Chapter 7

Alkenes and Alkynes I:
Properties and Synthesis.
Elimination Reactions
of Alkyl Halides

Created by
Professor William Tam & Dr. Phillis Chang

About The Authors

These PowerPoint Lecture Slides were created and prepared by Professor William Tam and his wife, Dr. Phillis Chang.

Professor William Tam received his B.Sc. at the University of Hong Kong in 1990 and his Ph.D. at the University of Toronto (Canada) in 1995. He was an NSERC postdoctoral fellow at the Imperial College (UK) and at Harvard University (USA). He joined the Department of Chemistry at the University of Guelph (Ontario, Canada) in 1998 and is currently a Full Professor and Associate Chair in the department. Professor Tam has received several awards in research and teaching, and according to *Essential Science Indicators*, he is currently ranked as the Top 1% most cited Chemists worldwide. He has published four books and over 80 scientific papers in top international journals such as *J. Am. Chem. Soc., Angew. Chem., Org. Lett.,* and *J. Org. Chem.*
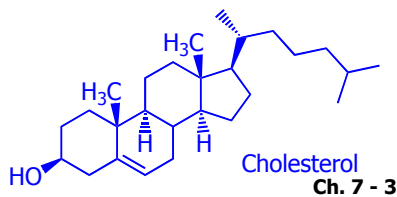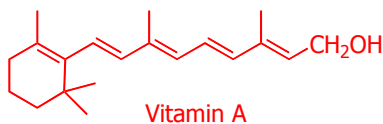
Dr. Phillis Chang received her B.Sc. at New York University (USA) in 1994, her M.Sc. and Ph.D. in 1997 and 2001 at the University of Guelph (Canada). She lives in Guelph with her husband, William, and their son, Matthew.
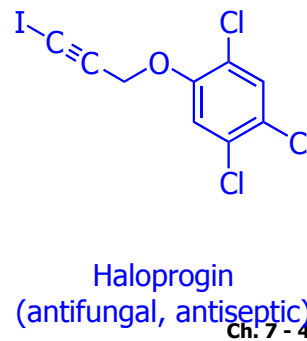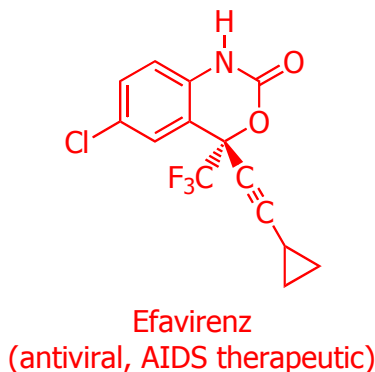
---

1. Introduction

❖ Alkenes
  - Hydrocarbons containing C=C
  - Old name: olefins

CH_2OH

Vitamin A

Cholesterol

HO

❖ Alkynes
  - Hydrocarbons containing C≡C
  - Common name: acetylenes

Efavirenz
(antiviral, AIDS therapeutic)
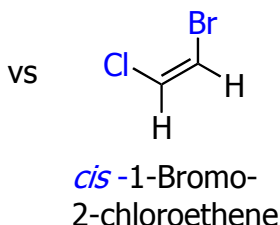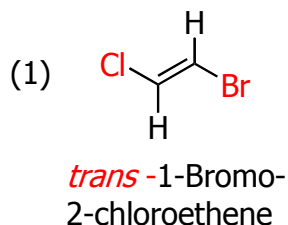
Haloprogin
(antifungal, antiseptic)

---

2. The (*E*) - (*Z*) System for Designating Alkene Diastereomers

❖ *Cis-Trans* System
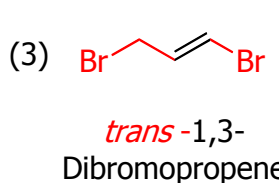 - Useful for 1,2-disubstituted alkenes
  - Examples:

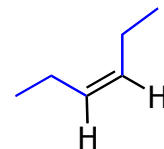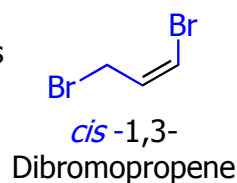(1)

trans-1-Bromo-2-chloroethene   vs   *cis*-1-Bromo-2-chloroethene

---

  - Examples

(2)   *trans*-3-Hexene   vs   *cis*-3-Hexene

(3)   *trans*-1,3-Dibromopropene   vs   *cis*-1,3-Dibromopropene
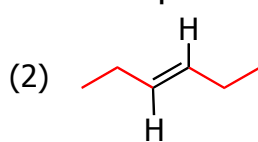
❖ *(E) - (Z)* System
  ● Difficulties encountered for trisubstituted and tetrasubstituted alkenes

e.g.   Cl—C=C(CH$_3$)(Br), H   *cis* or *trans*?
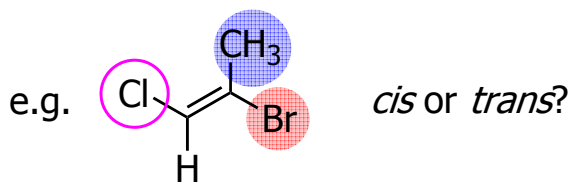
Cl is *cis* to CH$_3$
and *trans* to Br

❖ The Cahn-Ingold-Prelog *(E) - (Z)* Convention

  ● The system is based on the atomic number of the attached atom

 ● The higher the atomic number, the higher the priority

---

❖ The Cahn-Ingold-Prelog *(E) - (Z)* Convention
  ● *(E)* configuration – the highest priority groups are on the opposite side of the double bond
    ♦ "*E*" stands for "entgegen"; it means "opposite" in German
  ● *(Z)* configuration – the highest priority groups are on the same side of the double bond
    ♦ "*Z*" stands for "zusammer"; it means "together" in German

---

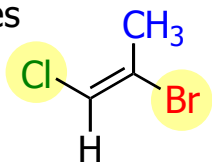● Examples

Cl—$\overset{1}{C}$=$\overset{2}{C}$(CH$_3$)(Br), H
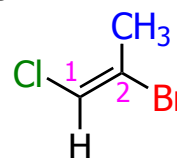
On carbon 2: Priority of Br > C
On carbon 1: Priority of Cl > H

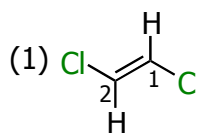⇒ highest priority groups are Br (on carbon 2) and Cl (on carbon 1)

● Examples

Cl—C=C(CH$_3$)(Br), H

⇒ *(E)*-2-Bromo-1-chloropropene

Cl—C=C(Br)(CH$_3$), H
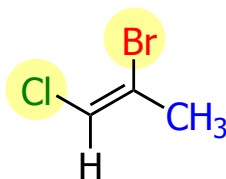
⇒ *(Z)*-2-Bromo-1-chloropropene

● Other examples

(1) Cl—$\overset{}{\underset{2}{C}}$=$\overset{1}{C}$—Cl (with H's)

(E)-1,2-Dichloroethene
[or *trans*-1,2-Dichloroethene]

C1: Cl > H
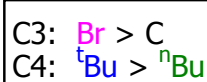C2: Cl > H

(2) Cl—$\overset{}{\underset{1}{C}}$=$\overset{2}{C}$—Cl, Br
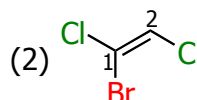
(Z)-1-Bromo-1,2-dichloroethene

C1: Br > Cl
C2: Cl > H

- Other examples

(3)

Br

C3: Br > C
C4: ^{t}Bu > ^{n}Bu
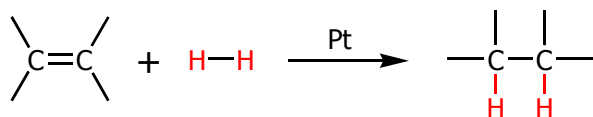
(Z)-3-Bromo-4-tert-butyl-3-octene
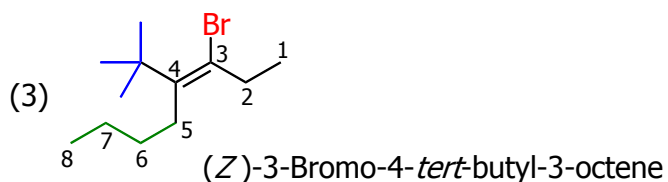
3. Relative Stabilities of Alkenes

❖ *Cis* and *trans* alkenes do not have the same stability

crowding

Less stable

More stable
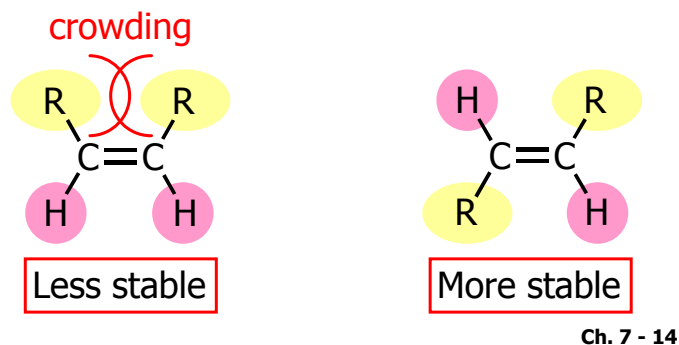
3A. Heat of Reaction

$$C=C + H-H \xrightarrow{Pt} -C-C-$$

❖ Heat of hydrogenation
- $\Delta H° \approx -120$ kJ/mol

+ H_2

7 kJ/mol

$\Delta H° = -127$ kJ/mol

+ H_2

5 kJ/mol   + H_2

$\Delta H° = -120$ kJ/mol

$\Delta H° = -115$ kJ/mol

Enthalpy
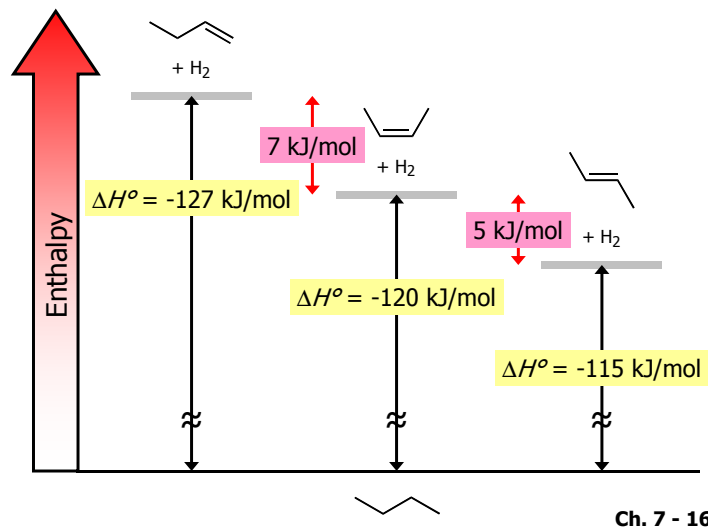
3B. Overall Relative Stabilities of Alkenes

❖ The greater the number of attached alkyl groups (i.e., the more highly substituted the carbon atoms of the double bond), the greater the alkene's stability.

❖ Relative Stabilities of Alkenes

tetra-substituted   >   tri-substituted   >   di-substituted   >   mono-substituted   >   un-substituted

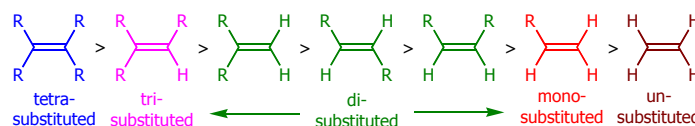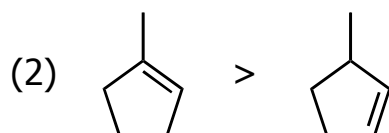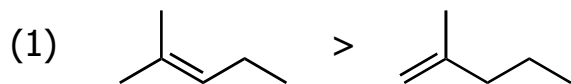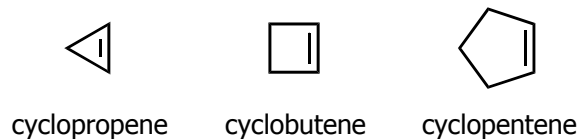❖ Examples of stabilities of alkenes

(1) >

(2) >

4. Cycloalkenes

❖ Cycloalkenes containing 5 carbon atoms or fewer exist only in the *cis* form

cyclopropene   cyclobutene   cyclopentene

❖ *Trans* – cyclohexene and *trans* – cycloheptene have a very short lifetime and have not been isolated

cyclohexene   Hypothetical
trans - cyclohexene
(too strained to exist at r.t.)
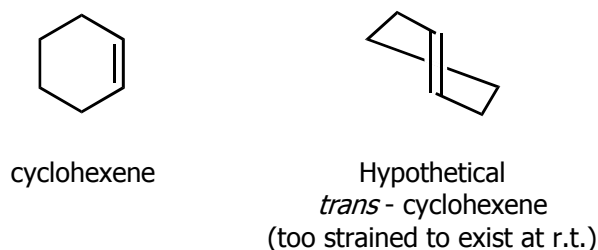
❖ *Trans* – cyclooctene has been isolated and is chiral and exists as a pair of enantiomers

cis - cyclooctene   *trans* - cyclooctenes
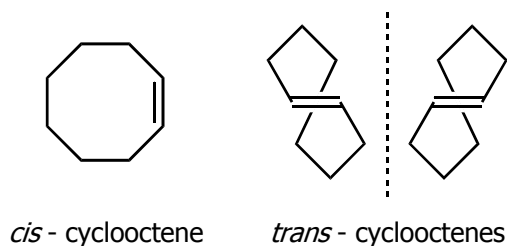
5. Synthesis of Alkenes via Elimination Reactions

❖ Dehydrohalogenation of Alkyl Halides
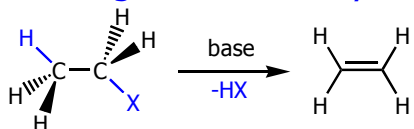
❖ Dehydration of Alcohols

6. Dehydrohalogenation of Alkyl Halides

❖ The best reaction conditions to use when synthesizing an alkene by **dehydrohalogenation** are those that promote an E2 mechanism

6A. How to Favor an E2 Mechanism

❖ Use a secondary or tertiary alkyl halide if possible. (Because steric hinderance in the substrate will inhibit substitution)

❖ When a synthesis must begin with a primary alkyl halide, use a bulky base. (Because the steric bulk of the base will inhibit substitution)

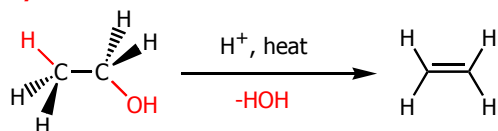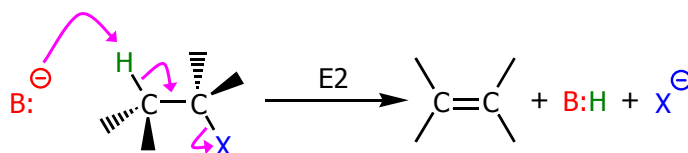❖ Use a high concentration of a strong and nonpolarizable base, such as an alkoxide. (Because a weak and polarizable base would not drive the reaction toward a bimolecular reaction, thereby allowing unimolecular processes (such as S_N1 or E1 reactions) to compete.
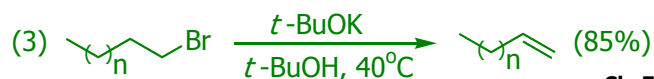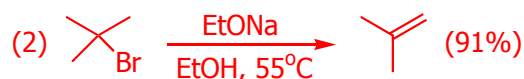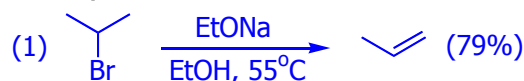
❖ Sodium ethoxide in ethanol (EtONa/EtOH) and potassium *tert-butoxide in tertbutyl* alcohol (t-BuOK/t-BuOH) are bases typically used to promote E2 reactions

❖ Use elevated temperature because heat generally favors elimination over substitution. (Because elimination reactions are entropically favored over substitution reactions)

6B. Zaitsev's Rule

❖ Examples of dehydrohalogenations where only a single elimination product is possible

(1) $\xrightarrow[\text{EtOH, 55}^\circ\text{C}]{\text{EtONa}}$ (79%)

(2) $\xrightarrow[\text{EtOH, 55}^\circ\text{C}]{\text{EtONa}}$ (91%)

(3) $\xrightarrow[\text{t-BuOH, 40}^\circ\text{C}]{\text{t-BuOK}}$ (85%)

❖ Rate = $k\left[H_3C-\underset{\underset{Br}{|}}{\overset{\overset{H}{|}}{C}}-CH_3\right]\left[EtO^\ominus\right]$

(2nd order overall) ⟹ bimolecular

− Hᵃ → 2-methyl-2-butene

− Hᵇ → 2-methyl-1-butene
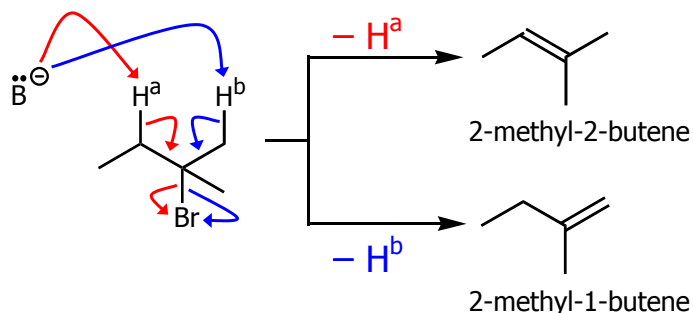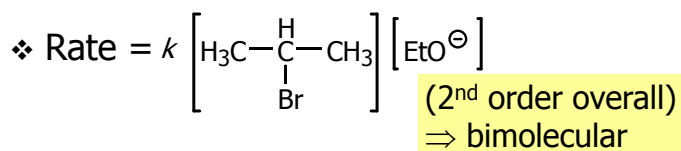
❖ When a small base is used (e.g. $EtO^\ominus$ or $HO^\ominus$) the major product will be the more highly substituted alkene (the more stable alkene)

❖ Examples:

(1) $\xrightarrow[\substack{\text{EtOH} \\ 70^\circ\text{C}}]{\text{NaOEt}}$ 69% + 31%

(eliminate Hᵃ) (eliminate Hᵇ)

(2) $\xrightarrow[\text{EtOH}]{\text{KOEt}}$ 51% + 18% + 31%

69%
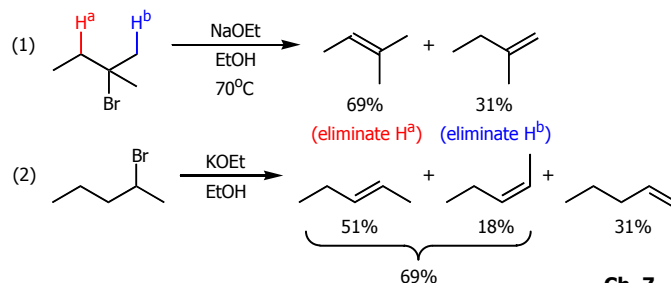
❖ Zaitsev's Rule
  ● In elimination reactions, the more highly substituted alkene product predominates
❖ Stability of alkenes

$$\underset{Me}{\overset{Me}{>}}C=C\underset{Me}{\overset{Me}{}} > \underset{Me}{\overset{Me}{}}C=C\underset{H}{\overset{Me}{}} > \underset{H}{\overset{Me}{}}C=C\underset{Me}{\overset{H}{}}$$
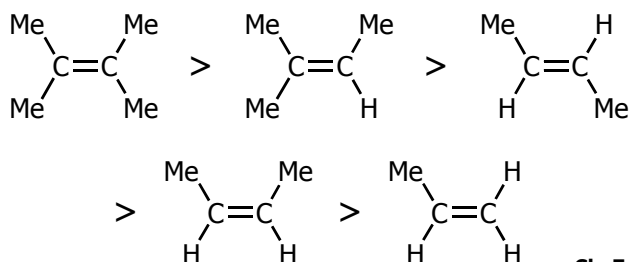
$$> \underset{H}{\overset{Me}{}}C=C\underset{H}{\overset{Me}{}} > \underset{H}{\overset{Me}{}}C=C\underset{H}{\overset{H}{}}$$
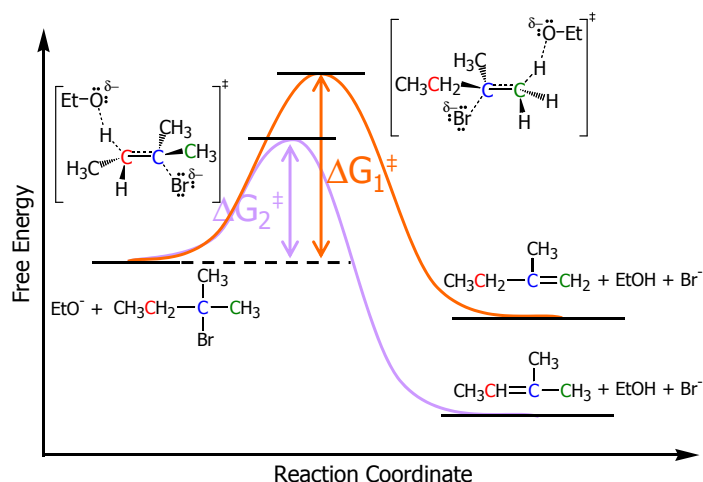
Mechanism for an E2 Reaction
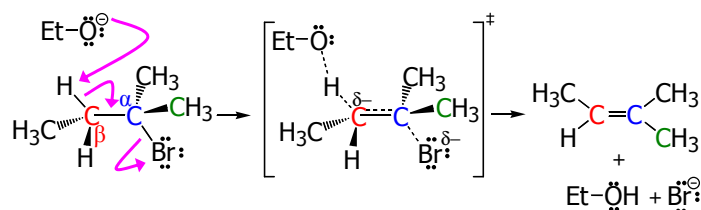
EtO⊖ removes a β proton; C–H breaks; new π bond forms and Br begins to depart

Partial bonds in the transition state: C–H and C–Br bonds break, new π C–C bond forms

C=C is fully formed and the other products are EtOH and Br⊖

Free Energy vs Reaction Coordinate

$\Delta G_1^{\ddagger}$ $\Delta G_2^{\ddagger}$

EtO⁻ + CH₃CH₂–C(CH₃)(Br)–CH₃

CH₃CH₂–C(CH₃)=CH₂ + EtOH + Br⁻
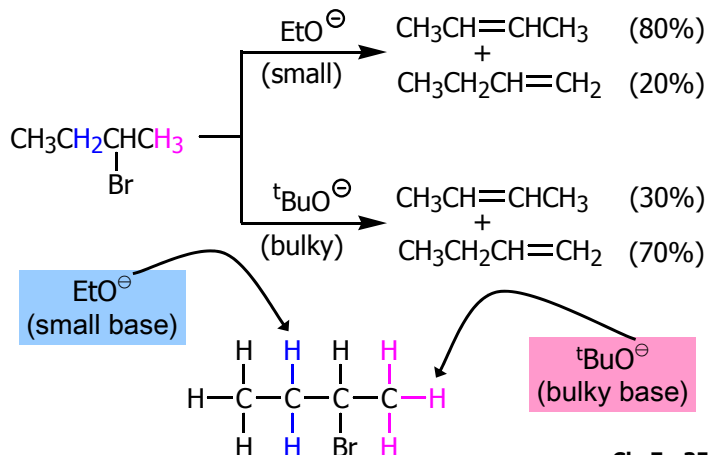
CH₃CH=C(CH₃)–CH₃ + EtOH + Br⁻

6C. Formation of the Less Substituted Alkene Using a Bulky Base

❖ Hofmann's Rule
  ● Most elimination reactions follow Zaitsev's rule in which the most stable alkenes are the major products. However, under some circumstances, the major elimination product is the less substituted, less stable alkene

● Case 1: using a bulky base

CH₃CH₂CHCH₃ with Br

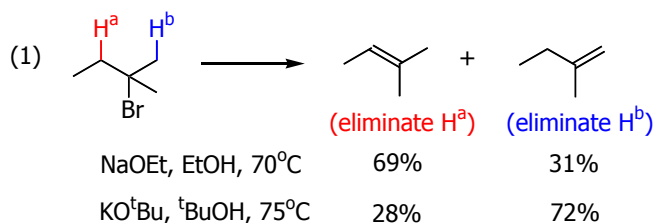EtO⊖ (small) → CH₃CH=CHCH₃ (80%) + CH₃CH₂CH=CH₂ (20%)

ᵗBuO⊖ (bulky) → CH₃CH=CHCH₃ (30%) + CH₃CH₂CH=CH₂ (70%)

EtO⊖ (small base)

ᵗBuO⊖ (bulky base)

● Case 2: with a bulky group next to the leaving halide

less crowded β-H

more crowded β-H

(mainly)
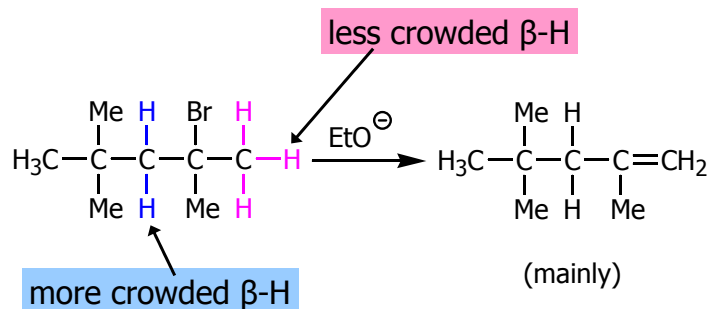
❖ Zaitsev Rule vs. Hofmann Rule

● Examples

(1)

	(eliminate H^a)	(eliminate H^b)
NaOEt, EtOH, 70°C	69%	31%
KO^{t}Bu, ^{t}BuOH, 75°C	28%	72%

● Examples

(2)

	(eliminate H^a)	(eliminate H^b)
NaOEt, EtOH, 70°C	91%	9%
KO^{t}Bu, ^{t}BuOH, 75°C	7%	93%
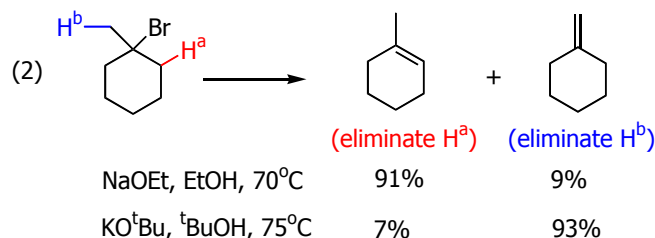
6D. **The Stereochemistry of E2 Reactions**

❖ The 5 atoms involved in the transition state of an E2 reaction (including the base) must lie in the same plane
❖ The *anti* coplanar conformation is the preferred transition state geometry
  ● The *anti* coplanar transition state is **staggered** (and therefore of lower energy), while the *syn* coplanar transition state is **eclipsed**
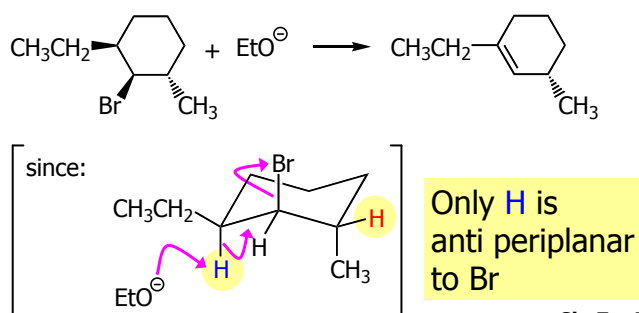
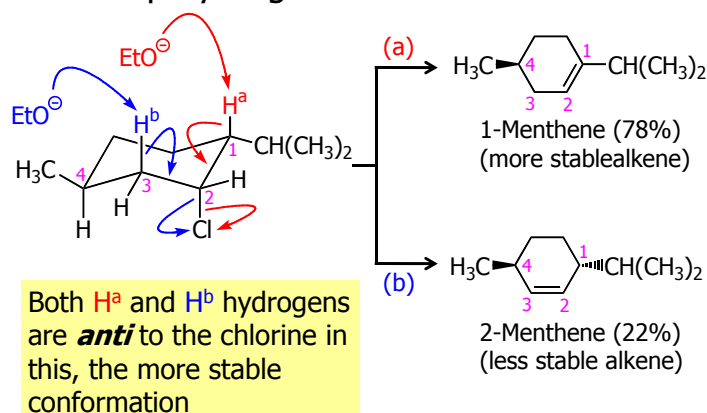*Anti* coplanar transition state (preferred)

Syn coplanar transition state (only with certain rigid molecules)
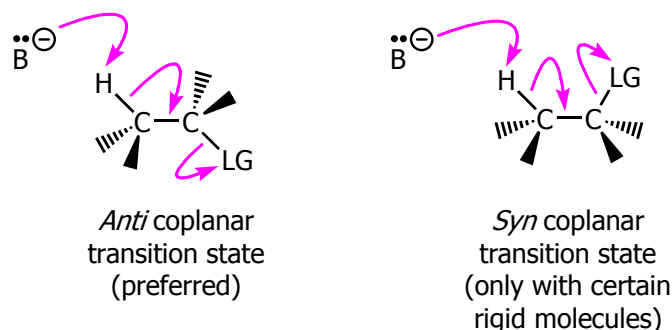
❖ Orientation Requirement
  ● H and Br have to be anti periplanar (*trans*-coplanar)
  ● Examples

since:

Only H is anti periplanar to Br

❖ E2 Elimination where there are two axial β hydrogens

(a) 1-Menthene (78%) (more stable alkene)

(b) 2-Menthene (22%) (less stable alkene)

Both H^a and H^b hydrogens are ***anti*** to the chlorine in this, the more stable conformation

❖ E2 elimination where the only axial β hydrogen is from a less stable Conformer
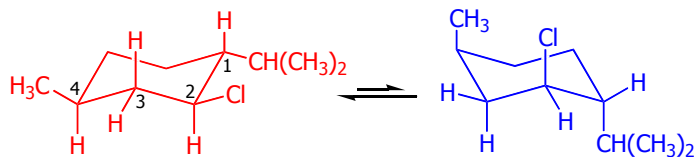
Ch. 7 - 43

The transition state for the E2 elimination is *anti* coplanar
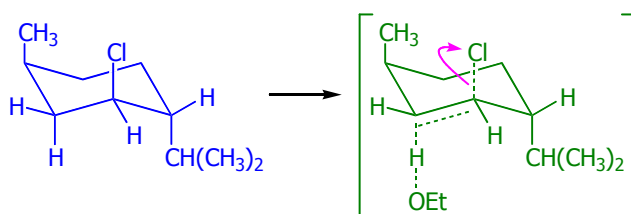
2-Menthene (100%)
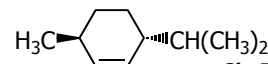
Ch. 7 - 44

7. Acid-Catalyzed Dehydration of Alcohols

❖ Most alcohols undergo **dehydration** (lose a molecule of water) to form an alkene when heated with a strong acid

Ch. 7 - 45

❖ The temperature and concentration of acid required to dehydrate an alcohol depend on the structure of the alcohol substrate
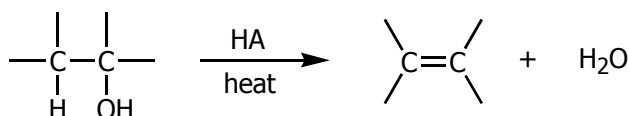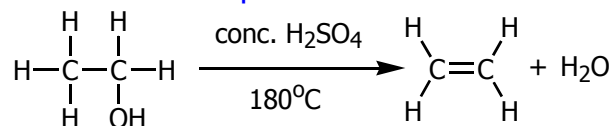
● Primary alcohols are the most difficult to dehydrate. Dehydration of ethanol, for example, requires concentrated sulfuric acid and a temperature of 180°C

Ethanol (a 1° alcohol)

Ch. 7 - 46

● Secondary alcohols usually dehydrate under milder conditions. Cyclohexanol, for example, dehydrates in 85% phosphoric acid at 165–170°C

Cyclohexanol

Cyclohexene
(80%)
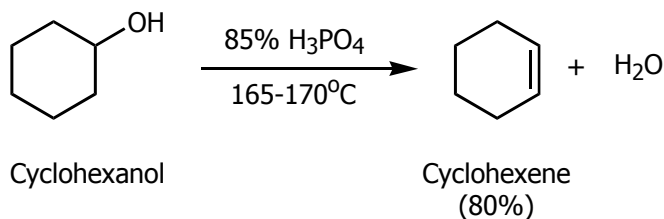
Ch. 7 - 47

● Tertiary alcohols are usually so easily dehydrated that extremely mild conditions can be used. *tert*-Butyl alcohol, for example, dehydrates in 20% aqueous sulfuric acid at a temperature of 85°C

tert-Butyl alcohol

2-Methylpropene
(84%)
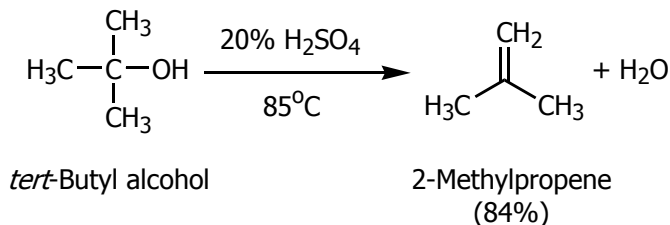
Ch. 7 - 48

- The relative ease with which alcohols will undergo dehydration is in the following order:
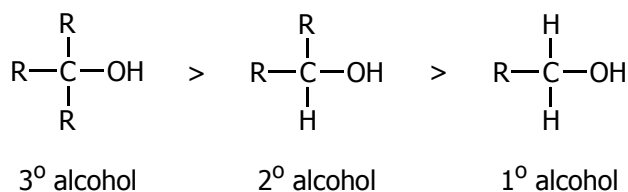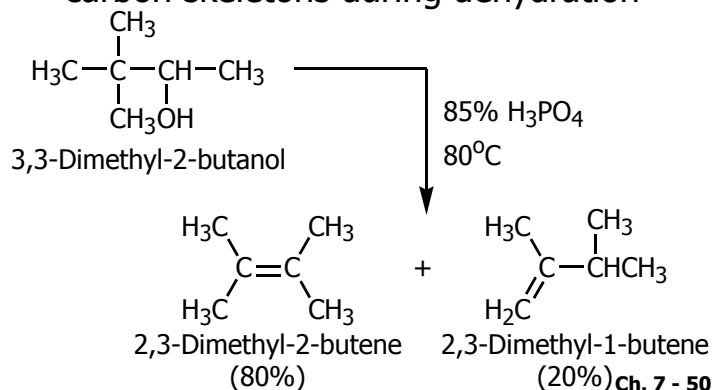
$$R-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{C}}-OH \quad > \quad R-\underset{\underset{H}{|}}{\overset{\overset{R}{|}}{C}}-OH \quad > \quad R-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-OH$$
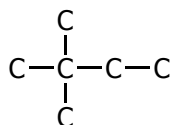
3° alcohol   2° alcohol   1° alcohol

Ch. 7 - 49

❖ Some primary and secondary alcohols also undergo rearrangements of their carbon skeletons during dehydration

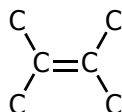$$H_3C-\underset{\underset{CH_3OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH-CH_3$$

3,3-Dimethyl-2-butanol

85% H_3PO_4
80°C

2,3-Dimethyl-2-butene (80%) + 2,3-Dimethyl-1-butene (20%)

Ch. 7 - 50

- Notice that the carbon skeleton of the reactant is

$$C-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}-C-C$$

while that of the product is

$$\underset{\underset{C}{}}{\overset{\overset{C}{}}{C}}=\underset{\underset{C}{}}{\overset{\overset{C}{}}{C}}$$
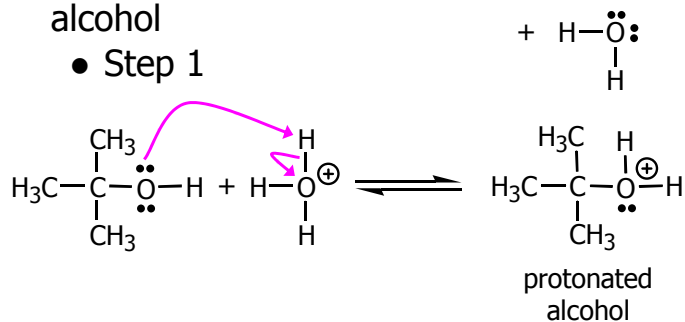
Ch. 7 - 51

7A. Mechanism for Dehydration of 2° & 3° Alcohols: An E1 Reaction

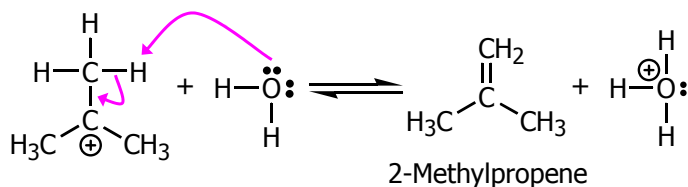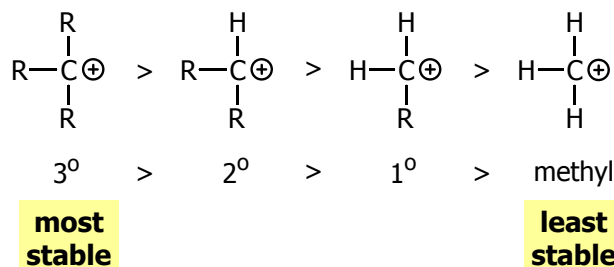❖ Consider the dehydration of *tert*-butyl alcohol
  - Step 1

protonated alcohol

$+ H-\overset{\cdot\cdot}{O}:$ with H

Ch. 7 - 52

- Step 2

a carbocation

$+ H-\overset{\cdot\cdot}{O}:$

- Step 3

2-Methylpropene

$+ H-\overset{\oplus}{\underset{H}{O}}:$
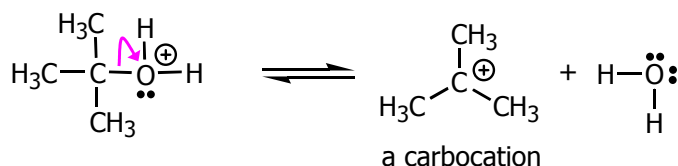
Ch. 7 - 53

7B. Carbocation Stability & the Transition State

❖ Recall

$$R-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{C}}{\oplus} \quad > \quad R-\underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}}{\oplus} \quad > \quad H-\underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}}{\oplus} \quad > \quad H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{\oplus}$$

3° >   2° >   1° >   methyl

most stable   least stable

Ch. 7 - 54
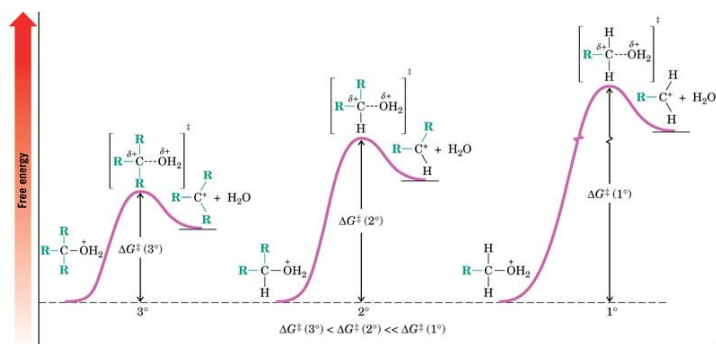
7C. A Mechanism for Dehydration of Primary Alcohols: An E2 Reaction

1° alcohol

protonated alcohol

fast

acid catalyst

slow r.d.s

+ A⁻

conjugate base

alkene
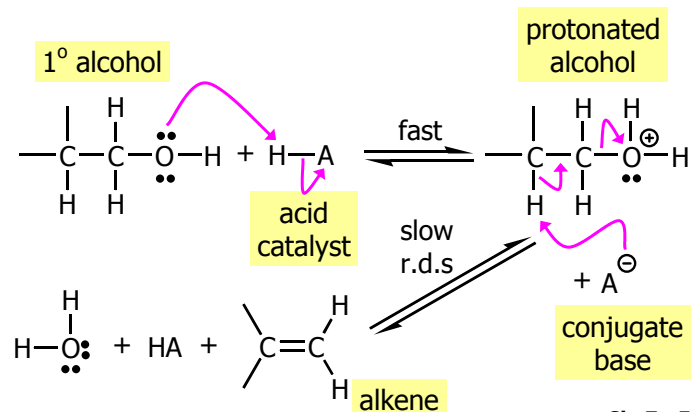
8. Carbocation Stability & Occurrence of Molecular Rearrangements

8A. Rearrangements during Dehydration of Secondary Alcohols

3,3-Dimethyl-2-butanol

85% H_3PO_4
heat

2,3-Dimethyl-2-butenol
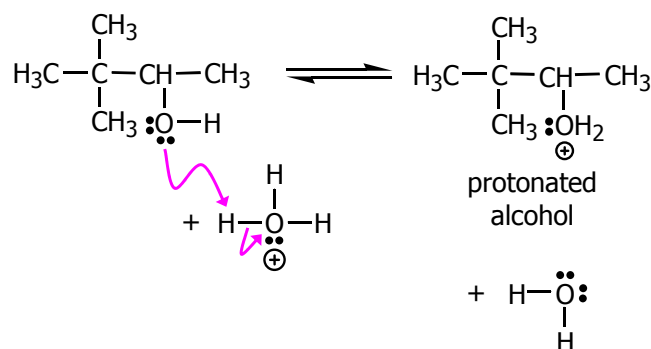(major product)

2,3-Dimethyl-1-butene
(minor product)

❖ Step 1

protonated alcohol

❖ Step 2

a 2° carbocation

❖ Step 3

2° carbocation
(less stable)

transition state

3° carbocation
(more stable)

The less stable 2° carbocation rearranges to a more stable 3° carbocation.

❖ Step 4

(a)

(b)

(a) or (b)

(a) (major) — less stable alkene

(b) (minor) — more stable alkene

HA + ... + HA
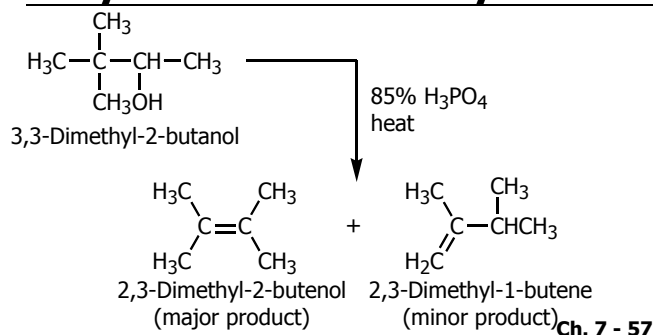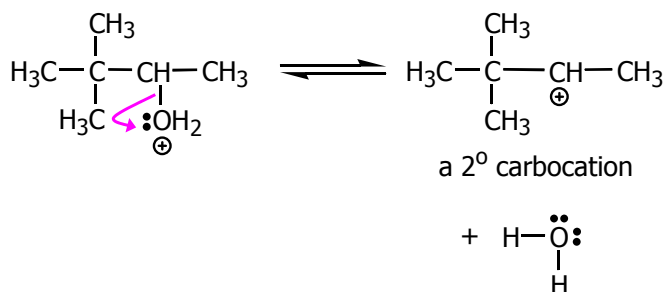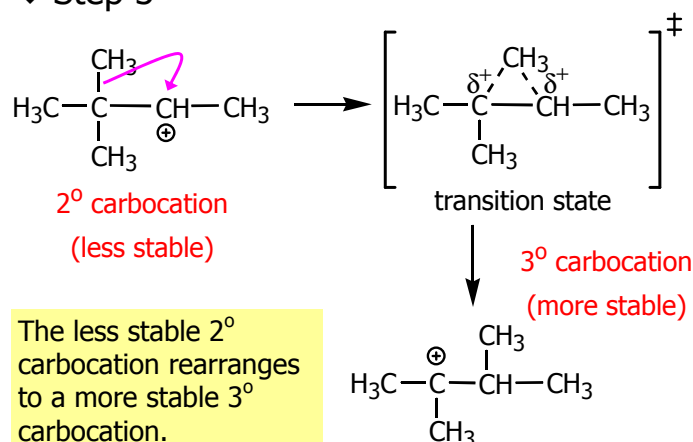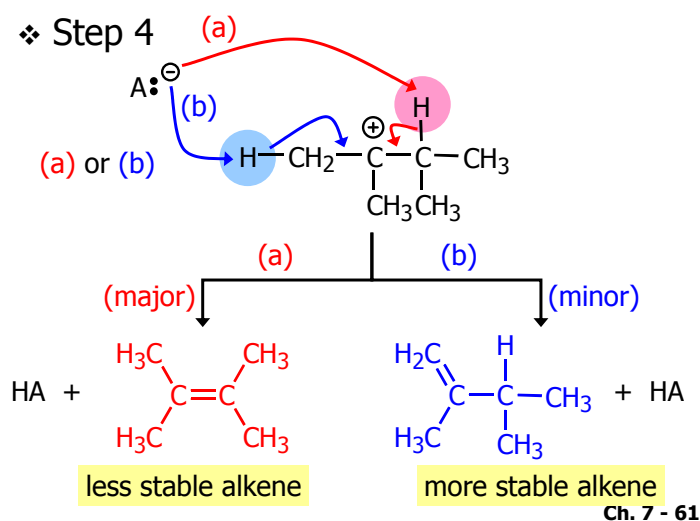
❖ Other common examples of carbocation rearrangements

● Migration of an allyl group

H_3C—C—CH—CH_3 $\xrightarrow[\text{migration}]{\text{methanide}}$ H_3C—C—C—CH_3

a 2° carbocation → 3° carbocation

● Migration of a hydride

H_3C—C—CH—CH_3 $\xrightarrow[\text{migration}]{\text{hydride}}$ H_3C—C—C—CH_3

a 2° carbocation → 3° carbocation
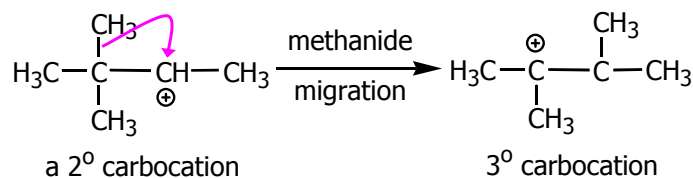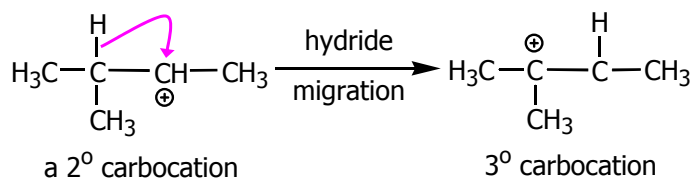
8B. Rearrangement after Dehydration of a Primary Alcohol

$\xrightleftharpoons{E2}$

$\xrightleftharpoons{\text{protonation}}$

$\xrightleftharpoons{\text{deprotonation}}$

---
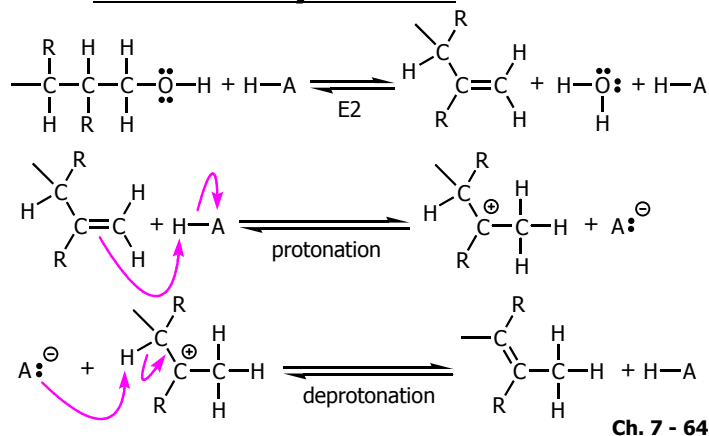
9. The Acidity of Terminal Alkynes

Acetylenic hydrogen

sp   sp²   sp³

H—C≡C—H   C=C   H—C—C—H

$pK_a = 25$ $pK_a = 44$ $pK_a = 50$
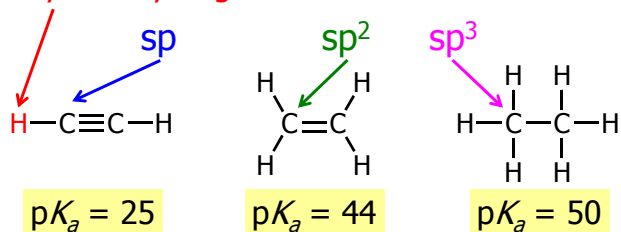
❖ Relative basicity of the conjugate base

$CH_3CH_2{:}^{\ominus} > CH_2{=}CH{:}^{\ominus} > CH{\equiv}CH{:}^{\ominus}$
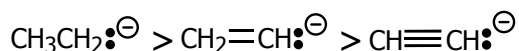
❖ Comparison of acidity and basicity of 1st row elements of the Periodic Table

● Relative acidity

$H{-}\ddot{O}H > H{-}\ddot{O}R > H{-}C{\equiv}CR > H{-}\ddot{N}H_2 > H{-}CH{=}CH_2 > H{-}CH_2CH_3$

| pK_a | 15.7 | 16-17 | 25 | 38 | 44 | 50 |

● Relative basicity

$^{\ominus}{:}\ddot{O}H < {}^{\ominus}{:}\ddot{O}R < {}^{\ominus}{:}C{\equiv}CR < {}^{\ominus}{:}\ddot{N}H_2 < {}^{\ominus}{:}CH{=}CH_2 < {}^{\ominus}{:}CH_2CH_3$
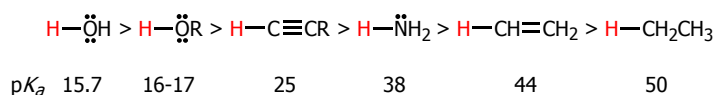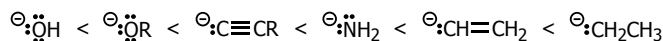
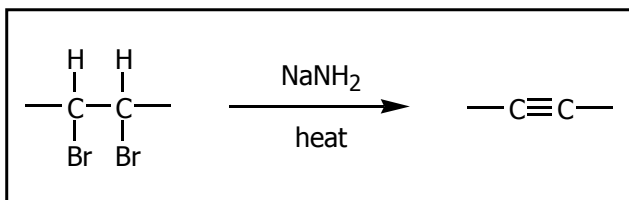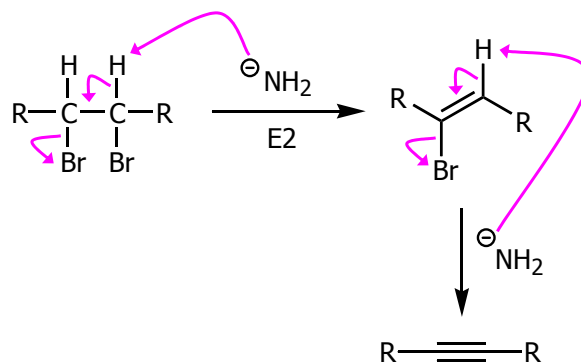## 10. Synthesis of Alkynes by Elimination Reactions

❖ Synthesis of Alkynes by Dehydrohalogenation of Vicinal Dihalides

---

❖ Mechanism

❖ Examples
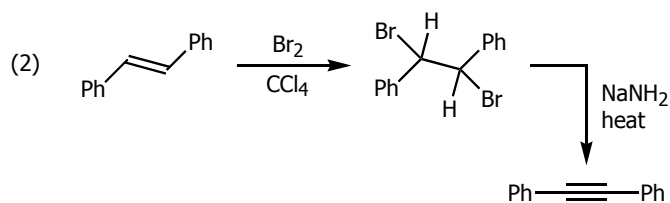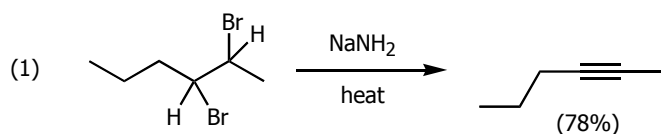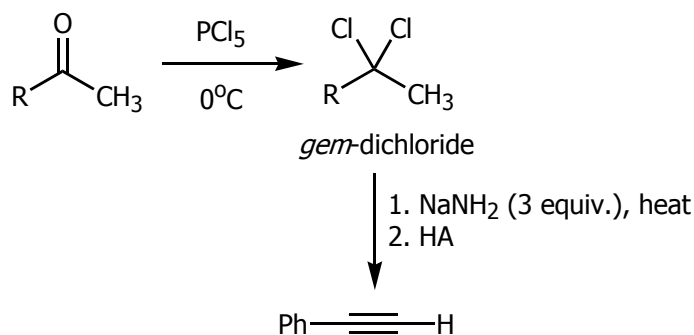
(1)

(78%)

(2)

Ph———Ph

❖ Synthesis of Alkynes by Dehydrohalogenation of Geminal Dihalides

gem-dichloride

1. NaNH$_2$ (3 equiv.), heat
2. HA

Ph———H

---

11. Replacement of the Acetylenic Hydrogen Atom of Terminal Alkynes

❖ The acetylide anion can be prepared by

$$R—\!\!\equiv\!\!—H \xrightarrow[\text{liq. NH}_3]{\text{NaNH}_2} R—\!\!\equiv\!\!—^{\ominus} Na^{\oplus} + NH_3$$
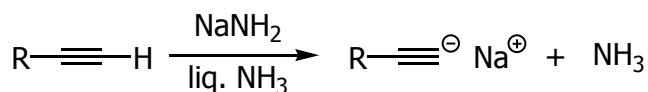
❖ Acetylide anions are useful intermediates for the synthesis of other alkynes

$$R—\!\!\equiv\!\!—^{\ominus} \quad R'—X \longrightarrow R—\!\!\equiv\!\!—R' + X^{\ominus}$$
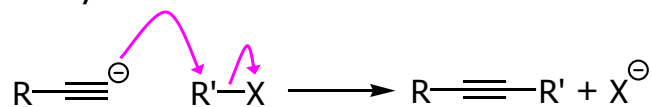
❖ ∵ 2nd step is an S$_N$2 reaction, usually only good for 1° R'

❖ 2° and 3° R' usually undergo E2 elimination

Examples

Ph≡≡H

NaNH₂
liq. NH₃

Ph≡≡⊖ Na⊕

CH₃—I

I

H

| S_N2 | E2 |

Ph—≡—CH₃

+

NaI

Ph—≡—H

+

+

I⊖

---
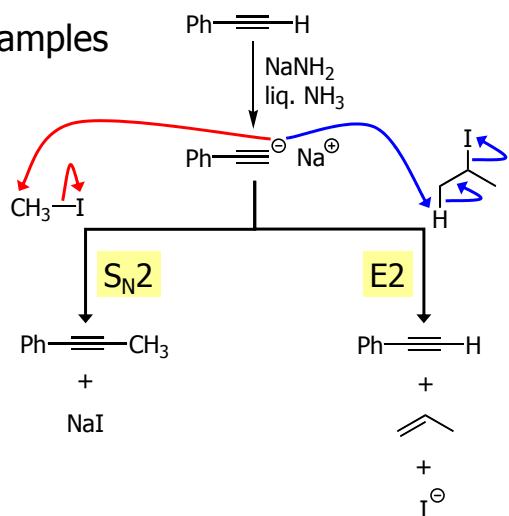
13. Hydrogenation of Alkenes

$$\text{C=C} \xrightarrow[\substack{\text{solvent} \\ \text{heat and pressure}}]{\substack{H_2 \\ \text{Pt, Pd or Ni}}} \text{—C—C—}$$
(with H H added)

$$—C≡C— \xrightarrow[\substack{\text{solvent} \\ \text{heat and pressure}}]{\substack{H_2 \\ \text{Pt, Pd or Ni}}} \text{—C—C—}$$
(with H H / H H added)
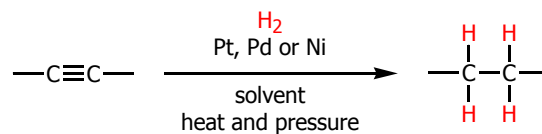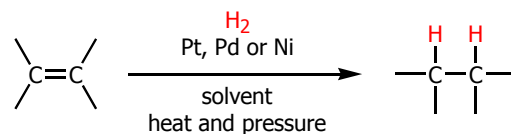
❖ Hydrogenation is an example of addition reaction

Examples

$$\text{(hept-1-ene)} \xrightarrow[\text{Rh(PPh}_3)_3\text{Cl}]{H_2} \text{(heptane, H H added)}$$

$$\text{(cyclohexene)} \xrightarrow[\text{Pd/C}]{H_2} \text{(cyclohexane, H H added)}$$
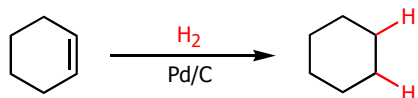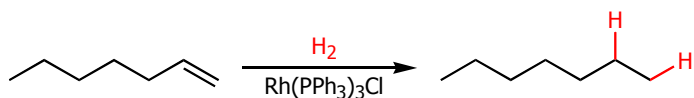
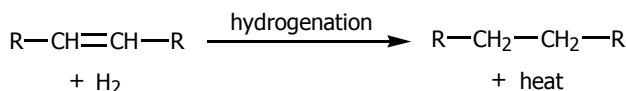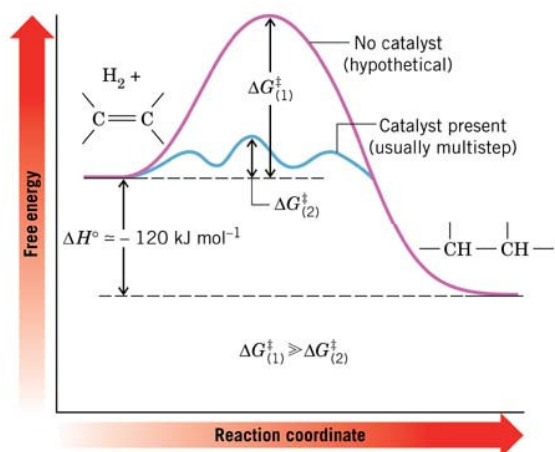
14. Hydrogenation: The Function of the Catalyst

❖ Hydrogenation of an alkene is an exothermic reaction
  • $\Delta H° ≈ -120$ kJ/mol

$$R—CH=CH—R \xrightarrow{\text{hydrogenation}} R—CH_2—CH_2—R$$
$$+ H_2 \qquad\qquad\qquad + \text{heat}$$

14A. Syn and Anti Additions

❖ An addition that places the parts of the reagent on the same side (or face) of the reactant is called **syn addition**

$$\text{C=C} + \text{X—Y} \longrightarrow \text{C—C} \quad \left.\begin{array}{c} \text{syn} \\ \text{addition} \end{array}\right.$$
(X and Y on same side)

$$\text{C=C} + \text{H—H} \xrightarrow{\text{Pt}} \text{C—C}$$
(H and H on same side)
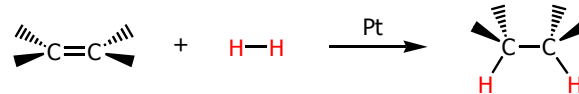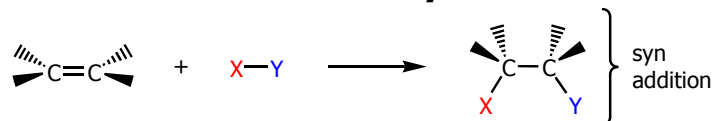
Catalytic hydrogenation is a **syn** addition.

- An **anti addition** places parts of the adding reagent on opposite faces of the reactant

$$\text{C=C} + \text{X—Y} \longrightarrow \begin{array}{c} \text{X} \\ | \\ \text{C—C} \\ | \\ \text{Y} \end{array} \Big\} \text{anti addition}$$
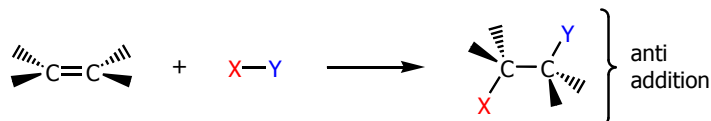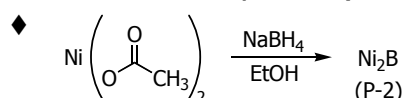
Ch. 7 - 79

15. Hydrogenation of Alkynes
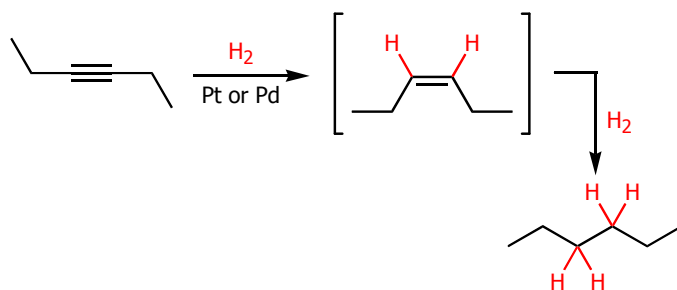
- Using the reaction conditions, alkynes are usually converted to alkanes and are difficult to stop at the alkene stage

Ch. 7 - 80

15A. Syn Addition of Hydrogen: Synthesis of *cis*-Alkenes

- Semi-hydrogenation of alkynes to alkenes can be achieved using either the Ni_2B (P-2) catalyst or the Lindlar's catalyst
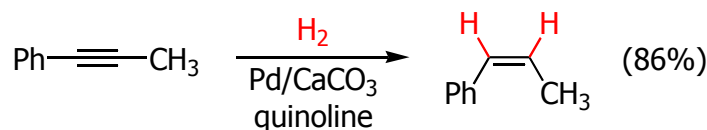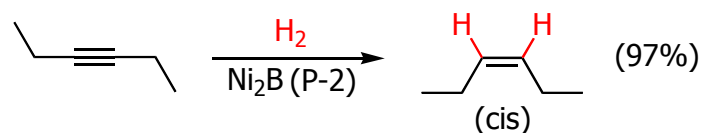 - Nickel boride compound (P-2 catalyst)
    - ♦

    $$Ni\left(\begin{array}{c} O \\ \| \\ O-CH_3 \end{array}\right)_2 \xrightarrow[\text{EtOH}]{\text{NaBH}_4} \begin{array}{c} Ni_2B \\ (P-2) \end{array}$$

  - Lindlar's catalyst
    - ♦ $Pd/CaCO_3$, quinoline

Ch. 7 - 81

- Semi-hydrogenation of alkynes using Ni_2B (P-2) or Lindlar's catalyst causes syn addition of hydrogen
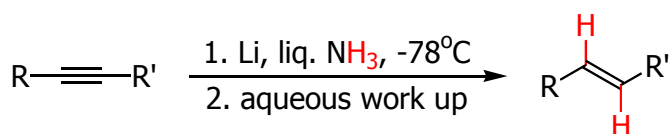 - Examples

Ch. 7 - 82

15B. Anti Addition of Hydrogen: Synthesis of *trans*-Alkenes

- Alkynes can be converted to *trans*-alkenes by dissolving metal reduction
- Anti addition of dihydrogen to the alkyne

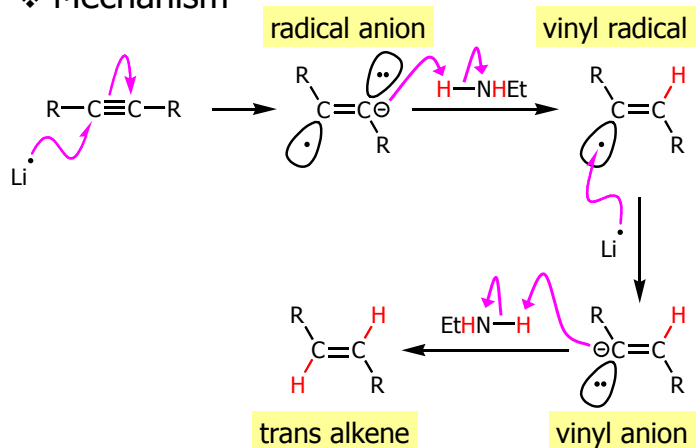$$R\text{—}\!\!\equiv\!\!\text{—}R' \xrightarrow[\text{2. aqueous work up}]{\text{1. Li, liq. NH}_3, -78^oC} \begin{array}{c} H \\ R \quad R' \\ H \end{array}$$

Ch. 7 - 83

- Example

1. Li, liq. $EtNH_2$, -78°C
2. NH_4Cl

anti addition

Ch. 7 - 84

❖ Mechanism
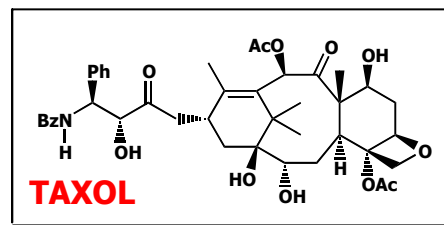

radical anion

vinyl radical

trans alkene

vinyl anion
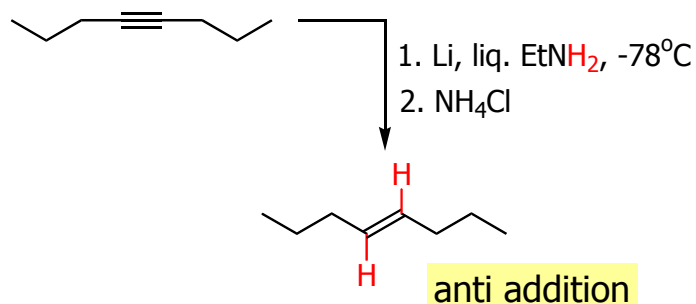
16. An Introduction to Organic Synthesis

16A. Why Do Organic Synthesis?

❖ To make naturally occurring compounds which are biologically active but difficult (or impossible) to obtain

TAXOL

Anti-tumor, anti-cancer agent

TAXOL

❖ Isolated from Pacific Yew tree

Leaves

Cones and Fruit

seed   pollen cones
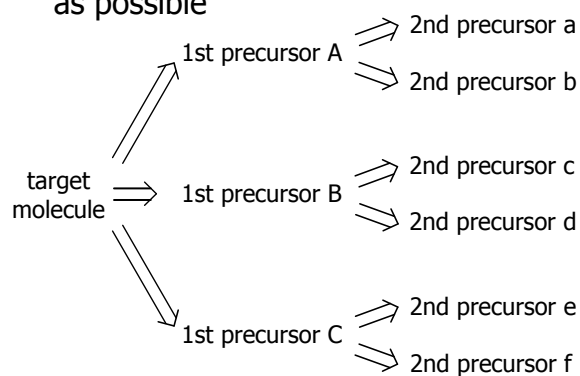usually appear on separate male and female trees

TAXOL

❖ Approved by the U.S. Food & Drug Administration in 1992 for treatment of several types of cancer, including breast cancer, lung cancer, and melanoma

❖ An estimation: a 100-year old yew tree must be sacrificed in order to obtain 300 mg of Taxol, just enough for one single dose for a cancer patient

❖ Obviously, synthetic organic chemistry methods that would lead to the synthesis of Taxol would be extremely useful

16B. Retrosynthetic Analysis

target molecule ⟹ 1st precursor ⟹ 2nd precursor ⟹⟹ starting compound
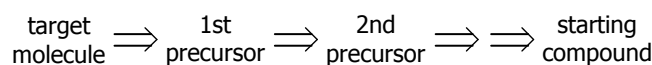
❖ When doing retrosynthetic analysis, it is necessary to generate as many possible precursors, hence different synthetic routes, as possible
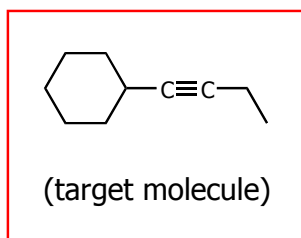
1st precursor A
⟹ 2nd precursor a
⟹ 2nd precursor b
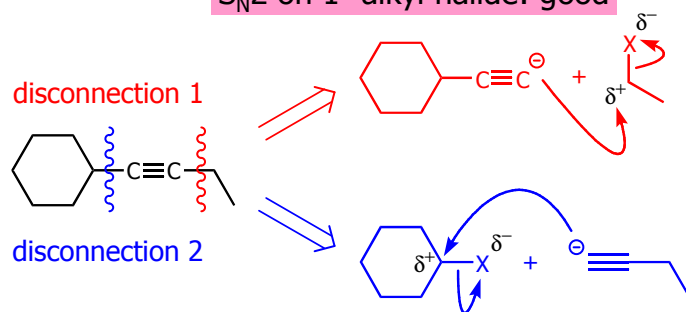
target molecule ⟹ 1st precursor B
⟹ 2nd precursor c
⟹ 2nd precursor d

1st precursor C
⟹ 2nd precursor e
⟹ 2nd precursor f

16C. Identifying Precursors

❖ Synthesis of

(target molecule)

❖ Retrosynthetic Analysis

S_N2 on $1°$ alkyl halide: good

disconnection 1

disconnection 2

S_N2 on $2°$ alkyl halide: poor
$\Rightarrow$ will get E2 as major pathway

❖ Synthesis

$NaNH_2$

liq. NH_3

(S_N2)

NaI +
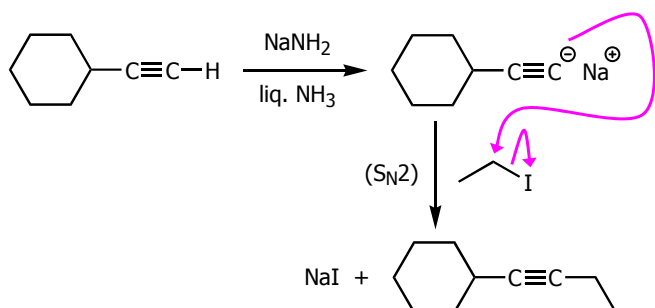
16D. Raison d'Etre

Summary of Methods for the Preparation of
Alkenes

(Dehydrohalogenation
of alkyl halides)

base, heat

H^+
heat   (Dehydration
of alcohols)

H_2, Ni_2B (P-2)
or Lindlar's catalyst
(give (Z)-alkenes)

Li, liq. NH_3
(give (E)-alkenes)

(Semi-
hydrogenation
of alkynes)

(Dissolving
metal reduction
of alkynes)

Summary of Methods for the Preparation of
Alkynes

(Dehydrohalogenation
of geminal dihalide)

$NaNH_2$
heat

$NaNH_2$
heat

(Dehydrohalogenation
of vicinal dihalide)

$R-C\equiv C-R'$

(Deprotonation of terminal
alkynes and S_N2 reaction of
the acetylide anion)

1. $NaNH_2$, liq. NH_3
2. R'-X (R' = $1°$ alkyl group)

$R-C\equiv C-H$

🔔 **END OF CHAPTER 7** 🔔