

3. The Nature of Organic Reactions: Alkenes

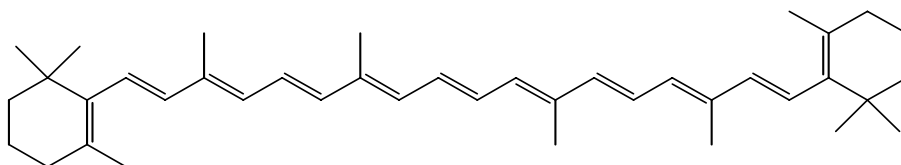
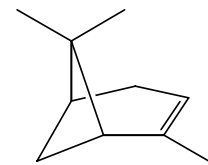
Alkenes (olefins): hydrocarbons that contain a carbon-carbon double bond, C=C.

Abundant in nature, playing important **biological roles**.

Ethylene (CH₂=CH₂) – a plant hormone that induces ripening in fruit.

α-Pinene – the major constituent of turpentine.

β-Carotene, an orange pigment responsible for the color of carrots, contains 11 double bonds and is a valuable dietary source of **vitamin A**.



[chapter_03_01.ppt](#)

3.1 Naming Alkenes

Unsaturation – alkenes have **fewer hydrogens** per carbon than related alkanes

Alkenes are named with the suffix **–ene** used in place of **–ane**.

Step 1. Name the parent hydrocarbon

Find the longest carbon chain that contains the double bond, and name the compound using the suffix **–ene**.

Step 2. Number the carbon atoms in the chain

Begin numbering at the end nearer the double bond

Step 3. Write the full name

Number the substituents according to their positions in the chain, and list them alphabetically.

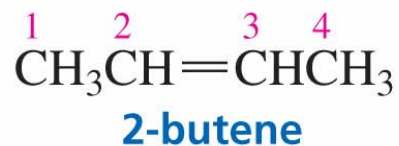
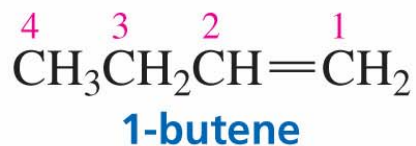
Indicate the position of the double bond by giving the number of the first alkene carbon and placing that number directly before the **–ene** suffix.

If more than one double bond is present, indicate the position of each and use one of the suffixes **–diene**, **–trene**, and so on.

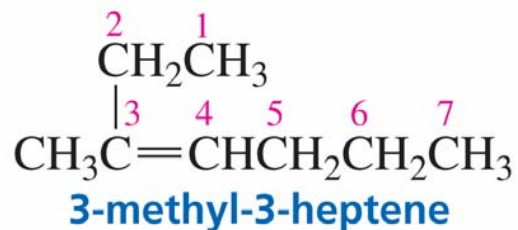
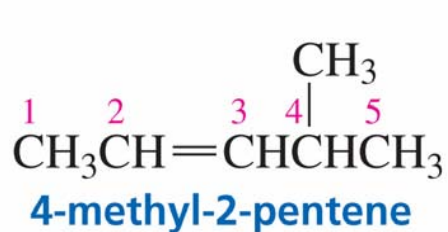
Cycloalkene

The double bond in cycloalkene is numbered as C1 and C2, and the first substituent has as low a number as possible.

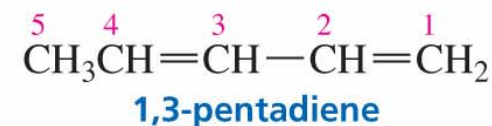
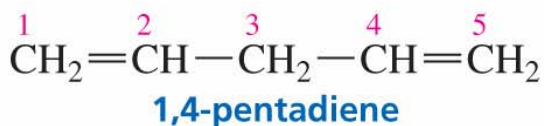
It is not necessary to specify the position of the double bond in the name



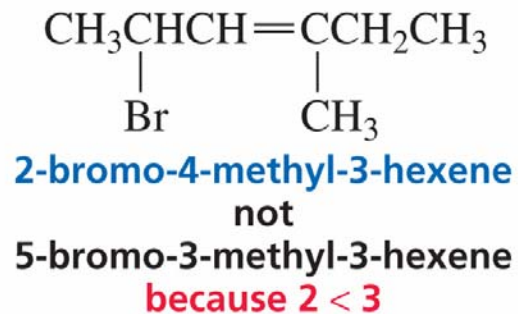
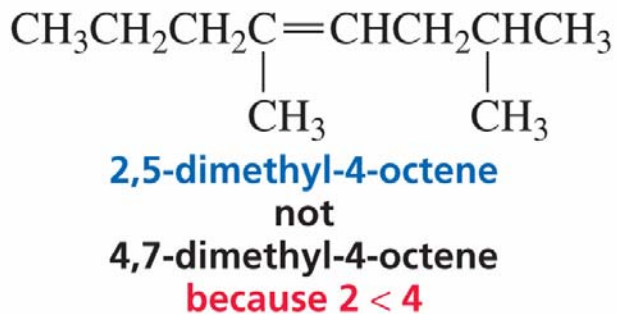
Copyright © 2006 Pearson Education, Inc.



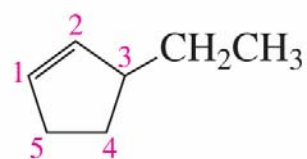
Copyright © 2006 Pearson Education, Inc.



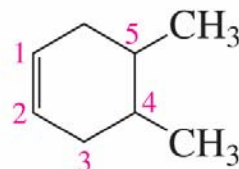
Copyright © 2006 Pearson Education, Inc.



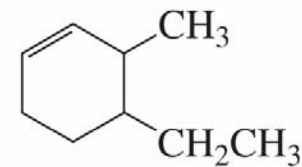
Copyright © 2006 Pearson Education, Inc.



3-ethylcyclopentene



4,5-dimethylcyclohexene



4-ethyl-3-methylcyclohexene

Copyright © 2006 Pearson Education, Inc.

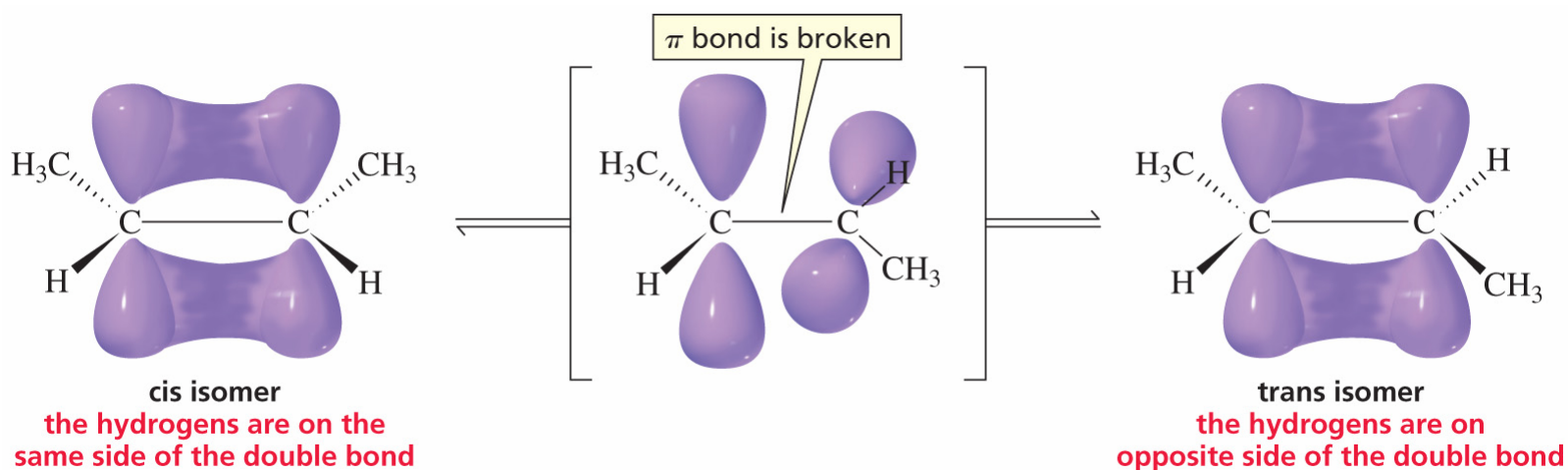
3.2 Electronic Structure of Alkenes

Two sp^2 hybridized carbon atoms form a σ bond by head-on overlap and a π bond by sideways overlap of **unhybridized p orbitals**.

Rotation around a double bond.

The energy barrier to rotation around a double bond must be at least as great as the strength of the π bond itself, estimated to be **268 kJ/mol** (64 kcal/mol).

* Rotation barrier for a single bond is only about **12 kJ/mol**.



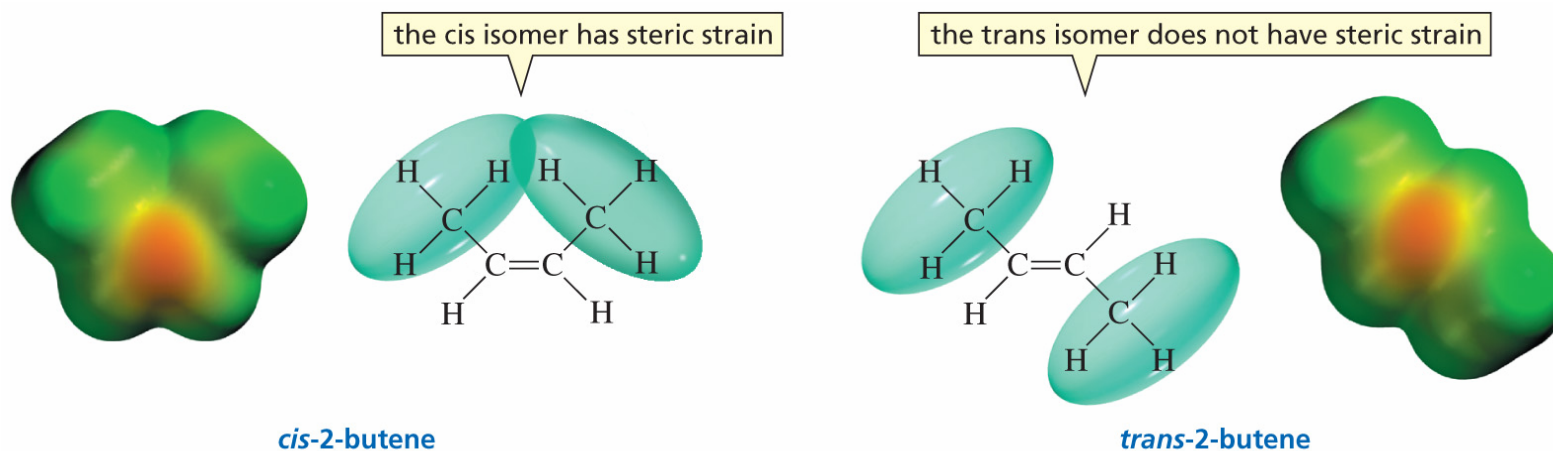
Copyright © 2006 Pearson Education, Inc.

3.3 Cis-Trans Isomers of Alkenes

Cis-Trans Isomerism: the chemical consequence of the lack of rotation around carbon-carbon double bonds.

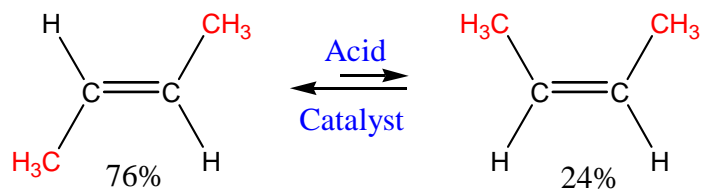
But-2-ene (or 2-butene) isomers

Because bond rotation can not occur at room temperature, the two but-2-ene isomers can not spontaneously interconvert and are different chemical compounds – *cis*-2-butene (or *cis*-but-2-ene) and *trans*-2-butene (or *trans*-but-2-ene).



Copyright © 2006 Pearson Education, Inc.

Interconversion of *cis* and *trans* alkenes with a strong acid catalyst or light



3.4 Sequence Rules: The E, Z Designation

General method of naming **tri-substituted** and **tetra-substituted** double bonds

E, Z system

Using **sequence rules** to assign **priorities** to the substituent groups on each of the double-bond carbons.

E (entgegen, opposite): if the higher-priority groups on each carbon are on opposite sides of the double bond.

Z (zusammen, together): if the higher-priority groups are on the same sides.



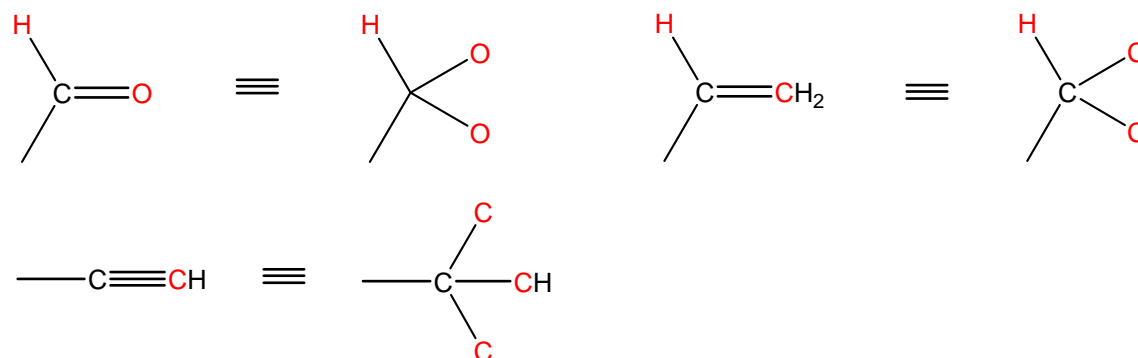
Copyright © 2006 Pearson Education, Inc.

The sequence rules: Cahn-Ingold-Prelog rules

Rule 1. Taking the double-bond carbons separately, look at the atoms directly attached to each carbon and rank them according to atomic number.

Rule 2. If a decision can't be reached by ranking the first atoms in the substituents, look at the second, third or fourth atoms away from the double-bond carbons until the first difference is found.

Rule 3. Multiple-bonded atoms are equivalent to the same number of single-bonded atoms.

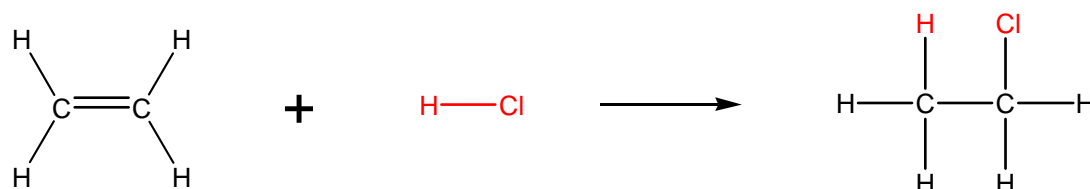


3.5 Kinds of Organic Reactions

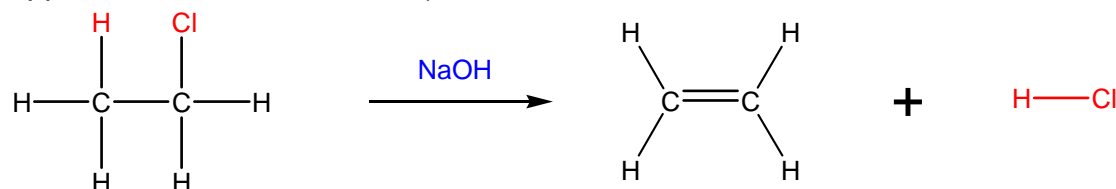
Organic chemical reactions can be organized by *what kinds* of reactions occur or by *how* reactions occur.

Four broad types of organic reaction

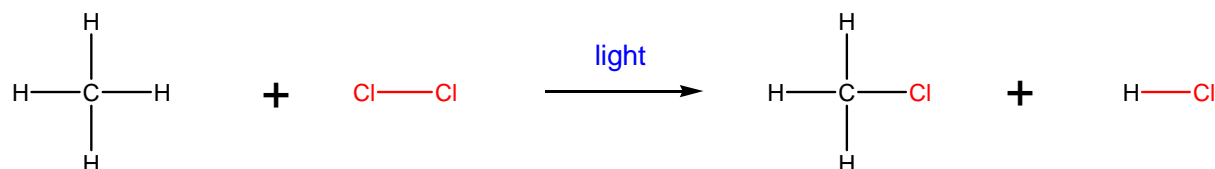
1. Addition reactions: when two reactants add together to form a single new product with no atoms “left over.”



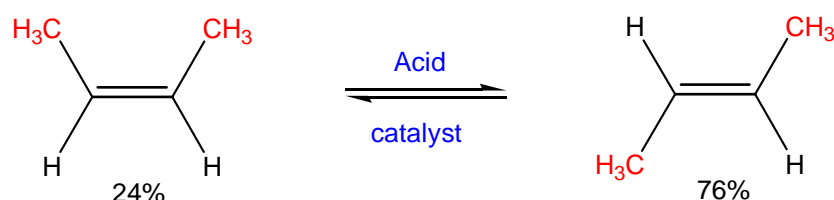
2. Elimination reactions: when a single reactant splits into two products (the opposite of addition reactions).



3. Substitution reactions: when two reactants exchange parts to give two new products.



4. Rearrangement reactions: when a single reactant undergoes a reorganization of bonds and atoms to yield a single isomeric product.



3.6 How Reactions Occur: Mechanisms

A reaction mechanism is detailed account of the motions of the valence electrons.

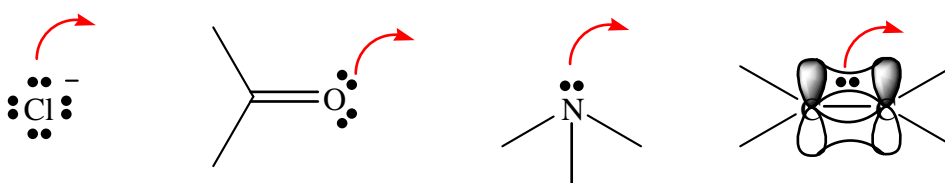
Mechanisms form the basis of a real chemical “intuition” and allow chemists to “dream” new reactions, reagents, and processes.

Mechanism is just a **model**, and represents our **best guess** as to what is occurring: No mechanism is known with 100% certainty.

A reaction mechanism is written as a series of chronologically ordered **steps**, with each step describing **the motion of one or more electrons**.

From a mechanism, we can tell when specific bonds are broken and when others are formed – **the timing of bond making and breaking**.

The electrons that initiate reactions are in accessible positions such as **π bonds** or **lone pairs**, not in the σ -bonds.



The electrons in lone pairs of ions or on oxygen or nitrogen as well as the π electrons of double bonds can initiate chemical reactions.

Terminologies in mechanism

► Based on the number of electrons that move

Polar reactions – two electrons move together when bonds are formed or broken.

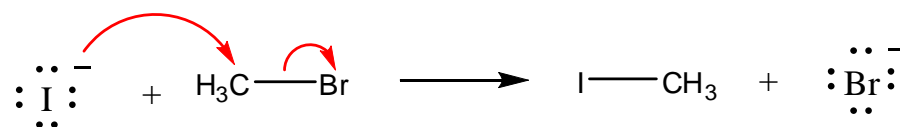
Radical reactions involve the movement of a lone electron.

Heterolytic (breaking) and Heterogenic (forming) – when the electrons are distributed unequally (electrons move in pairs): both electrons depart with a single atom or both are received from a single atom.

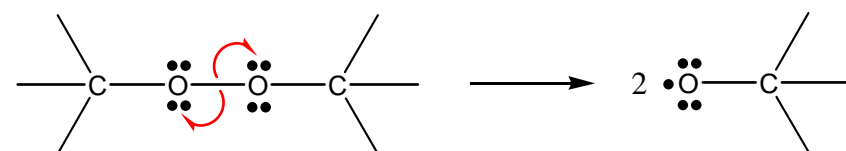
Homolytic (breaking) and Homogenic (forming) – when electrons are distributed evenly between atoms such as in radical processes.

(Examples)

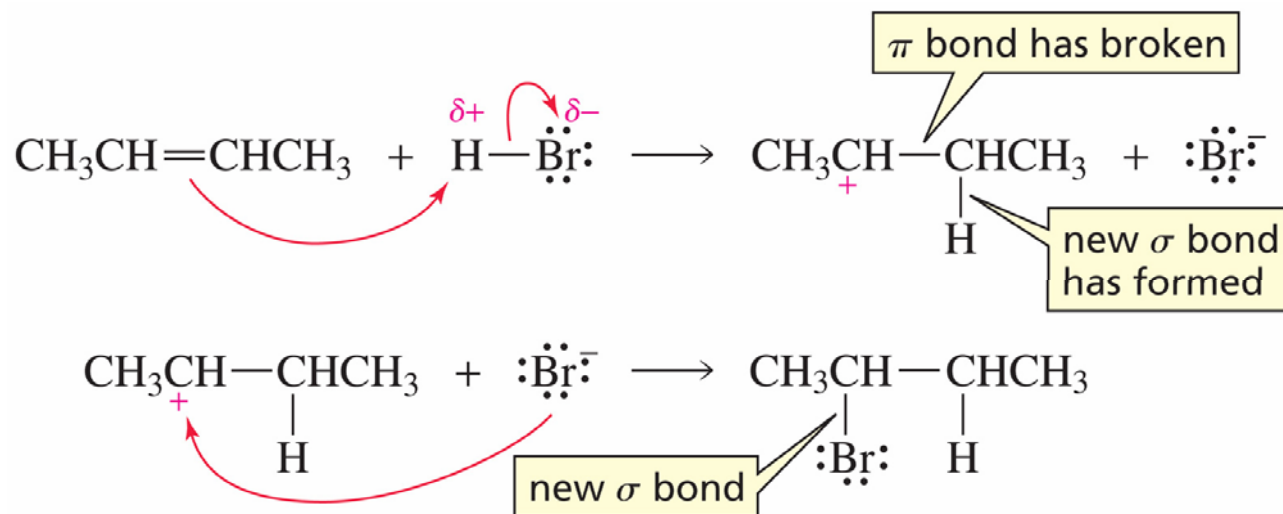
A polar substitution reaction: Heterolysis of the C-Br bond and **Heterogenesis** of the C-I bond.



A radical elimination reaction featuring **homolysis** of the O-O bond.



The mechanism of the electrophilic addition reaction of alkene with HBr



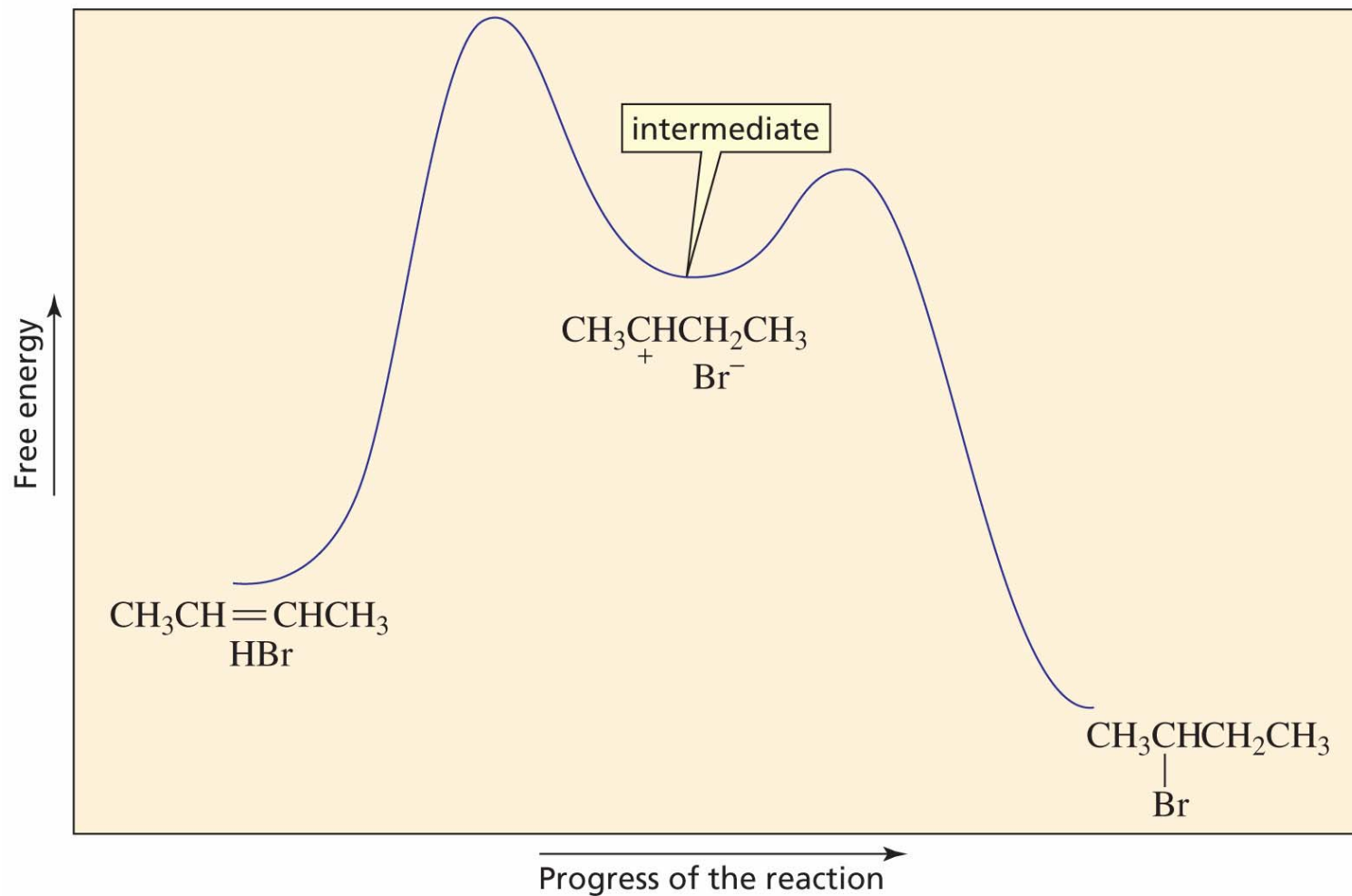
Copyright © 2006 Pearson Prentice Hall, Inc.

Step 1. Two electrons from the alkene π bond move to form a new σ bond between the H^+ and one of the alkene carbon atoms. The other alkene carbon atom, having lost its share of the π electrons, is now left with a vacant p orbital and only six valence electrons. This carbon atom carries a positive charge and is called a **carbocation (intermediate)**.

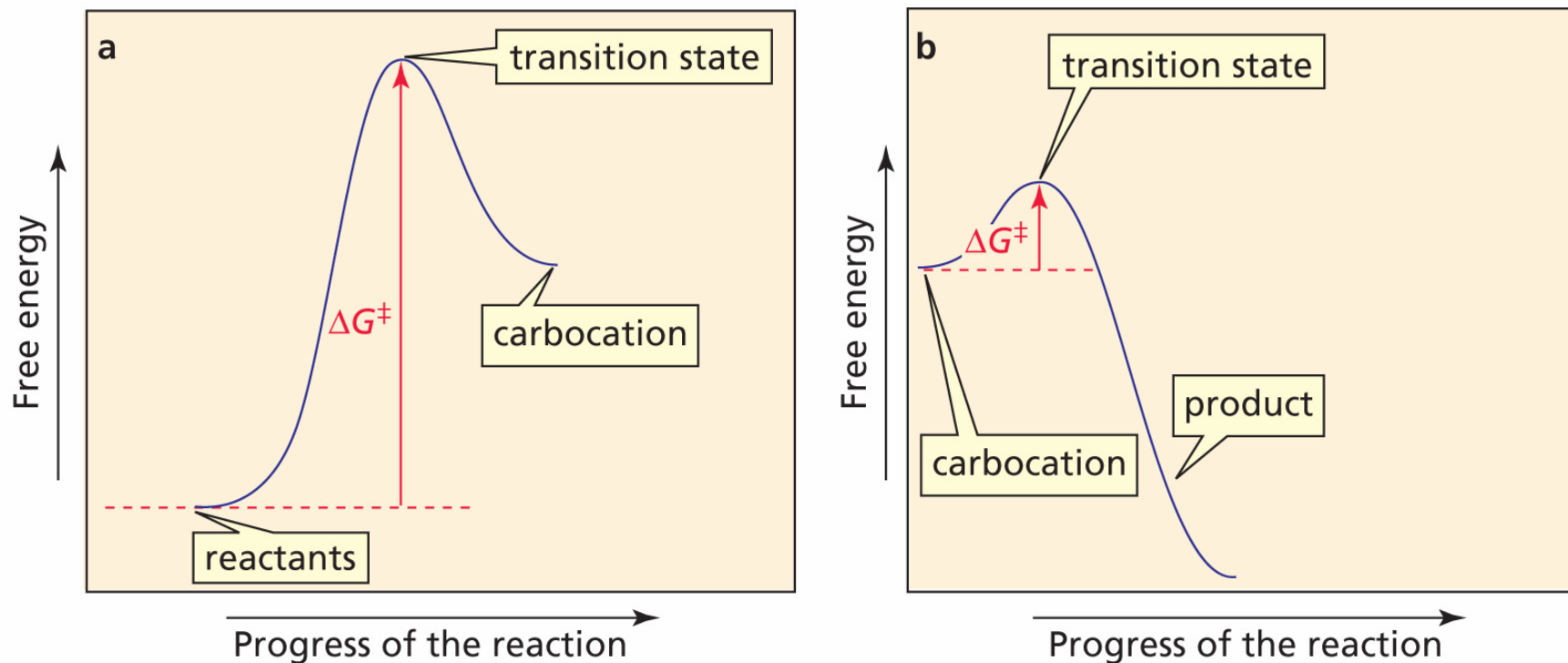
Step 2. The nucleophilic bromide ion donates an electron pair to form a new σ bond with the carbocation to form a stable and neutral addition product.

3.9 Describing a Reaction: Reaction Energy Diagrams and Transition States

Reaction energy diagrams: depicting the energy changes that occur during a reaction (**vertical axis: the total energy of all reactants, horizontal axis: the progress of the reaction**).



Copyright © 2006 Pearson Education, Inc.



Copyright © 2006 Pearson Education, Inc.

Transition state: a structure of **maximum energy** in the step; can not be isolated or directly observed.

Activation energy (E_{act}): the energy difference between reactants and transition states; helps determine **the rate of a reaction**.

Most organic reactions have activation energies in the range 40 to 125 kJ/mol (10-30 kcal/mol). Reactions with activation energies less than 80 kJ/mol take place spontaneously at or below room temperature.

Intermediate: a structure of **minimum energy** in the step (**carbocation intermediate**); can not be isolated, but can be observed in some cases by modern analytical equipment.

3.10 Describing a Reaction: Energetics and Catalysis

When will reaction occur?

Reactions where the product energy is less than the reactant energy proceed spontaneously.

How fast will reaction occur?

The rate of a reaction depends on its activation energy.

The higher the activation energy, the slower the reaction will proceed.

How can we speed up a reaction?

1. Giving the reactants more energy – increasing the temperature.
2. Looking for another mechanism – Adding new species (**catalyst**) can sometimes provide a different mechanism with a different activation barrier.

Catalyst: a compound that changes the rate of a chemical reaction by providing a new mechanism.

Catalysts increase reaction rates by lowering the activation energy.

Catalyst is not consumed in the reaction.

e.g. acid (H^+), metals, and enzymes.