



Chapter 4

Reactions of Alkenes and Alkynes

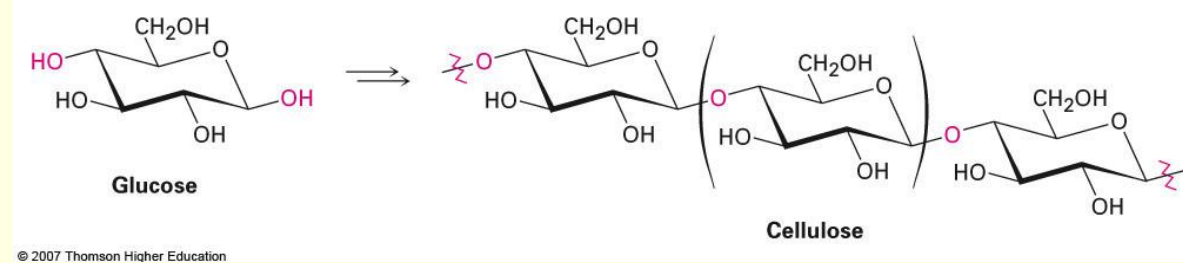
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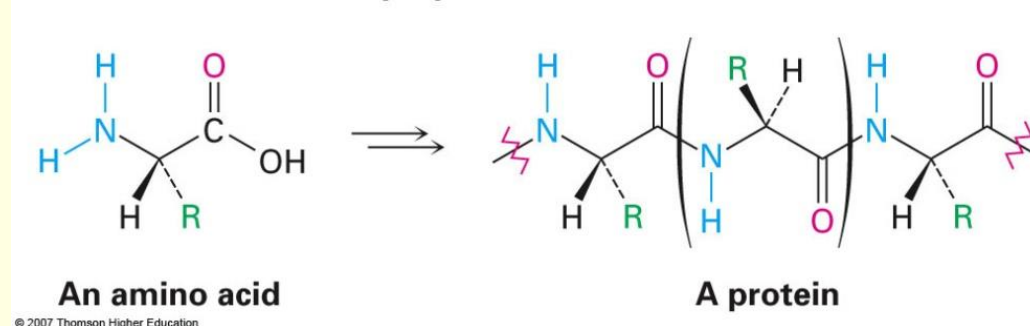
4.7 Addition of Radicals to Alkenes: Polymers

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

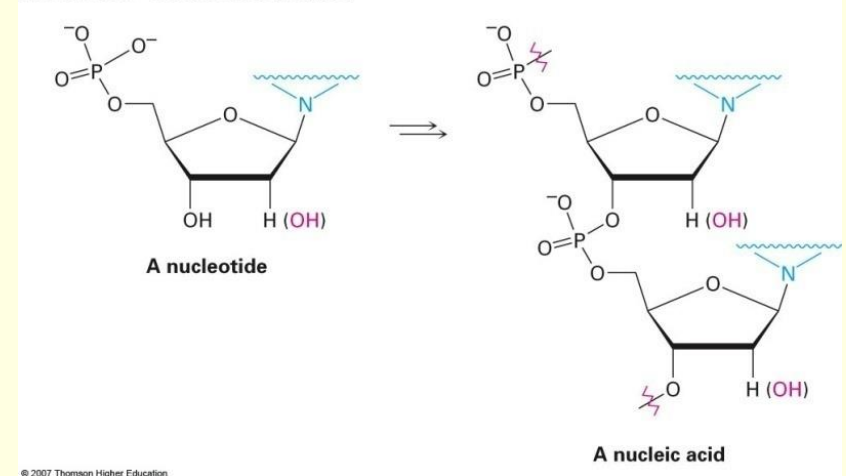
Cellulose—a glucose polymer



Protein—an amino acid polymer



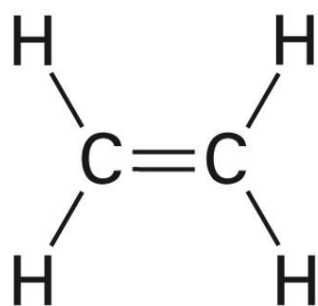
Nucleic acid—a nucleotide polymer



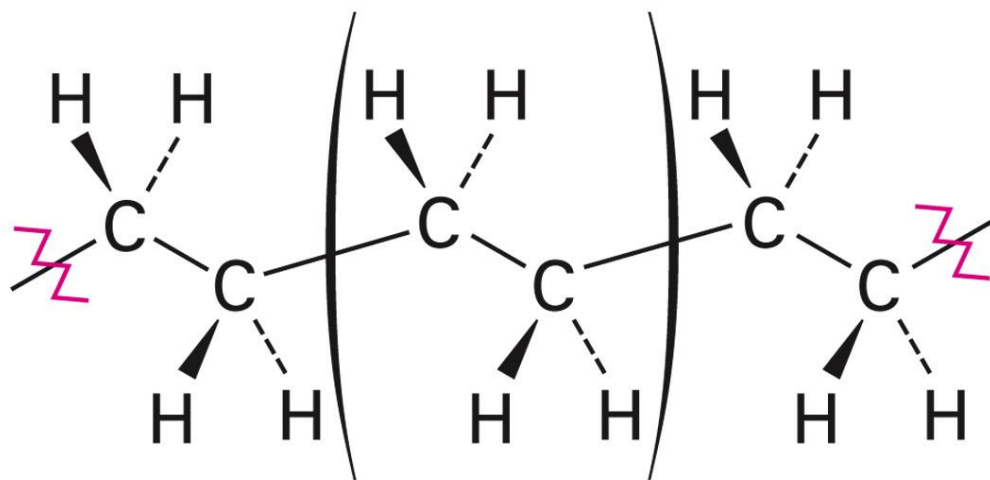
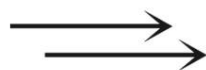
Free Radical Polymerization: Alkenes react with radical catalysts to undergo radical polymerization.

- Ethylene is polymerized to polyethylene.

Polyethylene—a synthetic alkene polymer

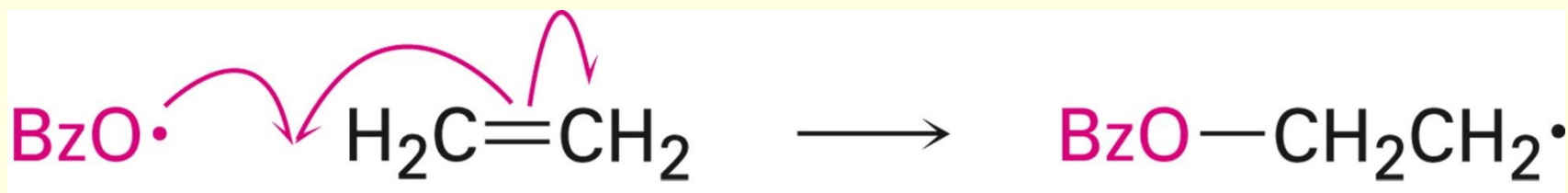
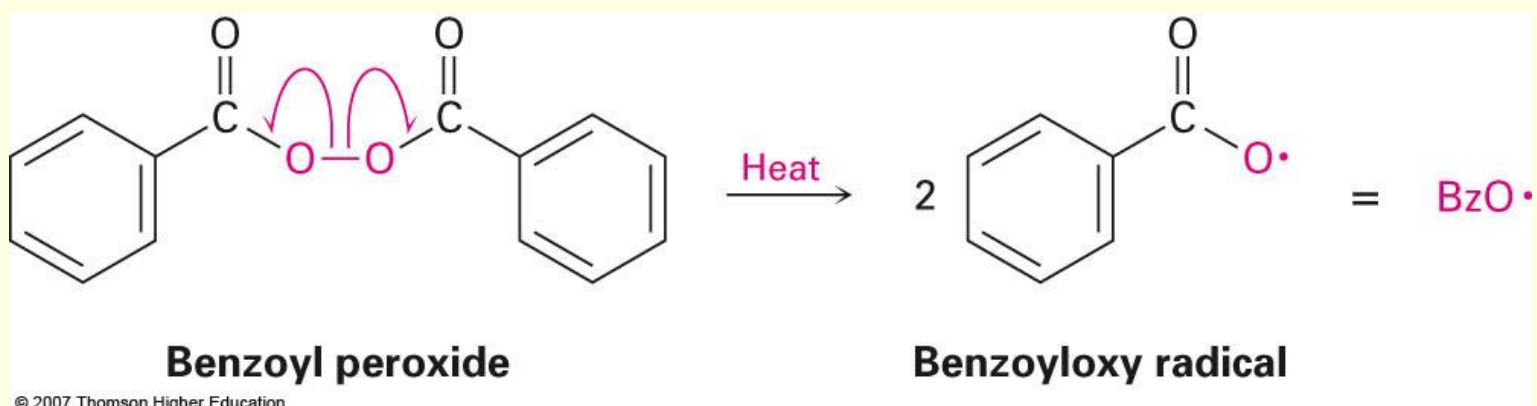


Ethylene



Polyethylene

- **Step 1: Initiation** - a few radicals are generated by the reaction of a molecule that readily **forms radicals** from a nonradical molecule

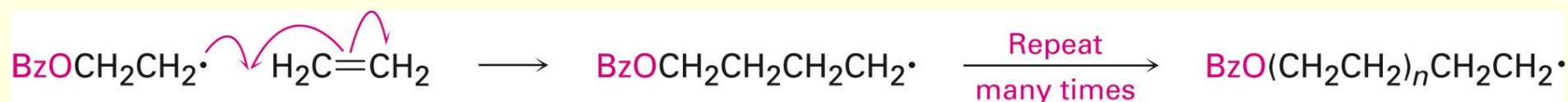


A benzoyloxy radical then adds to the C=C bond of ethylene to generate a **carbon radical**.

One electron from the carbon-carbon double bond pairs up with the odd electron on the benzoyloxy radical to form a C-O bond, and the other electron remains on carbon.

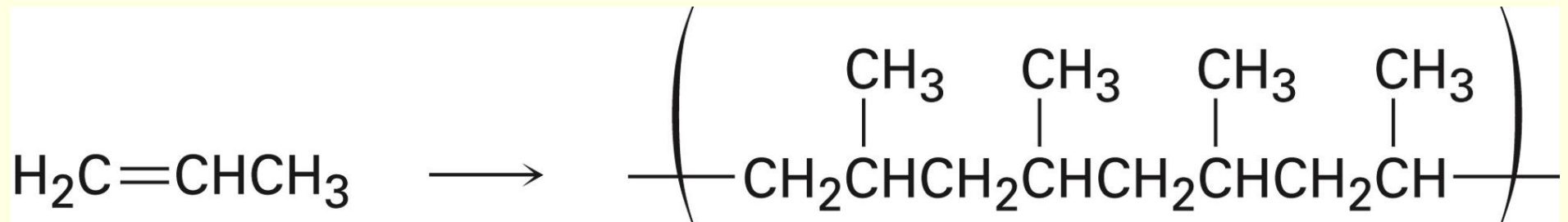
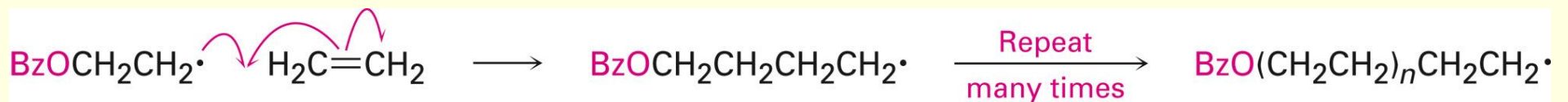
Step 2: Propagation

- 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



Propylene

Polypropylene

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

Monomer	Formula	Trade or common name of polymer	Uses
Ethylene	$\text{H}_2\text{C}=\text{CH}_2$	Polyethylene	Packaging, bottles
Propene (propylene)	$\text{H}_2\text{C}=\text{CHCH}_3$	Polypropylene	Moldings, rope, carpets
Chloroethylene (vinyl chloride)	$\text{H}_2\text{C}=\text{CHCl}$	Poly(vinyl chloride) Tedlar	Insulation, films, pipes
Styrene	$\text{H}_2\text{C}=\text{CHC}_6\text{H}_5$	Polystyrene	Foam, moldings
Tetrafluoroethylene	$\text{F}_2\text{C}=\text{CF}_2$	Teflon	Gaskets, nonstick coatings
Acrylonitrile	$\text{H}_2\text{C}=\text{CHCN}$	Orlon, Acrilan	Fibers
Methyl methacrylate	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_2\text{C}=\text{CCO}_2\text{CH}_3 \end{array}$	Plexiglas, Lucite	Paint, sheets, moldings
Vinyl acetate	$\text{H}_2\text{C}=\text{CHOCOCH}_3$	Poly(vinyl acetate)	Paint, adhesives, foams

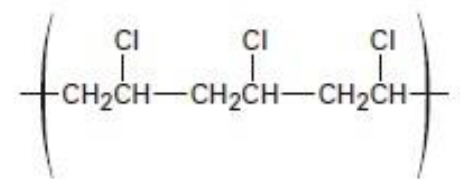
Worked Example 4.4

Predicting the Structure of a Polymer

Show the structure of poly(vinyl chloride), a polymer made from $\text{H}_2\text{C}=\text{CHCl}$, by drawing several repeating units.

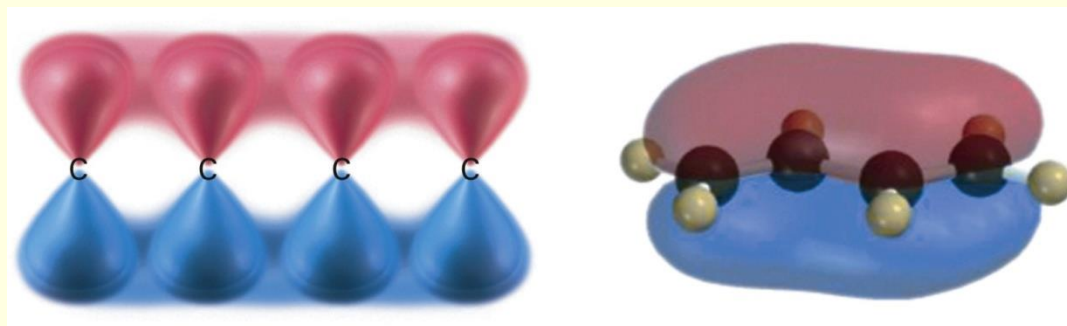
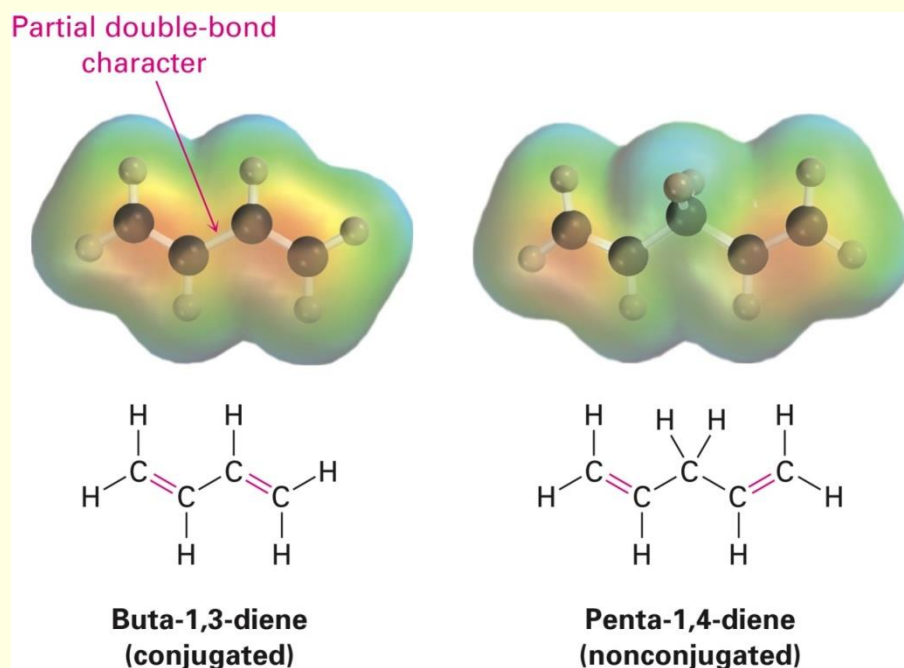
Strategy Imagine breaking the carbon–carbon double bond in the monomer unit, and then form single bonds by connecting numerous units together.

Solution The general structure of poly(vinyl chloride) is



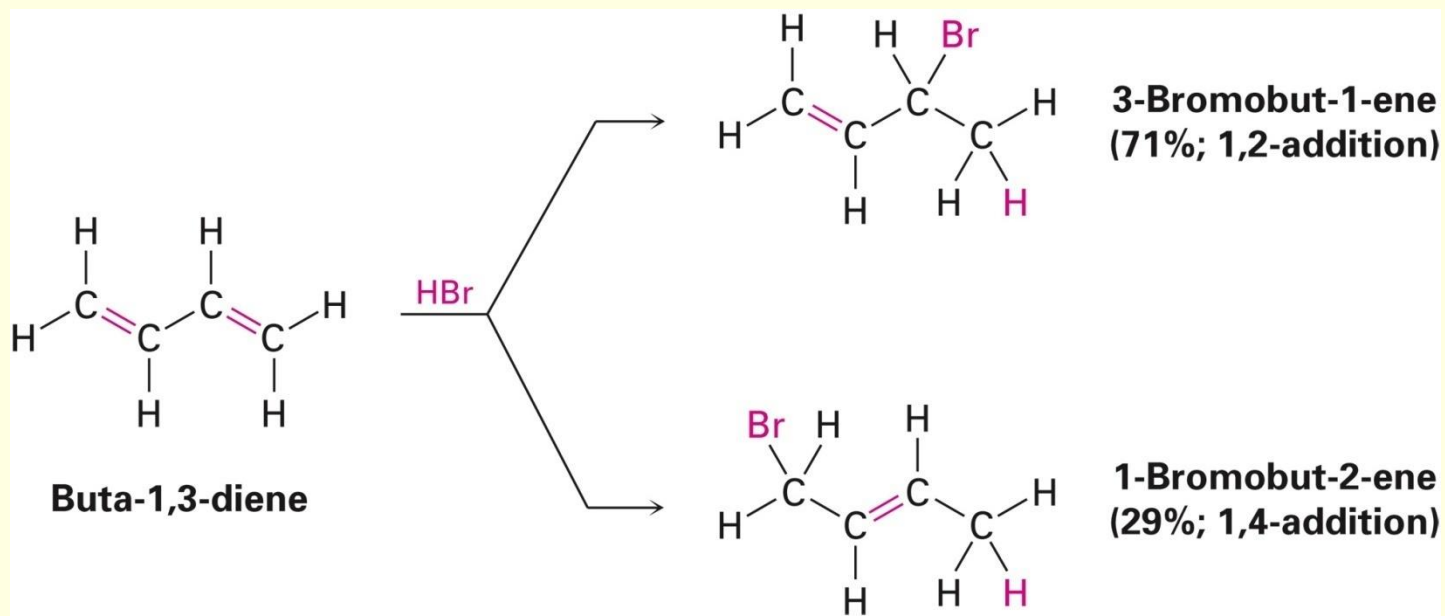
4.8 Conjugated Dienes

Alternating single and double bond: **conjugated**



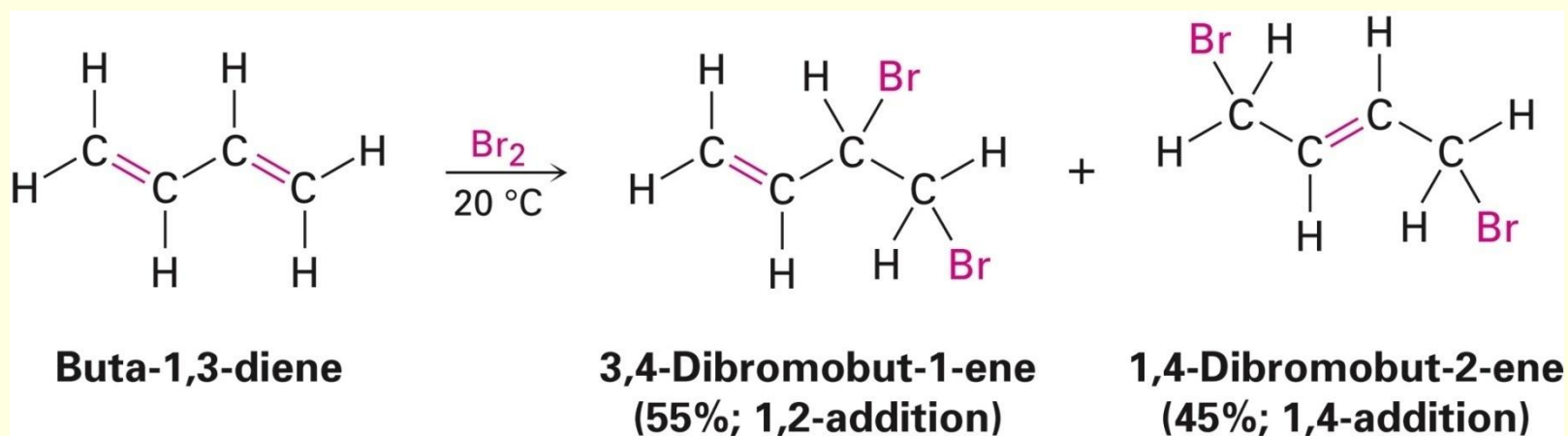
An orbital view of buta-1,3-diene

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



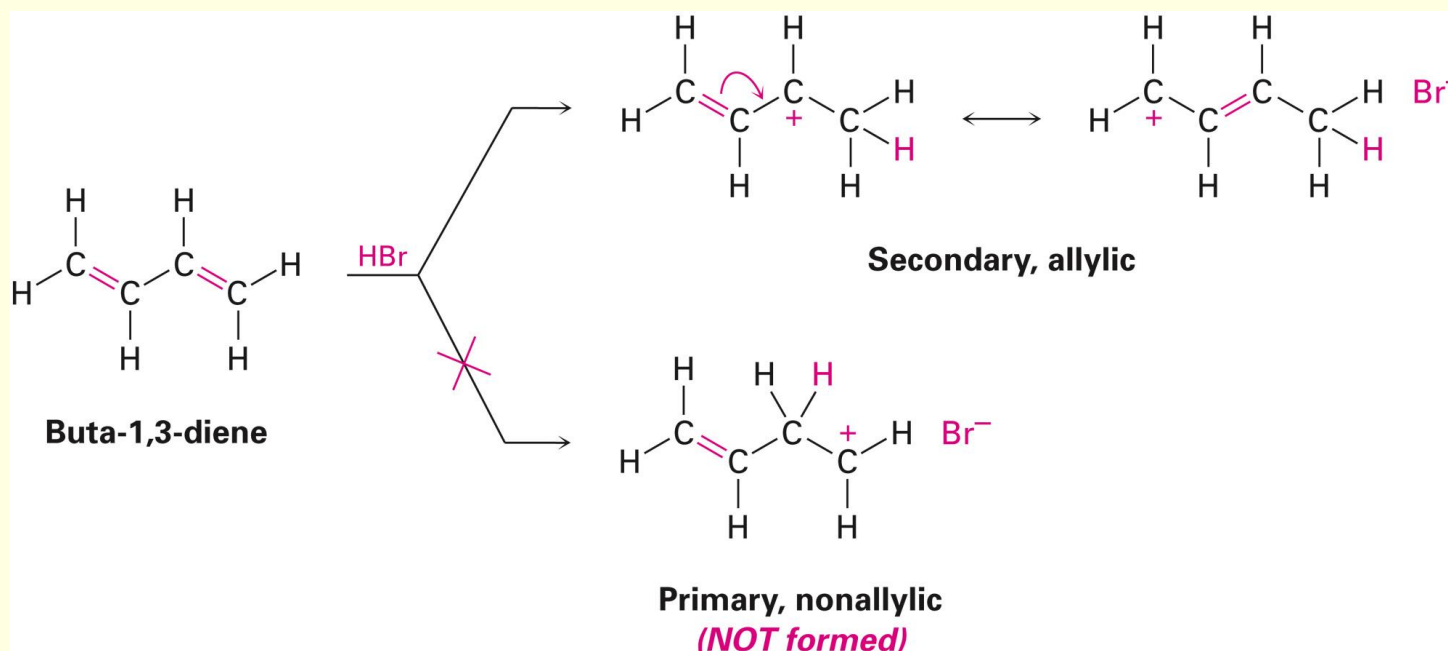
The double bond in this product has moved to a position between C2 and C3, and HBr has added to C1 and C4, a result described as **1,4-addition**.

3-Bromobut-1-ene is the typical Markovnikov product of **1,2-addition**, but 1-bromobut-2-ene appears unusual.



In the same way, Br₂ adds to buta-1,3-diene to give a mixture of 3,4-dibromobut-1-ene and 1,4-dibromobut-2-ene.

Allylic carbocation intermediate



How can we account for the formation of the 1,4-addition product?

The answer is that an *allylic carbocation* is involved as an intermediate in the reaction, where the word **allylic** means “next to a double bond.”

When H adds to an electron-rich bond of buta-1,3-diene, two carbocation intermediates are possible—a primary nonallylic carbocation and a secondary allylic carbocation.

Allylic carbocations are more stable and therefore form faster than less stable, nonallylic carbocations.

4.9 Stability of Allylic Carbocations: Resonance

Why are allylic carbocations particularly stable?

To see the answer, look at the orbital picture of an allylic carbocation in Figure 4.6. All three carbon atoms are ***sp*²-hybridized**, and **each has a *p* orbital**. Thus, the *p* orbital on the central carbon can **overlap equally well with *p* orbitals** on *either* of **the two neighboring carbons**, and the two *p* electrons are free to move about the entire three orbital array

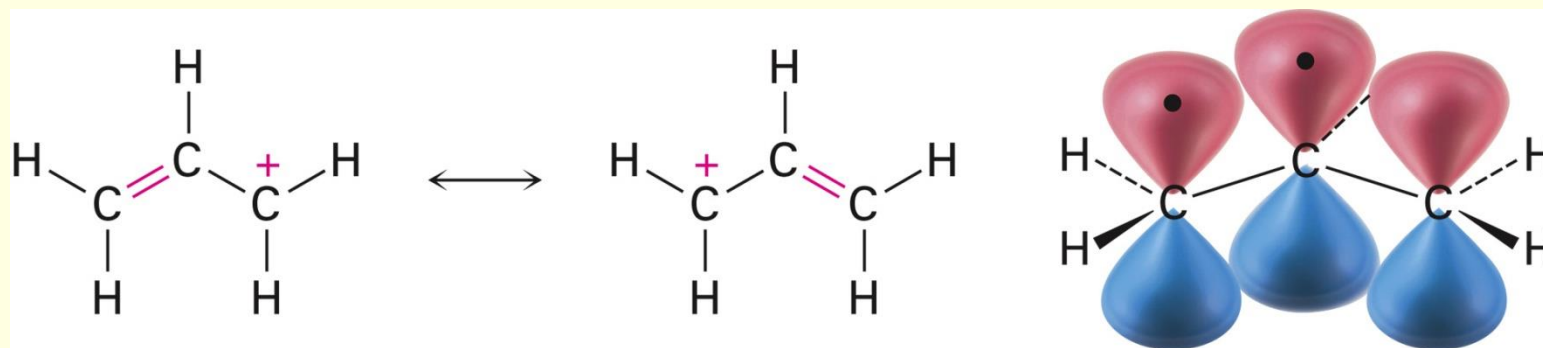
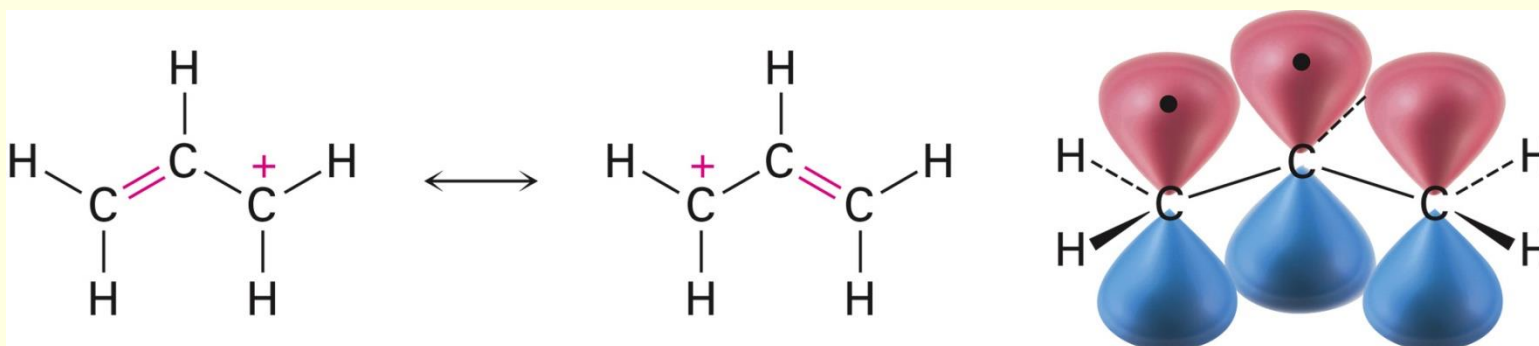


Figure 4.6 An orbital picture of an allylic carbocation. The vacant *p* orbital on the positively charged carbon **can overlap the double-bond *p* orbitals**. As a result, there are two ways to draw the structure.



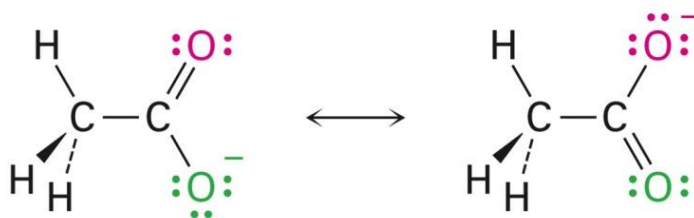
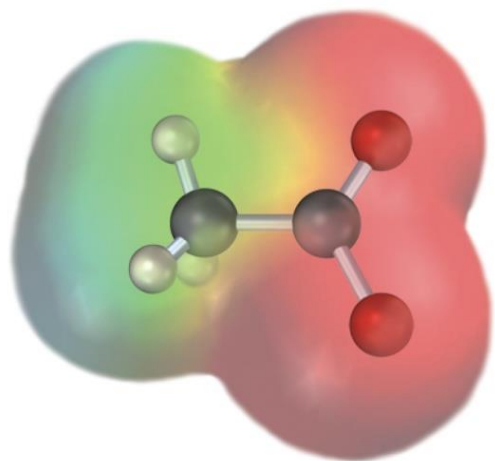
The two individual structures of an allylic carbocation are called **resonance forms**, and their special relationship is indicated by a **double headed arrow** placed between them.

The **only** difference between the resonance forms is the position of the bonding electrons.

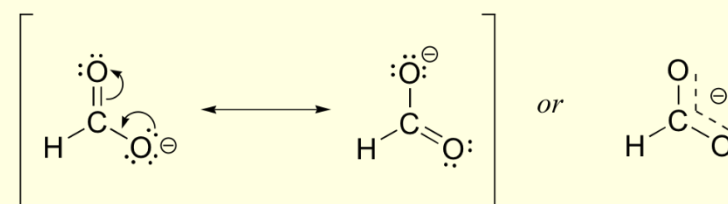
The atoms themselves remain in exactly the same place in both resonance forms, the **connections between atoms are the same**, and the **three-dimensional shapes of the resonance forms are the same**.

4.10 Drawing and Interpreting Resonance Forms

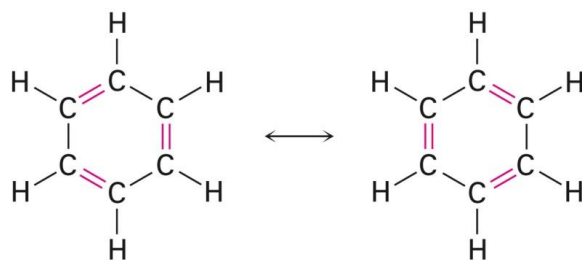
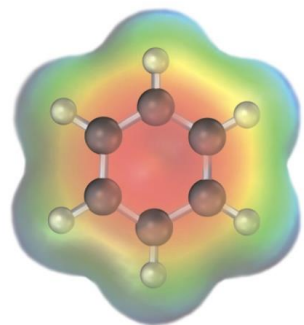
- Some molecules have structures that cannot be shown with a single representation
- In these cases we draw structures that contribute to the final structure but which differ in the position of the π bond(s) or lone pair(s)
- Such a structure is delocalized and is represented by **resonance forms**
-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



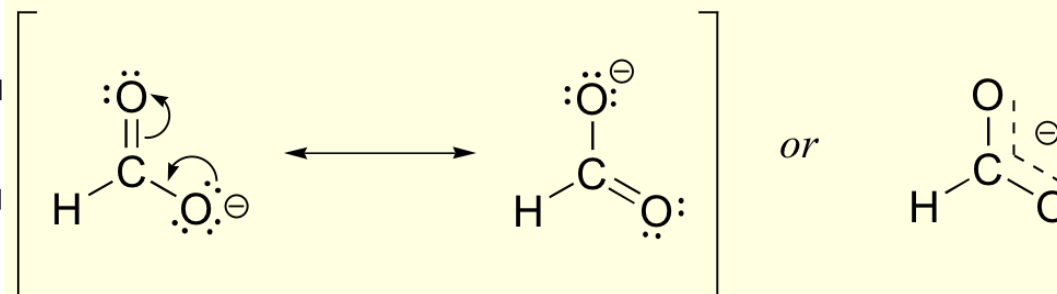
Acetate ion—two resonance forms



- 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**
- For 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

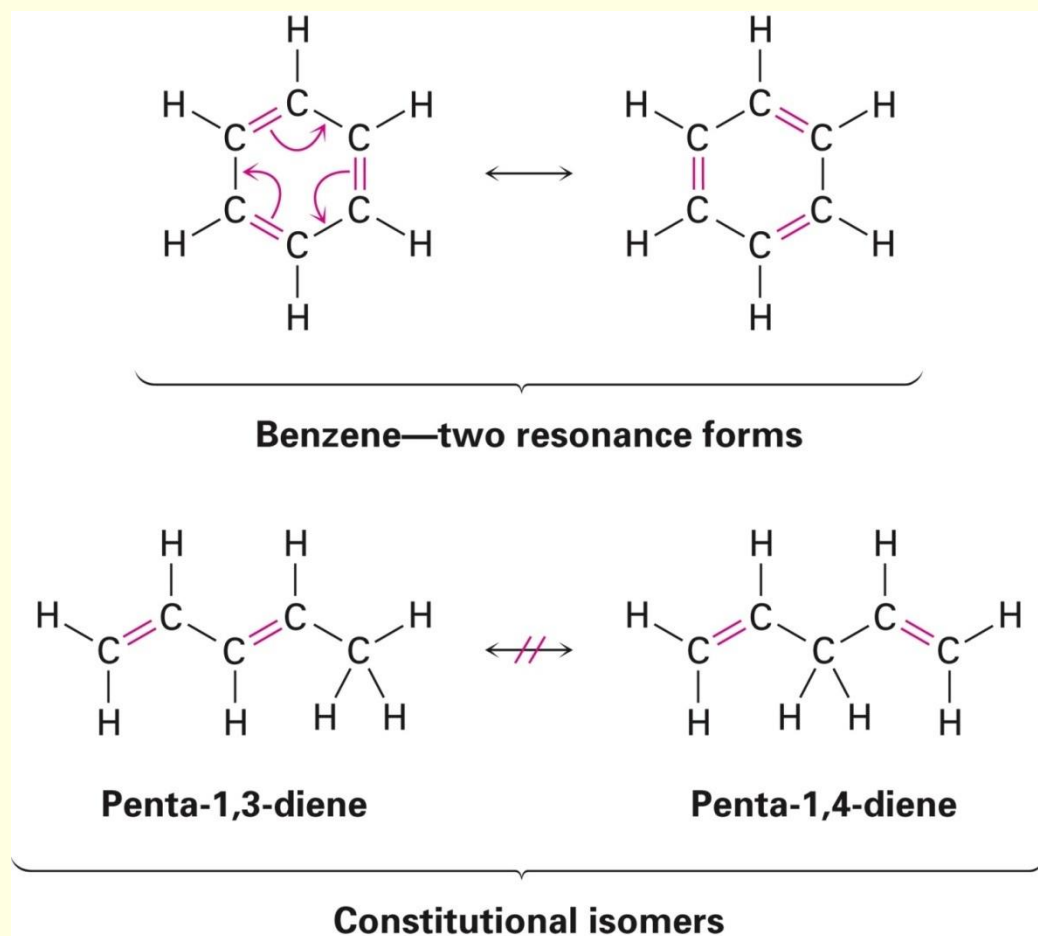


Benzene (two resonance forms)



resonance hybrid

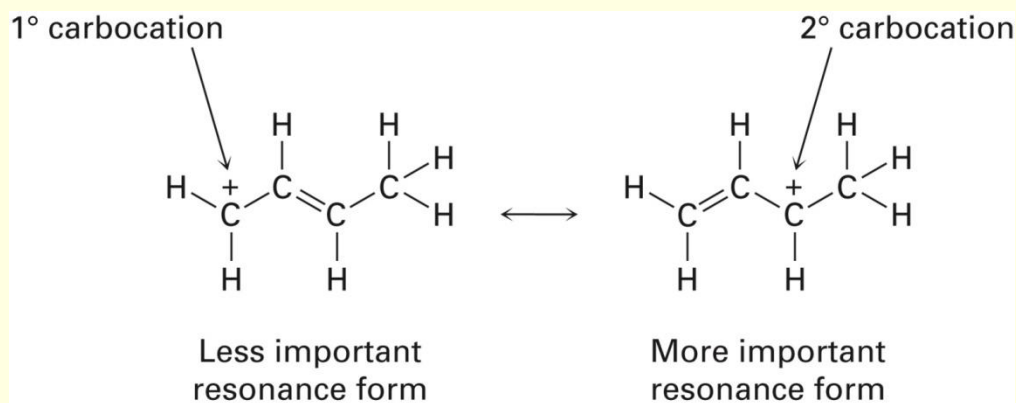
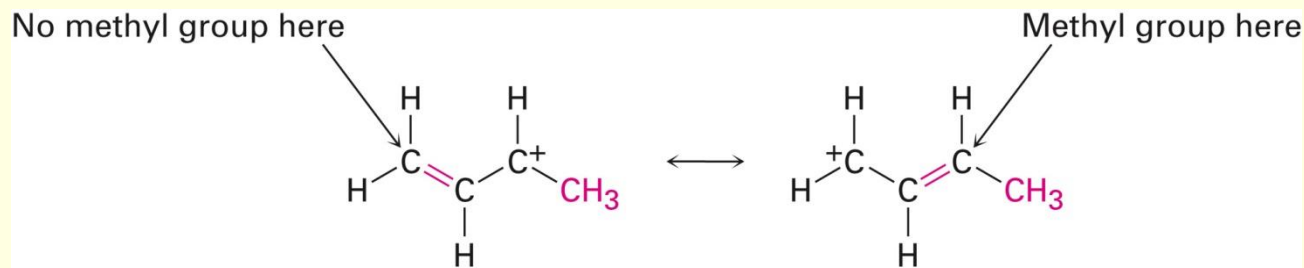
1. Individual resonance forms are **imaginary** - the real structure is a hybrid (only by knowing the contributors can you visualize the actual structure)
Substances like the allylic carbocation, the acetate ion, and benzene are no different from any other: **they have single, unchanging structures.**
2. Resonance forms differ only in the placement of their π or nonbonding electrons



In benzene, for example, the **electrons in the double bonds** move, but the six carbon and six hydrogen atoms remain in the same place.

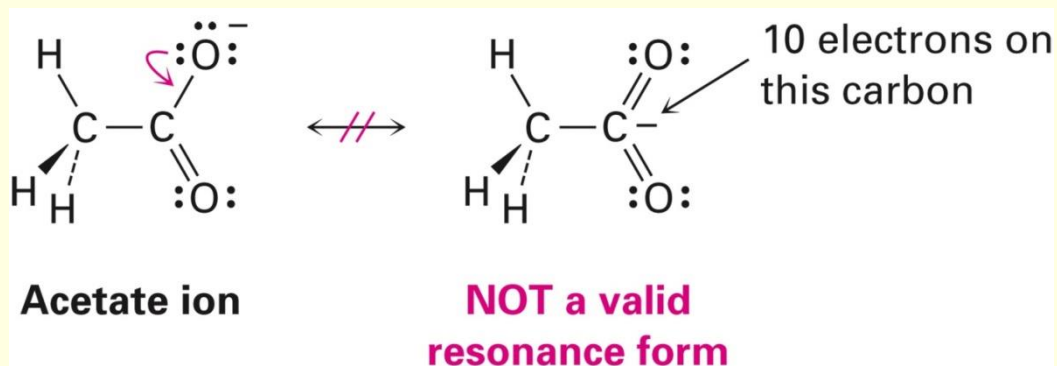
By contrast, two structures such as penta-1,3-diene and penta-1,4-diene are **not resonance** structures because their **hydrogen atoms don't occupy the same positions**. Instead, the two dienes are constitutional isomers

3. Different resonance forms of a substance don't have to be equivalent



Even though the two resonance forms aren't equivalent, both **contribute to the overall resonance hybrid.**

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



6 Resonance leads to stability.

The greater the number of resonance forms, the more stable the substance.

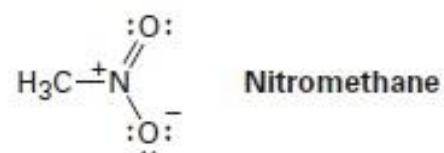
We've already seen, for example, that an allylic carbocation is more stable than a non allylic one.

In the same way, we'll see in the next chapter that a benzene ring is more stable than a cyclic alkene.

Worked Example 4.5

Using Resonance Structures

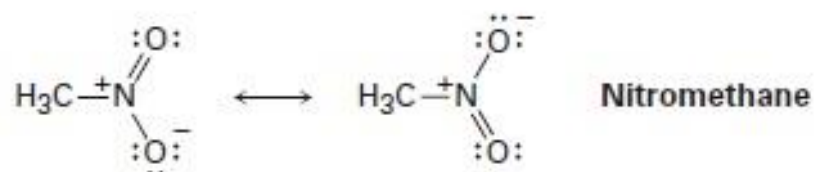
Use resonance structures to explain why the two N–O bonds of nitromethane are equivalent.



Strategy

Resonance forms differ only in the placement of π (multiple-bond) and nonbonding electrons. Nitromethane has two equivalent resonance forms, which can be drawn by showing the double bond either to the top oxygen or to the bottom oxygen. Only the positions of the electrons are different in the two forms.

Solution



Resonance forms differ only in the placement of π (multiple-bond) and nonbonding electrons.