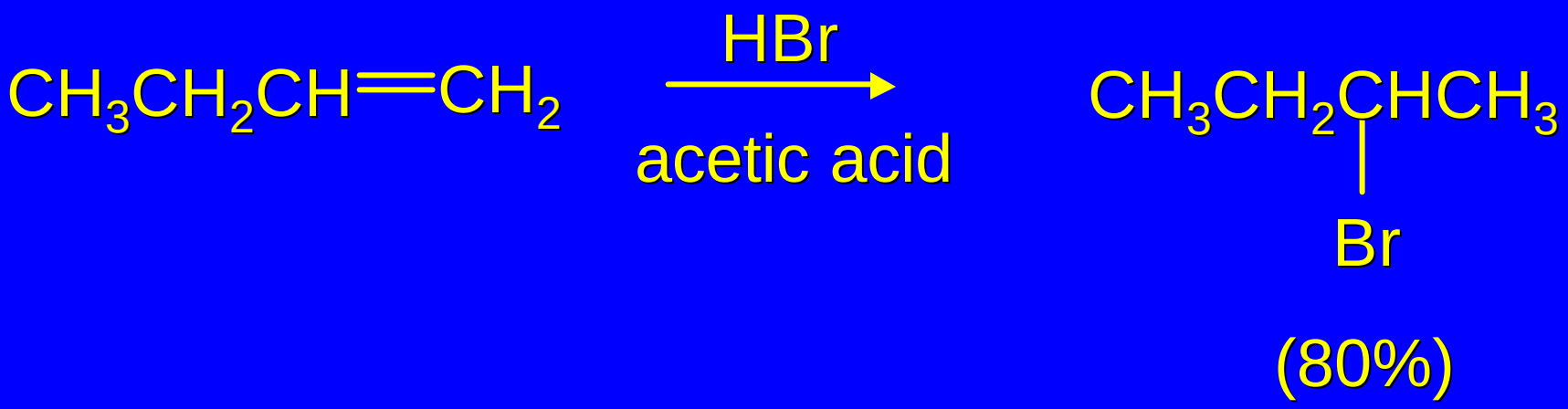
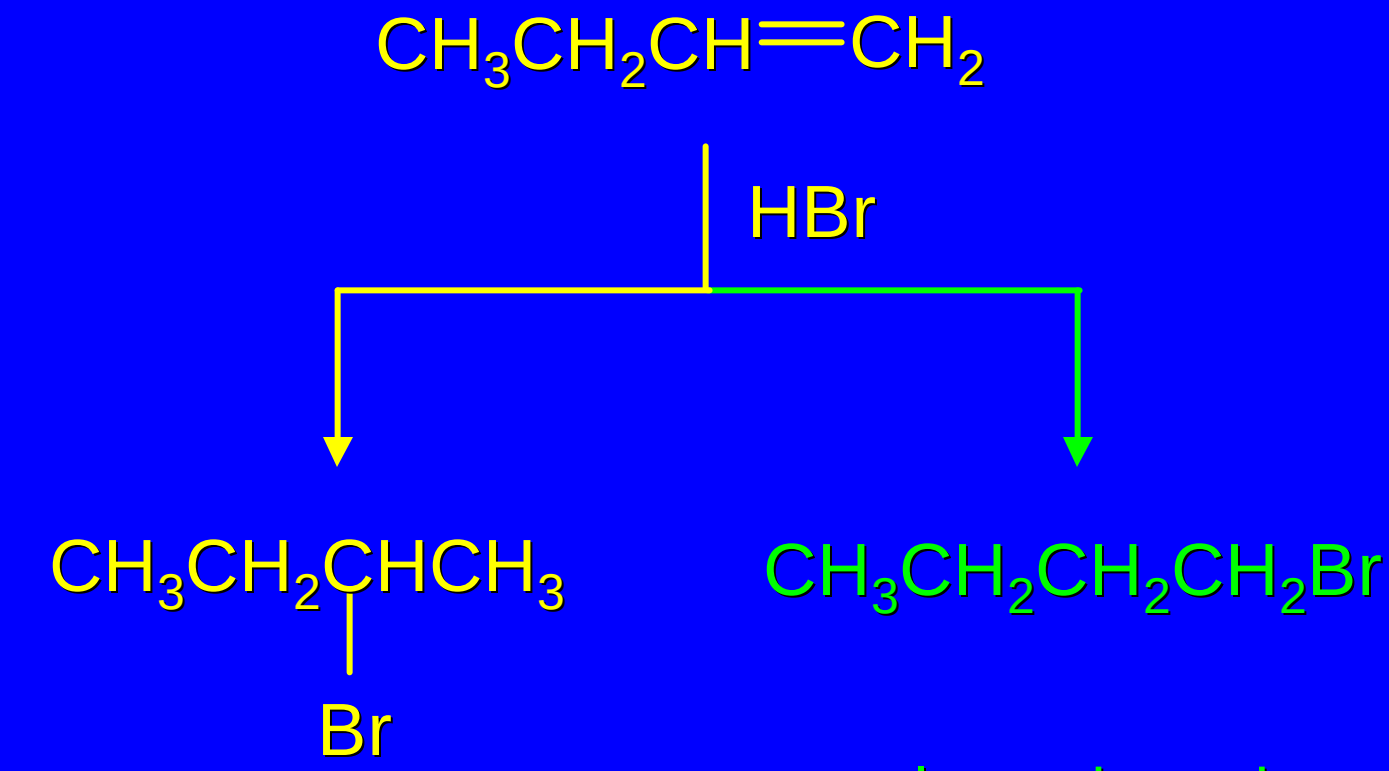
6.8
Free-radical Addition of HBr to Alkenes

The "peroxide effect"

Markovnikov's Rule



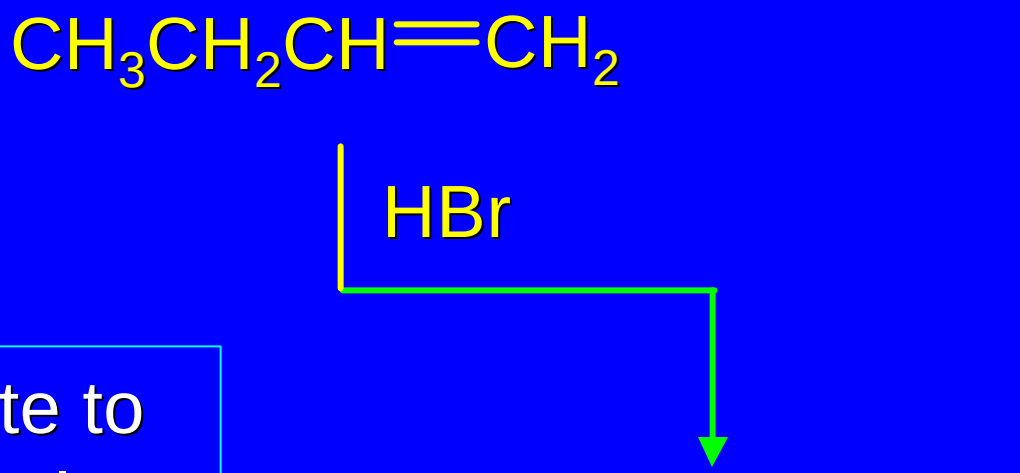
Addition of HBr to 1-Butene



only product in absence of peroxides

only product when peroxides added to reaction mixture

Addition of HBr to 1-Butene

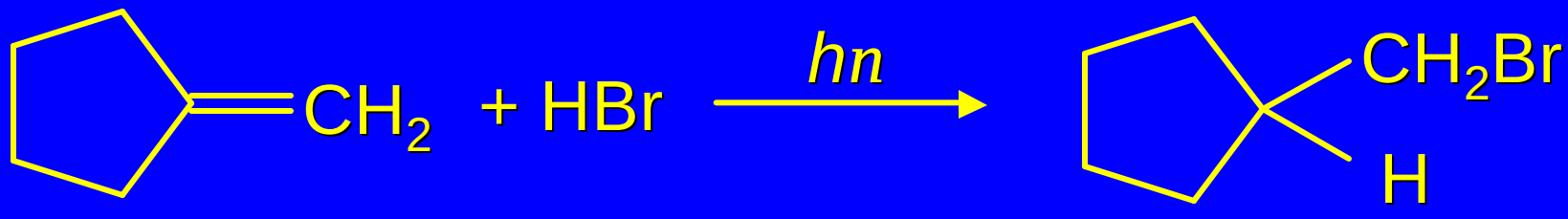


addition opposite to Markovnikov's rule

occurs with HBr (not HCl or HI)

only product when peroxides added to reaction mixture

Photochemical Addition of HBr



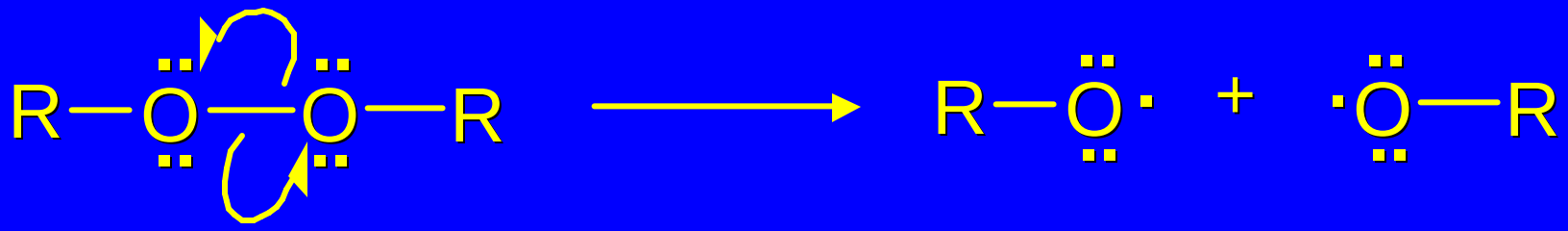
(60%)

Addition of HBr with a regiochemistry opposite to Markovnikov's rule can also occur when initiated with light with or without added peroxides.

Mechanism

Addition of HBr opposite to Markovnikov's rule proceeds by a free-radical chain mechanism.

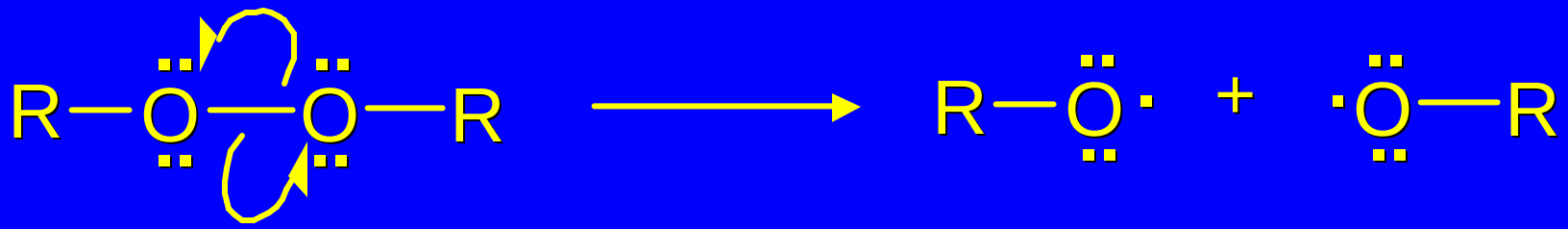
Initiation steps:

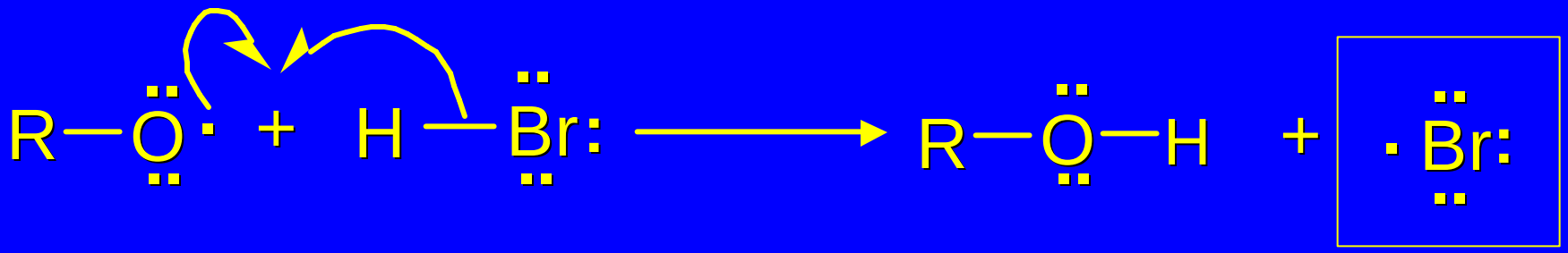


Mechanism

Addition of HBr opposite to Markovnikov's rule proceeds by a free-radical chain mechanism.

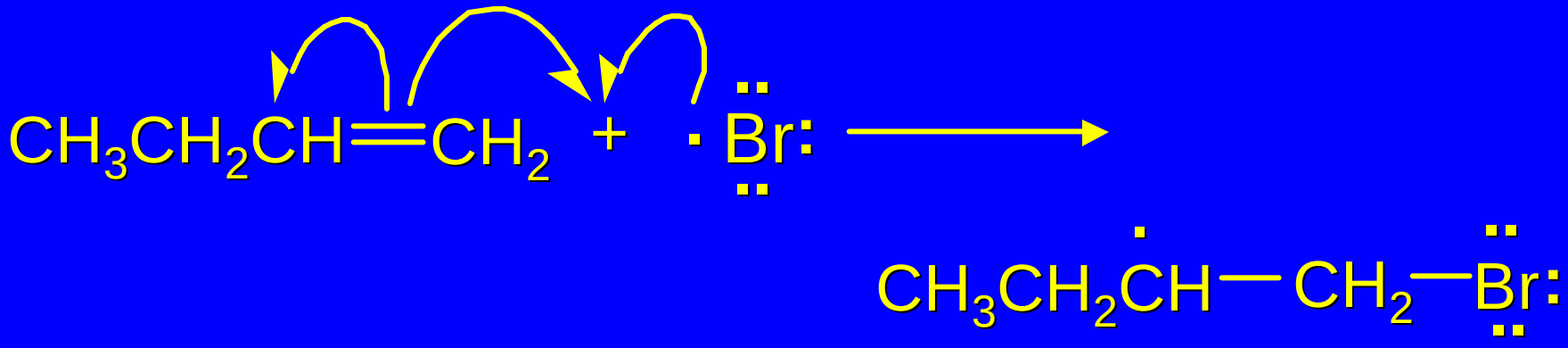
Initiation steps:





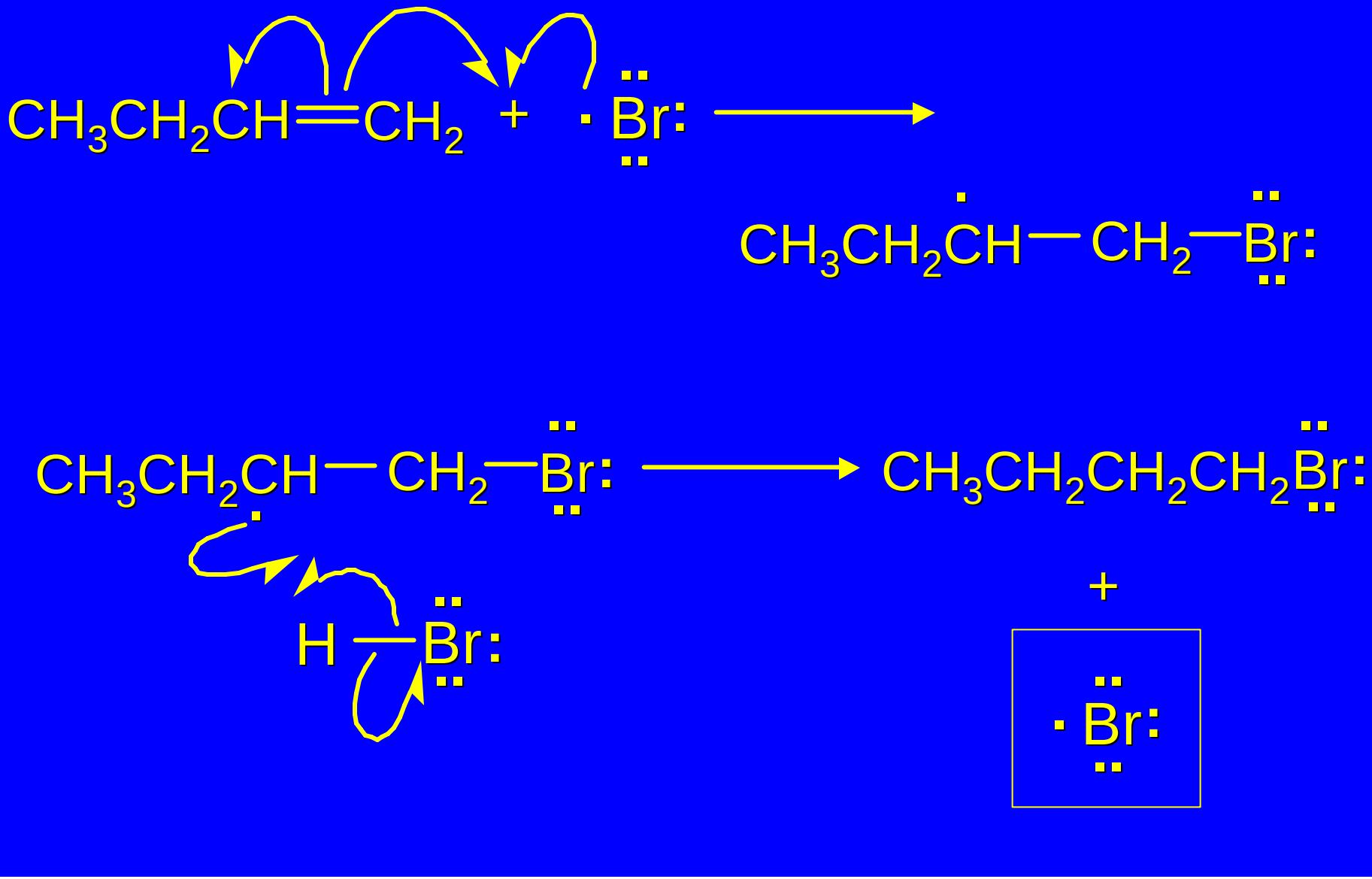
Mechanism

Propagation steps:



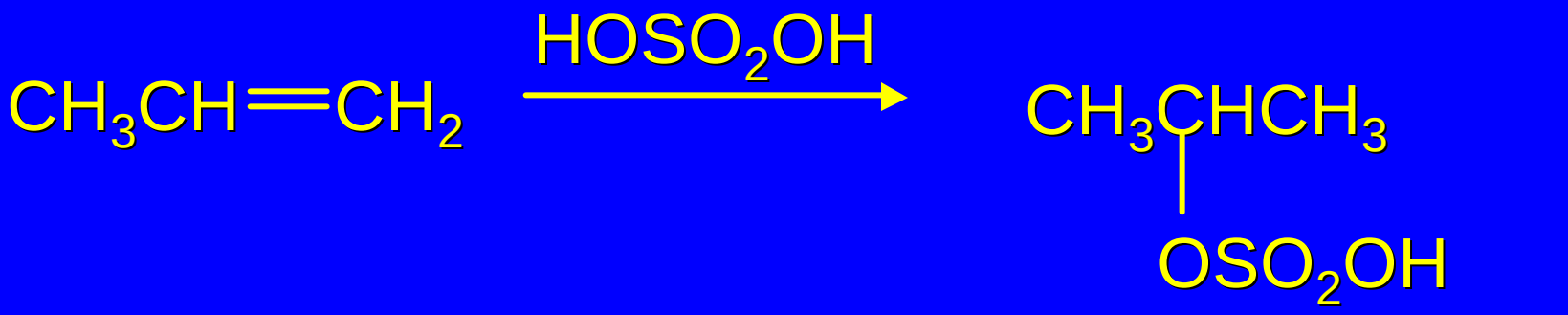
Mechanism

Propagation steps:



6.9
Addition of Sulfuric Acid to Alkenes

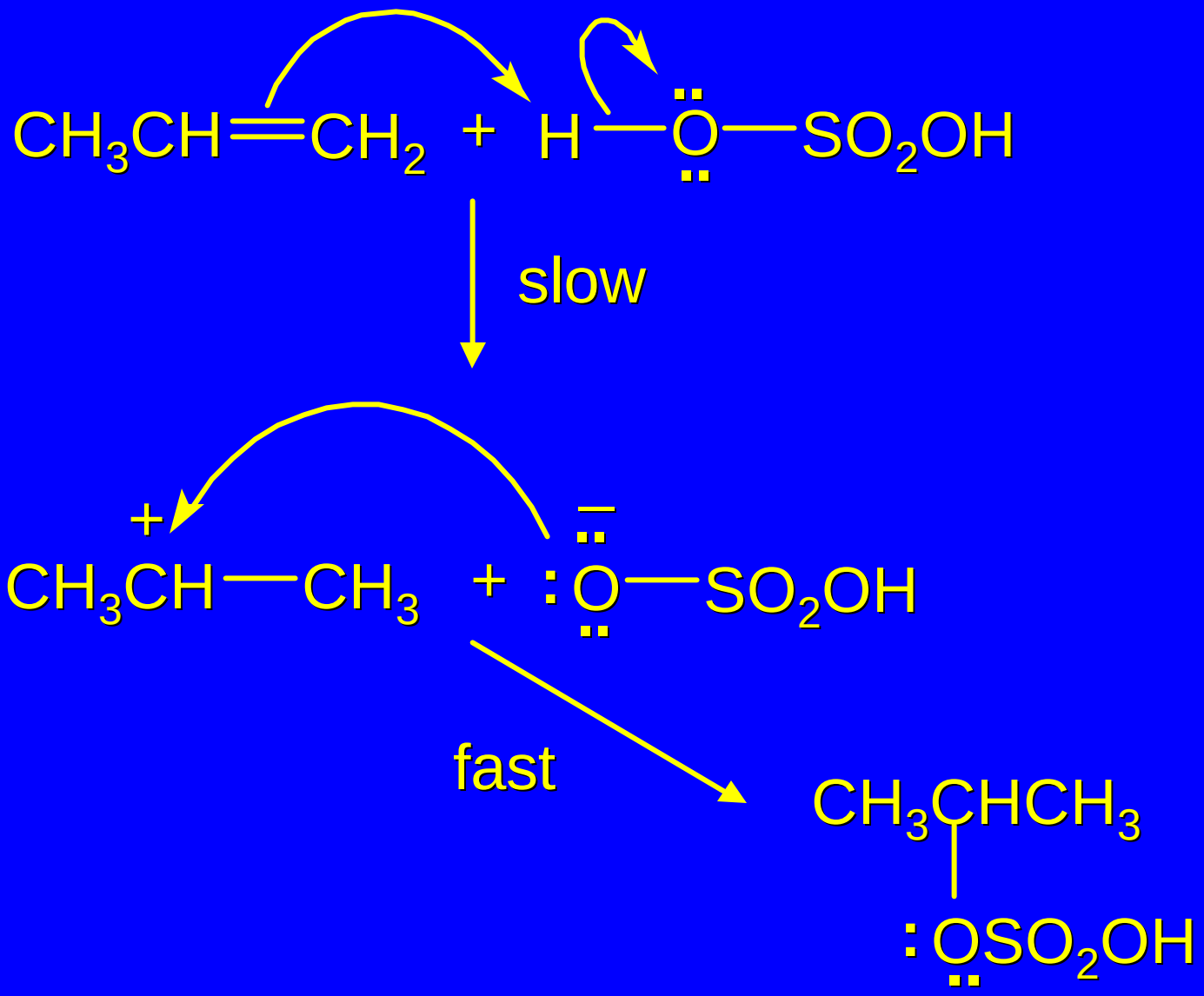
Addition of H_2SO_4



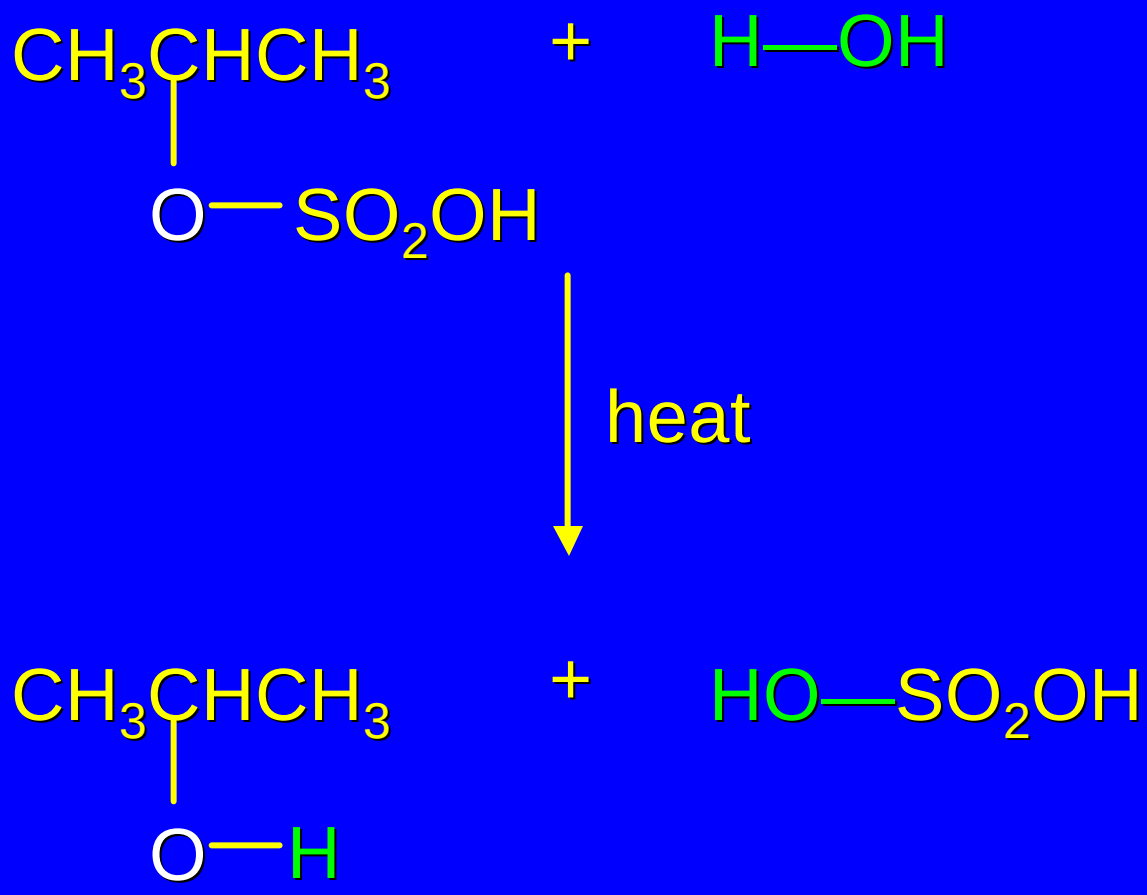
Isopropyl
hydrogen sulfate

follows Markovnikov's rule:
yields an alkyl hydrogen sulfate

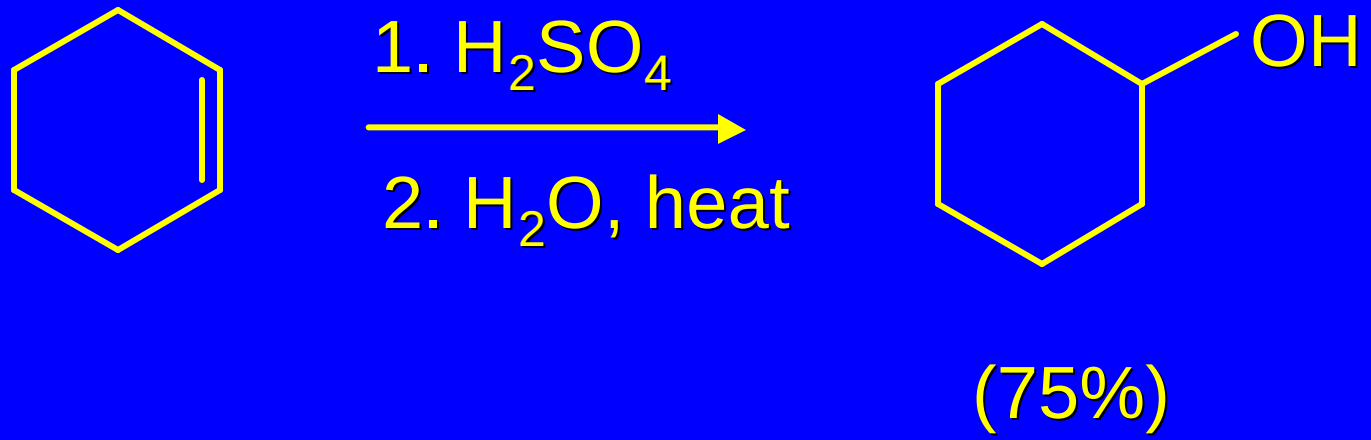
Mechanism


CH3CH=CH2 + H—O—SO2OH
slow
CH3CH—CH3 + :O—SO2OH
fast
CH3CHCH3
:OSO2OH

Alkyl hydrogen sulfates undergo hydrolysis in hot water



Application: Conversion of alkenes to alcohols



(75%)

But...

not all alkenes yield alkyl hydrogen sulfates on reaction with sulfuric acid

these do:

$H_2C=CH_2$, $RCH=CH_2$, and $RCH=CHR'$

these don't:

$R_2C=CH_2$, $R_2C=CH_2$, and $R_2C=CR_2$