Chemistry 351
Exam #2
November 13, 2019

Name: _____

Student Number: _____

Section Number: _____

TA: _____

INSTRUCTIONS:

This examination consists of 27 questions on 10 pages. Please make certain that your examination is complete.

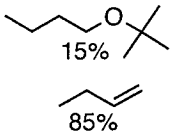
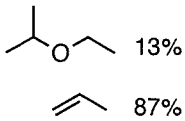
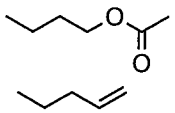
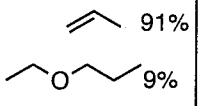
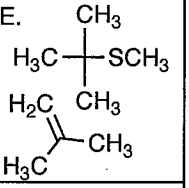
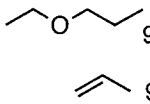
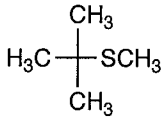
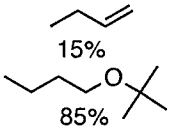
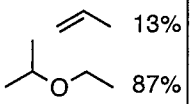
Write your name, student number, and section number **on both the examination and answer sheet. Be certain to bubble in your PID digits on the answer sheet. The absence of any of these identification items will result in the deduction of 2 points from your score.**

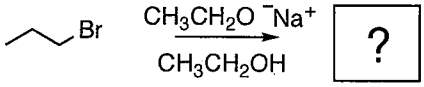
Questions 1-20 are each worth 3 points. Point totals for Questions 21-27 are indicated on the exam.

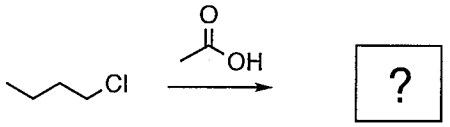
Write your answers to Questions 1- 20 on the enclosed answer sheet. **Write your answers to Questions 21-27 in the space provided on this examination.**

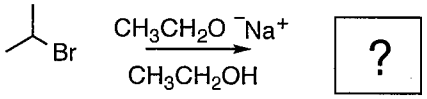
When you complete the examination, insert your answer sheet into your examination and then hand both in on the bench in front of the lecture hall in the spot indicated by your section number.

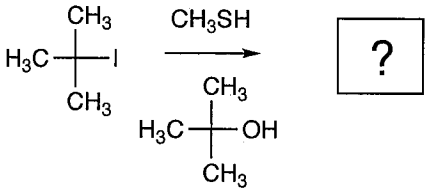
Questions 1-5 are to be answered from the following possibilities:

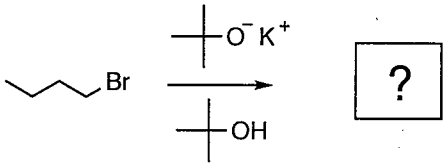
A. 	B. 	C. 	D. 	E. 
F. 	G. 	H. 	I. 	J. No Reaction

1. 

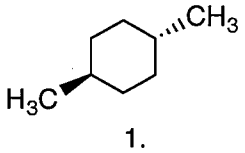
2. 

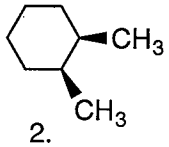
3. 

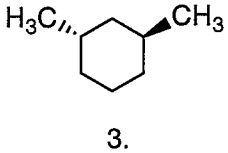
4. 

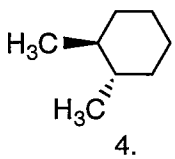
5. 

6. Identify which of the following dimethylcyclohexanes is chiral:


1.

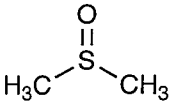
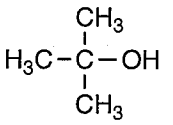
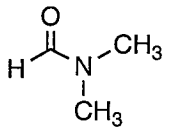
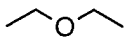
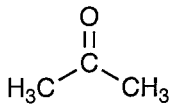

2.


3.

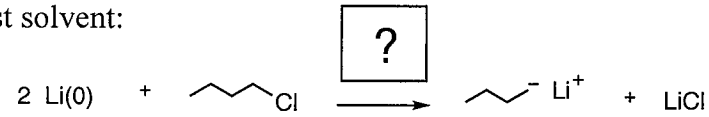

4.

a. 1 b. 2 c. 3 d. 4 e. 1,2 f. 1,3 g. 1,4 h. 2,3 i. 2,4 j. 3,4

Questions 7-10 are to be answered from the following possibilities:

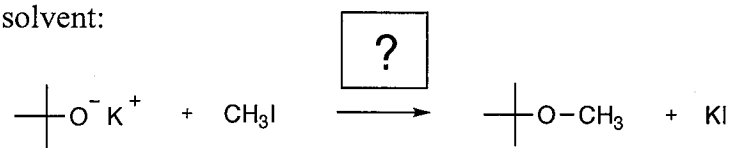
A. 	B. 	C. CH_3CH_2OH	D. 	E. $CH_3C{\equiv}N$
F. CF_3CH_2OH	G. 	H. 	I. CH_3CH_2SH	J. CH_3OH

7. Identify the best solvent:

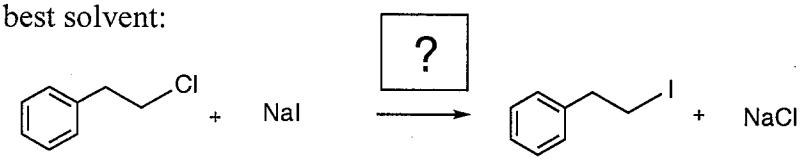


8. Identify the molecule whose conjugate base is destabilized due to steric crowding/interference with solvation.

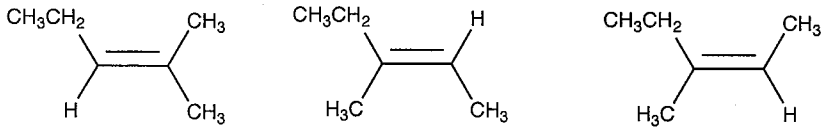
9. Identify the best solvent:

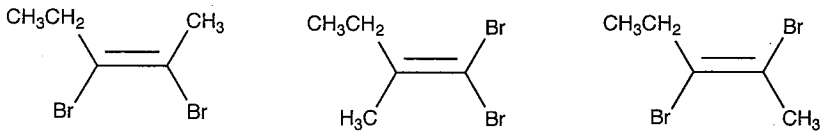


10. Identify the best solvent:



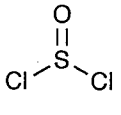
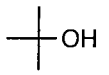
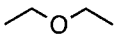
11. Which of the following alkenes have an *E* absolute configuration:

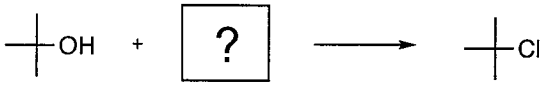


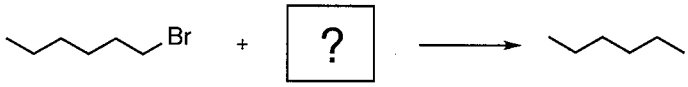


a. 1,4 b. 1,5 c. 1,6 d. 2,4 e. 2,5 f. 2,6 g. 3,4 h. 3,5 i. 3,6 j. 5,6

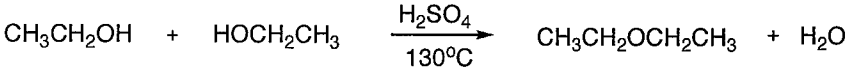
Questions 12-16 are to be answered from the following possibilities:

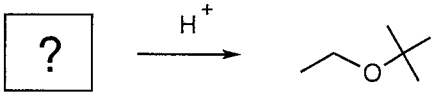
A. E2	B. 	C.  CH_3CH_2OH	D. S_N2	E. $NaBH_4$ CH_3OH
F.  $H_2C=CH_2$	G. S_N1	H. $LiAlH_4$ 	I. HCl	J. E1

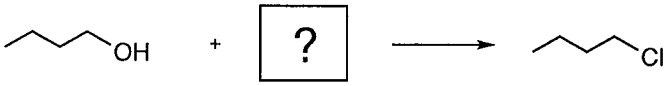
12. 

13. 

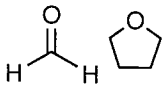
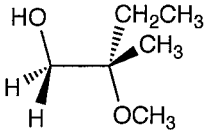
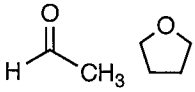
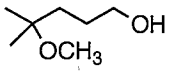
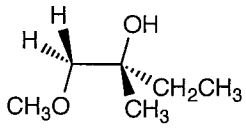
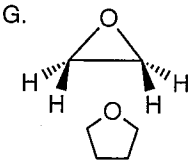
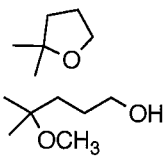
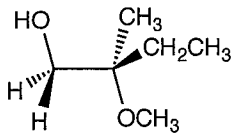
14. What is the mechanism of this conversion:

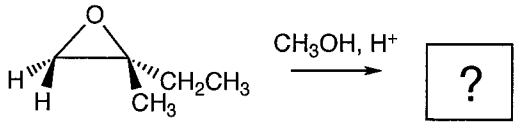


15. 

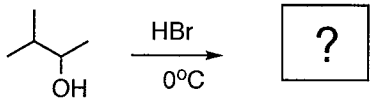
16. 

Questions 17-20 are to be answered from the following possibilities:

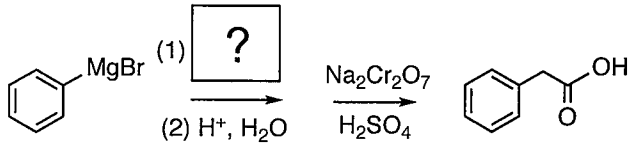
A. 	B.  H_2O	C. 	D. 	E. 
F. 	G. 	H. 	I.  H_2O	J. 

17. 

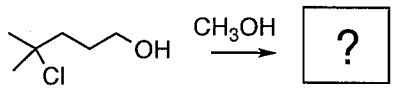
18. Identify the major product formed in this reaction:



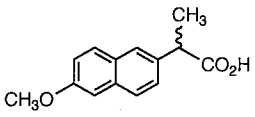
19. Identify the missing reagent in this synthesis:



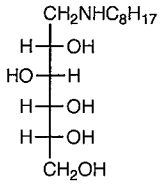
20.



21. (4 pts) (*R*,*S*)-Naproxen is resolved into its individual enantiomers using (+)-*N*-octyl-D-glucamine to afford the analgesic, antiinflammatory (*S*)-naproxen that has been purified away from the liver toxin (*R*)-naproxen.



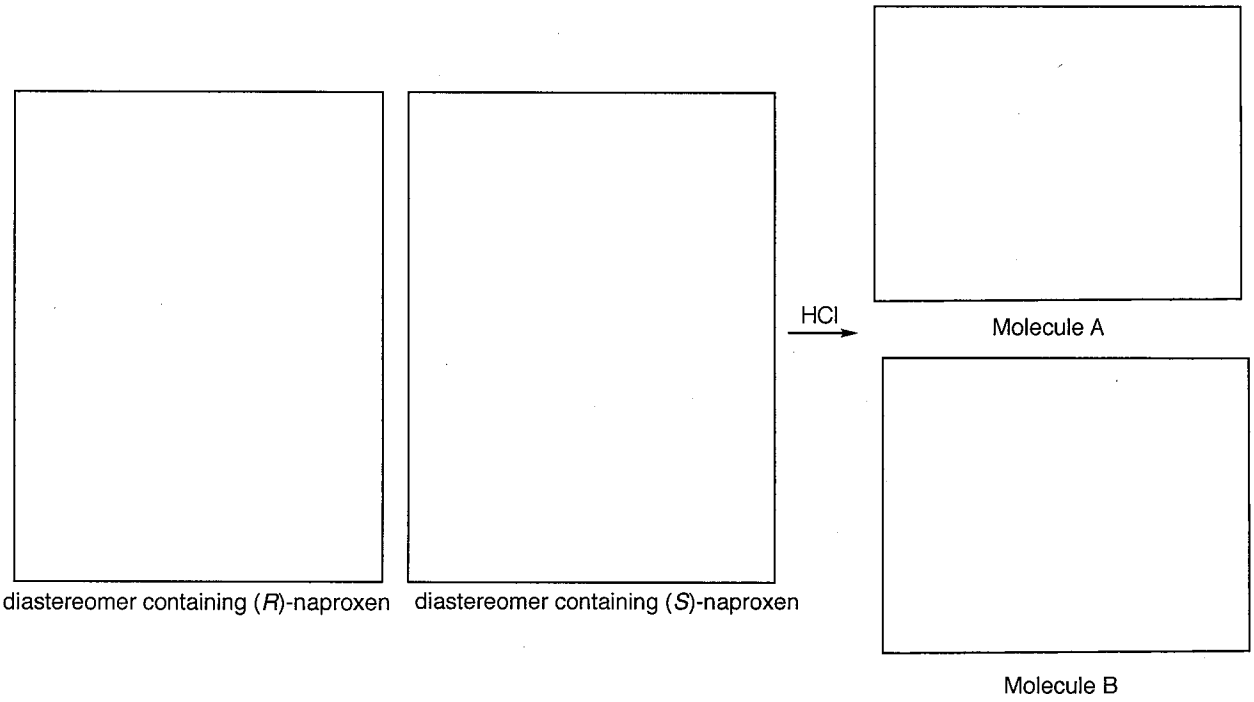
(R,S)-naproxen



(+)-N-octyl-D-glucamine

a. In the labeled boxes, provide the structures of the two diastereomers containing (*S*)-naproxen and (*R*)-naproxen from which the diastereomer containing (*S*)-naproxen selectively crystallizes from methanol/toluene.

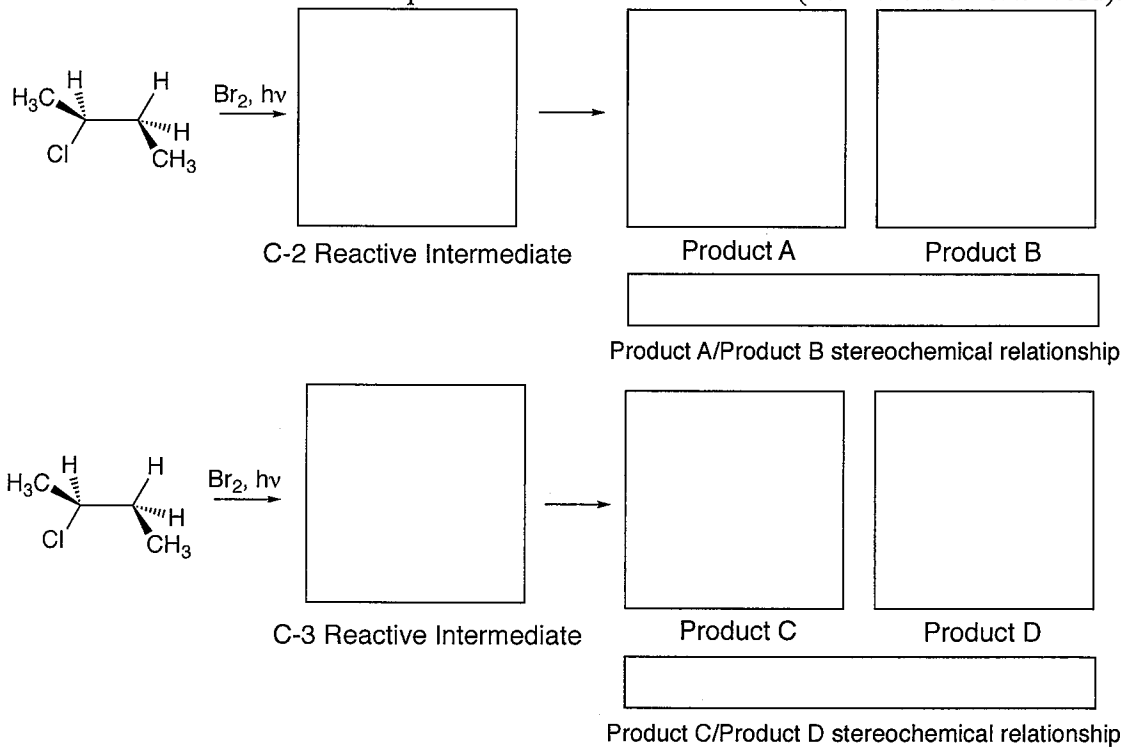
b. In the labeled boxes, provide the structure of Molecule A and Molecule B that result from treatment of the crystallized diastereomer containing (*S*)-naproxen with HCl.



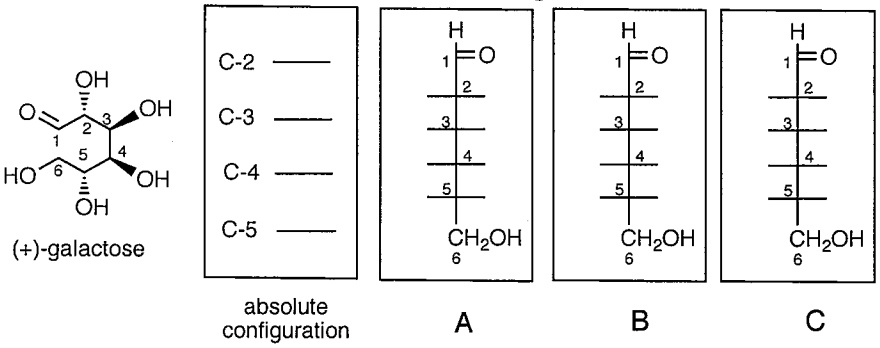
diastereomer containing (*R*)-naproxen

diastereomer containing (*S*)-naproxen

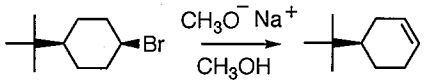
22. (8 pts) For the reaction of 2-*S*-chlorobutane with Br_2 and light, provide:
   a. the reactive intermediate resulting from exclusive reaction at C-2,
   b. the structure of Products A and B resulting from exclusive reaction at C-2,
   c. the stereochemical relationship of Product A and Product B (no more than one word),
   d. the reactive intermediate resulting from exclusive reaction at C-3,
   e. the structure of Products C and D resulting from exclusive reaction at C-2,
   f. the stereochemical relationship of Product C and Product D (no more than one word).



23. (8 pts) For the structure of (+)-galactose, provide in the labeled boxes:
   a. the absolute configurations of the stereocenters at C-2, C-3, C-4 and C-5,
   b. the completed Fischer projection of (+)-galactose in Box A,
   c. the completed Fischer projection of the stereoisomer of (+)-galactose in Box B that when dissolved with an equimolar amount of (+)-galactose results in a solution that does not rotate plane-polarized light,
   d. the completed Fischer projection of a diastereomer of (+)-galactose in Box C that has C-2, C-3, C-4 and C-5 stereocenters all with *S* absolute configurations.



24. (5 pts total) Elimination of bromide from *cis*-1-bromo-4-*t*-butylcyclohexane promoted by sodium methoxide in methanol.

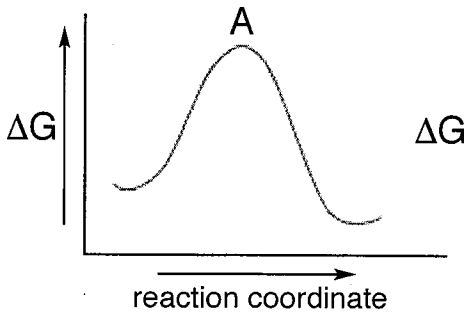


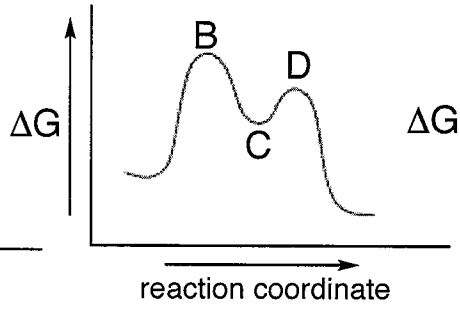
(a) In the labeled box, draw the most stable chair conformer of substrate *cis*-1-bromo-4-*t*-butylcyclohexane with the *t*-butyl group, bromine, and all ring hydrogen atoms shown.
(b) In the labeled box, provide the structure of a Reactive Intermediate or Transition State that precedes formation of 4-*t*-butyl-1-cyclohexene.
(c) For the Reactive Intermediate or Transition State, draw ALL arrows showing the flow of electrons during conversion of *cis*-1-bromo-4-*t*-butylcyclohexane into 4-*t*-butyl-1-cyclohexene.
(d) In the provided potential energy diagrams, CIRCLE THE SINGLE LETTER that corresponds to the position of the Reactive Intermediate or Transition State that precedes formation of 4-*t*-butyl-1-cyclohexene.
(e) In the labelled box, provide the rate expression for the conversion of *cis*-1-bromo-4-*t*-butylcyclohexane into 4-*t*-butyl-1-cyclohexene.

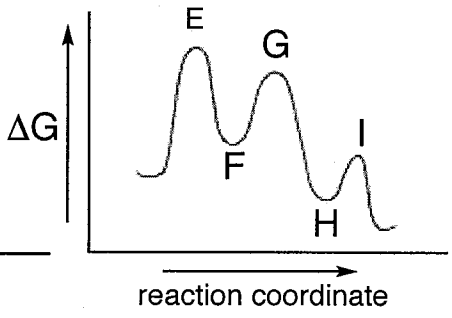
Most StableConformer:
cis-1-bromo-4-*t*-butylcyclohexane

CH_3O^- Na^+

Reactive Intermediate or Transition State



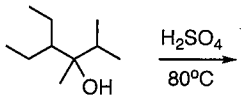




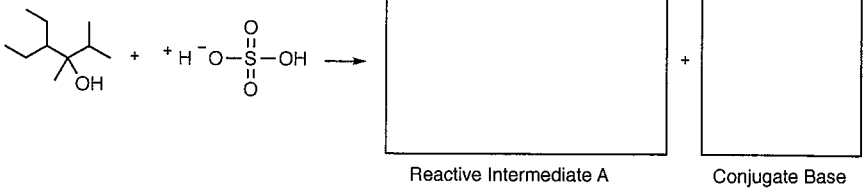
-d[substrate]/dt =

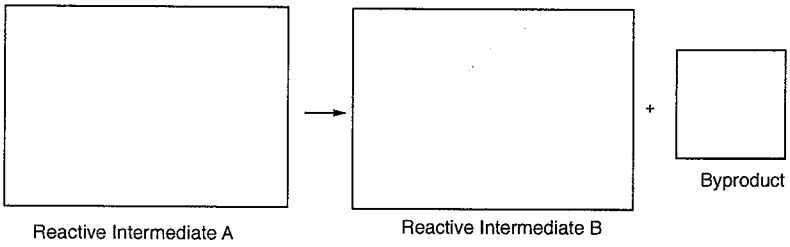
Rate Expression

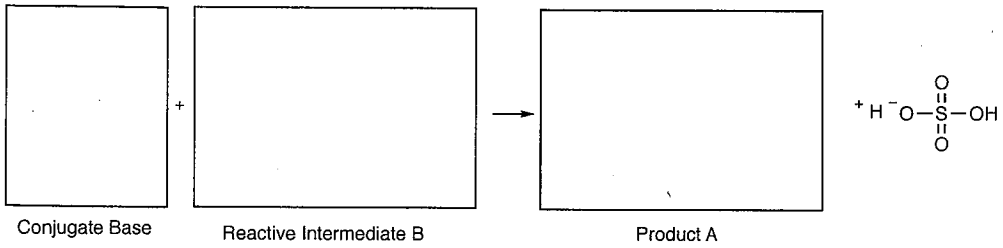
25. (5 pts) Three products are formed when 4-ethyl-2,3-dimethyl-3-hexanol is heated with sulfuric acid:

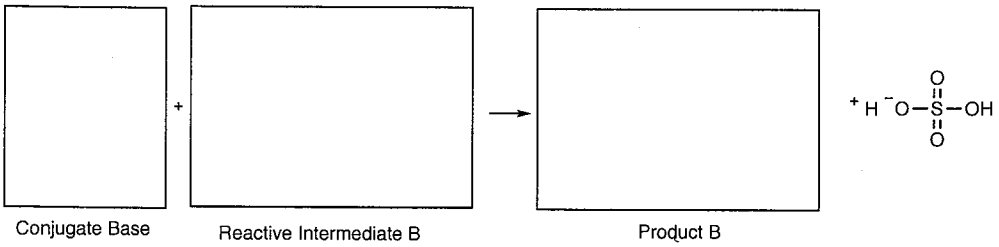


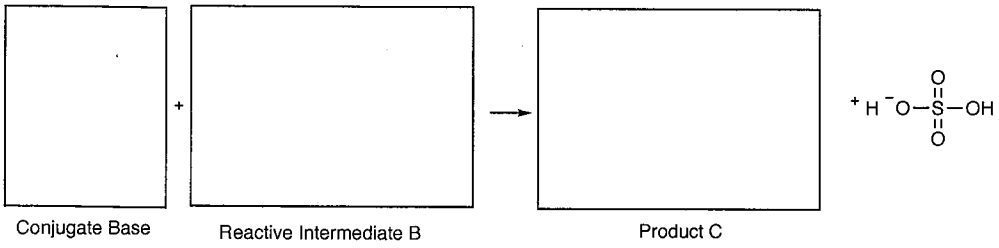
a. Provide the arrow(s) showing the flow of electrons in the reaction of 4-ethyl-2,3-dimethyl-3-hexanol with sulfuric acid leading to Reactive Intermediate A and a Conjugate Base.
b. In the labeled boxes, provide the structures of Reactive Intermediate A and Conjugate Base.
c. Provide the arrow(s) showing the flow of electrons during the conversion of Reactive Intermediate A into Reactive Intermediate B and a Byproduct.
d. In the labeled boxes, provide the structures of Reactive Intermediate B and the Byproduct.
e. Provide the arrow(s) showing the flow of electrons during reaction of the Conjugate Base with Reactive Intermediate B leading to Product A, Product B, and Product C.
f. In the labeled boxes, provide the structures of Product A, Product B, and Product C.



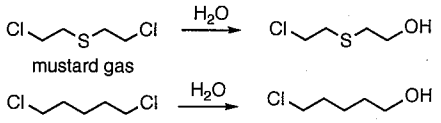








26. (6 pts) Mustard reacts thousands of times faster with water than 1,5-dichloropentane. This question deals with the dramatic increase in hydrolysis rate for mustard.



a. Provide the arrow(s) depicting the flow of electrons for the conversion of mustard gas into Reactive Intermediate A in water.

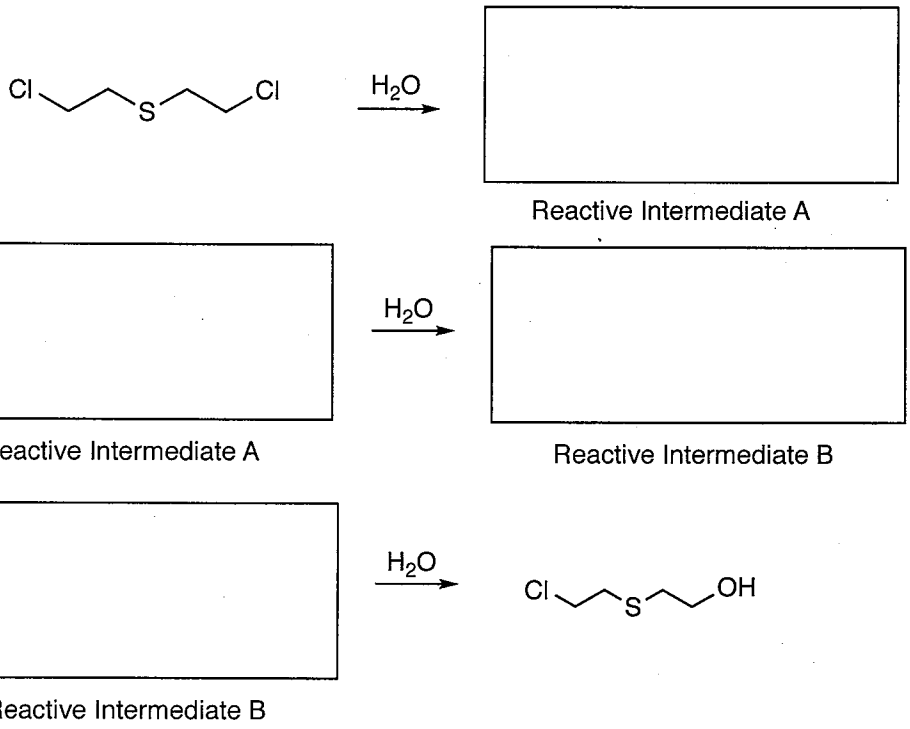
b. In the labeled box, provide the structure for Reactive Intermediate A.

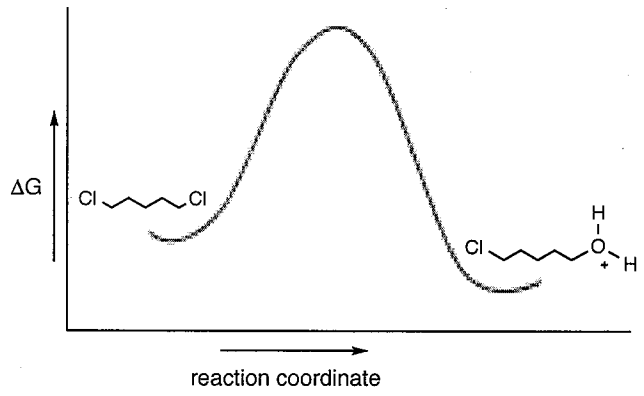
c. Provide the arrow(s) depicting the flow of electrons for conversion of Intermediate A into Intermediate B in water.

d. In the labeled box, provide the structure for Reactive Intermediate B.

e. Provide the arrow(s) depicting the flow of electrons for conversion of Intermediate B in water into partially hydrolyzed mustard.

f. Underneath the potential energy diagram for partial hydrolysis of 1,5-dichloropentane into an oxonium ion, provide a potential energy diagram for conversion of mustard gas into Reactive Intermediate B that explains the heightened reactivity of mustard gas with water. On the potential energy diagram, label where the mustard gas, Reactive Intermediate A, and Reactive Intermediate B are situated.





27. (4 pts)

a. In the labeled box, provide the structure of the Intermediate formed when 5-*(R)*-5-bromo-5-deuterio-1-pentanol is reacted with sodium hydride.

b. Provide the flow of electrons when the Intermediate undergoes reaction to afford the Product.

c. In the labeled box, provide the structure of the organic Product.