Ch. 7 Structure and Synthesis of Alkenes

7.1,2 Review

Bond Strength	
C-C σ Bond	83 kcal/mol
C=C π Bond	63 kcal/mol

- π Bonds are much weaker
- π Bonds are thus more breakable and more reactive

Double Bonds can't rotate

7.3 Elements of Unsaturation ("EU")
- **"Saturated Alkane"**: C_NH_{2N+2}
- **Unsaturated** Formula: Has less than the maximum 2N+2 number of hydrogens
- "**Element of Unsaturation**": Something that reduces the hydrogen count by two
  1. Double bond
  2. Ring

- Each element of unsaturation reduces the hydrogen count by two
- A molecule may well have several elements of unsaturation, each one progressively reducing it's hydrogen count by two.

Knowing how many elements of unsaturation are present helps to classify, and helps in isomer problems.

Calculating EU
General Concept

$$EU = \frac{\text{Theory \# H's - Actual \# H's}}{2}$$

For Formulas With Nothing
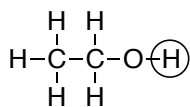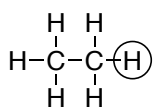Other than C, H, or O

$$EU = \frac{(2C + 2) - H}{2}$$

C = # C's
H = # H's
N = # N's
X - # halogens

For Formulas That May
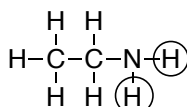Include Nitrogen or Halogens

$$EU = \frac{(2C + 2 + N) - (H + X)}{2}$$
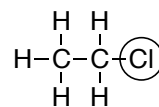
Heteroatom Effect:
- Oxygens: No effect
- Nitrogen: each nitrogen increases the theory # H's by 1
- Halogen: each halogen takes the place of a hydrogen and reduces the theory # H's by 1.

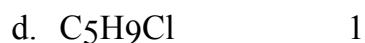Oxygen: no impact   Nitrogen: adds one   Halogen: replaces one

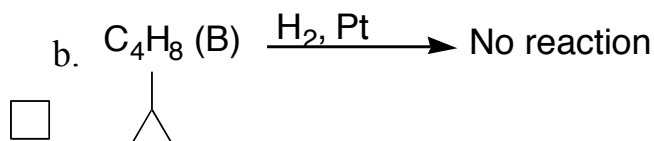1. Calculate how many elements of unsaturation are in the following formulas:

    a. C_5H_{12} 0

    b. C_4H_8 1

    c. C_3H_4O 2

    d. C_5H_9Cl 1
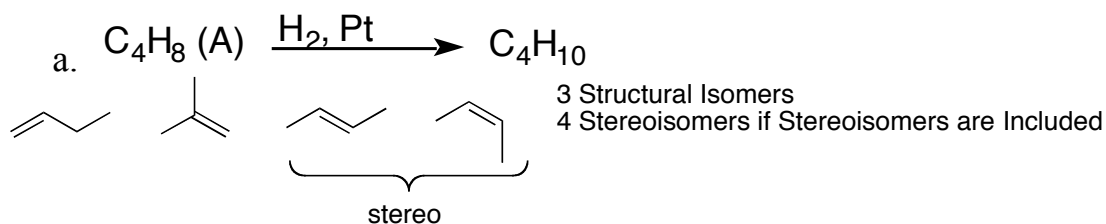
    e. $C_4H_{11}N$ 0

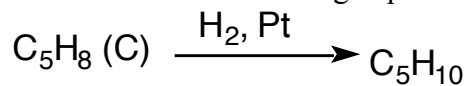Distinguishing Rings from Double Bonds by H_2/Pt Hydrogenation
- H_2/Pt will "saturate" **all** C=C double bonds by adding H_2 across each one.
- However, rings will not add hydrogen upon treatment with H_2/Pt
- Thus you can count how many of your EU's are rings versus double bonds
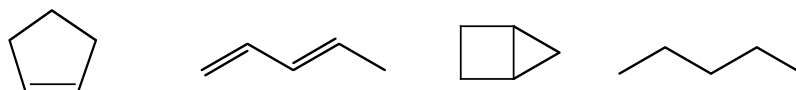- Note: 2H's add per 1 double bond
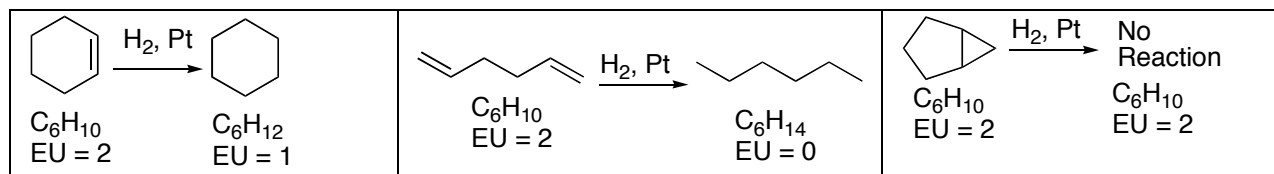
2. For C_4H_8 , draw all possible structures for isomer **A and isomer B,** given the following:

    a. C_4H_8 (A) $\xrightarrow{\text{H}_2,\ \text{Pt}}$ C_4H_{10}

3 Structural Isomers
4 Stereoisomers if Stereoisomers are Included

    b. C_4H_8 (B) $\xrightarrow{\text{H}_2,\ \text{Pt}}$ No reaction

3. Which of the following is possible for structure C?

C_5H_8 (C) $\xrightarrow{\text{H}_2,\ \text{Pt}}$ C_5H_{10} First one. One ring, one alkene.
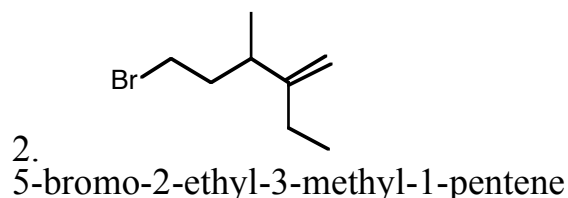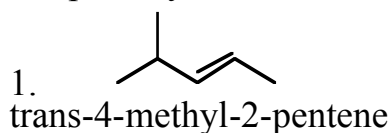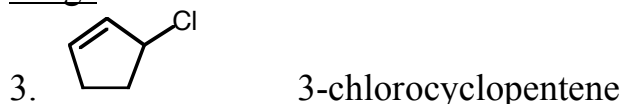
7.4,5 Nomenclature
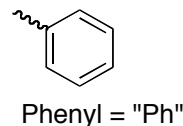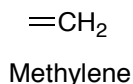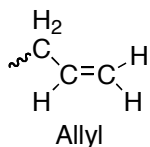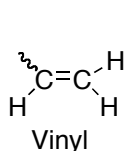A. When the Alkene is in the Core Name (the priority functional group)
    1. Number the longest continuous alkene-containing C-chain from the end
       nearest the alkene → core name = "x-…..ene"
    2. Designate the position of the alkene by using the lower-numbered of the two
       alkene carbons
    3. Attach and number substituents
    4. When alkene stereoisomer issues apply:
       • Designate stereochemistry as "E" or "Z" if the alkene is tri- or
         tetrasubstituted
       • If the alkene is di-substituted, you can use either E/Z or cis/trans to
         designate stereochemistry.
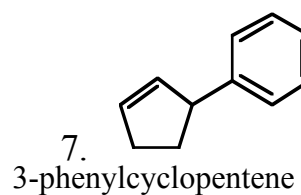
Give formal names for the following alkenes
Simple Acyclics

1.
trans-4-methyl-2-pentene

2.
5-bromo-2-ethyl-3-methyl-1-pentene

Rings

3.   3-chlorocyclopentene

B. Alkenes as Substitutents
    • Many functional groups have higher priority than alkenes, so that alkenes
      may need to be named as substituents rather than in the core name

Four to Memorize:

Vinyl   Allyl   =CH₂   Phenyl = "Ph"
                                          Methylene

Name the following:

4.
3-allylcyclohexene   5.   6.   7.
                        3-vinylcyclopentene   3-   3-phenylcyclopentene
                                              methylenecyclopentene
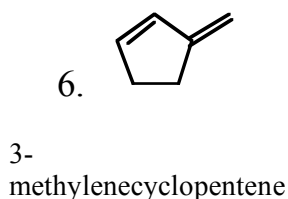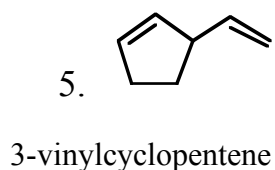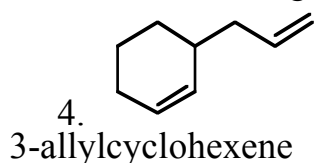
C. E-Z Nomenclature (7-5)
• Each carbon of an alkene has two attachments.
   1. Identify which of the two attachments on the left alkene carbon has higher priority.
   2. Then identify which attachment on the right alkene carbon has higher priority.
      • "Z" ("zusammen" = "together"): the priority attachments are cis
      • "E" ("entgegan = "opposite"): the priority attachments are trans

Z ("together")   E (opposite)   no Stereo
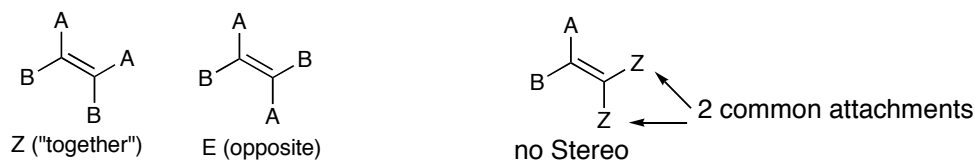
When does E/Z apply?
1. If either alkene carbon has two common attachments, than stereo doesn't apply
2. For tri- or tetrasubstituted alkenes (3 or 4 non-hydrogen attachments), E/Z must be used if there is stereochemistry
3. For di-substituted alkenes (one H on each alkene carbon), either E/Z or cis/trans designation can be used

Assign as Z or E
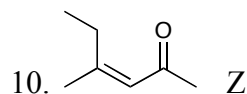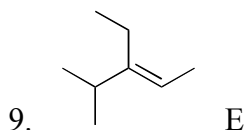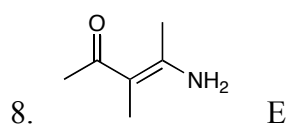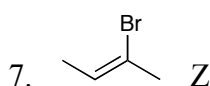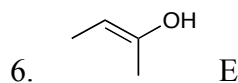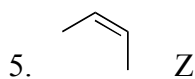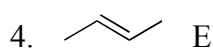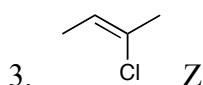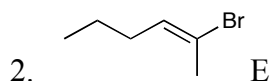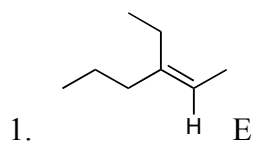
7.6   Alkenes and Polymers
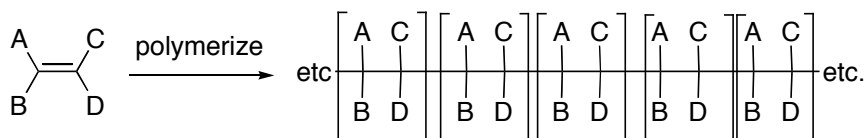
7.7 Alkene Stability Pattern

| tetra- subbed | tri- subbed | trans disubbed | 1,1- disubbed | cis disubbed | mono- subbed | un- subbed |

di-subbed

A. Increasing Substitution (# of non-hydrogens directly attached to alkene carbons) →
    Increased Stability
    • Why? Electronic Reasons.
        o Alkene carbons are somewhat electron poor due to the inferior overlap of pi
          bonds. (One carbon doesn't really "get" as much of the other carbon's electron
          as is the case in a nice sigma bond).
        o Since alkyl groups are electron donors, they stabilize electron-deficient alkene
          carbons.
        o Analogous to why electron-donating alkyls give the $3° > 2° > 1°$ stability pattern
          for cations and radicals

B. Trans is more stable than cis for 1,2-disubstituted alkenes
    • Why?
        o Steric Reasons

C. Measuring Relative Stability of Isomers by Heats of Hydrogenation or Heats of Combustion

ΔH = -30.3 kcal/mol
More exo, more energy released

common product

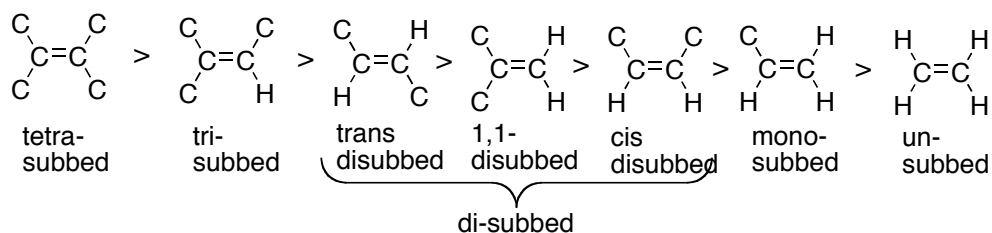ΔH = -26.9 kcal/mol
Less exo, less energy released
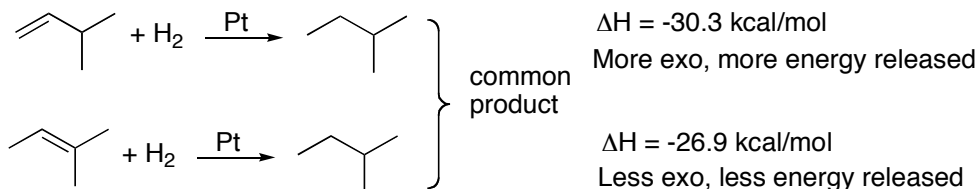
    • When 2 isomers can be converted to a common product, the relative magnitude of ΔH
      tells which isomer is more stable
    • The more heat released, the less stable the isomer. The less heat released, the more
      stable.
    • Heat of combustion works the same way (converts products to common CO_2 and H_2O)
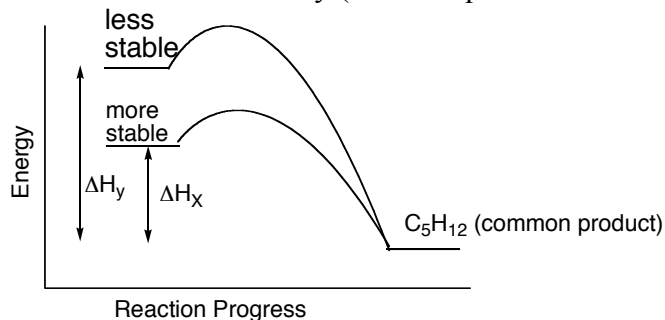
1. List the number of non-hydrogen substitutents on each alkene; rank the relative
    stability; rank by heat of hydrogenation, from 1 (most) to 4 (least)
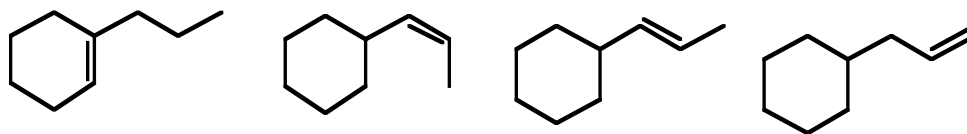
Stability: 1   3   2   4

Heat: 4   2   3   1

2. List the number of non-hydrogen substitutents on each alkene; rank the relative
    stability; When the following are burned, rank from the largest heat of combustion (1)
    to the smallest.

                        tetra   tri   mono
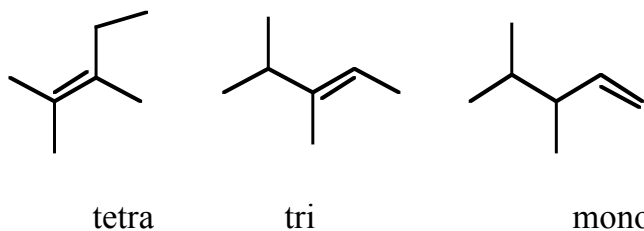
Stability:

Heat: 3   2   1

3. Which isomer is more stable, given the indicated heats of hydrogenation?

          80 kcal/mol   74 kcal/mol

              less   more
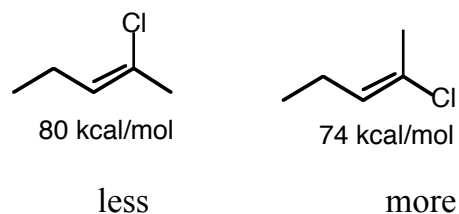
7.8 Physical Properties

7.9 Synthesis of Alkenes by E2 Elimination of Alkyl Halides (7.9A)
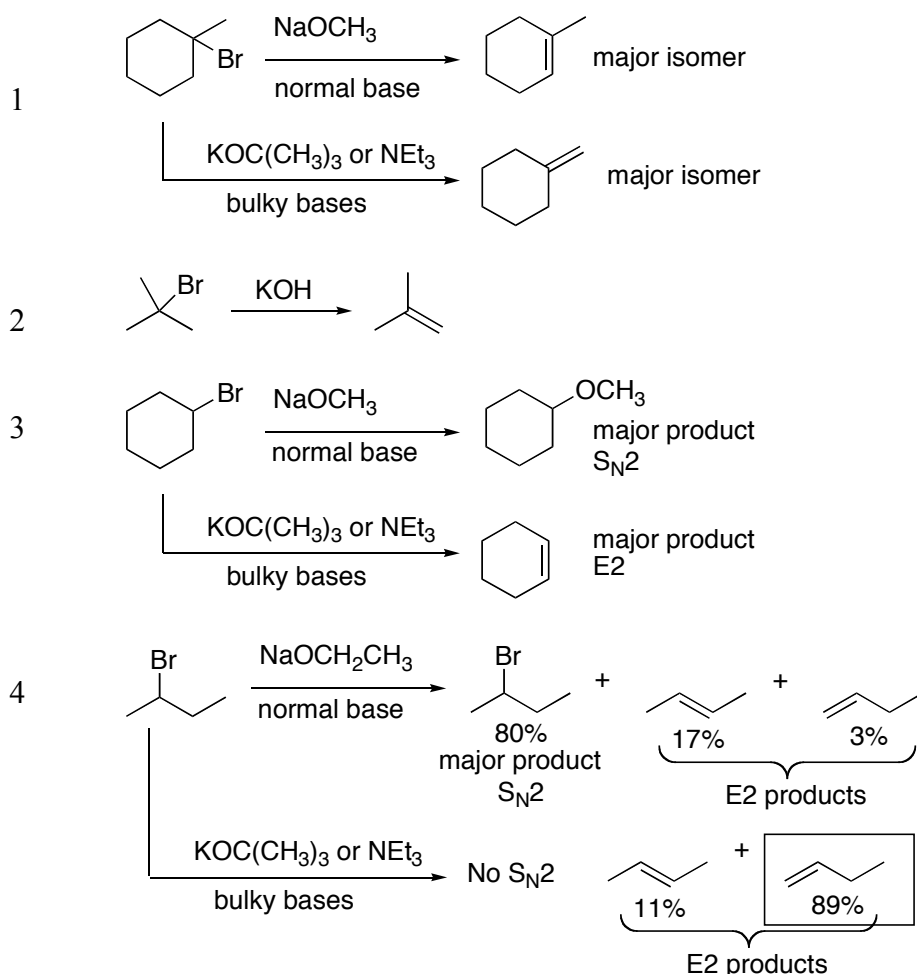
Factors to Consider
1. 3º R-X or 2º R-X
    a. 3º R-X gives E2 with any base
    b. 2º R-X gives largely S$_N$2 with **normal anions**.
    c. 2º R-X gives largely E2 with a **bulky base**. E2 prevails over S$_N$2
    •   Because S$_N$2 backside attack is so sterically sensitive, bulky bases have problems
        doing S$_N$2. Get E2 instead.

2. Base Size: Bulky Base versus Normal Base
    a. **Normal anions**:
    •   3º R-X give E2 only, no S$_N$2
    •   2º R-X give predominantly S$_N$2 rather than E2
    •   E2 elimiantions proceed with Zaytsev orientation: more-subbed alkene predominates
    b. **Bulky base**.
    •   3º R-X gives E2 only, no S$_N$2 .
    •   2º R-X gives E2 only, no S$_N$2 .
   •   E2's proceed via Hofmann orientation: less-subbed alkene predominates
        o   For steric reasons: base goes after less sterically hindered neighbor hydrogen
    •   2 Bulky Bases to Memorize:
        o   NEt$_3$ (Triethylamine)
        o   KOC(CH$_3$)$_3$ potassium t-butoxide

Bulky Bases: 2 to remember

$NEt_3 =$ [structure] "triethylamine"

Neutral
but amines
are basic
anyway

Normal Bases
NaOH, KOH, LiOH

$NaOCH_3$, $NaOCH_2CH_3$, $NaOCH_2CH_2CH_3$

$KOCH_3$, $KOCH_2CH_3$, $KOCH_2CH_2CH_3$

etc.

$KOC(CH_3)_3 = KOCMe_3 =$ [structure]
"potassium t-butoxide"
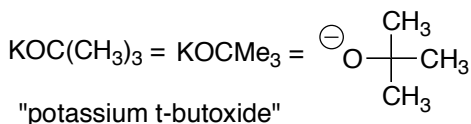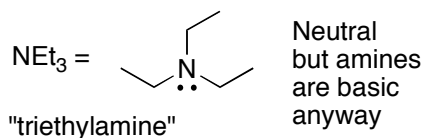
Bulky bases are:
1. Good S_N2 nucleophiles only for 1° R-X
2. Do clean E2 with both 3° R-X and 2° R-X
3. Give Hofmann elimination
(less substitued alkene major)

Normal bases are:
1. Anionic
2. Not especially bulky
3. Good S_N2 nucleophiles for 1° or 2° R-X
4. Only do clean E2 with 3° R-X
5. Give Zaitsev elimination
(more substitued alkene preferred)

3. Alkene Orientation: Zaytsev versus Hofmann Elimination
   a. **Zaytsev: most subbed alkene**
    • The major E2 product involves removal of a hydrogen from the most substituted neighbor carbon
    • This results in a maximally substituted, maximally stable alkene (product stability)
    • Normal-sized bases give predominantly Zaytsev elimination
    b. **Hofmann: least subbed alkene**
    • The major E2 product involves removal of a hydrogen from the least substituted neighbor carbon
    • This results in a less substituted, less stable alkene
    • Bulky bases give predominantly Hofmann elimination
    • Why: Steric reasons. A bulky base ends up having an easier time reaching a hydrogen on a less substituted carbon than on a more substituted carbon (transition-state stability-reactivity principle)

4. Stereochemistry: A trans-hydrogen is required.

5. Mechanism: Concerted.

Mech: [reaction mechanism structure] $+ H-OCH_3 + Br^{\ominus}$
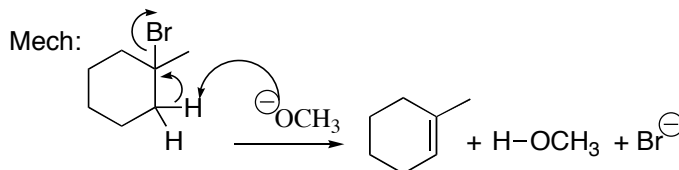
Predicting E2 Eliminations:
1. Is the base normal or bulky?
2. Is the R-X 3°, 2°, or 1°?
3. Will E2 or S_N2 occur predominantly?
4. Will you get Zaitsev or Hoffman elimination?
5. Is there a trans hydrogen available?

Draw the major Product for each of the following Reactions.

1.

Br ⟶ NaOH ⟶

NEt₃, heat ⟶

2.

Br ⟶ NaOCH₃ ⟶ OCH₃

KOC(Me)₃ ⟶

3.

NaOH ⟶ (HO, D, H, CH₃ product) + (D, CH₃ product)

To the extent that
E2 occurs, Zaytsev

NEt₃, heat ⟶ (D, H, CH₃ product)   Hofmann, no SN2

4.

NaOH ⟶ (HO, D, H, CH₃ product) + (D, CH₃ product)

SN2 major

To the extent that
E2 occurs, Zaytsev isn't possible
because of trans H requirement

NEt₃, heat ⟶ (D, CH₃ product)   Hofmann, no SN2

5.

Br ⟶ NEt₃
    or
    KOC(Me)3 ⟶

6.

Br ⟶ NEt₃
    or
    KOC(Me)3 ⟶   Bulky Base
                 so E2 Only

Indirect Route to Alkenes from Alkanes

Via 2 Reactions:
1. Bromination (reaction 1) followed by
2. Elimination (reaction 2)
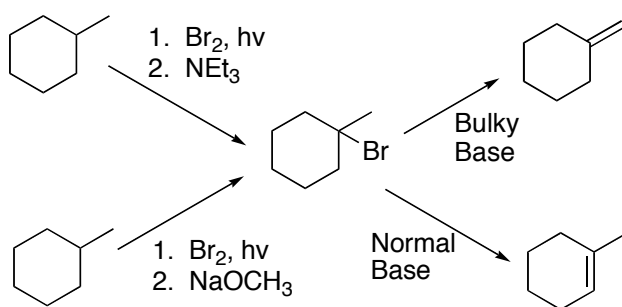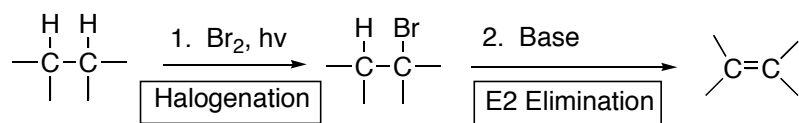
Provide Recipe:

7.10 Synthesis of Alkenes from Alcohol

General:

1

(+ isomers)

major

2

3

Observations:
- Zaytsev, not Hoffman elimination.
- No requirement for a trans hydrogen.
- Acidic conditions, need an acidic mechanism.

Mechanism (Memorize)
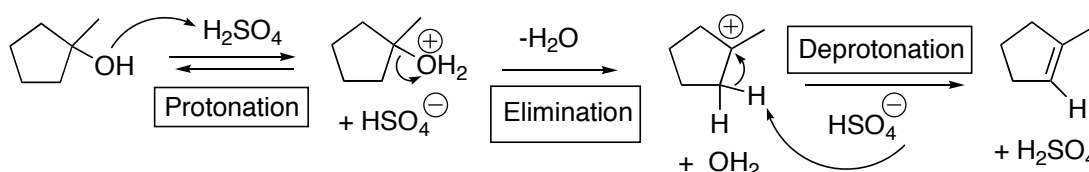
1. **3 steps: Protonation – Elimination – Deprotonation**
2. Protonation converts OH, a bad leaving group, into a very good leaving group (neutral water)
3. **Carbocation formation is slow step (like E1 mechanism)**
   - Cation stability dictates reactivity
   - Reactivity: allylic > 3° R-OH > 2° R-OH >>> 1° R-OH > vinyl, aryl
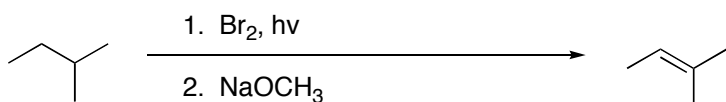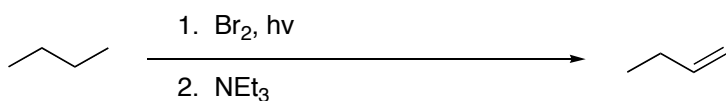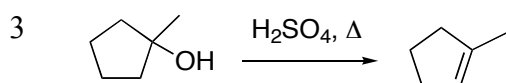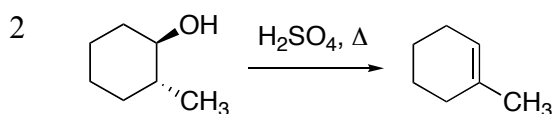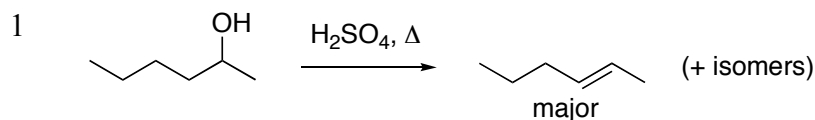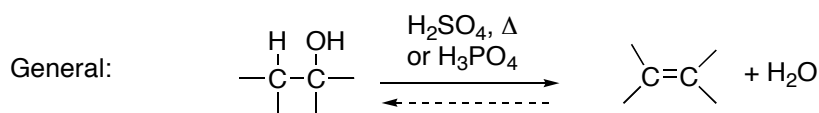   - Allylic, 3°, and 2° work; 1°, vinyl, and aryl do not.
4. C-H cleavage comes last.
5. Mechanism typical for acid-catalyzed processes: protonate-react-deprotonate. Protonation and deprotonation sandwich the key step.
6. Strong acidic conditions → intermediates should be positive, not negative
7. Because the cation is flat, and forgets original stereochemistry, there is no trans-H requirement.
8. The reaction is actually reversible, an equilibrium
9. Get complete E1, not S_N1, because the water that falls off in step 2 is converted to hydronium H_3O^+
10. Often the equilibrium is driven by distilling the alkene off as it forms. The alkene product has a much lower boiling point than the starting alcohol, based on both polarity (H-bonding is gone) and because of lower molecular weight.

Draw Products

1. OH H_2SO_4, heat

2. OH H_2SO_4, heat

3. OH H_2SO_4, heat

4.

Z = OH
H_2SO_4, heat
Zaytsev
Cis is OK

Z = Br
NaOCH₃
E2 must go
trans
+ SN2
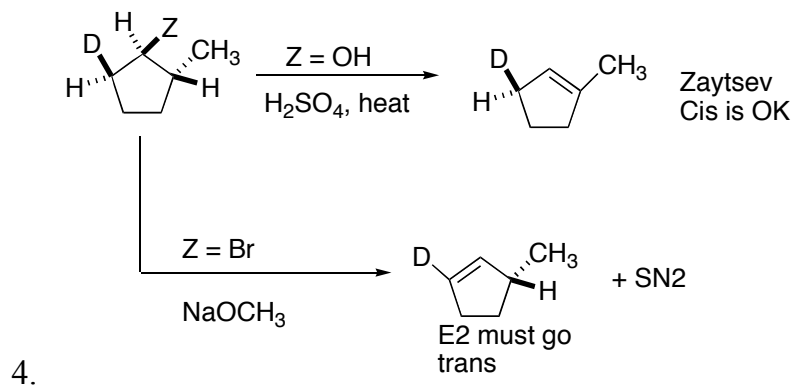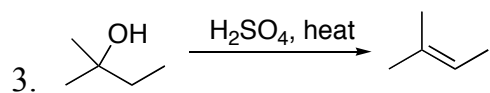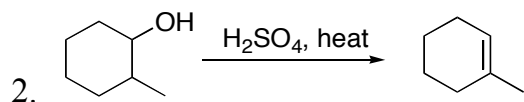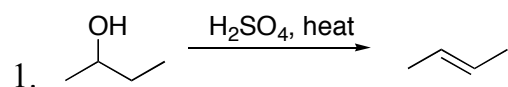
5. Rank the reactivity of the following toward H_2SO_4-catalyzed elimination (1 most). Why?
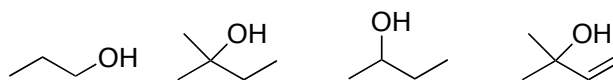
Key Issue: Cation Stability
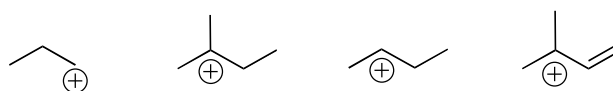
Reactivity: 4   2   3   1

Reaction Mechanisms (see p. 310)

A. Recognizing/Classifying as Radical, Cationic, or Anionic

1. Radical
   ▪ initiation requires both energy (either hv or Δ) and a weak, breakable heteroatom-
     heteroatom bond
        o Cl-Cl, Br-Br, O-O (peroxide), N-Br, etc..

   ┌───┐
   │ 2 Guides for That are Usually Reliable: │
   │ hv → radical mechanism   │
   │ peroxides → radical mechanism   │
   └───┘

2. Anionic
   ▪ **a strong anion/base appears in the recipe**
   ▪ no strong acids should appear in the recipe
   ▪ mechanisms should involve anionic intermediates and reactants, not strongly cationic
     ones
        • (except for do-nothing spectators like metal cations)
   ▪ The first step in the mechanism will involve the strong anion/base that appears in the
     recipe

3. Cationic
   ▪ **a strong acid/electrophile appears in the recipe**
   ▪ no strong anion/base should appear in the recipe
   ▪ mechanisms should involve cationic intermediates and reactants, not strongly anionic
     ones
        • (except for do-nothing spectators like halide or hydrogen sulfate anions)
   ▪ The first step in the mechanism will involve the acid that appears in the recipe. The last
     step will often involve a deprotonation step. Often the main step occurs in between the
     proton-on and proton-off steps

B. Miscellaneous Mechanism Tips

   1. Keep track of hydrogens on reacting carbons
   2. **Each step in a mechanism must balance**
   3. The types of intermediates involved (cation, anion, or radical) should be consistent
       with the reaction classification above
       a. **If the reaction is cationic, don't show anionic intermediates**
       b. **If the reaction is anionic, don't show cationic intermediates**
   4. Usually conditions are ionic.
   5. **Use a reactive species, whether strong anion or an acid, to start the first step**
       a. **If acidic, first step will involve protonation of the organic**
       b. **If anionic, the first step will involve the anion attacking the organic.**
   6. While it isn't always easy to figure out what is a good mechanism, you should often
       be able to eliminate an unreasonable mechanism.

1. Classify each mechanism as radical, cationic, or anionic.

a.   Cationic

b.   Radical

c.   Anionic

d.   Anionic

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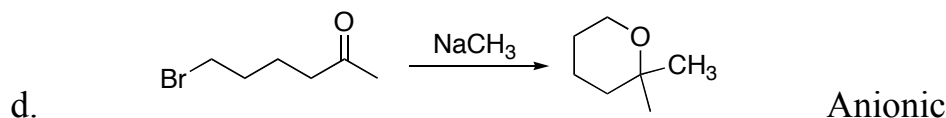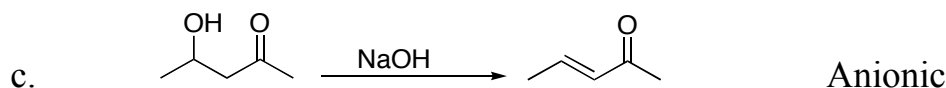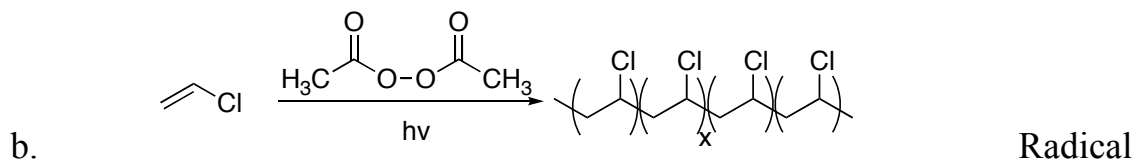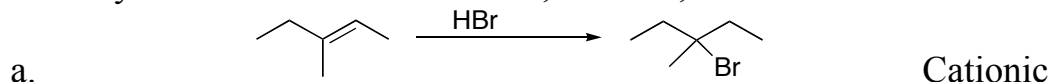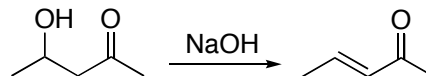
2. Which of the following mechanisms is reasonable or unreasonable for the transformation shown:

Identify recognition keys for things wrong with those that aren't right.

Problems

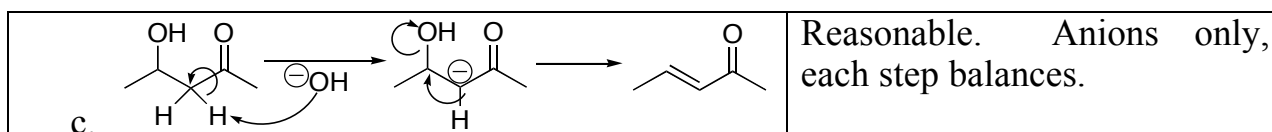|	
a.	Cation intermediate produced in step one
b.	Step 2 problems. a) oxygen left with 6 electrons b) where are the indicated arrows going to? The carbon already has four bonds, and there is no indication that anything is leaving. c) Atom balance. The carbon had two hydrogens going in, it looks to have only one coming out.
c.	Reasonable. Anions only, each step balances.

Q: Which of the following mechanisms is reasonable or unreasonable for the

transformation shown:

$$\text{(alkene)} \xrightarrow{\text{H}_2\text{O, H}^+} \text{(isopropanol, OH)}$$

- Identify recognition keys for things wrong with those that aren't right.

Problems

a.	a) Anion, should be cationic. b) Atom balance; where did water's oxygen go? c) Neutral water is too stable and weak to attack a neutral alkene
b.	a) Anion, should be cationic. b) No hydroxide in acid
c.	a) Doesn't use the acid proton b) Doesn't balance. Where did water's hydrogen go? c) Doesn't balance. How did alkene terminus go from 2 H's to three? d) Neutral alkene is too stable and weak to attack a neutral water.
d.	a) Doesn't use the acid proton in first step. b) Neutral alkene is too stable and weak to attack a neutral water. c) Atoms don't balance in first step d) Charge doesn't balance in first step e) Water is not an H-anion donor (step 2) f) If water actually did donate H-anion in step two, it would leave an OH-cation (not likely or possible!)
e	Good. a) Uses H+ in first step, as it should. b) All cation steps. c) Each step has charge and atom balance.