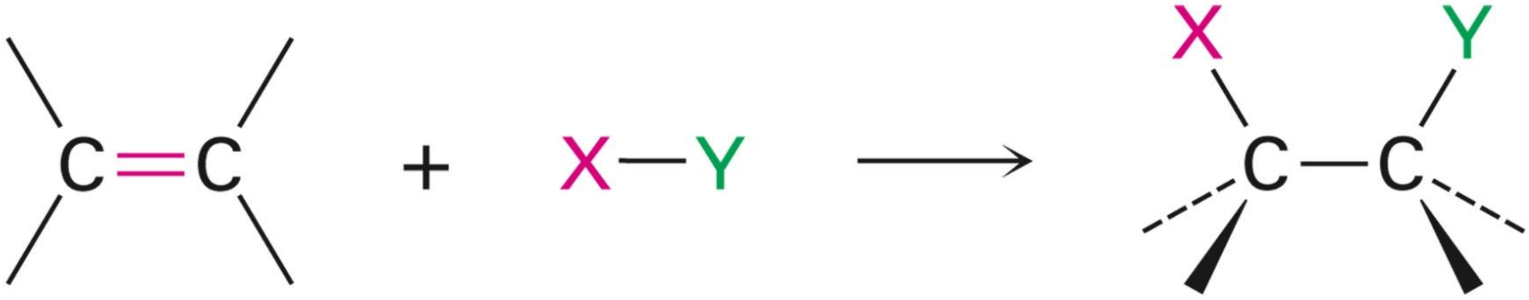
Reactions of Alkenes and Alkynes

McMurry, 'Fundamentals of Organic Chemistry', 7th Ed.

Chapter 4

Diverse Reactions of Alkenes

- **Alkenes react with many electrophiles to give useful products by addition (often through special reagents)**

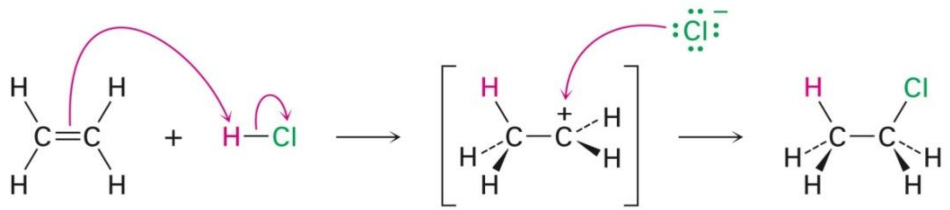


An alkene **An addition product**

Why this chapter?

- To begin a systematic description of major functional groups
- Begin to focus on general principles and patterns of reactivity that tie organic chemistry

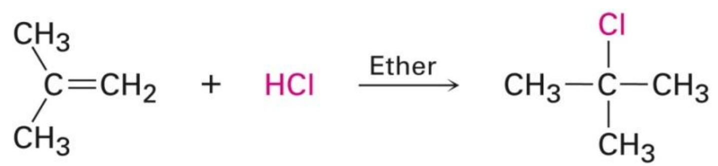
4.1 Addition of HX to Alkenes: Markovnikov’s Rule



Ethylene

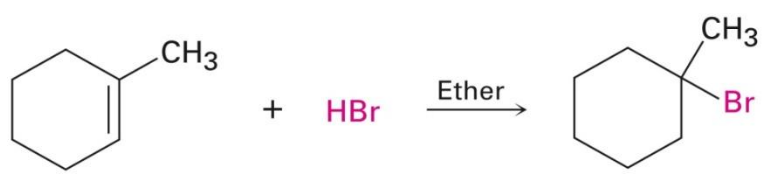
Carbocation intermediate

Chloroethane



2-Methylpropene

2-Chloro-2-methylpropane



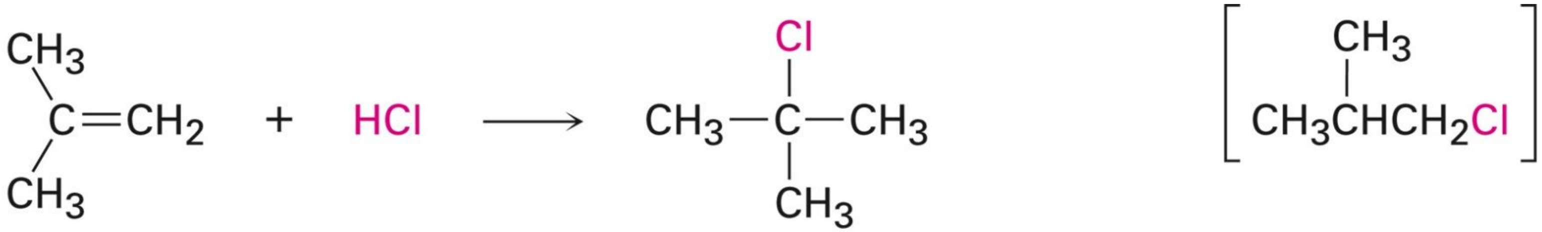
1-Methylcyclohexene

1-Bromo-1-methylcyclohexane

Pent-1-ene

2-Iodopentane

- In an unsymmetrical alkene, HX reagents can add in two different ways, but one way may be preferred over the other
- If one orientation predominates, the reaction is **regiospecific**
- **Markovnikov** observed in the 19th century that in the addition of HX to alkene, the H attaches to the carbon with fewer alkyl substituents and X attaches to the other end (to the one with more alkyl substituents)
  - This is **Markovnikov's rule**



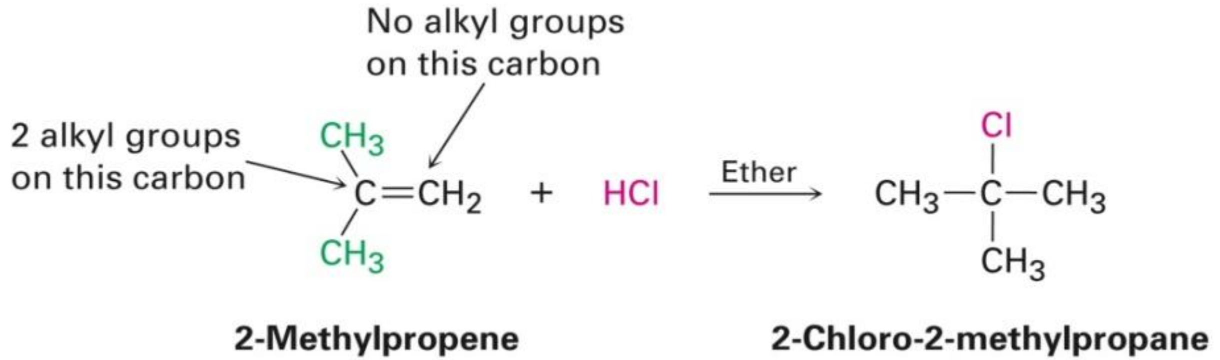
2-Methylpropene

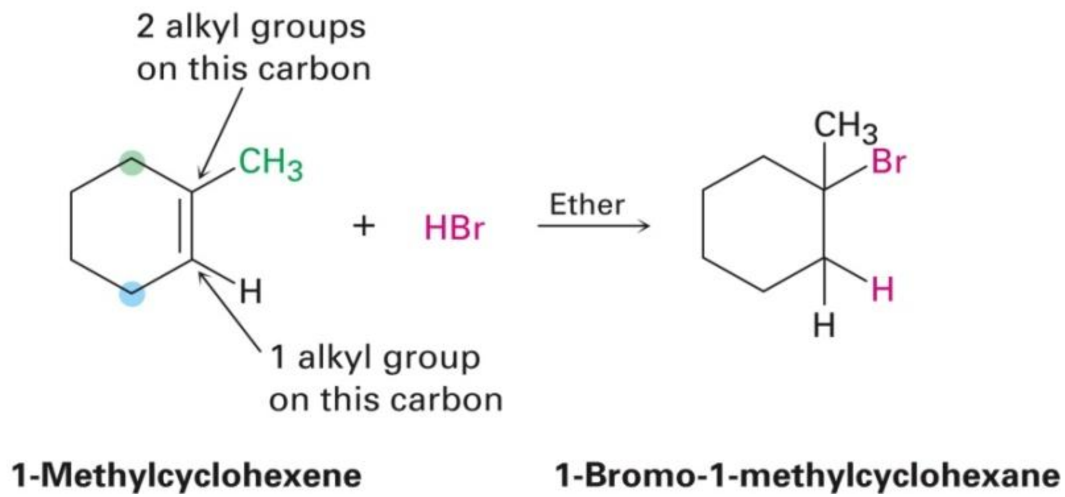
2-Chloro-2-methylpropane (sole product)

1-Chloro-2-methylpropane (*NOT formed*)

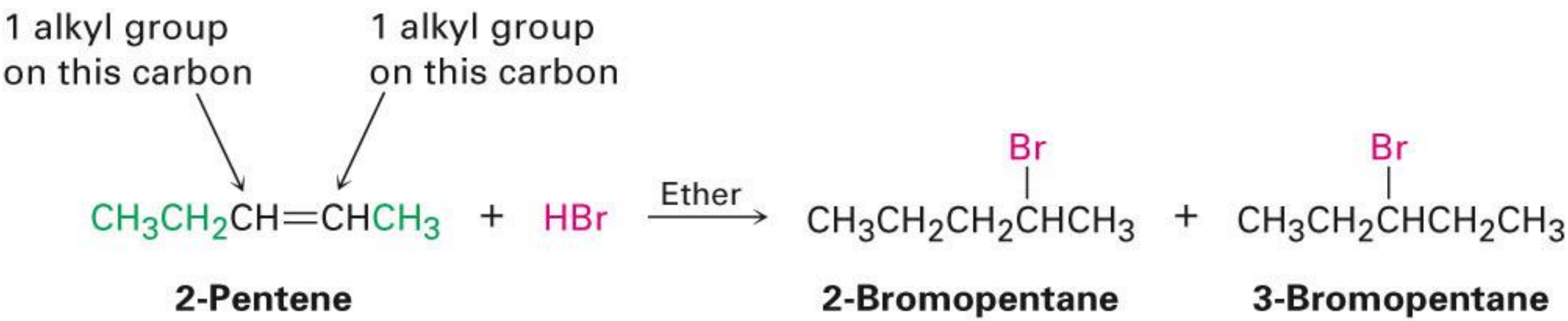
Markovnikov's Rule

- Addition of HCl to 2-methylpropene
- Regiospecific – one product forms where two are possible



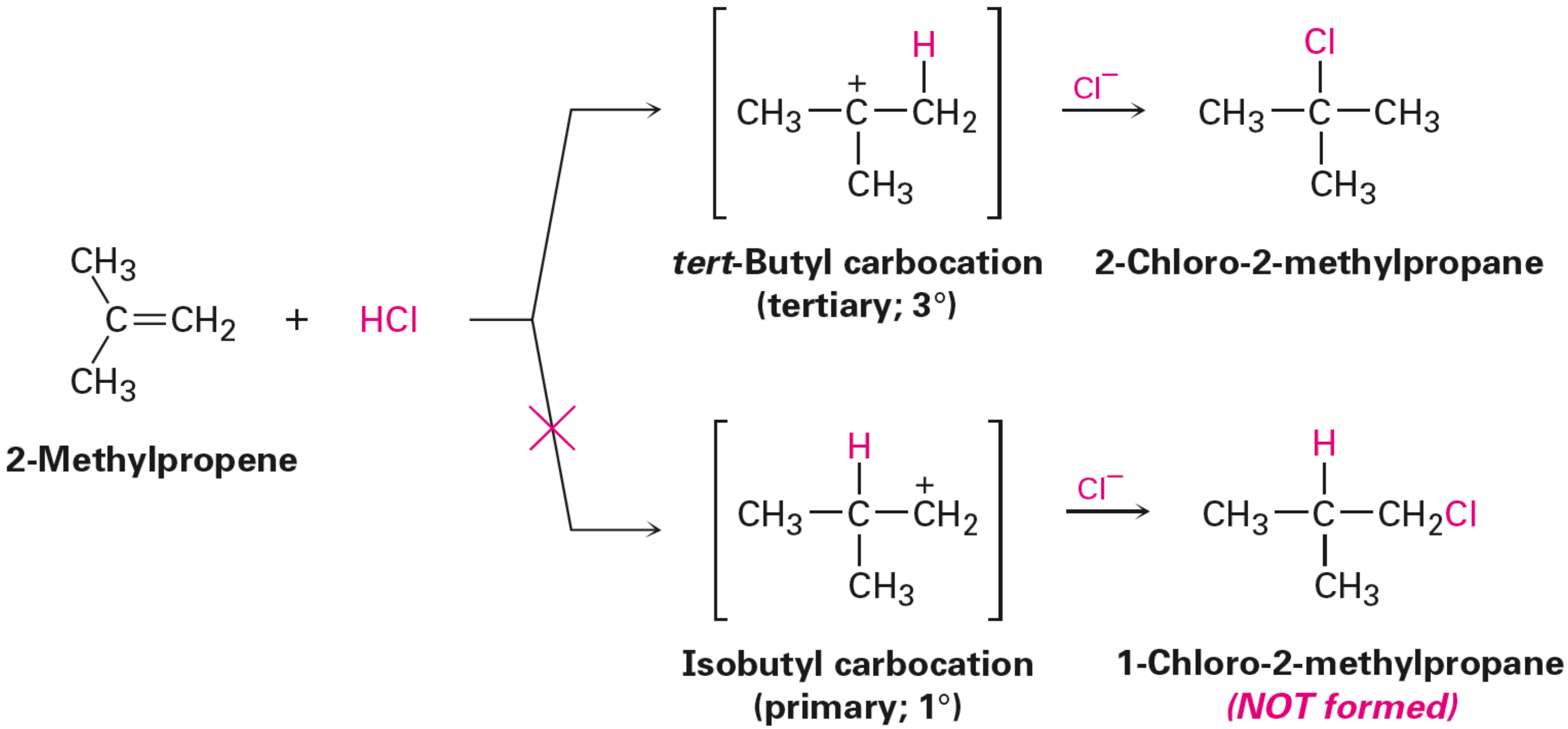


- **If both ends have similar substitution, then not regiospecific**



Markovnikov's Rule (restated)

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



4.2 Carbocation Structure and Stability

- **Carbocations are planar and the tricoordinate carbon is surrounded by only 6 electrons in *sp*^{2} orbitals**
- **The fourth orbital on carbon is a vacant *p*-orbital**
- **The stability of the carbocation (measured by energy needed to form it from R-X) is increased by the presence of alkyl substituents**

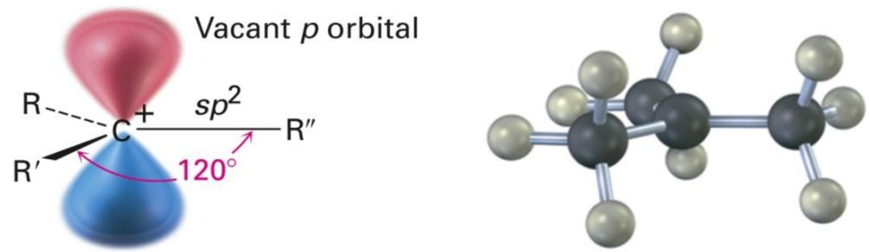
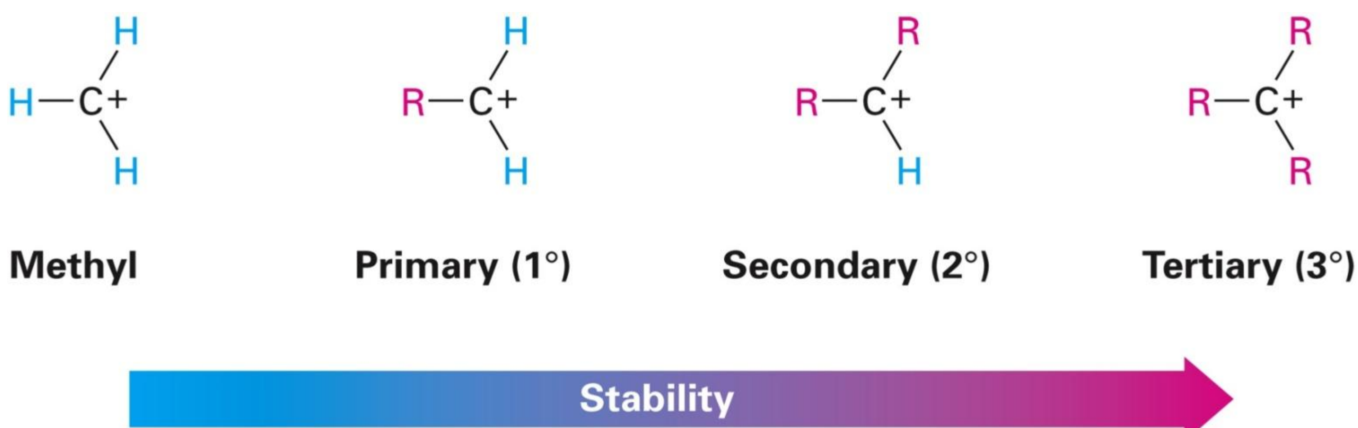
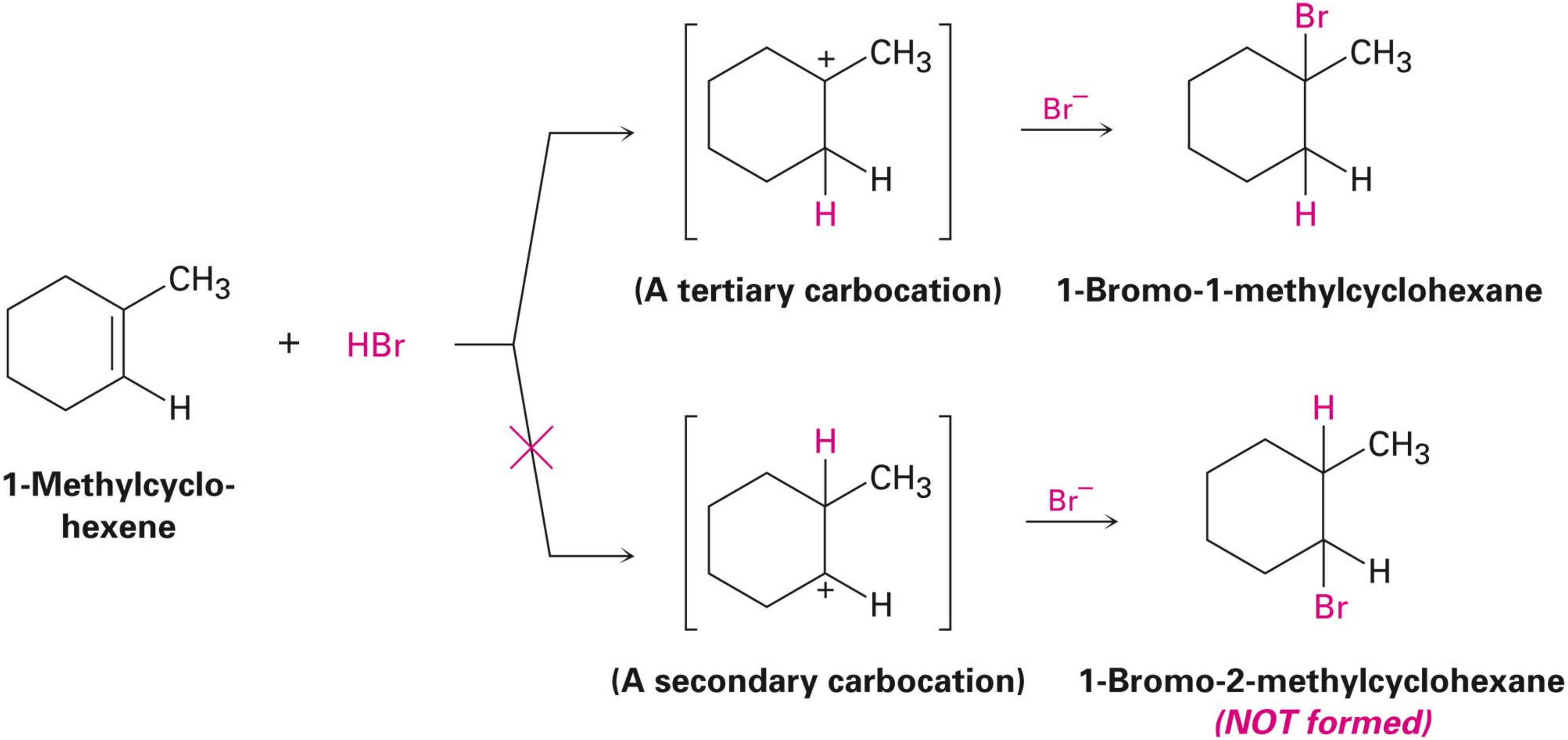


Figure 4.1 The structure of a carbocation.




CH3
H
+ HBr
1-Methylcyclo-
hexene
CH3
H
H
Br−
Br
CH3
H
H
(A tertiary carbocation)
1-Bromo-1-methylcyclohexane
H
CH3
H
Br−
H
CH3
H
Br
(A secondary carbocation)
1-Bromo-2-methylcyclohexane
(NOT formed)

4.3 Addition of Water to Alkenes

- **Hydration of an alkene** is the addition of H-OH to to give an alcohol
- Acid catalysts are used in high temperature industrial processes: ethylene is converted to ethanol

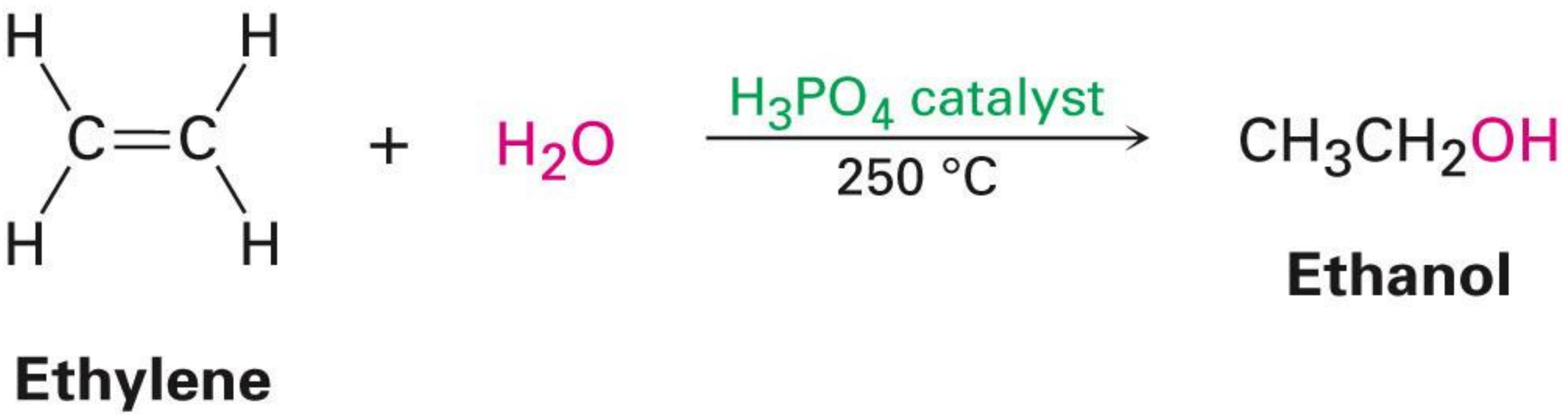


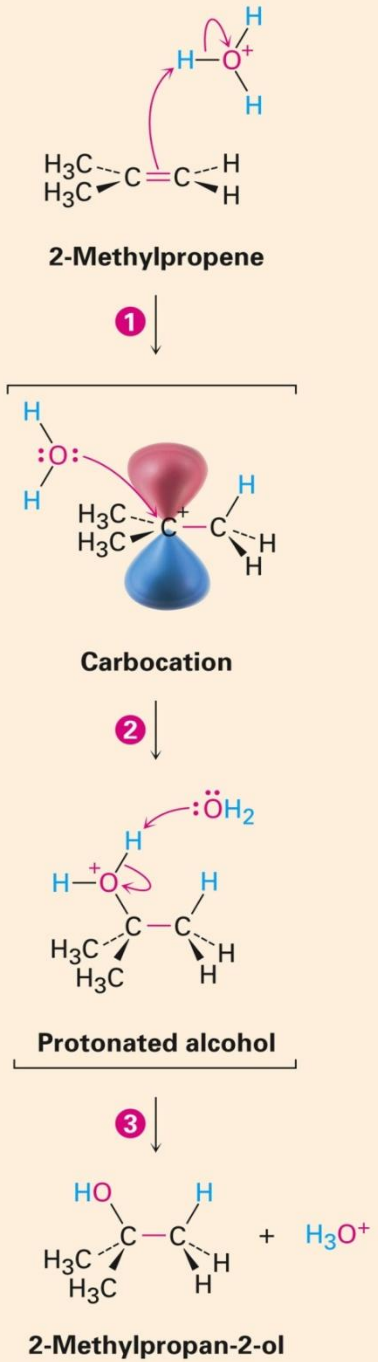
Figure 4.2 Mechanism of the acid-catalyzed hydration of an alkene to yield an alcohol.

Markovnikov's rule

1. A hydrogen atom on the electrophile H_3O^+ is attacked by π electrons from the nucleophilic double bond, forming a new C–H bond. This leaves the other carbon atom with a + charge and a vacant *p* orbital. Simultaneously, two electrons from the H–O bond move onto oxygen, giving neutral water.

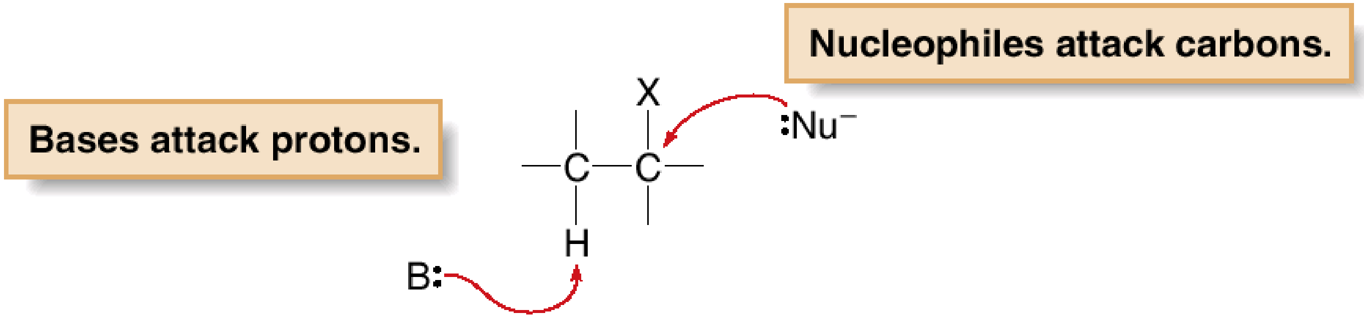
2. The nucleophile H_2O donates an electron pair to the positively charged carbon atom, forming a C–O bond and leaving a positive charge on oxygen in the protonated alcohol addition product.

3. Water acts as a base to remove H^+, regenerating H_3O^+ and yielding the neutral alcohol addition product.



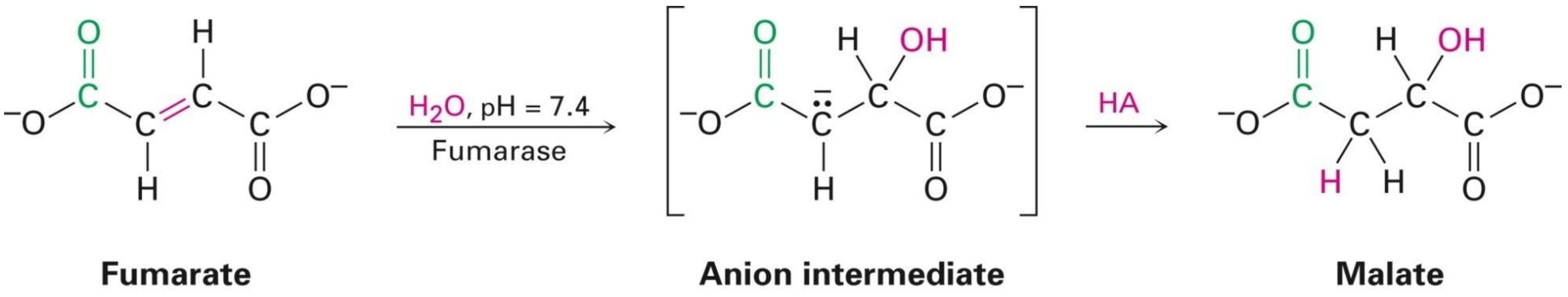
- **Nucleophiles and bases are structurally similar: both have a lone pair or a π bond**
- **They differ in what they attack**

- Bases attack protons. Nucleophiles attack other electron-deficient atoms (usually carbons).



Biological hydration

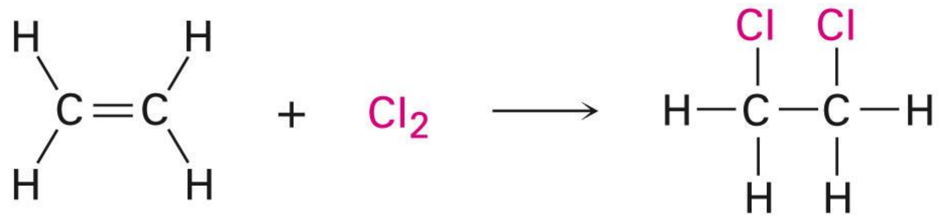
- **Usually require that the double bond be adjacent to a carbonyl group (C=O) for reaction to proceed**
- **For instance, Fumarate is hydrated to give malate as one step in the citric acid cycle of food metabolism**



4.4 Addition of Halogens to Alkenes

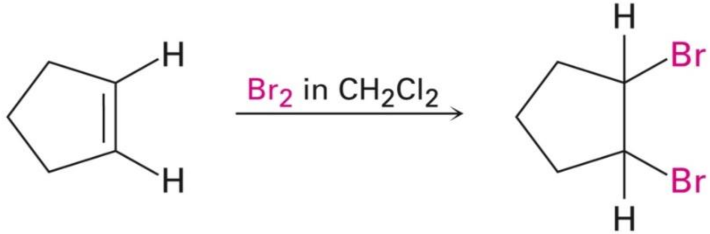
- Bromine and chlorine add to alkenes to give 1,2-dihaldes, an industrially important process
  - F_2 is too reactive and I_2 does not add
- Cl_2 reacts as Cl^+ Cl^-
- Br_2 is similar

Halogenation



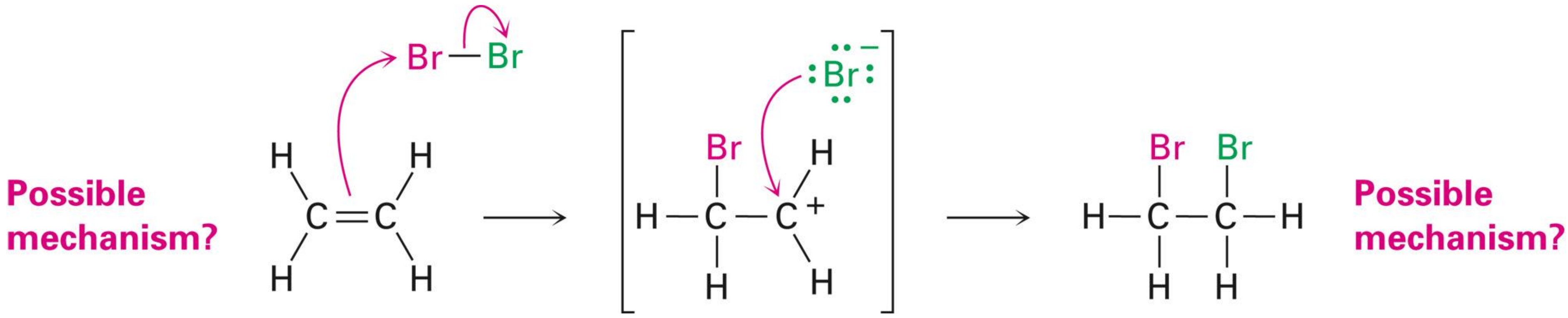
Ethylene

1,2-Dichloroethane (ethylene dichloride)



Cyclopentene

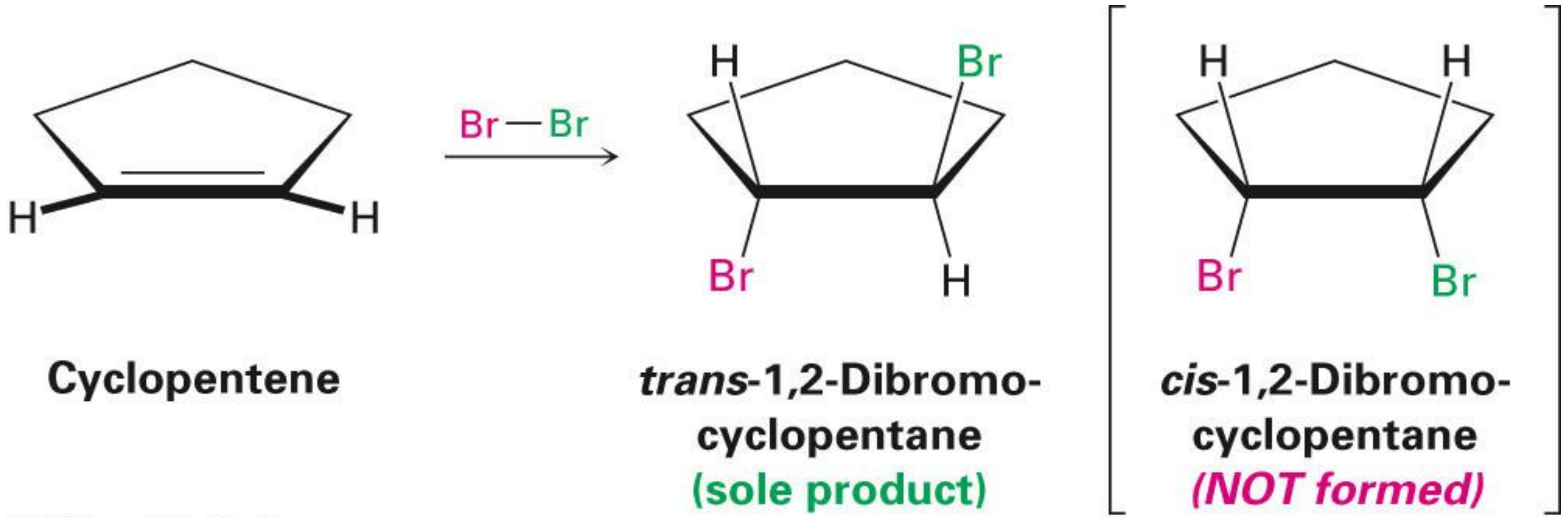
1,2-Dibromocyclopentane (95%)



- Although this mechanism looks reasonable, it’s not consistent with known facts because it doesn’t explain the stereochemical, or 3D, aspects of halogen addition

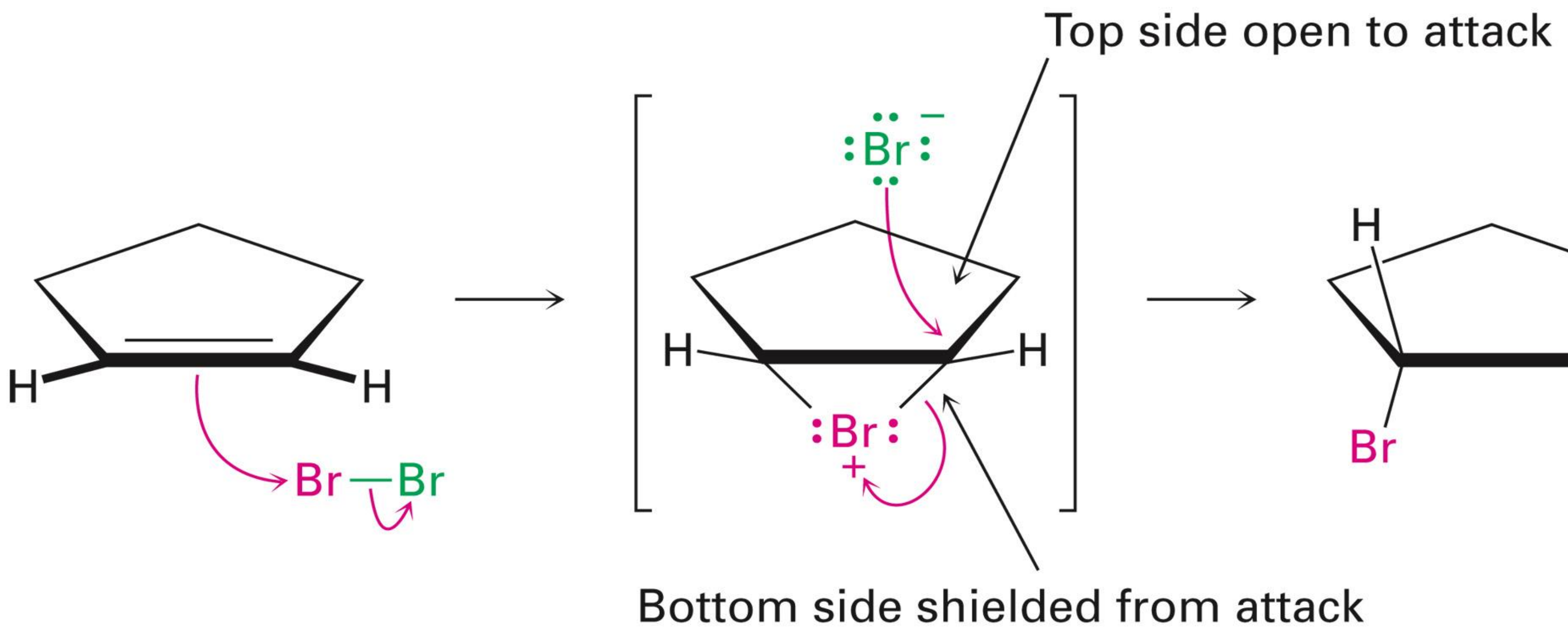
Addition of Br_2 to Cyclopentene

- **Addition is exclusively trans : anti stereochemistry**



Mechanism of Bromine Addition

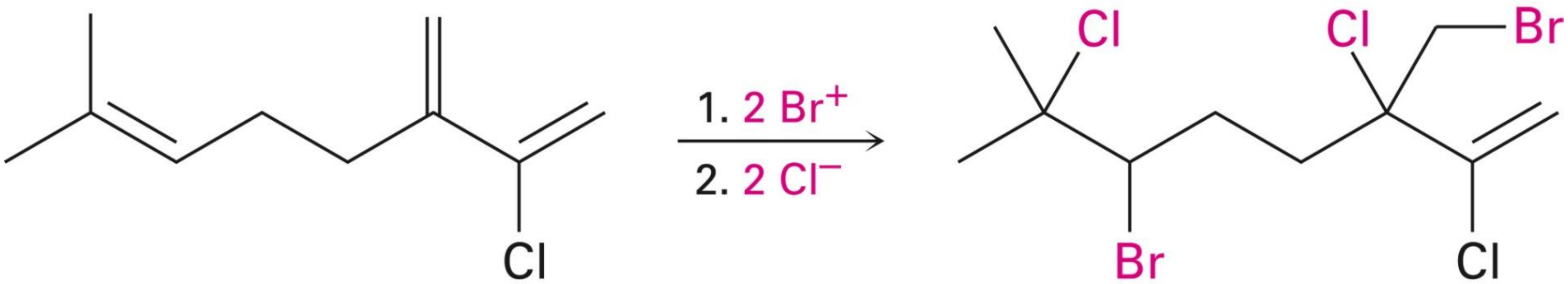
- Br^+ adds to an alkene producing a cyclic ion
- **Bromonium ion**, bromine shares charge with carbon
  - Gives trans addition



Cyclopentene **Bromonium ion intermediate** ***trans*-1,2-Dibromo-cyclopentane**

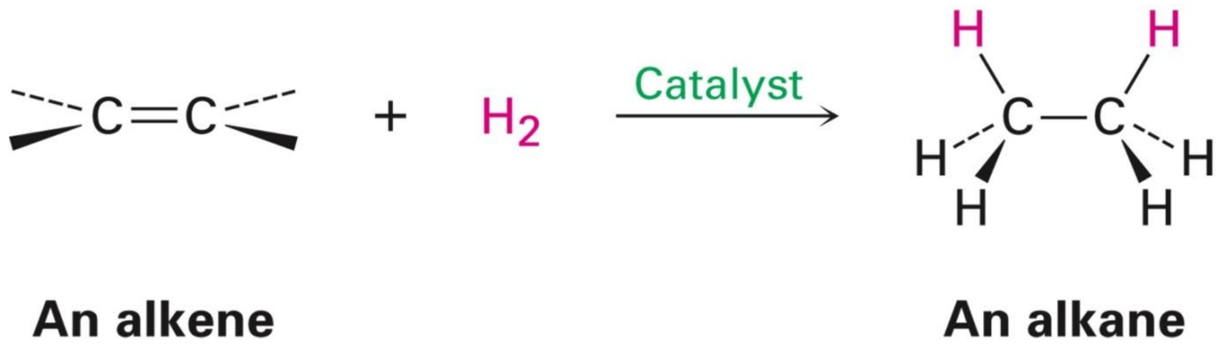
Figure 4.3 Mechanism of the addition of Br_2 to an alkene.

- Biological halogenation reaction
  - Carry out by enzymes called haloperoxidases



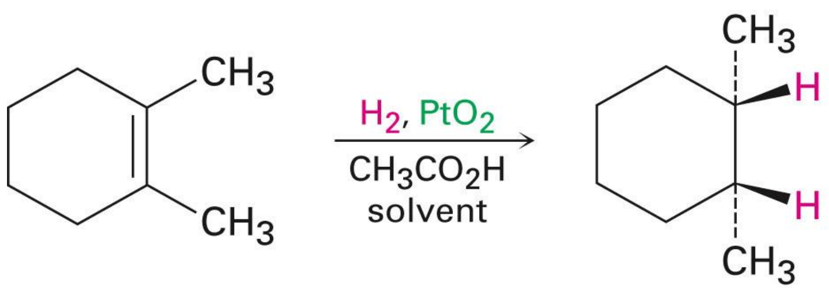
Halomon

4.5 Reduction of Alkenes: Hydrogenation



- Addition of H-H across C=C
- **Reduction** in general is addition of H_2 or removal of O from a molecule

- Requires Pt or Pd as powders on carbon and H_2
- Hydrogen is first adsorbed on catalyst
- Reaction is ***heterogeneous*** (process is not in solution)



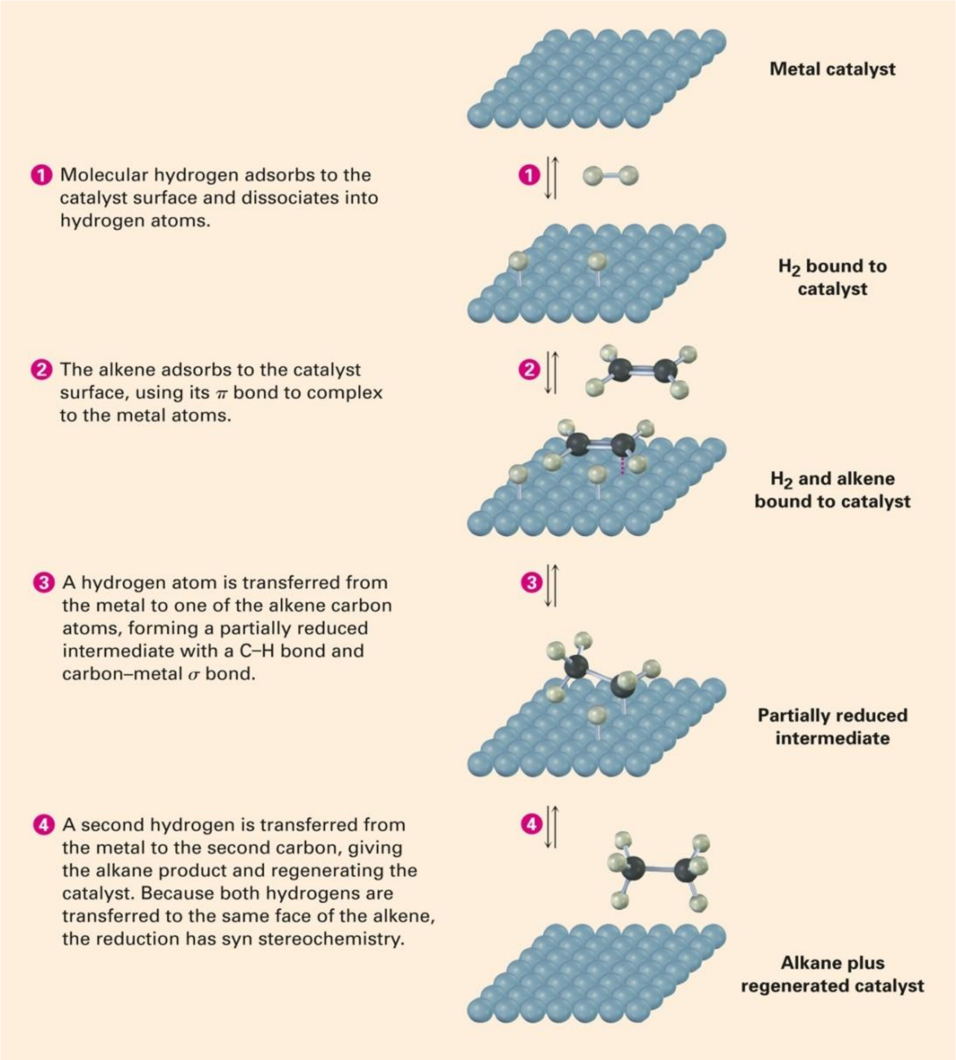
1,2-Dimethyl-cyclohexene

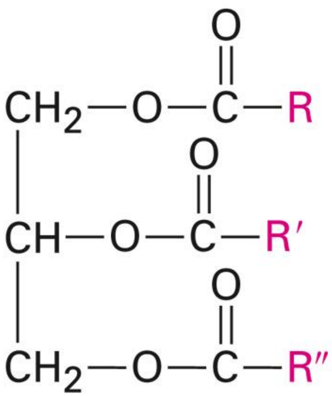
***cis*-1,2-Dimethyl-cyclohexane (82%)**

Mechanism of Catalytic Hydrogenation

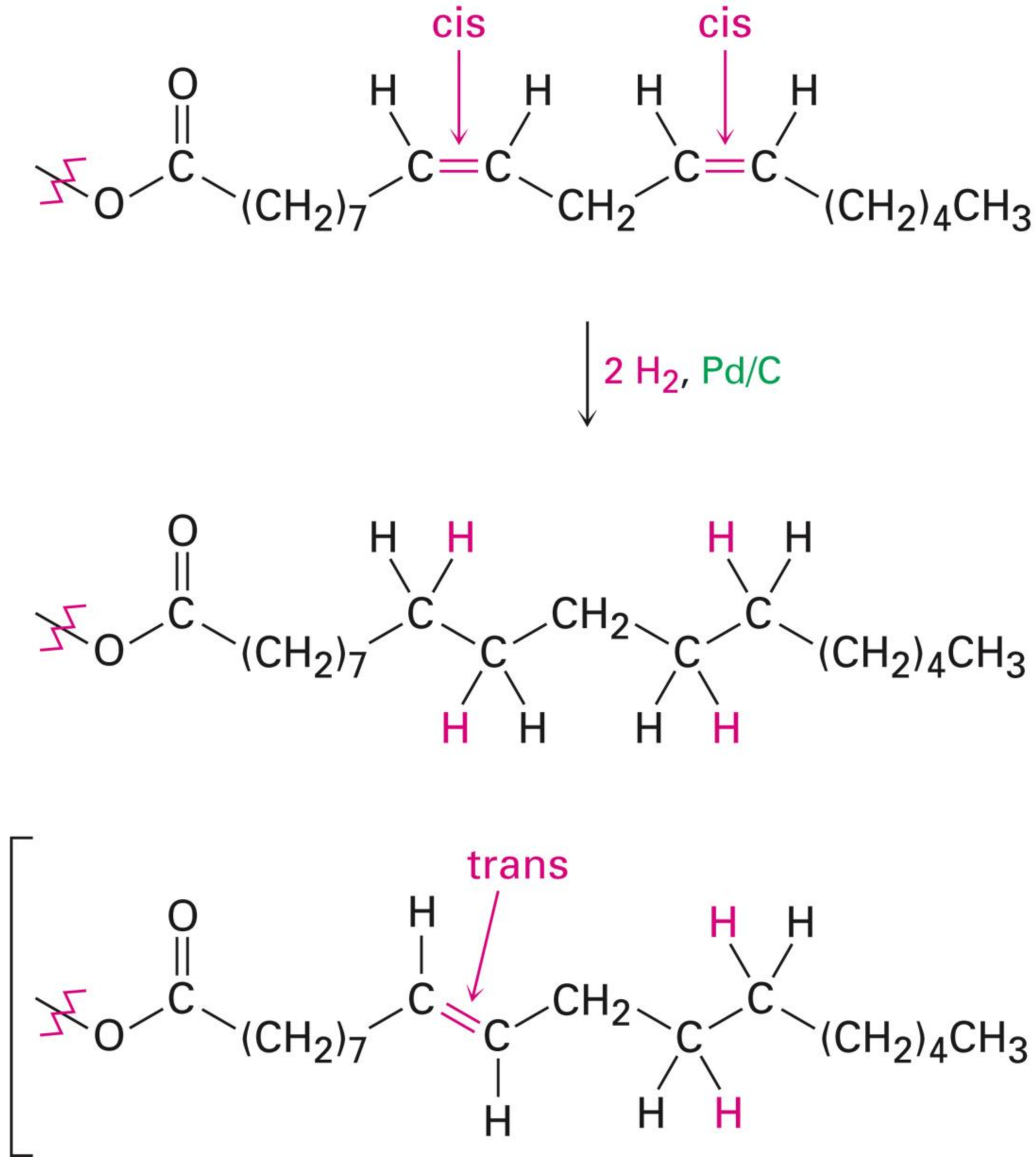
- Heterogeneous – reaction between phases
- Addition of H-H is **syn stereochemistry**

Figure 4.4 Mechanism of alkene hydrogenation.





A vegetable oil



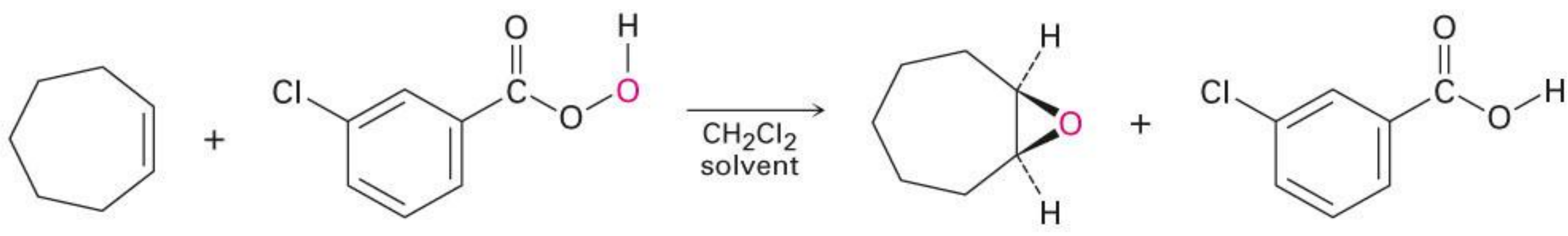
A polyunsaturated fatty acid in vegetable oil

A saturated fatty acid in margarine

A trans fatty acid

4.6 Oxidation of Alkenes: Epoxidation, Hydroxylation and Cleavage

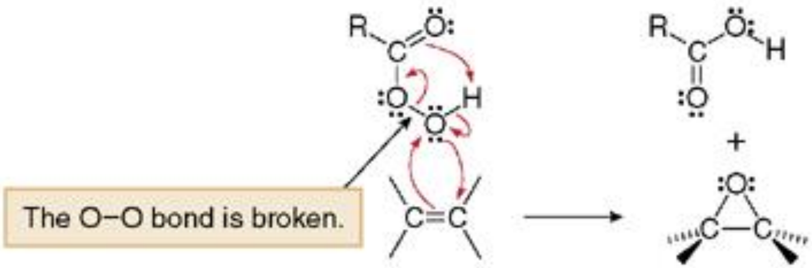
- Epoxidation results in a cyclic ether with an oxygen atom
- Stereochemistry of addition is syn
- Epoxide : oxirane



Cycloheptene | *meta*-Chloroperoxy-benzoic acid (mCPBA) | 1,2-Epoxy-cycloheptane | *meta*-Chloro-benzoic acid

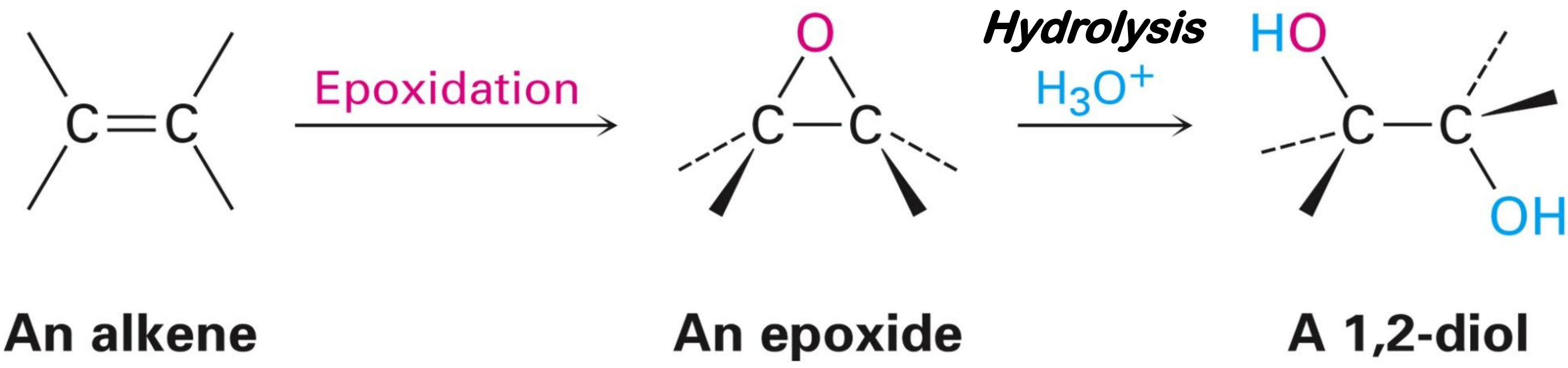
Mechanism: Epoxidation of an Alkene with a Peroxyacid

One step All bonds are broken or formed in a single step.

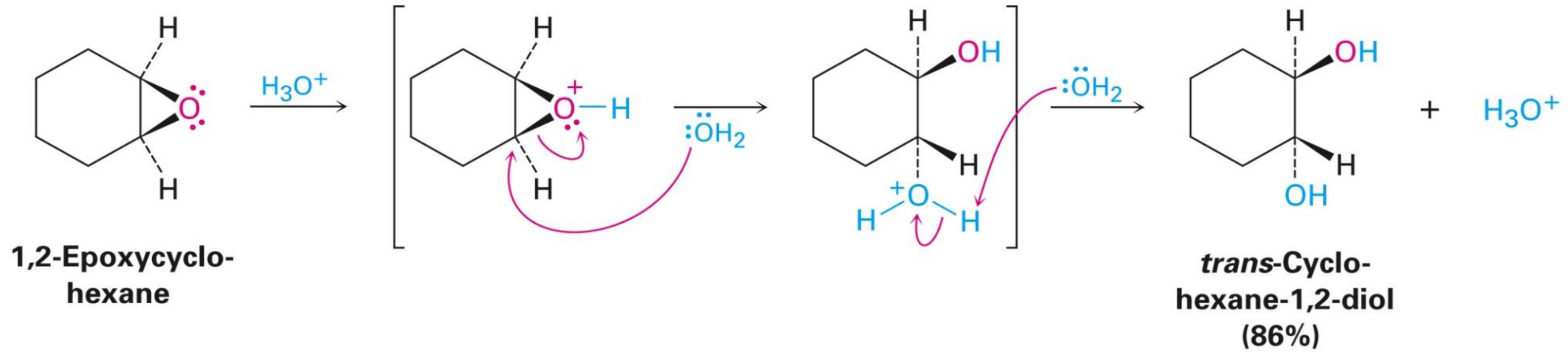


- Two C – O bonds are formed to one O atom with one electron pair from the peroxyacid and one from the π bond.
- The weak O – O bond is broken.

Acid catalyzed ring-opening reaction with water

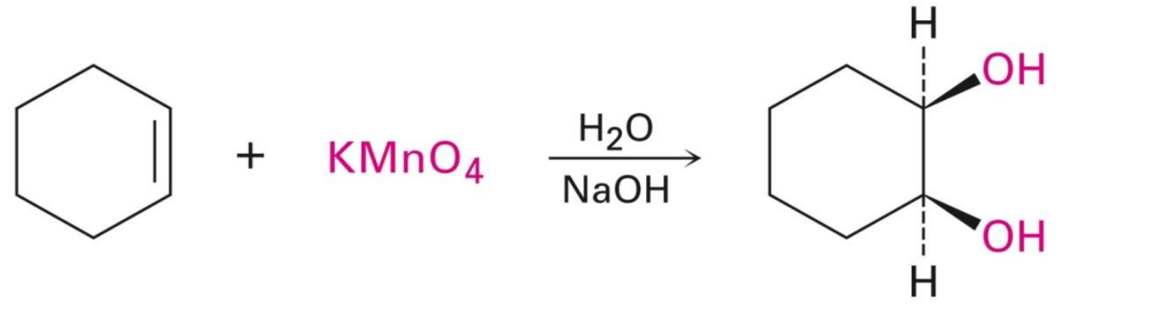


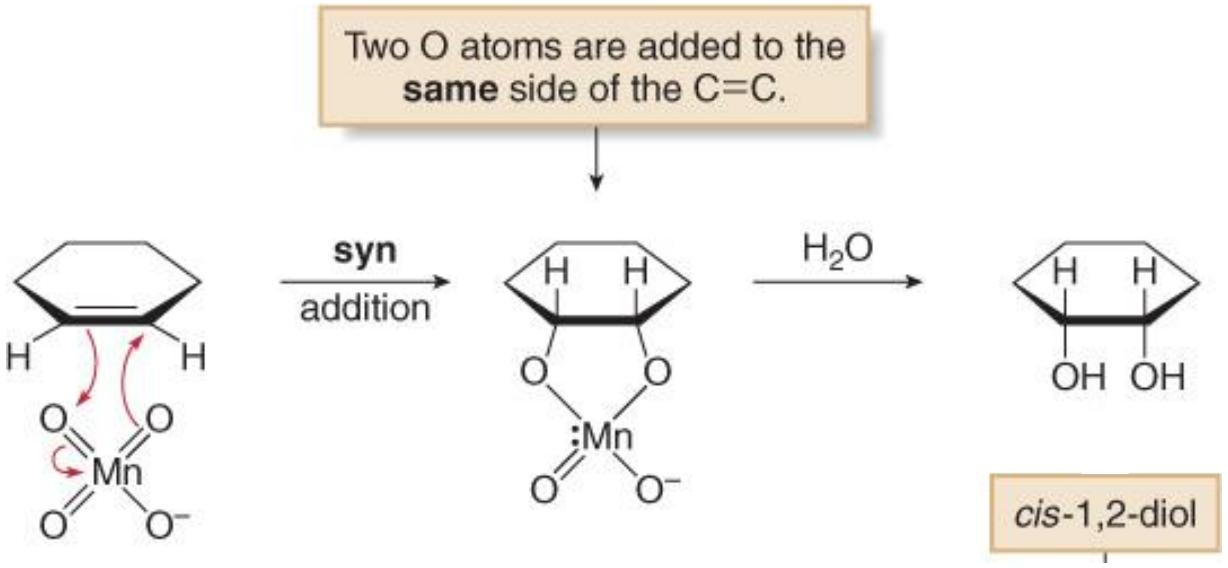
Hydroxylation



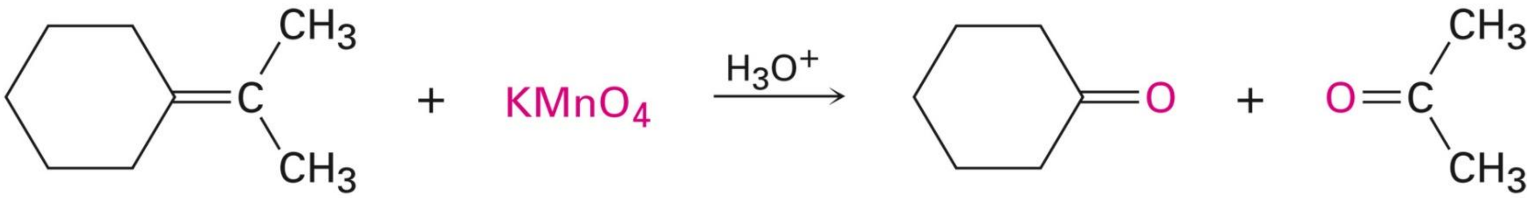
Reaction of the alkene with $KMnO_4$

- **Basic**



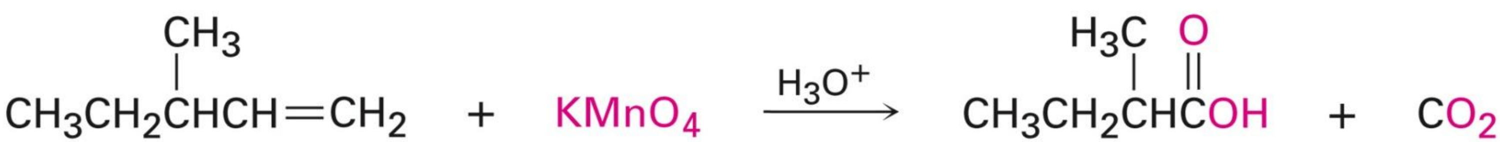


- **Acidic**



Isopropylidenecyclohexane **Cyclohexanone** **Acetone**

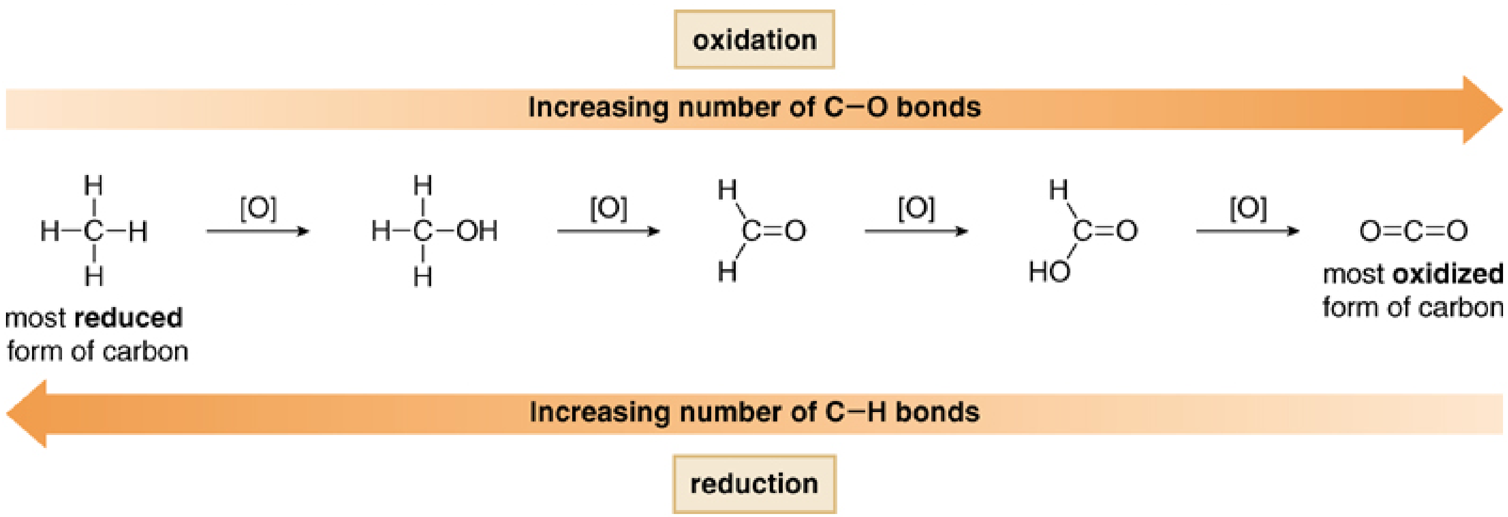
(two ketones)



3-Methylpent-1-ene **2-Methylbutanoic acid (45%)**

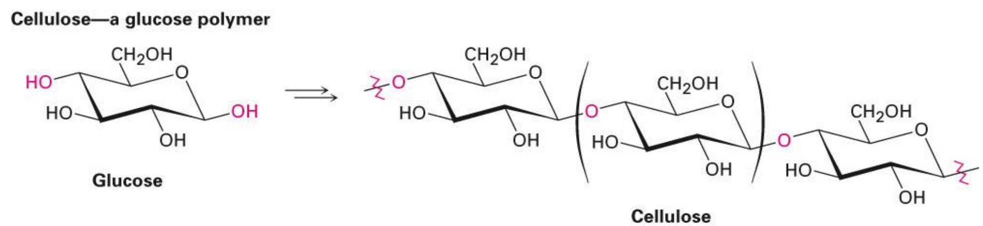
Oxidation and Reduction

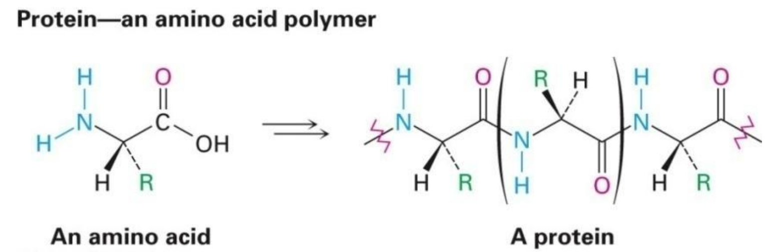
- *Oxidation* is the loss of electrons
- *Reduction* is the gain of electrons
- *Oxidation* results in an *increase* in the number of C—Z bonds; or *Oxidation* results in a *decrease* in the number of C—H bonds
- *Reduction* results in a *decrease* in the number of C—Z bonds; or *Reduction* results in an *increase* in the number of C—H bonds

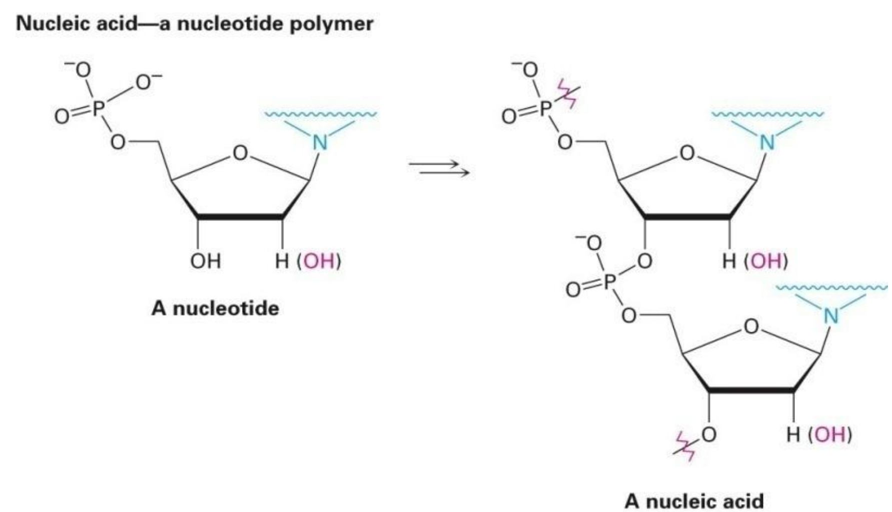


4.7 Addition of Radicals to Alkenes: Polymers

- A **polymer** is a very large molecule consisting of repeating units of simpler molecules (**monomers**), formed by *polymerization*





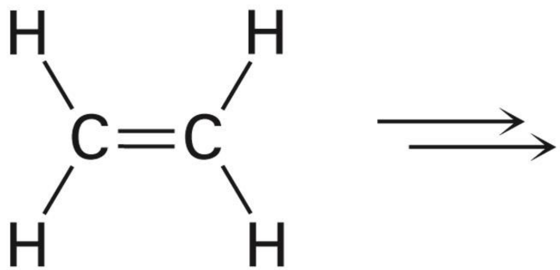


Biological polymers

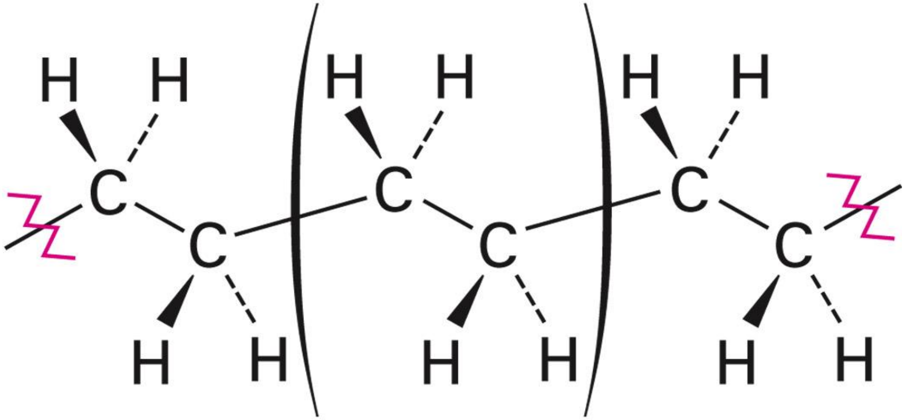
Free Radical Polymerization:

- **Alkenes react with radical catalysts to undergo radical polymerization**
  - **Ethylene is polymerized to polyethylene**

Polyethylene—a synthetic alkene polymer



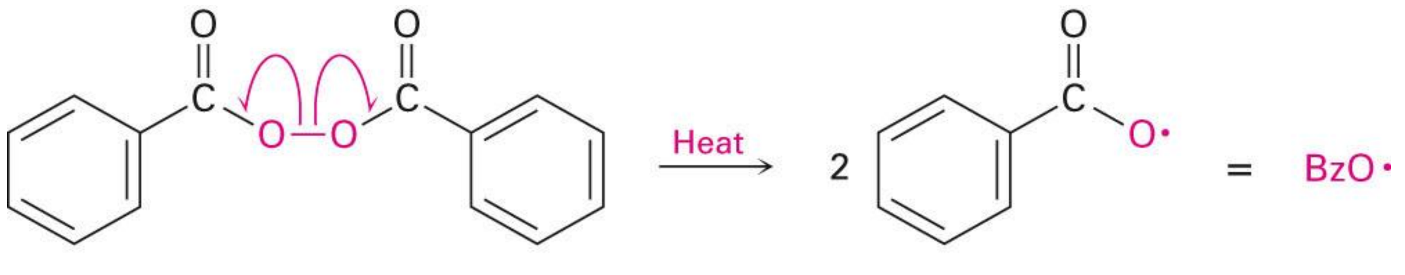
Ethylene



Polyethylene

Step 1: Initiation

- A few radicals are generated by the reaction of a molecule that readily forms radicals from a nonradical molecule
- A bond is broken *homolytically*

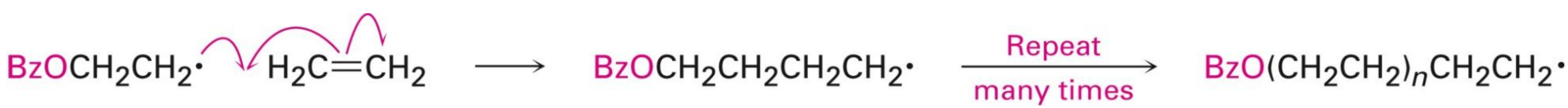


Benzoyl peroxide

Benzoyloxy radical

Step 2: Propagation

- Radical from initiation adds to alkene to generate alkene derived radical
- This radical adds to another alkene, and so on many times

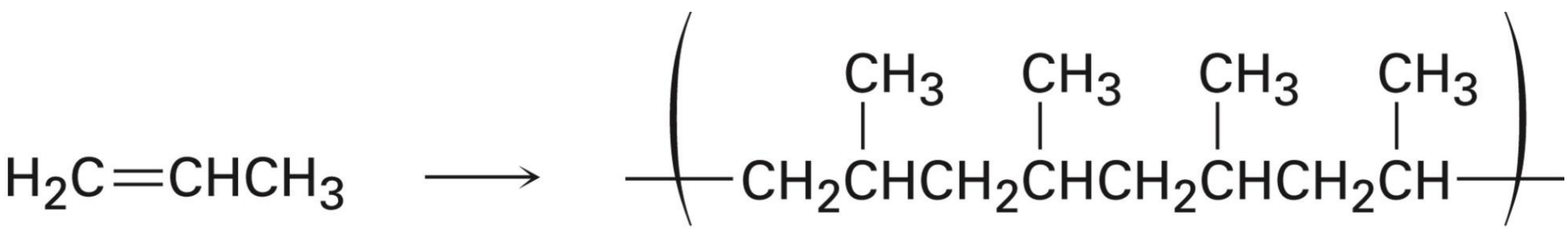


Step 3: Termination

- **Chain propagation ends when two radical chains combine**
- **Not controlled specifically but affected by reactivity and concentration**

$$2\ R{-}CH_2CH_2\cdot \longrightarrow R{-}CH_2CH_2CH_2CH_2{-}R$$

Vinyl monomers (substituted ethylenes)



Propylene **Polypropylene**

Table 4.1 **Some Alkene Polymers and Their Uses**

Monomer	Formula	Trade or common name of polymer	Uses
Ethylene	$H_2C{=}CH_2$	Polyethylene	Packaging, bottles
Propene (propylene)	$H_2C{=}CHCH_3$	Polypropylene	Moldings, rope, carpets
Chloroethylene (vinyl chloride)	$H_2C{=}CHCl$	Poly(vinyl chloride)	Insulation, films, pipes
		Tedlar	
Styrene	$H_2C{=}CHC_6H_5$	Polystyrene	Foam, moldings
Tetrafluoroethylene	$F_2C{=}CF_2$	Teflon	Gaskets, nonstick coatings
Acrylonitrile	$H_2C{=}CHCN$	Orlon, Acrilan	Fibers
Methyl methacrylate	$H_2C{=}C(CH_3)CO_2CH_3$	Plexiglas, Lucite	Paint, sheets, moldings
Vinyl acetate	$H_2C{=}CHOCOCH_3$	Poly(vinyl acetate)	Paint, adhesives, foams

4.8 Conjugated Dienes

Alternating single and double bond: conjugated

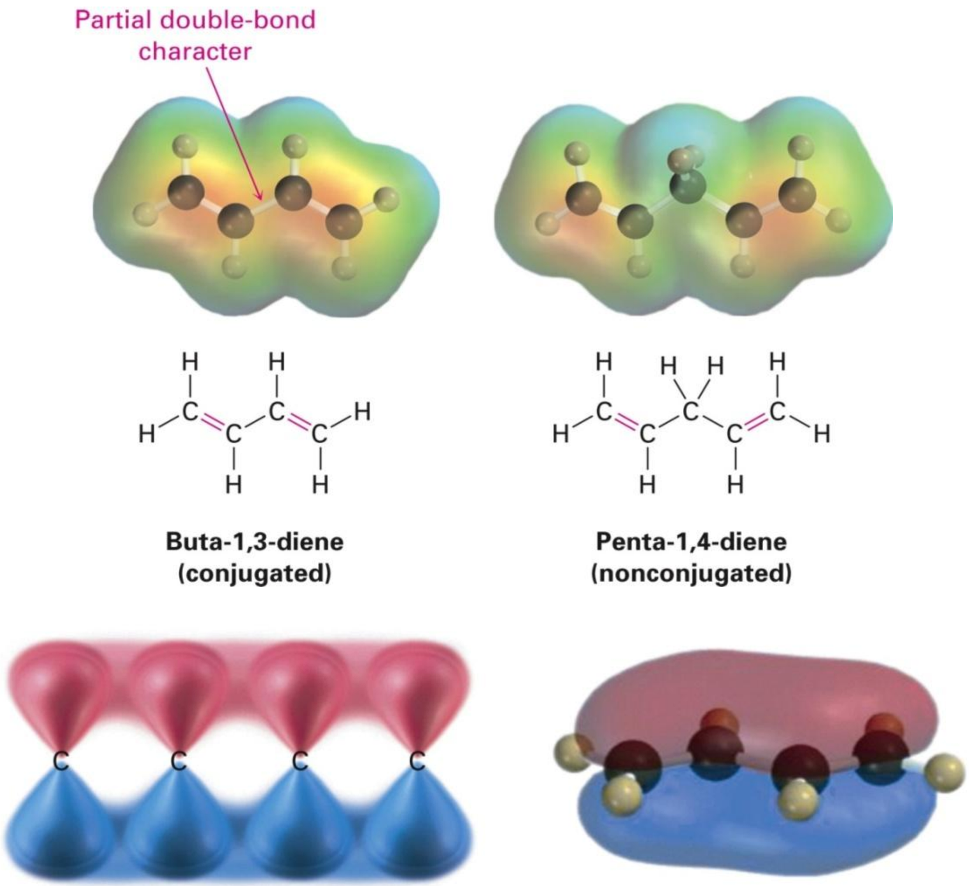
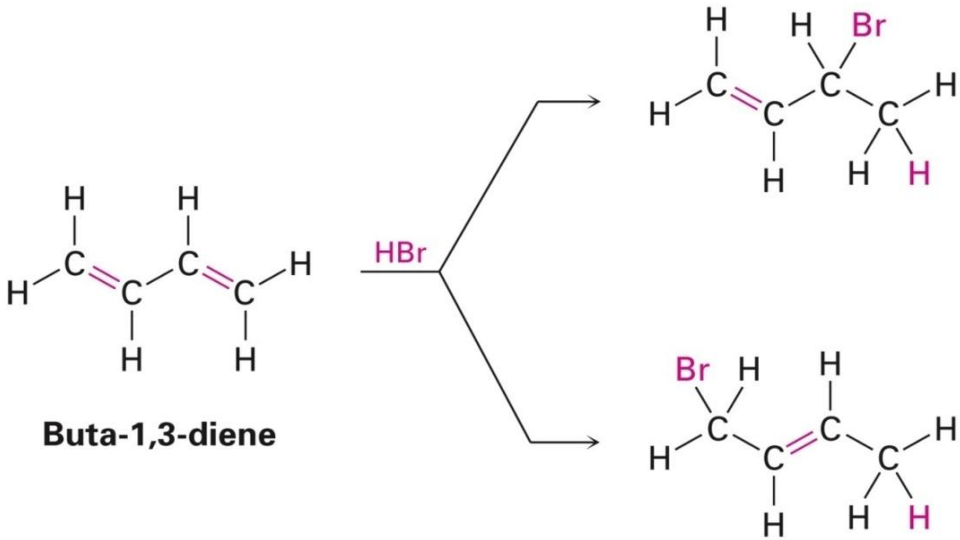


Figure 4.5 An orbital view of buta-1,3-diene.

1,2-addition vs. 1,4-addition

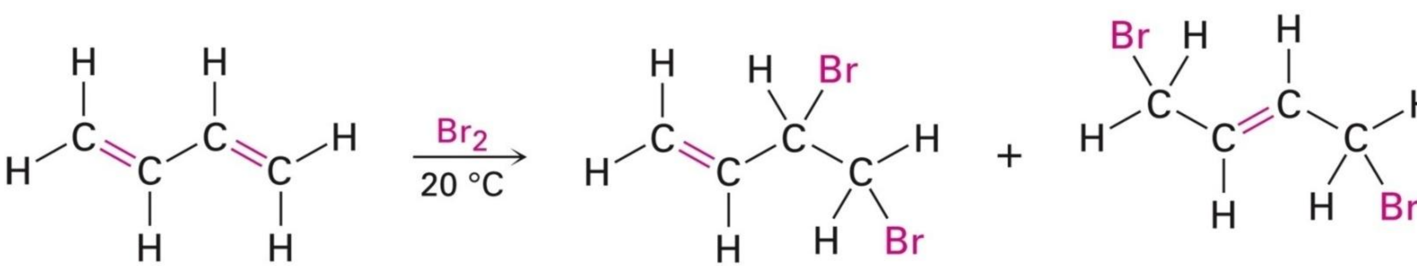


Buta-1,3-diene

3-Bromobut-1-ene
(71%; 1,2-addition)

Markovnikov's rule

1-Bromobut-2-ene
(29%; 1,4-addition)

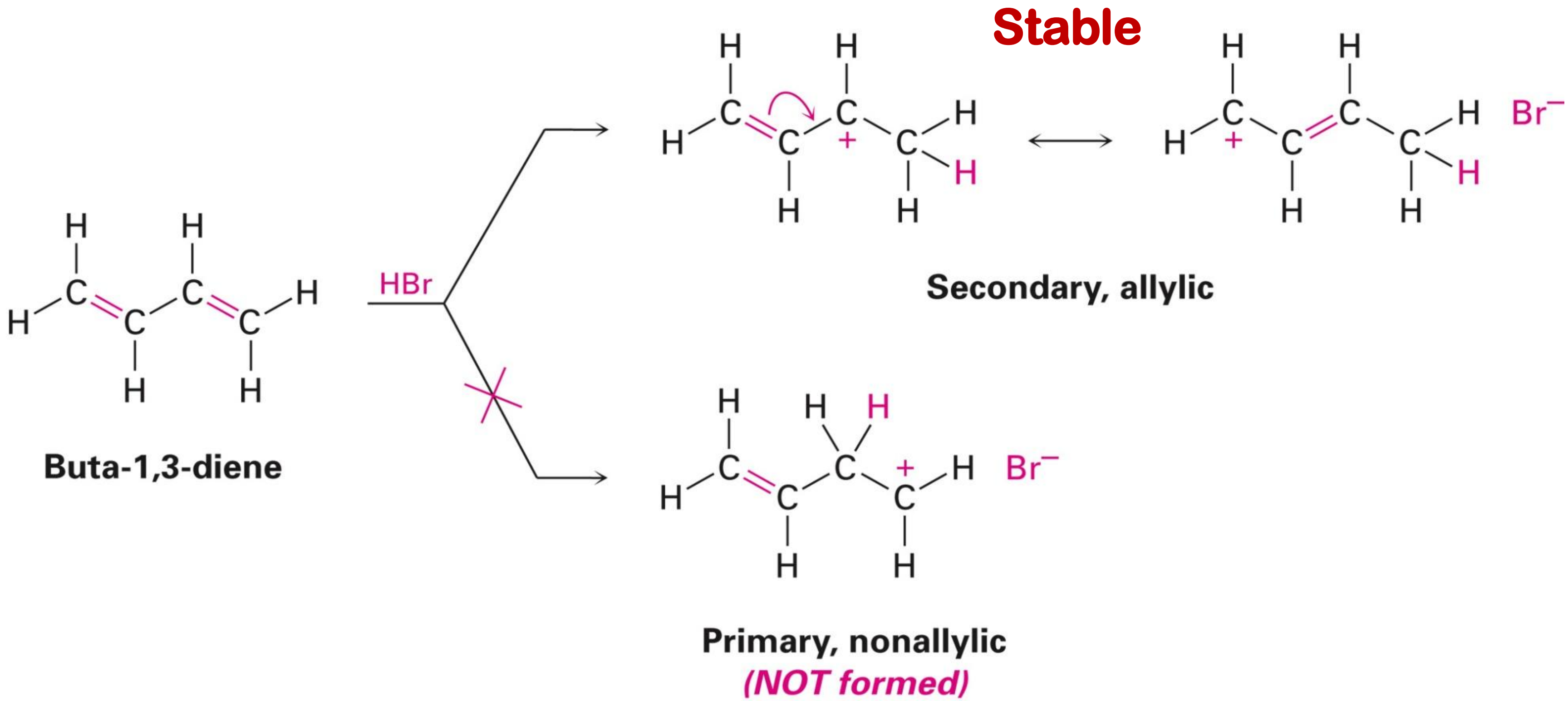


Buta-1,3-diene

3,4-Dibromobut-1-ene
(55%; 1,2-addition)

1,4-Dibromobut-2-ene
(45%; 1,4-addition)

Allylic carbocation intermediate



4.9 Stability of Allylic Carbocations: Resonance

- Some molecules are have structures that cannot be shown with a single representation
- In these cases we draw structures that contribute to the final structure but which differ in the position of the π bond(s) or lone pair(s)
- Such a structure is delocalized and is represented by **resonance forms**
- The resonance forms are connected by a double-headed arrow

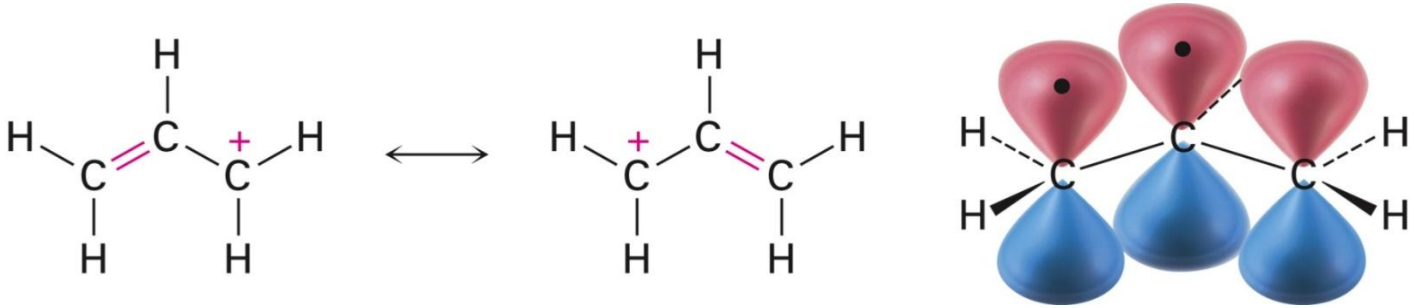
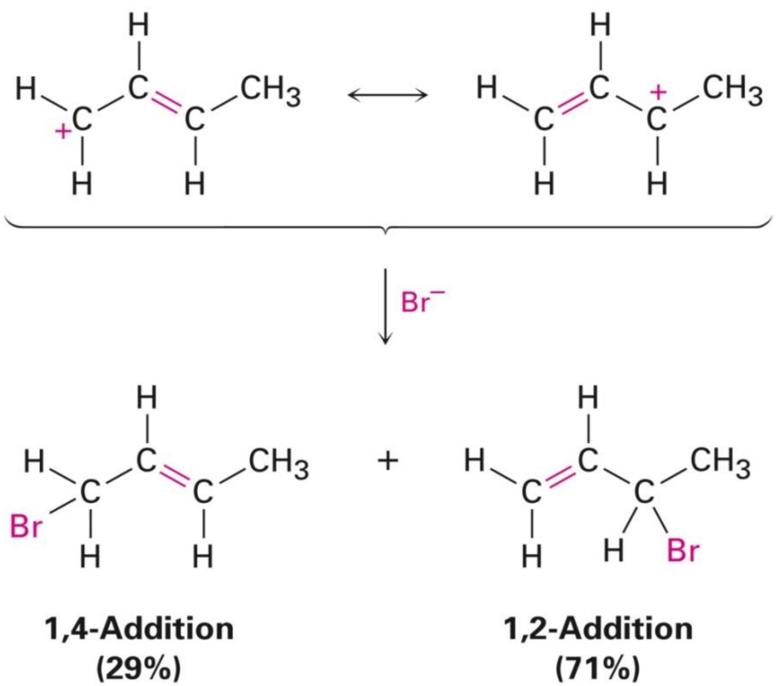
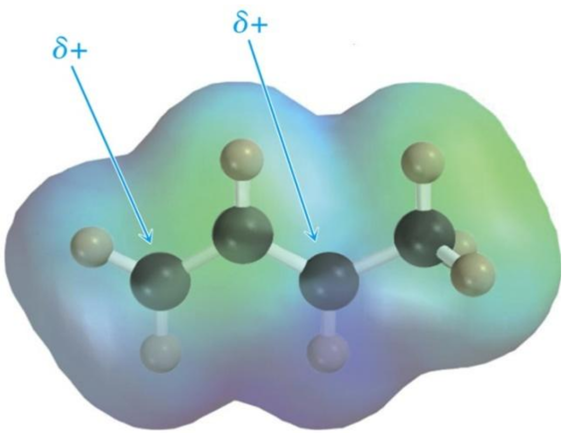
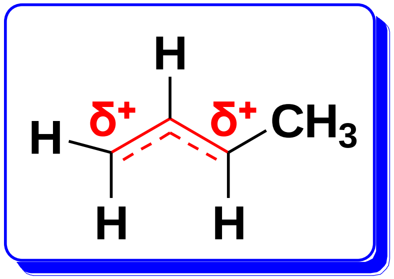


Figure 4.6 An orbital picture of an allylic carbocation.

- **A structure with resonance forms does not alternate between the forms**
- **Instead, it is a *hybrid* of the two resonance forms, so the structure is called a resonance hybrid**

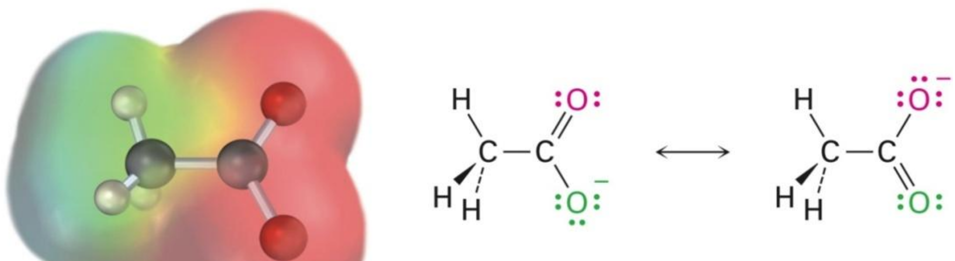






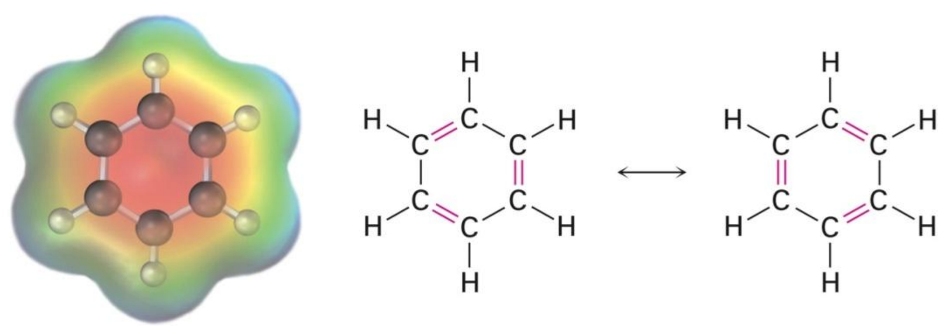
resonance *hybrid*

4.10 Drawing and Interpreting Resonance Forms



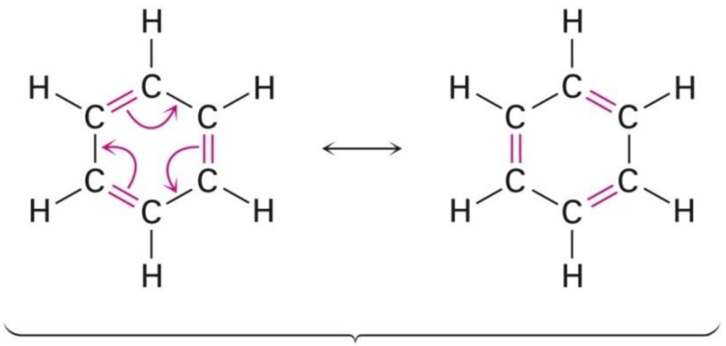
Acetate ion—two resonance forms

- As another example, benzene (C_6H_6) has two resonance forms with alternating double and single bonds
  - In the resonance hybrid, the actual structure, all its C-C bonds are equivalent, midway between double and single

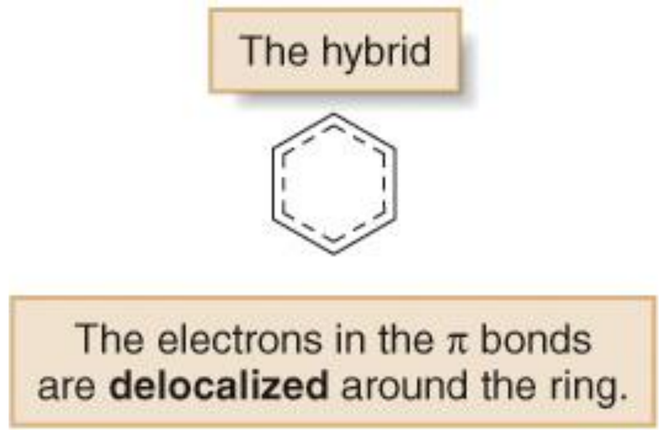


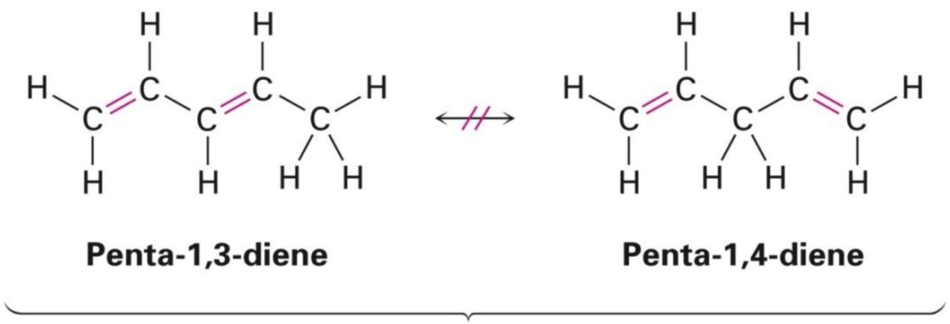
Benzene (two resonance forms)

- **Individual resonance forms are imaginary, not real** - the real structure is a hybrid (only by knowing the contributors can you visualize the actual structure)
- **Resonance forms differ only in the placement of their π or nonbonding electrons**



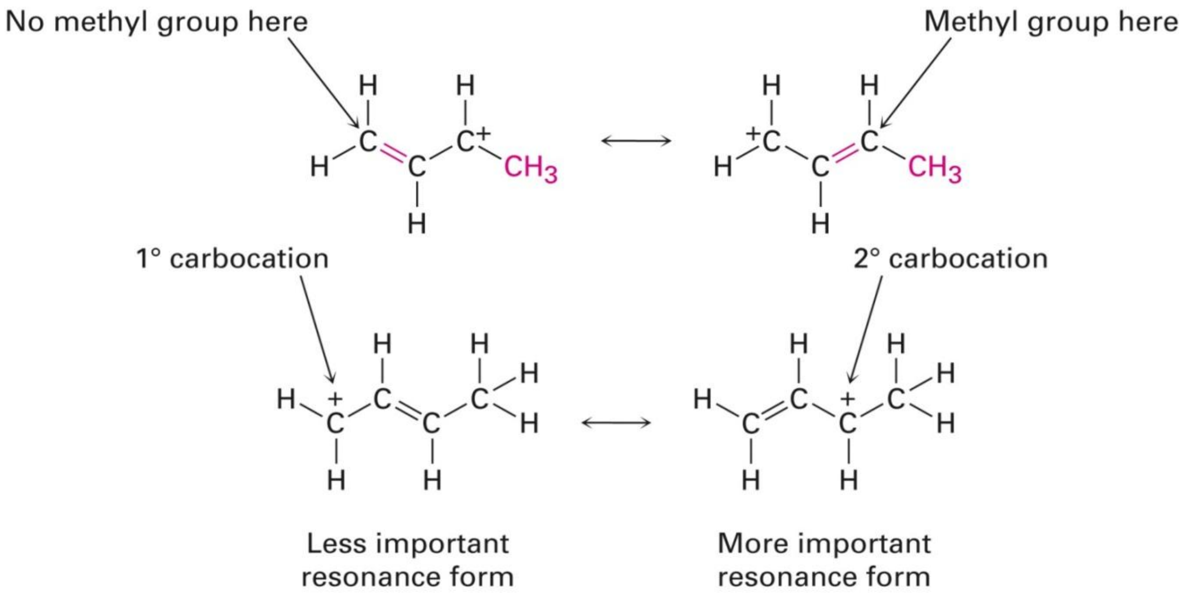
Benzene—two resonance forms



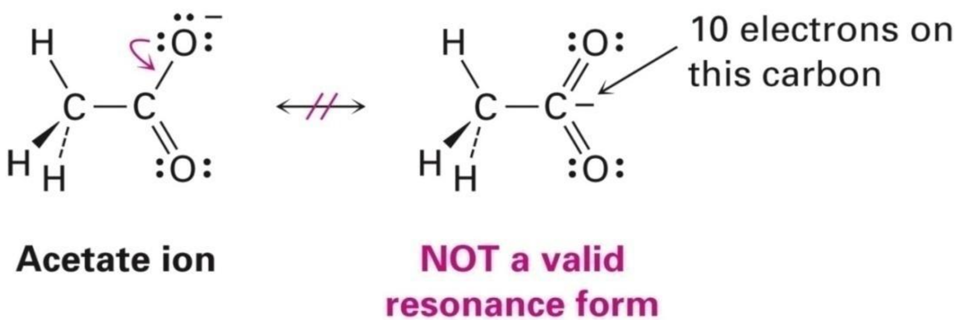


Constitutional isomers

- **Different resonance forms of a substance don't have to be equivalent**



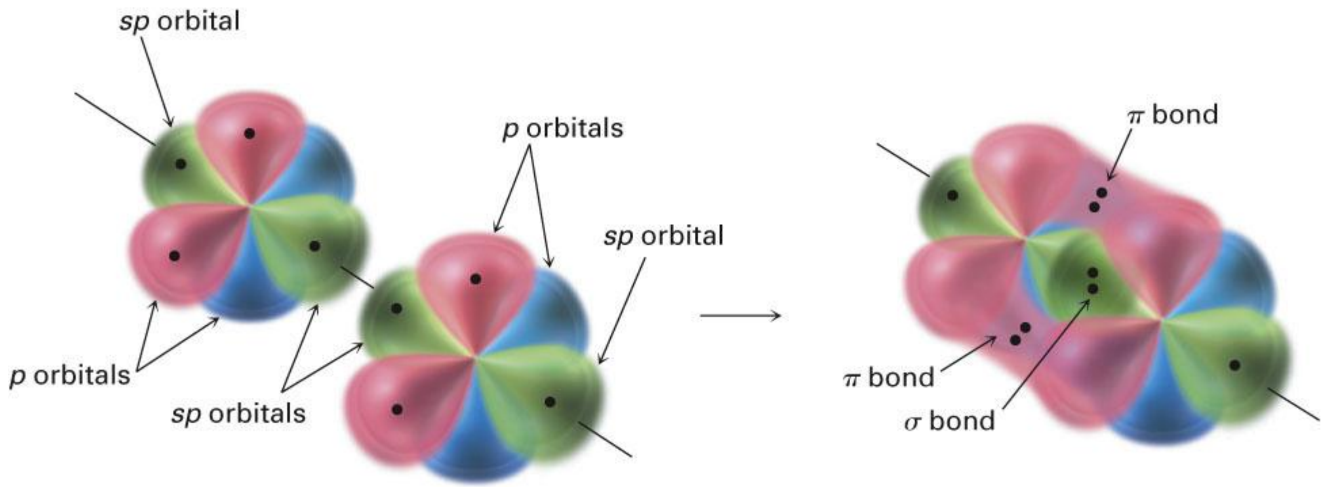
- **Resonance forms must be valid Lewis structures**: the octet rule applies



- **The resonance hybrid is more stable** than any individual resonance form would be

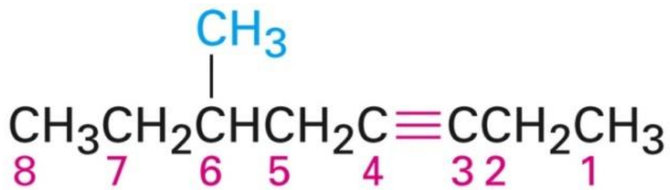
4.11 Alkynes and Their Reactions

- Carbon-carbon triple bond results from sp orbital on each C forming a sigma bond and unhybridized p_X and p_y orbitals forming π bonds (C_nH_{2n-2})
- The remaining sp orbitals form bonds to other atoms at 180° to C-C triple bond



Carbon–carbon triple bond

- General hydrocarbon rules apply with "-*yne*" as a suffix indicating an alkyne
- Numbering of chain with triple bond is set so that the smallest number possible for the first carbon of the triple bond



Begin numbering at the end nearer the triple bond.

6-Methyloct-3-yne

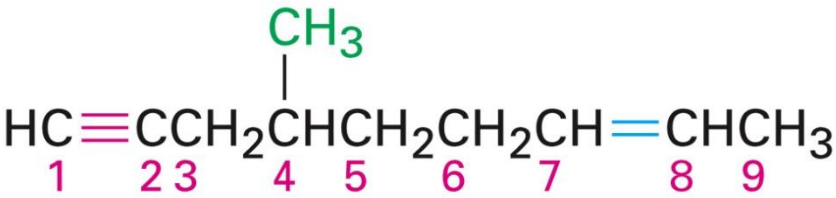
(Old name: 6-Methyl-3-octyne)

Double & Triple bonds: enyne

- **Numbering of the hydrocarbon chain starts from the end nearer the first multiple bond, whether double or triple**
- **If there is a choice in numbering, double bonds receive lower numbers than triple bonds**

Hept-1-en-6-yne

(Old name: 1-Hepten-6-yne)

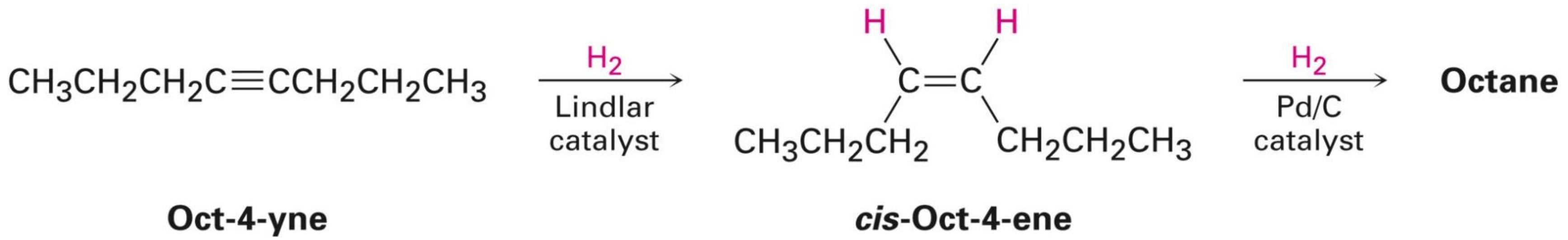


4-Methylnon-7-en-1-yne

(Old name: 4-Methyl-7-nonen-1-yne)

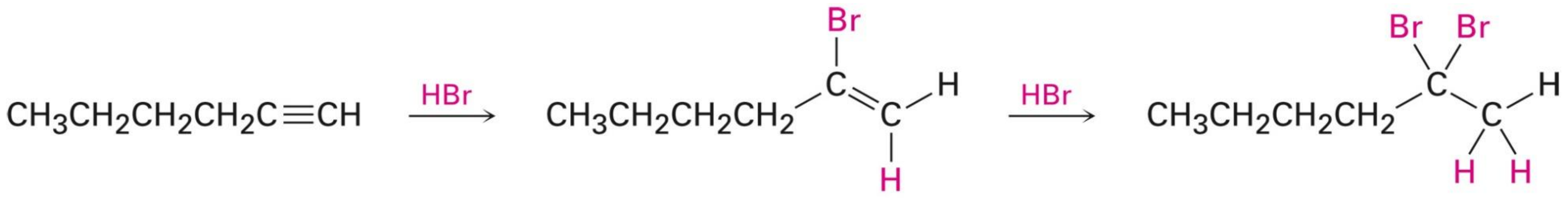
Alkyne Reactions : Addition of H_2

- Addition of H_2 over a metal catalyst (such as palladium on carbon, Pd/C) converts alkynes to alkanes (complete reduction)
- Addition of H_2 using chemically deactivated palladium on calcium carbonate as a catalyst (the ***Lindlar catalyst***) produces a cis alkene
- The two hydrogens add ***syn*** (from the same side of the triple bond)



Alkyne Reactions : Addition of HX

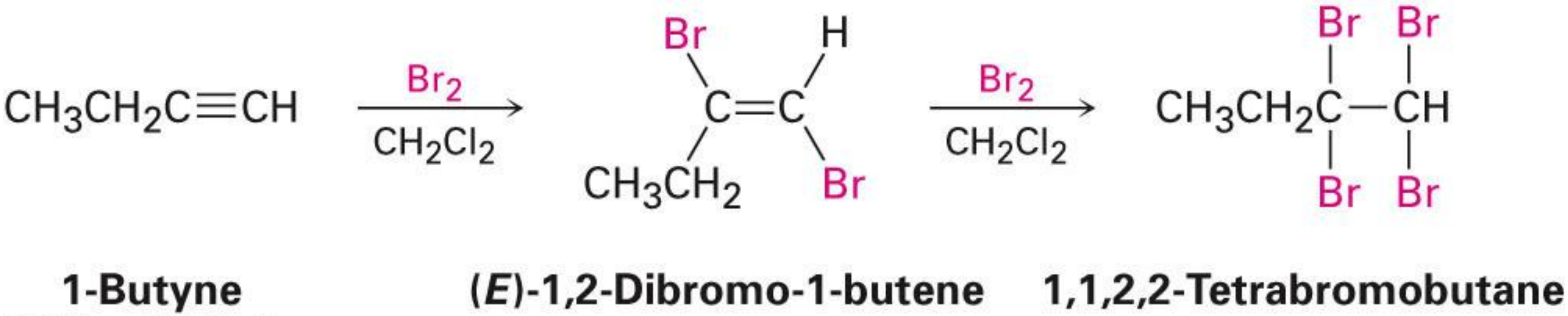
- **Addition reactions of alkynes are similar to those of alkenes**
- **Intermediate alkene reacts further with excess reagent**
- **Regiospecificity according to *Markovnikov's rule***



Hex-1-yne **2-Bromohex-1-ene** **2,2-Dibromohexane**

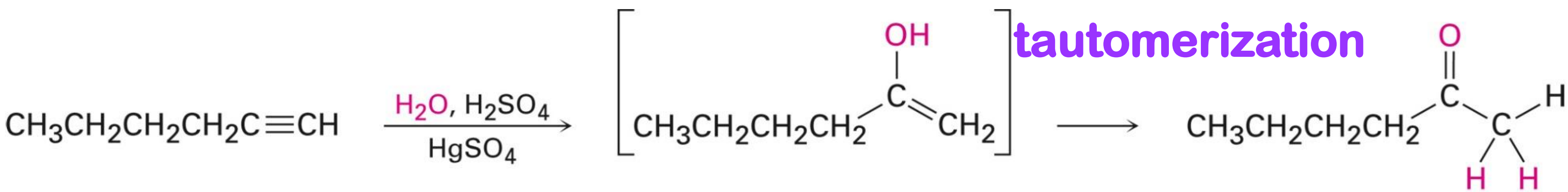
Alkyne Reactions : Addition of X_2

- **Initial addition gives *trans* intermediate**
- **Product with excess reagent is tetrahalide**

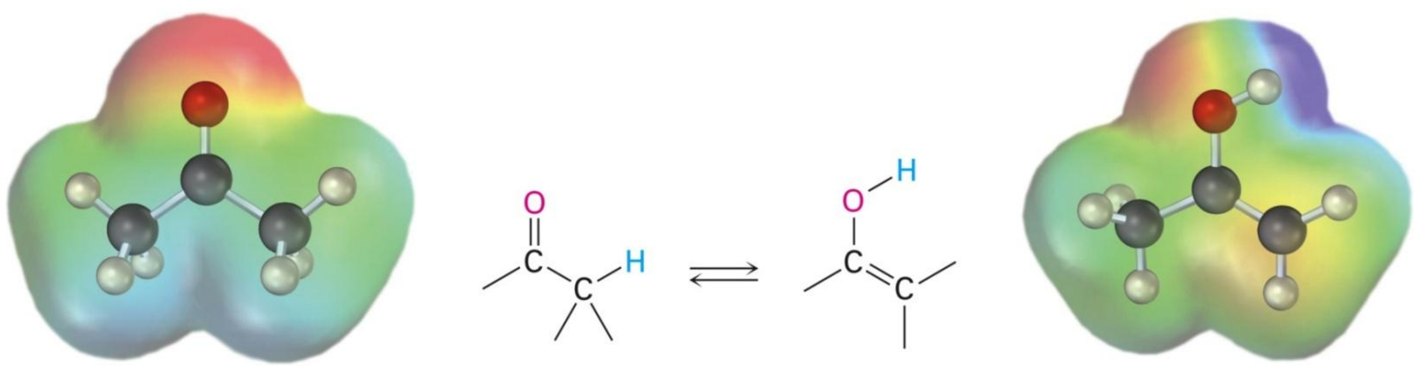


Alkyne Reactions : Addition of H_2O

- Addition of H-OH as in alkenes
  - Mercury (II) catalyzes ***Markovinikov's*** oriented addition

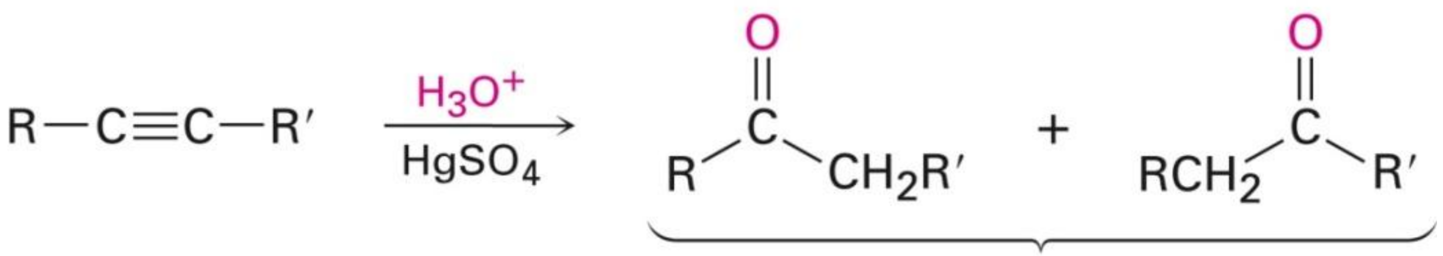


Hex-1-yne   An enol   Hexan-2-one (78%)



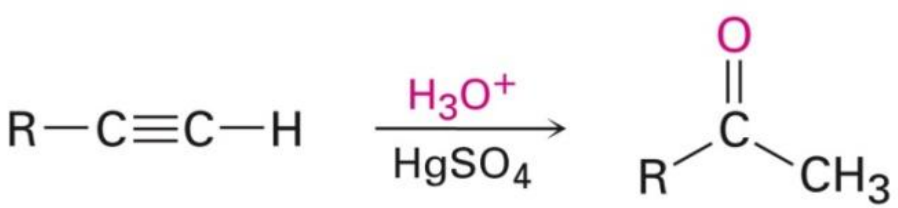
Keto tautomer   Enol tautomer

An internal alkyne



Mixture

A terminal alkyne

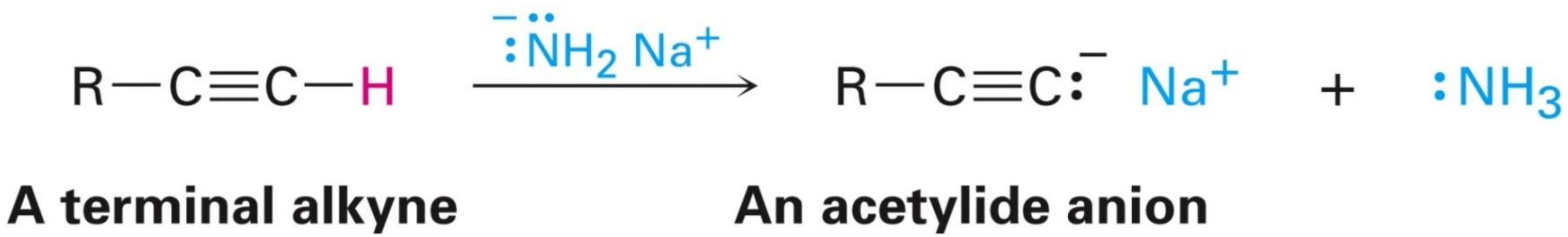


A methyl ketone

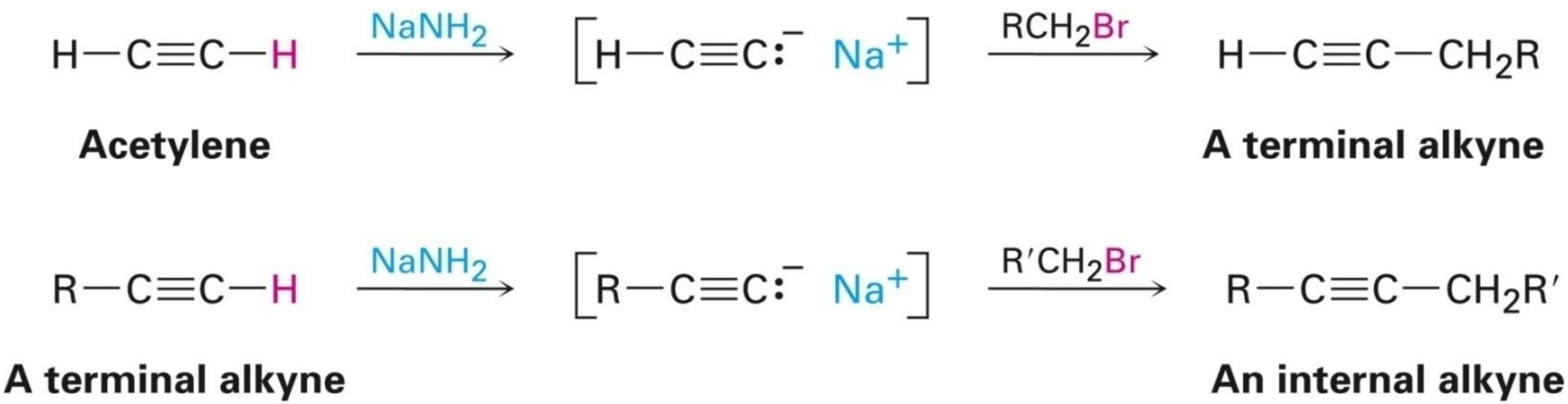
A single product

Alkyne Reactions: Formation of Acetylide Anions

- Terminal alkynes are weak Brønsted acids (alkenes and alkanes are much less acidic (pK_a ~ 25))
- Reaction of strong anhydrous bases with a terminal acetylene produces an **acetylide ion**



- Reaction with a ***primary alkyl halide*** **produces a hydrocarbon that contains carbons from both partners**



Natural Rubber