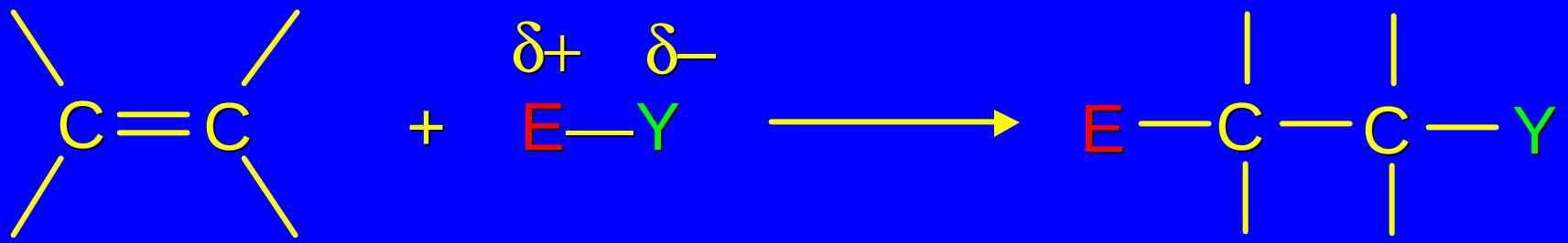
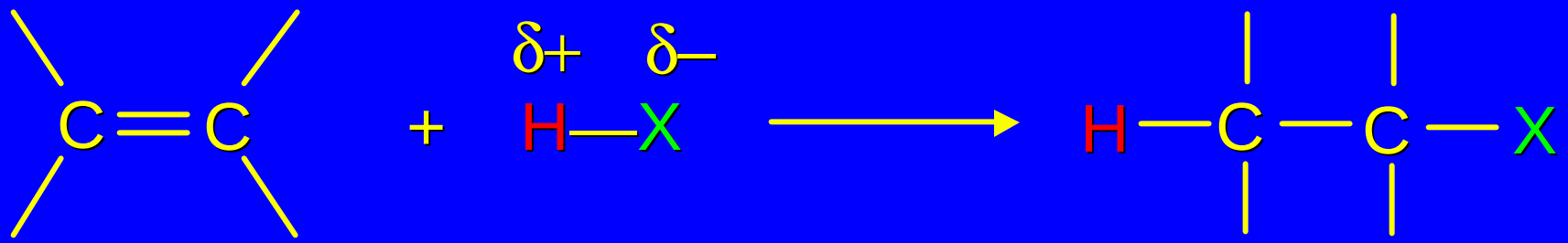
6.4
Electrophilic Addition of Hydrogen Halides to Alkenes

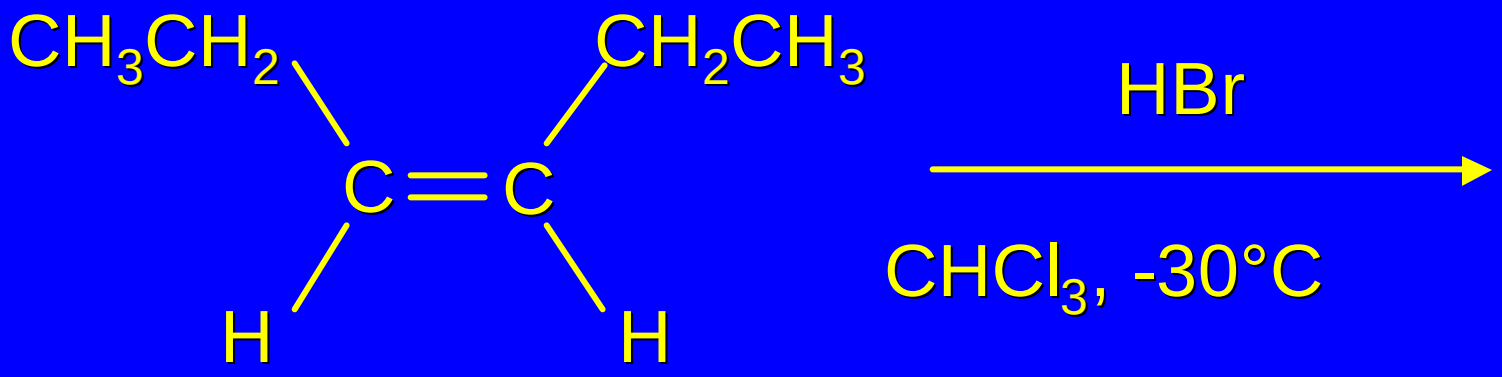
General equation for electrophilic addition



When EY is a hydrogen halide



Example



$CH_3CH_2CH_2CHCH_2CH_3$
|
Br

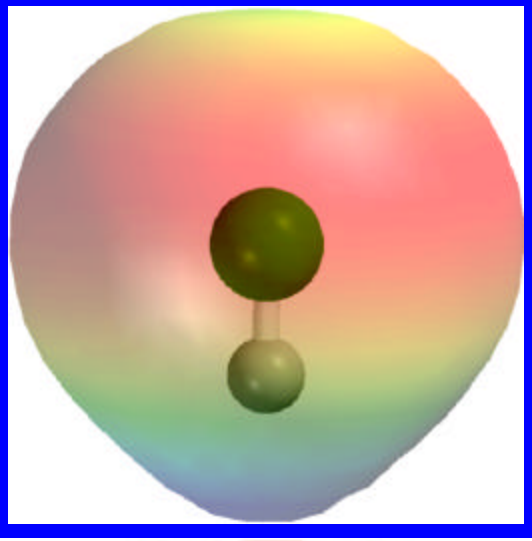
(76%)

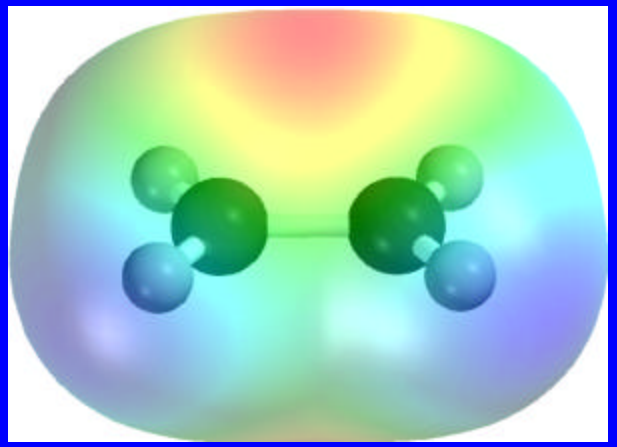
Mechanism

Electrophilic addition of hydrogen halides to alkenes proceeds by rate-determining formation of a carbocation intermediate.

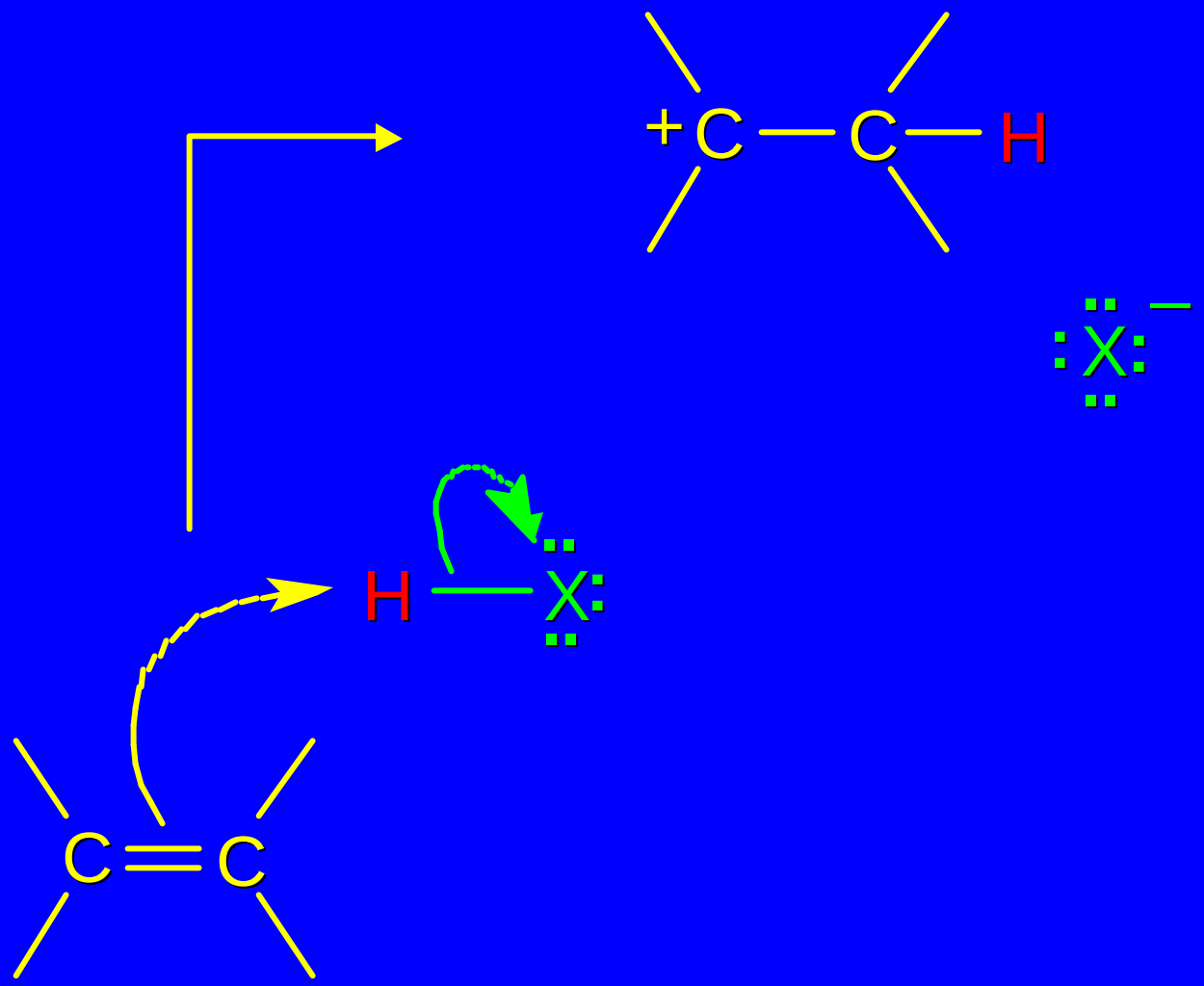
Mechanism

Electrons flow from the π system of the alkene (electron rich) toward the positively polarized proton of the hydrogen halide.

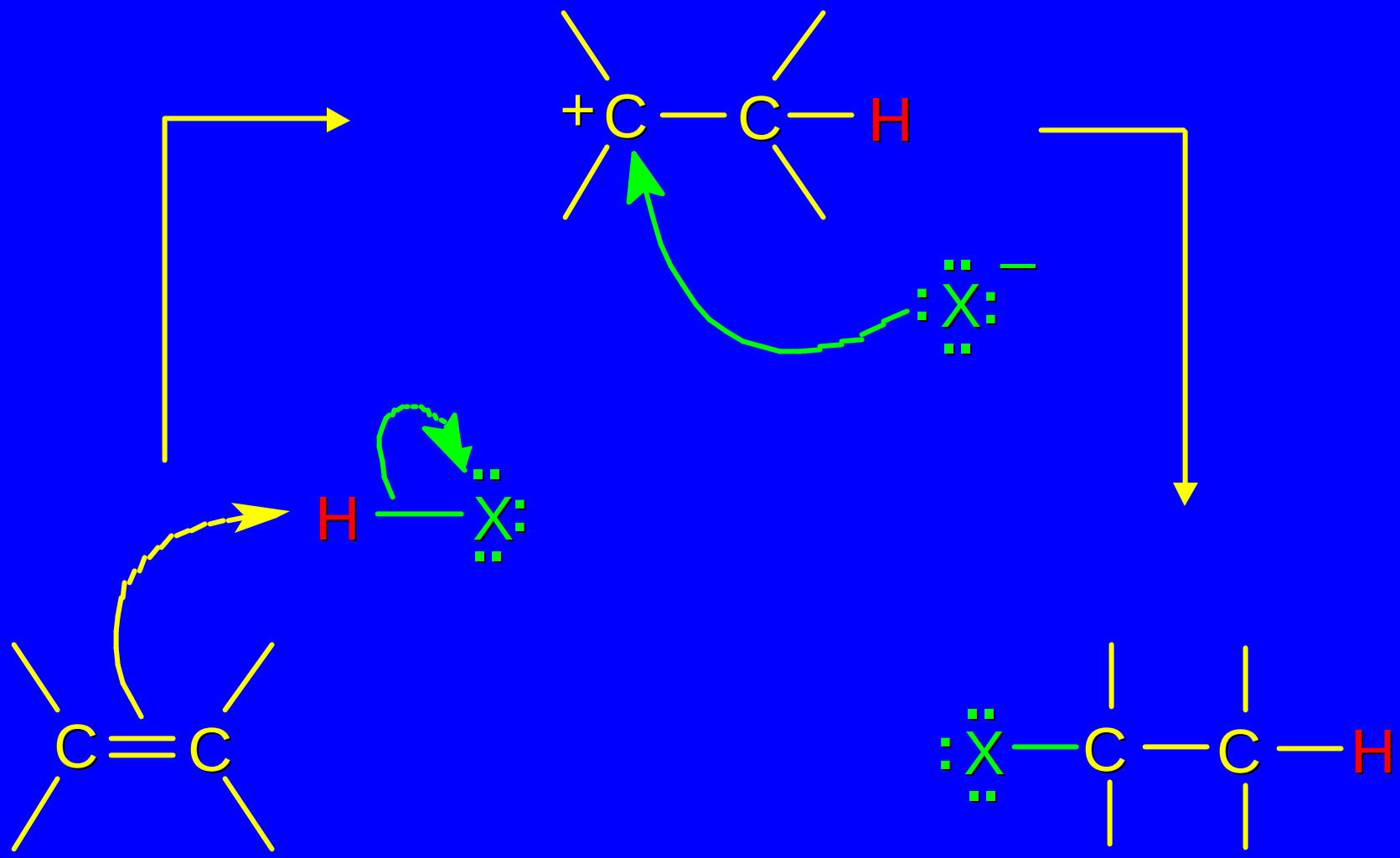




Mechanism



Mechanism

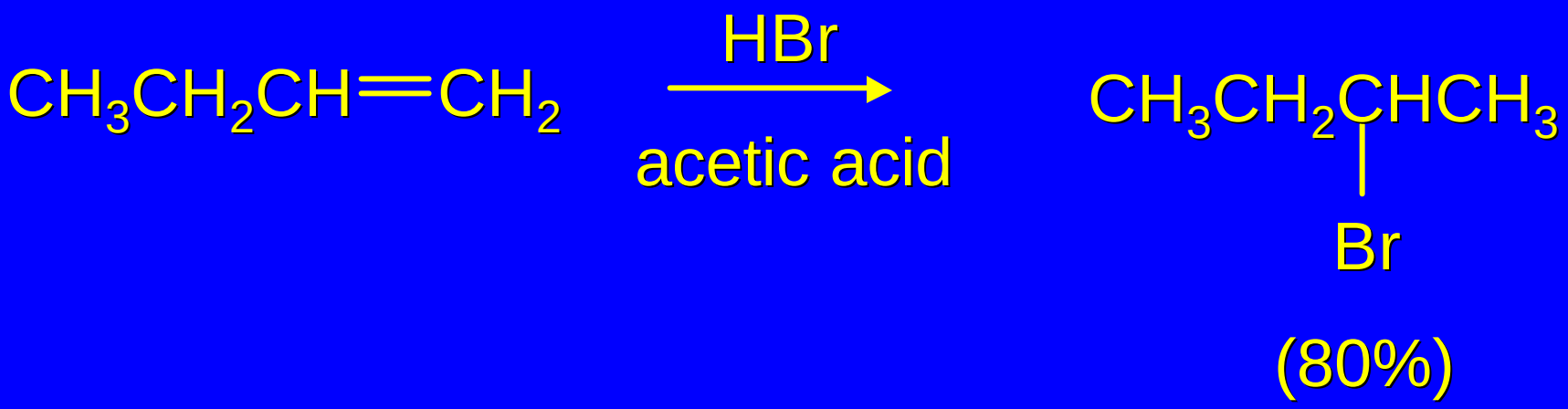


6.5
Regioselectivity of Hydrogen Halide Addition: Markovnikov's Rule

Markovnikov's Rule

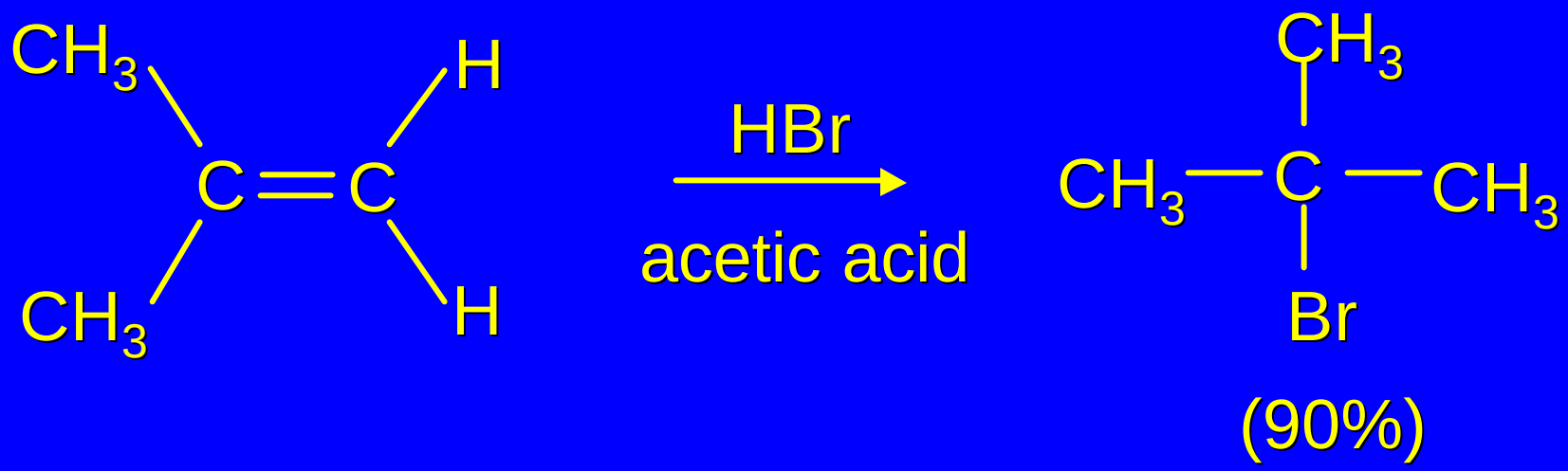
When an unsymmetrically substituted alkene reacts with a hydrogen halide, the hydrogen adds to the carbon that has the greater number of hydrogen substituents, and the halogen adds to the carbon that has the fewer hydrogen substituents.

Markovnikov's Rule



Example 1

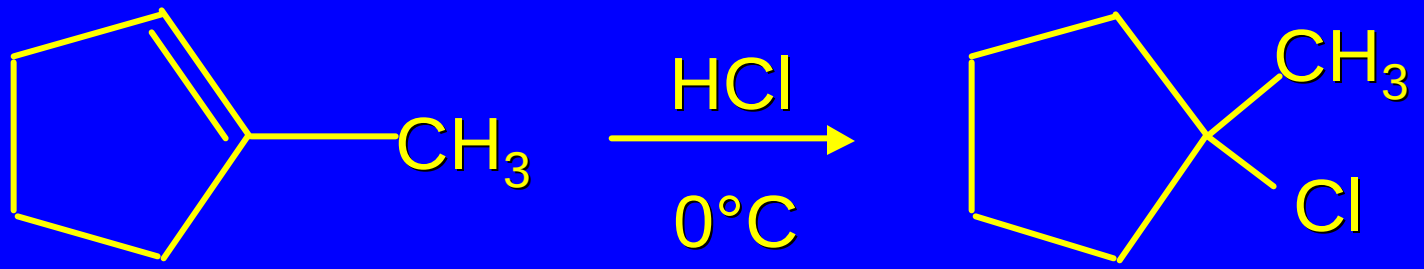
Markovnikov's Rule



(90%)

Example 2

Markovnikov's Rule



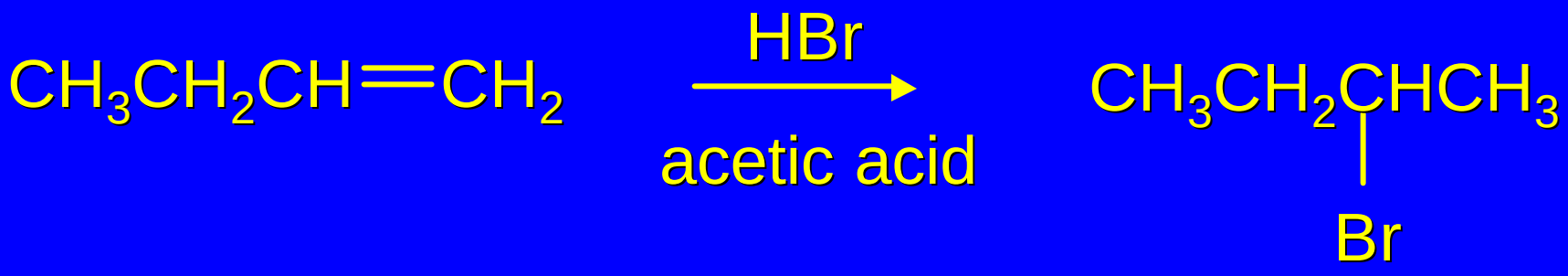
(100%)

Example 3

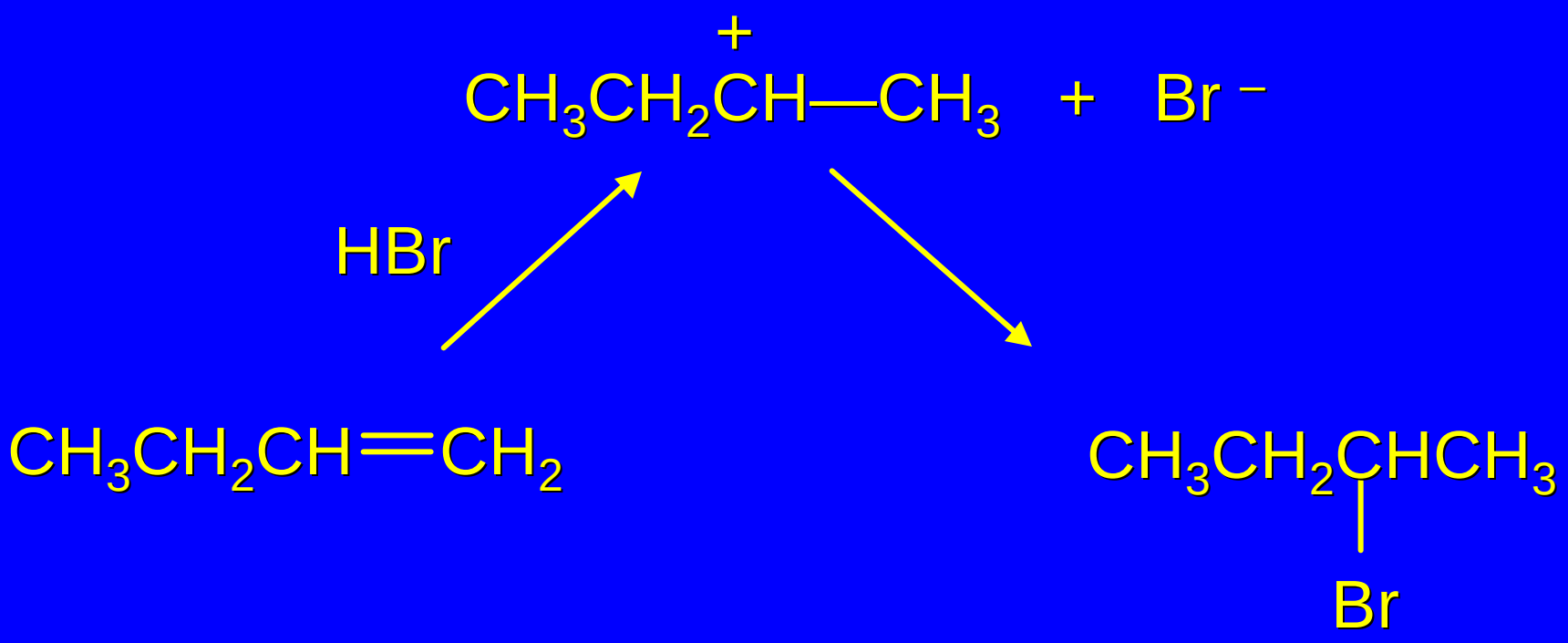
6.6
Mechanistic Basis
for
Markovnikov's Rule

Protonation of double bond occurs in direction that gives more stable of two possible carbocations.

Mechanistic Basis for Markovnikov's Rule: Example 1



Mechanistic Basis for Markovnikov's Rule: Example 1



Mechanistic Basis for Markovnikov's Rule: Example 1

$CH_3CH_2CH_2—\overset{+}{C}H_2$

primary carbocation is less stable: not formed

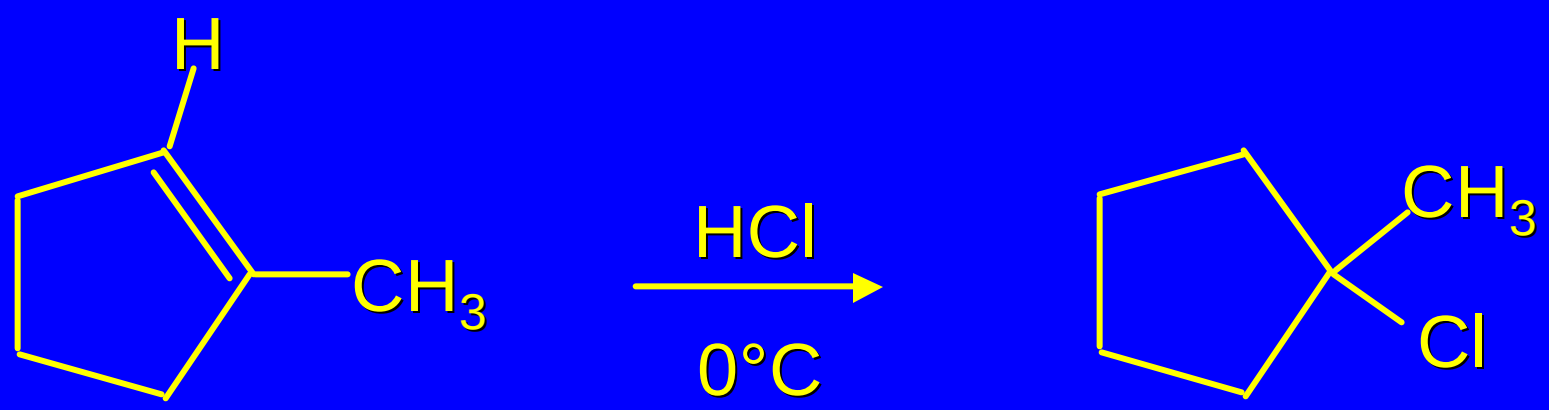
$CH_3CH_2\overset{+}{C}H—CH_3 \; + \; Br^-$

HBr

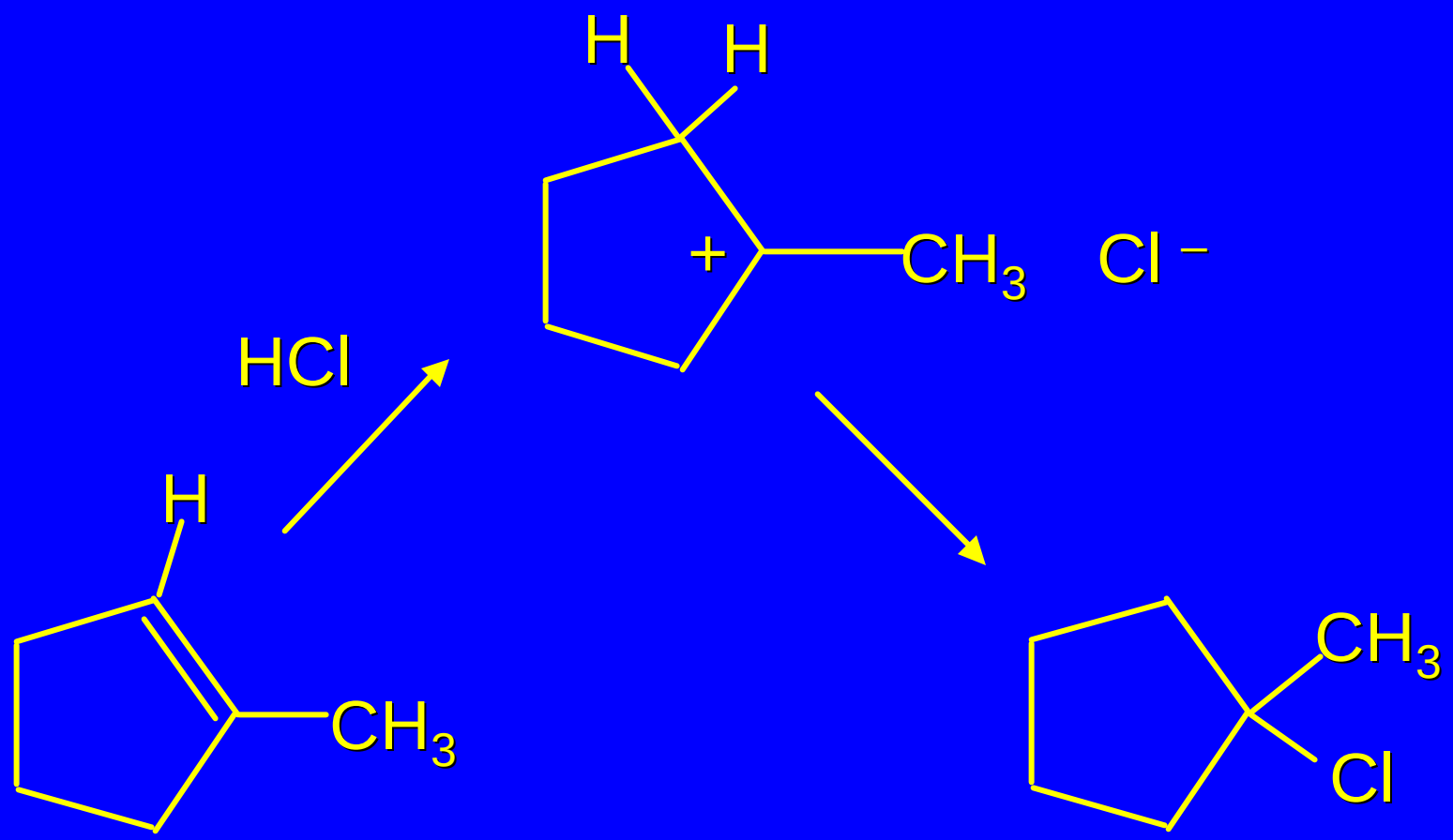
$CH_3CH_2CH{=}CH_2$

$CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$

Mechanistic Basis for Markovnikov's Rule: Example 3

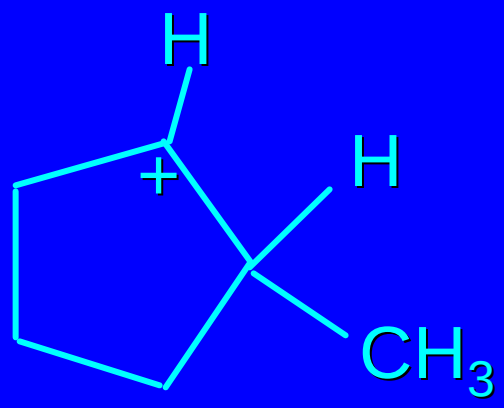


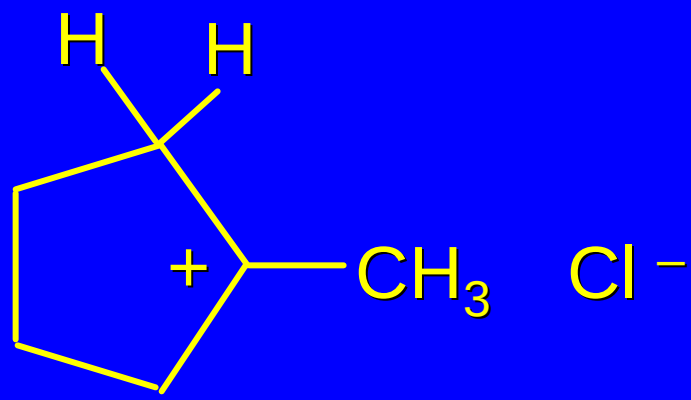
Mechanistic Basis for Markovnikov's Rule: Example 3

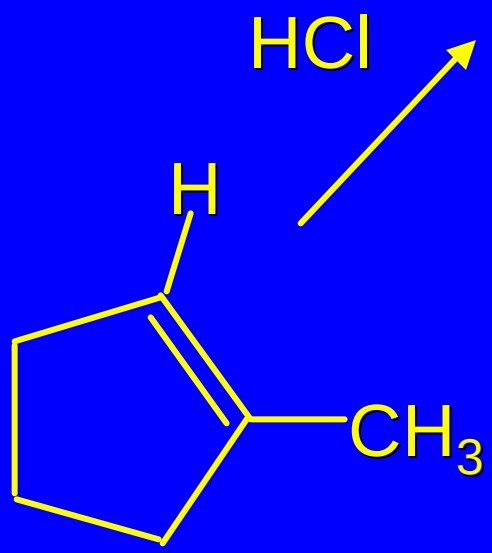


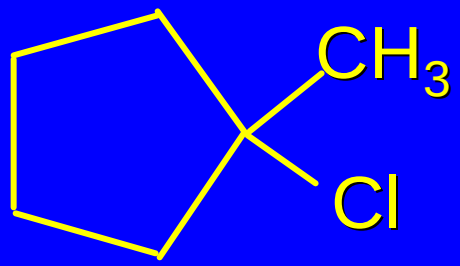
Mechanistic Basis for Markovnikov's Rule: Example 3

secondary carbocation is less stable: not formed









6.7
Carbocation Rearrangements in Hydrogen Halide Addition to Alkenes

Rearrangements sometimes occur