Department of Chemistry
University of Vermont

Chem 141
Fall, 1998
Exam 3

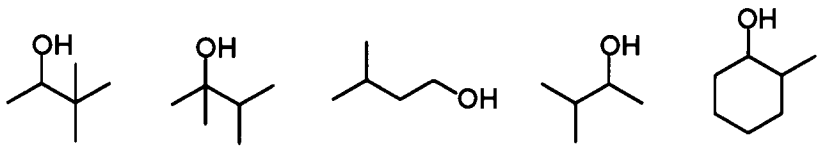
Name:

Problem	points (total)	Grader	**Score:**_____
	_____	_____	
	_____	_____	
	_____	_____	
	_____	_____	
	_____	_____	
	_____	_____	

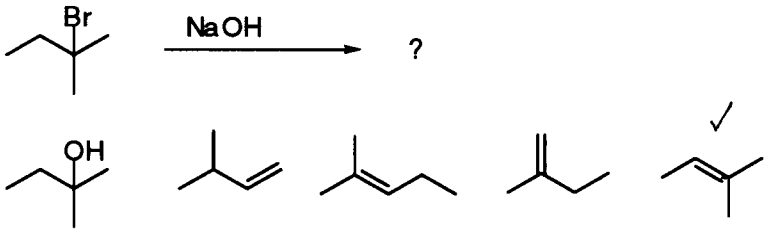
***** Special announcement *** the final exam is scheduled for dec 15th in the tennis courts**

For each question in this section, circle the correct answer. Each problem is worth 3 points.

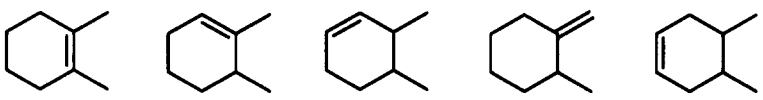
1. Which of the following alcohols would dehydrate most rapidly when treated with sulfuric acid?



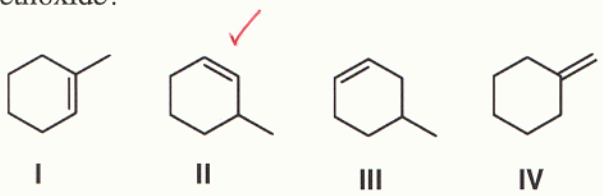
2. Which compound would you expect to be the major product of the following reaction?

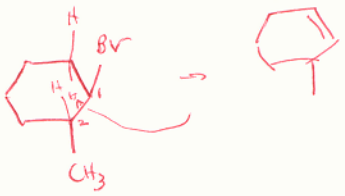


3. Which molecule would have the lowest heat of hydrogenation?



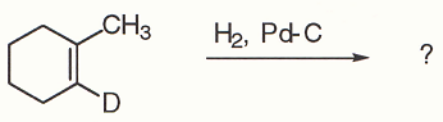
4. Which product (or products) would be formed in appreciable amounts when trans-1-bromo-2-methylcyclohexane undergoes dehydrohalogenation upon treatment with sodium ethoxide?

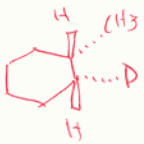


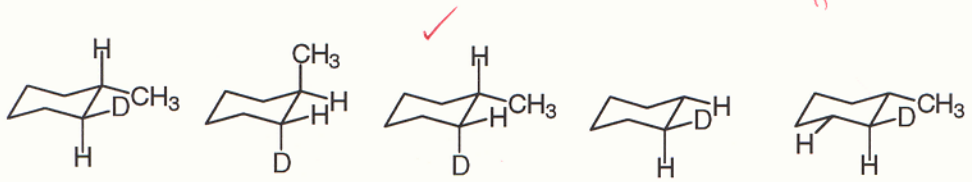


a) I
b) II
c) III
d) IV
e) more than one of the above

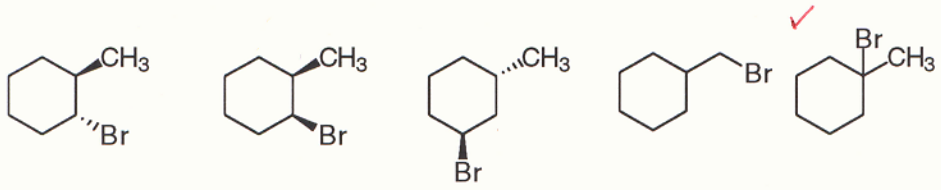
5.. Which would be the major product of the following reaction?

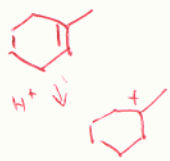




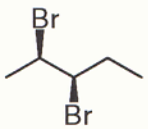


6. What would be the major product of the reaction of 1-methylcyclohexene with HBr?

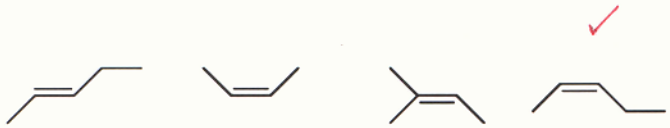


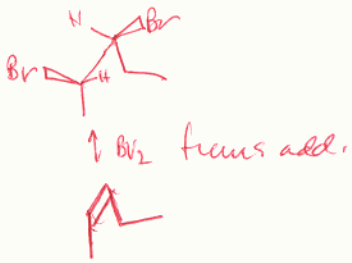


7. Reaction of which alkene with Br_2 would afford the dibromide shown below?

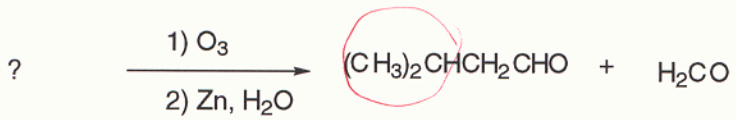


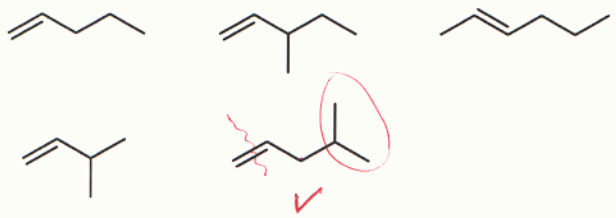
+ enatiomer



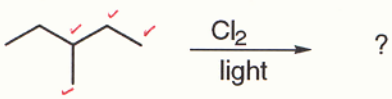


8. Which alkene would undergo the following reaction?





9. How many different constitutional isomers would be expected from the following reaction?



a. 2

b. 3

✓ c. 4

d. 5

e. 6

10. Which of these molecules is not expected to arise as the product of the high temperature chlorination of methane?

a. CCl_4

b. $CHCl_3$

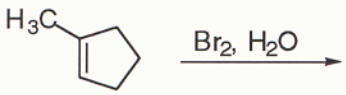
✓ c. CH_2CH_2

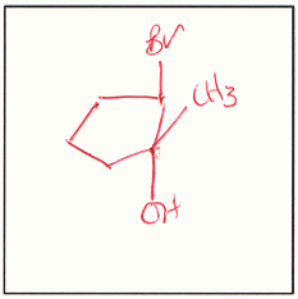
d. CH_3CH_3

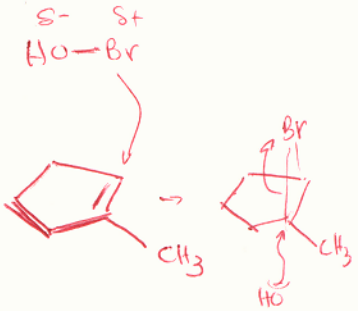
e. CH_2Cl_2

11. For the following section provide the major product expected for the reactions. Where appropriate show stereochemistry. If a reaction gives a racemic mixture you need only show one of the enantiomers. (15 points)

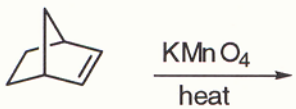
a.

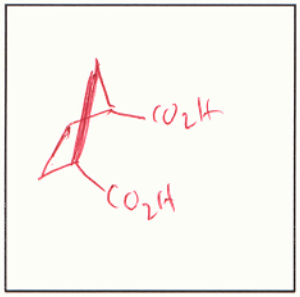




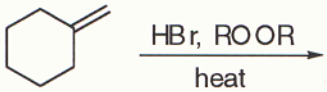


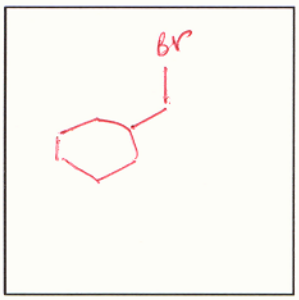
b.



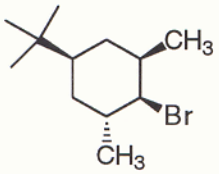


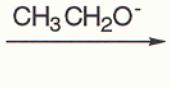
c.

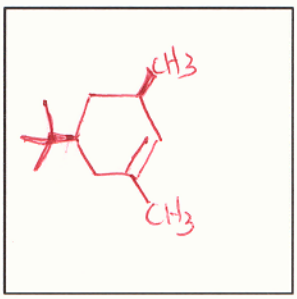


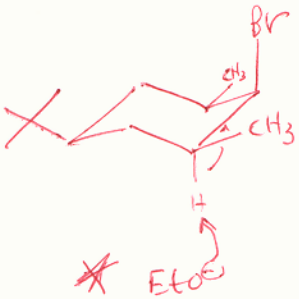


d.

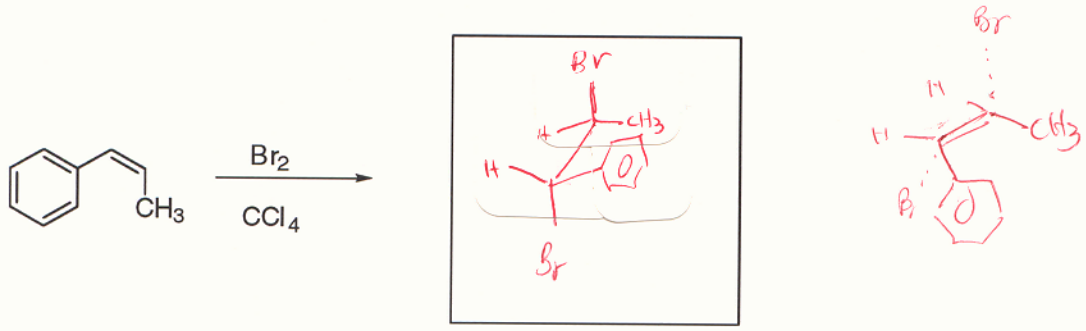






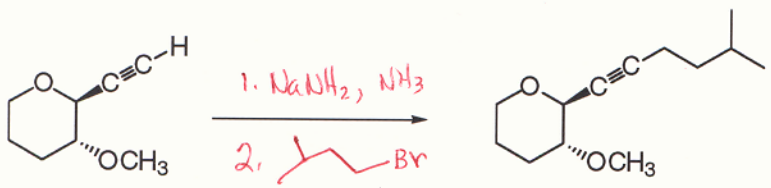


e.

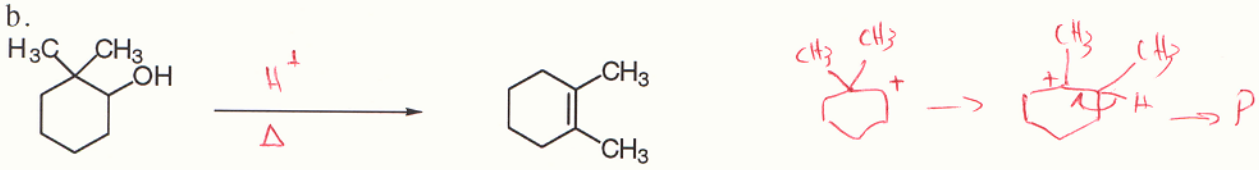


12. For the next section provide the missing reagents necessary to accomplish the following transformations. If a specific number of equivalents are required indicate so. If the reagents need to be added in a specific order indicate so. (18 points)

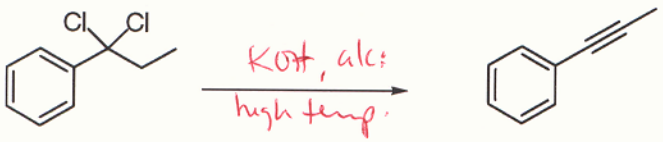
a.



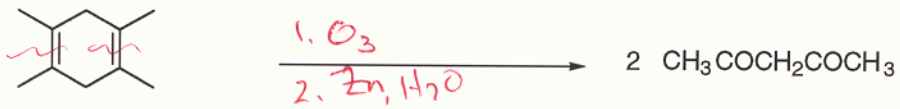
b.



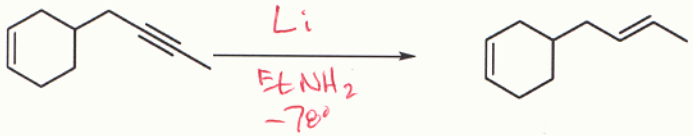
c.



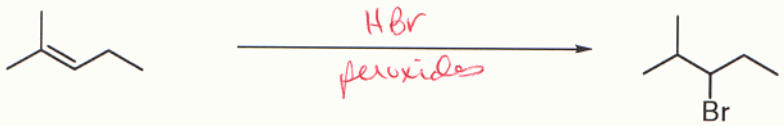
d.



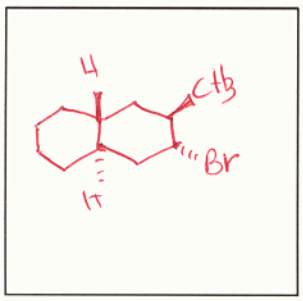
e.



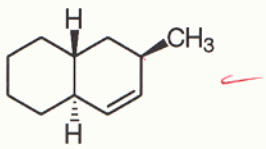
f.

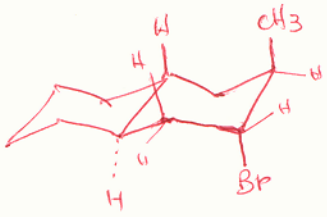


13. Provide the alkyl bromide that affords the compound below as a single product on treatment with sodium ethoxide. Be sure to include stereochemistry. (4 points)



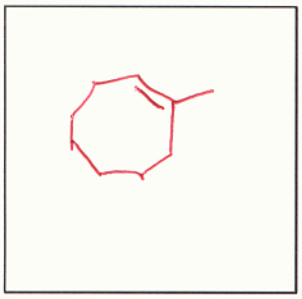
EtO^-





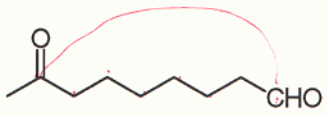
15. Provide the starting materials that would afford the specified products under the reaction conditions given. (9 points)

a.

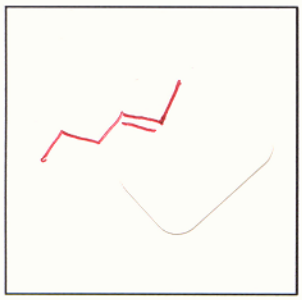


1) O_3

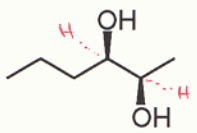
2) Zn



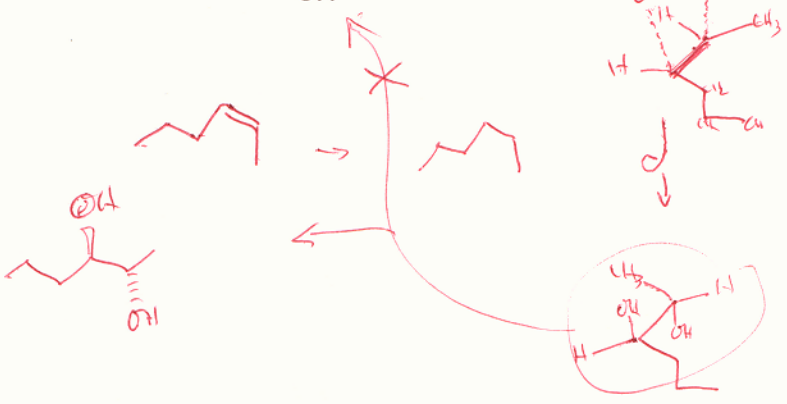
b.

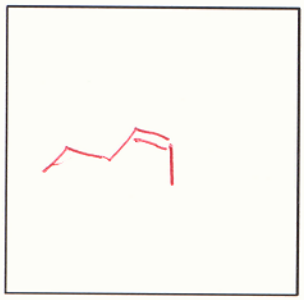


OsO_4, $NaHSO_3$

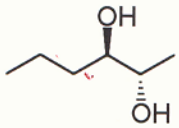


+ enantiomer



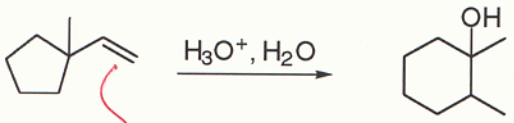


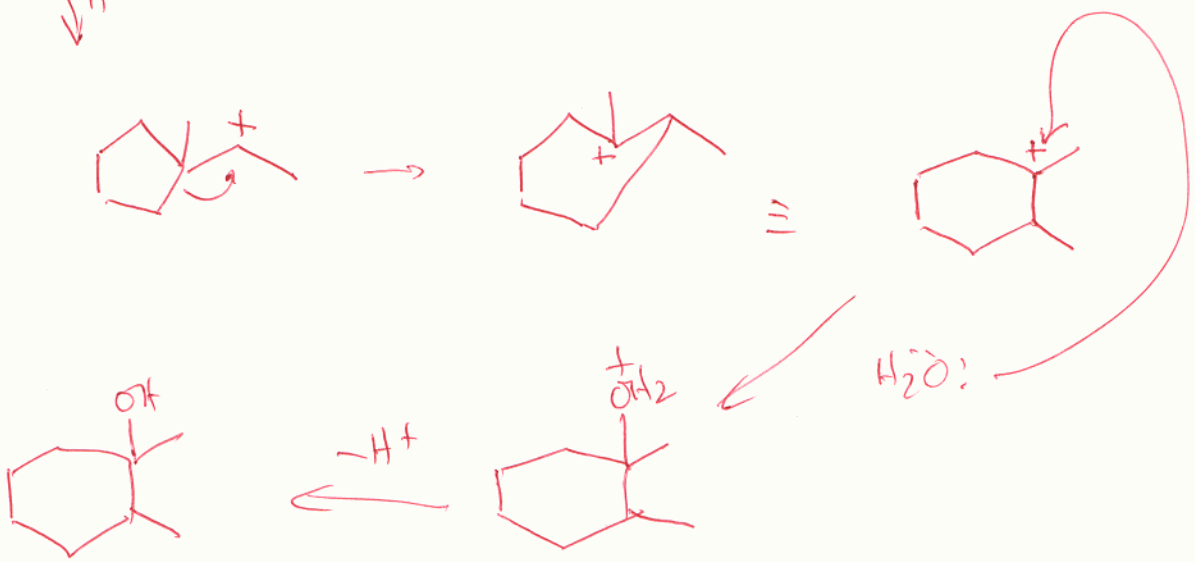
OsO_4, $NaHSO_3$



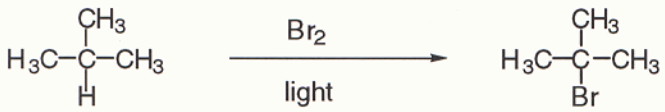
+ enantiomer

16. Provide a detailed curved arrow mechanism for the following transformation. (5 points)





17. Provide a detailed curved arrow mechanism for the two chain propagation steps of the following reaction. (5 points)



$Br_2 \xrightarrow{h\nu}$ 2 Br· initiation.

1) 

prop 1

2) 

prop 2

18. Zingiberene, a fragrant compound isolated from ginger, has the molecular formula $C_{15}H_{24}$ and is known to contain no triple bonds. (4 points)

(a) When zingiberene is subjected to catalytic hydrogenation using excess hydrogen a compound with the formula $C_{15}H_{30}$ is produced. How many double bonds does zingiberene have?

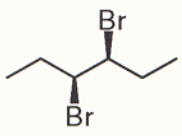
$C_{15}H_{30}$
$C_{15}H_{24}$
H_6 — $3\ H_2$ ∴ 3 d. bonds

(b) How many rings does zingiberene have?

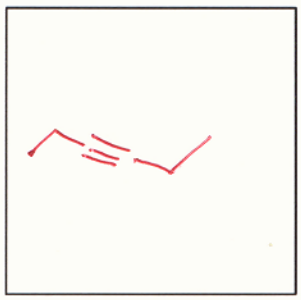
if saturated ~~world~~ hydrog. product would be $C_{15}H_{32}$ (i.e. C_nH_{2n+2})

∴ one ring must be present.

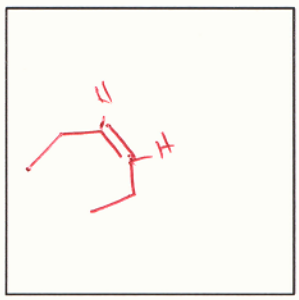
19. Treatment of compound **A** (C_6H_{10}) with H_2 in the presence of Lindlar's catalyst gives a compound **B** (C_6H_{12}). Reaction of compound **B** with Br_2 gives the dibromide **C**. Provide structures for **A** and **B**.



C



A



B

C_6H_{10} index of H def is 2.

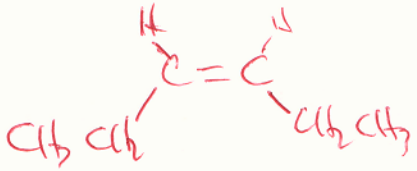
C_6H_{14}

H_{10}

4 ($1\pi - 2H_2$), or $C\equiv C \rightarrow C=C$ (Lindlar).

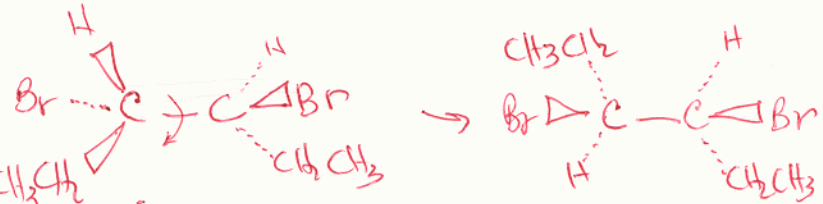
(A) $CH_3-CH_2-C\equiv C-CH_2-CH_3$

↓ Lindlar or Li/NH_3

(B) 

cis

↓ Br_2

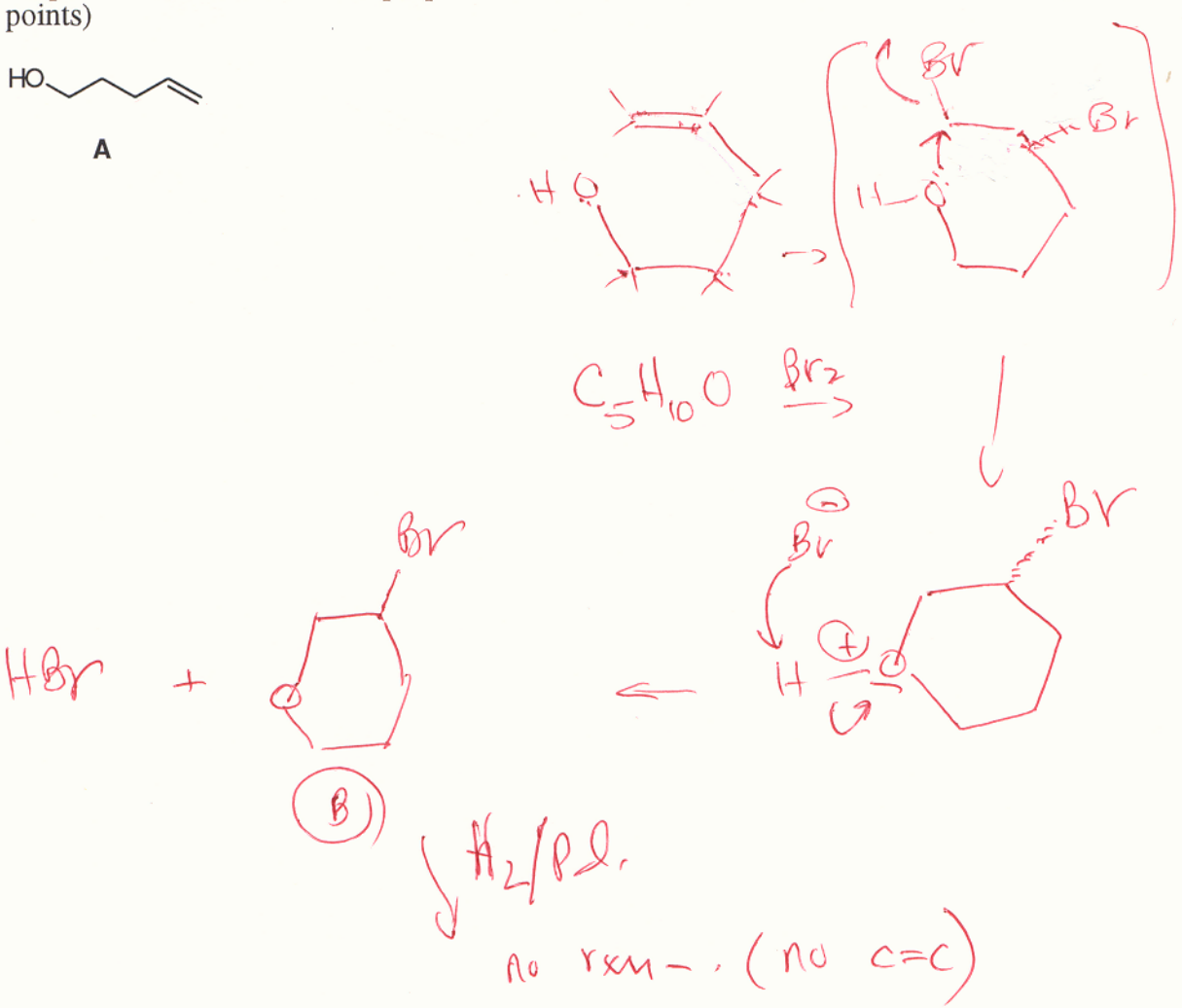


trans addition.

Extra Credit

Treatment of compound **A** with Br_2 in CCl_4 gives a compound **B** with the formula C_5H_9OBr (formula is consistent with index of hydrogen deficiency = 1) and 1 equivalent of HBr. Treatment of compound **B** with H_2 and Pd-C returned compound **B** unchanged. Propose a structure for **B** and propose a mechanism for the formation of **B** from **A**. (6 points)

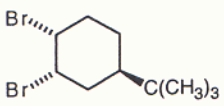
A



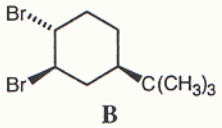
Questions 1-10 are multiple choice. Circle the best answer AND write it in the appropriate blank at the bottom of the page.

1. How many monochlorinated products (including stereoisomers) would be obtained in a reaction of 3-methylpentane with chlorine and light?
   A) four
   B) five
   C) six
   D) seven
   E) eight

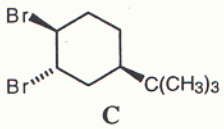
2. Which of the following vicinal dibromides would react most rapidly with zinc in ethanol?



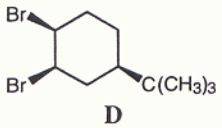
A



B



C

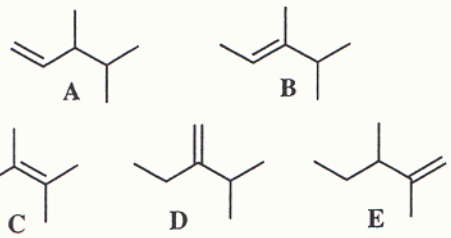


D

3. Which of the following results in initiation of a free radical chain halogenation?
   A) combination of two radicals
   B) homolysis of a bond
   C) formation of product by atom abstraction
   D) addition of a radical to an alkene
   E) both C and D result in initiation

4. In which of the following solvents would fluoride ion be a weaker nucleophile than iodide ion?
   A) water
   B) acetone: $(CH_3)_2C{=}O$
   C) diethyl ether: $CH_3CH_2OCH_2CH_3$
   D) dimethyl sulfoxide: $(CH_3)_2S{=}O$
   E) dimethylformamide: $(CH_3)_2NCHO$

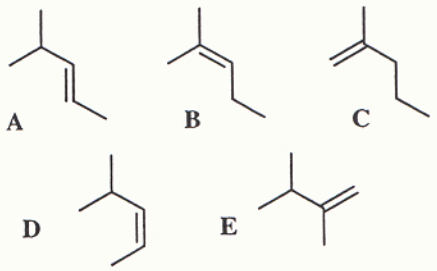
5. Which of the following alkenes would be least reactive in acid-catalyzed hydration?



6. What information can be predicted by Zaitsev's rule?
   A) whether debromination of a vicinal dibromide gives cis or trans alkene
   B) whether anti addition gives chiral or meso product
   C) which constitutional isomer is formed in electrophilic addition to an alkene
   D) which constitutional isomer is favored in dehydration of an alcohol
   E) relative reactivities in dehydrations of alcohols

7. Which of these reactions may be stereospecific?
   A) acid-catalyzed hydration of alkenes
   B) electrophilic addition of HBr to alkenes
   C) free radical addition of HBr to alkenes
   D) treatment of vicinal dihalides with excess $NaNH_2$
   E) treatment of vicinal dihalides with iodide ion

8. Which of the following alkenes would have the greatest heat of combustion?



9. Carbocation rearrangements commonly occur in which of the following types of reactions?
   A) acid-catalyzed hydration of alkenes
   B) solvolysis of alkyl halides
   C) electrophilic addition of HBr to alkenes
   D) all of the above
   E) none of the above

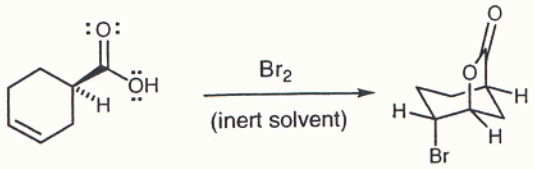
10. For which of the following reactions must regioselectivity often be considered in order to correctly predict the structures of the products?
    A) dihydroxylation of alkenes
    B) preparation of halohydrins
    C) ozonolysis of alkenes
    D) addition of bromine to alkynes
    E) catalytic hydrogenation of alkynes

Put your final answers to all of the multiple choice problems in the blanks below:

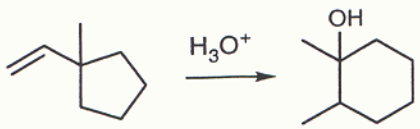
1.____ 2.____ 3.____ 4.____ 5.____ 6.____ 7.____ 8.____ 9.____ 10.____

For questions 11–15, write each answer neatly and clearly in the space provided.

11. Below is an example of a very useful reaction called "halolactonization", closely related to halohydrin formation. Show a detailed mechanism for this reaction which explains how the observed stereochemistry is formed in the product. Use curved arrows to illustrate the movement of electrons involved in each bonding change. (Hint: Note that there are non-bonding electrons on the carboxylic acid functional group.) (20 points)



12. Hydration of 1-methyl-1-vinylcyclopentane gives 1,2-dimethyl-1-cyclohexanol as shown below. Show a detailed mechanism which accounts for the formation of this product. Use curved arrows to illustrate the movement of electrons involved in each bonding change. (20 points)



13. An unknown liquid has been discovered in an unlabeled container in a busy airport. Because of security concerns, forensics experts are called upon to identify it. In their organic chemistry lab, experiments show that it is a pure compound **A** with molecular formula C_8H_{12}. Catalytic hydrogenation (H_2, Pd) of **A** gives a new compound **B** with the molecular formula C_8H_{16}. Heating **A** with potassium permanganate and aqueous base gives only succinic acid, a dicarboxylic acid with the structure $HO_2CCH_2CH_2CO_2H$.

a) Determine the index of hydrogen deficiency for **A** and **B**. (6 points)

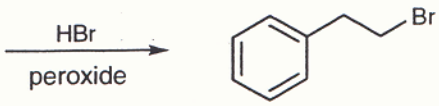
b) Identify the structures of **A** and **B**. (12 points)

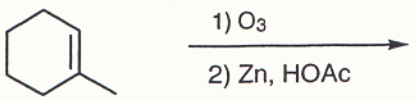
14. CHOOSE ONE OF THE FOLLOWING SYNTHESIS PROBLEMS. ONLY ONE WILL BE GRADED.
a) Show a synthesis of 2-bromo-1-pentene from 1-hexene and any other needed reagents. (Hint: Chop off one carbon!)
b) Show a synthesis of (3S,4S)-4-bromo-3-hexanol and its enantiomer from 1-butyne and any other needed reagents.
Use the back of the page for retrosynthetic analysis (not graded), and show your answer in the forward synthetic direction (graded). You do not need to show detailed mechanisms for this problem. (20 points)

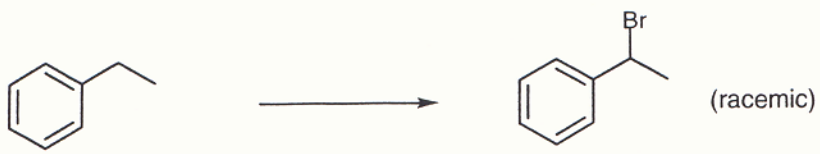
15. Provide reactants, reagents, or products to complete each of the following reactions. If more than one product is formed, identify major and minor products. For full credit, you must clearly indicate stereochemistry where appropriate.
(8 points each)

a) 

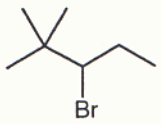
b) 

c) 

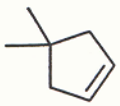
d) 

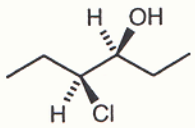
e) 

(racemic)

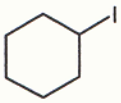
f) 

$\xrightarrow{NaOCH_3}$

g) 
$\xrightarrow{CH_2I_2,\ Zn(Cu)}$

h) $\xrightarrow[H_2O]{Cl_2}$ 

(racemic)

i) 

$\xrightarrow{HC\equiv C^{-}\ {}^{+}Na}$