Based on McMurry’s *Organic Chemistry*, 7th edition
Alkene - Hydrocarbon With Carbon-Carbon Double Bond

- Also called an olefin but alkene is better
- Includes many naturally occurring materials
  - Flavors, fragrances, vitamins

Temple, Cananga, and Safflower from nature.

Ethylene

α-Pinene

β-Carotene
(orange pigment and vitamin A precursor)
Why this Chapter?

- **C=C double bonds** are present in most organic and biological molecules

- To examine consequences of **alkene stereoisomerism**

- To focus on general alkene reaction: **electrophilic addition**
6.1 Industrial Preparation and Use of Alkenes

- Ethylene and propylene are the most important organic chemicals produced
- Made by thermal cracking of light alkanes (petroleum)
6.2 Calculating Degree of Unsaturation

- Relates molecular formula to possible structures
- **Degree of unsaturation**: number of multiple bonds or rings
- Formula for a saturated acyclic (سیرشده خطی) compound is $\text{C}_n\text{H}_{2n+2}$
- Each ring or multiple bond replaces 2 H's

Ethylene: $\text{C}_2\text{H}_4$
(fewer hydrogens—unsaturated)

Ethane: $\text{C}_2\text{H}_6$
(more hydrogens—saturated)
Example: $\text{C}_6\text{H}_{10}$

- Saturated is $\text{C}_6\text{H}_{14}$
  - Therefore 4 H's are not present
  - This has two degrees of unsaturation

- Two double bonds?
- or ring and double bond?

- or two rings?
- or triple bond?

MW $= 6 \times 12 + 10 \times 1 = 82$
Degree of Unsaturation With Other Elements

- **Organohalogens (X: F, Cl, Br, I)**
  - Halogen replaces hydrogen
  - C\(_4\)H\(_6\)Br\(_2\) and C\(_4\)H\(_8\) have one degree of unsaturation

  \[
  \text{BrCH}_2\text{CH} \equiv \text{CHCH}_2\text{Br} \quad \Rightarrow \quad \text{HCH}_2\text{CH} \equiv \text{CHCH}_2\text{H}
  \]

  \[
  \underline{\text{C}_4\text{H}_6\text{Br}_2} \quad \Rightarrow \quad \underline{\text{"C}_4\text{H}_8"} \quad \text{One unsaturation: one double bond}
  \]

- **Organoxygen compounds (C,H,O) - if connected by single bonds**
  - These don't affect the total count of H's

  \[
  \text{H}_2\text{C} \equiv \text{CHCH} \equiv \text{CHCH}_2\text{OH} \quad \Rightarrow \quad \text{H}_2\text{C} \equiv \text{CHCH} \equiv \text{CHCH}_2\text{H}
  \]

  \[
  \underline{\text{C}_5\text{H}_8\text{O}} \quad \Rightarrow \quad \underline{\text{"C}_5\text{H}_8"} \quad \text{Two unsaturations: two double bonds}
  \]
Organonitrogen compounds

- Nitrogen has three bonds
  - So if it connects where H was, it adds a connection point
  - Subtract one H for equivalent degree of unsaturation in hydrocarbon

\[
\text{C}_5\text{H}_9\text{N} = \text{“C}_5\text{H}_8”
\]

Two unsaturations: one ring and one double bond
Summary - Degree of Unsaturation

- **Method 1**
  - Add the number of halogens to the number of hydrogens.
  - Ignore the number of oxygens.
  - Subtract the number of nitrogens from the number of hydrogens.

- **Method 2**

\[
H_{\text{sat}} = 2C + 2 - X + N \quad \text{(ignore O, S)}
\]

Degree of Unsaturation = \[
\frac{H_{\text{sat}} - H_{\text{act}}}{2}
\]

- **Method 3**

\[
\text{Degree of Unsaturation} = \left( \frac{2 - \text{Número de órmos} + \text{Número de átomos de nitrogén}}{2} \right)
\]
Diazepam, marketed as an antianxiety medication under the name Valium, has three rings, eight double bonds, and the formula $\text{C}_{16}\text{H}_{?}\text{ClN}_2\text{O}$. How many hydrogens does diazepam have? (Calculate the answer; don’t count hydrogens in the structure.)

$$\text{No. H} + \text{No. X} = 32 + 1 = 33$$
$$- \text{ No. N} = 33 - 1 = 32$$
$$\text{C}_n\text{H}_{2n+2} = \text{C}_{20}\text{H}_{42}$$
$$42 - 32 = 10$$
$$10 / 2 = 5$$

$$\frac{2 + 20(4-2) + 32(1-2) + 1(1-2) + 1(3-2)}{2} = 5$$

$$\frac{-X + 35}{2} = 11$$
$$X = 13$$

$\text{C}_{16}\text{H}_{13}\text{ClN}_2\text{O}$
6.3 Naming of Alkenes

- **Name the parent** hydrocarbon—change ending to “–ene”
- Number carbons in chain so that double bond carbons have lowest possible numbers
- Alkenes higher priority than alkanes: even shorter chain
- Multiple “C=C“ are named as “diene” “triene” “tetraene” etc…

- Rings have “cyclo” prefix—double bond always C#1, C#2
Many Alkenes Are Known by Common Names

<table>
<thead>
<tr>
<th>Compound</th>
<th>Systematic name</th>
<th>Common name</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{C}≡\text{CH}_2$</td>
<td>Ethene</td>
<td>Ethylene</td>
</tr>
<tr>
<td>$\text{CH}_3\text{CH}≡\text{CH}_2$</td>
<td>Propene</td>
<td>Propylene</td>
</tr>
<tr>
<td>$\text{CH}_3\text{C}≡\text{CH}_2$</td>
<td>2-Methylpropene</td>
<td>Isobutylene</td>
</tr>
<tr>
<td>$\text{H}_2\text{C}≡\text{C}−\text{CH}=\text{CH}_2$</td>
<td>2-Methyl-1,3-butadiene</td>
<td>Isoprene</td>
</tr>
</tbody>
</table>

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6.4 *Cis-Trans* Isomerism in Alkenes

- Carbon atoms in a double bond are *sp*\(^2\)-hybridized
  - Three equivalent orbitals at 120° separation in plane
  - Fourth orbital is atomic *p* orbital
- Combination of electrons in two *sp*\(^2\) orbitals of two atoms forms *σ* bond between them
- Additive interaction of *p* orbitals creates a *π* bonding orbital
- Occupied *π* orbital *prevents rotation about* *σ*-bond
- Rotation prevented by *π* bond - high barrier, about 268 kJ/mole in ethylene
Rotation of $\pi$ Bond Is Prohibitive

- This prevents rotation about a carbon-carbon double bond (unlike a carbon-carbon single bond).
- Creates possible alternative structures
The presence of a carbon-carbon double bond can create two possible structures:

- **cis isomer** - two similar groups on same side of the double bond
- **trans isomer** - similar groups on opposite sides

Each carbon must have two different groups for these isomers to occur.
Cis, Trans Isomers Require That End Groups Must Differ in Pairs

- 180° rotation superposes

\[
\begin{align*}
\text{A} & \quad \text{D} \\
\text{C} = \text{C} & \quad = \\
\text{B} & \quad \text{D}
\end{align*}
\]

These two compounds are identical; they are not cis–trans isomers.

\[
\begin{align*}
\text{A} & \quad \text{D} \\
\text{C} = \text{C} & \quad \neq \\
\text{B} & \quad \text{E}
\end{align*}
\]

These two compounds are not identical; they are cis–trans isomers.

- Bottom pair cannot be superposed without breaking C=C
Neither compound is clearly “cis” or “trans”

- Substituents on C1 are different than those on C2

- We need to define “similarity” in a precise way to distinguish the two stereoisomers

- Cis, trans nomenclature only works for disubstituted double bonds

- E/Z Nomenclature for 3 or 4 substituents
E,Z Stereochemical Nomenclature

- Priority rules
  (قواعد ترتيب تقدم)
  of Cahn, Ingold, and Prelog

- Compare where higher priority groups are with respect to bond and designate as prefix

- **E** - *entgegen*, opposite sides

- **Z** - *zusammen*, together on the same side

\[ \text{Hi(C1)-Low(C1)-Hi(C2)-Lo(C2)} \]

\[ \text{E double bond (Higher-priority groups are on opposite sides.)} \]

\[ \text{Z double bond (Higher-priority groups are on the same side.)} \]
Isomers

- Constitutional isomers
  - Chain isomers
  - Position isomers
  - Functional group isomers

- Stereoisomers
  - Conformational isomers
  - Configurational isomers
    - E- and Z-isomers
    - Isomers with chiral centres
      - Enantiomers
      - Diastereomers
Ranking Priorities: Cahn-Ingold-Prelog Rules

RULE 1

- Must rank atoms that are connected at comparison point
- Higher **atomic number** gets higher priority
  - Br > Cl > S > P > O > N > C > H

(a) (E)-2-Chloro-2-butene

(b) (Z)-2-Chloro-2-butene
**Extended Comparison**

**RULE 2**

- If atomic numbers are the same, compare at next connection point at same distance
- Compare until something has higher atomic number
- Do not combine – always compare

![Chemical Structures](attachment:image.png)

- Lower: 
  - $\text{CH}_3$
  - $\text{C} - \text{CH}_3$
- Higher: 
  - $\text{H}$
  - $\text{C} - \text{CH}_3$
Dealing With Multiple Bonds:

**RULE 3**
- Substituent is drawn with connections shown and no double or triple bonds

![Diagram showing equivalent structures with and without multiple bonds](image)

This carbon is bonded to H, O, O.  
This oxygen is bonded to C, C.  
This carbon is bonded to H, O, O.  
This oxygen is bonded to C, C.
This carbon is bonded to H, C, C

This carbon is bonded to H, H, C, C

This carbon is bonded to H, C, C

This carbon is bonded to H, H, C, C

is equivalent to

This carbon is bonded to C, C, C

This carbon is bonded to H, C, C, C

This carbon is bonded to C, C, C

This carbon is bonded to H, H, C, C

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Cis alkenes are less stable than trans alkenes

- Compare heat given off on hydrogenation: $\Delta H^\circ$
- Less stable isomer is higher in energy
  - And gives off more heat
  - tetrasubstituted > trisubstituted > disubstituted > monosubstituted
- *hyperconjugation* (مزدوج شدن موقت) stabilizes

Trans (76%)  
Cis (24%)
Comparing Stabilities of Alkenes

- Evaluate heat given off when C=C is converted to C-C
- More stable alkene gives off less heat

(ΔG°_cis > ΔG°_trans)

γ / Λ kJ/mol
trans-Butene generates 4 kJ less heat than cis-butene

Cis isomer
\[ \Delta H^\circ_{\text{hydrog}} = -120 \text{ kJ/mol} \]

Trans isomer
\[ \Delta H^\circ_{\text{hydrog}} = -116 \text{ kJ/mol} \]

but the numbers aren’t exactly the same
4 kJ/mol (energy difference)
2.8 kJ/mole (equilibrium data)
for two reasons:
1. There is probably some experimental error, since heats of hydrogenation are difficult to measure accurately.
2. Heats of reaction and equilibrium constants don’t measure exactly the same thing.

Heats of reaction measure \( \Delta H^\circ \),
equilibrium constants measure \( \Delta G^\circ \) a
(slight difference between the two)
Alkenes become more stable with increasing substitution:

As a general rule, alkenes follow the stability order:

\[
\text{Tetrasubstituted} > \text{Trisubstituted} > \text{Disubstituted} > \text{Monosubstituted}
\]

This order of stability is due to:

- **Hyperconjugation** (مزدوج شدن موقت)
- **bond strength** (قدرت پیوند)
Hyperconjugation (مزدوج شدن موقت)

- Electrons in neighboring filled $\sigma$ orbital stabilize vacant antibonding $\pi$ orbital net positive interaction.

- در زمان هایی که اوربیتال پر نشده $\pi$ و اوربیتال پر $\sigma$ C=C بین اوربیتال ضدپیوندی پرنشده $\pi$ و اوربیتال پرنشده $\sigma$ C-H بروی استخلاف های مجاور برمی‌گردد.
- Alkyl groups are better than H
Hyperconjugation involves a sigma orbital component, usually a C-C or C-H bond.

Resonance involves pi orbitals.

Alternative Explanation: bond strength

$sp^3 - sp^2 > sp^3 - sp^3$ bond

2-Butene (more stable)
1-Butene (less stable)
6.7 Electrophilic Addition of Alkenes

- General reaction mechanism: electrophilic addition
- Attack of electrophile (such as HBr) on \( \pi \) bond of alkene
- Produces carbocation and bromide ion
- Carbocation is an electrophile, reacting with nucleophilic bromide ion

1. A hydrogen atom on the electrophile HBr is attacked by \( \pi \) electrons from the nucleophilic double bond, forming a new C–H bond. This leaves the other carbon atom with a + charge and a vacant \( \rho \) orbital. Simultaneously, two electrons from the H–Br bond move onto bromine, giving bromide anion.

2. Bromide ion donates an electron pair to the positively charged carbon atom, forming a C–Br bond and yielding the neutral addition product.
Electrophilic Addition Energy Path

- Two step process
- First transition state is high energy point
Electrophilic Addition for preparations

- The reaction is successful with HCl and with HI as well as HBr
- HI is generated from KI and phosphoric acid

\[
\text{CH}_3\text{C} = \text{CH}_2 + \text{HCl} \xrightarrow{\text{Ether}} \text{CH}_3\text{C} - \text{CH}_3
\]

2-Methylpropene

\[
\text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2 \xrightarrow{\text{KI, H}_3\text{PO}_4} \text{CH}_3\text{CH}_2\text{CH}_2\text{CHCH}_3
\]

1-Pentene (94%)

2-Iodopentane
6.8 Orientation of Electrophilic Addition: Markovnikov’s Rule

- In an unsymmetrical alkene, HX reagents can add in two different ways, but one way may be preferred over the other.

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}≡\text{CH}_2 \quad + \quad \text{HCl} \quad \rightarrow \quad \begin{cases} 
\text{CH}_3\text{CH}_2\text{CH}_2\text{CHCH}_3 & \text{Cl} \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} & \text{1-Chloropentane (sole product)} \\
\end{cases}
\]

- If one orientation predominates, the reaction is regiospecific (جهت ویژه).

- Markovnikov observed in the 19th century that in the addition of HX to alkene, the H attaches to the carbon with the most H’s and X attaches to the other end (to the one with the most alkyl substituents) This is Markovnikov’s rule.
Example of Markovnikov’s Rule

- Addition of HCl to 2-methylpropene

![Chemical structures showing the addition of HCl to 2-methylpropene and the formation of 2-Chloro-2-methylpropane.]

- Regiospecific – one product forms where two are possible

![Chemical structures showing regiospecific reaction examples.]

- If both ends have similar substitution,

![Chemical structures showing non-regiospecific reaction examples.]

then not regiospecific
Markovnikov’s Rule (restated) (به بیان دیگر)

- More highly substituted carbocation forms as intermediate rather than less highly substituted one
- Tertiary cations and associated transition states are more stable than primary cations

\[
\begin{align*}
\text{2-Methylpropene} & \quad + \quad \text{HCl} \\
\text{tert-Butyl carbocation (tertiary; 3°)} & \quad \xrightarrow{\text{Cl}^-} \quad \text{2-Chloro-2-methylpropane}
\end{align*}
\]

\[
\begin{align*}
\text{Isobutyl carbocation (primary; 1°)} & \quad \xrightarrow{\text{Cl}^-} \quad \text{1-Chloro-2-methylpropane (NOT formed)}
\end{align*}
\]
6.9 Carbocation Structure and Stability

- Carbocations are planar and the tricoordinate carbon is surrounded by only 6 electrons in $sp^2$ orbitals.
- The fourth orbital on carbon is a vacant $p$-orbital.
- The stability of the carbocation (measured by energy needed to form it from R-X) is increased by the presence of alkyl substituents (Hyperconjugation stabilizes C+).
• The stability of carbocation (R⁺) can be determined by measuring energy needed to form it from R-X:

\[ \text{R-X} \rightarrow \text{R}^+ + :\text{X}^- \]

• 3º alkyl halides dissociate to give R⁺ more easily than 2º and 1º.
Inductive stabilization of cation species

Hyperconjugation

Methyl: No alkyl groups donating electrons
Primary: One alkyl group donating electrons
Secondary: Two alkyl groups donating electrons
Tertiary: Three alkyl groups donating electrons

*Hyperconjugation*

Herče Tecdad g-rohehāy alkil biʃtary bi korbyn mibet mtaʃl bashed, چ-گالی الکترونی بیشتر و میزان کم الکترونی کربن مثبت (رنگ آبی) کاسته می‌شود.

• Hyperconjugation

Herče Tecdad g-rohehāy alkil wacoq br rooy korbokatyon biʃtary bashed, amkan biʃtary braid mzdug shden woy ejad korbokatyon bi yada r, wojood xwahed dašt.
If carbocation intermediate is more stable than another, why is the reaction through the more stable one faster?

پذیره هاموند چرا پایداری یک کربوکاتیون بر سرعت تشکیل آن اثر گذاشته و ساختار محصول نهایی را تعیین می‌کند؟

The relative stability of the intermediate is related to an equilibrium constant ($\Delta G^o$)

پایداری نسبی حدواسط کربوکاتیون به وسیله ($\Delta G^o$) تعیین می‌شود

The relative stability of the transition state (which describes the size of the rate constant) is the activation energy ($\Delta G^\ddagger$)

اما سرعت واکنش به وسیله انرژی فعال سازی ($\Delta G^\ddagger$) بدست می‌آید

The transition state is transient and cannot be examined

حالات گذار، حالات گذرایی هستند و به دلیل عمر بسیار کوتاه خود، قابل بررسی نیستند
Transition State Structures

- **A transition state** is the highest energy species in a reaction step.
- By definition, its structure is not stable enough to exist for one vibration.
- But the structure controls the rate of reaction.
- So we need to be able to guess about its properties in an informed way.
- We classify them in general ways and look for trends in reactivity – the conclusions are in the Hammond Postulate.

"The structure of the transition state resembles the structure of the nearest stable species. T.S. for Endergonic steps resemble products. T.S. for Exergonic steps resemble reactants."

---

ساختران یک حالت گذار به ساختران نزدیک ترین گونه شیمیایی پایدار شباهت دارد. مراحل انرژی خواه، از لحاظ ساختاری، به فرآورده‌های ت.S. مراحل انرژی زا، از لحاظ ساختاری به واکنش دهنده‌گان شباهت دارد.
Examination of the Hammond Postulate

- A transition state should be similar to an intermediate that is close in energy.

- Sequential states on a reaction path that are close in energy are likely to be close in structure - G. S. Hammond.
Competing Reactions and the Hammond Postulate

Normal Expectation: Faster reaction gives stable intermediate
Intermediate resembles transition state

تشکیل یک کربوکاتیون با پروتون دار شدن یک آلکن، مرحله ای انرژی خواه است. بنابراین حالت گذار پروتون دار شدن آلکن، از لحاظ ساختاری با یک عضو حدواسط کربوکاتیونی شباهت داشته باشد.
6.11 Mechanism of Electrophilic Addition: Rearrangements of Carbocations

- Carbocations undergo structural **rearrangements** following set patterns
- 1,2-H and 1,2-alkyl shifts occur
- Goes to give more stable carbocation
- Can go through less stable ions as intermediates

\[ \text{3-Methyl-1-butene} + \text{HCl} \rightarrow \text{2-Chloro-3-methylbutane (approx. 50%)} \]

\[ \text{3-Methyl-1-butene} + \text{HCl} \rightarrow \text{Hydride shift} \rightarrow \text{A 2° carbocation} \]

\[ \downarrow \text{Cl}^- \rightarrow \text{2-Chloro-3-methylbutane} \]

\[ \text{3-Methyl-1-butene} + \text{HCl} \rightarrow \text{A 2° carbocation} \]

\[ \downarrow \text{Cl}^- \rightarrow \text{2-Chloro-2-methylbutane} \]
Alkyl Shifts Can Also Occur

3,3-Dimethyl-1-butene + HCl → A 2° carbocation → Methyl shift → A 3° carbocation

2-Chloro-3,3-dimethylbutane 2-Chloro-2,3-dimethylbutane