

Chapter 5

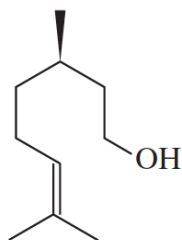


Alkenes Structure, Nomenclature, and an introduction to Reactivity • Thermodynamics and Kinetics

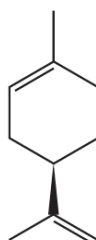
Paula Yurkanis Bruice
University of California,
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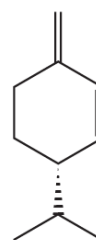
Alkenes



citronellol
in rose and
geranium oils



limonene
in lemon and
orange oils



β -phellandrene
oil of eucalyptus

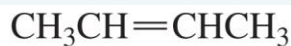
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Saturated and Unsaturated Hydrocarbons



an alkane

a saturated hydrocarbon



an alkene

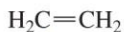
an unsaturated hydrocarbon

Saturated hydrocarbons have no double bonds.

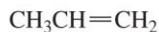
Unsaturated hydrocarbons have one or more double bonds.

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Nomenclature of Alkenes



systematic name: ethene
common name: ethylene



propene
propylene

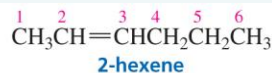
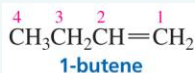


cyclopentene

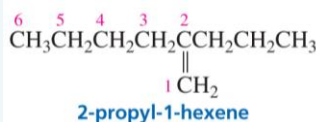


cyclohexene

Replace “ane” of alkane with “ene.”

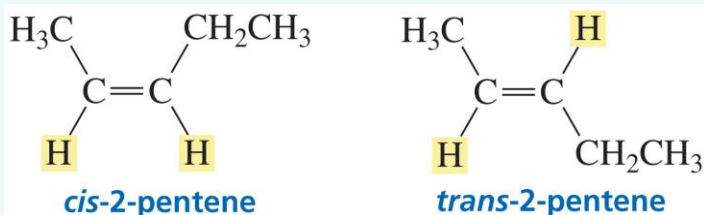


The functional group gets the lowest possible number.



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Stereoisomers of an Alkene are named using a *cis* or *trans* Prefix



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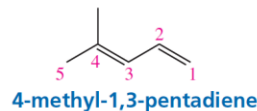
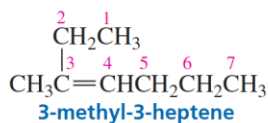
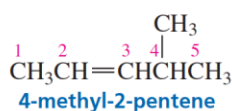
Nomenclature of Dienes



two double bonds = diene

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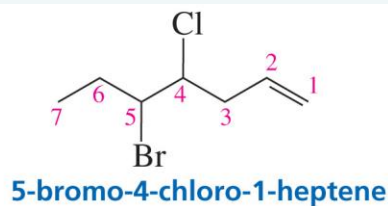
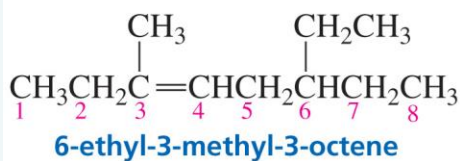
Nomenclature of Alkenes



Number in the direction so that the functional group gets the lowest number.

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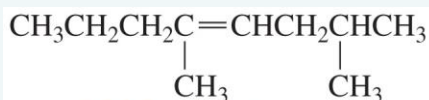
Nomenclature of Alkenes



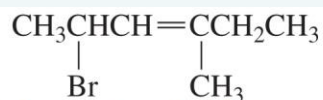
Substituents are stated in alphabetical order.

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Nomenclature of Alkenes



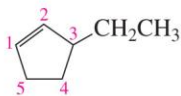
2,5-dimethyl-4-octene
not
4,7-dimethyl-4-octene
because $2 < 4$



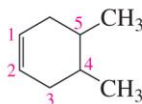
2-bromo-4-methyl-3-hexene
not
5-bromo-3-methyl-3-hexene
because $2 < 3$

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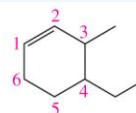
Nomenclature of Cyclic Alkenes



3-ethylcyclopentene



4,5-dimethylcyclohexene

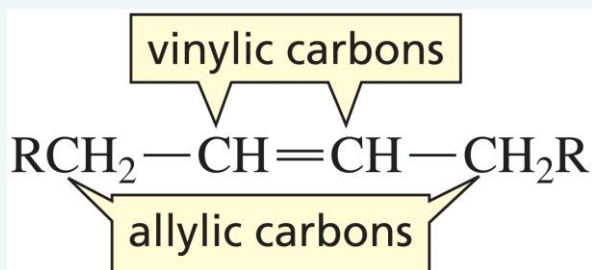


4-ethyl-3-methylcyclohexene

A number is not needed to denote the position of the functional group; **it is always between C1 and C2.**

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Vinylic and Allylic Carbons

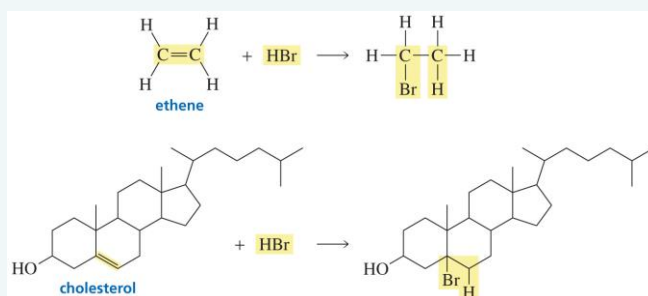


vinylic carbon: the sp^2 carbon of an alkene

allylic carbon: a carbon adjacent to a vinylic carbon

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Reactions of Organic Compounds

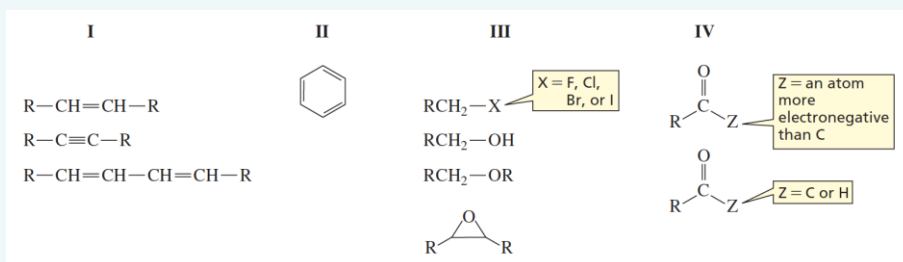


Organic compounds can be divided into **families**.

All members of a family react in the **same way**. The **family** a compound belongs to depends on its **functional group**.

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Each family can be put in one of four Groups

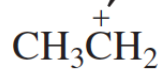


The families in a group react in similar ways.

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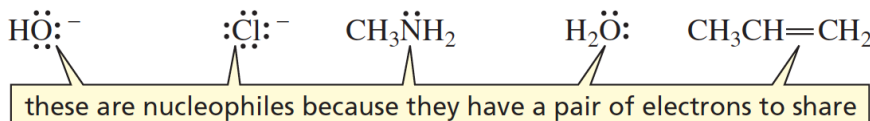
Electrophiles

these are electrophiles because they have a positive charge



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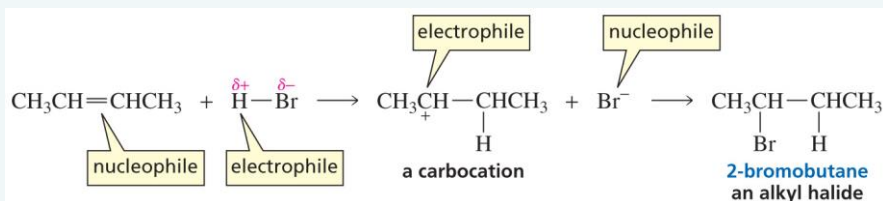
Nucleophiles



A nucleophile has
 a negative charge
 a lone pair
 a double bond

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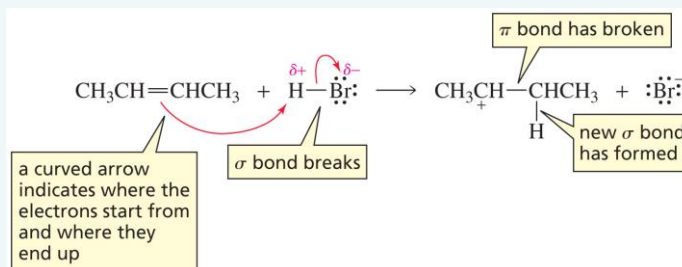
A Nucleophile reacts with an Electrophile



Your first organic reaction is a two-step reaction.

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Curved Arrows



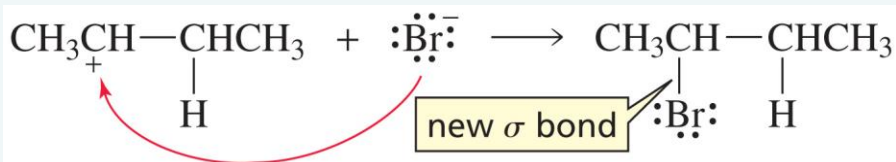
first step of the reaction

Curved arrows are used to show the **mechanism of a reaction**.

The **mechanism of a reaction** is the step-by-step description of the process by which reactants are converted into products.

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Curved Arrows

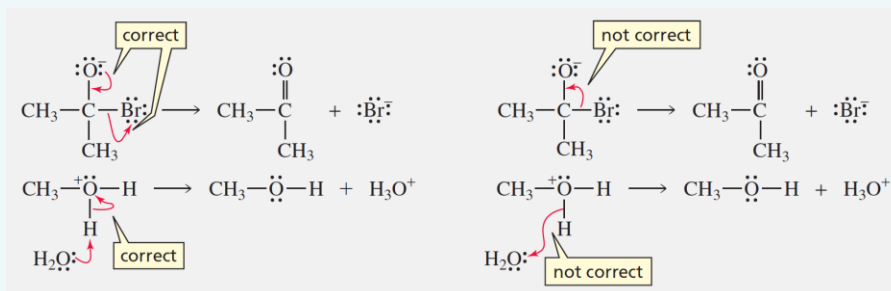


second step of the reaction

The curved arrow shows where the electrons **start from** and where they **end up**.

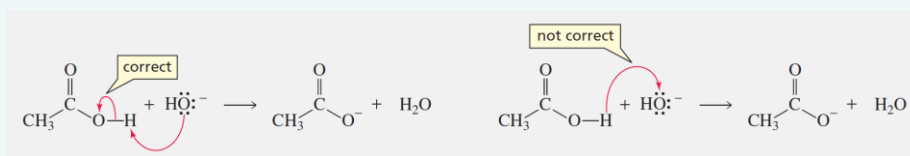
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How to draw Curved Arrows



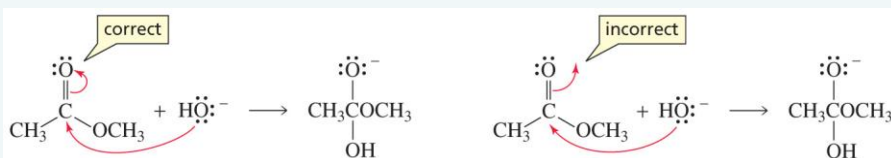
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How to draw Curved Arrows



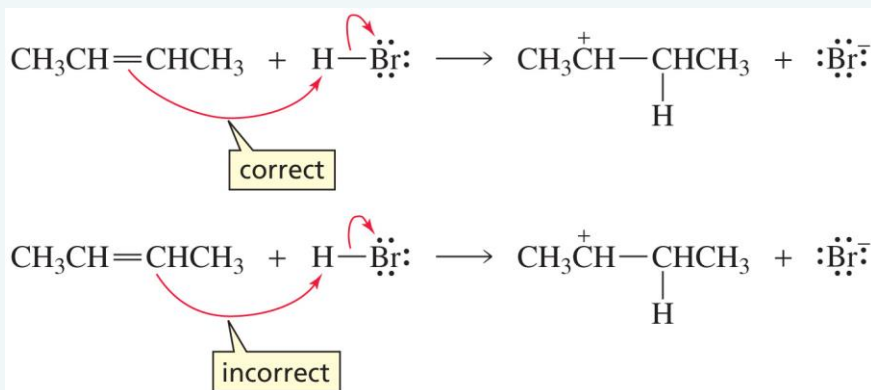
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How to draw Curved Arrows



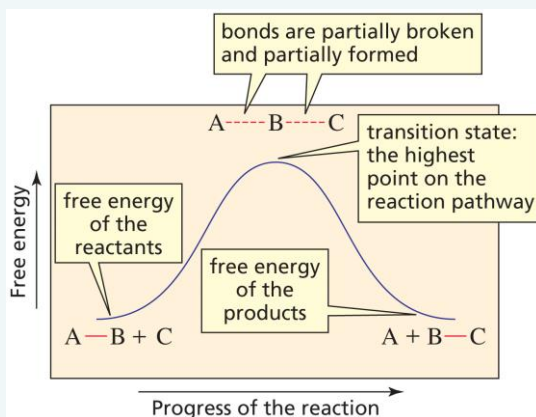
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How to draw Curved Arrows



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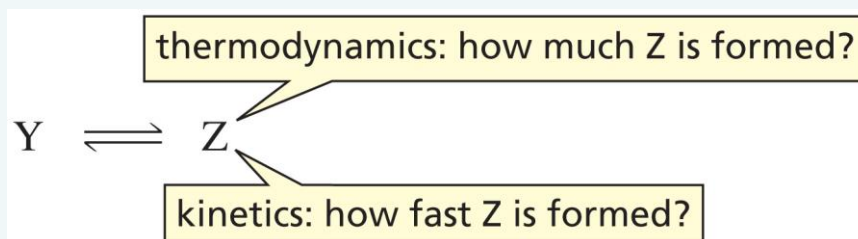
A Reaction Coordinate Diagram



A **reaction coordinate diagram** shows the **energy changes** that take place in each step of a reaction.

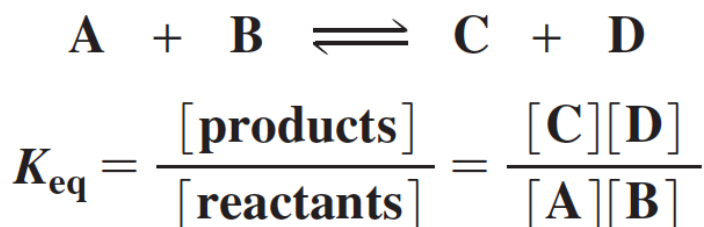
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Thermodynamics and Kinetics



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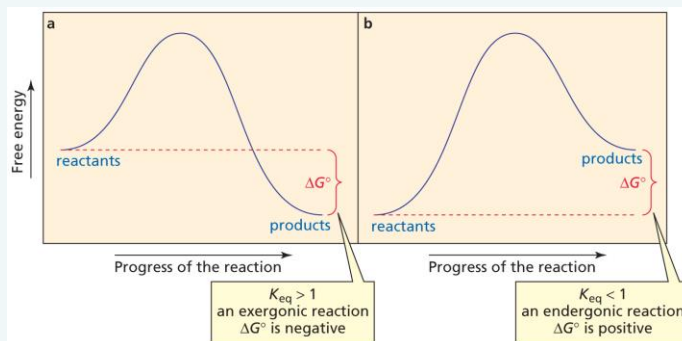
The Equilibrium Constant



The **equilibrium constant** gives the concentration of reactants and products at equilibrium.

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Exergonic and Endergonic Reactions



$$\Delta G^\circ = -RT \ln K_{\text{eq}}$$

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Gibbs Free-Energy Change (ΔG°)

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

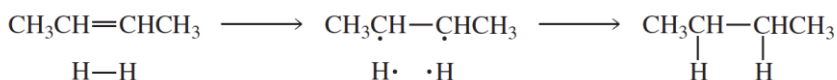
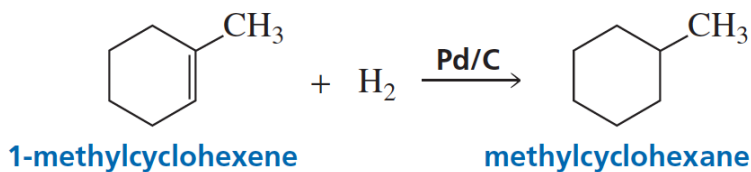
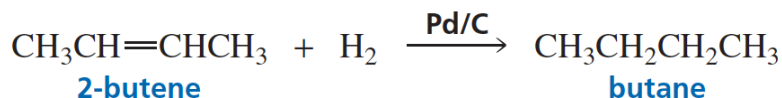
ΔG° = free energy of the products –
free energy of the reactants

ΔH° = heat required to break bonds –
heat released from forming bonds

ΔS° = freedom of motion of the products –
freedom of motion of the reactants

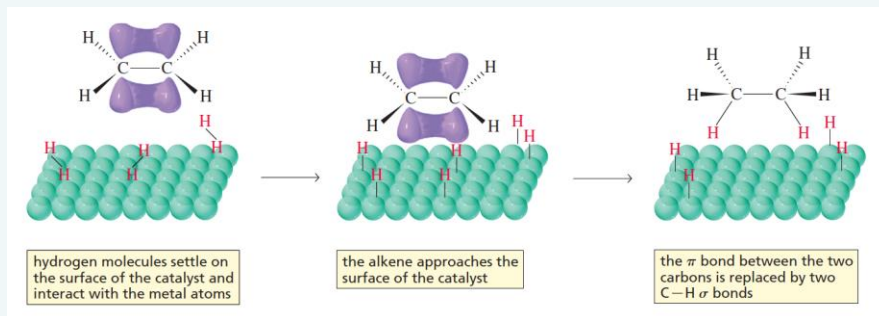
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A Reduction Reaction



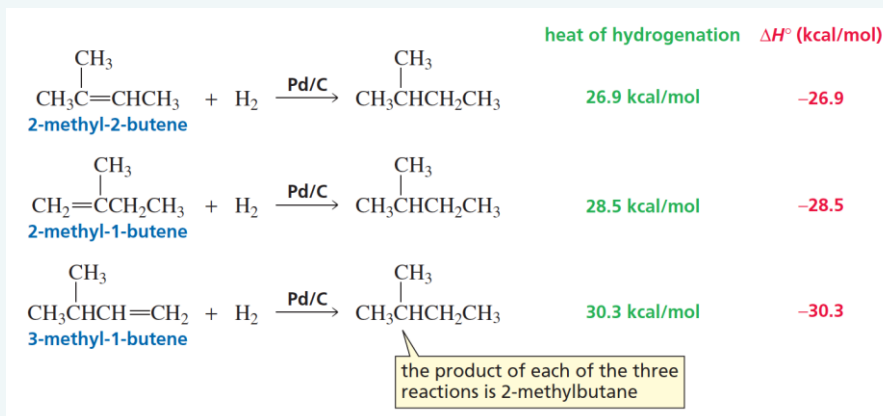
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Catalytic Hydrogenation



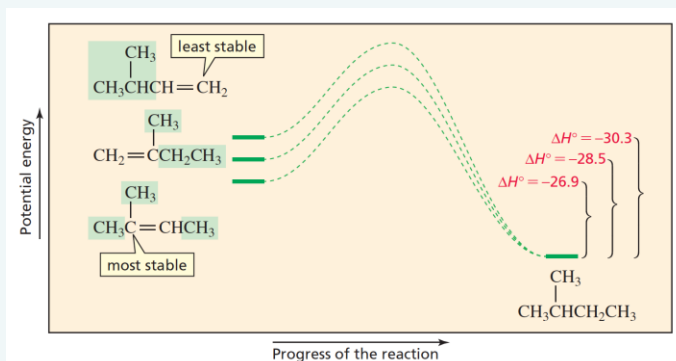
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Using ΔH° Values to determine the Relative Stabilities of Alkenes



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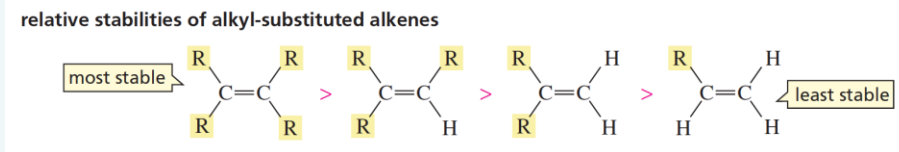
Using ΔH° Values to determine the Relative Stabilities of Alkenes



The relative energies (stabilities) of three alkenes that can be catalytically hydrogenated to 2-methylbutane. The most stable alkene has the smallest heat of hydrogenation. (Notice that when a reaction coordinate diagram shows ΔH° values, the y-axis is potential energy; when it shows ΔG° values, the y-axis is free energy [Figure 5.2].)

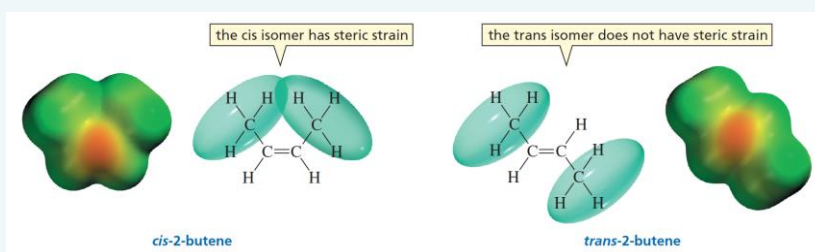
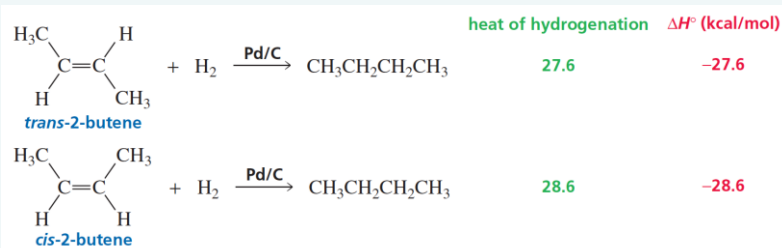
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Relative Stabilities of Alkenes



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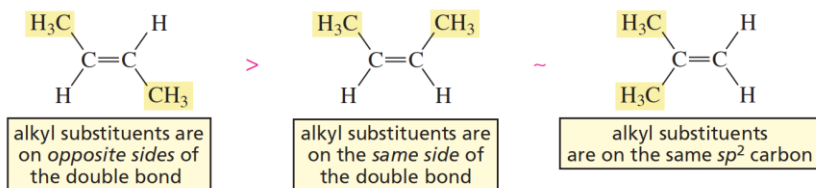
Relative Stabilities of Cis and Trans Alkenes



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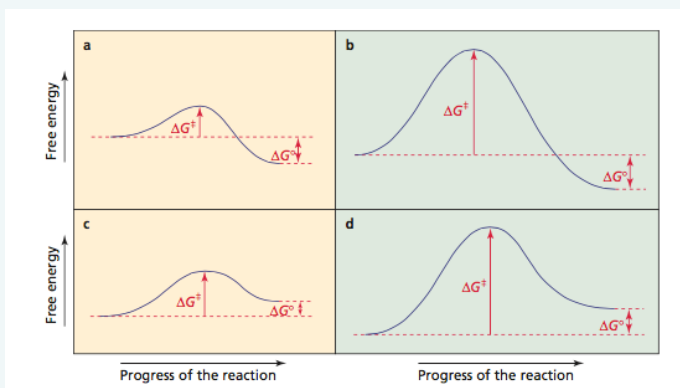
Relative Stabilities of Dialkyl-Substituted Alkenes

relative stabilities of dialkyl-substituted alkenes



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Kinetics: How fast is the product formed?



$\Delta G^\ddagger$ = free energy of the transition state - free energy of the reactants

The greater the energy barrier, the slower the reaction.

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Rate of a Reaction

$$\text{rate of a reaction} = \left(\frac{\text{number of collisions}}{\text{per unit of time}} \right) \times \left(\frac{\text{fraction with sufficient energy}}{\text{proper orientation}} \right) \times \left(\frac{\text{fraction with}}{\text{proper orientation}} \right)$$

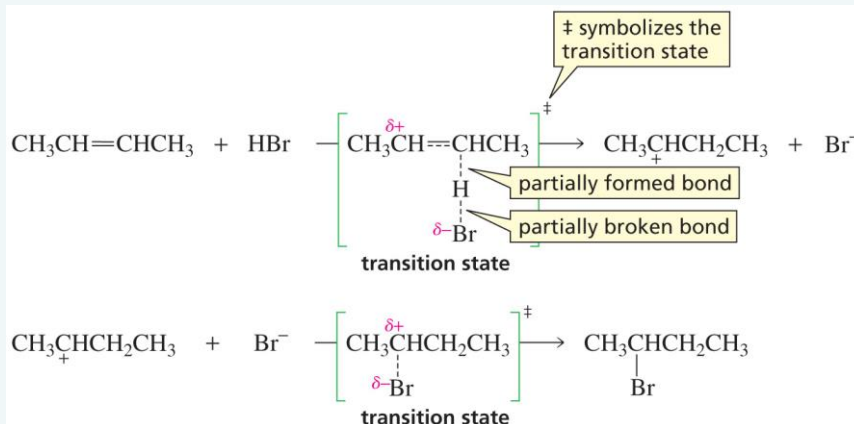
Increasing the **concentration** increases the rate.

Increasing the **temperature** increases the rate.

The rate can also be increased by a catalyst.

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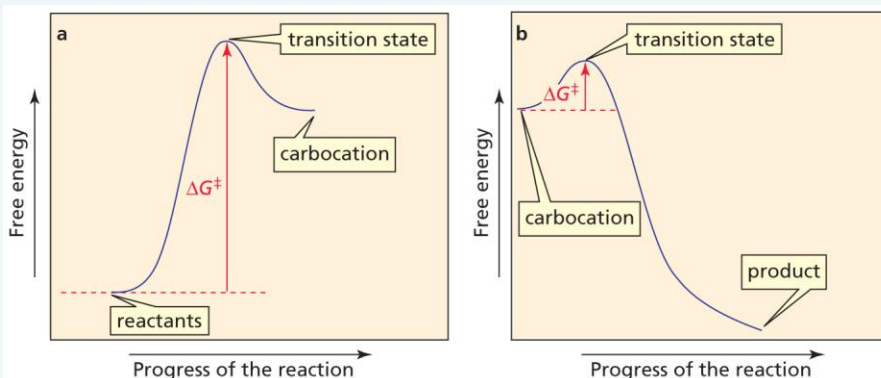
An Electrophilic Addition Reaction



Transition states have partially formed bonds.

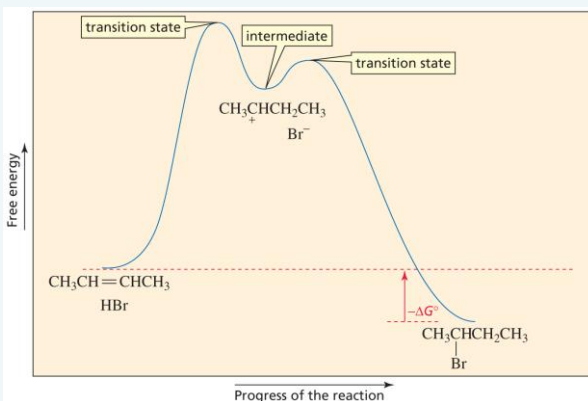
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Reaction Coordinate Diagram for each step of the addition of HBr to 2-Butene



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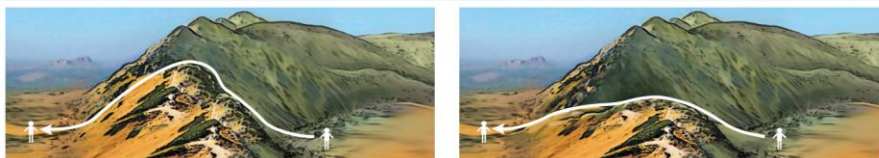
Reaction Coordinate Diagram for the addition of HBr to 2-Butene



The **rate-limiting step** of the reaction is the step that has its transition state at the **highest point** of the reaction coordinate diagram.

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A Catalyst



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

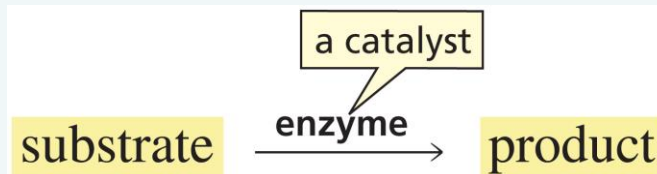
A catalyst **does not change** the energy of the starting point (the reactants) or the energy of the end point (the products).

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Enzymes

Most biological reactions require a catalyst.

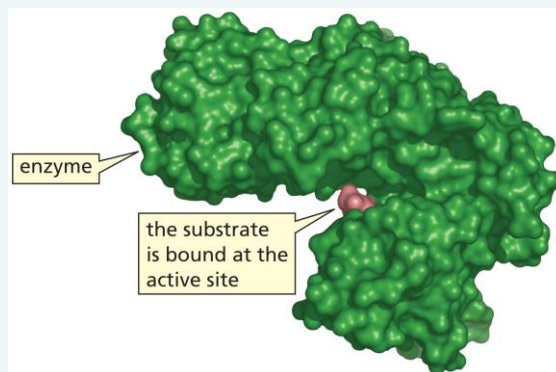
Most biological catalysts are proteins called **enzymes**.



The reactant of a biological reaction is called a **substrate**.

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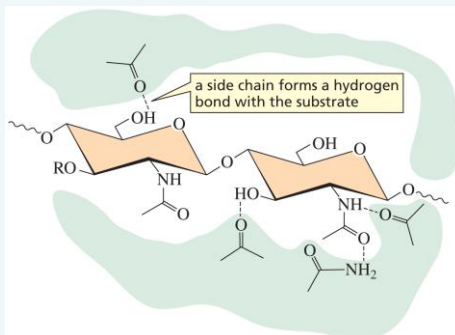
The Active Site of an Enzyme



An enzyme binds its **substrate** at its **active site**.

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Enzyme Side Chains that bind the Substrate

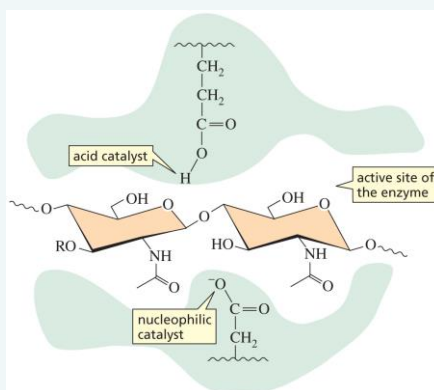


Some enzyme side chains **bind the substrate**.

Some enzyme side chains are **acids**, **bases**, and **nucleophiles** that **catalyze** the reaction.

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Enzyme Side Chains that catalyze the Reaction



Some enzyme side chains are **acids**, **bases**, and **nucleophiles** that **catalyze** the reaction.

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