Chapter 5

Alkenes:

Structures, Nomenclature, and an Introduction to Reactivity

Thermodynamics and Kinetics

p orbitals overlap to form a π bond

H_3C $\quad$ C $\qquad$ C $\quad CH_3$

H_3C $\qquad\qquad\qquad CH_3$

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Assigned reading:
Sections 5.1-5.4; omit 5.14
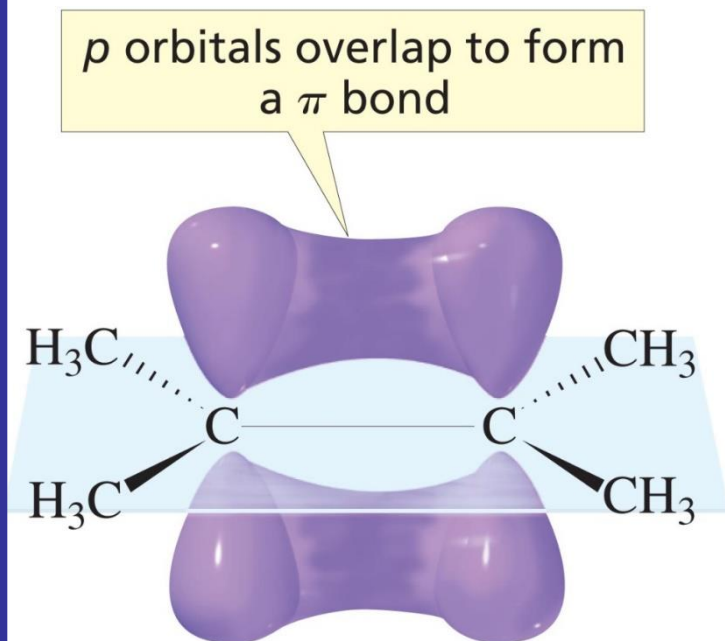
Chapter Objectives

- Name alkenes and substituted alkenes according to IUPAC rules.
- Know the structure (hybridization, bond angles) and which atoms lie in the same plane as each other.

- Work out from a general formula, how many unsaturations are present in a molecule.

- Understand & use the cis-trans, and the *E,Z*-system of nomenclature. Use the Cahn-Ingold-Prelog rules to determine priorities. (Chapter 4)

- Use curved arrows & electron movements to show the mechanism of what is happening when reactions take place. Understand the kinetics and thermodynamics of a reaction. Know where transition states & intermediates appear on an energy diagram, as well as what they represent.

- Understand the concept of "Rate Determining Step". Use the mechanism of reaction and the reaction co-ordinate diagram to describe the rate of reaction, and state whether the rate depends on one or two reactant concentrations.

- Understand the concepts of exothermic & endothermic reactions.
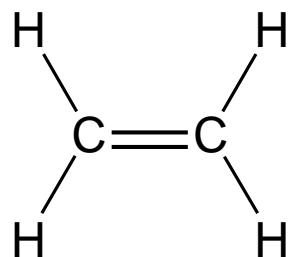
Alkenes (also called *olefins*)

Hydrocarbons containing C=C double bond

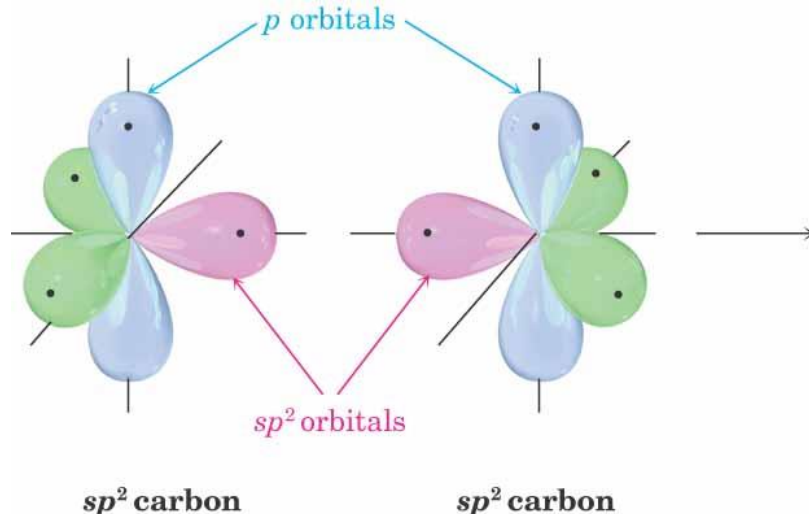**Unsaturated**: less H than alkane with same number of carbons

General *acyclic* **alkene** formula (for one double bond): $C_nH_{2n} = (CH_2)_n$
General *acyclic* **alkane** formula: $C_nH_{2n+2} = (CH_2)_nH_2$
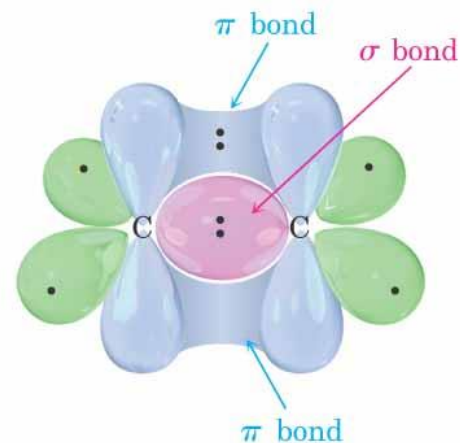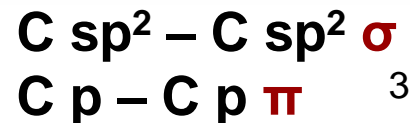General *cyclic* **alkene** formula (for one double bond): C_nH_{2n-2}

ethylene

C_2H_4

Planar-120°

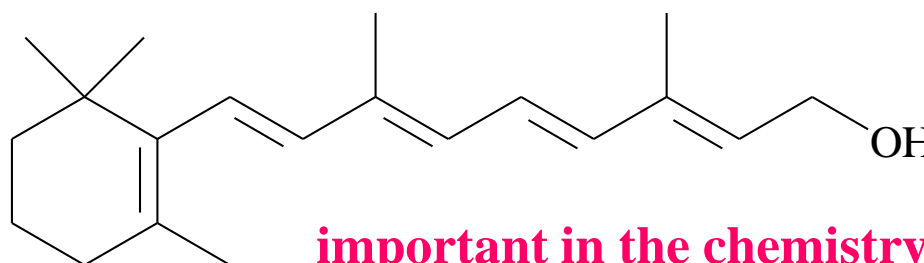**C sp^2 – C sp^2 σ**
C p – C p π

3

Why Study Alkenes?

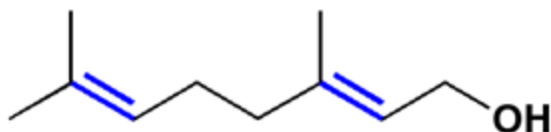- The **alkene** (C=C) functional group is of great importance both **industrially** and **biologically**...

- **Isobutene** (2-methylpropene) $(CH_3)_2C{=}CH_2$

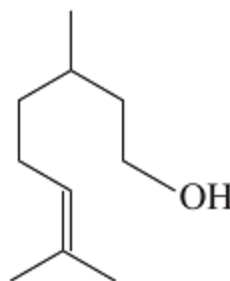 **used in the production of synthetic rubber**
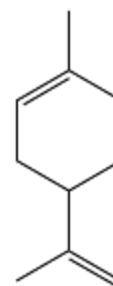
- **Vitamin A** (retinol)
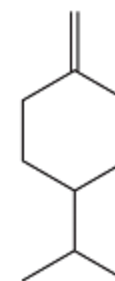

important in the chemistry of vision

Geraniol, a natural product used in perfumes

citronellol
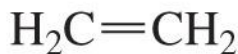in rose and
geranium oils

limonene
in lemon and
orange oils

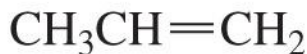**β-phellandrene**
oil of eucalyptus

4

Naming Alkenes (Suffix:ene)

1. Name the parent: find the longest carbon chain-MUST contain the double bond (both sp^2 carbons)

2. Number the chain: C=C must have LOWEST possible numbers-if equidistant from both ends, number closer to first branch point in chain. Functional group always gets lowest number, not the substituent.

3. Indicate the position of the double bond by giving the number of the FIRST alkene carbon-put this number immediately *before* parent name.

4. Name substituents alphabetically with their numbers before the parent name, as for alkanes. If two double bonds, suffix is "diene".

5. For rings-"cyclo" prefix; double bond is always located between C1 and C2. Substit given lowest number possible.

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Nomenclature of Alkenes

$H_2C=CH_2$ $\qquad$ $CH_3CH=CH_2$

systematic name: ethene $\qquad$ propene $\qquad$ cyclopentene $\qquad$ cyclohexene
common name: ethylene $\qquad$ propylene

Replace "ane" of alkane with "ene."

$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H=\overset{1}{C}H_2$
1-butene

$\overset{1}{C}H_3\overset{2}{C}H=\overset{3}{C}H\overset{4}{C}H_3$
2-butene

$\overset{1}{C}H_3\overset{2}{C}H=\overset{3}{C}H\overset{4}{C}H_2\overset{5}{C}H_2\overset{6}{C}H_3$
2-hexene

The functional group gets the lowest possible number.

$\overset{6}{C}H_3\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}CH_2CH_2CH_3$
$\|$
$\overset{1}{C}H_2$
2-propyl-1-hexene

Nomenclature of Alkenes

$$\underset{\text{4-methyl-2-pentene}}{\overset{\displaystyle \text{CH}_3}{\underset{1}{\text{CH}_3}\underset{2}{\text{CH}}=\underset{3}{\text{CH}}\underset{4}{\text{CH}}\underset{5}{\text{CH}_3}}}$$

4-methyl-2-pentene

$$\underset{\text{3-methyl-3-heptene}}{\overset{\displaystyle \underset{2}{\text{CH}_2}\underset{1}{\text{CH}_3}}{\underset{}{\text{CH}_3}\underset{3}{\text{C}}=\underset{4}{\text{CH}}\underset{5}{\text{CH}_2}\underset{6}{\text{CH}_2}\underset{7}{\text{CH}_3}}}$$

3-methyl-3-heptene

4-pentoxy-1-butene

4-methyl-1,3-pentadiene
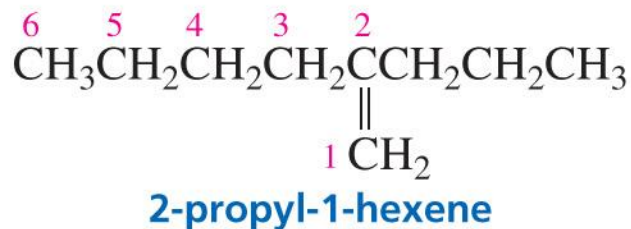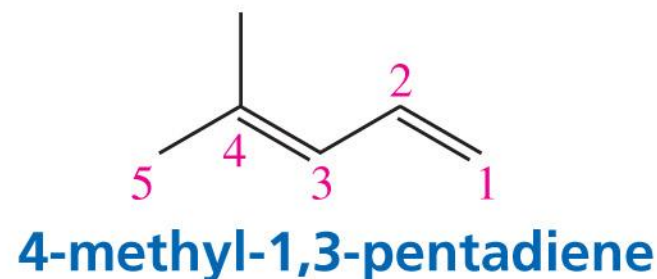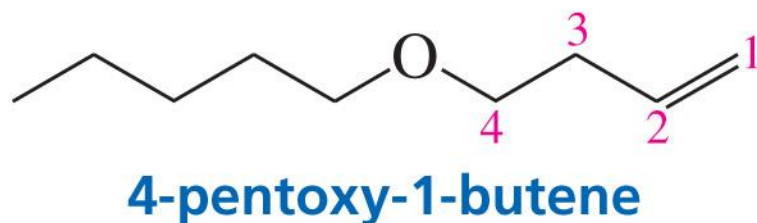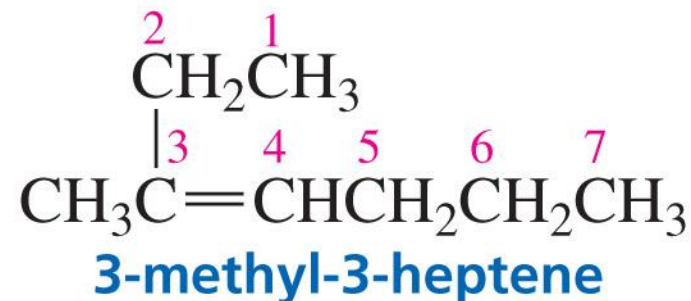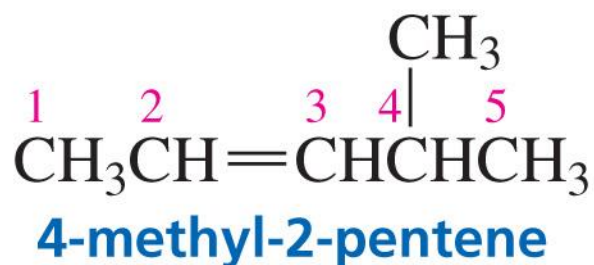
Number in the direction so that the functional group gets the lowest number.

Nomenclature of Alkenes

CH$_3$

CH$_2$CH$_3$

CH$_3$CH$_2$C=CHCH$_2$CHCH$_2$CH$_3$

1 2 3 4 5 6 7 8
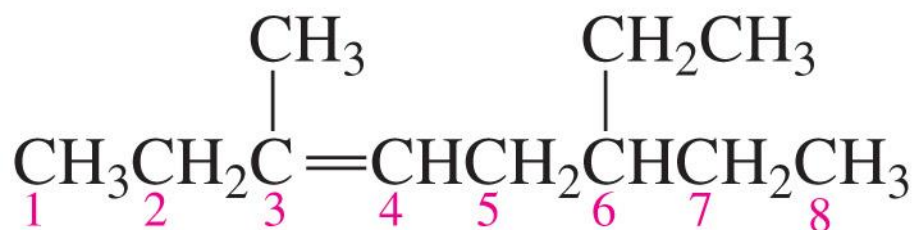
6-ethyl-3-methyl-3-octene

Cl

2 1

7 6 5 4 3

Br
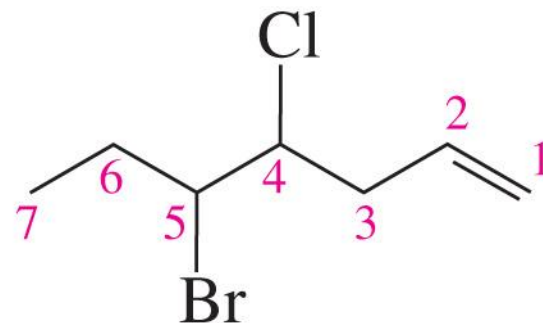
5-bromo-4-chloro-1-heptene

Substituents are stated in **alphabetical order.**

Nomenclature of Alkenes

$CH_3CH_2CH_2C$=$CHCH_2CHCH_3$
$\qquad\qquad\;|\qquad\qquad\qquad\;\;|$
$\qquad\qquad CH_3\qquad\qquad\;\; CH_3$
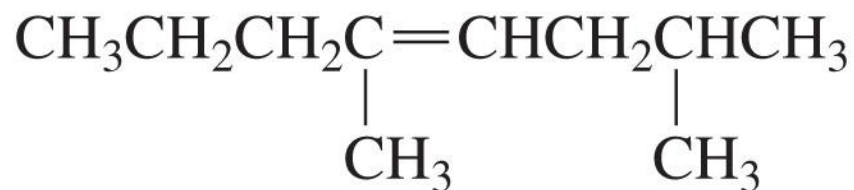
2,5-dimethyl-4-octene
not
4,7-dimethyl-4-octene
because 2 < 4

CH_3CHCH=CCH_2CH_3
$\qquad\;\;|\qquad\qquad\;|$
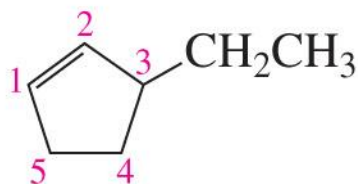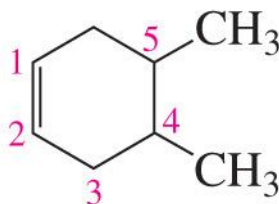$\qquad\;\; Br\qquad\quad\; CH_3$
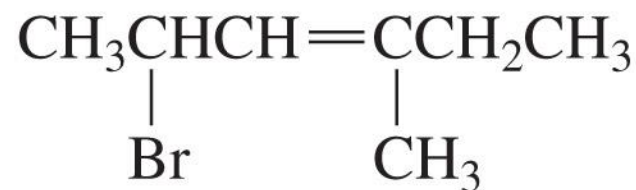
2-bromo-4-methyl-3-hexene
not
5-bromo-3-methyl-3-hexene
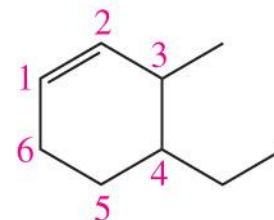because 2 < 3

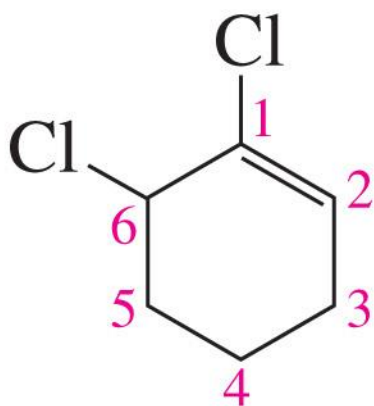# Nomenclature of Cyclic Alkenes

3-ethylcyclopentene

4,5-dimethylcyclohexene

4-ethyl-3-methylcyclohexene

A number is not needed to denote the position of the functional group;

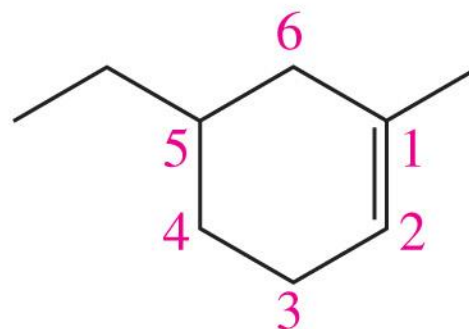**it is always between C1 and C2.**

Nomenclature of Alkenes

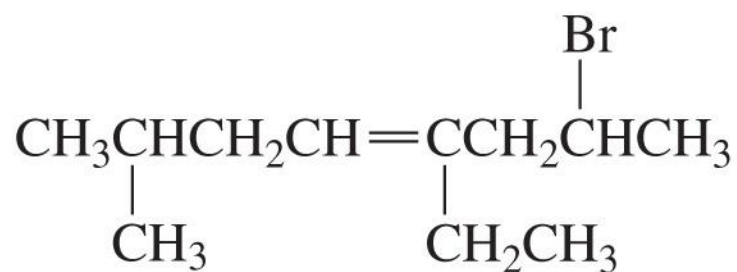**1,6-dichlorocyclohexene**
not
2,3-dichlorocyclohexene
because **1** < **2**

5-ethyl-1-methylcyclohexene
not
4-ethyl-2-methylcyclohexene
because **1** < **2**

Nomenclature of Alkenes

$$CH_3CHCH_2CH=CCH_2CHCH_3$$

with Br, CH₃, and CH₂CH₃ substituents:

Br (on the C after the double bond)

CH₃ (below the first CH)
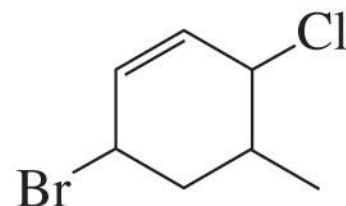
CH₂CH₃ (below the C after double bond)

2-bromo-4-ethyl-7-methyl-4-octene
not
7-bromo-5-ethyl-2-methyl-4-octene
because 4 < 5

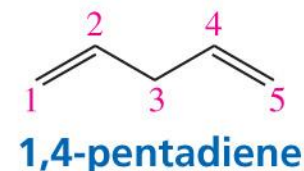**6-bromo-3-chloro-4-methylcyclohexene**
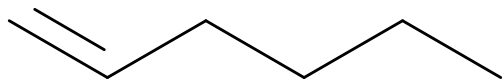not
3-bromo-6-chloro-5-methylcyclohexene
because 4 < 5

Nomenclature of Dienes

$$CH_3CH=CH-CH=CHCH_2CH_3$$

2,4-heptadiene

$$CH_3CH=CH-CH=CH_2$$

1,3-pentadiene
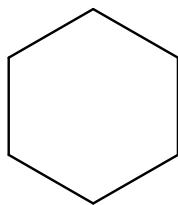
1,4-pentadiene
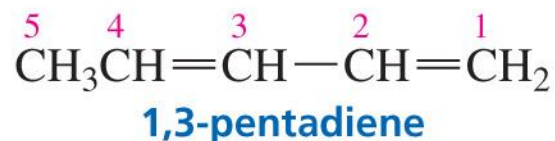
two double bonds = diene

Degree(s) Of Unsaturation (DOU)

- Alkenes are termed "**unsaturated**" compounds (contain one or more double bonds)

- 1-hexene has "**1 degree of unsaturation (D.O.U.)**" (one double bond)

1-hexene, C_6H_{12} (one double bond)

- Note: Degree of unsaturation: number of π bonds *or* rings

cyclohexane, C_6H_{12} - also 1 D.O.U. (one ring)

Degree(s) Of Unsaturation

- **Calculating D.O.U. for hydrocarbons:**

1) Look at formula (i.e. for 1-hexene = C_6H_{12})

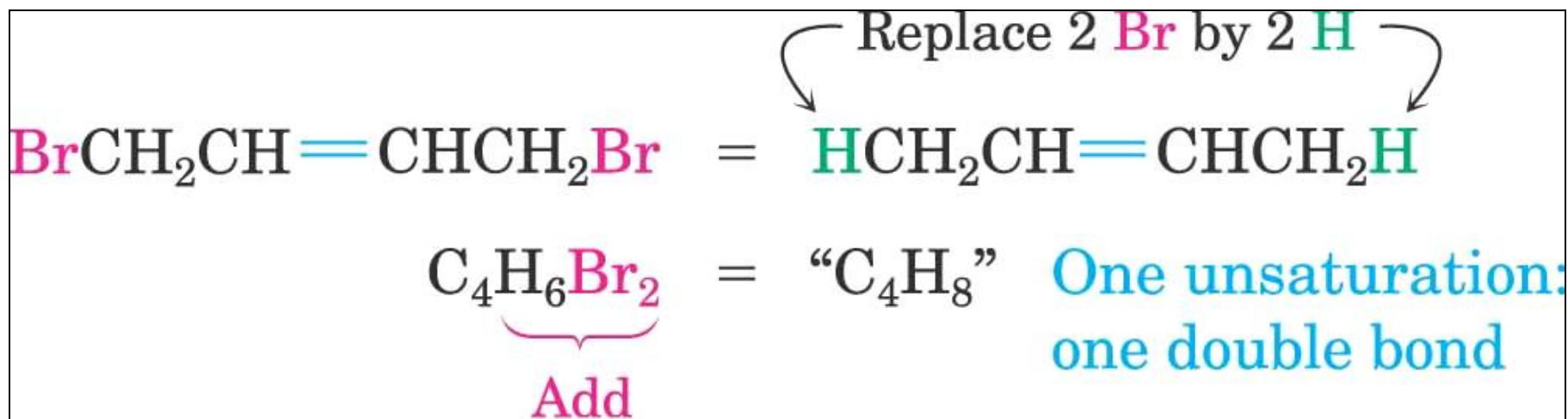2) Write formula of alkane with **same number of carbons**, i.e. $C_nH_{2n+2} = C_6H_{14}$

3) Calculate:

$$\frac{(\text{H's in alkane}) - (\text{H's in alkene})}{2}$$

= (14-12)/2

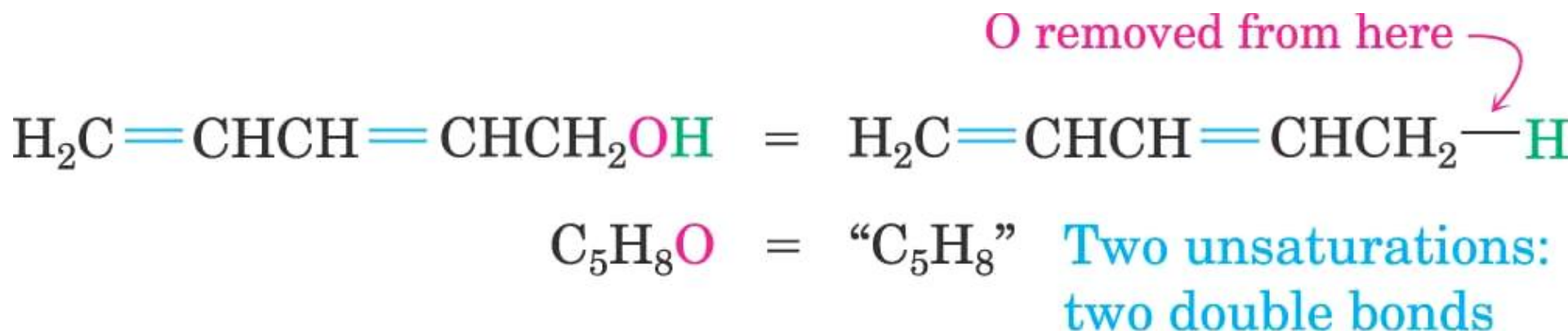= **1 degree of unsaturation**

Degree(s) Of Unsaturation

- What if other (hetero)atoms are in the formula?

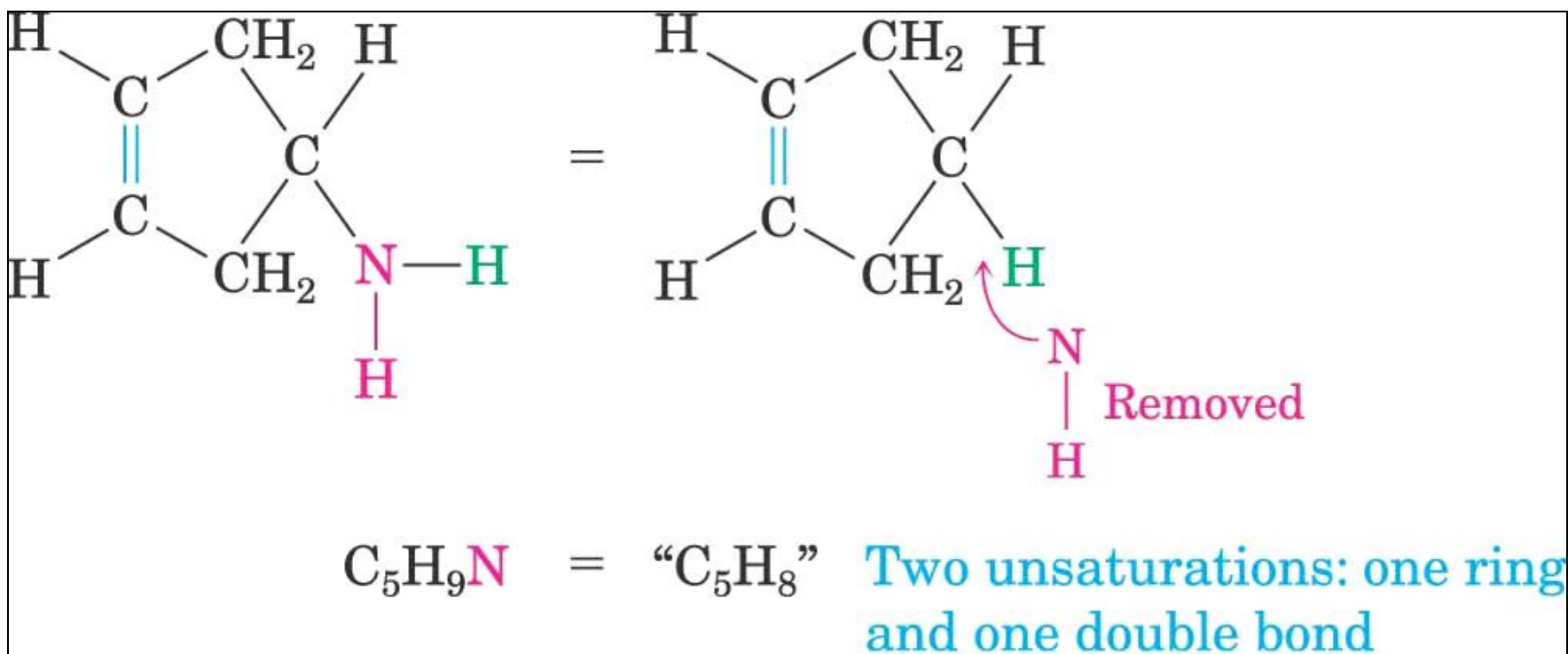- **Halogens** - replace each halogen with H and do same calculation, e.g. $C_5H_6BrCl = C_5H_8 = $ **2 D.O.U.**

$$\text{Replace 2 Br by 2 H}$$

$$BrCH_2CH=CHCH_2Br \ = \ HCH_2CH=CHCH_2H$$

$$C_4H_6Br_2 \ = \ \text{"}C_4H_8\text{"} \qquad \text{One unsaturation:}$$
$$\underbrace{}_{\text{Add}} \qquad \qquad \text{one double bond}$$

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Degree(s) Of Unsaturation

- **Oxygen** - remove from formula and do same calculation, e.g. $C_6H_6O_2 = C_6H_6 =$ **4 D.O.U.**

O removed from here

$$H_2C = CHCH = CHCH_2OH \quad = \quad H_2C = CHCH = CHCH_2 - H$$

$$C_5H_8O \quad = \quad \text{"} C_5H_8 \text{"} \quad \text{Two unsaturations: two double bonds}$$

Degree(s) Of Unsaturation

- **Nitrogen** – subtract number of N from H and do same calculation, e.g. $C_8H_{13}N = C_8H_{12} = $ **3 D.O.U**

$$C_5H_9N = \text{``}C_5H_8\text{''}$$ Two unsaturations: one ring and one double bond
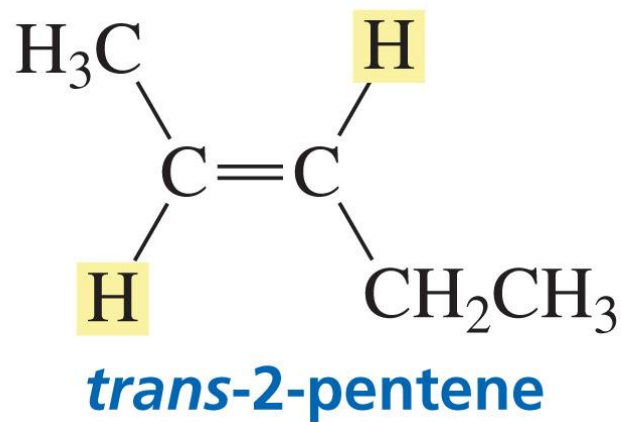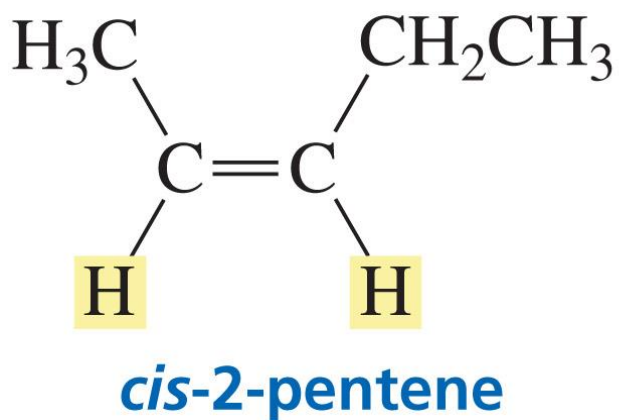
©2004 Thomson - Brooks/Cole

Degree of Unsaturation and Variation

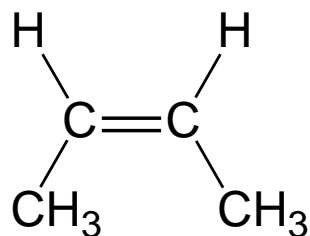- Compounds with the same degree of unsaturation can have many things in common and still be very different
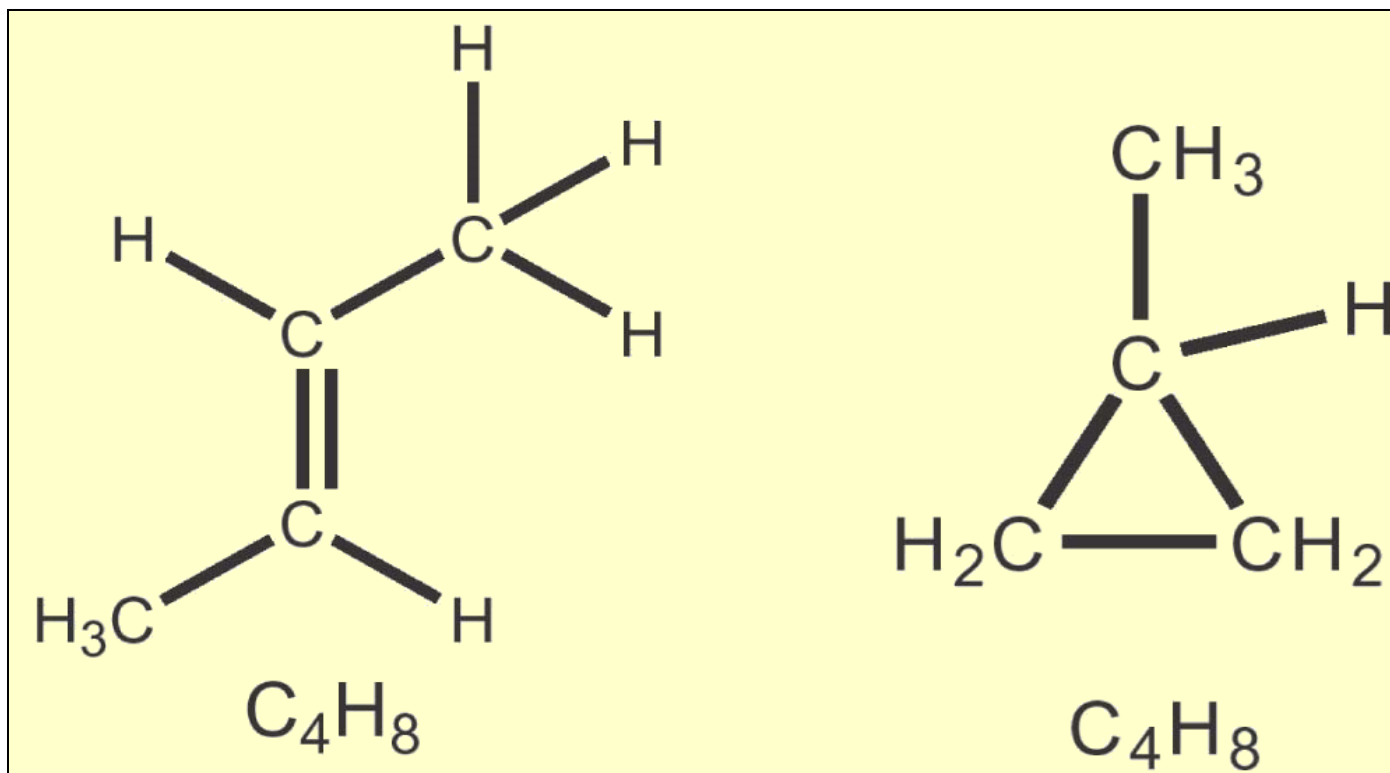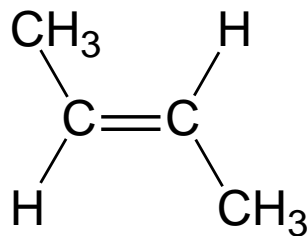
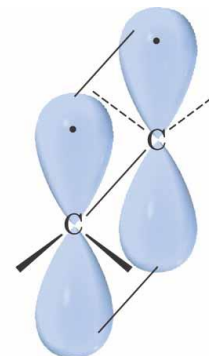# Stereoisomers are Named Using a *cis* or *trans* Prefix

cis-2-pentene   *trans*-2-pentene

Cis-Trans Isomerism in Alkenes
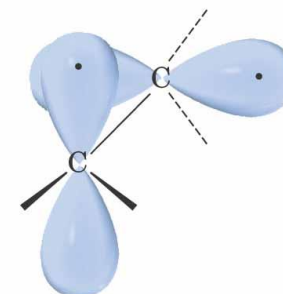## Consequence of no free rotation

___CIS___-2-butene
boiling point 3.7 ºC

___TRANS___-2-butene
boiling point 0.9 ºC

π bond
(*p* orbitals are parallel)

90°
rotation

Broken π bond after rotation
(*p* orbitals are perpendicular)

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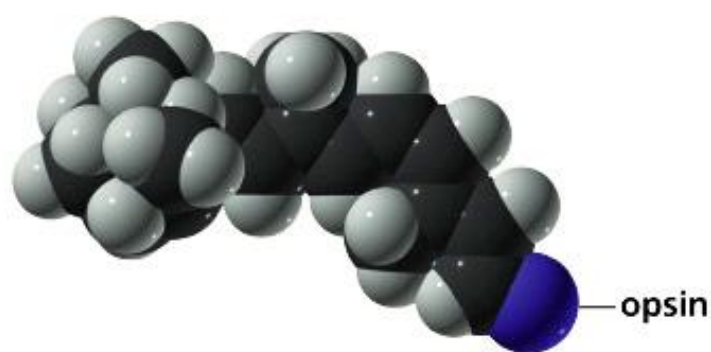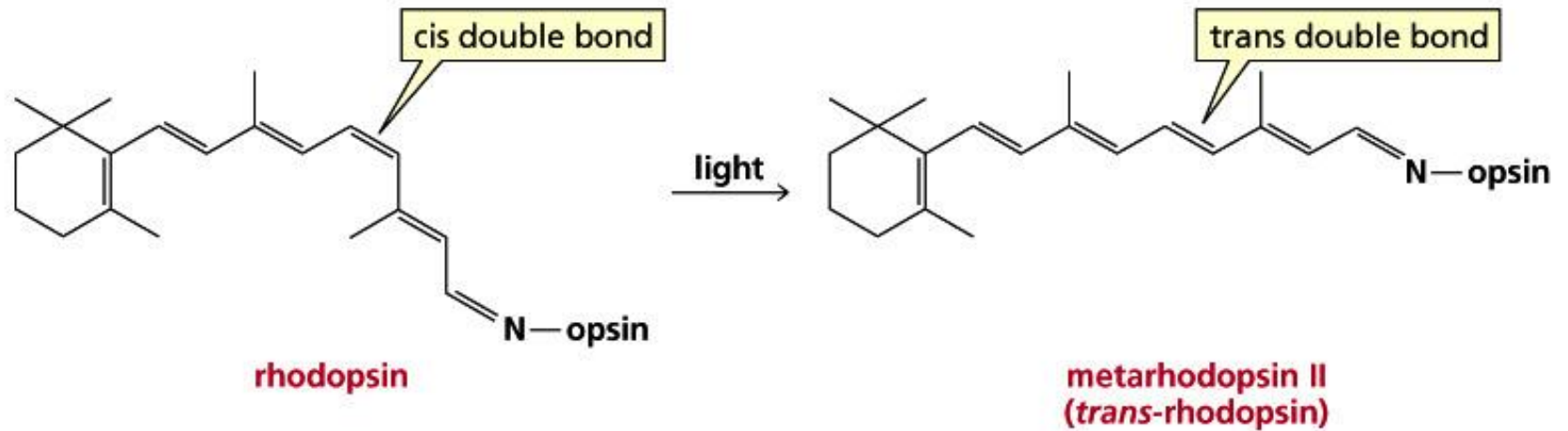
Cis isomer: two groups on __SAME__ side of C=C

Trans isomer: two groups on __OPPOSITE__ sides of C=C

cis and trans isomers are not possible for these compounds because
two substituents on an *sp*^{2} carbon are the same

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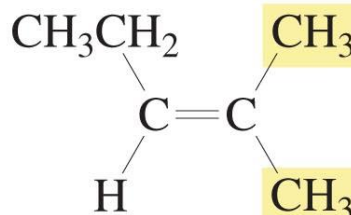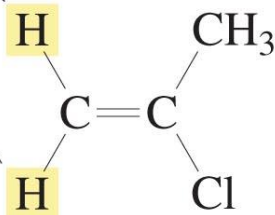
Each carbon must have two different groups for these isomers to exist.

Cis-Trans Interconversion in Vision

cis double bond

trans double bond

light

N—opsin

N—opsin

rhodopsin

metarhodopsin II
(*trans*-rhodopsin)

opsin

opsin

Sequence Rules: The *E,Z* Designation

- Neither compound is clearly "*cis*" or "*trans*"
  - Substituents on C1 are different than those on C2
  - We need to distinguish the two stereoisomers

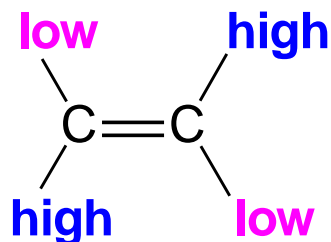- *Cis, trans* nomenclature only works for disubstituted double bonds
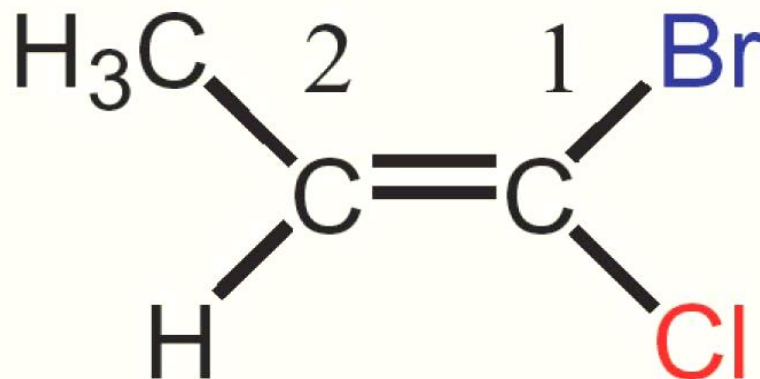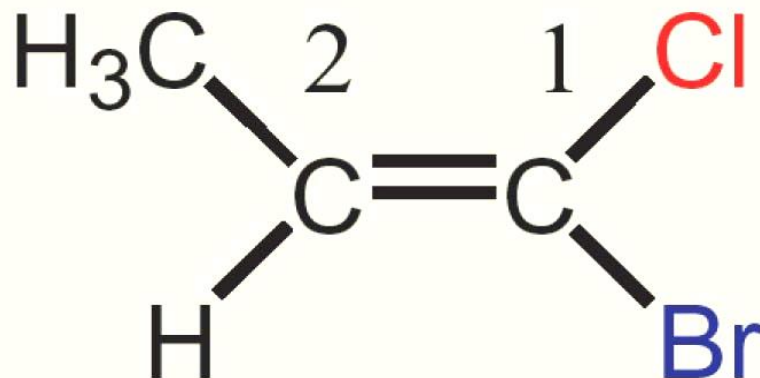
Sequence Rules: The *E,Z* Designation

Priorities are assigned to each group.

High priority groups on same side of double bond = __**Z**__ - designation (*zusammen*: together)

"zee zame zide"
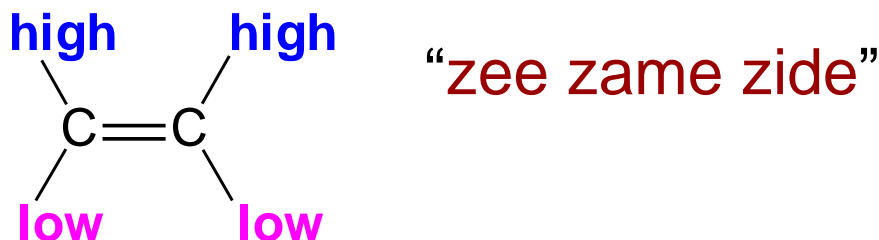
High priority groups on opposite side of double bond = _**E**_ -designation (*entgegen*: opposite sides)

Sequence Rules: The *E,Z* Designation (also used for *R/S*)
## *Cahn-Ingold-Prelog Rules*

1. Divide molecule in half by double bond.

2. Rank atoms directly attached to each C of double bond by ATOMIC NUMBER. (DO NOT USE MASS!!)

Br > Cl > O > N > C > H   **Higher atomic number = higher priority**
35   17   8   7   6   1

3. If atoms directly attached to sp^2 C of double bond the same – go to **next** atom (continue until "first point of difference" is reached)

4. Multiple bonded atoms (such as -C=O group) are equivalent to the same number of singly-bonded atoms (i.e. C bonded to two O atoms).

5. If two *isotopes* are compared, the *higher the mass number*, the higher the priority. (e.g. D > H)

Extended Comparison Example

- **-CH$_2$CH$_3$** has greater priority than **-CH$_3$** (first point of attachment the same (carbon) but **ethyl group has another carbon attached…**

$$H_3C\diagdown$$
$$\underset{H_3C\diagup}{CH}— \quad > \quad CH_3CH_2CH_2— \quad > \quad CH_3CH_2— \quad > \quad H_3C—$$
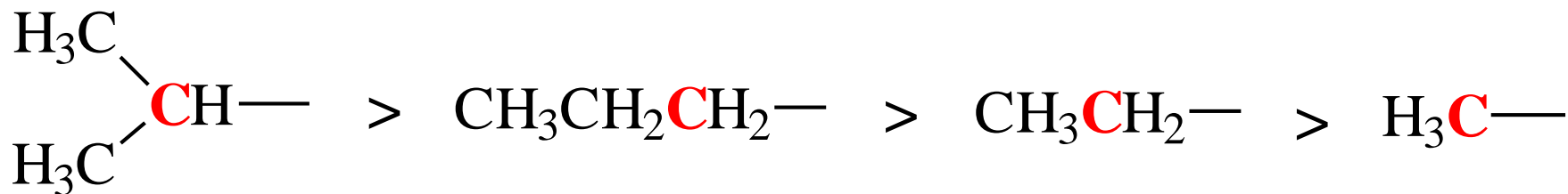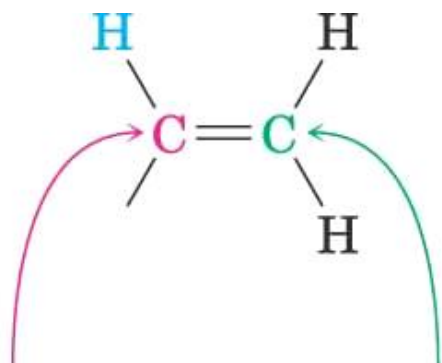
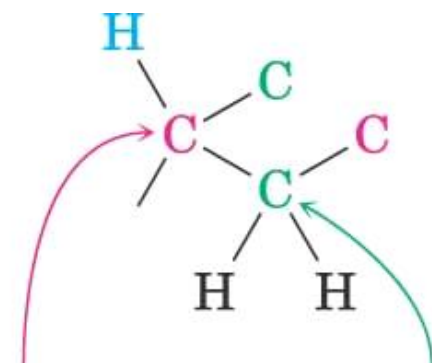**higher priority** $\longrightarrow$ **lower priority**

Dealing With Multiple Bonds

- Atoms attached to double or triple bonds are given "single bond equivalencies" <u>before</u> deciding the priorities
- Break open multiple bond, attach SAME atom to broken bonds as in original compound
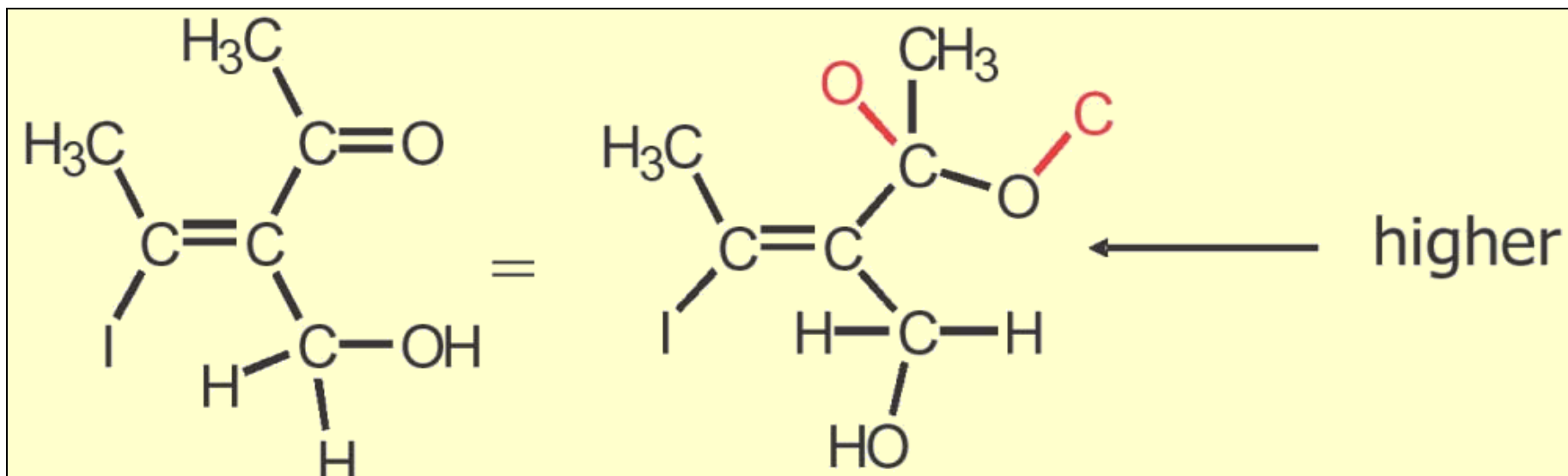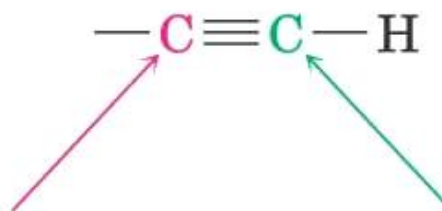
is equivalent to

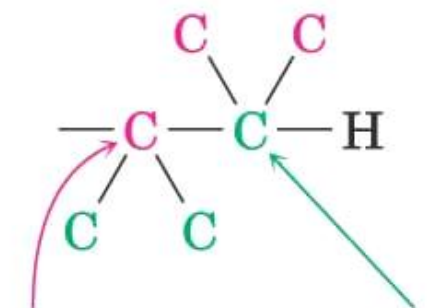This carbon is
bonded to
H, C, C

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

This carbon is
bonded to
H, C, C

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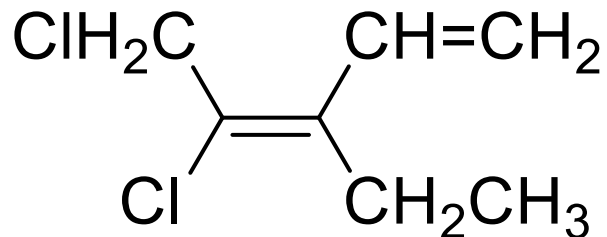is bonded to
H, H, C, C

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, C, C, C

©2004 Thomson - Brooks/Cole

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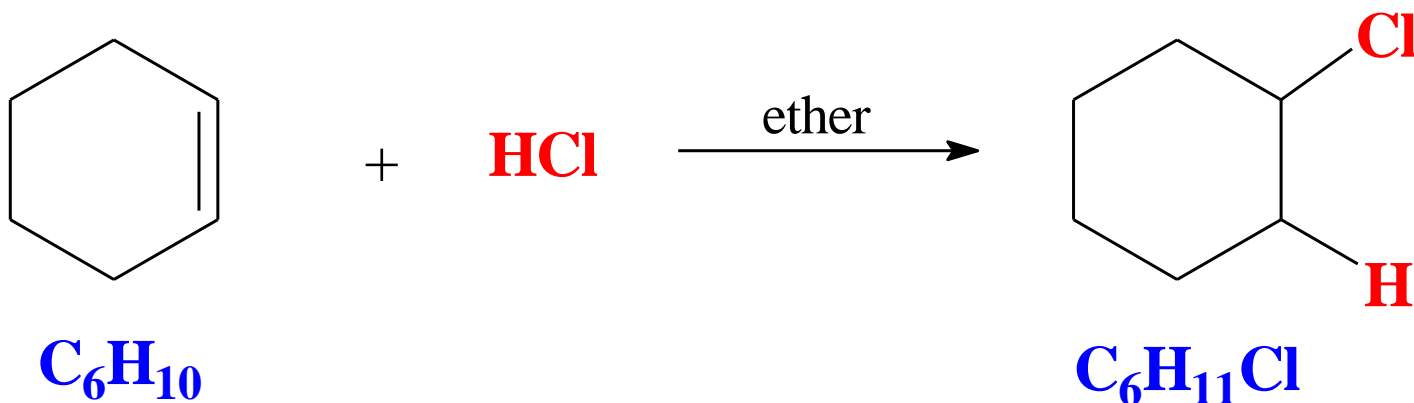# E/Z Examples

$$ClH_2C \qquad CH=CH_2$$
$$Cl \qquad CH_2CH_3$$

- Work out group priority on each alkene carbon

This is known as the "_____" isomer

Types Of Organic Reactions (1)

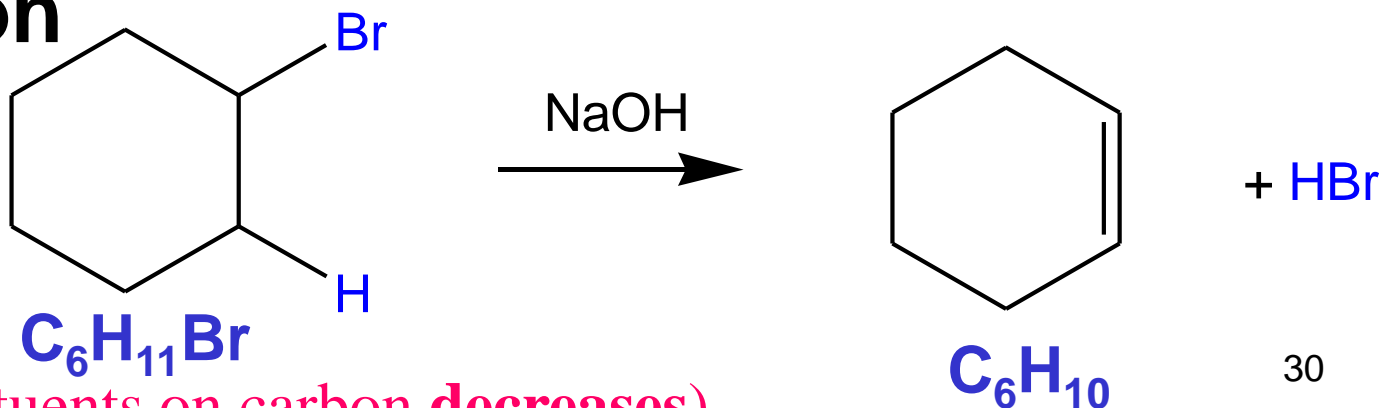- Most organic reactions can be identified as being one of the following types-

Addition

$+$ **HCl** $\xrightarrow{\text{ether}}$

C_6H_{10}

(number of substituents on carbon **increases**)

$C_6H_{11}Cl$

Elimination

$\xrightarrow{\text{NaOH}}$

$+$ HBr

$C_6H_{11}Br$

C_6H_{10}

(number of substituents on carbon **decreases**)

Types Of Organic Reactions (2)

Substitution
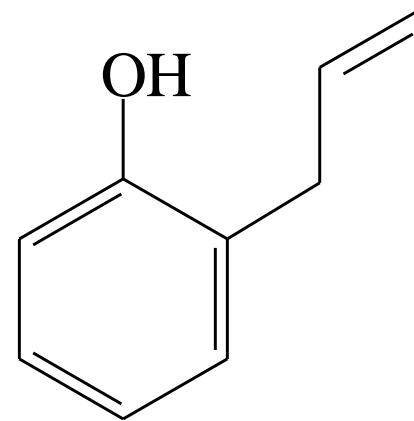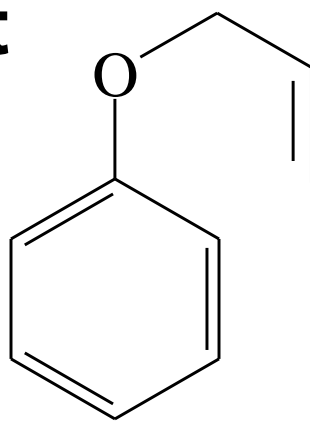
$$CH_3—I \; + \; {}^{-}CN \xrightarrow{\text{acetone}} CH_3—CN \; + \; I^{-}$$
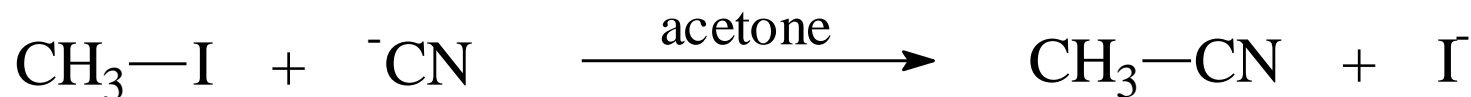
(number of substituents on carbon **stays the same**)

Rearrangement

(**atomic reorganization** forming an isomer)

heat

$C_9H_{10}O$ $C_9H_{10}O$

- In order for these reactions to proceed, bonds must be **broken** and **formed**

Breaking/Making Bonds (1)

- Covalent bonds are broken (formed) in **two** general ways:

Symmetrically

- This is _____bond cleavage - forming _____(species with an unpaired electron)

- A "fish-hook arrow"   represents movement of a **SINGLE electron -** less common, associated with **RADICAL** reactions
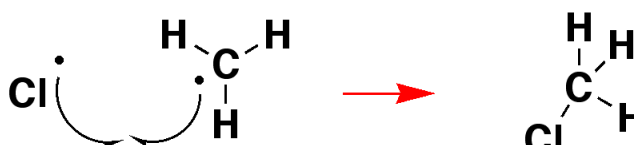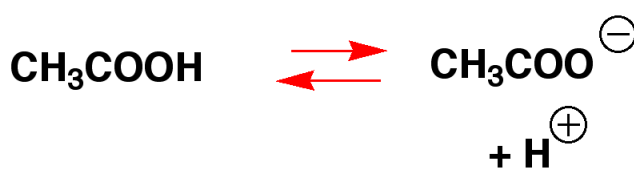
Unsymmetrically

- This is _____bond cleavage - forming _____(an anion and cation)

- A full-headed arrow   represents movement of an **electron PAIR**

- This electron movement is much more common, associated with **POLAR** reactions

CURVED ARROWS

In organic chemistry, a curved arrow indicates the movement of a pair of electrons.

Arrows in Organic Chemistry: Showing Processes
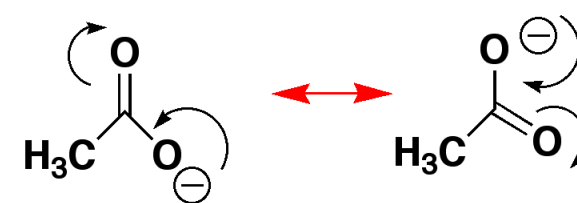
ARROW	USE	EXAMPLE

SHOW A REACTION

SHOW BETWEEN RESONANCE STRUCTURES

EQUILIBRIUM

CH_3COOH ⇌ $CH_3COO^{\ominus}$ + $H^{\oplus}$

NO REACTION

How to Draw Curved Arrows

How to Draw Curved Arrows

Correct Form:
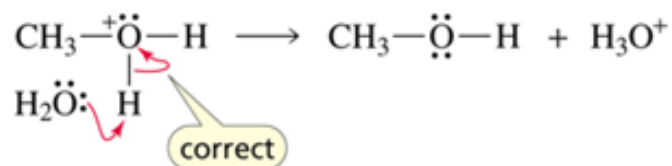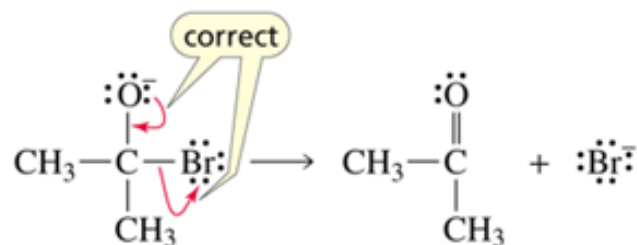
Incorrect Form:
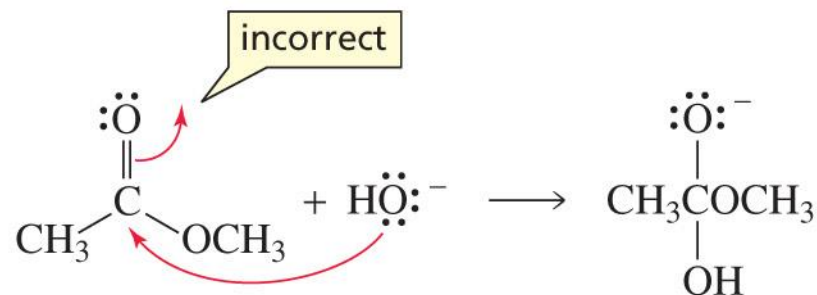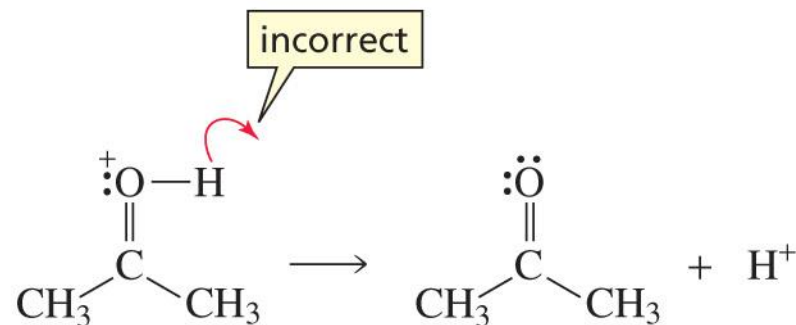
How to Draw Curved Arrows
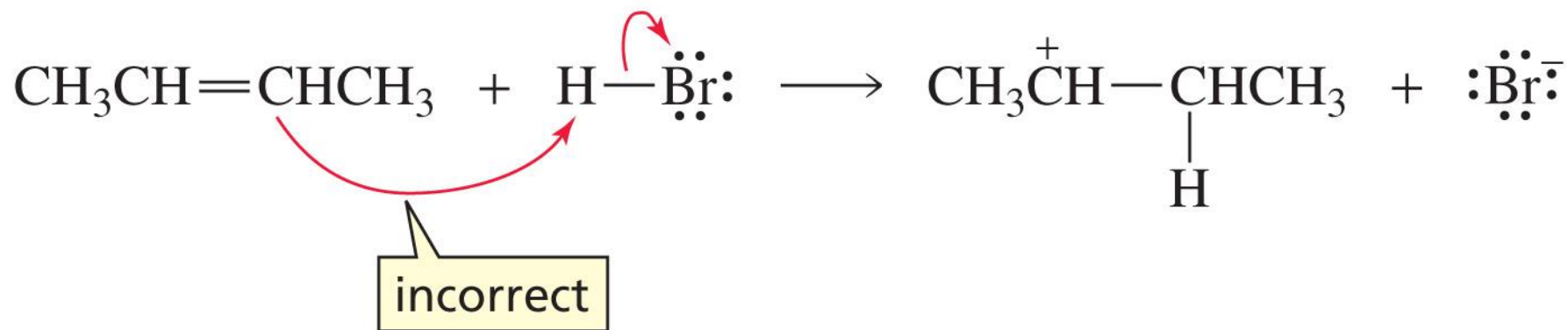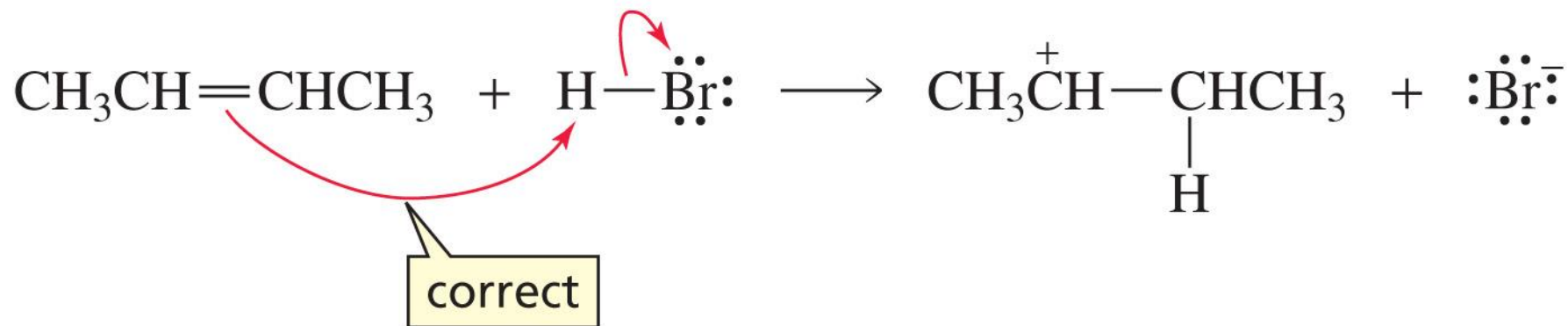
How Organic Reactions Occur: Mechanisms

- In a clock the hands move but the *mechanism* behind the face is what causes the movement

- In an organic reaction, we see the transformation that has occurred. *The mechanism describes the steps behind the changes that we can observe*

- Reactions occur in defined steps that lead from reactant to product

FUNDAMENTAL CONCEPT in POLAR REACTIONS

Electron rich atoms or molecules (_____)

are attracted to electron-deficient atoms or molecules

(_____)

Important Definitions

NUCLEOPHILE- "<u>Nucleus Loving</u>"; an electron **donor** (Lewis base), may be neutral (e.g. $:NH_3$, $H_2C=CH_2$) or negatively charged (e.g. HO^-, H_2O, Cl^-)

$$H\ddot{O}:^- \qquad :\ddot{C}l:^- \qquad CH_3\ddot{N}H_2 \qquad H_2\ddot{O}:$$

these are nucleophiles because they have a pair of electrons to share

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ELECTROPHILE- "<u>Electron Loving</u>"; an electron **acceptor** (Lewis acid), may be neutral (e.g. H_3B) or positively charged (e.g. H_3O^+)

$$H^+ \qquad CH_3\overset{+}{C}H_2 \qquad BH_3$$

these are electrophiles because they can accept a pair of electrons

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Nucleophiles and Electrophiles

- The nucleophile can be neutral or negatively charged

- The electrophile can be neutral or positively charged

Examples of nucleophilic/electrophilic carbons

Nucleophilic carbon

$\overset{+}{\delta}\qquad\overset{-}{\delta}$

Li—C

Na—C

Mg—C

$\overset{+}{\delta}\qquad\overset{-}{\delta}$

C—O

C—N

C—F

C—Cl

C—Br

C=O

C=N

C≡N

Electrophilic carbon

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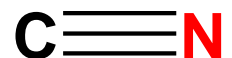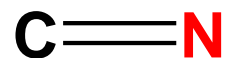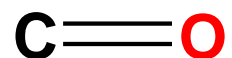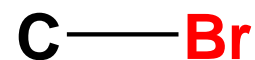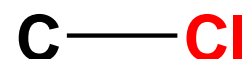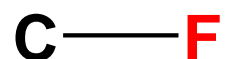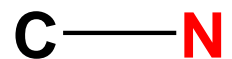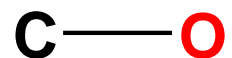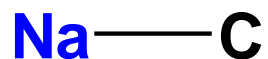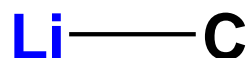
Example of Electrophilic Addition Reaction

Addition of HBr to Alkene
Overall reaction and mechanism:

What about energy?
First, we need to learn some terminology…..

Thermodynamics and Kinetics

Kinetics: The k_1 and k_{-1} values that provide the rate at which the reaction comes to equilibrium.

$$Y \rightleftharpoons Z$$

$$k_1$$

$$k_{-1}$$
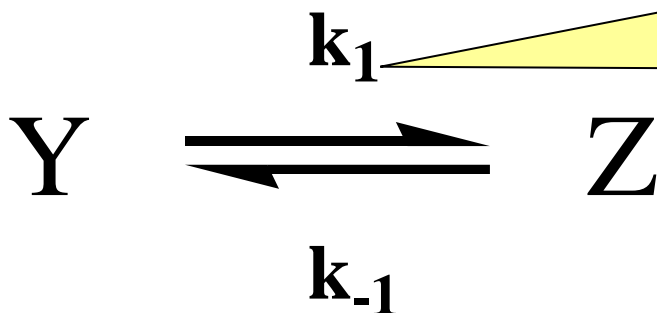
Thermodynamics: The K_{eq} value that provides the concentration at Z and Y at equilibrium.

$$K_{eq} = \frac{k_1}{k_{-1}} = \frac{[Z]}{[Y]}$$

thermodynamics: how much Z is formed?

$$Y \rightleftharpoons Z$$
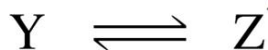
kinetics: how fast Z is formed?

Thermodynamics describes a reaction at equilibrium. Kinetics explains the rates of chemical reactions.

Reaction Energy Diagrams

Transition state:
-high energy structure
-"in between" reactants and products
-At energy maximum
-From transition state, reaction can go in either direction.
ΔG‡ (‡ double dagger)
-activation energy
-energy required to reach transition state
-determines the rate of reaction
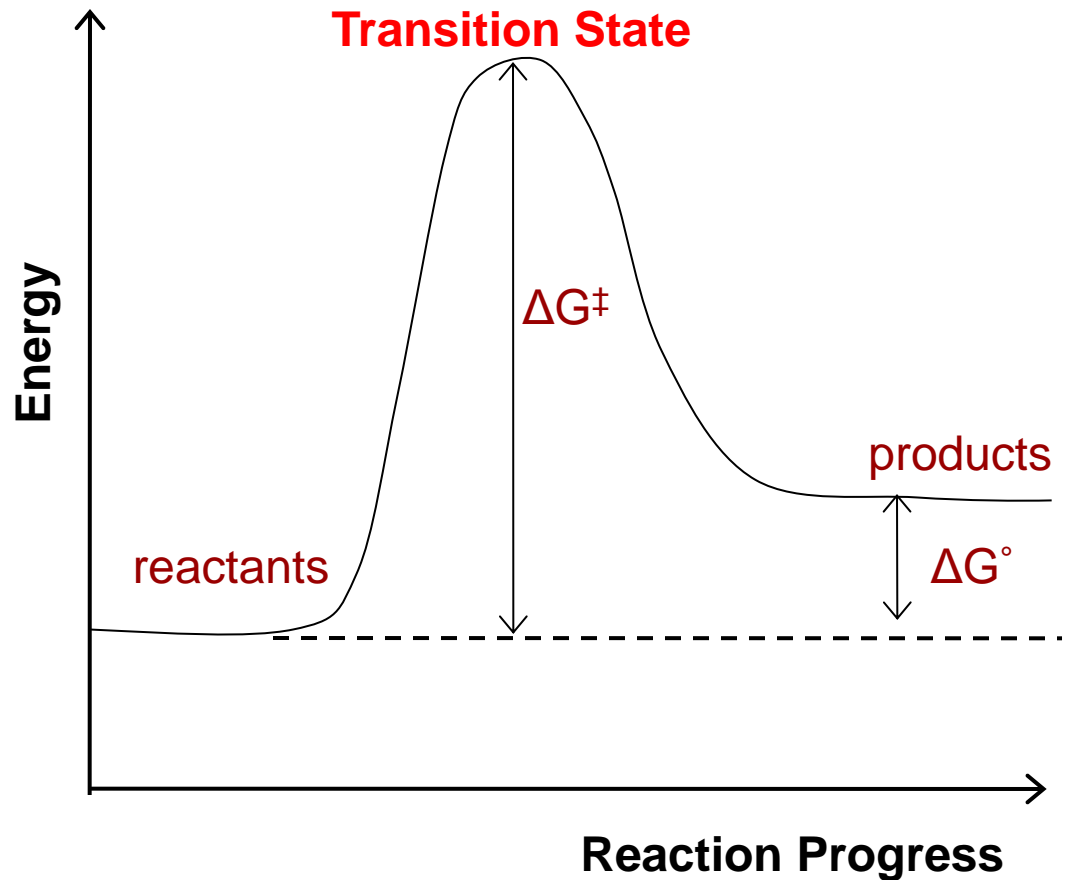
A Reaction Coordinate Diagram
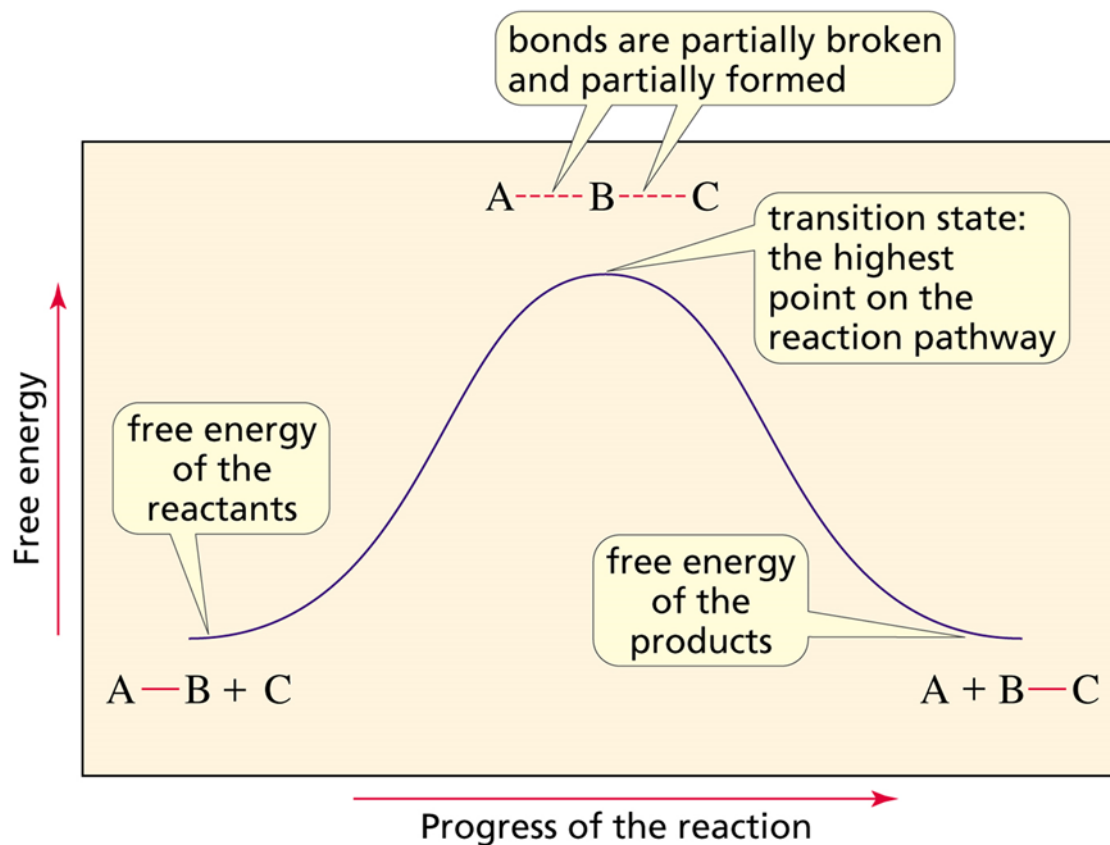
A reaction coordinate diagram shows the energy changes that take place in each step of a reaction.

Reaction Equilibria

We can write all reactions as equilibria:

$$a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$$

$$K_{eq} = \frac{[\text{Products}]}{[\text{Reactants}]} = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

equilibrium constant
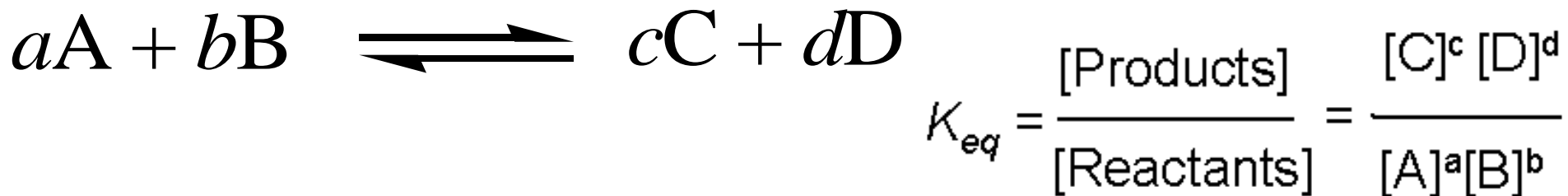
If Keq>1, forward reaction is favoured.
If Keq<1, reverse reaction is favoured.

What determines the size of K_{eq}?

Relative energies of reactants and products.

Gibbs Free Energy Change (ΔG°): standard free energy change at 1 atm and 298 K

ΔG° = free energy of products - free energy of reactants = $- RT \ln K_{eq}$
R = 8.315 J/(molK) or 1.986 cal/(molK), T = temperature (Kelvin)

Reaction Energy Changes

ΔG° = free energy of products - free energy of reactants = $- RT \ln K_{eq}$

If K **>** 1, ΔG° **<** 0 and the reaction is **spontaneous** (exergonic   ).
If K **<** 1, ΔG° **>** 0 and the reaction is **NOT spontaneous** (endergonic   ).

Exergonic process   **Endergonic process**
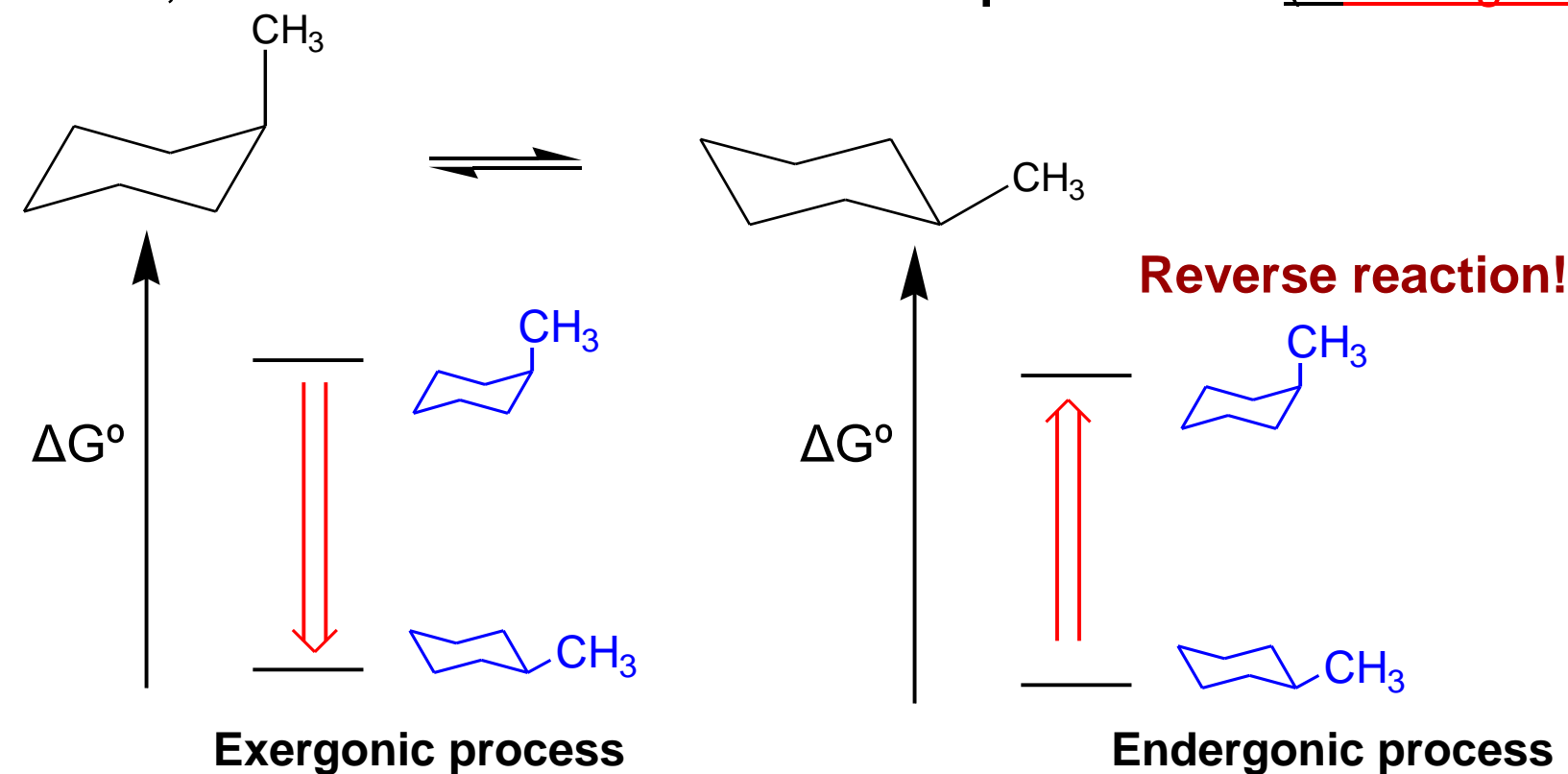
ΔG° can be considered in terms of **enthalpy** (ΔH°) and **entropy** (ΔS°).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Reaction Energy Diagrams
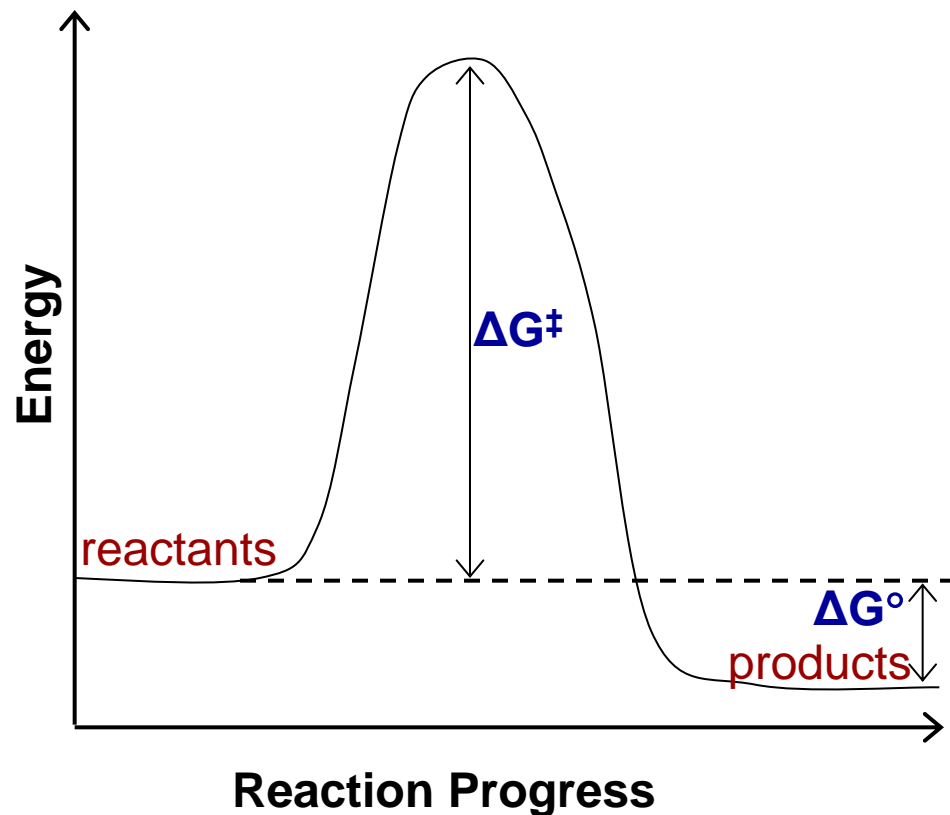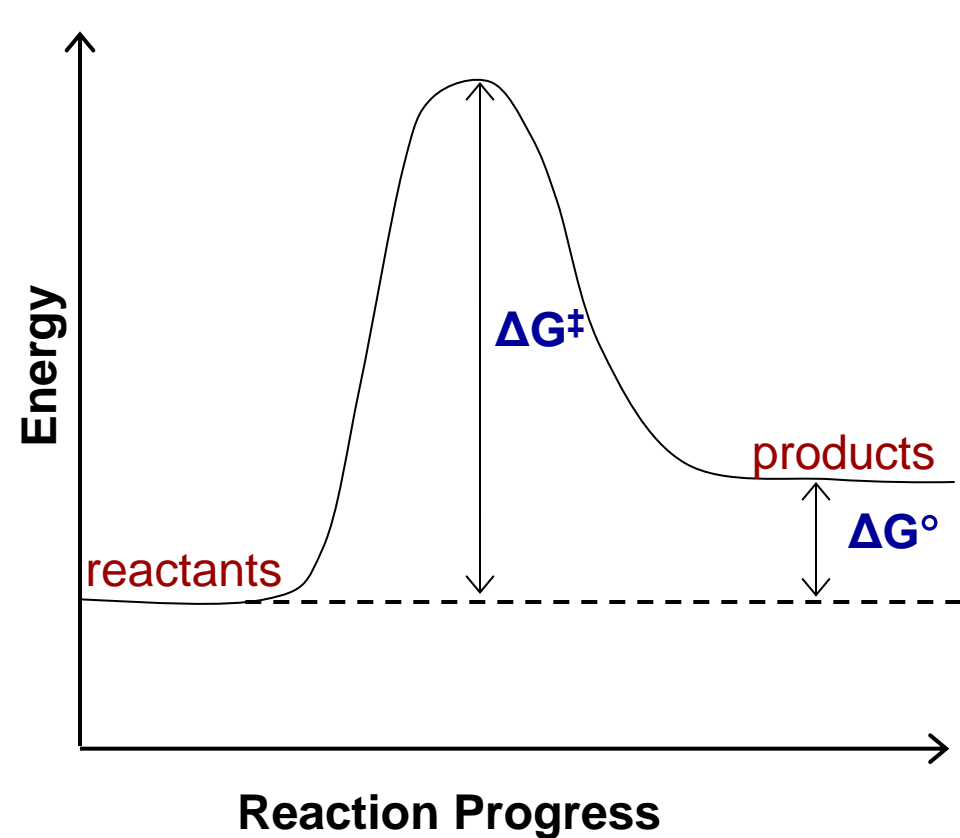
ΔG° related to equilibrium constant. Indicative of **"thermodynamic stability"**
ΔG‡ related to rate of the reaction. Indicative of **"kinetic stability"**

Enthalpy and Entropy

$\Delta H°$ (enthalpy) is the heat of the reaction and is a measure of the change in bonding energy in a reaction

$$\Delta G° = -RT \ln Keq = \Delta H° - T\Delta S°$$

If Keq > 15, use $\Delta H°$ to judge ease of reactions; otherwise use $\Delta G°$
$\Delta H° < 0$: _exothermic_____, heat released (bonds formed stronger than bonds broken)
$\Delta H° > 0$: _endothermic__, heat absorbed (bonds broken stronger than bonds formed)

$\Delta S°$ (entropy) is the change in freedom of motion that accompanies a reaction. (measure of disorder)

A + B ⇌ C $\Delta S°$ _negative_____.

A ⇌ B + C $\Delta S°$ ___positive_____.
What signs of $\Delta S°$ and $\Delta H°$ favour a spontaneous reaction?

Entropic Reactions

- **An entropic reaction results in a massive change in volume without heat evolution.**
- **Air bag deployment is a common entropic reaction.**
- **TATP is an entropic explosive used by terrorists.**
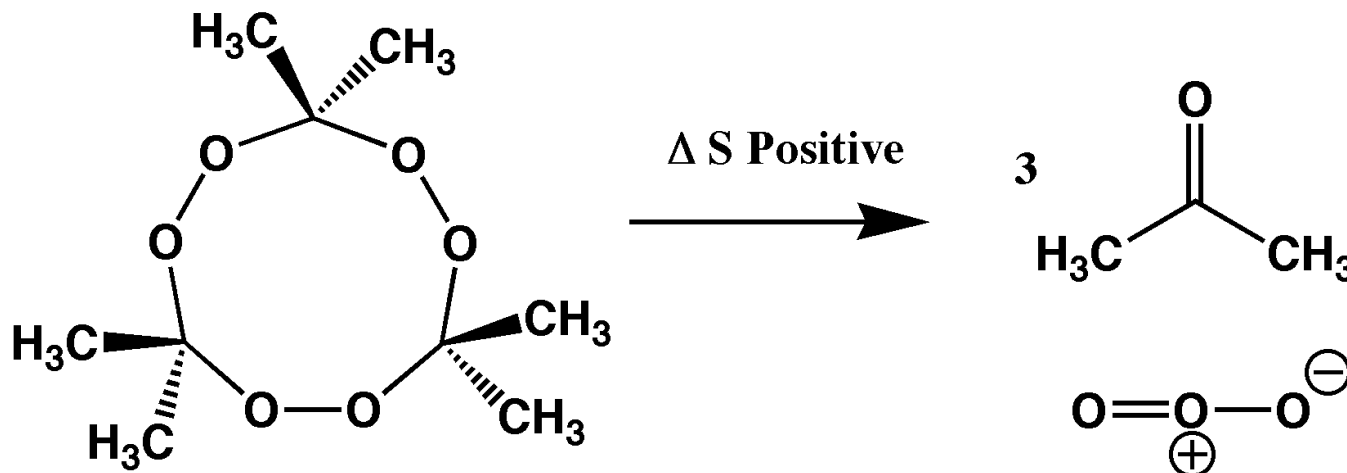
Triacetonetriperoxide (TATP)
called "Mother of Satan"

ΔS Positive

3

Increasing the Amount of a Product Formed in a Reaction

Le Chatelier's Principle: if an equilibrium is disturbed, the system will adjust to offset the disturbance

$$A + B \rightleftharpoons C + D$$
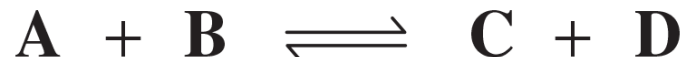
$$K_{eq} = \frac{[C][D]}{[A][B]}$$

Coupled Reactions: an endergonic reaction followed by an exergonic reaction

an endergonic reaction

an exergonic reaction

$$A \rightleftharpoons B \rightleftharpoons C$$
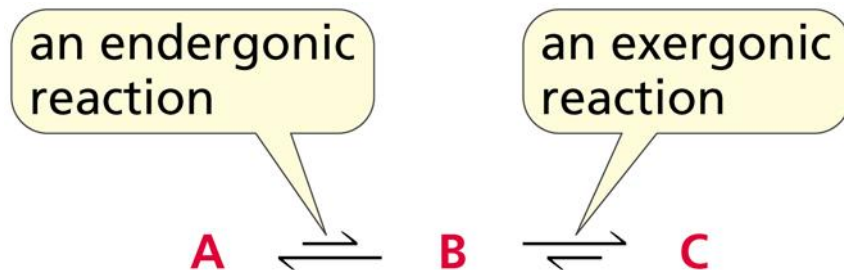
Catalytic Hydrogenation (1 of 2)

$$CH_3CH=CHCH_3 \ + \ H_2 \ \xrightarrow{\textbf{Pd/C}} \ CH_3CH_2CH_2CH_3$$

alkene   alkane

 + H$_2$ $\xrightarrow{\textbf{Pd/C}}$

alkene   alkane
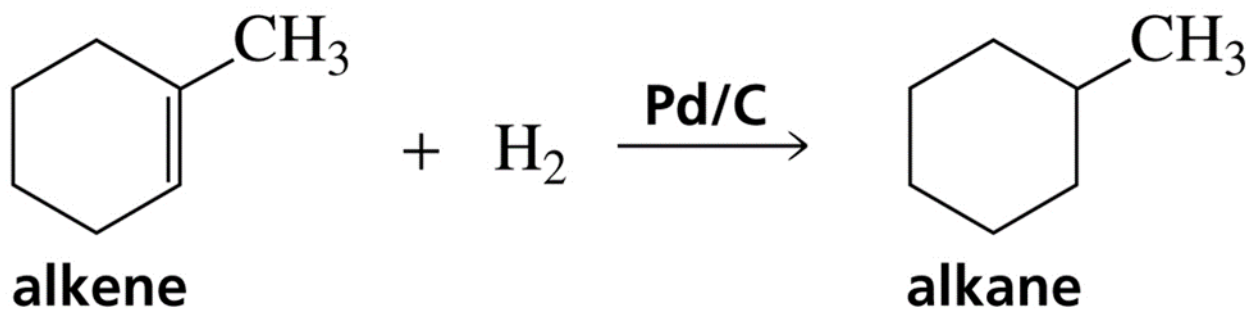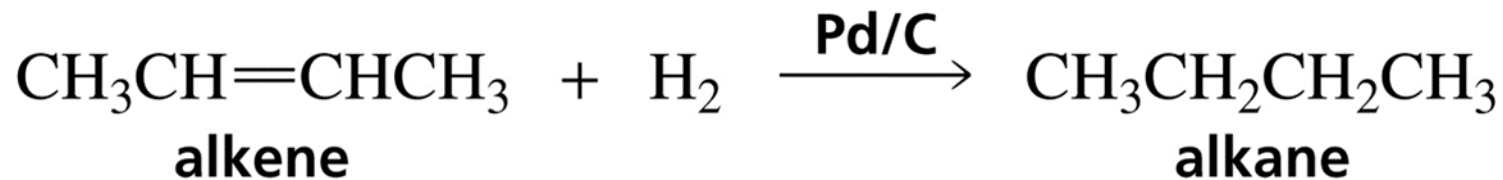
reduction reactions (the number of C–H bonds increases)

hydrogen molecules settle on the surface of the catalyst and interact with the metal atoms

the alkene approaches the surface of the catalyst

the π bond between the two carbons is replaced by two C—H σ bonds

$CH_3CH=CHCH_3 \longrightarrow CH_3\overset{.}{C}H-\overset{.}{C}HCH_3 \longrightarrow CH_3CH-CHCH_3$

$H-H \qquad\qquad H\cdot \quad \cdot H \qquad\qquad\qquad H \quad\;\; H$

Using Enthalpy Values to Determine the Relative Stabilities of Alkenes (1 of 2)

Reaction	Enthalpy of reaction (kcal/mol)	Heat of hydrogenation
$CH_3C{=}CHCH_3$ (with CH_3) $+ H_2 \xrightarrow{Pd/C} CH_3CHCH_2CH_3$ (with CH_3)	−26.9	26.9 kcal/mol
$CH_2{=}CCH_2CH_3$ (with CH_3) $+ H_2 \xrightarrow{Pd/C} CH_3CHCH_2CH_3$ (with CH_3)	−28.5	28.5 kcal/mol
$CH_3CHCH{=}CH_2$ (with CH_3) $+ H_2 \xrightarrow{Pd/C} CH_3CHCH_2CH_3$ (with CH_3)	−30.3	30.3 kcal/mol

The product of each of the three reactions is 2-methylbutane
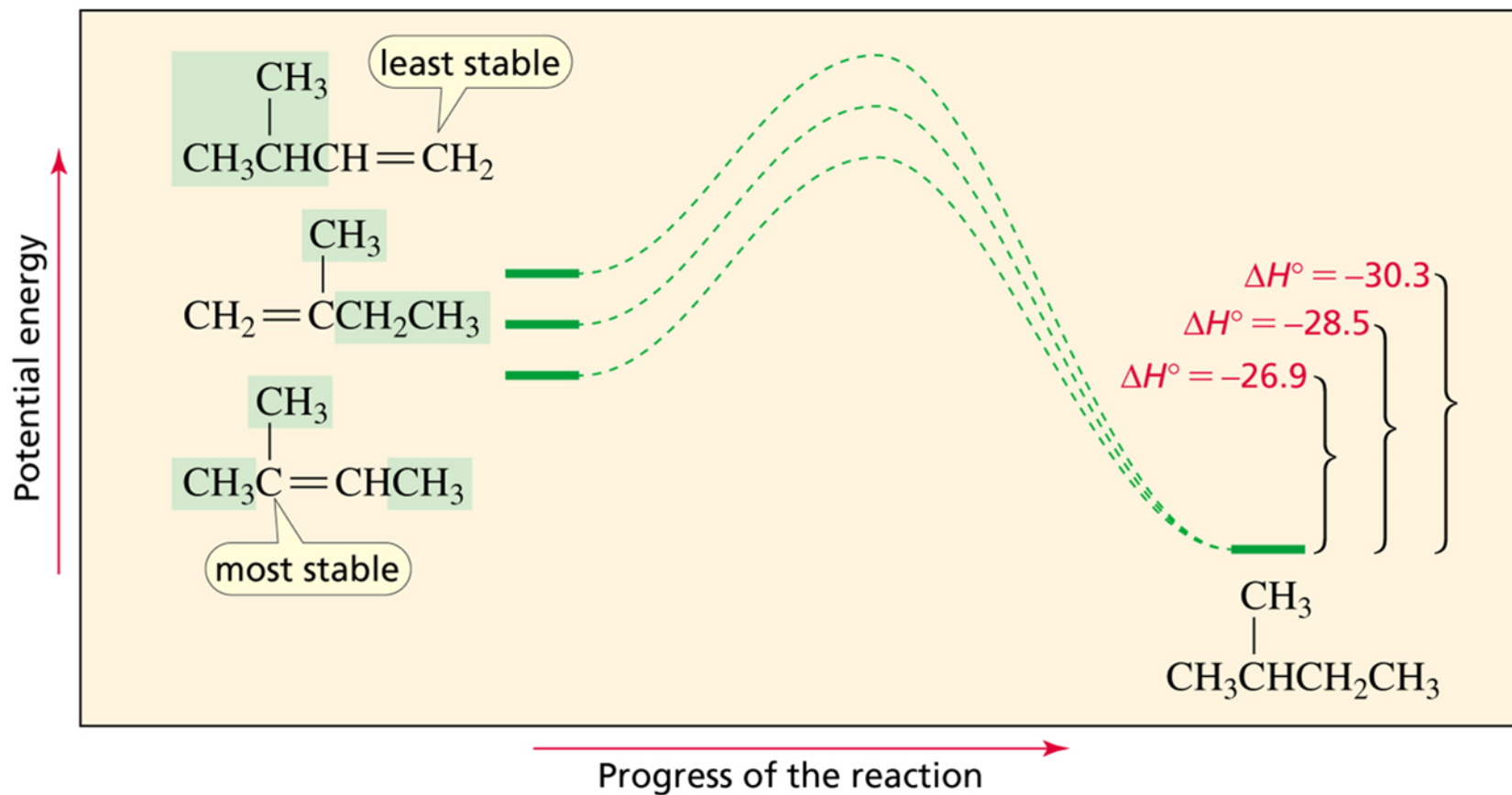
the more alkyl groups bonded to the *sp²* carbons, the more stable the alkene
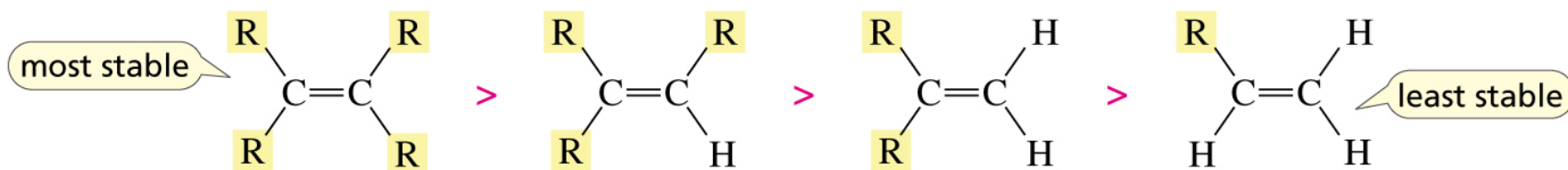
A Trans Alkene is More Stable Than a Cis Alkene

Reaction	Enthalpy of reaction (kcal/mol)	Heat of hydrogenation
trans-2-butene + H_2 →(Pd/C) $CH_3CH_2CH_2CH_3$	−27.6	27.6 kcal/mol
cis-2-butene + H_2 →(Pd/C) $CH_3CH_2CH_2CH_3$	−28.6	28.6 kcal/mol

the cis isomer has steric strain due to electron cloud overlap

the trans isomer does not have steric strain
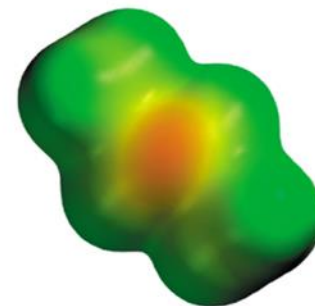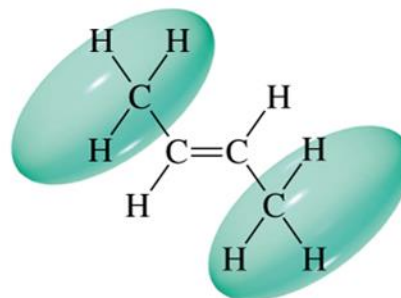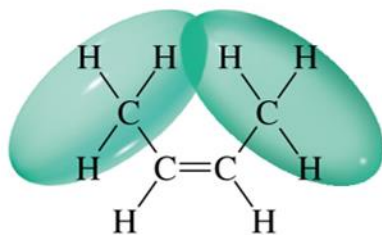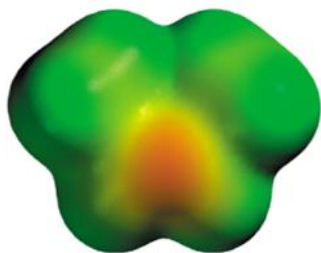
The Relative Stabilities of Alkenes (2 of 2)

the relative stabilities of alkenes that have two alkyl groups bonded to the sp^2 carbons

alkyl groups are on *opposite sides* of the double bond > alkyl groups are on the *same side* of the double bond ~ alkyl groups are on the same sp^2 carbon
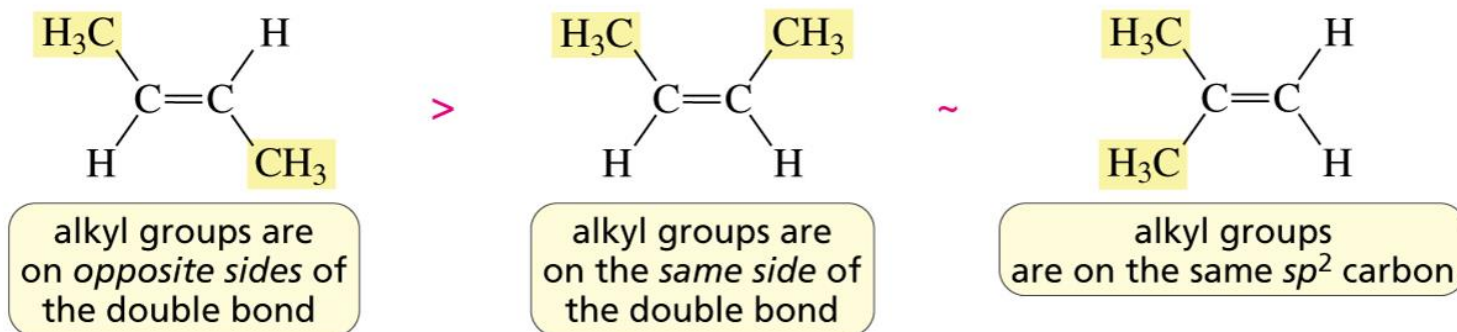
Kinetic and Thermodynamic Stability

Kinetic Stability is indicated by $\Delta G^{\neq}$

If $\Delta G^{\neq}$ is large, the reactant is kinetically stable because it reacts slowly.

If $\Delta G^{\neq}$ is small, the reactant is kinetically unstable because it reacts rapidly.

Thermodynamic Stability is indicated by $\Delta G°$

If $\Delta G° < 0$ the product is thermodynamically stable compared to the reactant.

If $\Delta G° > 0$ the product is thermodynamically unstable compared to the reactant.

Kinetics: How fast is the product formed?

Rate of a reaction =

$$\left(\begin{array}{c}\textbf{number of collisions}\\\textbf{per unit of time}\end{array}\right) \times \left(\begin{array}{c}\textbf{fraction with}\\\textbf{sufficient energy}\end{array}\right) \times \left(\begin{array}{c}\textbf{fraction with}\\\textbf{proper orientation}\end{array}\right)$$

$$A \longrightarrow B$$

$$\text{rate} \propto [A]$$

$$A + B \longrightarrow C + D$$
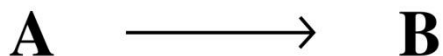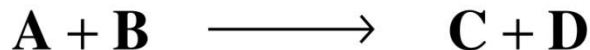
$$\text{rate} = k[A][B]$$

$$A + A \longrightarrow B$$
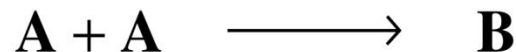
$$\text{rate} = k[A]^2$$

The rate-limiting step controls the overall rates of the reaction

$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$

$\Delta G^{\ddagger}$:
(free energy of transition state)- (free energy of reactants)

$\Delta H^{\ddagger}$:
(enthalpy of transition state) - (enthalpy of reactants)

$\Delta S^{\ddagger}$:
(entropy of transition state) - (entropy of reactants)

The free energy between the transition state and the reactants
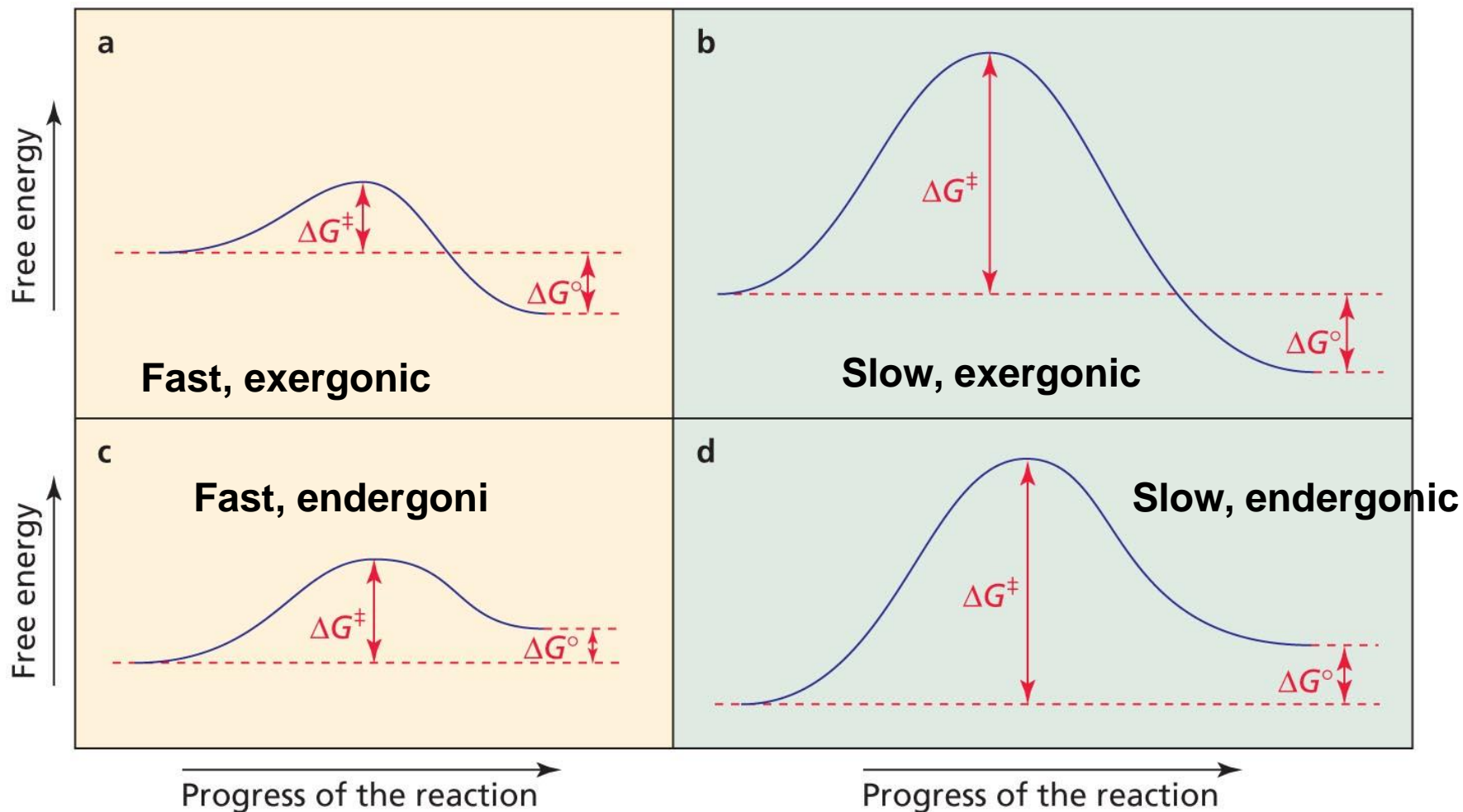
Rates and Rate Constants

First-order reaction

$$A \longrightarrow B$$

$$\text{rate} = k[A]$$

Units of first-order rate constant
k is time^{-1}

Units of the rate is M time^{-1}

Second-order reaction

$$A + B \longrightarrow C + D$$

$$\text{rate} = k[A][B]$$

$$A + A \longrightarrow B$$

$$\text{rate} = k[A]^2$$

Units of second-order rate constant
k is M^{-1}time^{-1}

Rate constants are **INDEPENDANT** of concentration. Rate is **DEPENDENT** on [ ].
Rate constants are quoted <u>at a given temperature</u>. Increasing temp. will increase the rate of reaction, and the rate constant. ($k \sim$ doubles for each 10°C rise in temp.)

65

Addition of HBr to Ethylene
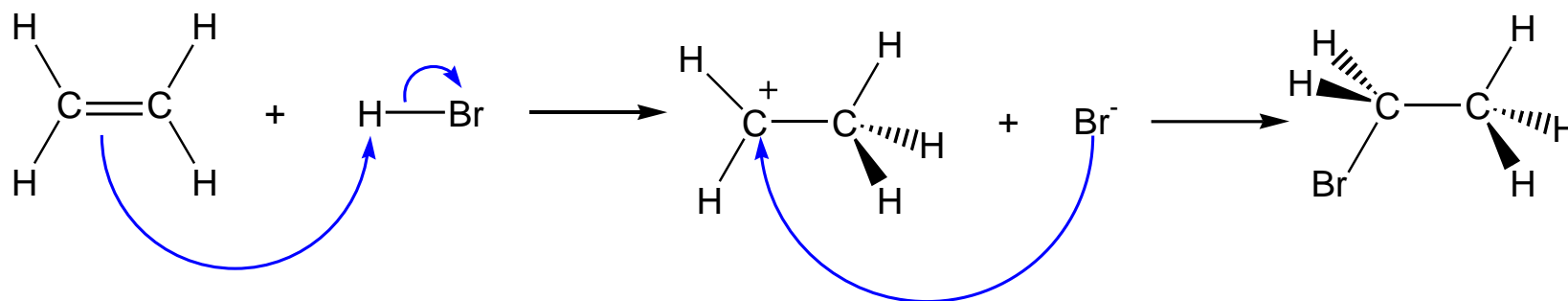
**carbocation
intermediate**

What about energy?

Reaction Coordinate Diagram for Each Step of the Addition of HBr to 2-Butene
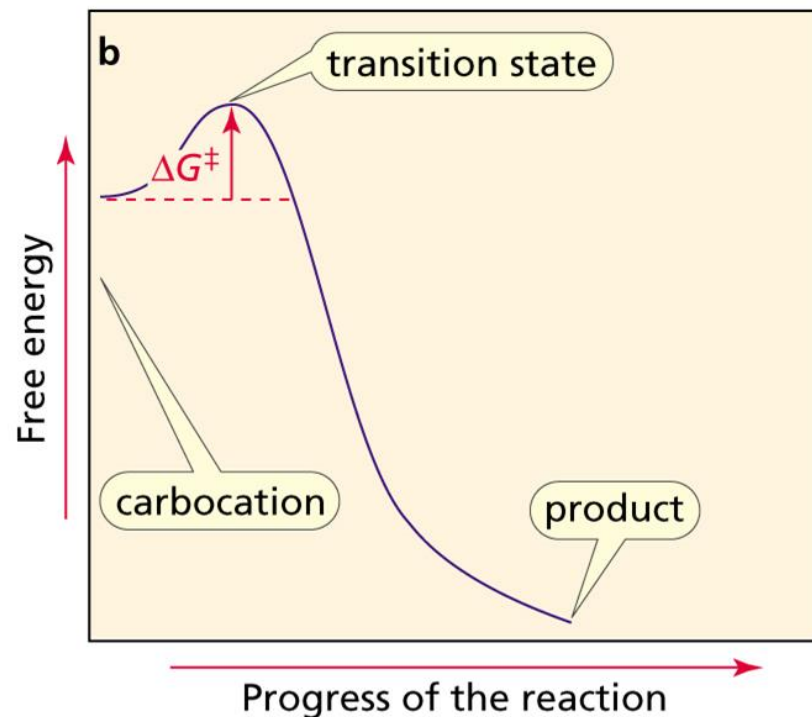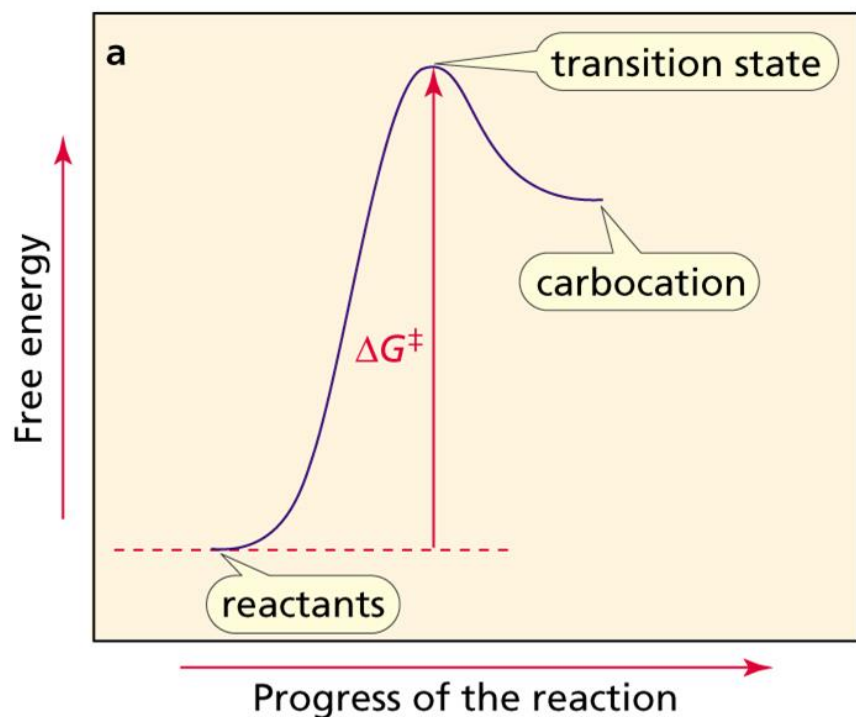
First transition state

Carbocation intermediate

Second transition state

$\Delta G_2^{\ddagger}$

$\overset{+}{CH_3CH_2}\ Br^-$

$\Delta G_1^{\ddagger}$

Energy

$H_2C{=}CH_2 + HBr$

$\Delta G°$

CH_3CH_2Br

Reaction progress $\longrightarrow$

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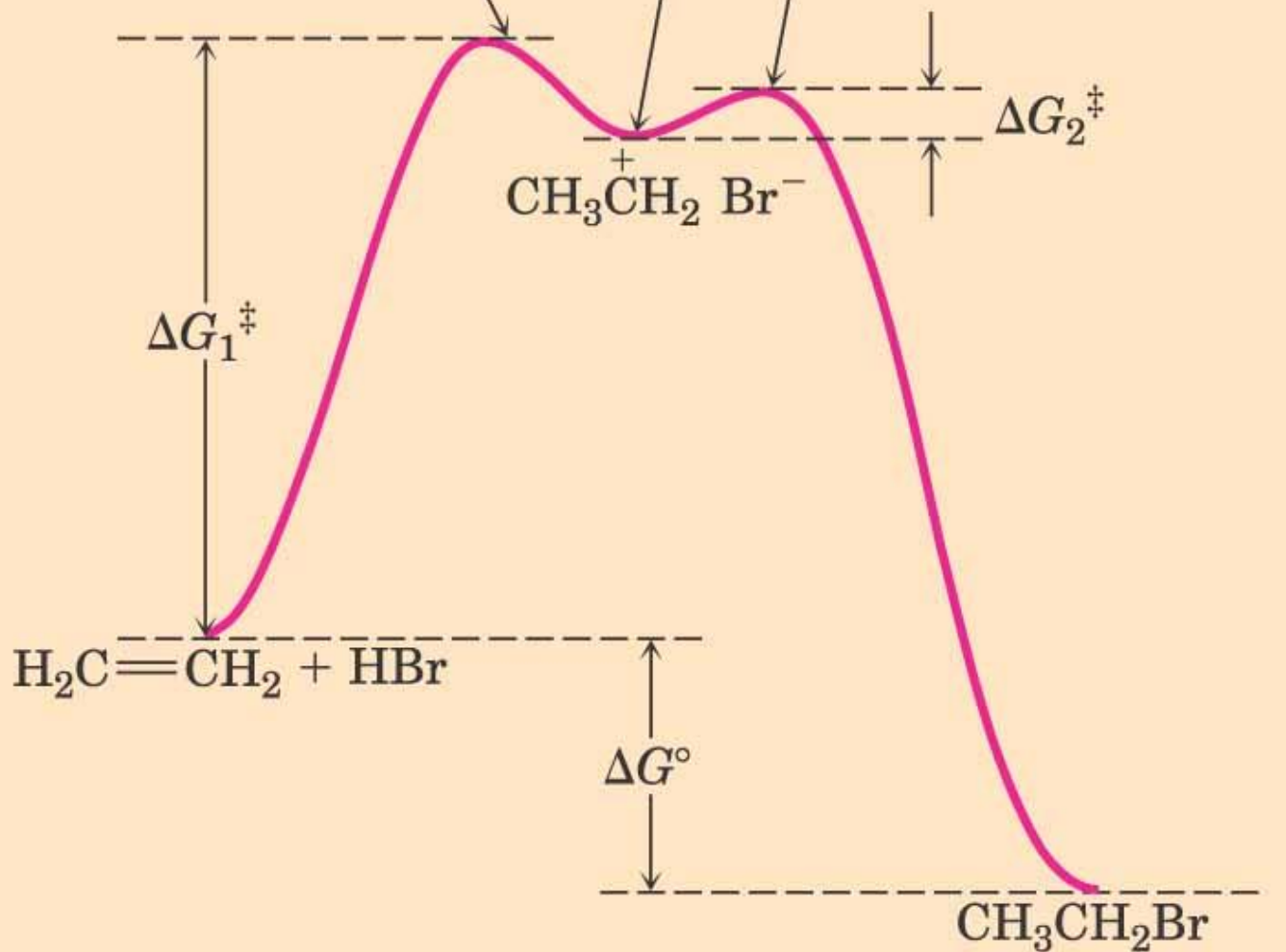
The Structure of the Transition State
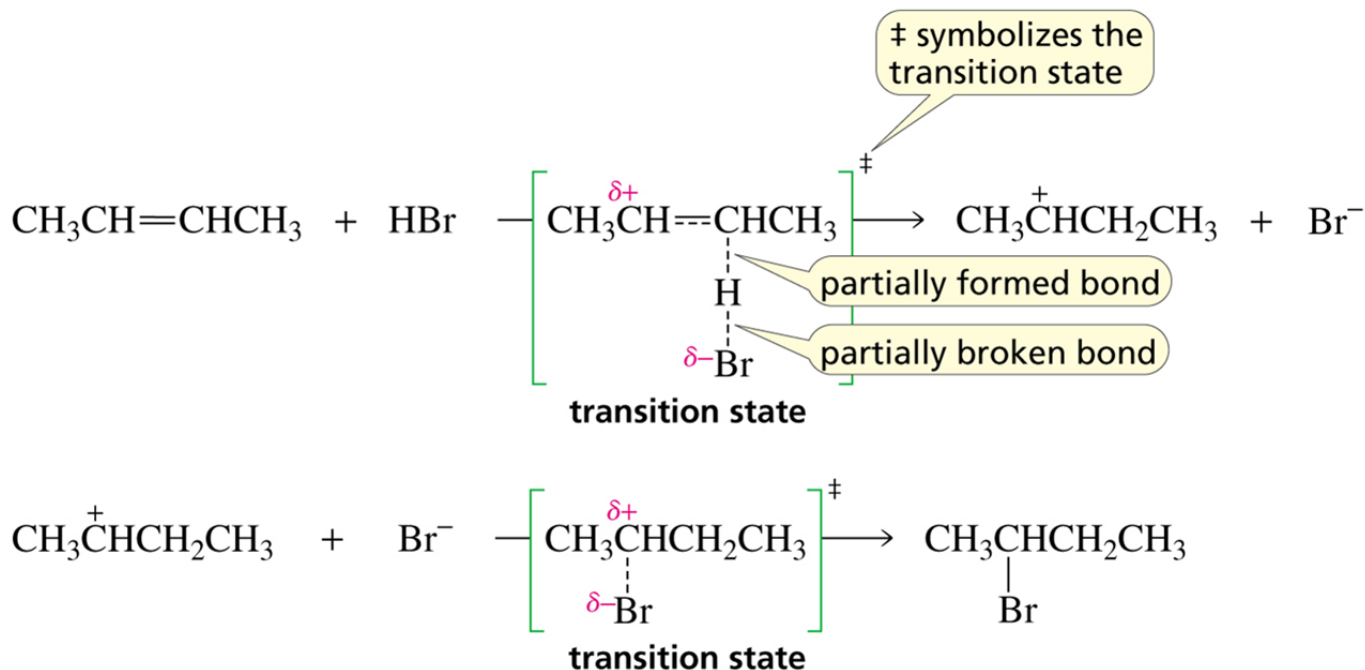
Transition states have partially formed bonds.

----- represents bonds breaking/forming

‡ (double dagger) indicates a **transition state**

Formation of C$^+$ via T.S.1 represents the **FIRST** mechanistic step

T.S.1 can turn into an **intermediate** species

Carbocation contains **completely formed and broken bonds**

C$^+$ breaks octet rule: Br$^-$ donates an electron pair and re-establishes octet around carbon (forms second transition state-T.S.2)

Formation of bromoethane via T.S.2 represents the **SECOND** mechanistic step

Mechanism proceeds in **TWO** steps, via **TWO** transition states and **ONE** intermediate

HBr addition energy diagram - summary

1) **Transition states** occupy **energy maxima**

2) **C$^+$** resides in an **energy well** (local energy minimum)

3) **Product** is **lower** in energy than reactants ($\Delta G° =$ negative, reaction thermodynamically favourable)

4) Reaction **rate** governed by **activation energy** associated with T.S.1 formation ($\Delta G_1^{\ddagger}$)

5) First reaction step (formation of **C$^+$**) is **RELATIVELY** slow and is **RATE DETERMINING** (slower than second reaction step)

• First step has a greater activation energy associated with it ($\Delta G_1^{\ddagger} > \Delta G_2^{\ddagger}$).… **WHY?**

A Catalyst

A catalyst provides a pathway for a reaction with a lower energy barrier.

A catalyst does not change the energy of the starting point (the reactants) or the energy of the end point (the products).

Key Concepts

- **Alkenes:** hydrocarbons containing double bonds. Suffix: "ene".
- **Degree of unsaturation**: number of pi bonds and rings
- **Cis/trans isomers**: geometrical isomers found in alkenes due to restriction of rotation around the double bond. Cis isomer has both H atoms on same side of double bond; trans isomer has H atoms on opposite sides of the double bond.
- *Z* and *E* **isomers** used in naming if more than two groups on the double bonded carbons. Z isomer has high priority groups on same side of double bond; E isomer has high priority groups on opposite sides of the double bond.
- **Cahn-Ingold-Prelog rules** used to assign priority. Higher atomic number = higher priority.
- Chemical reactions occur between a **nucleophile** (electron rich species) and **electrophile** (electron poor species).
- Alkenes are nucleophiles due to electron-rich pi bond, so they donate electrons in reactions.
- **Mechanisms** describe the step by step process of converting reactants to products and direction of electron flow is shown by using **curved arrows**.
- **Thermodynamics**: reaction at equilibrium; **Kinetics**: refers to rate of reaction. Energy changes of reaction shown by reaction coordinate diagram. **Transition state**: species at the energy maxima, very unstable, partially formed bonds. **Intermediate**: product of one step in reaction and reactant in next step, fully formed bonds.
- **Rate determining step**: step of reaction with highest energy of activation and T.S. at highest energy maxima.
- **Exergonic reaction**: Gibbs free energy is –ive; products more stable than reactants
- **Endergonic reaction**: Gibbs free energy is +ive; products less stable than reactants

Key Concepts

- $\Delta G° = \Delta H° - T\Delta S°$; $\Delta H°$ = change in enthalpy; $\Delta S°$ = change in entropy
- $\Delta G° = -RTlnK_{eq}$; identifies **thermodynamic stability**
- **Exothermic reaction**: enthalpy change is –ive; **Endothermic reaction**: enthalpy chang is +ive
- $\Delta G^{\ddagger}$ **:** Free energy of activation: energy barrier of reaction. Smaller value = faster reaction. Used to identify **kinetic stability.**
- **Rate of reaction**: dependent on rate constant, temperature and concentration of reactants.
- **Rate constant**: indicates how difficult it is to reach T.S.
- **First order reaction**: dependent on concentration of ONE reactant
- **Second order reaction**: dependent on concentration of TWO reactants