

Alkenes

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Alkenes and Alkynes

Hydrocarbons (contain only carbon and hydrogen)

a) **Saturated:** (Contain only single bonds)

Alkanes (C_nH_{2N+2})

Cycloalkanes (C_nH_{2N})

b) **Unsaturated:** contain

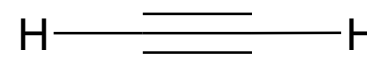
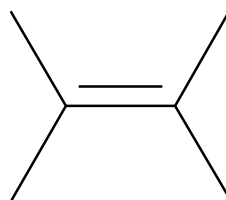
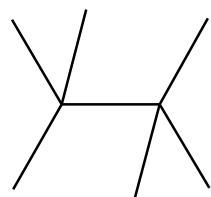
Alkenes: double bonds (C_nH_{2N})

Alkynes: triple bonds (C_nH_{2N-2})

Aromatic: benzene like compounds



Facts about double and triple bonds



bond angle

109.5

120 °

180 °

bond length

154 pm

134 pm

121 pm

rotation

possible

restricted

restricted

geometry

tetrahedral

triagonal planer

linear

Hypridization

sp³

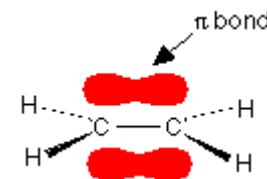
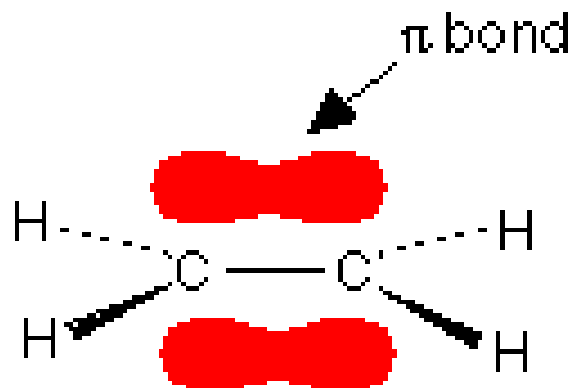
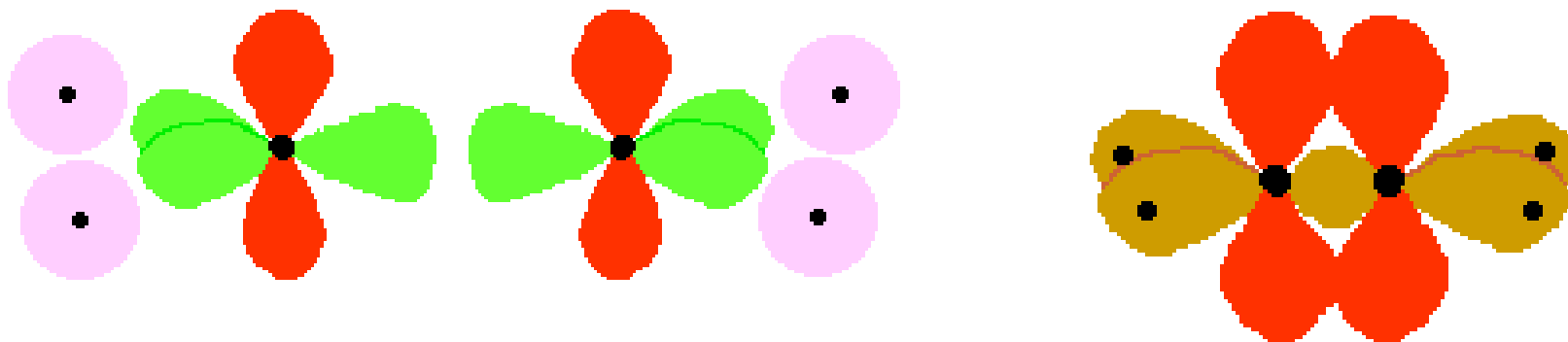
sp²

sp

Bond Length in Benzene

139 pm (plannar, sp² hypridized)



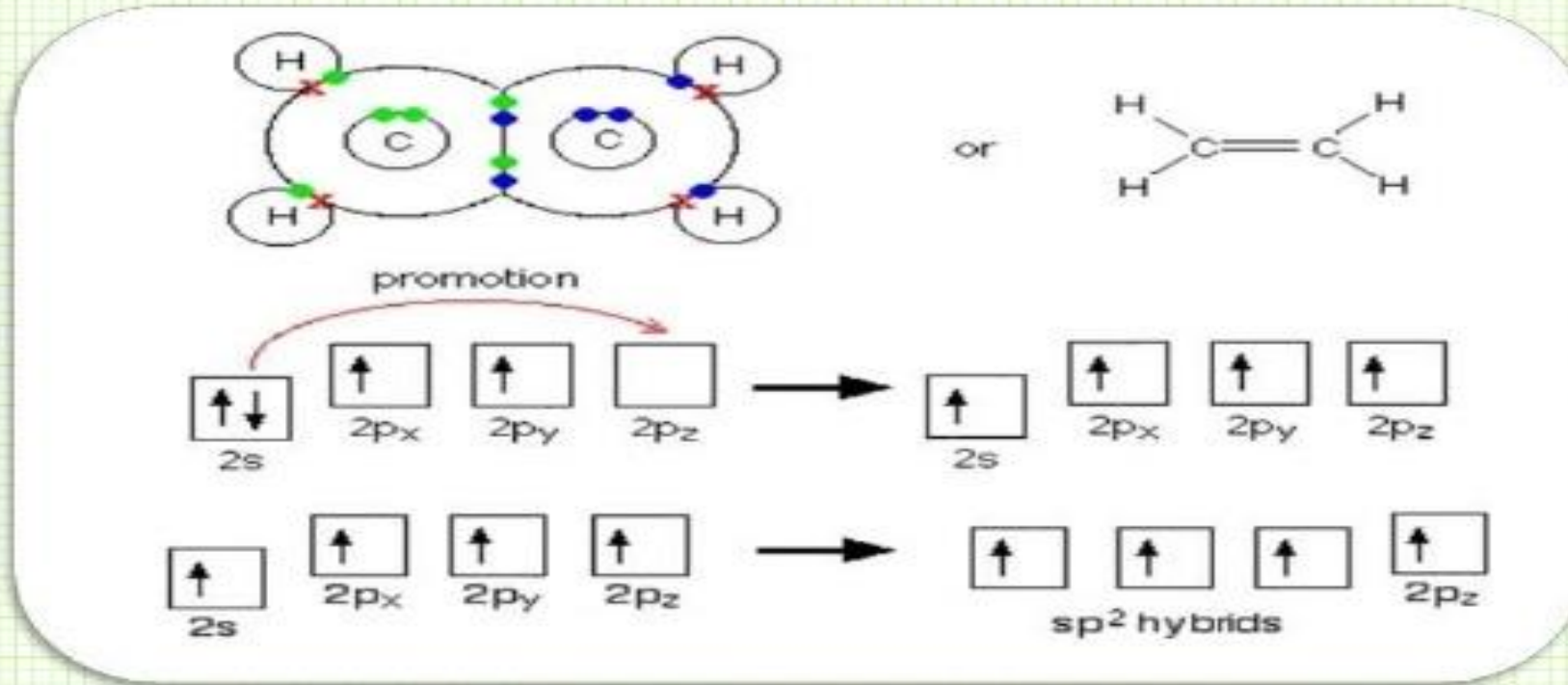


A pi bond is one in which the electrons in the p orbitals are held above and below the plane of the molecule.

The sigma bond is stronger than the pi bond.

A double bond is formed from a sigma bond and a pi bond, and so it is stronger than a single bond.

sp^2 Hybridization

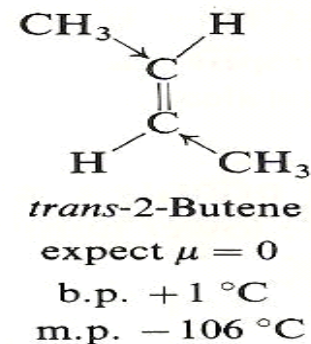
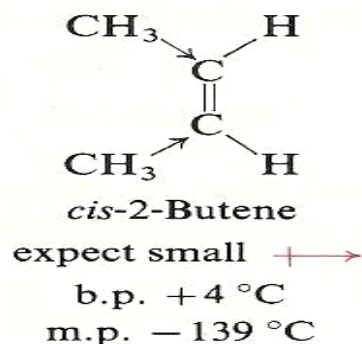


Summary

- sp^2 hybridization occurs when a C has 3 attached groups
- sp^2 hybrid orbital has 33% s and 67% p character
- the 3 sp^2 hybrids point towards the corners of a triangle at 120° to each other
- each sp^2 hybrid orbital is involved in a σ bond formation and the remaining p orbital forms the π bond
- a double bond as a $\sigma + \pi$ bond



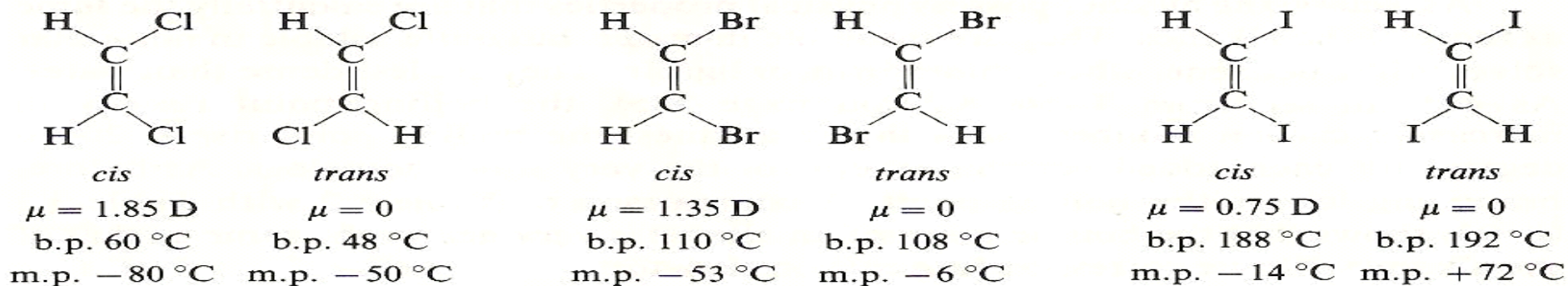
Physical Properties



measured directly, a small difference in polarity is reflected in the higher boiling point of the *cis* isomer.

This same relationship exists for many pairs of geometric isomers. Because of its higher polarity the *cis* isomer is generally the higher boiling of a pair; because of its lower symmetry it fits into a crystalline lattice more poorly, and thus generally has the lower melting point.

The differences in polarity, and hence the differences in melting point and boiling point, are greater for alkenes that contain elements whose electronegativities differ widely from that of carbon. For example:



- **Physical properties:**

- non-polar or weakly polar
- no hydrogen bonding
- relatively low mp/bp ~ alkanes
- water insoluble

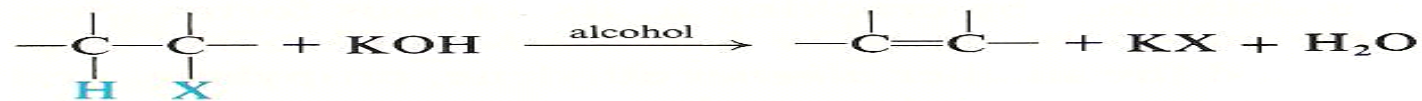
Importance:

- common group in biological molecules
- starting material for synthesis of many plastics



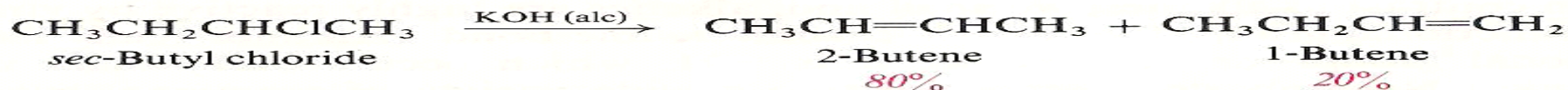
PREPARATION OF ALKENES

1. Dehydrohalogenation of alkyl halides. Discussed in Secs. 8.13 and 8.25.

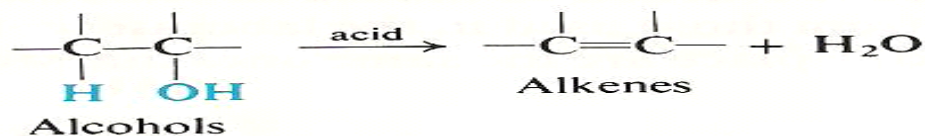


Ease of dehydrohalogenation
of alkyl halides
 $3^\circ > 2^\circ > 1^\circ$

Examples:

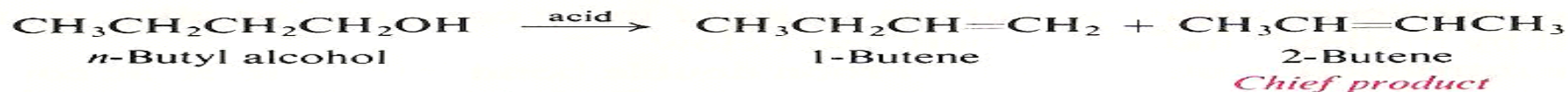
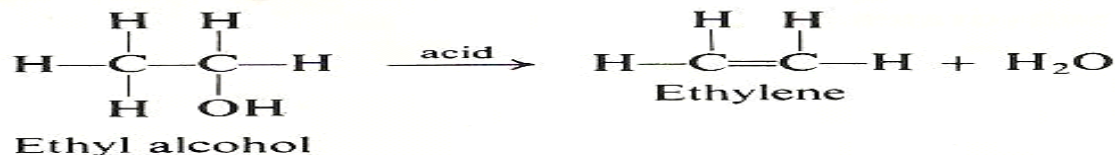


2. Dehydration of alcohols. Discussed in Sec. 8.26.



Ease of dehydration of alcohols
 $3^\circ > 2^\circ > 1^\circ$

Examples:



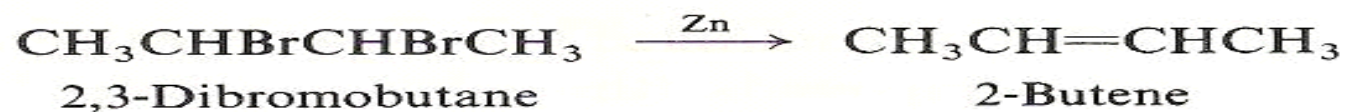
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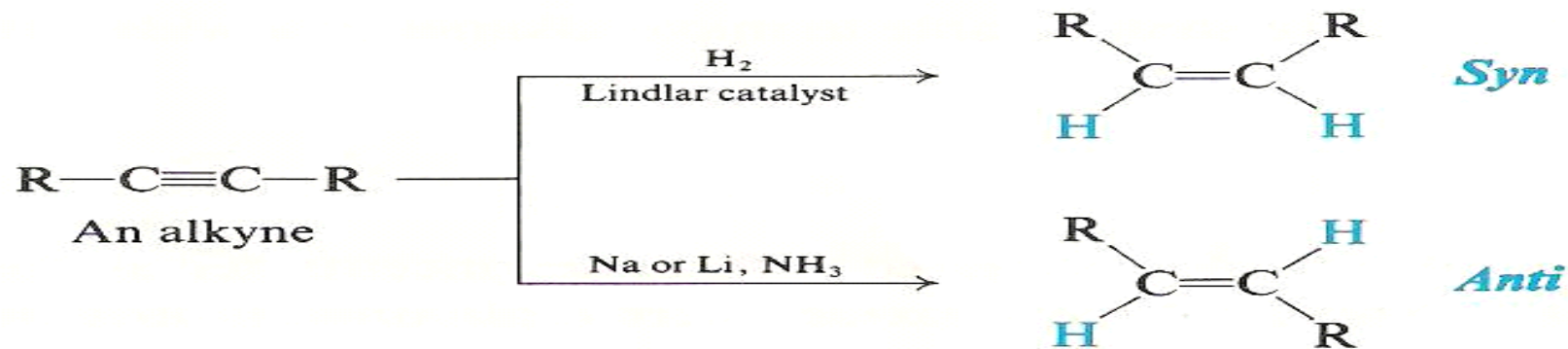
3. Dehalogenation of vicinal dihalides. Discussed in Sec. 8.12.



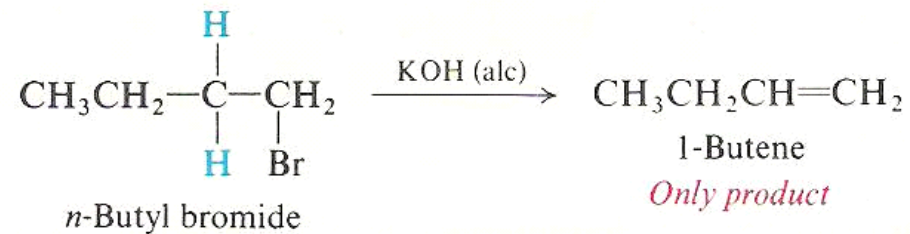
Example:



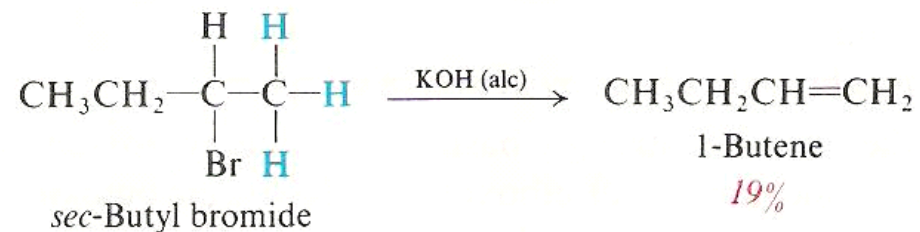
4. Reduction of alkynes. Discussed in Sec. 12.8.



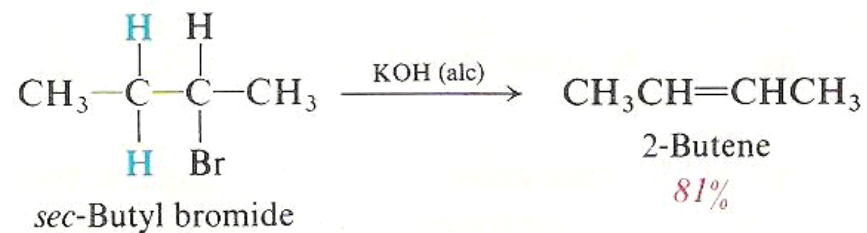
The more substituted alkene will form



and hence yields only 1-butene. *sec*-Butyl bromide, on the other hand, can lose hydrogen either from C-1,



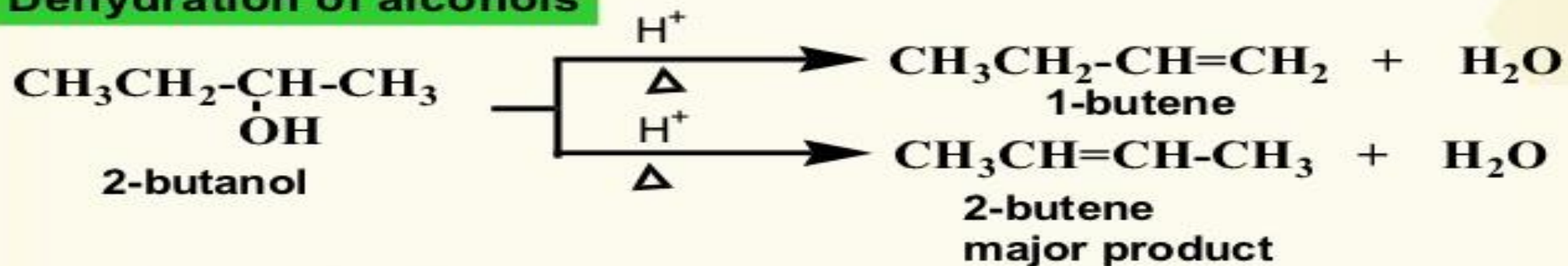
or from C-3,



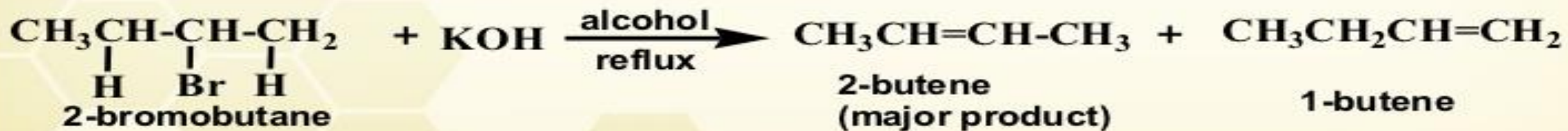
- Saytzeff rule:

- A reaction that produces an alkene would favour the formation of an alkene that has the **greatest number of substituents attached to the C=C group.**

Dehydration of alcohols



Dehydrohalogenation of haloalkanes



Saytzeff orientation:

In dehydrohalogenation the preferred product is the alkene that has the greater number of alkyl groups attached to the doubly bonded carbon atoms

(the more substituted alkene will form)

Ease of formation of alkenes:

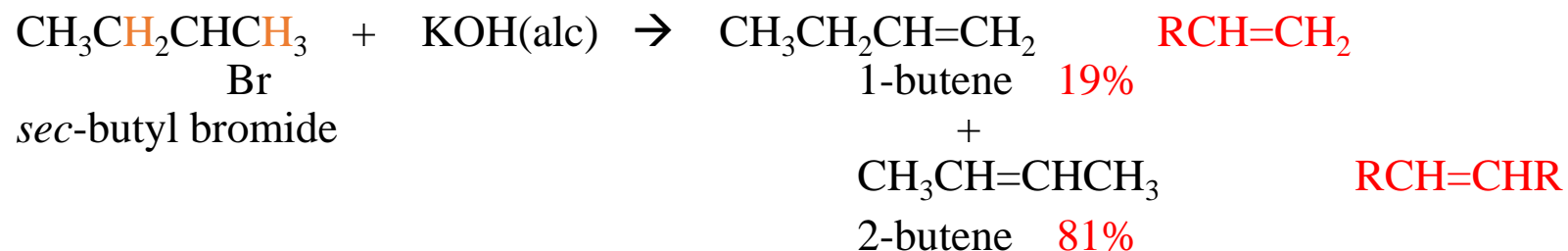


Stability of alkenes:

More no of the substitutes and more the stability of the alkenes



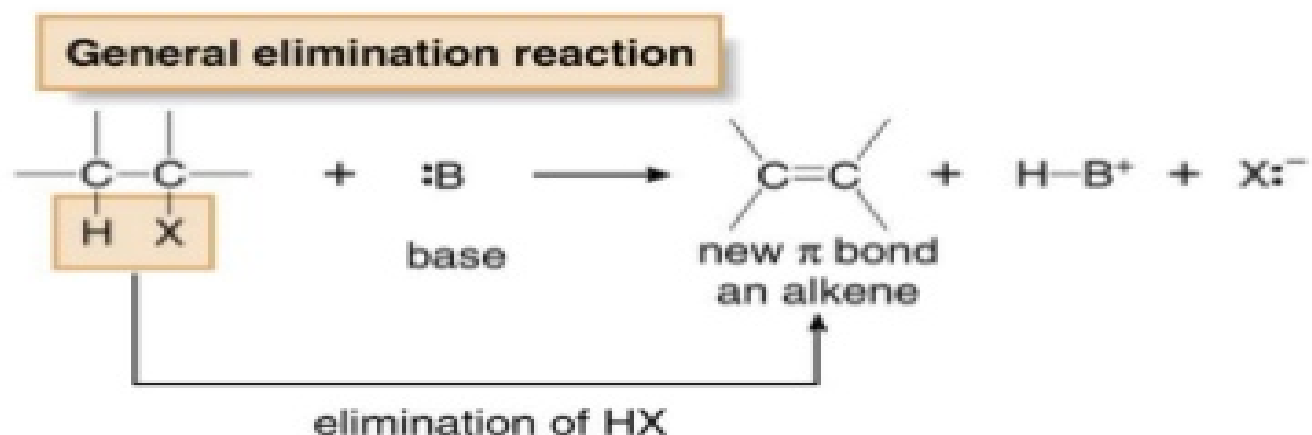
Example:



Elimination Reaction

Elimination reactions involve the loss of elements from the starting material to form a new π bond in the product.

Alkyl halides (RX) undergo elimination with bronsted bases. The elements of HX are lost and alkene are formed.



Leaving groups

X, OH, OR, N_2^+ , N_3 , H_2O^+ , NR_3^+ and SR_2^+

Classification

- α -elimination (1,1)
- β - elimination (1,2)
- γ - elimination (1,3)

β - elimination

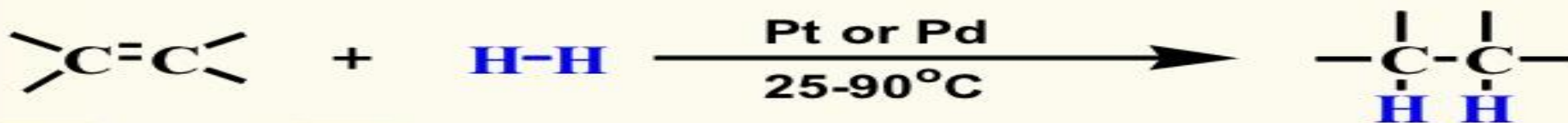
- E1
- E2
- E1CB



REACTIONS OF ALKENES

+ Catalytic hydrogenation:

- hydrogenation: addition of hydrogen to a double bond and triple bond to yield saturated product.
- alkenes will combine with hydrogen in the presence of a catalyst to form alkanes.



- Platinum (Pt) and palladium (Pd) – Catalysts
- Pt and Pd: temperature 25-90°C
- Nickel can also be used as a catalyst, but a higher temperature of 140°C – 200°C is needed.

EXAMPLES:



+ Addition of halogens:

i) In inert solvent:

- alkenes react with halogens at room temperature and in dark.
- the halogens is usually dissolved in an inert solvent such as dichloromethane (CH_2Cl_2) and tetrachloromethane (CCl_4).
- Iodine will not react with alkenes because it is less reactive than chlorine and bromine.
- Fluorine is very reactive. The reaction will produced explosion.



X-X = halogen such as Br_2 or Cl_2

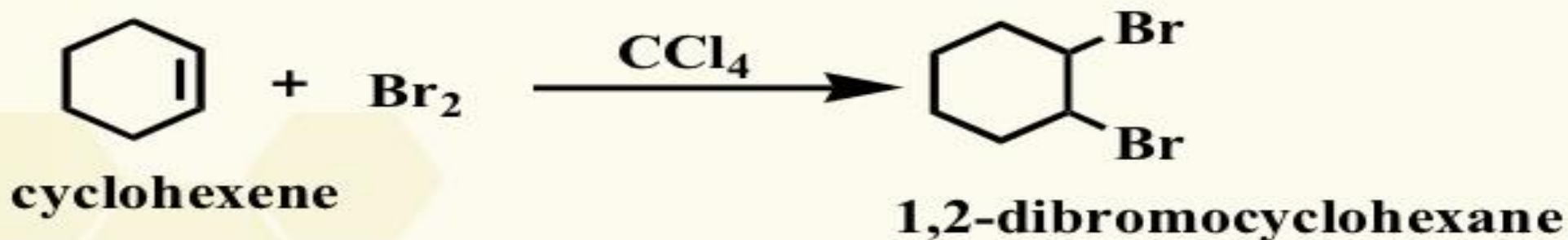
Inert solvent = CCl_4 or CH_2Cl_2



EXAMPLES:



* the red-brown colour of the bromine solution will fade and the solution becomes colourless.

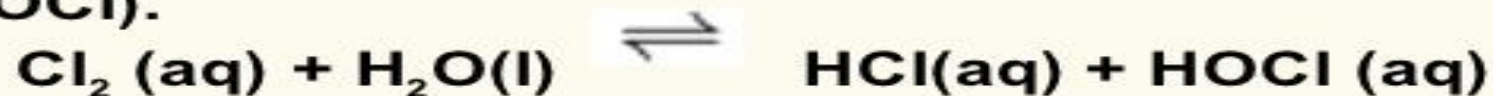


Addition of halogens:

ii) In water / aqueous medium:

- chlorine dissolves in water to form HCl and chloric (I) acid

(HOCl).



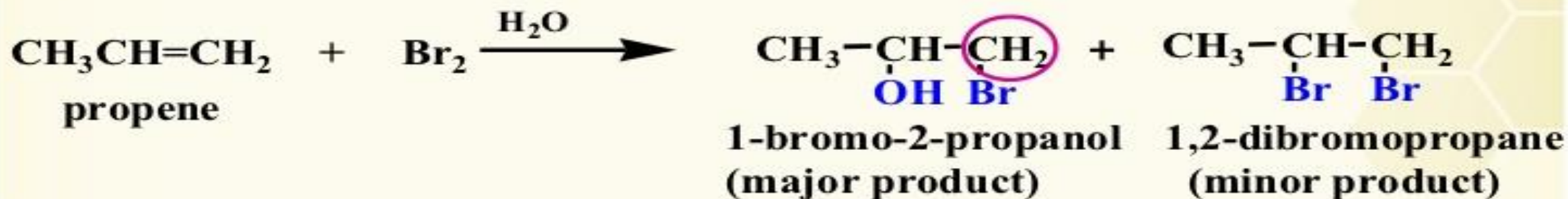
- same as bromine



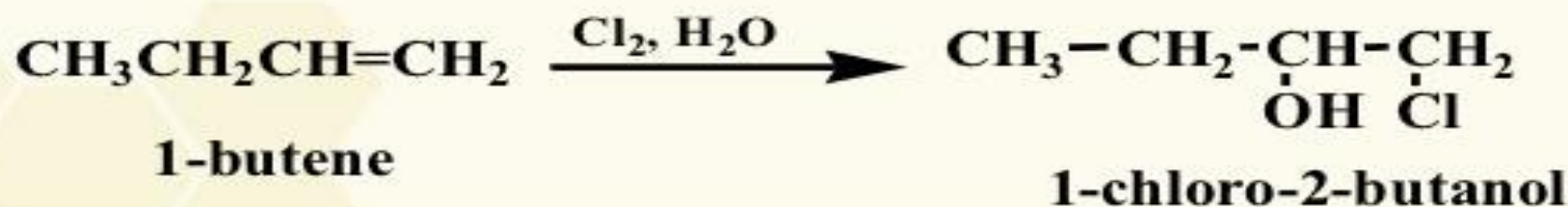
* **Reaction of alkenes with halogens in water** (eg. chlorine water and bromine water) produced **halohydrins** (an alcohol with a halogen on the adjacent carbon atom).



EXAMPLES:



* Br atom attached to the carbon atom of the double bond which has the **greater number of hydrogen atoms**.



• **Addition of hydrogen halides:**

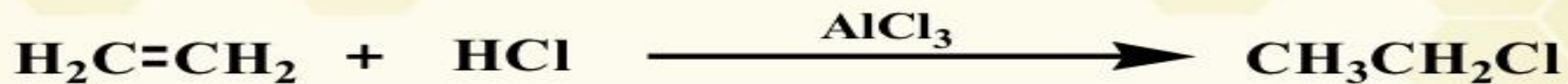
- Addition reaction with electrophilic reagents.
- Alkenes react with hydrogen halides (in gaseous state or in aqueous solution) to form addition products.
- The hydrogen and halogen atoms add across the double bond to form haloalkanes (alkyl halides).
- General equation:



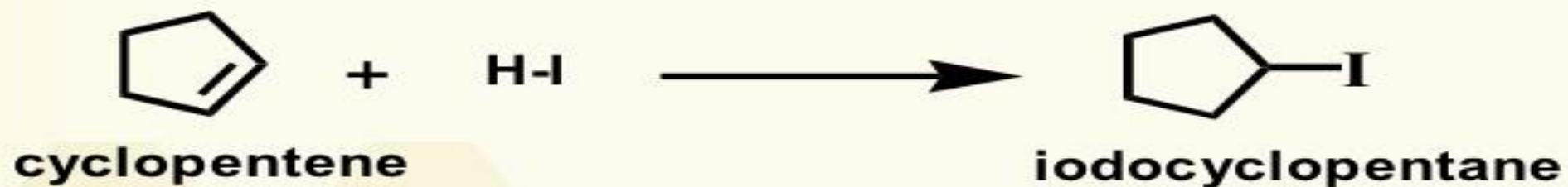
- Reactivity of hydrogen halides : HF < HCl < HBr < HI



* Reaction with HCl needs a catalyst such as AlCl_3



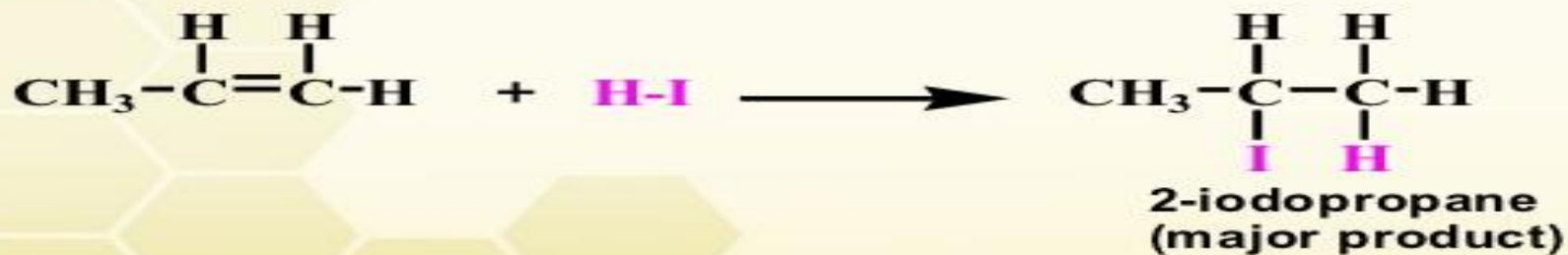
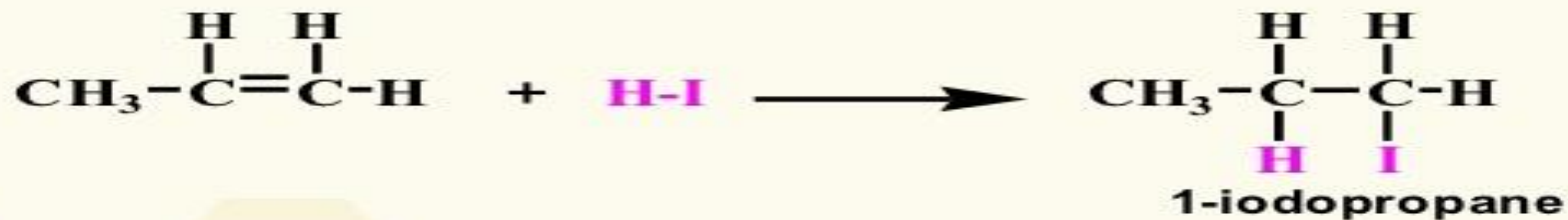
EXAMPLES:





MARKOVNIKOV'S RULE

- There are 2 possible products when hydrogen halides react with **an unsymmetrical alkene**.
- It is because hydrogen halide molecule can add to the C=C bond in two different ways.



Markovnikov's rules:

- the addition of HX to an unsymmetrical alkene, the **hydrogen atom attaches itself** to the carbon atom (of the double bond) with the **larger number of hydrogen atoms**.

Mechanism of electrophilic addition reactions:

- C=C : electron rich part of the alkene molecule
- Electrophiles: electron-seeking

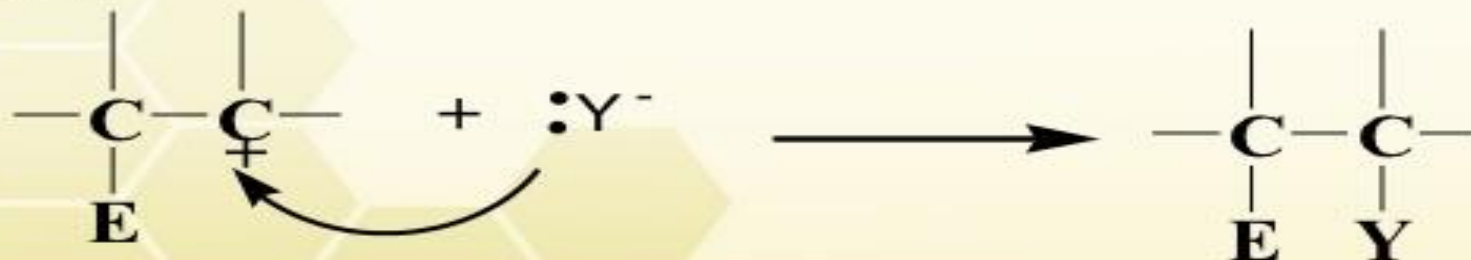
Step 1: Formation of carbocation.

Attack of the pi bond on the electrophile to form carbocation.

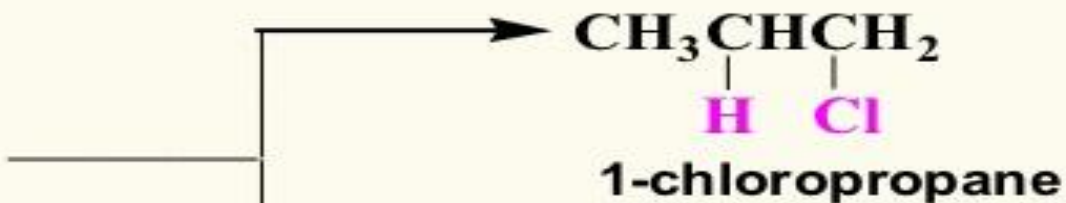
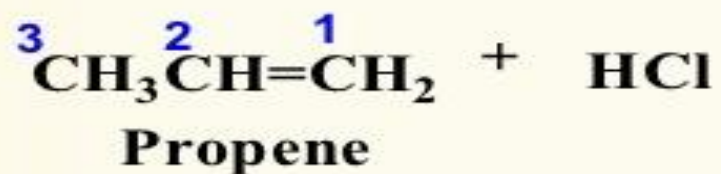


Step 2: Rapid reaction with a negative ion.

The negative ion (Y⁻) acts as nucleophile and attacks the positively charged carbon atom to give product of the addition reaction.

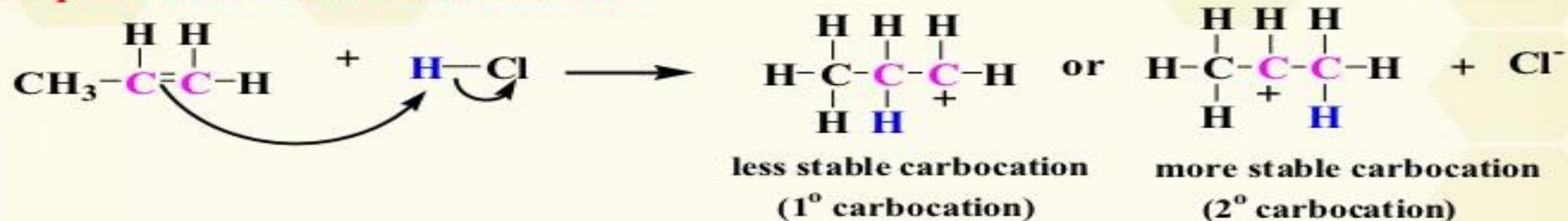


ADDITION OF HYDROGEN HALIDES TO UNSYMMETRICAL ALKENES AND MARKOVNIKOV'S RULE



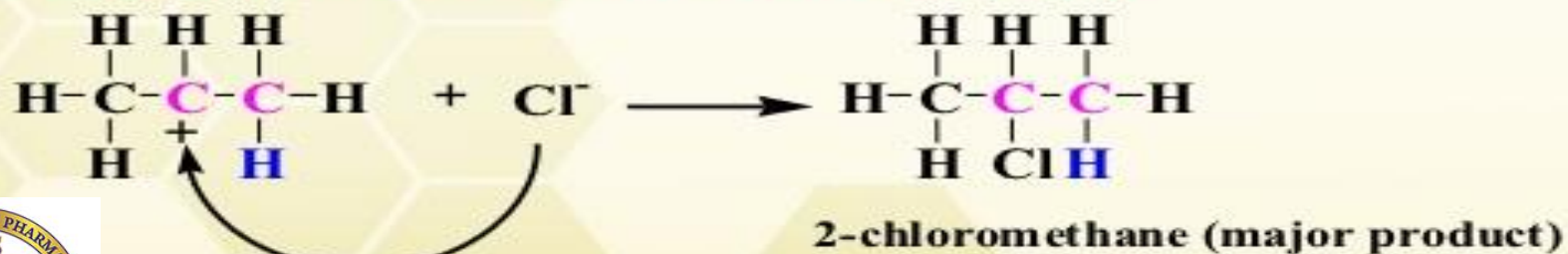
MECHANISM:

Step 1: Formation of carbocation



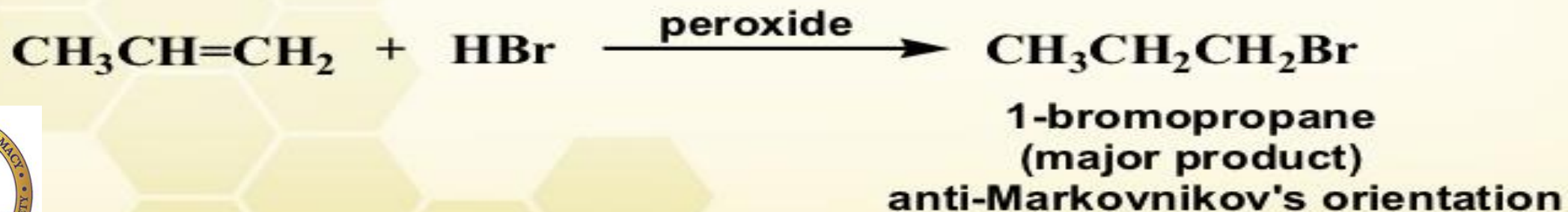
- 2° carbocation is more stable than 1° carbocation.
- 2° carbocation tends to persist longer, making it more likely to combine with Cl^- ion to form 2-chloromethane (basis of Markovnikov's rule).

Step 2: Rapid reaction with a negative ion



ANTI-MARKOVNIKOV'S RULE: FREE RADICAL ADDITION OF HYDROGEN BROMIDE

- When HBr is added to an alkene in the **absence of peroxides** it obey Markovnikov's rule.
- When HBr (not HCl or HI) reacts with unsymmetrical alkene in the **presence of peroxides** (compounds containing the O-O group) or oxygen, HBr adds in the **opposite direction to that predicted by Markovnikov's rule**.
- The product between propene and HBr under these conditions is 1-bromopropane and not 2-bromopropane.



- **Anti-Markovnikov's addition:**

- peroxide-catalysed addition of HBr occurs through a free radical addition rather than a polar electrophilic addition.

- also observed for the reaction between HBr and many different alkenes.

- not observed with HF, HCl or HI.



OZONOLYSIS OF ALKENES

- Ozonolysis:**

- The reaction of alkenes with ozone (O_3) to form an ozonide, followed by hydrolysis of the ozonide to produce aldehydes and /or ketone.

- Widely used to determine the position of the carbon-carbon double bond.

- Ozonolysis is milder and both ketone and aldehydes can be recovered without further oxidation.

