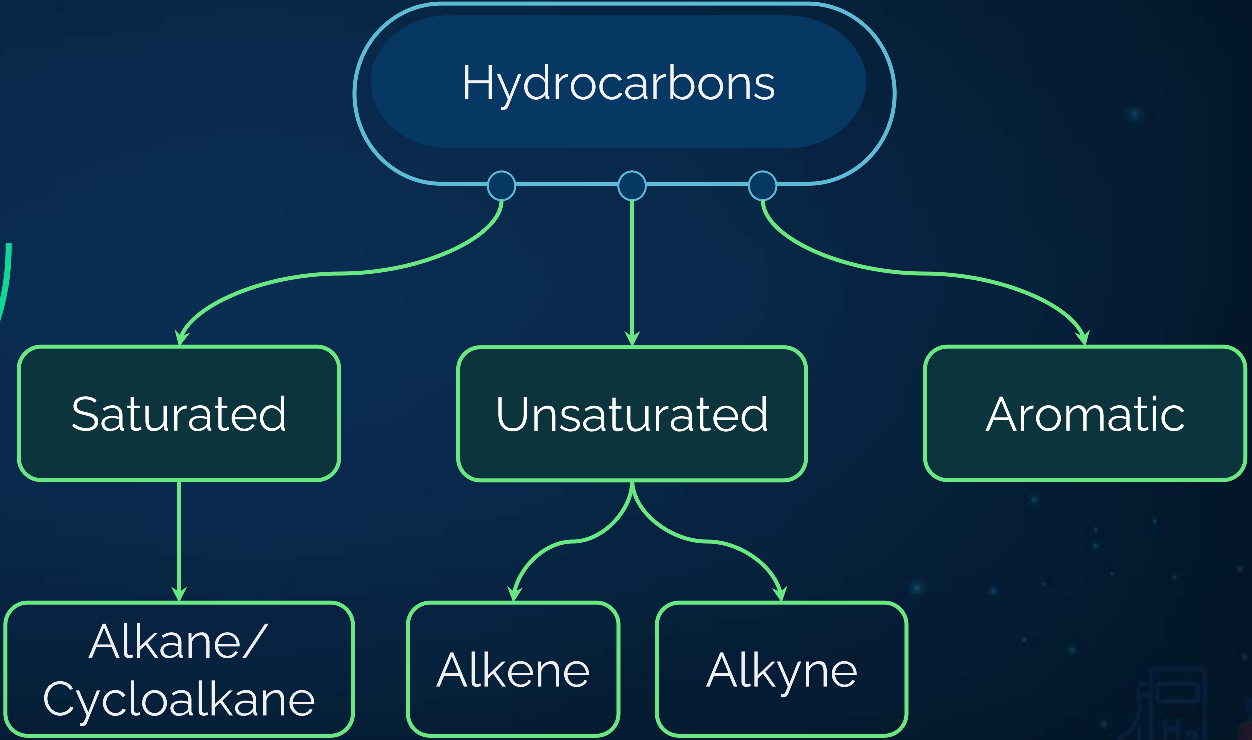
Welcome to

Aakash + BYJU'S LIVE

Hydrocarbons

Hydrocarbons

Compounds of only **Carbon and Hydrogen** are called Hydrocarbons.



Hydrocarbons

Saturated

Unsaturated

Aromatic

Alkane/ Cycloalkane

Alkene

Alkyne

Alkanes

General Formula C_nH_{2n+2}

Alkanes are called Paraffins

Little affinity towards many reagents

Preparation

1. **Catalytic Hydrogenation** of Alkenes or Alkynes → Addition of H_2 in the presence of a **catalyst**

Catalyst: **Ni/ Pt/ Pd**

Reducing Agent: **H_2 (g)**

Preparation of Alkanes from Alkenes and Alkynes

Catalytic Hydrogenation of Alkenes or Alkynes → Addition of H_2 in the presence of a **catalyst**

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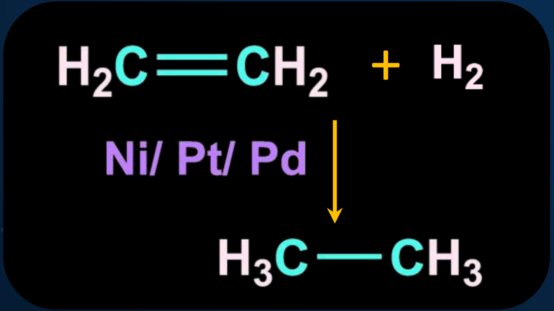
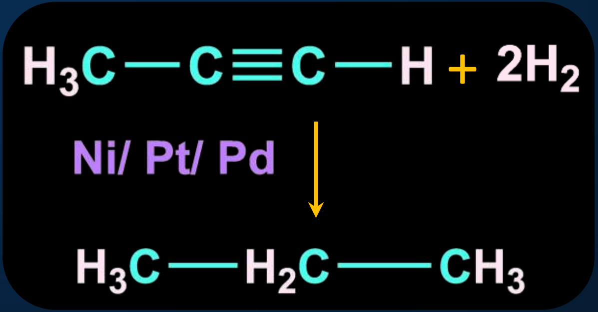


$$H_2C{=}CH_2 + H_2 \xrightarrow{\text{Ni/ Pt/ Pd}} H_3C{-}CH_3$$



$$H_3C{-}C{\equiv}C{-}H + 2H_2 \xrightarrow{\text{Ni/ Pt/ Pd}} H_3C{-}H_2C{-}CH_3$$

Pt and Pd catalyse the reaction **at room temperature,** but relatively **higher temperature and pressure** are required with **Ni catalysts.**

Preparation of Alkanes from Alkenes and Alkynes

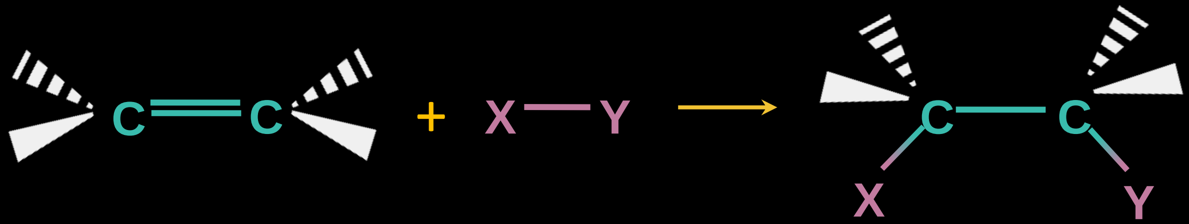
1. Substrate molecules are assumed to undergo **homolysis** into atoms at the **surface of the catalyst**.

2. The substrate is **adsorbed** on the surface of the catalyst and **hydrogenation** takes place.

Syn Addition

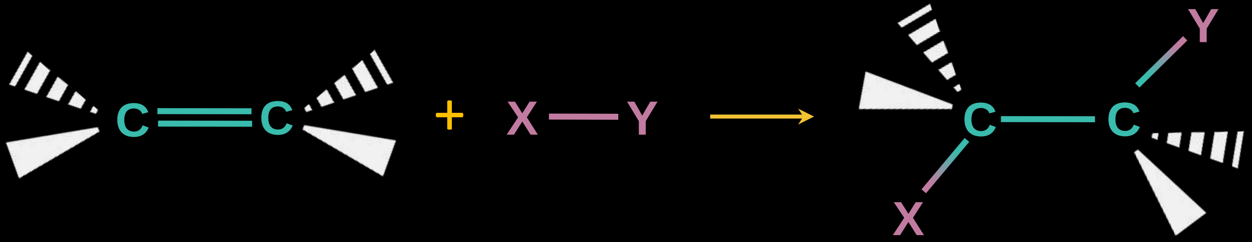
Catalytic H_2 addition is
a **syn** addition reaction.

An addition that places the parts
of the adding reagent on the **same
side (or face) of the reactant.**

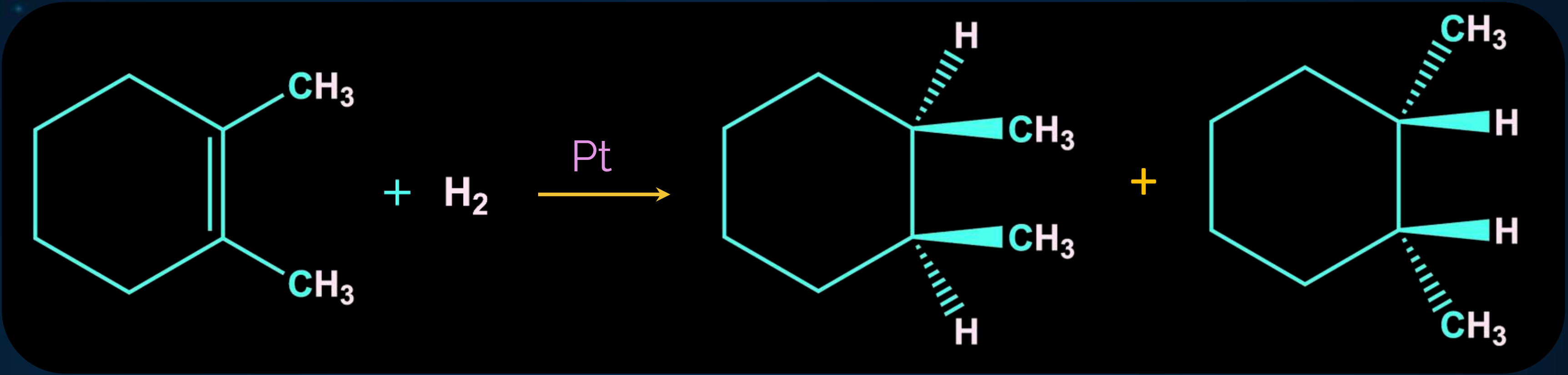


Anti Addition

An anti addition places the parts of the adding reagent **on the opposite faces of the reactant.**

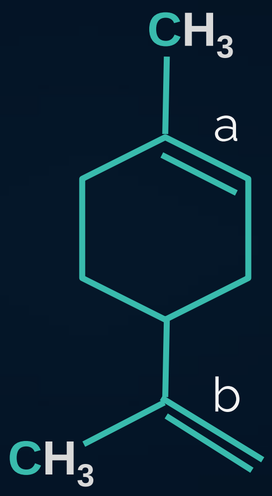


Preparation of Alkanes from Alkenes and Alkynes



The ease of reduction of an alkene **decreases** with the degree of substitution of the double bond.

Example



Order of reactivity: b > a

Ease of Reduction

Alkynes are more reactive than alkenes towards catalytic hydrogenation as they are **less hindered.**

Preparation of Alkanes from Alkyl Halides

1 From Alkyl Halides → By Reduction

Reagent: Zn, dil. HCl

$$CH_3-Cl \xrightarrow{\text{Zn, dil. HCl}} CH_4 + ZnCl_2$$

$$H_3C-H_2C-CH_2-Cl$$

$$\Big\downarrow \text{ Zn, dil. HCl}$$

$$H_3C-H_2C-CH_3 + ZnCl_2$$

Mechanism

$$Zn \longrightarrow Zn^{2+} + 2e^{-}$$

$$R - X + 2e^{-} \longrightarrow R^{-} + X^{-}$$

$$R^{-} + HCl \longrightarrow RH + Cl^{-}$$

Alkyl fluorides (R-F) cannot be reduced using Zn, dil. HCl as C-F bond is very strong.

Preparation of Alkanes from Alkyl Halides

2 From Alkyl Halides

By Reduction

Wurtz Reaction

Reagent: Na, dry ether

$$R-X + 2Na + X-R \xrightarrow{\text{dry ether}} R-R + 2NaX$$

$$Na \longrightarrow Na^{+} + e^{-}$$

$$R-X + e^{-} \longrightarrow R^{\bullet} + X^{-}$$

$$R^{\bullet} + R^{\bullet} \longrightarrow R-R$$

Wurtz Reaction

'Na' reacts **vigorously** with **water.**

Dry ether

Inert solvent is required to prevent interference with the reaction.

$$CH_3{-}Cl + 2Na + Cl{-}CH_3 \xrightarrow{\text{Dry ether}} H_3C{-}CH_3 + 2NaCl$$

Wurtz Reaction

$$CH_3-Cl + Na + Cl-H_2C-CH_3$$

$$\Big\downarrow \text{ Dry ether}$$

$$H_3C-H_2C-CH_3 + H_3C-CH_3$$

$$H_3C-H_2C-CH_2-CH_3 + NaCl$$

As the mixture of products are formed, yield of any product is not significant. Therefore, it's not preferable to use different alkyl halides.

Wurtz Reaction

Alkanes with both **odd** and **even** number of C are produced.

Mixture of products are formed in this reaction.

Wurtz reaction is generally used for the preparation of **higher alkanes** containing **even** number of carbon atoms.

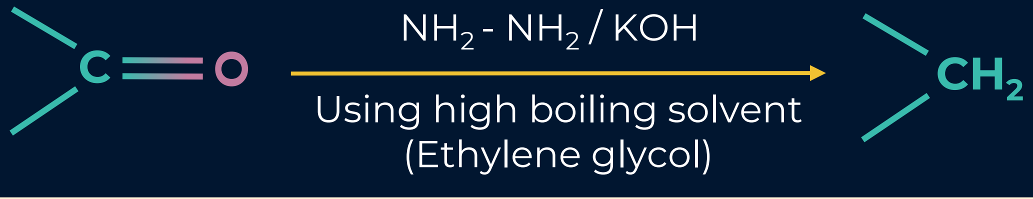
Clemmensen Reduction

It is used to prepare **alkanes** from **carbonyl compounds** (Aldehyde and ketones).

$$>C=O \xrightarrow{\text{Zn-Hg / Conc. HCl}} >CH_2$$

Wolff Kishner Reduction

Used to prepare alkane from carbonyl compounds.



$NH_2 - NH_2$ / KOH

Using high boiling solvent
(Ethylene glycol)

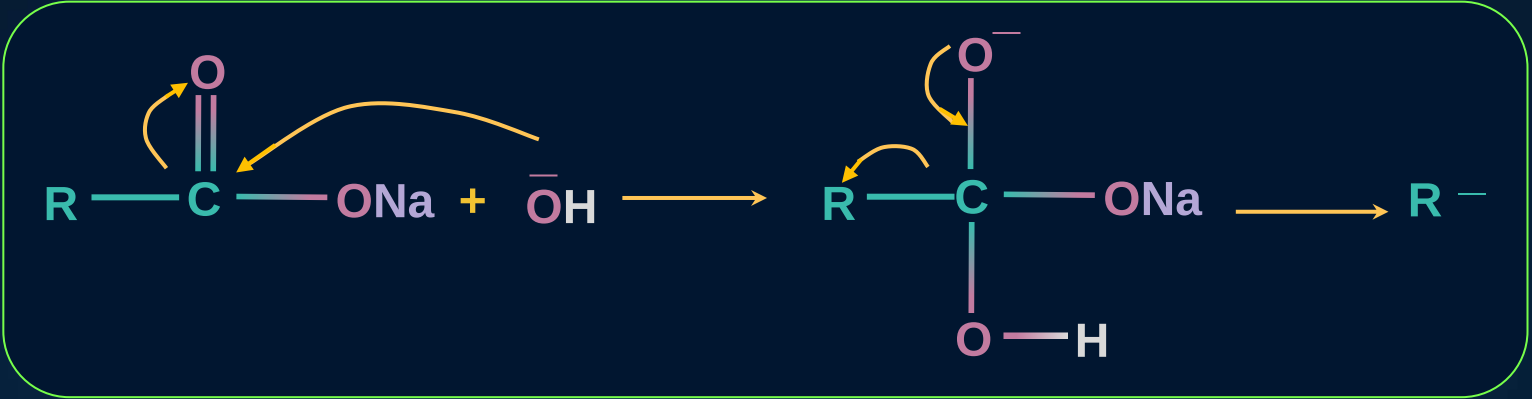
Decarboxylation by Soda Lime

Reaction in which carboxylic acid loses CO_2

Reagent: NaOH (Caustic soda) + CaO (Quick lime)

$$RCOONa + NaOH \xrightarrow[\Delta]{CaO} RH + Na_2CO_3$$

Mechanism



$$R-\overset{\overset{O}{\|}}{C}-ONa + \overset{-}{O}H \longrightarrow R-\underset{\underset{O-H}{|}}{\overset{\overset{O^-}{|}}{C}}-ONa \longrightarrow R^-$$

$$R^- \xrightarrow{NaHCO_3} Na_2CO_3 + RH$$

Rate $\propto$ Stability of carbanion

Decarboxylation by Soda Lime

Alkanes produced contain **one C atom less** than that in the carboxylate ion.

Kolbe’s Electrolysis Method

An aqueous solution of **‘Na’ salt** of a carboxylic acid on electrolysis gives an alkane containing **even number of C** atoms at the anode.

$$\begin{array}{c} R{-}COONa + R{-}COONa + 2H_2O \\ \Big\downarrow \text{ Electrolysis} \\ R{-}R + 2NaOH + 2CO_2 + H_2 \end{array}$$

Kolbe’s Electrolysis Method

At anode (**Oxidation**):

$$\begin{matrix}RCOO^{-} \\ + \\ RCOO^{-}\end{matrix} \xrightarrow{-2e^{-}} \begin{matrix}RCOO^{\bullet} \\ + \\ RCOO^{\bullet}\end{matrix} \xrightarrow{-2CO_2} 2R^{\bullet} \longrightarrow R-R + \underset{\text{Minor}}{RCOOR}$$

Kolbe's Electrolysis Method

At cathode (**Reduction**):

$$H_2O + e^- \longrightarrow {}^-OH + H^\bullet$$

$$2H^\bullet \longrightarrow H_2$$

On using two different types of **Na/K-salt of acids**, mixture of **three alkanes** is obtained.

As the reaction proceeds

pH of the reaction ↑

Physical Properties of Alkanes

1. Physical State
2. Color
3. Odour
4. Solubility
5. Boiling Point

Physical State of Alkanes

At 298 K

Number of C atoms in alkane	State
1 - 4	Gases
5 - 17	Liquids
≥ 18	Solids

Alkanes are **colourless** & **odourless.**

Like dissolves like

Alkanes (non-polar) are **insoluble in water** (polar) and **soluble** in other **non-polar** solvents.

Boiling Point of Alkanes

Boiling Point $\propto$ Van der waals Forces $\propto$ Molar mass

CH_4 < $H_3C—CH_3$ < $H_3C—H_2C—CH_3$

Remember!!

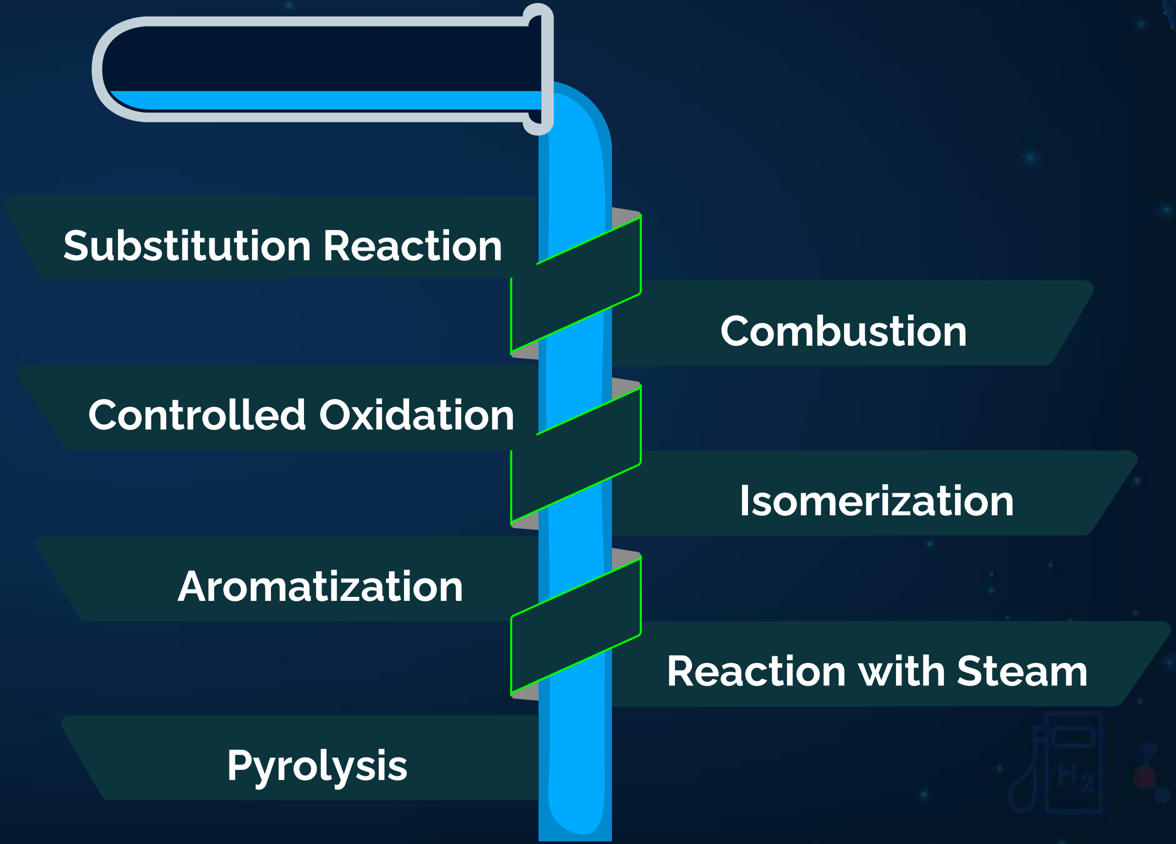
For the **same molar mass**, if

Branching ↑ → Overall surface area ↓ → Intermolecular attractive forces ↓ → Boiling point ↓

Chemical Properties of Alkanes

Alkanes are **inert to most reagents** under normal conditions.

But under certain conditions, they **can react.**



Substitution Reaction

Combustion

Controlled Oxidation

Isomerization

Aromatization

Reaction with Steam

Pyrolysis

Substitution Reaction of Alkanes

When one or more **H atoms of alkane are replaced** by an atom or a group of atom.

Halogenation

When one or more H atoms of an alkane are **replaced by halogens.**

Examples

$$CH_4 + Cl_2 \xrightarrow{\text{UV light}} CH_3Cl + HCl$$

$$CH_3Cl + Cl_2 \xrightarrow{\text{UV light}} CH_2Cl_2 + HCl$$

$$CH_2Cl_2 + Cl_2 \xrightarrow{\text{UV light}} CHCl_3 + HCl$$

$$CHCl_3 + Cl_2 \xrightarrow{\text{UV light}} CCl_4 + HCl$$

Mechanism of Halogenation

1. Initiation
2. Propagation
3. Termination

Initiation (Chain Reaction)

Homolytic cleavage of Cl_2 molecule takes place in the presence of heat or UV light

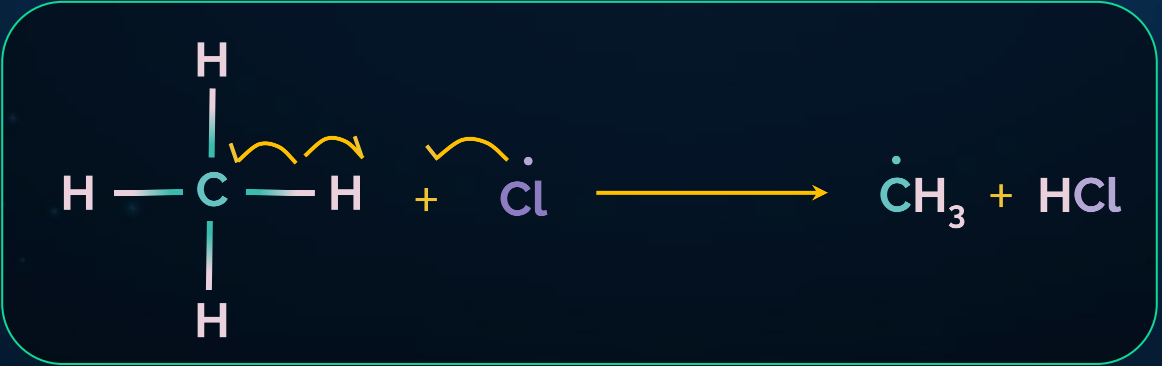
$$Cl-Cl \xrightarrow{\text{UV light}} Cl^{\bullet} + Cl^{\bullet}$$

Cl-Cl bond is weaker than C-C and C-H bonds. Hence, it is **easier to break**.

Propagation (Step I)

$\dot{Cl}$ attacks CH_4

Takes the reaction forward by breaking a C-H bond to generate $\dot{C}H_3$ **along** with HCl.



$$H-\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}-H + \dot{Cl} \longrightarrow \dot{C}H_3 + HCl$$

Propagation (Step II)

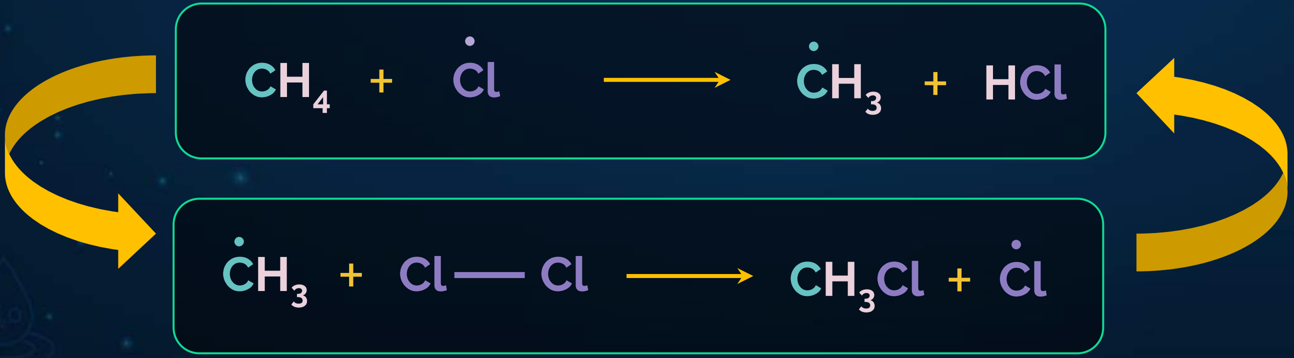
$\dot{C}H_3$ attacks Cl_2

$\dot{C}H_3$ attacks another molecule of Cl_2 to form CH_3- Cl and releases another $\dot{Cl}$.

$$\dot{C}H_3 + Cl - Cl \longrightarrow CH_3 - Cl + \dot{Cl}$$

Propagation

Step 1 and step 2 **repeat** themselves, thereby setting up a chain of reactions.



$$\mathrm{CH_4} + \dot{\mathrm{Cl}} \longrightarrow \dot{\mathrm{C}}\mathrm{H_3} + \mathrm{HCl}$$

$$\dot{\mathrm{C}}\mathrm{H_3} + \mathrm{Cl{-}Cl} \longrightarrow \mathrm{CH_3Cl} + \dot{\mathrm{Cl}}$$

Propagation

Other steps are also possible which generate **multi halogenated** products.

$$CH_3{-}Cl + \dot{C}l \longrightarrow \dot{C}H_2{-}Cl + HCl$$

$$\dot{C}H_2{-}Cl + Cl{-}Cl \longrightarrow CH_2Cl_2 + \dot{C}l$$

Termination

Coupling of any two radicals depletes the supply of reactive intermediates and terminates the chain.

Several pairings are possible for radical coupling termination steps.

Possible Termination Steps

$$\dot{C}l + \dot{C}l \longrightarrow Cl-Cl$$

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow H_3C-CH_3$$

$$\dot{C}H_3 + \dot{C}l \longrightarrow CH_3Cl$$

Inhibitors

A substance that **slows down** or **stops** the reaction is known as inhibitors. All reactive alkyl free radicals are consumed so reaction stops for a period of time.

$$R^{\bullet} + O_2 \longrightarrow R-O-O^{\bullet} + R^{\bullet} \longrightarrow R-O-O-R$$

Rate of Reaction of Alkanes with Halogens

I_2 < Br_2 < Cl_2 < F_2

Very slow and reversible

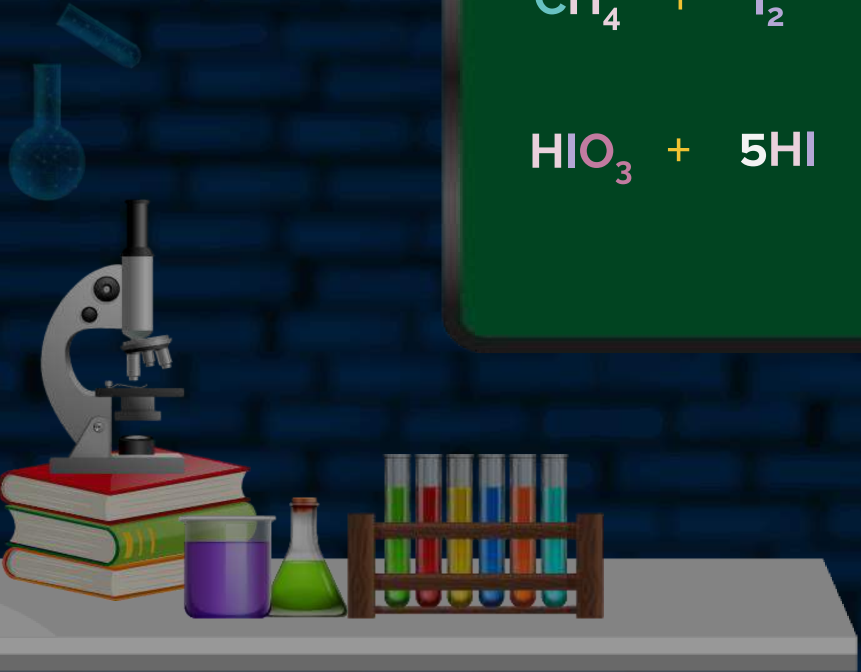
Carried out in presence of oxidising agents like **HIO_3/HNO_3**

Explosive, violent and uncontrollable

Iodination of Alkanes

$$CH_4 + I_2 \rightleftharpoons CH_3I + HI$$

$$HIO_3 + 5HI \longrightarrow 3I_2 + 3H_2O$$



Rate of Replacement of H from Alkanes

$3^\circ > 2^\circ > 1^\circ > \dot{C}H_3$

Rate of Halogenation $\propto$ Stability of **intermediate alkyl radical formed**

Remember!!

This is not the preferred way of producing alkyl halides from alkanes as

Multiple products are formed, resulting in **low yield.**

Combustion

The process of heating a substance **in the presence of sufficient air/O_2**

Alkanes are completely oxidised to **CO_2 & H_2O,** accompanied by the evolution of large amounts of heat.

General Reaction for Combustion

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right) O_2$$

$$\Big\downarrow$$

$$n\ CO_2 + (n+1)\ H_2O + \text{Heat}$$

Example of Combustion

$$C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l)$$

$\Delta_cH^\circ = -2875.84$ kJ/mol

Large amount of heat released during combustion

Alkanes are used as fuels

Heat of Combustion

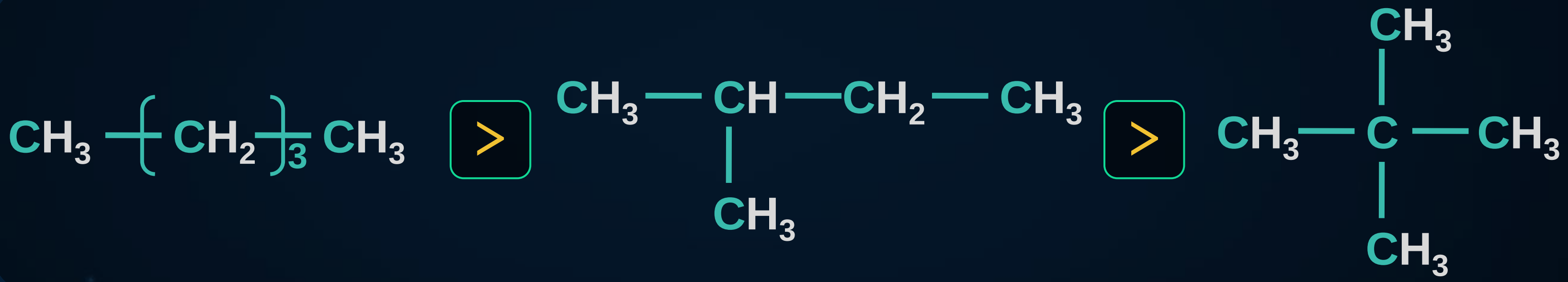
Heat of Combustion $\propto$ Number of C atoms

Example

$C_3H_8 > C_2H_6 > CH_4$

Heat of Combustion

$$\text{Heat of Combustion} \propto \frac{1}{\text{Branching of Alkane (in isomers)}}$$



$$CH_3\text{—}(CH_2)_3\text{—}CH_3 > CH_3\text{—}\underset{\underset{\displaystyle CH_3}{|}}{CH}\text{—}CH_2\text{—}CH_3 > CH_3\text{—}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\text{—}CH_3$$

Heat of Combustion

Heat of Combustion per CH_2 group $\propto$ $\dfrac{1}{\text{Size of ring (cycloalkane)}}$

Incomplete Combustion

Combustion in the **absence** of sufficient amount of air

$$CH_4\,(g) + O_2\,(g) \longrightarrow \underset{\text{Carbon black}}{C}\,(s) + 2\,H_2O\,(l)$$

Controlled Oxidation

Alkanes on heating in a **regulated supply of O_2 or air** at high pressure and in the presence of suitable catalysts, give a variety of oxidation products.

Controlled Oxidation of Alkanes

$$2CH_4 + O_2 \xrightarrow[100\ \text{atm}]{\text{Cu/523 K}} 2CH_3OH$$

$$CH_4 + O_2 \xrightarrow[\Delta]{Mo_2O_3} H_2O + HCHO$$

$$2C_2H_6 + 3O_2 \xrightarrow[\Delta]{(CH_3COO)_2Mn} 2CH_3COOH + 2H_2O$$

Oxidation of Alkanes

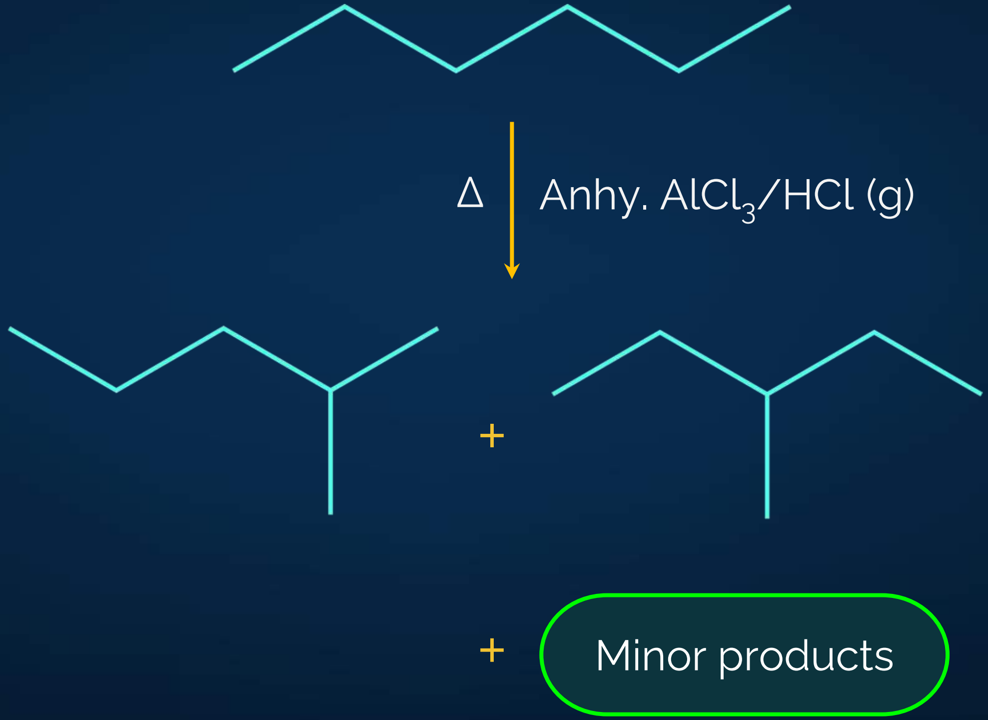
Generally, alkanes resist oxidation, but alkanes **having 3° H atom can be oxidised** to alcohol by $KMnO_4$.

$$(CH_3)_3CH \xrightarrow[\text{Oxidation}]{KMnO_4} (CH_3)_3C\text{-}OH$$

Isomerization of n-Hexane

$$\text{n-Alkanes} \xrightarrow[\Delta]{\text{Anhy. } AlCl_3/HCl\ (g)} \text{Branched alkanes}$$

Isomerization of n-Hexane



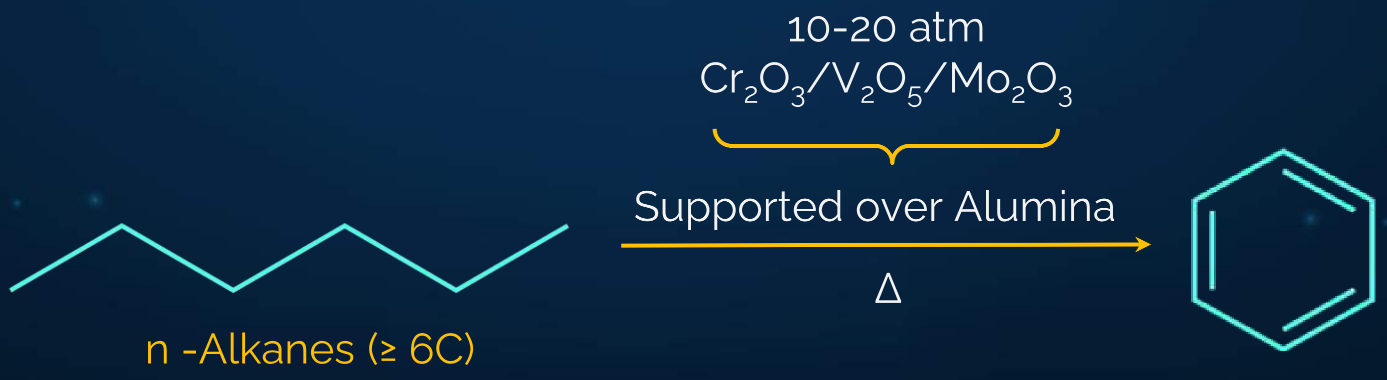
Δ Anhy. $AlCl_3$/HCl (g)

\+

\+ Minor products

Aromatisation

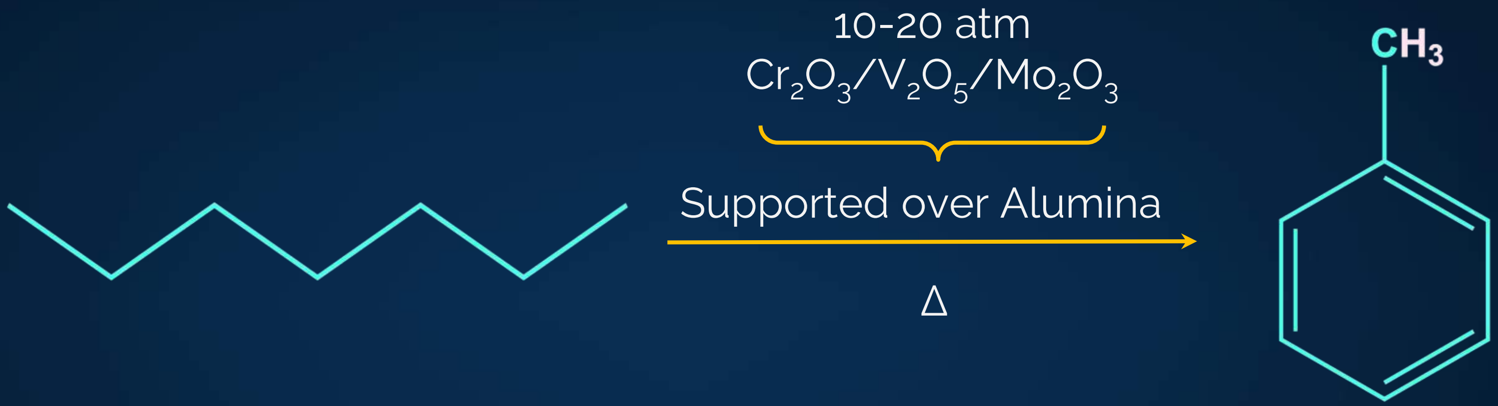
n-Alkanes with **6 or more C atoms**, on heating to **773 K** at **10-20 atm** pressure in the presence of oxides of **V/Mo/Cr** get dehydrogenated and cyclised to form benzene and its derivatives.



$$\xrightarrow[\Delta]{\substack{\text{10-20 atm} \\ \underbrace{Cr_2O_3/V_2O_5/Mo_2O_3}_{\text{Supported over Alumina}}}}$$

n -Alkanes (≥ 6C)

Aromatisation of n-Heptane



10-20 atm

$Cr_2O_3/V_2O_5/Mo_2O_3$

Supported over Alumina

Δ

Reaction with Steam

Methane reacts with steam at 1200 K in the presence of **nickel catalyst** to form **carbon monoxide** and **dihydrogen.**

$$CH_4 + H_2O \xrightarrow[\Delta\ (1270\ K)]{Ni} CO + 3H_2$$

Method used for the **industrial preparation of H_2**

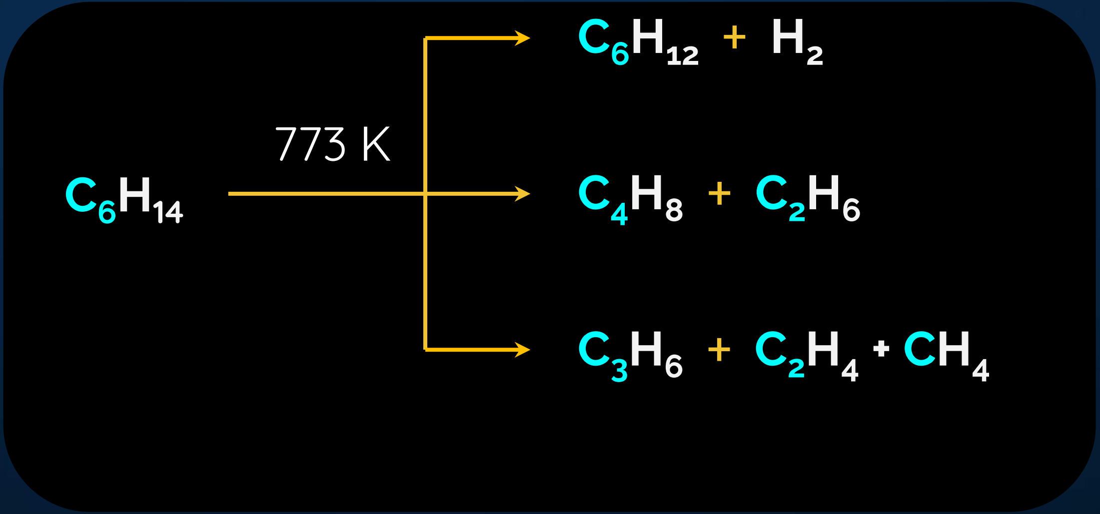
Pyrolysis/ Cracking

$$\text{Higher alkanes} \xrightarrow[\text{High temp}]{\Delta} \text{Lower alkanes/alkenes}$$

Heating of a substance in the **absence of air until it decomposes**.

Pyrolysis/ Cracking

Heating a substance in the **absence of air until it decomposes**.



$$C_6H_{14} \xrightarrow{773\ K} C_6H_{12} + H_2$$

$$C_6H_{14} \xrightarrow{773\ K} C_4H_8 + C_2H_6$$

$$C_6H_{14} \xrightarrow{773\ K} C_3H_6 + C_2H_4 + CH_4$$

Preparation of Oil Gas from Kerosene Oil

$$C_{12}H_{26} \xrightarrow[973\ K]{Ni/Pt/Pd} C_7H_{16} + C_5H_{10} + \text{Other products}$$

Dodecane

(A constituent of kerosene oil)

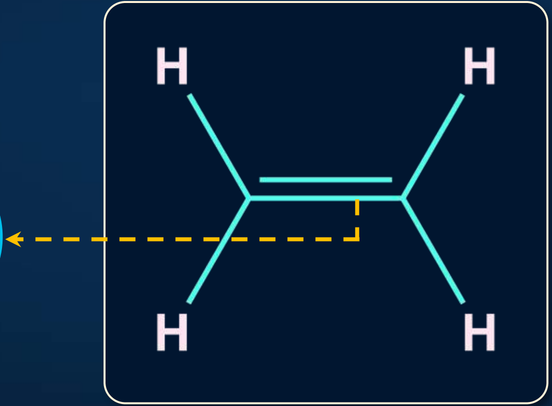
Alkenes/Olefins

Alkenes (C_nH_{2n})
are also known as olefins
(oil forming) since the first
member, ethene, was found
to form an **oily
liquid on reaction with
chlorine.**

General Formula	C_nH_{2n}

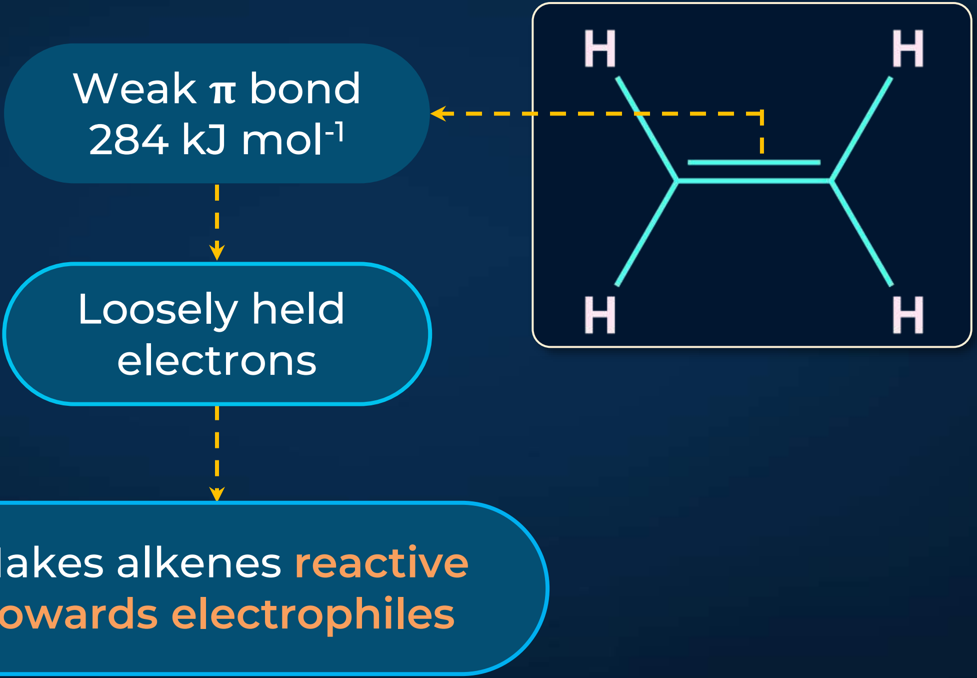
Alkenes

Bond strength and energy



Strong σ bond
397 kJ mol^{-1}

Alkenes



Weak π bond
284 kJ mol^{-1}

Loosely held electrons

Makes alkenes **reactive towards electrophiles**

Geometrical Isomers (G.I.)

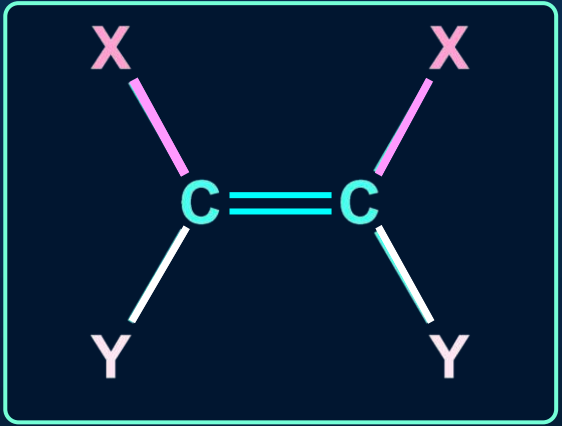
Isomers which possess the **same molecular** and **structural** formula but **differ in the arrangement** of atoms/groups in space due to restricted rotation.

Geometrical Isomers (G.I.)

π bond **prevents rotation**
because the orbitals overlap both
above & below the plane of atoms.

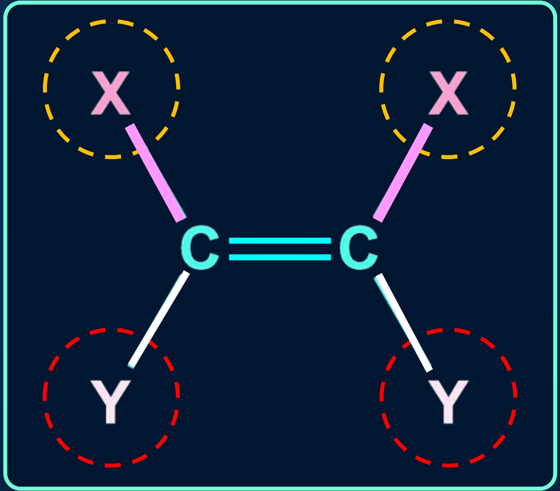
Conditions to Show G.I.

Restricted Rotation



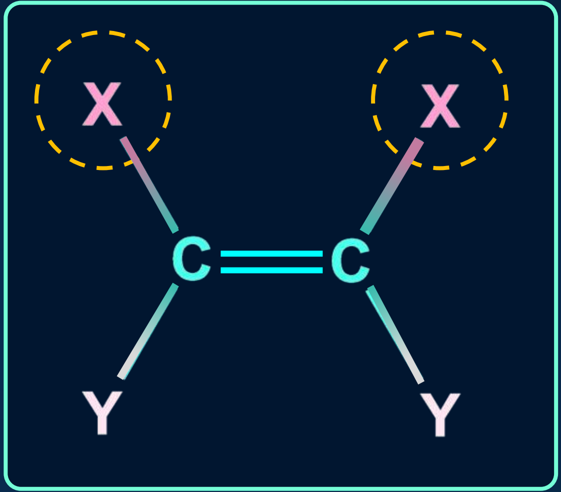
Conditions to Show G.I.

Different groups should be attached to each doubly bonded atom.



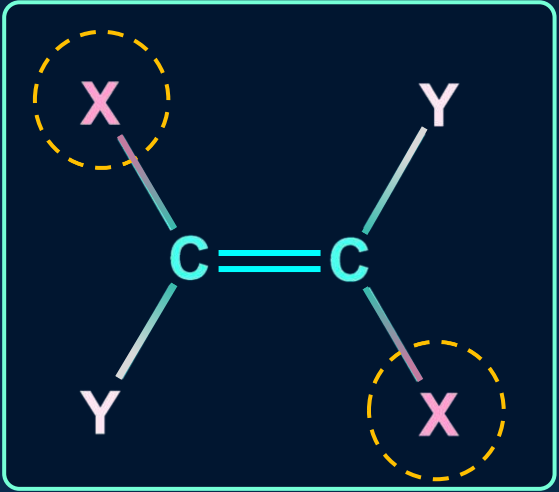
To show G.I, the groups responsible must be **nearly in the same plane**.

cis Form



Same groups lie
on the **same side**
of the double bond

trans Form



Same groups lie
on the **opposite sides**
of the double bond

Preparation of Alkenes from

- Alkynes
- Alkyl Halides
- Vicinal Dihalides
- Alcohols

Preparation of Alkenes from Alkynes

Hydrogenation of Alkynes

By **Partial Reduction**

Reagents

- Lindlar’s Catalyst
- Na/liq. NH_3

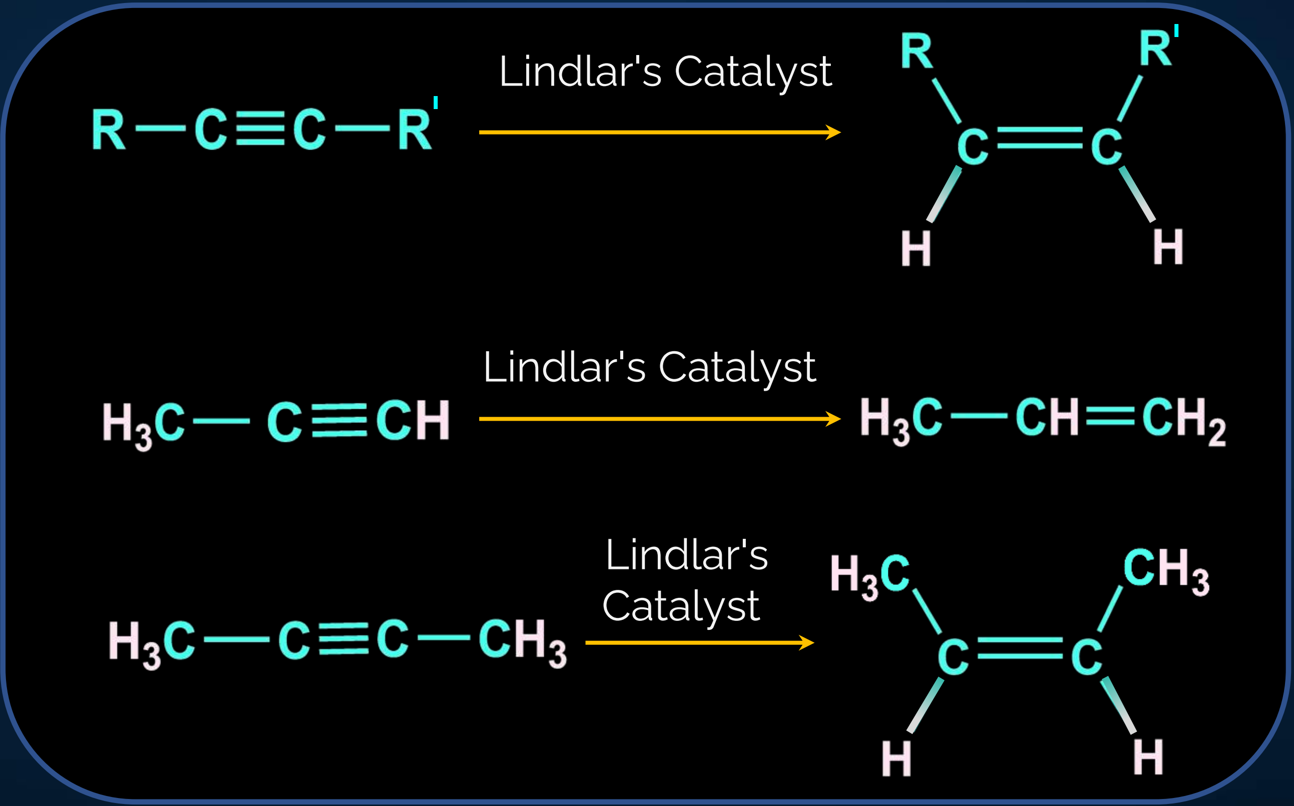
Lindlar's Catalyst

H_2/Pd, $CaCO_3$, quinoline

Poisoned palladium catalyst.
Composed of powdered calcium carbonate coated with palladium and poisoned with quinoline.

It produces cis alkenes from alkynes.

Preparation of Alkenes from Alkynes



$$R-C\equiv C-R' \xrightarrow{\text{Lindlar's Catalyst}} \text{cis-}RCH=CHR'$$

$$H_3C-C\equiv CH \xrightarrow{\text{Lindlar's Catalyst}} H_3C-CH=CH_2$$

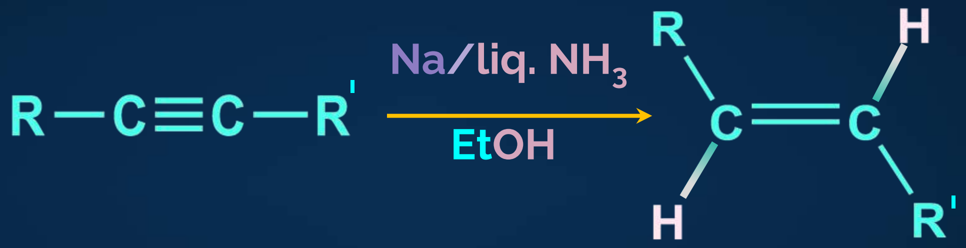
$$H_3C-C\equiv C-CH_3 \xrightarrow{\text{Lindlar's Catalyst}} \text{cis-}H_3C-CH=CH-CH_3$$

Preparation of Alkenes from Alkynes

$$H_3C-C\equiv C-H \xrightarrow{\text{Na/liq } NH_3} H_3C-C\equiv\overset{-}{C}\overset{+}{Na} + \frac{1}{2}H_2$$

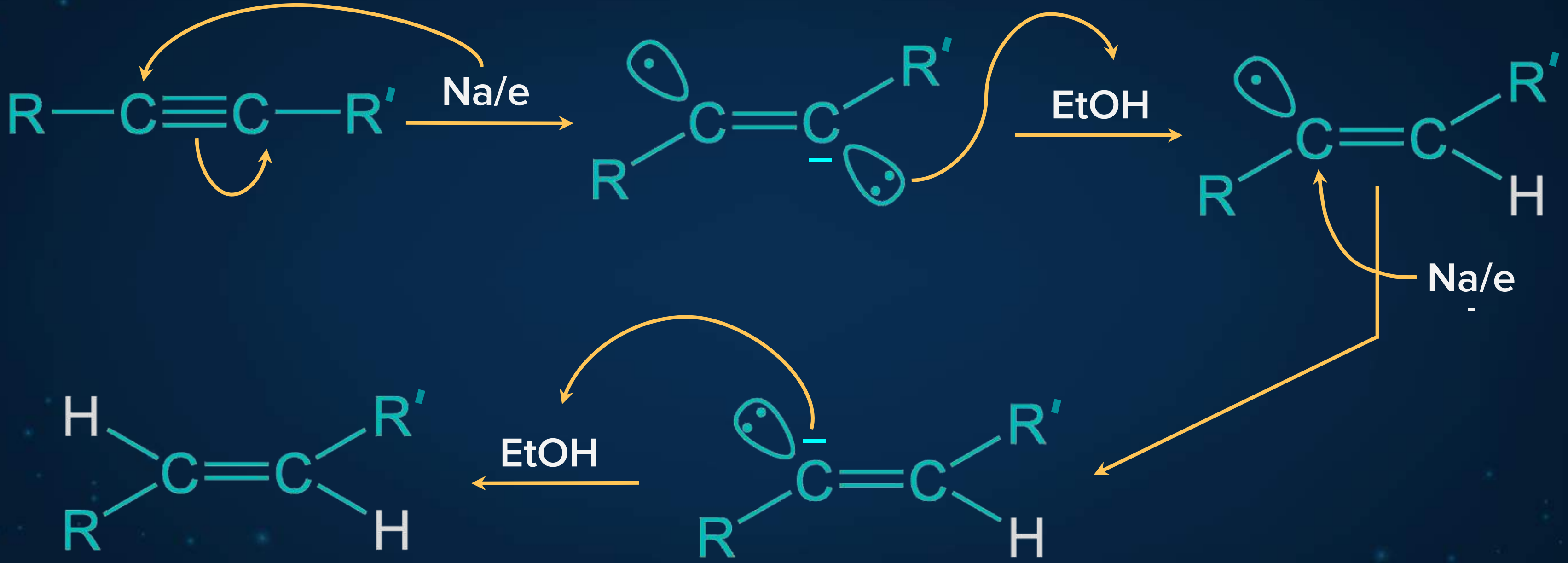
Terminal alkynes do not show Birch reduction, rather it shows **redox reaction** due to the acidic nature of terminal H.

Birch Reduction



It produces trans alkenes from alkynes.

Mechanism



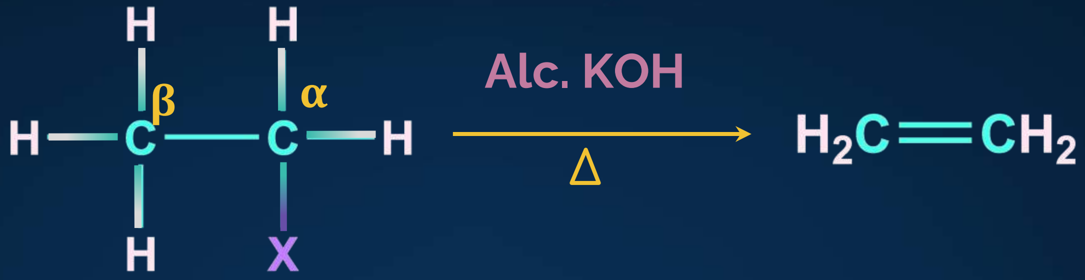
Preparation of Alkenes from Alkyl halides

By **Dehydrohalogenation**

Elimination of HX

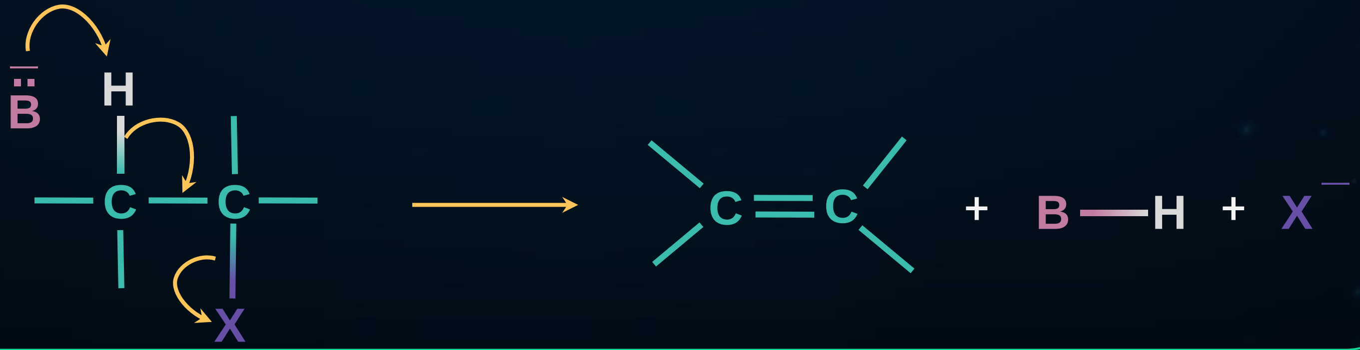
Reagent: **Alcoholic KOH**

Dehydrohalogenation of RX



X: Cl, Br, I

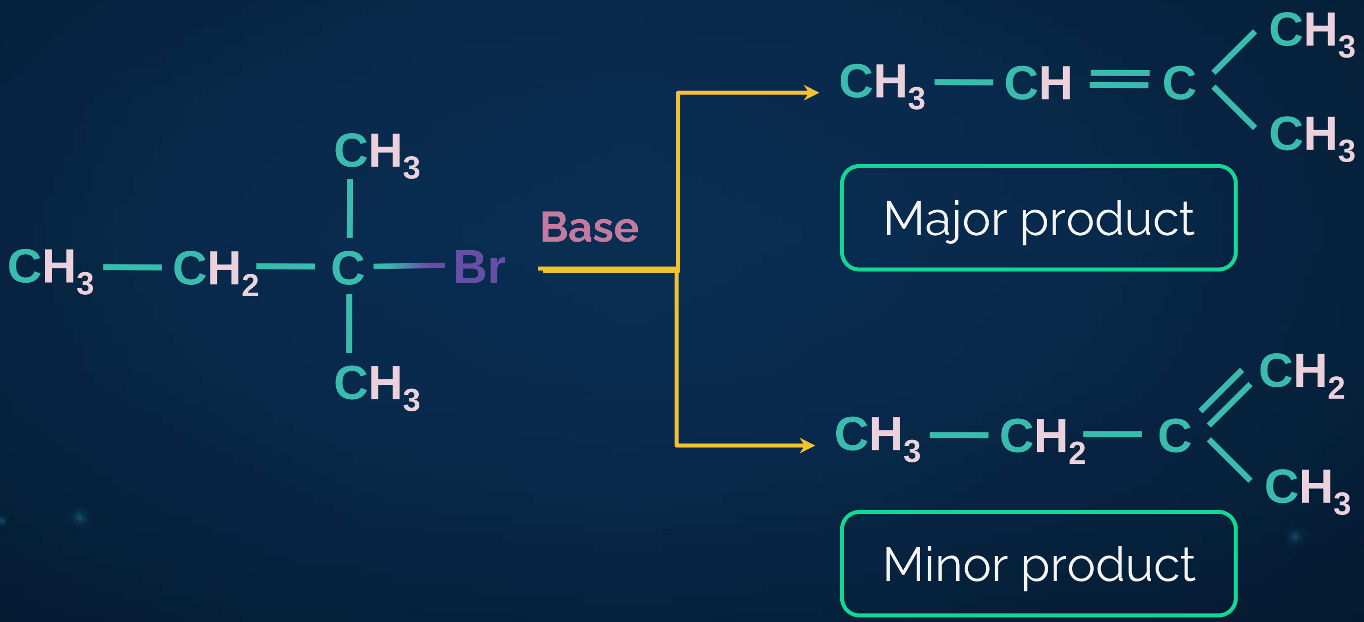
β-H is removed, hence called **β-Elimination reaction.**



Saytzeff or Zaitsev Rule

In most elimination reactions where there are 2 or more possible products, the predominant product will be the one with the **highly substituted double bond.**

Saytzeff or Zaitsev Rule



Dehydrohalogenation of RX

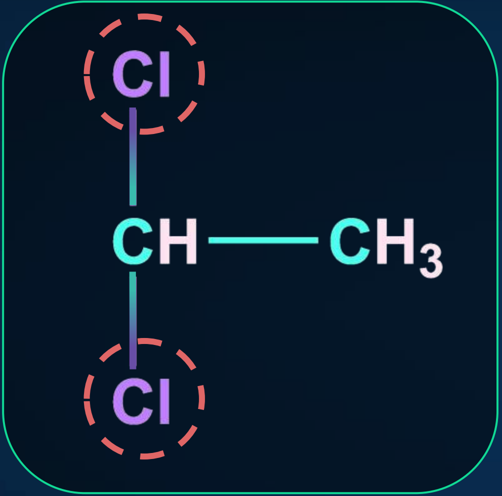
Reactivity

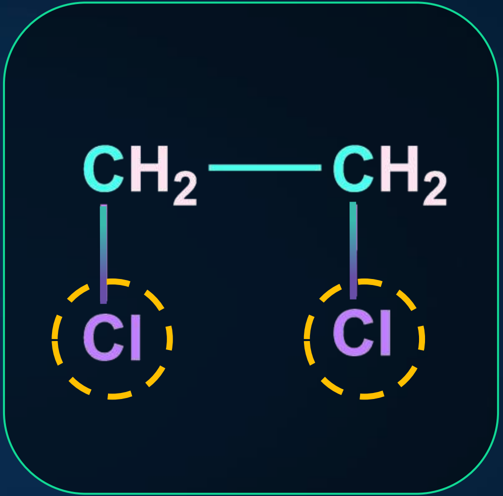
R-I > R-Br > R-Cl > R-F

Rate

3° Alkyl halide > 2° Alkyl halide > 1° Alkyl halide

Vicinal vs Geminal





1,1-Dichloroethane

Geminal Dihalide

1,2-Dichloroethane

Vicinal Dihalide

Preparation of Alkenes from Vicinal Dihalides

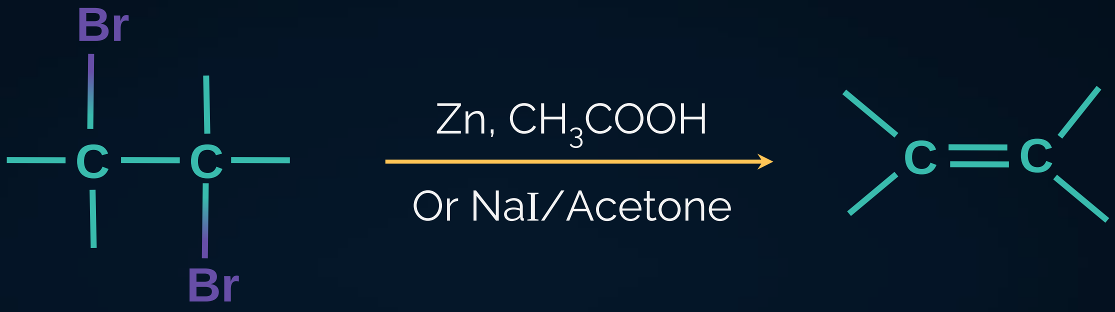
Elimination of X_2

By **Dehalogenation**

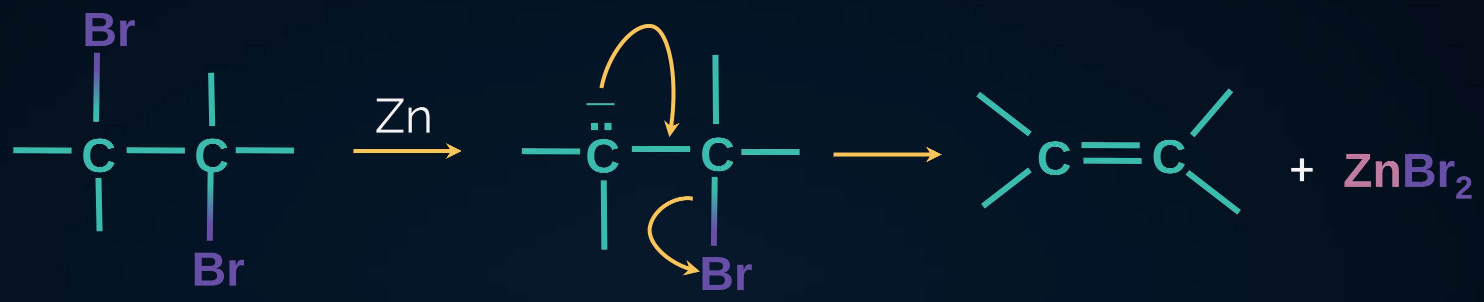
Reagent:

NaI in acetone or **Zn** in the presence of acetic acid or ethanol or **Zn**/Δ

Dehalogenation of Vicinal Dihalides



Mechanism



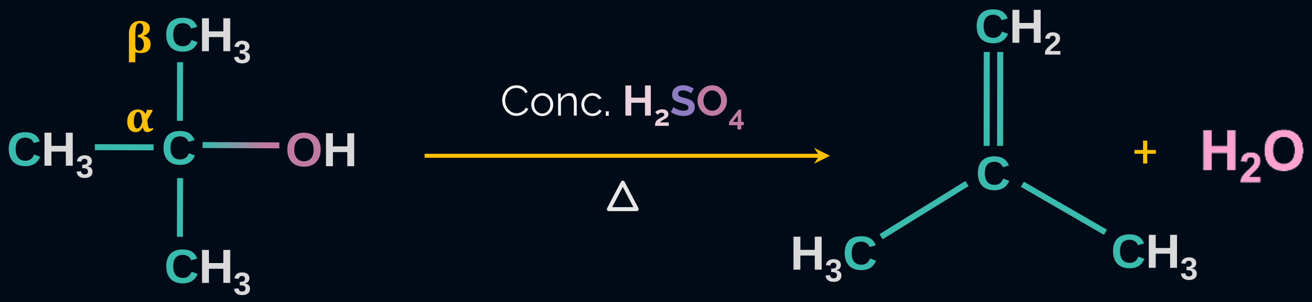
Preparation of Alkenes from Alcohols

By **acidic dehydration**

Elimination of H_2O

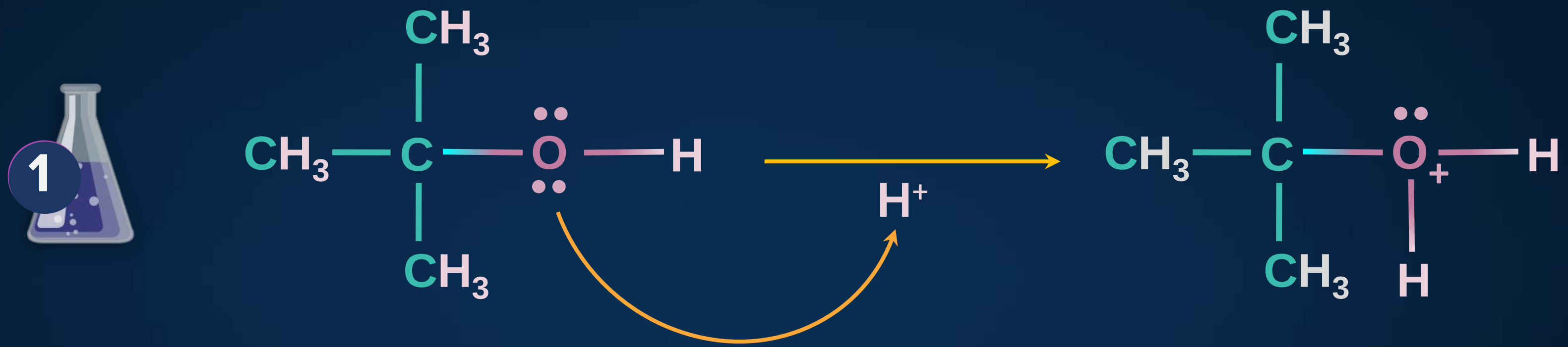
Reagent: Conc. H_2SO_4

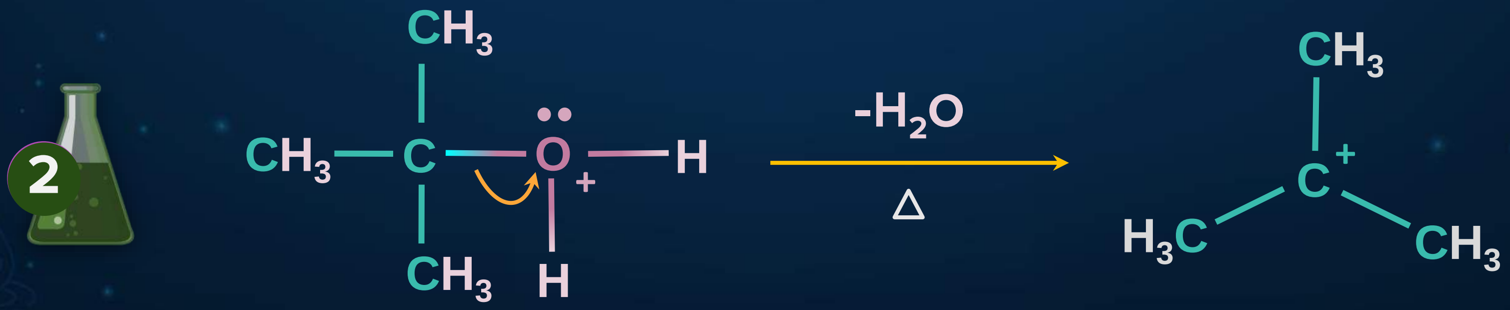
Dehydration of ROH



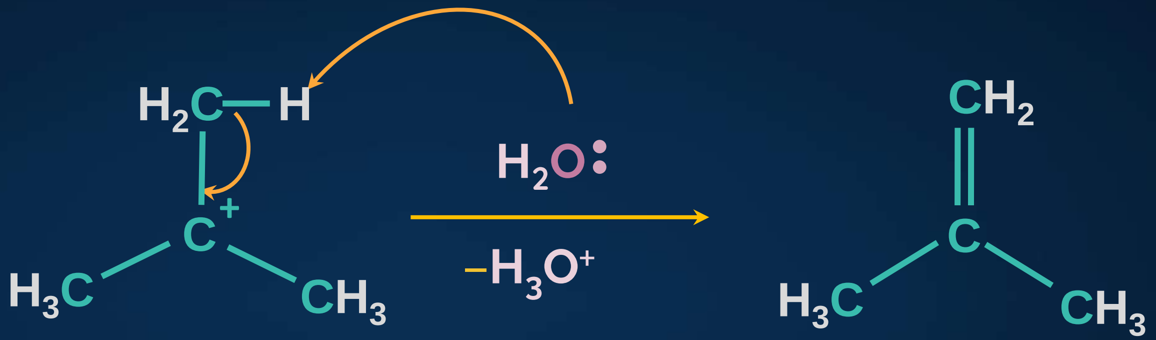
β-H is removed, hence it is called **β-elimination reaction**.

Mechanism


1
CH3
CH3—C—Ö—H
CH3
H+
CH3
CH3—C—Ö+—H
CH3 H


2
CH3
CH3—C—Ö+—H
CH3 H
-H2O
Δ
CH3
C+
H3C CH3

Mechanism

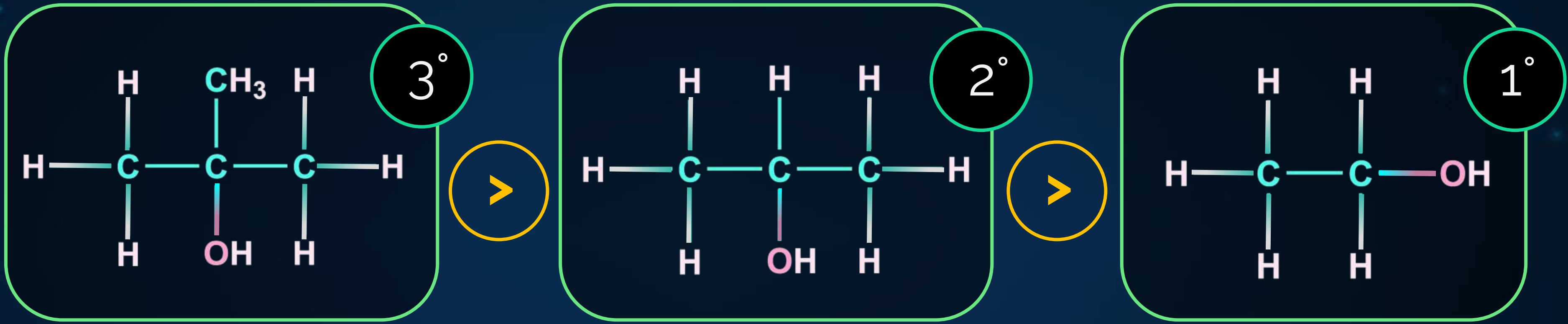


Ease of Dehydration

Ease of dehydration depends upon the **stability of the intermediate** (**carbocation**) formed.

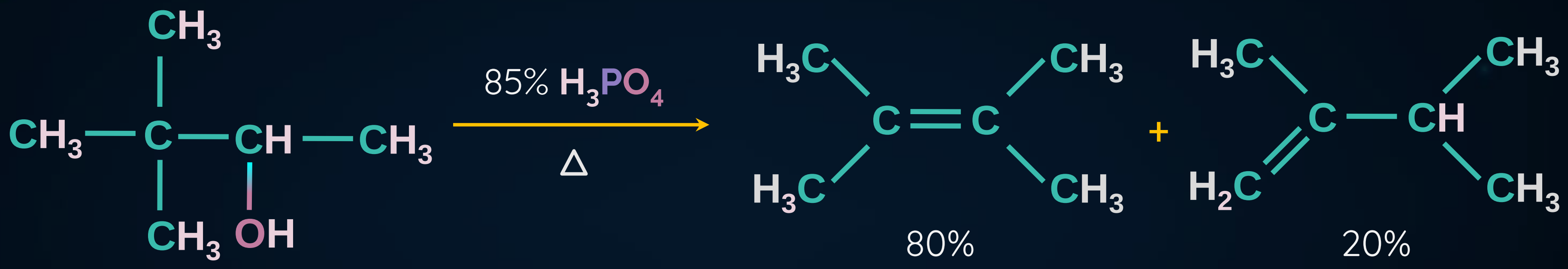
Some **primary & secondary** alcohols also undergo **rearrangements** of their carbon skeletons during dehydration.

Order of Reactivity of Alcohol



Some alcohols also **undergo rearrangements** in their carbon skeletons during dehydration.

Dehydration of ROH



Generally, in the dehydration of alcohols, **Saytzeff** products are the **major** products.

Remember!!

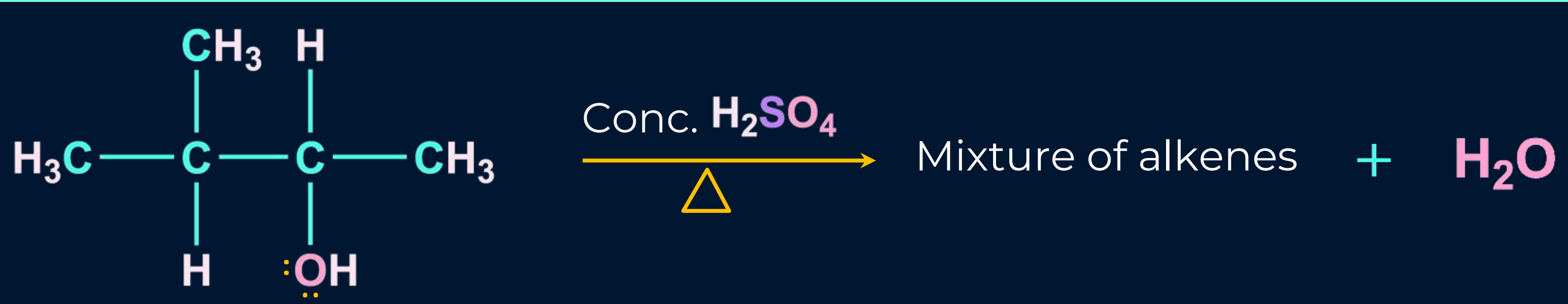
Migrating Tendency

Generally,

Alkyl < Phenyl < Hydride

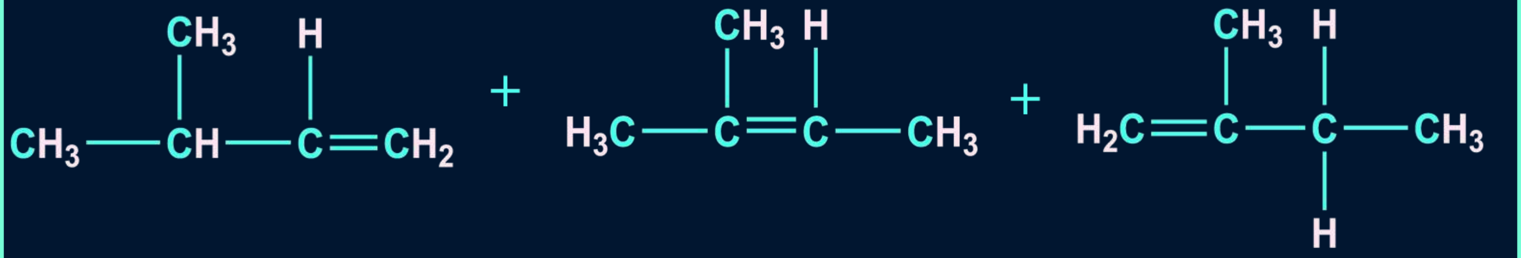
$1^\circ < 2^\circ < 3^\circ$

Dehydration of 3-Methylbutan-2-ol



$$H_3C-\underset{H}{\overset{CH_3}{C}}-\underset{:\ddot{O}H}{\overset{H}{C}}-CH_3 \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} \text{Mixture of alkenes} + H_2O$$

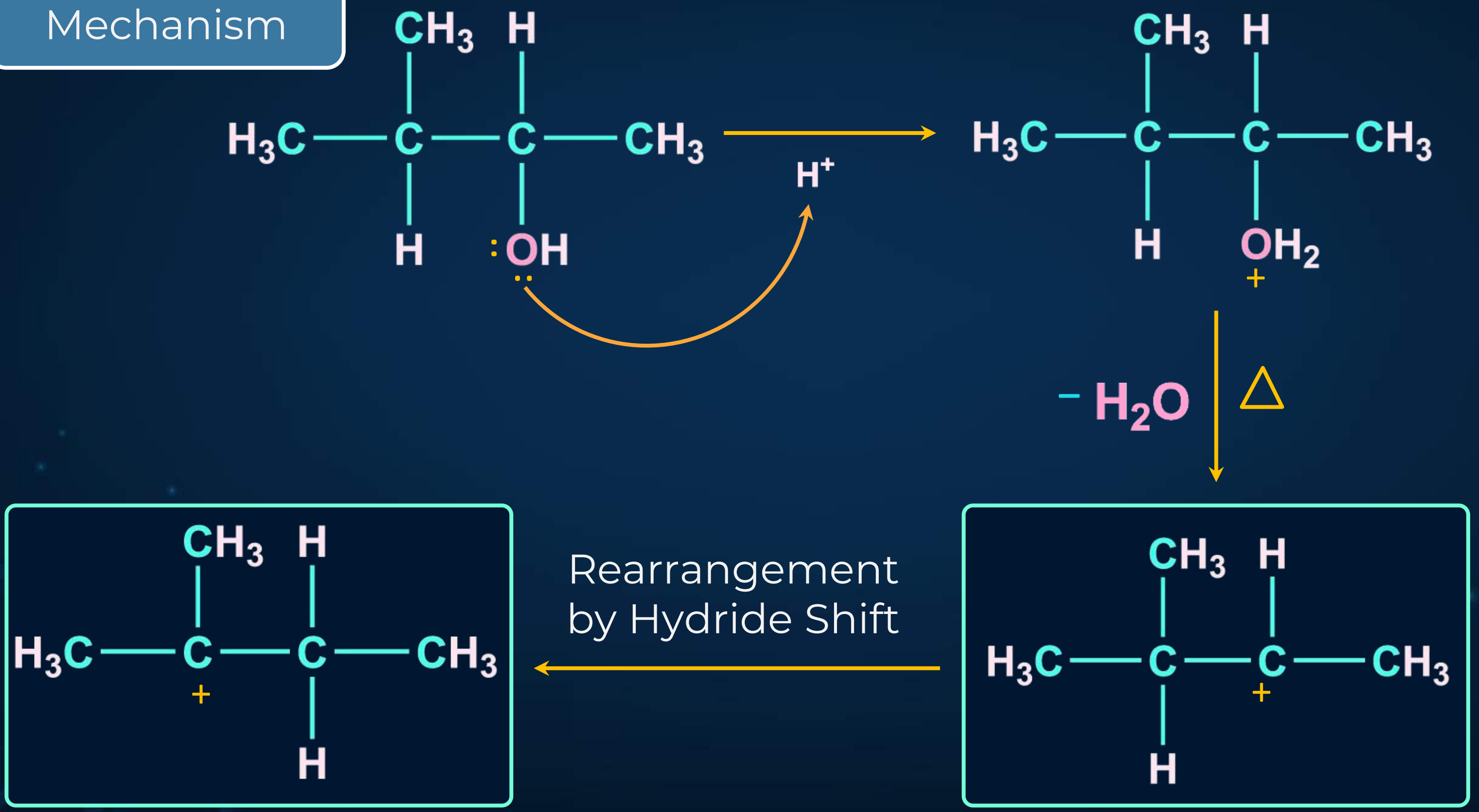
3 possible alkenes



$$CH_3-\overset{CH_3}{CH}-\overset{H}{C}=CH_2 + H_3C-\overset{CH_3}{C}=\overset{H}{C}-CH_3 + H_2C=\overset{CH_3}{C}-\underset{H}{\overset{H}{C}}-CH_3$$

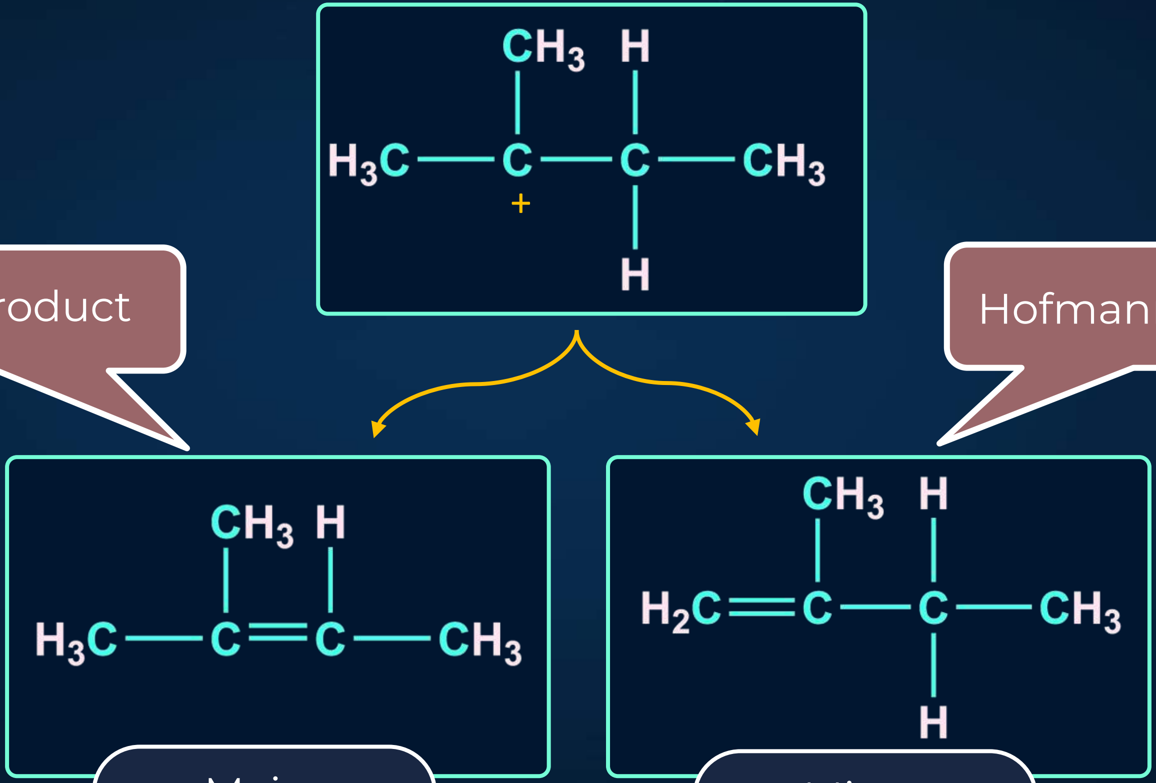
Dehydration of 3-Methylbutan-2-ol

Mechanism



Rearrangement by Hydride Shift

Dehydration of 3-Methylbutan-2-ol



Saytzeff product

Hofmann product

Major

Minor

Physical Properties of Alkenes

- **a** Physical State
- **b** Colour
- **c** Odour
- **d** Solubility
- **e** Boiling Point

Physical State of Alkenes

At 298 K,

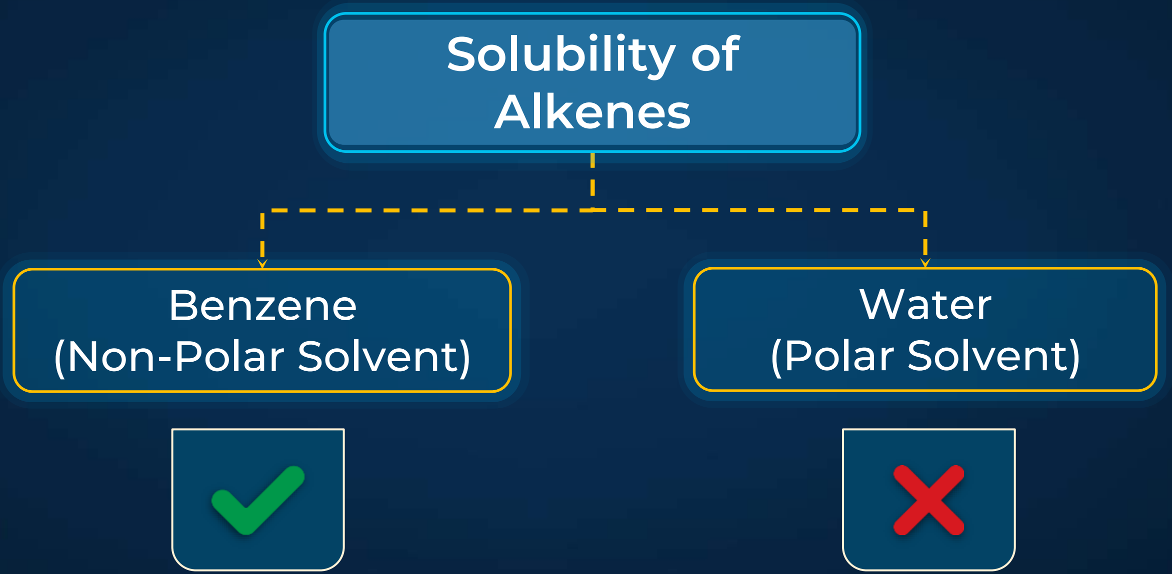
Number of C atoms in alkene	State
2 - 4	Gases
5 - 18	Liquids
≥ 19	Solids

Color and Odour of Alkenes

Alkenes are **colourless.**

Number of C atoms in alkene	Odour
2	Faint sweet smell
≥ 3	Odourless

Solubility of Alkenes



Solubility of Alkenes

Benzene
(Non-Polar Solvent)

✓

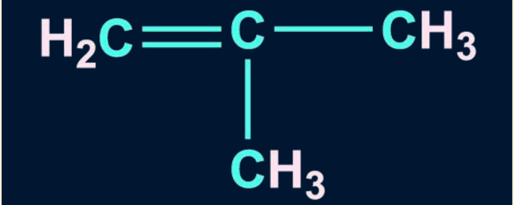
Water
(Polar Solvent)

✗

Boiling Point of Alkenes

Boiling point ∝ van der Waals force ∝ Molar mass

Like alkanes, **straight chain** alkenes also have **higher B.P.** than their isomeric **branched** counterparts.



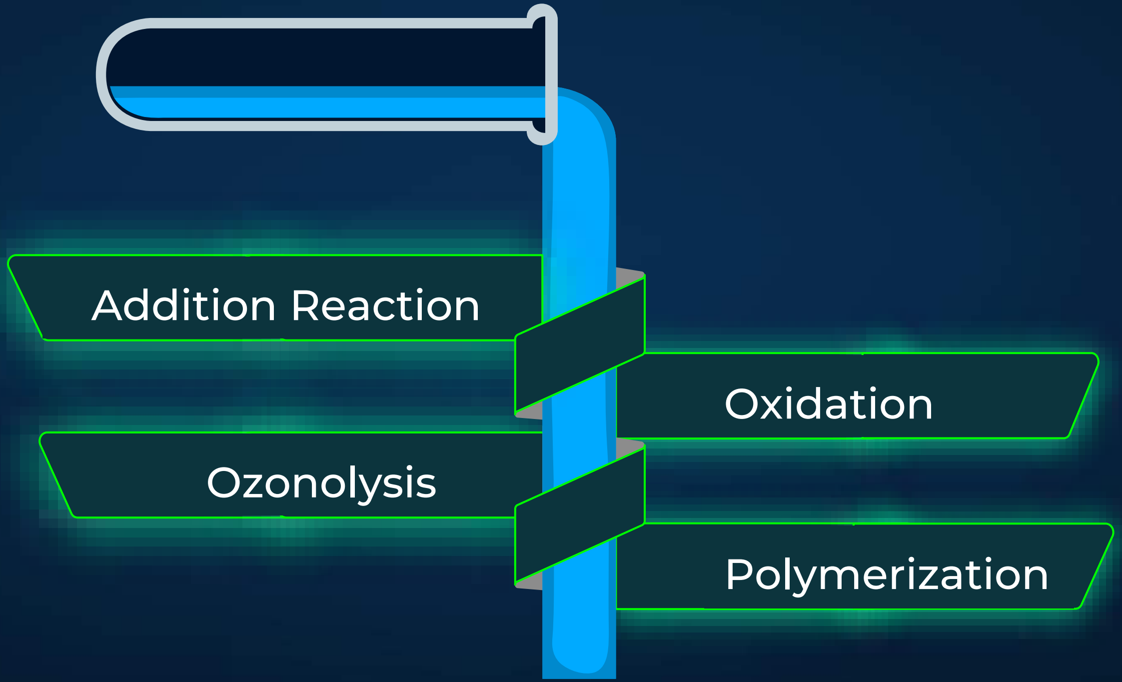
$$H_2C{=}C(CH_3){-}CH_3$$

2-Methylpropene
B.P.: -7 °C

$$H_2C{=}CH{-}CH_2{-}CH_3$$

But-1-ene
B.P.: -6.5 °C

Chemical Properties of Alkenes



Addition Reaction

Oxidation

Ozonolysis

Polymerization

Addition Reactions of Alkenes

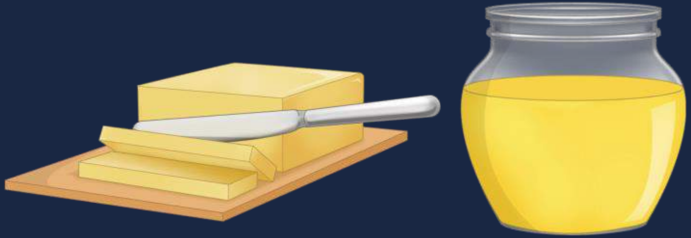
Alkenes are rich sources of
loosely held π electrons.

Addition of H_2

$$H_2C{=}CH_2 + H_2 \xrightarrow{\text{Ni/Pt/Pd}} CH_3{-}CH_3$$

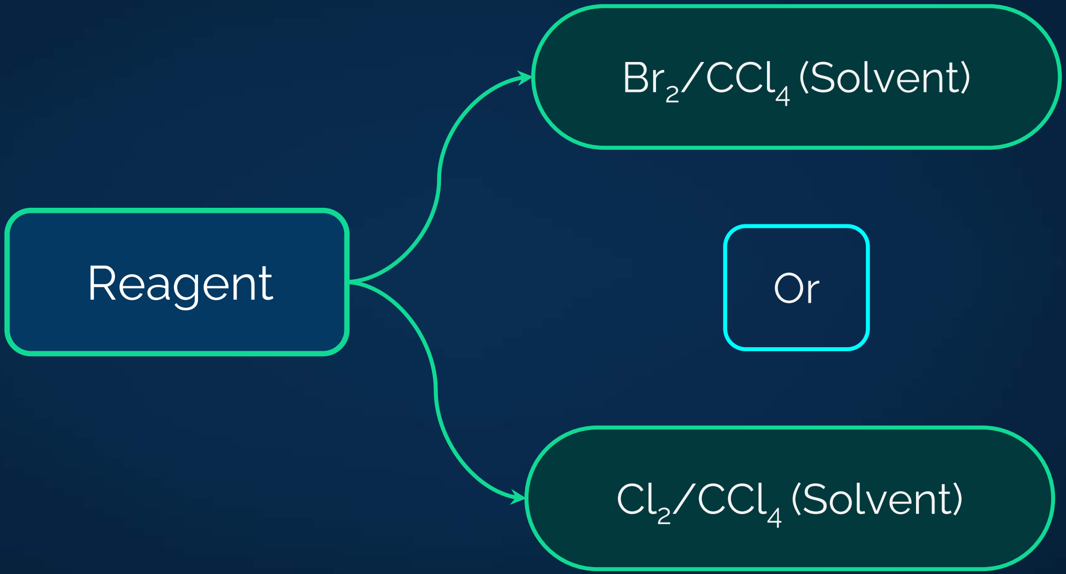
Vegetable Oils

$$\xrightarrow[\text{473 K, Ni}]{H_2}$$



Margarine and Vanaspati ghee

Addition of Halogens



Reagent

Br_2/CCl_4 (Solvent)

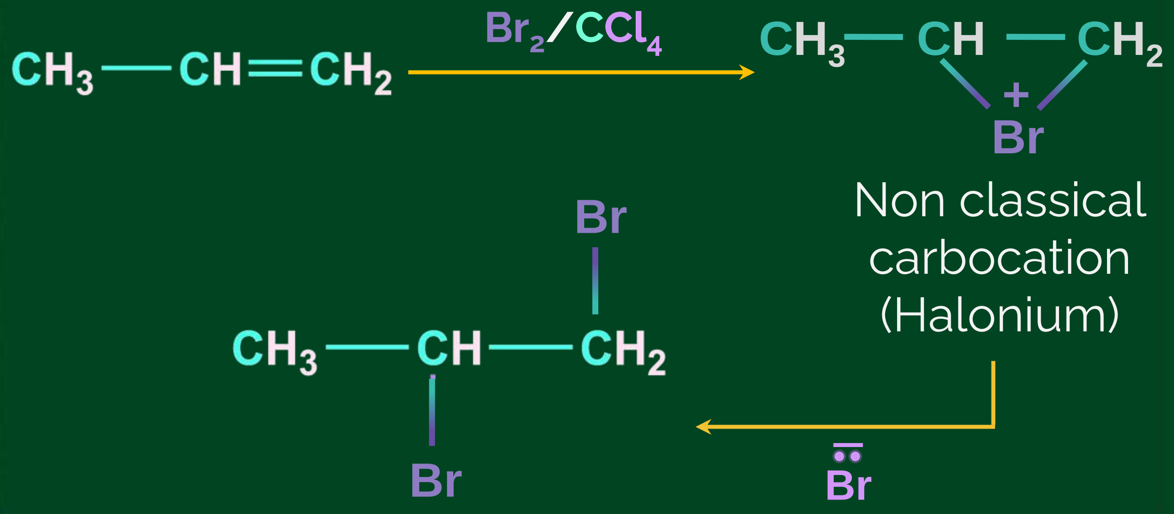
Or

Cl_2/CCl_4 (Solvent)

Addition of Halogens

Addition of halogens to alkenes is an example of **electrophilic addition reaction** involving **cyclic halonium ion** formation.

Addition of Halogens



$CH_3-CH=CH_2 \xrightarrow{Br_2/CCl_4} CH_3-\overset{+}{\underset{\overset{\frown}{Br}}{CH-CH_2}}$

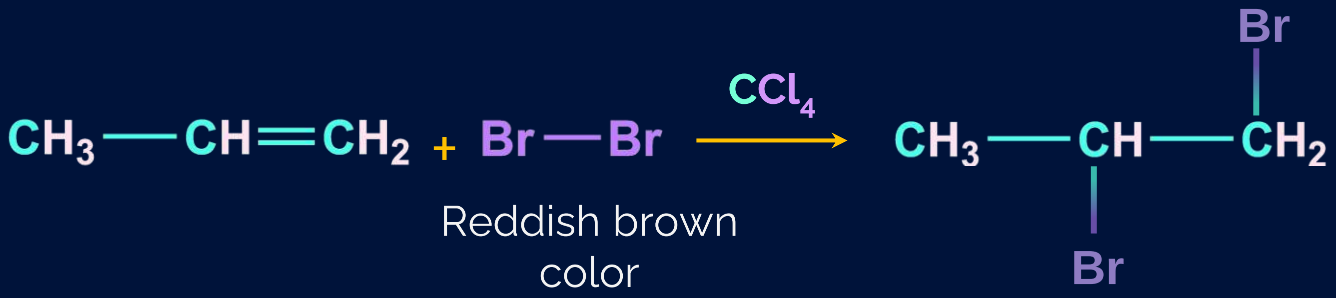
Non classical carbocation (Halonium)

$\xrightarrow{\ddot{\bar{Br}}}$ $CH_3-\underset{Br}{CH}-\overset{Br}{CH_2}$

Remarks

- Anti addition
- No rearrangement
- Non classical carbocation

Test for Unsaturation



$$CH_3-CH=CH_2 + Br-Br \xrightarrow{CCl_4} CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-\overset{\displaystyle Br}{\overset{|}{CH_2}}$$

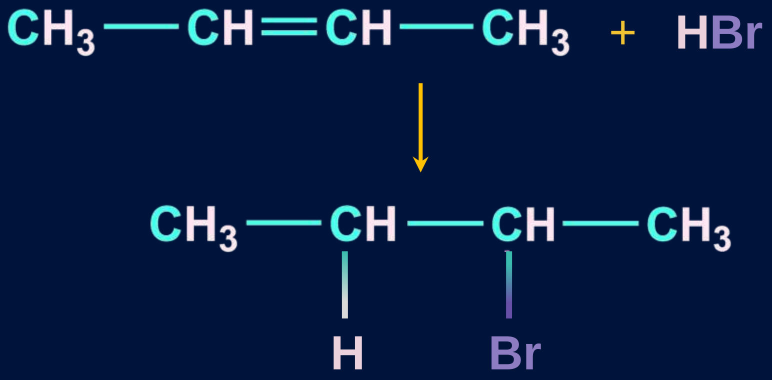
Reddish brown color

Colorless

Addition of Hydrogen Halides (HX)

Addition of HBr to a **symmetrical** alkene

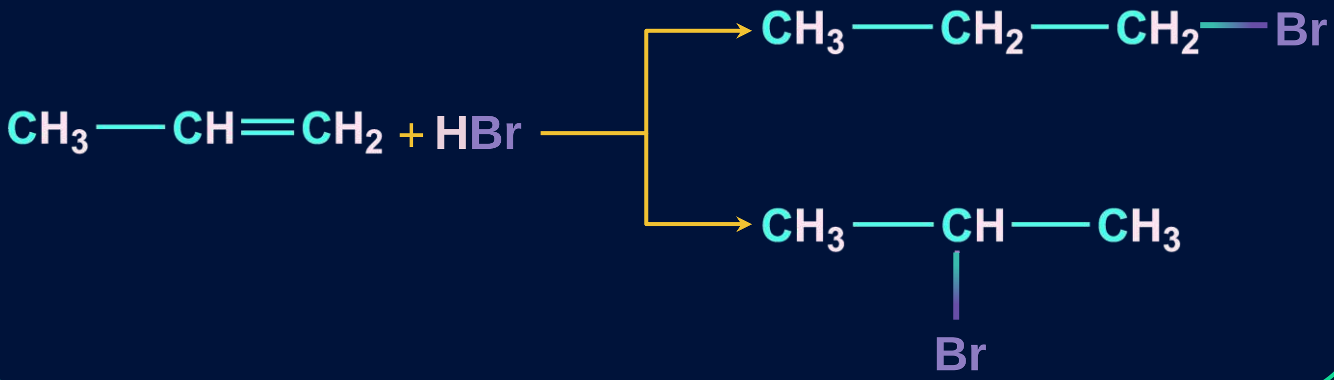
$$H_2C{=}CH_2 + HBr \longrightarrow \underset{\overset{|}{H}}{CH_2}-\underset{\overset{|}{Br}}{CH_2}$$



$$CH_3-CH{=}CH-CH_3 + HBr \longrightarrow CH_3-\underset{\overset{|}{H}}{CH}-\underset{\overset{|}{Br}}{CH}-CH_3$$

Addition of Hydrogen Halides (HX)

Addition of HBr to an **unsymmetrical** alkene.



$$CH_3-CH=CH_2 + HBr \rightarrow CH_3-CH_2-CH_2-Br$$

$$CH_3-CH=CH_2 + HBr \rightarrow CH_3-\underset{\overset{|}{Br}}{CH}-CH_3$$

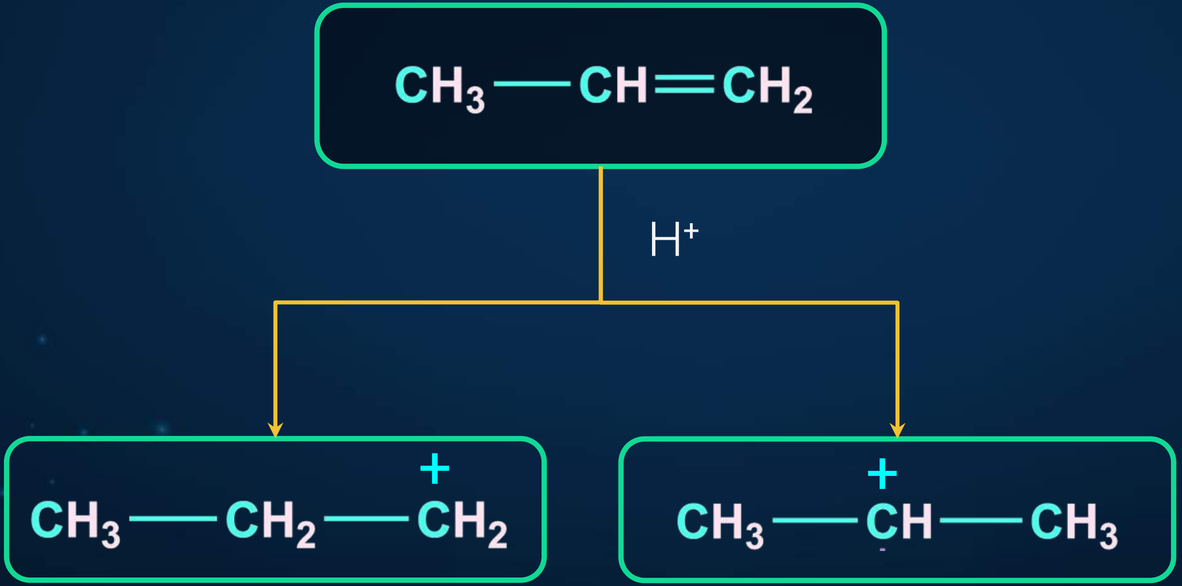
Markovnikov’s Rule

In the ionic addition of an **unsymmetrical reagent** to a double bond, the **positive portion** of the added reagent attaches itself to the carbon atom of the double bond, so as to yield the **more stable carbocation as an intermediate**.

Mechanism

1

Attack of double bond on H^+ (Electrophilic addition)



$CH_3—CH{=}CH_2$

H^+

$CH_3—CH_2—\overset{+}{C}H_2$

$CH_3—\overset{+}{C}H—CH_3$

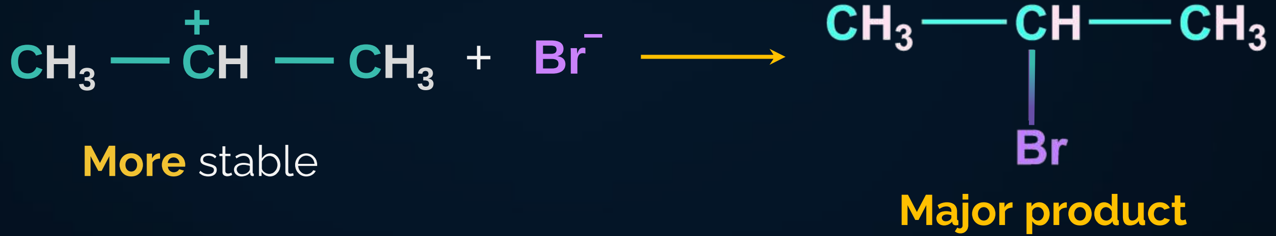
Less stable

More stable

Mechanism

2

Attack of Br^- on the carbocation

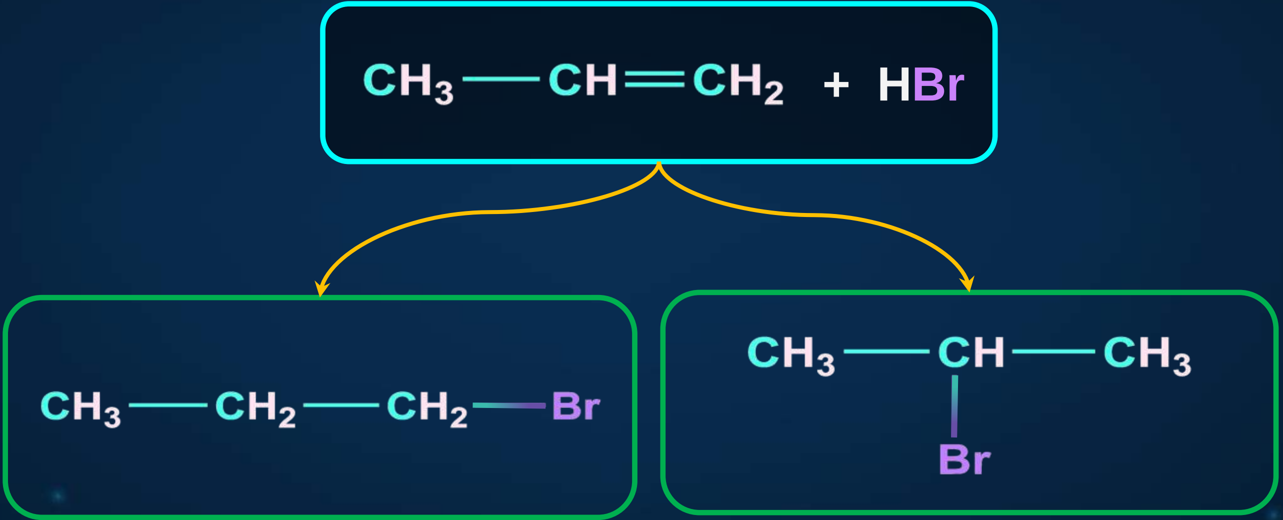


$$CH_3-\overset{+}{C}H-CH_3 + Br^- \longrightarrow CH_3-\underset{\underset{Br}{|}}{C}H-CH_3$$

More stable

Major product

Addition of Hydrogen Halides



$CH_3-CH=CH_2 + HBr$

$CH_3-CH_2-CH_2-Br$

Minor product

$CH_3-\underset{\underset{Br}{|}}{CH}-CH_3$

Major product

Addition of Hydrogen Halides

Order of reactivities of Hydrogen halides

$HF < HCl < HBr < HI$

Anti-Markovnikov Addition

When **alkenes** are treated with **HBr** in the presence of peroxides, anti-Markovnikov's addition occurs such that the **H - atom of HBr gets attached** to the C - atom with the **fewer H - atoms.**

Also known as **Peroxide** or **Kharasch effect.**

Anti-Markovnikov Addition

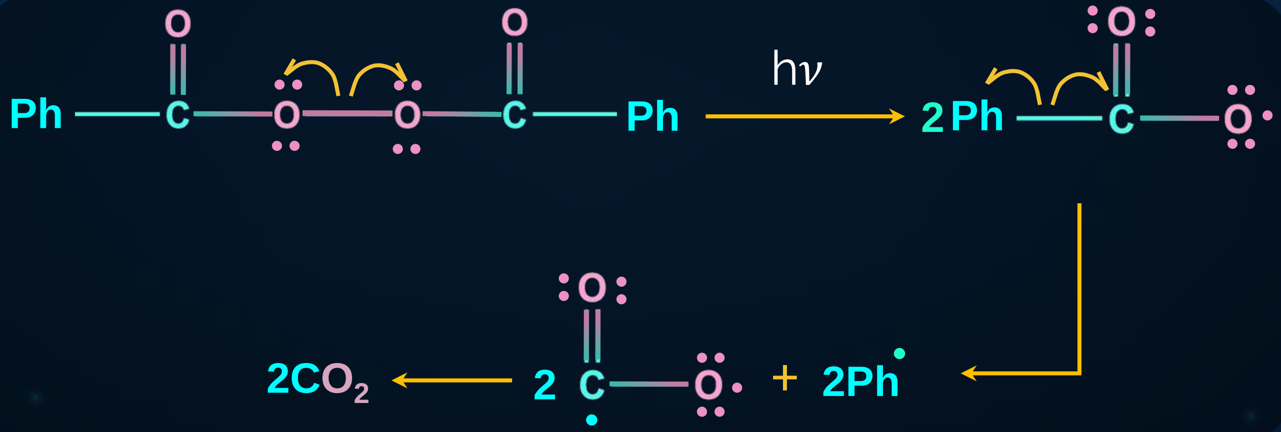
$$CH_3-CH=CH_2 + HBr \xrightarrow[h\nu]{(C_6H_5CO)_2O_2} CH_3-CH_2-CH_2-Br$$

The mechanism for anti-Markovnikov's addition of HBr is a **free radical chain reaction** initiated by a peroxide.

Chain Initiation

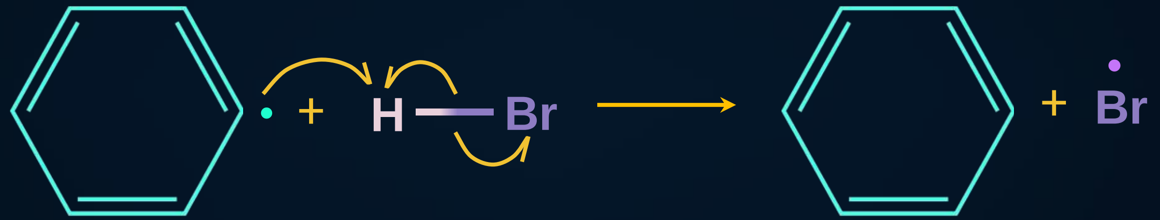
1

Generation of free radicals



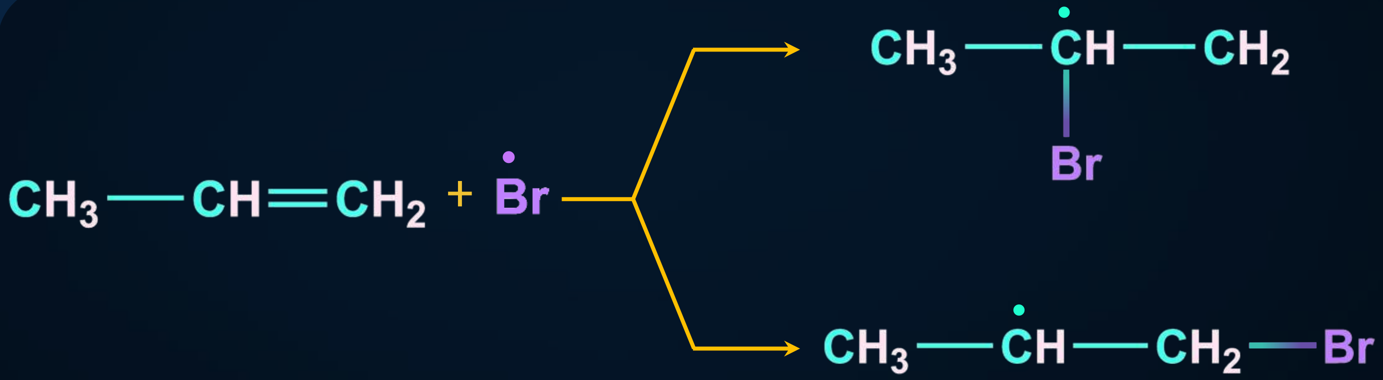
Chain Initiation

2 Attack of the formed free radical on HX



Chain Propagation

3 Attack of $\dot{X}$ on the alkene



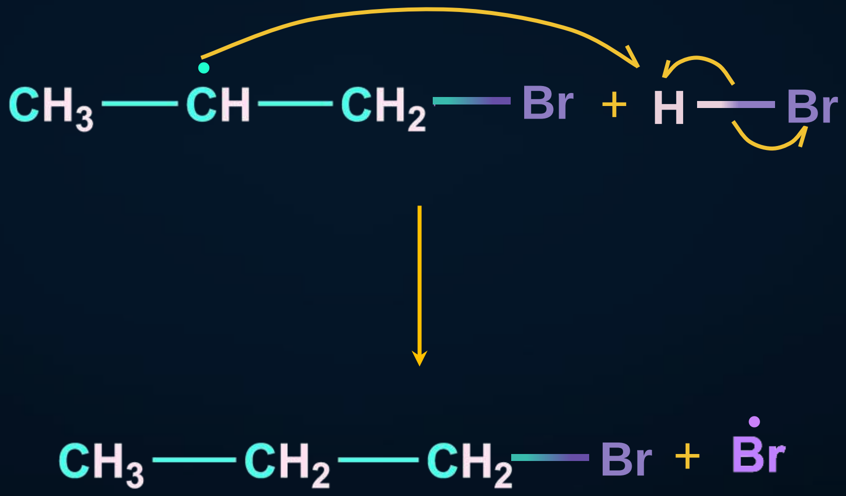
$$CH_3-CH=CH_2 + \dot{Br} \rightarrow CH_3-\underset{\substack{|\\ Br}}{\dot{C}H}-CH_2$$

$$CH_3-CH=CH_2 + \dot{Br} \rightarrow CH_3-\dot{C}H-CH_2-Br$$

1° Alkyl radical < 2° Alkyl radical < 3° Alkyl radical

Chain Propagation

4 Attack of the formed radical on HX



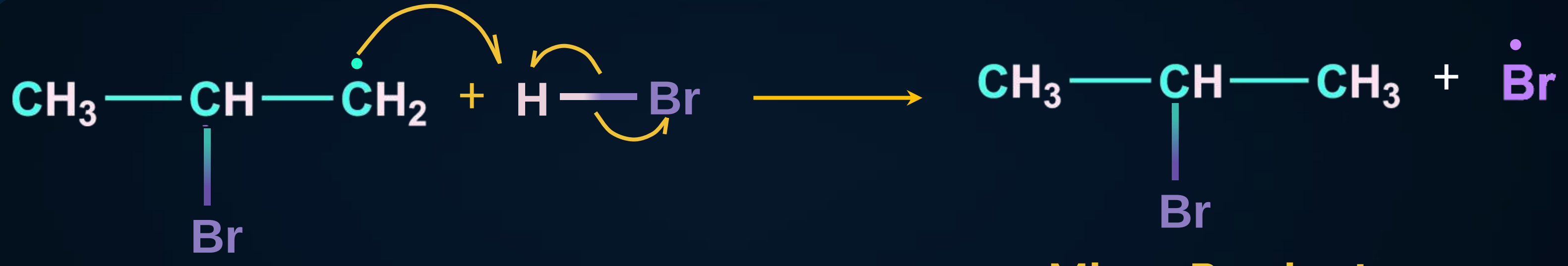
$$CH_3-\dot{C}H-CH_2-Br + H-Br \longrightarrow CH_3-CH_2-CH_2-Br + \dot{B}r$$

Major Product

Chain Propagation

4

Attack of the formed radical on HX



$$CH_3-\underset{\underset{Br}{|}}{CH}-\dot{C}H_2 + H-Br \longrightarrow CH_3-\underset{\underset{Br}{|}}{CH}-CH_3 + \dot{Br}$$

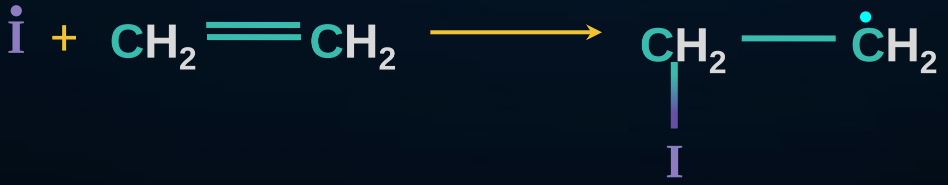
Minor Product

The formed **Br** radical reacts again with the alkene to setup a **chain of reactions**.

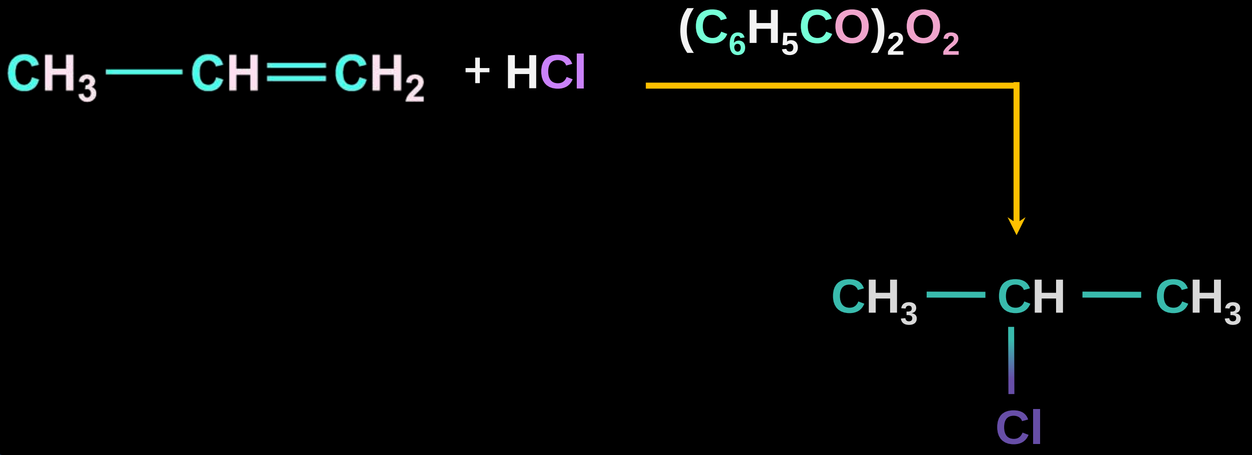
Cleavage of HCl or HF bond by alkyl radical is **endothermic**.

$$ClCH_2\dot{C}H_2 + HCl \longrightarrow ClCH_2CH_3 + \dot{Cl} \; ; \Delta H^\circ = +8 \text{ kJ/mol}$$

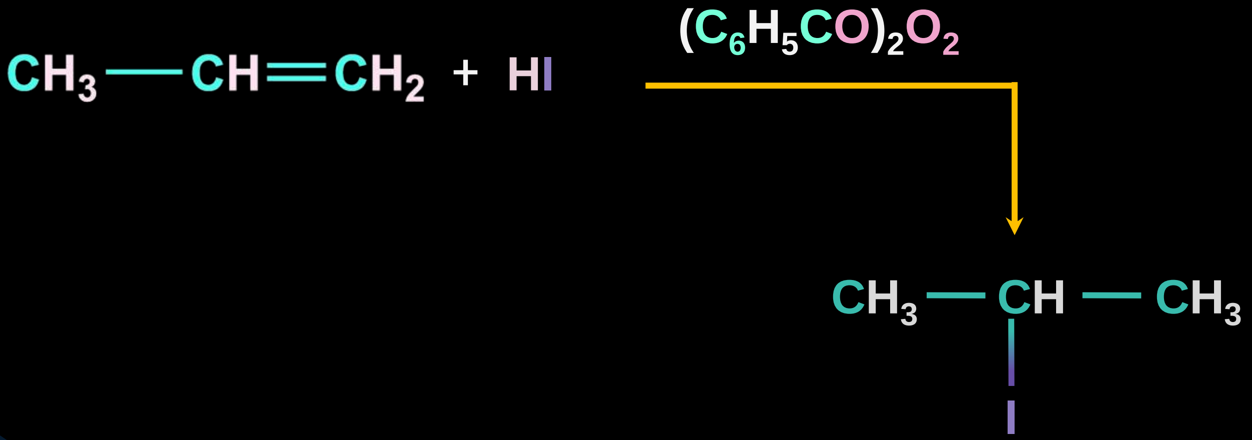
Reaction of alkene with $\dot{I}$ is **endothermic**.



$$\dot{I} + CH_2{=}CH_2 \longrightarrow \underset{\displaystyle I}{\underset{|}{C}}H_2{-}\dot{C}H_2 \; ; \Delta H^\circ = +33 \text{ kJ/mol}$$



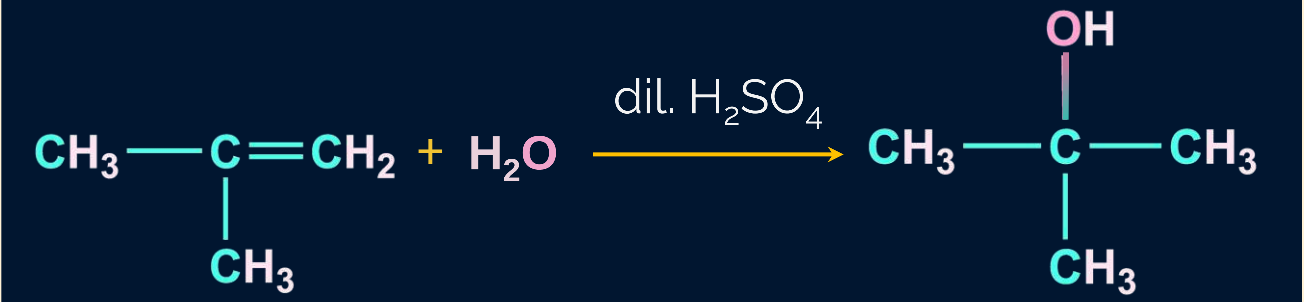
$$CH_3-CH=CH_2 + HCl \xrightarrow{(C_6H_5CO)_2O_2} CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3$$



$$CH_3-CH=CH_2 + HI \xrightarrow{(C_6H_5CO)_2O_2} CH_3-\underset{\underset{I}{|}}{CH}-CH_3$$

Addition of Water

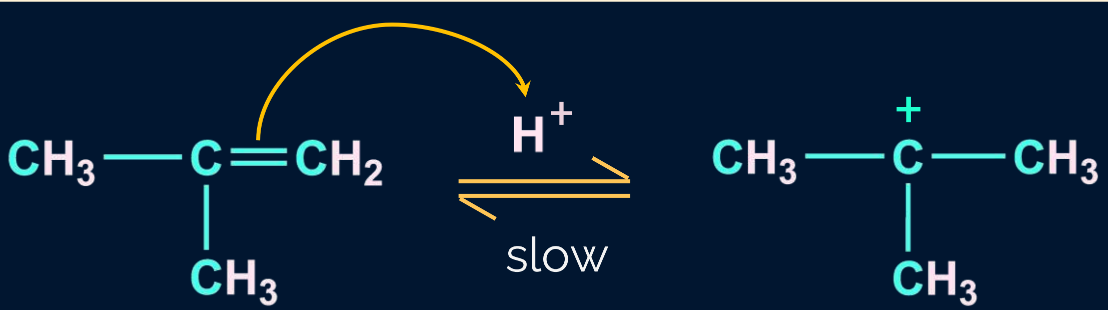
Addition of H_2O/H^+
to alkenes is a **Markovnikov addition**
reaction.



$$CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2 + H_2O \xrightarrow{\text{dil. } H_2SO_4} CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

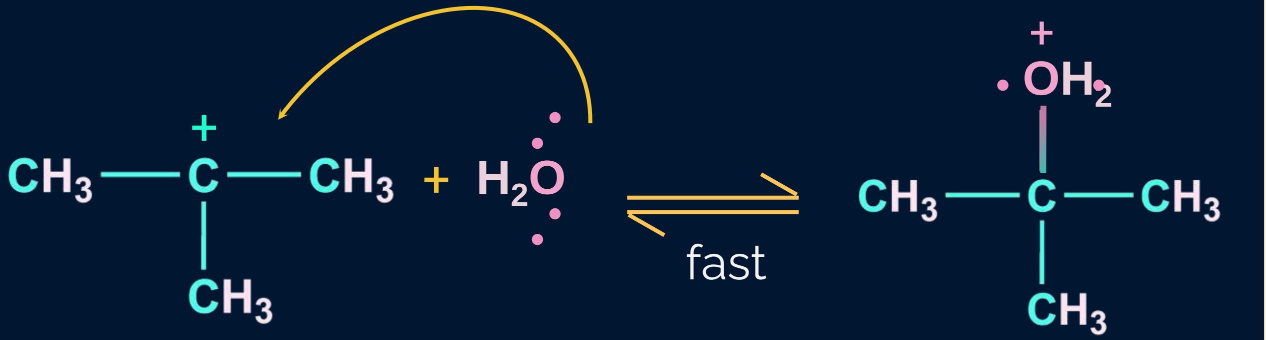
Mechanism

1



$$CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2 \underset{\text{slow}}{\overset{H^+}{\rightleftharpoons}} CH_3-\overset{+}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

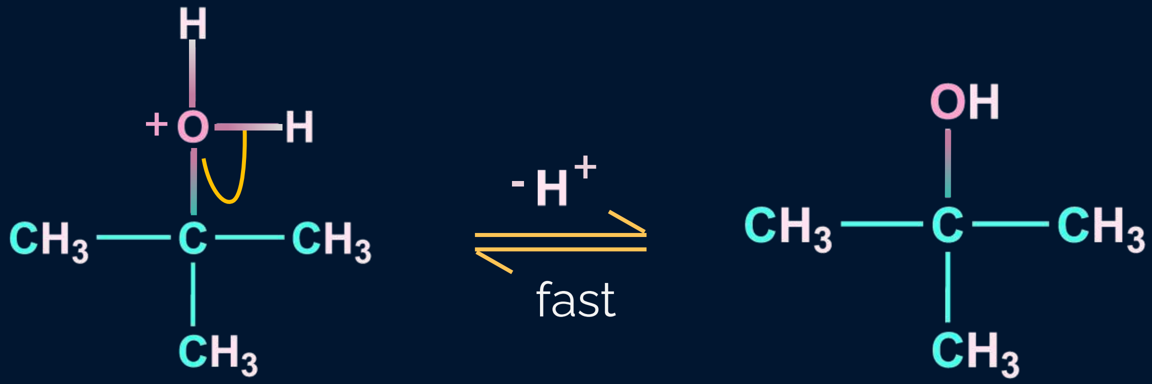
2



$$CH_3-\overset{+}{\underset{\underset{CH_3}{|}}{C}}-CH_3 + H_2\ddot{\underset{\cdot\cdot}{O}} \underset{\text{fast}}{\rightleftharpoons} CH_3-\overset{\overset{+}{\cdot OH_2}}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-CH_3$$

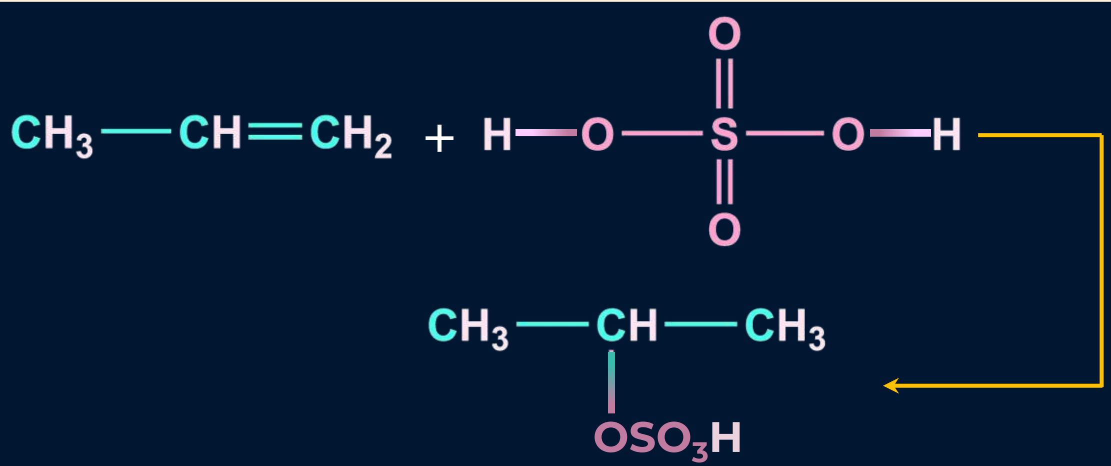
Mechanism

3



Addition of Sulphuric Acid

Addition of cold concentrated sulphuric acid to alkenes is a **Markovnikov addition** reaction.

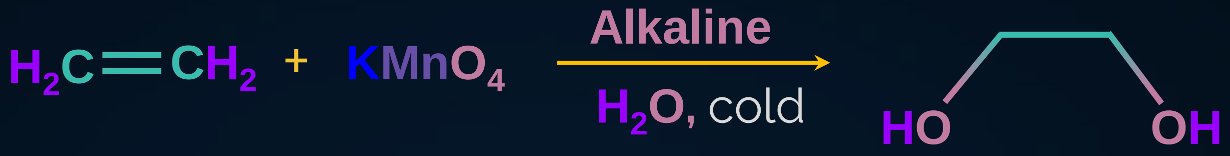


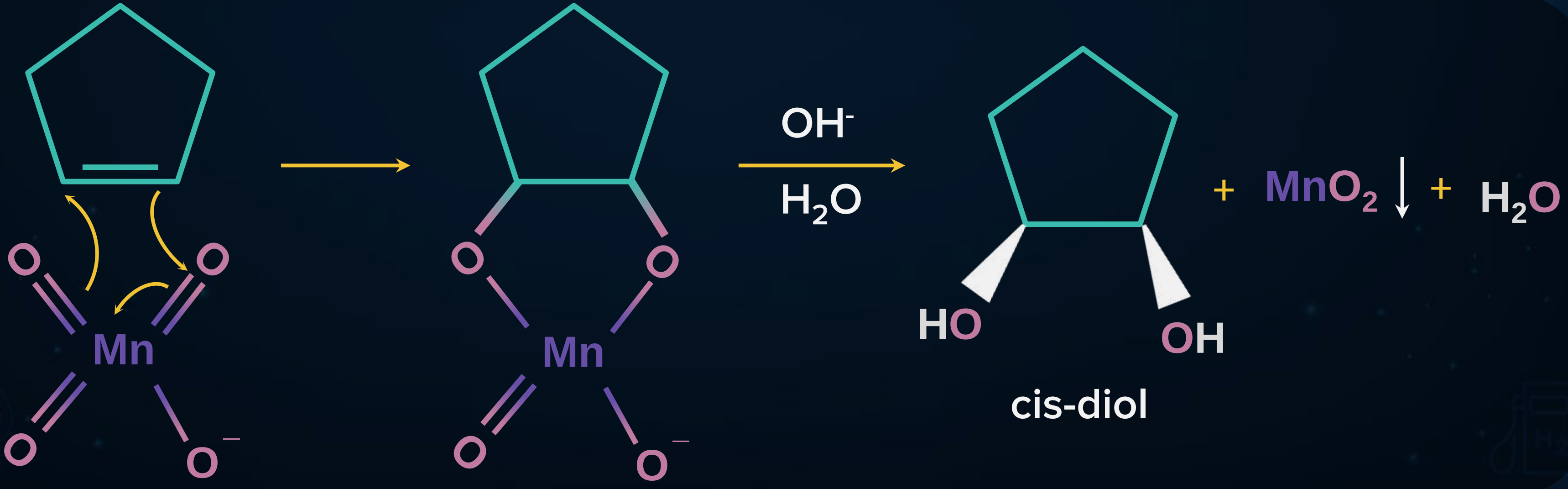
$$CH_3-CH=CH_2 + H-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-H \longrightarrow CH_3-\underset{\underset{OSO_3H}{|}}{CH}-CH_3$$

Oxidation of Alkenes

- Cold dil. alkaline $KMnO_4$ **(Baeyer's reagent)**
- Basic $KMnO_4$/ Acidic $K_2Cr_2O_7$

Oxidation using Baeyer's Reagent





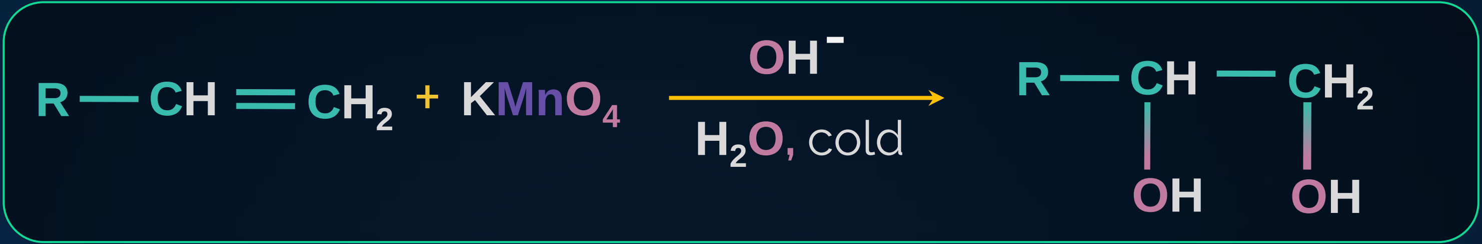
cis-diol

Oxidation using Baeyer's Reagent

This is used to **distinguish** between **saturated** (alkane) and **unsaturated** (alkene/alkyne) compounds.

$$R-CH_2-CH_3 + KMnO_4 \xrightarrow[H_2O,\ \text{cold}]{OH^-} \text{No reaction}$$

Oxidation using Baeyer's Reagent



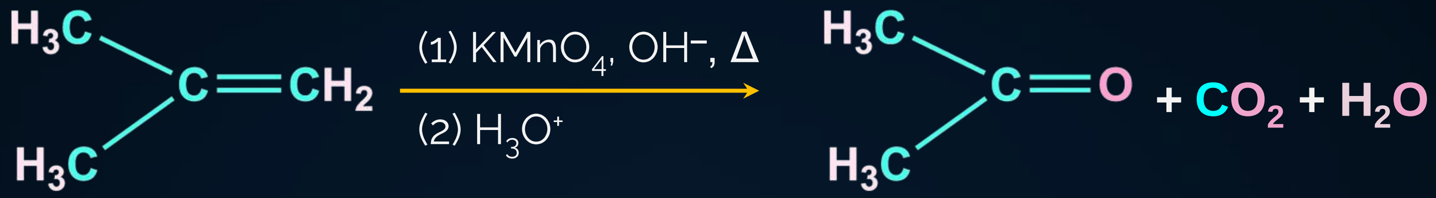
$$R-CH=CH_2 + KMnO_4 \xrightarrow[H_2O,\ \text{cold}]{OH^-} R-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle OH}{\underset{|}{CH_2}}$$

Purple color disappears

$$R-C\equiv C-R \xrightarrow{\text{Cold, dil. } KMnO_4} R-\overset{\displaystyle O}{\overset{\|}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-R$$

Purple color disappears

Oxidation using Basic $KMnO_4$/Acidified $K_2Cr_2O_7$



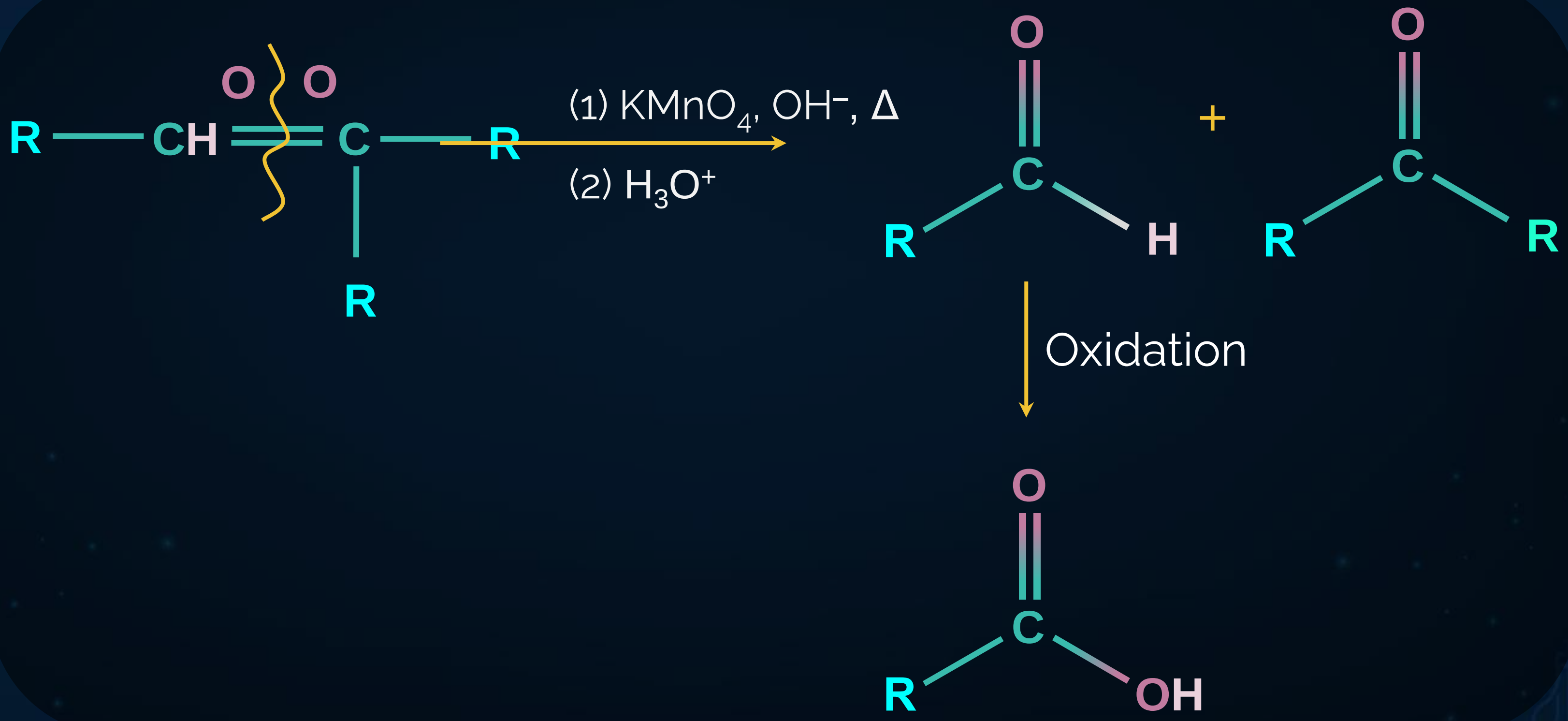
(1) $KMnO_4$, OH^-, Δ

(2) H_3O^+

$+ CO_2 + H_2O$

$$CH_3-CH=CH-CH_3 \xrightarrow[(2)\ H_3O^+]{(1)\ KMnO_4,\ OH^-,\ \Delta} 2CH_3COOH$$

Oxidation using Basic $KMnO_4$/Acidified $K_2Cr_2O_7$



Oxidation using Basic $KMnO_4$/Acidified $K_2Cr_2O_7$

$$R-C\equiv C-R' \xrightarrow[\text{(2) } H_3O^+]{\text{(1) } KMnO_4,\ OH^-,\ \Delta} RCO_2H + R'CO_2H$$

Ozonolysis

Alkenes, alkynes and polyalkenes on ozonolysis undergo **oxidative cleavage.** It can be **oxidative** or **reductive** ozonolysis depending upon the type of **reagents** used.

Reductive Ozonolysis

Reagents

i) O_3
ii) Zn or $(CH_3)_2S$ and H_2O or CH_3COOH

Products

Carbonyl compounds (aldehydes or ketones)

Oxidative Ozonolysis

Reagents

O_3 , H_2O

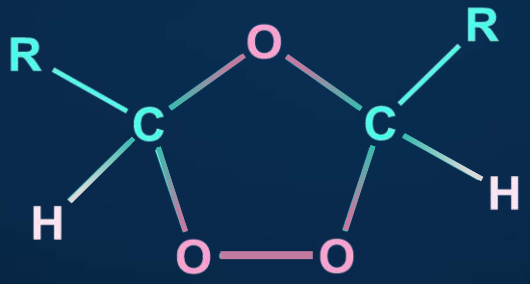
Products

Carboxylic Acid/Ketone

Ozonolysis

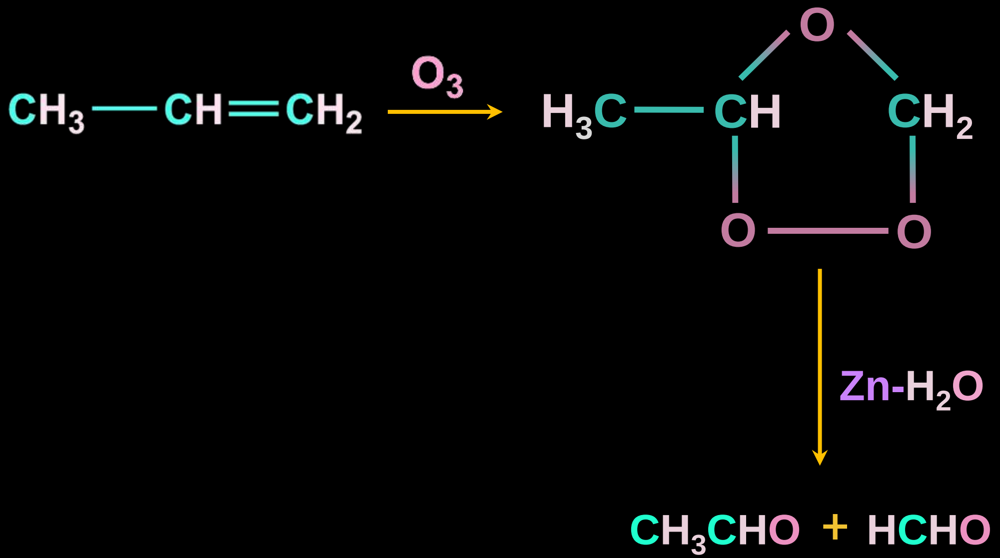
$$\text{Alkene} + O_3 \longrightarrow \text{Ozonide} \xrightarrow{\text{Zn-}H_2O} \text{Aldehyde/ Ketone}$$

Ozonide



Ozonide is a cyclic peroxide derivative

Ozonolysis



Polymerisation

Polymers are substances that consist of very large molecules that are made up of many **repeating subunits.**

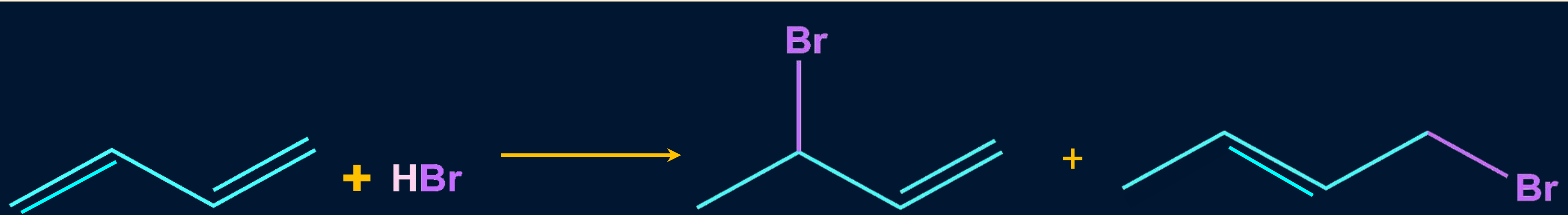
$$n\,H_2C{=}CH_2 \xrightarrow[\text{Catalyst}]{\text{High temp./Pressure}} -\!\!\left(CH_2-CH_2\right)_n\!\!-$$

Polythene

Alkadiene

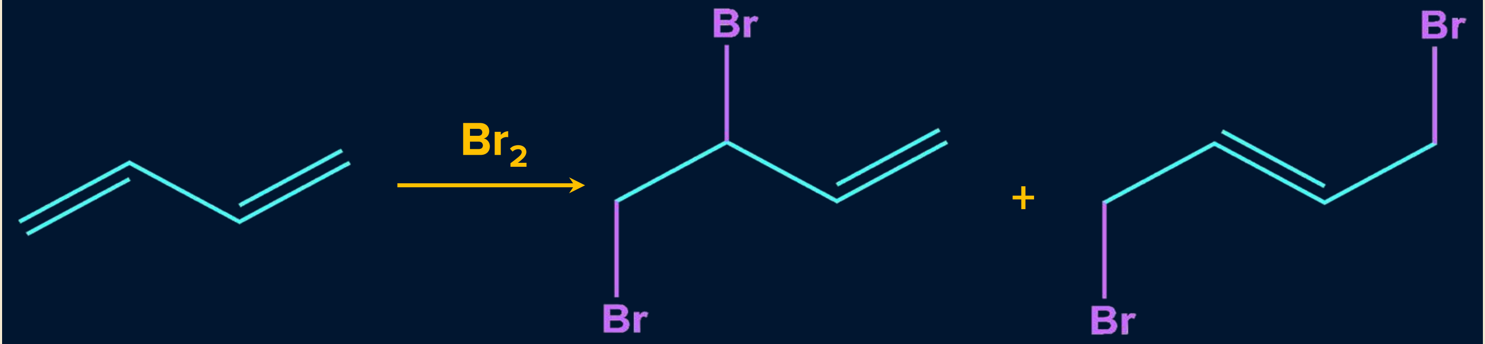
A **hydrocarbon** that contains two double bonds is called an **alkadiene.**

Chemical Properties



Major at -80 °C

Major at 40 °C



Major at -80 °C

Major at 40 °C

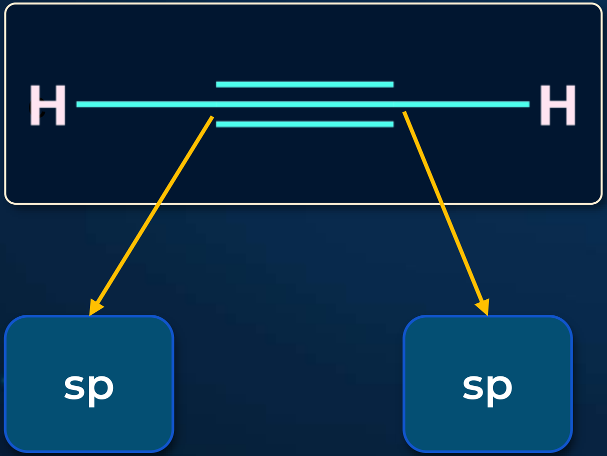
Alkynes

General Formula → C_nH_{2n-2}

Electron cloud between the two C atoms of an alkyne is **cylindrically symmetrical** about the internuclear axis.

Alkynes

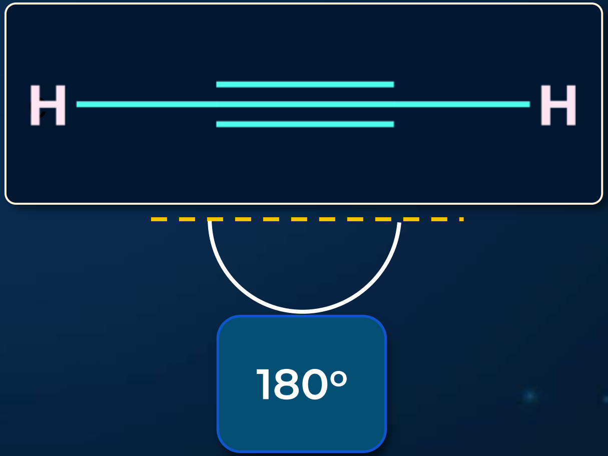
Hybridisation



sp

sp

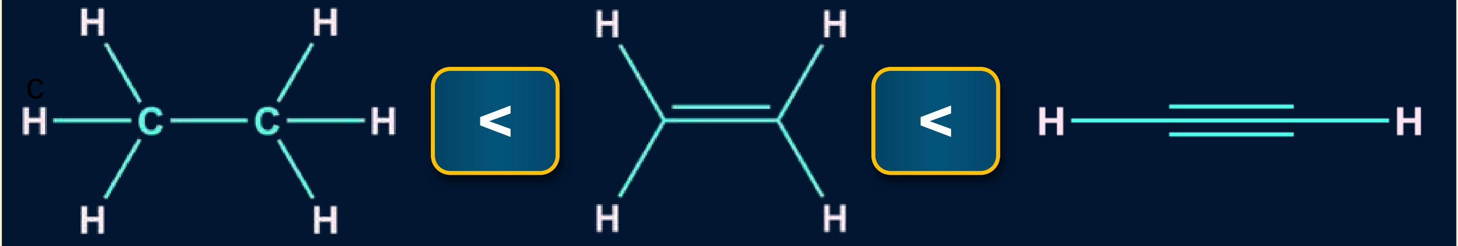
Bond angle



180°

Alkanes vs Alkenes vs Alkynes

Bond strength



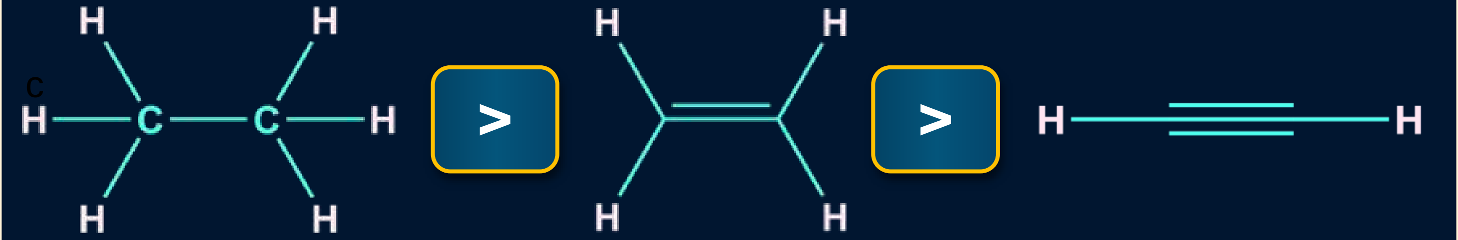
368 kJ mol^{-1}

636 kJ mol^{-1}

837 kJ mol^{-1}

Alkanes vs Alkenes vs Alkynes

C-C bond length



154 pm

134 pm

120 pm

Preparation of Alkynes

- From calcium carbide
- From vicinal dihalides
- From lower to higher alkynes
- Kolbe’s electrolysis method

Preparation from Calcium Carbide

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

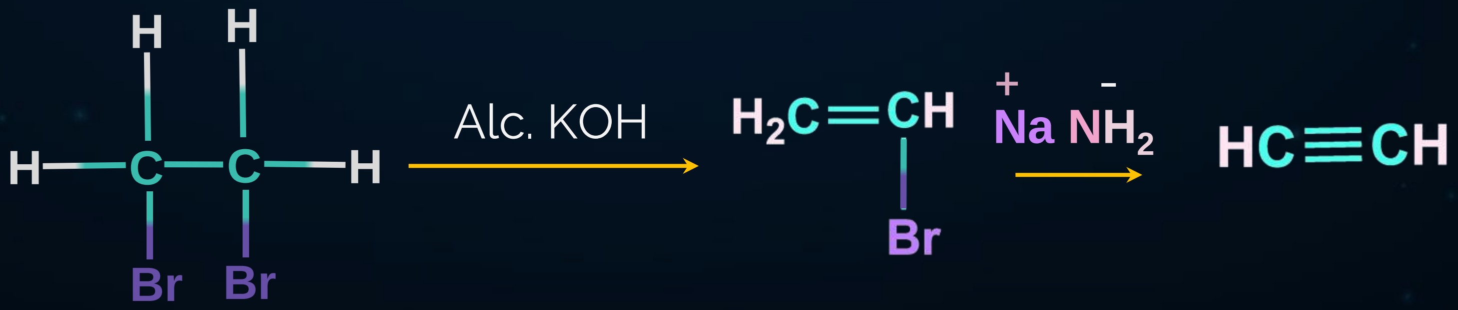
$$CaO + 3C \xrightarrow{\Delta} CaC_2 + CO$$

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

It is industrial method of preparation of **ethyne**

Preparation from Vicinal Dihalides

$$\text{Vicinal dihalide} \xrightarrow{\text{Alc. KOH}} \text{Alkenyl halide} \xrightarrow{Na^{+}NH_2^{-}} \text{Alkyne}$$



$$H\text{-}CH(Br)\text{-}CH(Br)\text{-}H \xrightarrow{\text{Alc. KOH}} H_2C{=}CH(Br) \xrightarrow{Na^{+}NH_2^{-}} HC{\equiv}CH$$

Preparation of Higher Alkynes from Lower Alkynes

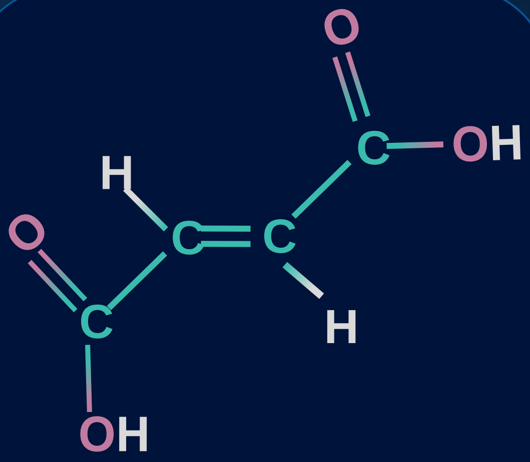
Lower alkyne reacts with strong base (**NaNH$_2$ in liquid NH$_3$**) to form a **sodium acetylide** which reacts with an **alkyl halide** to form a higher alkyne.

$$HC\equiv CH + NaNH_2 \xrightarrow{\text{liq. } NH_3} HC\equiv\overset{-}{C}Na^{+} + NH_3$$

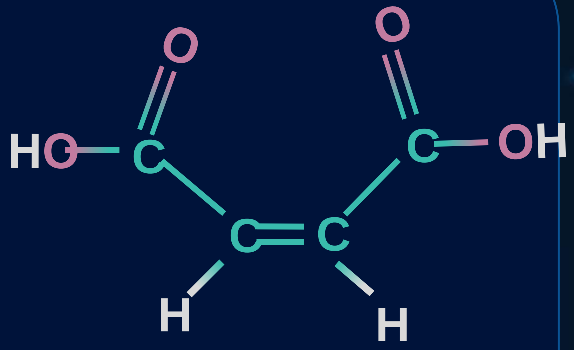
$$HC\equiv\overset{-}{C}Na^{+} + CH_3\text{-}Br \longrightarrow HC\equiv C-CH_3 + NaBr$$

Kolbe's Electrolysis Method

An aqueous solution of **'Na'/ 'K'** **salt of maleic acid** on electrolysis gives **ethyne** at the **anode.**

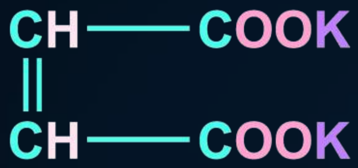


Fumaric acid



Maleic acid

Kolbe's Electrolysis Method



$$\begin{matrix}CH-COOK\\ \|\\ CH-COOK\end{matrix} + 2H_2O \xrightarrow{\text{Electrolysis}} HC\equiv CH + 2CO_2 + H_2 + 2KOH$$

Physical Properties of Alkynes

- **a** Physical State
- **b** Colour
- **c** Odour
- **d** Solubility
- **e** Boiling Point

Physical State of Alkynes

At 298 K,

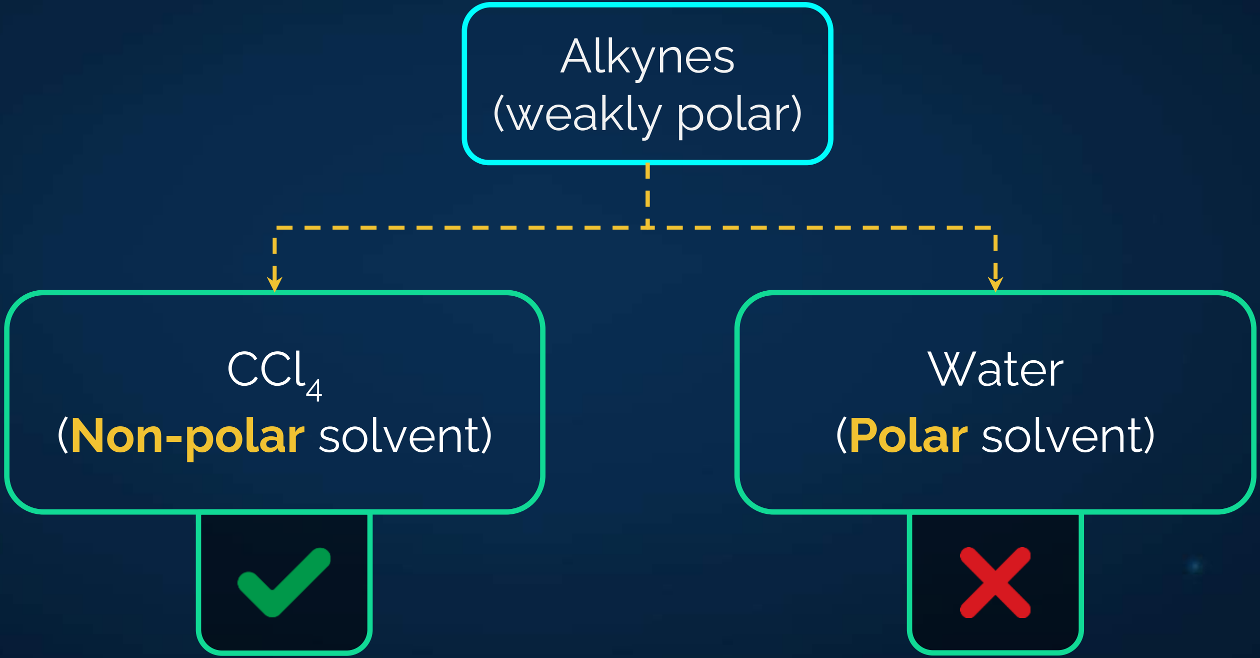
Number of C atoms in alkyne	State
2 - 4	Gases
5 - 12	Liquids
≥ 13	Solids

Colour and Odour of Alkynes

Alkynes are
colourless
& **odourless.**

An exception is **ethyne,** which has a characteristic **odour.**

Solubility of Alkynes



Alkynes
(weakly polar)

CCl_4
(**Non-polar** solvent)
✓

Water
(**Polar** solvent)
✗

Boiling Point of Alkynes

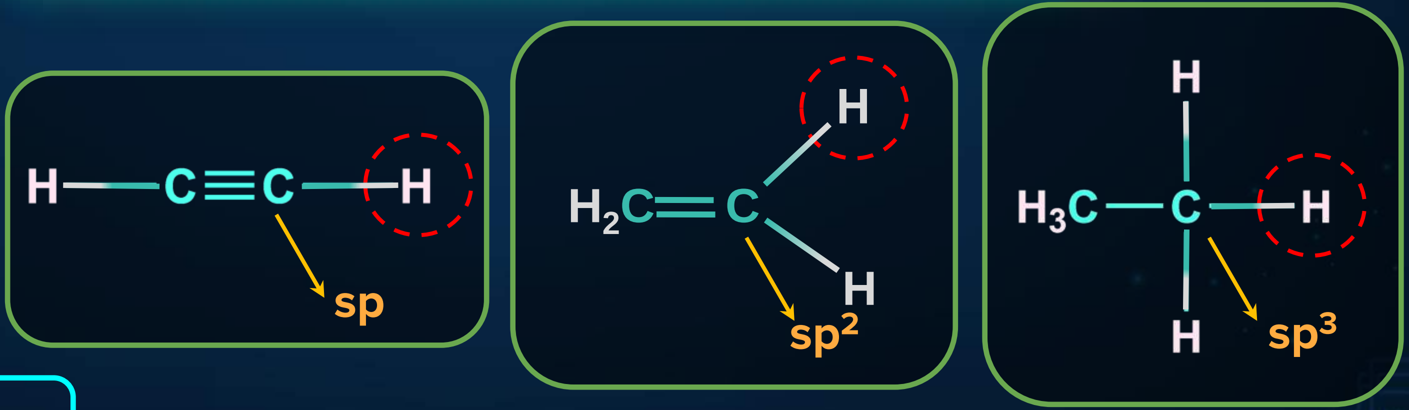
Boiling point $\propto$ van der Waals force $\propto$ Molar mass

Chemical Properties of Alkynes

- Acidic Nature
- Addition Reaction
- Oxidation
- Ozonolysis

Acidic Nature of Alkynes

H bonded to the carbon of a **terminal alkyne** is considerably **more acidic** than those bonded to carbons of an alkene or alkane.



% s-character	50%	33.3%	25%

Acidity of Hydrocarbon

% s ∝ Electronegativity of C atom ∝ Stability of the conjugate base ∝ Acidity of Hydrocarbon

$$H-C\equiv C-H + NaNH_2 \xrightarrow{\text{liq. } NH_3} H-C\equiv C^{-}Na + NH_3$$

$$H_3C-C\equiv C-H + NaNH_2 \xrightarrow{\text{liq. } NH_3} H_3C-C\equiv C^{-}Na + NH_3$$

Chemical Properties of Alkynes

Addition Reactions of Alkynes

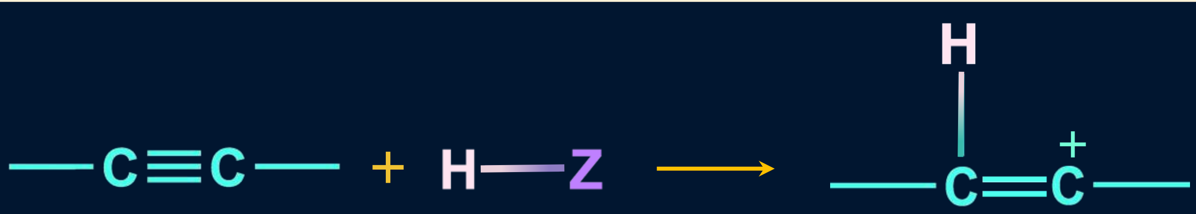
Takes place over the **triple bond**

So, it can add up **two molecules of H_2, X_2, HX** etc.

Addition of HZ to Alkyne

Let's consider the **addition** of a compound **HZ** to an **alkyne**.

Step 1: Addition of the electrophile

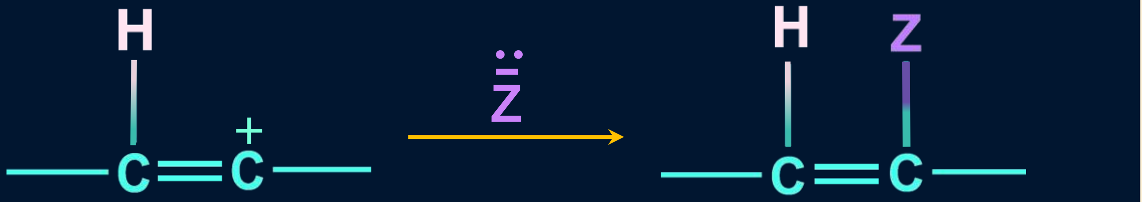


$$-C\equiv C- + H-Z \longrightarrow -\overset{H}{C}=\overset{+}{C}-$$

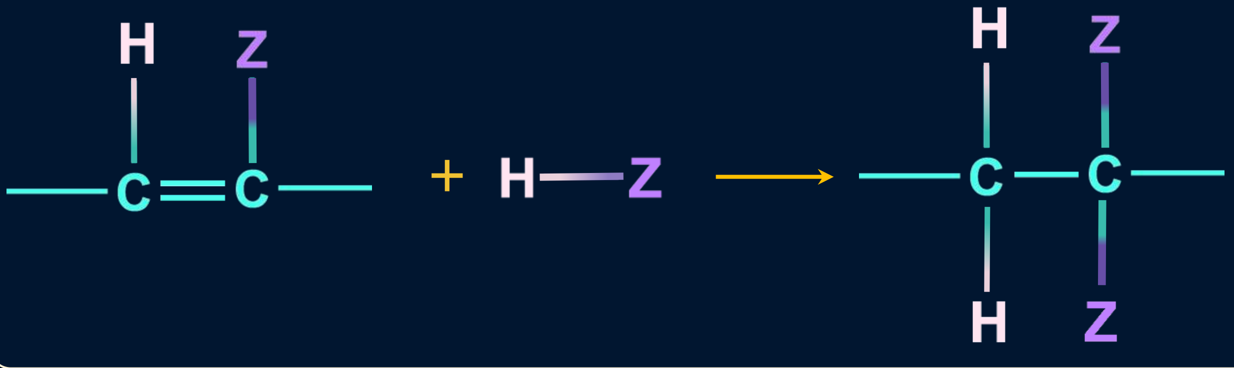
Product depends upon the
stability of the vinylic cation

Addition of HZ to Alkyne

Step 2: Addition of Z⁻



Similarly, another molecule of HZ reacts;



Addition Reactions of Alkynes

- Addition of H_2
- Addition of X_2
- Addition of HX
- Addition of H_2O

Addition of Dihydrogen

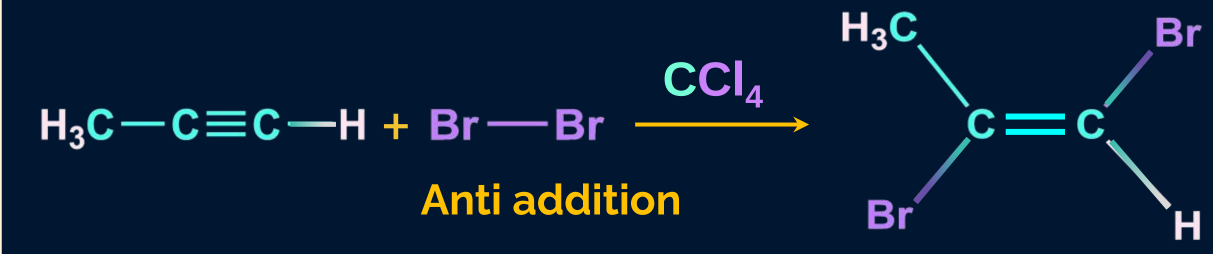
$$H_3C-C\equiv C-H + 2H_2 \xrightarrow{Ni/\ Pt/\ Pd} H_3C-H_2C-CH_3$$

Addition of Halogens

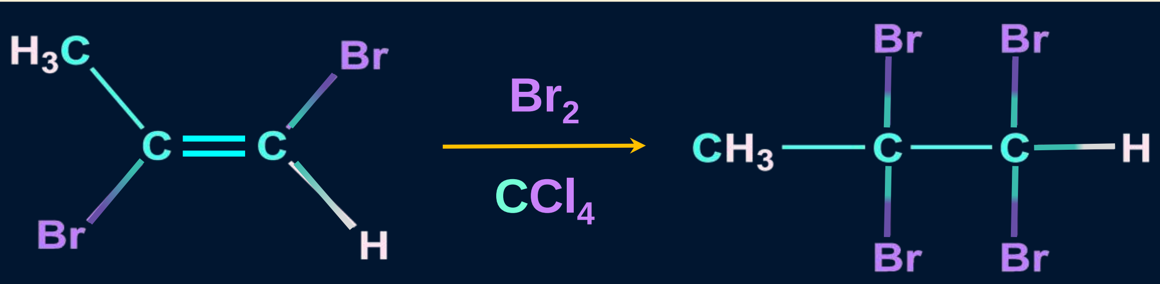
Alkynes react with a molecule of **X_2 (in CCl_4)** to form **1,2-Dihaloalkenes**

Further reaction of one more molecule of X_2 produces **tetra halogenated product**

Addition of Halogens



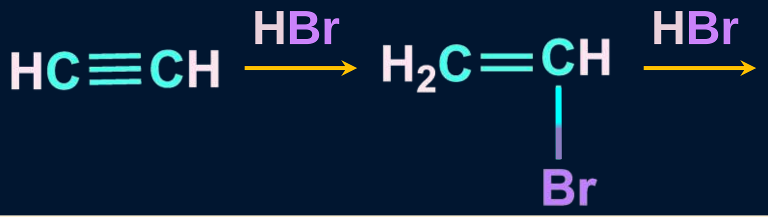
Anti addition



Reddish-brown colour decolourises

Addition of Hydrogen Halides

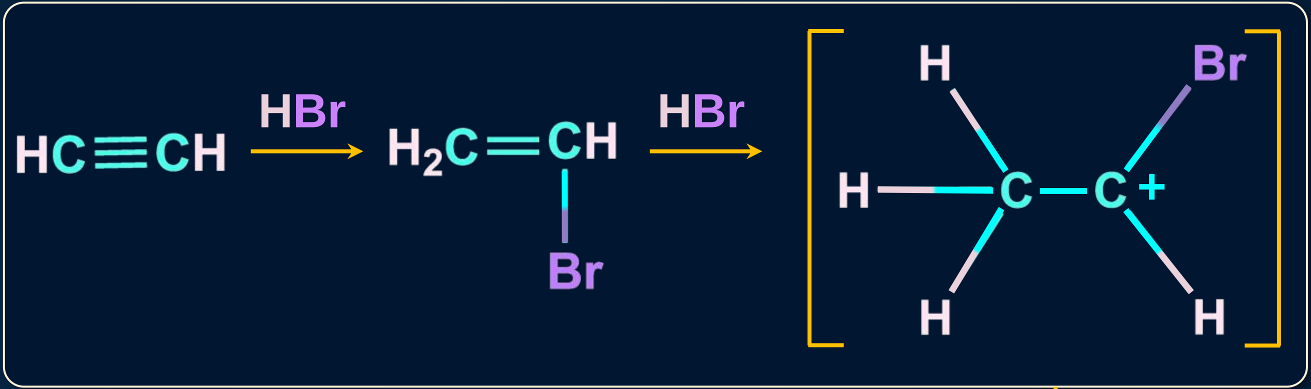
Alkynes react with one equivalent of HCl or HBr to form **haloalkenes** and with two equivalents to form **Geminal dihalides**.



$$HC\equiv CH \xrightarrow{HBr} H_2C=\underset{Br}{\underset{|}{C}}H \xrightarrow{HBr}$$

There are **two** possible carbocation intermediates

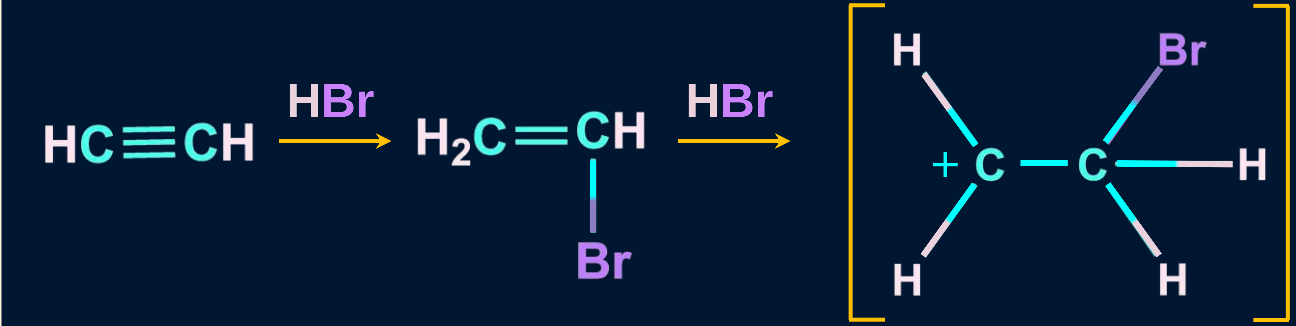
Addition of Hydrogen Halides



Stabilized through
+M effect of Br

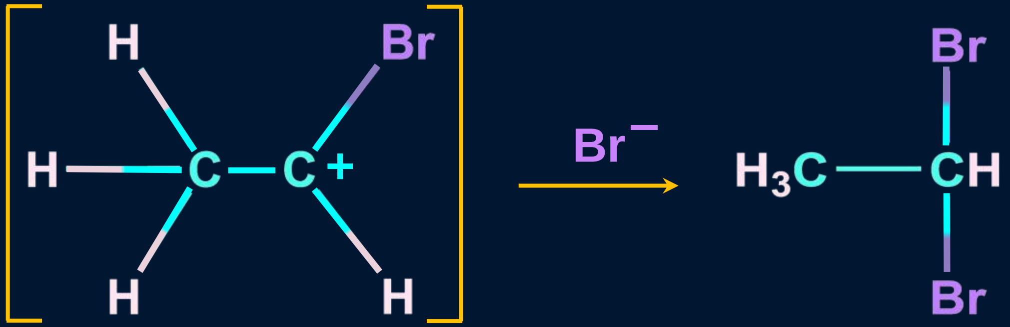
Intermediate **1**

Addition of Hydrogen Halides



Intermediate **2**

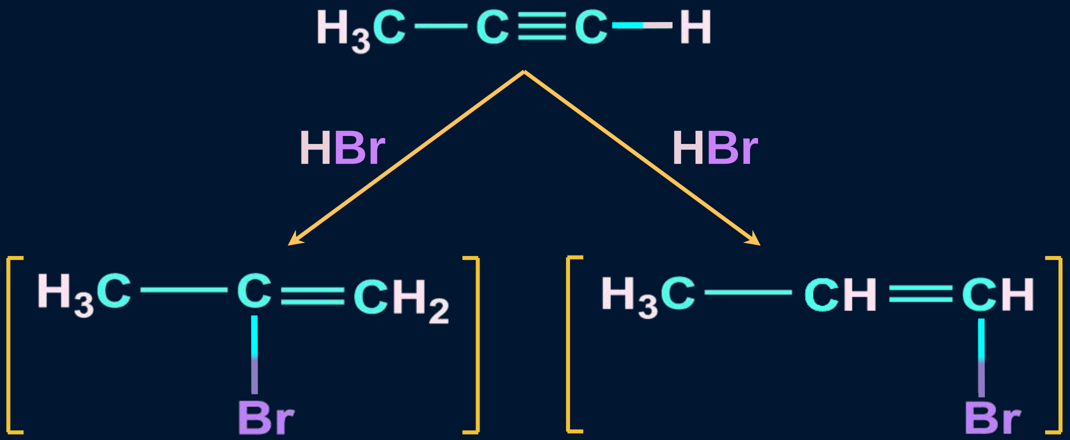
Addition of Hydrogen Halides



Intermediate **1**

Major product

Addition of Hydrogen Halides



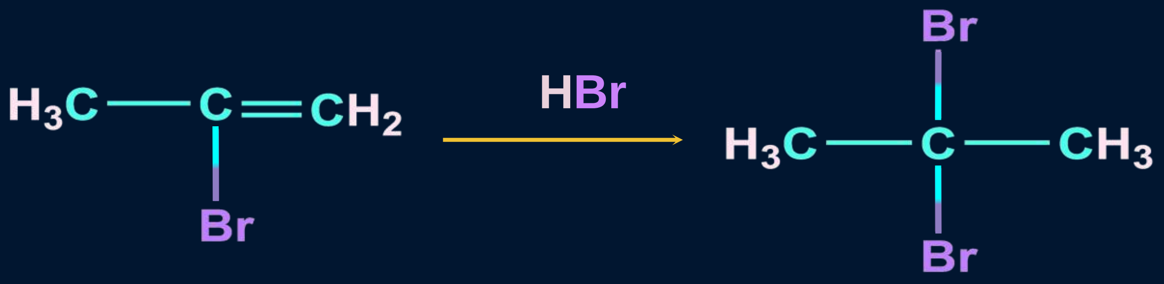
$$H_3C-C\equiv C-H \xrightarrow{HBr} \left[H_3C-\underset{\displaystyle Br}{\underset{|}{C}}=CH_2\right]$$

$$H_3C-C\equiv C-H \xrightarrow{HBr} \left[H_3C-CH=\underset{\displaystyle Br}{\underset{|}{CH}}\right]$$

Major

Minor

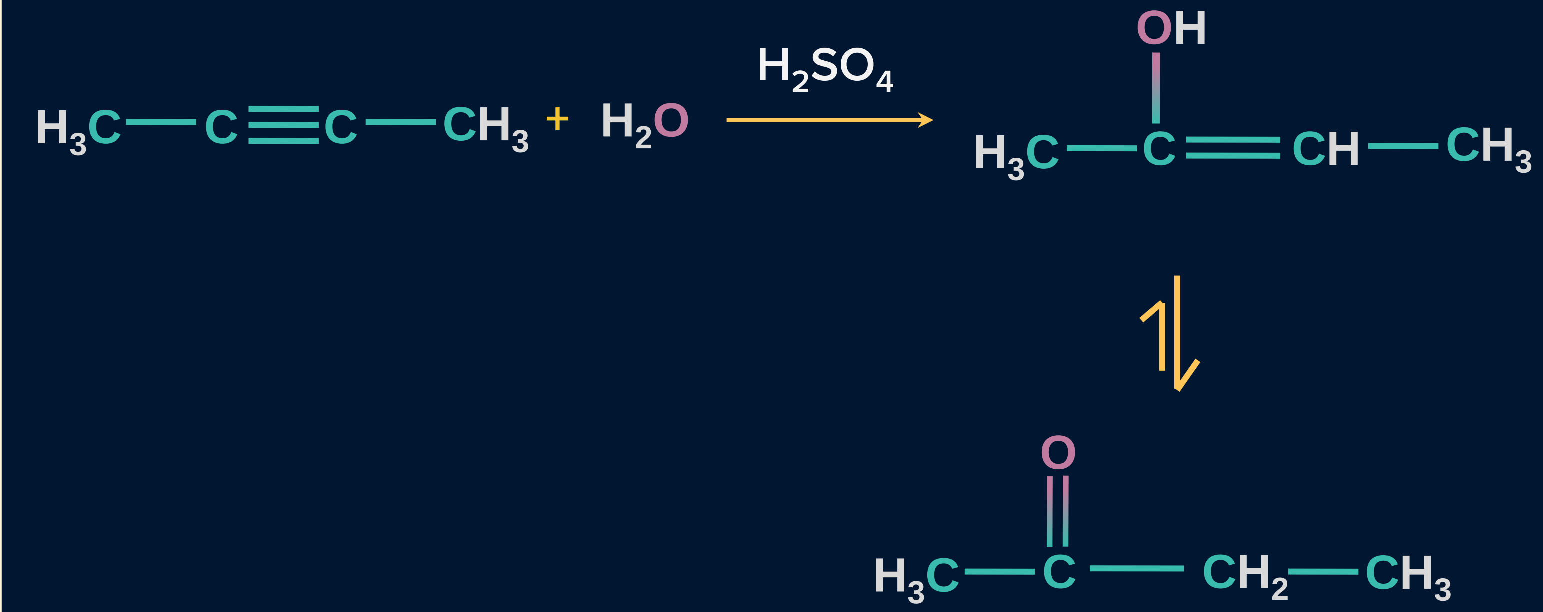
Addition of Hydrogen Halides



$$H_3C-\underset{\displaystyle Br}{\underset{|}{C}}=CH_2 \xrightarrow{HBr} H_3C-\overset{\displaystyle Br}{\overset{|}{\underset{\displaystyle Br}{\underset{|}{C}}}}-CH_3$$

Major product

Addition of Water



$$H_3C-C\equiv C-CH_3 + H_2O \xrightarrow{H_2SO_4} H_3C-\overset{OH}{\overset{|}{C}}=CH-CH_3$$

$$\rightleftharpoons$$

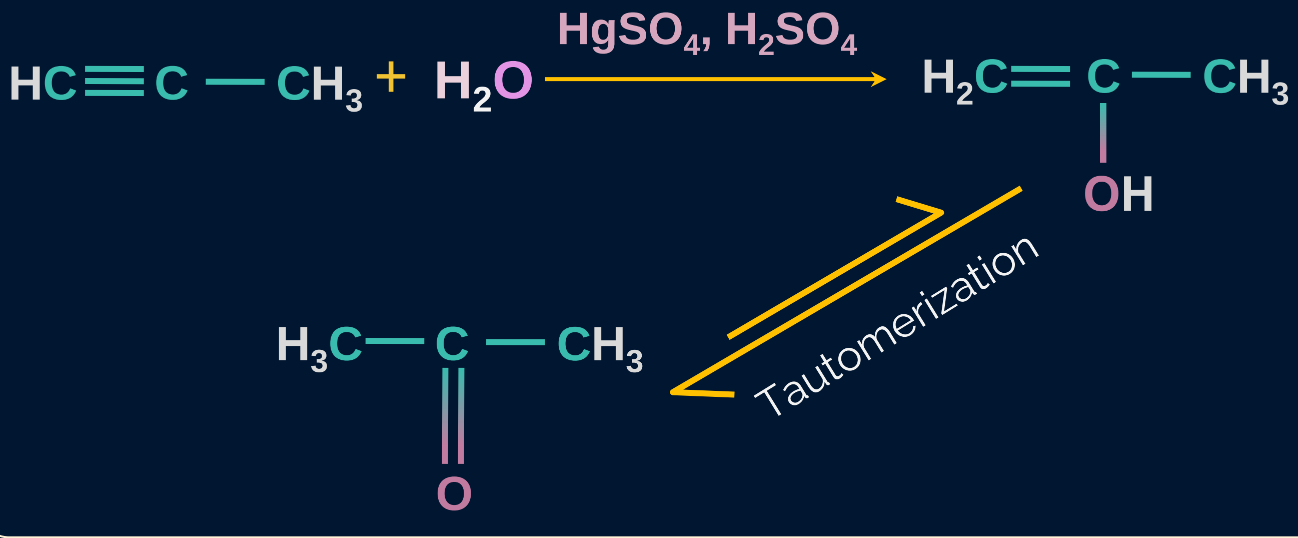
$$H_3C-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$$

Addition of Water

Terminal alkynes are **less reactive** than internal alkynes toward the addition of water.

Terminal alkynes will add water if **mercuric ion (Hg^{2+})** (catalyst) is added to the acidic mixture.

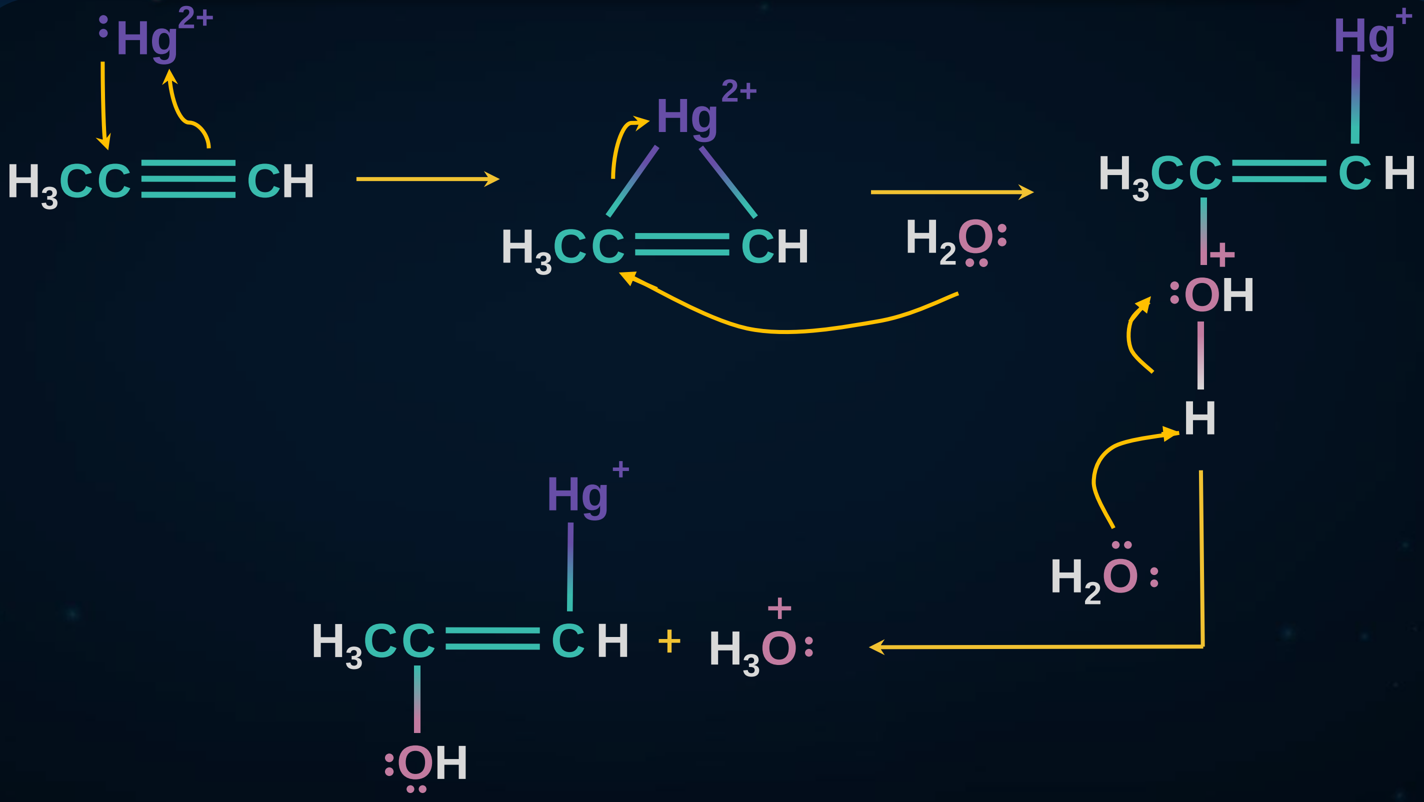
Addition of Water



$$HC\equiv C-CH_3 + H_2O \xrightarrow{HgSO_4,\ H_2SO_4} H_2C=\underset{\displaystyle OH}{\underset{|}{C}}-CH_3$$

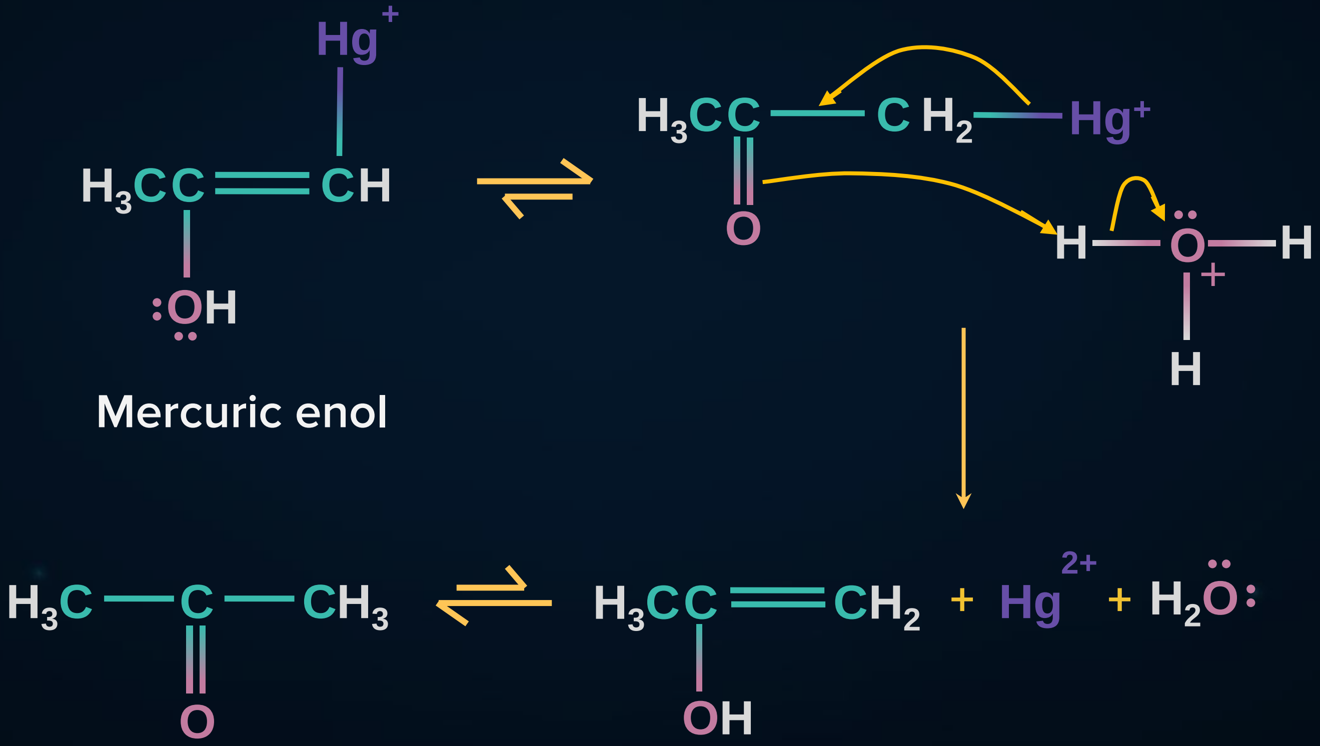
$$H_2C=\underset{\displaystyle OH}{\underset{|}{C}}-CH_3 \xrightleftharpoons{\text{Tautomerization}} H_3C-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3$$

Mechanism



Mercuric enol

Mechanism



Mercuric enol

$$H_3CC(OH)=CH-Hg^+ \rightleftharpoons H_3CC(=O)-CH_2-Hg^+ \xrightarrow{H_3O^+} H_3CC(OH)=CH_2 + Hg^{2+} + H_2\ddot{O}: \rightleftharpoons H_3C-C(=O)-CH_3$$

Note

01 Markovnikov’s addition

02 Bridged carbocation

03 No rearrangement takes place as non-classical carbocation is formed.

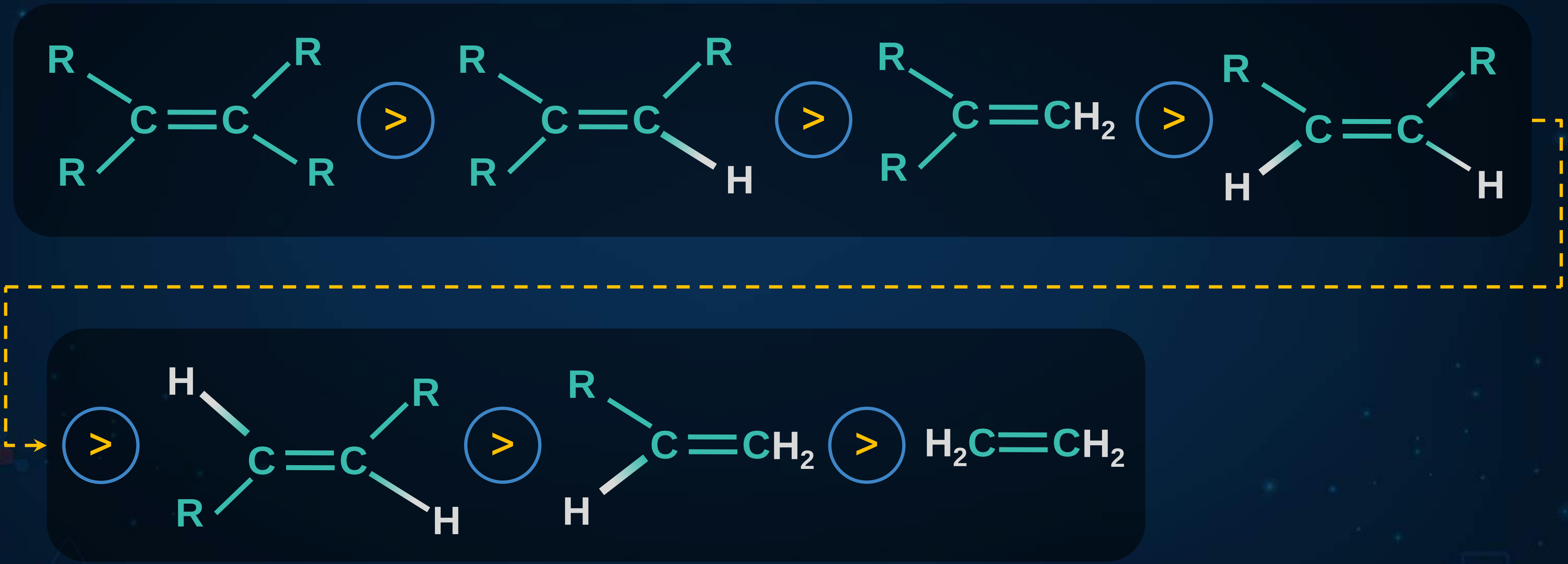
Reactivity of Alkene

Presence of **electron donating group (+M, +I)** at C=C increases reactivity

Presence of E.D.G. stabilises the intermediate carbocation

More stable the carbocation, more is the reactivity

Examples



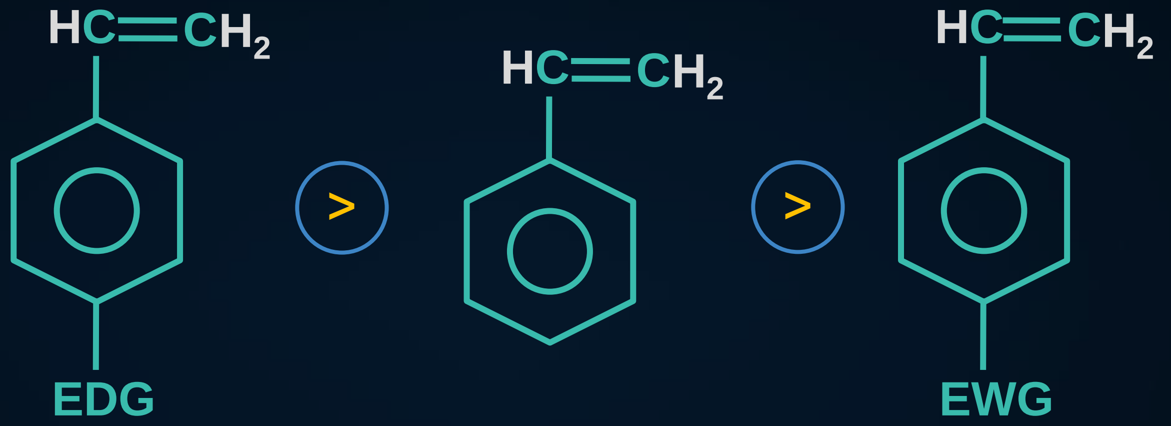
Examples

$EDG-HC{=}CH_2 > H_2C{=}CH_2 > EWG-HC{=}CH_2$

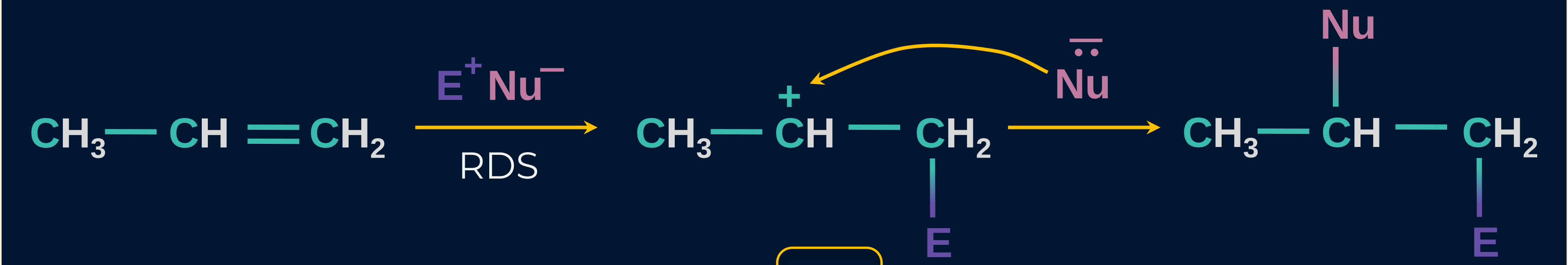
$H_3C-O-HC{=}CH_2 > H_2C{=}CH-CN$

$-CH{=}CH_2 > H_2C{=}CH_2$

Examples



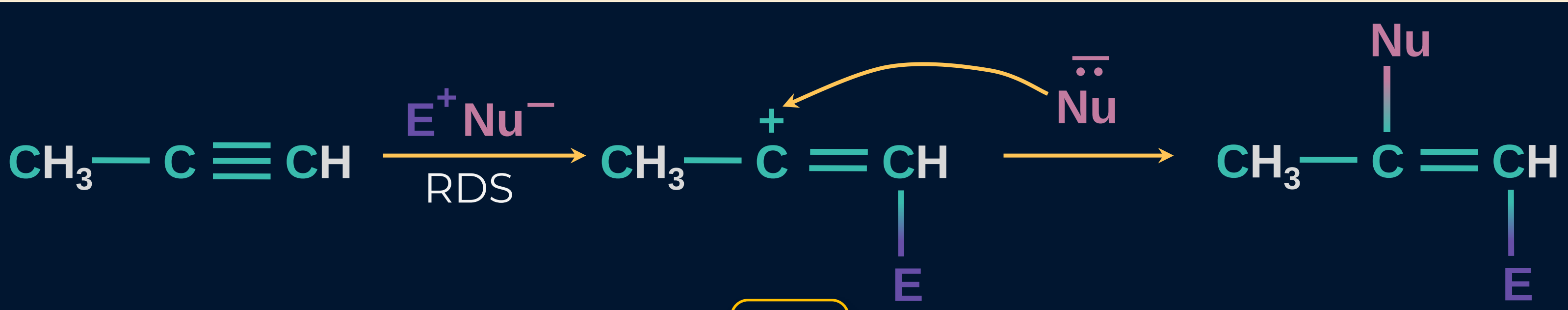
Alkene vs Alkyne



$$CH_3-CH=CH_2 \xrightarrow[\text{RDS}]{E^{+}Nu^{-}} CH_3-\overset{+}{C}H-\underset{\displaystyle E}{\underset{|}{CH_2}} \quad \overset{\overline{\cdot\cdot}}{Nu} \longrightarrow CH_3-\overset{\displaystyle Nu}{\overset{|}{C}H}-\underset{\displaystyle E}{\underset{|}{CH_2}}$$

A

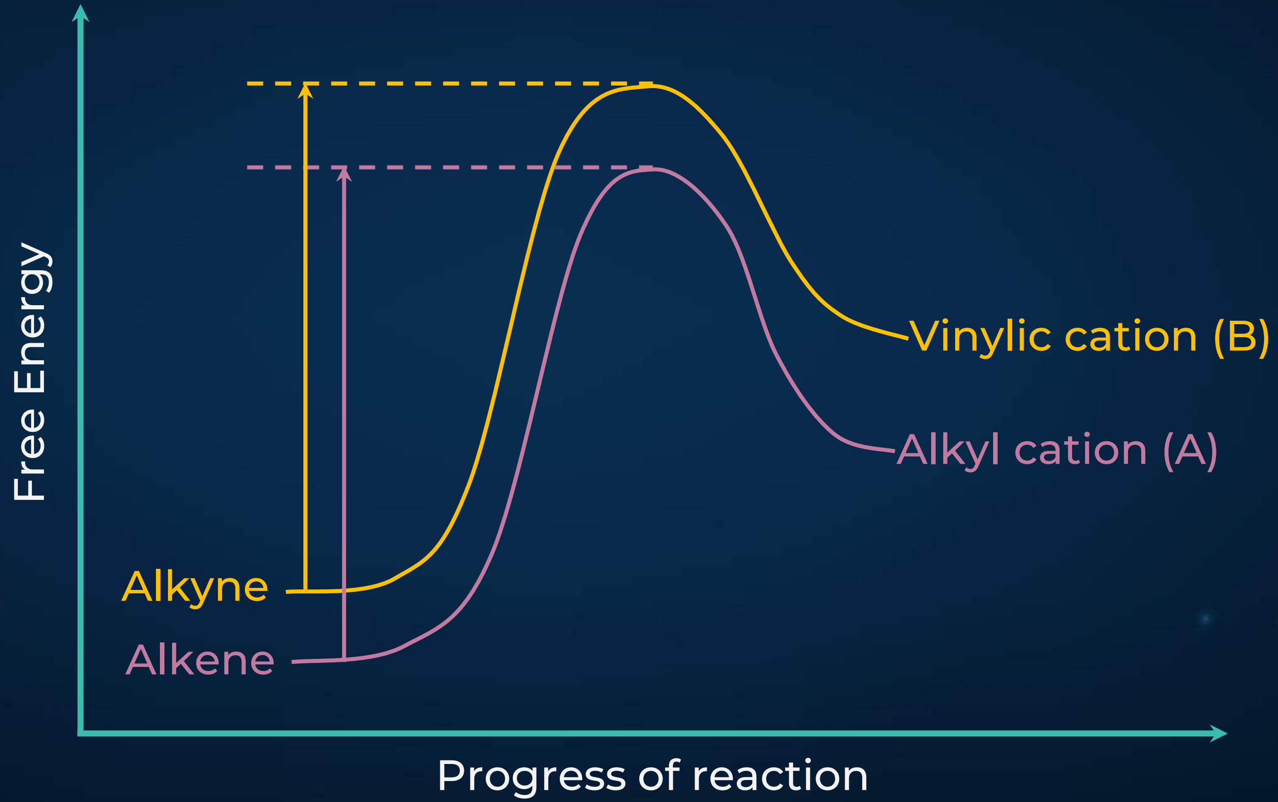
Alkene vs Alkyne



$$CH_3-C\equiv CH \xrightarrow[\text{RDS}]{E^+Nu^-} CH_3-\overset{+}{C}=\underset{\underset{E}{|}}{CH} \xrightarrow{\overline{\ddot{Nu}}} CH_3-\overset{\overset{Nu}{|}}{C}=\underset{\underset{E}{|}}{CH}$$

B

Alkene vs Alkyne



Alkene vs Alkyne

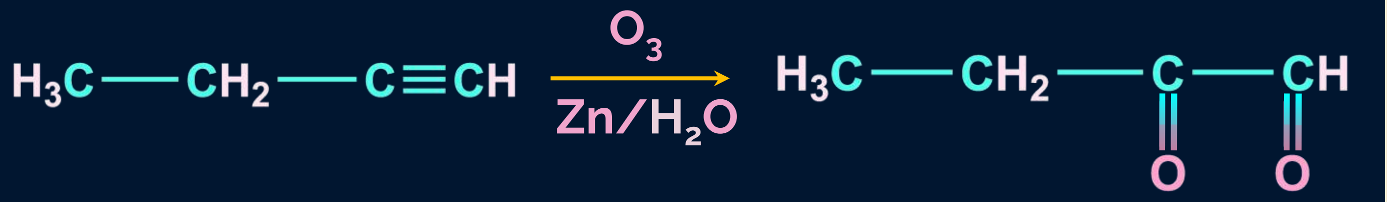
Stability: A > B

Electrophilic addition: Alkene > Alkyne

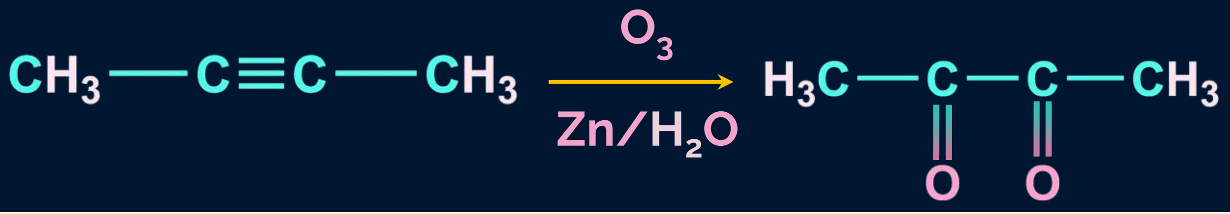
Points to Remember!!

When alkenes are in **conjugation** with alkynes, alkynes are more reactive towards electrophilic **addition reaction**.

Ozonolysis of Alkynes



$$H_3C-CH_2-C\equiv CH \xrightarrow[Zn/H_2O]{O_3} H_3C-CH_2-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{CH}$$

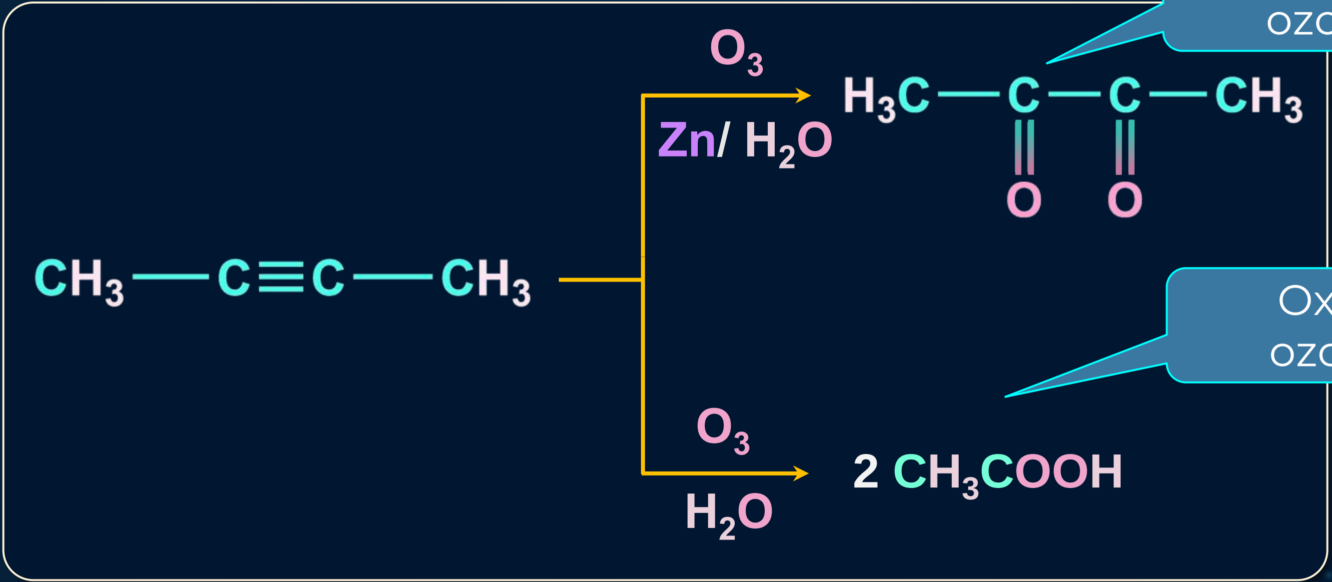


$$CH_3-C\equiv C-CH_3 \xrightarrow[Zn/H_2O]{O_3} H_3C-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-CH_3$$

Remember!

In the absence of Zn, **ozonolysis followed by hydrolysis** produces acid.

Ozonolysis of Alkynes



$$CH_3-C\equiv C-CH_3 \xrightarrow[Zn/\,H_2O]{O_3} H_3C-\underset{\overset{\|}{O}}{C}-\underset{\overset{\|}{O}}{C}-CH_3$$

$$CH_3-C\equiv C-CH_3 \xrightarrow[H_2O]{O_3} 2\,CH_3COOH$$

Reductive ozonolysis

Oxidative ozonolysis

Oxidation using Baeyer's Reagent

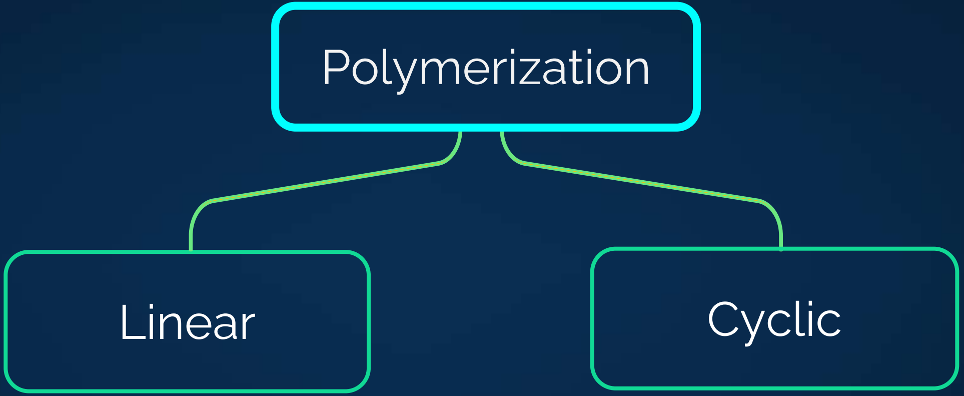
$$R-C\equiv C-R \xrightarrow{\text{Cold, dil. } KMnO_4} R-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-R$$

Purple color disappears

Oxidation using Basic $KMnO_4$/Acidified $K_2Cr_2O_7$

$$R-C\equiv C-R' \xrightarrow[\text{(2) } H_3O^+]{\text{(1) } KMnO_4,\ OH^-,\ \Delta} RCO_2H + R'CO_2H$$

Polymerization Reactions of Alkynes



Polymerization

Linear

Cyclic

Linear Polymerization of Alkynes

$$n\,(HC\equiv CH) \xrightarrow[\text{catalyst}]{\text{High temp./pressure}} -\!\!\left(HC=CH-CH=CH\right)_n\!\!-$$

Polyacetylene

Cyclic Polymerization of Alkynes

Ethyne on passing through a **red hot iron tube** at **873 K** undergoes cyclic polymerization to produce **benzene.**

Test for Terminal Alkynes

Terminal alkynes contain **acidic hydrogen.**

Test for Terminal Alkynes

Test for Terminal Alkynes

Tollen's reagent

$AgNO_3$ + NH_4OH or $[Ag(NH_3)_2]^+OH^-$

Ammoniacal Cuprous chloride

Cu_2Cl_2 + NH_4OH

Tollen’s Reagent

Tollen’s reagent gives **white precipitate (Silver alkynide)** with **terminal** alkynes.

$$R-C\equiv CH \xrightarrow{AgNO_3 + NH_4OH} R-C\equiv CAg$$

White precipitate

$$+\ NH_4NO_3$$

Ammoniacal Cuprous chloride

It gives **red precipitate** with **terminal alkynes.**

$$2\,R-C\equiv CH \xrightarrow{Cu_2Cl_2 + NH_4OH} \underset{\text{Red precipitate}}{R-C\equiv CCu} + 2NH_4Cl + 2H_2O$$

Test for Terminal Alkynes

Non-terminal alkynes do not react with Tollen’s reagent or Ammoniacal cuprous chloride

Lab Tests

Reagent	Alkane	Alkene	Alkyne (Terminal)
Br_2/H_2O solution	No effect	Decolorise	Decolorise
Cold dil. Alkaline $KMnO_4$ solution	No effect	Brown colour	Brown colour

Lab Tests

Reagent	Alkane	Alkene	Alkyne (Terminal)
Tollen's reagent	No effect	No effect	White ppt of silver acetanilide
Ammoniacal cuprous chloride solution	No effect	No effect	Red ppt of cuprous acetanilide

Aromatic Compounds

A **cyclic conjugated unsaturated** molecule or ion that is **stabilized by π electrons delocalisation.**

Aromatic Compounds

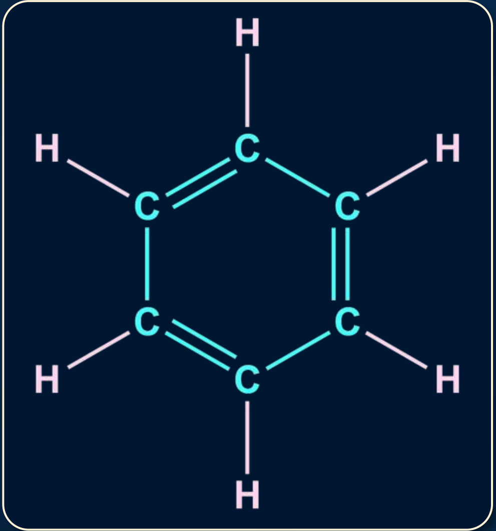
Huckel's Rule

Planar

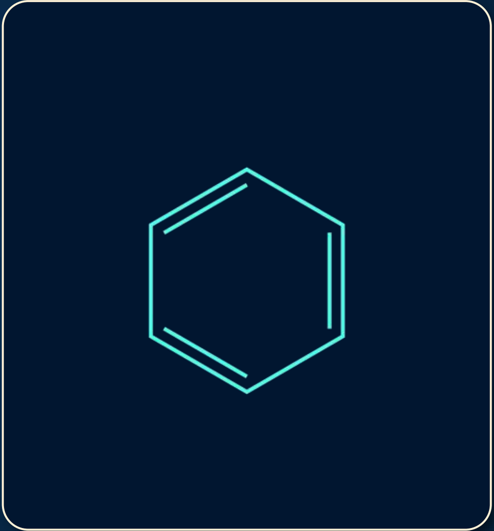
Fully Conjugated

Monocyclic system with $(4n + 2)\ \pi e^-$

Structure of Benzene

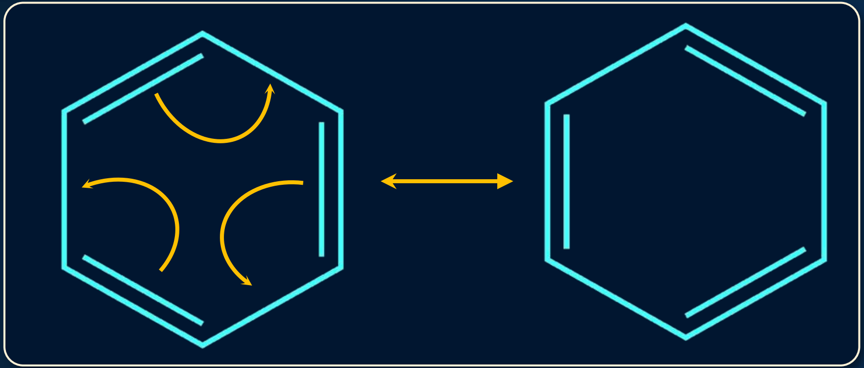


Structure of Benzene

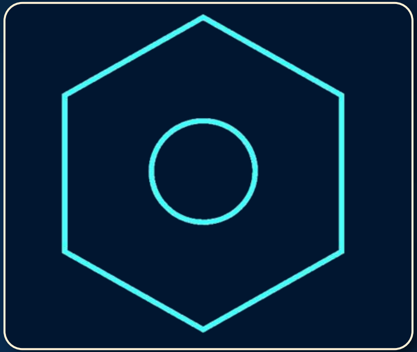


Bond line representation

Resonance in Benzene

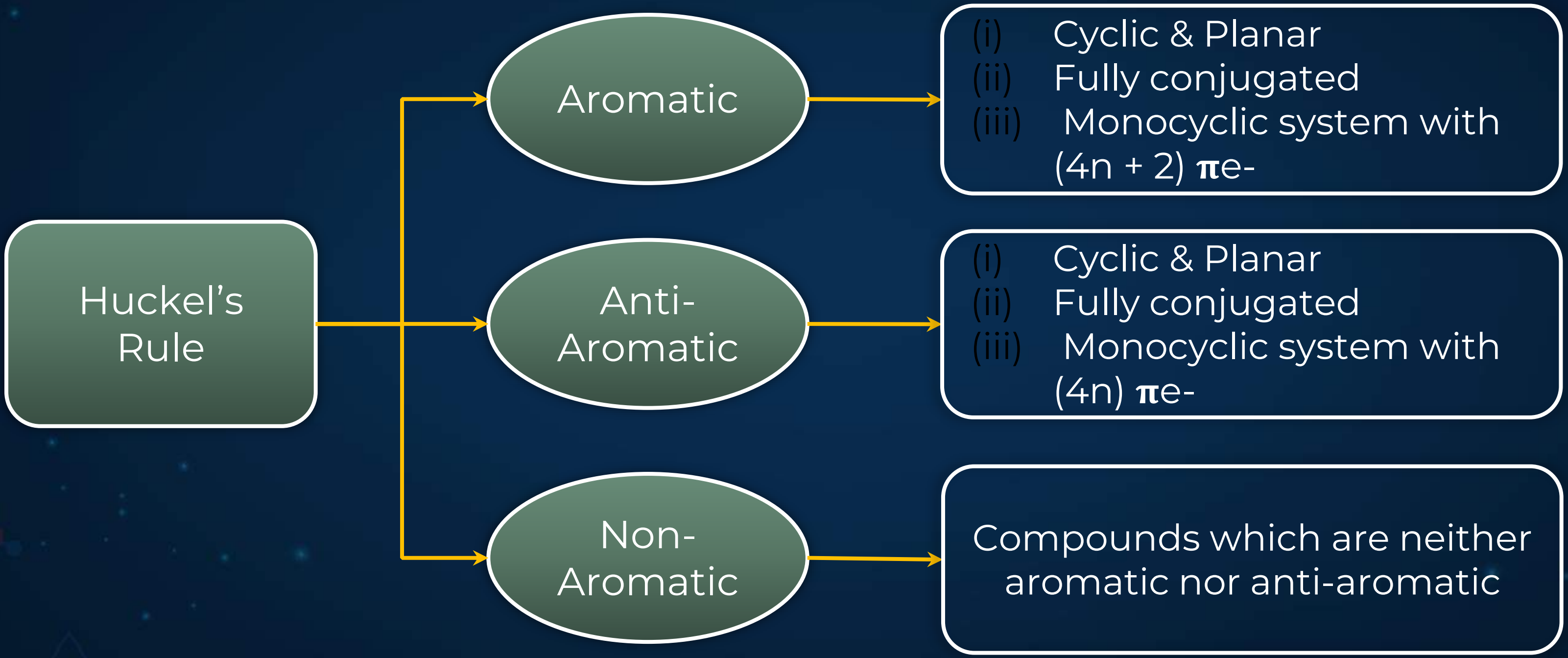


Resonating Structures



Resonance hybrid

Difference Between Aromatic, Anti-Aromatic & Non-Aromatic Compounds



Huckel's Rule

Aromatic

(i) Cyclic & Planar
(ii) Fully conjugated
(iii) Monocyclic system with (4n + 2) **π**e-

Anti-Aromatic

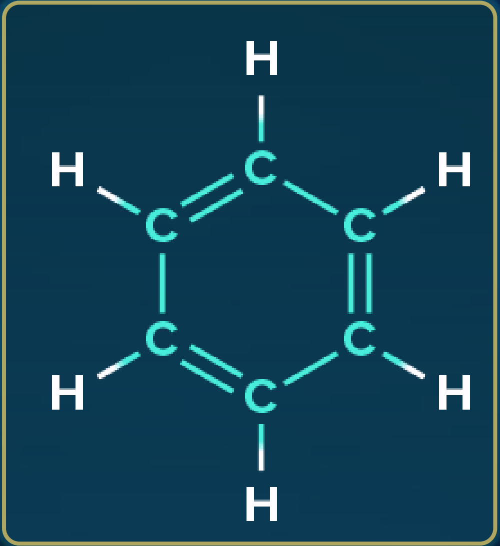
(i) Cyclic & Planar
(ii) Fully conjugated
(iii) Monocyclic system with (4n) **π**e-

Non-Aromatic

Compounds which are neither aromatic nor anti-aromatic

Aromatic Compounds

Example



Cyclic

Planar

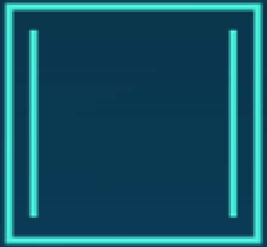
Fully conjugated

$(4n + 2)\ \pi\ e^-$
$= 6\ \pi\ e^-;\ (n = 1)$

Anti-Aromatic Compounds

Example

Cyclic



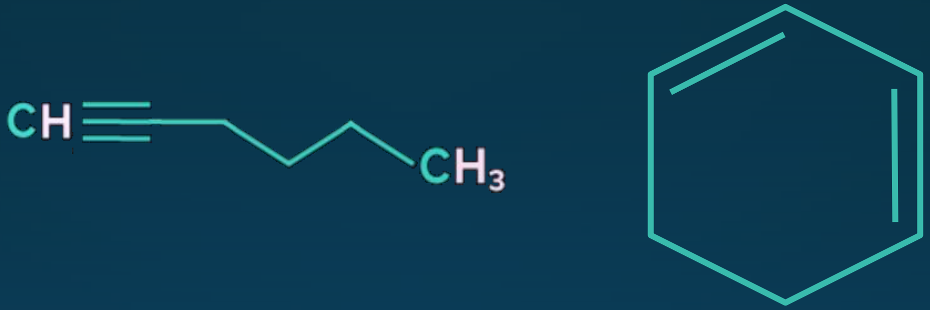
Planar

Fully conjugated

$4n\ \pi\ e^- = 4\ \pi\ e^-$
$(n = 1)$

Non-Aromatic Compounds

Example



Difference Between Aromatic, Anti-Aromatic & Non-Aromatic Compounds

Stability Order

Anti-Aromatic

Non-Aromatic

Aromatic

Least stable

Most stable

Preparation of Aromatic Hydrocarbons

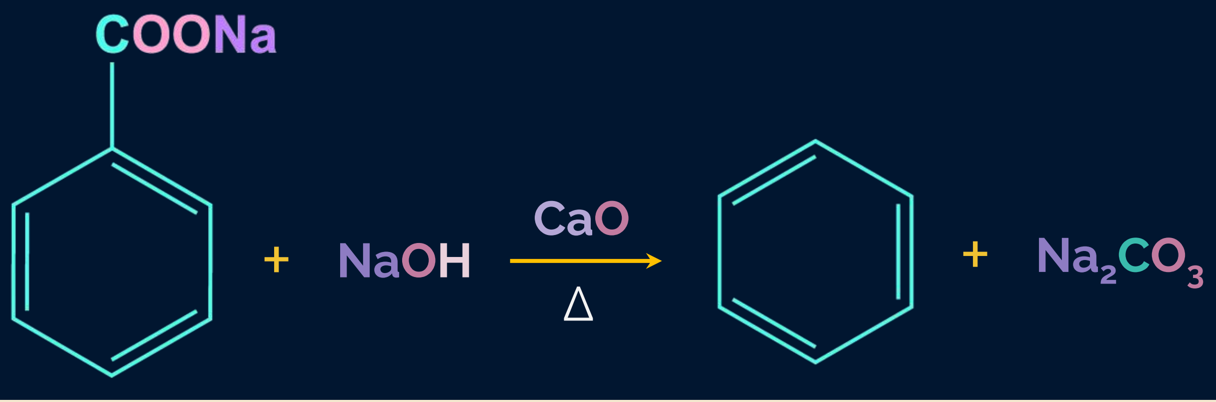
- Cyclisation of ethyne
- Decarboxylation of aromatic acids
- Reduction of phenol

Cyclic Trimerisation of Alkynes

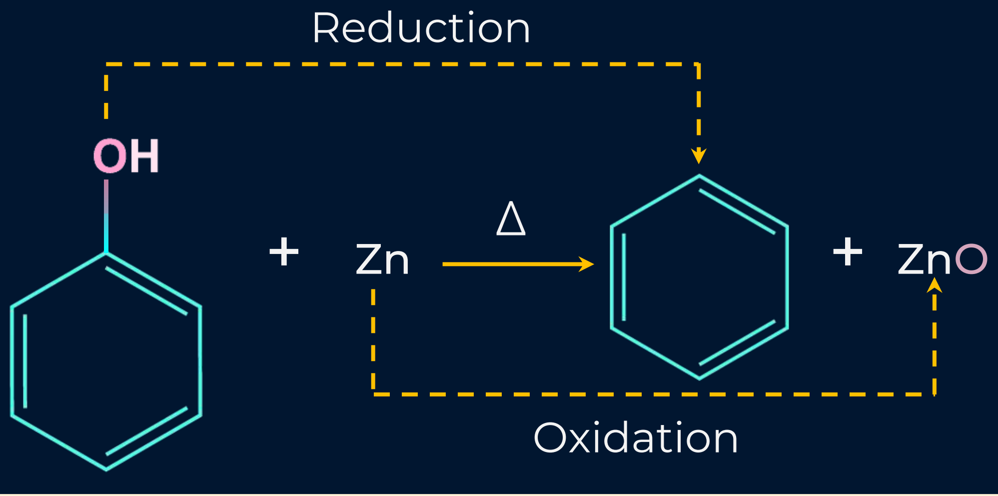
Cyclic trimerisation of ethyne with red hot iron produces benzene.

Decarboxylation of Aromatic Acid

Sodium salt of benzoic acid on heating with soda lime (NaOH + CaO) gives benzene.



Reduction of Phenol



Physical Properties of Aromatic Hydrocarbons

01 Physical State

02 Colour

03 Odour

04 Solubility

Physical States of Aromatic Hydrocarbons

Exists in solid or liquid state.

Aromatic hydrocarbons are colourless and have a characteristic aroma.

Characteristic Odour

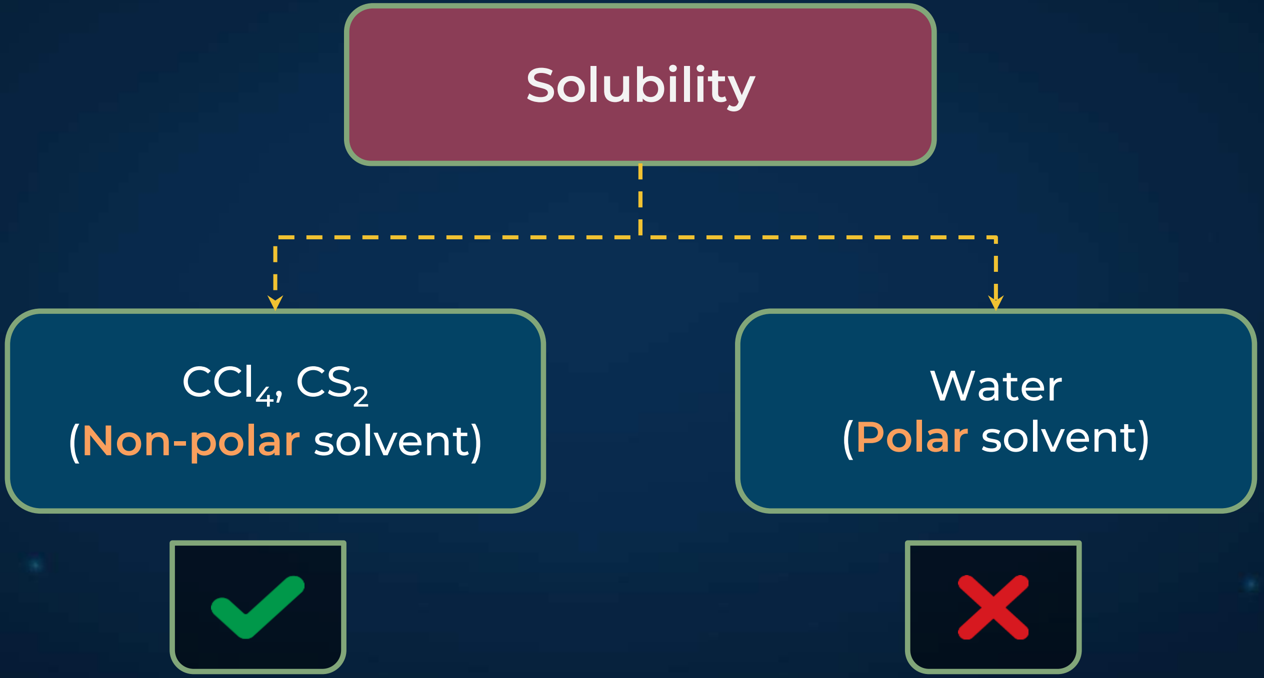
Unique smell

Moth repellent property

Naphthalene balls

Used in toilets and for the preservation of clothes

Solubility of Aromatic Hydrocarbons



Solubility

CCl_4, CS_2
(**Non-polar** solvent)

✓

Water
(**Polar** solvent)

✗

Chemical Properties of Aromatic Hydrocarbons

01 Electrophilic substitution

02 Addition reaction

03 Combustion

Electrophilic Substitution Reaction

Though benzene is susceptible to electrophilic attack, it generally undergoes **substitution reactions rather than addition reactions**.

Electrophilic substitution of benzene involves the reaction of an electrophile with an aromatic compound. Therefore, it is more precisely called as **Electrophilic Aromatic Substitution Reaction**.

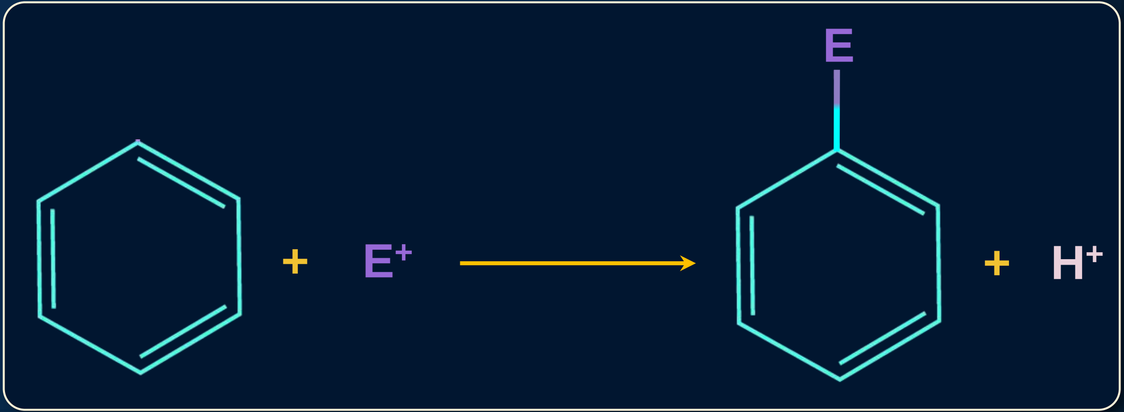
Electrophilic Substitution Reaction

S_EAr

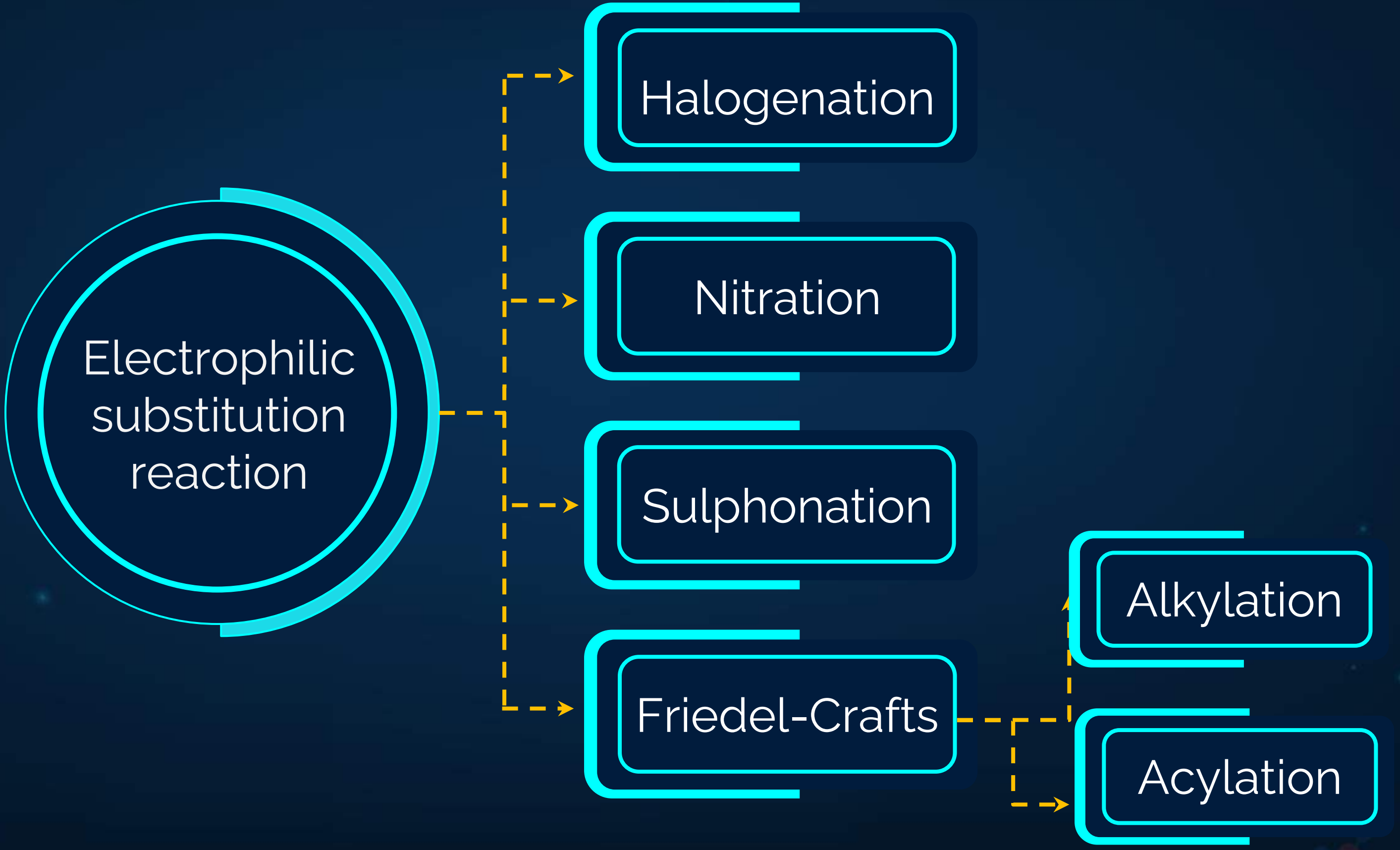
S Substitution

E Electrophilic

Ar Aromatic



Electrophilic Substitution Reaction



Electrophilic substitution reaction

- Halogenation
- Nitration
- Sulphonation
- Friedel-Crafts
  - Alkylation
  - Acylation

Mechanism

S_EAr of benzene takes place in 3 steps:

01 Generation of an electrophile

02 Formation of a carbocation intermediate

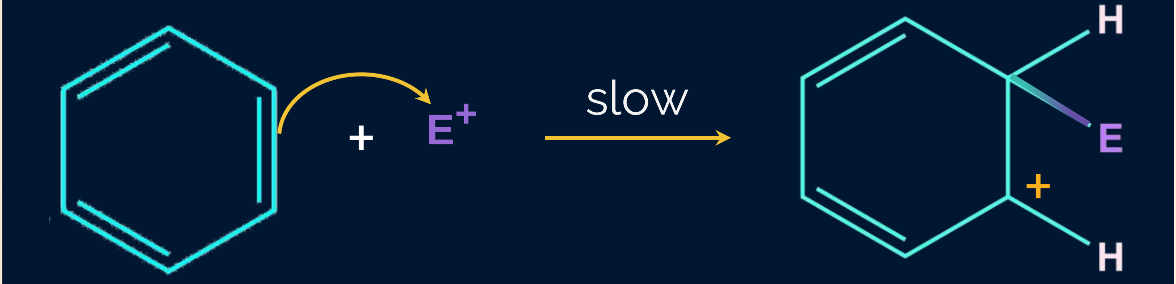
03 Removal of proton from the carbocation intermediate

Electrophiles for Different Electrophilic Substitutions

Reaction	Electrophile
Halogenation	Cl^+, Br^+, I^+
Nitration	NO_2^+
Sulphonation	SO_3
Friedel-Crafts	R^+, $RC\equiv O^+$

Formation of Carbocation Intermediate

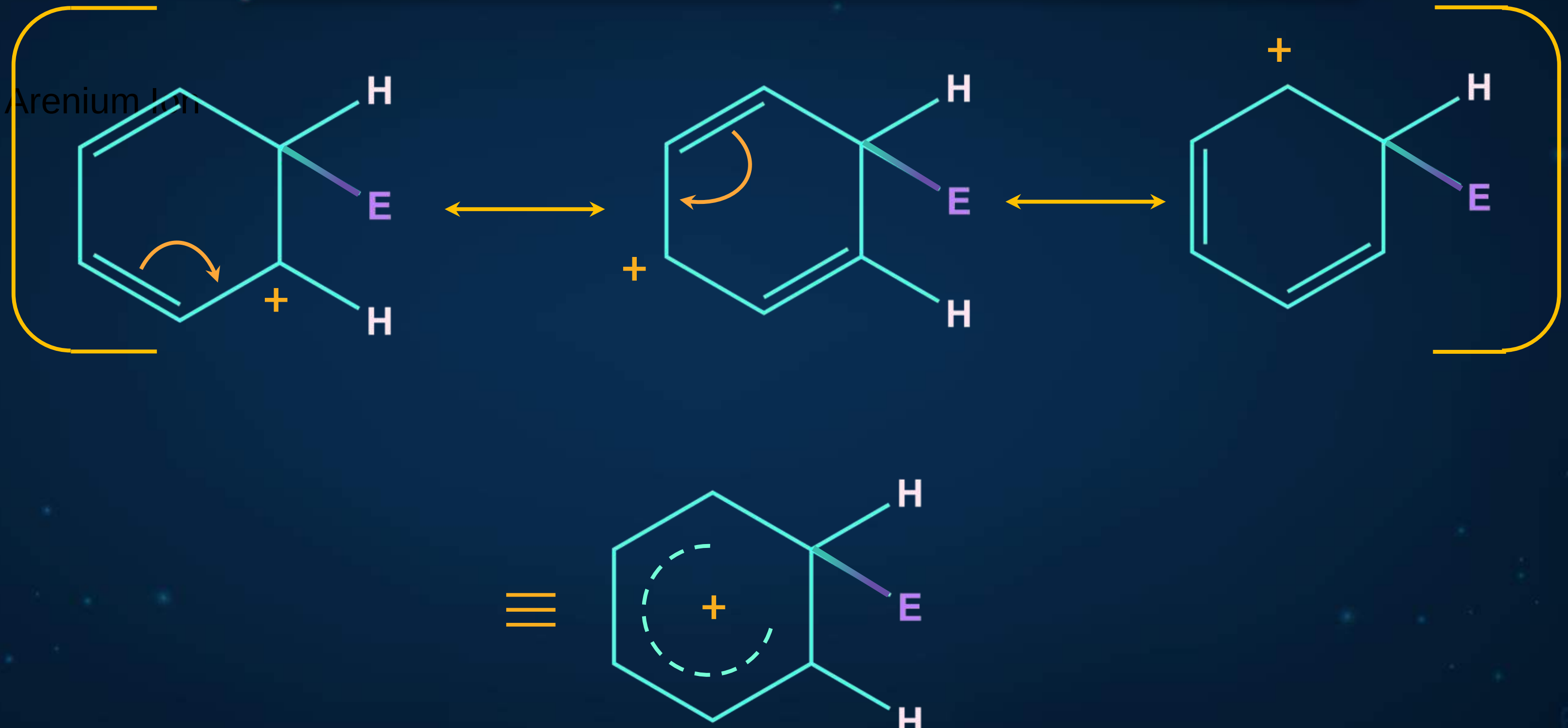
Attack of electrophile results in the formation of **arenium ion**



Arenium ion

Also known
as **sigma (σ) complex**
or **Wheland intermediate**

Arenium ion

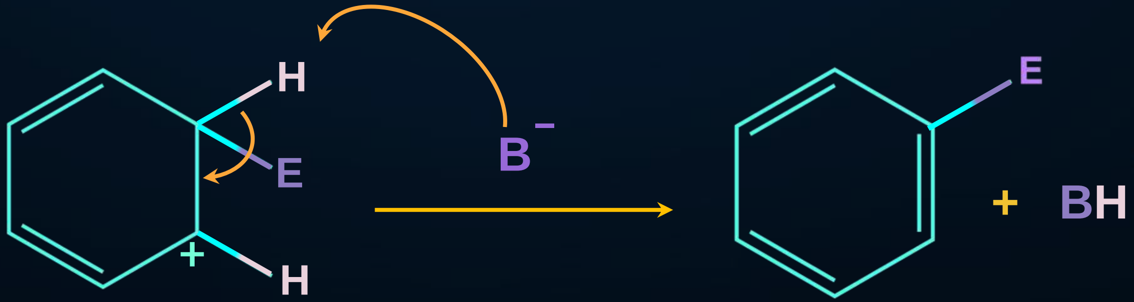


Arenium ion

Sigma complex/arenium ion is not aromatic due to the **sp³ hybridised carbon.**

Removal of Proton

To restore the aromatic character,
σ complex loses H^+ from the
sp^3 hybridised carbon.



Types of Electrophilic Substitution Reaction

Electrophilic substitution reaction

Halogenation

Nitration

Sulphonation

Friedel-Crafts

Alkylation

Acylation

Halogenation

Halogenation

Benzene reacts with **bromine or chlorine** in the presence of Lewis acids to give the corresponding **halogenated substitution products** in good yield.

Lewis acids typically used are **$AlCl_3$** or **$FeCl_3$** for chlorination, and **$FeBr_3$** for bromination.

Mechanism of Halogenation

01 Generation of the electrophile

02 Formation of arenium ion

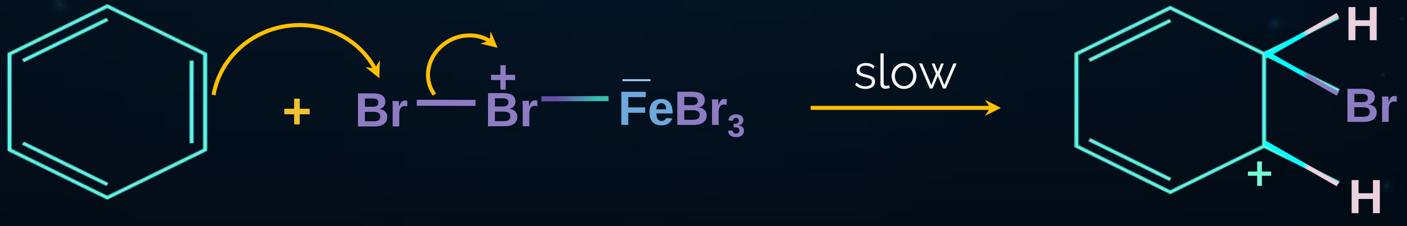
03 Removal of proton from the arenium ion

Mechanism of Halogenation

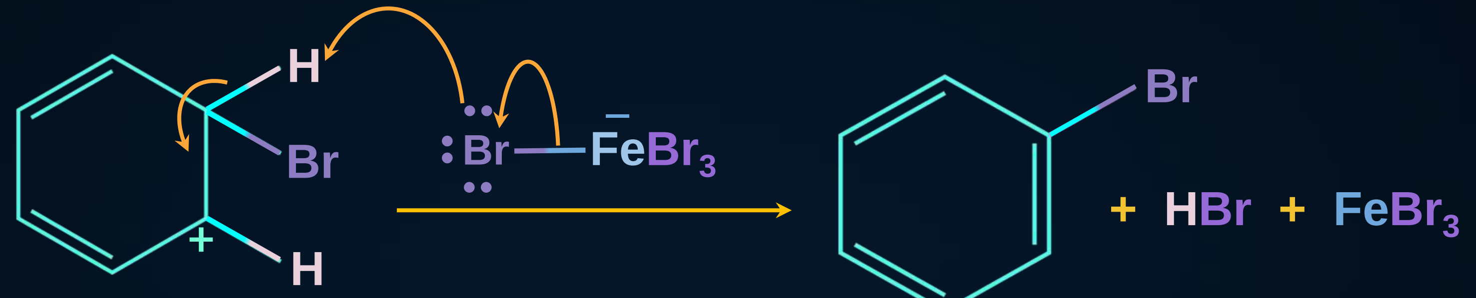
Generation of the electrophile

$$Br{-}Br + FeBr_3 \rightleftharpoons Br{-}\overset{+}{Br}{-}\overset{-}{Fe}Br_3$$

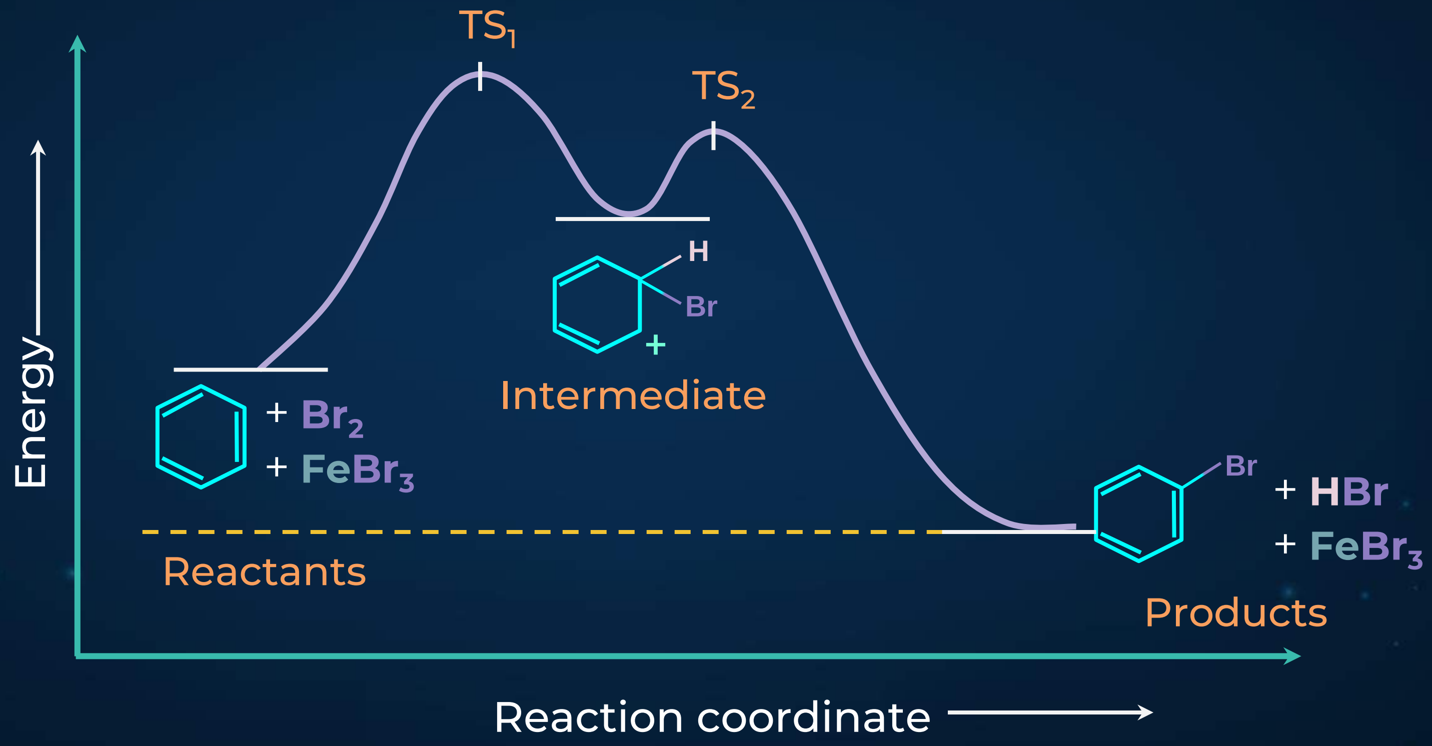
Formation of Arenium Ion



Removal of Proton



Energy Diagram-Bromination



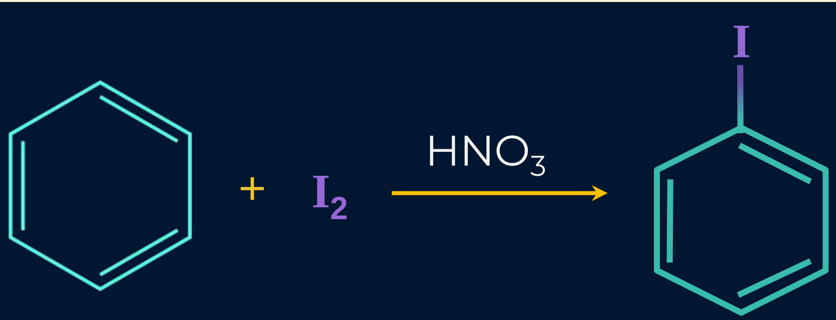
Fluorination of Benzene

Fluorine reacts so **rapidly** with benzene such that aromatic fluorination requires special conditions and apparatus.

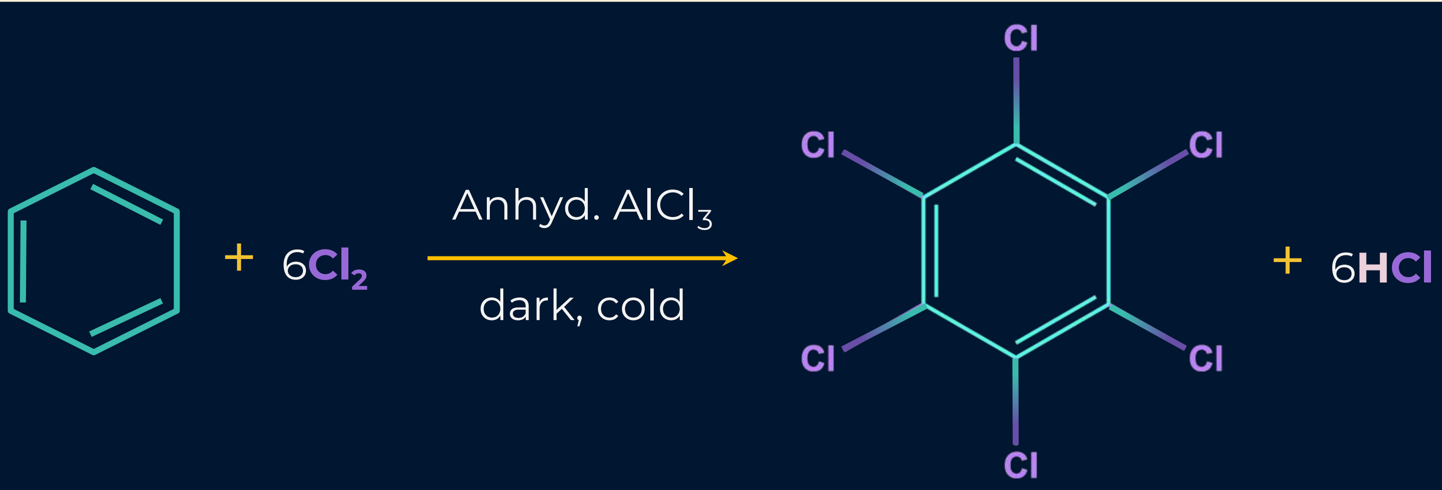
Even then, it is difficult to limit the reaction to **monofluorination**

Iodination of Benzene

Iodine is so **unreactive** that the reaction has to be carried out in the presence of an **oxidising agent** such as nitric acid

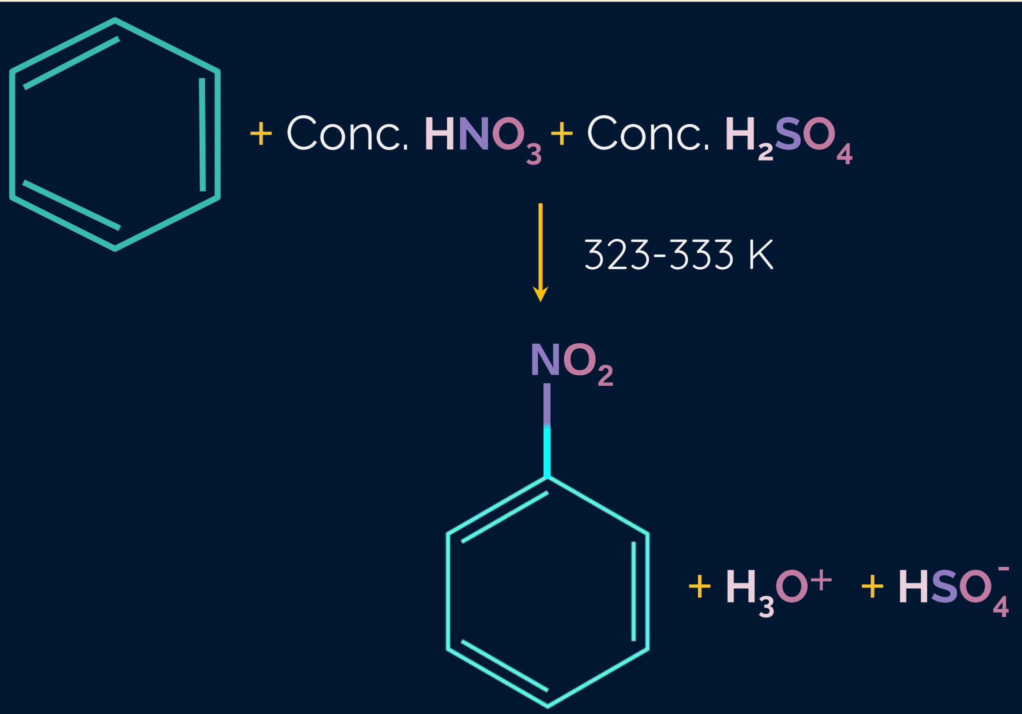


Electrophilic Substitution Reaction



Hexachlorobenzene

Nitration



+ Conc. HNO_3 + Conc. H_2SO_4

323-333 K

NO_2

+ H_3O^+ + HSO_4^-

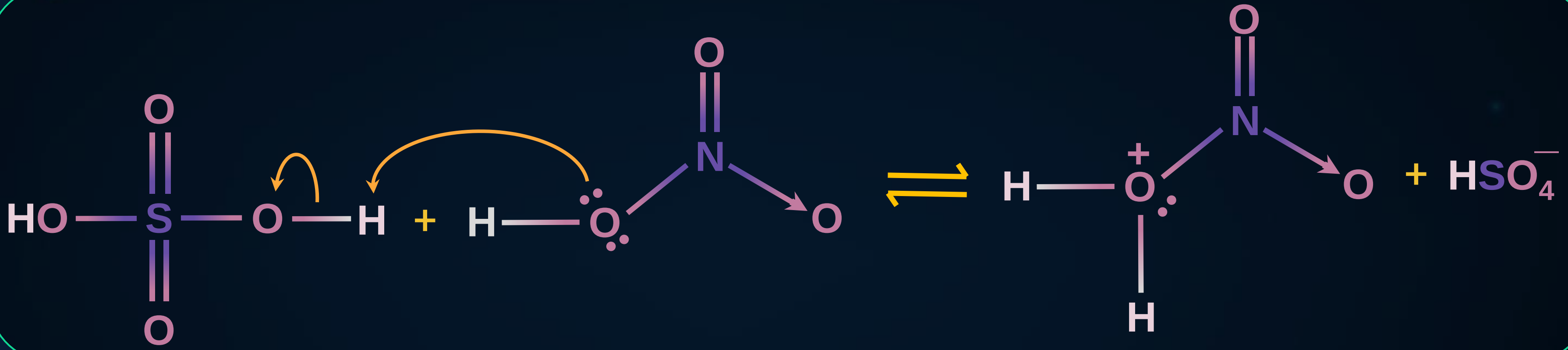
Mechanism of Nitration

01 Generation of the electrophile

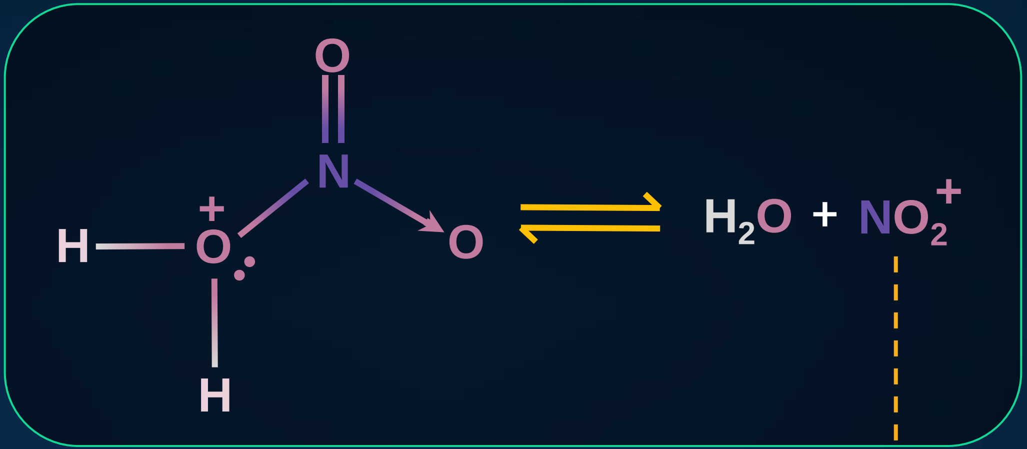
02 Formation of arenium ion

03 Removal of proton from the arenium ion

Generation of the Electrophile



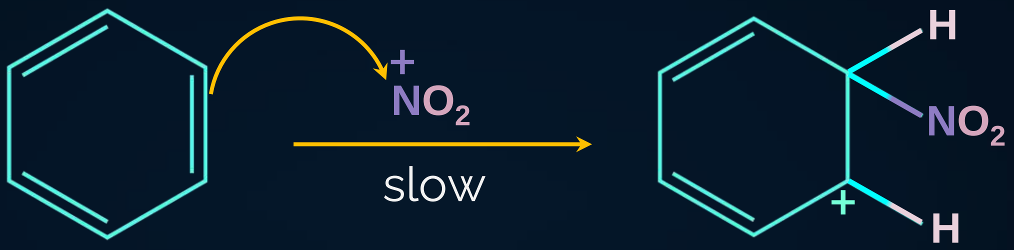
Generation of the Electrophile



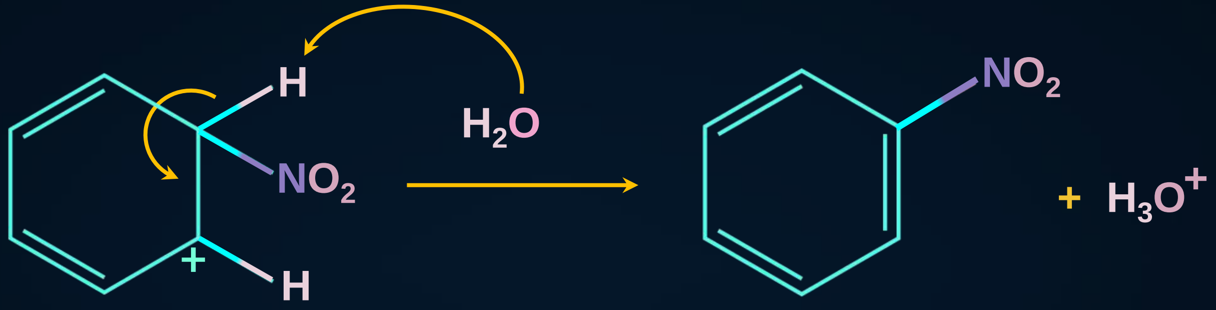
Electrophile

Nitronium ion

Formation of Arenium Ion



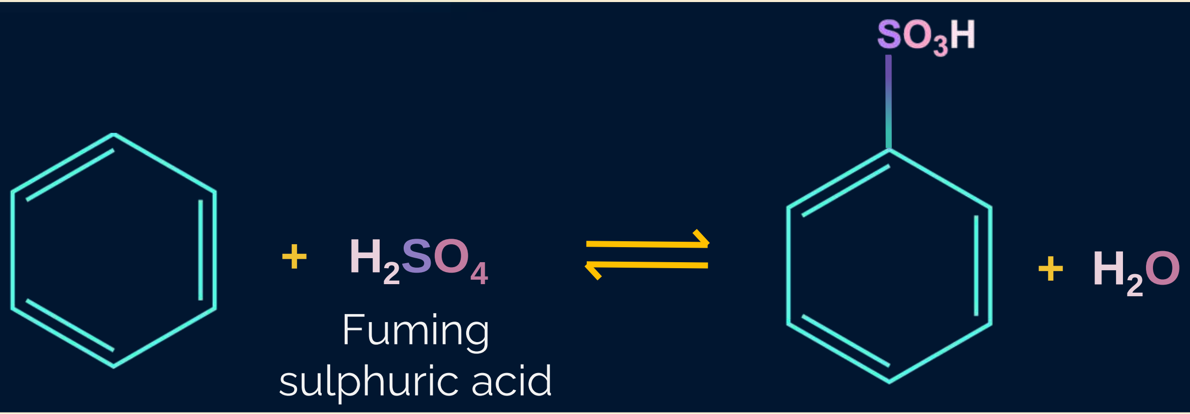
Removal of Proton



Slphonation

Benzene reacts with **fuming sulphuric acid** at room temperature to produce Benzenesulphonic acid.

Fuming sulphuric acid is sulphuric acid that contains added sulphur trioxide (**SO_3**)



Mechanism of Sulphonation

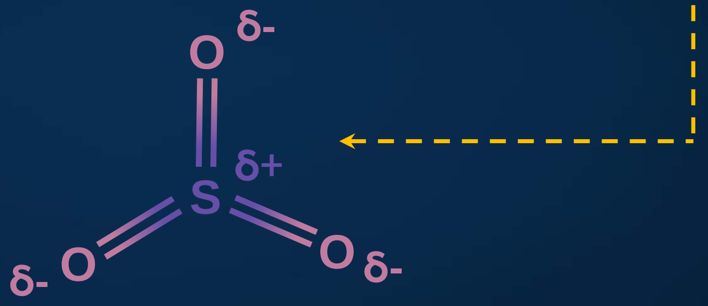
01 Generation of the electrophile

02 Formation of arenium ion

03 Removal of proton from the arenium ion

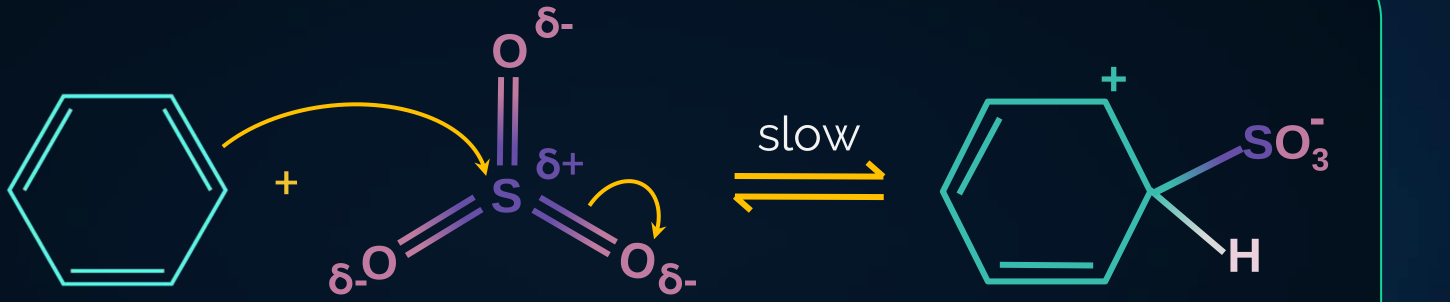
Generation of the Electrophile

$$H_2SO_4 + H_2SO_4 \rightleftharpoons H_3\overset{+}{O} + HSO_4^- + SO_3$$

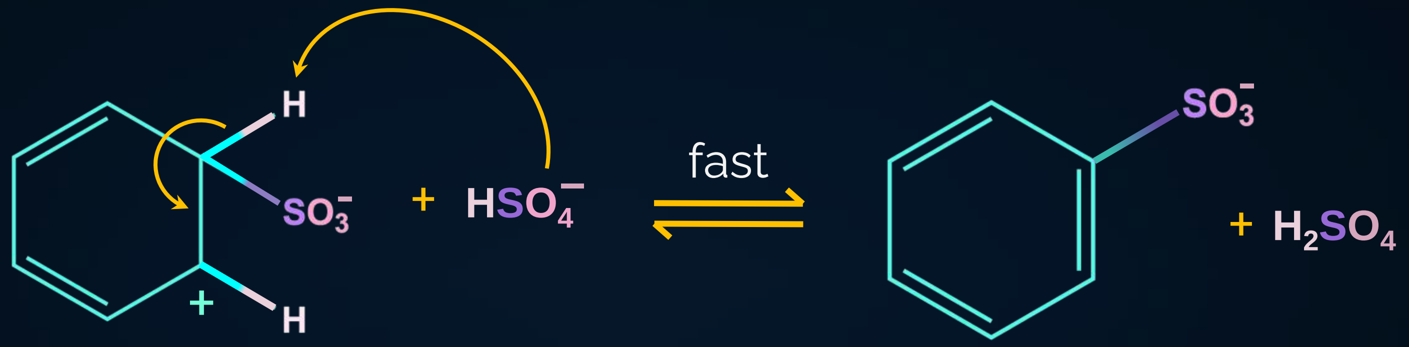


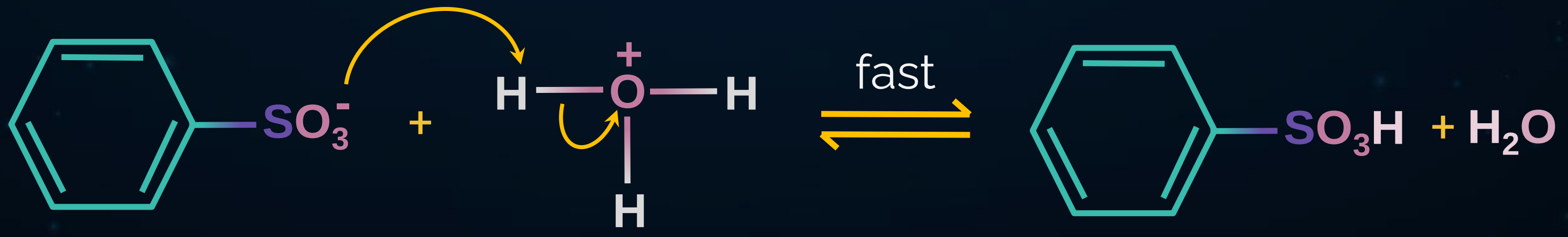
Electrophile:
Sulphur trioxide

Formation of Arenium Ion

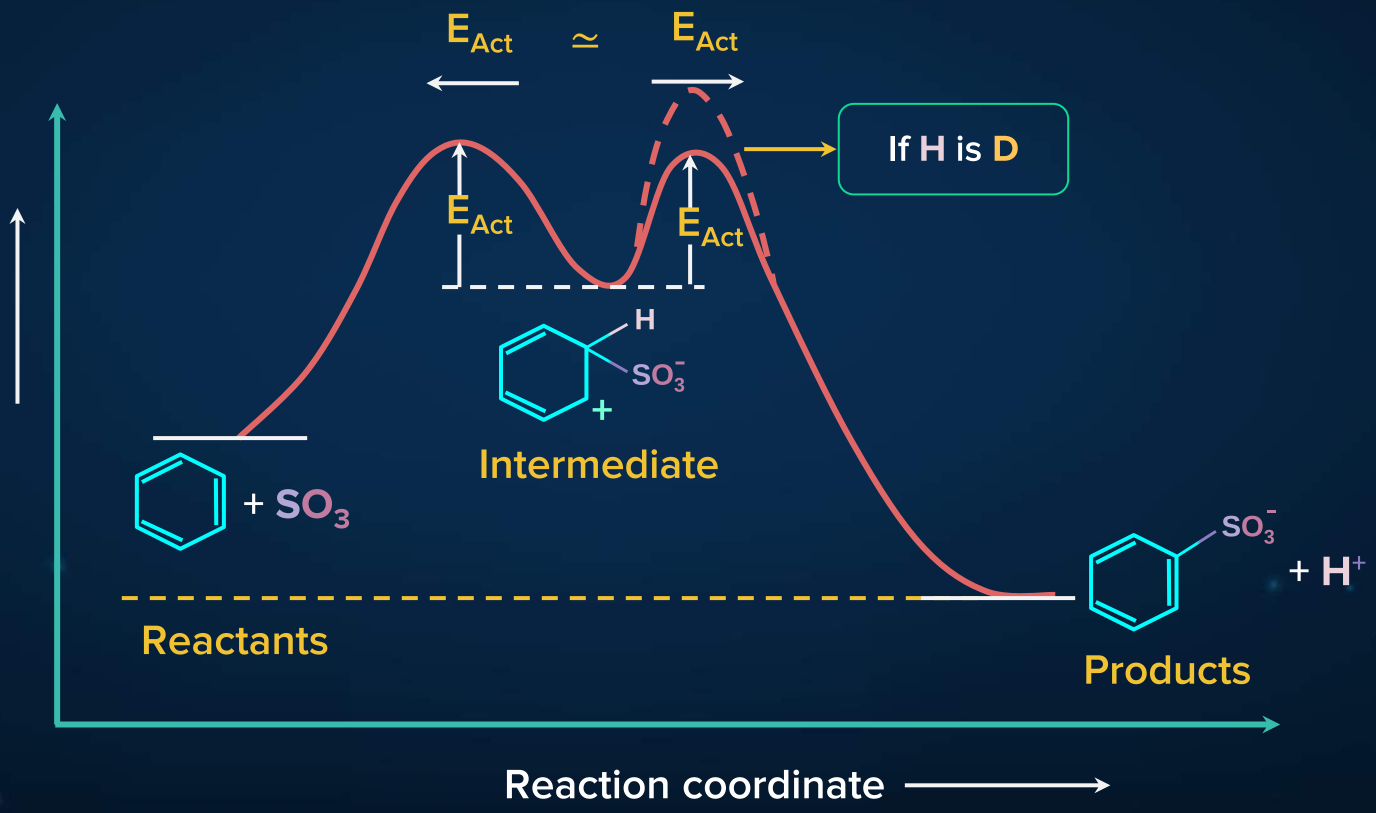


Removal of Proton





Energy Diagram



Isotope Effect

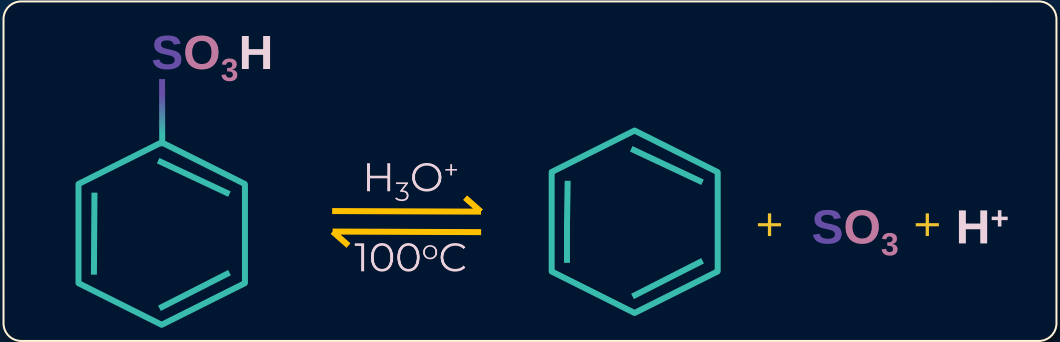
Rate of Sulphonation → $\underbrace{C_6H_6 > C_6D_6 > C_6T_6}$

Because the reaction can proceed in backward direction

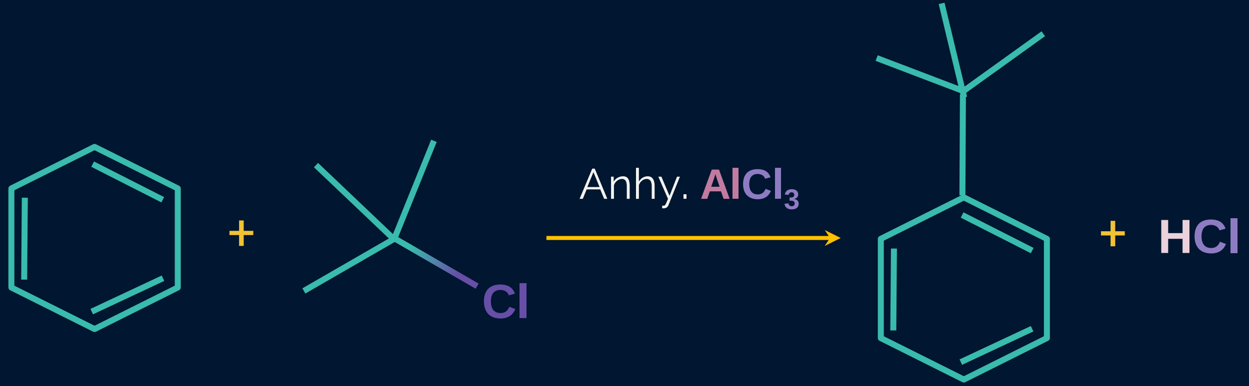
In case of iodination and sulphonation, **kinetic isotopic effect is observed.**

Did You Know?

Sulphonation of benzene is a **reversible reaction.** If Benzenesulphonic acid is heated in a dilute acid, the reaction proceeds in the reverse direction.



Friedel-Crafts Alkylation



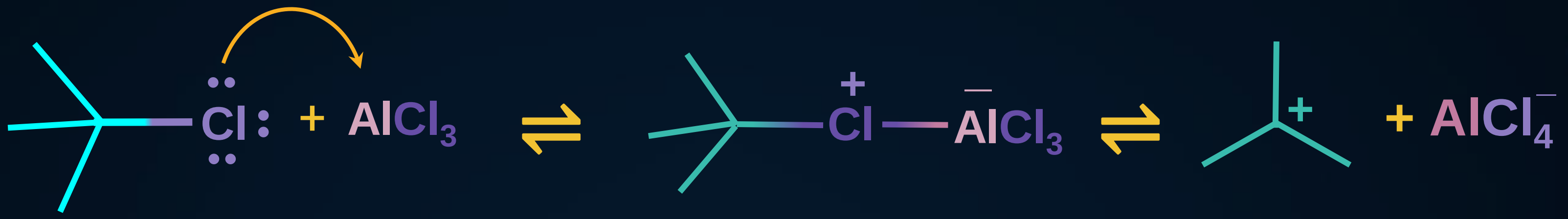
Mechanism of Alkylation

01 Generation of the electrophile

02 Formation of arenium ion

03 Removal of proton from the arenium ion

Generation of the Electrophile

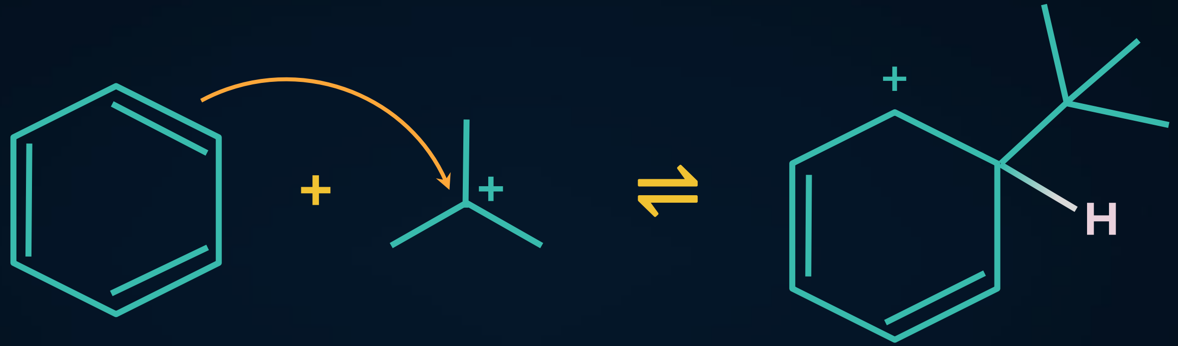


Order of overall reactivity of catalysts:

$AlBr_3$ > $AlCl_3$ > $FeCl_3$ > $SnCl_4$ > BCl_3

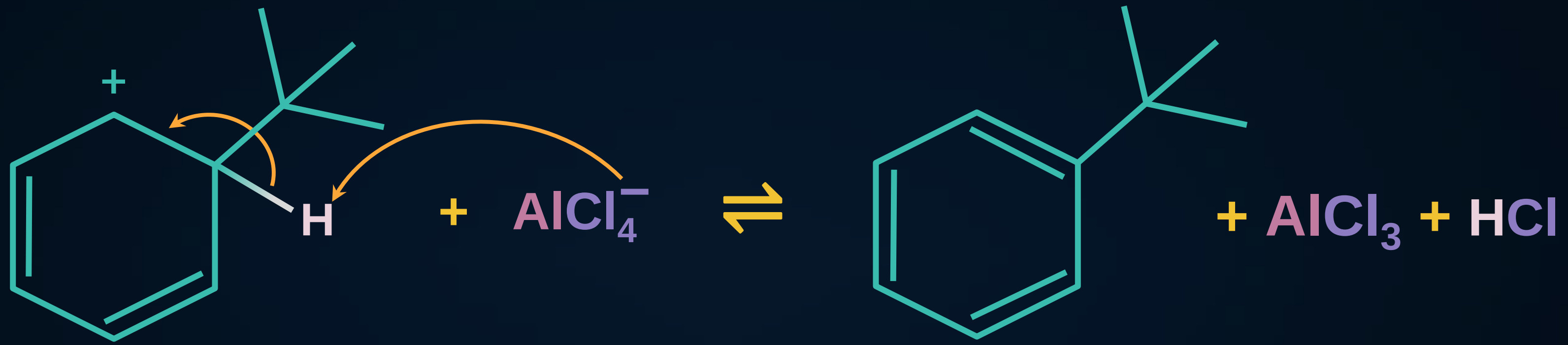
But the reactivity order in each case depends upon the **substrate, reagent and conditions**.

Formation of Arenium Ion



σ complex

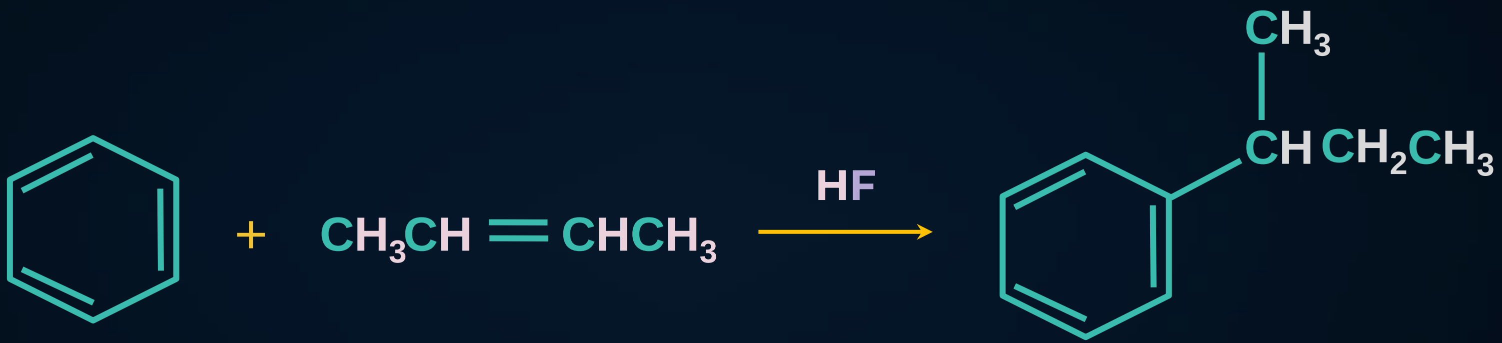
Removal of Proton



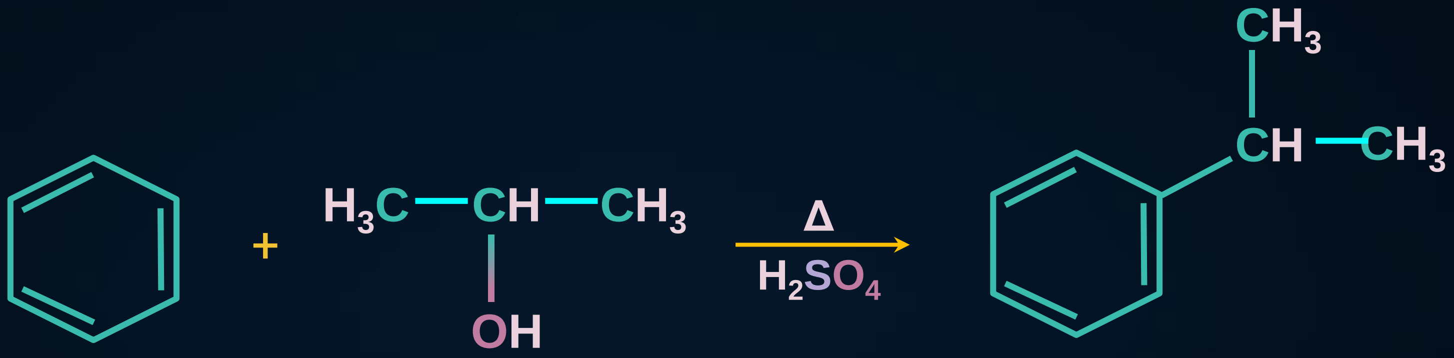
Order of **rate** of Friedel-Crafts Alkylation

R—F > R—Cl > R—Br > R—I

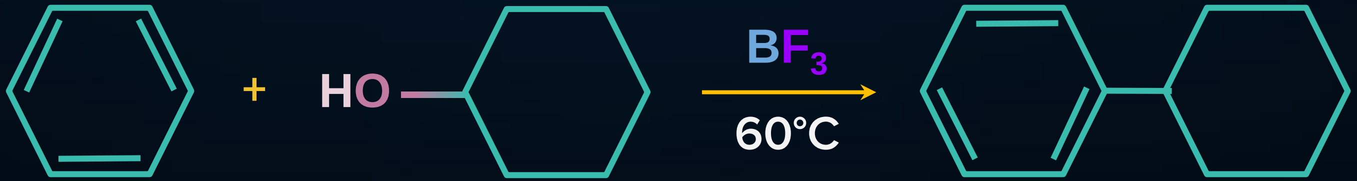
Alkylation of Benzene by an Alkene

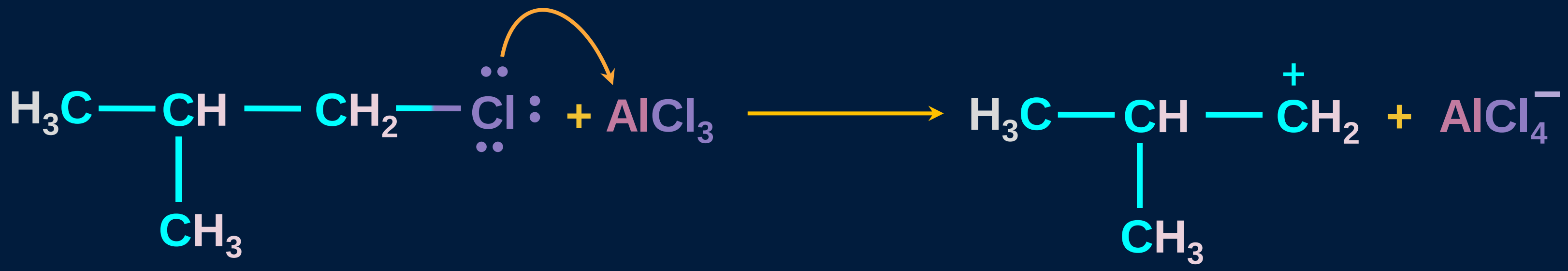


Alkylation of Benzene by an Alcohol



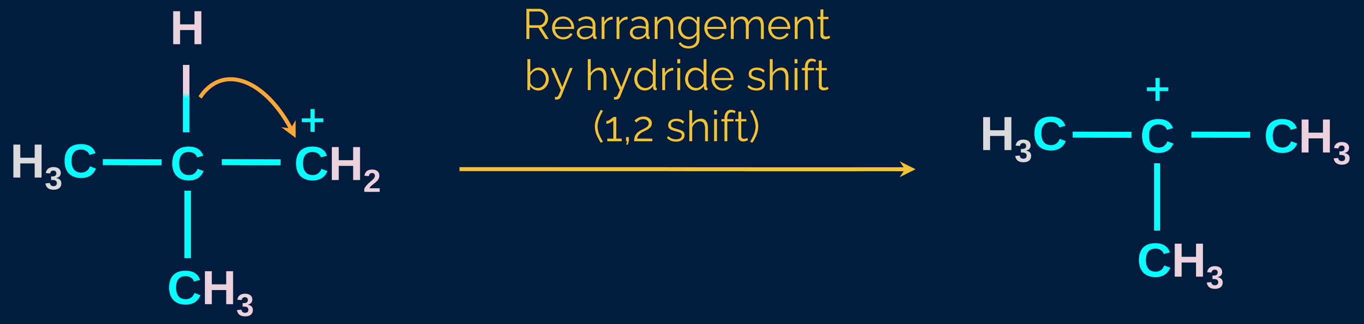
A mixture of an **alcohol** and an **acid** may also be used:





$$H_3C-\underset{\displaystyle CH_3}{\underset{|}{C}H}-CH_2-\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: + AlCl_3 \longrightarrow H_3C-\underset{\displaystyle CH_3}{\underset{|}{C}H}-\overset{+}{C}H_2 + AlCl_4^-$$

1° carbocation,
1 α-hydrogen



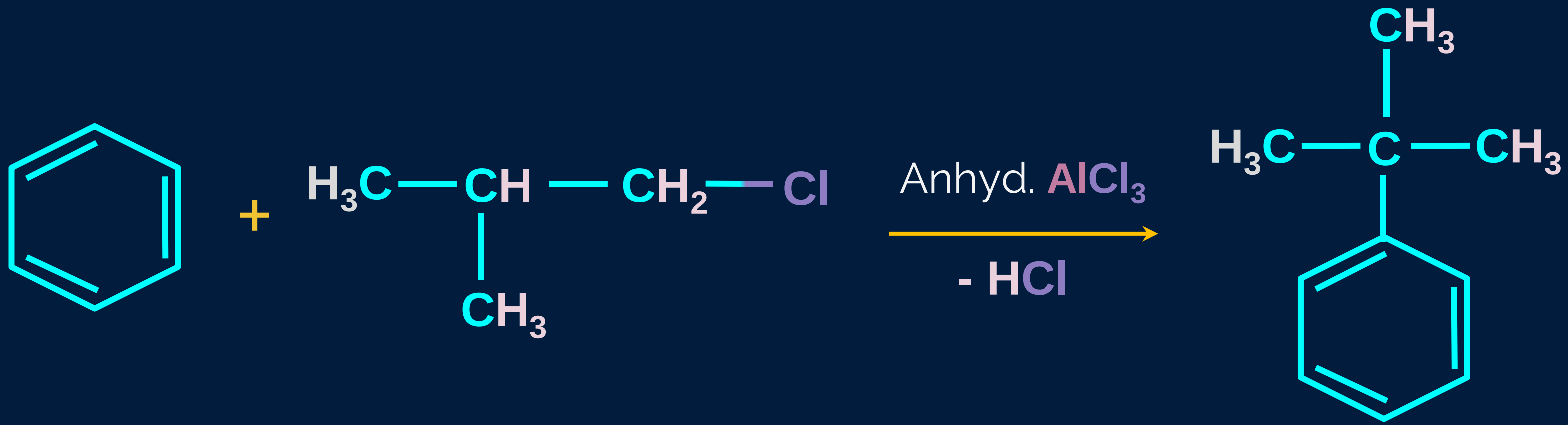
$$H_3C-\overset{\displaystyle H}{\underset{\displaystyle CH_3}{C}}-\overset{+}{C}H_2 \xrightarrow{\text{Rearrangement by hydride shift (1,2 shift)}} H_3C-\overset{+}{\underset{\displaystyle CH_3}{C}}-CH_3$$

Rearrangement
by hydride shift
(1,2 shift)

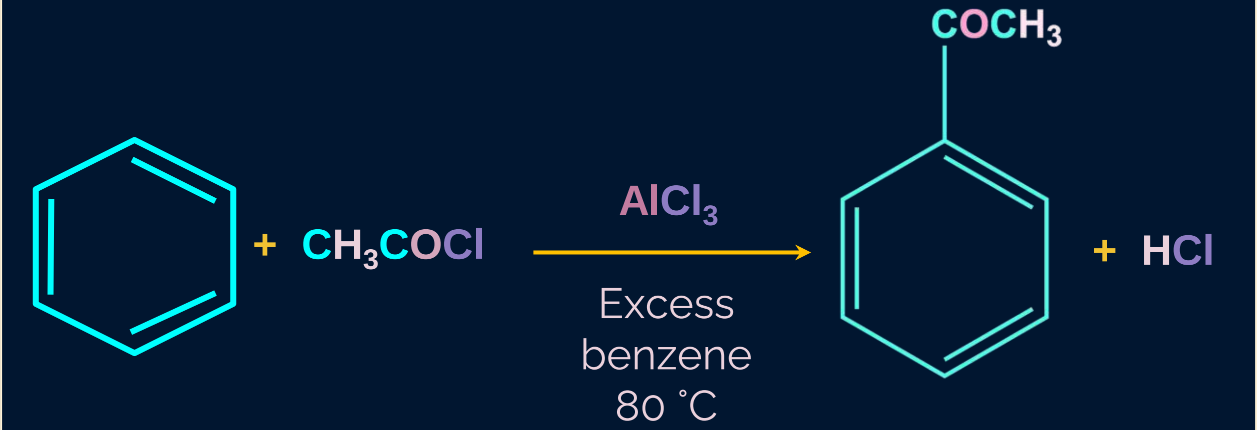
1° carbocation
1 α-hydrogen

3° carbocation
9 α-hydrogens

Friedel-Crafts Alkylation



Friedel-Crafts Acylation



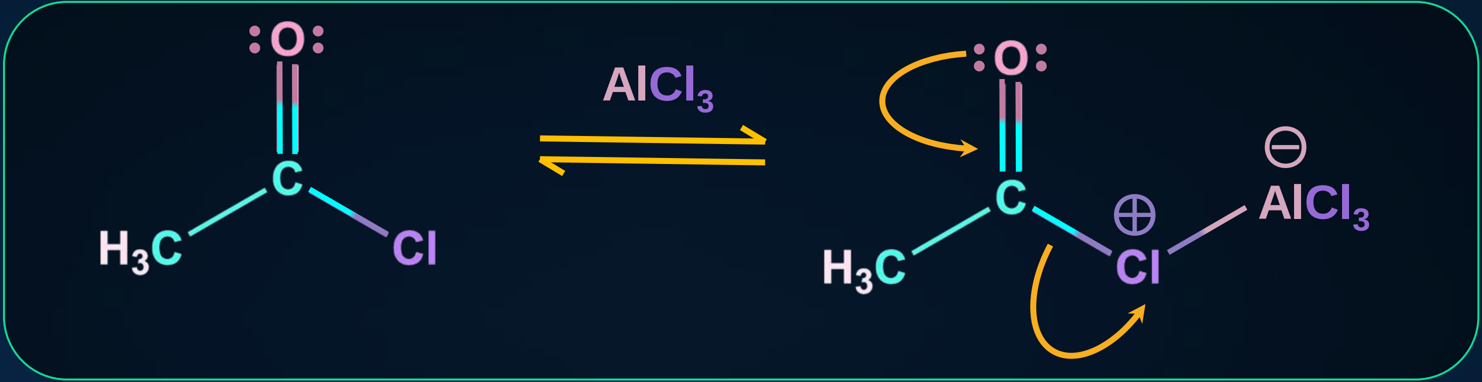
Mechanism of Acylation

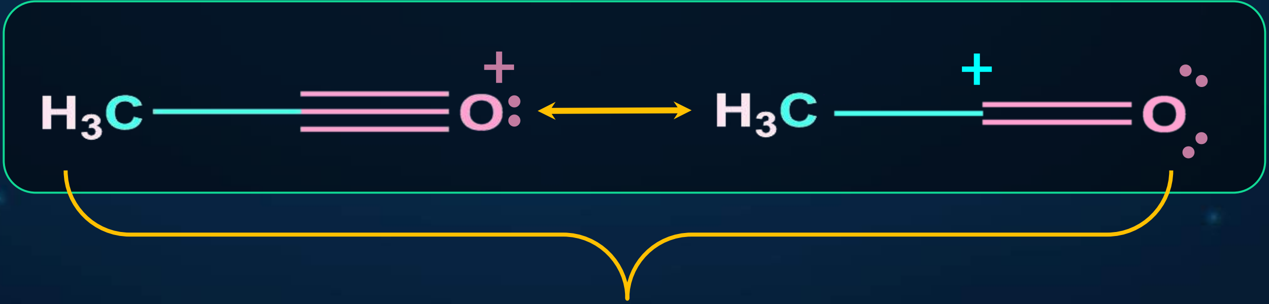
01 Generation of the electrophile

02 Formation of arenium ion

03 Removal of proton from the arenium ion

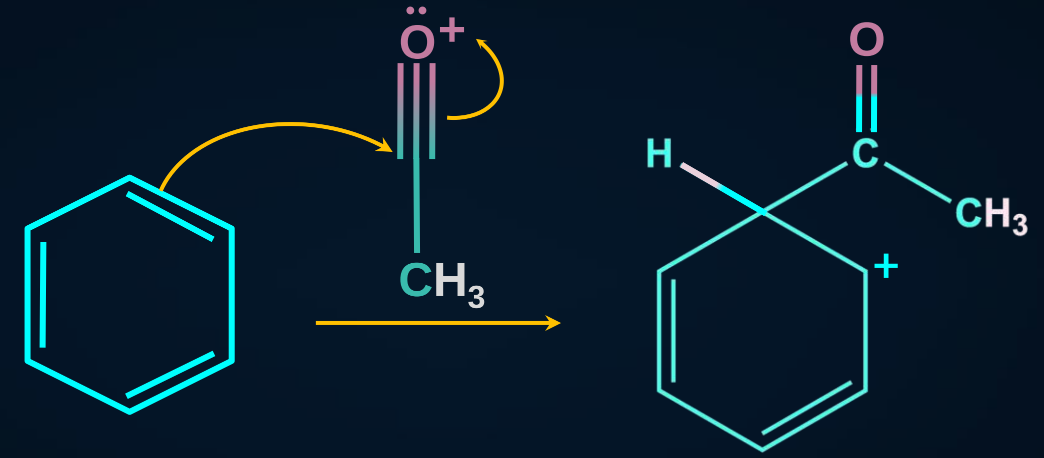
Generation of the Electrophile



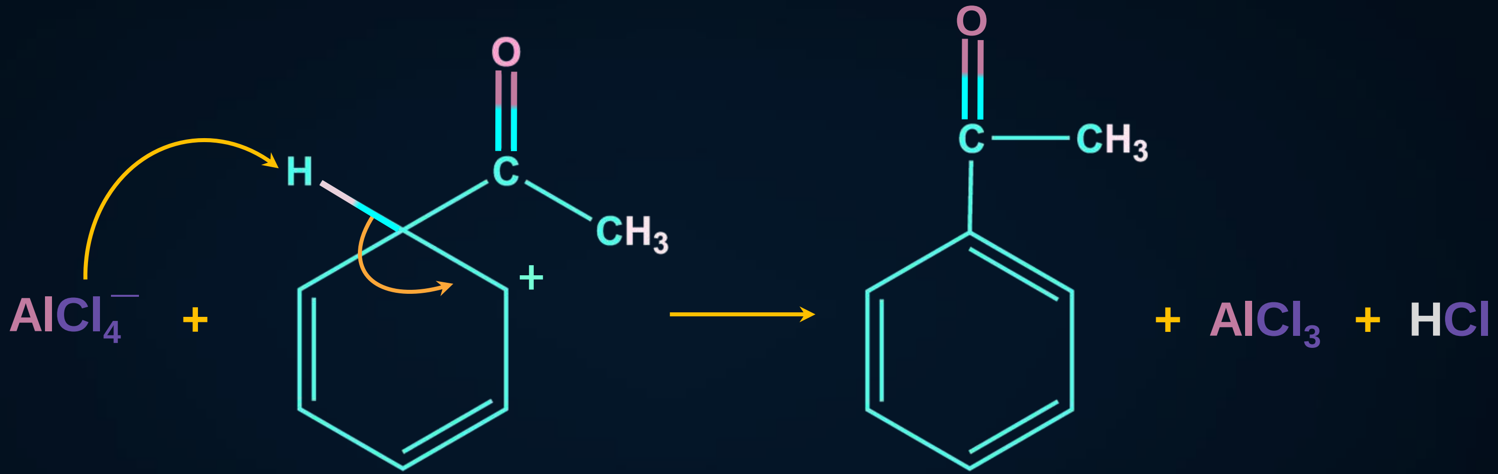


Acylium ion

Formation of Arenium Ion



Removal of Proton



Friedel-Crafts Acylation

Generally, the order of reactivity is:

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-F < R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl < R-\overset{\overset{\displaystyle O}{\|}}{C}-Br < R-\overset{\overset{\displaystyle O}{\|}}{C}-I$$

Limitations of Friedel-Crafts Reaction

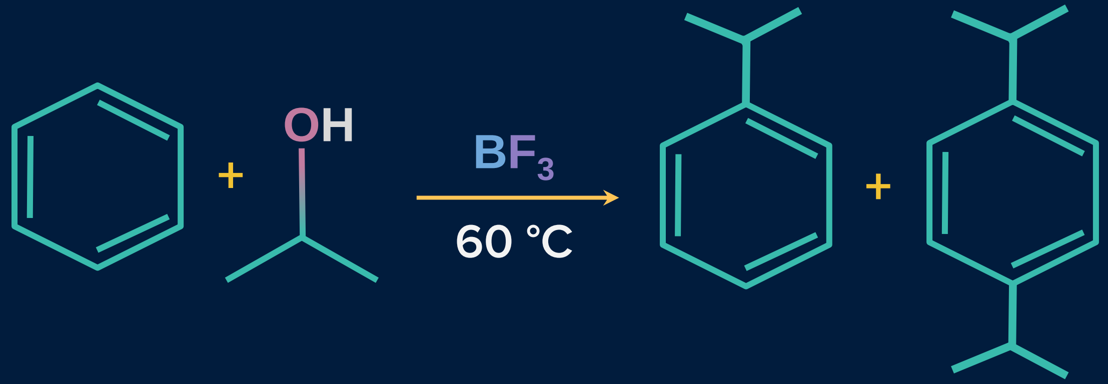
01

Highly reactive rings like aniline and **highly deactivated** rings like nitrobenzene, cyano-benzene **do not give** Friedel crafts reactions.

Limitations of Friedel-Crafts Reaction

02

Poly **alkylation is possible** but poly **acylation is not possible**.



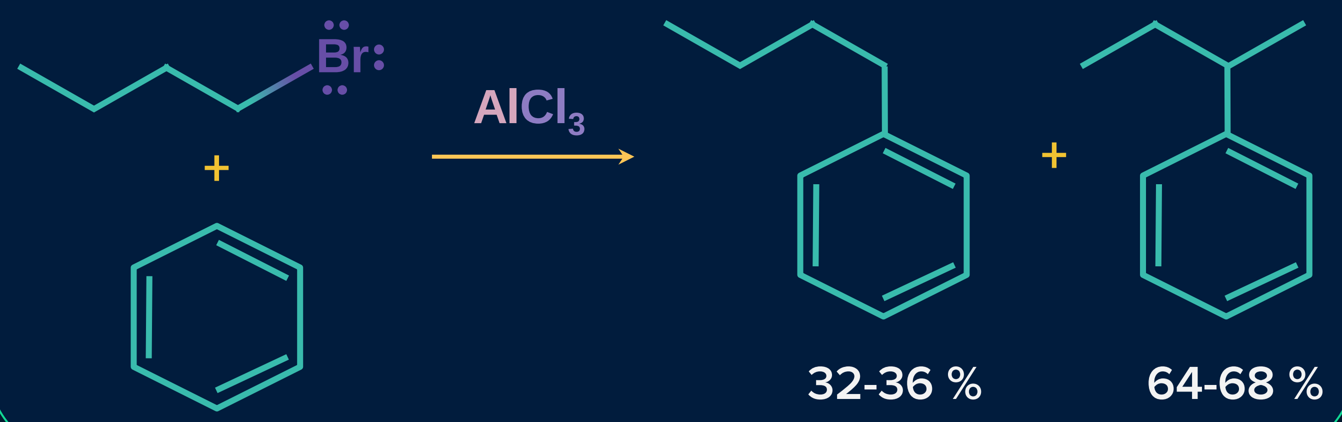
Why Poly Acylation is Not Possible?

After the first substitution, the ring becomes **deactivated** due to the presence of **–C=O** group. Thus, further substitution does not occur.

Limitations of Friedel-Crafts Reaction

03

Rearranged products may form in the Friedel crafts alkylation.



Limitations of Friedel-Crafts Reaction

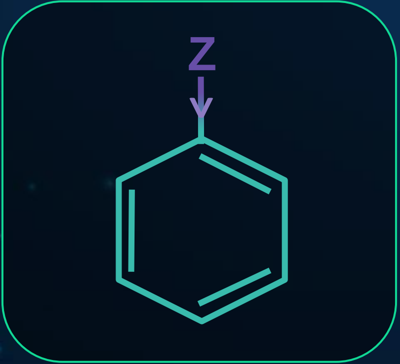
04

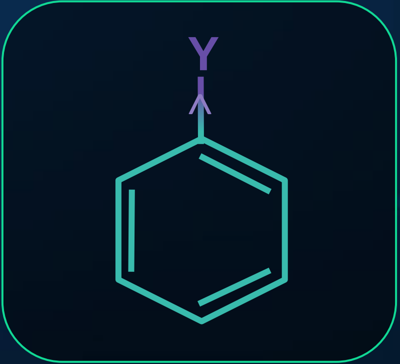
Aryl and vinylic halides cannot be used as the halide component because they do not form carbocations readily

Reactivity

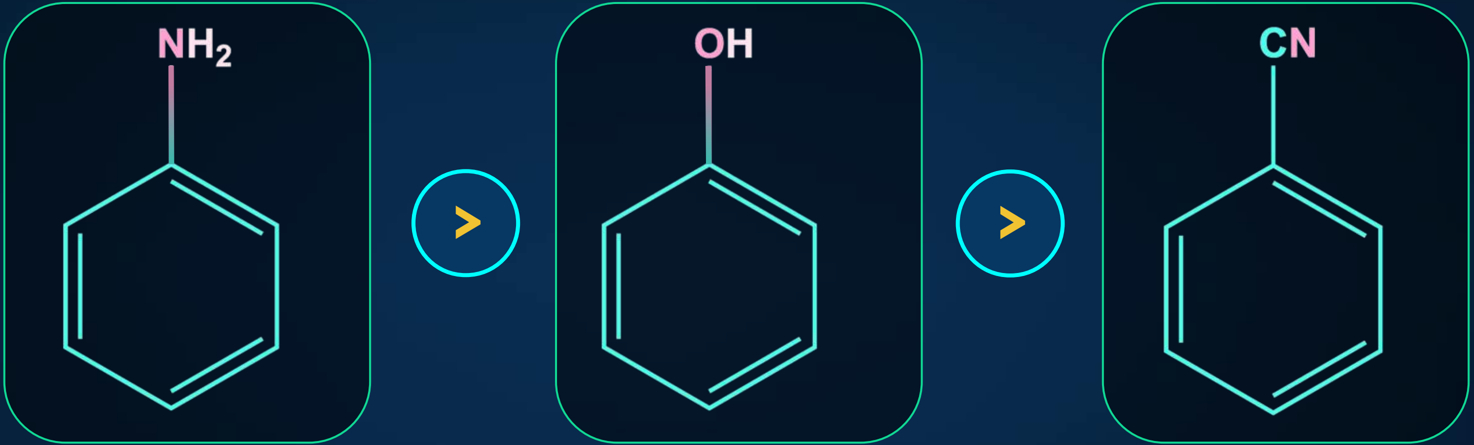
If a substituent increases the electron density of a ring, then the ring will be **more reactive** towards the electrophile.

If a substituent **decreases** the electron density of a ring, then the ring will be **less reactive** towards the electrophile.





Order of reactivities towards Electrophilic Substitution Reaction

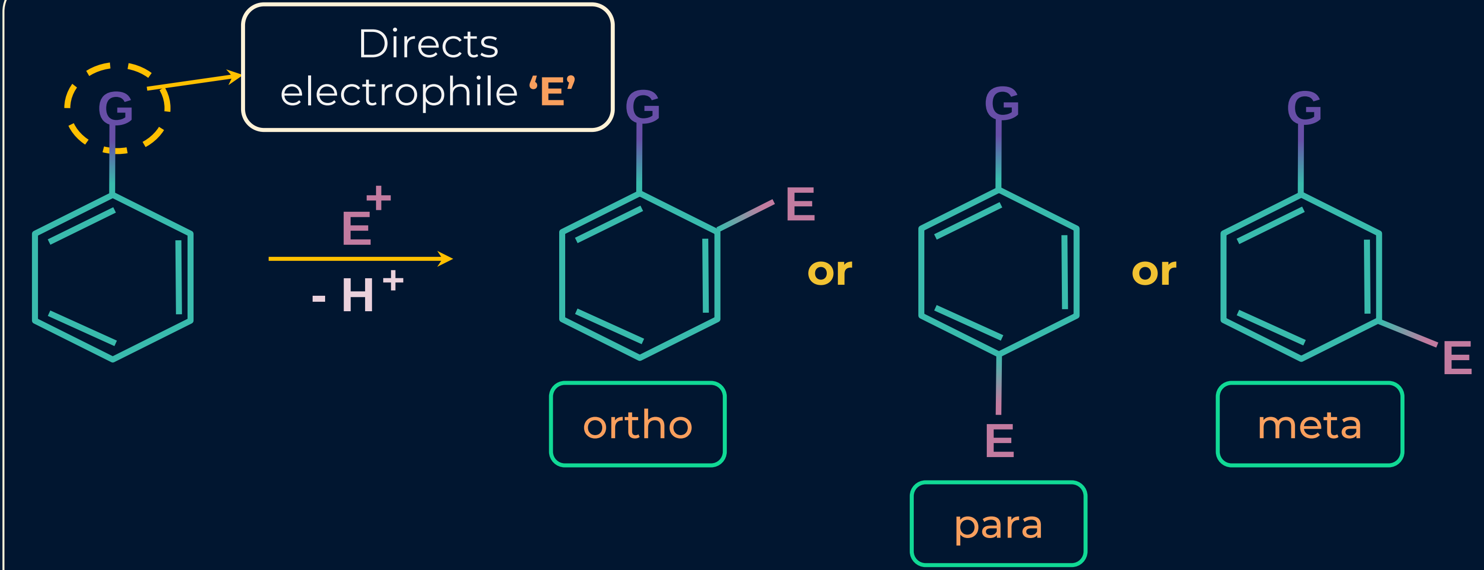


Effect of Substituent Groups in Monosubstituted Benzene

Effect of Substituemt Groups

When an **electrophilic** substitution reaction is performed on a **monosubstituted benzene**, the new group may be directed primarily to the **ortho, meta or para** position and the substitution may be **slower or faster** than with benzene itself.

Directive Influence of Groups



Directs electrophile **'E'**

$\xrightarrow[-H^+]{E^+}$

ortho

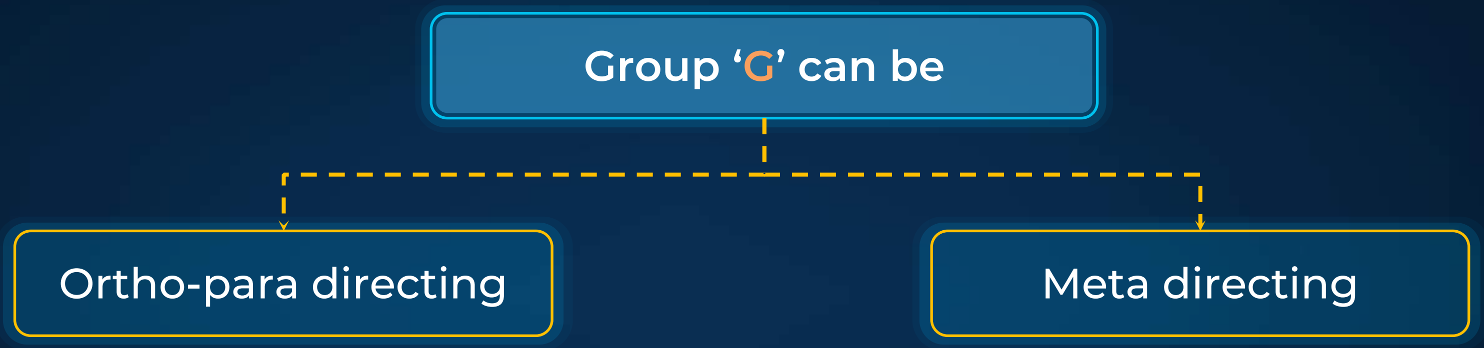
or

para

or

meta

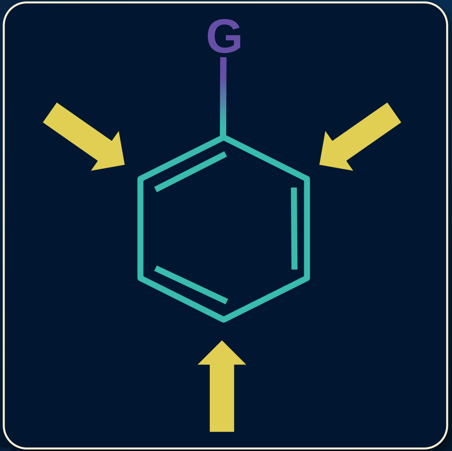
Directive Influence of Groups

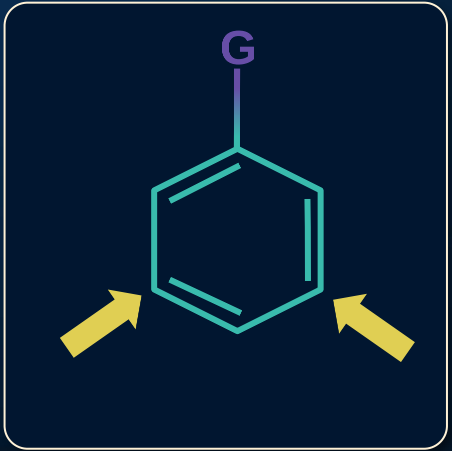


Group ‘G’ can be

Ortho-para directing

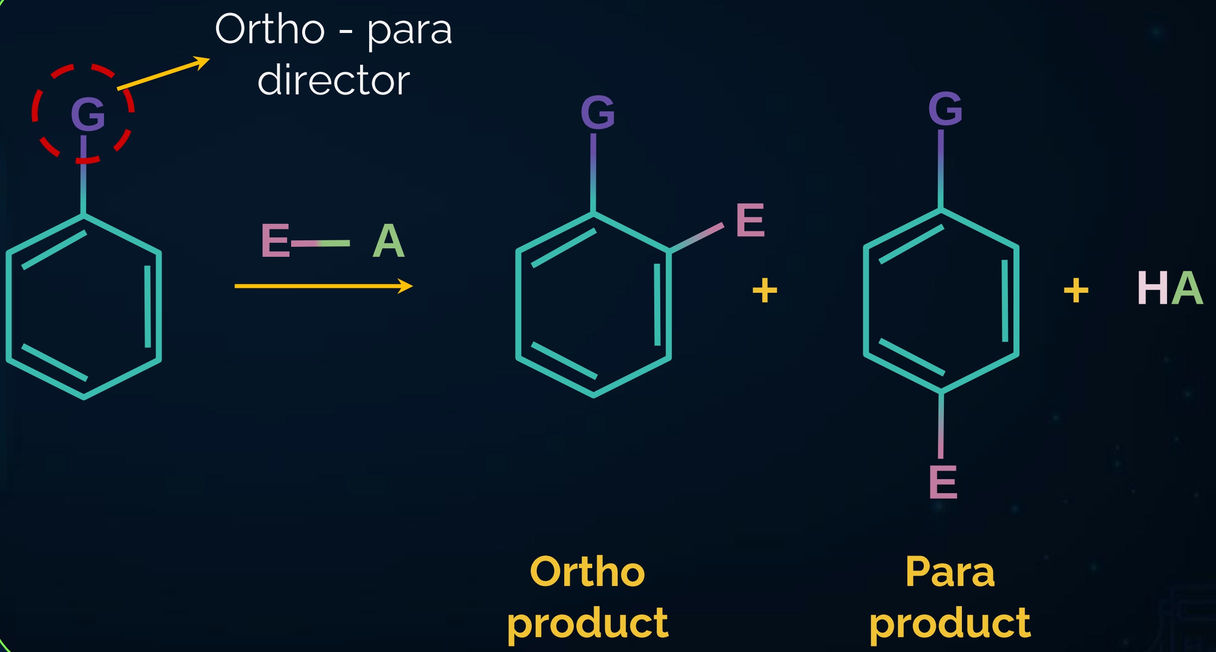
Meta directing





Ortho - Para Directing Groups

Ortho–para directors predominantly direct the incoming group to a position **ortho or para** to itself.



Ortho - Para Directing Groups

Generally, **electron releasing** groups (+M, +I) are **ortho-para directing** groups and activating towards **electrophilic** reactions.

Examples

$-O^-$, -OH , -OR , RCOO- , RCONH- , $-NH_2$, -NHR , $-CH_3$ etc.

Ortho-Para Directing Group: -OH

Ortho-para directing nature is decided by **+M effect** of -OH group.

Reactivity of benzene ring towards an electrophile increases by +M effect of -OH group.

Activating group

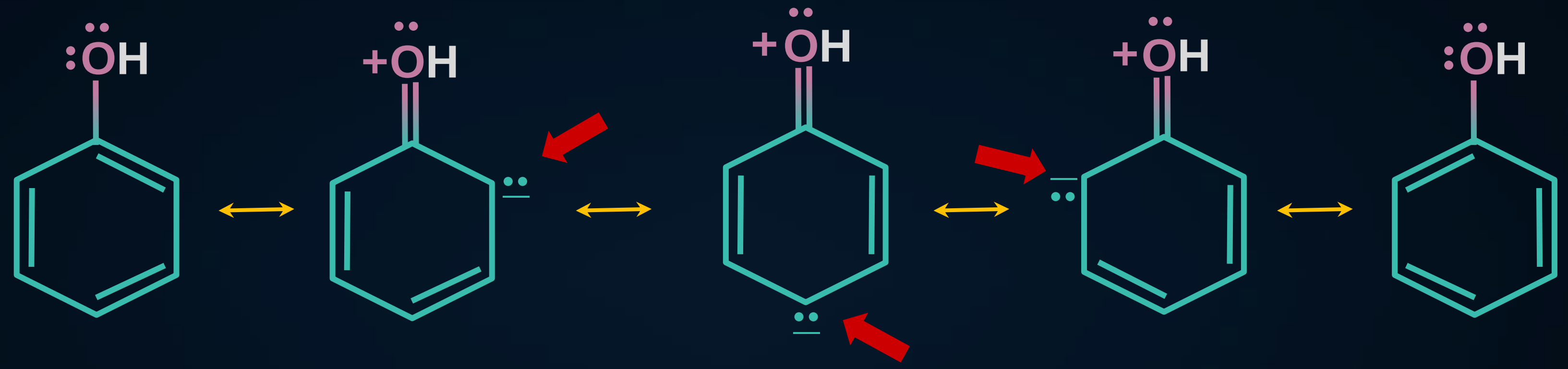
Order of Activating Effects of o-p Directing Groups

$-NH_2$ > -NHR > $-NR_2$ > -OH > -OR > -NHCOR > -OCOR > -R

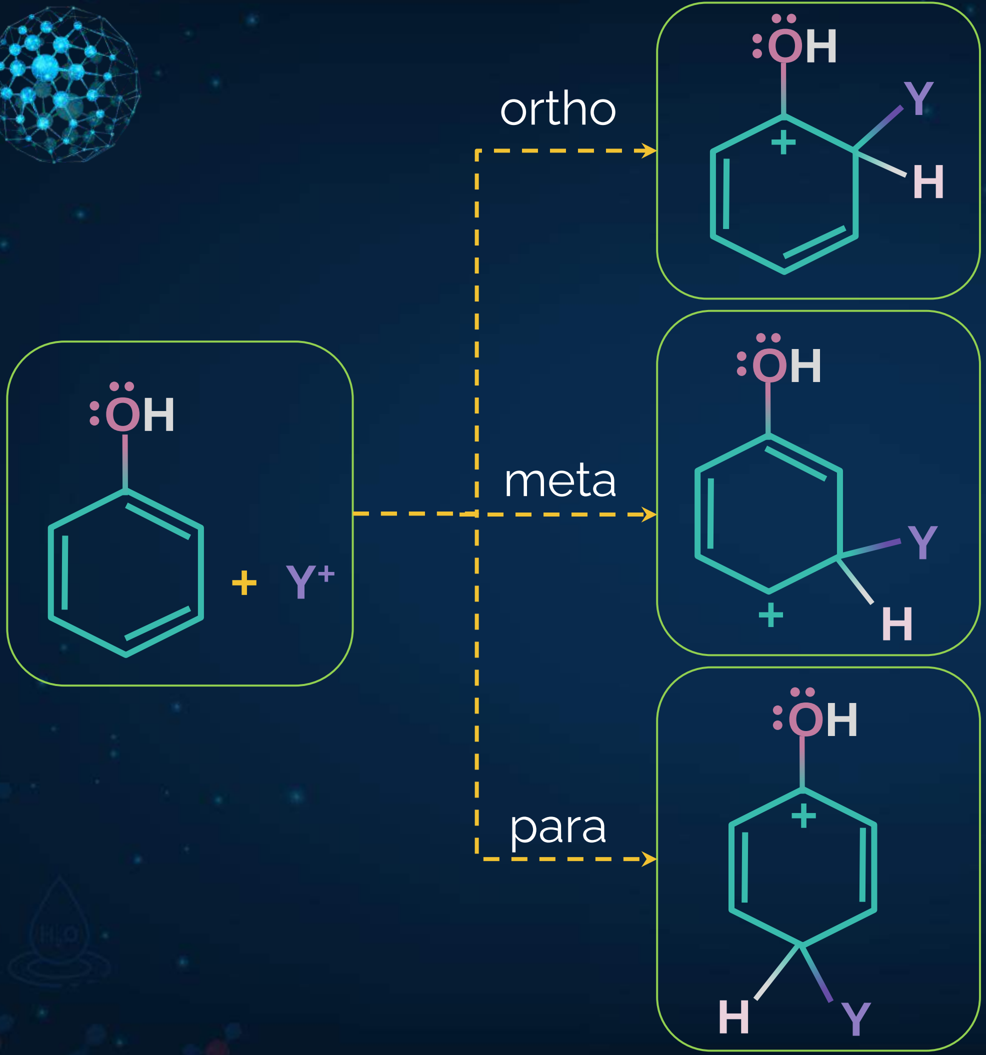
-OH group

- Ortho and para directing
- Activating group

Phenol - Resonating Structures



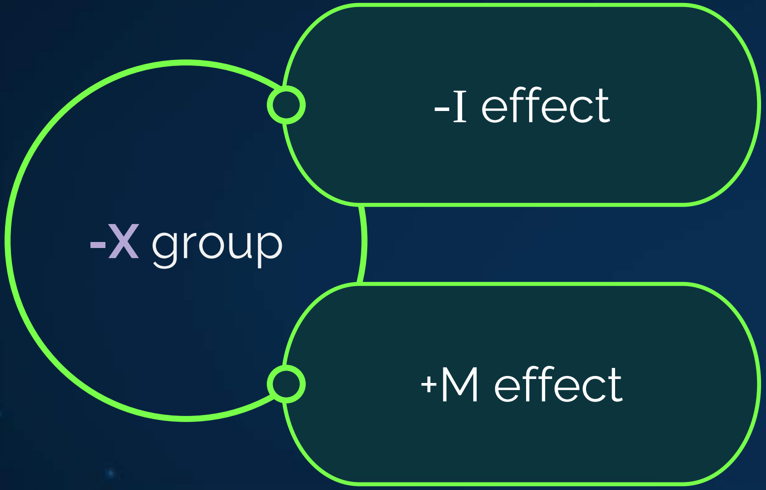
Electron density is more at **ortho and para** positions.



Relatively stable

Relatively stable

Ortho-Para Directing Group: Halogens

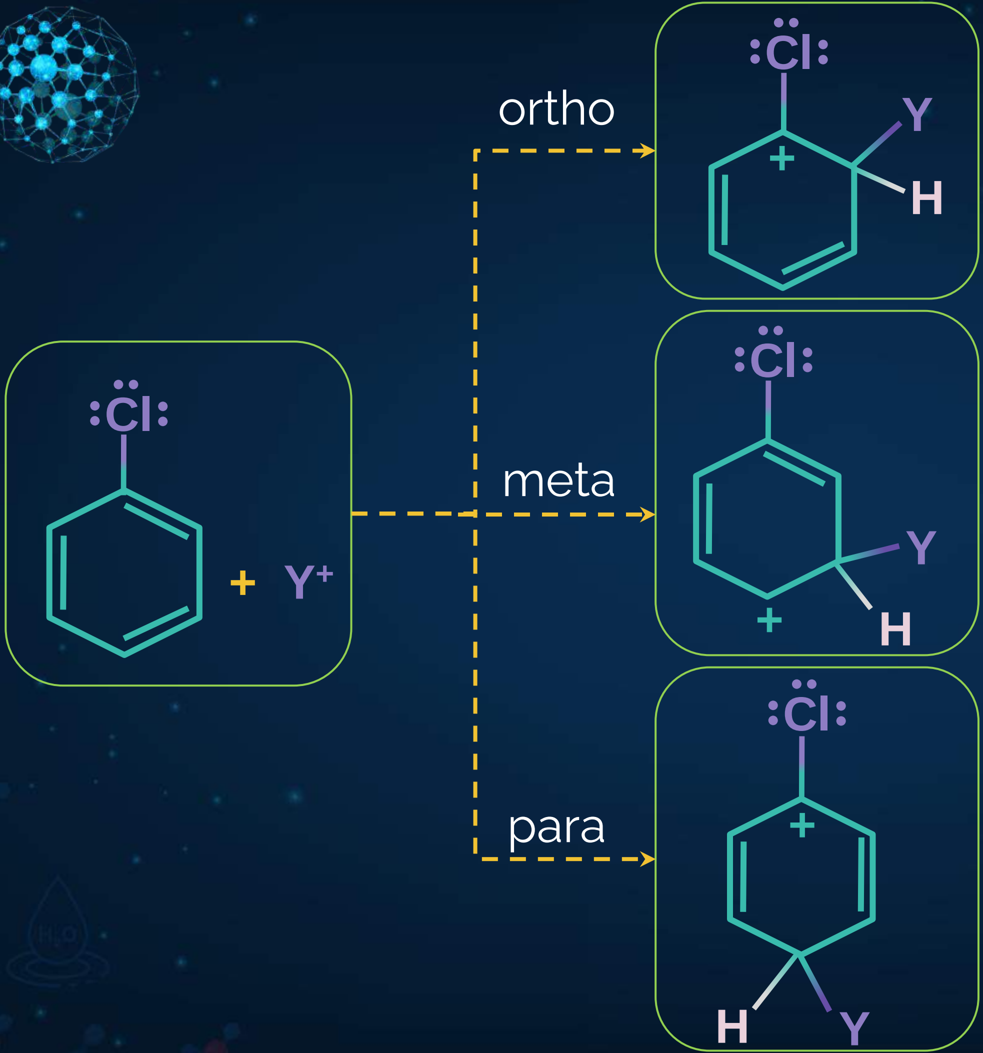


Ortho-para directing nature is decided by **+M effect** of halogens.

Reactivity of halobenzene towards electrophile **decreases** due to **–I effect** of halogens.

Deactivating Group

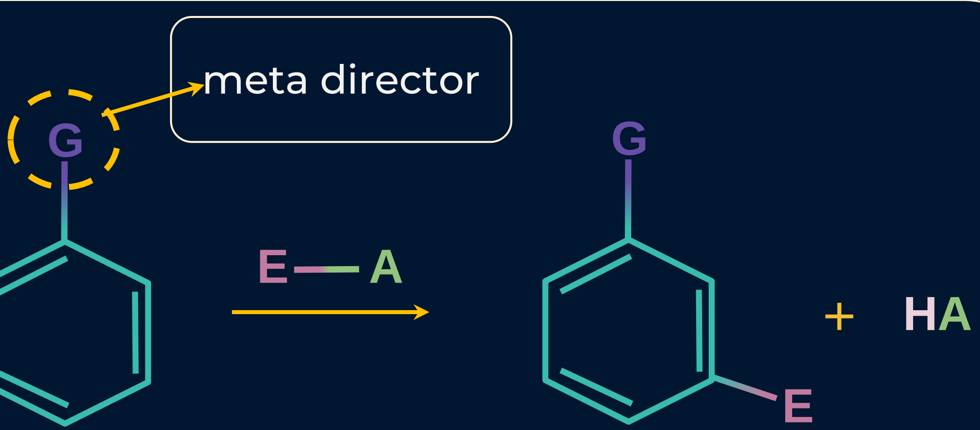
–I effect is more dominating than +M effect.



Relatively stable

Relatively stable

Meta Directing Groups



Examples

-NO_2, -CN, -CHO, -COR, -COOH, -COOR, -SO_3H, -CF_3, -CCl_3 etc.

Meta Directing Group: -CN

Meta directing nature is decided by **-M effect of -CN group.**

Reactivity of benzene ring towards an electrophile **decreases** by **-M effect of -CN.**

Deactivating group

Order of Deactivating Effects of Meta Directing Groups

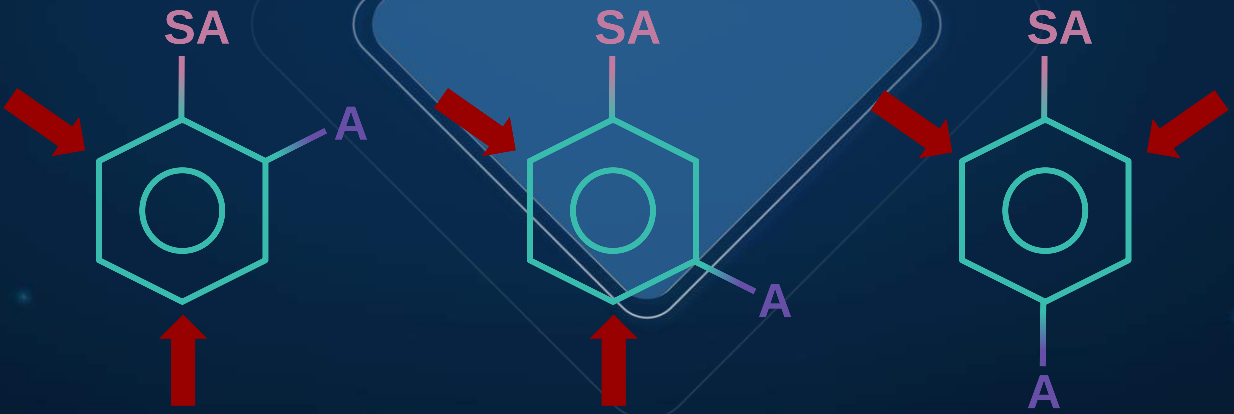
-NO_2 > -CN > -SO_3H > -CHO

> -$COCH_3$ > -COOH > -COOR > -X

Important Points

01

If **both** the groups are **activating groups,** then the position of the electrophile will be determined by the **stronger activator**.



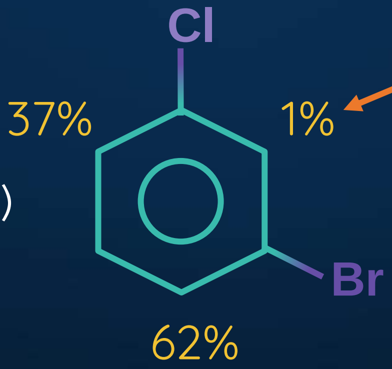
SA: Strong activator
A: Activator

Note

There is often **little substitution** between two groups that are **meta** to each other.

Very less substitution here

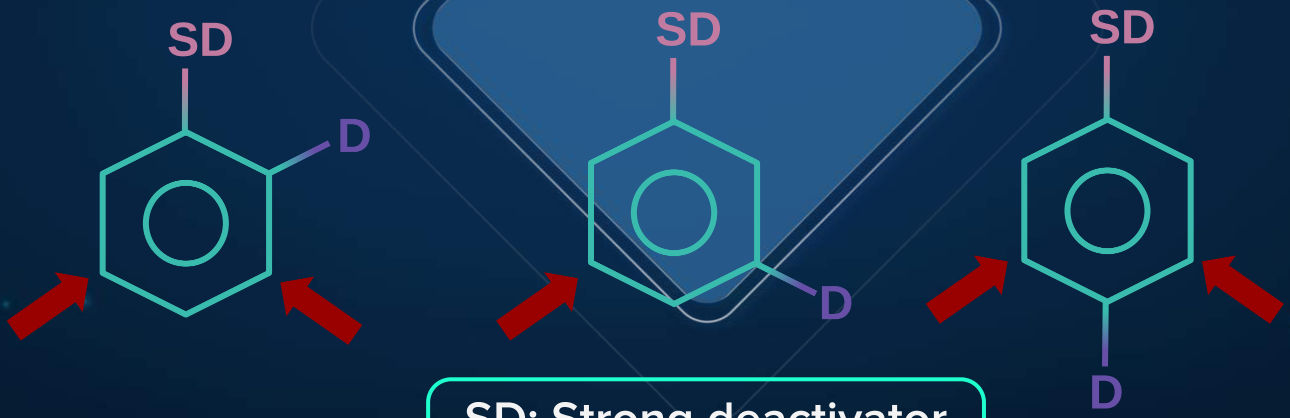
(% Nitro product)



Important Points

02

If **both** the groups are **deactivating** groups, then the **position of the electrophile** will be determined by the strong **deactivator.**

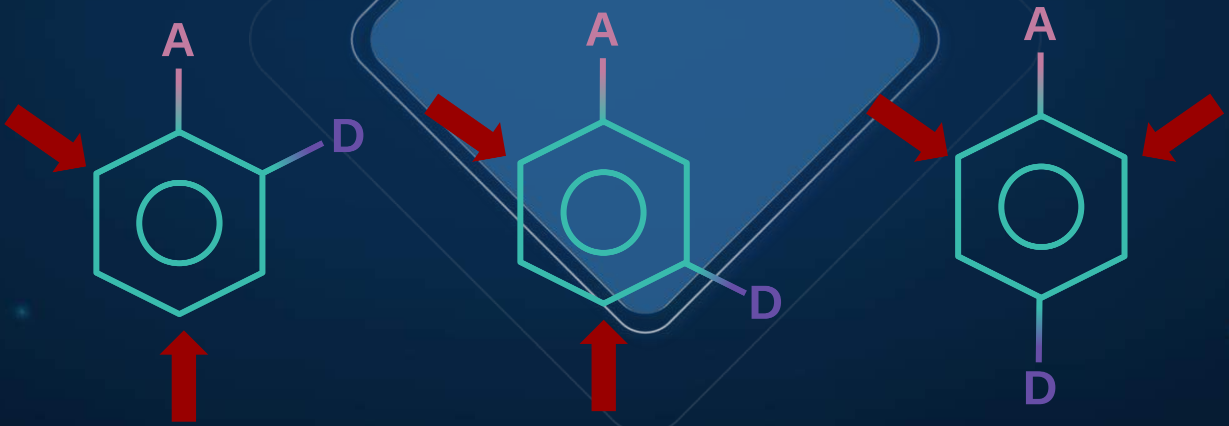


SD: Strong deactivator
D: Deactivator

Important Points

03

If **both activating** and **deactivating** groups are present, then the position of the electrophile will be determined by **the activating group**.



A: Activator
D: Deactivator

Chemical Properties

Addition Reaction

- Hydrogenation
- Halogenation

Hydrogenation of Aromatic Hydrocarbons

At high temperature and pressure, in the presence of **Ni catalyst**, hydrogenation of benzene slowly gives **cyclohexane.**

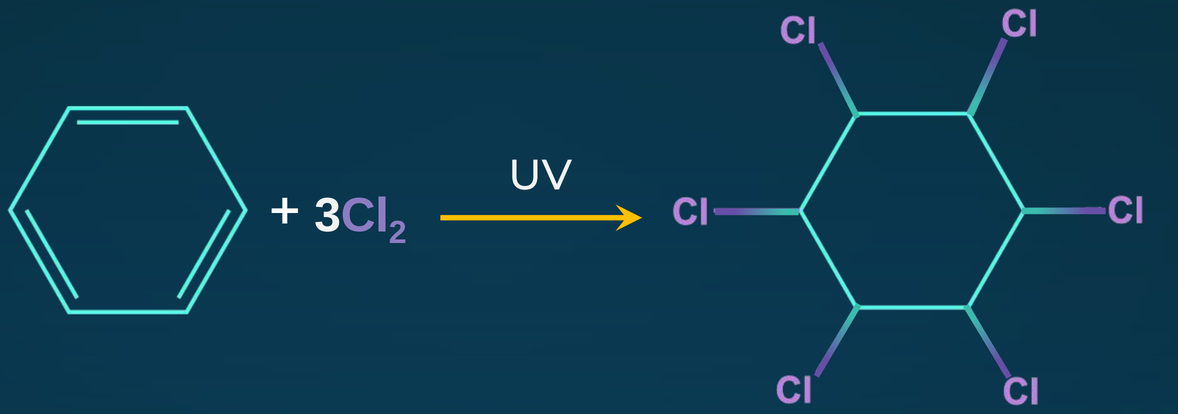
Combustion of Aromatic Hydrocarbons

When heated in air, benzene burns with a **sooty flame** producing CO_2 and H_2O.

Halogenation of Aromatic Hydrocarbons

Under **ultraviolet light**, chlorine adds to the benzene ring to give **Hexachloro-cyclohexane.**

Addition Reaction



Hexachlorocyclohexane
(Gammaxane)

Combustion of Aromatic Hydrocarbons

When heated in air, benzene burns with **a sooty flame** producing **CO_2** and **H_2O.**