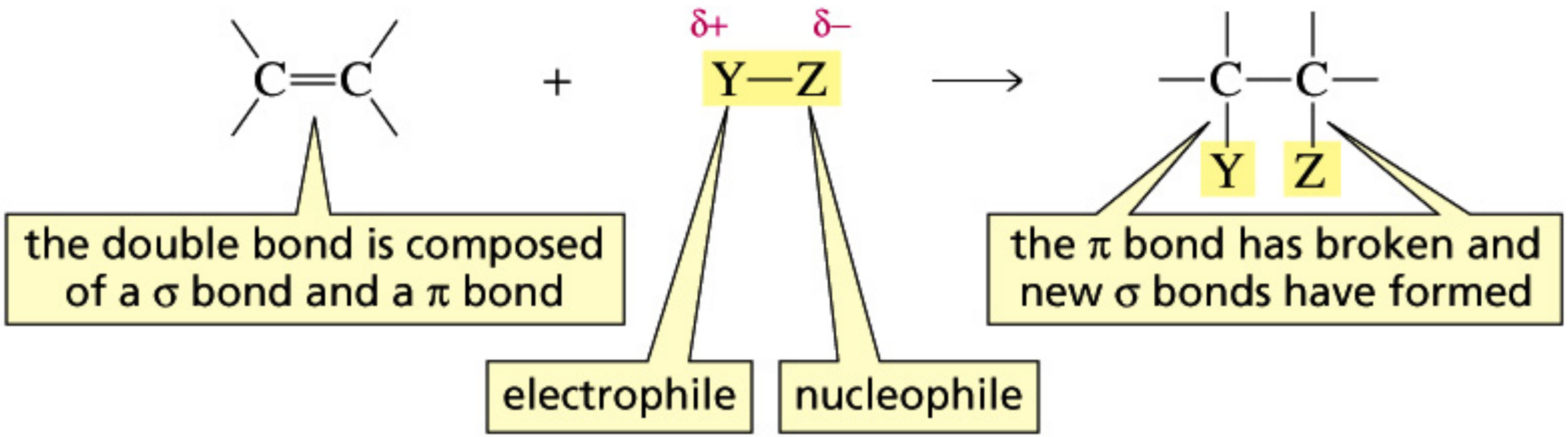
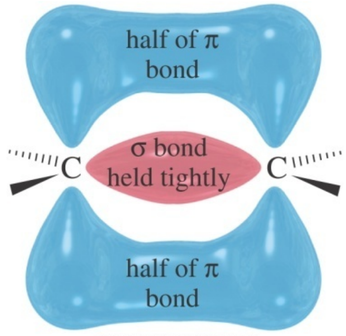
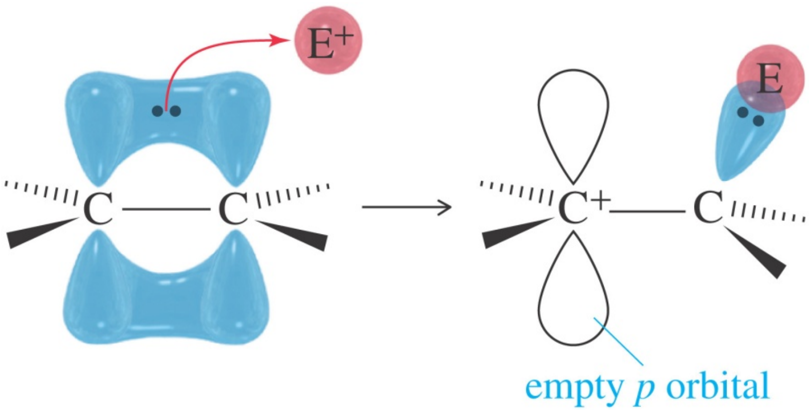
Electrophilic Addition of Alkenes



Bonding in Alkenes

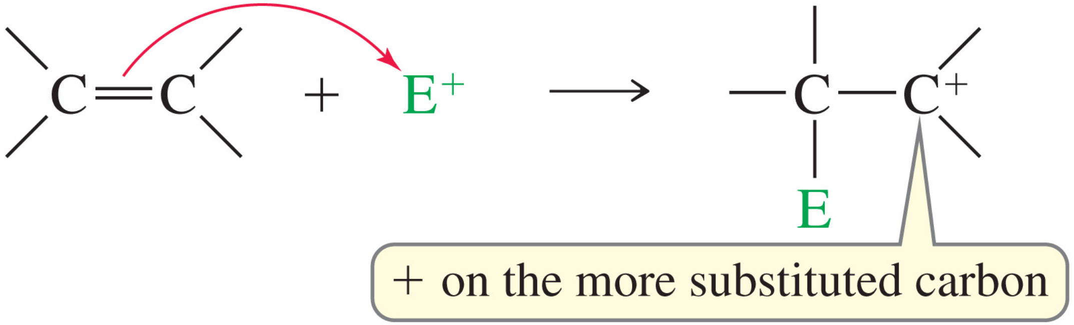
- Electrons in pi bond are loosely held.
- **The double bond acts as a nucleophile attacking electrophilic species**.
- Carbocations are intermediates in the reactions.
- These reactions are called ***electrophilic additions***.



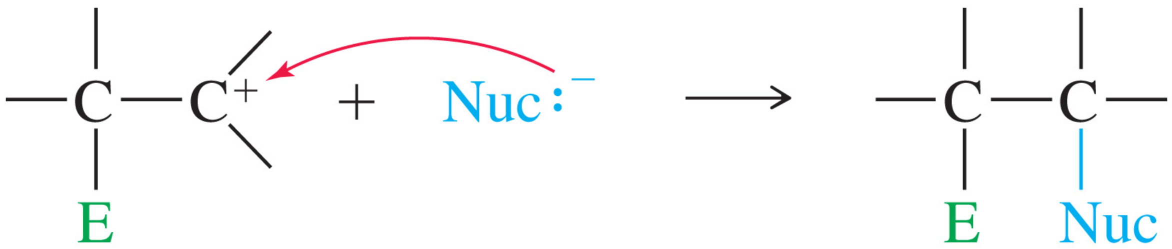


Electrophilic Addition

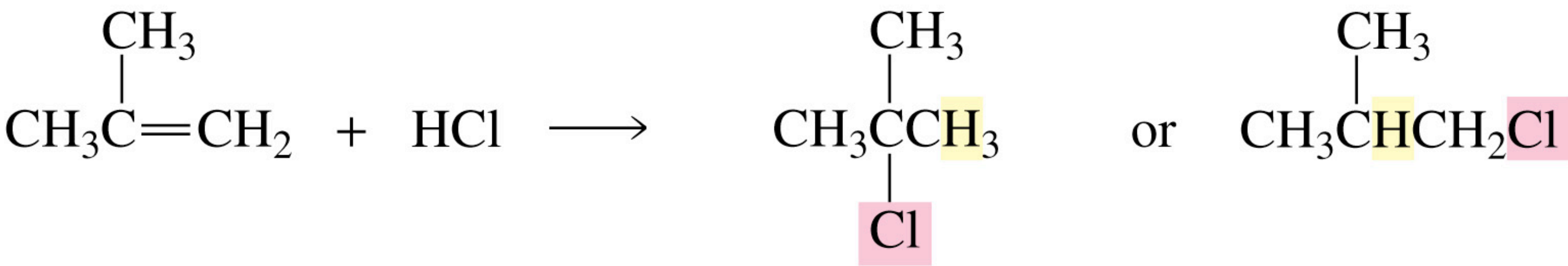
- **Step 1: Pi electrons attack the electrophile.**



- **Step 2: Nucleophile attacks the carbocation.**

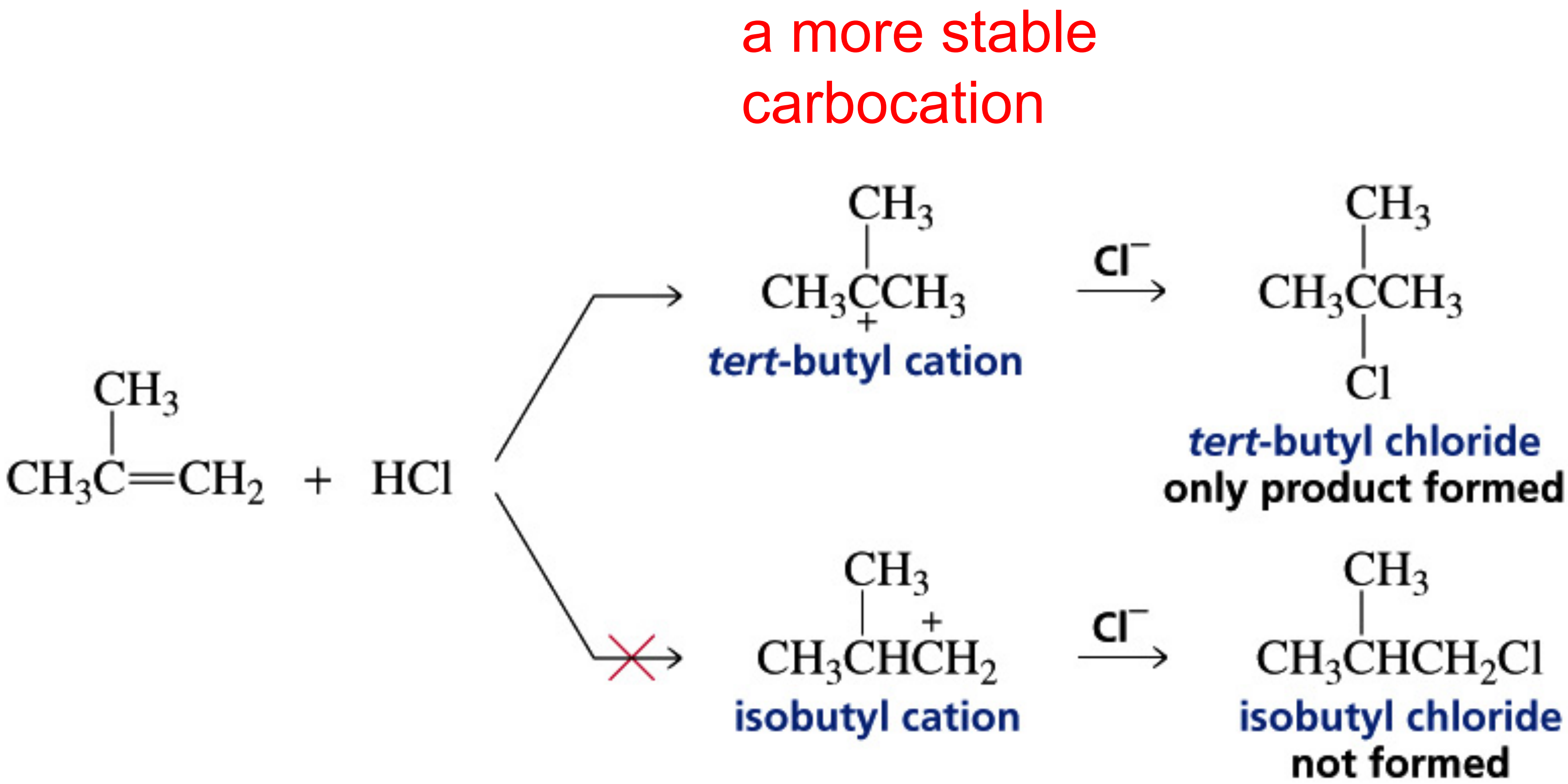


What is the product?

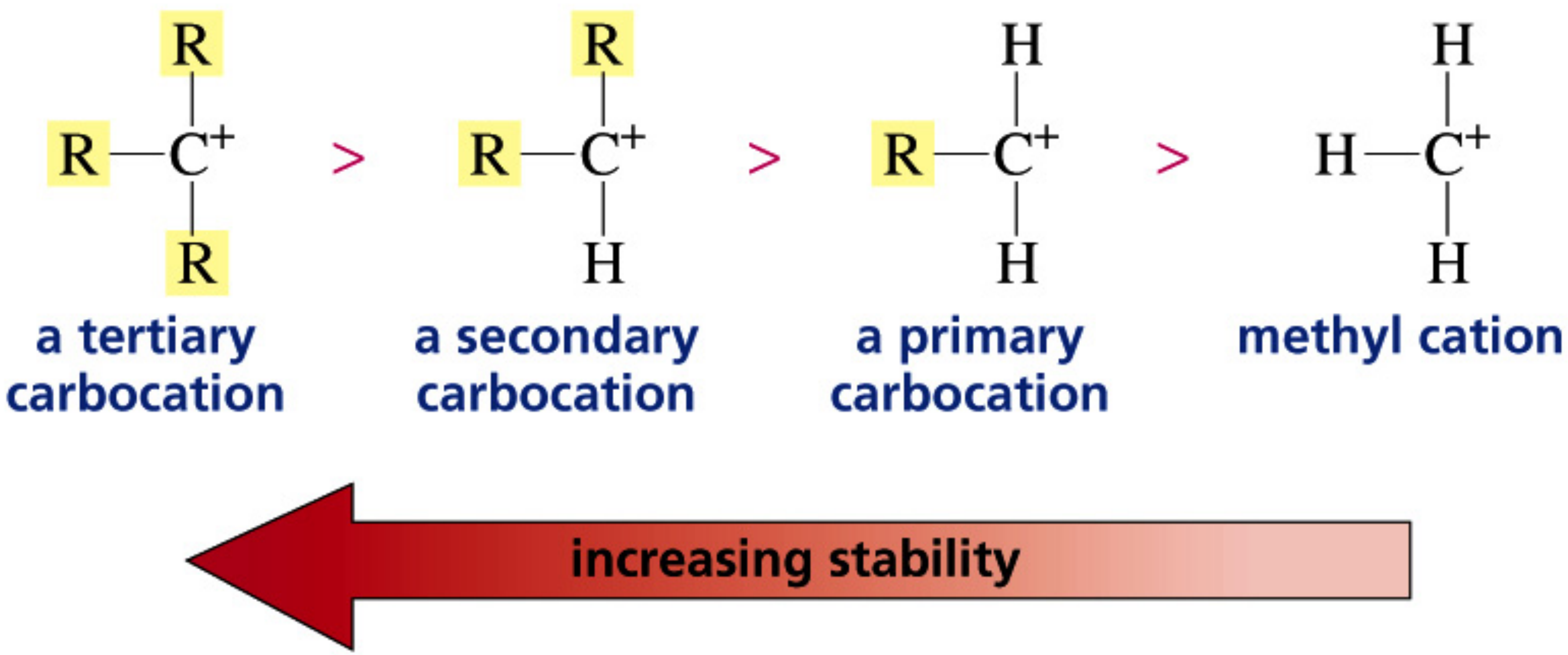


2-methylpropene — *tert*-butyl chloride — isobutyl chloride

Carbocation formation is the rate-limiting step

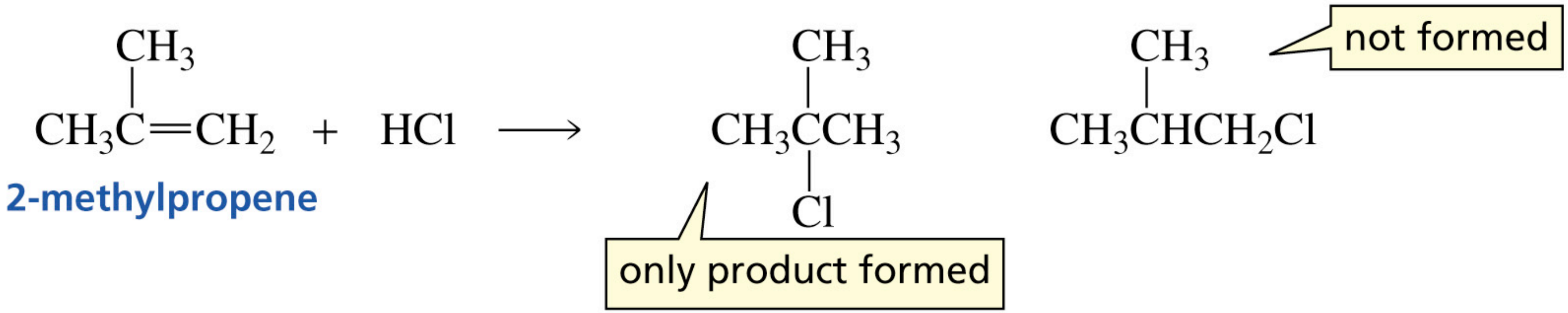


Carbocation Stabilities



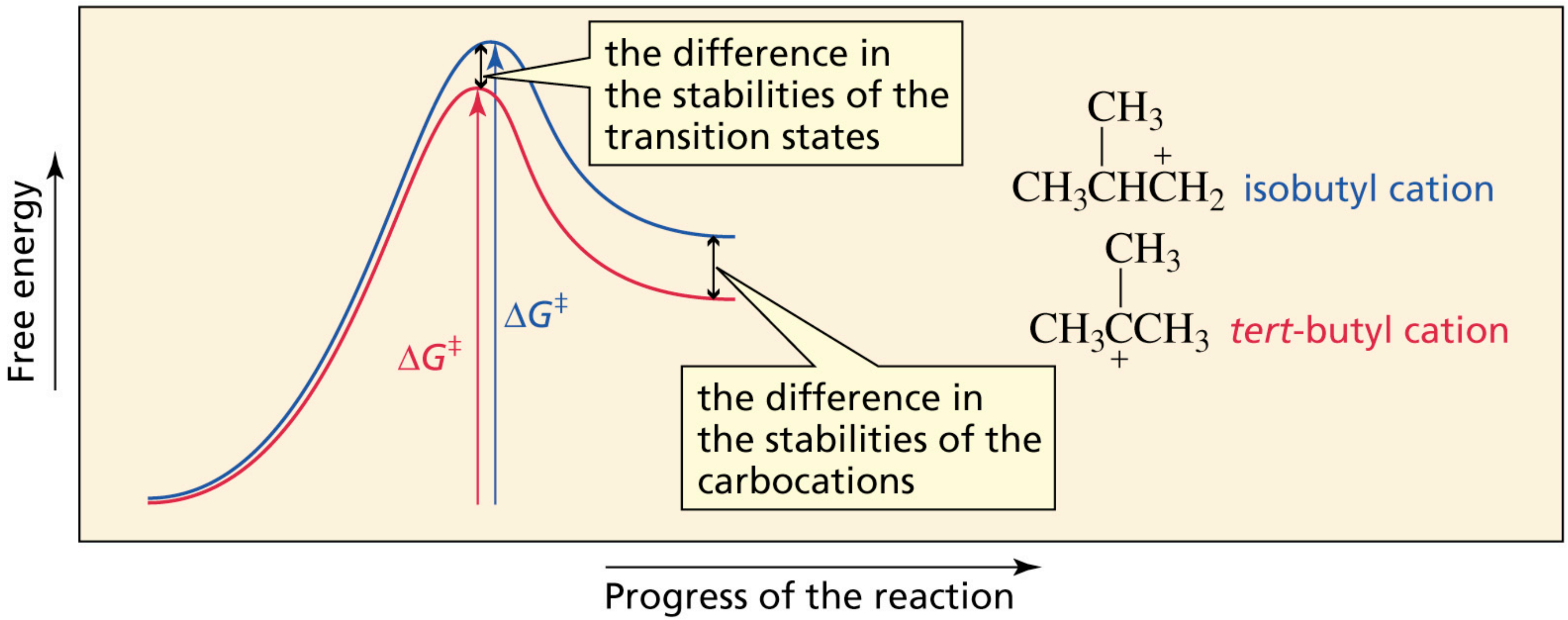
Markovnikov's Rule

The electrophile adds to the *sp*^{2} carbon that is bonded to the greater number of hydrogens



In a regioselective reaction, one constitutional isomer is the major or the only product

tert-Butyl cation is formed faster and it is more stable



Regioselectivity

- Markovnikov's Rule: The addition of a proton to the double bond of an alkene results in a product with the acidic proton bonded to the carbon atom that already holds the greater number of hydrogens.
- Markovnikov's Rule (extended): In an electrophilic addition to the alkene, the electrophile adds in such a way that it **generates the most stable intermediate**.

Synthesis of Bromobutane

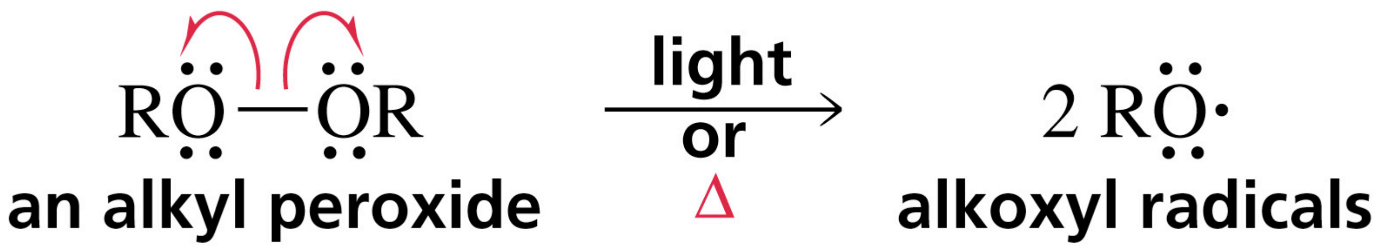
$$CH_3CH_2CH{=}CH_2 + HBr \longrightarrow CH_3CH_2\underset{}{\overset{Br}{\overset{|}{C}}}HCH_3$$

1-butene → 2-bromobutane

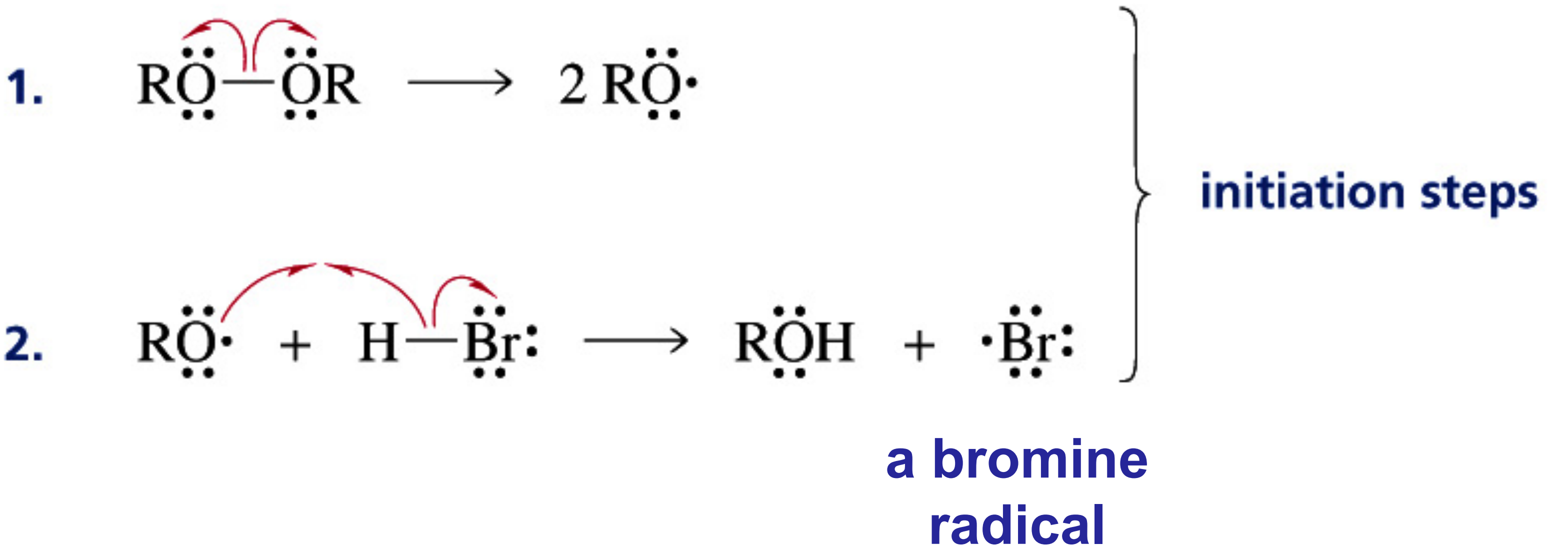
$$CH_3CH_2CH{=}CH_2 + HBr \xrightarrow{\text{peroxide}} CH_3CH_2CH_2CH_2Br$$

1-butene → 1-bromobutane

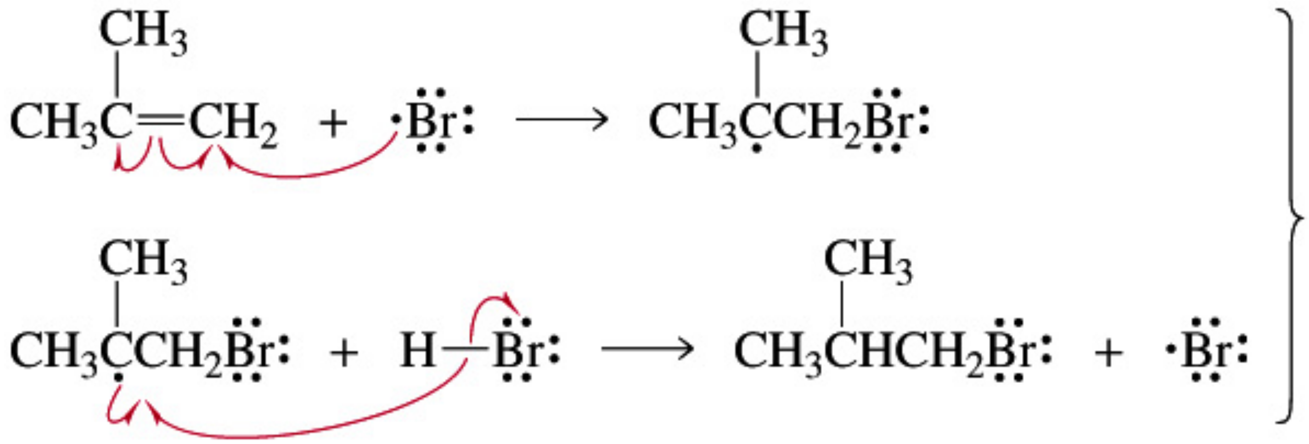
Generation of Radicals



Addition of Radicals to Alkene

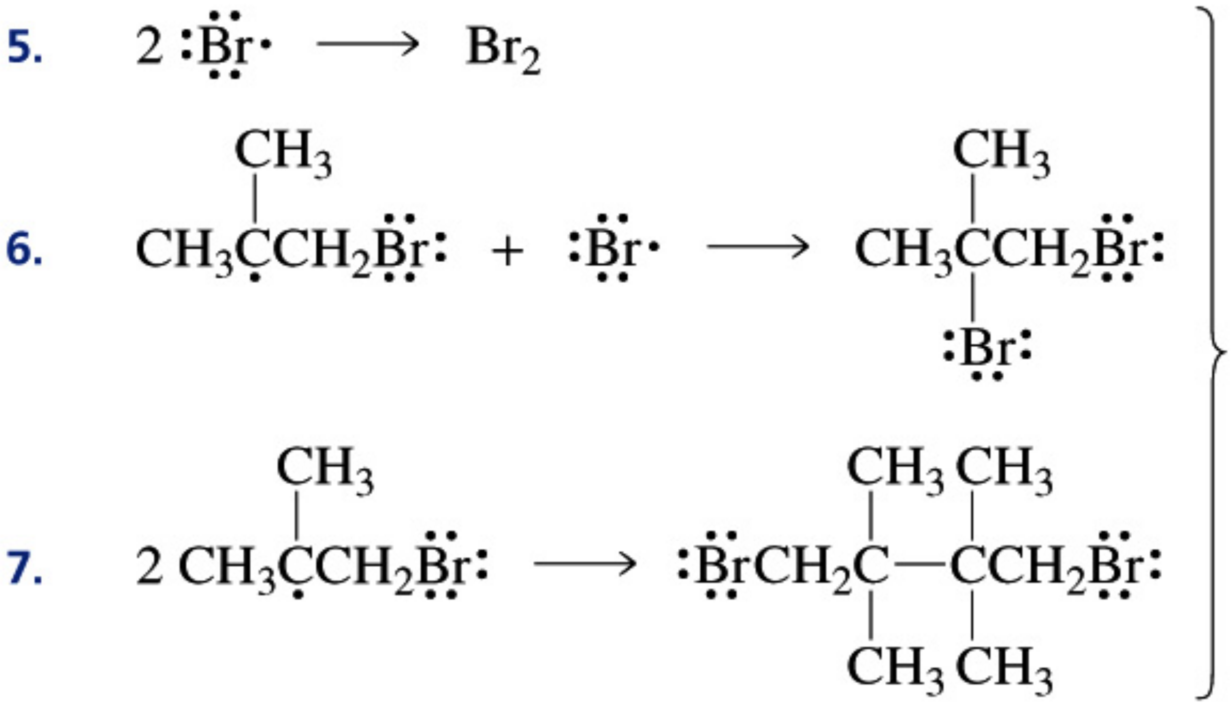


3.
4.



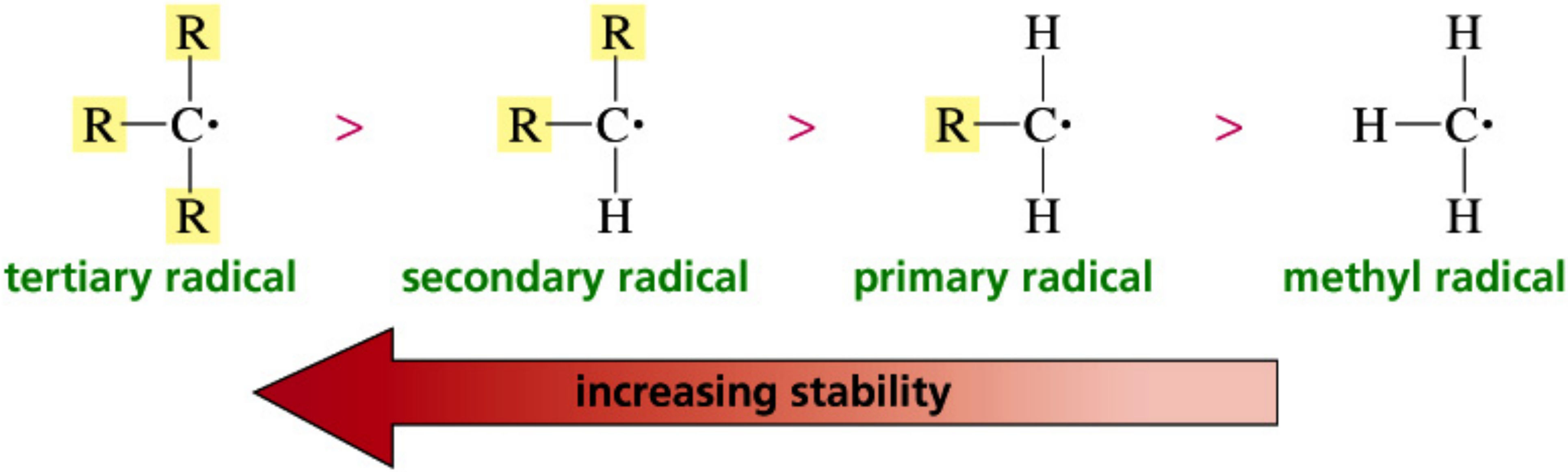
propagation steps

Addition of Radicals to Alkene



termination steps

Relative Stabilities of Alkyl Radicals



Free-Radical Addition of HBr

- In the presence of peroxides, HBr adds to an alkene to form the "anti-Markovnikov" product.
- Only HBr has the right bond energy.
- The HCl bond is too strong, so it will add according to Markovnikov's rule, even in the presence of peroxide.
- The HI bond tends to break heterolytically to form ions, it too will add according to Markovnikov's rule.