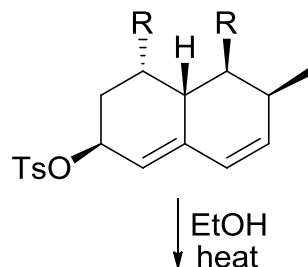


4. D. Below is a synthetic scheme that leads to Pravastatin. Fill in what is missing in the box. (3 pts)

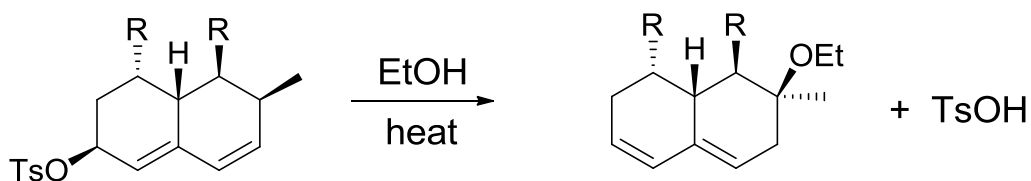


4. E. Add electron-pushing arrows to the reagents above to show the formation of products. (4 pts)

4. F. Predict the 6 mono-substituted products of the reaction below. Be sure to show all possible constitutional isomers as well as stereoisomers. Repeat answers will cancel out correct answers. Add appropriate groups and pi bonds to the templates in the box. (8 pts)

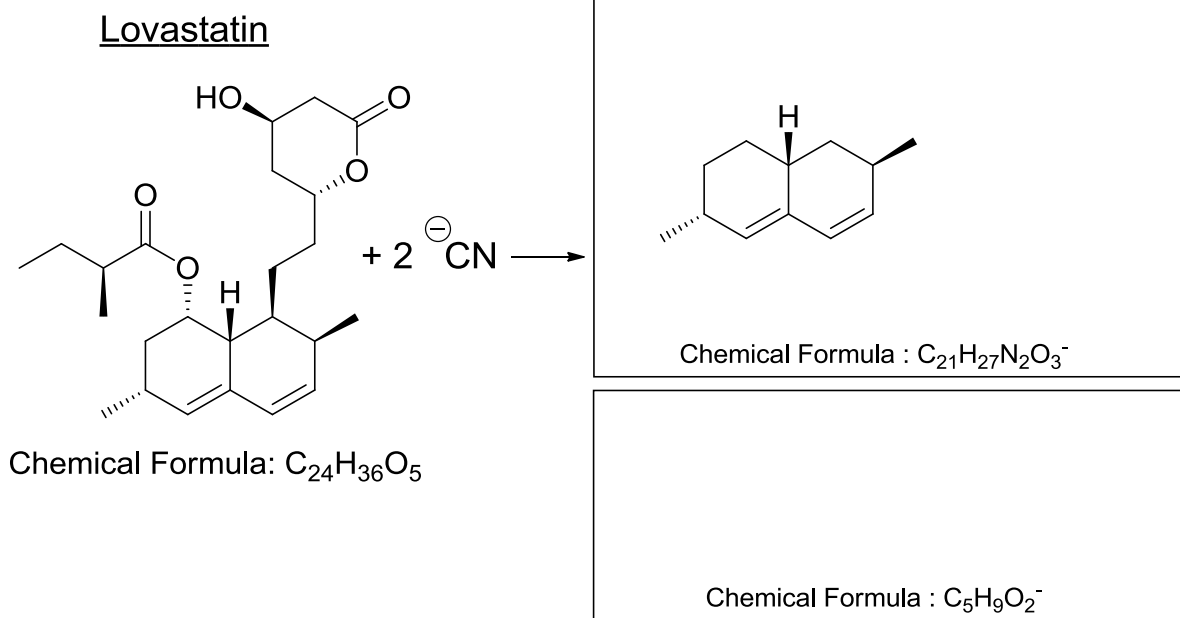


4. G. Draw an arrow-pushing mechanism for the following reaction. Be sure to clearly show formation of each product. (8 pts)

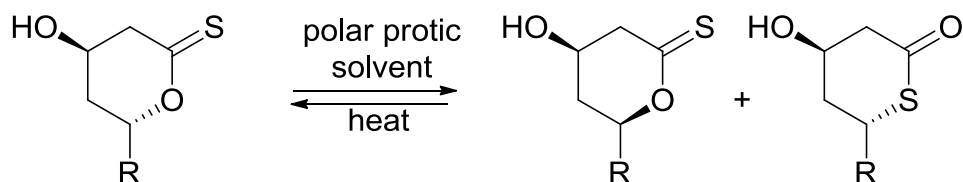




5. A. The conjugate bases of carboxylic acids (carboxylates) are decent leaving groups. Predict the products of the  $S_N2$  reaction below. Assume both cyanide groups attack the same molecule. Draw both of the organic products. A template has been provided. (5 pts)



5. B. Provide an electron pushing mechanism for the following equilibrium. Please indicate any stereodetermining steps. Show the formation of all products. (8 pts) (*Hint: 1st step is the leaving group leaves*)



### Frontier Molecular Orbital Theory - The Reckoning

6. Frontier Molecular Orbital Theory (FMO Theory) states that the HOMO of the nucleophile interacts with the LUMO of the electrophile. (22 pts)

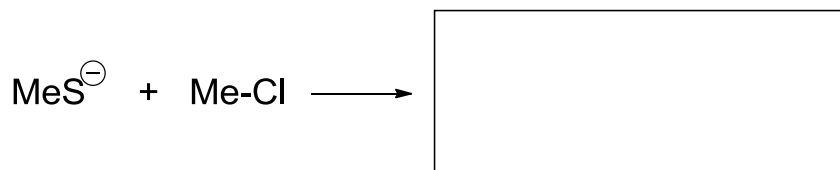
6. A. Circle the HOMO of  $\ominus$ SMe. The orbitals below are not in order.

$\sigma$ CH       $\sigma^*$ CS       $\sigma^*$ CH      nb S       $\sigma$ CS

6. B. Circle the LUMO of Me-Cl. The orbitals below are not in order.

$\sigma$ CH       $\sigma^*$ CCl       $\sigma^*$ CH      nb Cl       $\sigma$ CCl

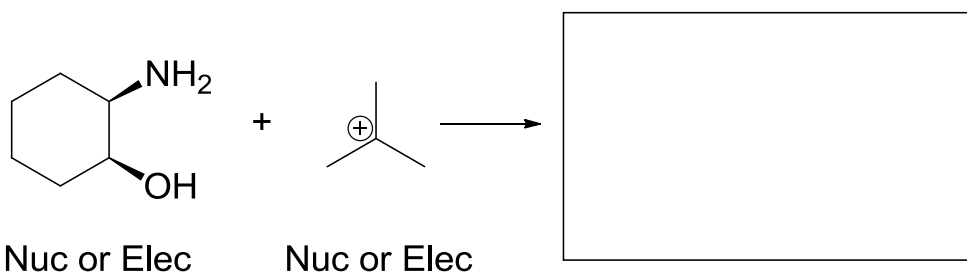
6. C. Based on FMO theory, predict the products of the reaction between  $\ominus$ SMe and MeCl.



6. D. Add electron-pushing arrows to the above reactants to clearly show the formation of your predicted products.

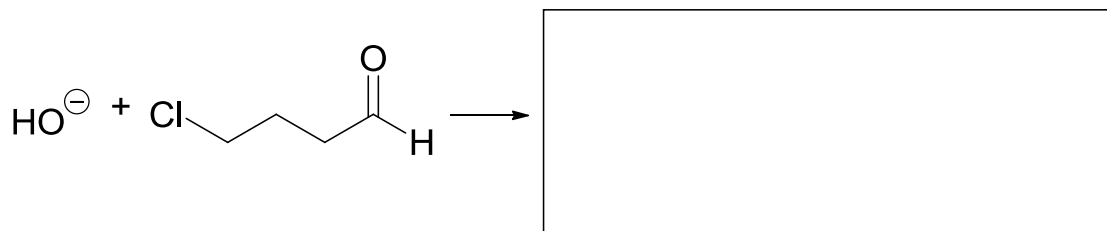
6. E. Label the stereocenters of the following molecules as R or S.

6. F. Circle the appropriate description of the below molecules. "Nuc" for the nucleophile and "Elec" for the electrophile.

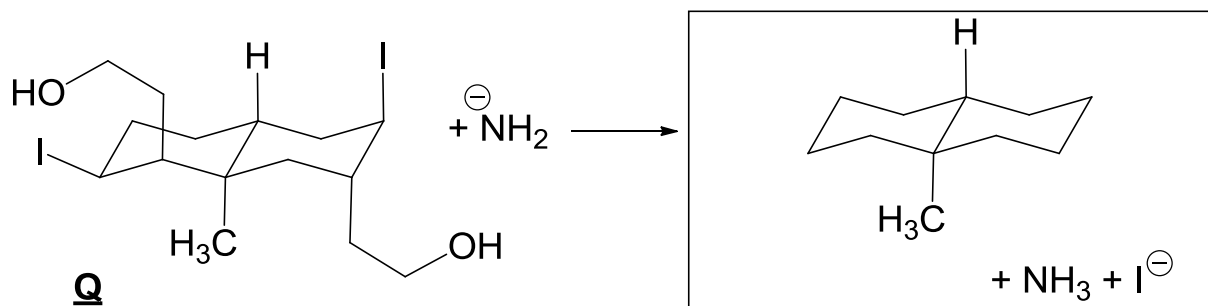


6. G. Predict the product of the above reaction based on FMO theory.

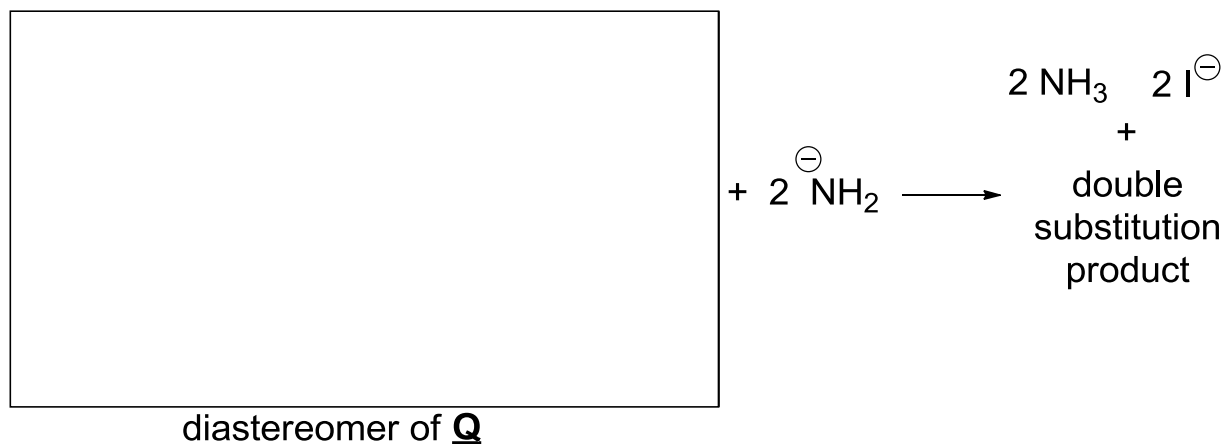
6. H. Predict the product of the following reaction based on FMO theory.



7. A. Predict the major mono-substitution product of the reaction below.  
**Add the appropriate groups to the template provided.** (3 pts)
7. B. In the space below the molecules, draw an electron-pushing mechanism that shows formation of the products. (8 pts)



7. C. Propose a diastereomer of compound **Q** that *can* undergo two intramolecular substitutions. (5 pts)



**You are incredible and have finished. Have a lovely night!**