CHAPTER FIVE

Reactions of Alkenes and Alkynes

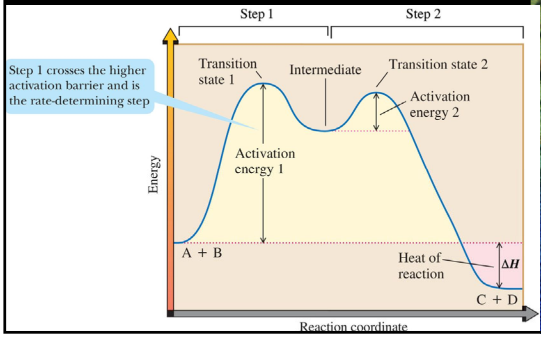
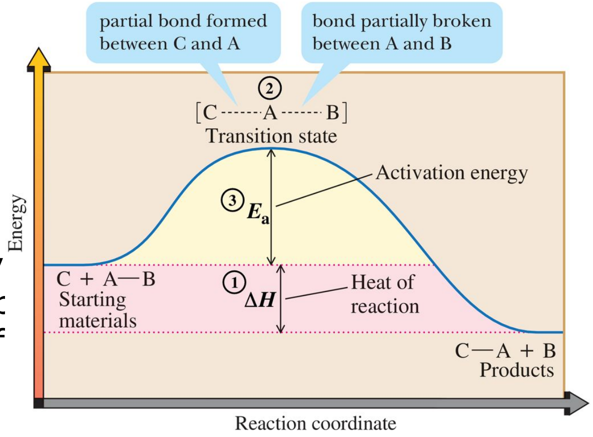


Table of Contents

1. **Energy profiles – Diagrams**
2. **Intermediates and Rate determining step**
3. **Mechanism patterns – Acid Base Chemistry**
4. **Addition Reactions of HX to Alkenes and Alkynes**
5. **Electrophilic Addition of Hydrogen Halides to Alkenes: Mechanisms**
6. **Markovnikov's Rule and Reaction Selectivity (Regioselectivity)**
7. **Carbocations and their relative stability**
8. **Ionic Addition to an Alkene**
9. **Addition of Water to Alkenes: Acid-Catalyzed Hydration**
10. **Electrophilic Addition of Bromine & Chlorine to Alkenes and Alkynes**
11. **Reduction of Alkenes and Alkynes**
12. **Heats of Hydrogenation**

Energy Diagram

- **Energy diagram**: A graph of the energy changes that occur during a chemical reaction; energy is plotted on the y-axis. Reaction progress on the x-axis.
- **Figure 5.1** An energy diagram for a one-step exothermic reaction of C and A-B to give C-A and B.



Energy Diagram

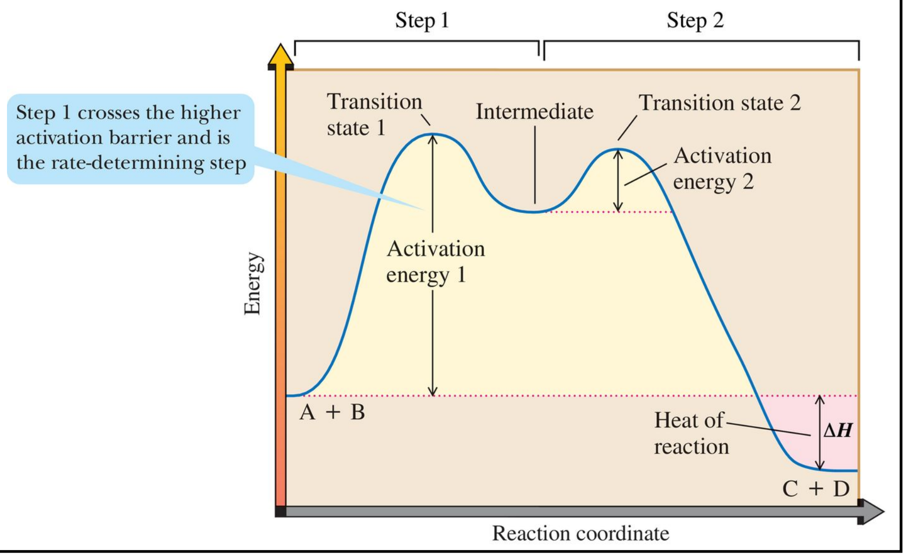
- **Transition state:** An unstable species of maximum energy formed during the course of a reaction; a maximum on an energy diagram.
- **Activation energy E_a:** The difference in energy between the reactants and the transition state.
  - E_a determines the rate of reaction.
  - **If the E_a is large**, very few molecular collisions occur with sufficient energy to reach the transition state, and the reaction is slow.
  - **If the E_a is small**, many collisions generate sufficient energy to reach the transition state, and the reaction is fast.

Energy Diagram

- Also shown on an energy diagram are:
  - **Heat of reaction ∆*H***: The difference in energy between reactants and products.
  - **Exothermic reaction**: A reaction in which the energy of the products is lower than the energy of the reactants; a reaction in which heat is liberated.
  - **Endothermic**: A reaction in which the energy of the products is higher than the energy of the reactants: a reaction in which heat is absorbed.

Energy Diagram

- **Figure 5.2** Energy diagram for a two-step exothermic reaction involving formation of a reaction intermediate.



Energy Diagram

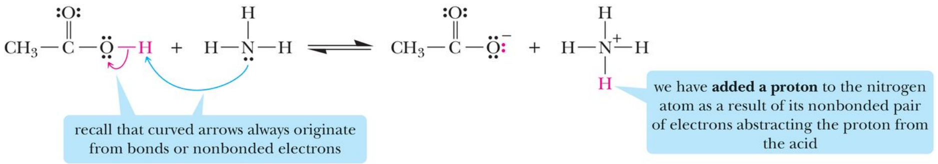
- **Reaction intermediate:** An energy minimum between two transition steps. Intermediates are highly reactive and rarely, if ever, can one be isolated.
- **Rate-determining step:** The step in a reaction sequence that crosses the highest energy barrier; the slowest step in a multistep reaction.

Reaction Mechanism

- A reaction mechanism is a step-by-step description of how a reaction occurs. It describes:
  - Which *bonds break* and which *new ones form*.
  - The order and relative rates of the various bond-breaking and bond-forming steps.
  - If the reaction takes place in solution, it describes the role of the solvent.
  - The role of the catalyst (if one is present).
  - The energy of the entire system during the reaction.
  - A reaction mechanism is NOT a list of reagents or of experimental conditions that bring about the chemical transformation.

Mechanism Patterns

- Before we discuss any particular reactions and their mechanisms, let us first analyze several of the common patterns to be seen in the mechanisms we will encounter.
- **Pattern 1: Add a Proton.** In Section 2.2, we saw how curved arrows can be used to show how a proton-transfer reaction takes place. In this example, curved arrows show the redistribution of valence electrons and the formation of a new covalent bond when a proton is transferred from acetic acid to ammonia.

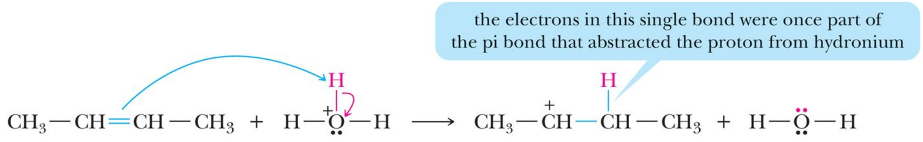


recall that curved arrows always originate from bonds or nonbonded electrons

we have **added a proton** to the nitrogen atom as a result of its nonbonded pair of electrons abstracting the proton from the acid

Mechanism Patterns

- **Pattern 1: Add a proton.** In this example, a proton is added across the pi bond of a C—C double bond to form a new C—H bond. Adding a proton is typical of all reactions that are catalyzed by an acid.



the electrons in this single bond were once part of the pi bond that abstracted the proton from hydronium

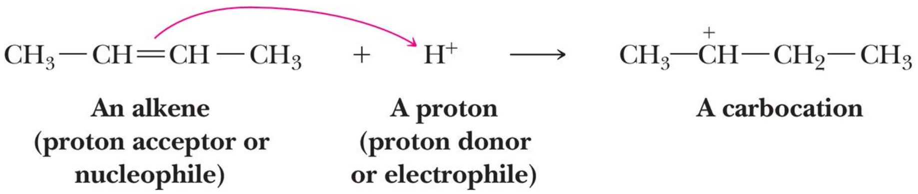
An alkene (proton acceptor or nucleophile)

Hydronium ion (proton donor or electrophile)

A carbocation

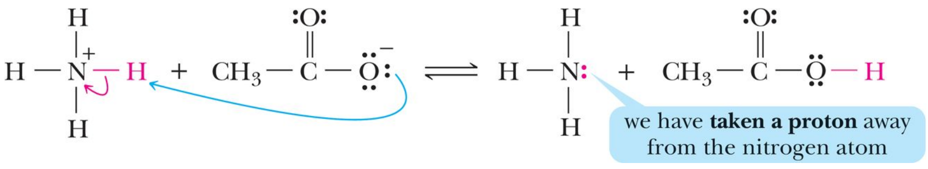
Mechanism Patterns

- **Pattern 1: Add a proton.** While it is most accurate to show proton transfer from H_3O^+ in aqueous solution, we will often simplify the equation to show just the proton H^+ and the formation of a new covalent bond.



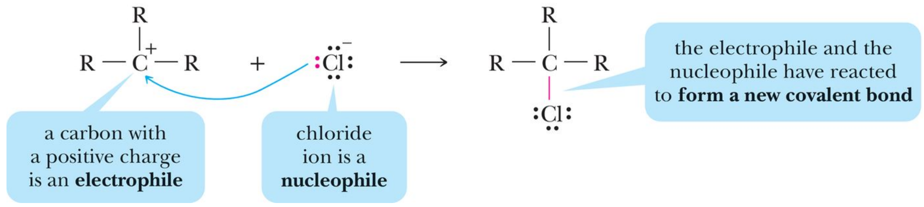
Mechanism Patterns

- **Pattern 2: Take a proton away.** Reversing Pattern 1 corresponds to taking a proton away. The mechanism for taking a proton away is similar to that for adding a proton, except that we focus our attention on the compound that loses the proton instead of the compound that adds a proton.



Mechanism Patterns

- **Pattern 3: Reaction of an electrophile and a nucleophile to form a new covalent bond.**
- **Electrophile:** an electron-poor species that can accept a pair of electrons to form a new covalent bond; a Lewis acid.
- **Nucleophile:** an electron-rich species that can donate a pair of electrons to form a new covalent bond; a Lewis base.



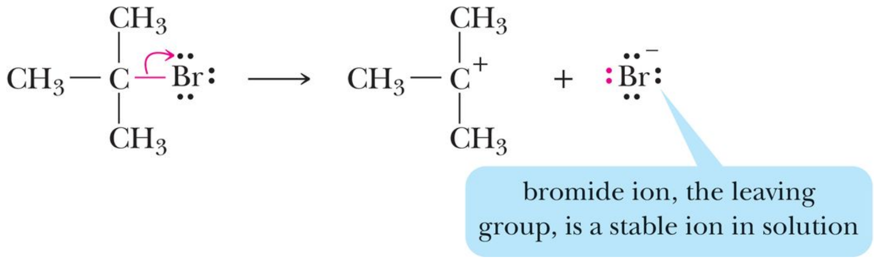
a carbon with a positive charge is an **electrophile**

chloride ion is a **nucleophile**

the electrophile and the nucleophile have reacted to **form a new covalent bond**

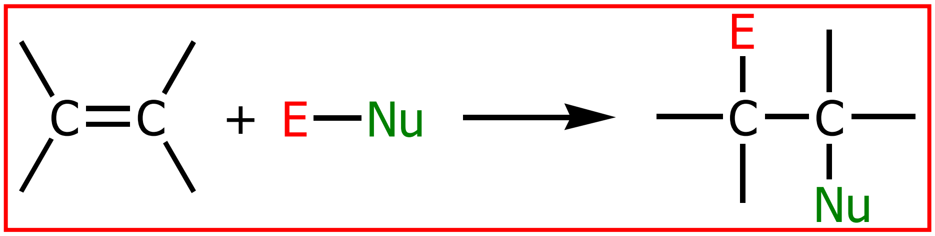
Mechanism Patterns

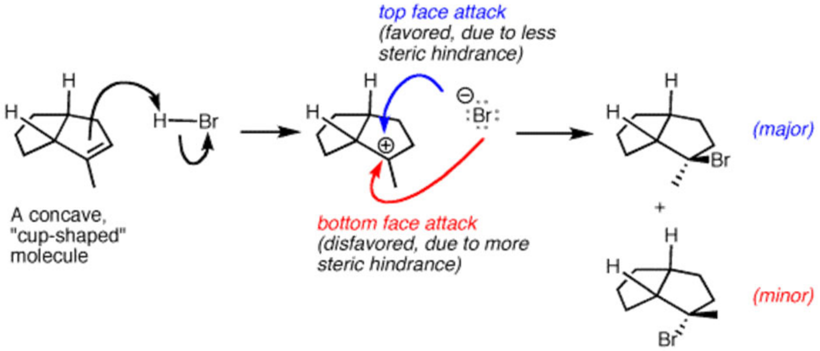
- **Pattern 5: Break a bond to form a stable molecule or ion.** A carbocation can be formed when a chemical species breaks off from a molecule, taking the electrons from the former single bond with it. The chemical species formed is called the leaving group. The bond breaks because doing so forms one or more stable ions or molecules.



bromide ion, the leaving group, is a stable ion in solution

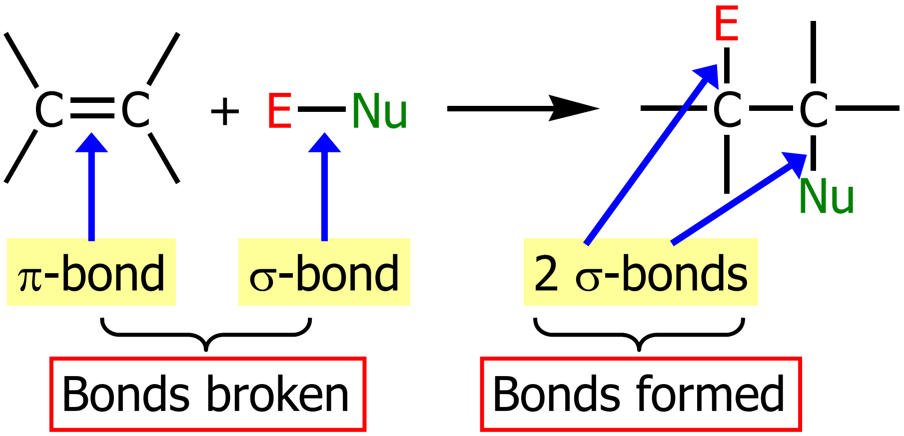
Addition Reactions of Alkenes





How To Understand Additions to Alkenes

- This is an addition reaction: E–Nu added across the double bond



π-bond

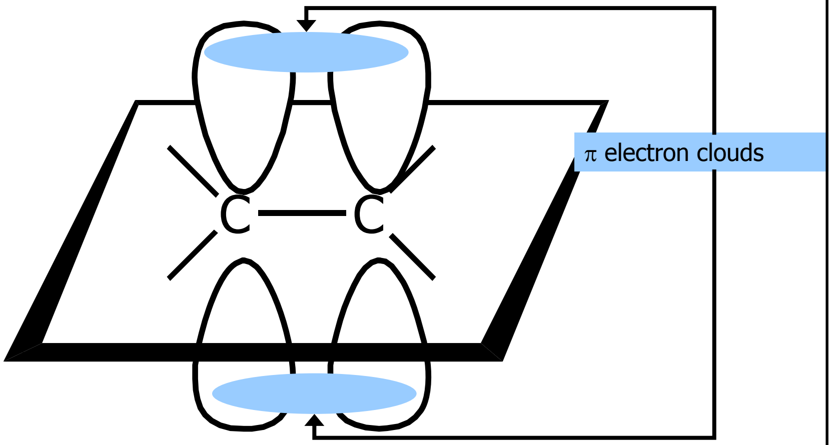
σ-bond

2 σ-bonds

Bonds broken

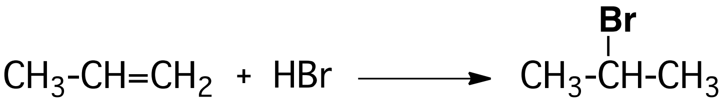
Bonds formed

- Since π bonds are formed from the overlapping of p orbitals, π electron clouds are above and below the plane of the double bond



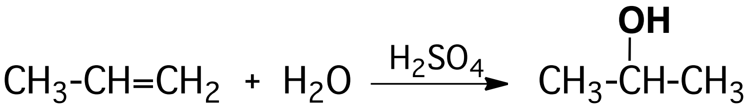
Electrophilic Additions to Alkenes

- **Addition of hydrogen halides (HCl, HBr, HI)**



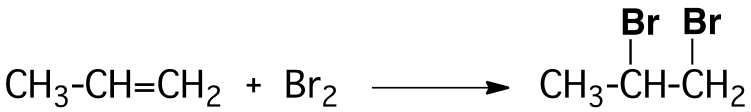
$$CH_3\text{-}CH{=}CH_2 + HBr \longrightarrow CH_3\text{-}\overset{\overset{\displaystyle Br}{|}}{C}H\text{-}CH_3$$

- **Addition of water (H_2O/H_2SO_4) Hydration**



$$CH_3\text{-}CH{=}CH_2 + H_2O \xrightarrow{H_2SO_4} CH_3\text{-}\overset{\overset{\displaystyle OH}{|}}{C}H\text{-}CH_3$$

- **Addition of halogens (Cl_2, Br_2) Halogenation**



$$CH_3\text{-}CH{=}CH_2 + Br_2 \longrightarrow CH_3\text{-}\overset{\overset{\displaystyle Br}{|}}{C}H\text{-}\overset{\overset{\displaystyle Br}{|}}{C}H_2$$

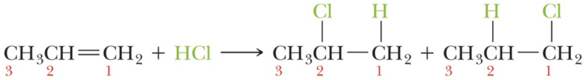
Addition of Hydrogen Halides

- Carried out with the pure reagents or in a polar solvent such as acetic acid.

$CH_2{=}CH_2 + HCl \longrightarrow \overset{H}{\overset{|}{CH_2}}{-}\overset{Cl}{\overset{|}{CH_2}}$

Ethylene Chloroethane

- Addition is regioselective.
  - **Regioselective reaction:** A reaction in which one direction of bond forming or bond breaking occurs in preference to all other directions.



$\underset{3}{CH_3}\underset{2}{CH}{=}\underset{1}{CH_2} + HCl \longrightarrow \underset{3}{CH_3}\underset{2}{\overset{Cl}{\overset{|}{CH}}}{-}\underset{1}{\overset{H}{\overset{|}{CH_2}}} + \underset{3}{CH_3}\underset{2}{\overset{H}{\overset{|}{CH}}}{-}\underset{1}{\overset{Cl}{\overset{|}{CH_2}}}$

Propene 2-Chloropropane 1-Chloropropane (not observed)

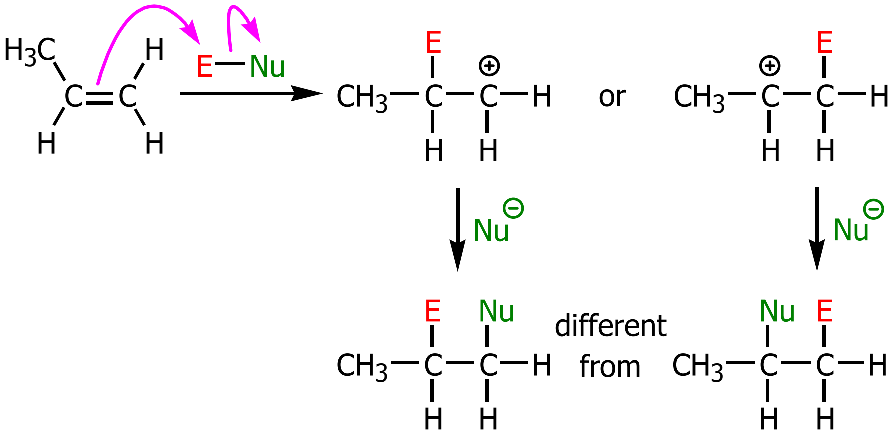
  - **Markovnikov's rule:** In additions of HX to a double bond, H adds to the carbon with the greater number of hydrogens already bonded to it.

- **Markovnikov's Rule**

- **In the electrophilic addition of an electrophile across an unsymmetrical alkene, the more highly substituted and *more stabilized carbocation* is formed as the intermediate in preference to the less highly substituted and less stable one (= *H^+ adds to the carbon with the greater number of hydrogens already bonded to it*)**

❖ Markovnikov's Rule

- For unsymmetrical alkenes, two *regioisomers* are possible



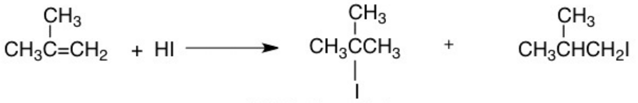
Minor!

Major!

Regioisomer: Constitutional isomer

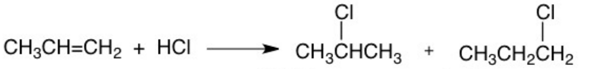
Regioselectivity

❖ Markovnikov's rule is but one example of regioselectivity. We will see more examples in this and later chapters.



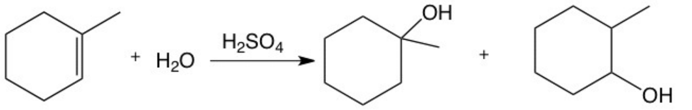
$CH_3C(CH_3)=CH_2 + HI \longrightarrow CH_3C(CH_3)(I)CH_3 + CH_3CH(CH_3)CH_2I$

2-Iodo-2-methylpropane (major product) **1-Iodo-2-methylpropane (not observed)**



$CH_3CH=CH_2 + HCl \longrightarrow CH_3CH(Cl)CH_3 + CH_3CH_2CH_2Cl$

2-Chloropropane (major product) **1--Chloropropane (not observed)**

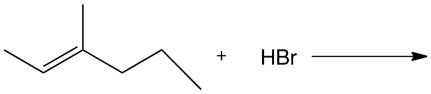


1-Methylcyclohexanol (major product) **2-Methylcyclohexanol (not observed)**

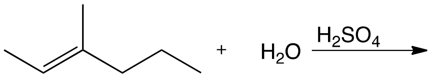
Markovnikov's Rule

- **Problem**: Complete these reactions by predicting the major product formed in each reaction.

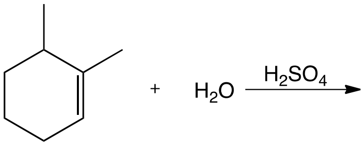
(a)



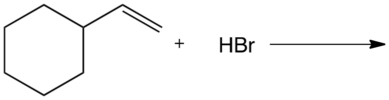
(b)



(c)

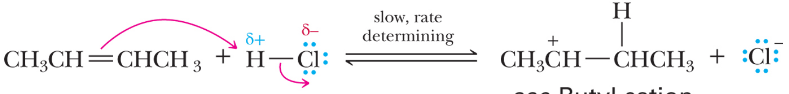


(d)



Addition of HCl to 2-Butene

- A two-step mechanism
  - **Step 1: Add a proton.** Formation of a *sec*-butyl cation, a 2° carbocation intermediate.

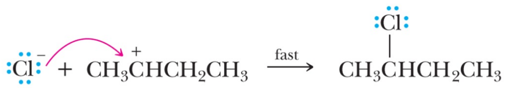


$$CH_3CH{=}CHCH_3 + \overset{\delta+}{H}-\overset{\delta-}{:\ddot{Cl}:} \xrightleftharpoons{\text{slow, rate determining}} CH_3\overset{+}{C}H-\overset{H}{\overset{|}{C}}HCH_3 + :\ddot{Cl}:^-$$

(a nucleophile) (an electrophile)

sec-Butyl cation
(a 2°carbocation
intermediate)

  - **Step 2: Reaction of an electrophile and a nucleophile to form a new covalent bond.** Reaction of the *sec*-butyl cation (an electrophile) with chloride ion (a nucleophile) completes the reaction.

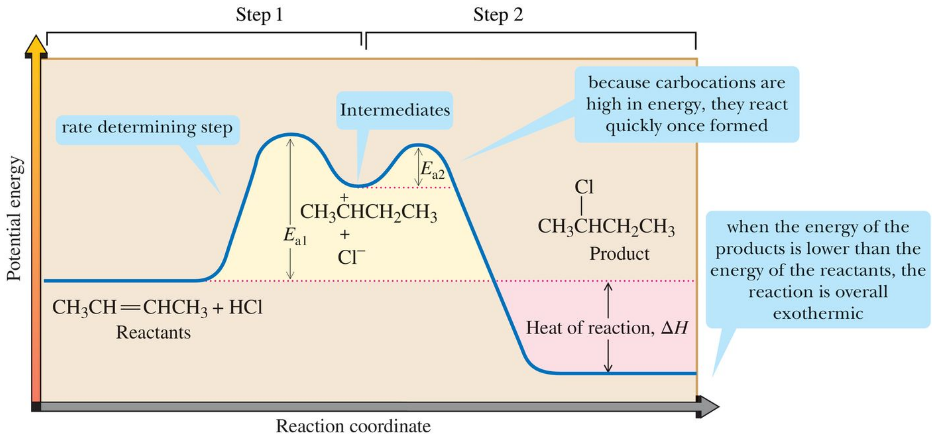


$$:\ddot{Cl}:^- + CH_3\overset{+}{C}HCH_2CH_3 \xrightarrow{\text{fast}} CH_3\overset{:\ddot{Cl}:}{\overset{|}{C}}HCH_2CH_3$$

Chloride ion	*sec*-Butyl cation	2-Chlorobutane
(a Lewis base)	(a Lewis acid)	
(a nucleophile)	(an electrophile)	

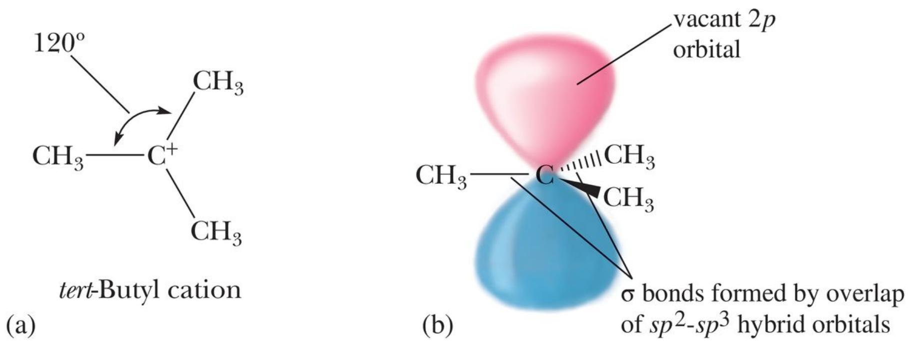
Addition of HCl to 2-Butene

- **Figure 5.4** Energy diagram for the two-step exothermic addition of HCl to 2-butene.



Carbocations

- **Figure 5.3** The structure of the tert-butyl cation.

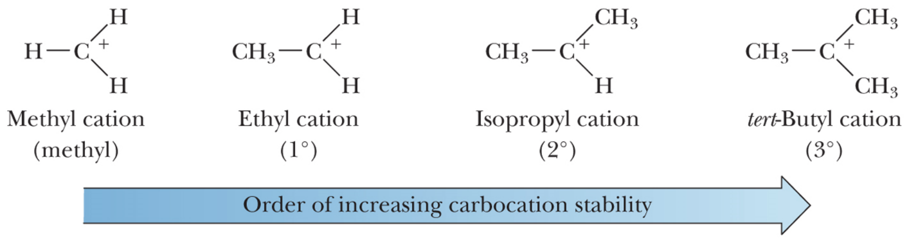


Carbocations

- **Carbocation:** A species containing a carbon atom that has three bonds to it, six electrons in its valence shell, and bears a positive charge.
  - Bond angles about the positively charged carbon are approximately 120°.
  - Carbon uses *sp*^{2} hybrid orbitals to form a sigma bond to each attached group.
  - The unhybridized 2*p* orbital lies perpendicular to the sigma bond framework and contains no electrons
- Carbocations are:
  - **Electrophiles:** that is, they are electron-loving.
  - **Lewis acids:** that is, they are electron-pair acceptors.

Carbocations

- A 3° carbocation is more stable than a 2° carbocation, and requires a lower activation energy for its formation.
- A 2° carbocation is, in turn, more stable than a 1° carbocation, and requires a lower activation energy for its formation.
- Methyl and 1° carbocations are so unstable that they are never observed in solution.

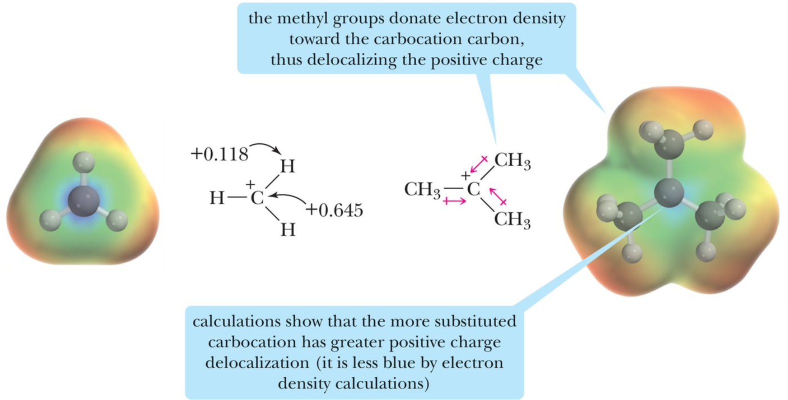


Relative Stability of Carbocations

- **Inductive effect**: The polarization of the electron density of a covalent bond as a result of the high electronegativity of a nearby atom.
    - The electronegativity of a carbon atom bearing a positive charge exerts an electron-withdrawing inductive effect that polarizes electrons of adjacent sigma bonds toward it.
    - Thus, the positive charge of a carbocation is not localized on the trivalent carbon, but rather is delocalized over nearby atoms as well.
    - The larger the area over which the positive charge is delocalized, the greater the stability of the cation.

The Inductive Effect

- **Figure 5.5** 3° Carbocations are more stable and require a lower activation energy for their formation than 2° carbocations. 1° and methyl carbocations are so difficult to form that they are never observed in solution or in any of the reactions we will discuss.

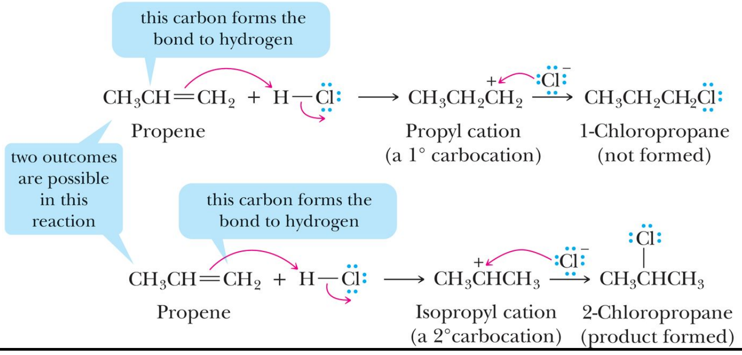


the methyl groups donate electron density toward the carbocation carbon, thus delocalizing the positive charge

calculations show that the more substituted carbocation has greater positive charge delocalization (it is less blue by electron density calculations)

Markovnikov’s Rule

- The chemical basis for the regioselectivity embodied in Markovnikov’s rule lies in the relative stabilities of carbocation intermediates. The reason why the proton of H—X adds to the less substituted carbon of the double bond is that this mode of addition leads to the more stable carbocation intermediate.



this carbon forms the bond to hydrogen

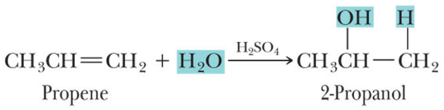
two outcomes are possible in this reaction

this carbon forms the bond to hydrogen

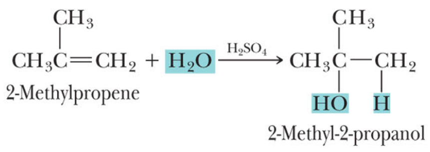
Addition of H_2O to an Alkene

- Addition of H_2O to an alkene is called hydration.
  - Acid-catalyzed hydration of an alkene is regioselective: hydrogen adds preferentially to the less substituted carbon of the double bond. Thus H–OH adds to alkenes in accordance with Markovnikov's rule.

EXAMPLE 1

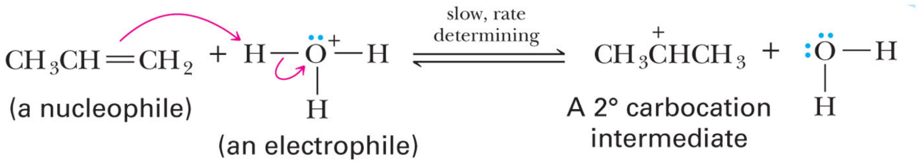


EXAMPLE 2



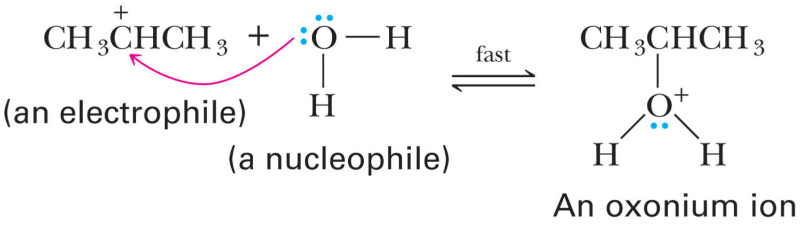
Addition of H_2O to an Alkene

- **Step 1: Add a proton.** Proton transfer from the acid catalyst (H_3O^+) to propene gives a 2° carbocation intermediate.



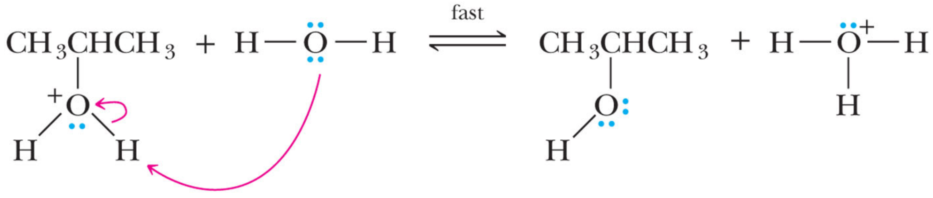
Addition of H_2O to an Alkene

- **Step 2: Reaction of a nucleophile and an electrophile to form a new covalent bond.** Reaction of the carbocation intermediate with water completes the valence shell of carbon and gives an oxonium ion.



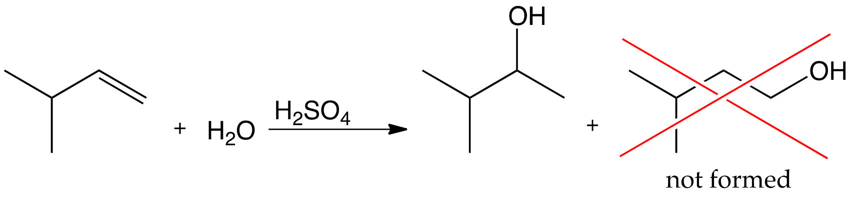
Addition of H_2O to an Alkene

- **Step 3: Take a proton away.** Proton transfer from the oxonium ion to water gives the alcohol and regenerates the acid catalyst.



Addition of H_2O to an Alkene

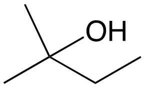
- **Problem:** Account for the fact that the acid-catalyzed hydration of alkenes can be used to prepare both 2° and 3° alcohols but, with the exception of ethanol, it cannot be used to prepare 1° alcohols.



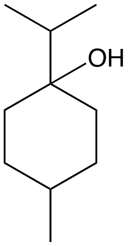
Addition of H_2O to an Alkene

- **Problem:** Draw the structural formula of an alkene that undergoes acid-catalyzed hydration to give each alcohol as the major product. More that one alkene may give each alcohol as the major product.

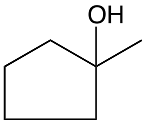
(a)



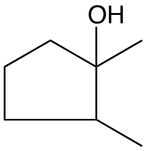
(b)



(c)

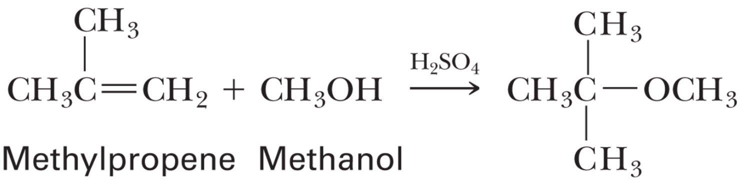


(d)



Addition of Cl_2 and Br_2

- **Problem:** Treatment of 2-methylpropene with methanol in the presence of an acid catalyst gives *tert*-butylmethyl ether. At one time this compound was added to gasoline to increase octane rating. Due to environmental concerns, however, it is no longer used for this purpose.
- Propose a mechanism for this reaction.



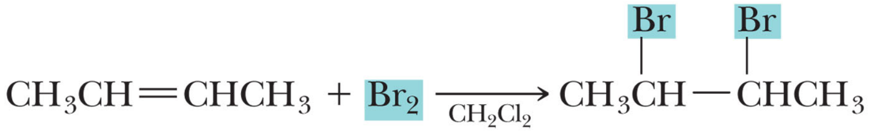
$$CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2 + CH_3OH \xrightarrow{H_2SO_4} CH_3\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}{-}OCH_3$$

2-Methylpropene Methanol

tert-Butyl methyl ether

Addition of Cl_2 and Br_2

- Carried out with either the pure reagents or in an inert solvent such as CH_2Cl_2.



$$CH_3CH{=}CHCH_3 + Br_2 \xrightarrow[CH_2Cl_2]{} CH_3\overset{\overset{Br}{|}}{C}H-\overset{\overset{Br}{|}}{C}HCH_3$$

2-Butene

2,3-Dibromobutane

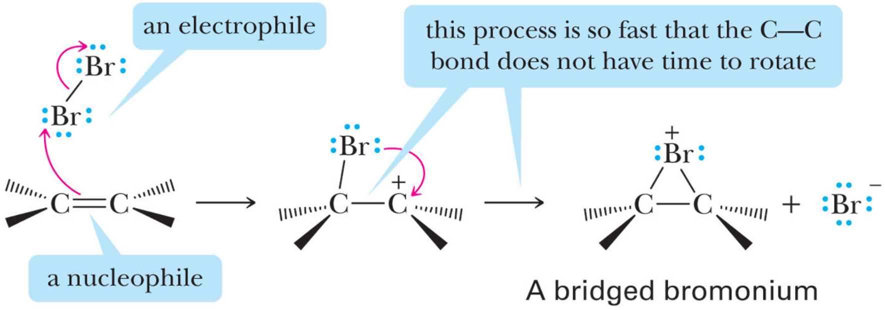
Addition of Cl2 and Br2

- Addition is stereoselective.
- **Stereoselective reaction:** A reaction in which one stereoisomer is formed or destroyed in preference to all others that might be formed or destroyed.
- Addition to a cycloalkene, for example, gives only a trans product. The reaction occurs with **anti-stereoselectivity.**

Charles D. Winters

Addition of Cl_2 and Br_2

- **Step 1: Reaction of a nucleophile and an electrophile to form a new covalent bond.** Reaction of the pi bond (a nucleophile) with bromine (an electrophile) gives a bridged bromonium ion intermediate



an electrophile

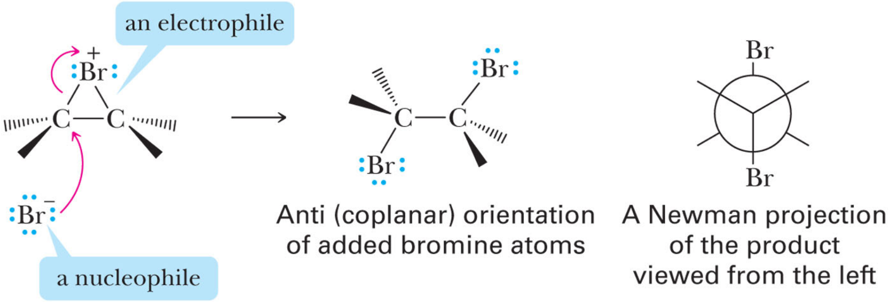
this process is so fast that the C—C bond does not have time to rotate

a nucleophile

A bridged bromonium ion intermediate

Addition of Cl_2 and Br_2

- **Step 2: Reaction of a nucleophile, and an electrophile to form a new covalent bond.** Attack of bromide ion from the side opposite the bridged bromonium ion opens the three-membered ring.



an electrophile

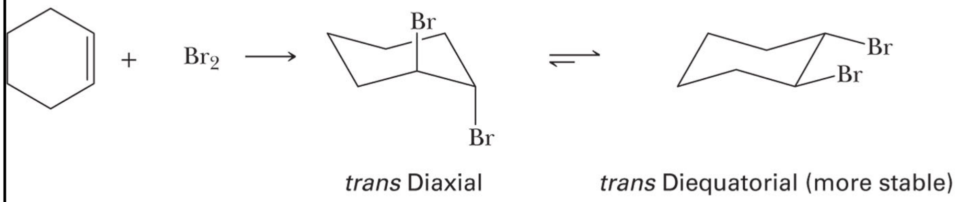
a nucleophile

Anti (coplanar) orientation of added bromine atoms

A Newman projection of the product viewed from the left

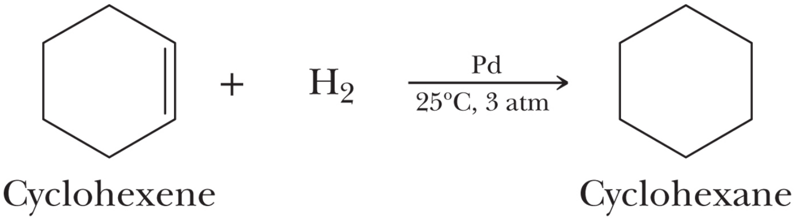
Addition of Cl_2 and Br_2

- The addition of chlorine or bromine to cyclohexene and its derivatives gives a *trans*-diaxial product because only axial positions on adjacent carbon atoms are anti and coplanar. The initial *trans*-diaxial conformation is in equilibrium with the more stable *trans*-diequatorial conformation.



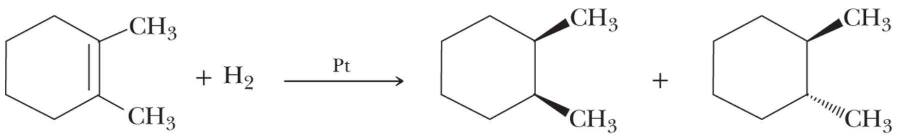
Reduction of Alkenes

- Alkenes react with H_2 in the presence of a transition metal catalyst to give alkanes.
  - The most commonly used catalysts are Pd, Pt, and Ni.
  - The reaction is called **catalytic reduction** or **catalytic hydrogenation.**



Reduction of Alkenes

- The most common pattern is syn addition of hydrogens; both hydrogens add to the same face of the double bond.
- Catalytic reduction is predominantly **syn stereoselective.**



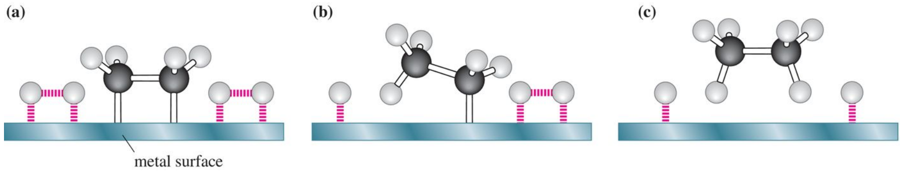
1,2-Dimethyl-cyclohexene

70% to 85%
cis-1,2-Dimethyl-cyclohexane

30% to 15%
trans-1,2-Dimethyl-cyclohexane

Catalytic Reduction of an Alkene

- **Figure 5.6** Syn addition of H_2 to an alkene involving a transition metal catalyst.
  - (a) H_2 and the alkene are absorbed on the catalyst.
  - (b) One H is transferred forming a new C-H bond.
  - (c) The second H is transferred. The alkane is released.



Heats of Hydrogenation

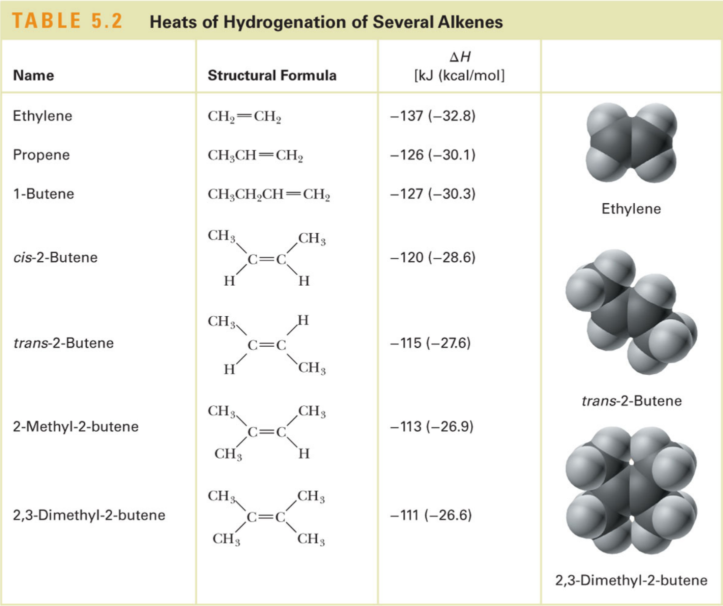


TABLE 5.2 **Heats of Hydrogenation of Several Alkenes**

Name	Structural Formula	ΔH [kJ (kcal/mol)]
Ethylene	$CH_2{=}CH_2$	−137 (−32.8)
Propene	$CH_3CH{=}CH_2$	−126 (−30.1)
1-Butene	$CH_3CH_2CH{=}CH_2$	−127 (−30.3)
cis-2-Butene	CH_3 CH_3 $C{=}C$ H H	−120 (−28.6)
trans-2-Butene	CH_3 H $C{=}C$ H CH_3	−115 (−27.6)
2-Methyl-2-butene	CH_3 CH_3 $C{=}C$ CH_3 H	−113 (−26.9)
2,3-Dimethyl-2-butene	CH_3 CH_3 $C{=}C$ CH_3 CH_3	−111 (−26.6)

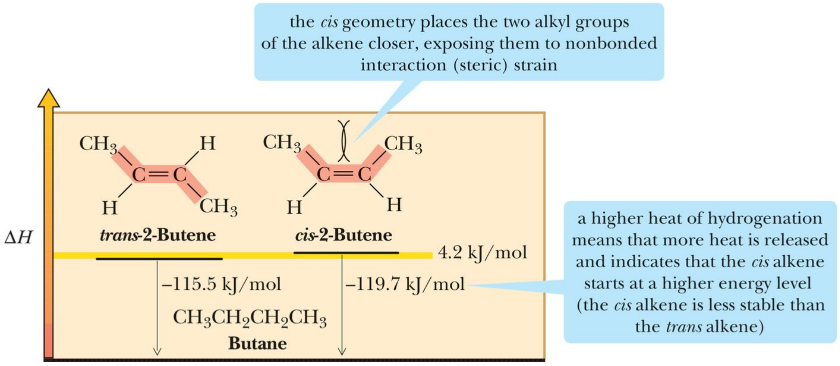
Heats of Hydrogenation

- Reduction involves net conversion of a weaker pi bond to a stronger sigma bond.
- The greater the degree of substitution of a double bond, the lower its heat of hydrogenation.
  - **The greater the degree of substitution, the more stable the double bond.**

- The heat of hydrogenation of a *trans* alkene is lower than that of an isomeric *cis* alkene.
  - **A *trans* alkene is more stable than its isomeric *cis* alkene.**
  - The difference is due to nonbonded interaction strain in the *cis* alkene.

Heats of Hydrogenation

- **Figure 5.7** Heats of hydrogenation of *cis*-2-butene and *trans*-2-butene.
- *trans*-2-butene is more stable than *cis*-2-butene by 4.2 kJ/mol.



the *cis* geometry places the two alkyl groups of the alkene closer, exposing them to nonbonded interaction (steric) strain

a higher heat of hydrogenation means that more heat is released and indicates that the *cis* alkene starts at a higher energy level (the *cis* alkene is less stable than the *trans* alkene)

Reactions of Alkynes

- As we saw in Chapter 4, one of the major differences between the chemistry of alkanes, alkenes, and alkynes is that terminal alkynes are weak acids.

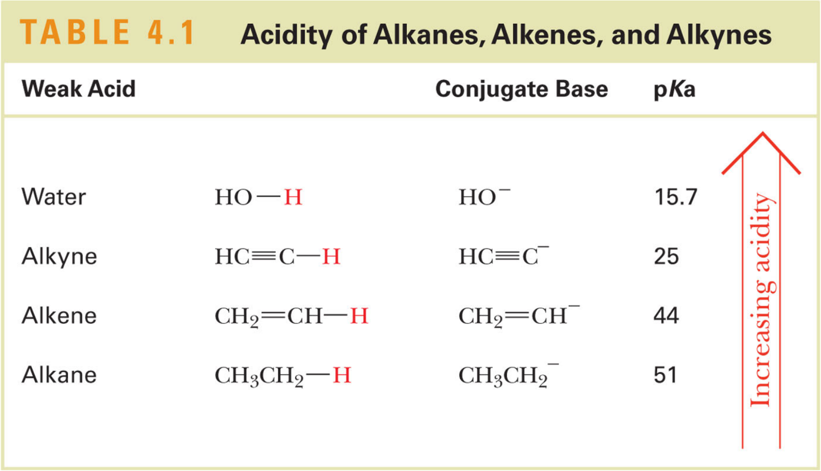
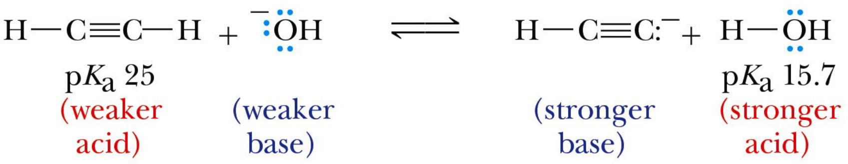


TABLE 4.1 Acidity of Alkanes, Alkenes, and Alkynes

Weak Acid		Conjugate Base	p*K*a
Water	HO—H	HO^-	15.7
Alkyne	HC≡C—H	$HC\equiv C^-$	25
Alkene	CH_2=CH—H	$CH_2=CH^-$	44
Alkane	CH_3CH_2—H	$CH_3CH_2^-$	51

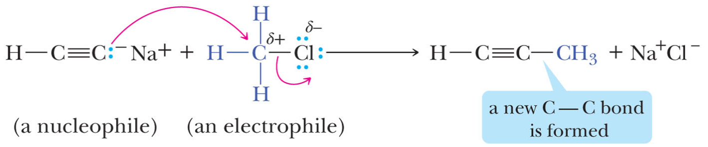
Alkylation of Terminal Alkynes

- ❖ Treatment of a 1-alkyne with a very strong base such as sodium amide, $NaNH_2$, converts the alkyne to an acetylide anion.



Acetylide Anions in Synthesis

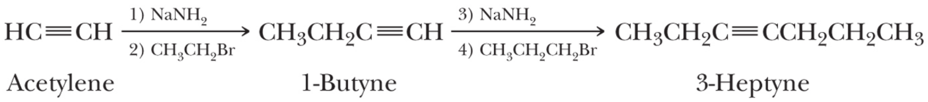
- ❖ An acetylide anion is both a strong base and a nucleophile. As a nucleophile, it can donate a pair of electrons to an electrophilic carbon atom and form a new carbon-carbon bond.



- ❖ In this example, the electrophile is the partially positive carbon of chloromethane. As the new carbon-carbon bond is formed, the carbon-halogen bond is broken.
- ❖ Because an alkyl group is added to the original alkyne, this reaction is called **alkylation**.

Acetylide Anions in Synthesis

- The importance of alkylation of acetylide anions is that the two-carbon molecule acetylene can be used to create larger carbon skeletons.

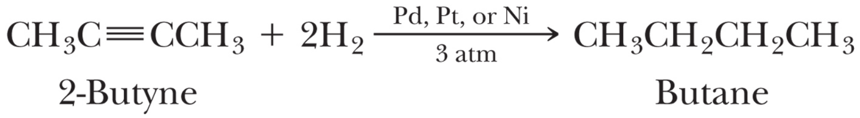


$$\underset{\text{Acetylene}}{HC{\equiv}CH} \xrightarrow[\text{2) } CH_3CH_2Br]{\text{1) } NaNH_2} \underset{\text{1-Butyne}}{CH_3CH_2C{\equiv}CH} \xrightarrow[\text{4) } CH_3CH_2CH_2Br]{\text{3) } NaNH_2} \underset{\text{3-Heptyne}}{CH_3CH_2C{\equiv}CCH_2CH_2CH_3}$$

- For reasons we will discuss fully in Chapter 7, this type of alkylation is successful only for methyl and primary alkyl halides (CH_3X and RCH_2X).

Reduction of Alkynes

- Treatment of an alkyne with H_2 in the presence of a transition metal catalyst, most commonly Pd, Pt, or Ni, results in addition of two moles of H_2 and conversion of the alkyne to an alkane.



$$\underset{\text{2-Butyne}}{CH_3C{\equiv}CCH_3} + 2H_2 \xrightarrow[\text{3 atm}]{\text{Pd, Pt, or Ni}} \underset{\text{Butane}}{CH_3CH_2CH_2CH_3}$$