Welcome to

Organic Chemistry: Some Basic Principles and Techniques



Wohler Theory

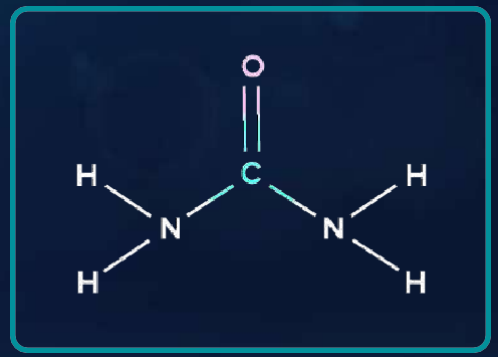
1828

Organic Compound - **UREA**

Synthesis of urea(organic compound) first time in lab by Wohler and synthesis of acetic acid by Kolbe(1845) and that of methane by Berthelot(1856) showed that organic compounds can be synthesized from inorganic sources in laboratory.

$NH_4^+NCO^-$

$\xrightarrow{\Delta}$



Ammonium Cyanate
(Inorganic)

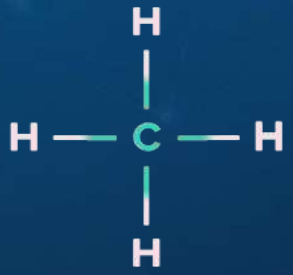
Urea
(Organic)

Organic Compounds

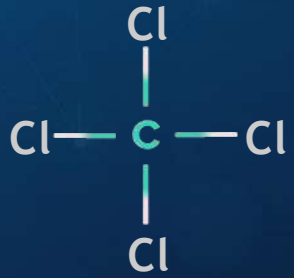
Compounds of carbon & hydrogen and their derivatives

The study of these compounds are done in a separate branch of chemistry called **Organic Chemistry**

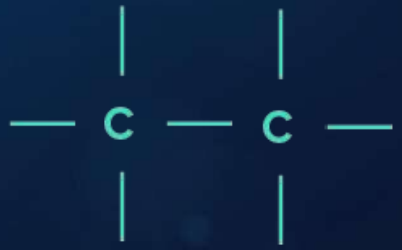
Tetravalency of Carbon and Catenation



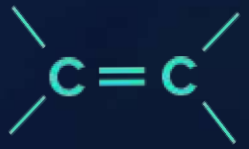
Methane



Tetrachloromethane

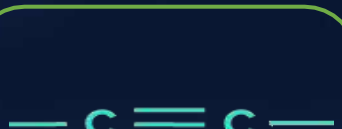


Single



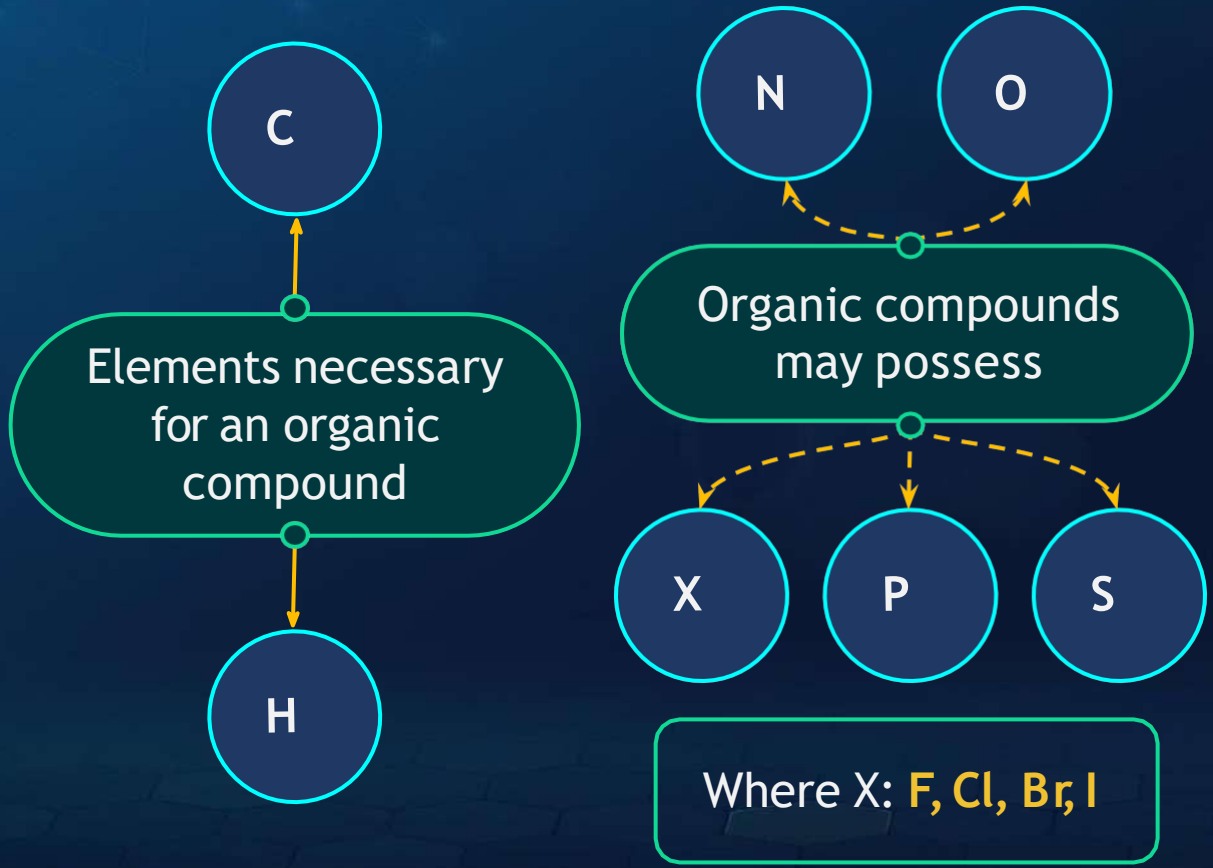
Double

Carbon has a unique tendency to form long chains with itself or with other elements.

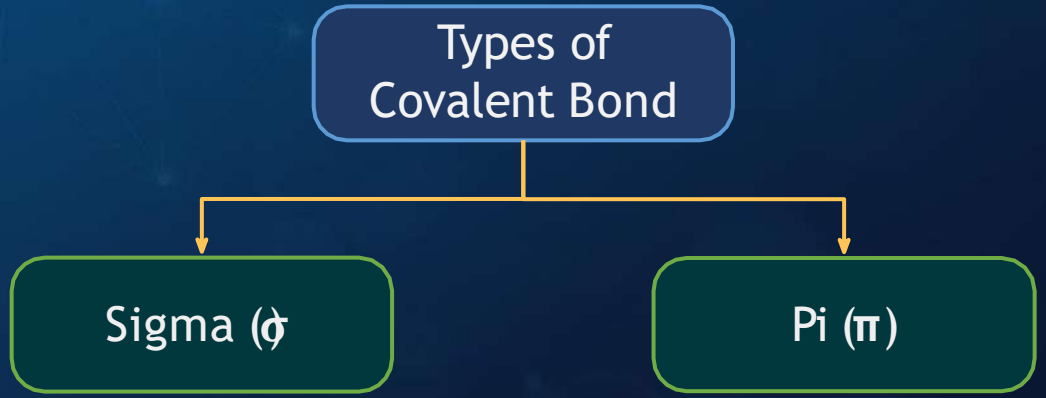


Triple

Tendency to form Bonds with other Non-metals



Bonding in Organic Compounds



Number of π bonds of a C atom	Hybridization of C
0	sp^3
1	sp^2
2	sp

Representation of Organic Molecules

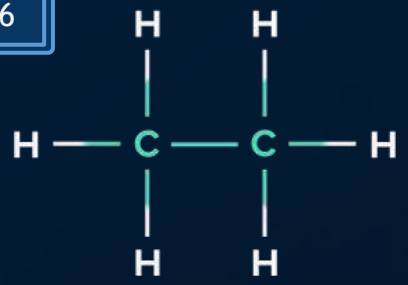
1. Molecular Formula
2. Structural Representation
   - 2.1. Complete Formula
   - 2.2. Condensed Formula
   - 2.3. Bond Line Formula

Shows the **exact number of different types of atoms** present in a molecule or a compound

Examples: C_3H_6 , C_4H_{10}

Structural Representation: Complete/Expanded Formula

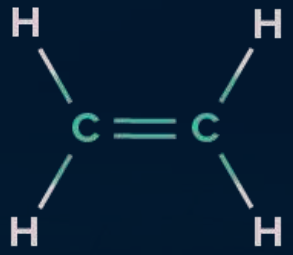
C_2H_6



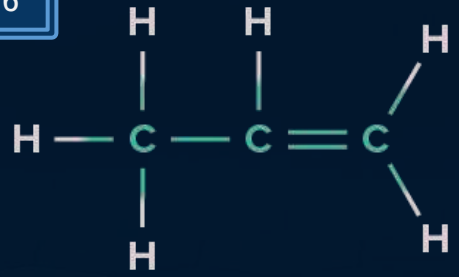
C_3H_8



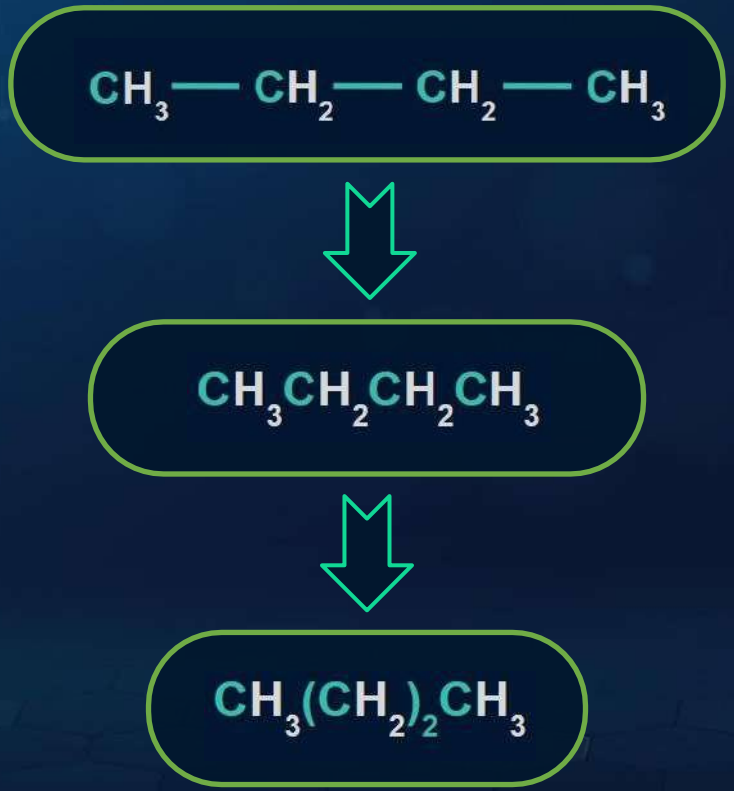
C_2H_4



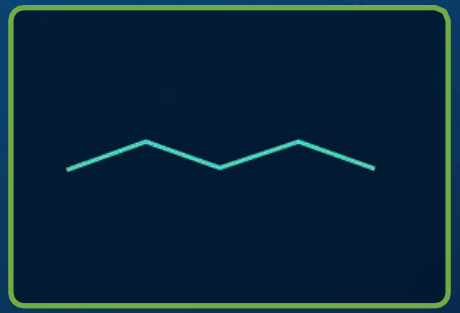
C_3H_6

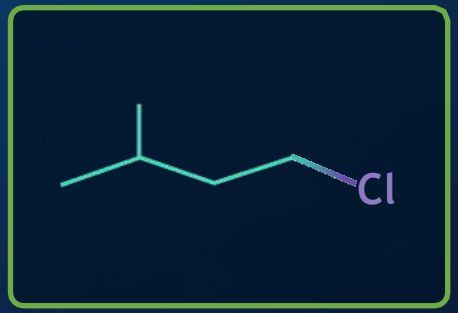


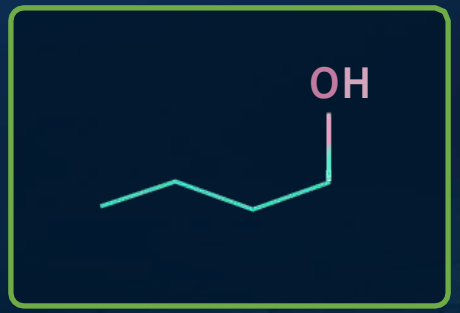
Condensed Formula

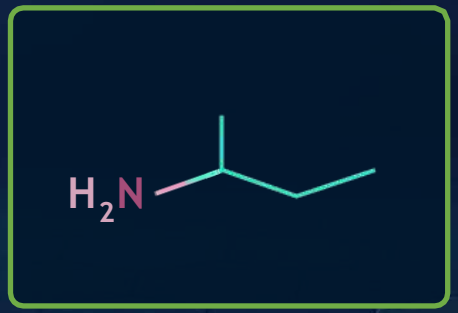


Bond Line Formula

1. 

3. 

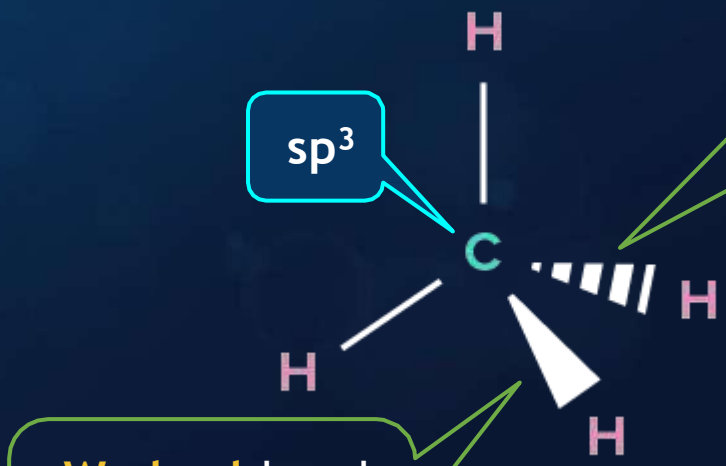
2. 

4. 

In this representation, C and H is not shown and C-C bond is shown in zig-zag fashion. The only atoms specifically written are oxygen, chlorine, nitrogen, etc,.

3D Representation of Organic Molecules

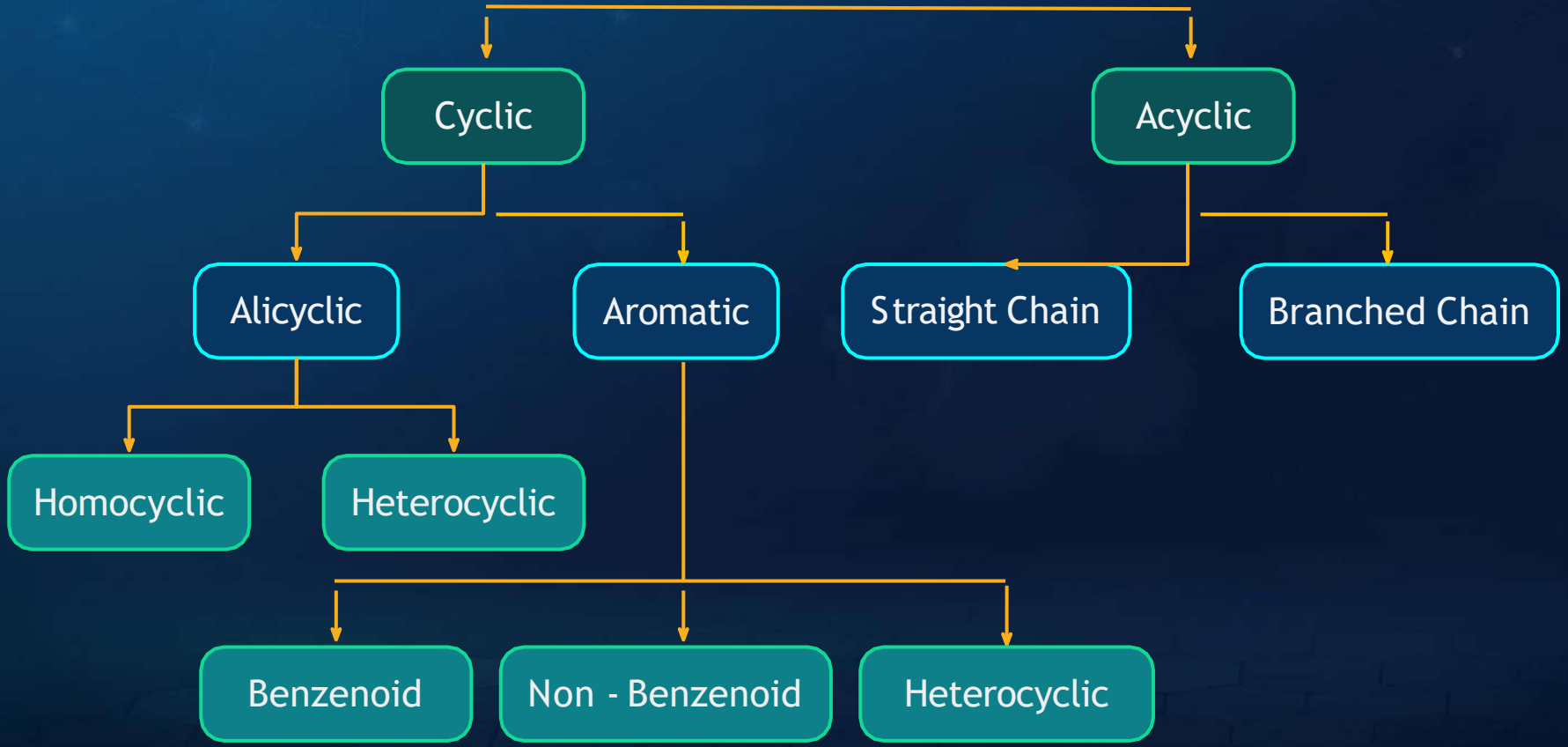
The structure of a molecule is shown using **dashes, wedges and straight lines**



Dashed bond (bond **away** from the observer)

Wedged bond (bond **towards** the observer)

Classification of Organic Compounds



Classification of Organic Compounds

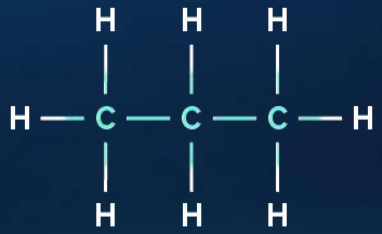
Organic Compounds

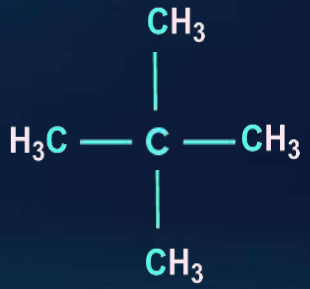
- Acyclic Compounds
- Cyclic Compounds



Classification of Organic Compounds

- Acyclic Compounds
  - Straight Chain
  - Branched Chain
- Cyclic Compounds
  - Alicyclic
  - Aromatic







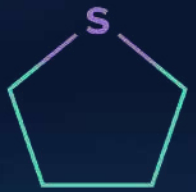


Classification of Organic Compounds

Alicyclic (Aliphatic Cyclic) Compounds

- Homocyclic
- Heterocyclic





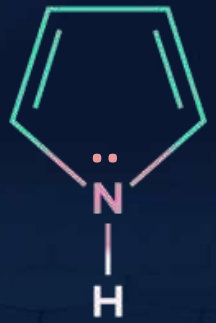
Classification of Organic Compounds

Aromatic Compounds

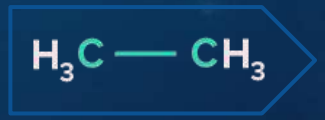
- Benzenoid
- Non-Benzenoid
- Heterocyclic



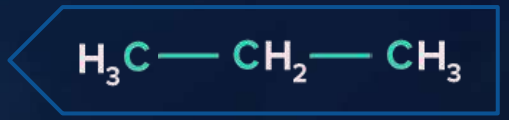




Hydrocarbons



Compounds that contain only **carbon** and **hydrogen**



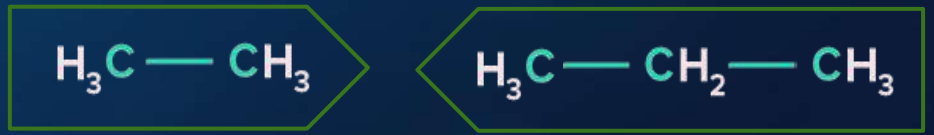
Hydrocarbons

Saturated

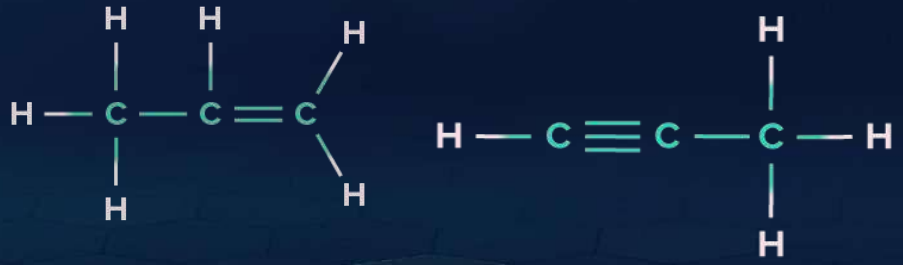
Unsaturated

Saturated and Unsaturated Hydrocarbons

If each **C atom** is joined to **four other atoms** (C or H), it has no potential to form more bonds and is therefore saturated.



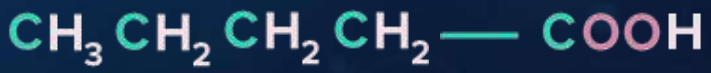
C atoms forming **C = C or C ≡ C** bonds have the potential to bond with at least one more monovalent atom and are therefore unsaturated.



Functional Group

Functional Group

The characteristic group of atom which decides the **physical and chemical properties** of an organic molecule.



A series of similarly constituted compounds in which the members possess the **same functional group**, have similar chemical characteristics and have a regular gradation in their physical properties.

Successive homologues differ by $-CH_2$ only

Naming

Common Name

Organic compounds were **assigned names** initially based on their origin or certain properties

Common Name → Acetic Acid

IUPAC Name → Ethanoic Acid

Examples

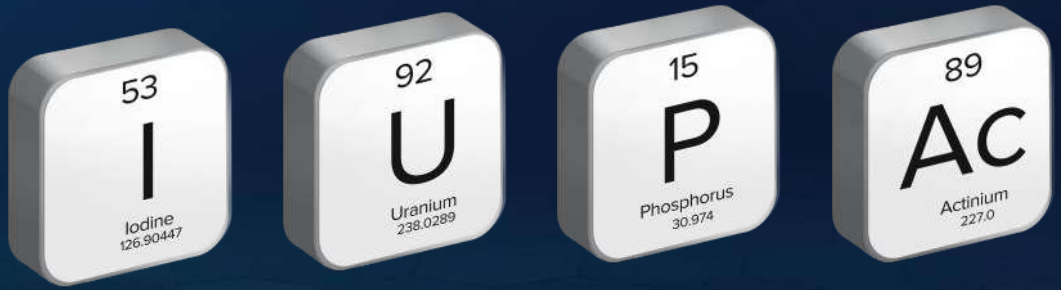
Citric acid → Citrus fruits

Formic acid → Red ants

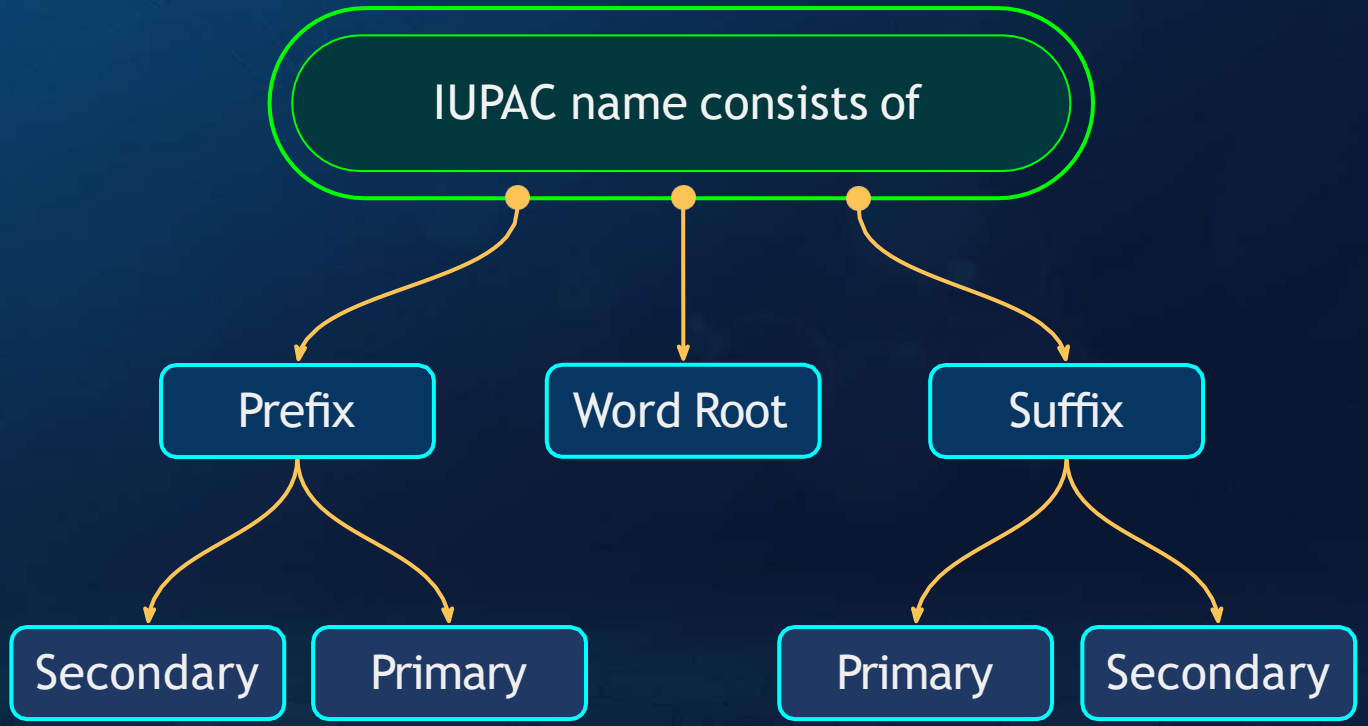
IUPAC

Standard rules set by

International **U**nion of **P**ure and **A**pplied **C**hemistry (IUPAC)



IUPAC Nomenclature



Word Root

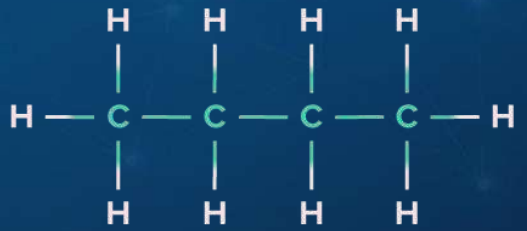
Number of carbon atoms in the parent chain	Word Root
1	Meth
2	Eth
3	Prop
4	But
5	Pent
6	Hex

Number of carbon atoms in the parent chain	Word Root
7	Hept
8	Oct
9	Non
10	Dec
11	Undec
12	Dodec

Primary Suffix

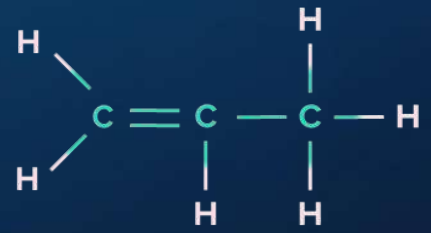
Carbon chain	Primary suffix	General name
Saturated	-ane	Alkane
Unsaturated with one double bond	-ene	Alkene
Unsaturated with one triple bond	-yne	Alkyne
Unsaturated with double bond and a	- enyne	Alkenyne

Naming Saturated Hydrocarbons



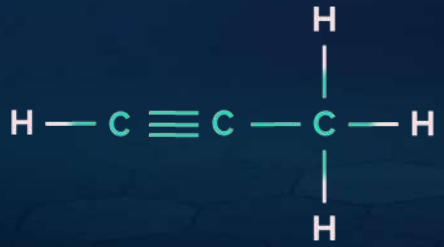
Word Root + Primary Suffix
But + ane

Butane



Word Root + Primary Suffix
Prop + ene

Propene



Word Root + Primary Suffix
Prop + yne

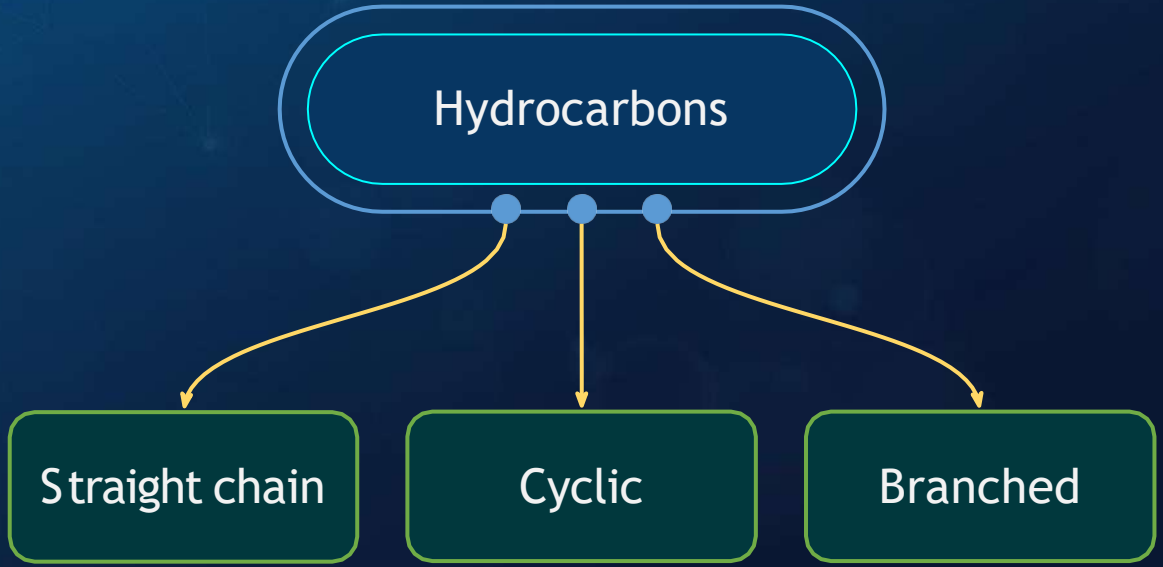
Propyne

Primary Prefix

A primary prefix is simply used to distinguish **cyclic from acyclic compounds**

Cyclo	+	Pent	+	ane	=	Cyclopentane
Primary Prefix		Word root		Primary Suffix		IUPAC name




Hydrocarbons
Straight chain
Cyclic
Branched

Straight Chain Hydrocarbon

Name	Molecular formula
Methane	CH_4
Ethane	C_2H_6
Propane	C_3H_8
Butane	C_4H_{10}
Pentane	C_5H_{12}
Hexane	C_6H_{14}

Name	Molecular formula
Heptane	C_7H_{16}
Octane	C_8H_{18}
Nonane	C_9H_{20}
Decane	$C_{10}H_{22}$
Undecane	$C_{11}H_{24}$
Dodecane	$C_{12}H_{26}$

Cyclic and Branched Hydrocarbon

Cyclic Hydrocarbons

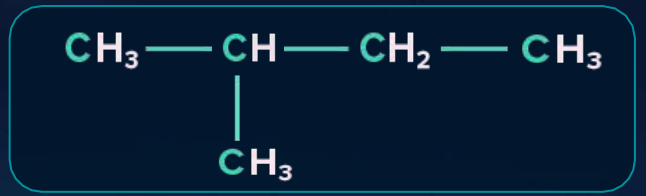


Cyclobutane



Cyclopentane

In branched chain hydrocarbons, **small chains of carbon atoms** are attached at **one or more carbon atoms of the parent chain.**



Alkyl Groups

An alkyl group is derived from a **saturated hydrocarbon** by **removing a hydrogen atom** from a carbon.

C_nH_{2n+2} (Alkane) $\xrightarrow{-H}$ C_nH_{2n+1} (Alkyl)

Alkane (C_nH_{2n+2}) $\xrightarrow{-H}$ Alk + yl (C_nH_{2n+1})

Alkene (C_nH_{2n}) $\xrightarrow{-H}$ Alken + yl (C_nH_{2n-1})

Alkyne (C_nH_{2n-2}) $\xrightarrow{-H}$ Alkyn + yl (C_nH_{2n-3})

Straight Chain Alkyl Groups

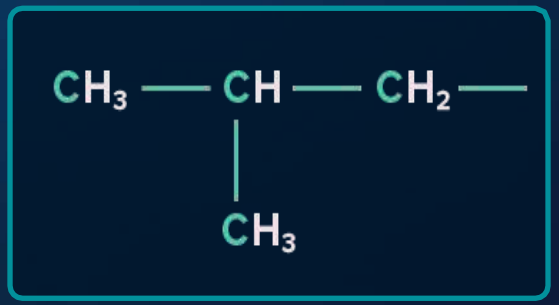
'yl' substitutes for 'ane' in corresponding alkane

Name	Molecular formula
Methyl	$-CH_3$
Ethyl	$-C_2H_5$
Propyl	$-C_3H_7$
Butyl	$-C_4H_9$
Pentyl	$-C_5H_{11}$

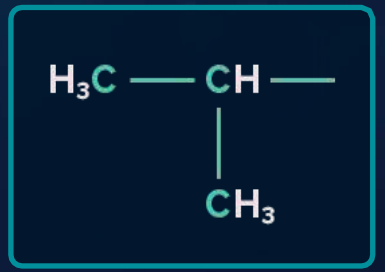
Some Important Alkyl Groups

Iso Group

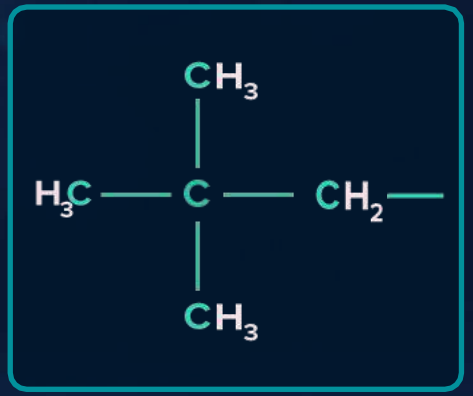
Neo Group



Isobutyl



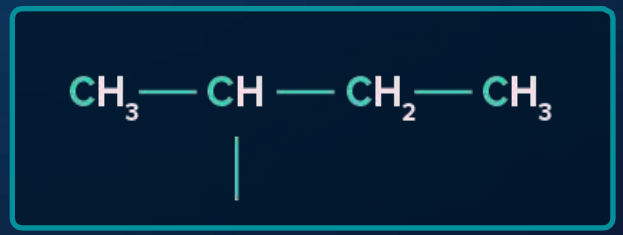
Isopropyl



Neopentyl

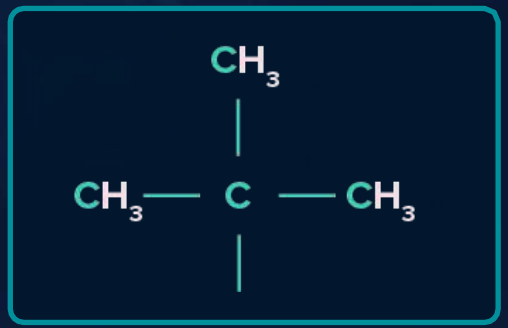
Some Important Alkyl Groups

Secondary Group (sec)

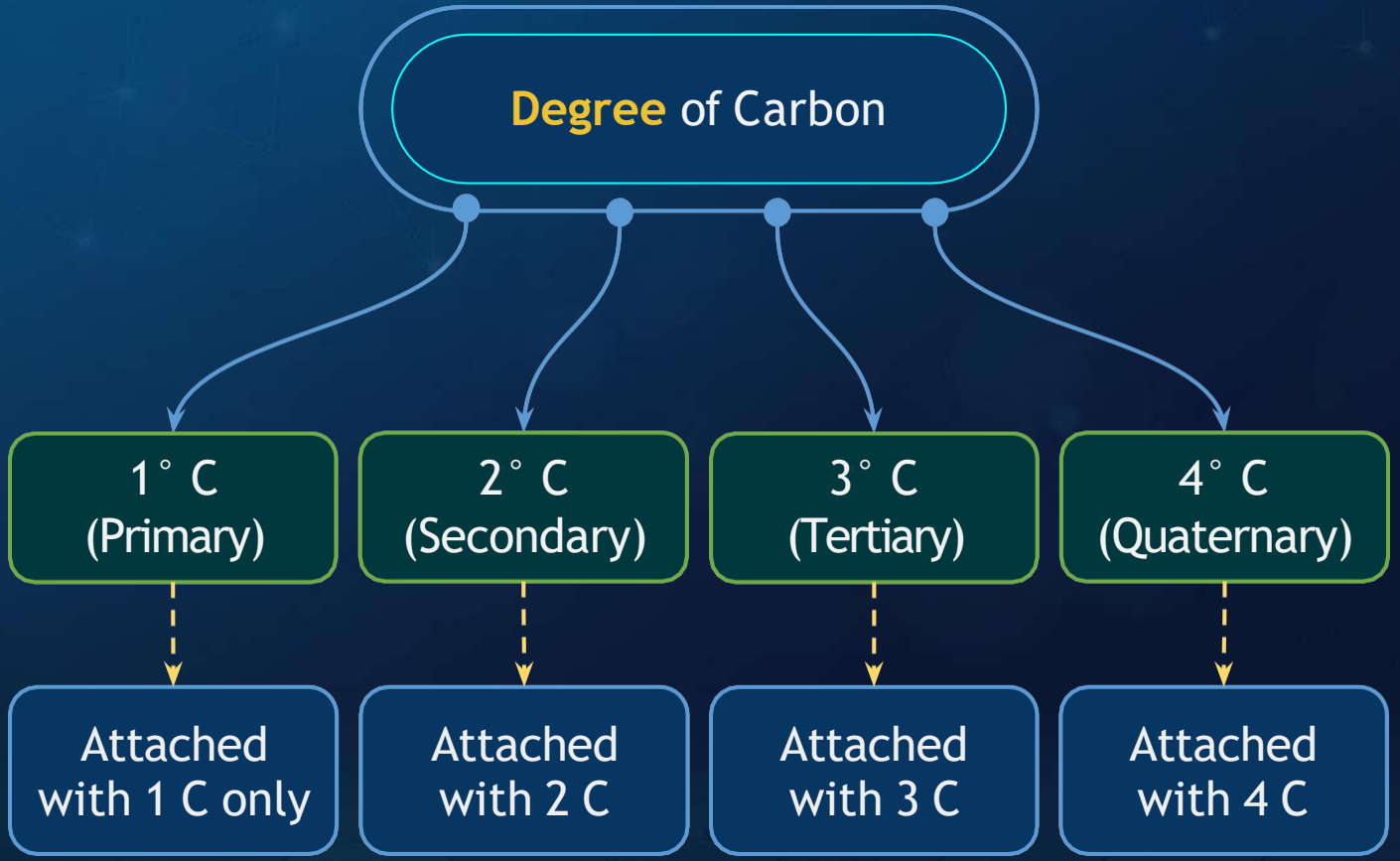


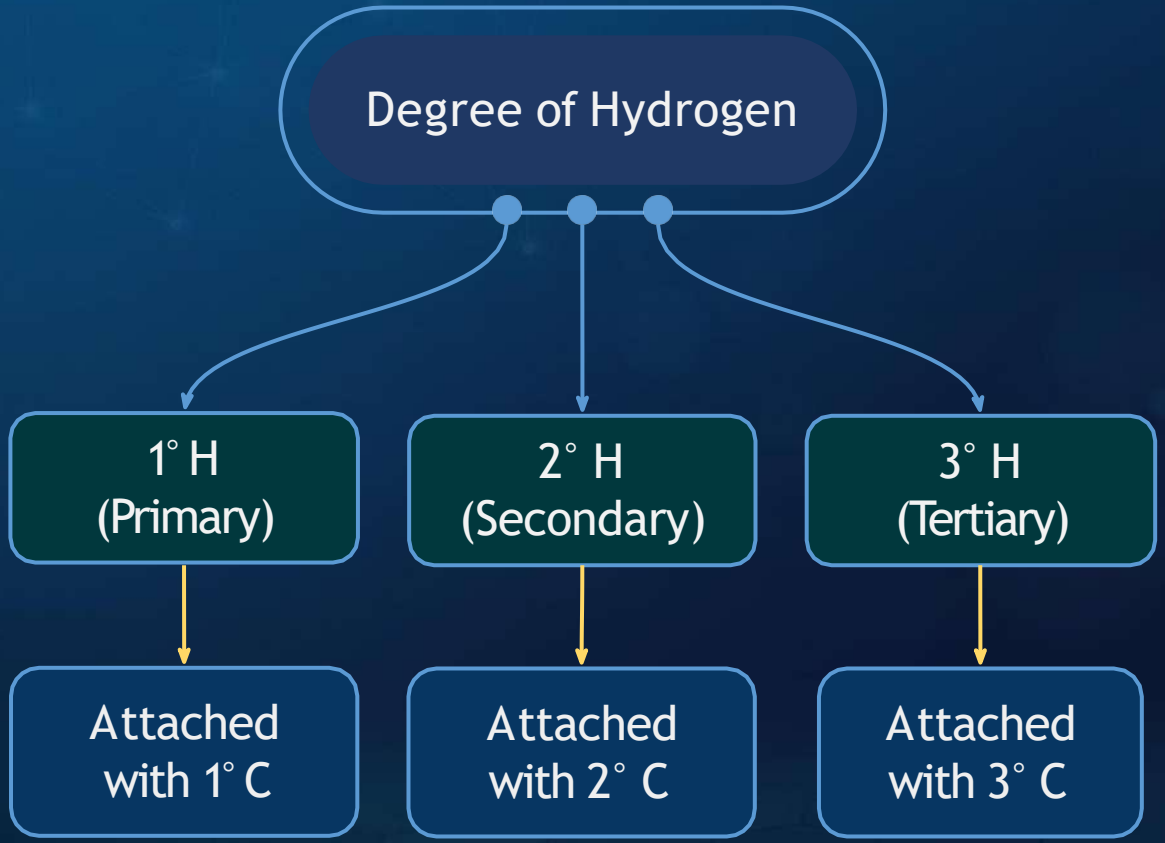
sec-Butyl

Tertiary Group (tert)



tert-Butyl

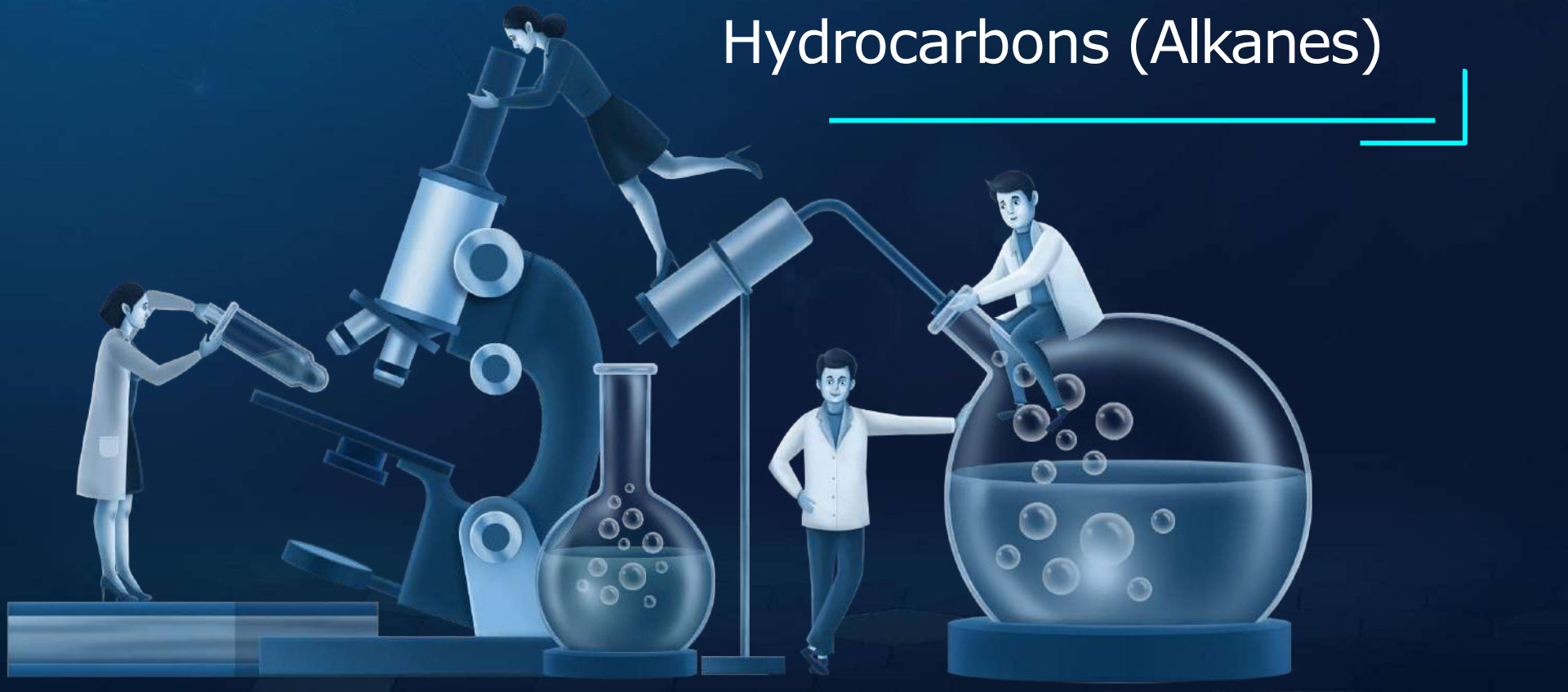

Degree of Carbon
1° C (Primary)
2° C (Secondary)
3° C (Tertiary)
4° C (Quaternary)
Attached with 1 C only
Attached with 2 C
Attached with 3 C
Attached with 4 C





4° (Quaternary) Carbon exists but 4° Hydrogen does not!

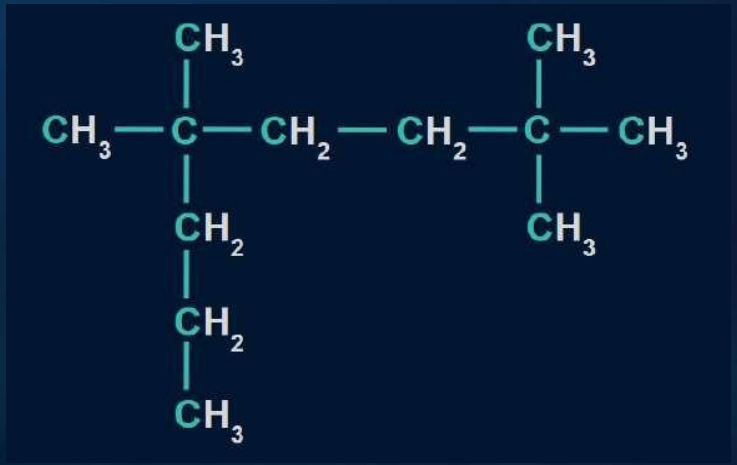
NomenclaĨure of SaĨuraĨed Hydrocarbons (Alkanes)

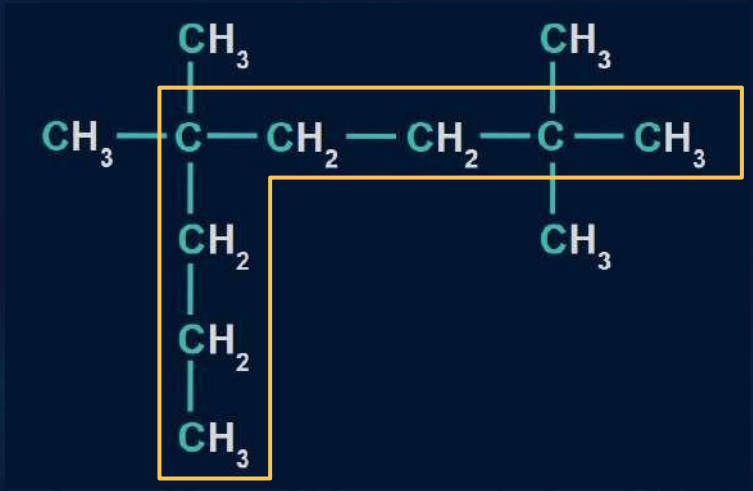


Determining the Parent Chain

Rule 1

Select the **longest** continuous carbon chain in the molecule. This chain is called the **parent chain.**



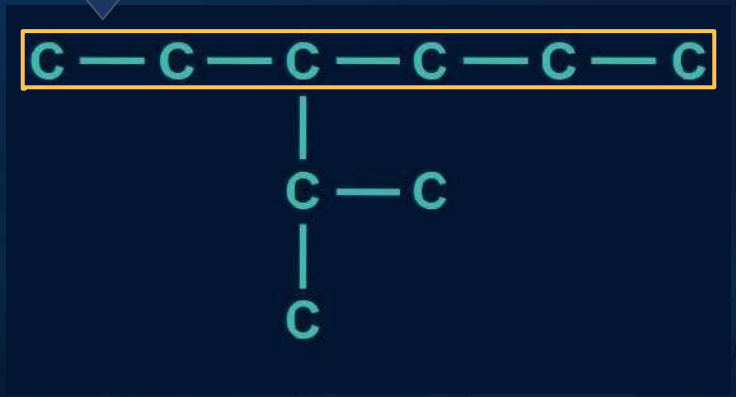


Chains with Equal Length

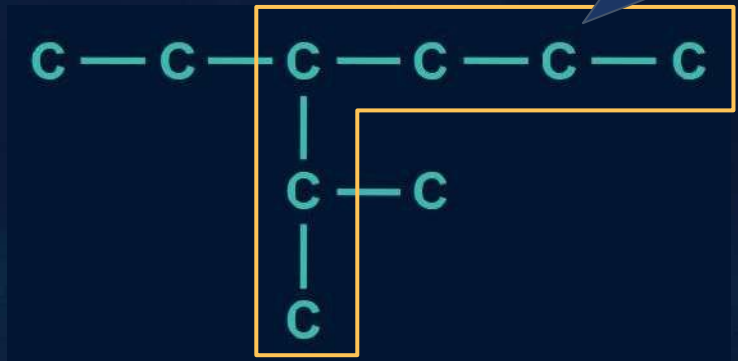
Rule 2

When chains of **equal lengths** are competing for selection, then the chain that has more number of substituents/branches is selected.

This chain has only one branch.



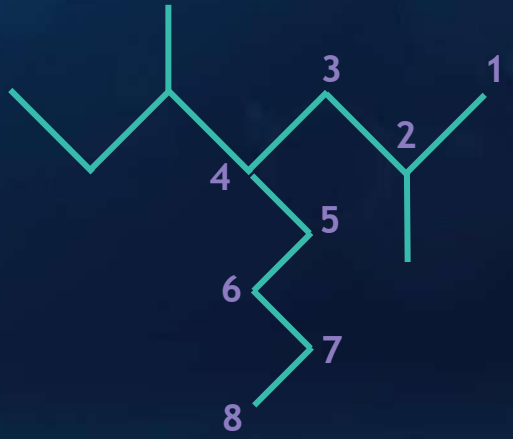
This chain is also 5 membered, but contains 2 side chains.



Chains with Equal Number of Substituents

Rule 3

When the **number of substituents are the same**, then the substituents at the **nearest positions** from either end is preferred for parent chain selection.



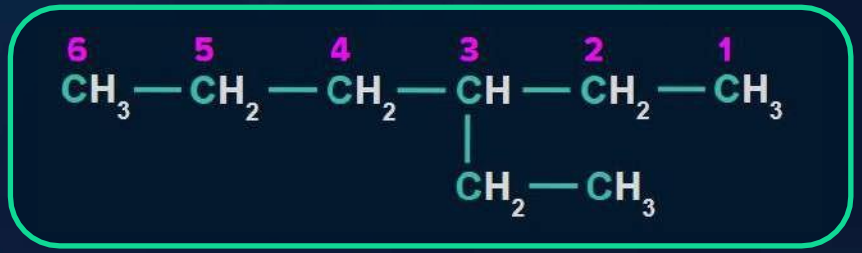
Assigning Locants

Numbering of Carbon Chain

The number that indicates the position of the substituent, side chain, multiple bonds or functional group.

Rule 1

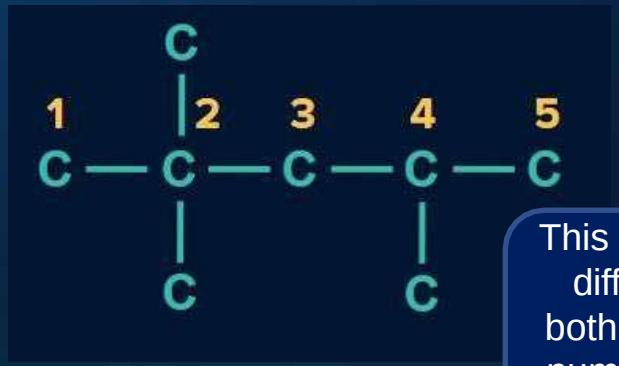
The **branched carbon** atom gets the **lowest** possible number

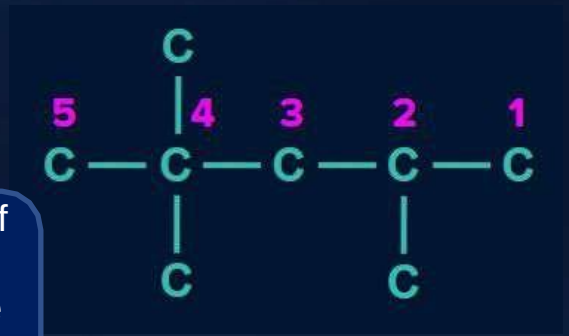


Numbering in the Presence of Multiple Substituents

Rule 2

When both the directions lead to a **tie in the lowest number**, choose the direction that gives the **first point of difference**





This is the first point of difference as from both the direction, the numbering starts with same number (2)

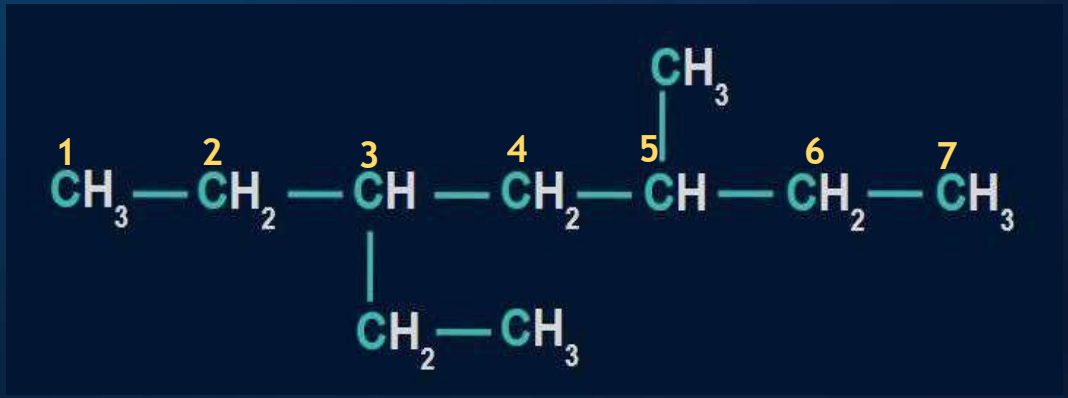
2,2,4

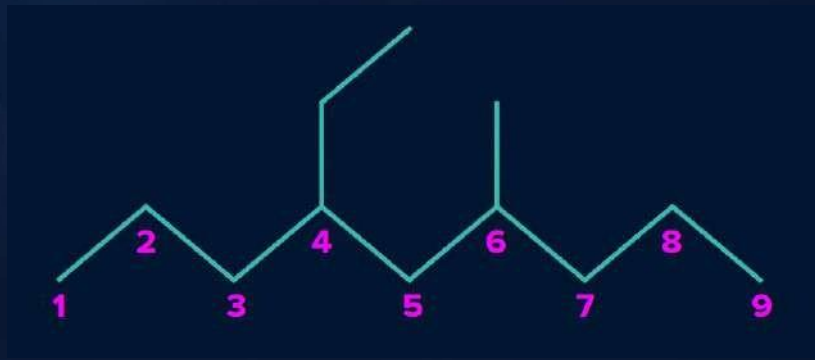
2,4,4

Substituents in Alphabetical Order

Rule 3

When numbering from either end results in the **same set of locants**, then the substituent coming first in the **alphabetical order** gets lower number.





The chain numbered from left to right is preferred because the substituent “ethyl” comes at C-3 while from right to left, at C-3, “methyl” substituent comes first. As ‘e’ comes before ‘m’, lowest number with “ethyl” substituent is correct.

In the IUPAC Name of a Compound

1. **Numbers** are separated from each other **by commas.**
2. Numbers are separated from words by **hyphens** and there is **no space** between the name of the substituents and the word root.
3. The locant **'1' is often omitted** when there is no ambiguity.
4. Locants are placed **immediately before the part of the name** to which they are related.

Secondary Prefix

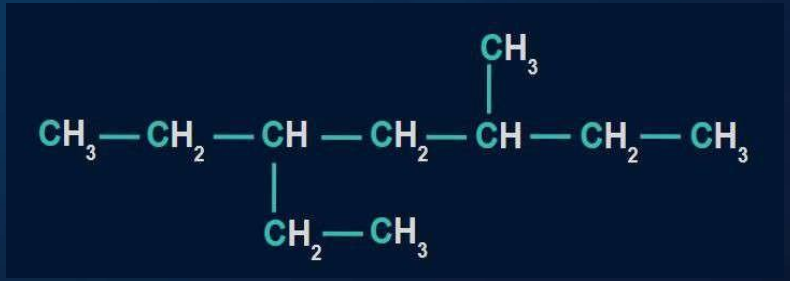
Secondary prefixes are added **immediately before the primary prefix** with their appropriate locations **in alphabetical order** to denote the side chains or substituent groups.

Substituent group	Secondary prefix
- R	Alkyl

Substituents in Alphabetical Order

Rule 1

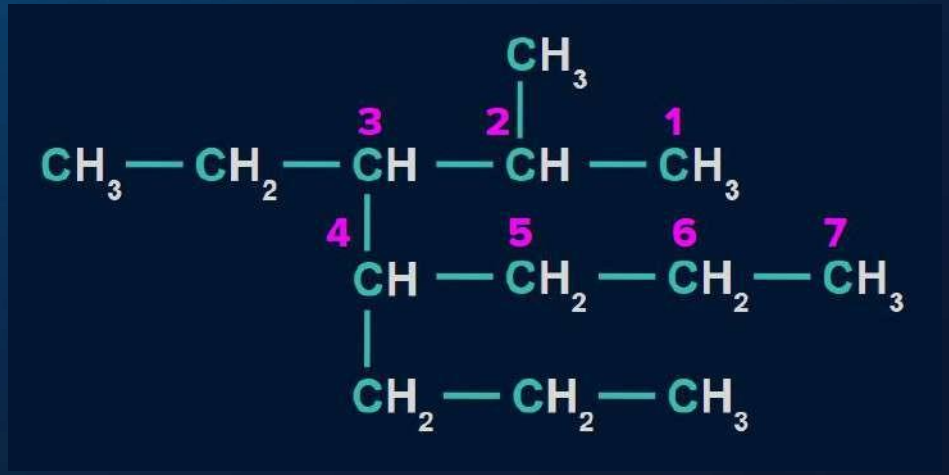
Secondary prefixes are written with their appropriate locations in the alphabetical order.



3-Ethyl-5-methylheptane

Secondary prefix	+	Primary prefix	+	Word root	+	Primary suffix
3-Ethyl-5-methyl	+	-	+	hept	+	ane

Substituents in Alphabetical Order



3-Ethyl-2-methyl-4-propylheptane

Occurrence of a Substituent More Than Once

Rule 2

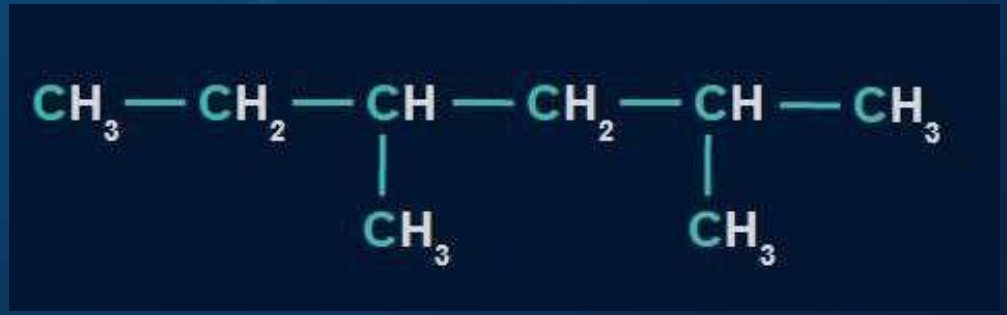
If the same substituent occurs more than once in the molecule, then **prefixes di, tri, tetra** are used to indicate how many times it appears.

- **di** → 2
- **tri** → 3
- **tetra** → 4

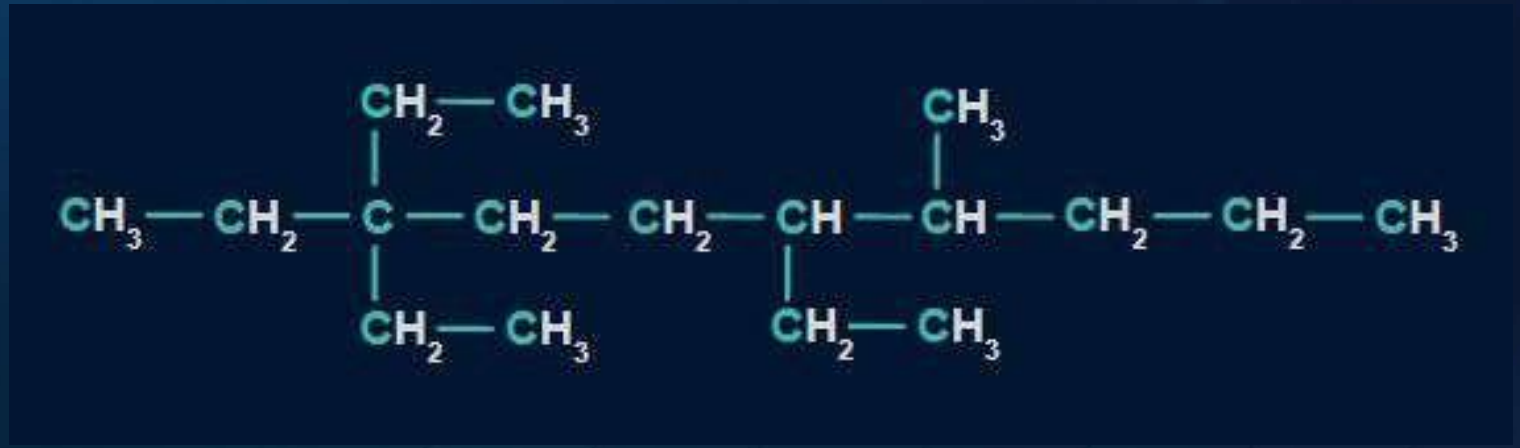


The prefixes di, tri, tetra are not considered in alphabetical order.

Occurrence of a Substituent More Than Once



2,4-Dimethylhexane



3,3,6-Triethyl-7-methyldecane

Complex Substituents

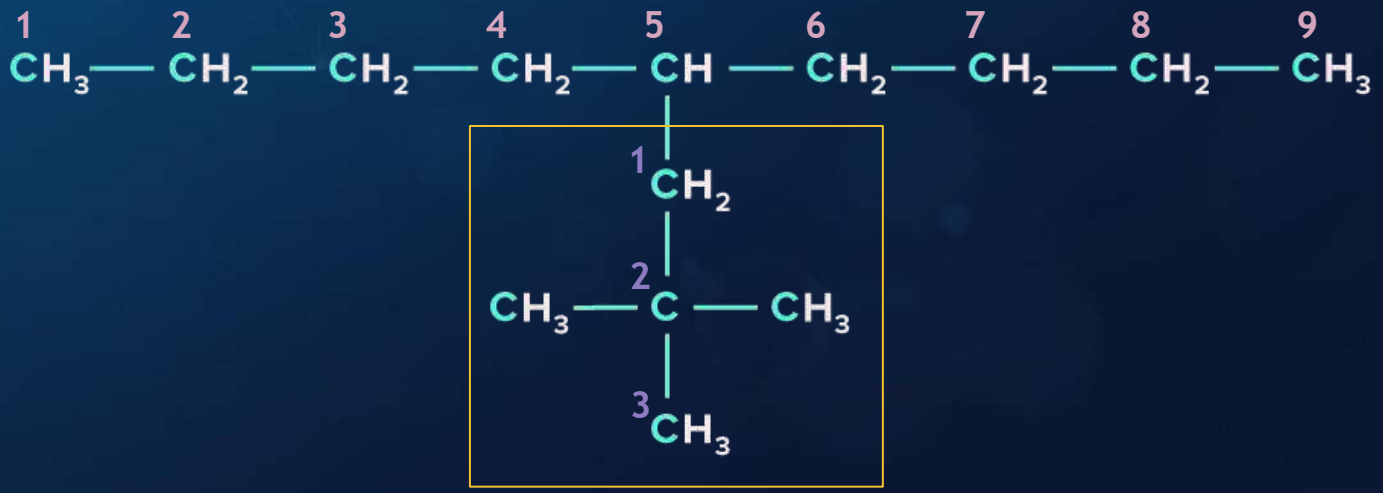
1. If **branching occurs within the side chain,** then it is considered as a **complex substituent.**

2. Numbering of complex substituent always starts from that **carbon connected directly to main chain.**



Name of the branched side chain is written in brackets to avoid confusion.

Complex Substituents

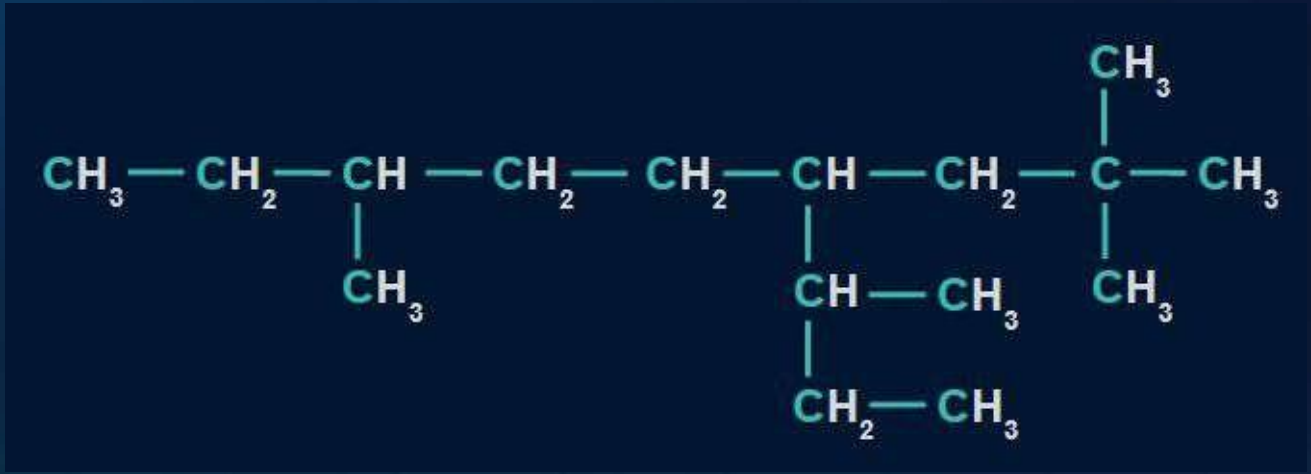


5-(2,2-Dimethylpropyl)nonane

Deciding the Alphabetical Order

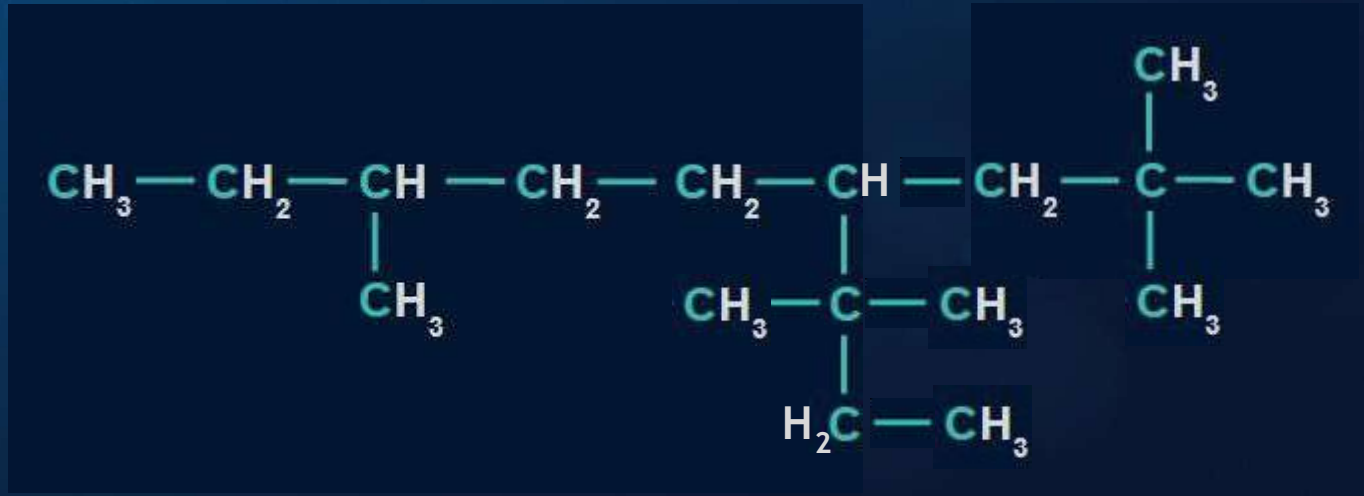
Rule 3

Prefixes di, tri, tetra etc., are **not considered in deciding the alphabetical order for simple substituents** but are considered for complex substituents.



2,2,7-Trimethyl-4-(1-methylpropyl)nonane

Deciding the Alphabetical Order



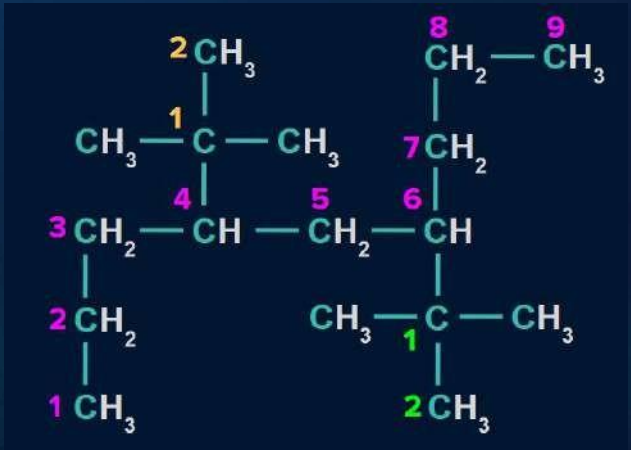
4-(1,1-Dimethylpropyl)-2,2,7-trimethylnonane

Presence of Similar Complex Substituents

Rule 4

If more than one similar complex substituents are present, then the numeral **prefixes bis, tris, tetrakis,** etc., are used.

bis → 2 | **tris → 3** | **tetrakis → 4**

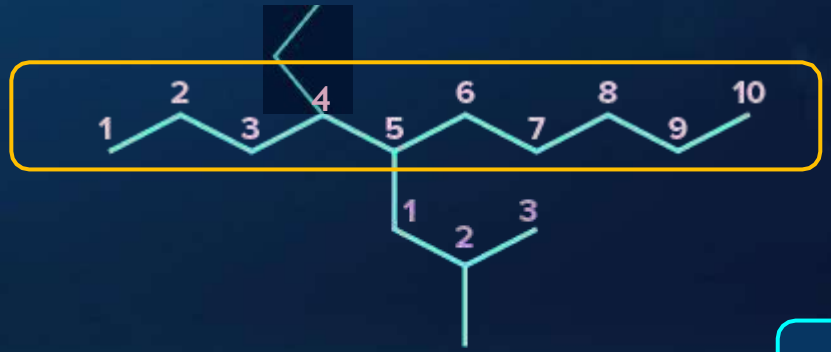


4,6-Bis(1,1-dimethylethyl)nonane

Deciding the Alphabetical Order

Rule 5

Iso & Neo are considered for the alphabetical order.



4-Ethyl-5-isobutyldecane

Or

4-Ethyl-5-(2-methylpropyl)decane

Point to Remember!!



Names such as **isopropyl, sec-butyl** and **tert-butyl** are acceptable substituent names in the IUPAC system. But systematic substituent names are preferable.

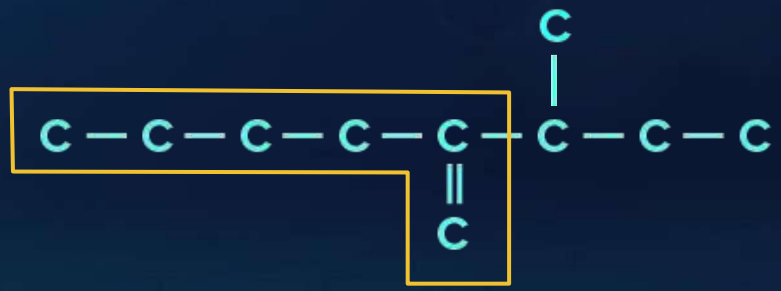
Nomenclature of Unsaturated Hydrocarbons



Parent Chain Selection

Selection of parent chain:

Maximum number of multiple bonds > Maximum number of carbon > Maximum number of substituents



Assigning Locants

Numbering of the parent chain:

Position of the multiple bond > Position of the substituents > Alphabetical order of the substituents

IUPAC Nomenclature of Polyenes/Poly-ynes

If **more than one multiple bond** is present, then we have to indicate their numbers using **di, tri, tetra,** etc., and their positions using **locants**

While naming polyenes and poly-ynes, alphabet '**a**' will be added just after word root.



1,3-But**a**diene OR But**a**-1,3-diene



1,3,5-Hex**a**triyne

OR

Hex**a**-1,3,5-triyne

Point to Remember!!

If both **double and triple bonds** are present in a structure,

Note !!!

While numbering	Lowest locant set is chosen
In case of a tie	Alkene is preferred over alkyne in assigning number
While naming,	'ene' comes before 'yne' alphabetically

Terminal **'e'** is **dropped** if it is followed by the alphabets **a, i, o, u or y**

Alkene/Alkyne as Substituent Groups

- Alkane → Alkyl
- Alkene → Alkenyl
- Alkyne → Alkynyl

Compound	IUPAC name	Common name
$-CH_2-CH=CH_2$	Prop-2-enyl	Allyl
$-CH=CH-CH_3$	Prop-1-enyl	-
$-CH=CH_2$	Ethenyl	Vinyl

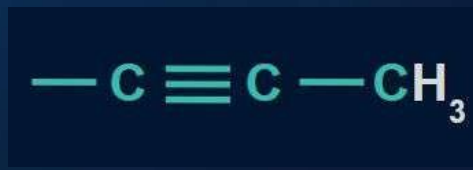


3-Ethenylpenta-1,4-diene

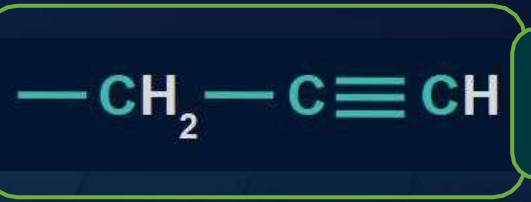
Examples



Ethynyl



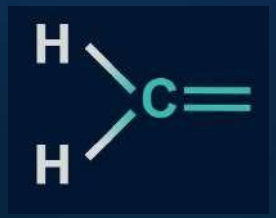
Prop-1-ynyl

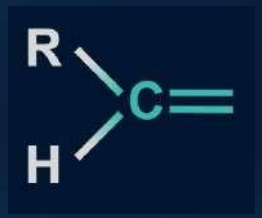


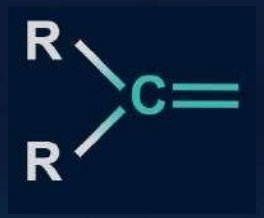
Prop-2-ynyl

Alkene/Alkyne as Substituent Groups

Alkylidene



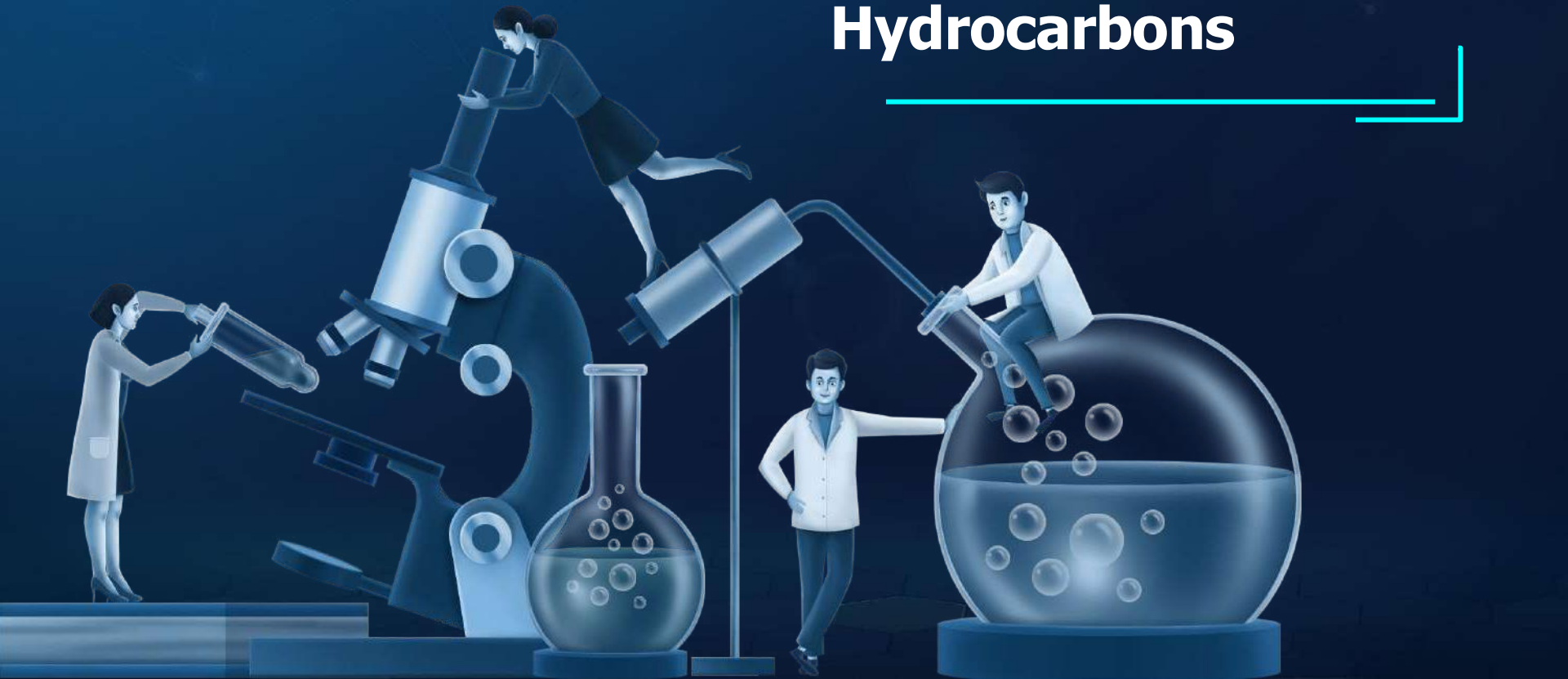






3-**Methylidene**penta-1,4-diene

Nomenclature of Cyclic Hydrocarbons



Parent Chain Selection

Rule for Selection of Parent Chain:

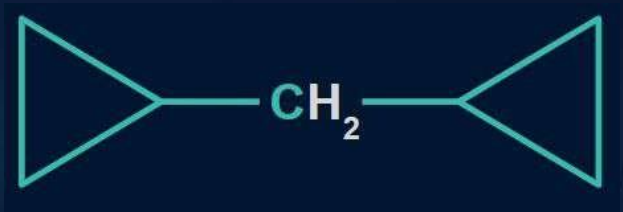
Maximum number of multiple bonds > Maximum number of carbon > Maximum number of substituents

All are same → Cyclic part - Parent chain

Remember!!

If more than one cyclic ring is attached to an open chain

Rings - **Substituent**
Open Chain - **Parent Chain**

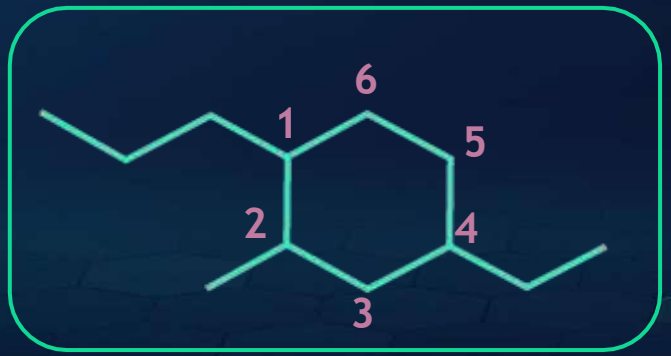


Assigning Locants

Numbering of the parent chain:

Position of the multiple bond > Position of the substituent > Alphabetical order of the substituents

If cyclic part is present as a **substituent** → Cyclo is considered in **alphabetical order**





Nomenclature of Organic Compounds with Functional Groups

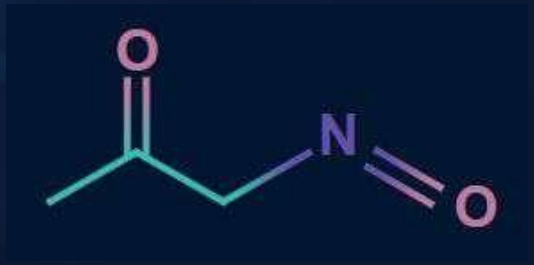
Nomenclature

A **secondary suffix** is added to the **primary suffix** to indicate the nature of the functional group present in the organic compound.

Nitroso Compounds (–NO)
Prefix: **nitroso**

Secondary Prefix

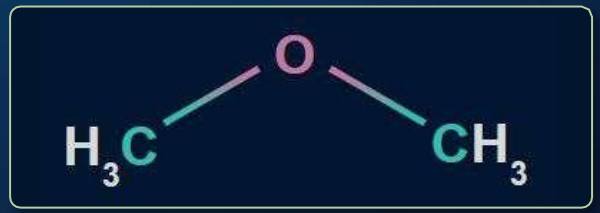
Substituent group	Secondary prefix
— R	Alkyl
— X	Halo
— NO_2	Nitro
— OR	Alkoxy
— NO	Nitroso

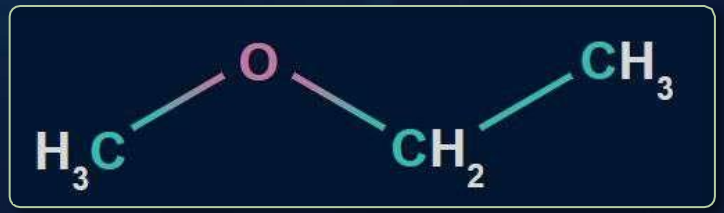


1-Nitroso-2-propanone

Ether

Ethers (R–O –R′)
Prefix **: (–alkoxy)**



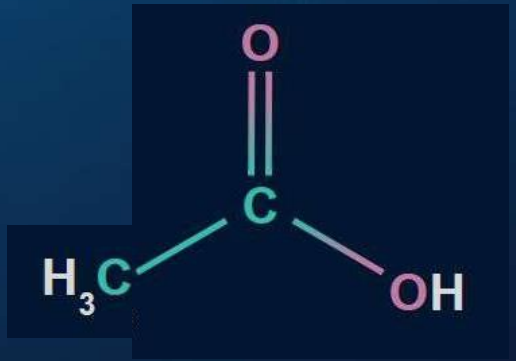


Methoxy methane

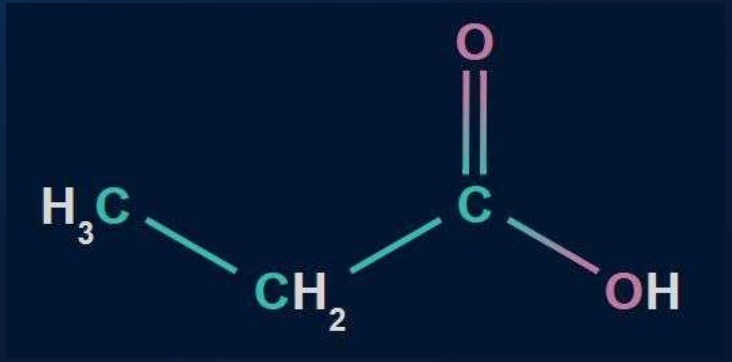
Methoxy ethane

Carboxylic Acids

Carboxylic acids (– COOH) - Suffix: –oic acid



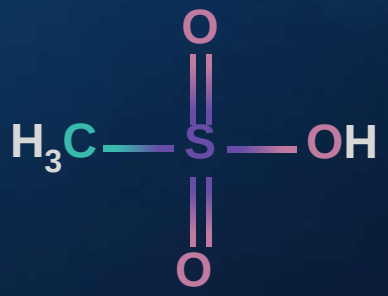
Ethanoic acid



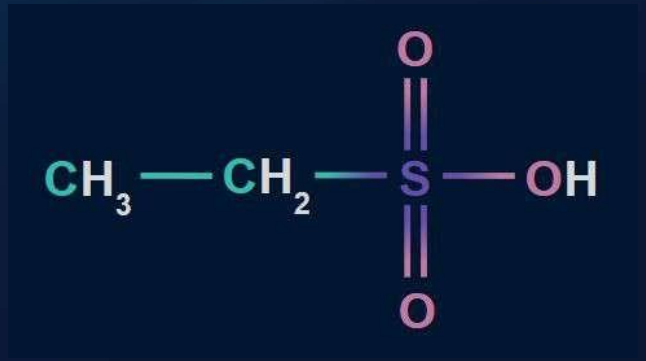
Propanoic acid

Sulphonic Acids

Sulphonic acids ($-SO_3H$)
Suffix: **–sulphonic acid**



Methanesulphonic acid

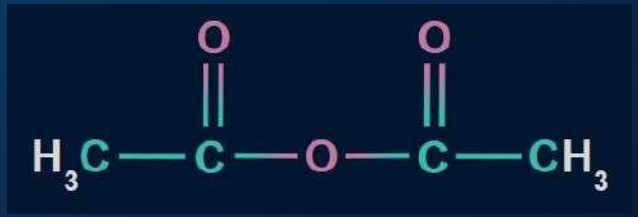


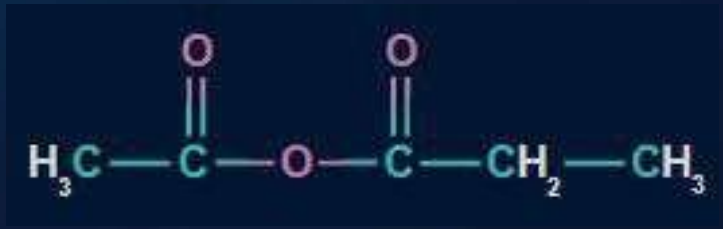
Ethanesulphonic acid

Acid Anhydride

Acid Anhydride (– COOCOR)

Suffix: **– oic anhydride**



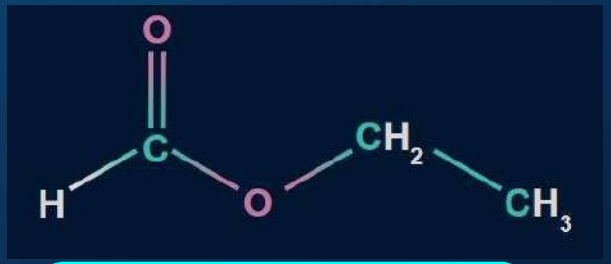


Ethanoic anhydride

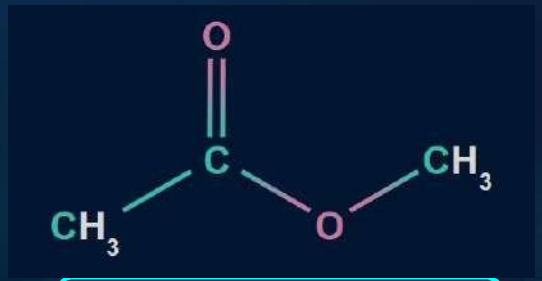
Ethanoic propanoic anhydride

Esters

Esters (–COOR)- Suffix: **–oate**



Ethyl methanoate

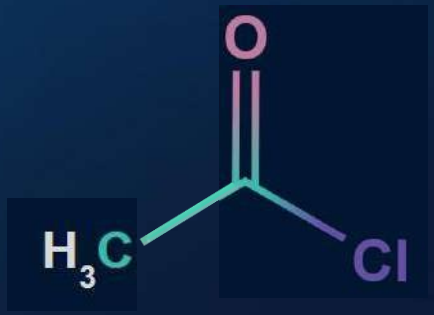


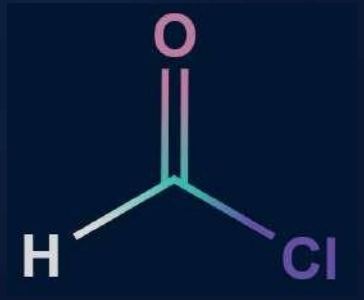
Methyl ethanoate

Name of group attached to the oxygen of ester should be written even before secondary prefix

Acid Halides

Acid Halides (–COX)
Suffix: **–oyl halide**





Ethan**oyl chloride**

Methan**oyl chloride**

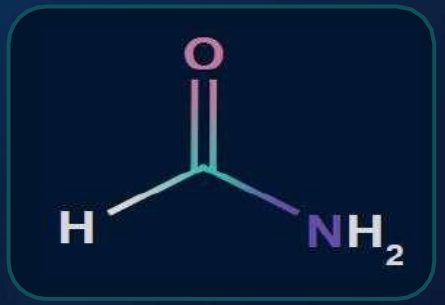
Amides

Amides
Suffix: **-amide**

$-CONH_2$ — 1º Amide

$-CONHR$ — 2º Amide

$-CONR_2$ — 3º Amide



Methan**amide**



Ethan**amide**

Amides

Name of groups attached to the nitrogen of amide should be **written alphabetically** and "**N**" prefix should be used for it as position



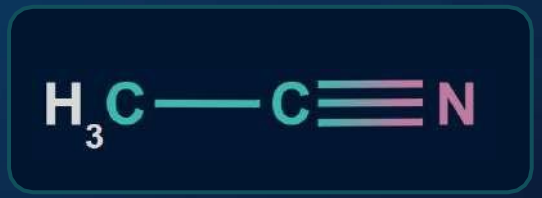
N-Methylethan**amide**



N,N-Dimethylethan**amide**

Cyanide

Cyanide (– C ≡ N)
Suffix: –nitrile





Ethanenitrile

Propanenitrile

Isocyanide

Isocyanide ($-\overset{+}{N}\equiv\overset{-}{C}$, $-N\rightleftharpoons C$)

Suffix: **–isonitrile**



Methan**isonitrile**



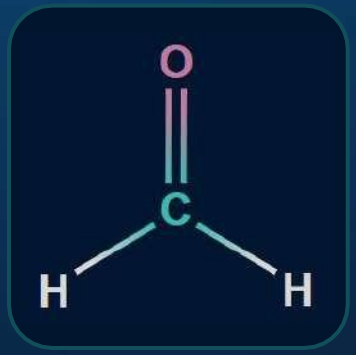
Propan-2-**isonitrile**

Cyanide and isocyanide are two different functional group. Also, cyanide has more priority over isocyanide.

Aldehydes and Ketones

Aldehydes (–CHO)
Suffix: **–al**

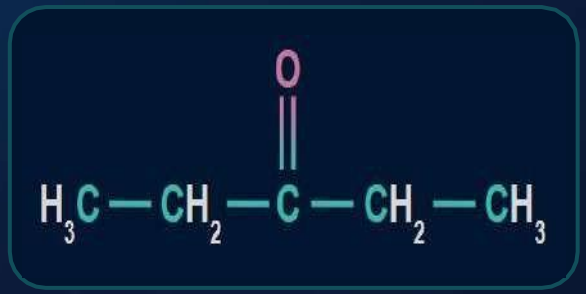
Ketones (>C=O)
Suffix: **–one**



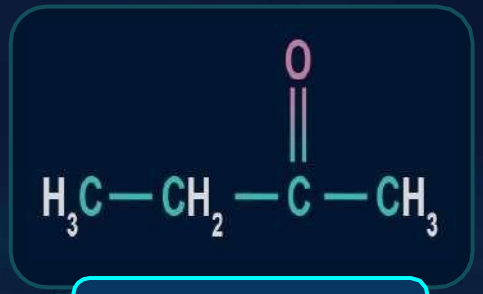
Methan**al**



Ethan**al**



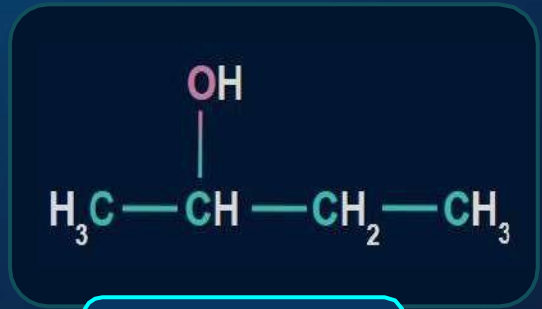
Pentan-3-**one**



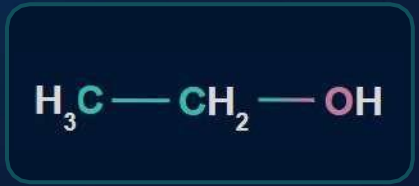
Butan-2-**one**

Alcohols and Thiols

Alcohols (– OH)
Suffix: **– ol**



Butan-2-**ol**

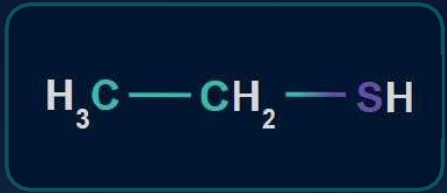


Ethan**ol**

Thiols (– SH)
Suffix: **–thiol**



Butane-2-**thiol**



Ethane**thiol**

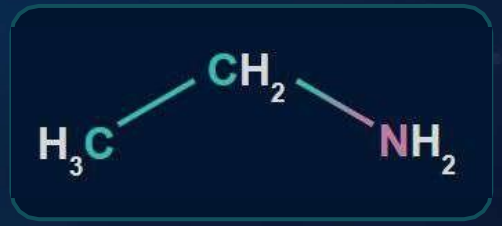
Amines

Amines
Suffix:
-amine

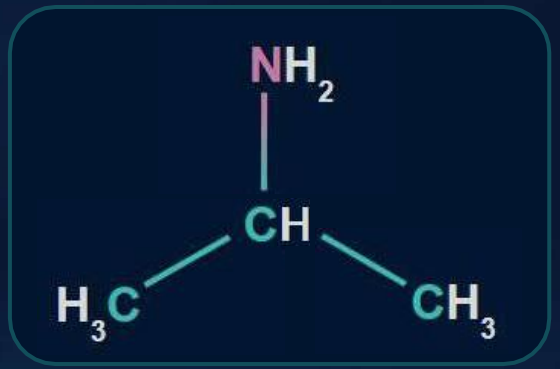
1º Amine
$-NH_2$

2º Amine
$-NHR$

3º Amine
$-NR_2$



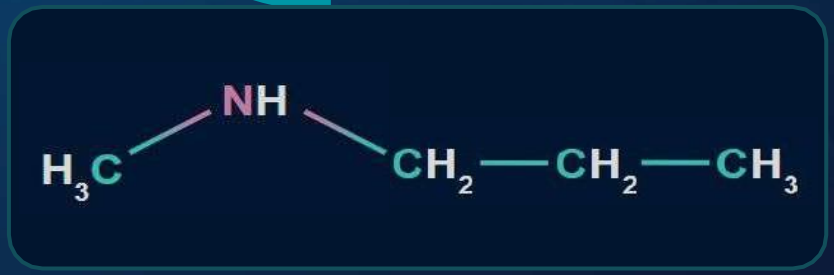
Ethan**amine**



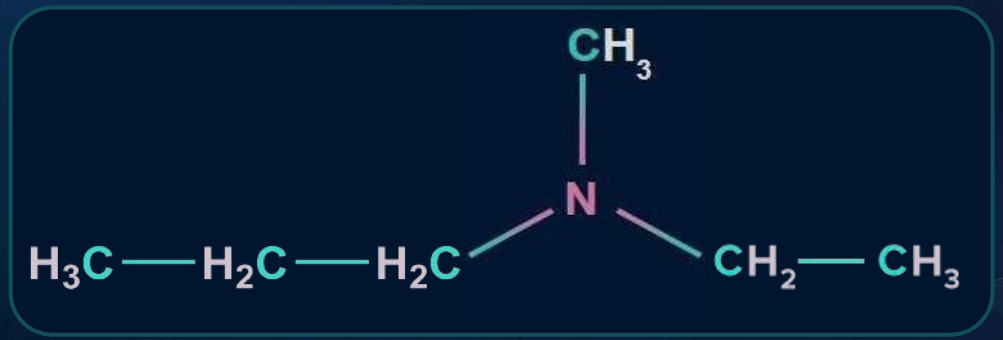
Propan-2-**amine**

Amines

Name of the groups attached to the nitrogen of amine should be **written alphabetically** and prefix "**N**" should be used for it as position.



N-Methylpropan**amine**



N-Ethyal-N-methylpropan**amine**


IUPAC Nomenclature of
Compounds Containing
Functional Groups

Parent Chain Selection

Main functional group > Same main functional group > Maximum number of multiple bonds

> Maximum number of C atoms > Maximum number of substituents

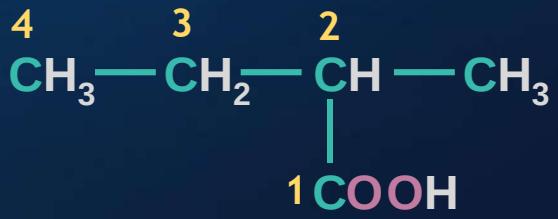
Assigning Locants

Main functional group > Same main functional group > Multiple bonds (ene > yne)

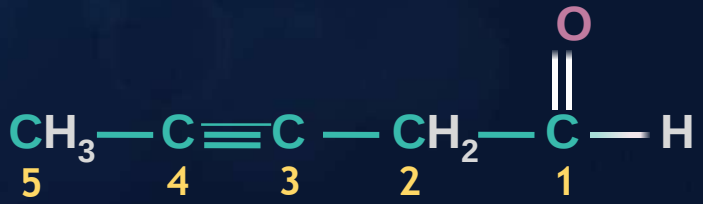
> Maximum number of side chains > When all things are identical, then alphabetical order

Assigning Locants

When a functional group such as
- COOH, -COOR, -COX, -$CONH_2$, -CN or - CHO
is present, it is always given **number '1'.**



2-Methylbutanoic acid



Pent-3-ynal

Point to Remember!!

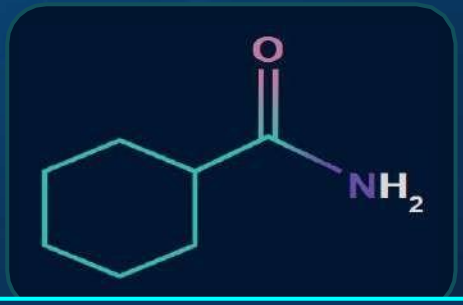
When some **carbon containing functional groups** are directly attached to a ring

The ring is taken as the **parent chain**

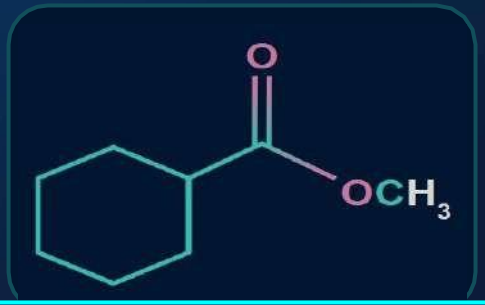
A **special suffix** is used for these functional groups.

Functional Group	Suffix
-CHO	Carbaldehyde
-COOH	Carboxylic Acid
-COX	Carbonyl halide
-COOR	Alkyl carboxylate
$-CONH_2$	Carboxamide
-CN	Carbonitrile

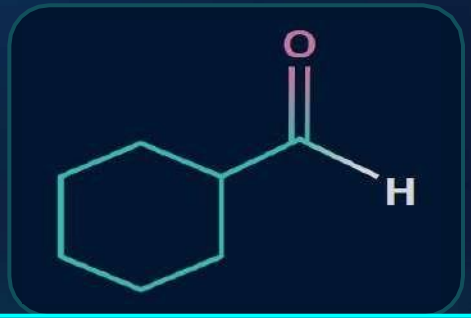
Examples



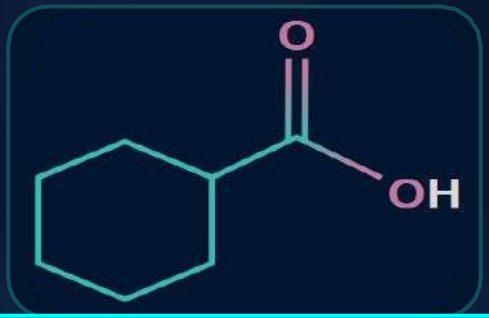
Cyclohexane**carboxamide**



Methylcyclohexane**carboxylate**



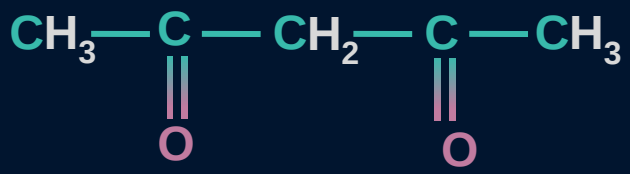
Cyclohexane**carbaldehyde**



Cyclohexane**carboxylic acid**

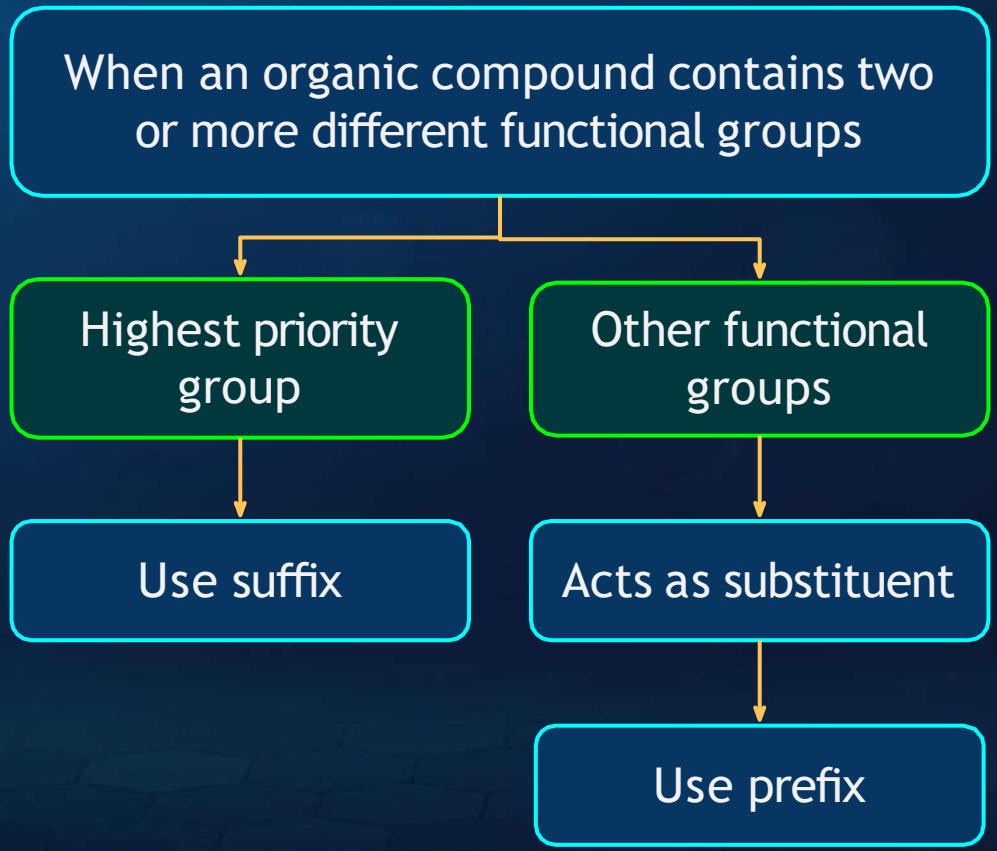
Naming Compounds Containing Functional Groups

If a compound contains two or more same functional groups, the numerical prefixes **di, tri, tetra** etc., are used.



Pentane-2,4-dione

Naming Compounds Containing Functional Groups



Principal Functional Group

The choice of the principal functional group is made on the basis of the priority table.



Name	Group	Prefix	Suffix
Carboxylic Acids	-COOH	-carboxy	-oic acid
Sulphonic Acid	$-SO_3H$	-sulpho	-sulphonic acid
Acid Anhydride	-COOCOR	-	-oic anhydride
Esters	-COOR	-alkoxy carbonyl	-oate
Acid halide	-COX	-halo carbonyl	-oyl halide
Amides	$-CONH_2$	-carbamoyl	-amide
Nitriles	-CN	-cyano	-nitrile
Isonitriles	-NC	-isocyano	-isonitrile
Aldehydes	-CHO	-formyl/oxo	-al
Ketones	>C=O	-oxo/keto	-one
Alcohols	-OH	-hydroxy	-ol
Thiols	-SH	-mercapto	-thiol
Amines	$-NH_2$	-amino	-amine

Some Important Points

Aldehydes (–CHO)
Prefix: **formyl/oxo**

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

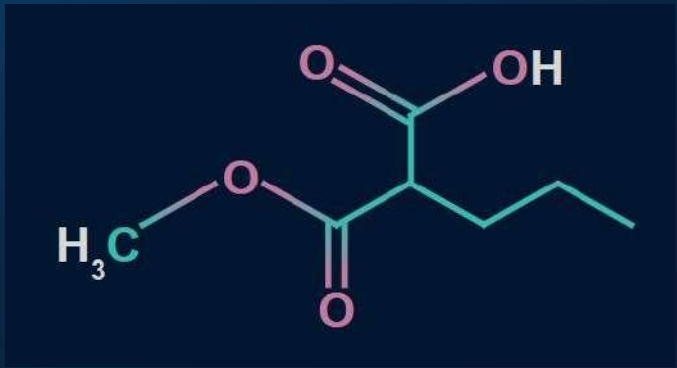


6-Oxohexanoic acid

Some Important Points

Esters (–COOR)
Prefix: **alkoxy carbonyl**

Used when C atom of ester is directly attached to the parent chain.

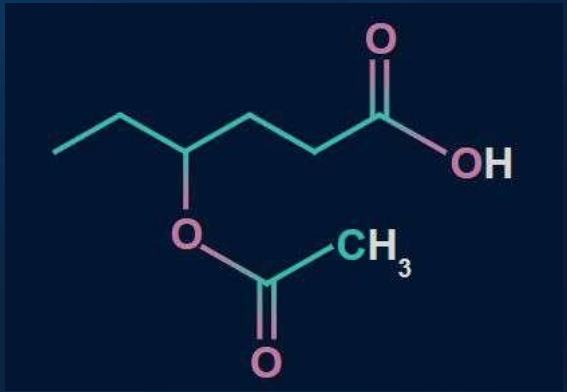


2-(Methoxycarbonyl)pentanoic acid

Some Important Points

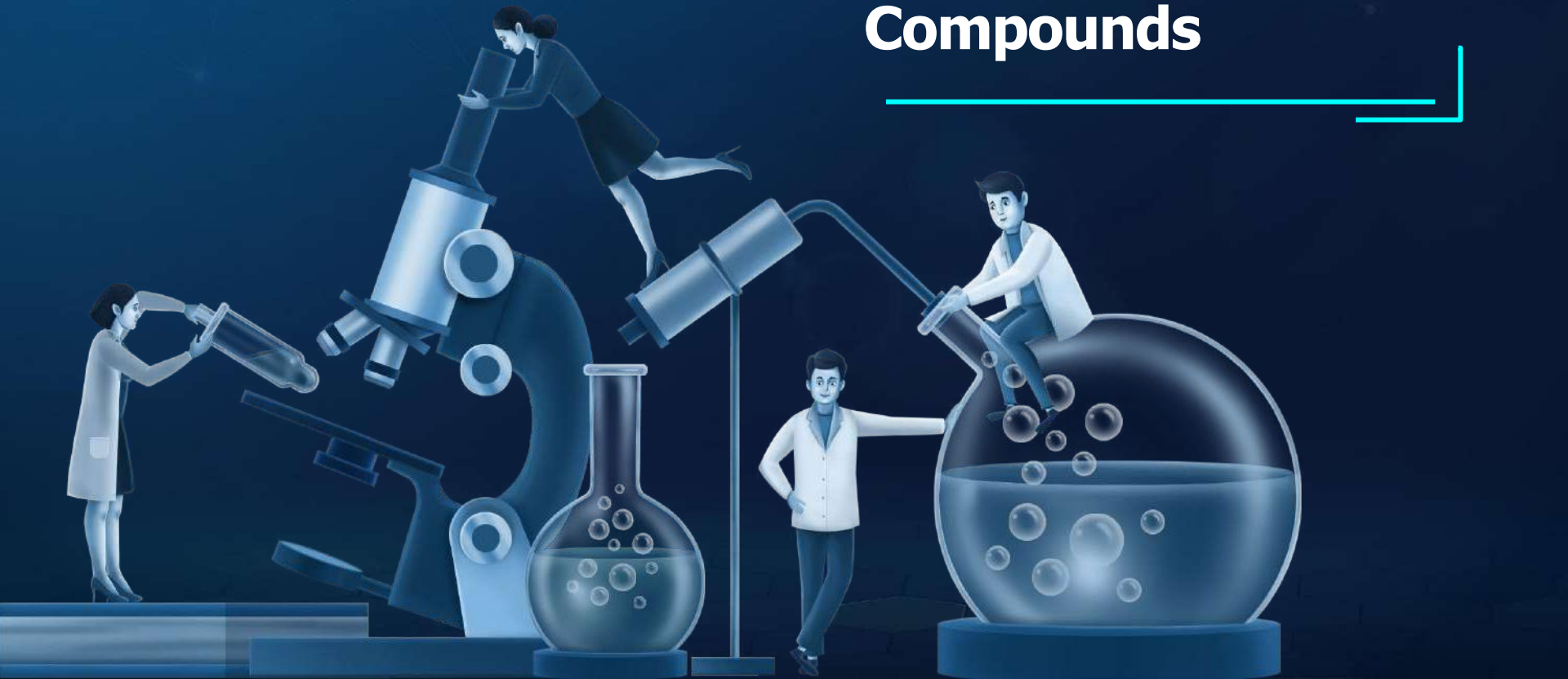
Esters (–COOR)
Prefix: **alkanoyloxy**

Used when O atom of ester is directly attached to parent chain.



4-(Ethanoyloxy)hexanoic acid

Nomenclature of Aromatic Compounds



Aromatic Compounds

Benzene is the simplest aromatic hydrocarbon

In many simple compounds, **benzene** is the **parent name** and the **substituent** is simply indicated by a **prefix**.

Examples



Fluorobenzene



Chlorobenzene



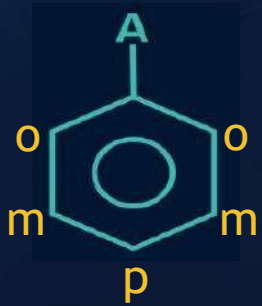
Bromobenzene

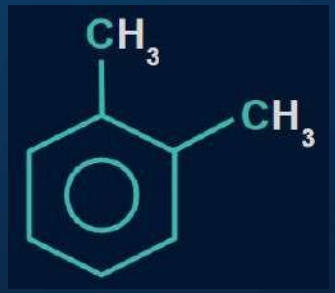


Nitrobenzene

Nomenclature of Benzene Derivatives

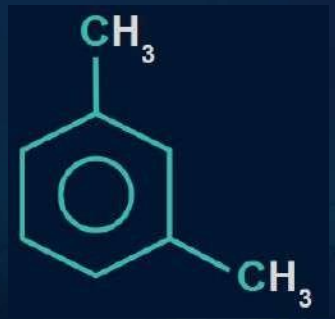
When two substituents are present, their relative positions are indicated by the prefixes **ortho-, meta- and para-** or by the use of numbers.





1,2-Dimethylbenzene

o-Dimethylbenzene



1,3-Dimethylbenzene

m-Dimethylbenzene

Nomenclature of Benzene Derivatives

If **more than two groups** are present on the benzene ring, their positions must be indicated by the use of **numbers**.

The benzene ring is numbered such that the **lowest possible numbers are given to the substituents**.

When more than two substituents are present and the substituents are different, they are listed in their **alphabetical order.**

Nomenclature of Benzene Derivatives



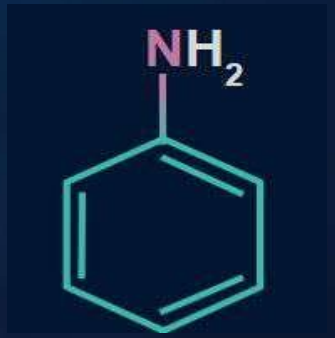
2-Bromo-1-chloro-5-fluoro-3-iodobenzene

When a substituent (or a functional group) together with the benzene ring gives a **new base name**, that substituent (or functional group) is assumed to be **in position 1and the new parent name is used.**

New Base Name







Phenol

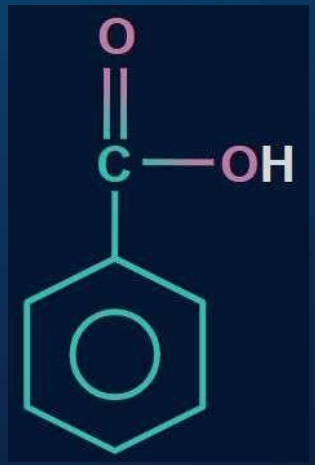
Methylbenzene

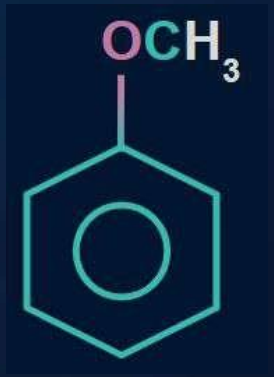
Benzenamine

Toluene

Aniline

New Base Name





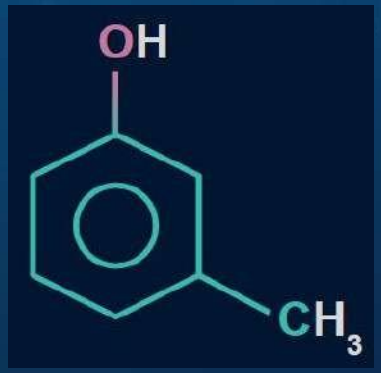
Benzenecarboxylic acid

Methoxybenzene

Benzoic Acid

Anisole

Naming with New Base Name



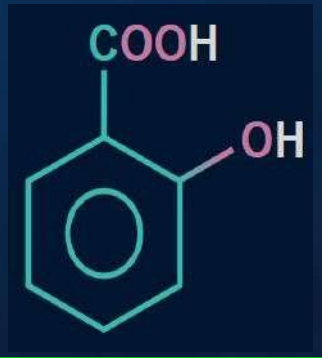
3-Methylphenol

m-Methylphenol

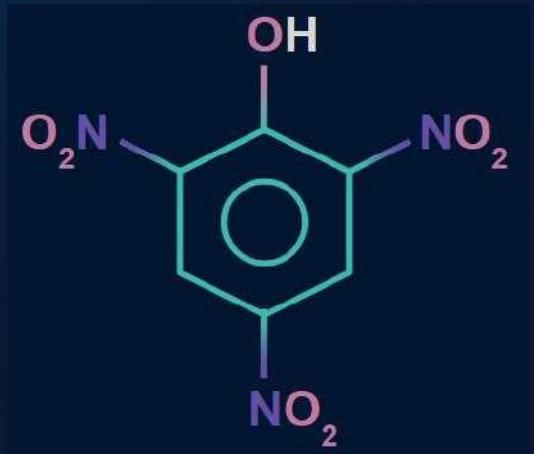


4-Methylphenol

p-Methylphenol



2-Hydroxybenzoic acid



2,4,6-Trinitrophenol

Nomenclature of Benzene Derivatives

When the $-C_6H_5$ (**-Ph**) group is named as a substituent, it is called a phenyl group.



Phenyl group



Phenyl group



Benzyl



Benzal

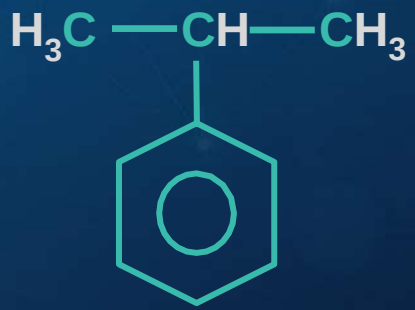
Nomenclature of Benzene Derivatives

A hydrocarbon composed of **one saturated chain and one benzene ring** is usually named as a derivative of the **larger structural unit.**

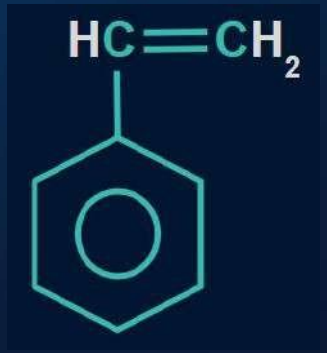
If an aromatic compound consists of an open and a closed chain

The principle chain will be the **open chain** if it contains **multiple bond(s), substituent(s) or functional group(s).**

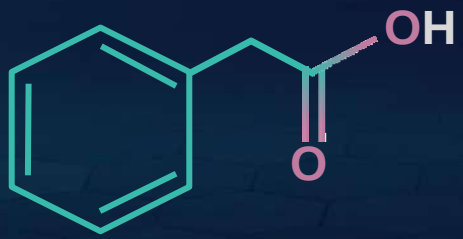
Benzene as Substituent



2-Phenylpropane



Phenylethene



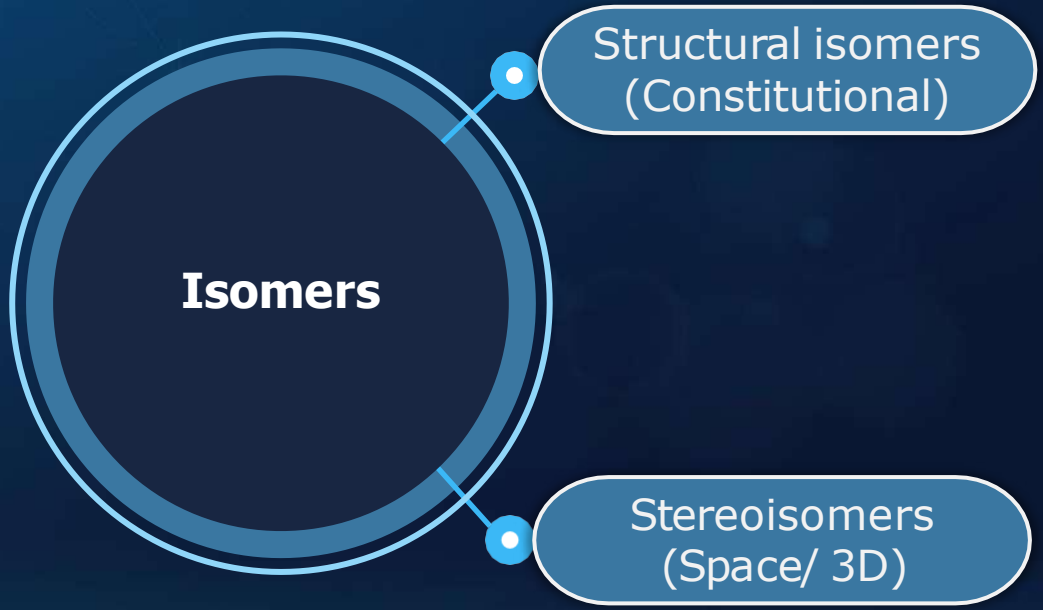
2-Phenylethanoic acid

Isomerism

Isomerism

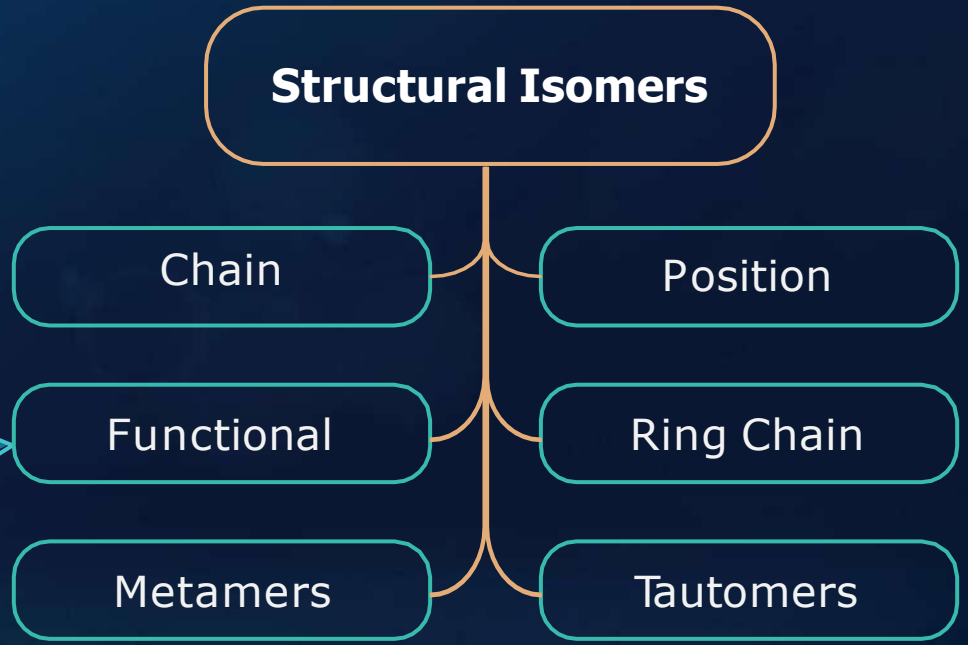
The phenomenon of existence of two or more compounds possessing the **same molecular formula but different properties** is known as isomerism. Such compounds are known as **isomers.**

Classification of Isomers



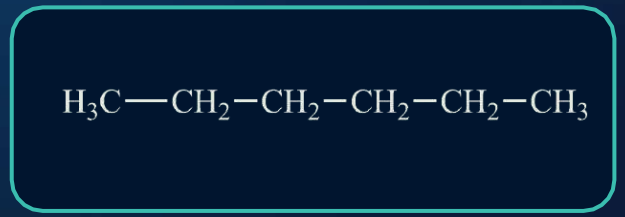
Structural Isomers

Compounds having the **same molecular formula but different structural formula** i.e., they differ in the bonding sequence of their atoms.

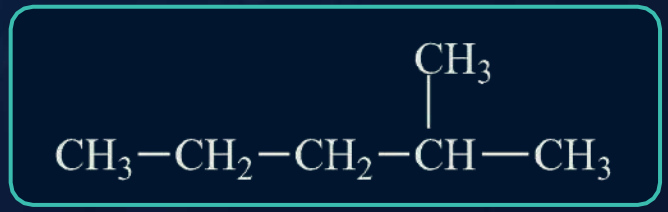


Structural Isomers

Example:
Straight chain n-hexane and branched chain 2-methylpentane are the structural isomers of C_6H_{14}.



n-hexane



2-Methylpentane

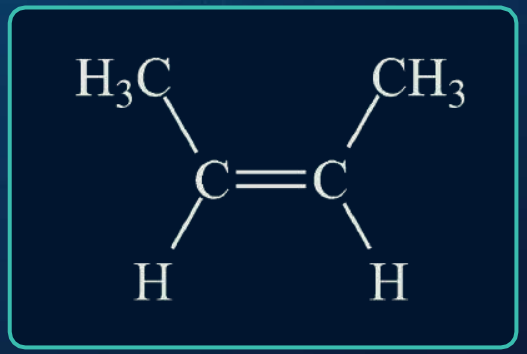
Structural isomers in C_6H_{14}

Stereo Isomers

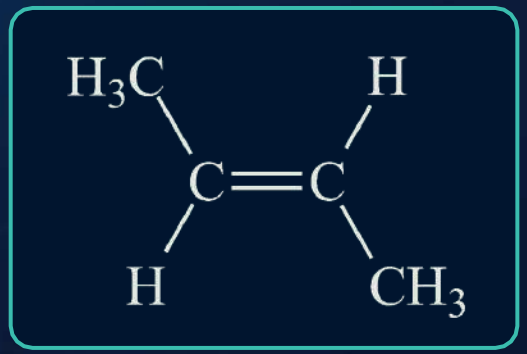
Isomers that have the **same bonding sequence** of atoms & groups but differ from each other only in the way their atoms are oriented in **space**

Stereo Isomers

Example:



cis-2-Butene



trans-2-Butene

Stereoisomers in But-2-ene

Chain Isomers

Compounds having the **same molecular formula** but **different carbon skeletons**

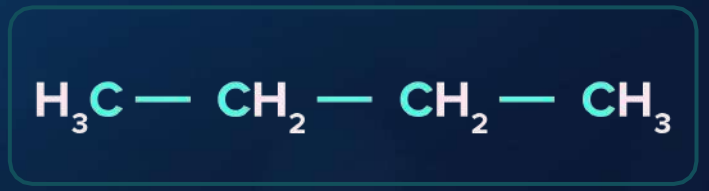
Different number of carbon atoms **in the main chain or in the side chains or both**



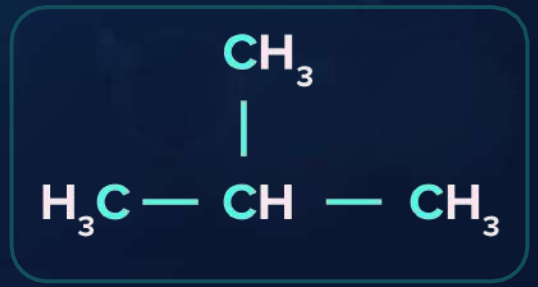
Example

C_4H_{10}

Butane



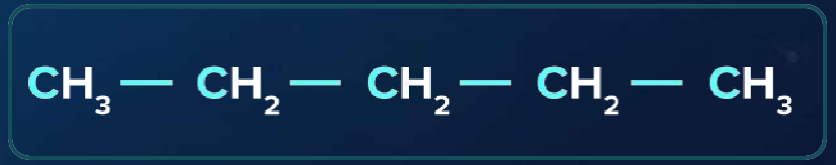
2-Methylpropane



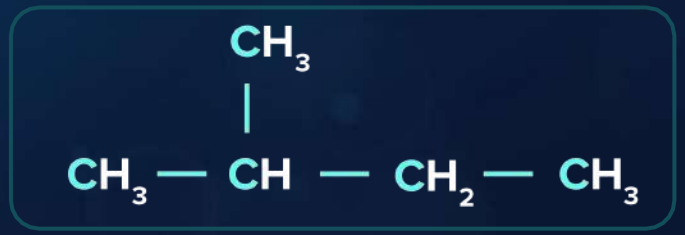
Example

C_5H_{12}

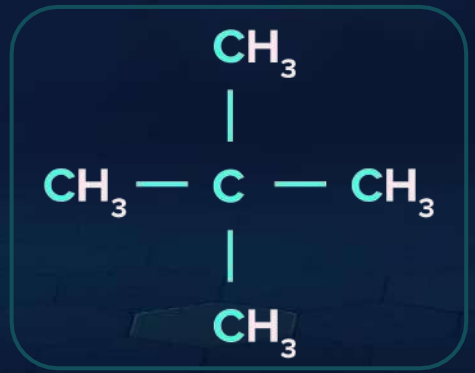
Pentane



2-Methylbutane



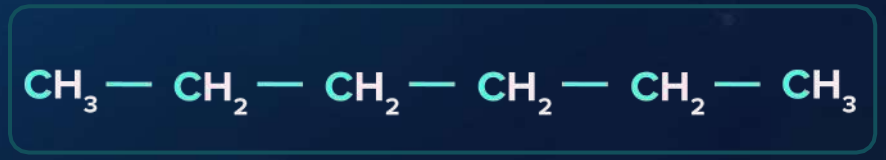
2,2-Dimethylpropane



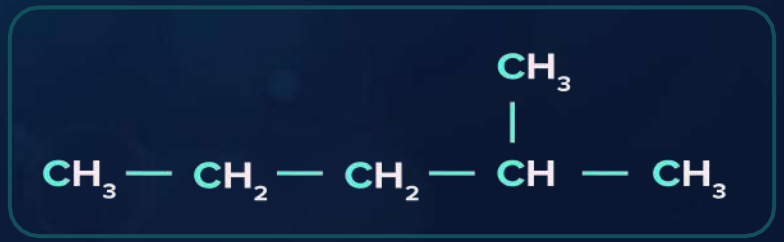
Example

C_6H_{14}

Hexane



2-Methylpentane



Position Isomers

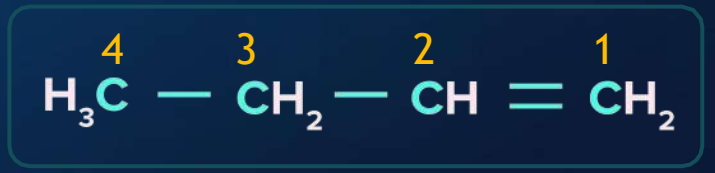
Compounds having the **same size of the main chain & the side chain** along with the same nature of functional group

But **differ in the position of** multiple bond/ functional group/ substituent

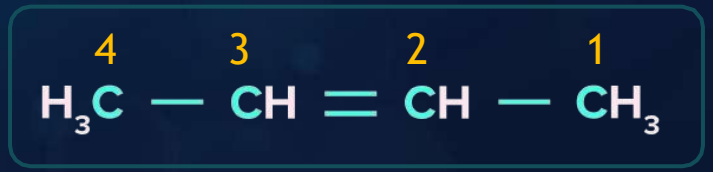
Example

C_4H_8

But-1-ene



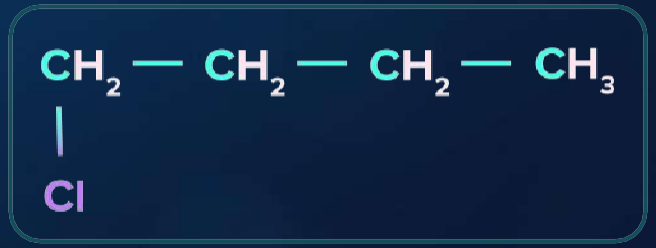
But-2-ene



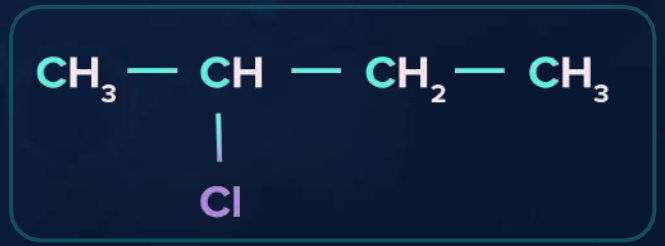
Example

C_4H_9Cl

1-Chlorobutane



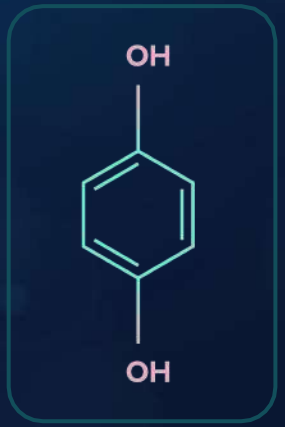
2-Chlorobutane



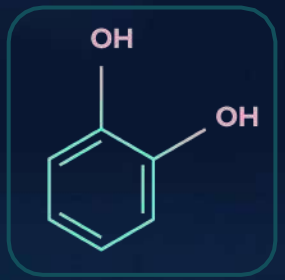
Example

$C_6H_6O_2$

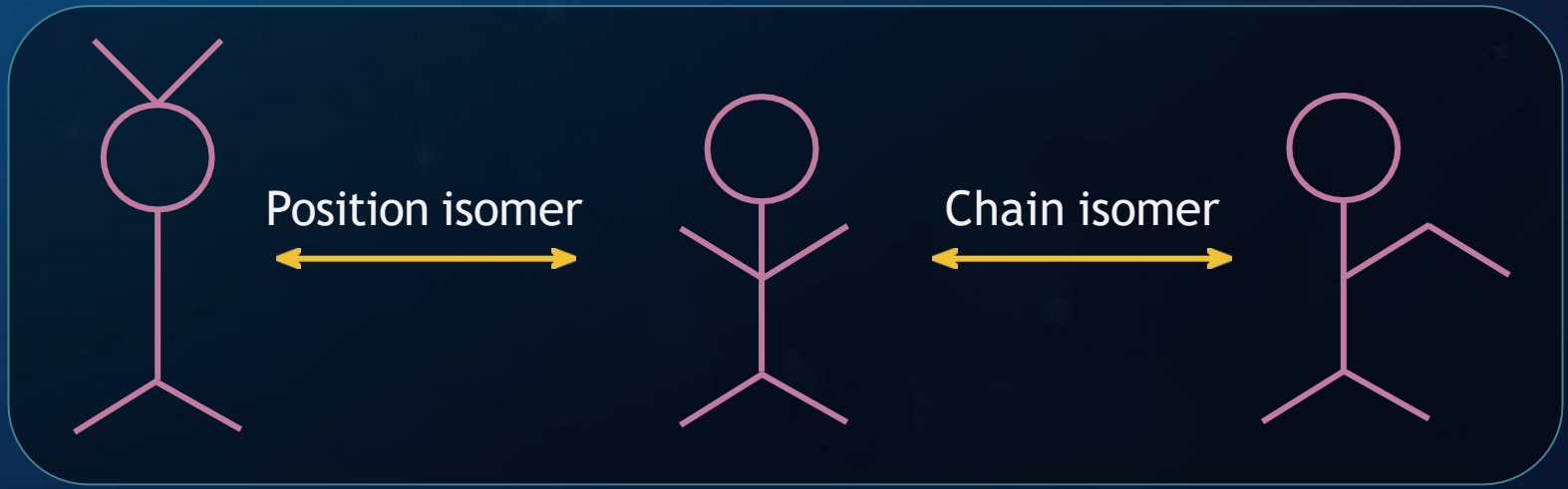
1,4-Benzenediol



1,2-Benzenediol



Example



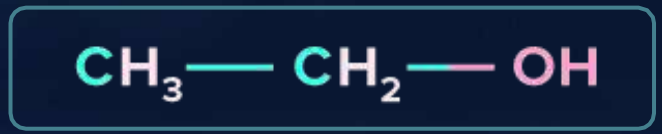
Functional Isomers

Compounds having the same molecular formula but **different functional groups**

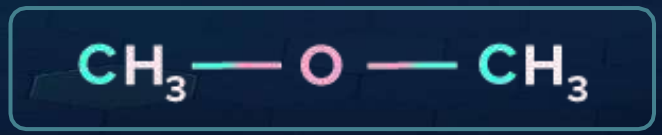
Examples

C_2H_6O

Ethanol



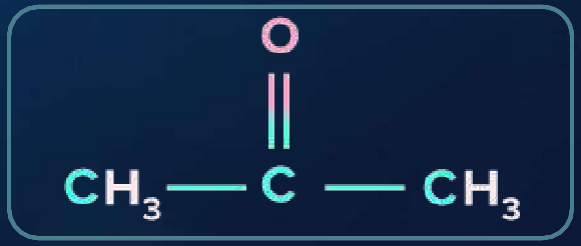
Methoxymethane



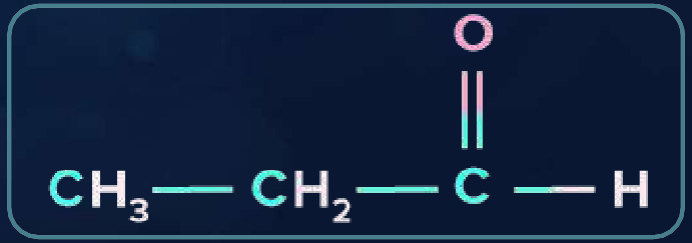
Examples

C_3H_6O

Propanone



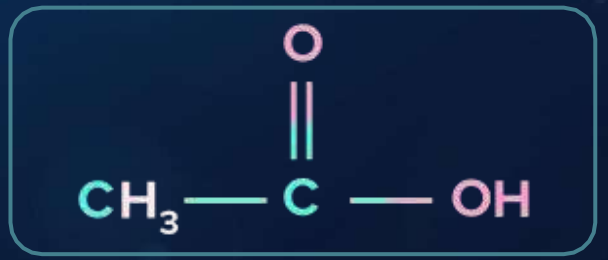
Propanal



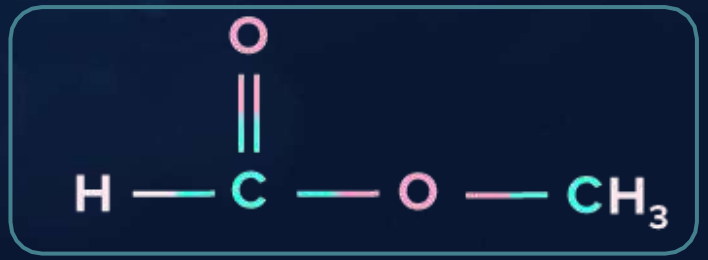
Examples

$C_2H_4O_2$

Ethanoic acid

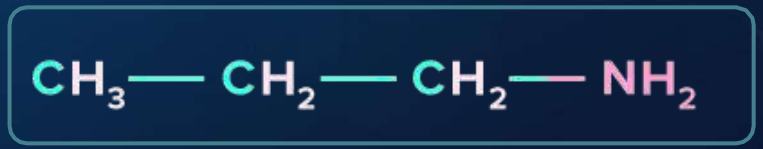


Methylmethanoate



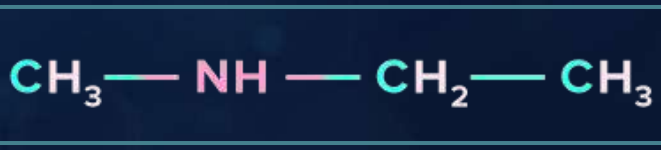
Examples

Propanamine

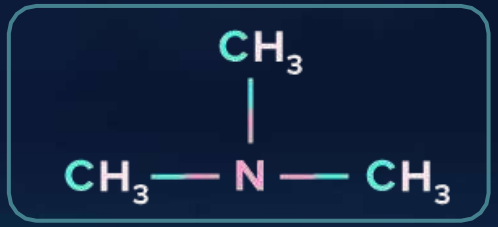


C_3H_9N

N-Methylethanamine

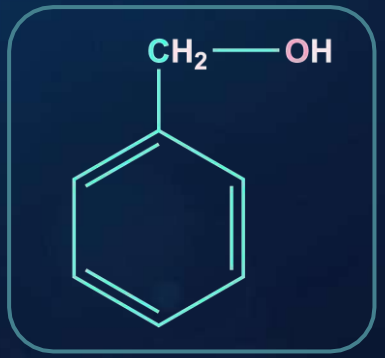


N,N-Dimethylmethanamine



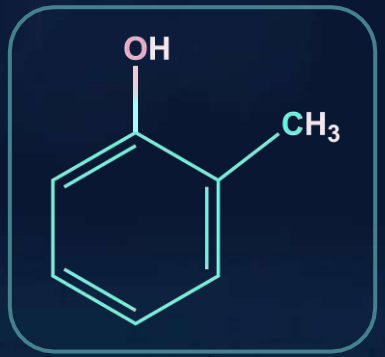
Examples

Benzyl alcohol



C_7H_8O

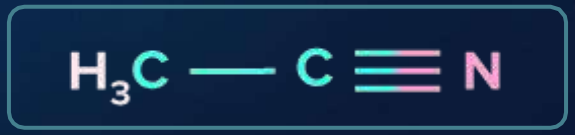
2-Methylphenol



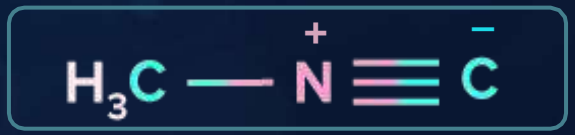
Examples

C_2H_3N

Ethanenitrile



Methyl isocyanide



Ring-Chain Isomers

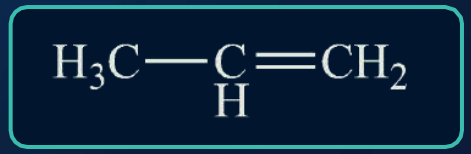
One isomer has a **ring** &
the other has an **aliphatic chain.**

Ring-Chain isomers are
also **functional isomers.**

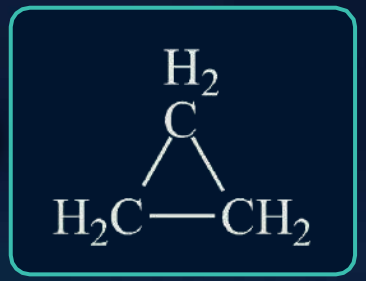
Example

C_3H_6

Propene



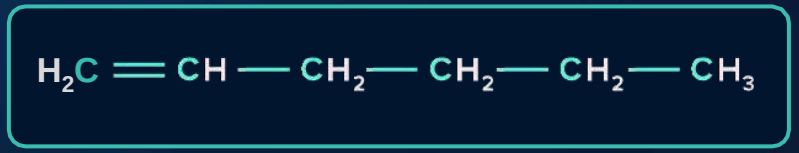
Cyclopropane



Example

C_6H_{12}

Hexene



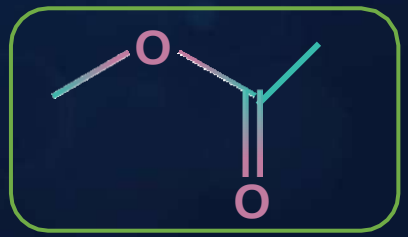
Cyclohexane

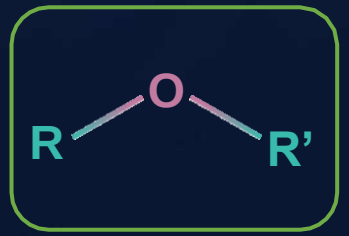


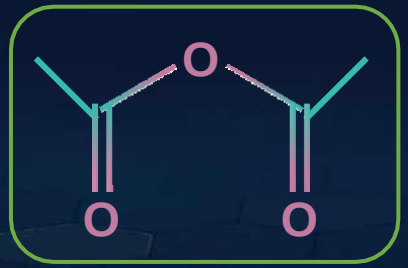
Metamers

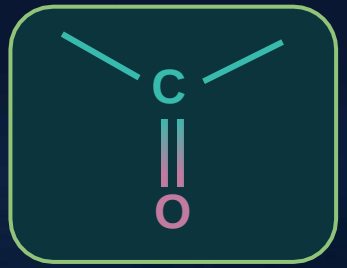
Compounds having the **same nature of functional groups but different nature of alkyl groups** along the polyvalent functional group

Polyvalent functional groups which show metamerism are:



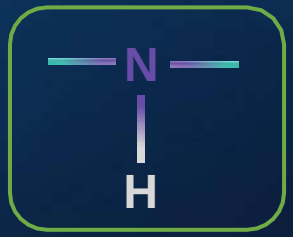


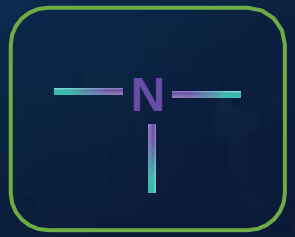


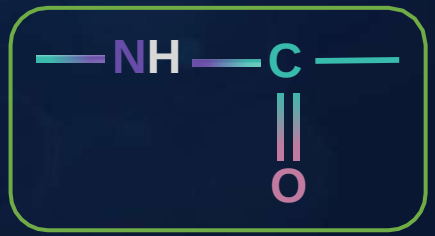


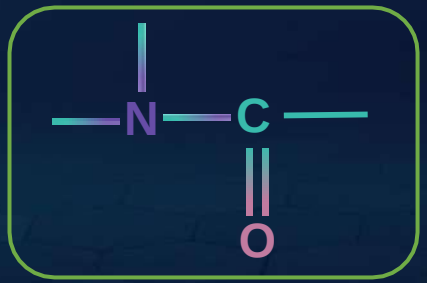
Metamers

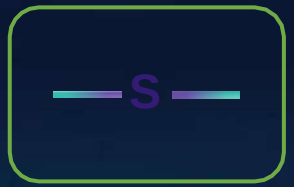
Polyvalent functional groups which show metamerism are:











Thioether

Metamers

$C_4H_{10}O$

Ethoxyethane



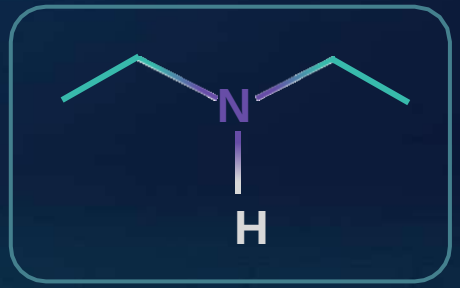
Methoxypropane



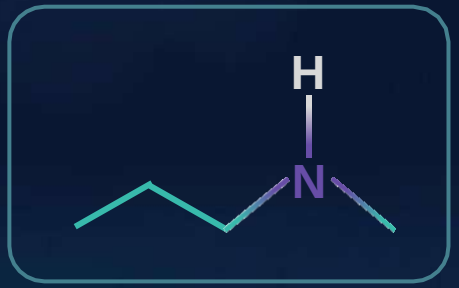
Metamers

$C_4H_{11}N$

N-Ethylethanamine



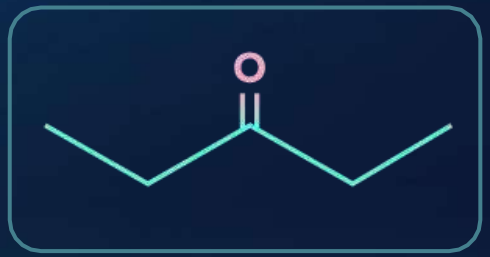
N-Methylpropanamine



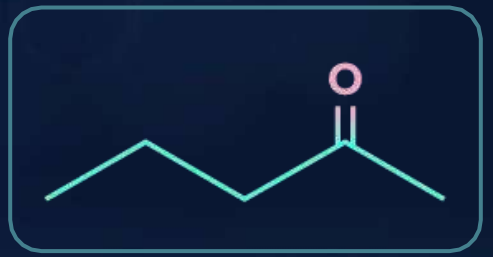
Metamers

$C_5H_{10}O$

Pentan-3-one



Pentan-2-one



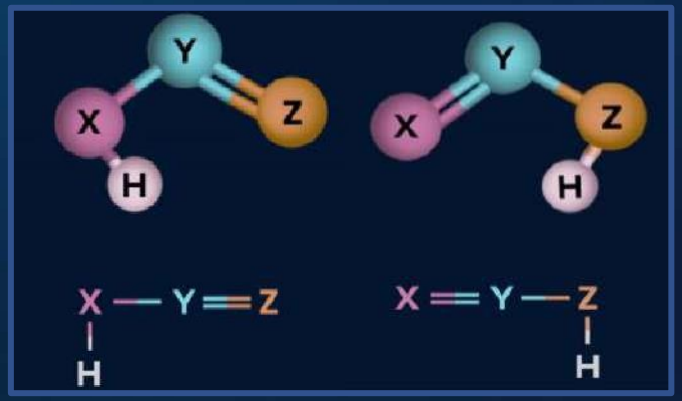
Tautomerism

Phenomenon by which a single compound exists in **two or more readily interconvertible structures** that differ in the relative positions of at least one atomic nucleus, generally hydrogen.

Isomers exhibiting tautomerism are called **tautomers.**

Tautomerism

Tautomers exist in **dynamic equilibrium** with each other.

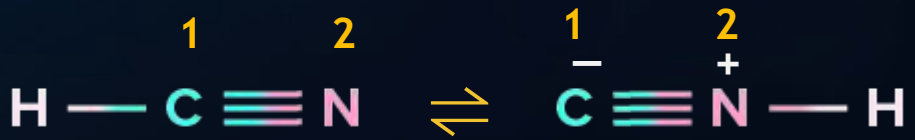


Tautomerism

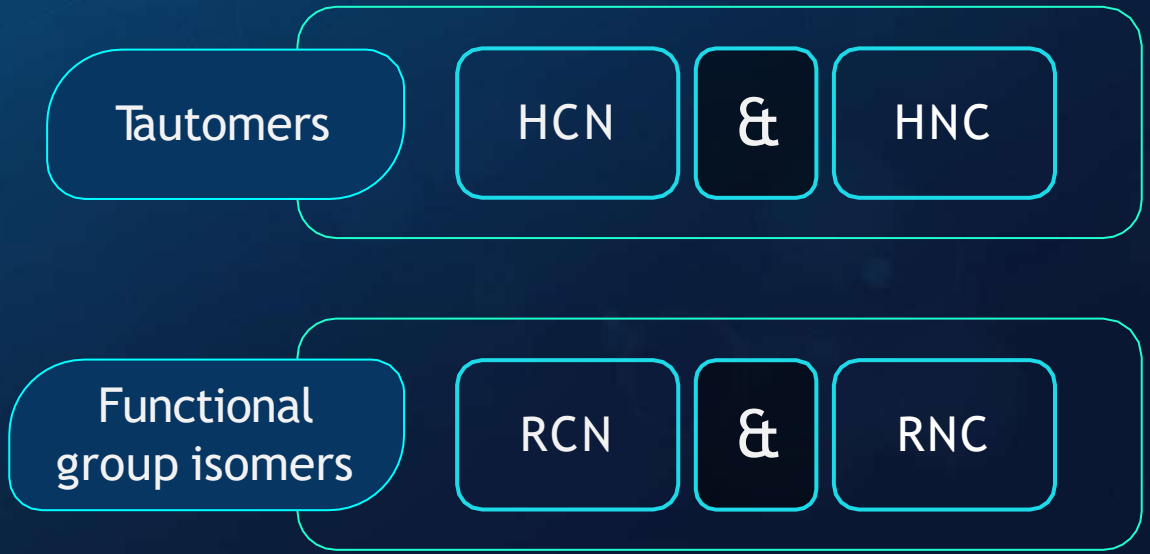
- Diad
- Triad

Diad Tautomerism

Movement of H atom between
1 ↔ 2 positions

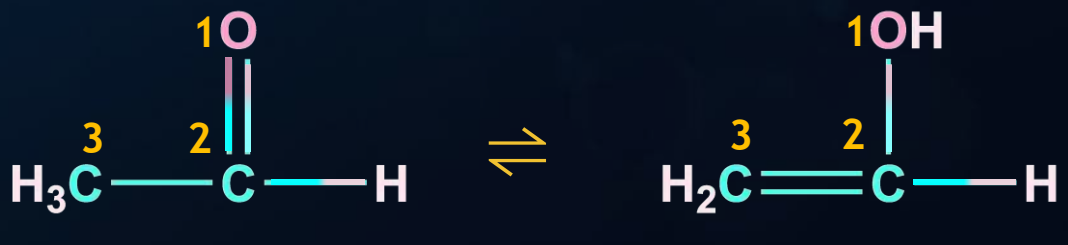


Diad Tautomerism



Triad Tautomerism

Movement of H atom between
1 ↔ 3 positions



Keto form ⇌ Enol form

Keto-enol Tautomerism

Conditions for Tautomerism

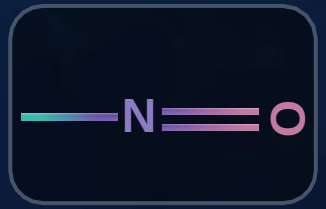
Usually present in the following functional groups



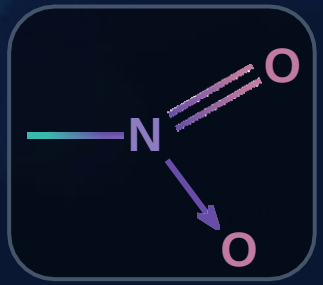
Carbonyl



Imine



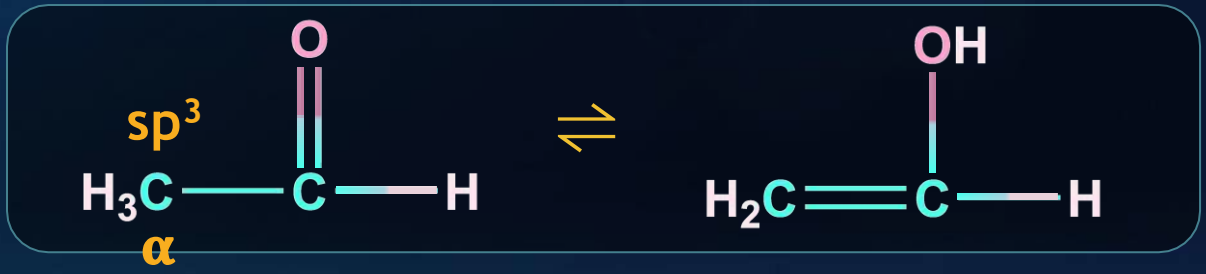
Nitroso



Nitro

Conditions for Tautomerism

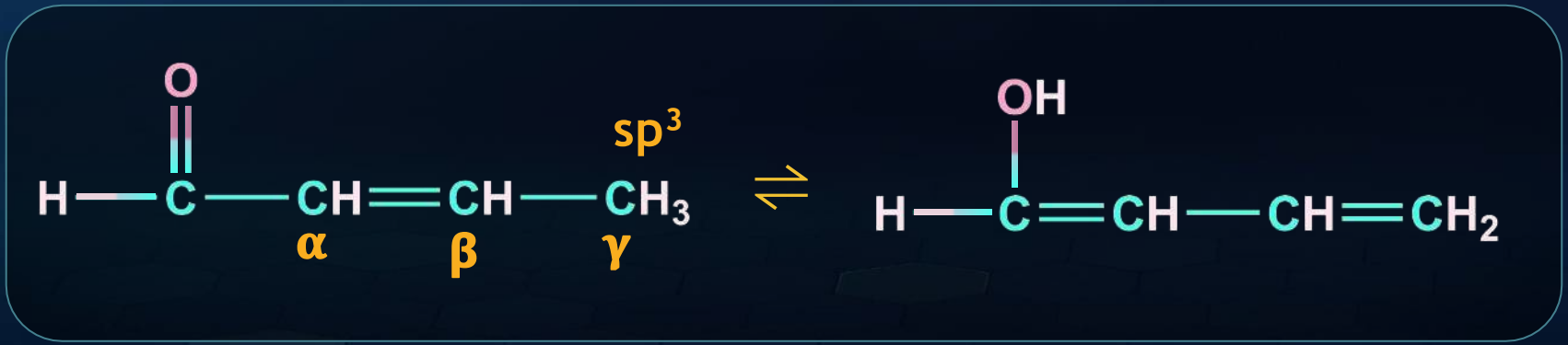
Presence of **at least one H atom** on the sp^3 hybridized **α-C** atom



Conditions for Tautomerism

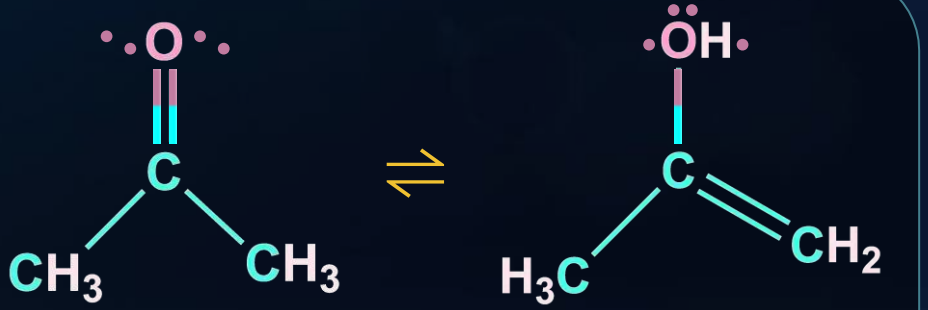
Tautomerism is possible if an α, δ **unsaturated carbonyl** compound contains a H at its sp^3 hybridised **γC** atom.





Keto-Enol Tautomerism

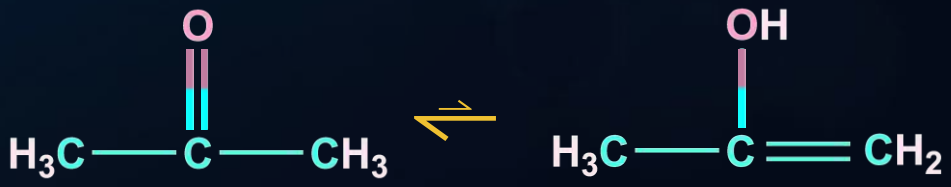
A form of tautomerism between a **carbonyl** compound containing **α-H** and its **enol** form.



Keto form ⇌ Enol form

Keto-Enol Tautomerism

Keto form of **mono carbonyl** compound is more stable than its enol form.



> 99 %

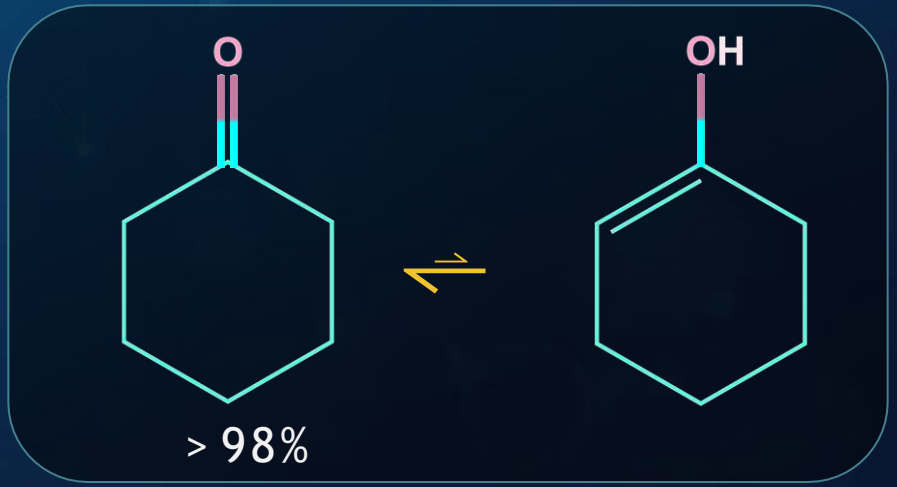
Keto-Enol Tautomerism

Tautomeric Form	Bonds Present	Sum of bond enthalpies
Keto form	C-H, C-C & C=O	~ 1500 kJ/mol
Enol form	C=C, C-O & O-H	~ 1452 kJ/mol

Keto form is thermodynamically more stable by 48 kJ/mol.



Examples





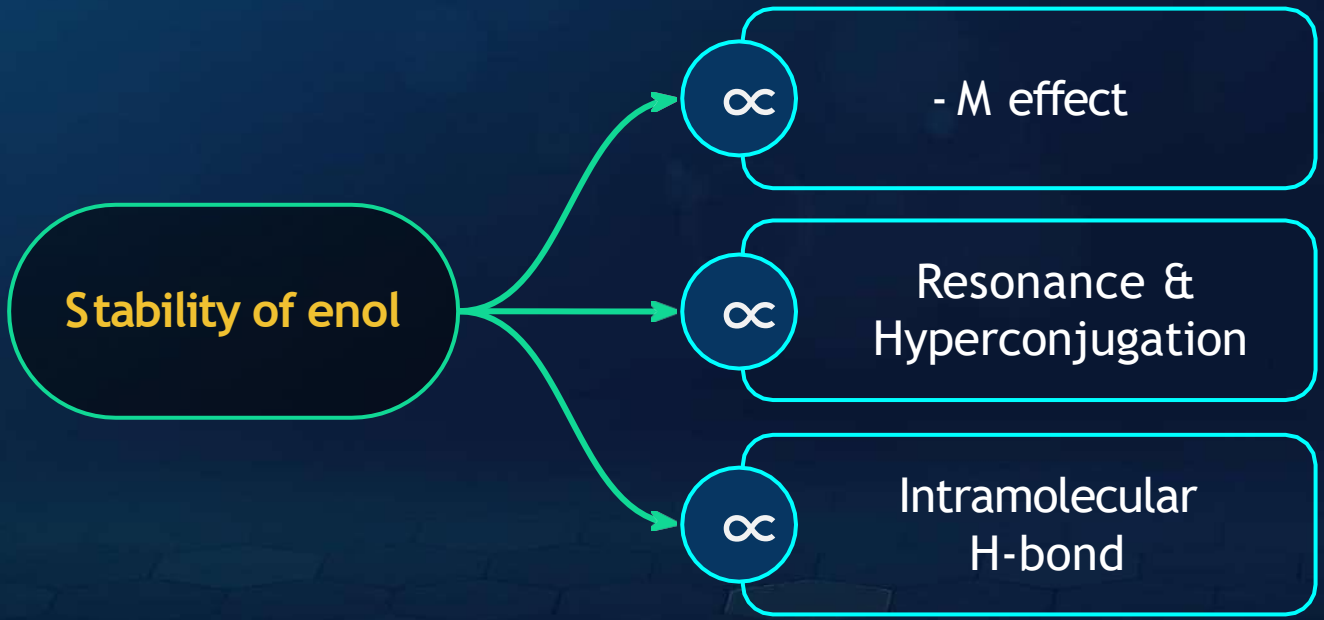
Keto-Enol Tautomerism

Keto form of **acyclic 1,2-Dicarbonyl** compound is more stable than its enol form.

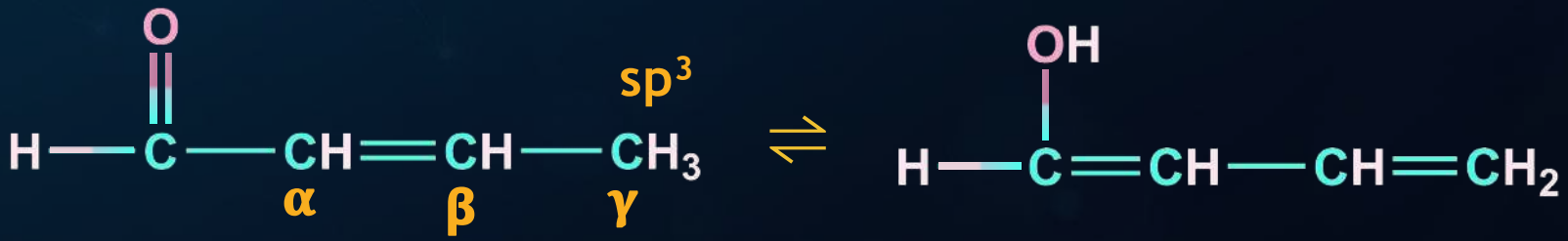


Keto-Enol Tautomerism

However, in certain cases, the %enol content predominates the %keto content!



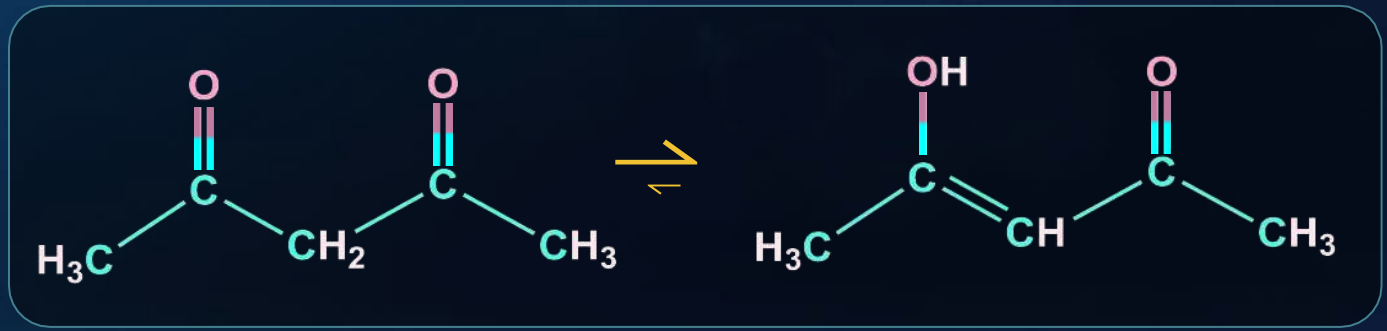
Keto-Enol Tautomerism



$$\%\text{Enol} \propto \frac{1}{\text{Polarity of solvent}}$$

β- Dicarbonyl Compounds

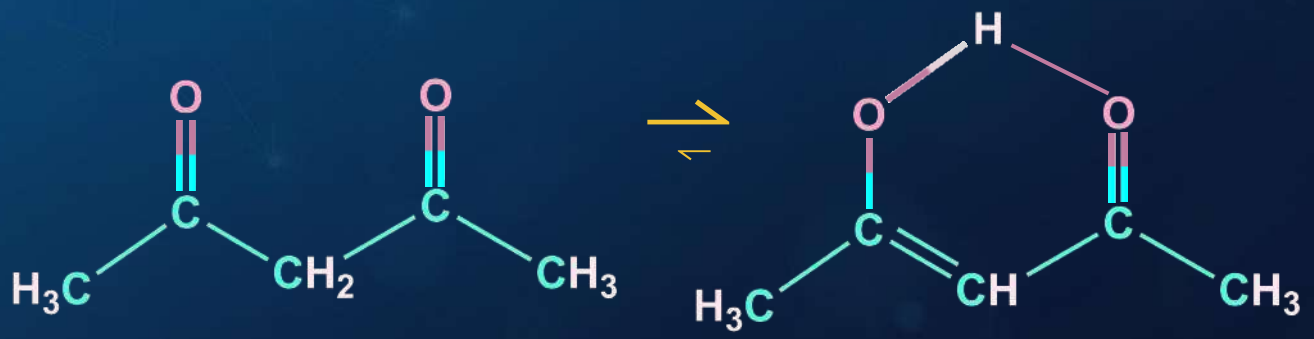
Molecules having two carbonyl groups **separated by one C atom.**



Keto form

Enol form
76%

Keto-Enol Tautomerism



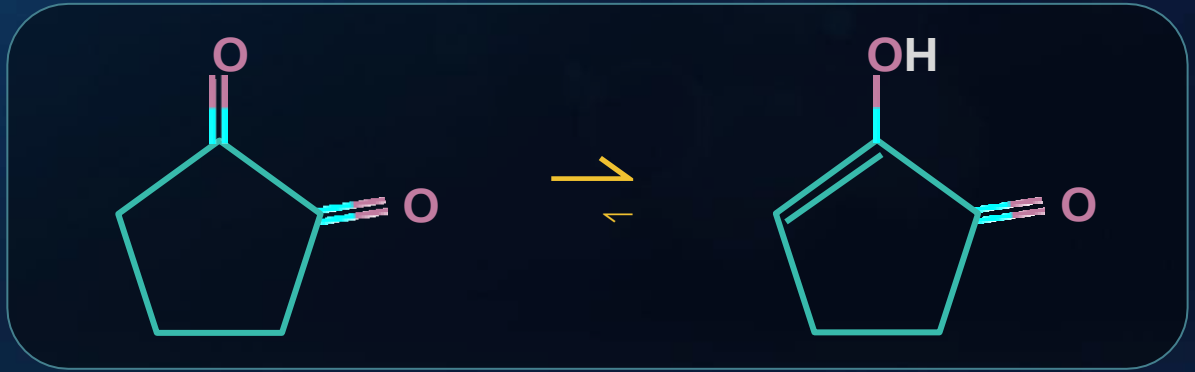
More stable due to

Resonance stabilisation of conjugated double bonds

H bonding in a cyclic form

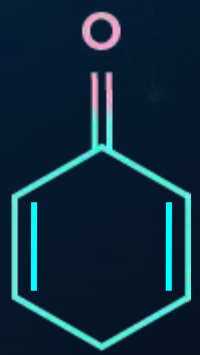
Keto-Enol Tautomerism

Enol form of **cyclic 1,2 Dicarbonyl** compound is more stable than its keto form.



Less stable,
Repulsion between >C=O groups

Keto-Enol Tautomerism





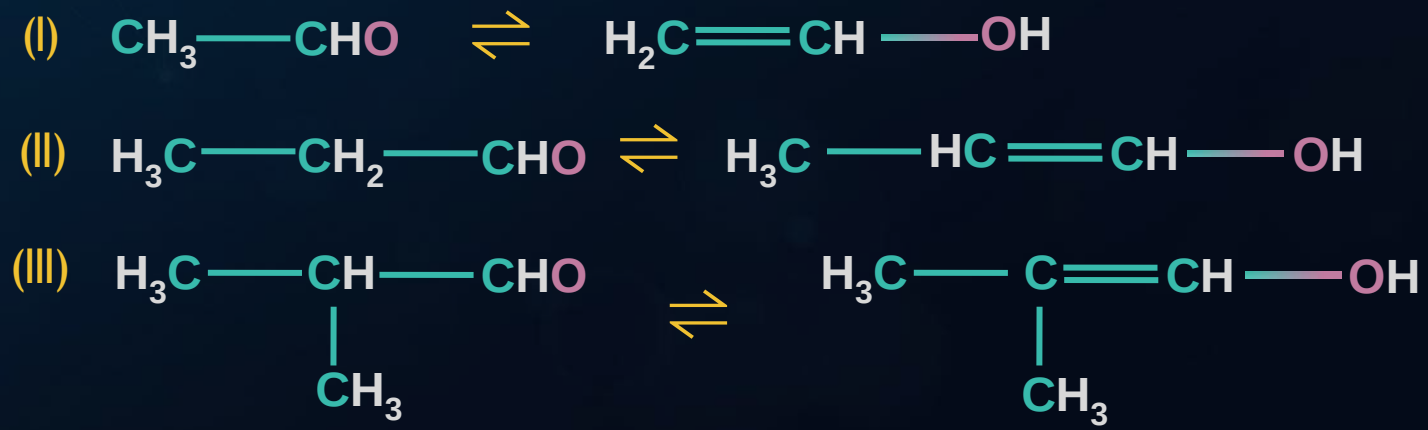


~ 100%

More stable due to Aromaticity

Keto-Enol Tautomerism

Percentage of **enol** increases with the **stability of Alkene**



% enol form

III > II > I

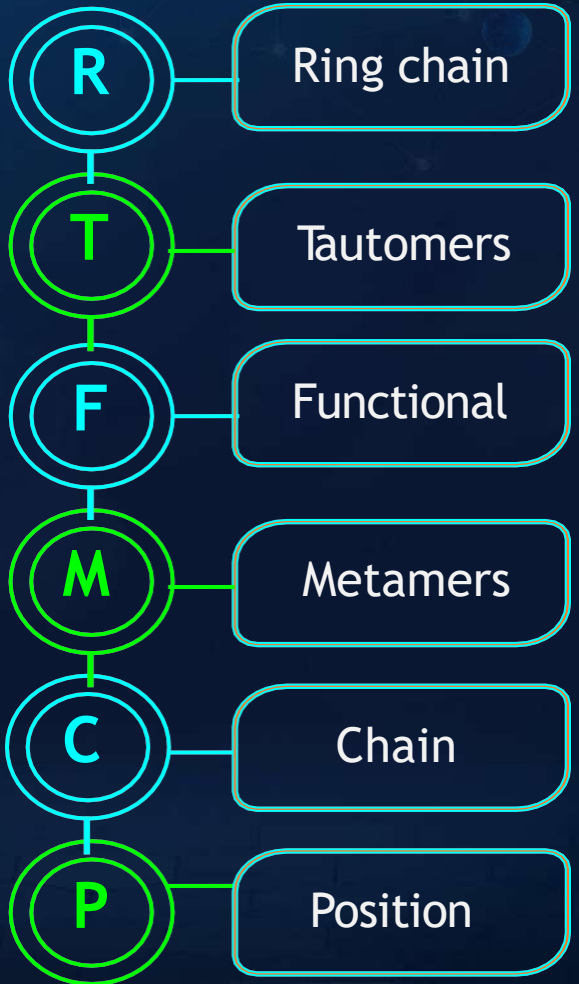
Keto-Enol Tautomerism

General order of **% enol**

Aromatic > β-Dicarbonyl > α-Dicarbonyl > Monocarbonyl

How to decide the type of isomerism if **multiple** types are possible?

Follow RTFMCP!!



Degree of Unsaturation

Difference in the number of **pairs of H atoms** between the compound under study and an **acyclic alkane** having the same number of 'C' atoms.

Double Bond Equivalent or Index of Hydrogen Deficiency

Sum of the number of **πbonds & rings** in a compound

Degree of Unsaturation

For a compound with molecular formula,

$C_aH_bX_cN_dO_e$

Where, **X** = Halogen

$$\text{Degree of unsaturation} = (a + 1) - \frac{(b + c - d)}{2}$$

Degree of Unsaturation

Interpretation

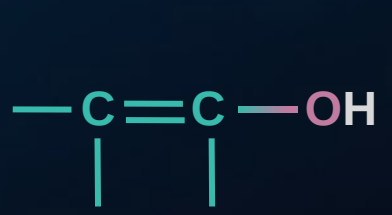
Degree of unsaturation	Meaning
1	One π bond or one ring
2	Two π bonds or two rings or one π bond & one ring

Application of DOU

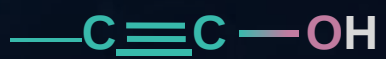
To calculate the **number of isomers** for a particular molecular formula.

Remember!!!

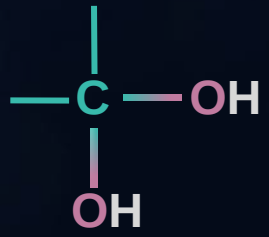
Following compounds **do not exist** at room temperature & therefore are **not considered** as structural isomers



(i)



(ii)

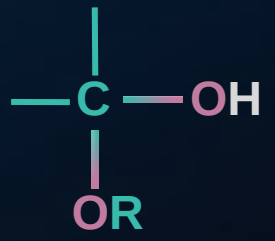


(iii)

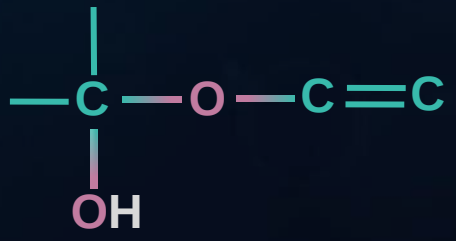
(iv) Any **peroxy** compound

Remember!!!

Following compounds **do not exist** at room temperature & therefore are **not considered** as structural isomers



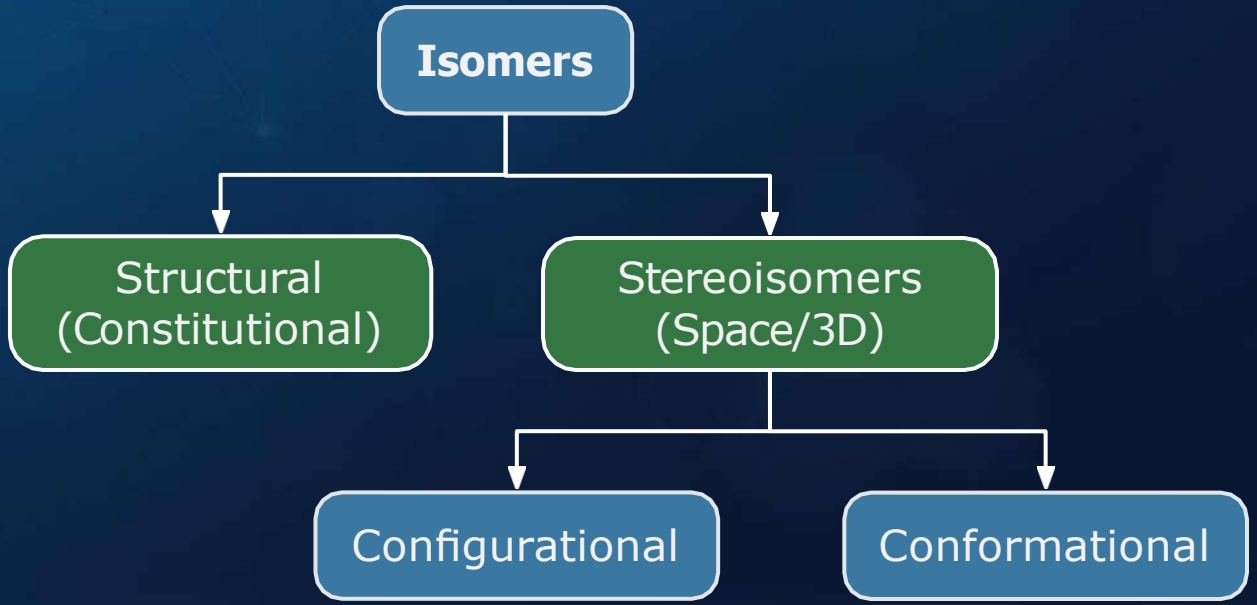
(v)



(vi)

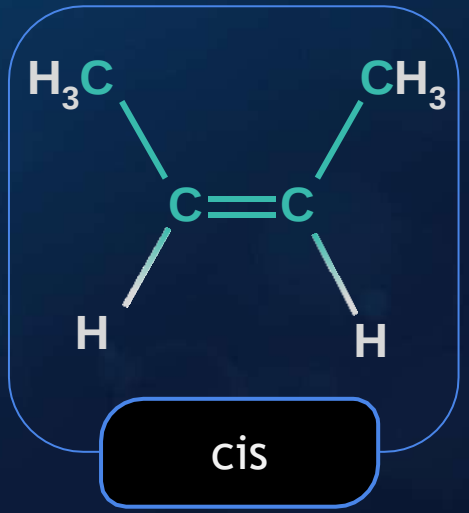
(vii)

Classification of Isomers

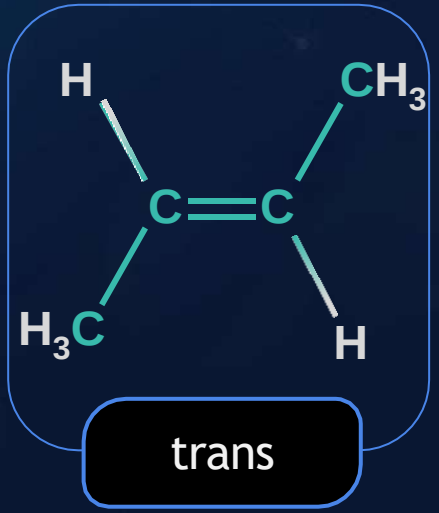


Configurational Isomers

Isomers which **differ in the configuration** i.e. the **spatial arrangement of atoms** that characterises a particular stereoisomer.



cis

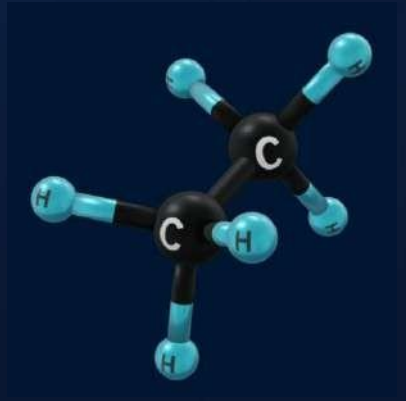


trans

Arises due to non-interconvertibility at room temperature.

Conformational Isomers

There are **infinite arrangements (conformations)** which arise due to the free rotation around the C-C σ bond, out of which different conformations corresponding to **energy minima** are called **conformers.**



Electron distribution in a σ bond is symmetrical around the internuclear axis

Permits free rotation (at room temperature) about the σ bond

Conformational Isomers

Basic structure of the molecule, bond lengths and bond angles remain the **same** in all the conformations.

Not true isomers.

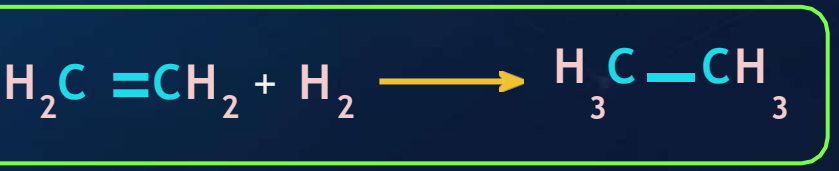
Less energy difference

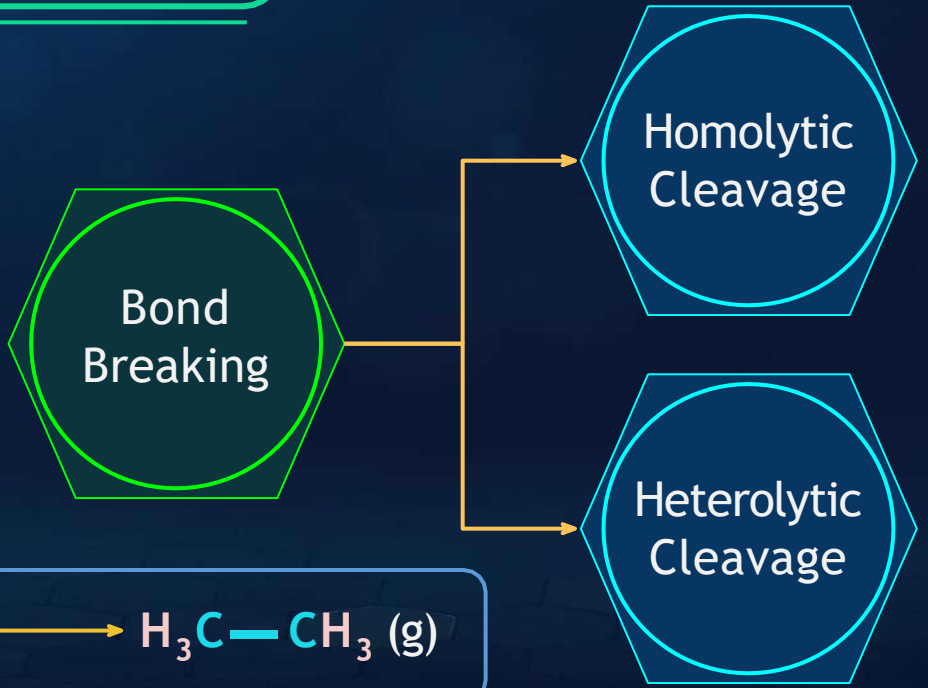
Interconverts rapidly.

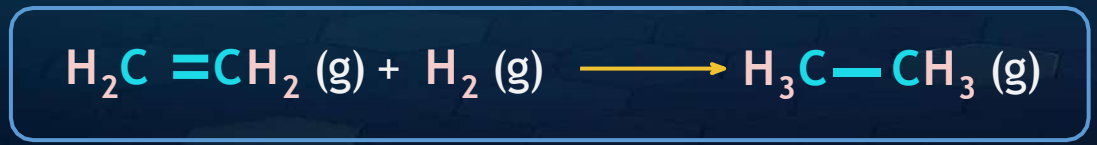
Conformational isomers are not to be considered while evaluating the number of isomers of any molecule.

General Organic Chemistry

During the course of a reaction, some bonds are **broken** and some new bonds are **formed**.

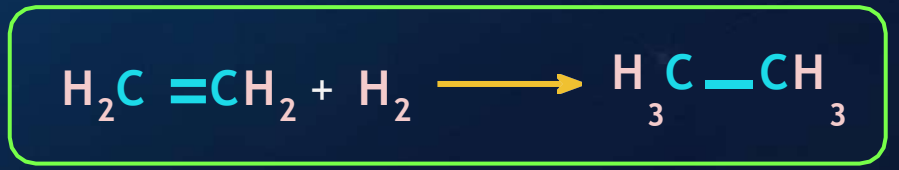


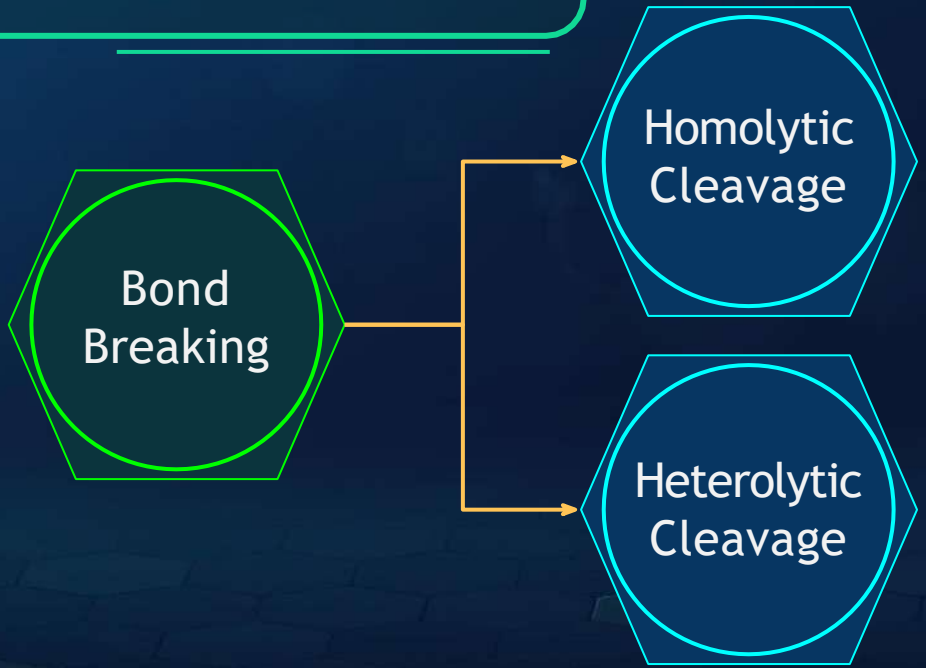




Bond Cleavage

During the course of a reaction, some bonds are **broken** and some new bonds are **formed**.





Bond Cleavage

Homolytic Cleavage

Bond breaks in such a way that each fragment takes away **one of the two electrons** of the bond

↓

Produce fragments with an unpaired electron called **free radical**

Represented by 

Heterolytic Cleavage

Bond breaks such that one fragment takes away **both the electrons** of the bond

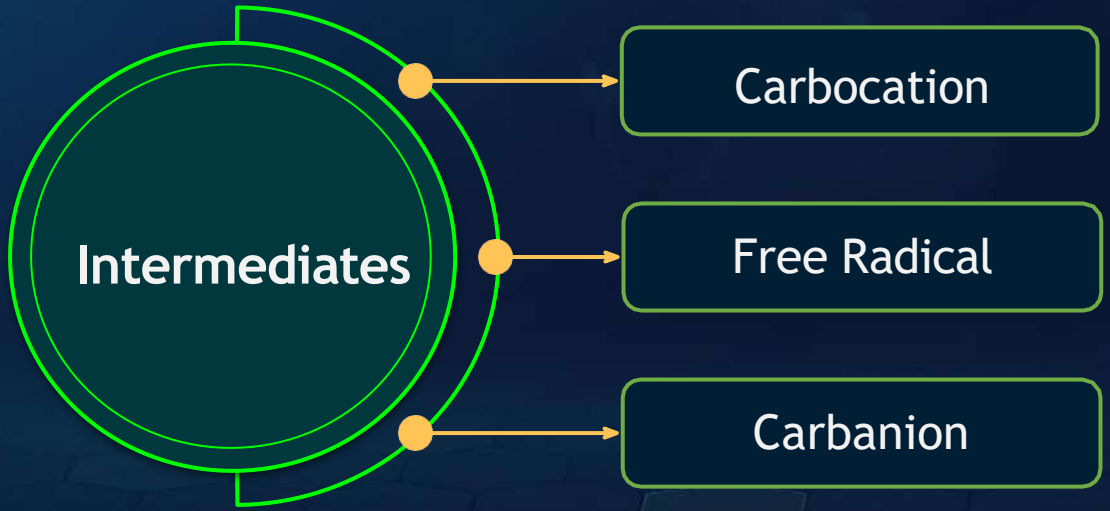
↓

Produces one **ion** & leaves the other fragment with an **empty orbital**

Represented by 

Intermediates

Reactive, short lived, highly energetic, unstable species that are formed in the course of organic reactions



Intermediates

Carbocation (CH_3^+)

A carbon intermediate which contains **three bond pairs & a positive charge** on it.

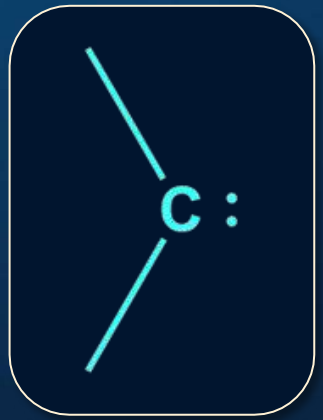
Free radical ($CH_3^{\cdot}$)

An **uncharged** intermediate which has **three bond pairs and an unpaired electron on the carbon.**

Carbanion ($\bar{C}H_3$)

A carbon intermediate which contains **three bond pairs and a negative charge** on it.

Carbene



Carbenes are **neutral reaction intermediates** having **bivalent** carbon

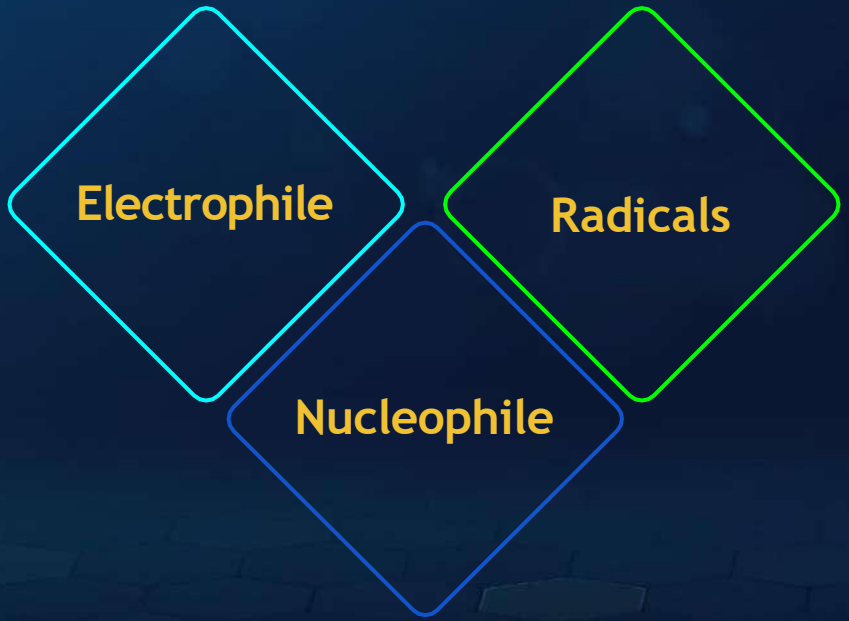
Which has two valence electrons distributed among two **non-bonding orbitals.**

Characteristics of Carbene

1. Reaction intermediate
2. Highly reactive
3. Highly unstable
4. Electron deficient
5. Carbon is divalent

Attacking Reagents

A reagent generates three type of attacking species.



Electrophile (E^+)

Electrophiles are **electron deficient species** which can accept a pair of electrons.

Examples

- Positively charged species: H^+, $\overset{+}{N}O_2$, $\overset{+}{C}H_3$
- Species with vacant orbitals on the central atom: PCl_5, SO_2, SO_3, BH_3

Nucleophile (Nu^-)

Nucleophiles are **electron rich species** having at least one unshared pair of electrons.

Examples: CN^-, OH^-, Br^-, I^-, NH_3, H_2O etc.

Free Radicals

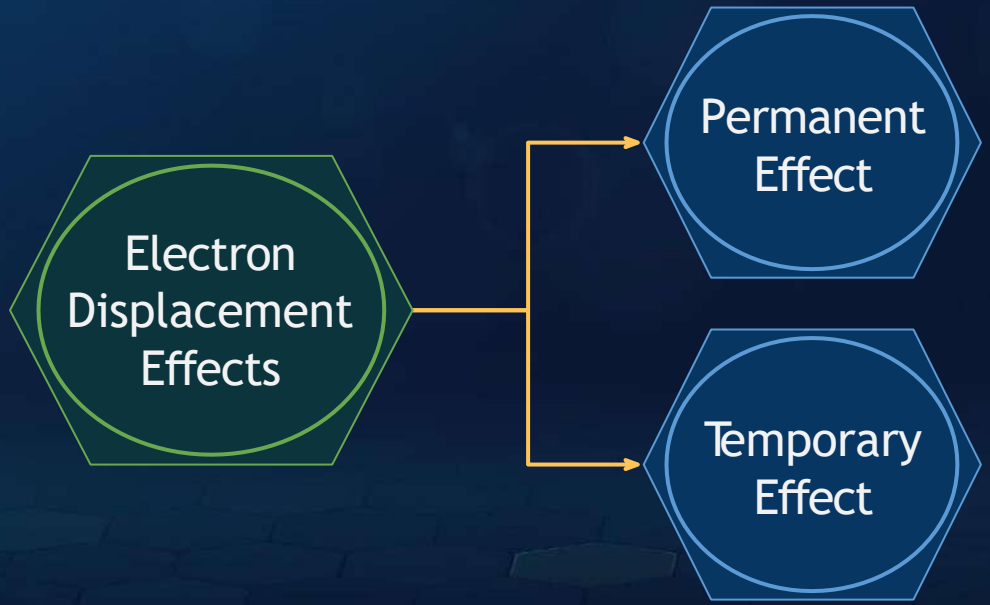
Free radicals are **electron deficient species** with an odd electron around an atom.

Examples

$\dot{C}H_3$, $\dot{C}_2H_5$, $C_2H_5\dot{O}$, $CH_3C\dot{O}O$, $\dot{X}$, etc.

Electron Displacement Effect

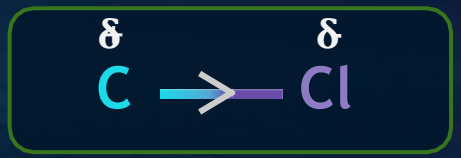
Effect which appears due to the electronic distribution or the **movement of electrons**



Permanent Effect

Permanent displacement of electrons causing **permanent polarisation of a bond.**

Arises due to the **influence of an/a atom/group** present in the molecule.



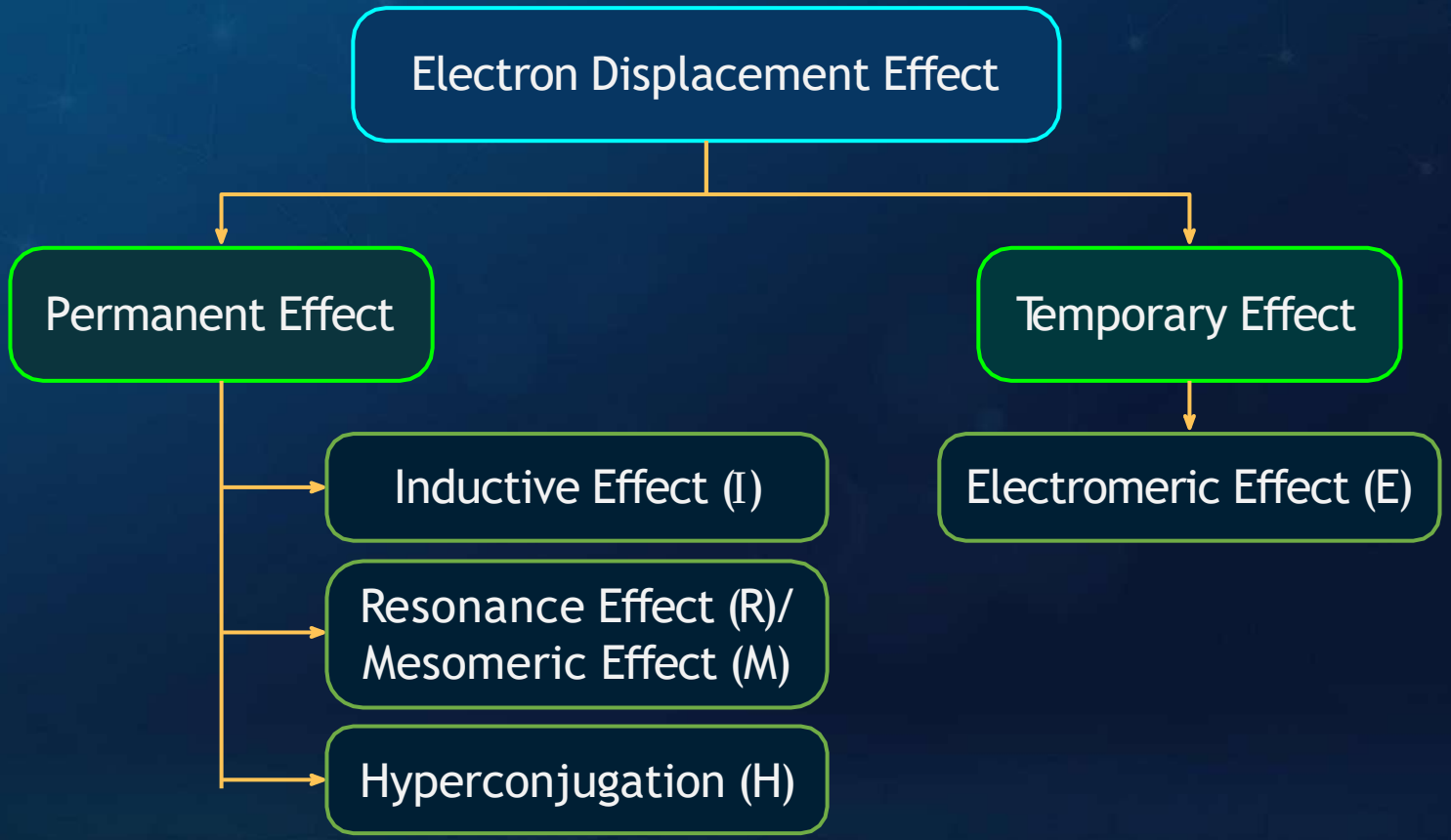
The fractional electronic charges on the two atoms in a polar covalent bond are called partial charges and are denoted by $\delta+/\delta-$

Temporary Effect

Temporary displacement of electrons in compounds having **multiple bonds.**

Observed only in the presence of an **attacking reagent.**




Electron Displacement Effect
Permanent Effect
Temporary Effect
Inductive Effect (I)
Resonance Effect (R)/
Mesomeric Effect (M)
Hyperconjugation (H)
Electromeric Effect (E)

Inductive Effect

Permanent displacement of **σ bond pair electrons** due to an adjacent polar bond.

- Displacement of electrons takes place due to the difference in E.N. of the two atoms
- Permanent electronic effect
- Polarisation of one bond caused by the polarisation of an adjacent bond

Inductive effect shows additive property

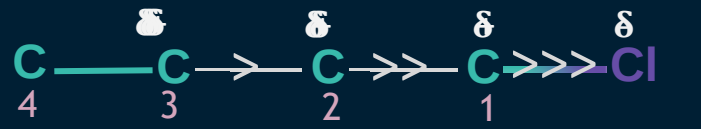
Characteristics of Inductive Effect

Operative through σ bond & does not involve π bond electrons.

Electrons never leave their original atomic orbital

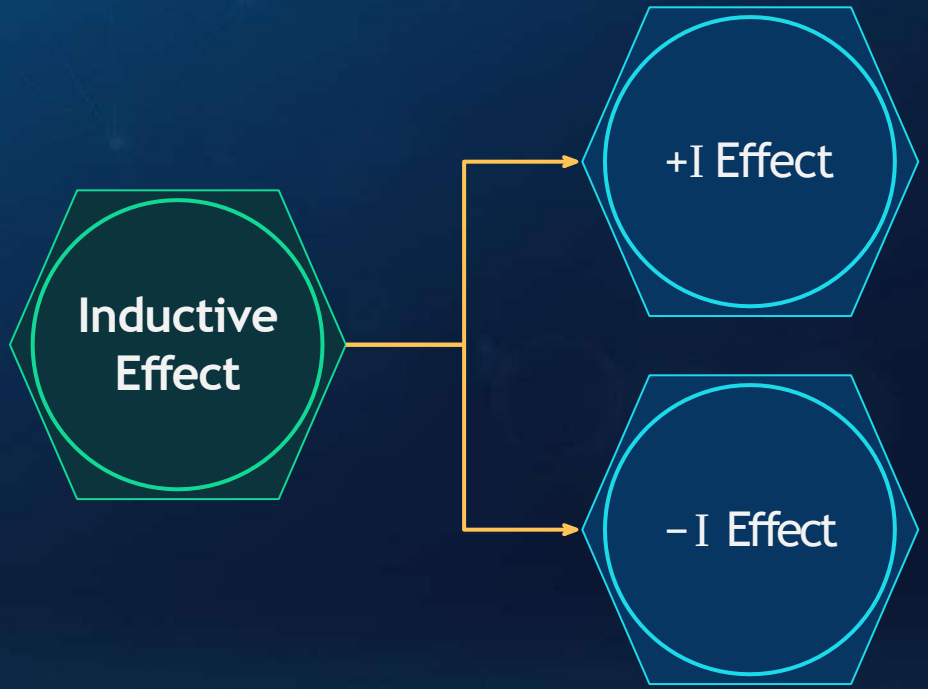
Distance dependent effect

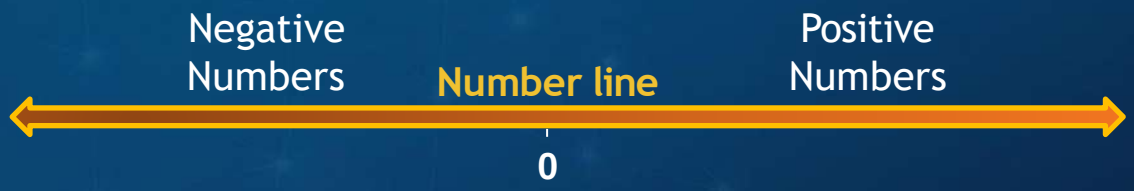
As distance **increases**, the strength of inductive effect **decreases.**

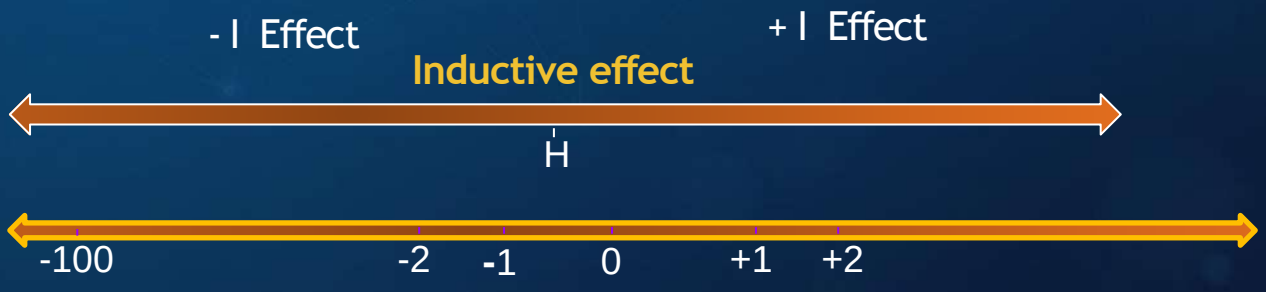


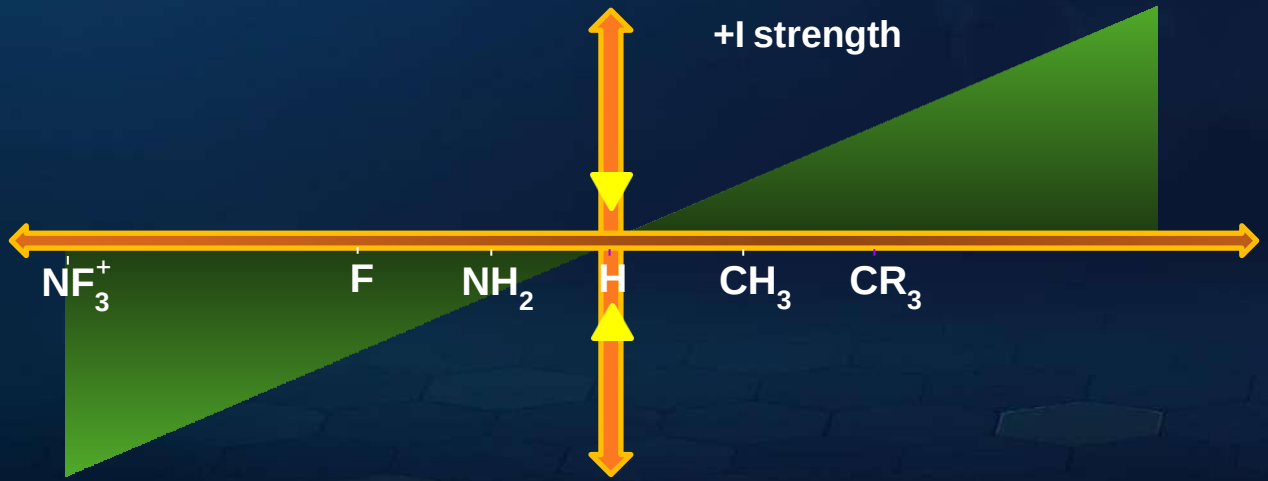
Negligible after 3rd C atom.

Inductive Effect









Electron donating/withdrawing capability is compared relative to hydrogen. Inductive effect of **hydrogen** is considered to be **zero.**

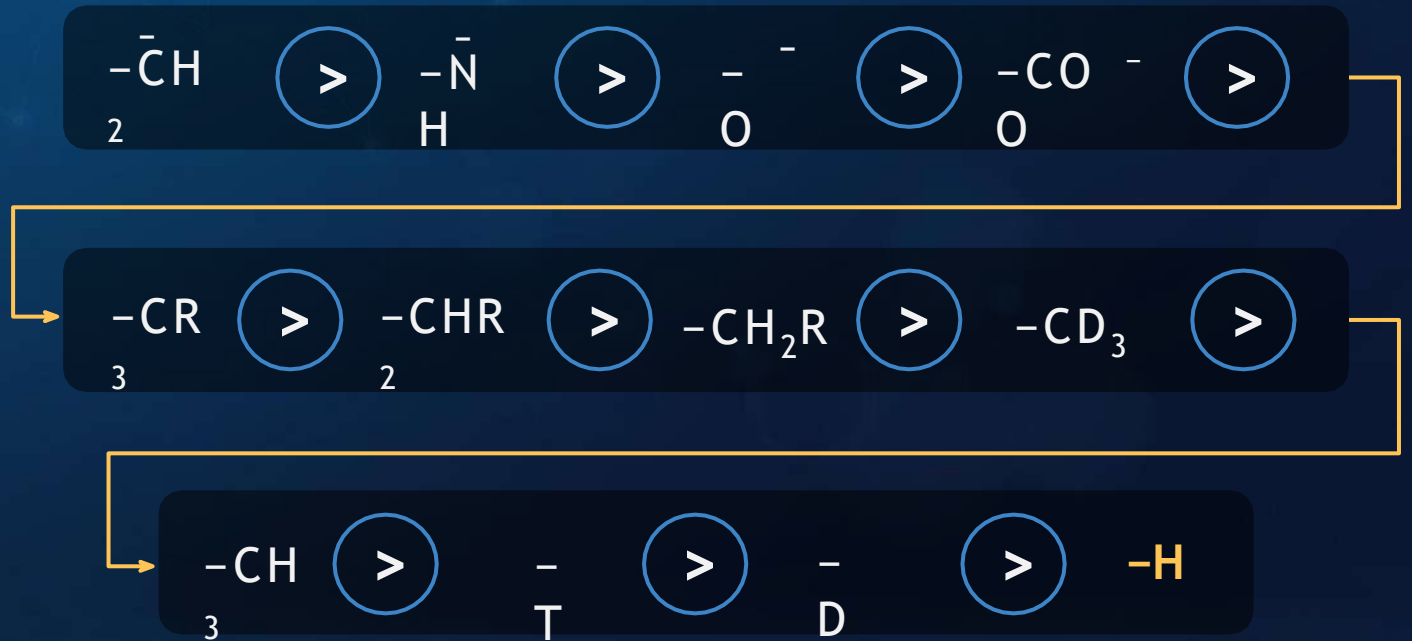
+I Effect

Permanent shift in electron density from the **electron donating group towards the carbon chain**

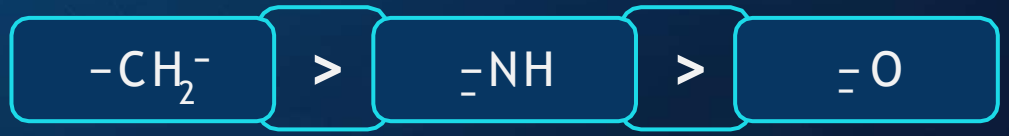
Shown by the group which **pushes the electron density** away from itself.

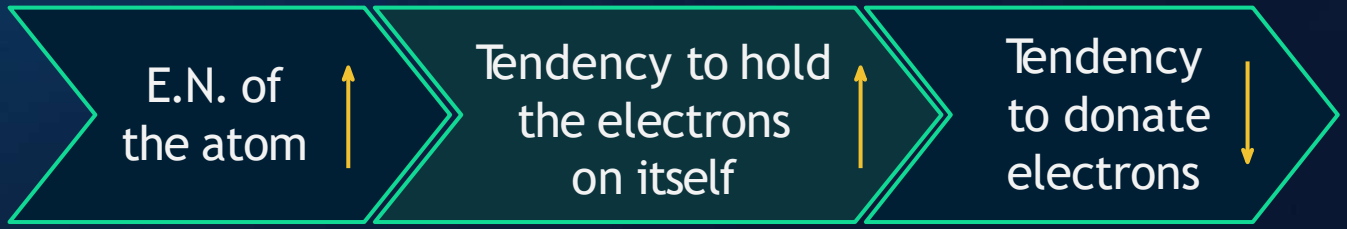
Example: Alkyl groups

Order of +I



Order of +I


$-CH_2^-$
>
$=NH$
>
$=O$


E.N. of the atom
Tendency to hold the electrons on itself
Tendency to donate electrons

Order of +I

$-C(CH_3)_3$ > $-CH(CH_3)_2$ > $-CH_2CH_3$ > $-CH_3$

3° alkyl > 2° alkyl > 1° alkyl

E.N. of C > E.N. of H → Electron density on C ↑ → Electron density is displaced away from the group

Order of +I

$-T$ > $-D$ > $-H$

–I Effect

Permanent shift in electron density **away from the carbon chain** towards the electron withdrawing group

Group which **withdraws electron density** towards itself.

Examples



Order of –I

$-\overset{+}{N}R_3$ > $-\overset{+}{N}H_3$ > $-NO_2$ > $-SO_2R$ > $-CN$ > $-CHO$

> $-COR$ > $-COOH$ > $-F$ > $-Cl$ > $-Br$ > $-I$

> $-OR$ > $-OH$ > $-C\equiv R$ > $-NH_2$ > $-Ph$ > $-CH=CR_2$

$-\overset{+}{N}H_3$ > $-NO_2$

Cations are **strong electron withdrawing groups** due to the presence of **+ve charge**.

Order of –I





Order of –I



Order of E.N.

N (sp) > N (sp^2) > C (sp) > N (sp^3) > C (sp^2) > C (sp^3)

More the % s-character → More will be E.N. → More will be –I



sp^2 sp

Order of –I

Order of –I groups

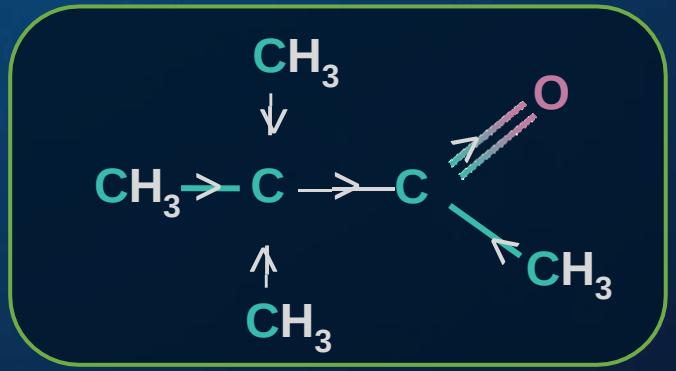
$-C\equiv CH$ > $-C_6H_5$ > $-CH=CH_2$

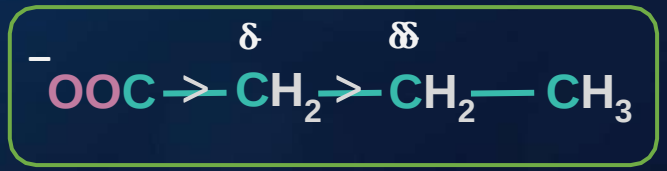
2C-sp | 6C-sp^2 | 2C-sp^2

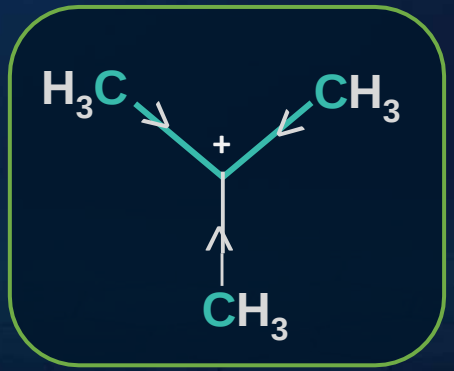
sp > sp^2

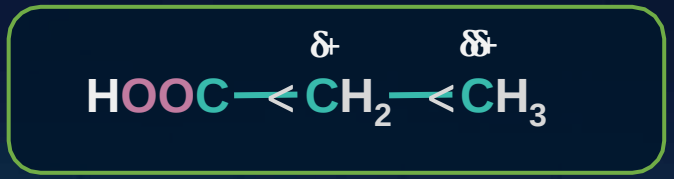
Electronegativity

Direction of Electron Displacements









Applications of Inductive Effect

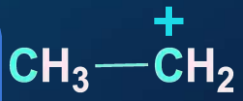
1. Relative stability of intermediates

2. Acidic/Basic Strength

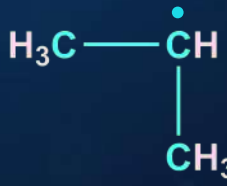
Intermediates

Electron deficient

- Carbocations

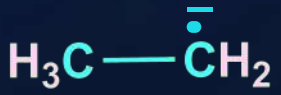


- Free radicals



Electron rich

- Carbanions



Stability of electron deficient species $\propto$ Electron donating group (+I)

Stability of electron rich species $\propto$ Electron withdrawing group (-I)

Acid Dissociation Constant for HA

$$HA \rightleftharpoons H^+ + A^-$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$pK_a = -\log K_a$$

Acidic strength $\propto$ Stability of the conjugate base

- $\propto$ Presence of E.W.G. (-I)
- $\propto \frac{1}{\text{Presence of E.D.G. (+I)}}$

For a Base 'B'

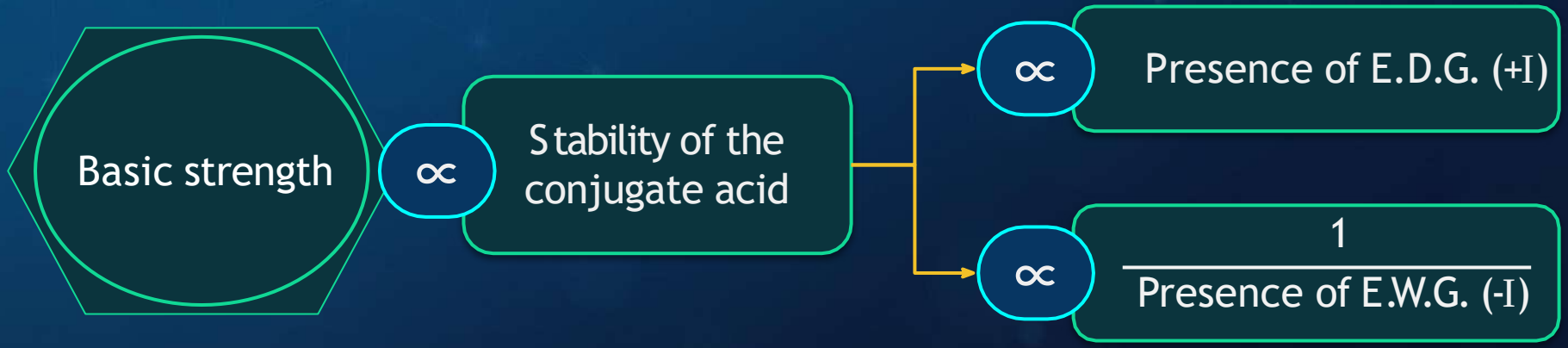
$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

$$pK_b = -\log K_b$$

Basic strength $\propto$ Stability of the conjugate acid

- $\propto$ Presence of E.D.G. (+I)
- $\propto \frac{1}{\text{Presence of E.W.G. (-I)}}$


Basic strength
∝
Stability of the conjugate acid
∝
Presence of E.D.G. (+I)
∝
1
Presence of E.W.G. (-I)



Resonance

Resonance

When two or more Lewis structures that **differ only in the distribution of electrons** can be written for a molecule, but no single Lewis structure is sufficient to describe the actual electron distribution, the molecule is said to show resonance.

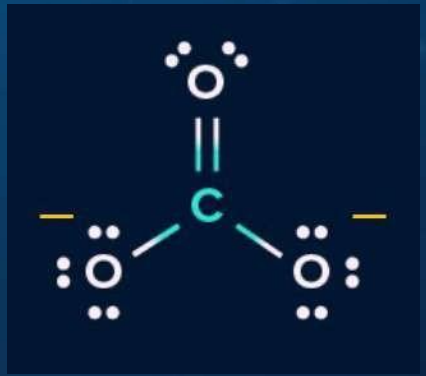


Bond length of C-C = 154 pm

Bond length of C=C = 134 pm

All bond lengths in benzene are equal = 139 pm

Resonance and Resonating structures

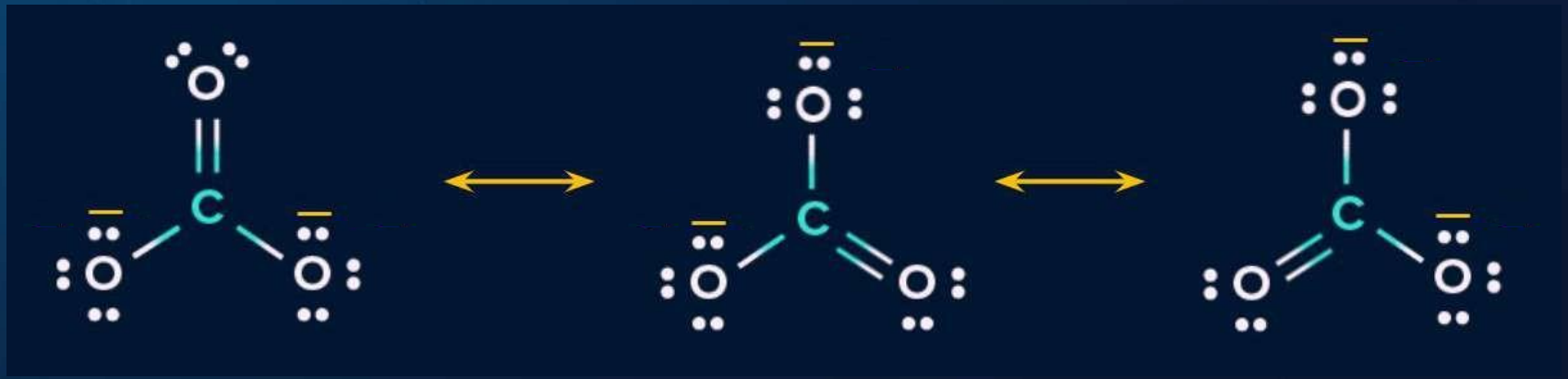


All the bond lengths in the carbonate ion are equal.

Various Lewis structures that can be written for a molecule are called **resonating structures/ contributing structures/canonical structures.**



Resonating Structures (R.S.)



Resonance Hybrid

Resonating structures are hypothetical, but contribute to the real structure which is called the **resonance hybrid**

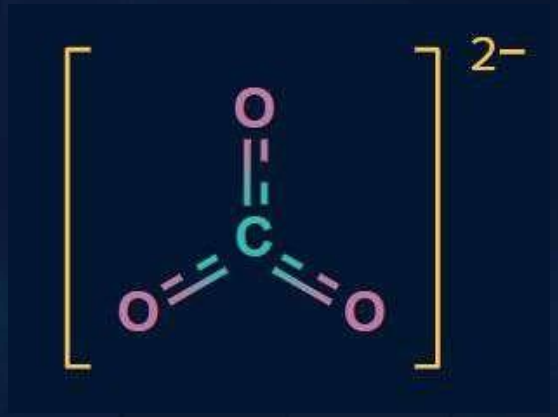
The resonance hybrid is **more stable than any other resonating structures**



Resonating structure

Resonating structure

Resonance Hybrid



Resonance

Delocalisation of π electrons

Planar structure, where π electron delocalisation takes place

At least 3 continuous parallel p-orbitals (or d-orbitals) on adjacent atoms

Parallel p-orbitals can be **half-filled, fully filled or vacant**

Conjugation

A given atom or a group is said to be in **conjugation when it is singly bonded to an unsaturated system** and has

- **Positive charge**
- **Multiple bonds**
- **Negative charge**
- **Lone pairs**

Types of Conjugation

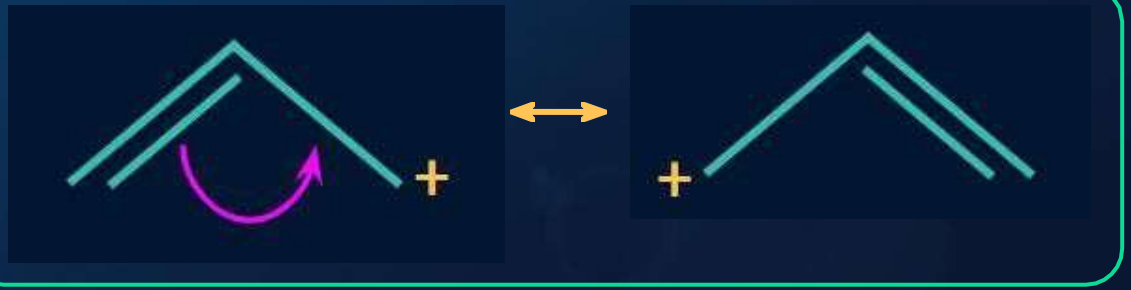
1 Conjugation between C=C and C=C





Types of Conjugation

2 Conjugation between a vacant orbital and C=C





Resonance Hybrid

Types of Conjugation

3

Conjugation between a non-bonded electron pair and C=C

πBond - Negative Charge Conjugation

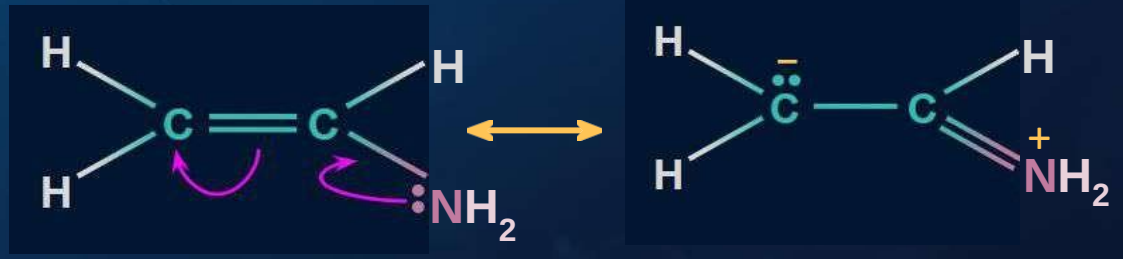




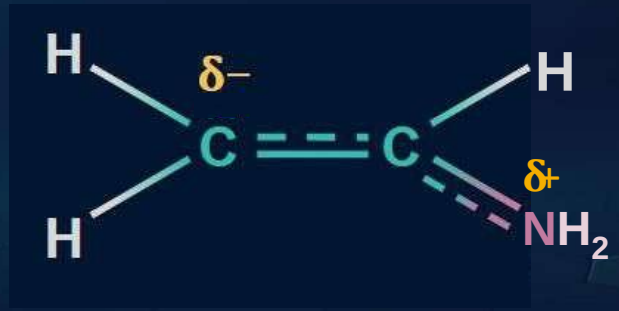
Resonance Hybrid

Types of Conjugation

πBond - Lone Pair Conjugation



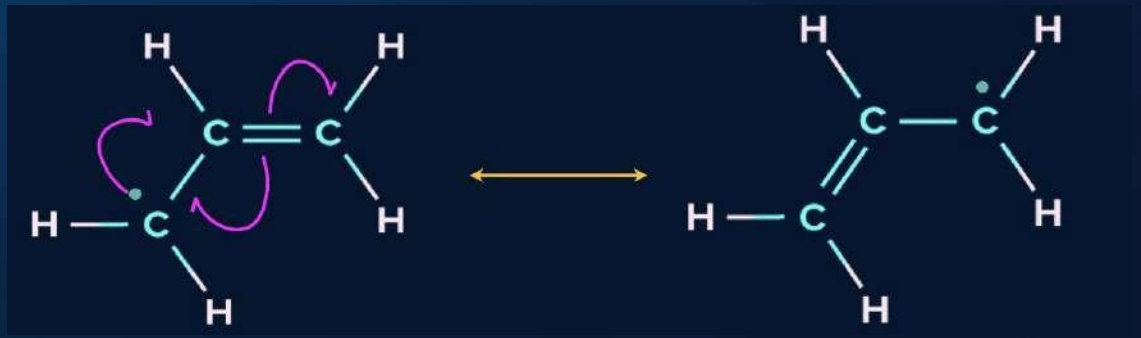
A B

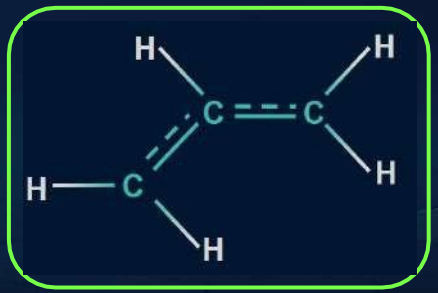


Resonance Hybrid

Types of Conjugation

4 Conjugation between an odd electron and C=C





Resonance Hybrid

Drawing Resonating Structures

Arrow is drawn **from the lone pair or the -ve charge** towards the conjugated system.

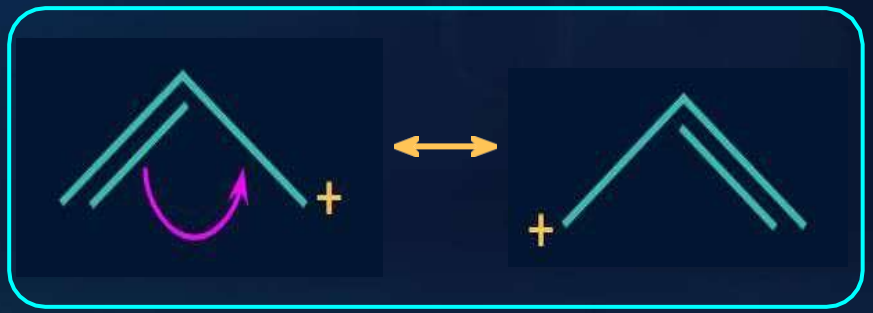
Arrow is drawn **from the conjugated system to the -X=Y** (-C=O, -N=O) bond or the vacant p-orbital or d-orbital





Drawing Resonating Structures

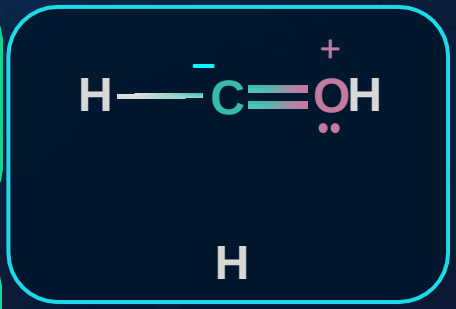
In case of conjugation of a double bond with a positive charge, **move the πelectrons and not the +ve charge.**



Rules for Resonating Structures

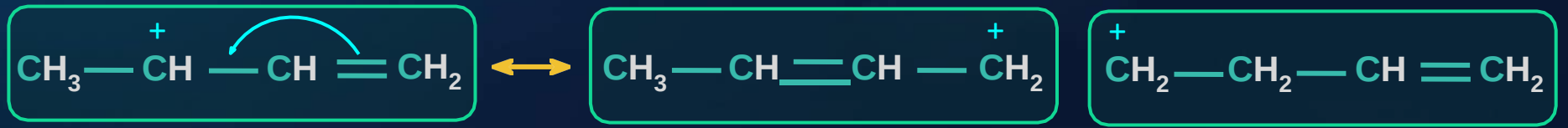
Rule 1

All the resonating structures must have a proper Lewis structure.



Rule 2

The positions of the nuclei of the atoms must remain the same in all the structures.



R.S. ✓

R.S. ✗

Rules for Resonating Structures

Rule 3

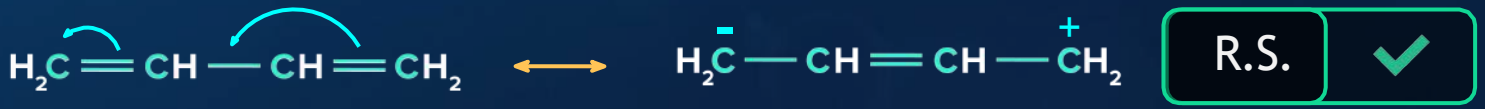
All atoms taking part in delocalisation must lie in a plane so that orbital overlapping becomes parallel to each other.

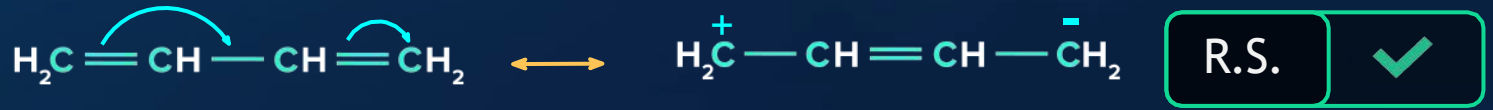


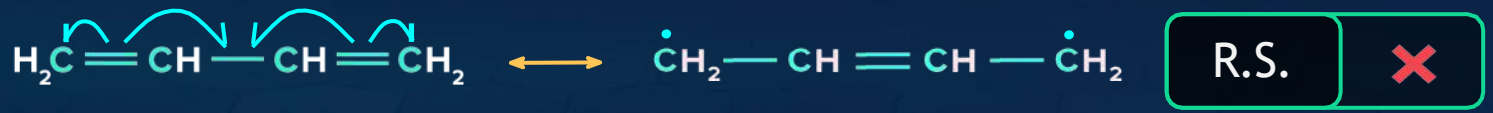
Rules for Resonating Structures

Rule 4

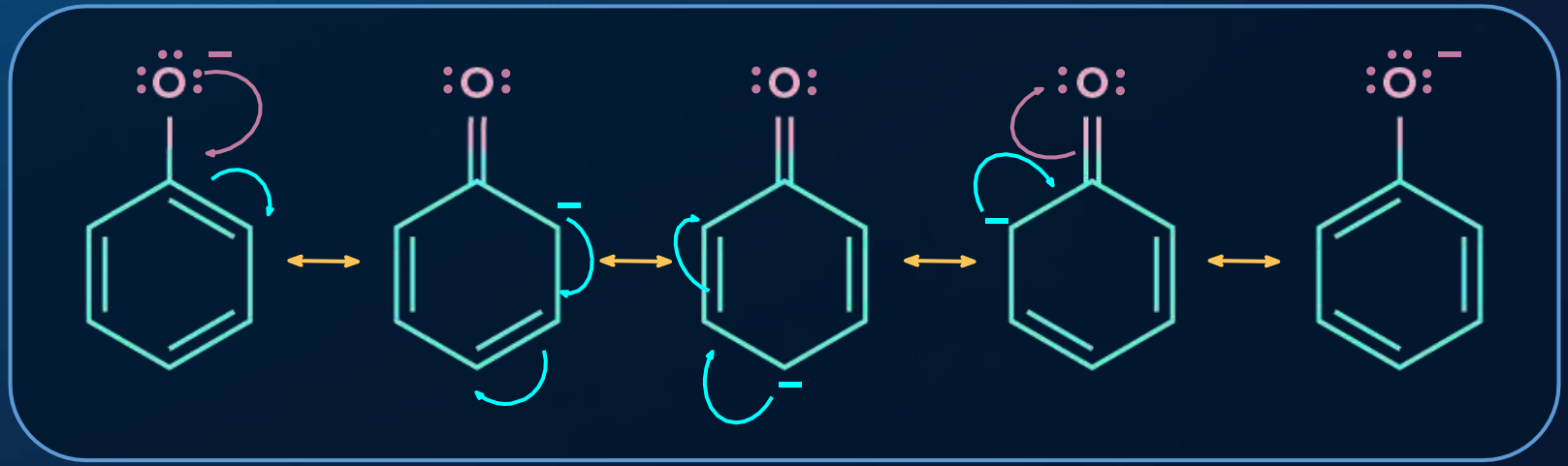
All canonical forms must have the same number of paired & unpaired electrons.







Resonating Structures of Phenoxide ion

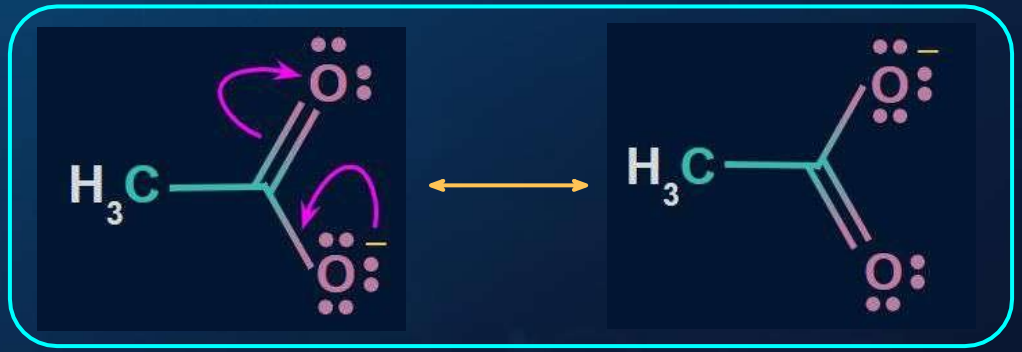


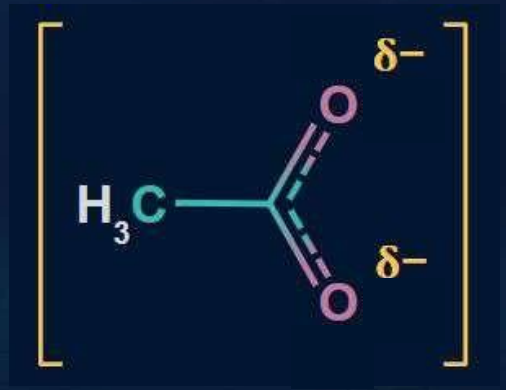
Resonating Structures

More the number of contributing resonating structures, more is the **stability** of the compound.

More the number of contributing **equivalent** resonating structures, more is the stability of the compound.

Equivalent Contributing Resonating Structures





Resonance

The energy of the actual molecule is **lower** than that of any of its resonating structures.

Delocalization is a stabilising phenomenon

All canonical forms **do not contribute equally** to the actual molecule.

Most stable resonating structure

Contributes **maximally** to the resonance hybrid

Least stable resonating structure

Contributes **minimally** to the resonance hybrid

Comparing the Stabilities of the Resonating Structures

1

Structures in which all of the atoms have a **complete valence shell of electrons** are stable.



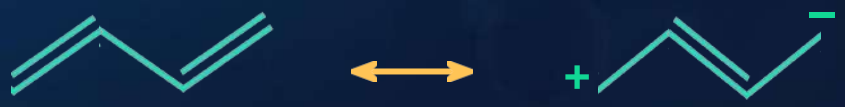
A

B

B is more stable than A

Comparing the Stabilities of the Resonating Structures

Structures which have **more covalent bonds** are **more stable** than other structures.



A

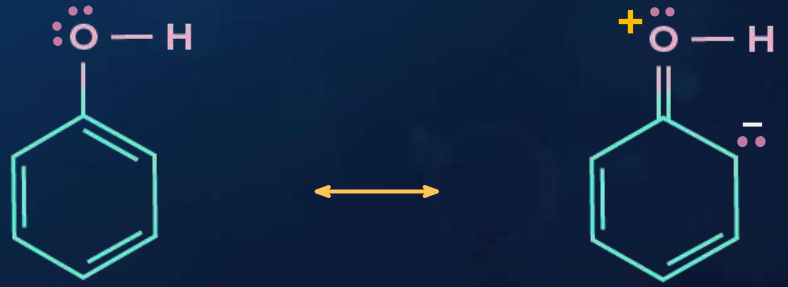
B

A is more stable than B

Comparing the Stabilities of the Resonating Structures

2

Non-polar structures are more stable.



A

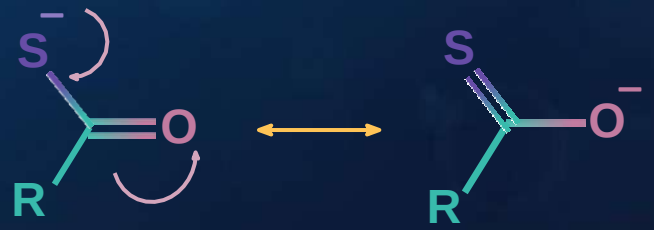
B

A is more stable than B

Comparing the Stabilities of the Resonating Structures

3

Any charge (+ve or -ve) is more stable on the **larger sized atom.**



Comparing across a group

A

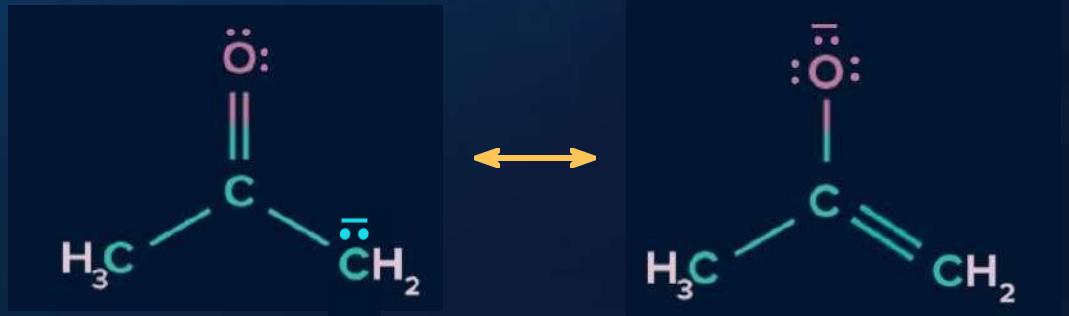
B

A is more stable than B

Comparing the Stabilities of the Resonating Structures

4

Structures that carry **-ve charge** on a **more E.N. atom** and **+ve charge** on a **less E.N. atom** are comparatively more stable.



A

B

Comparing across a period

B is more stable than A

Point to Remember!!

Distance between similar charges ↑ → Stability ↑

Distance between opposite charges ↑ → Stability ↓

Number of Benzenoid rings in the structure ↑ → Stability ↑

Resonance Energy



P.E. difference between the **most stable** resonance structure and the **resonance hybrid**.

Stability of the molecule $\propto$ Magnitude of Resonance Energy

Energy of the resonance hybrid - Energy of the most stable R.S. = Resonance Energy

Mesomeric Effect

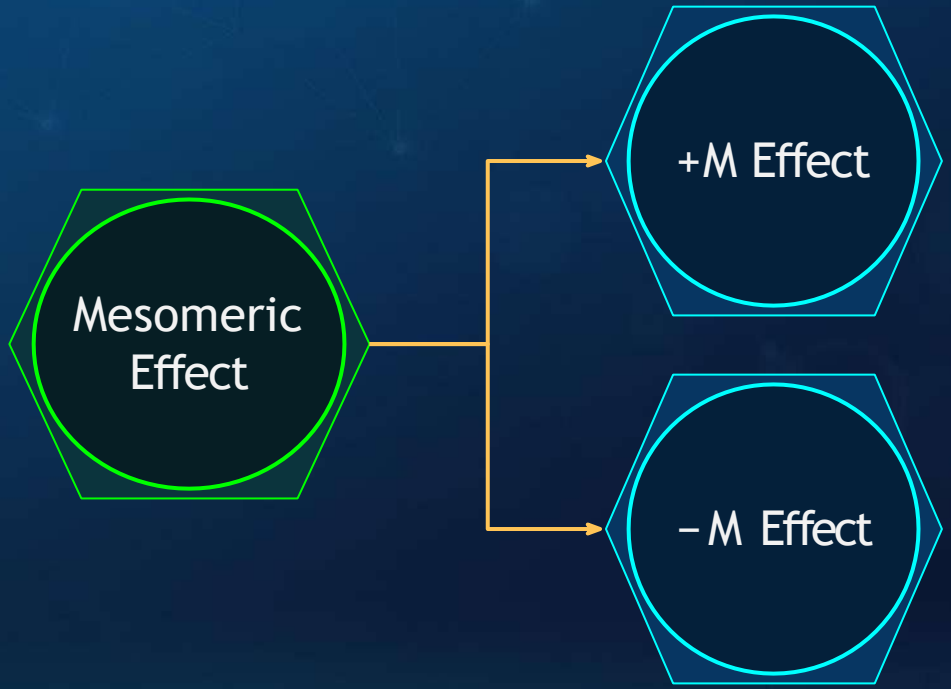
Permanent effect of **πelectron shifting** in a conjugated system.

Directional Resonance

Permanent effect

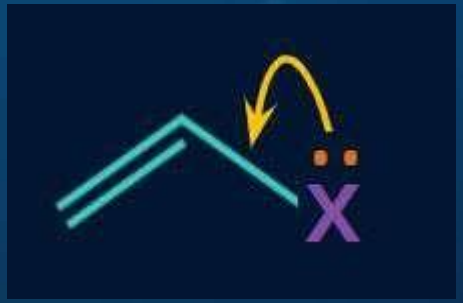
Distance independent effect

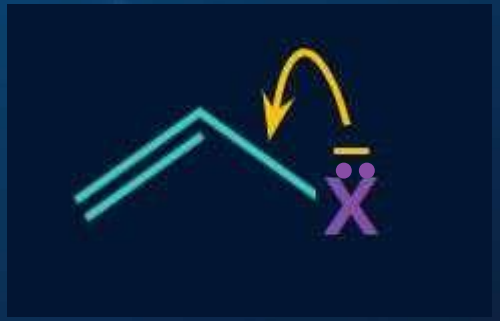
Types of Mesomeric Effects



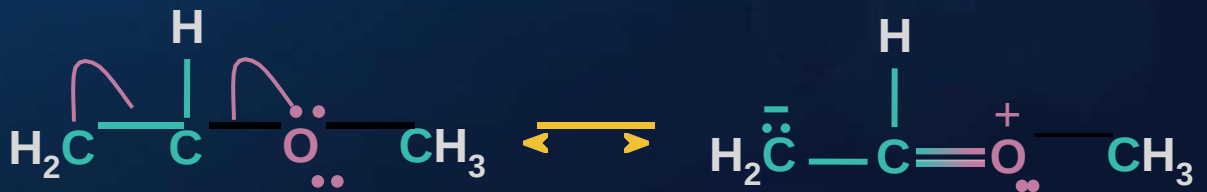
When the group **donates electron** to the conjugated system, it shows + M effect.

+M Effect

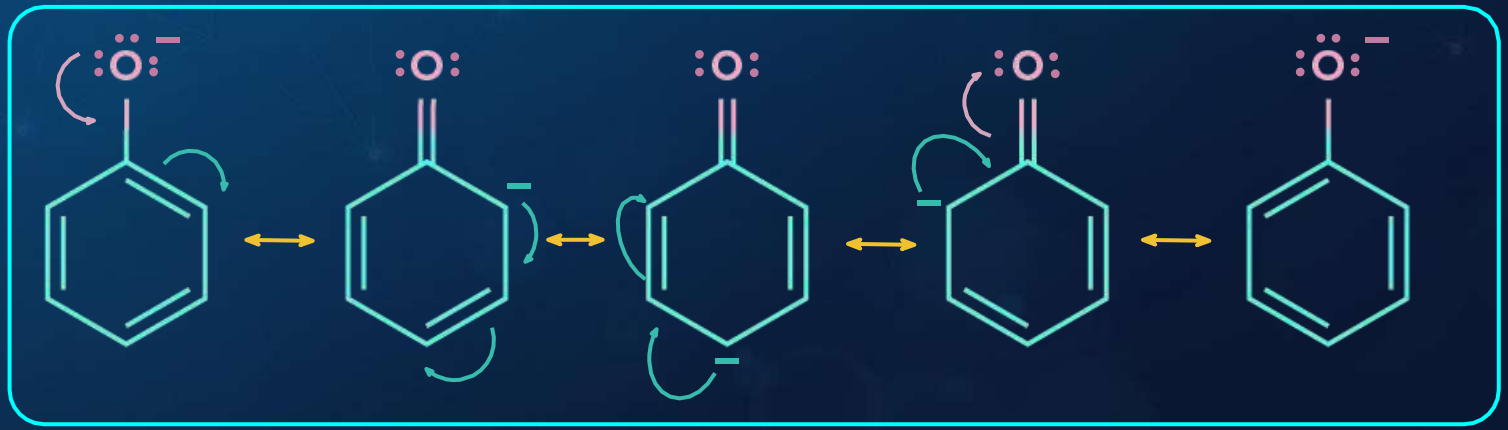




In general, the group attached to the conjugated system contains a **lone pair or a negative charge (unshared pair).**



Example



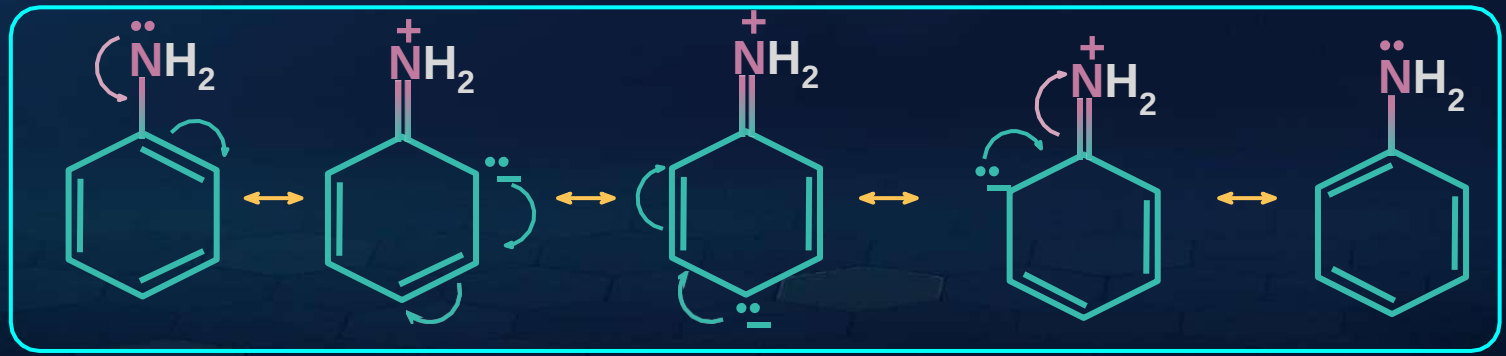
Positive Mesomeric effect (+M effect)

Relative order of +M groups

$-\ddot{O}^{-}$ > $-NH_2$ > $-NHR$ > $-NR_2$

$-OH$ > $-OR$ > $-NHCOR$ > $-OCOR$

$-Ph$ > $-F$ > $-Cl$ > $-Br$ > $-I$



Negative Mesomeric effect (-M effect)

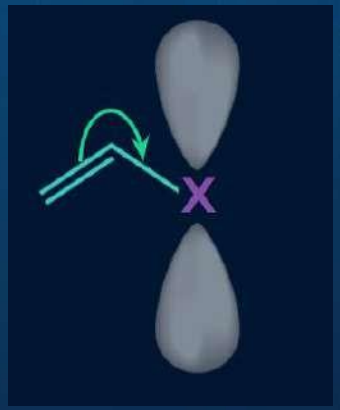
When the group withdraws electrons from the conjugated system, it shows - M effect.

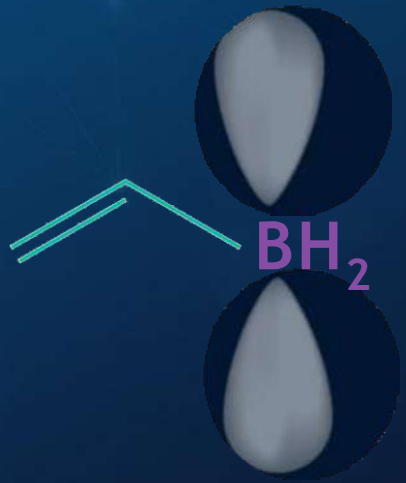
In general, the atom or the group attached directly to the conjugated system shall possess:

1. Vacant orbital
2. $-X=Y$
3. $-X\equiv Y$

E.N. (Y) > E.N. (X)

–M Effect









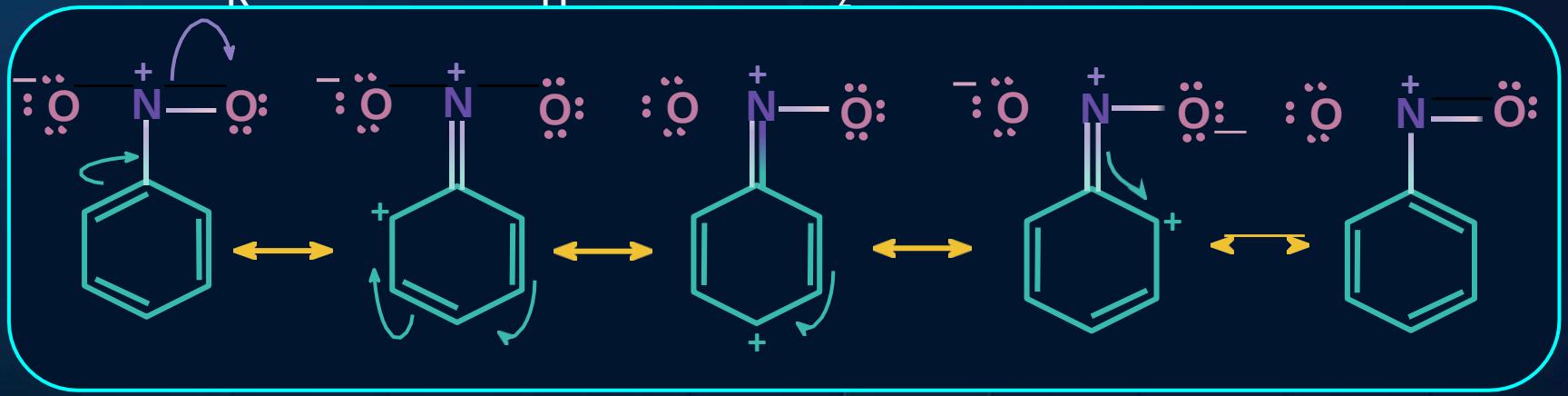
Vacant orbitals present in the group attached to the conjugated system

Electron withdrawing group attached to the conjugated system

Negative Mesomeric effect (-M effect)

$-NO_2$ > $-CN$ > $-CHO$ > $-COR$ > $-COOCO_R$

$-COO_R$ > $-COO_H$ > $-CONH_2$ > $-COO^-$



Flexible Groups

Atoms/ groups attached to the conjugated system which can show both +M/−M effect

−N=O, −SH, −Cl, -Phenyl, -CH=CH_2 etc.

Mesomeric Effect

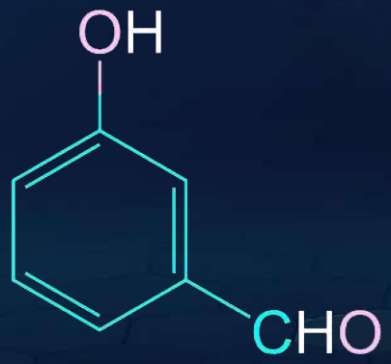
Distance independent effect

Generally **stronger** than Inductive effect

Does not operate at **meta** position

Brace Yourself!

When a **+M** group and a **−M** group are at **meta-positions** to each other, then they are not in conjugation with each other, but **conjugation with the benzene ring** exists.

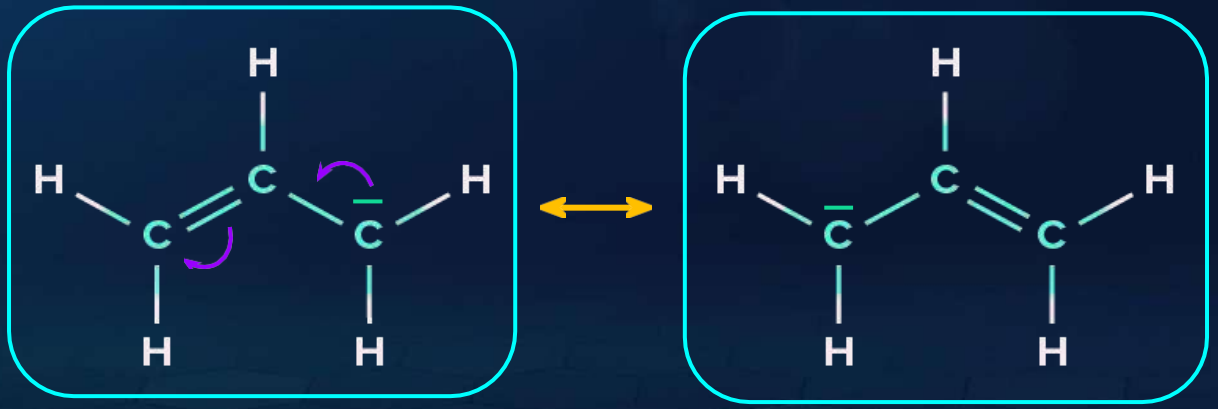


Applications of Resonance Effect

1. Stability of Intermediates
2. Bond Length
3. Acidic strength and Basic strength

Stability of Intermediates

Delocalisation of charge ↑ → Stability ↑



Bond Length

For a bond between two particular atoms,

Single bond > Partial double bond > Double bond > Partial triple bond > Triple bond



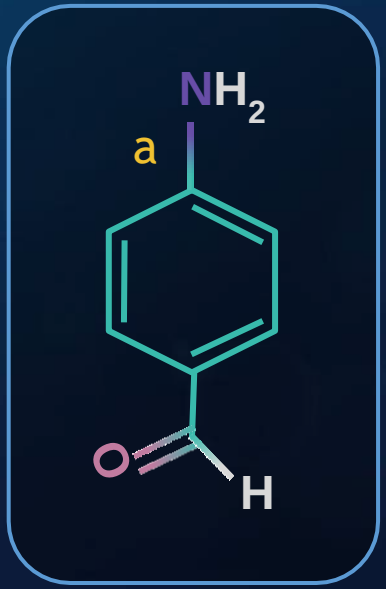


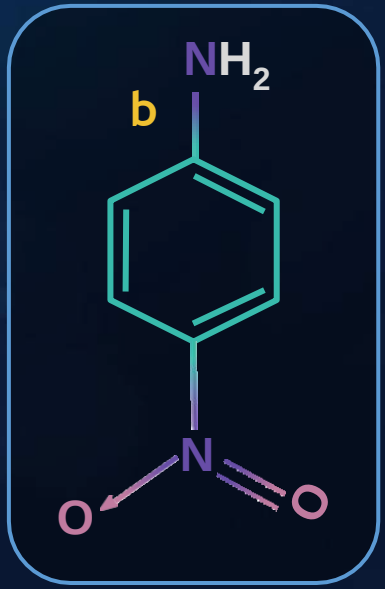
Partial double bond character due to conjugation of pi bonds

x > y

Example

As nitro group shows more –M effect, so, more electron density is given by NH_2 group to the ring resulting in more double bond character.





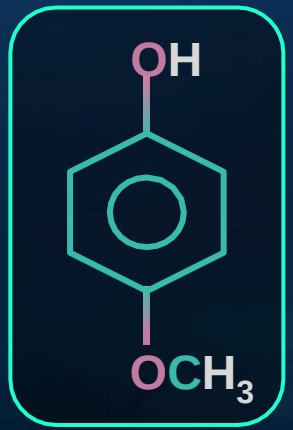
a > b

Acidic Strength

Delocalisation of charge of the conjugate base ↑ → Acidic strength ↑

+M effect ↑ → Acidic strength ↓

-M effect ↑ → Acidic strength ↑



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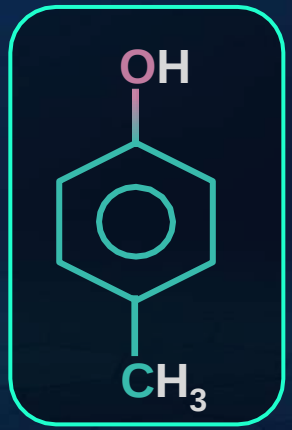

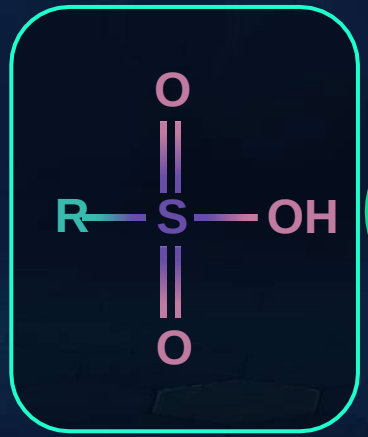

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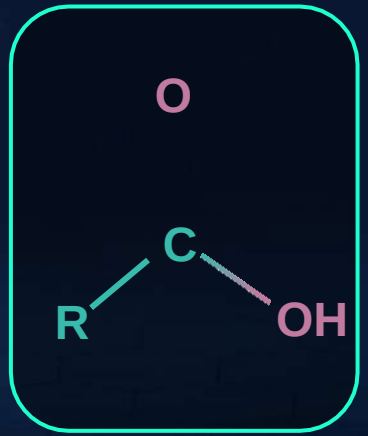
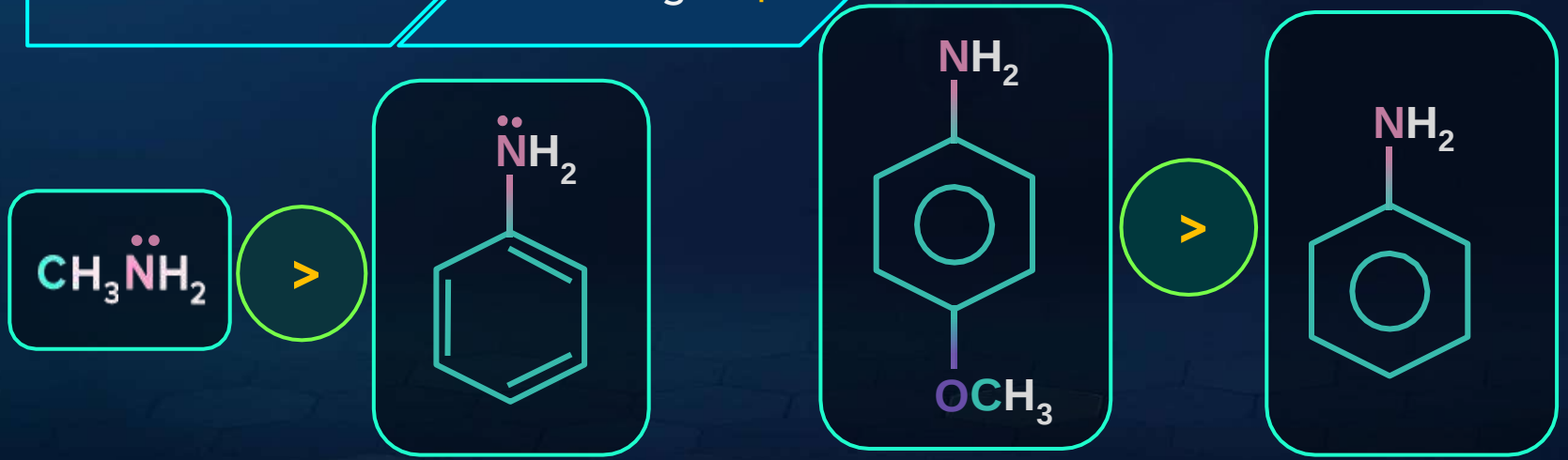


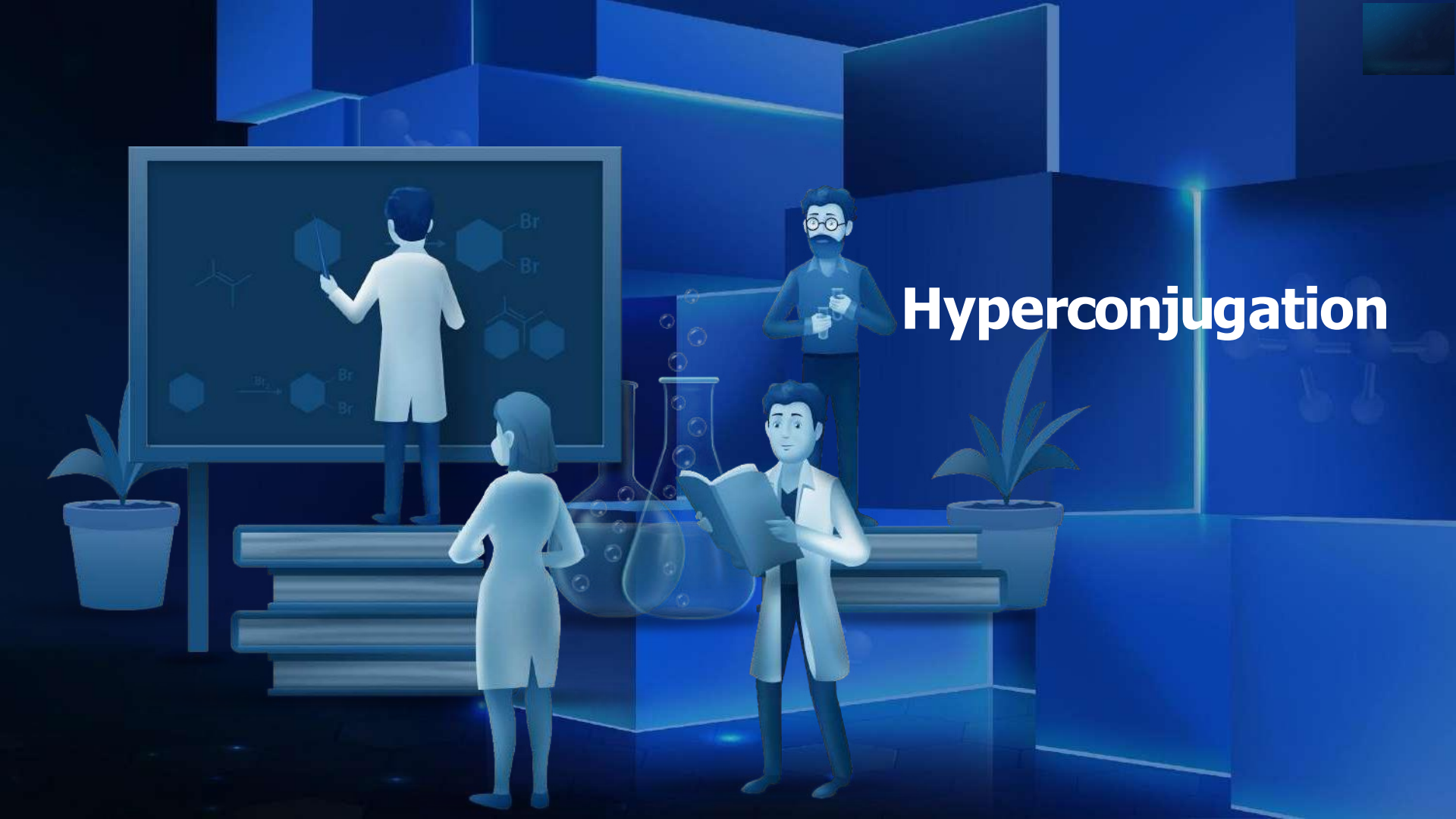
Basic Strength

Delocalization of lone pair of the base ↑ → Basic strength ↓

-M effect ↑ → Basic strength ↓

+M effect ↑ → Basic strength ↑




Hyperconjugation

Hyperconjugation

Other names of hyperconjugation

1. No bond resonance
2. Baker-Nathan Effect
3. σ- π resonance

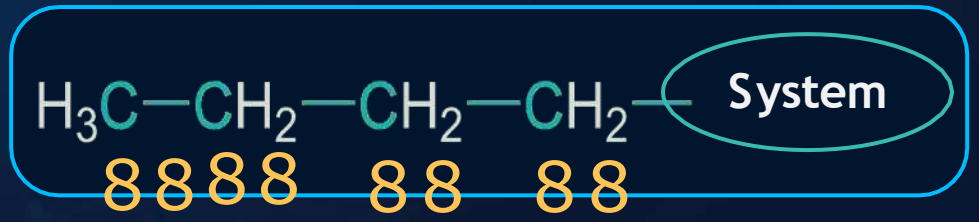
Delocalization of **σ-electrons with vacant p-orbital or antibonding π* orbital.**

Stability is increased due to the **delocalization of σ-πelectrons.**

Condition for Hyperconjugation

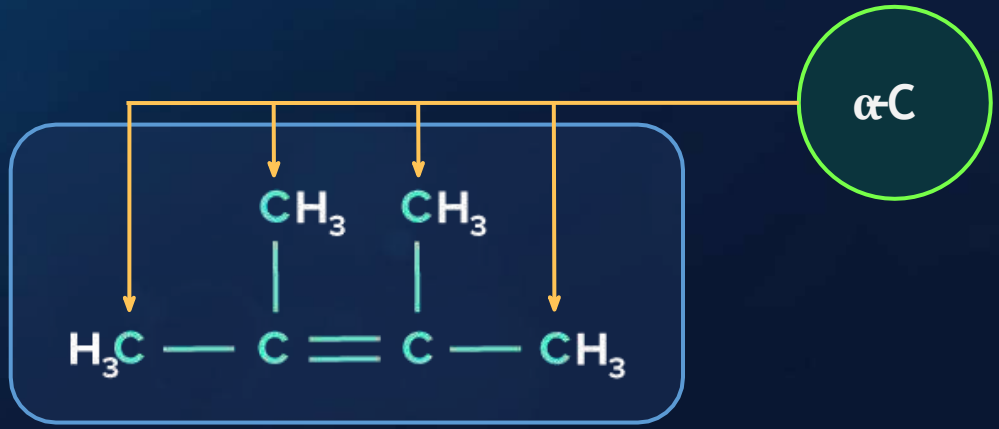
Presence of **at least one α-H** at the saturated carbon with respect to

- Alkene
- Benzene
- Carbocation
- Free radical



α–Carbon

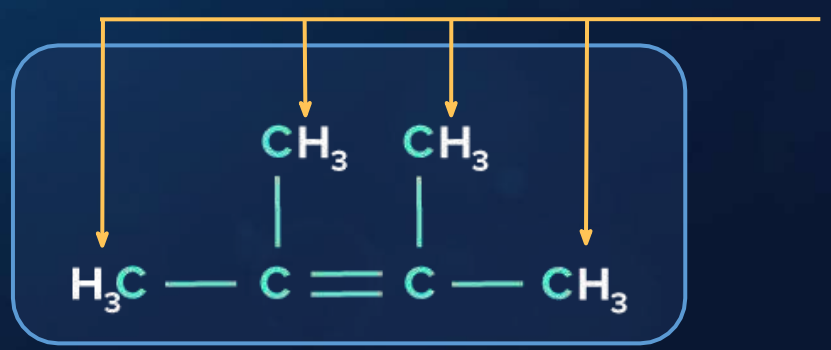
The carbon atom **directly bonded** to an atom, a group, a functional group or other elements of interest.



Total 4 α-C

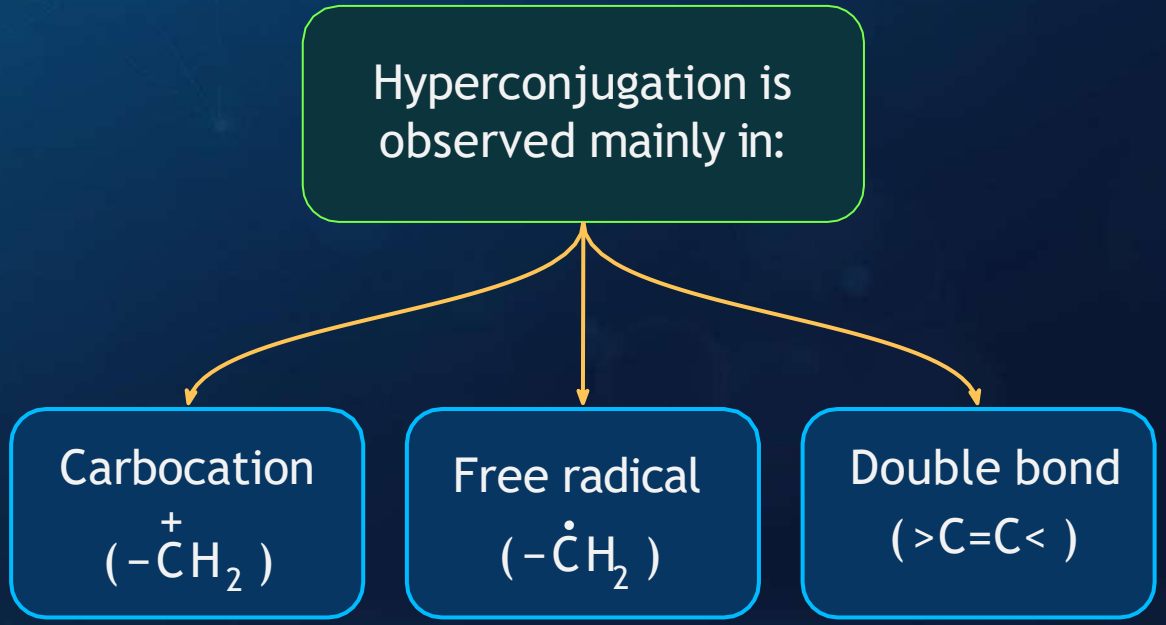
α–Hydrogen

The hydrogen atom **directly attached to the α – carbon.**

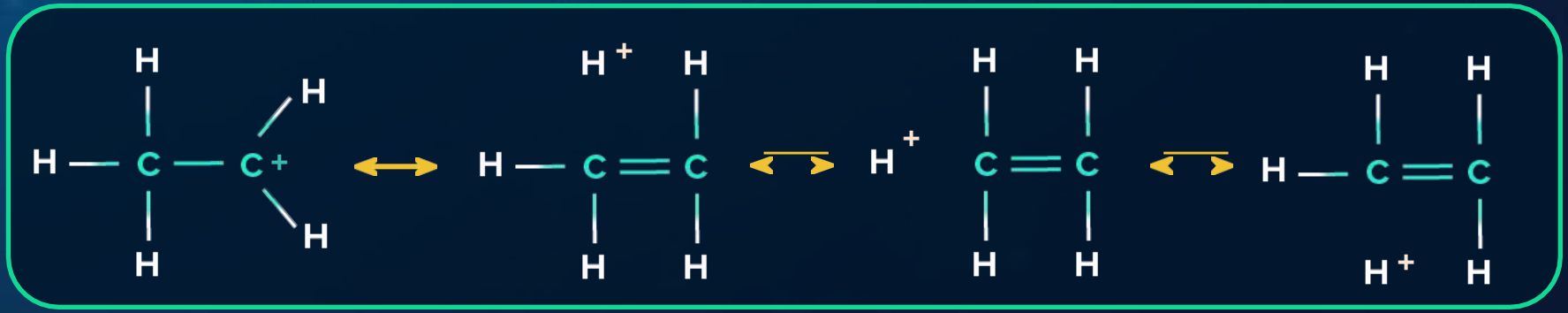


Total **12 α-H**

Hyperconjugation



Hyperconjugation in Ethyl Carbocation

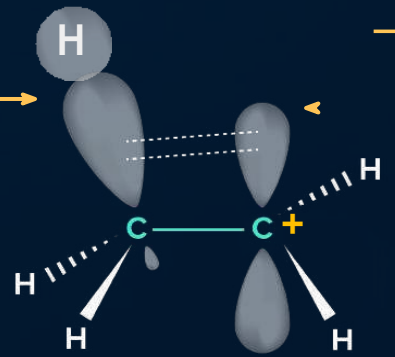


In Hyperconjugative structures, there is no covalent bond between 'C' & one of the 'H'.

So, Hyperconjugation is also known as **no-bond resonance.**

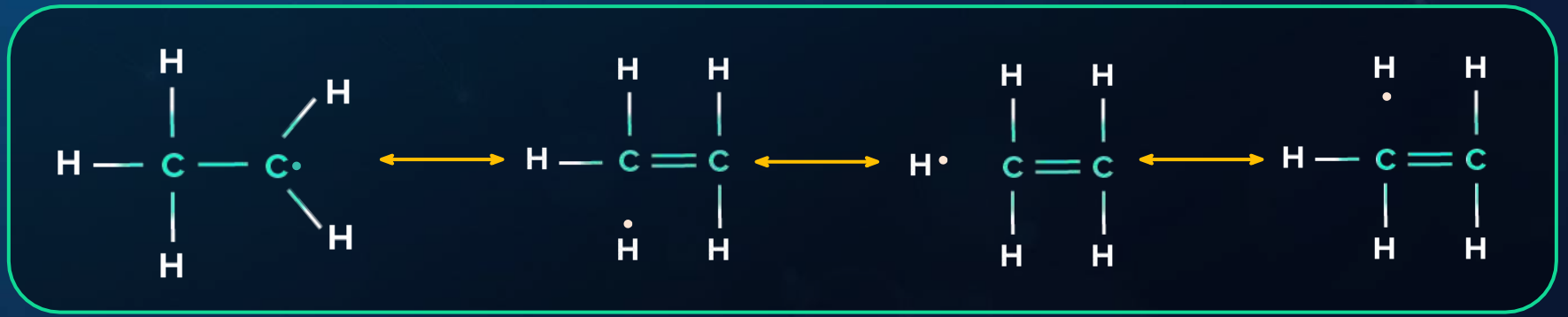
Hyperconjugation in Ethyl Carbocation

$C_{sp^3} - H_{1s}$ Bond

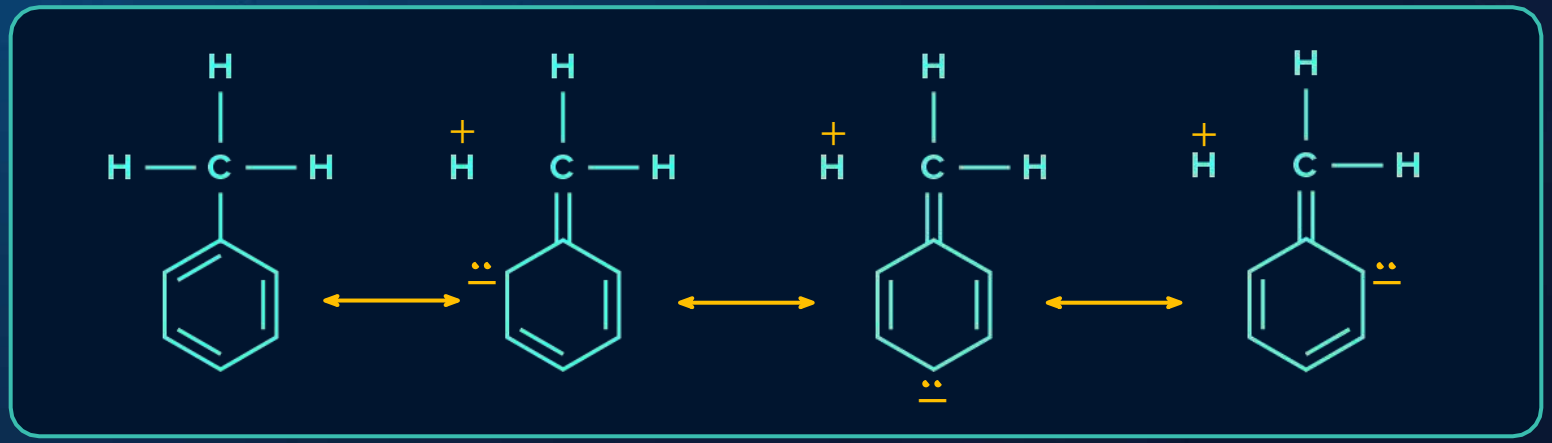


Empty 2p orbital of 'C'

Hyperconjugation in Ethyl Free Radical



Hyperconjugation in Benzenoid compounds



Similarly, six more structures can be drawn using other two hydrogens.

Hyperconjugation

Stability of the carbocation, free radical or alkene $\propto$ Number of no bond resonating structures due to hyperconjugation $=$ Number of α-hydrogens

Deuterium can also show hyperconjugation

C-D bond is stronger than C-H bond

Hyperconjugat-ion of C-D bond is weaker than C-H bond


Comparisons of
Electronic Effects

Comparisons of Electronic Effects

	Inductive effect	Mesomeric effect	Hyperconjugative effect
1	It is found in saturated and unsaturated compounds.	It involves complete shifting of π electrons of π bonds or lone pairs of electrons.	It is found in carbocation, carbon free radical and unsaturated compounds.

Comparisons of Electronic Effects

Inductive effect	Mesomeric effect	Hyperconjugative effect
It involves partial shifting of σ electrons.	It is found in unsaturated compounds especially having conjugated system.	It involves partial shifting of σ electrons into the adjacent p-orbital or anti-bonding π^*-orbital.

Comparisons of Electronic Effects

Inductive effect	Mesomeric effect	Hyperconjugative effect
The electron pair is slightly displaced from its position and thus, partial charges are developed.	The electron pair is completely transferred and thus, complete positive and negative charges are developed.	The electron pair is partially transferred.

Comparisons of Electronic Effects

Inductive effect	Mesomeric effect	Hyperconjugative effect
Distance dependent	Distance independent	Distance independent

Strength of Electronic Effects

Generally,

Mesomeric > Resonance > Hyperconjugation > Inductive

Generally, in case of Halogens,
-I effect dominates over **+M effect.**

Applications of Hyperconjugation Effect

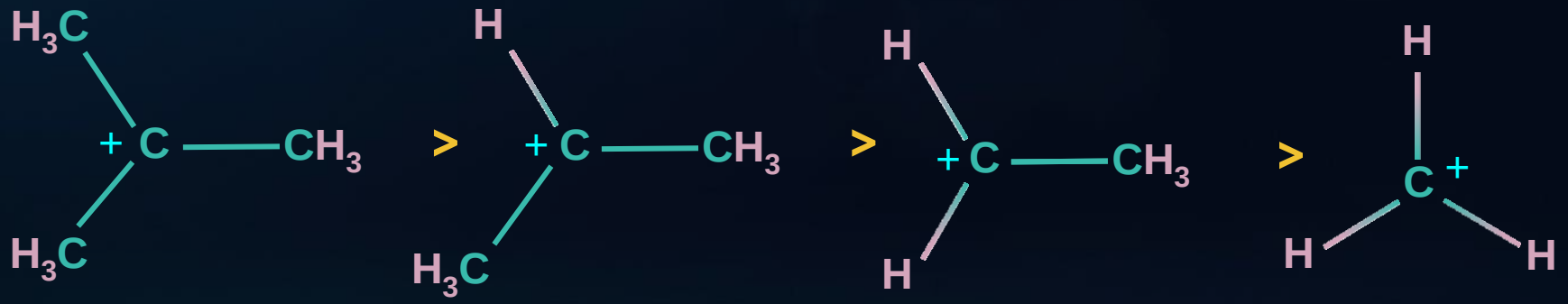
a. Stability of intermediates

b. Explains heat of hydrogenation

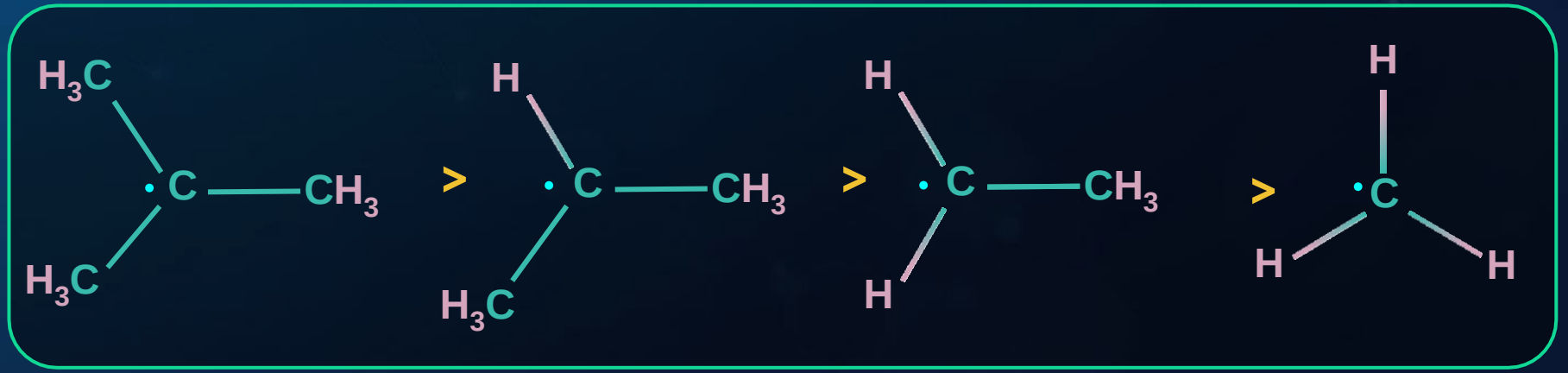
c. Bond Length

Stability of intermediates

Stability of **carbocation & free radical** $\propto$ Number of α-hydrogens



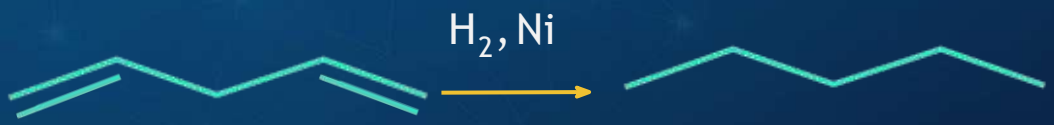
Stability of intermediates



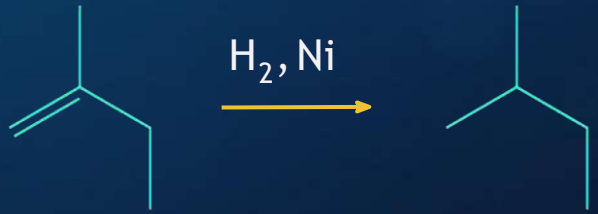
Heat of Hydrogenation

Enthalpy change that accompanies the **hydrogenation of 1 mol of a compound** to form a particular product

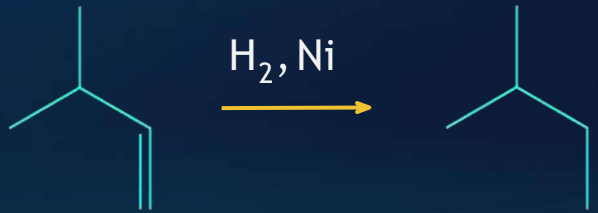
Heat of Hydrogenation



$\Delta H^\circ = -60.8$ kcal/mol



$\Delta H^\circ = -28.5$ kcal/mol



$\Delta H^\circ = -30.3$ kcal/mol

This heat of hydrogenation data tell us stable alkene have lesser heat of hydrogenation.

Heat of Hydrogenation

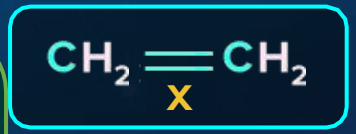
Heat of Hydrogenation $\propto$ Number of π bonds

Heat of Hydrogenation $\propto \frac{1}{\text{Stability of Alkenes}}$

Bond Length

Bond length is also affected by **Hyperconjugation**

Example



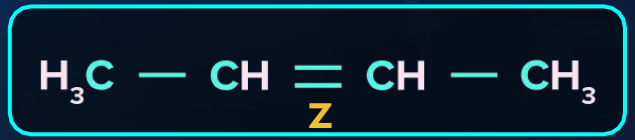
x

0 α-H



y

3 α-H



z

6 α-H

More the number of α-H, more the hyperconjugation and more involvement of double bond.

z > y > x

Electromeric Effect

Involves **complete shifting** of **π**electrons.

Temporary effect, since it is observed **only in the presence of an attacking reagent**

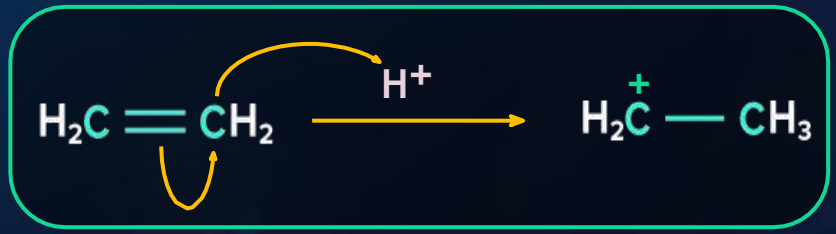
Types of Electromeric Effect

+ E Effect

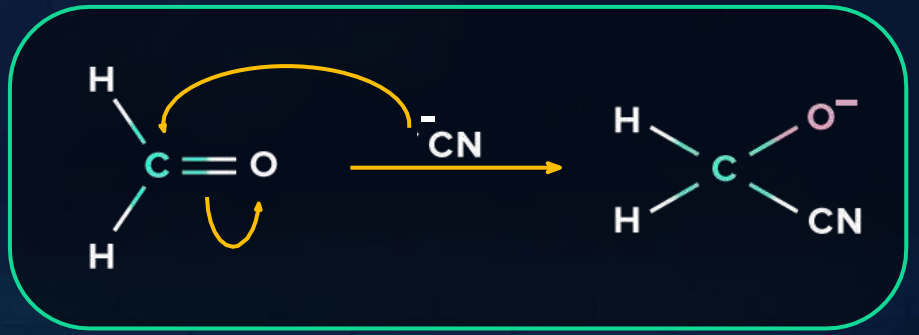
- E Effect

+E Effect and -E Effect

+E Effect: π electrons of the multiple bond are transferred to the atom to which the **reagent gets attached.**

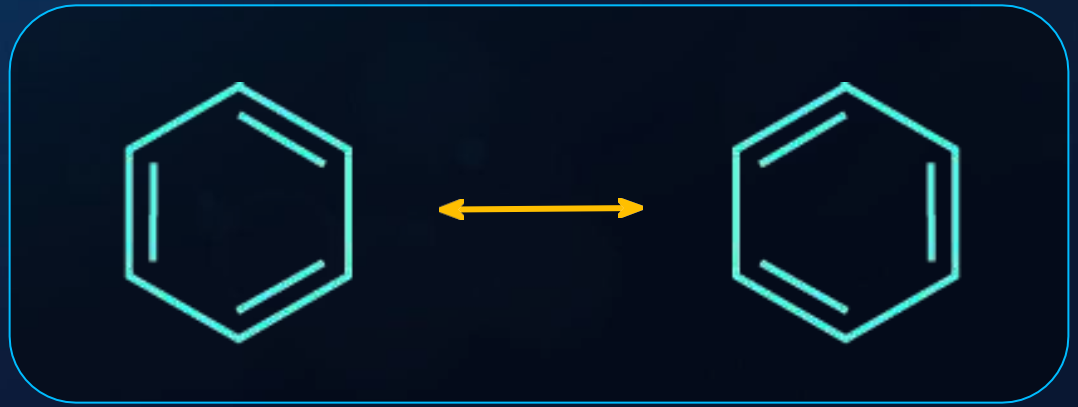


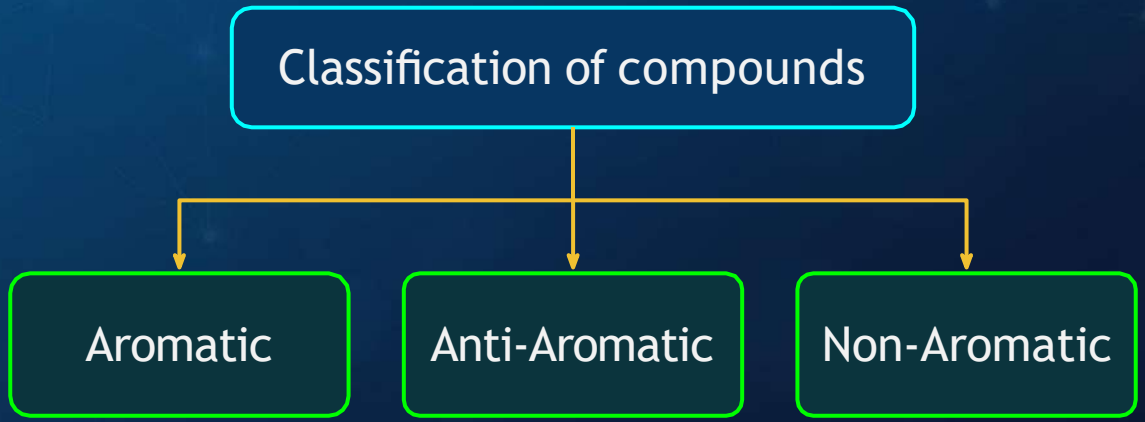
-E Effect: π electrons of the multiple bond are transferred to the atom to which the **reagent does not get attached.**



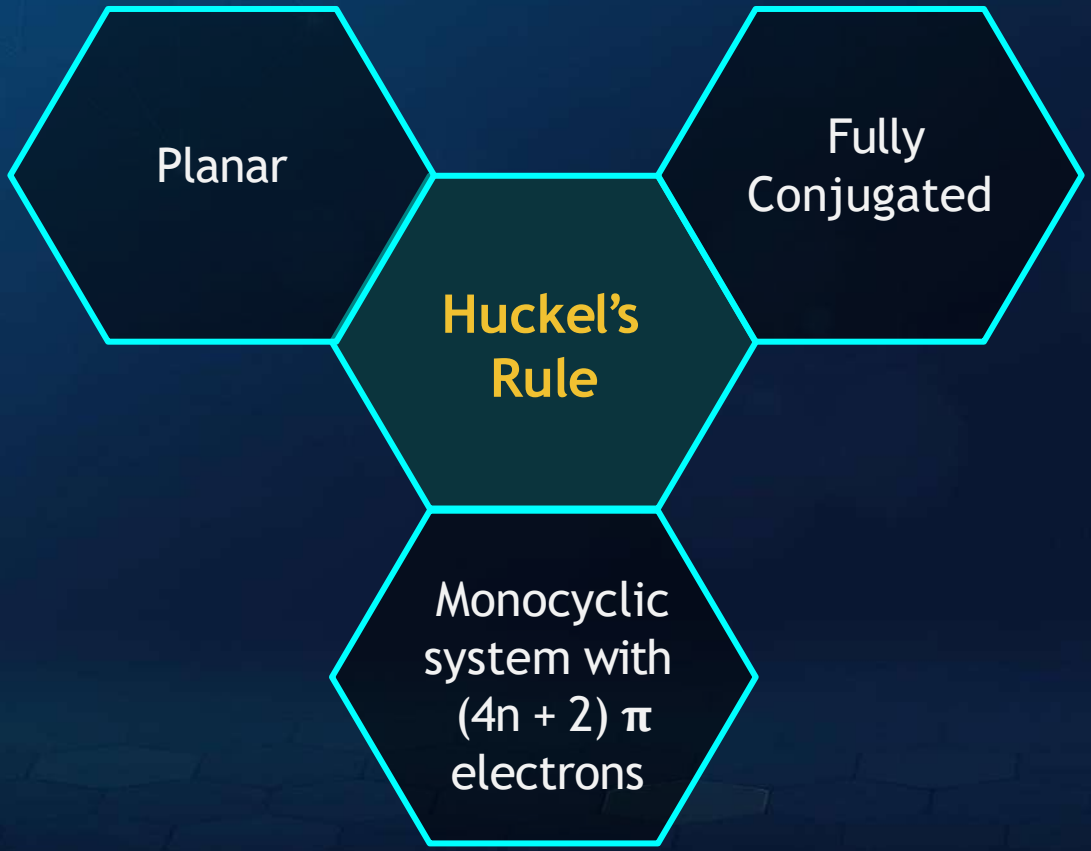
Aromaticity

A cyclic conjugated unsaturated molecule or ion that is stabilised by πelectron delocalisation.

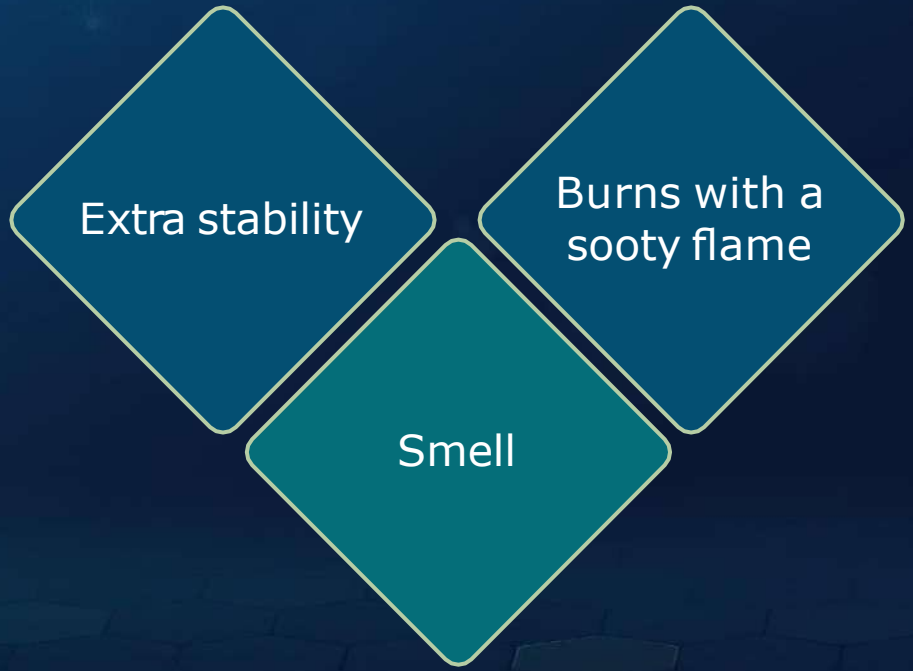



Classification of compounds
Aromatic
Anti-Aromatic
Non-Aromatic

Aromatic Compounds



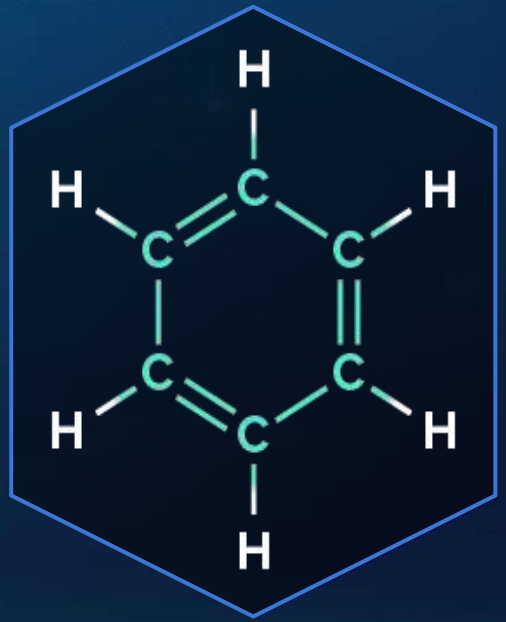
Characteristics of Aromaticity



Benzene as an Aromatic Compound

Cyclic

Planar



Fully conjugated

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

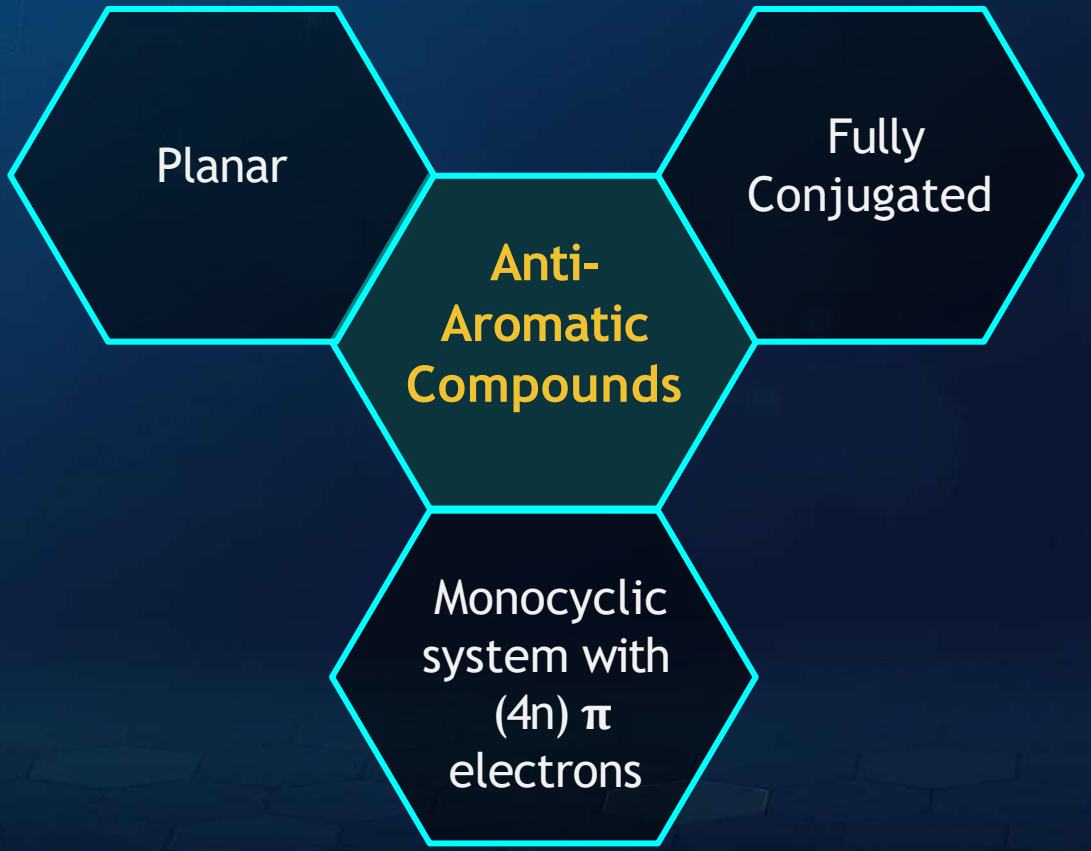
Aromatic hydrocarbons **having two or more benzene rings** fused together

Benzenoid Polycyclic Aromatic Hydrocarbons



Naphthalene | Anthracene | Phenanthrene

Anti-Aromatic Compounds



Cyclobutadiene as an Anti-Aromatic Compound

Cyclic

Planar



Fully conjugated

4n πe^- = 4 πe^-
(n = 1)

Non-Aromatic Compounds

Compounds which are neither aromatic nor anti-aromatic





Stability Order

Aromatic > Non-Aromatic > Anti-Aromatic

Annulene

It is the general name of **monocyclic** systems having **conjugated polyenes**

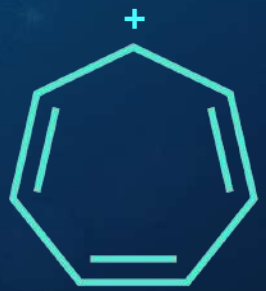
Example: **[8] - Annulene**



Ring size of annulene is indicated by **number in bracket**

Quasi-Aromatic

Aromatic compounds in which **+ve or -ve charge** (present in the ring) is a part of **Huckel's rule**



Tropylium cation

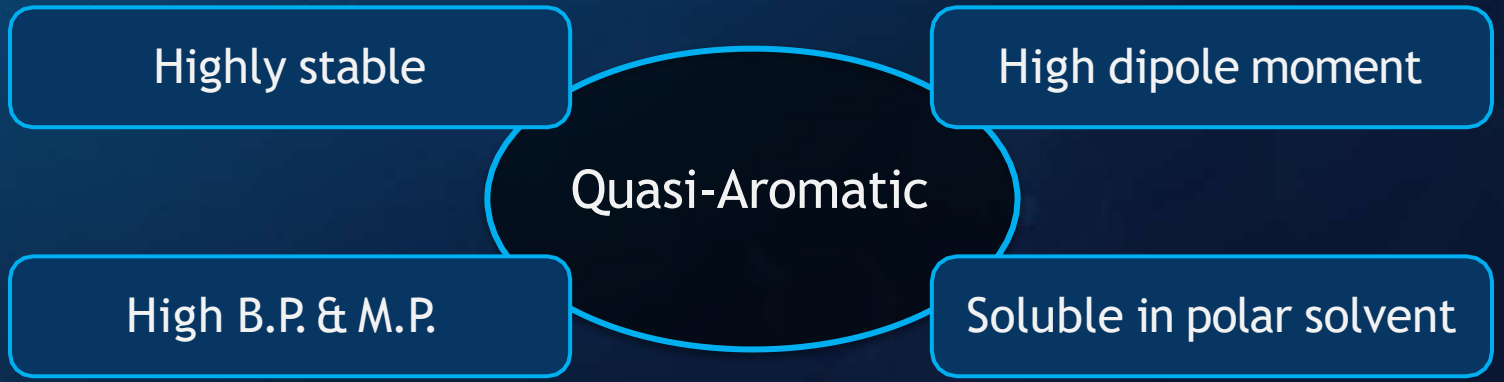


Cyclopentadienyl anion



Cyclopropenyl cation

Quasi-Aromatic



Which one is more stable?

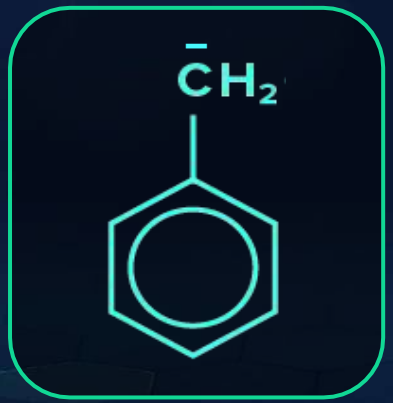


>



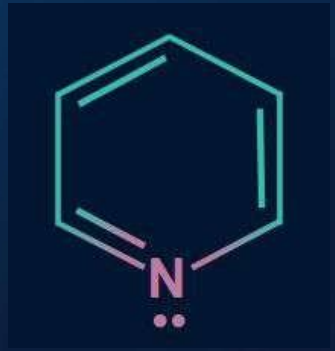


>

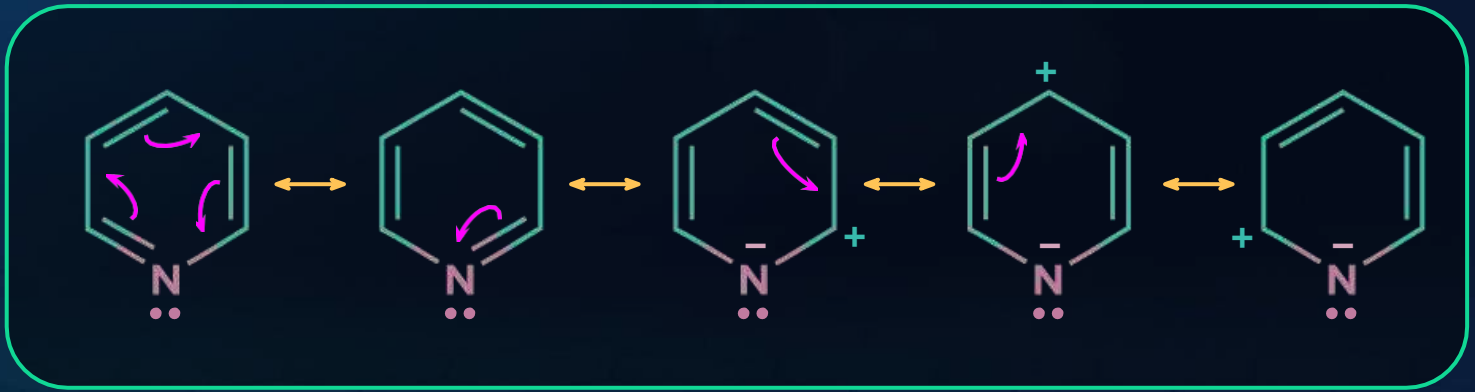


Heterocyclic Aromatic Compound

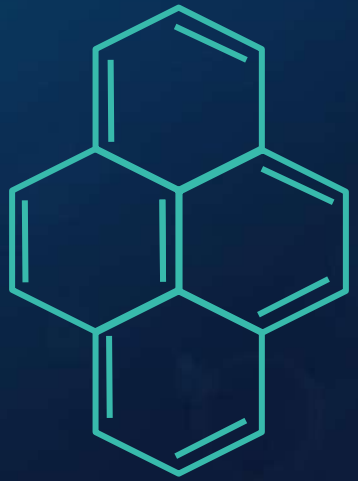
Cyclic compounds that include an element **other than carbon**



Pyridine



Peripheral Conjugation



Pyrene

Aromatic due to peripheral conjugation

Benzyne and Azulene

Benzyne is similar to benzene

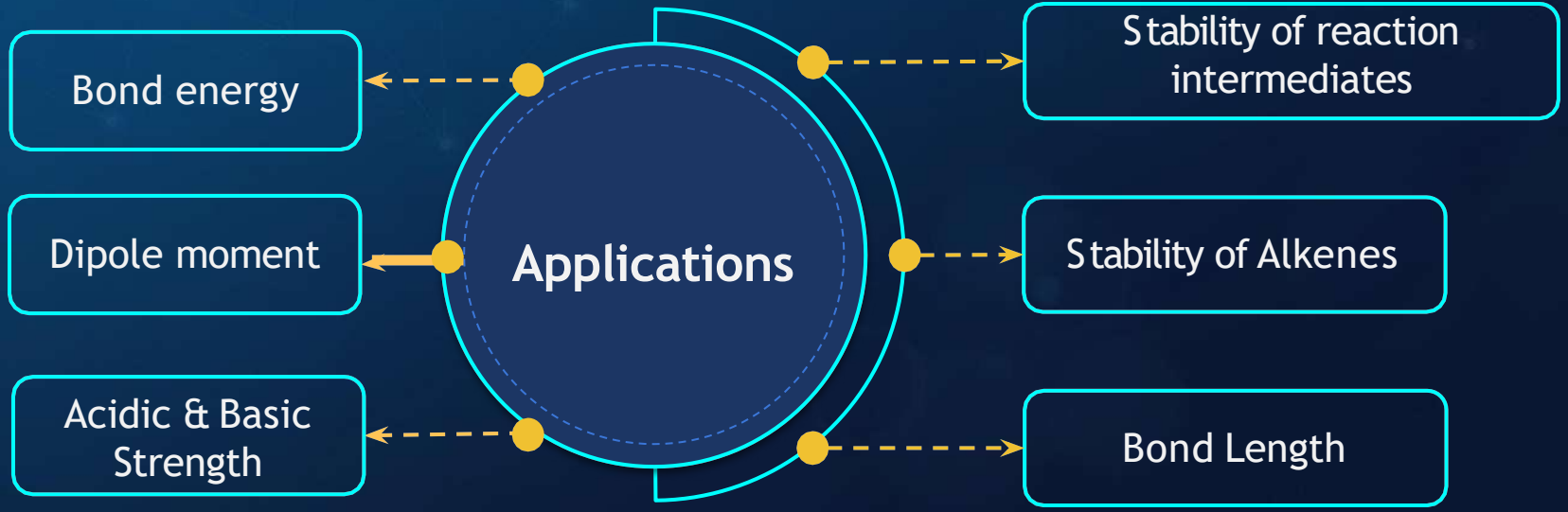
Additional weak bond formed by two sp^2 orbitals (in plane of ring)

Strained, but conjugation is maintained.

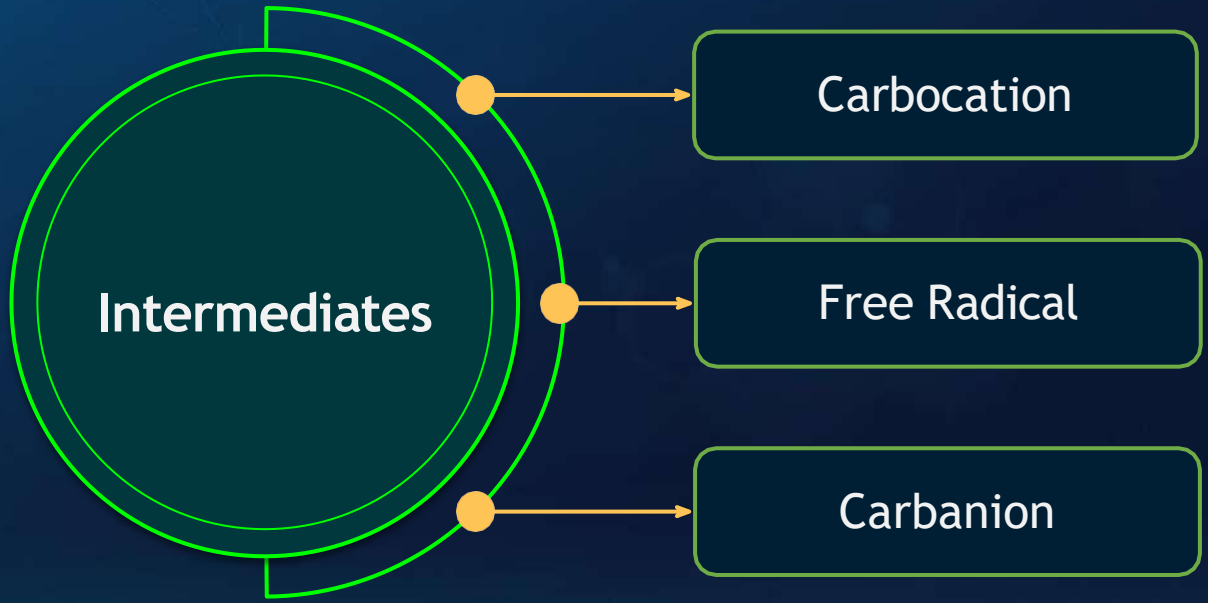
Aromatic

Azulenes are **fused non-benzenoid aromatic** compounds.

Applications of Electronic Effects



Stability of Reaction Intermediates



Carbocation

A carbon intermediate which contains **three bond pairs** & **a positive charge on it**.

Carbocation may be sp^2 or sp hybridized.

Carbocation (CH_3^+)

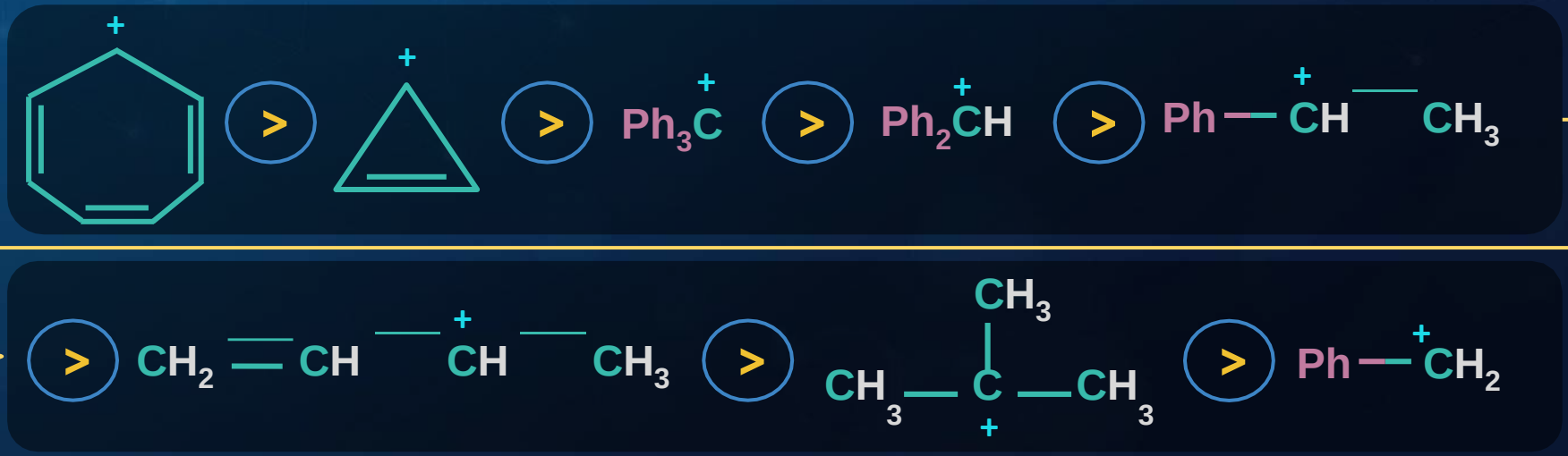
1. **6 electrons** in the outermost shell
2. All electrons are paired, hence it is **Diamagnetic.**
3. Lewis acid

Aromatic carbocations are highly stable.

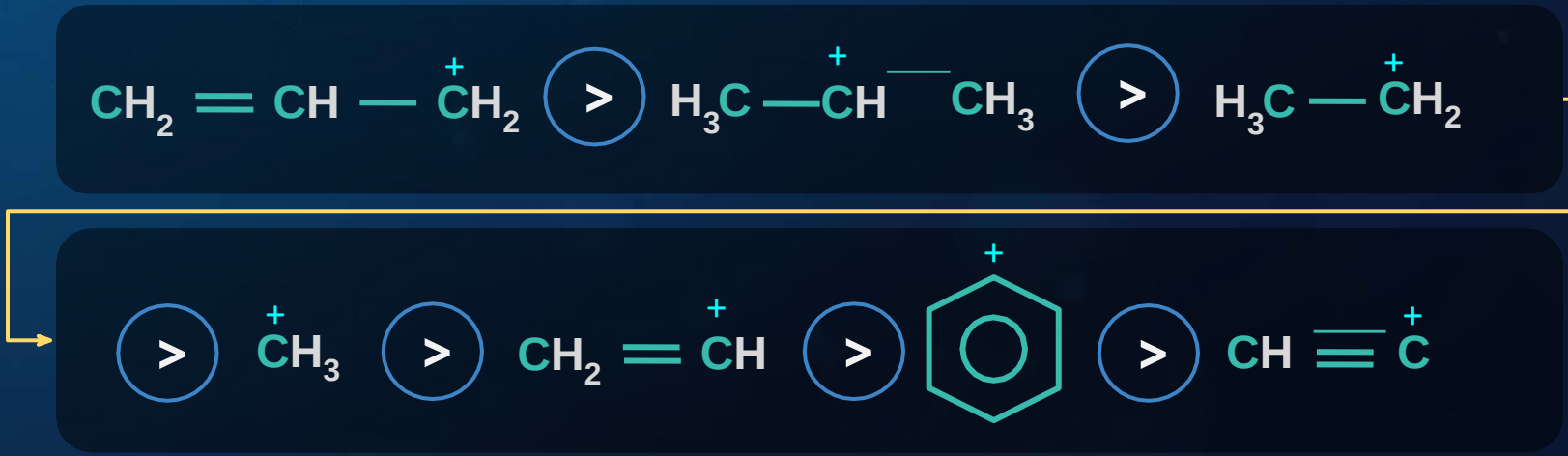
Stability of Carbocation

1. Mesomeric effect (+M)
2. Delocalisation of charge (Resonance)
3. Hyperconjugation (+H)
4. Inductive effect (+I)

Stability Order



Stability Order



Bredt's rule

Bicyclic molecules **cannot have bridge head C as sp^2 hybridized.**

Double bonds or carbocations at the bridge head of bridged bicyclic compounds are **highly unstable in small ring systems.**

Stability of Alicyclic Cations



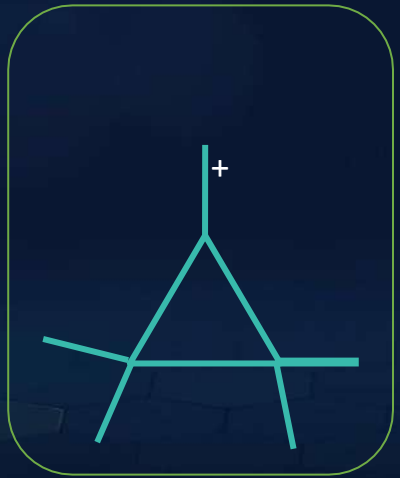
$$\text{Stability} \propto \frac{1}{\text{Strain}}$$

Point to Remember!!

Order of stability:



Special stability is a result of **conjugation** between the **bent orbitals** of the cyclopropyl ring and the **vacant p-orbital** of the cationic 'C'.



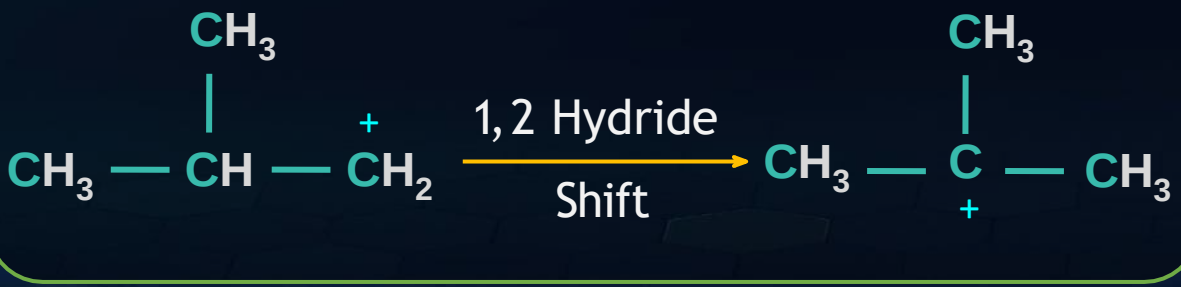
Rearrangement of Carbocations

Whenever a carbocation is formed in a reaction, **it may rearrange.**

Only those carbocations which can produce **more stable forms** will rearrange.

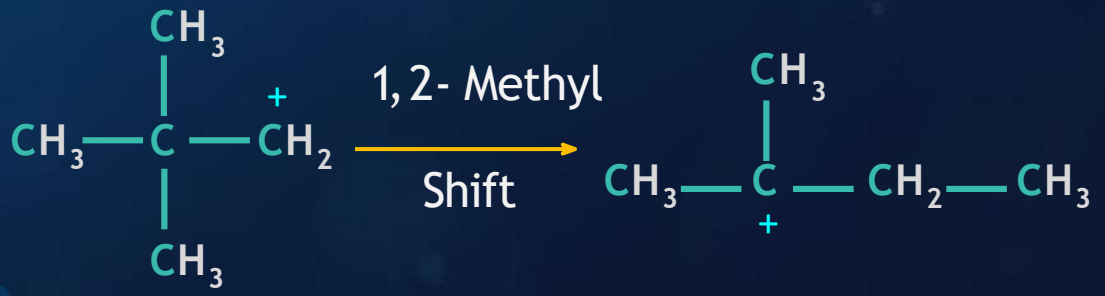
01

Shifting of H (1,2 shift)

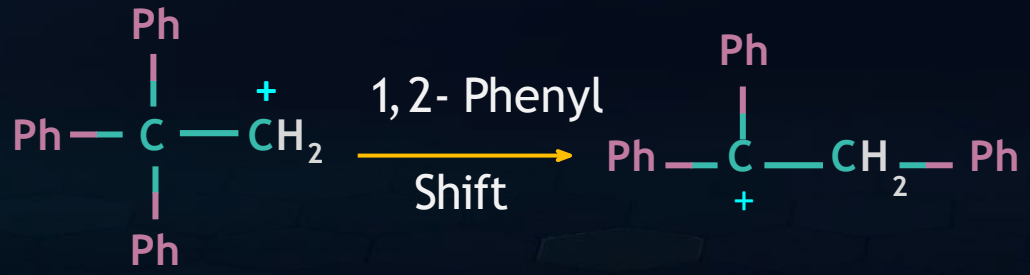


Rearrangement of Carbocations

02 Shifting of alkyl group (1,2 shift)



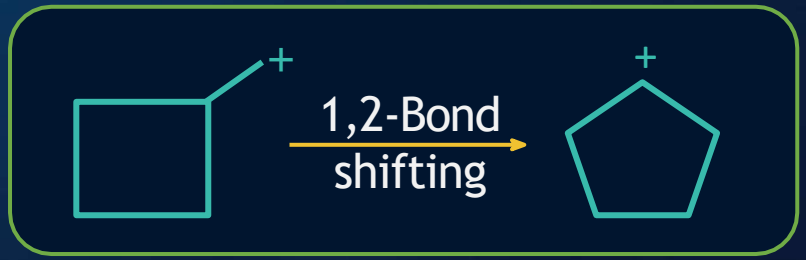
03 Shifting of aryl group (1,2 shift)

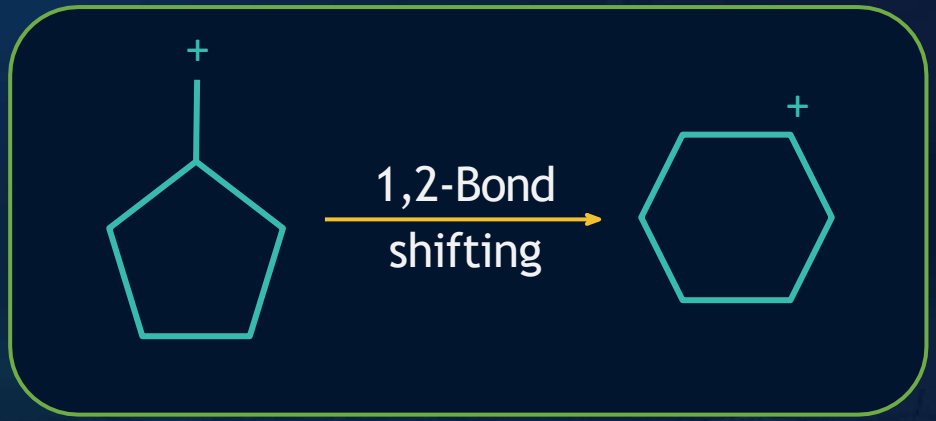


Rearrangement of Carbocations

04

Ring expansion

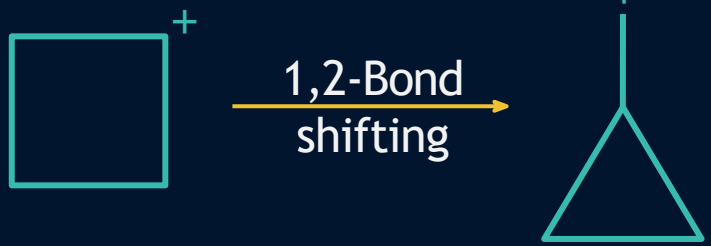




Rearrangement of Carbocations

05

Ring contraction



Point to Remember!!

Migrating Tendency

Generally,

Alkyl < Phenyl < Hydride

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

Free Radical ($\dot{C}H_3$)

An **uncharged** intermediate which has three bond pairs and **an unpaired electron** on carbon

Free radical can be **sp^2 or sp^3** hybridized.

1 **Odd electron species**

2 **7 electrons** in the outermost shell

3 Highly reactive

4 **Paramagnetic**

Stability of Free Radical

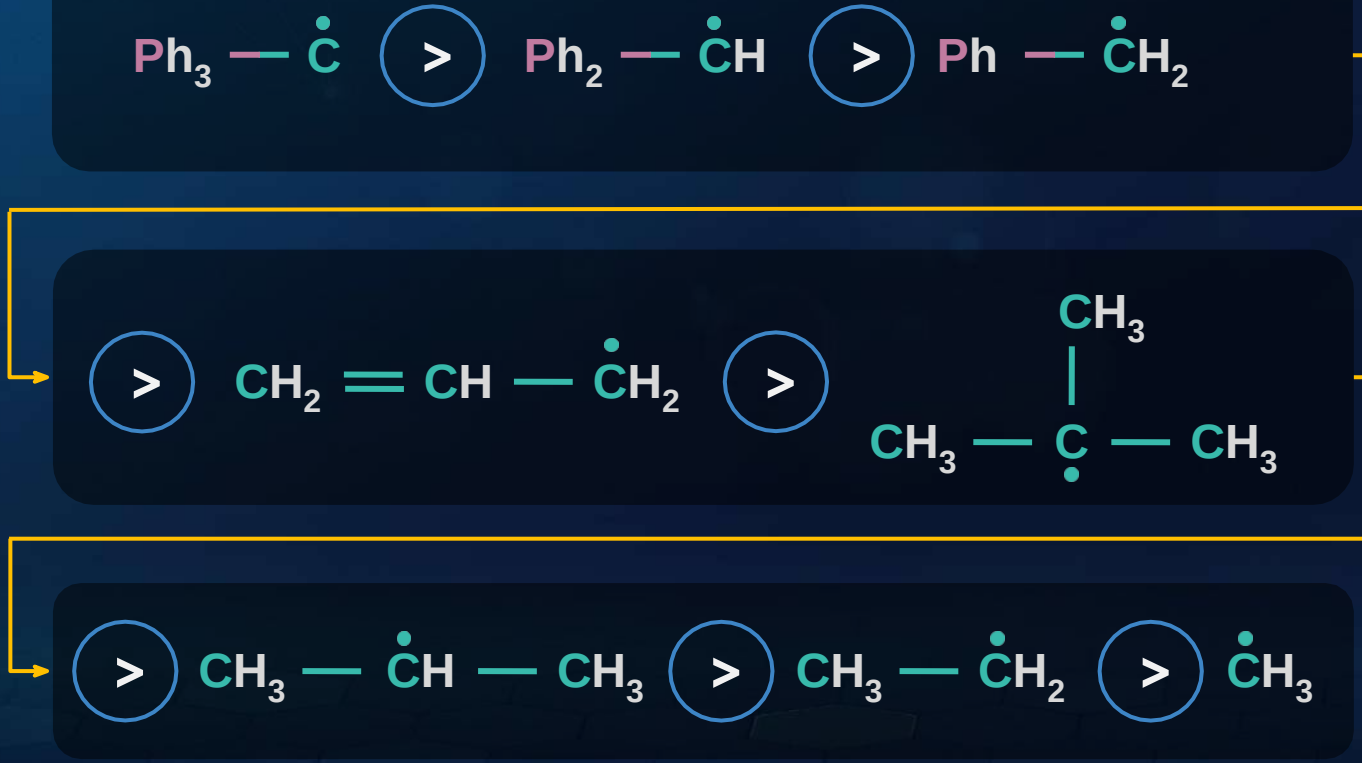
Free radicals are **electron deficient** species which are stabilized by **electron releasing groups.**

1) Delocalisation

2) Hyperconjugation

3) Inductive effect (+I)

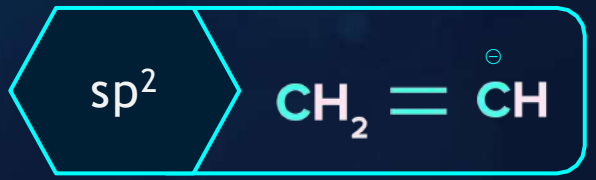
Stability order



Carbanions

A carbon intermediate which contains **three bond pairs** and a **negative charge** on it







Carbanions ($\ddot{C}H_3$)

1. **8 electrons** in the outermost shell
2. **Diamagnetic**
3. Lewis base

Stability of Carbanion

Mesomeric effect (-M)

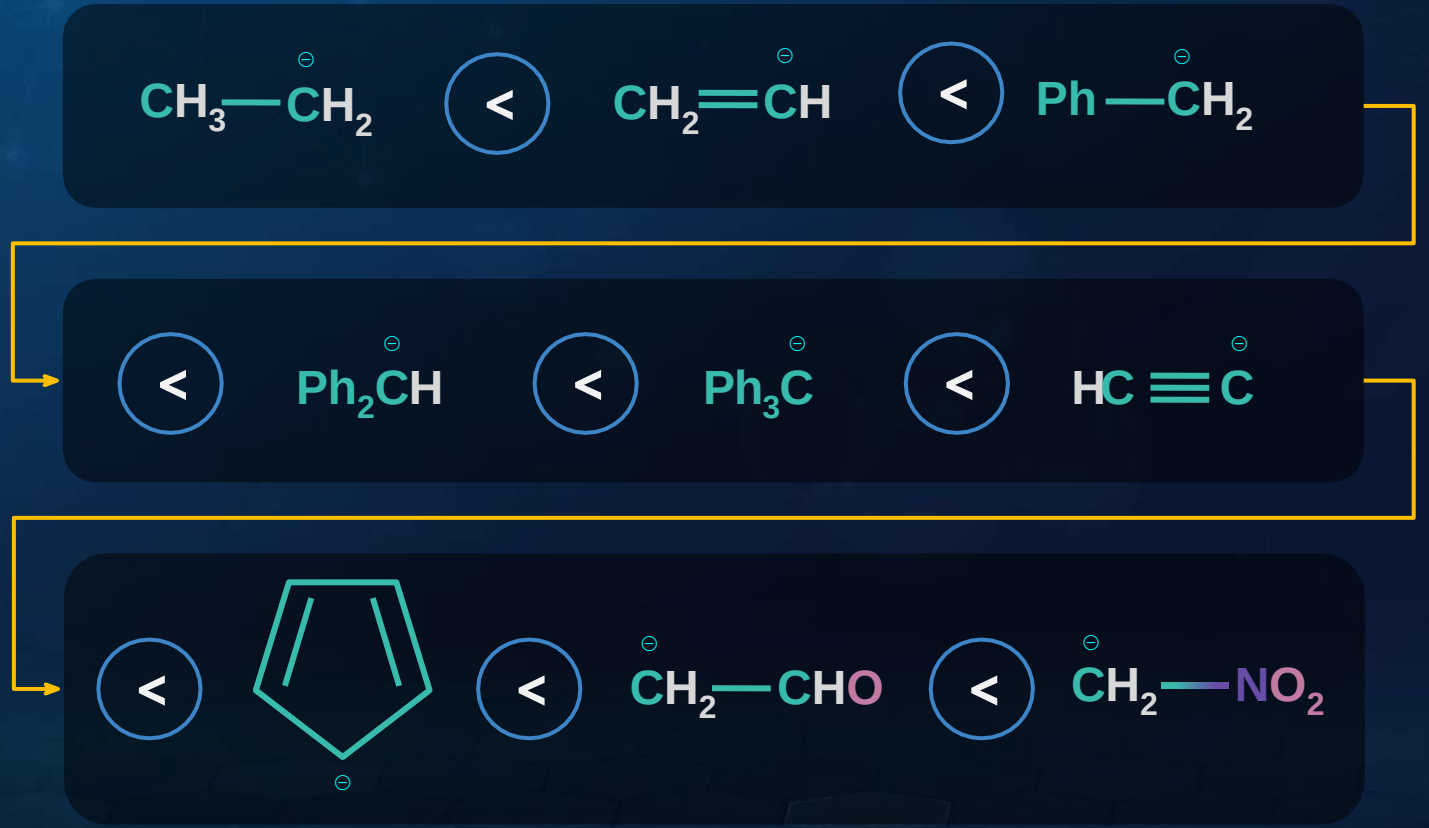
Delocalisation

Aromatic carbanion

Inductive effect (-I)

E.N. of the atom

Stability order



Comparison

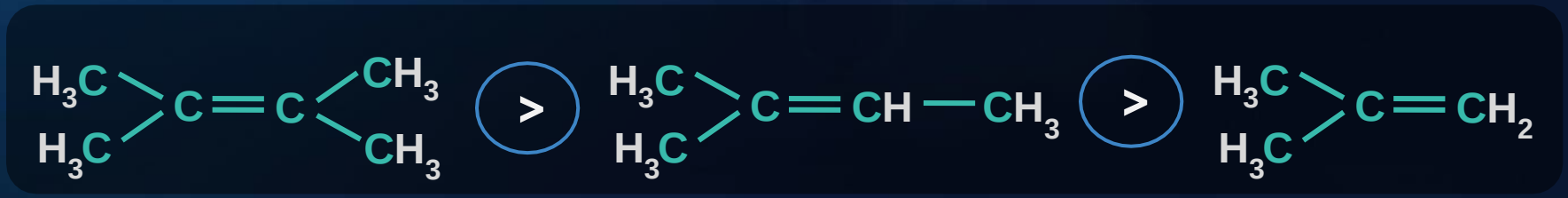
	Carbon free radical	Carbocation	Carbanion
Shape	Trigonal planar	Trigonal planar	Pyramidal
Hybridization	sp^2	sp^2, sp	sp^3, sp^2, sp
Number of e^- in the outermost shell	7	6	8

Stability of Alkenes

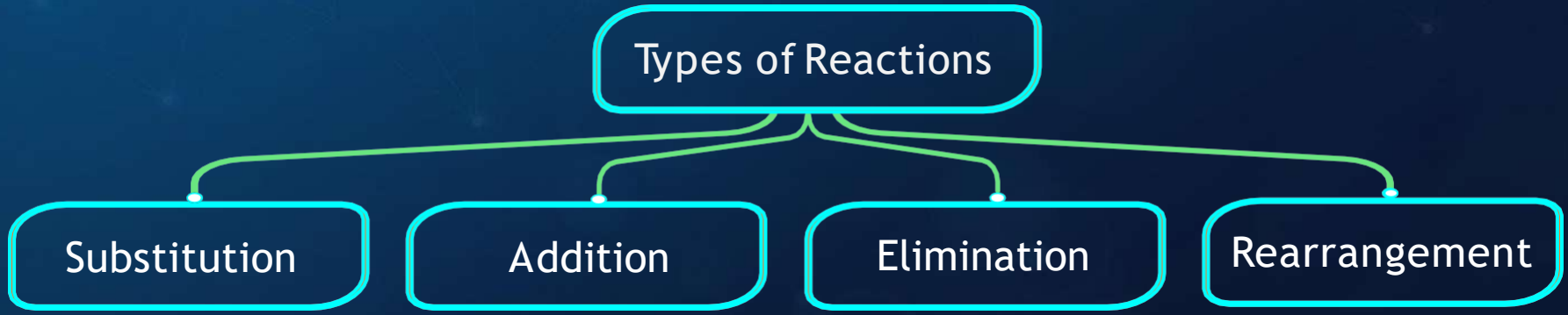
Stability of alkenes

∝ Delocalisation of π electrons

∝ Number of α-H






Types of Reactions
Substitution
Addition
Elimination
Rearrangement

Substitution Reaction



$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3{-}Cl + HCl$$

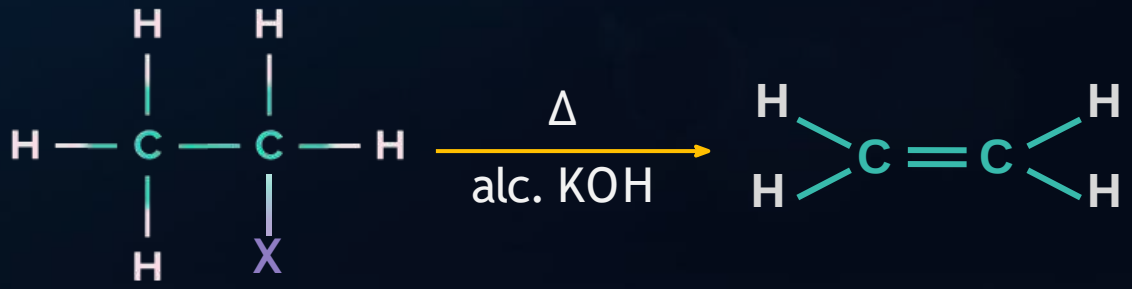
Addition Reaction



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

Elimination Reaction

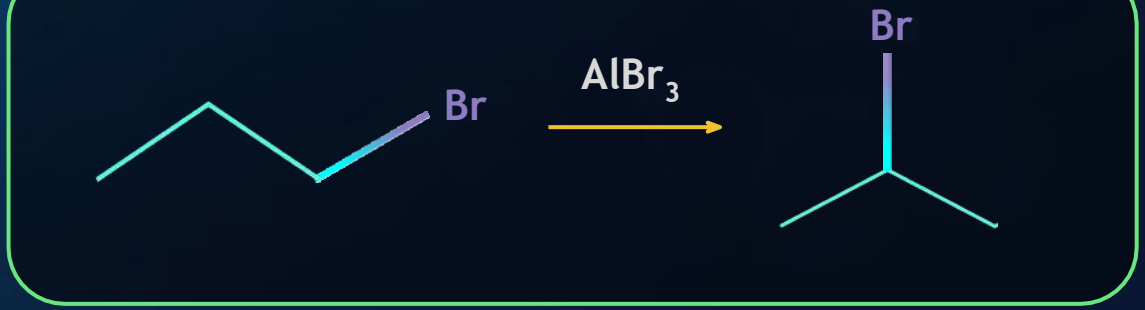




X = Cl, Br, I

Rearrangement Reaction





Purification

Purification

Removal of **undesirable impurities** associated with a particular organic compound i.e., to obtain the organic compound in **pure state.**

Crystallisation

Based on the principle of **solubility of compounds** (solutes), solutes tend to be more soluble in **hot liquids** (solvent) than in **cold liquids.**

If a **saturated hot solution** is allowed to **cool**, the solute is no longer soluble in the solvent and it **forms crystals** of the pure compound. The solid is filtered and dried.

Crystallisation

Examples

- **Sugar** mixed with **common salt** can be purified using ethanol.
- **Phthalic acid** mixed with **naphthalene** can be purified using hot water.

Sublimation

Certain organic substances **convert directly** from solid to vapour state on heating and vice-versa on cooling.

Solid $\underset{\text{Cool}}{\overset{\text{Heat}}{\rightleftharpoons}}$ **Vapours**

Sublimation

This process is very **useful** in the **separation** of a substance which sublimes on heating from a **non-volatile substance.**

Ex: Benzoic acid, naphthalene, anthracene, camphor, indigo, anthraquinone

Distillation

Used to **purify liquids** based on their **difference** in **boiling points.**

Vapour Pressure and Boiling Point

Vapour Pressure

Pressure exerted by the **vapours** over the **liquid** surface at **equilibrium**

Boiling point

Temperature at which the vapour pressure of a liquid is **equal** to the external pressure

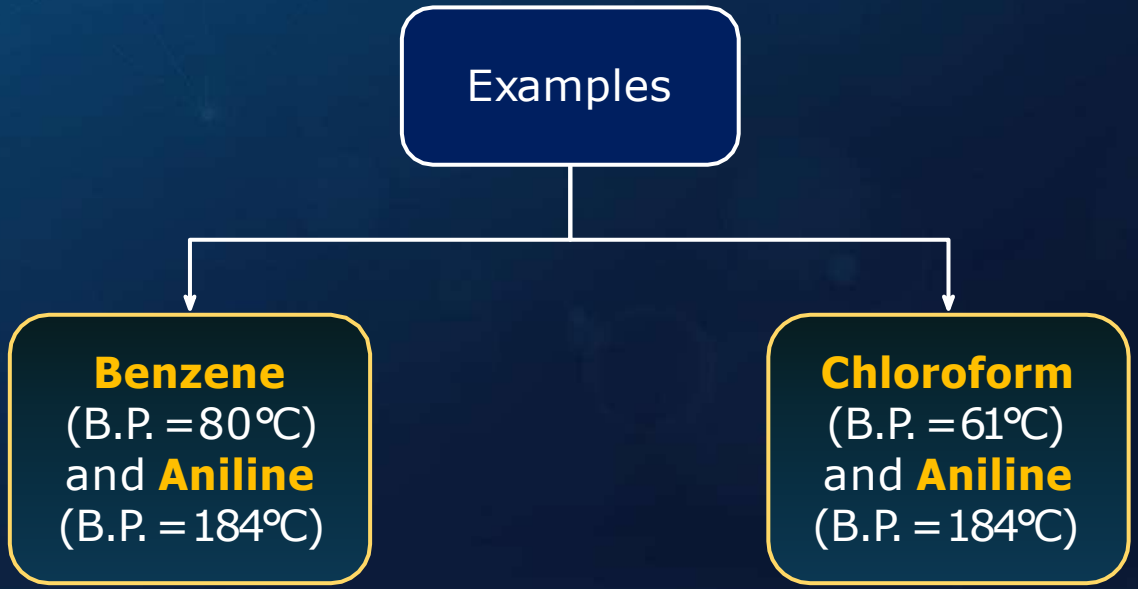

Types of Distillation
Simple
Fractional
Vacuum
Steam

Simple Distillation

It is applied only for **volatile liquids** which boil without decomposing at atmospheric pressure and contains **non-volatile impurities.**

It can also be used for **separating** liquids having sufficient difference in their **boiling points.**

Simple Distillation



Fractional Distillation

If the **boiling points** of the liquids to be separated are closer to each other, then **fractional distillation** is carried out using the **fractionating column.**

Fractional Distillation

Examples

- **Distillation** of petroleum, coal tar, and crude oil
- **Methanol** (B.P. = 65℃) and **Propanone** (B.P. = 57℃)
- **Benzene** (B.P. = 80℃) and **Toluene** (B.P. = 110℃)

Vacuum Distillation

Distillation under **reduced pressure**

Compounds which decompose at a temperature **below** their normal boiling point **cannot** be **distilled** at atmospheric pressure.

On reducing the **external pressure,** the liquid will **boil** at lower temperature.

Vacuum Distillation

Examples

Glycerine can be distilled at **180°C** (B.P. = 280°C) at lower pressure

Separation of glycerol from **spent-lye** in soap industries.

Steam Distillation

The liquid **boils** when the sum of vapour pressures due to the **organic liquid** (P_1) and that due to **water** (P_2) becomes **equal** to the **atmospheric pressure.**

Ex: 0-, m-, p-Chlorotoluenes,
o-, p-Nitrobenzene

Differential Extraction

The process of **separation** of an organic compound from its **aqueous solution** by shaking it with a suitable **organic solvent.**

Differential Extraction

The solvent should be **immiscible** with water and the organic compound to be **separated** should be **highly soluble** in it.

Ex: Benzoic acid can be extracted from water solution using benzene.

Chromatography

Used for the separation, isolation, purification, and identification of components of mixtures because of the distribution of components between a **liquid phase** (**mobile phase**) and a **solid phase** (**stationary phase**).

Chromatography

Separation of components of a mixture takes place as a result of **differential adsorption** on the **adsorption column.**

After the separation, the substances are extracted from the adsorbent using a suitable solvent, which is called **eluent.**

Adsorption and Adsorbent

Adsorption

Phenomenon of attracting and retaining the molecules of a substance **on the surface** of a liquid or a solid **resulting in a higher concentration** of the molecules on the surface

Adsorbent

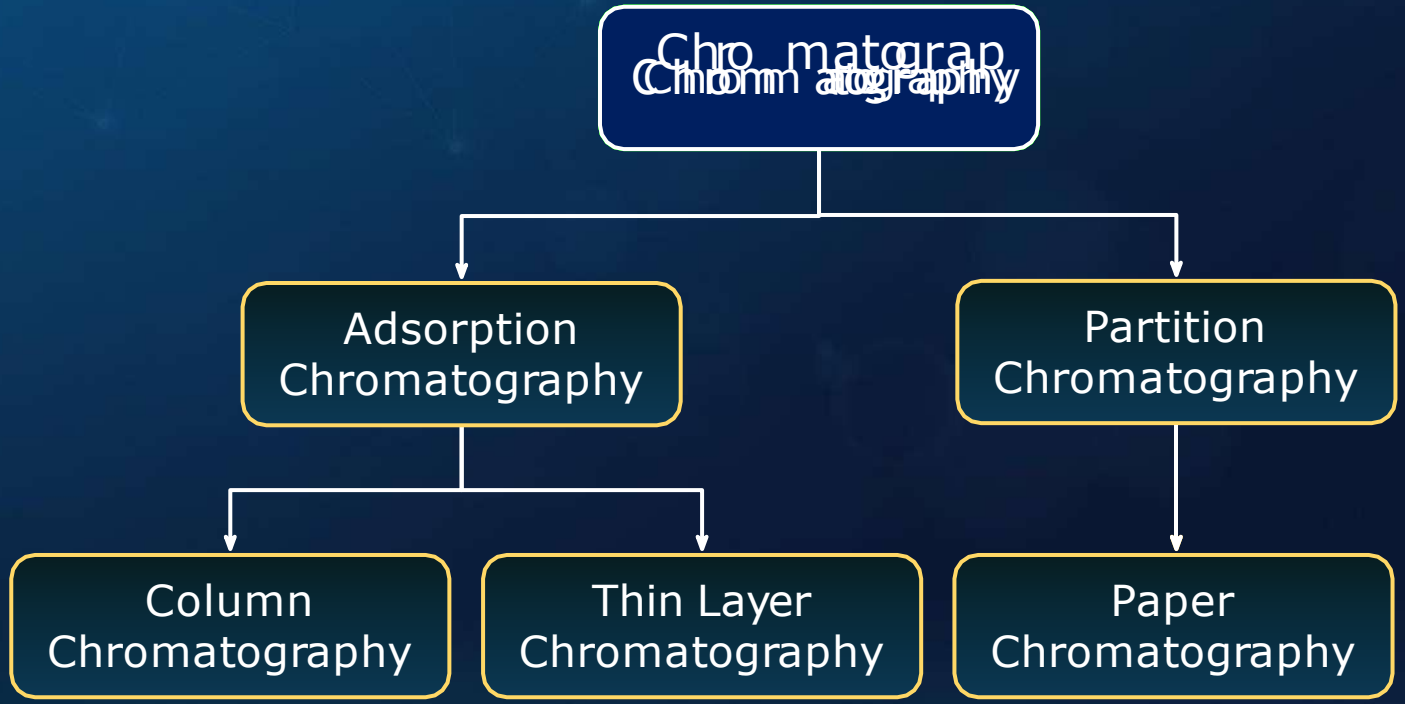
Substance on the surface of which adsorption occurs

Principle

Based upon the **differential adsorption** of various components of a mixture on a **suitable adsorbent**

Some components are more strongly adsorbed thus, travel at **different rates** and **get separated**

Types of Chromatography



Column Chromatography

Mixture is placed on the **top of the adsorbent column** packed in a glass tube.

↓

An appropriate **eluant,** which is a liquid or a mixture of liquids is allowed to flow **down the column** slowly.

↓

Separation of components takes place.

Thin Layer Chromatography (TLC)

Involves the separation of components of a mixture over a **thin layer of an adsorbent** coated on a glass plate.

A thin layer of an adsorbent (silica gel or alumina) is spread over the glass plate.

The glass plate is known as **thin layer chromatography plate** or **chromaplate.**

Thin Layer Chromatography (TLC)

Relative adsorption of each component of the mixture is expressed in terms of its **retardation factor** i.e. **R_f value**

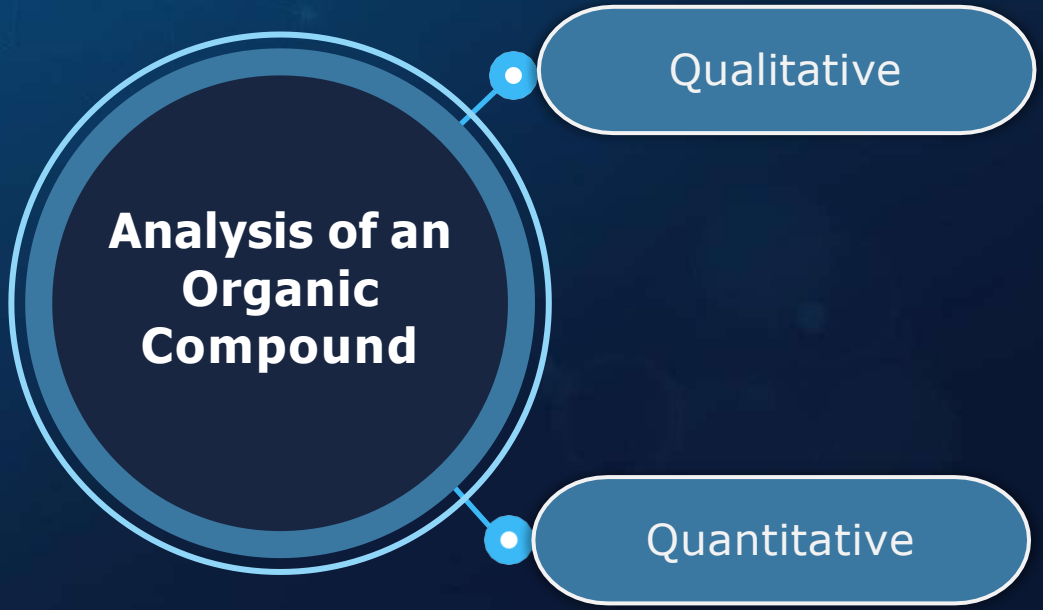
$$R_f = \frac{\text{Distance moved by the component from baseline}}{\text{Distance moved by the solvent from baseline}}$$

Partition Chromatography

It is based on the **continuous differential partitioning** of components of a mixture between the stationary and the mobile phases.

Paper Chromatography

Principle of paper chromatography is partition chromatography, wherein, the substances are distributed or **partitioned between the liquid phase** and the **stationary phase**.


Analysis of an Organic Compound
Qualitative
Quantitative

Qualitative Analysis

Identification of the elements present in an organic compound.

Detection of Elements

- Carbon and Hydrogen
- Nitrogen
- Sulphur
- Halogens
- Phosphorous

Detection of Carbon

Carbon is detected by **heating** the compound with **copper(II) oxide.**

Carbon present in the compound is **oxidised** to carbon dioxide.

Carbon dioxide is tested with **lime-water**, which develops **turbidity.**

$$C + 2CuO \xrightarrow{\Delta} CO_2 + 2Cu$$

$$CO_2 + Ca(OH)_2 \xrightarrow{\text{Lime water}} CaCO_3 \downarrow + H_2O$$

Precipitate
Milky/Turbid

Detection of Hydrogen

Hydrogen is detected by **heating** the compound with **copper(II) oxide.**

$$2H + CuO \xrightarrow{\Delta} H_2O + Cu$$

Hydrogen present in the compound is **oxidised** to water.

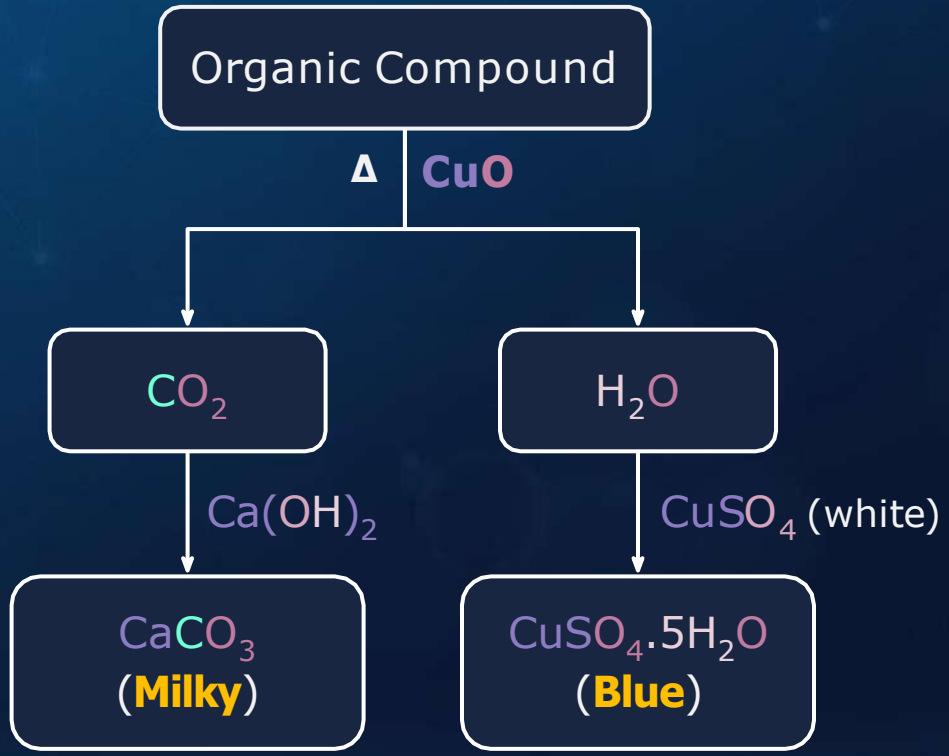
$$CuSO_4 + 5H_2O \longrightarrow CuSO_4.5H_2O$$

(Anhydrous)

Water is tested with **anhydrous copper sulphate,** which turns **blue.**

White

Blue


Organic Compound
Δ
CuO
CO_2
H_2O
$Ca(OH)_2$
$CuSO_4$ (white)
$CaCO_3$
(Milky)
$CuSO_4.5H_2O$
(Blue)

Sodium Fusion Extract

Elements present in the compound are converted from their **covalent form** to their **ionic form** by fusing the organic compound with sodium metal.

Organic compounds are reacted with **sodium** to convert them into their **ionic form,** which is **more reactive.**

$$Na + C + N \xrightarrow{\Delta} NaCN$$

$$2Na + S \xrightarrow{\Delta} Na_2S$$

$$Na + X \xrightarrow{\Delta} NaX$$

$$Na + C + N + S \xrightarrow{\Delta} NaSCN$$

Lassaigne's Test

Cyanide, sulphide, and halide of sodium so formed on sodium fusion are extracted from the fused mass by boiling it with distilled water. This extract is known as **Sodium Fusion Extract.**

Detection of Nitrogen

01 **Sodium Fusion Extract** is boiled with **Iron(II) sulphate** to form **Sodium hexacyanoferrate (II).**

$$FeSO_4 + 6NaCN \xrightarrow{\Delta} Na_4[Fe(CN)_6] + Na_2SO_4$$

Sodium hexacyanoferrate (II)

02 On heating with **sulphuric acid**, some **Fe^{2+} ions** are oxidised to **Fe^{3+} ions.**

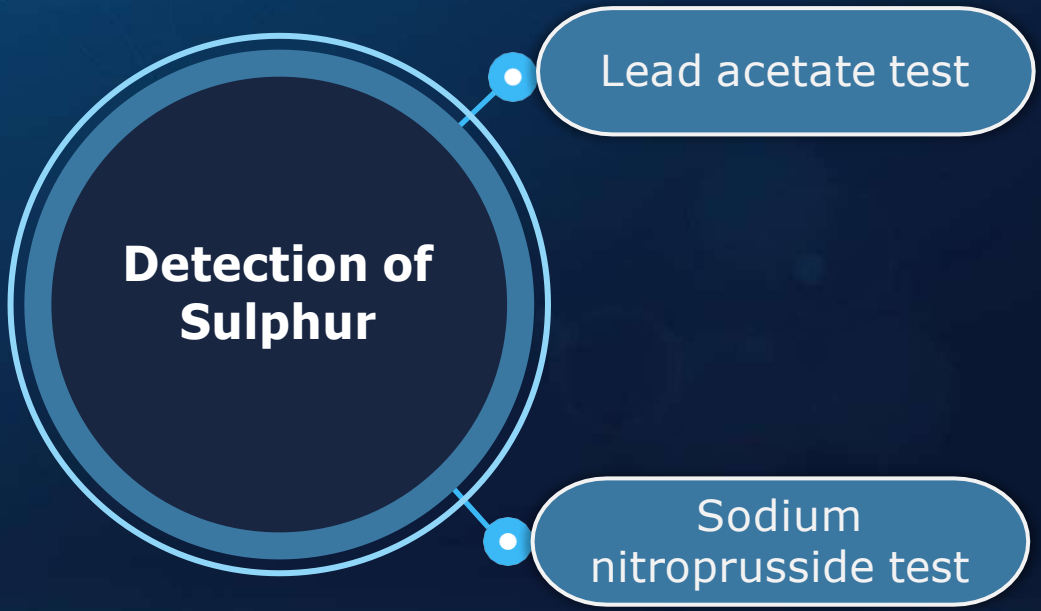
Detection of Nitrogen

03

Fe^{3+} reacts with **Sodium hexacyanoferrate (II)** to give **Prussian blue** colour of **Ferric ferrocyanide,** which confirms the presence of nitrogen.

$$3[Fe(CN_6)]^{4-} + 4Fe^{3+} \xrightarrow{xH_2O} \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3.xH_2O}$$

Test For Sulphur



Lead Acetate Test

Sodium Fusion Extract
is acidified with **acetic acid**
and **lead acetate** is added to it.

$$Na_2S + (CH_3COO)_2Pb \longrightarrow PbS + 2CH_3COONa$$

Black precipitate

Indicates
presence of S

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Sodium Nitroprusside Test

Sodium Fusion Extract is treated with **sodium nitroprusside**.



Violet

Indicates presence of S

Point to Remember!!

If **both nitrogen** and **sulphur** are present in an organic compound, then **sodium thiocyanate** is formed, which gives **blood red color** with neutral $FeCl_3$.



$$Na + C + N + S \longrightarrow NaSCN$$

$$\text{Neutral } FeCl_3 + NaSCN \longrightarrow Fe(SCN)_3$$

Blood red

Test for Halogens

Cyanide or sulphide of sodium formed during **Lassaigne's test** can **interfere with silver nitrate test** for halogens.

Sodium fusion extract is first **boiled** with concentrated **nitric acid** to **decompose** them.

Test for Halogens

$NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$

White ppt

AgCl is soluble in NH_4OH

$NaBr + AgNO_3 \longrightarrow AgBr + NaNO_3$

Pale yellow ppt

AgBr is sparingly soluble in NH_4OH

$NaI + AgNO_3 \longrightarrow AgI + NaNO_3$

Yellow ppt

AgI is insoluble in NH_4OH

Test for Phosphorous

Compound is heated with an oxidising agent **(sodium peroxide).** Phosphorus present in it gets oxidised to phosphate.

The solution is boiled with **nitric acid** and then treated with **ammonium molybdate.**

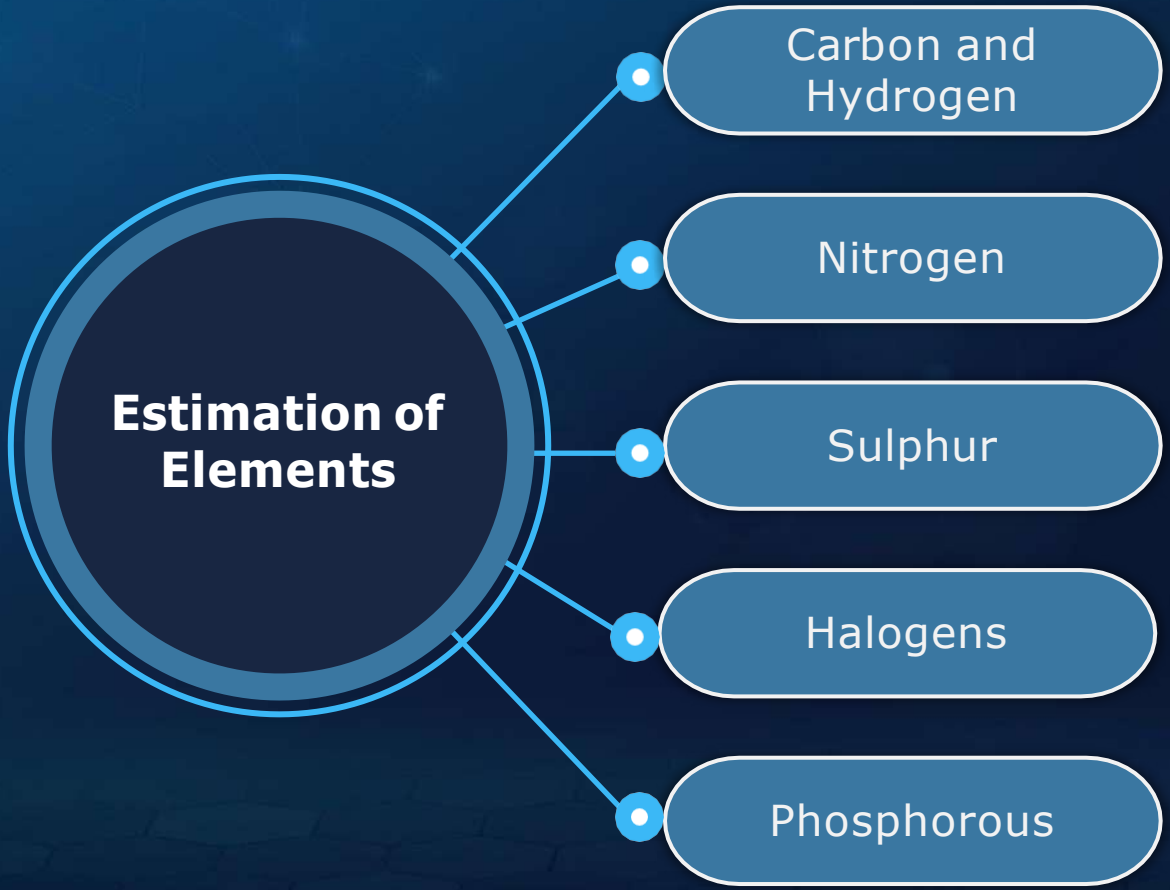
A **yellow** coloration or precipitate indicates the presence of phosphorus.

Test for Phosphorous

$$Na_3PO_4 + 3\,HNO_3 \longrightarrow H_3PO_4 + 3\,NaNO_3$$

$$H_3PO_4 + 12\,(NH_4)_2MoO_4 + 21\,HNO_3 \longrightarrow \underset{\text{yellow}}{(NH_4)_3PO_4.12MoO_3} + 21\,NH_4NO_3 + 12\,H_2O$$

Quantitative Analysis


Estimation of Elements
Carbon and Hydrogen
Nitrogen
Sulphur
Halogens
Phosphorous

Estimation of Carbon and Hydrogen

A known mass of the organic compound is heated with **dry copper oxide** in an atmosphere of air or oxygen free from moisture and carbon dioxide.

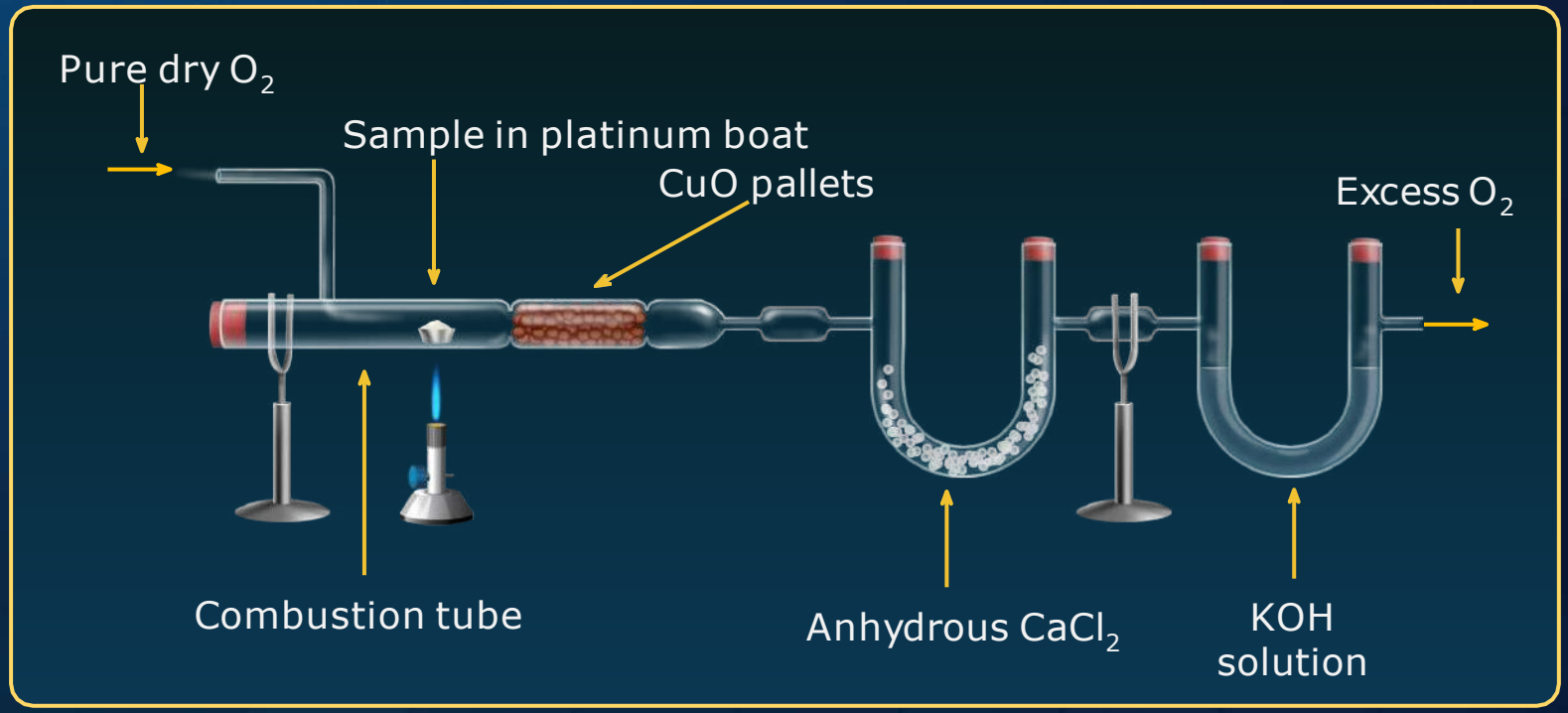
$$C + 2CuO \longrightarrow CO_2 + 2Cu$$

$$2H + CuO \longrightarrow H_2O + Cu$$

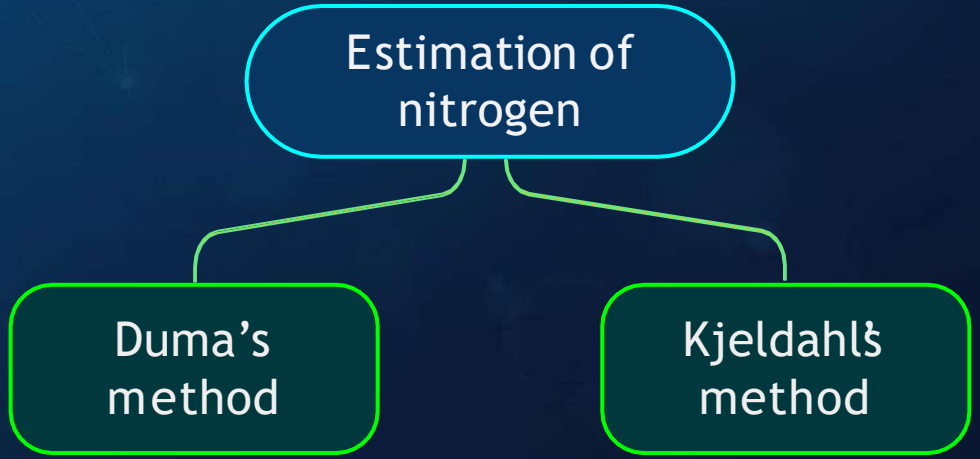
Estimation of Carbon and Hydrogen

CO_2 produced is collected in **potash bulb** (containing KOH), whereas **H_2O** is absorbed in **calcium chloride tube** (containing $CaCI_2$).

Estimation of Carbon and Hydrogen



Estimation of Nitrogen



Duma's Method

A known mass of the organic compound is **heated strongly** with excess of **copper oxide** in an atmosphere of carbon dioxide.

The **carbon and hydrogen** are converted to **CO_2 and H_2O**.

Nitrogen is set free as **N_2**.

Duma's Method

$$C + 2H + 3CuO \longrightarrow CO_2 + H_2O + 3Cu$$

Organic compound

$$2N + Cu \longrightarrow N_2 + \text{Oxides of nitrogen}$$

Organic compound

$$\text{Oxides of nitrogen} + Cu \longrightarrow N_2 + CuO$$

Duma's Method

N_2 is collected over the concentrated solution of KOH and its volume is measured at room temperature and atmospheric pressure.

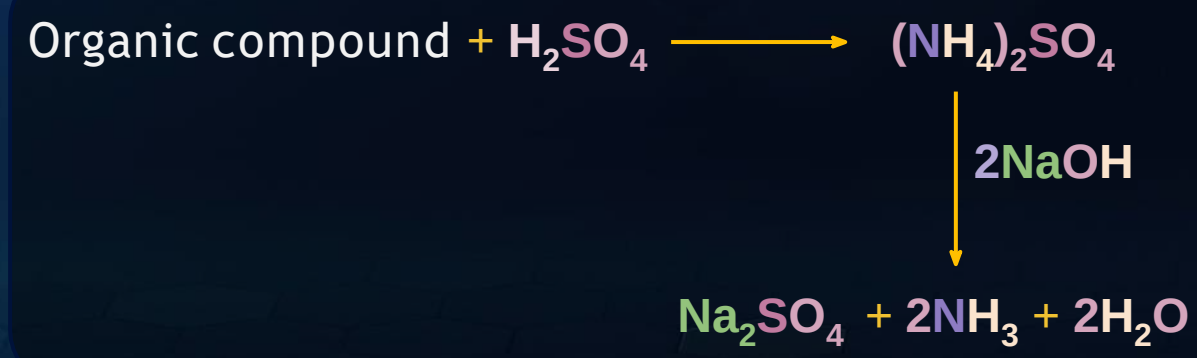
Kjeldahl's Method

A known mass of the organic compound containing **nitrogen** is heated with **concentrated sulphuric acid**. Nitrogen in the compound gets converted into **ammonium sulphate.**

Organic compound + conc. H_2SO_4 $\longrightarrow$ $(NH_4)_2SO_4$

Kjeldahl's Method

The resulting acid mixture is then heated with an excess of **sodium hydroxide.**



Kjeldahl's Method

The amount of **ammonia** produced is determined by estimating the amount of **sulphuric acid** consumed in the reaction.

The **acid left unused** is estimated by **titration** with some standard alkali.

Limitations of Kjeldahl's Method

This method is not applicable to compounds containing nitrogen in:

- **Nitro groups** ($-NO_2$)
- **Azo groups** ($- N = N -$)
- **Nitrogen present in the ring** (E.g: Pyridine)

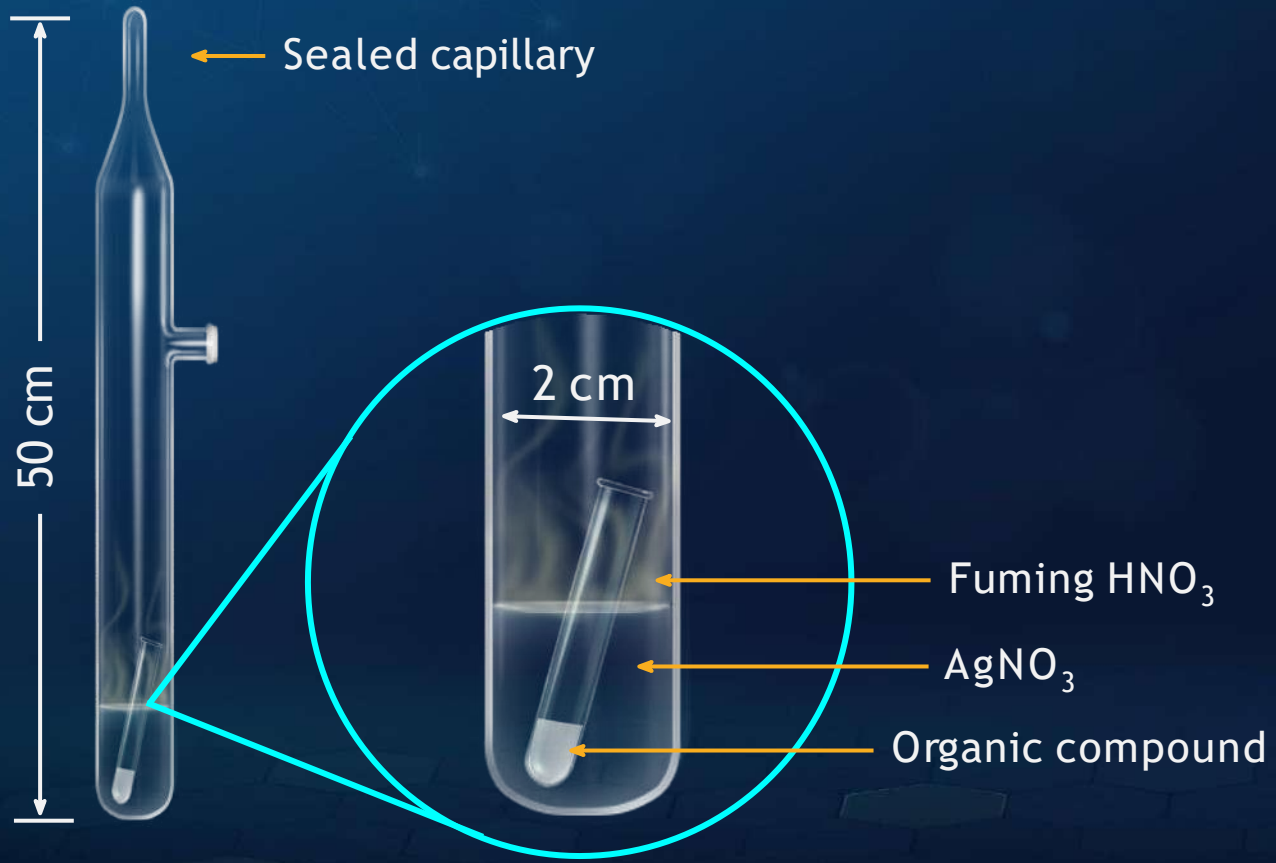
Estimation of Sulphur

Sulphur is estimated as **barium sulphate**.

The organic compound containing sulphur is taken in a **Carius tube containing HNO_3**, where sulphur is finally converted into **sulphuric acid**.

This sulphuric acid is passed through **excess $BaCl_2$** to get **$BaSO_4$**, which is then washed, dried & weighed.

Carius Method



Carius Method

Halogens are estimated as **silver halides**

Organic halide is treated with **acidified silver nitrate** solution to form **silver halide,** which is washed, dried & weighed.

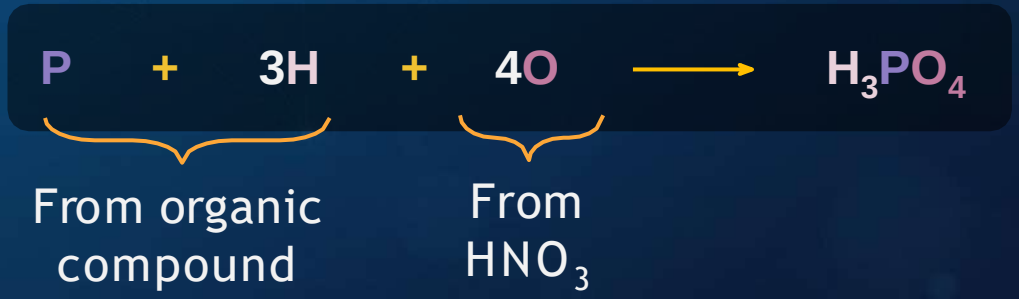
Estimation of Phosphorus

A known mass of the organic compound is **heated with fuming HNO_3**.

The phosphorus present in the organic compound is **oxidised to H_3PO_4**. The phosphoric acid thus formed is treated with **magnesia** mixture to get **$MgNH_4PO_4$** precipitate.

The precipitate is separated, dried and ignited to get **$Mg_2P_2O_7$**.

Estimation of Phosphorus



$$H_3PO_4 + \text{Magnesia mixture} \longrightarrow MgNH_4PO_4$$

$$2MgNH_4PO_4 \longrightarrow Mg_2P_2O_7 + 2NH_3 + H_2O$$

Estimation of Oxygen

The percentage of oxygen in an organic compound is usually found by **difference** between the **total percentage composition** (100) and **the sum of the percentages** of all other elements.