10.9
Preparation of Dienes

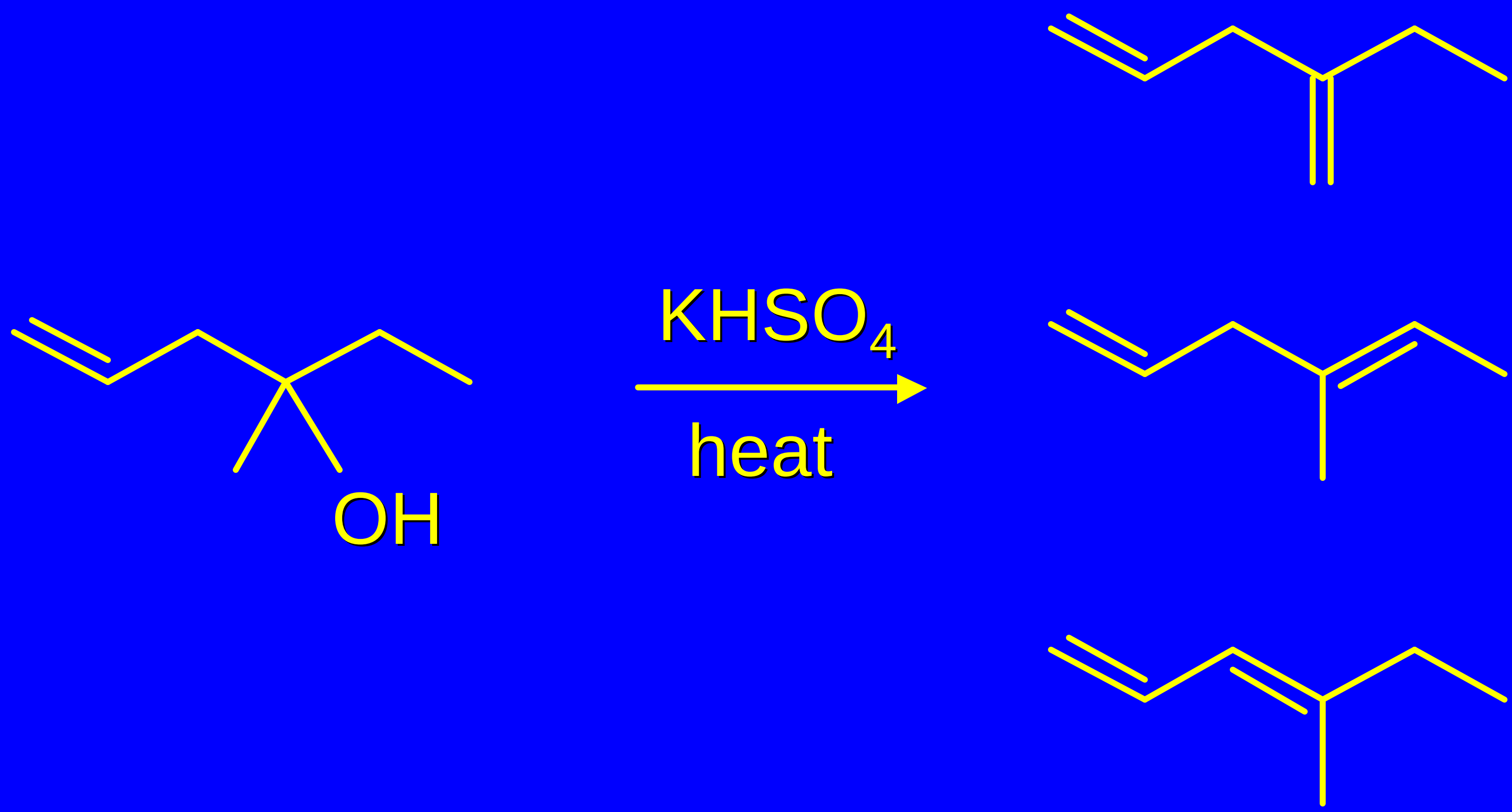
1,3-Butadiene

$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{chromia-alumina}]{590\text{-}675°C} H_2C{=}CHCH{=}CH_2 + 2H_2$$

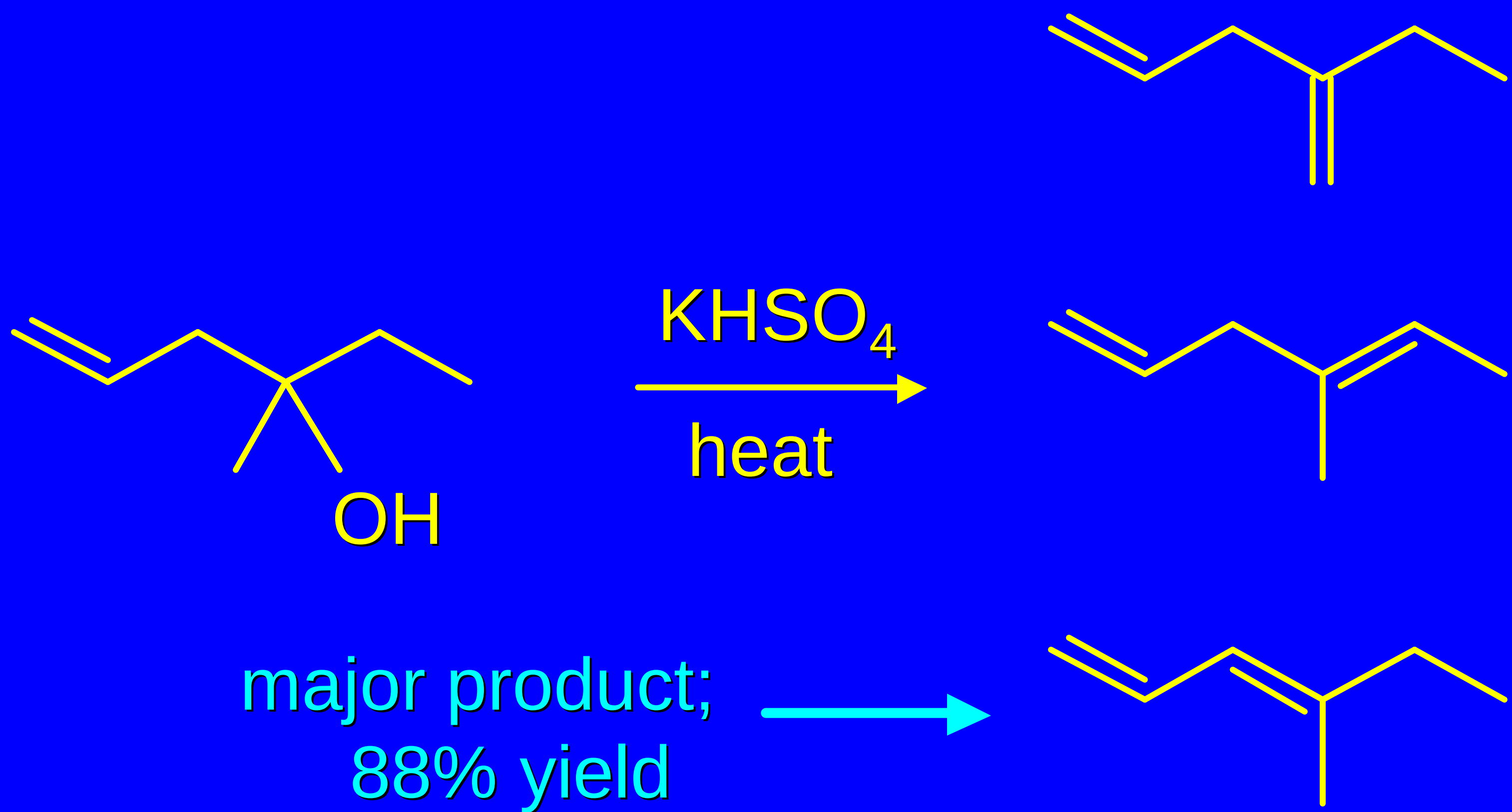
More than 4 billion pounds of 1,3-butadiene prepared by this method in U.S. each year

used to prepare synthetic rubber (See "Diene Polymers" box)

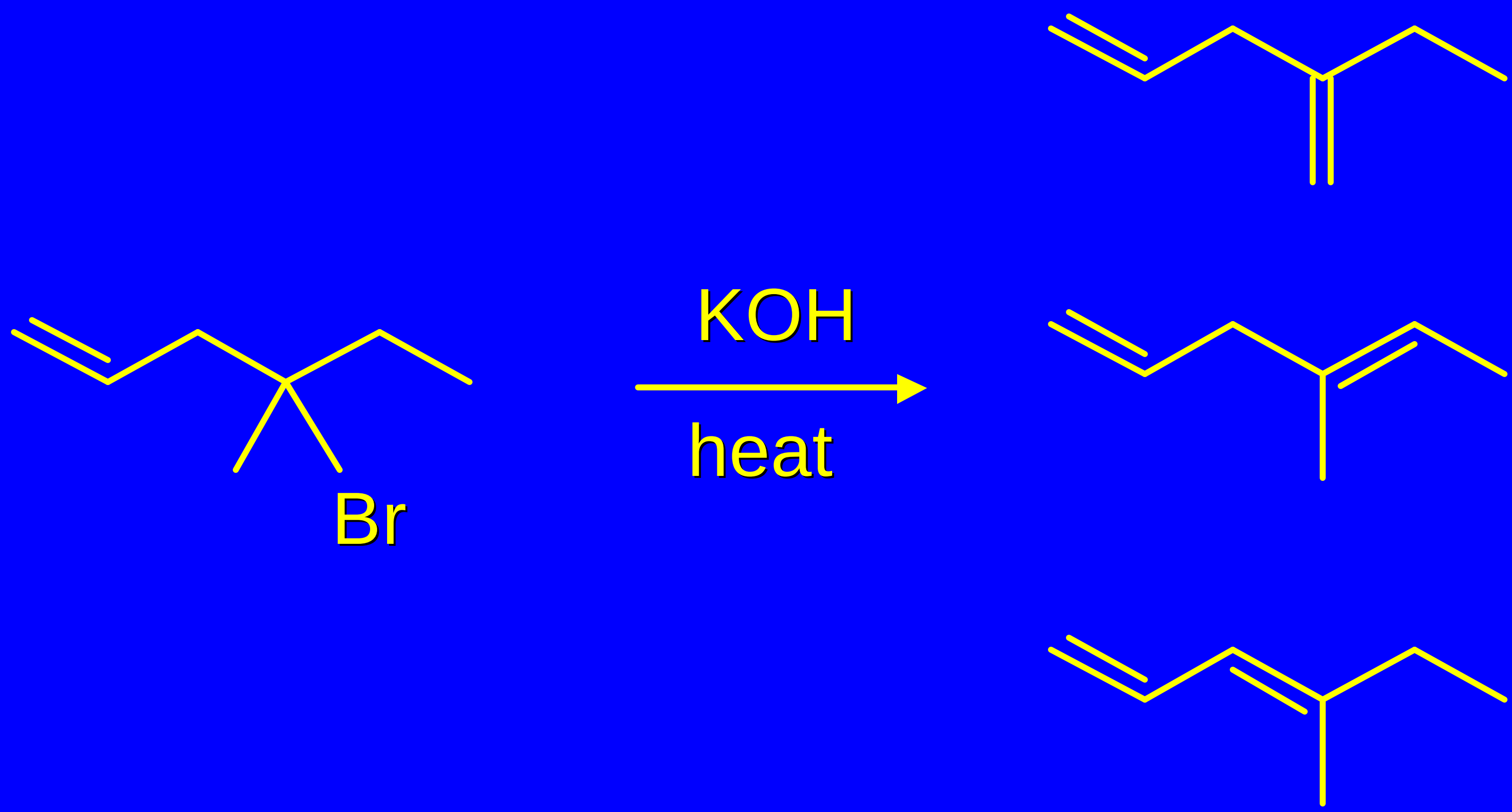
Dehydration of Alcohols



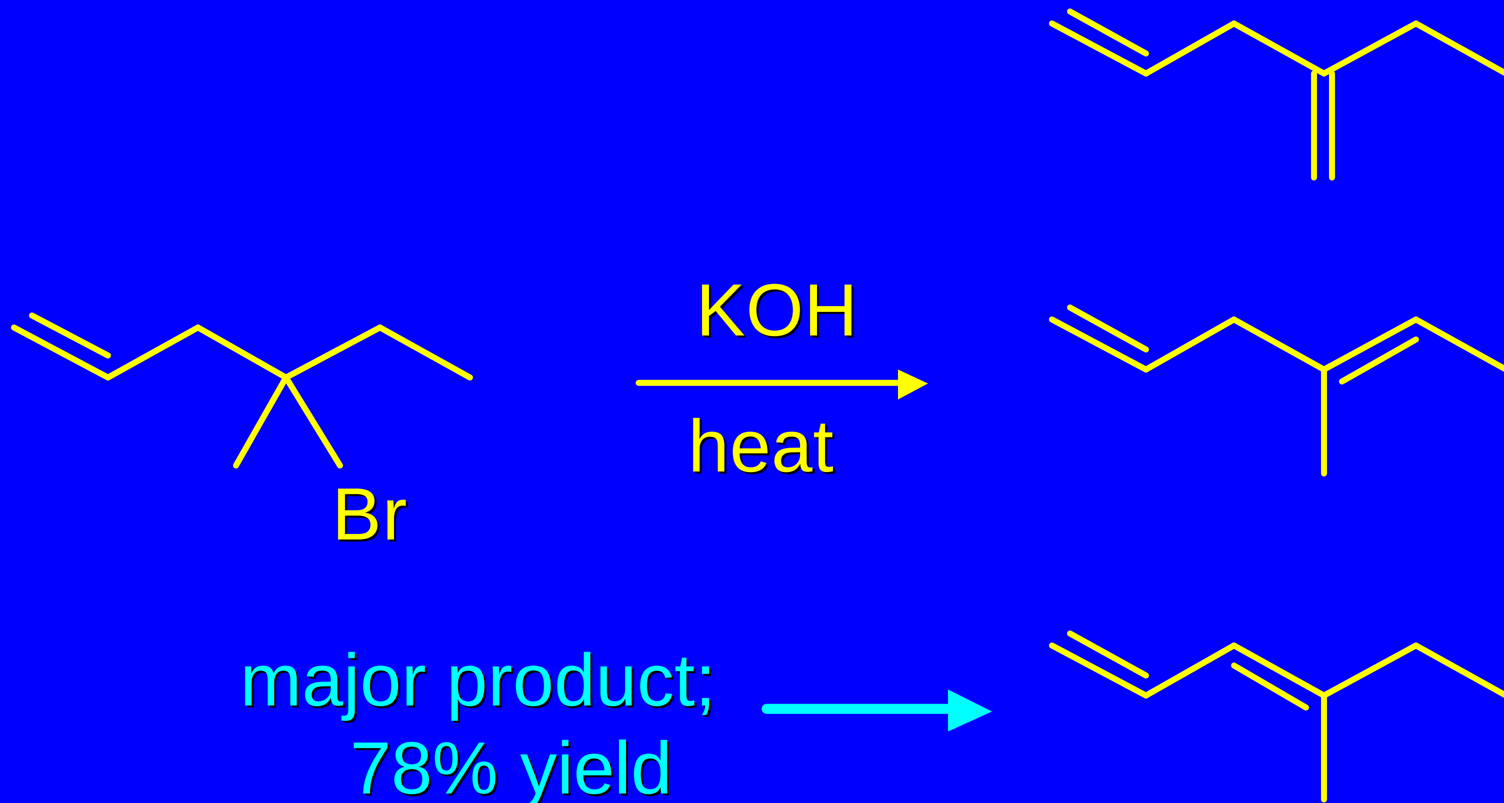
Dehydration of Alcohols



Dehydrohalogenation of Alkyl Halides



Dehydrohalogenation of Alkyl Halides



Reactions of Dienes

isolated dienes: double bonds react independently of one another

cumulated dienes: specialized topic

conjugated dienes: reactivity pattern requires us to think of conjugated diene system as a functional group of its own

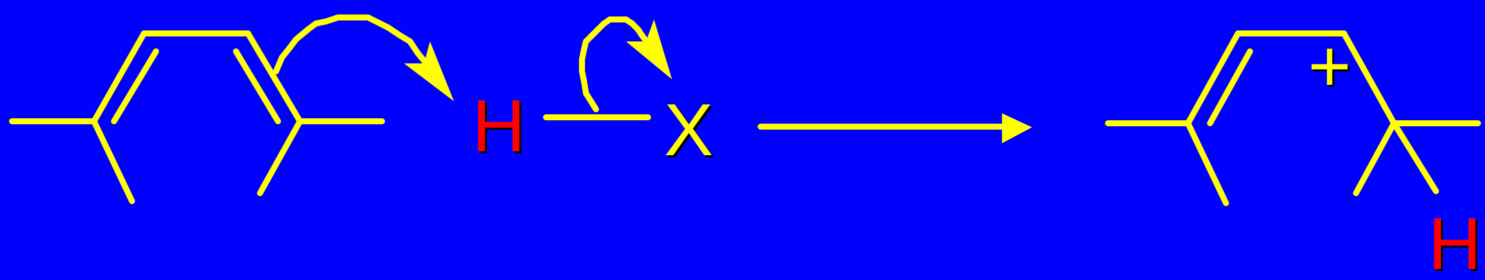
10.10

Addition of Hydrogen Halides

to

Conjugated Dienes

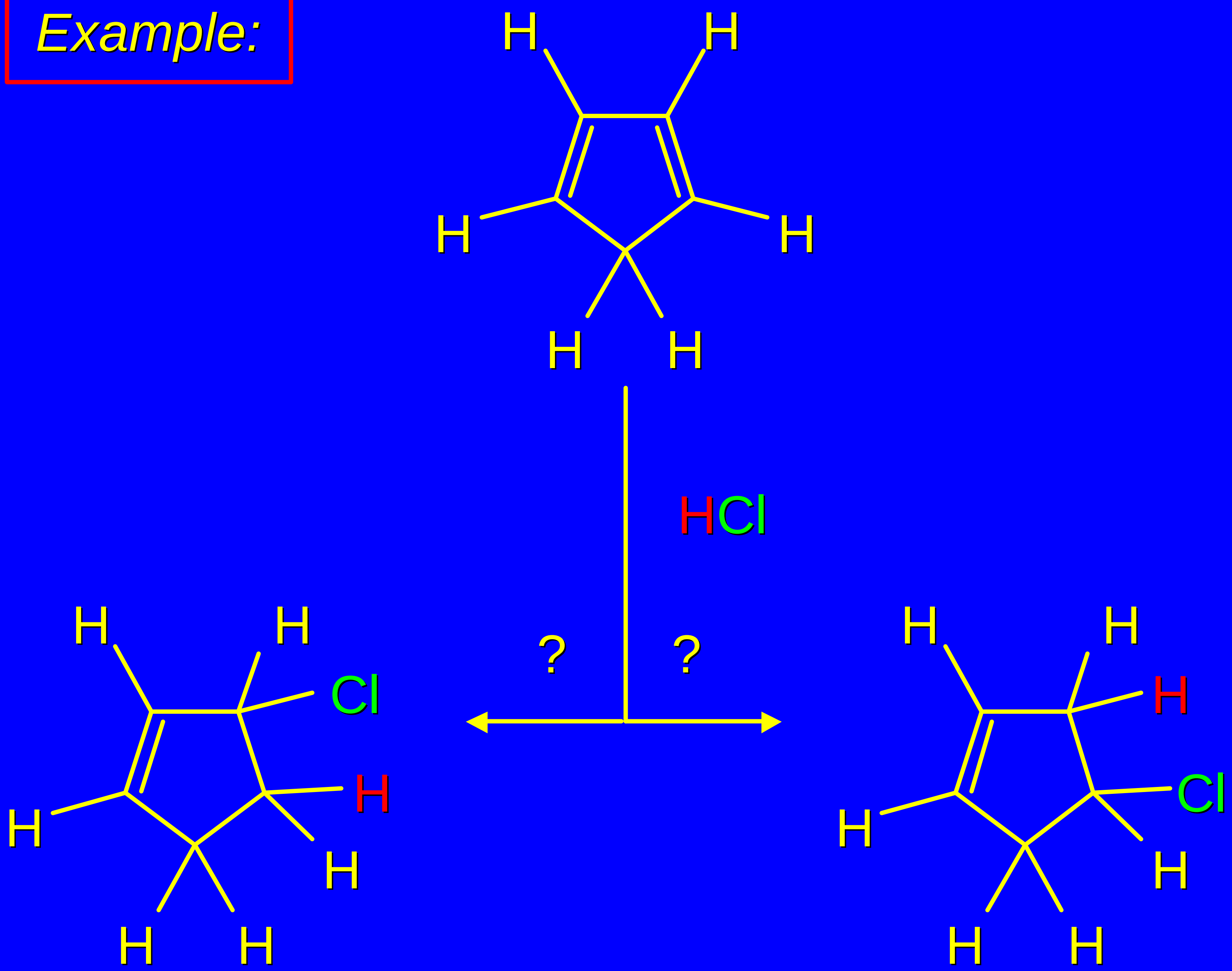
Electrophilic Addition to Conjugated Dienes



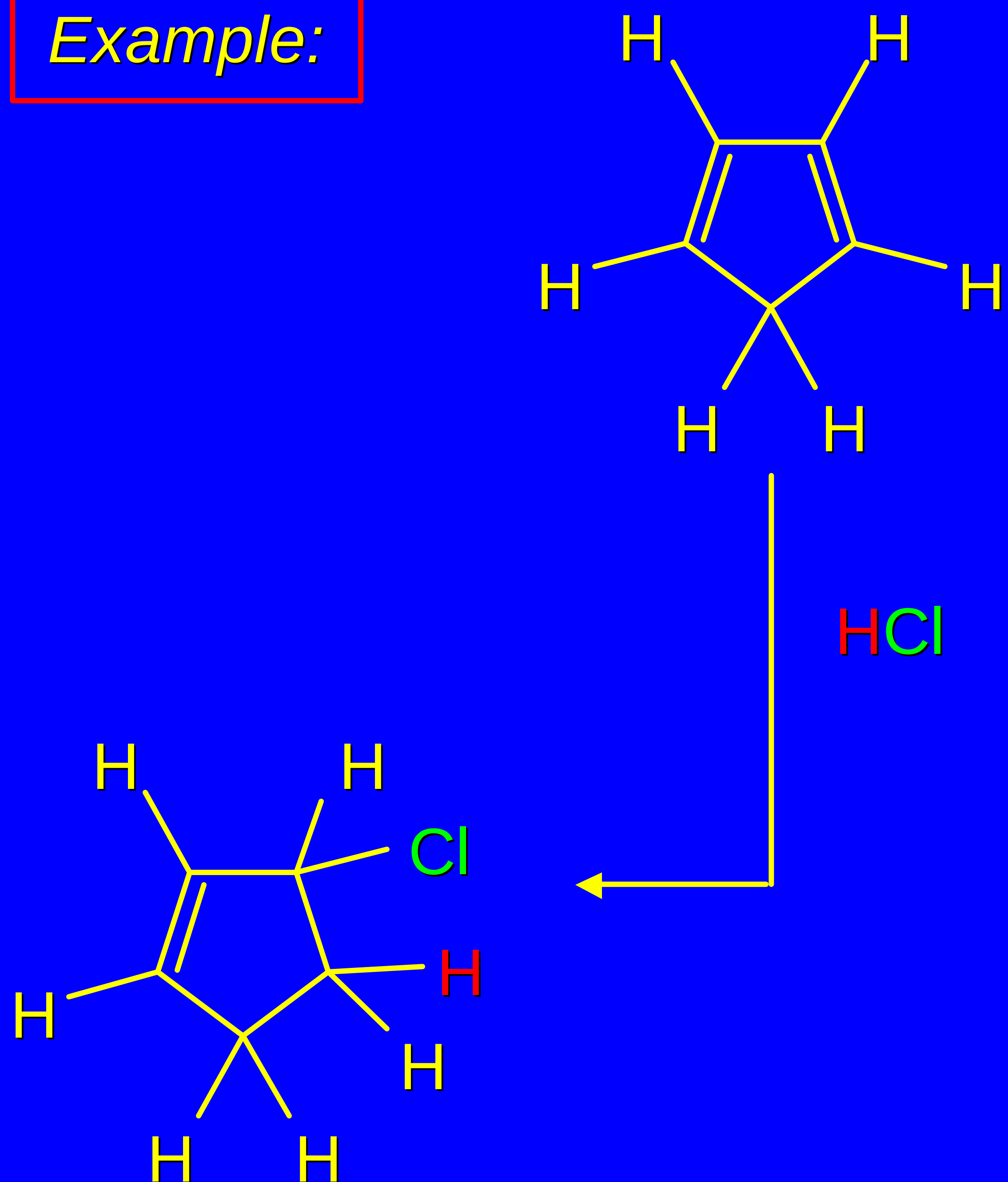
Proton adds to end of diene system

Carbocation formed is allylic

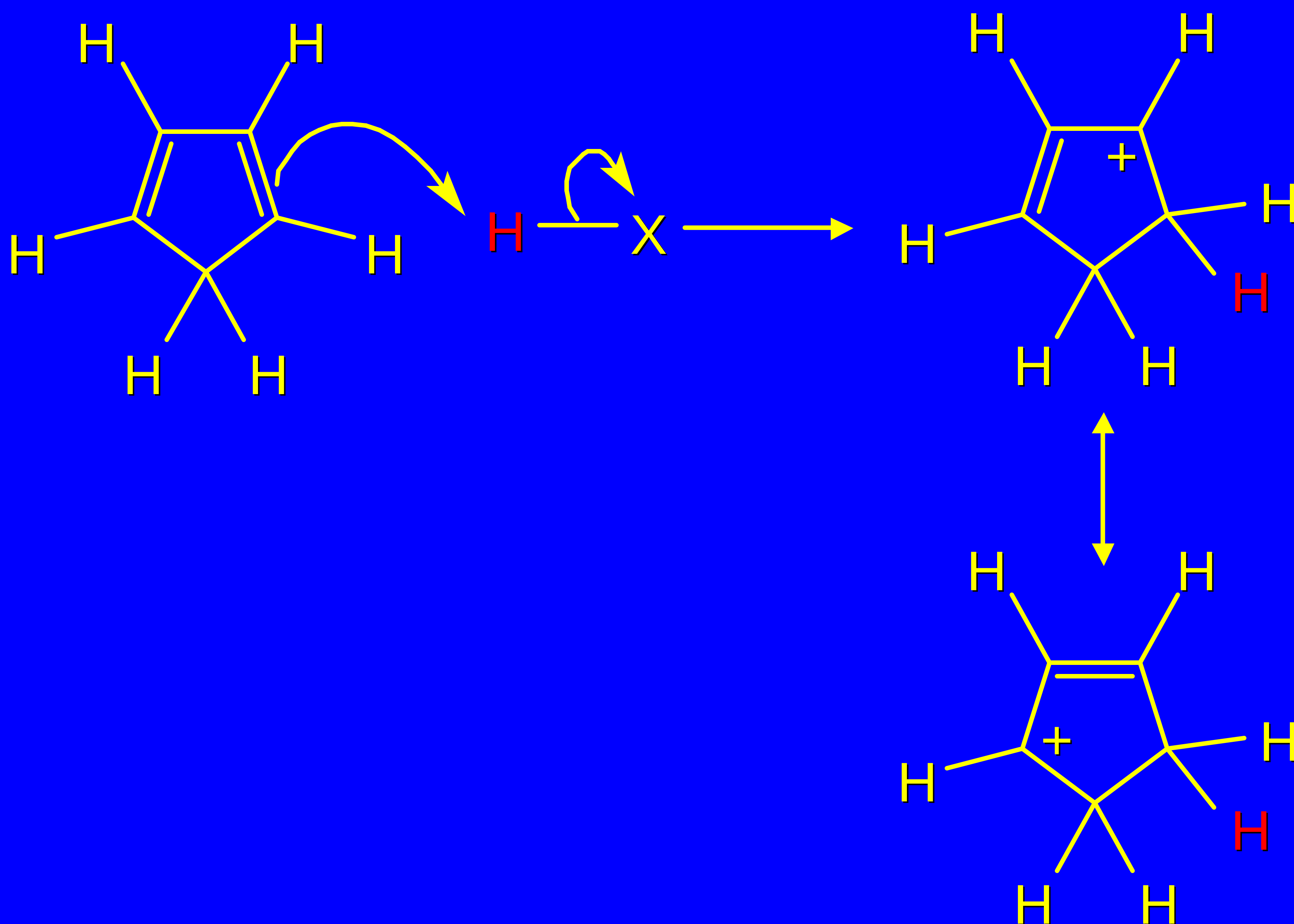
Example:



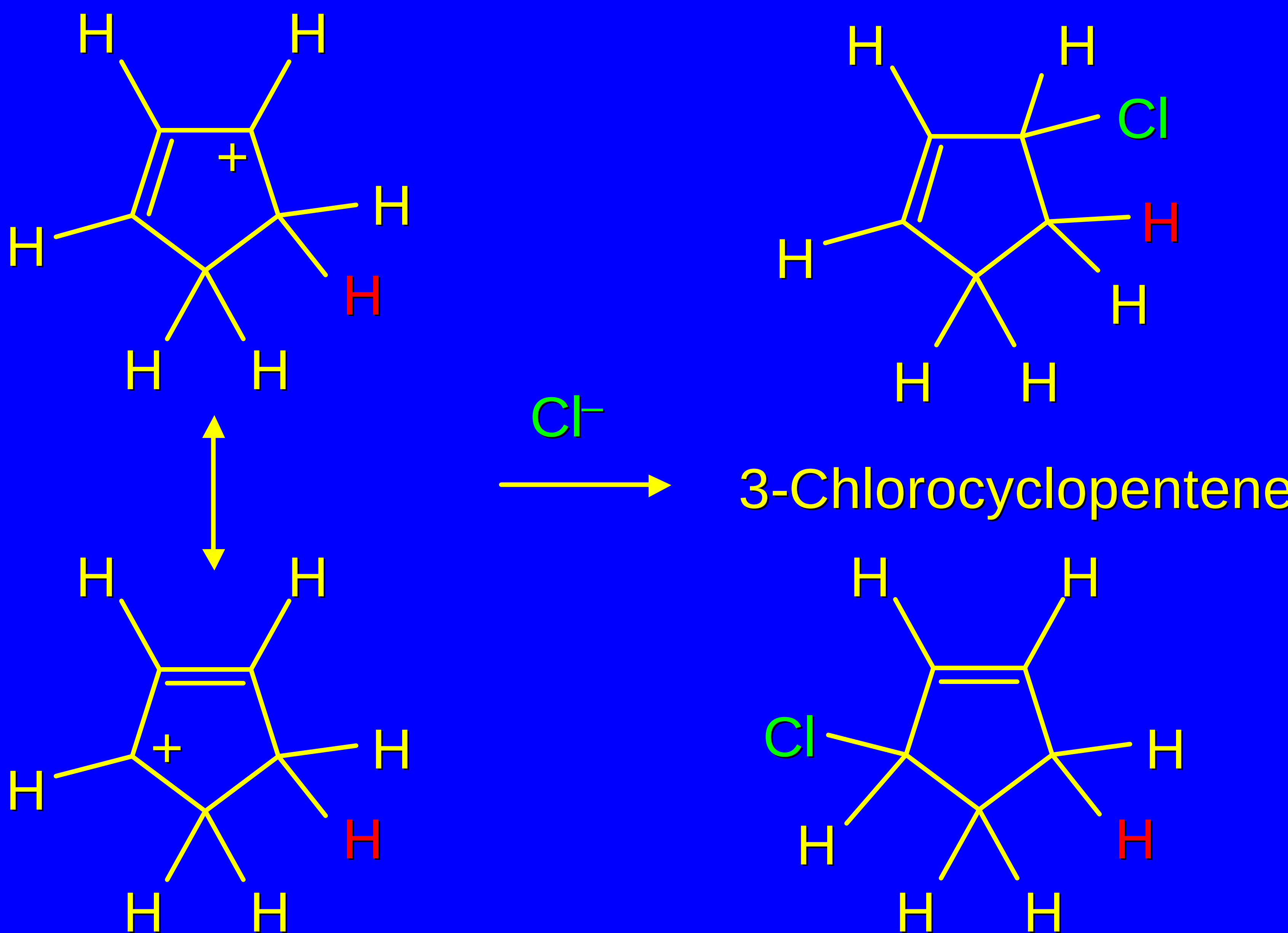
Example:



via:



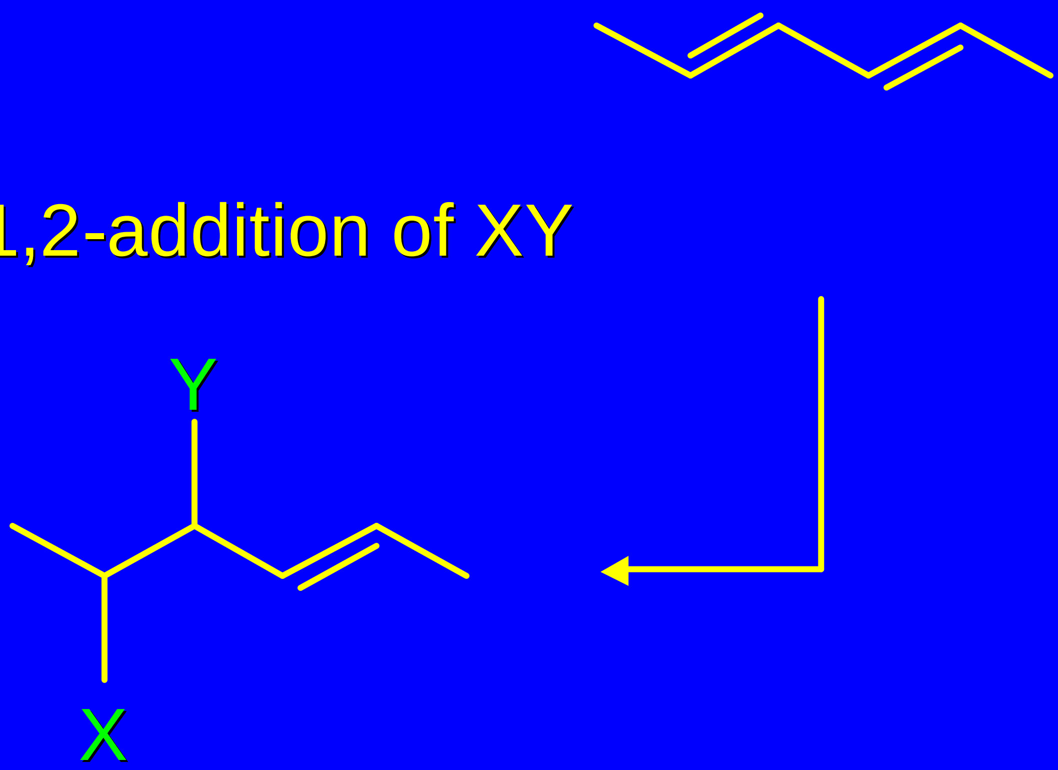
and:



3-Chlorocyclopentene

1,2-Addition versus 1,4-Addition

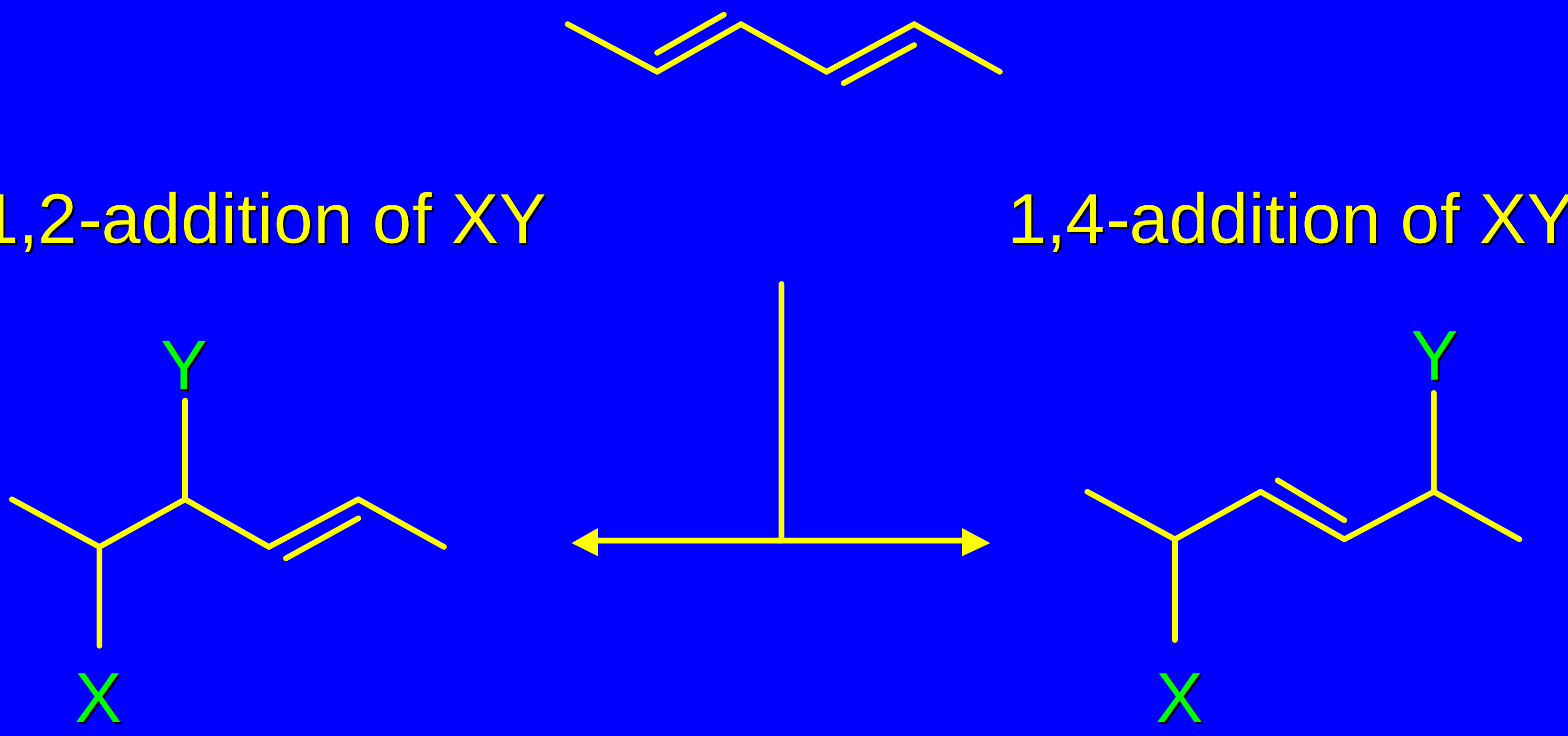
1,2-addition of XY



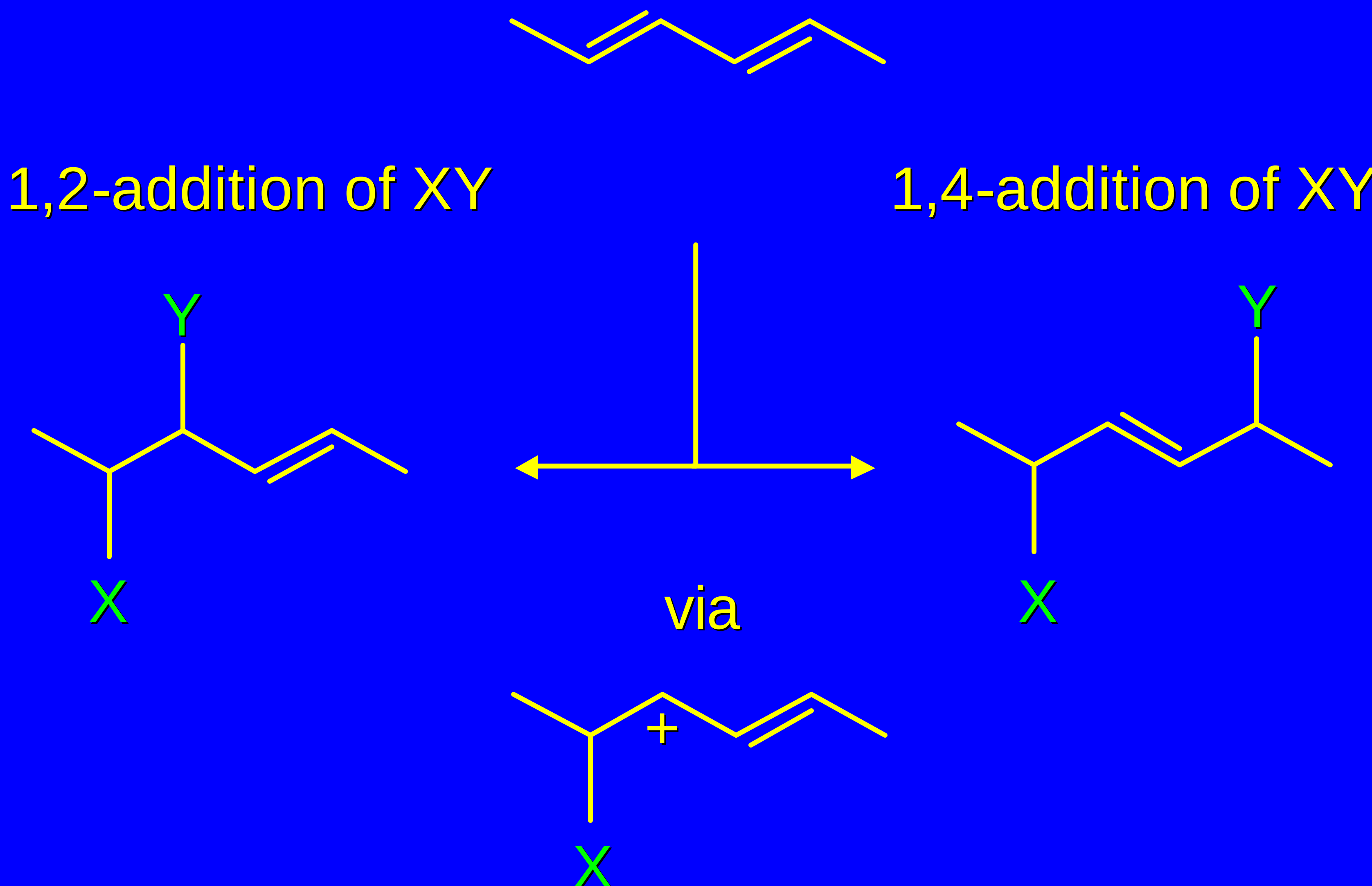
1,2-Addition versus 1,4-Addition

1,2-addition of XY

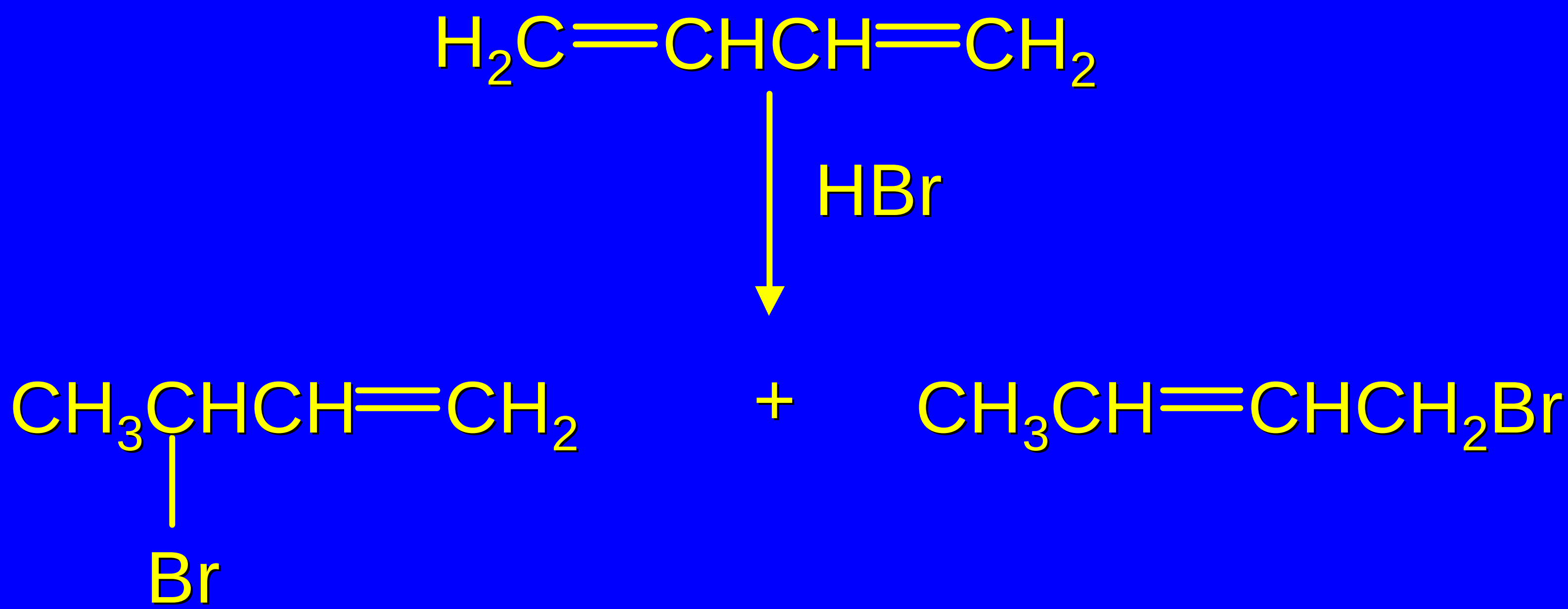
1,4-addition of XY



1,2-Addition versus 1,4-Addition



HBr Addition to 1,3-Butadiene



electrophilic addition

1,2 and 1,4-addition both observed

product ratio depends on temperature

Rationale

3-Bromo-1-butene is formed faster than 1-bromo-2-butene because allylic carbocations react with nucleophiles preferentially at the carbon that bears the greater share of positive charge.

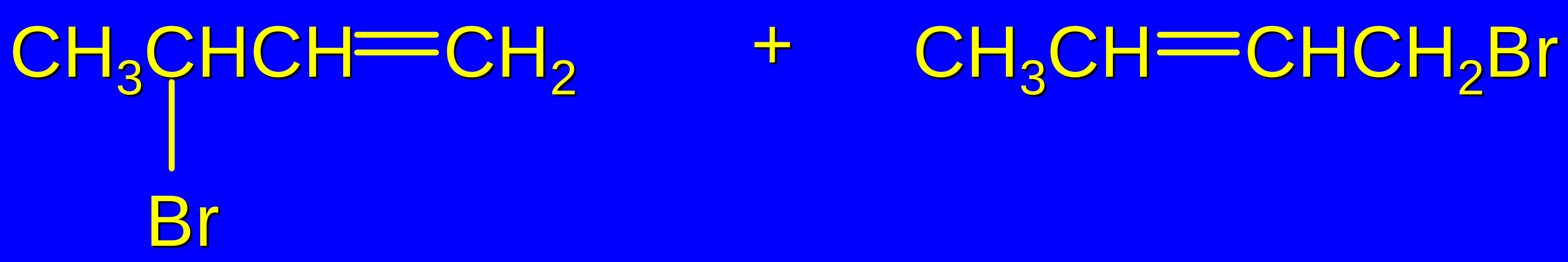
$$\underset{\substack{|\\ Br}}{CH_3CH}CH{=}CH_2 \qquad + \qquad CH_3CH{=}CHCH_2Br$$

via:

$$CH_3\overset{+}{C}HCH{=}CH_2 \longleftrightarrow CH_3CH{=}CH\overset{+}{C}H_2$$

Rationale

3-Bromo-1-butene is formed faster than 1-bromo-2-butene because allylic carbocations react with nucleophiles preferentially at the carbon that bears the greater share of positive charge.



formed faster

Rationale

1-Bromo-2-butene is more stable than 3-bromo-1-butene because it has a more highly substituted double bond.

$$CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCH{=}CH_2 \quad + \quad CH_3CH{=}CHCH_2Br$$

more stable

Rationale

The two products equilibrate at 25°C.
Once equilibrium is established, the more stable isomer predominates.

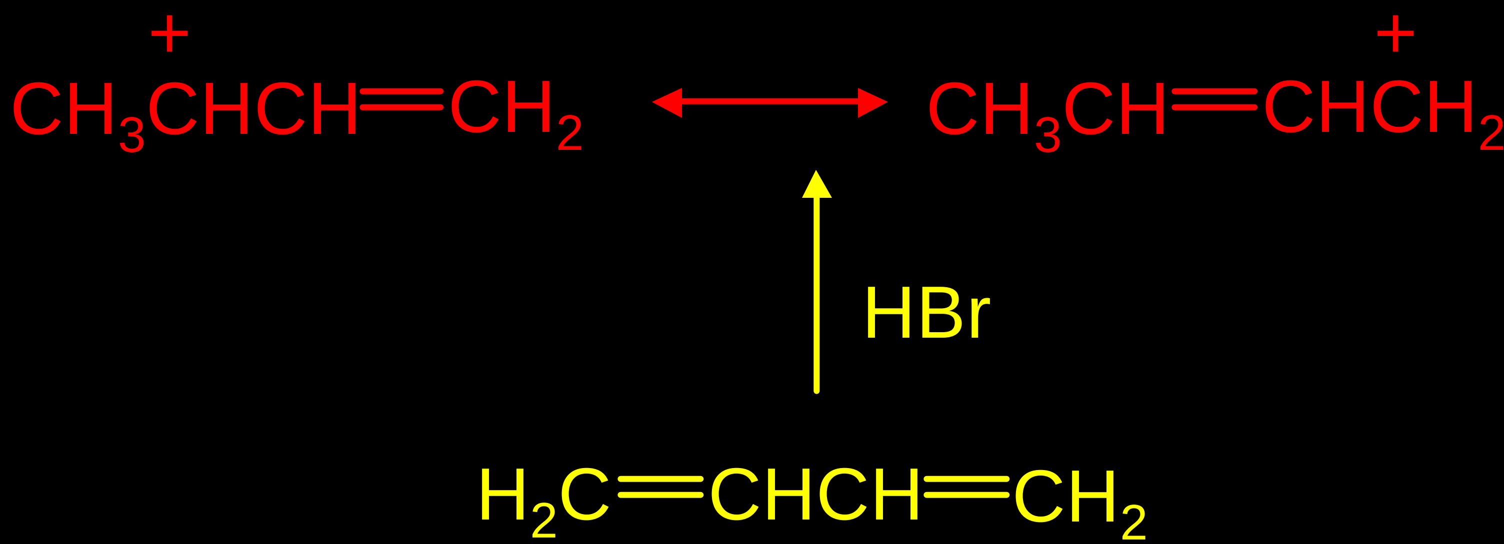
$$CH_3CH(Br)CH{=}CH_2 \rightleftharpoons CH_3CH{=}CHCH_2Br$$

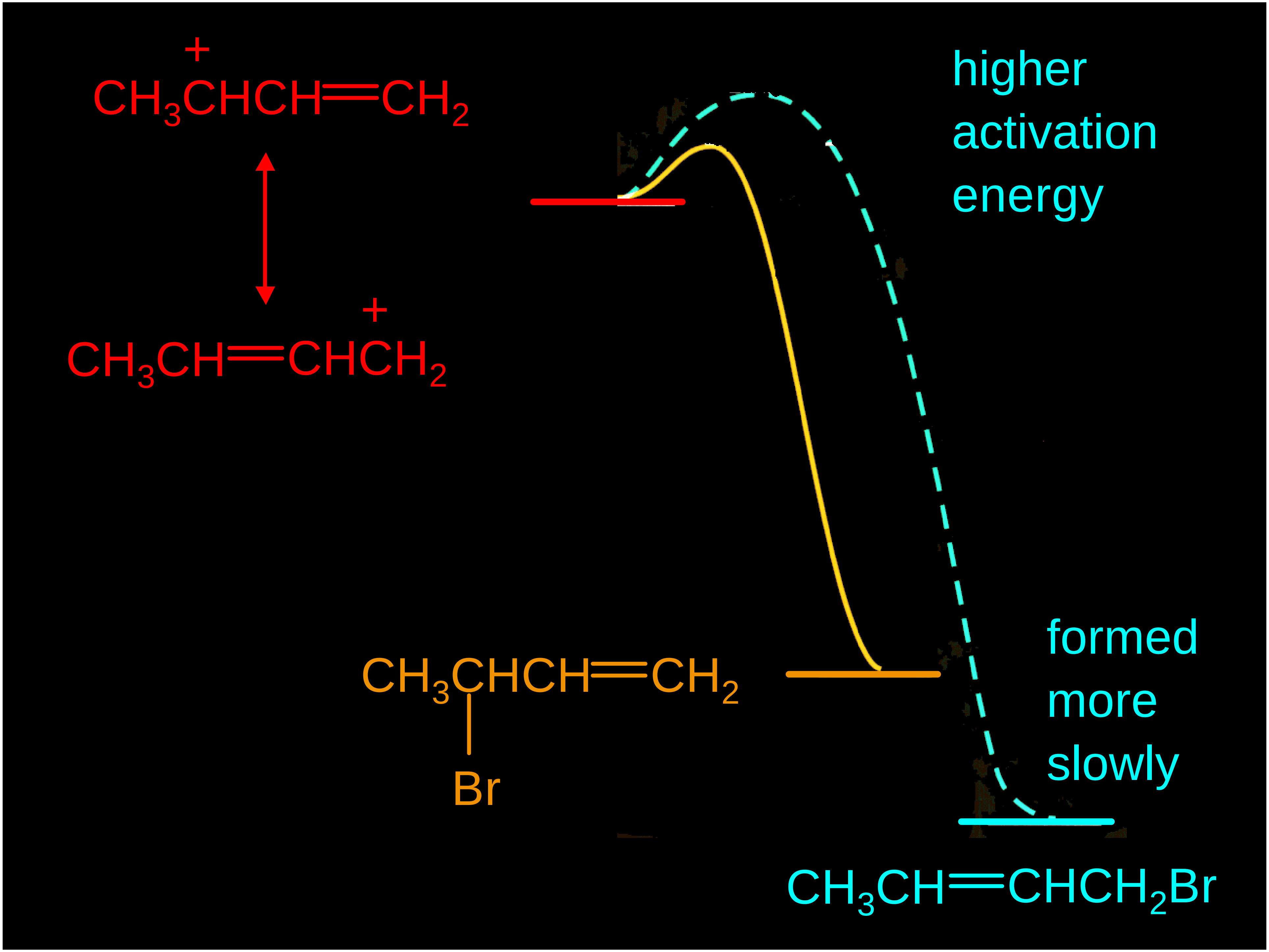
major product at -80°C	major product at 25°C
(formed faster)	(more stable)

Kinetic Control versus Thermodynamic Control

Kinetic control: major product is the one formed at the fastest rate

Thermodynamic control: major product is the one that is the most stable


CH3CHCH=CH2 (+)
CH3CH=CHCH2 (+)
HBr
H2C=CHCH=CH2

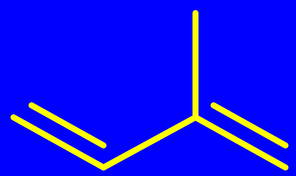

$CH_3\overset{+}{C}HCH{=}CH_2$
$CH_3CH{=}CH\overset{+}{C}H_2$
higher
activation
energy
$CH_3CHCH{=}CH_2$
Br
formed
more
slowly
$CH_3CH{=}CHCH_2Br$

Problem 10.10
(page 382)

Addition of hydrogen chloride to 2-methyl-1,3-butadiene is a kinetically controlled reaction and gives one product in much greater amounts than any isomers. What is this product?

Problem 10.10 (page 382)

Think mechanistically.

 + HCl

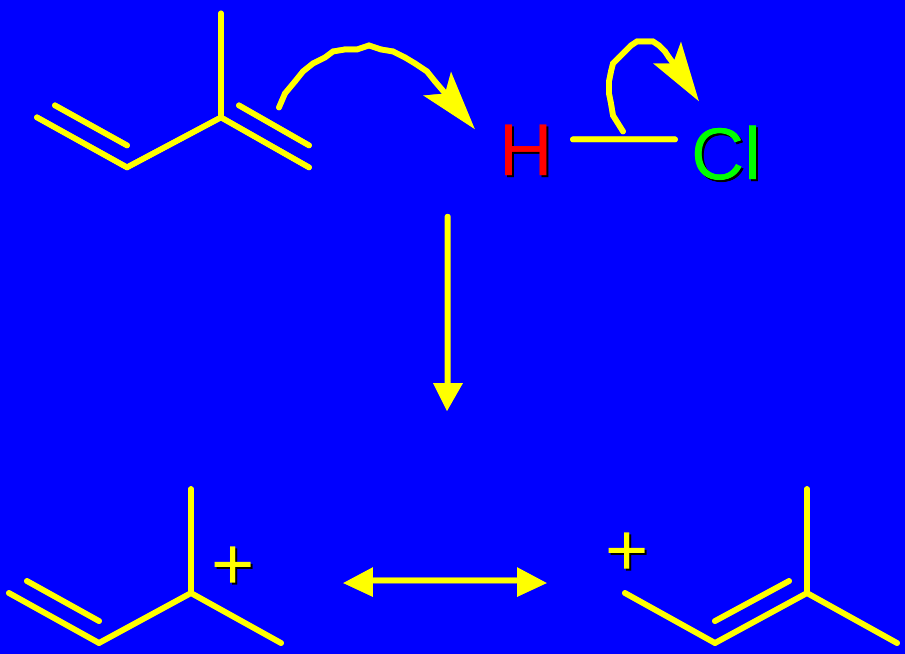
Protonation occurs:

- at end of diene system
- in direction that gives most stable carbocation

Kinetically controlled product corresponds to attack by chloride ion at carbon that has the greatest share of positive charge in the carbocation

Problem 10.10
(page 382)

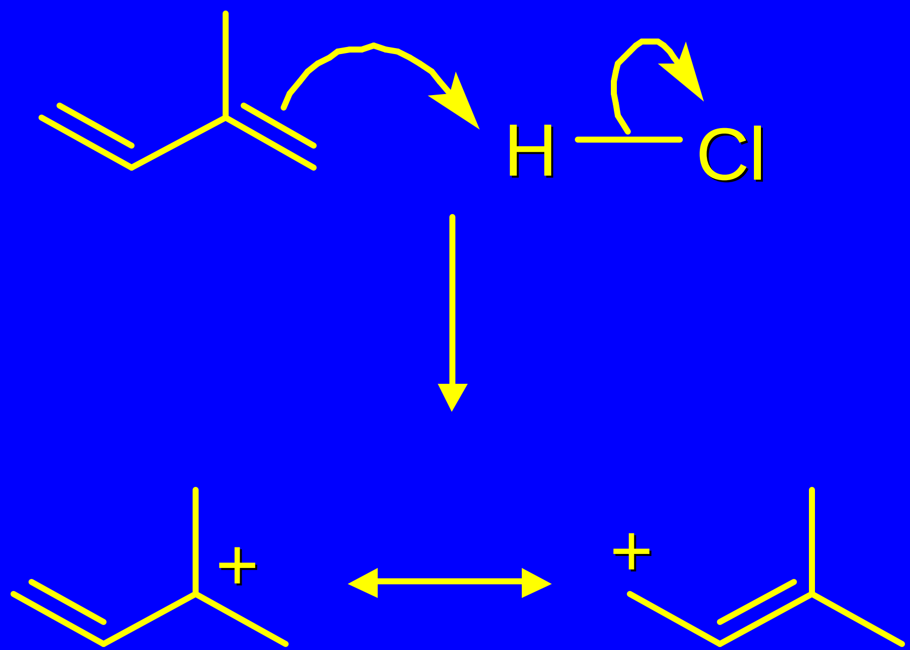
Think mechanistically



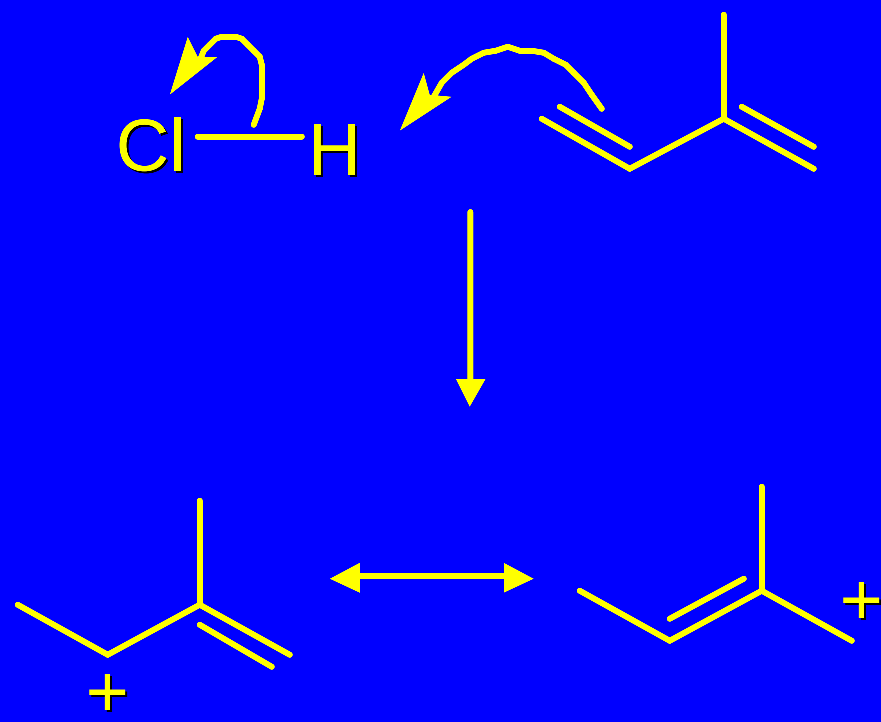
one resonance form is
tertiary carbocation;
other is primary

Think mechanistically

Problem 10.10
(page 382)



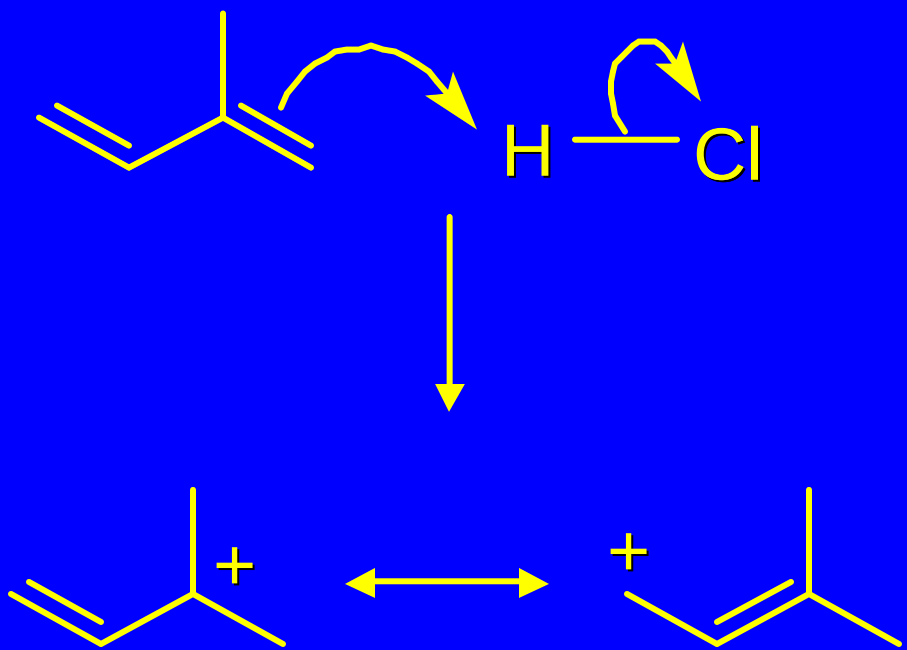
one resonance form is
tertiary carbocation;
other is primary



one resonance form is
secondary carbocation;
other is primary

Problem 10.10
(page 382)

Think mechanistically



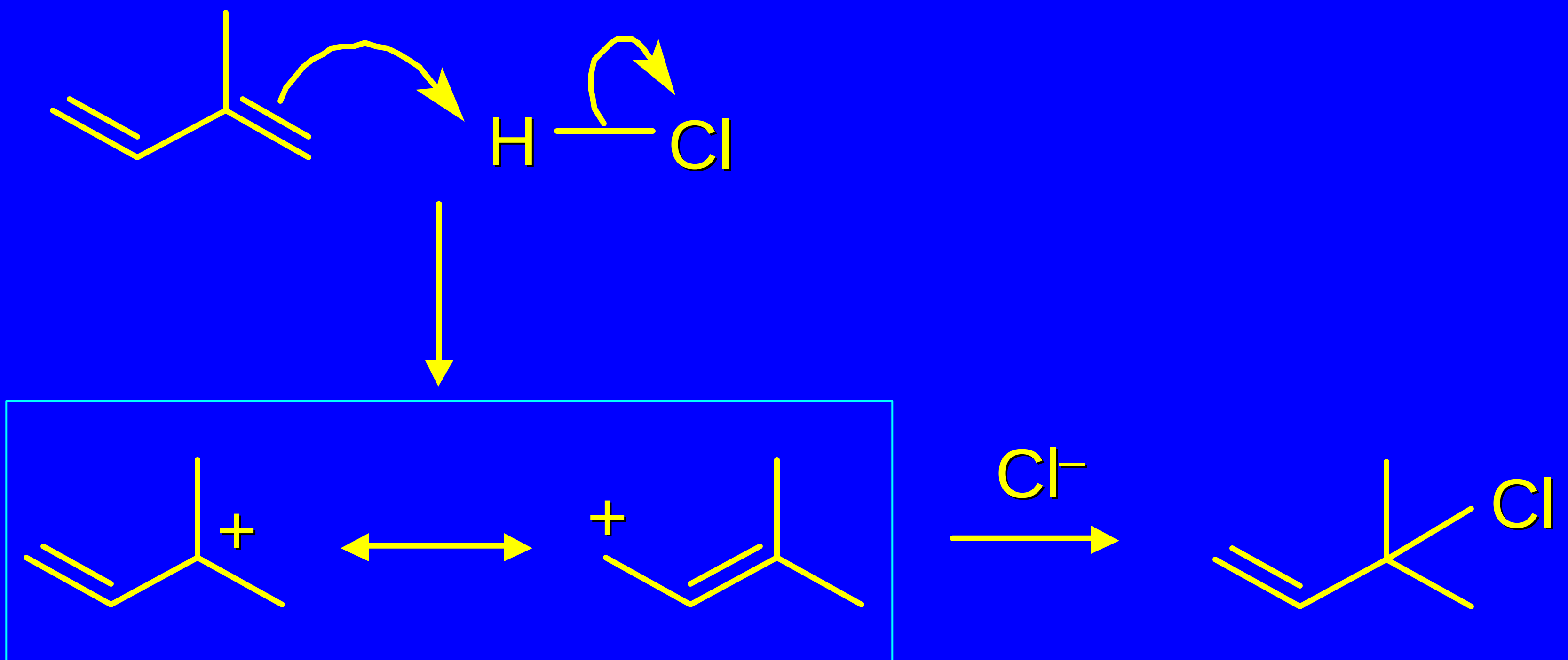
one resonance form is
tertiary carbocation;
other is primary

More stable carbocation

Is attacked by chloride ion at carbon that bears greater share of positive charge

Problem 10.10
(page 382)

Think mechanistically



one resonance form is
tertiary carbocation;
other is primary

major
product

10.11

Halogen Addition to Dienes

gives mixtures of 1,2 and
1,4-addition products

Example