# Alkene Reactions
# 1- Addition Reactions

*Dr. Sapna Gupta*

# Alkenes - Introduction

Alkene is a hydrocarbon functional group with at least double bond. The smallest alkene is $CH_2=CH_2$.

For all functional groups we will cover:

1. Nomenclature
2. Physical Properties
3. Applications
4. Synthesis
5. Reactions

For alkenes we have covered nomenclature, physical properties and synthesis (all elimination reactions from alkyl halides and dehydration of alcohols), in the previous chapter.

# Reactions of Alkenes

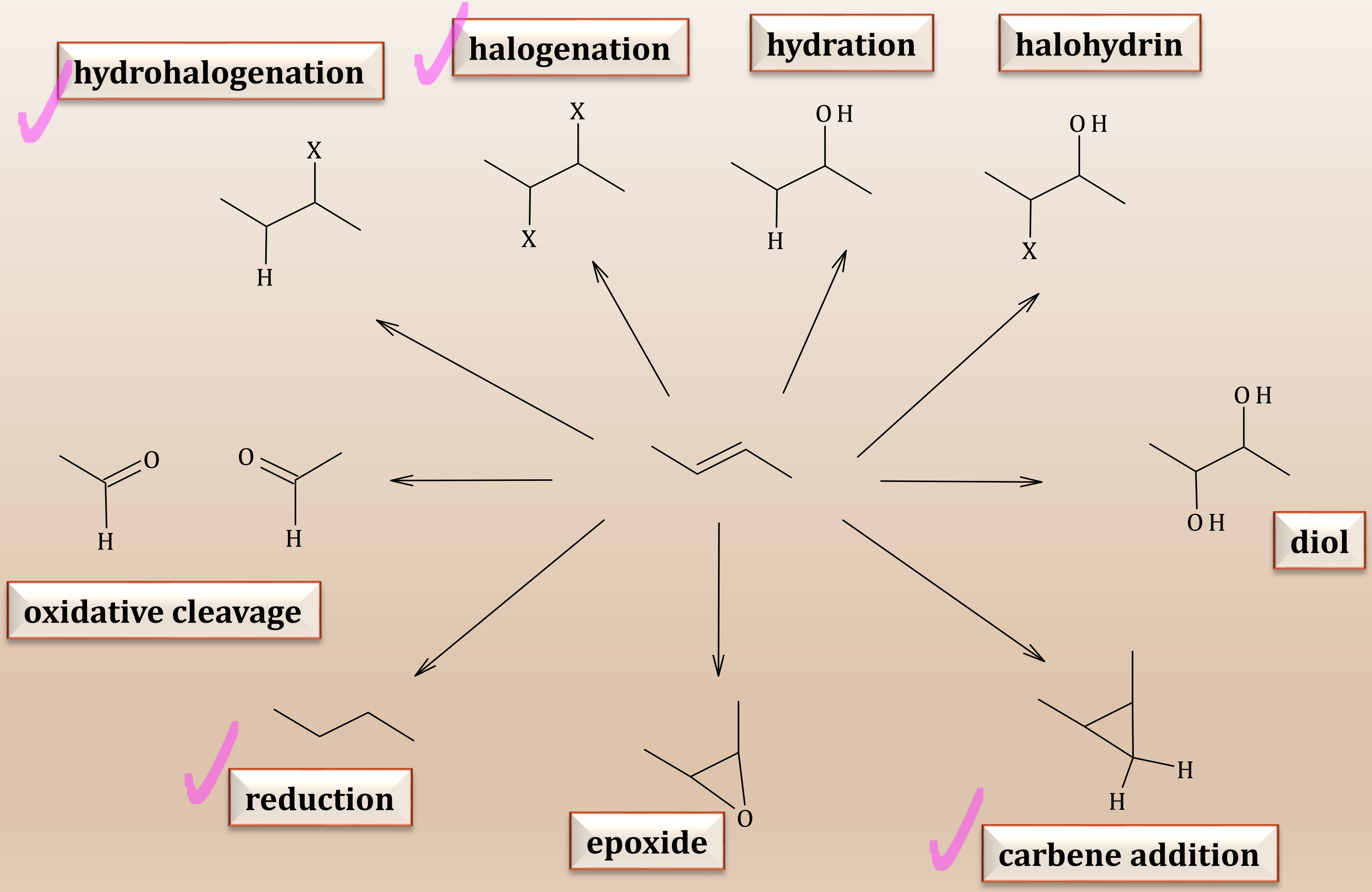
Most reactions of alkenes are addition because of the unsaturation of the double bond. Other reactions are oxidations.

Alkenes react with many electrophiles to give useful products by addition (often through special reagents). Reactions are shown on the next slide.

- Addition Reactions
  - Hydrohalogenation (HX)
  - Halogenation ($X_2$)
  - Hydration ($H_2O$)
  - Halohydrin ($X_2 + H_2O$)
  - Synthesis of diols
  - Carbene addition ($:CH_2$)
  - Epoxide formation
  - Hydrogenation ($H_2$) (reduction)
- Oxidative cleavage

# All Reactions

✓ *Covered in this power point.*



✓ **hydrohalogenation**

✓ **halogenation**

**hydration**

**halohydrin**

**diol**

✓ **carbene addition**

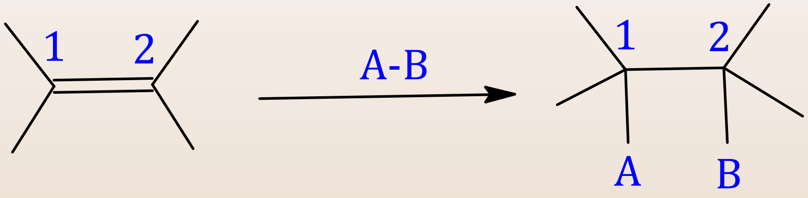
**epoxide**

✓ **reduction**

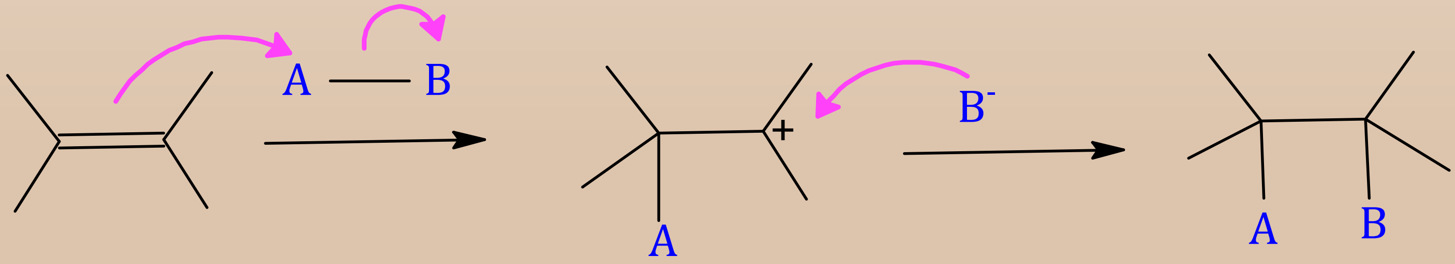
**oxidative cleavage**

# General Mechanism

All reactions of alkenes are addition reactions.



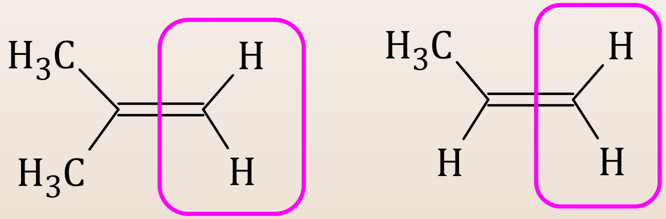
- Addition is 1,2-addition, which means that any atoms add on each of the carbon of the double bond.
- Alkene is the nucleophile in all reactions as it has the pi electrons and the reagent is the electrophile.
- Reactions products can depend on what kind of alkene is reacting, symmetric or asymmetric or terminal or internal. These alkenes are explained on the next slide.



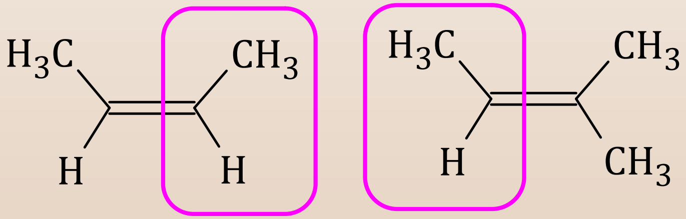
# Alkene Types

Alkenes can be classified as:

Symmetric – where alkene has equal number of carbons on the double bond and



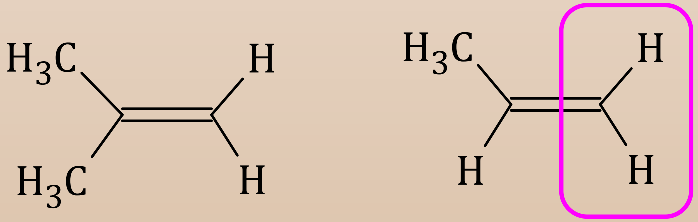
Asymmetric - where one carbon of the double bond has less



---

Alkenes can also be classified as:

Terminal – where alkene is on the first or last two carbons. These alkenes will usually have two hydrogens on one carbon.

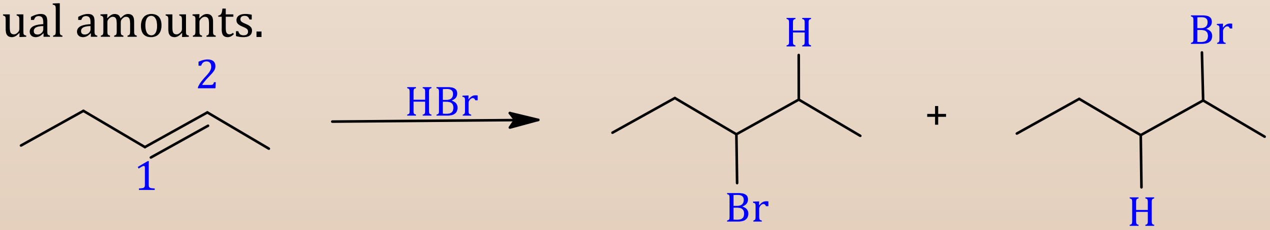


Internal - where double bond is within the chain. The double bond can be symmetric or asymmetric.

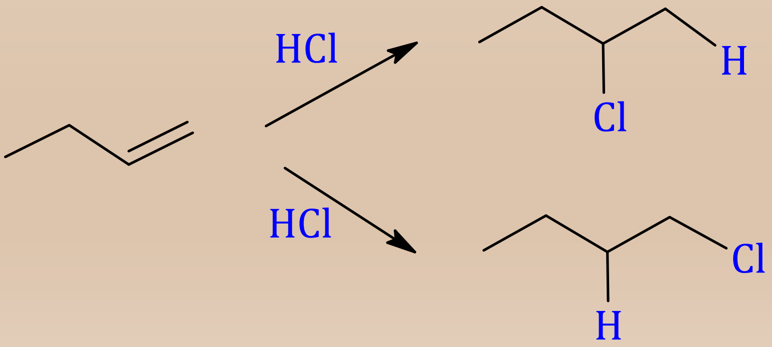
# Hydrohalogenation

Addition of HX to an alkene will lead to formation of an alkyl halide by adding H and X to the alkene. Hydrogen halide, HX, is generally in aqueous form, a haloacid, hydrochloric acid, hydrobromic acid etc.  This implies that the mechanism is acidic which means the mechanism is via carbocation intermediate.

**Symmetric alkene**. In addition to a symmetric alkene both products will form in equal amounts.



In an **asymmetric alkene** addition of any reagent with hydrogen in it, the H will go to the carbon with more H. (***Markovnikov's rule***).



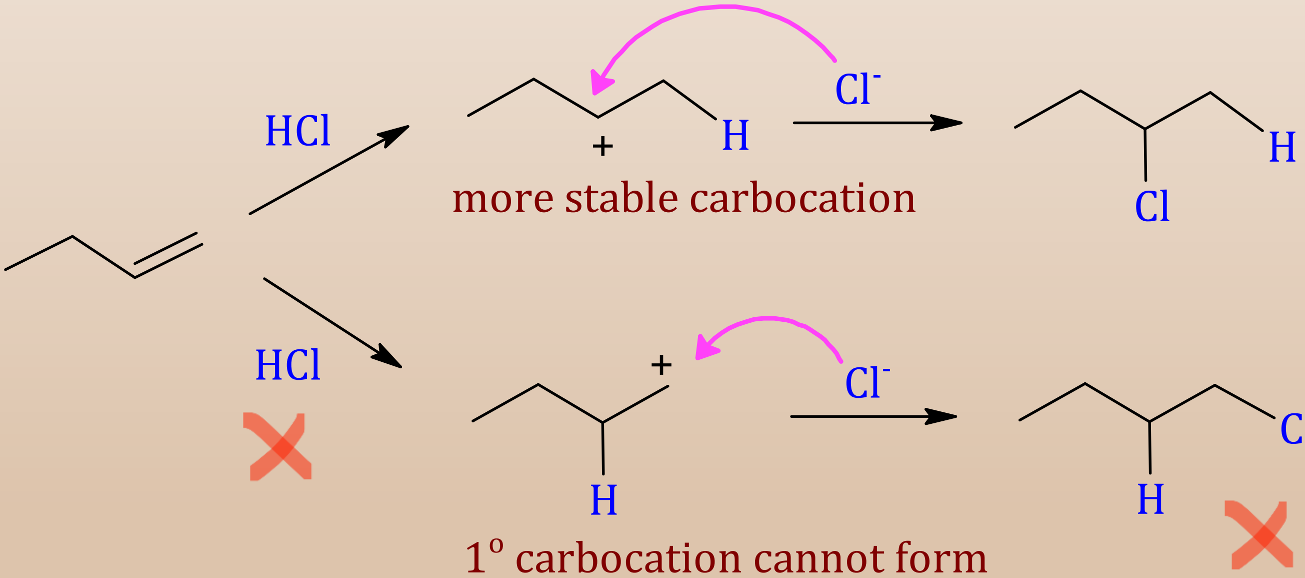
***Markovnikov's Product – only product***

***Anti-Markovnikov's Product – does not form***

# Hydrohalogenation - Mechanism

This rule was later understood when mechanism of reactions were established.

- During the first step a carbocation is formed – the more stable carbocation is preferred which leads to the ***Markovnikov's product*** being the main product.



more stable carbocation

***Markovnikov's Product – only product***

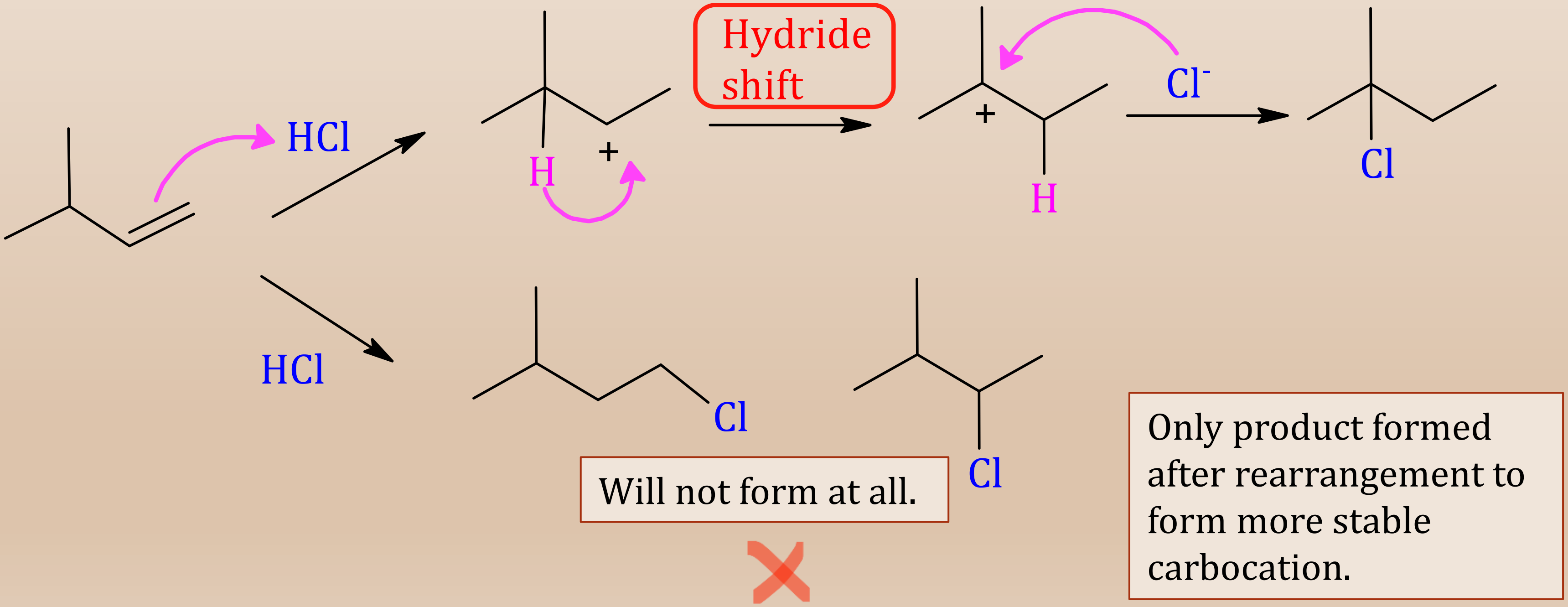
$1^o$ carbocation cannot form

***Anti-Markovnikov's Product – does not form***

# Rearrangement During Addition

As in any carbocation mechanism, the carbocation intermediate will undergo structural rearrangements to make carbocations more stable.

- Remember shifts are only 1,2 shifts of H, $CH_3$ or Ph. Only one shift occurs.
- Note: You don't have to write "Hydride shift" on the arrow. I am just writing it in case you wonder what I am doing.



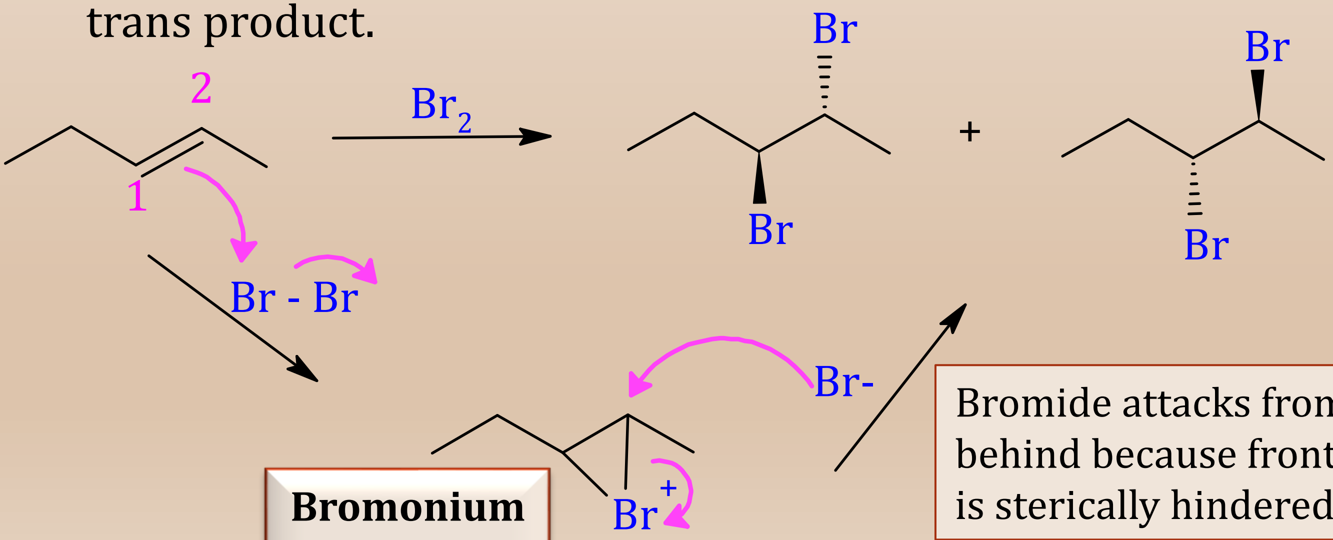
Will not form at all.

Only product formed after rearrangement to form more stable carbocation.

# Halogenation

Bromine ($Br_2$) and chlorine ($Cl_2$) add to alkenes to give 1,2-dihaldes. $F_2$ is too reactive and $I_2$ does not add in this type of reaction.

- There is no electrophile/nucleophile in $Cl_2$/$Br_2$ , they react as $Cl^+$ $Cl^-$ or $Br^+$ $Br^-$.
- $Br_2$ addition is accompanied by a color change because bromine is a brown-red liquid which disappears as it is added to the alkene. This is what it leads to being a good ***QUALITATIVE TEST***.
- ***Addition is ANTI (TRANS)*** as shown in the mechanism below. After the addition of the first bromine, a bromonium ion is formed. The bromide ion reacts with the 2nd carbon from behind since the front part is sterically hindered, giving a trans product.



**<u>Anti addition</u>**
Enantiomers are formed.

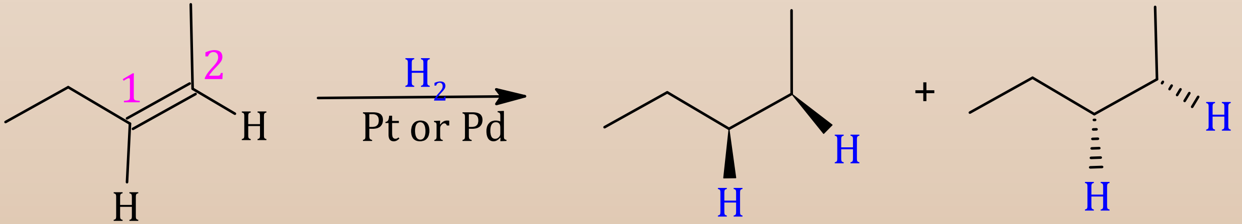
Bromide attacks from behind because front is sterically hindered.

**Bromonium ion.**

# Hydrogenation

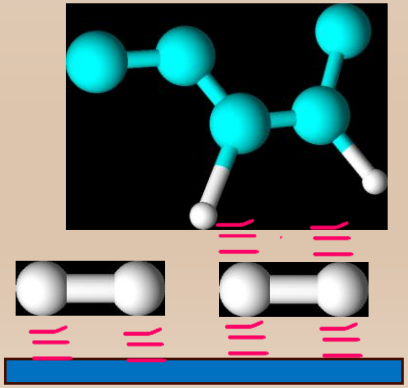
Addition of $H_2$/H-H across the double bond to give a 1,2-addition. This reaction is a reduction reaction as it is addition of $H_2$.

- This reaction requires a heavy metal, Pt, Pd or Ni as powdered (heterogeneous) catalyst. This is because hydrogen is a light gas and it is hard to get it in the correct orientation with respect to the alkene. The heavy metal adsorbs (surface property) the hydrogen for reaction. The metal is released at the end of the reaction.
- Since the hydrogen is adding from the same side, the ***addition is SYN.***

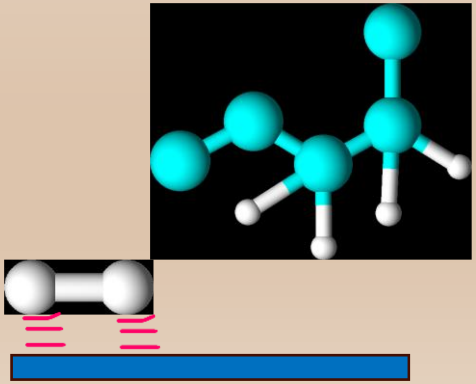


**Syn addition**
Enantiomers are formed.

$H_2$

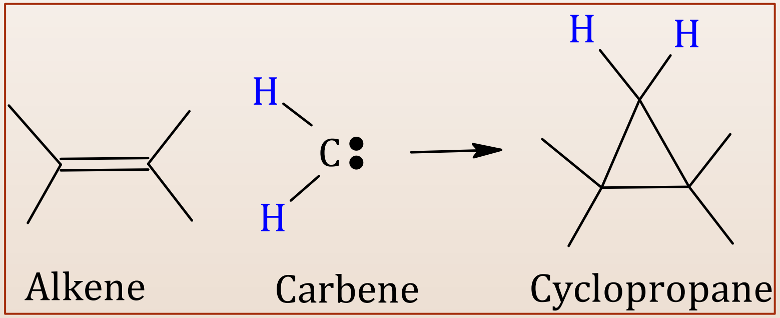


*The red lines show adsorption on the metal surface (blue).*

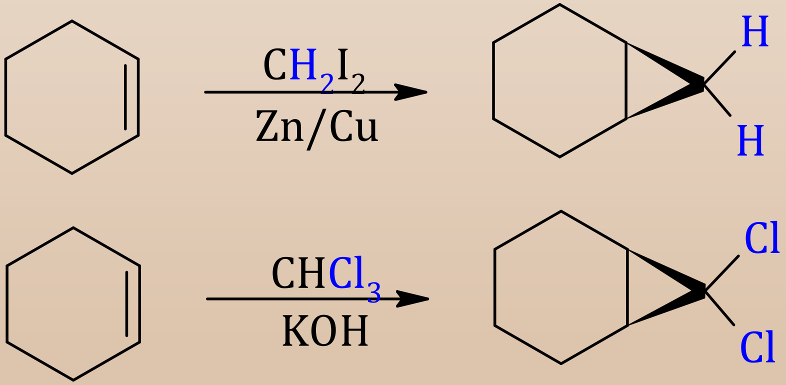


# Reaction with Carbene

**Carbene** is and intermediate that looks like "half of an alkene", hence the lone pair of electrons on the carbon.



- Carbenes are electronically neutral with six electrons in the outer shell ($CH_2$:).
- They add symmetrically across double bonds to form cyclopropanes. The product will be a syn addition and a pair of enantiomers will be formed.
- Another way to generate carbene is the Simmons-Smith reaction which is using a haloalkane with metals. A good way to add two halogens in the cyclopropane ring is to use chloroform with a strong base.



# Key Words/Concepts

- Electrophilic addition
- Markovnikov's addition
- Syn addition
- Anti addition
- Hydrohalogenation
- Halogenation
- Hydrogenation
- Carbene

*NOTE: All qualitative tests will be given in the last power point of this chapter.*