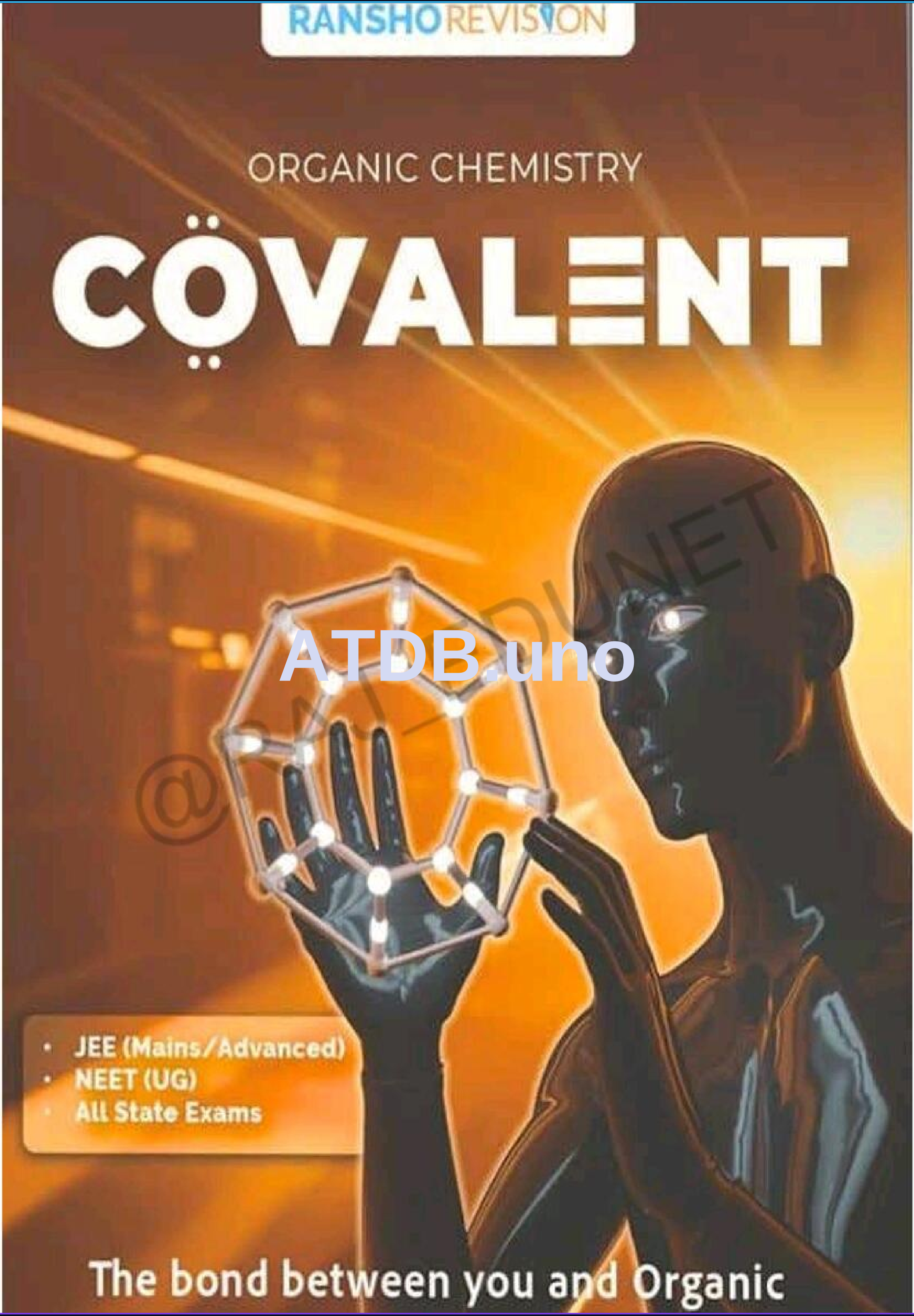
RANSHO REVISION



ORGANIC CHEMISTRY

COVALENT

- JEE (Mains/Advanced)
- NEET (UG)
- All State Exams

The bond between you and Organic

INDEX DETAILED

I. General Organic Chemsltry

II. Nomenclature

III. Stereochemistry

IV. Reactive Intermediates

V. Alkanes

VI. Electrophilic addition - Alkenes & Alkynes

VII. Electrophilic Substitution in Aromatics

VIII. Nucleophilic Substitution at Saturated C

IX. Nucleophilic Substitution - Aromatics

X. Carbonyls are often confused

XI. Nucleophilic addition, Aldehyde & Ketones

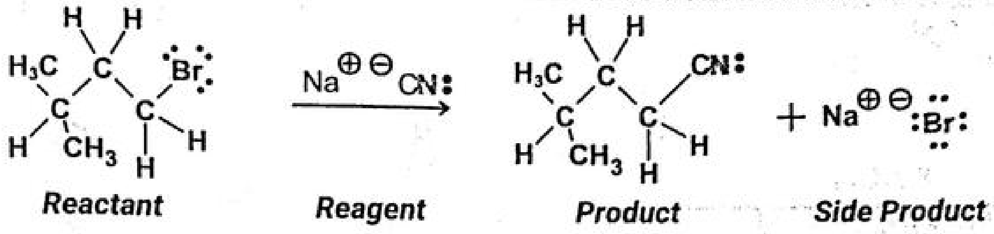
XII. Everything about Grignard Reagent

XIII. Carboxylic Acid Derivatives

Step Towards OrganiC 1

General Organic Chemistry

1 Introduction to a Organic Chemistry terms



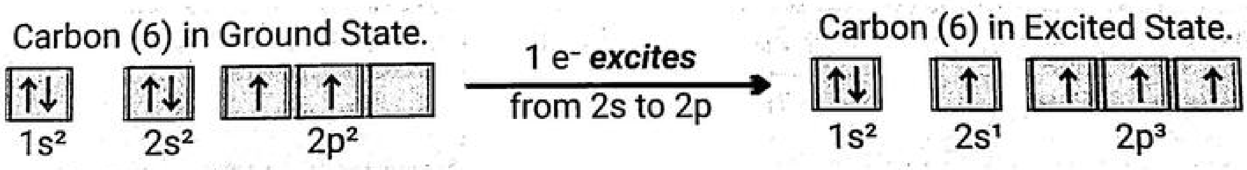
Organic chemistry boils down to three key ideas that control every reaction:

1. **General Organic Chemistry (GOC)**: The basics that make reactions happen. Think of it as the "go" signal for chemicals to change.
2. **Stereochemistry**: How molecules look in 3D. Different shapes can mean different results—super important to picture it!
3. **Reaction Mechanism**: The step-by-step path a reaction takes. Depends on what you start with and what you add.

That's it—rules, 3D shapes, and roadmaps run organic chemistry!

1.1 Carbon and its Tetravalency

- Class 10 taught us that Carbon rules organic chemistry—it's all about this one element! Why? Two big reasons:
  - **Tetra Valency**: Carbon can make 4 bonds, like a super connector.
  - **Catenation**: It loves linking up with itself, building chains and more!



- 2 Unpaired Electrons
- Cannot form 4 bonds

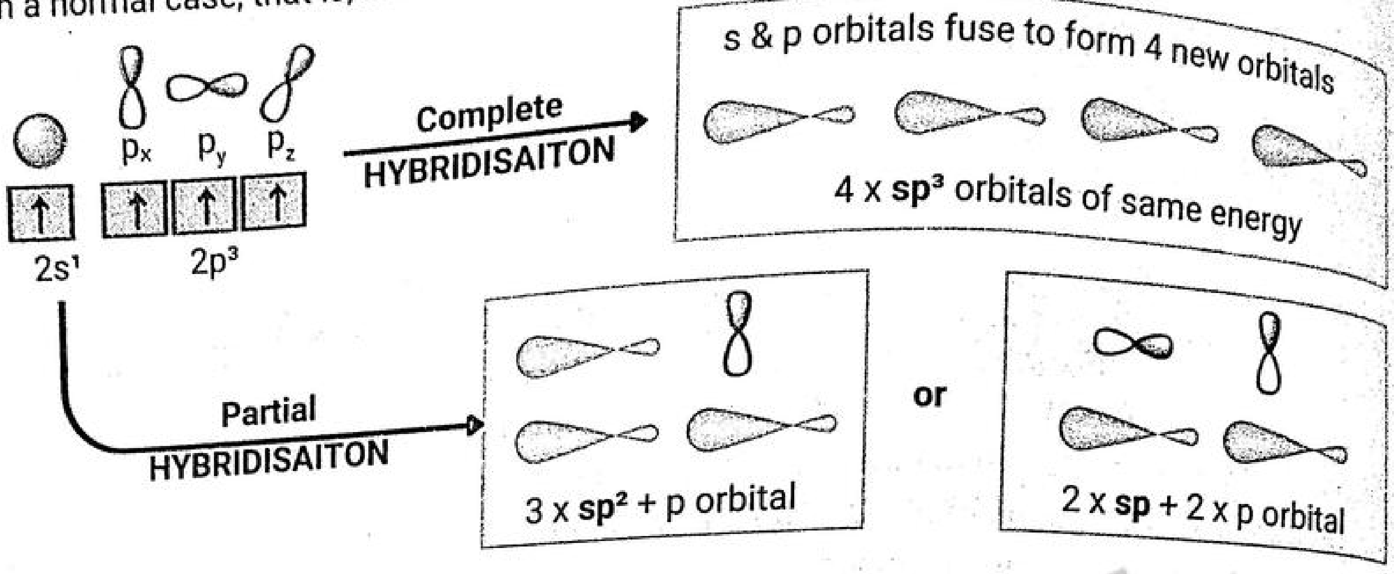
- 4 Unpaired Electrons
- Cannot form 4 bonds

Even with 4 unpaired electrons, Carbon struggles to bond. Why? The 2s-orbital's 1 electron and 2p-orbital's 3 electrons have an energy gap — fixed by something awesome! mentioned below.

HYBRIDISATION "Hybridisation fixes it! **s** and **p** orbitals mix into new ones, making Carbon ready to form 4 bonds!"

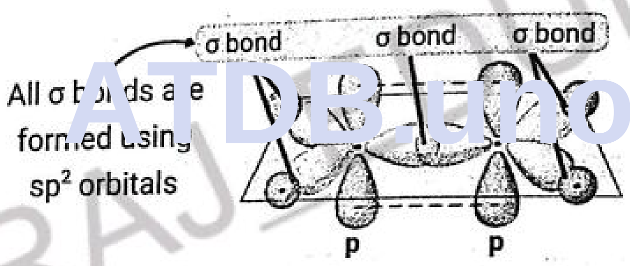
1.2 Hybridisation - The fusion of orbitals resulting in new ones

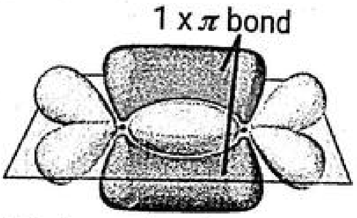
- In a normal case, that is, in excited state of carbon



- Note:
  - Sigma bonds contribute to single bonds & pi bonds to double/triple bonds
  - Sigma bonds come from sp, sp², or sp³ orbitals, but pi bonds? Always p orbitals!

For a simple molecule of Ethylene, i.e. $H_2C=CH_2$



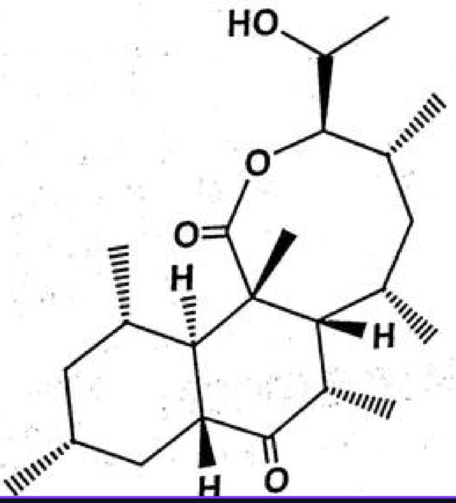


p orbitals overlap form one π bond

Hydrocarbon	Formula	Orbitals used for hybridisation	Orbitals Formed	Unhybridised p orbitals	Total orbitals
Alkanes	C_nH_{2n+2}	1s + 3p	4 x sp³	0	4
Alkenes	C_nH_{2n}	1s + 2p	3 x sp²	1	4
Alkynes	C_nH_{2n-2}	1s + 1p	2 x sp	2	4

FINDING HYBRIDISATION

Figuring out hybridisation in basic molecules is super simple! But what about those atoms in more complex compounds on the right? It might seem tricky at first, don't worry—we've got an easy trick to figure them all out!



1.2a Hybridisation - Finding the state of any molecule

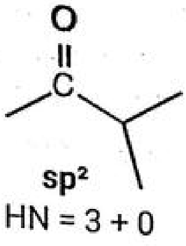
Hybridisation No. = No. of atoms connected (CA) **+ Lone pair on atom** (LP)

Hybridisation No.

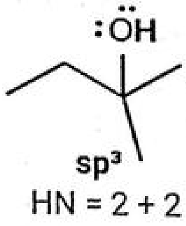
C.A. + LP	Hyb
2	sp
3	sp^2
4	sp^3

General Bonding of Atoms

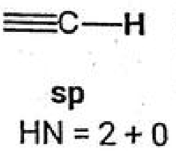
Atom	Bonds	L.P.
C	4	0
N	3	1
O	2	2
F	1	3



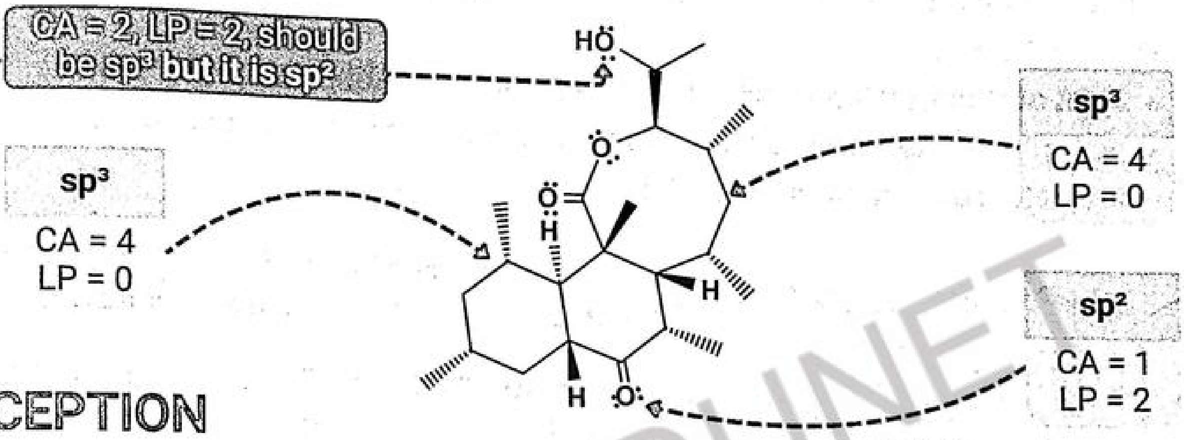
sp^2
HN = 3 + 0



sp^3
HN = 2 + 2

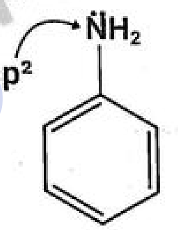


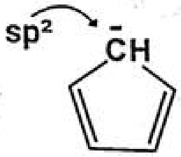
sp
HN = 2 + 0



EXCEPTION

When you've got lone pairs or even negative (-ve), positive (+ve), or radical charges hanging out in **conjugation**, something cool happens! The hybridisation shifts from sp^3 to sp^2.

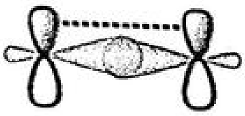




Common Thing that might become a mistake

H_3C-CH_3

This is a Single (sigma bond) formed between two sp3 orbitals

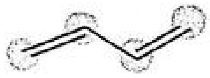


$H_2C=CH_2$

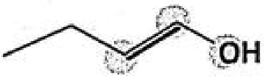
This is a double bond (mixture of sigma and pi bond)

1.3 Conjugation - The adjacent p orbitals

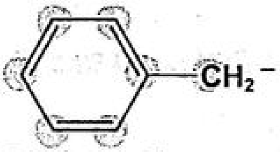
- When p orbitals from sp^2 atoms sit next to each other, they're called conjugated. This lets electrons spread out across them, creating resonance. For example
- *Every Heteroatom, Negative Charge or adjacent double bond contributes 2 π e-, whereas Radical contributes 1 π e-, and Carbocation contributes 0 π e-*



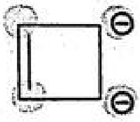
Conj. p = 4
π e⁻ = 4



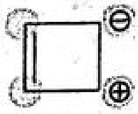
Conj. p = 3
π e⁻ = 4



Conj. p = 7
π e⁻ = 8



Con. p = 4
π e⁻ = 6

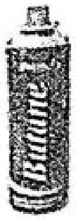


Conj. p = 4
π e⁻ = 4

1.4

Stability & Reactivity : ...

- Heat of combustion is the energy you get when an organic thing burns fully with oxygen.



Butane gas cans are picked over propane for camping stoves since they release more energy when burned. More heat of combustion means faster-cooking dal on your trip!

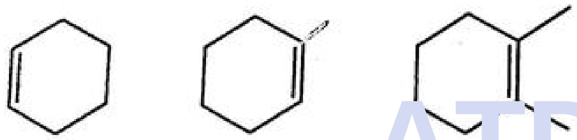
Butane	**Propane**
-2658 kJ mol^{-1}	-2220.1 kJ mol^{-1}
4 Carbon Atoms	**3 Carbon Atoms**
Less stable	**More stable**

- Overall, Remember, **More stability means less reactive**
  - **Heat of Combustion ∝ No. of carbons ∝ 1/Stability**
  - In Double Bonds,
    - **Heat of Combustion ∝ No. of Double bonds ∝ 1/Substitution**
    - ***For multiple double bonds, Heat of Combustion is lower for conjugated ones.***
  - In Rings, **Heat of Combustion per CH_2 ∝ Angle Strain**

HOC order

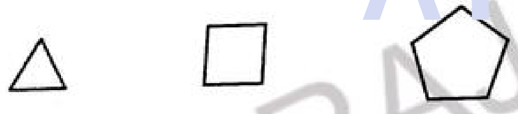
C has more π bonds than B and both C, B have more carbon atoms than A

C>B>A



C has 10αH's, B has 7αH's , A has 4αH's. Thus, C is most stable (Most substituted)

A>B>C



Angle strain has major role, **Cyclopropanes has the most angle strain** with internal angle of 60°. Thus, Highest HOC per CH_2

A>B>C

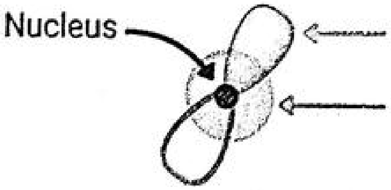
HOC order per CH_2

A B C

C's higher heat of combustion comes from two non-conjugated double bonds. **B has conjugated double bonds,** and A is with one double bond & fewer carbons

C>B>A

1.5 The Effects of Hybridisation & s-character



p orbitals are little far from nucleus

s orbital is closer to nucleus

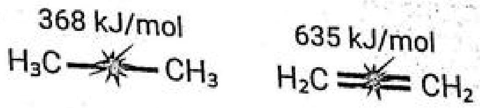
s-characters in hyb states		
sp^3	**sp^2**	**sp**
25%	**33%**	**50%**

- **Bond Length** : More the s character, shorter is the bond length
  - sp^3-sp^3 > sp^3-sp^2 > sp^2-sp^2 > sp^2-sp > sp-sp
  - Meaning, ***Ethene has shorter C-C bond than Ethane***

$H_3C\overset{1.53\text{Å}}{\text{—}}CH_3$ $\quad$ $H_2C\overset{1.33\text{Å}}{=}CH_2$

bond, More the strength of it

- sp^3-sp^3 < sp^3-sp^2 < sp^2-sp^2 < sp^2-sp < sp-sp
- Meaning, **C-C bond in Ethene is stronger than Ethane**



- **Electronegativity** : More the s character, More will be electronegativity (*discussed next)
  - More the electronegativity, better will be the hold of negative charge.

$$H_2C{=}CH_2 \xrightarrow{-H^+} H_2C{=}\overset{\ominus}{C}H$$

Ethene
Less Acidic

Less easily formed due to 33% s character

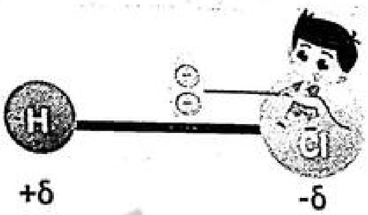
$$HC{\equiv}CH \xrightarrow{-H^+} HC{\equiv}C^{\ominus}$$

Ethyne
More Acidic

More easily formed due to 50% s character

1.6 Electronegativity

- Electronegativity is how much an atom tugs on electrons in a bond. Think of it like a tug-of-war over a rope! In HCl, chlorine's stronger and pulls the electrons closer, leaving hydrogen with less e⁻. So, chlorine gets a bit negative, and hydrogen ends up a bit positive!



- Remember the trick (Pronounced as *Fonkal Brish*) **FONClBrISH** ⟶ (Decreasing Electronegativity)

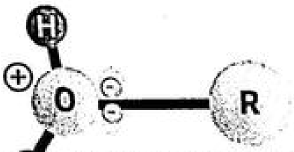
Negative charge is held better by more electronegative atom

Remember

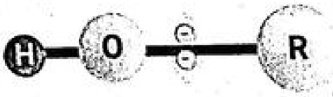
More electronegative element attracts electrons with higher force

Some important trends in Electronegativity you must know

1. **Increasing charge on En atom increases electronegativity:**
   a. $-\overset{\oplus}{O}H_2$ > $-OH$ (*+vely charged oxygen craves electrons more*)
   b. $-\overset{\oplus}{N}H_3$ > $-NH_2$ (*Similar for Nitrogen or any other En atom*)
2. **% s character increases electronegativity :**
   a. $(sp^3)^c < (sp^2)^c < (sp)^c$
   b. $(sp^3)^n < (sp)^c$ (*Alkyne C is more En than normal Nitrogen*)



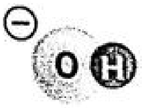
Electrons nearer to O



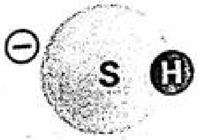
Electrons little far from O

1.7 Stability & Reactivity : Concept of Charge Density

- **Charge density?** Easy—it's how packed a charge is!
- **Smaller atom = Denser charge = More reactivity = Less stability!**



Oxygen : Smaller size
- More Charge density
- More Reactivity
- Less Stability



Sulphur : Bigger size
- Less Charge density
- Less Reactivity
- More Stability

But, along the Period, we consider electronegativity and not size!

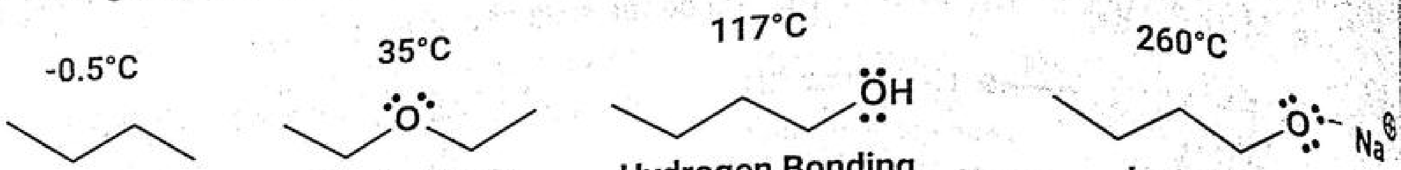
$$\overset{\ominus}{C}H_3 > \overset{\ominus}{N}H_2 > H\overset{\ominus}{O} > \overset{\ominus}{F}$$

- Most Reactive
- Least Stable
- Least Electronegative

- Least Reactive
- Most Stable
- Most Electronegative

1.8 Boiling Points in Organic Chemistry (General)

- To encounter the questions of B.P we need to understand the **concept of forces.**
  - **Stronger the force, Higher is the B.P.**



Vanderwaals forces — Weakest Forces — *Seen in Alkanes*

Dipole-Dipole — *Seen in Carbonyls, Ethers, Alkyl Halides*

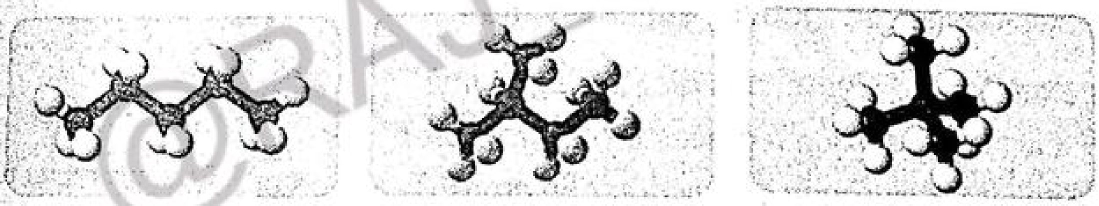
Hydrogen Bonding — *Seen in Alcohols, Phenols, Carboxylic acids*

Ionic Forces — Strongest Forces — Seen in Alkoxides, or tetrasubstituted Ammonium salts

- Apart from forces, two other factors influence the B.P. of a molecule
  - **Boiling points increase as the number of carbons is increased.**

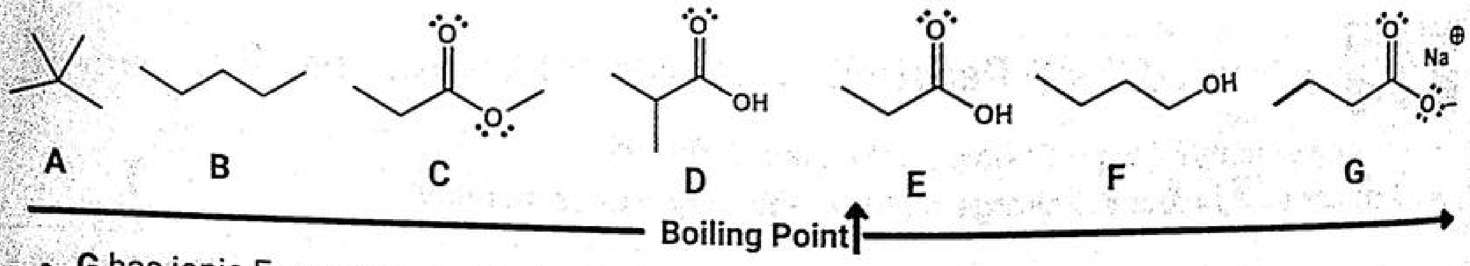
Methane CH_4 *(-161°C)* < Ethane C_2H_6 *(-88.6°C)* < Propane C_3H_8 *(-42°C)* < Butane C_4H_{10} *(-0.5°C)*.

- **Branching decreases boiling point.**



n-Pentane *(Unbranched)* > Isopentane *(Branched)* > Neopentane *(Highly Branched)*

The Ultimate order for Boiling point trend



- **G** has ionic Forces
- **F** has *H bonding*
- **E** has *H bonding* to a higher extent (Carboxylic acids have more BP than Alcohols)
- **D** has *H bonding* but branching decreases BP
- **C** has *Dipole Dipole Interactions.*
- **B** is an alkane with weak *vanderwaals* and **A** has *branching*. Thus, Lowest BP

1.9 Solvents

- Solvents in organic chemistry can only be divided into two major categories : polar and Non polar which can be further classified as followed :

Type	Definition	Examples	Key Reactions
Polar Protic	H bonded to Electro-ve Atom	H_2O, CH_3OH, CH_3CH_2OH, Acetic Acid	Favors SN1, stabilizes both cations & anions
Polar Aprotic	H not directly bonded to Electro-ve Atom	Acetone, DMSO, DMF, Acetonitrile	Favors SN2, solvates only cations
Non-Polar (Aromatic)	Weak/no dipole	Benzene, Toluene	Used in extractions & reactions
Non-Polar (Aliphatic)	Weak/no dipole	Hexane, Pentane	Used in chromatography
Non polar Ether-Based Solvents	Slight dipole, low polarity	Diethyl Ether, THF	Used in Grignard & organic reactions

1.10 Solubility

- Solubility of a compound depends on the forces that the compound has, Thus divided below

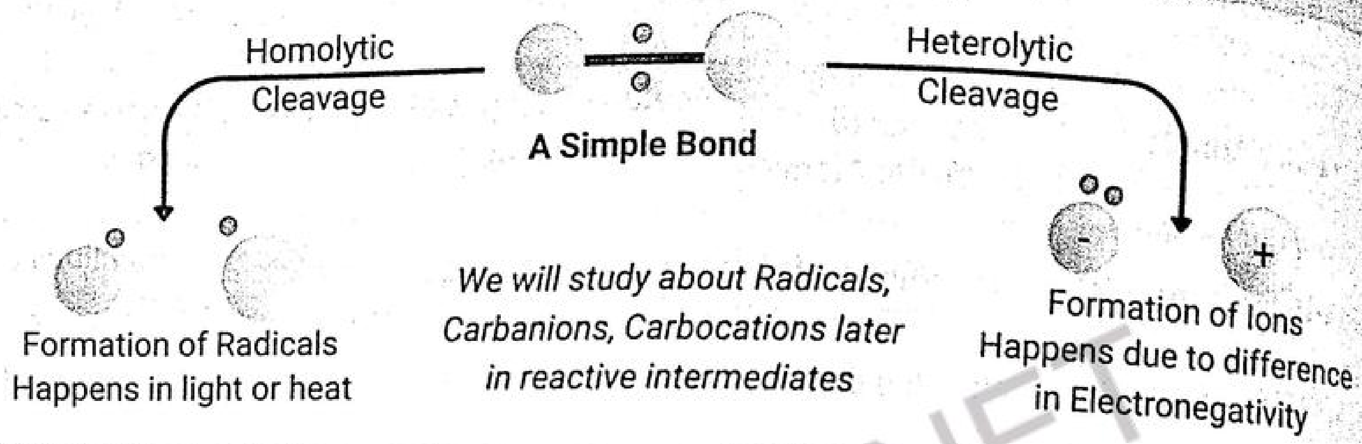
Intermolecular Force	Common in	Solubility in Water (Polar)	Solubility in Organic Solvents (Non-Polar)
Ionic Forces (Strongest)	Salts (NaCl, $RCOO^- Na^+$)	**Highly Soluble**	Insoluble
Hydrogen Bonding	Alcohols, Phenols, Carboxylic Acids	**Soluble**	Moderately Soluble
Dipole-Dipole Forces	Carbonyls, Alkyl Halides	Moderately Soluble	**Soluble**
Van der Waals Forces (Weakest)	Alkanes, Alkenes, Alkynes	Insoluble	**Highly Soluble**

- **Points to Note**
  - Alcohols are Water-soluble up to C4 due to hydrogen bonding. Solubility decreases as the carbon chain increases.
  - Carboxylic acids are more soluble than alcohols due to dimer formation.
  - Primary & secondary amines are soluble due to H-bonding.
    - **Tertiary amines are less soluble (no N-H bond for hydrogen bonding).**

2. Break, Make and Attack - The Organic Reactions

We've talked about bond strength (how tough bonds are), bond length (how long they stretch), and electronegativity (how atoms pull electrons). Now, let's get into the fun stuff—**why do organic reactions even happen?** It's all about what makes these molecules change and react!

2.1 Cleavage, How does it Break?

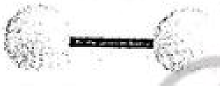


We will study about Radicals, Carbanions, Carbocations later in reactive intermediates

2.2 Electronic Displacement Effect


Difficult to break

Molecules with the same atoms on both sides is **non-polar**—no charges, totally chill! It won't react unless something from outside jumps in.


Easier to break

But a molecule with different atoms on each side? That makes a charge difference—great for starting a reaction when a bond breaks!

This charge difference sets up a **permanent effect** in molecules, driving reactions to happen!"

Types of Permanent Effects

Inductive Effect
Happens in sigma bonds

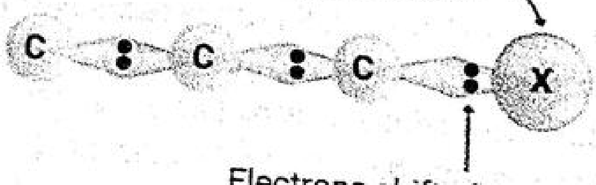
Mesomeric Effect
Happens in pi bonds

Hyperconjugation
Happens in sigma bonds usually C-H adjacent to p orbitals

2.2a Inductive Effect - Electrons inside **Sigma** Bond not in place

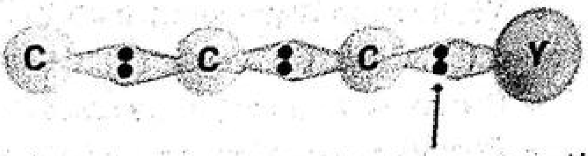
TWO CASES

An Electronegative Atom



Electrons shifted towards X

An Electropostive Atom



Electrons shifted away from Y

What happens because of it? The chain of carbon becomes positively or negatively charged depending upon the +I or -I group diminishing with distance.

$$C - \overset{+\delta\delta\delta}{C} \rightarrow \overset{+\delta\delta}{C} \rightarrow \overset{+\delta}{C} \rightarrow X$$

X is Electronegative Group **(-I)**

X can be $-NF_3^+ > -NR_3^+ > -SR_2^+ > -NH_3^+ > -NO_2 > -SO_3H > -CN > -CHO > -COOH > -F > -Cl > -Br > -I > -OR > -OH >$ Benzene > Alkene > H

$$C - \overset{-\delta\delta\delta}{C} \leftarrow \overset{-\delta\delta}{C} \leftarrow \overset{-\delta}{C} \leftarrow Y$$

Y is Electropositive Group **(+I)**

Y can be $-CH_3 < -CD_3 < -CT_3 < -C_2H_5 < -C_3H_7 < -C_4H_9 < -COO^- < -O^- < -NH^- < -CH_2^-$

Some Important points

1. **$-OH$ is a -I group** because oxygen acts like a regular electronegative atom, pulling electrons. But **$-O^-$? It's a strong +I group** since it's loaded with extra electrons to share!
    - Same deal: **$-NH_2$ is -I (pulls electrons)**, but **$-NH^-$ is +I (gives electrons)**.
2. **$-NH_3^+$ is a bigger -I than $-NH_2$** because that positive charge on nitrogen pulls electrons harder.
    - Same with **$-OH$ (-I) and $-OH_2^+$ (super strong -I due to the positive charge)**.
3. **$-O^- < -NH^- < -CH_2^-$ are stronger +I groups than plain alkyl groups** since they've got tons of electrons to push.
4. **Metals like Mg** in CH_3Mg can also be **+I**, sharing electrons.
5. A group can flip between +I and -I depending on what's attached to it! e.g.

$H_3C \rightarrow\rightarrow\rightarrow OH$

CH_3 acts as +I group

$H_3C \leftarrow\leftarrow\leftarrow O^-$

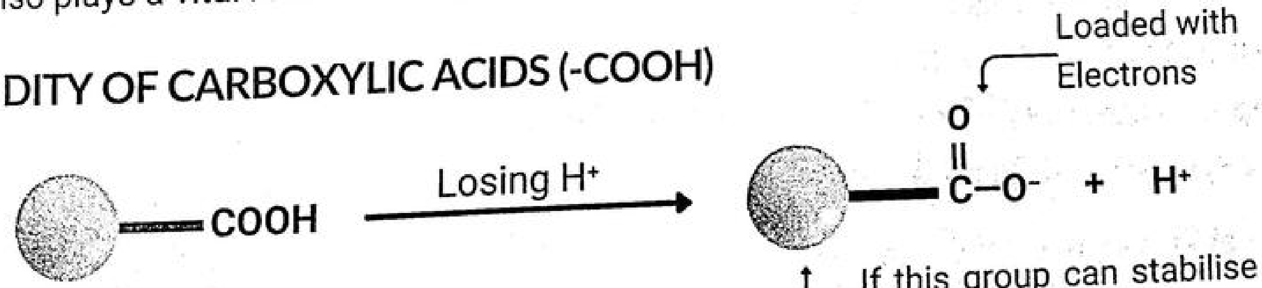
CH_3 acts as -I group

Why does it Matter?

Inductive Effect is like a push or pull on electrons that changes things!

1. For carboxylic acids or alcohols, it decides how easily they **give away H^+ (that's acidity)**.
2. For anilines, it controls how well they **grab H^+ (that's basicity)**.
3. It also plays a vital role in stability of Carbocation and Carbanion.

1. ACIDITY OF CARBOXYLIC ACIDS (-COOH)



If this group can stabilise COO^- by withdrawing electrons, The **acidity of precursor would increase**

⇒ **-I groups will increase** the acidity of carboxylic acid as it increases the stability of carboxylate ion (COO^-).

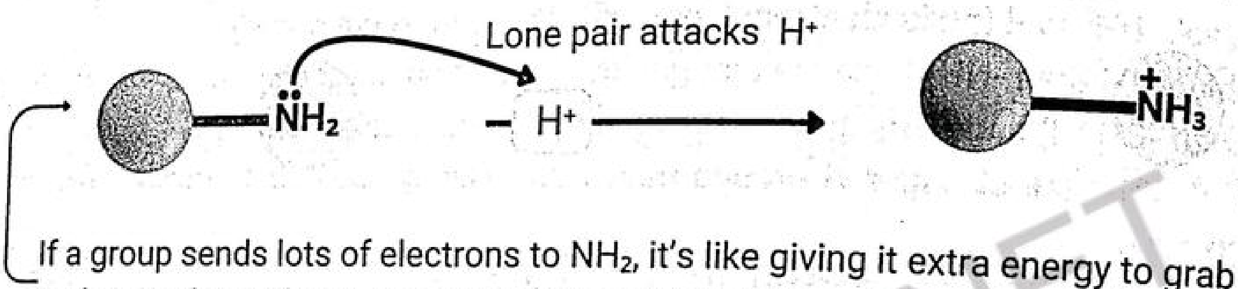
$Cl_3C-COOH$	$Cl_2CH-COOH$	$ClCH_2-COOH$	CH_3-COOH
Trichloroacetic Acid	Dichloroacetic Acid	Chloroacetic Acid	Acetic Acid

← **Increasing Acidity**

IMPORTANT

- **Increasing -I effect**
  - $NO_2CH_2COOH > FCH_2COOH > ClCH_2COOH > BrCH_2COOH,$
  - $F_3C\text{-}COOH > Cl_3C\text{-}COOH > Br_3C\text{-}COOH > I_3C\text{-}COOH$
- **Substituents on Benzene**
  - $CH_3\text{-}C_6H_5\text{-}COOH < C_6H_6\text{-}COOH < F\text{-}C_6H_5\text{-}COOH < Cl\text{-}C_6H_5\text{-}COOH < NO_2\text{-}C_6H5\text{-}COOH$
- **Distance Dependent Effect**
  - $ClCH_2CH_2CH_2COOH < ClCH_2CH_2COOH < ClCH_2COOH$
- **Going from +I Nature to -I Nature**
  - $(CH_3)_3C\text{-}COOH < CH_3COOH < CNCH_2COOH < SO_3HCH_2COOH$

2. BASICITY OF AMINES ($-NH_2$)



If a group sends lots of electrons to NH_2, it's like giving it extra energy to grab H^+. That makes it a better base, super ready to catch that H^+ and hang on!

Et_3N	**Et_2NH**	**$EtNH_2$**	**NH_3**
Triethyl Amine	Diethyl Amine	Ethyl Amine	Amine

← **+I groups Increases Basicity** ——

Some other basicity trends which might be helpful for exam

- **Going from -I Nature to +I Nature**
  - $(CF_3CH_2)_3N < (CF_3CH_2)_2NH < CF_3CH_2NH_2 < CH_3CH_2NH_2$
- **Trend with only -I effect**
  - $(CF_3)_3C\text{-}NH_2 < CF_3CH_2\text{-}NH_2$
- **Strong -I vs Strong +I**
  - $^+NH_3\text{-}CH_2\text{-}NH_2 < {}^-OOC\text{-}CH_2\text{-}NH_2$

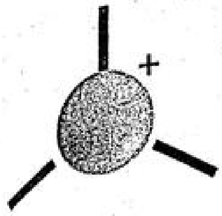
Exceptional Trends in case of amines

IMPORTANT

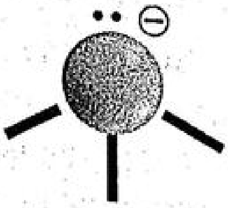
- $NH_3 < CH_3NH_2 < (CH_3)_2NH < (CH_3)_3N$ *(in Gas phase)*
- $NH_3 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$ *(in Aqueous Phase - Due to Solvation)*
- $NH_3 < CH_3CH_2NH_2 < (CH_3CH_2)_2NH < (CH_3CH_2)_3N$ *(in Gas phase)*
- $NH_3 < (CH_3CH_2)_3N < CH_3CH_2NH_2 < (CH_3CH_2)_2NH$ *(in Aqueous Phase - Due to Solvation)*

$(CH_3CH_2)_3N > (CH_3CH_2CH_2)_3N > ((CH_3)_2CH)_3N$ (*In both Gas and Aqueous phase - Sterically hindered Amines)*

3. STABILITY OF CARBOCATIONS AND CARBANIONS



Carbocation is electron deficient, any group that gives it electrons will make carbocation stable



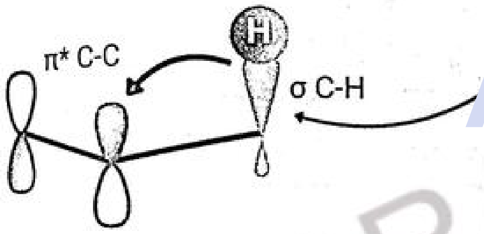
Carbanion is electron rich, any group that withdraws electrons, will make carbanion stable

Some stability trends which might be helpful for exam

IMPORTANT

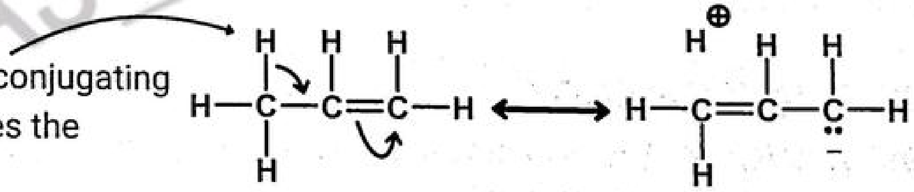
- **The effect of +I**
  - $CH_3^+ < CH_3CH_2^+ < (CH_3)_2CH^+ < (CH_3)_3C^+$ & $(CH_3)_3C^- < (CH_3)_2CH^- < CH_3CH_2^- < CH_3^-$
- **The Effect of -I**
  - $(CF_3)_3C^+ < (CF_3)_2CH^+ < CF_3CH_2^+ < CH_3CH_2^+$ & $CH_3^- < CF_3CH_2^- < (CF_3)_2CH^- < (CF_3)_3C^-$
- **Mixed Substituents**
  - $(CF_3)(CH_3)_2C^+ < (CH_3)_2CH^+ < (CH_3)_3C^+$ & $^-OOC\text{-}CH_2^- < CH_3^- < {}^+NH_3\text{-}CH_2^-$

2.2b Hyperconjugation : e⁻ in Sigma bond can move to adjacent p



When a σ C-H bond sits next to a p orbital or an sp² carbon, it can share its electrons. This creates a no-bond resonance structure, which helps make the whole thing more stable!

3 α C-H bonds can make 3 hyper conjugating resonance structures which makes the species stable



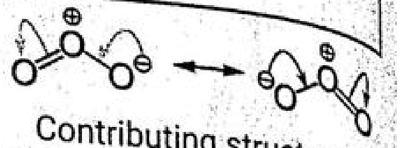
Some other hyperconjugation trends for alkenes & carbocations which might be helpful for exam

- **More Substituted Alkenes are more stable due to more α C-H bonds**
  - Ethene ($CH_2{=}CH_2$) < Propene ($CH_3\text{-}CH{=}CH_2$) < 2-Methylpropene ($(CH_3)_2C{=}CH_2$) < 2,3-Dimethylbut-2-ene ($(CH_3)_2C{=}C(CH_3)_2$)
- **Carbocations also becomes stable due to hyper conjugating structures**
- Methyl Carbocation (CH_3^+) < Ethyl Carbocation ($CH_3CH_2^+$) < Isopropyl Carbocation ($(CH_3)_2CH^+$) < Tert-Butyl Carbocation ($(CH_3)_3C^+$)

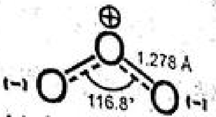
IMPORTANT

2.2c Resonance - Structures, Rules and Stability

- Before understanding mesomeric effect (One more displacement effect, we need to understand resonance)
  - **Resonance** in organic chemistry is when a molecule can be drawn in multiple ways by shifting electrons around, but it's really a blend of all those forms. Think of it like mixing colors—say, red and blue—to get one purple vibe that's the true molecule!



Contributing structures



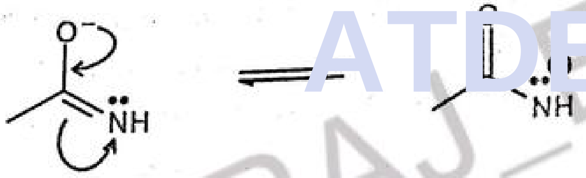
Hybrid of both

RULES FOR RESONANCE - HIGHLIGHTED : MORE STABLE

#1 : Less Charges are better

#2 : Octet Completion gives stability

#3 : -ve Charge on more Electronegative atom



#4 : +ve Charge on more substituted carbons

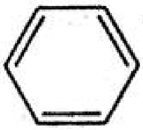
RESONANCE ENERGY

Energy difference between the theoretical value and the experimental value of energy(Real Value).

Resonance Energy ∝ Stability

A
2 π bonds

B
3 π bonds

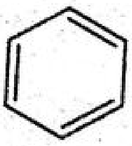


C
Aromatic structure

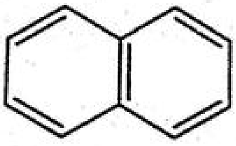
Resonance Energy : C >B > A

we will study this in a while

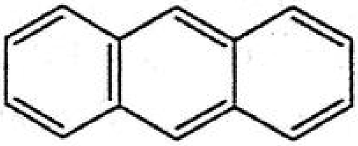
RESONANCE ENERGY PER RING



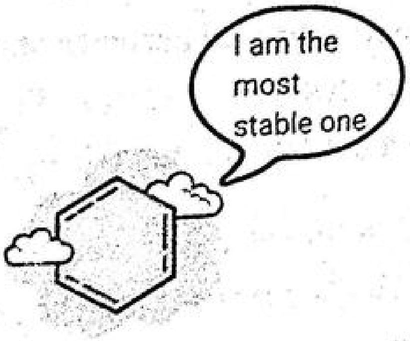
A



B



C



Resonance Energy : C >B > A (*more number of pi bonds*)

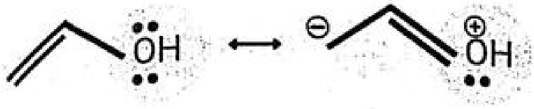
Resonance Energy Per ring : A > B > C (*Stability*)

RANSHOREVISION

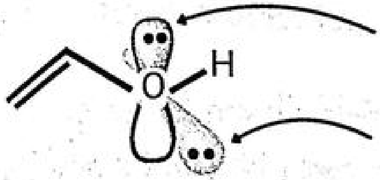
Remem are always in p orbitals

① 

This oxygen is sp³ hybridized, so it has 4 hybrid orbitals, and both its lone pairs chill in those sp³ orbitals!

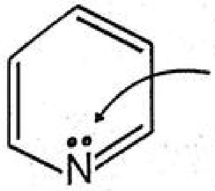
② 

Oxygen gets sp² hybridized when it's in conjugation, giving it 3 hybrid orbitals and 1 unhybridized p orbital!



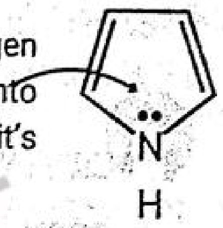
One lone pair in **p** orbital which is **involved in conjugation**

One lone pair sits in the **sp²** orbital, **not involved in conjugation**

③ 

The lone pair on nitrogen in pyridine **doesn't join resonance** because it's stuck in an sp² hybrid orbital, not a p orbital!

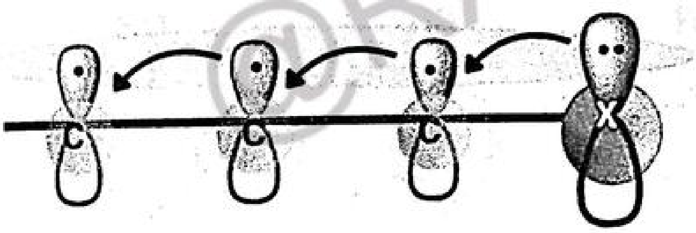
The lone pair on nitrogen in pyrrole jumps into resonance because it's ready in a p orbital!



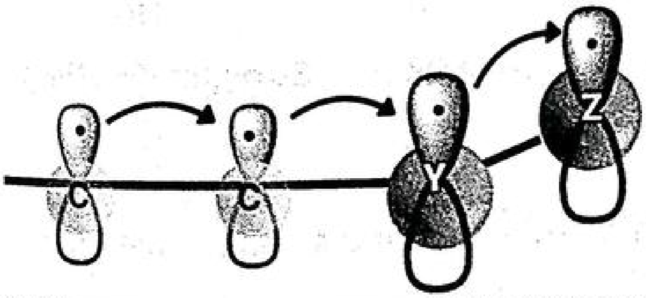
Final Conclusion

- A heteroatom that's sp³ hybridized and in conjugation switches to sp². Its lone pair moves to a p orbital, ready to join conjugation—like in pyrrole!
- But a heteroatom already sp² hybridized with a lone pair? That lone pair usually stays in an sp² orbital and skips conjugation—like in pyridine!

2.2d Mesomeric effect : The conjugated e⁻ in pi bond can delocalise



An atom or group with a lone pair lined up with p orbitals can share its electrons. This creates resonance structures, spreading the electrons towards the chain! this is **+M effect.**



An atom or group with a double bond next to p orbitals can pull electrons toward itself. This makes resonance structures, spreading electrons to the group—that's the -M effect!

Bond representation of +M effect

X can be -O⁻ > -NH$_2$ > -NHR > -OR > -NHCOR > -OCOR > -Ph > -F > -Cl > -Br > -I

Bond representation of -M effect

Y can be -NO$_2$ > -CN > -CHO > -C=O > -COOCOR > -COOR > -COOH > -CONH$_2$

Some Important points

1. **-O⁻ beats -OH as a +M group** because it's got tons of electrons to share, but it only donates through the p orbital—not the sp² ones
2. **Groups with C=O right on the chain (like -CHO or -COOH) show a -M effect,** with amide ($CONH_2$) being the weakest puller.
3. **-NHCOR isn't as good a +M group as -NHR** because the C=O grabs the lone pair from N, so there's less electrons to share with the chain

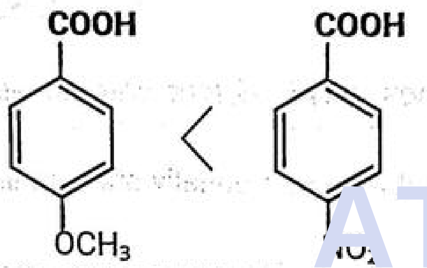
Why does it Matter? Similar to Inductive Effect, you know that!

Mesomeric Effect is like a push or pull on electrons **via pi bonds** which changes things

1. For carboxylic acids or alcohols, it decides how easily they **give away H^+ (that's acidity).**
2. For anilines, it controls how well they **grab H^+ (that's basicity).**
3. It also plays a vital role in stability of Carbocation and Carbanion.

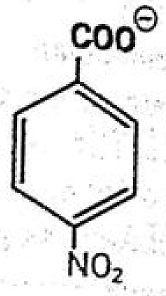
1. ACIDITY OF BENZOIC ACIDS (Ph-COOH) AND PHENOLS (Ph-OH)

❶



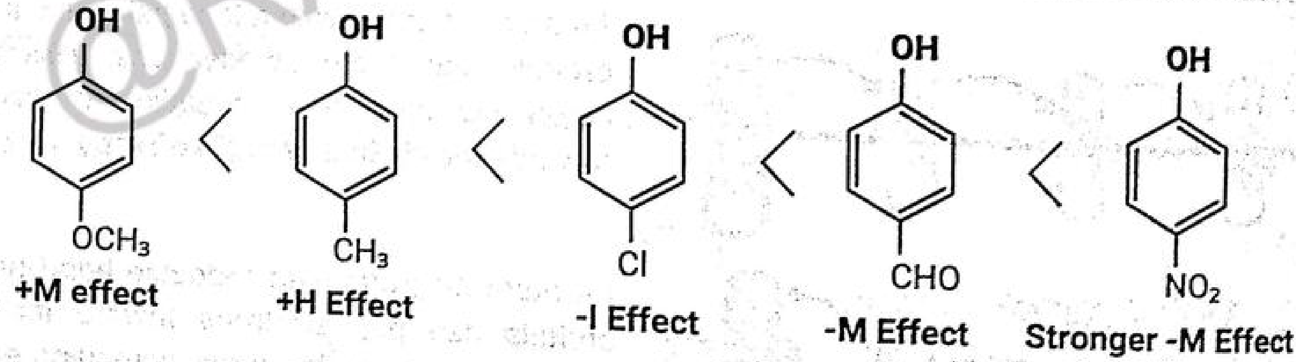
+M effect **-M effect**

p-Nitrobenzoic acid beats p-methoxybenzoic acid in acidity because the -M effect of NO_2 pulls electrons away from the benzoate ion, making it less electron-rich!



p-nitro benzoate ion

❷

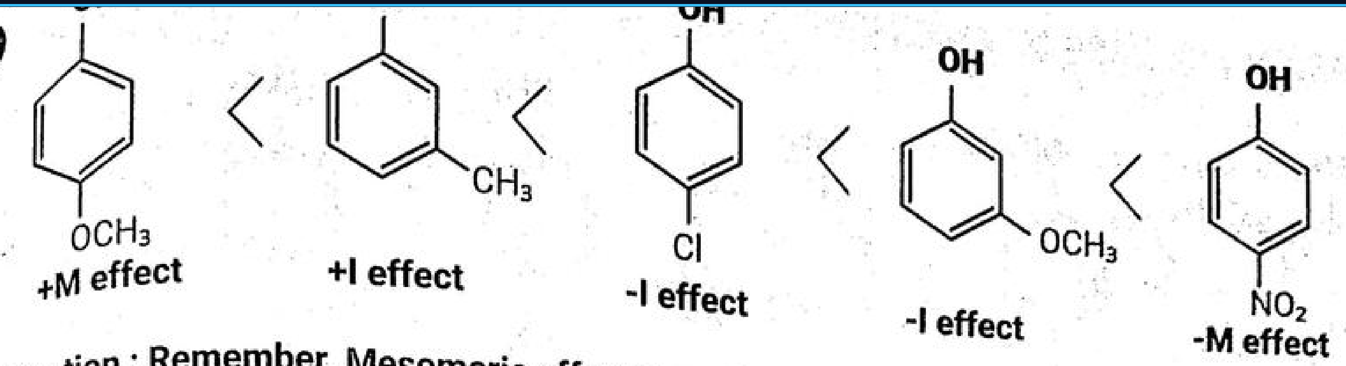


+M effect **+H Effect** **-I Effect** **-M Effect** **Stronger -M Effect**

Explaination

1. p-Methoxybenzoic acid lowers phenol's acidity with its +M effect (it also has -I, but +M wins big time!).
2. p-Methylphenol cuts phenol's acidity a bit with +H (hyperconjugation), which donates less than a normal +M gp.
3. p-Chlorobenzene boosts acidity slightly with -I (inductive)—**halogens have lone pairs, but their mesomeric effect is non considerable (it is very tiny).**
4. The -M effect of CHO ramps up acidity.
5. The -M effect of NO_2, stronger than CHO, pumps up acidity even more!

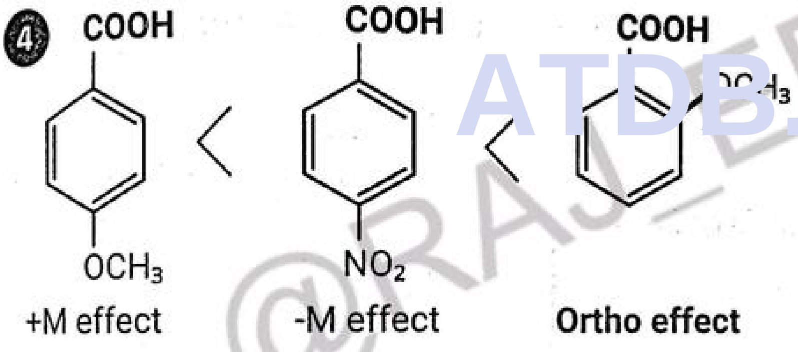
③



Explaination : **Remember, Mesomeric effect doesn't happen on meta position.** **IMPORTANT**

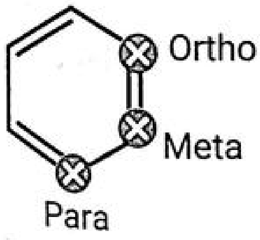
1. p-Methoxybenzoic acid lowers phenol's acidity with its +M effect (it also has -I, but +M wins big time!).
2. m-Methylphenol cuts phenol's acidity a bit with +I (Inductive effect), which donates the electrons to ring but lesser than +M.
3. p-Chlorobenzene boosts acidity slightly with -I (inductive)—**halogens have lone pairs, but their mesomeric effect is non considerable (it is very tiny).**
4. The -I effect of OCH_3 boosts acidity since there's no -M effect due to meta position—negative effects like -I always make things more acidic!
5. The -M effect of NO_2, stronger than -I effect of CHO, pumps up acidity even more!

④

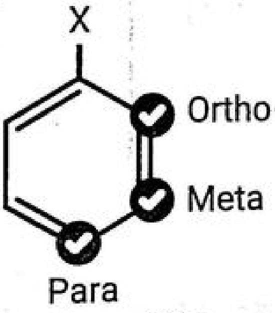


OCH_3 is a +M group which decreases acidity but **in case of benzoic acid.** NOTE : Any substituent when placed on ortho position increases the acidity of benzoic acid to much higher extent.

Benzene doesn't have ortho, meta, para positions until a group is attached



Benzene without substituent

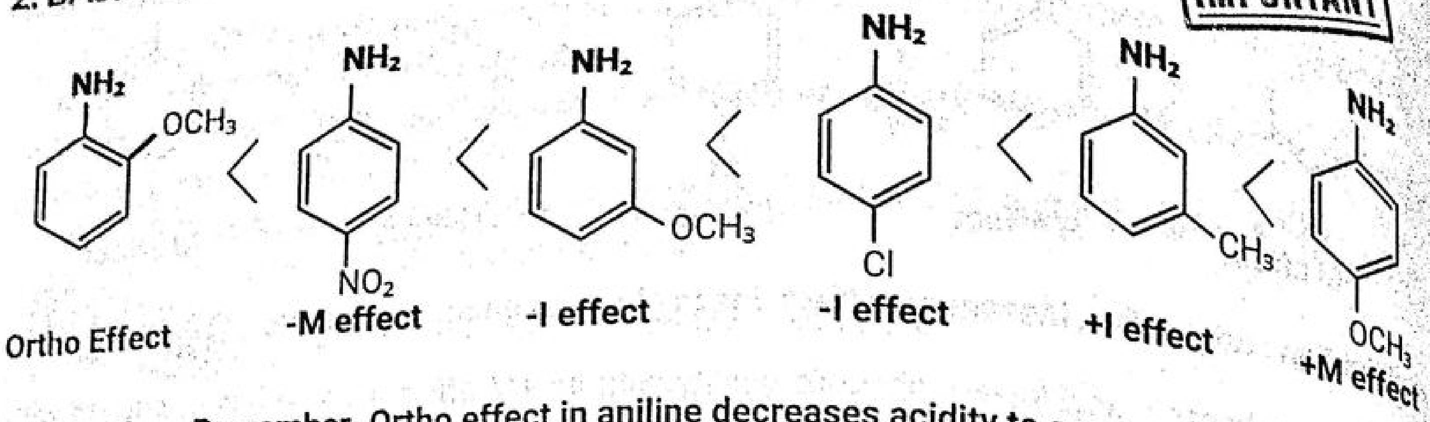


Benzene with substituent

Benzene doesn't come with ortho, meta, or para spots built in—they only show up once you stick a substituent on it! and the positions are only with respect to substituent.

2. BASICITY IN CASE OF ANI

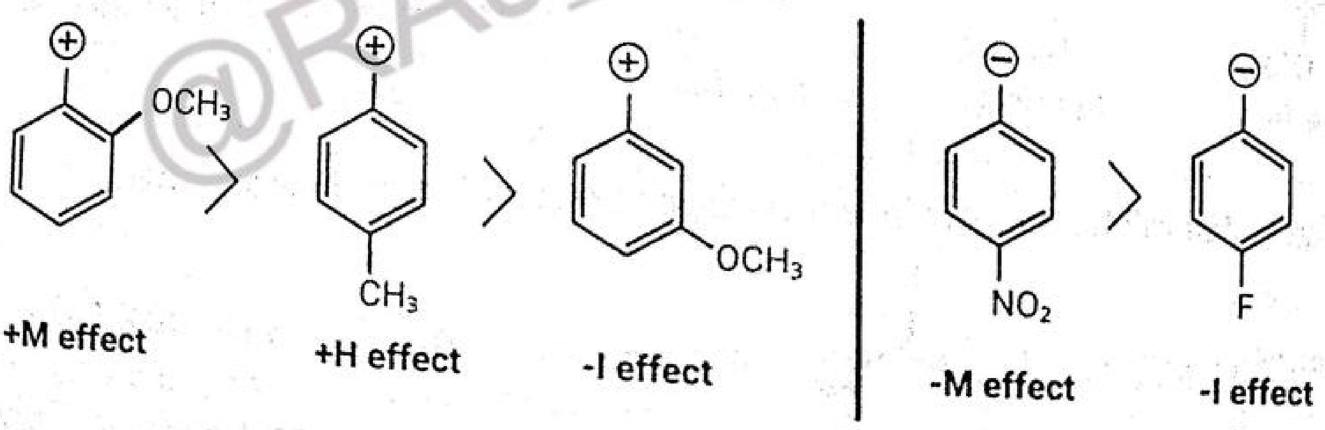
IMPORTANT



Explaination : Remember, Ortho effect in aniline decreases acidity to a very high extent

1. o-Methoxybenzoic acid lowers aniline basicity with its ortho effect though it has +M effect, it doesn't work.
2. p-Nitroaniline decreases the basicity with it's -M effect which withdraws the electrons from the ring.
3. The -I effect of OCH_3 decreases the basicity of aniline because the +M doesn't operate on meta position.
4. p-Chloroaniline decreases the basicity with the -I effect, halogens have lone pairs, but their mesomeric effect is non considerable (it is very tiny).
5. The +I effect of CH_3 boosts acidity since there's no +H effect due to meta position—Positive effects like +I makes things more basic.
6. The +M effect of OCH_3 is the strongest increasing the basicity to highest.

3. STABILITY OF CARBOCATIONS AND ANIONS



FINALLY,

EFFECT	ACIDITY	BASICITY	CARBOCATION STABILITY	CARBANION STABILITY
+I/+H/+M	Decreases	Increases	Increases	Decreases
-I/-H/-M	Increases	Decreases	Decreases	Increases

2.3 Aromaticity : Extra stability to specific species

Some compounds are super stable thanks to a special set of rules called Hückel's rule of aromaticity. If a compound follows these rules, we put the 'aromatic' label on it!

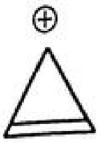
AROMATICITY				
CYCLIC	PLANAR	CONJUGATED	RULE	
✓	✓	✓	(4n + 2) πe-	**Aromatic**
✓	✓	✓	4n πe-	**Anti Aromatic**
May be	May be	May be	NO RULE	**NON Aromatic**

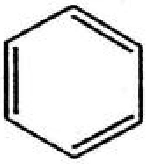
Before proceeding, Remember two things

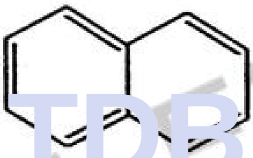
1. When in conjugation (adjacent p orbitals) contribution of πe- is as followed.
   - **Double bond = 2; Carbanion = 2; Carbocation = 0; Heteroatom = 2; Free Radical = 1**
2. **Aromatic > Non Aromatic > Anti Aromatic** in terms of stability

Aromatic-A

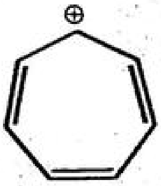
IMPORTANT

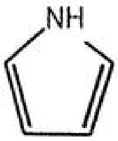

Cyclopropenyl cation
2πe-

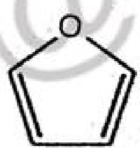

Benzene
6πe-

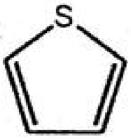

Napthalene
10πe-

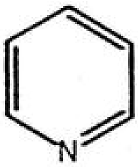

Cyclopentadienyl anion
6πe-

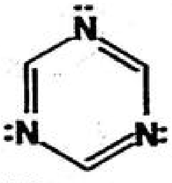

Tropylium Cation
6πe-

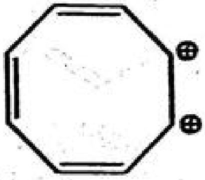

Pyrolle
6πe-

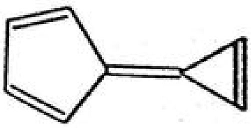

Furan
6πe-

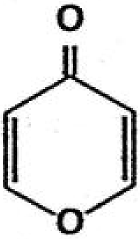

Thiophene
6πe-

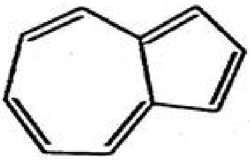

Pyridine
6πe-

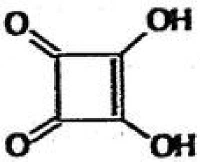

Nitrogen doesn't donate
6πe-

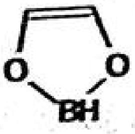

6πe-


6πe- + 2πe-
Bond Rotation Easier

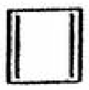

6πe-
Oxygen donates in resonance


10πe-
Aromatic in Polar state (**high Dipole moment)**


6πe-

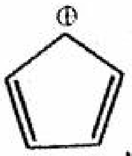

6πe-
Oxygen donates

Anti-Aromatic



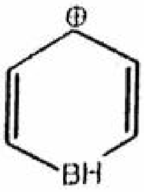
Cyclo butadiene

$4\pi e^-$



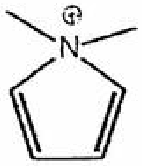
Cyclopentadienyl cation

$4\pi e^-$

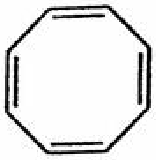


$4\pi e^-$

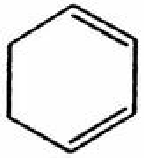
Non Aromatic



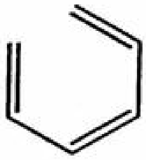
Non Conjugated



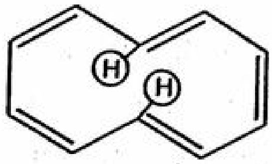
Non Planar



Non Conjugated



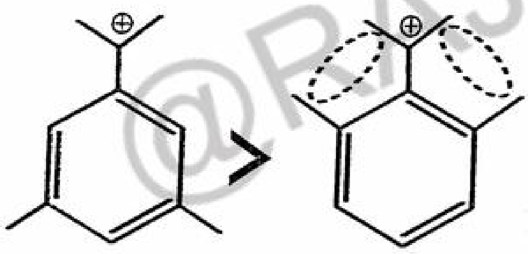
Non Cyclic



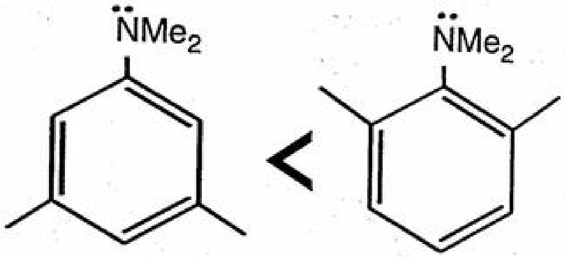
Non Planar

2.4 Steric Inhibition of Resonance

When a bulky group at the ortho spot pushes things around, the -sp² group twists out of shape and stops being flat. That blocks resonance—*meet steric inhibition of resonance!*



More stable, since the charge flows smoothly around the ring. The other one's all twisted, so the charge can't spread



More basic because nitrogen's twisted out of the ring in second one and doesn't share its lone pair with benzene ring

SIR applied by all bulky groups except OH, H, OR, NH_2, F etc.

SIR applied on all sp² Groups

2.5

Electrophiles and Nucleophiles

80% of organic chemistry reactions are a showdown between an electrophile and a nucleophile. Spotting them in a reaction makes things way easier!

IMPORTANT

Electrophiles : Electrons loving species : Also regarded as **Lewis acid** in Organic Chemistry

1. Compounds with incomplete octet	**BF_3, $AlCl_3$, etc.**
2. Compounds with available d-orbitals	**PF_3, $SnCl_2$, $SnCl_4$ etc**
3. Multiple bonds with dissimilar electronegativity	**$O=C=O$**
4. Sextet of electrons	**Carbenes**
5. All Simple Cations	**Na^+, Ag^+, Mg^{+2}, H^+ etc**

Nucleophiles : Nucleus loving species : Also regarded as **Lewis base** in Organic Chemistry

1. Molecules with lone pair	**$\dot{N}H_3$, $H_2\ddot{O}$, $R\text{-}\ddot{O}H$, py etc.**
2. Unsaturated Hydrocarbons	**$R_2C=CR_2$, $RC\equiv RC$**
3. Multiple bonds with dissimilar electronegativity	**$O=C=O$**
4. All Simple Anions	**Cl^-, OH^-, SH^-, Br^- etc**

2.6

Acidity and Basicity - The last thing you should know

We've tackled acidity and basicity with mesomeric and inductive effects already. Now, let's blend those trends to make exam prep a breeze for you!

Some Mixed Acidity Trends

1. $(CH_3)_3COH < (CH_3)_2CHOH < CH_3CH_2OH < CH_3OH$ *(+I decreases acidity)*
2. $CH_3CH_2OH < ClCH_2CH_2OH < FCH_2CH_2OH$ *(-I of halogens increases acidity)*
3. $CH_3OH < CH_3COOH$ *(Carboxylic acids are stronger than alcohols due to stabilised carboxylate)*
4. $CH_3CH_2OH < C_6H_5OH < p\text{-}NO_2\text{-}C_6H_5OH$ *(-M of Nitro increases Acidity compared to normal phenol which is higher acidic than normal Ethanol)*
5. $HOOC\text{-}CH_2\text{-}CH_2\text{-}COOH < HOOC\text{-}CH_2\text{-}COOH < HOOC\text{-}CCl_2\text{-}COOH$ *(The second COOH group exerts a –I effect, increasing acidity. Cl atoms further enhance the –I effect)*
6. $(CF_3)_3C\text{-}COOH < F_3C\text{-}COOH$ *(Steric hinderance distorts carboxylate ion, decreasing acidity)*
7. $C_6H_5\text{-}COOH < p\text{-}NO_2\text{-}C_6H_5\text{-}COOH < o\text{-}Cl\text{-}C_6H_5\text{-}COOH$ *(ortho effect of Benzoic acid)*
8. ${}^-OOC\text{-}CH_2\text{-}COOH < CH_3COOH < {}^+NH_3\text{-}CH_2\text{-}COOH$ *(Strong -I effect of ${}^+NH_3$)*

Basicity Trends

1. $p\text{-}NO_2\text{-}C_6H_5\text{-}NH_2 < C_6H_5\text{-}NH_2 < p\text{-}CH_3\text{-}C_6H_5\text{-}NH_2$
2. $C_6H_5\text{-}NH_2 < CH_3CH_2NH_2$ *(Aniline's nitrogen is in conjugation losing it's electrons, thus, less basic)*
3. $C_6H_5\text{-}C\equiv N < C_6H_5\text{-}NH_2 < CH_3CH_2NH_2$ *($(sp)^n$ is more electronegative than $(sp^3)^n$ thus it holds electrons to might tigher, making it less basic, The middle one is $(sp_2)^n$)*
4. $(CH_3)_3N < (CH_3CH_2)_3N < (CH_3CH_2CH_2)_3N$ *(Larger alkyl groups balance +I and solvation)*
5. $C_6H_5\text{-}NH_2 < p\text{-}CH_3\text{-}C_6H_5\text{-}NH_2 < o\text{-}CH_3\text{-}C_6H_5\text{-}NH_2$
6. $C_6H_5\text{-}NH_2 < (CH_3)_2NH < (NH_2)_2C{=}NH$ ***(Guanidine's resonance-stabilized conjugate acid makes it very basic.)***

Summing up Acidity in a easy method - Cardio Method

- **C - CHARGE**

  More positive charge, More Acidity **$H_3O^+ > H_2O > OH^-$**

- **A - ATOM**

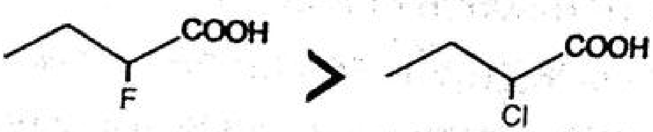
  Along Group & Period Acidity Increases **$CH_4 < NH_3 < H_2O < HF$ & $HF < HCl < HBr < HI$**

- **R - RESONANCE**

  Resonating Conj. bases have stronger acids **Ethanol < Phenol** Phenoxide is stable

- **DI - DIPOLE INDUCTION**

  More acidic due to stronger -I of F



- **O - ORBITALS**

  Terminal Alkynes (sp) > Alkenes (sp^2) > Alkanes (sp^3)

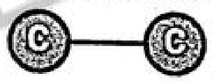
Step Towards Organic 2
Nomenclature

1. Introduction to Organic Nomenclature

With millions of organic compounds discovered so far, we cannot rely on calling them by common names like "alcohol," "vinegar," or "acetone"- because many compounds can share the same common name or have none at all. **IUPAC (International Union of Pure and Applied Chemistry)** gives us a universal set of rules to name each compound in such a way that its structure is reflected in the name itself.

1.1 Basic structure for nomenclature

PREFIX — WORD ROOT — PRIMARY SUFFIX — SECONDARY SUFFIX

PREFIX	WORD ROOT	PRIMARY SUFFIX	SECONDARY SUFFIX
Tells about: Substituents, Halogens, other groups	**Tells about:** Number of carbons in the longest chain	**Tells about:** Type of carbon- carbon bond 	**Tells about:** Indicates the main functional group

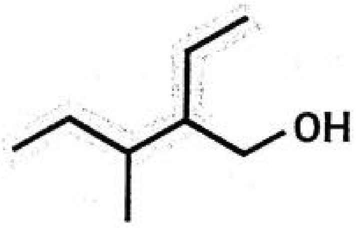
1.2 Finding the WORD ROOT

This tells us how many carbon atoms are present in the **PARENT CHAIN** *(longest continuous carbon chain).*

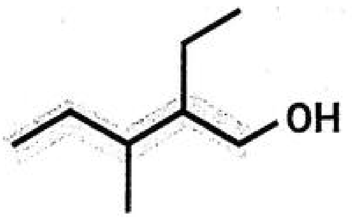
FINDING THE PARENT CHAIN

Finding the Parent chain involves- **"3 golden rules"**

RULE 1- **The parent chain must include the main functional group.**



Chain A



Chain B

- Chain A contains more number of carbon atoms. (It might tempt you!)
- Chain B has main functional group. (but 5 C atoms)
- So, **Chain B** is the Parent Chain.

RULE 2- The chain must include all double or triple bonds.

If a chain with a double bond is shorter than one without it, still prefer the one with the double bond.

Example- This is a 5- Carbon chain and not 4 carbon with one double bond!

RULE 3- Length of the chain is important, yet choose the chain with more substituents.

When two chains of equal length exist, pick the one with more branches or side groups, so the full name can reflect maximum detail.

Once you have selected the parent carbon chain, Its time to find the WORD ROOT.

No. of Carbons	Word root	No. of Carbons	Word root
1	Meth	6	Hex
2	Eth	7	Hept
3	Prop	8	Oct
4	But	9	Non
5	Pent	10	Dec

1.3 Finding the PRIMARY SUFFIX

Tells us about the type of carbon-carbon bonds in the main chain:

C-C Bonds	Primary suffix	Representation
Single bond	-ane	H_3C-CH_3
Double bond	-ene	$H_2C=CH_2$
Triple bond	-yne	$HC\equiv CH$

1.4 Finding the SECONDARY SUFFIX

Indicates the main **functional group** in the molecule:

Functional group	Suffix	Functional group	Suffix
Alcohols (**-OH**)	-ol	Aldehyde (**-CHO**)	-al
Ketone (**R-CO-R'**)	-one	Carboxylic acid (**-COOH**)	-oic acid
Ester (**R-COO-R)**	-oate	Thione (**R-CS-R'**)	-thione
Amine (**R-NH_2**)	-amine	Amide (**R-CO-NH_2**)	-amide

Functional group	Suffix	Functional group	Suffix
Acid halides (**-CO-X**)	-oyl halides	Cynides (**-CN**)	-nitrile

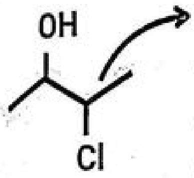
1.5 Finding the PREFIX

Tells us about the substituents, halogens and other functional groups.

Functional group	Prefix	Functional group	Prefix
Azo (**-N=N-**)	azo	Nitro (**-NO$_2$**)	nitro
Nitroso (**NO**)	nitroso	Halides (**-X**)	halo
Ether (**-O-**)	alkoxy	Epoxides (C–C with O bridge)	epoxy
Alkane (**-R**)	alkyl	Alcohols (**-OH**)	hydroxy
Cynides (**-CN**)	cyano	Carboxylic acid (**-COOH**)	carboxy

Note- Prefixes are written in an alphabetical order, and in case of repeated groups use- di-, tri-, tetra- etc.

Example- Let's see what can we infer from this molecule!



- The longest chain has 4 carbons as highlighted- **But (Word root)**
- All bonds are single- **ane (Primary suffix)**
- We see alcohol group attached (main functional group)- **ol (Secondary suffix)**
- We also find chlorine attached- **Chloro (Prefix)**

Name of the molecule- **3-Chlorobutan-2-ol**

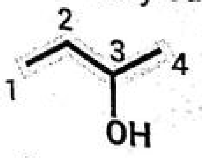
But, what are these numbers?

1.6 Numbering the Carbon chain

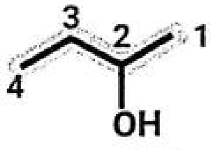
Once you've selected the correct parent chain (based on functional group, multiple bonds, and length), then you need to assign numbers to the carbon atoms in that chain. But this isn't just random numbering! The goal is to give the lowest possible numbers to the most important features in a strict priority order. 3 rules define the numbering of the chain-

RULE 1- **Give the Lowest Number to the Main Functional Group.**

The most important functional group must get the lowest possible locant. This group decides the secondary suffix in the name and is your top priority during numbering.



Butan-3-ol

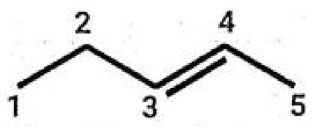


Butan-2-ol

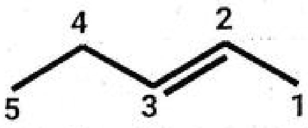
Since -OH is the main priority group, the numbering will start from the right side- hence, the **correct name** is **Butan-2-ol**

RULE 2- If No Functional Group, Prioritize Multiple Bonds (Double/Triple)

If there's no functional group, then the position of double (C=C) or triple (C≡C) bonds decides the numbering. The carbon where the multiple bond starts must get the lowest number possibl



Pent-3-ene



Pent-2-ene

As we prioritise the double bonds, the **correct name** will be **Pent-2-ene.**

RULE 3- Substituents tend to be named after the functional groups and multiple bonds.

If the positions of the functional group and double/triple bonds are already minimized, only then do you consider substituents (like methyl, chloro, bromo, etc.) for numbering.

Priority order: Functional group > Multiple bonds > Substituents

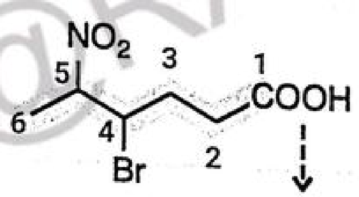
1.7 Priority Order of Functional Groups

In IUPAC nomenclature, if a molecule contains more than one functional group, you must choose only one as the main functional group (which decides the suffix in the name). The rest are treated as substituents and are written as prefixes in the name.

Sulphonic acid > Carboxylic acid > Ester > Acid chloride > Amide > Nitrile > Aldehyde > Ketone > Alcohol > Amines > nitro > Halo > Alkyl

Learn by- Some Cool Explorers Always Ask Naughty Aliens Kindly About Amazing New Hidden Adventures.

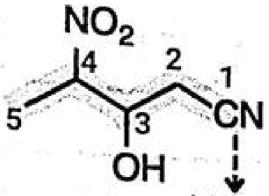
Example-



Main functional group- Carboxylic acid

2-Bromo-3-nitropentanoic acid

4-Bromo-5-Nitrohexanoic acid



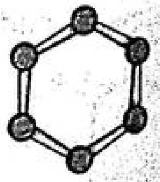
Main functional group- ~~Carboxylic acid~~ Nitrile

3-Hydroxy-4-nitropentanenitrile

2 Special Cases in IUPAC Nomenclature

While the standard rules of IUPAC nomenclature work for most organic compounds, some structures require special attention due to their unique frameworks or the presence of multiple features. Let's break these down into three important categories:

- Cyclic Compounds
- Aromatic compounds
- Bicyclic compounds

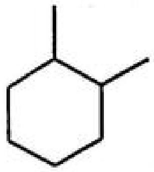


2.1 IUPAC for Cyclic compounds

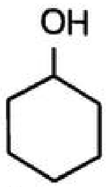
Cyclic compounds are organic molecules in which the carbon atoms are connected to form a ring structure.

How to Name:

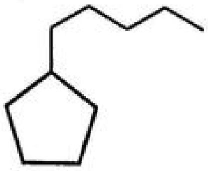
- Use the prefix *"cyclo"* before the word root.
- Numbering starts from the substituent or functional group that gives the lowest locants.



1,2-Dimethylcyclohexane

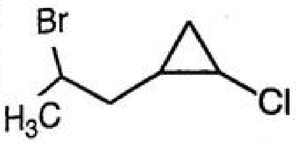


Cyclohexanol

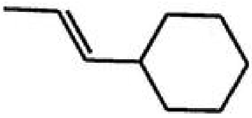


Pentyl cyclopentane

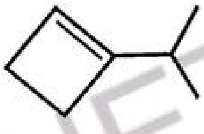
Note- If the ring and the chain both have same no. of C- atoms; give priority to ring.



1-(2-bromo-propyl)- 2-chlorocyclopropane



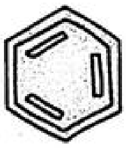
prop-1-en-1ylcyclohexane



1-Isopropylcyclobutane

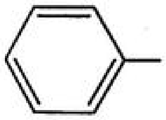
2.2 IUPAC for Aromatic compounds

Aromatic compounds are based on benzene rings and its substituted forms.

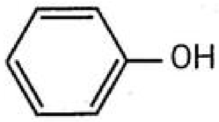


How to name:

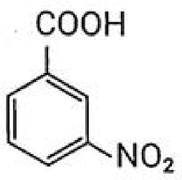
- Parent = Benzene.
- Substituents are treated as prefixes.
- If there's a functional group with high priority (e.g., –COOH, –OH), the base changes. (e.g.- benzoic acid, phenol).



Methylbenzene
(Toluene)

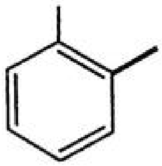
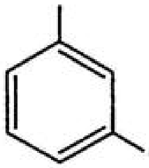
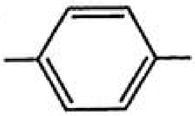


Hydroxybenzene
(Phenol)



3-Nitrobenzoic acid

This is also written as m- nitrobenzoic acid (Here, m= meta)

Ortho position	Meta Position	Para Position
1,2 substitution	**1,3 substitution**	**1,4 substitution**
		

2.3 IUPAC for Bicyclic compounds

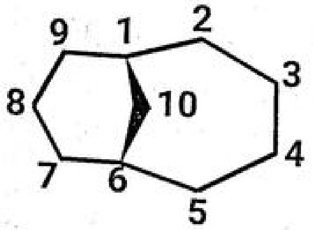
BRIDGED BICYCLIC-

Compounds that contain 2/ more rings sharing non- adjacent atoms.

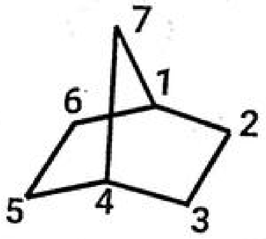
How to name:

- Count the total no. of carbons to get the word root.
- Use the prefix Bicyclo.
- Count no. of carbons in big ring, small ring, and bridge (write in the format- [big.small.bri

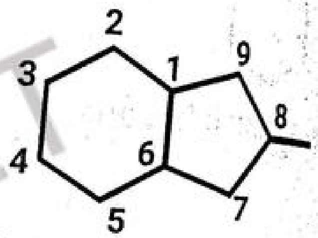
Note- The counting is done as- Big ring→ Small ring→ Bridge



Bicyclo [4.3.1] decane



Bicyclo [2.2.1] decane



8- Methyl bicyclo [4.3.0] Nonane

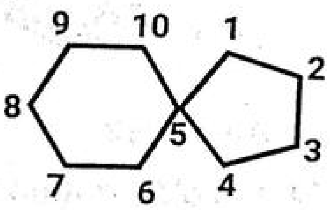
SPIROCYCLIC-

Organic molecules featuring at least two rings that share a single atom

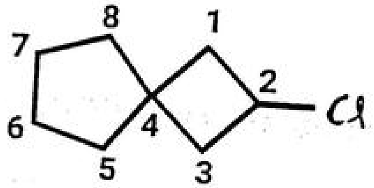
How to name:

- Count the total no. of carbons to get the word root.
- Use the prefix Spiro.
- Count no. of carbons in big ring and small ring (write in the format- [big.small])

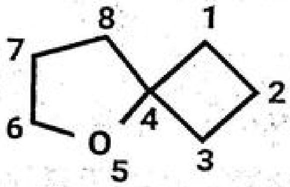
Note- The counting is done as- Small ring→ Big ring



Spiro [5.4] decane



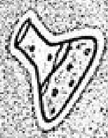
2- chlorospiro [3.4] octane



5- Oxaspiro [3.4] octane

THE CASE OF OXA-SPIRAL COMPOUNDS

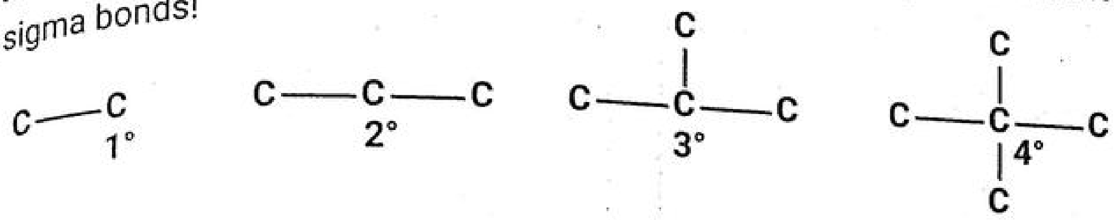
- Everything is done in the same way, except oxygen is also counted for the word root.
- Also while counting the rings, oxygen is counted too.



Steorechemistry/Isomerism

1. Degree of an atom

- An atom, like carbon, gets called 1°, 2°, or 3° based on how many other atoms it's hooked to with sigma bonds!



1.1 Degree of Unsaturation - Less Hydrogens

Let's see how some compounds match up with their alkane pals!

Compound	Alkane Counterpart	Hydrogen Deficiency	Degree of Unsaturation
Ethene ($CH_2=CH_2$)	Ethane, CH_3-CH_3	2 fewer hydrogens	**1** (1 Double bond)
Benzene (C_6H_6)	Hexane, C_6H_{14}	8 fewer hydrogens	**4** (1 Ring + 3 Double bonds)
Cyclohexene (C_6H_{10})	Hexane, C_6H_{14}	4 fewer hydrogens	**2** (1 Ring + 1 Double bond)

The **Degree of Unsaturation (DoU)** counts the rings and multiple bonds in a molecule compared to a saturated alkane. It shows how many pairs of hydrogens are "missing."

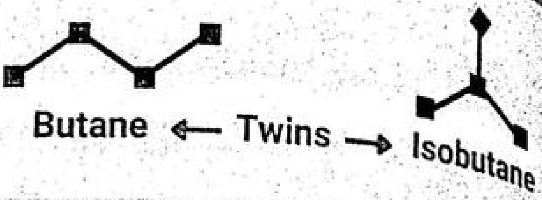
For $C_xH_yN_nO_oX_x$ (X = halogen): $\frac{2C + 2 + N - H - X}{2}$

Examples

1. **Ethyne** (C_2H_2) - One Triple Bond
    - Ethyne, C_2H_2, has DoU = (2(2) + 2 - 2) / 2 = 2. One triple bond (2 units).
2. **1,3-Butadiene** (C_4H_6) - Two Double Bonds
    - 1,3-Butadiene, C_4H_6, has DoU = (2(4) + 2 - 6) / 2 = 2. Two double bonds (2 units).
3. **Pyridine** (C_5H_5N) - Aromatic with Nitrogen
    - Pyridine, C_5H_5N, has DoU = (2(5) + 2 + 1 - 5) / 2 = 4. One ring + 3 effective double bonds (aromatic).
4. **Chloroform** ($CHCl_3$) - Halogen-Containing Compound
    - Chloroform, $CHCl_3$, has DoU = (2(1) + 2 - 1 - 3) / 2 = 0. No rings or multiple bonds.
5. **Acetone** (C_3H_6O) - Carbonyl Compound
    - Acetone, C_3H_6O, has DoU = (2(3) + 2 - 6) / 2 = 1. One C=O double bond (1 unit).

2. Isomerism

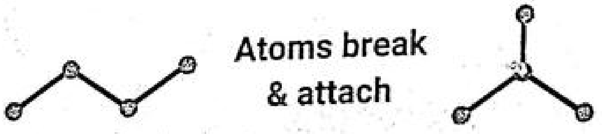
Isomerism is like a chemistry magic trick! Molecules with the same "pieces" (like C_4H_{10}) can look different —like building a straight or branched shape with the same LEGO bricks. Same stuff, different styles!



2.1 Types of Isomerism

Structural Isomerism

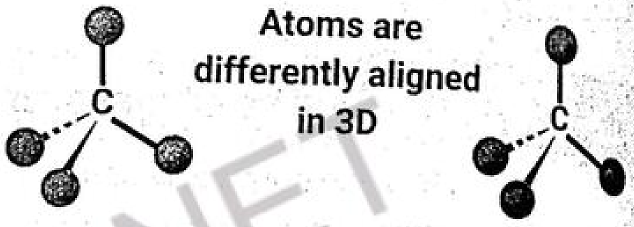
Different structure but same molecular formula



- Chain isomerism
- Position isomerism
- Functional isomerism
- Metamerism
- Tautomerism

Stereoisomerism

Different 3d arrangement but same molecular formula

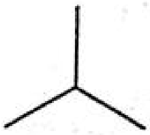


They both seem identical, but are they?

- Geometrical isomerism
- Configurational Isomers
- Confirmational isomerism

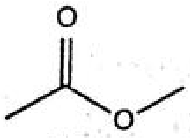
2.2 Structural Isomers

n-butane

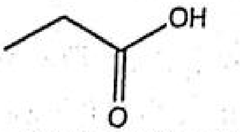


Iso-butane

- **Chain isomerism :** Arrangement of carbon chain is different



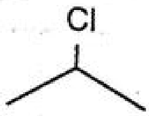
Ester



Carboxylic acid

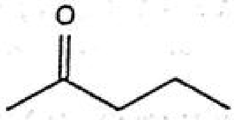
- **Functional isomerism :** Different Functional groups

1-Chloropropane

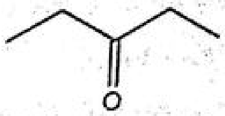


~~Iso-butane~~ 2-Chloro Propane

- **Position isomerism :** Position of Functional group is different



~~Ester~~ (2-Pentanone)



~~Carboxylic acid~~ (3-Pentanone)

- **Metamerism :** Different alkyl gps on two sides of functional groups

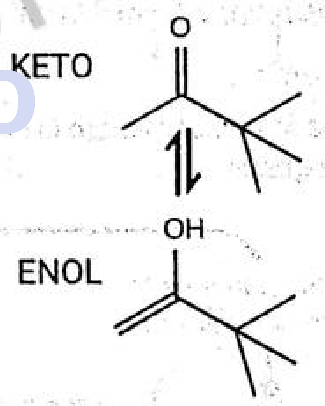
Exam Oriented Question : How many chain isomers can are there for X **IMPORTANT**

Below table summarises all the possible number of isomers for Alkanes, alkenes and alkynes

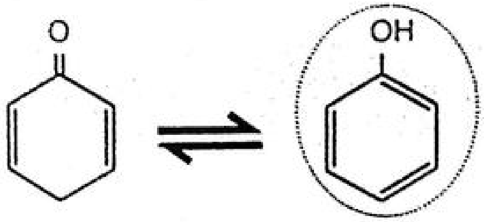
Carbon Atoms (n)	Alkanes (C_nH_{2n+2})	Number of Isomers	Alkenes (C_nH_{2n})	Number of Isomers	Alkynes (C_nH_{2n-2})	Number of Isomers
2	C_2H_6	1	C_2H_4	1	C_2H_2	1
3	C_3H_8	1	C_3H_6	2	C_3H_4	2
4	C_4H_{10}	2	C_4H_8	5	C_4H_6	7
5	C_5H_{12}	3	C_5H_{10}	7	C_5H_8	14
6	C_6H_{14}	5	C_6H_{12}	17	C_6H_{10}	39
7	C_7H_{16}	9	C_7H_{14}	36	C_7H_{12}	94
8	C_8H_{18}	18	C_8H_{16}	99	C_8H_{14}	263

For other formulas like C_8H_{10}, First find Degree of Unsaturation and then produce the isomers

- **Tautomerism**
  - Interconvertible structures that are different in terms of the relative position of one atomic nucleus which is generally the hydrogen
  - **Need to have an α-H for inter-convertibility**
  - Keto is more stable than enol due to C=O stronger bond but in some cases, enol concentration is higher.

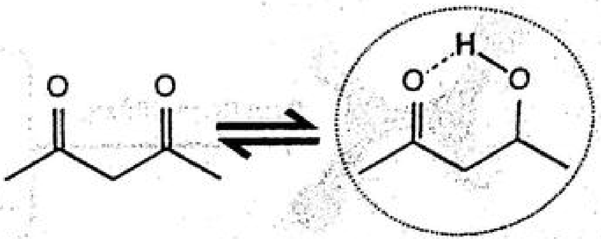


In some cases, Enol content can also become high



More stable due to **aromaticity** in case of phenol.

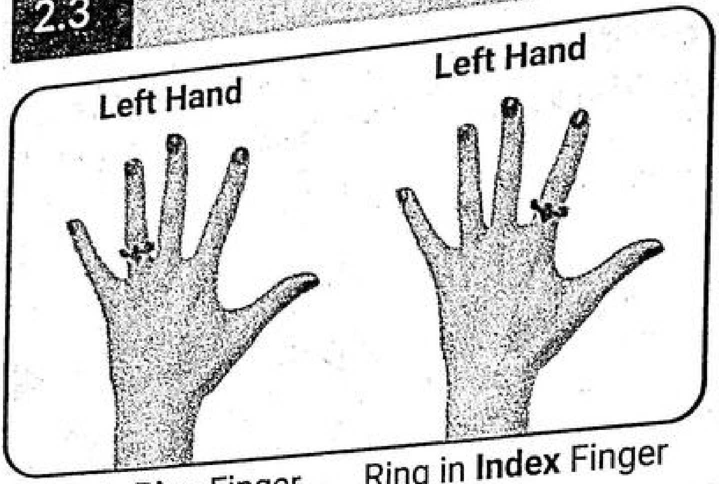
Enol can also be higher due to **intramolecular H-Bonding**



Order. of Enol-Content due to hydrogen bonding

β-diketo > Ket-aldehyde> β-Aldehyde > Di-ester > Ketone > aldehyde

2.3 Stereoisomerism

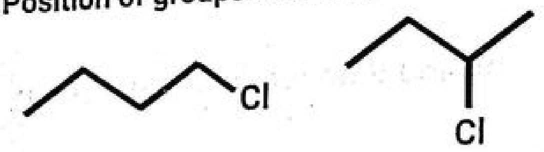


Ring in **Ring** Finger Ring in **Index** Finger

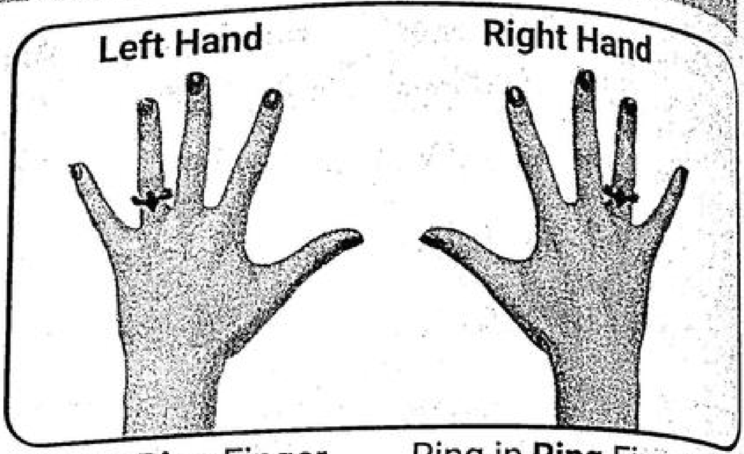
Rings in different fingers but same hand

This is Structural Isomerism

Position of groups different, Chain is same



Chlorine (Group) attached in different positions



Ring in **Ring** Finger Ring in **Ring** Finger

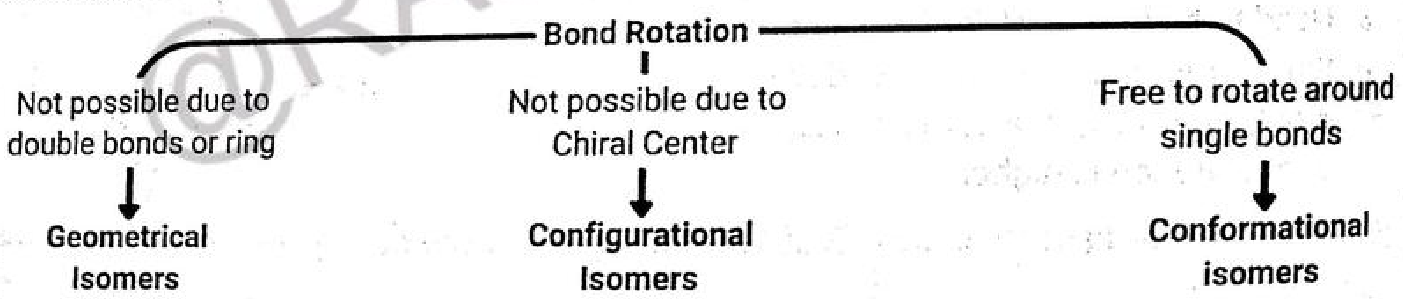
Rings in same finger but different hand in 3D

This is Stereoisomerism

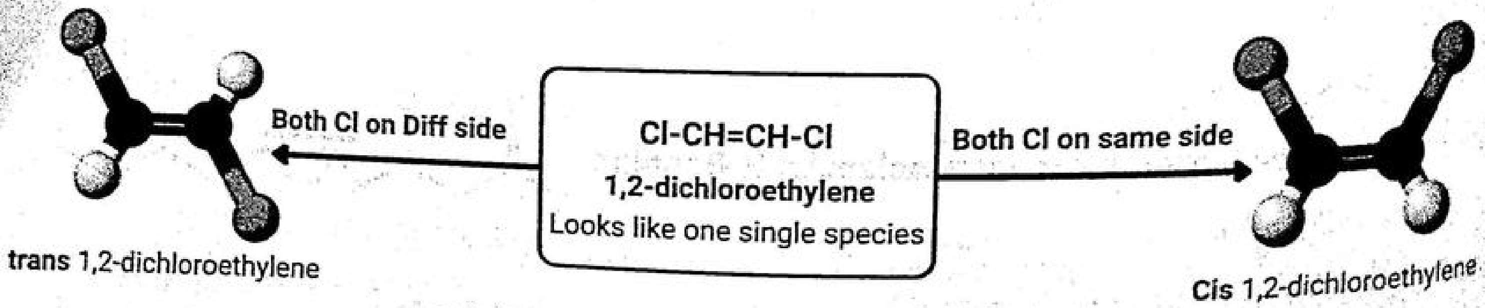
Position of groups Same, Species looks different in 3D

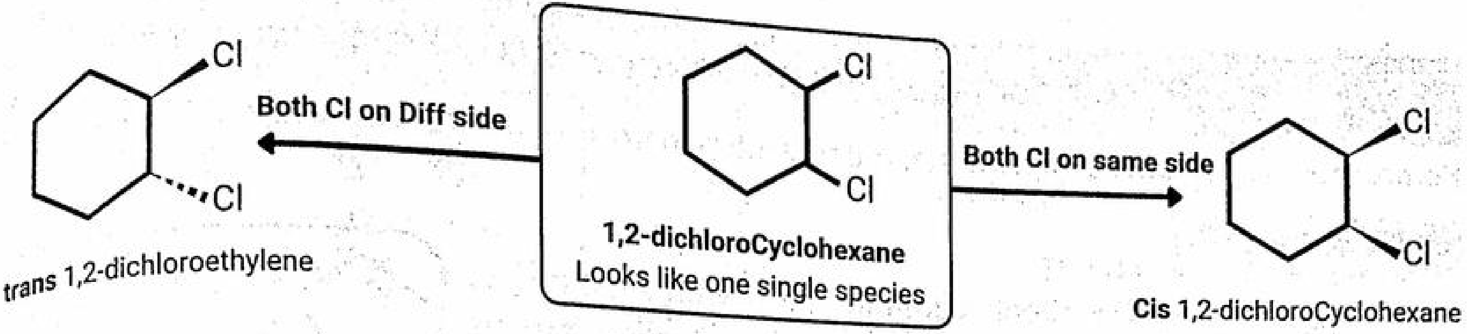
Chlorine (Group) attached in same position but arrangement is different in 3D

- Now the stereoisomerism is directly connected to bond rotation and thus we can categorise it in 3 subcatogories.



2.4 Geometrical isomerism





trans 1,2-dichloroethylene

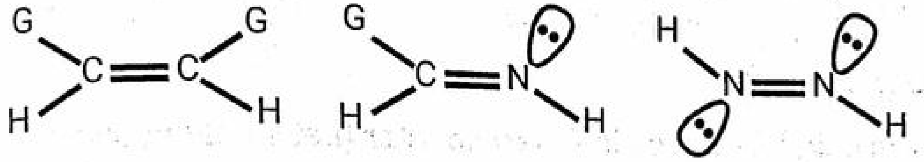
1,2-dichloroCyclohexane
Looks like one single species

Cis 1,2-dichloroCyclohexane

- **How to find geometrical isomers in a given compound?**

1. First find out whether the system given lies under the **Accepted** Double bond or ring system with bond rotation restriction

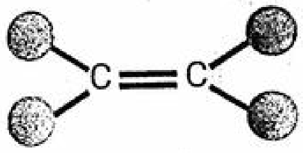
Accepted Double bond system



Accepted Ring System

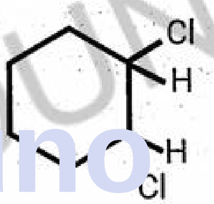
Any ring which is 3,4,5,6 membered with adjacent atoms being connected

2. After confirming above, Confirm whether on each side substituents are different

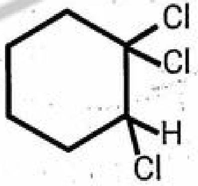


Shows G.I.

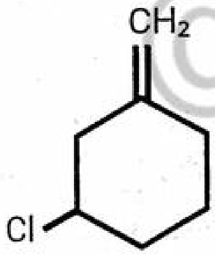
Doesn't show G.I.



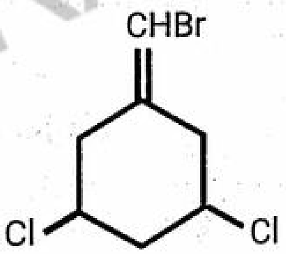
Shows G.I.



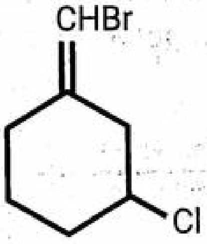
Doesn't show G.I.



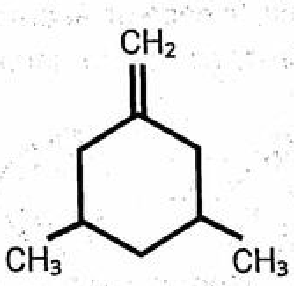
Doesn't show G.I.



Doesn't show G.I.



Shows G.I.



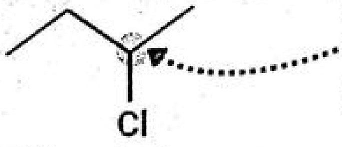
Doesn't show G.I.

IMPORTANT

2.5 Configurational Isomers (Enantiomers and Diastereomers)

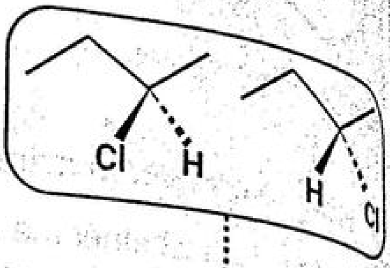
Before proceeding towards the configurational isomerism, we need to understand a few terms

CHIRAL CENTER



2-Chloro butane

Look carefully, the carbon marked is connected to 4 different atoms/groups (*Fourth being Hydrogen*).

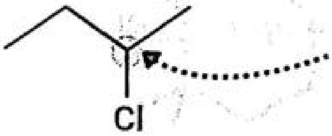


A center with 4 different groups attached leading to two or more different isomers is called **Chiral Center**

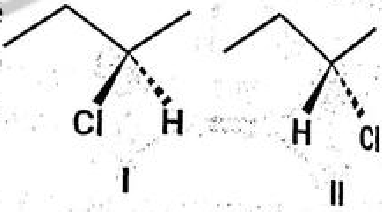
Formation of two different type of structures (3D Arrangements), due to a chiral center

but there is another term mixed with chiral Center called **Stereocenter** (Let's understand it)

STEREOCENTER

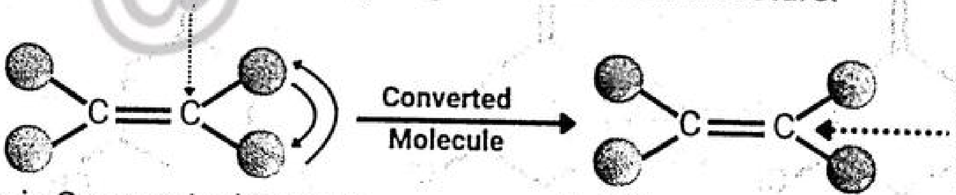


Since at this point (The chiral center) if the two groups (Cl and H are swapped), two different isomers appear. The center will be called a Stereocenter



But Remember, **All Chiral Centres are Stereocentres but all Stereocentres are not Chiral Centres**

Example, In case of Geometrical Isomers, this is a special spot in this molecule where, if you swap the atoms/groups around it, you get a whole new structure!



This is Geometrical Isomer

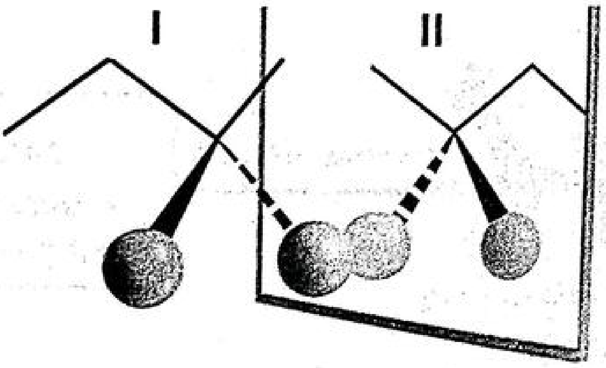
A different Compound

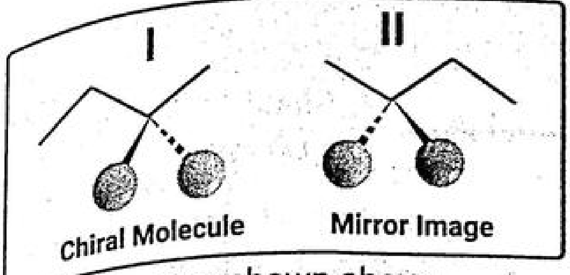
But this is **NOT** a Chiral Center since four different atoms are not connected

CHIRALITY

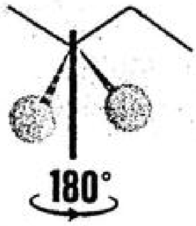
A chiral molecule can form two different versions (called isomers) that are like mirror images of each other and can only be changed into one another by swapping two atoms or groups.

Are these two molecules really not same? Let's Visualise.

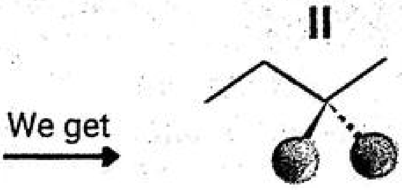




The ones shown above



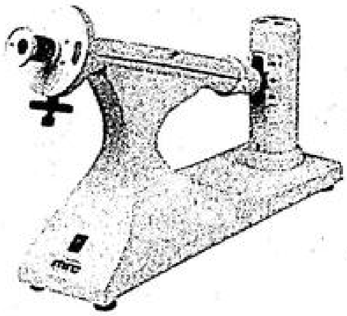
Rotating molecule II 180°



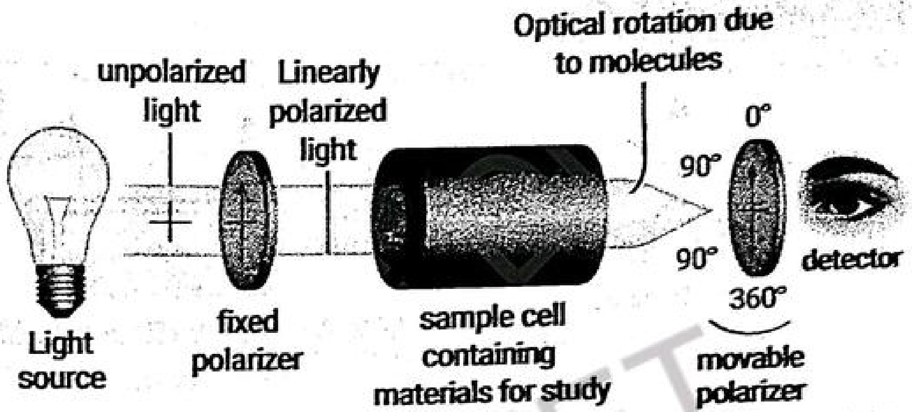
This is totally different from **molecule I** considering both atoms have different orientation

Also, **Chirality unpacks new property called optical activity, Let's Understand**

OPTICAL ACTIVITY

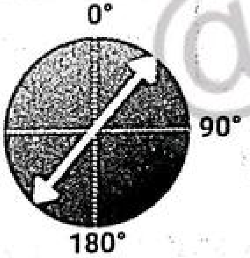


This is a polarimeter



Polarimeter has these stages of analysing the material in sample cell

- When the sample cell contains only water, the plane polarised light doesn't rotate
- When the sample cell contains a chiral molecule, the plane polarised light is rotate by some °
  - This means Chiral molecules are **Optically active.**
  - Mirror Images rotates Plane polarised light in exactly opposite directions.



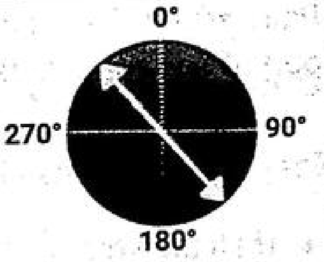
Rotates by +50°

Dextrototatory

Exactly **opposite** Rotation of Plane polarised light for Mirror Images

Rotates by -50°

Levorotatory



- Observed rotation α may vary with concentration and length, so we define specific rotation [α] as $[\alpha]_\lambda^T = \frac{\alpha}{l \times c}$

$$\text{Optical purity} = \frac{[\alpha]_{\text{mixture of + \& -}}}{[\alpha]_{\text{pure isomer (+/-)}}} \times 100$$

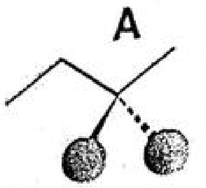
ENANTIOMERS

Atom (Especially Carbon) with 4 Different Atoms connected → Generates Chiral Molecule → A Chiral Molecule has Chirality

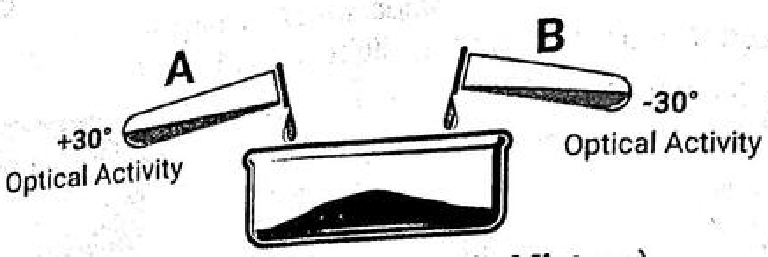
↓

Chirality Means there are two isomers which are optically Active → Those two isomers are nothing but **Enantiomers**

RACEMIC MIXTURE

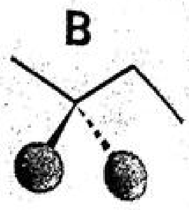


Chiral Molecule



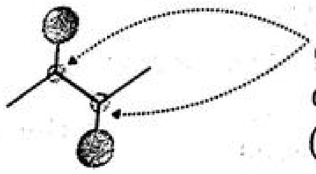
50% A + 50% B **(Racemic Mixture)**

Optically Inactive 0°

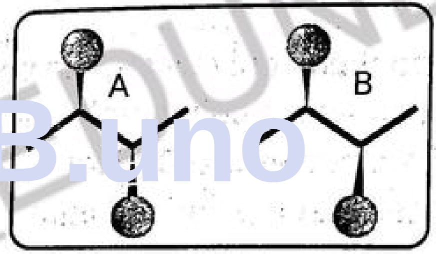


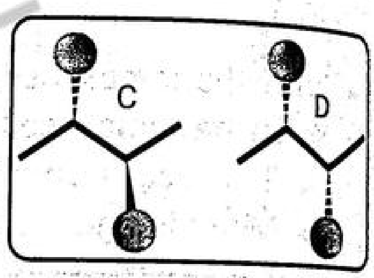
Mirror Image

DIASTEREOMERS - WHEN TWO CHIRAL CENTERS MEET



Two chiral centres can create 4 possible outcomes (Stereoisomers)





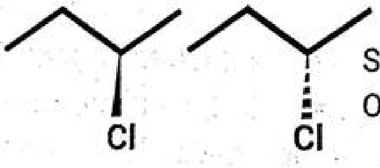
Pairs which are not mirror images but part of stereoisomers are Diastereomers.

- A & B are not mirror images
- C & D are not mirror images

} **Diastereomers**

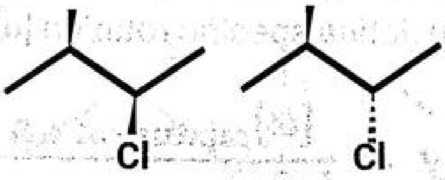
Easy trick to guess Enantiomers and Diastereomers just by viewing it

- If all the Wedge/dash changes on going from one stereoisomer to other as dash/wedge relationship is enantiomers.
- If either one or all except one wedge/dash changes, the relationship is diastereomers.



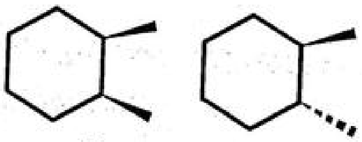
Enantiomers

Single Chiral Center
One Wedge other Dash



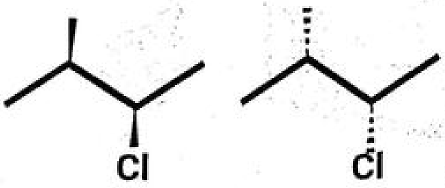
Diastereomers

Two Chiral Center
Only one wedge
changes to Dash



Diastereomers

Two Chiral Center
Only one wedge
changes to Dash



Enantiomers

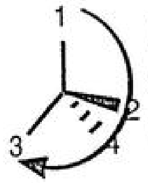
Two Chiral Center
Both wedge changes
to dash

2.6 Nomenclature to study before configurational isomers

The four compounds above (A, B, C, D) are the same molecule but with different 3D arrangements, making them tricky to name. We need a simple naming system to tell them apart based on their 3D structure.

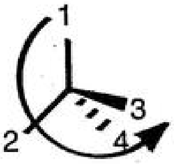
CIP RULES FOR R/S NOMECULATURE

1. **Find the Chiral Center** : Look for a carbon with four different groups, like in 2-chlorobutane (CH_3-CHCl-CH_2CH_3).
2. **Assign Priorities:**
   - **Atomic Number**: Highest atomic number gets priority 1, lowest gets 4. In 2-chlorobutane: Cl (1), H (4).
   - **Break Ties**: If tied (e.g., CH_3 vs. CH_2CH_3), check the next atoms. CH_2CH_3 (C, H, H) > CH_3 (H, H, H), so CH_2CH_3 (2), CH_3 (3).
   - **Multiple Bonds**: Double/triple bonds count as multiple atoms (e.g., C=O is like C bonded to two O's).
3. **Orient the Molecule**: Point the lowest priority (4, like H) away from you (use a Fischer projection if needed).
4. **Check the Order**: Look at 1 → 2 → 3:
   - Clockwise = **R** (right).
   - Counterclockwise = **S** (left).
   - Example: In 2-chlorobutane with H away, it Cl (1) → CH_2CH_3 (2) → CH_3 (3) is clockwise, it's R.
5. **If 4 Isn't Away** (but in front) : Find the order, then take the opposite.

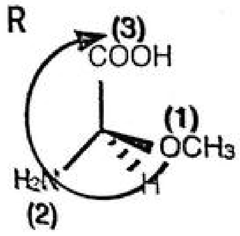


If curve arrow rotates **Clockwise: R**

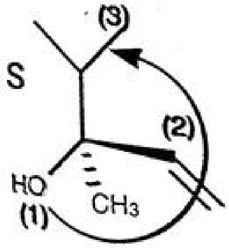
Priority Order :
I > Br > Cl > SO_3H > SH > F > OR > OH > NO_2> NR_2 > COOR > COOH > RCOR > RCHO > ROH > CN > Ph > T > D > H



If curve arrow rotates **Anticlockwise: S**



- OCH_3 > NR_2 > COOH > H {*Atomic number are O > N > C > H*}
  - 4th group is at the dash
- The arrow shows a clockwise direction : **R**

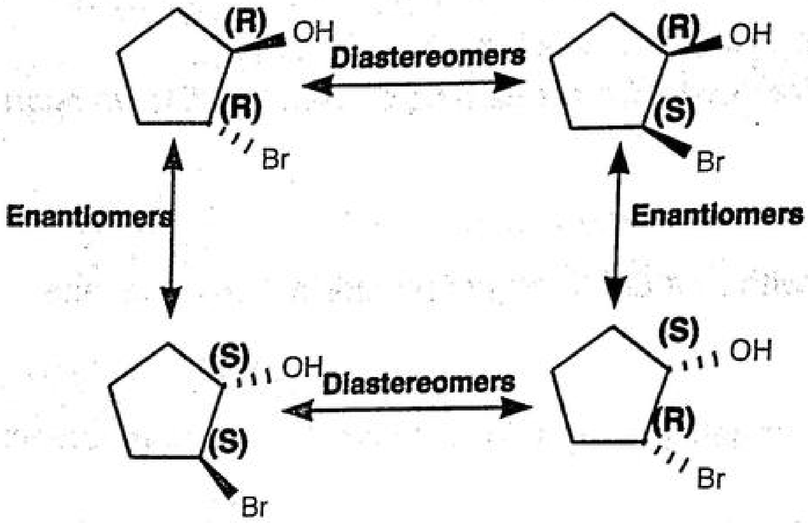


- OH > CH=CH_2 > CH_3(CH)CH_3 > CH_3
  - OH (O, atomic number 8) → 1
  - CH=CH_2 (double bond counts as C, C, H) → 2
  - $CH(CH_3)_2$ (C, bonded to C, C, H) → 3
  - CH_3 (C, bonded to H, H, H) → 4

IMPORTANT

Double bond has higher priority than Isopropyl

Easy trick to guess Enantiomers and Diastereomers using R/S

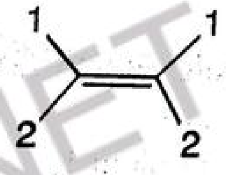


- If all the configuration changes on going from one stereoisomer to other relationship is **enantiomers.**
- If either one or all except one configuration changes, the relationship is **diastereomers.**

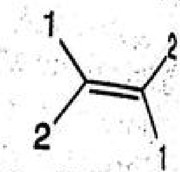
2.7 E/Z Nomenclature for Double bonds

Mark a line in between Alkene and Prioritise the right-handed and left-handed atoms as 1,2 according to atomic numbers.

- If Priority 1 lay on same side, Configuration: Z
- If laying on opposite side, Configuration: E



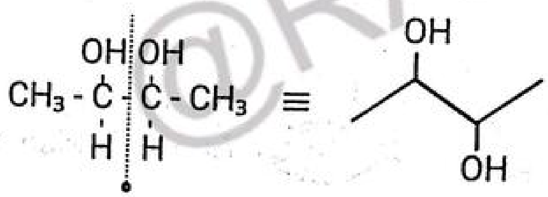
Configuration: **Z**



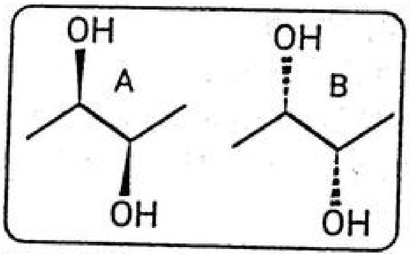
Configuration: E

2.8 Meso compound : POS changes outcome

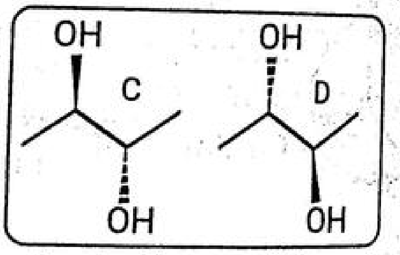
- Let's Imagine a compound : 2,3-Hydroxybutane, Which has two chiral centers.
  - 2 chiral center means it will have 4 possible stereoisomers, but will it have 4?



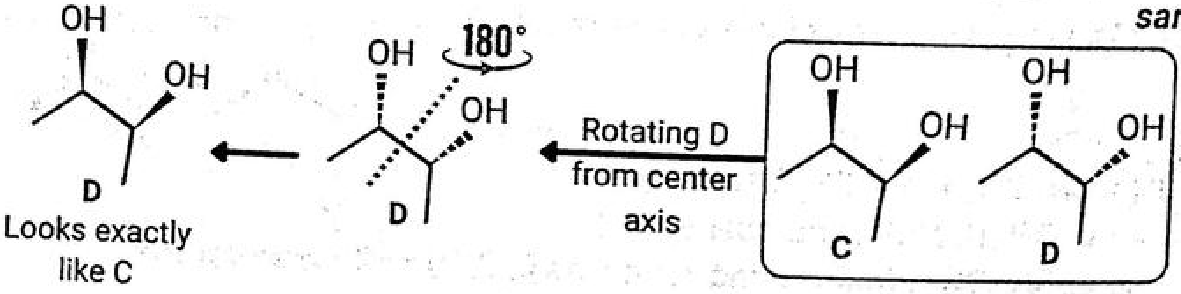
Plane of Symmetry



Two different compounds
Enantiomers



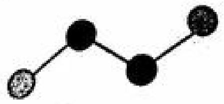
Looks like two different compounds but are same compounds



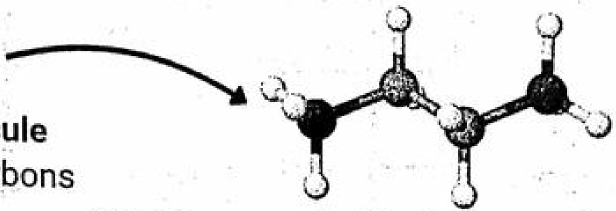
Rotating right side of the molecule

- If a compound has a plane of symmetry (POS), it can form a meso compound, which looks the same as its mirror image. Even though it has chiral centers, we treat it as a single compound, not two different ones
- **Meso compounds are optically Inactive**

2.9 Fischer, Newman and Saw horse Projection



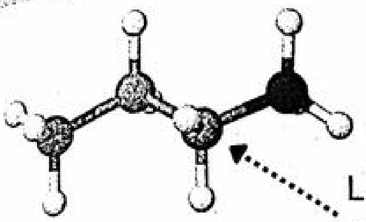
Normal Butane Molecule
All Colors represent Carbons



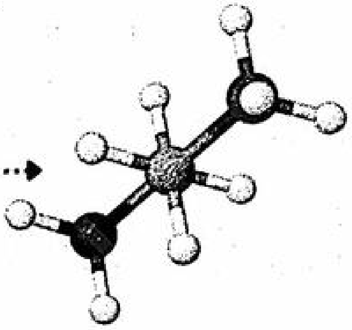
Now focus on the black/grey Carbons

Normal view of a molecule in Zig Zag

NEW MAN PROJECTION



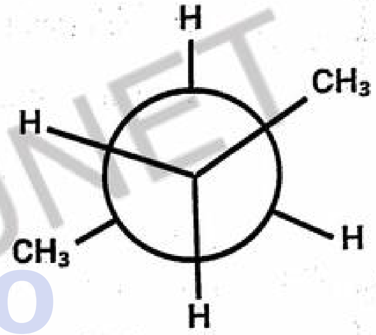
Look here like you are looking C-C black grey bond in middle



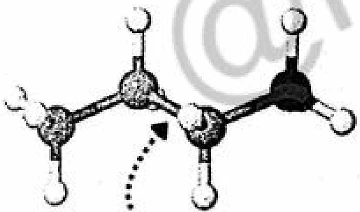
It will look something like this

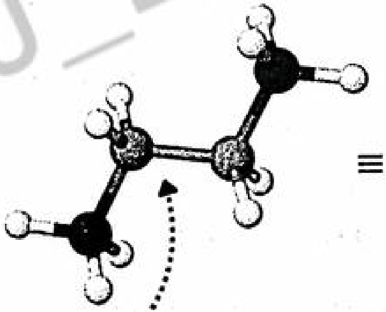
- Newman Projection is a way of looking at a C–C bond so that you don't see the bond itself, but only the atoms attached to the front and back carbon.
- It can be represented by a circle in front and bonds coming out of it.

≡

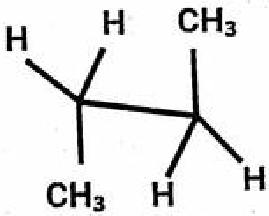


SAW HORSE PROJECTION





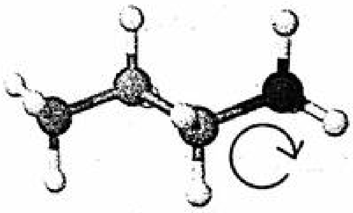
≡



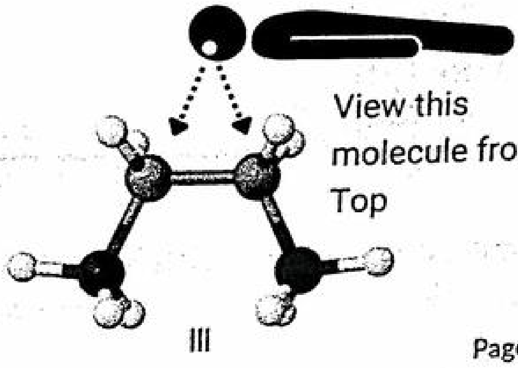
Look directly on the bond now

- Sawhorse projection is a way of showing a molecule by looking at the C–C bond from an angle, so you can see both carbon atoms and all the atoms attached to them clearly.

FISCHER PROJECTION



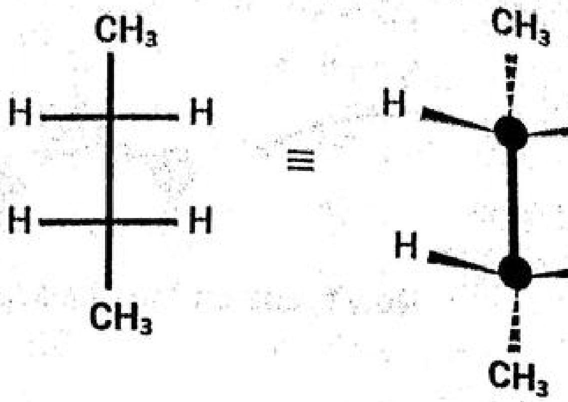
Rotate this molecule such that the groups come on the same side



View this molecule from Top

It can be represented as this

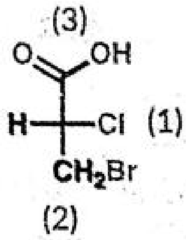
1. Dash molecules on vertical line
2. Wedge molecule on horizontal line



It will appear like this

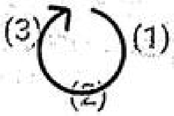
Determining R/S Configuration in Fischer Projection

Same rules apply except, here the #4 priority group should be in the vertical position (Which is actually Dash line), If #4 priority group is on horizontal line, Reverse the configuration



Cl> CH_2Br > COOH

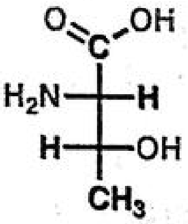
Br has higher atomic number than O



Clock wise rotation

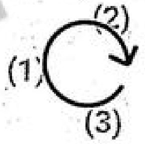
Should be R

But since, the #4 group is on horizontal line, **The configuration changes to S**



Centre 1 : NH_2 > COOH > C(OH)(CH_3) > H

N has higher atomic number than C



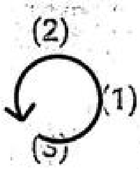
Clock wise rotation

Should be R

But since, the #4 group is on horizontal line, **The configuration changes to S**

Centre 2 : OH > *C(NH_2)(COOH)(H)* > CH_3 > H

N has higher atomic number than C



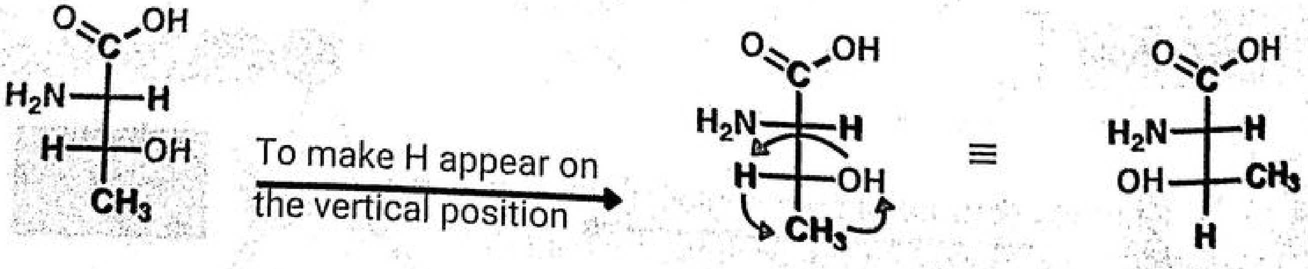
Anticlock wise rotation

Should be S

But since, the #4 group is on horizontal line, **The configuration changes to R**

To determine enantiomers and Diastereomers in Fischer projection, Remember to find out R/S Configuration and apply the trick you learned above

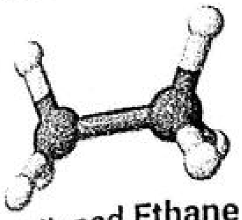
Remember : To change the position of an atom in Fischer projection, you need to rotate all the atoms on that chiral center.



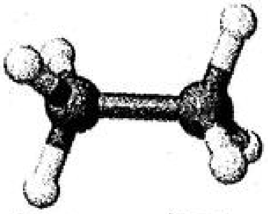
Never change position of only two atoms as it will change the configuration and make a different molecule

2.10 Conformational Isomers

Conformational isomers (or conformers) are different forms of the same molecule that can be changed into one another by just rotating around a single bond.



Eclipsed Ethane
Highest Energy due to H-H Repulsions



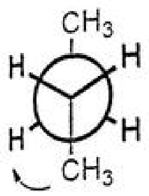
Staggered Ethane
Lowest Energy due to no H-H Repulsions

When the C-C bond in ethane rotates, it can form many different shapes. Each shape has a different angle and a different amount of energy. Out of all these shapes, there are two main ones:

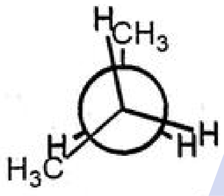
- **Staggered** – this is the most stable
- **Eclipsed** – this is the least stable

All the conformations between Staggered and eclipsed are called ***SKEW*** *conformations*

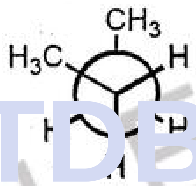
- **Torsional Strain :** Strain due to repulsion of electrons
- **Van der Waals Strain** : Strain due to bulky groups like alkyl
  - The Torsional and Vanderwaal strain is high in case of eclipsed structured thus, Staggered > Eclipsed.



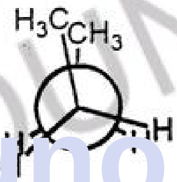
A
staggered
anti



B
eclipsed
anticlinal



C
staggered
gauche



D
eclipsed
synperiplanar

- **Stability order** : Antiperiplanar > Gauche > Anticlinical > Syn Periplanar
- Gauche becomes more stable in case of *H-bonding involvement.*
  - e.g. 2-Fluoroethanol, gauche is more stable
- Other cases for G-CH_2-CH_2-OH, where Gauche is more stable is when G = -OH, -NH_2, -NR_2, -CHO, -COOH.

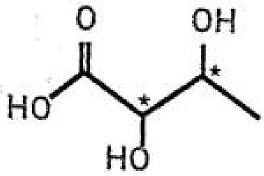
2.11 Total number of stereoisomers

Molecules without POS	Molecules with POS	
n even or odd	n odd	n even
2^n d/l forms, no meso forms	2^{n-1} Total forms	$2^{n-1} + 2^{\left(\frac{n}{2}\right)-1}$ d/l forms Meso forms

n = number of Chiral Centers

Remember, when double bonds are present in addition to Chiral centers, total stereoisomers increases due to Geometrical isomerism + Optical isomerism

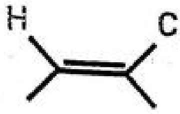
①



- No. of Chiral Centers : 2
- Plane of Symmetry : Absent
- Formula applied : 2^n

Total : $2^2 = 4$

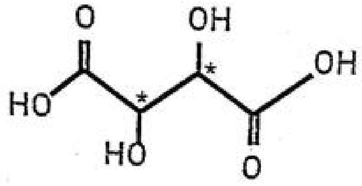
②



- No. of Stereo Centers : 1
- Plane of Symmetry : Absent
- Formula applied : 2^n

Total : 2

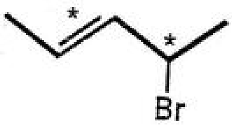
③



- No. of Chiral Centers : 2
- Plane of Symmetry : Present
- Formula applied : $\underbrace{2^{n-1}}_{\text{d/l forms}} + \underbrace{2^{\left(\frac{n}{2}\right)-1}}_{\text{Meso forms}}$

Total : $2^{2-1} + 2^0 = \underbrace{2}_{\text{d/l forms}} + \underbrace{1}_{\text{Meso forms}}$

④



- No. of Stereo Centers : 1(Double bond) + 1(Chiral Centere) = 2
- Plane of Symmetry : Absent
- Formula applied : $2^n \times 2^d$

Total : $2^1 \times 2^1 = 4$

⑤ $CH_3-\overset{*}{C}H(OH)-\overset{*}{C}H=CH-\overset{*}{C}H(CH_3)-Cl$

IMPORTANT

- No. of Stereo Centers : 1(Double bond) + 2(Chiral Centere) = 3
- Plane of Symmetry : Absent
- Formula applied : $2^n \times 2^d$

Total : $2^2 \times 2^1 = 8$

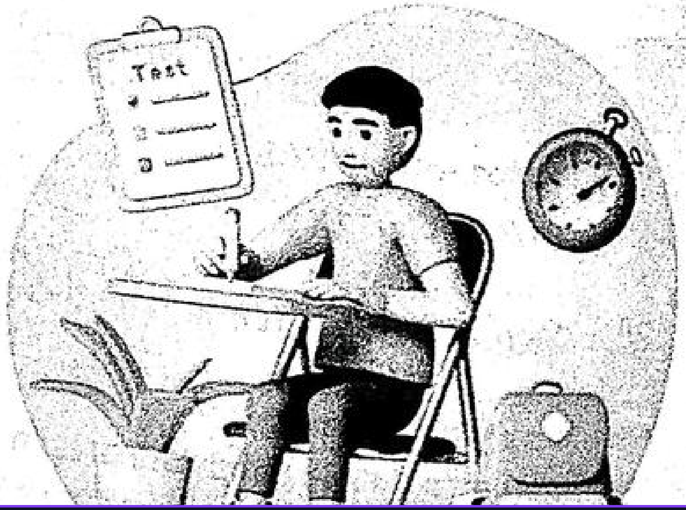
⑥ $Cl-\overset{*}{C}H(Ph)-\overset{*}{C}H(Ph)-Cl$

- No. of Stereo Centers : 2(Chiral Centere)
- Plane of Symmetry : Absent
- Formula applied : $\underbrace{2^{n-1}}_{\text{d/l forms}} + \underbrace{2^{\left(\frac{n}{2}\right)-1}}_{\text{Meso forms}}$

Total : $2^{2-1} + 2^0 = \underbrace{2}_{\text{d/l forms}} + \underbrace{1}_{\text{Meso forms}}$

Types of Questions in Exam

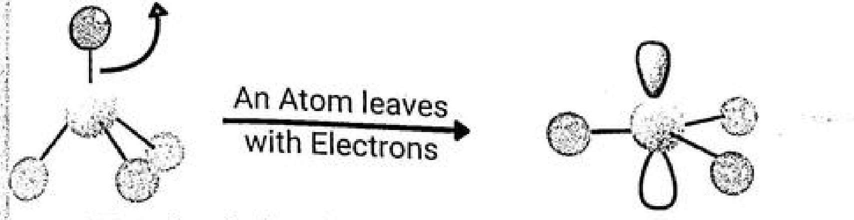
- **Molecules with no POS (NO MESO)**
  - Only chiral centres
  - Chiral centres + Double bonds
- **Molecules with POS (MESO Present)**
  - Only **even** Chiral Centre
  - Only **odd** Chiral Centre



Step Towards Organic 4

Reactive Intermediates

1 Carbocation - The deficiency is killing it

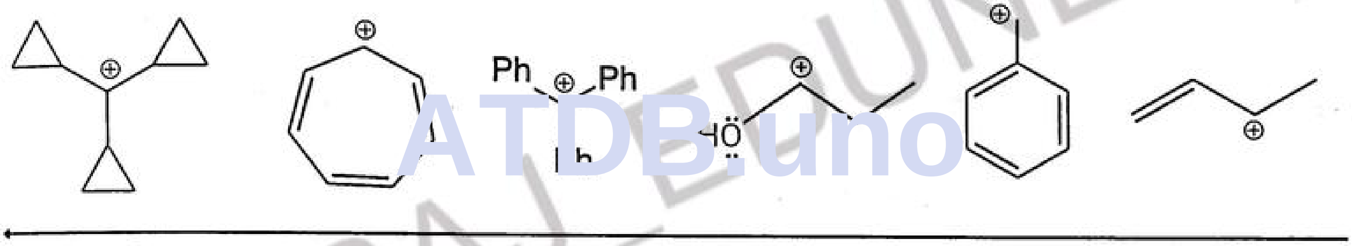


Normal Tetrahedral molecule
One atom leaving with electrons

State of Carbon with a
deficiency of electrons

- **Electrons** : 6
- **Shape** : Trigonal Planar, sp²
- **Special features**
  - Vacant p Orbital which shows carbocation
  - Nucleophile can attack either from above or below

1.1 Stability of Carbocations - Anything that gives electrons



Dancing Resonance

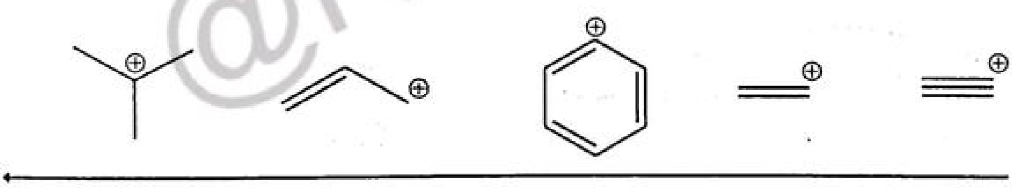
Aromaticity

High Resonance
3 Ph Attached

Mesomeric
Adjacent L.P.

Resonance
1 Ph

Resonance
One double bond
2° Carbocation



Hyperconjugation
9 α-Hydrogens

Resonance
One double bond
1° Carbocation

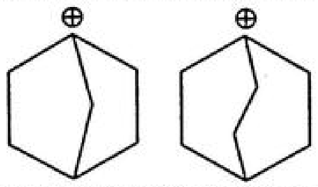
Unstable sp Carbocations
Directly attached to unsaturated carbons

IMPORTANT

- sp-hybridized carbocations are highly unstable due to their linear geometry, which prevents proper orbital overlap for stabilization.

The Ultimate Stability Order	Dancing Resonance > Aromaticity > Mesomeric > Equivalent Resonance > Regular Resonance > Hyperconjugation > Inductive > S-character

Only carbocation which can never be stable

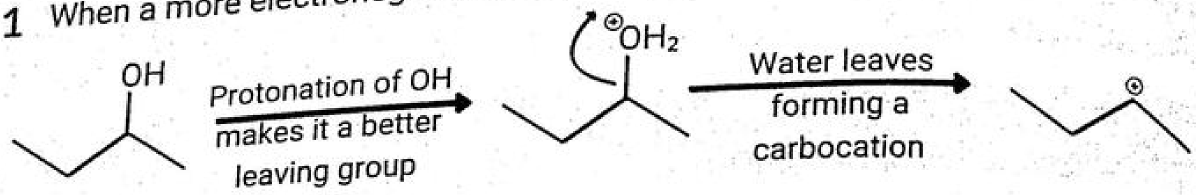


Bridgehead carbocations are not stable due to non planarity
Unstable Carbocations

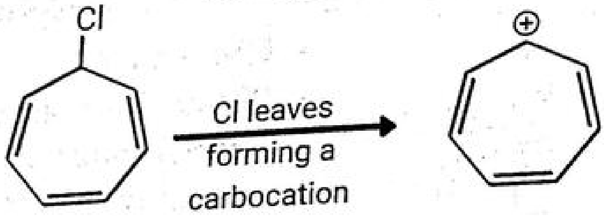
1.2 How are carbocations formed

Method 1 When a more electronegative group leaves with its lone pair of electrons

Reaction A



Reaction B

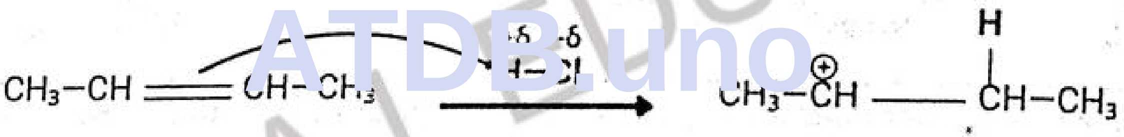


Points to note :

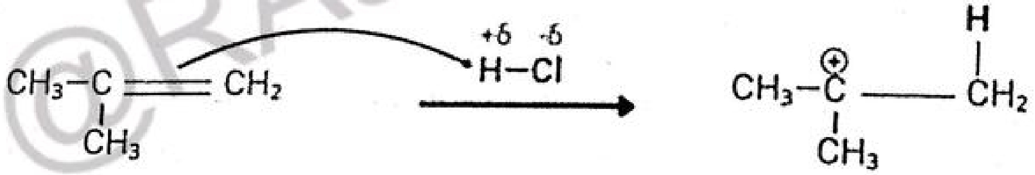
- +ve charge on O doesn't mean it is deficient of electrons. (Oxygen donates a lone pair to H^+)
    - Water is a better leaving group than OH
- Reaction B is faster than Reaction A, since the carbocation formed in B is more stable due to aromaticity

Method 2 When a double bond gets influenced by external species (Electrophile)

Reaction A



Reaction B



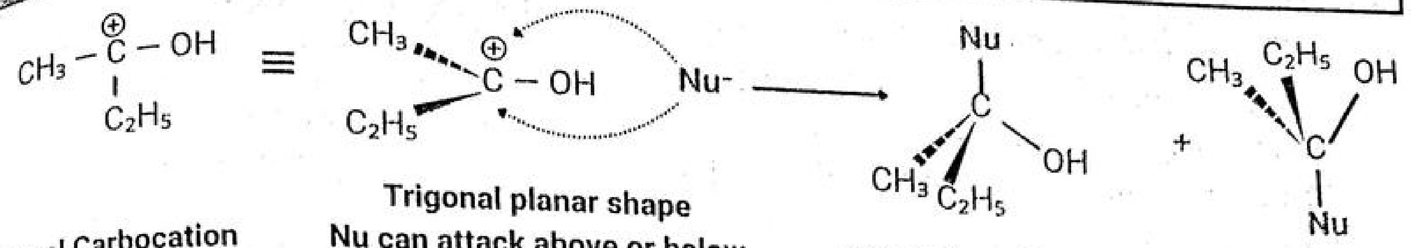
Points to note :

- Double bond is neutral and only forms a carbocation in the presence of an electrophile
- Carbocation is formed on the place where it is more stable.
- Reaction B happens faster than A since more stable carbocation is being formed.

1.3 What do carbocations do after they are formed?

- They can proceed only doing 4 types of reactions
    a. Attack of Nucleophile
    b. Elimination of Hydrogen from nearest carbon to form double bond
    c. Rearrangement due to Hydride or Alkyl Shift
    d. Ring Expansion or Contraction

1.3a Nucleophilic attack on Carbocation



Normal Carbocation

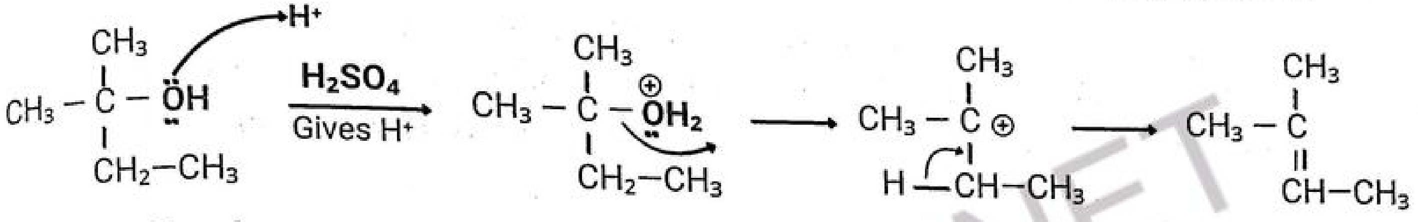
Trigonal planar shape
Nu can attack above or below

Attack from above

Attack from below

1.3b Elimination of Hydrogen from Nearest carbon

If no nucleophile is around, the carbocation often loses a hydrogen and forms a double bond. This usually happens in acid-catalyzed reactions, like when alcohols lose water (dehydration).



Protonation of alcoholic OH

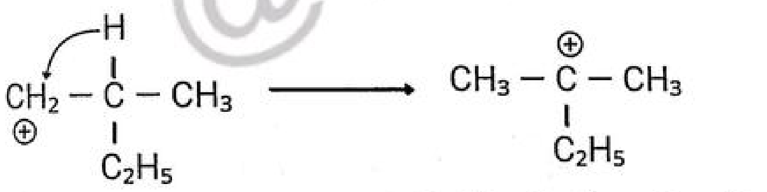
Water leaves forming a carbocation

No Nucleophile present,
H Leaves forming a double bond

1.3c Rearrangement due to hydride and Alkyl shift

Before reacting, carbocations often rearrange to become more stable.
Only after that, they go for nucleophilic attack or elimination to form a double bond.

HYDRIDE SHIFT



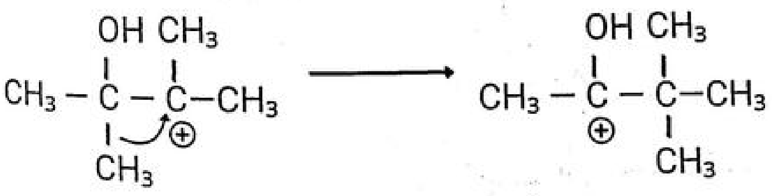
Normal Carbocation A
Undergoes Hydride shift

Stable Carbocation B
No further rearrangments

Why is B more stable?

- 3° carbocation compared to 1° in A
- More Hyperconjugation effect

ALKYL SHIFT



Stable 3° Carbocation A
Undergoes Alkyl shift

More stable Carbocation B
No further rearrangments

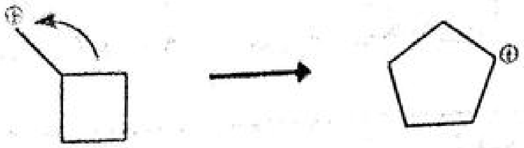
Why is B more stable?

- Adjacent OH group donates lone pairs to stabilize via the mesomeric effect

1.3d Ring Expansion or Contraction

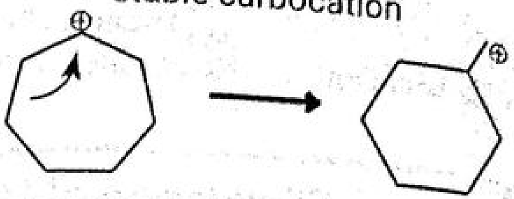
Ring Expansion (More Common)

Happens when a small ring (like 3 or 4 membered) opens up or becomes a bigger ring (like 5 or 6 membered)



Ring Contraction (Less Common)

Happens when a carbocation rearranges and a smaller ring is formed that results in a more stable carbocation



1.4 Rearrangements due to Carbocations (Higher level)

We have already studied the type of rearrangements but still need to cover the advanced part of it.

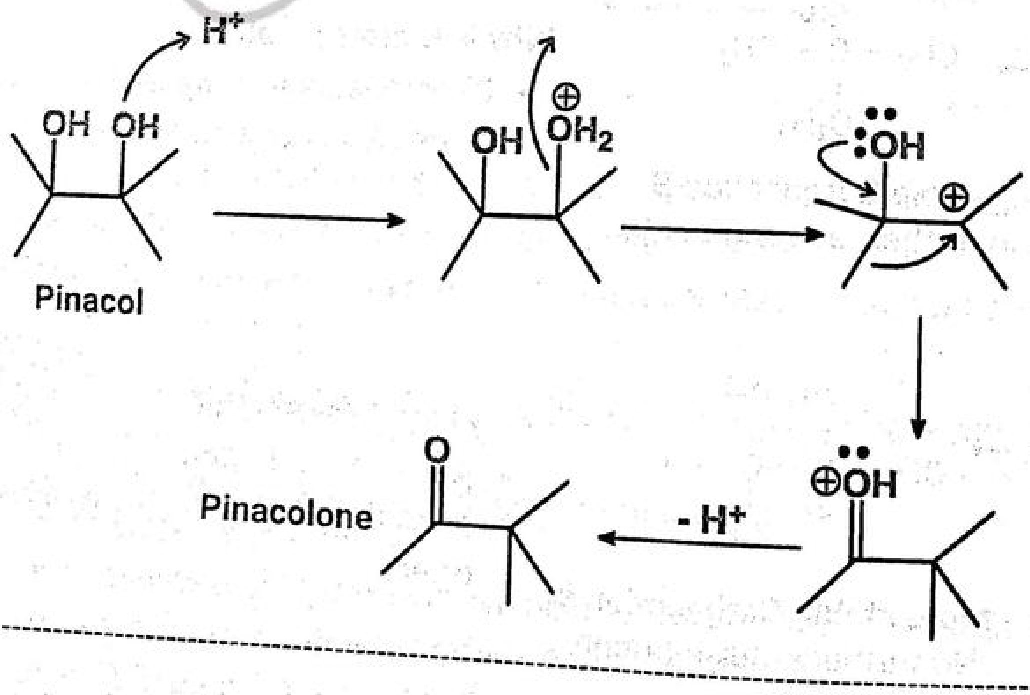
Note: Formation of a More Stable Carbocation is the reason for the carbocation to undergo rearrangement. Here are some common conditions that lead to rearrangements.

- Primary → Secondary
- Secondary → Tertiary
- Allylic → More Resonance-stabilized
- Benzylic → More delocalized system
- Ring strain relief (expansion from 4-membered to 5/6

☑ *Golden Rule: Carbocations rearrange if the new carbocation is more stable due to inductive effects, hyperconjugation, or resonance.*

One of the most important rearrangements is the **Pinacol-Pinacolone Rearrangement**

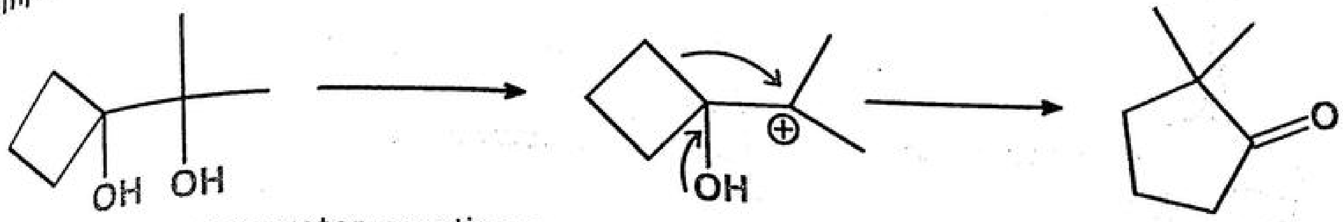
Pinacol-Pinacolone



A vicinal diol (Pinacol) on heating with acid rearranges to form a ketone (Pinacolone) via methyl shift and a carbocation intermediate.

NAME 1 REACTION

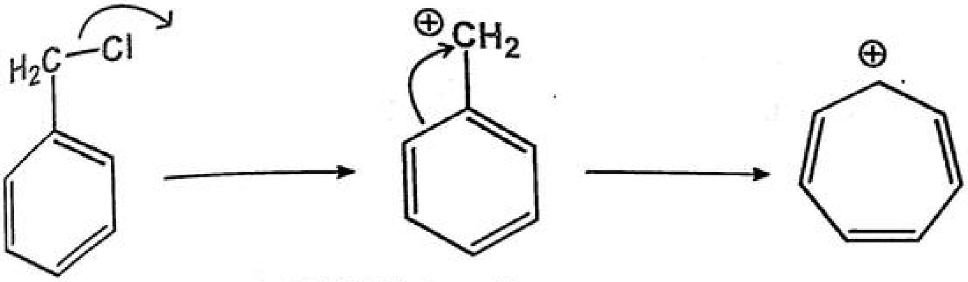
Important Example – Pinacol-Pinacolone



Acid removes water, creating a carbocation

Rearrangement to form 5 membered ring

Other cases where carbocation rearrangement is observed



Chlorine leaves to form a stable benzyl Carbocation

It rearranges to form a more stable tropylium cation

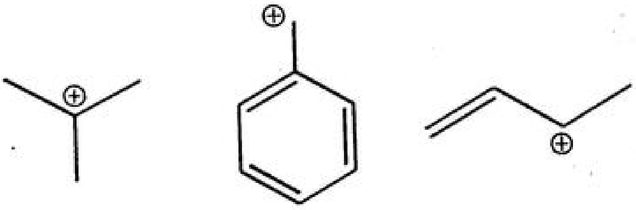
Benzene is also aromatic but rearrangement happens because Tropylium cation is more stable due to delocalization over seven carbons, compared to six in benzene.

1.5 Types of Carbocations (Advanced)

Classical Carbocation

A classical carbocation is the "normal" carbocation you've studied so far:

- Carbon atom holds a positive charge
- Has sp² hybridization
- Has an empty p-orbital
- Charge is localized on one carbon



In all the examples above, the Positive charge is located at a Single carbon, One at a time

Structure: Planar (trigonal)

Stabilized by: Hyperconjugation, resonance, inductive effect

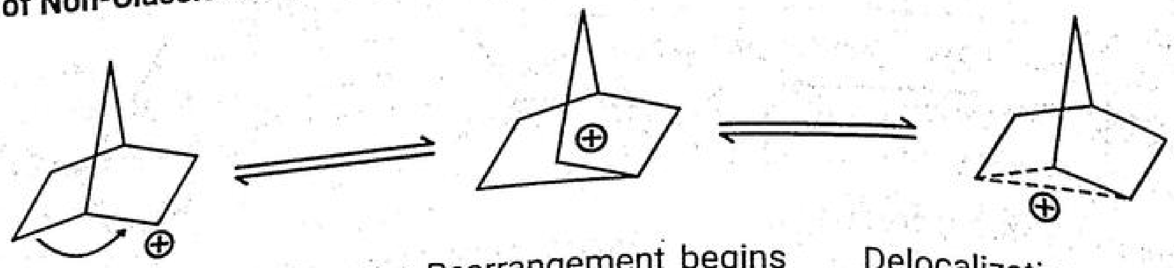
Non-Classical Carbocation

- A non-classical carbocation is one in which the positive charge is delocalized over more than one carbon atom using bridging orbitals.
- Electrons from adjacent σ-bonds or π-bonds delocalize to stabilize the cation
- 3-center, 2-electron bond is formed (banana bond)
- It's like a hybrid of multiple classical structures

Structure: Not strictly planar; can be bridged or cyclic

Stabilized by: Charge delocalization via orbital overlap (not just hyperconjugation)

Example of Non-Classical Carbocation

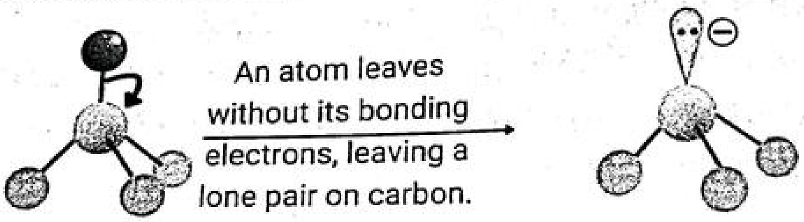


The initial carbocation is formed on the bridgehead carbon in a norbornyl system, which is unstable in classical form.

Rearrangement begins as adjacent C–C σ bond overlaps with empty p-orbital.

Delocalization via 3-center 2-electron bond across the bridge → formation of non-classical carbocation.

2. Carbanion – Too many electrons cause instability



An atom leaves without its bonding electrons, leaving a lone pair on carbon.

Normal Tetrahedral molecule

Carbon has a complete octet but lacks one bond, giving it a negative charge.

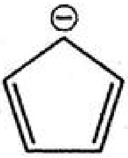
- **Electrons** : 8
- **Shape** : Pyramidal, sp^3
- **Special features**
  - Lone pairs are present in sp^3 orbital
  - The hybridisation changes to sp^2, if it is in conjugation.

2.1 Stability of Carbanions - Anything that takes away electrons

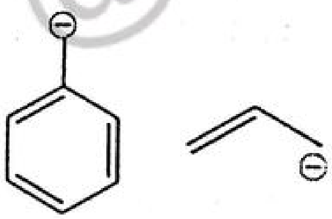
Factors : Aromaticity > Resonance > Back bonding > S-character > Inductive

Stabilised by : - Effects like -M > -H > -I

IMPORTANT



Aromaticity



Resonance

$\overset{\ominus}{C}H_2-NO_2$

-M effect

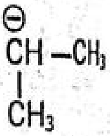
$\overset{\ominus}{C}H_2-Cl$

-I effect

s-character

$\overset{\ominus}{C}H_3$

Methyl anion



$\overset{\ominus}{C}H(CH_3)-CH_3$

2° Anion

2.2 How are Carbanions formed in Organic Chemistry?

There are two main ways to form a carbanion in organic chemistry:

1. Removal of a leaving group in such a way that the bonding electrons stay on the carbon.
2. Use Grignard reagents or similar organometallic compounds where carbon behaves like a carbanion due to its nucleophilic nature.

Meth ydrogen (H^+), leaving electrons on carbon

Reaction A $CH_3-NO_2 + OH^- \rightarrow \overset{\ominus}{C}H_2-NO_2 + H_2O$

Reaction B $NO_2-CH_2-NO_2 + OH^- \rightarrow NO_2-\overset{\ominus}{C}H_2-NO_2 + H_2O$

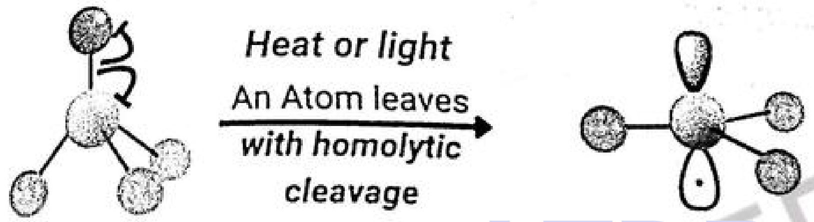
Points to note :

- OH^- acts as a strong base
- The carbanion is stabilized by the −M (mesomeric) effect of the NO_2 group
- Reaction B is faster than A due to the more stable carbanion.

Method 2 When carbon is connected to Organometallic Reagents (Grignard / Organolithium)

CH_3-MgBr is actually CH_3^- $MgBr^+$ *the bond is polar covalent, not ionic in reality.*

3. Free Radicals - Odd-Electron Species



Normal Tetrahedral molecule

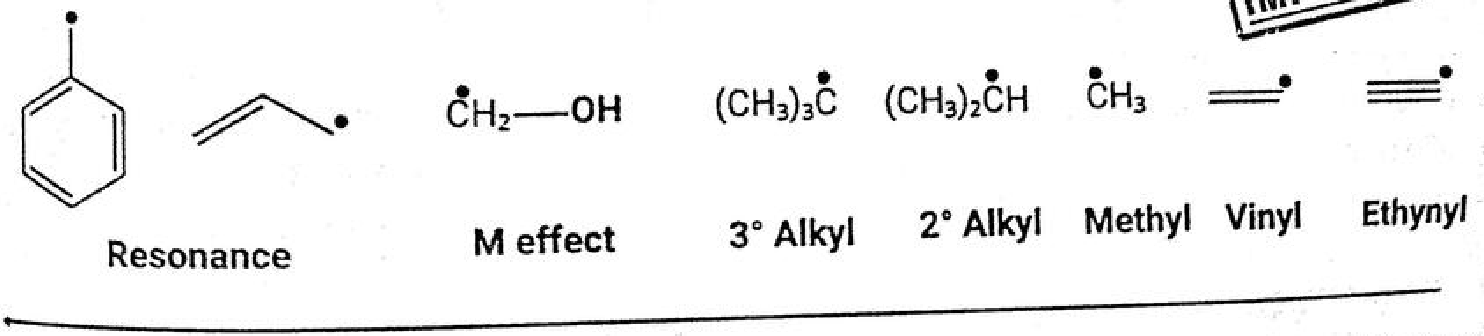
State of Carbon with an odd number of electrons, making it electron-deficient

- **Electrons:** 7
- **Shape:** Trigonal Planar or Slightly Bent, sp^2
- **Special features:**
  - Contains one unpaired electron in a p orbital
  - Can react with radicals, electrophiles, or nucleophiles

3.1 Stability of Free Radicals - Anything that delocalises

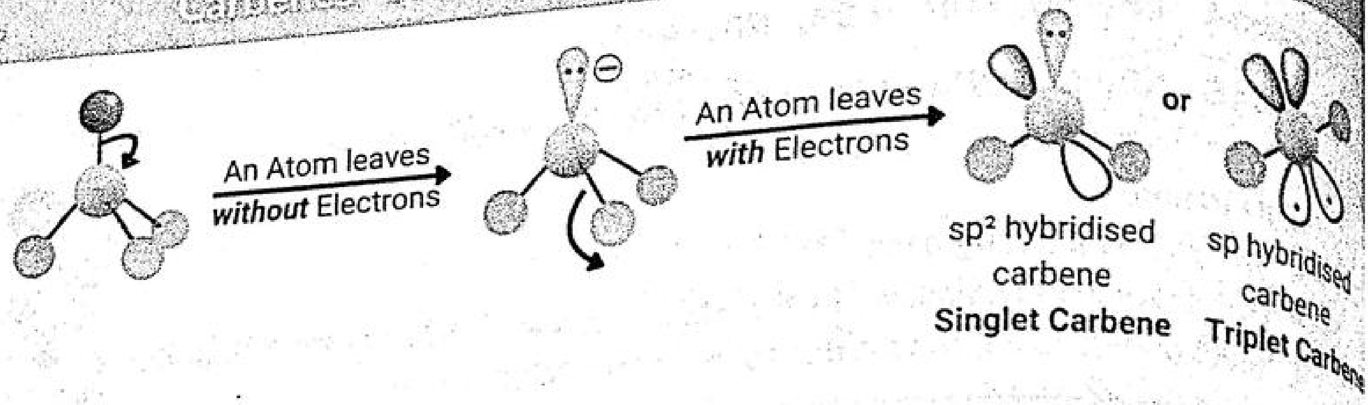
The Ultimate Stability Order	Benzylic > Allylic > Lone pair adjacent (Mesomeric) > 3° Alkyl > 2° Alkyl > 1° Alkyl > Methyl > Vinyl (sp^2) > Ethynyl (sp)

IMPORTANT



Radicals in Organic chemistry are formed by homolytic bond cleavage, usually initiated by heat, light, or radical initiators (like peroxides)

4. Carbenes - A Unique Type of Elec



4.1 How are Carbenes formed in Organic Chemistry?

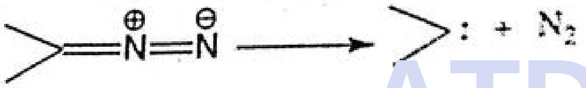
Method 1 Base-Induced Alpha-Elimination

$$CHCl_3 \xrightarrow{NaOH} {}^{-}CCl_3 \xrightarrow[-Cl]{} :CCl_2$$

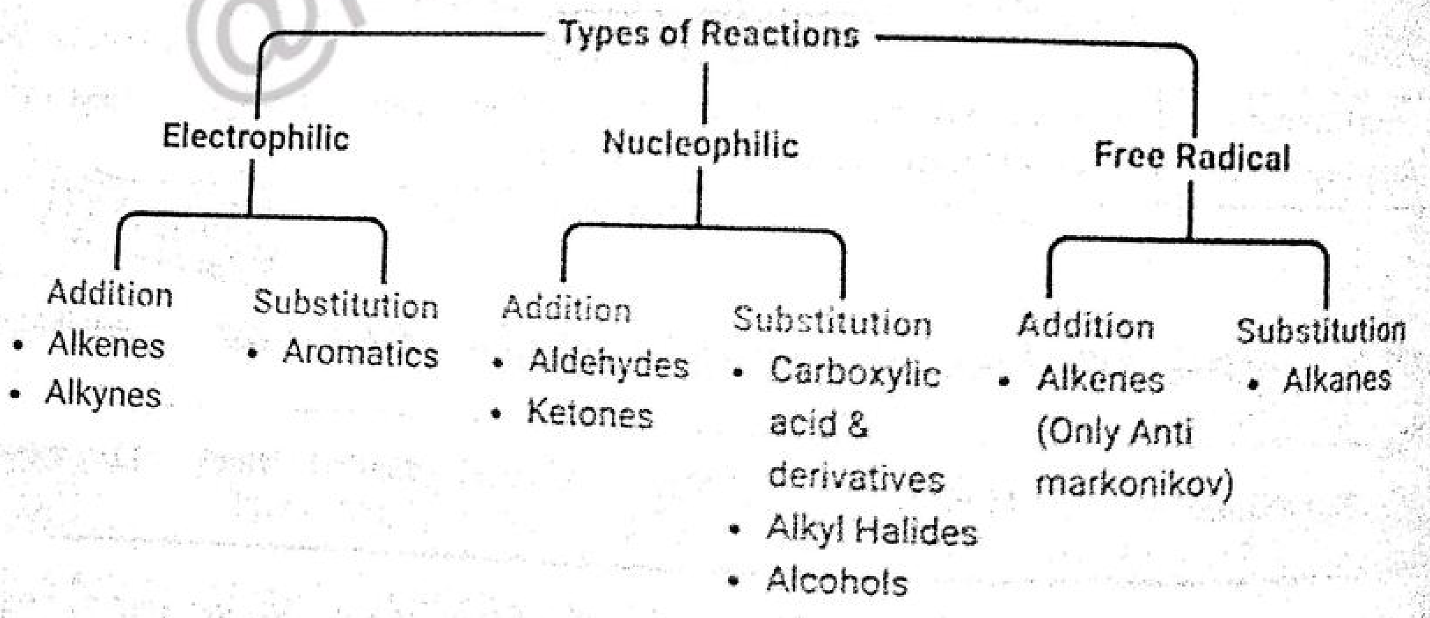
dichlorocarbene

Dichlorocarbene (:CCl₂) is formed via alpha-elimination.

Method 2 Thermal or Photochemical Decomposition of Diazo Compounds



Types of Reactions Commonly Encountered in Organic Chemistry



Electrophilic
- Addition
  - Alkenes
  - Alkynes
- Substitution
  - Aromatics

Nucleophilic
- Addition
  - Aldehydes
  - Ketones
- Substitution
  - Carboxylic acid & derivatives
  - Alkyl Halides
  - Alcohols

Free Radical
- Addition
  - Alkenes (Only Anti markonikov)
- Substitution
  - Alkanes

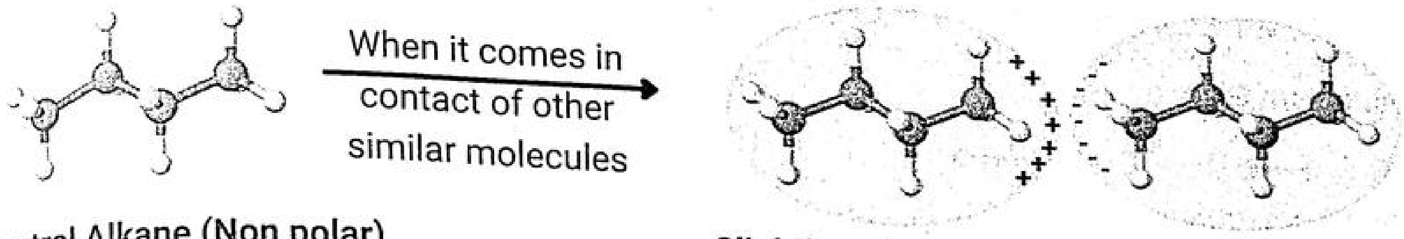
Other Types of Reactions: **Elimination & Rearrangement** (will be covered during the course)

Step Towards Organic 5

Alkanes - Start of Reaction Mechanism

Alkanes are less reactive than alkenes and alkynes. Why?

- **C-C (sigma)** bond energy is around 348 kJ/mol, and **C-H bond** energy is 412 kJ/mol.
- The bonds are non-polar in nature, so there are no charges to initiate the reaction.
- They do not contain electronegative elements (like N, O, or F) to help initiate reactions.



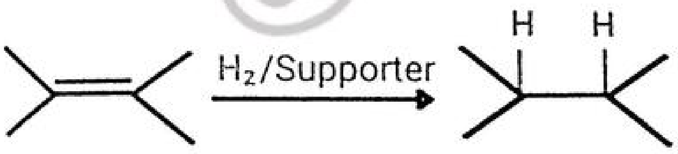
Neutral Alkane (Non polar)
No Forces

Slightly polarized alkane (due to induced dipole)
Vander Waals Forces (Weak forces)

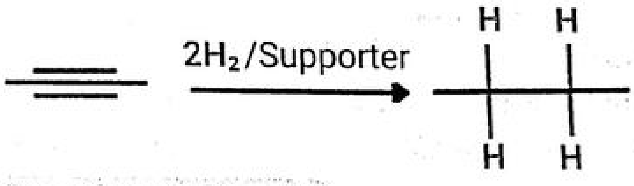
1. How do they form?

- **From Alkenes & Alkynes** : Hydrogenation (H_2, Ni/Pd)
- **From Alkyl Halides** : Wurtz Reaction ($2RX + Na \rightarrow R\text{-}R$) & Reduction (Zn/HCl, $LiAlH_4$)
- **From Carboxylic Acids** : Decarboxylation (NaOH + CaO) & Kolbe's Electrolysis
- **From Grignard Reagent** : Hydrolysis of Grignard compounds with water or alcohol

1.1 Hydrogenation



Reaction of Alkenes



Reaction of Alkynes

- **Catalysts:** Pt, Pd, Raney Ni, or Ru can be used
- **Mechanism Insight**: Metal surface adsorption and hydrogenation
- **Orientation** : Hydrogen adds from the same side **(Syn addition – leads to Cis product)**
- **Speed** : Rate of Hydrogenation ∝ 1/Steric Crowding
- **Heat of Hydrogenation** : More stable alkenes have lower heat of hydrogenation
- The process of converting unsaturated vegetable oils (having C=C bonds) into saturated fats by adding hydrogen using a metal catalyst (Ni, Pd, Pt) is **Hydrogenation of Oils**
  - Used in the production of margarine and vanaspati ghee.
  - Unsaturated Oil + $H_2 \rightarrow$ Saturated Fat (**Catalyst**: Ni; **Conditions**: ~200°C, High **Pressure**)

1.2 From Alkyl Halides

Wurtz Reaction

Free Radical

$$2R{-}X + 2Na \xrightarrow{\text{Dry Ether}} R{-}R$$

X = Halogen (Cl, Br, I)

NAME 2 REACTION

- It is easy to prepare symmetrical Alkanes using this method in dry ether.
  - **Ethane :** $2CH_3Br + 2Na \rightarrow \mathbf{C_2H_6} + 2NaBr$ & **Butane** : $2C_2H_5Br + 2Na \rightarrow \mathbf{C_4H_{10}} + 2NaBr$
- Unsymmetrical alkanes can also be prepared using different alkyl halides
  - This leads to multiple products, making the reaction non-selective.
  - $CH_3Br + C_2H_5Br + 2Na \rightarrow \mathbf{CH_3CH_2CH_3 + CH_3CH_3 + C_2H_5C_2H_5} + 2NaBr$

IMPORTANT

Mechanism Glance

$R{-}X \longrightarrow R\cdot + X\cdot$ — *R–X undergoes homolysis to form Radicals*

$X\cdot \xrightarrow{Na\cdot} R\cdot + X^-$ — *Na donates one electron to the halogen atom (X), converting it to X⁻.*

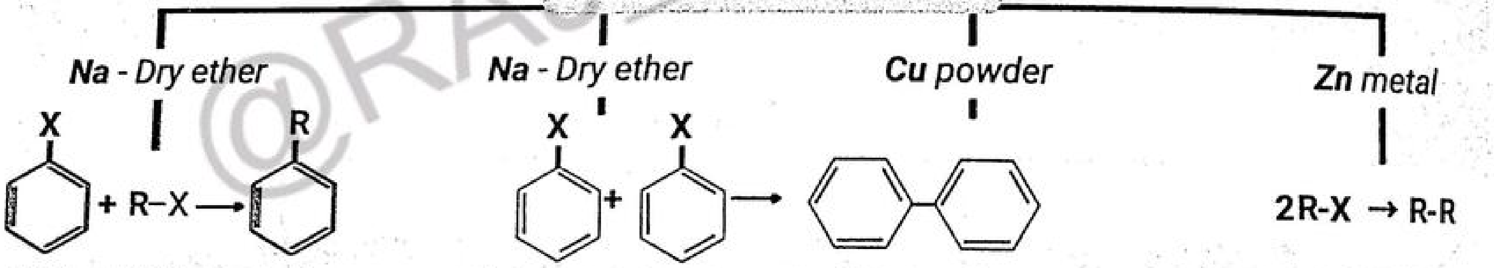
$R\cdot \quad \cdot R \longrightarrow R{-}R$ — *free radical (R•) combines with another to form the alkane (R–R).*

$Na^+ + X^- \longrightarrow NaX$ — *X⁻ connects with Na⁺ to form NaX*

Limitations

- ◎ It works best for even-numbered alkanes (R–R type products).
- ⚠ Tertiary alkyl halides undergo elimination (E2) instead of substitution, leading to alkenes.
- Rate of radical formation : R–I > R–Br > R–Cl > R–F

Variation of Wurtz Reaction



Wurtz - Fittig Reaction *Side : **2NaX***

Fittig Reaction *Side : **2NaX***

Ullmann Reaction *Side : **CuX***

Frankland Reaction *Side : **ZnX_2***

Corey house

$$R{-}X + Li + \underset{\textit{Gilman Reagent}}{R'_2CuLi} \longrightarrow R{-}R' + R'Cu + LiX$$

NAME 3 REACTION

- **Gilmann Reagent :** R'_2CuLi is formed by $2R'{-}Li + CuX \rightarrow R'_2CuLi + LiI$
- Best for methyl and primary alkyl halides
- ✗ **Tertiary alkyl halides** → Poor yield due to elimination
- Selective for C–C bond formation
- ⊘ **Not suitable** for forming **unsymmetrical** alkanes via branching
- Useful in alkyl-alkyl coupling without side products **(better than Wurtz for selectivity)**

Example

1.3 From Carboxylic Acids

Kolbe's Electrolysis

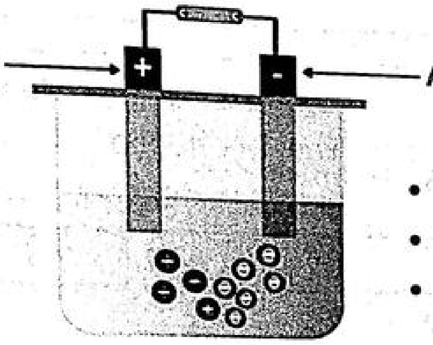
Free Radical $R\text{-}COONa \xrightarrow[\text{Electrolysis}]{\text{Aqueous}} R\text{-}R + CO_2 + H_2 + 2OH^-$ **NAME REACTION 4**

$R\text{-}COO^- \rightarrow 2R\cdot + CO_2$

$2R\cdot \rightarrow R\text{-}R$

Coupling of Free Radicals

Alkanes are formed in this step by coupling of free radicals.



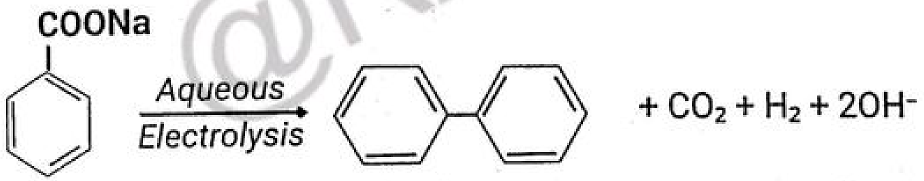
Anode $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

- Hydrogen gas (H_2) is released.
- OH^- ions remain in the solution.
- Species involved: **Water**

- Produces symmetrical alkanes with even number of carbon atoms only.
- **Does NOT work for preparing methane (CH_4)**
- Useful for alkanes where both alkyl groups are the same.
- With $HCOO^- \rightarrow H_2 + CO_2$ (No alkane is formed in this case)

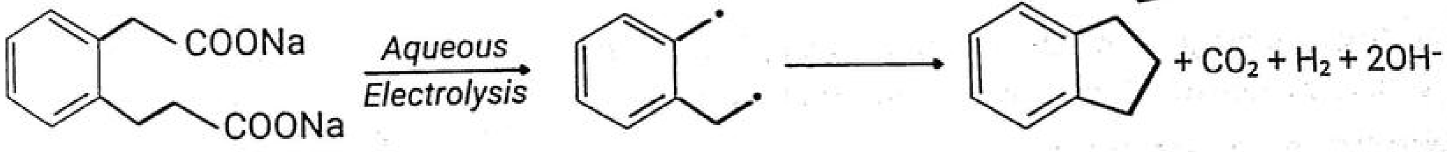
TRICKY Examples

①



IMPORTANT

②



Decarboxylation

Carbanion

$$\underset{\substack{\uparrow\\ \text{Extra Carbon}}}{R\text{-}COOH} + \underbrace{NaOH + CaO}_{\text{Soda Lime}} \xrightarrow{\text{Heat}} \underset{\substack{\uparrow\\ \text{One less Carbon}}}{R\text{-}H} + Na_2CO_3$$

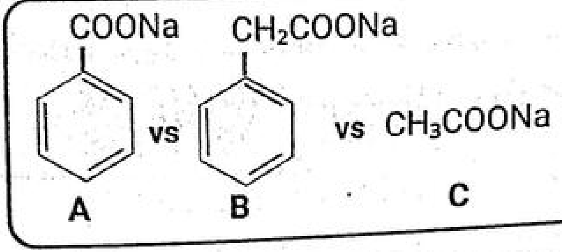
- $NaOH + CaO$ = Soda lime **(CaO prevents charring & absorbs moisture).**
- Only simple (non-branched) alkanes are efficiently formed; poor yields with tertiary acids due to competing elimination."
- Cannot be used for formic acid (HCOOH) → gives $H_2 + CO_2$ instead.

Mechanism Glance

$R{-}COOH + NaOH \rightarrow R{-}COO^-Na^+$

Carboxylic acid reacts with NaOH to form carboxylate ion

On heating, the carboxylate ion releases CO_2, forming R^-, which then abstracts a proton from the solution.



Which undergoes decarboxylation fastest among A,B & C?

Since carbanion is the intermediate after release of CO_2, **B will be Fastest** due to formation of Benzyl Anion.

CH_3COONa **vs** NO_2CH_2COONa

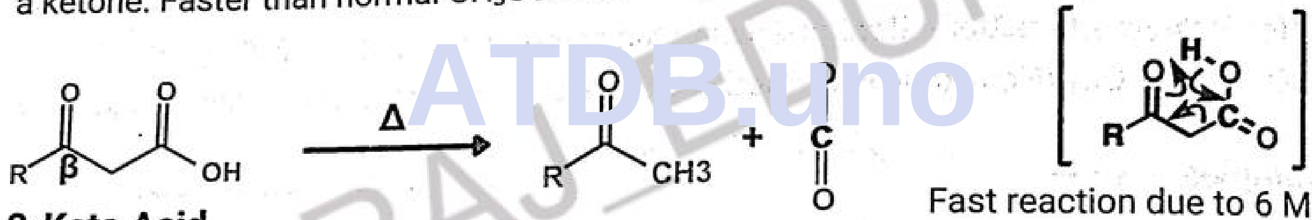
A **B**

Which undergoes decarboxylation fastest among A & B

The -M effect of NO_2 in B will stabilise the anion to a greater extent compared to normal methyl in A

β-Keto Acids on Heating

β-Keto acids contain a ketone group at the β-position (i.e., two carbons away) from the carboxylic acid group. When beta-keto acids are heated, they spontaneously lose CO2 to give a ketone. Faster than normal CH_3COONa.



β-Keto Acid

Fast reaction due to 6 Membered cyclic intermediate formation

1.4 Reaction with Grignard reagent, R–MgX

(R = alkyl or aryl group, X = Cl, Br, I)

- Grignard reagent acts as a **strong nucleophile** or a **base**.
- In formation of alkanes, the role of Grignard is purely as base.

IMPORTANT

Grignard Reagent as base

$$R{-}MgX + H{-}Y \longrightarrow R{-}H + MgX{-}Y$$

- Where **H–Y is a proton donor like water, alcohol, terminal alkyne, amine, etc.**
- Order of Acidity of H-Y is $\mathbf{HC{\equiv}CH > H_2O > ROH > NH_3}$

Examples

- $CH_3MgBr + CH_3CH_2OH \rightarrow CH_4 + CH_3CH_2OMgBr$ **(Reaction with Alcohol)**
- $C_2H_5MgBr + HC{\equiv}CH \rightarrow C_2H_6 + HC{\equiv}CMgBr$ **(Reaction with Terminal Alkyne)**
- $CH_3MgBr + NH_3 \rightarrow CH_4 + NH_2MgBr$ **(Reaction with Ammonia)**

2. How do they React?

- Alkanes undergo free radical reactions because their bonds are non-polar, making it difficult to form carbocations or carbanions.
- Some important reactions they go under are **Free radical Halogenation, Aromatisation, Combustion in presence of Oxygen.**

2.1 Free Radical Halogenation

- Order of **Reactivity** of Halogens : $F_2 > Cl_2 > Br_2 > I_2$ (Ease of homolysis + exothermic nature)
- Order of **Selectivity** of Halogens : $I_2 > Br_2 > Cl_2 > F_2$ (Based on preference for stable radicals)

Halogenation of Alkanes

$$R\text{-}H + X_2 \longrightarrow R\text{-}X + HX \qquad X = F, Cl, Br, I$$

Steps of Reaction

Initiation

$Cl_2 \rightarrow 2Cl\cdot$

Homolytic cleavage of halogen molecule

Propagation

$Cl\cdot + CH_4 \rightarrow CH_3\cdot + HCl$ ← **Rate Determining**

$CH_3\cdot + Cl_2 \rightarrow CH_3Cl + Cl\cdot$

The alkyl radical continues to attack more alkane molecules, propagating the chain.

Termination

$Cl\cdot + Cl\cdot \rightarrow Cl_2$

$CH_3\cdot + Cl\cdot \rightarrow CH_3Cl$

$CH_3\cdot + CH_3\cdot \rightarrow C_2H_6$

Two radicals combine

- A normal reaction of propane with X (halogen) would look like
  - $CH_3\text{-}CH_2\text{-}CH_3 + \mathbf{X_2} \rightarrow CH_3\text{-}CH\mathbf{X}\text{-}CH_3\ (2°) \rightarrow CH_2\mathbf{X}\text{-}CH_2\text{-}CH_3\ (1°)$

Reaction	Product Type	% with Cl_2	% with Br_2
$CH_3\text{-}CHX\text{-}CH_3$	2° (Secondary)	55.9%	96.5%
$CH_2X\text{-}CH_2\text{-}CH_3$	1° (Primary)	44.1%	3.5%

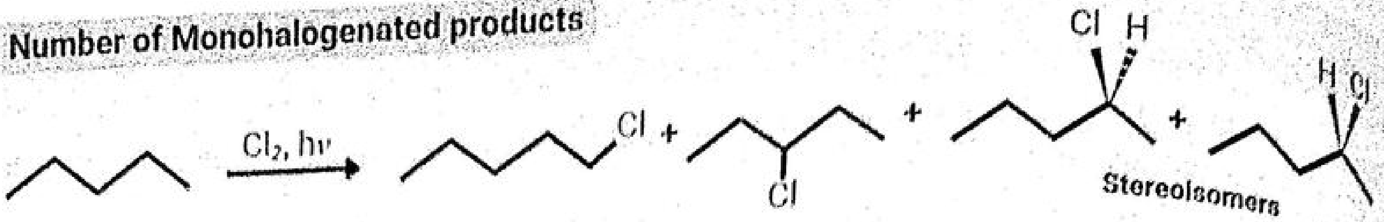
With Br_2, the reaction is more **selective favouring** the 2° product in the ratio 96.5 : 3.5

Reactivity and Selectivity of different halogens

Halogen	Reactivity	Selectivity 🎯	Reason
F_2	Very high	Very low ✗	Bonds form too fast; no time for selectivity
Cl_2	Moderate	Moderate ✗	Energy needed to break C−H bond ≈ Energy Released
Br_2	Low	High	More energy needed, so prefers stable radical
I_2	No reaction ✗	–	Endothermic reaction → *doesn't proceed*

- **Br_2 prefers tertiary > secondary > primary even more than Cl_2.**

Number of Monohalogenated products



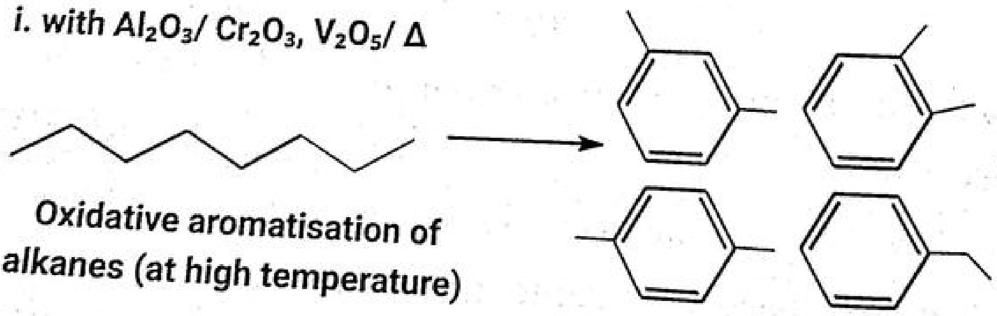
Number of Unique monochlorinated products = 3
Total Products including stereoisomers = 4

IMPORTANT

Alkane	Monochlorinated Products	Chiral Centers Present?" or "Stereoisomers?	Total Products (incl. stereoisomers)
Methane (CH_4)	1	No	1
Ethane (CH_3-CH_3)	1	No	1
Propane ($CH_3-CH_2-CH_3$)	2 (1° & 2°)	No	2
n-Butane	2 (1° & 2°)	No	2
n-Pentane	3 unique positions → 1 + 1 + 2	Yes (at 2° asymmetric C)	4
Isopentane (2-methylbutane)	3	Yes (at asymmetric 2°)	4
Neopentane (2,2-dimethylpropane)	1	No (all 1° equivalent)	1
2-Methylpentane	4 unique positions	Yes (possible chiral centers)	5 or more (depends on symmetry)

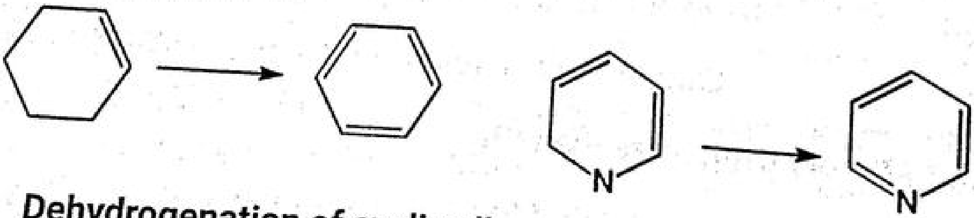
2.2 Aromatisation Reactions

i. with Al_2O_3/ Cr_2O_3, V_2O_5/ Δ



Oxidative aromatisation of alkanes (at high temperature)

ii. with Pd/C or Se



Dehydrogenation of cyclic alkanes to aromatic compounds

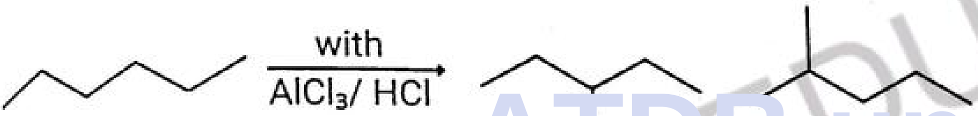
2.3 Combustion of Alkanes

- **General Reaction for Complete Combustion** $C_nH_{2n+2} + (3n+1)/2\ O_2 \rightarrow n\ CO_2 + (n+1)\ H_2O$
  - Example for propane (C_3H_8): $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$
- **Incomplete Combustion :** Produces CO (carbon monoxide) or even C (soot)
  - $2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O$
  - $CH_4 + O_2 \rightarrow C + 2H_2O$

Controlled Oxidation of Alkanes

Reaction	Catalyst	Forming
$CH_4 + O_2 \rightarrow CH_3OH$	Cu/523K/100 atm	Methonol
$CH_4 + O_2 \rightarrow HCHO$	Mo_2O_3, Δ	Formaldehyde
$2CH_3CH_3 + 3O_2 \rightarrow 2CH_3COOH + 2H_2O$	$(CH_3COO)_2Mn$	Acetic Acid
$(CH_3)_3CH \rightarrow (CH_3)_3COH$	$KMnO_4$	Tert-butyl Alcohol

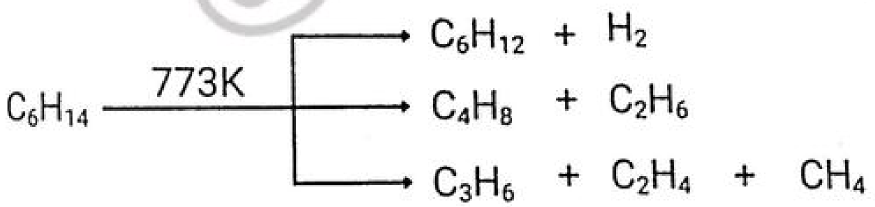
2.4 Isomerism with $AlCl_3$



Here, an isomerized product forms due to carbocation rearrangement.

2.5 Pyrolysis of big compounds

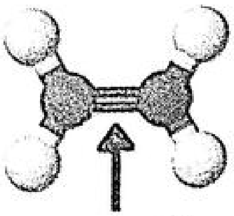
- $C_nH_{2n+2} \rightarrow$ alkanes + alkenes + H_2 + coke (carbon)



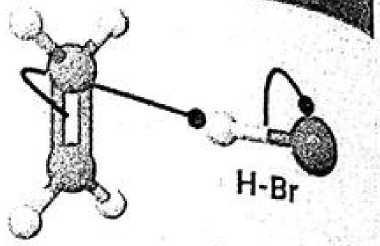
Feature	Detail
Reaction Type	Free radical thermal decomposition
Reactivity Order	Higher for larger alkanes
Not Selective	Mixture of products
Bonds Broken	C–C and C–H
Forms	Alkanes, Alkenes, H_2, Coke

Electrophilic addition - Alkenes and Alkynes

1. The Main Reactions and Reactivity of Alkenes and Alkynes


π + σ bond

The π bond has loosely held electrons held electrons which are available to be donated to other species. Due to this nucleophilic nature of Pi bonds, they prefer to undergo Electrophilic addition reaction.



Alkene attacking H of H-Br

1.1 Reactivity of Alkenes and Alkynes

- Since alkenes and alkynes prefer to undergo Electrophilic addition reactions, The functional groups which provides electrons to alkenes and alkynes will increase the rate of the reaction.
- Although alkynes contain two π bonds, their electrons are more tightly held due to greater s-character (sp-hybridized carbon = more electronegative).
  - This makes the π electrons in alkynes less available for attack by electrophiles.

Within Alkenes: What Makes Some Alkenes More Reactive?

IMPORTANT

- **More Substituted Alkenes are More Reactive** (due to more stable carbocations formed).
  - Tertiary > Secondary > Primary > Ethene
- **Electron-Donating Groups (EDGs) Increase Reactivity**
  - e.g. Alkyl groups donate electrons by +I effect, stabilizing the π bond and the carbocation.
- **Conjugation Increases Reactivity**
  - e.g. $CH_2=CH-Ph$ (styrene) is more reactive due to resonance with phenyl ring.

1. $CH_2=CCl_2$ (EWG Cl decreases reactivity)
2. $CH_2=CH_2$ (unsubstituted)
3. $CH_2=CH-CH_3$ (mono-substituted)
4. $CH_2=CH-CH=CH_2$ (conjugated diene)
5. $(CH_3)_2C=CH_2$ (highly substituted)
6. $CH_2=CH-Ph$ (conjugation with phenyl)
7. $CH_2=CH-OCH_3$ (resonance donor)

Least Reactive

Some major examples from the perspective of JEE

↓ **Most Reactive**

Within Alky

- **Terminal vs Internal Alkynes**
  - Terminal alkynes are less reactive than internal alkynes toward electrophilic addition.
- **Resonance or Conjugation Increases Reactivity**
  - $CH\equiv C-Ph$ (phenylacetylene) shows resonance and may have slightly altered reactivity.

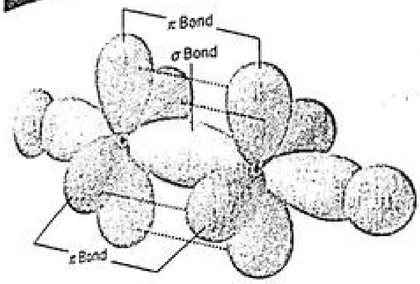
1. $HC\equiv C-CF_3$ (Strong −I effect of CF_3 pulls electrons)
2. $HC\equiv CH$ (Terminal alkyne, unstable intermediate)
3. $HC\equiv C-CH_3$ (+I effect of CH_3 helps a bit)
4. $CH_3-C\equiv C-CH_3$ (Internal alkyne, more stable intermediate)
5. $Ph-C\equiv CH$ (Phenyl group gives some stabilization)
6. $CH_3-C\equiv C-Ph$ (Internal + conjugation with phenyl)
7. $Ph-C\equiv C-Ph$ (Full conjugation with two phenyl groups)

Least Reactive

Some major examples from the perspective of JEE

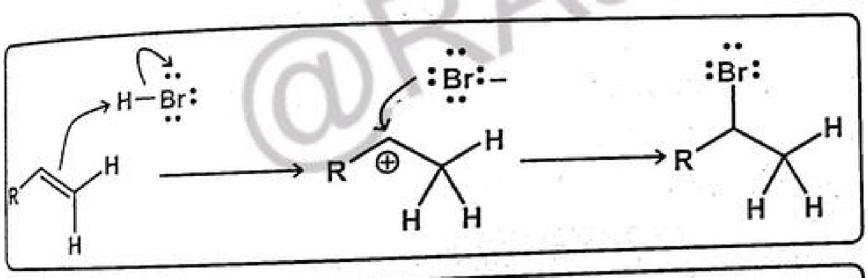
Most Reactive

2. Electrophilic addition Reactions to Alkenes and Alkynes



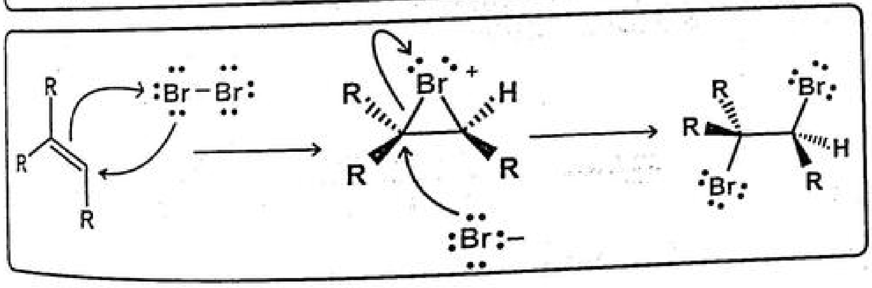
3d arrangement of Alkynes

- Alkenes and alkynes react in similar ways (Like a nucleophile), but alkynes have two pi bonds compared to one in Alkene, so there are a few small differences
- There are specific pathways with which the unsaturated carbon chains react. Distributed in three major categories, they are as followed.

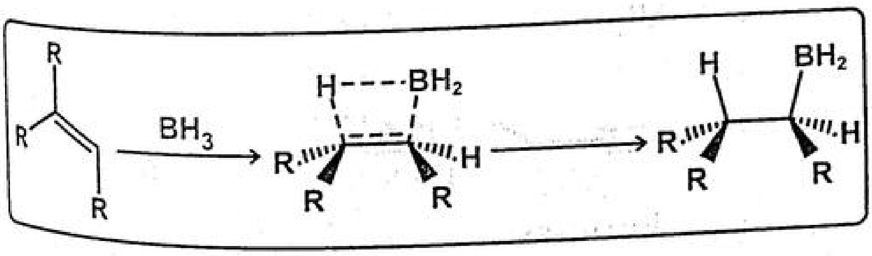


The Carbocation Pathway
Syn + Anti Addition

Addition of HCl, HBr, HI, H_3O^+

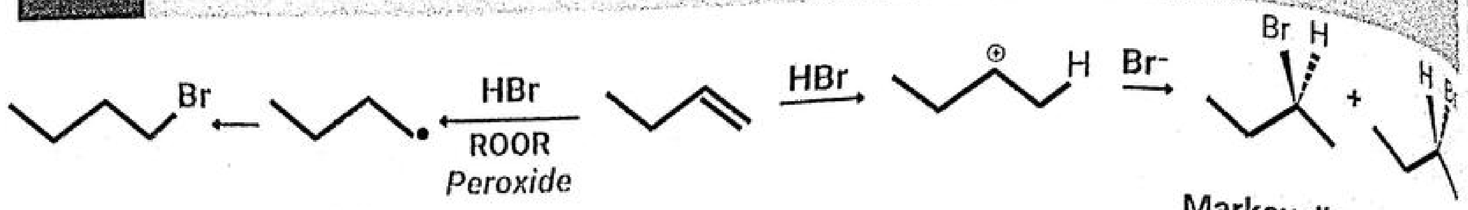


The 3-Membered Ring Pathway
Anti Addition
Addition of Cl_2, Br_2, Br_2/H_2O, Oxymercuration Demercuration, Epoxide opening



The One-way Pathway
Syn Addition
Hydroboration oxidation, Hydrogenation, Epoxidation, Dihydroxylation, Cyclopropanation

2.1 Markovnikov and AntiMarkovnikov Addition

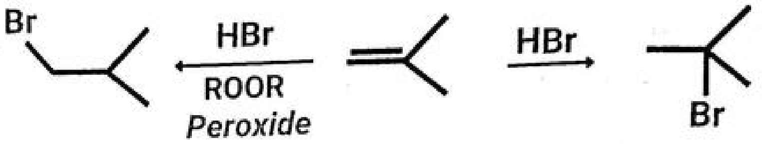


Anti-Markovnikov Addition
Free radical forms on less substituted carbon due to peroxide effect.

Markovnikov Addition
Carbocation forms on more stable side
Syn + Anti Addition possible

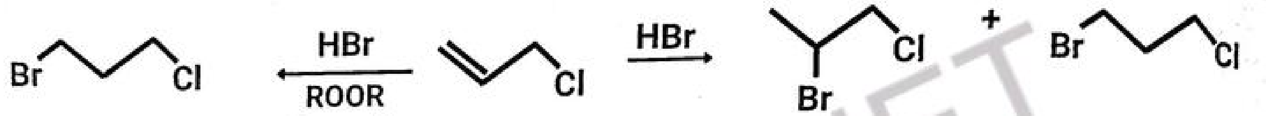
Some more tricky examples

① **Anti-Markovnikov Product**



Markovnikov Product

②



Anti-Markovnikov Product | **Markovnikov Product** (Minor) | **Anti-Markovnikov Product** (Major)

Markovnikov Product should be major with HBr but the carbocation being formed is not stable due to -CHCl present (-I effect)

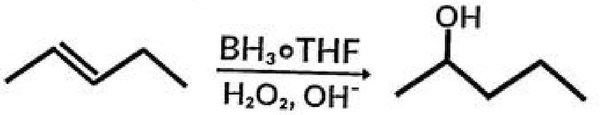
- Thus, Antimarkonikov product leads in both

IMPORTANT

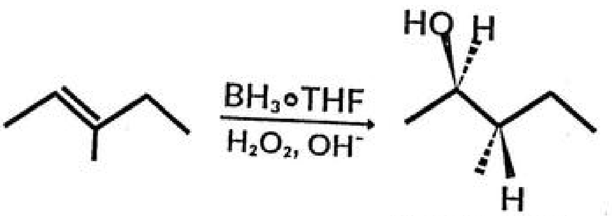
2.2 Hydroboration - Oxidation (Anti-Markonikov for Water)

- Hydroboration-oxidation is a two-step reaction of alkenes or alkynes that converts them into alcohols or carbonyl compounds (aldehydes/ketones).
- It follows **anti-Markovnikov rule and syn addition.**

Hydroboration Oxidation in Alkenes



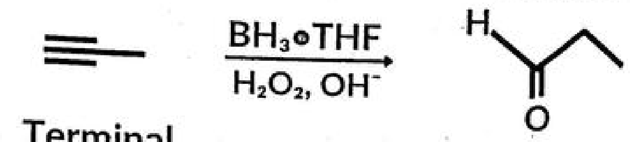
AntiMarkonikov Addition of OH



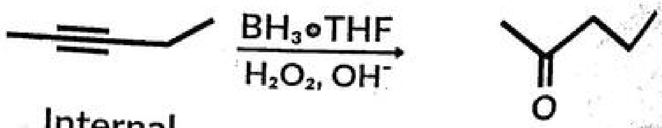
Syn Addition of OH and H

In Alkynes

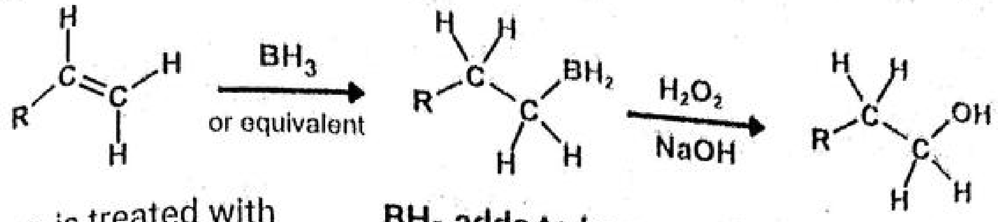
NAME 5 REACTION



Terminal Alkynes | Aldehydes



Internal Alkynes | Ketones



Alkene is treated with borane (BH_3) or any one of similar reagents.

BH_3 adds to less hindered site and H to more substituted site

Then H_2O_2/OH- oxidizes the B–C bond to B-OH bond

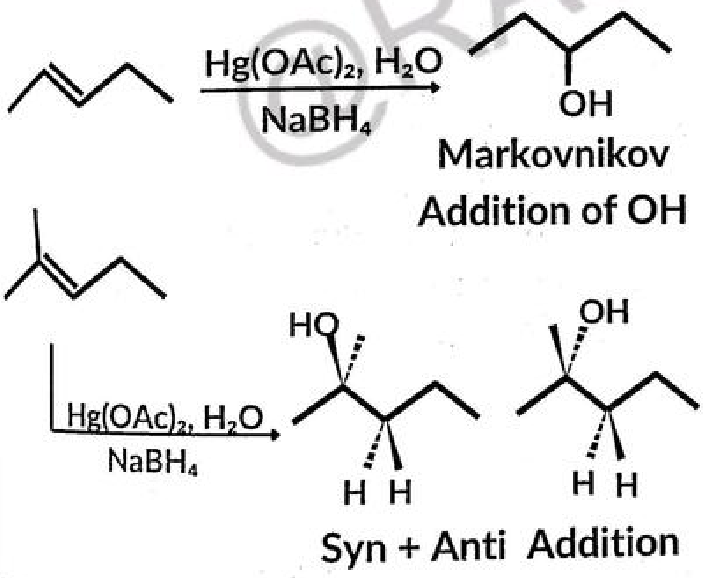
- Other Reagents which can be used : $(Sia)_2BH$ (disiamylborane) or 9-BBN for alkynes (to avoid over-addition) or B_2H_6 for alkenes
- No carbocation involved = No rearrangement happens
- Aromatic double bonds (like in benzene, styrene) do not react
- Always check for steric hindrance (bulky boranes prefer less hindered side)

2.3 Oxymercuration-Demercuration (Markovnikov for Water)

- Oxymercuration-demercuration is a two-step electrophilic addition reaction that converts alkenes into alcohols, following the Markovnikov rule — without forming a carbocation, so no rearrangement happens.
- OH to more substituted carbon, H to less substituted carbon
- No syn/anti preference → mixture possible

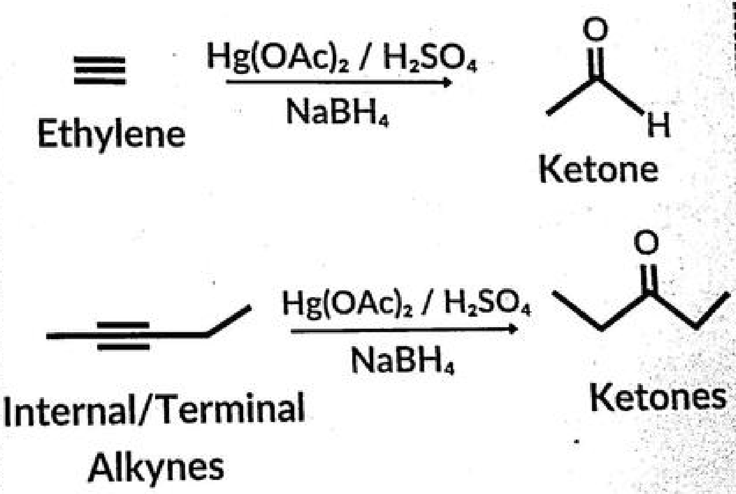
IMPORTANT

Oxymercuration-Demercuration in Alkenes

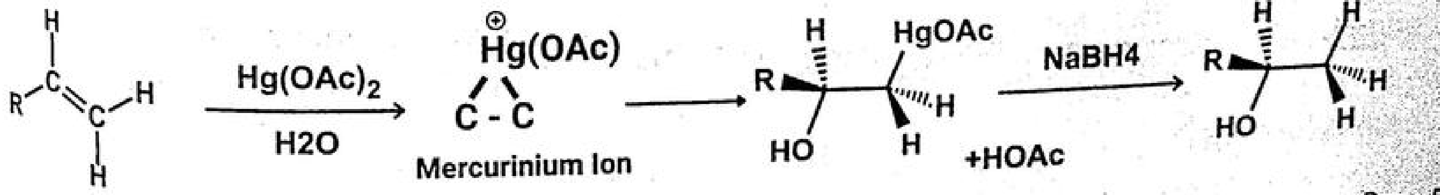


In Alkynes

NAME 6 REACTION



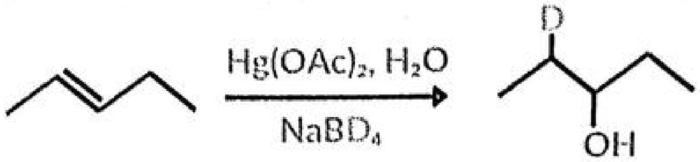
Mechanism Glance



Electrophilic Addi

- $Hg(OAc)_2$ adds across the double bond, forming a bridged mercurinium ion.
- H_2O attacks the more substituted carbon, giving Markovnikov addition of –OH.
- $NaBH_4$ replaces the HgOAc group with hydrogen, yielding the final alcohol.

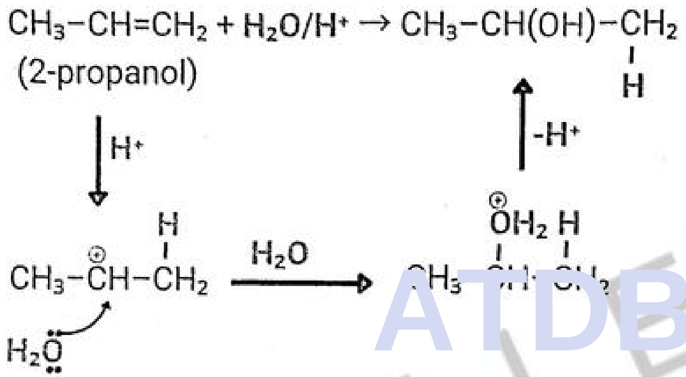
In case of deuteriated Sodium borohydride, $NaBD_4$



Deuterium (D) goes to the less substituted carbon

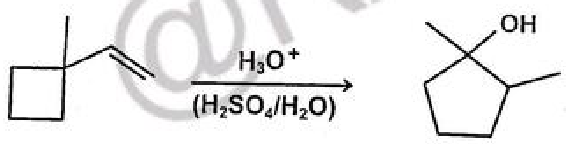
2.4 Hydrolysis of Alkenes and Alkynes - Markonikov addition

- "Hydrolysis" in this context generally refers to addition of water (H_2O) across double (C=C) or triple bonds (C≡C) to form alcohols or carbonyl compounds.
- Goes via **Carbocation intermediate.**

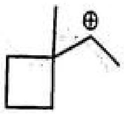


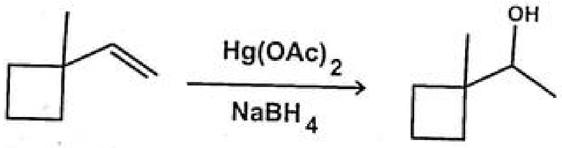
- H^+ adds to less substituted carbon → forms more stable carbocation.
- H_2O attacks the carbocation → forms an oxonium ion ($-OH_2^+$).
- Another H_2O removes a proton from OH_2^+ → gives the final alcohol.

Why is Hydrolysis different than Oxymercuration Demercuration? (Both are Markonikov)



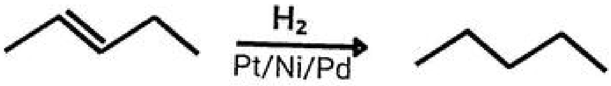
The carbocation formed due to H^+ can rearrange to form 5 membered ring





Since there is no carbocation rearrangement, the alcohol is formed on the more substituted side in same compound

2.5 Hydrogenation of Alkenes and Alkynes

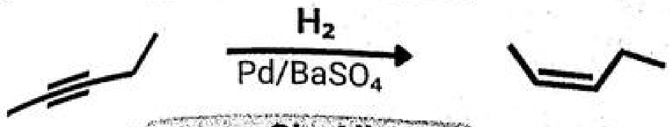


Hydrogenation is syn addition of hydrogen over the double bond

Alkynes require hydrogenation twice to convert into alkanes

To ochemistry (Cis or trans), we have special
Reactions

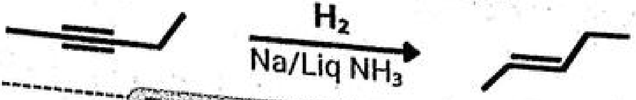
Lindlar's Catalyst



Forms Cis Alkenes

Mechanism Tip: The poisoned catalyst (with Pb & quinoline) slows down the reaction, preventing full hydrogenation.

Birch Method Reduction

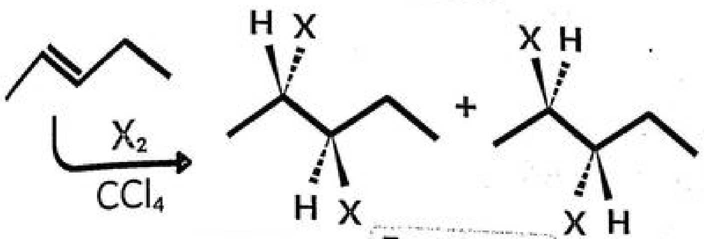


Forms Trans Alkenes

Mechanism Tip: Involves radical anion intermediate

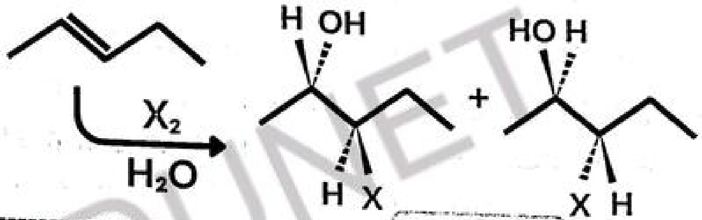
2.6 Addition of Halogens to Alkenes

Halogen with CCl4



Enantiomers

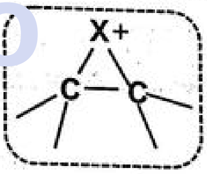
Halogen with Water/Alcohol



Enantiomers

Mechanism Tip: Both the reactions always form a cyclic halonium ion first, NOT a carbocation!

- The alkene attacks X_2, forming a three-membered halonium ion ring
- This ring is then opened by X^-, which attacks the opposite side (backside attack)
- In case of polar solvent, Water (or alcohol) attacks from the opposite side of the ring



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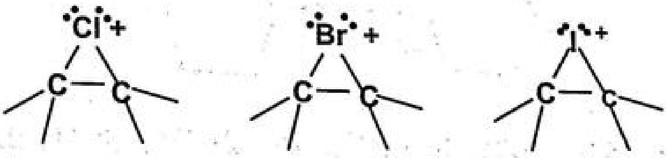


Stereochemistry is very important for the Halogenation of Alkenes and Alkynes, It is important to deduce Meso Compounds, Enantiomers, Diastereomers in the compounds.

Example (Alkene)	Reagents Used	Product Formed	Stereochemistry	Product Type
Cis-2-butene	Br_2 / CCl_4	2,3-dibromobutane	Anti addition	Pair of enantiomers
Trans-2-butene	Br_2 / CCl_4	2,3-dibromobutane	Anti addition	Meso compound
Cyclohexene	Br_2 / CCl_4	trans-1,2-dibromocyclohexane	Anti addition	Pair of enantiomers
Propene	Br_2 / H_2O	$CH_3-CH(OH)-CH_2Br$	OH on more substituted C	Racemic Mixture
2-Methylpropene	Cl_2 / H_2O	$(CH_3)_2C(OH)-CH_2Cl$	OH on more substituted C	Racemic Mixture

$CH_2{=}CH{-}CH_2OH$ (Allyl alcohol)	Br_2 / H_2O			Racemic Mi
1-Methylcyclohexene	Br_2 / CCl_4	trans-1,2-dibromo-1-methylcyclohexane	Anti addition on ring	Pair of enantiom

A pair of enantiomers together constitutes a racemic mixture.

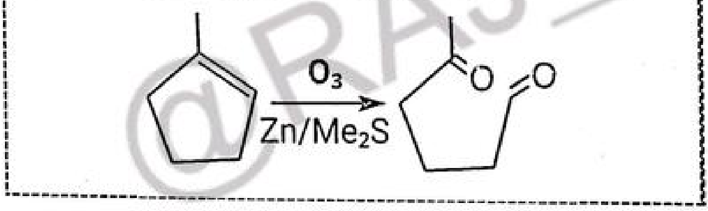
Trick for electrophilic add. stereochemistry to alkenes

1. **CSM :** Cis alkene - **S**yn Addition - **M**eso Product
2. **TSR :** Trans alkene - **S**yn Addition - **R**acemic Product
3. **CAR :** Cis alkene - **A**nti Addition - **R**acemic Product
4. **TAM :** Trans alkene - **A**nti Addition - **M**eso Product

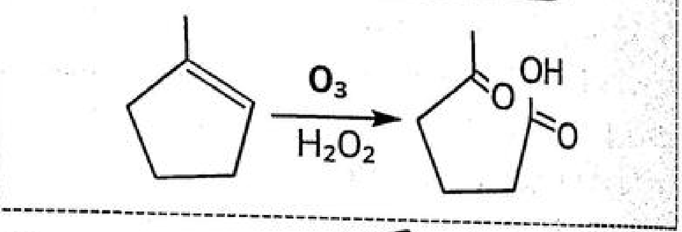
2.7 Ozonolysis of Alkenes and Alkynes

- Ozonolysis is an oxidative cleavage reaction of alkenes or alkynes using ozone (O_3) to brea C=C or C≡C bonds and form carbonyl compounds.
- Reagents Used
  - **O_3 (ozone)** – to cleave the double/triple bond Followed by
    - **Zn/H_2O or $(CH_3)_2S$** → Reductive ozonolysis
    - **H_2O_2** → Oxidative ozonolysis

Reductive Ozonolysis



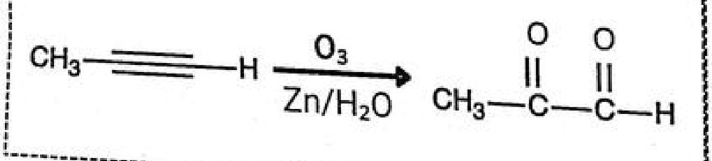
Oxidative Ozonolysis



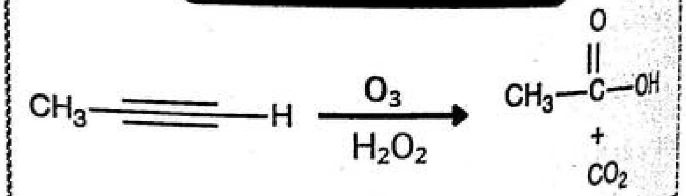
- Monosubstituted Carbon, Zn/Me_2S: **Aldehyde**
- Monosubstituted Carbon, H_2O_2 : **Carboxylic Acid**
- Disubstituted Carbon with either : **Ketone**

IMPORTANT

Reductive Ozonolysis



Oxidative Ozonolysis



- Reductive Ozonolysis gives **diketones**
- Oxidative give acids.**Terminal alkynes give CO_2.**

IMPORTANT

Some oth

Reagent & Purpose	**Reaction Example**
$NaNH_2$ Generates alkynyl carbanions (from terminal alkynes)	• $HC\equiv CH + NaNH_2 \rightarrow HC\equiv C^{-}Na^{+}$
NBS : N-Bromosuccinimide Allylic bromination	• $CH_2{=}CH{-}CH_3$ + NBS in hν → $CH_2{=}CH{-}CH_2Br$
Per-acid (e.g. mCPBA) Epoxidation of alkenes	• $CH_2{=}CH{-}CH_3$ + mCPBA→ epoxide (oxirane ring formed)
Cold, dilute $KMnO_4$ / OsO_4 Syn dihydroxylation (cis diol)	• $CH_2{=}CH{-}CH_3 + KMnO_4$ (cold)→ $CHOH{-}CHOH{-}CH_3$
Hot $KMnO_4$ Oxidative cleavage (like ozonolysis)	• $CH_3{-}CH{=}CH_2$ + hot $KMnO_4 \rightarrow CH_3COOH + CO_2$

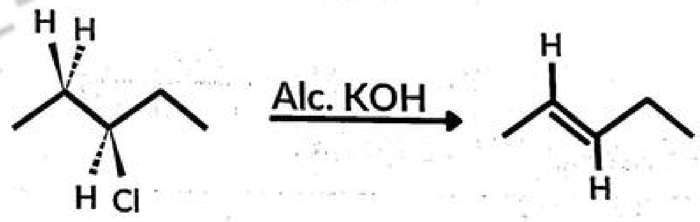
3. Other Important Reagents in Alkene/Alkyne Chemistry

Below are some important reactions for the formation of alkanes which can come in form of conversion or theory

3.1 From Halogens

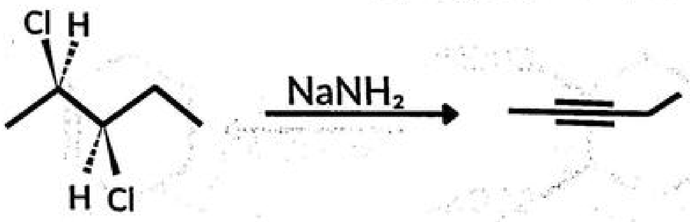
1. Dehydrohalogenation with Alc. KOH

- Alc. KOH used once to form alkene from Alkyl halides.
- H and Cl should be anti-periplanar for E2 elimination. (Discussed Later)



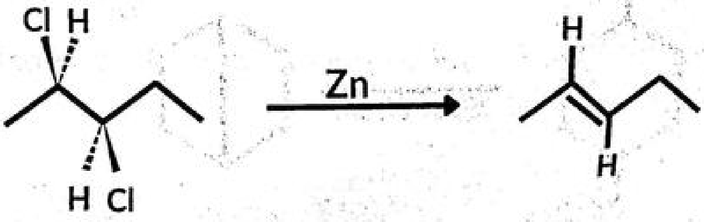
2. Dehydrohalogenation with $NaNH_2$

- $NaNH_2$ used twice to form alkyne from vicinal dihalides.
- H and Cl should be anti-periplanar for E2 elimination. (Discussed Later)



3. Forming alkene from Vicinal Dihalides

- Zn takes away vicinal dihalides by forming $ZnCl_2$
- Both Cl atoms should be in the same plane for elimination to occur.



3.2 From Hydrolysis of Carbides

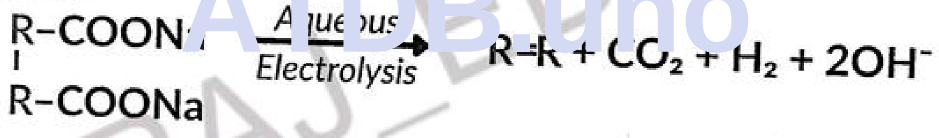
Carbide Compound	Reaction with Water	Product Formed	Hydrocarbon
Calcium carbide (CaC_2)	$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$	Ethyne (Acetylene)	Alkyne
Magnesium carbide (Mg_2C_3)	$Mg_2C_3 + 4H_2O \rightarrow 2Mg(OH)_2 + C_3H_4$	Propyne (Methylacetylene)	Alkyne
Beryllium carbide (Be_2C)	$Be_2C + 4H_2O \rightarrow 2Be(OH)_2 + CH_4$	Methane	Alkane
Aluminium carbide (Al_4C_3)	$Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4$	Methane	Alkane

Remember : A-B-C Rule : Aluminium-Beryllium gives CH_4

3.3 Kolbe's Electrolysis Reaction

- You might remember, Kolbe's Electrolysis in Alkanes, it is very similar to that

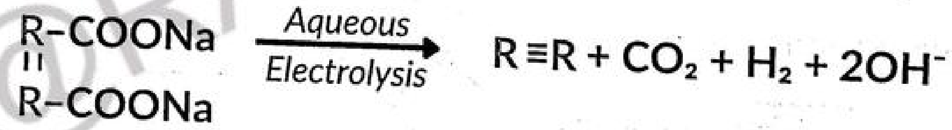
Kolbe's Electrolysis



$$\begin{array}{l} R-COONa \\ \quad | \\ R-COONa \end{array} \xrightarrow[\text{Electrolysis}]{\text{Aqueous}} R=R + CO_2 + H_2 + 2OH^-$$

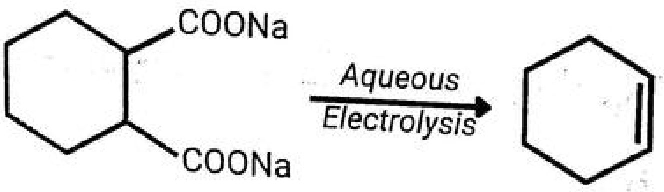
NAME 7 REACTION

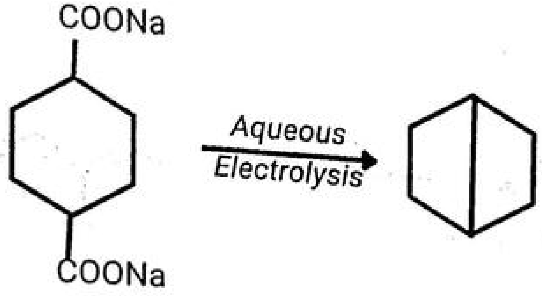
Free Radical



$$\begin{array}{l} R-COONa \\ \quad \| \\ R-COONa \end{array} \xrightarrow[\text{Electrolysis}]{\text{Aqueous}} R\equiv R + CO_2 + H_2 + 2OH^-$$

Some Tricky examples

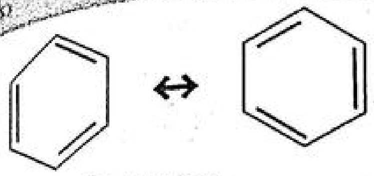




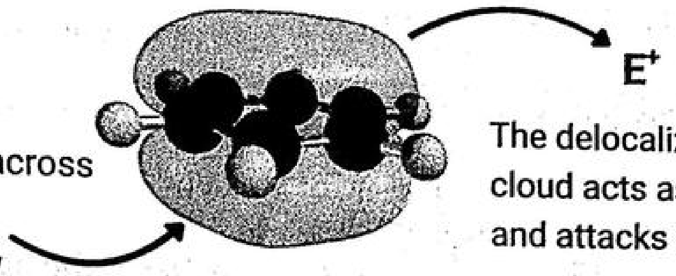
Step Towards Organic 7

Electrophilic Substitution in Aromatics

1. Why and how do Aromatics undergo Electrophilic substitution?



- This is Benzene
- Electron density is delocalized across all carbon atoms.
- Electron cloud above and below



The delocalized π-electron cloud acts as a nucleophile and attacks electrophiles.

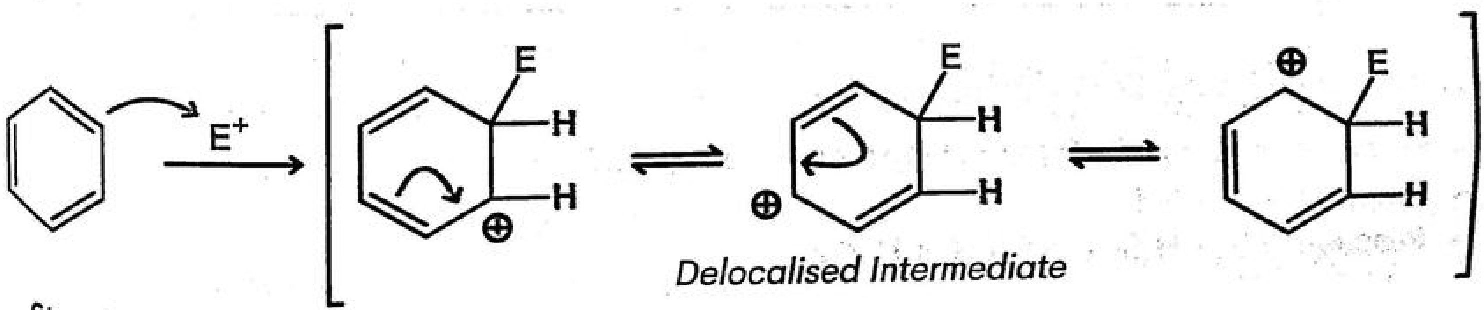
1.1 Mechanism view of the E.A.S.

IMPORTANT

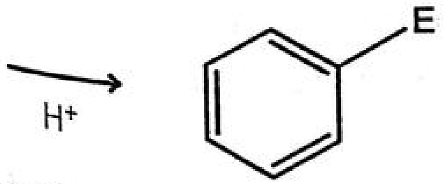
Step 1 : Generation of Electrophile

Name	Reagent	Lewis Acid / Catalyst	Electrophile (E⁺)
Nitration	HNO_3	H_2SO_4	NO_2^+
Chlorination	Cl_2	$FeCl_3$ or $AlCl_3$	Cl^+
Bromination	Br_2	$FeBr_3$ or $AlBr_3$	Br^+
Friedel–Crafts Alkylation	R–X (alkyl halide)	AlX_3 (mostly $AlCl_3$)	R^+ (carbocation)
Friedel–Crafts Acylation	R–CO–X (acyl halide)	AlX_3 (mostly $AlCl_3$)	R–C⁺=O (acylium ion)
Sulfonation	SO_3	H_2SO_4	SO_3H^+ or protonated SO_3

Step 2 : Attack of Benzene on Electrophile



Step 3 : Regain of Aromaticity



Addition of E⁺ breaks aromaticity. Loss of H⁺ brings it back. That's why it's substitution, not addition!

Nitration using HNO_3, H_2SO_4

- H_2SO_4 acts as an acid giving H^+ to HNO_3 forming NO_2^+
- $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$

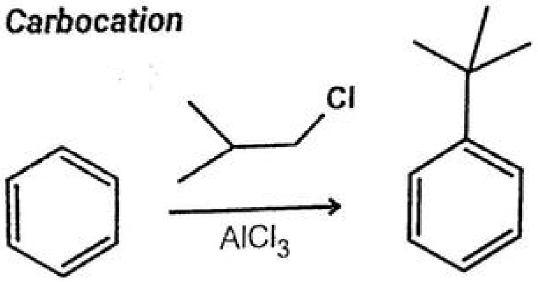
Halogenation using $Cl_2/Br_2 + FeCl_3/FeBr_3$

- $FeCl_3/FeBr_3$ is a **Lewis acid** – polarizes the halogen molecule.
- It forms Cl^+ or Br^+ electrophile.
- Reaction: $Cl_2 + FeCl_3 \rightarrow Cl^+ + FeCl_4^-$

Friedel-Crafts Alkylation using $R\text{-}X + AlCl_3$

NAME REACTION 8

Carbocation

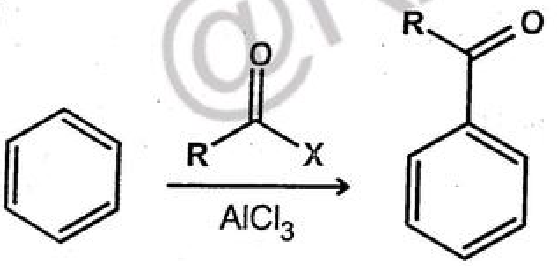


- $AlCl_3$ abstracts the halide (X^-) from the alkyl halide (R–X), forming a carbocation (R^+), which may rearrange
- Electrophile formed = R^+ (alkyl carbocation)
- Reaction: $R\text{–}Cl + AlCl_3 \rightarrow R^+ + AlCl_4^-$

- Carbocation in the above case rearranges via hydride shift to form 3° carbocation

Friedel-Crafts Acylation using $R\text{–}CO\text{–}X + AlCl_3$

NAME REACTION 9



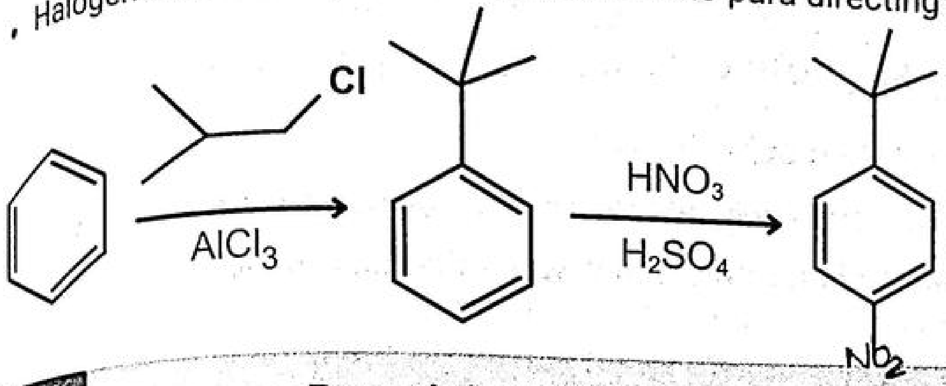
- $AlCl_3$ removes X^- from acyl halide to form Acylium ion ($R\text{–}C^+\equiv O$).
- Acylium ion is resonance-stabilized – very stable E^+.
- Reaction : $R\text{–}CO\text{–}Cl + AlCl_3 \rightarrow R\text{–}C^+\equiv O + AlCl_4^-$

Sulfonation using $SO_3 + H_2SO_4$

- H_2SO_4 protonates SO_3, forming SO_3H^+ or protonated SO_3.
- Electrophile = SO_3H^+
- Reaction : $SO_3 + H_2SO_4 \rightarrow SO_3H^+ + HSO_4^-$

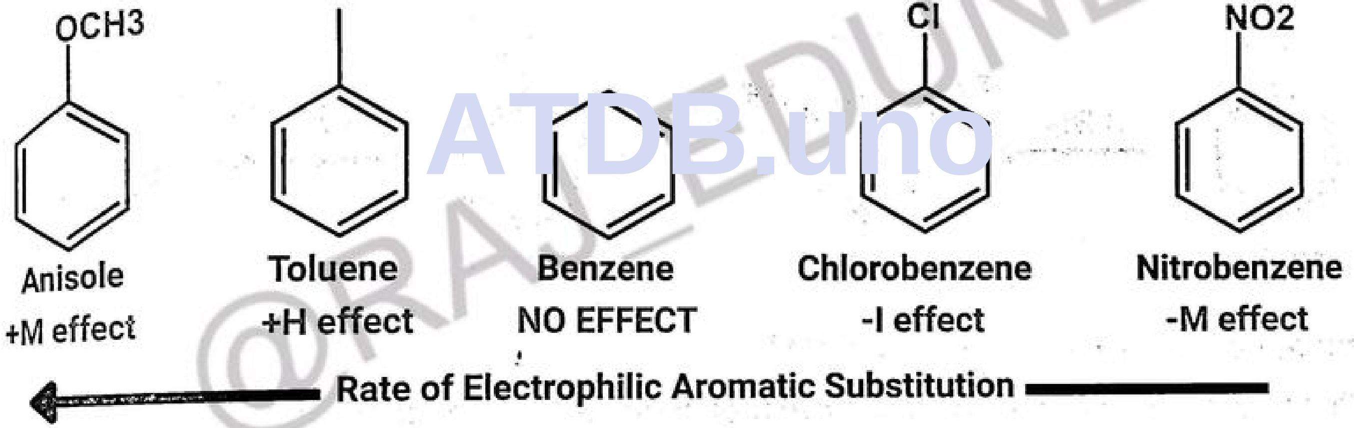
Fac	ecting	meta-Directing
Activating groups	-OH, -OR, $-NH_2$, $-NR_2$ and other +M Groups	-----------
Deactivating Groups	**Halogens**	$-NO_2$, -CHO, -COOH, -COOR and other -M Groups

- Friedal Craft Alkylation proceeds via formation of carbocation which undergo rearrangement for stability.
- Halogens are the only deactivating and ortho para directing gp.



- $AlCl_3$ generates a carbocation which rearranges to form 3 degree attaching to benzene ring
- Nitration of B gives para product

1.2 Reactivity of Substituted Aromatic Rings



+M, H, I effects increases electron density on the benzene ring by donating electrons

Other Examples

IMPORTANT

- Fluorobenzene > Chlorobenzene > Bromobenzene > Iodobenzene
- m-Nitrobenzene > o-Nitrobenzene ≈ p-Nitrobenzene *(meta has only -I effect)*
- Aniline > Acetanilide > Toluene > Benzene *(Free $-NH_2$ activates more than protected $-NHCOCH_3$, which is still better than $-CH_3$)*
- Phenol > Anisole > Benzene > Chlorobenzene *($-OH$ gives stronger +M effect than $-OCH_3$)*
- Biphenyl > Benzene *(Extra conjugation in biphenyl gives more electron density)*
- Mesitylene > Toluene > Benzene *(More methyl groups = more hyperconjugation)*
- Phenol > Benzoic acid *(Phenol is activating due to +M; benzoic acid has −M and −I)*

Compound	Substituent Type	Reactivity Towards EAS
Aniline ($-NH_2$)	Strong +M	☆☆☆☆☆ (Very Fast)
Phenol ($-OH$)	Strong +M	☆☆☆☆
Anisole ($-OCH_3$)	+M	☆☆☆
Toluene ($-CH_3$)	+H	☆☆
Benzene ($-H$)	Neutral	☆
Chlorobenzene ($-Cl$)	−I / weak +M	⚠ (Slow)
Nitrobenzene ($-NO_2$)	Strong −M	⊘ (Very Slow)

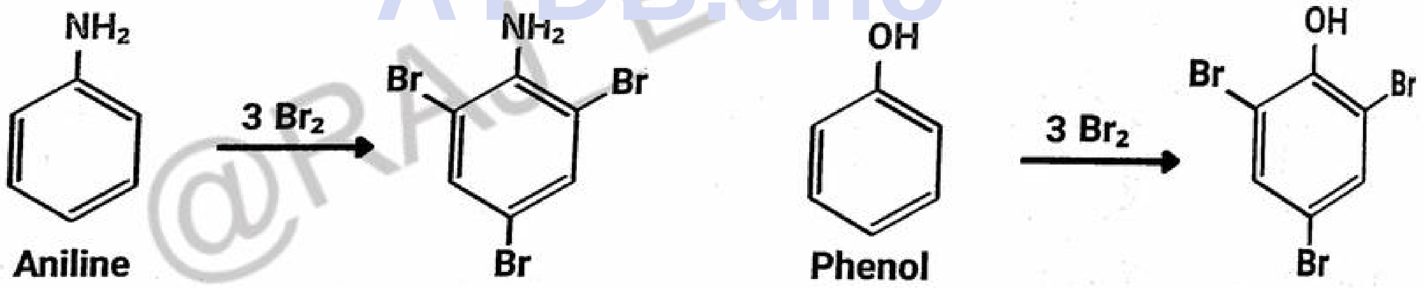
More donation means more reaction

more withdrawal means more hesitation!

Does it matter, if aniline of Phenol Reacts fast?

Yes, it matters. Both aniline and phenol are highly reactive towards electrophilic substitution due to their strong +M groups. They react so fast with bromine water that tribrominated products are formed instantly:

- Phenol → 2,4,6-tribromophenol
- Aniline → 2,4,6-tribromoaniline



Do we have a solution to this problem?

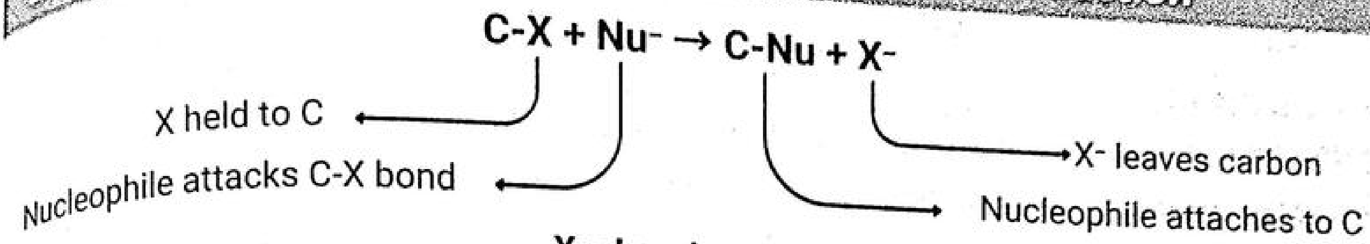
Yes, Specific methods can help us achieve monosubstitution as followed

Compound	Problem	Solution
Phenol	Overreaction	Use dil. Br_2 in CCl_4
Aniline	Overreaction	Protect $-NH_2$ by converting to acetanilide first

Step Towards Organic 8

Nucleophilic Substitution at Saturated Carbon

1. Substitution at Saturated carbon - Introduction



$$C\text{-}X + Nu^- \rightarrow C\text{-}Nu + X^-$$

X = Leaving Group

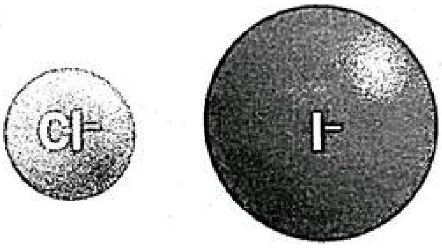
- There are two main ways in which nucleophilic substitution reactions can happen: S_N^1 and S_N^2.
- But before we understand them, it's important to know about "X" – the leaving group.
- **The better the leaving group, the faster the reaction happens.**
- A good leaving group makes it easier for the nucleophile to come in and take its place.

1.1 Leaving group ability of X

- What does a leaving group do? **It departs as a stable anion (X^-)**
- How can we make it better? ***If it's stable as (X^-) it would want to leave***

Example

- Reaction 1 : $CH_3{-}Cl + OH^- \rightarrow CH_3{-}OH + \mathbf{Cl^-}$
  (Cl act as a leaving group)
- Reaction 2 : $CH_3{-}I + OH^- \rightarrow CH_3{-}OH + \mathbf{I^-}$
  (I act as a leaving group)



Reaction 2 is much faster than reaction 1 since I^- is more stable than Cl^- due to bigger charge accommodating more electrons easily.

Can we predict good leaving groups easily? **Definitely**

If we compare I^- and Cl^- as leaving groups, we look at their conjugate acids: HI and HCl. Now, HI is a much stronger acid than HCl. That means the ion it gives (I^-) is more stable. So, I^- is a better leaving group than Cl^-.

Better leaving groups come from stronger acids.
To compare two leaving groups, just check which one has the stronger conjugate acid (i.e., lower pKa).
Lower the pKa → better the leaving group.

Different Leaving groups and their ability based on Conjugate acids

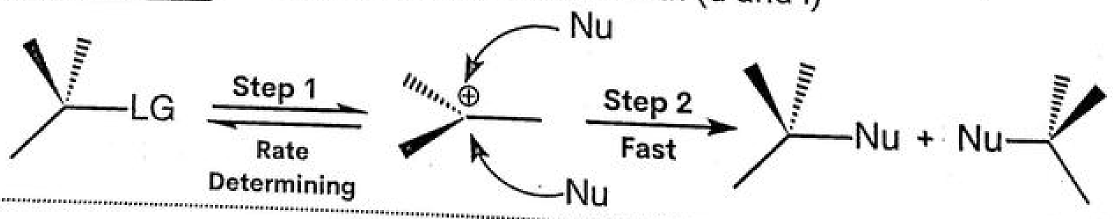
Leaving Group (LG)	Conjugate Acid (HA)	pKa	Leaving Group Ability
TsO⁻ (Tosylate)	TsOH	−3	☆☆☆ Excellent
I^-	HI	−10	☆☆☆ Excellent
Br^-	HBr	−9	☆☆☆ Excellent
Cl^-	HCl	−7	☆☆ Very Good
H_2O (from OH after protonation)	H_3O^+	−1.7	☆☆ Good
MsO⁻ (Mesylate)	MsOH	−2	☆☆ Good
AcO⁻ (Acetate)	AcOH	4.8	☆ Moderate
OH^-	H_2O	15.7	⊘ Poor
NH_2^-	NH_3	~38	⊘⊘ Very Poor
H^-	H_2	~35	⊘⊘⊘ Worst
CH_3^-	CH_4	~50	✕ Not a leaving group

Few points you must note from this

- **Halogens are good leaving groups** (Thus, alkyl halides undergo Nu Substitution)
- **OH is not a good leaving group and should be converted into one**
  - OH → H_2O using protonation with acids (Water is a good leaving group)
  - OH → OTs using TsCl (TsOH is a good leaving group)
  - OH → Cl/Br using PCl_5/PCl_3, $SOCl_2$ etc.
- **NH_2 is also not a good leaving group**

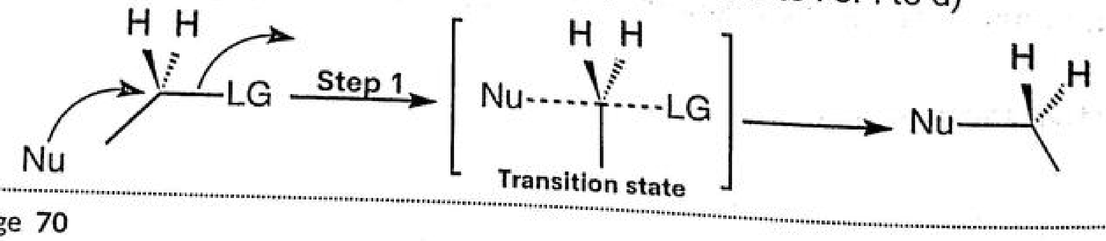
1.2 The Two Mechanisms of Substitution : $S_N{}^1$ and $S_N{}^2$

$S_N{}^1$ REACTION Forms Racemic mixture both (d and l)



Carbocation Pathway
Can rearrange to form more stable carbocation

$S_N{}^2$ REACTION Undergoes Inversion (d converts to l or l to d)



No carbocation involved.
Thus no Rearrangement possible

Feature	$S_N{}^1$ (Unimolecular)	$S_N{}^2$ (Bimolecular)
Order of Reaction	First order	Second order
Rate Law	Rate = k[Substrate]	Rate = k[Substrate][Nu^-]
Key Factor	Carbocation stability	Steric hindrance
Substrate Reactivity	3° > 2° >> 1°	1° > 2° >> 3°
Type of Nucleophile	Weak/neutral nucleophile (e.g., H_2O, ROH)	Strong/negatively charged nucleophile (e.g., OH^-, CN^-)
Solvent	Polar protic (e.g., H_2O, alcohol)	Polar aprotic (e.g., DMSO, acetone)
Stereochemistry	Racemization (Retention + Inversion)	Inversion of configuration only (Walden inversion)
Intermediate Formed	Carbocation	No intermediate; single transition state
Effect of Substituents	Electron-releasing groups increase rate	Electron-withdrawing groups increase rate
Energy Profile	Two humps (stepwise: carbocation + Nu^- attack)	One hump (single-step concerted mechanism)
Good Leaving Group?	Required	Required

1.3 Trends in Nucleophilicity: How Nucleophiles Become Stronger

Factor	Trend	Example / Explanation
Charge	Increases with negative charge	$OH^- > H_2O$ (More electron density = better attacker)
Across a Period (→)	Decreases with increasing electronegativity	$CH_3^- > NH_2^- > OH^- > F^-$ (More electronegative = holds electrons tightly)
Down the Group (in Polar Protic Solvent)	Increases down the group	$I^- > Br^- > Cl^- > F^-$ (Larger ions less solvated → more free to attack)
Down the Group (in Polar Aprotic Solvent)	Decreases down the group	$I^- < Br^- < Cl^- < F^-$ (No H-bonding → smaller ions stay stronger)

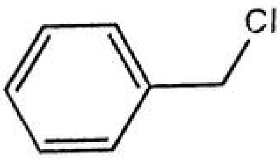
The Basic Mistake : **Nucleophilicity vs Basicity** : OH^- is a base as well as nucleophile.

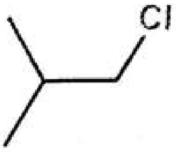
- **Nucleophilicity:** How fast a species attacks a carbon (focus = rate of reaction).
- **Basicity:** How strongly a species grabs a proton (H^+) (focus = equilibrium).
- Nucleophile = Reacts with carbon → Used in SN reactions
- Base = Reacts with H^+ → Used in acid-base reactions
- I^- is a better nucleophile than F^- (less solvated, attacks faster)
- F^- is a stronger base than I^- (holds H^+ more tightly)

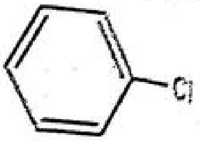
1.4 Trend of Substrate - How substrate decides mechanism

Substrate	Me-X	R-CH₂-X	R₂CH-X	R₃C-X
SN2	Excellent	GOOD	Bad	Poor
SN1	Bad	Bad	Ok-Ok	Excellent

IMPORTANT







Substrate	Benzylic / Allylic Halide	Neopentyl Halide	Vinyl Halides Haloarene
SN2	GOOD	Bad	Not Possible due to Partial Double bond Character
SN1	GOOD	Bad	

2. Substitution of Alkyl Halides/Alcohols/Ethers with Nucleophiles

Reaction **R-X + Reagent (With Nu) → R-Nu**

- Alkyl halides have a polar C–X bond, making carbon δ⁺ and electrophilic.
- The electron-deficient carbon is attacked by nucleophiles in substitution reactions.
- Sometimes the nucleophilic site can be different from imagined, Below are reactions

2.1 Some Important Reagents reacting with Alkyl halide

Reagent	Product Formed	Reaction Type / Name	Special Notes
KCN	R–CN	Cyanide Substitution	Forms alkyl cyanide (nitrile) via S_N^2
AgCN	R–NC	Isocyanide Formation	Ag^+ leads to N-attachment
KNO_2	R–ONO	Nitroester Formation	From ionic NO_2^- (O–N=O)
$AgNO_2$	R–NO_2	Nitro Compound	Ag^+ directs C–N bond (N-attachment)
Moist Ag_2O	R–OH	Alcohol Formation	Moisture gives water nucleophile
Dry Ag_2O	R–O–R	Ether Formation	S_N^2 etherification
AgF	R–F	**Swartz Reaction**	Used to introduce fluorine NAME 10 REACTION
NaI (in acetone)	R–I	**Finkelstein Reaction**	I^- replaces Cl^- or Br^- in S_N^2 NAME 11 REACTION

2.2 Reaction to form long chain Ethers

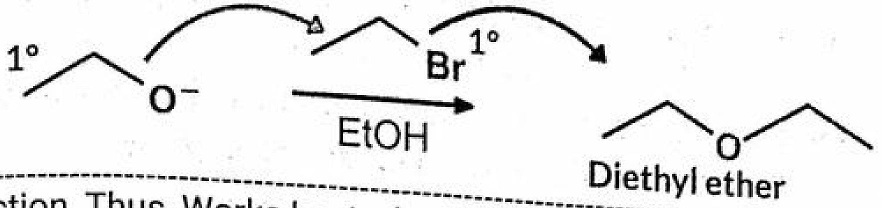
We Know : **R-X + Reagent (With Nu) → R-Nu**

- If we suppose the reagent to be an Alkoxide ion, R-O⁻, it will form an ether

Williamson Synthesis

$$R{-}O^- + R'{-}X \rightarrow R{-}O{-}R' + X^-$$

$S_N{}^2$ Reaction



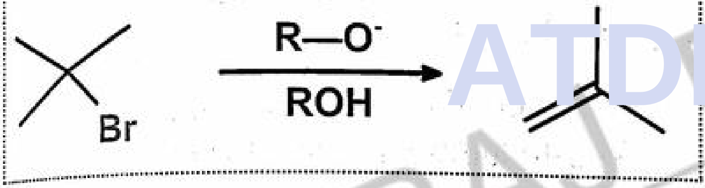
NAME 12 REACTION

- It's an SN2 reaction, Thus, Works best when **alkyl halide is primary**, because $S_N{}^2$ is hindered by bulky groups.

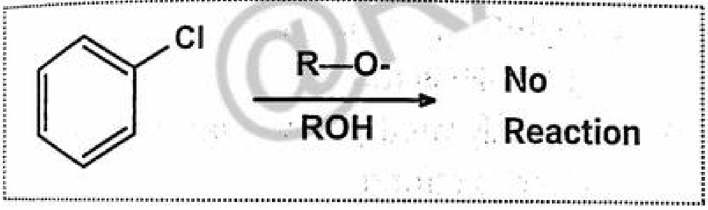
Some Examples

- $CH_3I + C_2H_5ONa \rightarrow C_2H_5OCH_3 + NaI$
- $C_6H_5CH_2Br + CH_3ONa \rightarrow C_6H_5CH_2OCH_3 + NaBr$ *(Benzyl halide is very reactive in SN2!)*
- $C_6H_5ONa + CH_3I \rightarrow C_6H_5OCH_3 + NaI$

Some not so possible Examples



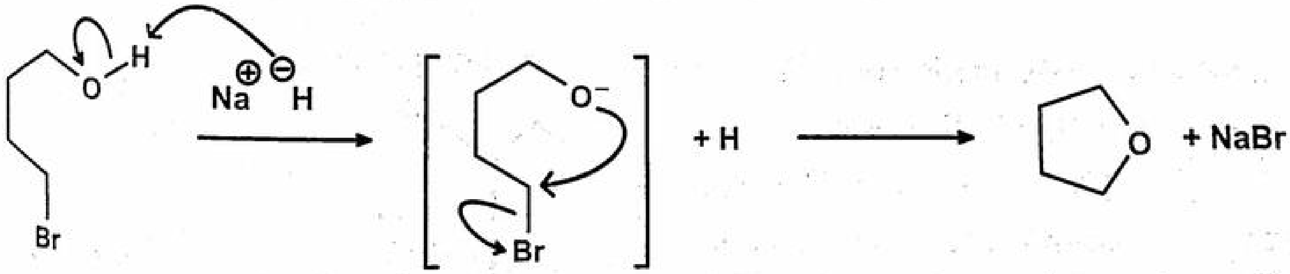
With tertiary alkyl halides, the Williamson ether reaction fails completely, and only **alkenes** are obtained.



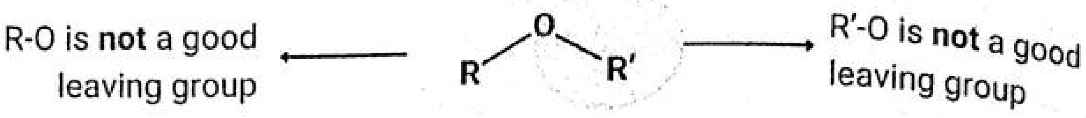
Aryl halides and vinyl halides do not undergo Williamson synthesis

IMPORTANT

Intramolecular Williamson Synthesis

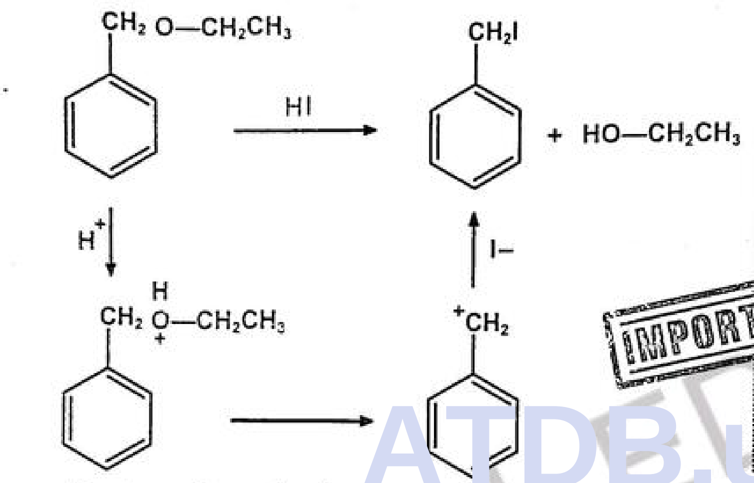


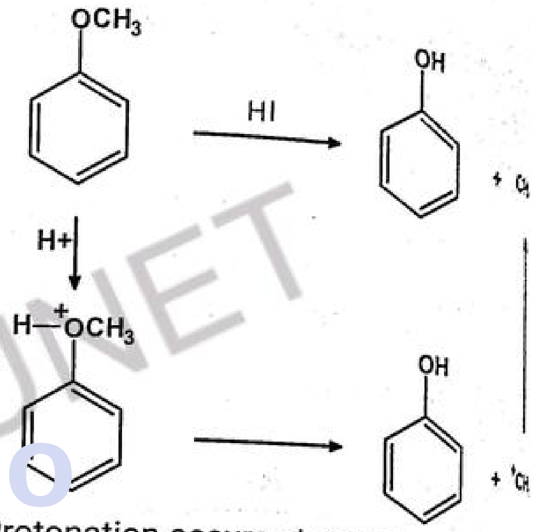
2.3 A Reaction of Ethers with HI involving S_N1 or S_N2



Ether

- But, Ethers react with concentrated HI (or HBr) to undergo cleavage and form:
  - An alkyl halide (R–I)
  - And an alcohol (R′–OH) or another alkyl halide (R′–I) depending on the conditions
- **Proceeds via SN1 or SN2 mechanism depending on the alkyl group**



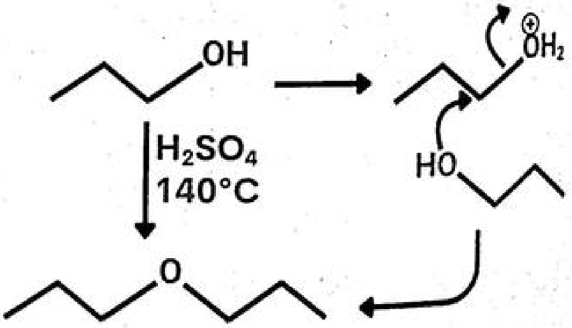


- Protonation of ether → makes it reactive
- Benzyl group leaves easily (forms stable carbocation)
- I⁻ attacks benzyl carbocation → forms benzyl iodide ($Ph–CH_2I$)
- Ethyl group becomes ethanol (CH_3CH_2OH)
- SN1 mechanism (benzyl is stable)

- Protonation occurs at oxygen
- CH_3^+ leaves and reacts with I⁻ → forms methyl iodide (CH_3I)
- Aryl–O bond doesn't break, so phenol (Ph–OH) is formed
- Only methyl side cleaved – aryl-O bond is strong

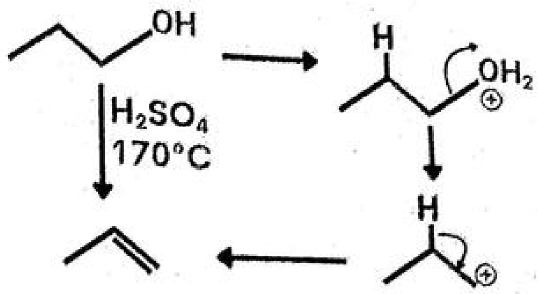
2.4 Dehydration of Alcohols to form Ethers via

- **At 413 K (~140°C) → Formation of Ether**
  - Reaction: 2 R–OH → R–O–R + H_2O
  - $C_2H_5OH + C_2H_5OH \rightarrow C_2H_5–O–C_2H_5 + H_2O$
  - This is called **dehydration** to form ethers
  - **Follows acid-catalyzed S_N2 mechanism**



Protonation: One alcohol is protonated to form $R–OH_2^+$ (good leaving group).
Attack: Another alcohol molecule attacks → kicks out H_2O (S_N2-like step).
Deprotonation: Final product is ether (R–O–R).

- *But the reacti*
- → *Formation of Alkene*
  - R–CH_2–CH_2–OH → R–CH=CH_2 + H_2O
  - C_2H_5OH → CH_2=CH_2 + H_2O
  - This is called **dehydration** to form Alkenes
  - **Follows acid-catalyzed E1 mechanism (via carbocation) Studied later**



Protonation of –OH group : Alcohol reacts with H^+ (H_2SO_4) → forms protonated alcohol (R–OH_2^+)
Loss of Water : The protonated alcohol loses H_2O → forms a carbocation (R^+)
Elimination of H^+ : A base (like HSO_4^-) abstracts a β-hydrogen → double bond forms

2.5 Conversion of OH group to a better leaving group

- As told earlier, OH can be converted to a better leaving group by converting it into Halogens or OTs, Some of the reactions below are the conversions

Reagent	Reaction	Mechanism	Stereochemistry
HX (X = Cl, Br, I)	R–OH + HX → R–X + H_2O	S_N1 carbocation	Inversion + Retention (racemic)
Red P / PBr_3 / PBr_5	R–OH + PBr_3 → R–Br + H_3PO_3	S_N2	Inversion of configuration
PCl_5	R–OH + PCl_5 → R–Cl + $POCl_3$ + HCl	Likely S_N2	Inversion of configuration
$SOCl_2$ (Darzens)	R–OH + $SOCl_2$ → R–Cl + SO_2 + HCl	SNi (internal attack)	Retention of configuration
$SOCl_2$ + Pyridine	R–OH + $SOCl_2$ + py. → R–Cl + SO_2 + HCl	S_N2	Inversion of configuration
TsCl / TsOH	R–OH + TsCl → R–OTs	-	No change (Used to make –OH a better LG)

Stereochemistry in SN1 depends on carbocation stability; for 1° alcohols, SN2 dominates.

2.6 OH into better leaving group via Lucas Reagent

- Lucas reagent is made of **Conc. HCl + Anhydrous $ZnCl_2$**
- Used for: Converting alcohols to alkyl chlorides (R–Cl)
- Mechanism: Follows SN1 for 3° and 2° alcohols
- **Test Use: Differentiates 1°, 2°, and 3° alcohols based on turbidity**

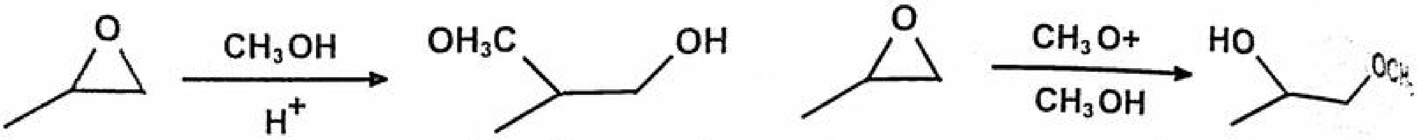
$(CH_3)_3C$–OH [3°] + HCl → $(CH_3)_3C^+$ ***stable carbocation*** → $(CH_3)_3C$–Cl + H_2O

Nucleophil

Type of Alcohol	Turbidity Appears	Reason
3° Alcohol	Immediately	Stable 3° carbocation (fast S_N^1)
2° Alcohol	Within 5 minutes	Moderate carbocation stability
1° Alcohol	No turbidity / very slow	Unstable carbocation (S_N^1 doesn't proceed)

2.7 Nucleophilic substitution in case of Epoxides

- Epoxides are three-membered cyclic ethers — highly strained and reactive toward nucleophiles.
- Now depending on the medium, where the nucleophile attacks changes:



2-methoxy-1-propanol

1-methoxy-2-propanol

In Acidic Medium (H⁺)

- The epoxide oxygen gets protonated first → becomes more electrophilic.
- The nucleophile (like CH_3OH) then attacks the more substituted carbon.
- This happens because protonation creates partial carbocation-like character at the more stable (substituted) position → favors S_N^1-like behavior.

In Basic Medium

- The nucleophile directly attacks the less hindered (less substituted) carbon.
- No protonation happens first → so no carbocation-like intermediate.
- The attack is a pure backside S_N^2 attack.

IMPORTANT

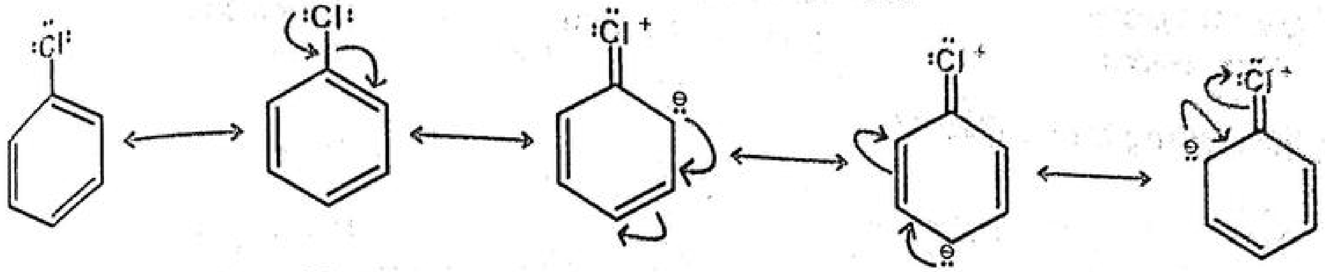
Acidic → Attacks More Substituted (due to + charge)
Basic → Attacks Less Substituted (due to S_N^2 nature)

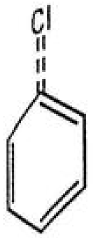
Step Towards Organic 9

Nucleophilic Substitution in Aromatics

1 Haloarenes do not undergo Nucleophilic sub. normally

Resonating structures of Chlorobenzene





The partial Double bond Character in Haloarenes

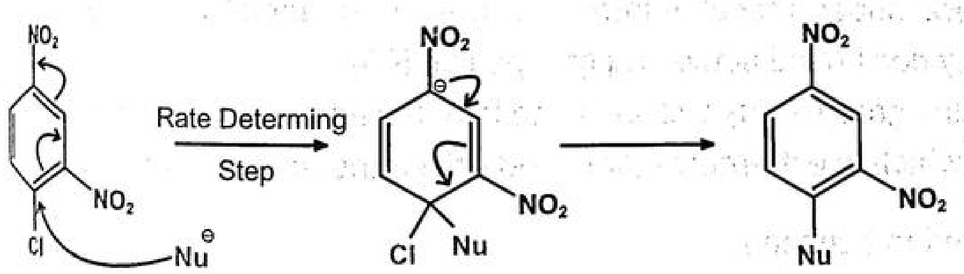
- The C–Cl bond becomes stronger and shorter than a typical single bond.
- The bond is less polar, making the carbon atom less electrophilic.
- This reduces the tendency of nucleophiles to attack the carbon attached to the halogen.

Ⓐ **No SN1 or SN2** : Because of this partial double bond character,

- $S_N{}^1$ mechanism is unfavorable because the intermediate (a carbocation) would be highly unstable in an aromatic system.
- $S_N{}^2$ mechanism is hindered due to the planar structure of the benzene ring, which does not allow backside attack easily.

11 A Possible Mechanism S_NAr (Addition-Elimination)

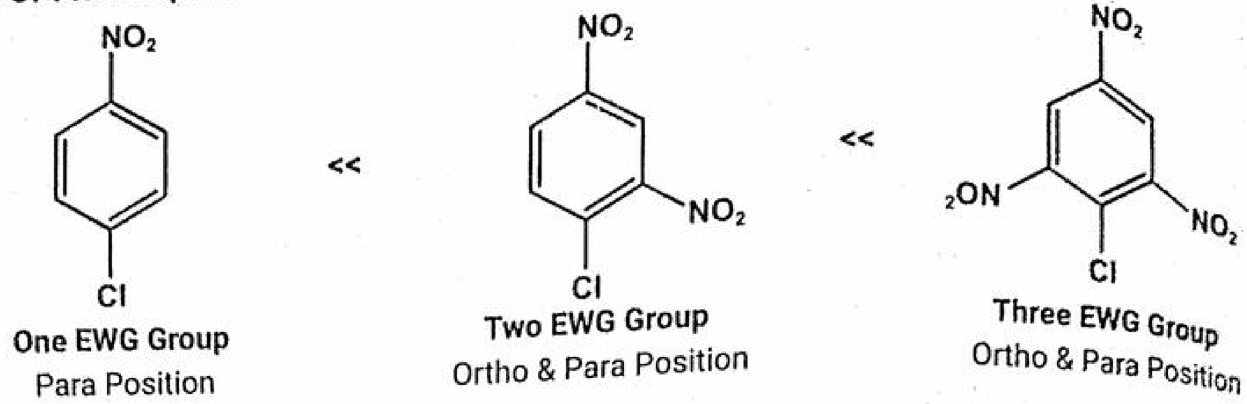
We know, SN1 or SN2, are not possible in Haloarenes but if we have EWG groups present in Ortho/para positions, the substitution reaction is possible via S_NAr mechanism.



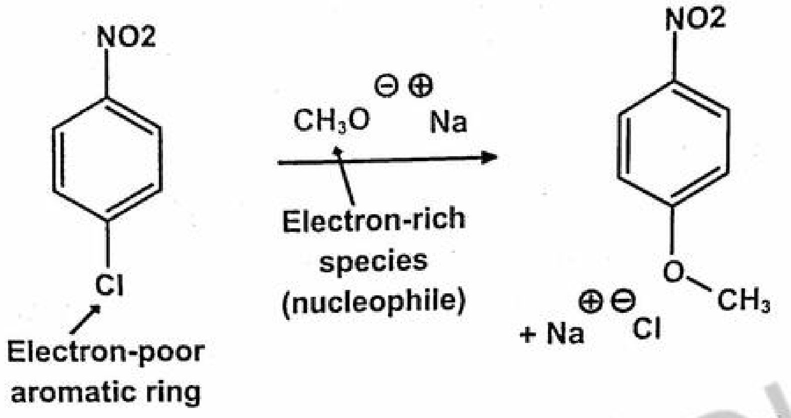
Nucleophile attacks the ring → forms Meisenheimer complex (slow step).
Cl^- leaves, restoring aromaticity.

- The rate-determining step is attack of the aromatic ring by the nucleophile, **which disrupts aromaticity.**
- NO_2 groups stabilize the intermediate by delocalizing the negative charge.
- Electron-withdrawing groups on o,p position to L.G., help to stabilize the -ve charge.
- **Ar-F > Ar-Cl > Ar-Br > Ar-I**, Since it makes the carbon site of attack more electropositive.

Rate of Nucleophilic Aromatic Substitution?

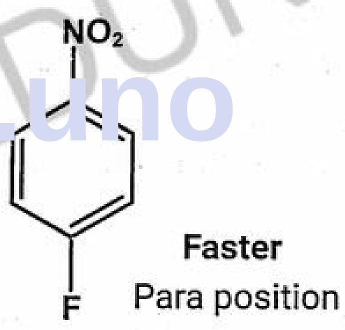


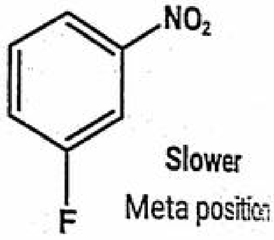
Example making things clearer



What doesn't work in this?

If we have the EWG groups in meta position to the halogens, the reaction will either not take place or will happen very slow

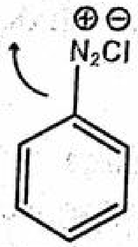




1.2 Diazonium Salts can help in Nucleophilic sub in Aromatics SNAr1

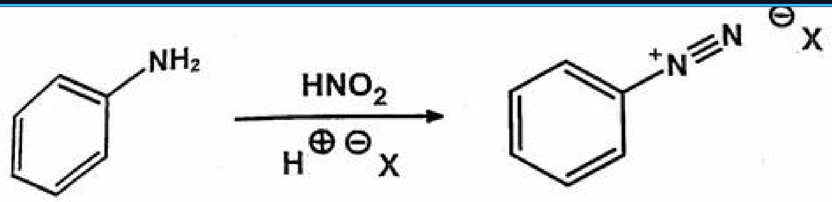
- Benzene diazonium salts are super reactive intermediates — especially in substitution reactions. The best part? They don't need activating groups like NO_2
- That's because the diazonium group ($-N_2^+$) is an excellent leaving group — and when it leaves, it escapes as N_2 gas, which is extremely stable and drives the reaction forward.

This is **Diazonium salt** attached to benzene in which N2 is always ready to leave

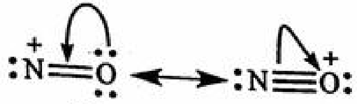


But how do we form this?

- **Via Anilines**

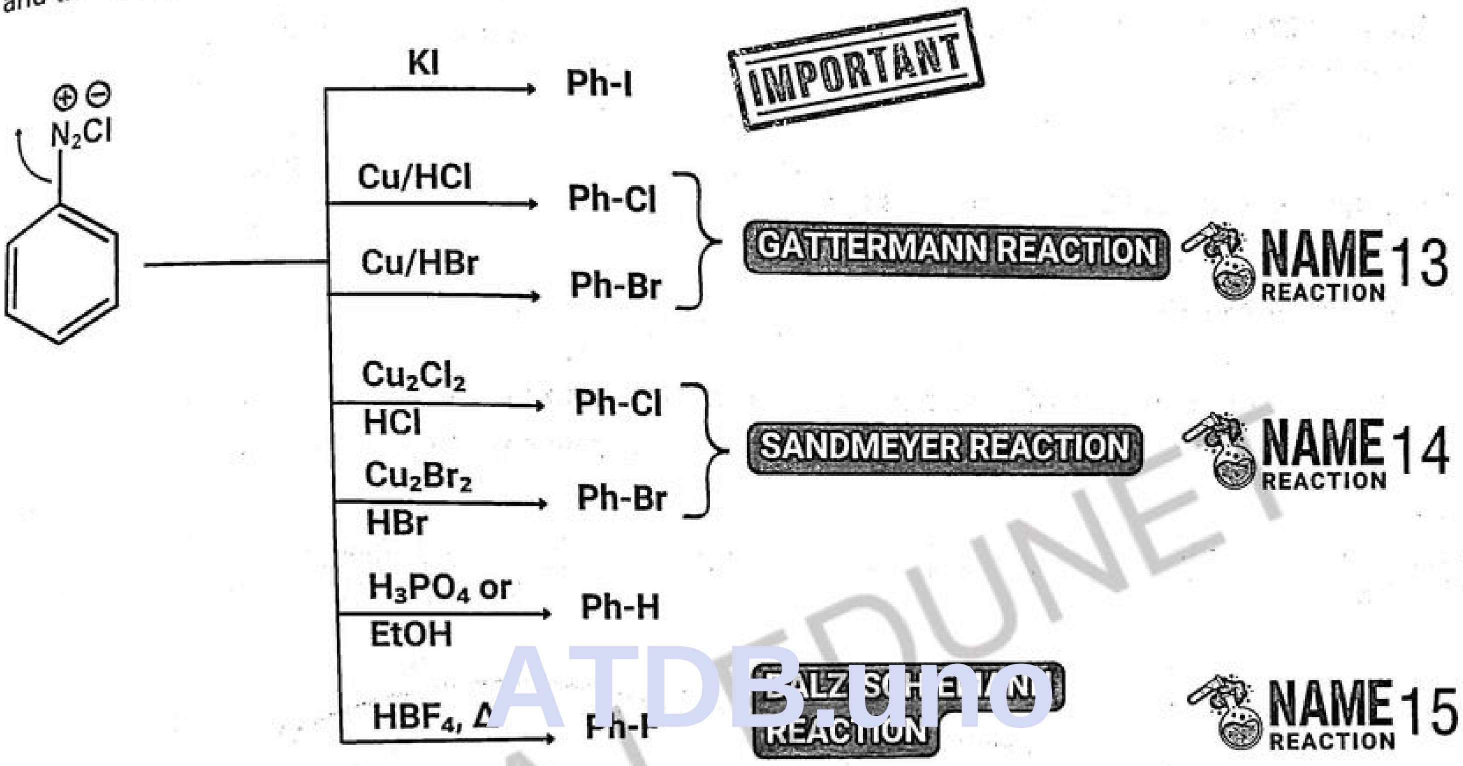


Intermediate involved?



Nitrosonium ion

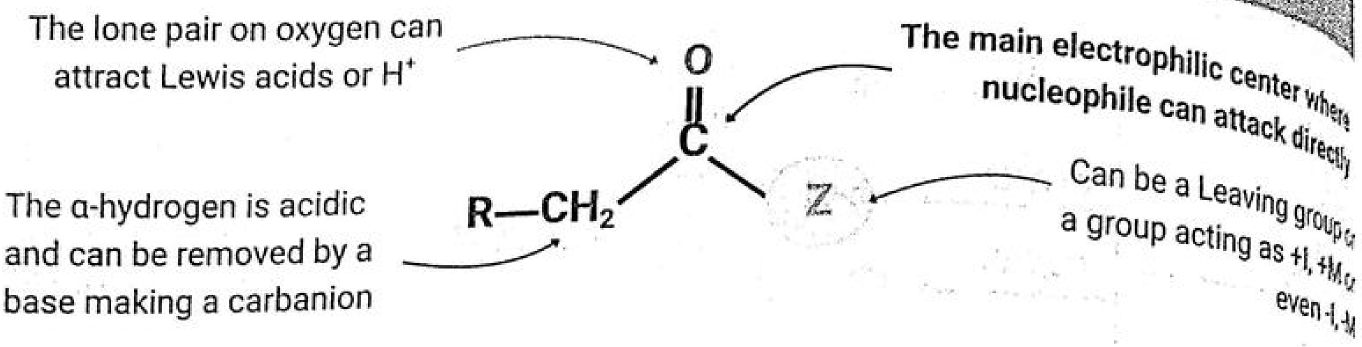
Treatment of an aromatic amine with nitrous acid (or sodium nitrite, which is converted to nitrous acid in the presence of acid) in the presence of a strong acid like HCl results in the loss of H_2O and the formation of a new N-N triple bond.



Bonus step for Organic 10

Carbonyls are often confused

1. Why is carbonyl so important?



The lone pair on oxygen can attract Lewis acids or H^+

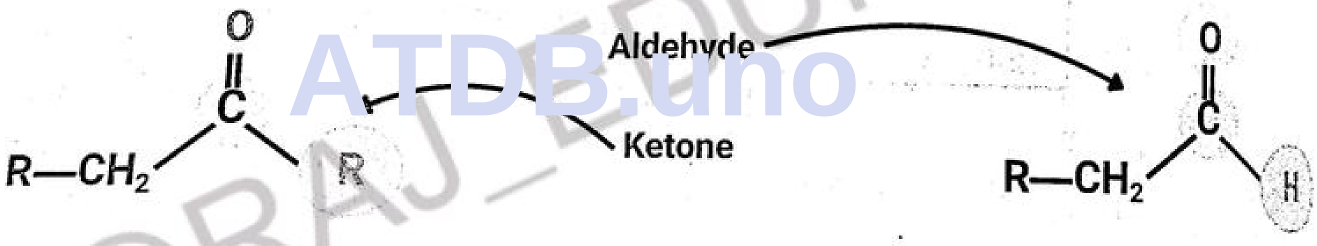
The main electrophilic center where nucleophile can attack directly

The α-hydrogen is acidic and can be removed by a base making a carbanion

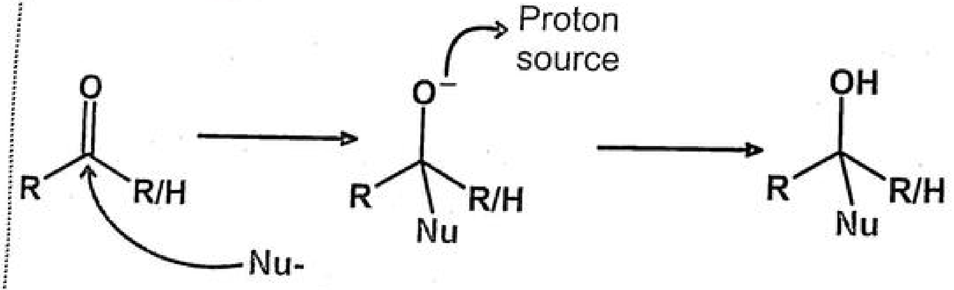
Can be a Leaving group or a group acting as +I, +M or even -I, -M

- The four different types of possibilities in carbonyl compounds make them special.
- Depending upon the group on the right **Z**, the reaction mechanism can be of two types.

1.1 The Nucleophilic addition when Z = any Alkyl chain or Hydrogen



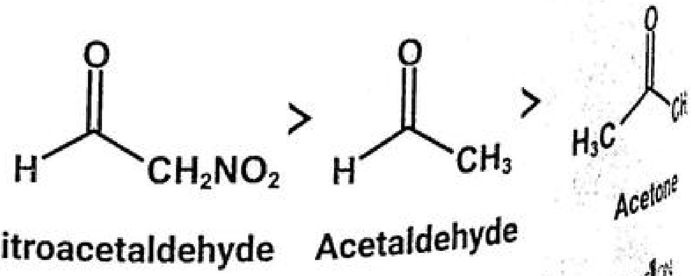
Mechnism of Nucleophilic addition



- Nucleophile attacks electrophilic carbon of the C=O group → forms tetrahedral intermediate.
- O⁻ gets protonated by a proton source
- ✕ Not substitution because no group is replaced – nucleophile adds, and nothing leaves.

Reactivity order of Aldehyde Ketones

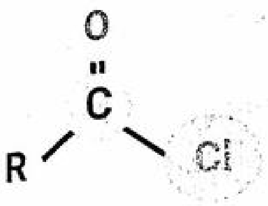
- Reactivity ∝ Electron Deficiency of Carbon
- -M, -H, -I effects increases reactivity
- Aldehydes are more reactive than ketones

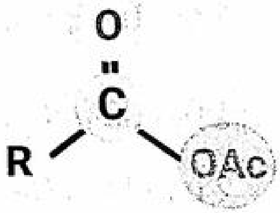


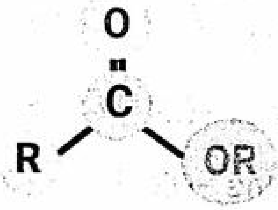
Some important trends in Reactivity

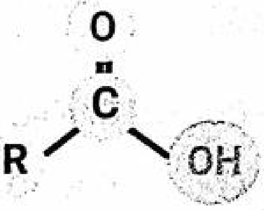
1. Aliphatic Aldehydes > Aromatic Aldehydes *(Resonance stabilised Aromatic Aldehydes)*
2. HCHO > CH_3CHO > CH_3COCH_3 *(+I of methyl decreases reactivity)*
3. p-NO_2–C_6H_4–CHO > Benzaldehyde > p-CH_3–C_6H_4–CHO *(-M of NO_2 decreases electron density on ring and carbonyl making it more elctrophilic)*
4. Cyclopropanone > Cyclobutanone > Cyclopentanone > Acyclic ketones *(Small rings are more reactive due to angle strain)*

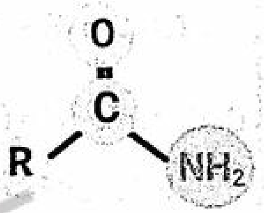
1.2 The Nucleophilic Substituion when Z = Cl, OAc, OH, NH_2


Acyl Halide

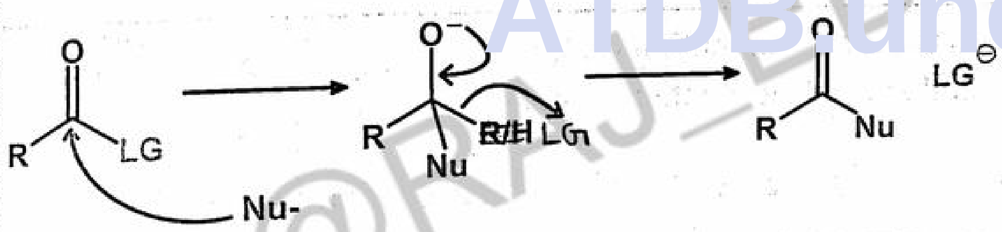

Anhydride


Ester


Carboxylic acid


Amide

Mechnism of Nucleophilic addition



- Nu⁻ attacks the carbonyl carbon → forms tetrahedral intermediate.
- O⁻ collapses back, reforming the C=O bond.
- LG⁻ leaves, giving final substituted carbonyl product.

Reactivity order of carboxylic acid derivatives

- Leaving group Tendency = -Cl > -$COCH_3$ > -OCH_3 > -OH > -NH_2
- Reactivity: Acyl Chloride > Anhydride > Ester > Carboxylic acids >Amide.
- R-C=O group is known as acyl group.

2. Oxidation Level of Organic Compounds

Compound / Functional Group	Structure Clue	Oxidation Level (0–4)	Why (No. of electronegative atoms attached)
Alkane (CH_4, CH_3-CH_3)	No O, N, halogen	0	No electronegative atoms
Alcohol ($R-CH_2-OH$)	One OH group	1	1 bond to O
Diol ($R-CH(OH)-CH_3$)	Two OH groups	2	2 bonds to O
Aldehyde ($R-CHO$)	One =O + one H	2	1 double bond to O = 2 electronegative bonds
Ketone ($R-CO-R'$)	One =O between two C	2	1 double bond to O = 2
Carboxylic acid ($R-COOH$)	One =O + one −OH	3	2 bonds to O in total (1 OH + 1 =O)
Ester ($R-COOR'$)	One =O + one −OR	3	2 bonds to O
Carbonic acid derivative ($R-O-CO-OH$)	3 Oxygens	4	3 bonds to O (1 OR + 1 OH + 1 =O)
Carbon dioxide (CO_2)	O=C=O	4	2 double bonds to O = 4 electronegative bonds

- To go from Lower Oxidation level to higher : **Oxidation** Happens
- To go from higher to Lower Oxidation level : **Reduction** Happens

IMPORTANT

2.1 Hydride Donors to Lower O.L. of Carbonyl Compounds

Functional Group	$LiAlH_4$	$NaBH_4$	DIBAL-H (−78 °C)	$BH_3·THF$
Aldehyde	☑ → $R-CH_2OH$	☑ → $R-CH_2OH$	✗	✗
Ketone	☑ → R_2CHOH	☑ → R_2CHOH	✗	✗
Carboxylic Acid	☑ → $R-CH_2OH$	✗	✗	☑ → $R-CH_2OH$
Ester	☑ → 2° Alcohols	✗	☑ → Aldehyde	✗
Amide	☑ → Amine	✗	✗	✗
Nitrile	☑ → Amine	✗	☑ → Aldehyde	✗

Step Towards Organic 11

Nucleophilic addition to Aldehyde and Ketones

1. Before that, How do they form?

- We have already discussed few reactions which forms aldehyde, ketones, like **hydroboration oxidation, oxymercuration demercuration** from alkynes.
- Apart from above, Aldehyde or ketones can form only via either Oxidation or Reduction.

1.1 Oxidation Reactions to form Aldehyde/Ketones

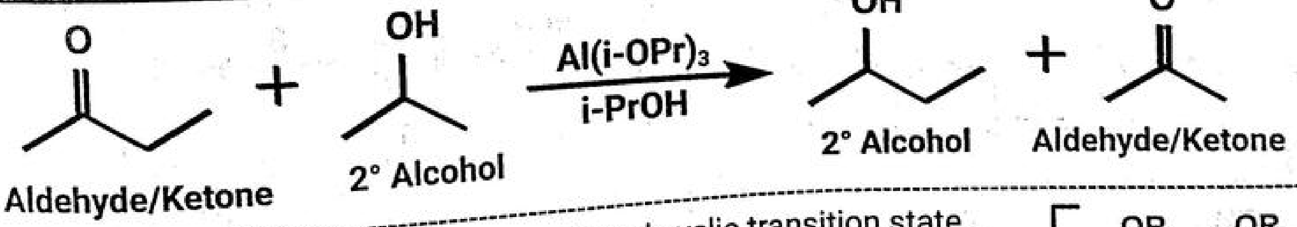
Conversion of Alcohols to Aldehydes or Ketones via Oxidation

Oxidizing Agent	Converts	Remarks
PCC (Pyridinium Chlorochromate)	1° OH → Aldehyde 2° OH → Ketone	Mild and selective. No water = no overoxidation to acid.
PDC (Pyridinium Dichromate)	1° OH → Aldehyde 2° OH → Ketone	Similar to PCC, slightly stronger, used in non-aqueous medium.
Cu or ZnO (Dehydrogenation)	1° OH → Aldehyde 2° OH → Ketone	Done by heating vapours of alcohol over metal catalyst (Cu, ZnO).
Jones Reagent ($CrO_3 + H_2SO_4$ in acetone)	1° OH → Carboxylic Acid 2° OH → Ketone	Strong oxidizer. Not used for aldehyde prep due to overoxidation.
Collins Reagent (CrO_3 + pyridine in CH_2Cl_2)	1° OH → Aldehyde only	Used in anhydrous conditions to stop at aldehyde. Milder than Jones.

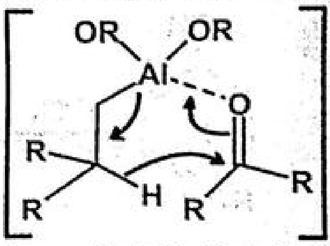
The Reaction performing both Oxidation and Reduction

Meerwein Pondorff Varley and Oppenauer oxidation

NAME 16 REACTION



- The reaction proceeds via a six-membered cyclic transition state.
- The hydride from the secondary alcohol (e.g., isopropanol) is transferred to the carbonyl carbon of the aldehyde or ketone.
- The carbonyl gets reduced to alcohol, and the secondary alcohol becomes a ketone (acetone).
- **Forward rxn** : MPV Reduction, **Backward rxn** : Oppenauer Oxidation

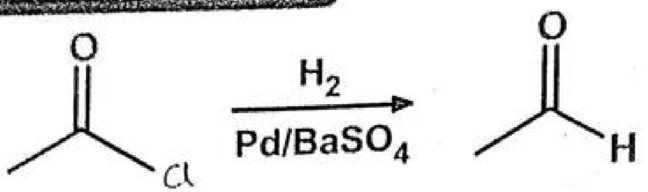


Intermediate in Reaction

1.2 Reduction Reactions to form Aldehyde/Ketones

Reduction of Acid Chloride

Rosenmund Reduction

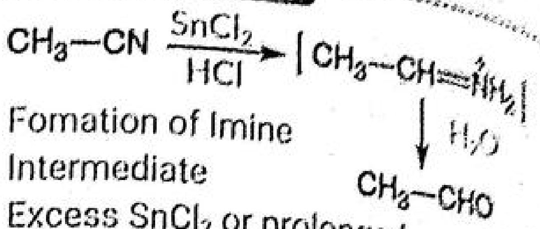


- $BaSO_4$ reduces activity of Pd,
- Poisons like Quinoline-S, Xylene is added

NAME 17 REACTION

Reduction of Nitriles

Stephens Reduction



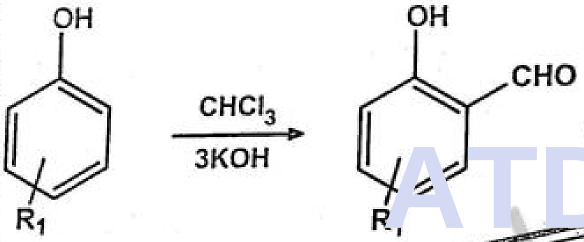
$$CH_3-CN \xrightarrow[HCl]{SnCl_2} [CH_3-CH=\overset{+}{N}H_2] \xrightarrow{H_2O} CH_3-CHO$$

- Fomation of Imine Intermediate
- Excess $SnCl_2$ or prolonged reaction can sometimes lead to primary amine

NAME 18 REACTION

1.3 Other important Name Reactions to form Benzene Aldehydes

Riemer Tiemann Reaction

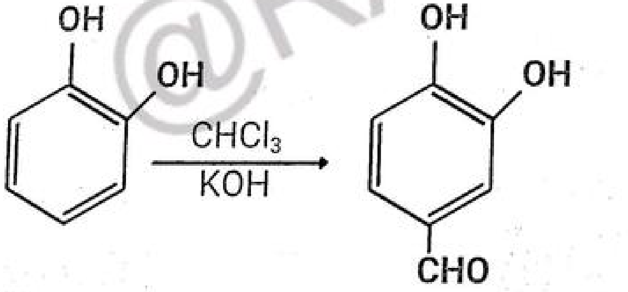


- Carbene is the intermediate
- **Used for** : Introducing –CHO group (formylation) at the ortho-position of phenols.
- Mainly ortho-hydroxybenzaldehyde (salicylaldehyde) minor para product.

NAME 19 REACTION

Important Examples

①



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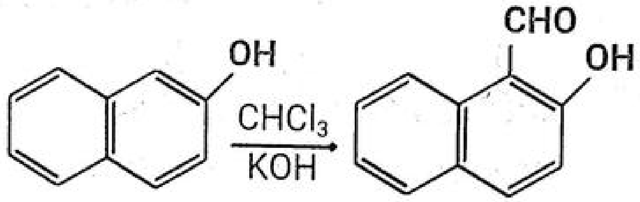

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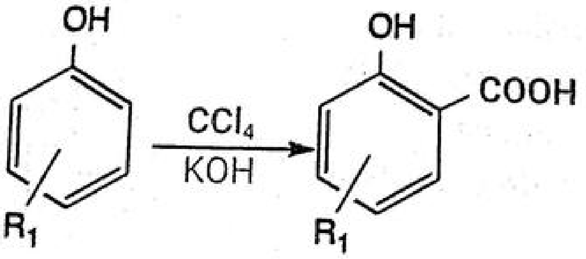
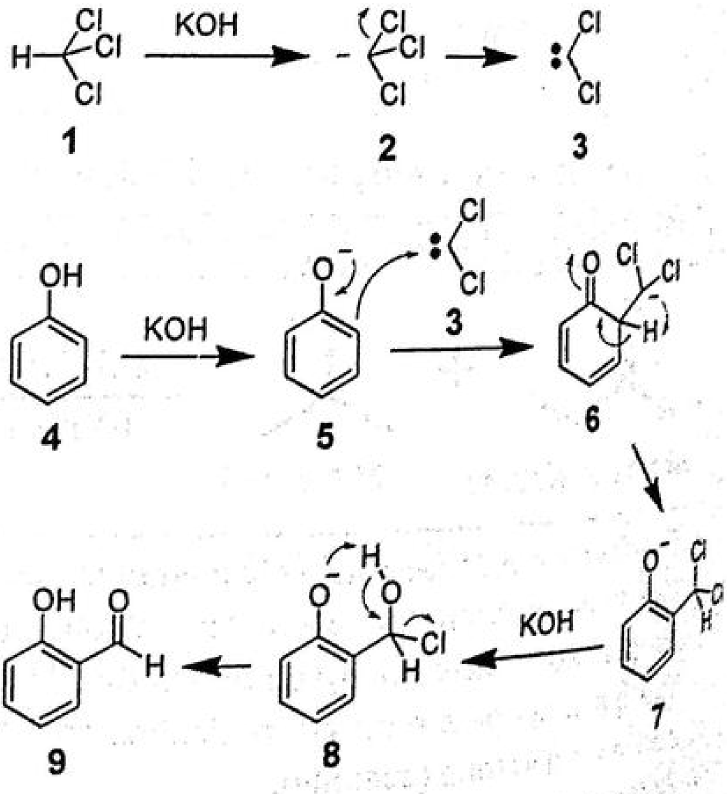
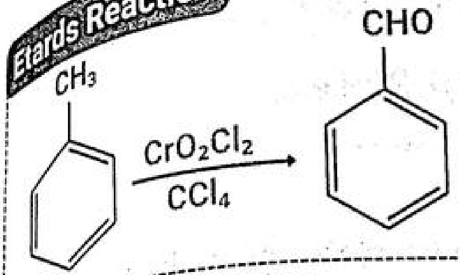


Mechanistic Glance



When CCl_4 is used, the resultant is COOH and not CHO

Etards Reaction

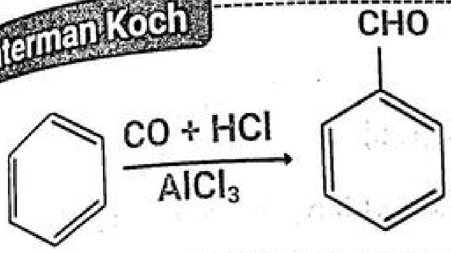


- Convert toluene ($C_6H_5-CH_3$) into benzaldehyde (C_6H_5-CHO)
- Chromyl chloride forms a complex with the benzylic hydrogen and oxidizes the $-CH_3$ group to $-CHO$.

NAME 20 REACTION

The two name reactions to convert Benzene to Benzaldehyde

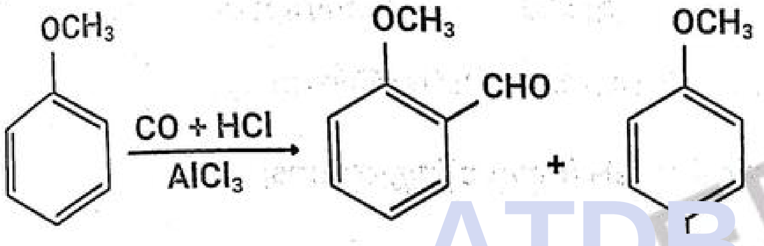
Gaterman Koch



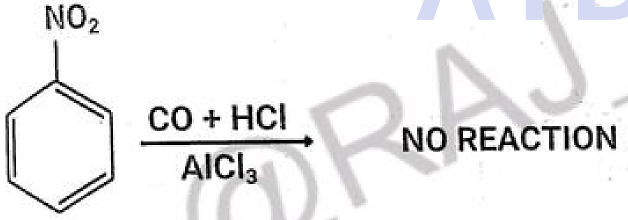
- Reaction of CO + HCl Generates $H-C^{+}=O$ (Formylium ion)
- It is attacked by benzene ring via Electrophilic aromatic substitution

NAME 21 REACTION

Important Examples

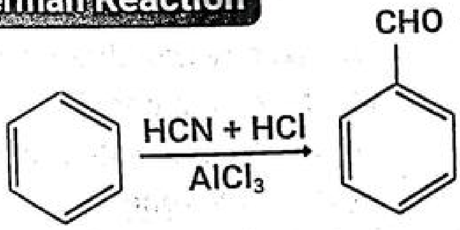


OCH_3 is a +M group activating ortho and para positions for the external Electrophile



NO_2 withdraws electrons from the ring and thus an external electrophile like formylium ion couldn't react

Gaterman Reaction



- If CO is unavailable we use HCN + HCl
- Intermediate formed is : $ClCH=NH^{+}CN$ (Electrophile)
- Similar to Gaterman Koch

NAME 22 REACTION

2. Nucleophilic Addition via different nucleophiles

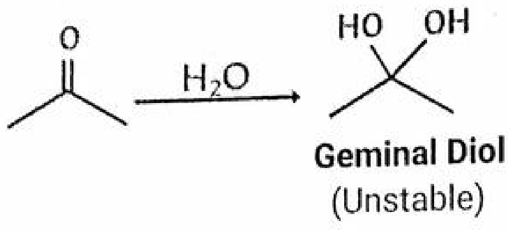
- Various nucleophiles can be added to Aldehyde and ketones, we will study the important ones step by step.

Nucleophile	Product Formed	Special Use
CN^- (HCN)	Cyanohydrin	Synthesis intermediate
$NaHSO_3$	Bisulfite addition compound	Purification

2.1 Nucleophiles with attacking atom as Oxygen

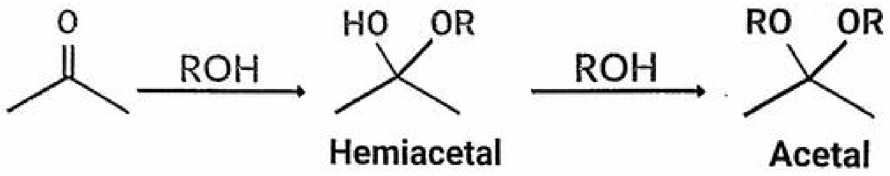
- Some nucleophiles with attacking atom as oxygen can be H_2O, ROH etc.

Addition of water - Formation of Geminal Diols



- Aldehyde gives more stable gem-diol than ketone (less steric hindrance)
- No catalyst needed, but acid/base can accelerate the reaction.

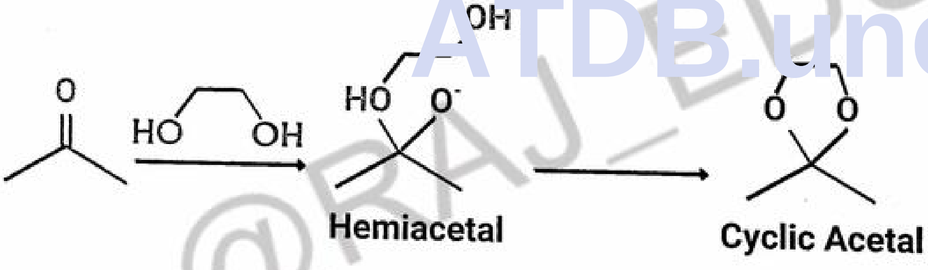
Addition of Alcohols - Formation of Acetals (Protecting groups)



- Aldehyde reacts with alcohol → Hemiacetal → Acetal
- Ketones can also form hemi/acetals, but less stable.

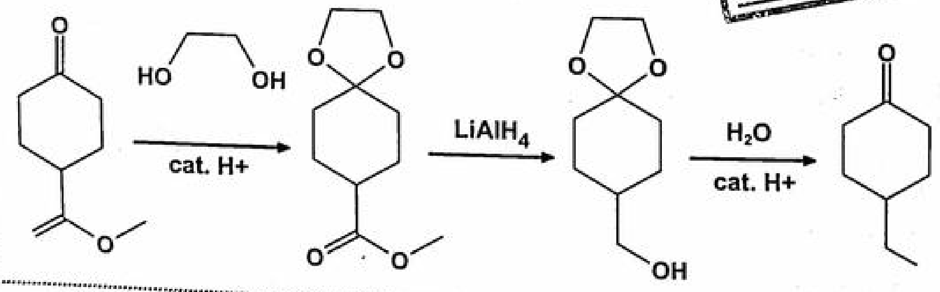
Used to protect carbonyl groups during synthesis (**Acetal as protecting group**)

Addition of Alcohols - Formation of Cyclic Acetals (Protecting groups)



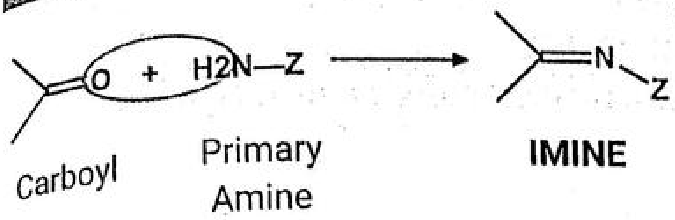
Acetals acting as protecting group

IMPORTANT



- $LiAlH_4$ reduces both ketone and ester to alcohol.
- To reduce only ester, we have to protect ketone.
- Making an acetal of ketone protects it from reduction

2.2 Nucleophiles with attacking atom as Nitrogen



Easy Shortcut for Reaction of ***Amines***

- The nitrogen of the primary amine (NH_2–Z) donates its lone pair to the electrophilic carbonyl carbon, forming a tetrahedral intermediate.
- A proton transfer occurs, making the hydroxyl group a better leaving group.
- Water (H_2O) is eliminated, resulting in the formation of a C=N–Z (imine) bond.

Reagent (NH_2–Z)	Product Type	General Product Formula	Z Group
NH_2–OH (Hydroxylamine)	Oxime	R_2C=N–OH	–OH
NH_2–NH_2 (Hydrazine)	Hydrazone	R_2C=N–NH_2	–NH_2
NH_2–Ph (Phenylhydrazine)	Phenylhydrazone	R_2C=N–NHPh	–NH–C_6H_5
NH_2–$CONH_2$ (Semicarbazide)	Semicarbazone	R_2C=N–NH–CO–NH_2	–NH–CO–NH_2

3. Distinguishing Tests for Aldehyde and Ketones

Compound	2,4 DNP Test	Sodium Bisulfite Test	Tollens' Test	Benedict's Test	Fehling's Test	Iodoform Test
Aldehyde	☑	☑	☑	☑ Aliphatic only	☑ Aliphatic only	☑ Only Ethanal
Ketone	☑	☑ Only methyl ketones	✗	☑ Only α-hydroxy methyl ketones	✗	☑ Only methyl ketones
Formaldehyde	☑	☑	☑	☑	☑	✗
Acetaldehyde	☑	☑	☑	☑	☑	☑
Benzaldehyde	☑	☑	☑	✗	✗	✗
Acetophenone	☑	✗	✗	✗	✗	☑
Benzophenone	☑	✗	✗	✗	✗	✗

IMPORTANT

Why Benzaldehyde Passes Tollen's but Fails Benedict's/Fehling's:

- Tollen's reagent (Ag^+) oxidizes both aliphatic and aromatic aldehydes.
- Benedict's and Fehling's (Cu^{2+}) oxidize only aliphatic aldehydes, not aromatic ones.

Why Benzophenone & Acetophenone Fail Most Tests:

- They are ketones, which don't react with mild oxidizing agents like Tollen's or Fehling's.
- Aromatic rings reduce carbonyl reactivity via resonance, making nucleophilic additions harder.
- Benzophenone lacks CH_3-CO-, so it fails the iodoform test.
- Acetophenone passes iodoform test because it has a methyl ketone group (CH_3-CO-).

Test Details

Tollens' Test

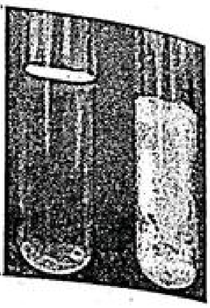
Reagent: Ammoniacal silver nitrate → $2[Ag(NH_3)_2]^+ + OH^-$

Detects: Aldehydes only (both aliphatic and aromatic)

Reaction: Aldehyde gets oxidized to carboxylic acid, Ag^+ gets reduced to Ag

Observation: Formation of shiny silver mirror on the inner wall of the test tube

Not for : Ketones (they resist oxidation under these mild conditions)



Benedict's test

- **Reagent**: Copper(II) citrate complex → $Cu(C_6H_5O_7)^{2-}$ in alkaline medium
- **Detects**: Aliphatic aldehydes (and some α-hydroxy ketones)
- **Reaction**: Aldehyde → carboxylic acid; $Cu^{2+} \rightarrow Cu_2O$ (Cu^+)
- **Observation**: Formation of brick-red precipitate of Cu_2O
- **Fails For**: Aromatic aldehydes (e.g., benzaldehyde)

Fehling's Test

- **Reagent**:
  - **Fehling A**: $CuSO_4 \cdot 5H_2O$
  - **Fehling B**: Alkaline solution of Rochelle's Salt (sodium potassium tartrate)
- **Detects**: Aliphatic aldehydes only
- **Reaction**: Aldehyde → carboxylic acid; $Cu^{2+} \rightarrow Cu_2O$
- **Observation**: Red precipitate of Cu_2O
- **Fails For**: Aromatic aldehydes and ketones

Iodoform Test

- **Reagent**: $I_2 + NaOH$ (or $KI + NaOCl$)
- **Detects**:
  - Methyl ketones (CH_3-CO-R)
  - Compounds with $CH_3-CH(OH)-$ group (on oxidation)
- **Reaction**: $R-CO-CH_3 \rightarrow R-COO^- + CHI_3$
- **Observation**: Formation of yellow precipitate of CHI_3 (iodoform) with antiseptic smell
- **Positive For**: Acetophenone, acetaldehyde, ethanol
- **Negative For**: Benzaldehyde, benzophenone

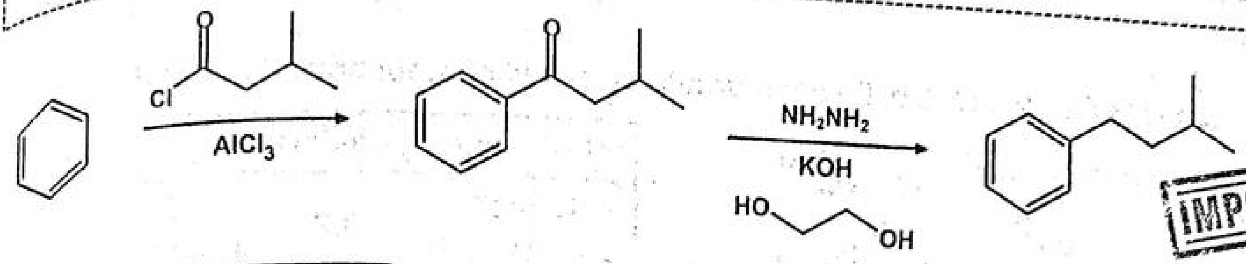
4. Removing C=O

Wolff Kishner Reaction

$R-CO-R' + NH_2NH_2 + KOH \rightarrow R-CH_2-R' + N_2\uparrow + H_2O$

Strongly basic, high temperature

NAME23 REACTION



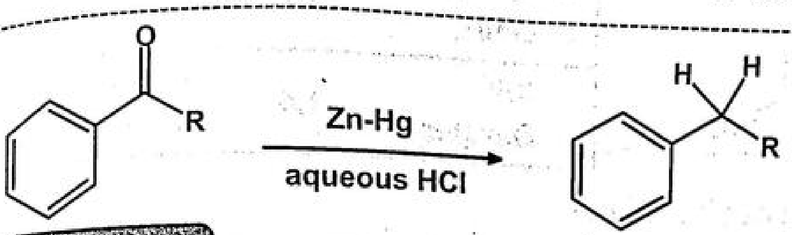
IMPORTANT

Clemmensen Reduction

$R-CO-R' + Zn(Hg) + HCl \rightarrow R-CH_2-R' + H_2O$

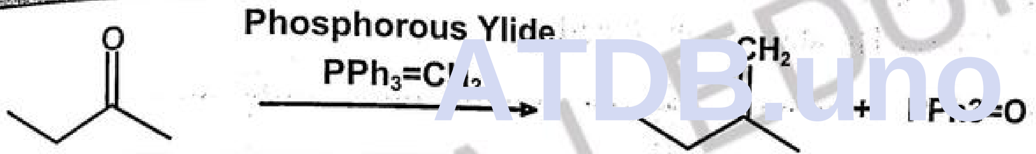
Strongly acidic, room or mild heating

NAME24 REACTION



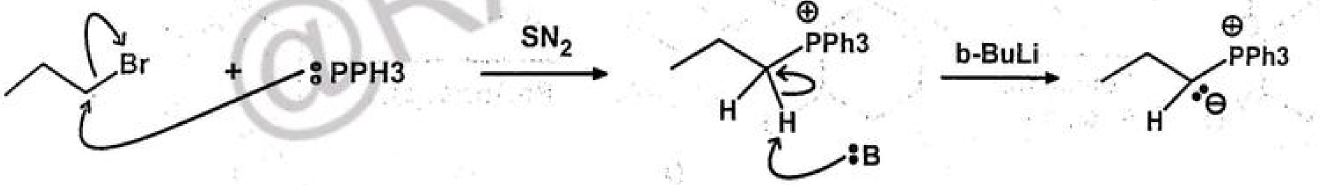
Wittig Reaction

NAME25 REACTION



IMPORTANT

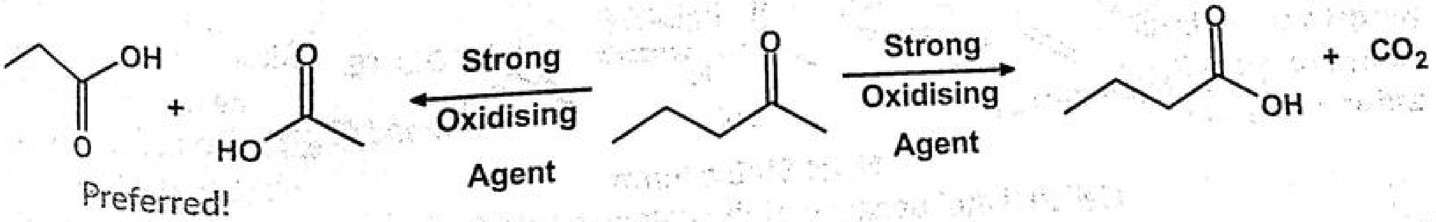
How to form Phosphorous Ylide?



- The Reaction proceeds towards elimination of P=O since oxygen has higher affinity towards Phosphorous than Oxygen. **Wittig is stereoselective (usually gives Z-alkene)**

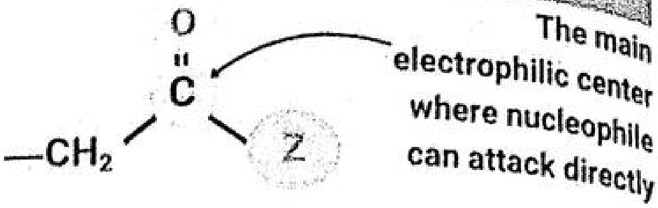
5. Breaking sides of Ketones, C=O Selectively - Popoff's Rule

During the oxidation of an unsymmetrical ketone, the C–CO bond breaks in such a way that the smaller alkyl group remains attached to carbonyl carbon to form a carboxylic acid, while the larger group is cleaved and further oxidized (usually to another acid, formic acid, or CO_2).



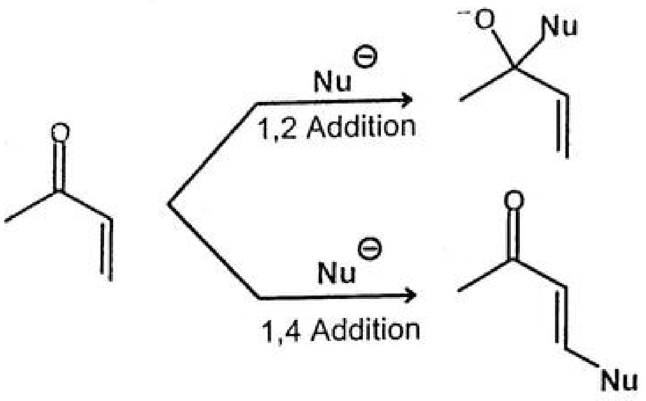
6. 1,2 vs 1,4 Nucleophilic Addition in Aldehydes and Ketones

When we consider the Nucleophilic substitution on a carbonyl carbon, the nucleophile always attacks at the Carbon in C=O (carbonyl).



The main electrophilic center where nucleophile can attack directly

But the case changes when we take α, β - unsaturated carbonyl compounds into consideration.

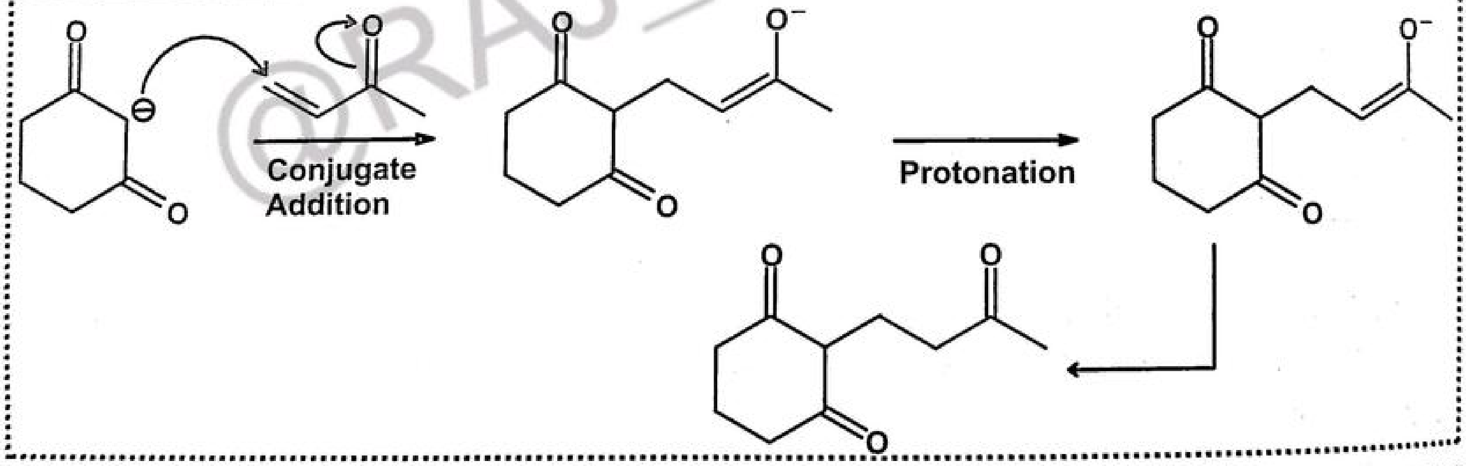


Nucleophile	Addition	Why?
• R–MgX • R–Li	1,2	Hard nucleophile; attacks C=O directly
• R_2CuLi	1,4	Softer nucleophile; prefers β-carbon
• $NaBH_4$ • $LiAlH_4$	1,2	Direct hydride attack on C=O
• CN^- • Enolates	1,4	Delocalized, prefers conjugate attack

- **The 1,4 Attack of Enolates (Acting as nucleophiles)**

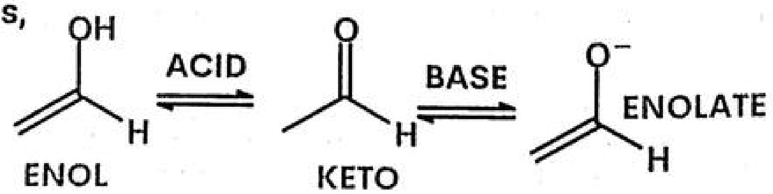
  Michael addition is a 1,4-conjugate addition of a nucleophile to an α,β-unsaturated carbonyl compound, forming a stabilized product via the β-carbon.

Michael Addition



7. Enolates - The part to study name Reactions

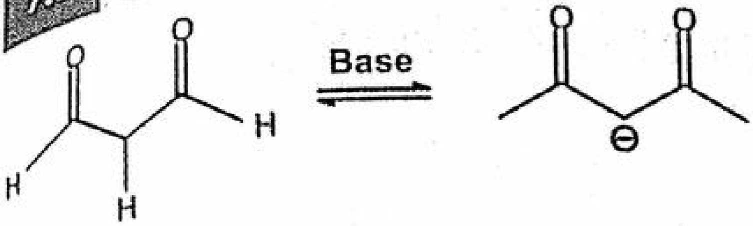
Under acidic conditions,
One hydrogen shifts, and you get a double bond between carbons (C=C) and an –OH group.



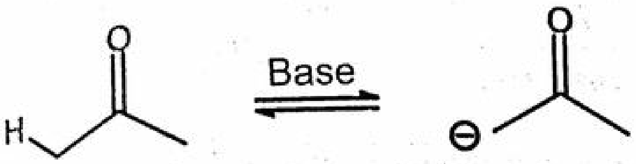
Under Basic conditions,
A base removes a hydrogen from the carbon next to the C=O. This creates a negative charge, which is stabilized by the oxygen.

Most Stable Form
Called "keto" because of the ketone or aldehyde group.

7.1 To form Enolate : Ease of Abstraction of H varies

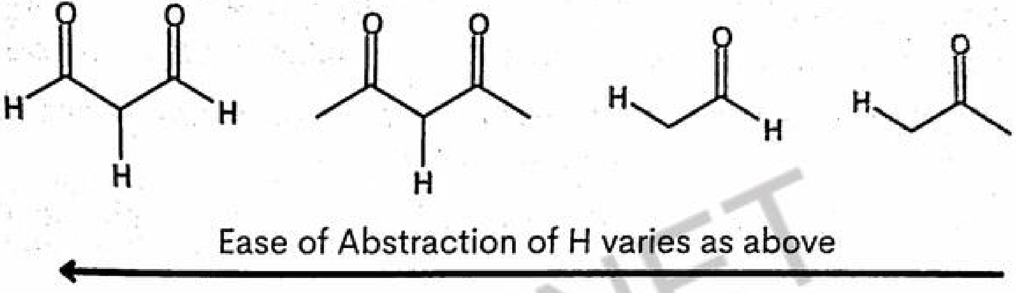


Two carbonyls stabilize the enolate via resonance → very acidic α-H



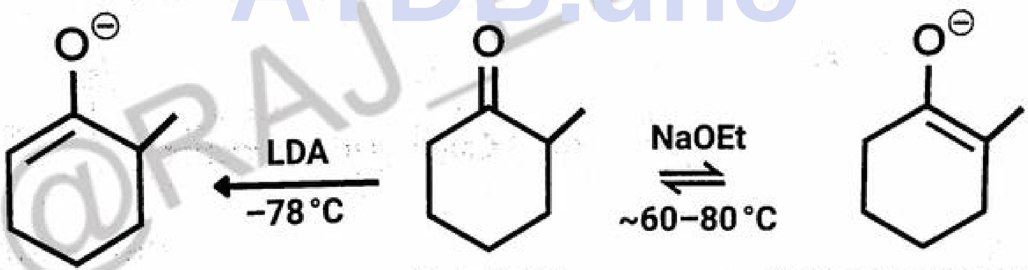
Only one carbonyl to stabilize the enolate

Remember : "More carbonyl = more stable enolate = easier H+ loss"



Ease of Abstraction of H varies as above

7.2 Kinetic vs Thermodynamic Enolates



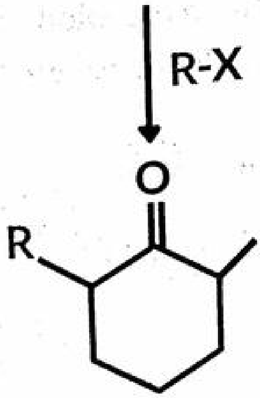
Less substituted enolate
Fast, irreversible abstraction of less hindered α-H

Keto form

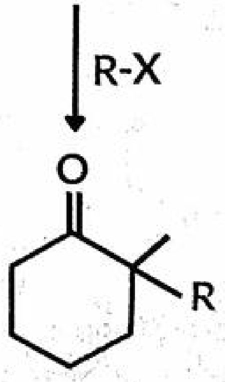
More substituted enolate
Reversible, equilibrium-favored

Bulky, strong base (e.g., LDA) and Low temperature (≈ −78 °C) gives **Kinetic Product**

Small, weaker base (e.g., NaOEt, NaOH) andHigh temperature (reflux or warm, 60−80 °C) gives **Thermodynamic Product**



Thermodynamic Product



Kinetic Product

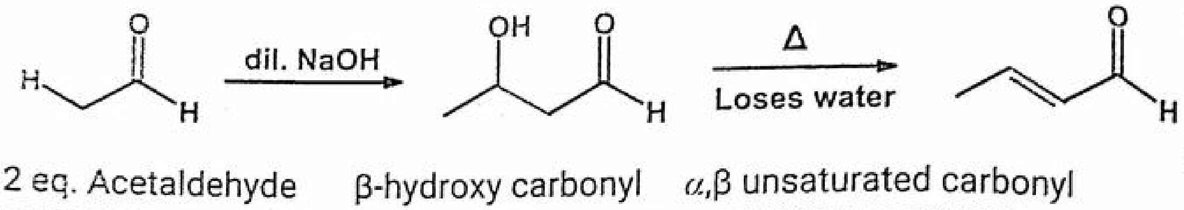
8. Most Important Reactions of Enolates

8.1 Alpha-H atoms in both Reactants

Aldol Condensation

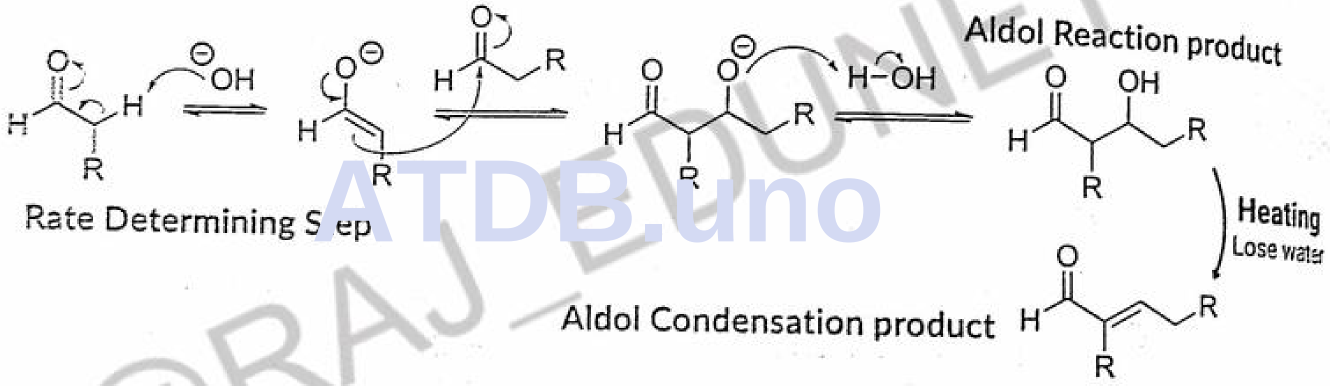
IMPORTANT

NAME 27 REACTION



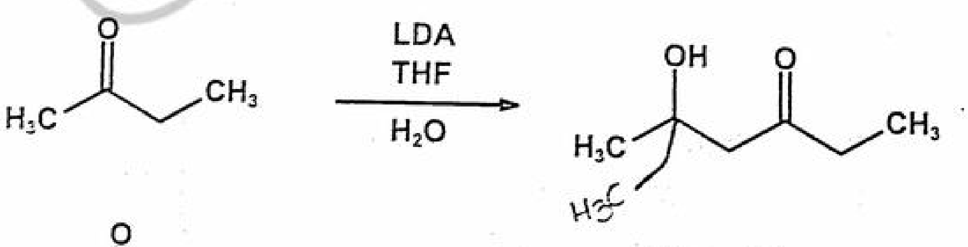
When aldehydes or ketones having at least one α-hydrogen are treated with dilute base, they undergo nucleophilic addition followed by condensation, forming a β-hydroxy aldehyde or ketone.

- Aldehydes are more reactive due to less steric hindrance and more electrophilicity.
- Only compounds with at least one α-H participate
- Benzaldehyde and Formaldehyde (H−CHO) does not undergo aldol



Examples

①



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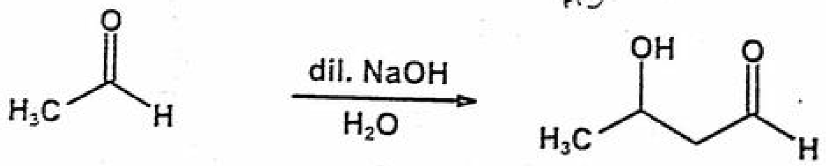

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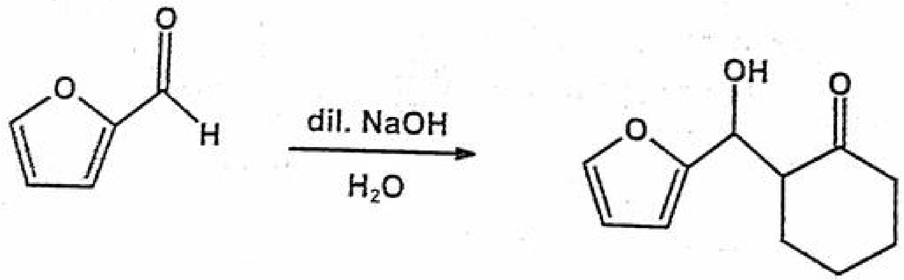
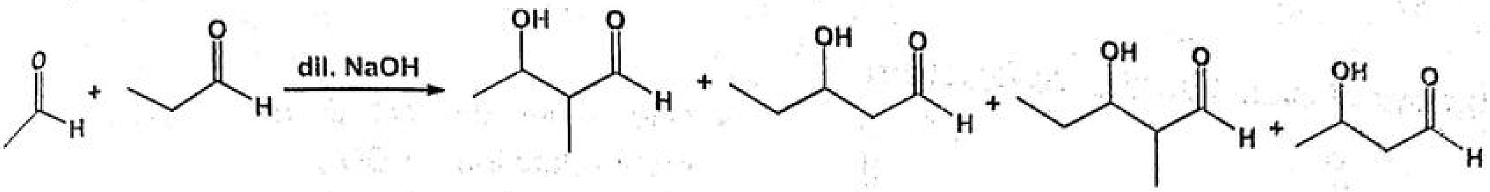
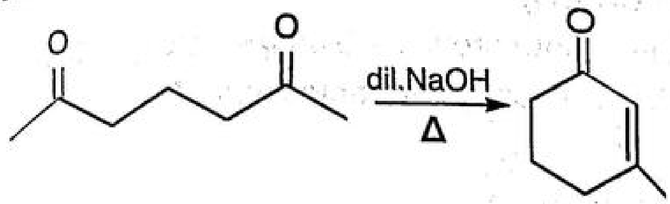


Crossed Aldol Reaction

- If Compound A and Compound B both have at least one α-hydrogen:
  - A + B → multiple possible aldol products
- This happens because both can form enolates, and both can act as electrophiles, leading to a mixture of products.



Intramolecular aldol Reaction

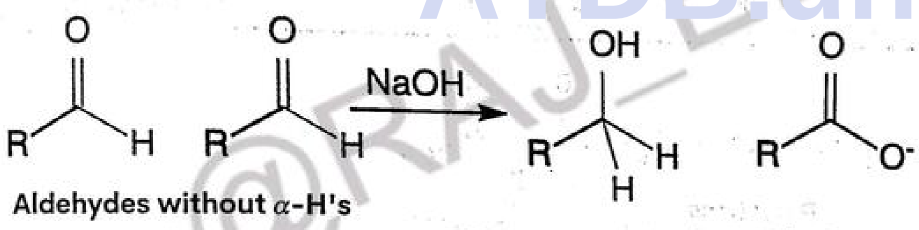


- Preferentially forms 5- or 6-membered rings (stable)

It's an aldol condensation that happens within the same molecule — when a molecule has two carbonyl groups(aldehyde or ketone), and one of them forms an enolate that attacks the other.

8.2 No Alpha H in any reactant

Cannizaro Reaction

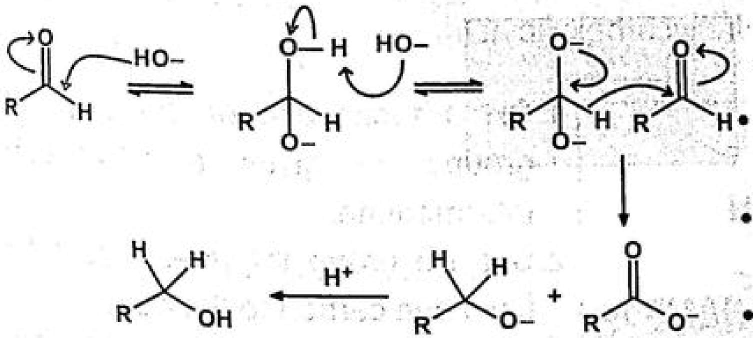


Aldehydes without α-H's

IMPORTANT

NAME28 REACTION

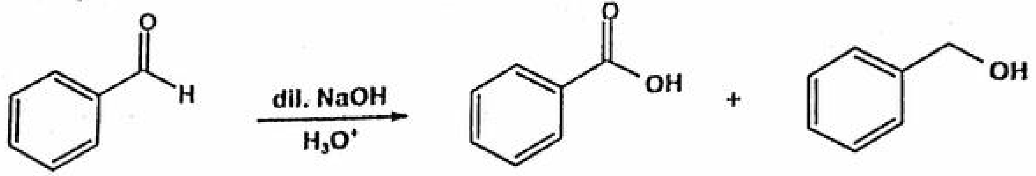
- A disproportionation reaction in which non-enolizable aldehydes (i.e., no α-hydrogens) react with strong base to give:
  - One molecule of alcohol (reduced)
  - One molecule of carboxylic acid salt (oxidized) which is hydrolysed to form Acid.



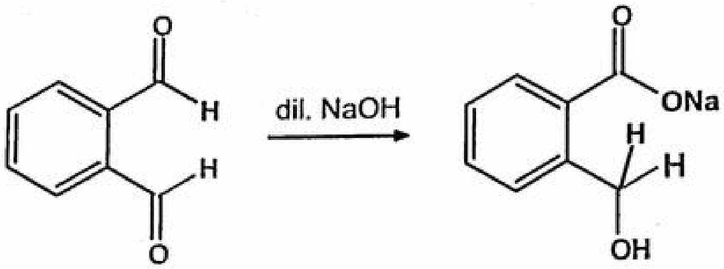
Rate Determining Step

- OH⁻ attacks the carbonyl carbon → forms a tetrahedral intermediate
- This **intermediate transfers a hydride** (H⁻) to another aldehyde molecule
- Acidification gives carboxylic acid (if needed)

Example



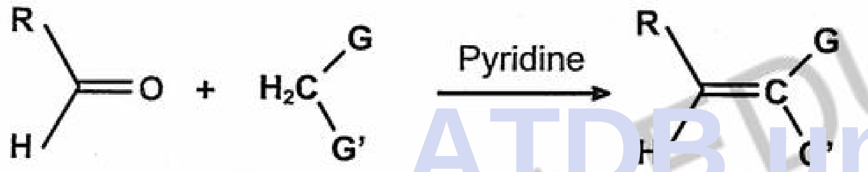
Intramolecular Cannizzaro Reaction



- One aldehyde group gets oxidized → carboxylate ion (–COO-)
- The other aldehyde gets reduced → alcohol (–CH_2OH)
- Since both groups are on the same molecule, the reaction is intramolecular.

8.3 Knoevengal Reaction

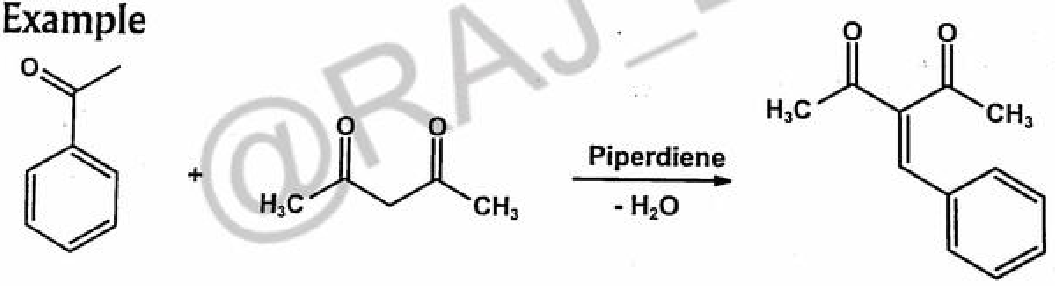
- It is a condensation reaction between an aldehyde or ketone and a compound containing **active methylene hydrogens.**



G and G' are Electron withdrawing -M groups

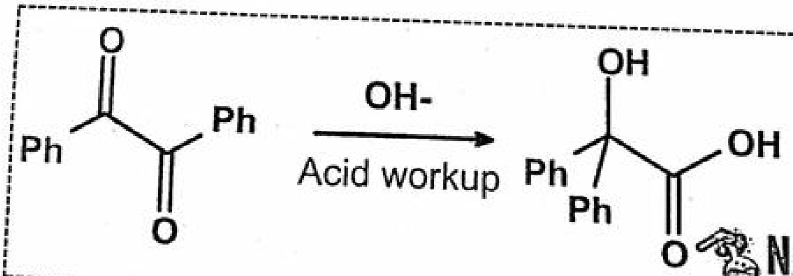
NAME25 REACTION

Example



8.4 Benzil-Benzilic Rearrangement

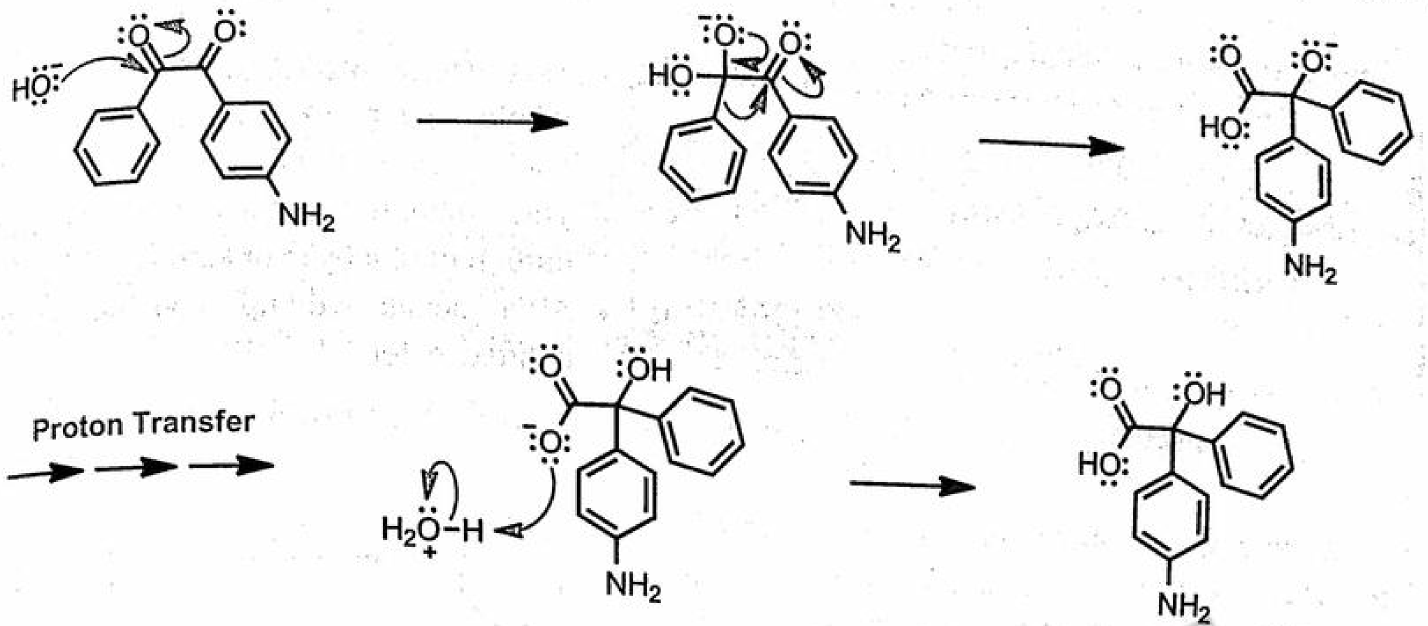
- When benzil **(a 1,2-diketone)** is treated with a strong base (like NaOH), it undergoes rearrangement to form **benzilic acid**, an α-hydroxycarboxylic acid.



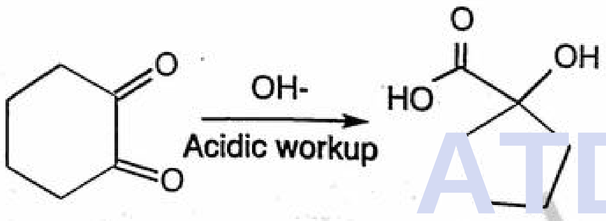
NAME26 REACTION

1. OH⁻ attacks one of the carbonyl groups → gives a tetrahedral intermediate.
2. One Ph group migrates (1,2-shift) from one carbon to the other
3. Generates a Carboxylic acid after acidic work and a tertiary alcohol

- Important fact to note : OH- attacks the carbonyl which is more electrophilic, Like in example below, It doesn't connect to carbonyl carbon which is connected to benzene with NH_2 (+M gp.)



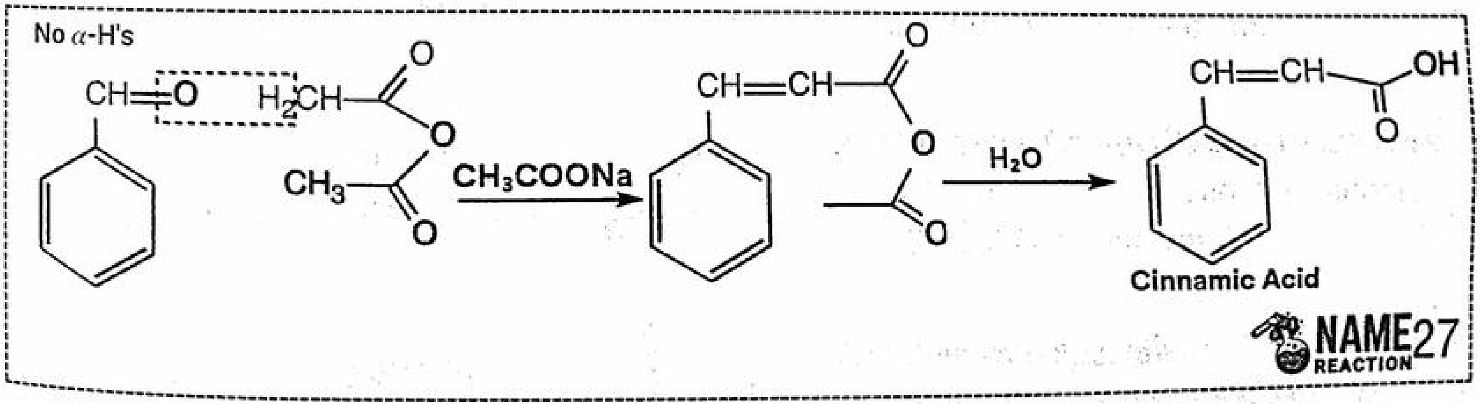
Ring contraction with benzil benzilic acid rearrangement



- In normal Benzil rearrangement, a phenyl or alkyl group shifts → no ring contraction.
- But in cyclic 1,2-diketones, the migrating group is part of the ring, so when it moves, it shortens the original ring.

8.5 Perkin Reaction

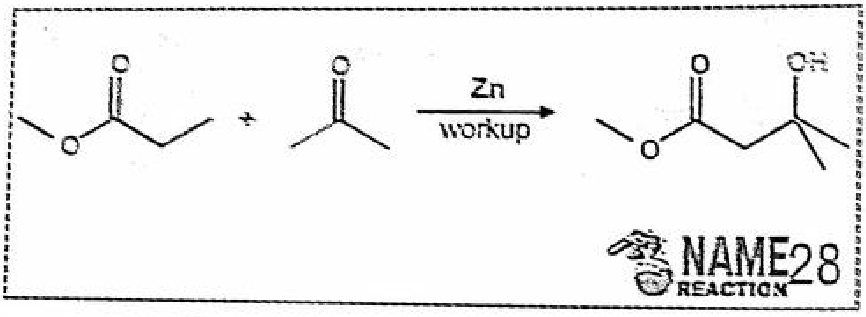
- The Perkin Reaction is a base-catalyzed condensation between an aromatic aldehyde and an acid anhydride in the presence of a weak base (like sodium salt of the acid) to form α,β-unsaturated carboxylic acids.



8.6

Reformatsky Reaction

- A reaction in which an **α-halo ester** reacts with an aldehyde or ketone in the presence of zinc metal to form a **β-hydroxy ester.**

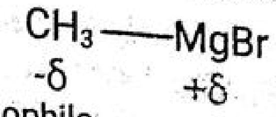


- Zinc inserts into the C–Br bond of the α-halo ester → forms organozinc enolate (Reformatsky reagent)
- This enolate attacks the carbonyl carbon of aldehyde or ketone
- After acidic workup, you get a β-hydroxy ester

Everything about Grignard Reagent

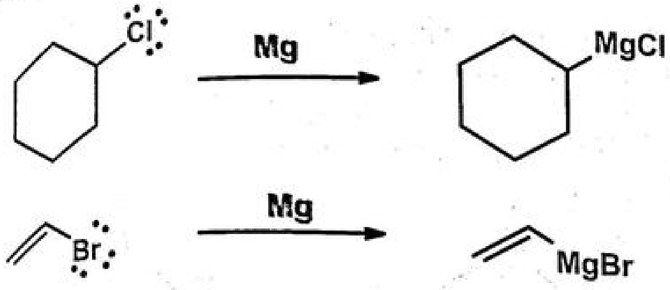
1. All types of Reaction that Grignard can undergo

- Grignard has a unique property that the alkane attached to Magnesium acts as nucleophile.
- Thus it undergoes all sorts of reactions, Acting as a base or nucleophile.



$\underset{-\delta}{CH_3}\text{——}\underset{+\delta}{MgBr}$

1.1 How do Grignards usually form in Organic Chemistry



Grignard reagents are made by reacting alkyl or alkenyl halides (Cl, Br, or I) with magnesium metal. Magnesium inserts itself between the carbon and halogen, forming RMgX. Bromides and iodides react more easily than chlorides.

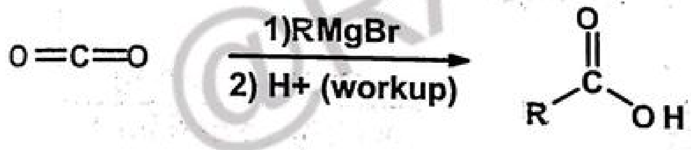
1.2 Grignards Reacting with different species

IMPORTANT

❶ $R\,MgBr \xrightarrow{R-OH} R-H$

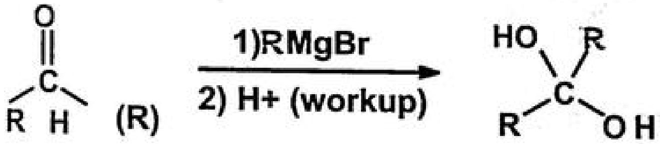
- **Reaction with Slightly acidic H**
  - Forms Alkanes (Already studied)

❷



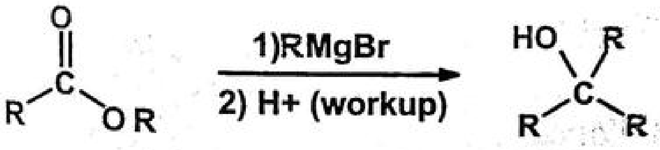
- **Reaction with Carbon Dioxide**
  - Forms Carboxylic Acid

❸



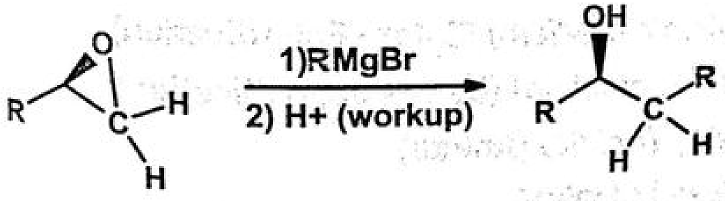
- **Reaction with Aldehyde or Ketones**
  - Adds once, Aldehydes → 1° Alcohol and Ketones → 3° Alcohols

❹



- **Reaction with Carboxylic acid Derivatives**
  - Adds twice to form Tertiary alcohol (Except First derivative)

❺



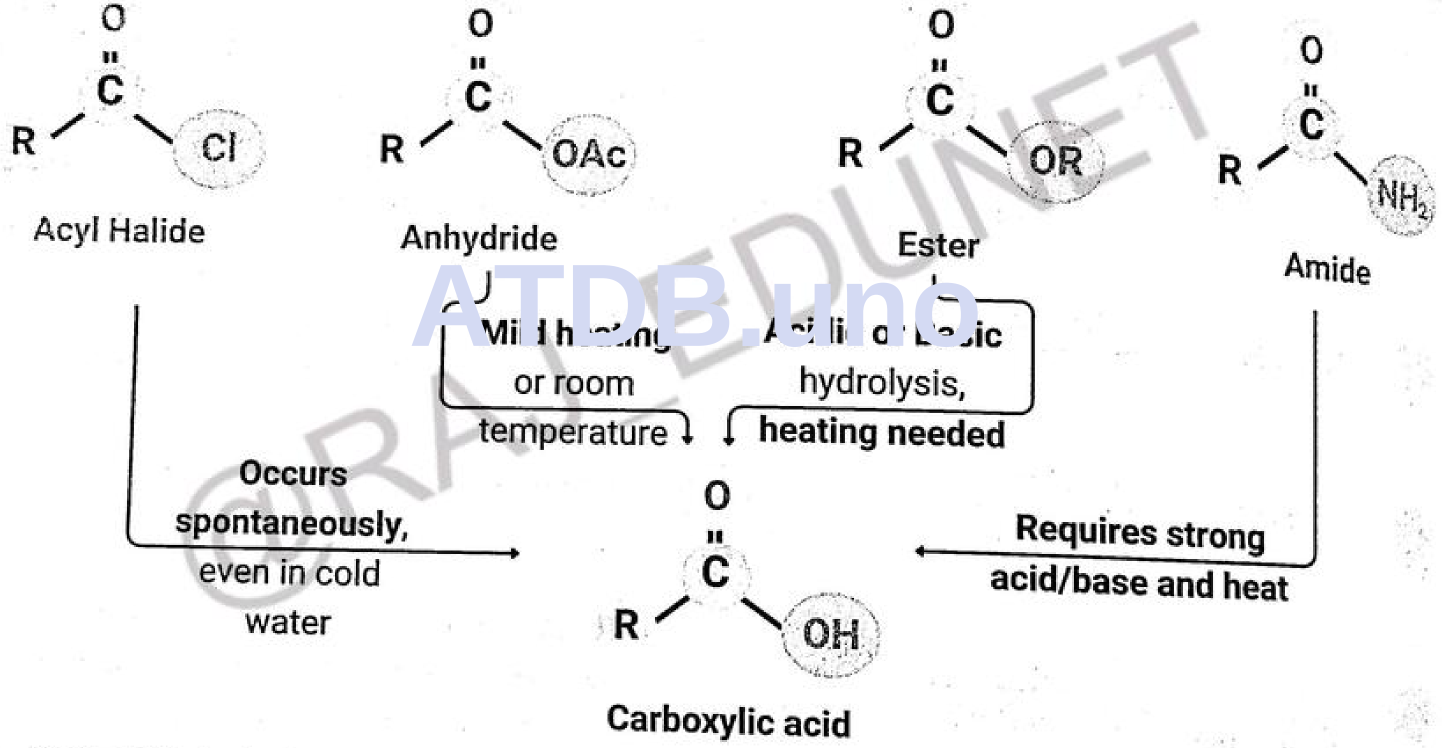
- **Reaction with Epoxides**
  - Adds to Less substituted side, ring breaks to form alcohol

Step Towards Organic 13
Carboxylic Acid Derivatives

1. Important Concepts about Carboxylic Acid Derivatives

- We have already studied, how carboxylic acids are made.
  - By using Jones reagent on 1° Alcohol.
  - By using Grignard Reagent on CO_2
- The other famous methods to make Carboxylic acid is to do Hydrolysis of it's own Derivatives depending upon the condition used or via oxidation using $KMnO_4$

1.1 Hydrolysis of Carboxylic acid Derivatives

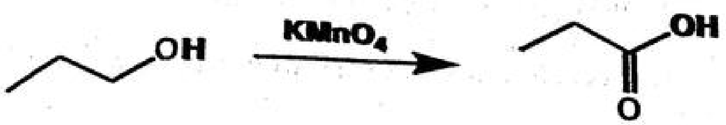


- **Ease of Hydrolysis**
  - Acid Chloride > Acid Anhydride > Ester > Amide
- **Individual Reactions**
  - $R-CO-Cl + H_2O \rightarrow R-COOH + HCl$ **(Acid Chloride)**
  - $(R-CO)_2O + H_2O \rightarrow 2\ R-COOH$ **(Anhydride)**
  - $R-CO-OR' + H_2O \rightleftharpoons R-COOH + R'OH$ *(Acidic medium)* **(Ester - Esterification)**
  - $R-CO-OR' + OH^- \rightarrow R-COO^- + R'OH$ *(Basic medium)* **(Ester - Saponification)**
  - $R-CO-NH_2 + H_2O + H^+ \rightarrow R-COOH + NH_4^+$ *(Acidic)* **(Amide)**
  - $R-CO-NH_2 + OH^- \rightarrow R-COO^- + NH_3$ *(Basic)* **(Amide)**

IMPORTANT

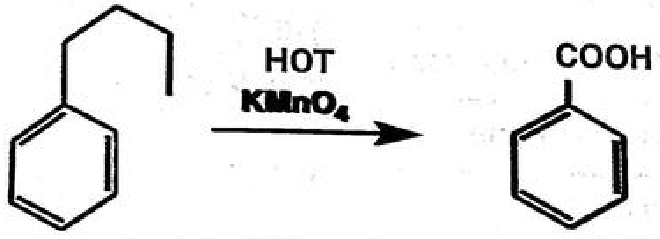
1.2 Oxidation to form Carboxylic Acid Derivatives using $KMnO_4$

- Potassium permanganate ($KMnO_4$) is a strong oxidizing agent, and it's commonly used in organic chemistry to oxidize various compounds into carboxylic acids.

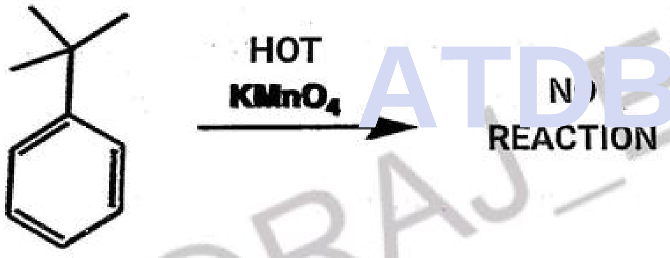


Oxidation of Primary Alcohols to Carboxylic Acids

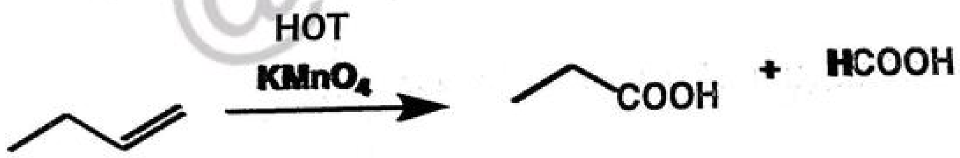
Oxidation of Aldehydes to Carboxylic Acids



Oxidation of Alkyl Side Chains in Aromatic Compounds



Oxidation of Alkyl Side Chains Doesn't happen due to no Alpha-H Present



Terminal alkenes give formic acid (HCOOH) or CO_2 upon further oxidation.

1.3 Interconversion of Carboxylic acid Derivatives

- We know that carboxylic acid derivatives undergo Nucleophilic acyl substituion, Thus we can interconvert them into each other by replacing the group already present.
- Flowchart below will help you remember all the reagents used in interconverting them.

R–COOH	R–COCl (Acid Chloride)	$SOCl_2$ / PCl_5 /
R–COOH	$(R–CO)_2O$ (Anhydride)	Heat with P_2O_5 or dehydrating agent
R–COOH	R–COOR' (Ester)	R'OH + H^+ (Fischer esterification)
R–COOH	$R–CONH_2$ (Amide)	Convert to acid chloride, then use NH_3
R-COOH	$R–COOCH_3$	React with CH_2N_2
R–COCl	$(R–CO)_2O$	React with $RCOO^-$ (carboxylate salt)
R–COCl	R–COOR'	R'OH (alcohol)
R–COCl	$R–CONH_2$	NH_3 or amine
$(R–CO)_2O$	R–COOR'	R'OH (Alcoholysis) IMPORTANT
$(R–CO)_2O$	$R–CONH_2$	NH_3 or amine
R–COOR'	$R–CONH_2$	NH_3 + heat

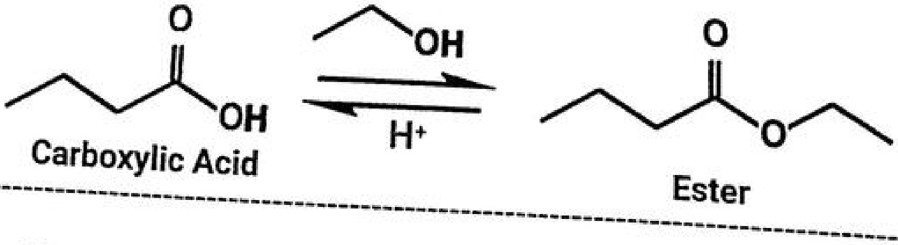
Elucidations

1. Amides cannot be interconverted into any other derivative due to it's stability. Thus we first convert it into RCOOH using hydrolysis under drastic conditions and then into other derivatives.
2. RCOCl can be easily interconverted into any derivative using alchol, carboxylate and Amine due to it's high reactivity.
3. **P_2O_5 is a great Dehydrating agent** to remove water and form Anhydrides or Nitriles.
   a. **Reaction with Acids**
      - $2\ R–COOH + P_2O_5 \rightarrow (R–CO)_2O + H_2O$ (Forms Anhydrides)
   b. **Reaction with Amides**
      - $R–CONH_2 + P_2O_5 \rightarrow R–CN + H_2O$ (Forms Nitriles)

1.4 More About Fischer Esterification and Saponification

- **Fischer Esterification** – formation of esters *(Acid Catalysed Reaction - Reversible)*
- **Saponification** – breakdown of esters *(Base Catalysed Reaction)*

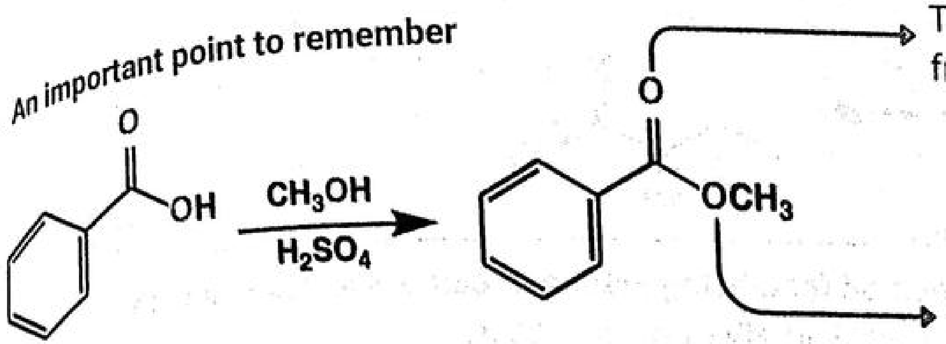
Fischer Esterification



NAME 29 REACTION

RANSHOREVISION

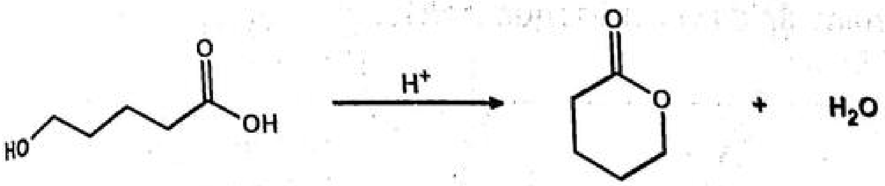
- *An important point to remember*



This oxygen comes from **Carboxylic acid.**

This oxygen comes from **Alcohol.**

- **Intramolecular Esterification gives Lactone**



This works best for 5 to 6 membered rings

Saponification

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$$

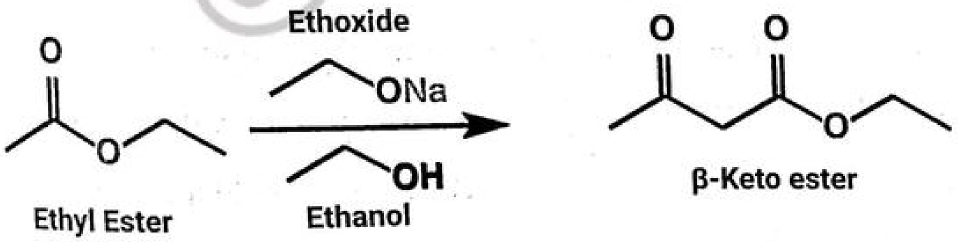
Ester **Carboxylate ion** **Ethanol**

NAME 29 REACTION

- This reaction is irreversible and commonly used in soap-making where esters of fatty acids are hydrolyzed to form soap (the salt of a fatty acid) and glycerol.

1.5 Important Name Reactions in Carboxylic Acids

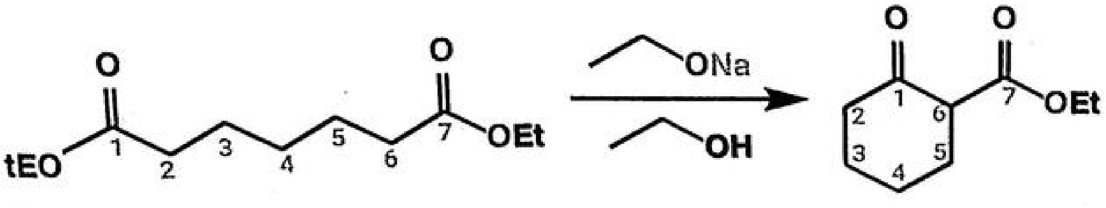
Claisen condensation



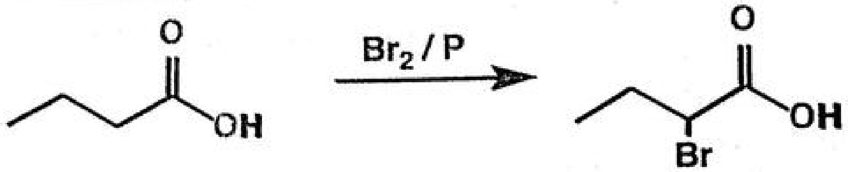
The base used is exactly the alkoxide of the Group attached to atom in ester

NAME 30 REACTION

- The ester must have at least one α-hydrogen (adjacent to the carbonyl group).
- No α-hydrogen = no enolate ion = no reaction.
- Claisen condensation is just aldol of esters with a leaving group
- **Intramolecular Claisen Condensation : Also known as Dieckmann Condensation**



HVZ Reaction

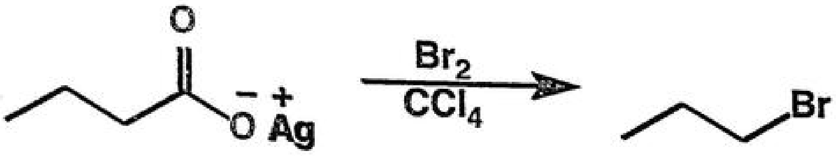


The HVZ reaction is used to halogenate the α-position

NAME 31 REACTION

- HVZ is the only standard method for α-halogenation of carboxylic acids directly
- No α-H = no HVZ (e.g., in formic acid, HVZ doesn't occur)
- Intermediate : Acyl halide (R–COX) and its enol form
- Red phosphorus (P) is essential
- Best Use : Used to prepare α-amino acids via subsequent NH_3 substitution

Hundsdiecker Reaction



Decarboxylative halogenation via radical mechanism

NAME 32 REACTION

- Note : Loss of one carbon atom (chain shortens!)
- Works best with alkyl groups; aryl groups are less reactive
    - E.g., benzoic acid fails due to poor formation of aryl radicals or instability.
- By Products : CO_2 and AgBr

2. Acidity of Alcohol, Phenols and Carboxylic Acid tested with $NaHCO_3$

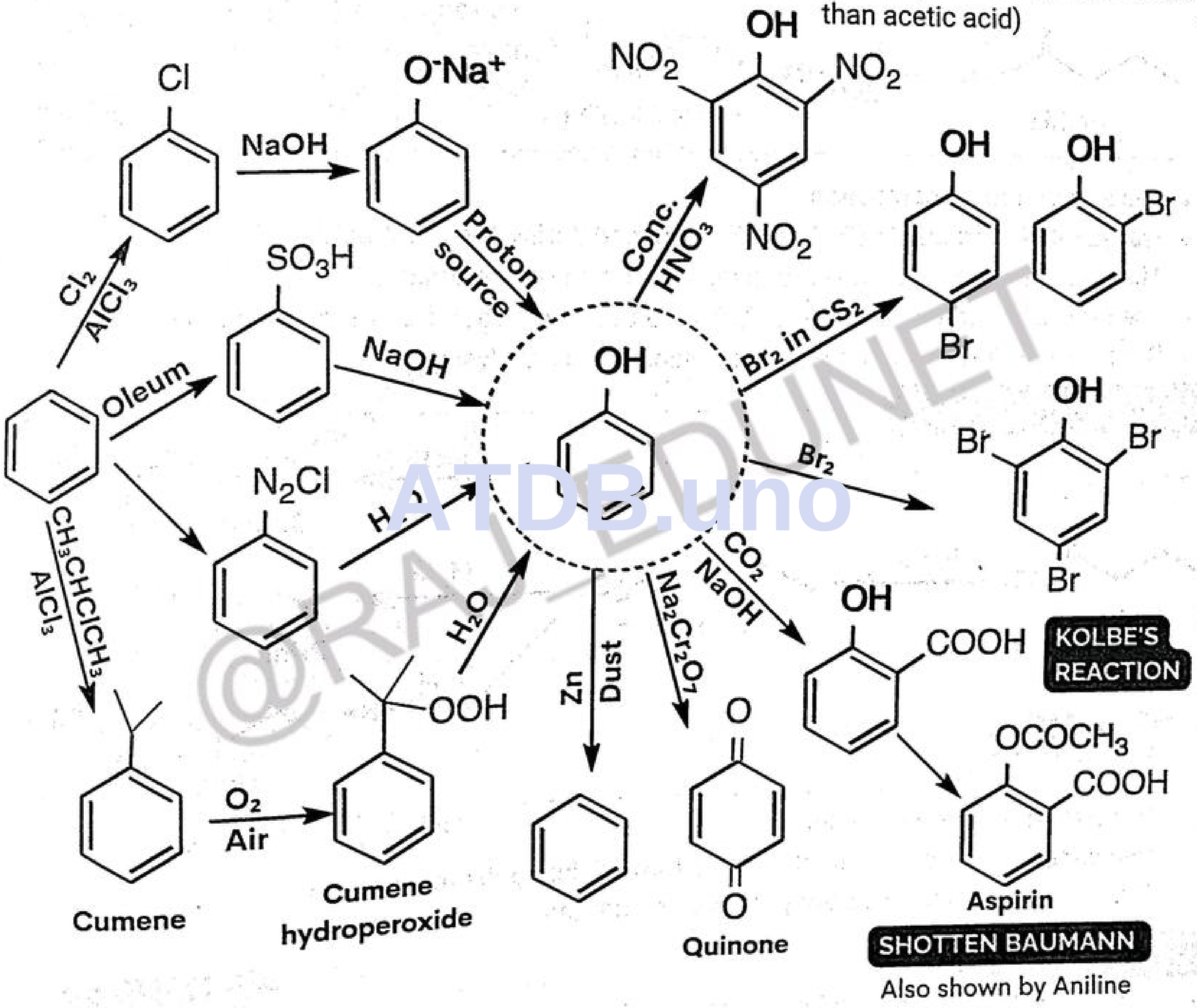
Compound	Rxn with $NaHCO_3$?	Gas Evolved?	Reason
Carboxylic Acid	☑ Yes	☑ CO_2 evolved	Strong enough to neutralize bicarbonate
Phenol	✗ No	✗ No	Too weak to react with bicarbonate
Alcohol	✗ No	✗ No	Even weaker acid than phenol

- If a compound gives brisk effervescence with $NaHCO_3$, it contains a carboxylic acid group.
- This is a standard test to distinguish carboxylic acids from phenols.

Step towards Organic 14

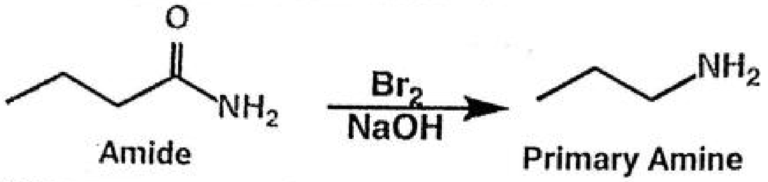
All Reactions of Phenols

Picric Acid is one of the most acidic phenols (more acidic than acetic acid)



Remaining Reactions of Amines

Hoffmann Bromamide Reaction

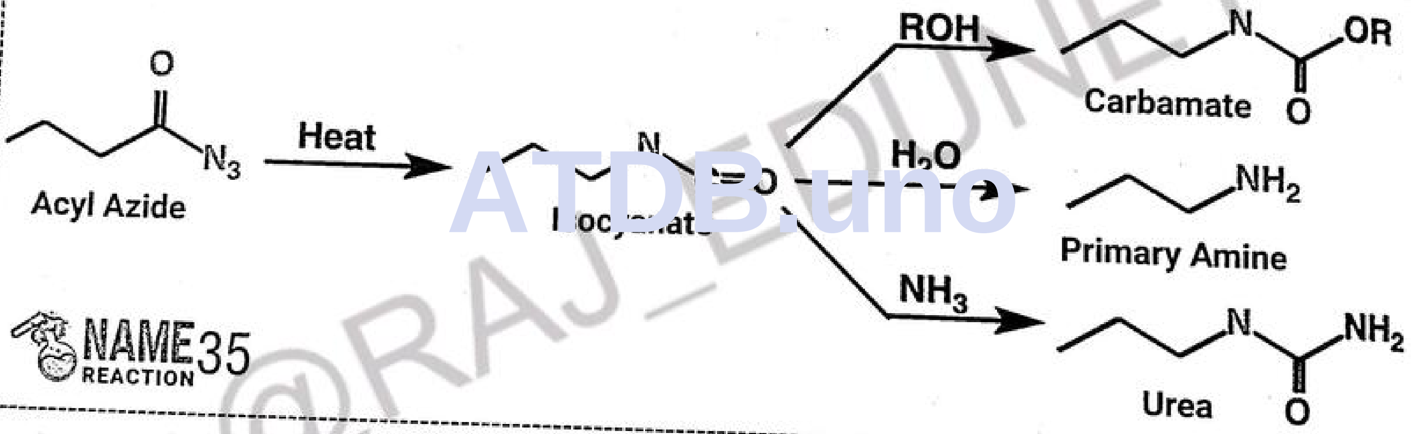


An amide reacts with bromine (Br_2) and a strong base (NaOH) to give a primary amine, with one carbon less than the original amide.

NAME 34 REACTION

- It is a **rearrangement** reaction.
- **Isocyanate intermediate (R−N=C=O) is formed during the mechanism.**
- The product amine has one carbon less than the starting amide.
- The R-group migrates from the carbonyl carbon to nitrogen (rearrangement step).
- Bromination → Rearrangement → Isocyanate → Hydrolysis

Curtius Rearrangement



- It is a **rearrangement** reaction.
- **Isocyanate** intermediate (R−N=C=O) is formed during the mechanism.
- R group migrates from carbonyl carbon to nitrogen

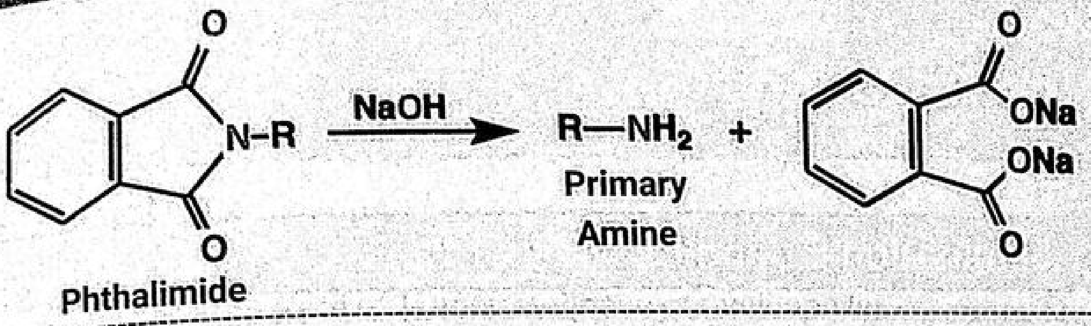
Schmidt Reaction

NAME 36 REACTION

It is a rearrangement where carboxylic acids, ketones, or aldehydes react with hydrazoic acid (HN_3) in acidic medium to form amines, amides, or N-formyl derivatives

Reactant	**Reagents**	**Product**	**Evolved**	**Intermediate Formed**
Carboxylic Acid	$HN_3 + H^+$ (conc. H_2SO_4)	Primary Amine ($R-NH_2$)	$CO_2 + N_2$	Isocyanate (R−NCO)
Ketone	$HN_3 + H^+$	N-substituted Amide	N_2	Azidohydrin / Nitrene
Aldehyde	$HN_3 + H^+$	N-formyl derivative (R−NH−CHO)	N_2	Nitrene / Isocyanate

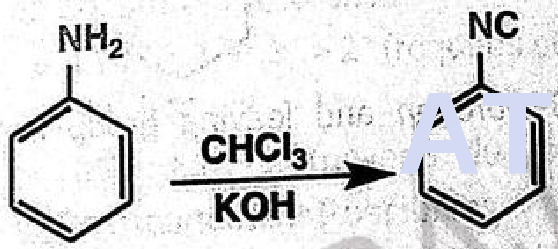
Gabriel Pthalamide Reaction



Phthalimide

- ✗ Not suitable for aryl halides (e.g., C_6H_5-Br) or tertiary alkyl halides.
- ✗ Does not work for secondary or tertiary amines.
- ✗ Requires careful hydrolysis conditions to avoid side products.

Carbylamine Reaction



The Carbylamine reaction (also known as the isocyanide test) is a chemical test where primary amines (both aliphatic and aromatic) react with chloroform ($CHCl_3$) and alcoholic KOH to produce foul-smelling isocyanides (R–NC).

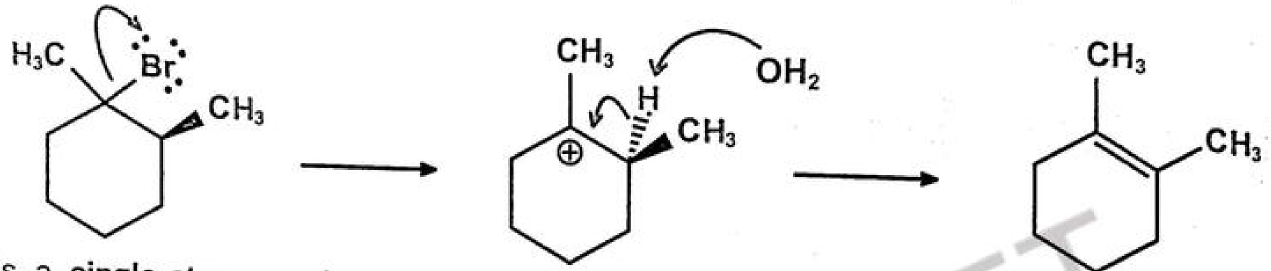
- **Not Given By:**
  - Secondary and tertiary amines
  - Amides, anilides, nitro compounds, alcohols, etc.
- **Intermediate :** Dichlorocarbene (CCl_2)
- **Observation :** Foul smell (confirmation of primary amine). No gas evolved but pungent smell of isocyanide.
- Used as Tests for Primary amines only.

Step Towards Organic 16

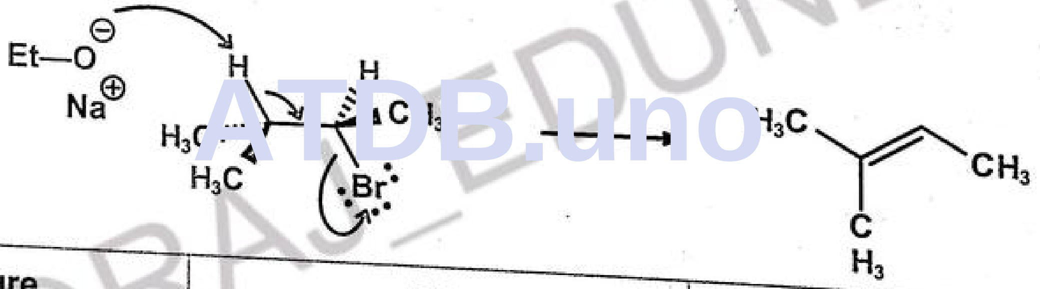
Elimination Reactions

1. Elimination E1 and E2 Mechanisms

E1 is a **two-step** elimination where the *leaving group leaves first*, forming a carbocation, followed by base-induced proton removal to form an alkene.



E2 is a **single-step** reaction where *base abstracts β-hydrogen* and leaving group leaves simultaneously → alkene forms.



Feature	E1	E2
Steps	Two-step (carbocation formed)	One-step (concerted)
Rate depends on	Only substrate	Substrate + base
Carbocation formed?	Yes	No
Rearrangement possible?	Yes	No
Base strength	Weak base sufficient	Requires strong base
Favored substrates	3° > 2°	3° ≈ 2° ≈ 1°
Solvent	Polar protic (e.g., H_2O, ROH)	Polar aprotic / strong base
Stereochemistry	Not specific	Anti-periplanar required

1.1 Key Differences – E1 vs E2 vs SN1 vs SN2

IMPORTANT

- **Number of Steps**
  - E1 / SN1 → Two-step (carbocation intermediate)
  - E2 / SN2 → One-step (concerted mechanism)
- **Rate Law**
  - E1 / SN1 → Rate ∝ [substrate]
  - E2 / SN2 → Rate ∝ [substrate][base or nucleophile]
- **Reagent Type**
  - E1 / SN1 → Weak base/nucleophile
  - E2 / SN2 → Strong base/nucleophile
    - E2 often uses bulky base (e.g., t-BuO-)
    - SN2 prefers small, unhindered nucleophiles (e.g., CN-)
- **Substrate Preference**
  - E1 / SN1 → 3° > 2° (requires stable carbocation)
  - E2 → 3° > 2° > 1°
  - SN2 → 1° > 2° (never 3° due to steric hindrance)
- **Rearrangement Possibility**
  - E1 / SN1 → Possible (via carbocation shift)
  - E2 / SN2 → Not possible
- **Stereochemistry**
  - E2 → Requires anti-periplanar β-H and leaving group
  - SN2 → Gives inversion of configuration
  - E1 / SN1 → No stereochemical control (may give mixtures)
- **Solvent Type**
  - E1 / SN1 → Polar protic (stabilizes carbocation)
  - E2 / SN2 → Polar aprotic preferred (faster reaction)

Examples

1. $CH_3CH_2Br + NaCN \rightarrow CH_3CH_2CN + NaBr$
   - 1° alkyl halide, Strong nucleophile (CN-), No bulky base or carbocation **(SN2)**
2. $(CH_3)_3C{-}Br + H_2O \rightarrow (CH_3)_3C{-}OH + HBr$
   - 3° alkyl halide, Weak nucleophile (H_2O), Polar protic solvent, Carbocation forms ***(SN1)***
3. $CH_3CHBrCH_3 + t\text{-}BuO^- \rightarrow CH_3CH{=}CH_2 + t\text{-}BuOH + Br^-$
   - Strong bulky base (t-BuO-), β-H available, No carbocation, One-step *elimination* ***(E2)***
4. $(CH_3)_3C{-}Br + EtOH$ (heat) $\rightarrow (CH_3)_2C{=}CH_2 + HBr$
   - 3° alkyl halide, Weak base (EtOH), Carbocation formed, Heat favors *elimination (E1)*

Step Towards Organic 17

Practical Organic Chemistry

1. Tests for Organic Groups Analysis

1.1 Liebig's Test

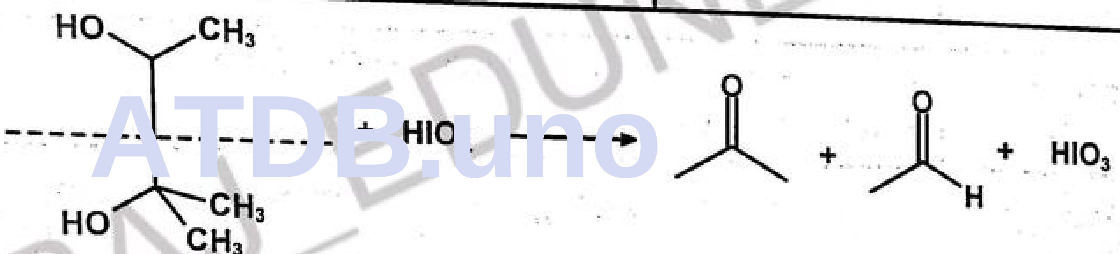
Element	Reaction	Observation
Carbon (C)	$C + CuO \rightarrow CO_2$	CO_2 turns lime water milky due to $Ca(HCO_3)_2$
Hydrogen (H)	$H + CuO \rightarrow H_2O$	Moist $CuSO_4$ turns blue ($CuSO_4 \cdot 5H_2O$)

1.2 Lassaigne's Test – Sodium Fusion Extract

Nitrogen (N) NaCN formed	$NaCN + Fe^{2+} \rightarrow [Fe(CN)_6]^{4-}$ Adding Fe^{3+}, $\mathbf{Fe_4[Fe(CN)_6]_3.xH_2O}$	- $Fe_4[Fe(CN)_6]_3.xH_2O$ **Prussian Blue** - NH2-NH2 doesn't give this test
Halogen (X) NaX formed	First Sodium Extract boiled with HNO_3 - $NaCl + AgNO_3 \rightarrow$ **AgCl (white ppt)** - $NaBr + AgNO_3 \rightarrow$ **AgBr (pale yellow)** - $NaI + AgNO_3 \rightarrow$ **AgI (Yellow)**	On Adding Ammonium Hydroxide - AgCl Dissolves - AgBr partially dissolves - AgI doesn't dissolve in NH_4Cl
Sulphur (S) Na_2S formed	Na_2S + Lead Acetate → **Black ppt** of $PbS.2CH_3COONa$ $Na_2S + Na_2[Fe(NO)(CN)_5] \rightarrow Na_3[Fe(NOS)(CN)_5]$ **Thionitroprusside (Violet)**	
S & N together	$NaSCN + FeCl_3 \rightarrow [Fe(SCN)]^{2+}$	$[Fe(SCN)]^{2+}$ has Blood Red Colour
Phosphorous (P)	Solution boiled with nitric acid and then treated with Ammonium molybdate	Ammonium Phosphomolybdate $(NH_4)_3PMo_{12}O_{40}$ is yellow in colour

1.3 Test for Functional Groups

ALCOHOL

Na Metal Test	Sodium Alkoxide is formed and H_2 **Released**	Given By all alcohols
Lucas Reagent Test	**ALREADY DISCUSSED**	
Jone's Oxidation	**Orange Red** Colour Cr^{6+} to **Green** Colour Cr^{3+}	Test for 1°, 2° Alcohol
Victor Meyer's test	Alcohol + P/I_2 + $AgNO_2$ + $NaNO_2$/HCl + KOH	1° : Red colour ; 2° : Blue Colour
CAN test	**Yellow colour** of Ceric Amm. Nitrate, $(NH_4)_2Ce(NO_3)_6$ **changes to Red to colourless**	Test for 1°, 2° Alcohol, Slow for 3° alcohols
Periodic Acid test Given by Diols	 **Iodine goes from +7 oxidation state to +5 Oxidation state**	

ALDEHYDE AND KETONES – All Tests Already Discussed

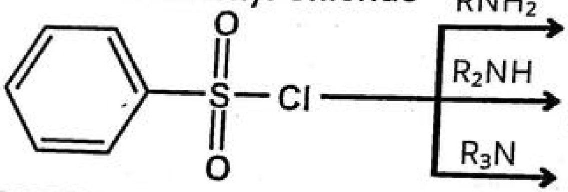
TESTS FOR UNSATURATION

Br_2 in CCl_4	**Red Brown Colour** of Bromine **Disappears**	Given by Alkenes and Alkynes
Baeyers test	**Purple Colour** of $KMnO_4$ **Disappears**	Given by Alkenes, Alkynes, Aldehyde and Alcohol

PHENOLS

CAN Test	Gives **black/brown ppt** with Ceric ammonium Nitrate
$KMnO_4$ Test	Reduces potassium permanganate solution and undergo oxidation to **quinones.**
$FeCl_3$ Test	Forms **Violet Colour Complex** with $FeCl_3$
Bromine Water	**2,4,6tribromophenol** is formed which is white in colour **(Brown dissappears)**

AMINES AND THEIR SALTS

Nitrous Acid Test	- $RNH_2 + HONO \rightarrow ROH + H_2O + N_2$ - $R_2NH + HONO \rightarrow R_2N{-}NO + H_2O$ - $R_3N + HONO \rightarrow R_3NH^+ONO^-$	- Nitrogen gas seen in form of bubbles - Yellow Oily Nitrosamine - Soluble Nitrite salts
Azo-Dye Test	Aniline on Reaction with $NaNO_2$ + HCl forms Diazonium which on reaction with Napthan-2-ol gives Azo dye **(Scarlet Red in Colour)**	
Libermann Nitroso test	$R_2NH + HONO \rightarrow R_2N{-}NO$ Nitrosamines when heated with Phenol and conc. H_2SO_4 is added, Green colour is formed which turns Blue with an alkali. (Only 2° amines)	
Hinsberg Test	**Benzene Sulfonyl Chloride**  **N-Alkylbenzenesulfonamide** Compound formed is soluble in alkali **N.N - Dialkylbenzenesulfonamide** Compound formed is insoluble in alkali **No Reaction**	
Carbylamine Test	- $CH_3CH_2NH_2 + CHCl_3 + 3KOH \rightarrow CH_3CH_2NC$ - (Offensive smell of isocyanide with 1°)	

2. Elemental Estimation

2.1 CARBON, HYDROGEN AND NITROGEN ESTIMATION

Combustion Method (C & H)

General Reaction : $C_xH_y + (x + y/4)O_2 \rightarrow xCO_2 + (y/2)H_2O$

Element	Reaction	Absorber	Formula
Carbon (C)	$C \rightarrow CO_2$	KOH	%C = (12/44) × (mass of CO_2 / mass of compound) × 100
Hydrogen (H)	$H \rightarrow H_2O$	$CaCl_2$	%H = (2/18) × (mass of H_2O / mass of compound) × 100

- A measured mass of an organic compound undergoes combustion with excess oxygen and copper(II) oxide, resulting in the oxidation of carbon to carbon dioxide and hydrogen to water.
- The resulting water and carbon dioxide are measured by passing through U-tubes with calcium chloride and potassium hydroxide. By checking the increase in weights of these tubes, they calculate the percentages of carbon and hydrogen in the substance.

DUMAS METHOD (Estimation of Nitrogen – by Volume Measurement)

Step	Details
Reaction	$C_xH_yN_z + (2x + y/2)CuO \rightarrow xCO_2 + y/2H_2O + z/2N_2 + (2x + y/2)Cu$
Gas Collection	• Organic compound is heated strongly with excess copper oxide (CuO) in a carbon dioxide-free atmosphere. • Nitrogen in the compound is converted to free nitrogen gas (N_2). • CO_2 formed is absorbed by KOH, and the volume of N_2 is measured
Volume Correction	**Adjusted to NTP using: (P - aqueous tension) × $V_1 / T_1 = V_2 / T_2$** *Here, V_2 represents the value of Volume of Nitrogen at NTP and V_1 represents the volume at T_1*
Final Formula	**%N = (28 × V_2 × 100) / (22400 × mass of compound)**

✐ Example:

A 0.2 g organic sample gives 25 mL of N_2 at NTP. Find % of nitrogen.

% N = (28 × 0.025 × 100) / (22.4 × 0.2)
= 15.625%

KJELDAHL'S METHOD (Estimation of Nitrogen – by Ammonia Measurement)

Step	Reaction
Principle	• Organic nitrogen is converted into $(NH_4)_2SO_4$ by digestion with H_2SO_4 (and catalyst like Cu/Se). • Upon making alkaline, NH_3 gas is liberated. • NH_3 is absorbed in HCl or H_2SO_4 and estimated by back titration.
Digestion	Organic-N + $H_2SO_4 \rightarrow (NH_4)_2SO_4$
Alkaline Treatment	$(NH_4)_2SO_4 + 2NaOH \rightarrow 2NH_3\uparrow + Na_2SO_4 + 2H_2O$
Absorption	$NH_3 + HCl \rightarrow NH_4Cl$
Final Formula	**%N = (1.4 × N × (V - v)) / mass of compound** • *N = Normality of the standard acid used (usually HCl or H_2SO_4)* • *V = Volume (in mL) of acid taken to absorb ammonia (total acid used)* • *v = Volume (in mL) of base (e.g. NaOH) used in back titration (amount of acid neutralized)*

***Not suitable for nitro, azo compounds or nitrogen in aromatic rings like pyridine.**

0.25 g of an organic compound required 25 mL of N/10 HCl.
Back titrated with 10 mL of N/10 NaOH.

% N = [(25 – 10) × 0.1 × 14 × 100] / (1000 × 0.25)
= 8.4%

2.2 CARIUS METHOD (Estimation of Halogens)

An organic compound undergoes oxidation by fuming nitric acid with silver nitrate in a Carius tube. Carbon and hydrogen become carbon dioxide and water, while halogens form silver halides, which are filtered, washed, dried, and weighed.

Halogen	Precipitate Formed	Formula
Cl	AgCl (White ppt)	%Cl = (35.5 / 143.5) × (mass of AgCl / mass of compound) × 100
Br	AgBr (Pale yellow ppt)	%Br = (80 / 188) × (mass of AgBr / mass of compound) × 100
I	AgI (Yellow ppt)	%I = (127 / 235) × (mass of AgI / mass of compound) × 100

2.3 Estimating Sulphur and Phosphorous

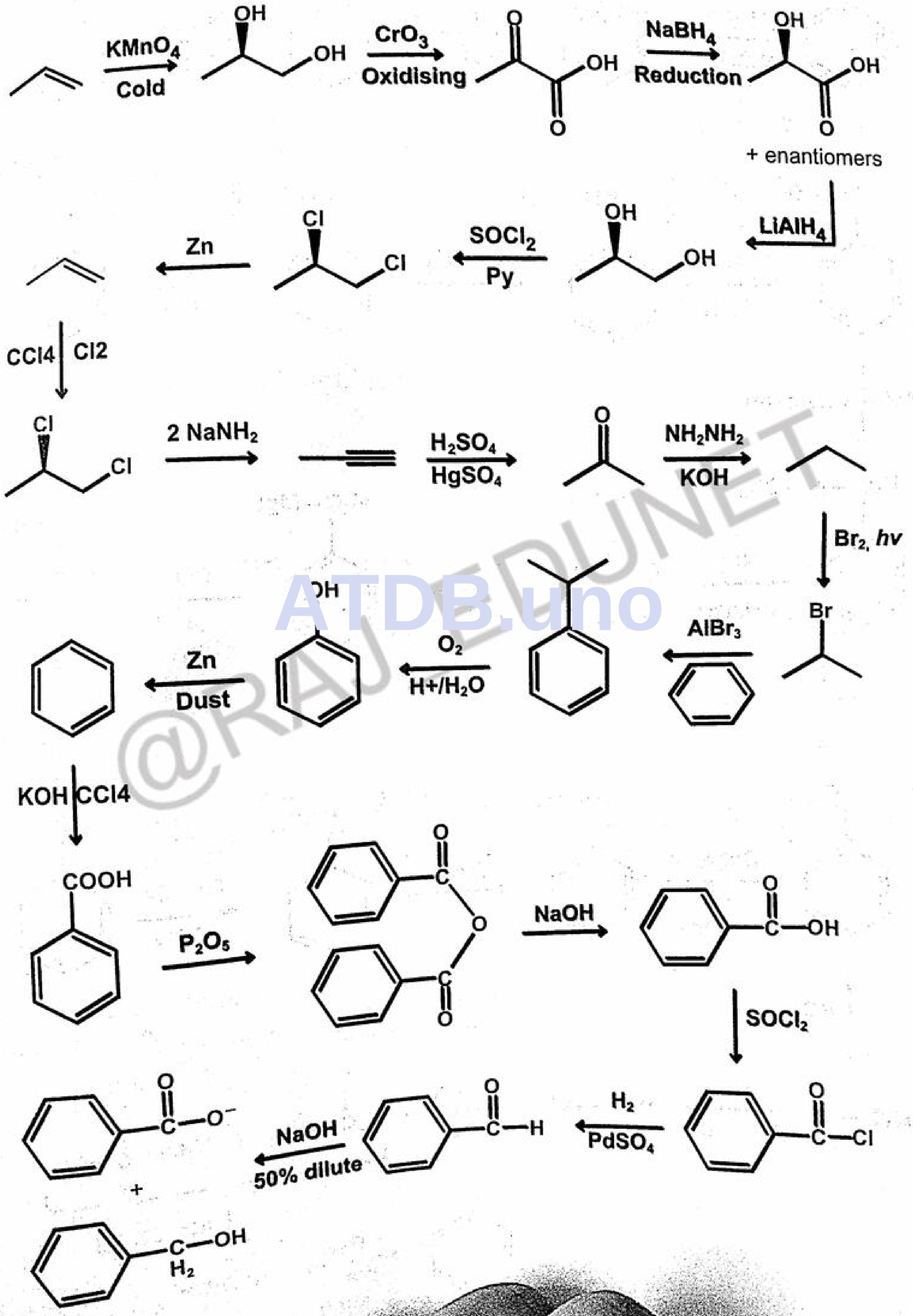
An organic compound is heated with sodium peroxide or fuming nitric acid in a Carius tube. The resulting sulfur is oxidized to sulfuric acid, precipitated as barium sulfate, and its mass used to calculate the %S.

Reaction Type	Product Formed	Formula
Oxidation (using Na_2O_2 or HNO_3)	$BaSO_4$ (white ppt)	%S = (32 / 233) × (mass of $BaSO_4$ / mass of compound) × 100

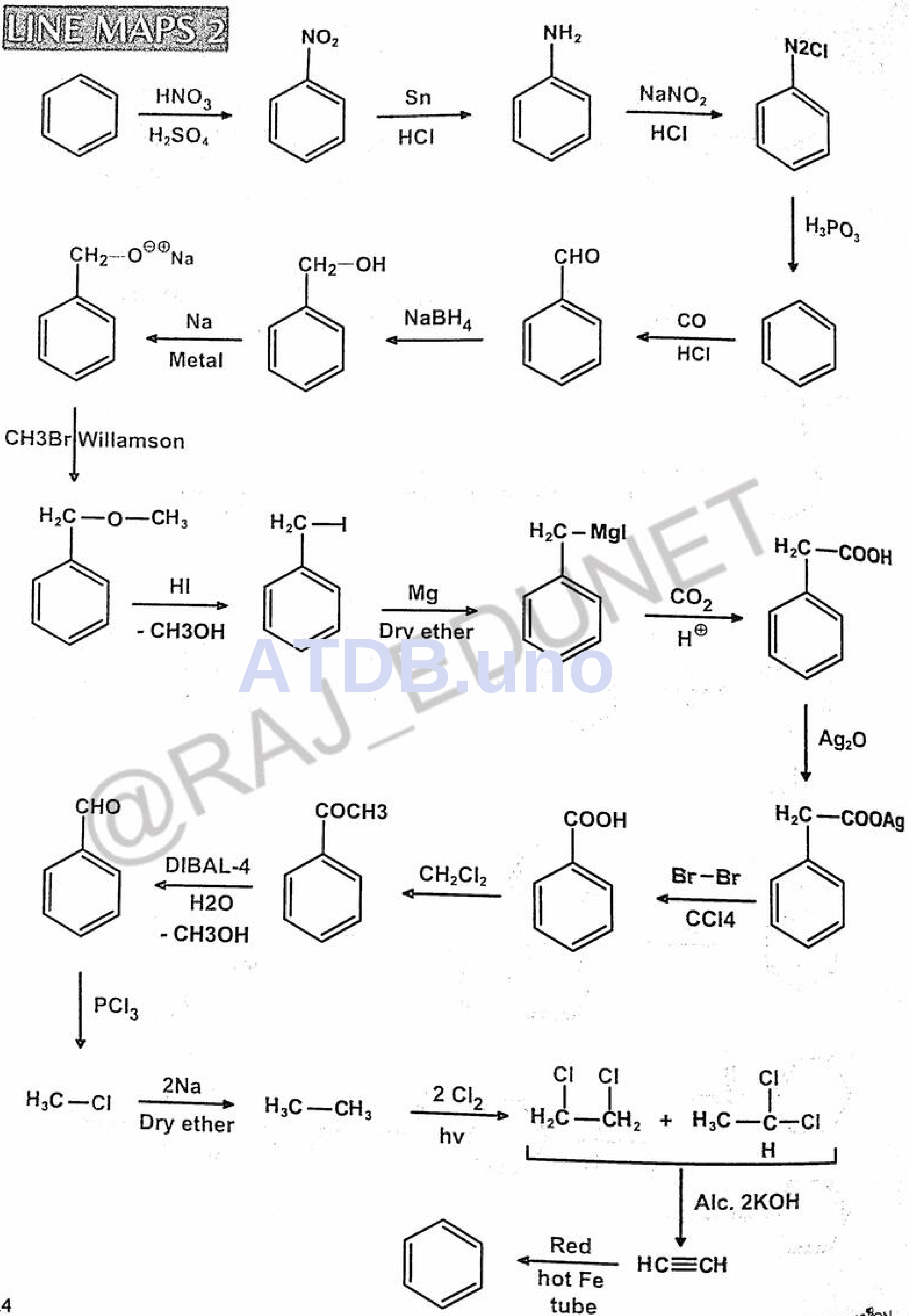
An organic compound, when heated with fuming nitric acid, oxidizes phosphorus to phosphoric acid. This is then precipitated as ammonium phosphomolybdate or $MgNH_4PO_4$ to determine the phosphorus percentage.

Precipitate	Comp. Formed	Formula
APM (Yellow ppt)	$(NH_4)_3PMo_{12}O_{40}$	%P = (62 / 222) × (mass of APM / mass of compound) × 100
MPP (White ppt)	$Mg_2P_2O_7$	%P = (31 / 1877) × (mass of MPP / mass of compound) × 100

LINE MAPS 1

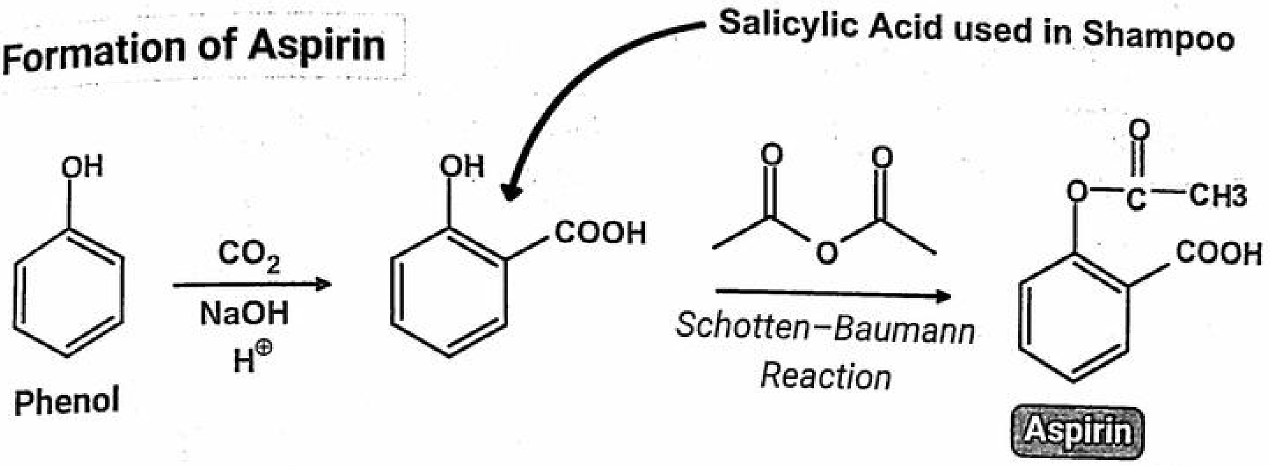

KMnO4
Cold
OH
OH
CrO3
Oxidising
O
OH
O
NaBH4
Reduction
OH
OH
O
+ enantiomers
LiAlH4
OH
OH
SOCl2
Py
Cl
Cl
Zn
CCl4
Cl2
Cl
Cl
2 NaNH2
H2SO4
HgSO4
O
NH2NH2
KOH
Br2, hv
Br
AlBr3
O2
H+/H2O
OH
Zn
Dust
KOH
CCl4
COOH
P2O5
O
C
O
C
O
NaOH
O
C
OH
SOCl2
O
C
Cl
H2
PdSO4
O
C
H
NaOH
50% dilute
O
C
O−
+
C
H2
OH

LINE MAPS 2

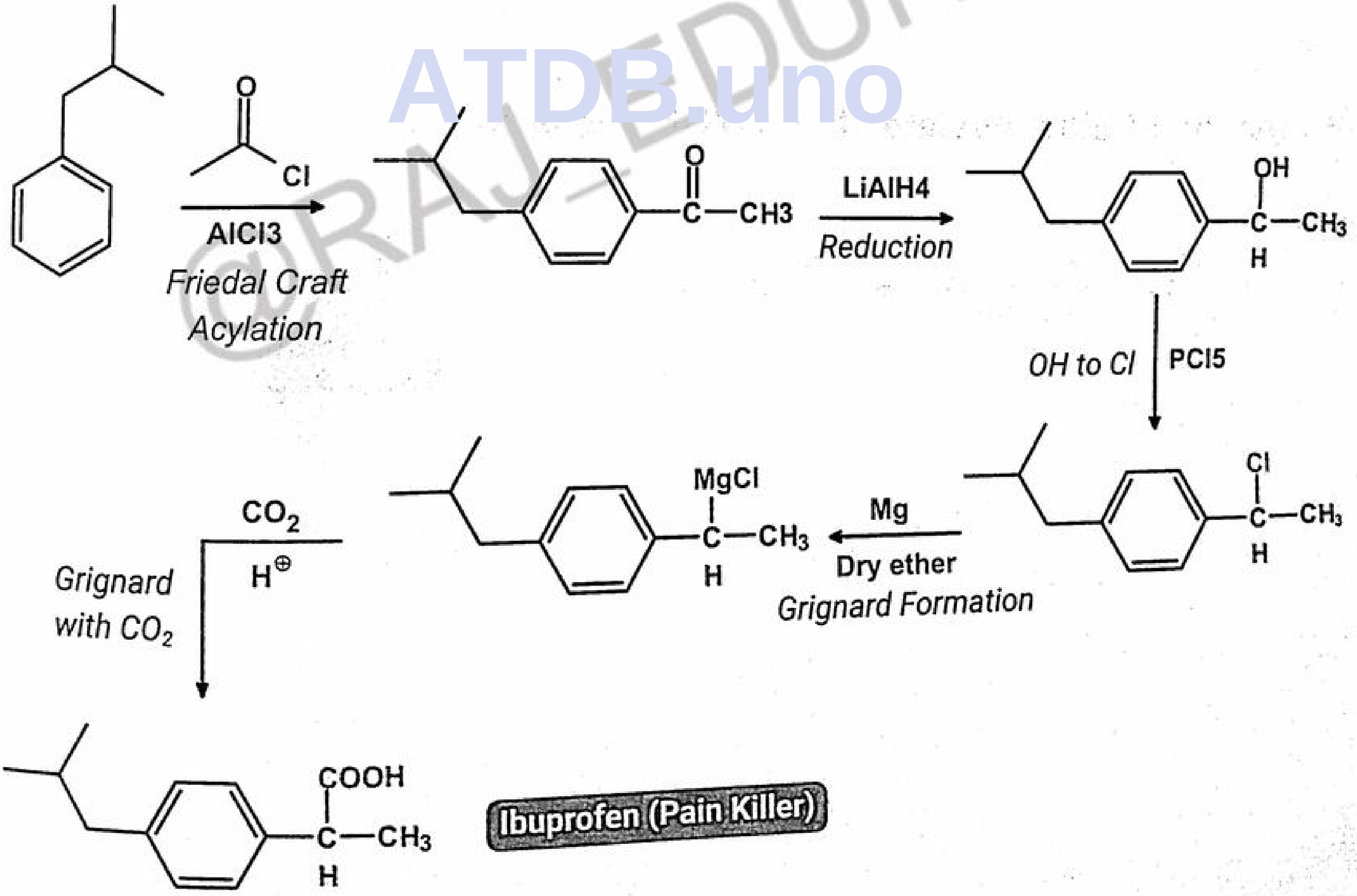

NO₂
HNO₃
H₂SO₄
NH₂
Sn
HCl
N2Cl
NaNO₂
HCl
H₃PO₃
CO
HCl
CHO
NaBH₄
CH₂—OH
Na
Metal
CH₂—O⊖⊕Na
CH3Br Willamson
H₂C—O—CH₃
HI
- CH3OH
H₂C—I
Mg
Dry ether
H₂C—MgI
CO₂
H⊕
H₂C—COOH
Ag₂O
H₂C—COOAg
Br—Br
CCl4
COOH
CH₂Cl₂
COCH3
DIBAL-4
H2O
- CH3OH
CHO
PCl₃
H₃C—Cl
2Na
Dry ether
H₃C—CH₃
2 Cl₂
hv
Cl Cl
H₂C—CH₂
+
Cl
H₃C—C—Cl
H
Alc. 2KOH
HC≡CH
Red
hot Fe
tube

Some Reactions to form products you might be familiar with

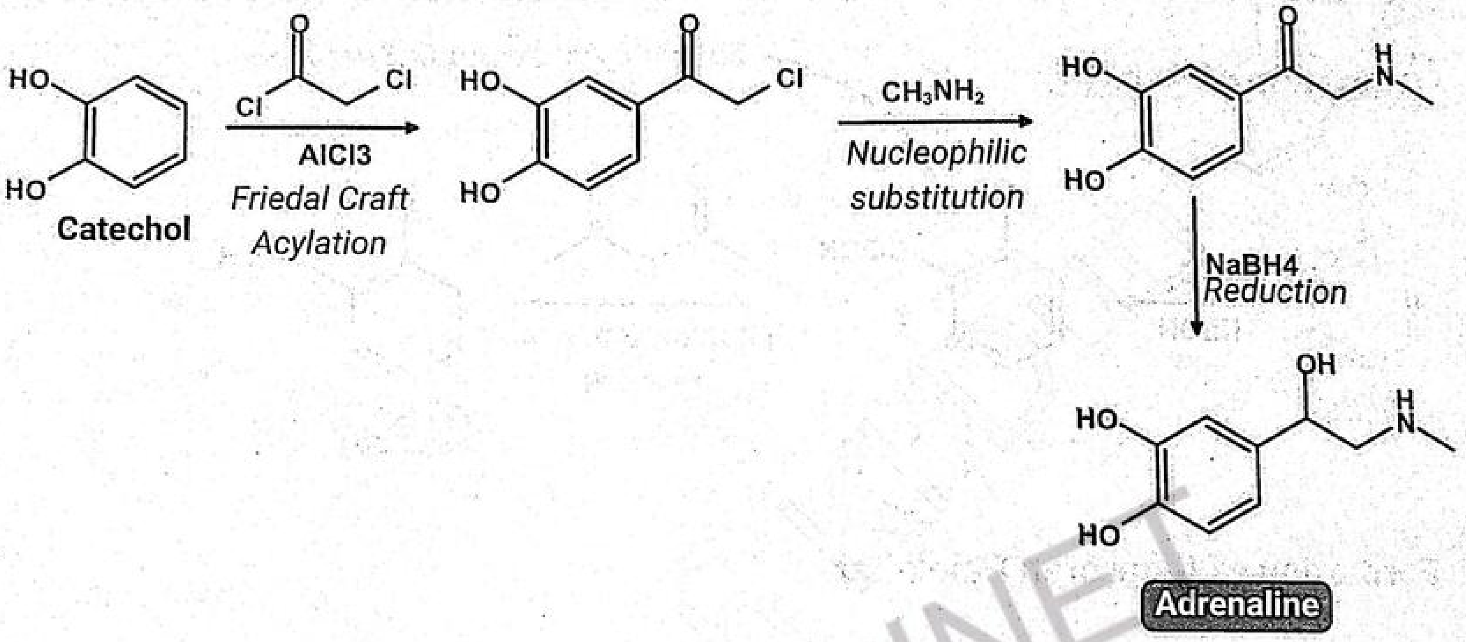
Formation of Aspirin



Formation of Ibuprofen Painkiller



Formation of Adrenaline - Flight or Fight Mechanism



Formation of Ethyl Acetate - Nail Polish Remove