OC Mega Revision

• Live at 8:00 PM

5th April - 24th April


SD Card Included
PRAHAAR JEE T-22
PHASE-3


PRAHAAR
NEET T-22


JEE T-22
Warriors 1.0-For Droppers

What you get inside the course?

- Study from Kota's **Top IITian Faculties**
- **650+ Hours of PCM Videos** Lectures with best Visualisation
- **30000+** Solved Qs
- Personalised date wise Time-table
- Live **4-Layered Doubt Solving** System
- Personalised 3-Layered **One to One Mentorship**
- **115** Fully Solved Topic wise segregated **Practice Sheets** with **homework index & video solutions**
- Solved **Prev 10 years Chapterwise Qs**
- Quick Revision Video Lectures and **90+ Mind Maps**
- **97 JEE Main** and **94 JEE advanced** 1hr Topic wise **Tests**
- 3 Hour Regular Review tests and Test Series
- Instant Test Analysis Report
- Regular Motivation and Strategy Sessions

Complete Chemistry Mega Revision Timetable

5 April

✓ IUPAC + GOC

7 April

✓ Structural + Stereo Isomerism

9 April

Hydrocarbon

12 April

Haloalkane & Haloarenes

14 April

Alcohol, Phenol & Ether

16 April

Carbonyl Compounds

19 April

Oxidation, Reduction, Carboxylic Acid & amines

21 April

Polymer & Environmental Chem

23 April

Biomolecule and CIEL

Organic Chemistry Mega Revision Imp Qs Timetable

6 April
IUPAC + GOC

8 April
Structural + Stereo Isomerism

10 April
Hydrocarbon

13 April
Haloalkane & Haloarenes

15 April
Alcohol, Phenol & Ether

17 April
Carbonyl Compounds

20 April
Oxidation, Reduction, Carboxylic Acid & amines

22 April
Polymer & Environmental Chem

24 April
Biomolecule and CIEL

I Love Chemistry


Samjho, dekho & yaad karo

Alkane(C_nH_{2n+2})

Electrophile
+
Nucleophile ♡

Alkanes do not react with chemical reagents such as dil. and conc. HCl, dil. & conc. H_2SO_4, dil. & conc. HNO_3, Caustic soda, acidic & basic $K_2Cr_2O_7$, $KMnO_4$ etc. That is why alkanes are called paraffins. (Parum = little, affins = reactivity).

Methods of Preparation

hawa X

(1) From alkenes and alkynes

(Catalytic Hydrogenation)

Reactive

$$\underset{\text{Alkene}}{\mathrm{R-CH=CH-R}} + \mathrm{H_2} \xrightarrow{\text{Catalyst}} \underset{\text{Alkane}}{\mathrm{R-CH_2-CH_2-R}}$$

Catalyst

A substance that **increases or decreases the rate of a chemical reaction** without itself undergoing any **permanent** chemical change.

vegetable oil

(a) Pd/Pt at ordinary T&P.

(b) Ni, 200–300° C (Sabatier & Sandren's reaction)

(c) Raney Nickel at room temp.

Catalyst is taken in powdered form.

(2) From Alkyl Halides

$C - X \longrightarrow C - \underset{\downarrow}{H}$

small in size

✓

$$R - X + H_2 \longrightarrow \boxed{R - H} + \boxed{HX}$$

(i) Zn + HCl $\rightarrow H_2\uparrow$

(ii) Zn + CH_3 COOH $\rightarrow H_2\uparrow$

(3) From alkyl halide (By Wurtz reaction)

e^-

$\overset{\delta+}{R}\overset{e^- e^-}{-}X$ X^- X^-

$\dot{R}-\dot{R}$

$$\dot{R}-\boxed{X + 2Na + X}-\dot{R} \xrightarrow[\text{Ether}]{\text{Dry}} \underset{2}{R-R} + 2NaX$$

1. **Methane can not be prepared by this method. The alkane produced is higher and symmetrical i.e. it contains double the number of carbon atoms present in the alkyl halide taken.**

2. **Two different alkyl halides, on Wurtz reaction give all possible alkanes.**

BP ≈ CP ≈

$$\dot{C}H_3X + \dot{C}_2H_5X \longrightarrow \left.\begin{array}{l} CH_3-CH_3 \\ C_2H_5-C_2H_5 \\ CH_3-CH_2-CH_3 \end{array}\right\} \text{Mixture}$$

Separation Not Possible

$$R—X + 2Na + X—R \xrightarrow[\text{Ether}]{\text{Dry}} R—R + 2NaX$$

(a) Two moles of alkyl halide treated with Na in presence of dry ether. If ether is wet then we obtain alcohol.

Zn

$$2Na + H_2O \longrightarrow \underline{2NaOH} + \overset{\frown}{H_2}$$

$$CH_3I + Na\overline{OH} \xrightarrow[S_N2]{} CH_3OH + NaI$$

Methanol

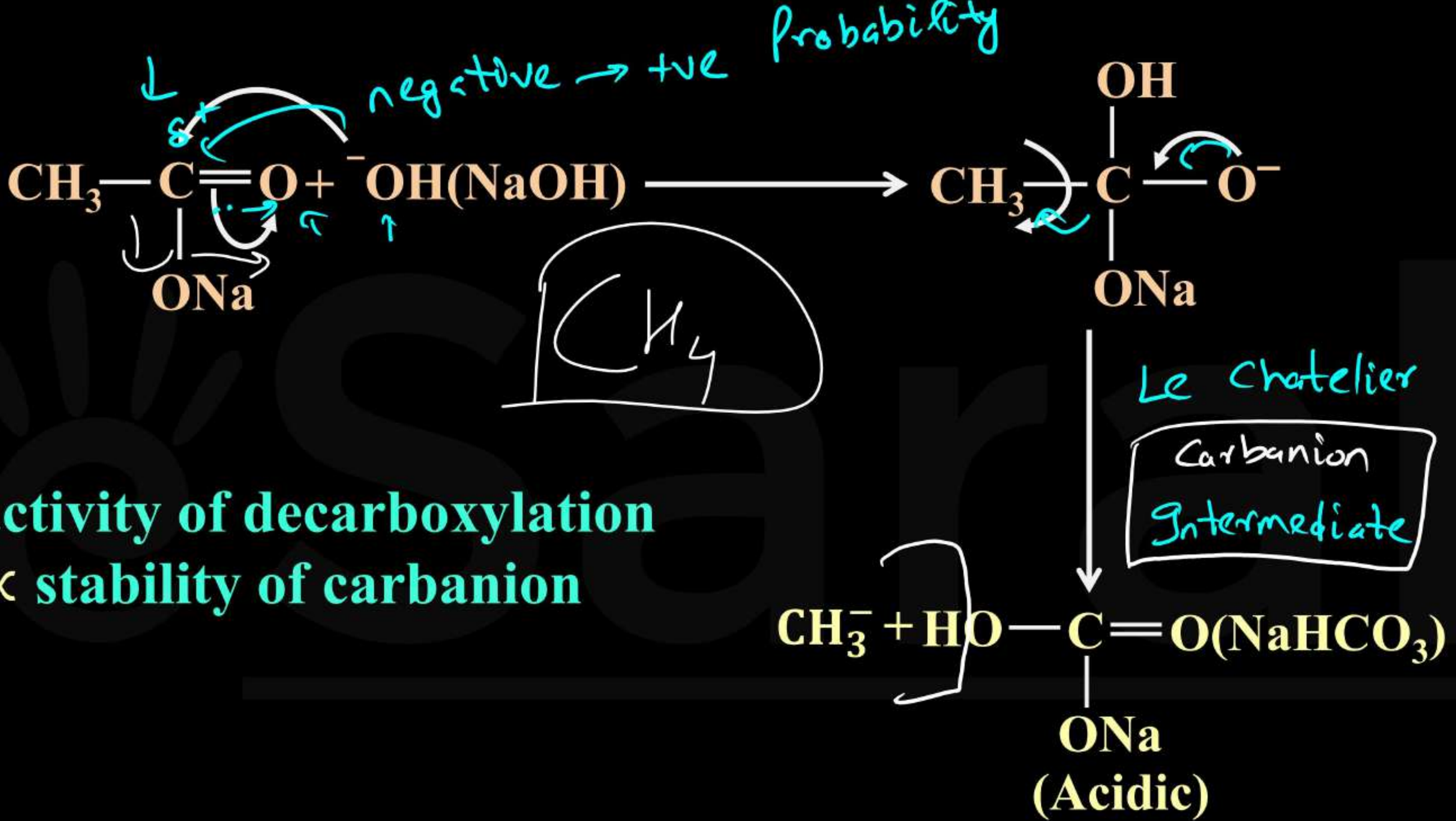
(4) From Frankland Reagent

If Zn is used in place of Na, the reaction is named as Frankland reaction.

(5) From Carboxylic Acid
(By Decarboxylation)

$$\mathrm{RCOONa + NaOH \xrightarrow[CaO]{\Delta} R-H + Na_2CO_3}$$

Soda Lime



Reactivity of decarboxylation
∝ stability of carbanion

H—H

Learn

$$\text{HCOONa} + \text{NaOH (CaO)} \xrightarrow{\Delta} H_2 + Na_2CO_3$$

Q) Give reactivity order for decarboxylation of the following.

$\underset{\text{I}}{CH_3-\underset{sp^3}{\overline{C}H_2}-COOH}$ $\underset{\text{II}}{CH_2=\underset{sp^2}{\underline{C}H}-COOH}$ $\underset{\text{III}}{CH\equiv \underset{sp}{C}-COOH}$

(1) I > II > III

[✓ (2) III > II > I]

(3) III > I > II

(4) None is correct

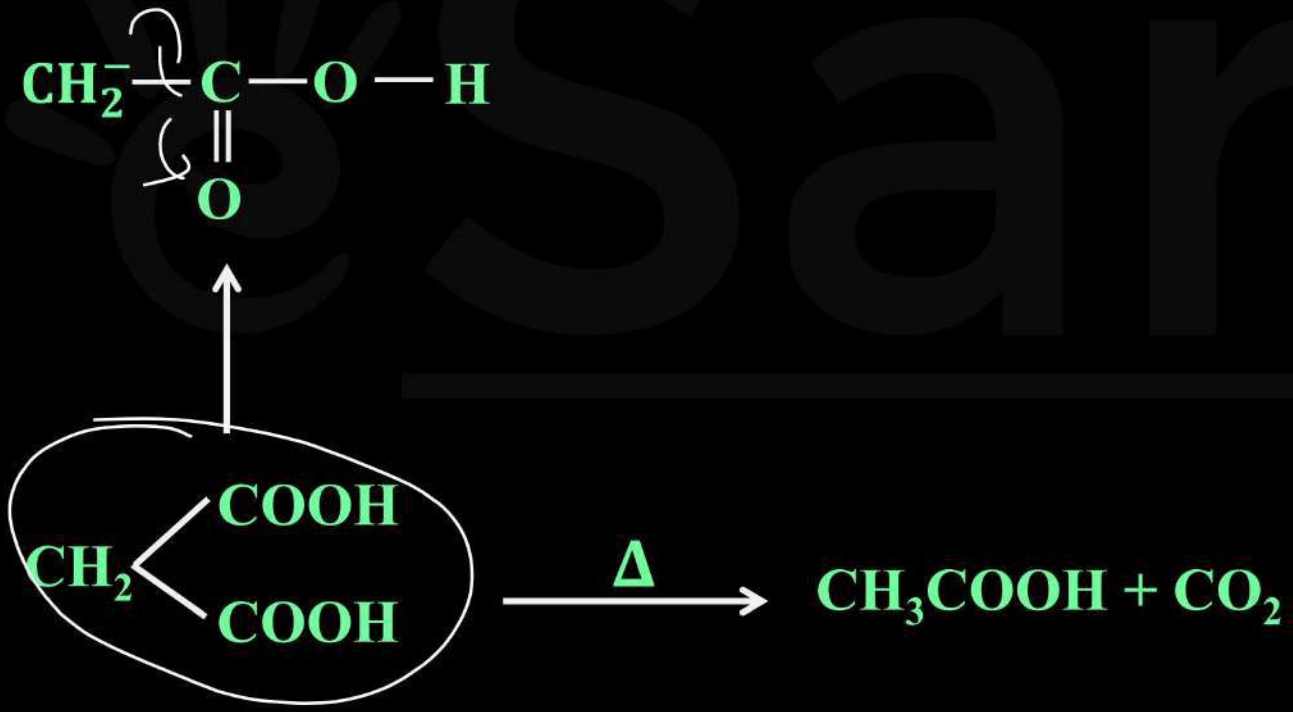
%s↑ EN↑ Carbanion↑ rate↑

Ans. (2)

$\underset{\text{I}}{CH_3-CH_2^-}$ $\underset{\text{II}}{CH_2=CH^-}$ $\underset{\text{III}}{CH\equiv C^-}$

Key Point

If in a compound two carboxylic groups are present and they are attached to same carbon atom then also decarboxylation of one of the carboxylic groups takes place simply on heating.



$$CH_2^{-}-\overset{\overset{}{}}{C}(=O)-O-H$$

$$CH_2(COOH)_2 \xrightarrow{\Delta} CH_3COOH + CO_2$$

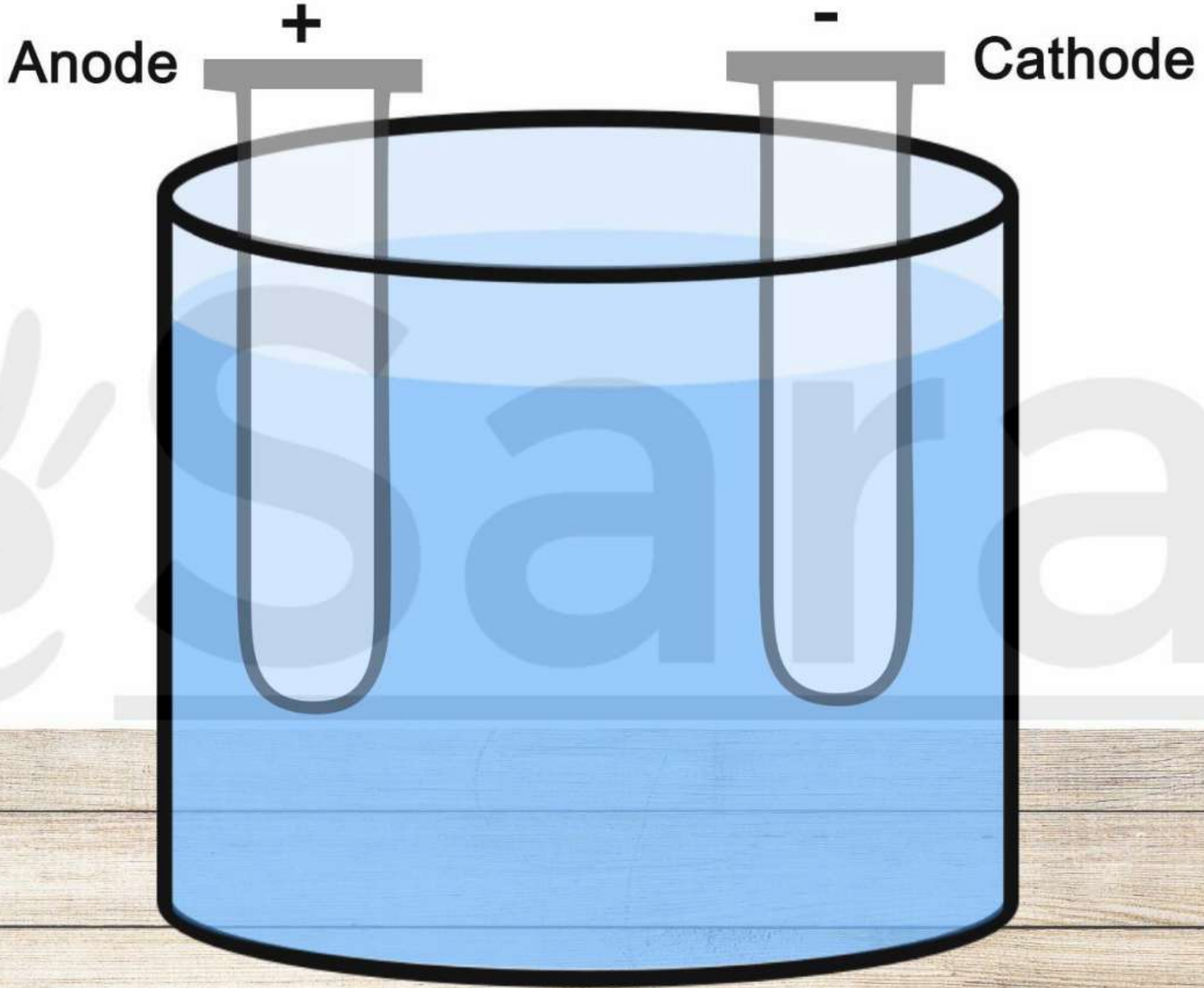
(6) From carboxylic acid (By Kolbe's process)

FR mechanism

Alkanes are formed on electrolysis of concentrated aqueous solution of sodium or potassium salt of saturated monocarboxylic acids.

methane ✗

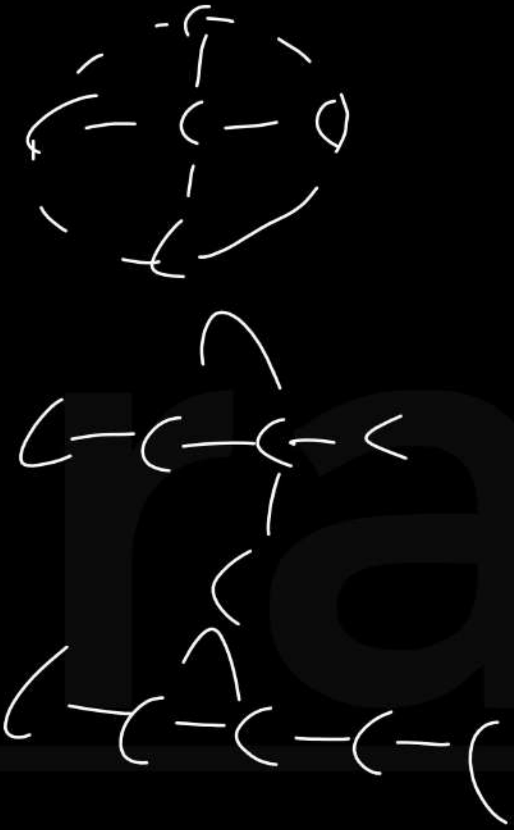
$$2RCOONa + 2H_2O \xrightarrow{\text{Electrolysis}} \underbrace{R-R+2CO_2}_{\text{At Anode}} + \underbrace{2NaOH + H_2}_{\text{At cathode}}$$


Anode
+
-
Cathode

$$\text{Boiling point} \propto \frac{1}{\text{number of side chain}}$$

For side chain containing compounds the shape approaches spherical which results in decrease in Vanderwaal forces (as surface area decreases)

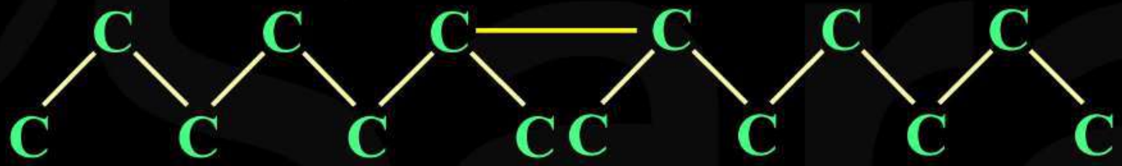
Thus boiling point
n–Pentane > Isopentane > neopentane



Melting Point

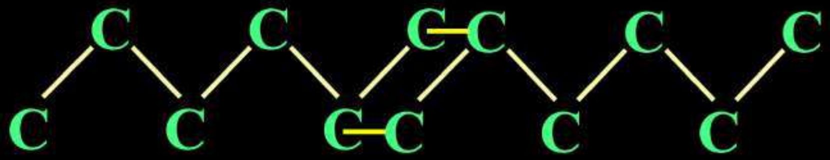
Odd number of carbon

Ineffective Packing



Even number of carbon

Effective Packing



Oxidation

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right) O_2 \longrightarrow nCO_2 + (n+1)\,H_2O\ (\Delta H = -ve)$$

$$2CH_4 + 3O_2 \longrightarrow 2CO + 4H_2O$$

$$CH_4 + O_2 \longrightarrow C + 2H_2O$$

C–black (used in printing) VVV Imp

Catalytic Oxidation

(i) **Alkanes are easily converted to alcohols and aldehydes under controlled catalytic oxidation.**

Imp

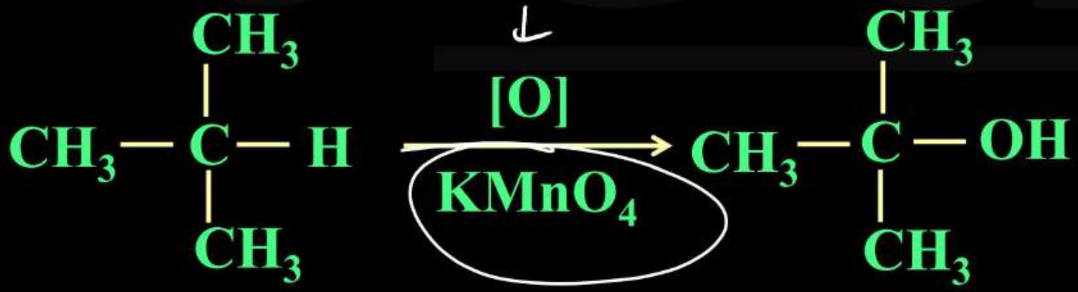
$$2CH_4 + O_2 \xrightarrow[\text{High P and T}]{\text{Red hot Cu or Fe tube}} 2CH_3OH$$

$$CH_4 + O_2 \xrightarrow[230^0\ C,100atm]{Mo_2O_3} HCHO + H_2O$$

Alkanes on oxidation in presence of manganese acetate give fatty acids.

$$CH_3(CH_2)_nCH_3 \xrightarrow[\text{High Temp}]{(CH_3COO)_2\ Mn} CH_3(CH_2)_n\,COOH$$

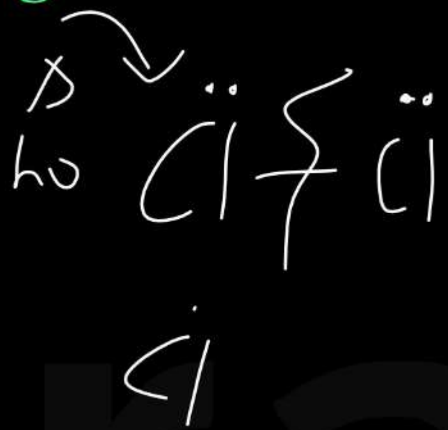
Tertiary alkanes are oxidized to give tertiary alcohols by $KMnO_4$.



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-H \xrightarrow[KMnO_4]{[O]} CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OH$$

Halogenation

Mechanism for Halogenation



Step I Chain Initiation Step

$$Cl : Cl \xrightarrow[\text{Or } \Delta]{\text{UV/ } h\nu} Cl^{\bullet} + Cl^{\bullet}$$

Step II Chain Propagation Step

$$Cl^{\bullet} + H : CH_3 \longrightarrow H : Cl + {}^{\bullet}CH_3$$

Methyl Free Radical

Carbon Free Radical Intermediate

$${}^{\bullet}CH_3 + Cl : Cl \longrightarrow CH_3Cl + {}^{\bullet}Cl$$

Step III Chain Termination Step

$$Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl_2$$

$$CH_3^{\bullet} + {}^{\bullet}Cl \longrightarrow CH_3Cl$$

$$CH_3^{\bullet} + {}^{\bullet}CH_3 \longrightarrow CH_3CH_3$$

The reactivity order for halogens is

$F_2 > Cl_2 > Br_2 > I_2$

sunlight → dhamaka

$CH_4 + I_2 \rightleftharpoons CH_3I + HI$

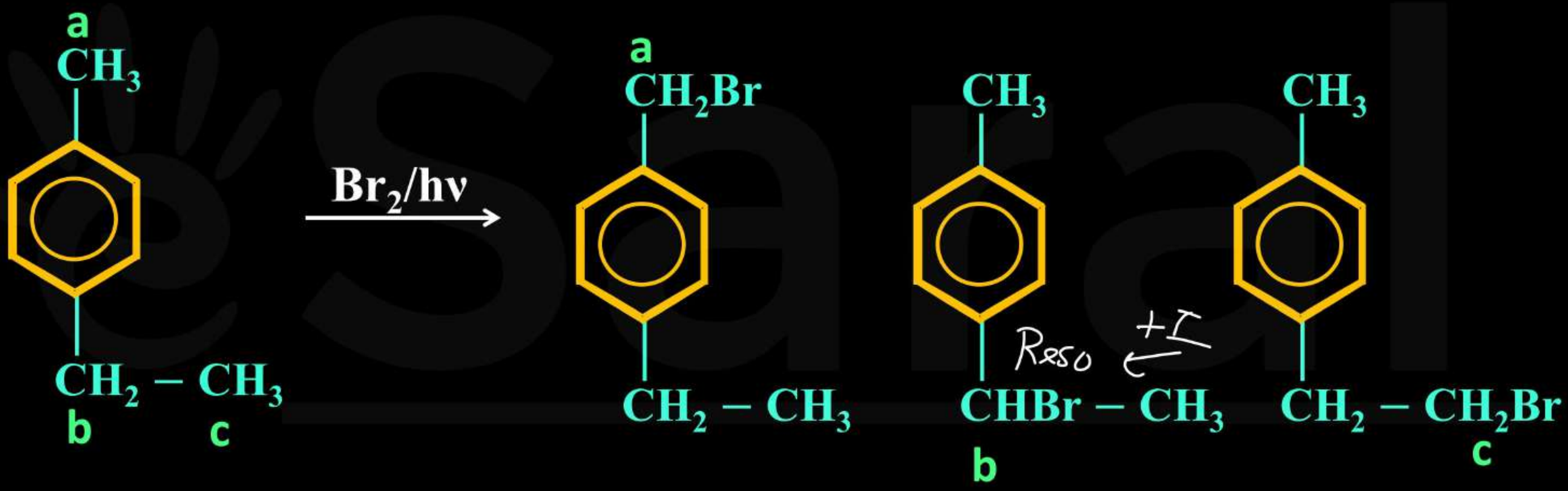
$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$

LeChatelier's Principle

Iodination may be carried out in the presence of an oxidising agent such as HIO_3, HIO_4, HNO_3, HgO etc. which destroy HI.

Q) Decreasing order of concentration of products formed on Bromination is?

FR ↑ product ↑ ror ↑



b > a> c

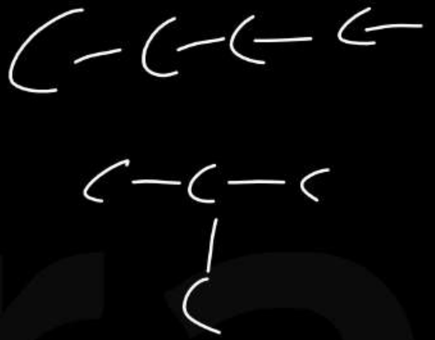
Nitration (Vapour Phase Nitration)

HNO$_3$

lp-lp

$$R-H + H\ddot{O}-NO_2 \xrightarrow{400\text{–}500^0C} \boxed{R-NO_2} + H_2O$$

$$OH^{\cdot} + NO_2^{\cdot}$$



VVV Imp

$$CH_3-CH_3 + HNO_3 \xrightarrow{450°C} CH_3CH_2NO_2 + CH_3NO_2 + H_2O$$

$$CH_3CH_2CH_3 + HNO_3 \xrightarrow{450°C}$$

1–Nitro propane	25%
2–Nitro propane	40%
Nitroethane	10%
Nitromethane	25%

Sulphonation

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-H + HO-SO_3H \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-SO_3H + H_2O$$

2–Methyl propane

2–Methyl propane–2–Sulphonic acid

Isomerization

✓✓✓✓✓✓✓✓ Imp

⇓

Petroleum

↓

Qu↑ ↑ octane value ∝ volatility

$BP \propto \frac{1}{\text{volatility}}$

agent

$$CH_3-CH_2-CH_2-CH_3 \xrightarrow{AlCl_3+HCl} CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_3$$

N-butane **Isobutane**

$$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-CH_2-CH_3 \xrightarrow{AlCl_3+HCl} CH_3-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-CH_3$$

Hydroforming or Dehydrogenation or Cyclisation or Catalytic Reforming or Aromatization

Superstar

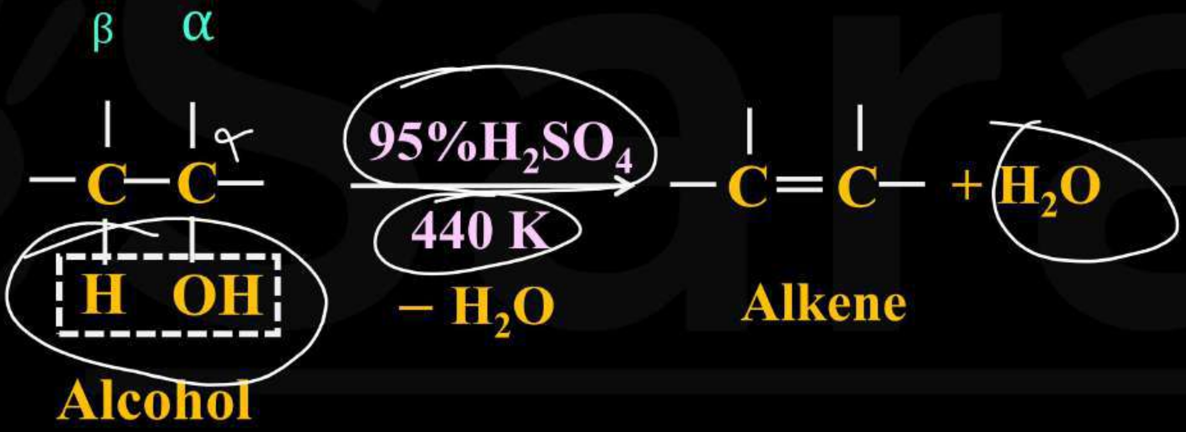
n — hexane $\xrightarrow[500^0C]{Cr_2O_3/Al_2O_3}$  $+ 4H_2$

[illegible]

ALKENE

Methods of Preparation

(1) From Alcohols (Dehydration)

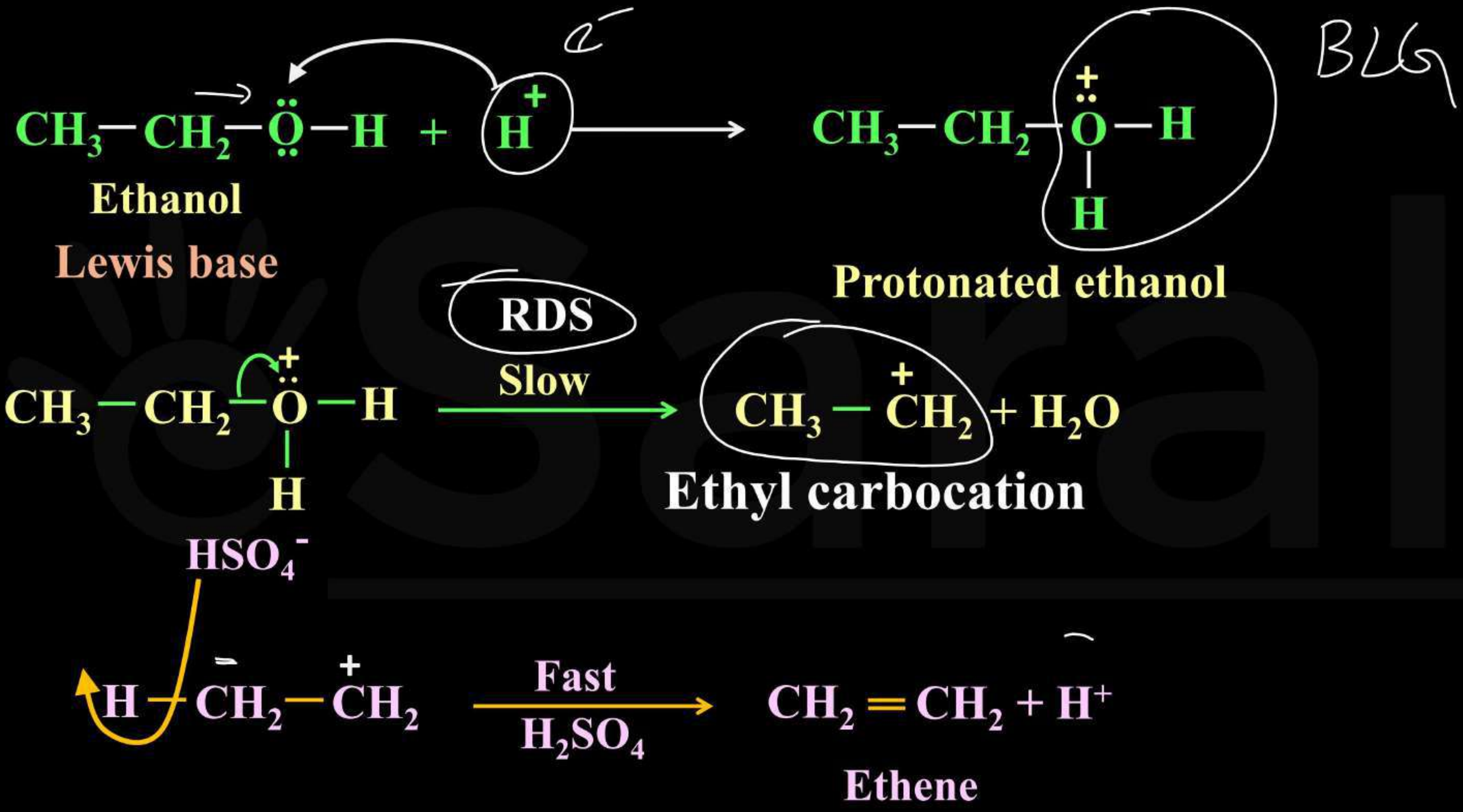


$$\overset{\beta}{-\overset{|}{\underset{\underset{H}{|}}{C}}}-\overset{\alpha}{\overset{|}{\underset{\underset{OH}{|}}{C}}}- \xrightarrow[440\text{ K}]{95\%H_2SO_4} -\overset{|}{C}=\overset{|}{C}- + H_2O$$

β–elimination or α, β–elimination

1. **For dehydration following catalyst can be used**
   Conc. H_2SO_4, H_3PO_4, $KHSO_4$ etc.
2. **Endothermic Reaction**
3. **Higher temperature is required for dehydration.**

Mechanism of Reaction



$$CH_3-CH_2-\ddot{\underset{\cdot\cdot}{O}}-H + H^+ \longrightarrow CH_3-CH_2-\overset{+}{\ddot{O}}(H)-H$$

$$CH_3-CH_2-\overset{+}{\ddot{O}}(H)-H \xrightarrow[]{\boxed{\text{RDS}}\ \text{Slow}} CH_3-\overset{+}{C}H_2 + H_2O$$

$$H-CH_2-\overset{+}{C}H_2 \xrightarrow[H_2SO_4]{\text{Fast}} CH_2=CH_2 + H^+$$

E1 Mechanism

C^+ intermediate

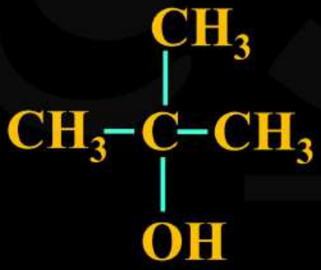
1. Reaction involves E1(unimolecular elimination) mechanism.

$$CH_3-CH_2-\underset{\displaystyle H}{\overset{+}{\ddot{O}}}-H \xrightarrow[\text{(RDS).}]{\text{Slow}} CH_3-\overset{+}{C}H_2 + H_2O$$

Ethyl carbocation

Rate: r = k$[R\text{–}OH_2^+]$

Proportionate to only one substrate.



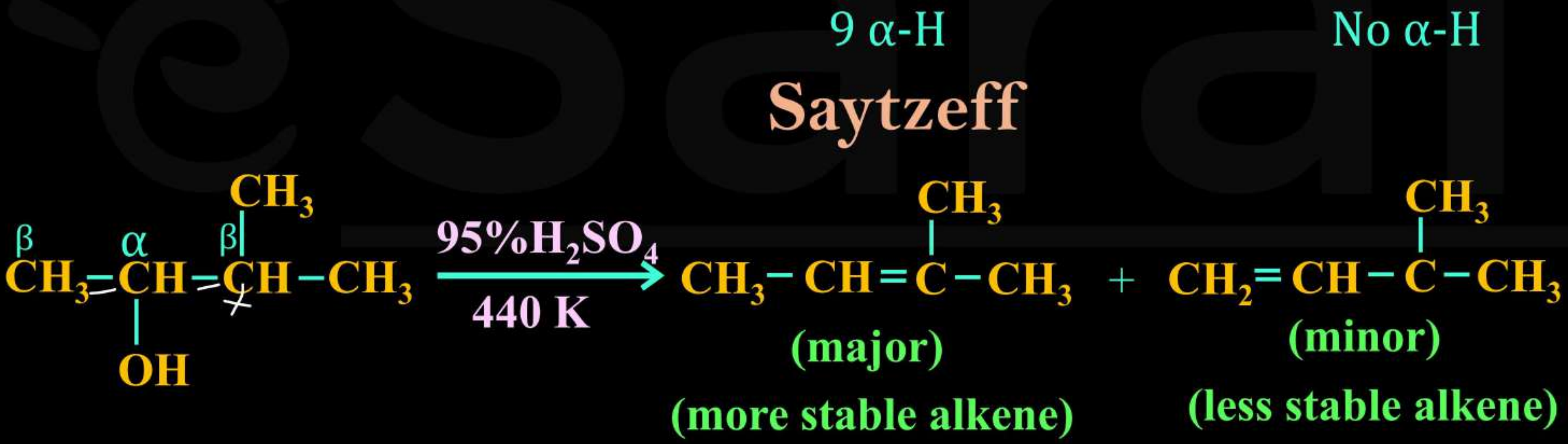
$$CH_3-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3 \xrightarrow[363\ K]{30\%H_2SO_4}$$

$$CH_3-CH_2-OH \xrightarrow[440\ K]{95\%H_2SO_4}$$

Saytzeff Rule

more α-H

The product with the most highly substituted (more alkylated) double bond will predominate. This rule is called the Saytzeff or Zaitsev rule. More alkylated product is called the Saytzeff Product.



9 α-H

No α-H

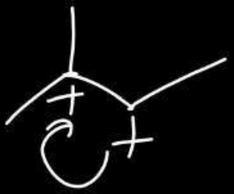
Saytzeff

$$\overset{\beta}{CH_3}-\underset{OH}{\overset{\alpha}{CH}}-\overset{\overset{CH_3}{\beta|}}{CH}-CH_3 \xrightarrow[440\ K]{95\%H_2SO_4} CH_3-CH=\overset{CH_3}{C}-CH_3 + CH_2=CH-\overset{CH_3}{C}-CH_3$$

(major)
(more stable alkene)

(minor)
(less stable alkene)

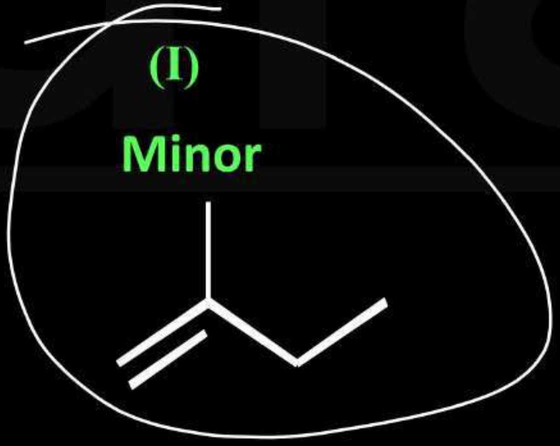
lp →



C^+ rearrangement

(I) Minor

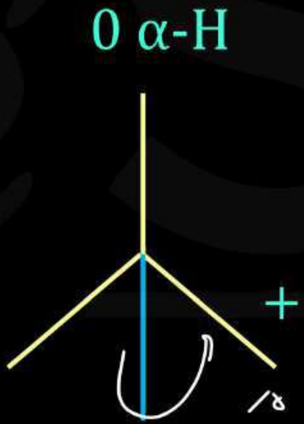
(II) Major

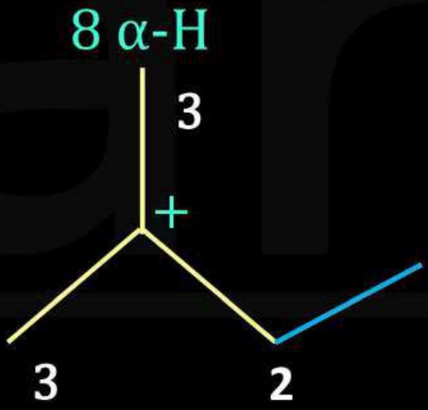


(I)

Minor

Carbocation Rearrangement



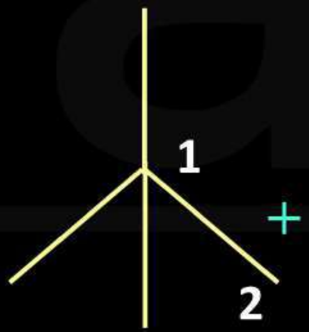


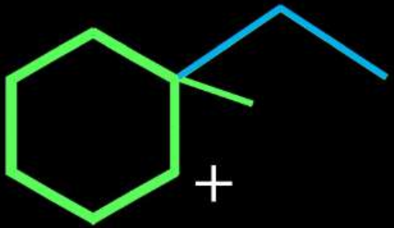
Note

(i) It's an example of 1, 2 shift.

(ii) 3-MCTS (3 membered cyclic transition state) involved

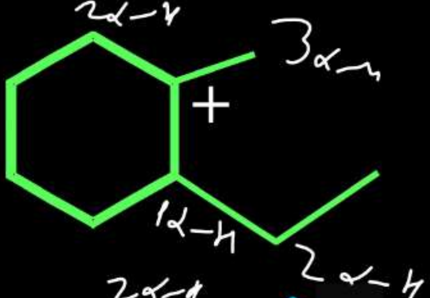
(iii) Migration takes place according to stability of Carbocation. That group migrates which leads to increased stability of C^+





1(Et)

6 α-H

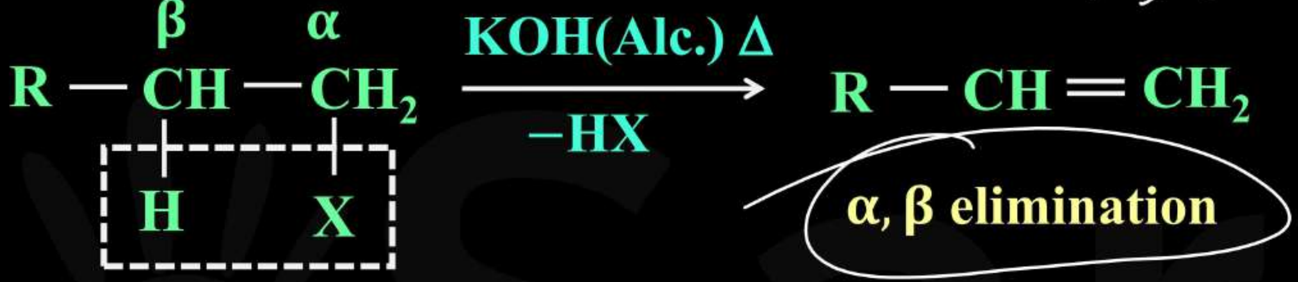


5 α-H

(Dancing Resonance)

2) From Alkyl halide (By dehydrohalogenation)

↳ stable



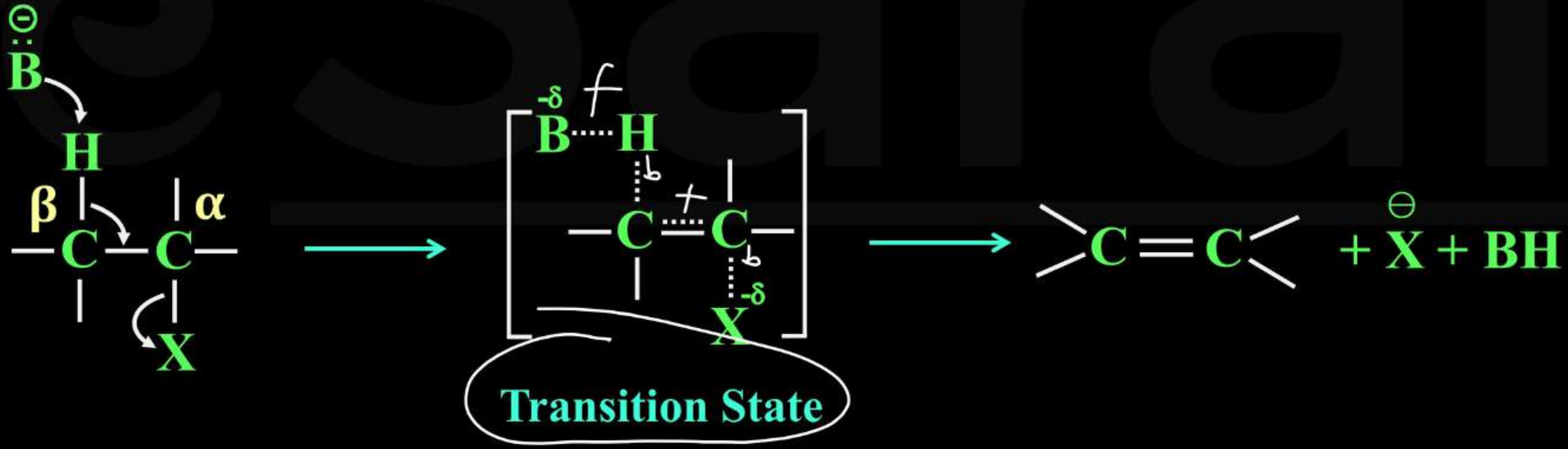
$$R-\overset{\beta}{\underset{H}{CH}}-\overset{\alpha}{\underset{X}{CH_2}} \xrightarrow[-HX]{KOH(Alc.)\ \Delta} R-CH=CH_2$$

α, β elimination

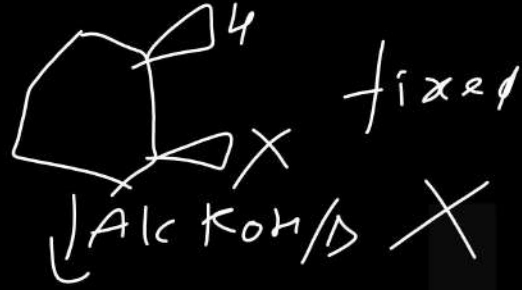
Saytzeff

$$CH_3-\overset{\beta_2}{CH_2}-\overset{\alpha}{\underset{X}{CH}}-\overset{\beta_1}{CH_3} \xrightarrow{KOH(Alc.)} \underset{\text{Major}}{CH_3-CH=CH-CH_3} + \underset{\text{Minor}}{CH_3-CH_2-CH=CH_2}$$

Mechanism (E2)



Characteristics of E2 Reaction

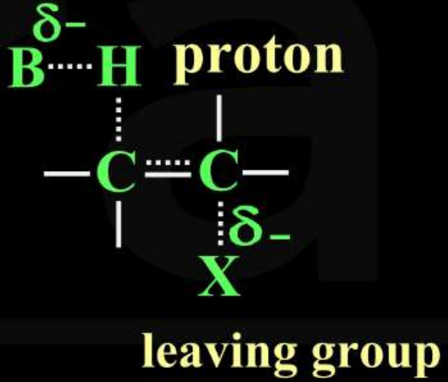


(i) This is a single step, bimolecular reaction

Rate = k [R – X] [B^-]

(ii) Rearrangement is not possible, since carbocation is not formed.

(iii) The proton & leaving group should be anti to each other or at an angle of 180 to each other.



(iii) Reactivity order for alkyl halide towards E2 reaction is given as

R – I > R – Br > R – Cl > R – F

(R – X bond breaking involved)

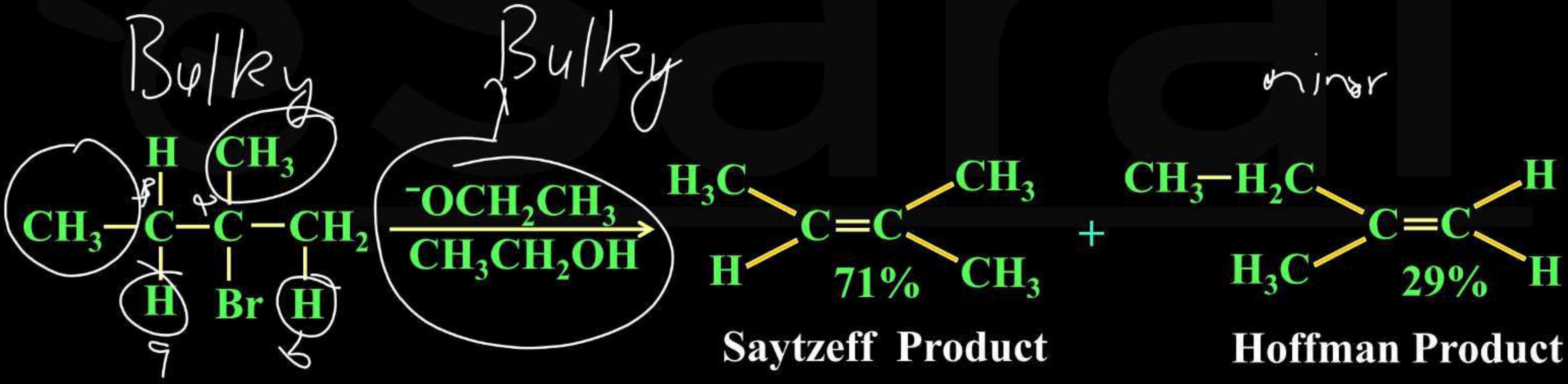
(iv) Reactivity order for alkyl group towards E2 reaction is given as

Tertiary > secondary > primary → Product stability

Formation of The Hoffmann Product

↳ less stable

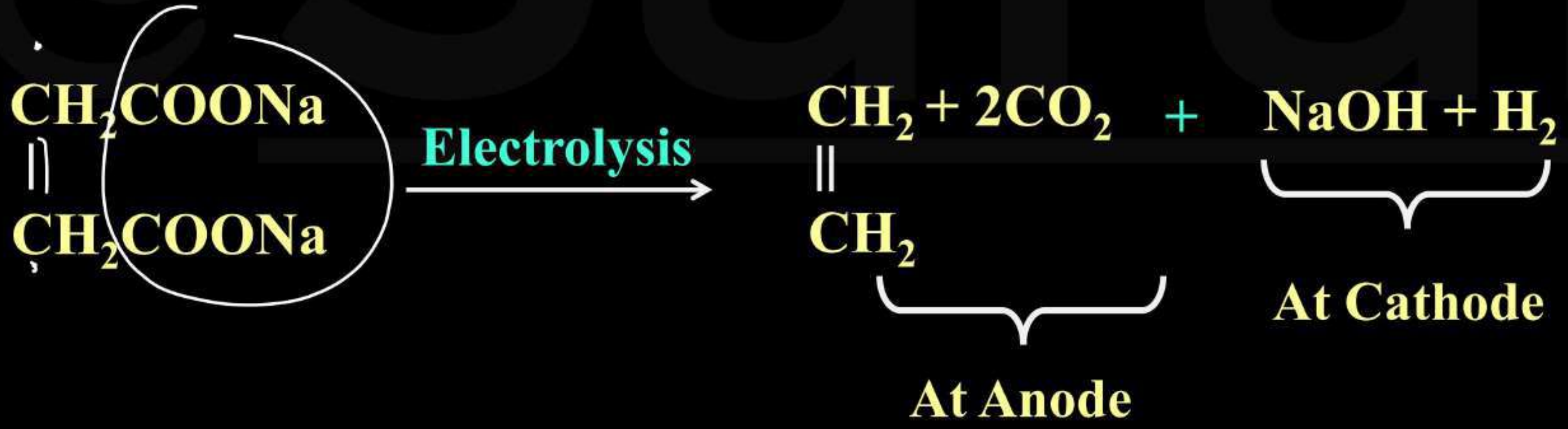
3° → major (Hoffmann)



Saytzeff Product

Hoffman Product

Kolbe's Method



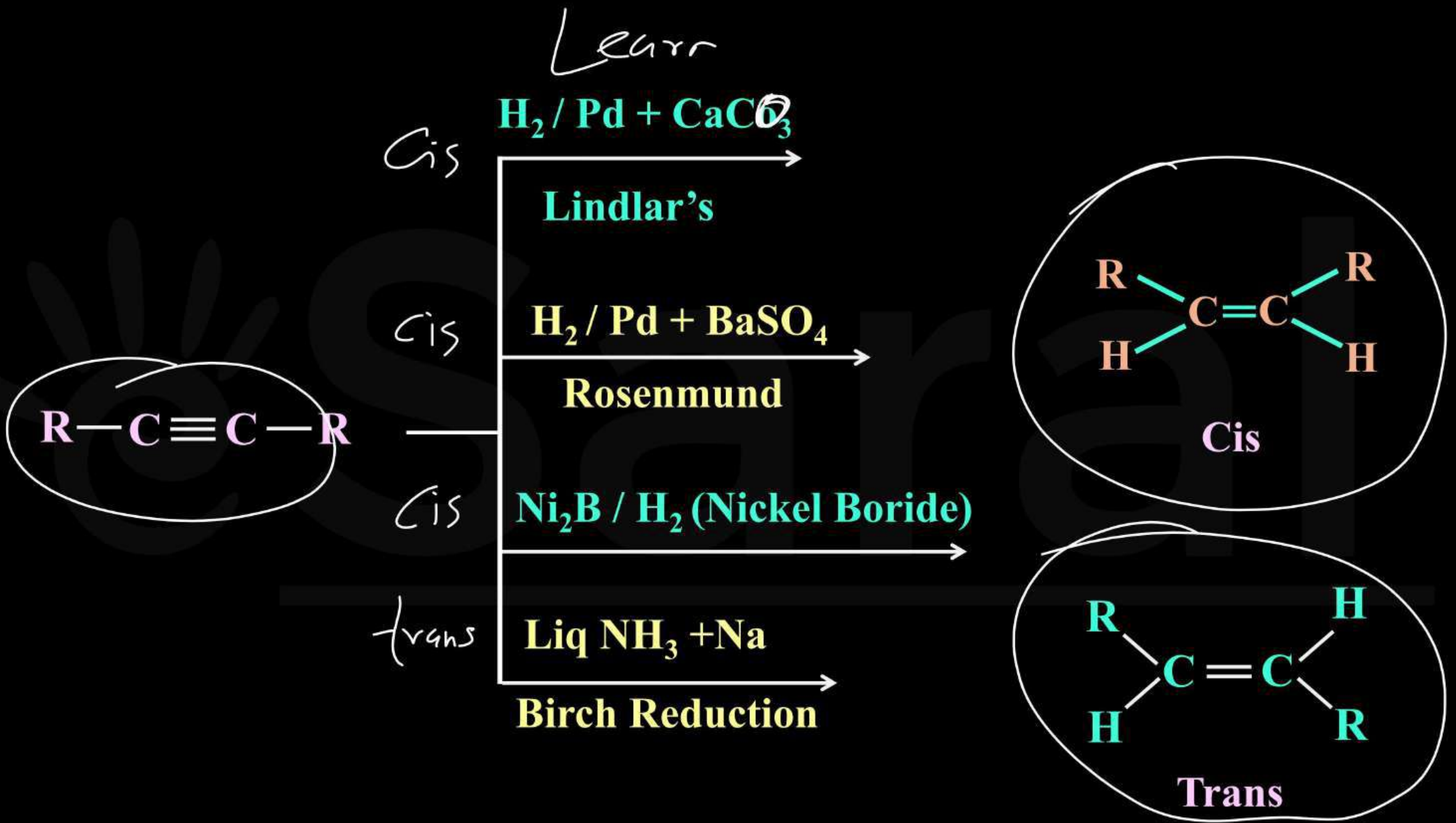
$$\begin{matrix}CH_2COONa\\ \| \\ CH_2COONa\end{matrix} \xrightarrow{\text{Electrolysis}} \underbrace{\begin{matrix}CH_2 + 2CO_2\\ \| \\ CH_2\end{matrix}}_{\text{At Anode}} + \underbrace{NaOH + H_2}_{\text{At Cathode}}$$

Hydrogenation of Alkyne

$$R-C\equiv C-R \xrightarrow{\overset{\text{stop}}{H_2/\,Pd}} R-CH_2-CH_2-R \quad \times$$

Catalytic Hydrogenation of Alkynes in presence of Poisoned Catalyst

Learn



$R-C\equiv C-R$

Cis H_2 / Pd + $CaCO_3$

Lindlar's

Cis H_2 / Pd + $BaSO_4$

Rosenmund

Cis Ni_2B / H_2 (Nickel Boride)

trans Liq NH_3 +Na

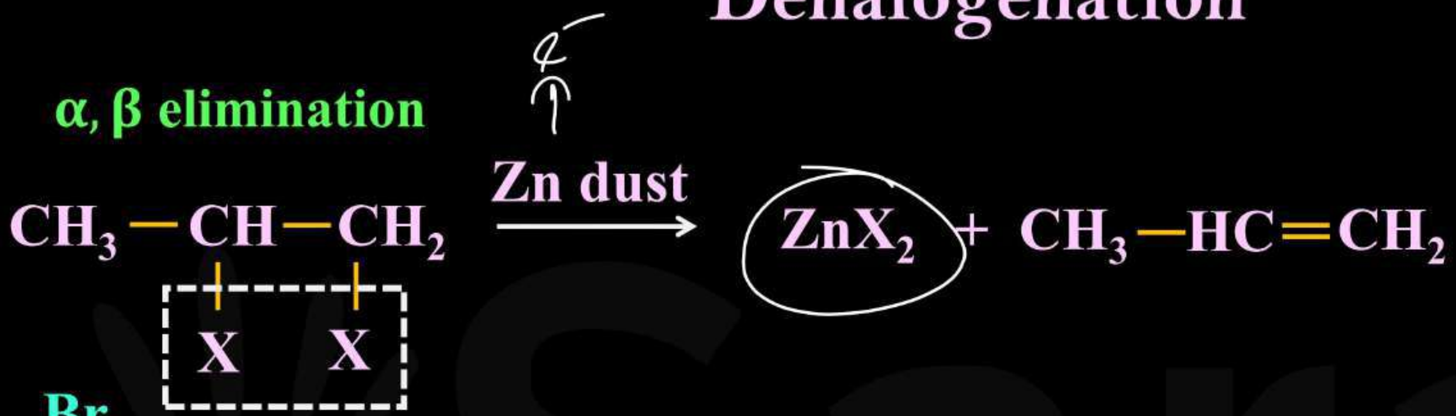
Birch Reduction

Cis

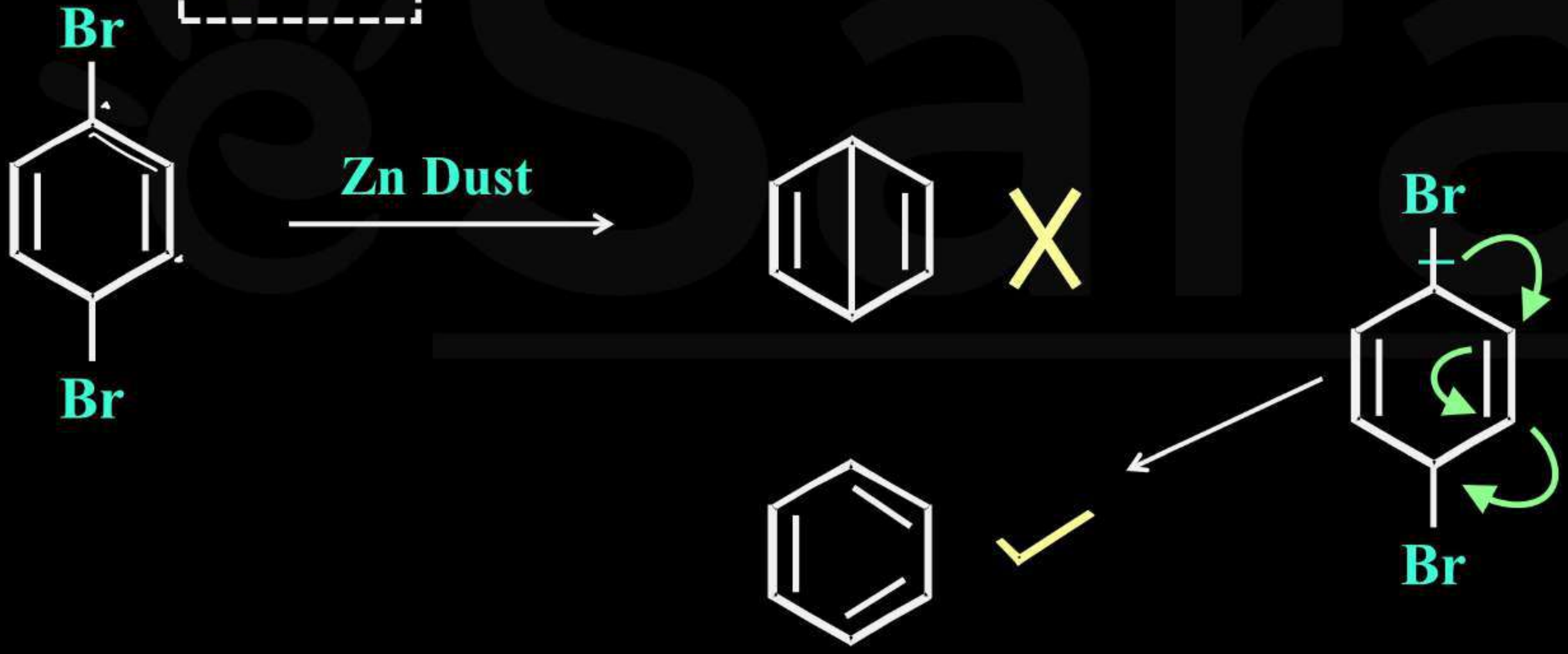
Trans

Dehalogenation

α, β elimination



$$CH_3-\underset{X}{CH}-\underset{X}{CH_2} \xrightarrow{\text{Zn dust}} ZnX_2 + CH_3-HC=CH_2$$



Wittig Reaction

Phosphorous Ylide or Wittig Reagent

Chemical Properties of Alkene

Addition Reaction

(1) Addition of H_2

$$R - CH = CH_2 + H_2 \xrightarrow{\text{Ni , Pt or Pd}} R\text{-}CH_2\text{-}CH_3 + \text{Heat of Hydrogenation}$$

Electrophilic Addition Reactions

$$-\overset{|}{C}=\overset{|}{C}- \; + \; \overset{+}{X}Y \longrightarrow -\underset{X}{\overset{|}{\underset{|}{C}}}-\underset{Y}{\overset{|}{\underset{|}{C}}}-$$

ē density

nucleophile

Alkene **Attacking Molecule** **Addition Product**

Addition of Halogen Acid

$$R-\overset{+}{C}H=CH-R+\overset{+}{H}X \xrightarrow[\text{rearrangement}]{C^{+}\text{ mechanism}} R-\overset{X}{\overset{|}{CH}}-\overset{H}{\overset{|}{CH}}-R$$

(i) The order of reactivity of hydrogen halide is : HI > HBr > HCl > HF

(ii) The rate of reaction is directly proportional to carbocation stability

(iii) Addition of HX on unsymmetrical alkenes ($R-CH=CH_2$) takes place according to Markovnikov's rule.

Markovnikov's Rule

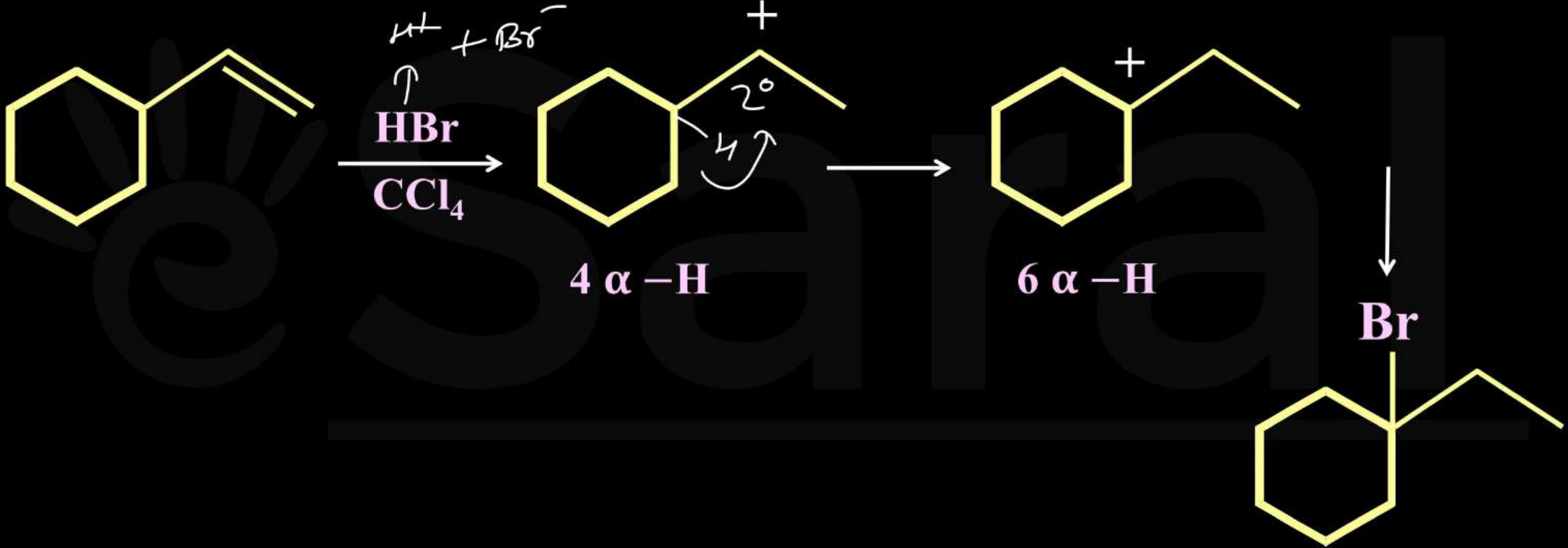
When a molecule of HX adds up on unsymmetrical unsaturated hydrocarbon, the halogen atom goes to the unsaturated carbon atom bearing lesser number of hydrogen atoms.

$$R-\overset{1}{C}H=\overset{2}{C}H_{2}\,\cancel{-R}+HX\longrightarrow R-\overset{X}{\overset{|}{CH}}-\overset{H}{\overset{|}{CH_{3}}}\,\cancel{-R}$$

Failure of Markovnikov's Rule

Markovnikov's rule can also be stated as, the electrophilic addition to unsymmetrical alkenes always occurs through the formation of a more stable carbocation intermediate.

It is not true always, Carbocation rearrangement happens wherever applicable.


H+ + Br⁻
HBr
CCl4
+
2°
4
4 α −H
+
6 α −H
Br

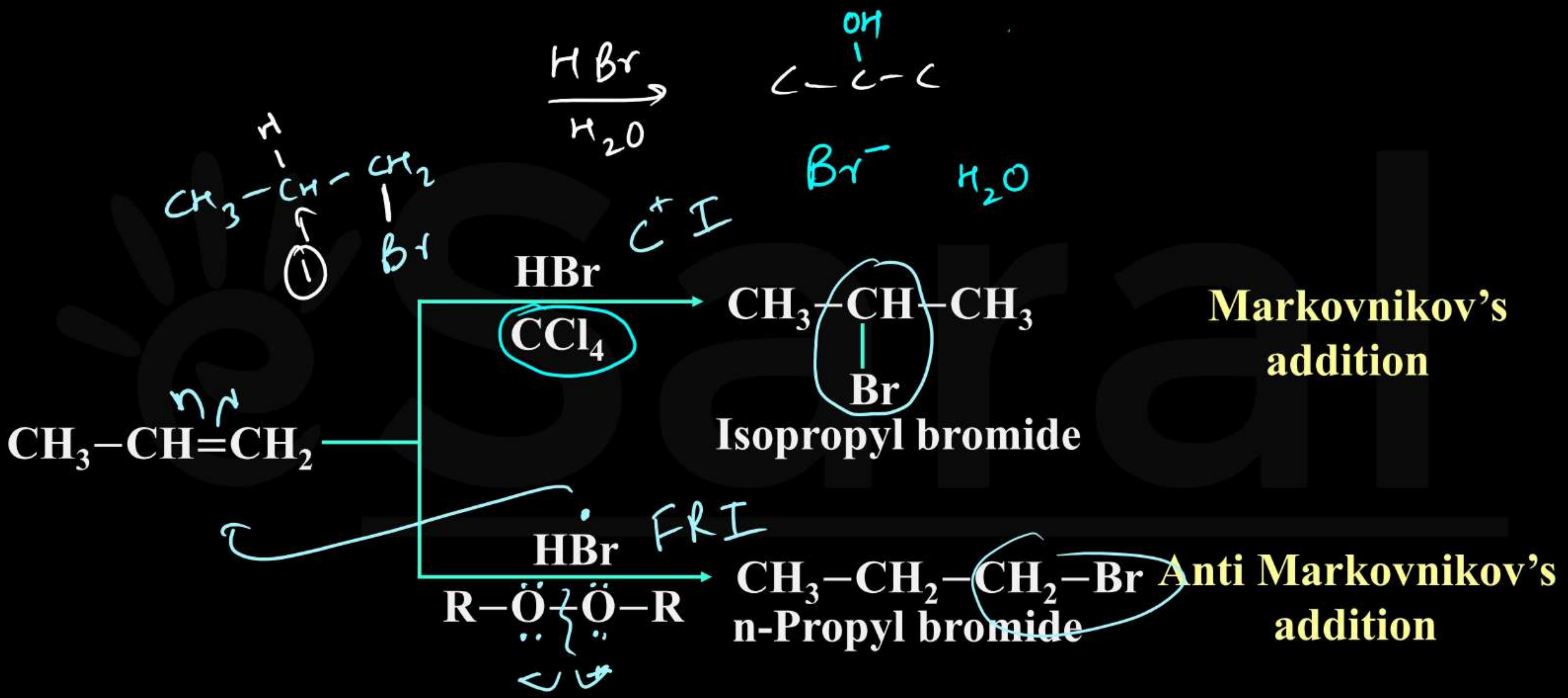
HBr addition

In the presence of peroxides the addition of HBr on unsaturated unsymmetrical alkene takes place contrary to Markovnikov's rule. This is called peroxide effect and is due to the difference in the mechanism of the addition. This effect is also known as Kharasch effect.

$$CH_3-\overset{H}{\overset{|}{C}H}-\underset{Br}{\underset{|}{CH_2}} \qquad \xrightarrow[H_2O]{HBr} \qquad C-\overset{OH}{\overset{|}{C}}-C$$

C^+ I

Br^- H_2O



$$CH_3-CH=CH_2 \xrightarrow[CCl_4]{HBr} CH_3-\underset{Br}{\underset{|}{CH}}-CH_3$$

Isopropyl bromide

Markovnikov's addition

$$CH_3-CH=CH_2 \xrightarrow[R-\ddot{O}-\ddot{O}-R]{HBr} CH_3-CH_2-CH_2-Br$$

n-Propyl bromide

Anti Markovnikov's addition

FRI

Q) Why HCl and HI do not give antimarkovnikov’s products in the presence of peroxides?

C^+

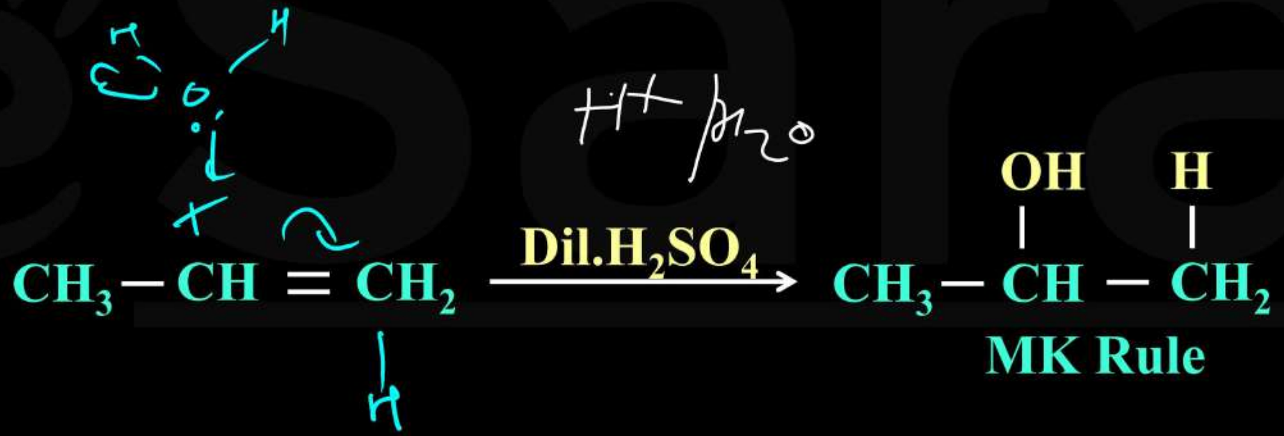
$\xrightarrow[CCl_4/\text{peroxide}]{HCl}$

Sol. (a) The H — Cl bond is stronger than H—Br, hence not broken by alkoxy free radical.

(b) The H — I bond is weaker than H—Br bond. It is broken by the alkoxy free radicals obtained from peroxides, but the addition of iodine atom on alkene is endothermic. Therefore iodine atoms so formed combine with each other to yield iodine.

Addition of Water (Hydration of Alkenes)

Propene and higher alkenes react with water in the presence of acid to form alcohol. This reaction is known as the hydration reaction. Intermediate in this reaction is carbocation, so rearrangement will take place.



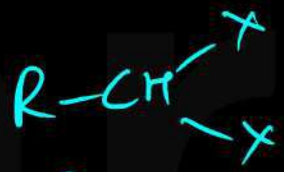
$$CH_3-CH=CH_2 \xrightarrow{Dil.H_2SO_4} CH_3-\overset{OH}{\overset{|}{CH}}-\overset{H}{\overset{|}{CH_2}}$$

MK Rule

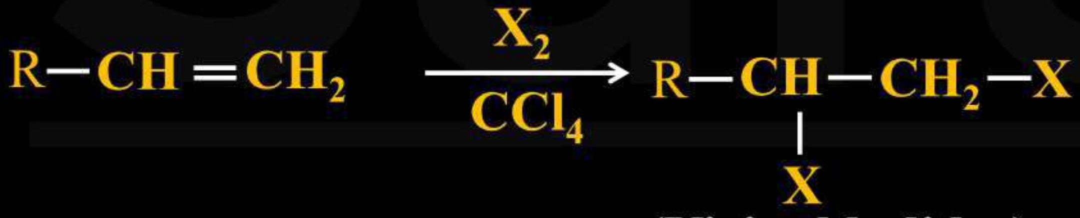
Addition of X_2 on Alkene

Sawaal

Special



Gem

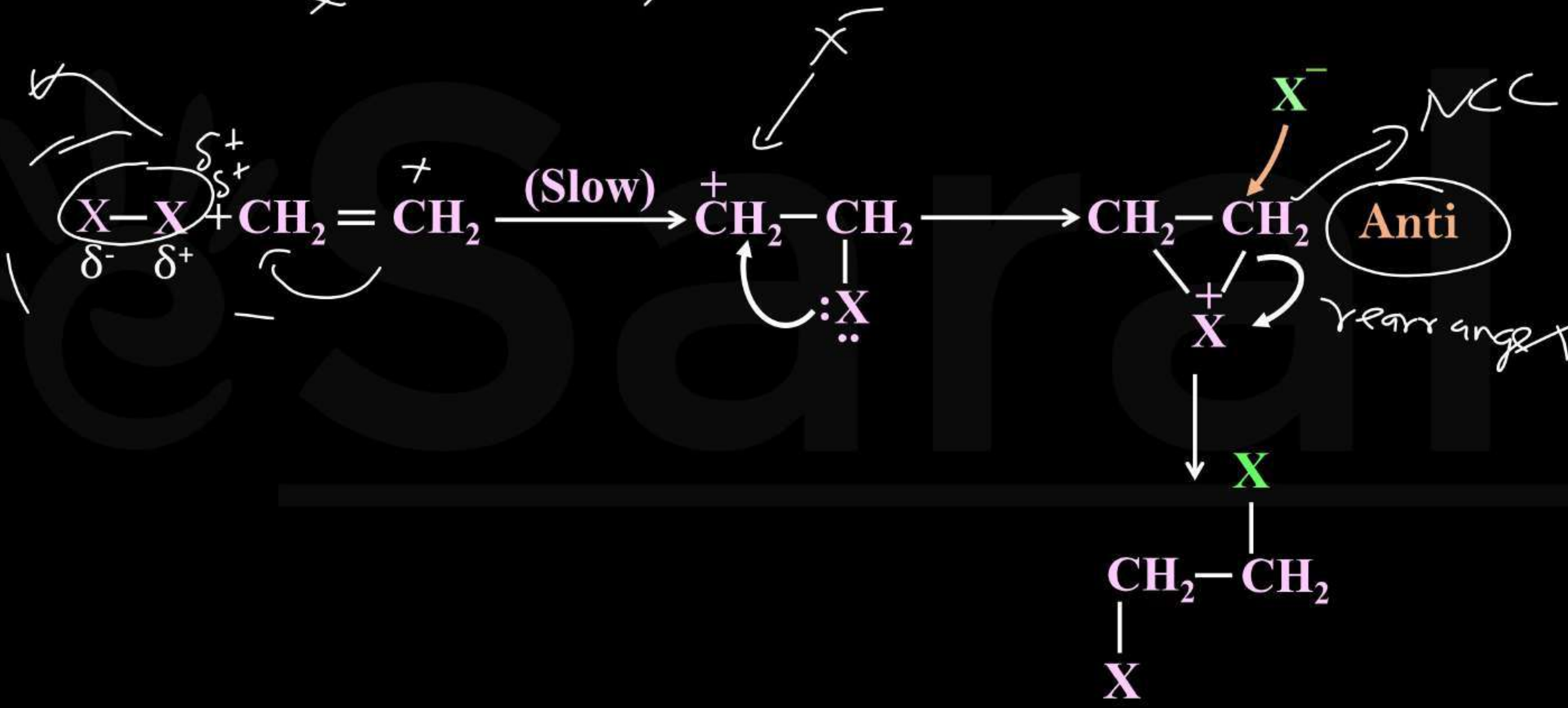


$$R-CH=CH_2 \xrightarrow[CCl_4]{X_2} R-\underset{\displaystyle X}{\underset{|}{CH}}-CH_2-X$$

(Vicinal halides)

Mechanism

X_2
X
X



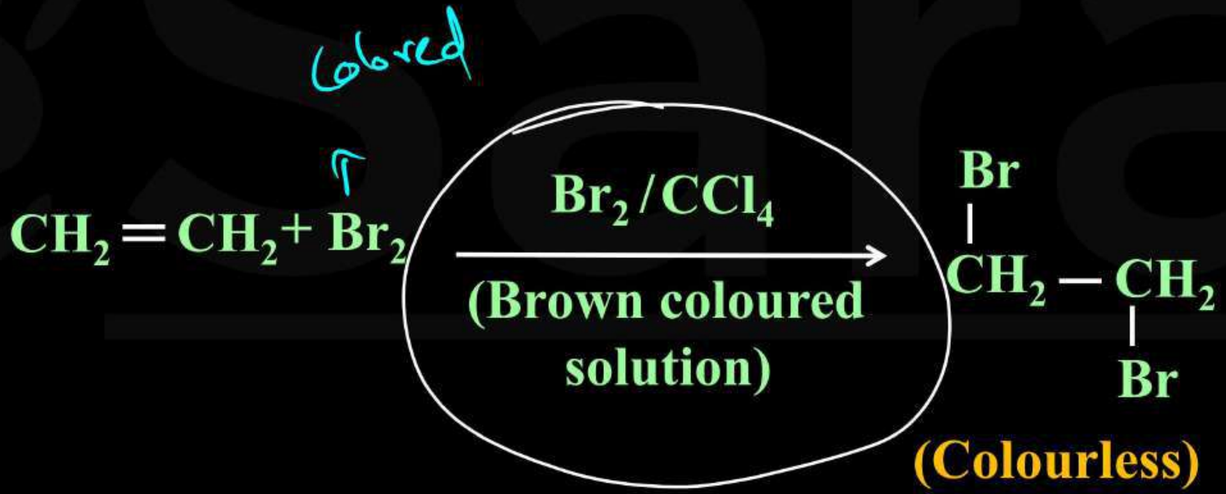
δ+
δ+
$\overset{\delta^-}{X}-\overset{\delta^+}{X} + CH_2 = \overset{+}{C}H_2$
(Slow)
$\overset{+}{C}H_2 - CH_2 - :\ddot{X}$
X
X^-
$CH_2 - CH_2$
$\overset{+}{X}$
Anti
NCC
rearrangt
$X - CH_2 - CH_2 - X$

Test of Unsaturation

POC

Bromine Water Test

Brown-red

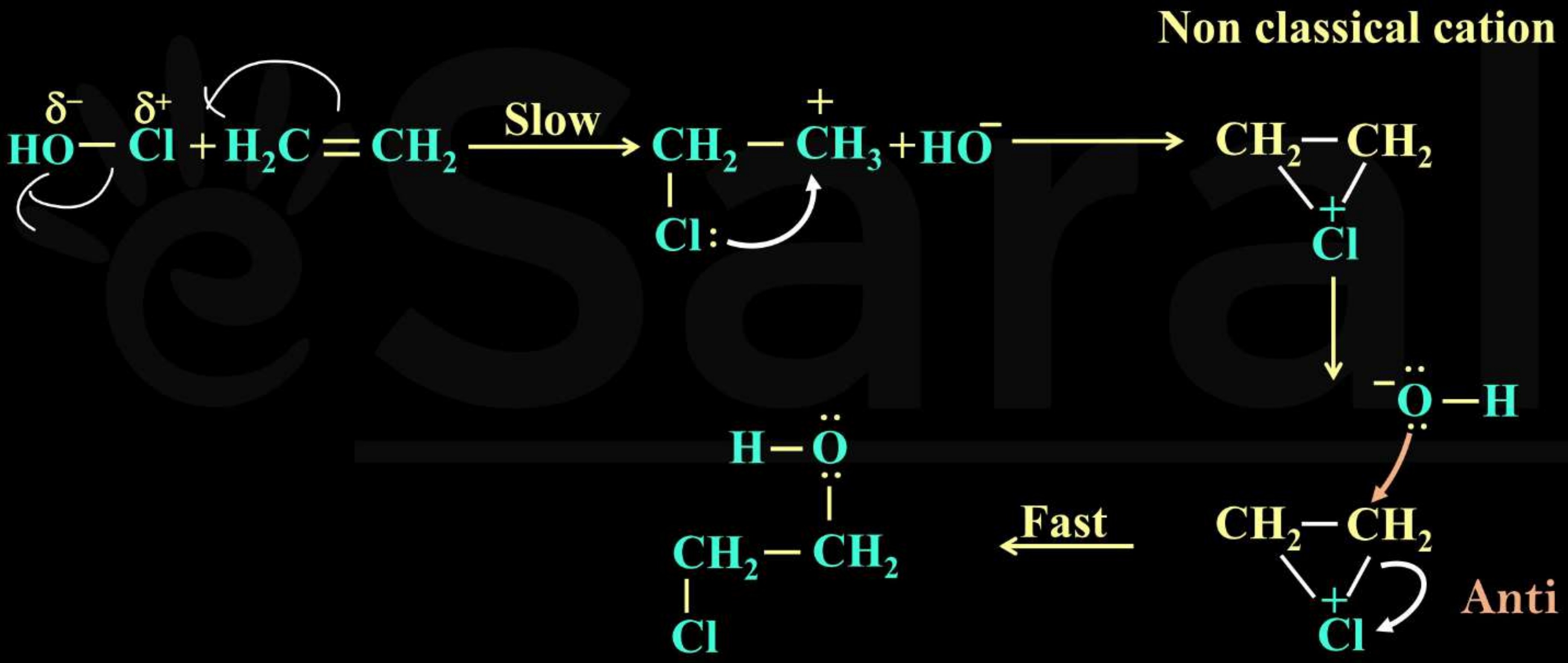


colored

$$CH_2{=}CH_2 + Br_2 \xrightarrow[\text{(Brown coloured solution)}]{Br_2/CCl_4} \underset{\underset{Br}{|}}{\overset{\overset{Br}{|}}{CH_2}}-\underset{\underset{Br}{|}}{CH_2}$$

(Colourless)

Addition Of Hypohalous Acid Or X_2/H_2O or HOX

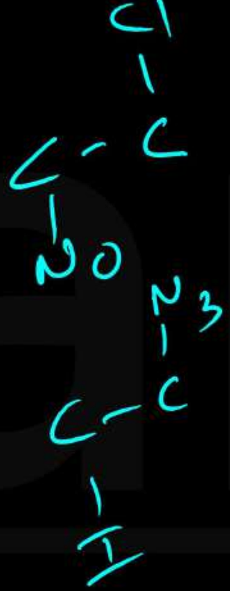


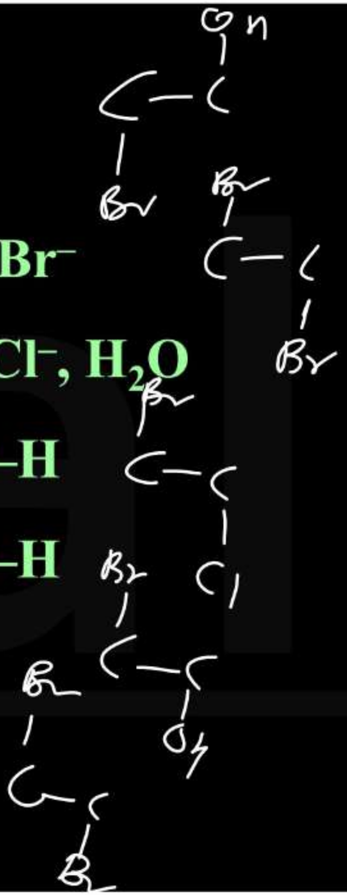
E–Nu	E^+	Nu^-
HCl	H^+ ×	Cl^-
HBr	H^+ ×	Br^-
HI	H^+	I^-
DI	D^+	I^-
H_2SO_4 Hydration	H^+	OSO_3H^-
H_2O/H^+	H^+	H_2O
ROH/H^+	H^+	ROH
CH_3COOH/H^+	H^+	CH_3COOH

Classical ✓
Carbocation
↓
Carbo
Rearrangement ✓

NCL

Br_2/CCl_4 ✓	Br^+	Br^-
Cl_2/CS_2 ✓	Cl^+	Cl^-
Br_2/H_2O ✓	Br^+	H_2O/Br^-
(Br_2 water in brine)	Br^+	Br^-, Cl^-, H_2O
HOCl	Cl^+	H–O–H
HOBr	Br^+	H–O–H
NOCl	$\overset{+}{NO}$	Cl^-
IN_3	I^+	N_3^-

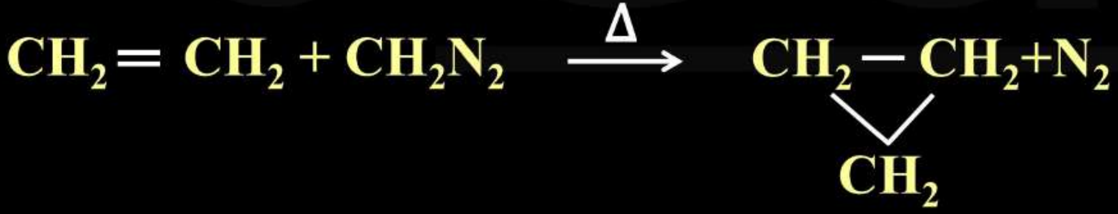




Addition of Carbene

$:CH_2 \rightarrow$ Carbene

The addition of carbene to alkene is carried out by diazomethane CH_2N_2. Carbene group obtained from diazomethane is added to alkene and gives cycloalkanes.



$$CH_2 = CH_2 + CH_2N_2 \xrightarrow{\Delta} \underbrace{CH_2 - CH_2}_{CH_2} + N_2$$

Oxidation Reaction

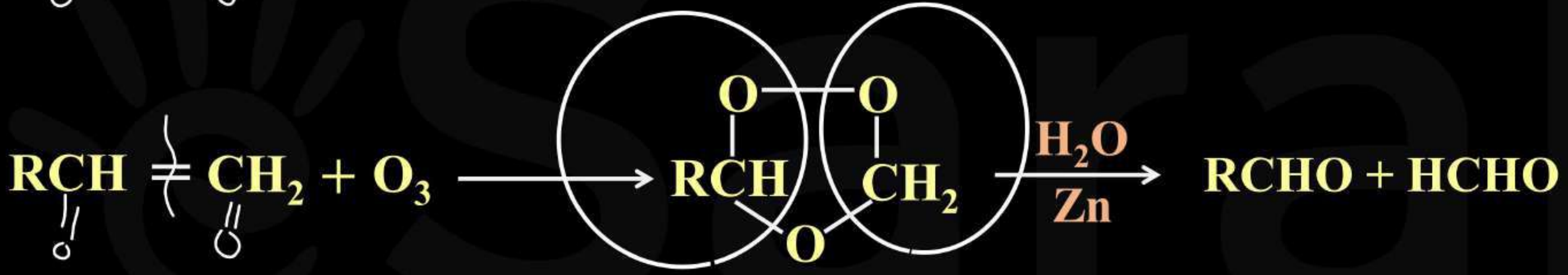
1. Alkene On Combustion Gives CO_2 And H_2O

$$C_nH_{2n} + \frac{3n}{2}O_2 \longrightarrow nCO_2 + nH_2O$$

2. Ozonolysis (A Test For Unsaturation In Molecule)

Reductive | Oxidative

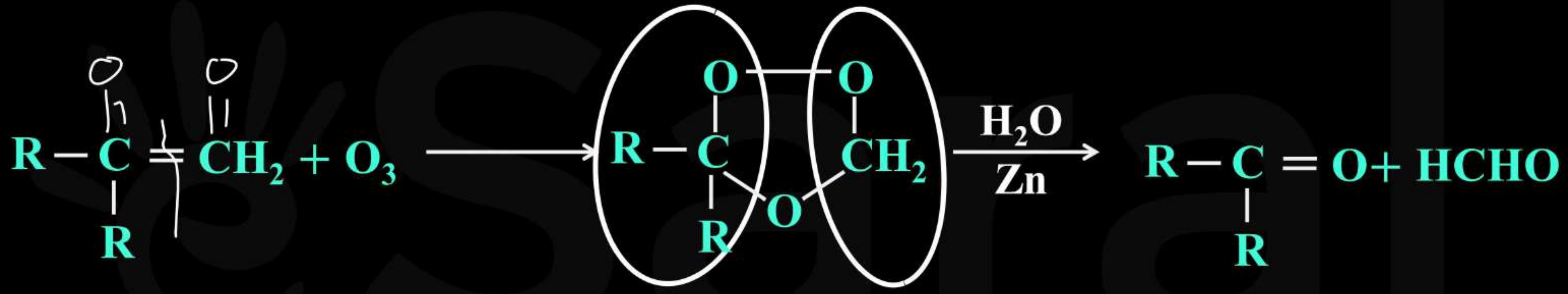
$$RCH=CH_2 + O_3 \xrightarrow[Zn]{H_2O} RCHO + HCHO$$



$$RCH=CH_2 + O_3 \longrightarrow \text{Ozonide} \xrightarrow[Zn]{H_2O} RCHO + HCHO$$

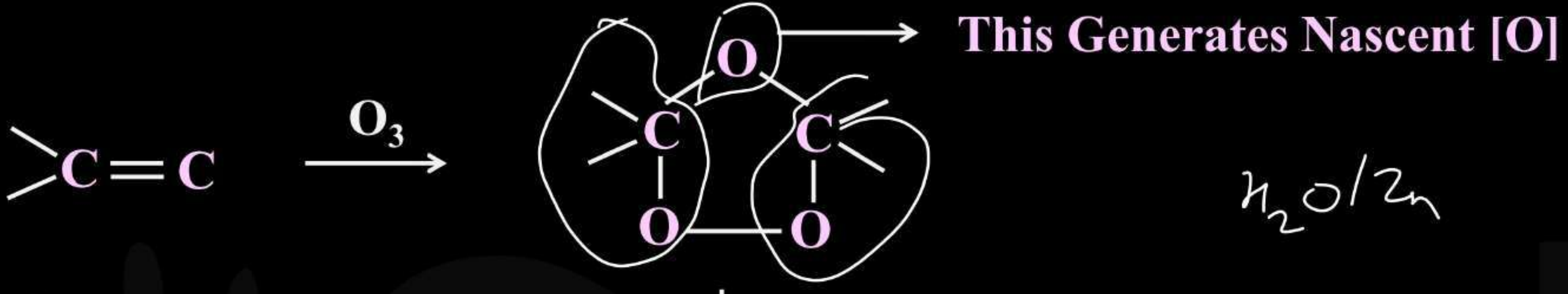
Ozone

Ozonide



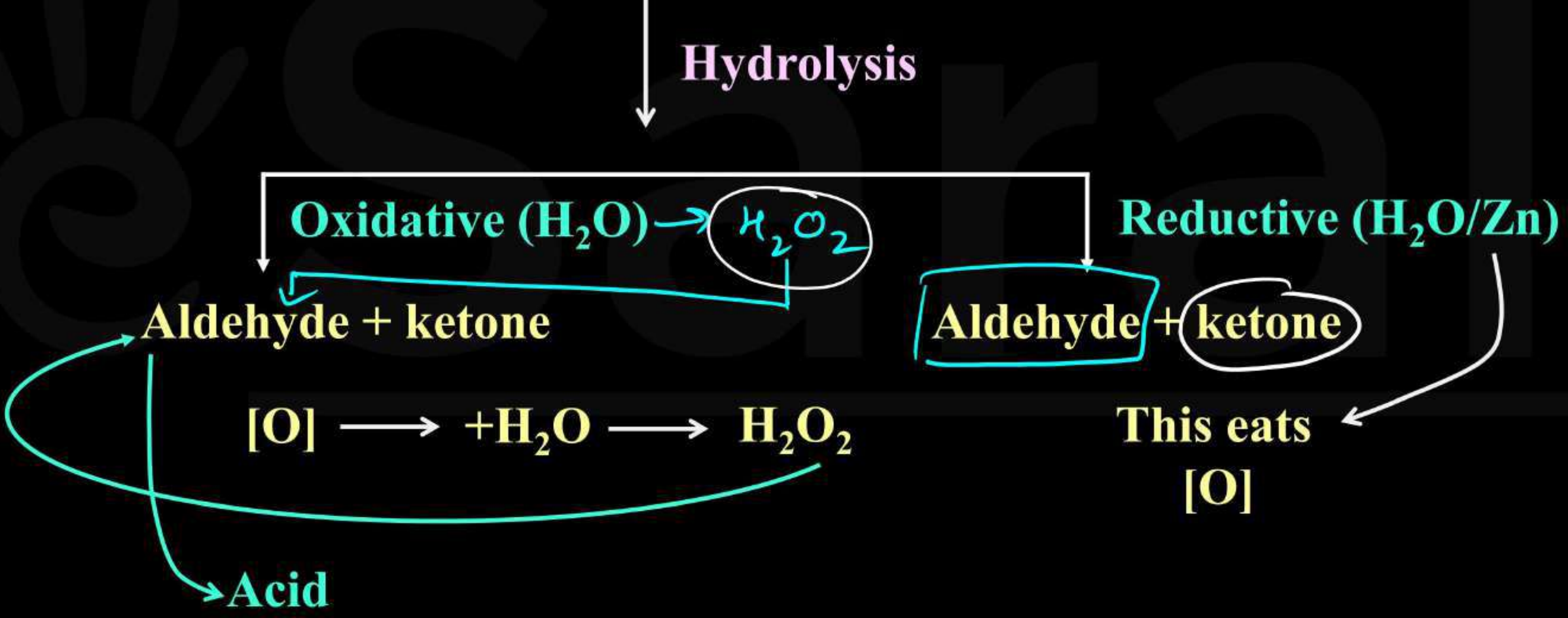
Unbranched alkene $\longrightarrow$ **aldehyde**

Branched alkene $\longrightarrow$ **ketone**



This Generates Nascent [O]

H_2O/Zn



Hydrolysis

Oxidative (H_2O) → H_2O_2

Reductive (H_2O/Zn)

Aldehyde + ketone

Aldehyde + ketone

$[O] \longrightarrow +H_2O \longrightarrow H_2O_2$

This eats [O]

Acid

Note

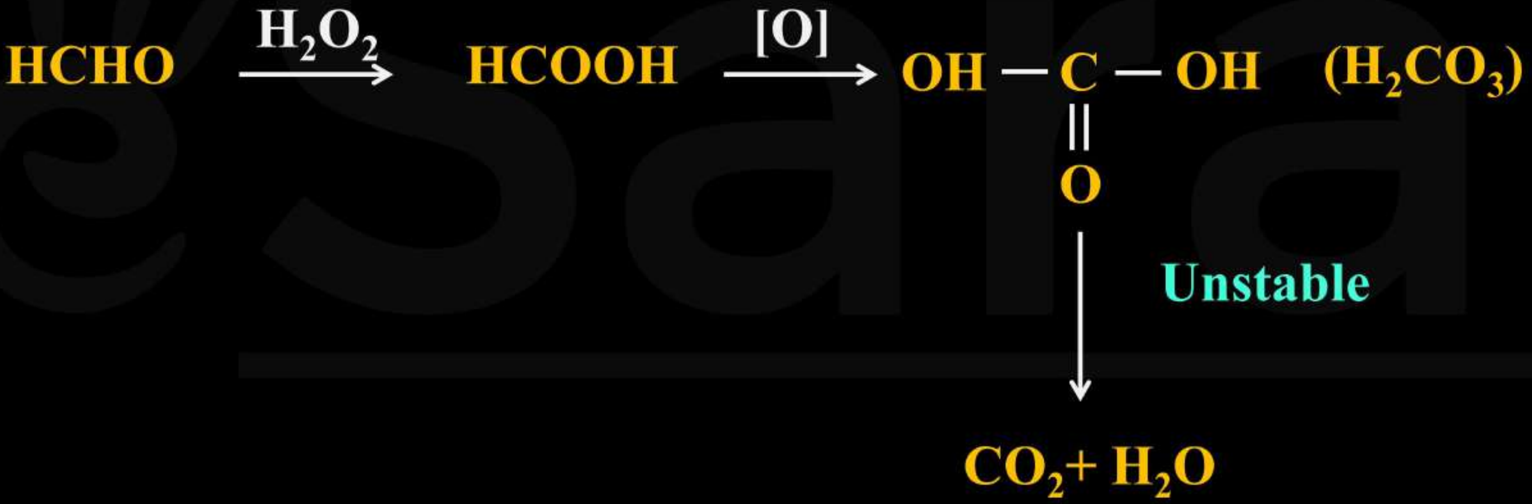
If aldehyde formed is formaldehyde (in Oxidative) then

$CH_2=CH_2 \xrightarrow[H_2O]{O_3} 2HCHO$

$HCOOH \rightarrow H_2CO_3 \rightarrow H_2O$

CO_2

H_2CO_3

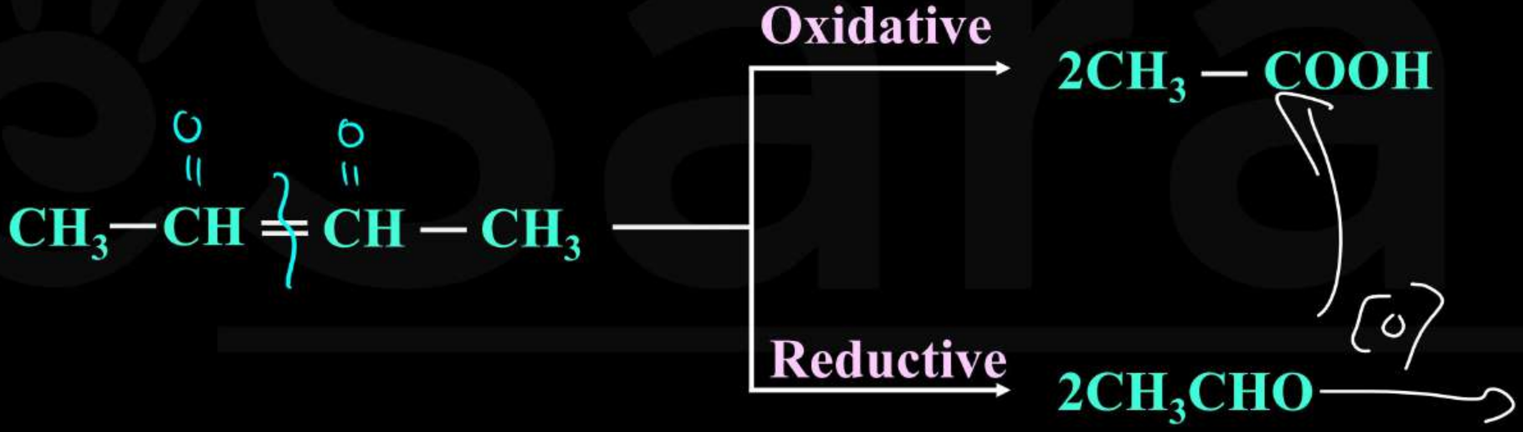


$$HCHO \xrightarrow{H_2O_2} HCOOH \xrightarrow{[O]} OH-\underset{\underset{O}{\|}}{C}-OH \quad (H_2CO_3)$$

Unstable

$$\downarrow$$

$$CO_2 + H_2O$$



$CH_3-\overset{\overset{O}{\|}}{CH}=\overset{\overset{O}{\|}}{CH}-CH_3$

Oxidative $\rightarrow 2CH_3-COOH$

Reductive $\rightarrow 2CH_3CHO$

$2CH_3CHO \xrightarrow{[O]} 2CH_3-COOH$

3. Hydroxylation (Formation of Vicinal Alcohol)

Oxidation By Baeyer's Reagent (A Test For Unsaturation)

(Bayer’s Reagent)

$$CH_3-CH=CH_2+H_2O+[O]\xrightarrow[273K]{\text{dil. }KMnO_4}CH_3-\overset{OH}{\overset{|}{CH}}-\overset{OH}{\overset{|}{CH_2}}$$

Propane -1,2- diol

Oxidation By Strong Oxidising Agent
(Oxidative Cleavage)

Oxidative ozonolysis

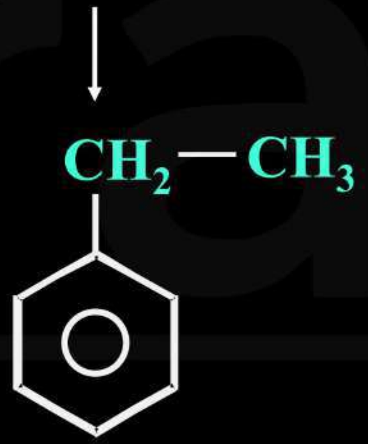
The alkenes are readily oxidised to acid or ketone by means of acid permanganate ($KMnO_4/H^+$) or acid dichromate ($K_2Cr_2O_7/H^+$). If HCOOH is formed, it further oxidises to CO_2 and H_2O. No further oxidation of ketones will take place.

Substitution Reaction
(Allylic and Benzylic Substitution)

Allylic

$$\overset{\downarrow}{CH_3}-CH=CH_2$$

Benzylic

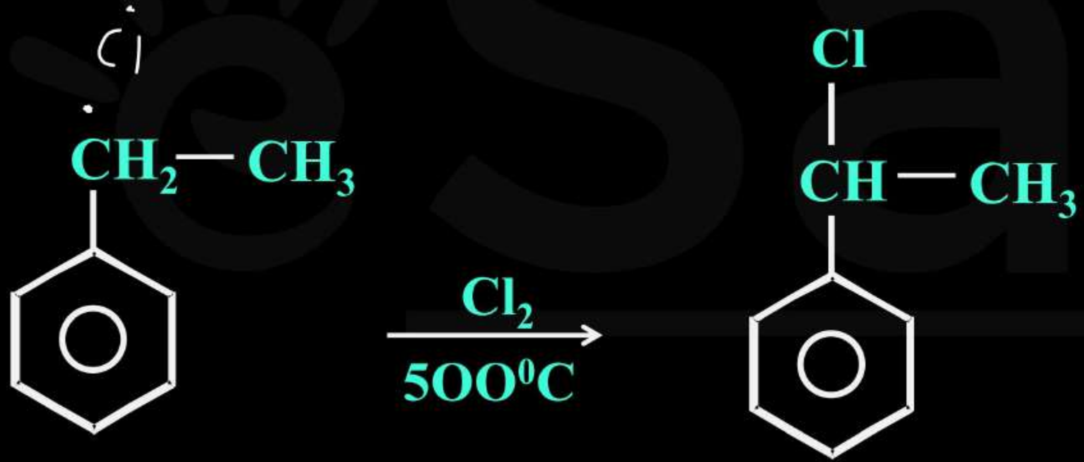


$$CH_3-CH=CH_2+Cl_2 \xrightarrow{500°C} Cl\dot{C}H_2-\dot{C}H=CH_2+HCl$$

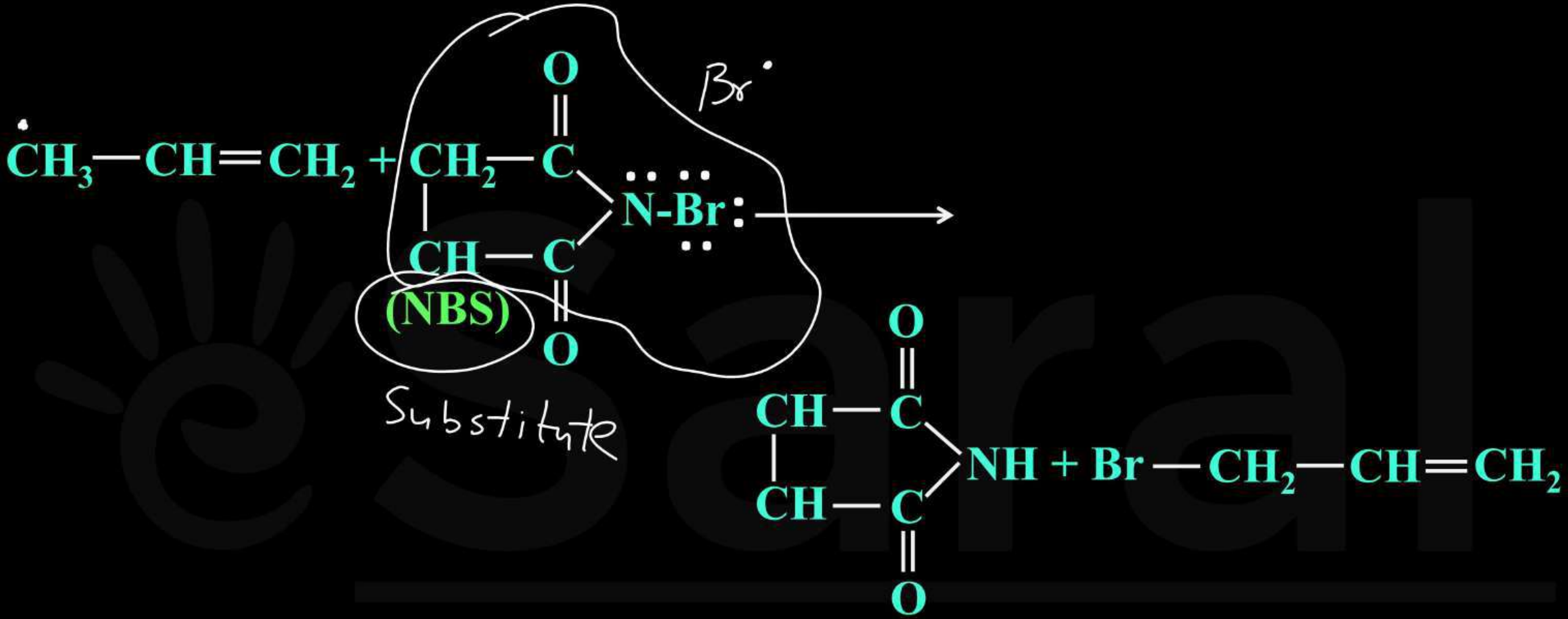
$\dot{Cl}$

Allyl chloride

(3-Chloro prop-1-ene)



$$C_6H_5-CH_2-CH_3 \xrightarrow[500^0C]{Cl_2} C_6H_5-CH(Cl)-CH_3$$



Substitution reaction is not given by ethene, because allylic or benzylic position is absent.

Polymerization

$$n(CH_2{=}CH_2) \xrightarrow[\text{Catalyst}]{\text{High T/P}} \left(CH_2 - CH_2 \right)_n$$

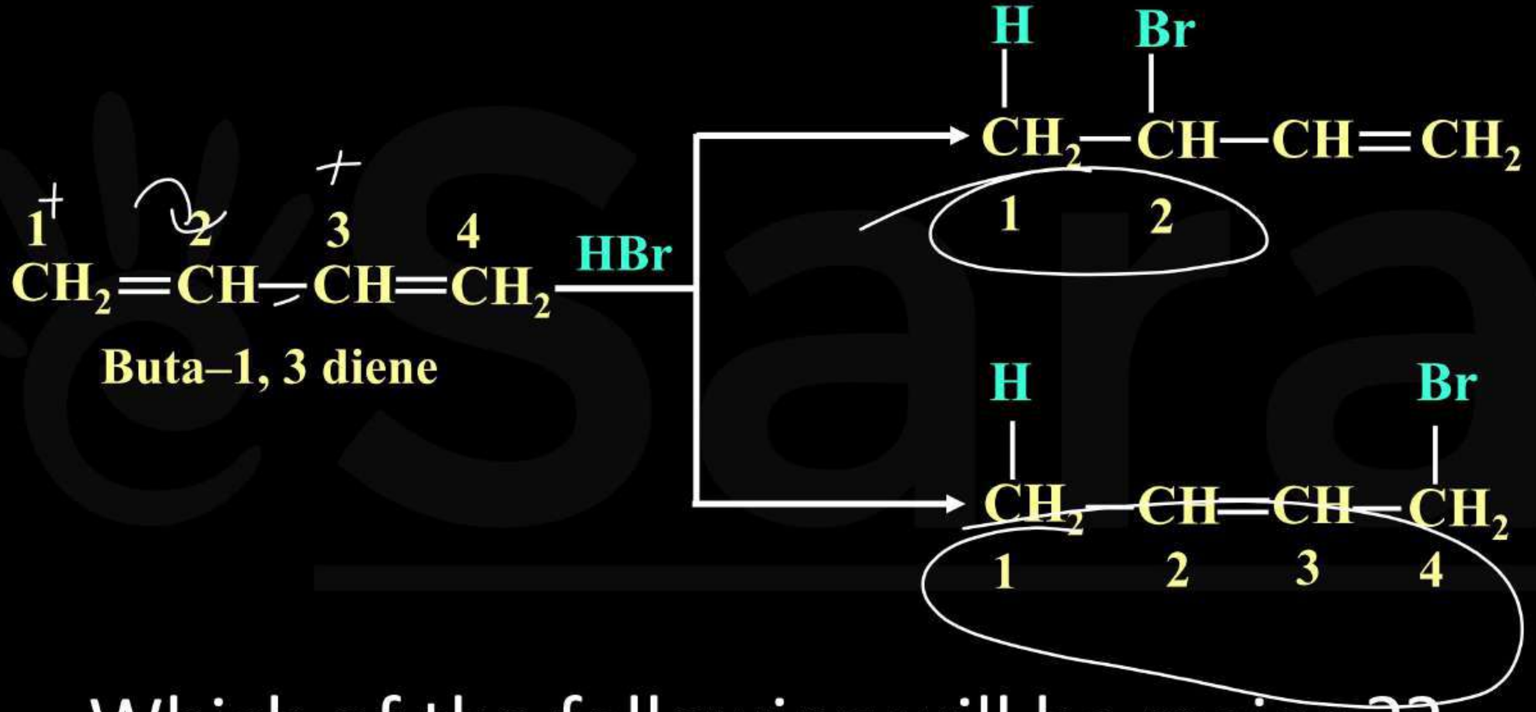
Polythene

Monomer

Polymer

Addition Reaction of Conjugated Diene

$CH_2{=}CH{-}CH{=}CH_2$



$$\overset{\overset{+}{1}}{CH_2}{=}\overset{2}{CH}{-}\overset{\overset{+}{3}}{CH}{=}\overset{4}{CH_2} \xrightarrow{HBr}$$

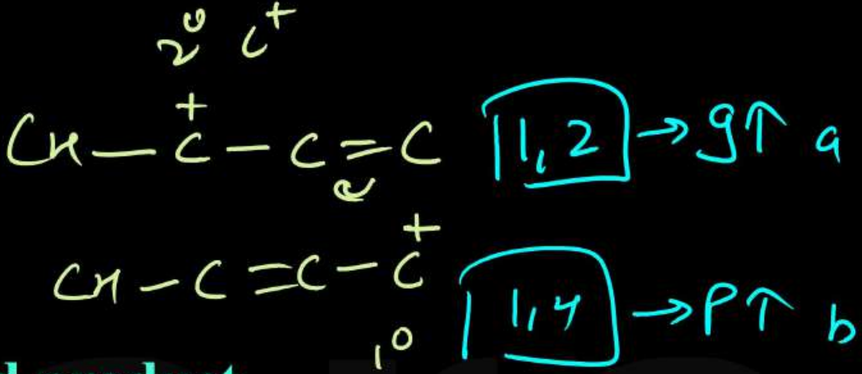
Buta–1, 3 diene

$$\overset{H}{\underset{1}{CH_2}}{-}\overset{Br}{\underset{2}{CH}}{-}CH{=}CH_2$$

$$\overset{H}{\underset{1}{CH_2}}{-}\underset{2}{CH}{=}\underset{3}{CH}{-}\overset{Br}{\underset{4}{CH_2}}$$

Which of the following will be major ??

KCP vs TCP



(i) KCP ⇒ Kinetically controlled product

⇒ Product which is quickly formed

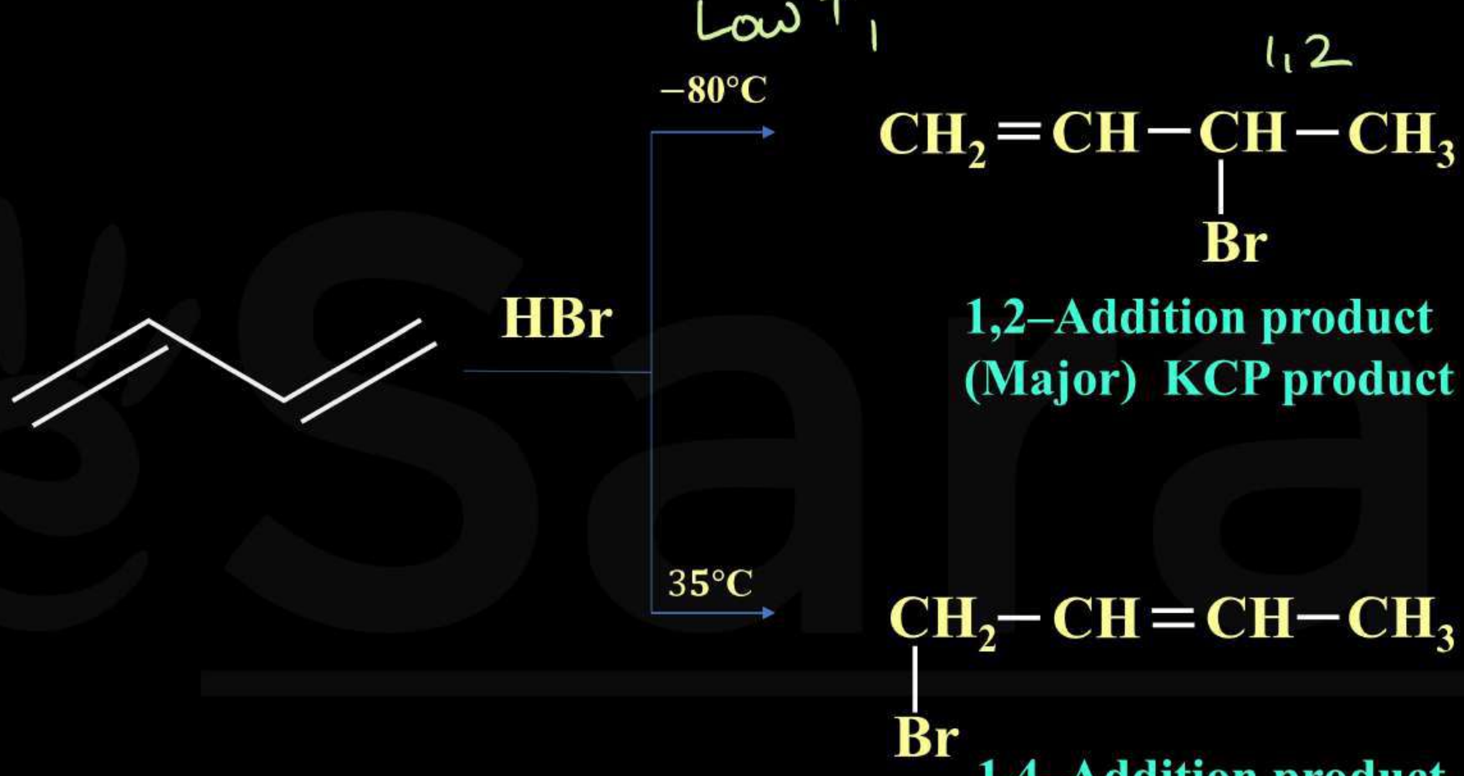
⇒ Product formed by lowest activation energy → Intermediate

T↓ Int↑

(ii) TCP ⇒ Thermodynamically controlled product

⇒ Most stable → product

T↑ Pro↑



$$CH_2=CH-\underset{Br}{CH}-CH_3$$

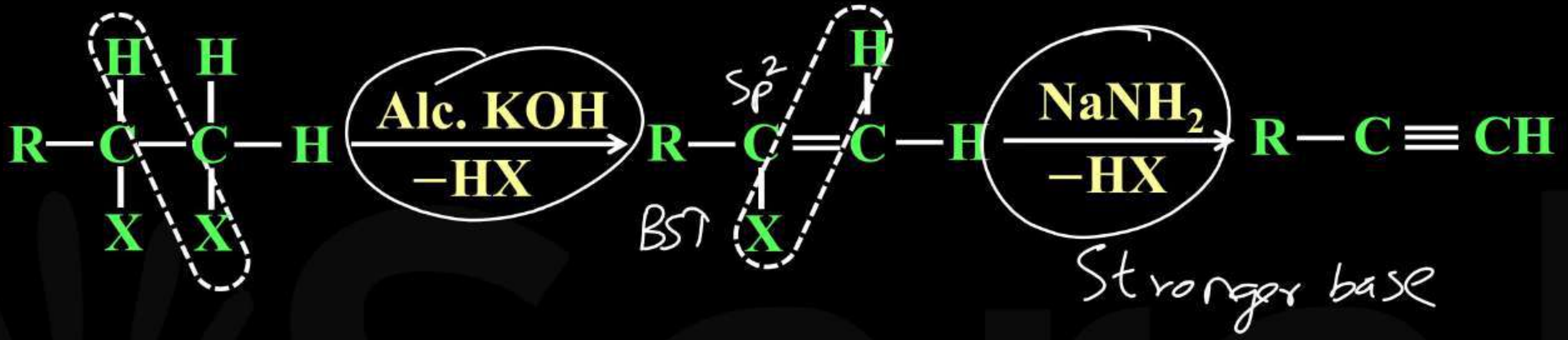
1,2–Addition product
(Major) KCP product

$$\underset{Br}{CH_2}-CH=CH-CH_3$$

1,4–Addition product
(Major) TCP product

Alkyne

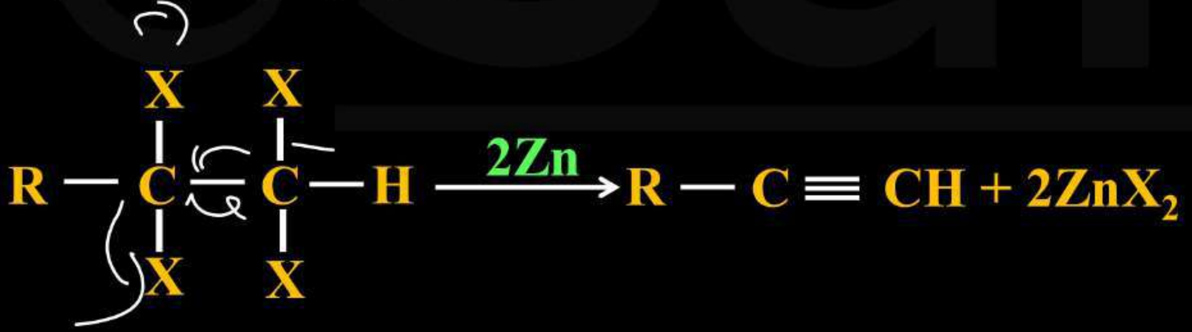
From Vicinal Dihalides (By Dehydrohalogenation)



$$R-\underset{X}{\overset{H}{C}}-\underset{X}{\overset{H}{C}}-H \xrightarrow[-HX]{\text{Alc. KOH}} R-\underset{X}{C}=\overset{H}{C}-H \xrightarrow[-HX]{NaNH_2} R-C\equiv CH$$

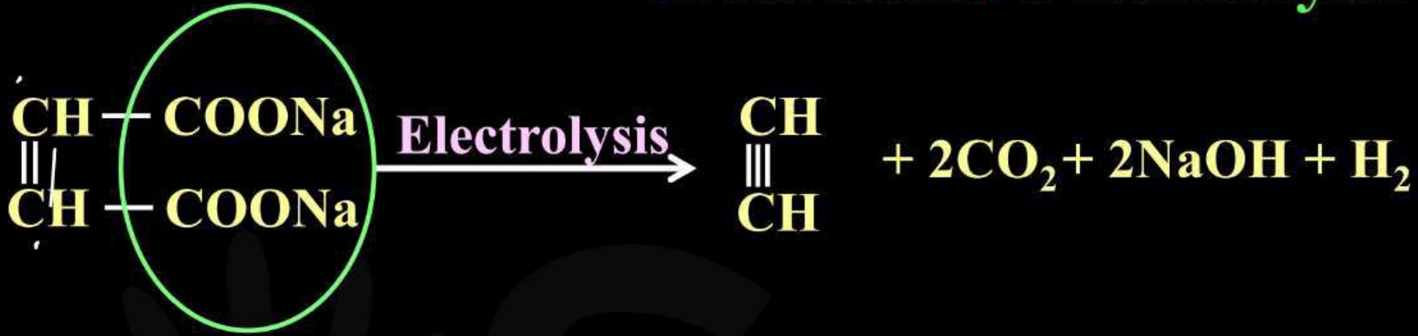
Dehalogenation of Tetrahalo Alkane

By heating 1, 1, 2, 2 - tetra halo alkane with Zn dust.



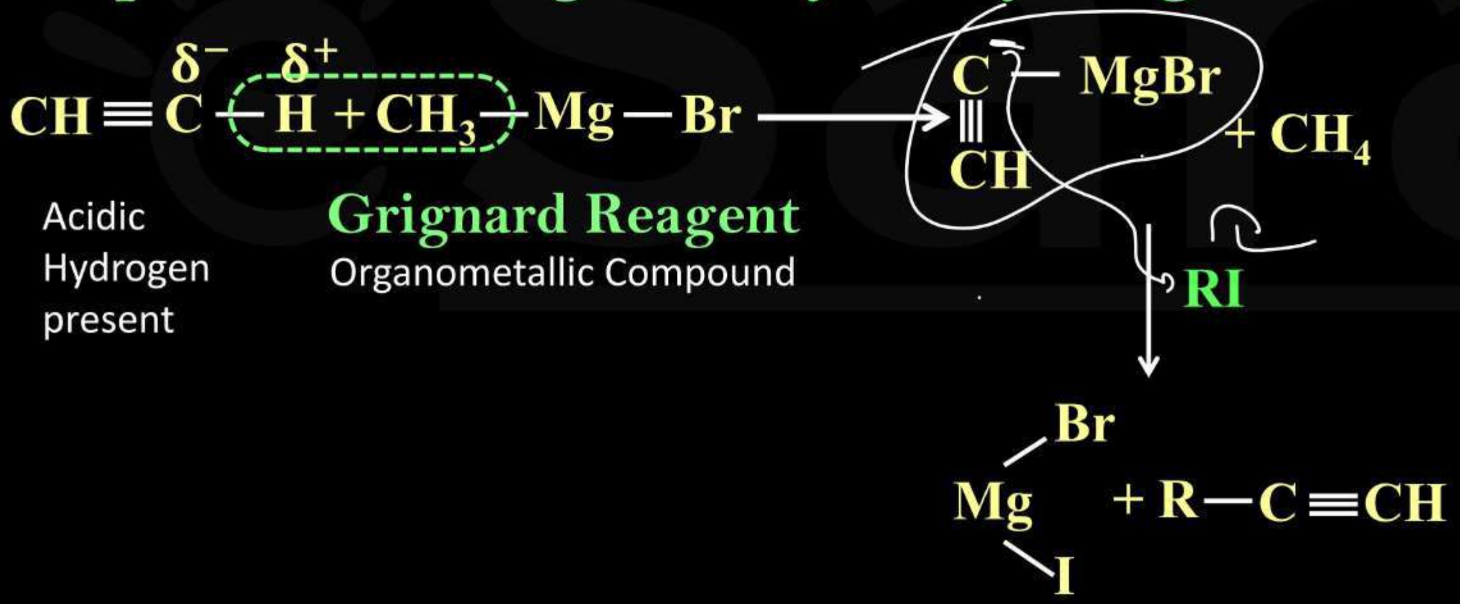
$$R-\underset{X}{\overset{X}{C}}-\underset{X}{\overset{X}{C}}-H \xrightarrow{2Zn} R-C\equiv CH+2ZnX_2$$

From Kolbe's electrolysis



$$\begin{matrix}CH-COONa\\ \|\\ CH-COONa\end{matrix}\xrightarrow{\text{Electrolysis}}\begin{matrix}CH\\ |||\\ CH\end{matrix}+2CO_2+2NaOH+H_2$$

Preparation of Higher Alkynes By Grignard Reagent



$$CH\equiv\overset{\delta^-}{C}-\overset{\delta^+}{H}+CH_3-Mg-Br\longrightarrow\begin{matrix}C^{-}-MgBr\\ |||\\ CH\end{matrix}+CH_4$$

$$\xrightarrow{RI}Mg\begin{matrix}Br\\ I\end{matrix}+R-C\equiv CH$$

Acidic Hydrogen present

Grignard Reagent

Organometallic Compound

Preparation of Ethyne or Acetylene

(a) From Metal carbide [Laboratory method]

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

From Haloform (CHI_3, $CHCl_3$)

$$CHI_3 + 6Ag + I_3CH \longrightarrow CH\equiv CH + 6AgI$$

(b) Presence of acidic hydrogen atom

$C \equiv C - H$

↓

acidic

Addition reaction

$C \equiv C \xrightarrow{E^+}$

(a) Addition of hydrogen

$C \equiv C^-$ CB is stable

sp

↓

EN ↑

Electrophilic Addition

$+$

$C = C$

sp^2

↓

E

↓

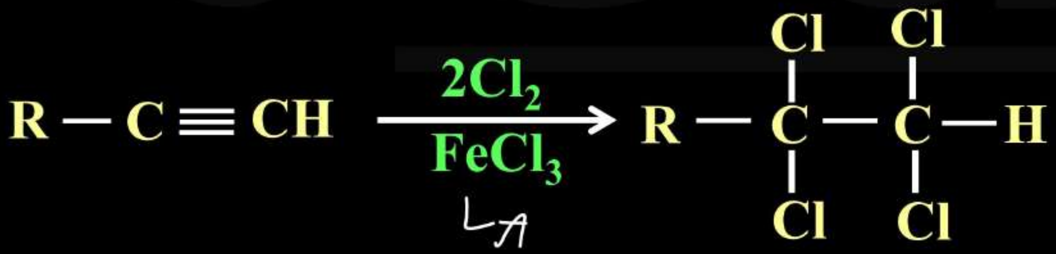
Intermediate ↓ ror ↓

The characteristic reaction of alkynes is electrophilic addition but the reactivity of alkynes towards electrophilic addition is less than alkenes.

Addition of Halogens

Reactivity order of Halogens $Cl_2 > Br_2 > I_2$

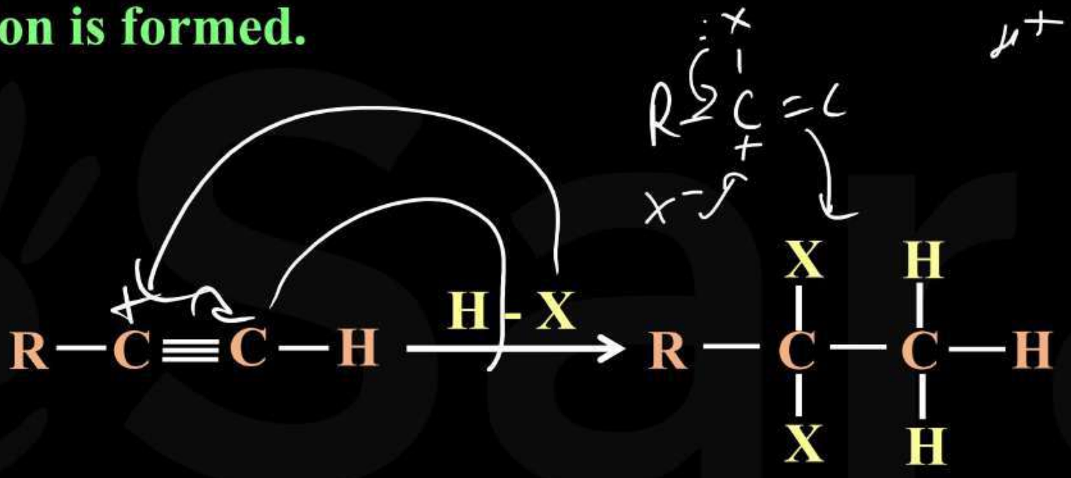
Alkynes react with Cl_2 or Br_2 in dark in presence of metal halide and form di and tetra halo derivatives.



$$R-C\equiv CH \xrightarrow[\substack{FeCl_3 \\ \text{LA}}]{2Cl_2} R-\underset{Cl}{\overset{Cl}{C}}-\underset{Cl}{\overset{Cl}{C}}-H$$

Addition of Halogen Acids (H – X)

Addition according to Markovnikov's Rule. Both the times Markovnikov's rule is applicable. Also no carbocation rearrangement will talke place here as vinylic cation is formed.

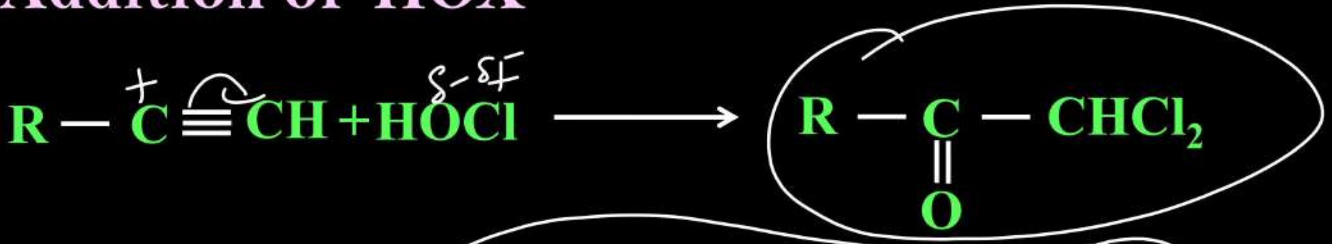


(Gem dihalides major product)

Reactivity order of H – X

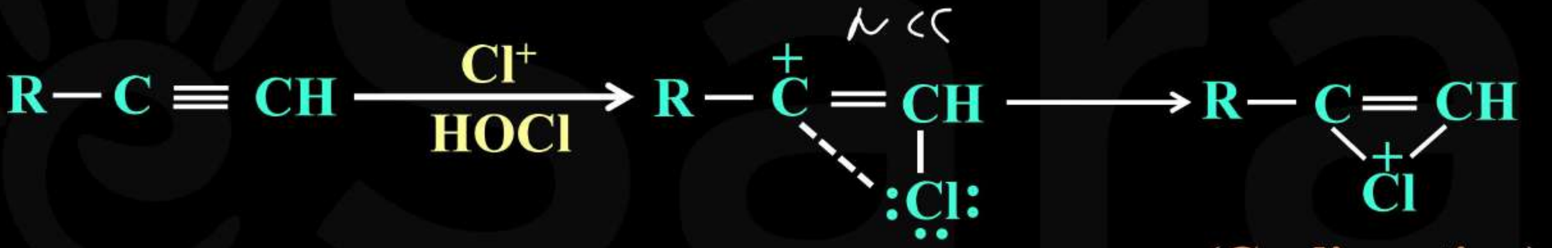
HI > HBr > HCl > HF

Addition of HOX

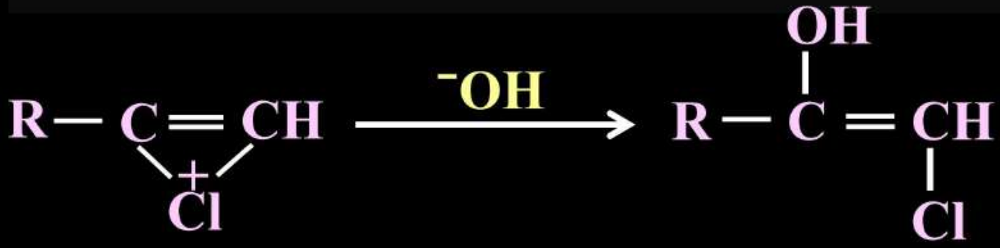


$$R-\overset{+}{C}\equiv CH + H\overset{\delta-\ \delta+}{OCl} \longrightarrow R-\underset{\underset{O}{\|}}{C}-CHCl_2$$

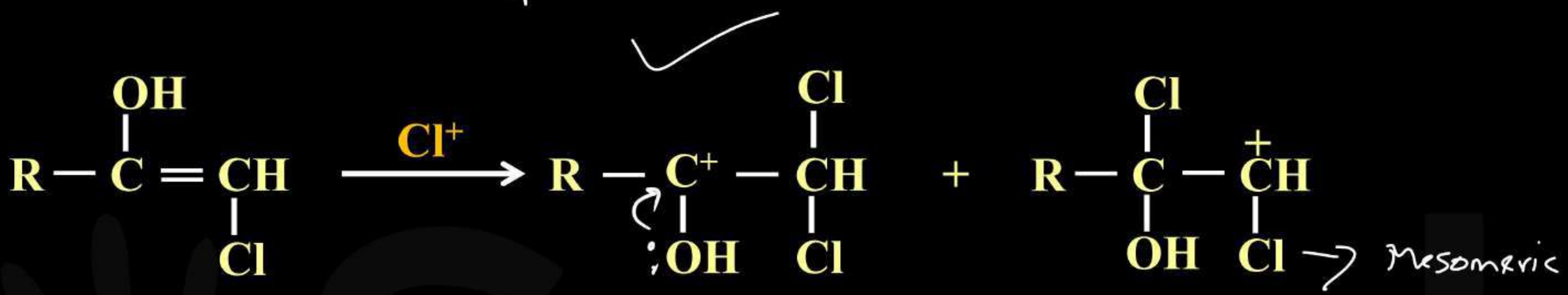
Reactivity order HOCl > HOBr > HOI Learn



(Cyclic cation)



+M



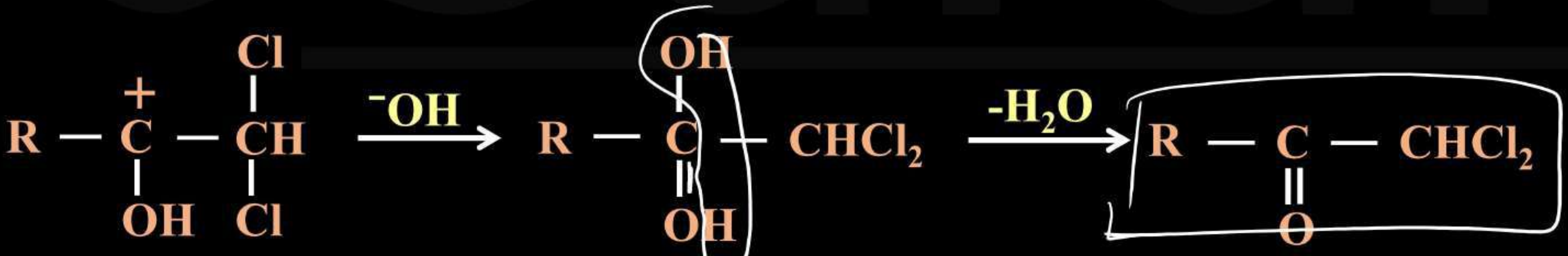
$$R-\overset{\overset{OH}{|}}{C}=\underset{\underset{Cl}{|}}{CH}\xrightarrow{Cl^+}R-\underset{\underset{:OH}{|}}{C^+}-\overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{CH}}+R-\overset{\overset{Cl}{|}}{\underset{\underset{OH}{|}}{C}}-\underset{\underset{Cl}{|}}{\overset{+}{C}H}$$

Mesomeric

(more stable due to +M of OH group)

(less + M of Cl - Atom)

4 membered
CTS → H-bonding

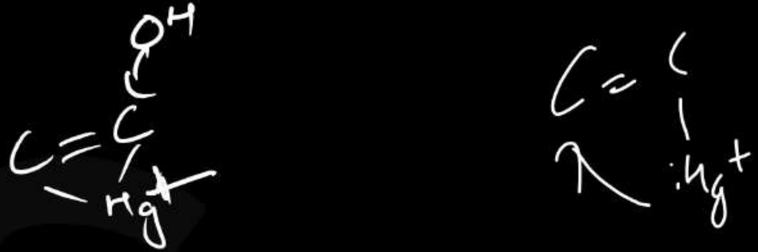


$$R-\underset{\underset{OH}{|}}{\overset{+}{C}}-\overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{CH}}\xrightarrow{^-OH}R-\overset{\overset{OH}{|}}{\underset{\underset{OH}{||}}{C}}-CHCl_2\xrightarrow{-H_2O}\boxed{R-\underset{\underset{O}{||}}{C}-CHCl_2}$$

(Unstable)

(Dichloro ketones)

Nucleophilic addition reaction



$\boxed{H_2O}$

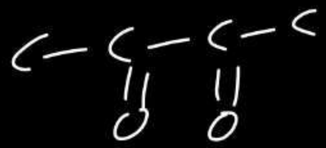
$$CH \equiv CH \xrightarrow[\text{dil } H_2SO_4]{1\% \ HgSO_4} CH_2 = CH - OH \rightleftharpoons \boxed{CH_3 - CHO}$$

Enol unstable

Oxidation Reactions

$C-C\equiv C-C$

(a) Combustion



$$C-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-C$$

$C\equiv C$

$$C_nH_{2n-2} + \frac{3n-1}{2}O_2 \longrightarrow nCO_2 + (n-1)\,H_2O + \text{Heat}$$

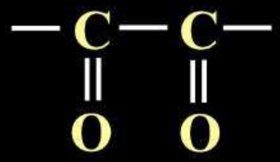
CH_3COOH

Oxidation With Acidic $KMnO_4$ or $K_2Cr_2O_7$

In presence of acidic $KMnO_4$ or acidic $K_2Cr_2O_7$ alkynes are oxidized to monocarboxylic acids.

(c) Oxidation With Ozone (O_3)

In the ozonolysis both sp C-atoms are converted into



$$-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-$$

Substitution Reaction

Formation of metallic derivatives

Only 1-alkynes give substitution reaction and show acidic characters

$$\equiv\overset{\delta^-}{C} - \overset{+\delta}{H}$$

Q) Which of the following reagents can be used to distinguish between A & B ?

POC

$AgNO_3 + NH_4OH$

$Cu_2Cl_2 + NH_4OH$

→ Red ppt

substitution ✓

1-alkyne

✓

×

–

A

B

1) Tollen's reagent → Silver Mirror

2) Ammonical Cuprous Chloride

3) Br_2/CCl_4

4) Bayer's Reagent

} Test of unsaturation

Cyclic Polymerisation

$3CH \equiv CH \xrightarrow[\text{Iron tube}]{\text{Red hot}}$

Benzene

Most important

Laboratory Test for alkynes(Test is used for presence of unsaturation in compound)

Functional Group	Reagent	Observation
$-C \equiv C-$	(1) Bayer's Reagent Alk.dil.Cold $KMnO_4$	Pink Colour disappears
	(2) Br_2/H_2O	Red Brown Colour decolourises
	O_3 (Ozone)	Acid Formed

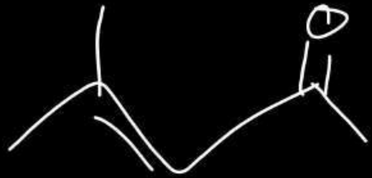
POC

Laboratory test of terminal alkynes(Test is used for distinguishing between alkenes and 1-alkynes or 1-alkyne and 2-alkyne.)

Functional Group	Reagent	Observation	Reaction
$R-C\equiv C-H$	(1) Cuprous chloride $+NH_4OH$	Red ppt.	$R-C\equiv CH+CuCl \xrightarrow{NH_4OH} R-C\equiv C-Cu\downarrow$(red ppt)
	(2) $AgNO_3+NH_4OH$ Tollens reagent	White ppt. (silver mirror test)	$R-C\equiv CH + Ag \rightarrow R-C\equiv C\,Ag$ (white ppt)
	(3) Na in ether	Colourless gas	$HC\equiv CH + 2Na \rightarrow Na-C\equiv C-Na + H_2\uparrow$

Aromatic Hydrocarbons [Arenes]

General Methods of Preparation



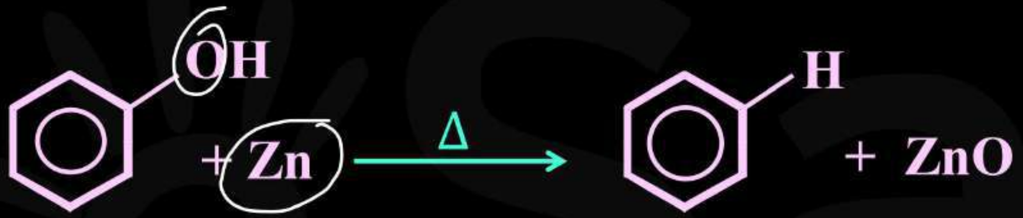
(i) From alkanes

$$\text{n – Hexane} \xrightarrow[600^\circ C]{Cr_2O_3/Al_2O_3} \text{Benzene} + 4H_2$$

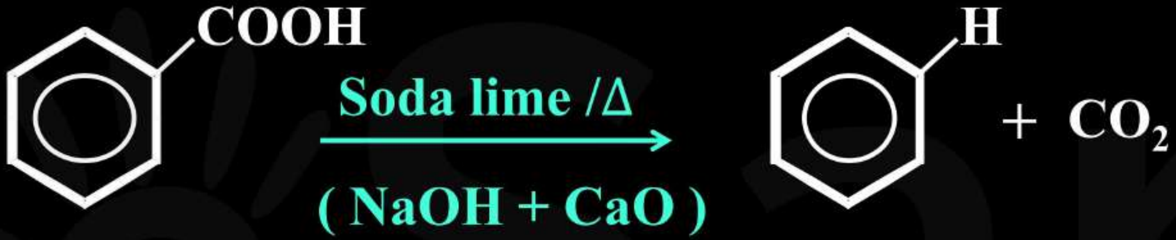
From Alkyne (By Cyclic Polymerisation)

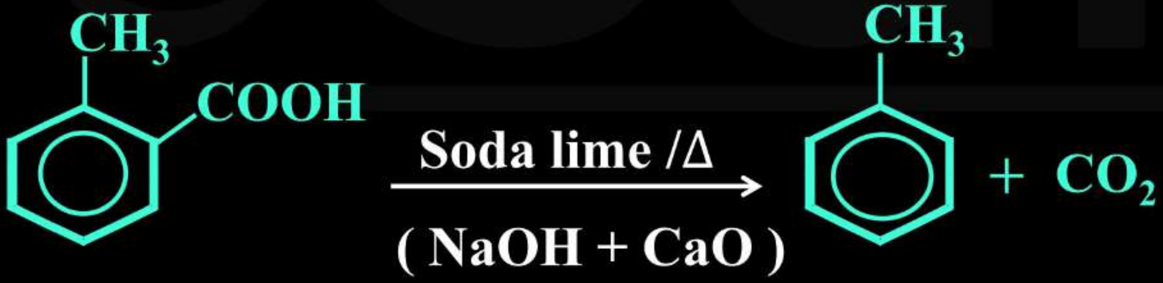
$$3CH \equiv CH \xrightarrow{\text{Red hot iron tube}}$$

From Phenolic Compounds (By Deoxygenation)

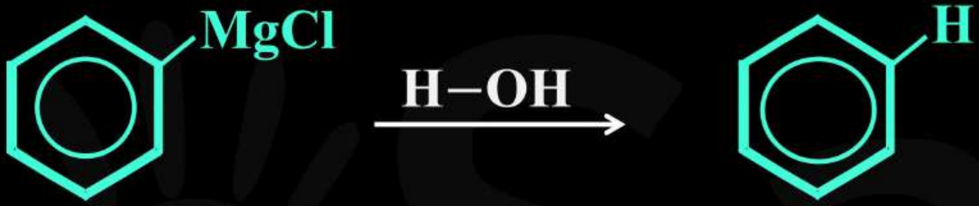


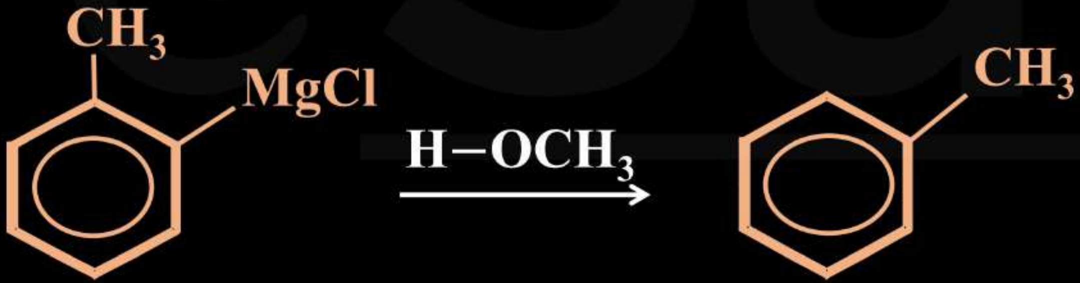
From Carboxylic Acids (By Decarboxylation)





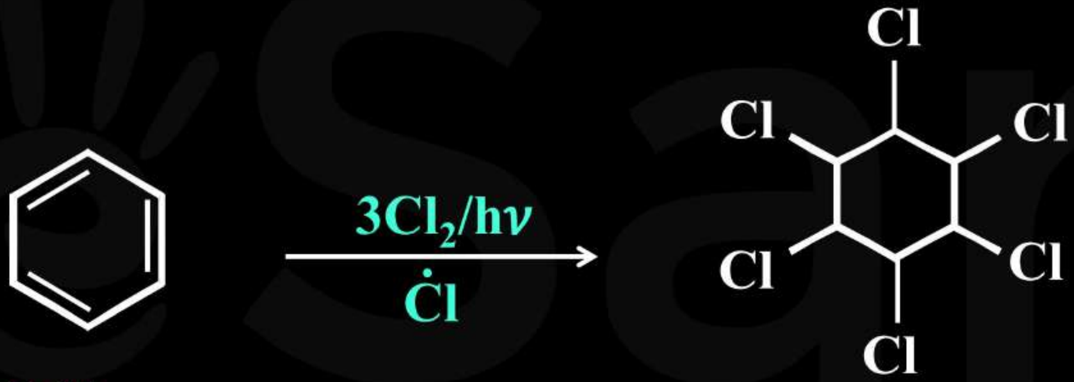
By Grignard Reagent





(i) Addition of X_2

Imp



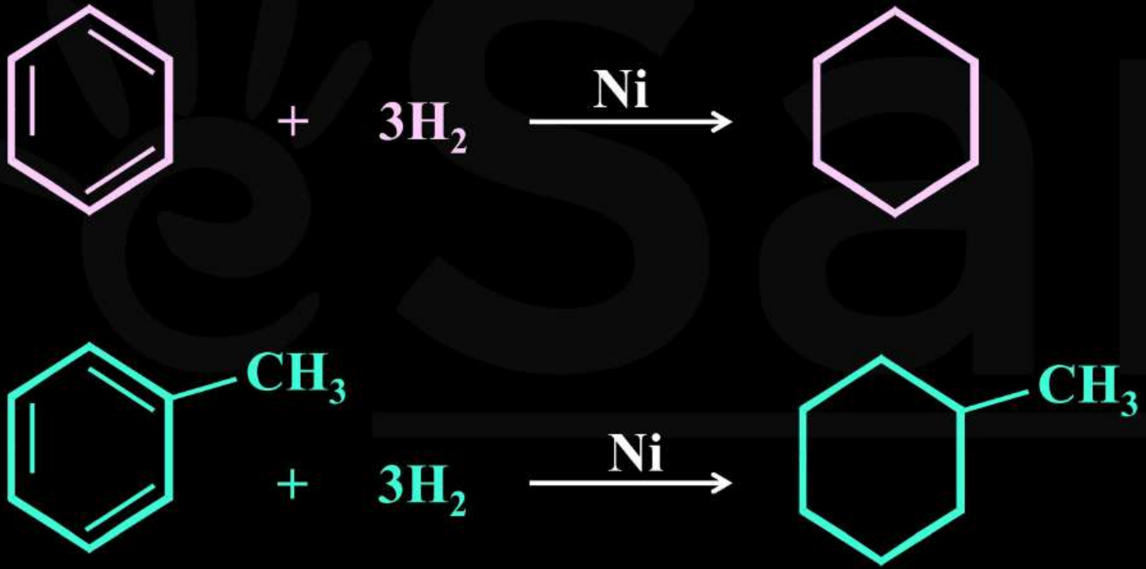
C_6H_6
Aromatic compound

Benzene hexachloride

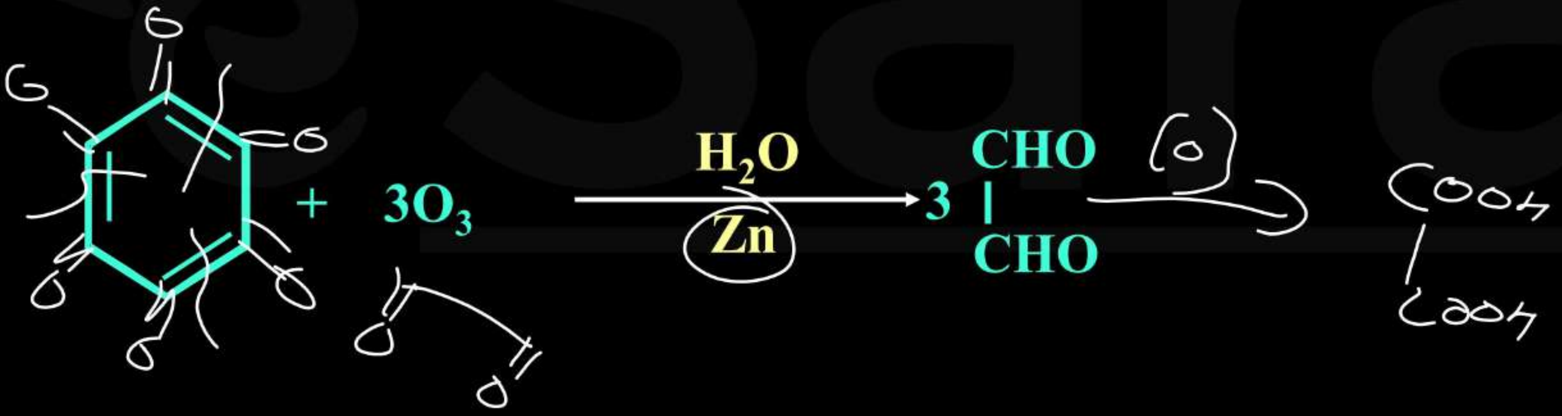
BHC or 666 or Gammexane or lindane

*BHC is used as powerful insecticide

Addition of H_2



Addition of O_3(Ozonolysis)



$$+\ 3O_3 \xrightarrow[\boxed{Zn}]{H_2O} 3\begin{array}{c}CHO\\|\\CHO\end{array} \xrightarrow{(O)} \begin{array}{c}COOH\\|\\COOH\end{array}$$

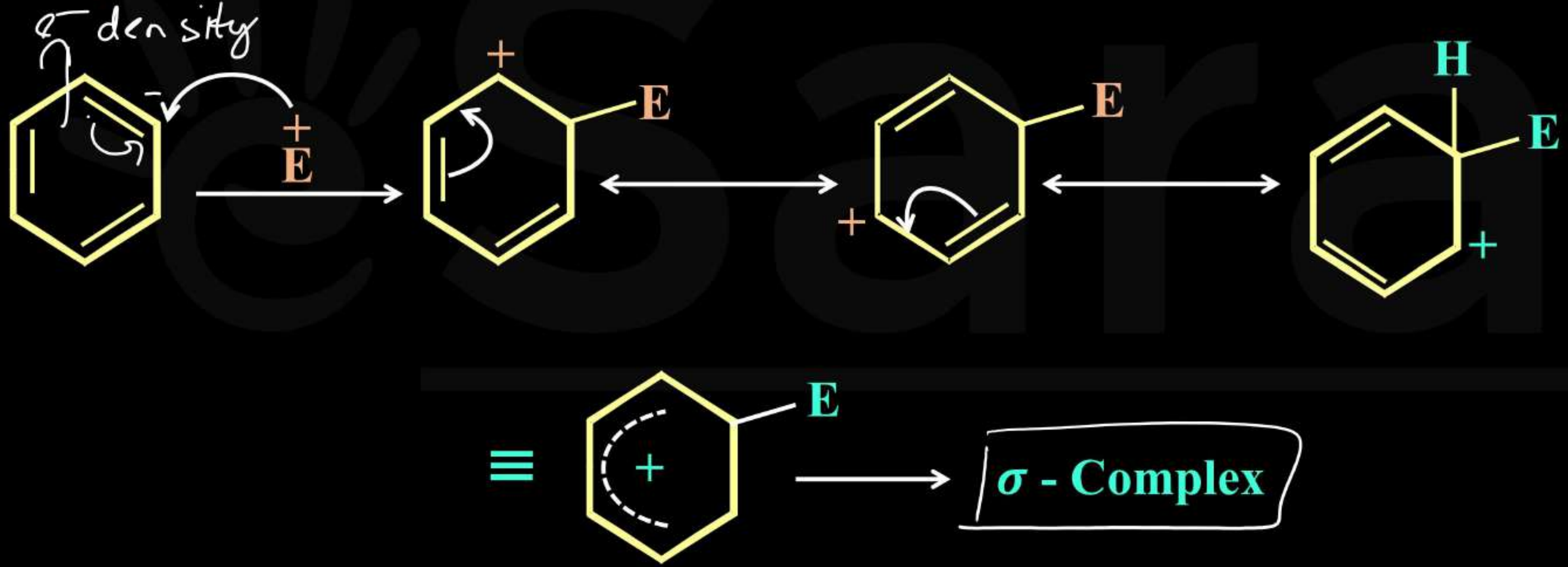
Electrophilic Substitution Reaction [ESR]

Characteristic reaction of arenes is ESR

Mechanism

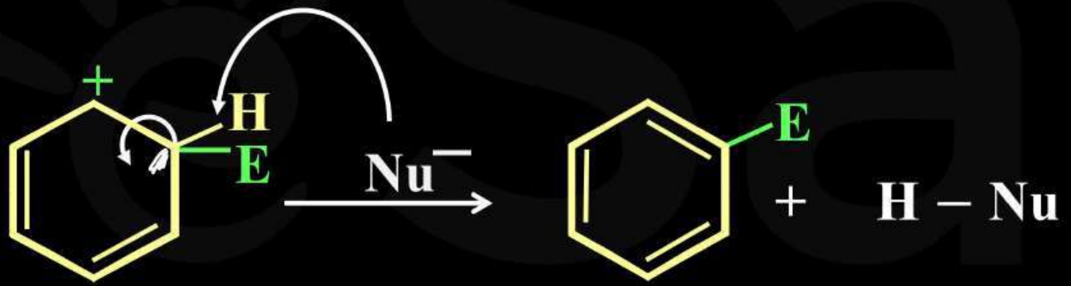
Step I : Formation of E^+ $E - Nu \xrightarrow{\text{Catalyst}} E^+ + Nu^-$

Step II : Attack of E^+

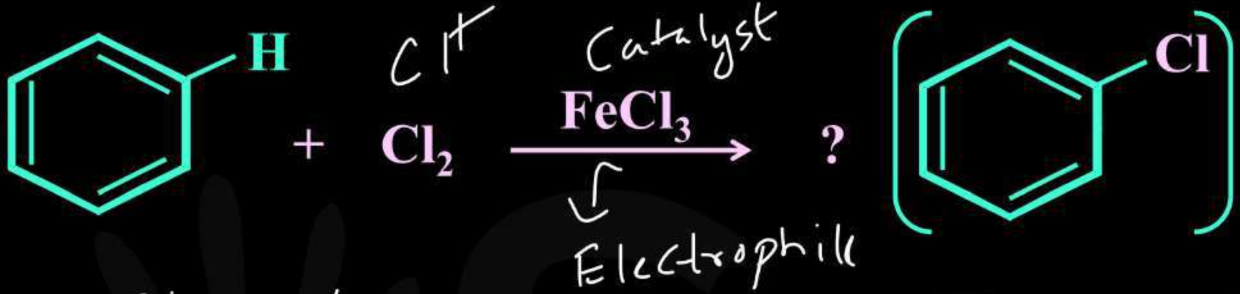


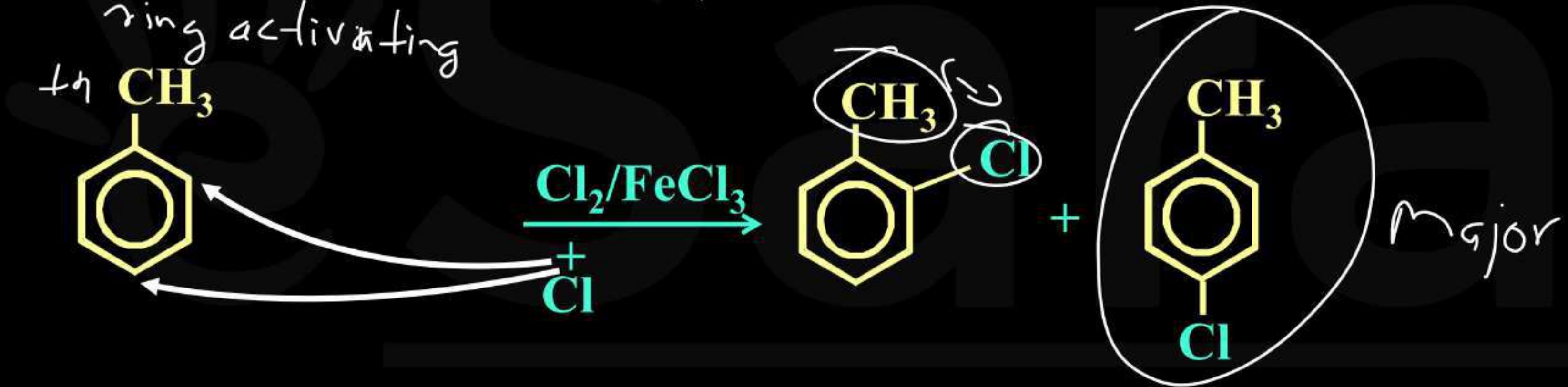
σ - Complex

Step III : Abstraction of H^+
(To retain it's aromaticity)



Halogenation

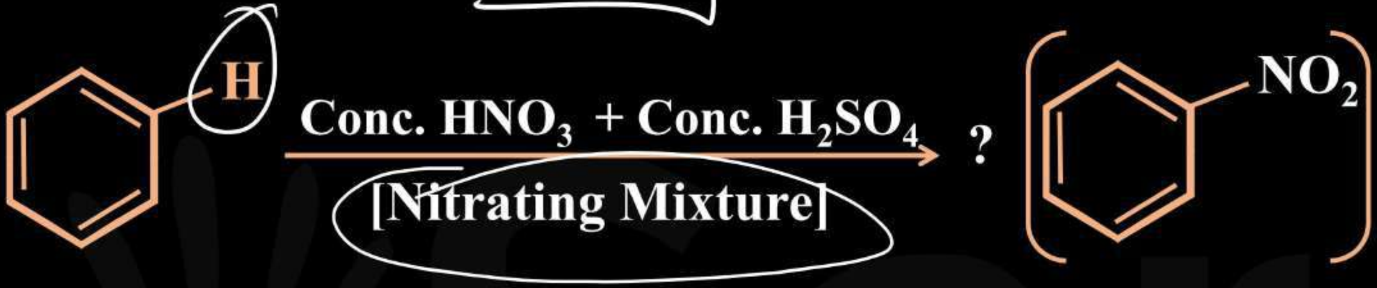




Note: CH_3 group in toluene is o/p directing and activating group.

Nitration

$\boxed{\overset{+}{NO_2}}$



H

Conc. HNO_3 + Conc. H_2SO_4

[Nitrating Mixture]

?

NO_2

Sulphonation

SO_34

H

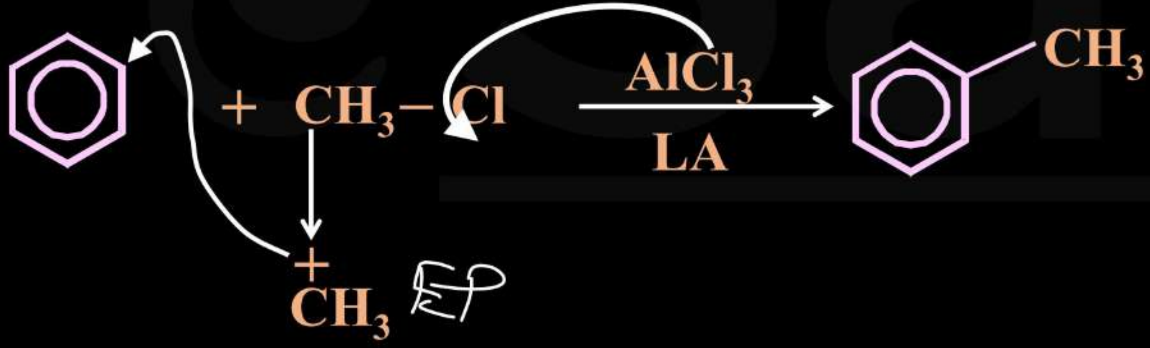
Conc.H_2SO_4

SO_3H

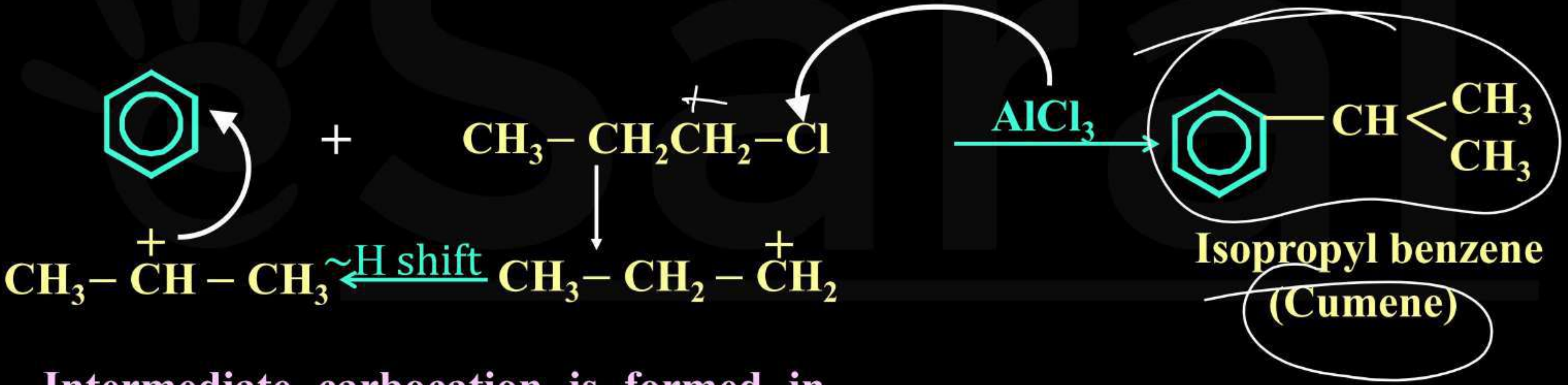
Friedel Crafts Reaction [FCR]

Alkylation or acylation of arenes in presence of lewis acid [$FeCl_3$, $AlCl_3$ or $ZnCl_2$...] is called as FCR. CS_2 or nitrobenzene is used as solvent in FCR.

Friedal Crafts Alkylation



Q)



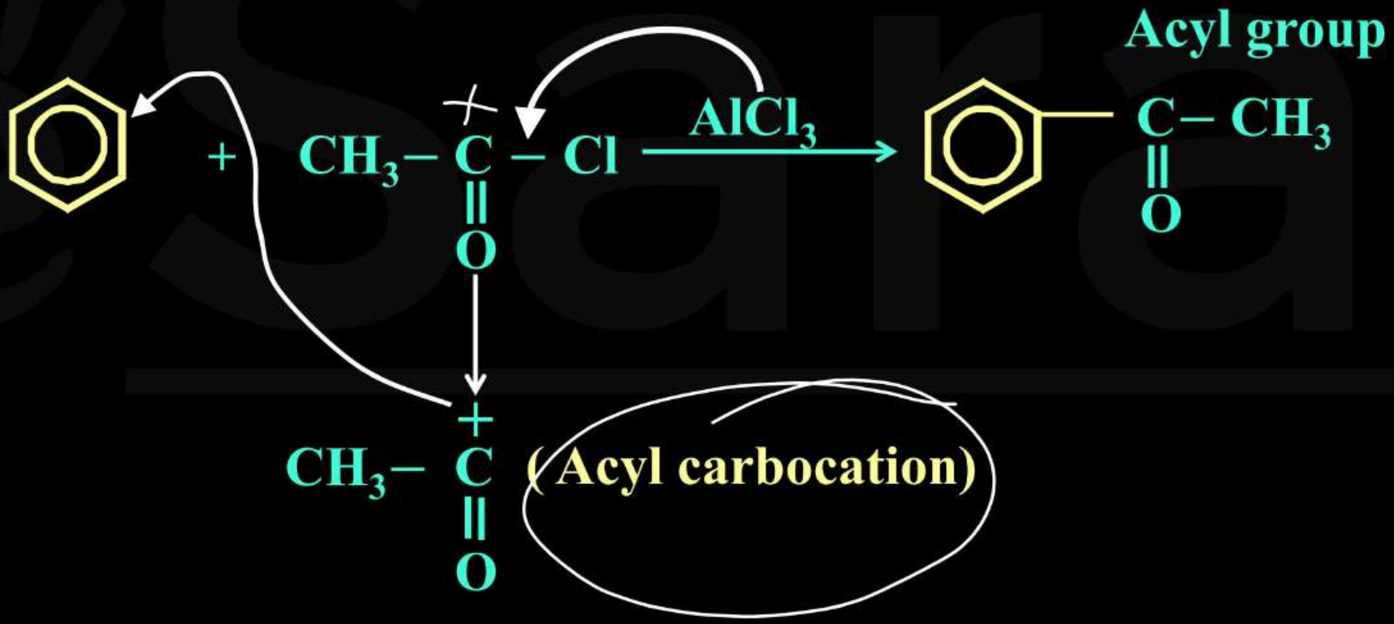
$$C_6H_6 + CH_3-CH_2CH_2-Cl \xrightarrow{AlCl_3} C_6H_5-CH(CH_3)_2$$

$$CH_3-\overset{+}{C}H-CH_3 \xleftarrow{\sim H\ shift} CH_3-CH_2-\overset{+}{C}H_2$$

Isopropyl benzene
(Cumene)

Intermediate carbocation is formed in FCR so rearrangement possible.

Friedal Crafts Acylation

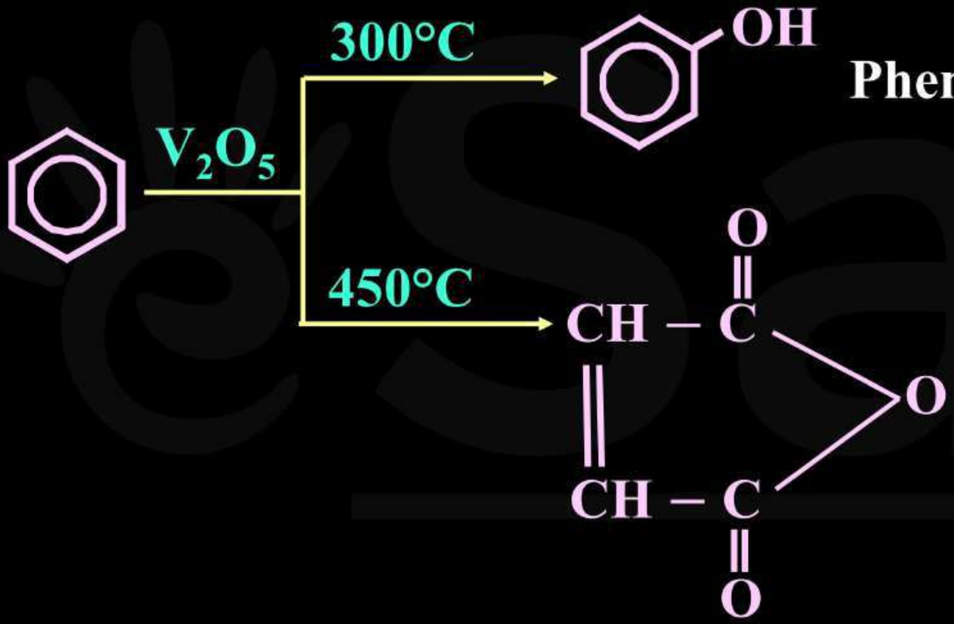


Oxidation Reactions

Combustion

$$C_6H_6 + \frac{15}{2}O_2 \longrightarrow 6CO_2 + 3H_2O$$

Catalytic Oxidation



Phenol

Maleic anhydride

Learn

Side chain Oxidation

$KMnO_4 \mid K_2Cr_2O_7$

$Ph-CH_3$

$Ph-COCl$

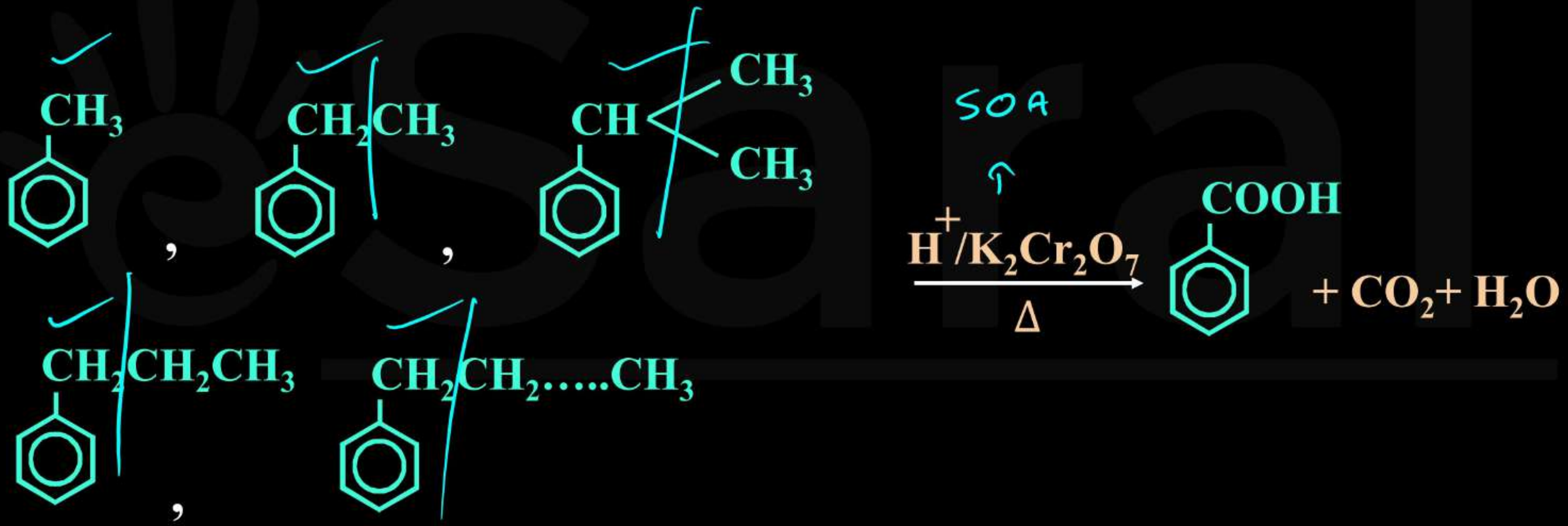
$\xrightarrow{} Ph-COOH$

Atleast one benzylic –H containing alkyl benzene gives benzoic acid in presence of strong oxidising agent.

$Ph-CH_2-CH_3 \xrightarrow{SOA} Ph-COOH$

$Ph-C(CH_3)_3 \xrightarrow{SOA} \times$

⑤


CH_3
CH_2CH_3
$CH(CH_3)_2$
$CH_2CH_2CH_3$
$CH_2CH_2.....CH_3$
SOA
$H^+/K_2Cr_2O_7$
Δ
COOH
$+ CO_2 + H_2O$

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