Exam 2 Summer 2017

Name Key Seat Number_____

Student ID_____

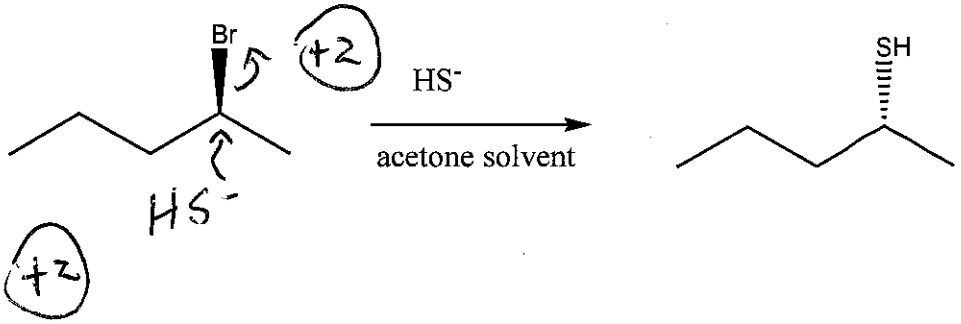
The exam consists of 8 questions worth 104 points on a total of 10 pages. It will be scored out of 100 points. The maximum score you may receive is 100 points.

1. _____/14
2. _____/12
3. _____/12
4. _____/12
5. _____/12
6. _____/12
7. _____/16
8. _____/14

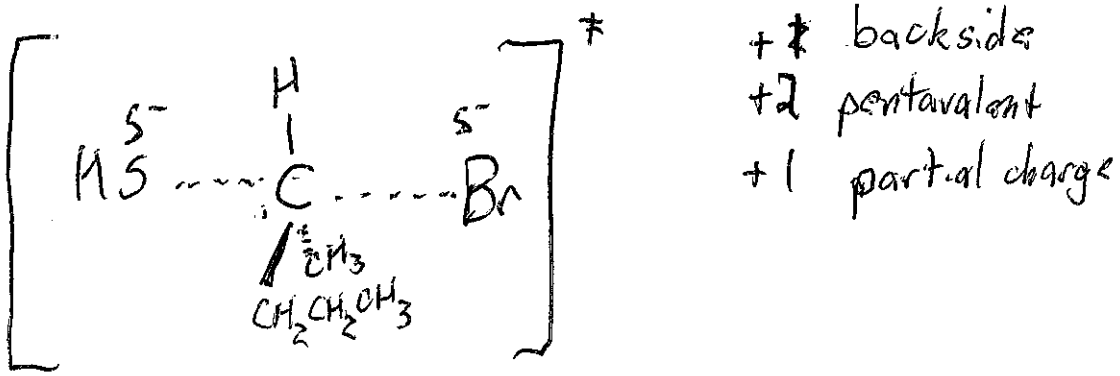
Total:

Regrading: All requests for regrades must be submitted in writing within 48 hours of the return of the exam. You must explicitly state what has been misgraded and why it is an error. The entire exam will be regraded, which could result in points being added or deducted overall.

1. (14pts) Draw an arrow mechanism for the following bimolecular substitution reaction.



In the space below, draw a structure of the transition state for the rate determining step of the reaction:



Would you expect the following changes to the reaction to make the rate of the reaction faster, slower, or stay the same? if S_N2 ; if S_N1 +1 each

Change the nucleophile to H_2S: slower ; unchanged

Change the solvent to CH_3CH_2OH: slower ; faster

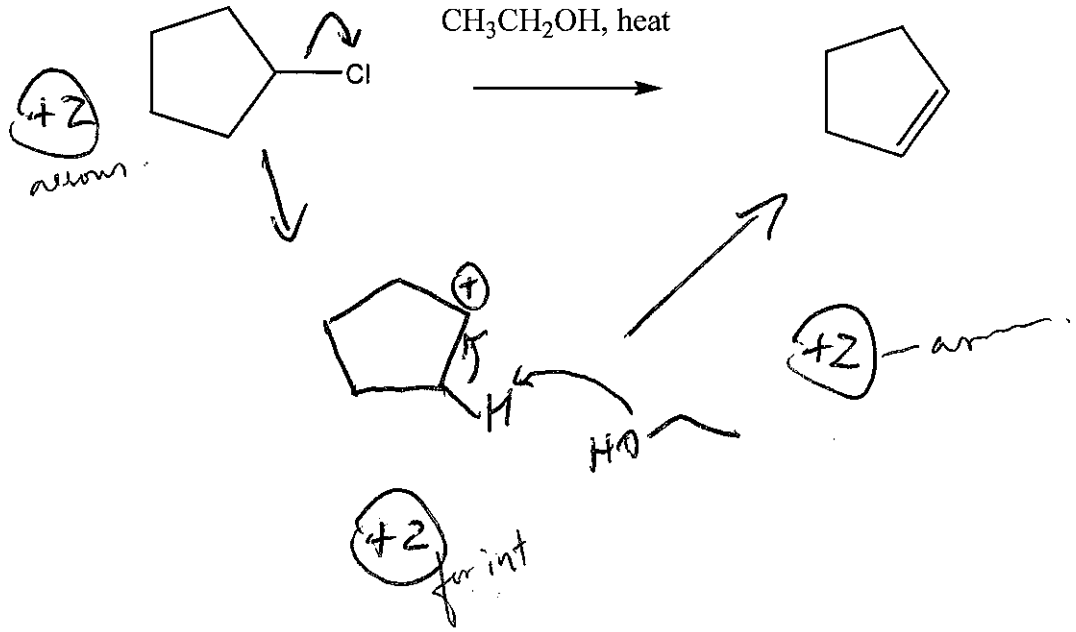
Change the substrate to (R)-2-bromopentane: no effect ; N/A

Heat the reaction: Faster ; faster

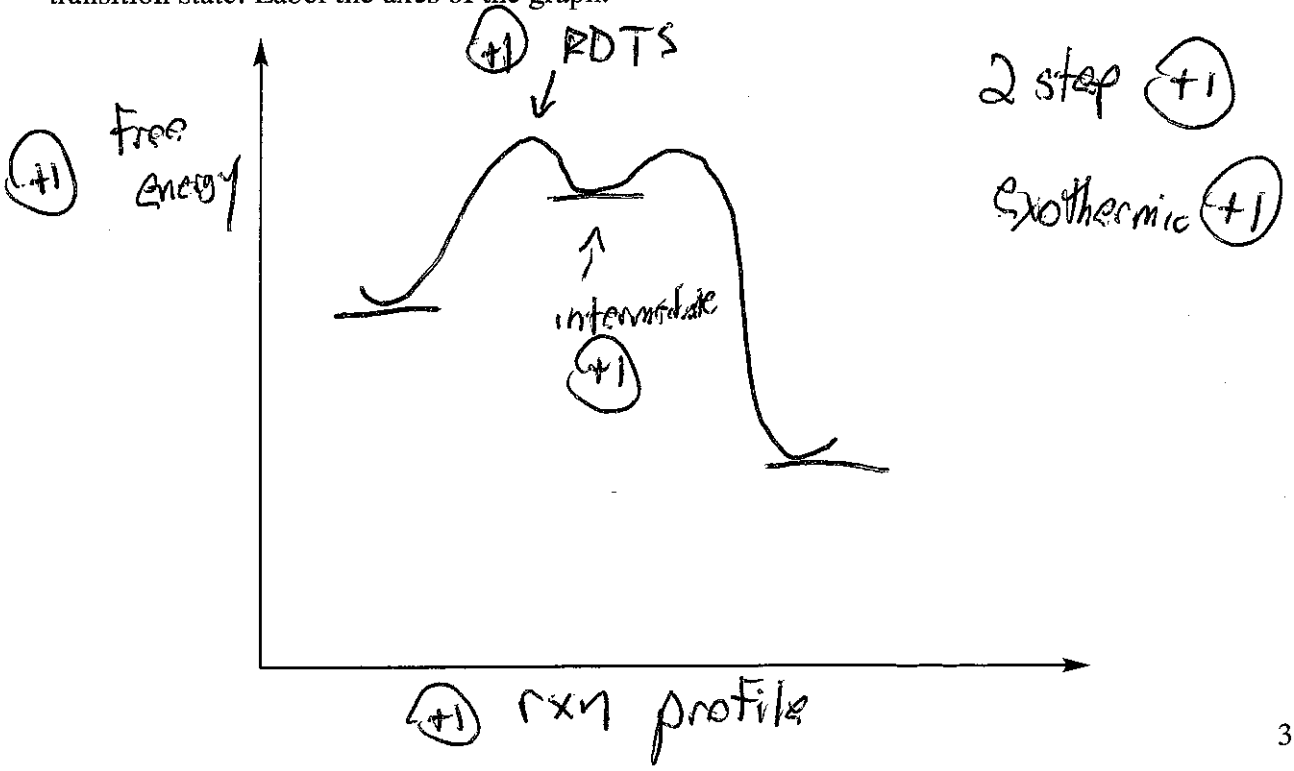
Change the leaving group to HO^-: slower ; slower

Change the substrate to 2-bromo-2-methylpentane: slower ; faster

2. (12pts) Draw an arrow mechanism for the following E1 elimination reaction, including all intermediates.

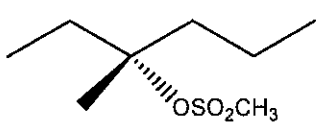


Draw an energy diagram based on the mechanism you proposed, assuming that the reaction is exothermic overall. On the energy diagram, label the intermediate and the rate determining transition state. Label the axes of the graph.



3. (12pts) Choose TWO of the following THREE <u>substitution</u> reactions. Propose a major product for the reaction and label the mechanism of formation of the product as Sn1 or Sn2. Clearly mark the one you do not want graded or else the first two will be graded.

A.

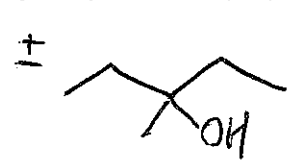


H_2O

S_N1

+2

optically inactive $C_7H_{16}O$ compound

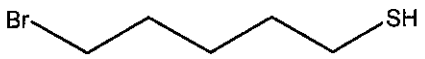


+4

stereochem

-2

B.



HO^-

DMF

+2

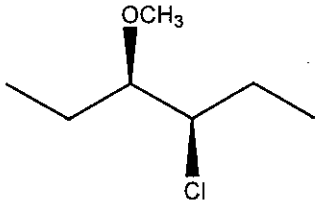
S_N2

$C_5H_{10}S$ product

+4

-2

C.



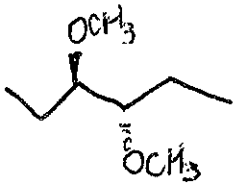
CH_3O^-

acetone

+2

S_N2

optically inactive $C_8H_{18}O_2$ compound

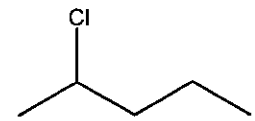


+4

-2

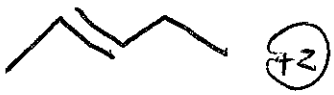
stereo

4. (12pts) Choose 3 of the following 4 ELIMINATION reactions, and indicate whether the reaction mechanism will be E1 or E2. Predict the major product(s) of the three reactions you chose. Be sure to include proper stereochemistry. Put an "X" in the box you do not want graded, or else the first three will be graded.



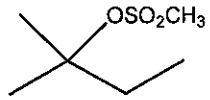
HO^-
DMF

E1 or E2? E2 (+2)



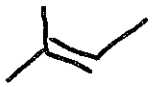
(+2)

+1



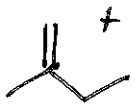
CH_3OH

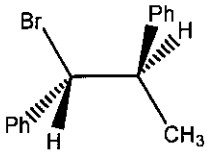
E1 or E2? E1 (+2)



(+2)

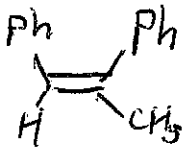
+1



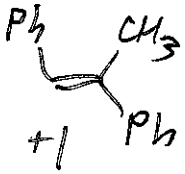


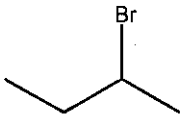
CH_3O^-

E1 or E2? E2 (+2)



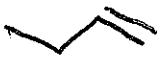
(+2)





$(CH_3)_3CO^-$

E1 or E2? E2 (+2)

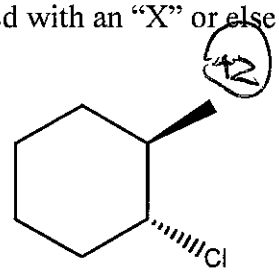


(+2)

+1

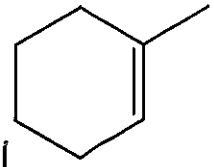
5. (12pts) Indicate which of the reagents or starting materials is necessary for 3 of the following 4 transformations, then EXPLAIN your choice. CLEARLY MARK the one you do not want graded with an "X" or else the first three will be graded.

A.



12

a. weak base
b. strong base
c. weak nucleophile
d. strong nucleophile

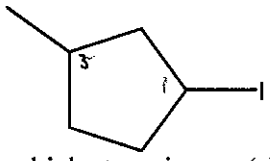


or a and c

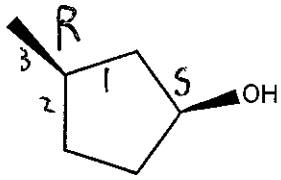
12

Must go through E1 to get this regiochem - no antiperiplanar βH

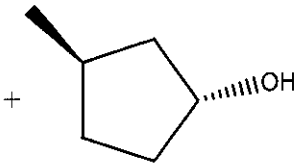
B.



water, heat



+



which stereoisomer(s)?

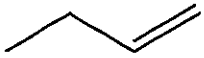
a. (1R, 3R)
b. (1R, 3S)
c. (1S, 3S)
d. (1S, 3R)

E1 leads to racemation, so either stereocenter at carbon #1

C.

a. 1-bromobutane
b. R-2-bromobutane
c. S-2-bromobutane
d. racemic 2-bromobutane

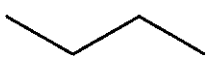
CH_3O^-



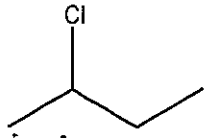
major product

E2 with unhindered base - all other choices would give the more substituted alkene

D.

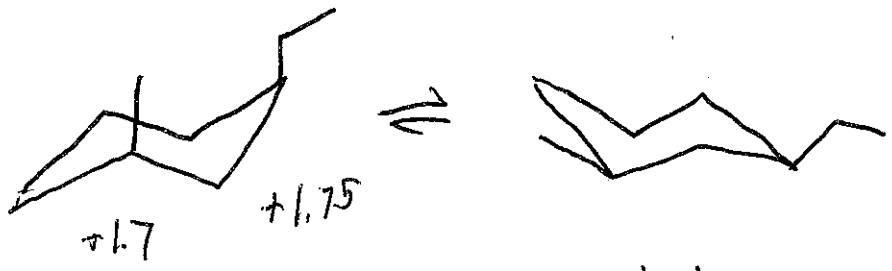


a. HCl
b. Cl_2, light
c. NaCl



This requires radical halogenation

6. (12pts) Draw two chair conformations for cis-1-ethyl-3-methylcyclohexane.



+2 chairs
+1 cis
+1 1,3

+2 axial/equatorial

Use data from the table below to determine the difference in stability between the two conformations in kcal/mol.

Substituent in axial position	ΔG° (kcal/mol)
-H	0
$-CH_3$	1.7
$-CH_2CH_3$	1.75
$-CH(CH_3)_2$	2.2
$-C(CH_3)_3$	5.0

$\Delta G^\circ = +3.45$

+4

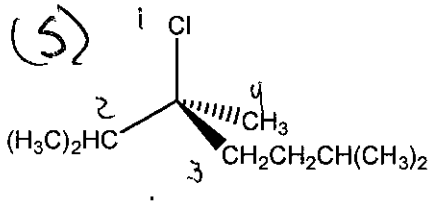
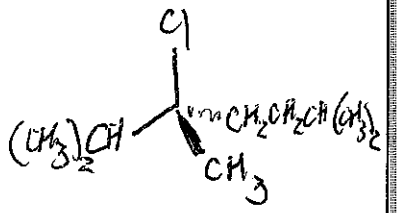
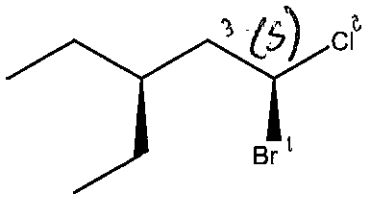
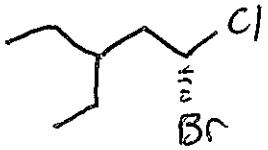
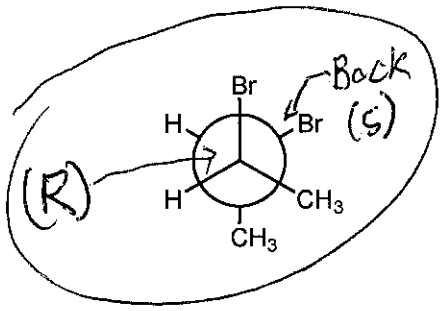
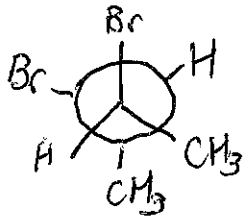
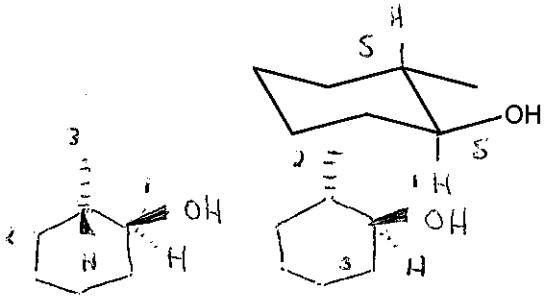
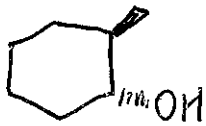
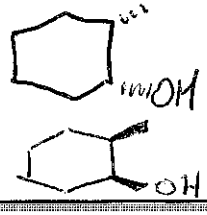
Use the thermodynamic rule of thumb to approximate the percentage of each conformation at equilibrium: 90%/10%, 99%/1%, 99.9%/0.1%, or in between those values.

+2 Between 99%/1% and 99.9%/.1%

7. (16pts) On the compounds below, mark each chiral center R or S, as appropriate. In the boxes next to them, draw their enantiomer and draw one diastereomer. If the compound does not have an enantiomer or diastereomer, write "None" in the appropriate box. Blank boxes will be marked incorrect.

+1 each (6pts)

+1 each (8 pts)

	enantiomer	diastereeomer
		None
		None
	None	
		

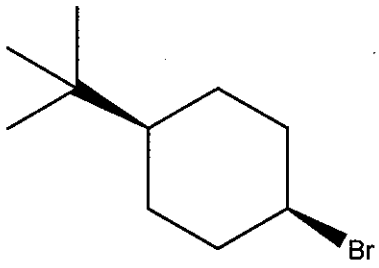
Circle any of the compound above that are meso compounds.

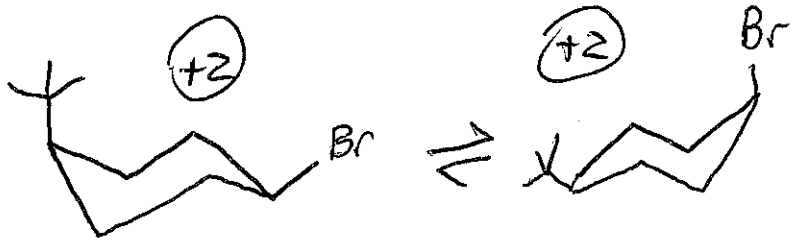
+2 for correct meso

-1 for any additional

} Minimum score = zero

8. (14pts) Draw two chair conformations for the compound below. Which of the two is the more stable structure? Which of the two is the reactive conformation for an E2 reaction?

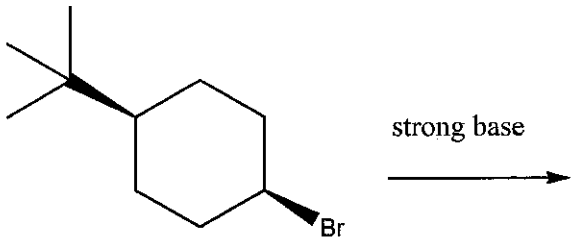


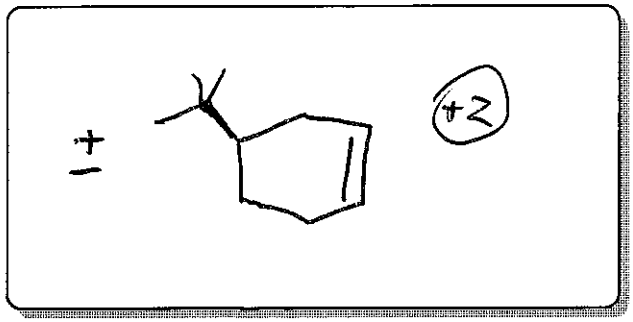


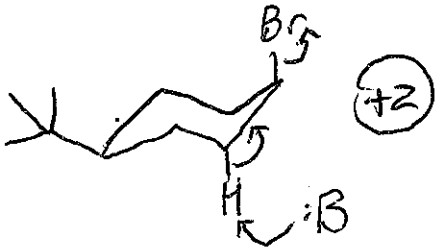
+2 ★ more stable

+2 ★ reactive

Draw a mechanism for the elimination of this molecule under E2 conditions. Be sure to draw the starting material in its reactive conformation. What product(s) are produced?







Is the product of this reaction optically active or optically inactive? Explain.

+2 inactive - racemic mix