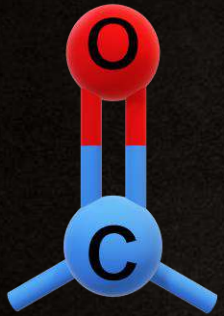
Welcome to

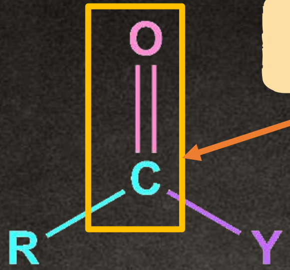
Aakash + BYJU'S LIVE

Aldehydes, Ketones and Carboxylic Acids

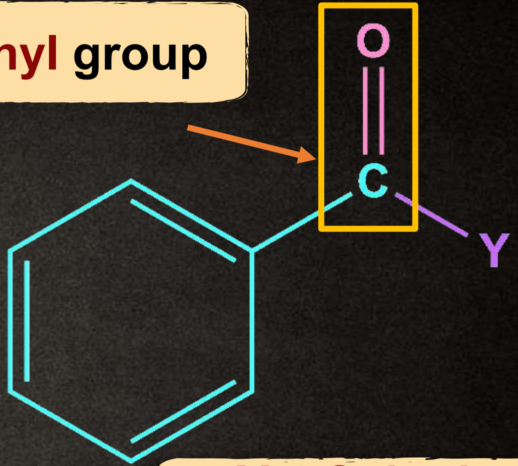
Carbonyl Compounds

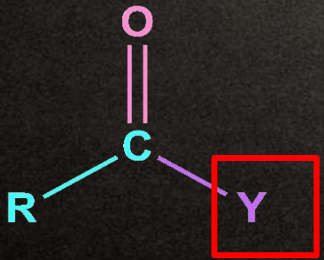


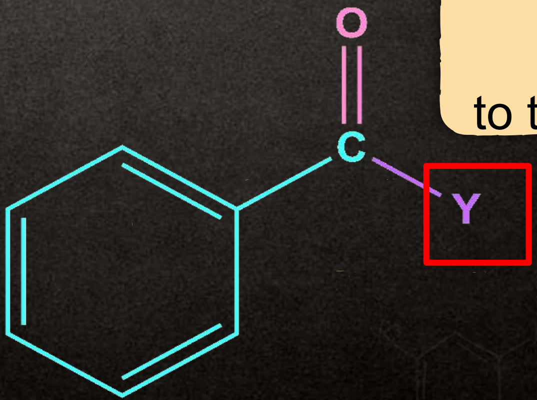
A carbonyl group



A carbonyl group







Y = Substituents
attached
to the **carbonyl group**

Classification of Carbonyl Compounds

Based on the **type of ‘Y’, carbonyl compounds** are classified as

Class I

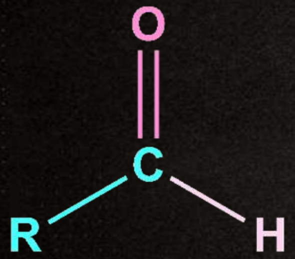
Carbonyl compounds with groups that **cannot be replaced** by a **nucleophile**

Class II

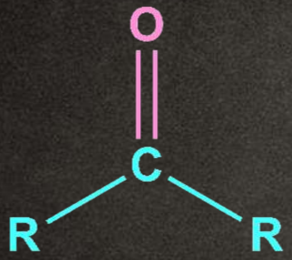
Carbonyl compounds with groups that **can be replaced** by a **nucleophile**

Carbonyl Compounds: Class I and Class II

Class I

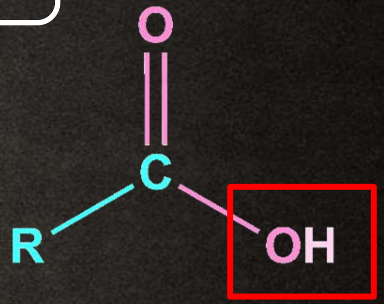


Aldehyde



Ketone

Class II

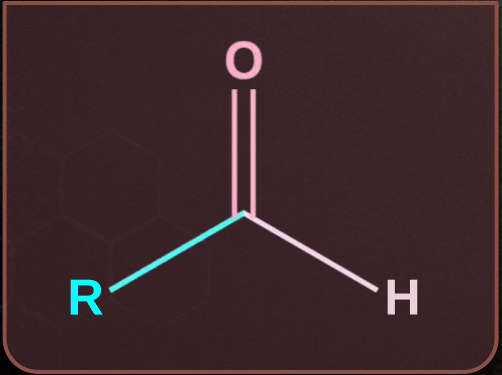


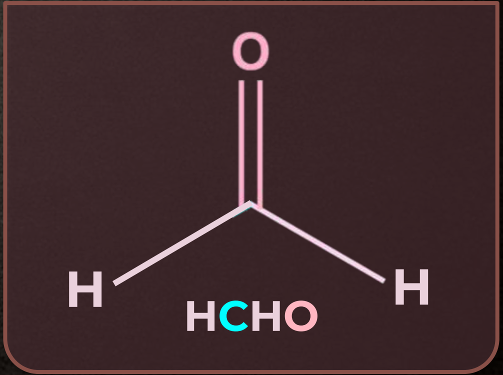
Carboxylic acid

Carbonyl Compounds

Aldehydes have a carbonyl group bonded to a **carbon** atom on one side and a **hydrogen** atom on the other side

Formaldehyde is an **exception** because it has hydrogen atoms on both sides.

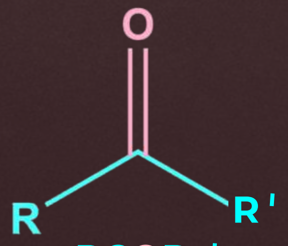




HCHO

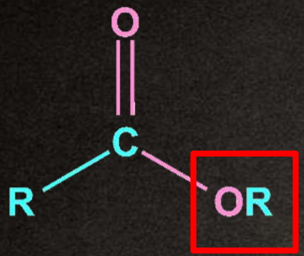
Carbonyl Compounds

Ketones have a carbonyl group bonded to carbon atoms on **both sides.**

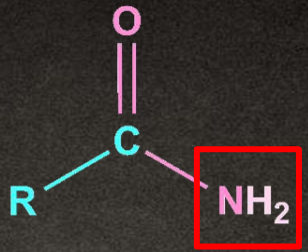


RCOR '

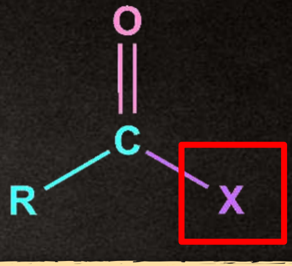
Carboxylic Acid and Its Derivatives



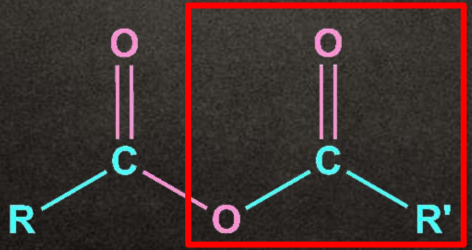
Ester



Amide



Acid halide



Anhydride

Aldehydes and Ketones

- Nomenclature
- Structure
- Preparation
- Properties
- Uses

Nomenclature of Aldehydes and Ketones

Nomenclature

- IUPAC
- Common names

IUPAC Nomenclature of Aldehydes and Ketones

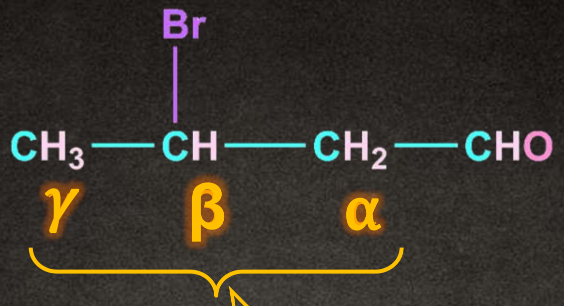
Aldehydes (−CHO)
Prefix: formyl/oxo

Oxo is used as a prefix when ‘C’ of ‘CHO’ is included in the parent chain, or else ‘formyl’ is used.

6-Oxohexanoic acid

Common Names of Aldehydes and Ketones

When common names are used, the position of the substituent is designated by lowercase Greek letters (**alpha, beta, and gamma**). The carbonyl's C is not designated, but the C adjacent to carbonyl's C is **alpha c**, next adjacent to alpha c-**beta c** then next adjacent to beta c-**gamma c**, and so on.



$$\underset{\gamma}{CH_3}-\underset{\beta}{\overset{Br}{\overset{|}{CH}}}-\underset{\alpha}{CH_2}-CHO$$

Position of the substituent

Systematic name

3-Bromobutanal

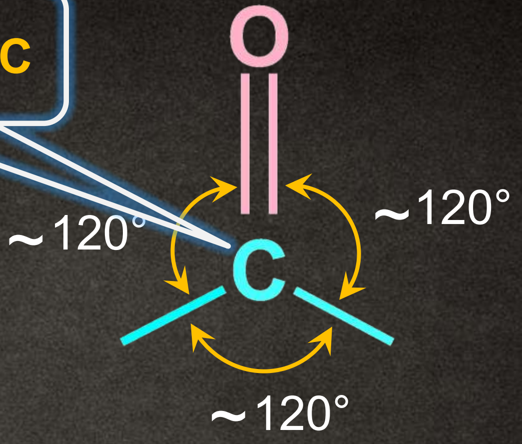
Common name

β-Bromobutyraldehyde

The position of a substituent is designated by a **lowercase Greek letter** when common names are used.

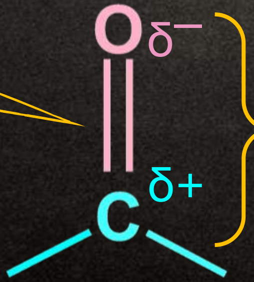
Structure of Carbonyl Compounds

sp^2 hybridised C



Trigonal planar

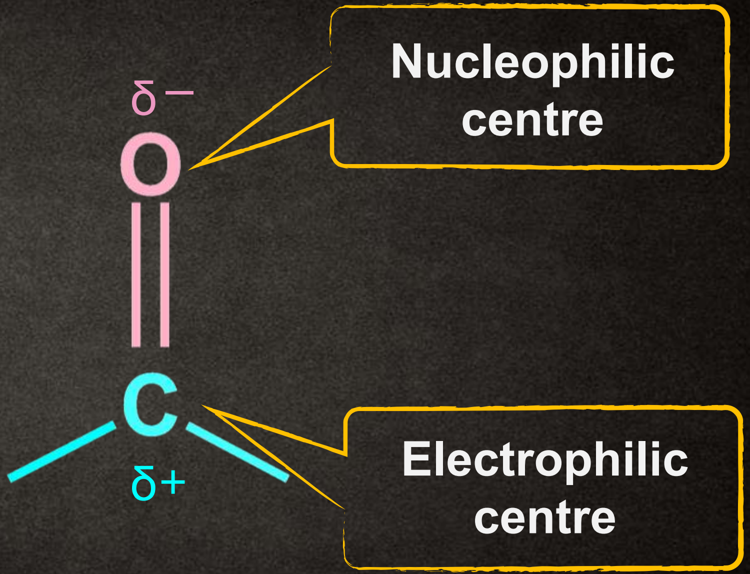
Polarised bond



Electronegativity of **oxygen** > Electronegativity of **carbon**

Structure of Carbonyl Compounds

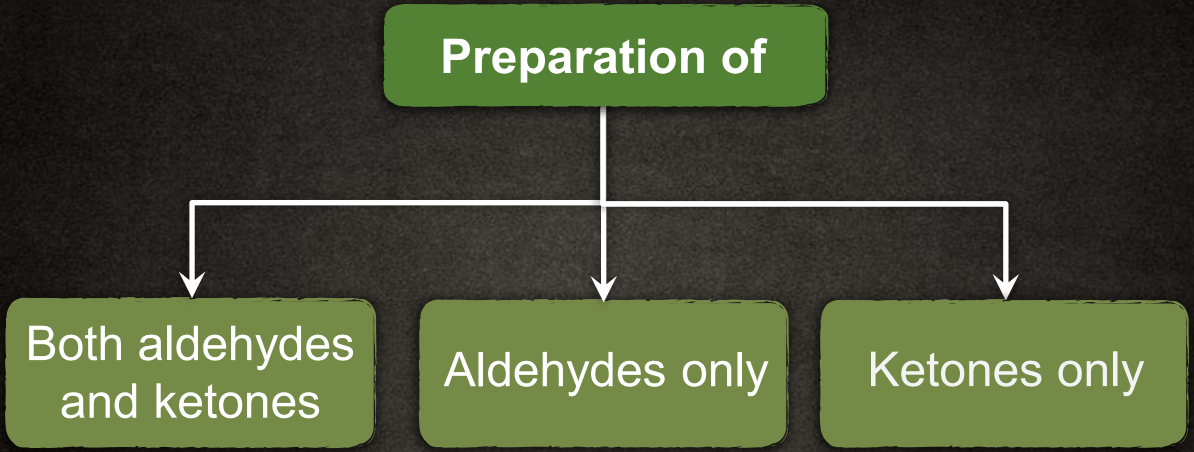
Oxygen acts as **nucleophilic** centre whereas carbon acts as an **electrophilic** centre.



Nucleophilic centre

Electrophilic centre

Preparation of Aldehydes and Ketones



Preparation of

- Both aldehydes and ketones
- Aldehydes only
- Ketones only

Preparation of Aldehydes and Ketones

Preparation via

- Oxidation of alcohols
- Dehydrogenation of alcohols
- Hydrocarbons
  - Ozonolysis
  - Hydration of alkynes
  - Alkaline hydrolysis of gem dihalides

Oxidation of Alcohols

$$\text{Primary alcohol} \xrightarrow{\text{PCC}} \text{Aldehydes}$$

$$\text{Secondary alcohol} \xrightarrow{CrO_3/K_2Cr_2O_7} \text{Ketones}$$

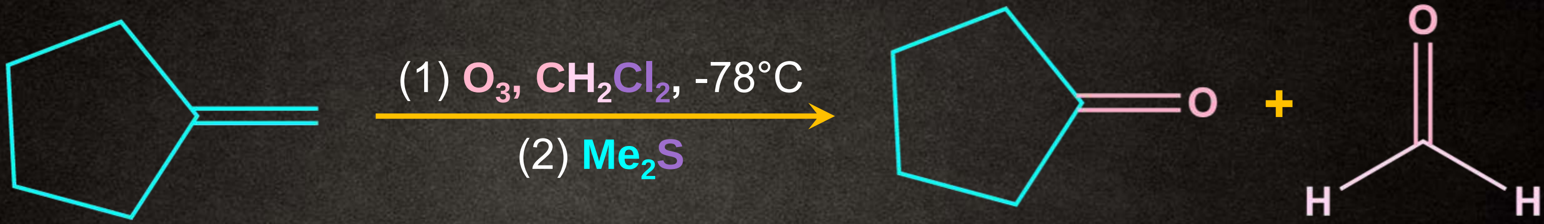
Dehydrogenation of Alcohols

$$\begin{matrix}\text{1° alcohol} \\ (RCH_2OH)\end{matrix} \xrightarrow[-H_2]{Cu/300^\circ C} \begin{matrix}\text{Aldehyde} \\ (R\text{-}CH{=}O)\end{matrix}$$

$$\begin{matrix}\text{2° alcohol} \\ (R_2CHOH)\end{matrix} \xrightarrow[-H_2]{Cu/300^\circ C} \begin{matrix}\text{Ketone} \\ (R_2C{=}O)\end{matrix}$$

$$\text{3° alcohol} \xrightarrow[-H_2O]{Cu/300^\circ C} \begin{matrix}\text{Alkene (Here dehydration} \\ \text{takes place)}\end{matrix}$$

Ozonolysis

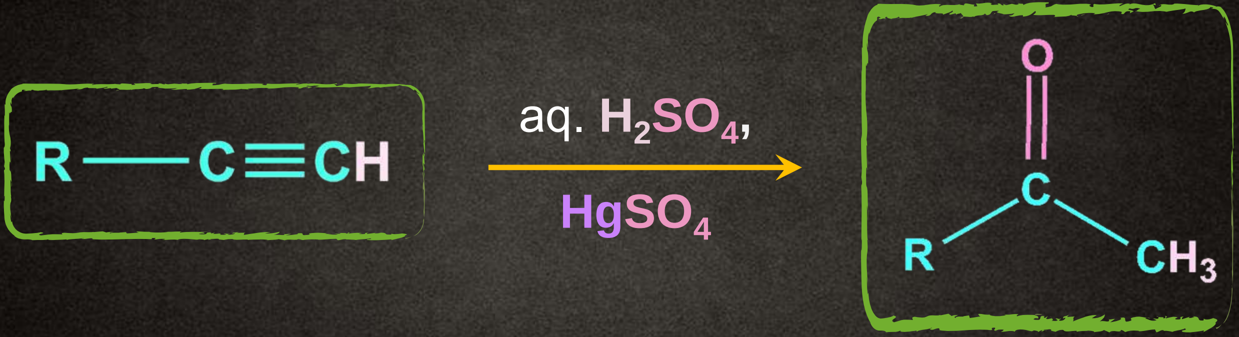


(1) O_3, CH_2Cl_2, -78°C

(2) Me_2S

Kucherov Reaction

General reaction:

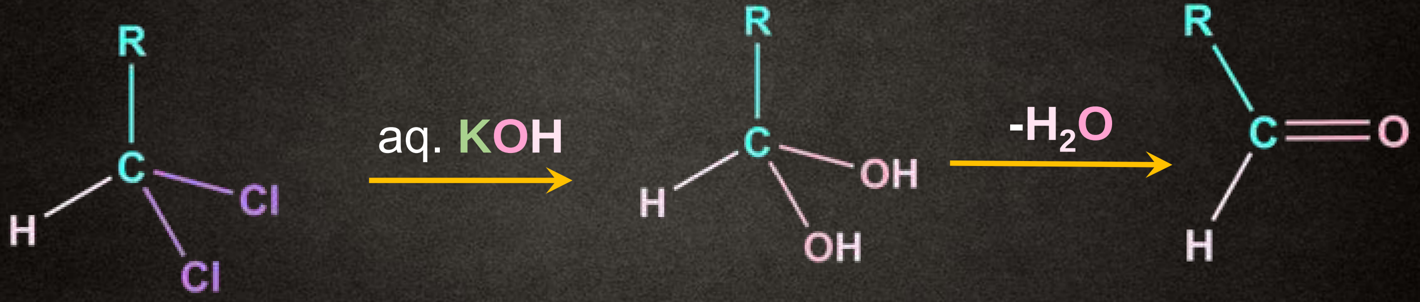


Kucherov reaction

Only **acetylene** produces **aldehyde**, otherwise all **alkynes** produce **ketone.**

Alkaline Hydrolysis of Gem-dihalides

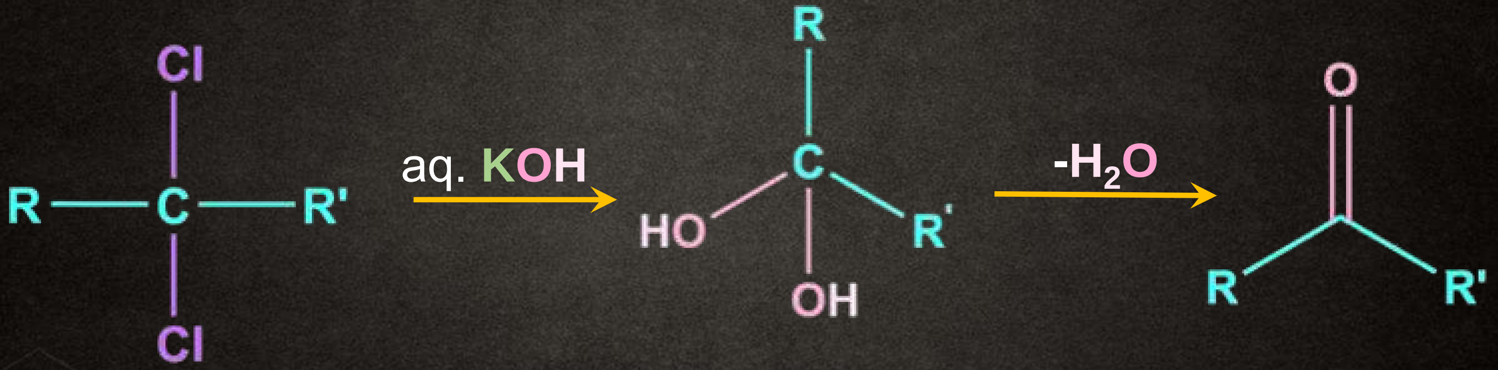
From terminal gem-halides



Terminal gem-dihalides → **Aldehydes**

Alkaline Hydrolysis of Gem-dihalides

From non-terminal gem-halides



Non-terminal gem-dihalides → **Ketones**

Preparation of Aldehydes

Preparation of aldehydes from

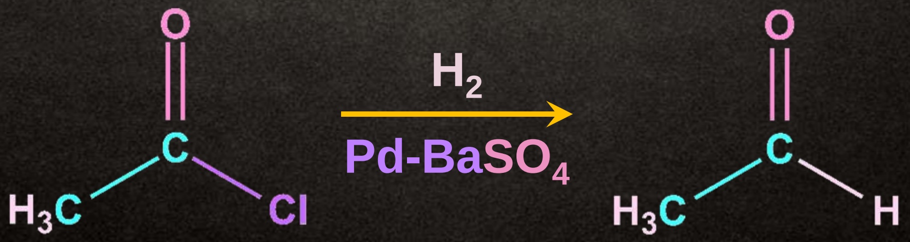
- Acid chloride
- Nitrile and ester
- Hydrocarbons

Rosenmund Reduction

$$\text{Acid chloride} \xrightarrow[\text{Pd-BaSO}_4]{H_2} \text{Aldehyde}$$

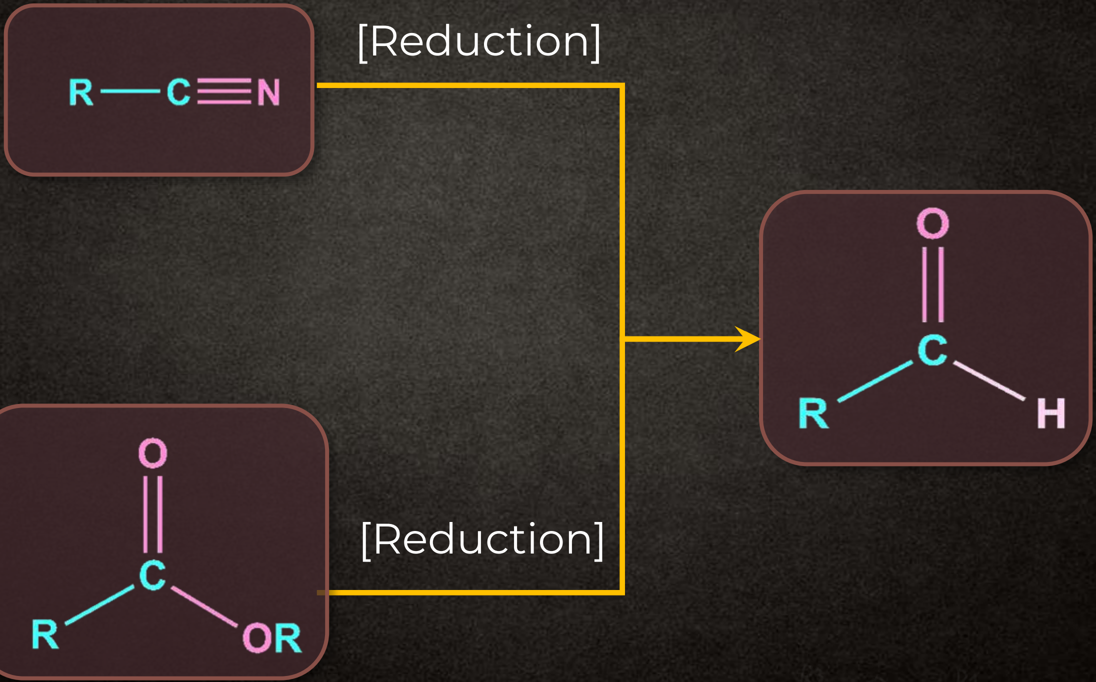
Lindlar’s catalyst

Example:



Preparation of Aldehydes from Nitrile and Ester

General reaction:



[Reduction]

[Reduction]

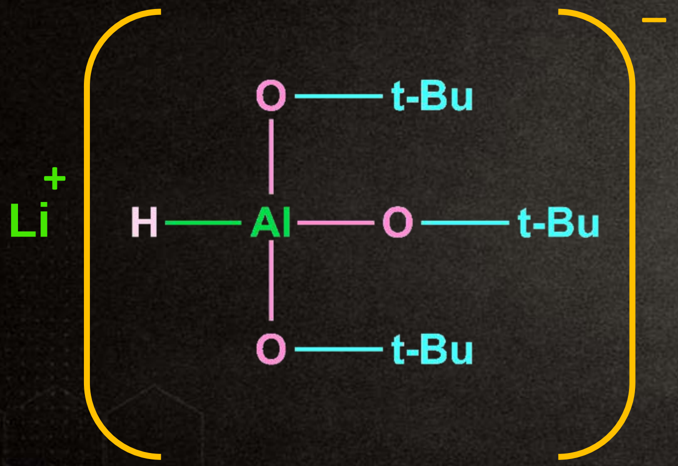
Preparation of Aldehydes

Reduction

- From **derivatives of LiAlH$_4$**
- From **Stephen reaction**

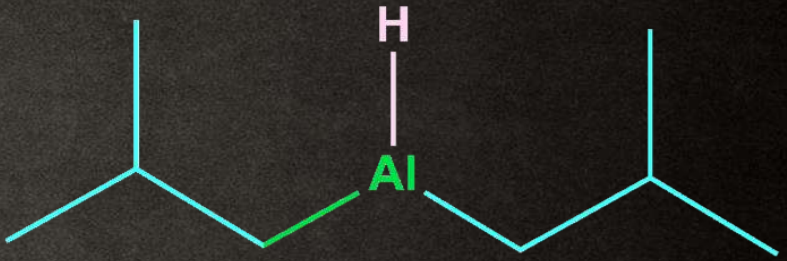
Derivatives of $LiAlH_4$

Derivative 1:



$LiAlH(O\text{-}t\text{-}Bu)_3$

Derivative 2:



DIBAL-H

$AlH(i\text{-}Bu)_2$

In general, **double bonds** are **not reduced** by DIBAL-H.

Preparation of Aldehydes

Example:

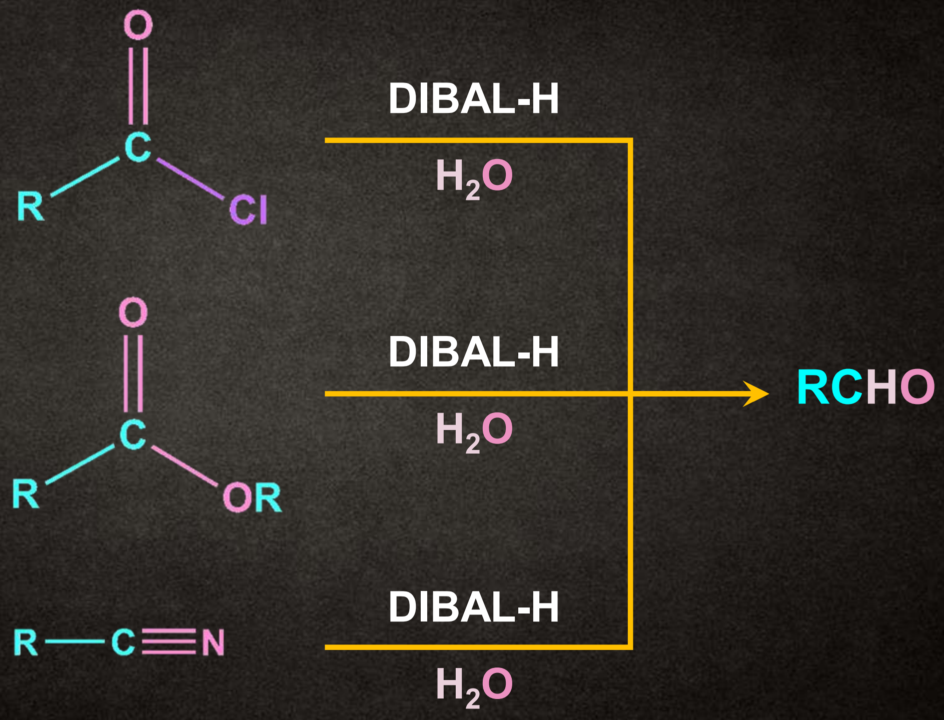
$$RCN \xrightarrow[H_2O]{LiAlH(O\text{-}t\text{-}Bu)_3} RCHO$$

$$\begin{tikzcd} CH_3CH{=}CHCH_2CH_2CN \arrow[d, "LiAlH(O\text{-}t\text{-}Bu)_3"', "H_2O"] \\ CH_3CH{=}CHCH_2CH_2CHO \end{tikzcd}$$

$$RCN \xrightarrow{DIBAL\text{-}H} RCHO$$

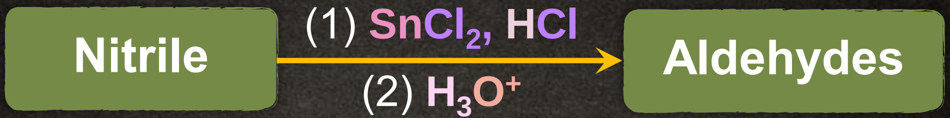
$$\begin{tikzcd} CH_3CH{=}CHCH_2CH_2CN \arrow[d, "DIBAL\text{-}H"] \\ CH_3CH{=}CHCH_2CH_2CHO \end{tikzcd}$$

Preparation of Aldehydes

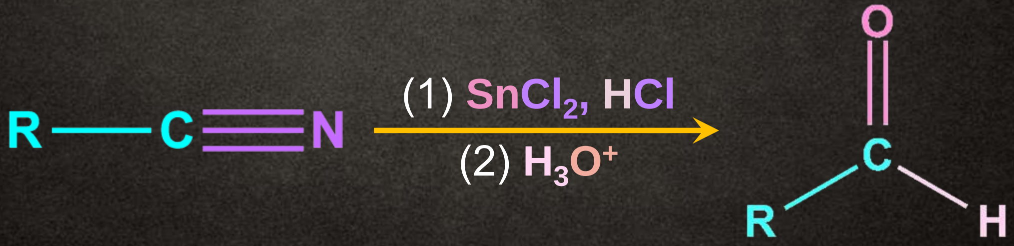


Stephen Reaction

General reaction:



Nitrile $\xrightarrow[\text{(2) } H_3O^+]{\text{(1) } SnCl_2,\ HCl}$ **Aldehydes**



$R-C\equiv N \xrightarrow[\text{(2) } H_3O^+]{\text{(1) } SnCl_2,\ HCl}$ R–CHO

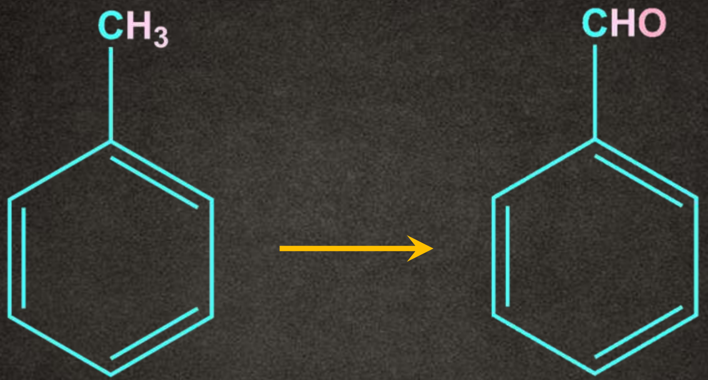
Preparation of Aldehydes

From hydrocarbons

- Oxidation of methyl benzene
  - By chromyl chloride(Etard Reaction)
  - By chromic oxide
- Side chain chlorination of methyl benzene
- Gattermann–Koch reaction

Etard Reaction

Reaction:

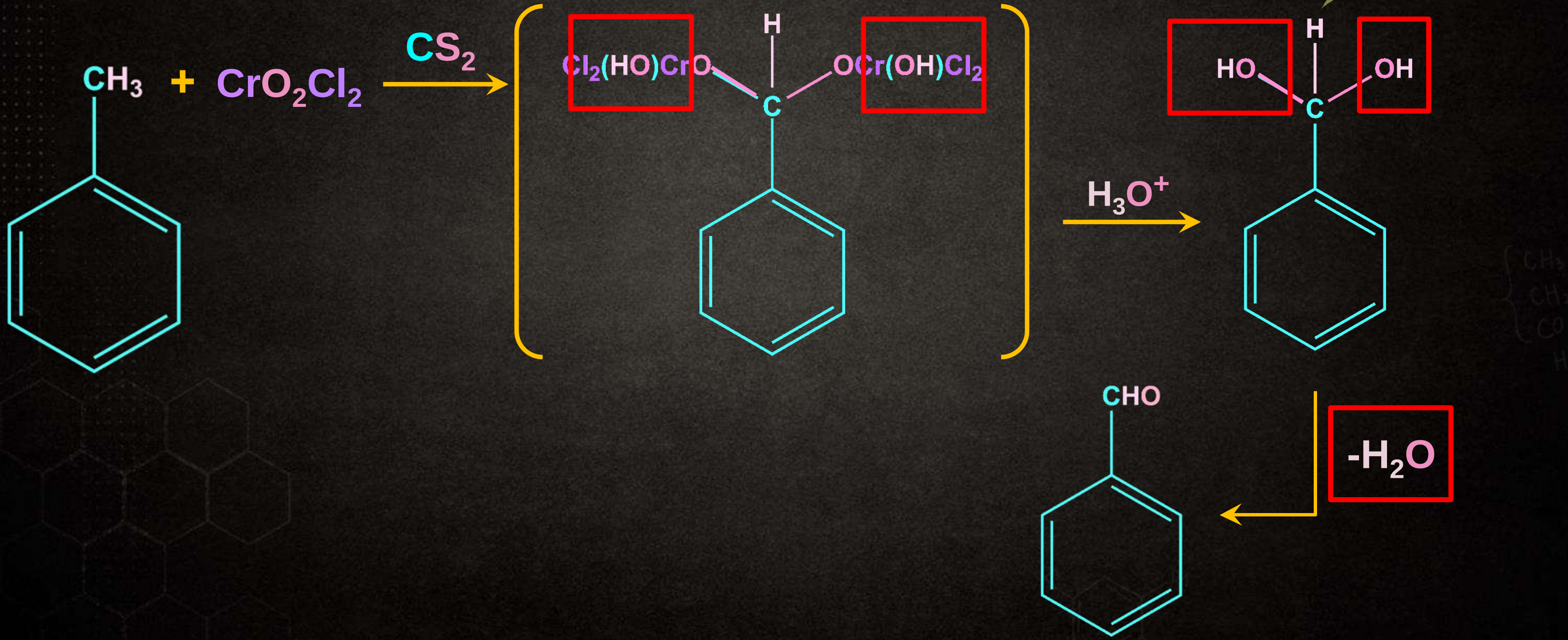


Reagents used

CrO_2Cl_2, CS_2, H_3O^+

Etard Reaction

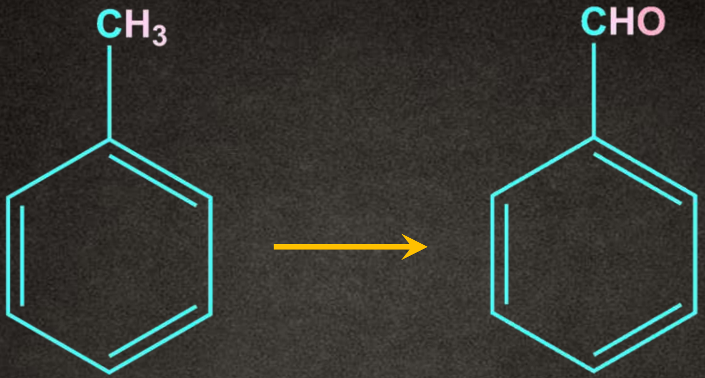
Reaction:



Unstable

Oxidation of Toluene by Chromic Oxide

Reaction:



Reagents used

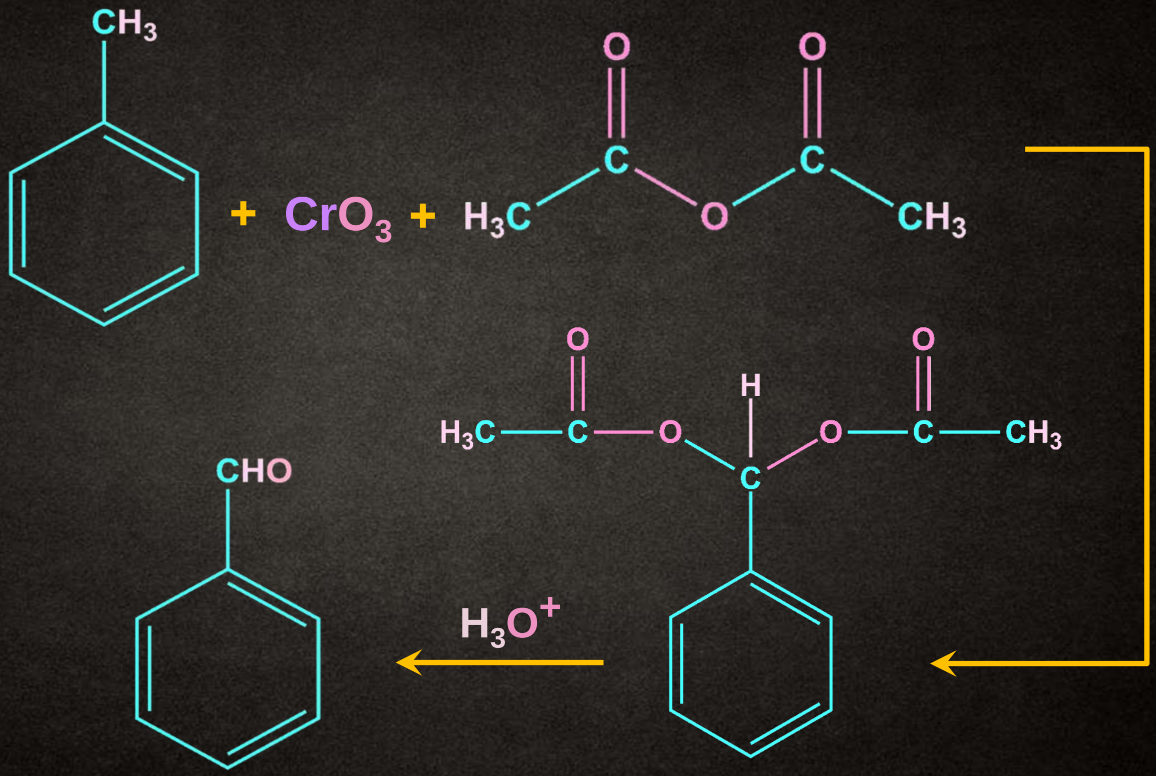
1) CrO_3, $(CH_3CO)_2O$

At 273–283 K

2) H_3O^+, Δ

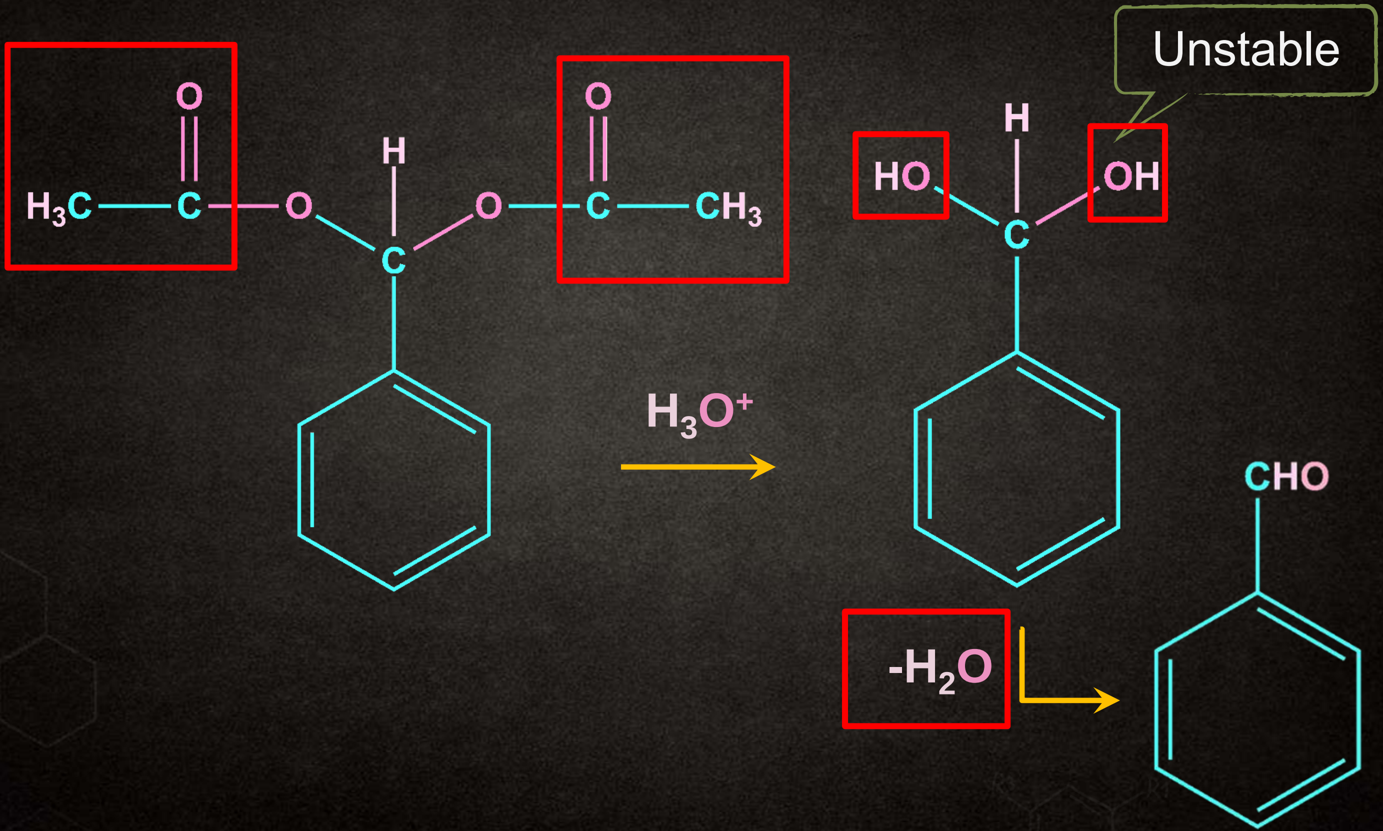
Oxidation of Toluene by Chromic Oxide

Reaction:



Benzaldehyde

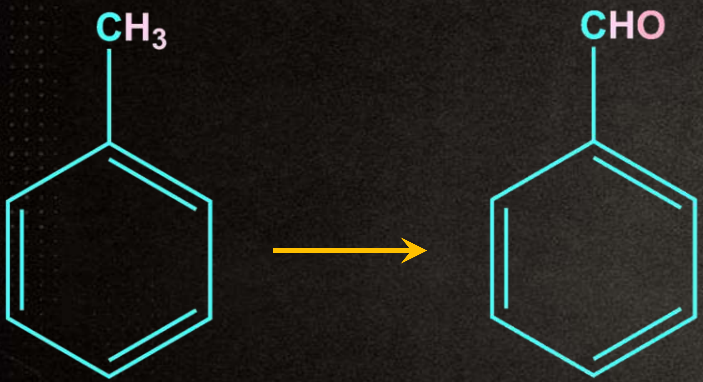
Oxidation of Toluene by Chromic Oxide

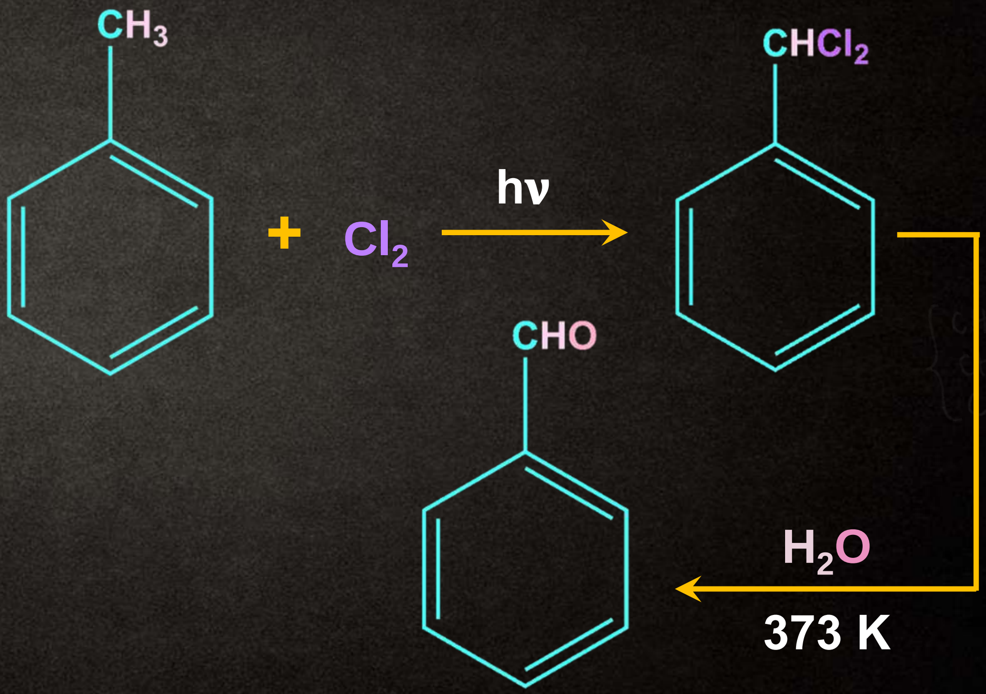


Unstable

Side Chain Chlorination of Methyl Benzene

Reaction:



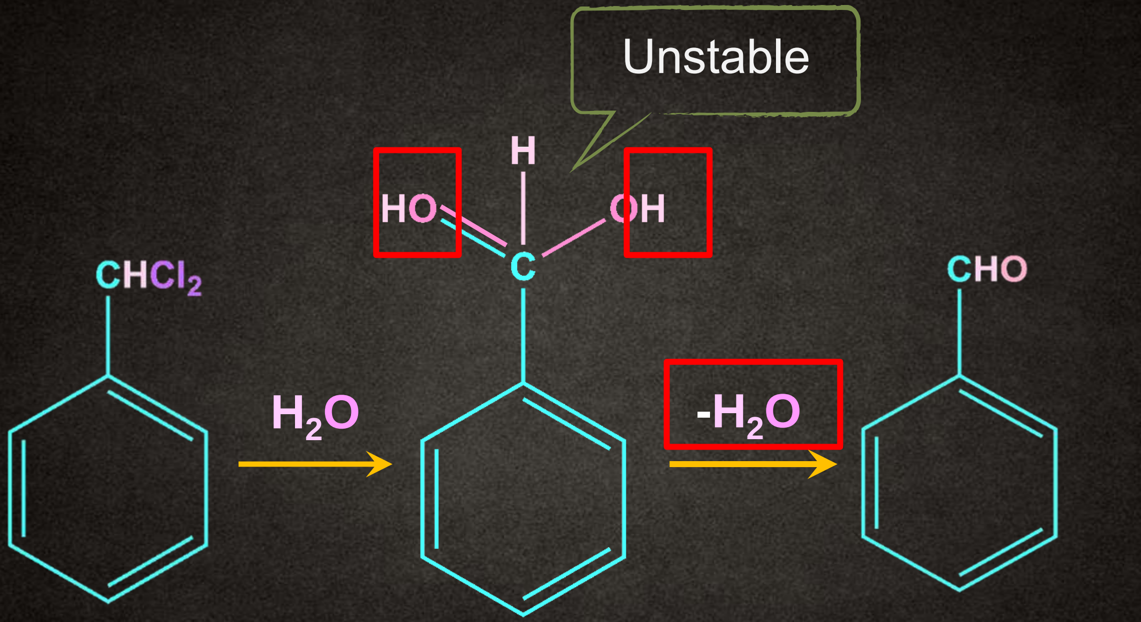


Benzaldehyde

Reagents used

1) Cl_2, hν
2) H_2O, 373 K

Side Chain Chlorination of Methyl Benzene

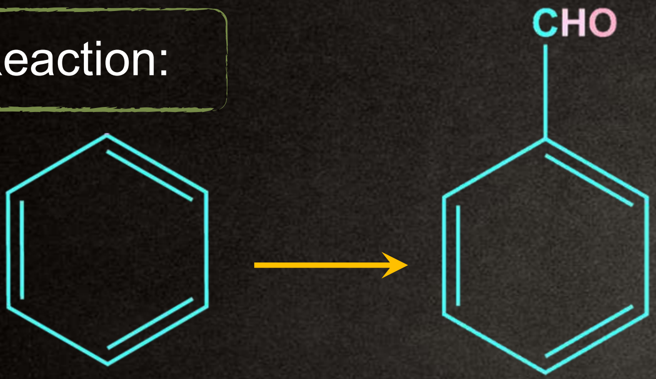


Benzal chloride

Benzaldehyde

Gattermann–Koch Reaction

Reaction:



Reagents used

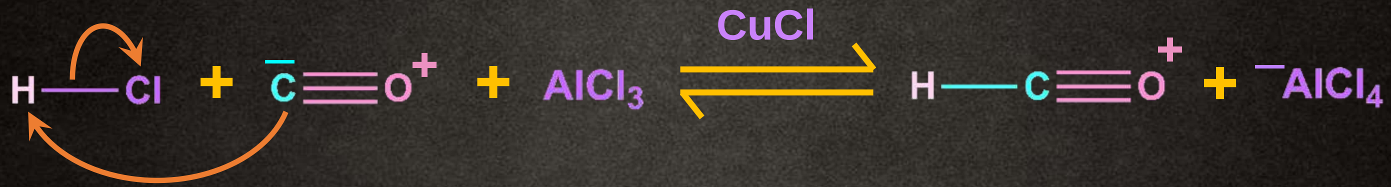
1) CO, HCl
2) Anhydrous $AlCl_3$/CuCl

Gattermann–Koch reaction occurs by **electrophilic substitution mechanism.**

The reaction occurs in **two steps.**

Steps Involved in Gattermann–Koch Reaction

Step 1 Formation of electrophile

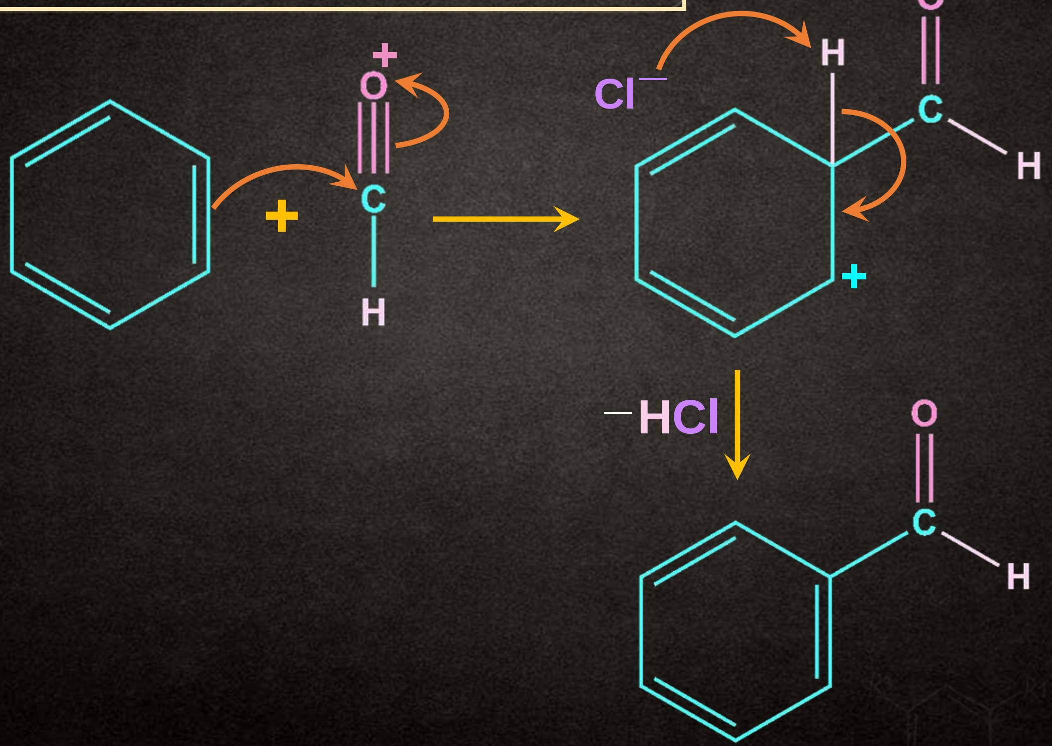


$$H-Cl + \bar{C}\equiv O^{+} + AlCl_3 \xrightleftharpoons{CuCl} H-C\equiv O^{+} + {}^{-}AlCl_4$$

Electrophilic substitution on benzene

Step 2

Electrophilic substitution on benzene



Methods to prepare only aldehydes

- From acid chloride — **Rosenmund's** reduction
- From nitrile — **Stephen's** reaction
- From toluene — **Etard's** reaction
- From benzene — **Gattermann–Koch** reaction

Preparation of Ketones

Preparation of ketones from

- Acid chloride
- Nitrile
- Friedel−Crafts acylation

Preparation of Ketones from Acid Chloride

Acyl chlorides → **Ketones**

Reagent used

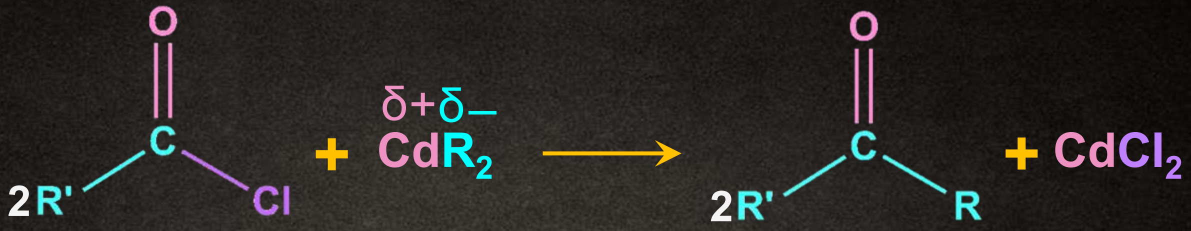
Dialkyl cadmium

$$2\ XM\overset{\delta+}{g}\boxed{\overset{\delta}{R}\quad+\quad\overset{\delta+}{Cd}}\overset{\delta-}{Cl_2}\longrightarrow\boxed{CdR_2}\quad+\quad 2\ Mg(X)Cl$$

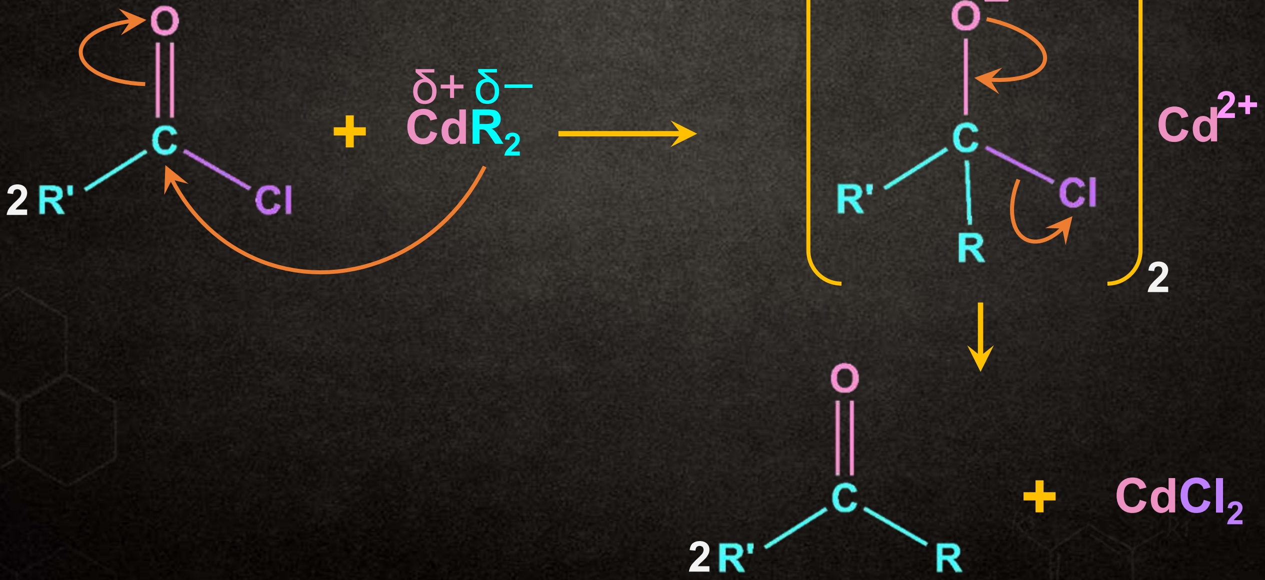
Dialkyl cadmium

Preparation of Ketones from Acid Chloride

General reaction:



Mechanism:



Preparation of Ketones

Example:

$$2\ C_2H_5COCl + Cd(CH_3)_2 \longrightarrow 2\ C_2H_5COCH_3 + CdCl_2$$

Preparation of Ketones from Nitriles

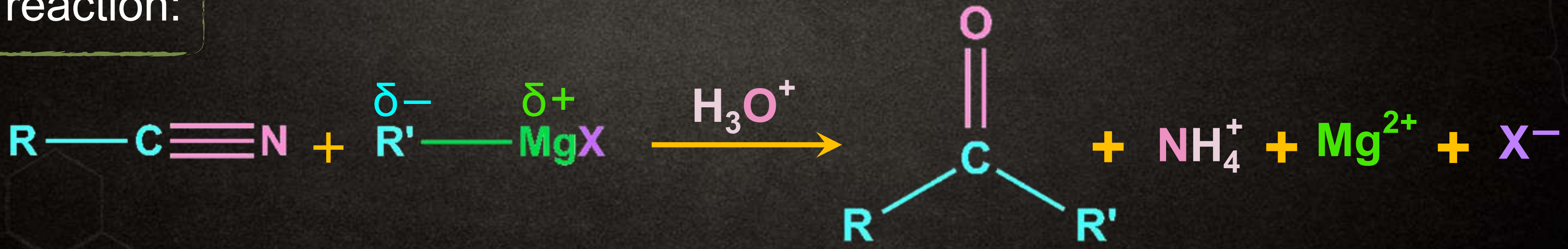
Nitriles → **Ketones**

Reagents used

1) RMgBr, ether
2) H_3O^+

Grignard reagent

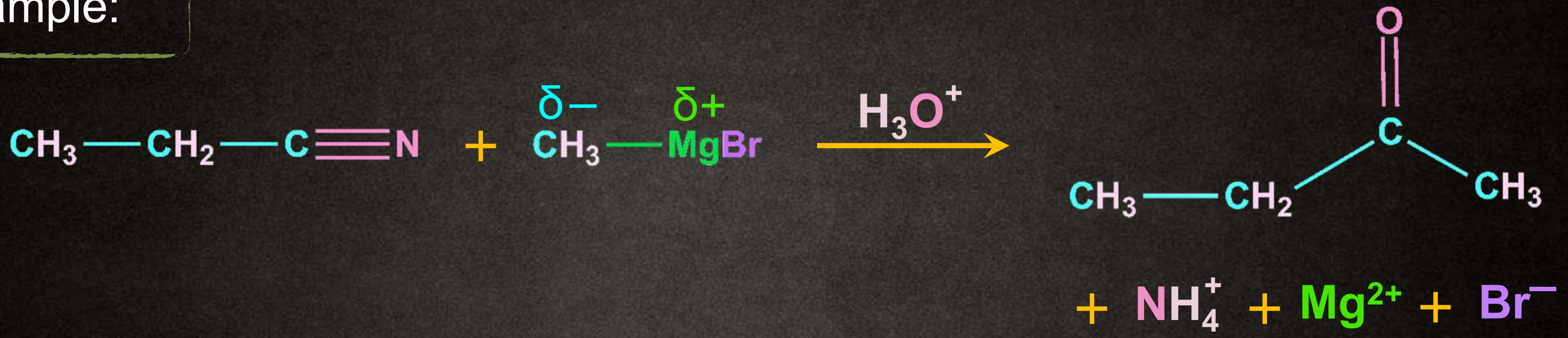
General reaction:



$$R-C\equiv N + \overset{\delta-}{R'}-\overset{\delta+}{MgX} \xrightarrow{H_3O^+} R-\overset{\overset{\displaystyle O}{\|}}{C}-R' + NH_4^+ + Mg^{2+} + X^-$$

Preparation of Ketones from Nitriles

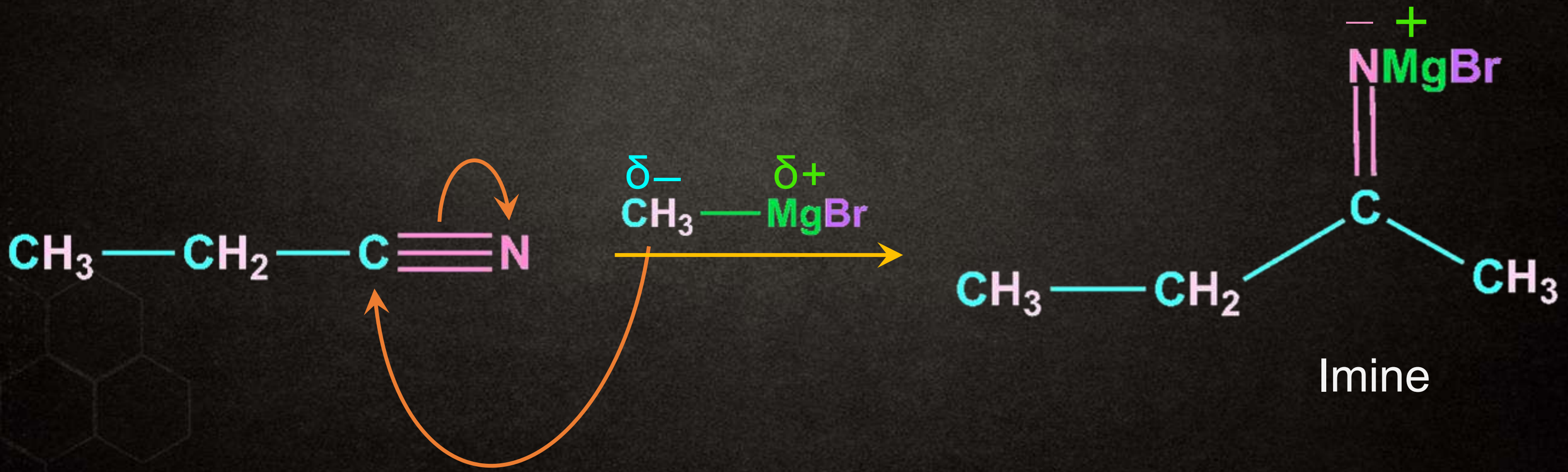
Example:



$$CH_3-CH_2-C\equiv N + \overset{\delta-}{CH_3}-\overset{\delta+}{MgBr} \xrightarrow{H_3O^+} CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + NH_4^+ + Mg^{2+} + Br^-$$

Steps Involved in the Reaction of Grignard Reagent with Alkyl Cyanide

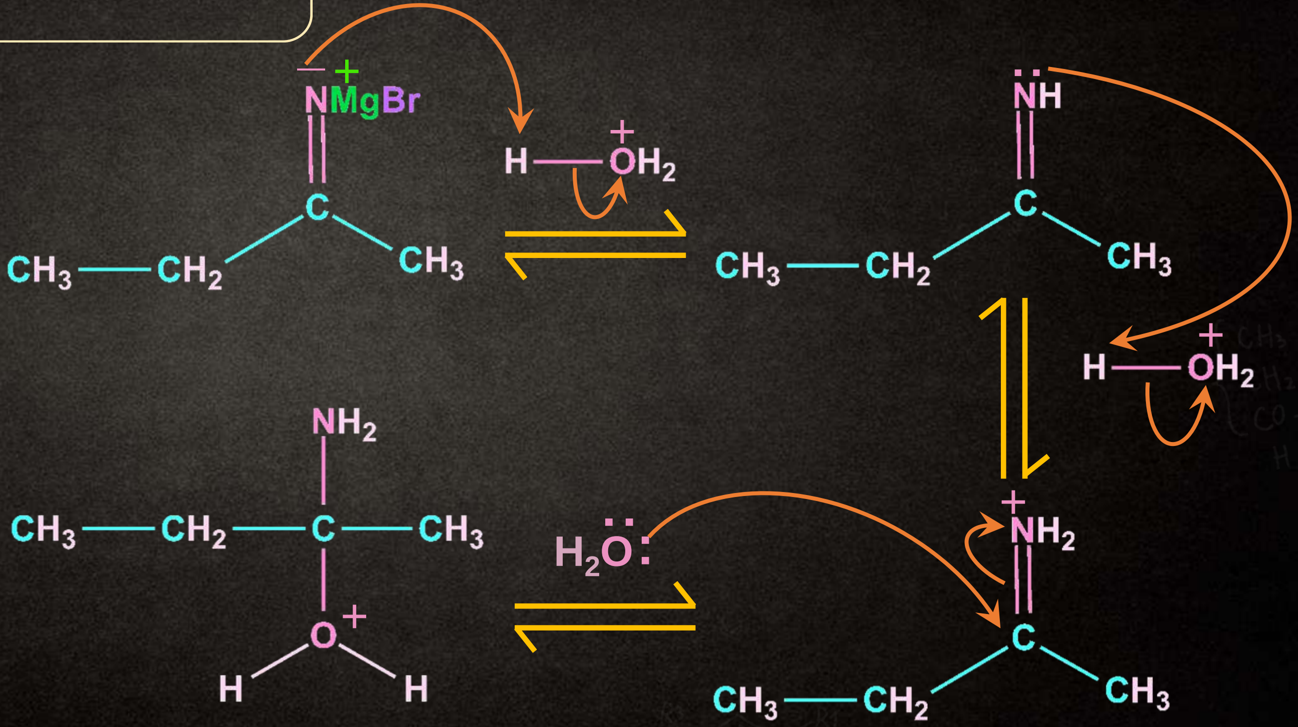
Step 1 Nucleophilic attack



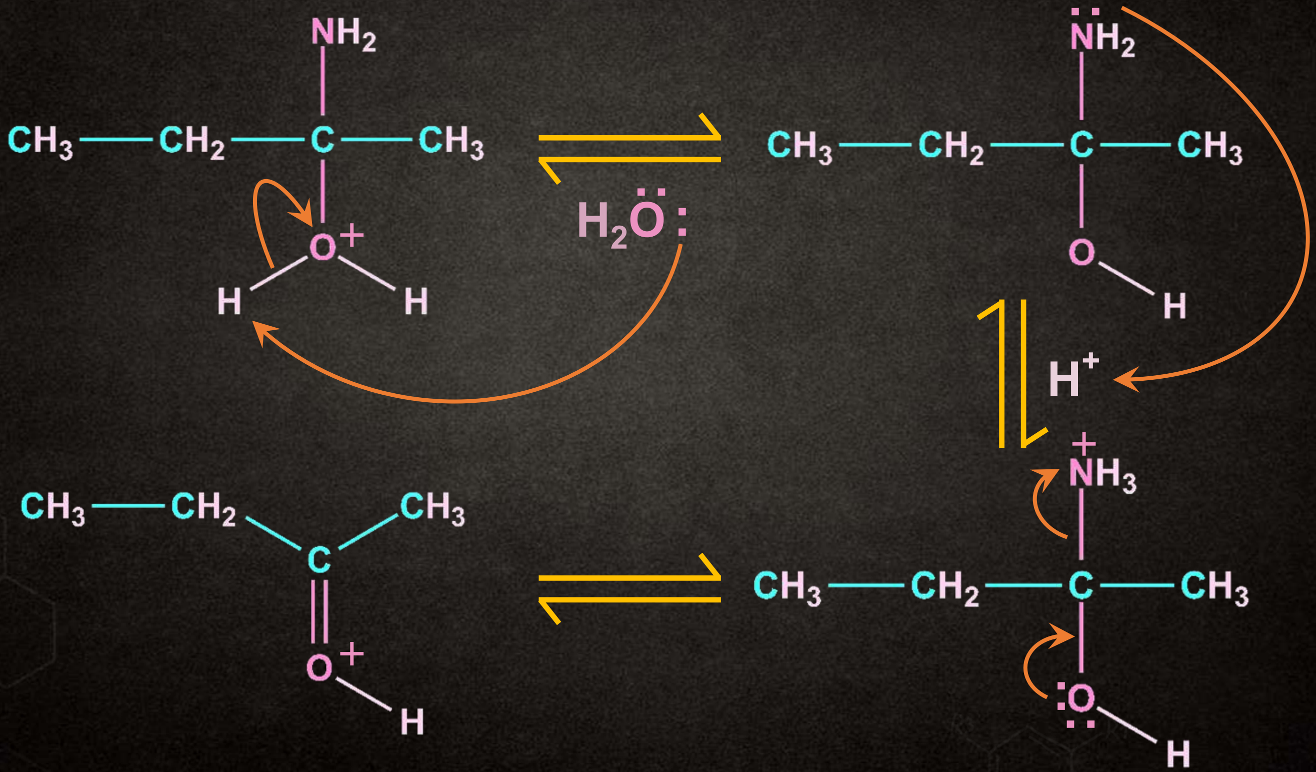
Imine

Hydrolysis of Imine

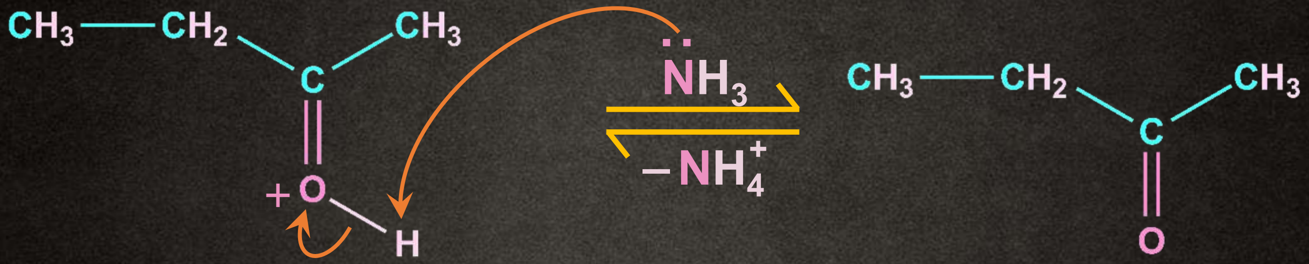
Step 2 Hydrolysis of imine



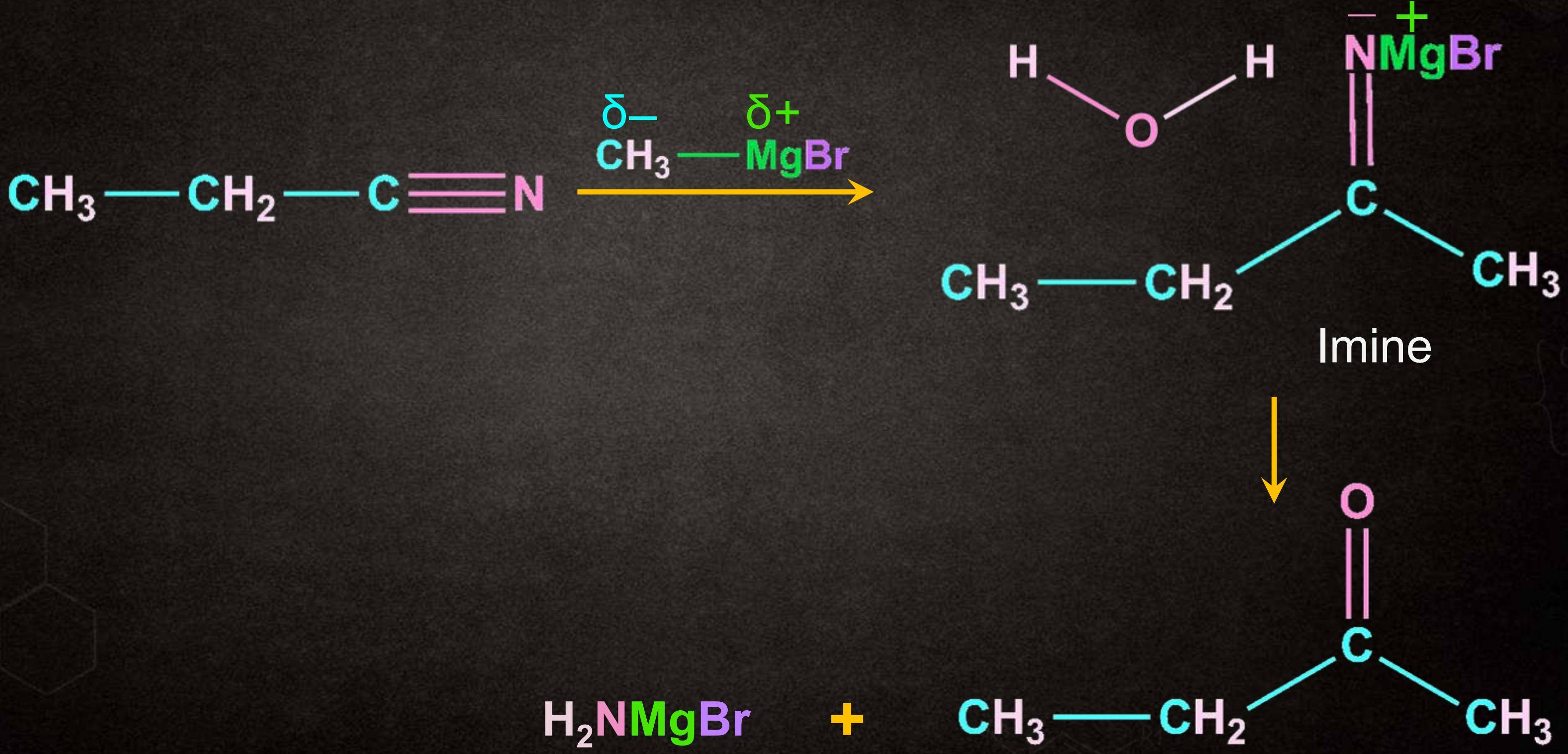
Hydrolysis of Imine



Hydrolysis of Imine



Preparation of Ketones from Nitriles



Friedel–Crafts Acylation

$$C_6H_6 + CH_3COCl \xrightarrow[AlCl_3]{Dry} C_6H_5COCH_3 + HCl$$

Acetophenone

RCO is added to the benzene ring in this reaction.

Physical Properties of Aldehydes and Ketones

Physical Properties

- Odour
- Boiling Point
- Physical State
- Solubility

• Odour

The lower aldehydes have sharp **pungent** odour.

Size of aldehydes ↑

The odour becomes less pungent & **more fragrant**

• Boiling Point

Boiling point	Reason
The boiling points of aldehydes and ketones are **higher** than those of hydrocarbons and ethers of comparable molar masses.	The weak molecular association in aldehydes and ketones arising out of the **dipole-dipole** interactions.

• Boiling Point

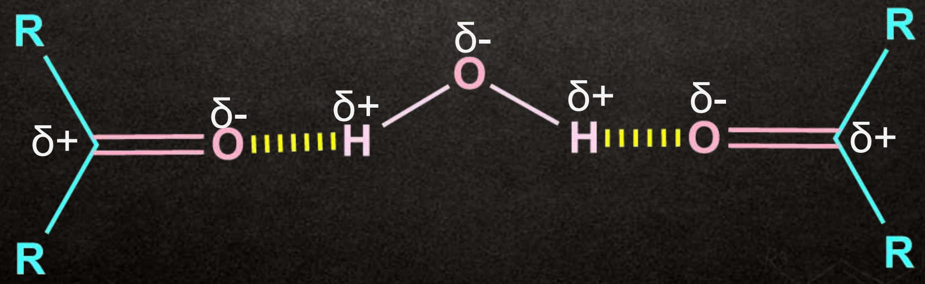
Boiling point	Reason
The boiling points of aldehydes and ketones are **lower** than those of alcohols of similar molar masses.	The **absence** of **intermolecular H-bonding** in aldehydes and ketones

• Physical State

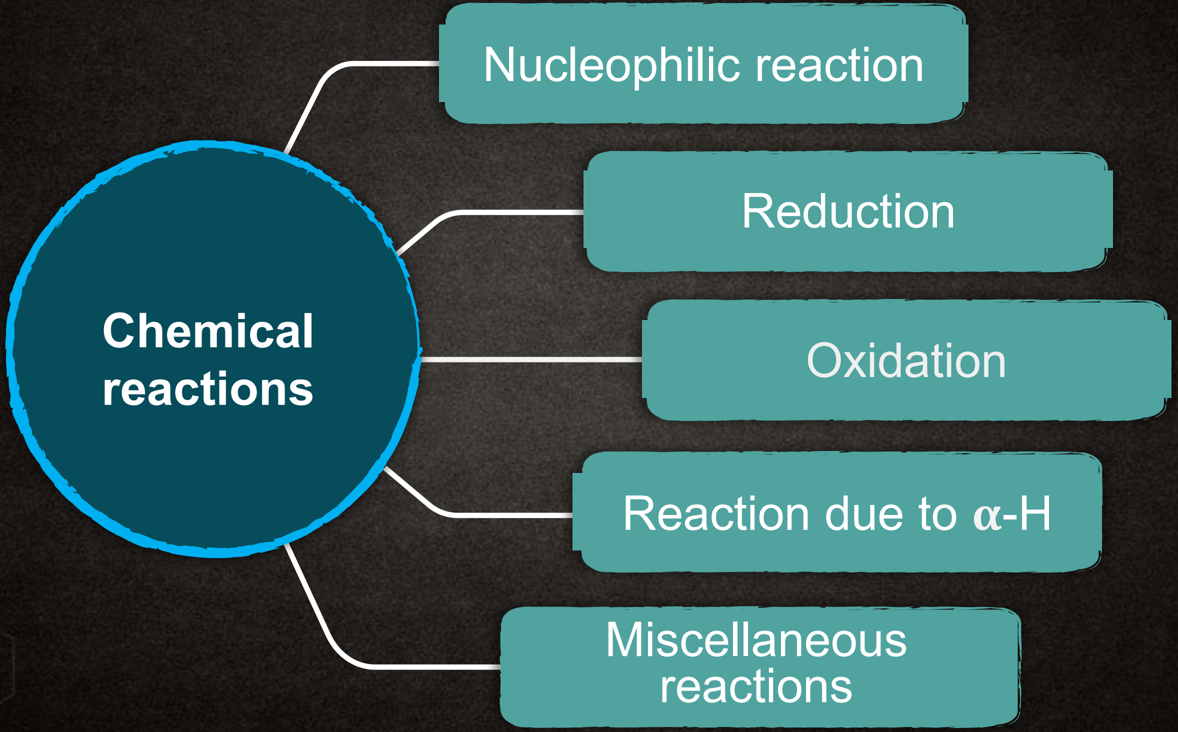
Methanal	Gas at room temperature
Ethanal	Volatile liquid
Other aldehydes and ketones	Liquid or solid at room temperature

• Solubility

Solubility	Reason
The lower members of aldehydes and ketones are **miscible** with water in all proportions.	They form **hydrogen bonds** with water.



Chemical Properties of Aldehydes and Ketones

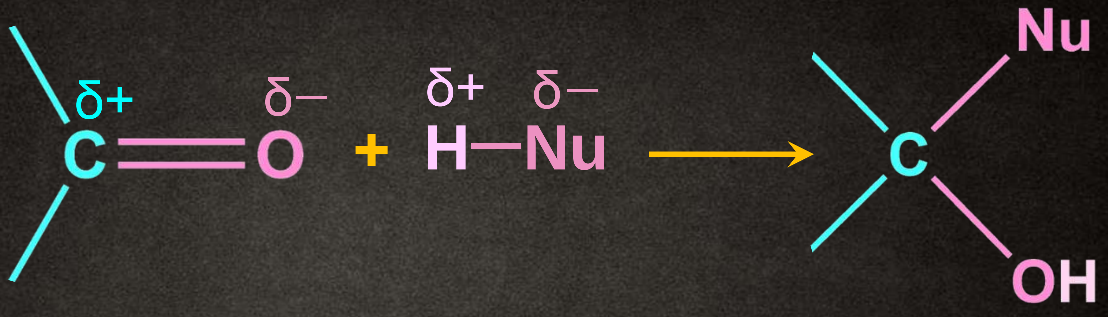


Chemical reactions

- Nucleophilic reaction
- Reduction
- Oxidation
- Reaction due to α-H
- Miscellaneous reactions

Nucleophilic Addition Reaction

General reaction



Mechanism

Step 1 **Addition of nucleophile**

Step 2 **Protonation**

Addition of Nucleophile

Rate-determining step

sp^3 - hybridised C

sp^2 - hybridised C

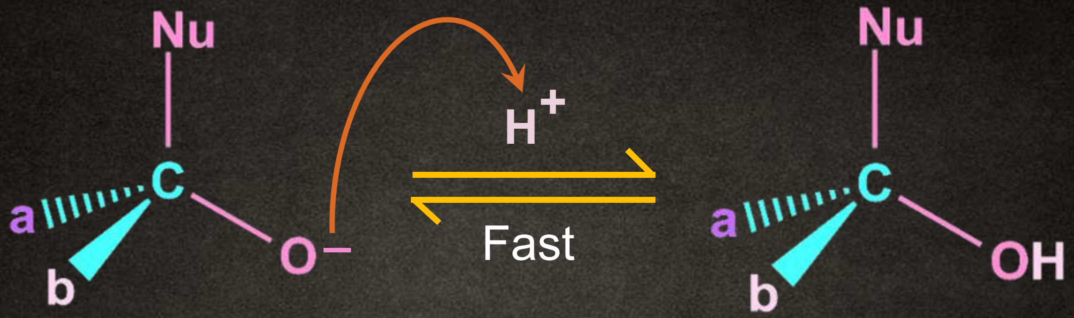
Perpendicular attack to the plane of C=O bond

Addition of Nucleophile

sp^3 hybridised C

Tetrahedral intermediate

Protonation

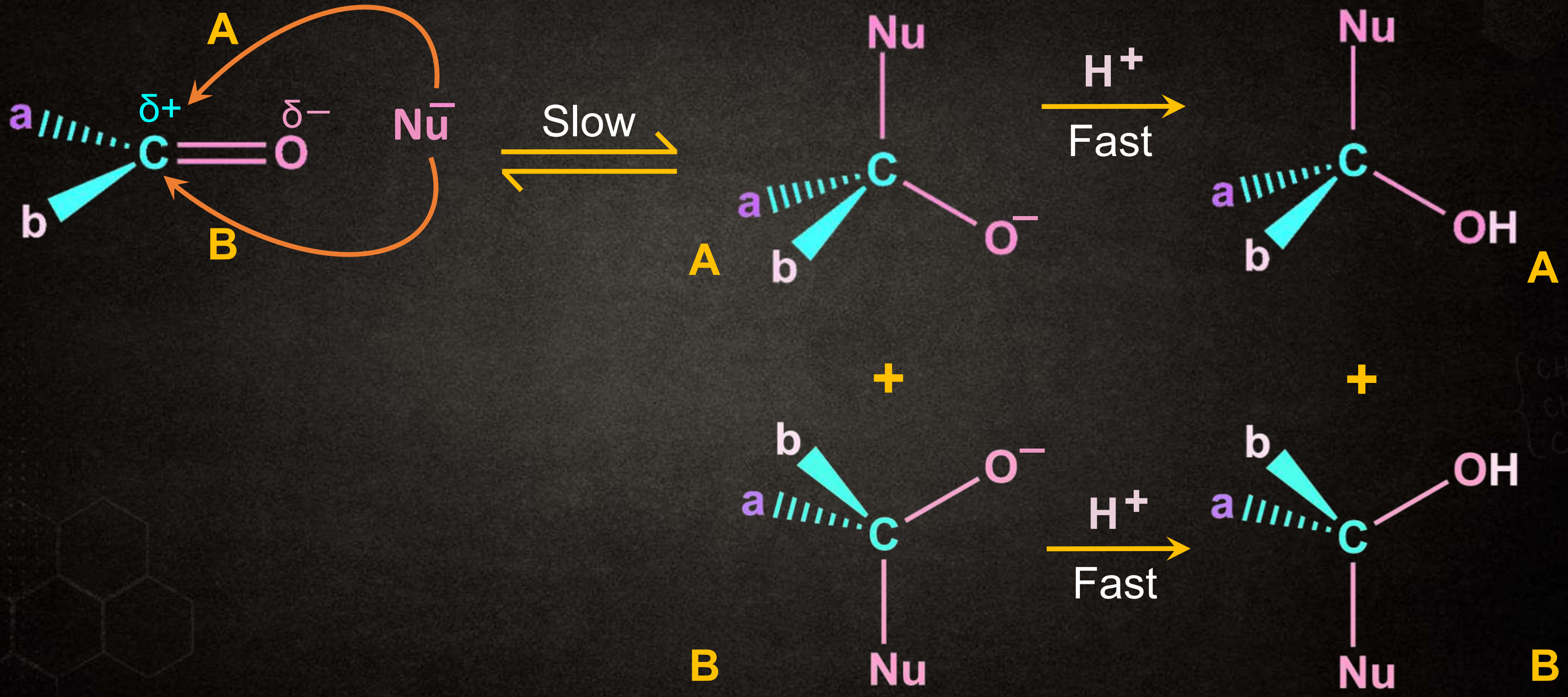


Stereochemistry of Nucleophilic Addition

If the **groups attached** to the carbonyl are **different,**

Nucleophilic addition reaction leads to **racemisation.**

Stereochemistry of Nucleophilic Addition



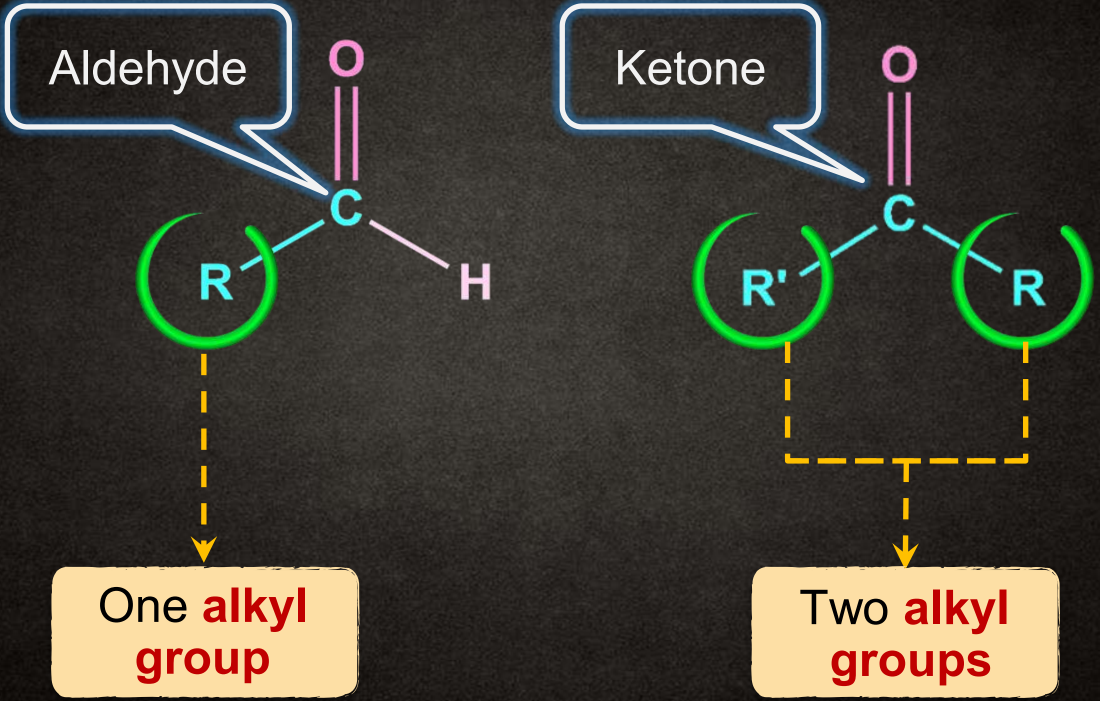
Relative Reactivity: Aldehydes vs Ketones

Reactivity depends on

- Steric factor
- Electronic factor

Generally, **aldehydes** are **more reactive** than **ketones** due to **less steric hindrance.**

Steric Factor: Aldehydes vs Ketones



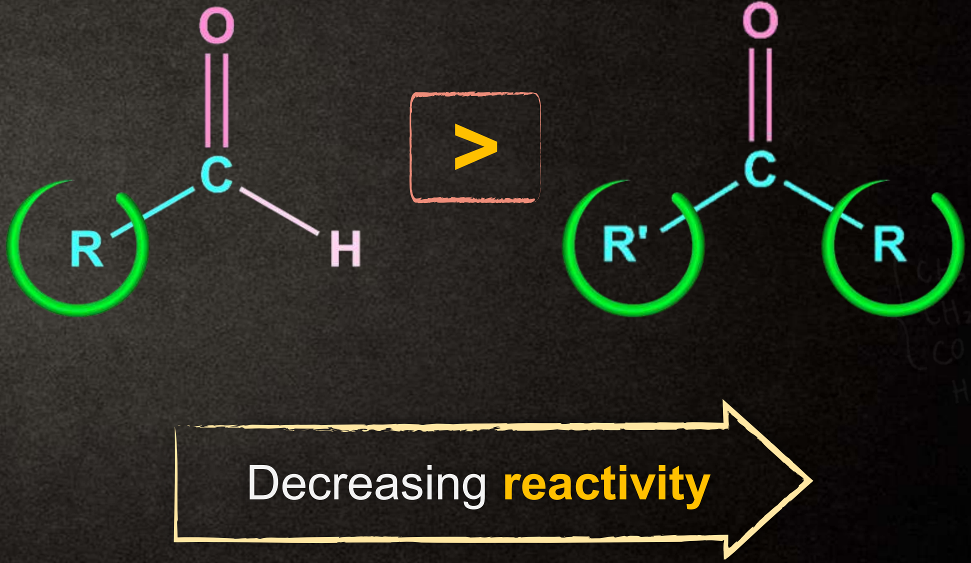
One **alkyl group**

Two **alkyl groups**

Steric Factor: Aldehydes vs Ketones

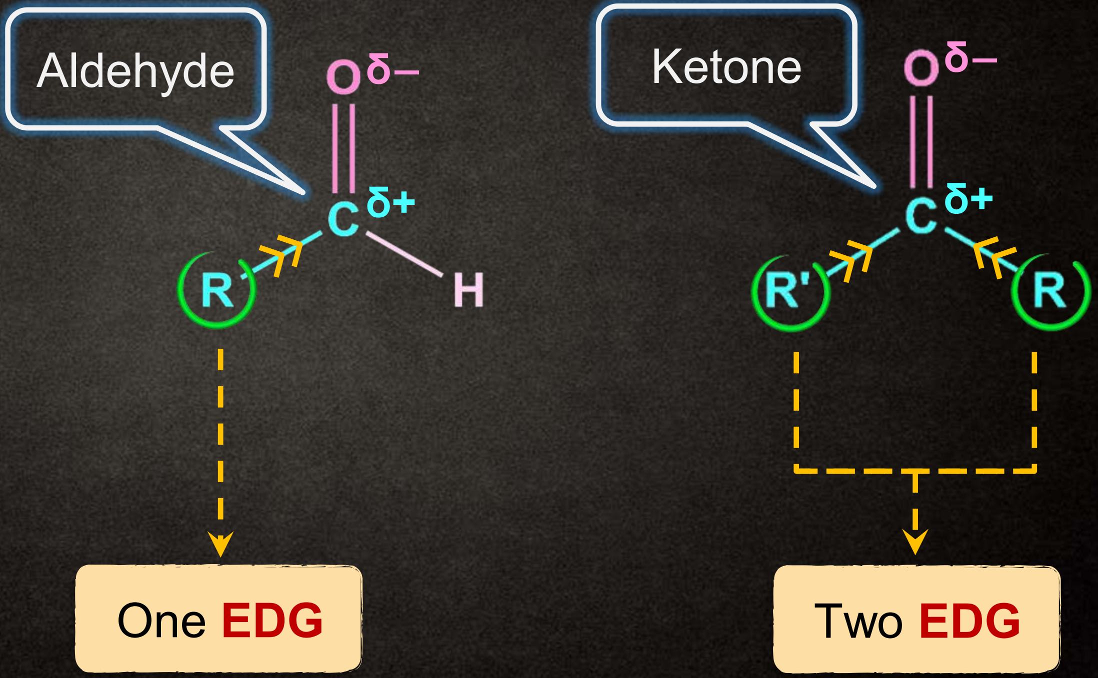
The carbonyl carbon of an aldehyde is **more** accessible to a nucleophile.

It is because the **hydrogen** attached to the carbonyl carbon of an aldehyde is **smaller** than the second alkyl group attached to the carbonyl carbon of a ketone.

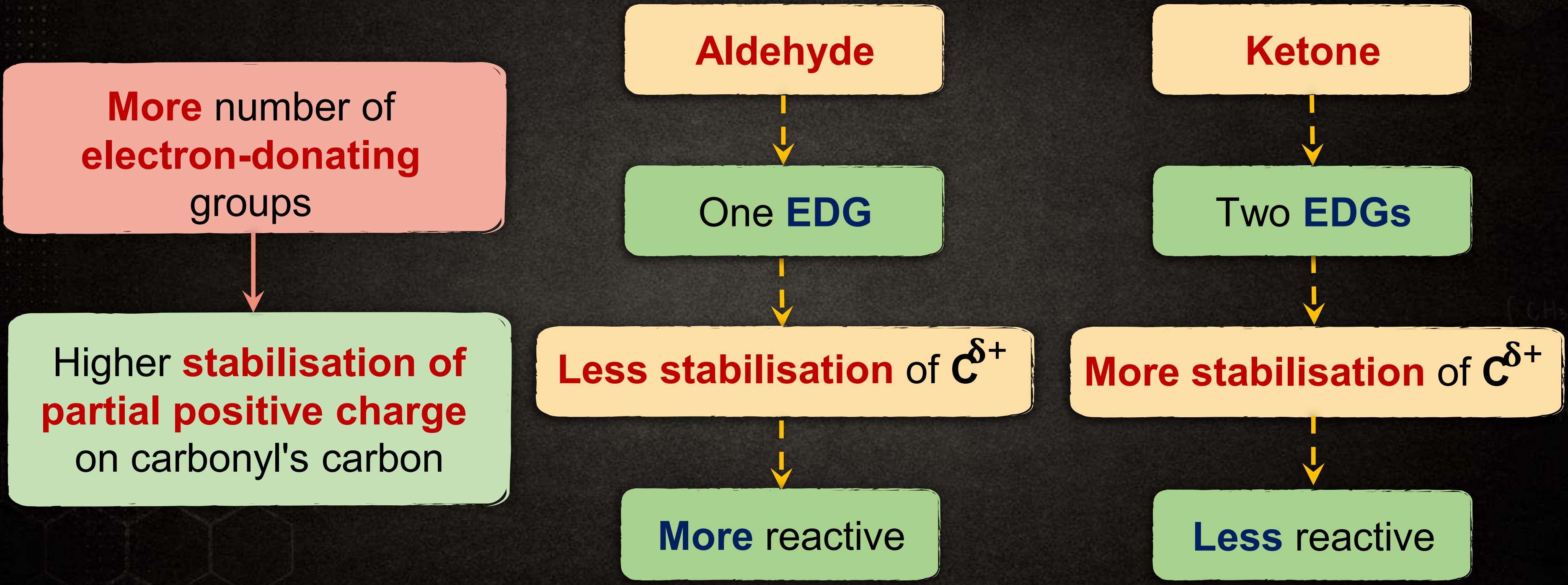


Decreasing **reactivity**

Electronic Factor: Aldehydes vs Ketones



Electronic Factor: Aldehydes vs Ketones



More number of **electron-donating** groups

Higher **stabilisation of partial positive charge** on carbonyl's carbon

Aldehyde

One **EDG**

Less stabilisation of $C^{\delta+}$

More reactive

Ketone

Two **EDGs**

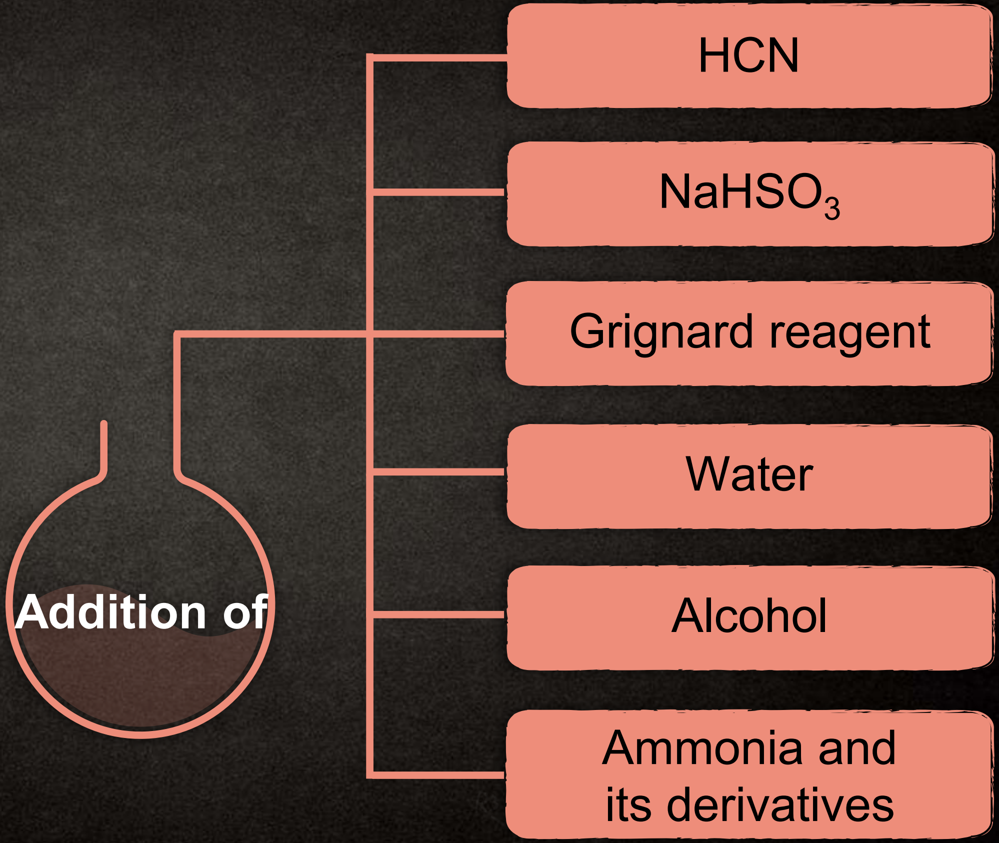
More stabilisation of $C^{\delta+}$

Less reactive

Electronic Factor: Aldehydes vs Ketones

Decreasing **reactivity**

Nucleophilic Addition Reactions

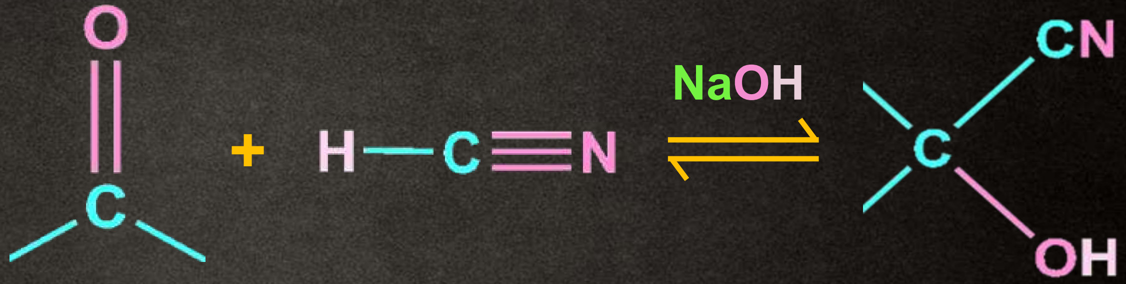


Addition of

- HCN
- $NaHSO_3$
- Grignard reagent
- Water
- Alcohol
- Ammonia and its derivatives

Nucleophilic Addition of HCN

General reaction



Cyanohydri
n

Steps Involved in the Addition of HCN

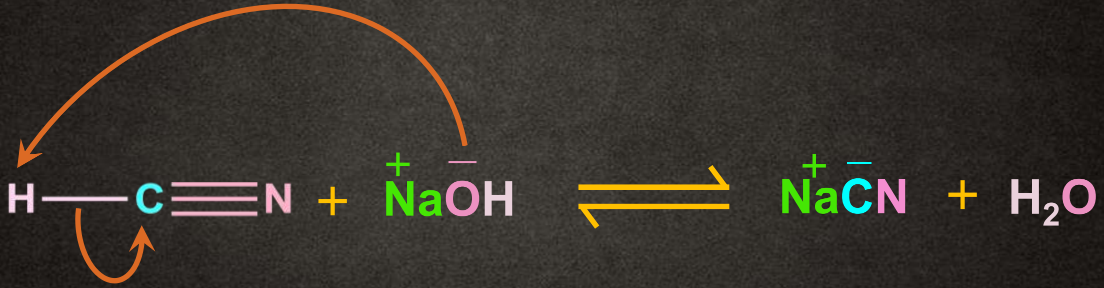
Step 1 Formation of a strong nucleophile

Step 2 Nucleophilic attack on the carbonyl carbon

Step 3 Protonation of the intermediate

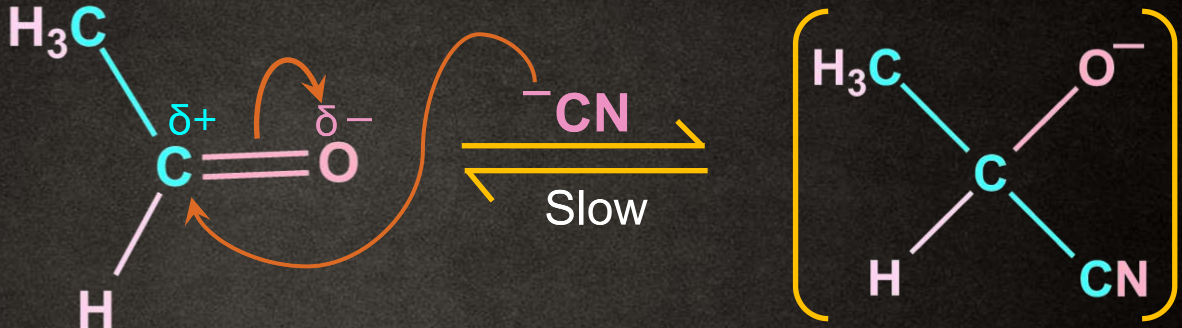
Formation of Strong Nucleophile

HCN is a weak nucleophile, its nucleophilicity is increased when a base takes proton from it.



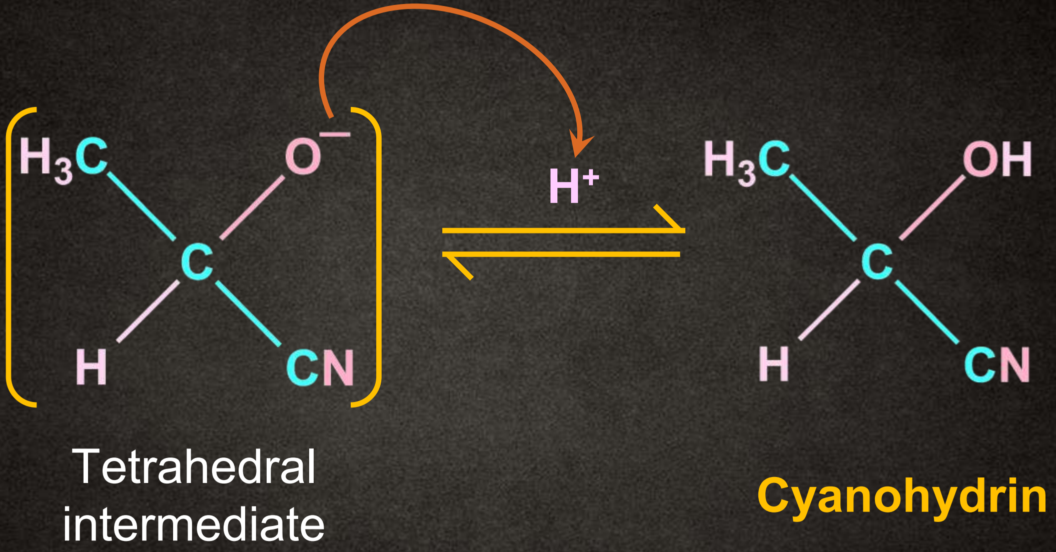
$$H-C\equiv N + \overset{+}{Na}\overset{-}{O}H \rightleftharpoons \overset{+}{Na}\overset{-}{C}N + H_2O$$

Nucleophilic Attack on Carbonyl Carbon



Tetrahedral intermediate

Protonation of Intermediate



Tetrahedral intermediate

Cyanohydrin

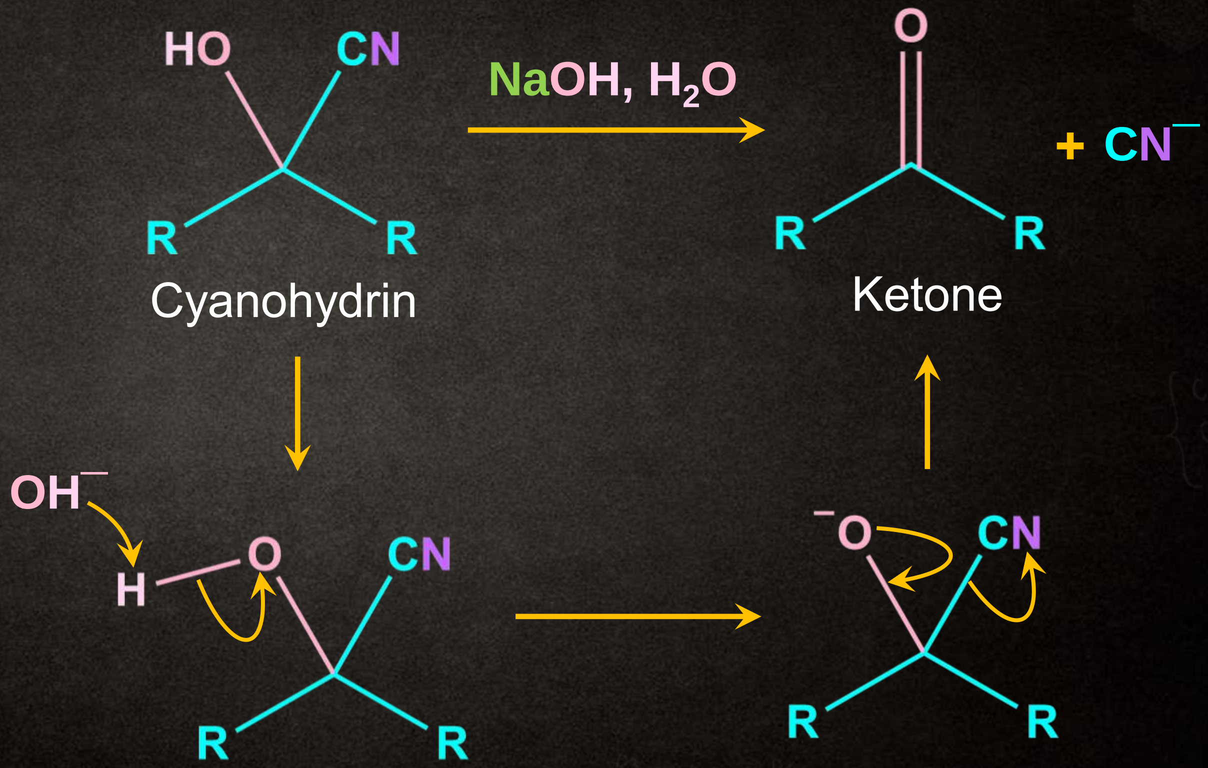
Nucleophilic Addition of HCN

KCN and **H_2SO_4** can also be used as a **source of CN^-** ion.

Cyanohydrin formation is **reversible**

Just dissolving a cyanohydrin in **water** can give back the aldehyde or ketone, and aqueous base usually **decomposes** cyanohydrins completely.

Nucleophilic Addition of HCN



Nucleophilic Addition of HCN

The equilibrium is **more favourable for aldehyde** cyanohydrins than for ketone cyanohydrins

Reason

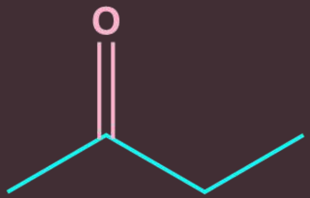
The **size** of the groups attached to the carbonyl carbon atom

More steric hinderance

Lesser accessibility for the nucleophile

Equilibrium shifts to the **LHS.**

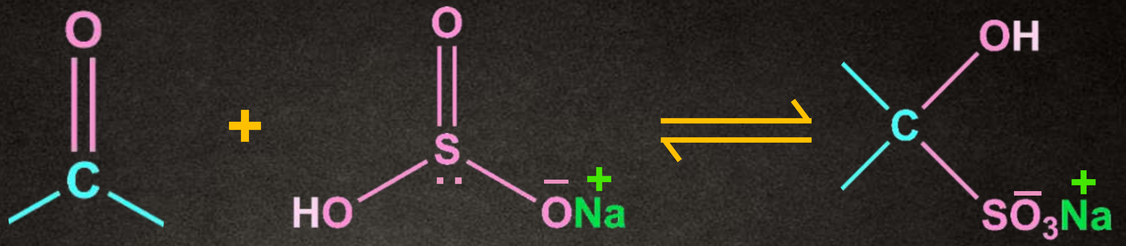
Nucleophilic Addition of HCN

Aldehyde or ketone	K_{eq}
PhCHO	212
	28

Cyanohydrins are very useful compounds in synthesizing many other organic compounds such as **α-hydroxy acids, amino acids, etc.**

Nucleophilic Addition of $NaHSO_3$

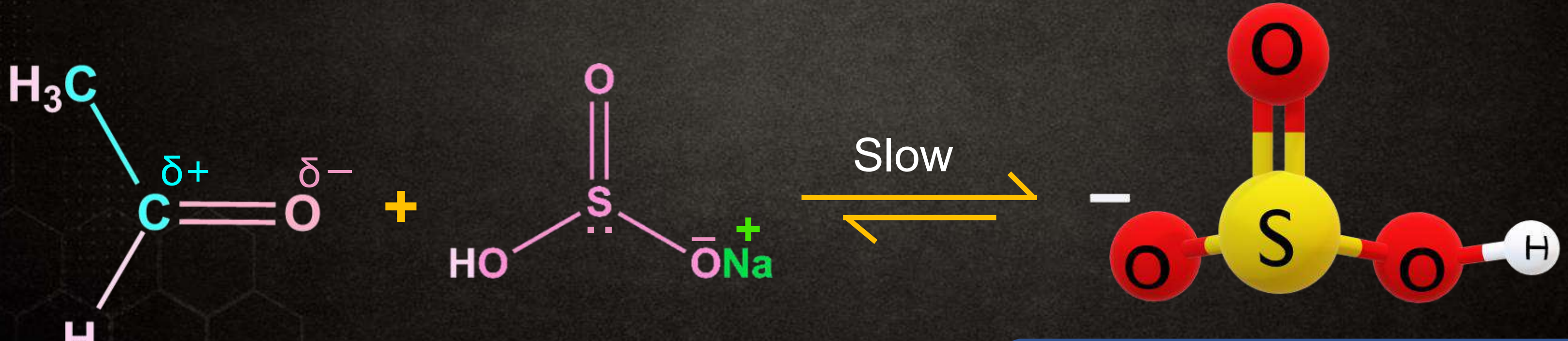
General reaction



Bisulphite addition compound

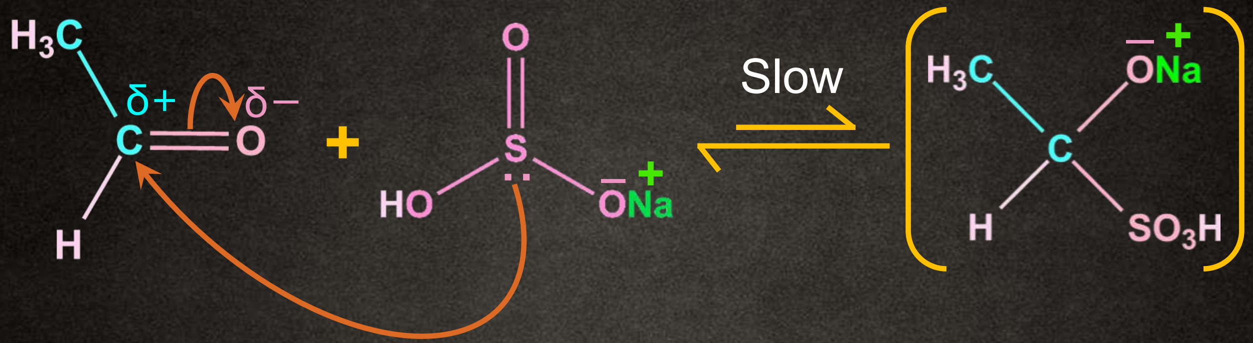
Nucleophilic Attack on Carbonyl Carbon

Step 1 Nucleophilic attack on the carbonyl carbon



The **S-site** is **more** nucleophilic than the **O-site.**

Nucleophilic Attack on Carbonyl Carbon



The **nucleophile** added in the **slow step**, which is **RDS,** and hence, this reaction known as **'nucleophilic addition'.**

Proton Transfer

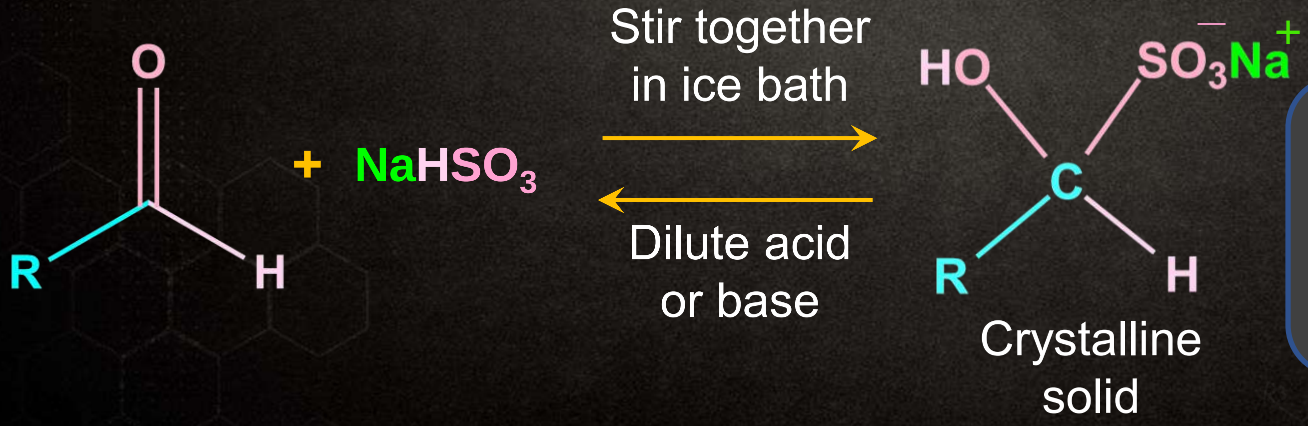
Step 2 **Proton transfer**

Since the reaction is **reversible,**

The **addition product** can be converted back into **carbonyl compounds** using **mineral acids.**

Point to Remember!

This method can be used for the **purification of aldehydes** from other organic compounds.



Stir together in ice bath

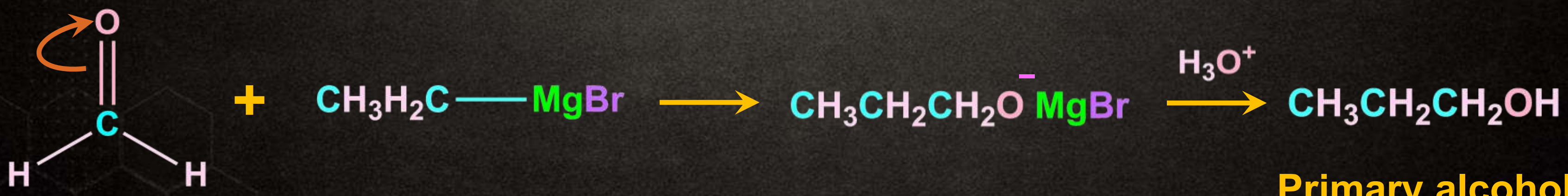
Dilute acid or base

Crystalline solid

In case of **ketones,** the equilibrium of the reaction is shifted in the **left direction.**

Nucleophilic Addition of Grignard Reagent

Reagent	Reactant	Product
Grignard reagent	Formaldehyde	Primary alcohol
	An aldehyde other than formaldehyde	Secondary alcohol
	Ketone	Tertiary alcohol

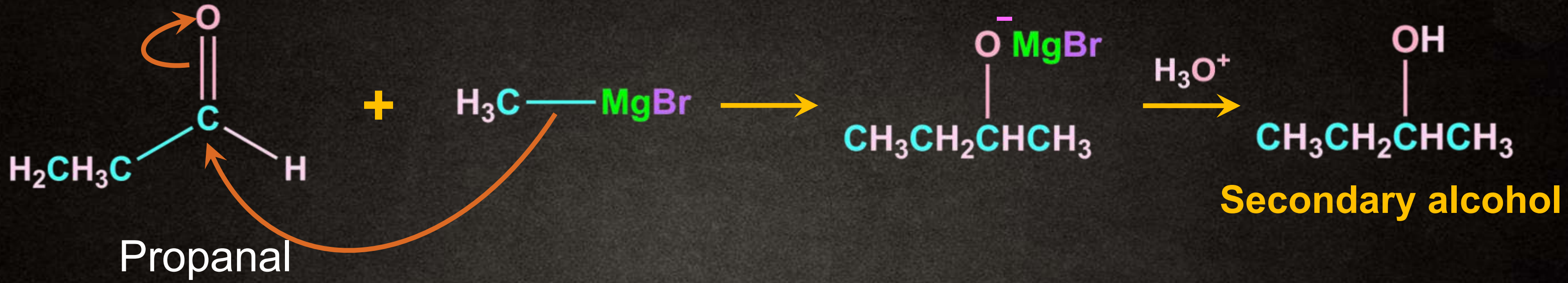


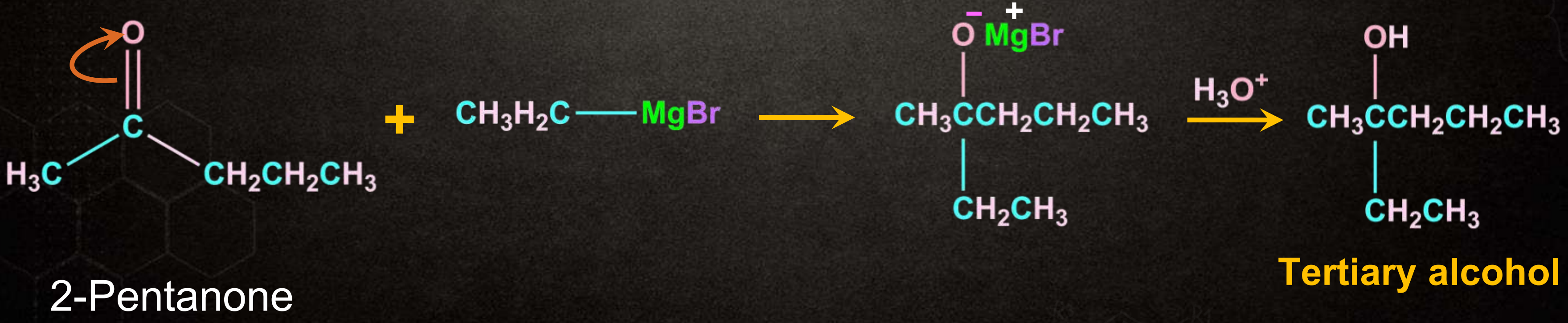
$$HCHO + CH_3H_2C{-}MgBr \longrightarrow CH_3CH_2CH_2\overset{-}{O}\,MgBr \xrightarrow{H_3O^+} CH_3CH_2CH_2OH$$

Formaldehyde

Primary alcohol

Nucleophilic Addition of Grignard Reagent



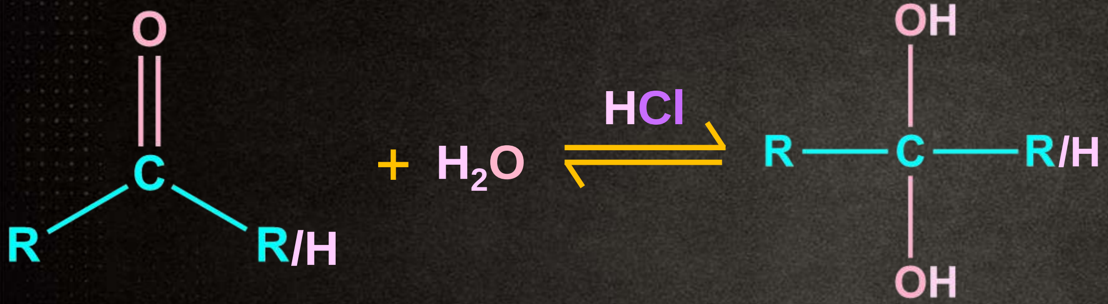


Nucleophilic Addition Reactions

Addition of

- HCN
- $NaHSO_3$
- Grignard reagent
- Water
- Alcohol
- Ammonia and its derivatives

Nucleophilic Addition–Elimination of Water



An aldehyde
or a ketone

A **gem-diol**
A hydrate

Water is a poor nucleophile. Therefore, it adds relatively slowly to a carbonyl group.

The rate of the reaction is **increased** by an **acid catalyst**.

Nucleophilic Addition–Elimination of Water

The **addition of water** to an aldehyde or a ketone forms a **hydrate**.

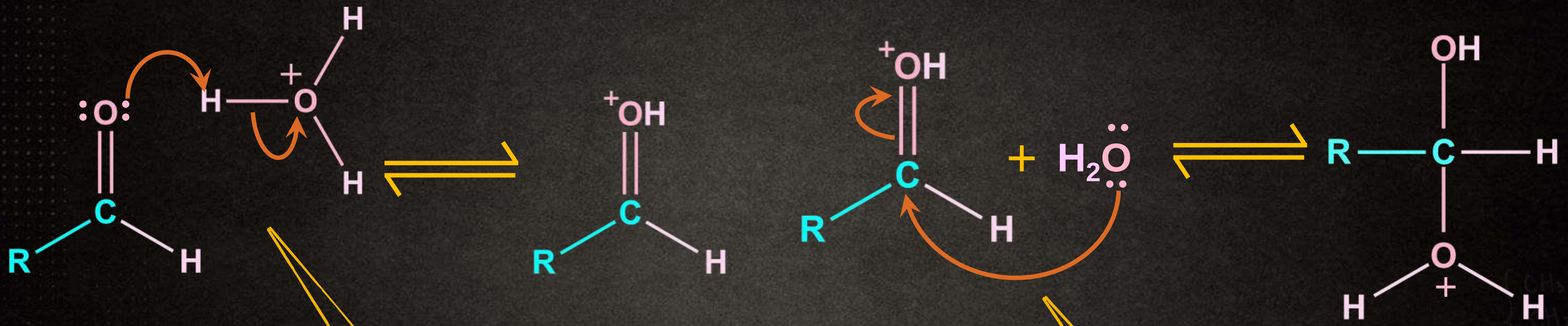
A molecule with **two –OH groups** bonded to the **same carbon**, also called **gem-diols.**

Step 1 **Protonation**

Step 2 **Nucleophilic attack of water**

Step 3 **Deprotonation**

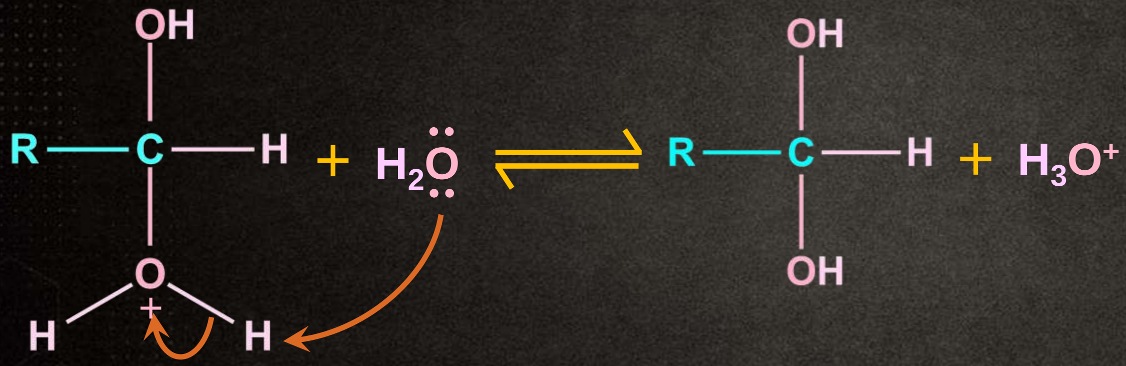
Mechanism for Acid–Catalyzed Hydrate Formation



The acid protonates the carbonyl oxygen

The nucleophile adds to the carbonyl carbon

Mechanism for Acid–Catalyzed Hydrate Formation



Generally, simple aldehydes are **hydrated to some extent** while simple ketones are not.

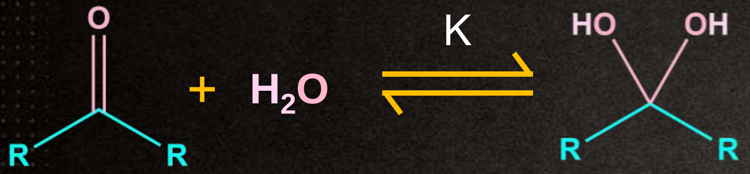
Aqueous solution of formaldehyde is **completely hydrated**.

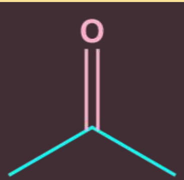
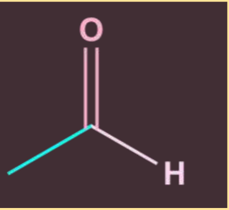
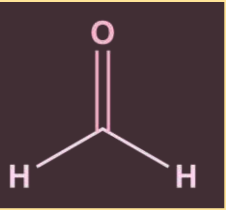
Nucleophilic Addition–Elimination of Water

The **extent** to which an aldehyde or a ketone is hydrated in an aqueous solution **depends on** the **substituents** attached to the carbonyl group.

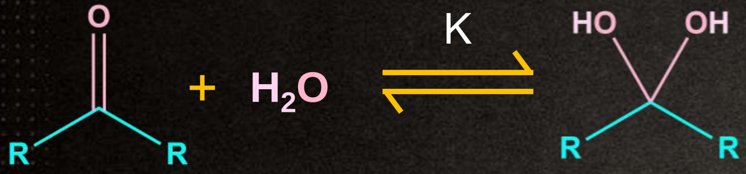
Substituent	Effect
Electron-donating, **bulky** (such as methyl groups of acetone)	**Decreases** the percentage of hydrate present at equilibrium
Electron-withdrawing, **small** (the hydrogens of formaldehyde)	**Increases** the percentage of hydrate present at equilibrium

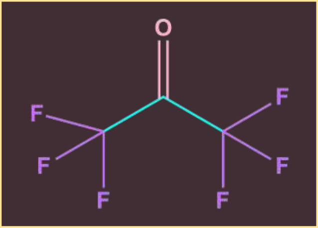
Steric Factor



Name	Structure	Equilibrium constant K
Acetone		0.001
Acetaldehyde		1.06
Formaldehyde		2280

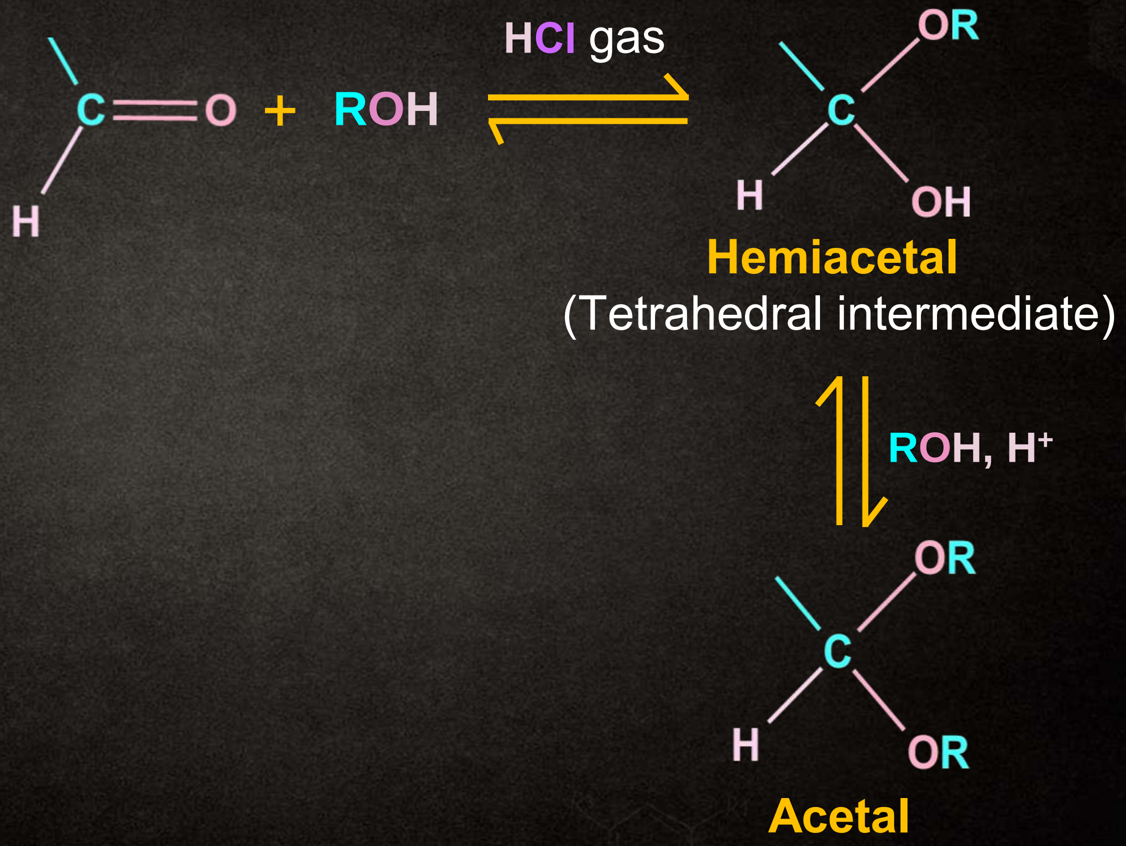
Electronic Factor



Name	Structure	Equilibrium constant K
Acetone		0.001
Chloral	 	1.06
Hexafluoro-acetone	 	2280

Nucleophilic Addition of Alcohol

General reaction:



HCl gas

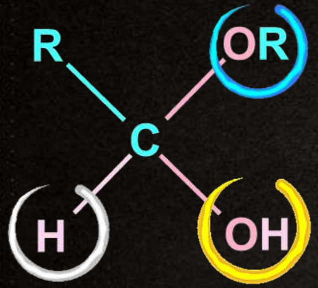
Hemiacetal

(Tetrahedral intermediate)

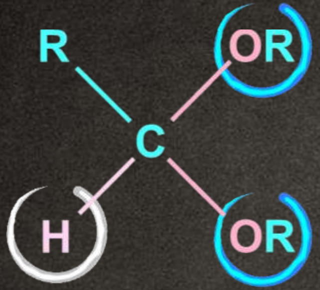
ROH, H^+

Acetal

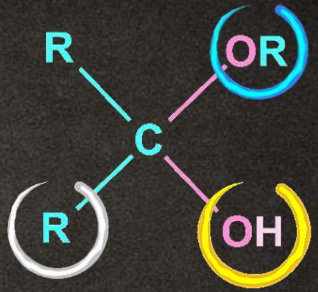
Structures of Hemiacetal, Acetal, Hemiketal and Ketal



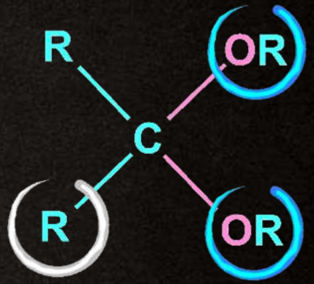
Hemiacetal



Acetal



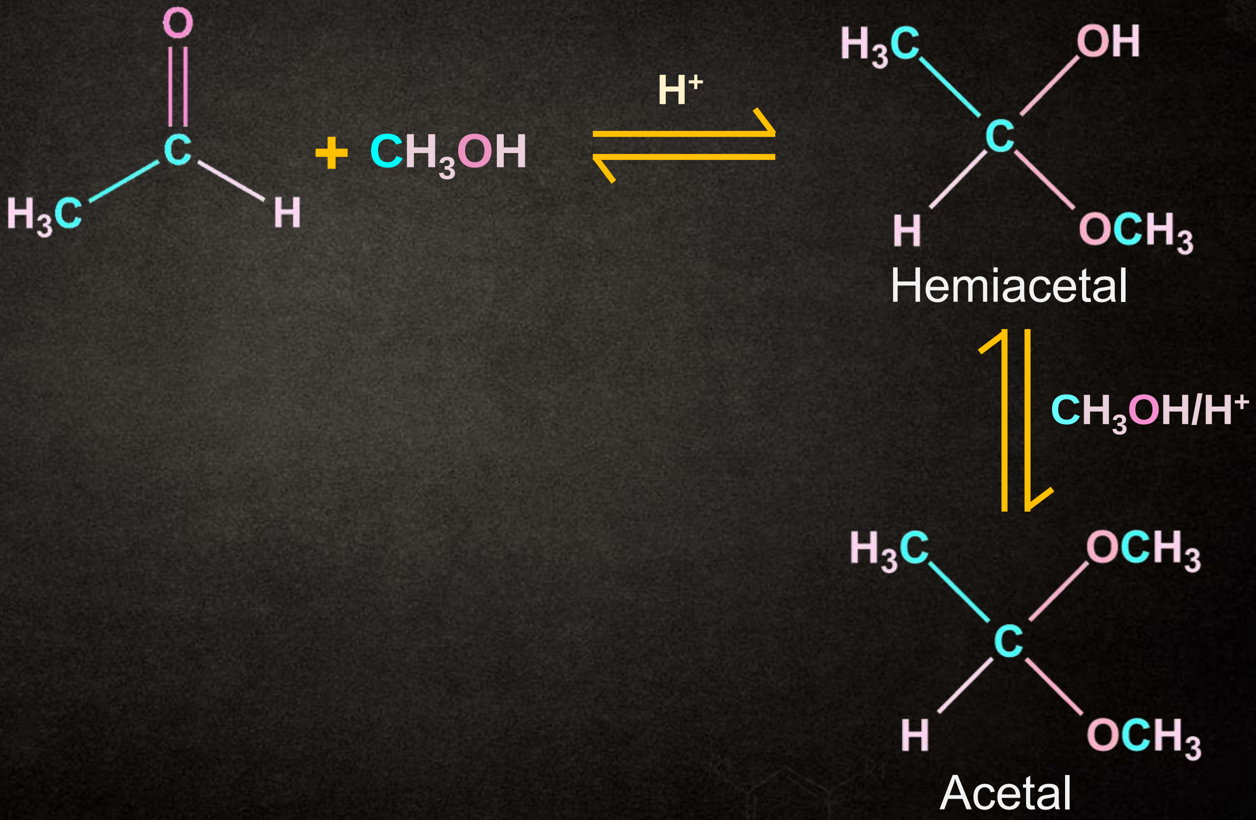
Hemiketal



Ketal

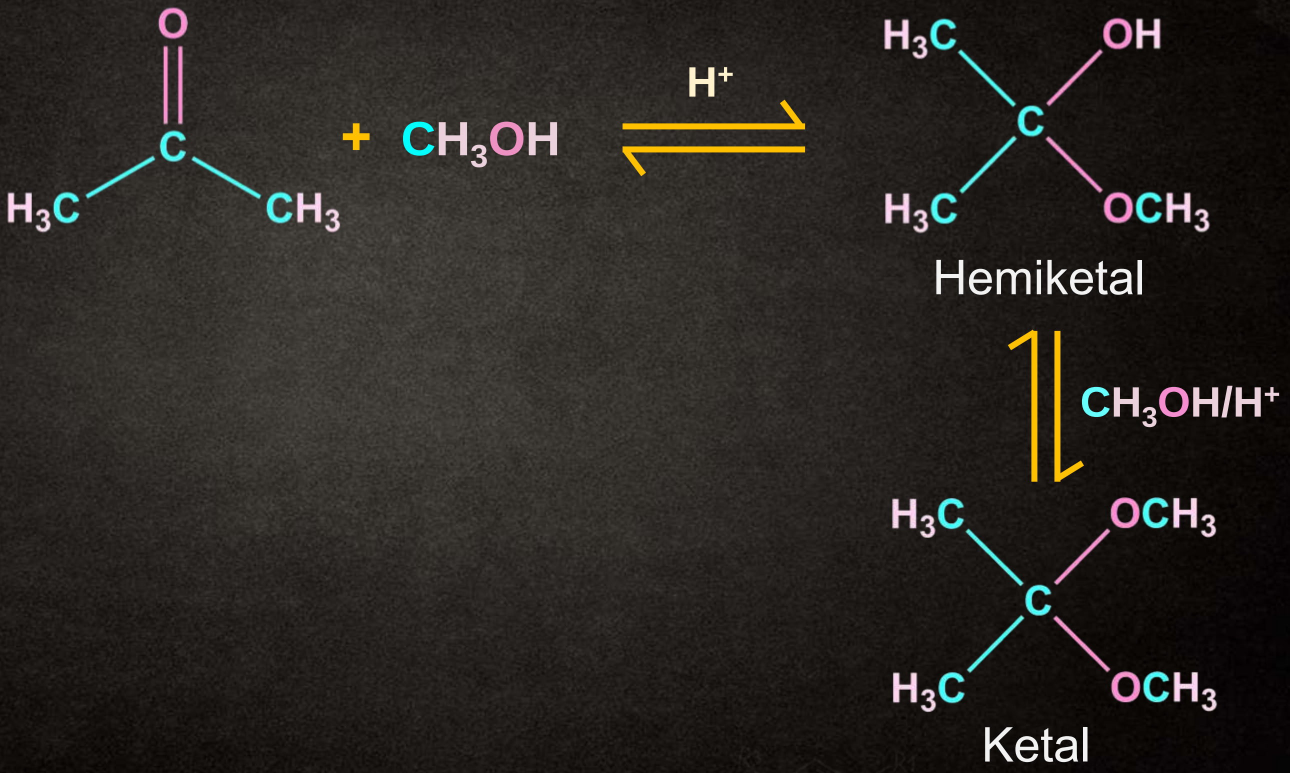
EXAMPLE

Nucleophilic Addition of Alcohol



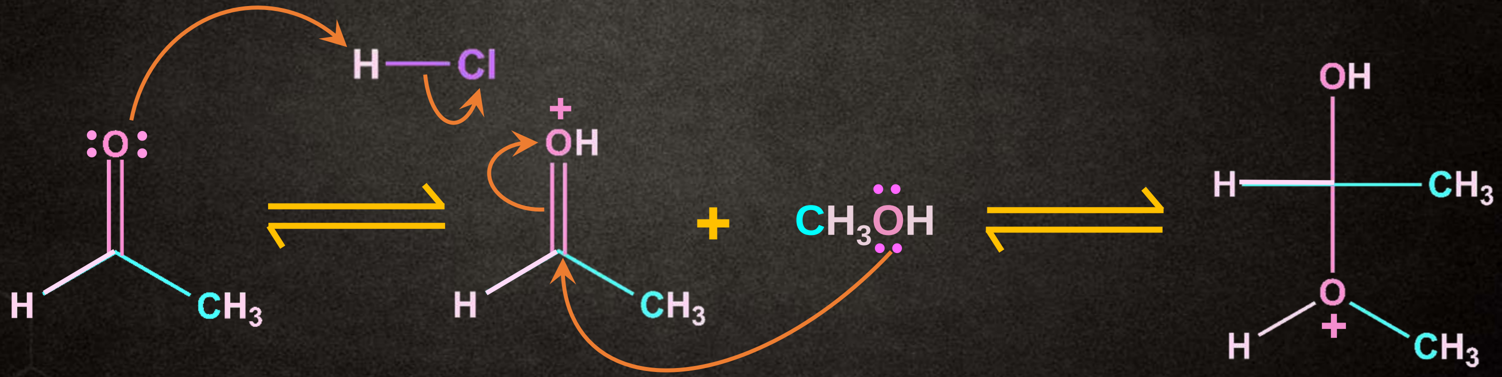
EXAMPLE

Nucleophilic Addition of Alcohol

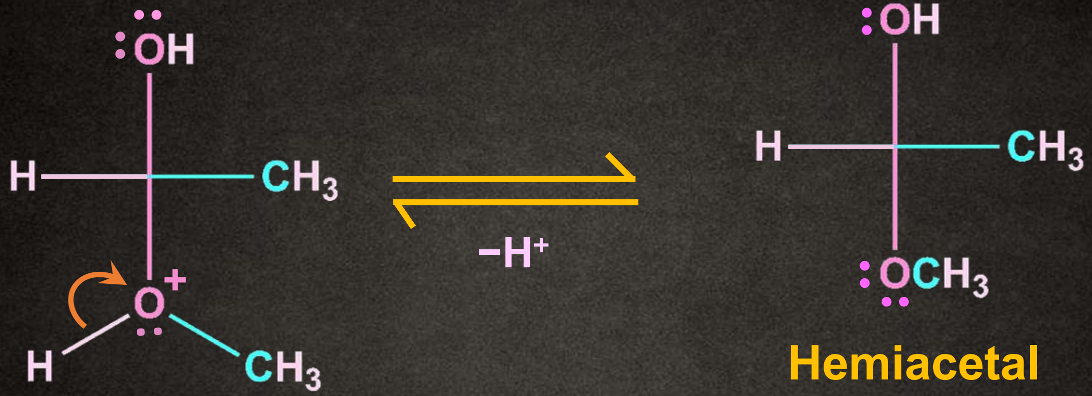


Steps Involved in Nucleophilic Addition of Alcohol

Step 1 **Formation of a hemiacetal**



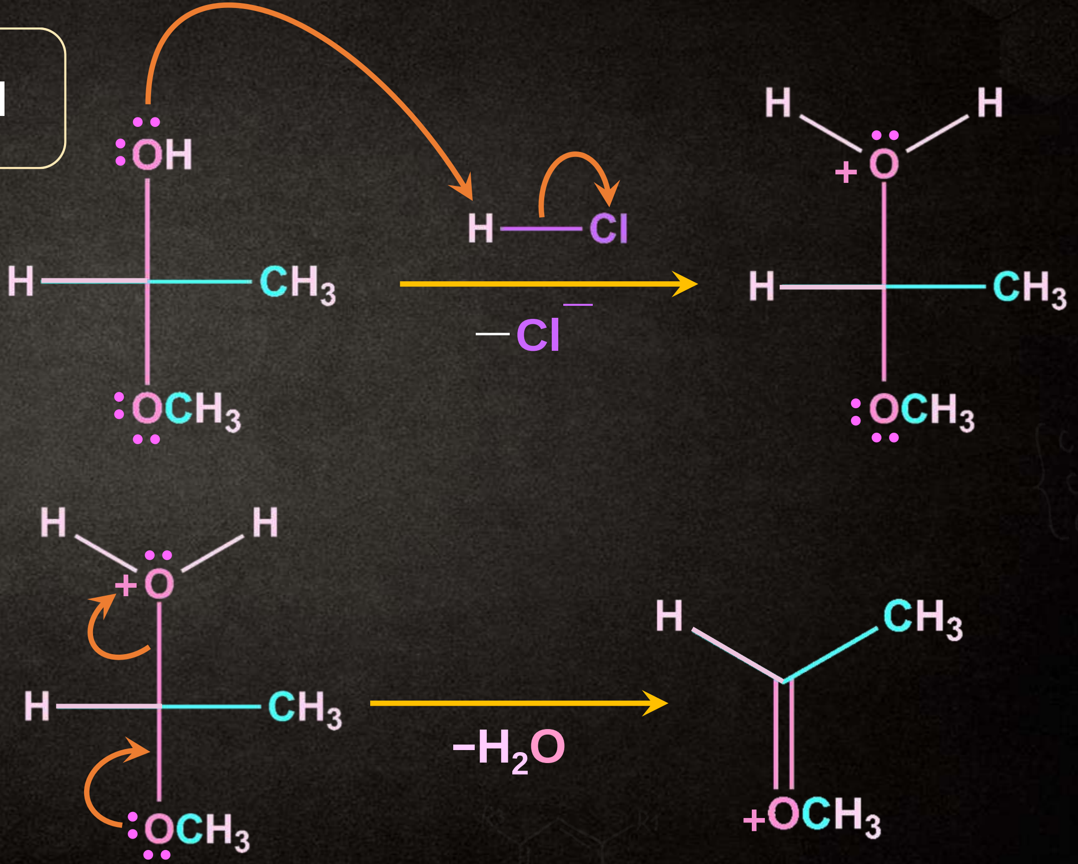
Formation of a Hemiacetal



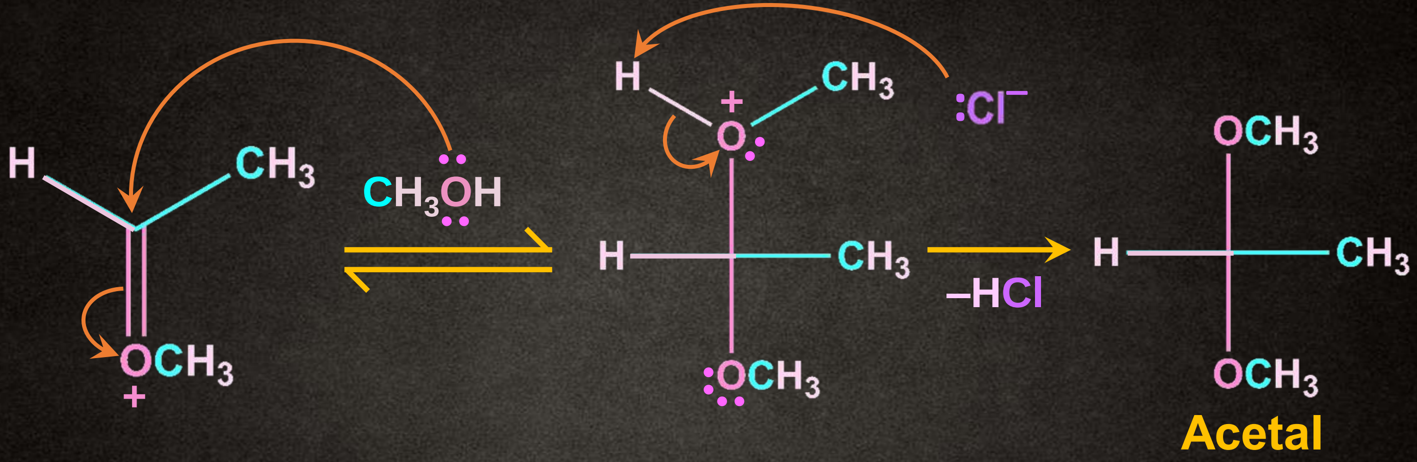
Hemiacetal

Formation of an Acetal

Step 2 Formation of an acetal



Formation of an Acetal



Note!

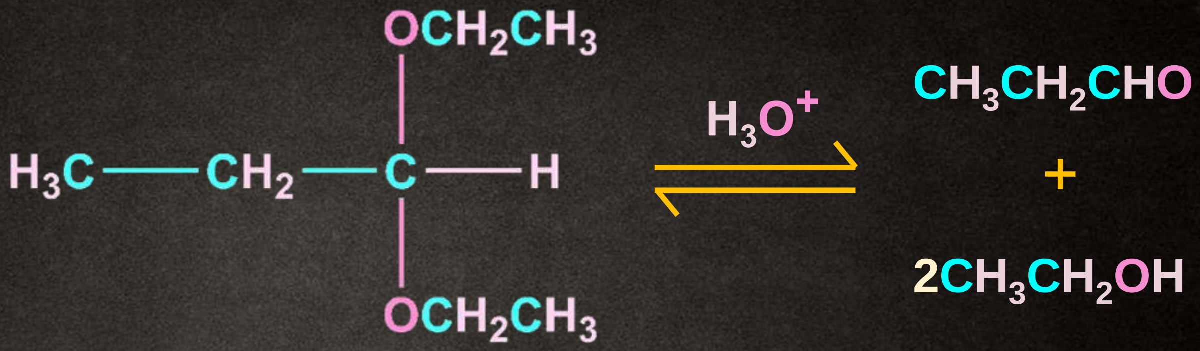
Generally,

Acyclic hemiacetals and hemiketals are **not stable in the aqueous phase**. Hence, they **cannot be isolated.**

Acetals and ketals **can be transformed back** to the respective aldehydes and ketones **by using mineral acids**.

Conversion of Acetals and Ketals

Example:



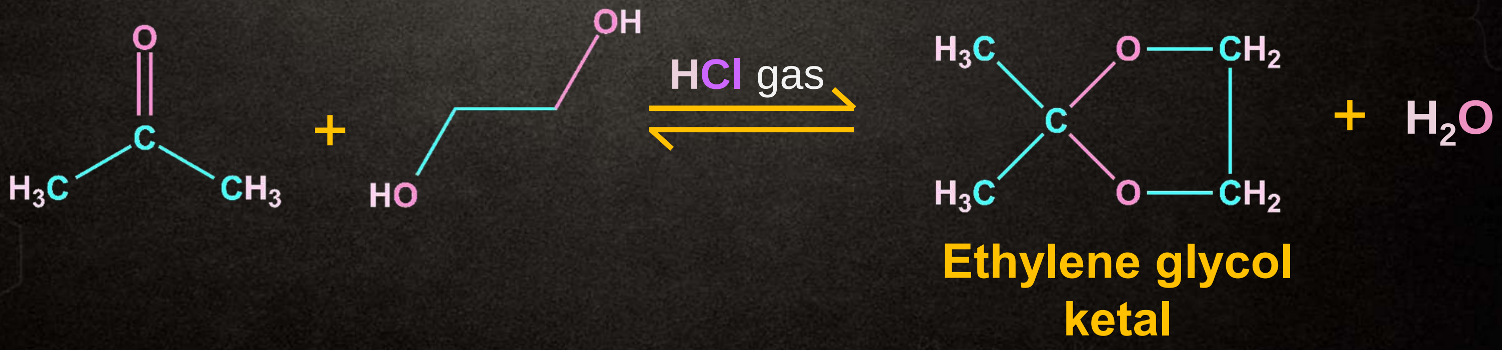
$$H_3C-CH_2-\underset{OCH_2CH_3}{\overset{OCH_2CH_3}{C}}-H \underset{}{\overset{H_3O^+}{\rightleftharpoons}} CH_3CH_2CHO + 2CH_3CH_2OH$$

Acetal

Nucleophilic Addition of Alcohol

Cyclic acetals and **ketals** are formed in the presence of **dihydric** or **trihydric alcohols.**

Example:



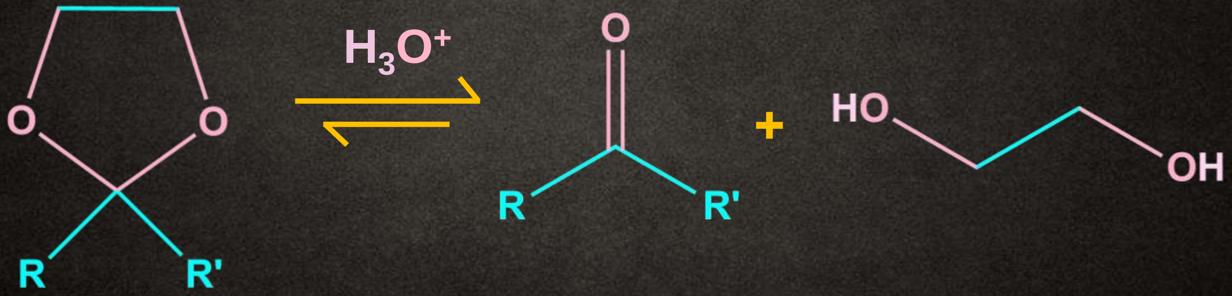
Ethylene glycol ketal

Trick to Remember!

Ethylene glycol ketal

Cyclic Acetals

Cyclic acetal too, can be **reversed** by treating the acetal with aqueous acid

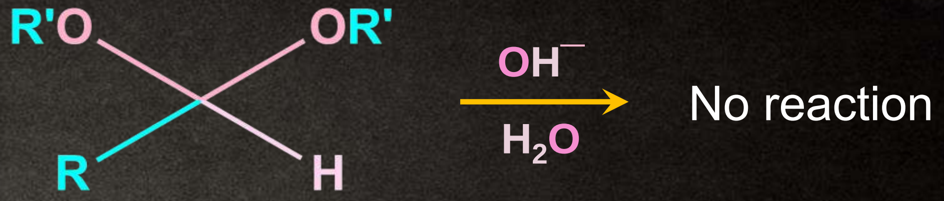


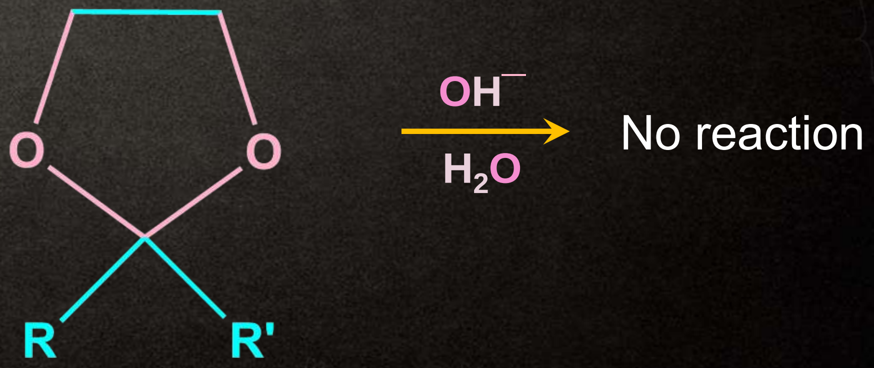
Acetals as Protecting Groups

Although acetals are hydrolysed to aldehydes and ketones in **aqueous acid**, acetals are **stable** in basic solutions

Acetals are used to protect aldehydes and ketones from undesired reactions in basic solutions.

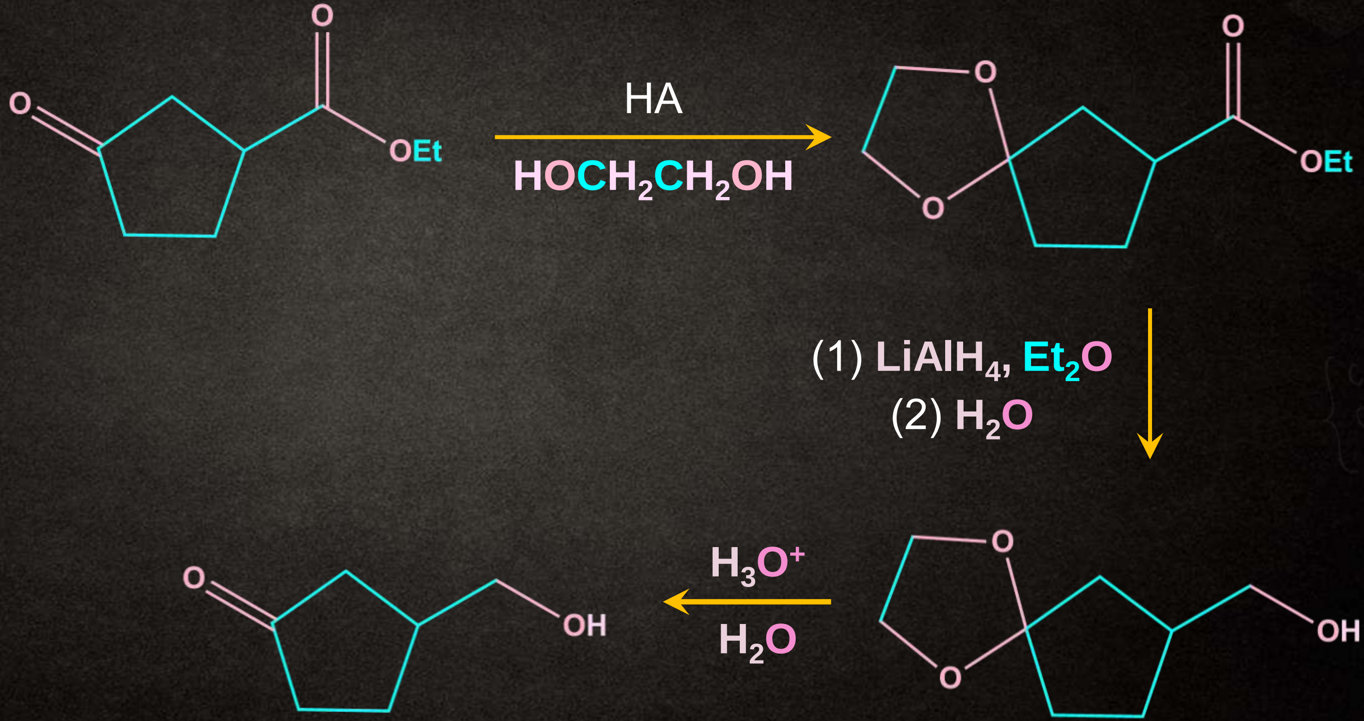
Protecting group





Acetals as Protecting Groups

EXAMPLE



HA

$HOCH_2CH_2OH$

(1) $LiAlH_4$, Et_2O

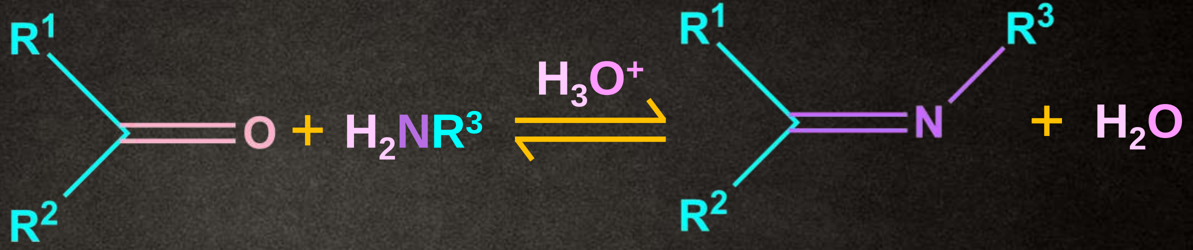
(2) H_2O

H_3O^+

H_2O

Addition of Ammonia and Its Derivatives

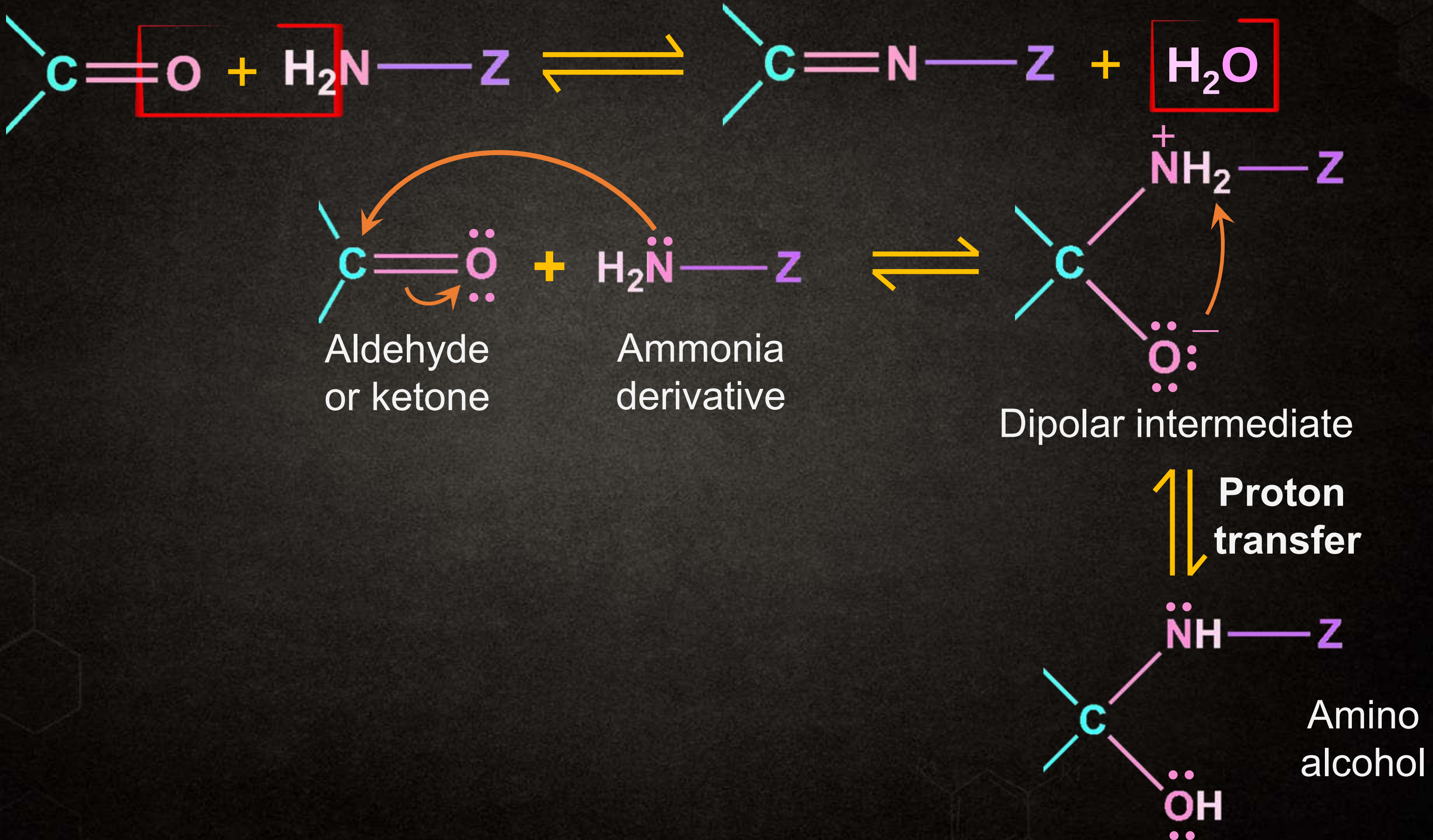
General reaction:



Aldehydes and ketones react with primary amines to form **imines.**

They have a **carbon–nitrogen double bond**

Addition-Elimination of Ammonia and Its Derivatives



$$C=O + H_2N-Z \rightleftharpoons C=N-Z + H_2O$$

Aldehyde or ketone

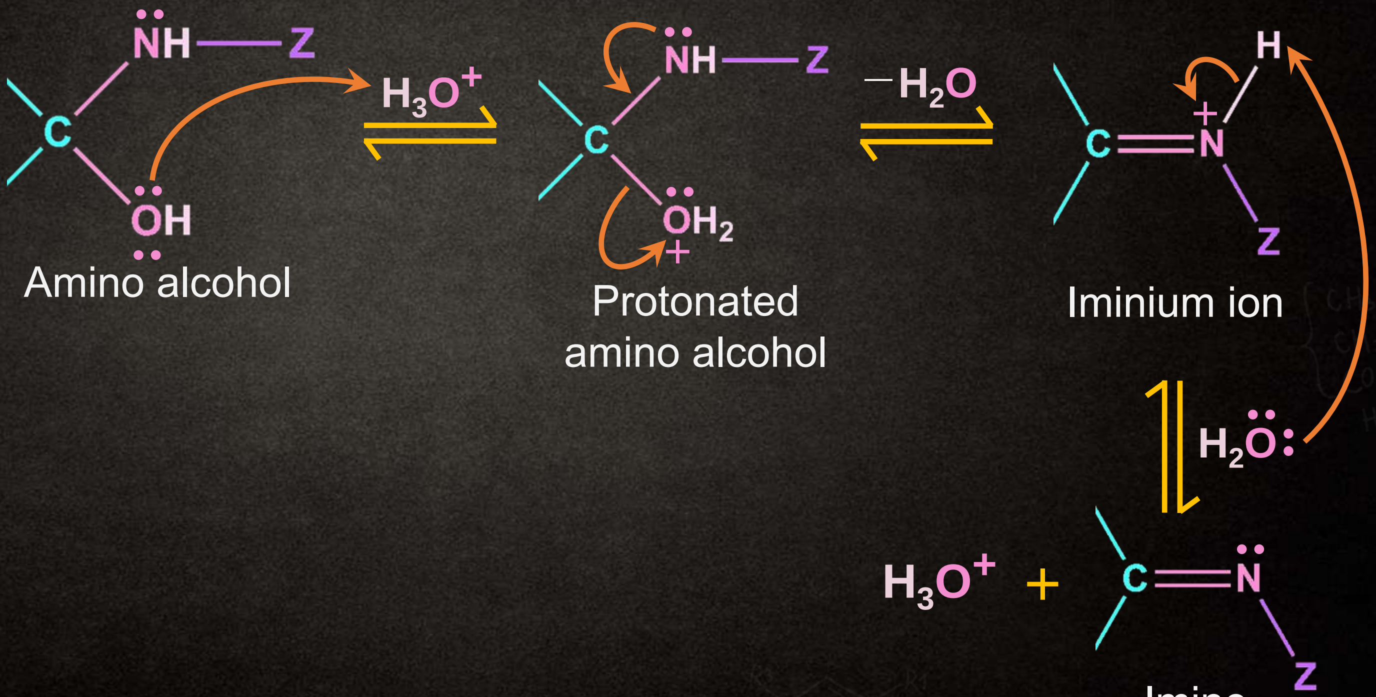
Ammonia derivative

Dipolar intermediate

Proton transfer

Amino alcohol

Addition of Ammonia and Its Derivatives



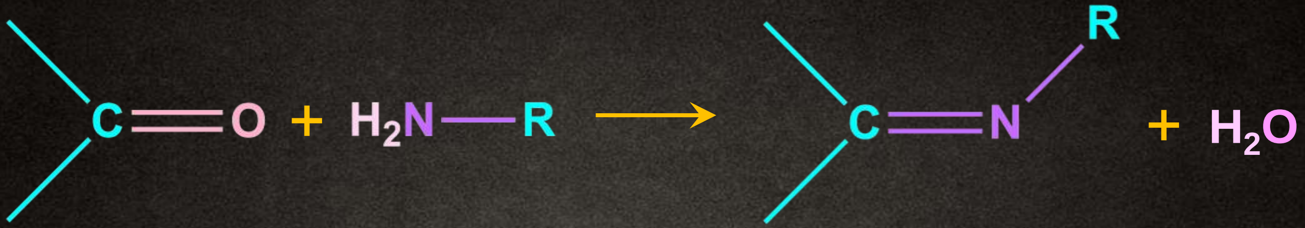
Amino alcohol

Protonated amino alcohol

Iminium ion

Imine

Imine



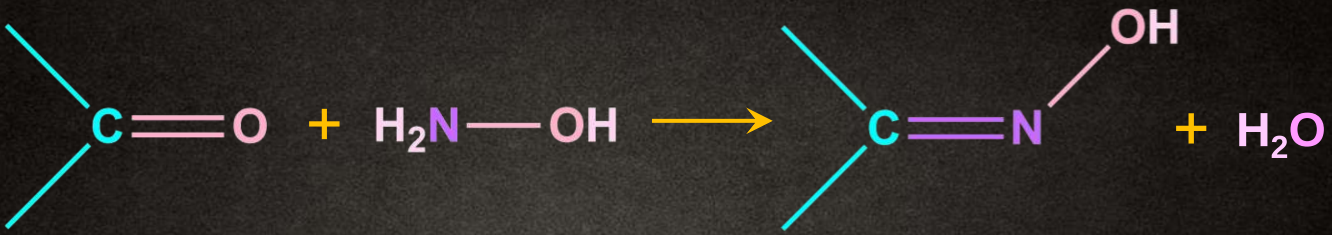
Aldehyde
or ketone

1° amine

Imine

Imine formation: Reaction with a primary amine

Oxime



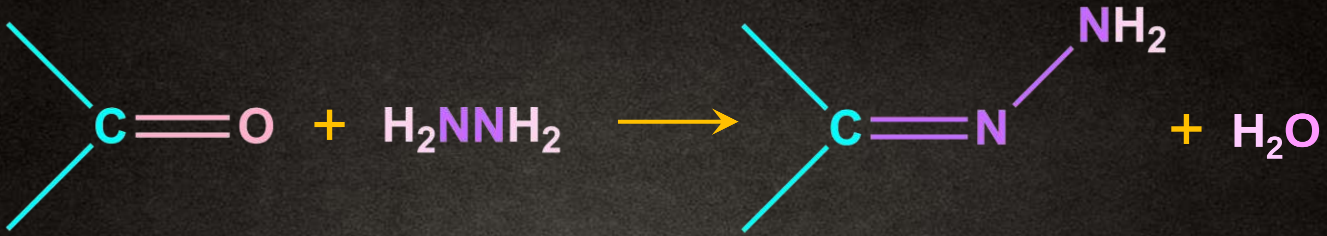
Aldehyde
or ketone

Hydroxylamine

An oxime

Oxime formation: Reaction with hydroxylamine

Hydrazone



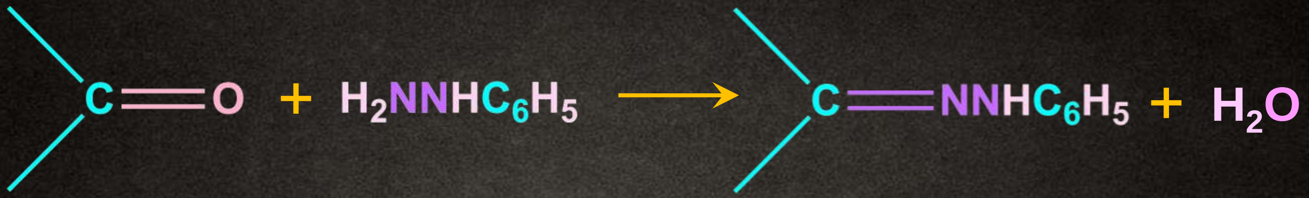
Aldehyde
or ketone

Hydrazine

A hydrazone

Hydrazone formation:
Reaction with hydrazine

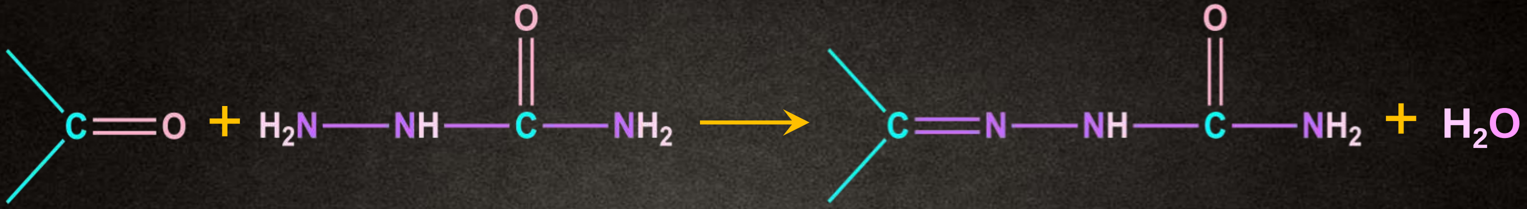
Phenylhydrazone



Phenylhydrazine A phenylhydrazone

Substituted hydrazone formation:
Reactions with phenylhydrazine

Semicarbazone

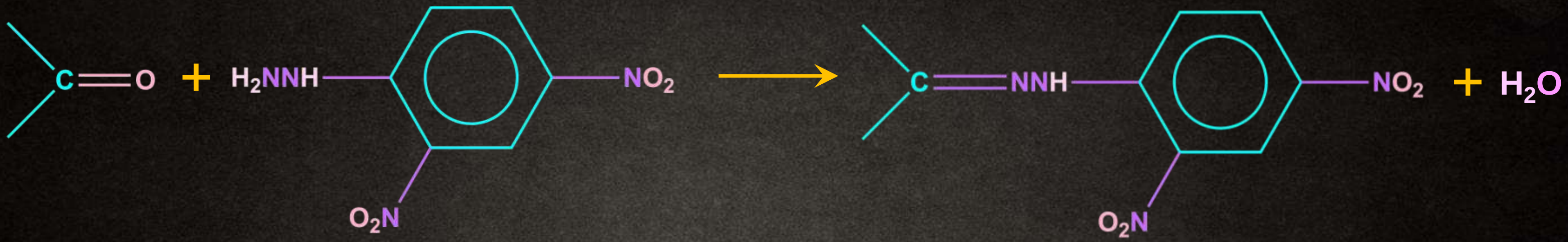


Semicarbazide

Semicarbazone

Semicarbazone formation:
Reactions with semicarbazide

2,4-Dinitrophenylhydrazone

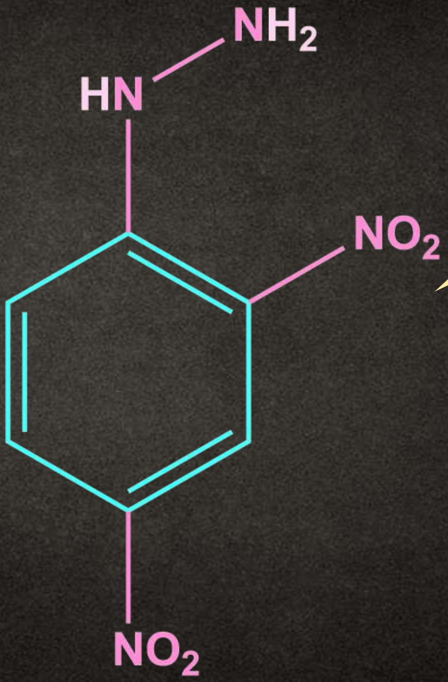


2,4-Dinitrophenylhydrazine

2,4-Dinitrophenylhydrazone

Substituted hydrazone formation:
Reactions with 2,4-dinitrophenylhydrazine

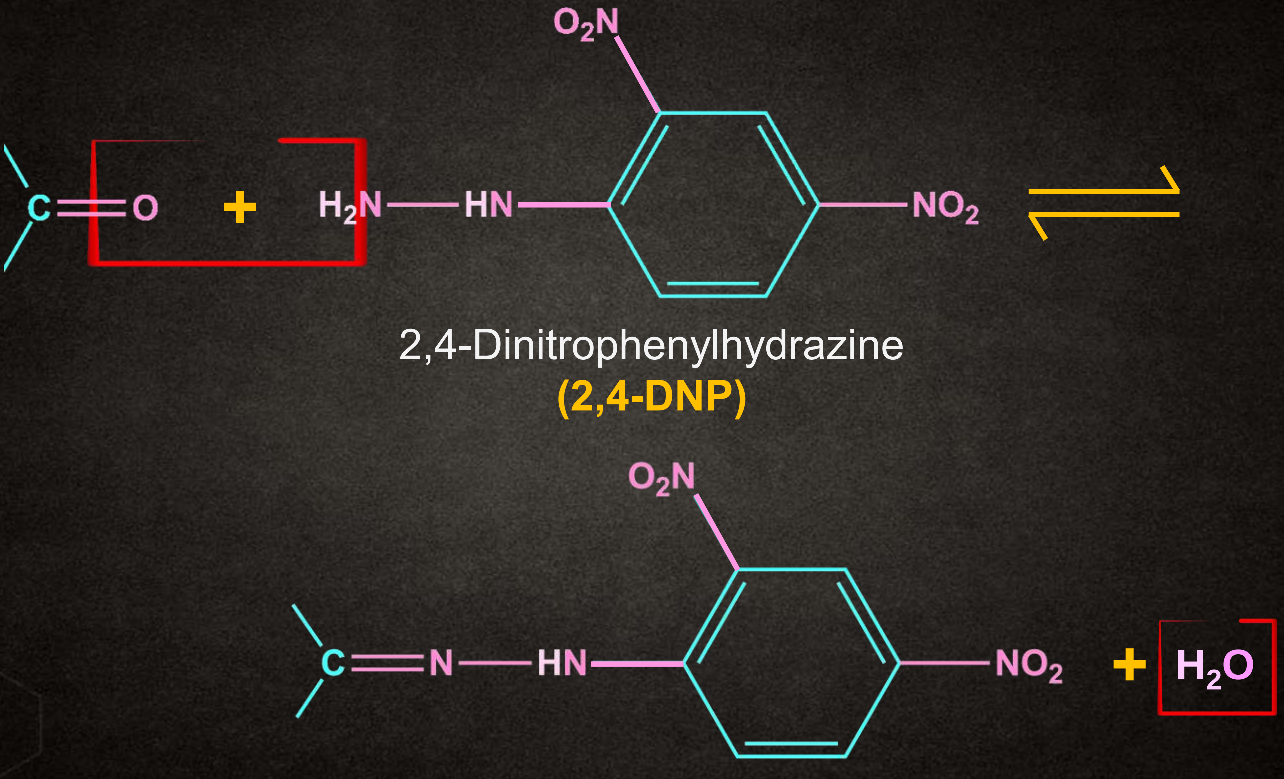
Structure of 2,4-DNP



2,4-Dinitrophenylhydrazine

Used for **identification** of aldehydes and ketones

Addition of Ammonia and Its Derivatives



2,4-Dinitrophenylhydrazine

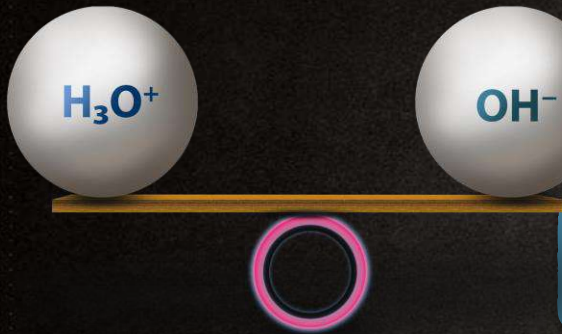
(2,4-DNP)

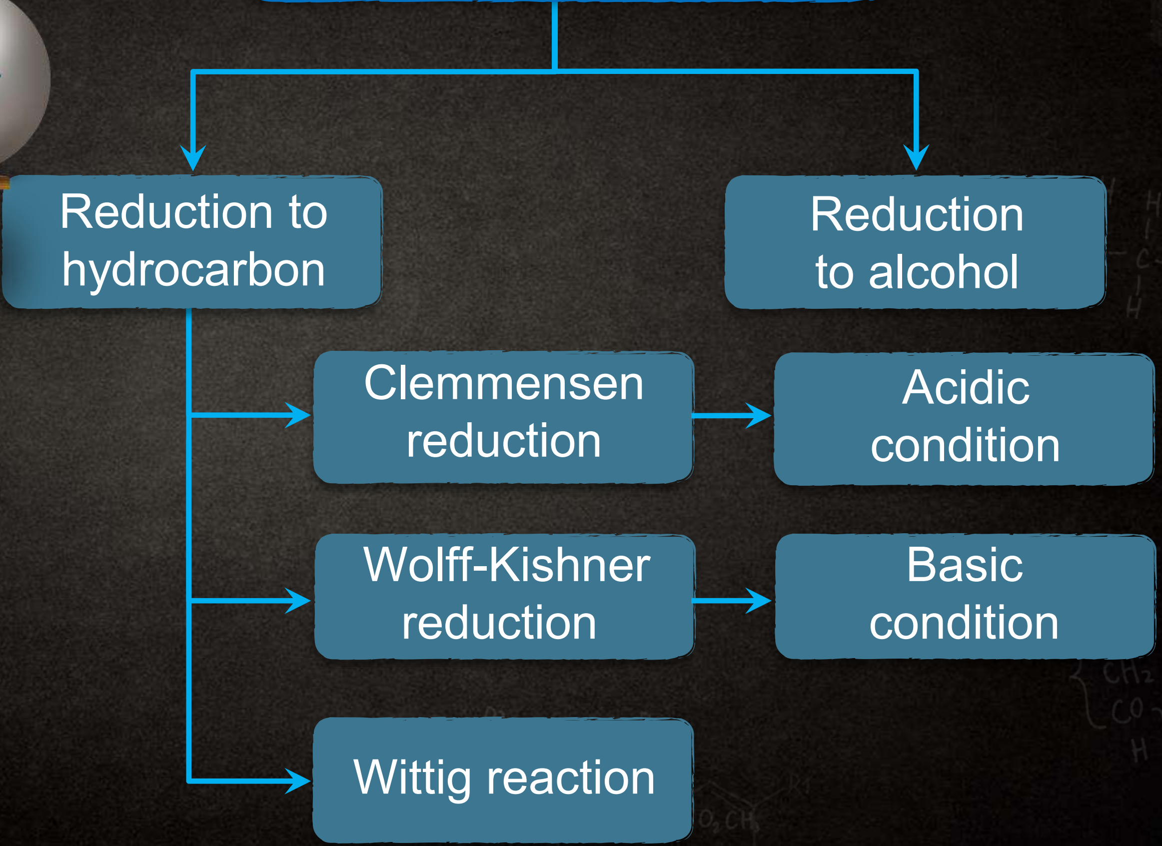
2,4-Dinitrophenylhydrazone

2,4-DNP Test

2,4-DNP derivatives are **yellow**, **orange**, or **red** solids **used for the detection of aldehydes and ketones** among the mixture of organic compounds.

Reduction of aldehydes and ketones

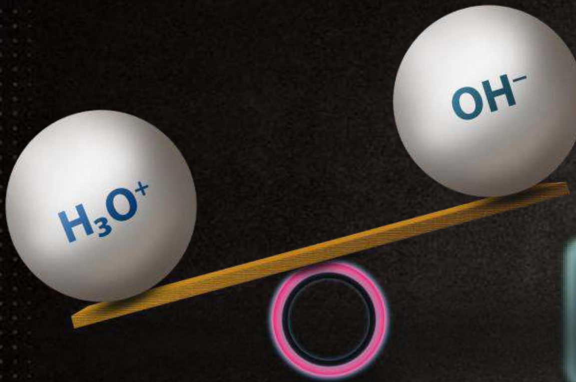




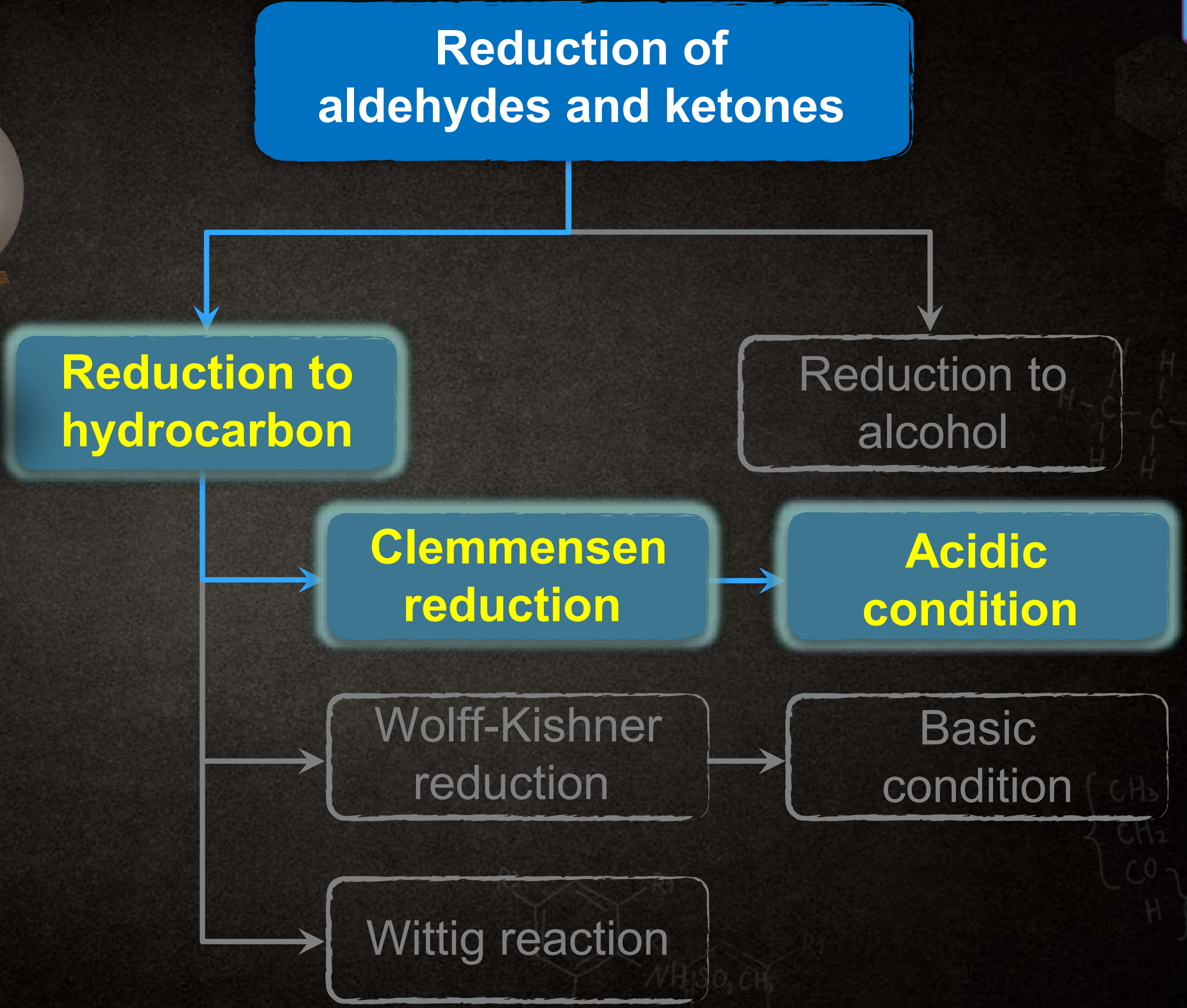
Reduction to hydrocarbon

- Clemmensen reduction → Acidic condition
- Wolff-Kishner reduction → Basic condition
- Wittig reaction

Reduction to alcohol



Reduction of aldehydes and ketones



Reduction to hydrocarbon

Reduction to alcohol

Clemmensen reduction → Acidic condition

Wolff-Kishner reduction → Basic condition

Wittig reaction

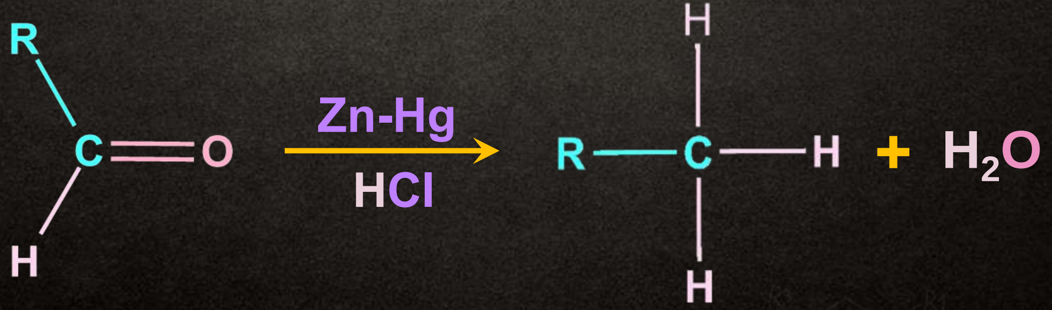
Clemmensen Reduction

Aldehyde/Ketone

Hydrocarbon

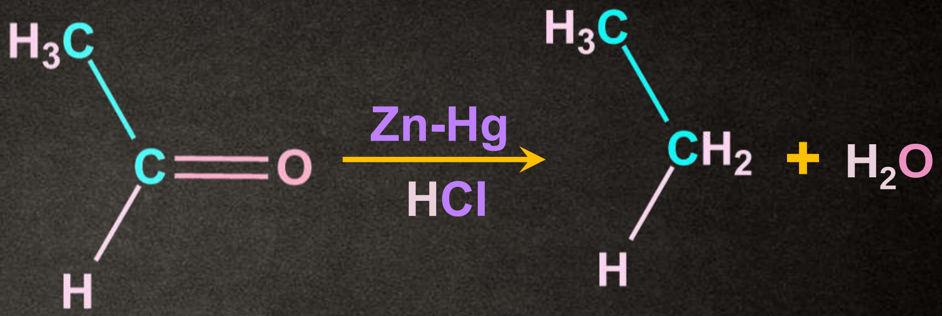
Reagents used → Zn-Hg, HCl

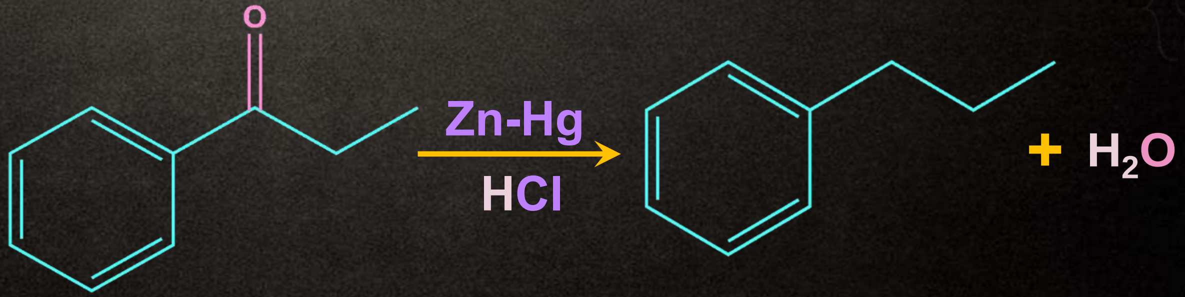
General reaction



Clemmensen Reduction

EXAMPLE





Note!

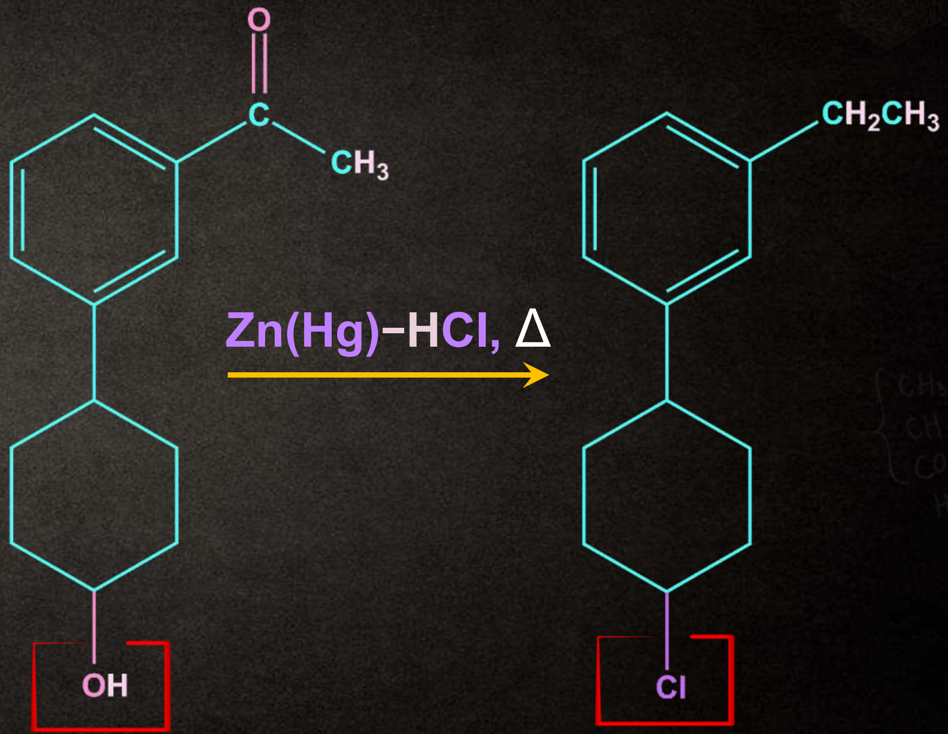
Due to the presence of **acidic conditions (Zn-Hg/HCl), Clemmensen reduction** fails for **acid-sensitive** substrates. For these cases, **Wolff-Kishner reduction** is quite useful.

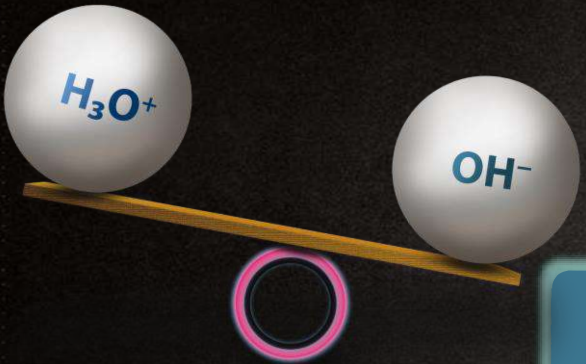
Eg: –OH

Clemmensen Reduction

EXAMPLE

This is not a good method to reduce carbonyl for acid sensitive substrates.





Reduction of aldehydes and ketones

- **Reduction to hydrocarbon**
  - Clemmensen reduction → Acidic condition
  - **Wolff-Kishner reduction** → **Basic condition**
  - Wittig reaction
- Reduction to alcohol

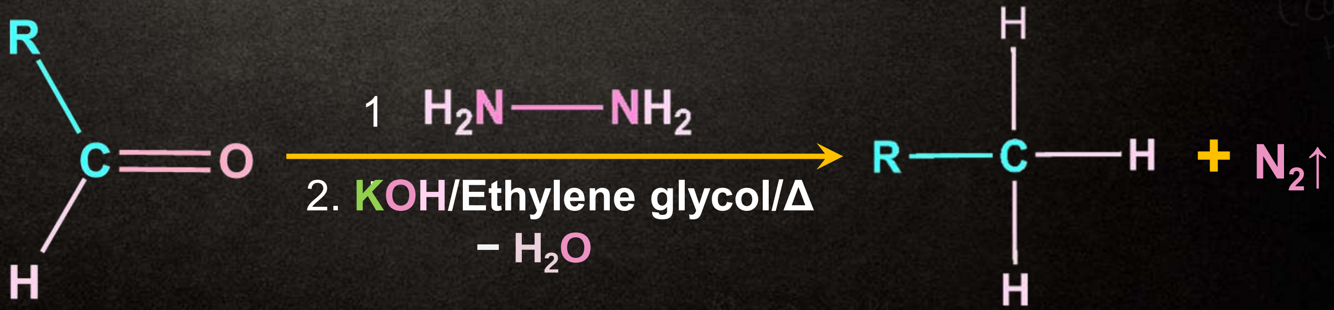
Wolff-Kishner Reduction

Aldehyde/Ketone

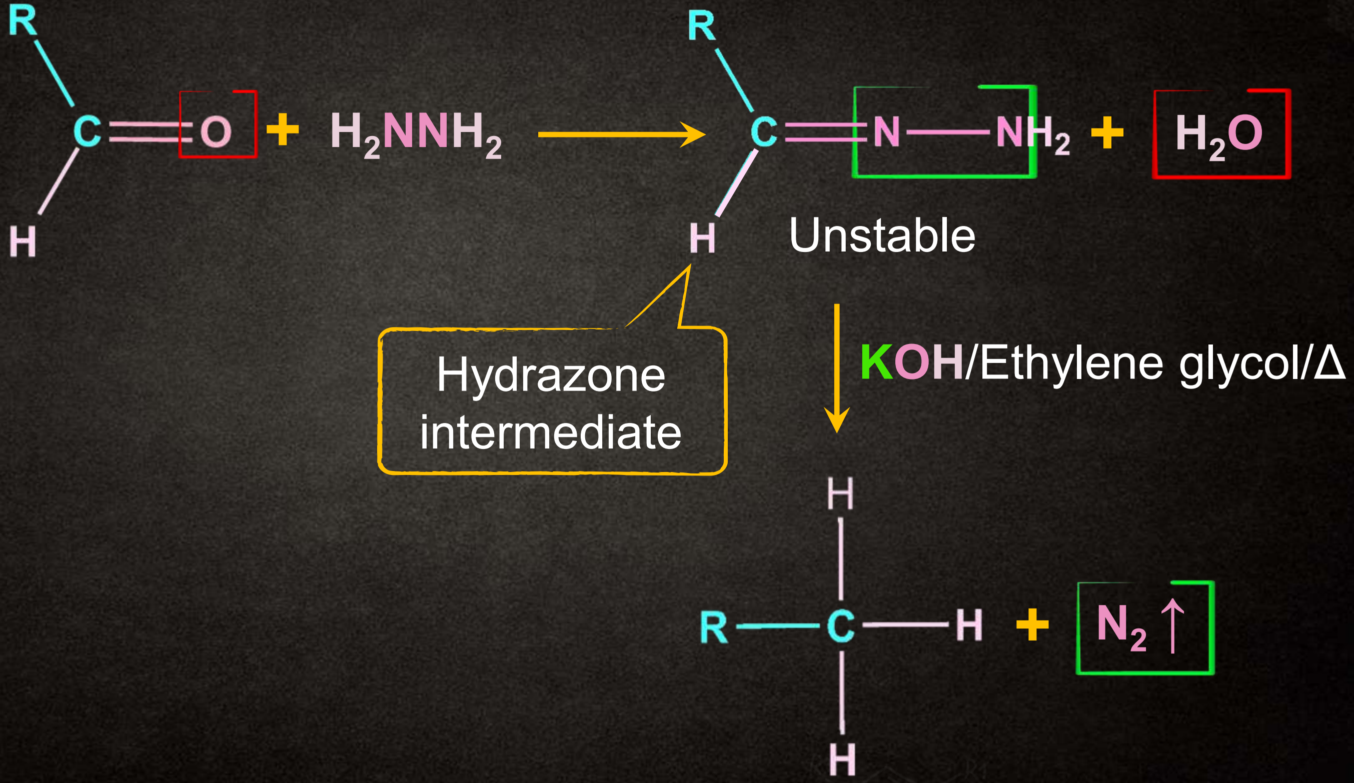
Hydrocarbon

Reagents used → NH_2NH_2, KOH/Δ

General reaction



Wolff-Kishner Reduction



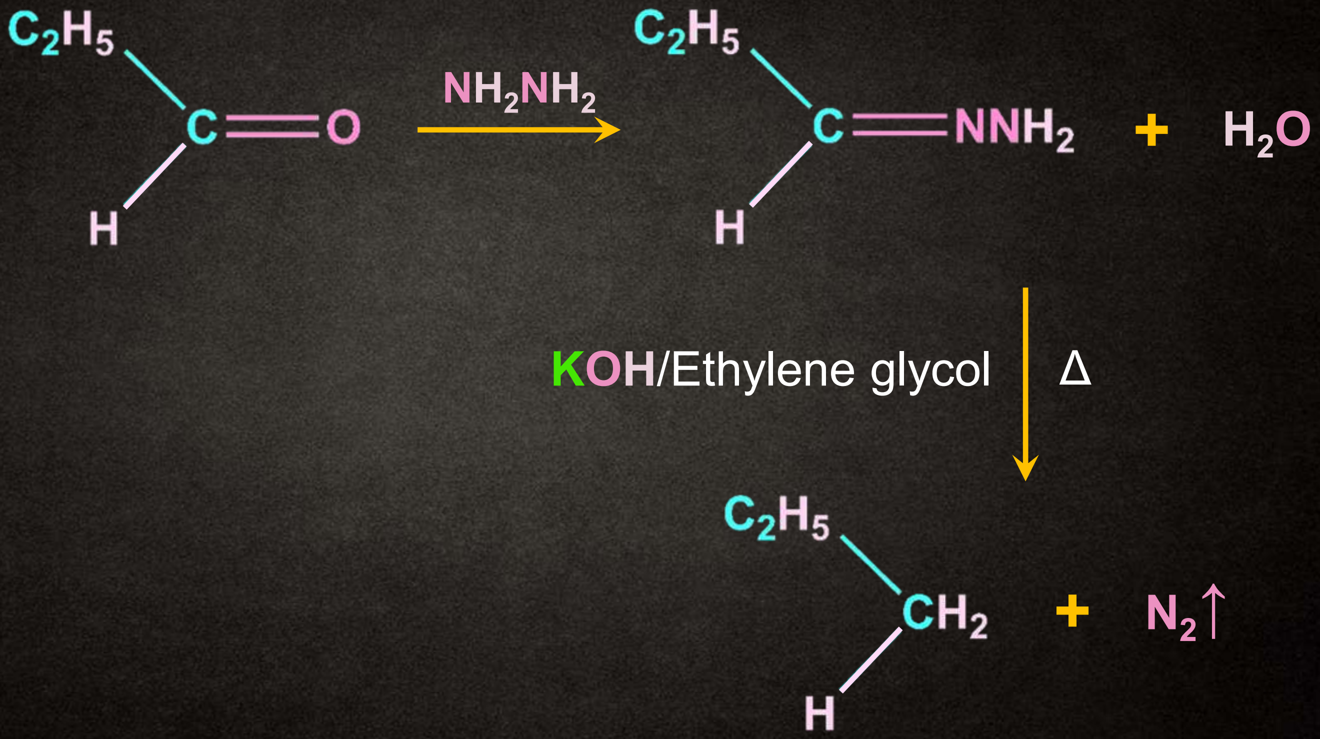
Unstable

Hydrazone intermediate

KOH/Ethylene glycol/Δ

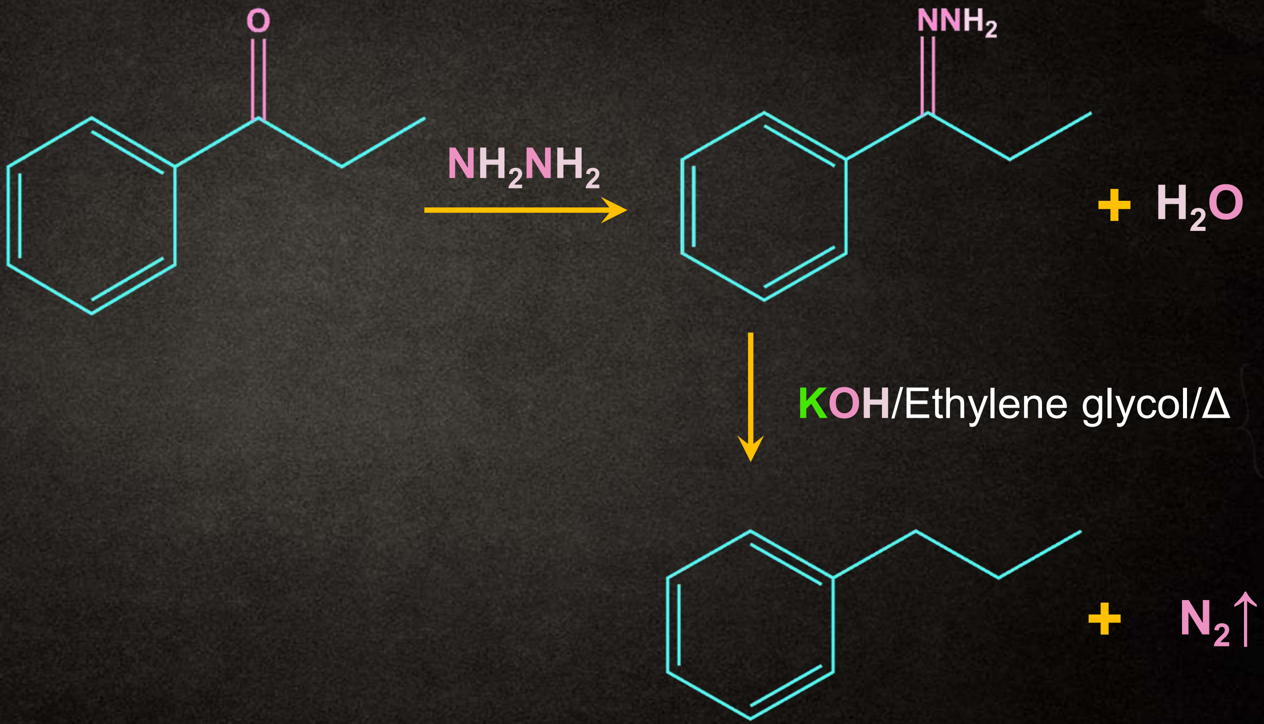
Wolff-Kishner Reduction

EXAMPLE



Wolff-Kishner Reduction

EXAMPLE



NH_2NH_2

$+ H_2O$

KOH/Ethylene glycol/Δ

$+ N_2\uparrow$

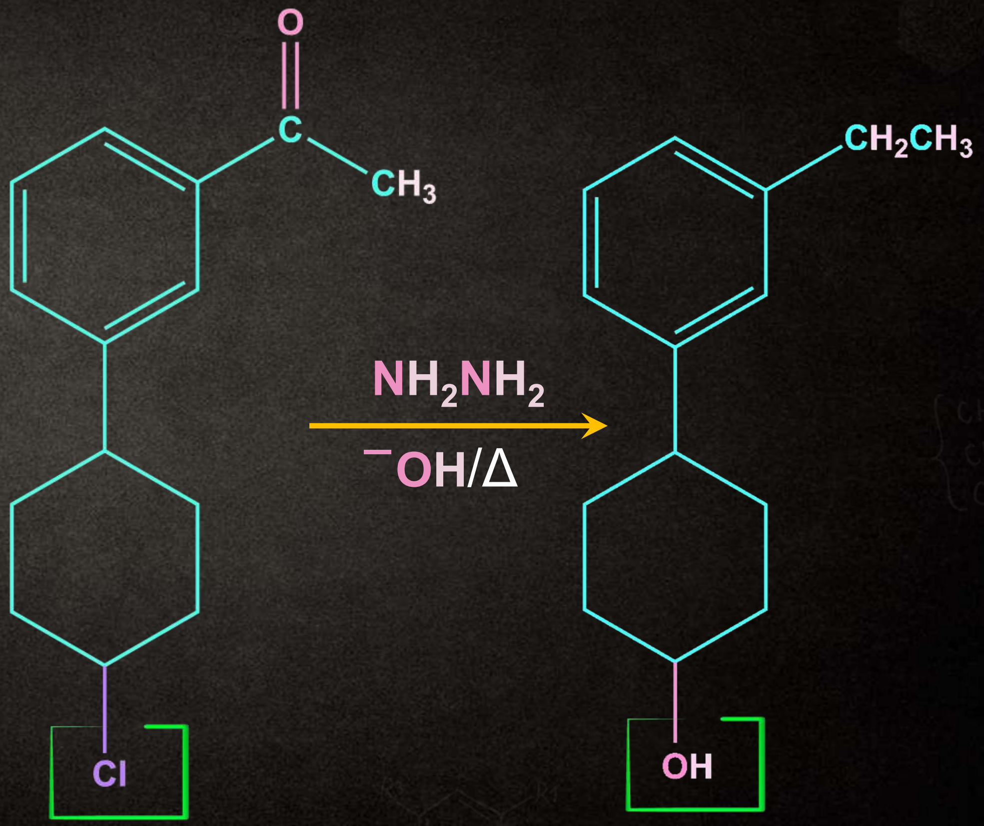
Note!

Eg: **-Cl**, **-COOH**

Due to the presence of **basic conditions (NH_2NH_2/KOH)**, Wolff-Kishner reduction **fails for base-sensitive substrates.** In these cases, we use **Clemmensen reduction.**

Wolff-Kishner Reduction

EXAMPLE



Reduction to Alcohol

$$\text{Aldehyde} \xrightarrow[\text{Reduction}]{[H]} 1^\circ \text{ alcohol}$$

$$\text{Ketone} \xrightarrow[\text{Reduction}]{[H]} 2^\circ \text{ alcohol}$$

General reaction

Aldehyde

Primary alcohol

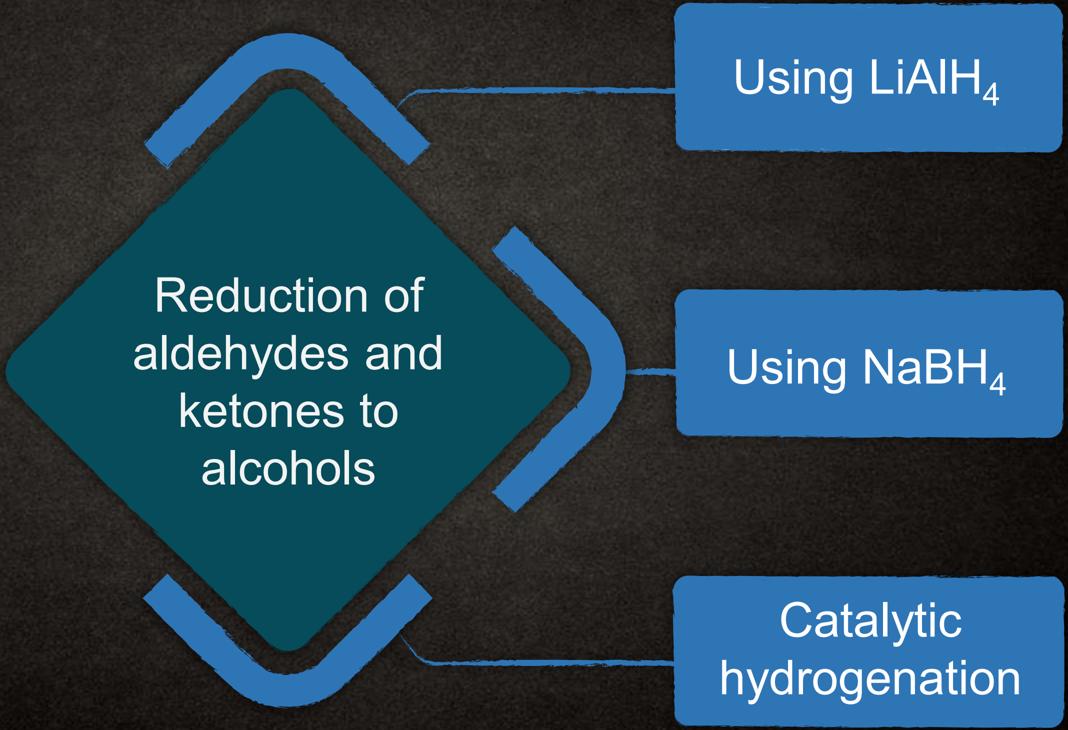
Reduction to Alcohol

General reaction

Ketone

2° alcohol

Reduction to Alcohol



Reduction of aldehydes and ketones to alcohols

Using $LiAlH_4$

Using $NaBH_4$

Catalytic hydrogenation

Recall!

Reduced by **$NaBH_4$**

Not reduced by **$NaBH_4$**

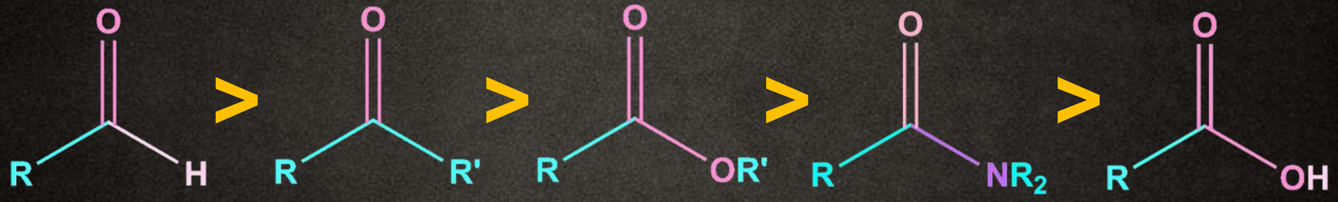
Aldehyde

Ketone

Ester

Amide

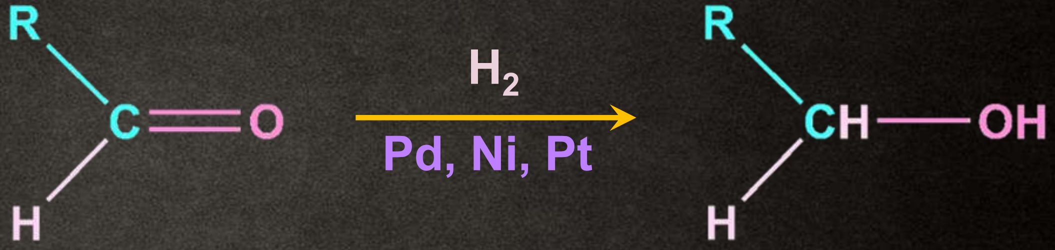
Carboxylic acid



Reduced by **$LiAlH_4$**

Catalytic Hydrogenation

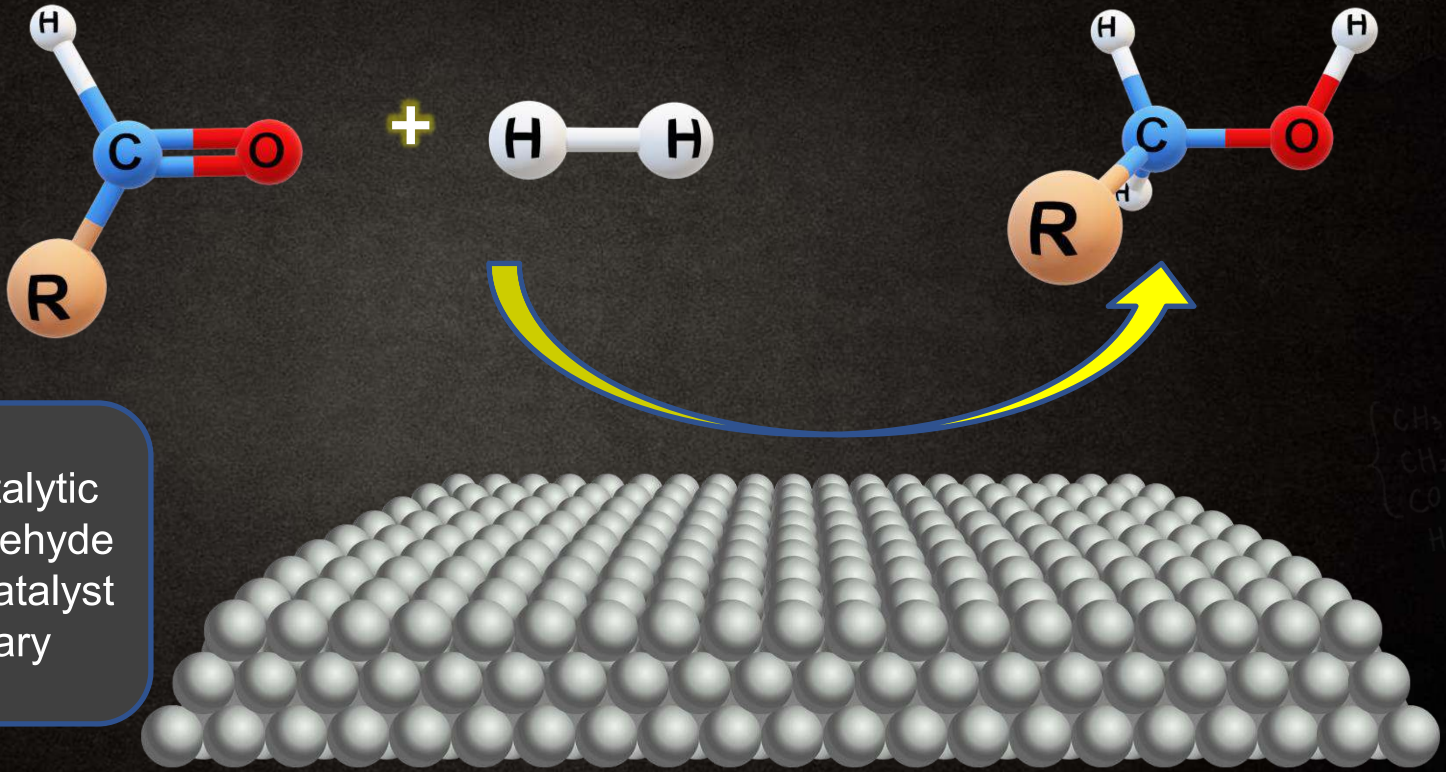
General reaction



Aldehyde

1° alcohol

Catalytic Hydrogenation

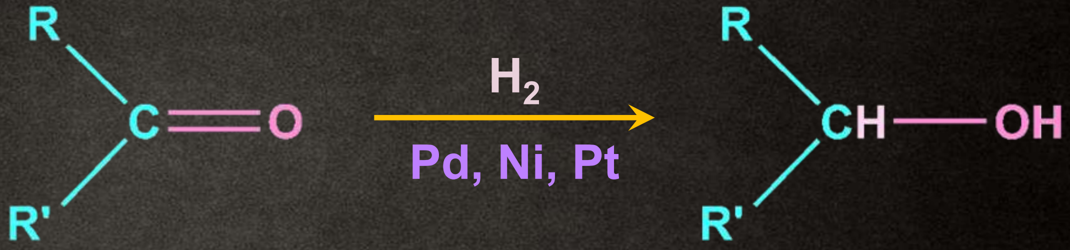


General pictorial representation of catalytic hydrogenation of aldehyde when passed over catalyst surface to form primary alcohol.

Catalyst bed

Catalytic Hydrogenation

General reaction

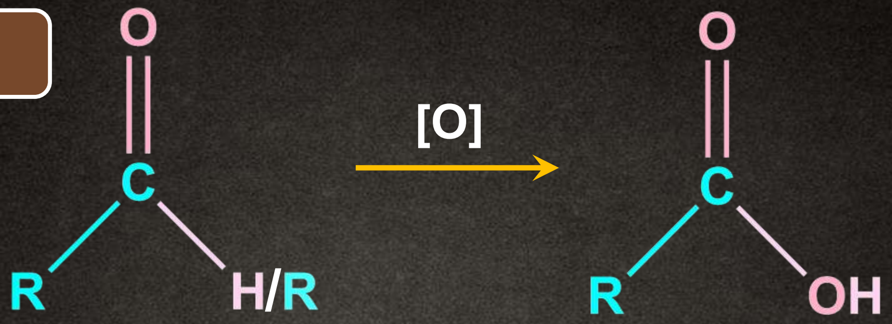


Ketone

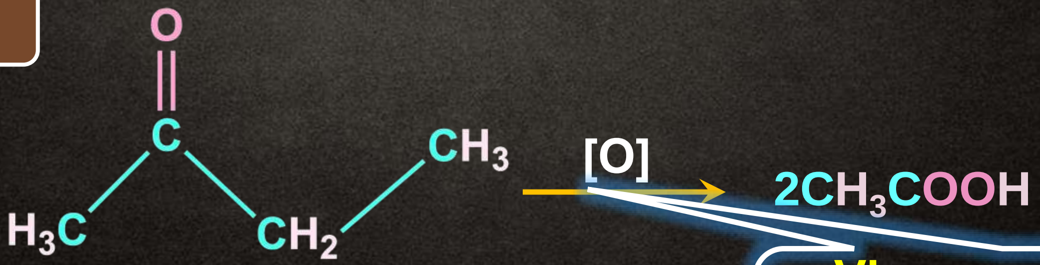
2° alcohol

Oxidation of Aldehyde and Ketone

Oxidation of Aldehydes



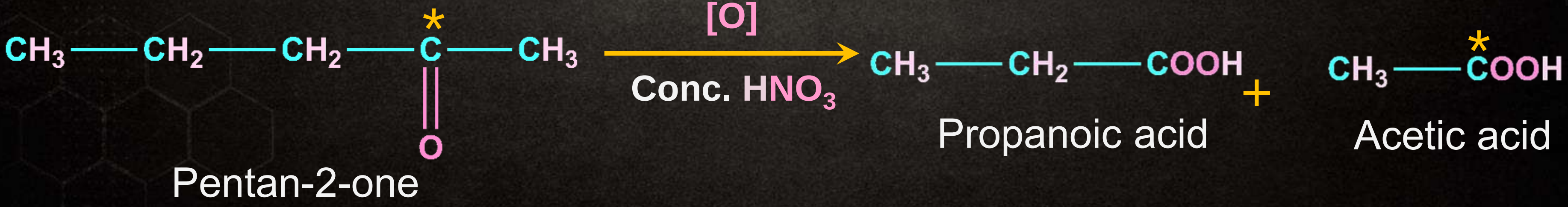
Oxidation of Ketone



Vigorous oxidation
(strong oxidant at elevated temperature)

Popoff's Rule

The rule states that
during the **oxidation of unsymmetrical** ketone,
the cleavage of the **C–CO bond**
happens in such a way that
the **keto group is always**
with the smaller alkyl group.



$$CH_3-CH_2-CH_2-\overset{*}{\underset{\underset{O}{\|}}{C}}-CH_3 \xrightarrow[\text{Conc. } HNO_3]{[O]} CH_3-CH_2-COOH + CH_3-\overset{*}{C}OOH$$

Pentan-2-one

Propanoic acid

Acetic acid

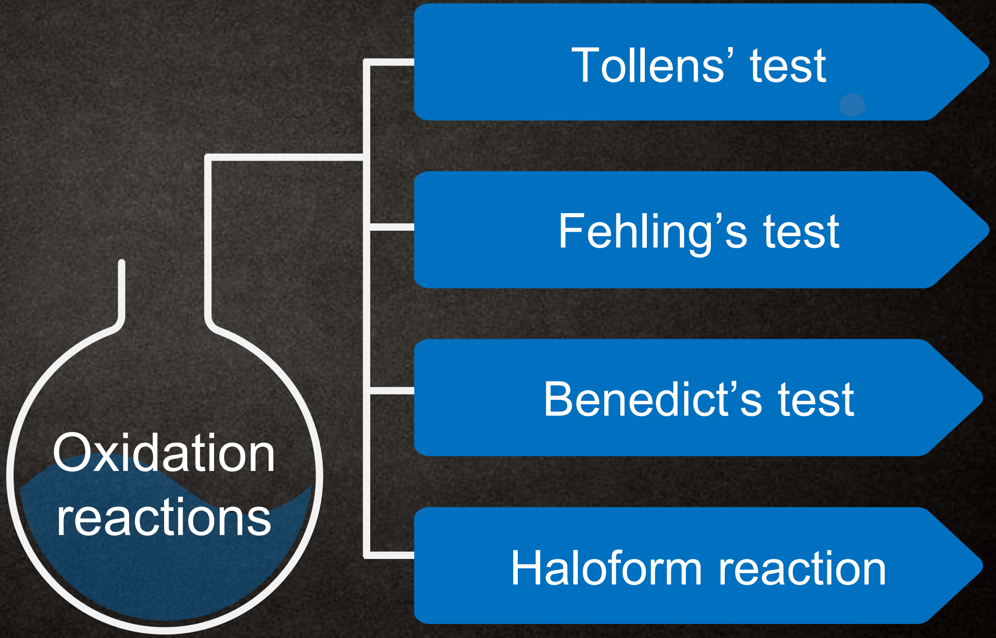
Oxidation of Aldehyde

$$\text{RCHO} \xrightarrow{[O]} \text{RCOOH}$$

Oxidation of an aldehyde to an acid can be done with a **strong** oxidising agent such as **$KMnO_4$, HNO_3, $K_2Cr_2O_7$**

Also, with **mild** oxidising agents like **Tollens'** and **Fehling's reagents**

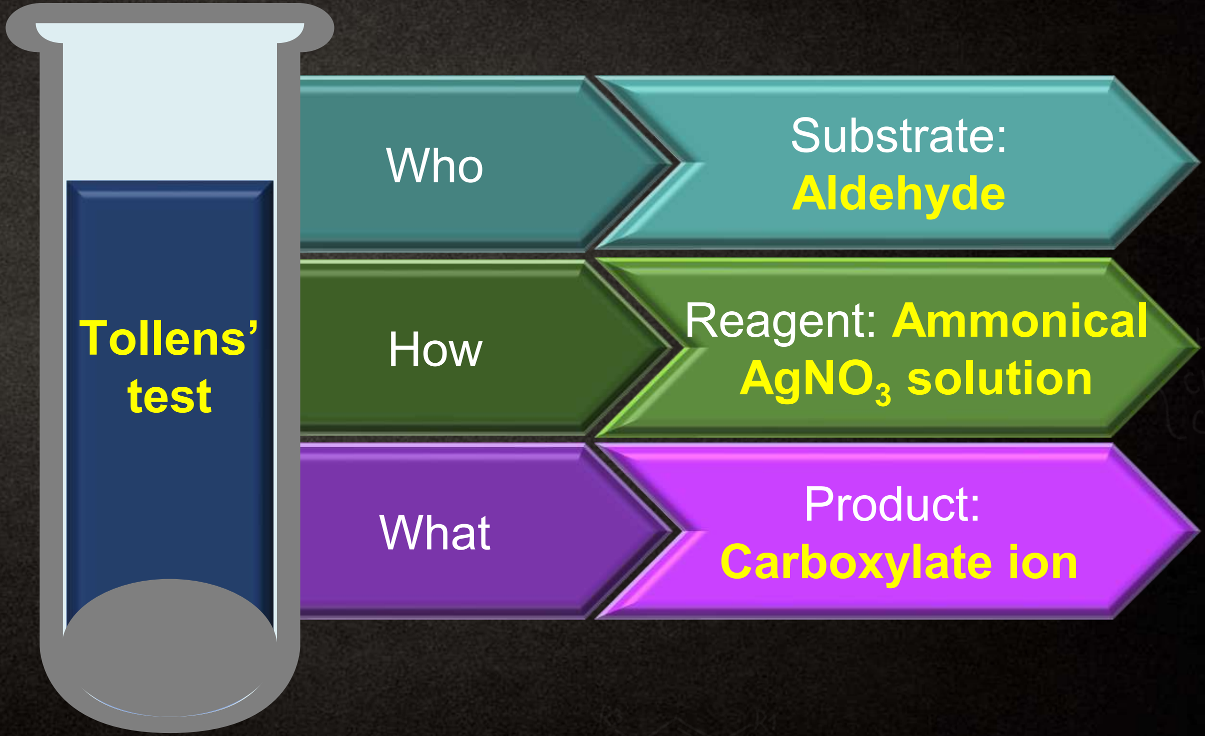
Oxidation Reactions of Aldehydes and Ketones



Oxidation reactions

- Tollens' test
- Fehling's test
- Benedict's test
- Haloform reaction

Tollens' Test



Tollens' test

Who — Substrate: **Aldehyde**

How — Reagent: **Ammonical $AgNO_3$ solution**

What — Product: **Carboxylate ion**

Tollens' Test

General reaction

$$\underset{\text{Aldehyde}}{RCHO} + \underset{\text{Tollens' reagent}}{2[Ag(NH_3)_2]^+} + 3OH^-$$

$$\downarrow$$

$$\underset{\text{Carboxylate anion}}{RCOO^-} + \underset{\text{Silver mirror}}{2Ag\downarrow} + 2H_2O + 4NH_3$$

This reaction is also known as **silver mirror test**

Preparation of Tollens’ Reagent

$$2Ag(NO_3) + 2NH_4OH \longrightarrow Ag_2O + 2NH_4(NO_3) + H_2O$$

Silver nitrate

Ammonium
hydroxide

$$Ag_2O + 4NH_4OH \longrightarrow 2[Ag(NH_3)_2]^{+}OH^{-} + 3H_2O$$

Tollens’
reagent

Oxidation of Aldehyde by Tollens' Reagent

$$2[Ag(NH_3)_2]^+ + 3OH^- \xrightarrow{\text{Reduced to}} 2Ag\downarrow$$

Tollens' reagent

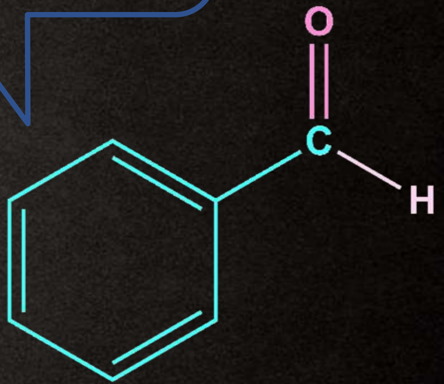
Silver mirror

$$RCHO \xrightarrow{\text{Oxidised to}} RCOO^-$$

Aldehyde

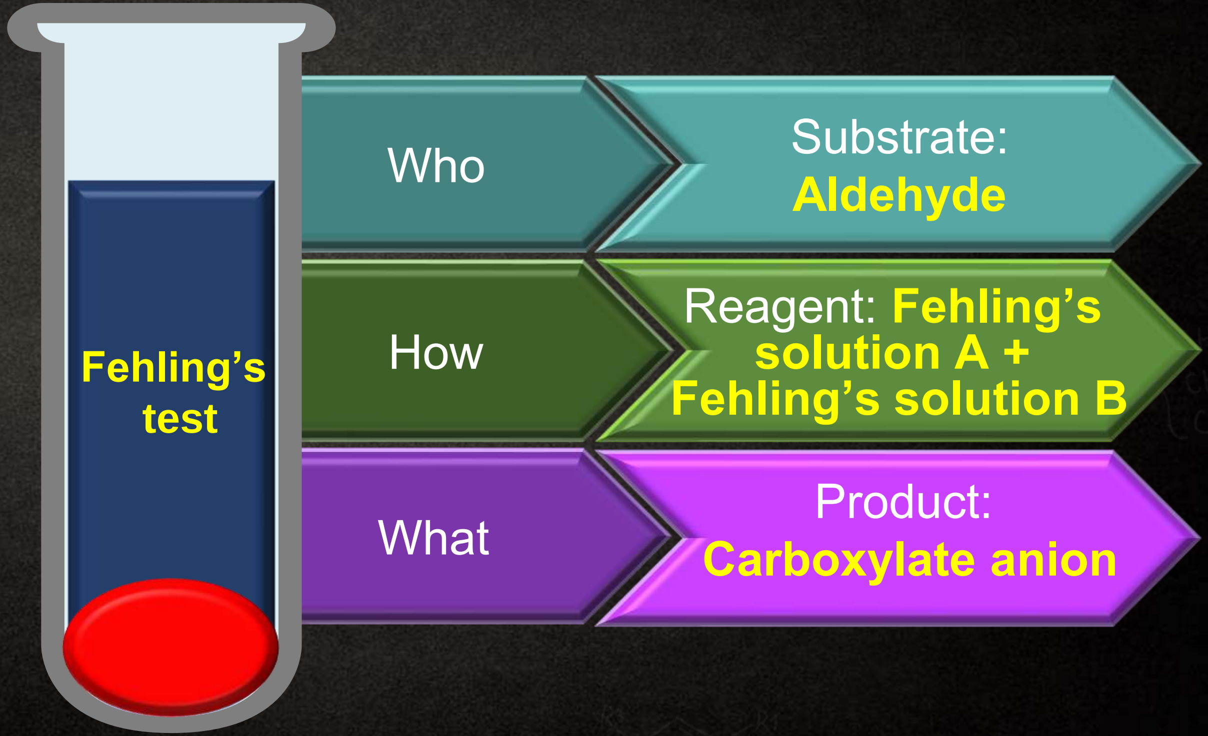
Carboxylate anion

Gives **positive** **Tollen's test**



All aromatic aldehydes give **Tollens' test.**

Fehling’s Test



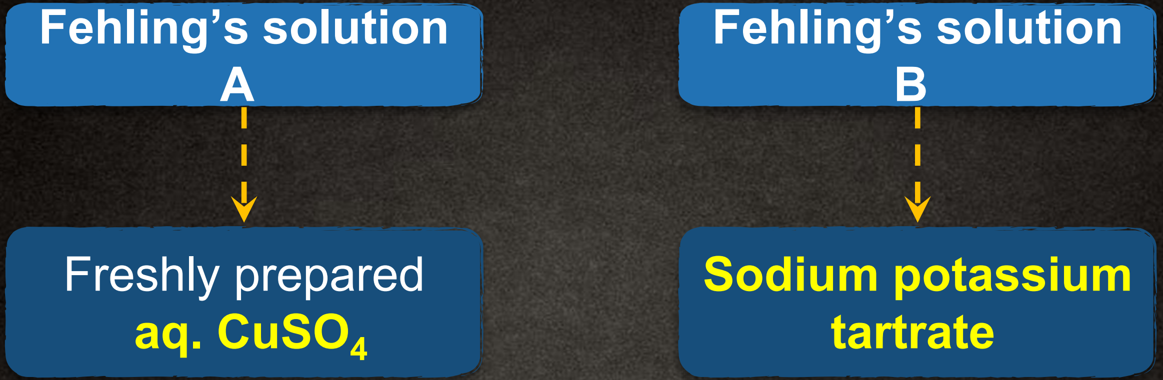
Fehling’s test

Who — Substrate: **Aldehyde**

How — Reagent: **Fehling’s solution A + Fehling’s solution B**

What — Product: **Carboxylate anion**

Fehling's Test



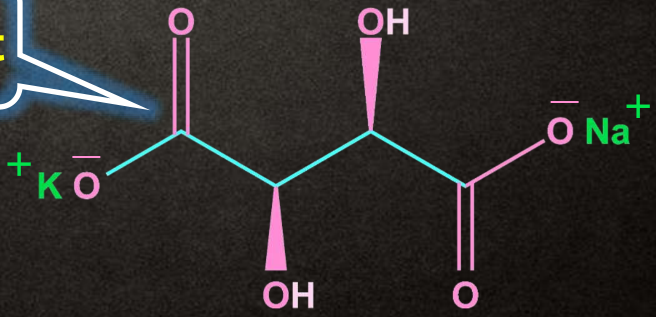
Fehling's solution A

Freshly prepared **aq. $CuSO_4$**

Fehling's solution B

Sodium potassium tartrate

Rochelle's salt



Fehling's Test

General reaction

$RCHO$ + $2Cu^{2+}$ + $5OH^{-}$

Aldehyde

Fehling's solution

$$\downarrow$$

$RCOO^{-}$ + $Cu_2O\downarrow$ + $3H_2O$

Carboxylate anion

Red-brown ppt

Fehling's Test

$$\mathrm{RCHO} \xrightarrow{\text{Oxidised to}} \mathrm{RCOO^-}$$

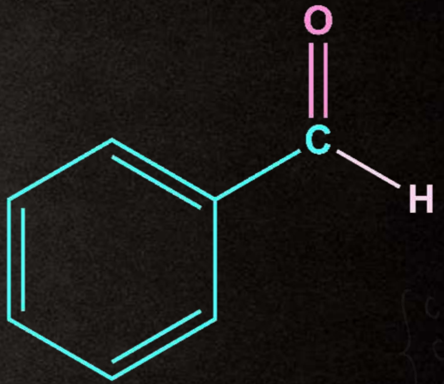
Aldehyde

Carboxylate anion

$$\mathrm{2Cu^{2+}} \xrightarrow{\text{Reduced to}} \mathrm{Cu_2O}\downarrow$$

Red-brown ppt

Does not give Fehling's test



All aromatic aldehydes
do not give Fehling's test

Benedict's Test

General reaction

$$\underset{\text{Aldehyde}}{RCHO} + \underset{\text{Benedict's reagent}}{Cu(Citrate)_2^{2-}} + 5OH^{-}$$

$$\downarrow$$

$$\underset{\text{Carboxylate anion}}{RCOO^{-}} + \underset{\text{Brick red ppt}}{Cu_2O\downarrow} + 3H_2O$$

$$\text{Aq. } CuSO_4 + \textbf{Sodium citrate}$$

$$\downarrow$$

$$Cu(Citrate)_2^{2-}$$

Benedict's reagent

Blue colour

Trick to Remember!

$$2Cu^{2+} \xrightarrow{\text{Reduction}} Cu_2O$$

$$RCHO \xrightarrow{\text{Oxidation}} RCOO^-$$

Aldehyde

Carboxylate anion

Benedict's and **Fehling's** reagents have similar behaviour.

Comparison of Tollens' and Fehling's Tests

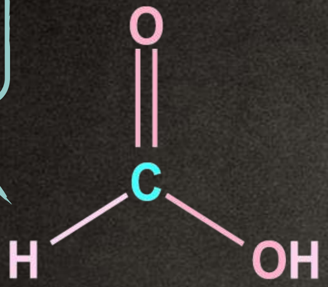
Compound	Tollens' test	Fehling's test
Aliphatic aldehyde	✓	✓
Aromatic aldehyde	✓	✗
Aliphatic ketone	✗	✗
Acetal	✗	✗
Ketal	✗	✗
Hemiacetal	✓	✓

Comparison of Tollens' and Fehling's Tests

Compound	Tollens' test	Fehling's test
α-Hydroxy ketone (terminal)	✓	✓
Carboxylic acid	✗	✗
Formic acid (HCOOH)	✓	✓

Comparison of Tollens' and Fehling's Tests

Presence of an **aldehydic C–H** bond

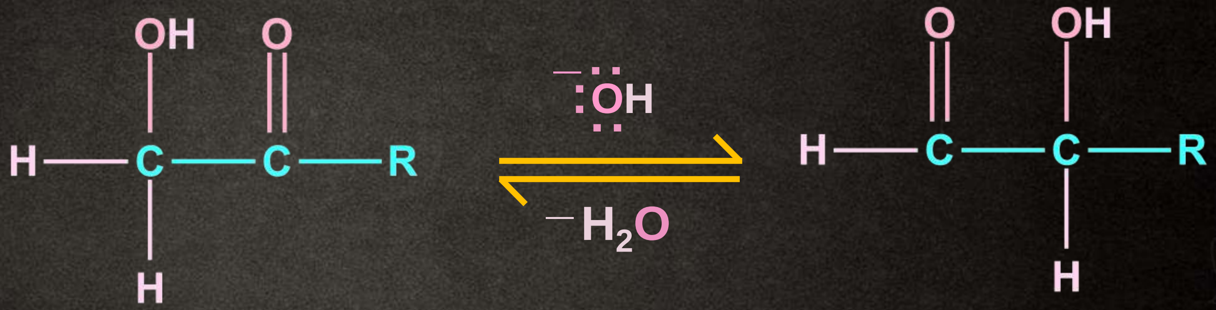


As a result, this bond can be **oxidised further** in the presence of mild oxidising agents such as **Tollens'** and **Fehling's reagents.**

***α*-Hydroxy ketones** give **Tollens'** and **Fehling's tests** because they can be converted into ***α*-hydroxy aldehydes** under basic conditions.

Tautomerism in α-Hydroxy Ketones

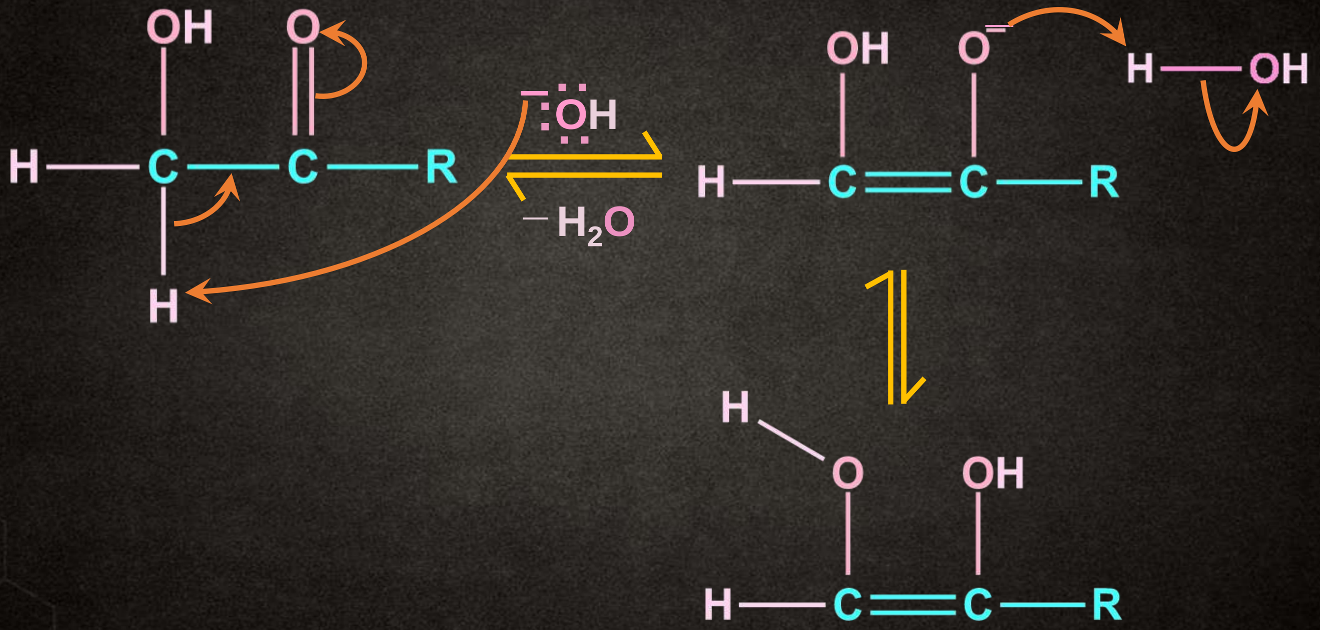
General reaction



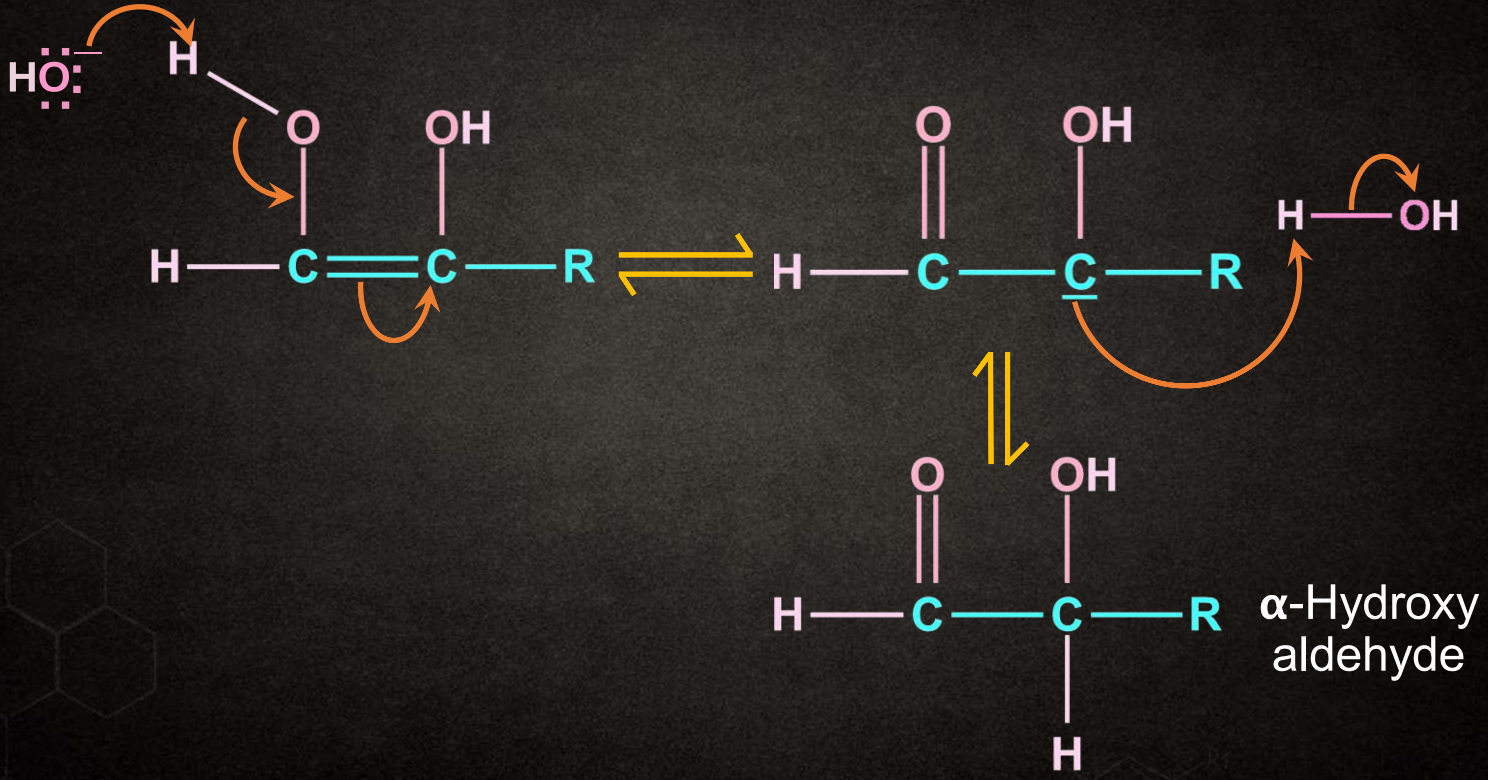
α-Hydroxy ketone
(terminal)

α-Hydroxy
aldehyde

Tautomerism in α-Hydroxy Ketones



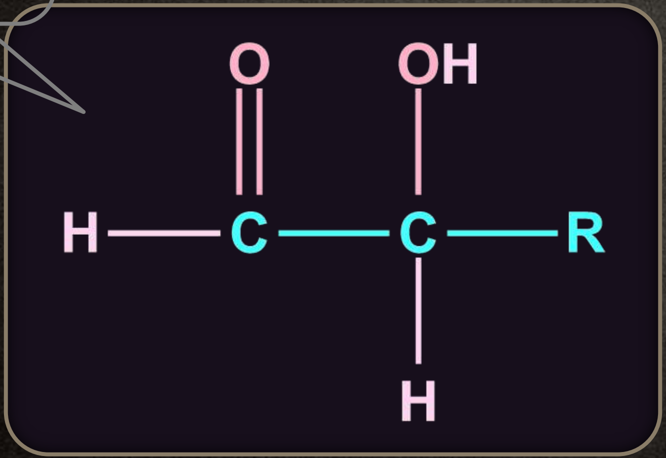
Tautomerism in α-Hydroxy Ketones



α-Hydroxy aldehyde

Tautomerism in α-Hydroxy Ketones

Gives **positive** Tollens’ and Fehling’s tests



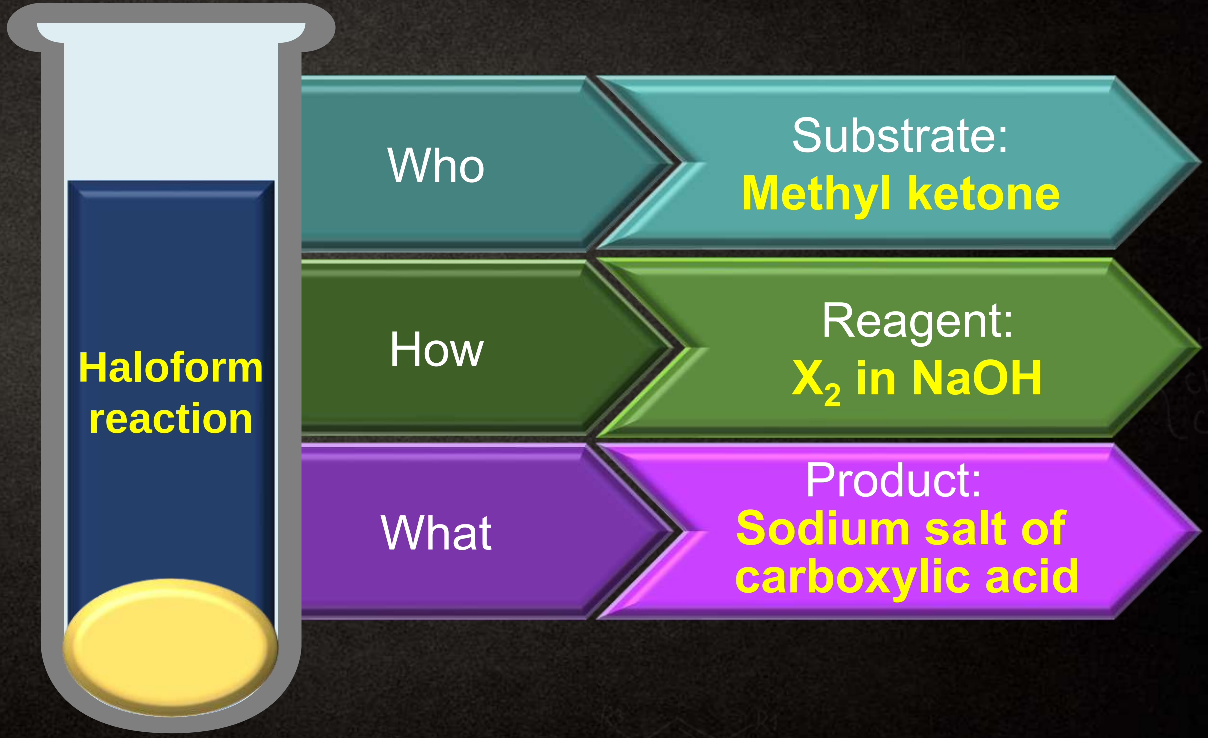
$$\mathrm{H-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-R}$$

α-Hydroxy aldehyde

Eg: Benzoin

Some **non-terminal** alpha-hydroxy aldehyde/ketone also gives **positive Tollens' test**.

Haloform Reaction



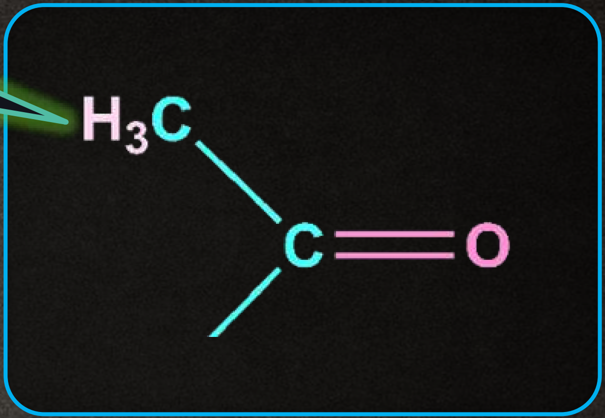
Haloform reaction

Who → Substrate: **Methyl ketone**

How → Reagent: **X_2 in NaOH**

What → Product: **Sodium salt of carboxylic acid**

Haloform Reaction



Methyl ketone

Aldehydes and **ketones** have at least one **methyl group** attached to the carbonyl carbon atom.

Iodoform Reaction

CHI_3

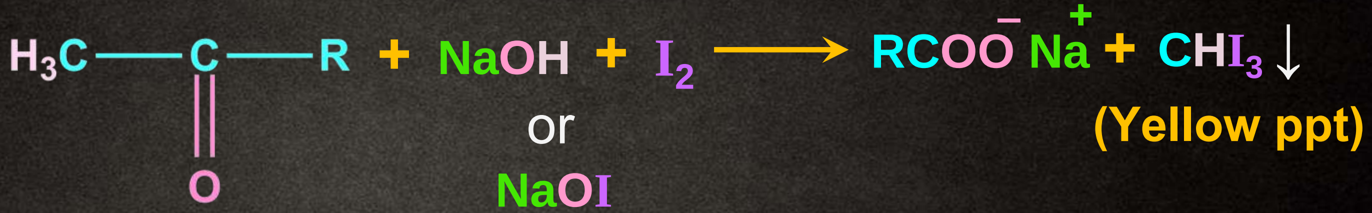
Yellow crystalline solid

Distinct **M.P** and **B.P**

Easily **identifiable**

Iodoform Reaction

General reaction



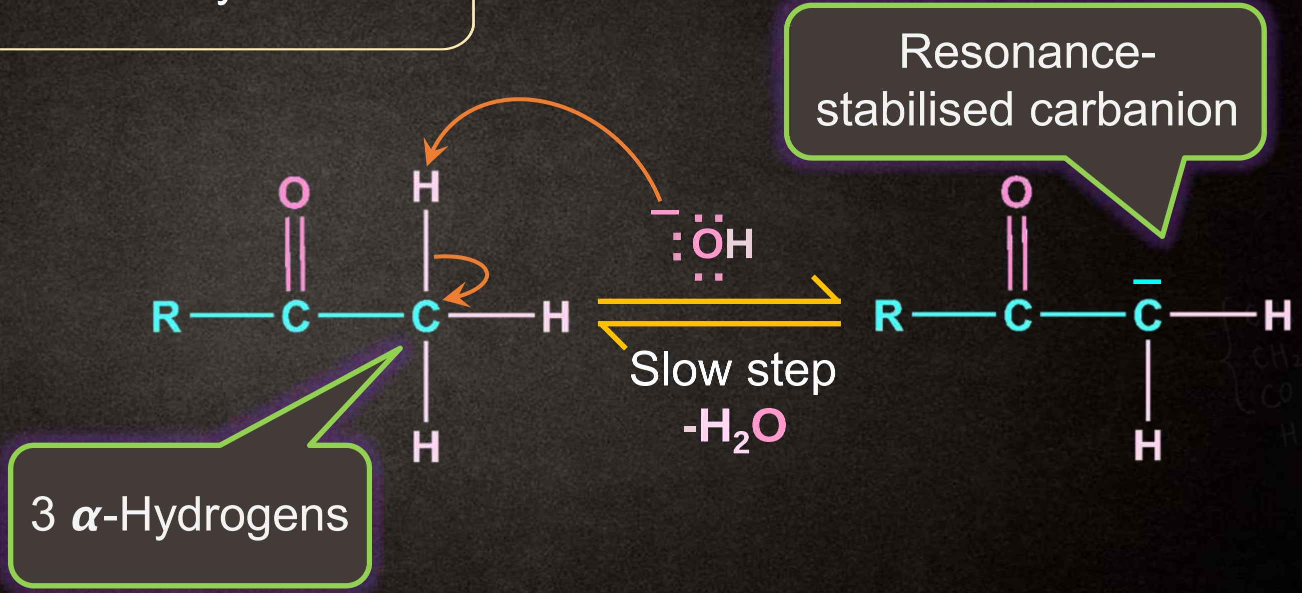
$$H_3C-\underset{\underset{\displaystyle O}{\|}}{C}-R + \underset{\underset{\displaystyle NaOI}{\text{or}}}{NaOH + I_2} \longrightarrow RCOO^{-}\,Na^{+} + \underset{\text{(Yellow ppt)}}{CHI_3\downarrow}$$

Formation of NaOI

$$\underset{\underset{\text{diluted)}}{\text{(Cold and}}}{2\,NaOH} + I_2 \longrightarrow NaOI + NaI + H_2O$$

Halogenation of Methyl Ketone

Step 1 Halogenation of methyl ketone



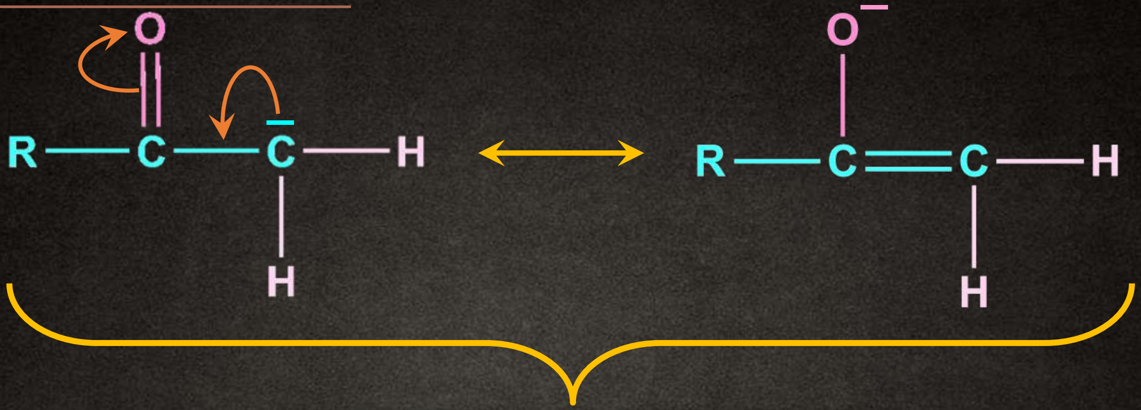
Resonance-stabilised carbanion

Slow step

$-H_2O$

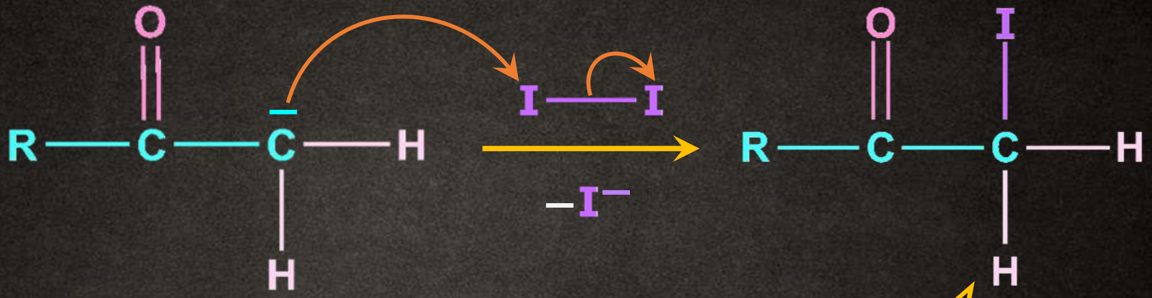
3 α-Hydrogens

Halogenation of Methyl Ketone



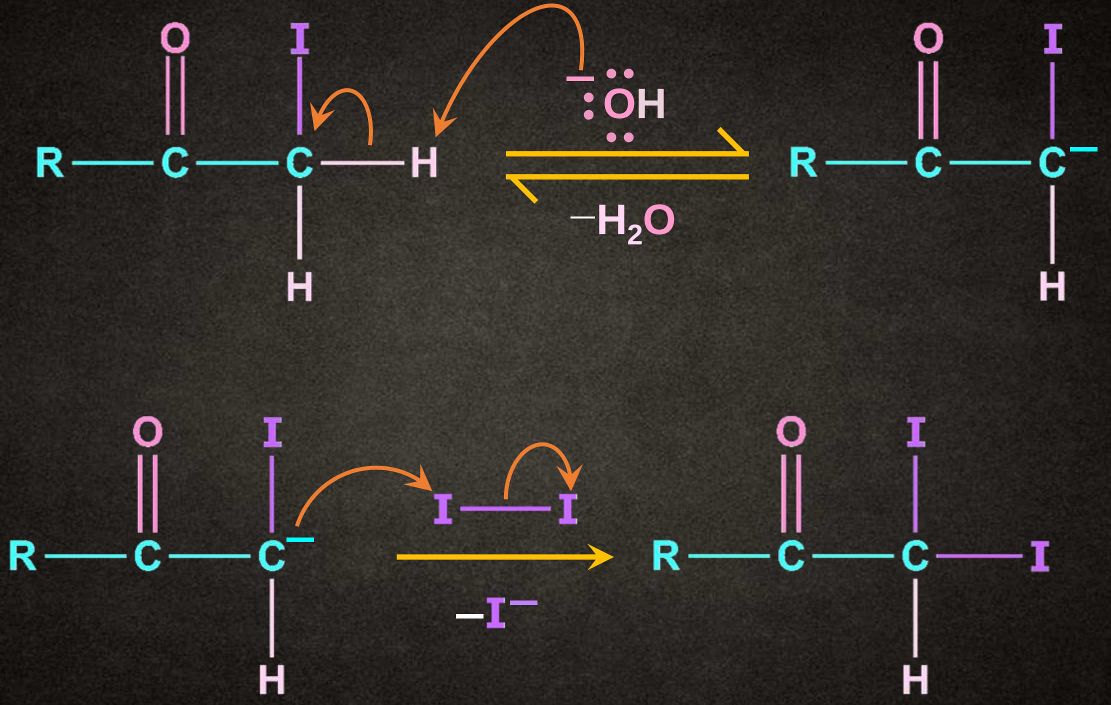
Resonating structures

Halogenation of Methyl Ketone

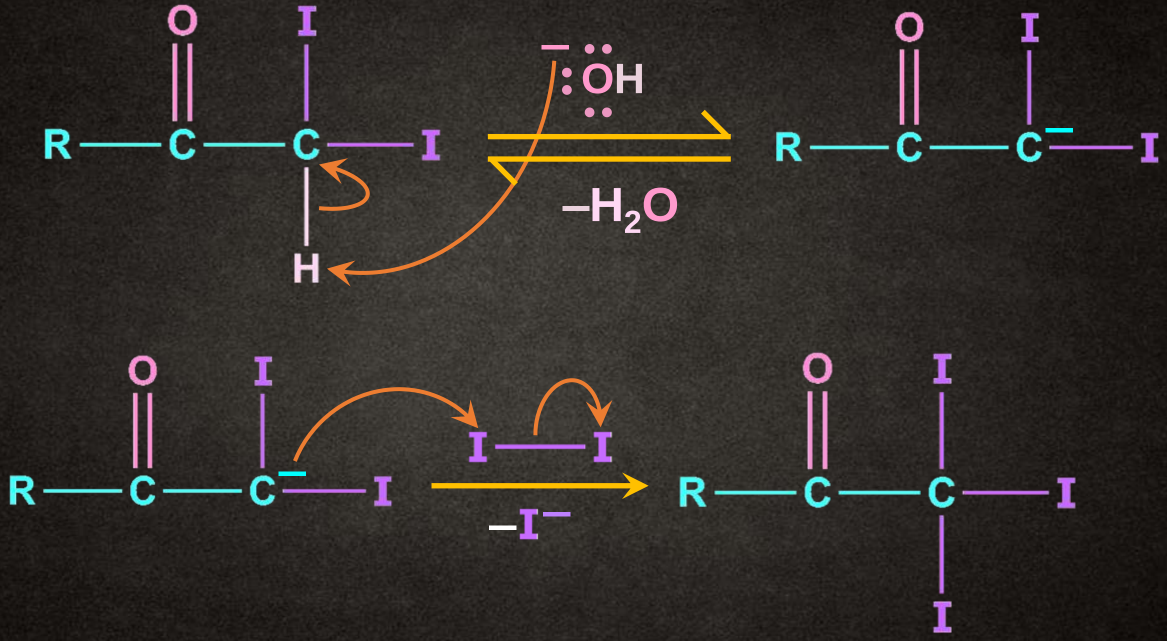


Abstraction of the remaining α-hydrogen becomes easier

Halogenation of Methyl Ketone



Halogenation of Methyl Ketone

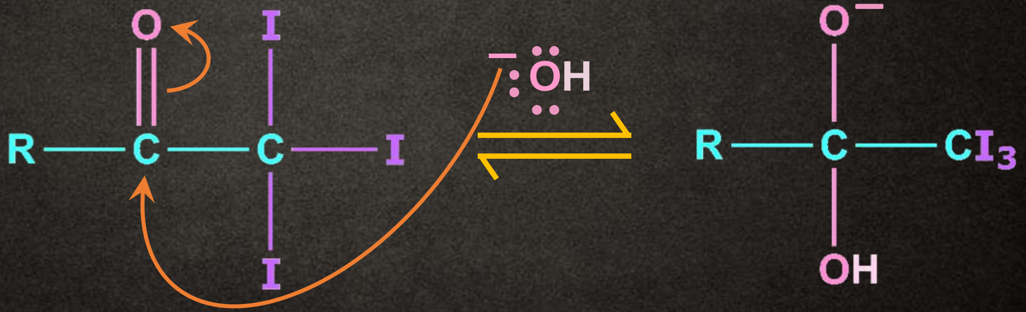


Triiodo-substituted alkyl ketone

Formation of Iodoform

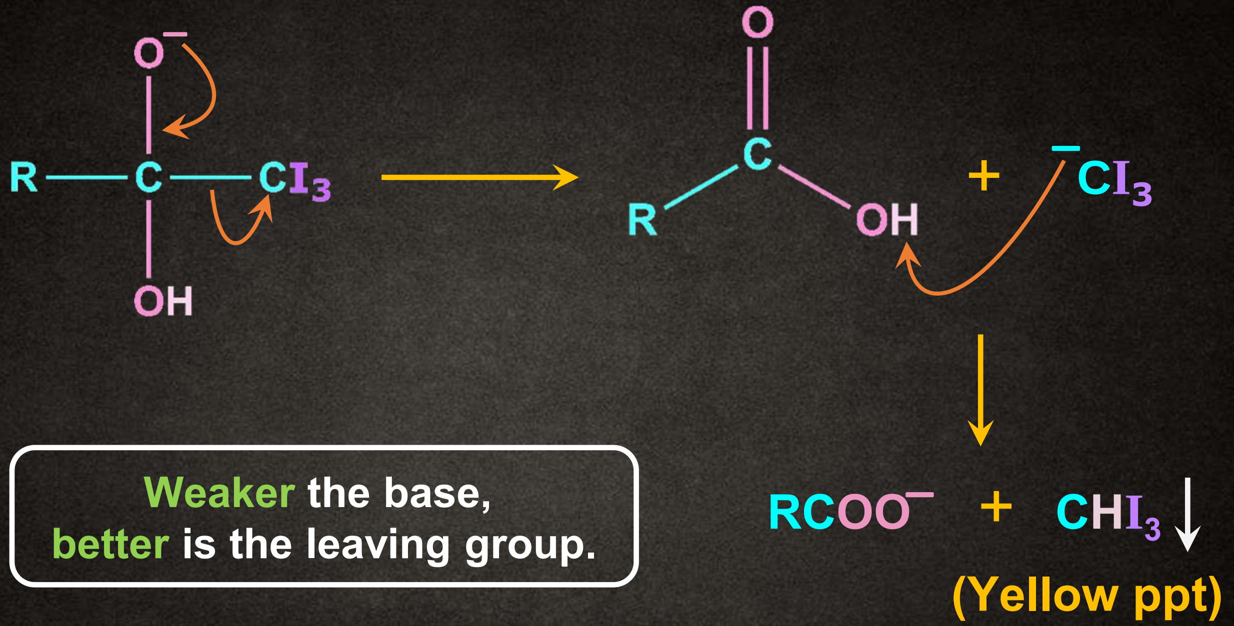
Step 2

Formation of iodoform



Triiodo-substituted
alkyl ketone

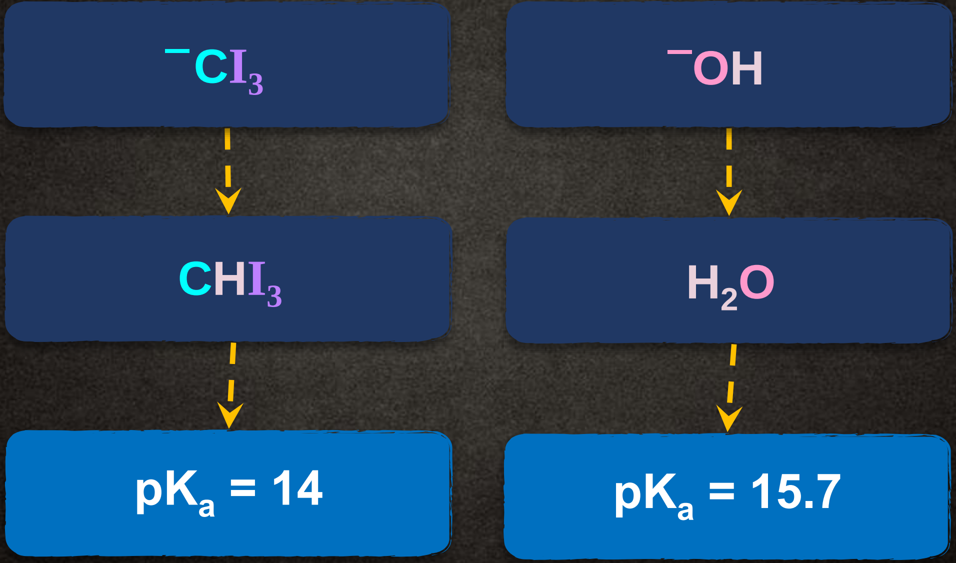
Formation of Iodoform



(Yellow ppt)

Weaker the base,
better is the leaving group.

Iodoform Reaction



$^{-}CI_3$

CHI_3

$pK_a = 14$

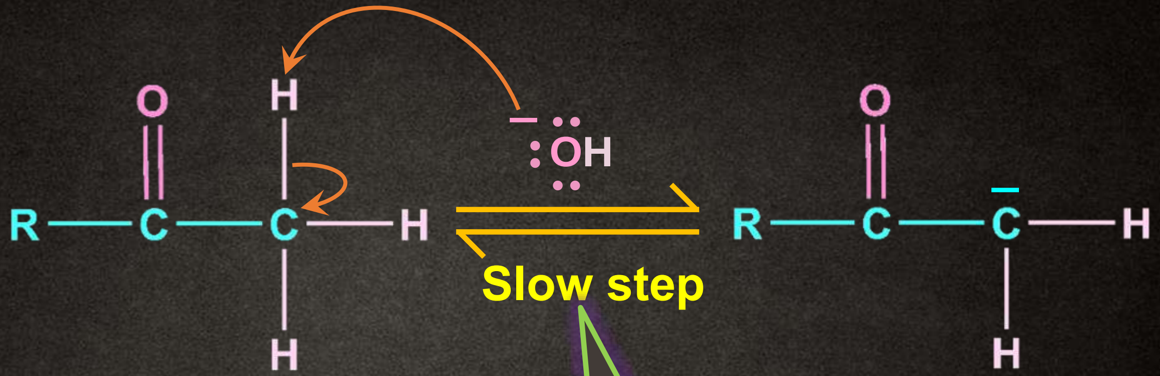
^{-}OH

H_2O

$pK_a = 15.7$

Halogenation of Methyl Ketone

Step -1



Slow step

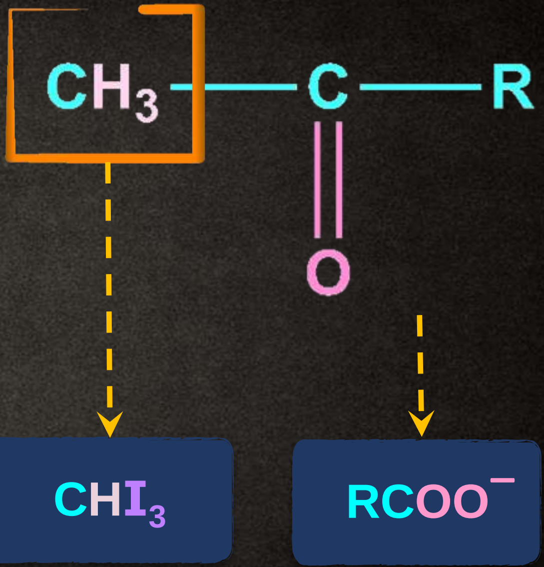
RDS

Note!

Since **enolate formation** is the **RDS**, the addition of **halogen does not** affect the **rate** of haloform reaction.

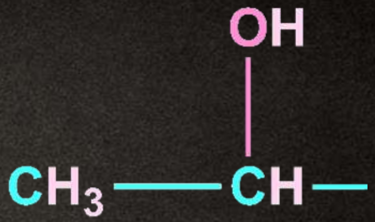
Reactivity order of halogens in haloform reaction:

Cl_2 = Br_2 = I_2



Note!

Haloform reaction is used to **detect** the **methyl ketone group** in organic compounds.

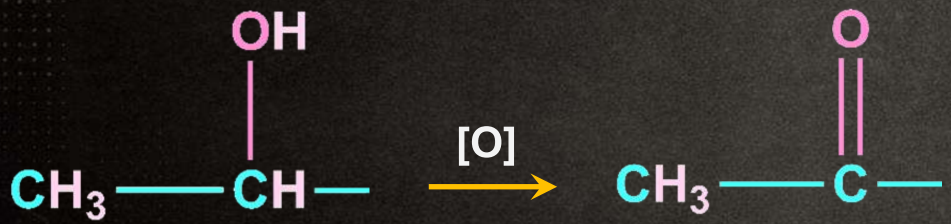


$$CH_3-\overset{\overset{OH}{|}}{CH}-$$

This shows a **positive haloform test.**

Iodoform Test

NaOH + I_2 is a **mild oxidising agent** and can easily oxidise.



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

Gives
iodoform test

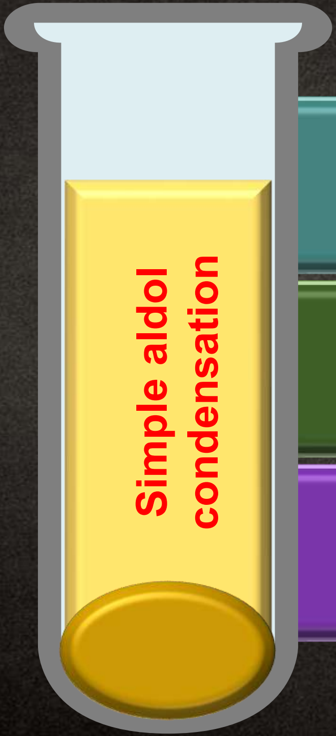
If any group/atom **that has a lone pair** is directly attached to the **carbonyl carbon** of methyl ketone, then it **will not show iodoform test**.

Eg: **–OH**, **–OR**, **–NH_2**

Note!

In case of halogenation of a ketone/aldehyde in an **acidic medium, monohalogenation occurs**.

Simple Aldol Condensation



Simple aldol condensation

Who	Substrate: **Carbonyl having at least one α-H**
How	Reagents: **NaOH, Na_2CO_3, $Ba(OH)_2$**
What	Product: **α,β-Unsaturated carbonyl compound**

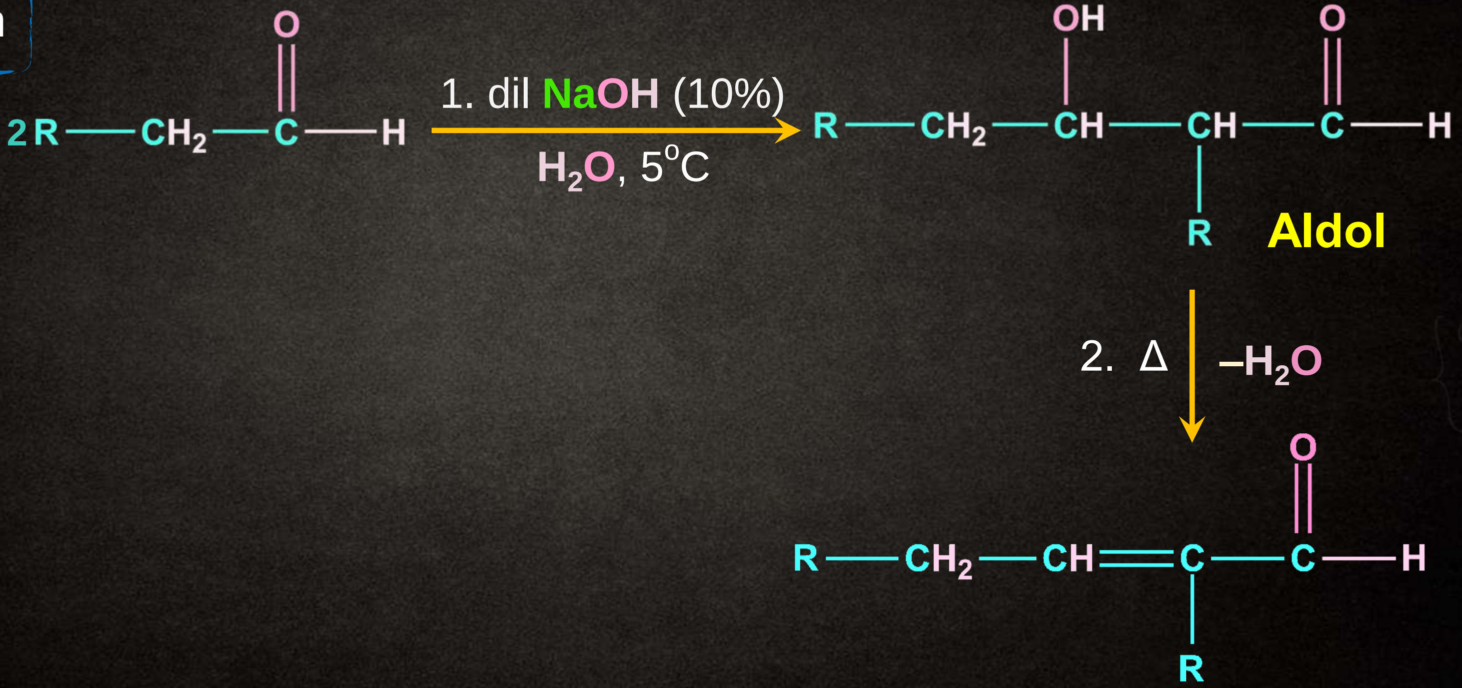
Simple Aldol Condensation

Necessary condition

- For an aldol reaction → Aldehyde or ketone with atleast **1 α-H**
- For aldol condensation → Aldehyde or ketone with atleast **2 α-H**

Simple Aldol Condensation

General reaction



$$2R-CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow[H_2O,\ 5^{o}C]{1.\ \text{dil NaOH (10\%)}} R-CH_2-\overset{OH}{\overset{|}{C}H}-\underset{R}{\underset{|}{C}H}-\overset{O}{\overset{\|}{C}}-H$$

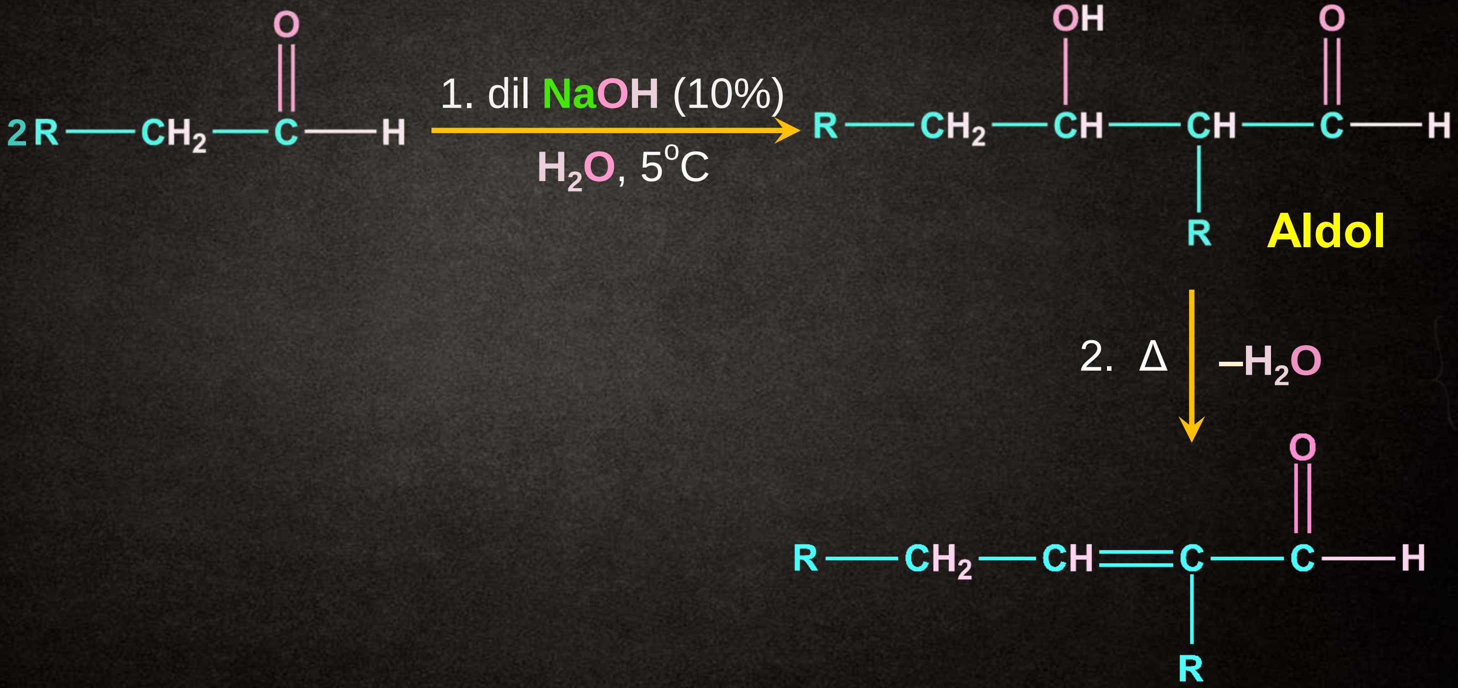
Aldol

$$\Big\downarrow 2.\ \Delta \quad -H_2O$$

$$R-CH_2-CH=\underset{R}{\underset{|}{C}}-\overset{O}{\overset{\|}{C}}-H$$

α,β–Unsaturated aldehyde

Simple Aldol Condensation



$$2R-CH_2-\overset{\overset{O}{\|}}{C}-H \xrightarrow[H_2O,\ 5^{o}C]{\text{1. dil NaOH (10\%)}} R-CH_2-\overset{\overset{OH}{|}}{CH}-\underset{\underset{R}{|}}{CH}-\overset{\overset{O}{\|}}{C}-H$$

Aldol

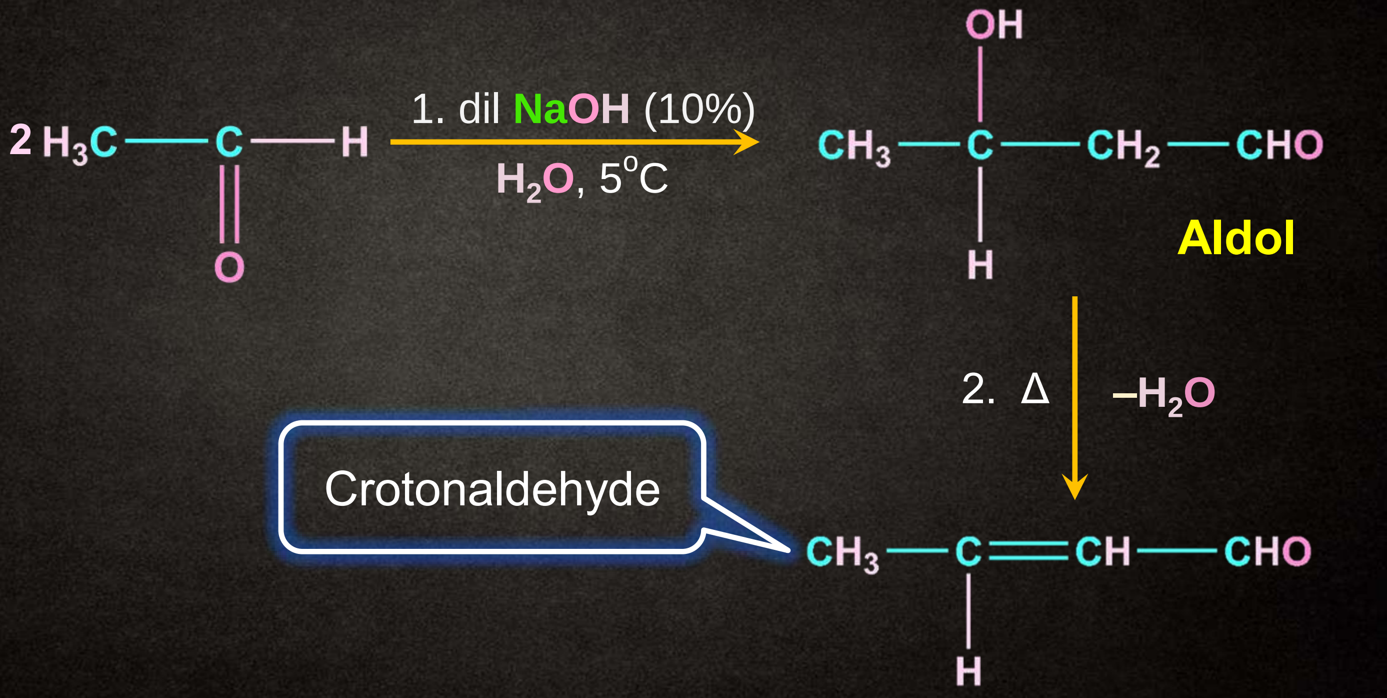
$$\Big\downarrow \text{2. } \Delta \quad -H_2O$$

$$R-CH_2-CH=\underset{\underset{R}{|}}{C}-\overset{\overset{O}{\|}}{C}-H$$

α,β–Unsaturated aldehyde

Simple Aldol Condensation

EXAMPLE



$$2\,H_3C-\underset{\overset{\|}{O}}{C}-H \xrightarrow[H_2O,\ 5^{o}C]{1.\ \text{dil NaOH (10\%)}} CH_3-\underset{H}{\overset{OH}{C}}-CH_2-CHO$$

Aldol

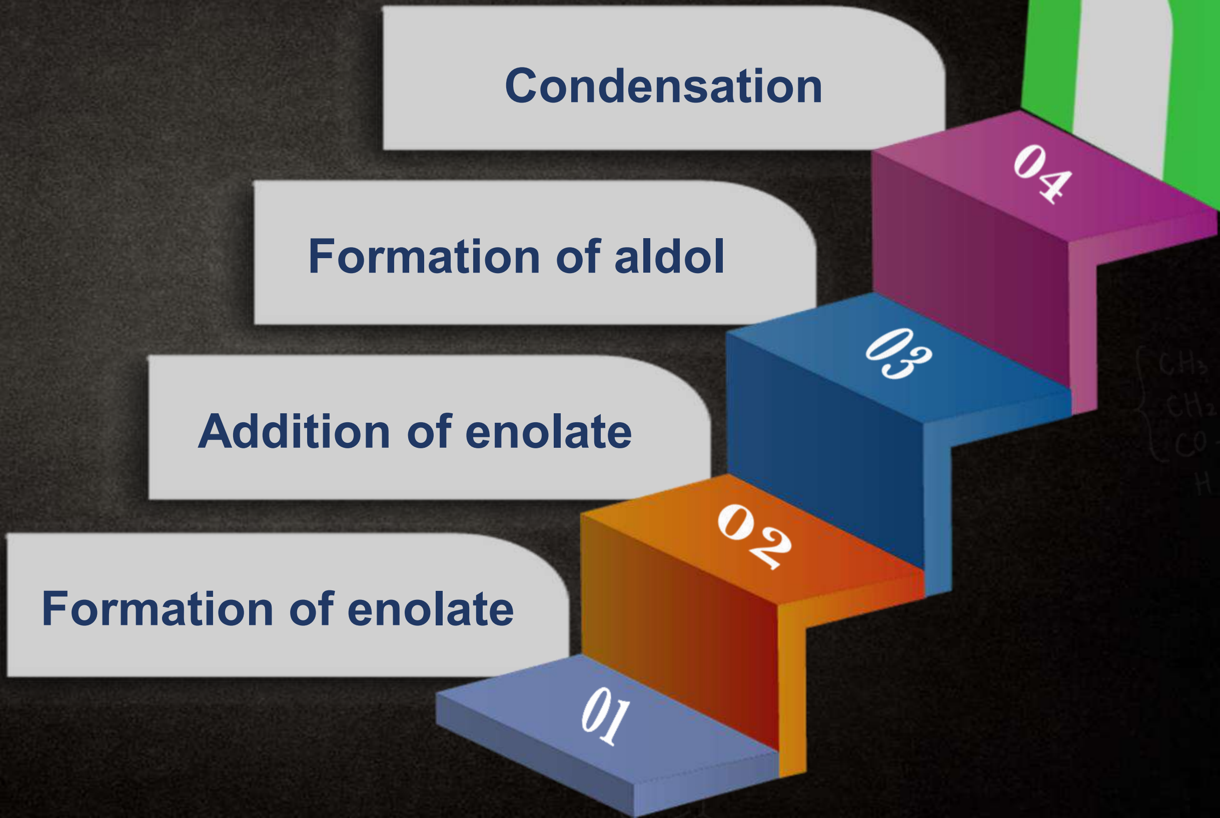
$$\xrightarrow[-H_2O]{2.\ \Delta}$$

$$CH_3-\underset{H}{C}=CH-CHO$$

Crotonaldehyde

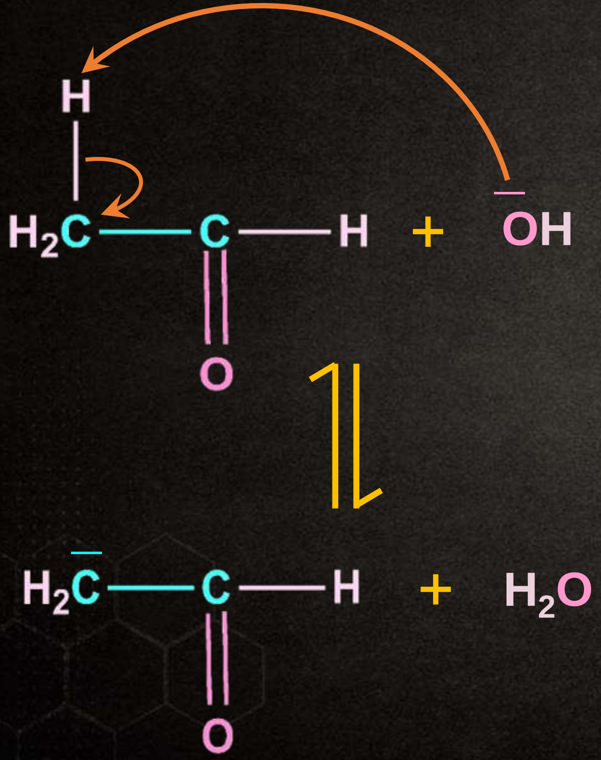
α,β–Unsaturated aldehyde

Steps Involved in Simple Aldol Condensation

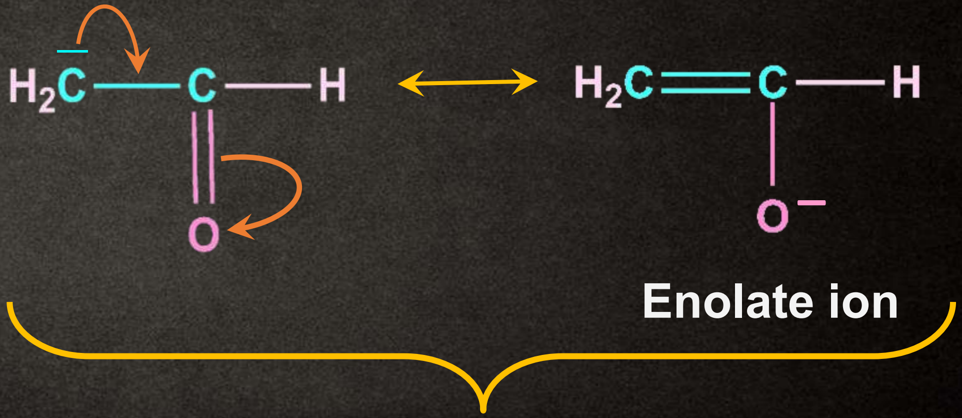


1. Formation of enolate
2. Addition of enolate
3. Formation of aldol
4. Condensation

Enolate Formation



$$H_2C(H)-C(=O)-H + \bar{O}H \rightleftharpoons H_2\bar{C}-C(=O)-H + H_2O$$

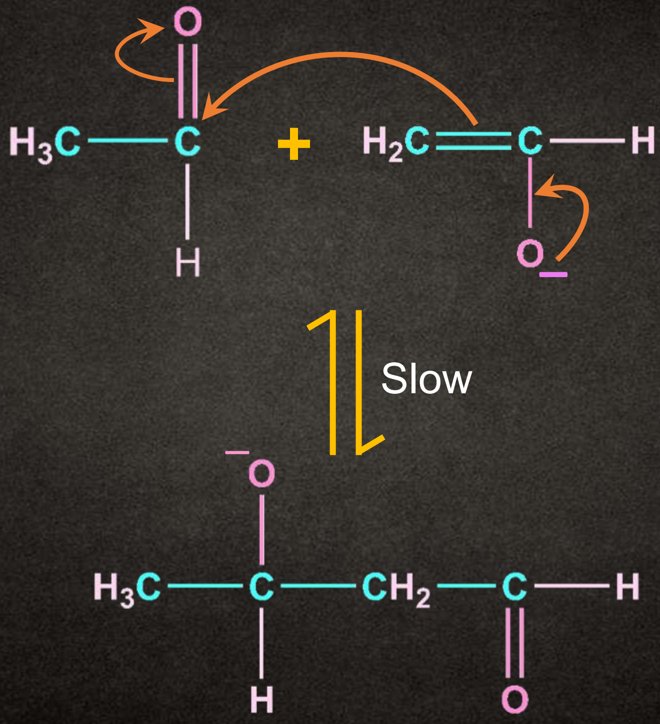


$$H_2\bar{C}-C(=O)-H \longleftrightarrow H_2C=C(O^-)-H$$

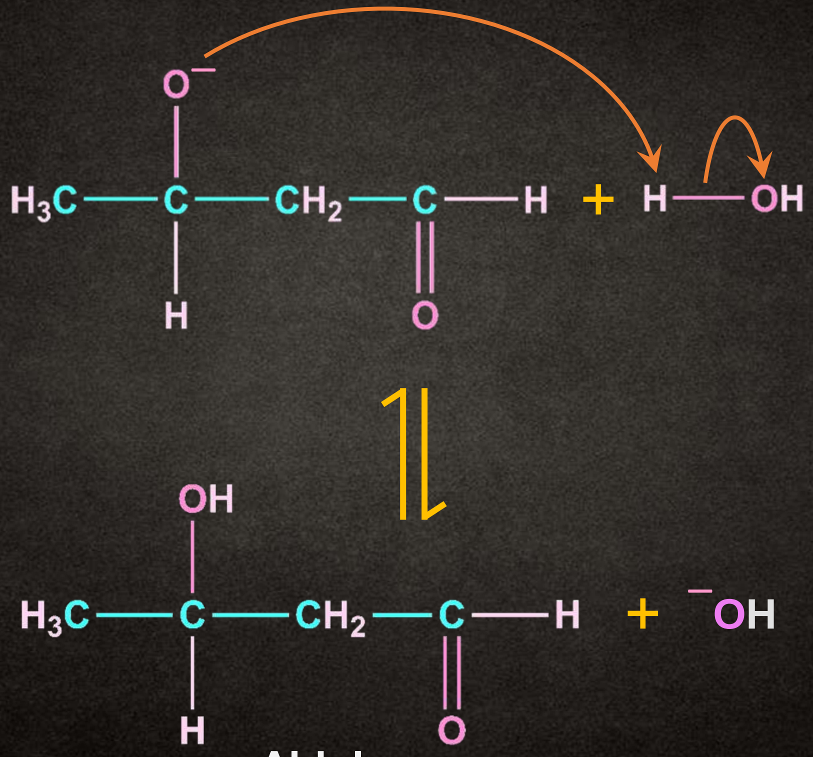
Enolate ion

Resonating structures

Addition of Enolate

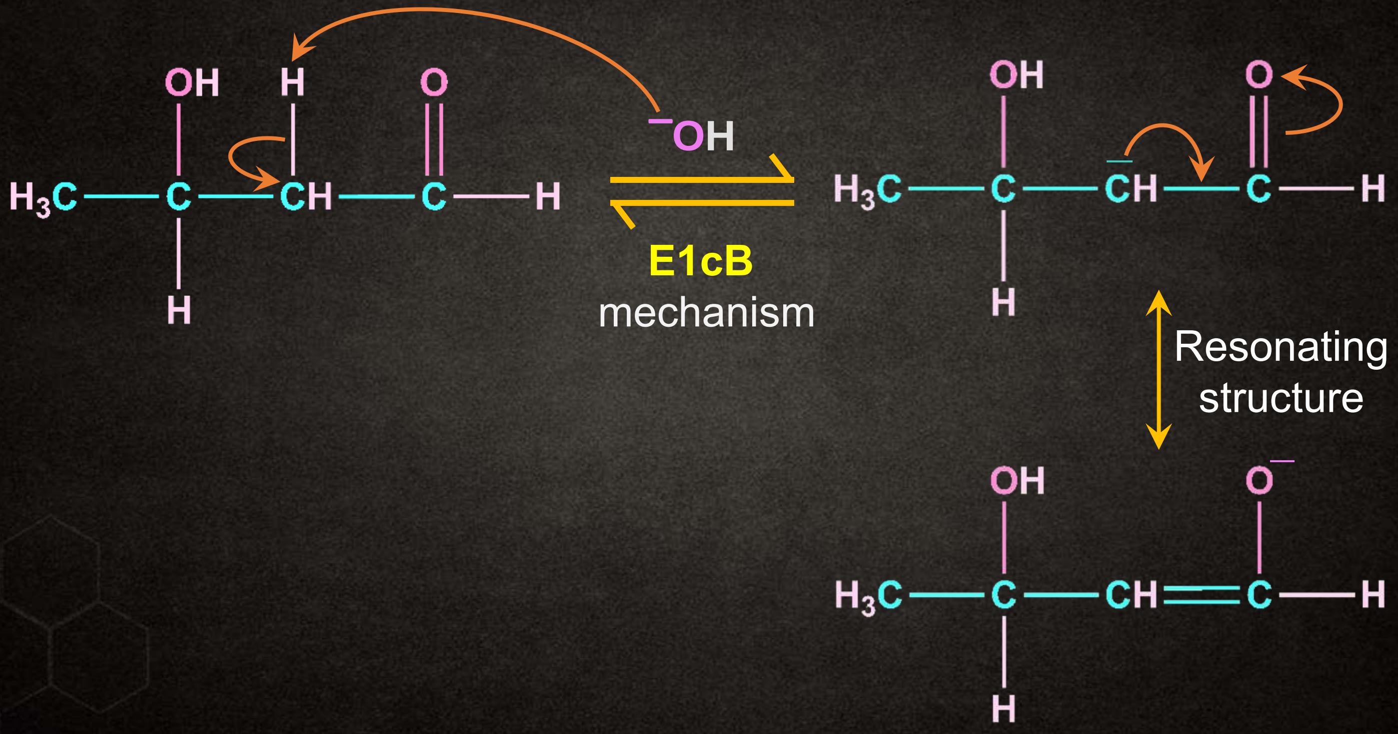


Formation of an Aldol

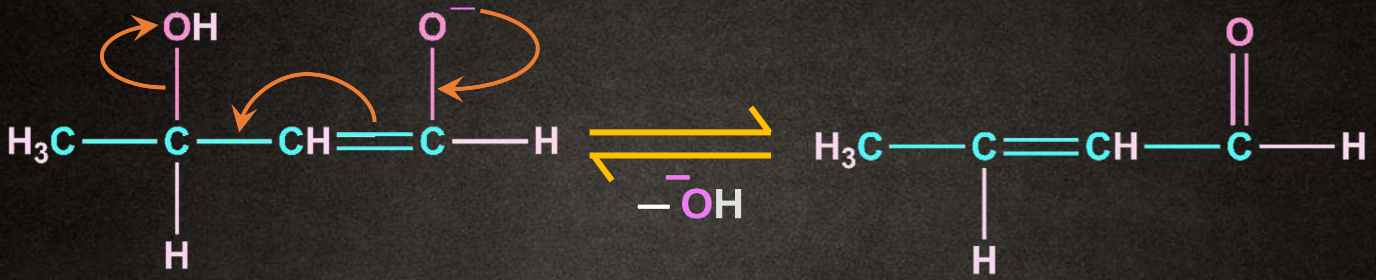


Aldol

Condensation

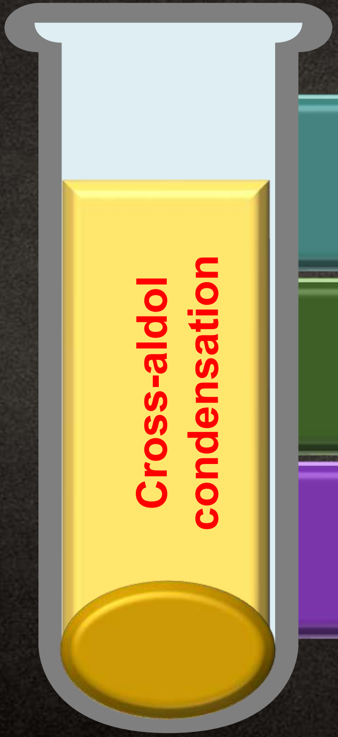


Condensation



α,β–Unsaturated aldehyde

Cross–Aldol Condensation



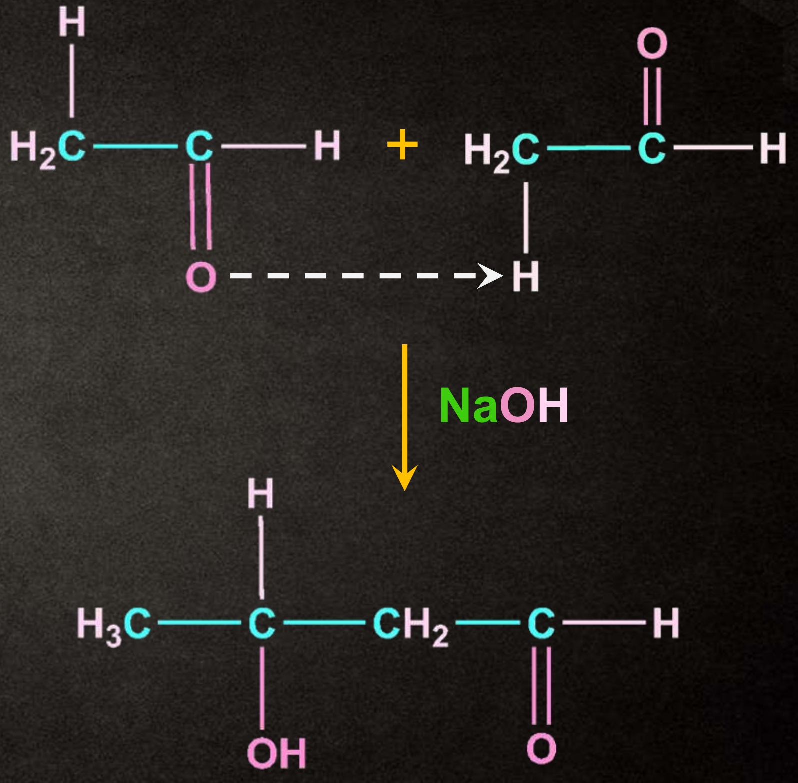
Who	Substrate: **Two different carbonyls having at least one α–H**
How	Reagents: **NaOH, $Ba(OH)_2$, KOH**
What	Product: **α,β–unsaturated carbonyl compound**

Example

Four types of products can result in a cross-aldol reaction

Product 1 Self-aldol

$$2\ CH_3CHO \xrightarrow[\text{ii) } \Delta]{\text{i) Dil. NaOH, 5°C}}$$



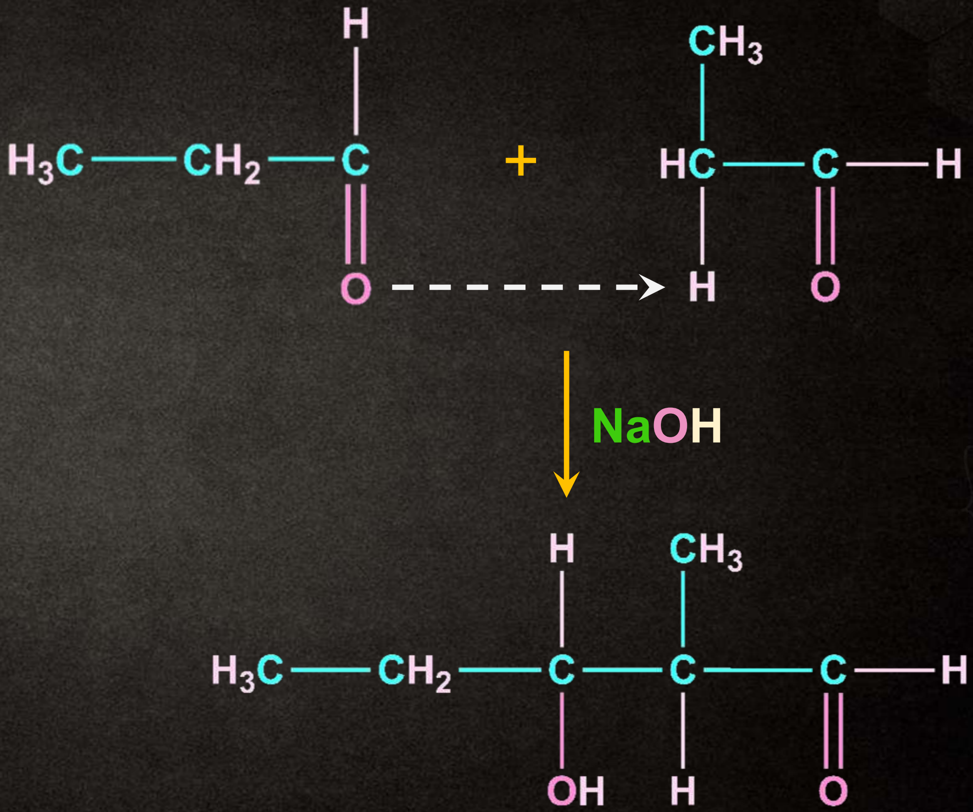
Aldol

Example

Four types of products can result in a cross-aldol reaction

Product 2 Self-aldol

$$2\ CH_3CH_2CHO \xrightarrow[\text{ii) }\Delta]{\text{i) Dil. NaOH, 5°C}}$$



Aldol

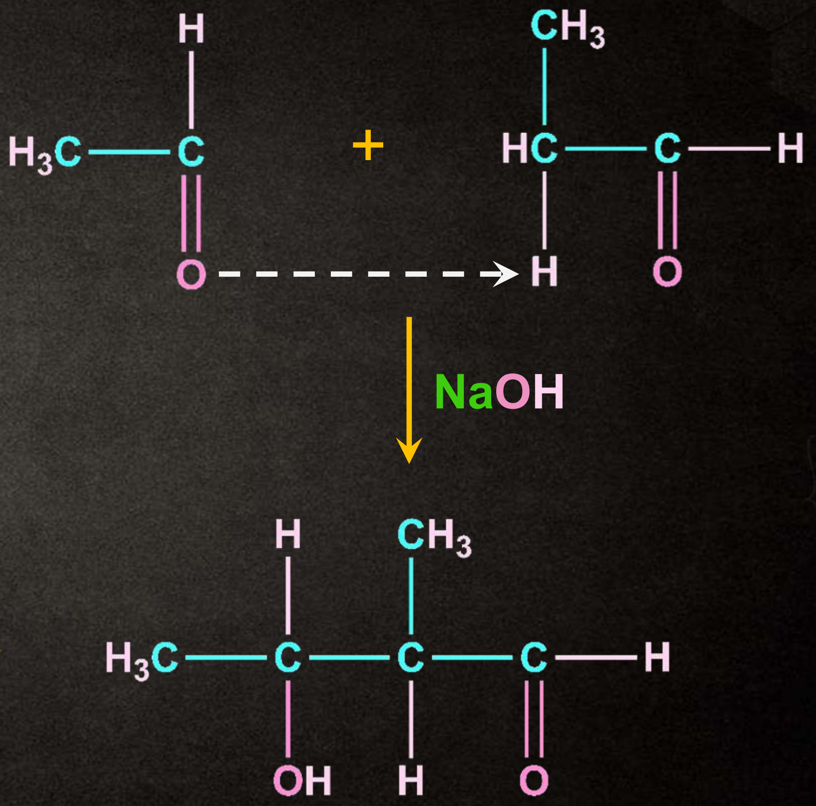
Example

Four types of products can result in a cross-aldol reaction

Product 3

Cross-aldol

$$CH_3CHO + CH_3CH_2CHO \xrightarrow[\text{ii) }\Delta]{\text{i) Dil. NaOH, 5°C}}$$



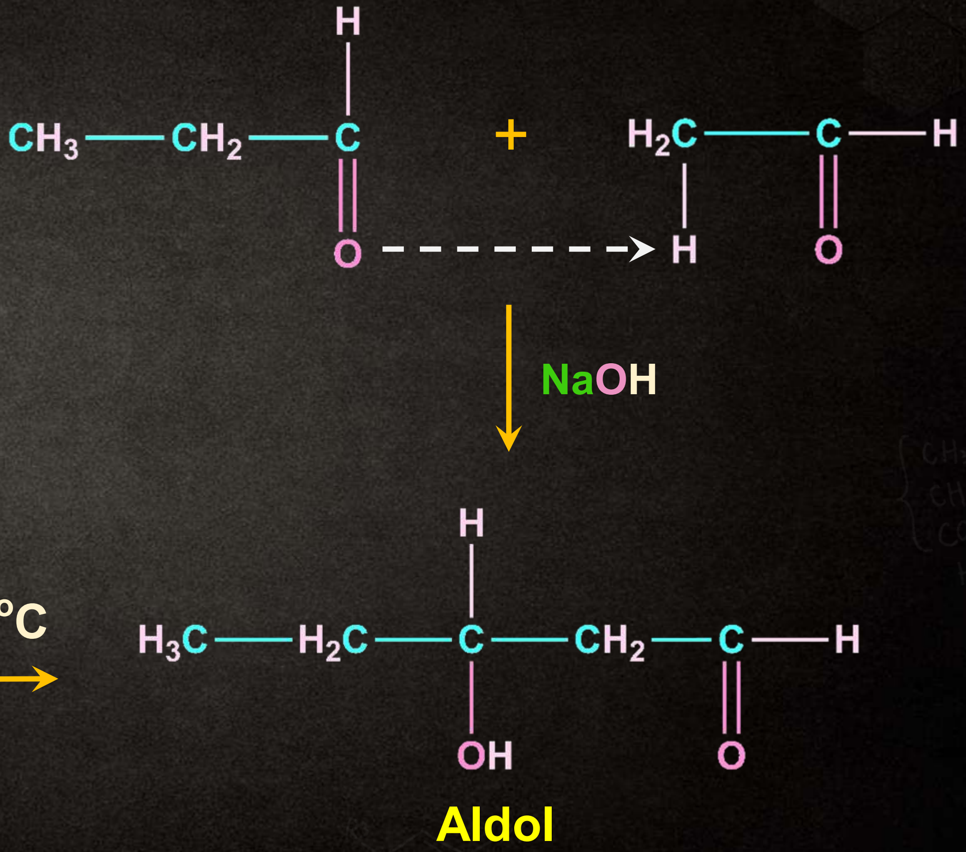
Aldol

Example

Four types of products can result in a cross-aldol reaction

Product 4 Cross-aldol

$$CH_3CH_2CHO + CH_3CHO \xrightarrow[\text{ii) }\Delta]{\text{i) Dil. NaOH, 5°C}}$$

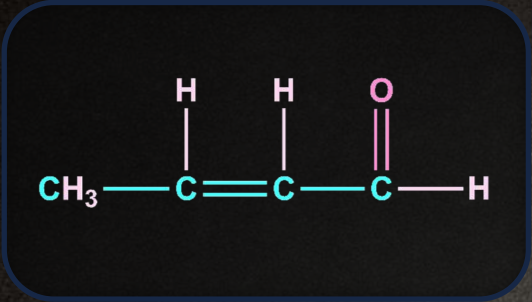


Factors Affecting the Stability of the Product

1. **Stability** of enolate

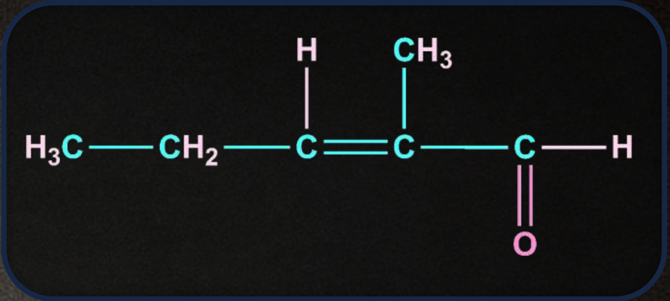
2. Attack of enolate will occur on the carbonyl carbon that is **more electron deficient**.

Factors Affecting the Stability of the Product



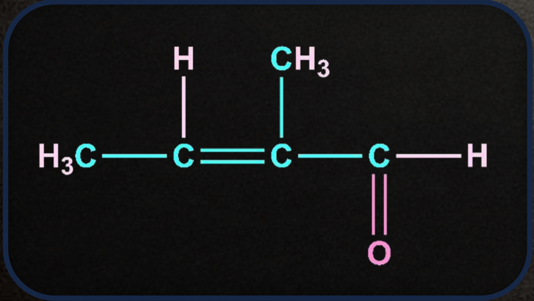
$CH_3-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-H$

Product I



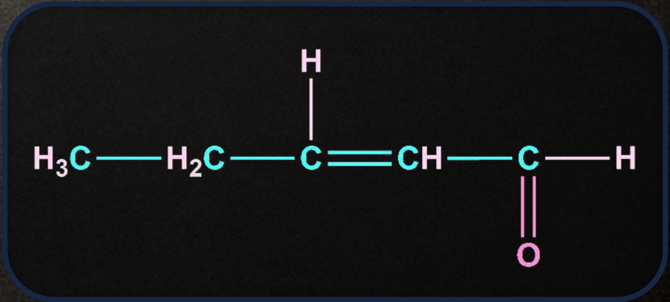
$H_3C-CH_2-\overset{H}{\overset{|}{C}}=\overset{CH_3}{\overset{|}{C}}-\underset{O}{\underset{\|}{C}}-H$

Product II



$H_3C-\overset{H}{\overset{|}{C}}=\overset{CH_3}{\overset{|}{C}}-\underset{O}{\underset{\|}{C}}-H$

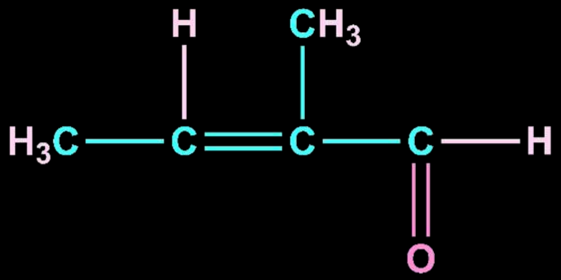
Product III



$H_3C-H_2C-\overset{H}{\overset{|}{C}}=CH-\underset{O}{\underset{\|}{C}}-H$

Product IV

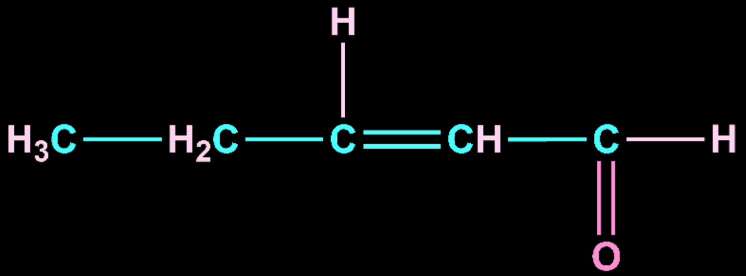
Factors Affecting the Stability of the Product



$H_3C-\overset{H}{\overset{|}{C}}=\overset{CH_3}{\overset{|}{C}}-\underset{\underset{O}{\|}}{C}-H$

Product III

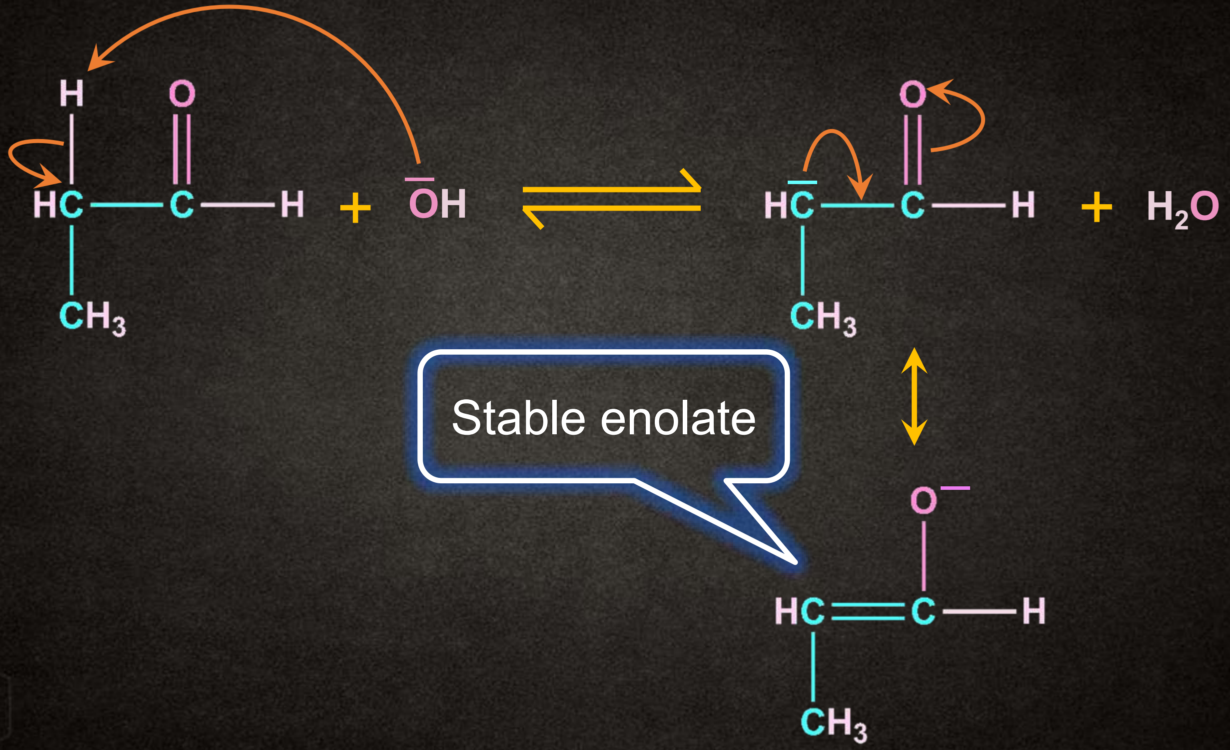
Major product



$H_3C-H_2C-\overset{H}{\overset{|}{C}}=CH-\underset{\underset{O}{\|}}{C}-H$

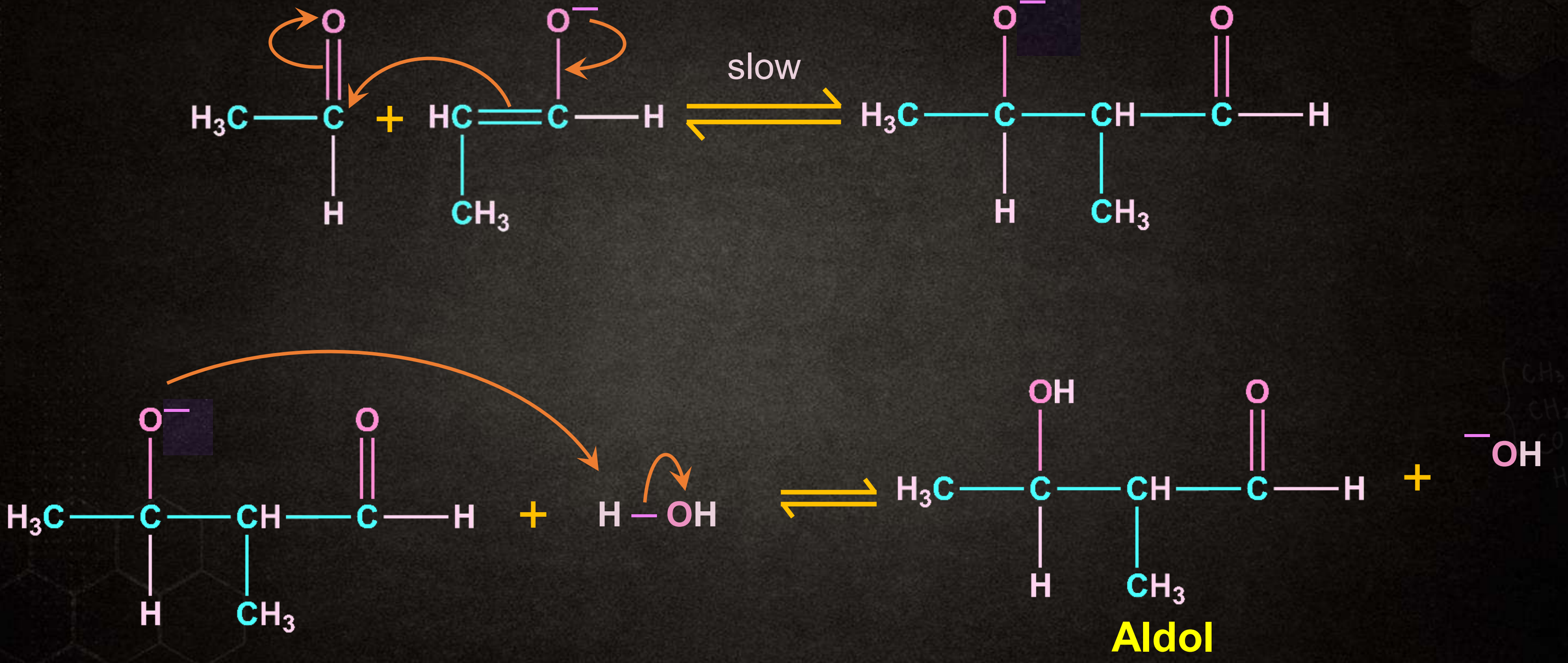
Product IV

Mechanism of Cross–Aldol Condensation

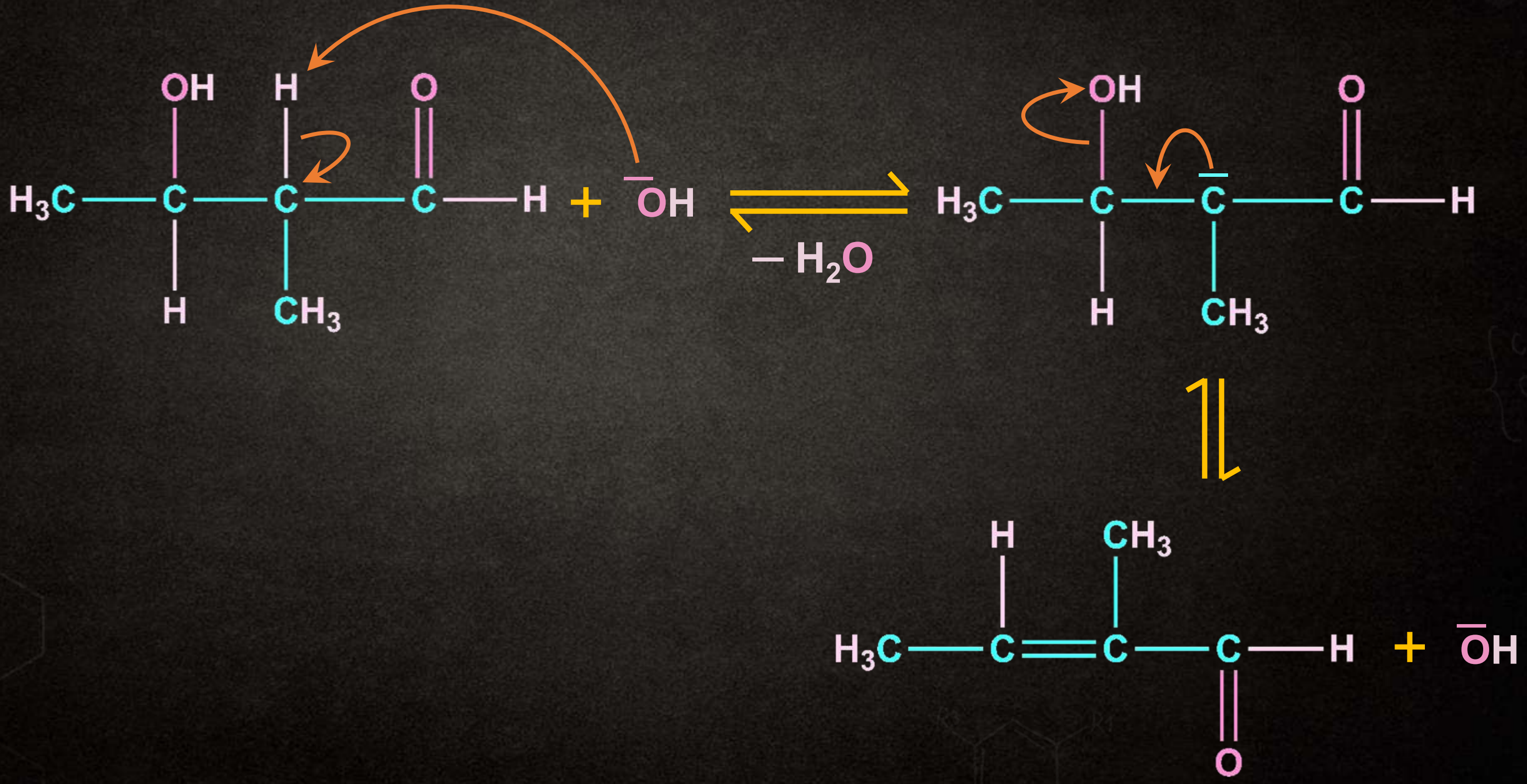


Stable enolate

Mechanism of Cross–Aldol Condensation



Mechanism of Cross–Aldol Condensation



Chemical Properties of Aldehydes and Ketones

Miscellaneous reactions

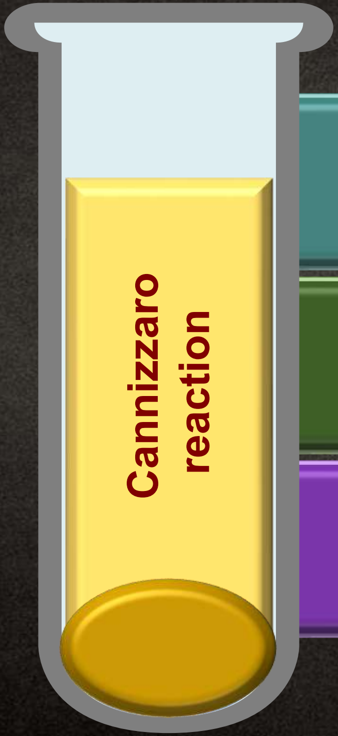
- Cannizzaro reaction
- Electrophilic substitution reaction

Cannizzaro Reaction

Cannizzaro reaction

- Cannizzaro
- Cross–Cannizzaro
- Intramolecular Cannizzaro

Cannizzaro Reaction



Who — Substrate: **Aldehydes with no α-hydrogen**

How — Reagent: **Conc. NaOH (50%), Δ**

What — Product: **Salt of carboxylic acid and alcohol**

Cannizzaro Reaction

Generally, aldehydes with no α-H undergo

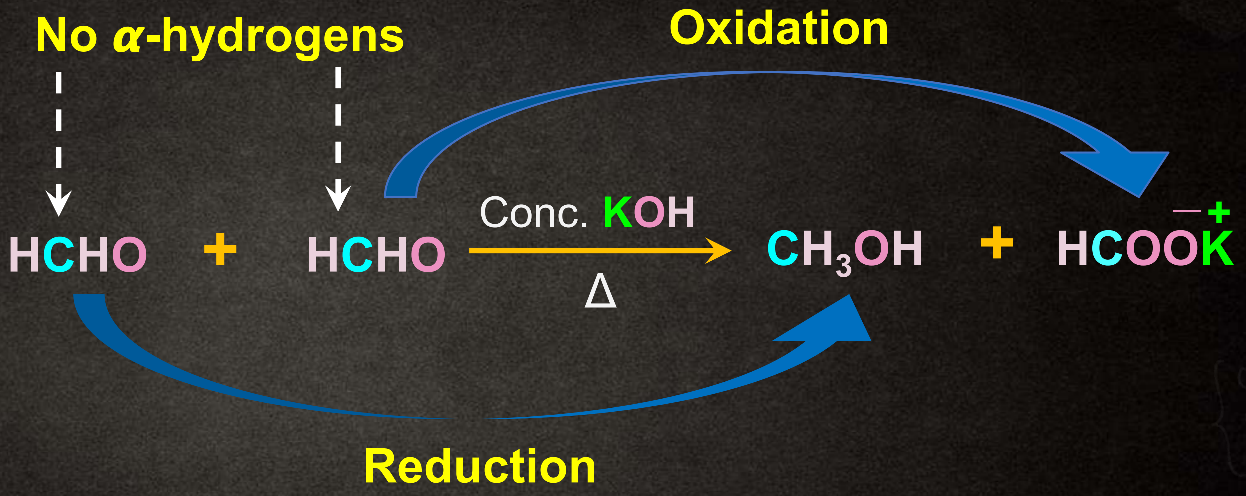
Self-oxidation and self-reduction

Disproportionation

On treatment with a strong base

Cannizzaro Reaction

Reaction



No α-hydrogens

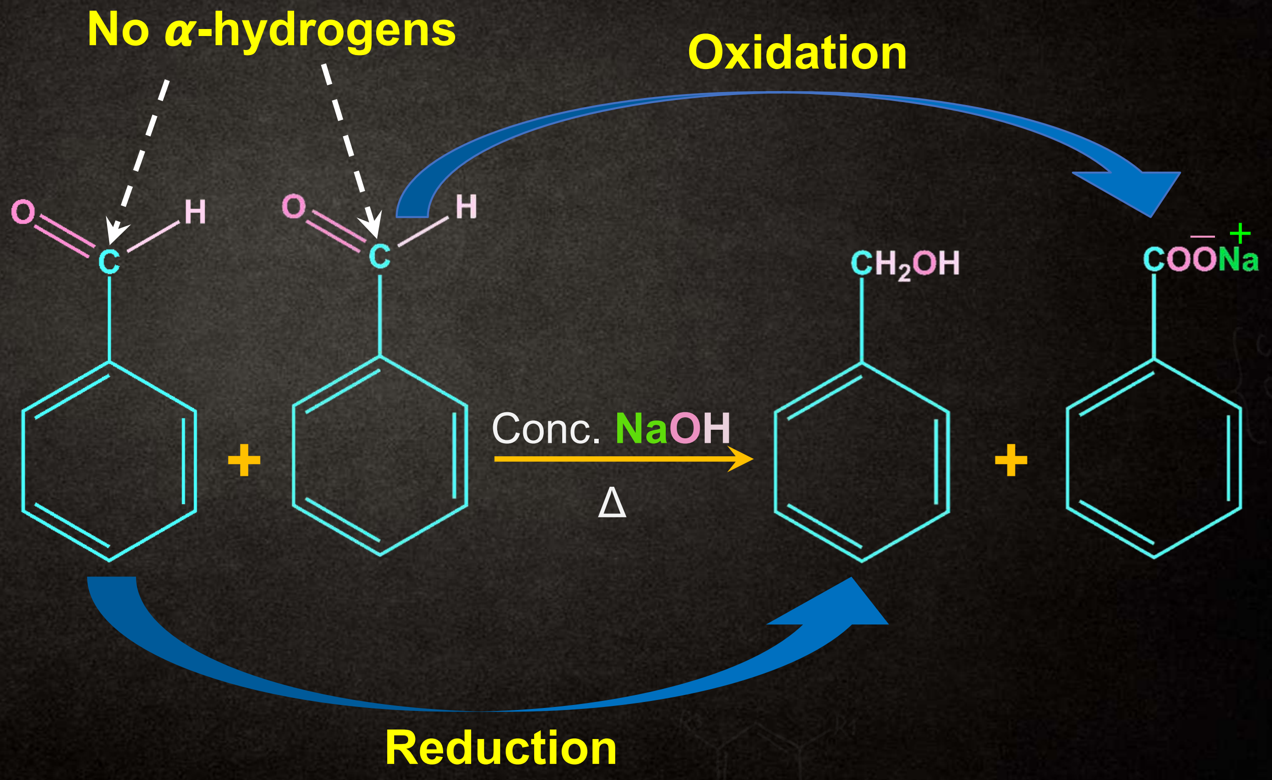
Oxidation

$$HCHO + HCHO \xrightarrow[\Delta]{\text{Conc. KOH}} CH_3OH + HCO\overset{-}{O}\overset{+}{K}$$

Reduction

Cannizzaro Reaction

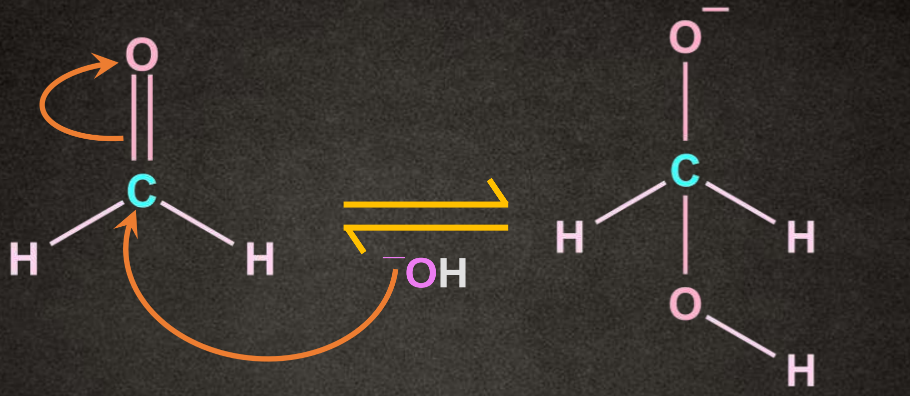
Reaction



Steps Involved in Cannizzaro Reaction

Step 1	Nucleophilic attack of hydroxide
Step 2	Hydride transfer
Step 3	Proton transfer

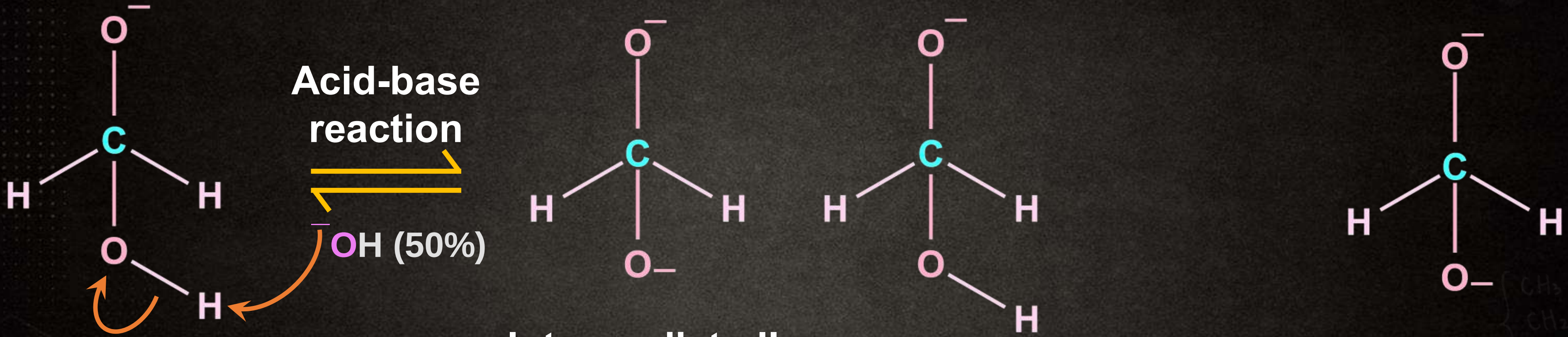
Nucleophilic Attack of Hydroxide



Intermediate–I

Monoxide anion

Nucleophilic Attack of Hydroxide



Intermediate-II

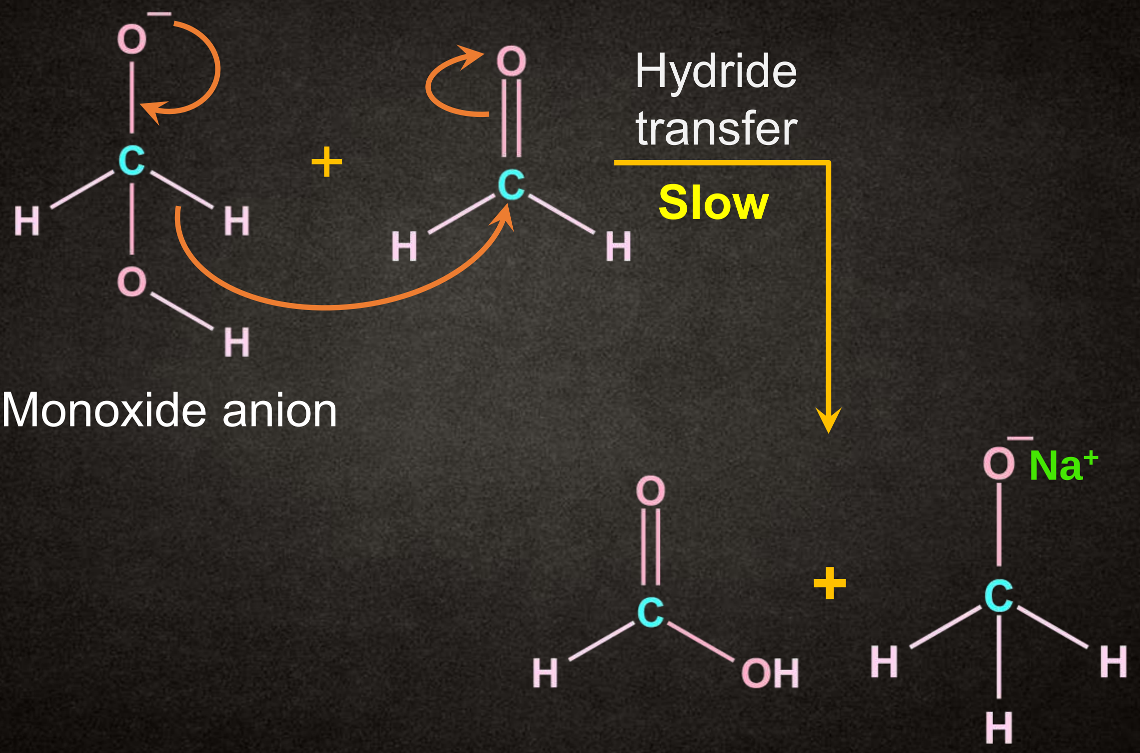
Intermediate-I

Intermediate-II

Dioxide anion

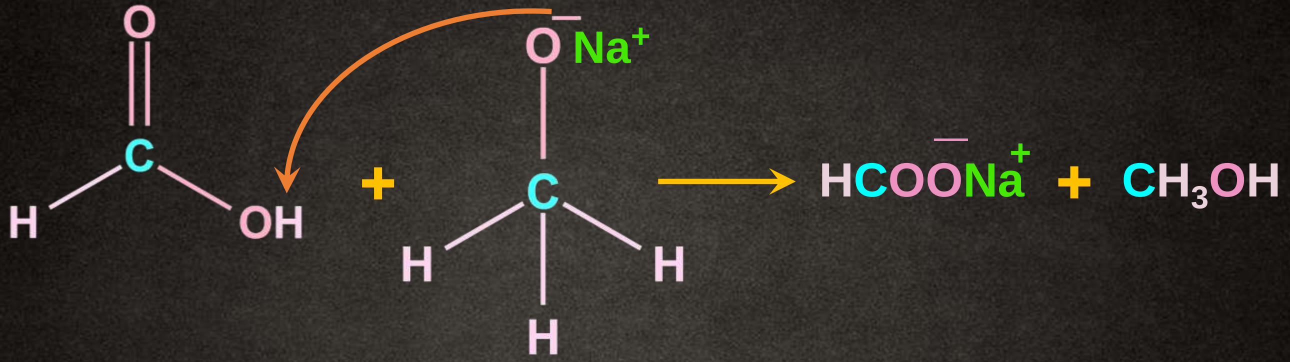
Both **intermediates are formed** in this reaction.

Hydride Transfer

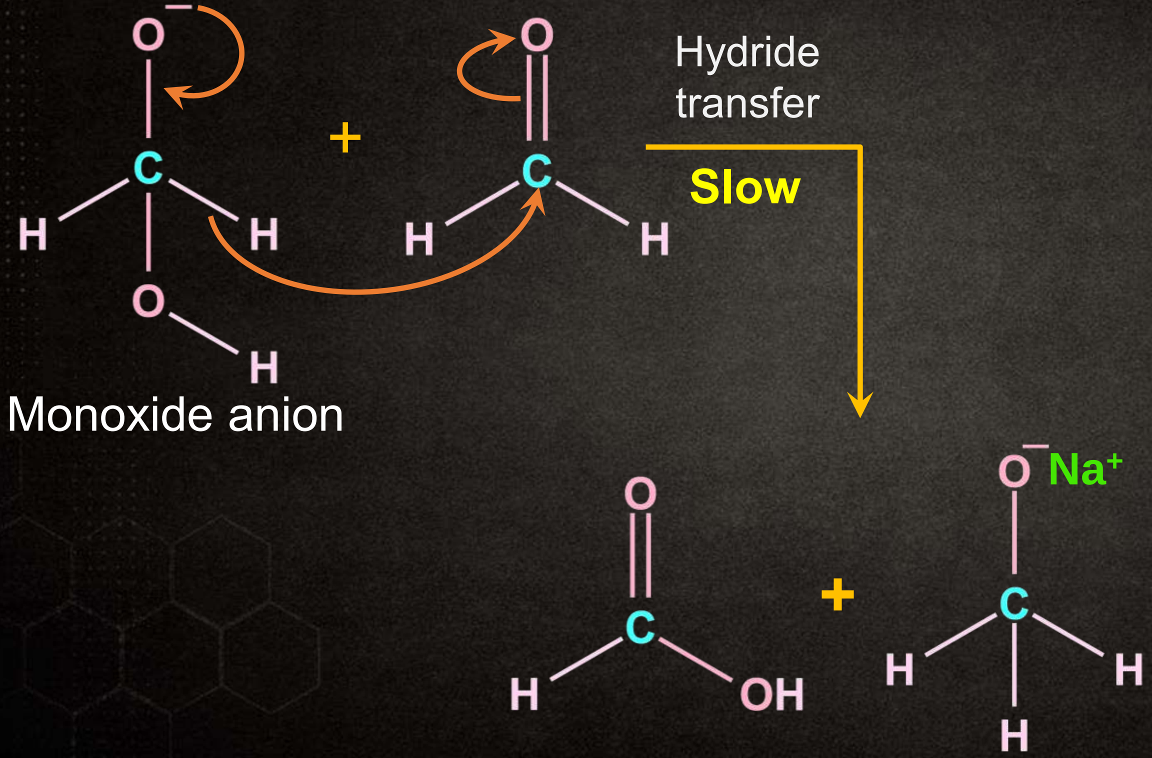


Monoxide anion

Proton Transfer



Hydride Transfer



Hydride transfer is the **rate-determining step** in **Cannizzaro reaction.**

Cross-Cannizzaro Reaction

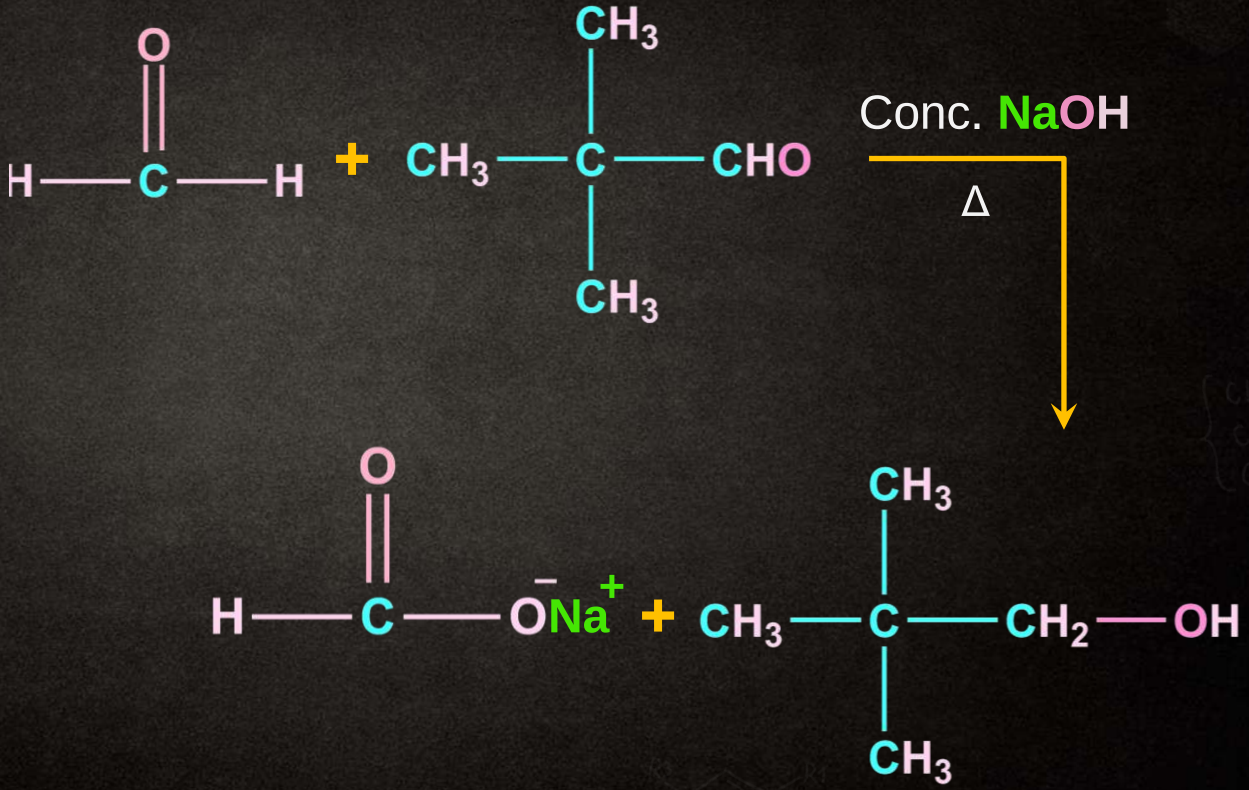
If we have **two different aldehydes** in the Cannizzaro reaction

It is known as a **Cross–Cannizzaro** reaction

The compound that is more reactive towards **nucleophilic addition reaction** undergoes **oxidation,** while the other one undergoes **reduction.**

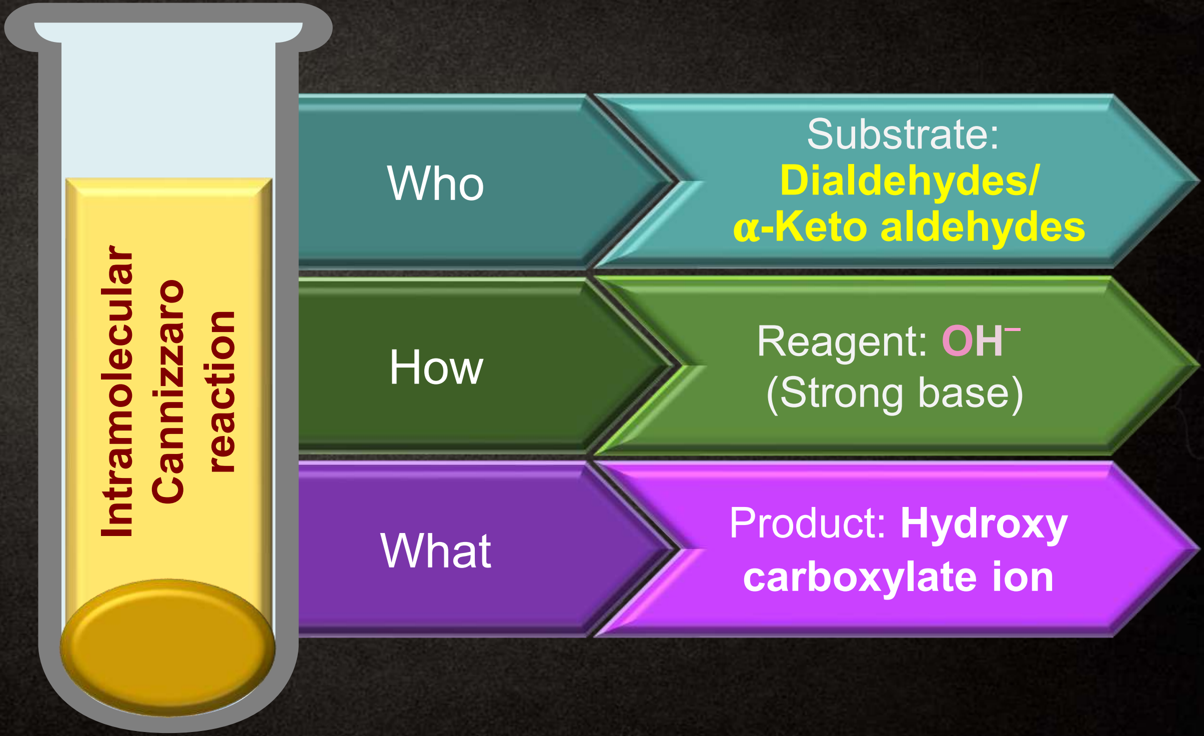
Cross-Cannizzaro Reaction

EXAMPLE



$$H-\overset{\overset{\displaystyle O}{\|}}{C}-H + CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CHO \xrightarrow[\Delta]{\text{Conc. NaOH}} H-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{-}{O}Na^{+} + CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2-OH$$

Intramolecular Cannizzaro Reaction



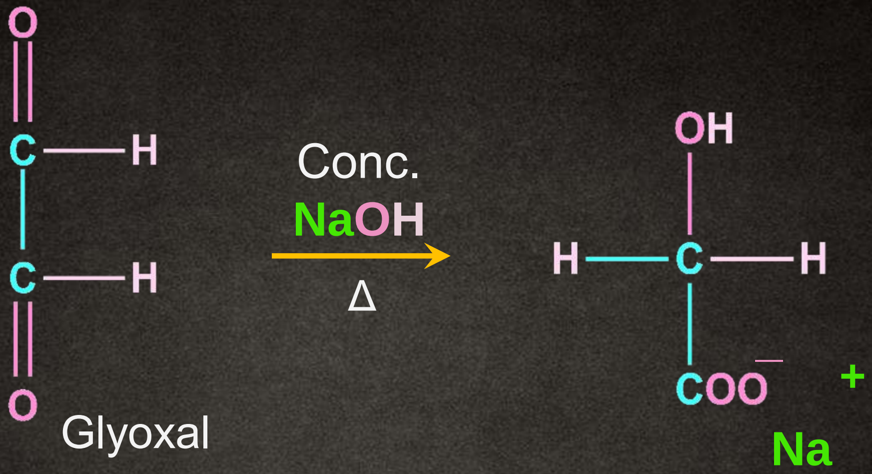
Intramolecular Cannizzaro reaction

Who — Substrate: **Dialdehydes/ α-Keto aldehydes**

How — Reagent: **OH^-** (Strong base)

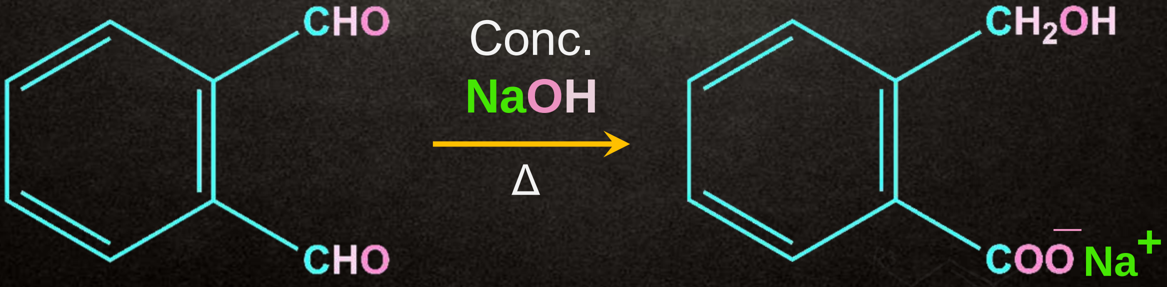
What — Product: **Hydroxy carboxylate ion**

Intramolecular Cannizzaro Reaction

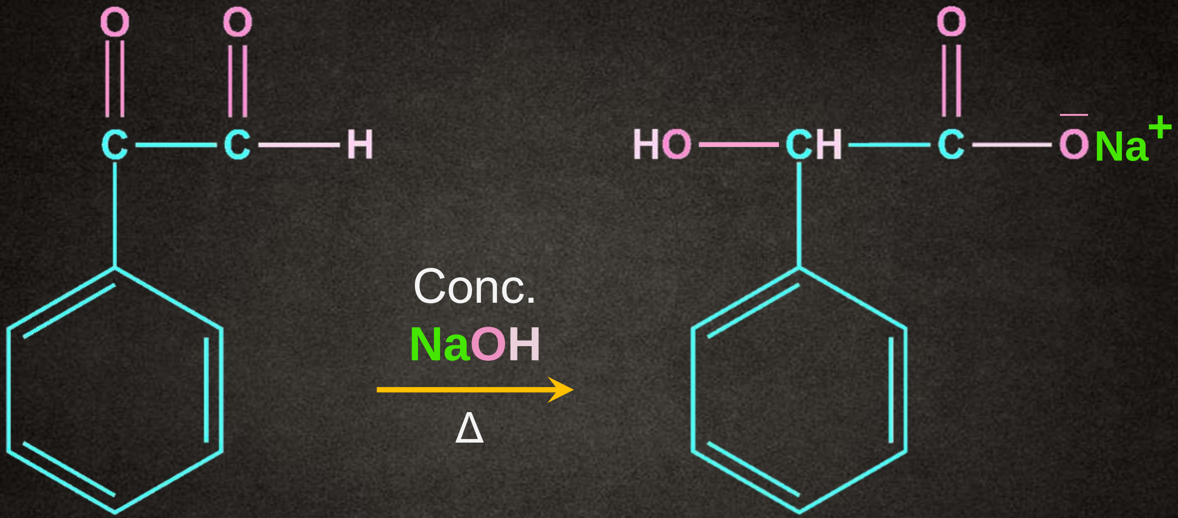


Glyoxal

Glycolate ion



Intramolecular Cannizzaro Reaction



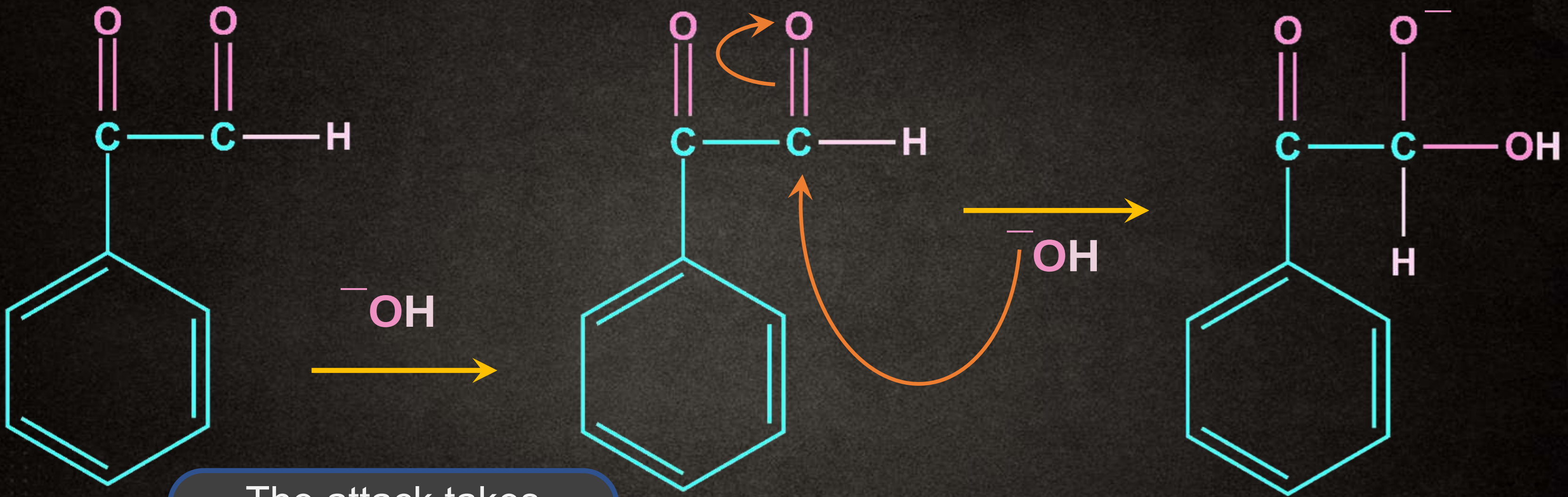
Steps Involved in Intramolecular Cannizzaro Reaction

03 Proton transfer

02 Intramolecular hydride transfer

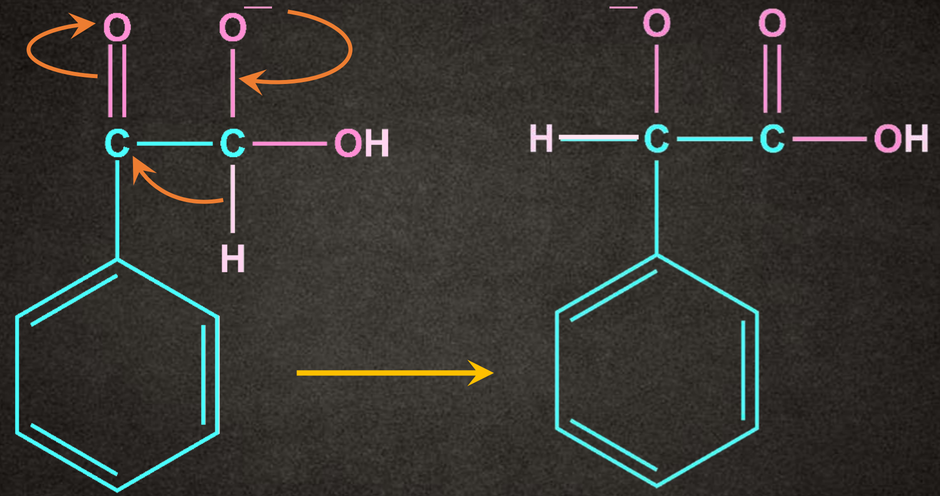
01 Nucleophilic attack of hydroxide

Nucleophilic Attack of Hydroxide

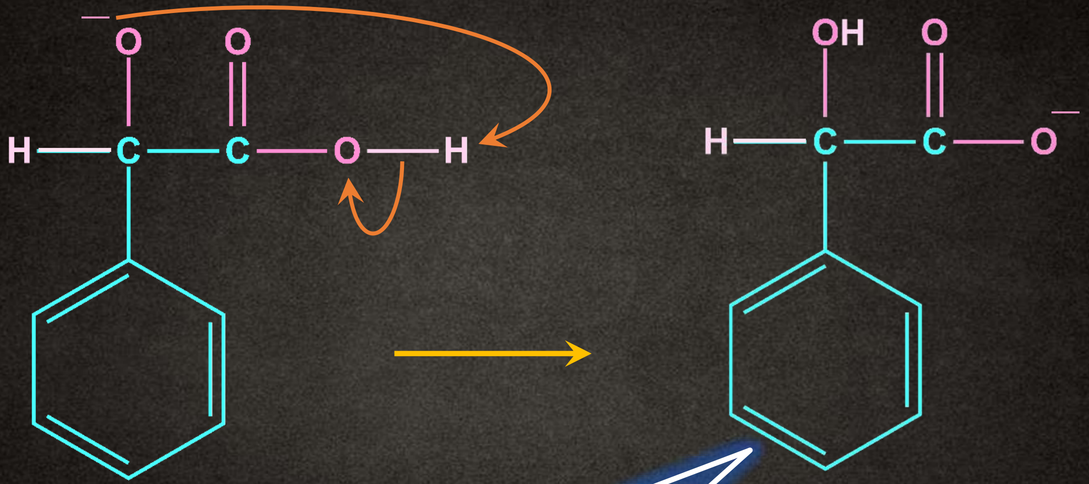


The attack takes place on the carbonyl carbon that is **more electrophilic**.

Intramolecular Hydride Transfer



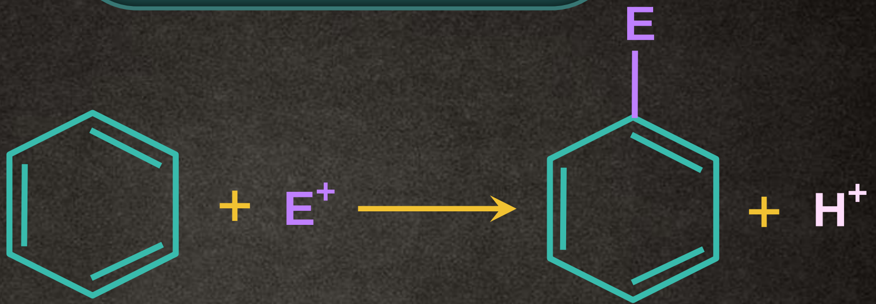
Proton Transfer



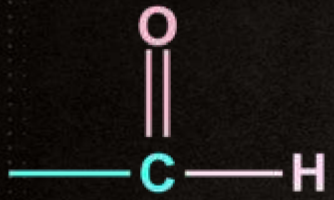
Salt of **mandelic acid**

Electrophilic Substitution Reaction

General reaction

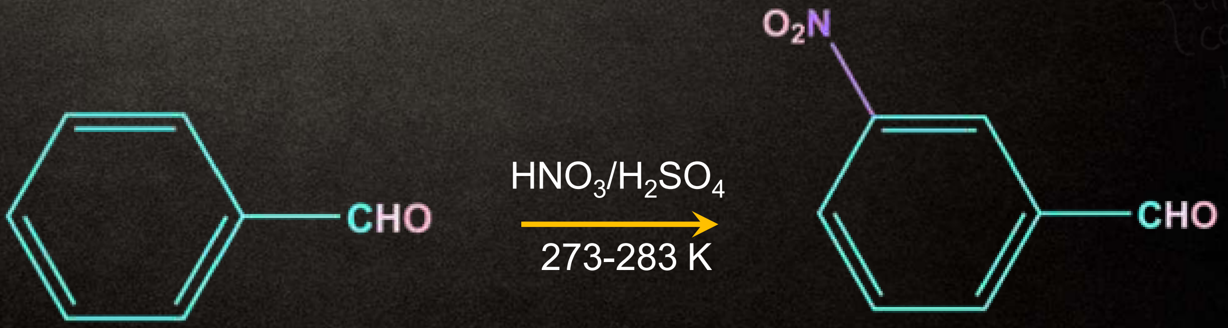


Electrophilic Substitution Reaction



Deactivating group and **meta directing**

Here, -CHO group is deactivating and meta directing. So, the electrophile is added to meta position in this reaction and rate of reaction will be slow due to deactivating nature of –CHO group.



Uses of Aldehyde and Ketone

Most of the ketones like acetone and ethyl methyl ketone are used as most commonly **industrial solvent.**

Aldehydes and **ketones** are known for their **sweet** and sometimes **pungent odors.** Because of their pleasant fragrances aldehyde and ketone containing molecules are often found in **perfumes.**

Acetone is used as a **nail polish remover.**

Urea formaldehyde resin are used an **adhesive** and are favored whenever strong structural joints are required.

Act as **starting materials & reagents** for the synthesis of **other products.**

Aldehyde and **ketone** are used in **dye industry.**

Uses of Aldehyde and Ketone

Formaldehyde is used as a preservative.

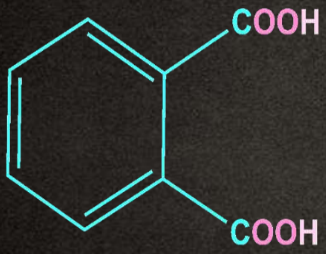
A 40% solution of formaldehyde is known as **formalin**. It is used for the preservation of biological specimens as it is a disinfectant, germicide, and antiseptic in nature. It prevents the growth of bacteria that cause decaying.

Carboxylic acids

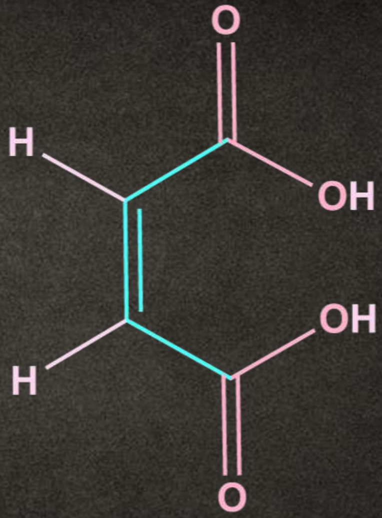
- Nomenclature
- Structure
- Preparation
- Chemical properties
- Uses

Common Names of Carboxylic Acids

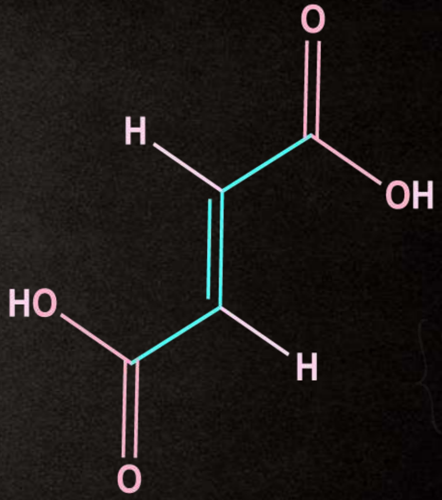
Benzoic acid



Phthalic acid



cis-Butenedioic acid (Maleic acid)

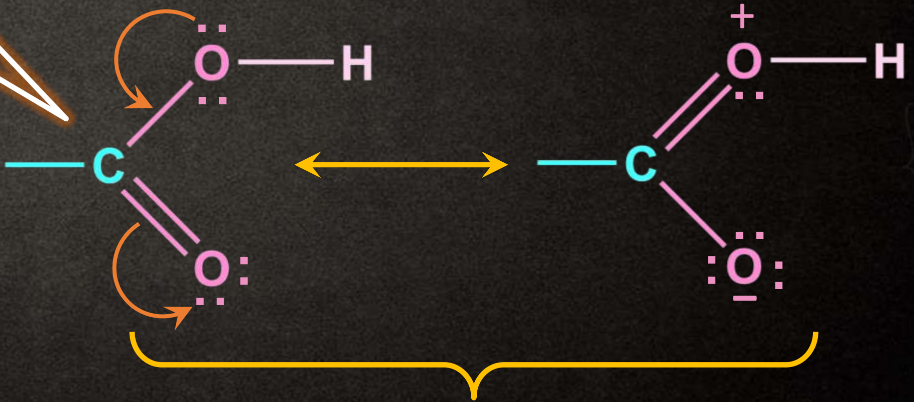


trans-Butenedioic acid (Fumaric acid)

Resonance in Carboxylic Acids

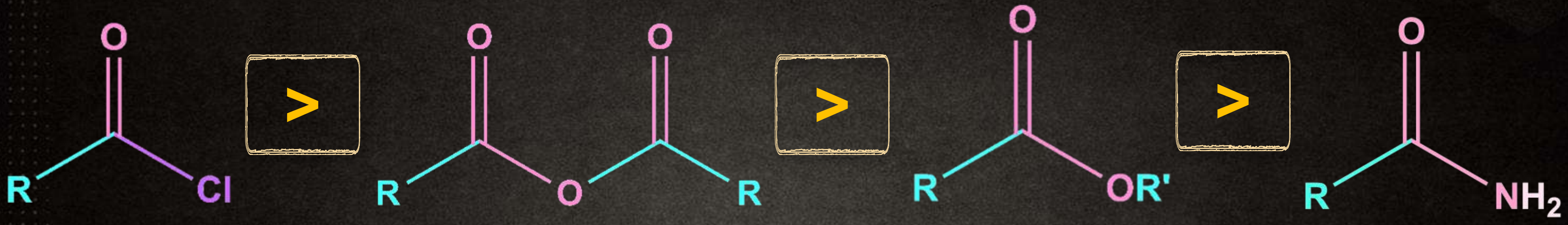
Carboxylic acid's C is **less electrophilic** than an aldehydic carbon.

Resonance phenomenon occurs in carboxylic acids.

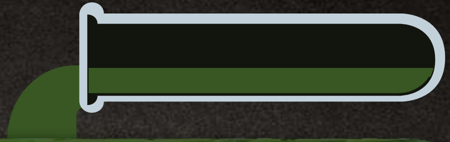


Resonating structures

Relative Reactivity of Acyl Compounds



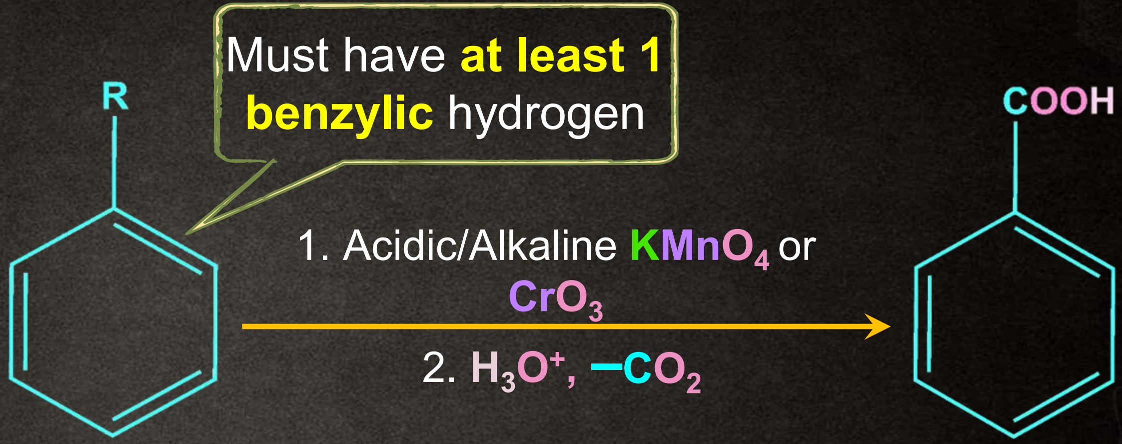
Preparation of Carboxylic Acids



- From 1° alcohol and aldehyde
- From alkyl benzenes
- From nitriles and amides
- From Grignard reagents
- From acyl halides and anhydrides
- From esters

Preparation from Alkyl Benzenes

General reaction

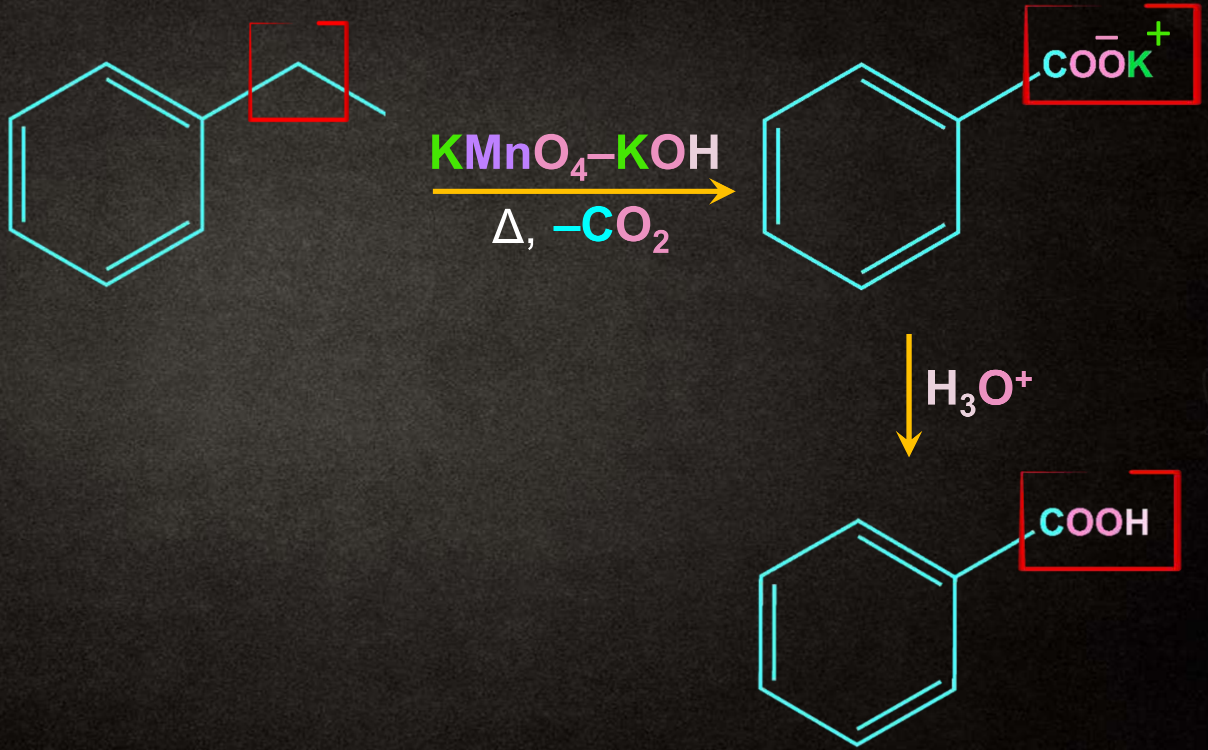

Must have **at least 1 benzylic** hydrogen

1. Acidic/Alkaline $KMnO_4$ or CrO_3

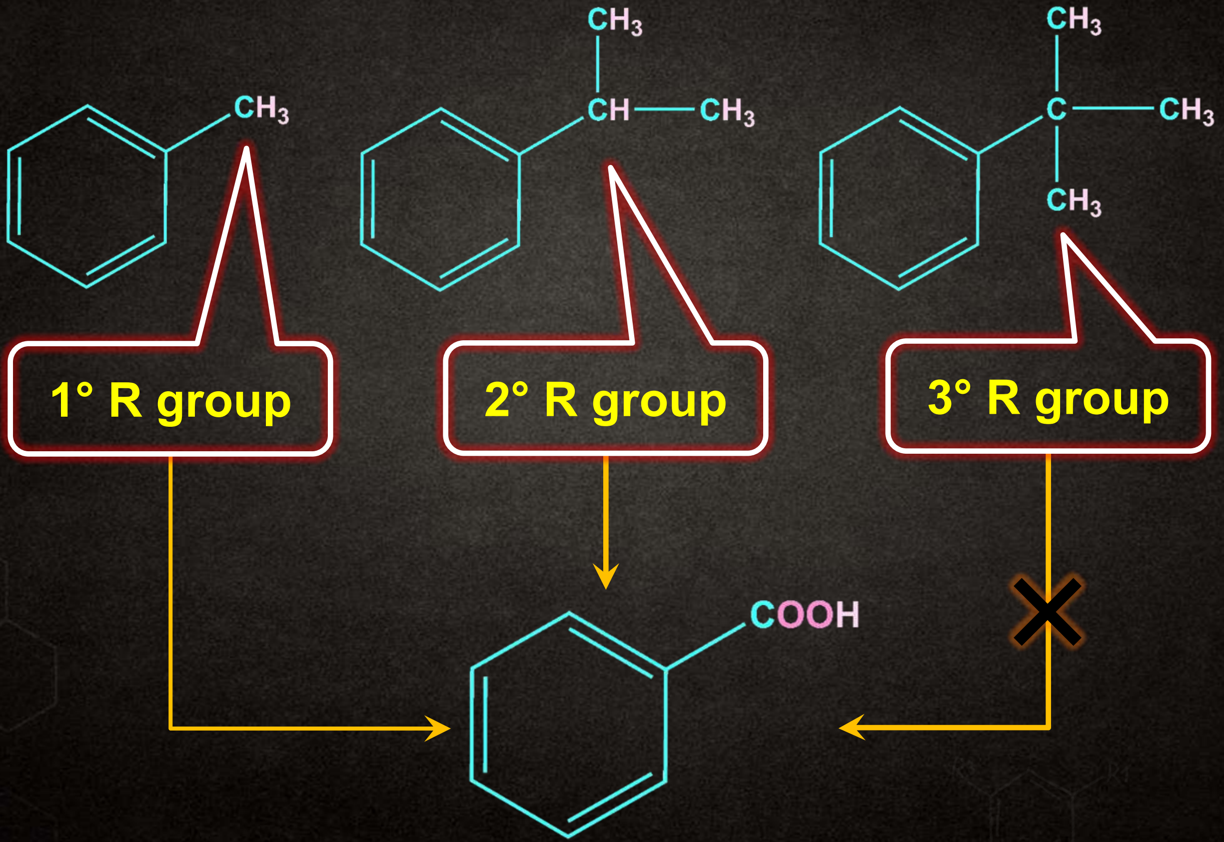
2. H_3O^+, $-CO_2$

Preparation from Alkyl Benzenes

EXAMPLE



Oxidation with KMnO$_4$–KOH



1° R group

2° R group

3° R group

Preparation from Alkyl Benzene

If a **tertiary group** or any **alkyl group with no benzylic-H** is present on benzene ring, then it will not undergo vigorous oxidation in the presence of **$KMnO_4$-KOH.**

Preparation from Nitriles

$RCN \longrightarrow RCOOH$

Reagents used ⇢ $H^+/OH^-/H_2O, \Delta$

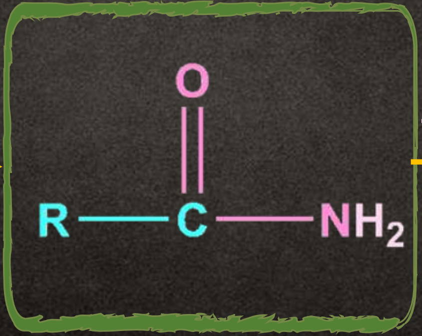
$$RCN \xrightarrow[-NH_3]{H_3O^+,\ \Delta} RCOOH$$

Hydrolysis of cyanide in **acidic** conditions

Preparation from Nitriles

$$CH_3-C\equiv N \xrightarrow[-NH_3]{H_3O^+,\ \Delta} CH_3-COOH$$

General reaction



$$RCN \xrightarrow{^-OH/H_2O} R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[-NH_3]{^-OH/H_2O,\ \Delta} RCOO^-$$

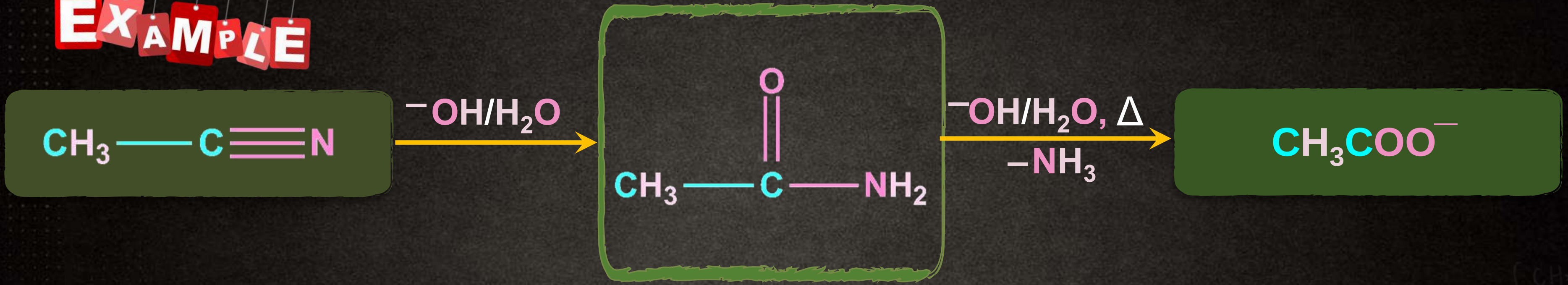
Amide

Hydrolysis of cyanide in **basic** conditions

We get caboxylate ion on heating; otherwise hydrolysis stops at amide.

Preparation from Nitriles

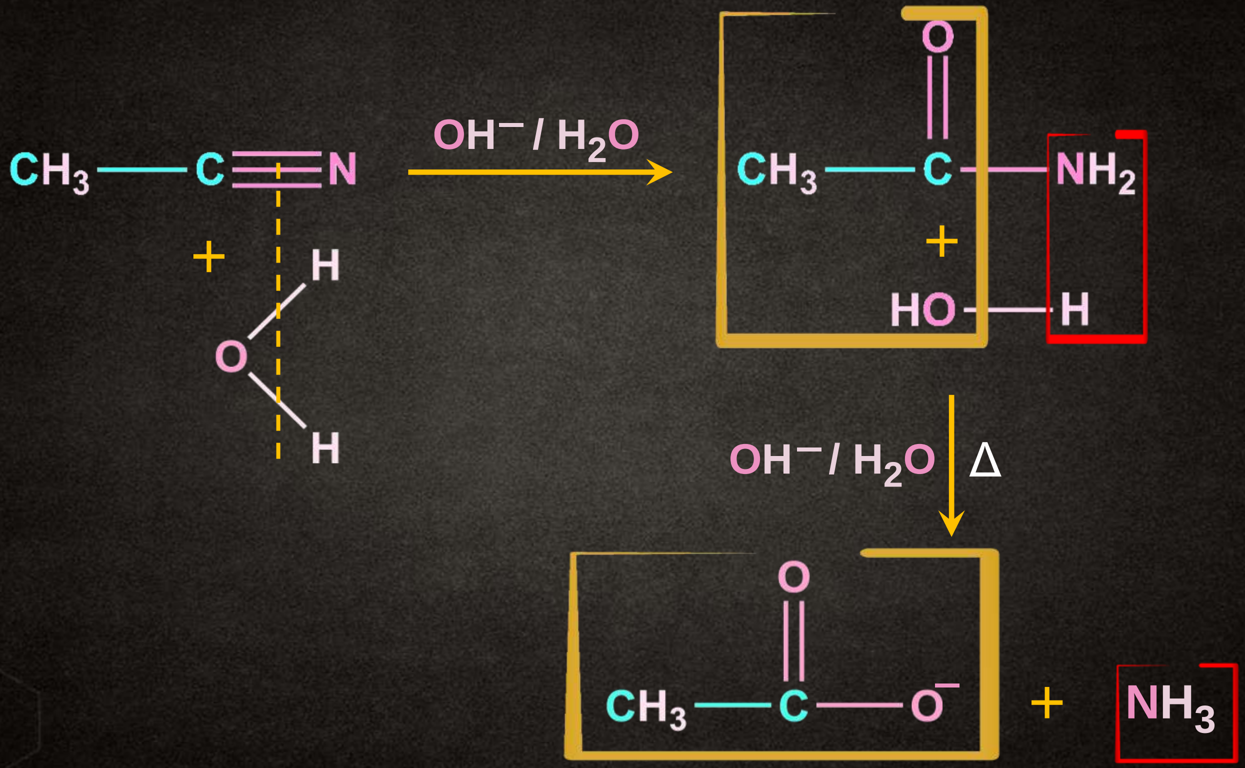
EXAMPLE



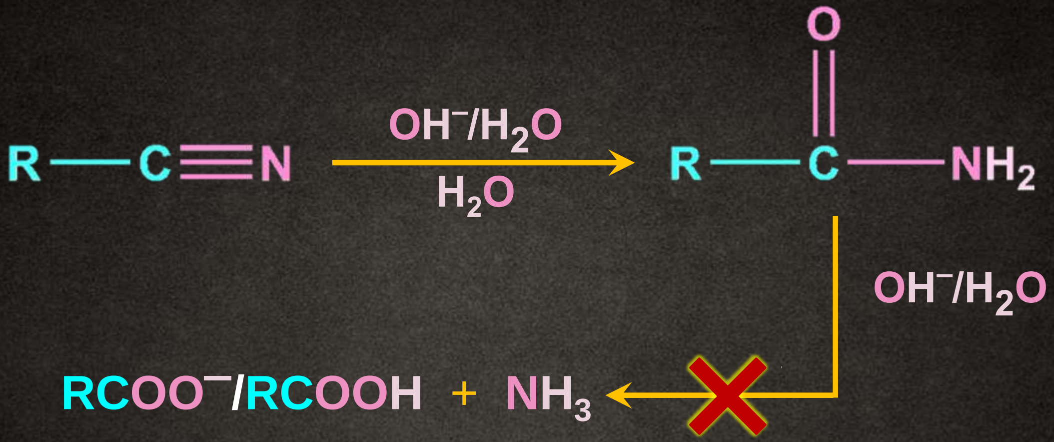
$$CH_3-C\equiv N \xrightarrow{^-OH/H_2O} CH_3-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow[-NH_3]{^-OH/H_2O,\ \Delta} CH_3COO^-$$

Amide

Hydrolysis of Nitriles



Note



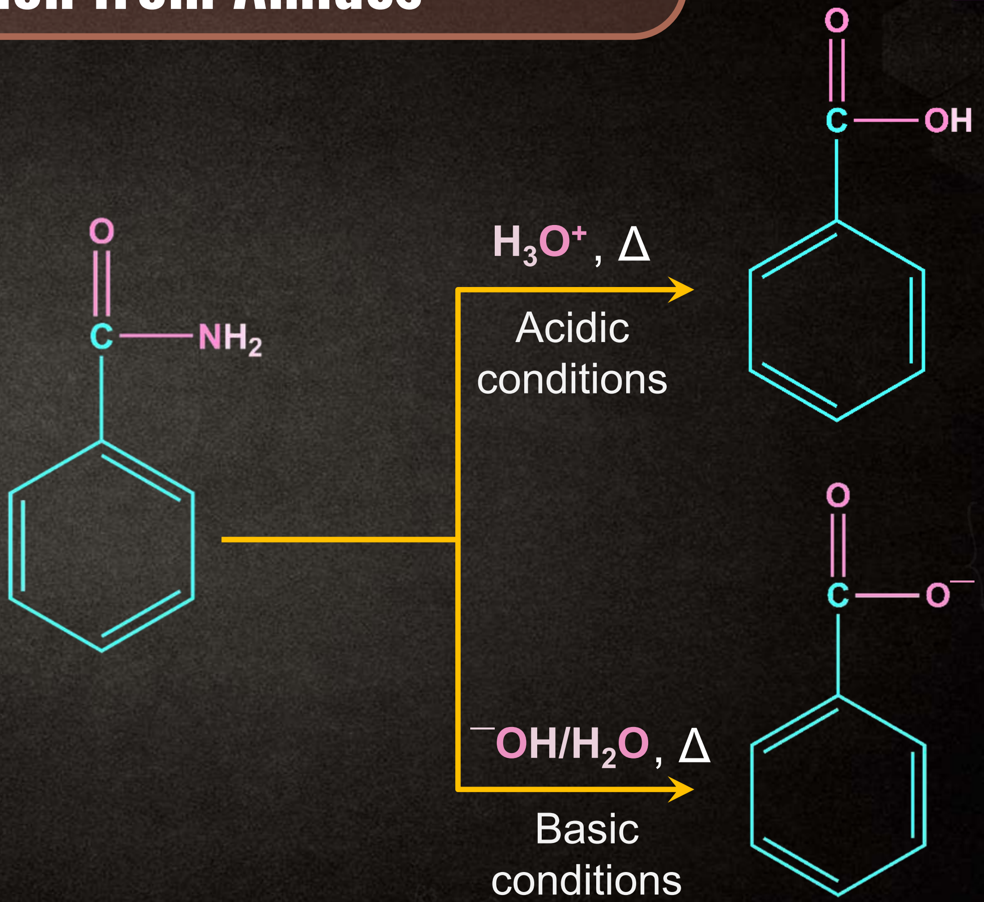
$$R-C\equiv N \xrightarrow[H_2O]{OH^-/H_2O} R-\overset{\overset{O}{\|}}{C}-NH_2$$

$$RCOO^-/RCOOH + NH_3 \cancel{\xleftarrow{OH^-/H_2O}} R-\overset{\overset{O}{\|}}{C}-NH_2$$

Mild conditions are used to **stop** the reaction at the **amide** stage.

Preparation from Amides

EXAMPLE



H_3O^+, Δ

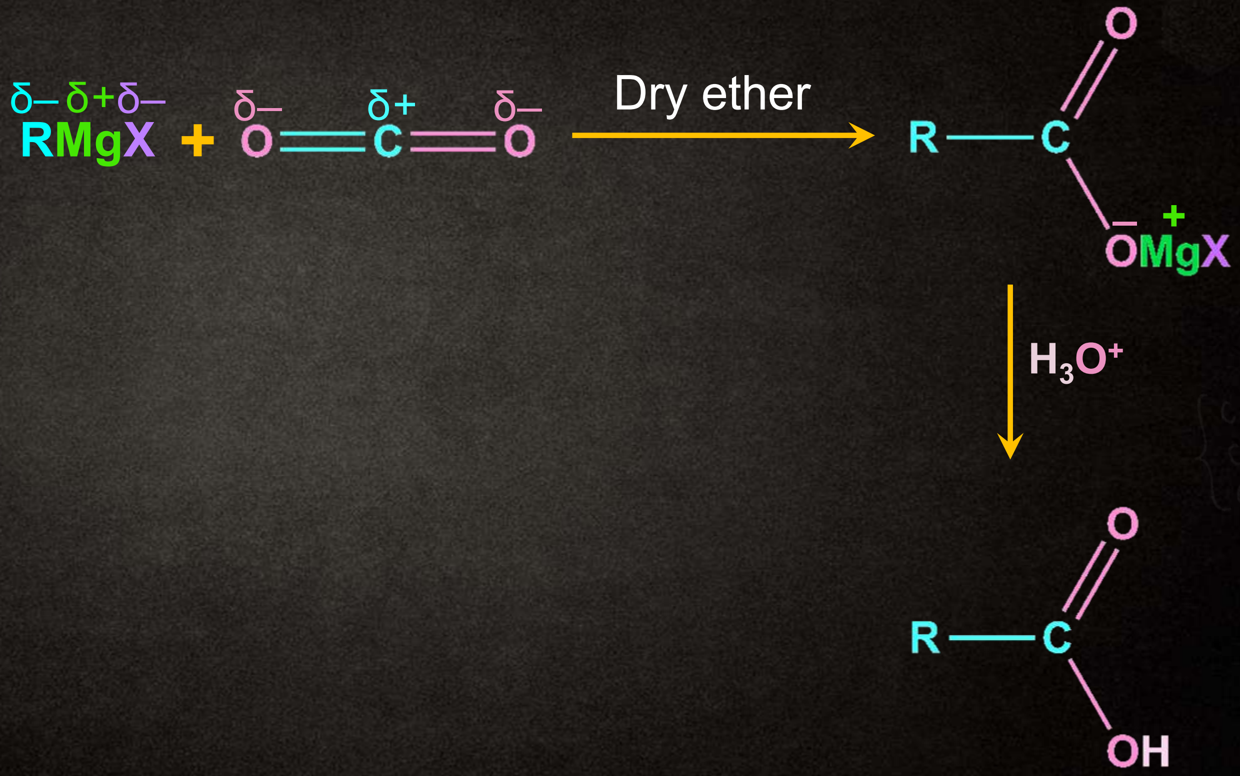
Acidic conditions

$^-OH/H_2O$, Δ

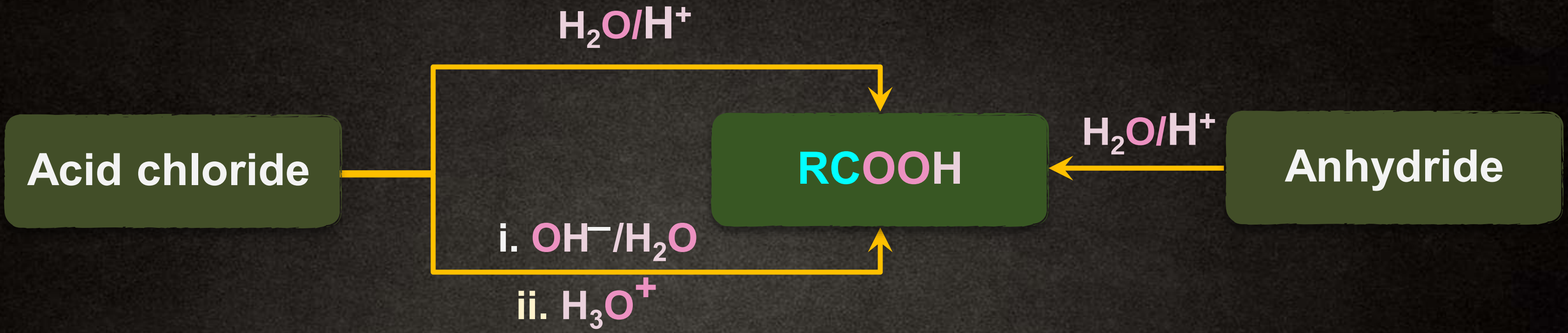
Basic conditions

Recall

General reaction



Preparation from Acyl Halides and Acid Anhydrides



H_2O/H^+

Acid chloride

RCOOH

H_2O/H^+

Anhydride

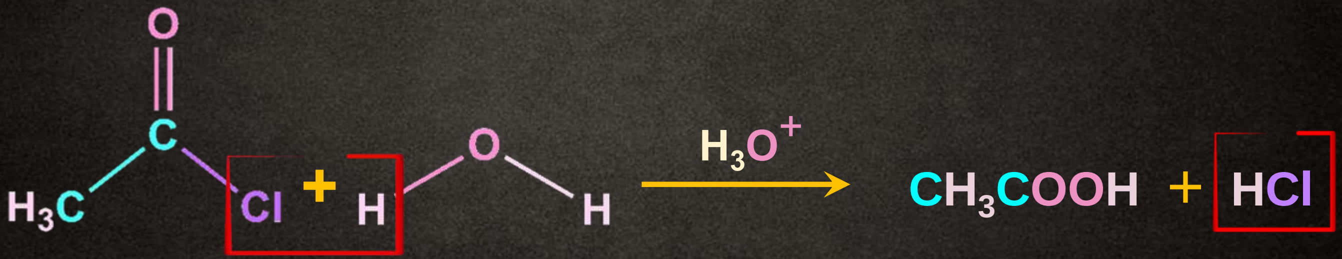
i. OH^-/H_2O

ii. H_3O^+

Preparation from Acid Chlorides

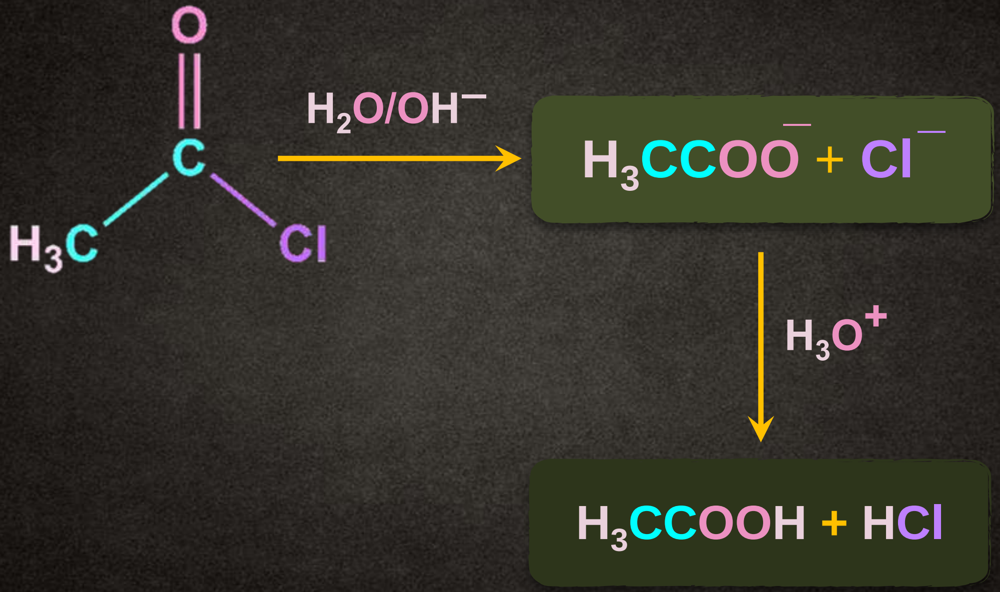
EXAMPLE

$$CH_3COCl \xrightarrow[-Cl^{-}]{H_2O} CH_3COOH$$



$$\xrightarrow{H_3O^+} CH_3COOH + \boxed{HCl}$$

Preparation from Acid Chlorides



H_2O/OH^-

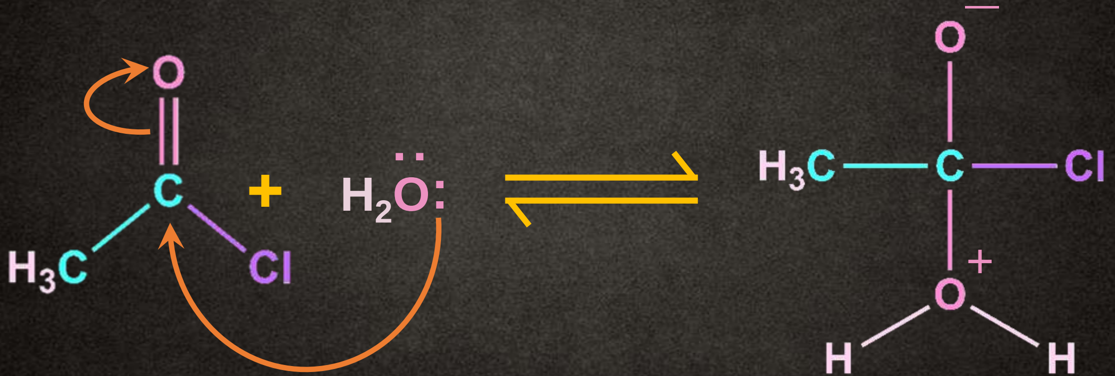
$H_3CCOO^- + Cl^-$

H_3O^+

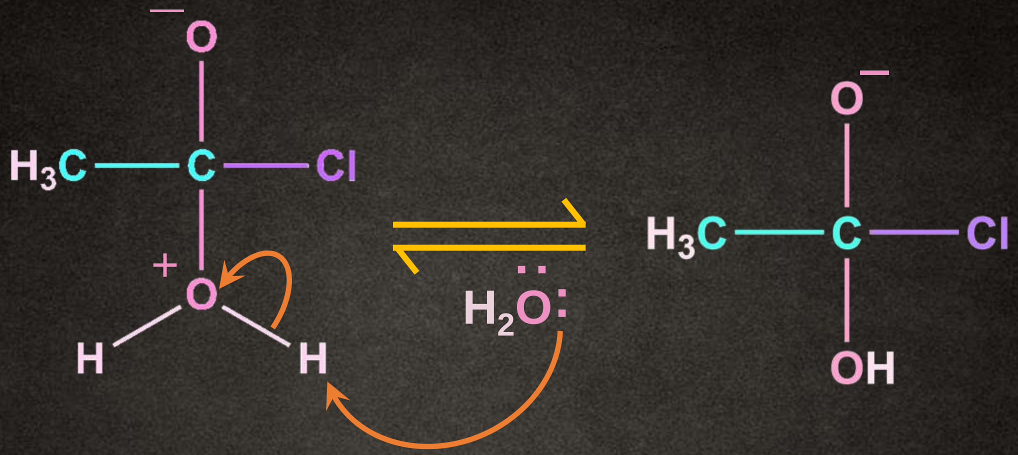
$H_3CCOOH + HCl$

Steps Involved in the Hydrolysis of Acid Chloride

Step 1 Attack of the nucleophile

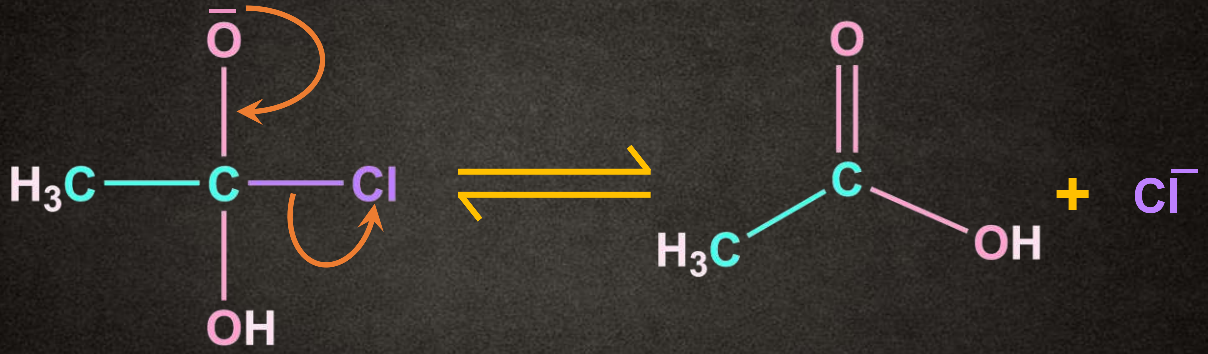


Attack of the Nucleophile

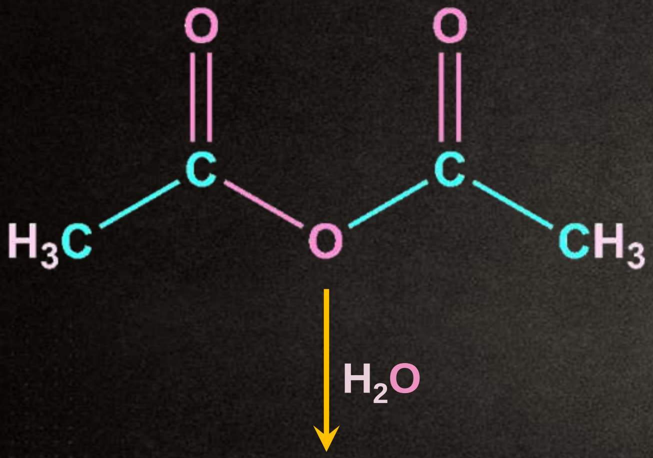


Removal of the Leaving Group

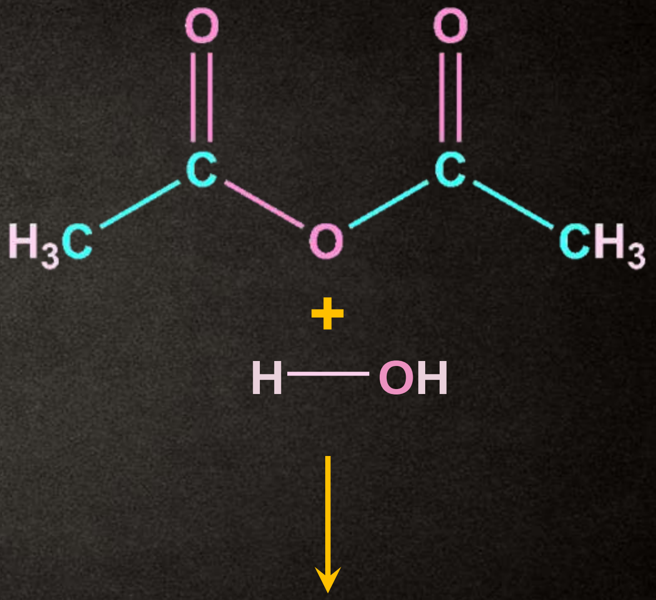
Step 2 Removal of the leaving group



Preparation from Acid Anhydrides



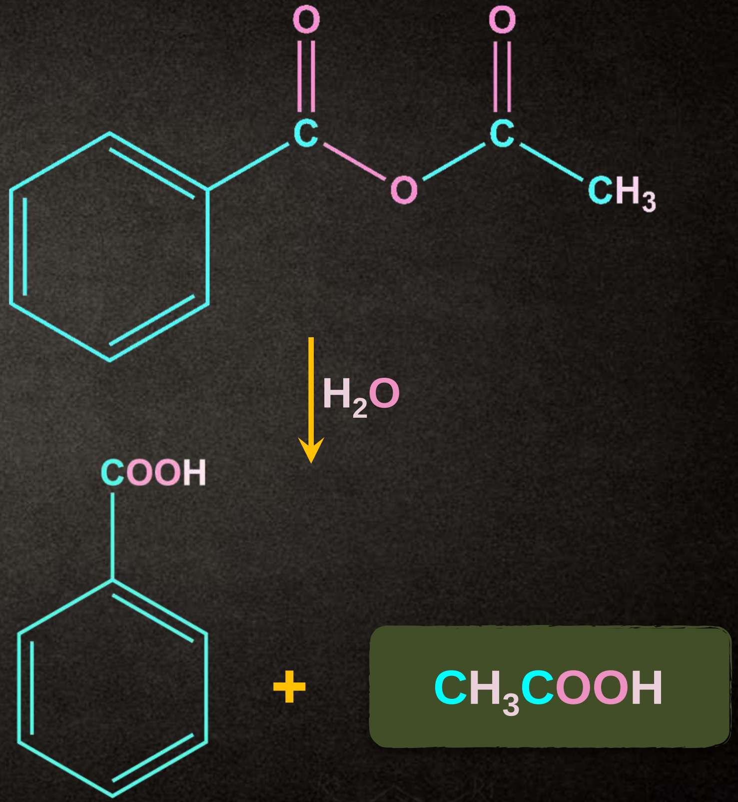
$2\ CH_3COOH$



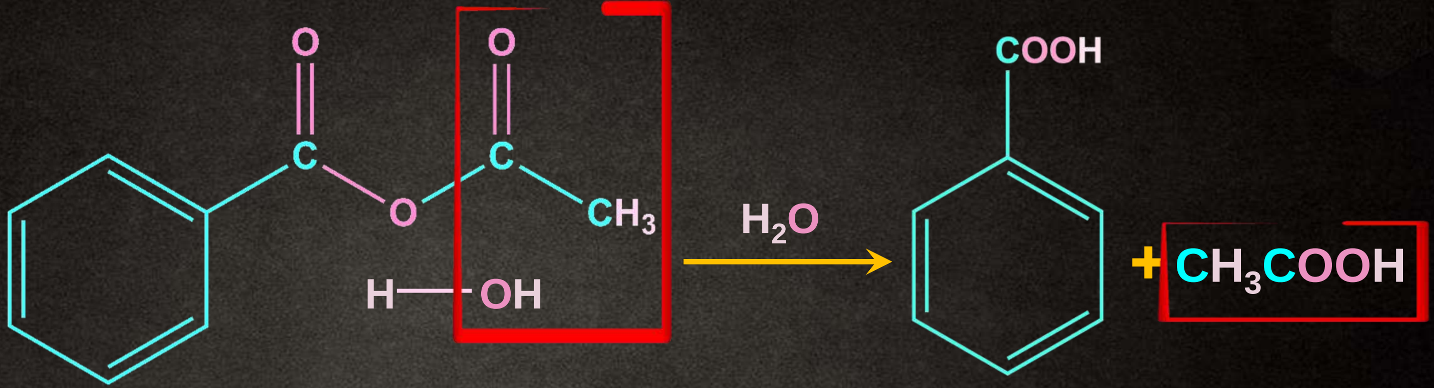
$CH_3COOH + \boxed{CH_3COOH}$

Preparation from Acid Anhydrides

A mixture of **carboxylic acids** is obtained with different **alkyl/aryl** groups.

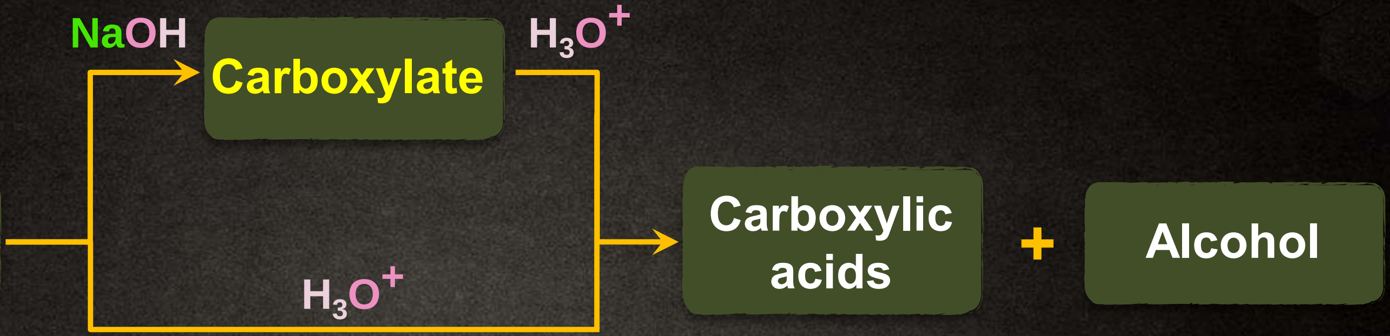


Preparation from Acid Anhydrides



Preparation from Esters

General reaction



NaOH

Carboxylate

H_3O^+

Ester

H_3O^+

Carboxylic acids

+

Alcohol

Basic hydrolysis of ester

$$C_2H_5COOC_2H_5 \overset{NaOH}{\rightleftharpoons} C_2H_5CO\bar{O}Na^+ + C_2H_5OH \xrightarrow{H_3O^+} C_2H_5COOH + C_2H_5OH$$

Preparation from Esters

EXAMPLE

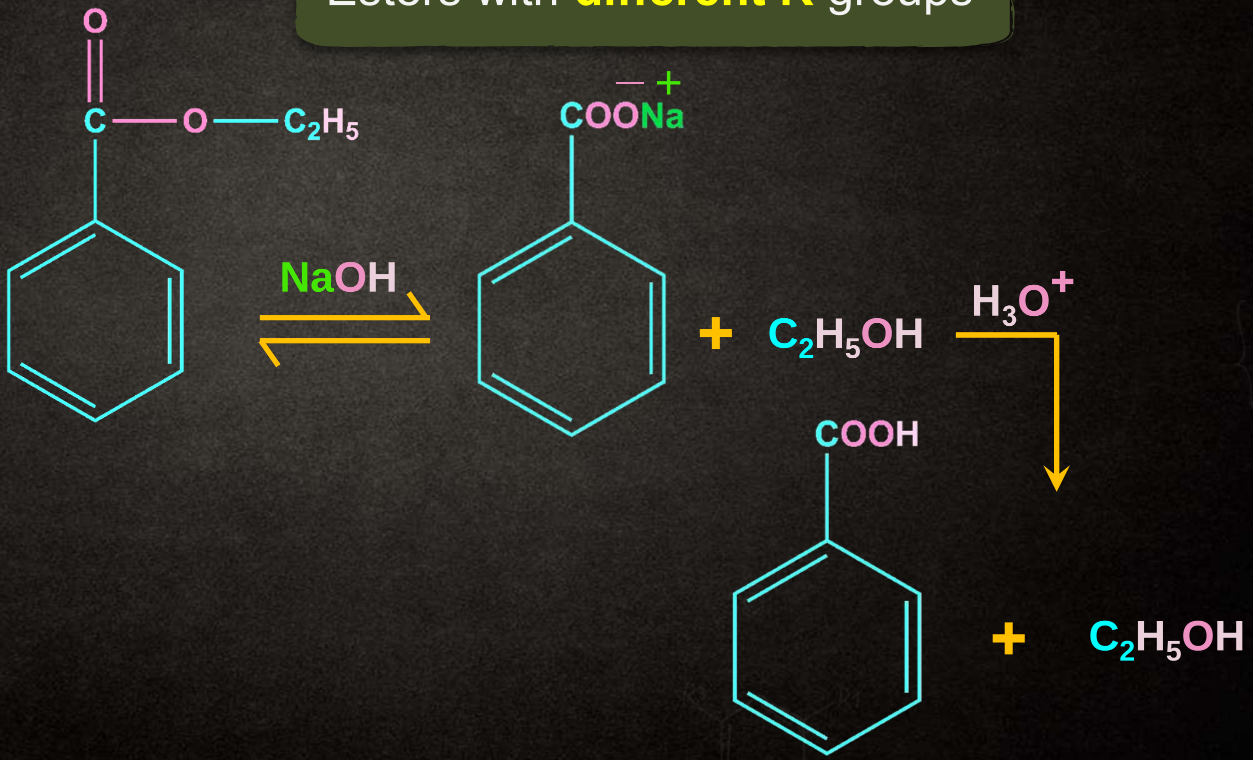
Acidic hydrolysis of ester

$$C_2H_5COOC_2H_5 \xrightleftharpoons{H_3O^+} C_2H_5COOH + C_2H_5OH$$

Preparation from Esters

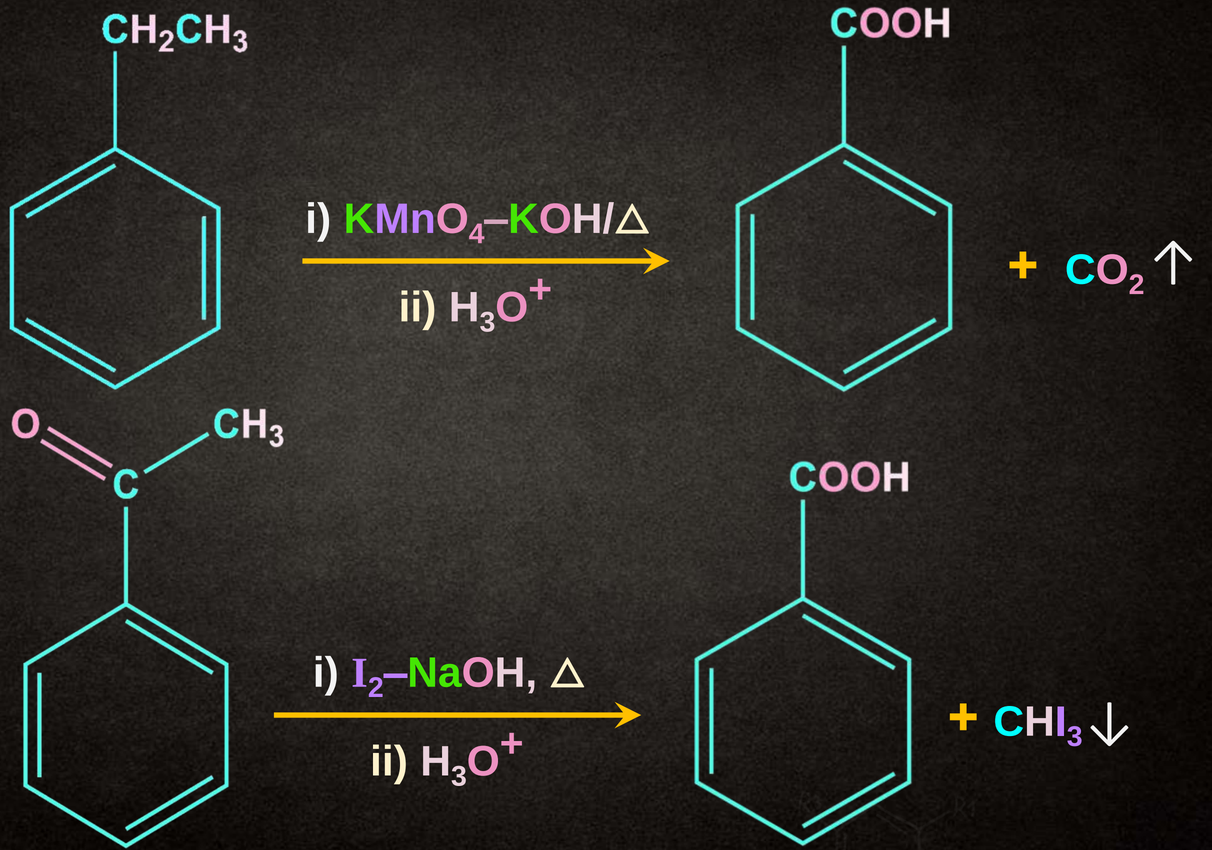
EXAMPLE

Esters with **different R groups**



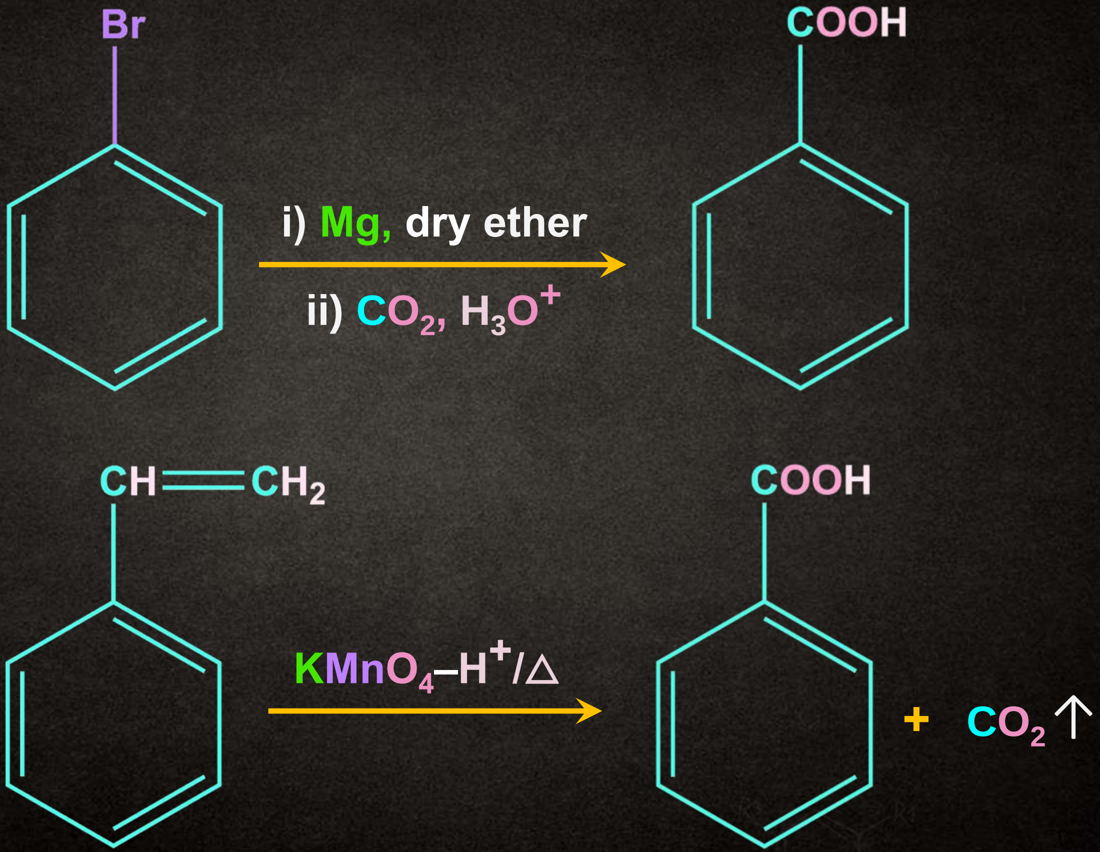
Preparation of Benzoic Acid

Reaction



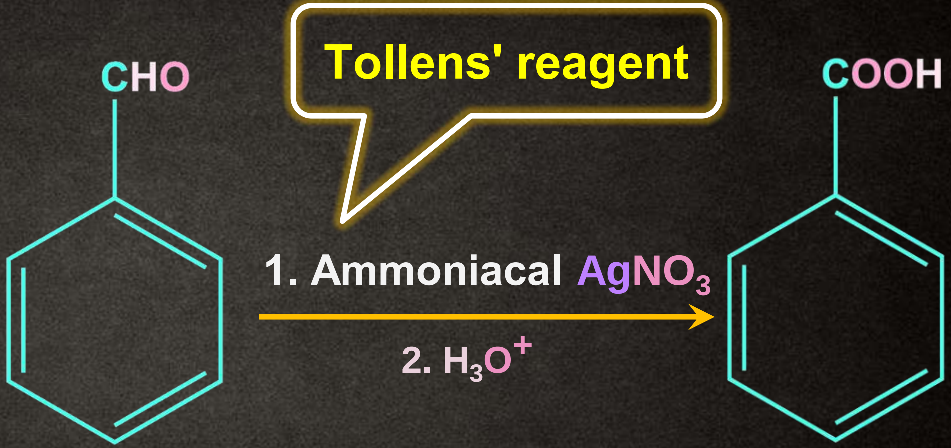
Preparation of Benzoic Acid

Reaction



Preparation of Benzoic Acid

Reaction



Tollens' reagent

1. Ammoniacal $AgNO_3$

2. H_3O^+

Preparation of Dicarboxylic Acids

Preparation methods of dicarboxylic acids

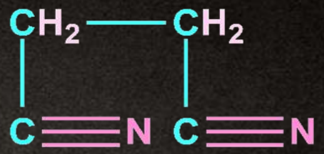
- Hydrolysis of dinitrile compounds
- Oxidation by $KMnO_4$
- Oxidative ozonolysis

Dinitrile Compounds

EXAMPLE

$N\equiv C-CH_2-C\equiv N$

Geminal dinitrile



$CH_2(C\equiv N)-CH_2(C\equiv N)$

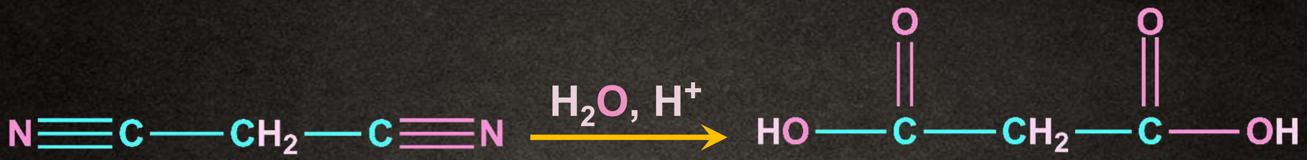
Vicinal dinitrile

Preparation

$$CH_2(Cl)-CH_2(Cl) + 2KCN \xrightarrow{S_N2} CH_2(C\equiv N)-CH_2(C\equiv N)$$

Preparation from Dinitrile Compounds

EXAMPLE



$$N\equiv C-CH_2-C\equiv N \xrightarrow{H_2O,\ H^+} HO-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-OH$$

Malonic acid

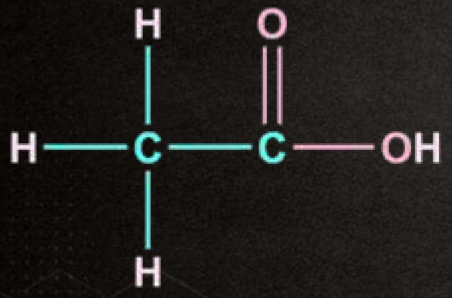
Hydrolysis of dinitrile compound yields carboxylic acid

Physical Properties

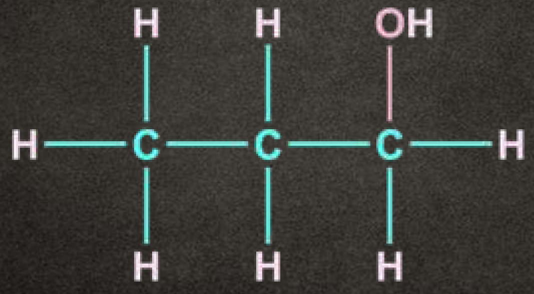
- Boiling point
- Physical state
- Odour
- Solubility

Boiling Point of Carboxylic Acids

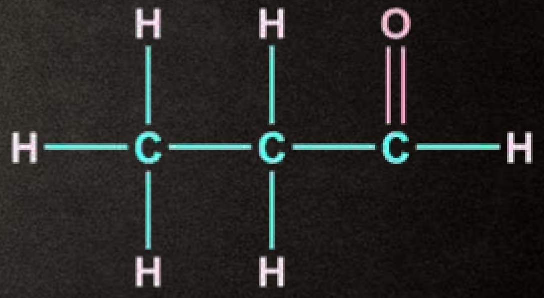
B.P. of carboxylic acids are **higher** than that of **alcohols, ketones** or **aldehydes** of similar molar mass.



Acetic Acid
(b.p.= 118℃)

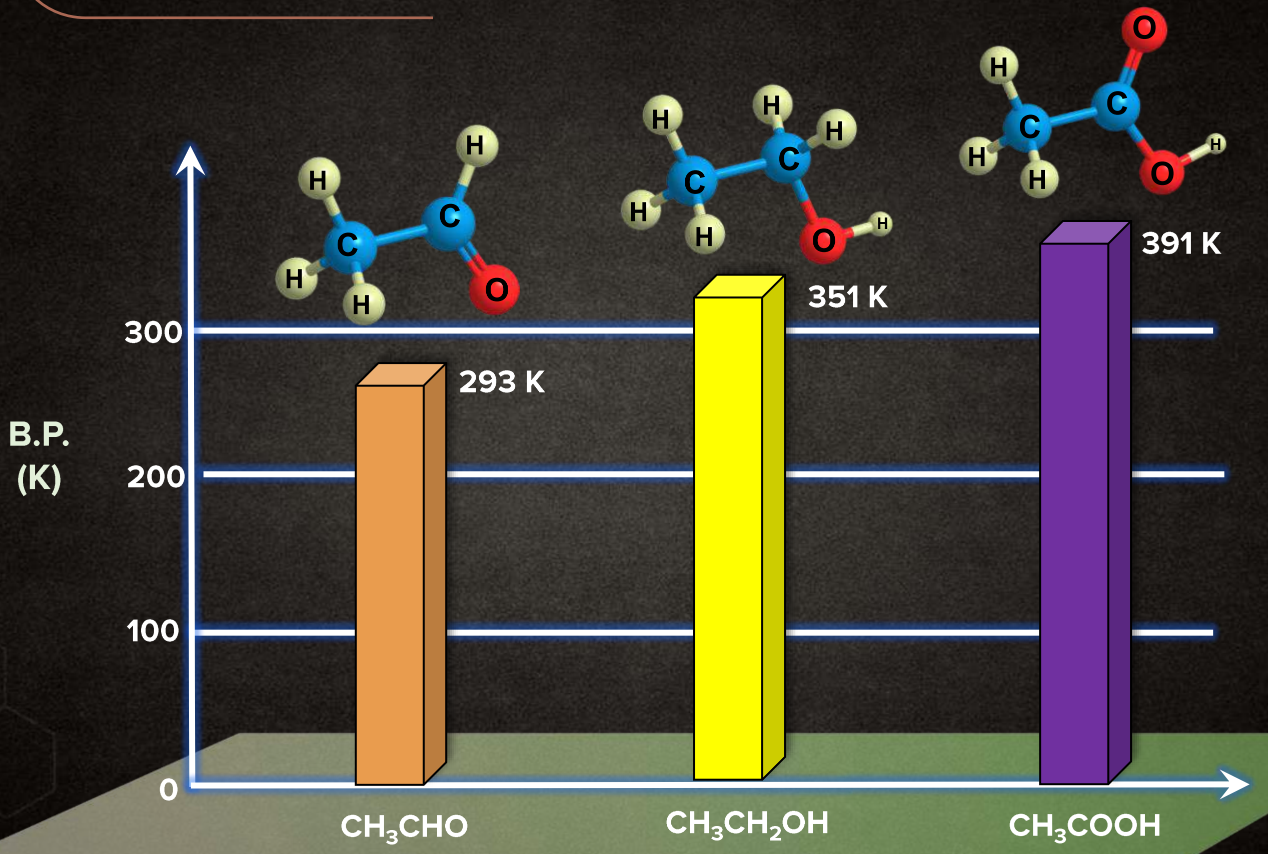


Propanol
(b.p.= 97℃)



Propanal
(b.p.= 49℃)

Boiling Point of Carboxylic Acids



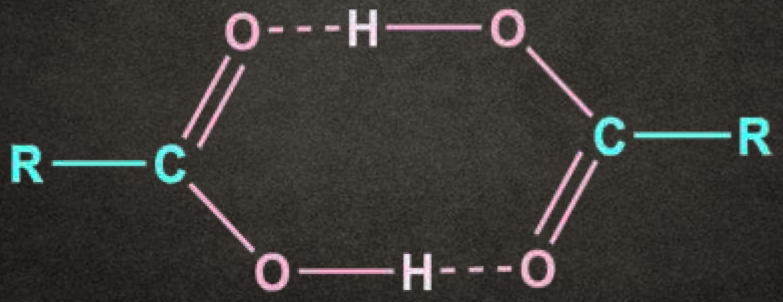
CH_3CHO

CH_3CH_2OH

CH_3COOH

Boiling Point of Carboxylic Acids

High B.P. of **carboxylic acids** is the result of the formation of a stable **H-bonded dimer.**



Physical State

Aliphatic carboxylic acids upto nine carbon atoms

Colourless liquids at room temperature

Higher acids

Wax-like solids due to their low volatility

Methanoic acid

Ethanoic acid

Propanoic acid

Butanoic acid

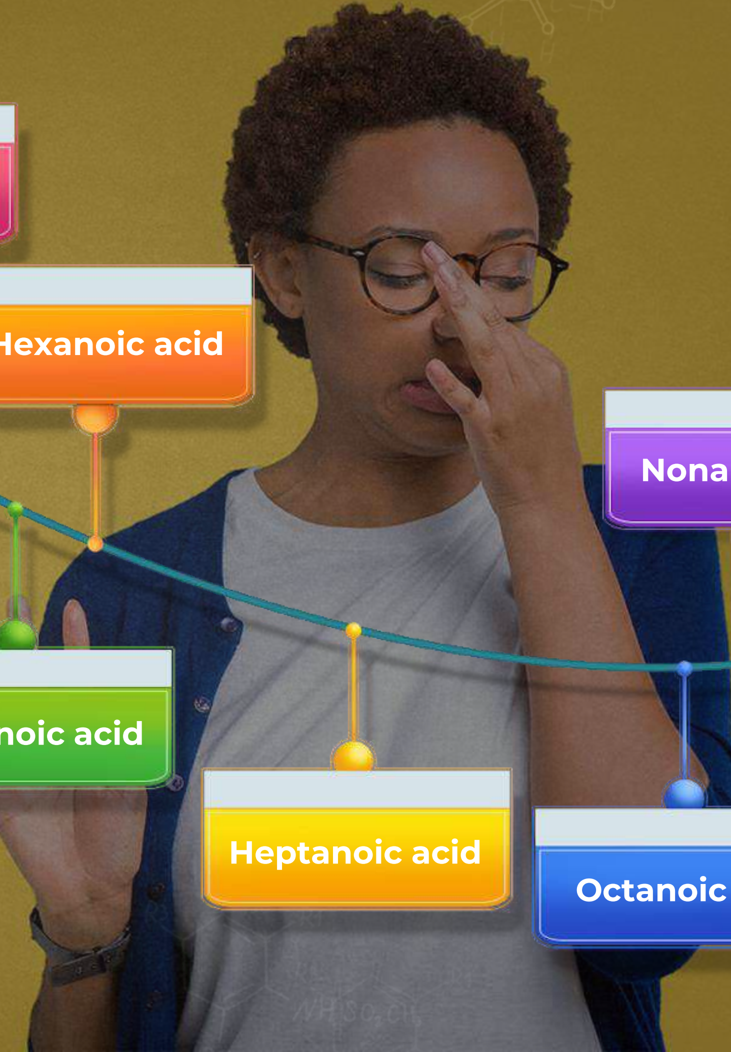
Pentanoic acid

Hexanoic acid

Heptanoic acid

Octanoic acid

Nonanoic acid



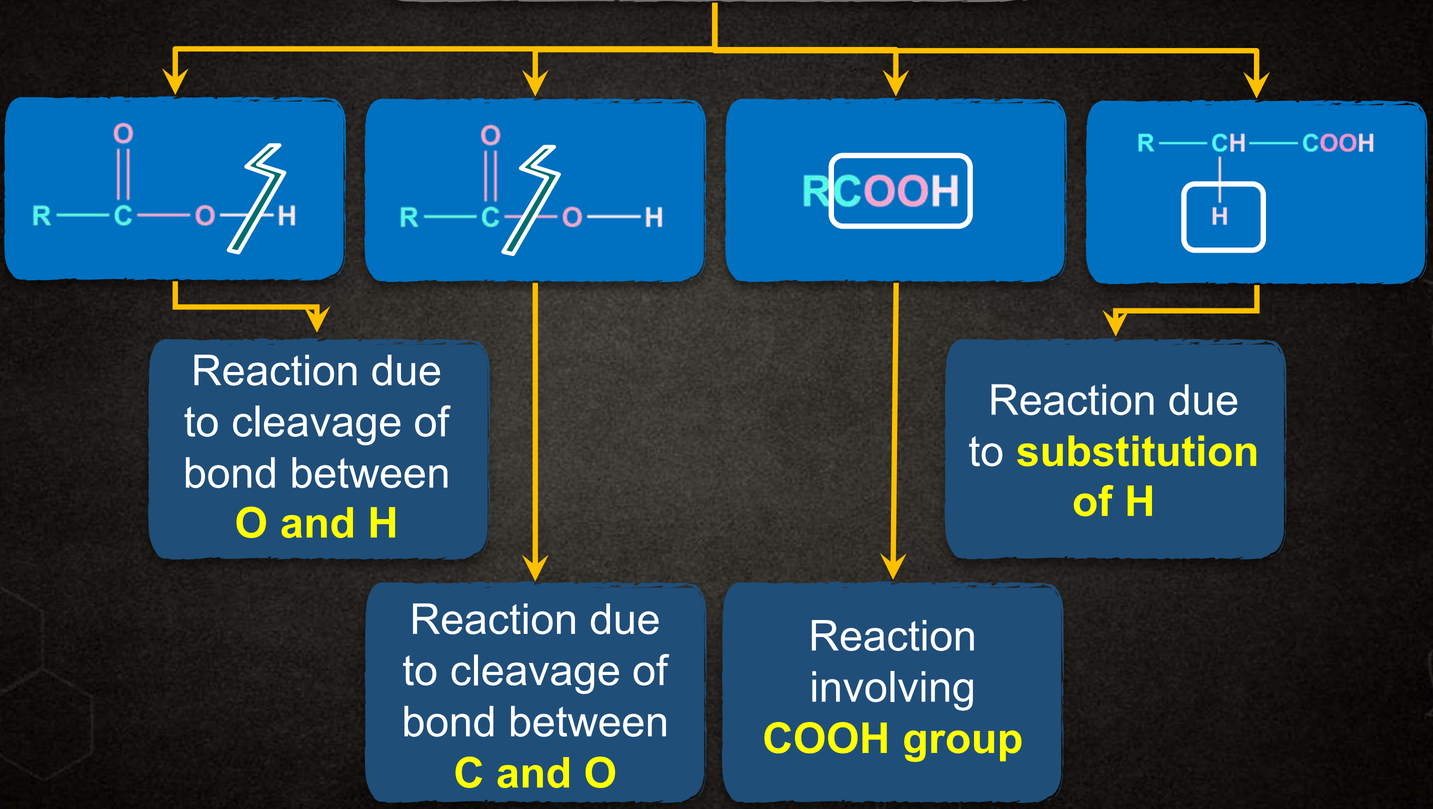
Odour

Aliphatic carboxylic acids upto nine carbon atoms have unpleasant odours.

Solubility

Carboxylic acids form hydrogen bonds with H2O and the lower molar mass aliphatic carboxylic acids (upto 4 carbon atoms) are miscible with water

Reactions of carboxylic acids are classified as



Reaction due to cleavage of bond between **O and H**

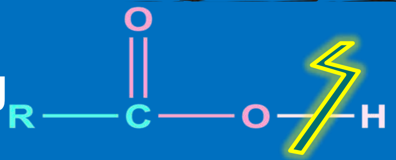
Reaction due to cleavage of bond between **C and O**

Reaction involving **COOH group**

Reaction due to **substitution of H**

Reactions of Carboxylic Acids

Reactions involving



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

- Acidity
- Reaction with metals
- Reaction with alkalies

Recall

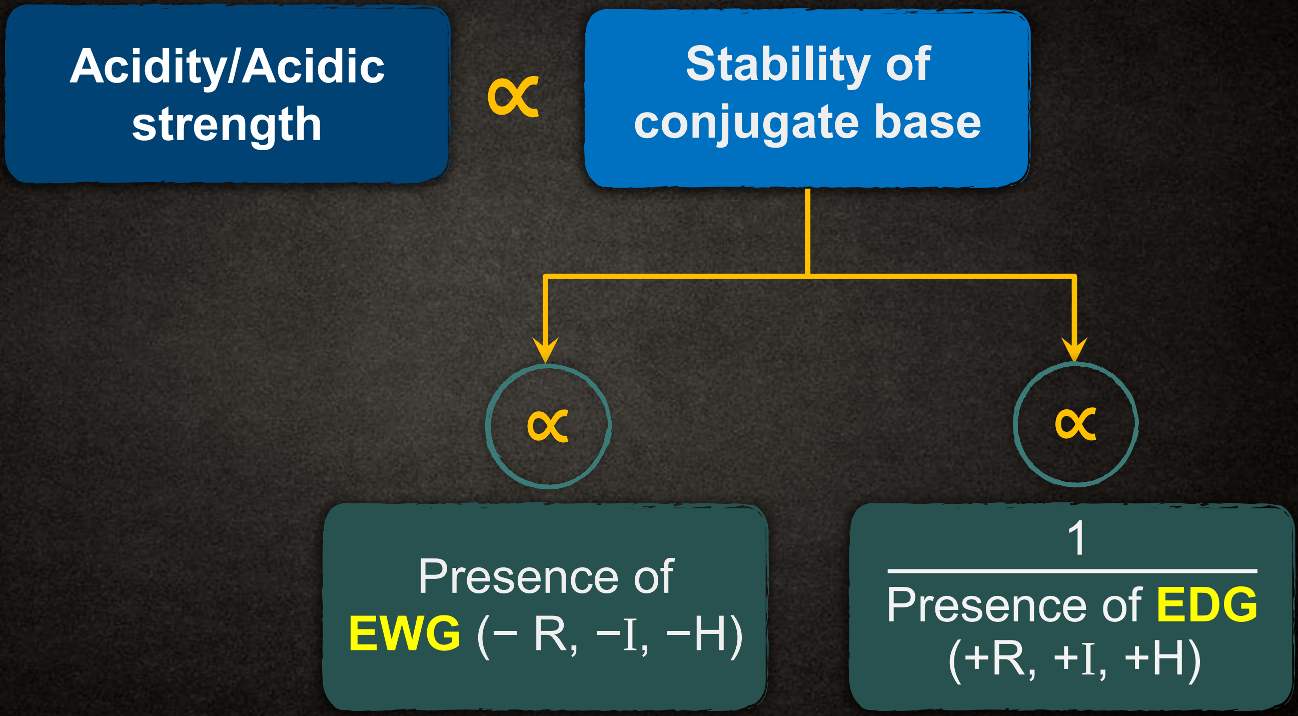
Acidic strength $\propto$ K_a $\propto$ $\frac{1}{pK_a}$ $\propto$ $\frac{1}{pH}$

Where

$pK_a = -\log_{10}K_a$

$pK_a = \log_{10}\left(\frac{1}{K_a}\right)$

Recall



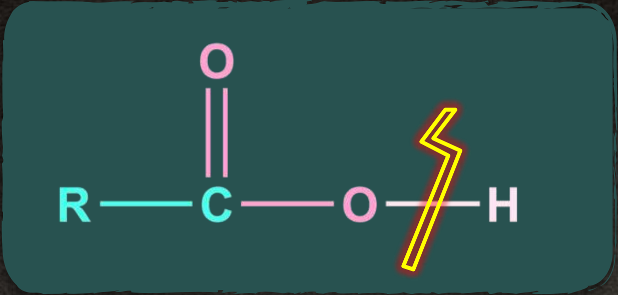
Acidity/Acidic strength $\propto$ **Stability of conjugate base**

$\propto$ Presence of **EWG** (− R, −I, −H)

$\propto$ $\frac{1}{\text{Presence of } \textbf{EDG} \text{ (+R, +I, +H)}}$

Reactions with Active Metals

General reaction



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

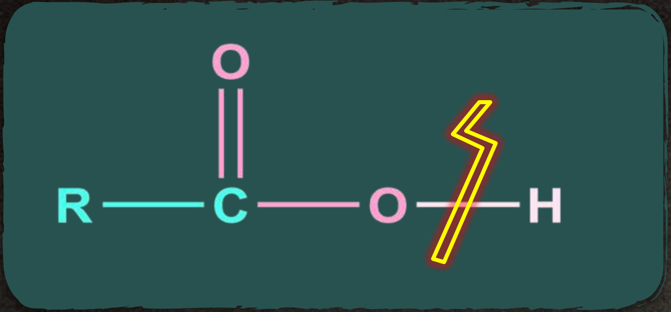
Carboxylic acid → Carboxylate ion + $H_2\uparrow$

Reagents used → Active metals

$$2CH_3COOH + 2Na \longrightarrow 2CH_3CO\overset{-}{O}\overset{+}{Na} + H_2\uparrow$$

Reactions with Alkalies

General reaction



Carboxylic acid → **Carboxylate ion** + H_2O

Reagents used → NaOH/KOH

$$CH_3COOH + NaOH \longrightarrow CH_3CO\overset{-}{O}Na^{+} + H_2O$$

$$C_2H_5COOH + KOH \longrightarrow C_2H_5CO\overset{-}{O}K^{+} + H_2O$$

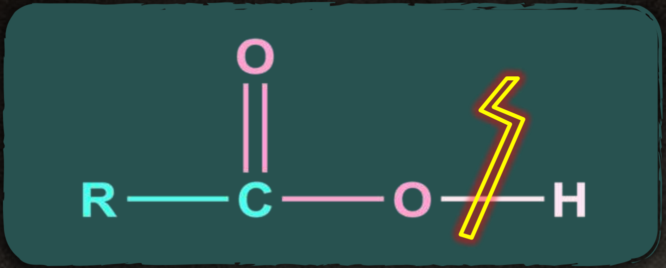
Carboxylic acids also react with weaker bases such as **bicarbonates** and release **CO_2**.

This reaction is used to **detect** the **carboxylic group** in an organic compound.

This reaction is known as **bicarbonate test.**

Bicarbonate Test

General reaction



$R-\overset{\overset{O}{\|}}{C}-O-H$

Carboxylic acid → Carboxylate ion + $CO_2\uparrow$ + H_2O

Reagents used → Bicarbonates of alkali

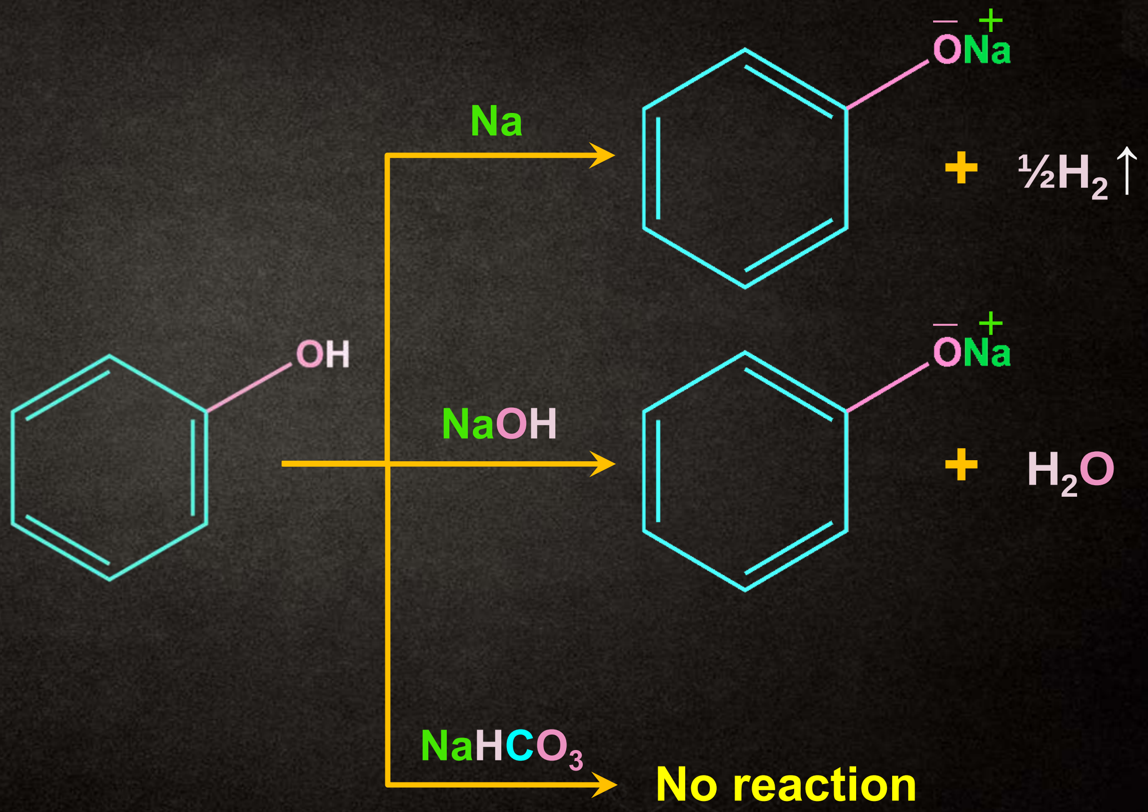
$$CH_3COOH + NaHCO_3 \longrightarrow CH_3CO\overset{-}{O}\overset{+}{Na} + H_2O + CO_2\uparrow$$

Bicarbonate Test

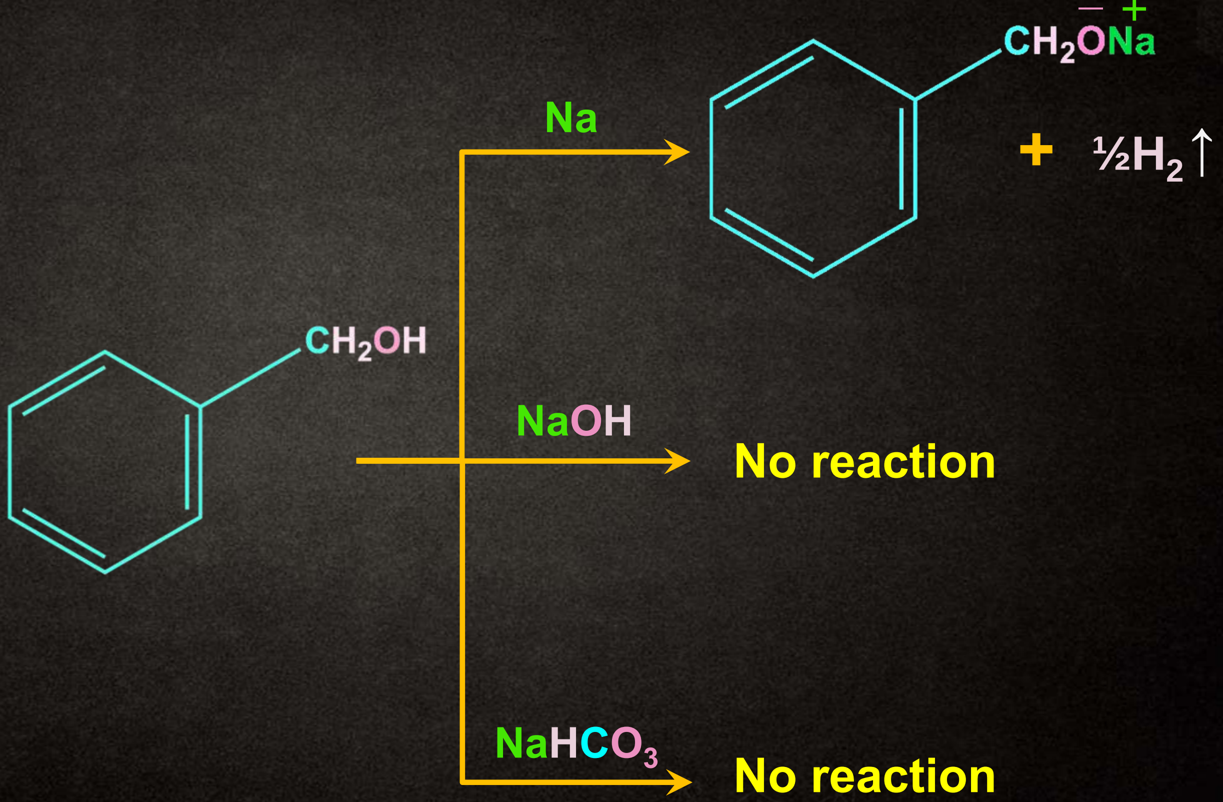
Generally, compounds that are **more acidic than phenol** give **bicarbonate test.**

It is a general criteria to check the compounds that give this test. However, this is not a thumb rule because there are many compounds that are more acidic than phenol but do not give this test.

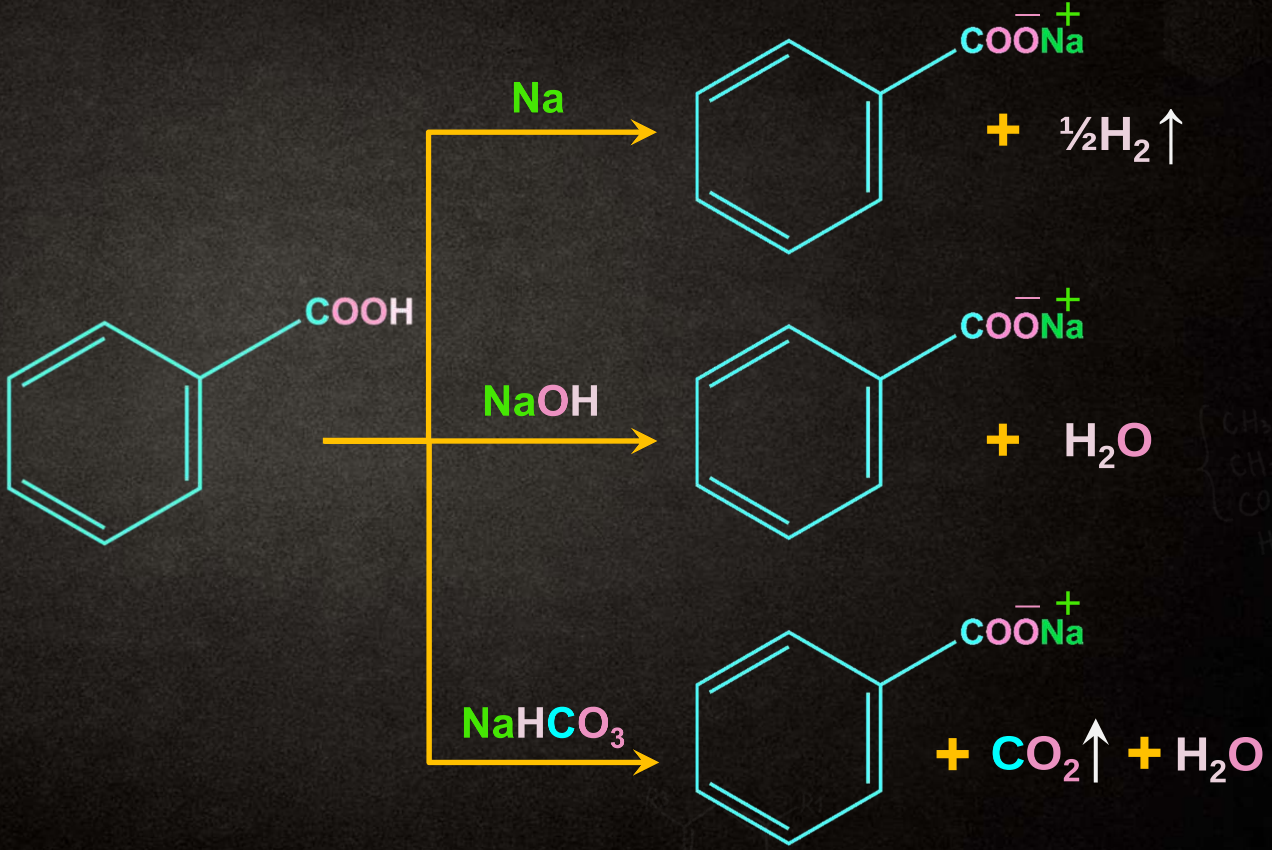
Reaction of Phenol with Na, NaOH, and $NaHCO_3$



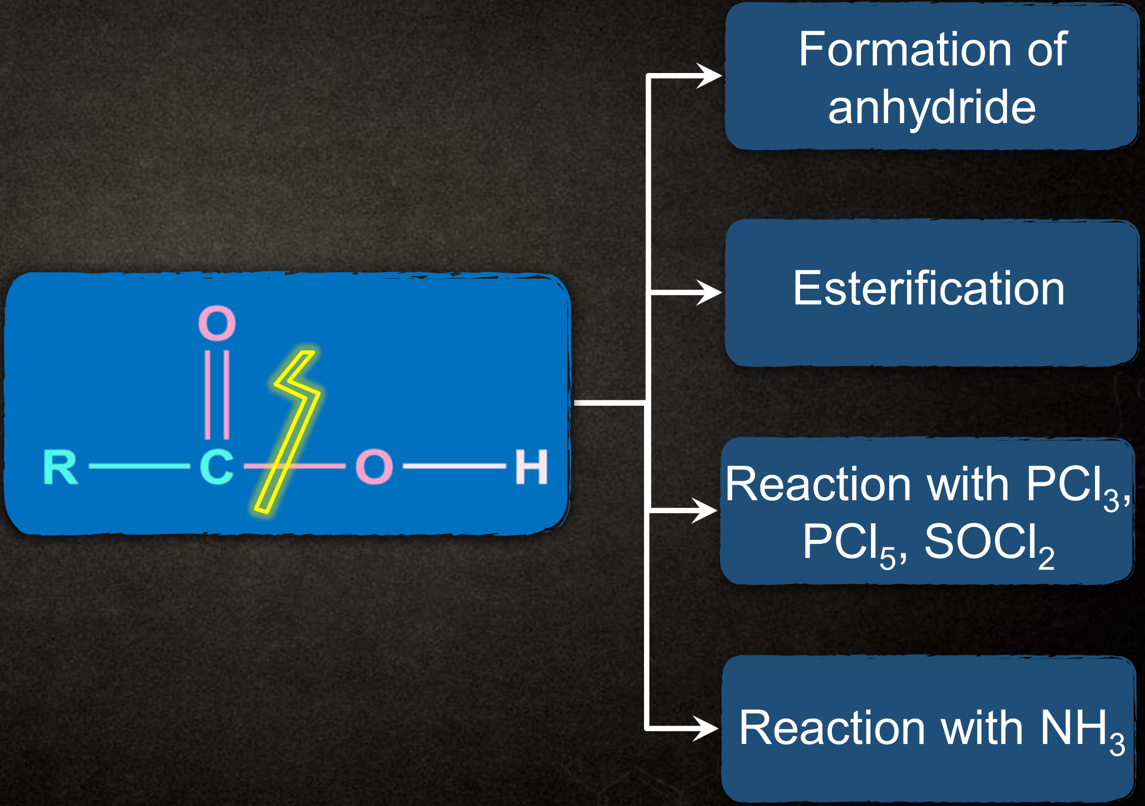
Reaction of Benzyl Alcohol with Na, NaOH, and $NaHCO_3$



Reaction of Benzoic Acid with Na, NaOH, and $NaHCO_3$



Reactions of Carboxylic Acids



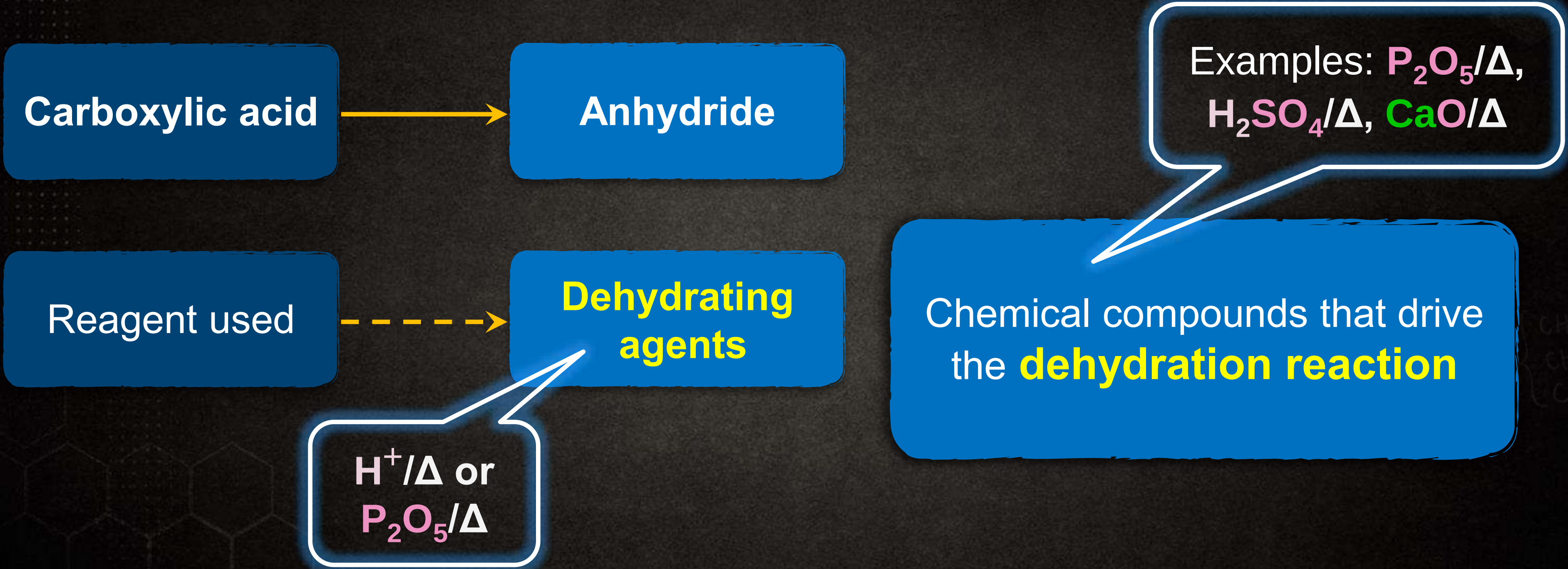
Formation of anhydride

Esterification

Reaction with PCl_3, PCl_5, $SOCl_2$

Reaction with NH_3

Formation of Anhydride



Carboxylic acid → **Anhydride**

Reagent used → **Dehydrating agents**

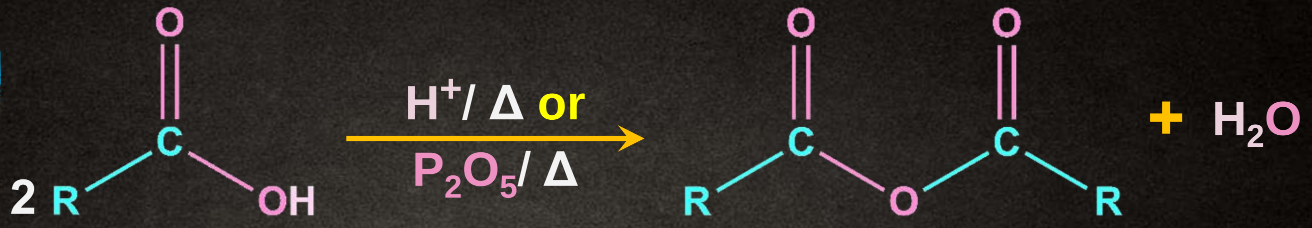
H^+/Δ or P_2O_5/Δ

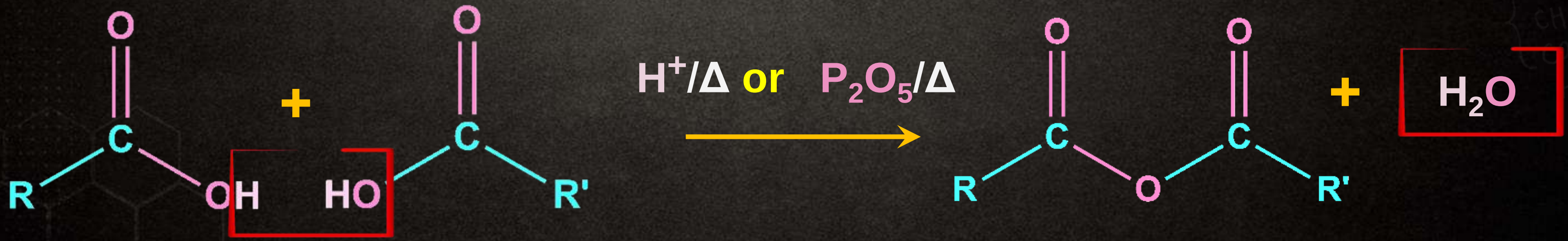
Chemical compounds that drive the **dehydration reaction**

Examples: P_2O_5/Δ, H_2SO_4/Δ, CaO/Δ

Formation of Anhydride

General reaction





Esterification

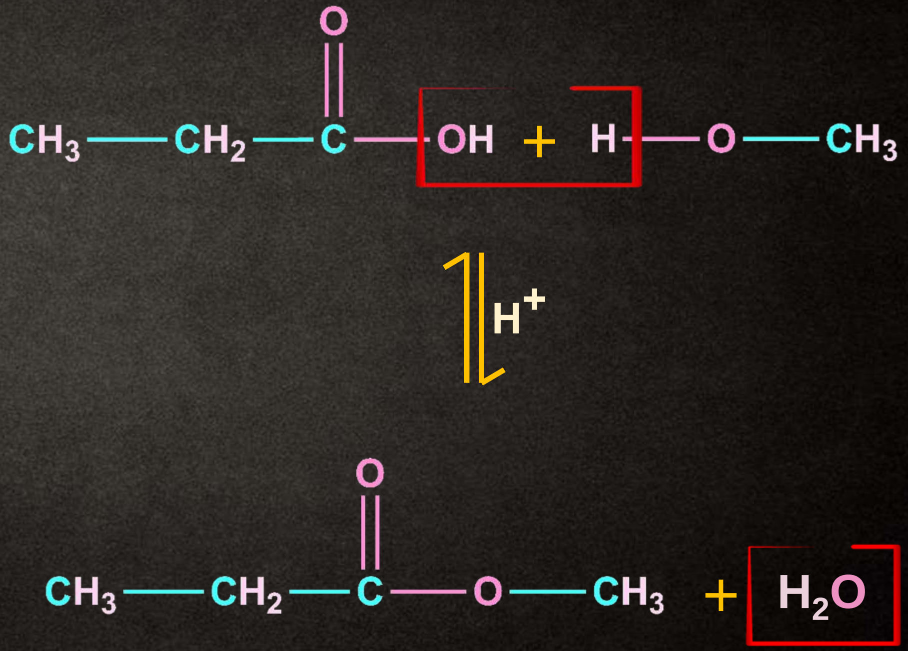
Carboxylic acid → **Esters**

Reagent used → **Alcohols/Phenols + Conc. H_2SO_4/HCl (g)**

$$RCOOH + R'OH \xrightleftharpoons{H^+} RCOOR' + H_2O$$

Esterification

$$C_2H_5COOH + CH_3OH \overset{H^+}{\rightleftharpoons} C_2H_5COOCH_3 + H_2O$$



$$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-\boxed{OH + H}-O-CH_3 \overset{H^+}{\rightleftharpoons} CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_3 + \boxed{H_2O}$$

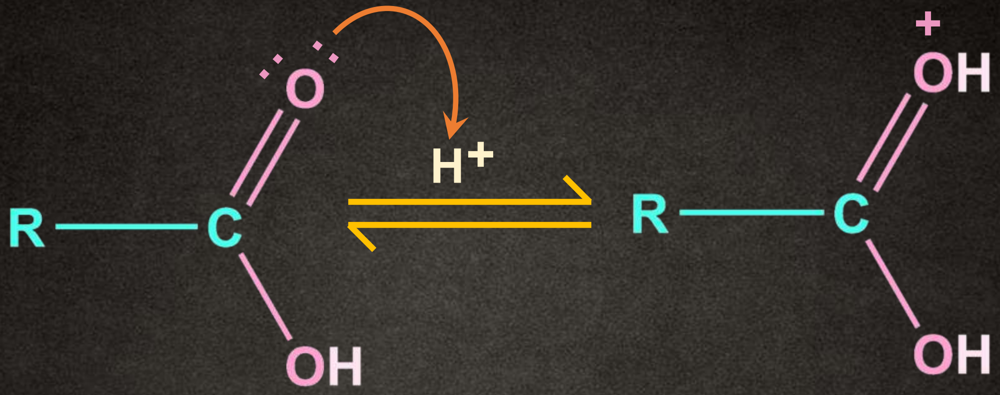
Steps Involved in Esterification

Protonation of carboxylic acid

Nucleophilic attack of alcohol

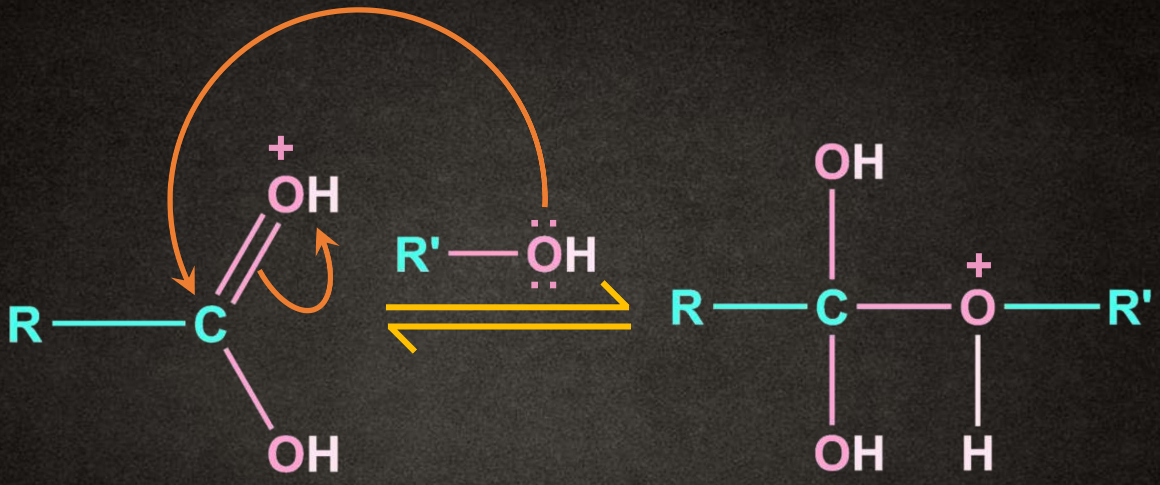
Formation of ester

Protonation of Carboxylic Acid



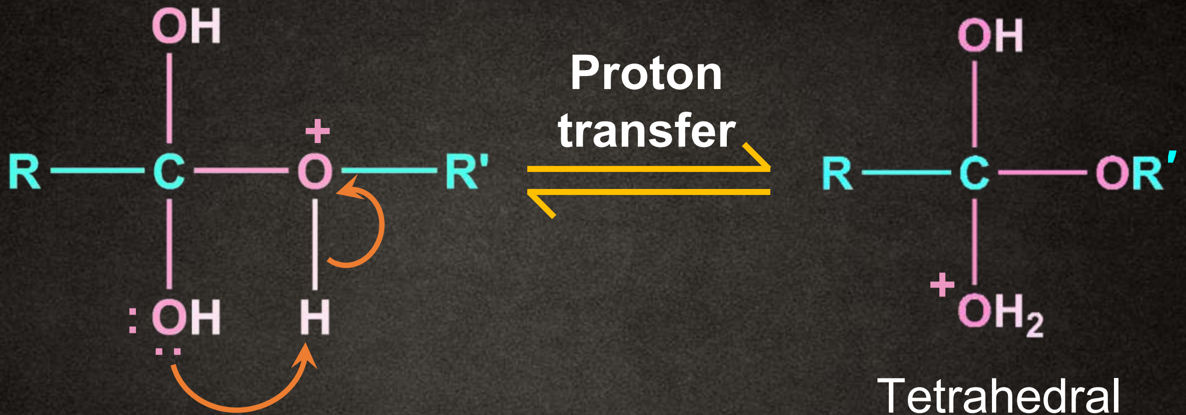
Carboxylic acid

Nucleophilic Attack of Alcohol



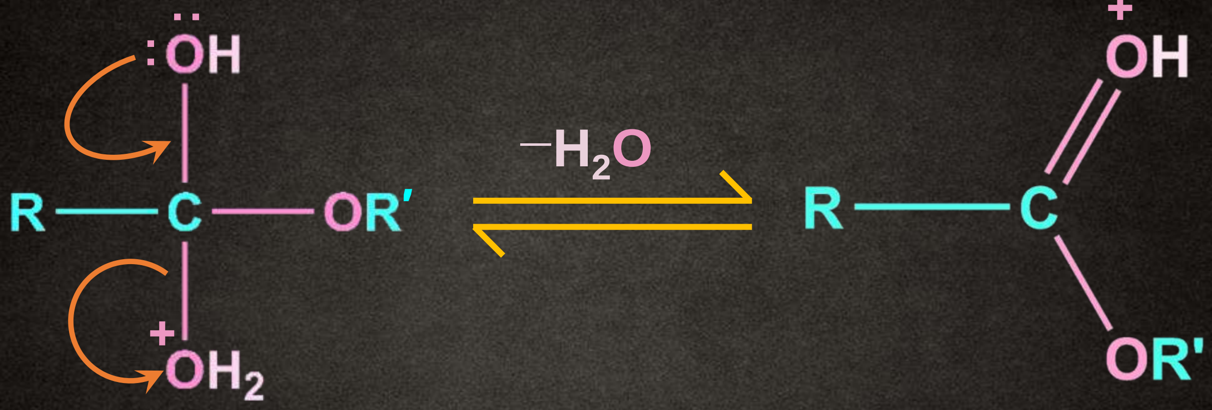
Tetrahedral
intermediate

Formation of Ester



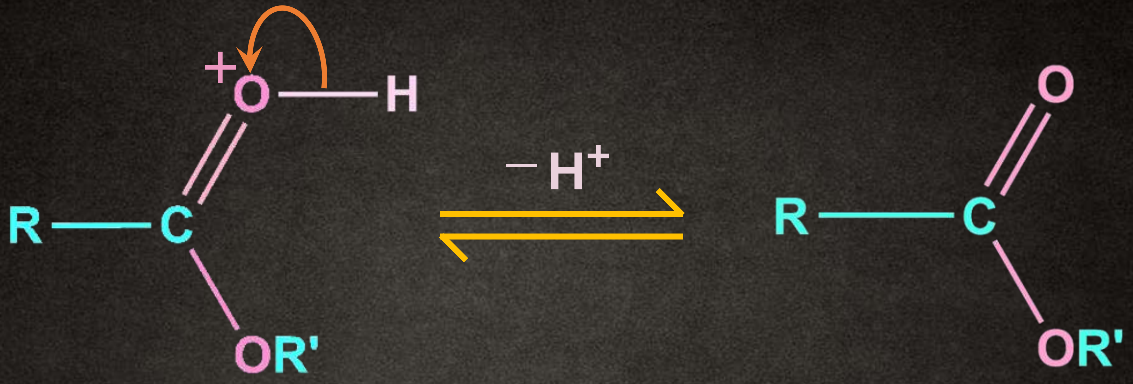
Tetrahedral intermediate

Formation of Ester



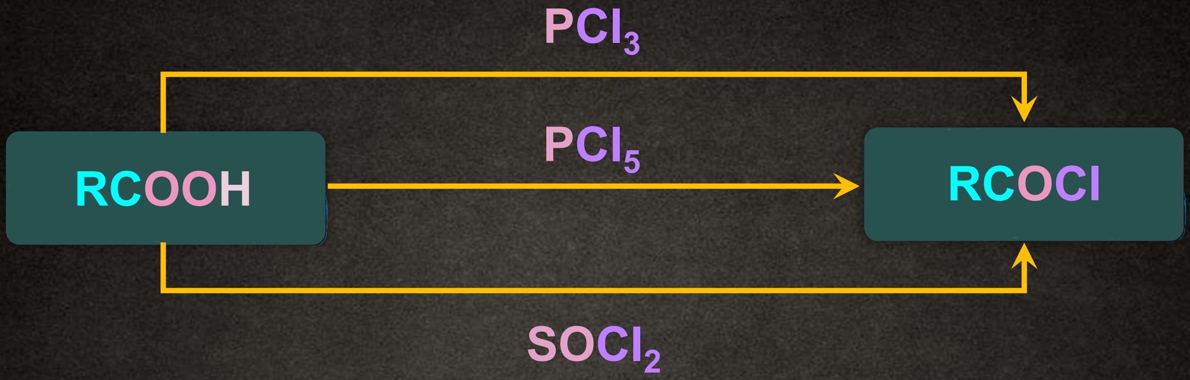
Tetrahedral intermediate

Formation of Ester



Ester

Reaction with PCl_3, PCl_5, $SOCl_2$



PCl_3

PCl_5

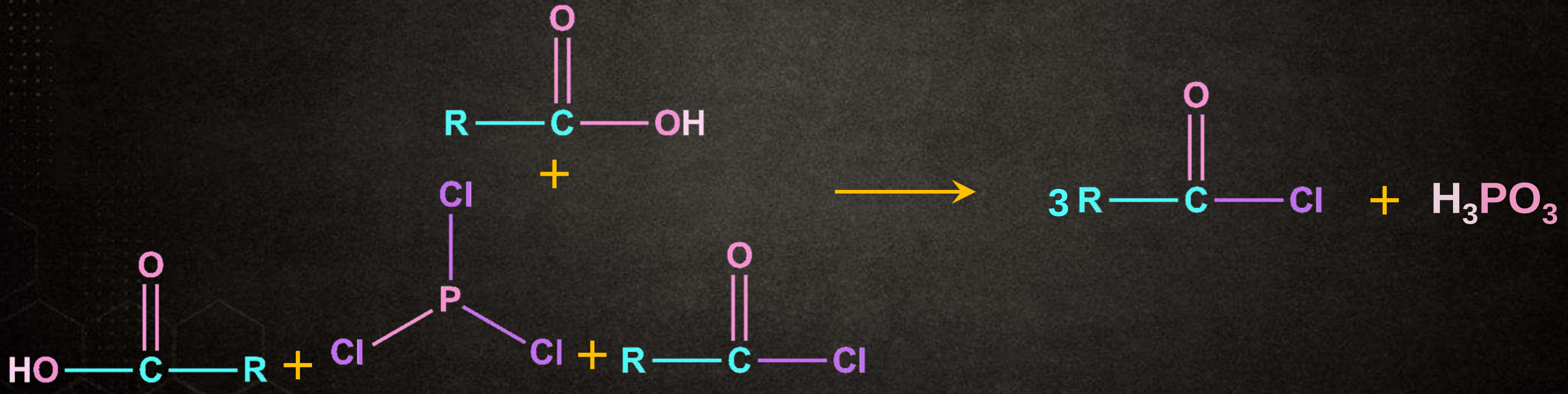
$RCOOH \rightarrow RCOCl$

$SOCl_2$

Reaction of Carboxylic Acid with PCl_3

General reaction

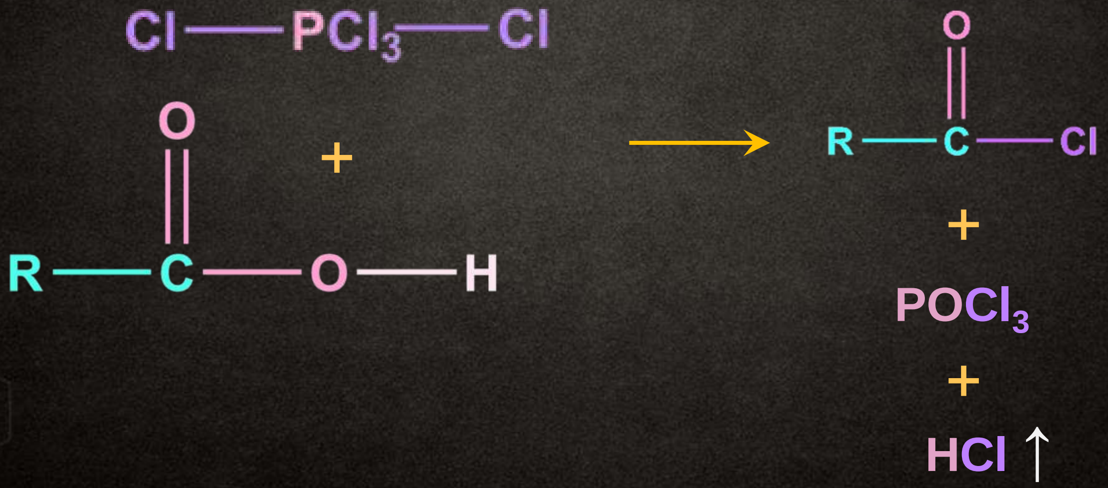
$$3\,RCOOH + PCl_3 \longrightarrow 3\,RCOCl + H_3PO_3$$



Reaction of Carboxylic Acid with PCl_5

General reaction

$RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl\uparrow$

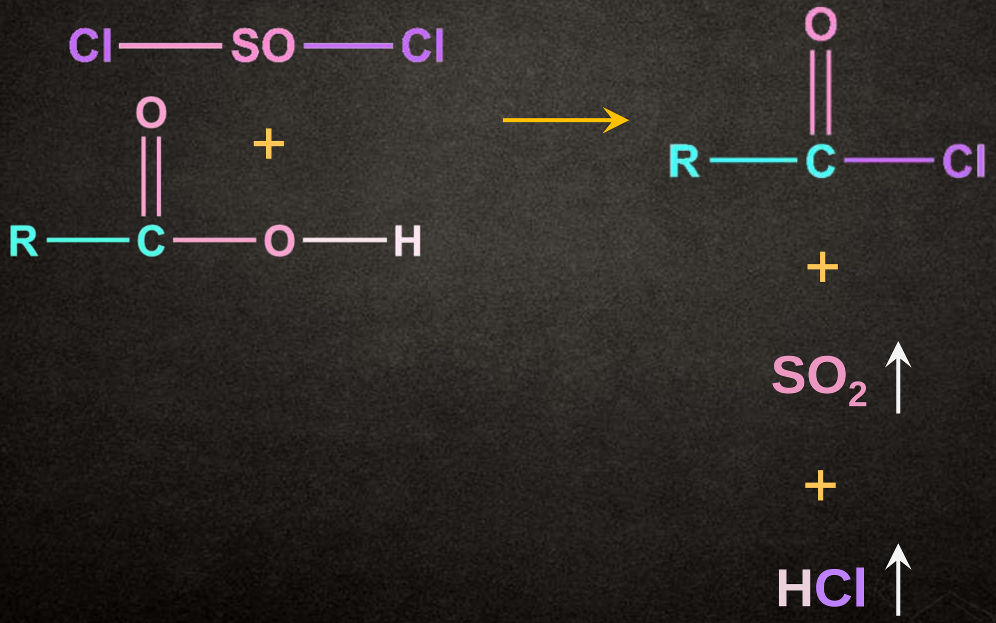


$$Cl{-}PCl_3{-}Cl + R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}H \longrightarrow R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Cl + POCl_3 + HCl\uparrow$$

Reaction of Carboxylic Acid with $SOCl_2$

General reaction

$$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2\uparrow + HCl\uparrow$$



Reaction with PCl_3, PCl_5, $SOCl_2$

EXAMPLE

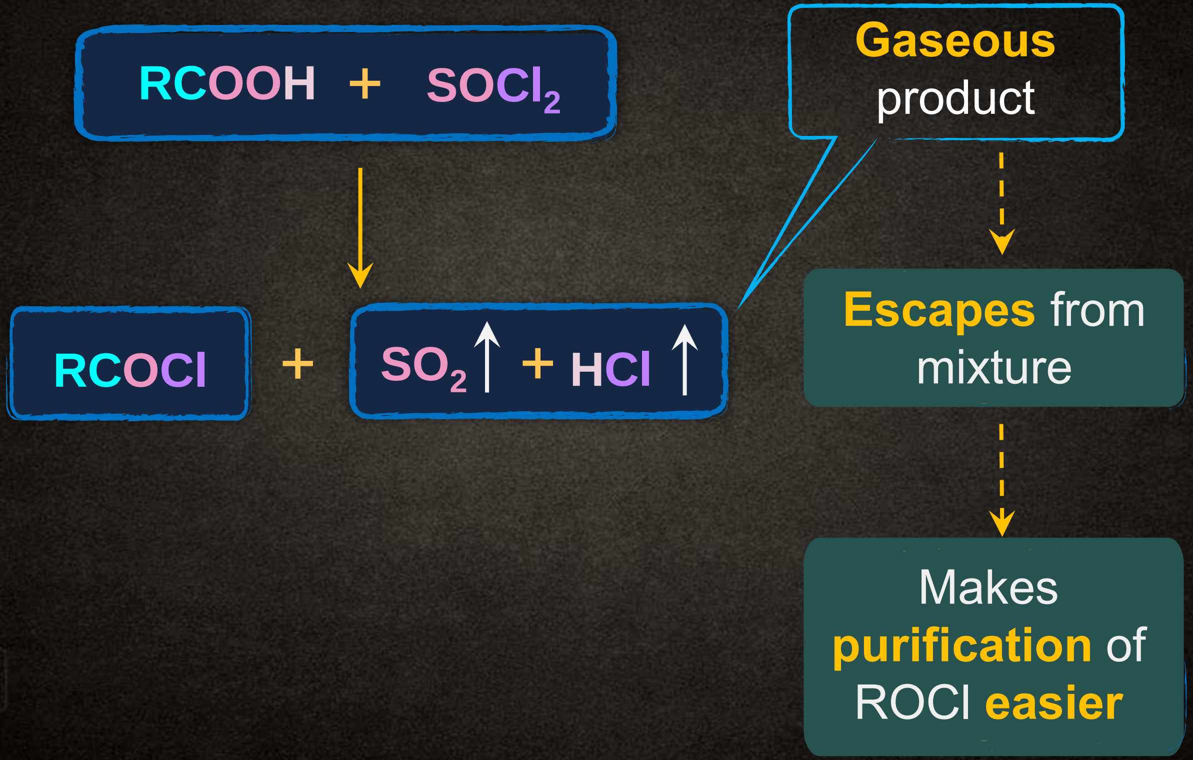
$$3CH_3COOH + PCl_3 \longrightarrow 3CH_3COCl + H_3PO_3$$

$$CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl\uparrow$$

$$CH_3COOH + SOCl_2 \longrightarrow CH_3COCl + SO_2\uparrow + HCl\uparrow$$

Preferred reagent

Reaction of Carboxylic Acid with $SOCl_2$



$RCOOH + SOCl_2$

$\downarrow$

$RCOCl + SO_2\uparrow + HCl\uparrow$

Gaseous product

Escapes from mixture

Makes **purification** of ROCl **easier**

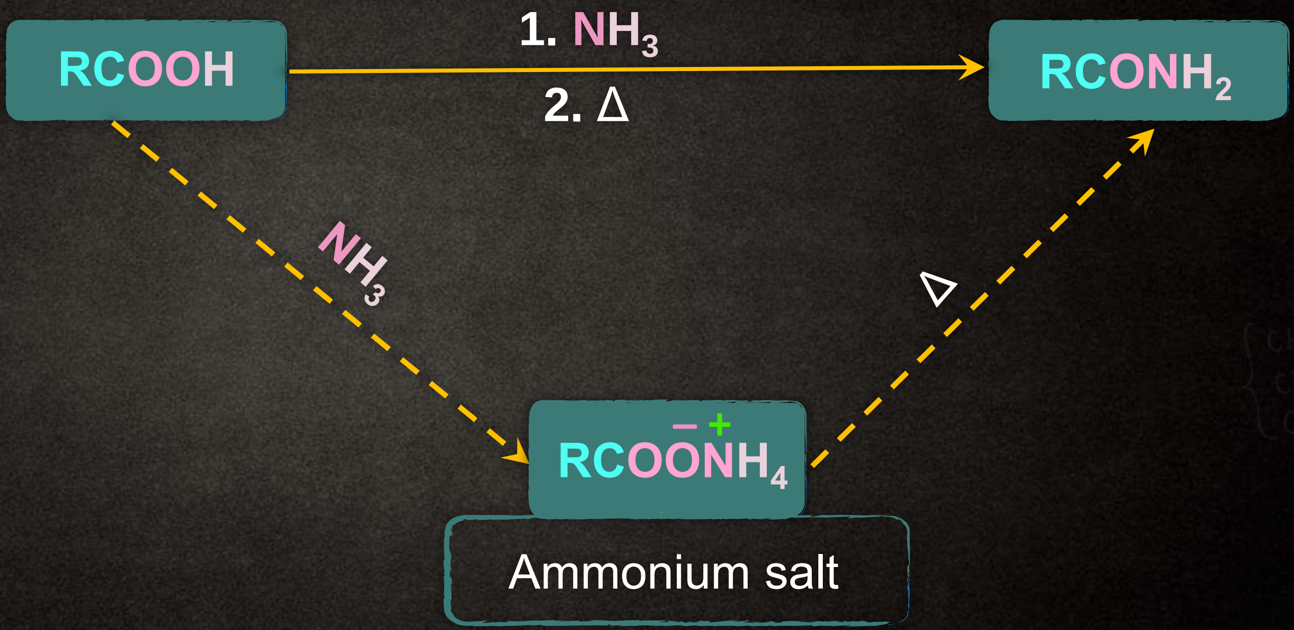
Reaction with NH_3

Carboxylic acid → Amide

Reagents used → (i) NH_3 (ii) Δ

Reaction with NH_3

General reaction



$$RCOOH \xrightarrow[2.\ \Delta]{1.\ NH_3} RCONH_2$$

$$RCOOH \xrightarrow{NH_3} RCO\overset{-}{O}\overset{+}{N}H_4 \xrightarrow{\Delta} RCONH_2$$

Ammonium salt

Reaction with NH_3

EXAMPLE

$$CH_3COOH + NH_3 \rightleftharpoons CH_3CO\overset{-}{O}\overset{+}{N}H_4$$

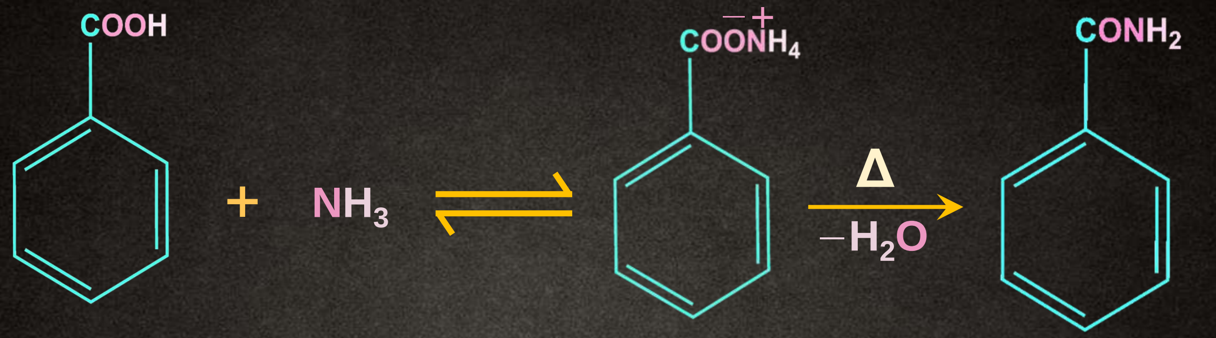
Ethanoic acid　Ammonia　Ammonium acetate

$$\Big\downarrow {-H_2O} \;\; \Delta$$

$$CH_3CONH_2$$

Ethanamide

Reaction with NH_3

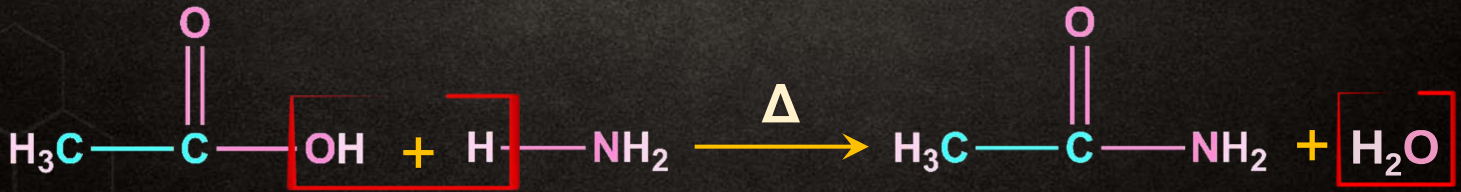


Benzoic acid

Ammonia

Ammonium benzoate

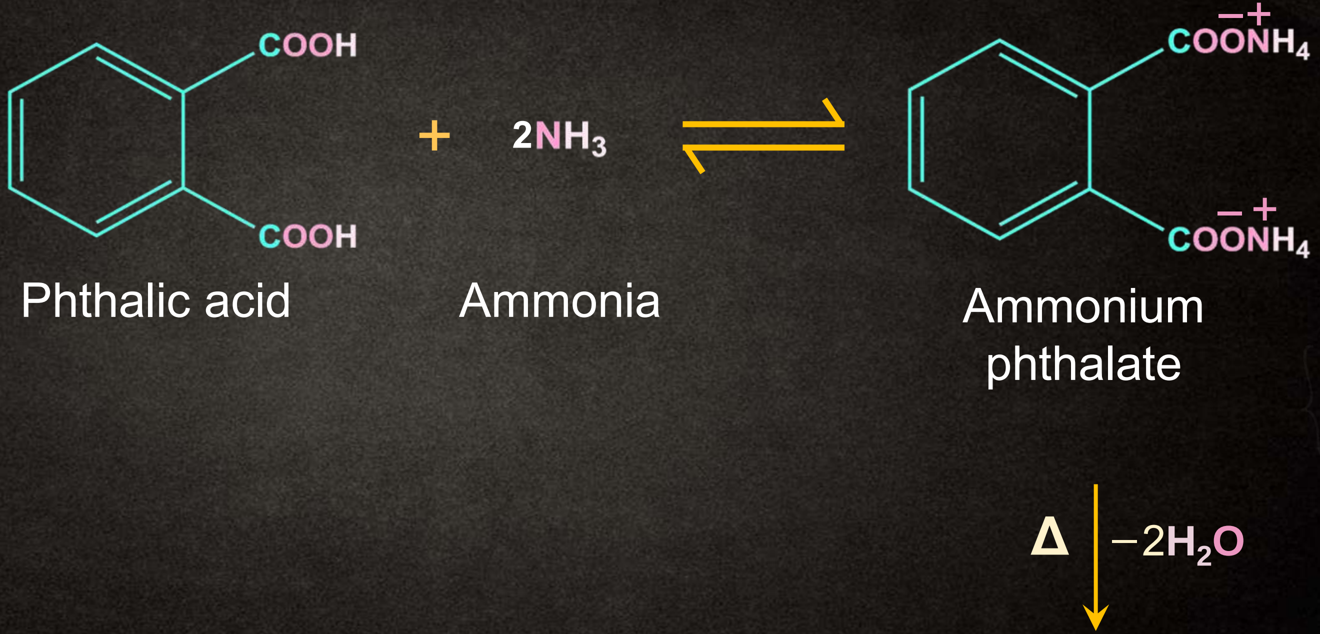
Benzamide



$$H_3C-\overset{\overset{O}{\|}}{C}-\boxed{OH\ +\ H}-NH_2 \xrightarrow{\Delta} H_3C-\overset{\overset{O}{\|}}{C}-NH_2 + \boxed{H_2O}$$

Reaction with NH_3

EXAMPLE



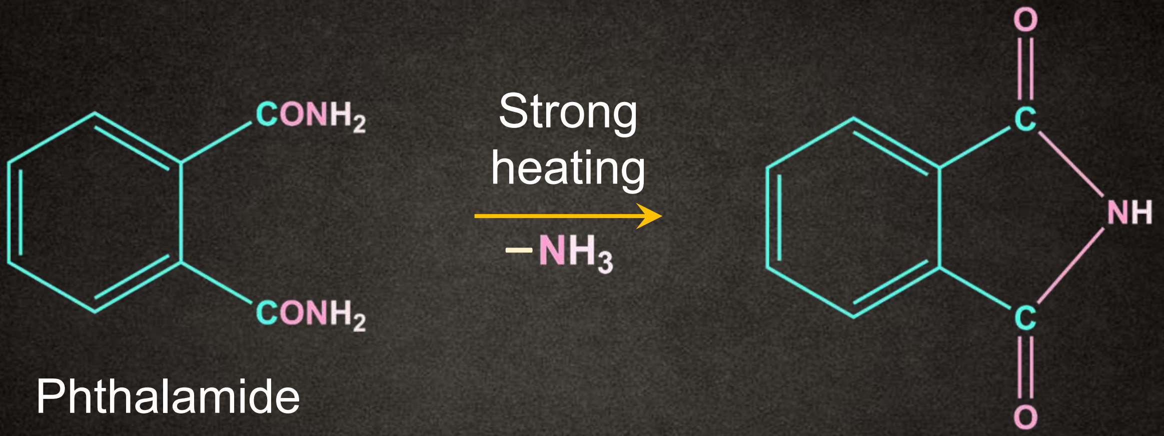
Phthalic acid

Ammonia

Ammonium phthalate

Phthalamide

Reaction with NH_3



Phthalamide

Phthalimide

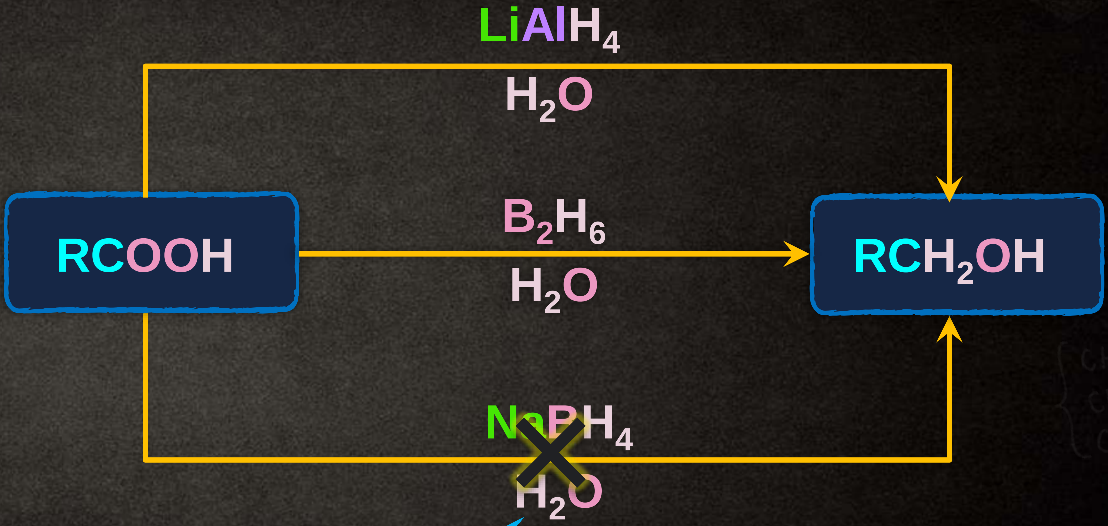
Reactions of Carboxylic Acids

Reactions involving $R\boxed{COOH}$

- Reduction
- Decarboxylation

Reduction of Carboxylic Acids

General reaction



$$RCOOH \xrightarrow[H_2O]{LiAlH_4} RCH_2OH$$

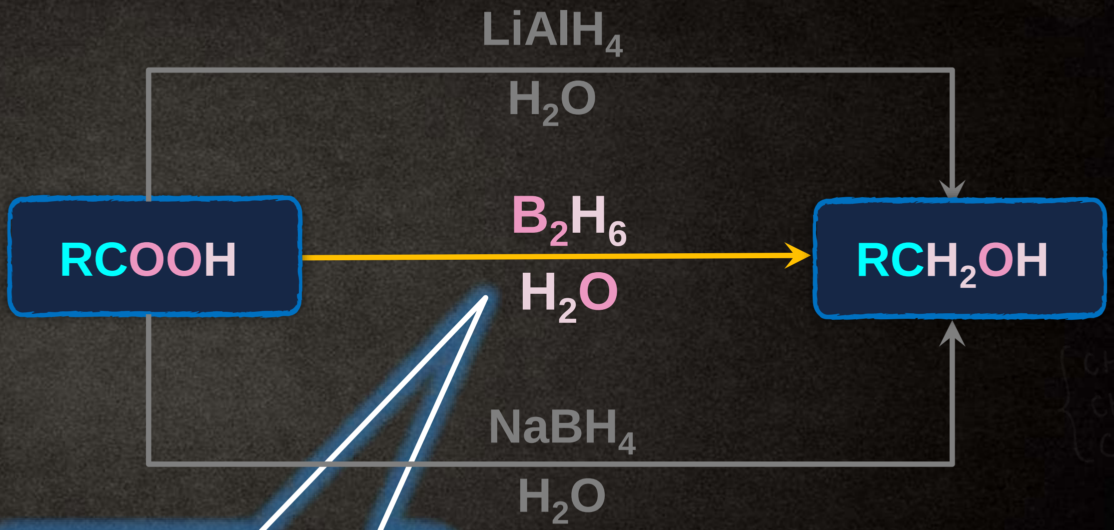
$$RCOOH \xrightarrow[H_2O]{B_2H_6} RCH_2OH$$

$$RCOOH \xrightarrow[H_2O]{\cancel{NaBH_4}} RCH_2OH$$

Not strong enough to reduce COOH

Reduction of Carboxylic Acids

General reaction



$RCOOH \xrightarrow[H_2O]{B_2H_6} RCH_2OH$

$RCOOH \xrightarrow[H_2O]{LiAlH_4} RCH_2OH$

$RCOOH \xrightarrow[H_2O]{NaBH_4} RCH_2OH$

Selective reducing agent for carboxylic acid

Note

In general,

Reduction of carboxylic acid is preferred with **diborane** because it **does not** easily reduce other functional groups such as **ester, nitro, halo,** etc.

Decarboxylation of Carboxylic Acids

Sodium carboxylate → Hydrocarbons

Reagent used → $NaOH + CaO/\Delta$

3:1 ratio

Decarboxylation of Carboxylic Acids

General reaction

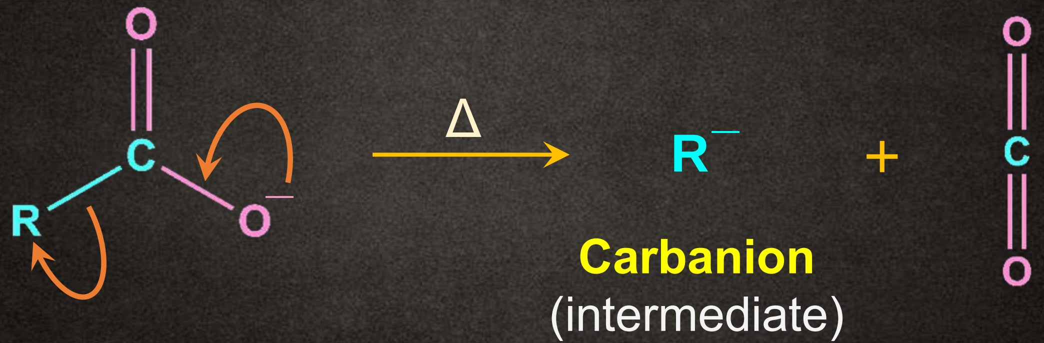
$$RCO\bar{O}\overset{+}{Na} \xrightarrow[\Delta]{NaOH + CaO} R{-}H + Na_2CO_3$$

Soda–lime process

$$CH_3CO\bar{O}\overset{+}{Na} \xrightarrow[\Delta]{NaOH + CaO} CH_4\uparrow + Na_2CO_3$$

Steps Involved in Soda–Lime Process

Step 1 Decarboxylation



Carbanion
(intermediate)

Abstraction of Proton

Step 2 Abstraction of proton

$$R^{-} + H{-}OH \longrightarrow R{-}H + {}^{-}OH$$

Uses of CaO

01

As CaO is **porous**, it increases the **surface area** of the mixture, thereby facilitating **decarboxylation** by absorbing CO_2.

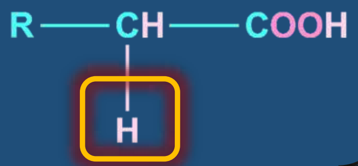
02

CaO absorbs CO_2 only to form $CaCO_3$, but since NaOH is present in the solution, it **reacts further** with **$CaCO_3$ to give Na_2CO_3**.

This reaction is considered as the **heating effect** of carboxylic acid.

Reactions of Carboxylic Acids

Reactions involving



$\mathrm{R-\underset{\underset{H}{|}}{C}H-COOH}$

Halogenation

Ring substitution

Halogenation

Carboxylic acid → α-Halocarboxylic acid

Hell–Volhard–Zelinsky halogenation reaction

Reagents used → (i) X_2/Red P (X = Br, Cl)
(ii) H_2O

HVZ Reaction

HVZ reaction

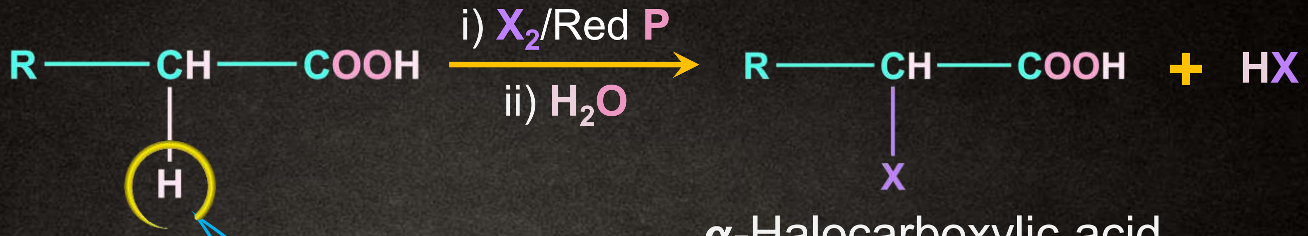
Who — Substrate: **Carboxylic acid**

How — Reagents: **Red P/X_2 and H_2O**

What — Product: **α-Halo-carboxylic acid**

HVZ Reaction

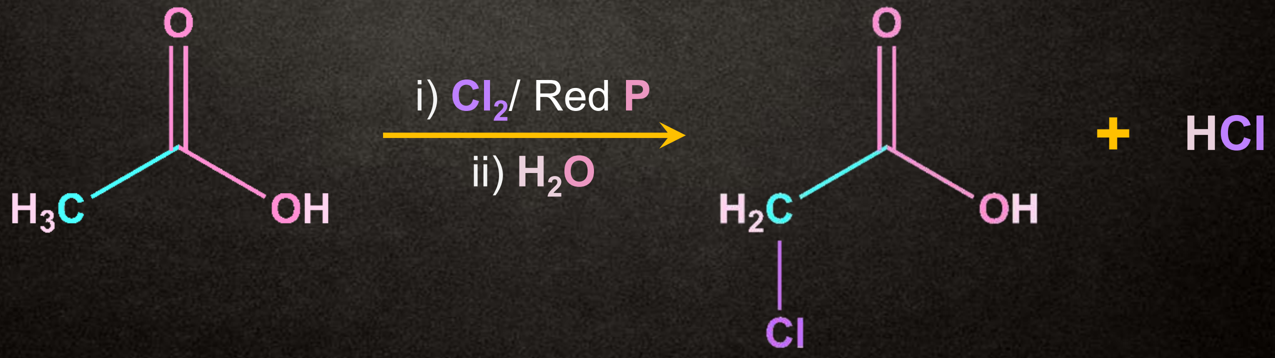
General reaction



$$R-\underset{\underset{H}{|}}{CH}-COOH \xrightarrow[\text{ii) } H_2O]{\text{i) } X_2/\text{Red } P} R-\underset{\underset{X}{|}}{CH}-COOH + HX$$

α-H atom

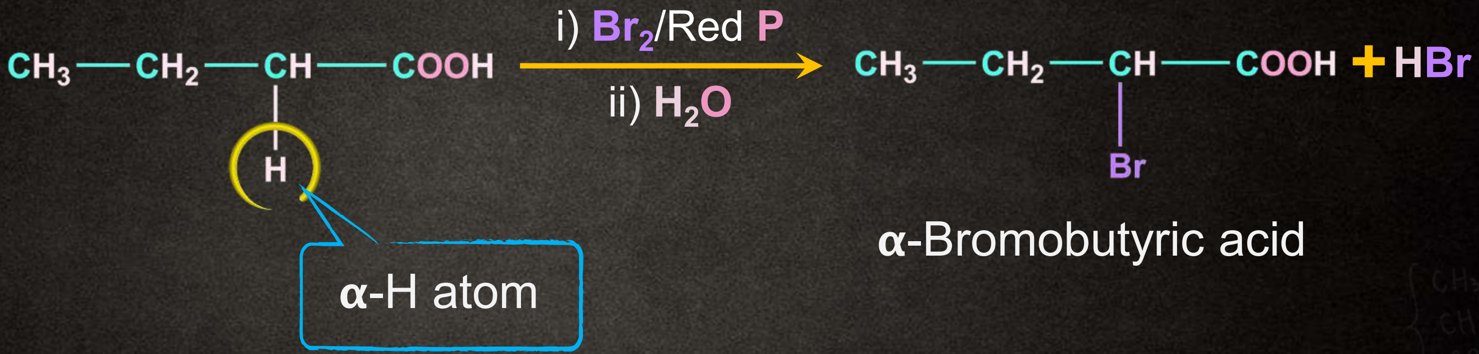
α-Halocarboxylic acid



α-Chloroacetic acid

HVZ Reaction

EXAMPLE

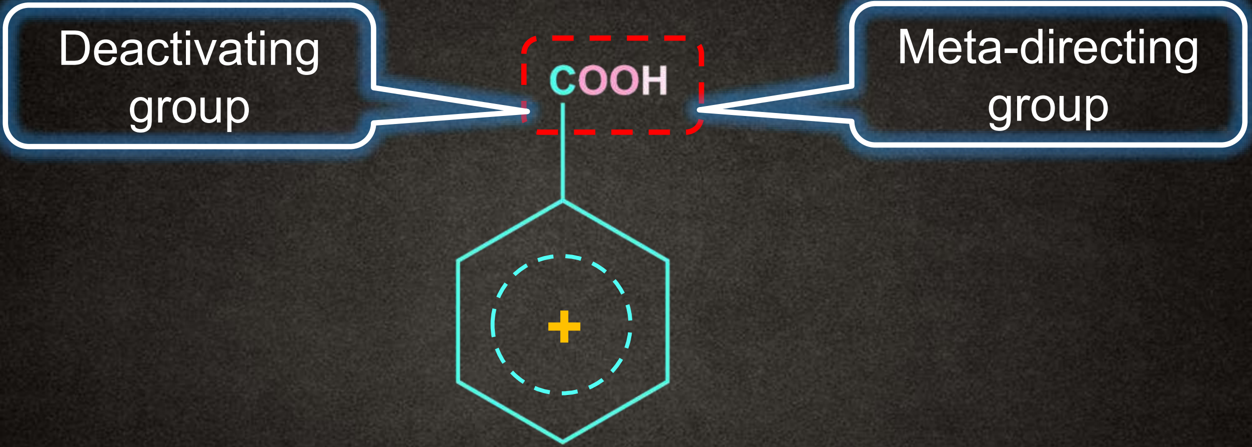


$$CH_3-CH_2-\underset{\underset{H}{|}}{CH}-COOH \xrightarrow[\text{ii) } H_2O]{\text{i) } Br_2/\text{Red P}} CH_3-CH_2-\underset{\underset{Br}{|}}{CH}-COOH + HBr$$

α-H atom

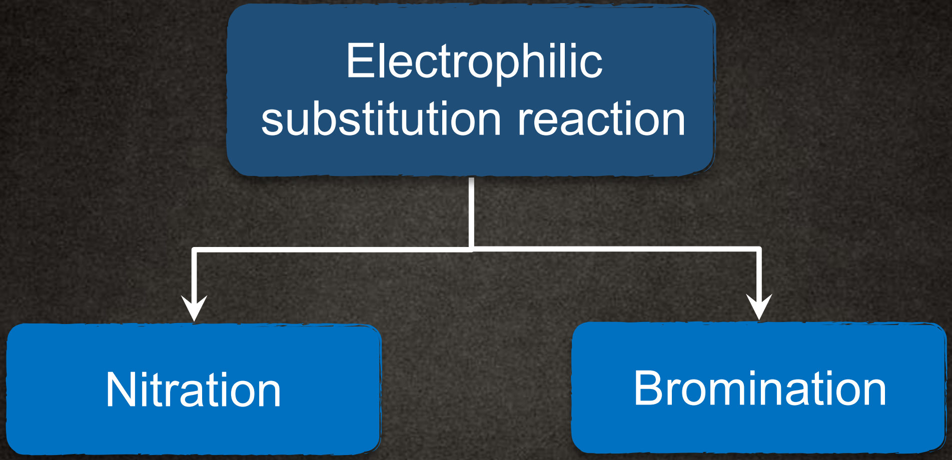
α-Bromobutyric acid

Recall



Electrophilic substitution reaction

Ring Substitution Reaction



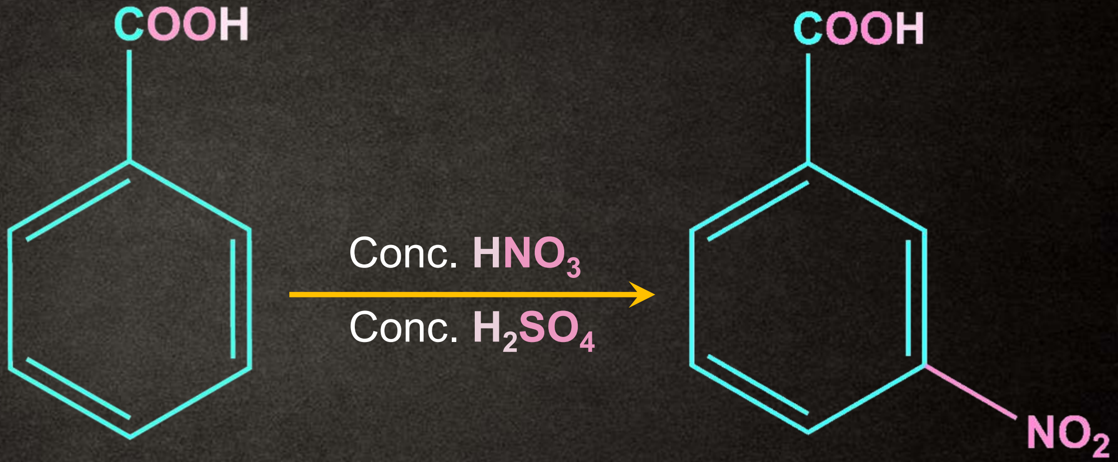
Electrophilic substitution reaction

Nitration

Bromination

Nitration of Aromatic Carboxylic Acids

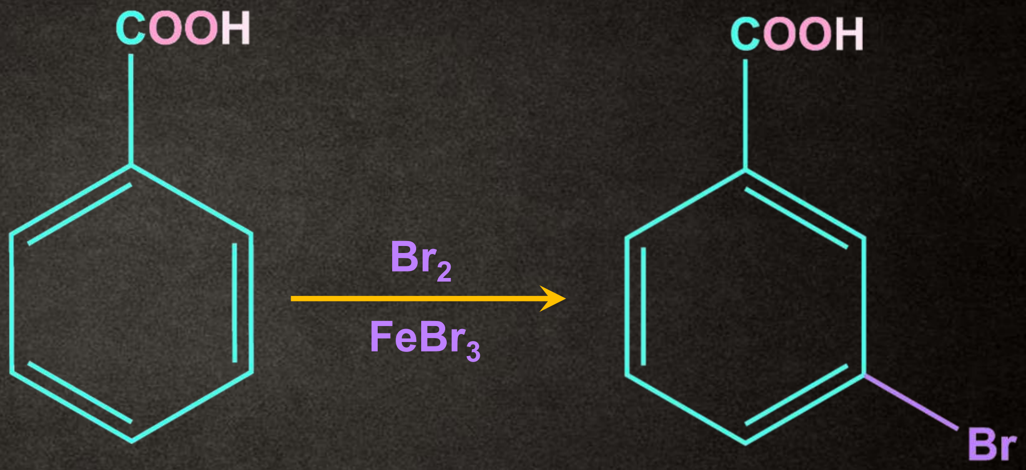
Reaction



m-Nitrobenzoic acid

Bromination of Aromatic Carboxylic Acids

Reaction



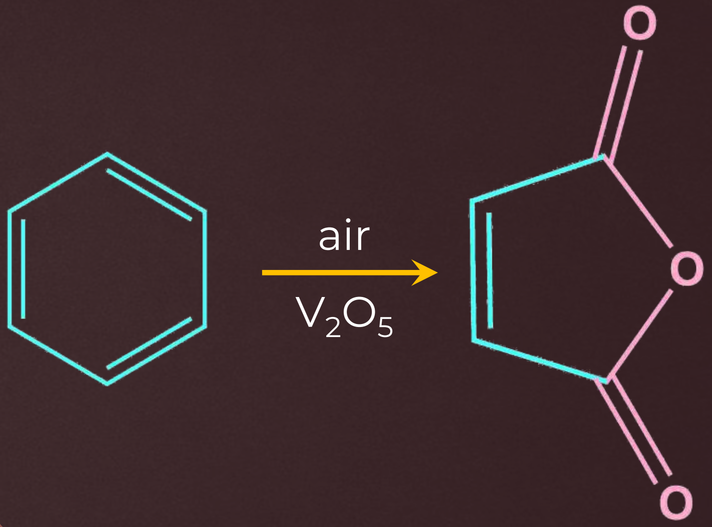
m-Bromobenzoic acid

Note

Carboxylic acids do not undergo **Friedel–Crafts reaction** because the **carboxyl group** is **deactivating** and the catalyst **$AlCl_3$** (Lewis acid) gets bonded to the **carboxyl group**.

Oxidation

Aromatic rings can be cleaved with strong **oxidising agents**. Reagent that oxidises aromatic rings is air catalysed by **V_2O_5**.

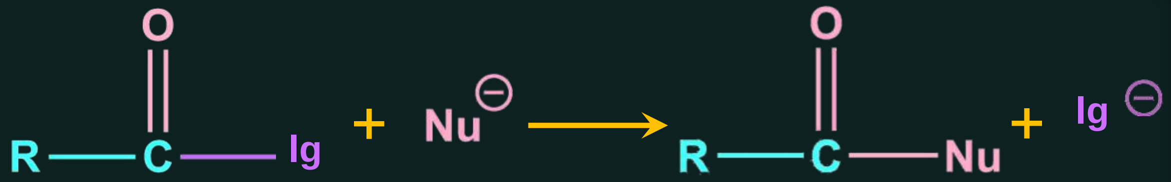


Bimolecular Nucleophilic Substitution Reaction with Tetrahedral Intermediate (S_N2Th)

S_N2Th

S_N2Th is a characteristic reaction of **acid and its derivatives** (acid halide, anhydride, ester, and amide).

General reaction



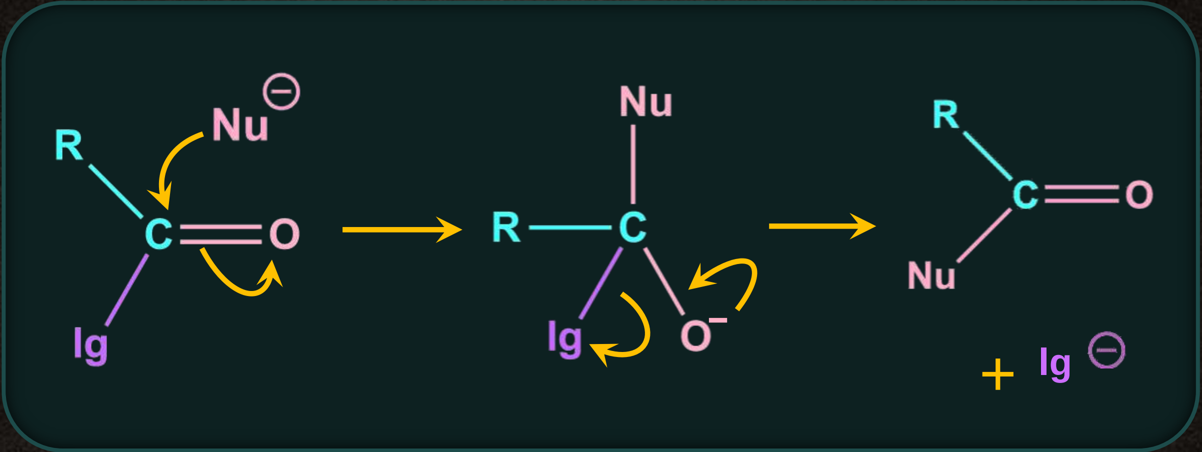
$$R-\overset{O}{\overset{\|}{C}}-lg + Nu^{\ominus} \longrightarrow R-\overset{O}{\overset{\|}{C}}-Nu + lg^{\ominus}$$

S_N2Th

Nucleophilic acyl substitution usually takes place by an **addition-elimination** mechanism.

The incoming nucleophile adds to the carbonyl to form a **tetrasubstituted intermediate**

Mechanism



S_N2Th

A pair of non-bonding electrons on the oxygen **reforms the π bond**.

And either **Ig^- or Nu^-** is eliminated with its bonding electrons.

S_N2Th

Which will be eliminated?
Ig or Nu?

Depends on their **basicity**

Weaker base is the **better leaving group**.

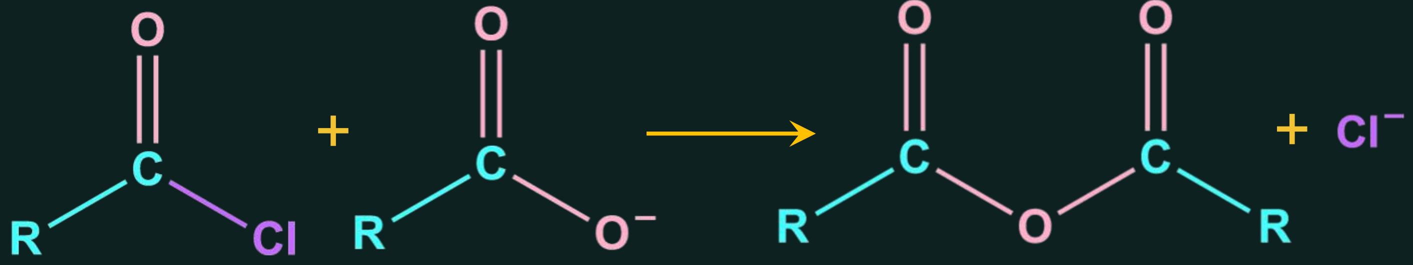
Weaker base is preferentially **eliminated**.

S_N2Th

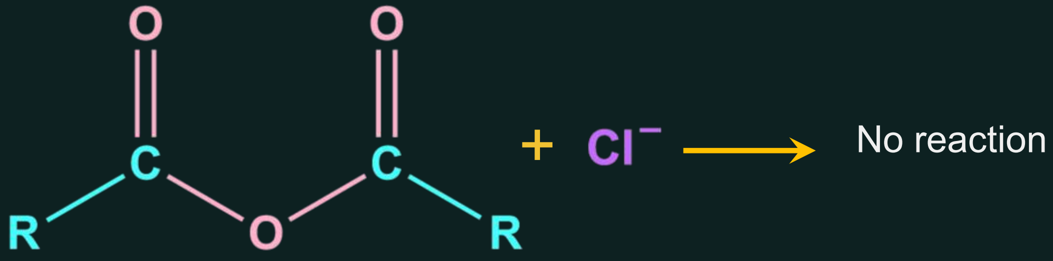
$$R-\overset{\overset{O}{\|}}{C}-Ig + Nu^{\ominus} \longrightarrow R-\overset{\overset{O}{\|}}{C}-Nu + Ig^{\ominus}$$

Basicity of $Ig^{\ominus}$ should be less than that of $Nu^{\ominus}$

Examples



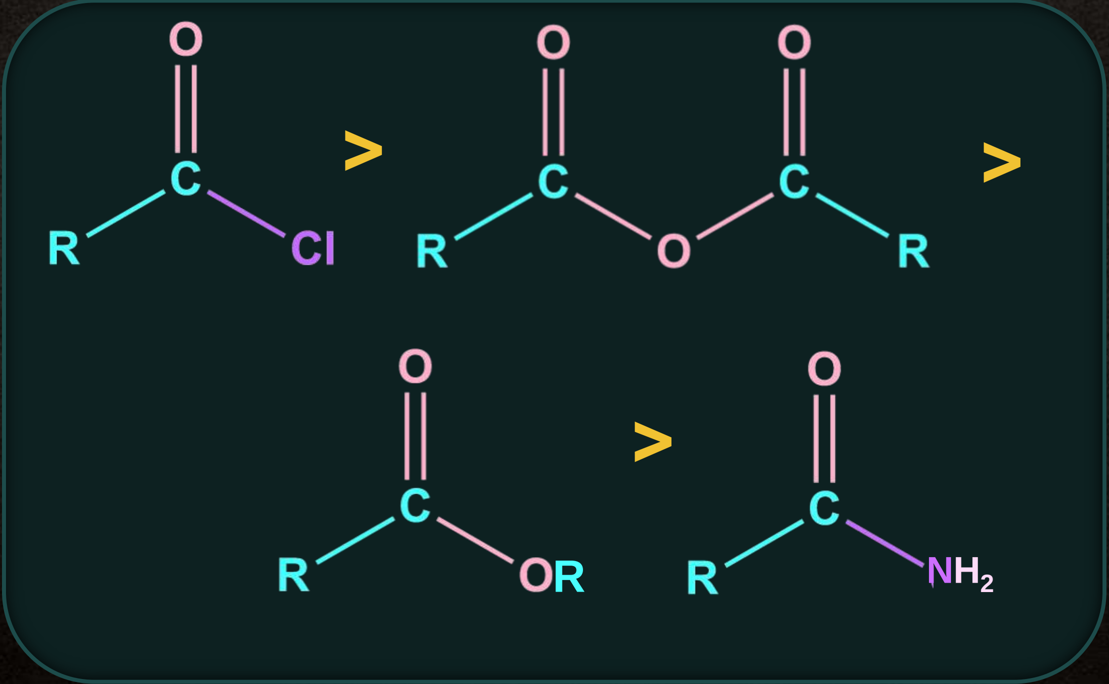
S_N2Th



An anhydride **cannot be converted** into an acyl chloride because a chloride ion is a **weaker base** than a carboxylate ion.

S_N2Th

Reactivity order



Uses of Carboxylic Acids

Methanoic acid is used in the rubber industry.

Ethanoic acid in the form of **vinegar** is used in the food industry.

Esters of benzoic acid are used in perfumery.

Higher fatty acids
are used for the manufacture of soaps and detergents.