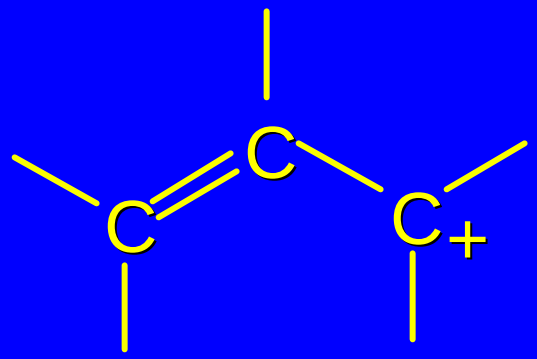
# Chapter 10
# Conjugation in Alkadienes and Allylic Systems

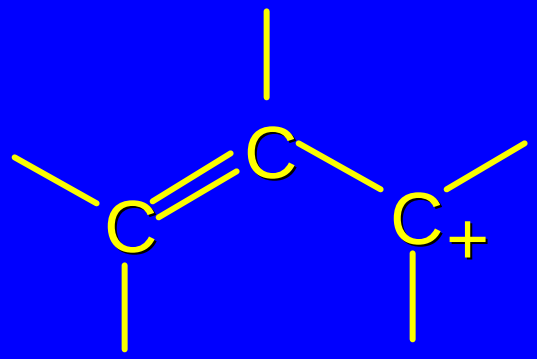
*conjugare is a Latin verb meaning "to link or yoke together"*

# *The Double Bond as a Substituent*

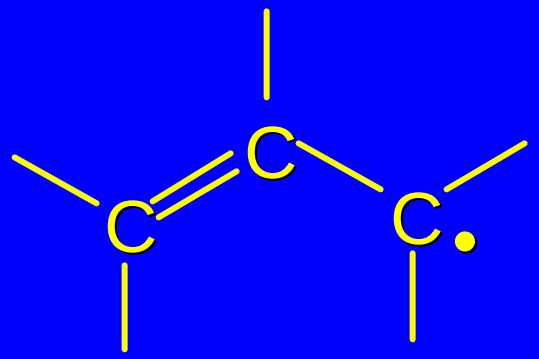



*allylic carbocation*

# *The Double Bond as a Substituent*

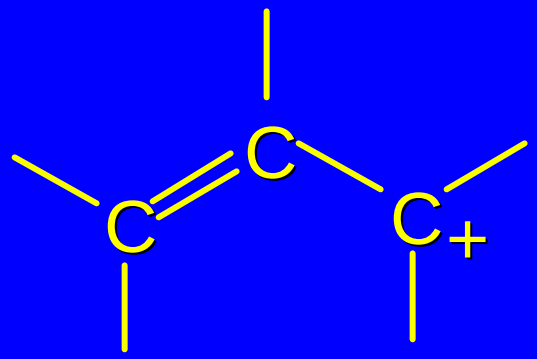



*allylic carbocation*

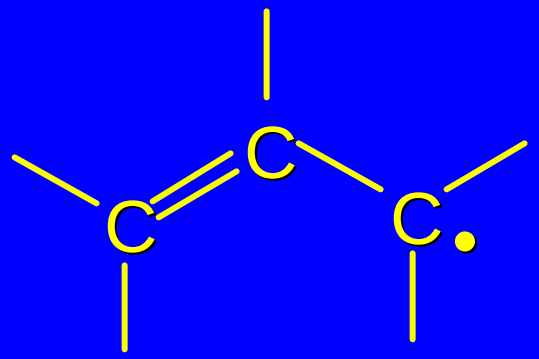



*allylic radical*

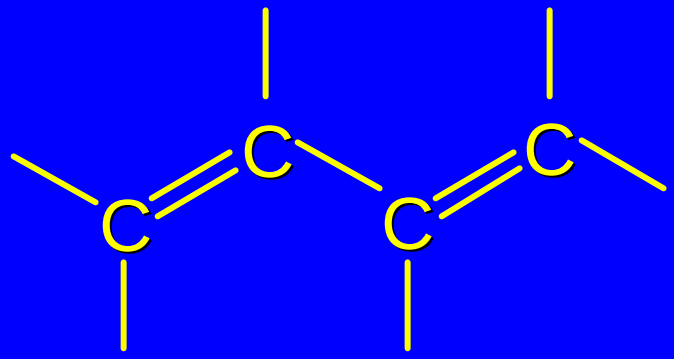
# *The Double Bond as a Substituent*




*allylic carbocation*



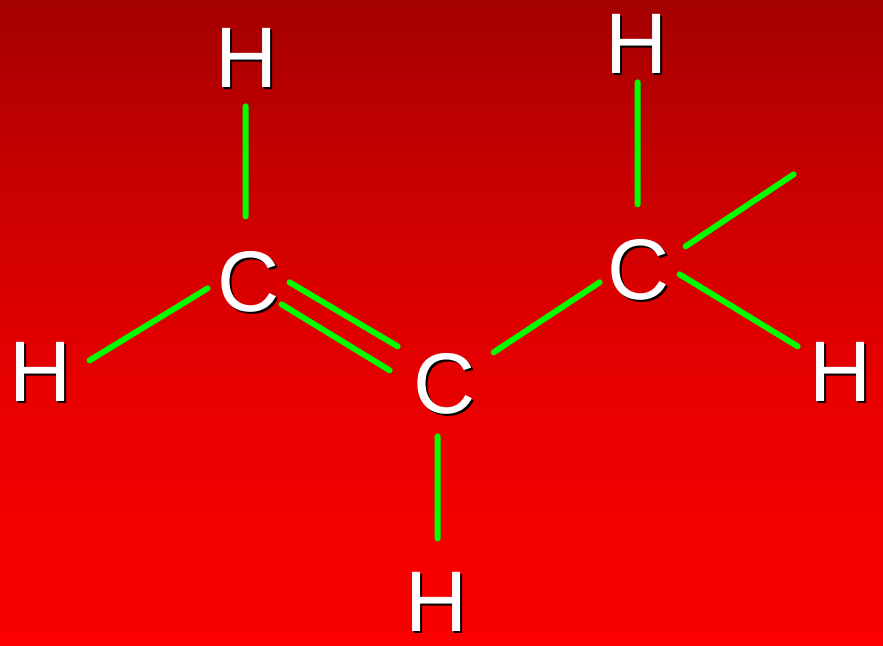

*allylic radical*



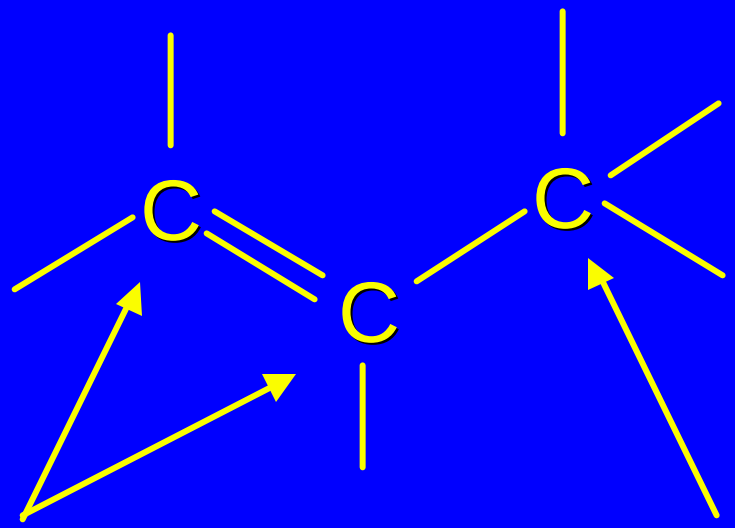

*conjugated diene*

# 10.1

# The Allyl Group



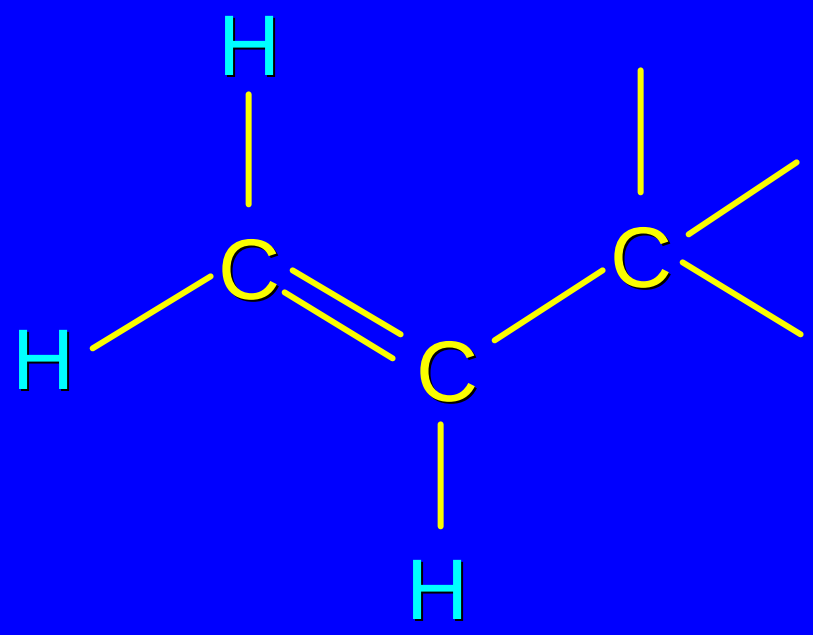
# *Vinylic versus Allylic*




vinylic carbons

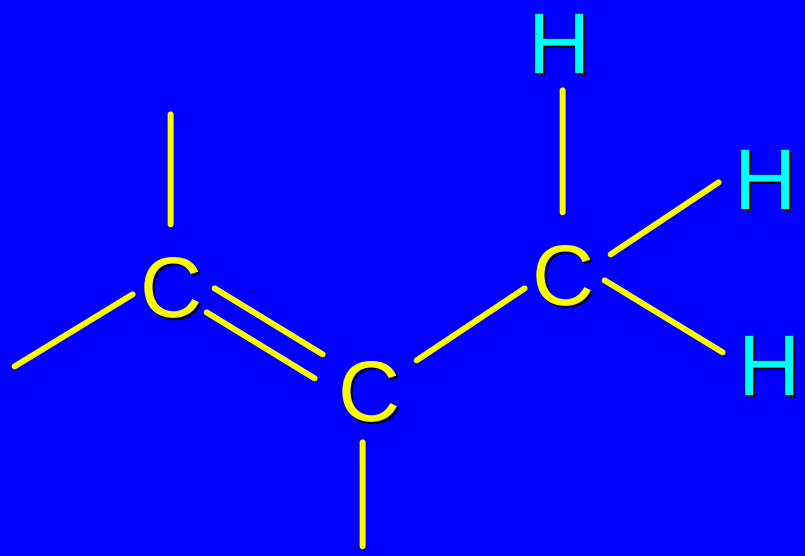
allylic carbon

# *Vinylic versus Allylic*



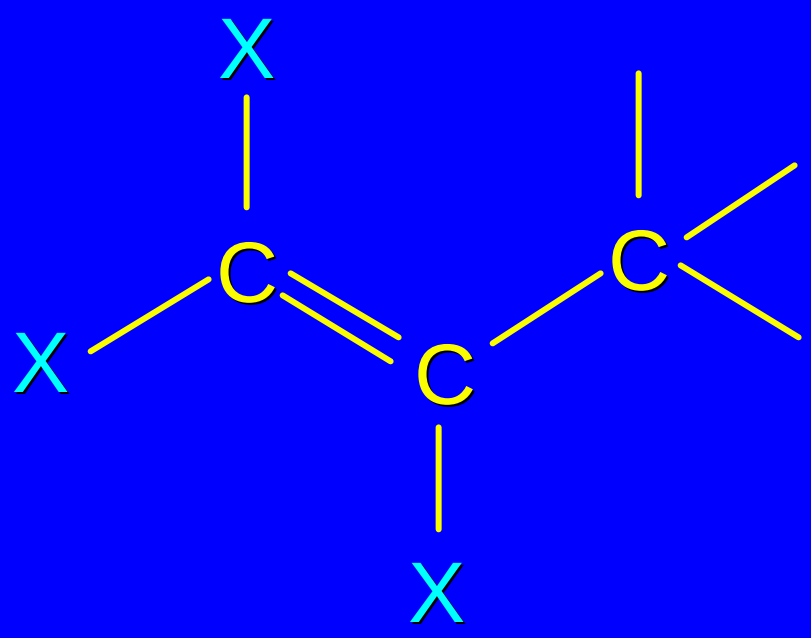

vinylic hydrogens are attached to vinylic carbons

# *Vinylic versus Allylic*



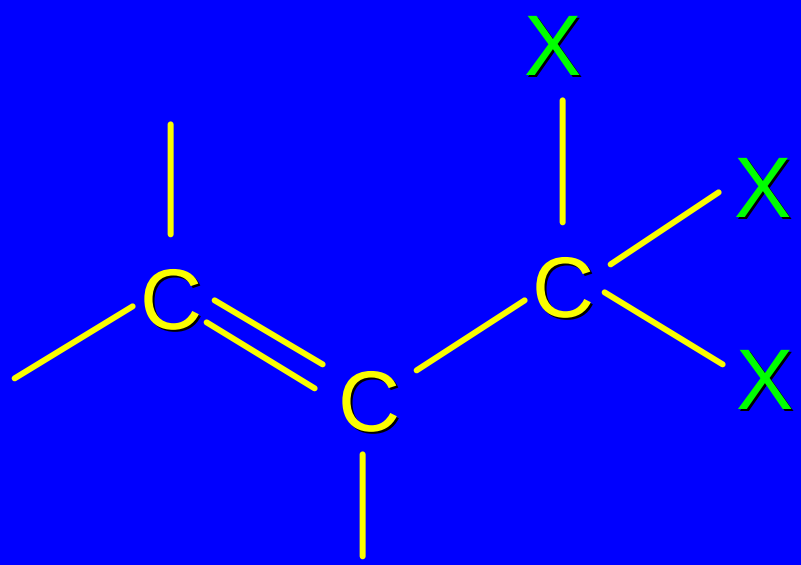

allylic hydrogens are attached to allylic carbons

# *Vinylic versus Allylic*




vinylic substituents are attached to vinylic carbons

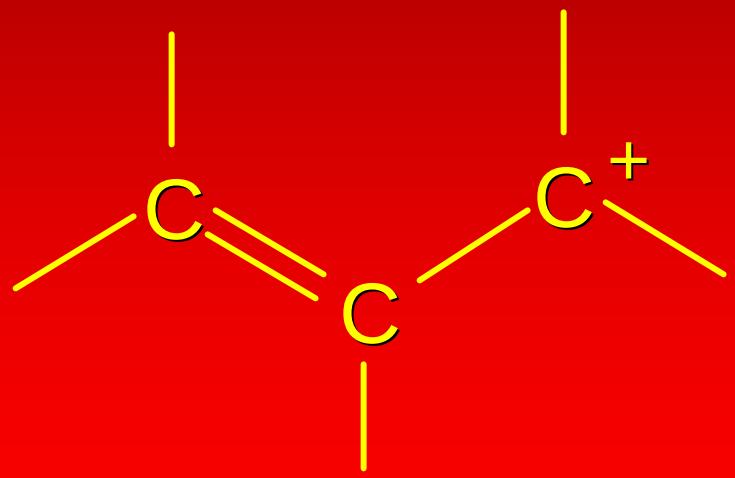
# *Vinylic versus Allylic*




allylic substituents are attached to allylic carbons

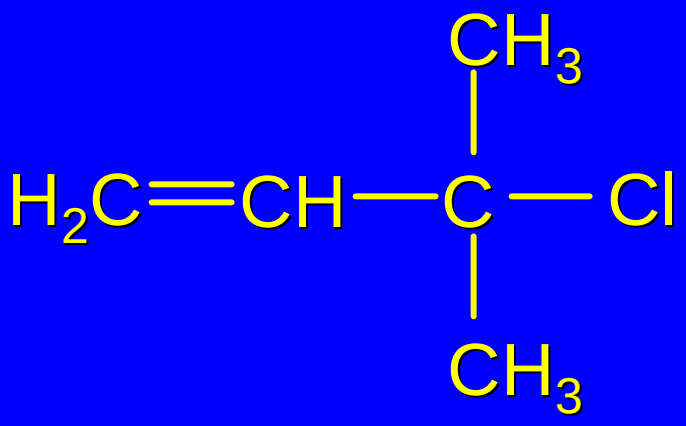
# 10.2

# Allylic Carbocations

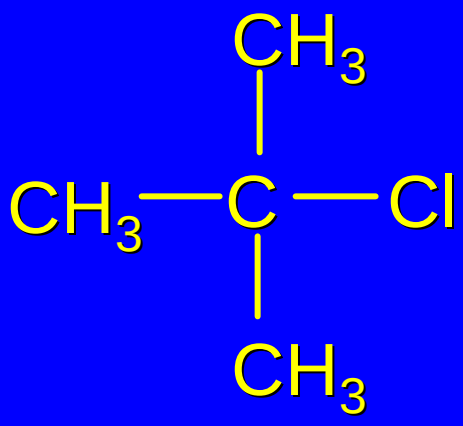


# *Allylic Carbocations*

the fact that a tertiary allylic halide undergoes solvolysis ($S_N1$) faster than a simple tertiary alkyl halide



123

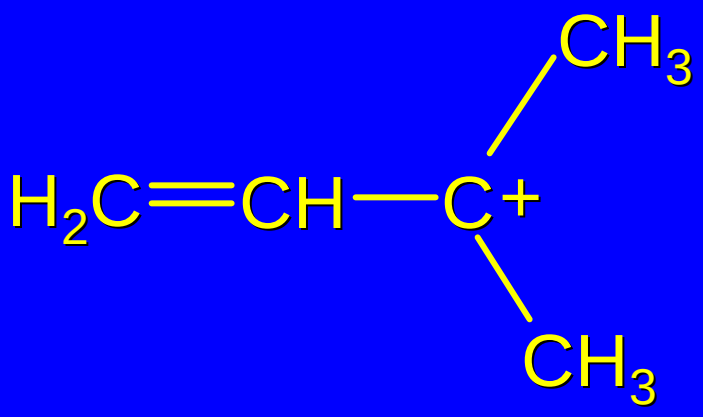


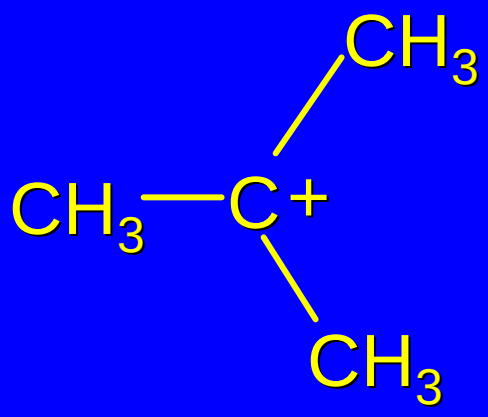
1

relative rates: (ethanolysis, 45°C)

# *Allylic Carbocations*

provides good evidence for the conclusion that allylic carbocations are more stable than other carbocations

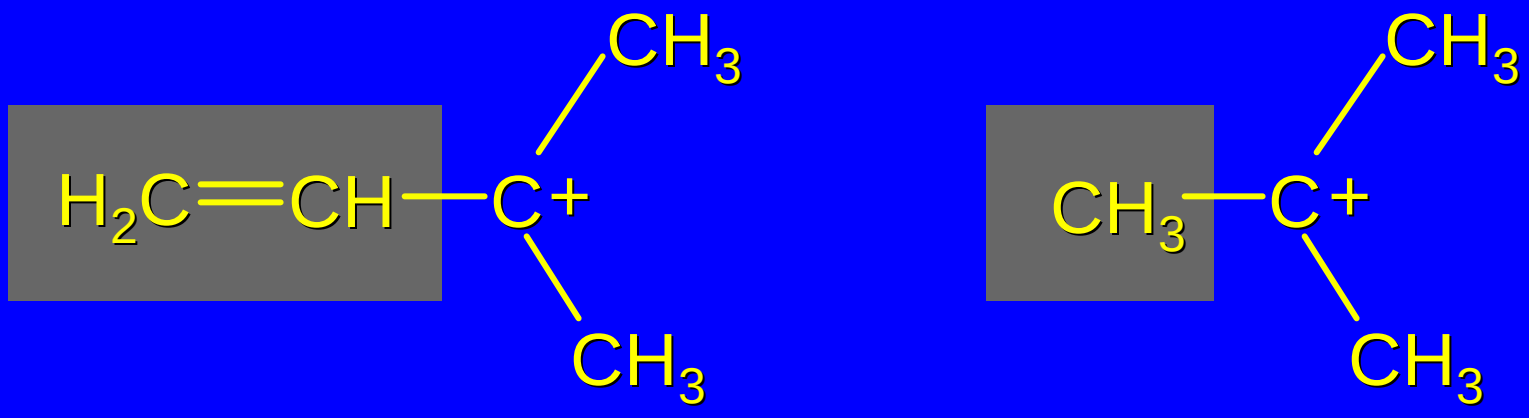



formed faster

# *Allylic Carbocations*

provides good evidence for the conclusion that allylic carbocations are more stable than other carbocations




$H_2C{=}CH{-}$ stabilizes C+ better than $CH_3{-}$

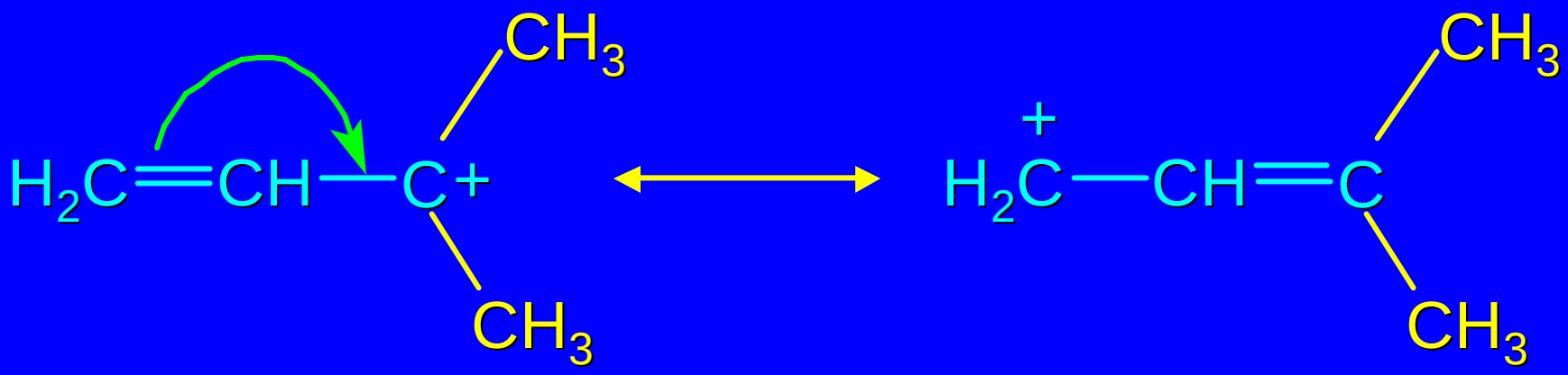
# *Stabilization of Allylic Carbocations*

Delocalization of electrons in the double bond stabilizes the carbocation

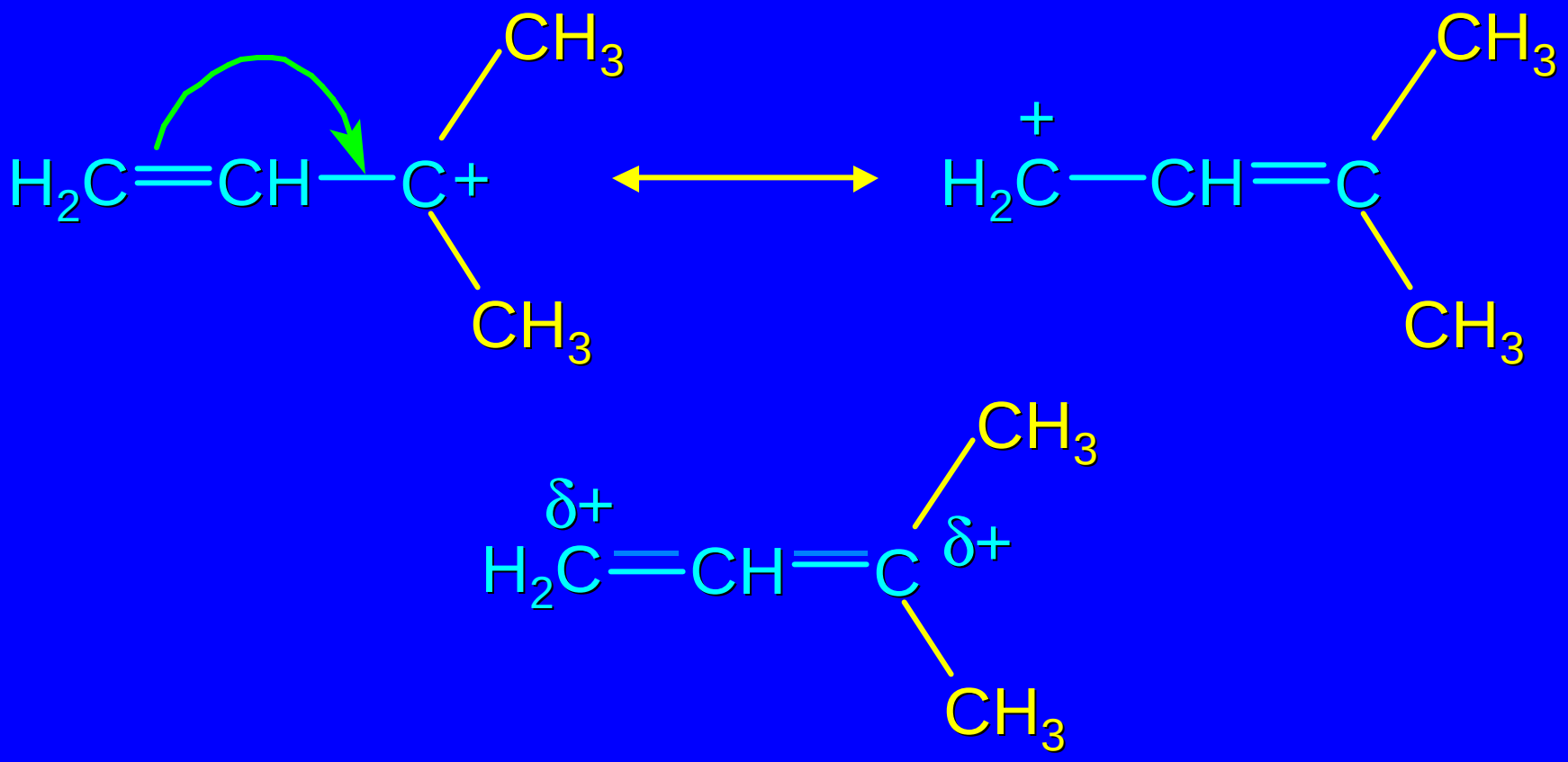
resonance model

orbital overlap model

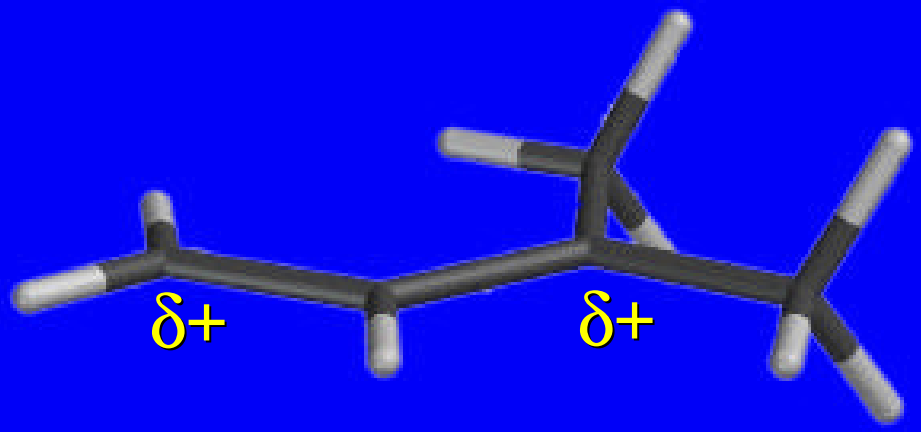
# *Resonance Model*



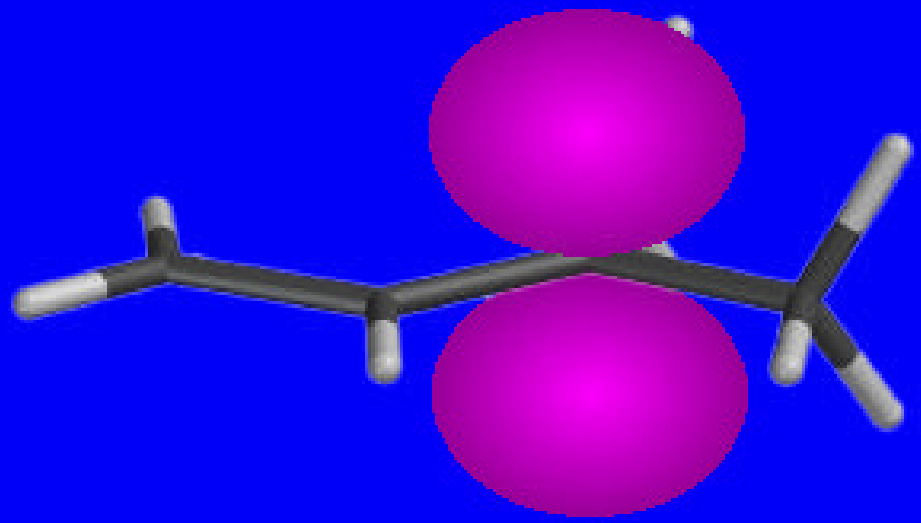
# *Resonance Model*



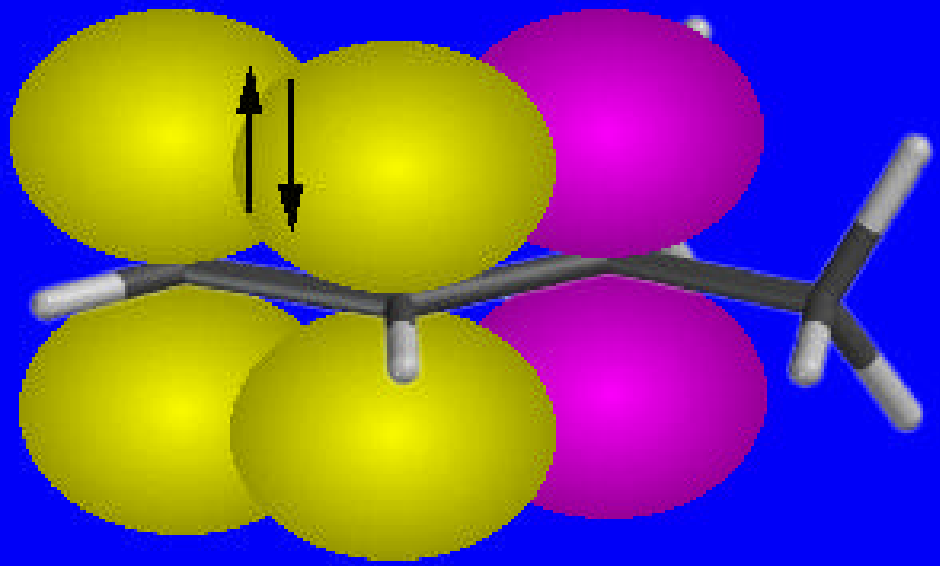
# *Orbital Overlap Model*



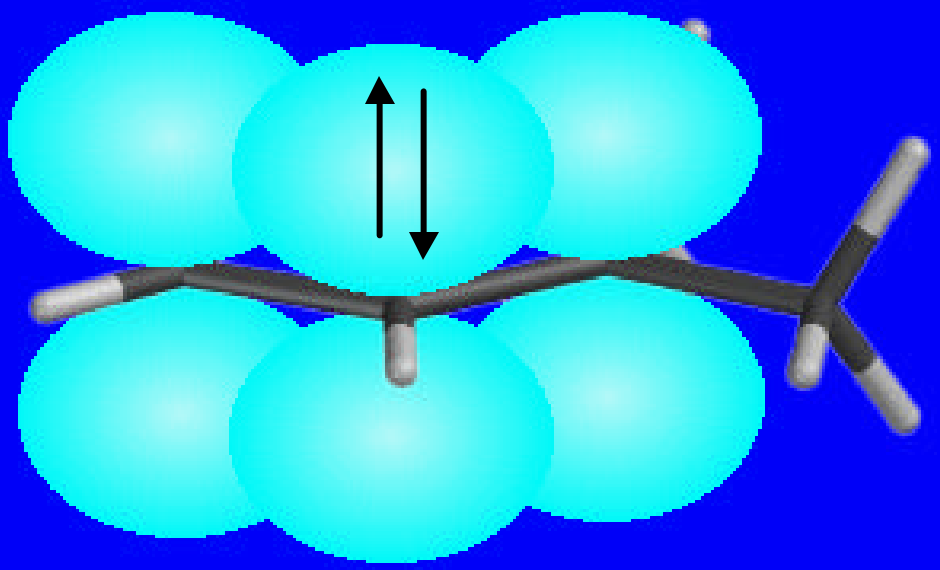
# *Orbital Overlap Model*



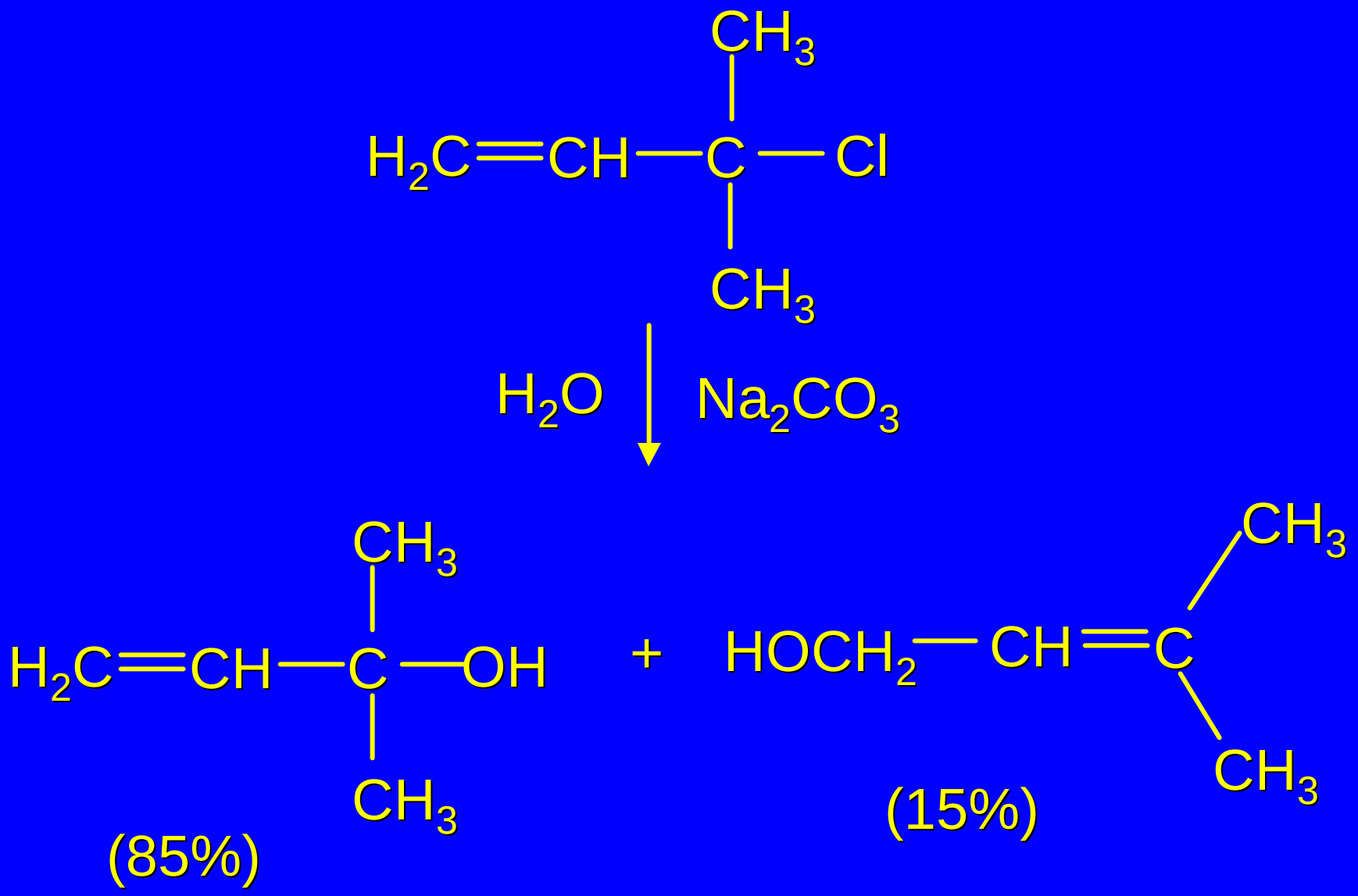
# *Orbital Overlap Model*



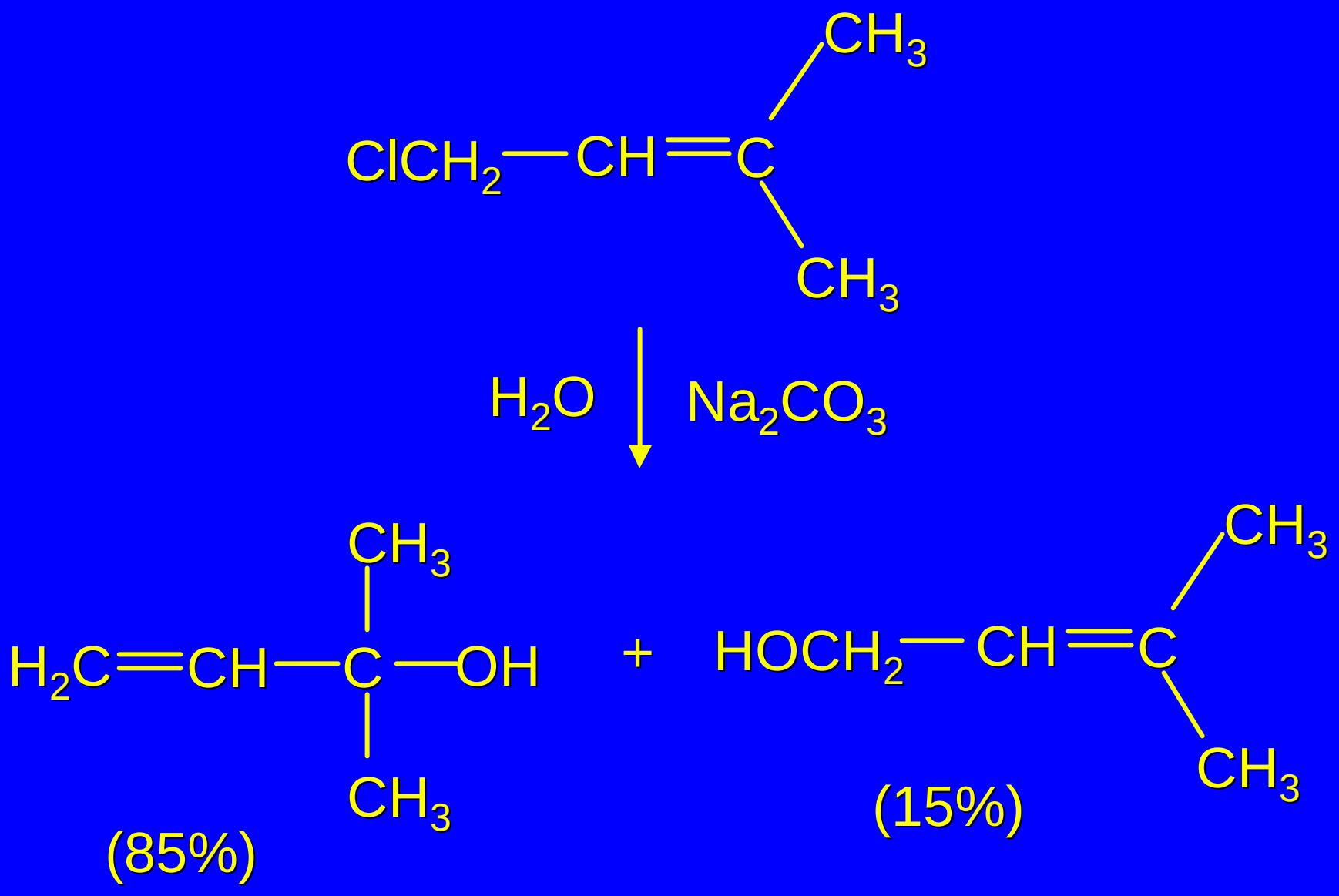
# *Orbital Overlap Model*



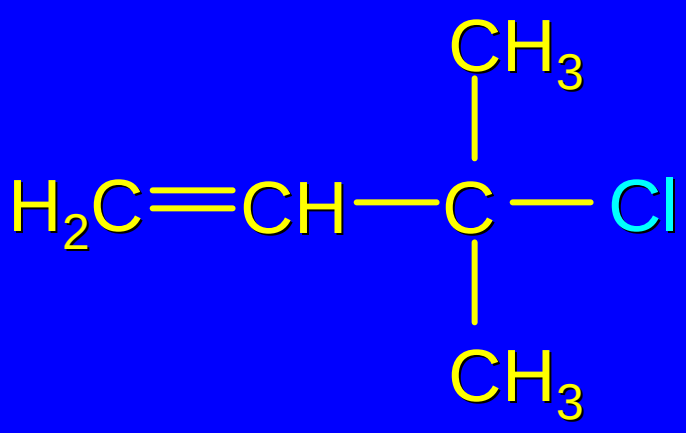
# *Hydrolysis of an Allylic Halide*



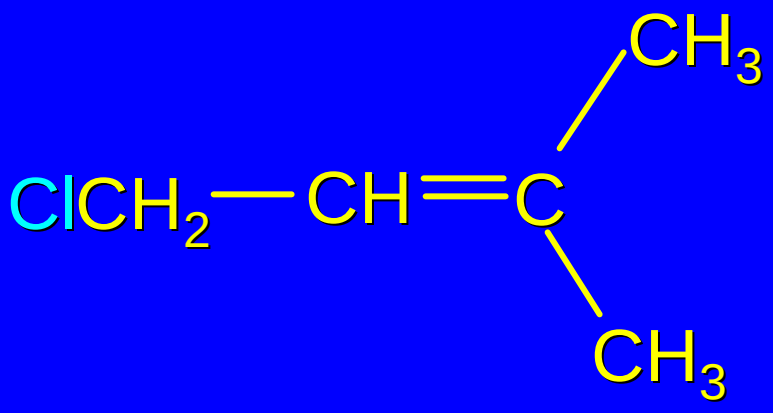
# *Corollary Experiment*




give the same products because they form the same carbocation



and



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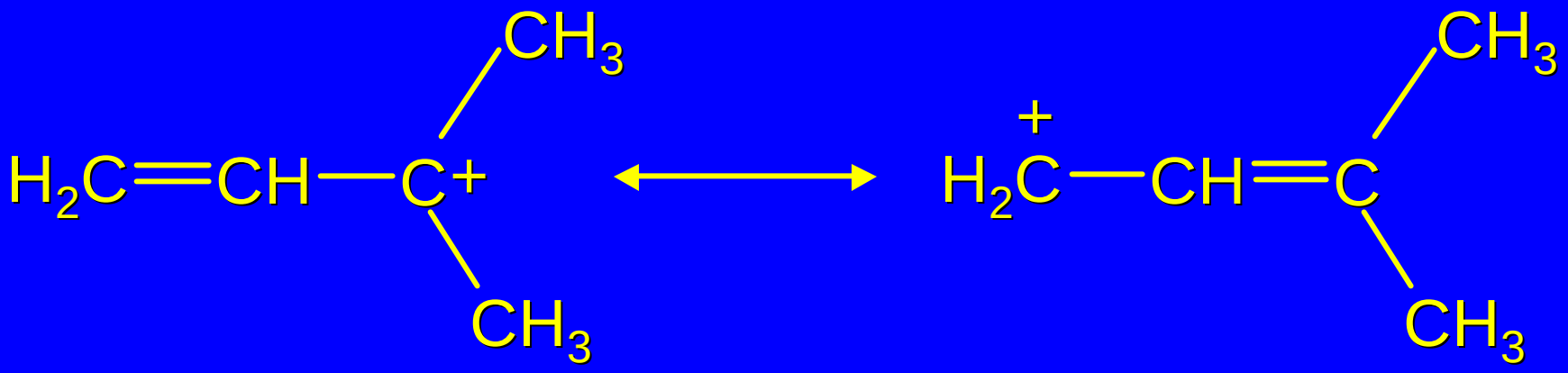
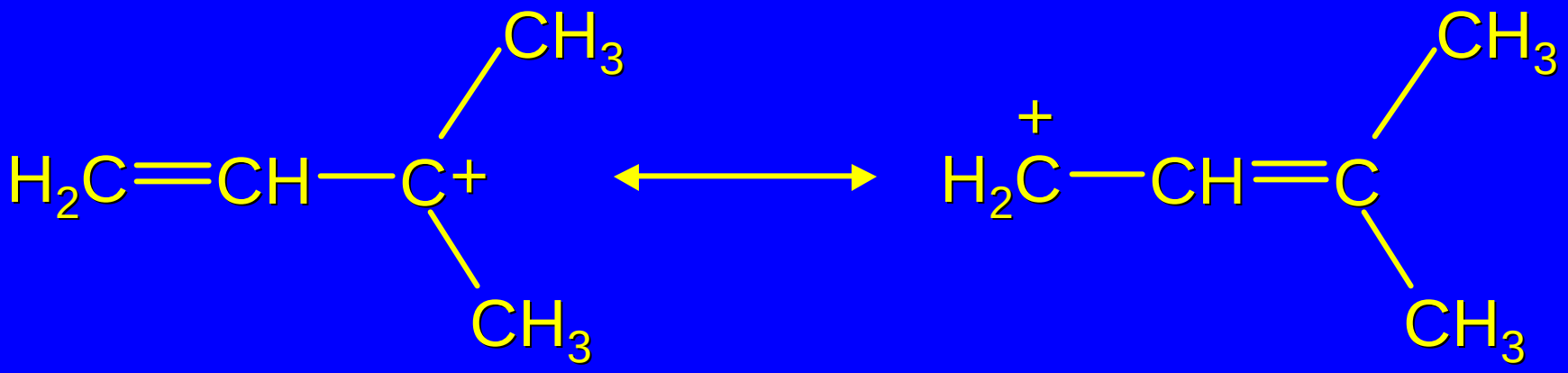
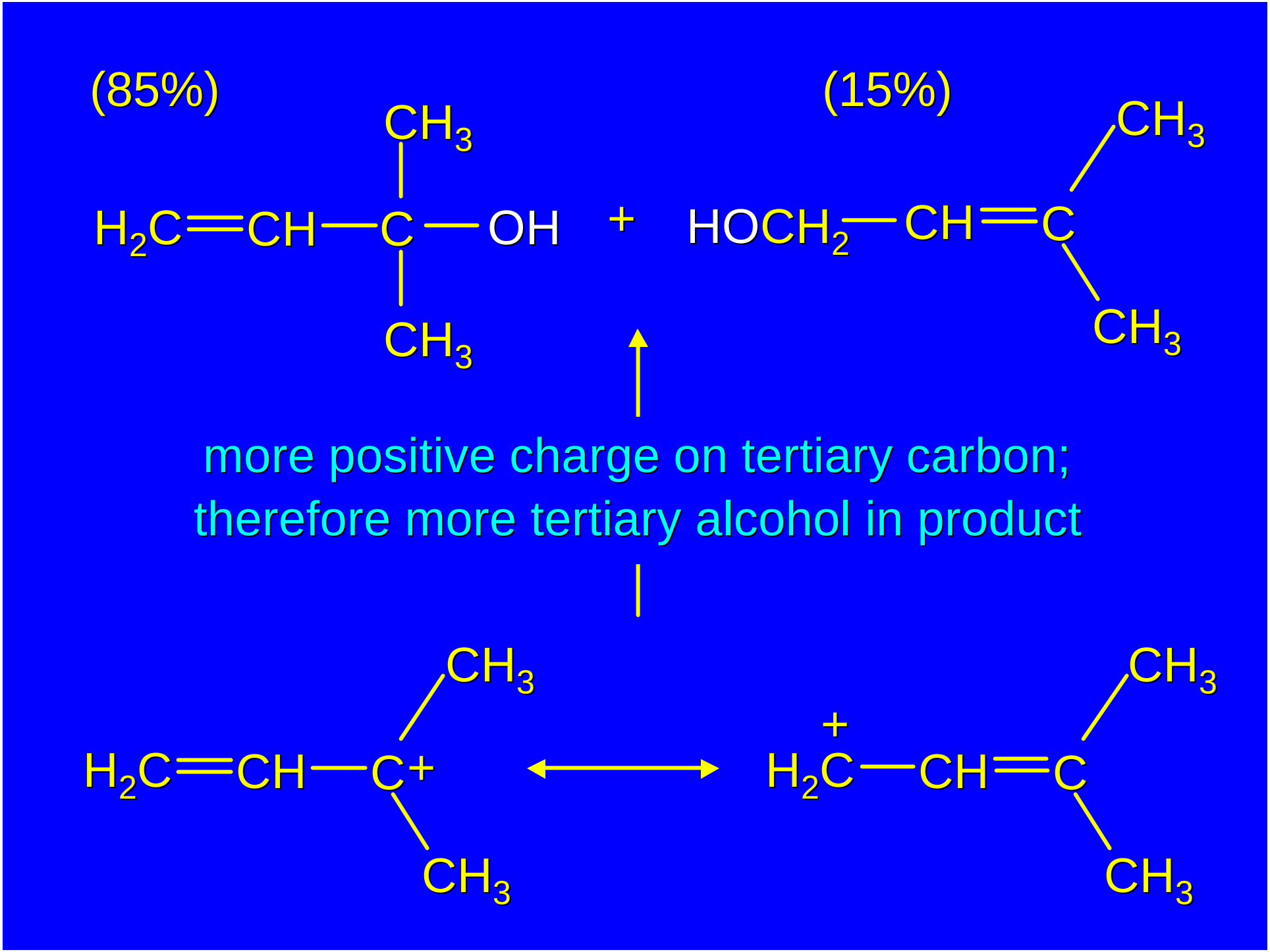


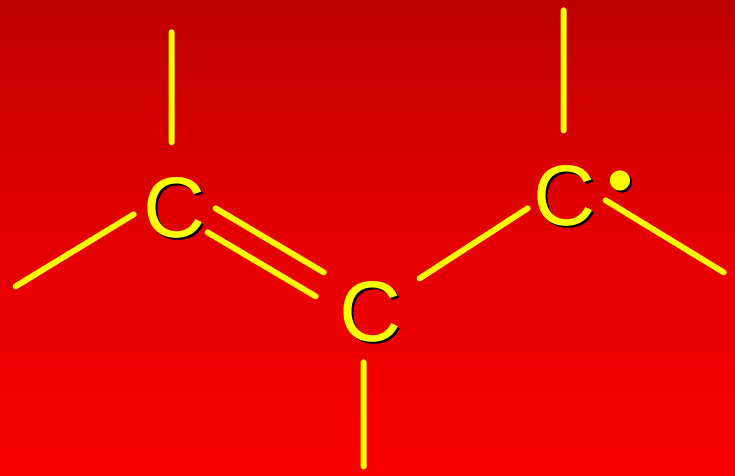
more positive charge on tertiary carbon;
therefore more tertiary alcohol in product



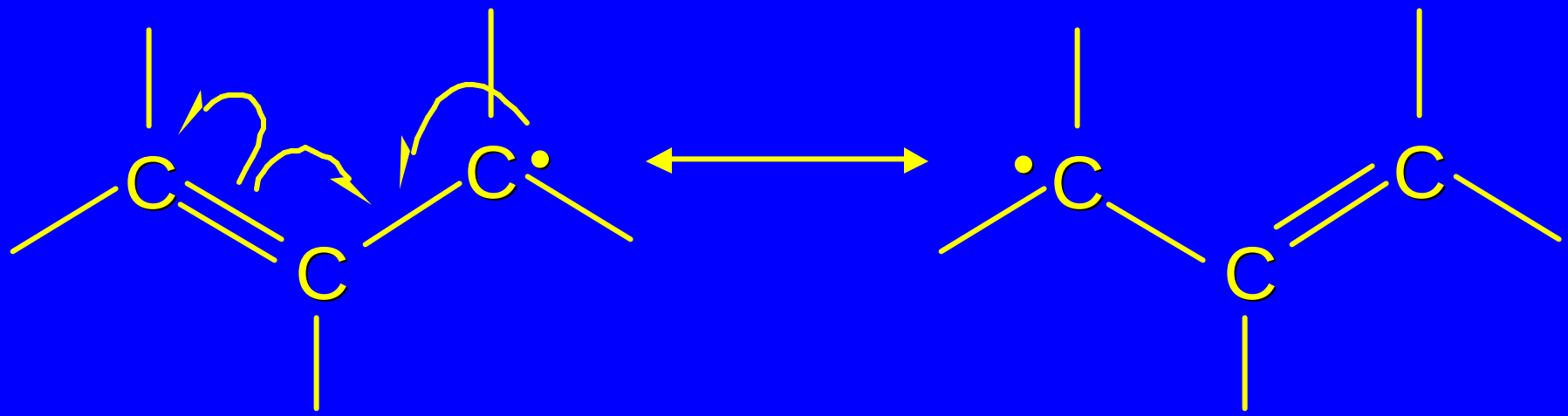

(85%)
(15%)
more positive charge on tertiary carbon;
therefore more tertiary alcohol in product

# 10.3

# Allylic Free Radicals



*Allylic free radicals are stabilized by electron delocalization*



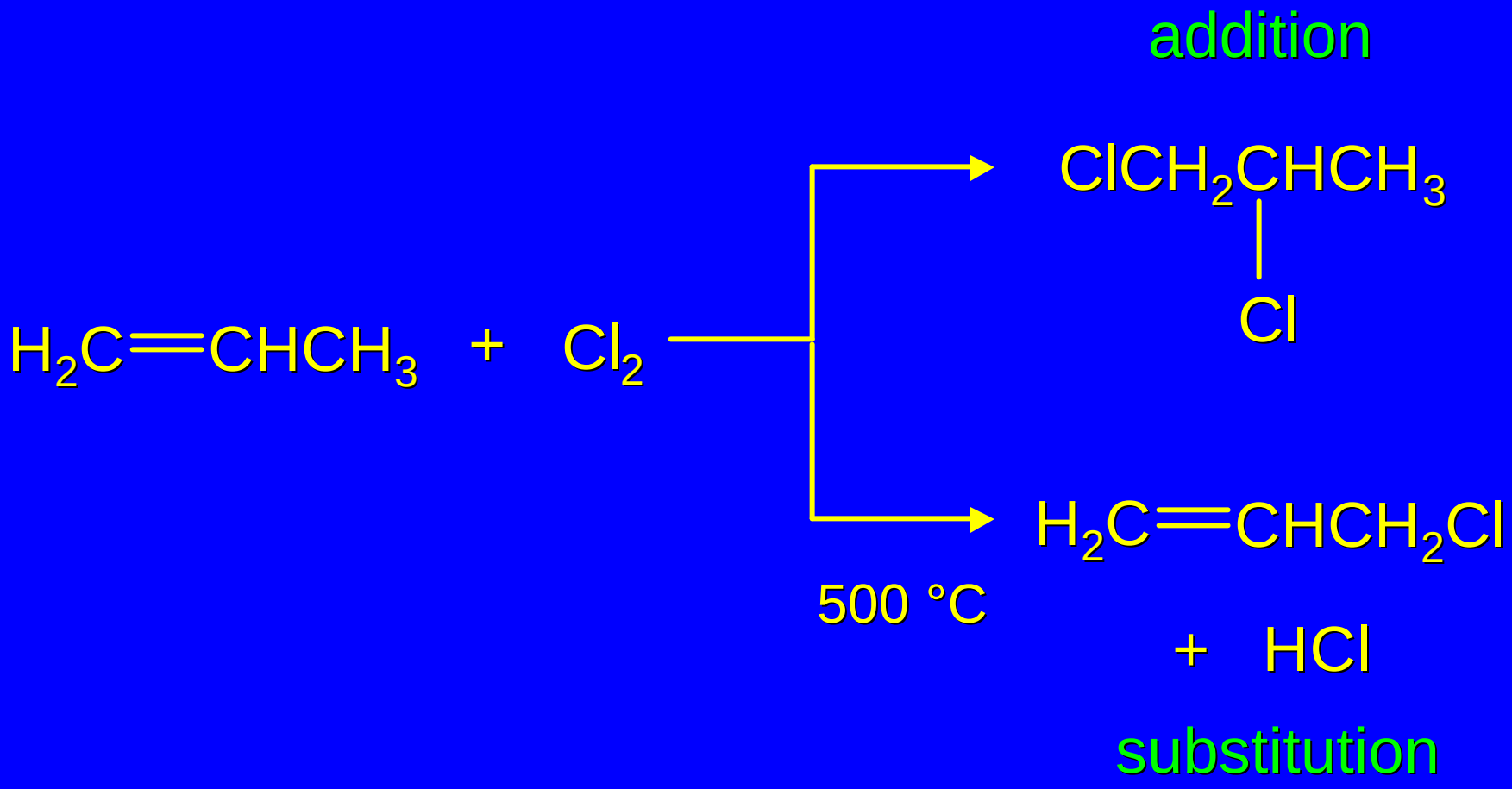
*Free-radical stabilities are related to bond-dissociation energies*



C—H bond is weaker in propene because resulting radical (allyl) is more stable than radical (propyl) from propane

# 10.4
# Allylic Halogenation

# *Chlorination of Propene*



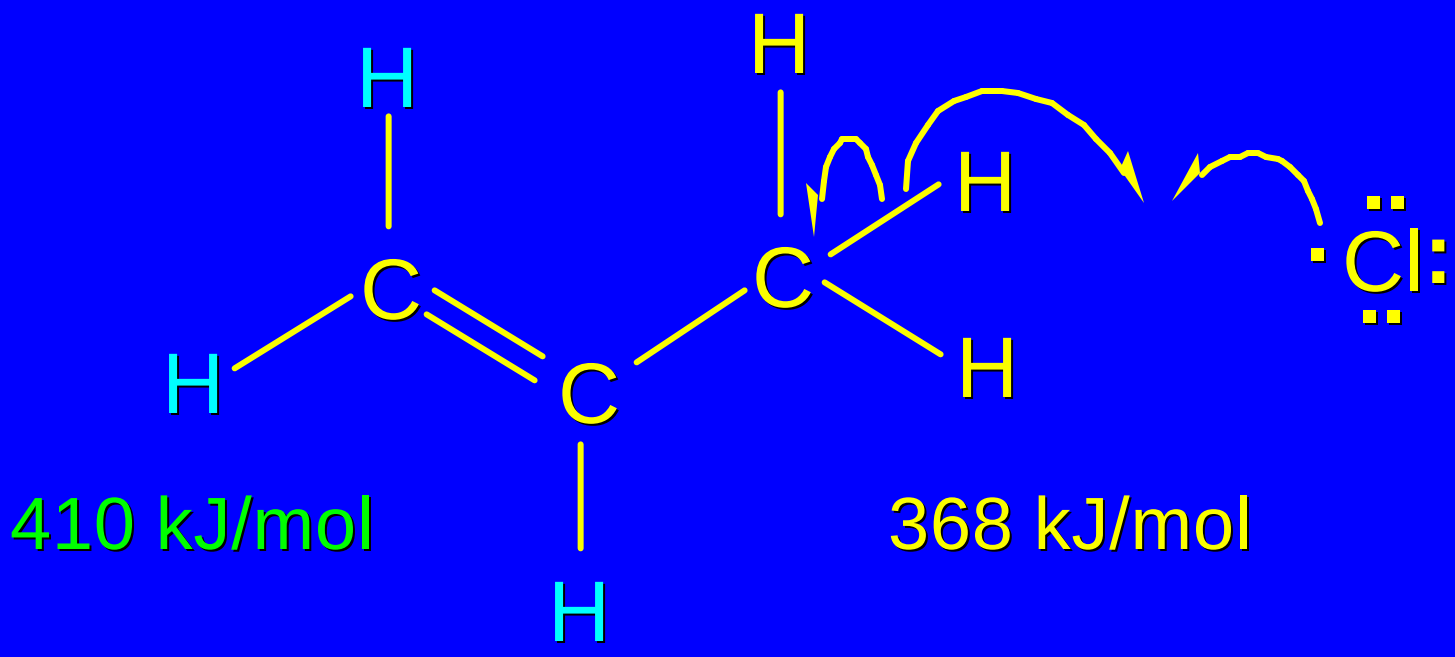
# *Allylic Halogenation*

selective for replacement of allylic hydrogen

free radical mechanism

allylic radical is intermediate

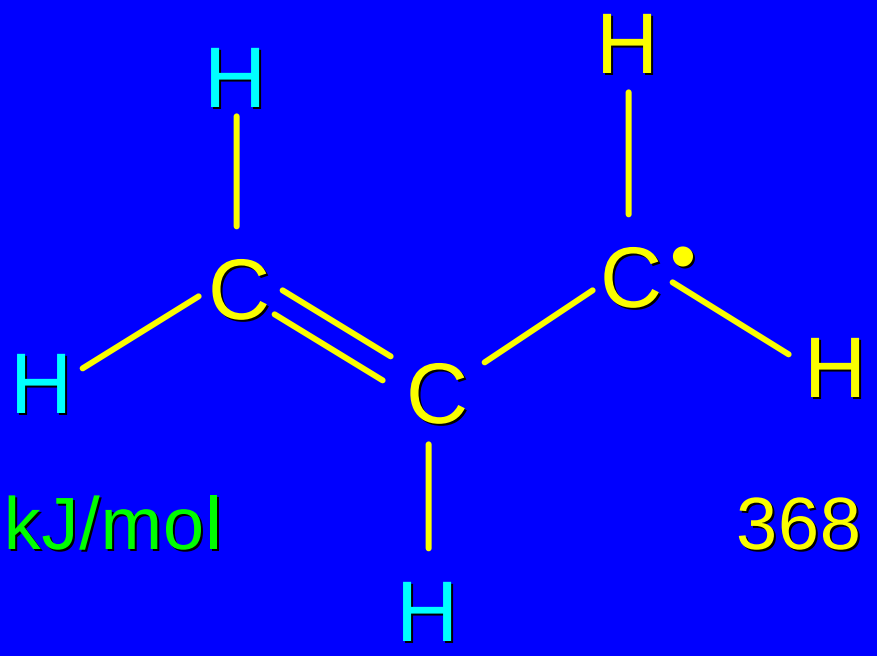
## *Hydrogen-atom abstraction step*



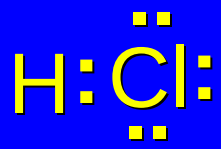

allylic C—H bond weaker than vinylic

chlorine atom abstracts allylic H in propagation step

## *Hydrogen-atom abstraction step*



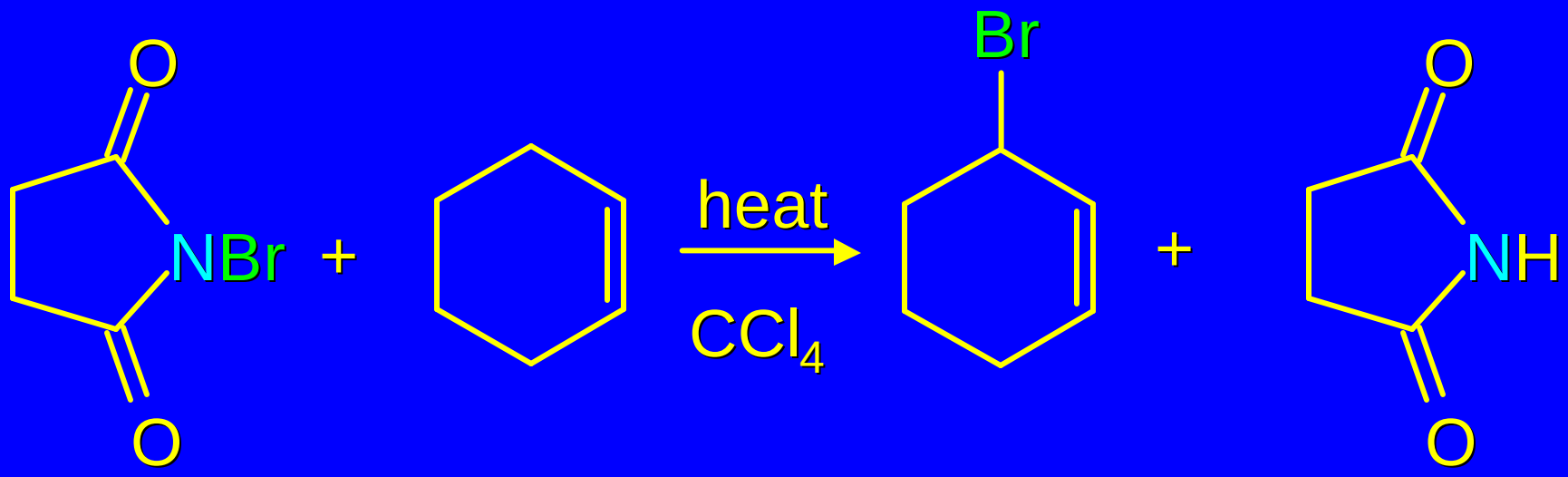

410 kJ/mol




368 kJ/mol

# *N-Bromosuccinimide*

reagent used (instead of $Br_2$) for allylic bromination




(82-87%)

## *Limited Scope*

Allylic halogenation is only used when:

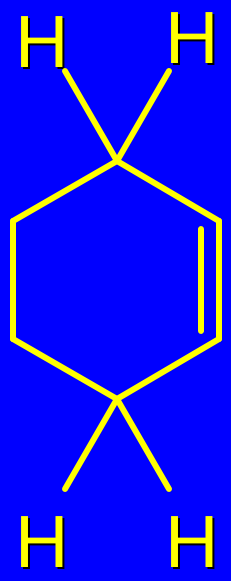
all of the allylic hydrogens are equivalent

and

the resonance forms of allylic radical are equivalent

*Example*

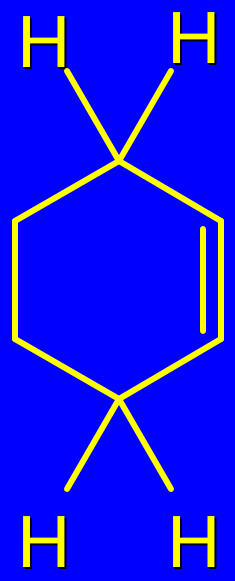
Cyclohexene satisfies both requirements



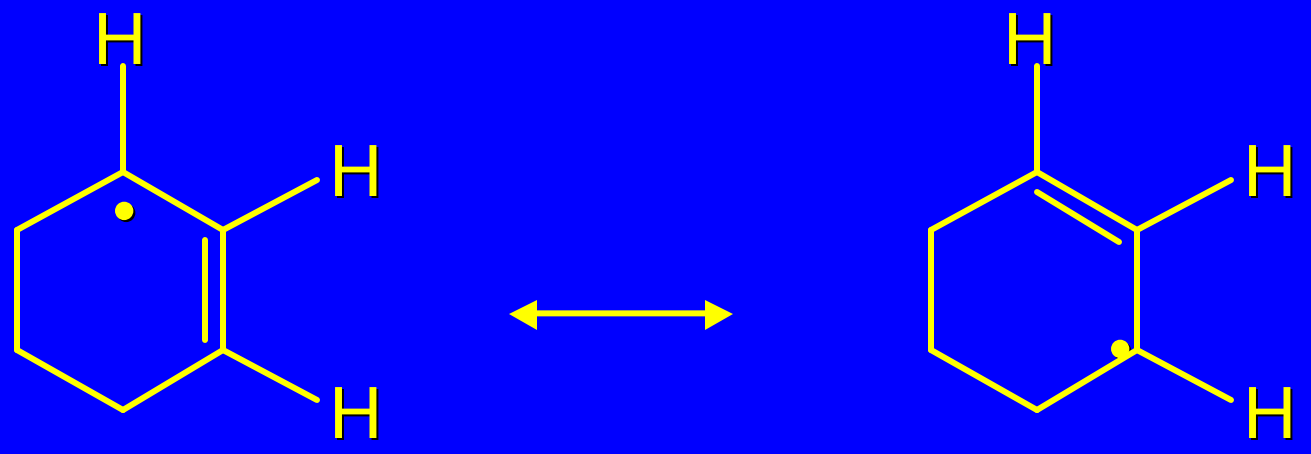

All allylic hydrogens are equivalent

*Example*

Cyclohexene satisfies both requirements




All allylic hydrogens are equivalent



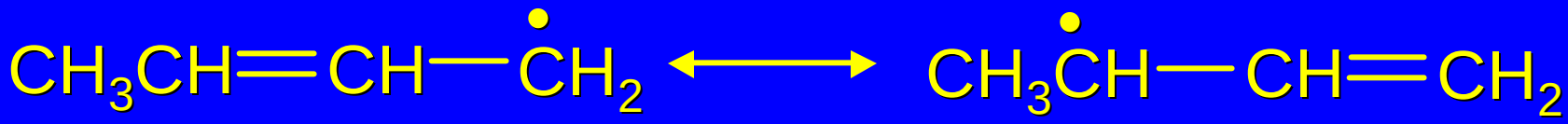

Both resonance forms are equivalent

*Example*

2-Butene $CH_3CH{=}CHCH_3$

All allylic hydrogens are equivalent

But



Two resonance forms are not equivalent; gives mixture of isomeric allylic bromides.