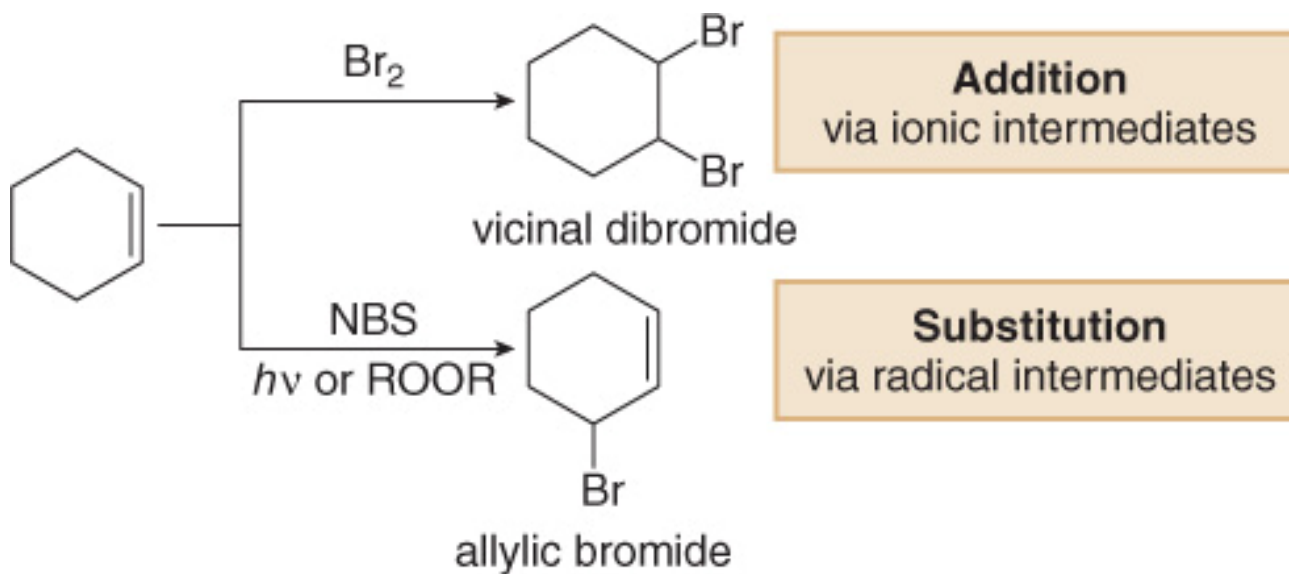


# Radical Reactions

## Radical Halogenation at an Allylic Carbon

Thus, an alkene with allylic C—H bonds undergoes two different reactions depending on the reaction conditions.

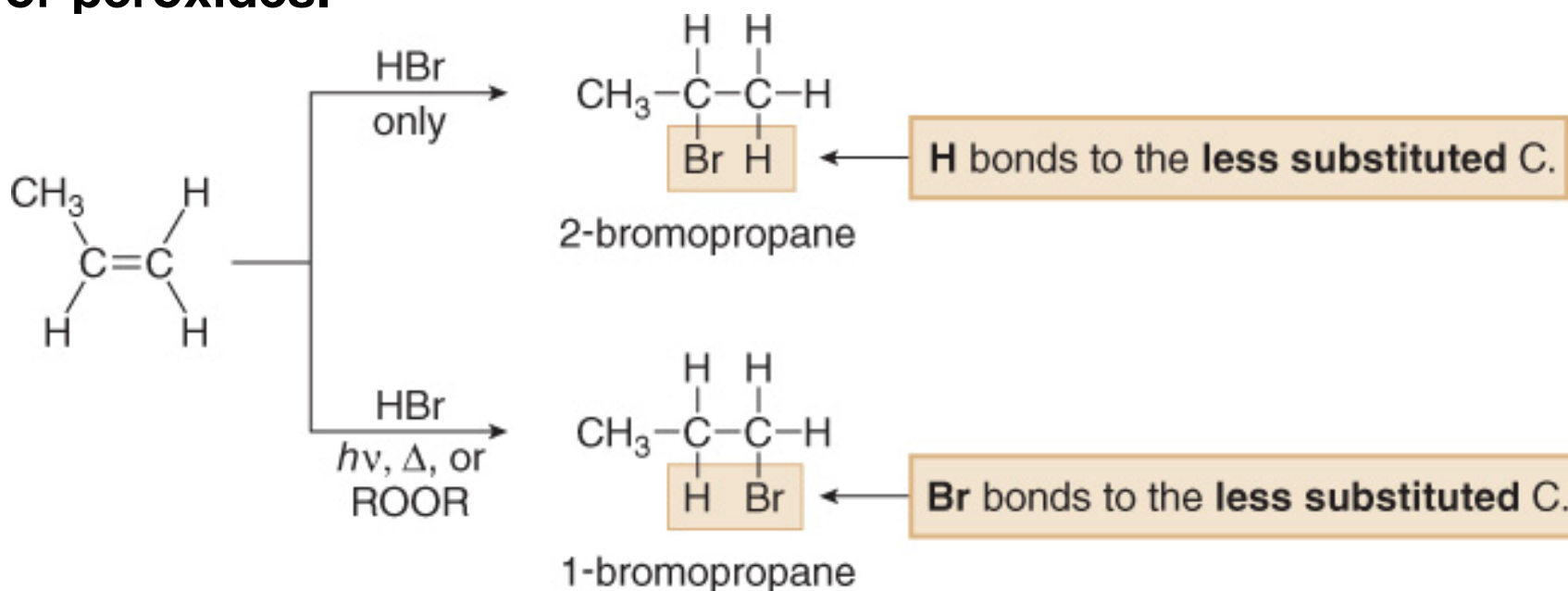




# Radical Reactions

## Radical Additions to Double Bonds

- HBr adds to alkenes to form alkyl bromides in the presence of heat, light, or peroxides.
- The regioselectivity of the addition to unsymmetrical alkenes is different from that in addition of HBr in the absence of heat, light or peroxides.



- The addition of HBr to alkenes in the presence of heat, light or peroxides proceeds via a radical mechanism.

# Radical Reactions

## Radical Additions to Double Bonds

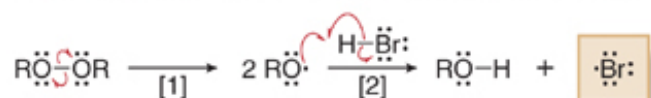
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### Mechanism 15.4 Radical Addition of HBr to an Alkene

#### Initiation

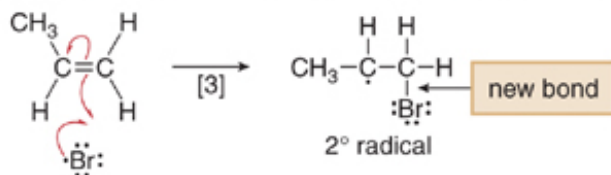
Steps [1] and [2] Abstraction of H from HBr occurs by a two-step process.



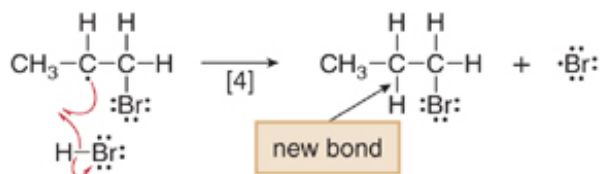
- With ROOR to initiate the reaction, two steps are needed to form Br $\cdot$ . Homolysis of the weak O–O bond of the peroxide forms RO $\cdot$ , which abstracts a hydrogen atom from HBr to form Br $\cdot$ .

#### Propagation

Steps [3] and [4] The  $\pi$  bond is broken and the C–H and C–Br  $\sigma$  bonds are formed.



- Chain propagation occurs in two steps, and in each step one radical is consumed and another is formed.
- The first step of propagation forms the C–Br bond when the Br $\cdot$  radical adds to the terminal carbon, leading to a 2° carbon radical.

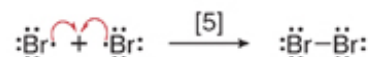


- The 2° radical abstracts a H atom from HBr, forming the new C–H bond and completing the addition reaction. Because a new Br $\cdot$  radical is also formed in this step, Steps [3] and [4] occur repeatedly.

Repeat Steps [3], [4], [3], [4], and so forth.

#### Termination

Step [5] Two radicals react to form a bond.



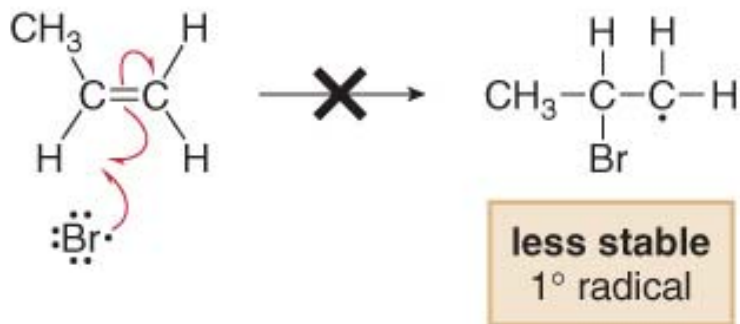
- To terminate the chain, two radicals (for example two Br $\cdot$  radicals) react with each other to form a stable bond, preventing further propagation via Steps [3] and [4].

# Radical Reactions

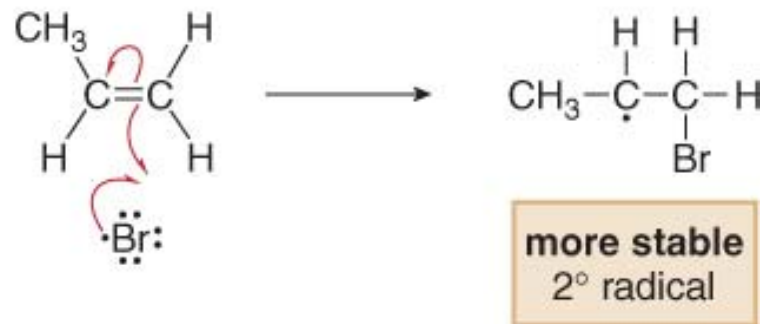
## Radical Additions to Double Bonds

- Note that in the first propagation step, the addition of  $\text{Br}\cdot$  to the double bond, there are two possible paths:
  1. Path [A] forms the less stable  $1^\circ$  radical.
  2. Path [B] forms the more stable  $2^\circ$  radical.
- The more stable  $2^\circ$  radical forms faster, so Path [B] is preferred.

Path [A]:  
Does NOT occur



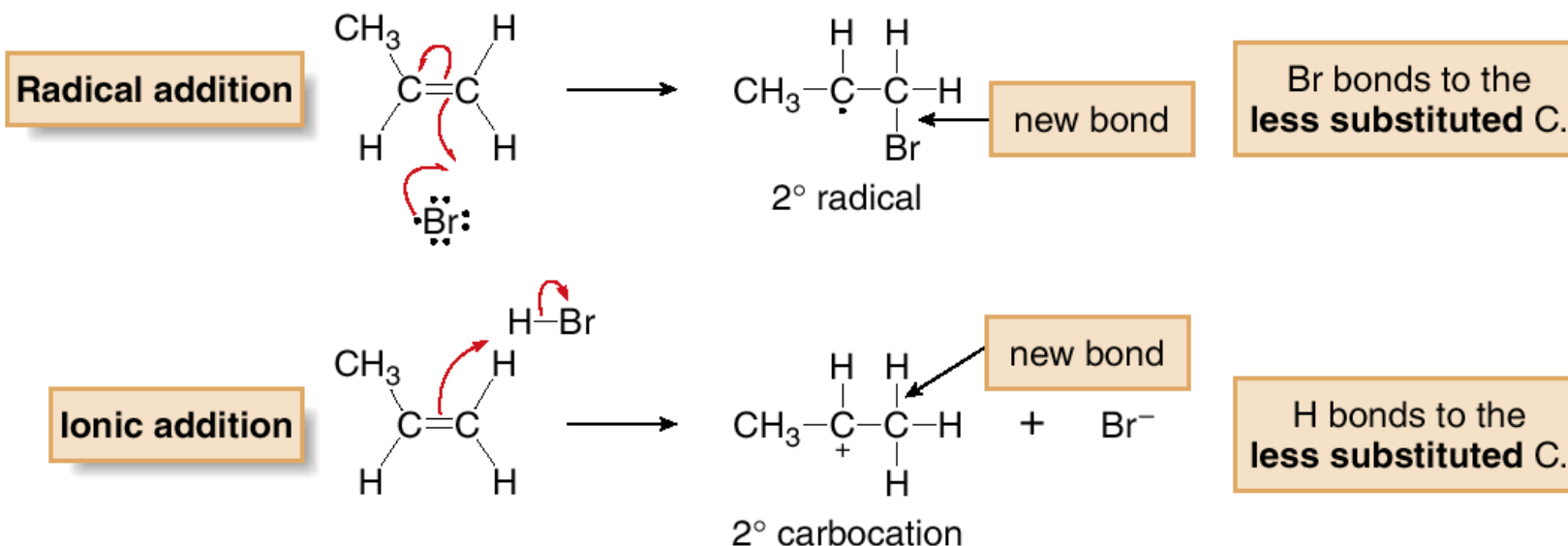
Path [B]:  
Preferred path



# Radical Reactions

## Radical Additions to Double Bonds

- The radical mechanism illustrates why the regioselectivity of HBr addition is different depending on the reaction conditions.

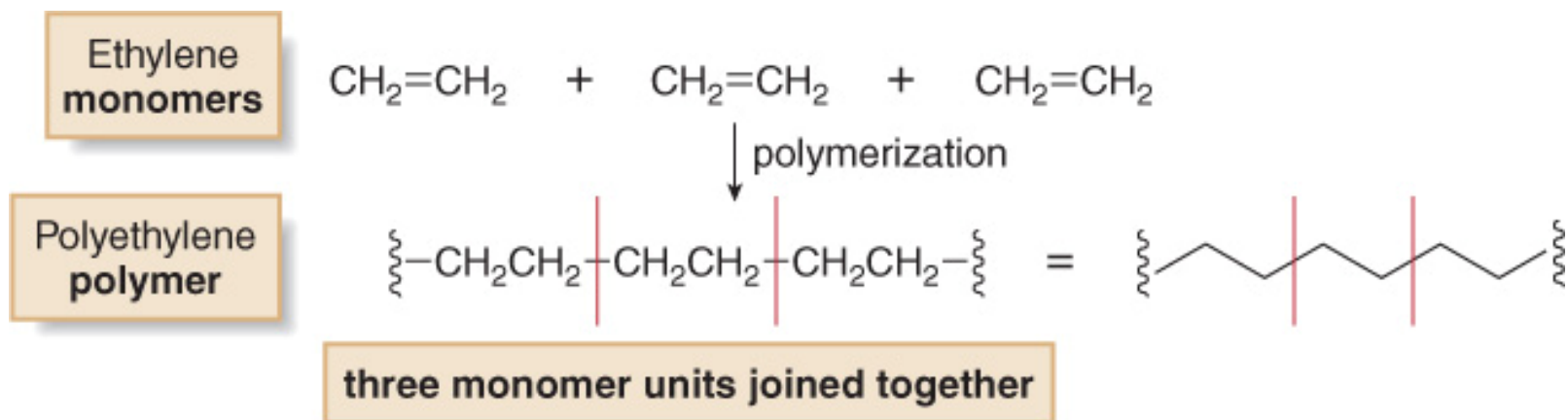


- In radical addition (HBr with added light, heat, or ROOR), *Br· adds first* to generate the more stable radical.
- In ionic addition (HBr alone), *H<sup>+</sup> adds first* to generate the more stable carbocation.

# Radical Reactions

## Polymers and Polymerization

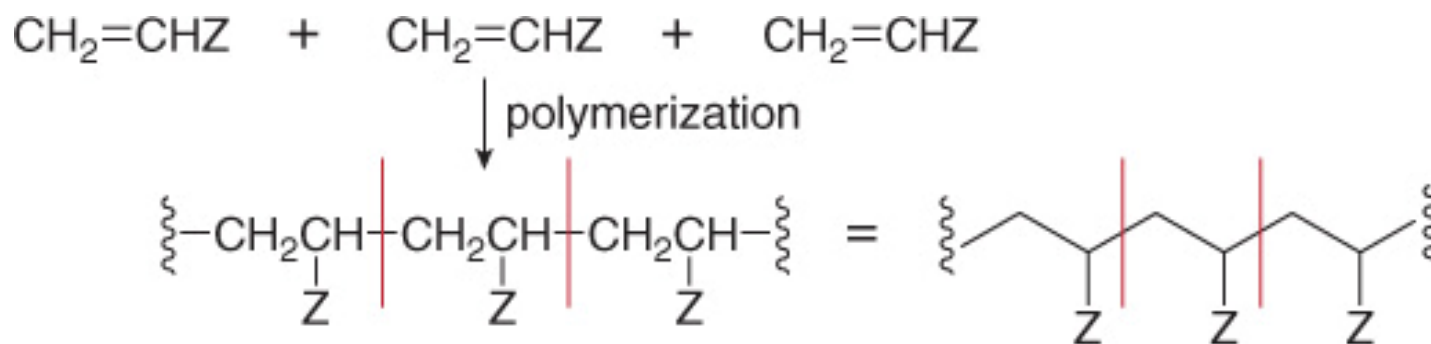
- **Polymers** are large molecules made up of repeating units of smaller molecules called **monomers**. They include biologically important compounds such as proteins and carbohydrates, as well as synthetic plastics such as polyethylene, polyvinyl chloride (PVC) and polystyrene.
- **Polymerization** is the joining together of monomers to make polymers. For example, joining ethylene monomers together forms the polymer polyethylene, a plastic used in milk containers and plastic bags.



# Radical Reactions

## Polymers and Polymerization

- Many ethylene derivatives having the general structure  $\text{CH}_2=\text{CHZ}$  are also used as monomers for polymerization.
- The identity of Z affects the physical properties of the resulting polymer.
- Polymerization of  $\text{CH}_2=\text{CHZ}$  usually affords polymers with Z groups on every other carbon atom in the chain.



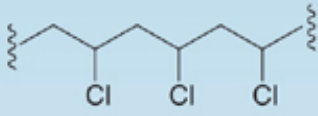

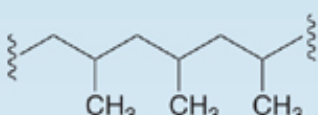


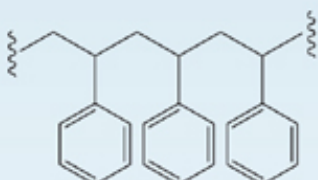

three monomer units joined together

# Polymers and Polymerization

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**Table 15.2**

**Common Industrial Monomers and Polymers**

Monomer	Polymer	Consumer product
$\text{CH}_2=\text{CHCl}$ vinyl chloride	 poly(vinyl chloride) PVC	 PVC pipes
$\text{CH}_2=\text{CHCH}_3$ propene	 polypropylene	 polypropylene carpeting
$\text{CH}_2=\text{CH}$ -  styrene	 polystyrene	 Styrofoam products

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# Radical Reactions

## Polymers and Polymerization

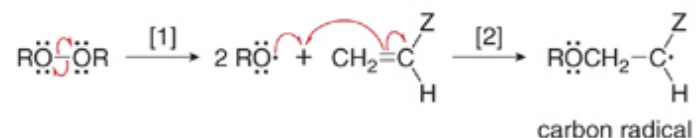
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### Mechanism 15.5 Radical Polymerization of $\text{CH}_2=\text{CHZ}$

#### Initiation

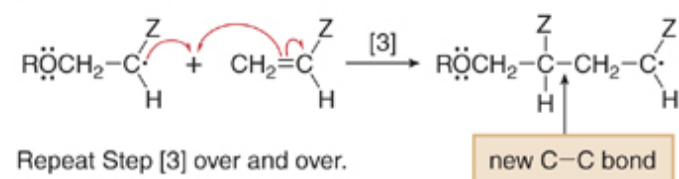
Steps [1] and [2] A carbon radical is formed by a two-step process.



- Chain initiation begins with homolysis of the weak O–O bond of the peroxide to form  $\text{RO}\cdot$ , which then adds to a molecule of monomer to form a carbon radical.

#### Propagation

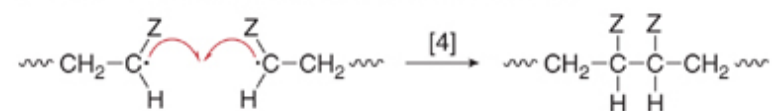
Step [3] The polymer chain grows.



- Chain propagation consists of a single step that joins monomer units together.
- In Step [3], the carbon radical formed during initiation adds to another alkene molecule to form a new C–C bond and another carbon radical. Addition always forms the more substituted carbon radical—that is, the **unpaired electron is always located on the carbon atom having the Z substituent**.
- This carbon radical reacts with more monomer, so that Step [3] occurs repeatedly, and the polymer chain grows. Each time a carbon radical adds to a double bond, a **new C–C bond** and a new carbon radical are formed.

#### Termination

Step [4] Two radicals combine to form a bond.



- To terminate the chain, two radicals combine to form a stable bond, thus ending the polymerization process.

# Radical Reactions

## Polymers and Polymerization

- In radical polymerization, the more substituted radical always adds to the less substituted end of the double bond, a process called **head-to-tail polymerization**.

