OC Mega Revision

• **Live** at 8:00 PM

5th April - 24th April

Complete Chemistry Mega Revision Timetable

5 April

IUPAC + GOC

6–10

7 April

Structural + Stereo Isomerism

6–10

9 April

Hydrocarbon

6–8

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

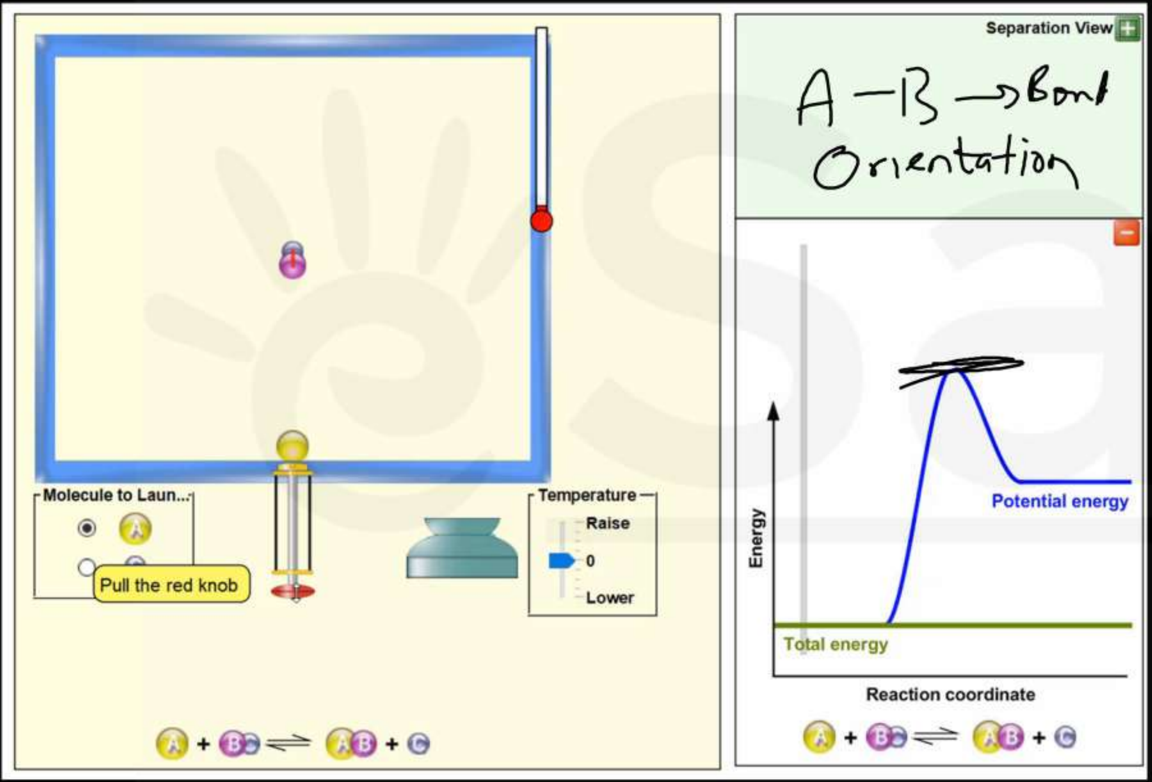
Haloalkanes and Haloarenes

$$A + B \xrightarrow[\text{Conditions}]{} C - A$$

$$\text{Reactant} \longrightarrow \text{Product}$$

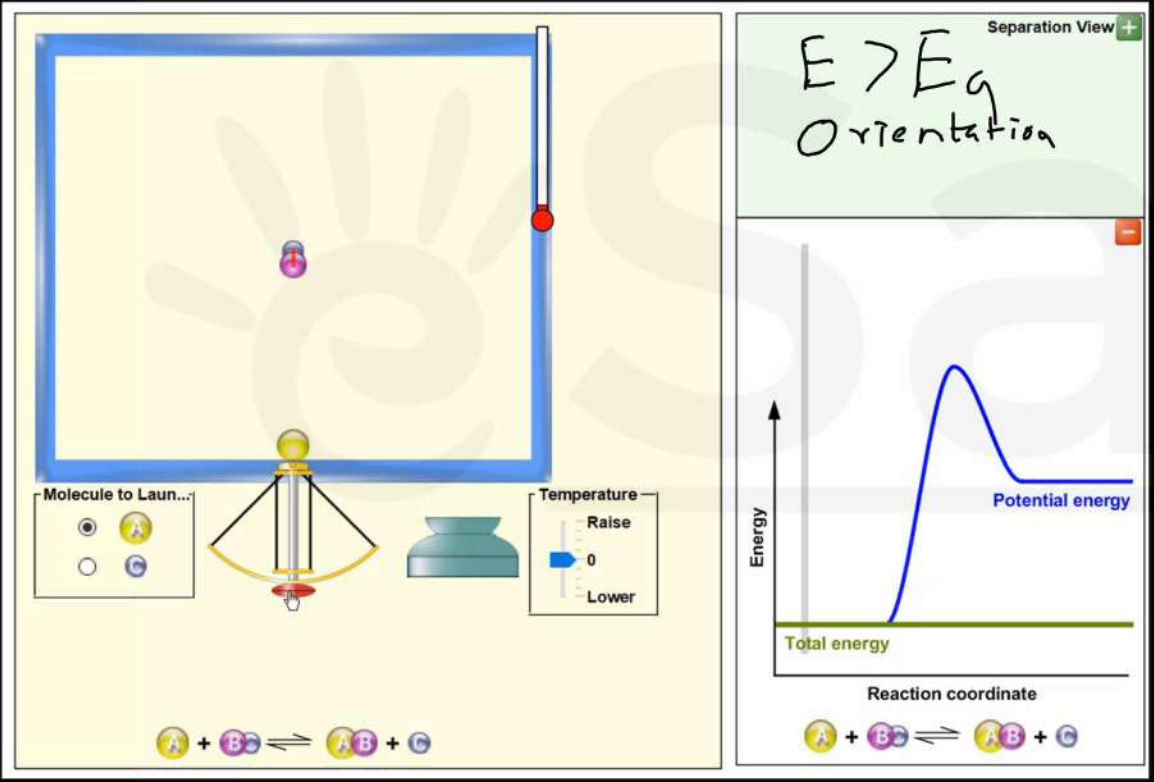
What is Chemistry?

What is a Chemical reaction?



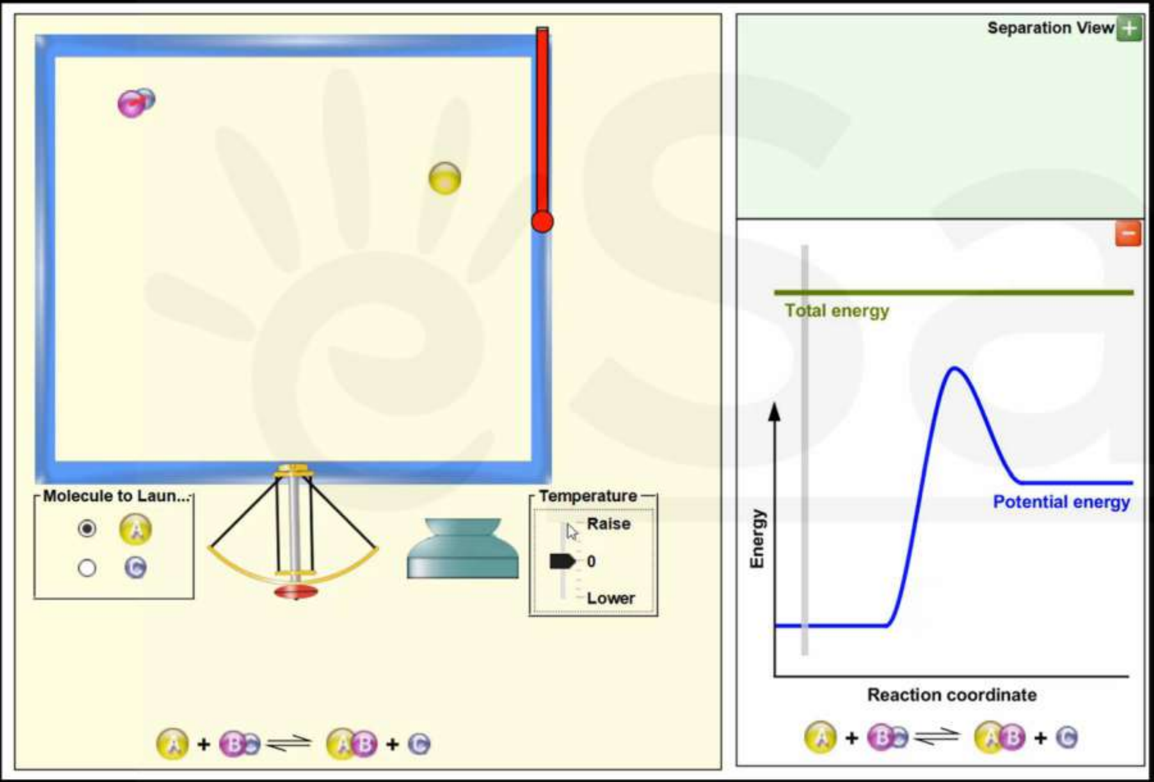
A — B → Bond

Orientation



$E > E_a$

Orientation


Separation View
Molecule to Laun...
● A
○ C
Temperature
Raise
0
Lower
A + BC ⇌ AB + C
Total energy
Potential energy
Energy
Reaction coordinate
A + BC ⇌ AB + C

Substrate

Attacking Species

Stability of Transition State

Stability of Product

Temperature

Solvent

Orientation

Electrophiles are of following types

(1) Positively charged electrophiles

$H^+, Br^+, Cl^+, I^+, \overset{+}{N}O_2, R_3C^+, \overset{+}{N}O$ etc.

(2) Neutral Electrophiles

$\overset{\delta+}{S}O_3, \overset{\delta+}{B}F_3, AlCl_3, ZnCl_2, FeCl_3,$
RCOCl, $(RCO)_2O$ etc.

Nucleophiles (Nucleus Loving)

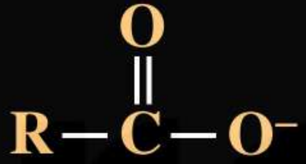
+ve
neutral

It is an electron rich species.

(1) Negatively charged nucleophiles

no one wants
a charge

$\bar{H}$, $\bar{O}H$, $\bar{O}-R$, $\bar{C}H_3$, $\bar{X}$, $\bar{S}H$, $\bar{R}-\bar{S}$, $N\bar{O}_2$,



$R-\overset{\overset{\displaystyle O}{\|}}{C}-O^-$

(2) Neutral nucleophiles

$R-\ddot{N}H_2$, $\ddot{N}H_3$, $\ddot{N}H_2-\ddot{N}H_2$, $H-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-H$,

$R-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-H$, $R-\ddot{O}-R$,

$H-\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}-H$, $R-\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}-H$, $R-\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}-R$, $\ddot{P}H_3$,

(3) Pi bonded organic compounds

$CH_2 = CH_2$, , $CH_2 = CH - CH = CH_2$, etc.

(4) Ambident Nucleophile

$\bar{C} \equiv \ddot{N}$, $\bar{O} - \ddot{N} = O$, etc.

Solvent & it's Role

Charges are formed
↓
Bina solvent ✗

A Solvent provides a medium, a place, for the substrate and attacking species to react.

Other than this it can also affect the rate of reaction.

S_N1
S_N2

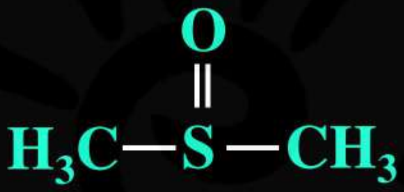
Reactants need a place
↓
Solvent

Solvent

- Non polar
  - CCl_4
- Polar
  - ± Polar protic
    - H_2O
  - Polar aprotic +
    - DMF

Examples of polar aprotic

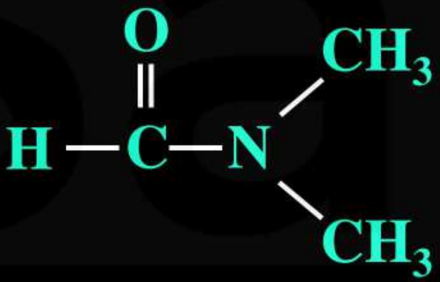
Learn



$H_3C-\overset{\overset{\displaystyle O}{\|}}{S}-CH_3$

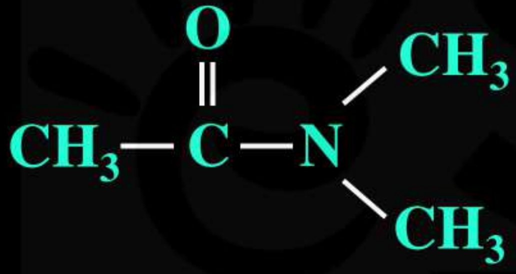
DMSO

(Dimethyl sulphoxide)

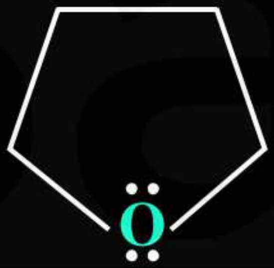


DMF

(Dimethyl formamide)

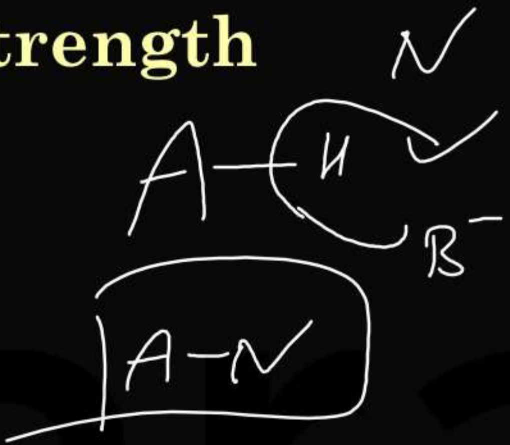


DMA
(Dimethyl acetamide)



THF
(Tetrahydrofuran)

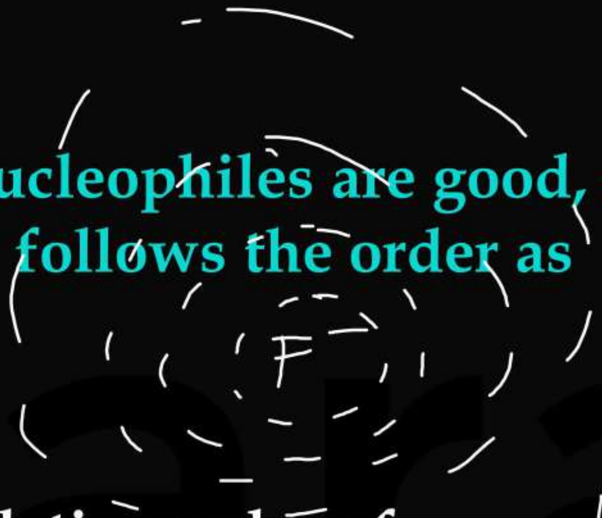
Nucleophilicity Vs Basic strength



Nucleophilicity is defined as the tendency of any species to give electron pair to an electron deficient centre, while basic strength is the ability of the species to remove H^+ ion from an acid.

Effect of The Solvent

In polar protic solvent large nucleophiles are good, and the Nucleophilicity of halide ions follows the order as



Ion—dipole

$F^- < Cl^- < Br^- < I^-$

↳ paani

In polar aprotic solvent, the relative order of Nucleophilicity of halide ions is given as

$F^- > Cl^- > Br^- > I^-$

(as no Solvation of anion takes place by aprotic solvent).

Key point

PP

BS $F^- > Cl^- > Br^- > I^-$ N PP $I^- > Br^- > Cl^- > F^-$

PA

BS $F^- > Cl^- > Br^- > I^-$ N PA $F^- > Cl^- > Br^- > I^-$

$F \cdots H^+$

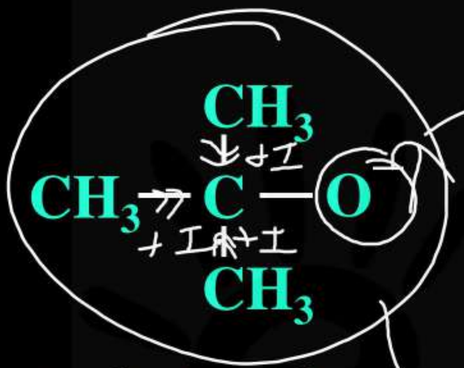
Basic strength of halides follows the same order as nucleophilicity in polar aprotic solvent but in polar protic solvent like H_2O they follow the reverse order of Nucleophilicity.

Steric Effects on Nucleophilicity

e⁻ rich ←

↳ Bond Banayega

→ +H extract



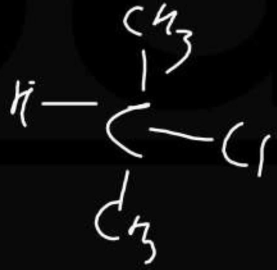
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O^-$$

(Stronger base, yet weaker nucleophile. Cannot approach the carbon atom so easily.)

Size ↓

t - butoxide

SN2



$CH_3-CH_2-O^-$

ethoxide

(Weaker base, yet stronger nucleophile)

Leaving Group Ability

-ve charge

$\boxed{X^{\ominus}} \rightarrow LG$

$Nu \frown C - X$

LG Ab ∝ stability of CA

[L.G. Ability ∝ Stability of Conjugate base or anion (Lg$^{\ominus}$)]

$C - I$ $\quad$ $\boxed{I^{-}}$

$C - F$ $\quad$ F^{-}

Weaker is the base better is the leaving group.

F^{-}

Cl^{-}

Br^{-}

I^{-}

Order Of Leaving Ability Of Some Groups

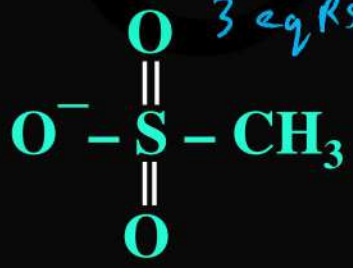
LG ∝ stab of -ve charge

(1) $-\overset{-}{I} > -\overset{-}{Br} > -\overset{-}{Cl} > -\overset{-}{F}$

Same group size

(2) $CH_3^- < NH_2^- < OH^- < F^-$ Same period EN

3 eq RS 2 eq RS Reso

(3) 

$O^- - \overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}} - CH_3 > R - COO^- > PhO^- > HO^- > \overset{+I}{R}O^-$

N_2 and water are good LGs

$R-\overset{+}{N}\equiv N$ & $R-\overset{+}{O}-H$ with H below O

Preparation of Alkyl Halide

CH_3Cl

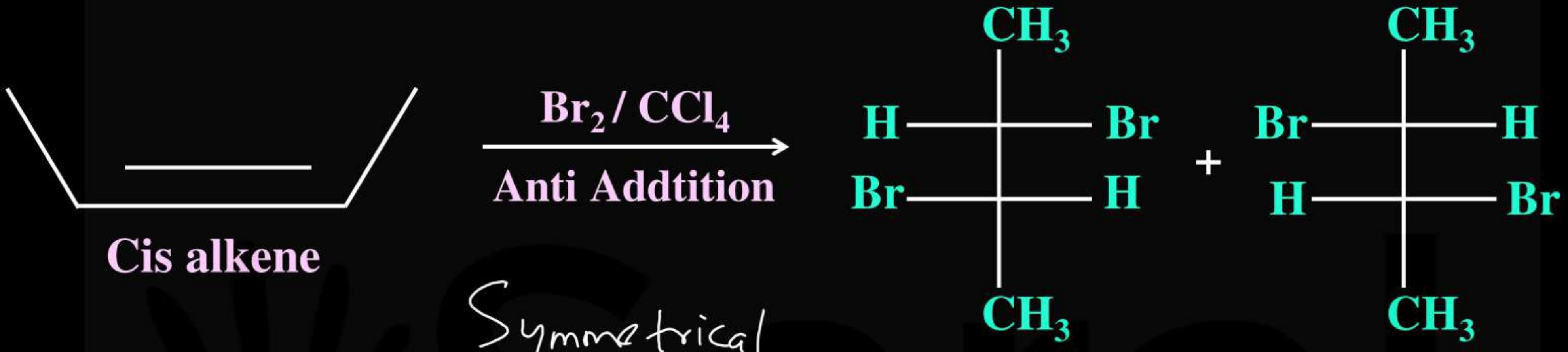
Addition of HX

Addition of X_2

$$\underset{Cl}{CH_2}-\underset{Cl}{CH_2}$$

By Electrophilic Substitution Reaction

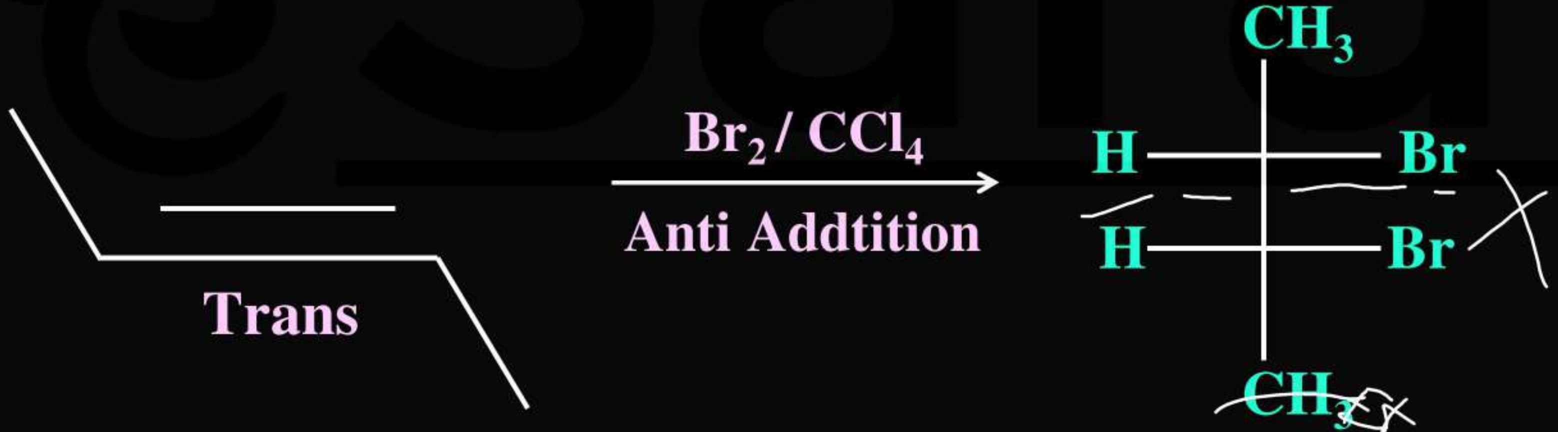
Halogenation



Cis alkene

Symmetrical

Racemic Mixture



Trans

(Meso/POS)

For Symmetric Alkene

Learn

Alkene Type	Type of Addition	Product Type
Cis	Syn	Meso
Cis	Anti	Racemic Mixture
Trans	Anti	Meso
Trans	Syn	Racemic Mixture

Unimolecular Nucleophilic Substitution Reaction (S_N1)

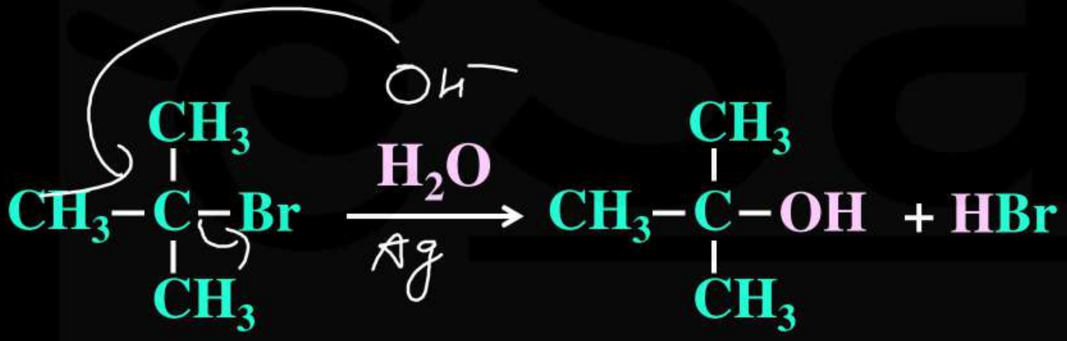
↳ First order

↓ sp^2 ↑ + —

Me_3C^+ + Br^- Ag^+

C^+ stable

S_N1 in Haloalkanes



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br \xrightarrow[Ag]{OH^- \; H_2O} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH + HBr$$

(3° alkyl halide)

$Br^- \rightarrow LA$

X^-

(1.) **Substrate must be bulky.**

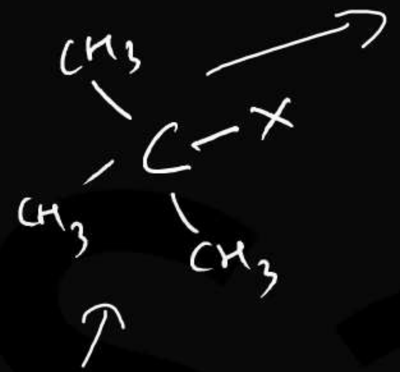
(2.) **Weak or neutral nucleophile with low concentration**

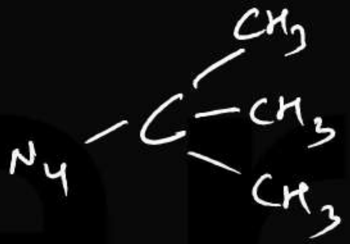
5) Racemic mixture sp^2 Intermediate

(3) **In presence of polar protic solvent.**

(4.) **In presence of Lewis acid .**

45% Retension
55% Inversion





In most of the case the product has usually of 5-20% inverted product and 80-95% racemised species. Thus reaction proceeds with partial racemisation and some inversion.

C^+ → rearrangement

$CH_3\overset{+}{O}H^+$

$$CH_3-\underset{H}{\overset{CH_3}{C}}-CH_2-Br \xrightarrow[S_N1]{CH_3\ddot{O}H / Ag^+} CH_3-\underset{OCH_3}{\overset{CH_3}{C}}-CH_3$$

(carbocation rearrangement)

Q) Arrange the following compounds in increasing order of rate of S_N1 reaction?

$r_{S_N1} \propto$ [substrate]

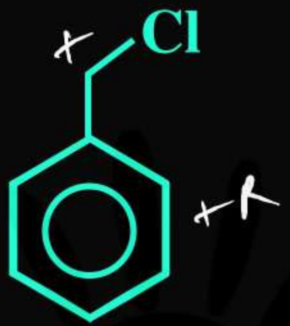
$\propto$ stability of C^+

rxr $\propto$ stab of C^+

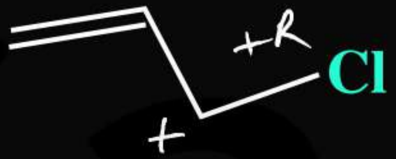
$\downarrow$

S_N1

(1)



(2)

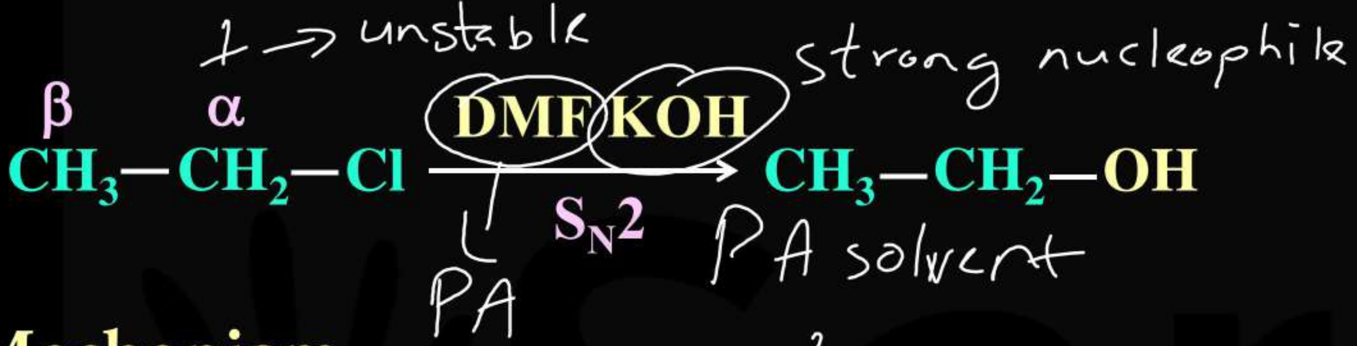


(3) $\overset{+I}{CH_3}-\overset{+}{CH_2}-Cl$

(4) $CH_2=\underset{sp^2}{\overset{+}{CH}}-Cl$

Sol. 1 > 2 > 3 > 4

Bimolecular Nucleophilic Substitution Reaction (S_N2)



$$\overset{\beta}{CH_3}-\overset{\alpha}{CH_2}-Cl \xrightarrow[S_N2]{DMF\ KOH} CH_3-CH_2-OH$$

① less bulky subs

② Strong Nu

③ PA solvent

Mechanism

Transition state

-ve charge

(1) Characteristics of S_N2 Reactions

(A) Nucleophile attacks on the substrate from just opposite side to the leaving group.

(B) Hybridisation of the carbon at which substitution occurs changes from sp^3 to sp^2 in the transition state

S_N1 two step

1) C^+ form

2) Nu attach

nu conc ↑ rate ↑

(C) It is S_N2 **bimolecular, one step concerted process**

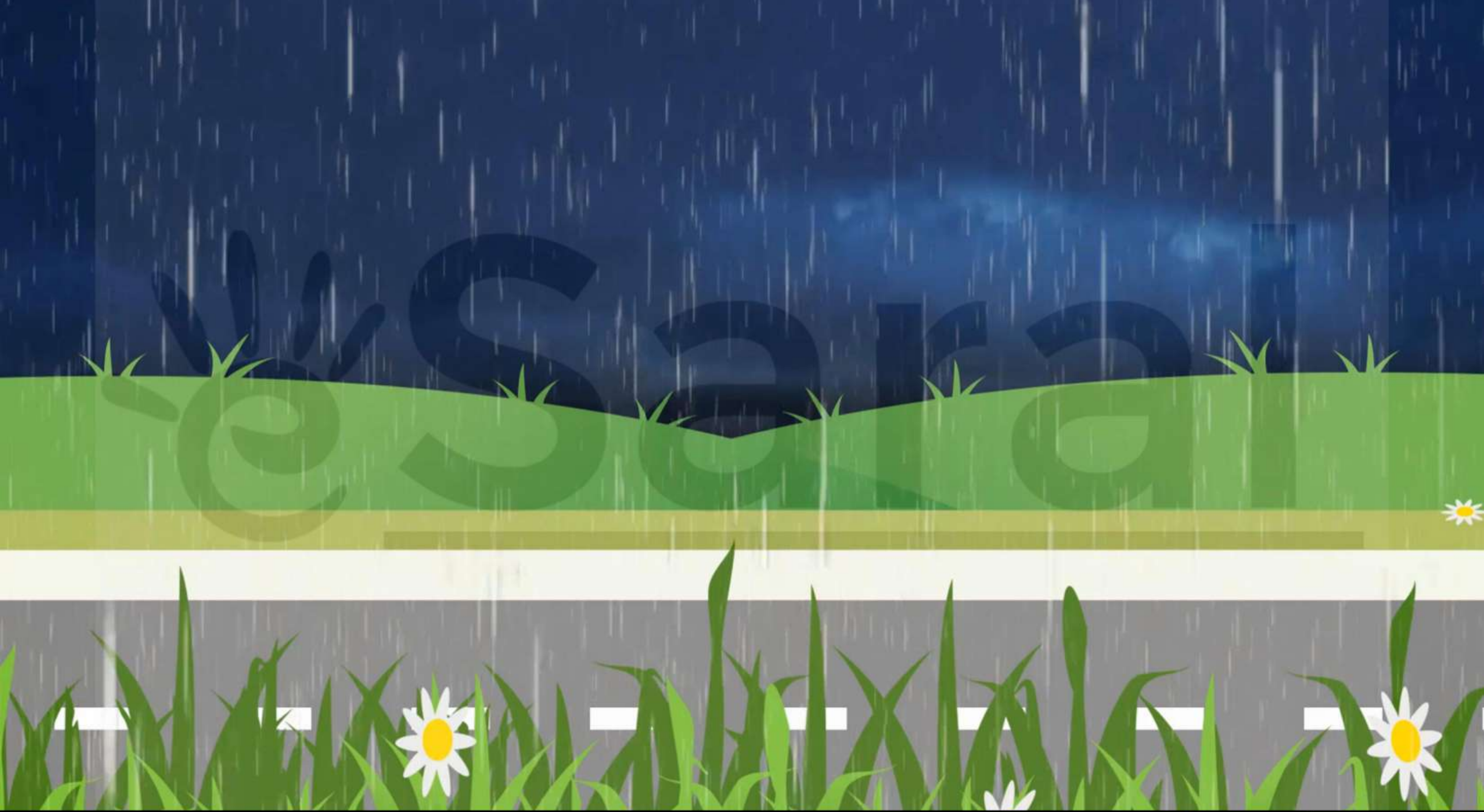
rate ∝ [alkyl halide] [nucleophile]

rate = k[alkyl halide] [nucleophile]

This mode of attack causes an inversion of configuration at the carbon atom that is the target of nucleophilic attack.

This inversion is also known as Walden inversion.


eSaral



Favourable conditions

(1) Smaller least stericly hindered substrate.

(2) Strong nucleophile.

(3) High concentration of nucleophile.

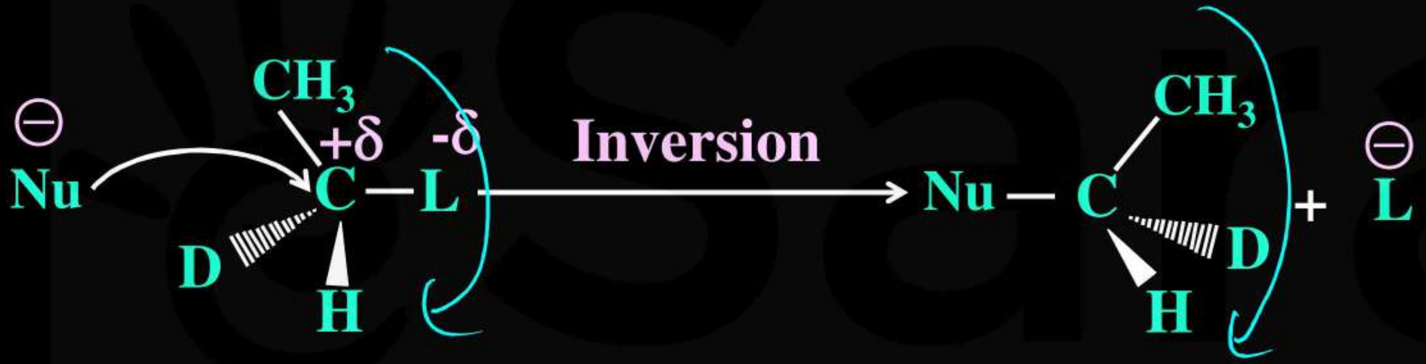
(4.) In alkaline medium.

(5.) In presence of polar aprotic solvent.

Important Point

R → S ✗

Inversion ✓
absolute config ✗



It is always not necessary that absolute configuration will change.

(B) Presence of Unsaturation on β-Carbons

$\overset{\delta-}{Nu}-C-\overset{\delta-}{X}$

TS in S_N2 is -ve charged

Presence of unsaturation on β carbon in primary alkyl halide increases rate of S_N2 , that's why allyl halide and benzyl halides are good substrate for S_N2

As transition state is negatively charged so presence of electron withdrawing group or negative charge stabilising factors increases the rate of S_N2 reaction.

Preparation of Alkyl Halide

By alcohols

C^+

S_N1 Path

$$R-CH_2-OH \xrightarrow[\substack{ZnCl_2 \\ \text{Lewis Acid}}]{H-Cl} RCH_2-Cl$$

Reactivity order for alcohol

Reactivity ∝ stability of intermediate carbocation

so reactivity order is

Tertiary alc. > Secondary alcohol > Pri. alc.

Note

$HCl + ZnCl_2$ is called as Lucas reagent, alcohol gives turbidity with Lucas reagent.

By the action of Phosphorus Halides (S_N2 Path)

$R-OH + PCl_5 \rightarrow R-Cl + POCl_3 + HCl$ inversion

PCl_5

PCl_3

By reaction with Thionyl Chloride - (Darzens Reaction)

$R-OH + SOCl_2 \longrightarrow R-Cl + SO_2\uparrow + HCl\uparrow$

~~Product~~

S_N2 Path and inversion with pyridine

S_Ni mechanism and retention for alcohols in absence of pyridine

The side products are gaseous, which escape from the reaction mixture and hence giving very good yield.

By halide exchange

Finkelstein reaction

$$R-Cl \text{ or } R-Br + KI \xrightarrow[S_N2 \text{ Path}]{\text{Dry Acetone}} R-I + KCl \text{ or } KBr$$

Swarts Reaction

✓✓✓✓✓ Imp

$$2CH_3Cl + HgF_2 \xrightarrow[S_N2 \text{ Path}]{} 2CH_3-F + HgCl_2$$

Sandmeyer's Reaction

Aryl Halides

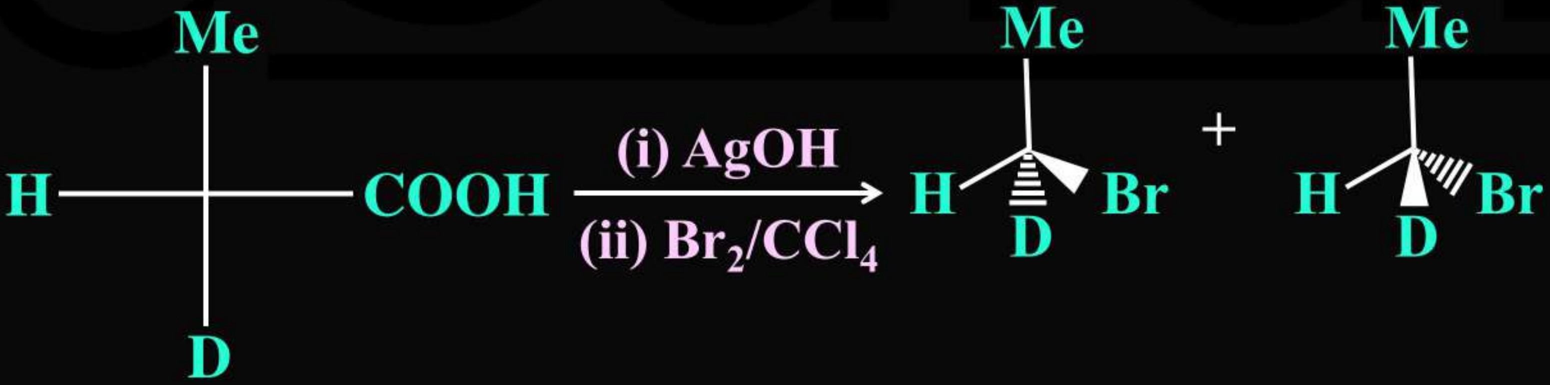
Borodine Hunsdiecker Reaction

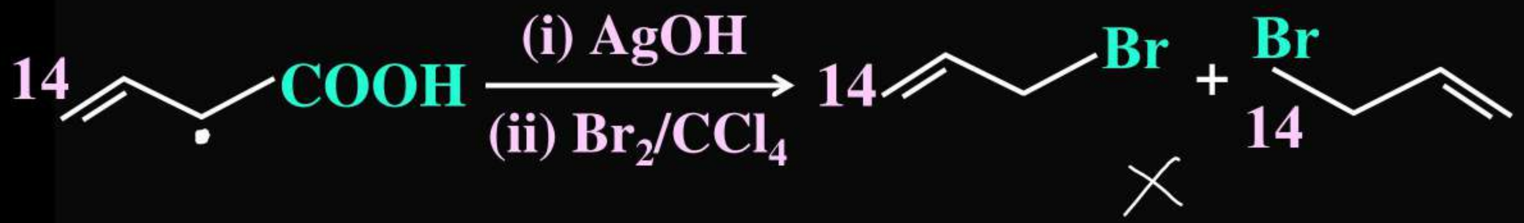
(±) Racemic Mixture
↓
planar intermediate

$R-\overline{C}-OOAg + Br_2 \xrightarrow{CCl_4} R-Br + CO_2 + AgBr$

(i) Radical intermediate is involved. → planar intermediate

(ii) Degradation (Carbon length reduces) reaction.



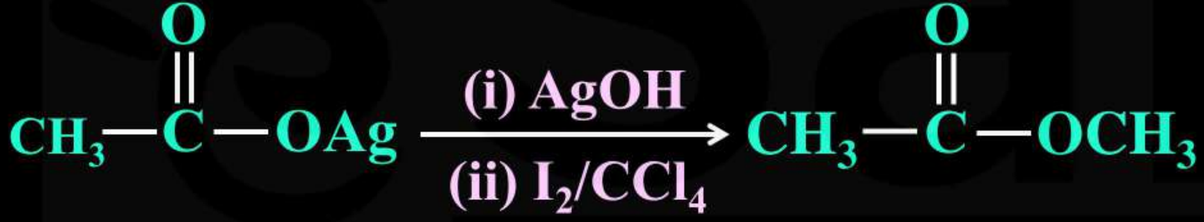


no of products

1

If I_2 is taken instead of Br_2 ester is formed.

It is called **Birnbaum Simonini** reaction.



$$CH_3-\overset{O}{\overset{\|}{C}}-OAg \xrightarrow[\text{(ii) } I_2/CCl_4]{\text{(i) AgOH}} CH_3-\overset{O}{\overset{\|}{C}}-OCH_3$$

Elimination Reaction

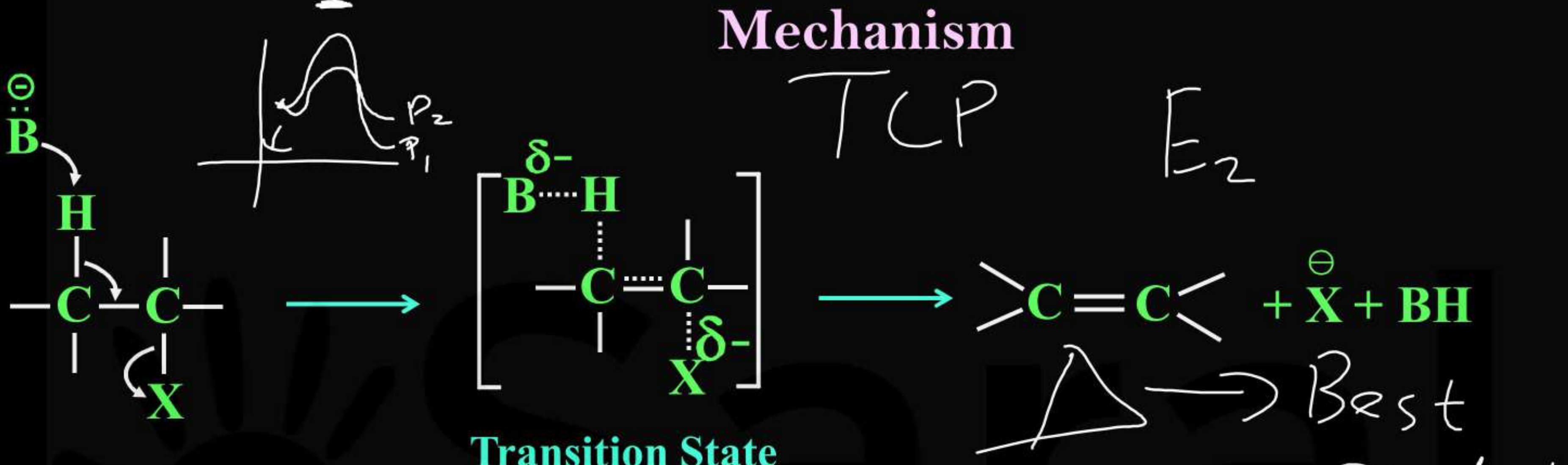
E2	**E1**	**E1cB**	**E_i**
Elimination Reaction With molecularity = 2	Unimolecular Elimination Reaction	Elimination Conjugate Base Reaction	Elimination Internal Reaction

Bimolecular Elimination Reaction (E2)

Dehydrohalogenation is the elimination of a hydrogen and a halogen from an alkyl halide to form an alkene.

$$CH_3CH_2Cl \xrightarrow[\Delta]{\text{Alc. KOH}} CH_3 = CH_2$$

Mechanism



Transition State

(i) This is a single step, bimolecular reaction

Rate = k [R – X] [B^-]

Reactivity order for alkyl group towards E2 reaction is given as
Tertiary > secondary > primary

Chlorocyclooctane

No of products
②

2 products
cis and trans

Stereo Chemistry of E2 reactions

E2 reaction is an example of anti-elimination in which both H and leaving group are anti to each other.

Unimolecular Elimination Reaction (E1)

Proton and leaving group depart in two different step.

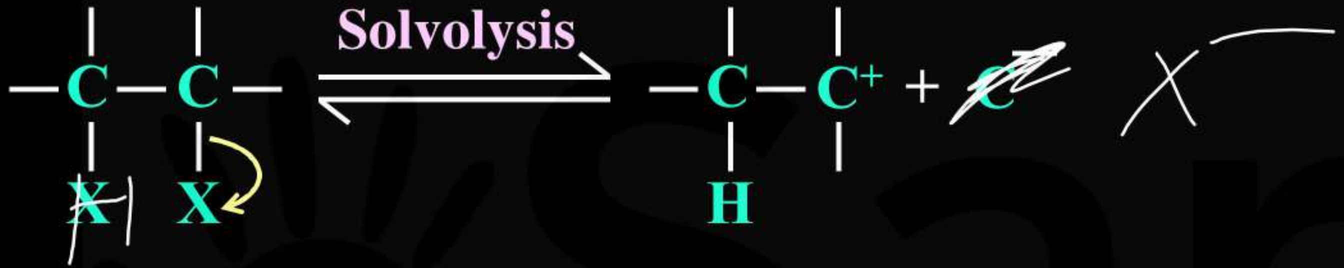
First step - Slow step involves ionisation to form carbocation

Second step - Abstraction of proton

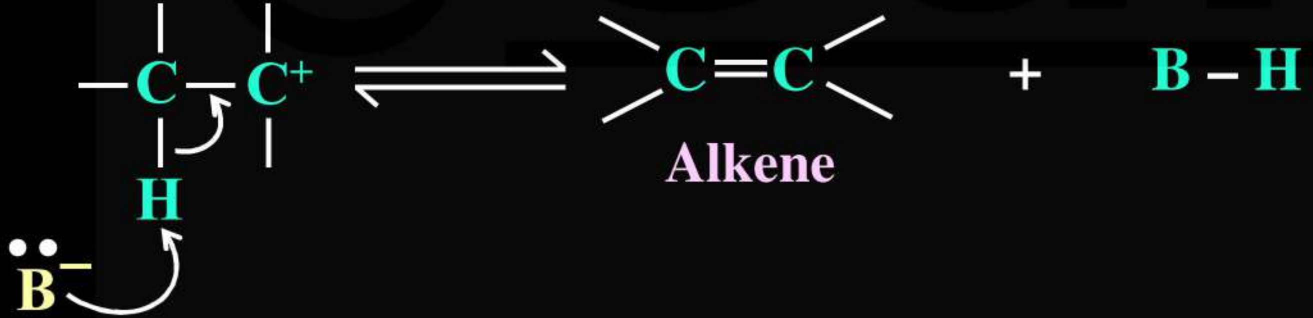
Mechanism

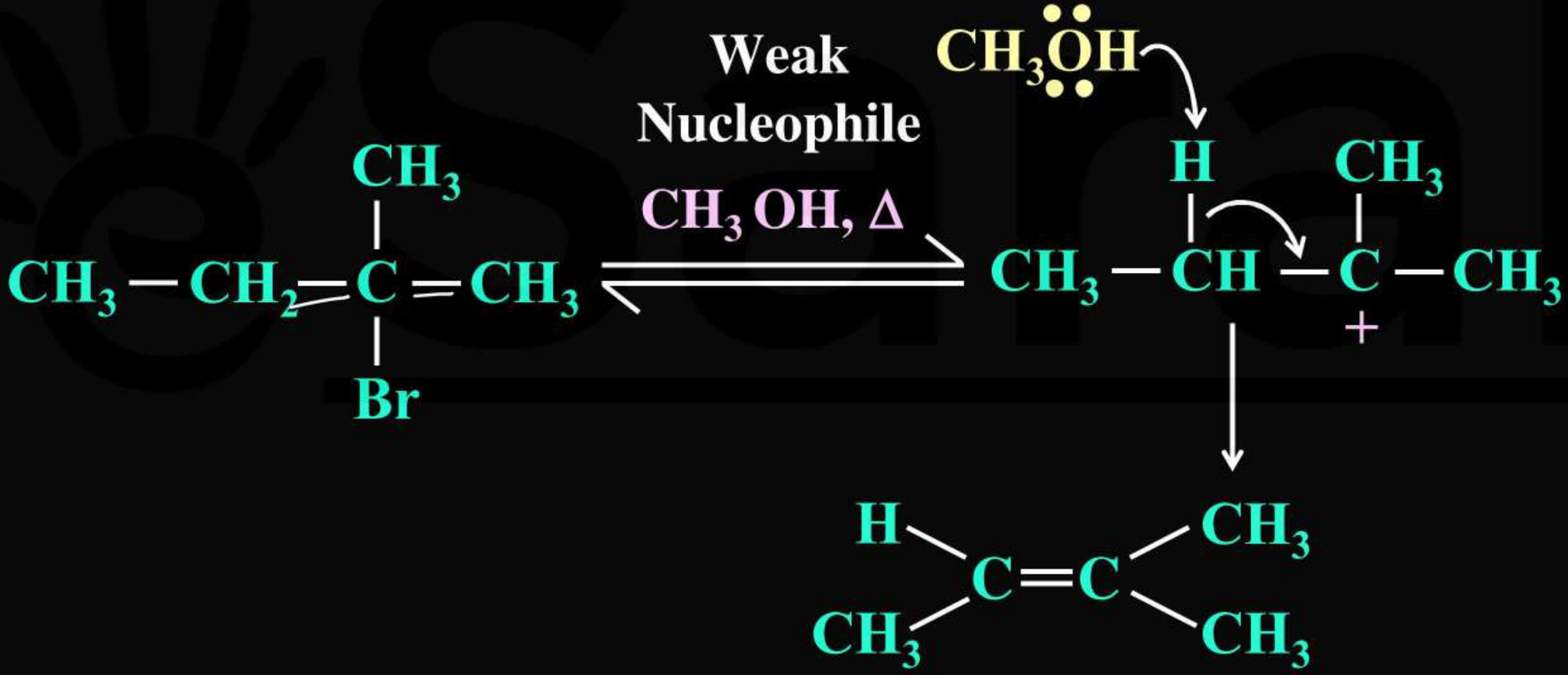
C^+ intermediate → rearrangement

Step 1



Step 2




Weak
Nucleophile
CH₃ OH, Δ
CH₃
CH₃ — CH₂ — C — CH₃
Br
CH₃ÖH
H
CH₃
CH₃ — CH — C — CH₃
+
H
CH₃
C = C
CH₃
CH₃

(1) Characteristics of E1 Reaction

(A) It is unimolecular, two step process.

(B) It is a first order reaction.

$$\text{Rate} \propto [\text{Alkylhalide}]^1$$
$$\text{Rate} = k\,[\text{Alkylhalide}]^1$$

(C) Reaction intermediate is carbocation, so rearrangment is possible.

(D) In the second step, a base abstracts a proton from the carbon atom adjacent to the carbocation, and forms alkene.

3.Elimination Internal (Ei) Or Pyrolytic Syn-elimination

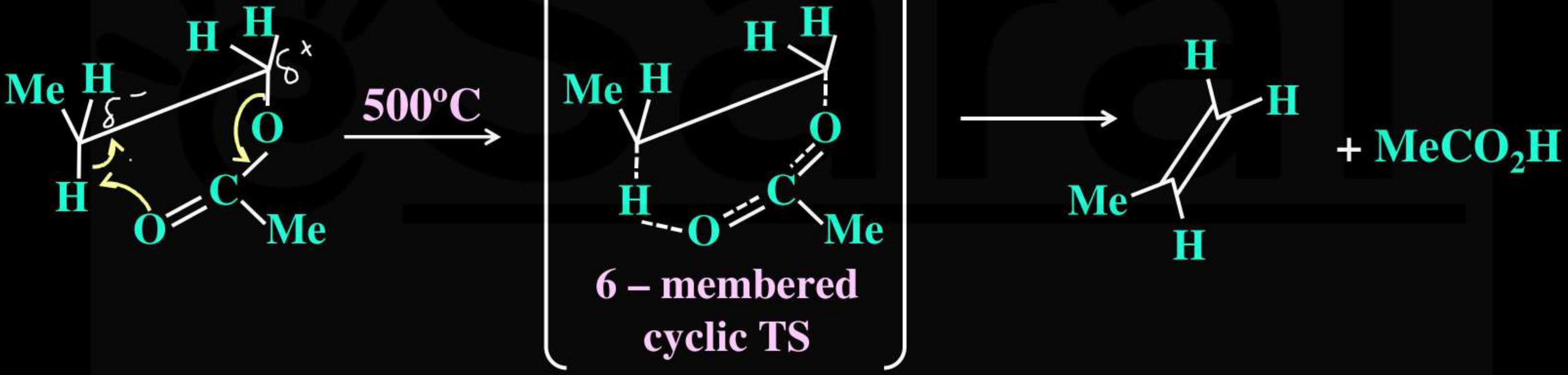
These elimination reaction occur through formation of cyclic transition state involving only one molecule of substrate.

(1) Pyrolysis of Esters (E_i)

उष्मा

6 MCTS

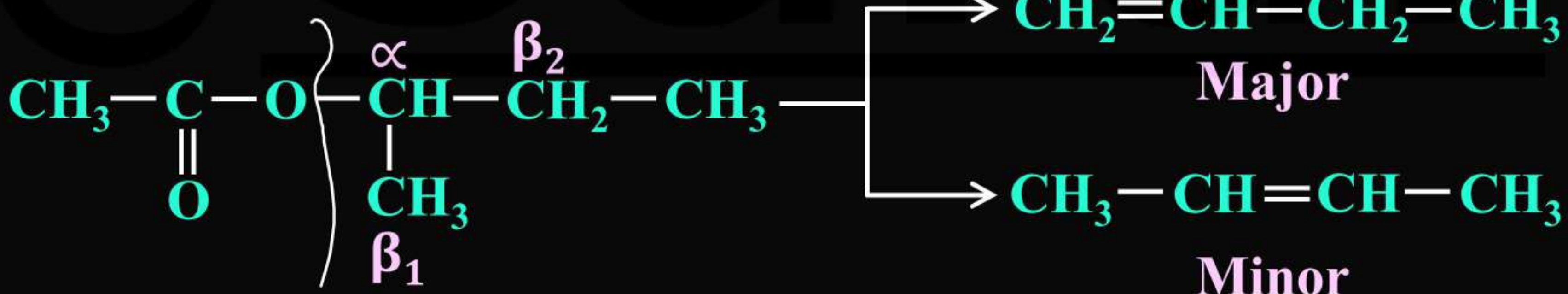
5 MCTS



500°C

6 – membered cyclic TS

+ $MeCO_2H$



$$CH_3-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{\underset{\beta_1}{CH_3}}{|}}{\overset{\alpha}{CH}}-\overset{\beta_2}{CH_2}-CH_3 \longrightarrow \begin{cases} CH_2{=}CH-CH_2-CH_3 \\ CH_3-CH{=}CH-CH_3 \end{cases}$$

Less hindered

major

4. Unimolecular Conjugate Base Reaction (E1cB Reaction)

नाकटे LG

In the E1cB H leaves first and then the X(when X is a poor leaving group). This is a two step process, the intermediate is a carbanion.

For E1cB

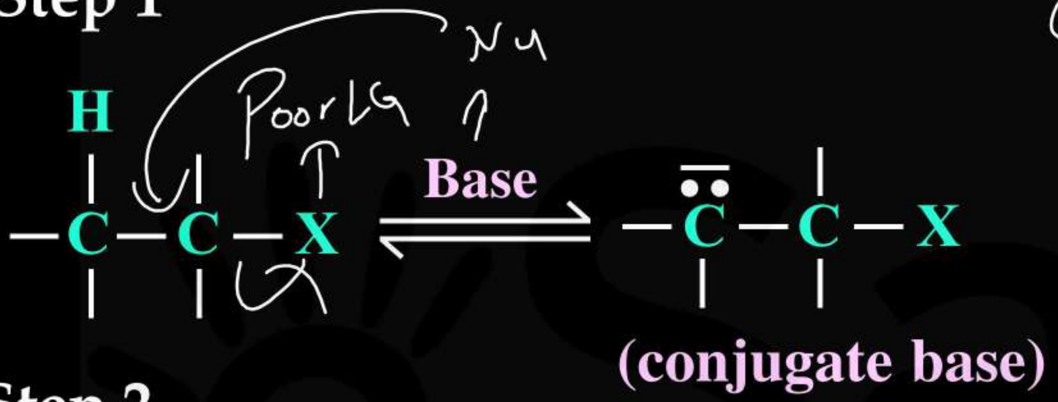
(i) Substrate must be containing acidic hydrogens

(ii) Poor leaving groups(For example F and NR_3.)

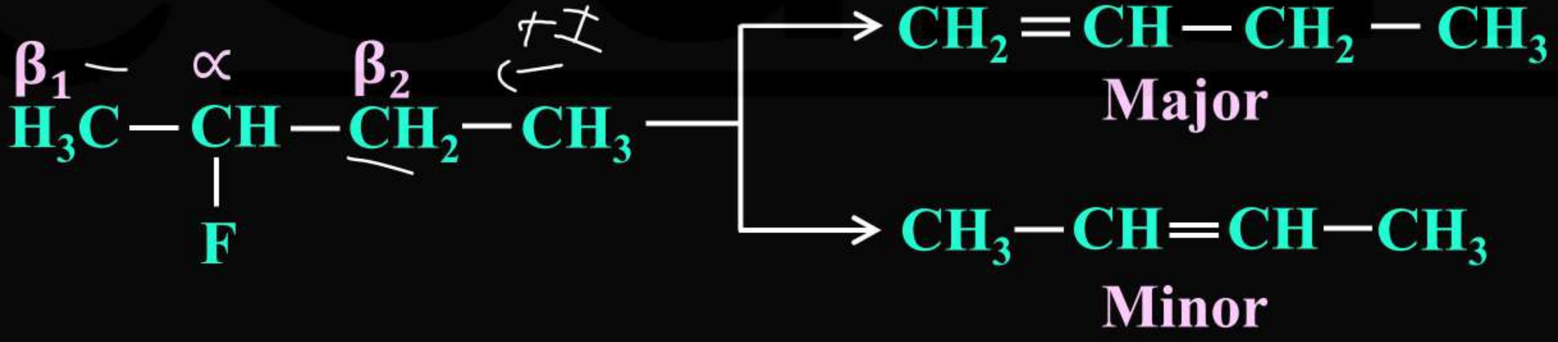
Mechanism

Step 1

C^{-} intermediate

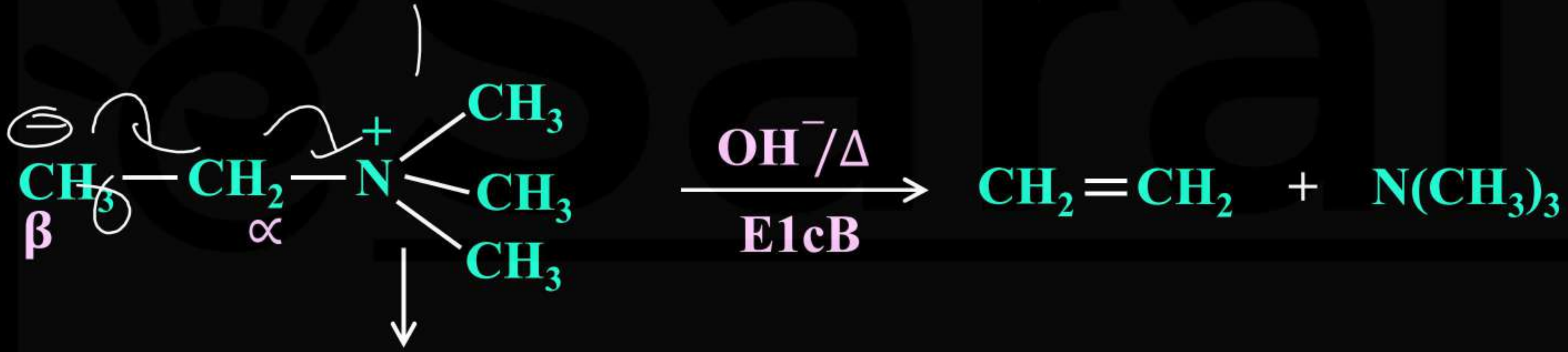


Step 2



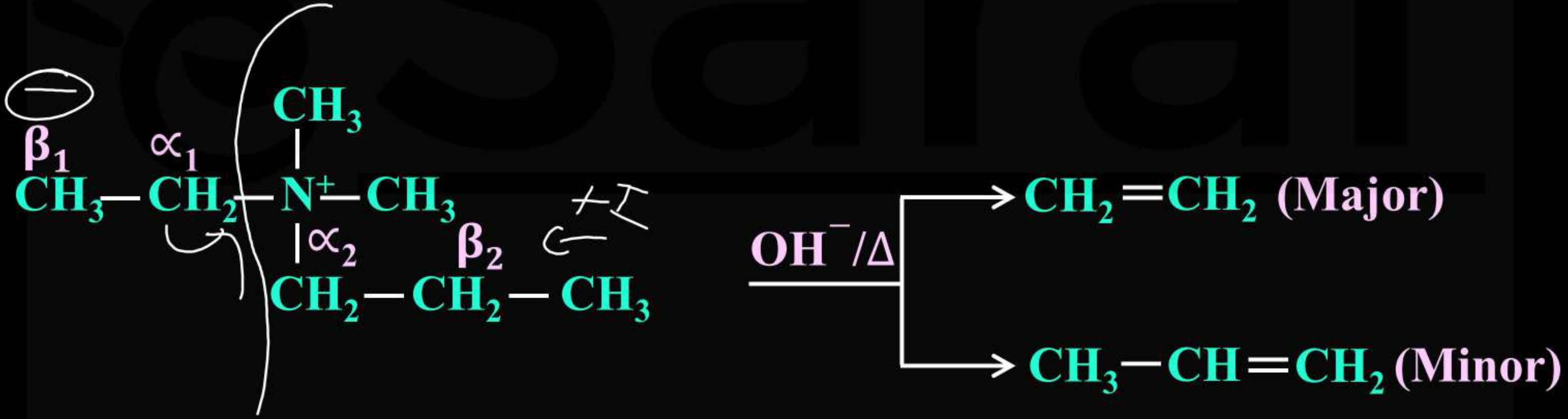
$$H_3C-\underset{F}{CH}-CH_2-CH_3 \rightarrow CH_2=CH-CH_2-CH_3 \text{ (Major)} + CH_3-CH=CH-CH_3 \text{ (Minor)}$$

Pyrolysis of Tetra Alkyl Ammonium Hydroxide (Application of E1cB)



$$\overset{\beta}{CH_3}-\overset{\alpha}{CH_2}-\overset{+}{N}(CH_3)_3 \xrightarrow[\text{E1cB}]{OH^-/\Delta} CH_2=CH_2 + N(CH_3)_3$$

Poor leaving group



$$\overset{\beta_1}{CH_3}-\overset{\alpha_1}{CH_2}-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_2-\overset{\beta_2}{CH_2}-CH_3}{|\,\alpha_2}}{N^+}}-CH_3$$

$$\xrightarrow{OH^-/\Delta}\ CH_2=CH_2\ \textbf{(Major)}$$

$$\xrightarrow{OH^-/\Delta}\ CH_3-CH=CH_2\ \textbf{(Minor)}$$

Sabse Imp Table

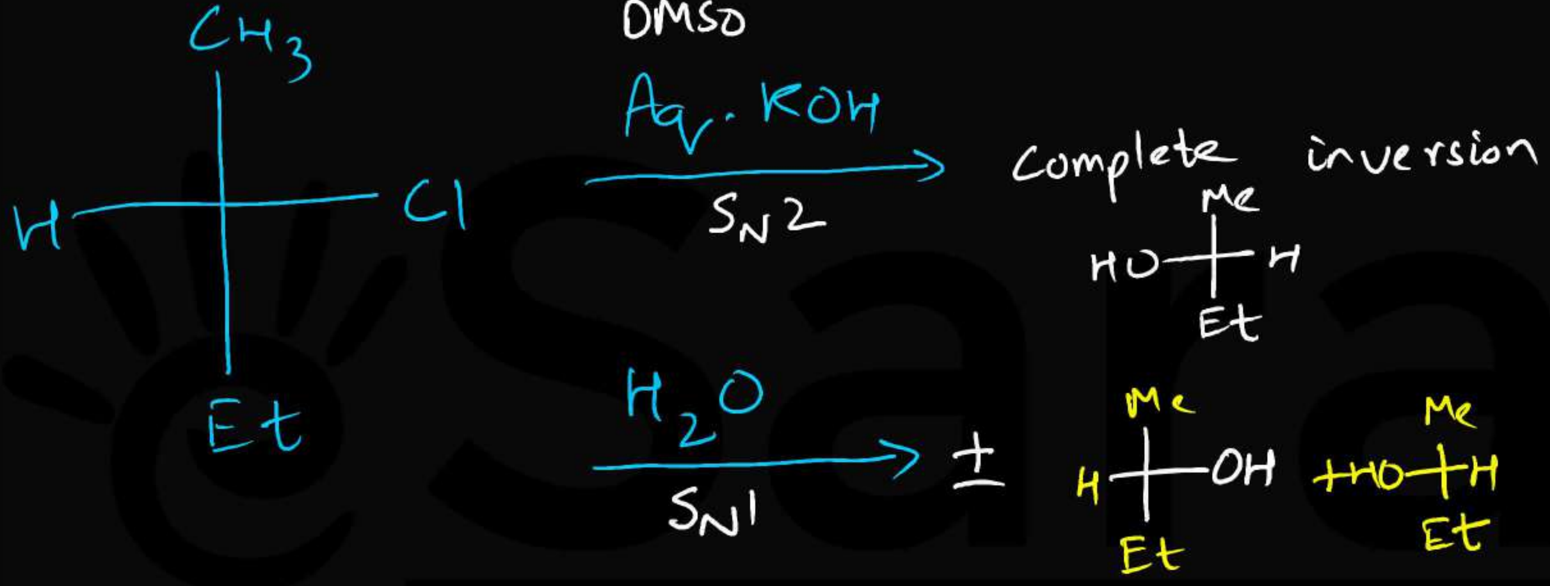
Elimination ↑ strong Base

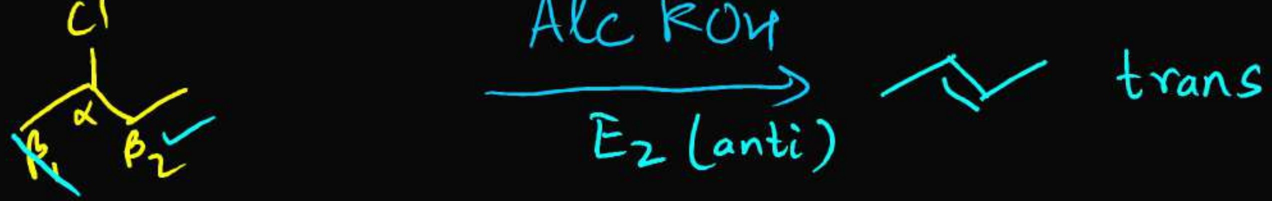
Strong Nu/Base

Weak nucleophile ↑

Substrate	Alc. KOH	Aq. KOH	H_2O
1° halide	$S_N < E$	$S_N2 > E$	×
2° halide	$S_N < E$	$S_N2 \geq E_2$	$S_N1 > E$
3° halide	$S_N < E$	$S_N1 < E_1$	$S_N1 > E$

2° halide

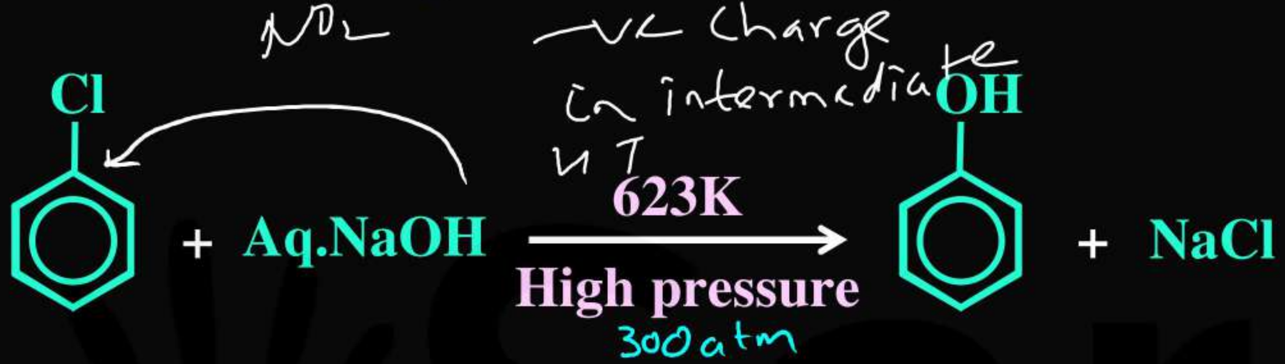

CH3
H
Cl
Et
DMSO
Aq. KOH
SN2
complete inversion
Me
HO
H
Et
H2O
SN1
±
Me
H
OH
Et
Me
HO
H
Et


Cl
α
β1
β2
Alc KOH
E2 (anti)
trans

Chemical Properties of Aryl Halides

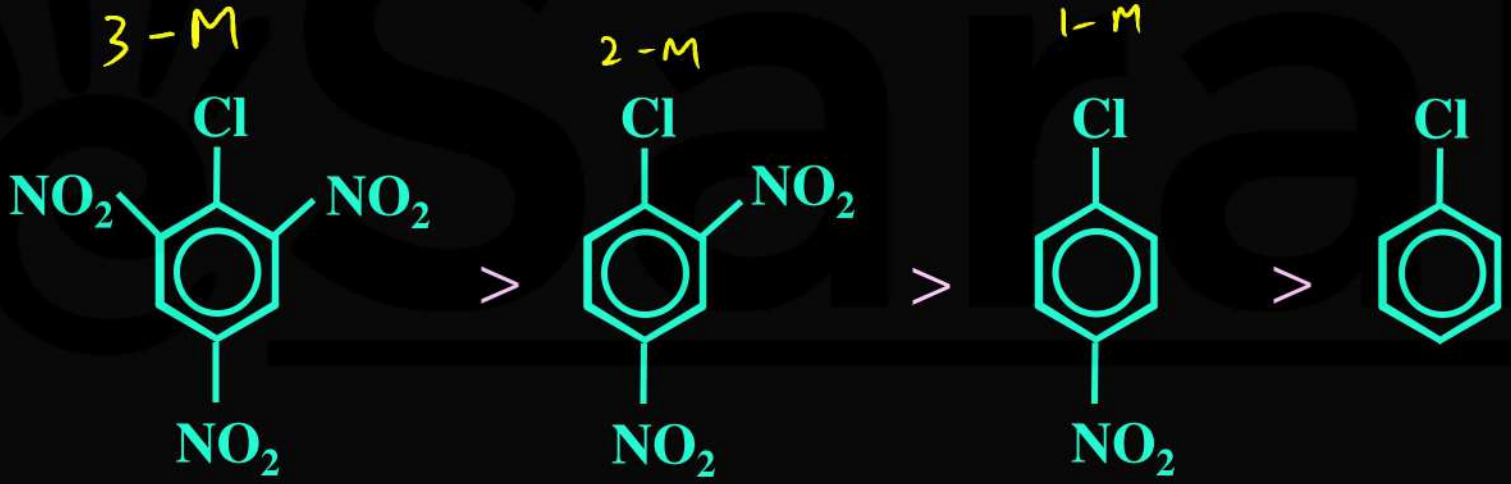
VVV Imp

(1)



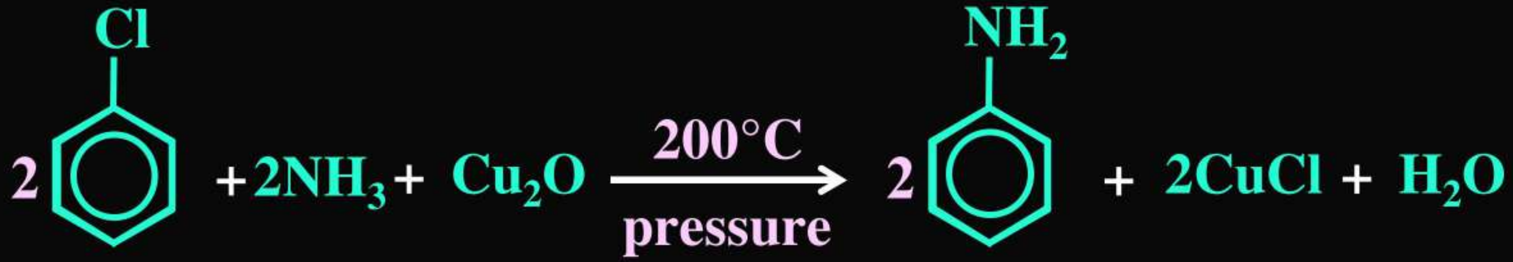
Presence of deactivating group in ortho and para position makes the nucleophilic substitution easier.

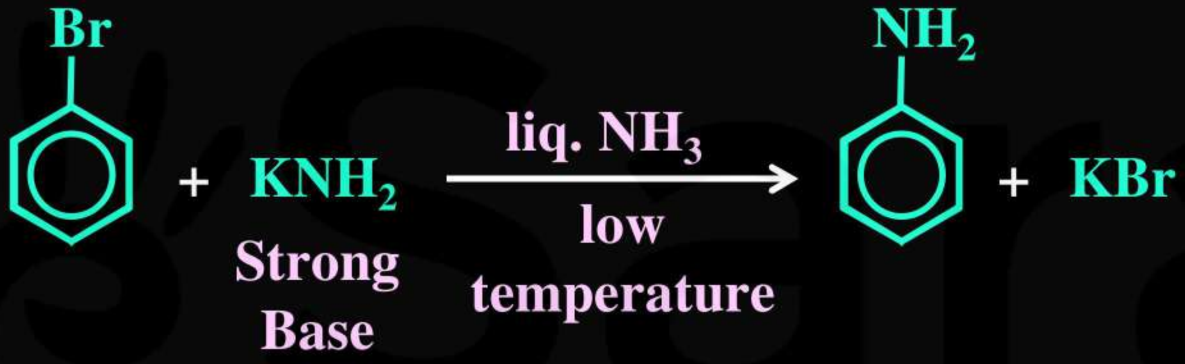
Reactivity Order (Towards Nucleophilic Substitution)

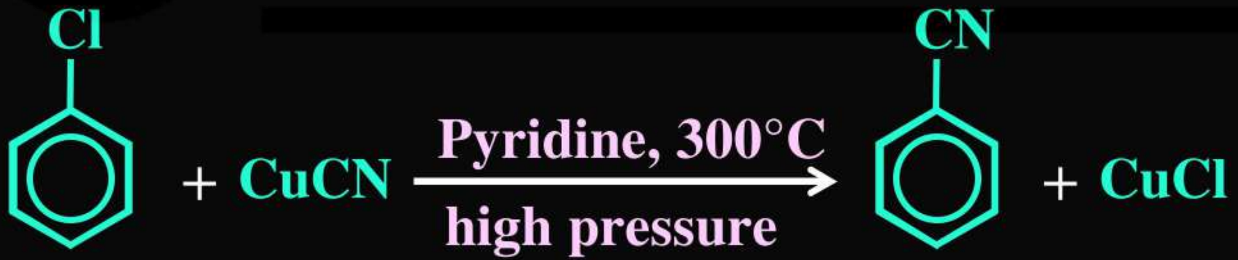


Warm   368 K   443 K   623 K

(2)

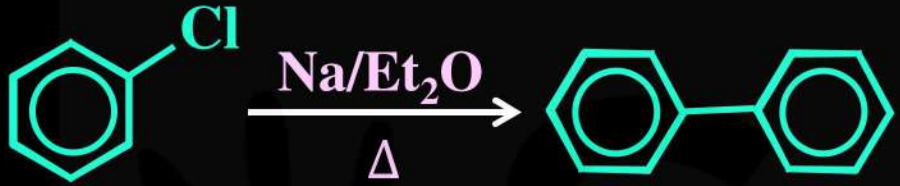

Cl
2
+ 2NH3 + Cu2O
200°C
pressure
NH2
2
+ 2CuCl + H2O


Br
+ KNH2
Strong
Base
liq. NH3
low
temperature
NH2
+ KBr


Cl
+ CuCN
Pyridine, 300°C
high pressure
CN
+ CuCl

Fitting Reaction (Aryl Halide)

Ar – Ar



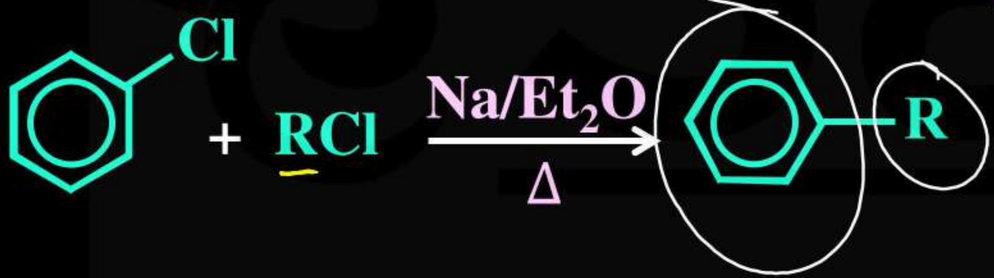
Biphenyl

Wurtz-Fitting Reaction(Alkyl-Aryl)

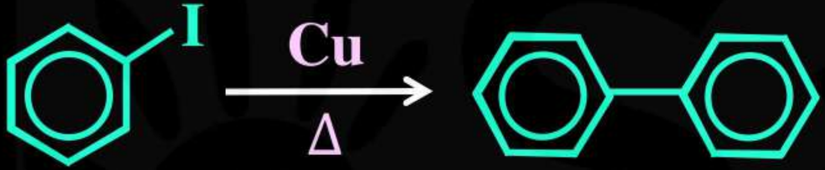
$R-X + R-X \xrightarrow[Et_2O]{Na}$ Wurtz $R-R$

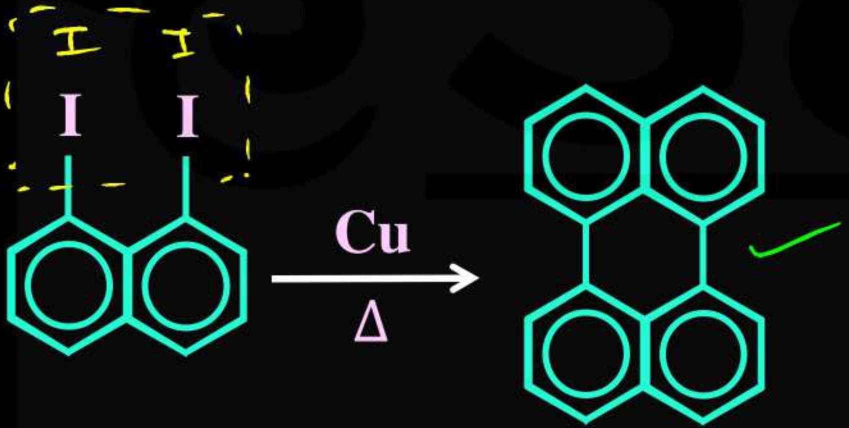
$Ph-X + Ph-X \xrightarrow[Et_2O]{Na}$ Fittig $Ar-Ar$

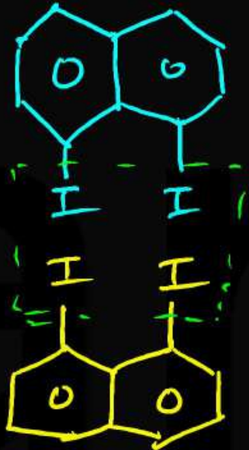
$Ph-X + R-X \xrightarrow[Et_2O]{Na}$ Wurtz-Fittig $R-Ar$



Ullmann Reaction







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Abhinav Baranwal


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Shivam Anand


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Upadhyay Meet


99.10 %ile
Sharnam Kansal


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Divyam


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Kanishk Singh

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