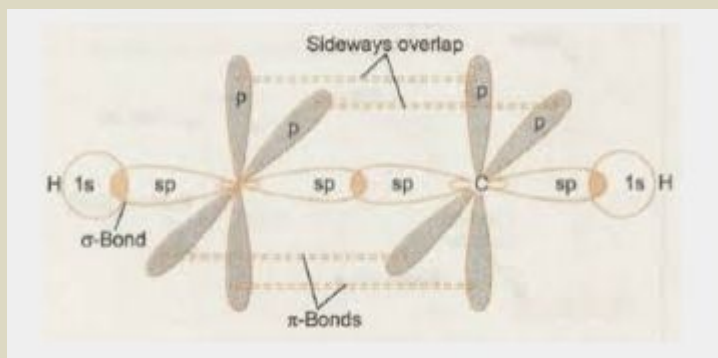
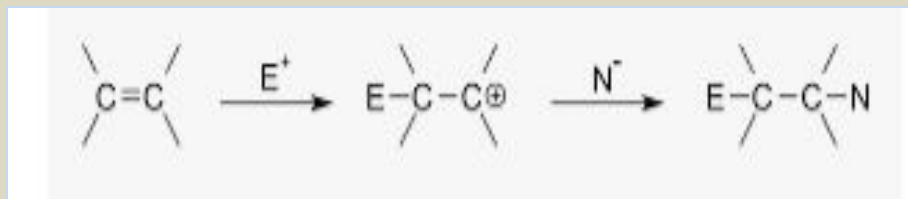


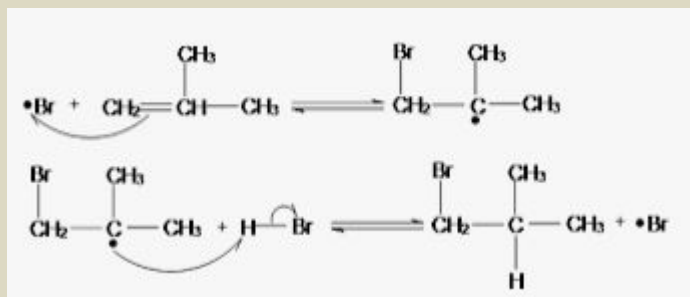
## *Addition Reactions Of Carbon Carbon Multiple Bond - Hydrogenation, Halogenation, Hydrohalogenation*



- A C-C multiple bond is composed of a sigma bond and one or two pi bonds. Being weakly held by the two atomic nuclei, a pair of pi electrons are readily available for reaction.
- Usually **addition** is the characteristic reaction of a pi bond. Ions and free radicals may add across a multiple bond, accordingly the additions are said to be a) ionic or polar addition b) radical addition.
- The examples of the above reactions are:
  - a)



- b)



- In the case of an ionic reaction an electrophile or nucleophile (or a positive or negative pole of a dipole) initiates the processes of addition. When a electrophile initiates the process, the reaction is termed as electrophilic addition, whereas a reaction initiated by a nucleophile (or a negative pole of a dipole) is said to be a nucleophilic addition reaction. An addition reaction to a c-c multiple bond may take place in two separate steps or in a single step.
- **Electrophilic addition to  $C=C$  :**

Two double bonded carbon atoms and four other atoms bonded to the carbons of c-c moiety lie in a plane. The pi orbital, with its weakly held electron pair remains perpendicular to the plane, one lobe of the pi orbital lies above the plane and the other below it. Thus the two double bonded carbon atoms become sandwiched between negative charge clouds, these in their turn, shield the carbon atoms from attack by nucleophiles and make them react readily with electrophiles.

- Electrophilic addition to the double bond is the most common type of reactions which this functional group undergoes. Electrophilic addition to a  $C=C$  usually occurs in two steps:

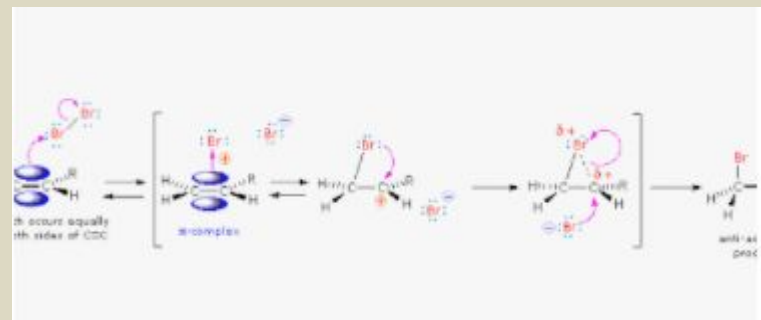
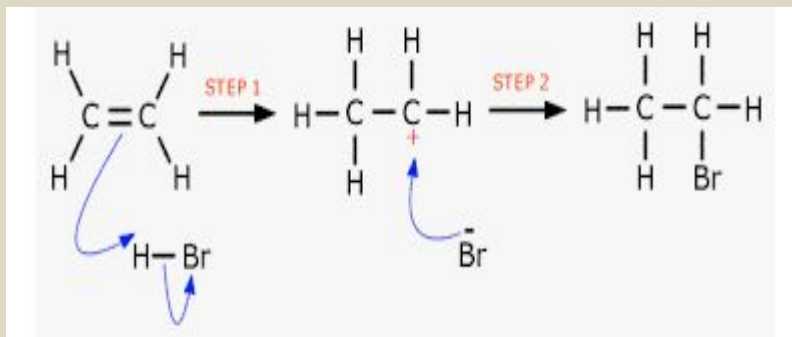
### Step 1:

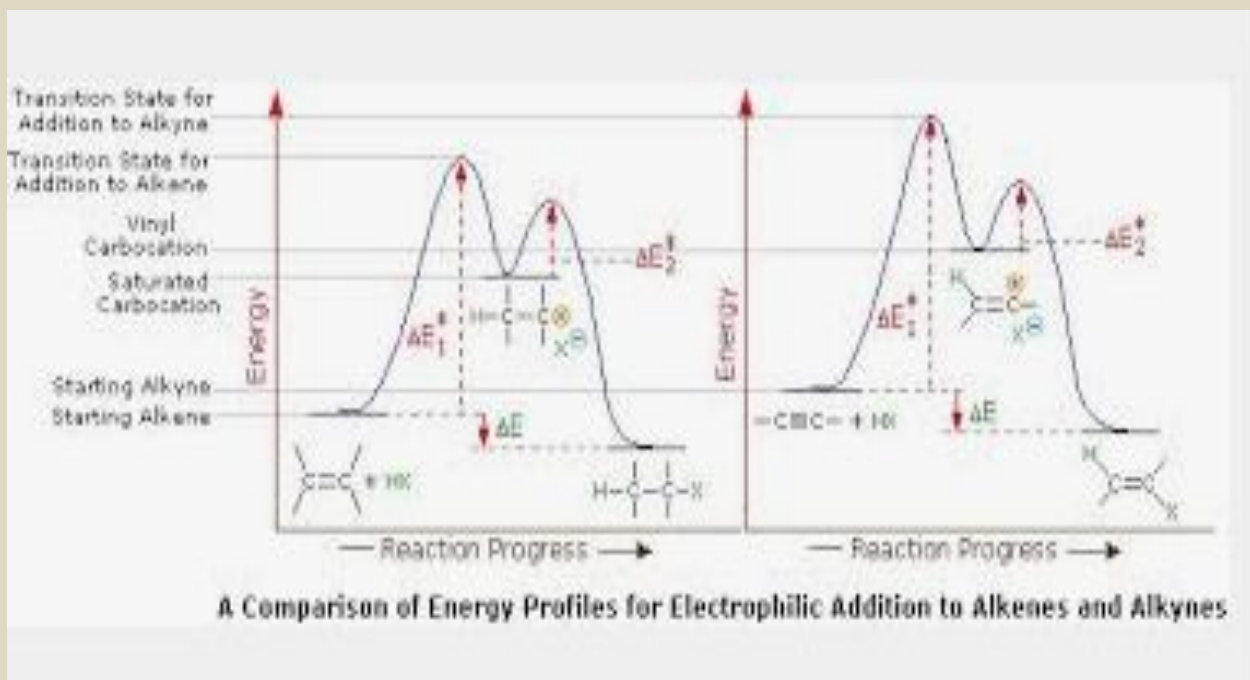
The incoming electrophile with its vacant orbital attacks the pi cloud in a perpendicular direction from above or below the plane to form pi-complex. If the electrophile possesses a lone pair of nonbonded electrons, then a three membered cyclic cation results.

This step is slow step and hence this is the rate determining step.

### Step 2:

In this step the intermediate, the carbeneum ion or the three membered cyclic cation, combines with a nucleophile to produce the addition product. It is a fast step.





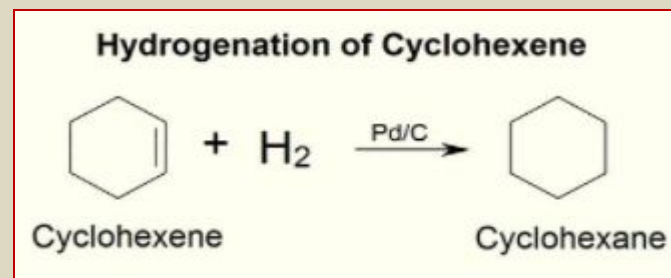
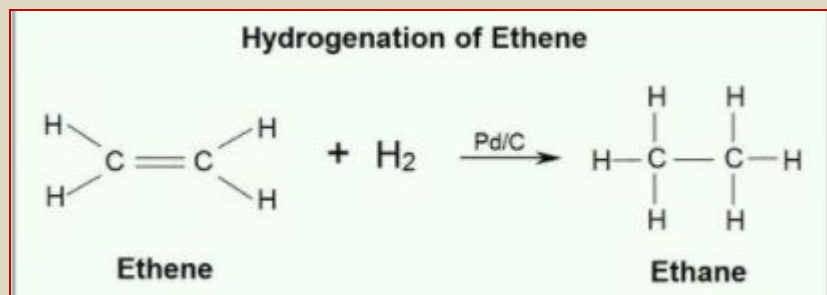
Since step 1, the electrophilic addition to c-c double bond is the slow step and the T.S of this step involves both the substrate and the reagent, the electrophile, the reaction is expected to follow the second order kinetics.

$$\text{The rate} = K[\text{substrate}][\text{reagent}]$$

## •Hydrogenation of alkene:

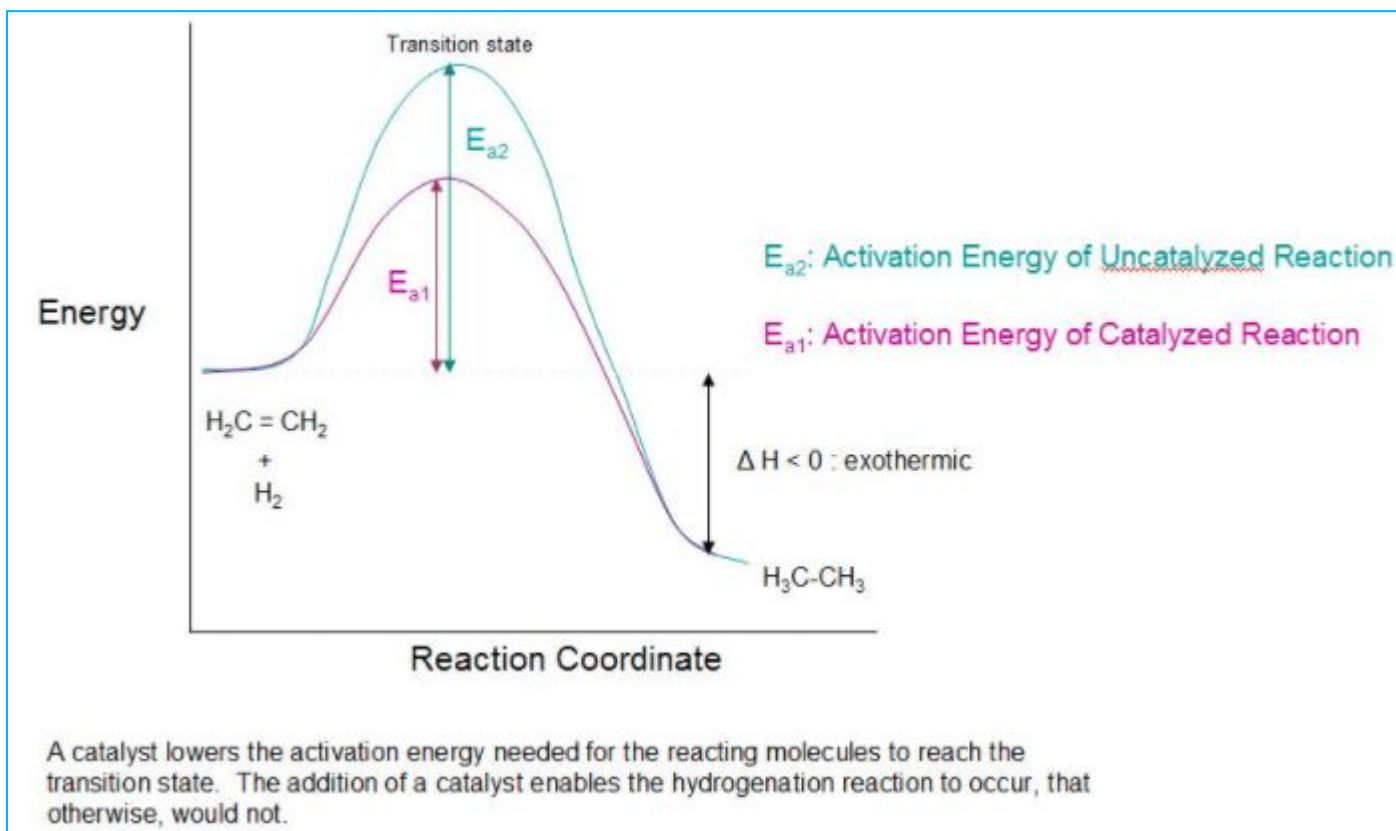
Addition

of hydrogen to a carbon-carbon double bond is called hydrogenation. This is an example of addition reaction of alkene. **Two hydrogen atoms are added across the double bond of an alkene**, resulting in a saturated alkane. Hydrogenation of a double bond is a thermodynamically favorable reaction because it forms a more stable (lower energy) product. In other words, the energy of the product is lower than the energy of the reactant; thus it is exothermic (heat is released). The heat released is called the heat of hydrogenation, which is an indicator of a molecule's stability.

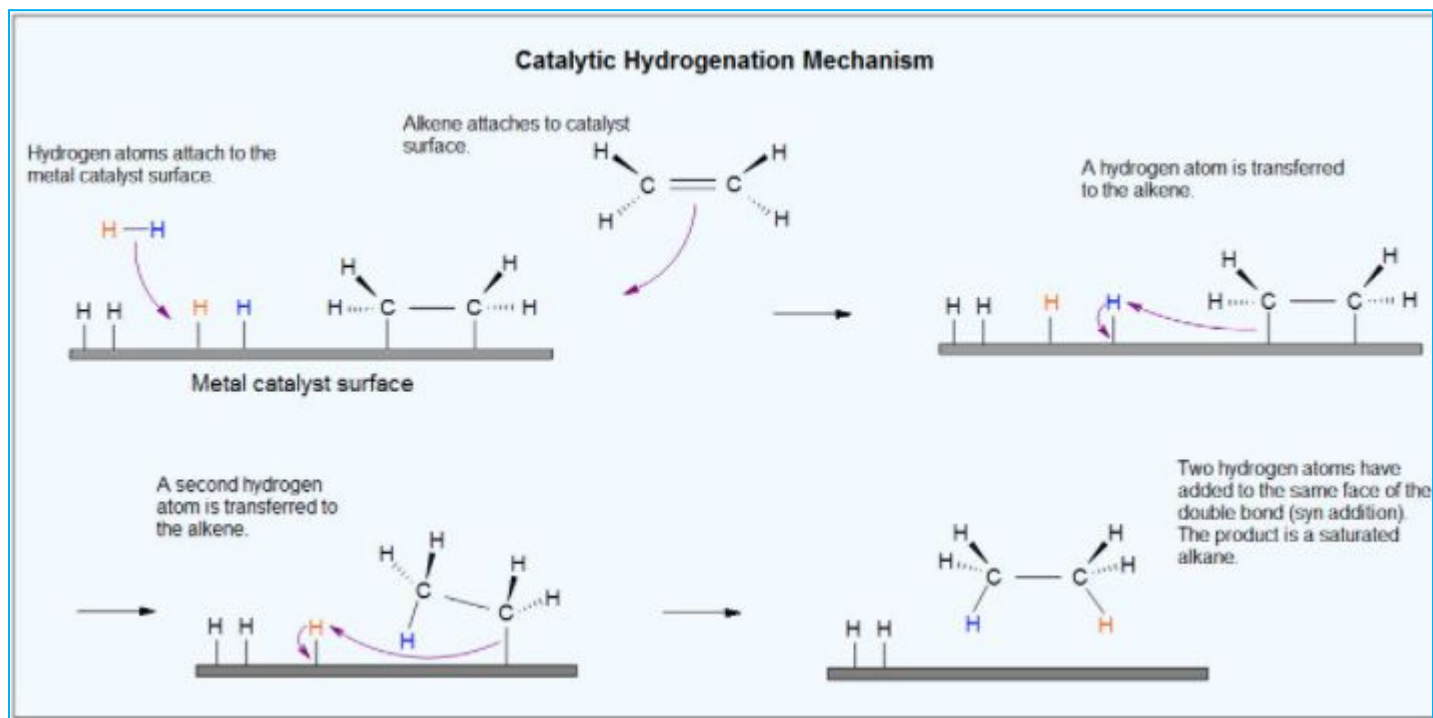


•Although the overall hydrogenation reaction is exothermic, high activation energy prevents it from taking place under normal conditions. This restriction may be circumvented by the use of a catalyst. The most commonly used metal catalysts are nickel, palladium and platinum.

# Energy profile diagram of hydrogenation of alkene



# Mechanism of catalytic hydrogenation

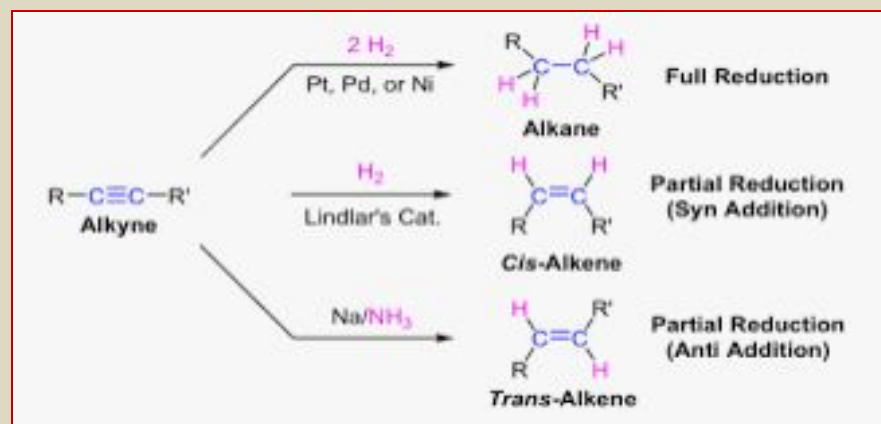




- **Hydrogenation of alkyne :**

Alkynes can be fully hydrogenated into alkanes with the help of a platinum catalyst. However, the use of two other catalysts can be used to hydrogenate alkynes to alkanes. These catalysts are:

Palladium dispersed on carbon (Pd/C) and finely dispersed nickel (Raney-Ni).



- Partial reduction of alkynes with Lindlar's catalyst gives *Cis*-alkene through syn addition and partial reduction of alkynes with sodium/liquid ammonia gives *Trans*-alkene through trans addition.

- **Halogenation of alkene:**

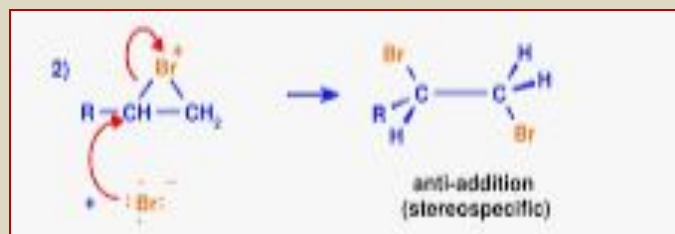
Halogens (chlorine and bromine) combine with alkenes to form vicinal dihalides. The reaction may occur in the absence of light and becomes rapid in the presence of Lewis acids. This fact led to the conclusion that reaction occurs by an ionic mechanism. Studies have shown that ionic mechanism of addition to alkenes follows the course of electrophilic addition reaction.

The most familiar of the addition reactions is the addition reaction of bromine in carbon tetrachloride or acetic acid to C-C multiple bonds. In this reaction decolourisation of bromine occurs without evolution of hydrogen bromide and thus constitutes a classical test for unsaturation. A two step mechanism involving a three membered cyclic bromonium ion as an intermediate has been proposed for bromination (halogenation) of alkene.

- **Step 1:** Electrophilic attack by the reagent (bromine or chlorine) and the formation of cyclic bromonium (or chloronium) ion via a pi-complex.



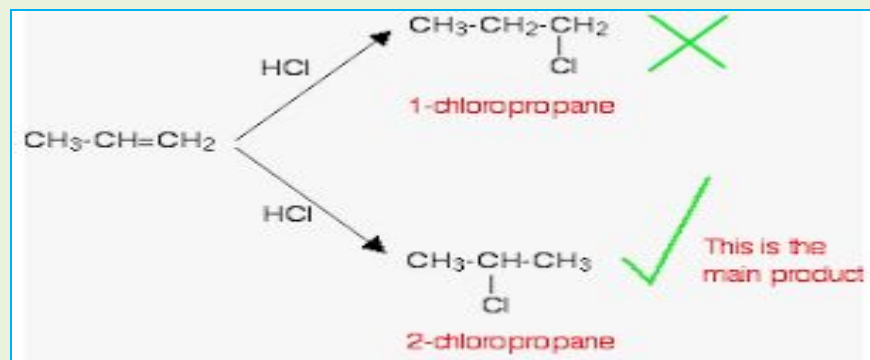
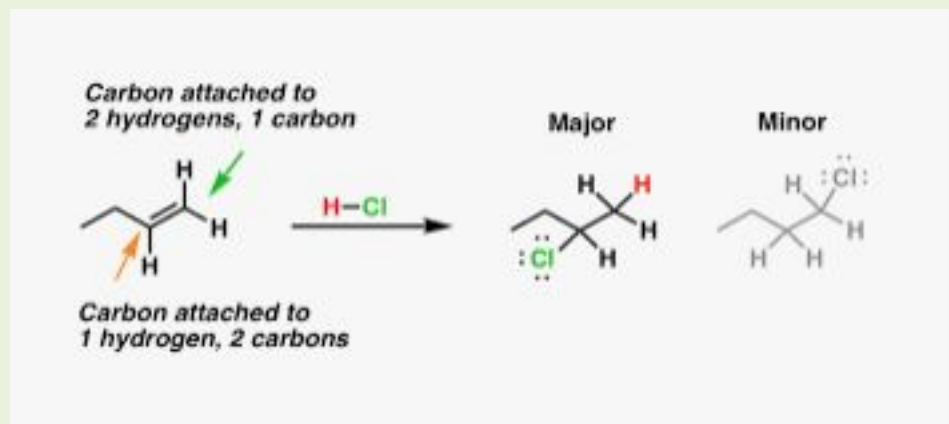
- **Step 2:** Nucleophilic attack by the bromide (chloride) ion from the sterically unhindered position i.e from the opposite side of the ring on either carbon atom to produce trans addition product. Formation of bridged bromonium ion prevents addition of two bromine atoms from the same side, that is cis addition. Lastly ring takes place with the formation of vicinal bromide or chloride. This step is fast. This is an example of a stereospecific reaction.



- It is not normally possible to add fluorine directly to olefinic double bond because the reaction is so exothermic that bond cleavage of the alkenes take place. The electrophilic addition reaction between fluorine and c-c double bond is carried out at a very low temperature and xenonfluoride may be used as a reagent under controlled condition. This is a non stereospecific reaction in which cis addition predominates.
- It has been observed that the addition reaction between an alkene and iodine is a reversible one and the equilibrium lies over the reactant side.

# Hydrohalogenation of alkene :

The hydrohalogenation of alkenes involves **breaking a carbon to carbon double bond, followed by the electrophilic addition of a hydrogen atom and halogen**. The halide will add to the more substituted carbon following Markovnikov's rule. The product is a haloalkane also called an alkyl halide.



## Summary of Hydrohalogenation Mechanism:

- Nucleophilic pi bond reaches for electrophilic H in H-X, pi bond breaks in the process
- H adds to the less substituted carbon atom following Markovnikov's rule
- More substituted carbon is now deficient getting a formal charge of +1
- Negative halide in solution attacks the carbocation forming a bond
- Product is a haloalkane – also known as alkyl halide

## Key Reaction Notes:

- This reaction has a carbocation intermediate and therefore follows Markovnikov's rule
- Look out for carbocation rearrangements
- This reaction must be carried out in an 'inert' solvent
- This reaction is regioselective – halide adds to more substituted carbon

- We have seen that the electrophilic addition of hydrogen halides to alkenes produces alkyl halides according to the Markovnikov's rule: **Alkynes undergo hydrohalogenation following a similar pattern.**

