

Chapter **3**...

**Electrophilic Addition to
>C=C< Bond and -C≡C- Bond**

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(i) Addition of Hydrogen

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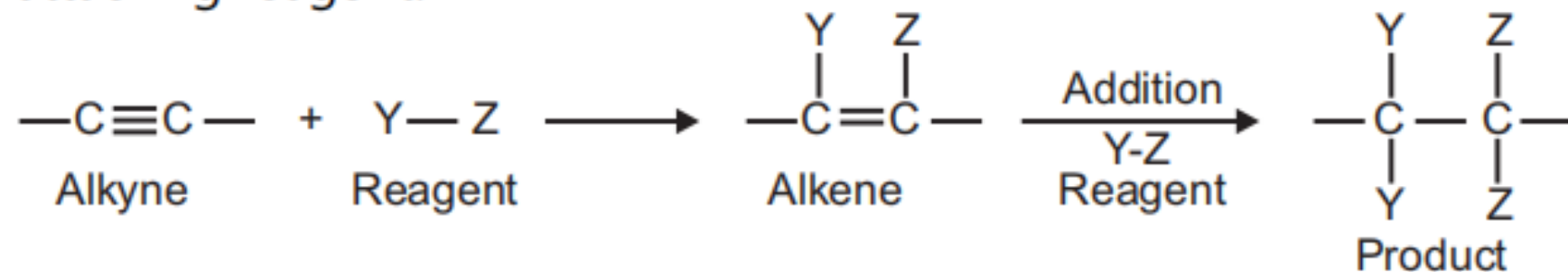
3.3 Formation of Metal Acetylides

- Exercise

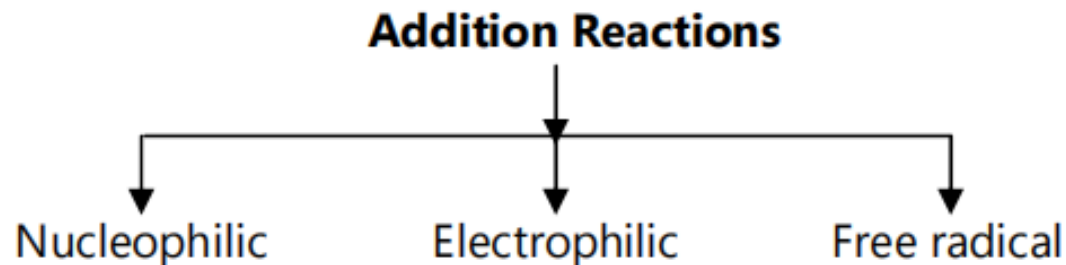
3.1 Addition to Carbon-Carbon Double Bond (>C = C<)

3.1.1 Introduction

A reaction in which two molecules combine to yield a single molecule of product is called as addition reaction. In this reaction the product contains all the atoms of the substrate as well as that of the attacking reagent.



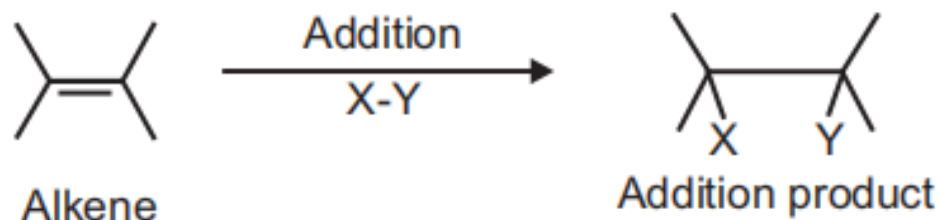
Due to addition reaction the unsaturated compound is converted into saturated compounds (change in hybridization from $sp \rightarrow sp^2 \rightarrow sp^3$).



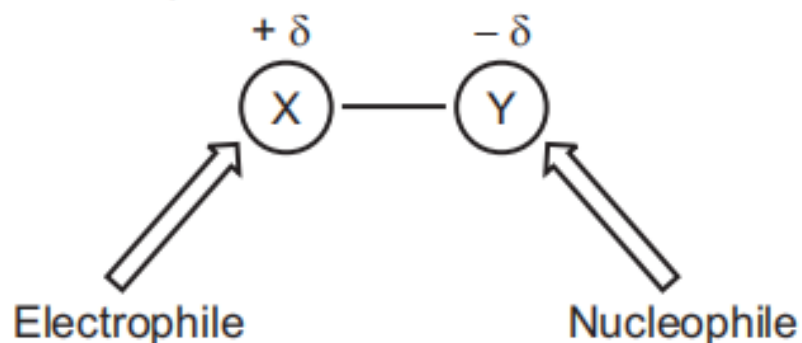
In this chapter, we will consider electrophilic addition reactions.

3.1.3 Mechanism of Electrophilic Addition to $>C=C<$ Bond

The general reaction of addition on $C=C$ bond is as follows.



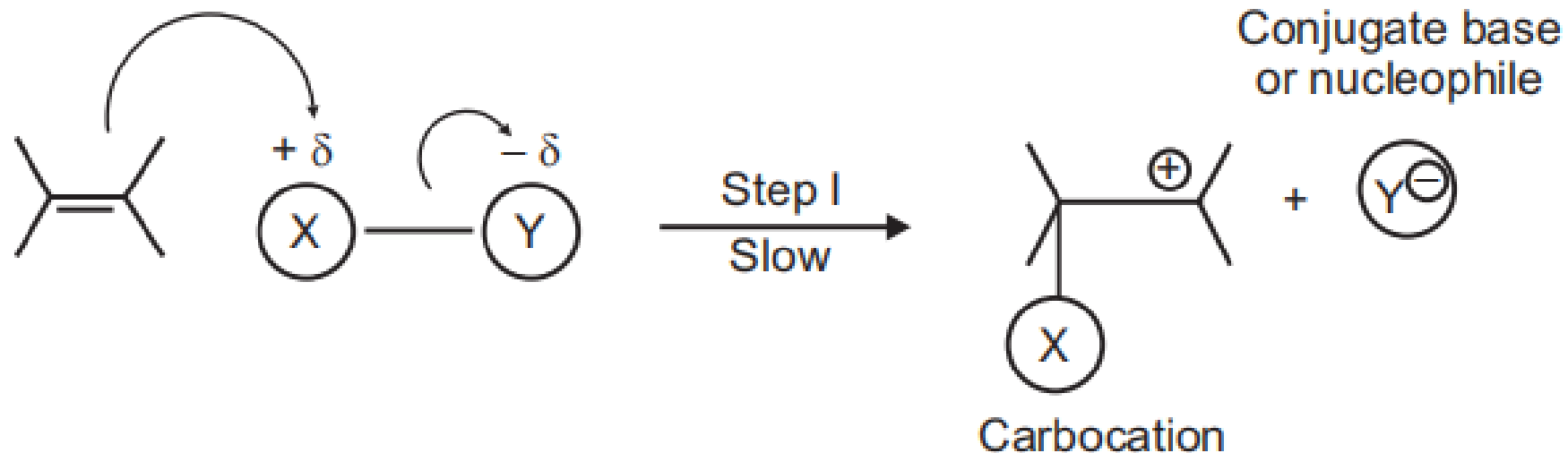
Consider Y is more electronegative (hence electron rich) than X (hence electron deficient).



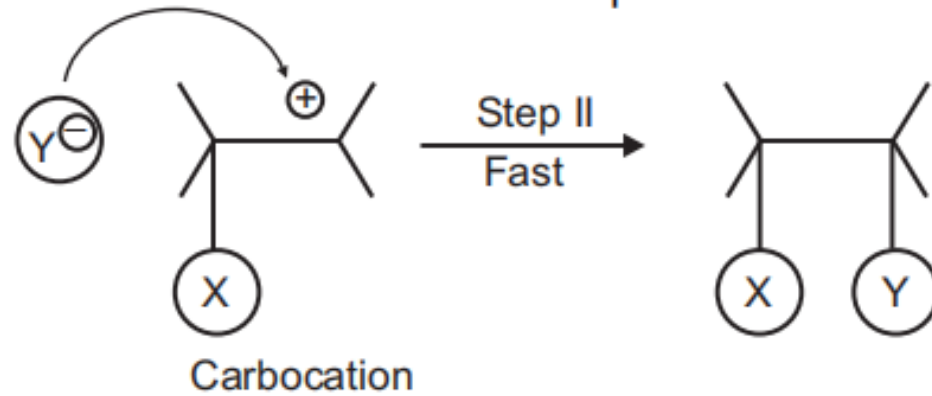
The mechanism of electrophilic addition to $C=C$ bond involves following two steps :

- (1) Formation of carbocation.
- (2) Attachment of base to carbocation.

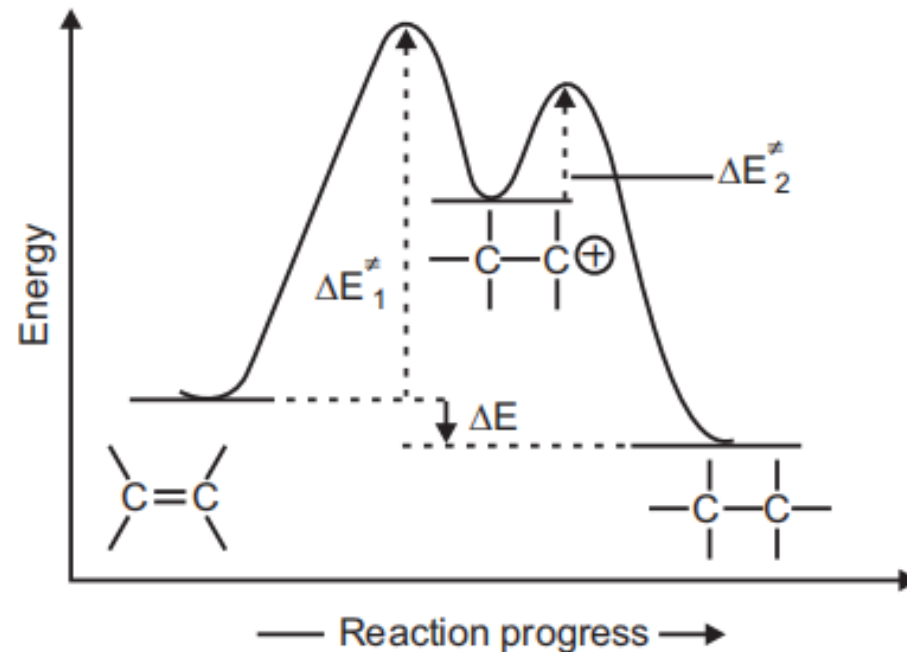
(1) Step I : Formation of carbocation : This is the slow step which involves the addition of the electrophile ($X^+ = H^+$) to the C=C bond. The π electrons of the alkene (C=C bond) attack the H^+ forming the C-H bond and leave the +ve charge on the other carbon to form a carbocation.



(2) Step II : Attachment of base to carbocation : This step is the fast step which involves the attack of the conjugate base to the carbocation to form the desired addition product.



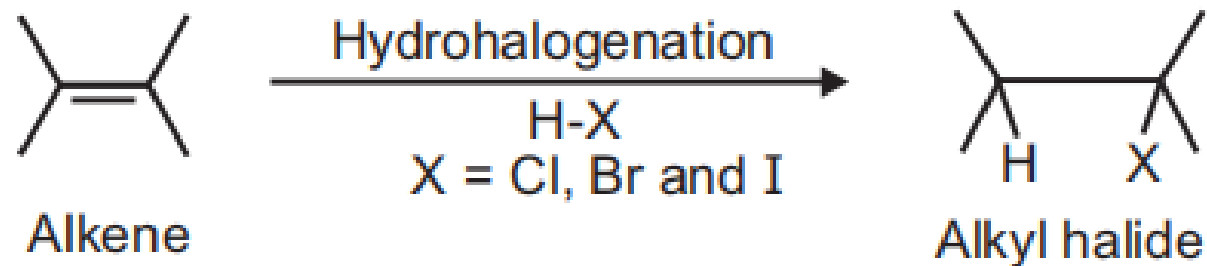
The energy profile diagram for the above reaction mechanism is shown below.



3.1.4 Addition of Hydrogen Halide (Hydrohalogenation)

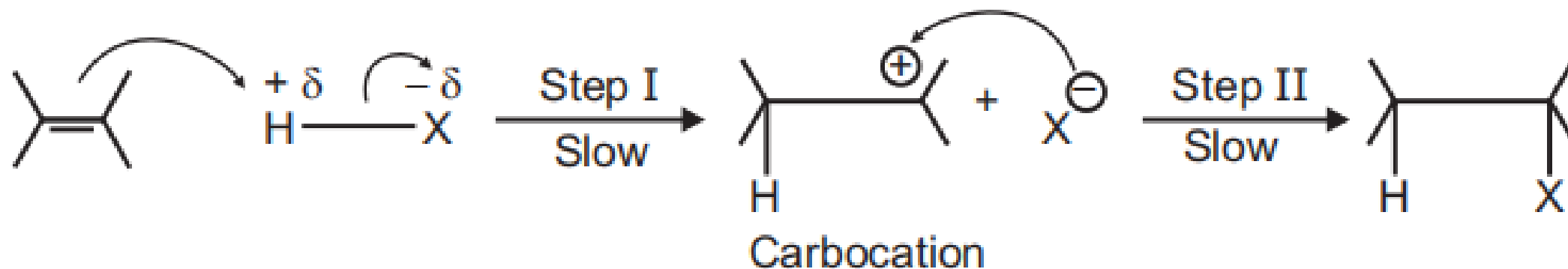
1. Reaction :

The addition of hydrogen halide (HX ; HCl, HBr and HI) across C=C bond to form alkyl halide is called as hydrohalogenation.



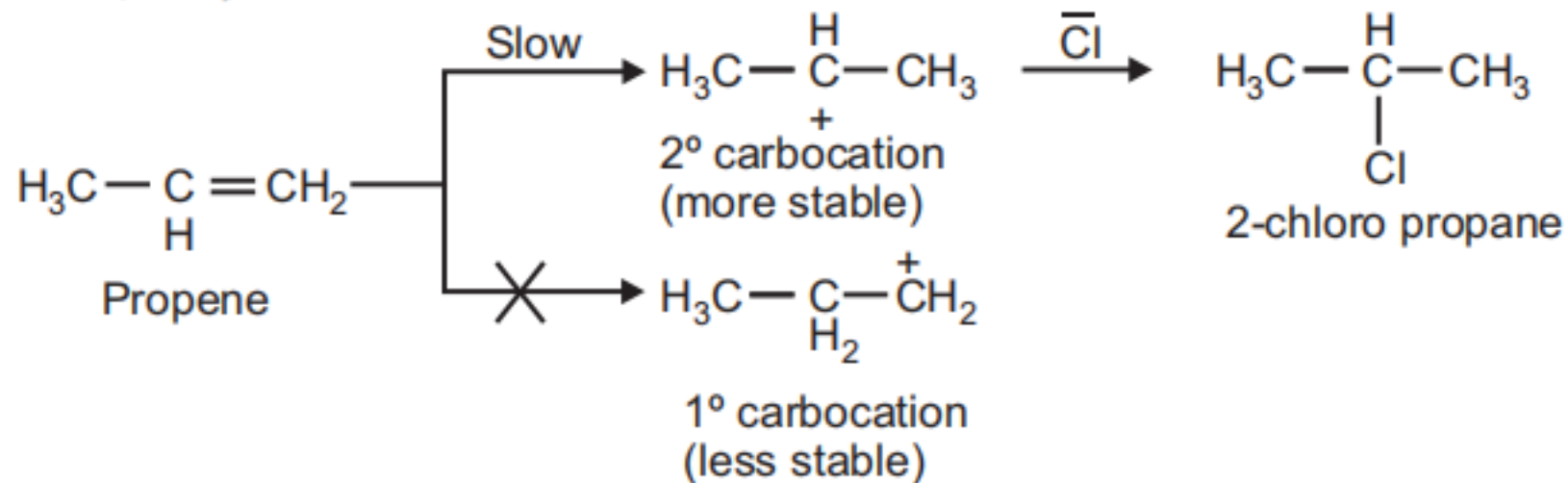
2. Mechanism :

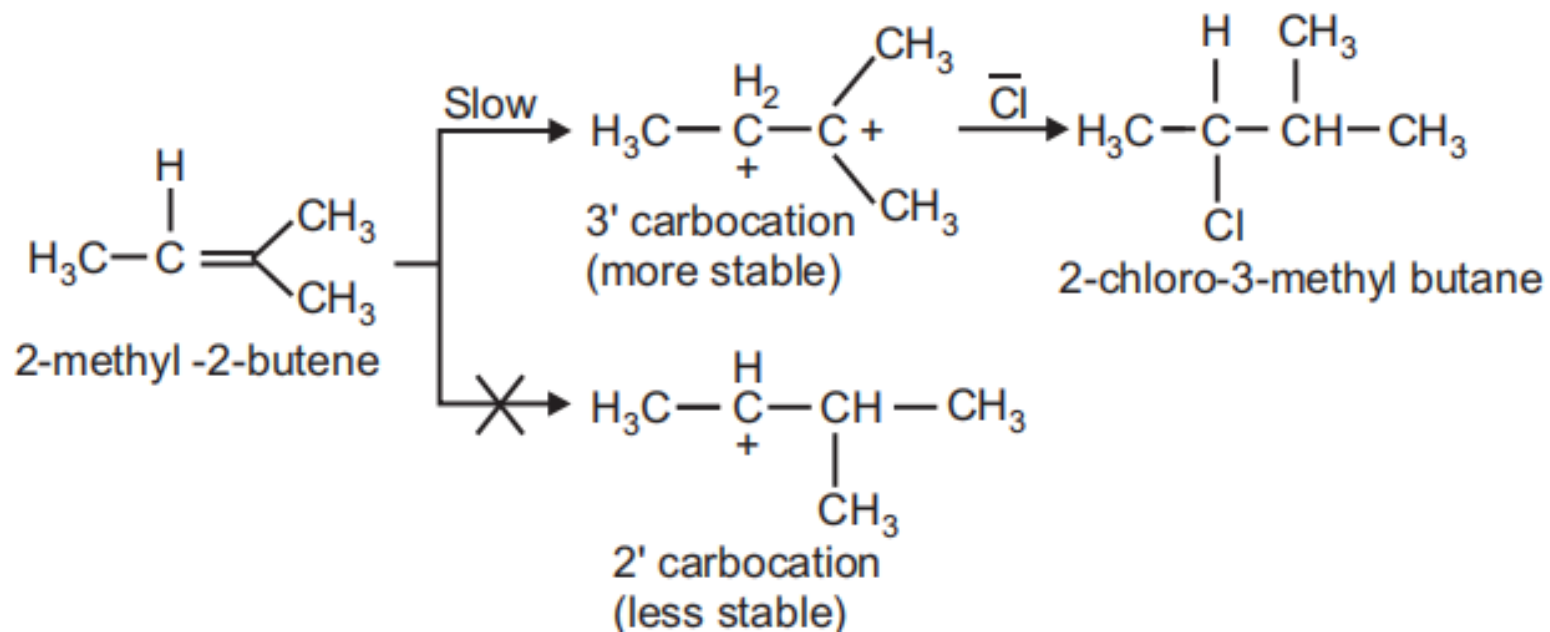
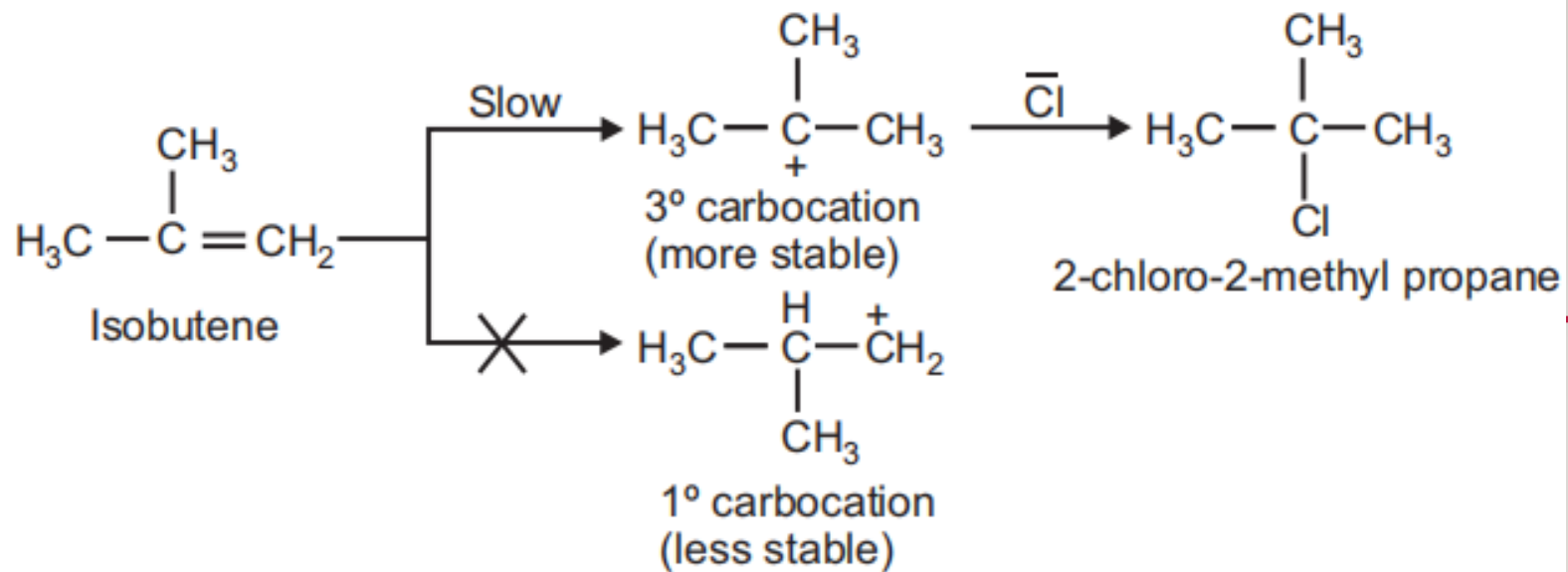
The reactions of alkenes with acids like HCl follow Markovnikov's rule: the major product formed is that where the hydrogen adds to the carbon containing the most hydrogens. In this reaction, C=C (π bond) attacks on the H-Cl bond to form an intermediate carbocation, which is then attacked by the chloride ion leading to the formation of the alkyl halide.



3. Orientation and Reactivity (Markovnikoff's rule) :

Regiochemistry : As we saw in the last part, reactions of alkenes with acids like HCl follow Markovnikov's rule: the major product formed is that where the hydrogen adds to the carbon containing the most hydrogens. Only one product is possible for the above reaction. Consider the addition of hydrogen chloride to three typical olefins : propene, isobutene and 2-methyl-2-butene. In accordance to Markovnikov's rule which states that **the negative part of the addendum (reagent) adds to that carbon which has less number of hydrogen atoms**. Hence, propene yields isopropyl chloride, isobutene yields tert-butyl chloride and 2-methyl-2-butene yields tert-pentyl chloride.

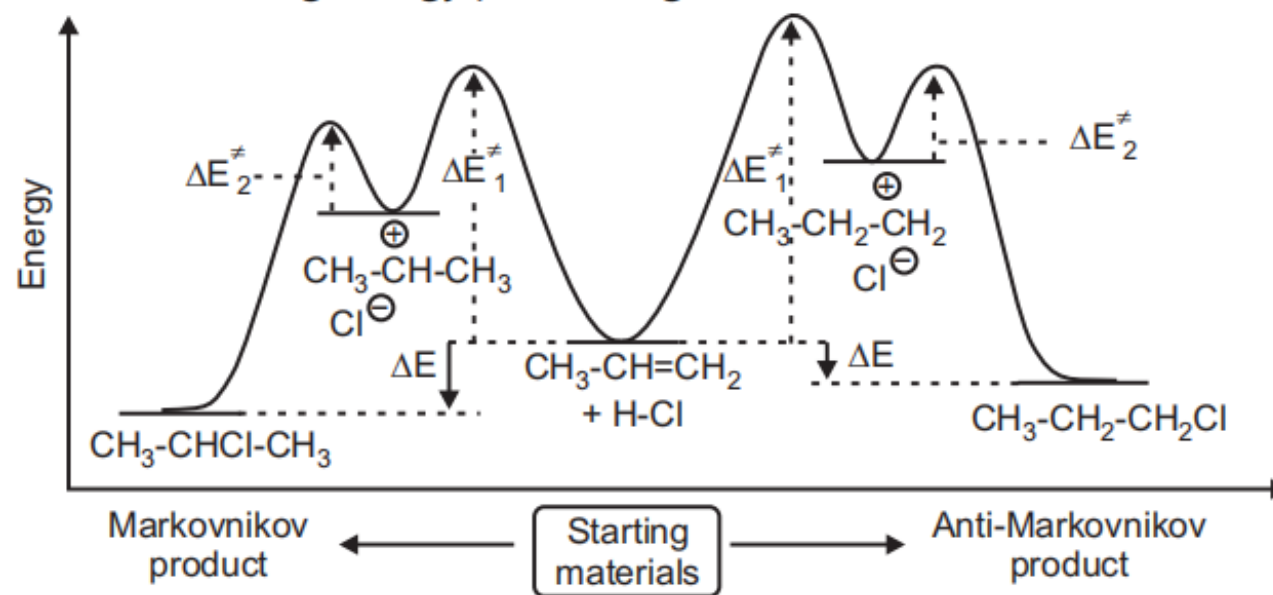




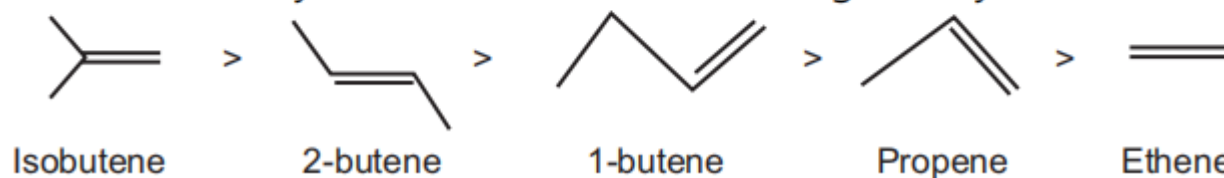
The stability of carbocation : $3^\circ > 2^\circ > 1^\circ > \text{CH}_3^+$

Thus the more stable carbocation gave main product of the reaction by reacting with Cl^- .

The following energy profile diagram summarizes these features.



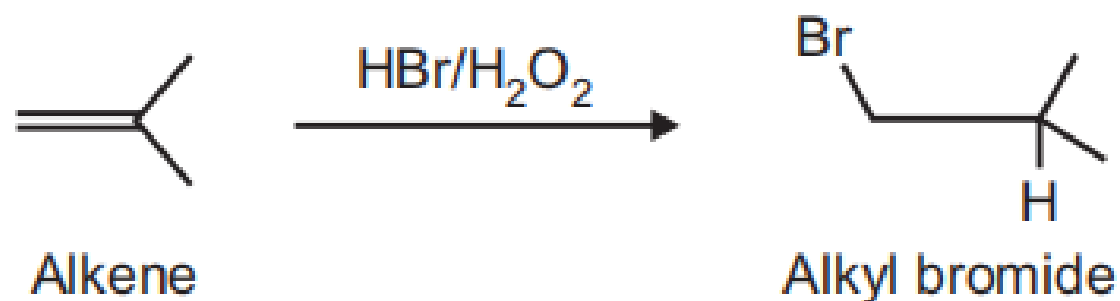
Thus the rate of addition of hydrogen ion to double bond depends on the stability of the carbocation being formed. This factor determines not only the **orientation** of an addition to a single alkene but also the **relative reactivities** of different alkenes. Following the order of reactivity towards addition of acids is generally observed.



4. Anti-Markovnikoff's Addition (Peroxide Effect) :

When HBr adds to an unsymmetrical alkene in the presence of peroxide, light or other free radicals, the direction of addition is exactly reversed as compared to the Markovnikov's rule. This effect is called **peroxide** or **Kharasch effect**.

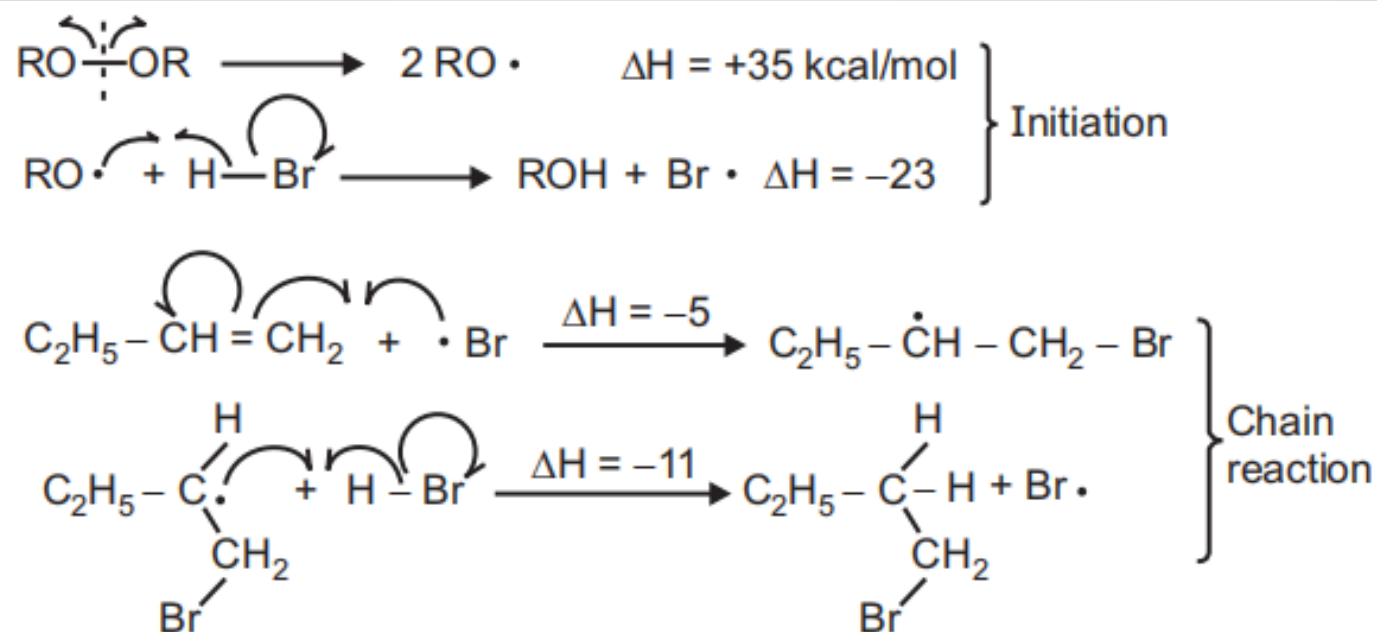
Here the halogen adds to the less substituted carbon instead of the more substituted one, as is normally the case in Markovnikov's reactions.



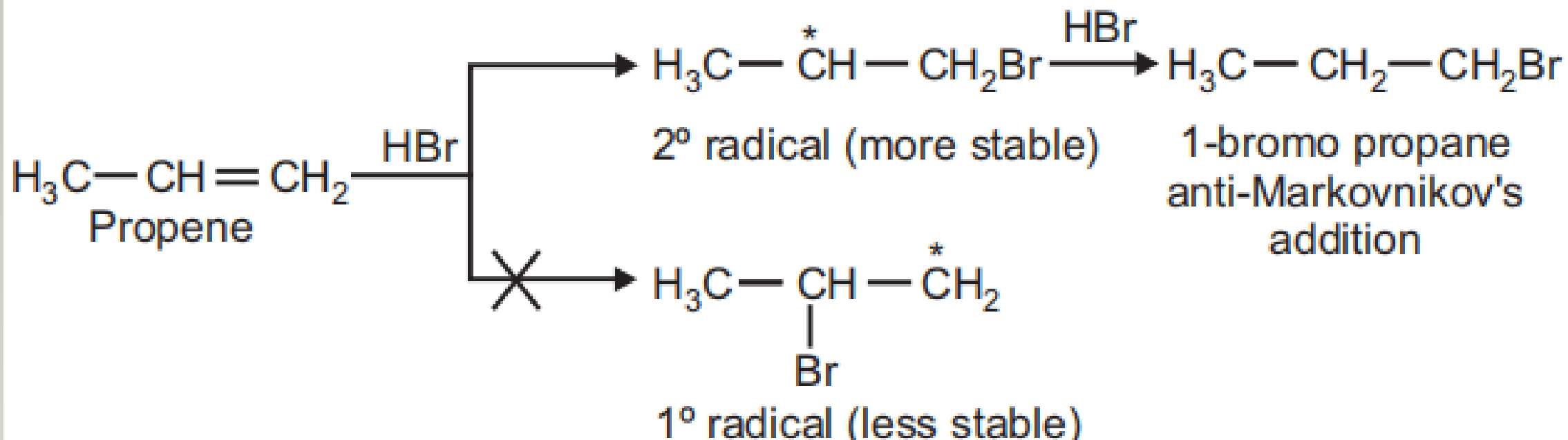
Step-I : Initiation: Decomposition of the peroxide yields free radical. The free radical abstracts hydrogen from HBr to form a bromine atom.

Step-II : Propagation : In this step, the bromine atom attaches to one of the doubly bonded carbons; in doing so it uses its odd electron and one of the π -electrons. The other carbon atom is left with an odd electron and the alkene in turn is converted to a free radical. The free radical then abstracts hydrogen from HBr. Addition is now complete and a new bromine atom is generated to continue the chain reaction.

Step-III : Termination : In this the radicals combine to create waste products. For example, two bromine radicals combine to give bromine.



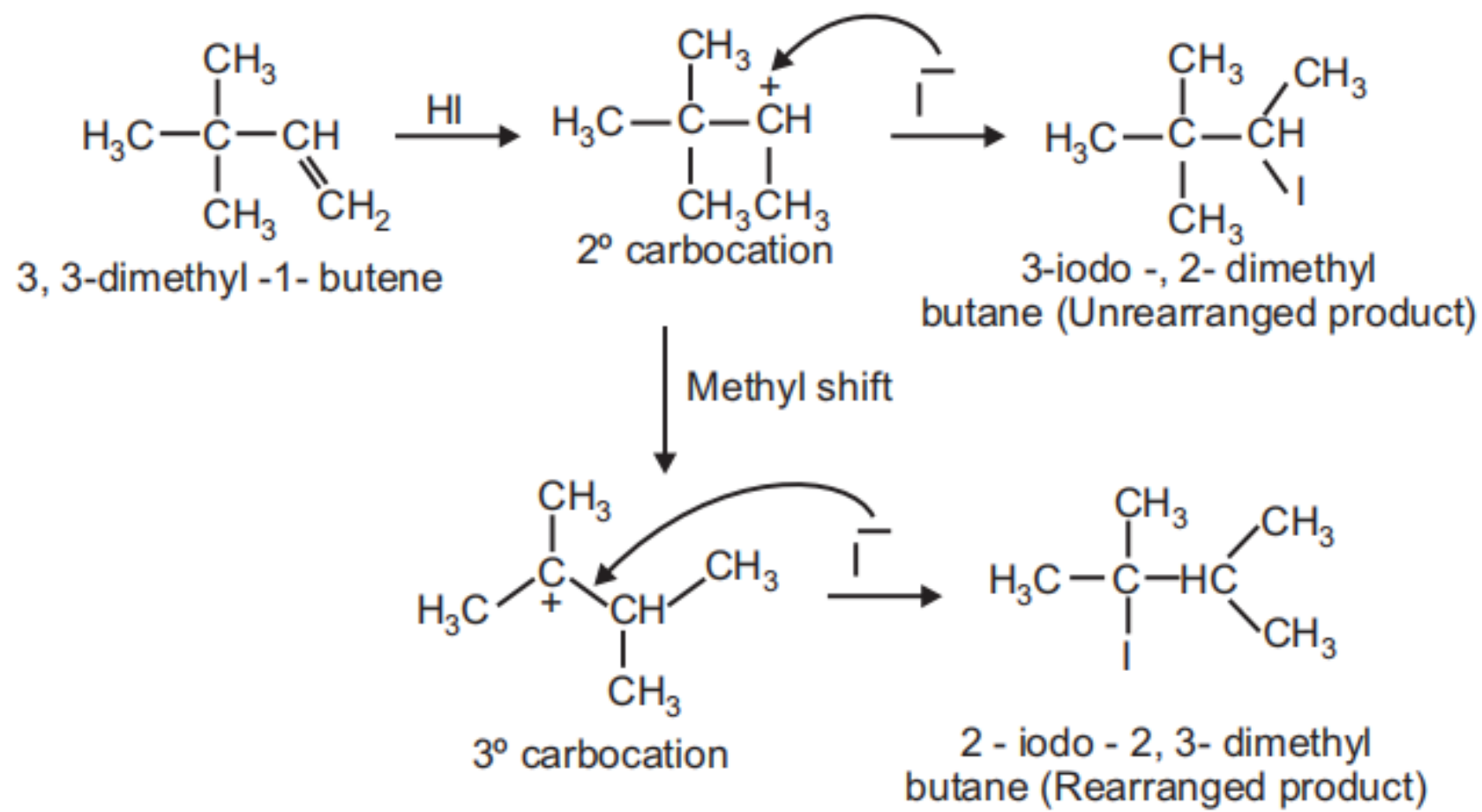
Example :



Note : *HCl and HI do not show peroxide effect as chloride radical is too reactive, while iodide radical formation is too sluggish. They add according to Markovnikov's rule.*

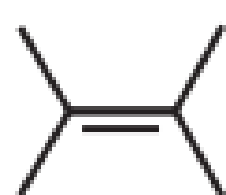
5. Rearrangements (Support for formation of carbocation) :

When the structure permits the electrophilic addition, reaction is accompanied by rearrangements. These rearrangements follow the same pattern as that of the carbocations in S_N1 reactions. For example, addition of HI to 3, 3-dimethyl-1-butene yields not only the expected 3-iodo-2, 2-dimethyl butane but also 2-iodo-2, 3-dimethyl butane.

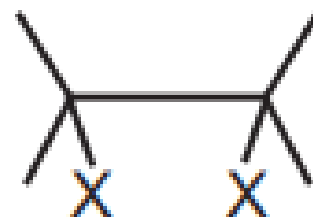
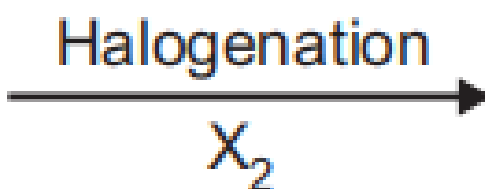


3.1.5 Addition of Halogen (Halogenation)

Reaction : Halogens undergo electrophilic addition with C=C bond to form vicinal dihalides (1,2-dihaloalkane). Bromine and chlorine in the presence of CCl_4 add to double bonds to give vicinal dibromo or dichloro derivatives, iodine however, fails to react.



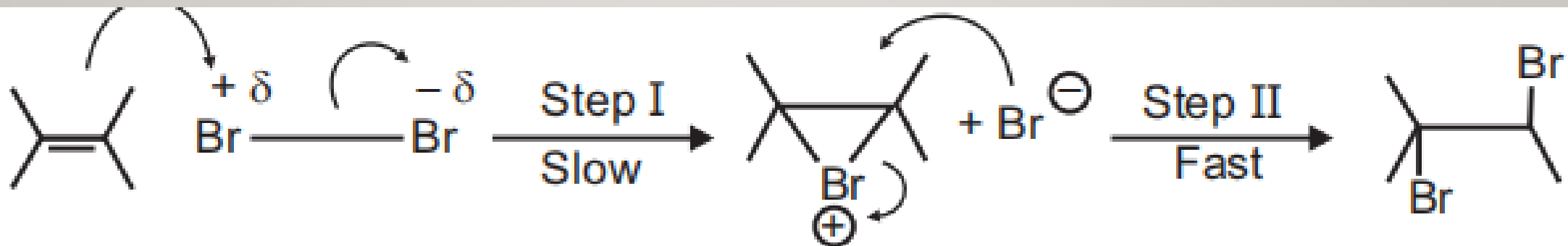
Alkene



Vicinal
1, 2-Dihaloalkane

X = Cl: Chlorination

X = Br: Bromination



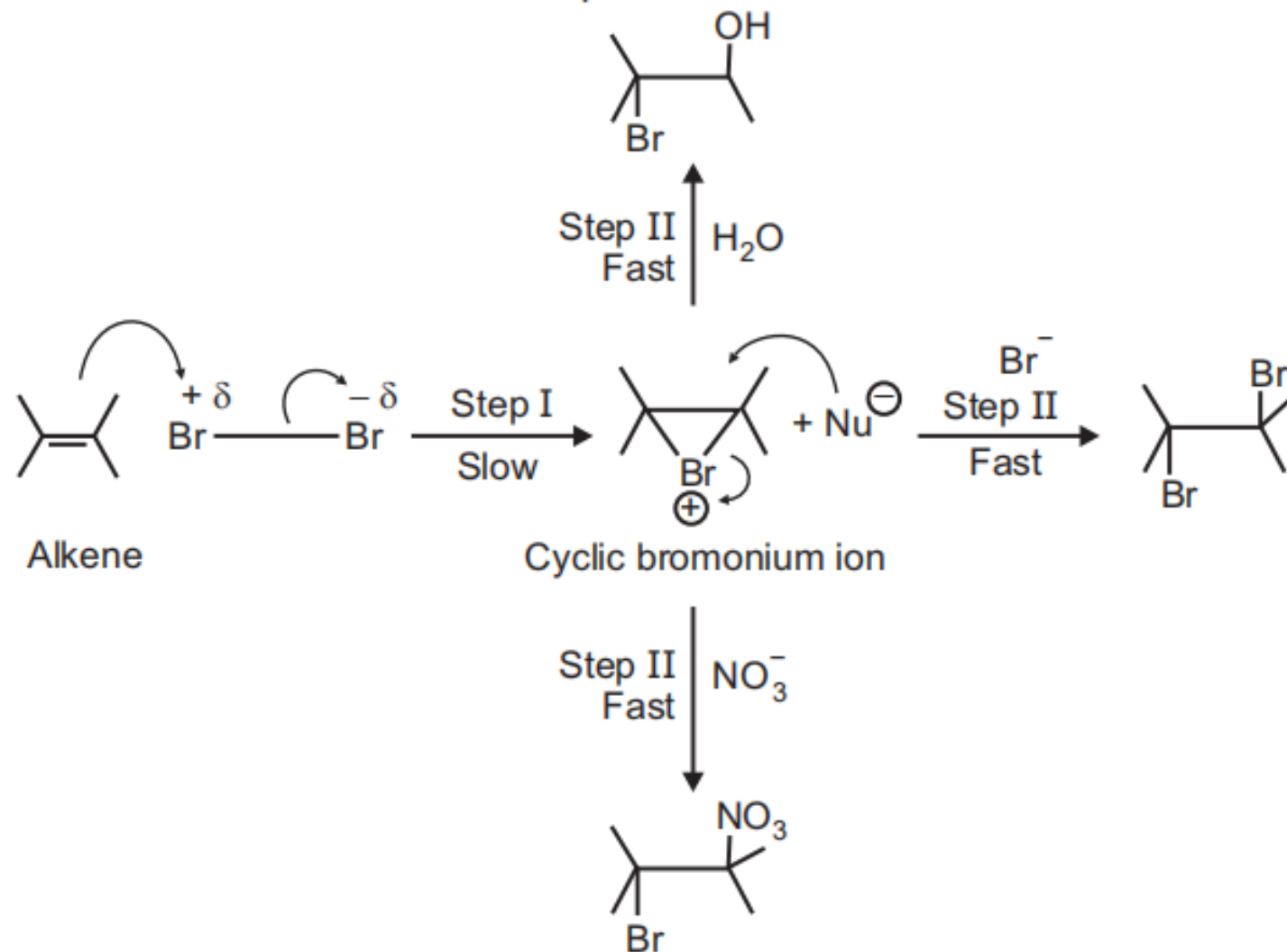
Cyclic bromonium ion

This mechanism is supported by the following observations.

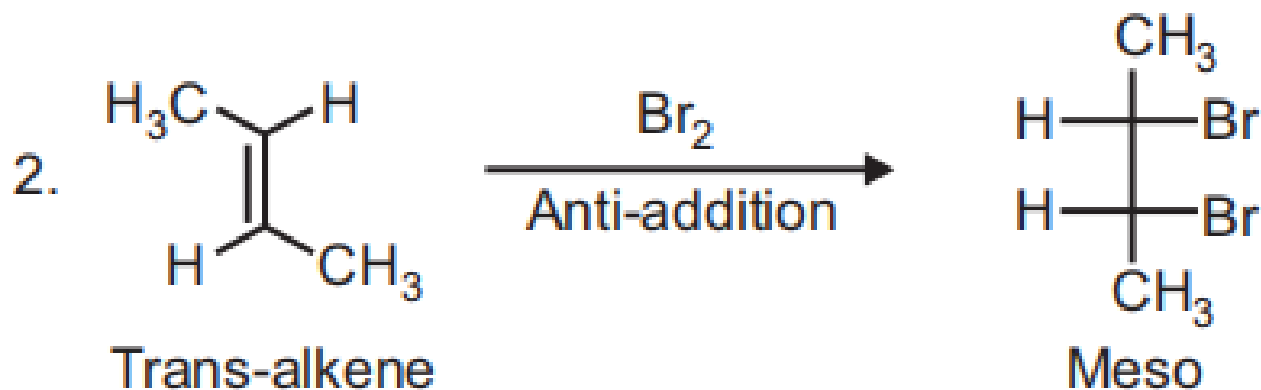
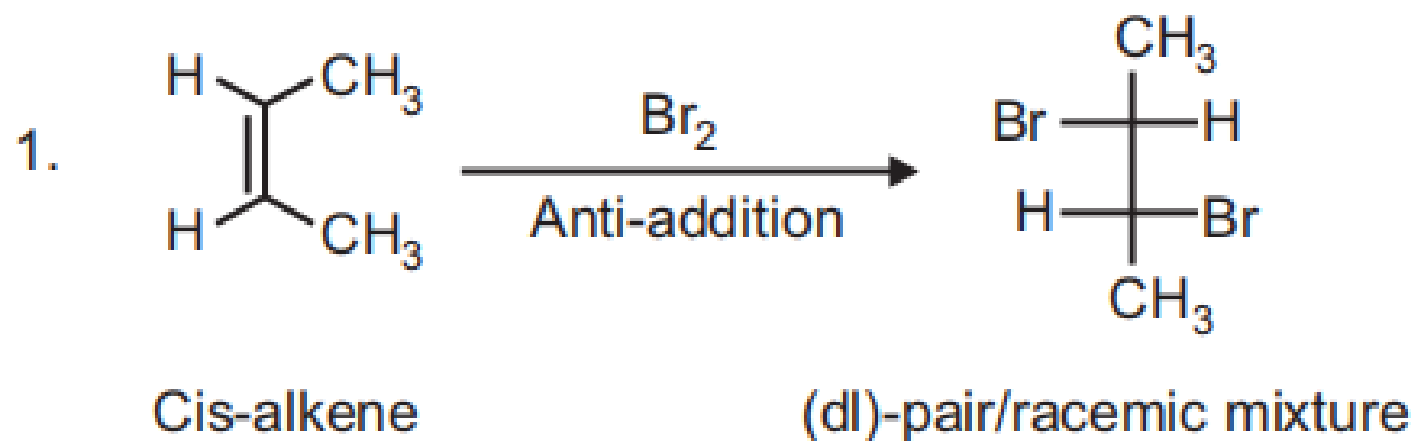
(i) Kinetics : Kinetic studies on the rate of reaction show that the rate of bromination depends on the concentration of alkene as well as bromine. Therefore, it is a bimolecular electrophilic addition reaction.

$$\text{Rate} \propto [\text{alkene}] [\text{Br}_2]$$

(iii) Effect of nucleophile : Support for the halonium ion intermediate comes from the evidence that if the reaction is carried out in the presence of added nucleophile like Cl^- , NO_3^- , H_2O etc. in addition to the formation of dibromo product, bromo-chloro or bromo-nitro or bromo-alcohol products are also observed.

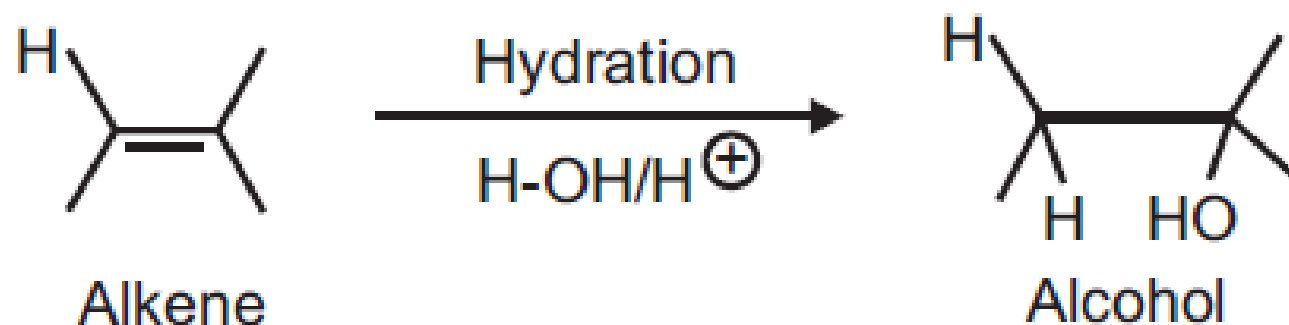


(iv) Stereochemistry (Anti addition) (Stereospecific reaction) : Since two bromines add in opposite direction, the resultant product has two bromines anti to each other. Thus, trans-2-butene gives meso product, while the cis-isomer gives racemic product.



3.1.6 Addition of Water (Hydration)

Reaction : The acid catalyzed addition of water to the C=C bond is known as **hydration** of alkenes. This reaction is a useful method for the conversion of alkenes into alcohols. The acids most commonly used to catalyze the hydration of alkenes are dilute solutions of sulphuric and phosphoric acid.

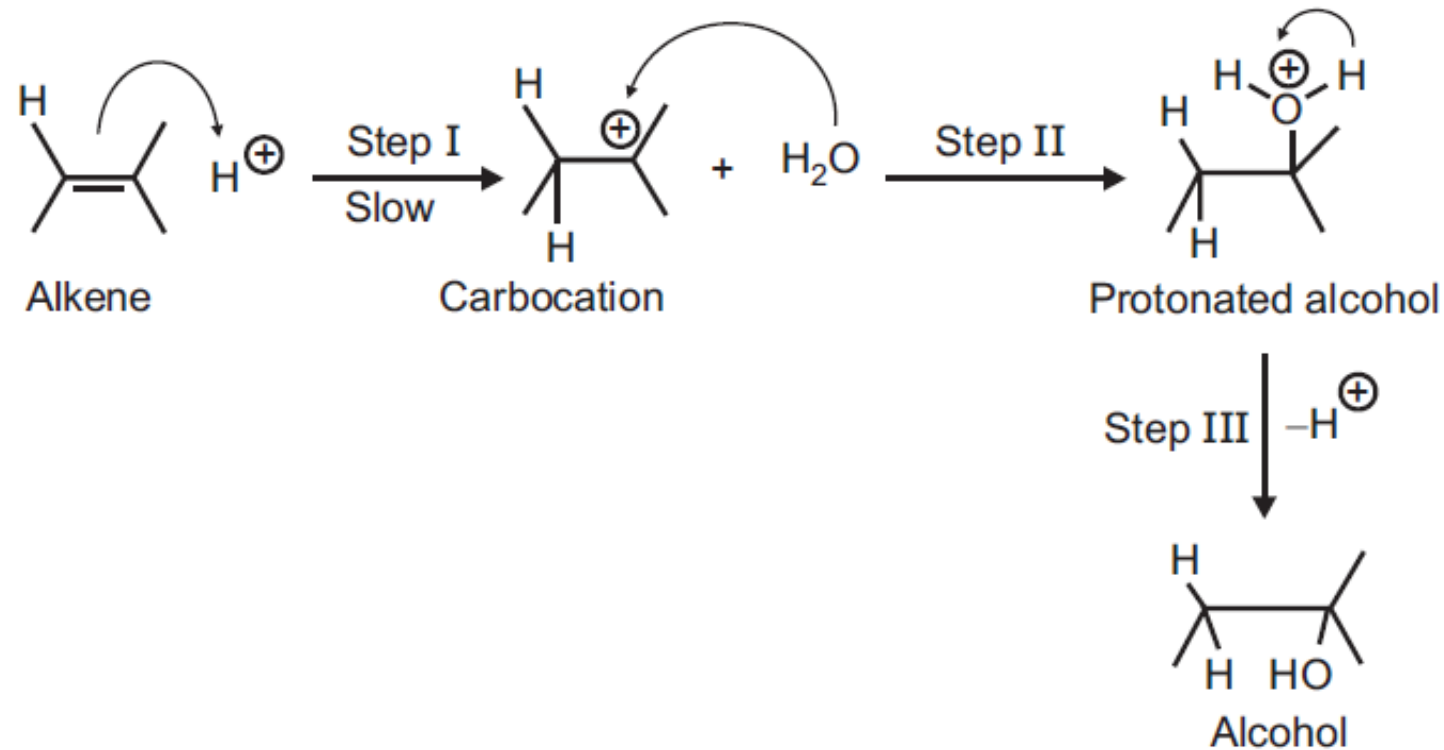


Mechanism : Hydration of alkenes is usually regioselective and it follows Markovnikov's rule. The mechanism for hydration of an alkene is as follows :

(i) Step-I : The first step is the protonation of the alkene to yield a carbocation. This step is the rate determining step.

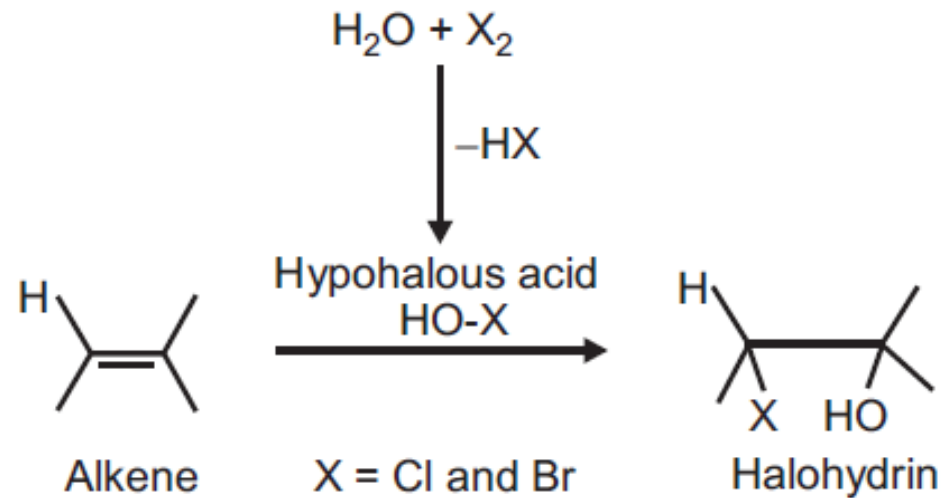
(ii) Step-II : The carbocation of the reaction reacts with nucleophile, i.e. H_2O to form a protonated alcohol.

(iii) Step-III : A transfer of proton to a molecule of water leads to the formation of the product.

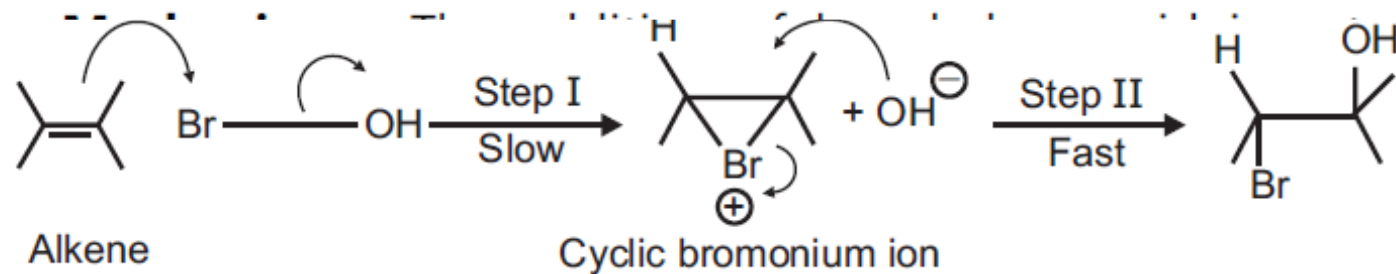


3.1.7 Addition of Hypohalous Acids (HOX)

Reaction : Addition of halogens in the presence of water yield compounds containing halogen and hydroxyl group on the adjacent carbon atoms. These compounds are known as halohydrins. Hypohalous acids are produced by the reaction of halogens and water.

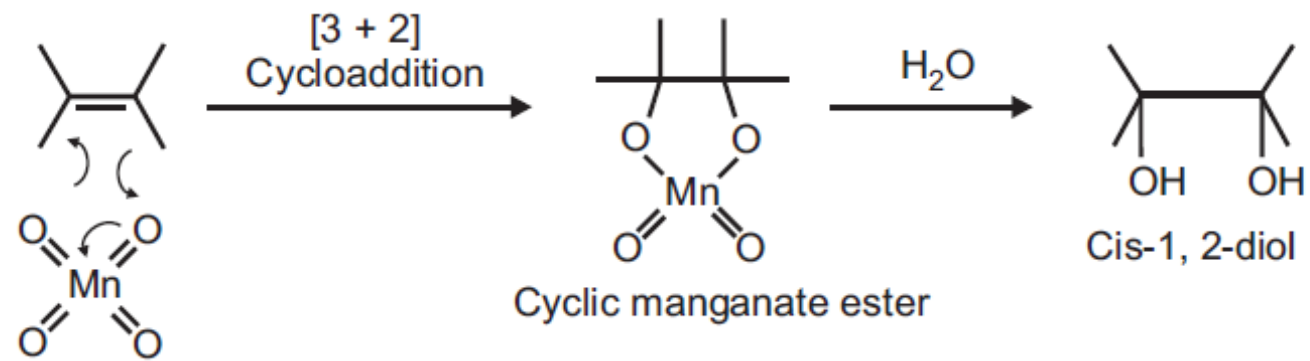
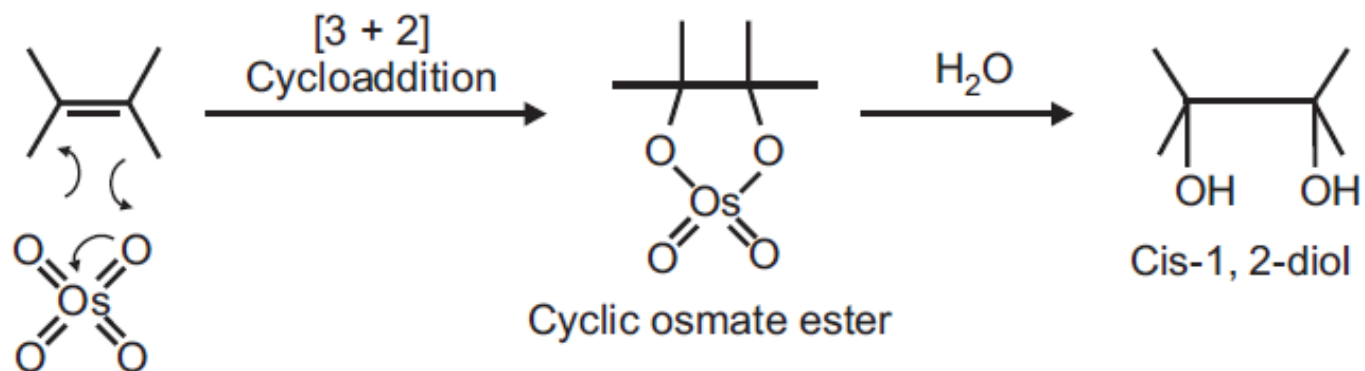
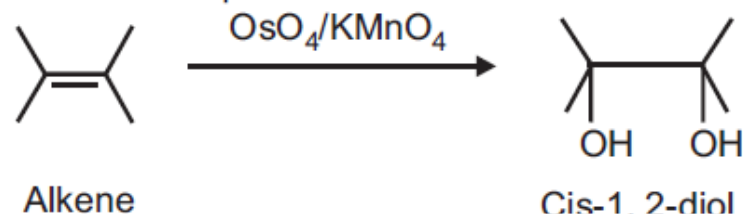


X = Cl: Chlorohydrin
X = Br: Bromohydrin



3.1.8 Hydroxylation (Formation of 1,2-Diols)

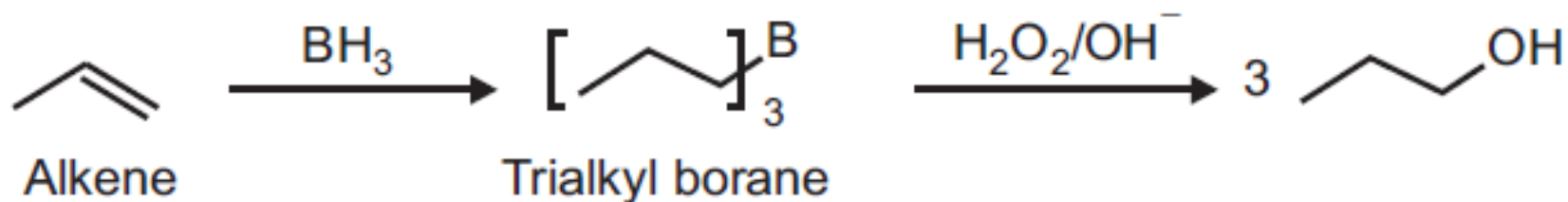
1. Reaction : Addition of hydroxyl groups across the C=C bond of an alkene giving 1, 2-diol (glycol) is known as hydroxylation. This reaction can be carried out by number of reagents. For example, OsO_4 , alkaline KMnO_4 and per acid.



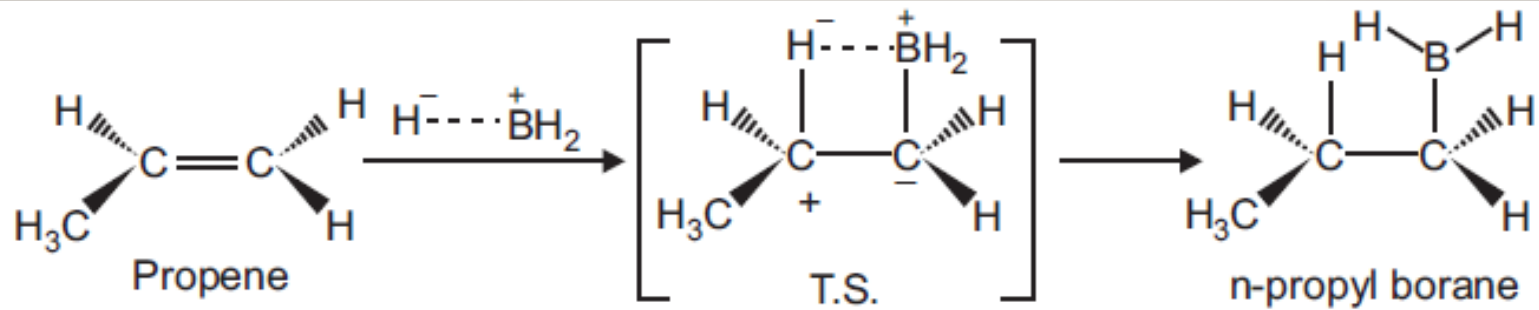
However, KMnO_4 being a strong oxidizing agent can further oxidize 1, 2-diol into two molecules of acid.

3.1.9 Hydroboration - Oxidation (Formation of Alcohols)

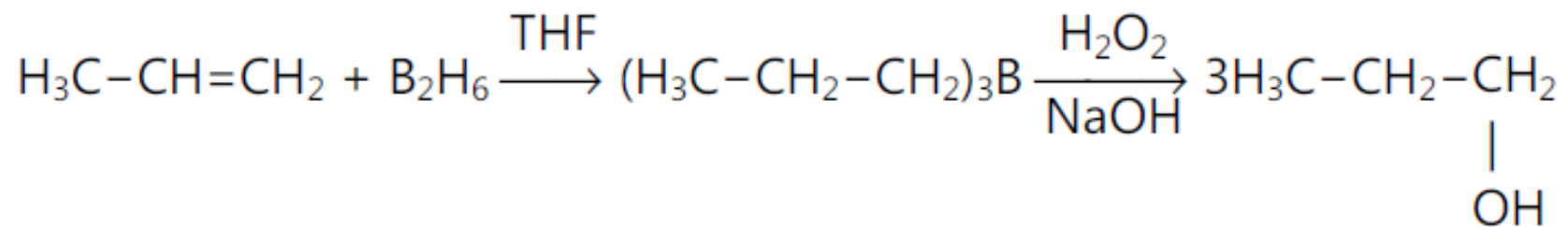
Addition of borane ($\text{BH}_3/\text{B}_2\text{H}_6$) on $\text{C}=\text{C}$ bond forming alkyl borane is called as hydroboration, which on oxidation with alkaline peroxide yields alcohol. This reaction was reported by Prof. H. C. Brown for which he received Nobel Prize in 1979.



Boron adds to the less substituted carbon atom, while H to the more substituted carbon atom. The $\text{C}-\text{B}$ bond is then oxidized to $\text{C}-\text{O}$ bond to yield the alcohol. The overall reaction is the addition of H_2O molecule across the $\text{C}=\text{C}$ bond similar to hydration, however, in this case the addition is anti-Markovnikov.

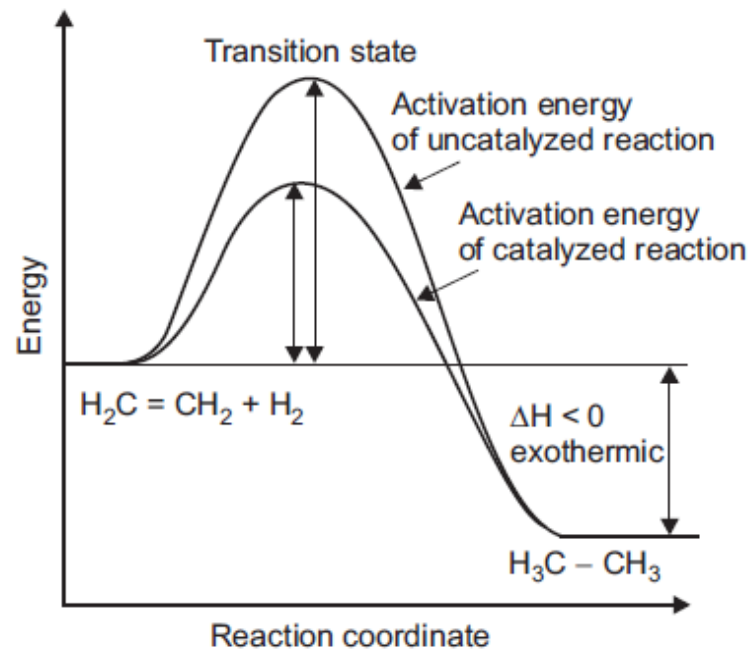


For example,

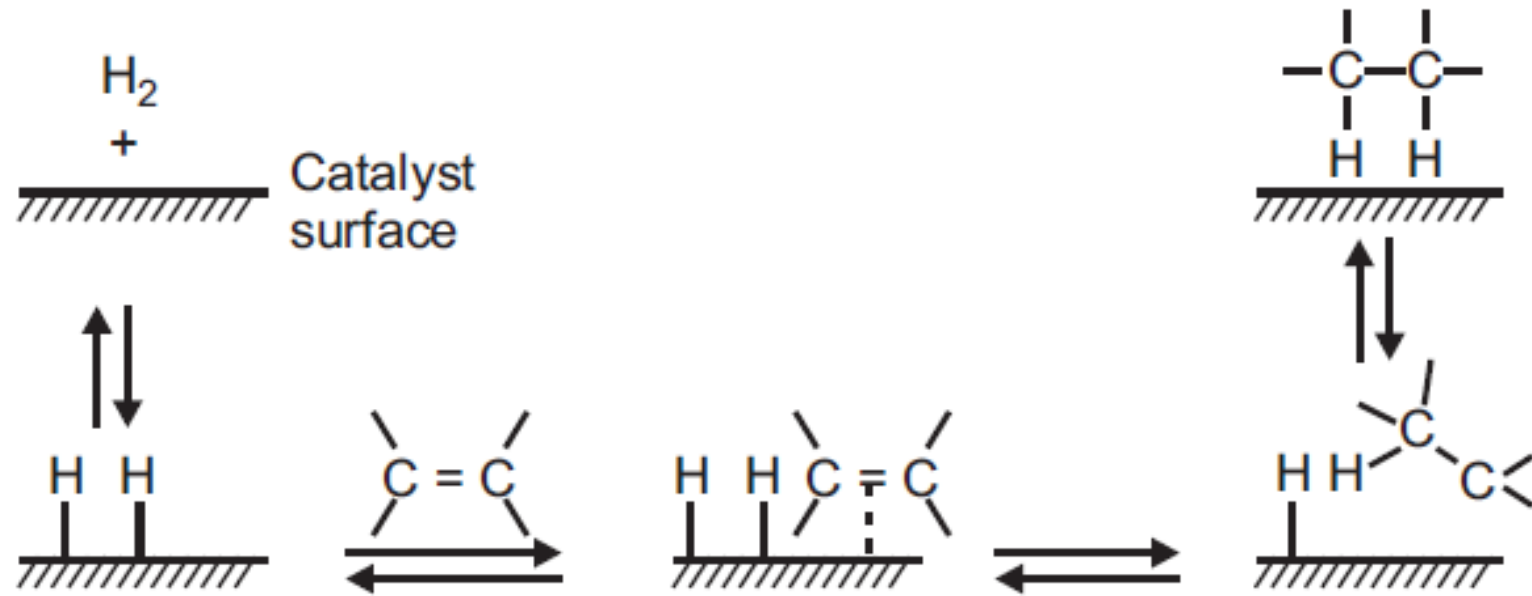


3.1.10 Hydrogenation (Addition of H₂)

Reaction : Hydrogenation is a general method for the conversion of C=C bond into C–C bond in almost any kind of compound. It is an exothermic reaction : two σ bonds (C–H) being formed are stronger than the σ bond (H–H) and π bond being broken. The quantity of heat evolved when one mole of an unsaturated compound is hydrogenated is called as **heat of hydrogenation**. Although hydrogenation is exothermic reaction, it proceeds at a negligible rate in the absence of a catalyst, even at elevated temperature. The uncatalysed reactions therefore must have very large activation energy. The function of the catalyst is to lower the energy of activation so that the reaction proceeds rapidly at room temperature. Metal catalysts like Ni, Pt, Pd, Ru, Rh etc. are generally employed for hydrogenation reaction of alkenes.



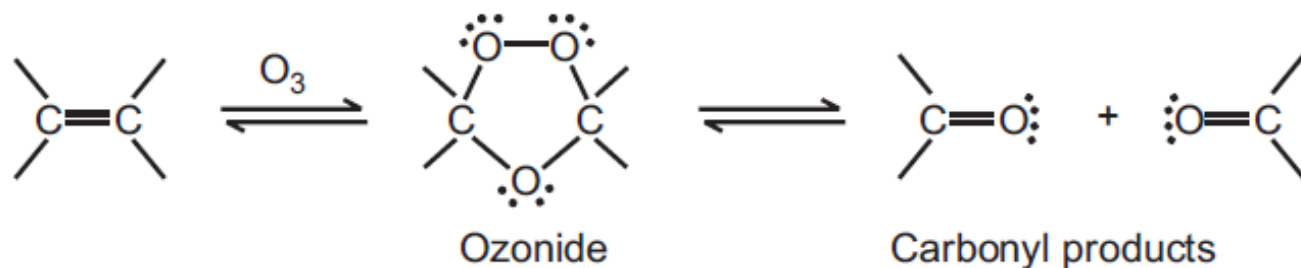
Mechanism : Heterogeneous hydrogenation involves chemisorption (adsorption-desorption) process.



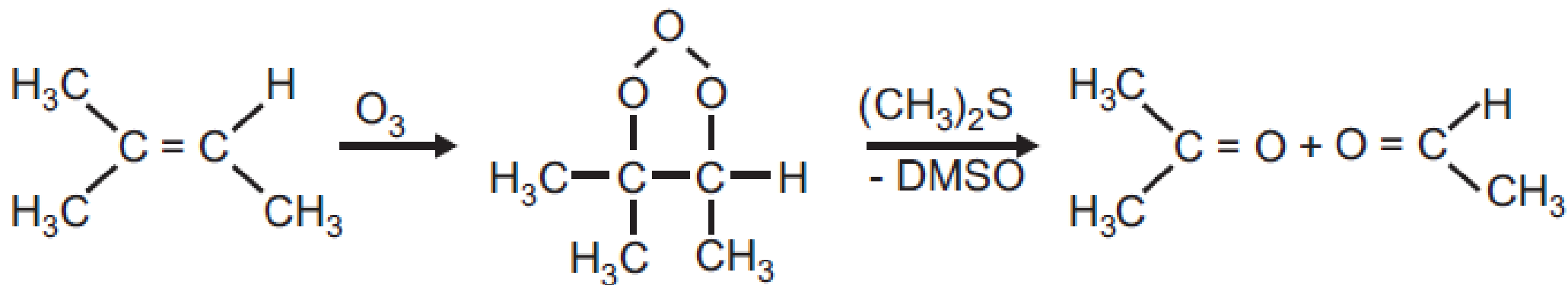
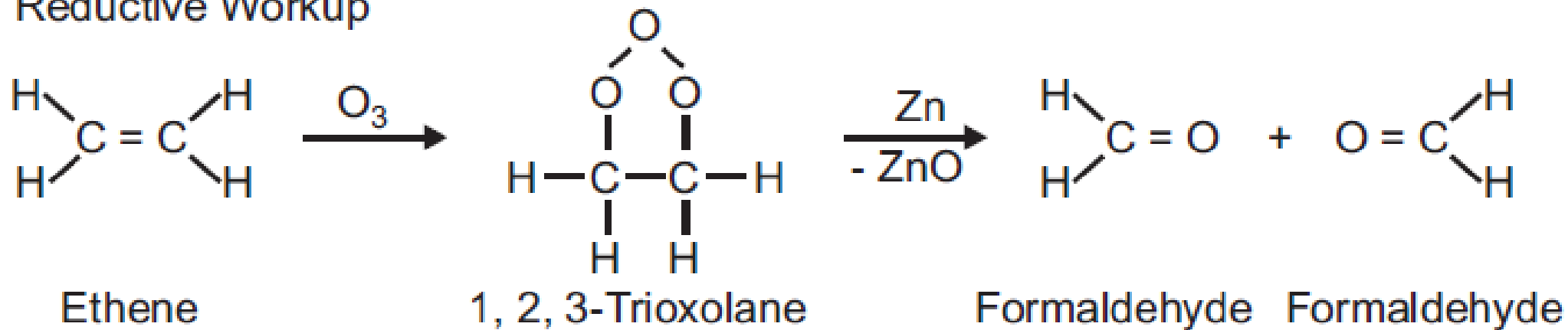
3.1.11 Ozonolysis (Addition of O₃)

Reaction : Ozonolysis is a cleavage reaction in which the C=C bond is completely cleaved into aldehydes/ketones. Ozone is used for this reaction, therefore, the name is ozonolysis.

This reaction is carried out in two steps : addition of ozone to the double bond to form an ozonide which on hydrolysis yield aldehydes/ketones. Ozone gas is passed into a solution of alkaline dissolved in CCl₄ at low temperature. Ozonides are not isolated as they are explosive, but are treated with water in the presence of reducing agent like Zn metal. This is to avoid the formation of H₂O₂ which would otherwise further oxidize the resultant aldehydes and ketones.



Reductive Workup



3.2 Addition to Carbon-Carbon Triple Bond ($-\text{C}\equiv\text{C}-$)

3.2.1 Introduction

Similar to alkenes, alkynes undergo electrophilic addition reactions due to presence of the loosely held π -electrons. Addition of halogens, hydrogen and hydrogen halides (HX) to alkynes is much like addition to alkenes, except that, here two molecules of the reagent can be consumed for each triple bond. By selecting proper conditions, the addition reaction can be stopped at first stage giving alkenes.

Besides addition reactions, terminal alkynes ($\text{R}-\text{C}\equiv\text{C}-\text{H}$) undergo displacement reaction due to more acidic hydrogen atom held by triply bonded carbon. Such reactions provide the best route to the important organometallic compounds.

(i) **Addition of Hydrogen : Hydrogenation :**

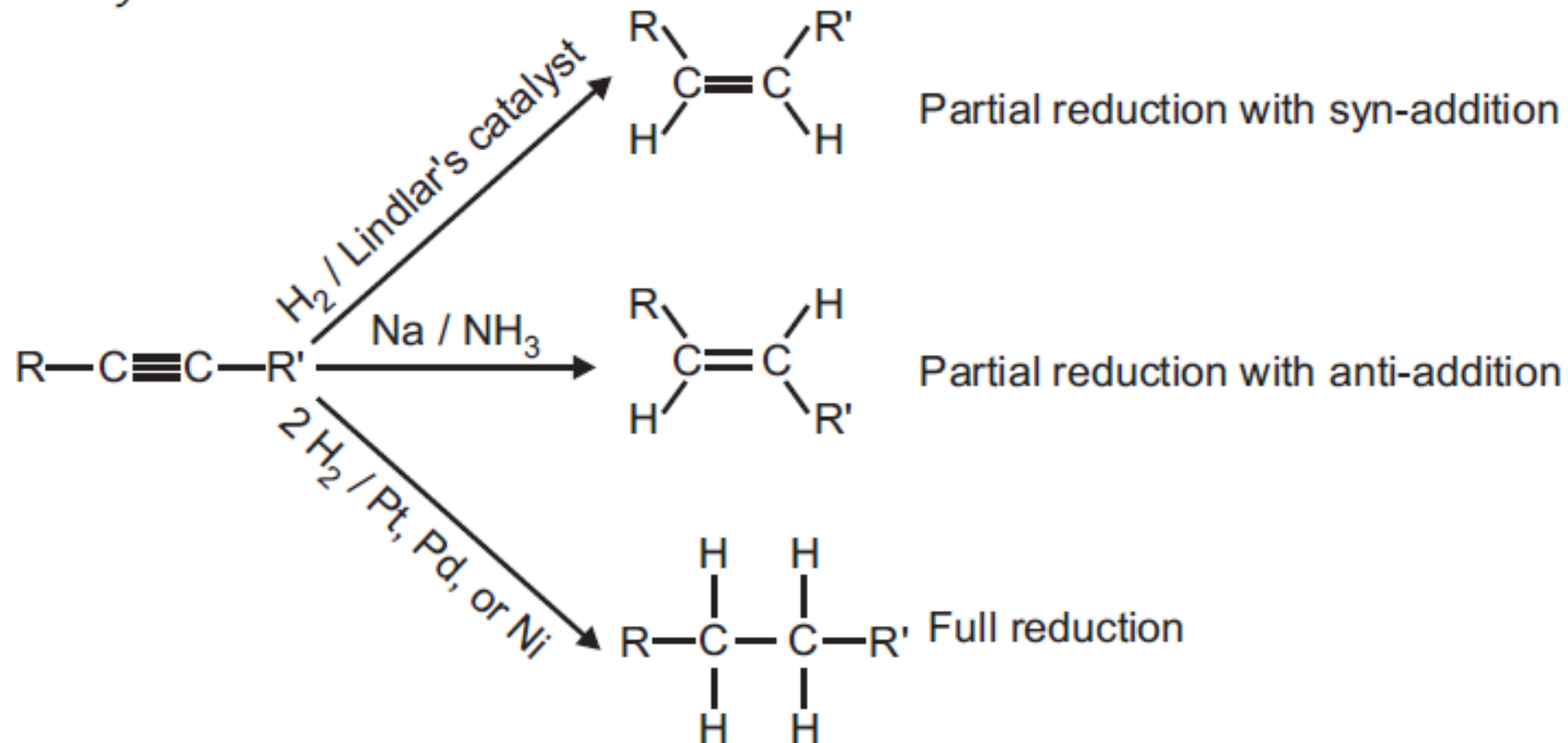
Alkynes can undergo reduction reactions similar to alkenes and are also called hydrogenation reactions. With the presence of two pi bonds within the carbon-carbon triple bonds, the reduction reactions can be partial or complete depending on the reagents.

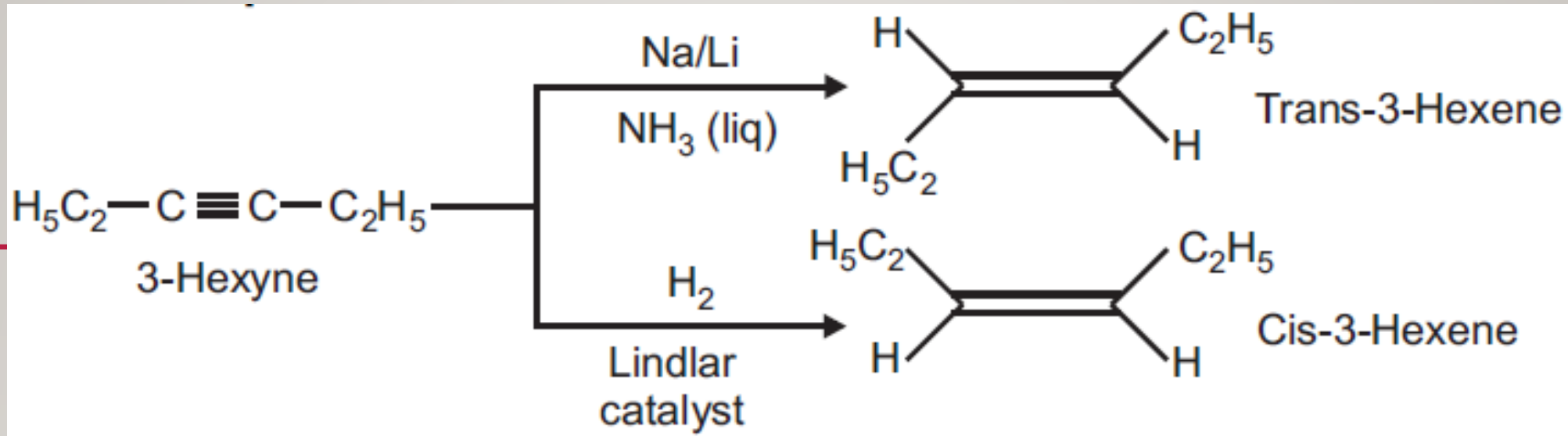
Types : The two most significant alkyne reduction reactions are summarized below.

(a) Complete reduction : The complete reduction is carried out in the presence of metal catalysts like Pd/Pt/Ni. Addition of hydrogen molecule to alkyne is syn addition giving first an alkene, which then react with second molecule of hydrogen and get reduced to alkane.

(b) Partial reduction : It is carried out using $(\text{Na}+\text{NH}_3)$ or Lindlar's catalyst. If the alkyne is not a terminal alkyne then it yields

either a *cis* or *trans* alkene depending on the choice of the reagent. Predominantly the *trans*-isomer is obtained by reduction of alkynes with sodium or lithium in liquid ammonia. Almost entirely *cis* alkene is obtained by hydrogenation with palladium catalyst called as *Lindlar's catalyst*.

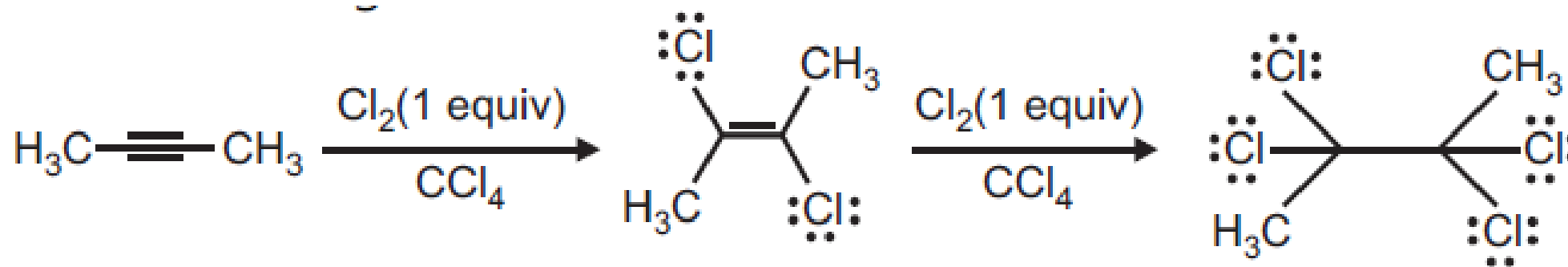




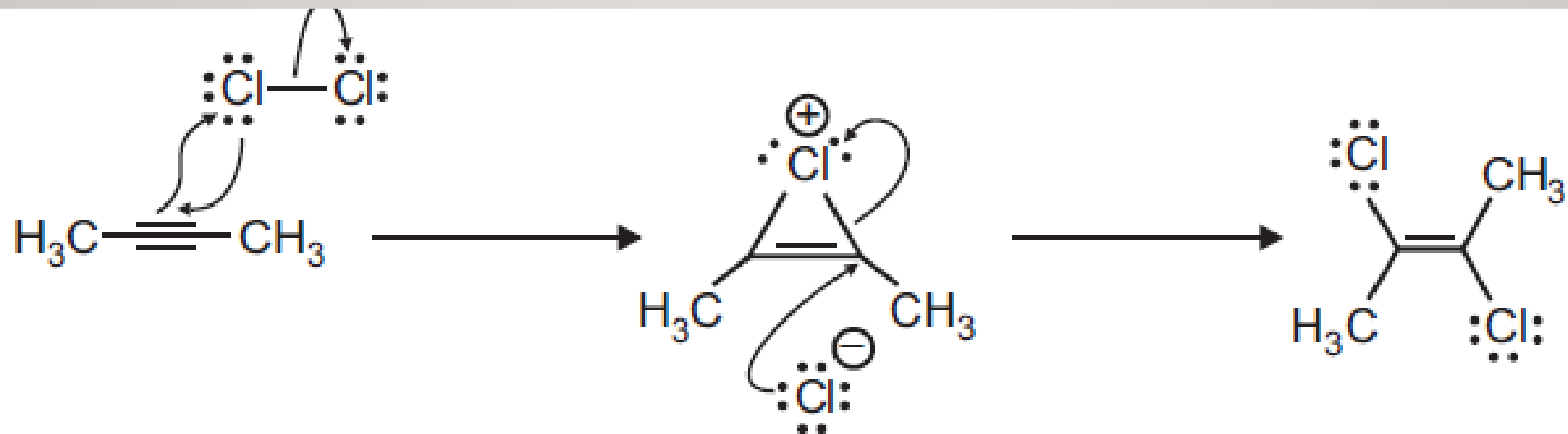
(ii) Addition of Halogen : Halogenation :

Electrophilic addition of halogens to alkyne is much slower than alkenes. The reason for this difference in the reactivity is attributed to the greater difficulty in the formation of the cyclic halonium ion in case of alkynes. However, one mole of halogen gives vicinal dihalo alkene. The second mole of halogen then adds to give vicinal tetrahalo alkene.

The reaction of alkynes with electrophiles such as Cl_2 , Br_2 and I_2 does give very similar results to what is observed with alkenes.



Trans product obtained



Bridged-ion intermediate

Similar mechanism for Br_2 and I_2

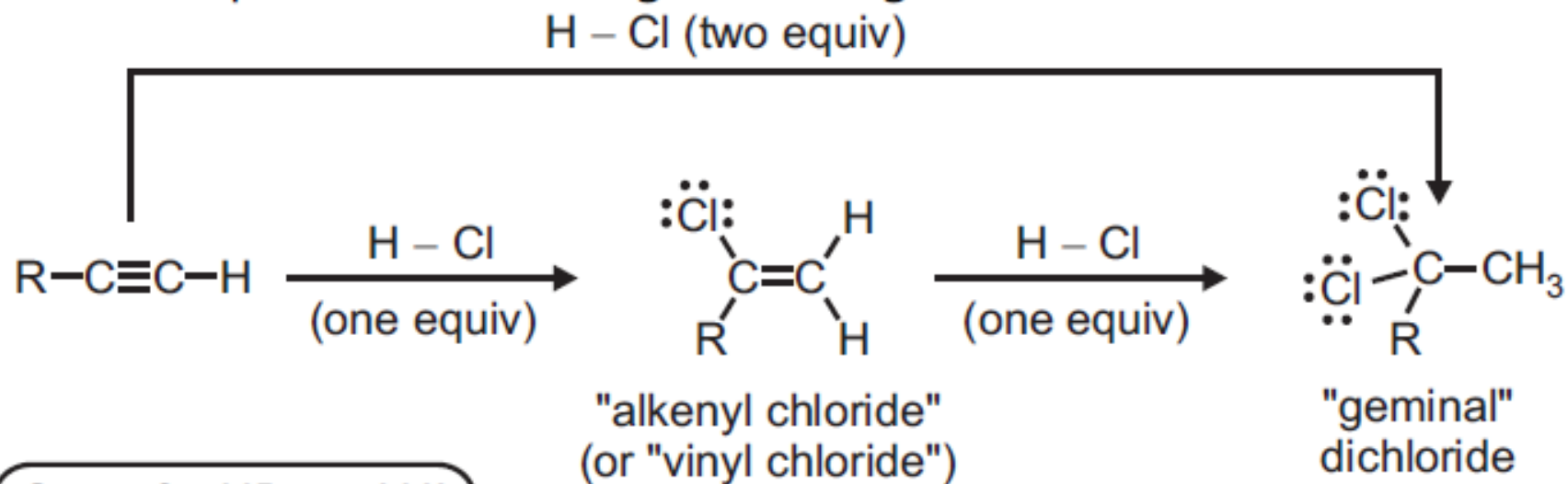
(iii) Addition of Hydrogen halides : Hydrohalogenation :

Alkynes on treatment with HX (X = Cl, Br, I) initially give haloalkene, which on further reaction with HX give dihaloalkane.

Addition to Acids to Alkynes

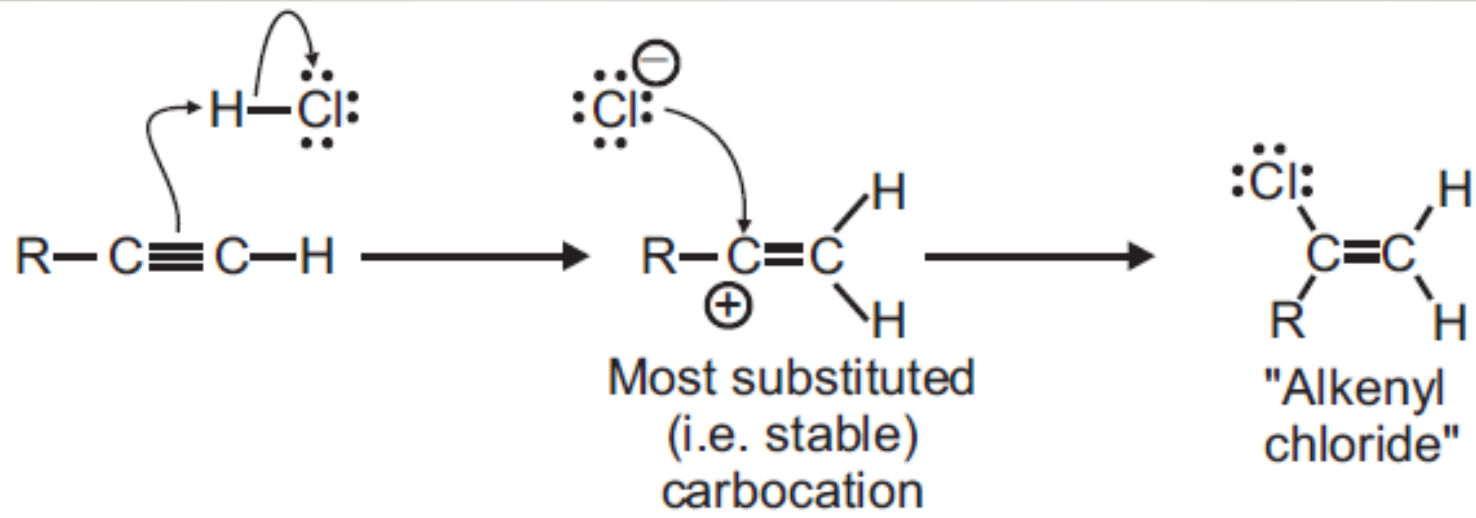
One equivalent of acid gives the alkenyl halide ("vinyl halide").

Two equivalents of acid gives the "geminal dihalide".

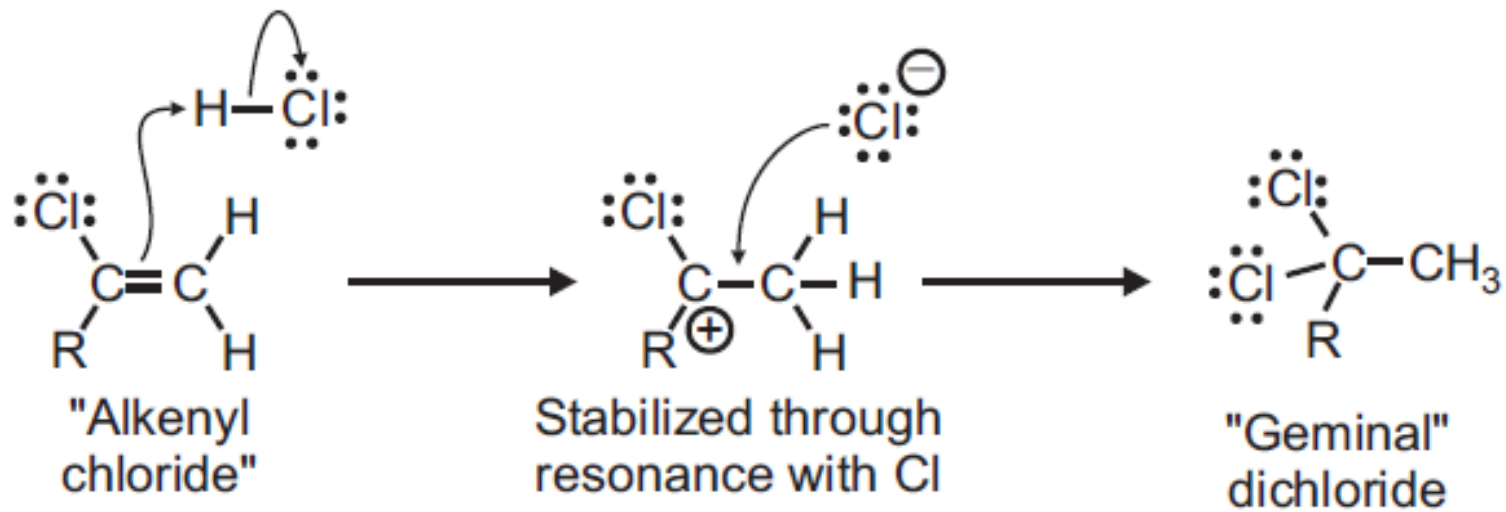


Same for HBr and HI

*note: "Markovnikov" addition
(Cl adds to most substituted carbon)*

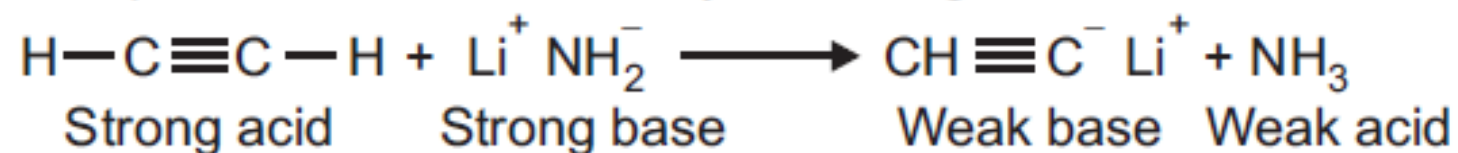


Addition of second equivalent:

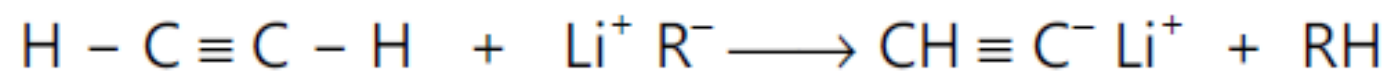


3.3 Formation of Metal Acetylides

A triply bonded carbon atom is more electronegative than a doubly or singly bonded carbon atom. As a result, hydrogen atom attached to a triply bonded carbon atom as in acetylene or any terminal alkyne shows appreciable acidity. Metals like sodium, lithium, magnesium react with acetylene to liberate hydrogen gas and form metal acetylide. The acetylene proton as compared to that of ammonia or alkane is strongly acidic. When acetylene reacts with lithium amide, it gives ammonia and lithium acetylide. The weak acid, $\text{H}-\text{NH}_2$ is displaced from its salt by a stronger acid $\text{HC} \equiv \text{C}-\text{H}$.



Similarly, acetylene is stronger acid than alkene. When a terminal alkyne is treated with alkyl magnesium bromide or alkyl lithium, the alkene is displaced from its salt and the metal acetylide is obtained.



Strong acid Strong base Weak base Weak acid



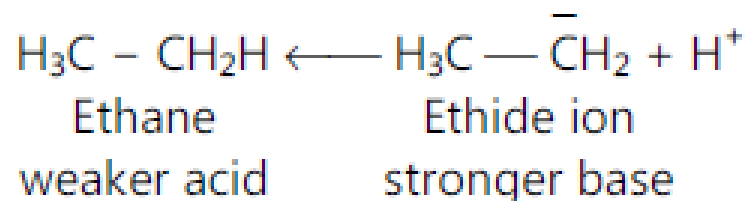
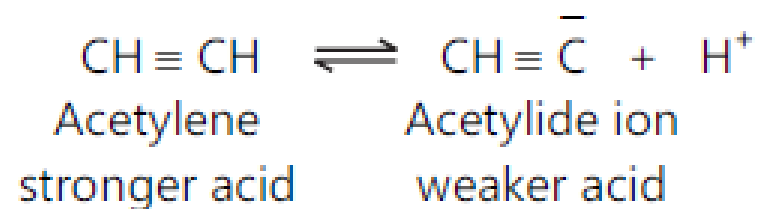
Strong acid Strong base Weak base Weak acid

When lithium acetylide reacts with water, hydroxide ion is formed and acetylene is liberated, Thus acetylene is weaker than water.

Thus, the relative acidities of the following organic compounds are in the order :



To account for the fact that acetylene is a stronger acid than ethane; a possible explanation is the electronic configuration of anions. In the acetylide ion, the unshared pair of electrons occupies the sp orbital; in the ethide anion the unshared pair of electrons occupies the sp^3 orbital.



The availability of this pair for sharing with acids determines the basicity of the anion. Now, compared to an sp^3 orbital, an sp orbital has less p character and more s character. An electron in a p orbital is at a distance from the nucleus and is held relatively loosely; an electron in s orbital on the other hand, is close to the nucleus and is held more strongly. The acetylide ion is therefore weaker base as compared to ethide ion. Thus acetylene is a stronger acid than ethane.