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Organic Chemistry I Drill (CHEM2210D) - Module 8 - Alkenes and eliminations

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ALKENES – STRUCTURE, PROPERTIES, AND SYNTHESIS

A STUDENT SHOULD BE ABLE TO:

1. Give the IUPAC name when given the structure, and draw the structure given the name of open-chain alkenes using the *E-Z* system for designating alkene diastereomers. Give the IUPAC name of monocyclic alkenes. (Note: *cis* and *trans* isomerism was discussed in Module 4)
2. Interpret heat of hydrogenation and heat of combustion data in terms of alkene stabilities, and predict relative stabilities, and relative heats of hydrogenation and combustion using your knowledge of these stabilities. In acyclic alkenes, the order of stability is:

tetrasubstituted > trisubstituted > disubstituted > monosubstituted
also, *trans*-disubstituted > *cis*-disubstituted

3. Predict the product or products given the starting materials and reaction conditions for the following reactions:

Dehydrohalogenation, the removal of a halogen atom and a hydrogen atom from adjacent carbons (and the removal of 2 HX using NaNH₂). The most stable alkene is usually the major product if more than one product is possible.

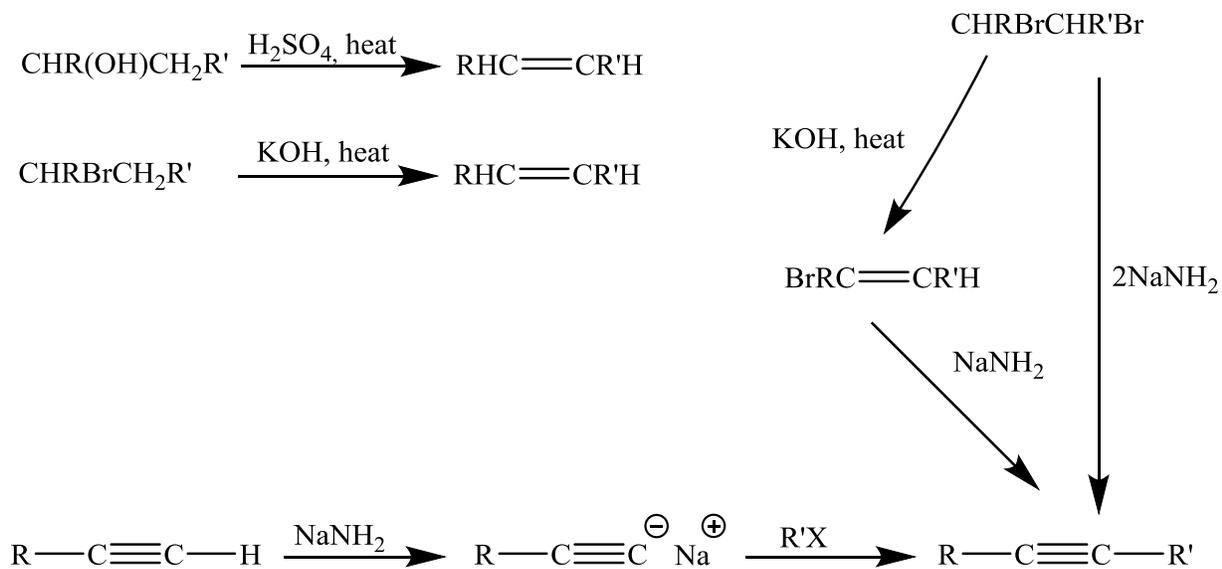
Exceptions: When no hydrogen is available *anti* to the halogen atom; when the extremely bulky *tert*-butoxide ion is used as the base; and when S_N2 is a more favorable reaction.

Dehydration, the acid-catalyzed removal of the elements of H₂O from an alcohol. The more stable alkene is the major product; the product may arise via the rearrangement of the original carbon skeleton. 1° ROH do not dehydrate easily.

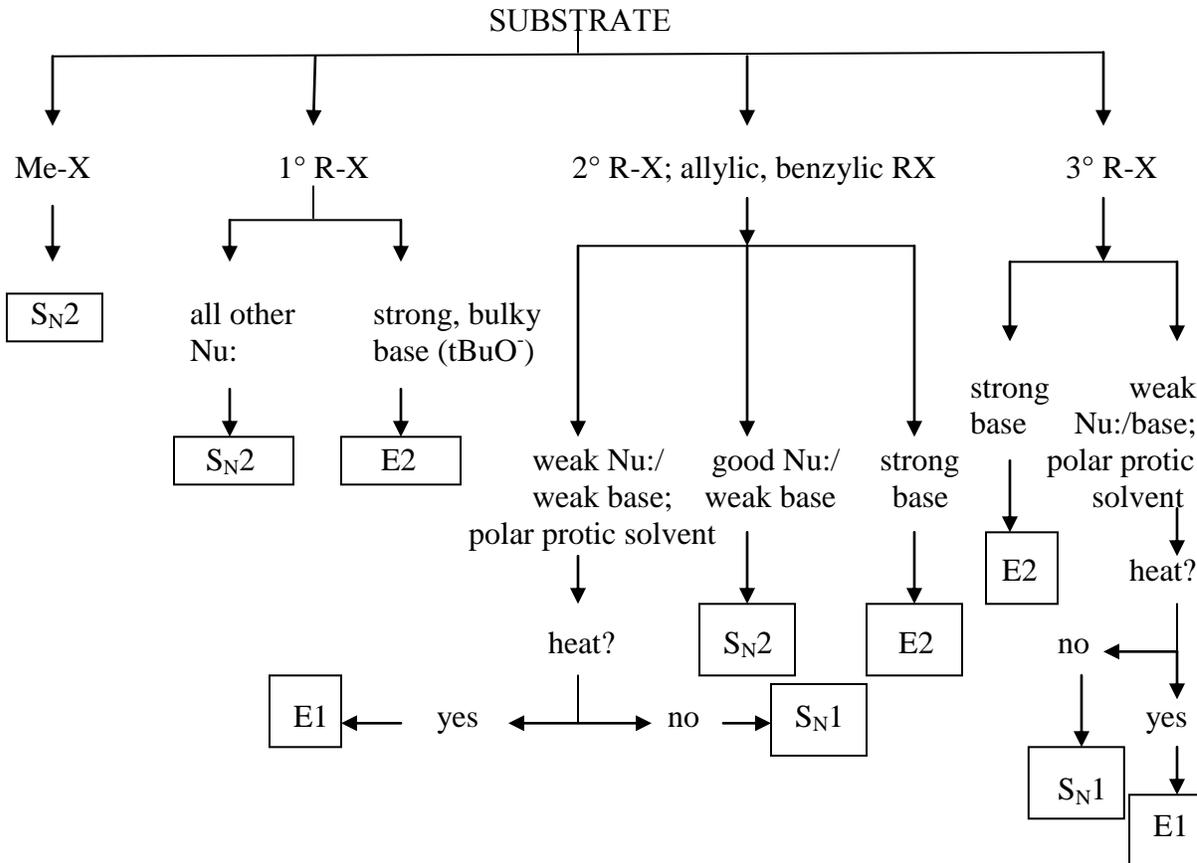
Acetylide ions + RX. Elimination (E2) takes place when the alkyl halide is 2° or 3°; substitution (S_N2) is favored with 1° RX or CH₃X.

4. Propose complete mechanisms for dehydrohalogenation and dehydration reactions, and predict and interpret experimental results based on knowledge of that mechanism. Carbocations are intermediates in the dehydration of 2° and 3° alcohols. Less stable carbocations will rearrange to more stable carbocations when possible.
5. Propose syntheses of alkenes and alkynes using the reactions given in objective 4 above, plus reactions recalled from previous chapters. For a summary of important reactions see the next page.
6. Calculate Hydrogen Deficiency Index from a given molecular formula or structure, and, from the same information plus hydrogenation or equivalent data, calculate the number of rings present.

The following chart summarizes some of the important reactions of this and previous chapters. Knowledge of reaction sequences is useful in solving synthesis problems, which are notoriously difficult for many students in Organic Chemistry. One of the best ways to learn the reactions in a chapter, in fact, is to make a chart like this for yourself. Once you finish the next drill module, you will know many more reactions to add to this chart and to connect functional groups.



Substitutions versus Eliminations:



To best prepare for this module, please work appropriate Skill Builder problems in the textbook.

A STUDENT WHO HAS MASTERED THE OBJECTIVES FOR THIS UNIT SHOULD BE ABLE TO SOLVE THE FOLLOWING PROBLEMS AND RELATED ONES:

1.1 Draw the structures of each of the following compounds.

a) (*E*)-3-hexene

b) 3-isopropylcyclobutene

c) (*Z*)-2-pentene

d) (*Z*)-1-bromo-1-chloro-1-hexene

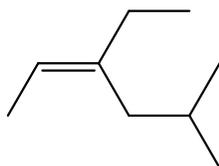
e) (*E,R*)-4-methyl-2-hexene

f) (*S*)-4-bromo-2-pentyne

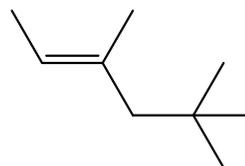
g) (*E*)-2-chloro-1-cyclopropyl-1-butene

1.2 Name each of the following compounds.

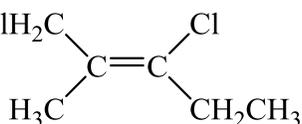
a)



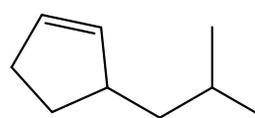
b)



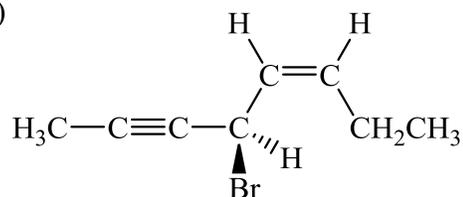
c)



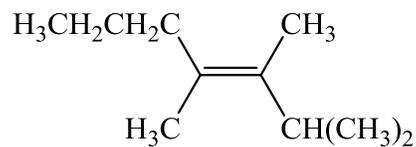
d)



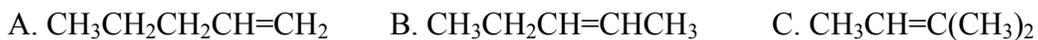
e)



f)



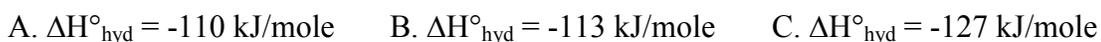
- 2.1 a) Which of the following compounds is the most stable?
 b) Which has the greatest heat of combustion?



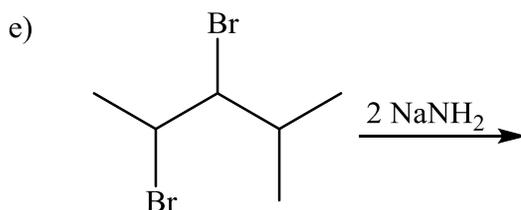
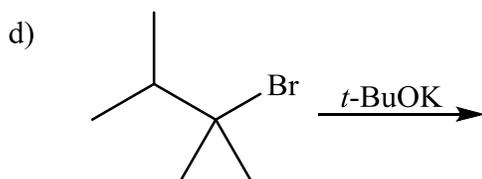
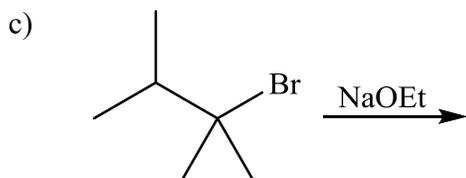
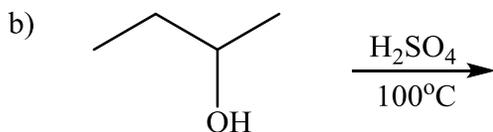
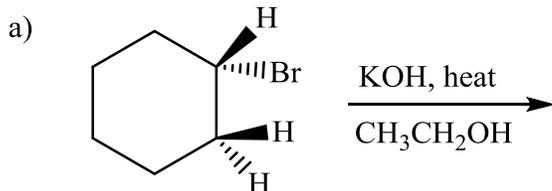
- 2.2 Number the compounds shown in order of increasing stability (1 = least stable, etc.)



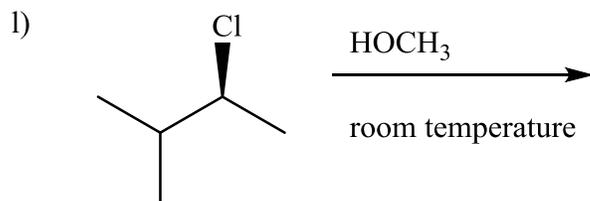
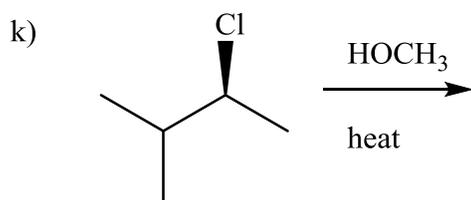
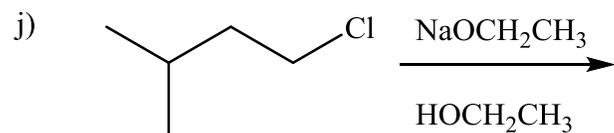
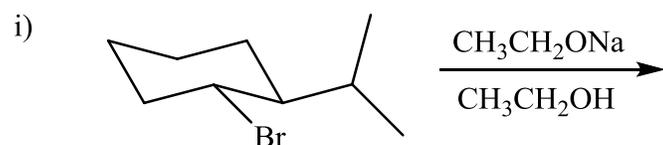
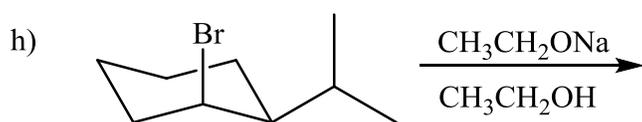
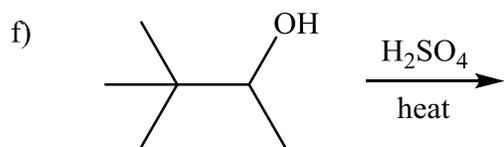
- 2.3 Based on the heats of hydrogenation given, which of these alkenes is the least stable?



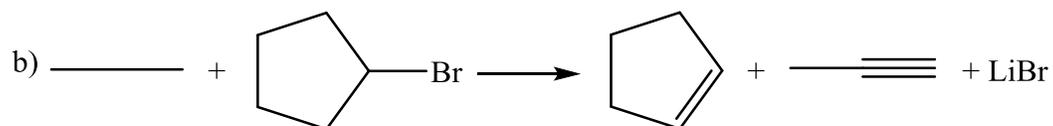
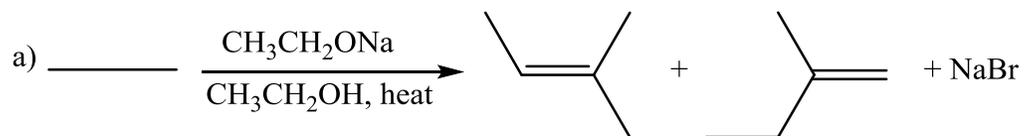
- 3.1 Predict the organic product or products of each of these reactions. If more than one organic product forms, indicate which is the major product.



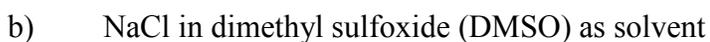
3.1 Predict the organic product or products, continued.



3.2 Fill in the blanks with the reagents necessary to complete the following reactions.



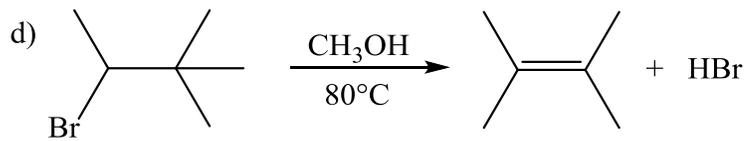
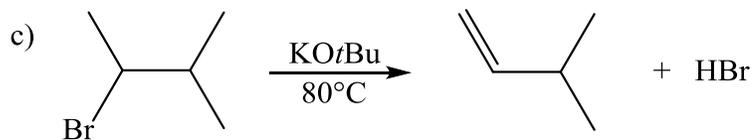
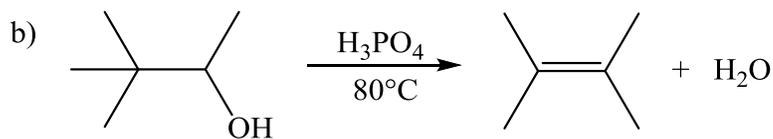
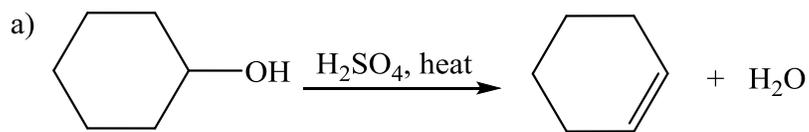
3.3 Identify the reaction mechanism when 2-bromopentane reacts with each of the following reagents:



3.4 The substrate 2-bromobutane reacts with one the following reagents. Classify each reagent as a nucleophile, strong base, good nucleophile, weak base, or weak nucleophile and identify the most likely mechanism for this reaction (E1, E2, S_N1 or S_N2).

Reagent	Classification	Likely Mechanism
HO ⁻		
Cl ⁻		
⁻ CN		
H ⁻		
CH ₃ OH		
(CH ₃) ₃ O ⁻		
N ₃ ⁻		
CH ₃ C≡C ⁻		

4.1 Propose complete mechanisms for the reactions shown. Add lone pairs and needed H atoms as necessary.



5.1 Propose a synthesis of the following compounds from the given starting materials. You may also use any needed inorganic reagents and solvents you may need.

a) $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{CH}_3$ from $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$ and CH_3Br

b) $\text{CH}_3\text{C}\equiv\text{CCH}_3$ from $\text{CH}_3\text{CHBrCHBrCH}_3$

c) $\text{CH}_3(\text{CH}_2)_{10}\text{CH}=\text{CH}_2$ from $\text{CH}_3(\text{CH}_2)_{10}\text{CHBrCH}_3$

6.1 Calculate the hydrogen deficiency index of the following compounds.

a) C_7H_{12}

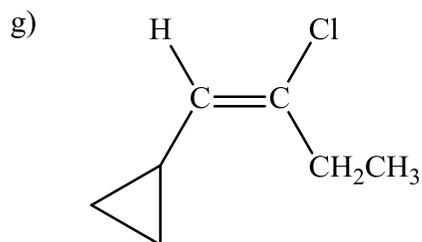
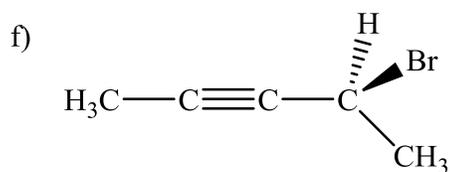
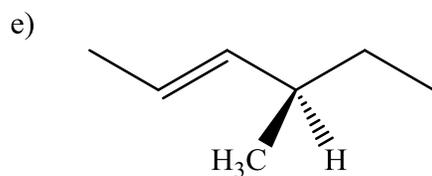
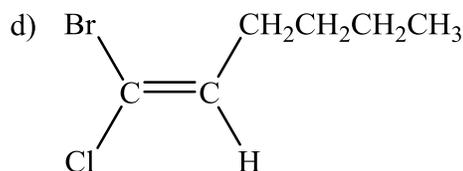
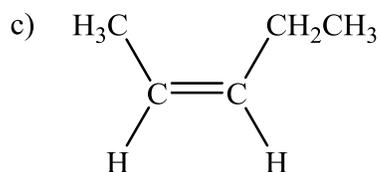
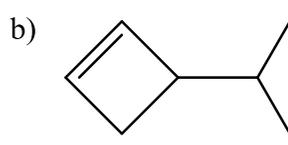
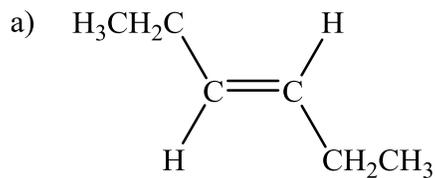
b) C_5H_{10}

c) $\text{C}_{10}\text{H}_{14}$

6.2 An unknown compound has the molecular formula C_6H_8 and absorbs two moles of hydrogen on treatment with H_2/Pt to yield cyclohexane. (Only pi bonds, not rings, absorb H_2 .) a) What is the hydrogen deficiency index of the compound? b) Draw a possible structure for the unknown.

SOLUTIONS TO SAMPLE PROBLEMS:

1.1 Structures:



1.2 Names:

a) (Z)-3-ethyl-5-methyl-2-hexene

b) (E)-3,5,5-trimethyl-2-hexene

c) (Z)-1,3-dichloro-2-methyl-2-pentene

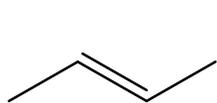
d) 3-isobutylcyclopentene

e) (Z,R)-4-bromo-5-octene-2-yne

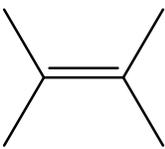
f) (E)-2,3,4-trimethyl-3-heptene

2.1 a) Most stable: C Greatest heat of combustion: A

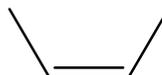
2.2 Number the compounds shown in order of increasing stability (1 = least stable, etc.)



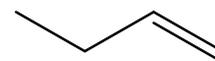
3



4 (most stable)



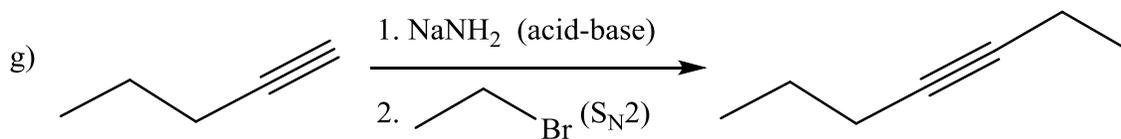
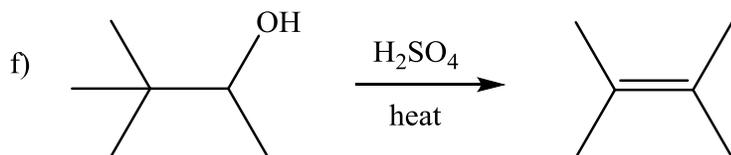
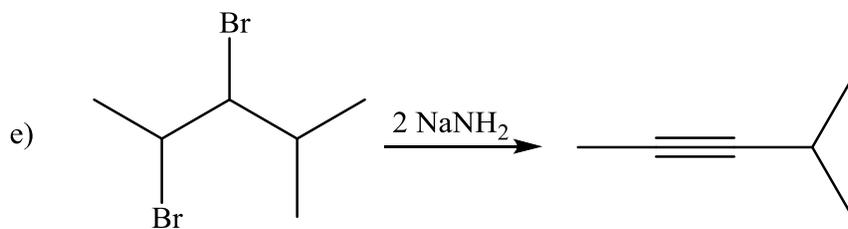
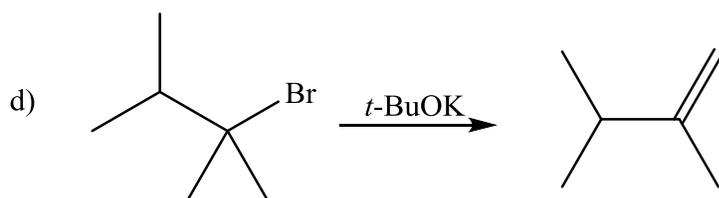
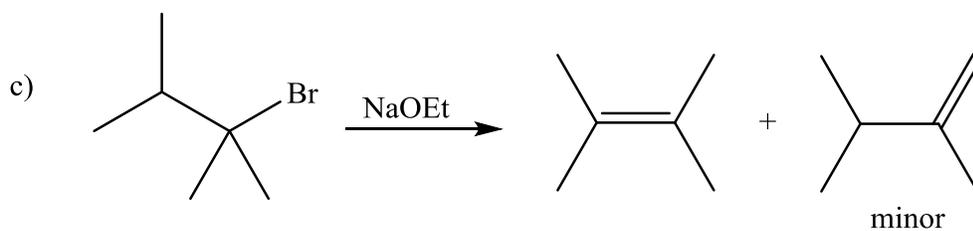
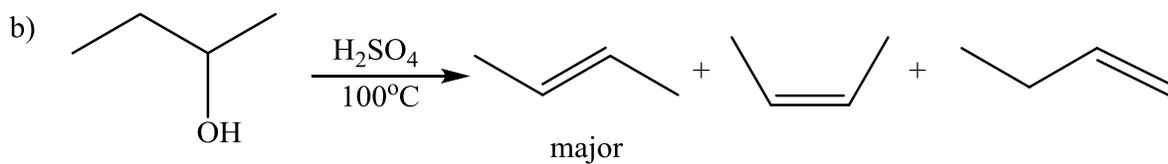
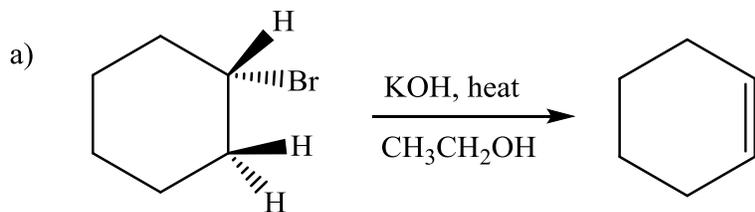
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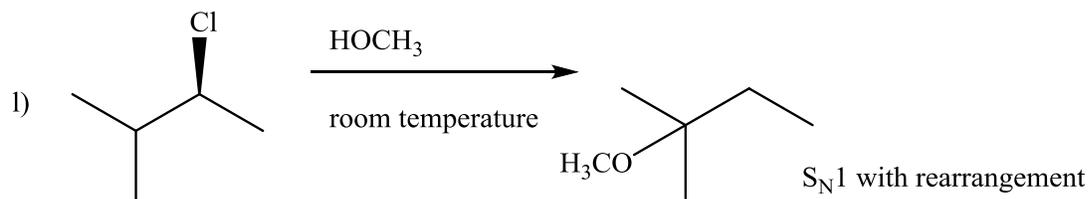
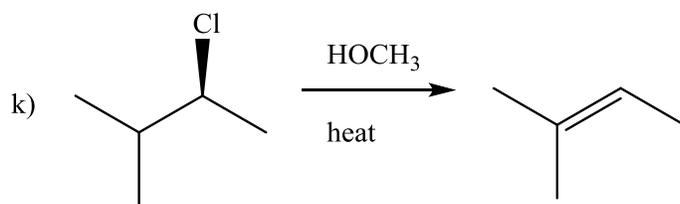
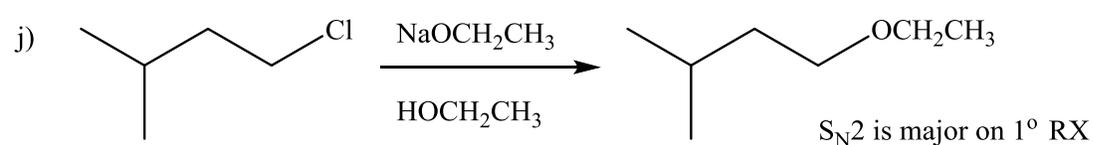
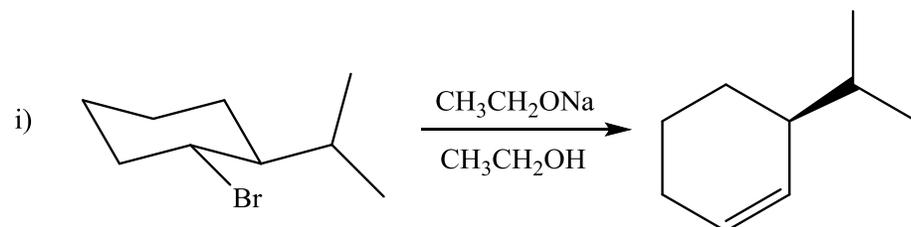
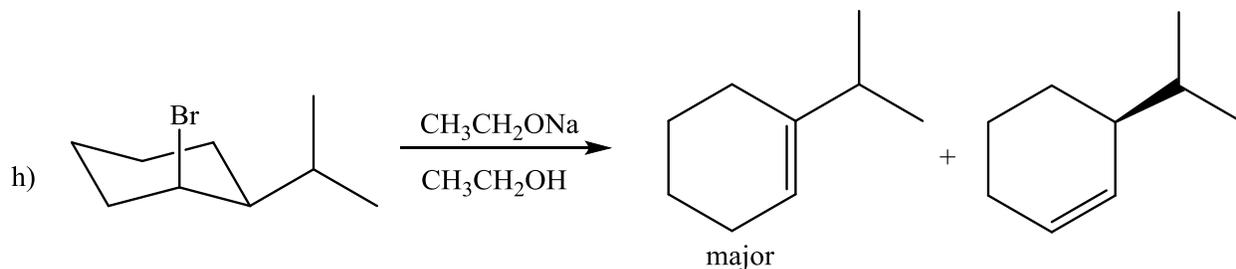
1 (least stable)

2.3 The least stable alkene of this group: C

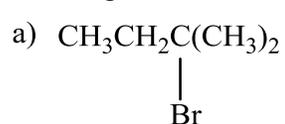
3.1 Predict the organic product or products of these reactions.



3.1 Continued:



3.2 The reagents necessary to complete the reactions are:



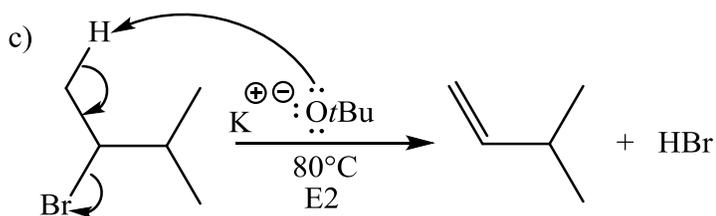
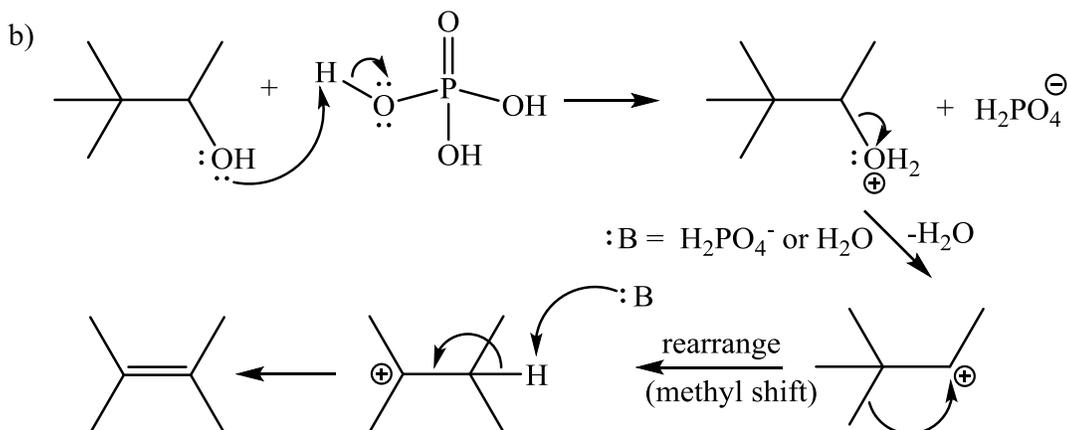
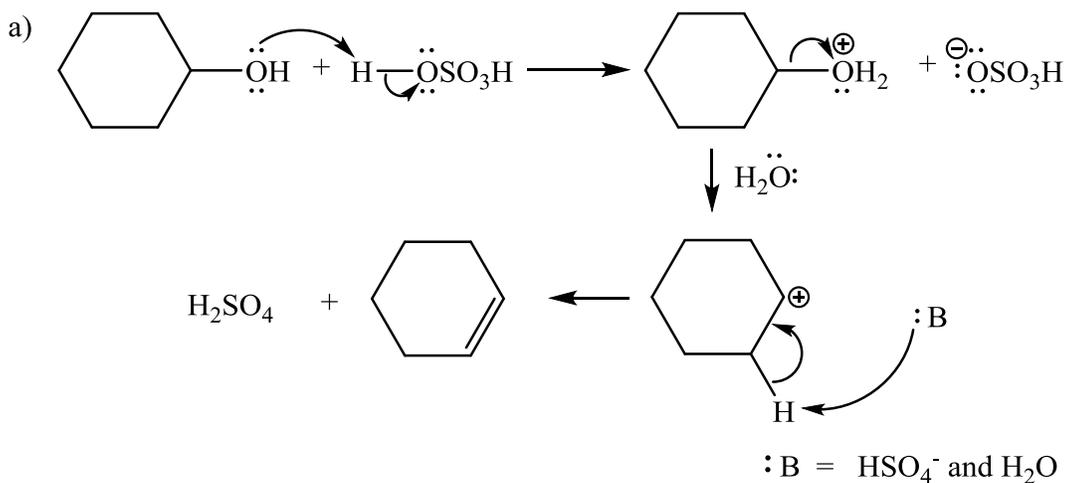
3.3 Identify the reaction mechanism when 2-bromopentane reacts with:

- a) $\text{NaOCH}_2\text{CH}_3$
 $\text{E}2$: 2° substrate with strong base (also strong nucleophile, but the base strength matters most here).
- b) NaCl in dimethyl sulfoxide (DMSO) as solvent
 $\text{S}_{\text{N}}2$: 2° substrate with weak base (i.e., not $\text{E}2$) that is a strong nucleophile. DMSO (polar, aprotic) is ideal for $\text{S}_{\text{N}}2$, and fine for $\text{E}2$, but shuts down $\text{E}1/\text{S}_{\text{N}}1$.

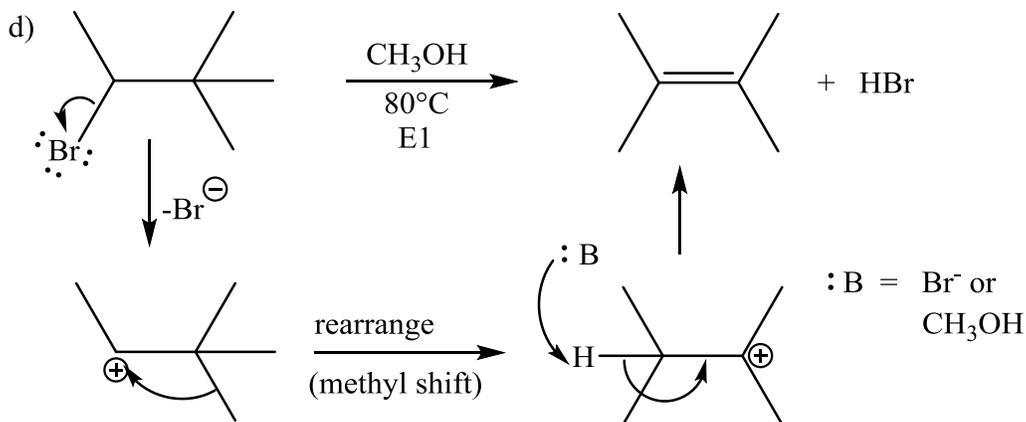
3.4

Reagent	Classification	Major Mechanism
HO^-	Strong base	E2
Cl^-	Nucleophile	$\text{S}_{\text{N}}2$
CN^-	Nucleophile	$\text{S}_{\text{N}}2$
H^-	Strong Base	E2
CH_3OH	weak nucleophile	$\text{S}_{\text{N}}1$,
$(\text{CH}_3)_3\text{O}^-$	Strong base	E2
N_3^-	Nucleophile	$\text{S}_{\text{N}}2$
$\text{CH}_3\text{C}\equiv\text{C}^-$	Strong base	E2

4.1 Mechanisms:



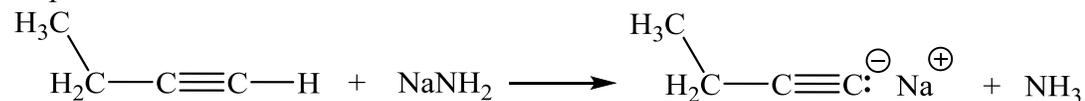
4.1



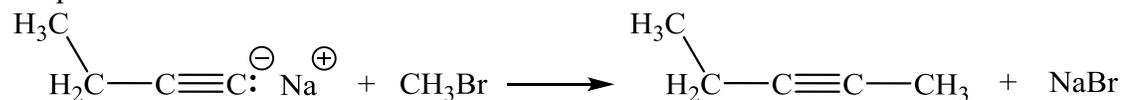
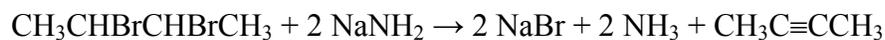
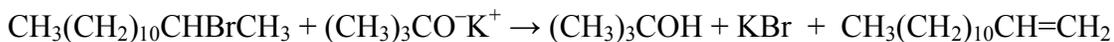
5.1 Synthesis:

a) $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{CH}_3$ from $\text{CH}_3\text{CH}_2\text{C}\equiv\text{C-H}$ and CH_3Br

Step 1:

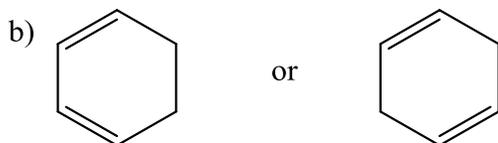


Step 2:

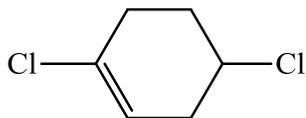
b) $\text{CH}_3\text{C}\equiv\text{CCH}_3$ from $\text{CH}_3\text{CHBrCHBrCH}_3$ c) $\text{CH}_3(\text{CH}_2)_{10}\text{CH}=\text{CH}_2$ from $\text{CH}_3(\text{CH}_2)_{10}\text{CHBrCH}_3$ 

(Note: The base $(\text{CH}_3)_3\text{CO}^-\text{K}^+$ was used here because it is both strong and bulky. A base without both of these characteristics will give the wrong product here.)

6.1 a) 2 b) 1 c) 4

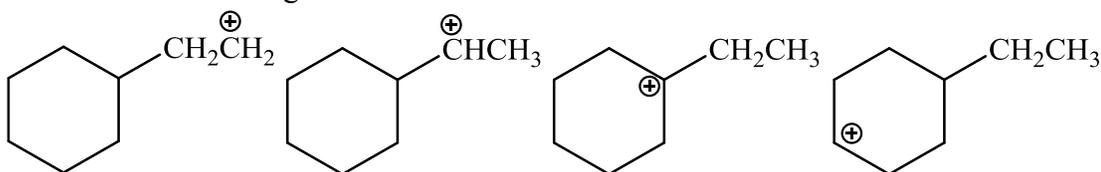
6.2 a) HDI = 3; must have 2 pi bonds because it absorbs 2 moles of H_2 

1. Name: 2. Draw: (Z)-1-chloro-2-ethyl-1-pentene

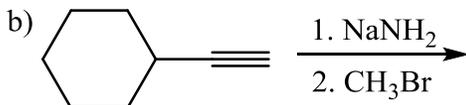
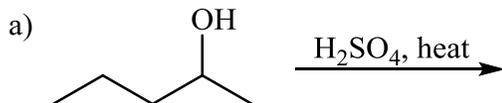


3. Which of these gives off the MOST heat when it reacts with an excess of O₂?
- A. (CH₃)₂CHCH=CHCH(CH₃)₂ B. (CH₃)₂CH(CH₂)₃CH=CH₂
C. (CH₃)₂C=C(CH₂CH₃)₂ D. (CH₃)₂C=CH(CH₂)₃CH₃

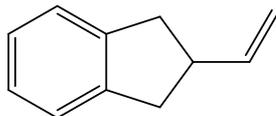
4. Which of the following is the MOST stable?



5. Predict the major product of each of the reactions given below



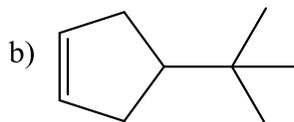
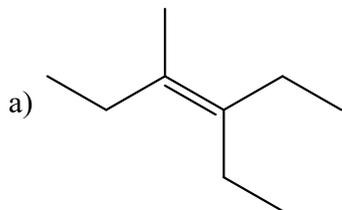
6. a) What is the hydrogen deficiency index of the compound shown? b) What is the hydrogen deficiency index of C₁₄H₂₄?



7. Propose a synthesis of CH₃CCCH₃ from CH₃Br, CH₃CCH, and any other needed reagents.

8. Propose a mechanism for (CH₃)₃C-OH $\xrightarrow{\text{H}_3\text{PO}_4, \Delta}$ (CH₃)₂C=CH₂ + H₂O

1. Give the IUPAC name of each of the following compounds.

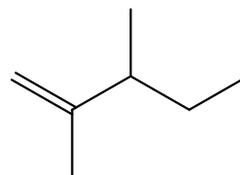
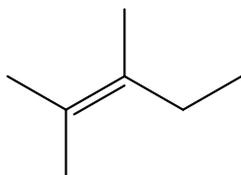
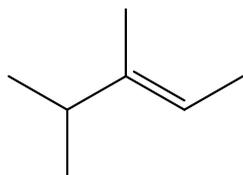


2. Draw the structure of each of the following compounds.

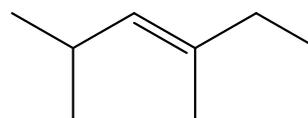
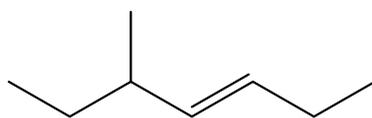
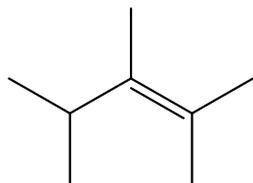
a) (Z)-2-bromo-2-hexene

b) 3-isopropylcycloheptene

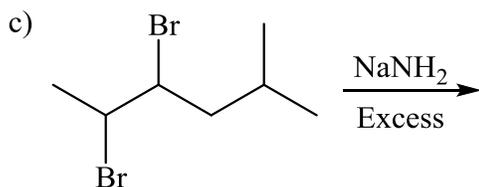
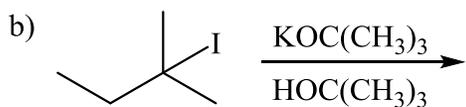
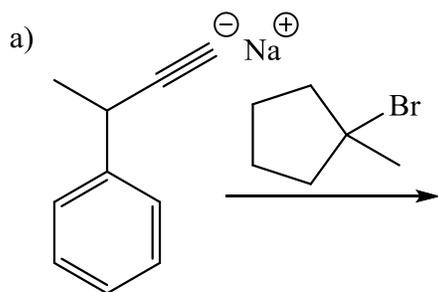
3. Which of the following compounds is the most stable? Which is the least stable?



4. Which of the following compounds has the greatest enthalpy (heat) of combustion?
Which has the smallest?



5. Predict the products of each of the following reactions. Where there are major and minor products for a reaction, indicate which product is the major one.



6. Propose a synthesis of 5-methyl-2-heptyne from 1-bromo-2-methylbutane.

7. Propose a complete mechanism for the following reaction.

