

PRACTICE EXAM 2A

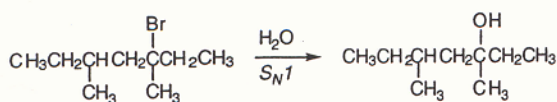
(Some ACID BASE QUESTIONS TOO)

Questions 1-20 are multiple choice. Choose the best answer and blacken the appropriate circle on your answer sheet.

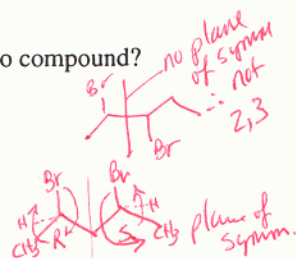
- Which of these is NOT a Lewis acid?
A) AlCl_3
B) H^+
C) BCl_3
D) H_2S
E) CH_3^+
- Which of the following pairs of reactants would undergo no reaction?
A) aqueous $\text{NaOH} + \text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$
B) ethene + $\text{CH}_3\text{CH}_2\text{ONa}$ (in ethanol)
C) ethyne + CH_3Li (in hexane)
D) ethanol + NaNH_2 (in liquid NH_3)
E) $\text{CH}_3\text{CO}_2\text{Na} + \text{aqueous HCl}$
- If a neutral organic substance X has a pK_a of 10 and is insoluble in distilled water, what happens when it is added to 1 M aqueous sodium hydroxide?
A) substance X gains a hydroxide ion
B) substance X remains insoluble
C) substance X becomes a water-soluble salt
D) substance X loses a proton
E) more than one of the above
- Which of the following is true about every compound with (R) configuration?
A) it is not superimposable on its mirror image
B) it will have (+) specific rotation
C) it will have (-) specific rotation
D) it is superimposable on its (S)-enantiomer
E) it is racemic
- According to the Lewis definition, a base is:
A) proton donor
B) electron pair donor
C) hydroxide ion donor
D) hydrogen ion donor
E) electron pair acceptor
- What properties are different when comparing a pair of enantiomers?
A) chemical reactivity toward ACHIRAL reagents
B) chemical reactivity toward CHIRAL reagents
C) density
D) melting point
E) boiling point
- Which statement is true of a meso compound?
A) it will have optical activity
B) there are no planes of symmetry
C) it is not superimposable on its mirror image
D) it is an achiral diastereomer
E) it is a mixture of R and S enantiomers
- The sex attractant ($\text{C}_{10}\text{H}_{18}\text{O}_2$) of the carpet beetle is not optically active. Based only on this observation, the substance must:
A) be a meso compound
B) be racemic
C) contain no stereocenters
D) have a plane of symmetry
E) any of the above could be correct
- Which statement is NOT true of nucleophilic substitution reactions?
A) $\text{S}_\text{N}1$ proceeds through a carbocation intermediate
B) $\text{S}_\text{N}2$ occurs with inversion of configuration
C) rates of both $\text{S}_\text{N}1$ and $\text{S}_\text{N}2$ increase at higher temperatures
D) rates of both $\text{S}_\text{N}1$ and $\text{S}_\text{N}2$ increase with higher concentrations of R-X
E) rates of both $\text{S}_\text{N}1$ and $\text{S}_\text{N}2$ increase with higher concentrations of Nu
- In the following equilibrium, which two substances are both behaving as acids?
$$\text{CH}_3\text{NH}_3^+ + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{NH}_2 + \text{H}_3\text{O}^+$$

A) CH_3NH_3^+ and H_2O
B) CH_3NH_3^+ and CH_3NH_2
C) H_2O and H_3O^+
D) CH_3NH_3^+ and H_3O^+
E) CH_3NH_2 and H_2O
- Which of the following is the poorest leaving group?
A) Cl^-
B) Br^-
C) CH_3CO_2^-
D) CH_3O^-
E) HSO_4^-

13. For the following S_N1 reaction, choose the statement which best describes the stereochemistry of the products:



- A) the product is a mixture of diastereomers
☒ B) the product is a mixture of enantiomers
 C) the product is a single diastereomer
 D) the product is a single enantiomer
 E) the product is achiral
14. Which of the following is a meso compound?
- A) (2R,3R)-2,3-dibromopentane
 B) (2R,3S)-2,3-dibromopentane
 C) (2R,4R)-2,4-dibromopentane
☒ D) (2R,4S)-2,4-dibromopentane
 E) none of the above



17. The term *resolution* best describes which of the following processes:
- ☒ A) separation of enantiomers
 B) conversion of chiral compounds to achiral
 C) returning a salt to an aqueous solution
 D) a reaction with no effect on bonds to a stereocenter
 E) changing configuration from R to S (or S to R)

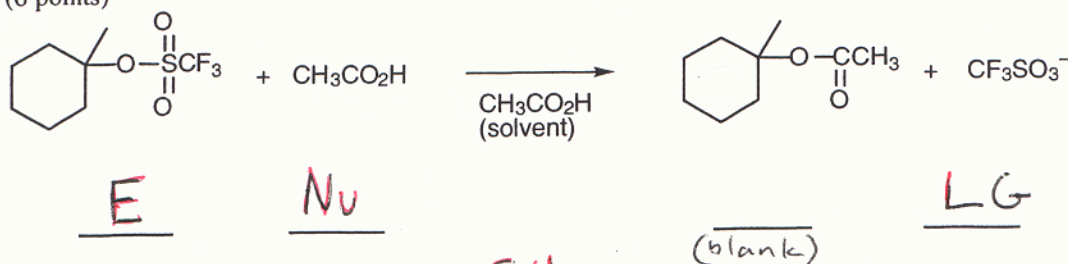
18. Which of the following would be expected to lead to increased rates of S_N1 reactions?
- A) resonance-stabilization of the carbocation
 B) alkyl groups attached to the carbocation
 C) stabilization of the carbocation by solvent
 D) lowering ΔG^\ddagger of the first step
☒ E) all of the above

19. Which of the following is true of hydrocarbons and their carbanions?
- ☒ A) C-H bonds of sp -hybridized carbon are more acidic than those of sp^2 -hybridized carbon
 B) C-H bonds of sp^2 -hybridized carbon are more acidic than those of sp -hybridized carbon
 C) C-H bonds of sp^3 -hybridized carbon are more acidic than those of sp^2 -hybridized carbon
 D) carbanions with less s-character are less basic
 E) all of the above are true

20. Which alkyl halide would be most effective in a nucleophilic substitution reaction with OH^- ?
- A) 2-bromo-2-methylpentane
 B) 2-bromo-3-methylpentane
 C) 1-bromo-2,2-dimethylpentane
☒ D) 1-bromo-4-methylpentane - primary and unhindered.
 E) 2-bromopentane

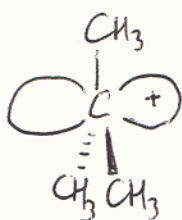
For questions 21–27, write each answer neatly and clearly in the space provided. (Please use reverse side if you need scratch paper.)

21. a) Identify the nucleophile (Nu), substrate (electrophile, E), and leaving group (LG) in the following nucleophilic substitution reaction. Place an appropriate abbreviation (Nu, E, LG) in 3 of the 4 blanks below. (6 points)



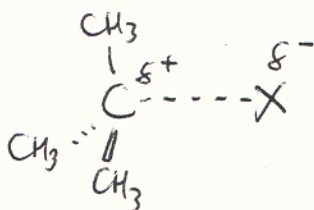
- b) The above reaction likely proceeds by the S_N1 mechanism and is a special type of nucleophilic substitution reaction which is also known as solvolysis. (4 points)

22. a) Draw a three-dimensional representation of the carbocation intermediate formed upon heterolysis of *tert*-butyl bromide. Include the shape of the orbital associated with the positive charge. Use dashed or wedged bonds if appropriate. (8 points)

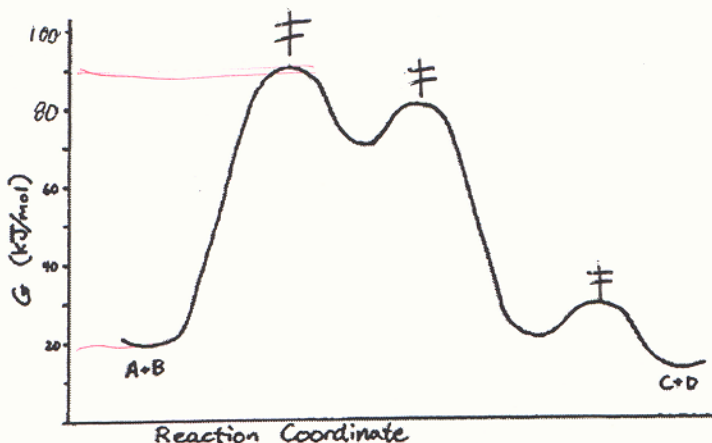


planar, sp^2 hybridized, empty p orbital has the + charge

- b) Draw the transition state for the heterolysis of *tert*-butyl bromide, showing partial charges on the appropriate atoms. Use dashed or wedged bonds if appropriate. (8 points)



- c) A carbocation would also form upon heterolysis of methyl bromide. This carbocation is: more less (circle one) stable than the one in part a) above because it has fewer alkyl groups to stabilize the C^+ (6 points)
(for full credit, your answer must be clear and concise)
or no resonance or no overlap of C-H σ orbitals with C^+ p orbital
23. Consider the free-energy reaction coordinate diagram below to answer each of the questions which follow. (12 points)

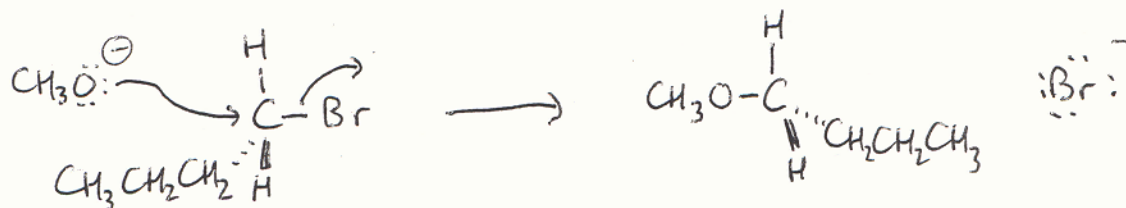


- a) The free energy change for the reaction $A+B \rightarrow C+D$ is approximately -10 kJ/mol (round to the nearest 10)
- b) The reaction $A+B \rightarrow C+D$ is: endergonic exergonic (circle one)
- c) The free energy of activation ΔG^\ddagger of the slowest step is approximately 70 kJ/mol (round to the nearest 10)
- d) Clearly indicate the location of all transition states on the reaction coordinate diagram using this label: ‡

must have sign!
must not be negative

3 points each

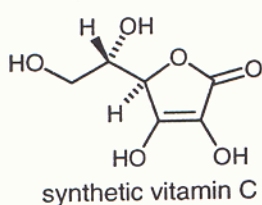
24. The nucleophilic substitution reaction of 1-bromobutane with sodium methoxide (CH_3ONa) likely proceeds by the $\text{S}_\text{N}2$ mechanism. Show the detailed mechanism of this reaction. Use curved arrows to illustrate the movement of electrons involved in each bonding change. (10 points) 2 points



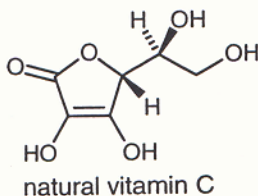
correct reactants, Lewis str. (2)
 correct arrows (4)
 correct prod (2)
~~and step (2)~~

8 points, stereochemistry not required, \neq not required

25. Identify the relationship between each of the following pairs of compounds. Select from the following terms: constitutional isomers, diastereomers, enantiomers, or identical. (12 points)

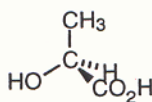


and



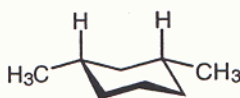
identical

and



identical

and



identical

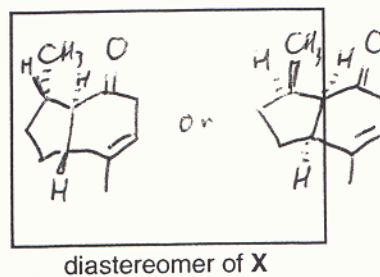
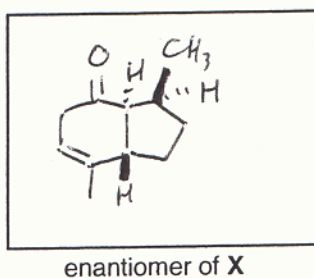
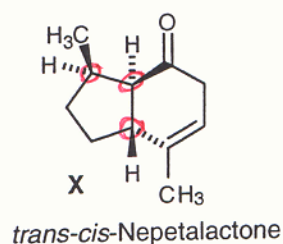
4 points each

a Fischer Projection

26. The active ingredient in catnip oil which makes it a good insect repellent is *trans-cis*-nepetalactone (X). (see below right)

a) How many stereoisomers of nepetalactone are possible? $2^3 = 8$ (2 points)

b) In the boxes below, draw a structure which is enantiomeric to X and a structure which is diastereomeric to X. (8 points)

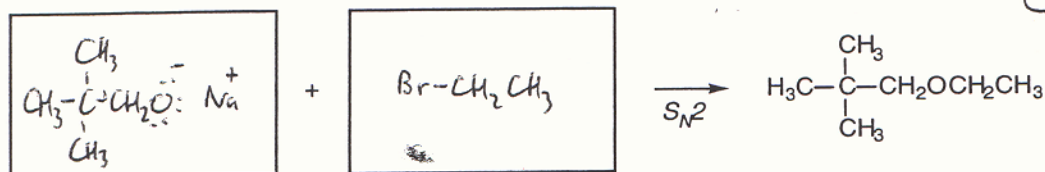
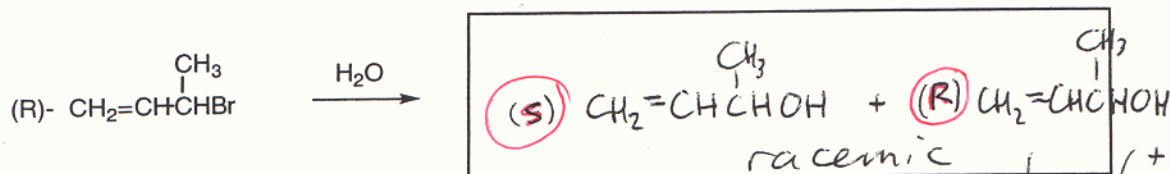
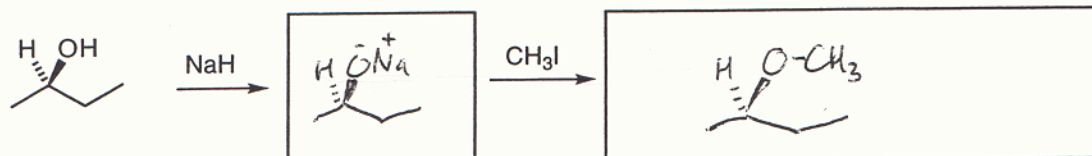
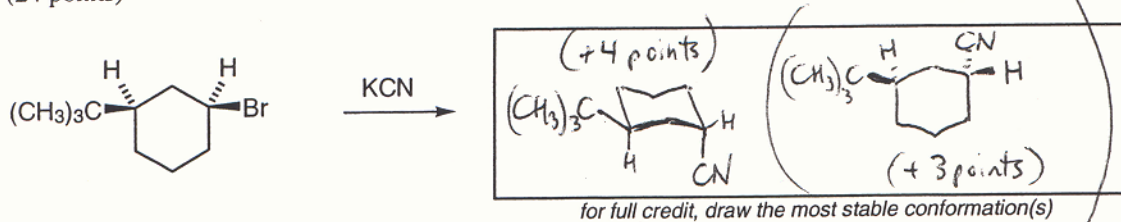


4 points each

or several others
 (must have only 1 or 2 stereocenters inverted from X)

4 points for each box

27. Provide reactants, reagents, or organic products needed to complete the following reactions. Clearly indicate configurations if stereoisomers are possible. (You need not show inorganic byproducts.) (24 points)



must use ethyl group as electrophilic partner

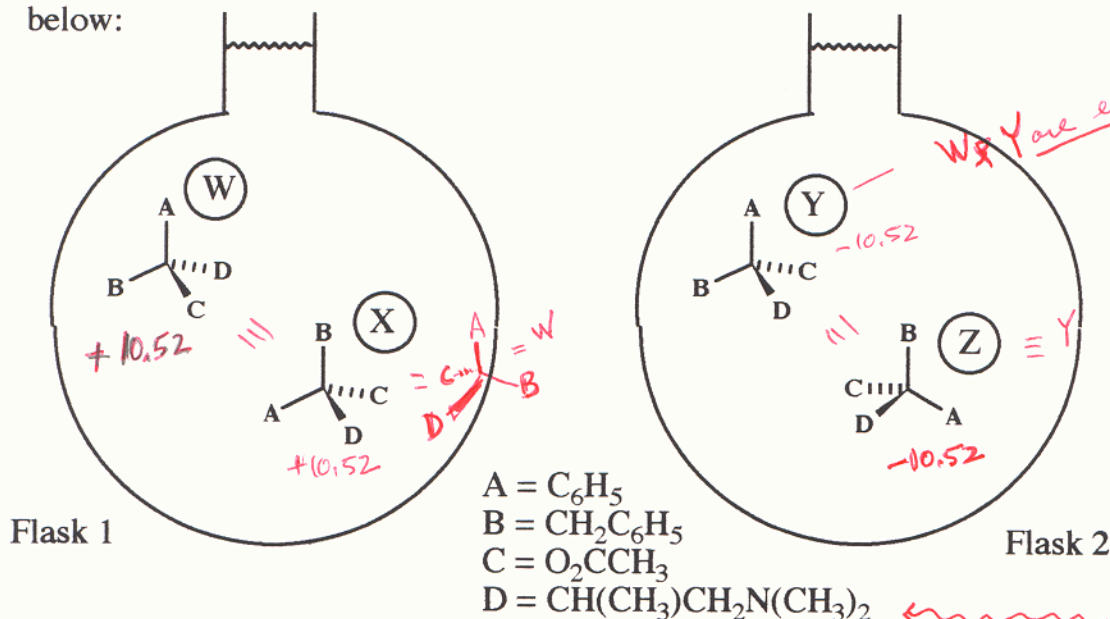
+ 2 points if only 1 product given and racemic not indicated

PRACTICE EXAM 2B

(18)

1. The narcotic analgesic Darvon™ is shown in various ways in the two flasks below. Each of the structures in each flask represents a mole of that species. The solution volume is 1 liter. The solvent is achiral. Assume that the specific rotation of species W is $+10.52^\circ$. Answer the questions below:

red ink is work - not on original exam



W & Y are enantiomers

NOTE

a. Is the rotation of the solution in flask 1 +, - or 0? +

b. Mixing equal volumes of solution from flask 1 and flask 2 would give a solution with a net rotation of? 0

c. Explain your answer to question b. you create a racemate

d. Which flask, if any, contains a meso compound? neither
If neither, indicate this.

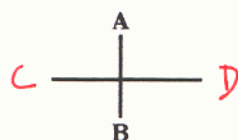
e. Which flask will yield a pure compound when the solvent is evaporated off? both

f. What is the configuration of compound Z, R or S? S

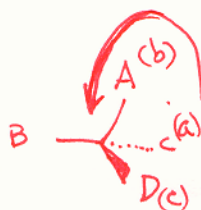
g. What is the specific rotation for Y? -10.52

h. What is the specific rotation of X? +10.52

i. A correct Fischer projection formula for W is (complete the structure below):



Counterclockwise
 $\therefore S$

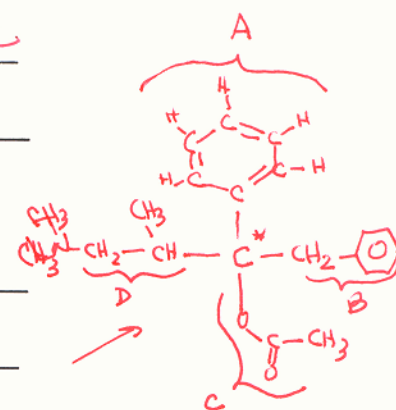


equiv to C=C

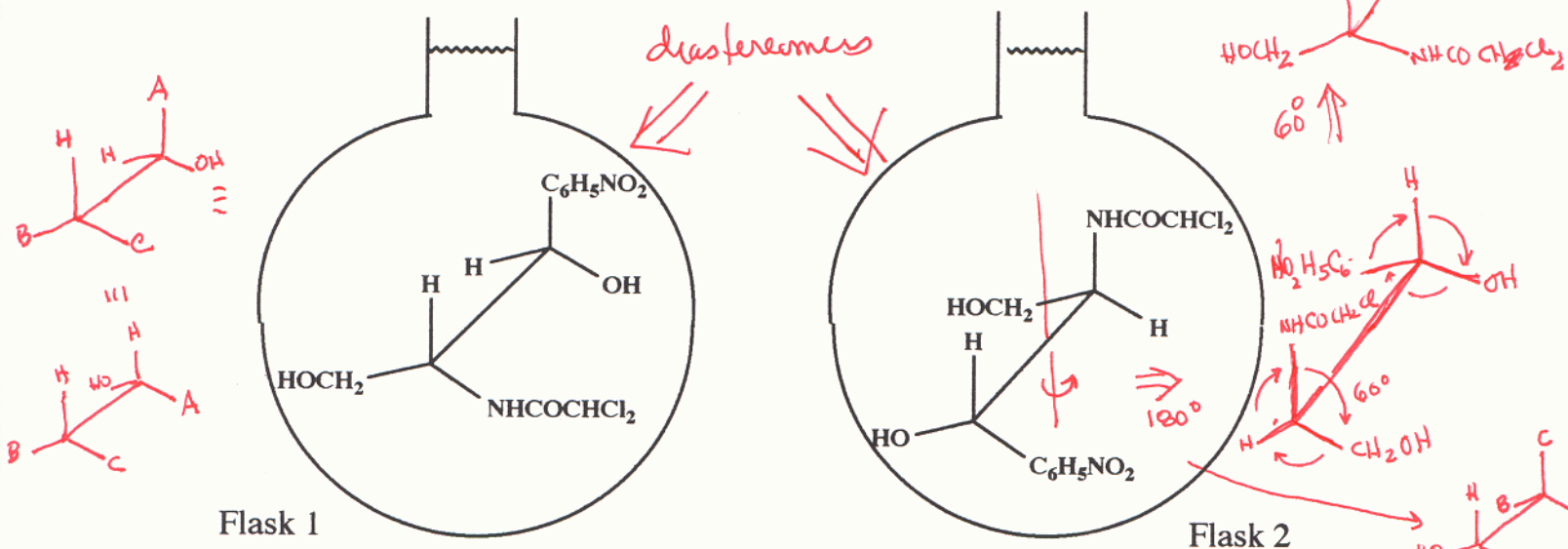


priorities

- * C is a) high
- B is d) low
- A is b) 2nd high
- D is c) 3rd high



- (12) 2. Shown below are two representations of the antibiotic Chloramphenicol. Each structure represents a mole of that species in a liter of solution (concentration = 1 Molar). Assume that the specific rotation for the species in flask 1 is -7.3 degrees. Answer the questions below.



- a. The specific rotation of the solution in flask 2 must be +7.3 degrees (T or F?) F
- b. Which flask contains a meso compound (if any)? neither
- c. Would mixing flasks 1 and 2 yield a racemate? no
- d. Are the compounds in the flasks meso compounds, enantiomers diastereomers, structural isomers or just different conformations of a single compound? diastereomers
- e. Must the compound in flask 1 necessarily melt at the same temperature as the compound in flask 2? no

f. What is the relationship of the

structure on the right

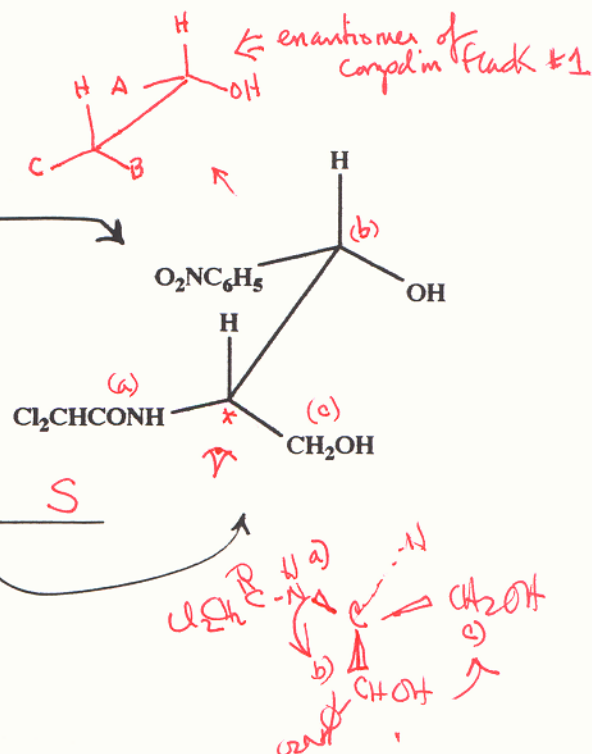
to the structure in flask 1? enantiomer

to the structure in flask 2? diastereomer

What is the configuration (R or S) of the carbon

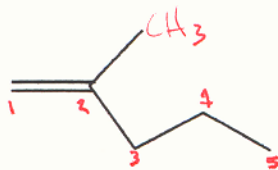
bearing the CH_2OH group in the structure on the right? S

do these problems with groups labeled A, B, C, ~~H and OH~~ and it is easier —.

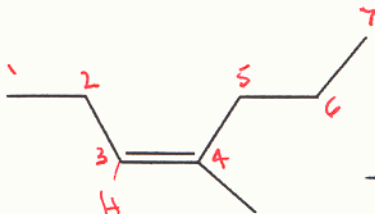


(6)

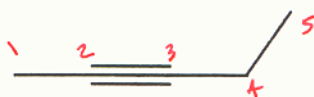
3. Name the following (use E/Z where appropriate) :



2-methyl-1-pentene
~~2-methyl-1-heptene~~



Z-4-methyl-3-heptene



2-pentyne

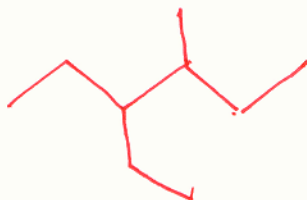
(6)

4. Draw the following:

cis-1,3-dimethylcyclohexane (draw most stable conformation):



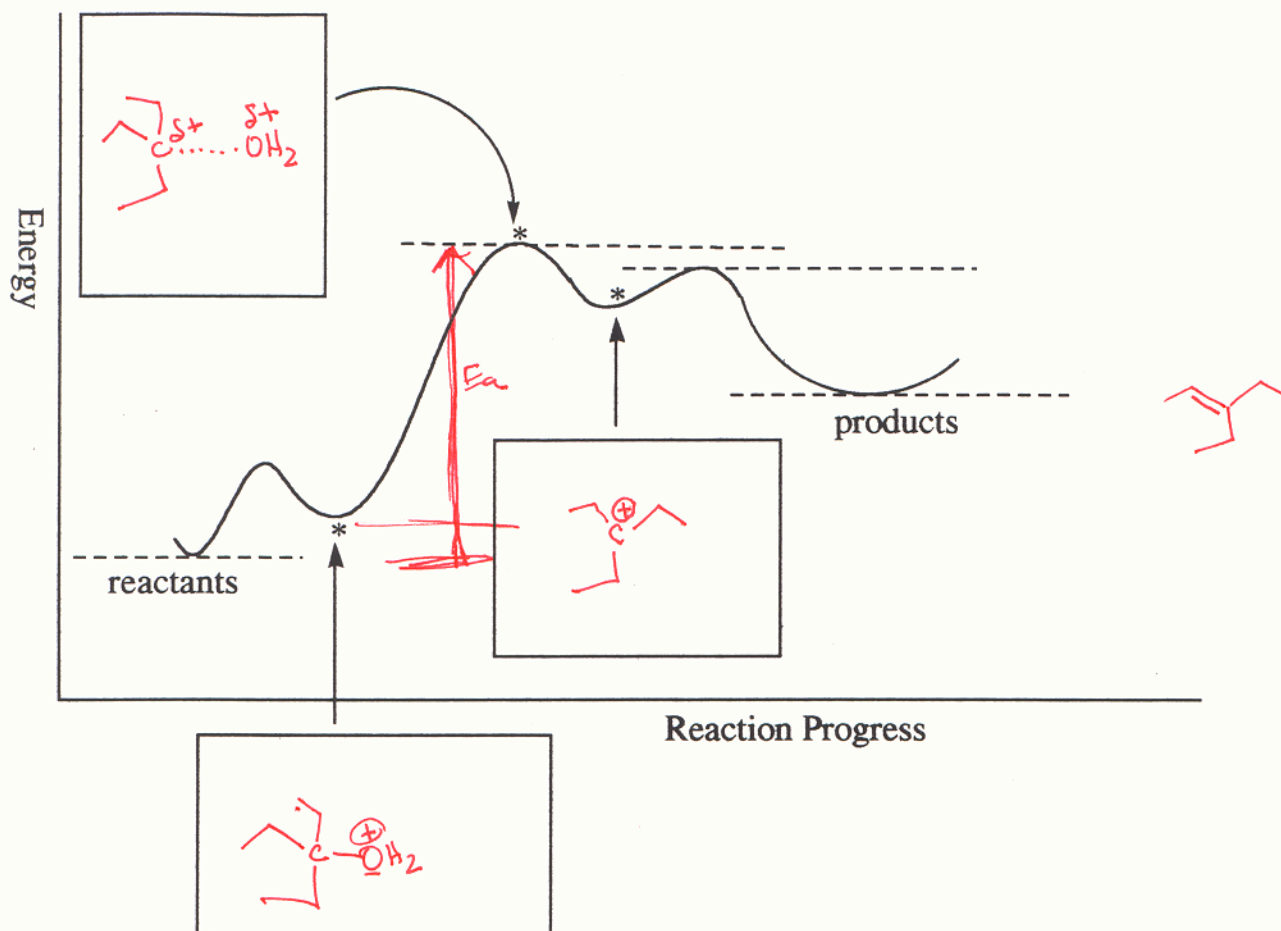
3-ethyl-4-methylhexane:



5-methyl-2-hexanol:



- (15) 4. A qualitative reaction coordinate for the reaction of $(\text{CH}_3\text{CH}_2)_3\text{COH}$ in aqueous acid to yield 3-ethyl-2-pentene is shown below:



Indicate in the boxes the species at each of the respective points indicated by the arrows on the reaction coordinate curve. Use line bond structures to simplify. On the diagram, show the activation energy for the reaction.

Is this reaction $\text{S}_{\text{N}}1$, E-1, $\text{S}_{\text{N}}2$ or E-2? E-1

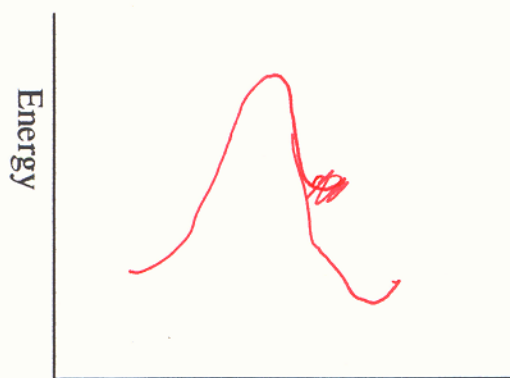
What would happen to the rate of the reaction if the temperature was increased?

rate ↑

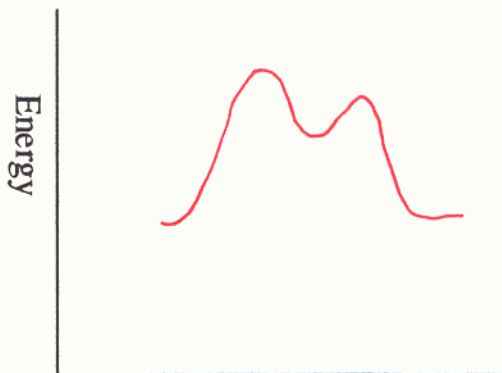
Write the rate law for the process corresponding to the reaction represented by the above reaction coordinate. Assume that H_3O^+ is in excess and that its concentration remains constant (i.e., it does not appear in the rate law)



- (12) 5. Draw qualitative reaction coordinates for the reaction of 2-bromoethane with aqueous potassium hydroxide and for the reaction of 2-chloro-2-methylpropane with aqueous sodium hydroxide. Draw that coordinate for the substitution reaction in each case. You need not draw species on the curves as in the previous problem....just qualitative curves will be enough.
- not needed in name



Reaction Progress

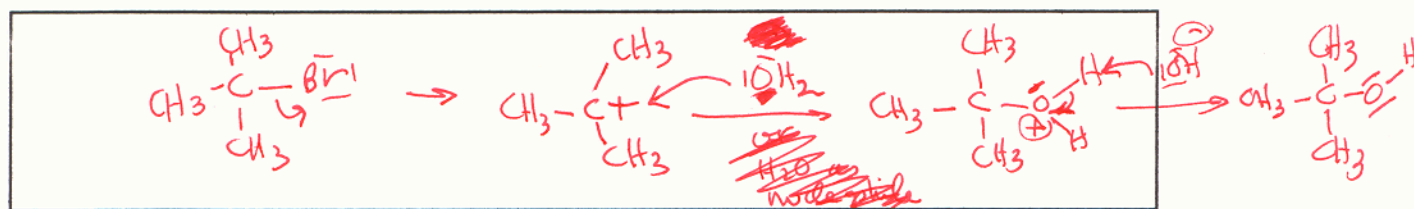
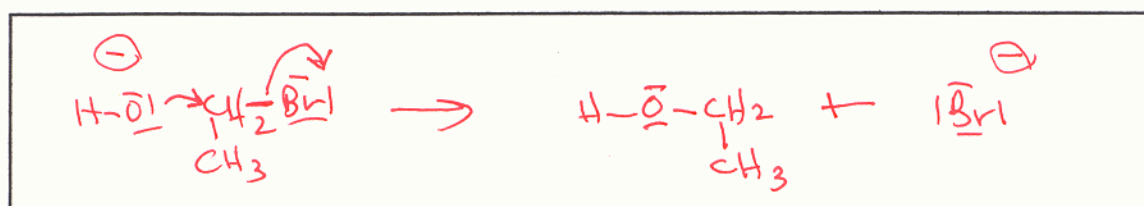


Reaction Progress

2-chloro-2-methylpropane



Write a detailed curved arrow mechanism for each reaction:



The rate law for the 2-bromoethane reaction is: Rate = $k [\text{OH}^-] [\text{CH}_3\text{CH}_2\text{Br}]$

What would happen to the rate of the 2-bromoethane reaction if the concentration of hydroxide and the concentration of 2-bromoethane were both doubled?

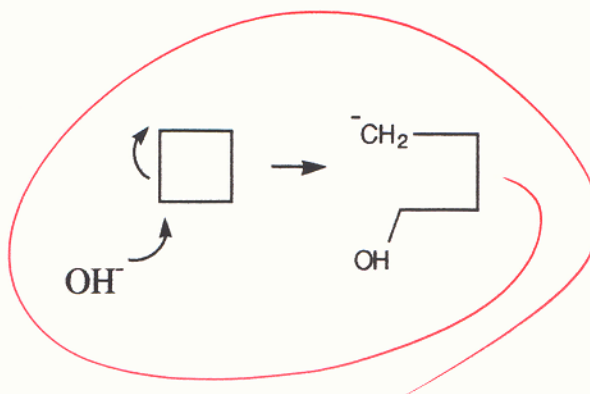
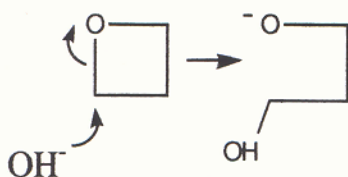
rate would quadruple

What kind of reaction ($\text{S}_{\text{N}}1$ or $\text{S}_{\text{N}}2$) is the 2-chloro-2-methylpropane reaction?

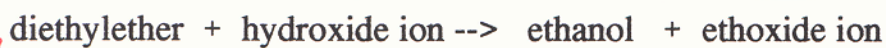
$\text{S}_{\text{N}}1$

(11) 6. In the following problems, circle the correct answer:

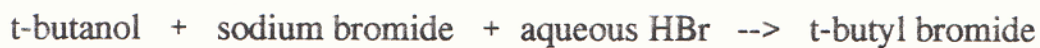
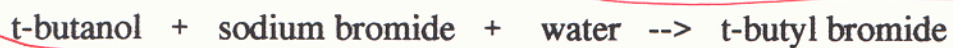
a. Which is slower?



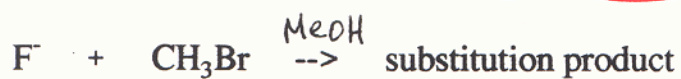
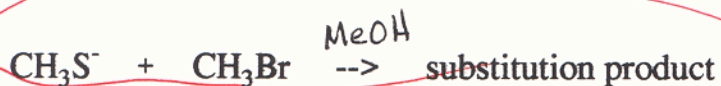
b. Which is faster?



c. Which is slowest?



d. Which is fastest



e. Which is fastest?

t-butyl chloride hydrolyzes to t-butanol in a mixture of 40% acetone and 60% water

t-butyl chloride hydrolyzes to t-butanol in a mixture of 15% acetone and 75% water

f. Which is fastest?

methyl chloride reacting with bromide ion in DMSO to give methyl bromide and chloride ion.

methyl chloride reacting with bromide ion in CH_3OCH_3 to give methyl bromide and chloride ion.

g. Which gives the most elimination product?

2-iodo-2-methylpropane + MeO^-



1-iodopentane + MeO^-



h. Which is the most nucleophilic towards iodoethane in ethanol?

BH_3

NH_3

i. Which gives a charged (ionic) organic product?

triethylamine + ethyl bromide

$\text{CH}_3\text{N}^-\text{H}^+\text{K}^+$ + ethylbromide

J. Which is slowest?

t-butyl chloride solvolysis
in water

t-butyl chloride solvolysis
in ethanol

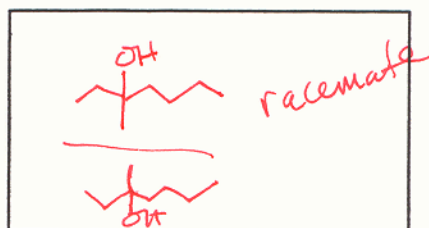
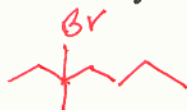
K. Which is the strongest nucleophile?

CH_3NH_2

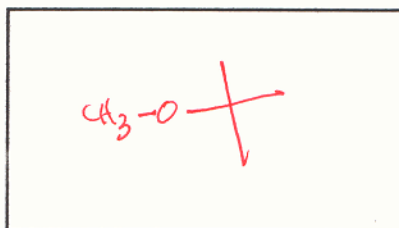
CH_3NH_3^+

(II) 7. For the following reactions, write the products in the boxes to the right of the reactants:

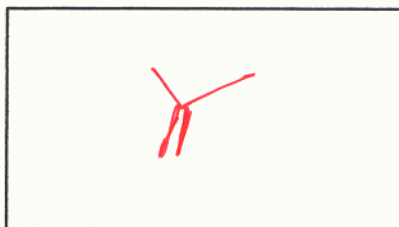
S-3-bromo-3 methylheptane in MeOH at 25°C



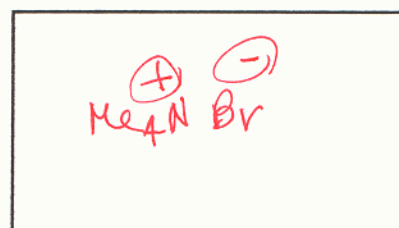
methyl iodide at 50°C in t-butanol/Kt-butoxide



t-butyl iodide and methoxide



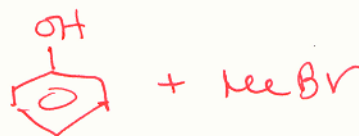
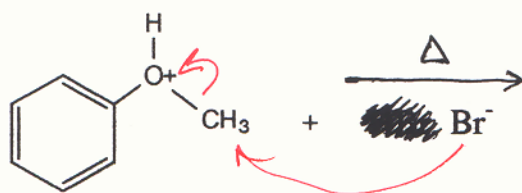
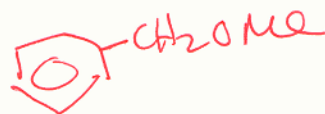
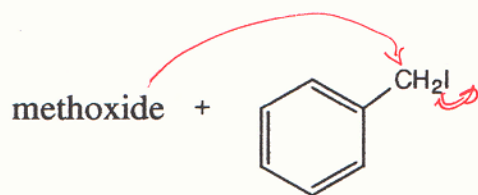
trimethylamine and methylbromide



2-chloro-2,3-dimethylbutane + t-butoxide



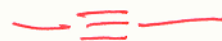
2 products!



$(\text{CH}_3)_3\text{P} + \text{CH}_3\text{Br}$



2,3-dibromobutane + 2 NaNH₂



C₄H₆ (contains a triple bond)

neopentyl alcohol + acid (heat)

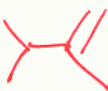
two products here



major



minor

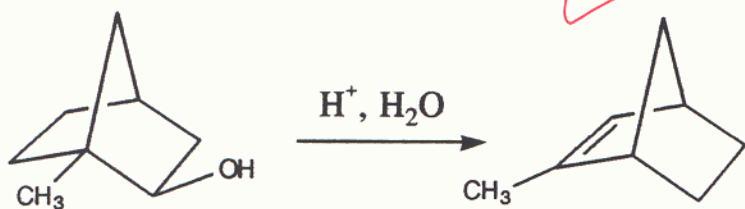
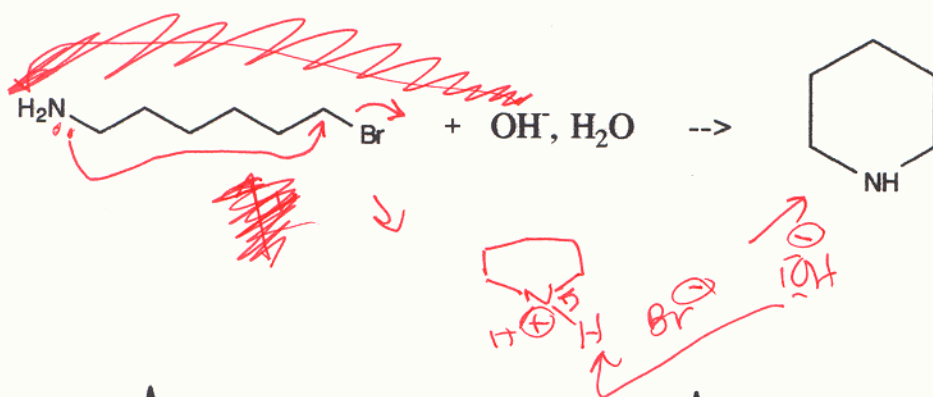
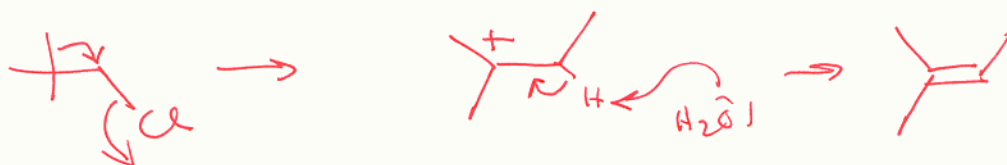


must have both products for credit

8. Draw curved arrow mechanisms for the following:

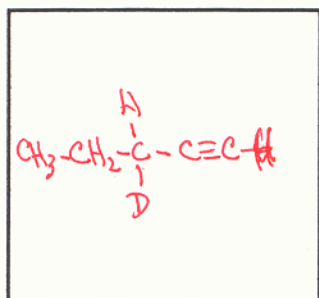
(6)

neopentyl chloride + H_2O \rightarrow 2-methyl-2-butene

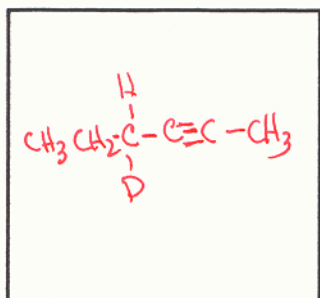


D is in the middle - see (A) below in workspace

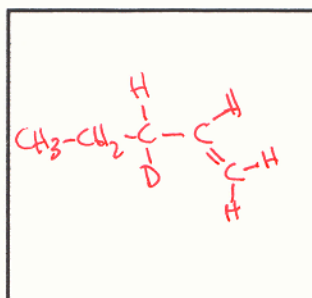
9. (4) A Chiral compound C_5H_7D , A, reacts with $NaNH_2$ in liquid ammonia to give the sodium salt of an organic anion. Adding CH_3Br to this anion yields B, C_6H_9D . B absorbs two moles of H_2 in the presence of a platinum catalyst to yield 3-deuteriohexane. Compound A absorbs one mole of H_2 in the presence of a platinum catalyst to give C, C_5H_9D , which is also chiral. C rapidly absorbs a second mole of H_2 to give D, $C_5H_{11}D$, which is not chiral. Hydrogenation of Z-3-deuterio-2-pentene with H_2 and a platinum catalyst also yields D. What are the structures of A, B, C and D?



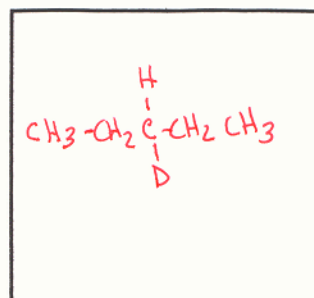
A



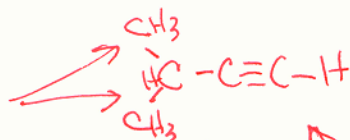
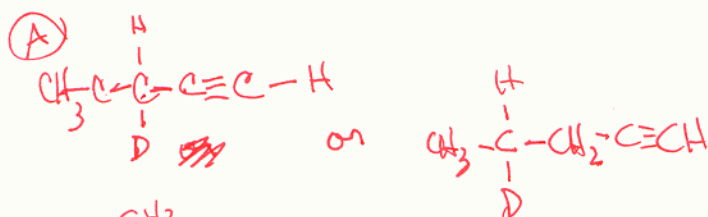
B



C

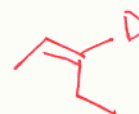


D



must be
terminal
alkyne
(alkyne)

NOT
CHIRAL
if D on
either position



Z-3-deuterio-2-pentene