Chemistry 112A, Midterm 2

Thursday, November 16, 2006

Student name: Answer Key

Student signature: ____________________

Write TA's full name (section number) or Lecture Only: ____________________

1. Please make sure that the exam has 8 pages including this one.
2. Please write your answers in the spaces provided.
3. Write clearly; illegible or ambiguous answers will be considered incorrect.
4. Only writing implements are allowed **(No Calculators)**.

GOOD LUCK!

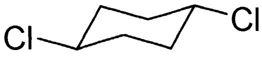
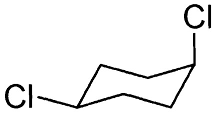
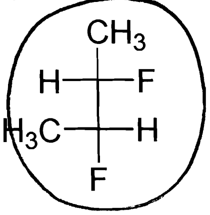
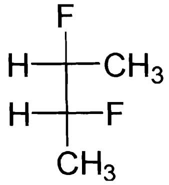
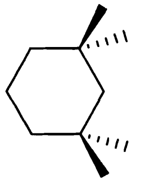
1.	60 points	______
2.	25 points	______
3.	8 points	______
4.	34 points	______
5.	20 points	______
6.	8 points	______
7.	8 points	______
8.	12 points	______
Total	**175 points**	______

MINI-PERIODIC TABLE

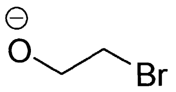
I	II	III	IV	V	VI	VII	VIII
H							**He**
Li	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
K	**Ca**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**

1. Answer the following questions. Every wrong answer cancels a correct answer (60 points).

(a). **Circle** the compound(s) that are meso compounds (6 points).

(b). **Number** the starting materials that cyclize fastest to slowest via an S_N2 reaction [1 = **fastest**] (6 points).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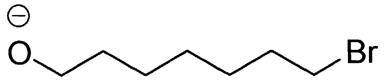
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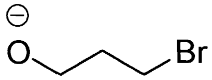
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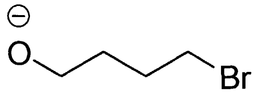
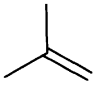
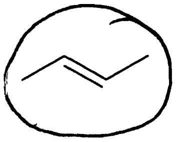
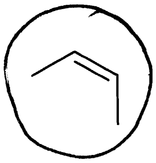
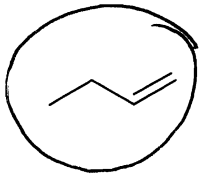
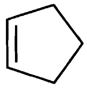
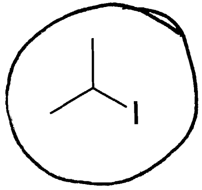
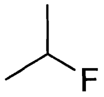
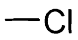
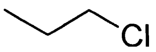
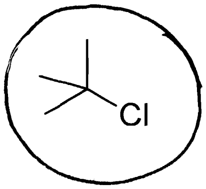

1

(c). **Circle** the alkene(s) listed below that upon reaction with HBr would give a racemic chiral product rather than an achiral product (6 points).

(d). **Circle** the alkyl halide(s) below that would undergo an S_N1 reaction more rapidly than isopropyl chloride (6 points).

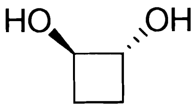
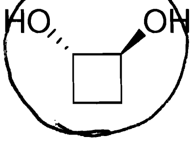
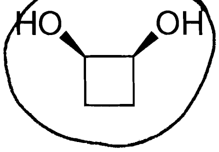
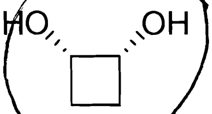
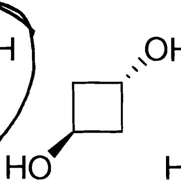
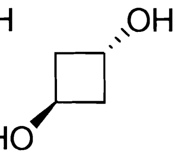
(e). **Circle** the correct statement(s) (6 points).

1. If a compound has a diastereomer it must be chiral.
2. Compounds that do not have any asymmetric carbons cannot be chiral.
[✓ 3.] If two stereoisomers are not enantiomers then they must be diastereomers.
4. All stereocenters are asymmetric carbons.
[✓ 5.] The reaction of a chiral compound with an achiral reagent can provide two product diastereomers in unequal amounts.

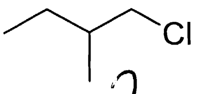
(f). **Circle** the correct statement(s) (6 points).

[✓ 1.] Chloride anion is a **faster** S_N2 nucleophile than iodide anion in aprotic solvents.
2. Chloride anion is a **faster** S_N2 nucleophile than iodide anion in protic solvents.
[✓ 3.] S_N1 and E1 reactions proceed via the same intermediate.
4. The rate of E1 reactions does not depend of solvent.
[✓ 5.] Primary alkyl halides cannot react by an E1 mechanism.

(g). **Circle** the compound(s) that contain **(S)** stereocenter(s) (6 points).

(h). **Number** the alkyl halides that provide the fastest to slowest S_N2 reaction [1 = **fastest**] (6 points).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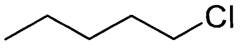
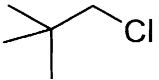

1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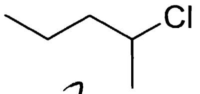
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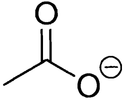
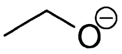
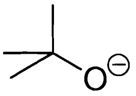
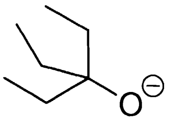
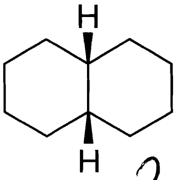
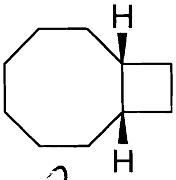
(i). **Circle** the nucleophile(s) that would react with isopropyl iodide primarily by S_N2 rather than elimination ~~[4 = fastest]~~ (6 points).

(j). **Number** the bicyclic $C_{10}H_{18}$ hydrocarbons according to their heats of formation, i.e., relative stability [1 = **most** stable] (6 points):


2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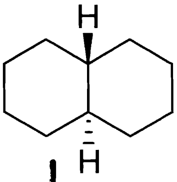
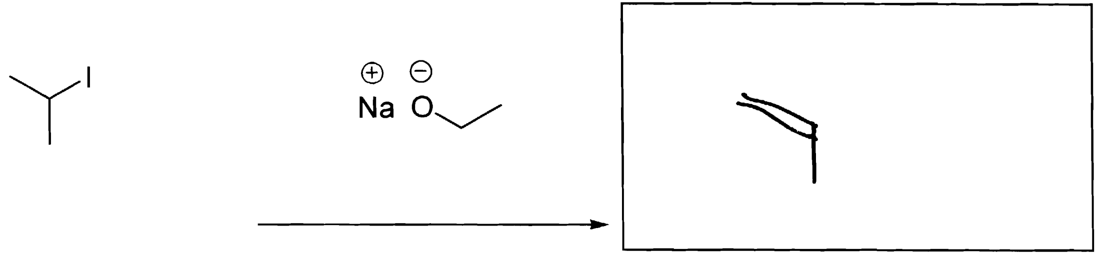
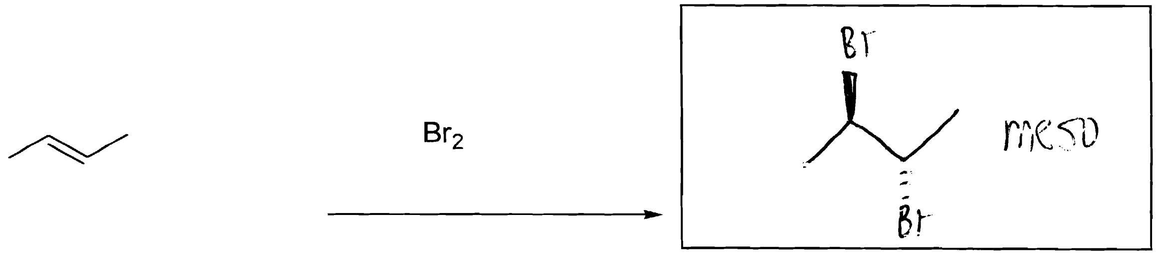

1

2. For each of the following reactions supply the missing starting materials, reagents, or major organic products in the space provided. Show the stereochemistry of the product. If the product is chiral indicate whether or not it is racemic (25 points total).

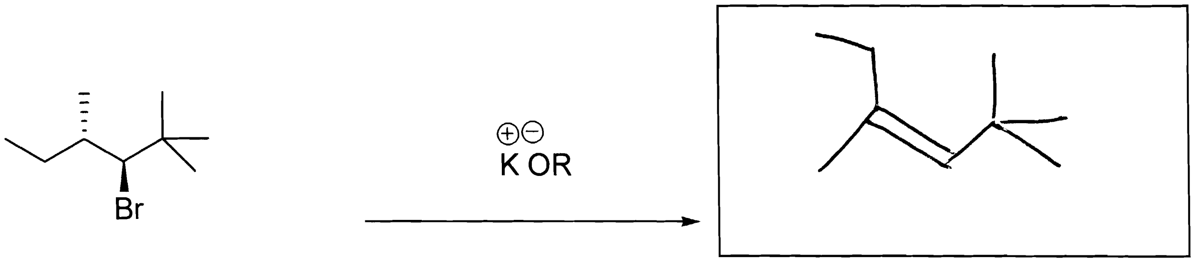
(a)

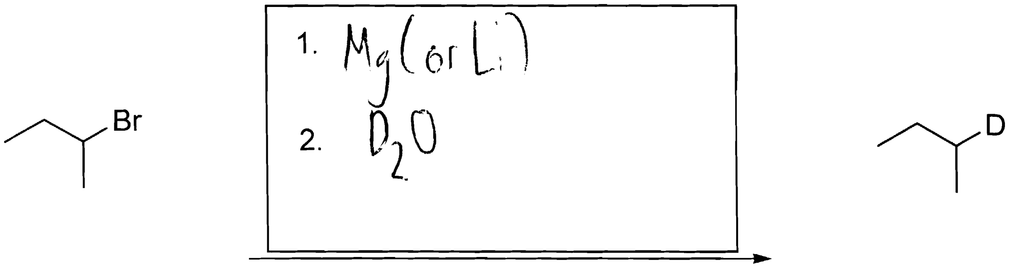


(b)

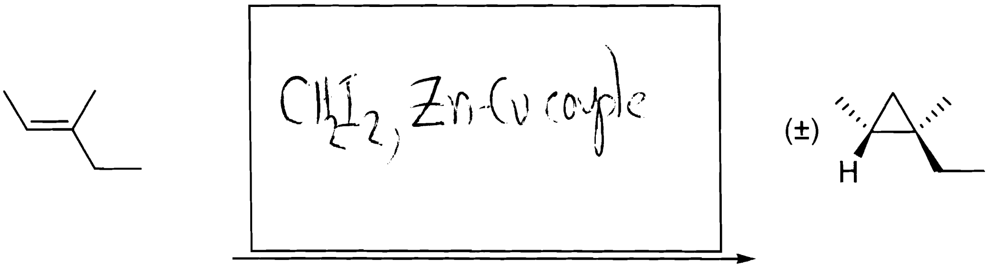


meso

(c) 

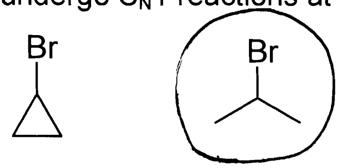
(d) 

1. Mg (or Li)
2. D_2O

(e) 

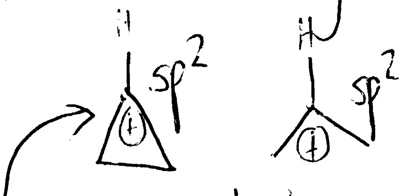
CH_2I_2, Zn-Cu couple

3. The two alkyl bromides shown below undergo S_N1 reactions at very different reaction rates.



a. **Circle** the alkyl bromide that undergoes the **fastest** S_N1 reaction (2 points)
b. Briefly explain the rationale for your answer (6 points).

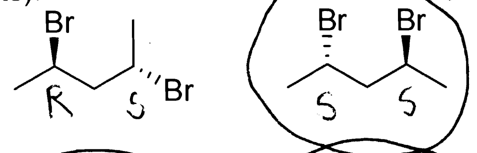
Even though both cation intermediates are 2°, the cyclopropyl cation is much higher in energy.



increased ring strain in going from $sp^3 \rightarrow sp^2$ hybrid makes intermediate cation (and t.s.) higher in energy

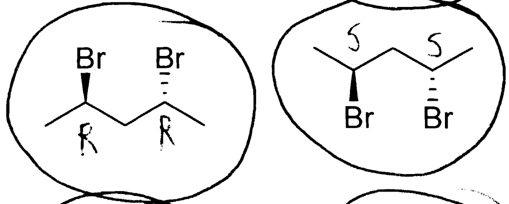
4. For each of the following pairs of structures **assign** the isomeric relationship, i.e., diastereomeric, enantiomeric, or identical (includes conformational). In addition, **circle** all of the compounds that are chiral (34 points).

(a)



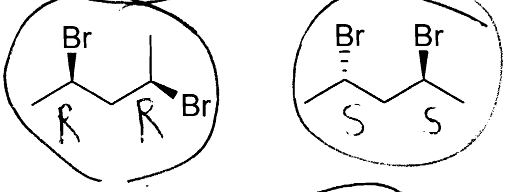
diastereomers

(b)



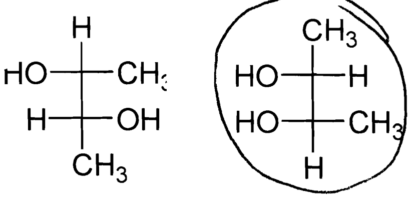
enantiomers

(c)



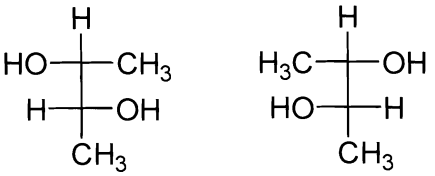
enantiomers

(d)



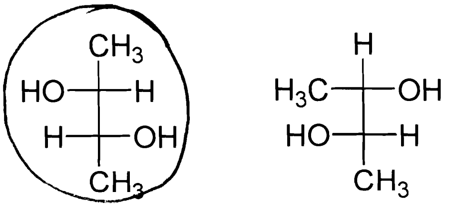
diastereomers

(e)



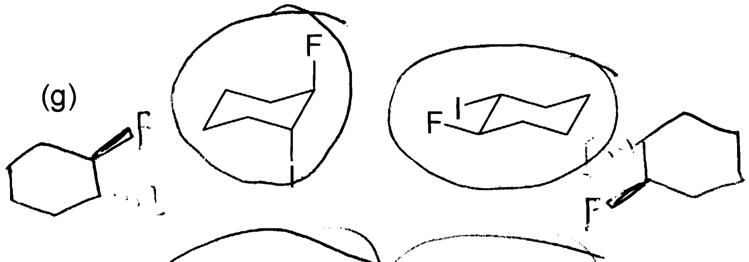
identical

(f)



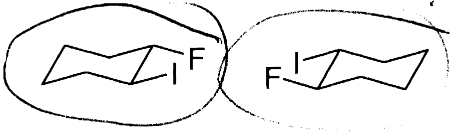
diastereomers

(g)



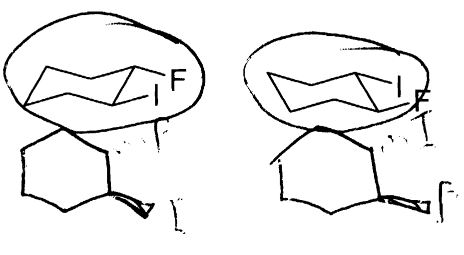
identical

(h)



enantiomers

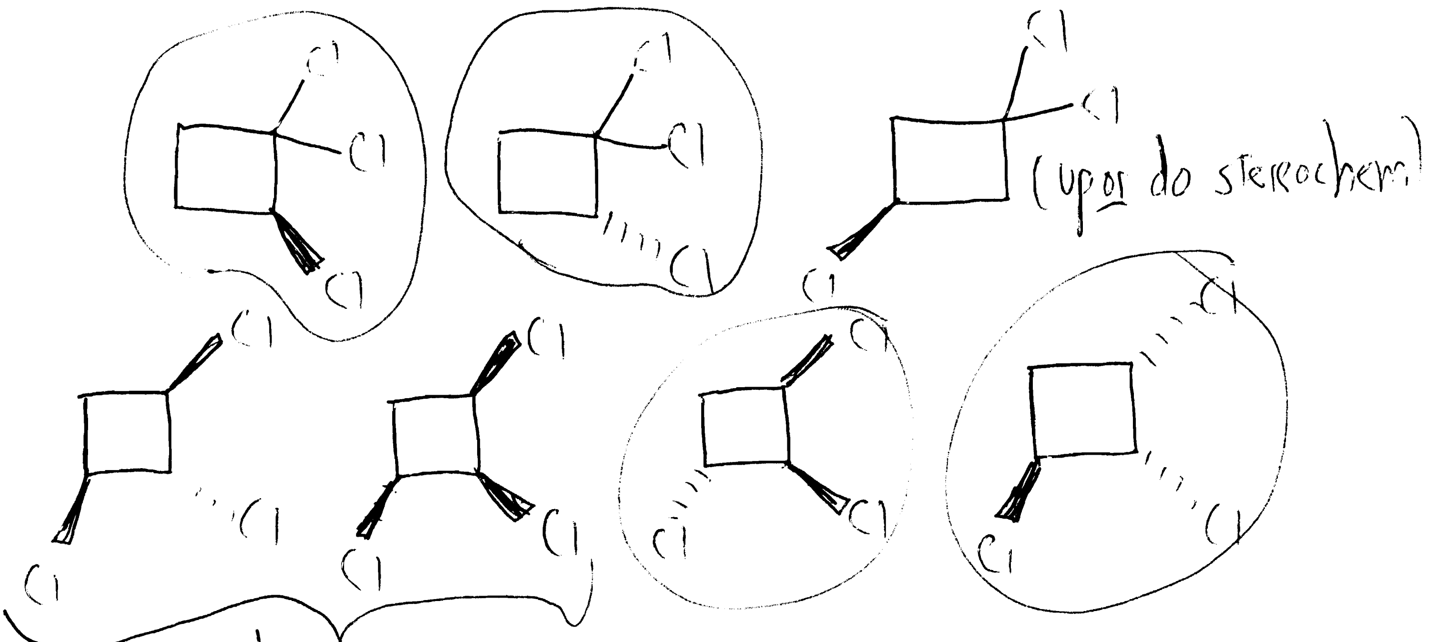
(i)



identical

5a. Draw **all** of the possible isomers of trichlorocyclobutane (**Four**-membered ring with **three** chlorines attached). List enantiomers, but points will be marked off for writing the same structure twice (16 points).

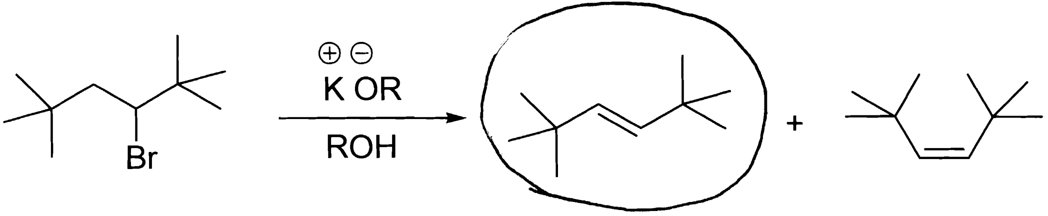
5b. Circle the chiral compounds (4 points).



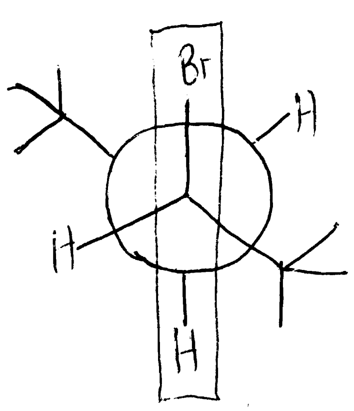
(up or do stereochem)

meso cmpds
(could also show view from opposite face)

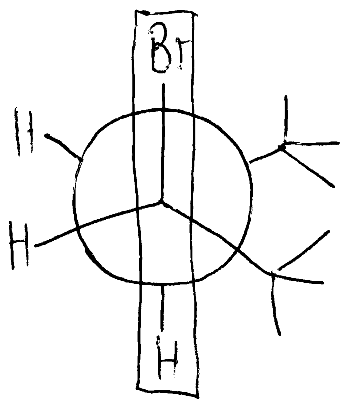
6. Treatment of the compound below with base results almost exclusively in **one** alkene stereoisomer.



a. **Circle** the stereoisomer that is primarily formed (2 points).
b. Use **Newman** projections of the starting material to explain the reaction stereoselectivity (6 points).

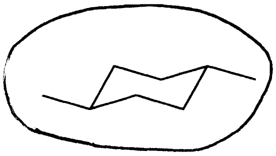


t-Bu groups anti - low energy conform. (trans product)



t-Bu groups - gauche - high energy (cis product)

7. Two dimethylcyclohexane constitutional isomers are shown below in their low energy conformations.



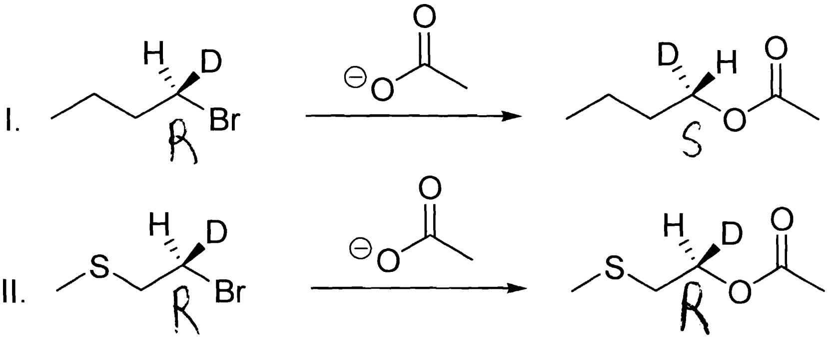
a. **Circle** the isomer for which the **smallest** amount of the chair flipped conformation is present at equilibrium (2 points).
b. Briefly **explain** your reasoning (6 points).

1. The circled isomer has only anti-methyl interactions with ring C-C bonds in its low energy conformation.

2. The other isomer has a gauche (unfavorable) interaction between the two methyl groups in the Low energy conformation.

3. The high energy conformations of both compounds have comparable interactions and energies.

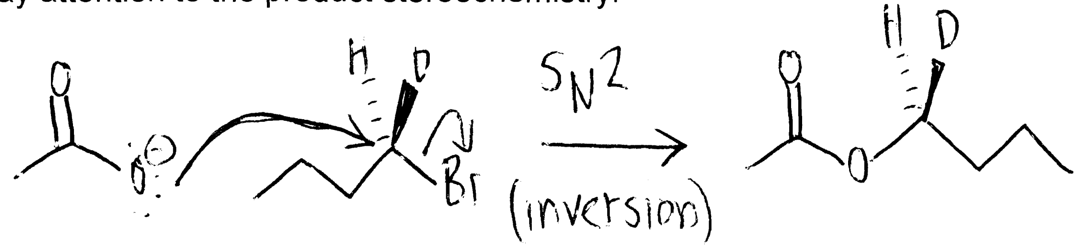
8. Two substitution reactions are shown below.



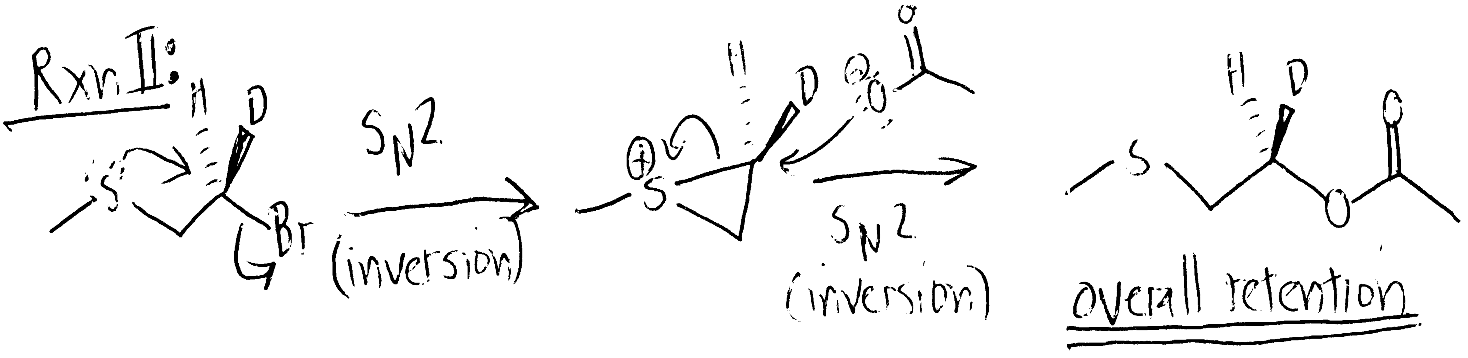
a. Assign the (R) or (S) configuration to the stereocenters in **each** of the starting materials and products (2 points).

b. Provide a mechanism for **each** reaction (10 points).
Hint: Pay attention to the product stereochemistry.

Rxn I:



Rxn II:



overall retention