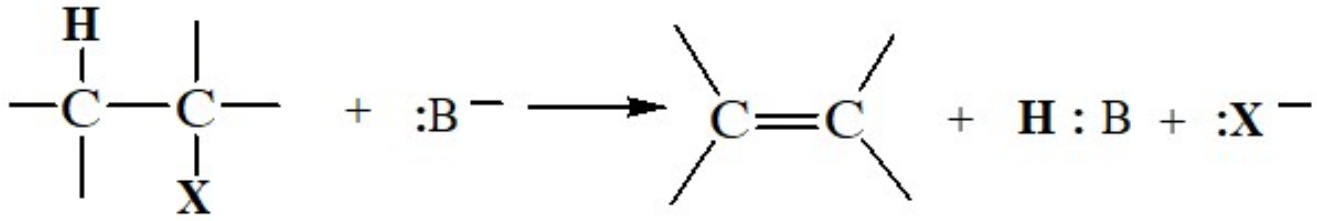
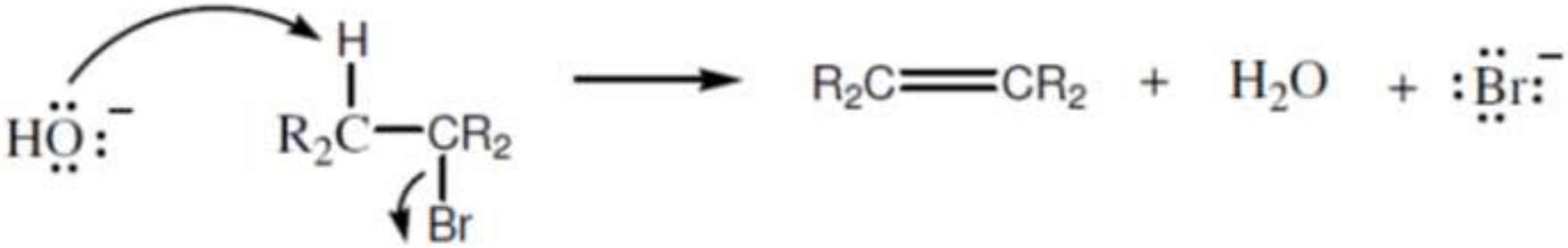
4.2 ELIMINATION REACTIONS

An elimination reaction is a type of organic reaction in which two substituents (two atoms or groups) are removed from a molecule



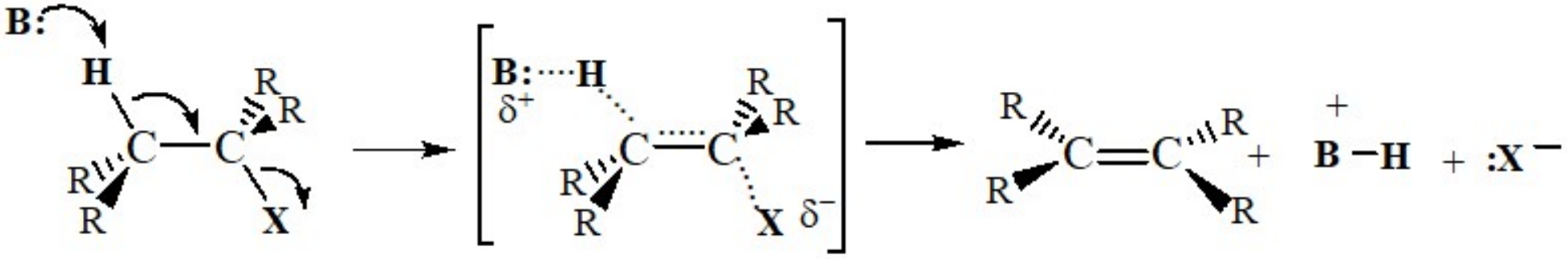
- base removes H^+ as X^- leaves

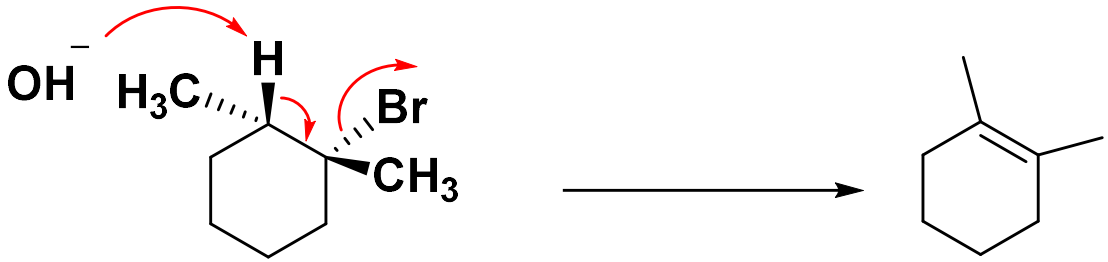


E2 and E1 Mechanism

E2 Elimination Mechanism

- concerted (single step)
- all bond-breaking and bond-forming steps are concerted
- the H and X eliminated must be aligned anti to one another

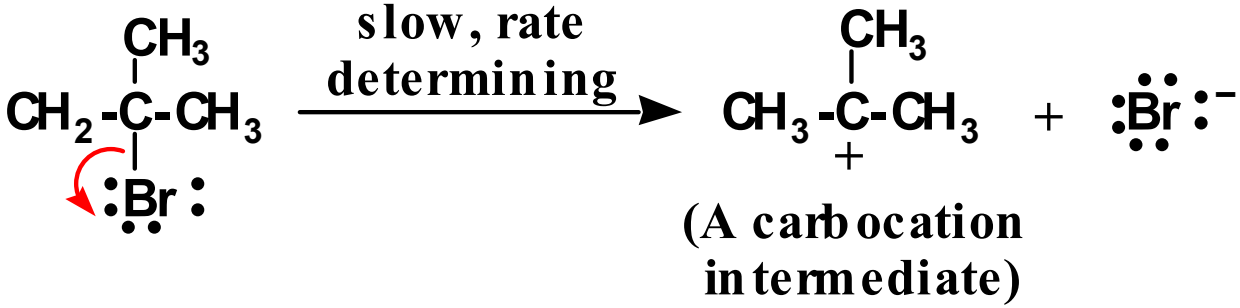




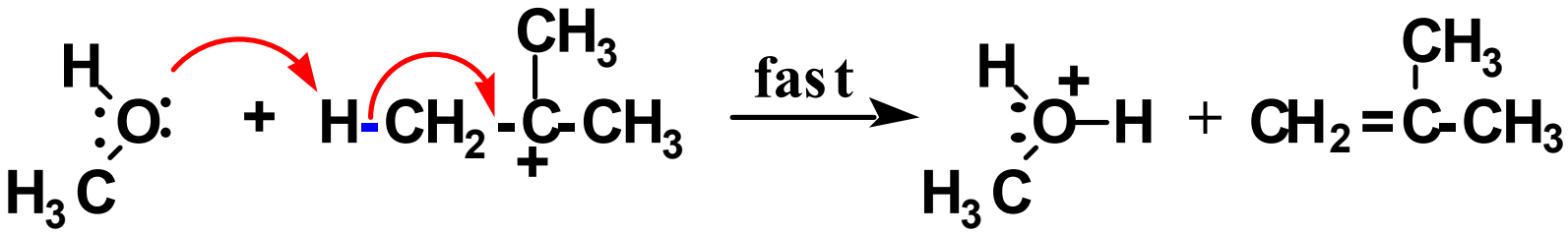
E1 Elimination Mechanism

- two-step mechanism

Step 1: ionization of C-X gives a carbocation intermediate

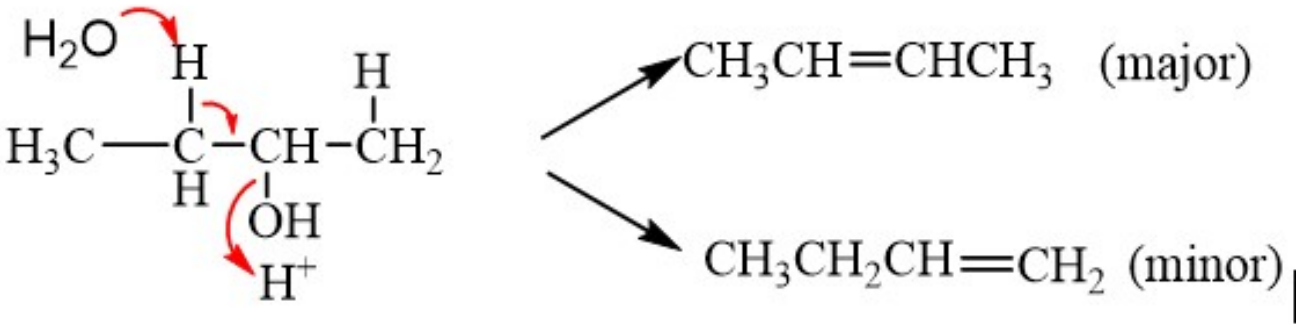


Step 2: proton transfer from the carbocation intermediate to a base (in this case, the solvent) gives the alkene

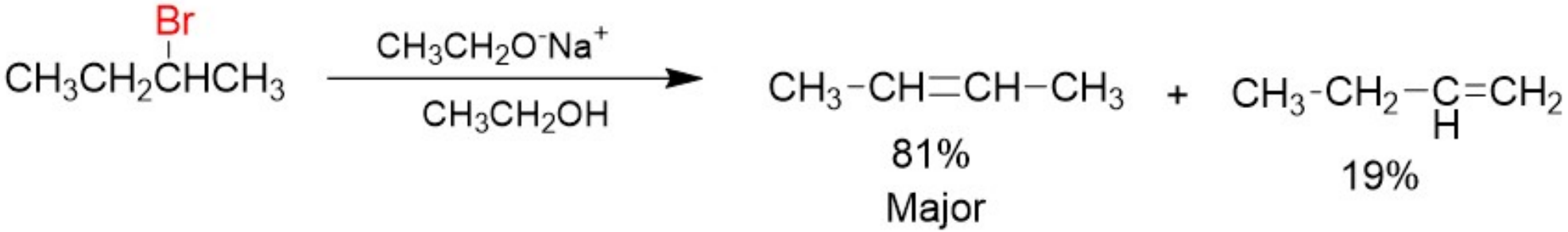


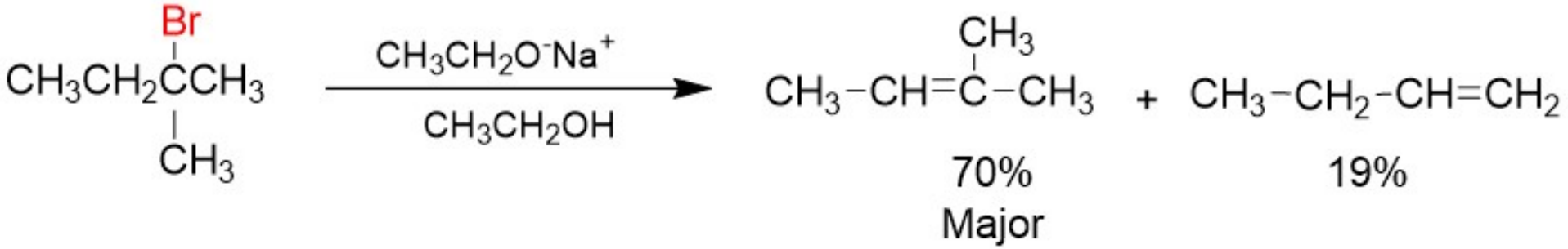
Zaitsev's Rule

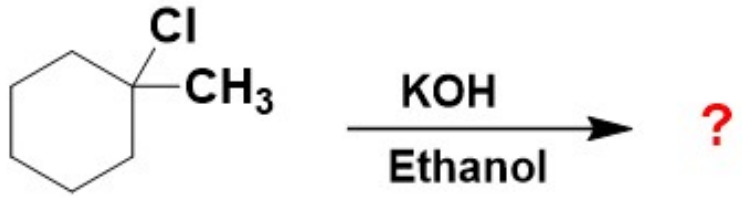
- Elimination reactions almost always give mixtures of alkene products.
- Zaitsev's rule states that if more than one alkene can be formed by an elimination reaction, the more stable alkene is the major product.

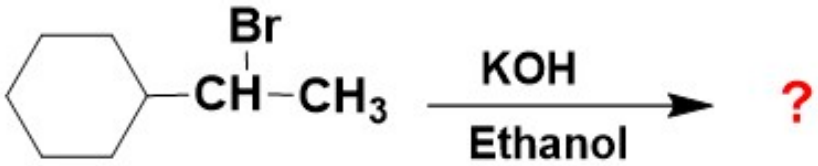


more highly substituted C=C double bond is more stable due to the electron donating properties of the alkyl group.


Br
CH3CH2CHCH3
CH3CH2O-Na+
CH3CH2OH
CH3-CH=CH-CH3
81%
Major
+
CH3-CH2-C=CH2
H
19%

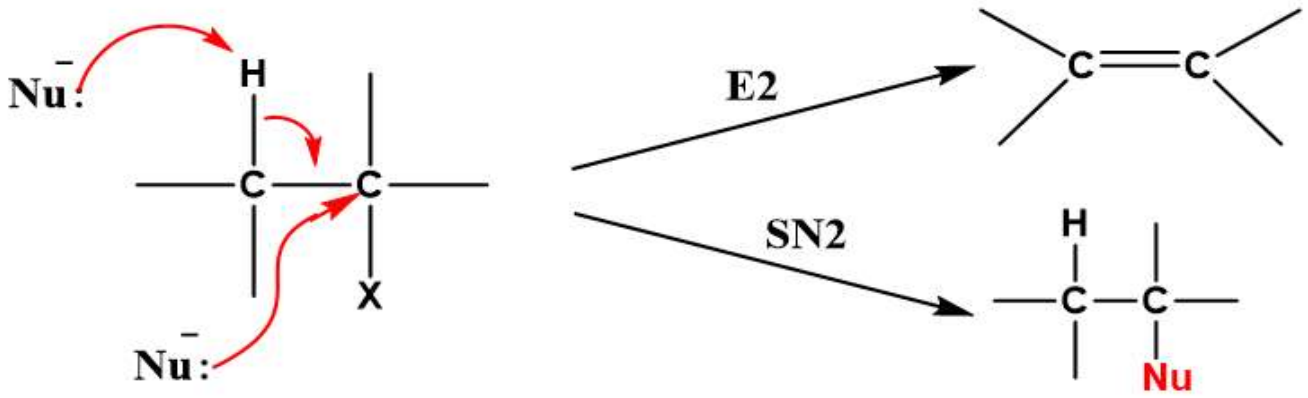

Br
CH3CH2CCH3
CH3
CH3CH2O-Na+
CH3CH2OH
CH3
CH3-CH=C-CH3
70%
Major
+
CH3-CH2-CH=CH2
19%


Cl
CH3
KOH
Ethanol
?


Br
CH-CH3
KOH
Ethanol
?

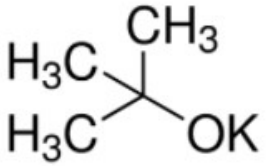
Elimination versus Substitution

Nucleophilic substitution and elimination reactions often compete. Since bases are nucleophilic, they can undergo substitution



$$CH_3CHCH_3 \xrightarrow[CH_3CH_2OH]{CH_3CH_2O^-Na^+} CH_3{-}CH{=}CH_2 \;(87\%) \;+\; CH_3{-}CH(OCH_2CH_3){-}CH_3 \;(13\%)$$

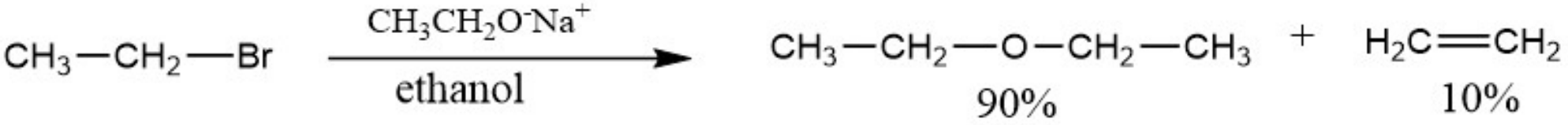
- **to favor elimination:** use a strong, hindered base
  e.g., KOtBu (Potassium *tert*-butoxide)



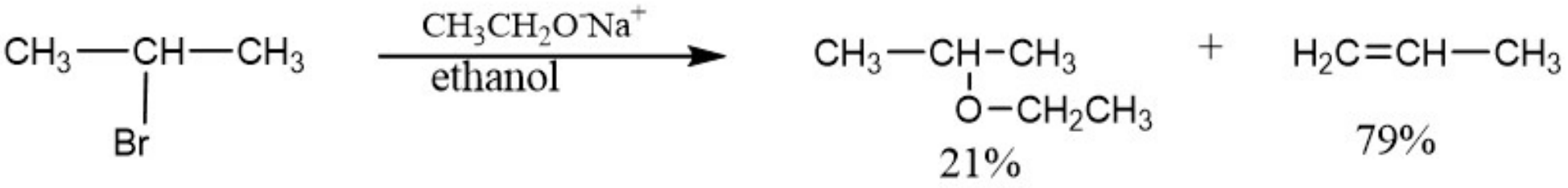
- **to favor substitution:** use a small, unhindered nucleophile

- **reactivity Patterns**

With 1° halide substitution is highly favoured

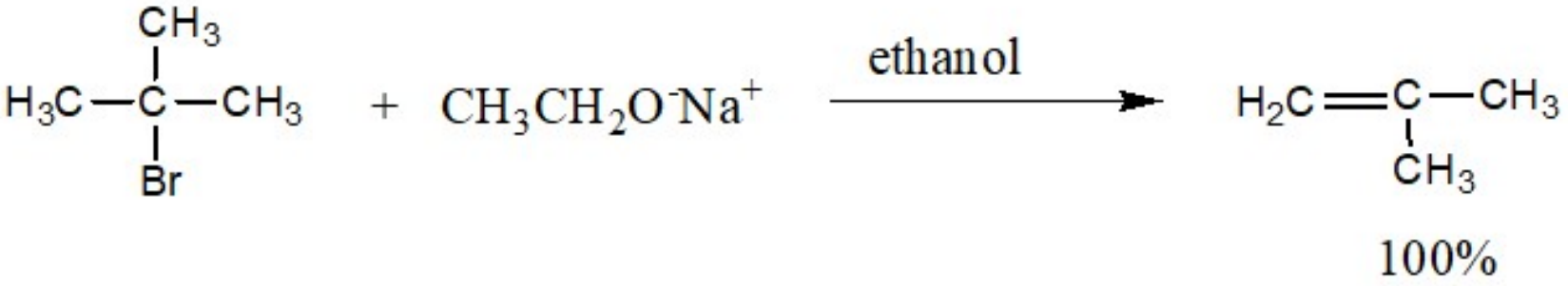


With 2° halide elimination favoured



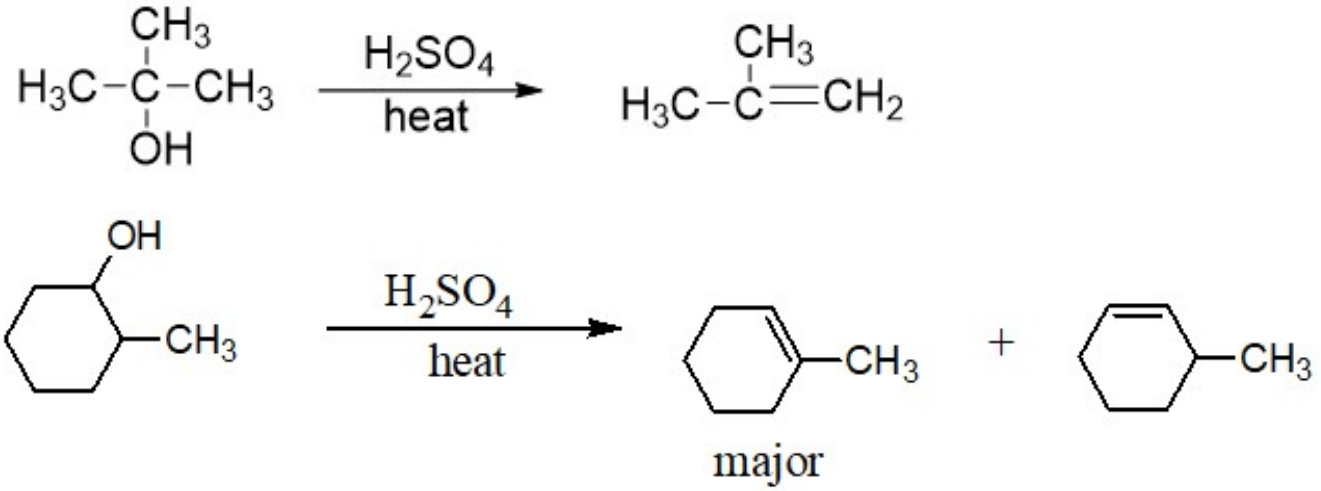
steric effect makes substitution difficult

With 3° halide elimination highly favoured

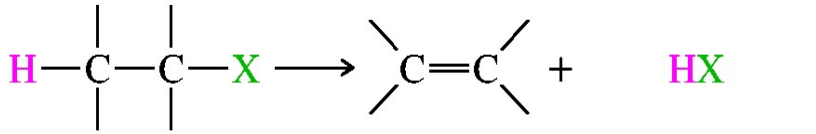


Applications of Elimination Reactions

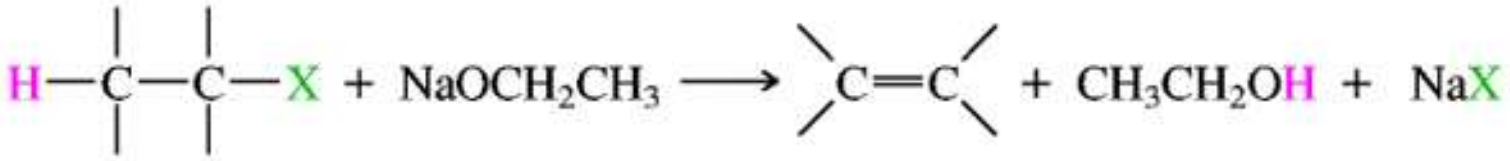
1. Dehydration of alcohol

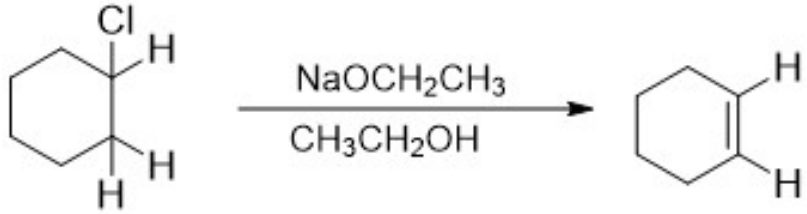


2. Dehydrohalogination

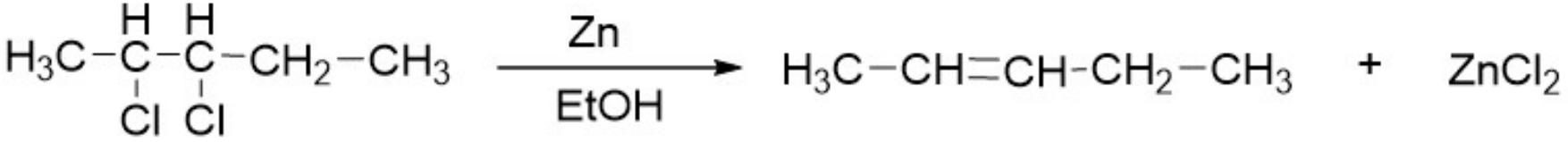


Alkyl halide Alkene Hydrogen halide

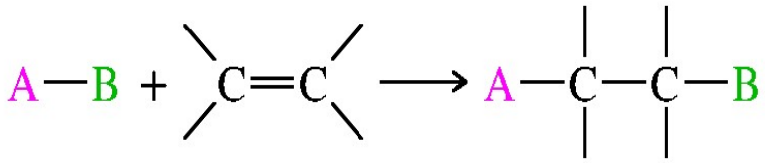




3. Elimination of vicinal dihalides

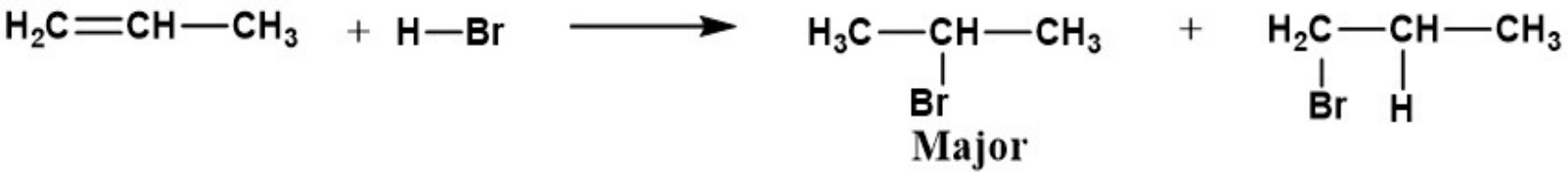


4.3 ADDITION REACTIONS

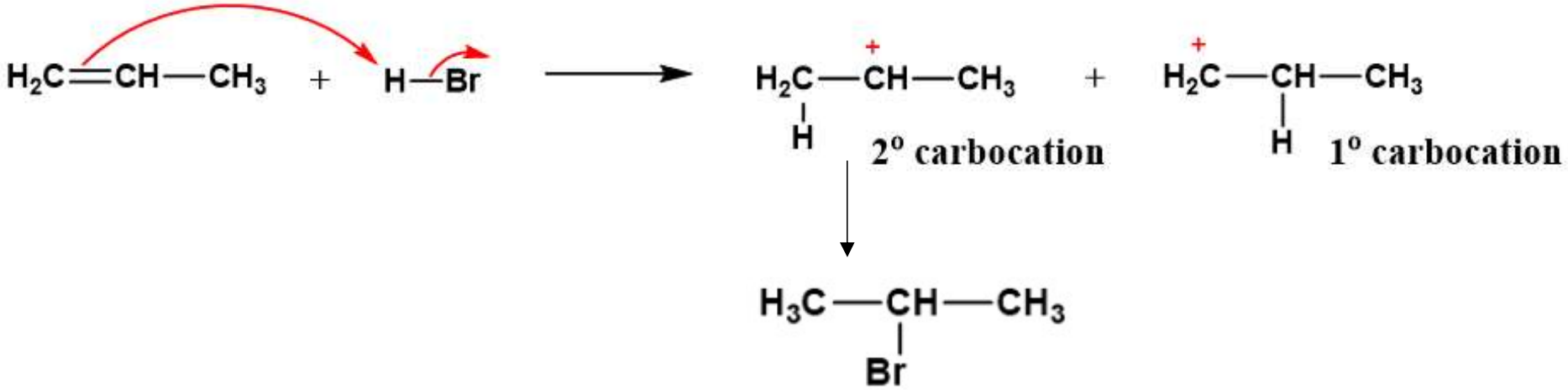


Rules for Addition Reactions

Markovnikov's Rule: addition reaction pass through the formation of more stable carbocation as an intermediate.



mechanism

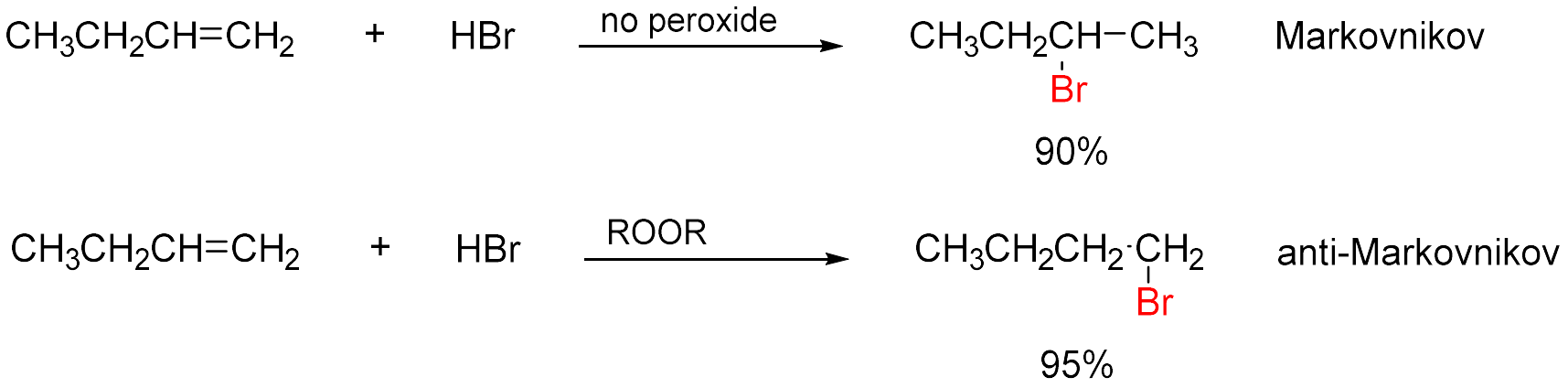


The reaction tends to pass through more stable carbocation.

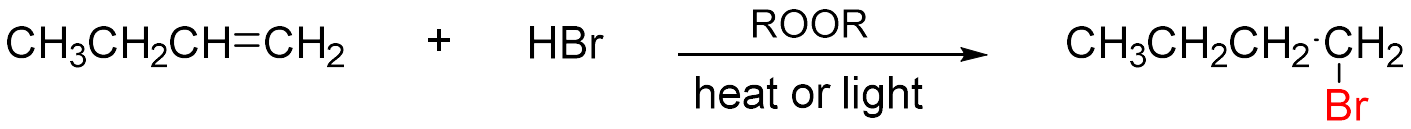
Carbocation stability: 3° > 2° > 1°

Anti-Markovnikov's (Radical) addition

Addition of HX on double bond in the presence of peroxides follow anti-Markovnikov's rule



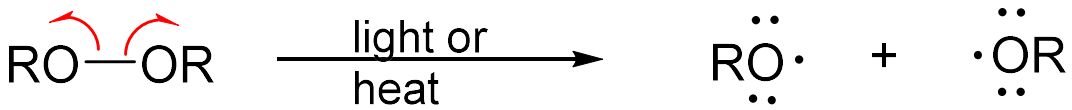
The overall reaction



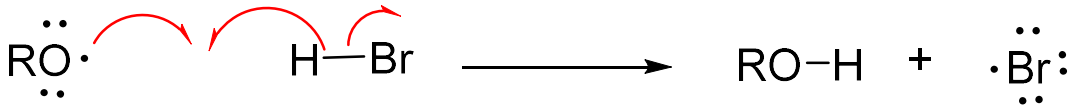
Mechanism

a) Initiation

Step 1 : dissociation of a peroxide in to two radicals

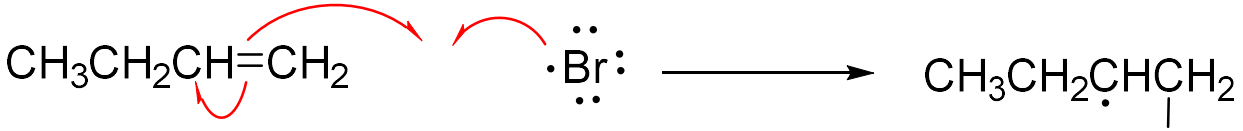


Step 2: Hydrogen atom abstraction from hydrogen bromide by an alkoxy radical:



(b) Chain propagation

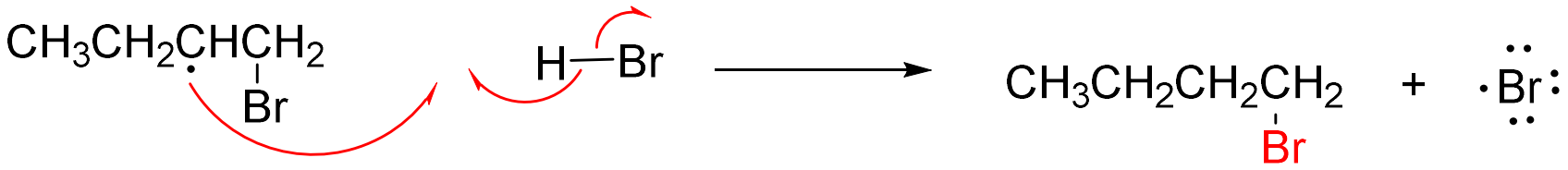
Step 3: Addition of a bromine atom to the alkene:



2°

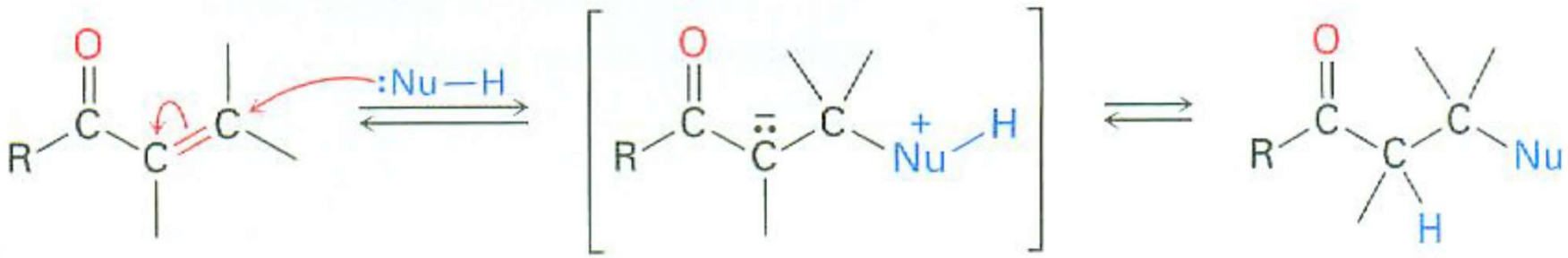
A secondary alkyl radical is more stable than a primary radical.

Step 4: Abstraction of a hydrogen atom from hydrogen bromide by the free radical formed in step 3:

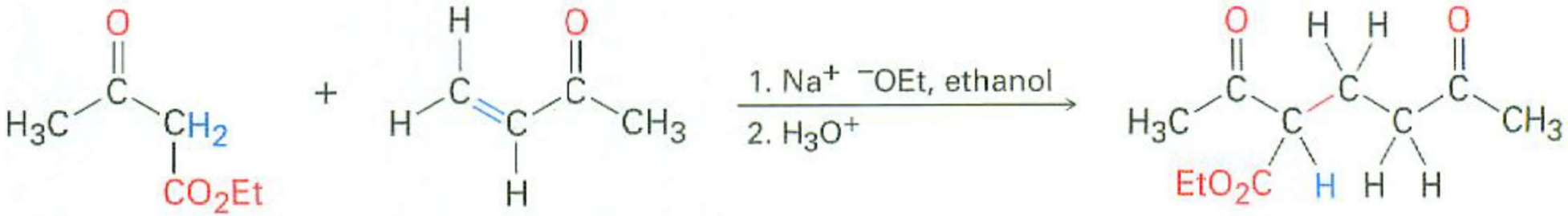


Michael addition

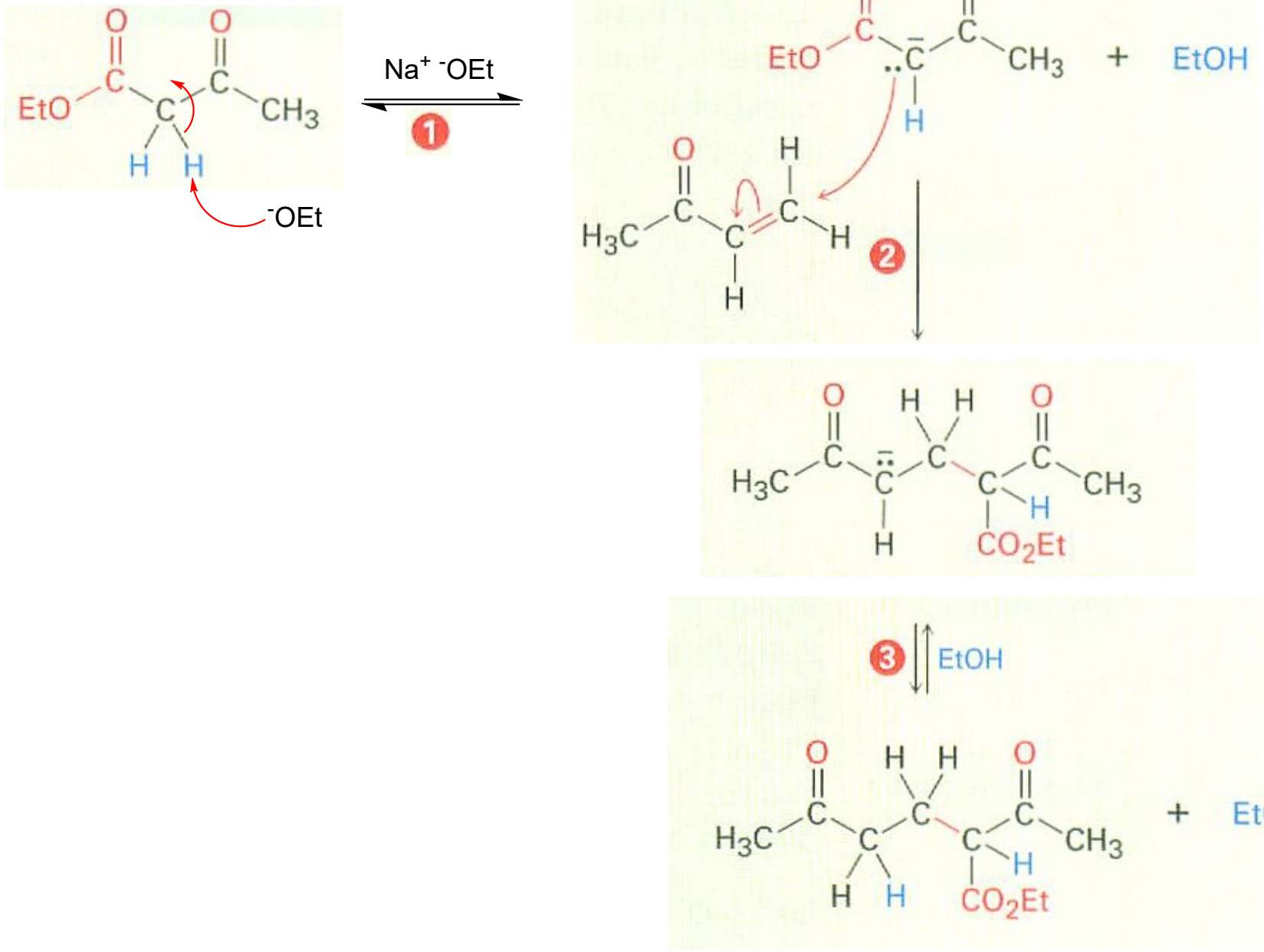
Michael addition is the nucleophilic addition of a carbanions or another nucleophile to an α, β-unsaturated ketones.



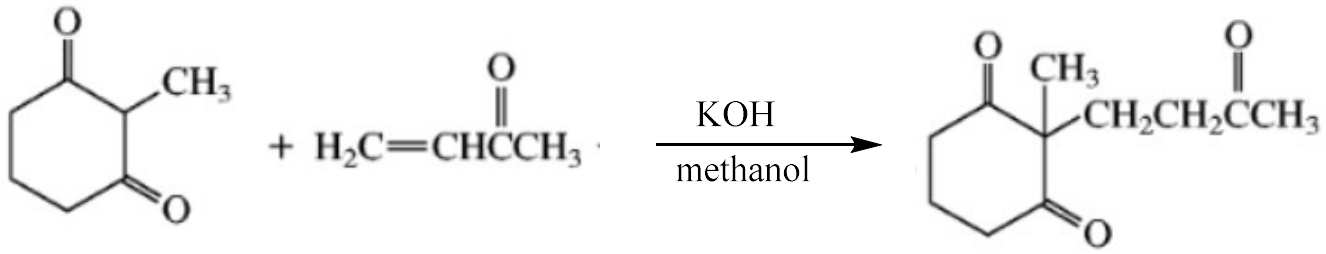
The best Michael reaction are those that take place when a particular stable enolate ion such as derived from a β-keto ester or other 1,3-dicarbonyl compounds adds to an α, β-unsaturated ketones .



Mechanism

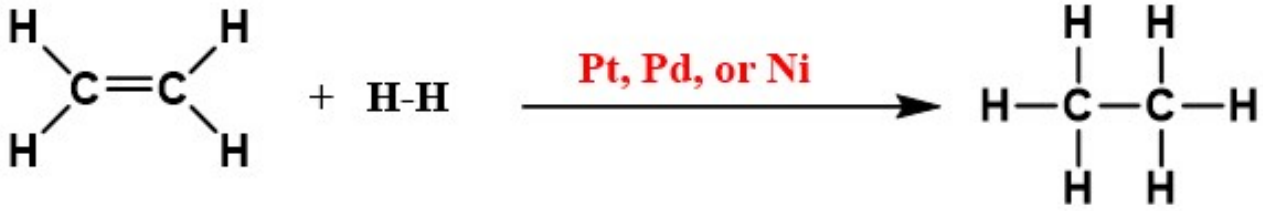

EtO
O
O
CH3
H
H
-OEt
Na+ -OEt
1
EtO
CH3
+
EtOH
H3C
H
2
H3C
H
H
CO2Et
3
EtOH
H3C
CH3
CO2Et
+
EtO−

E.g



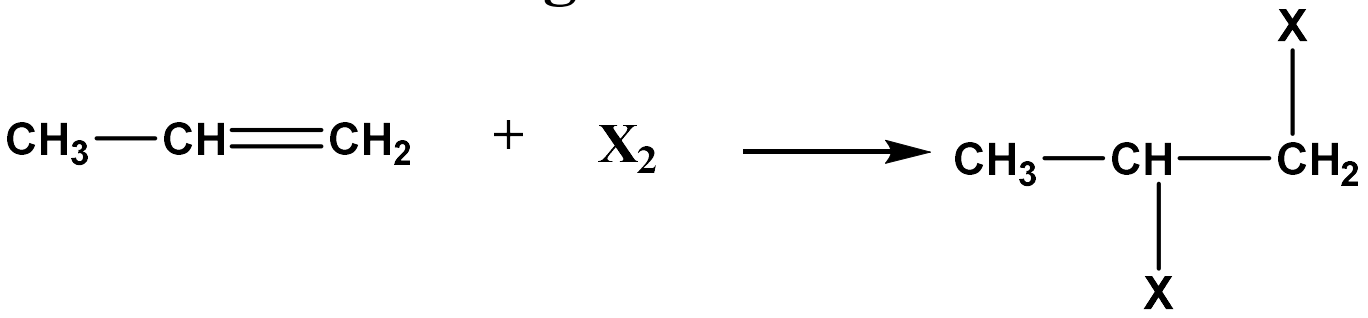
Examples of Addition Reactions

1. Hydrogenation

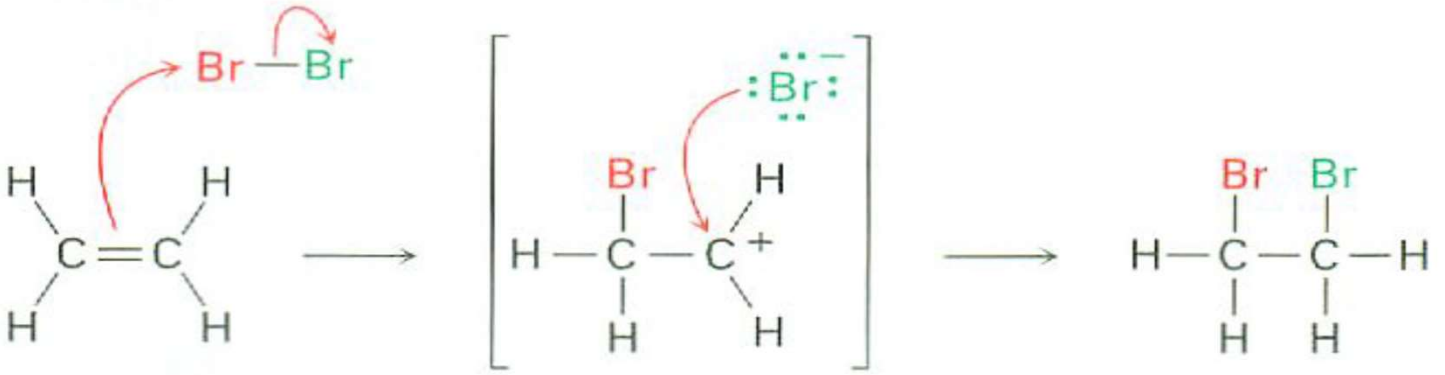


$(CH_3)_2C{=}CHCH_3 + H_2 \xrightarrow{Pt} (CH_3)_2CHCH_2CH_3$

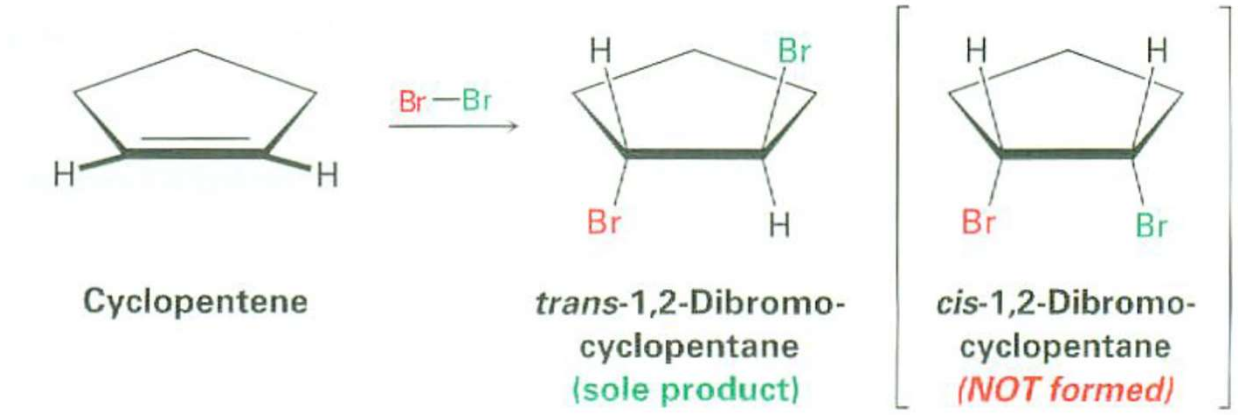
2. Addition of Halogens



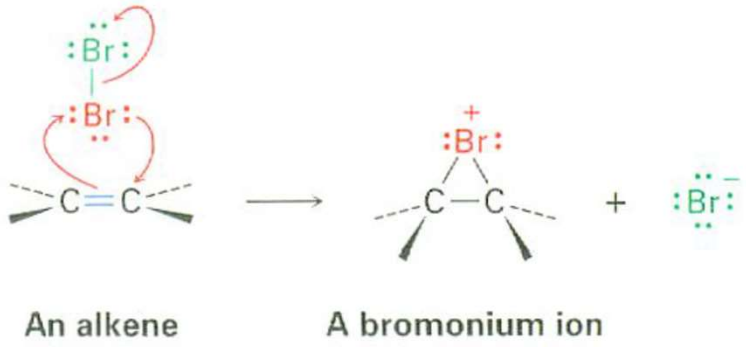
vicinal dihalide

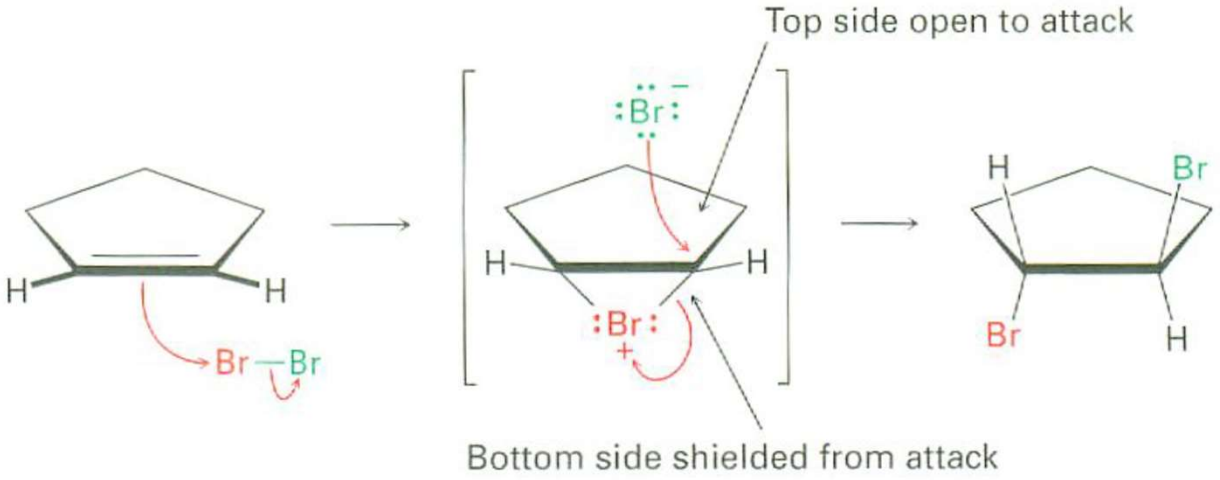


- anti-stereochemistry-two new groups are added to opposite sides of the original pi bond

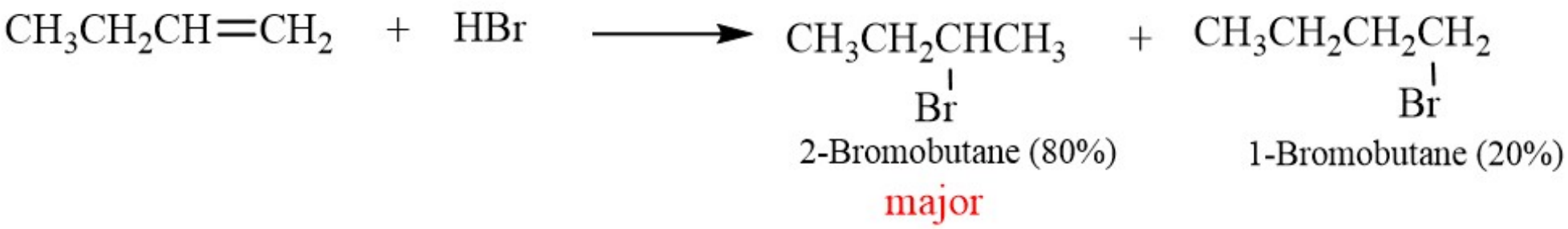


The reaction intermediate is not a carbocation but is instead a bromonium ion, R_2Br^+. Formed by addition of Br^+ to the alkene.

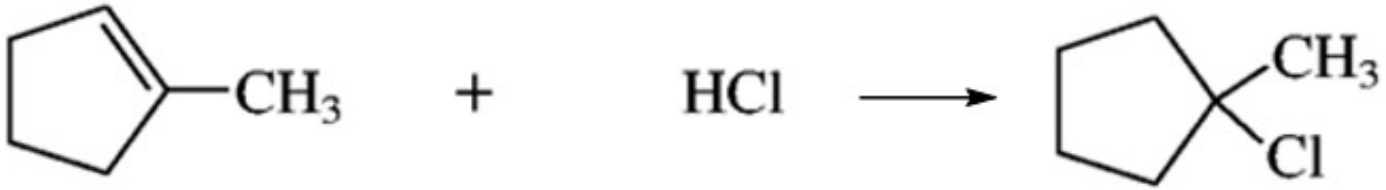




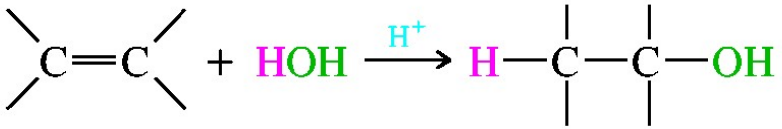
3. Addition of Hydrogen Halide (HX)



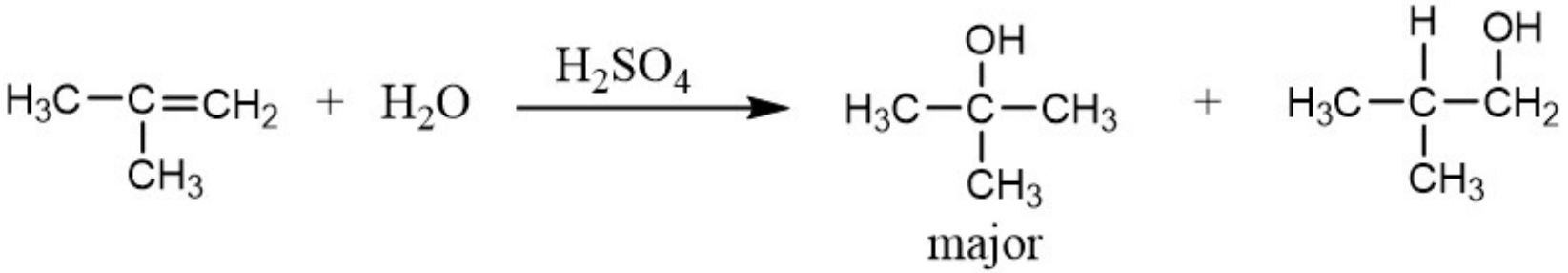
The major product is determined by Markovnikov's rule



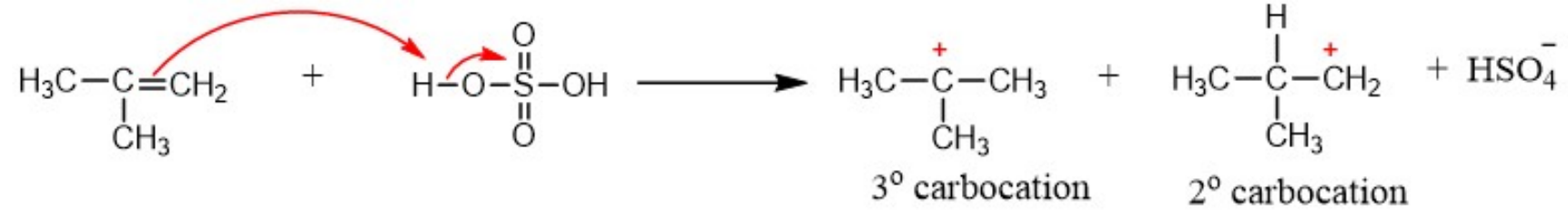
4. Addition of water (Hydration)

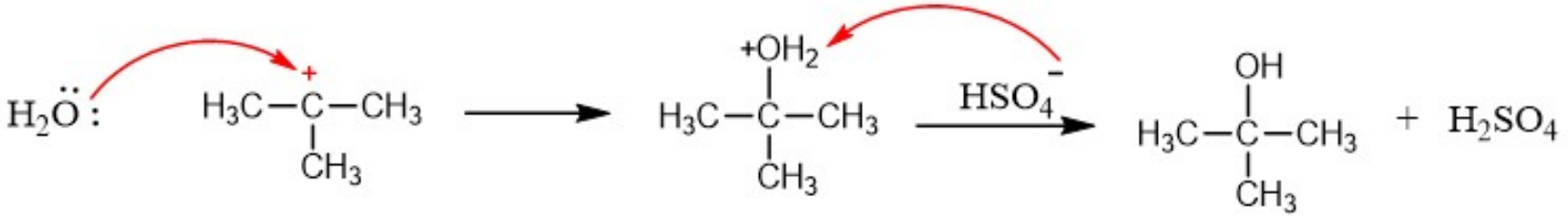


Alkene Water Alcohol

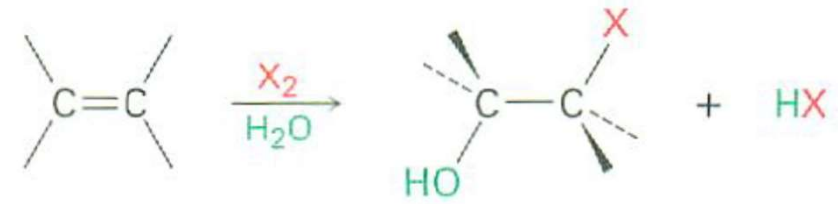


The reaction follows Markovnikov's rule.





5. Halohydrin formation

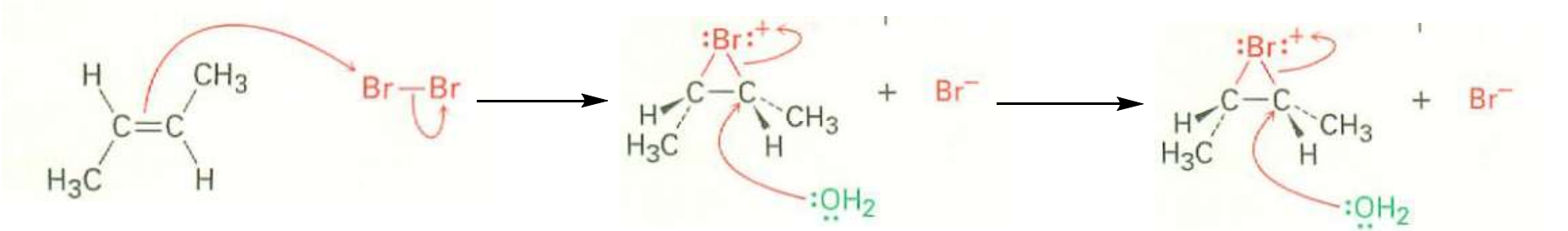


An alkene A halohydrin

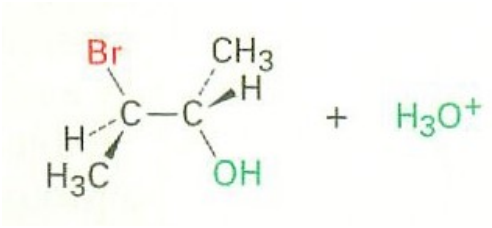
$$H_2C{=}CH_2 + Br_2 \xrightarrow{H_2O} HOCH_2CH_2Br$$

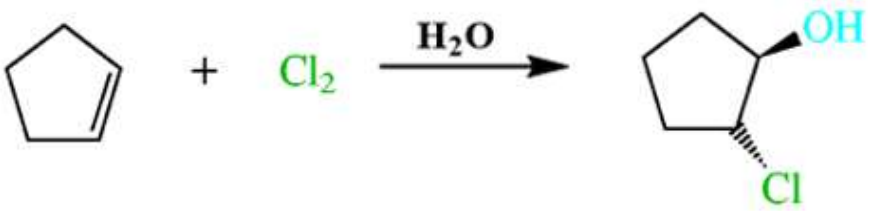
2-Bromoethanol (70%)

Mechanism

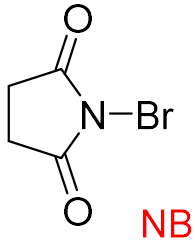


Bromonium ion intermediate produced





N-bromosuccinimide (NBS) commonly used as a source of Br_2



NBS is a stable, easily handled compound that slowly decomposes in water to yield Br_2. Br_2 itself can also be used in the reaction, but it is more dangerous and more difficult to handle than NBS