# 8.

# BASIC PRINCIPLES OF ORGANIC CHEMISTRY

## 1. INTRODUCTION

What is organic chemistry?

Organic chemistry is the study of most carbon compounds with the exception of a few (e.g., $CO_2$ and carbonate salts). While inorganic chemistry deals with the study of all other compounds.

## 2. PROPERTIES OF ORGANIC COMPOUNDS

In general, organic compounds.

**(a)** Are far more in number than inorganic compounds. This is due to the catenation property of the C atom. Carbon has the ability to form bonds with almost every other element (Other than the noble gases), forming long chains as well as ring compounds. Moreover, C compounds exist as many isomers.

**(b)** React more slowly and require higher temperatures for reactions to take place.

**(c)** Are less stable and sometimes decompose on heating to compounds of lower energy levels.

**(d)** Undergo more complex reactions and produce more side reaction products.

**(e)** Are largely insoluble in water.

**(f)** Have generally lower melting and boiling points.

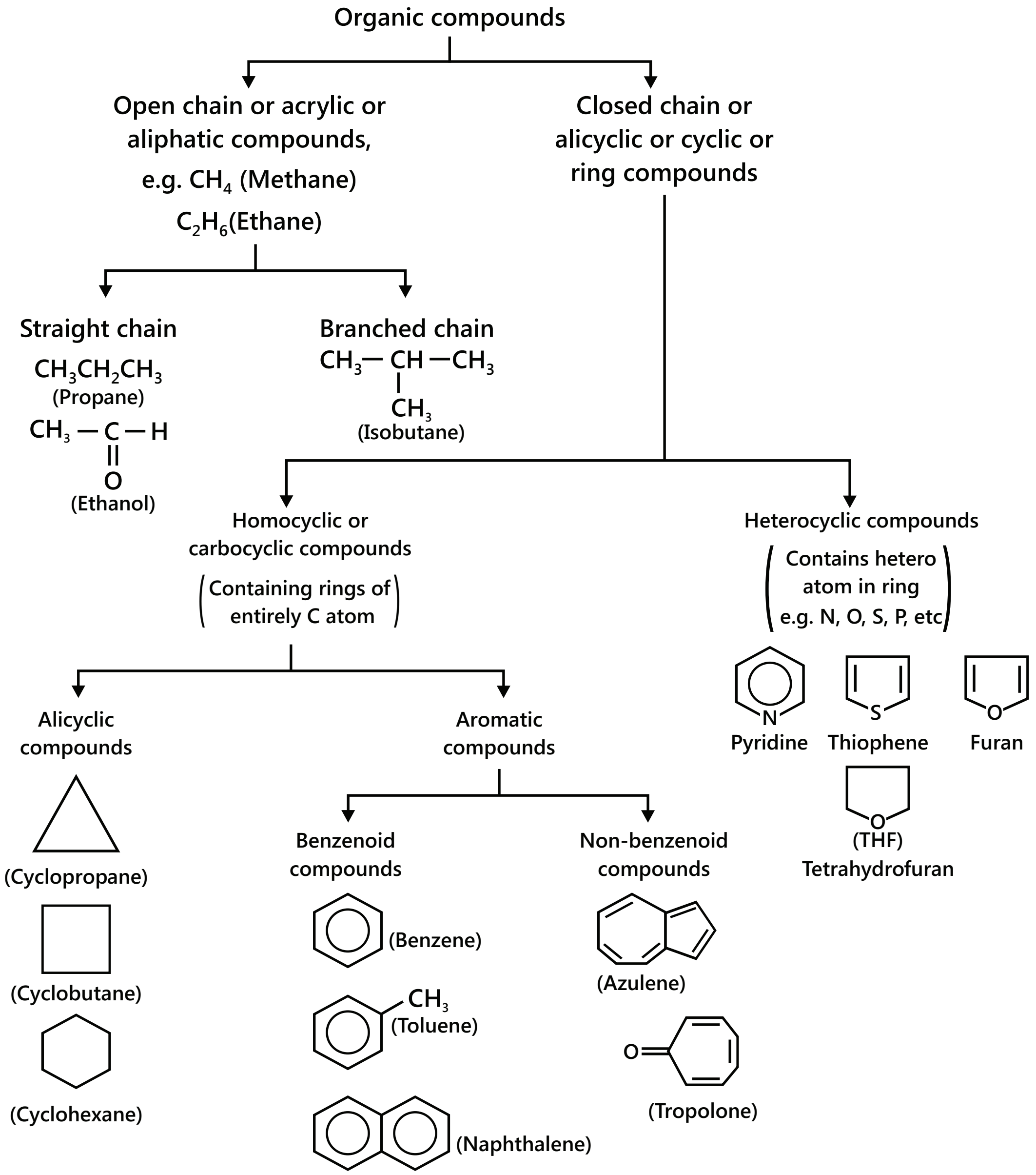
**(g)** Are classified into families of compounds such as carboxylic acids, which have similar reactive groups and chemical properties.

**(h)** Are mostly obtained from animals or plants as opposed to the mineral origin of inorganic compounds.

## 3. CLASSIFICATION OF ORGANIC COMPOUNDS

They are classified follows:

Classification of organic compounds is basically based on the functional group. The chemical properties of compound depends on the properties of the functional group present in it. The rest of the molecule simply affects the physical properties, e.g., m.p., b.p., density etc. and has very little effect on its chemical properties.



**Flowchart 8.1:** Classification of organic compound

**Homologous Series**

Organic compounds containing one particular characteristic group or functional group constitute a homologous series, e.g., alkanes, alkenes, haloalkanes, alkanols, alkanals, alkanones, alkanoic acids amines etc.

# 4. NOMENCLATURE OF ORGANIC COMPOUNDS

## 4.1 Trivial or Common Names

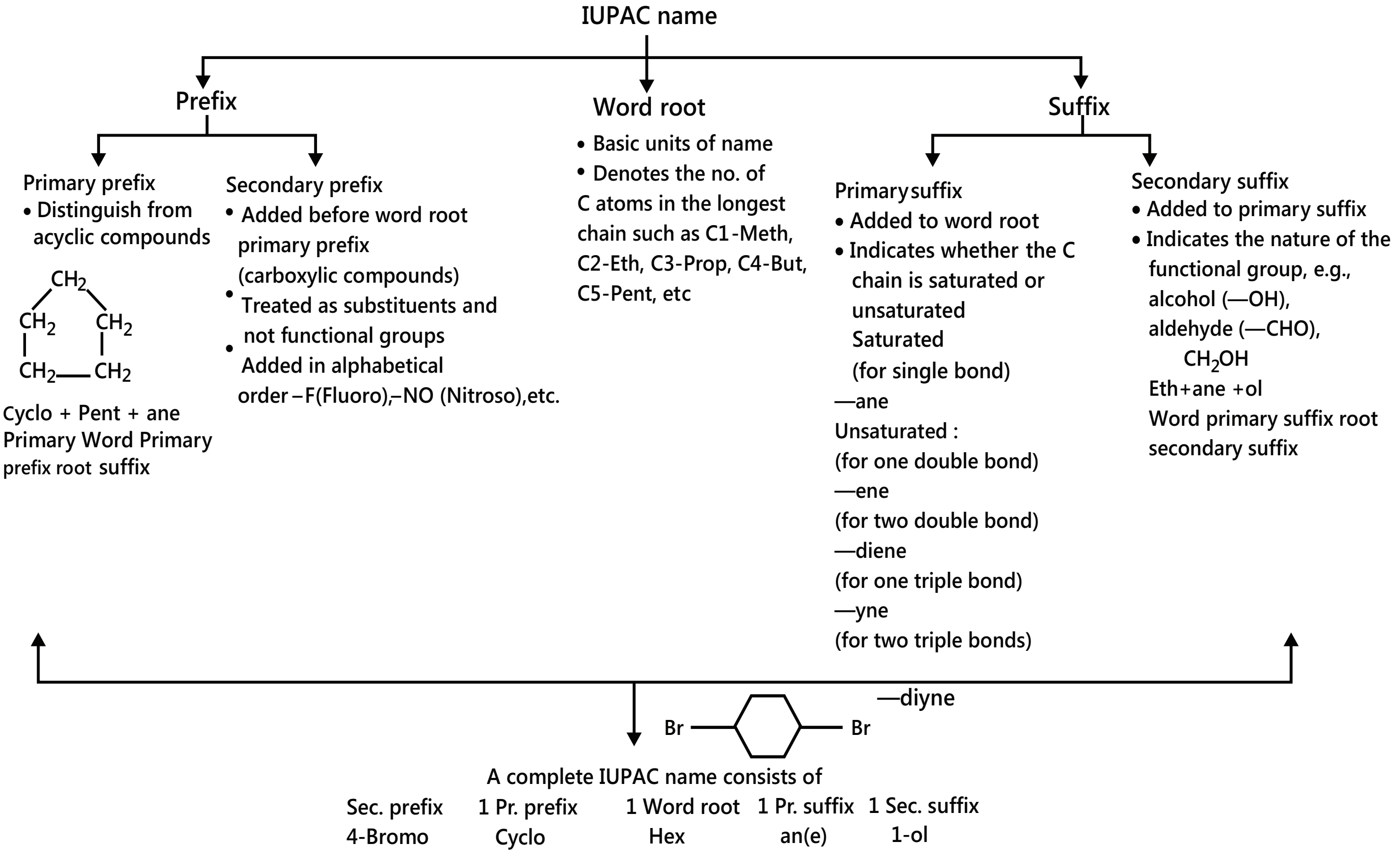
In the earlier days, because of the absence of IUPAC names, the names of the compounds were dependent on the source from which the compound was obtained. Even today, in spite of IUPAC nomenclature some of the common names are still at use. In some case, where the IUPAC name is very tedious we prefer to use common names, for example lactic acid, sucrose etc.

**Table 8.1:** Common names of organic compounds, their sources, and structures

| S.No | Common name | Source | Structure |
|---|---|---|---|
| 1. | Formic acid | Formica (red ant) | HCOOH |
| 2. | Acetic acid | Acetum (vinegar) | MeCOOH |
| 3. | Propionic acid | Portopion (first fat) | $MeCH_2COOH$ |
| 4. | Butyric acid | Butyrum (butter) | $MeCH_2CH_2COOH$ |
| 5. | Valeric acid | Valerian (shrub) | $Me(CH_2)_3COOH$ |
| 6. | Caproic acid | Caper (Goat) | $Me(CH_2)_4COOH$ |
| 7. | Urea | Urine | $NH_2CONH_2$ |
| 8. | Malic acid | Malum (apple) | $CH_2COOH$<br>\|<br>CH(OH)COOH |
| 9. | Methyl alcohol | Methu hule (Mehtu-wine, hule = wood) | MeOH |

## 4.2 IUPAC Names

The IUPAC nomenclature of organic compounds is a systematic method of naming organic compounds as recommended by the International Union of Pure and Applied Chemistry (IUPAC). This system uses substitutive nomenclature, which is based on the principal group, and principal chain. The IUPAC rules for the naming of alkanes from the basis of the substitutive nomenclature of most other compounds -



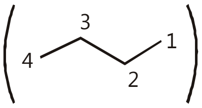
**Flowchart 8.2:** IUPAC nomenclature of organic compound

## 4.3 IUPAC and Common Names of Some Functional Groups and Classes of Organic Compounds

### 4.3.1 IUPAC Rules for Saturated Hydrocarbons

**1. Alkanes:** General formula: $C_nH_{2n+2}$ IUPAC group suffix: - ane

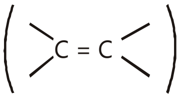
E.g. $(H_3\overset{4}{C}\overset{3}{C}H_2\,\overset{2}{C}H_2\overset{1}{C}H_3)$
or
$(Me(CH_2)_2Me)$



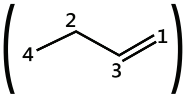
Butane (IUPAC name)

**2. Alkenes:** General Formula: $C_nH_{2n} \Rightarrow \left(\begin{array}{l}\text{suffix} = -\text{ene}\\ \text{Alkane}\dfrac{-\text{ane}}{+\text{ene}}\text{alkene}\end{array}\right)$

Functional group structure:



E.g. **i.** $(\overset{1}{C}H_2 = \overset{2}{C}H\overset{3}{C}H_2\overset{4}{C}H_3)$ **or**



**But-1-ene (IUPAC)**

**3. Alkyne:** General formula: $C_nH_{2n-2}$ $\left(\begin{array}{l}\text{suffix} = -\text{yne}\\ \text{Alkane}\xrightarrow[+\text{yne}]{-\text{ane}}\text{Alkyne}\end{array}\right)$

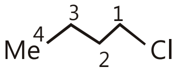
Functional group structure: $(-C \equiv C-)$

E.g. **i.** $\mathbf{HC \equiv CH}$ **or** $\mathbf{H - \equiv - H}$ Ethyne (IUPAC) Acetylene (Common name)

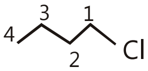
**4. Halides:** General formula: $C_nH_{2n+1}X$ (X = F, Cl, Br, I) (RX) suffix = Halo

Functional group structure – X

E.g. $\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2Cl$ or



or



(1-Chlorobutane)

**5. Alcohols:** General formula: $C_nH_{2n+1}OH$ (R – OH)

IUPAC suffix: – ol Common name = Alcohol IUPAC prefix: -Hydroxy.

$\text{Alkan}\textcircled{e}\xrightarrow[+\text{ol}]{-\text{e}}\text{Alkanol}$

Functional group structure: – OH

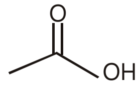
| Example | IUPAC name | Common name |
|---|---|---|
| i. $CH_3OH$ | Methanol | Methyl alcohol or Carbinol or Zerone |

**6. Carboxylic acids:** General formula: $C_nH_{2n+1}COOH$ (R – COOH)

IUPAC suffix: -oic acid  Common name = Acid  IUPAC perfix : - Carboxy

$$\text{Alkan}\textcircled{e} \xrightarrow[+\text{oic acid}]{-e} \text{Alkanol}$$

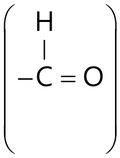
Functional group structure: (–COOH)

| **Example** | **IUPAC name** | **Common name** |
|---|---|---|
| HCOOH or  | Methanoic acid | Formic acid |

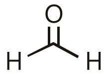
**7. Aldehydes:** General formula: $C_n2_{n+1}$ . CHO (R – CHO)

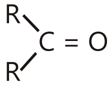
IUPAC suffix: - al  Common name = Aldehyde  IUPAC prefix: Formyl or oxo-

$$\text{Alkane} \xrightarrow[+\text{al}]{-e} \text{Alkanal}$$

Functional group structure: (–CHO) or 

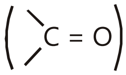
$$\left( \begin{array}{c} \text{H} \\ | \\ -\text{C} = \text{O} \end{array} \right)$$

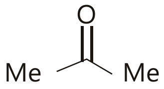
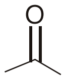
| **Example** | **IUPAC name** | **Common name** (derived from acid) |
|---|---|---|
| HCHO or  | Methanal | Formaldehyde |

**8. Ketones**: General formula: 

IUPAC suffix: - one  Common name; Ketone  IUPAC prefix; – oxo,

$$\text{Alkan}\textcircled{e} \xrightarrow[+\text{ one}]{-e} \text{Alkanone}$$

Functional group structure: 

| **Example** | **IUPAC name** | **Common name** |
|---|---|---|
| $CH_3COCH_3$ or  or  | Propan-2-one | Acetone |

**9. Nitriles:** General formula: $C_nH_{2n+1}$ CN ($R - C \equiv N$)

IUPAC suffix: nitrile  Common name: Cyanide  IUPAC prefix: Cyano

$$\text{Alkane} \xrightarrow[+\text{nitrile}]{-e} \text{Alkan}\textcircled{e}\text{nitrile}$$

(e is not dropped)

Functional group structure: ( $-C \equiv N$)

| Example | IUPAC name | Common name |
|---|---|---|
| $\overset{2}{C}H_3\overset{1}{C}N$ or $\overset{2}{Me}-\overset{1}{C}\equiv N$ or $(^{2}-\overset{1}{C}\equiv N)$ | Ethane nitrile | Methyl cyanide<br>or<br>Acetonitrile |

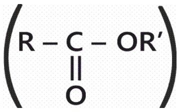
**10. Ethers:** General formula: (R – O – R′)

IUPAC suffix: -- Common name: (Ether)

IUPAC prefix: alkoxy (smaller chain) alkane (larger chain)

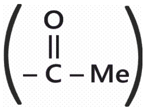
Functional group structure: (R – O – R′)

| Example | IUPAC name | Common name |
|---|---|---|
| $CH_3 - O - CH_3$ or $(CH_3)_2O$ or $Me_2O$ | Methoxy methane | Dimethyl ether |

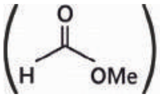
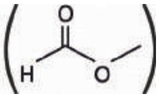
**11. Esters**: General formula: 

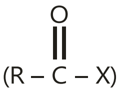
$$\left(R - \underset{\underset{O}{\parallel}}{C} - OR'\right)$$

IUPAC suffix: -oate IUPAC prefix: alkoxy carbonyl

Functional group structure: (–COOR) or 

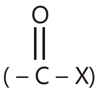
$$\left(-\overset{\overset{O}{\parallel}}{C} - Me\right)$$

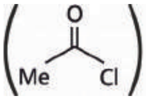
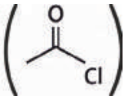
| Example | IUPAC name | Common name |
|---|---|---|
| $HCOOCH_3$ or  or  | Methyl methanoate | Methyl formate |

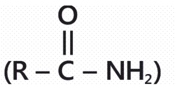
**12. Acyl halides**: General formula:  $(R - \overset{\overset{O}{\parallel}}{C} - X)$ (X = F, Cl, Br, I)

IUPAC suffix: -oyl halide IUPAC prefix: halocarbonyl

Alkane $\xrightarrow[\text{oyl halide}]{-e}$ Alkanoyl halide

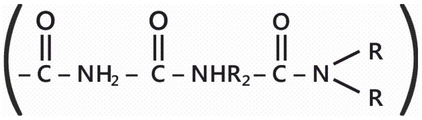
Functional group structure:  $( - \overset{\overset{O}{\parallel}}{C} - X)$

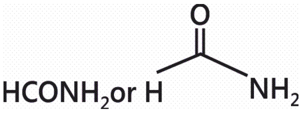
| Example | IUPAC name | Common name (derived from acid) |
|---|---|---|
| $CH_3COCl$ or  or  | Ethanoyl chloride | Formyl chloride |

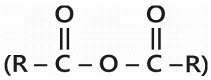
**13. Amides:** General formula:  $(R-\overset{\overset{O}{\|}}{C}-NH_2)$

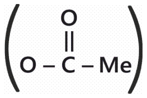
IUPAC suffix: amide IUPAC prefix: Carbamyl

Alkane $\xrightarrow[+\text{ amide}]{-e}$ Alkanomide

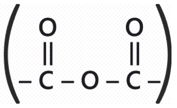
Functional group structure:  $\left(-\overset{\overset{O}{\|}}{C}-NH_2-\overset{\overset{O}{\|}}{C}-NHR_2-\overset{\overset{O}{\|}}{C}-NR_2\right)$

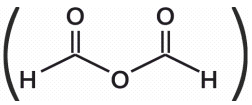
| **Example** | **IUPAC name** | **Common name** |
|---|---|---|
|  $HCONH_2$ or | Methanamide | Formamide |

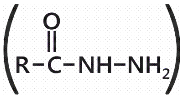
**14. Anhydrides:** General formula:  $(R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R)$

IUPAC suffix: – oic anhydride IUPAC prefix: Acetoxy or acytyloxy or  $\left(O-\overset{\overset{O}{\|}}{C}-Me\right)$

Alkanoic acid $\xrightarrow[+\text{anhydride}]{-\text{acid}}$ Alkanoic anhydride

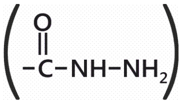
Functional group structure: (–COOCO–) or  $\left(-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-\right)$

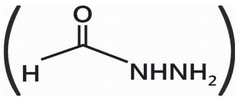
| **Example** | **IUPAC name** | **Common name (derived from acid)** |
|---|---|---|
| HCOOCH or $(HCO_2)$ or  | Methanoic anhydride | Formic anhydride |

**15. Acid hydrazides:** General formula:  $\left(R-\overset{\overset{O}{\|}}{C}-NH-NH_2\right)$

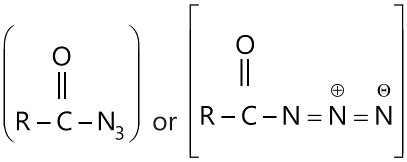
IUPAC suffix – hydrazide IUPAC prefix: --

Alkanoic acid $\xrightarrow[+\text{hydrazide}]{-\text{ic acid}}$ Alkanohydrazide

Functional group structure: $(-CONHNH_2)$ or  $\left(-\overset{\overset{O}{\|}}{C}-NH-NH_2\right)$

| **Example** | **IUPAC name** | **Common name** (derived from acid) |
|---|---|---|
| $HCONHNH_2$ or  | Methanohydrazide | Formyl hydrazide |

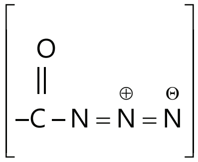
**16. Acid azides:** General formula:



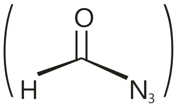
$$\left(R-\overset{\overset{\displaystyle O}{\|}}{C}-N_3\right) \text{ or } \left[R-\overset{\overset{\displaystyle O}{\|}}{C}-N=\overset{\oplus}{N}=\overset{\ominus}{N}\right]$$

IUPAC suffix: azide Alkanoic acid $\xrightarrow[+\text{azide}]{-\text{ic acid}}$ Alkanoazide

Functional group structure: (–$CON_3$) or



$$\left[-\overset{\overset{\displaystyle O}{\|}}{C}-N=\overset{\oplus}{N}=\overset{\ominus}{N}\right]$$

| Example | IUPAC name | Common name |
|---|---|---|
| $HCON_3$ or  | Methanoazide | Formyl azide |

**17. Thioalcohols or Thiols or Mercaptans:** General formula: (RSH)

IUPAC suffix: thiol IUPAC prefix: mercapto

Functional group structure: (–SH) Alkane $\xrightarrow[+\text{thiol}]{-e}$ Alkan thiol

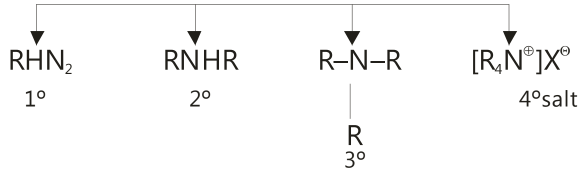
| Example | IUPAC name | Common name (derived from acid) |
|---|---|---|
| $CH_3SH$ or MeSH or | Methanthiol | Methyl thioalcohol or Methylmercaptan |

**18. Thioethers:** General formula: (R – S – R)

IUPAC suffix: thioether IUPAC prefix: --

| Example | IUPAC name | Common name (derived from acid) |
|---|---|---|
| $CH_3SCH_3$ ore MeSMe or $Me_2S$ | Methyl thio ether or<br>(Methyl thio) Methane | Dimethyl sulphide |

**19. Amines**: General formula:

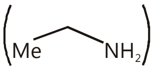
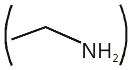


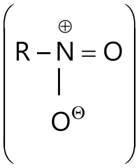
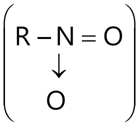
$$\underset{1^\circ}{RHN_2} \quad \underset{2^\circ}{RNHR} \quad \underset{3^\circ}{R-\underset{\displaystyle R}{\underset{|}{N}}-R} \quad \underset{4^\circ\text{salt}}{[R_4N^{\oplus}]X^{\ominus}}$$

IUPAC suffix: amine IUPAC prefix: amino

Alkane $\xrightarrow[+\text{amine}]{-e}$ Alkanamine

Functional group structure: –$NH_2$, (1°), >NH(2°), >N – (3°)

| Example | IUPAC name | Common name |
|---|---|---|
| $CH_3CH_2NH_2$ or $EtNH_2$ or  or  | Ethan amine | Ethyl amine |

**20. Nitro compounds:** General formula: ($RNO_2$) or  $\left(R-\overset{\oplus}{N}(-O^{\ominus})=O\right)$ or  $\left(R-\underset{\downarrow\atop O}{N}=O\right)$

IUPAC suffix: -- IUPAC prefix: nitro

Functional group structure: ($-NO_2$)

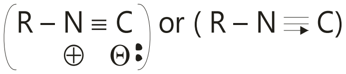
| Example | IUPAC name |
|---|---|
| $CH_3NO_2$ | Nitro methane |

**21. Alkyl nitrites:** General formula: ($R-O-N=O$) IUPAC suffix: nitrite

Functional group structure: ($-O-N=O$)

| Example | IUPAC Name |
|---|---|
| **i.** $CH_3-ONO$ or $Me-O-N=O$ | Methyl nitrite |
| **ii.** $CH_3CH_2CH_2ONO$ or $Pr-O-N=O$ | Propyl nitrite |

**22. Alkyl isocyanides or Isonitriles:**

General formula:  $\left(R-\underset{\oplus}{N}\equiv\underset{\ominus:}{C}\right)$ or $(R-N\rightrightarrows C)$

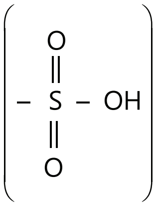
According to an IUPAC recommendation the substituent – NC is termed as carbylamino. Thus, $CH_3NC$ is carbylamino methane and so on. However, this name is not in use.

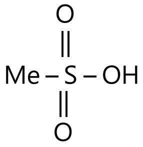
For naming isocyanides, iso is prefixed to the name of the corresponding cyano/nitrile compound. In another mode the suffix carbylamine is added to the name of the alkyl group.

| Example | Common name |
|---|---|
| $CH_3NC$ | Methyl isocyanide or Acetoisonitrile or Methyl carbylamine |

**23. Sulphonic acids:** General formula: ($R-SO_3H$)

IUPAC suffix: sulphonic acid IUPAC prefix: sulpho

Functional group structure: ($R-SO_3H$) or  $\left(-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH\right)$

| Example | IUPAC name |
|---|---|
| $CH_3SO_3H$ or  $Me-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH$ | Methyl sulphonic acid |

**24. Imines:** General formula: RCXH = NH

IUPAC suffix: imine IUPAC prefix: None

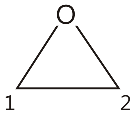
$\text{Alkane} \xrightarrow[+\text{al imine}]{-\text{e}} \text{Alkanal imine}$

Functional group structure: (–CH = NH)

| **Example** | **IUPAC name** | **Common name** |
|---|---|---|
| HCH = NH | Methanalimine | Formaldimine |

**25. Cyclic ethers:** General formula: O atom ring

IUPAC suffix: -- IUPAC prefix: epoxy

| **Example** | **IUPAC name** | **Common name** |
|---|---|---|
|  | Oxirane or 1,2-epoxy ethane | Ethylene oxide |

## 4.3.2 IUPAC Rules for Saturated Hydrocarbons

**(a)** The longest possible chain (parent chain) is selected. The chain should be continuous.

**(b)** C atoms which are not included in this chain are considered substituents (side chain)

**(c)** In case of two equal chains having the same length, the one with the larger number of side chains or alkyl groups in selected.

**(d)** Numbering of C atoms in the parent chain starts from that end where the substituent acquires the lowest position numbers or locant.

**(e)** Lowest sum rule: In case of two or more substituents, numbering is done is such a way that the sum of position number substituent or location is the lowest

**(f)** Position and substituent name are separated with a case (-)

**(g)** In case of more than one substituent, they are prefixed by their respective locants in alphabetical order.

## 4.3.3 IUPAC Rules for Unsaturated Hydrocarbons

**(a)** All the rules of alkanes are also applicable there,

**(b)** The parent or the longest chain is selected irrespective of the = or $\sigma$ bonds.

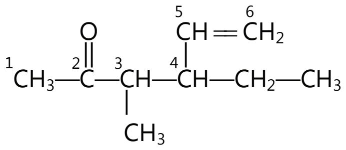
**(c)** The numbering is done from the end which is nearer to the = bond, and according to the lowest sum of locant rule.

**(d)** The numbering or sum rule will follow the alphabetical order of the substituent.

## 4.3.4 IUPAC Rules for Functional Groups

While numbering the longest chain, the function group should acquire the lowest number followed by other substituent and the family of multiple bonds even if it violates the lowest sum rule.

E.g.

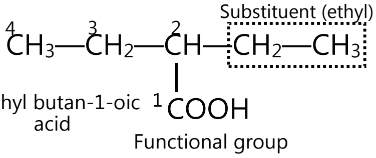


C$=$O (Functional group) acquires the lowest number $CH_3$ (Substituent methyl $CH=CH_2$($=$bond)

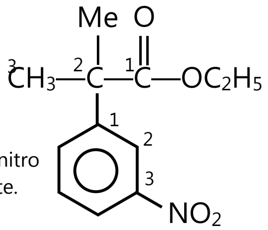
### 4.3.5 IUPAC Rules for Chain Terminating Functional Groups (-CHO, -COOH, -CONH$_2$, -COCl)

These chain terminating groups are included in the numbering, starting from the end where it acquires the lowest number followed by other substituent's in alphabetical order.

E.g.



2-Ethyl butan-1-oic acid



Ethyl 2-methyl-2-(3-nitro phenyl) propanoate.

### 4.3.6 IUPAC Rules for Polyfunctional Compounds

In case of polyfunctional compounds, one of the functional groups is chosen as the principal functional group and the compound is named on that basis. The remaining functional group which are subordinate functional groups, are named as substituents using the appropriate prefixes.

The decreasing order of priority of some functional groups is

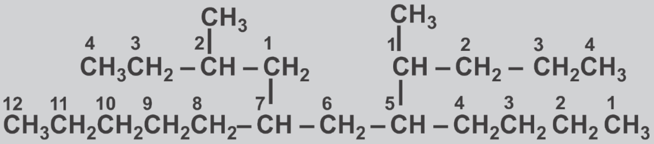
$-COOH > -SO_3H > -COOR$ (ester) $> -COCl$ (acylhalide) $> -CONH_2$ (amide) $> -C\equiv N$ (nitriles) $> -CH=O$ (aldehyde) $> \ >C=O$ (keto) $> -OH$ (alcohol) $> -NH_2$ (amine) $> \ >C=C$ (alkene) $> -C\equiv C-$ (alkyne)

The $-R$ (alkyl group), Ph or $C_6H_5-$(phenyl), halogens (F, Cl, Br, I) $-NO_2$ alkoxy ($-OR$). Etc., are always prefix substituents. Thus, a compound containing both an alcohol and a keto group is named hydroxyl alkanone since the keto group is preferred to the hydroxyl group.

## PLANCESS CONCEPTS

- When the names of two or more substituents are composed of Identical Words

  The priority of citation is given to the substituent which has the first cited point of difference with in the complex substituent. e.g.



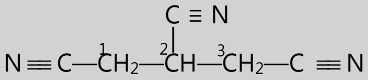
5(1-Methylbutyl) -7-(2-methylbutyl) dodecane

## PLANCESS CONCEPTS

- **Poly-Functional Compounds containing more than two like-functional groups**

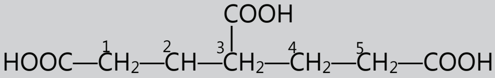
  According to the latest convention (1993 recommendation for IUPAC nomenclature), if an unbranded carbon chain is directly linked to more than two like-functional groups, then the organic compound is named as a derivative of the parent alkane which does not include the carbon atoms of the functional groups.

  E.g.

  **i.** 

  $$N\equiv C-\overset{1}{C}H_2-\overset{\overset{C\equiv N}{|}}{\overset{2}{C}H}-\overset{3}{C}H_2-C\equiv N$$

  Propane-1,2,3-tricarbonitrile
  (Not 3-cyanopentane-1, 5-dinitrilic)

  **ii.** 

  $$HOOC-\overset{1}{C}H_2-\overset{2}{C}H-\overset{\overset{COOH}{|}}{\overset{3}{C}H_2}-\overset{4}{C}H_2-\overset{5}{C}H_2-COOH$$

  Pentane-1,3,5-tricarboxylic acid
  (Not 4-carboxyheptane-1,7-dioic acid)

- **When both double and triple Bonds are present in the compound**

  In such cases, their locants are written immediately before their respective suffixes and the terminal 'e' from the suffix 'ene' is dropped while writing their complete names. It may be emphasized here that such unsaturated compounds are always named as derivatives of alkyne rather than alkene.

  E.g.

  **i.** $\overset{5}{C}H_3-\overset{4}{C}H=\overset{3}{C}H-\overset{2}{C}\equiv\overset{1}{C}H$

  Pent+3-en(e)+1-yne
  = Pent-3-en-1-yne
  (Formerly 3-Penten-1-yne)

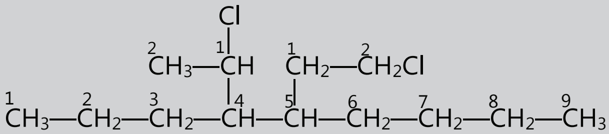
  **ii.** $H\overset{5}{C}\equiv\overset{4}{C}-\overset{3}{C}H_2-\overset{2}{C}H=\overset{1}{C}H_2$

  Pent-1-en(e) + 4-yne
  = Pent 1-en-4-yne
  (Formerly 1-Penten-4-yne)

- **When two or more prefixes consist of identical Roman letters (words):**

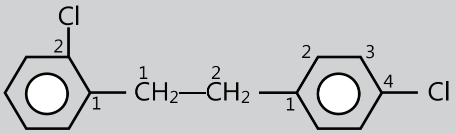
  The priority for citation is given to that group which contains the lowest locant at the first point of difference.

  e.g.

  **i.** 

  $$\overset{1}{C}H_3-\overset{2}{C}H_2-\overset{3}{C}H_2-\overset{\overset{\overset{2}{C}H_3-\overset{\overset{Cl}{|}}{\overset{1}{C}H}}{|}}{\overset{4}{C}H}-\overset{\overset{\overset{1}{C}H_2-\overset{2}{C}H_2Cl}{|}}{\overset{5}{C}H}-\overset{6}{C}H_2-\overset{7}{C}H_2-\overset{8}{C}H_2-\overset{9}{C}H_3$$

  4-(1-chloroethyl)-5-(2-chloroethyl) nonane

  **ii.** 

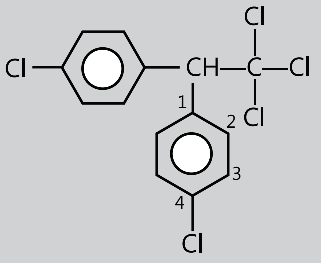
  1-(2-chlorophenyl)-2-(4-chlorophenyl) ethane

## PLANCESS CONCEPTS

- **When the Organic molecular contains more than one similar complex substituents**

  In such case, the numerical prefixes, such as di, tri, tetra etc,. are replaced by bis, tris, tetrakis, etc., respectively.

  E.g.



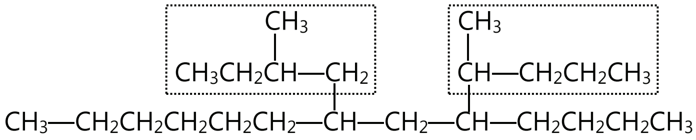
1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane

- **When all the three like groups are not directly linked to the unbranched carbon chain**

  The two like groups are included in the parent chain while the third group which forms the side chain is considered a substituent group.

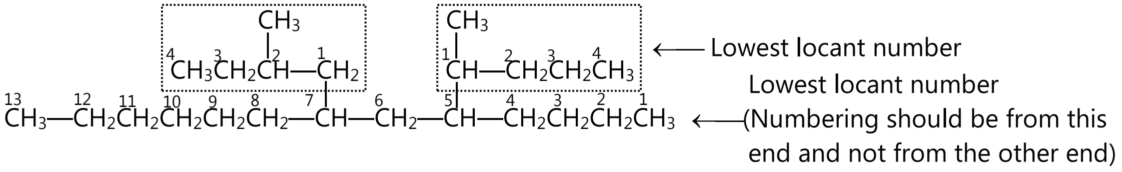
**Vaibhav Krishnan (JEE 2010, AIR 44**)

**Illustration 1:** Write the IUPAC name of the following compound: **(JEE ADVANCED)**



$$CH_3-CH_2CH_2CH_2CH_2CH_2-\overset{\overset{\displaystyle CH_3CH_2\overset{\overset{CH_3}{|}}{CH}-CH_2}{|}}{CH}-CH_2-\overset{\overset{\displaystyle \overset{\overset{CH_3}{|}}{CH}-CH_2CH_2CH_3}{|}}{CH}-CH_2CH_2CH_2CH_3$$

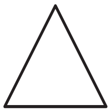
**Sol:** In case of a complex substituent and other substituents, the complex substituent begins with the first letter of its complete name. In case of two same complex substituents, one with the lowest positional number or locant is named first. This called priority citation.

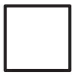


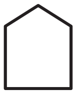
The IUPAC name of this compound is 5-(1-methyl butyl)-7-(2-methyl butyl) tridecane Priority of citation (5 < 7, 1 < 2); Locant 1 comes before 2.

### 4.3.7 IUPAC Rules for Alicyclic Compounds

1. IUPAC suffix: ane, ene, yne IUPAC prefix: cyclo

I. 

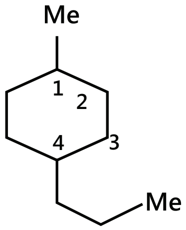
II. 

III. 

Two or more alkyl groups or other substituent's are present in the ring, their positions are indicated, e.g., 1,2,3 …., etc. The substituent which comes first in the alphabetical order is give n the lowest number, as per the lowest sum rule, e.g.

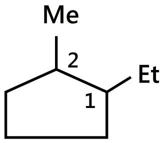
**2.** **(a)** If the ring contains equal or more number of C atoms than the alkyl groups attached to it, is named as an alkyl cycloalkane.

(I)



**1- Methyl-4-propylcyloexane**

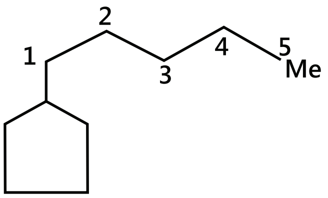
(II)



**1- Ethyl-2-2methyl cyclopentane**

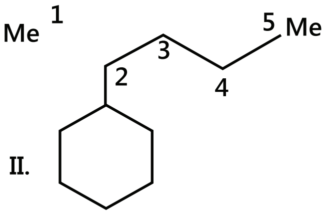
**(b)** If the ring contains lesser number of C atoms than the alkyl groups attached to it, is named cycloalkyl alkane, e.g.,

I.



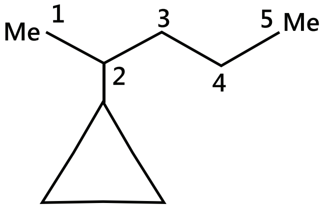
**(Same number of C atoms in ring and side chain)**
**Pentyl cylopentane**
**(Alkly cylcloalkane)**

II.



**(Ring contains more C atoms than side chain)**
**2-Cyclopropyl pentane**
**(Cycloalkyl alkane)**

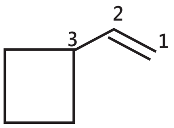
III.



**(Ring contains less C atoms than side chain)**
**2-Pemtyl cyclohexane**
**(Alkly cylcloalkane)**

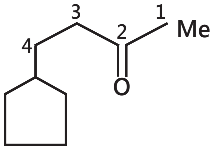
**(c)** If the side chain constrains a functional group or a multiple bond, then the alicyclic ring is considered substituent irrespective of the size of the ring, e.g.,

I.



**3-Cyclobutyl prop-1-ene**

II.



**4-Cyclopentyl but -3-en-2-one**

## 4.3.8 IUPAC Names of Bicyclo Compounds

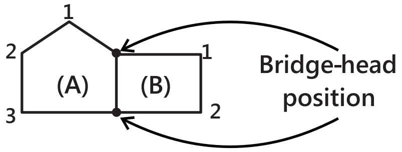
Compounds with two fused cycloalkane rings are called bicyclo compounds. They are cyclo alkanes having two or more atoms in common.

The prefix bicycle is followed by the name of the alkane whose number of C atoms is equal to number of C atoms in the two rings.

The bracketed numbers show the number of C atoms (except bridge-head position C atoms) in each bridge and they are cited in decreasing order.

E.g.

**(a)**

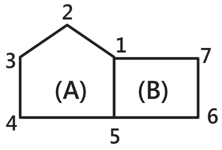


**(i)** Number of C atoms in ring A = 3

**(ii)** Number of C atoms in ring B = 2

**(iii)** Number of C atoms between bridge-head position = 0

**(iv)** Total C atoms = 3 (in ring A) + 2(in ring B) + 2 (Bridge-head position) = 7

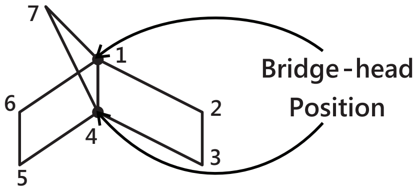


**(Numbering starts from the bridgehead to the larger ring and then back to the smaller ring.)**

## 4.3.9 IUPAC Names of Tricyclo Compounds

Compounds with three fused rings are called tricyclo compounds. The prefix tricyclo is followed by the name of alkane whose number of C atoms is equal to the number of C atoms in the rings.

E.g.



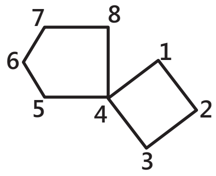
Tricyclo [2.2.1.0] heptane

The bracketed numbers show the number of C atoms (except the bridge-head position) in each bridge and they are cited in decreasing order.

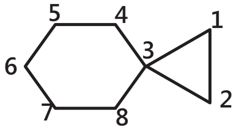
## 4.3.10 IUPAC Names of Spiranes

Spiranes are polycyclics that share only one C atom. In substituted spiranes, the numbering is started next to the fused C atom in the lower-member ring.

E.g.



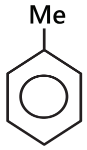
Spiro [3, 4] octane



Spiro [2.5] octane

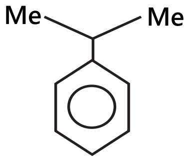
### 4.3.11 IUPAC Name of Aromatic Compounds

**(a)** No specific rules are required to name aromatic compounds. However, they are named substituted benzene, e.g.

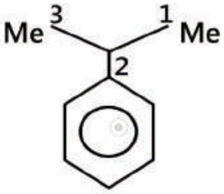


Methyl beznene
(Toluene)

**(b)** When larger and complex groups are attached to the benzene ring, the molecule is named as an alkane, alkene, etc., and benzene as side chain derivatives, abbreviated as, Ph –, or $C_6H_5$ – Ph – or ϕ. When the benzene ring contains some substituent's, it is abbreviated as Ar – .



Isoperopylbenznen or
2-Phenyl propane or



2-Phenyl propanoic
acid

## 4.4 Writing the Structural Formula from the Given IUPAC Name

The IUPAC name of an organic compound consists of the following parts:

a. Root word b. 1° suffix c. 2° suffix d. 1° prefix e. 2° prefix

**(a)** Root word indicates the longest chain thus, first locate the longest chain from the root word. Write the number of C atoms in a straight chain or in zigzag manner (for bond line structure) and then number them from any end.

**(b)** 1° suffix (-ane, -ene, or -yne) indicates the nature of the chain. Put the multiple bonds at proper places in the chain.

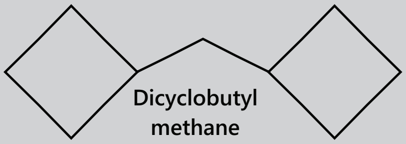
**(c)** 2° suffix indicates the principal functional group. Put it at a proper place in the chain.

**(d)** Prefixes are the substituents or secondary functional groups. Put them at a proper place with the help of locants.

**(e)** Add H atoms to satisfy valences of each C atom if stick formula is used. If the structure is written bond line, then there is no need of adding H atoms.

**PLANCESS CONCEPTS**

- If more than one alicyclic ring is attached to a single chain, then the compound is named as cycloalkyl alkane (i.e., derivative of alkane) irrespective of the number of C atoms in the ring or the chain, e.g.,

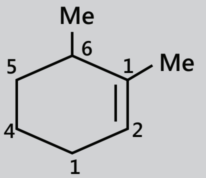


Dicyclobutyl
methane

## PLANCESS CONCEPTS

- If double or triple (multiple) bonds and some other substituents are present in the ring. The numbering is done in such a way that the multiple bond gets the lowest number, e.g.

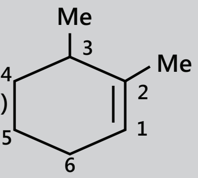
(I)



1,6-Dimethyl cyclohex-1-en
(correct)

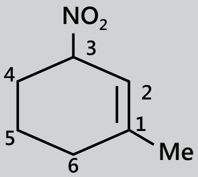
[ Lowest number for Me substituent and also for double bond. although it violates lowest sum rule ]

(not)



2,3-Dimethyl cyclohex-1-ene
(incorrect)

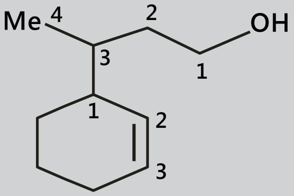
(II)



1-Methyl-3-nitro
cyclohex-1-ene

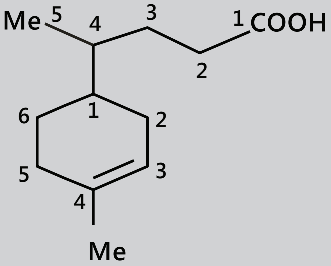
- If the ring contains a multiple bond and the side chain contains functional group, then the ring is considered the substituent and the compound is named a derivative of the side chain, e.g.,

I.



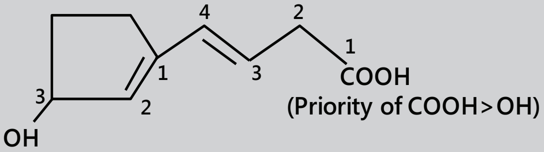
3–(Cyclohex-2-enyl)
butan-1-ol

I.



4-(4-Methyl cyclohex-3-enyl)
Pentanoic acid

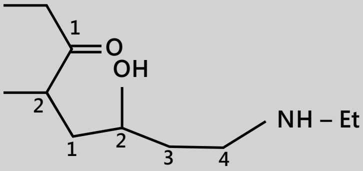
- If the ring and side chain both contain functional groups, then
  - **(i)** If the side chain constrains higher priority of of functional group then the compound is named the derivative of the side chain



(Priority of COOH>OH)

4-(3-Hydroxy cyclopent-1-enyl) but-3-en-1-oic acid

  - **(ii)** If the ring contains higher priority of functional group, then the compound is named the derivative of the alicyclic ring, e.g.,

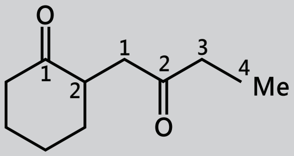


2-(4-Amino ethyl-2-hydroxy butlyl)

## PLANCESS CONCEPTS

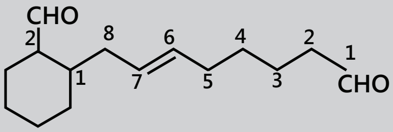
- If both the side chain and the alicyclic ring contain the same functional group, then it is of two types.

  **(i)** If the number of C atoms of the alicyclic ring is equal or greater than that of the side chain, then it is named the derivative of the alicyclic ring. e.g.,



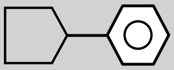
**2-(2-Oxobutyl)cyclohexan-1-one**

  **(ii)** If the number of C atoms of the side chain is greater than that of the alicyclic ring, then it is named the derivative of the side chain. e.g.,

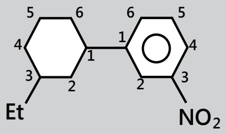


**8-(2-Formyl cyclohexyl ) oct-6-en-1-al**

- If an alicyclic ring is directly attached to the benzene ring, it is named the derivative of benzene. e.g.,



**Cyclopentyl benzene**

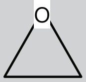


**1-(3-Ethyl cyclohexyl)-**
**3-nitro benzene**

- Naming of cyclic ethers

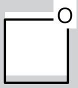
  The IUPAC names for cyclic ether $(CH_2)_nO$, where n = 2,3,4,5 and 6.

**a.**



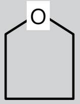
**Oxirane**

**b.**



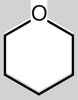
**Oxetane**

**c.**



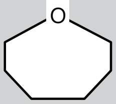
**Oxolane**

**d.**



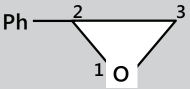
**Oxane**

**e.**



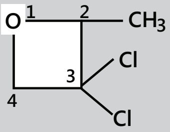
**Oxepane**

f.



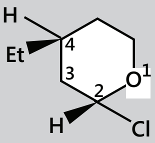
**Phenyloxirane**

g.



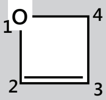
**3,3-Dichloro-2-methyl**
**oxetane**

h.



**trans-2-chloro-4-ethyloxane**

i.



**Oxetane**

- Mono-substituted benzene compounds :

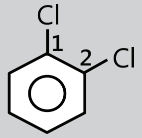
  According to IUPAC nomenclature, the substituent is placed as prefix and benzene as suffix.

  However, common names (written in bracket) of many substituted compound are commonly used, e.g- Toluene, Phenol etc.

## PLANCESS CONCEPTS

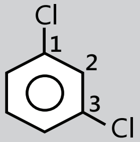
- If the benzene ring is disubstituted, the substituents are located at the lowest number. In the trivial system of nomenclature, the terms ortho (o), meta (m) and para (p) are used as prefixes to indicate the relative positions 1,2 - ; 1,3 -, and 1,4- respectively, e.g.

I.



**1,2-Dichloro benzene**
**(o-Dichloro benzene)**

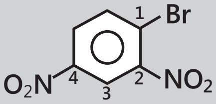
II.



**1,3-Dichloro benzene**
**(m-Dichloro benzene)**

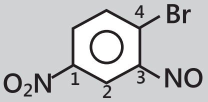
- If the benzene ring is tri- or higher substituted, then the compounds are named by identifying the substituent position on the ring by following the lowest locant sum rule. The substituent of the base compound is given the number 1 and then the direction of the numbering is selected such that the next substituent gets the lowest number. The substituent's are written in the name in alphabetical order, e.g.,

I.



(1-Bromo-2,4-dinitro benzne)
(not 4- Bromo- 1,3 -dinitro benzne)

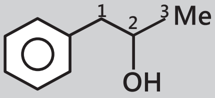
not



(Lowest sum = 1 + 2 + 4 =7)
(Highest sum = 4 + 1 + 3 = 8)

- When a benzene ring is attached to an alkane with a functional group, it is considered as a substituent instead of a parent. The name for benzene as substituent is phenyl ($C_6H_5$–) also abbreviated as Ph, e.g.,

I.

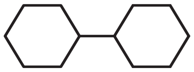


1-Phenyl propan-2-ol

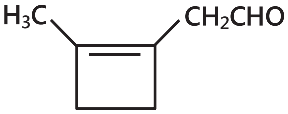
**Nikhil Khandelwal (JEE 2010, AIR 443)**

**Illustration 2:** Give the IUPAC name of the following compounds: **(JEE MAIN)**

I.

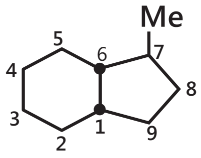


II.

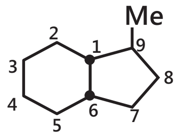


**Sol:** i. Cyclohexylcyclohexane ii. 2-(2-Methylcylobut-1-enyl) ethanal

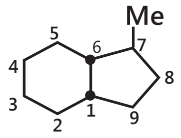
**Illustration 3:** Write the IUPAC Name for **(JEE MAIN)**



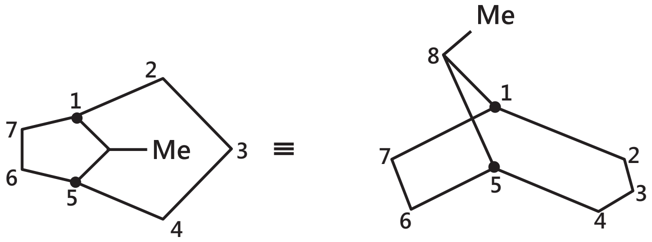
**Sol:**



**Wrong numbering**
since the position
of the substituent is at C-9



**Correct numbering**
since the position
of the substituent is at
the lowest number ,i.e .,
at C-7

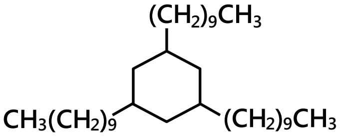


IUPAC name: 7-Methyl bicycle [4.3.0] nonane

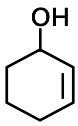
Numbering from the longest bridge-head (i.e., from the larger ring) to the next longest bridge-head (i.e., to the smaller ring.)

**Illustration 4:** Write the IUPAC name: **(JEE ADVANCED)**

I.



II.



**Sol:** (i) 1,3,5-Tris(decyl)cyclohexane ; (ii) Cyclohex-2-en-1-ol

# 5. GENERAL ORGANIC CHEMISTRY

## 5.1 Basics of GOC

### 5.1.1 Theory of Development of Quantum Mechanics

The Quantum theory was developed by Erwin Schrödinger. He worked on a mathematical model for the motion of electrons based on wave functions. This whole model was based on the fact that electron have a dual nature i.e., they show properties of both particles as well as waves. This theory led to the idea of atomic orbitals.

**Atomic orbital:** Due to the dual nature of electrons, the Schrodinger wave equation came up. However, the wave equation fails to tell us exactly where the electron is at any particular moment, or the speed with which it is moving. All it tells us is the probability of finding the electron at any particular place. The region in space where the electron is most likely to be, is known as an orbital. These orbitals are of different kinds, and are hence dispersed about the nucleus in specific ways. The particular shape of orbital that an electron occupies, depends: upon the energy of the electron.

By knowing the shapes of these orbitals and there dispositions with respect to each other, we can be more precise in conveniently explaining the arrangement in the space of the atoms forming the nucleus and as a result, determine its physical and chemical behaviors.

### 5.1.2 Covalent Bonding

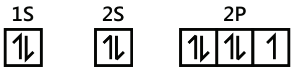
Covalent bonds, make up compounds of carbon. This bond is of chief importance in the study of organic chemistry.

**Overlap Theory:** According to this theory, for a covalent bond to the formed, the atoms must be located sufficiently close together so that an orbital of one atom overlaps with the other. Each orbital must contain single (unpaired) electrons. When this happens, single bond orbitals are occupied by both electrons. The two electrons that occupy the orbital must have opposite spins i.e. it must be paired.

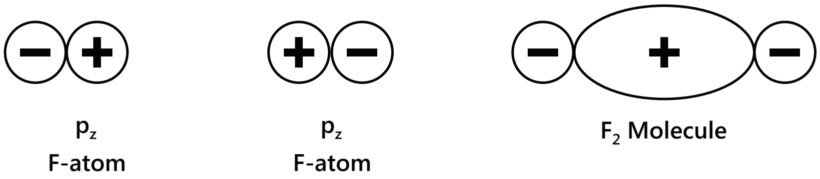
This arrangement contains less energy and hence is more stable.

E.g. F atom

Valence shell contains 7 electrons



The two F-atom some together and overlap through their p-orbital

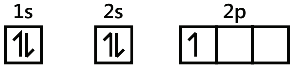


$BeCl_2$ molecule

**$BeCl_2$:** The electronic configuration of Be atom can be represented as 

Be atom in order to take part in covalent bonding must have single electron orbitals.

Electronic Configuration of Be atoms just about to get bonded to chlorine atoms.

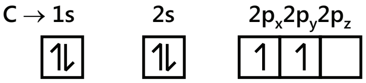


This leads to the idea that Be forms two different kinds of overlaps with every chlorine atom i.e. one Be-Cl bond s-p overlap and other Be-Cl bond p-p overlap which would result in two different types of Be-Cl bonds having different bond energies and bond lengths.

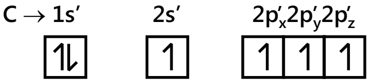
But experiments have shown that both the Be-Cl bonds in $BeCl_2$ are identical. So the theory of overlap is not applicable everywhere

Even if you consider the molecule of $CH_4$ . Here, the central atom is carbon. The electronic configuration of carbon is

$$C \rightarrow 1s^2 \quad 2s^2 \quad 2p_x^1 \ 2p_y^1$$



Just before combining with the 4H–atoms the electronic configuration of carbon becomes

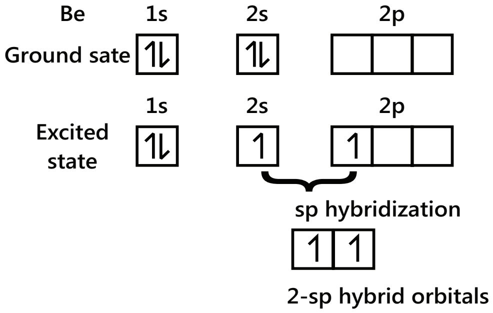


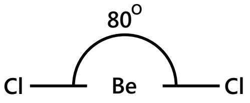
Here again we will find that according to the theory of overlap, there are 3 p-s overlaps and one s-s overlap meaning that the bonds are not identical, but experiments have shown beyond doubt that the 4 C–H bonds are all equivalent.

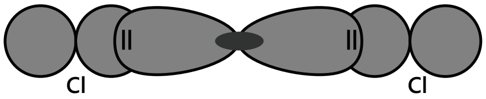
Hence we apply the concept of hybridization.

**Hybridization:** It is the process of mixing up of non-degenerate atomic orbitals of the atom to form degenerate orbitals called hybrid orbitals each having the greatest degree of directionality.

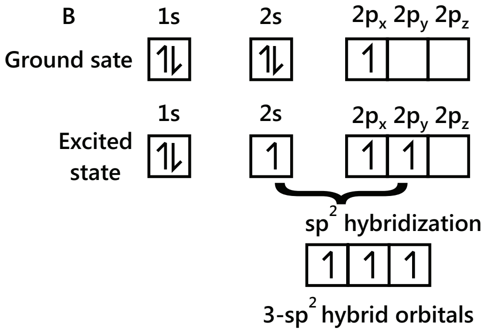
### Hybrid orbitals: sp



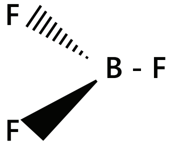




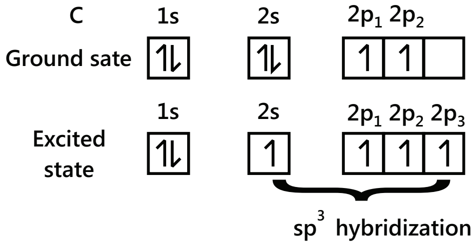
### Hybrid orbitals: Sp²

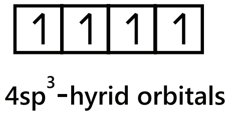


$BF_3$ is trigonal planar



### Hybrid Orbital –sp³





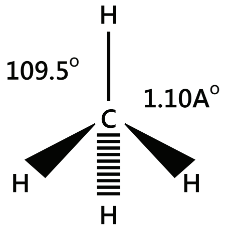
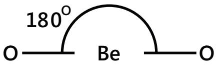
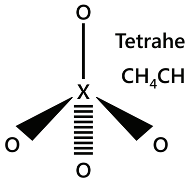
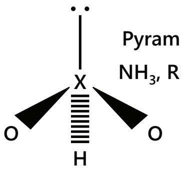
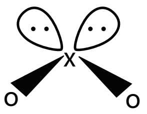


**Table 8.2:** Shape and geometry of the compound depending upon the hybridization

| S. No. | Hybridization | Number of lone pair | Geometry | Shape and example |
|---|---|---|---|---|
| 1. | sp<br>BeF$_2$ | 0 | Linear |  <br>BeF$_2$<br>CH ≡ CH |
| 2. | sp$^3$ | 0 | Trigonal Planar | Angular or bond<br>BF$_3$, CH$_2$=CH$_2$ |
| 3. | sp$^3$ | 0 | Tetrahedral |  <br>Tetrahedral<br>$CH_4CH_2H_6$ |
| 4. | sp$^3$ | 1 | Tetrahedral |  <br>Pyramidal<br>$NH_3$, $RNH_2$ |
| 5. | sp$^3$ | 2 | Tetrahedral |  <br>Angular<br>or<br>bend<br>$H_2O$ |

### 5.1.3 Polarity in Molecule

Each time a covalent bonds is formed between the same atoms, then the electrons are shared equally between the two atoms forming the bond e.g. $F_2$, $H_2$, etc. However, when the covalent bond is formed between two dissimilar atoms then there is an unequal sharing of electrons resulting in the electron of the covalent bond being drawn closer to the more electronegative atom, resulting in a bond dipole. e.g. HCl, HBr etc.

The polarized covalent bond due to the difference of electro negativity may be shown as

$\overset{\delta+}{H}-\overset{\delta-}{F} \quad \underset{\text{H–F}}{+\!\!\!\longrightarrow} \quad \overset{\delta+}{H}-\overset{\delta-}{Cl} \quad \underset{\text{H–Cl}}{+\!\!\!\longrightarrow}$

The polarity in a bond arises from the difference in electronegativity of the atoms participating in the bond formation.

The greater the difference in the electronegativity between the atoms bonded, the greater will be the polarity of the bond. Electronegativity order of some elements is below:

| F | > O | > Cl | ~ N | > Br | > C | ~ S | > I | > P | ~ H | > Si | > Al | > Mg | > Li | > Na | > K |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 4.0 | 3.5 | 3.0 | 3.0 | 2.8 | 2.5 | 2.5 | 2.4 | 2.1 | 2.1 | 1.8 | 1.5 | 1.2 | 1.0 | 0.9 | 0.8 |

Electronegativity of carbon and hydrogen are close enough, hence C-H bonds do not have much polarity.

H – O
H – F
H – Cl
H – N

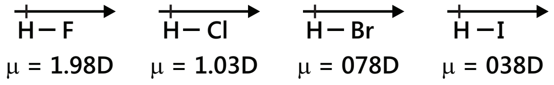
Even C – X, C – O and C – N bonds are also polar

Dipole moment = charge × distance

Bond polarity contributes greatly to the physical and chemical properties of molecules.

### Dipole Moments of Covalent Molecules

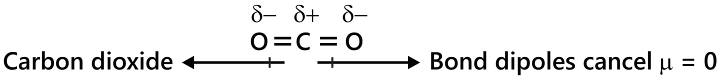
**(a)** For a distant molecule with different atoms, the level dipole is also the dipole moment.

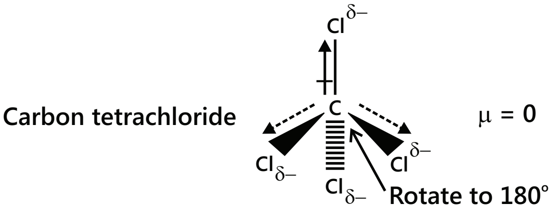


**(b)** For diatomic molecules with the same atoms there is no bond dipole e.g., H—H and I — I

**(c)** The overall dipole moment of a molecule containing more than two atoms is the vector sum of the individual bond dipole moments.

A molecule may contain polar bonds but has no overall dipole moment if the shape of the molecule is such that the individual bond moments cancel out.





## 5.1.4 Molecular Interactions

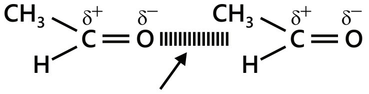
It is found that covalent compounds exist as solids, liquids and gases. So what forces hold neutral molecules together?

Like interionic forces, these forces seem to be, electrostatic in nature, involving the attraction of +ve charge for negative charge (a) Dipole-Dipole interactions (b) Vander waal's forces.

### Dipole-Dipole Interactions

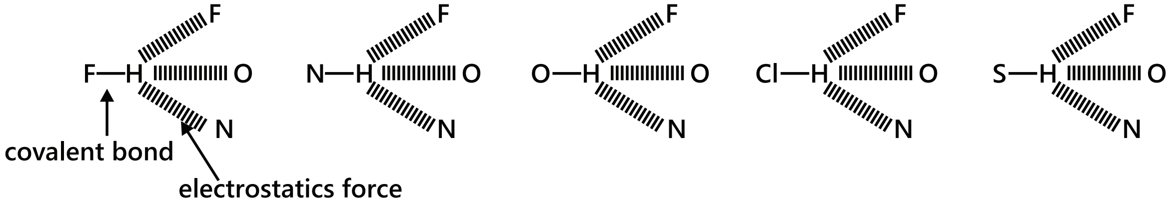
**(a)** This exists mainly in polar molecules. Here there is attraction of the positive end of one polar molecule for the negative end of another polar molecule.

In acetaldehyde the relatively –ve



As a result of dipole-dipole interactions the molecules are generally near to each other more strongly than all the non-polar molecules of comparable molecular mass.

**(b)** H–bonding [king of dipole-dipole interaction]. Here the H-atom seems to act as a bridge between two electronegative atoms, holding one by a covalent bond and the other by purely an electrostatic force.



Also the strength of hydrogen bonding order is

F||||||||||||H > O ||||||||||||H >>>> N||||||||||||H.

### 5.1.5 Non-Polar Forces

It has been found that even non- polar molecules solidify and hence there must be some forces which exist in order for this to happen. Such attractive forces are called Van der Waal forces. Quantum mechanics accounts for the existence of these forces, as it states that the average distribution of charge about e.g., $CCl_4$ molecule is symmetrical, so there is no net dipole moment. However, electrons move about, so at any instant the distributions become distorted leading to a small dipole. This momentary dipole induces another small dipole moment in another molecule and so on and so forth to the neighbouring molecules.

Though the momentary dipole and induced dipoles are constantly changing, the net result is the attraction between the two molecules.

These Van der Waals forces have a very short range, they act only between the portions of different molecules that are in close contact in between the surfaces of molecules.

(a) Van der Waals forces are directly proportional to molecular mass.

(b) Van der Waals forces are directly proportional to surface area.

The molecular forces of attraction are very useful in comparing the rates of evaporation, vapour pressures, boiling points, melting points, viscosity, etc.

## PLANCESS CONCEPTS

**(a) Hybridization:** Some special case of hybridization are –

- **(i)** Carbanion is $sp^3$ hybridized.
- **(ii)** Carbocation is $sp^2$ hybridized.
- **(iii)** $CH_3$ Radical is $sp^2$ hybridized while $CF_3$ is $sp^3$ hybridized. Electronegativity of fluorine is responsible for the latter case.
- **(iv)** Triplet carbine is sp hybridized while singlet carbene is $sp^2$ hybridized.

**(a) Polarity:**

- **(i)** Dipole moment = q x d
- **(ii)** Polarity determines many physical factors like intermolecular interaction, boiling and melting points, solubility.
- **(iii)** Greater the polarity, greater is the intermolecular interaction.
- **(iv)** Greater the polarity, higher are the boiling and melting points.
- **(v)** Polar molecules are soluble in polar solvent while non-polar molecules are soluble in non-polar solvent.

**(a) Molecular interactions:**

- **(i)** Dipole-dipole interactions – attraction between two polar molecules.
- **(ii)** Van der Waals forces – increases with increase in molecular weights.
- **(iii)** Hydrogen bonding – occurs with hydrogen attached with fluorine, nitrogen and oxygen only.
- **(iv)** Magnitude of molecular interaction – H bonding > Dipole – dipole interactions > Van der waals forces.

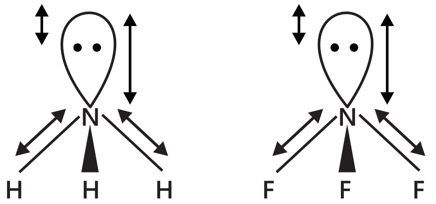
**Saurabh Gupta (JEE 2010, AIR 443)**

**Illustration 5:** Explain why μ of $NH_3$ > $NF_3$? **(JEE MAIN)**

**Sol:** Explain this question by taking into account the direction of contribution of N-H and N-F bond and the lone pair electrons.

In $NH_3$, the net moment of (N – H) bonds and the contribution from the LP eletrons (lone pair electrons) are in the same direction and are additive. The net moment of the (N – F) bonds opposes the dipole effect of the LP electrons in the $NH_3$ and the resultant is less μ. So μ of $NH_3$ > $NF_3$.

i.



($sp^3$ H.O.)
(a)

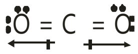
($sp^3$ H.O.)
(b)

**Illustration 6:** Explain why μ of $CH_3Cl$ > $CH_3F$ > $CH_3Br$ > $CH_3I$ **(JEE MAIN)**

**Sol:** The electro-negativities of halogens decrease from F to I so μ of HF > HCl > HBr > HI, but μ of $CH_3F$ is smaller than $CH_3Cl$ due to shorter (C – F) bond distance, although EN of F is greater than that of Cl.

**Illustration 7:** Explain why $CO_2$ has dipole moment zero whereas for $SO_2$ its non-zero? **(JEE ADVANCED)**

**Sol:** In $CO_2$, C is sp hybridized and linear. The dipole moments of (C – O) are equal and in opposite directions and cancel each other. Hence, μ is zero.



In $SO_2$ , S is $sp^2$ hybridized having one LP on S atom. The (O – S – O) bond angle is nearly 120º; (S – O) bond moment does not cancel and shows a net resultant μ.

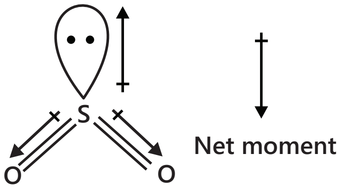


**Illustration 8:** Explain why the lone pairs of electrons has no effect on the μ of $PH_3$.The bond angle in $PH_3$ is 92º **(JEE ADVANCED)**

**Sol:** The 92º bond angle suggests that P uses three p atomic orbitals in forming bonds with H, with one LP $\bar{e}$ in 3s atomic orbital, i.e., P in $PH_3$ is $sp^2$ hybridized (unlike $NH_3$, in which N is $sp^3$ hybridized)

Therefore, due to the presence of LP $\vec{e}$ s in 3s atomic orbital of P, which is spherical symmetrical, the polarity of the molecule is not affected enough to affect the polarity of the molecule, the $\vec{e}$ 's must be in a directional orbital. Moreover, EN of P and H are nearly same, so $PH_3$ molecule is almost nonpolar,

**Illustration 9:** (a) Describe heterolytic (polar) bond cleavage of:

i. AgI, ii. $\overset{\oplus}{N}\overset{\ominus}{B}F_3$ iii. $[Cu(OH_2)_4]^{\ominus}$

(b) Name the reverse of heterolytic cleavage.

(c) Describe hemolytic bond cleavage of $CH_3 – CO – CO – CH_3$.

(d) Compare the relative energies of singlet and triplet carbenes.

(e) Of $X_2C$ : (singlet) and $X_2Cl$ :(triplet), which is stable ?

(f) Of $F_3C$ :, $Cl_2C$:, $Br_2C$ :, $I_2C$ : (singlet), which is more stable ?

(g) Compare and explain the difference in the IE and EA of $^{+}CH_3$. **(JEE ADVANCED)**

**Sol:** (a) (i) $Ag - I \rightarrow Ag^{+} + I^{-}$ (More EN atoms acquire negative charge.)

(ii) $H_3\overset{\oplus\ominus}{NB}F_3 \longrightarrow H_3N : BF_3$ (Bonded atoms with formal charges give uncharged products.)

(iii) $[Cu(OH_2)_4]^{2+} \longrightarrow Cu^{2+} + 4H_2O$

(b) Coordinates covalent bonding.

(c) $H_3C - CO - CO - CH_3 \rightarrow \underset{(\text{A radical})}{2CH_3CO^{\bullet}}$

(d) Triplet carbene has lower energy because with two $e^-$'s in different orbitals there is less electrostatic repulsion than when both are in the same orbital.

(e) $X_2C$: Singlet is more stable, because of the lone pair of electrons on X which can overlap laterally with the empty orbital.

(f) $F_3C$ is the most stable singlet, since F and C are in the same period of the periodic table and are about the same size permitting a more efficient overlap (2p(F) –2p(C) ore $p\pi - p\pi$ bond). Moreover, (F – C) bond length is the shortest bond length and provides a more extensive lateral overlap.

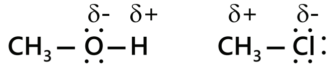
(g) The EA is less than IE. When – $CH_3$ gains an $e^-$ to become carbanion, C acquires a stable octet of $e^-$s. When it loses an $e^-$, it becomes unstable with only 6 $e^-$ s.

# 6. ELECTRONIC EFFECTS

## 6.1 Inductive Effect

The Inductive effect is an electronic effect due to the polarization of **σ bonds** within a molecule or ion.

- This is typically due to an electronegativity difference between the atoms at either end of the bond.
- The more electronegative atom pulls the electrons in the bond towards itself creating some bond polarity for example the O-H and C-Cl bonds in the following examples:



$$CH_3 - \overset{\delta-}{\ddot{O}} - \overset{\delta+}{H} \qquad \overset{\delta+}{CH_3} - \overset{\delta-}{Cl}$$

The inductive effect is divided into two types depending on their strength of electron withdrawing or electron releasing nature with respect to hydrogen.

**(a) Negative inductive effect (-I):** The electron withdrawing nature of groups or atoms is called the negative inductive effect. It is indicated by -I. Following are the examples of groups in the decreasing order of their -I effect:

$NH_3$ + > $NO_2$ > CN > $SO_3H$ > CHO > CO > COOH >COCl> $CONH_2$ > F >Cl> Br > I > OH > OR > $NH_2$ > $C_6H_5$ > H

**(b) Positive inductive effect (+I):** It refers to the electron releasing nature of the groups or atoms and is denoted by +I. Following are the examples of groups in the decreasing order of their +I effect.

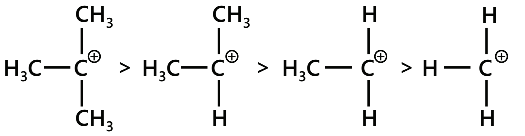
$C(CH_3)_3$ > $CH(CH_3)_2$ > $CH_2CH_3$ > $CH_3$ > H

**Why do alkyl groups show a positive inductive effect?**

Though the C-H bond is practically considered as non-polar, there is partial positive charge on hydrogen atom and partial negative charge on carbon atom. Therefore each hydrogen atom acts as electron donating group. This cumulative donation turns the alkyl moiety into an electron donating group.

### 6.1.1 Applications of Inductive Effect

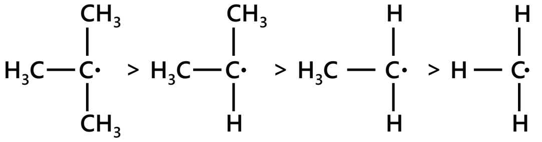
**(a) Stability of Carbonium Ions:** The stability of carbonium ions increases with the increase in the number of alkyl groups due to their +I effect. The alkyl groups release electrons to carbon, bearing a positive charge and thus stabilizes the ion. The order of stability of carbonium ions is:



$$H_3C-\underset{CH_3}{\overset{CH_3}{C^{\oplus}}} > H_3C-\underset{H}{\overset{CH_3}{C^{\oplus}}} > H_3C-\underset{H}{\overset{H}{C^{\oplus}}} > H-\underset{H}{\overset{H}{C^{\oplus}}}$$

3° 2° 1° Methyl

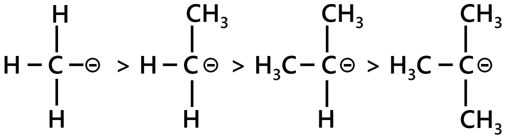
**(b) Stability of Free Radicals:** In the same way the stability of free radicals increases with increase in the number of alkyl groups. Thus the stability of different free radicals is:



$$H_3C-\underset{CH_3}{\overset{CH_3}{C\cdot}} > H_3C-\underset{H}{\overset{CH_3}{C\cdot}} > H_3C-\underset{H}{\overset{H}{C\cdot}} > H-\underset{H}{\overset{H}{C\cdot}}$$

3° 2° 1° Methyl

**(c) Stability of Carbanions:** However the stability of carbanions decreases with increase in the number of alkyl groups since the electron donating alkyl groups destabilize the carbanions by increasing the electron density. Thus the order of stability of carbanions is:



$$H-\underset{H}{\overset{H}{C}}-\ominus > H-\underset{H}{\overset{CH_3}{C}}\ominus > H_3C-\underset{H}{\overset{CH_3}{C}}\ominus > H_3C-\underset{CH_3}{\overset{CH_3}{C}}\ominus$$

Methyl 1° 2° 3°

**(d) Acidic Strength of Carboxylic Acids and Phenols:** The electron withdrawing groups (-I) decrease the negative charge on the carboxylate ion by stabilizing it. Hence the acidic strength increases when -I groups are present.

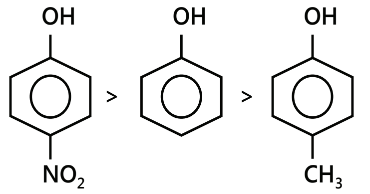
However the +I groups decrease the acidic strength.

E.g. (i) The acidic strength increases with increase in the number of electron withdrawing Fluorine atoms as shown below.

$CH_3COOH < CH_2FCOOH < CHF_2COOH < CF_3COOH$

(ii) Formic acid is a stronger acid than acetic acid since the $-CH_3$ group destabilizes the carboxylate ion. On the same lines, the acidic strength of phenols increases when -I groups are present on the ring.

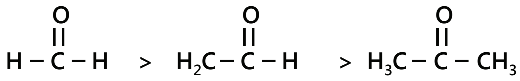
E.g. p-nitrophenol is a stronger acid than phenol since the $-NO_2$ group is a -I group and withdraws electron density. Whereas the para-cresol is a weaker acid than phenol since the $-CH_3$ group shows a positive (+I) inductive effect. Therefore the decreasing order of acidic strength is:



p-nitrophenol phenol p-cresol

**(e)** **Basic strength of amines:** The electron donating groups like alkyl groups increase the basic strength of amines whereas the electron with drawing groups like aryl groups decrease the basic nature. Therefore alkyl amines are stronger Lewis bases than ammonia, whereas aryl amines are weaker than ammonia. Thus the order of basic strength of alkyl and aryl amines with respect to ammonia is: $CH_3NH_2 > NH_3 > C_6H_5NH_2$

**(f)** **Reactivity of Carbonyl Compounds:** The +I groups increase the electron density at the carbonyl carbon. Hence their reactivity towards nucleophiles decreases. Thus, formaldehyde is more reactive than acetaldehyde and acetone towards nucleophilic addition reactions. Thus the order of reactivity follows:

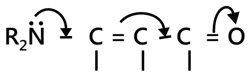


$$\mathrm{H-\overset{\overset{O}{||}}{C}-H \;>\; H_2C-\overset{\overset{O}{||}}{C}-H \;>\; H_3C-\overset{\overset{O}{||}}{C}-CH_3}$$

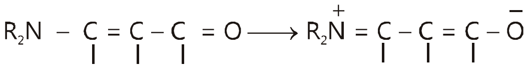
Formaldehyde Acetaldehyde Acetone

## 6.2 Electromeric Effect

A molecular polarizing effect occurring by an intermolecular electron displacement (sometimes called the 'conjugative mechanism' and, previously, the 'tautomeric mechanism') characterized by the substitution of one electron pair for another within the same atomic octet of electrons. It can be indicated by curved arrows symbolizing the displacement of electron pairs, as in:



$$R_2\ddot{N}\;\underset{|}{C}=\underset{|}{C}\;\underset{|}{C}=O$$



$$R_2N-\underset{|}{C}=\underset{|}{C}-\underset{|}{C}=O \longrightarrow R_2\overset{+}{N}=\underset{|}{C}-\underset{|}{C}=\underset{|}{C}-\overline{O}$$

which represents the hypothetical electron shift -

## 6.3 Mesomeric Effect

The Mesomeric effect (on reaction rates, ionization equilibria, etc.) is attributed to a substituent due to the overlap of its p- or π-orbitals with the p- or π-orbitals of the rest of the molecular entity. Delocalization is thereby introduced or extended, and electronic charge may flow to or from the substituent. The effect is symbolized by M. Strictly understood, the mesomeric effect operates in the ground electronic state of the molecule. When the molecule undergoes electronic excitation or its energy is increased on the way to the transition state of a chemical reaction, the mesomeric effect may be enhanced by the electromeric effect, but this term is not much used, and the mesmeric and electromeric effects tend to be assumed to be taken in the term resonance effect of a substituent. Mesomeric effect is divided into 2 parts on basis of withdrawal or donation of electrons.

**Negative resonance or mesomeric effect (-M or -R):** It is shown by substituents or groups that withdraw electrons by the delocalization mechanism from rest of the molecule and are denoted by -M or -R. The electron density on rest of the molecular entity is decreased due to this effect.

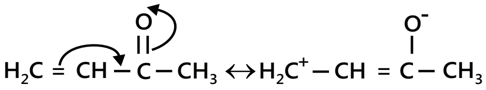
E.g. $-NO_2$, Carbonyl group (C=O), -C≡N, -COOH, $-SO_3H$ etc.

**Positive resonance or mesomeric effect (+M or +R):** The groups show a positive mesomeric effect when they release electrons to the rest of the molecule by delocalization. These groups are denoted by +M or +R. Due to this effect, the electron density on rest of the molecular entity is increased.

E.g. -OH, -OR, -SH, -SR, $-NH_2$, $-NR_2$ etc.

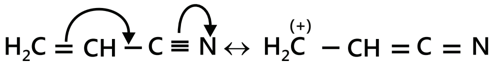
**Applications of Resonance Effect (Or) Mesomeric Effect**

**(a)** The negative resonance effect (-R or -M) of the carbonyl group is shown below. It withdraws electrons by delocalization of π electrons and reduces the electron density particularly on 3rd carbon.



$$H_2C=CH-\overset{\overset{O}{||}}{C}-CH_3 \leftrightarrow H_2C^+-CH=\overset{\overset{O^-}{|}}{C}-CH_3$$

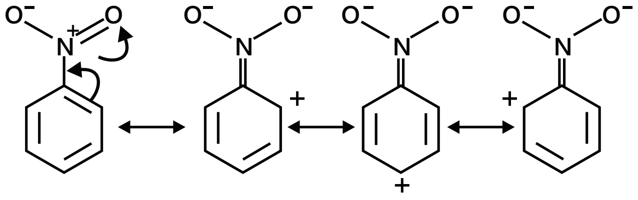
**(b)** The negative mesomeric effect (-R or -M) shown by the cyanide group in acrylonitrile is illustrated below. The electron density on the third carbon decreases due to delocalization of π electrons towards cyanide group.



$$H_2C = CH - C \equiv N \leftrightarrow H_2\overset{(+)}{C} - CH = C = N$$

Because of negative resonance effect, the above compounds act as good acceptors.

**(c)** The nitro group, -NO$_2$, in nitrobenzene shows -M effect due to the delocalization of conjugated π electrons as shown below. Note that the electron density on the benzene ring is decreased particularly on ortho and para positions.



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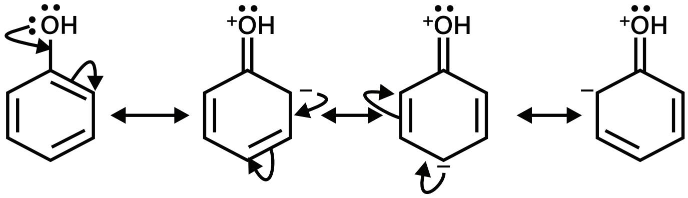
This is the reason for why nitro group deactivates the benzene ring towards the electrophilic substitution reaction.

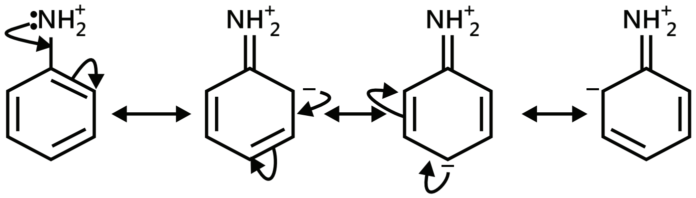
**(d)** In phenol, the -OH group shows +M effect due to the delocalization of a lone pair on the oxygen atom towards the ring.



Thus the electron density on the benzene ring is increased particularly on ortho and para positions.

Hence phenol is more reactive towards electrophilic substitution reactions. The substitution is favoured more at ortho and para positions.

**(e)** The -NH$_2$ group in aniline also exhibits +R effect. It releases electrons towards the benzene ring through delocalization. As a result, the electron density on the benzene ring increases particularly at the ortho and para positions. Thus, aniline activates the ring towards electrophilic substitution.

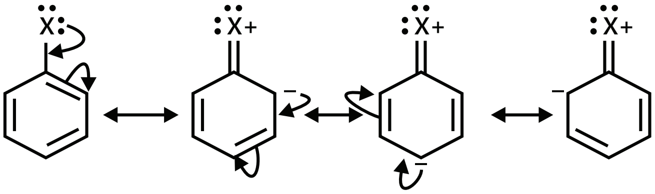


It is also worth mentioning that the electron density on nitrogen in aniline decreases due to the delocalization which is the reason for its less basic strength when compared to ammonia and alkyl amines.

### Inductive Effect Vs Resonance Effect

In most cases, the resonance effect is stronger and outweighs inductive effect.

For example, the -OH and -NH$_2$ groups withdraw electrons by the inductive effect (-I). However they also release electrons by delocalization of lone pairs (+R effect). Since the resonance effect is stronger than the inductive effect the net result is of the electron releasing to rest of the molecule. This is clearly observed in phenol and aniline, which are more reactive than benzene towards electrophilic substitution reactions.

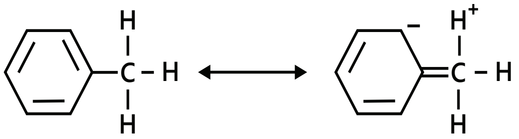


Whereas the inductive effect is stronger than the resonance effect in case of halogen atoms. These are electronegative and hence exhibit -I effect. However, at the same time they also release electrons by the delocalization (+R effect) of the lone pair. This is evident in the case of the reactivity of halobenzenes, which are less reactive than benzene towards electrophilic substitution due to -I effect of halogens.

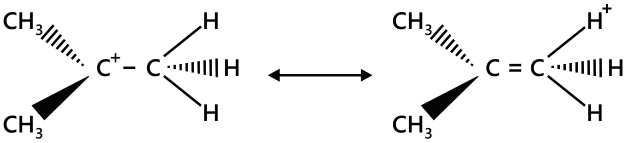
However, it is interesting to note that the substitution is directed at ortho and para positions rather than meta position. It can be ascribed to the fact that the electron density is increased at ortho and para positions due to +R effect of halogens as shown below.

## 6.4 Hyper Conjugation

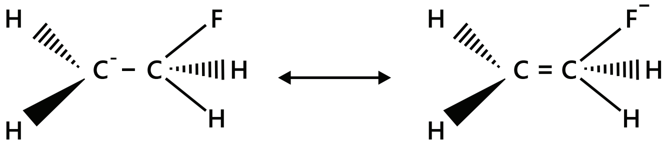
The displacement of $\sigma$-electrons towards the multiple bond occurs when there are hydrogens on the $\alpha$-carbon (which is adjacent to the multiple bond). This results in the polarization of the multiple bond. In the formalism that separates bonds into $\sigma$ and $\pi$ types, hyper conjugation is the interaction of $\sigma$-bonds (e.g. C–H, C–C, etc.) with a $\pi$ network. This conjugation between electrons of single (H-C) bond with multiple bonds is called hyperconjugation. This occurs when the sigma (s) electrons of the H-C bond that is attached to an unsaturated system, such as double bond or a benzene ring, enter into conjugation with the unsaturated system. This interaction is customarily illustrated by contributing structures, e.g. for toluene (below), sometimes said to be an example of 'heterovalent' or 'sacrificial hyper conjugation', so named because the contributing structure contains one two-electron bond less than the normal Lewis formula for toluene:



At present, there is no evidence for sacrificial hyper conjugation in neutral hydrocarbons. The concept of hyper conjugation is also applied to carbonium ions and radicals, where the interaction is now between $\sigma$-bonds and an unfilled or partially filled $\pi$- or p-orbital. A contributing structure illustrating this for the *tert*-butylcation is:



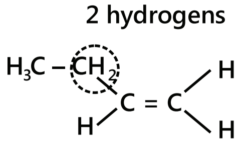
This latter example is sometimes called an example of 'isovalent hyper-conjugation' (the contributing structure containing the same number of two-electron bonds as the normal Lewis formula). Both structures shown on the right hand side are also examples of 'double bond-no-bond resonance'. The interaction between filled π- or p-orbitals and adjacent antibonding $\sigma^*$ orbitals is referred to as 'negative hyperconjugation', as for example in the fluoroethyl anion:



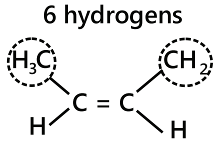
### Consequences and Applications of Hyperconjugation

**(a) Stability of alkenes:** A general rule is that, the stability of alkenes increases with increase in the number of alkyl groups (containing hydrogens) on the double bond. It is due to the increase in the number of contributing no bond resonance structures.

For example, 2-butene is more stable than 1-butene. This is because in 2-butene, there are six hydrogens involved in hyperconjugation whereas there are only two hydrogens involved in case of 1-butene. Hence the contributing structures in 2-butene are more and is more stable than 1-butene.

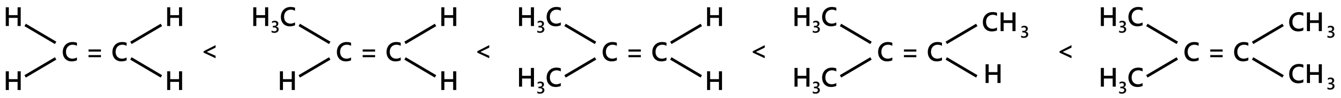


1-butene

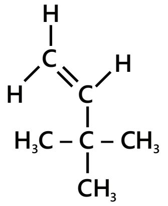


2-butene

The increasing order of stability of alkenes with increases in the number of methyl groups on the double bond is depicted below.



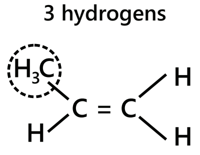
This order is supported by the heat of hydrogenation data of these alkenes. The values of heats of hydrogenation decrease with the increase in the stability of alkenes. Also the heats of formation of more substituted alkenes are higher than expected. However it is important to note that the alkyl groups attached to the double bond must contain at least one hydrogen atom for hyperconjugation. For example, in case of the following alkene containing a tert-butyl group on doubly bonded carbon, the hyperconjugation is not possible.



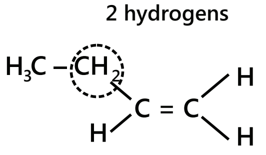
No H atoms on a carbon
Hence no hyperconjugation.

It is also important to note that the effect of hyperconjugation is stronger than the inductive effect.

For example, the positive inductive effect of ethyl group is stronger than that of methyl group. Hence, based on inductive effect, 1-butene is expected to be more stable than propene. However propene is more stable than 1-butene. This is because there are three hydrogens on α-methyl group involved in hyperconjugation. Whereas, in 1-butene there are only two hydrogen atoms on -$CH_2$ group that can take part in hyperconjugation.



propene

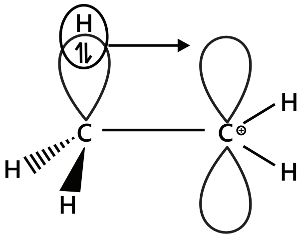


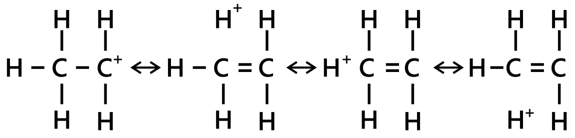
1-butene

**(b) Stability of carbocations (carbonium ions):** The ethyl carbocation, $CH_3$-$CH_2$+ is more stable than the methyl carbocation, $CH_3$+.

This is because, the σ-electrons of the α-C-H bond in ethyl group are delocalized into the empty p-orbital of the positive carbon center and thus by giving rise to the 'no bond resonance structures' as shown below.

Whereas hyperconjugation is not possible in methyl carbocation and hence is less stable.

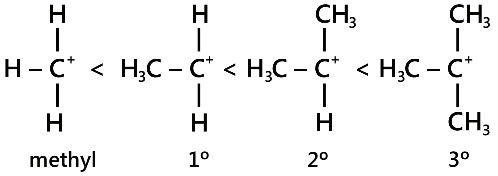




hyperconjugation in ethyl carboninum ion

In general, the stability of carbonium ions increases with the increase in the number of alkyl groups (containing hydrogen) attached to the positively charged carbon due to increase in the number of contributing structures to hyperconjugation.

Note: This type of hyperconjugation can also referred to as isovalent hyperconjugation since there is no decrease in the number bonds in the no bond resonance forms. Thus the increasing order of stability of carbocations can be given as: methyl < primary < secondary < tertiary as depicted below:

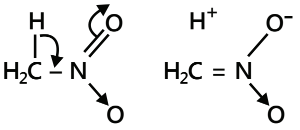


$$H-\overset{H}{\underset{H}{C^+}} < H_3C-\overset{H}{\underset{H}{C^+}} < H_3C-\overset{CH_3}{\underset{H}{C^+}} < H_3C-\overset{CH_3}{\underset{CH_3}{C^+}}$$

**(c)** **Stability of free radicals:** The stability of free radicals is influenced by hyperconjugation as in case of carbonium ions. The $\sigma$-electrons of the $\alpha$-C-H bond can be delocalized into the p-orbital of carbon containing an odd electron. Due to hyperconjugation, the stability of free radicals also follow the same order as that of carbonium ions i.e., methyl < primary < secondary < tertiary.

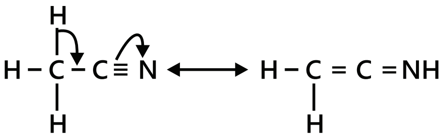
**(d)** **Dipole moment and bond length:** The dipole moment of the molecules is greatly affected due to hyperconjugation since the contributing structures show considerable polarity. The bond lengths are also altered due to change in the bond order during hyperconjugation. The single bond may get a partial double bond character and vice versa.

E.g. The observed dipole moment of nitro methane is greater than the calculated value due to hyperconjugation. The observed C –N bond length is also less than the expected value due to same reason.

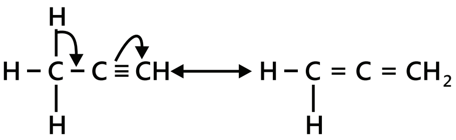


Hyperconjugation in nitroethane

The same arguments can be applied to shortening of C-C bond adjacent to -C≡N in acetonitrile and also the C-C bond adjacent to the -C≡C in propyne. Also note that the observed dipole moments are again different from their expected values.



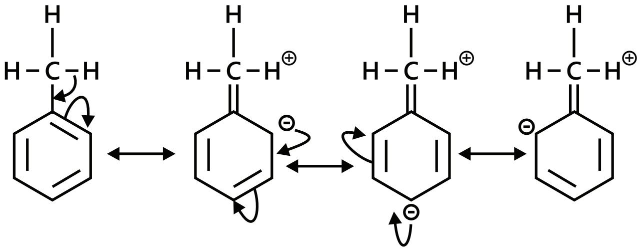
Acetonitrile



Propyne

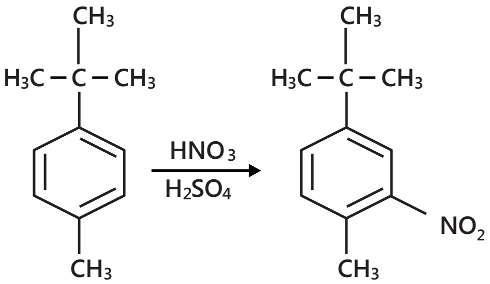
**(e)** **Reactivity & orientation of electrophilic substitution on benzene ring:** In Toluene, the methyl group releases electrons towards the benzene ring partly due to the inductive effect and mainly due to hyperconjugation. Thus the reactivity of the ring towards electrophilic substitution increases and the substitution is directed at ortho and para positions to the methyl group.

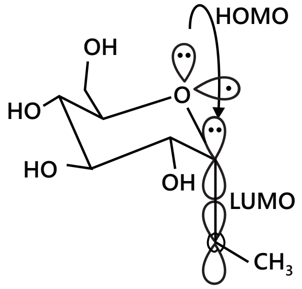
The no bond resonance forms of toluene due to hyperconjugation are shown below.



Hyperconjugation in toluene

From the above diagram, it can be seen clearly that the electron density on the benzene ring is increased especially at ortho and para positions. Since the hyperconjugation overpowers the inductive effect, the substitution (e.g. nitration) on the following disubstituted benzene occurs ortho to the methyl group. In the tert-butyl group, there are no hydrogens on the carbon directly attached to the benzene ring. Hence it cannot be involved in hyperconjugation.

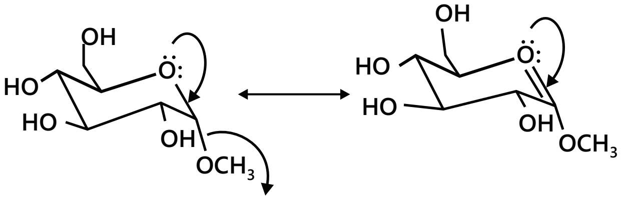




**Anit periplanar arrangement is only possible in α from**

Also note that the tert-butyl group is bulky and hinders the approach of electrophile.

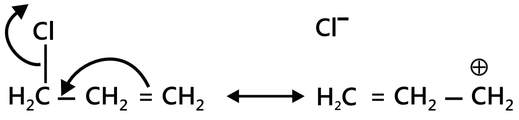
**(f)** **Anomeric effect:** The general tendency of anomeric substituents to prefer an axial position is called the Anomeric effect. For example, the α-methyl glucoside is more stable than the β-methyl glucoside due to hyperconjugation. In α-methyl glucoside, the non-bonding HOMO with a pair of electrons on the ring oxygen is antiperiplanar to the antibonding LUMO of C-O bond in the methoxy group. This allows hyperconjugation between them and thus stabilizes the α-form.



**Hyperconjugation in α-D-methylglucosicle**

Whereas, in β-methyl glucoside the methoxy group is at an equatorial position and cannot involve in hyperconjugation since it is not antiperiplanar to the lone pair on the ring oxygen. Therefore β-methyl glucoside is less stable than the α- methyl glucoside.

**(g)** **Reverse hyperconjugation:** In case of α-halo alkenes, the delocalization of electrons occurs towards the halogen group through the hyperconjugative mechanism. It is referred to as reverse hyperconjugation. The dipole moments of α-halo alkenes are augmented due to this phenomenon.



$$\overset{Cl}{H_2C} - CH_2 = CH_2 \longleftrightarrow Cl^- \quad H_2C = CH_2 - \overset{\oplus}{CH_2}$$

**reverse hyperconjugation**

## PLANCESS CONCEPTS

**(a)** Inductive effect : It operatives through sigma bonds and is permanent effect

**(b)** Mesomeric effect : It operates through pi bonds and is permanent effect.

**(c)** Resonance effects :

**(i)** Conditions –

- Same positions of atoms.
- Same number of paired and unpaired elections
- The should differ only in the arrangement of electrons

**(ii)** Misconception –

- The canonical forms have no real existence.
- The molecule does not exist for a certain fraction of time in one canonical from and other fractions of time in other canonical forms.
- The molecule as such has a single structure which is the resonance hybrid of the canonical forms and which cannot be represented by a single Lewis structure,

**(d)** Hyperconjugation : it involves the delocalization of the σ electrons of the C-H bond with the unshared p- orbital.

**(e)** Electromeric effect: It involves temporary polarization in the presence of a polar reagent.

**(f)** Generally the mesomeric effect is the strongest followed hyperconjugation and then the inductive effect.

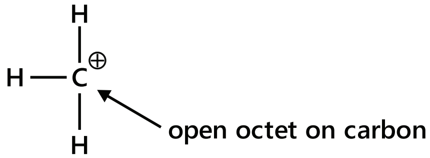
**Neeraj Toshniwal (JEE 2010, AIR 443)**

# 7. REACTION INTERMEDIATES

## 7.1 Carbocations

### 7.1.1 Introduction

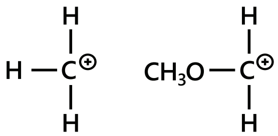
A molecule in which a carbon atoms bears three bonds and a positive charge is called a carbocation. Carbocations are generally unstable because they do not have eight electrons to satisfy the octet rule.



### 7.1.2 Classification of Carbocation

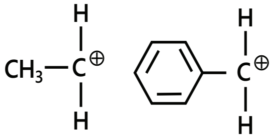
In order to understand carbocations, we need to learn some basic carbocation nomenclature. A primary carbocation is one in which there is one carbon group attached to the carbon bearing the positive charge. A secondary carbocation is one in which there are two carbons attached to the carbon bearing the positive charge. Likewise, a tertiary carbocation is one in which there are three carbons attached to the carbon bearing the positive charge.

Methyl carbocations



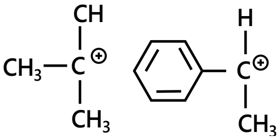
No C – C′ bonds

Primary (1°) carbocations



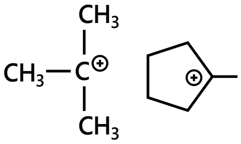
One C–C′ bonds

Secondary (2°) carbocations



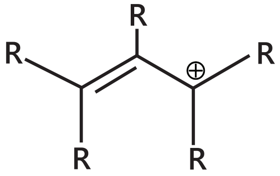
Two C – $C^+$ bonds

Tertiary (3°) carbocations

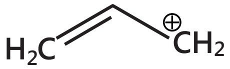


Three C – $C^-$ bonds

If the carbon bearing the positive charge is immediately adjacent to a carbon-carbon double bonds, the carboacation is called an allylic carbocation. The simplest case (all R—H) is called the allyl carbocation.

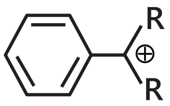


**Generic allylic carbocation**

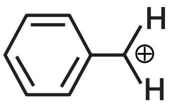


**The allyl carbocation**

If the carbon bearing the positive charge is immediately adjacent to benzene ring, the carbocation is termed a benzylic carbocation. The simplest case is called the benzyl carbocation.

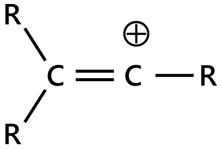


**Gneric benzylic carbocation**

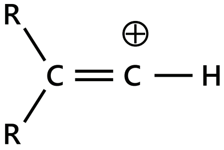


**The benzyl carbocation**

If the carbon bearing the positive charge is part of an alkene, the carbocation is termed a vinylic carbocation. The simplest case is called the vinyl carbocation. Note that the carbon bearing the positive charge has two attachments and thus adopts sp hybridations and linear geometry.

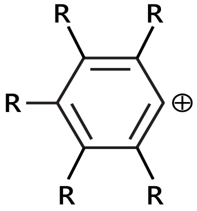


**Gneric benzylic carbocation**

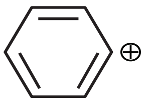


**The vinyl carbocation**

If the carbon bearing the positive charge is part of a benzene ring, the carbocation is termed as an aryl carbocation. The simplest case is called the phenyl carbocation.



**Generic aryl carbocation**

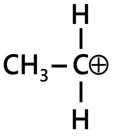


**The phenyl carbocation**

### 7.1.3 Carbocation Stability

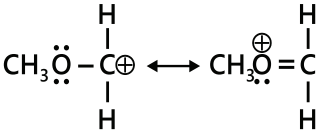
The stability of carbocations is dependent upon a few factors. One factor that decides the stability of a carbocation is resonance. Resonance is a stabilizing feature to a carbocation because it delocalizes the positive charge and creates additional bonding between adjacent atoms. Decreasing the electron deficiency increases the stability.

Consider the following:



$$\mathrm{CH_3{-}}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\oplus$$

**NO resonance**



$$\mathrm{CH_3\ddot{\underset{\cdot\cdot}{O}}{-}}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\oplus \longleftrightarrow \mathrm{CH_3}\overset{\oplus}{\underset{\cdot\cdot}{\mathrm{O}}}{=}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}$$

**Resonance**

The structure on the left does not have any resonance contributors in which electrons are donated to the carbon with the open octet. Compare this with the carbocations that has resonance and a delocalized positive charge. Charge delocalization imparts stability, so the structure with resonance is lower in energy.

In the example shown above, an oxygen atom lone pair is involved in resonance that stabilizes a Allylic and benzylic carbocations enjoy resonance stabilization by delocalization of the positive charge to the adjacent $\pi$ bond(s). Vinylic and aryl carbocations do not enjoy resonance stabilization because their p electron clouds are perpendicular to the vacant p orbitals of the carbocation. (Recall that resonance requires the interacting orbitals to be parallel so they can overlap. Without overlap there can be no resonance.)

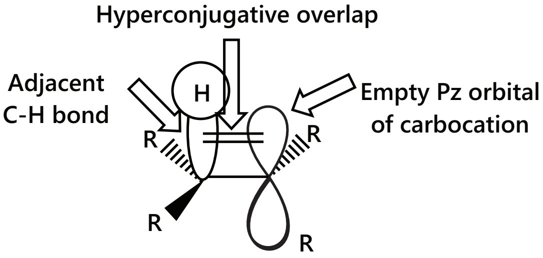
Note the influence of the inductive effect versus the resonance on the energies of these molecules. The oxygen atom that is bonded to the carbocation on the right is more electronegative than the corresponding hydrogen atom in the left-hand structure. We would think that the inductive effect would pull electron density away from the carbocation, making it higher in energy. In this case, the carbocation stabilization by resonance electron donation is a more significant factor than carbocation destabilization by inductive electrons withdrawal.

Methyl and primary carbocations without resonance are very unstable, and should never be invoked in a reaction mechanism unless no other pathway is possible. More stable carbocations (secondary or tertiary with resonance, or any carbocation with resonance) are sufficiently stable to be formed in a mechanism under reasonable reaction conditions.

The second factor that should be considered when thinking about carbocation stability is the number of carbons attached to the carbon carrying the positive charge. We look at the number of

bonding electrons that are attached to the carbocation because those bonding electrons will help in alleviating the positive charge. Bonding electrons from adjacent s bonds may overlap with the unoccupied p orbital of the carbocation.

This phenomenon is termed hyper conjugation. Since the overlap supplies electron density to the electron-deficient carbocation carbon, we predict that increasing the number of hyper conjugative interactions increases carbocation stability. Extending this idea, we predict that increasing the number of bonds adjacent to the carbocation by increasing the number of alkyl groups attached to the carbocation carbon results in an increases in carbocation stability. For example, a tertiary carbocation should be more stable than a secondary carbocation. This predication is accurate.



This suggests that any adjacent bonding electron pair will participate in carbocation hyperconjugation. However, only C—H and C—C bonds provide a significant level of increased stability.

Despite the importance of both the factors of resonance and hyperconjugation, resonance usually wins out. For example. a primary carbocation with resonance is more stable than a secondary carbocation without resonance and is usually more stable than a tertiary carbocation without resonance.

**The general rules for carbocation stability can be summarized as follows.**

(a) Increasing substitution increases stability.

$CH_3^+$ (methyl; least stable) < $RCH_2^+$ (1°) <$R_2CH^+$ (2°) < $R_3C^+$ (3° ; most stable)

(b) Resonance is more important than substitution. For example, a secondary carbocation without resonance is generally less stable than a primary carbocation with resonance.

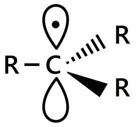
In vinylic carbocation, the positive charge is assigned to a carbon with sp hybridization. How does this influence the carbocation's stability? A sp orbital has more character than an $sp^2$ orbital. Electrons in an s orbital are closer to the nucleus and therefore more tightly held than electrons in a p orbital. This can be taken to mean that the electronegativity of carbon increases with the increasing s character. Thus sp carbon (most s character, most electronegative) > $sp^2$ > $sp^3$ (least s character; least electronegative). Electronegativity is a measure of electron attraction. So the stability of a cation is affected by the electronegativity of the atom bearing the positive charge. The more electronegative the atom, the less stable the cation. A vinylic carbocation carries the positive charge on a sp carbon which is more electronegative than an $sp^2$ carbon of an alkyl carbocation. Therefore a primary vinylic carbocation is less stable then a primary alkyl carbocation. Similar reasoning explains why an aryl carbocation is less stable than a typical secondary alkyl carbocation such as cyclohexyl carbocation.

Because of their reduced stability, vinyl and aryl carbocations are not often encountered.

## 7.2 Free Radical

A molecular entity such as $\cdot CH_3$ or $\cdot SnH_3$ or $\cdot Cl$ possessing an unpaired electron. (In these formulae, the dot symbolizing the unpaired electron should be placed so as to indicate the atom of highest spin density, if this is possible.) Paramagnetic metal ions are not normally regarded as radicals. However, similarities have been found between certain paramagnetic metal ions and radicals. Depending upon the core atom that possesses the unpaired electron, the radicals can be described as carbon-, oxygen-, nitrogen-, metal-centred radicals. If the unpaired electron occupies an orbital having considerable s or more or less pure p character, the respective radicals are termed σ- or π-radicals. In the past, the term 'radical' was used to designate a substituent group bound to a molecular entity, as opposed to 'free radical', which nowadays is simply called radical. The bound entities may be called groups or substituents, but should no longer be called radicals.

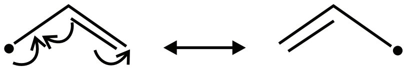
**Radical Structure:** We can present the general radical as $R_3C$.



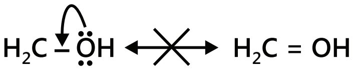
Note that the radical is NOT charged (its reactivity and electrophilic nature does not come from a charge but from its unpaired electron). Also, note how the radical looks $sp^2$ with a planar configuration. The unpaired electron occupies the unhybridized 2p orbital.

**Radical Stability:** Like carbocations, radicals are electron deficient. Therefore, we can think of the same factors in carbocation stability and see if they apply in radical stability:

**Resonance:** Like carbocations, radicals can gain stability through resonance. That is, a radial with resonance that can delocalize the electron deficiency is more stable. Recall that reactions tend to produce the more stable product. Therefore, reactions will tend towards the more stable radical. This will become important when we are considering a radical reaction and determining the favoured product:



However, unlike carbocations, radicals do not gain resonance from lone pairs. Why?



$H_2\dot{C} - \ddot{\underset{..}{O}}H \not\leftrightarrow H_2C = OH$

Look at this resonance stabilization step carefully; note that the carbon has 9 electrons attributed to it. This is not possible .

Number of substituents: We know that radicals are electron deficient species. Therefore, stability is increased with increasing numbers of electron-donating substituents, such as alkyl group:

$\dot{C}H_3 < R\dot{C}H_2 < R_2\dot{C}H < R_3\dot{C}$

Recall that we have almost never worked with methyl carbocations. However, methyl radicals are sometimes considered because unlike carbocations, methyl radicals are only missing one electron (not a pair of electrons) and thus are slightly more stable than the methyl carbocation.

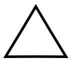
## 7.3 Carbanion

A **carbanion** is an anion in which carbon has an unshared pair of electrons and bears a negative charge usually with three substituents for a total of eight valence electrons.[1] The carbanion exists in a trigonal pyramidal geometry. Formally, a carbanion is the conjugate base of a **carbon acid**.

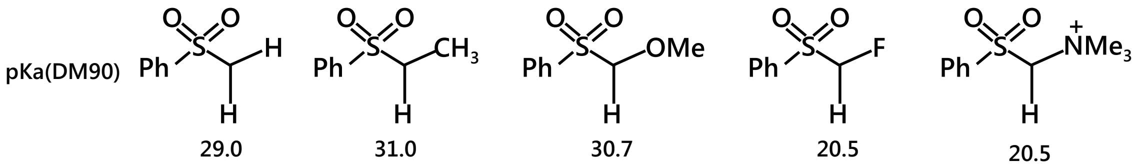
$R_3CH + B \rightarrow R_3C^- + H—B$ where B stands for the base. A carbanion is one of several reactive intermediates in organic chemistry.

### 7.3.1 Effect of Substituents on Carbanion Stability

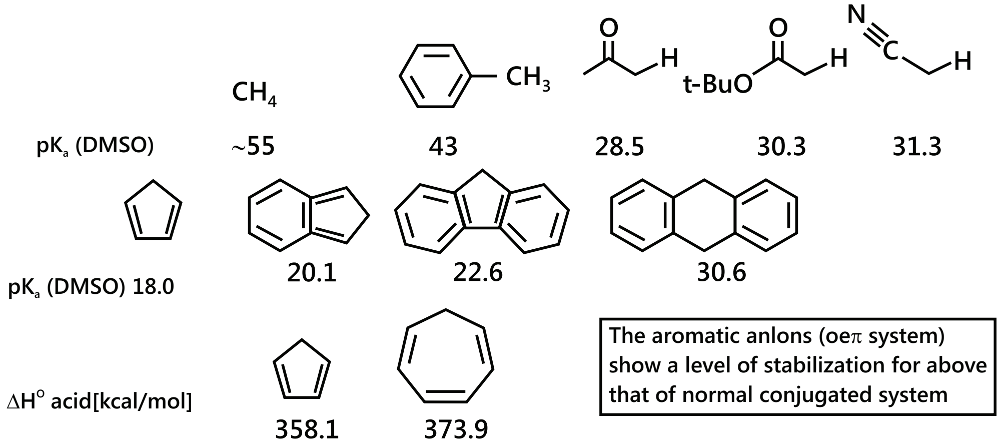
**(a)** **Hybridization:** In almost all areas of organometallic chemistry the primary subdivision of reactivity types is by the hybridization of the C-M carbon atom (methyl/alkyl, vinyl/aryl, alkynyl). A key second subdivision is the presence of conjugating substituents (allyl/allenyl/propargyl/benzyl). The fractional s-character of the C-H bonds has a major effect on the kinetic and thermodynamic acidity of the carbon acid. Only s-orbitals have electron density at the nucleus, and a lone pair with highly fractional s character has its electron density closer to the nucleus, and is hence stabilized. This can be easily seen in the gas-phase acidity of the prototypical C-H types, ethane, ethylene and acetylene, as well as for cyclopropane, where the hybridization of the C—H types, ethane, ethylene and acetlylene, as well as for cyclopropane, where the hybridization of the C—H bond is similar to that in ethylene.

| | $CH_3-CH_3$ |  | $CH_2=CH_2$ | $CH\equiv CH$ |
|---|---|---|---|---|
| $\Delta H^{o}$ acid (kcal/mol) | 420 | 411 | 406 | 375 |

**(b)** **Inductive effects:** Electron-withdrawing substituents will inductively stabilize negative charges on nearby carbons. These effects are complex, since electronegative substituents interact with carbanions in other ways as well (e.g. O and F substituents have lone pairs, which tends to destabilize adjacent carbanion centers.)



**(c) Conjugation and Delocalization:** Delocalization of negative charge, especially onto electronegative atoms, provides potent stabilizations of carbanionic centers. Since almost all conjugating substituents are also more electronegative than H or $CH_3$, there is usually a significant inductive contribution to the stabilization.



The aromatic anlons (oeπ system) show a level of stabilization for above that of normal conjugated system

**(d) Lone Pair Effects:** For the first low elements N, O, F and sometimes also for higher elements, the presence of lone pairs has a strong destabilizing effect on a directly bonded carbanion centre. This has several effects on carbanion structure : there are substantial rotational barriers around the C—C bond and the carbanion center is usually more pyramidal in nature.

Measurement of CH acidities in solution

pK = 0-16 direct measurements in water.

pK = 0-33 Direct measurements in dimethyl sulfoxide (DMSO).

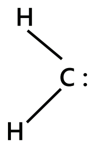
pk = 33-45 Direct measurements in THF and ether on ion pairs

pK = 45+ Only indirect measurements in nonpolar solvents.

- Kinetic acidities
- Bronsted equation Ka = ak
- Usually only on contact ion pairs
- Aggregates are frequently present
- Gas phase acidities ($\Delta H°_{acid}$)

## 7.4 Carbene

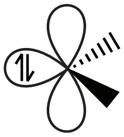
In chemistry, a **carbene** is a molecule containing a neutral carbon atom with a valence of two and two unshared valence electrons. The general formula is R-(C**:**)-R′ or R=C**:**. The term "carbene" may also refer to the specific compound $H_2C$**:** , also called methylene, the parent hydride from which all other carbene compounds are formally derived. Carbenes are classified as either singlets or triplets depending upon their electronic structure. Most carbenes are very short lived, although persistent carbenes are known. One well studied carbene is $Cl_2C$**:** or dichlorocarbene, which can be generated *in situ* from chloroform and a strong base.



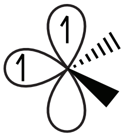
**methylene (carbene)**

### 7.4.1 Structure and Bonding

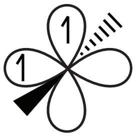
**Singlet and Triplet Carbenes**



singlet



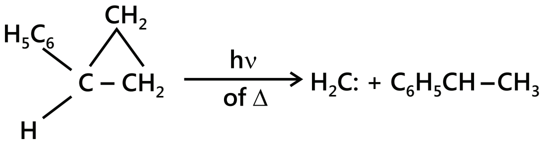
triplet

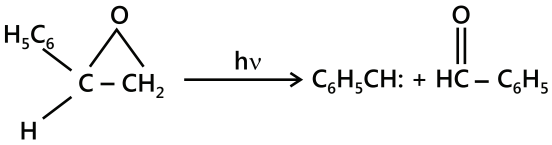


triplet

The two classes of carbenes are singlet and triplet carbenes. Singlet carbenes are spin-paired. In the language of valence bond theory, the molecule adopts a $sp^2$ hybrid structure. Triplet carbenes have two unpaired electrons. They may be either linear or bent, i.e. sp or $sp^2$ hybridized, respectively. Most carbenes have a nonlinear triplet ground state, except for those with nitrogen, oxygen, or sulfur atoms, and halides directly bonded to the divalent carbon. Carbenes are called singlet or triplet depending on the electronic spins they possess. Triplet carbenes are paramagnetic and may be observed by electron spin resonance spectroscopy if they persist long enough. The total spin of singlet carbenes is zero while that of triplet carbenes is one .Bond angles are 125-140° for triplet methylene and 102° for singlet methylene (as determined by EPR). Triplet carbenes are generally stable in the gaseous state, while singlet carbenes occur more often in aqueous media. For simple hydrocarbons, triplet carbenes usually have energies 8 kcal/mol (33 kJ/mol) lower than singlet carbenes. thus, in general, triplet is the more stable state (the ground state) and singlet is the excited state species. Substituents that can donate electron pairs may stabilize the singlet state by delocalizing the pair into an empty p-orbital.

**Formation:** From photochemical or thermal cleavage of cyclopropanes and oxiranes



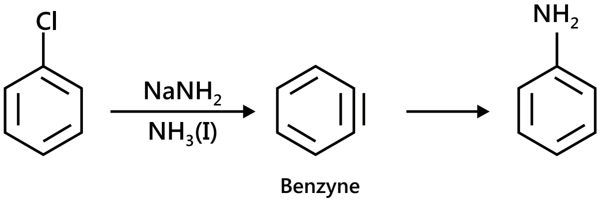


## 7.5 Nitrene

In chemistry, a **nitrene** (R-N:) is the nitrogen analogue of a carbene. The nitrogen atom has only 6 valence electrons and is therefore considered an electrophile. A nitrene is a reactive intermediate and is involved in many chemical reactions. In the most simple nitrene, the linear Imidogen (:N-H), two of the 6 available electrons form a covalent bond with hydrogen, two others create a free electron pair and the two remaining electrons occupy electrons in each of the p orbitals and the high energy form is the singlet state with an electron pair filling one p orbital and leaving the other one vacant. $R-\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}:$ nitrene

## 7.6 Benzyne

**Arynes** or **benzynes** are highly reactive species derived from an aromatic ring by removal of two ortho substituents. Arynes usually are best described as having a strained triple bond; however, they possess some biradical character as well.



## PLANCESS CONCEPTS

**(a) Carbocation**

- **(i)** They cannot be optically active because of their planar structure.
- **(ii)** Stability: Electron donating groups and hyperconjugation stabilizes the carbocation whereas the electron withdrawing group destabilizes the carbocation.
- **(iii)** Generally aromatic cations are the most stable
- **(iv)** Methyl cyclopropyl cation is exceptionally stable.
- **(v)** Tert-butyl cation is also very stable due to a larger number of hyperconjugating structures and the inductive effect of 3 alkyl groups.

**(b) Carbanion**

- **(i)** They can be optically active.
- **(ii)** Stability: Electron donating groups destabilize the carbanion whereas the electron withdrawing group stabilizes the carbanion.
- **(iii)** Aromatic carbanions are generally most stable.

**(c) Carbenes:** Are an electron deficient species with 6 electrons.

- **(i)** Triplet: They have 2 unpaired electrons in 2 different orbitals.
- **(ii)** Singlet: They have two paired electrons in a single orbital.

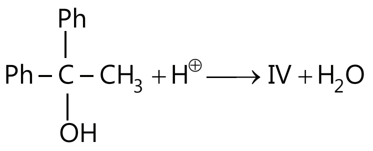
**Aman Gour (JEE 2010, AIR 443)**

**Illustration 10:** Name the intermediate species formed in the following reactions:

a. $CH_3CH_2-\underset{\oplus}{N}\equiv\underset{\bullet\bullet}{N}\longrightarrow I+:N\equiv N:$

b. $CH_3CH_2-C\equiv C-H+\overset{\oplus\ominus}{K NH_2}\longrightarrow II+H_3$

c. $Ph-CH=CH-Me+HBr\longrightarrow III+Br^-$

d. 
$Ph-\overset{\overset{\displaystyle Ph}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CH_3+H^{\oplus}\longrightarrow IV+H_2O$

e. $CH_3CH_2\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}H\xrightarrow{-\bar{e}}V\longrightarrow VI+CH_3$

f. $CH_3-\overset{\bullet\bullet}{N}=\overset{\bullet\bullet}{N}-CH_3\xrightarrow{\Delta}VII+N_2$

g. $CH_3-CHI_2+Zn/Cu\xrightarrow{\Delta}VIII+ZnI_2$

h. $PhCH_2Cl+AlCl_3\longrightarrow IX+[AlCl_4]^{\ominus}$

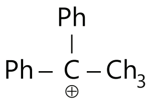
i. $CH_3-C\equiv C-CH_3+Li\xrightarrow[C_2H_5OH]{liq.NH_3}X+Li^{\oplus}$ **(JEE ADVANCED)**

**Sol:**

a. $CH_3\overset{\oplus}{C}H_2$ (Carbocation)

b. $CH_3CH_2 - C \equiv C^{\ominus} K^{\oplus}$ (carbanion)

c. $Ph\overset{\oplus}{C}H - CH_2Me$ ($2^{o}$ Benzylic carbocation)

d. 

$Ph - \underset{\oplus}{\overset{\overset{Ph}{|}}{C}} - Ch_3$

e. **$[CH_3CH_2 - \dot{O}\!: - H]^{\oplus}$ (Radical cation, loss of $e^-$ s from O atom can occur since it has higher energy than bonded $e^-$ S)**

**$[\dot{C}H_3 + CH_2 = \underset{\cdot\cdot}{\overset{\oplus}{O}} - H \leftrightarrow \overset{\oplus}{C}H_2 - \underset{\cdot\cdot}{\overset{\cdot\cdot}{O}} - H]$**

**(Resonance stabilised cation)**

f. $2CH_3$- (free radical)

g. Simmons – Smith reaction

($CH_3CH$:) (singlet carbene)

h. $Ph\overset{\oplus}{C}H_2$ (Benzyl carbocation)

i. $(X)\underset{1}{C}H_3 - \underset{2}{C} - \underset{3}{\overset{\overset{\cdot\cdot}{\oplus}}{C}} - \underset{4}{CH_3}$ (Radical anion $C^2$ is vinyl radical and $C^3$ is vinyl carbanion.

# 8. ACIDITY AND BASICITY IN ORGANIC COMPOUNDS

## 8.1 Acidity

Five key factors that influence acidity:

**Factor #1 – Charge:** Removal of a proton, $H^+$, decreases the formal charge on an atom or molecule by one unit. This is, of course, is the easiest to do when an atom bears a charge of +1 in the first place, and becomes progressively more difficult as the overall charge becomes negative. The acidity trends reflect this:

Acidity increases with the increasing positive charge on an atom.

| | | | | | |
|---|---|---|---|---|---|
| | $HO^{\ominus}$ | < | $H_2O$ | < | $H_3O^{\oplus}$ |
| pKa | | | 15.7 | | –1.7 |

$$\xrightarrow{\text{increasing acidity}}$$

| | | | | | |
|---|---|---|---|---|---|
| | $NH_2^{\ominus}$ | < | $NH_3$ | < | $NH_4^{\oplus}$ |
| pKa | | | 38 | | 9.2 |

Note that once a conjugate base ($B^-$) is negative, a second deprotonation will make the dianion ($B^{2-}$). While far from impossible, forming the dianion can be difficult due to the build-up of negative charge and the corresponding electronic repulsions that result.

**Factor #2 – The Role of the Atom:** This point causes a lot of confusion due to the presence of two seemingly conflicting trends. Here's the first point: acidity increases as we go across a row in the periodic table. This makes sense, right? It makes sense that HF is more electronegative than $H_2O$, $NH_3$, and $CH_4$ due to the greater electronegativity of fluorine versus oxygen, nitrogen, and carbon. A fluorine bearing a negative charge is a happy fluorine.

But here's the seemingly strange thing. HF itself is not a "strong" acid, at least not in the sense that it ionizes completely in water. HF is a weaker acid than HCl, HBr, and HI. What's going on here?

Across the periodic table, acidity increases with electronegativity

| | $CH_4$ < | $NH_3$ < | $H_2O$ < | HF |
|---|---|---|---|---|
| pKa | ~50 | 38 | 15.7 | 3.2 |
| Electronegativity | 2.5 | 3.0 | 3.4 | 4.0 |

but down the periodic table, acidity increases with size.

| | HF < | HCl < | HBr < | HI |
|---|---|---|---|---|
| pKa | 3.2 | –8.0 | –9.0 | –10 |
| Electronegativity | 4.0 | 3.0 | 2.8 | 2.5 |
| Ionic radius (picometres) | 133 | 181 | 196 | 220 |

Also holds for oxygen versus sulphur .....

| | $H_2O$ | < | $H_2S$ |
|---|---|---|---|
| pKa | 15.7 | | 7.0 |
| | $H_3COH$ | < | $H_3CSH$ |
| pKa | 15.5 | | 10 |

You could make two arguments for why this is. The first reason has to do with the shorter (and stronger) H-F bond as compared to the larger hydrogen halides. The second has to do with the stability of the conjugate base. The fluoride anion, $F^-$ is a tiny and vicious little beast, with the smallest ionic radius of any other ion bearing a single negative charge. Its charge is therefore spread over a smaller volume than those of the larger halides, which is energetically unfavourable: for one thing, $F^-$ begs for solvation, which will lead to a lower entropy term in the $\Delta G$. Note that this trend also holds for $H_2O$ and $H_2S$, with $H_2S$ being about 10 million times more acidic.

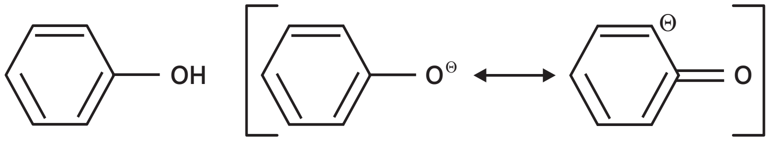
**Factor #3 – Resonance:** A huge stabilizing factor for a conjugate base is if the negative charge can be delocalized through resonance. The classic examples are with phenol ($C_6H_5OH$) which is about a million times more acidic than water. Remember, any structural feature that increases the stability of the conjugate base will increase acidity.

**Key question:** Can the lone pair of the conjugate base participate in resonance with an adjacent $\pi$ bond?

Resonance will increases the stability of the conjugate base (therefore in increasing acidity) because the negative charge can be delocalized

**Example.1** Contrast methanol versus phenol:

$CH_3OH$

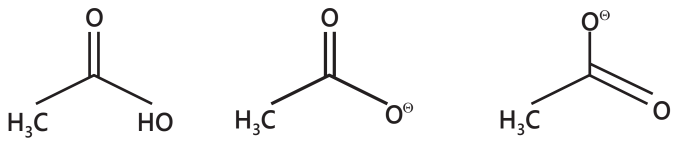


pKa 15 < 10 more acidic

The anion of phenol can be stabilized through resonance

**Example.2** Alcohols (e.g. methanol) versus carboxylic acids

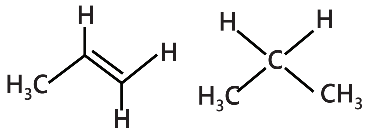
$CH_3OH$



pKa 15 < 4 more acidic

The anion of phenol can be stabilized through resonance

**Question:** Which proton (in red) would you expect to be more acidic?



With acetic acid (pKa of ~5).

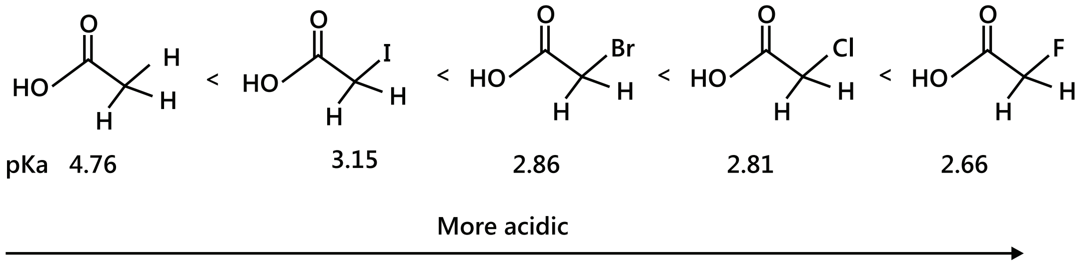
Watch out though – it isn't enough for a π system to simply be adjacent to a proton – the electrons of the conjugate base have to be in an orbital which allows for the effective overlap.

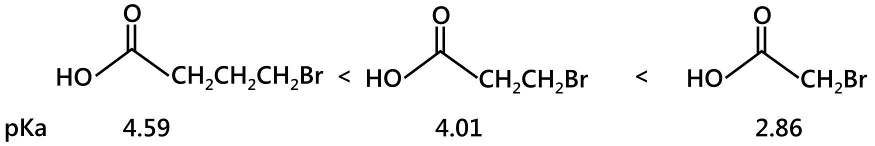
**Factor #4 – Inductive effects:** Electronegative atoms can draw negative charge toward themselves, which can lead to considerable stabilization of conjugate bases. Check out these examples:

Electronegativity and inductive effects:

Two principles – electron withdrawing substituents can increase the acidity of 8 nearby atoms, which increases with electronegativity and decreases with increasing distance to the atom.

Electronegativity increases in the order F > Cl > Br > I :





Predictably, this effect is going to be related to two major factors: The electronegativity of the element (the more electronegative, the more acidic) and the distance between the electronegative element and the negative charge.

**Factor #5 – Orbitals:** Again, the acidity relates nicely to the stability of the conjugate base, and the stability of the conjugate base depends on how well it can accommodate its newfound pair of electrons. The more s character in the orbital, the closer the electrons will be to the nucleus, and the lower in energy (= stable! ) they will be. The higher the s-character of bond to hydrogen, the more acidic it will be.

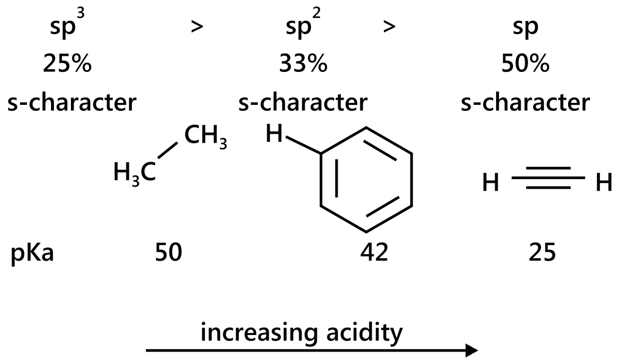


**Illustration 11:** Arrange the following: **(JEE MAIN)**

a. In decreasing order of $pK_b$

I. $C_2H_5NH_2$ II. PhNHMe III. $(C_2H_5)_2NH$ IV. $PhNH_2$

b. In increasing order of basic strength

I. $PhNH_2$ II. $PhNMe_2$ III. $(C_2H_5)_2NH$ IV. $MeNH_2$

c. I. $PhNH_2$ II. P-nitroaniline III. p-Toluidine

d. I. $PhNH_2$ II. PhNHMe III. $PhCH_2NH_2$

e. In decreasing order of basic strength in gas phase.

I. $C_2H_5NH_2$ II. $(C_2H_5)_2NH$ III. $(C_2H_5)_3N$ IV. $NH_3$

**Sol:** The electron donating groups like alkyl groups increase the basic strength of amines whereas the electron with drawing groups like aryl groups decrease the basic nature.

a. IV < II < I < III (aromatic amine < EDG, –Me increase basicity <1° amine < 2° amine)

b. I < II < IV < III (aromatic amine < EDG, –2Me increase basicity < 1°amine < 2° amine)

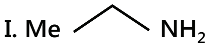
c. II < I < III < (EWG, $-NO_2$, decrease and EDG, $-CH_3$, increase basicity)

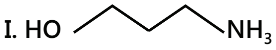
d. I < II < III (aromatic amine < EDG, – Me increase basicity < benzylamine, aliphatic amine)

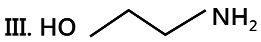
e. IV < I < II < III (–Me increase basicity)

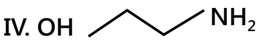
**Illustration 12:** Arrange the following in decreasing order of basicities **(JEE MAIN)**

a.









b. I. $EtNH_2$ II. $MeCONH_2$ III. $PhCONH_2$

c. I. $PrNH_2$ II. $HC \equiv C—CH_2NH_2$ III. $H_2C = CH—CH_2NH_2$

**Sol:** a. I > II > III > IV

The –I effect of OH group decreases the electron density on N atom, and thus decrease its basicity. If –I effect is large distance operating from $(-NH_2)$, then the base is stronger, and vice versa, So, basicity II > III > IV.

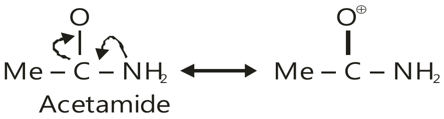
(I) is the strongest base due to +I effect of $(MeCH_2)$ group,

b. I > III > II

i. The +I effect of (Et–) group increases the electron density on N atom and thus increases

basicity and is the strongest base.

ii. (C = O) is EWG and decreases the basicity by the delocalization of electron density from N to O.

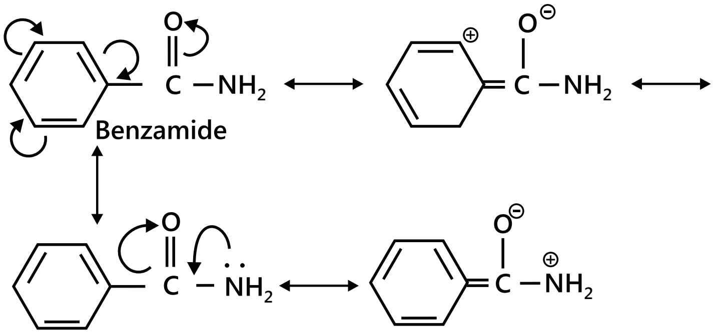


$$\mathrm{Me-\overset{O}{\overset{|}{C}}-NH_2} \longleftrightarrow \mathrm{Me-\overset{O^{\oplus}}{\overset{|}{C}}-NH_2}$$

Acetamide

Both the amides are weaker bases then amine. Unlike amines, amides are amphoteric in nature, i.e., they are insoluble in aqueous acids and do not form salts..

iii. In benzamide $(PhCONH_2)$, there is cross conjugation of (C = O) with Ph groups and with $NH_2$ group, as shown below.

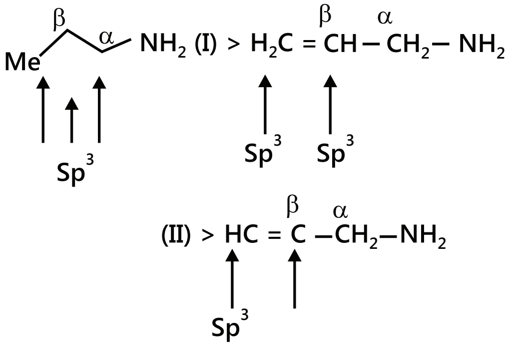


Therefore, electron density on N in benzamide (III) is slightly more than aliphatic amide (II), So, (III) is more basic than (II). Hence, basicity order is $EtNH_2 > PhCONH_2 > MeCONH_2$.

c. Static of hybridization decides the basic character. Basic order is $sp^3 > sp^2 > sp$ hybrid orbitals.

Conversely, the more the s character (as in sp hybrid orbitals) of β-C atom, the more is the electron withdrawing -I effect, and weaker the base. So, the basicity order is:

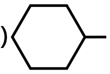
(I)



Alternatively, electron withdrawing -I effect of:

$HC \equiv C-CH_2- > \quad CH_2 = CH—CH_2— \quad > \quad CH_3—CH_2—CH_2—$

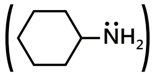
Propargyl Allyl Propyl

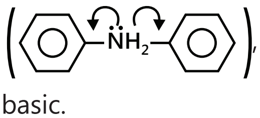
**Illustration 13:** a. **(I)**  **$NH_3$ II. $PH_2NH$ (III) $PhNH_2$** **(JEE MAIN)**

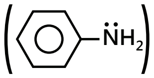
b. Write the conjugate base and conjugate acid of (I) $HOCH_2CH_2NH_2$.

**Sol:** The electron donating groups like alkyl groups increase the basic strength of amines whereas the electron with drawing groups like aryl groups decrease the basic nature.

a. I > III > II

In (I)  electron density on Na atom is localized and hence most base.

In (II) , electron density on N atom can be delocalized in both the Ph rings and is hence, least basic.

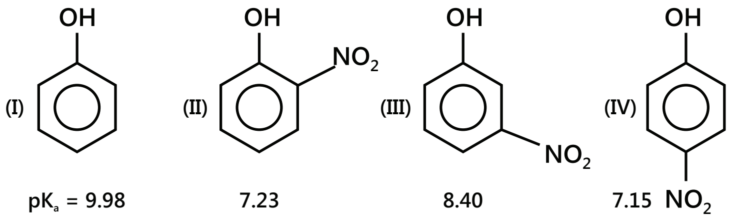

In (III) electron density on N atom is delocalized only in one Ph ring, and hence is less basic than (I) and more basic than (II).

Moreover, (I) is an aliphatic (cyclic) amine, and (II) and (III) are aromatic amines which are less basic than (I), In aromatic amines, L.P. electron on N atoms are delocalized into the ring mainly at o and p positions, thereby weakening the basicity.

b. i. In (I) (HO—CH$_2$—CH$_2$—NH$_2$, OH is more acidic then NH$_2$, So, conjugate base of (I) is O$^\ominus$—CH$_2$—CH—NH$_2$.

ii. In (I) NH$_2$ is more basic than OH, so conjugate acid of (I) is HO —CH$_2$—CH$_2$— $\overset{\oplus}{\text{N}}\text{H}_3$

**Illustration 14:** Compare the acidity of substituted phenolic compounds: **(JEE MAIN)**



**Sol:** Due to – Inductive effect and – Resonance effect of (–NO$_2$) group, in both II and IV, but (–I) at o$^n$ > p$^n$, II should be a stronger acid than IV. But is stronger than II. This is due to intermolecular Hydrogen Bonding formed between hydrogen of OH and Nitro group in II, which results in the release of H$^\oplus$ slightly difficult than in IV.

Acidic character: should be II > IV > III > I. But, the observed order is IV > II> III> I (p$^n$ > o$^n$ > m$^n$ > phenol)

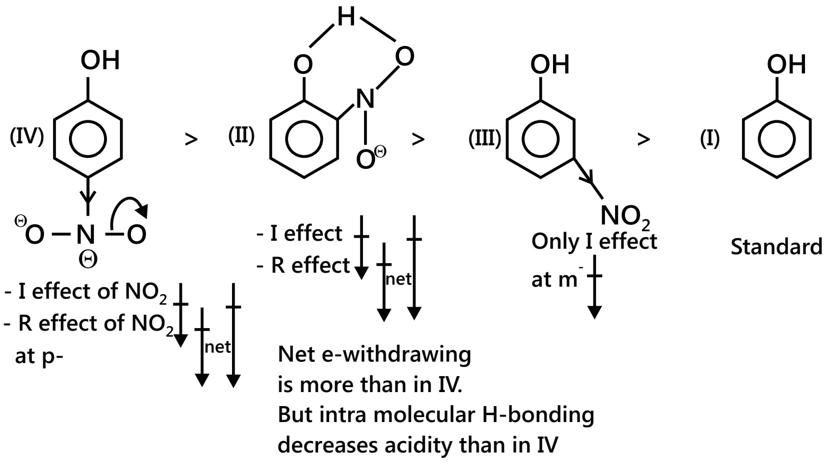
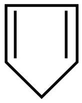
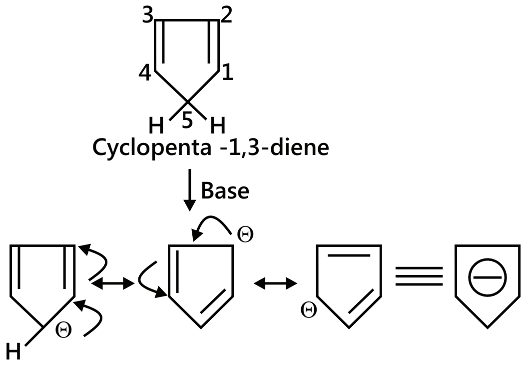


**Illustration 15:** Give the resonance structures of the conjugate base of the following: **(JEE MAIN)**

I.  II. Ph–CH$_2$–Ph

**Sol:**



(Aromatic) six $e^-$ system in delocalization

$$Ph-CH_2-Ph \xrightarrow{Base} Ph-CH-Ph$$

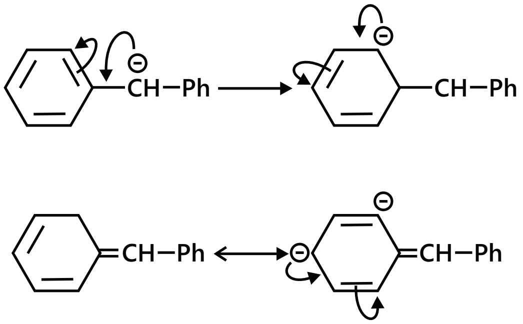
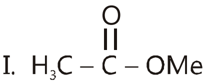
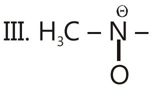


**Illustration 16:** Give the decreasing order of acidities of: **(JEE ADVANCED)**



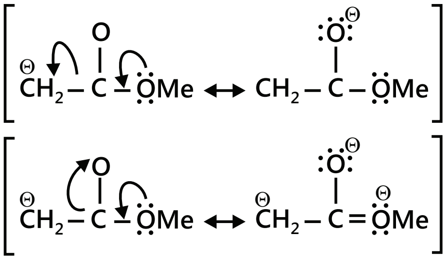
I. $H_3C-\overset{\overset{\large O}{||}}{C}-OMe$ II. $H_3C-CH=O$



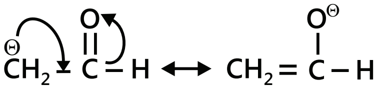
III. $H_3C-\overset{\ominus}{\underset{\underset{\large O}{|}}{N}}-O$ and explain.

**Sol:** Extent of Acidity of any compound depends on the stability of carbanion formed. More stable the anion, more acidic is the parent compound.

In the anion of (I), due to the cross conjugation with the delocalization of the negative charge on ($CH_2$) group and the O atoms of (OMe) group, complement each other, thereby making the anion a stronger base, hence its parent compound is a weak acid.



The negative charge on the anion of (II) is delocalized to the more electronegative O atom.



However, the negative charge on the anion of (III) is most extensively delocalized to two more electronegative O atoms. Moreover, – I effect of $N^{\oplus}$ provides additional stabilization.

Hence, the anion of (III) is more stabilized than the anion of (II), which in turn is more stabilized than the anion of (I).

Stability order of anion is: III > II > I.

Acidic order is: III > II > I.

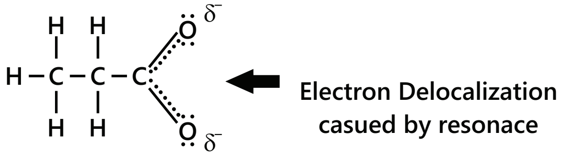
## 8.2 Basicity

So what are the various factors that can influence basicity?

- Resonance
- Electro-negativity
- Size of atomic radius
- Inductive effect
- Formal charges

**1. Resonance:** Let us recall that resonance delocalizes electrons. If an atom is involved in resonance, it has a negative formal charge, it delocalizes that formal charge.

**Example:**

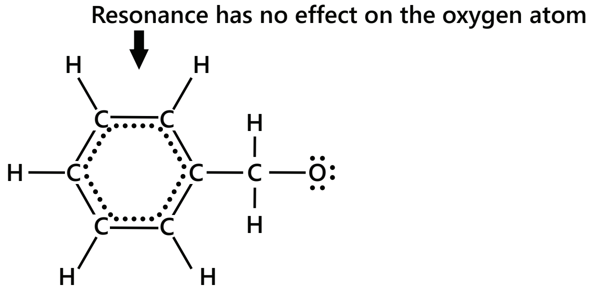


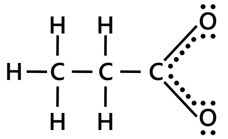
In the $CH_3CH_2CO_2$ – molecule, the oxygen atoms are the ones donating electrons to the hydrogen, these oxygen atoms have dilute negative charges, due to resonance, electrons as well as the negative charges are delocalized. This decreases electron density and thus elasticity.

**Key point:** Resonance usually DELOCALIZES electrons from the atom, thus REDUCING electron density. This causes the molecule to have a lower basicity!

Because resonance does not ALWAYS reduce basicity. Sometimes it has no effect on it.

E.g.



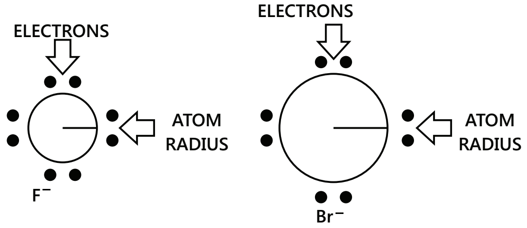


If a basic atom is not involved in resonance, then resonance has no impact on the molecule's basicity! This is because the atom's electron density is not delocalized!

**2. Atomic radius:** Atoms with smaller atomic radii will have greater electron density, increasing basicity. Atoms with larger atomic radii will have less electron density, reducing basicity.

Key point: LARGER atomic radius means LOWER Basicity, SMALLER atomic radius means HIGHER basicity.

**Example:** What the difference between F – and Br -?



Br has a larger atomic radius than F.

Notice how the electrons on the $F^-$ are covering more of the atom than compared to that of $Br^-$.

$F^-$ has a greater electron density that $Br^-$

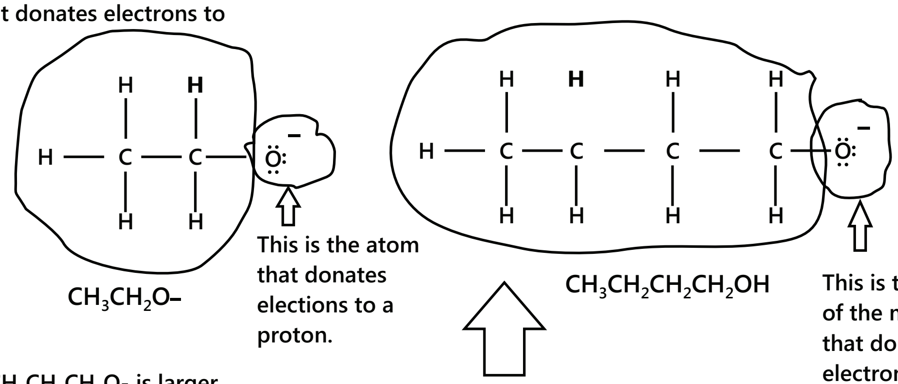
Therefore, $Br^-$ is less basic than $F^-$,

We only consider atomic radius of the atom that donates electrons to the hydrogen proton.

The atomic radius concept will not work between $CH_3CH_2O$ – and $CH_3CHCH_2CH_2O$-

This is because the carbon hydrogen chain is not the one donating electrons to a proton, the oxygen is, of course we can say the $CH_3CH_2CH_2CH_2O$- has greater London Dispersion Forces, but that's a different story.

The $CH_3CH_2$ part of the Molecule has no impact on the oxygen atom, the one that donates electrons to the proton.



This is the atom that donates elections to a proton.

$CH_3CH_2O$–

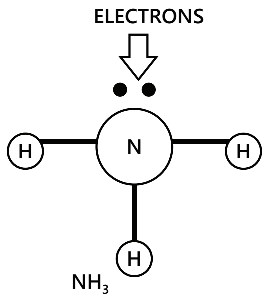
$CH_3CH_2CH_2CH_2OH$

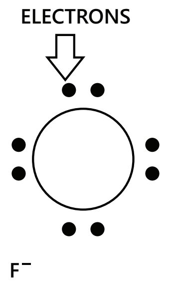
This is the part of the molecule that donates electrons to a proton

Although $CH_3CH_2CH_2O$- is larger than $CH_3CH_2O$-, their level of basicity is not influenced by the size if the molecule, only the oxygen atom is the one donating Electrons to $H^+$. When we compare basicity by using atomic radius, We only consider the electron Donating atom.

The $CH_3CH_2CH_2$ part of the molecule has no impact on the oxygen atom, the one that donates electrons to the proton.

**3. Electronegativity:** When atom has greater electronegativity, this means that the atom is greedier for electrons. It is less willing to share its electron pairs with a proton, reducing the atoms' likelihood to bond with the proton. This reduces basicity.





**Key point:** If the atom donating electrons to the proton has high electronegativity, then the molecule containing that atom has lower basicity.

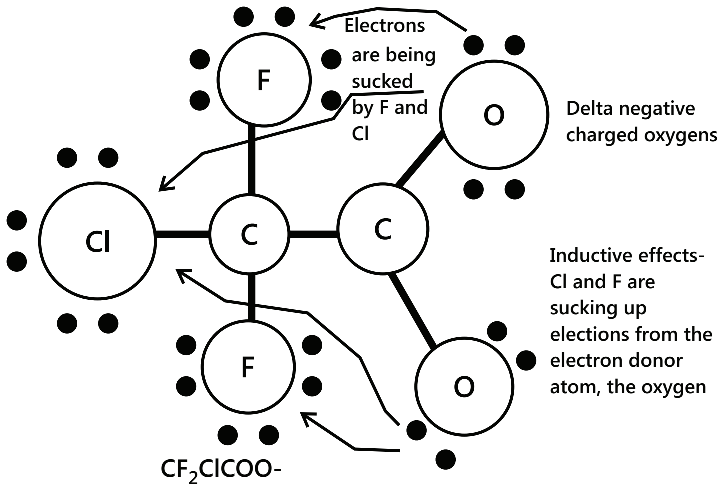
**Example:** $NH_3$ vs F -

The electron donating atoms are N and $F^-$.

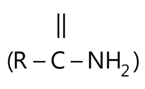
F has a higher electronegativity than N, it is less willing to donate electrons to the proton. This reduces the likelihood that F will form a bond with H, meaning that F is the less basic out of the two.

**4. Inductive effect:** The inductive effect is when other atoms within the molecule can take or are given electrons from the atom donating electrons to a proton. Atoms that do not donate electrons to protons can influence basicity as well. Example of inductive effect taking electrons away.

$CF_2ClCOO–$



The atoms involved in the inductive effect are the F, Cl, Br. Since, these atoms are electronegative, the atoms take electrons away from the $O^-$ which acts as the electron donating atom. The closer the atoms are to the electron donating atom, the larger the inductive effect. $CF_2ClCO_2^-$ has a larger inductive effect than $CF_2ClCH_2CO_2^-$

**Illustration 17:** Why Amides  $(R-\overset{\overset{\Large O}{\|}}{C}-NH_2)$ are less basic than Amines ($RNH_2$) **(JEE MAIN)**

**Sol:** Amides are resonance, stabilized by the Lone Pair electrons on N atom, thus resulting in the lack of availability of electrons on N atom.

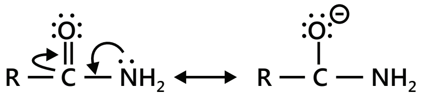
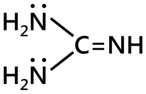


**Illustration 18:** a. Which N of guanidine (I) is more basic and is more likely to be protonated?

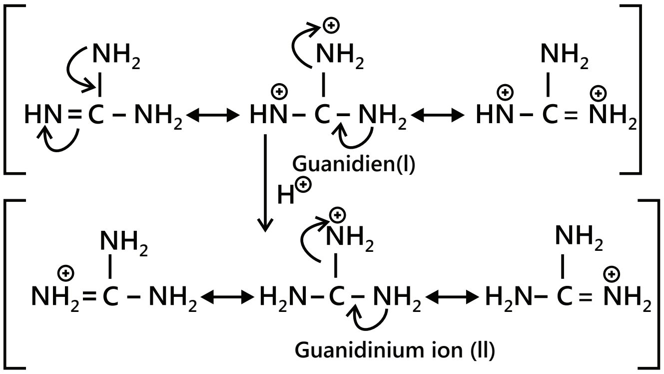
b. Why guanidine is the strongest organic N-base ($K'_b \equiv 1$)? **(JEE ADVANCED)**

**Sol:** a. The lesser the s character (as in $sp^3$ HO's), the stronger is the base. The N atom of $NH_2$ group is $sp^3$ hybridized with less s character than N of the imino (–NH) group, So, $NH_2$ group is more basic and is more likely to accept a proton from a water solvent.



**Guanidine(I)**

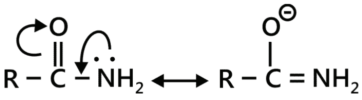
b. Both guanidine and its conjugate acid, the guanidinium ion, are stabilized by delocalization as shown below:



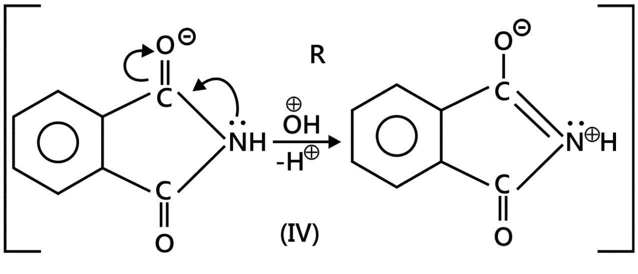
Guanidinium cation (II) is stabilized by the contribution of three exactly equivalent structures, whereas guanidine (I) has the resonating structures involving charge separation. Thus, the conjugate acid is a more stable chain the base and guanidine is therefore, a strong base.

**Illustration 19:** Why amides (III) are weakly basic (amphoteric), whereas phthalimide (IV) is an acid? **(JEE ADVANCED)**

**Sol:** Due to more resonance hybrid and extensive delocalisation in phthalimide anion, its parent compound shows acidic character.



(III)



## 9. THE ATTACKING REAGENT

The attacking reagents are classified into two main groups.

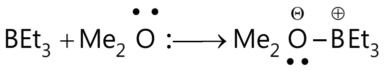
**(a)** **Electrophiles:** The species which carry +ve charge or are electron deficient are called electrophiles. These species attack regions of high electron density in a molecule.

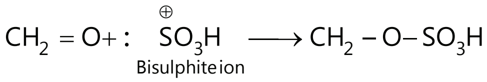
- **(i)** Positively charged electrophiles. $H^+$, $CH_3^+$, $NO_2^+$, $NO^+$, $Bi^+$, $R–C^+=O$
- **(ii)** Neutral electrophiles $SO_3$, $RCOCl$, $(RCO)_2O$, $AlCl_3$, $ZlCl_3$, $BF_3$

**(b)** **Nucleophile:** Those species which carry a negative cleavage/electron rich species or which have some pair of electrons are called nucleophiles. They attack regions of low electron density.

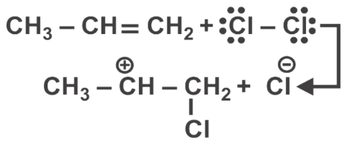
- **(i)** Negatively charge: $Br^-$, $CH^-$, $CH_2^-$, $CH_3^-$
- **(ii)** Neutral Nucleophiles: $NH_3$, $ROH$, $ROR$, $H_2O$, $RNH_2$

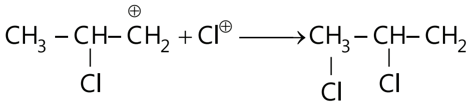
**Illustration 20:** Designate the species (A) and (B) as electrophile (E) or nucleophile (Nu) in the following reactions:

a.

$$BEt_3 + Me_2\ddot{O}: \longrightarrow Me_2\overset{\ominus}{\underset{\cdot\cdot}{O}}-\overset{\oplus}{B}Et_3$$

b.

$$CH_2 = O + :\underset{\text{Bisulphite ion}}{\overset{\oplus}{SO_3H}} \longrightarrow CH_2-O-SO_3H$$

c. $C_2H_5Cl + :CN:^{\ominus} \rightarrow C_2H_5 - CN + Cl^{\oplus}$

d.

$$CH_3-CH=CH_2 + :\ddot{\underset{\cdot\cdot}{Cl}}-\ddot{\underset{\cdot\cdot}{Cl}}: \longrightarrow CH_3-\overset{\oplus}{CH}-\underset{\underset{Cl}{|}}{CH_2} + \overset{\ominus}{Cl}$$

e.

$$CH_3-\underset{\underset{Cl}{|}}{CH}-\overset{\oplus}{CH_2} + Cl^{\oplus} \longrightarrow CH_3-\underset{\underset{Cl}{|}}{CH}-\underset{\underset{Cl}{|}}{CH_2}$$

**(JEE MAIN)**

**Sol:**

| Reaction | (a) | (b) | (c) | (d) |
|---|---|---|---|---|
| Species A | E | E | E | Nu |
| Species B | Nu | Nu | Nu | E |

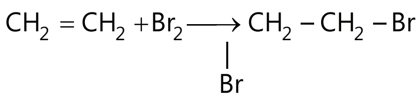
## 10. TYPES OF ORGANIC REACTIONS

The organic reactions are of following types:

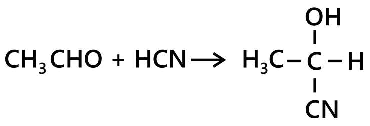
1. Addition Reactions 2. Substitution Reactions 3. Elimination Reactions

**(a)** **Addition Reactions:** The reactions in which the attacking reagent adds up to the substrate molecule is called a addition reaction. e.g. $CH_2 = CH_2 + HBr$ ¾→ $CH_3 – CH_2 – Br$

- **(i)** Electrophilic addition Reactions

E.g.

$$CH_2 = CH_2 + Br_2 \longrightarrow \underset{\underset{Br}{|}}{CH_2}-CH_2-Br$$

**(ii)** Nucleophilic addition Reactions

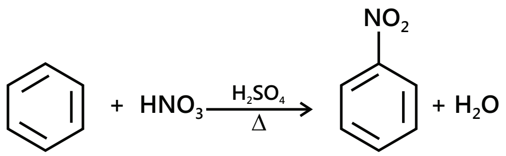
E.g. 

$$CH_3CHO + HCN \rightarrow H_3C-\underset{CN}{\overset{OH}{C}}-H$$

**(iii)** (c) Free radical addition Reactions

E.g. $CH_3 - CH = CH_2 + HBr \xrightarrow{\text{Peroxide}} CH_3CH_2{-}CH_2Br$

**(b)** **Substitution Reaction:** The replacement of an atom ore a group from a molecule by different atom or group is known as substitution reaction. e.g. $CH_3OH + HBr \rightarrow CH_3Br + H_2O$

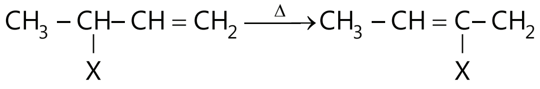


Substitution reactions are of three types: (a) Nucleophilic substitutions reactions (b) Electrophilic substitution reactions (c) Free radical substitution reactions.

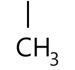
**(c)** **Elimination Reactions:** These reactions are the reverse of the addition reaction and involve the loss of atoms or group of atoms from a molecule to form a multiple linkage. Most commonly, loss of atoms or groups occurs from adjacent carbon atoms to yield an olefin.

E.g. $CH_3CH_2 \xrightarrow{\text{alc.KOH}} CH_2 = CH_2 + HCl$

**(d)** **Rearrangement:** Rearrangement reactions involve either the migration of functional group to another position in the molecule containing a double bond or change the sequences of atoms forming the base carbon skeleton of the molecule to form a product with a new structure.

E.g. 

$$CH_3 - \underset{X}{CH} - CH = CH_2 \xrightarrow{\Delta} CH_3 - CH = \underset{X}{C} - CH_2$$



$$CH_3CH_2CH_2CH_3 \xrightarrow{AlCl_3} \underset{CH_3}{CH_3} - CH_2 - CH_3$$

## PLANCESS CONCEPTS

**Acids :** Some important points:

**(a)** More stable the conjugate base more acidic is the molecule.

**(b)** In case of phenols –M groups at ortho and para positions enhances the acidic strength while +M groups decreases the acidic strength to a drastic extent.

**(c)** In case of benzoic acids -M groups at ortho and para positions enhances the acidic strength while +M groups decreases the acidic strength. But, ortho substituted carboxylic acids are more acidic compared to para and meta due to the ortho effect

**(d)** Even –I effect increases the acidic strength to some extent by withdrawing the electrons through $\sigma$ bonds and +I effect decreases the acidic strength.

## PLANCESS CONCEPTS

**(e)** Generally thiols are acidic compared to alcohols because its conjugate base is more stable than alkoxide due to its lower charge density.

**(f)** Acidity of Trinitrophenols are comparable to carboxylic acid and this gives effervescence with $NaHCO_3$.

**Bases :** Some important points:

**(a)** More easily the lone pair can be donated, more basic are the Nitrogen containing compounds.

**(b)** Aniline is less basic compared to amines because the lone pair is delocalized.

**(c)** In water the order of basicity is secondary > primary > tertiary

**Attacking reagent :**

**(a)** Rate of electrophilic reaction increases with the increase in negative charge density and decreases with increase in steric hindrance.

**(b)** Rate of nucleophilic reaction increases with the increase in positive charge density and decreases with the increases in steric hindrance.

**(c)** Generally nucleophilic strength decreases along the period and increases on moving down the group.

**B Rajiv Reddy (JEE 2010, AIR 443)**

# POINTS TO REMEMBER

**(a)** **Inductive Effect:** The Inductive effect is an electronic effect due to the polarization of σ bonds within a molecule or ion.

**(i)** Negative inductive effect (-I): The electron withdrawing nature of groups or atoms is called the negative inductive effect. It is indicated by -I. Following are the examples of groups in the decreasing order of their -I effect:

$NH_3+ > NO_2 > CN > SO_3H > CHO > CO > COOH > COCl > CONH_2 > F > Cl > Br > I > OH > OR > NH_2 > C_6H_5 > H$

**(ii)** Positive inductive effect (+I): It refers to the electron releasing nature of the groups or atoms and is denoted by +I. Following are the examples of groups in the decreasing order of their +I effect.

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

**Application of Inductive Effect:**

**Stability of carbonium ions:** The stability of carbonium ions increases with the increase in the number of alkyl groups due to their +I effect.

**Stability of free radicals:** In the same way the stability of free radicals increases with increase in the number of alkyl groups. Thus the stability of different free radicals is:

**Stability of carbanions:** Stability of carbanions decreases with increase in the number of alkyl groups since the electron donating alkyl groups destabilize the carbanions by increasing the electron density.

**Acidic strength of carboxylic acids and phenols:** The electron withdrawing groups (-I) decrease the negative charge on the carboxylate ion by stabilizing it. Hence the acidic strength increases when -I groups are present.

However the +I groups decrease the acidic strength.

**Basic strength of amines:** The electron donating groups like alkyl groups increase the basic strength of amines whereas the electron with drawing groups like aryl groups decrease the basic nature.

**Reactivity of carbonyl compounds:** The +I groups increase the electron density at the carbonyl carbon. Hence their reactivity towards nucleophiles decreases.

**(b) Mesomeric Effect:** The Mesomeric effect (on reaction rates, ionization equilibria, etc.) is attributed to a substituent due to the overlap of its p- or π-orbitals with the p- or π-orbitals of the rest of the molecular entity. Delocalization is thereby introduced or extended, and electronic charge may flow to or from the substituent.

- **(i) Negative resonance or mesomeric effect (-M or -R):** It is shown by substituents or groups that withdraw electrons by the delocalization mechanism from rest of the molecule and are denoted by -M or -R. The electron density on rest of the molecular entity is decreased due to this effect.

  E.g. $-NO_2$, Carbonyl group (C=O), $-C \equiv N$, -COOH, $-SO_3H$ etc.

- **(ii) Positive resonance or mesomeric effect (+M or +R):** The groups show a positive mesomeric effect when they release electrons to the rest of the molecule by delocalization. These groups are denoted by +M or +R. Due to this effect, the electron density on rest of the molecular entity is increased.

  E.g. -OH, -OR, -SH, -SR, $-NH_2$, $-NR_2$ etc.

**(c) Hyperconjugation:** In the formalism that separates bonds into $\sigma$ and $\pi$ types, hyperconjugation is the interaction of $\sigma$-bonds (e.g. C–H, C–C, etc.) with a $\pi$ network.

**Applications of hyperconjugation:**

- **(i)** Stability of alkenes:
- **(ii)** Stability of carbocations (carbonium ions):
- **(iii)** Stability of free radicals:
- **(iv)** Dipole moment & bond length:
- **(v)** Reactivity & orientation of electrophilic substitution on benzene ring:
- **(vi)** Anomeric effect:
- **(vii)** Reverse hyperconjugation:

**(d) Factors that influence acidity:**

- **(i) Charge-** Acidity increases with the increasing positive charge on an atom.
- **(ii) The Role of the Atom-** Across the periodic table, acidity increases with electronegativity but down the periodic table, acidity increases with size.
- **(iii) Resonance-** Any structural feature that increases the stability of the conjugate base will increase acidity.
- **(iv) Inductive effects-** Electron with drawing substituents can increase the acidity of 8 nearby atoms, which increases with electronegativity and decreases with increasing distance to the atom.
- **(v) Orbitals-** The higher the s-character of bond to hydrogen, the more acidic it will be.

**(e) Factors that influence Basicity:**

- **(i) Resonance-** Resonance usually DELOCALIZES electrons from the atom, thus REDUCING electron density. This causes the molecule to have a lower basicity!
- **(ii) Electro-negativity-** When atom has greater electronegativity, this means that the atom is greedier for electrons. It is less willing to share its electron pairs with a proton, reducing the atoms' likelihood to bond with the proton. This reduces basicity.
- **(iii) Size of atomic radius-** LARGER atomic radius means LOWER Basicity, SMALLER atomic radius means HIGHER basicity.
- **(iv) Inductive effect-** The inductive effect is when other atoms within the molecule can take or are given electrons from the atom donating electrons to a proton.

# Solved Examples

## JEE Main/Boards

**Example 1:** RSH (Thiols or Mercaptans) (pKa = 11) are more acidic than alcohols (pKa = 17).

**Sol:** This can be explained by considering the comparative size of sulphur and oxygen and bond dissociation energies of S-H and O-H.

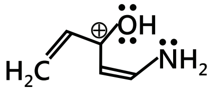
**i.** The S atom is larger and is more polarised than the O atom. S compounds are more powerful nucleophiles and compounds containing (SH) groups are stronger acids than their oxygen analogues. Also, $C_2H_5S^-$ ion is a stronger nucleophile than $C_2H_5O^-$ ion.

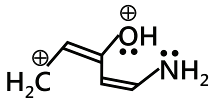
**ii.** Bond dissociation energy of (S–H) bonds of thiols 9~330 kJ) is much less than (O–H) bond of a alcohols (~420 kJ). Thiols undergo oxidative coupling reaction with mild OA alcohol do not undergo such reaction.

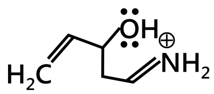
$2RS–H + H_2O_2 \rightarrow RS–SR$ (Disulfide) $+ 2H_2O$

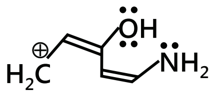
In alcohols, the oxidation takes place at the weaker (C–H) (~360 kJ) bond rather than at the stronger (O–H) bond.

**Example 2:** Which of the following is the most stable resonance structure?

(A) 

(B) 

(C) 

(D) 

**Sol: (C)** Structure (C) is the most stable resonance structure.

i. Number of covalent bonds in (A) and (B) = 13.

ii. Number of covalent bonds in (C) and (D) = 14.

iii. In (C), positive charge is on N, whereas in (D), it is on O atom. Since N is less EN (electronegative) than O, (C) is more stable.

**Example 3:** Give the stability order of the following resonance structures is -

I. $H_2C=\overset{\oplus}{N}=\overset{\ominus}{N}$ II. $H_2\overset{\oplus}{C}–N=\overset{\ominus}{N}$

III. $H_2\overset{\ominus}{C}–\overset{\oplus}{N}\equiv N$ IV. $H_2\overset{\ominus}{C}–N=\overset{\oplus}{N}$

**Sol:** The lesser the charge separation more stable the resonating structure.

(I) and (III) have less charge separation. But in (III), charge is on an electropositive C atom. Therefore, (I) is more stable than (III). Since both have six covalent bonds, so (I) is more stable than (III) (I > III).

Both (II) and (IV) have five covalent bonds, but (II) is more stable than (IV) because in (II) positive charge is on electropositive C atom and negative charge is on EN (electronegative) N atom, whereas in (IV) it is reversed.

Therefore, II > IV.

So, the stability order is I > III > II > IV.

**Example 4:** Dibasic acids are stronger than monobasic acids.

**Sol:** Dicarboxylic acids are stronger than monocarboxylic acids because (–COOH) group is an e-withdrawing group.

Order of acidity: Oxalic > Malonic > Succinic > Glutaric > Adipic > Butanoic acid.

$pK_{a1}$ = 1.27 2.86 4.21 4.34 4.41 4.82

$pK_{a2}$ = 4.27 5.70 5.64 5.27 5.28

The above order of dibasic acid is due to an increasing number of alkyl group (e-donating group) or increasing number of $\sigma$-bonds between (–COOH) and ($–COO^-$).

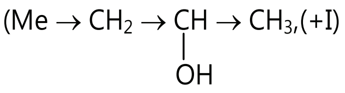
**Example 5:** Arrange the following in the decreasing order of acidity:

| | |
|---|---|
| i. 1. n-Butanol | 2. Methyl alcohol |
| 3. sec-Butanol | 4. tert-Butanol |
| ii. 1. HCOOH | 2. $CH_3COOH$ |
| 3. $C_2H_5COOH$ | 4. $C_6H_5COOH$ |
| 5. $(CH_3)_2CHCOOH$ | 6. $CH_2ClCOOH$ |

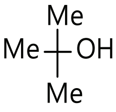
**Sol:** Electron withdrawing group increases the acidic character and Electron Donating Group decreases the acidic character.

i. 1 > 4 > 2 > 3

$CH_3 \rightarrow CH_2 \rightarrow CH_2 \rightarrow CH_2–OH$ (+I effect of Bu > Me)



$(Me \rightarrow CH_2 \rightarrow \underset{\substack{|\\ OH}}{CH} \rightarrow CH_3,(+I)$

(+I effect of Et and Me > Me)  $Me-\overset{Me}{\underset{Me}{C}}-OH$ +I effect of three Me groups)

ii. 6 > 1 > 4 > 2 > 3 > 5

(In (6) –I effect of Cl > (1) (standard) > (4) + R > –I of Ph > (2) +I effect of Me > (3) effect of two Me groups)

**Example 6:** Arrange the following in decreasing order of acidity:

i. 1. o-Hydroxybenzoic acid

2. p-Hydroxybenzoic acid

3. 2,6-Dihydroxybenzoic acid

ii. 1. HCOOH 2. $C_6H_5COOH$

3. $C_6H_5OH$ 4. HCl

iii. 1. RCOOH 2. ROH

3. RH 4. $NH_3$

5. HOH 6. CH=CH

**Sol:** (i) 3 > 1 > 2

(3) Intramolecular H-bonding from two sides > (I) Intramolecular H-bonding from one side > (2) –I and +R effects of OH group at p-position; net effect is e-donating.

ii. 4 > 1 > 2 > 3

(4) Inorganic acid > (1) Formic acid (standard) > (2) Benzoic acid, –I and +R of Ph group; net e–donating > (3) Phenol.

iii. 1 > 5 > 2 > 6 > 4 > 3

(1) Acid > (5) $H_2O$ > (2) Alcohol > (6) HC=CH (sp character) > (4) $NH_3$ > (3) Alkane ($sp^3$ character)

**Example 7:** Arrange the following in decreasing order of basicity:

i. 1. RCN 2. $RNH_2$ 3. R–N=CH–R

ii. 1. $C_2H_5NH_2$ 2. $(iso\text{-}C_3H_7)_3N$

3. $CH_3CONH_2$ 4. $CH_3\overset{\oplus}{N}HNa^{\oplus}$

iii. 1. $\overset{\ominus}{NH_2}$ 2. $HC\equiv C^-$ 3. $^-OH$

4. $^-OR$ 5. $R^-$ 6. $RCOO^-$

**Sol:** i. 2 > 3 > 1

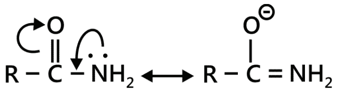
[(2) 1°R–$NH_2$($sp^3$) > (3) R–N=CH–R($sp^2$) > (1) R–C≡N (sp) character]

Basicity: $sp^3 > sp^2 >$ sp character

ii. 4 > 1 > 2 > 3

(4) Anion of 1° amine $CH_3-\overset{\ominus}{\ddot{\underset{\cdot\cdot}{N}}}H_2$

LP e⁻s density increases > (1) 1° amine > (2) 3° amine > (3) amide due to the resonance, non-availability of LP electrons, hence weakest)



iii. 5 > 1 > 2 > 4 > 3 > 6

Convert conjugate base into acid by adding $H^{\ominus}$, find the acidic character and then reverse the order after removing $H^{\oplus}$ ions that would be the order for basic character.

Acidity: RCOOH > $H_2O$ > ROH

(6) (3) (4)

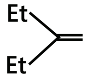
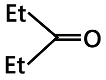
> CH=CH > $NH_3$ > RH

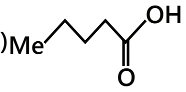
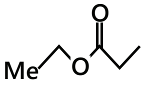
(2) (1) (5)

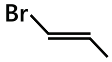
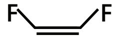
Basicity: $RCOO^{\ominus} < {}^-OH < RO^- < CH\equiv C^{\ominus} < \overset{\oplus}{NH_2} < R^-$

(6 < 3 < 4 < 2 < 1 < 5)

**Example 8:** Which of the following pairs would have higher boiling points?

a. (I)  (II) 

b. (I)  (II) 

c. (I)  (II) 

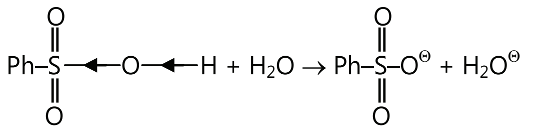
**Sol:** a. (II) because carbonyl group is more polar than double bond.

b. (I) acid forms dimmer due to H-bonding.

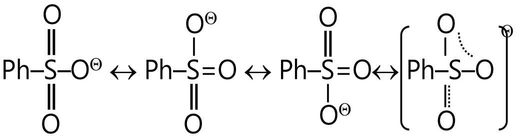
c. (II) cis-compound has high dipole moment (μ), so more polar than trans-compound (μ = 0).

**Example 9:** Sulphonic acids are stronger acids than carboxylic acids

**Sol:**


$Ph-\overset{O}{\underset{O}{S}}\leftarrow O\leftarrow H + H_2O \rightarrow Ph-\overset{O}{\underset{O}{S}}-O^{\ominus} + H_2O^{\ominus}$

Benzone sulphoric acid Benzone sulphonate ion



$$\mathrm{Ph{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}O^{\ominus} \leftrightarrow Ph{-}\overset{\overset{O^{\ominus}}{|}}{\underset{\underset{O}{\|}}{S}}{=}O \leftrightarrow Ph{-}\overset{\overset{O}{\|}}{\underset{\underset{O^{\ominus}}{|}}{S}}{=}O \leftrightarrow \left[Ph{-}\overset{\overset{O}{|}}{\underset{\underset{O}{\vdots}}{S}}{-}O\right]^{\ominus}}$$

Oxygen being more EN than S, the sulphonyl group ($-SO_2-$) having two oxygen atoms greatly facilitates the release of H atom of ($-SO_2OH$) group as hydronium ion as shown above.

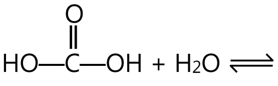
i. Due to the release of a portion, the replacement of (–OH) group is difficult. Hence, esters and amides of sulphuric acids are not formed directly but through their acid chlorides.

ii. Once the sulphonate anion is formed, it is stabilized due to the dispersal of negative charge over three oxygen atoms

Benzene sulphonic acid is a stronger acid than benzoic acid due to greater stabilisation of benzene sulphonate ion than the carboxylate ion.

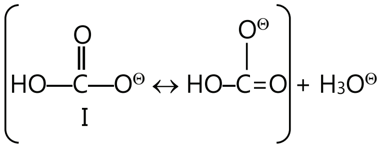
**Example 10:** Carbonic Acid ($H_2CO_3$) is a stronger acid than phenol.

**Sol:** In carbonate anion negative charge is delocalised over two oxygen atom thus it is more stable. As the resonating structure is stable, parent compound is More acidic.



$$\mathrm{HO{-}\overset{\overset{O}{\|}}{C}{-}OH + H_2O \rightleftharpoons}$$

Carbonic acid



$$\left[\mathrm{HO{-}\underset{I}{\overset{\overset{O}{\|}}{C}}{-}O^{\ominus} \leftrightarrow HO{-}\overset{\overset{O^{\ominus}}{|}}{C}{=}O}\right] + \mathrm{H_3O^{\ominus}}$$

Resonance structure of bicarbonate ion

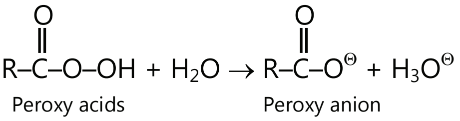
Resonating structures I and II of the bicarbonate ions are equivalent, whereas the resonating structures of the phenoxide ion are non-equivalent. Hence, the bicarbonate ion is relatively more stable.

## JEE Advanced/Boards

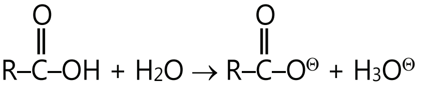
**Example 1:** Peroxy Acids $\left(\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}O{-}OH}\right)$ are Much Weaker than Acids $\left(\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}OH}\right)$

**Sol:** The negative charge on Peroxy anion is localized and hence is not resonance stabilized.

Acid anion is stabilized by resonance as explained earlier.



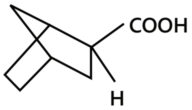
$$\mathrm{\underset{Peroxy\ acids}{R{-}\overset{\overset{O}{\|}}{C}{-}O{-}OH} + H_2O \rightarrow \underset{Peroxy\ anion}{R{-}\overset{\overset{O}{\|}}{C}{-}O^{\ominus}} + H_3O^{\ominus}}$$



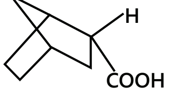
$$\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}OH + H_2O \rightarrow R{-}\overset{\overset{O}{\|}}{C}{-}O^{\ominus} + H_3O^{\ominus}}$$

**Example 2:** Exo-2-Norborane Carboxylic Acid (I) is more acidic then endo-Isomer (II)

**Sol:** Exo-bicyclo [2,2,1]-2-heptanoic acid (I)



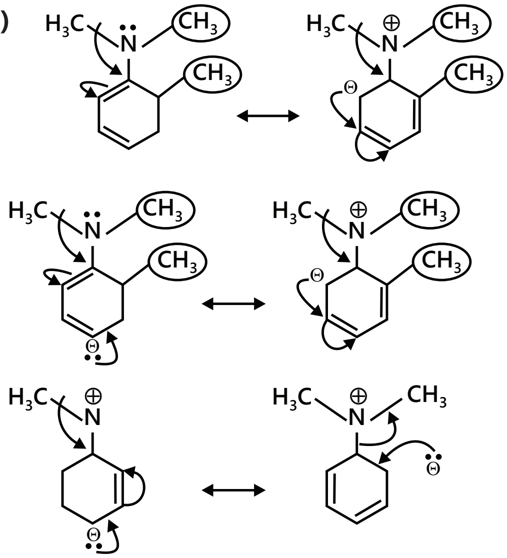
**exo-bicyclo [2,2,1]-2-heptanoic acid (I)**



Here, exo ($-COO^{o}$) is less hindered and is thus more exposed to solvent and as a result more acidic.

**Example 3:** Compare the basicity of (a)N,N-dimethyl-o-toluidine and N-dimethyl aniline.(b)Bemzoquinoclidine and N,N-dimethyl aniline(c) p=Cyanophenol and 5-methyl p-cyanophenol (d) 2,43,6-DNP and Aniline(e) Trimethyl amine ,pyridine and acetonitrile

**Sol: (A)**

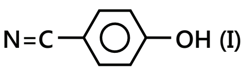


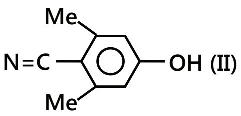
The extent of stabilization due to delocalization is lesser in N, N-dimethyl-o-toluidine than in N, N-dimethyl aniline because in it the (–$CH_3$) group at the o-position and (–$CH_3$) group at nitrogen of the amine group are close enough and the steric hindrance between these groups inhibits the nitrogen atom of the amino group and the benzene ring to become coplanar. Thus, the lone pair of $e^-$s over nitrogen is less delocalized in N, N-dimethyl-o-toluidine and therefore, it is more basic of the two.

**(B)** Benzoquinoclidine is a stronger base than N, N dialkyl aniline derivative, i.e., N, N-dimethylaniline.

In II, LP of $e^-$s on nitrogen is sterically hindered, whereas in I, the groups are only on one side and the pair can be donated comparatively more readily, resulting in (I) being the more basic of the two.

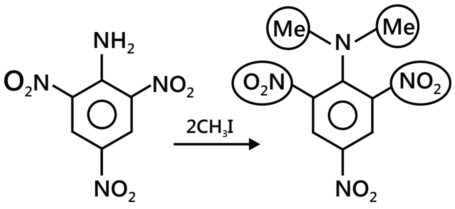
**(C)** The reason why acidity of p-cyanophenol (I) and 3, 5-dimethyl p-cyanophenol (II) is approximately the same is explained below.



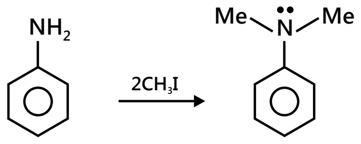


There is no steric inhibition of resonance in both due to the linear cyano group.

**(D)** From the reactions given below it is clear that methylation increases the basicity of 2, 4, 6-trinitro-aniline (I) by 40,000 times, whereas nearly triples the basicity of aniline.

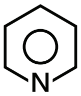


(I) (II)



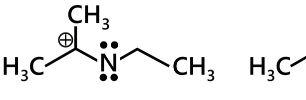
(III) (IV)

**(E) Basic character:**

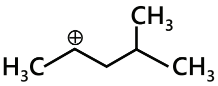
$(CH_3)_3N$ >  > $CH_3-C\equiv N$

**($sp^3$ > $so^2$ > sp, for basic character)**

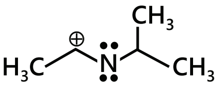
**Example 4:** Gives the correct stability order of the following species:



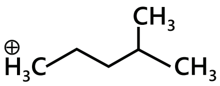
(I)



(II)

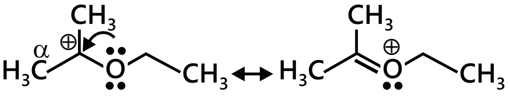


(III)



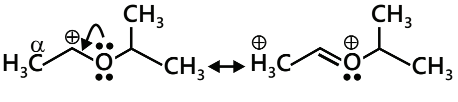
(IV)

**Sol:** i. (I) is most stable, since it is stabilized by resonance and has six α-H atoms (hyperconjugation).



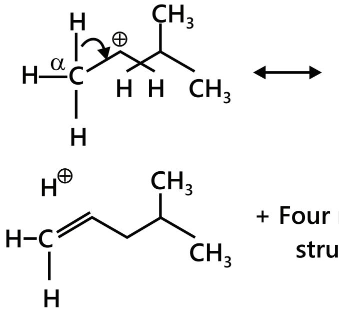
(I) (II)

ii. (III) is less stable than (I) but more stable than (II) and (IV), since it is also stabilized by resonance and has three α-H atoms (hyperconjugation).



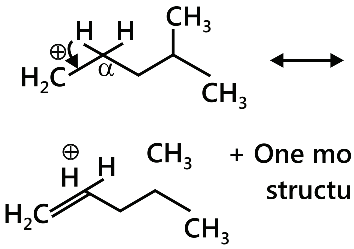
(III) (IV)

iii. (II) is more stable than (IV) and is stabilised only by hyperconjugative structure (five α-H atoms).



+ Four more H.C. structures

(IV) is least stable; it has only two α-H atoms.



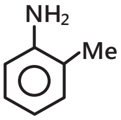
+ One more H.C. structures

So, the stability order is I > III > II > IV.

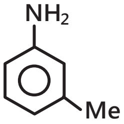
**Example 5:** Compare the basicity of substituted aromatic amines:

(I)


**Aniline**
**$pK_b = 9.42$**

(II)


**o-Toluidine**
**9.61**

(III)


**m-Toluidine**
**9.31**

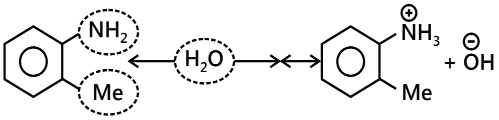
(IV)


**p-Toluidine**
**8.92**

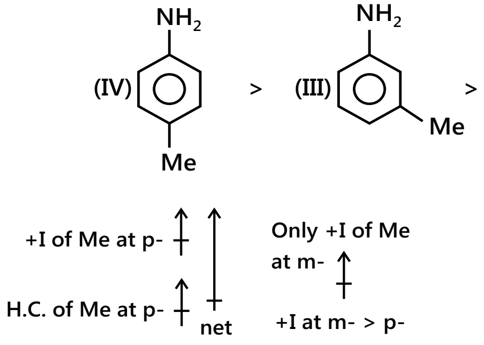
**Sol:** Basic character: IV > III > I > II

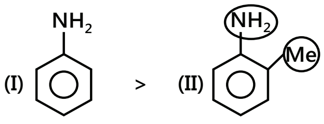
(p- > m- > Anilline > o-)

According to +I and H.C. effects, o-isomer (II) should be the strongest base. Due to ortho effect, basic character is decreased. In this case, ortho effect is due to steric hindrance of (Me) group, over the ($NH_2$) group ; this results in the protonation of ($NH_2$) group becoming more difficult (salvation effect), hence the basicity decreases.

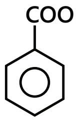


In general, basicity order of methyl-substituted aromatic amine is the reverse of the acidic order of methyl-substituted acid.

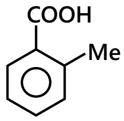




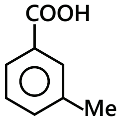
**Example 6:** Compare the acidity of substituted aromatic acids

(I)


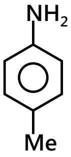
**Benzoic acid**
**$pK_a = 4.17$**

(II)


**o-Toluic acid**
**3.91**

(III)


**o-Toluic acid**
**4.27**

(IV)


**p-toluic acid**
**4.37**

**Sol:** Basic character: II > I > III > IV (o- > B.A. >m- > p-).

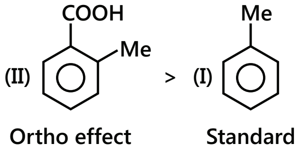
In II, there is ortho effect, strongest acid.

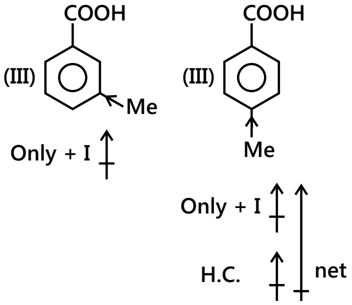
So, o-substituted acid, containing EWG or EDG, is the strongest acid its isomers (except in case of o-amino benzoic acid)

Acidic character of phenolic compound in (a): o- > B.A. > m- > p-

Place o-methyl substituted at the strongest position, keeping the rest of the order same as in Me-substituted phenol.

Explanation:





# JEE Main/Boards

## Exercise 1

**Q.1** Explain tetravalency of carbon.

**Q.2** Why does carbon undergo hybridization prior to bond formation.

**Q.3** Draw the orbital diagram of methane and ethane molecules indicating the hybridization involved.

**Q.4** Which of the following has higher melting point and why?

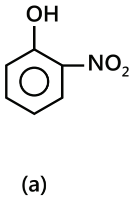
(i) Fumaric acid (ii) Maleic acid

**Q.5** What is the effect of type of hybridization on

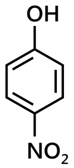
(i) Bond length (ii) Bond strength.

**Q.6** Draw bond-line formulae for (a) tert-butylcyclopentane, (b) cyclohexanone.

**Q.7** Which is more soluble and why?



(a)



(b)

**Q.8** Write condensed and bond-line structural formulae for all the possible isomers of molecular formula

(i) $C_6H_{14}$ (ii) $C_6H_{10}$

(iii) $C_8H_{10}$ (iv) $C_8H_{18}$

(v) $C_3H_8O$ (vi) $C_3H_8O_2$

(vii) $C_4H_{10}O$ (viii) $C_6H_{11}NO_2$

**Q.9** What is a functional group? Write the functional groups of the following:

(i) Thioalochol (ii) Isothiocyanate

(iii) Thiocyanate and (iv) Sulhponic acid

(v) Suplhones (vi) Sulphoxides

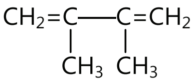
**Q.10** What are homocyclic and heterocyclic compounds? Given two examples with their names.

**Q.11** Hydrazine does not show a positive test for Lassaigne's test of nitrogen. Why?

**Q.12** Giving reason arrange the following in increasing order of reactivity towards HBr.

$CH_2=CH–C_2H_5$, $CH_3CH=CHCH_3$, $CH_2=CHCH=CH_2$,

$CH_3–CH=CH–CH=CH_2$ and



$CH_2=\underset{CH_3}{\underset{|}{C}}-\underset{CH_3}{\underset{|}{C}}=CH_2$

**Q.13** What is homologous series? Given its important characteristics. Write the first four homologues of alcohols and give their IUPAC names.

**Q.14** Explain in the following terms with one example in each case, (i) word root (ii) primary and secondary suffixes and prefixes.

**Q.15** 0.2018 gm of silver salt of dibasic acid gives 0.1073 gms of silver on complete ignition. What is the molecular weight of the acid?

**Q.16** When is the process of fraction crystallization employed?

**Q.17** 0.3168 gms of the platinic chloride of a mono acidic base gave 0.1036 gms of platinum, what is the molecular weight of the base?

**Q.18** How will you separate two components when: (a) their boiling points differ by a few degrees,

(a) They are soluble in the same solvent.

(b) They are almost immiscible in water but are volatile in steam?

**Q.19** What is resonance effect? What are its various types? In what respects, does the resonance effect differ from inductive effect?

**Q.20** Common upon the statement: 'Usual order of inductive effects of the alkyl groups is often reversed when attached to a double or a benzene ring.' Name the electronic effect and illustrate your answer with suitable examples.

**Q.21** Explain hyperconjugation effect.

**Q.22** What is principle of column chromatograph?

**Q.23** Explain the principle of steam distillation.

**Q.24** When is the process of fractional distillation employed?

## Exercise 2

### Single Correct Choice Type

**Q.1** Which of the following species have a trigonal planar shape?

(A) $:CH_3^-$ (B) $CH_3^+$ (C) $BF_4^-$ (D) $SiH_4$

**Q.2** A nucleophile must necessarily have -

(A) An overall positive charge

(B) An overall negative charge

(C) An unpaired electron

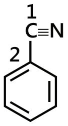
(D) A lone pair of electrons

**Q.3** Which of the following has a bond formed by overlap of $sp^3$–$sp^2$ hybrid orbitals?

(A) $CH_3–C\equiv C\ CH_3$ (B) $CH_3–CH=CH–CH_3$

(C) $CH_2=CH–CH=CH_2$ (D) $HC\equiv C_2H_4$

**Q.4** The bond between carbon atoms (1) and carbon atom (2) in compound,



(A) $sp^3$ and $sp^2$ (B) $sp^2$–$sp^3$

(C) sp and $sp^2$ (D) sp and sp

**Q.5** In the compound $CH_2=CH–CH_2–CH_2–CH_2–C\equiv CH$, the $C_2$–$C_3$ bond is of the type is -

(A) sp – $sp^2$ (B) $sp^3$ – $sp^3$

(C) sp – $sp^2$ (D) $sp^2$ – $sp^3$

**Q.6** Which of the following species has a trigonal planar shape?

(A) $CH_3^-$ (B) $CH_3^+$ (C) $BF_4^-$ (D) $\dot{C}H_3$

**Q.7** The stability order of alkenes is given as $CH_3–CH=CH_2$ > $CH_2=CH_2$, the reactivity order towards electrophilic addition reaction is given by

(A) $CH_2=CH_2$ > $CH_3–CH=CH_2$

(B) $CH_3–CH=CH_2$ > $CH_2=CH_2$

(C) $CH_3–CH=CH_2$ equal to $CH_2=CH_2$

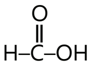
(D) None of these

**Q.8** Carbanion is

(A) An electrophile (B) A nucleophile

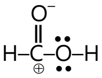
(C) A zwitter ion (D) A free radial

**Q.9** Formic acid is considered as a resonance hybrid of the four structures.



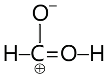
$H-\overset{\overset{O}{\parallel}}{C}-OH$

(I)



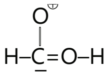
$H-\underset{\oplus}{\overset{\overset{O^-}{\parallel}}{C}}-\ddot{\underset{\cdot\cdot}{O}}-H$

(II)



$H-\underset{\oplus}{\overset{\overset{O^-}{|}}{C}}=O-H$

(III)



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

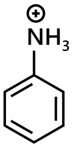
(IV)

Which of the following order is correct for the stability of the four contributing structures?

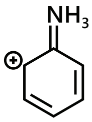
(A) I > II > III> IV (B) I > II > IV > III

(C) I > III > II > IV (D) none of these

**Q.10** Examine the following two structures for the anilinium ion and choose the correct statement from the ones given below.



(I)



(II)

(A) II is not an acceptable canonical structure because carbonium ions are less stable than ammonium ion

(B) II is not an acceptable structure because it is non-aromatic

(C) II is not an acceptable canonical structure because the nitrogen has 10 valence electrons

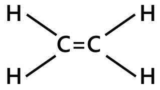
(D) II is an acceptable canonical structure

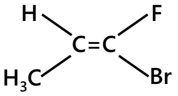
**Q.11** $HC\equiv CH \xrightarrow[H_2SO_4]{HgSO_4} (A) \xrightarrow[5°C]{dil.\ OH^-} (B)$. Give the IUPAC name of B.

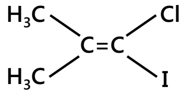
(A) 2-butenal (B) 3-hydroxybutanal

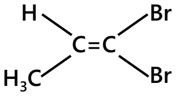
(C) 3-formyl 2-propanol (D) 4-oxo-2-propanol

**Q.12** Geometrical isomerism is shown by

(A)


(B)


(C)


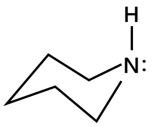
(D)


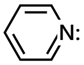
**Q.13** Polarisation of electrons in acrolein may be written as

(A) $\overset{\delta_-}{C}H_2 = CH - \overset{\delta_+}{C}H = O$ (B) $\overset{\delta_-}{C}H_2 = CH - CH = \overset{\delta_+}{O}$

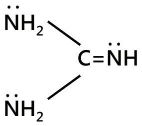
(C) $\overset{\delta_-}{C}H_2 = \overset{\delta_+}{C}H - CH = O$ (D) $\overset{\delta_+}{C}H_2 - CH = CH - \overset{\delta_-}{O}$

**Q.14** What is the basic strength order

A.


B.


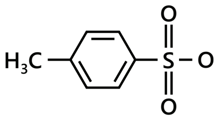
C. CH-C≡N:

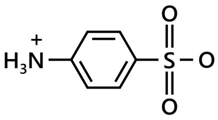
D.


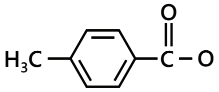
(A) A > B > C > D (B) D > A > B > C

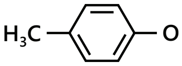
(C) D > C > A > B (D) C > D > A > B

**Q.15** The leaving group ability of the following will be expressed in the order

1.


2.


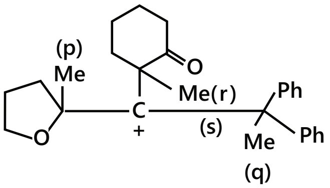
3.


4.


(A) 1 > 2 > 3 > 4 (B) 2 > 1 > 3 > 4

(C) 4 > 3 > 2 > 1 (D) 2 > 4 > 3 > 1

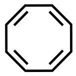
**Q.16** The rearrangement of following carbocation will occur with the shifting of group ... to yield the most stable carbocation

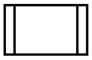


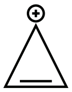
(A) Me – (p) (B) Me – (q)

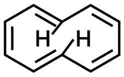
(C) Me – (r) (D) bond – (s)

**Q.17** Which of the following is aromatic

(A)


(B)


(C)


(D)


**Q.18** In the identification of phosphorus, the phosphorus in the organic compound is converted to $PO_4^{3-}$ using

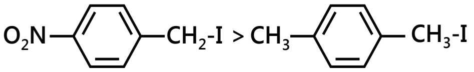
(A) NaOH (B) $Na_2O$

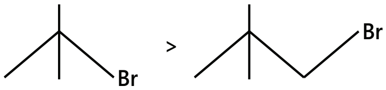
(C) $Na_2O_2$ (D) $NaO_2$

**Q.19** The correct reactivity order(s) for $S_N1$ reaction is/are

1. Ph–Br < Ph–$CH_2$–Br

2. Ph–Br > $PhCH_2Cl$

3.


4.


(A) 1, 2, 3 (B) 2, 4 (C) 1, 4 (D) 2, 3, 4

**Q.20** The incorrect statement about $S_N1$ reaction is (When only α-C atom is chiral)

(A) A stereoisomer is formed

(B) Two step reaction

(C) Rearrangement takes place

(D) The rate is independent of concentration of nucleophile

**Q.21** The acidic strength of chloro substituted benzoic acid is

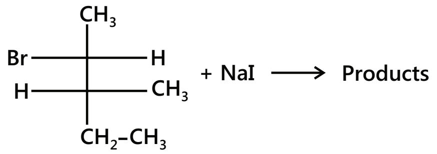
(A) Benzoic acid>o-chloro > m-chloro > p-hloro

(B) o-chloro > m-chloro>p-chloro>benzoic acid

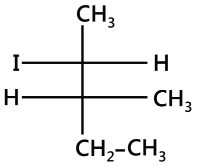
(C) m-chloro>o-chloro> p-chloro >benzoic acid

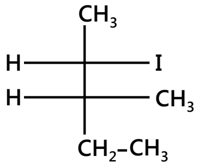
(D) None of these

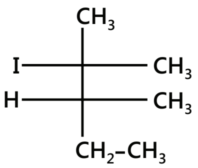
**Q.22**

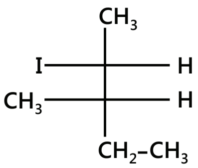


Product of reaction is:

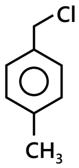
(A)


(B)


(C)


(D)


**Q.23** Which of the following is most reactive towards $S_N2$ reaction?

(A)


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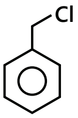

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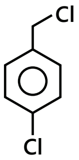

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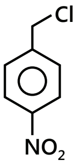


**Q.24** Magnesia mixture used during estimation of phosphorous is -

(A) $MgCl_2$ + $NH_4Cl$

(B) $HgCl_2$ + $NH_4Cl$ + little of $NH_3$

(C) $HgCl_2$ + $NH_4Cl$

(D) $MgCl_2$ + $NH_4Cl$ + little of $NH_3$

**Q.25** In the Kjeldal's estimation of nitrogen in the form of $NH_3$ small amounts of $K_2SO_4$ is added to the system -

(A) Here $K_2SO_4$ acts as a catalyst

(B) To provide common ion effect for dissociation of $CuSO_3$

(C) $K_2SO_4$ is responsible for converting $NH_3$ to $(NH_4)_2SO_4$

(D) $K_2SO_4$ raises the boiling point of $H_2SO_4$

**Q.26** The compound having maximum enol content -

(A) $CH_3CH_2CHO$ (B) $CH_3COCH_3$

(C) $CH_3CHO$ (D) $CH_3COCH_2COCH_3$

**Q.27** In which of the following pairs the difference in dipole moment is maximum -

(A) cis and trans 1,2-Dichloro ethane

(B) cis and trans 1-chloropropene

(C) o-Xylene, m-xylene

(D) Dipole moment does not change with configuration

**Q.28** The stability of carbenes is -

(A) Singlet carbene > Triplet carbine

(B) Singlet carbene = Triplet carbine

(C) Singlet carbene < Triplet carbine

(D) Cannot be predicted

**Q.29** The number of isomeric chloro butanes formed by the monochlorination of n-butane are -

(A) 1 (B) 2 (C) 3 (D) None of these

**Q.30** The reactivity order of HCHO, ArCHO, ArCOAr, ArCOR, RCOR is towards nucleophilic attack is -

(A) HCHO > ArCHO > ArCOAr > ArCOR > RCOR

(B) HCHO > ArCOAr > ArCHO > ArCOR > RCOR

(C) HCHO > ArCHO > RCOR > ArCOAr > RCOAr

(D) None of these

**Q.31** The number of meso forms for glucose are

(A) 1 (B) 2

(C) 3 (D) None of these

**Q.32** The Lassaigne's extract is boiled with dil. $HNO_3$ before testing for halogens such that -

(A) AgX is soluble in $HNO_3$

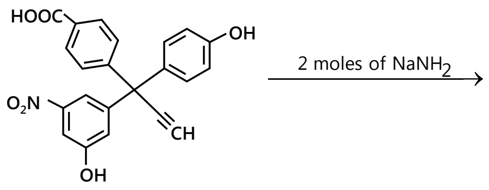
(B) $Na_2S$ and NaCN are decomposed by $HNO_3$

(C) $Ag_2S$ is soluble in $HNO_3$

(D) AgCN is soluble in $HNO_3$

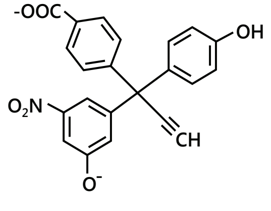
## Previous Years' Questions

**Q. 1**



The product A will be - ***(2003)***

(A)



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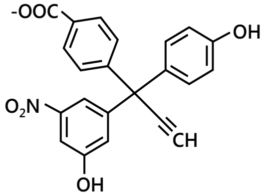

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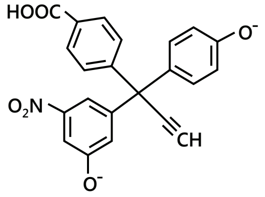

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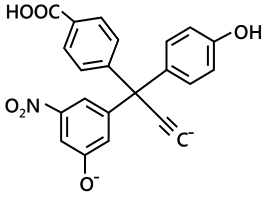
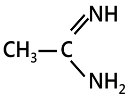


**Q.2** The correct order of basicity of the following compounds is - ***(2001)***

(1)



$CH_3-C(=NH)NH_2$

(2) $CH_3CH_2NH_2$

(3) $(CH_3)_2NH$

(4) $CH_3CONH_2$

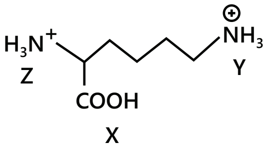
(A) 2 > 1 > 3 > 4

(B) 1 > 3 > 2 > 4

(C) 3 > 1 > 2 > 4

(D) 1 > 2 > 3 > 4

**Q.3** Arrange in order of increasing acidic strength ***(2004)***



(A) X > Z > Y

(B) Z < X > Y

(C) X > Y > Z

(D) Z > X > Y

**Q.4** Which of the following, has the most acidic hydrogen? ***(2000)***

(A) 3-hexanone

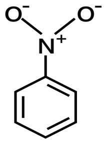
(B) 2,4-hexanedione

(C) 2,5-hexanedione

(D) 2,3-hexanedione

**Q.5** The most unlikely representation of resonance structure of p-nitrophenoxide ion is ***(1999)***

(A)



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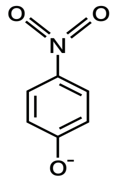

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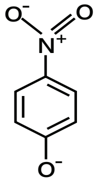
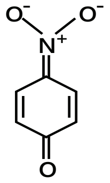


(D)



**Q.6** The correct stability order of the following resonance structures is - ***(2009)***

$H_2C=\overset{+}{N}=\overset{-}{N}$ (I)

$H_2\overset{+}{C}-N=\overset{-}{N}$ (II)

$H_2\overset{-}{C}-\overset{+}{N}\equiv N$ (III)

$H_2\overset{-}{C}-N=\overset{+}{N}$ (IV)

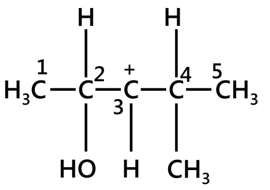
(A) (I) > (II) > (IV) > (III)

(B) (I) > (III) > (II) > (IV)

(C) (II) > (I) > (III) > (IV)

(D) (III) > (I) > (IV) > (II)

**Q.7** In the following carbocation, H/$CH_3$ that is most likely to migrate to the positively charged carbon is ***(2009)***



(A) $CH_3$ at C-4

(B) H at C-4

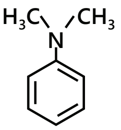
(C) $CH_3$ at C-2

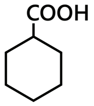
(D) H at C-2

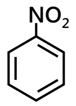
**Q.8** Hyperconjugation involves overlap of the following orbitals – ***(2008)***

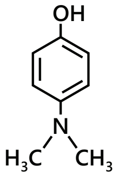
(A) $\sigma$-s (B) $\sigma$-p (C) p-p (D) $\pi$-p

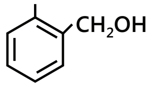
**Q.9** Amongst the following, the total number of compound soluble in aqueous NaOH is – ***(2010)***

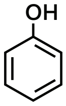


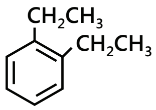


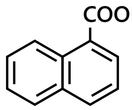




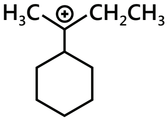








**Q.10** The total number of contributing structures showing hyper conjugation (involving C-H bonds) for the following carbocation is ***(2011)***



**Q.11** The optically active tartaric acid is named as D-(+)-tartaric acid because it has positive ***(1999)***

(A) Optical rotation and is derived from D-glucose

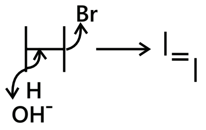
(B) pH in organic solvent

(C) Optical rotation and is derived from D(+) glyceraldehydes

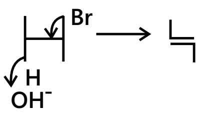
(D) Optical rotation only when substituted by deuterium

**Q.12** Dehydrohalogenation in presence of $OH^-$ is correctly represented by – ***(2004)***

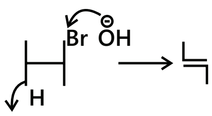
(A)



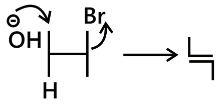
(B)



(C)



(D)



**Q.13** Which one of the following species is most stable ***(1995)***

(A) $p-O_2N-C_6H_4-\overset{+}{C}H_2$ (B) $p-CH_3O-C_6H_4-\overset{+}{C}H_2$

(C) $p-Cl-C_6H_4-\overset{+}{C}H_2$ (D) $C_6H_5-\overset{+}{C}H_2$

**Q.14** Which of the following has the highest nucleophilicity - ***(2000)***

(A) $F^-$ (B) $OH^-$ (C) $CH_3^-$ (D) $NH_2^-$

**Q.15** Dipole moment is shown by - ***(1986)***

(A) 1, 4-dichloro benzene

(B) Cis-1, 2-dichloro ethene

(C) Trans-1,2dichloro-2-pentene

(D) Trans-1,2dichloro ethene

**Q.16** The molecules that will have dipole moment are – ***(1992)***

(A) 2,2-dimethyl propane

(B) Trans-2-pentene

(C) Cis-3-hexene

(D) 2,2,3,3-tetramethyl butane

**Q.17** Only two isomers of monochloro product is possible of - ***(1986)***

(A) n-butane (B) 2,4-dimethyl pentane

(C) Benzene (D) 1-methyl propane

Each of the questions given below consists of two statements, an assertion (Assertion) and reason (Reason). Select the number corresponding to the appropriate alternative as follows

(A) If both assertion and reason are true and reason is the correct explanation of assertion.

(B) If both assertion and reason are true and reason is not the correct explanation of assertion.

(C) If assertion is true but reason is false.

(D) If assertion is false but reason is true.

**Q.18 Assertion:** Carbon-oxygen bonds are of equal length in carbonate ion. ***(1993)***

**Reason:** Bond length decreases with the multiplicity of bond between two atoms.

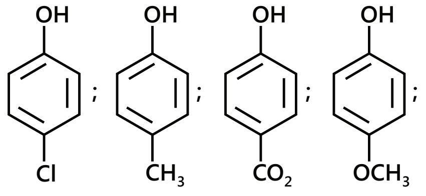
**Q.19 Assertion:** Boiling points of cis-isomers are higher than trans-isomers. ***(1997)***

**Reason:** Dipole moments of cis-isomers are higher than trans-isomers.

**Q.20 Assertion:** Diastereoisomers have different physical properties. ***(1986)***

**Reason:** They are non-superimposable mirror images.

**Q.21** Arrange the following compounds in order of decreasing acidity: ***(2013)***

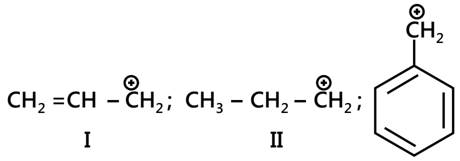


(I) (II) (III) (IV)

(A) II > IV > I > III (B) I > II > III > IV

(C) III > I > II > IV (D) IV > III > I > II

**Q.22** The order of stability of the following carbocation: is: ***(2013)***



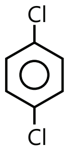
$CH_2=CH-\overset{\oplus}{C}H_2$; $CH_3-CH_2-\overset{\oplus}{C}H_2$;

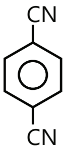
I II III

(A) III > II > I (B) II > III > I

(C) I > II > III (D) III > I > II

**Q.23** For which of the following molecule significant $\mu \neq 0$ ? **(2014)**

(a) 

(b) 

(c) 

(d) 

(A) Only (c) (B) (c) and (d)

(C) Only (a) (D) (a) and (b)

## JEE Advanced/Boards

## Exercise 1

**Q.1** Explain the term hybridization. Why does carbon undergo hybridization? Explain the different types of hybridizations carbon atom can undergo?

**Q.2** In terms of hybridization of carbon atom, discuss briefly the shapes of methane, ethane, ethene and ethyne?

**Q.3** Explain?

(a) Although boron trifluoride is insoluble in trimethylamine, it is soluble in triphenylamine.

(b) Which $CX_2$(X = F, Cl, Br, I) is the most stable radical and why?

**Q.4** Discuss classification of hydrocarbons into various types and illustrate each class by taking two examples?

**Q.5** Explain the following giving examples?

(i) Functional group

(ii) Homologous series and its characteristics

**Q.6** Sulphanilic acid although has acidic as well as basic group, it is soluble in alkali but insoluble in mineral acids. Explain.

**Q.7** What is meant by hybridization ? Discuss its various type giving at least one example in each case.

**Q.8** Define tautomerism. Discuss briefly keto-enol tautomerism in aldehydes and ketones. Also discuss the conditions under which enol form predominates.

**Q.9** Write equations for the acid base reaction that would occur when each of the following compounds of solution are mixed. In each case label the stronger acid and stronger base and the weaker acid and weaker base.

(a) $NaNH_2$ is added to acetylene

(b) gaseous $NH_3$ is add to ethyl lithium in hexane

(c) $C_2H_5OH$ is added to a solution of

$HC \equiv c^{-}Na+$ in liquid $NH_3$.

(d) NaH is added to $H_3COH$.

**Q.10** Give a brief account of the various types of electronic effects in a covalent molecule.

**Q.11** Define and explain the term resonance with suitable examples. Comment upon the relative contributions of the various resonance structures.

**Q.12** What is hyperconjugation effect? How does it differ from resonance effect. Briefly discuss the significance of hyperconjugation effect.

**Q.13** How are free radicals, carbocations and carbanions produced? Discuss their relative stabilities.

**Q.14** Cyclohexanol is more soluble in water 1-hexanol why?

**Q.15** 1, 5-Pentanediol is soluble and 1-pentanol is slightly soluble in $H_2O$. Justify the statement.

**Q.16** 1° and 2° amides tend to exist as dimmer in solid and pure liquid state.

**Q.17** Give an account of common types of organic reactions with suitable examples.

**Q.18** Explain the following with one example in each case.

(i) Homolytic fission

(ii) Heterolytic fission of covalent bonds.

**Q.19** What are electrophiles and nucleophiles? Explain with examples.

**Q.20** What are reactive intermediates? How are they generated by bond fission?

**Q.21** Discuss the stability of carbanions on the basis of inductive effects.

**Q.22** Explain the following:

(a) p-chlorobenzene is more soluble in n-propyl alcohol than methyl alcohol, while o-dichlorobenzene is less soluble in n-propyl alcohol than methanol.

(b) Heterolytic cleavage requires more energy than homolytic cleavage.

**Q.23** How many isomers of molecular formula $C_3H_7NO$ are possible when all isomers have 'amide' group. If one of the isomer has different properties, name that isomer and give reason of different characteristics.

**Q.24** Explain the following reactions:

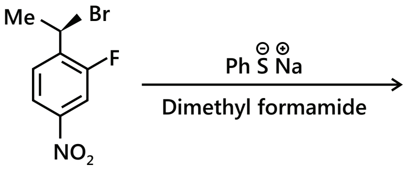
(i) Substitution
(ii) Addition
(iii) Elimination
(iv) Rearrangement
(v) Isomerization
(vi) Condensation
(v) Pericyclic

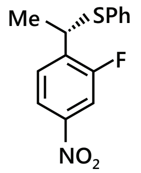
**Q.25** Sulphanilic acid although has acidic as well as basic group, it is soluble in alkali but insoluble in mineral acids. Explain.

# Exercise 2

### Single Correct Choice Type

**Q.1** The major product of the following reaction is



(A)


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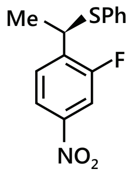

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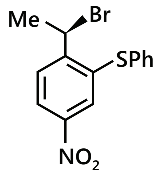
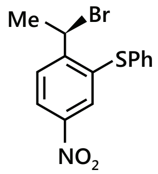
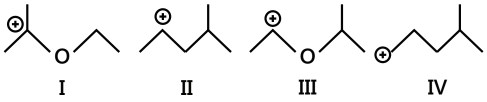


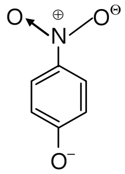
(D)


**Q. 2** The correct stability order for the following species is



(A) II > IV > I > III
(B) I > II > III > IV
(C) II > I > IV > III
(D) I > III > II > IV

**Q.3** The most unlikely representation of resonance structure of p-nitrophenoxide ion is

(A)


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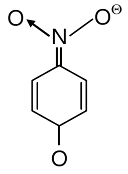
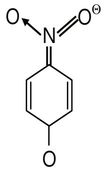
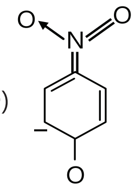


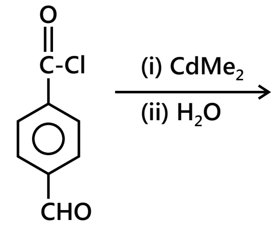
(C)


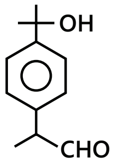
(D)


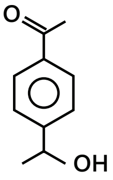
**Q.4** Which of the following is an electrophile?

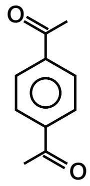
(A) $AlCl_4^-$ (B) $BCl_3$ (C) $NH_3$ (D) $CH_3OH$

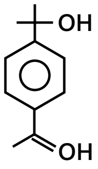
**Q.5** Product of the following reaction is



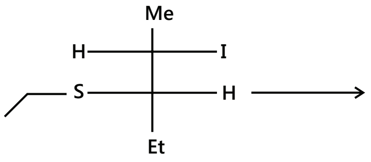
(A)


(B)


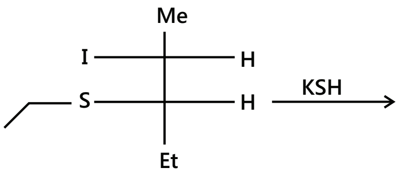
(C)


(D)


**Q.6** Reaction A:



Reaction B:



(A) Products are same and mechanism is also same

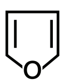
(B) Products are same but mechanism is different

(C) Products are different but mechanism is same

(D) Products are different and mechanism is also different

**Q.7** The stability order of the compounds

**A.**


**B.**


(A) A < B (B) A > B

(C) A = B (D) Stabilities cannot be compared

**Q.8** The acidic strength of chloro substituted benzoic acid is

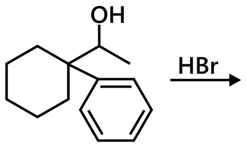
(A) Benzoic acid>o-chloro>m-chloro>p-chloro

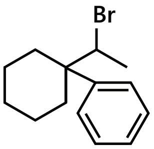
(B) o-chloro>m-chloro>p-chloro>benzoic acid

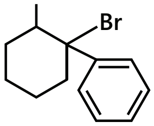
(C) m-chloro>o-chloro>p-chloro>benzoic acid

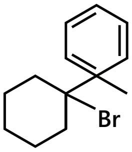
(D) None of these

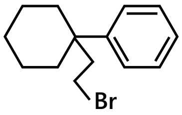
**Q.9** The major product of following reaction is



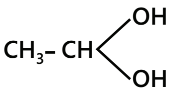
**(A)**


**(B)**


**(C)**


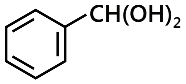
**(D)**


**Q.10** Which one among the following geminal dihydroxy compound is most stable -

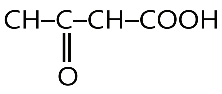
(A)

$\mathrm{CH_3{-}\ CH}\!<\!\begin{smallmatrix}\mathrm{OH}\\ \mathrm{OH}\end{smallmatrix}$

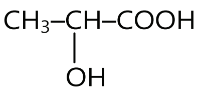
(B) $CH_3{-}C(OH)_2{-}CH_3$

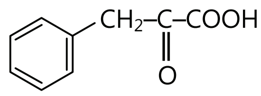
(C) $CCl_3{-}CH(OH)_2$

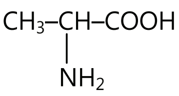
(D)


**Q.11** Which of the following can undergo decarboxylation reactions most easily

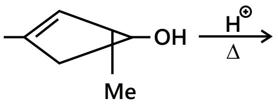
(A)

$\mathrm{CH{-}\underset{\underset{O}{\|}}{C}{-}CH{-}COOH}$

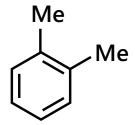
(B)

$\mathrm{CH_3{-}\underset{\underset{OH}{|}}{CH}{-}COOH}$

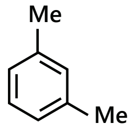
(C)


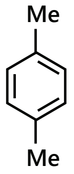
(D)

$\mathrm{CH_3{-}\underset{\underset{NH_2}{|}}{CH}{-}COOH}$

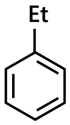
**Q.12** Write the product of the following reaction:



(A) 

(B) 

(C) 

(D) 

**Q.13** Select the incorrect option amongst the following statements

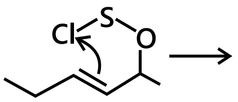
(A) Bimolecular elimination of alkyl halides is a stereospecific reaction

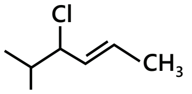
(B) In $S_N2$ reaction a single isomer is the only product

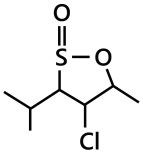
(C) n-Propyl alcohol dehydrates in strongly basic conditions by E1cB mechanism

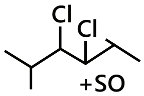
(D) 3-Hydroxypropanal dehydrates in strongly basic conditions by E1cB mechanism

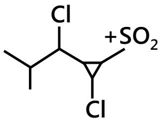
**Q.14** Which of the following is the most likely product from the reaction illustrated by the curved arrows in the formula?

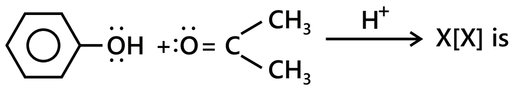


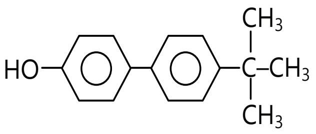
(A) 

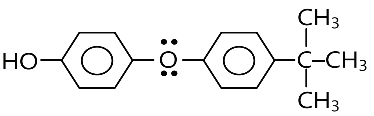
(B) 

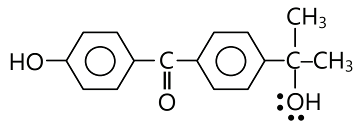
(C) 

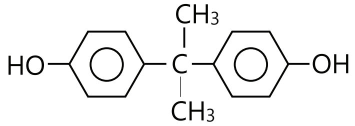
(D) 

**Q.15** 

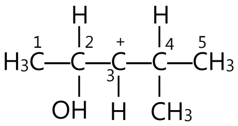
(A) 

(B) 

(C) 

(D) 

**Q.16** In the following carbocation, H/$CH_3$ that is most likely to migrate to the positively charged carbon is


$H_3\overset{1}{C}-\underset{OH}{\overset{H}{\overset{2}{C}}}-\underset{H}{\overset{+}{\overset{3}{C}}}-\underset{CH_3}{\overset{H}{\overset{4}{C}}}-\overset{5}{C}H_3$

(A) $CH_3$ at C-4 (B) $CH_3COCH_3$

(C) $CH_3CHO$ (D) H at $C_2$

**Q.17** The compound having maximum enol content -

(A) $CH_3CH_2CHO$ (B) $CH_3COCH_3$

(C) $CH_3CHO$ (D) $CH_3COCH_2COCH_3$

**Q.18** Which of the following statement is correct?

(A) Trimethylmenthyl and triphenylmethyl radicals, both being 3° free radical, equally exist in solution

(B) Stability order of carbanions always follows reverse order to that of corresponding carbocations

(C) Among the simple alkyl carbocations, the most stable one is $\overset{+}{C}H_3$ because here the positive charge is dispersed only to small extent

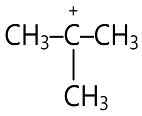
(D) None of these

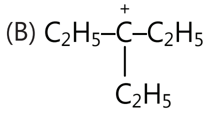
**Q.19** The heat of hydrogenation of benzene is 49.8 Kcal/mole while its resonance energy is 36.0 Kcal/mole. Then the heat of hydrogenation of cyclohexene is -

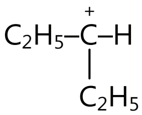
(A) 28.6 K cal/mole (B) 13.8 K cal/mole

(C) 85.8 K cal/mole (D) 36.0 K cal/mole

**Q.20** Which carbocation among the following is most stable -

(A) 
$CH_3-\underset{CH_3}{\overset{+}{C}}-CH_3$

(B) 
$C_2H_5-\underset{C_2H_5}{\overset{+}{C}}-C_2H_5$

(C) 
$C_2H_5-\underset{C_2H_5}{\overset{+}{C}}-H$

(D) $CH_2{-}CH{-}CH_2^+$

**Multiple Correct Choice Type**

**Q.21** Resonance structure of a molecule should have –

(A) Identical arrangement of atoms

(B) Nearly the same energy content

(C) The same number of paired electrons

(D) Identical bonding

**Comprehension Type**

**Paragraph 1 (Q.22 to 24)**

Conformation are structures obtained byrotation around $\sigma$ bonds without breaking and remaking the bonds. Ethane has staggered and eclipsed conformations. Staggered conformation is more stable than eclipsed conformation.

**Q.22** The total number of possible conformation of ethane are -

(A) 2 (B) 3 (C) Infinite (D) Zero

**Q.23** Which conformation of cyclohexane is most stable?

(A) Chair (B) Boat

(C) Half-chair (D) Half-boat

**Q.24** Which of the following is correct?

(A) Conformations cannot be isolated due to less difference in their energy

(B) Conformations can be isolated

(C) Conformations are obtained by breaking and remaking the bonds

(D) Conformations are same as configurational isomers

**Paragraph 2 (Q.25 to 27)**

Those compounds which rotate plane polarised light are optically active compounds. They must be chiral, i.e. should not have any plane of symmetry. They should have chiral carbon atom. Meso compounds have internal plane of symmetry.

**Q.25** Which of the following alkane shows optical isomerism?

(A) 2-methyl pentane (B) 3-methyl pentane

(C) 2,3-dimethyl pentane (D) Both (B) and (C)

**Q.26** Which the following are pair of enantiomers?

(A) d-glucose and l-glucose

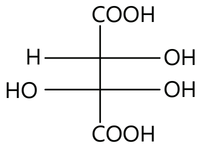
(B) Glucose and L-glucose

(C) Racemic-tartaric acid

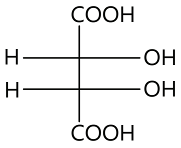
(D) Meso-tartaric acid

**Q.27** Which of the following is meso compounds?

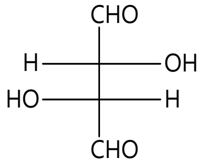
(A)



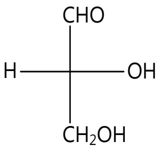
(B)



(C)



(D)



**Assertion Reasoning Type**

Each of the questions given below consists of two statements, an assertion (Assertion) and reason (Reason). Select the number corresponding to the appropriate alternative as follows

(A) If both assertion and reason are true and reason is the correct explanation of assertion.

(B) If both assertion and reason are true and reason is not the correct explanation of assertion.

(C) If assertion is true but reason is false.

(D) If assertion is false but reason is true.

**Q.28 Assertion:** Trophylium cation is more stable than $(CH_3)_3C^+$.

**Reason:** It is stabilized by both resonance effect and inductive effect.

**Q.29 Assertion:** In benzyne, two out of six carbon atoms are sp-hybridised.

**Reason:** Benzyne has one $C \equiv C$ bond.

**Q.30 Assertion:** $PH_3$ is stronger nucleophile than $NH_3$.

**Reason:** $PH_3$ is stronger base than $NH_3$.

**Q.31 Assertion**: The carbocation $CF_3-\overset{\oplus}{C}H_2$ is less stable than $\overset{\oplus}{C}F_3$.

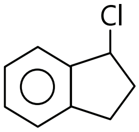
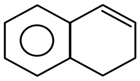
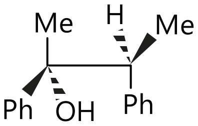
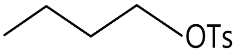
**Reason:** In case of $CF_3-\overset{\oplus}{C}H_2$, $CF_3$ is strong electron withdrawing, therefore increases +ve, charge whereas in $\overset{\oplus}{CF_3}$, lone pair of F overlap with vacant p-orbital of carbon reducing +ve charge by pπ-pπ bonding or back bonding.

### Match the Columns

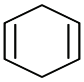
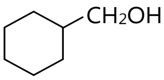
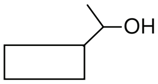
**Q.32** Match the following:

| **Column I** | | **Column II** | |
|---|---|---|---|
| (A) | Carbocations | (p) | E1 |
| (B) | Tetrahedral transition state | (q) | Nucleophilic-addition |
| (C) | Pentavalent transition state | (r) | $S_N2$ |
| (D) | Carbonyl compounds | (s) | C=C + HX |

**Q.33** Match the compounds given in column I with their reactions given column II

| **Column I** | | **Column II** | |
|---|---|---|---|
| (A) |  | (p) | Halogenation |
| (B) |  | (q) | Electrophilic addition reactions |
| (C) |  | (r) | Nucleophilic addition reactions |
| (D) |  | (s) | Elimination reaction $E_1$ or $E_2$) |
| | | (t) | Formation of carbocation intermediate |

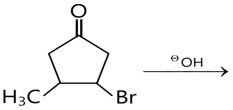
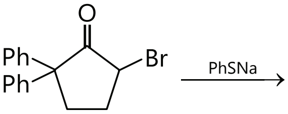
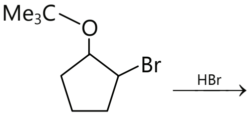
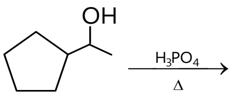
**Q.34** Match the following:

| **Column I** | | **Column II** | |
|---|---|---|---|
| (A) | $(CH_3)_2C{=}CH_2$ + HBr | (p) | 1° carbocation |
| (B) |  + $CHBr_3$ + $(CH_3)_3COK$ | (q) | 2° carbocation |
| (C) |  + $H^+$ | (r) | 3° carbocation |
| (D) |  | (s) | Carbene |

**Q.35** Match the following:

| **Column I** | | **Column II** | |
|---|---|---|---|
| (A) | Carbocation | (p) | Reaction with ethylene |
| (B) | Carbanions | (q) | Reaction with opposite species |
| (C) | Carbenes | (r) | Rearrangement |
| (D) | Free adicals | (s) | Disproportionation |

**Q.36** Match the following:

| **Column I** | | **Column II** | |
|---|---|---|---|
| (A) |  | (p) | $E_2$(Major) |
| (B) |  | (q) | $E_1$(Major) |
| (C) |  | (r) | $S_N1$(Major) |
| (D) |  | (s) | $S_N2$(Major) |
| | | (t) | $E_1CB$(Major) |

## Previous Years' Questions

**Q.1** For 1-methoxy-1, 3-butadienium ion which of the following resonating structure is least stable? ***(2005)***

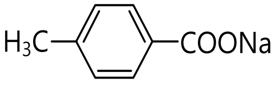
(A) $\overset{\ominus}{C}H_2 - \overset{\oplus}{C}H - CH = CH - O - CH_3$

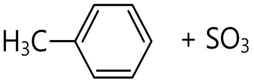
(B) $CH_2 - CH = CH - CH = O - CH_3$

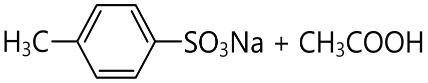
(C) $CH_2 = CH_2 - \overset{\oplus}{C}H = \overset{\ominus}{C}H - O - CH_3$

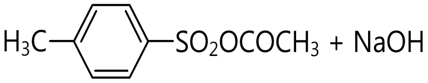
(D) $CH_2 = CH - \overset{\ominus}{C}H - CH = \overset{\oplus}{O} - CH_3$

**Q.2** Which of the following is obtained when 4-methylbenzene sulphonic acid is hydrolysed with excess of sodium acetate ? ***(2005)***

(A) 

(B) 

(C) 

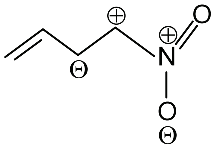
(D) 

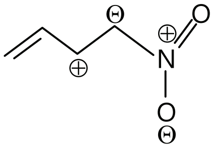
**Q.3** When benzene sulphonic acid and p-nitrophenol are treated with $NaHCO_3$, the gases released respectively are ***(2006)***

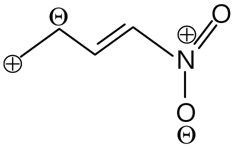
(A) $SO_2$, $NO_2$ (B) $SO_2$, NO

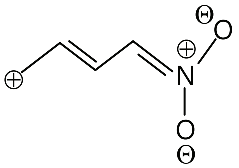
(C) $SO_2$, $CO_2$ (D) $CO_2$, $CO_2$

**Q.4** Among the following least stable resonance structure is – ***(2007)***

(A) 

(B) 

(C) 

(D) 

**Q.5** Phenol is less acidic than - ***(1986)***

(A) Acetic acid (B) p-methoxy phenol

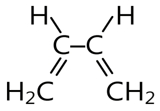
(C) p-nitrophenol (D) Ethanol

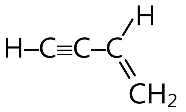
**Q.6** The compound in which C uses its $sp^3$-hybrid orbitals for bond formation is ***(2000)***

(A) HCOOH (B) $(H_2N)_2CO$

(C) $(CH_3)_3COH$ (D) $CH_3CHO$

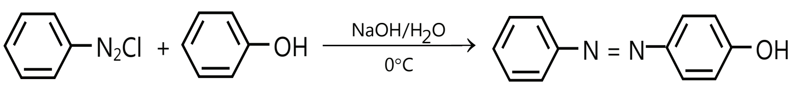
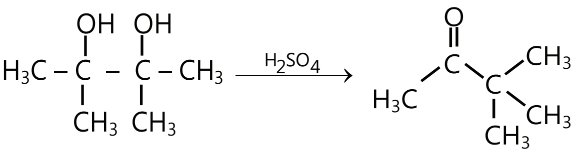
**Q.7** Amongst the given options, the compound(s) in which all the atoms are in one plane in all the possible conformations (if any), is (are) ***(2011)***

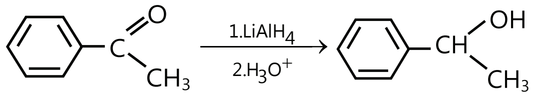
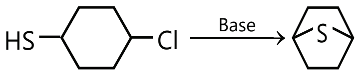
(A) 

(B) 

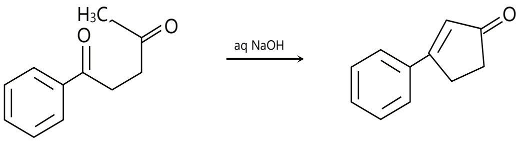
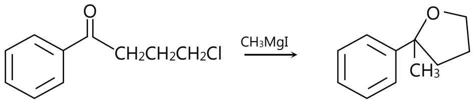
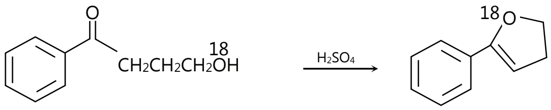
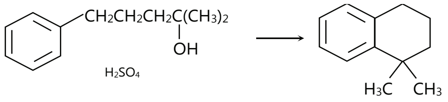
(C) $H_2C=C=O$ (D) $H_2C=C=CH_2$

**Q.8** ***(2010)***

| | **Column I** | | **Column II** |
|---|---|---|---|
| (A) |  | (p) | Racemic mixture |
| (B) |  | (q) | Addition reaction |

| | | | |
|---|---|---|---|
| (C) |  | (r) | Substitution reaction |
| (D) |  | (s) | Coupling reaction |
| | | (t) | Carbocation intermediate |

**Q.9** Match the reactions in column I with appropriate type of steps/reactive intermediate involved in these reactions as given in column II ***(2011)***

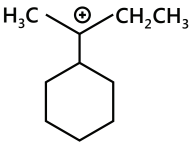
| | **Column I** | | **Column II** |
|---|---|---|---|
| (A) |  | (p) | Nucleophilic substitution |
| (B) |  | (q) | Electrophilic substitution |
| (C) |  | (r) | Dehydration |
| (D) |  | (s) | Nucleophilic addition |
| | | (t) | Carbanion |

**Q.10** Give reasons for the following $CH_2=CH^-$ is more basic than $HC\equiv C^-$. **(2000)**

**Q.11** Match the following with their $K_a$ values ***(2003)***

| | | | |
|---|---|---|---|
| (A) | Benzoic acid | (p) | $10.2 \times 10^{-5}$ |
| (B) | p-nitrobenzoic acid | (q) | $3.3 \times 10^{-5}$ |
| (C) | p-chlorobenzoic acid | (r) | $6.4 \times 10^{-5}$ |
| (D) | p-methylbenzoic acid | (s) | $36.2 \times 10^{-5}$ |

**Q.12** The total number of contributing structures showing hyper conjugation (involving $C-H$ bonds) for the following carbocation is ***(2011)***



**Q.13** Among the following compounds, the most acidic is ***(2011)***

(A) p-nitrophenol

(B) p-hydroxybenzoic acid

(C) o-hydroxybenzoic acid

(D) p-toluic acid

**Q.14** In allene $\left(C_3H_4\right)$, the type (s) of hybridization of the carbon atoms is (are) ***(2012)***

(A) sp and $sp_3$ (B) sp and $sp_2$

(C) only $sp^2$ (D) $sp^2$ and $sp^3$

**Q.15** The hyper conjugative stabilities of tert – butyl action and 2 - butane respectively, are due to ***(2013)***

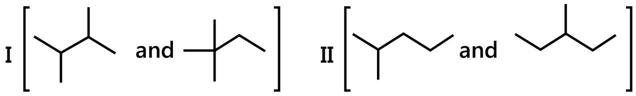
(A) $\sigma \rightarrow p$ (empty) and $\sigma \rightarrow \pi$ electron delocalisation

(B) $\sigma \rightarrow \sigma$ and $\sigma \rightarrow \pi$ electron delocalisation's.

(C) $\sigma \rightarrow p$ (filled) and $\sigma \rightarrow \pi$ electron delocalisation's

(D) P(filled) $\rightarrow \sigma$ and $\sigma \rightarrow \pi$ electron delocalisation's

**Q.16** Isomers of hexane, based on their branching, can be divided into three distinct classes as shown in the figure.



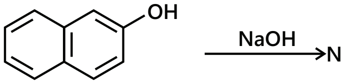
***(2014)***

The correct order of their boiling point is

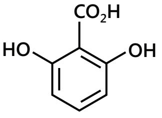
(A) I > II > II (B) III > II > I

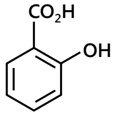
(C) II > III > I (D) III > I > II

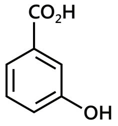
**Q.17** The number of resonance structures for N is ***(2015)***

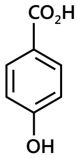


**Q.18** The correct order of acidity for the following compounds is ***(2016)***


I


II


III


IV

(A) I > II > III > IV (B) III > I > II > IV

(C) III > IV > II > I (D) I > III > IV > II

# **PlancEssential** Questions

## JEE Main/Boards

### Exercise 1

Q.1 (iii) Q.3 Q.12 (iii)

Q.17 (vi, ii) Q.19 (iv) Q.22 (ii) Q.27

### Exercise 2

Q.2 Q.14 Q.19 Q.27

### Previous Years' Questions

Q.1 Q.5 Q.10

## JEE Advanced/Boards

### Exercise 1

Q.2 Q.6(4) Q.7(4)

Q.14 Q.23 Q.29

### Exercise 2

Q.8 Q.19 Q.21 Q.23

### Previous Years' Questions

Q.2 Q.4

# Answer Key

## JEE Main/Boards

### Exercise 1

**Q.15** 192 **Q.26** 93.14 g

### Exercise 2

**Single Correct Choice Type**

**Q.1** B **Q.2** D **Q.3** B **Q.4** C **Q.5** D **Q.6** B
**Q.7** B **Q.8** B **Q.9** B **Q.10** C **Q.11** B **Q.12** B
**Q.13** D **Q.14** B **Q.15** B **Q.16** D **Q.17** C **Q.18** C
**Q.19** C **Q.20** A **Q.21** B **Q.22** B **Q.23** D **Q.24** D
**Q.25** D **Q.26** D **Q.27** A **Q.28** C **Q.29** B **Q.30** D
**Q.31** D **Q.32** B

### Previous Years' Questions

**Q.1** C **Q.2** A **Q.3** B **Q.4** C **Q.5** A, B, D **Q.6** C
**Q.7** D **Q.8** B **Q.9** 4 **Q.10** B **Q.11** C **Q.12** A
**Q.13** B **Q.14** C **Q.15** B **Q.16** C **Q.17** A, D **Q.21** C
**Q.22** D **Q.23** B

## JEE Advanced/Boards

### Exercise 2

**Single Correct Choice Type**

**Q.1** A **Q.2** B **Q.3** C **Q.4** B **Q.5** C **Q.6** C
**Q.7** A **Q.8** B **Q.9** C **Q.10** C **Q.11** A **Q.12** B
**Q.13** C **Q.14** A **Q.15** D **Q.16** D **Q.17** A **Q.18** D
**Q.19** A **Q.20** A

**Multiple Correct Choice Type**

**Q.21** A, B, C

**Comprehension Type**

**Q.22** C **Q.23** A **Q.24** A **Q.25** C **Q.26** A **Q.27** C

**Assertion Reasoning Type**

**Q.28** A **Q.29** A **Q.30** C **Q.31** A

**Matric Match Type**

**Q.32** A → p, s; B → q; C → r; D → q

**Q.33** A → p, r, s, t; B → p, q, r, s,t; C → p, r, s, t; D → p, r, t

**Q.34** A → p, r; B → r, s; C → p, r; D → q, r

**Q.35** A → p, r; B → S; C → p, s; D → q, r, s

**Q.36** A →t; B →p; C →r; D →t, b→ p; C→ r; D→ q

## Previous Years' Questions

**Q.1** C **Q.2** C **Q.3** D **Q.4** A **Q.5** B,D **Q.6** C,D

**Q.7** B, C **Q.8** A → r, s ; B → t ; C→ p, q; D→r **Q.9** A → r, s, t ; B → p, s ; C → r, s ; D → q, r

**Q.11** A → r; B → s; C → p; D → q **Q.12** 6 **Q.13** C **Q.14** B **Q.15** A

**Q.16** B **Q.17** 7 **Q.18** A

# Solutions

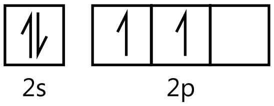
## JEE Main/Boards

## Exercise 1

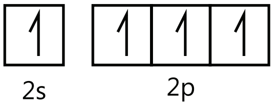
**Sol 1:** Configuration of C: [He] $2s^2 2p^2$

It has four electrons in its outermost shell

Ground state :



Excited state :



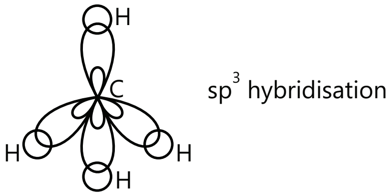
Thus, it has 4 unpaired electrons which its uses in bond forming thus making it tetravalent.

**Sol 2:** Carbon undergo hybridization due to following reasons

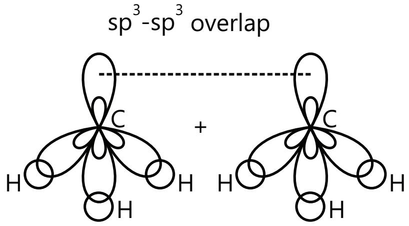
(i) Hybridised orbitals are equivalent in energy (degenerate) and have more effective overlapping

(ii) Hybridised orbitals are directional in nature

**Sol 3:** Methane:



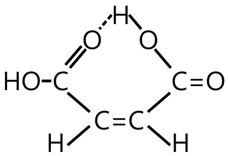
Ethane :



Both carbon $sp^3$

**Sol 4:** Fumaric acid has higher metling point as maleic acid has intramolecular H-bonding whereas fumaric acid has intermolecular bonding

Maleic acid :

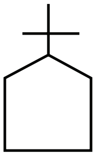


**Sol 5:** (i) Bond length: Bond length decreases with increasing s character in overlapping orbitals for ex., $sp^3$ has the largest bond length and sp has the least (for carbon compounds)

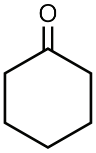
(ii) Bond strength: Bond strength follows opposite order to bond length

**Sol 6:**

(a) Tert-butylcyclopentane

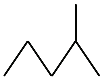
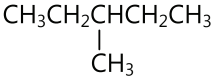
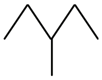
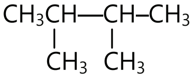
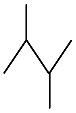
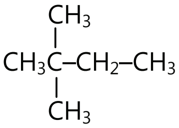
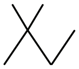


(b) Cylohexanone

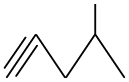
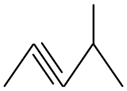
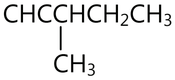
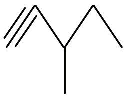


**Sol 7:** (ii) (p-nitrophenol) is more soluble than (i) (o-nitrophenol) as the extent of hydrogen bonding with solvent will be less in (i) due to steric hindrance by a bukly $NO_2$-group

**Sol 8:** (i) $C_6H_{14}$

| Condensed | Bond line |
|---|---|
| $CH_3CH_2CH_2CH_2CH_2CH_3$ |  |
| $CH_3CH_2CH_2CHCH_3CH_3$ |  |
|  $CH_3CH_2\underset{\mid\atop CH_3}{C}HCH_2CH_3$ |  |
|  $CH_3\underset{\mid\atop CH_3}{C}H—\underset{\mid\atop CH_3}{C}H–CH_3$ |  |
|  $CH_3\overset{CH_3\atop \mid}{\underset{\mid\atop CH_3}{C}}–CH_2–CH_3$ |  |

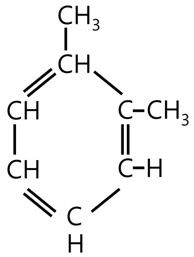
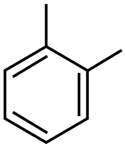
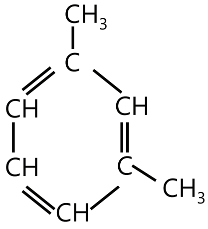
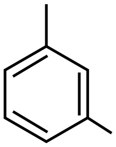
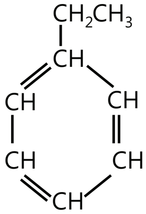
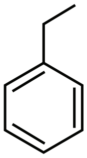
(ii) $C_6H_{10}$

| Condensed | Bond line |
|---|---|
| $CHCCH_2CH_2CH_2CH_3$ |  |
| $CH_3CCCH_2CH_2CH_3$ |  |
| $CH_3CH_2CCCH_2CH_3$ |  |
| $CHCCH_2CHCH_3CH_3$ |  |
| $CH_3CCCHCH_3CH_3$ |  |
|  $CHC\underset{\mid\atop CH_3}{C}HCH_2CH_3$ |  |

(iii) $C_8H_{10}$

Degree of unsaturation = $8 - \frac{10}{2} + 1 = 4$

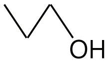
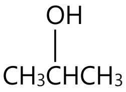
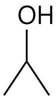
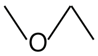
I am drawing those isomers only which contains a benzene ring.

| Condensed | Bond line |
|---|---|
|  |  |
|  |  |
|  |  |

(iv) $C_8H_{18}$

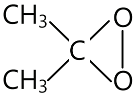
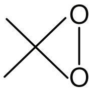
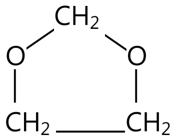
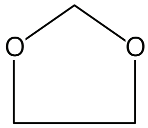
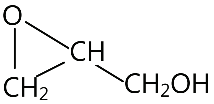
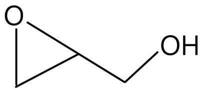
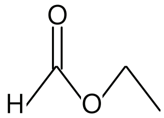
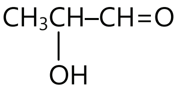
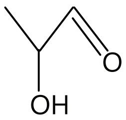
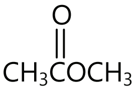
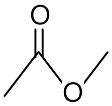
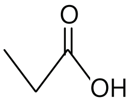
18 isomers

(v) $C_3H_8O$

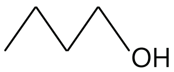
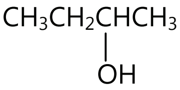
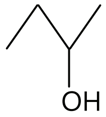
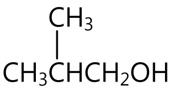
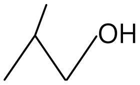
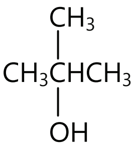
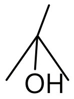
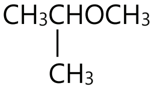
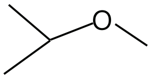
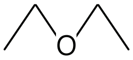
| Condensed | Bond line |
|---|---|
| $CH_3CH_2CH_2OH$ |  |
|  $CH_3\overset{OH\atop\mid}{C}HCH_3$ |  |
| $CH_3OCH_2CH_3$ |  |

(vi) $C_3H_6O_2$

Degree of unsaturation = 1

| Condensed | Bond line |
|---|---|
|  |  |
|  |  |
|  |  |
| $CH_3CH_2OCHO$ |  |
|  $CH_3\underset{OH}{\underset{\vert}{C}}H-CH=O$ |  |
|  $CH_3\overset{O}{\overset{\Vert}{C}}OCH_3$ |  |
| $CH_3CH_2COOH$ |  |

(vii) $C_4H_{10}O$

| Condensed | Bond line |
|---|---|
| $CH_3CH_2CH_2CH_2OH$ |  |
|  $CH_3CH_2\underset{OH}{\underset{\vert}{C}}HCH_3$ |  |
|  $CH_3\overset{CH_3}{\overset{\vert}{C}}HCH_2OH$ |  |
|  $CH_3\underset{OH}{\underset{\vert}{\overset{CH_3}{\overset{\vert}{C}}}}HCH_3$ |  |
| $CH_3CH_2CH_2OCH_3$ |  |
|  $CH_3\underset{CH_3}{\underset{\vert}{C}}HOCH_3$ |  |
| $CH_3CH_2OCH_2CH_3$ |  |

(viii) $C_6H_{11}NO_2$

More than 20 molecules

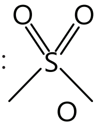
**Sol 9:** Functional group is a specific group of atoms or bonds within molecules that are responsible for the characteristic chemical reaction of those molecules.

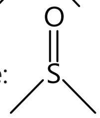
(i) Thialcohol:–SOH

(ii) Isothiocyanate: S=C=N–

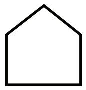
(iii) Thiocyanate:–S=C=N$^-$

(iv) Sulphonic acid: –$SO_3H$

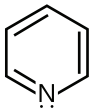
(v) Sulphones: 

(vi) Sulphoxide: 

**Sol 10:** Hemicyclic compounds is a cyclic compound that has only one single element as constituent of ring.

E.g.: Cyclopentane : 

Heterocyclic compounds is a cyclic compound that has atoms of atleast two different elements as members of its ring (s)

E.g.: Pyridine : 

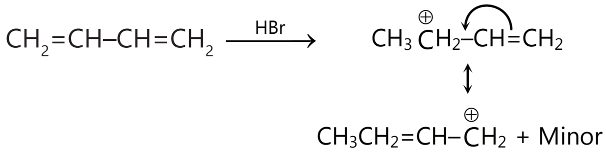
**Sol 11:** Hydrazine (H–N=N–H) does not give a +ve test for Lassaigne's test of Nitrogen because it cannot produce NaCN.

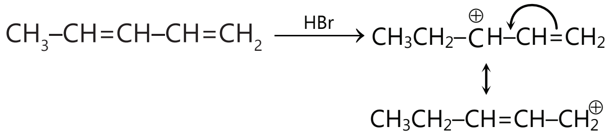
**Sol 12:** (i) $CH_2=CH-C_2H_5 \xrightarrow{HBr}$

$CH_3-\overset{\oplus}{C}H-C_2H_5 + \overset{\oplus}{C}H_2-CH_2CH_2C_2H_5$

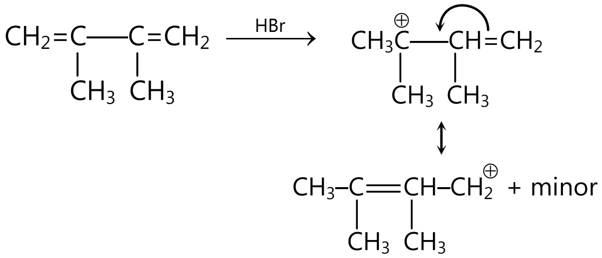
(ii) $CH_3CH=CHCH_3 \xrightarrow{HBr}$

$CH_3CH_2\overset{\oplus}{C}HCH_3 + CH_3\overset{\oplus}{C}HCH_2CH_3$

(iii)


(iv)


+ minor but stable than III minor

(v)


Thus, we see on the basis of resonance and inductive effects (v) > (iv) > (iii) > (ii) > (i)

**Sol 13:** Homologous series is a series of compounds with a similar general formula, usually varying by a single parameter such as the length of the chain.

Members of a homologous series usually have similar physical and chemical properties

Many physical properties, eg. Boiling point gradually increase with molecular mass

Alcohol series:

Methyl alcohol $CH_3OH$

Ethyl alcohol $C_2H_5OH$

Propyl alcohol $C_3H_7OH$

Butyl alcohol $C_4H_9OH$

**Sol 14:** Refer theory

**Sol 15:** $R_1Ag_2 \rightarrow 2Ag + \text{other}$

Let molecular weight of salt be M.

Then 1 mole of $R_2$ Ag gives 2 moles of Ag

$$\therefore\ 2 \times \frac{0.2018}{M} = \frac{0.1073}{108} \Rightarrow M = 406.23$$

Molecular weight of organic compound

$= 406.23 - (2 \times 108) \times 2 = 192.23$

**Sol 16:** Fractional crystallization is a method of refining substances based on difference in solubility (especially when the difference in solubility is low)

**Sol 17:** For platinic chloride method, we have

$$\frac{w}{2M+410} = \frac{x}{195}$$

$$\frac{w}{2M}\ \frac{0.3168}{2M+410} = \frac{0.1036}{195}$$

$2M + 410 = 596.3$

$M = 93.14$ g

**Sol 18:** (a) Fractional Distillation

(b) Crystallisation (c) Steam Distillation

**Sol 19:** For definition and types of resonance effect refer text.

It differs from inductive effect as resonance effects involves actual movement of electrons contrary to inductive effect in which there is no actual movement but just development of polarity.

Because of this, resonance effect is more stronger than inductive effect.

**Sol 20:** The reversal occurs due to hyperconjugation effect, which is an extension of the resonance effect. The inductive effect will depend on the number of hyperconjugation structures which will depend on the number of $\alpha$–H

For $H_3C$– max inductive effect (3$\alpha$H)

$H_2CH_3C$–2 $\alpha$ H

$(CH_3)$ CH–1 $\alpha$ H

$(CH_3)_3C$–0 $\alpha$ H

Thus order of hypercongugation effect

$CH_3– > CH_3CH_2– > (CH_3)\ _2C– > (CH_3)\ _3C–$

Whereas inductive effect follows reverse order

**Sol 21:** Refer text

**Sol 22:** Chromatography is based upon the principal of distributing the components of a given organic mixture between two medium. One of which is stationary and other is mobile.

**Sol 23:** Refer text

**Sol 24:** Fractional distillation is employed when the liquids which have to be separated have very little difference in their boiling point temperatures (~10 – 15K)

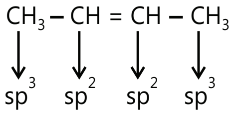
## Exercise 2

### Single Correct Choice Type

**Sol 1: (B)** In $CH_3^+$, C has a $sp^2$ structure, making its shape trigonal planar

**Sol 2: (D)** A nucleophile must have a lone pair of electons

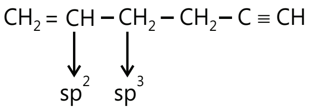
**Sol 3: (B)**



$$\underset{\underset{sp^3}{\downarrow}}{CH_3} - \underset{\underset{sp^2}{\downarrow}}{CH} = \underset{\underset{sp^2}{\downarrow}}{CH} - \underset{\underset{sp^3}{\downarrow}}{CH_3}$$

**Sol 4: (C)** $C_1$ is sp and $C_2$ is $sp^2$

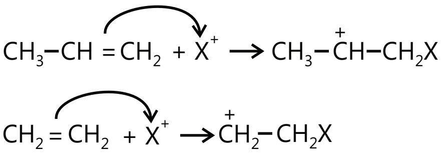
**Sol 5: (D)**



$$CH_2 = \underset{\underset{sp^2}{\downarrow}}{CH} - \underset{\underset{sp^3}{\downarrow}}{CH_2} - CH_2 - C \equiv CH$$

**Sol 6: (B)** In $CH_3^+$, C has a $sp^2$ structure, making its shape trigonal planar

**Sol 7: (B)**



$$CH_3-CH=CH_2 + X^+ \longrightarrow CH_3-\overset{+}{C}H-CH_2X$$

$$CH_2=CH_2 + X^+ \longrightarrow \overset{+}{C}H_2-CH_2X$$

The resulting carbocation is more stable for $CH_3$–CH=$CH_2$ due to more number of hyperconjugation structures

**Sol 8: (B)** Carbanion is a nucleophile as its has a negative and lone pair of electrons.

**Sol 9: (C)** In (I) → No charge separation.

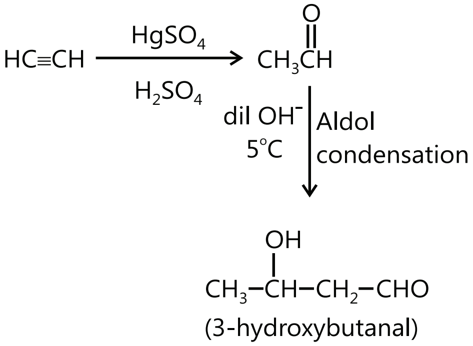
(II) → Complete octet on every atom

(III) → Positive charge on Carbon atom

(IV) → Negative charge on Carbon atom

**Sol 10: (C)** In II, N has 10 valence electrons which is not possible, as N is period 2 element

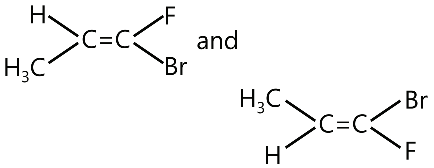
**Sol 11: (B)**



$$HC\equiv CH \xrightarrow[H_2SO_4]{HgSO_4} CH_3\overset{O}{\overset{\|}{C}}H \xrightarrow[5^\circ C]{\text{dil } OH^- \text{ Aldol condensation}} CH_3-\overset{OH}{\overset{|}{C}H}-CH_2-CHO$$

(3-hydroxybutanal)

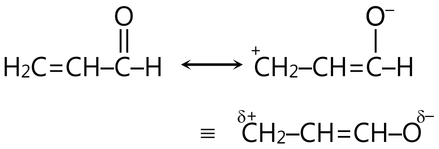
**Sol 12: (B)**



Are geometric isomers

For rest cannot show geometrical isomerism as they contains same group on C atom.

**Sol 13: (D)**



$$H_2C=CH-\overset{O}{\overset{\|}{C}}-H \longleftrightarrow \overset{+}{C}H_2-CH=\overset{O^-}{\overset{|}{C}}-H$$

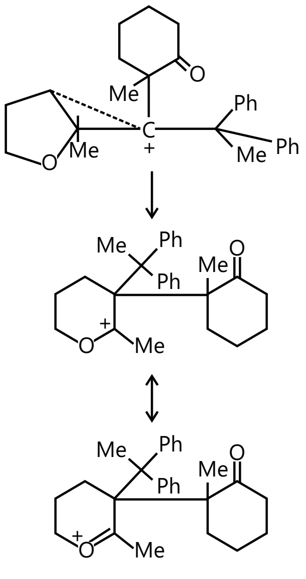
$$\equiv \overset{\delta+}{C}H_2-CH=CH-\overset{\delta-}{O}$$

**Sol 14: (B)** (D) is most stable because of the enhanced stability of resulting carbocation due to conjugation. In (A) lone pair of N is not conjugated and also $CH_2$C–N single bond have more +I effect than C–N double bond making it basic than (B) $CH_3$–C has least +I effect

**Sol 15: (B)** $RSO_3^-$ group is the best leaving group. In 1 and 2, 2 will be more stable due to more – I effect of $NH_3^+$ and 3 > 4 in stability

∴ 2 > 1 > 3 > 4

**Sol 16: (D)**



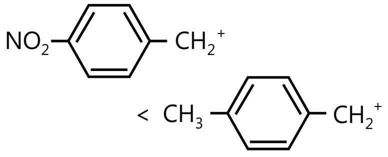
Here the positive charge is greatly Stabilise as all the atoms have complete octet.

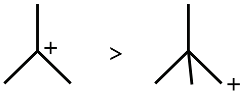
**Sol 17: (C)** Its ring ontains 2$\pi$ electrons, so it follows huckel s rule

**Sol 18: (C)** $5Na_2O_2+2P \xrightarrow{\text{fuse}} 2Na_3PO_4 + 2Na_2O$

**Sol 19: (C)** Reactivity order for $S_N1$ reaction depends upon the stability of resulting carbocation.

Ph.$CH_2^+$ > $Ph^+$, since Ph–$CH_2^+$ is a benzyl cation (due to –I and –M effect of $NO_2^-$)



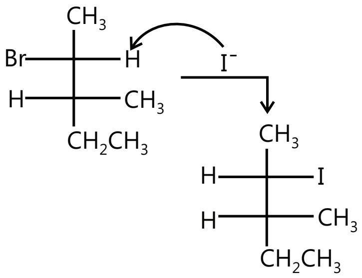


($\because$ tertiary carbocation > secondary carbocation)

**Sol 20: (A)** $S_N1$ reaction yield a racemic mixture

**Sol 21: (B)** –Cl group have –I effect which stabilizes the anion and it decreases with distance.

**Sol 22: (B)**

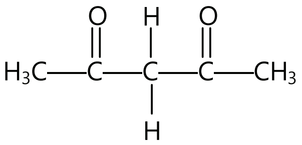


**Sol 23: (D)** For a compound to be reactive towards $S_N2$ reaction, the resulting carbocation should be least stable. Here, the resulting carbocation is least stable in (d) due to strong –M effect of $–NO_2$ group.

**Sol 24: (D)** Magnesia mixture is $MgCl_2 + NH_4Cl$ + little of $NH_3$

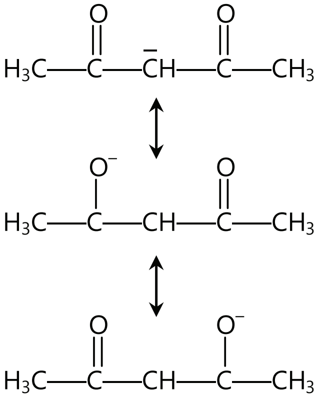
**Sol 25: (D)** $K_2SO_4$ raises the boiling point of water.

**Sol 26: (D)**



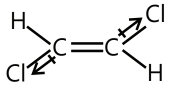
$$H_3C-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{O}{\|}}{C}-CH_3$$

Enol ate form is



This structure is stabilised most by resonance

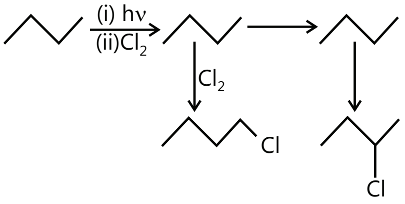
**Sol 27: (A)** For trans 1,2-Dichloroethene, dipole moment is 0



Which causes maximum difference in dipole moment between its cis and trans form. For others, trans form also has some dipole moment.

**Sol 28: (C)** Triplet carbene is more stable than singlet carbene because of the more repulsion between electrons in singlet carbene compared to triplet carbene.

**Sol 29: (B)**



Total number of isomeric chloro butanes = 2

**Sol 30: (D)** Reactivity will be most for the compound which has most positive charge density on carbonyl carbon. Noting this, order will be:

ArCOAr > ArCHO > ArCOR > HCHO >ArCOAr>

**Sol 31: (D)** There are no meso forms for glucose.

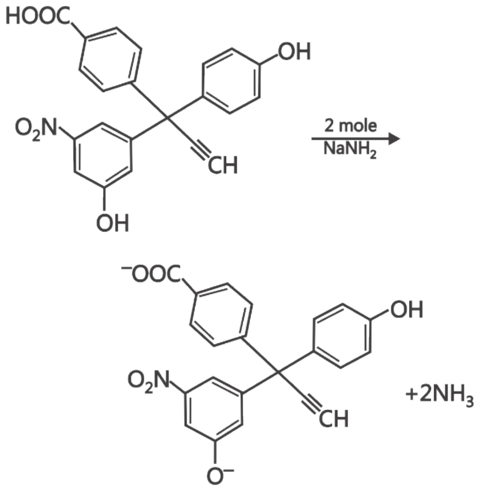
**Sol 32: (B)** Its necessary to remove S and N before testing for halogens.

## Previous Years' Questions

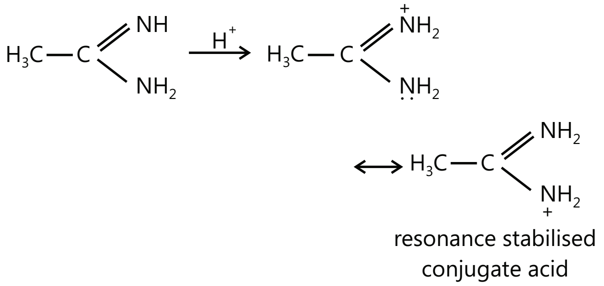
**Sol 1: (C)** In general, the order of acid strength is

$$-C\equiv CH < ROH < H_2O < PhOH < R-COOH$$

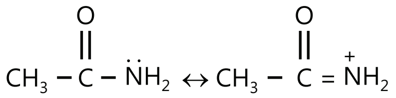
Therefore, during stepwise neutralisation of given acid, -COOH will be neutralised first. In the second step, the phenolic –OH, assisted by –I effect of $-NO_2$ at Meta position will be neutralised.



**Sol 2: (A)** I is most basic due to formation of resonance stablised conjugate acid



IV is amide, least basic



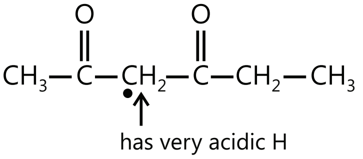
$$CH_3-\overset{\overset{O}{\|}}{C}-\ddot{N}H_2 \leftrightarrow CH_3-\overset{\overset{O}{\|}}{C}=\overset{+}{N}H_2$$

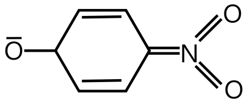
lone pair is part of delocation

Also, among alkyl amines, 2° is more basic than 1° amine. Hence , Overall order of basic strength is 1 > 3 > 2 > 4

**Sol 3: (B)** Carboxylic acid is stronger acid than ammonium ion, hence –COOH(X) is most acidic. $Z(\overset{+}{N}H_3)$ is more acidic than $Y(\overset{+}{N}H_3)$ due to –I effect of –COOH on Z. Hence, overall acid strength order is X > Z > Y

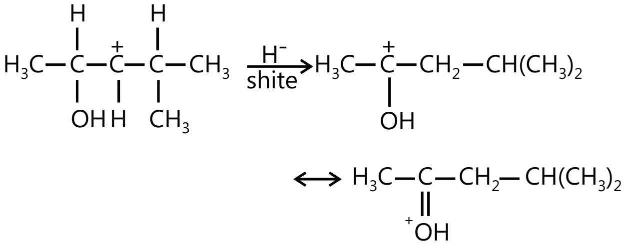
**Sol 4: (C)** A methylene ($-CH_2-$) with carbonyl on both side is highly acidic.



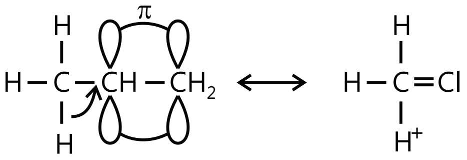
**Sol 5: (A, B, D)**  Octet of nitrogen is violated.

**Sol 6: (C)** I is most stable because it has more covalent bonds and negative charge on electronegative nitrogen. III is more stable than II and IV due to greater number of covalent bonds. Between II and IV, II is more stable since, it has negative charge on electronegative atom and positive charge on electropositive atom. Hence, overall stability order is I > III> II > IV

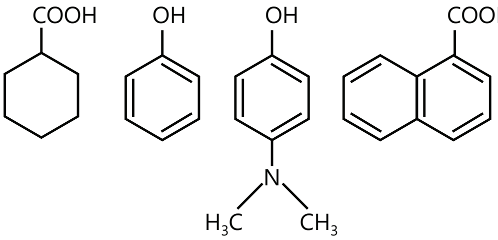
**Sol 7: (D)** H at C-2 will migrate giving resonance stabilized carbocation



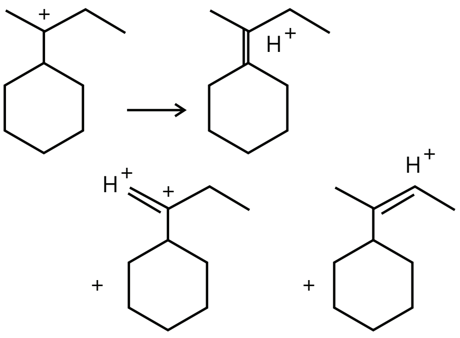
**Sol 8: (B)** The σ-electrons of C-H bond is delocalized with p-orbitals of π-bond.



**Sol 9: (4)** Aromatic alcohols and carboxylic acids forms salt with NaOH, will dissolve in aqueous NaOH:



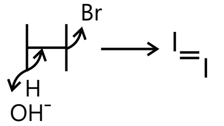
**Sol 10: (B)** These are total $6\alpha-H$ to $sp^2$ carbon and they all can participate in hyper conjugation.

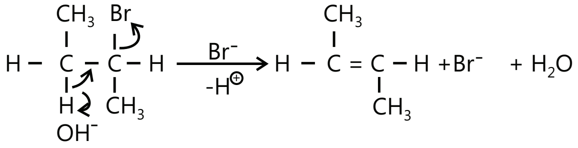


Three structures Two structures

**Sol 11: (C)** D(+)-tartaric acid has positive optical rotation and is derived from D(+) glyceraldehyde.

**Sol 12: (A)**

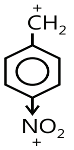




$$H-\underset{\underset{OH^-}{H}}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{Br}{C}}-H \xrightarrow[-H^{\oplus}]{Br^-} H-\overset{CH_3}{C}=\underset{CH_3}{C}-H + Br^- + H_2O$$

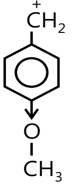
**Sol 13: (B)**

Nitro-group is electron withdrawing therefore decreases stability.



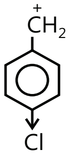
Methoxy group is electron releasing.

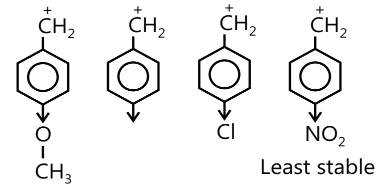
Therefore increases stability by donating electron.



Chlorine is also electron withdrawing but its effect is less than $-NO_2$ group.

Hence, correct order of stability.





Most stable Least stable

**Sol 14: (C)** $CH_3^-$ has the highest nucleophilicty.

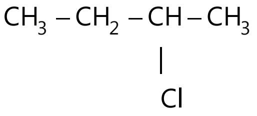
**Sol 15: (B)** In cis isomer the carbon-chlorine dipole reinforces and henece ther is large molecualr dipole.

**Sol 16: (C)** (A) and (D) are symmetric alkanes, hence these are non polar, while (B) and (C) are symmetric alkenes hence they posses dipole momnet. But B is trans.

**Sol 17: (A, D)** n-butane has following two isomeric monochloro derivatives

$CH_3–CH_2–CH_2–CH_2Cl$

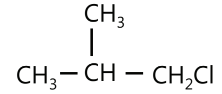
1-chloro butane and



$$CH_3-CH_2-\underset{Cl}{CH}-CH_3$$

2–chloro butane

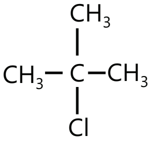
2-methyl propane as following two isomeric monochloro derivatives.



$$CH_3-\overset{CH_3}{CH}-CH_2Cl$$

2-methyl-1-chloropropane

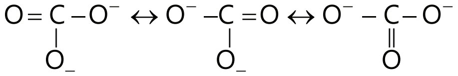
and



$$CH_3-\underset{Cl}{\overset{CH_3}{C}}-CH_3$$

2-methyl-2-chloropropane

**Sol 18:** $CO_3^{2-}$ shows resonance and thus all the three bonds are of identical bond length.



$$O=\underset{O^-}{C}-O^- \leftrightarrow O^- -\underset{O^-}{C}=O \leftrightarrow O^- -\underset{\underset{O}{\|}}{C}-O^-$$

**Sol 19:** Boiling points of isomeric compounds depend on dipole-dipole interactions and cis-isomers have greater dipole moment (more polar) than trans-isomers (less polar).

**Sol 20:** Diastereoisomers are mirror images.

**Sol 21: (C)** Acidic nature order $(III) > (I) > (II) > (IV)$

**Sol 22: (D)** On the basis of number of resonating structure $(III) > (I) > (II)$

**Sol 23: (B)** Quinol (c) and thioquinol (d) do not have $\mu = 0$ due to nonlinear alignment.

## JEE Advanced/Boards

## Exercise 1

**Sol 1:** Hybridisation is the concept of mixing atomic orbitals into new hybrid orbitals suitable for the pairing of electrons to form chemical bonds. Now, talking about carbon, it can hybridize on three different ways, because his valence shell orbitals allows him to do so.

He can hybridize (mix) his valence orbitals to generate sets of equivalent sp, sp2 or sp3 orbitals.

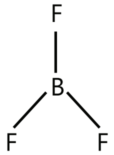
**Sol 2:** Methane: In methane, carbon is $sp^3$ hybridised making the shape tetrahedral.

Ethane: In ethane, both the carbon atoms are $sp^3$ hybridised making its shape tetrahedral with respect to each carbon atom

Ethene: In ethene both are carbon atoms are $sp^2$ hybridised making its shape trigonal planar with respect to each carbon atom.

Ethyne: In ethyne both carbon atoms are sp hybridized making its geometry linear.

**Sol 3:** (a) Boron trifloride



Here, B has only 2 electrons in its valence shell making a lewis acid.

On the other hand, nitrogen has a lone pair of electron in both $(CH_3)$ N and (PH) $_3$N making them Lewis base.

But, in (PH) $_3$N lone pair is resonance stabilised by conjugation with three phenyl rings making availability for lone pair towards co-ordination.

(b) $:CF_2$ is the most stability due to the back bonding between vacant orbital of C and the filled p orbital of F reducing the electron deficiency on C carbon.

**Sol 4:** The classifications for hydrocarbons, defined by IUPAC nomenclature of organic chemistry are as follows:

(a) Saturated hydrocarbon: The general formula for saturated hydrocarbons is $C_nH_{2n+2}$

Example: methane, ethane

(b) Unsaturated hydrocarbons: These with one double bond are called akenes have the formula $C_nH_{2n}$

Example: Ethene, propene.

Those containing triple bonds are called alkynes, with general formula $C_nH_{2n-2}$

Example: Acetylene, Propyne

(c) Cycloalkanes are hydrocarbons: The general formula for a saturated hydrocarbon containing one ring is $C_nH_{2n}$. Example: cyclopropane, cyclobutane

(d) Aromatic hydrocarbons: Also known as arenes, are hydrocarbons that have at least one aromatic ring. E.g. benzene, naphthalene

**Sol 5:** (i) Functional group is an atom or group of atoms that replaces hydrogen in an organic compoundand that defines the structure of a family of compounds and determines theproperties of the family. E.g. Alkyl, Phenyl

(ii) A homologous series is a group of chemicals which have similar chemical properties and can be represented by a general formula. Homologous series are 'families' of organic compounds

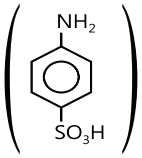
They share common characteristics:

(a) They all contain the same functional group. This gives the homologous series name.

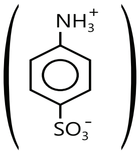
(b) They differ in formula from one member to the next by one -CH2- unit

(c) They show a steady change in physical properties from one member to the next. The alkanes, alkenes and cycloalkanes are examples of homologous series

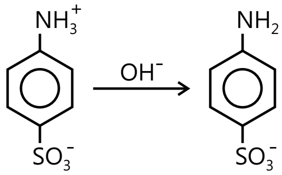
**Sol 6:** Sulphanilic acid



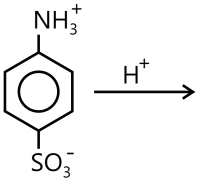
exist as a Zwitter ion



Now,



(Soluble in base) (as OH– is more basic than $-NH_2$)



No reaction (insoluble)

($H^+$ is less acidic the $-SO_3H$)

**Sol 7:** Hybridization happens when atomic orbitals mix to form new atomic orbitals. The new orbitals have the same total electron capacity as the old ones. The properties and energies of the new, hybridized orbitals are an 'average' of the original unhybridized orbitals

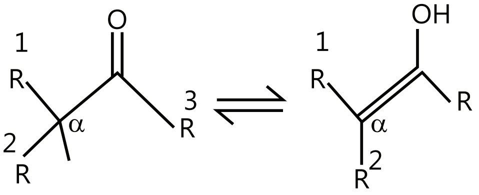
$sp^3$ hybridization : Tetrahedrally coordinated carbon.e.g- Methane

$sp^2$ hybridisation: In ethene molecule carbon $sp^2$ hybridises, because one π (pi) bond is required for the double bond between the carbons and only three σ bonds are formed per carbon atom.

sp hybridisation :The chemical bonding in acetylene (ethyne) ($C_2H_2$) consists of sp–sp overlap between the two carbon atoms forming a σ bond and two additional π bonds formed by p–p overlap.

**Sol 8:** Tautomers are constitutional isomers of organic compounds that readily interconvert by chemical reaction called tautomerisation. This reaction commonly results in the formal migration of a hydrogen atom or proton, accompanied by a switch of a single bond and adjacent double bond, The concept of tauromerization is called tautomerism

Keto-enol tautomerism refers to a chemical equailibrium between a keto form (a ketone or an aldehyde) and an enol (an alcohol)

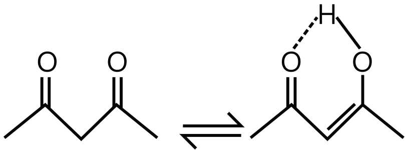


Keto enol

Conditions:

(i) Presence of conjugated double bonds in enol form

(ii) Due to favourable hydrogen bonding interactions



Keto form
(24 %)

(iii) Sometimes under slightly acidic or basic conditions

**Sol 9:** (a) $NaNH_2 + C_2H_2 \longrightarrow$

$NH_2–CH≡C–NH_2 + Na^+ + NH_3$

Strong acid: $NH_2^-$

Weak acid: $C_2H_2$

Weak base: $NH_3$

Strong base: $H–C≡C^-$

(b) $EtLi \xrightarrow[\text{hexane}]{NH_3} LiNH_2 + Et\ (C_2H_6)$

Strong base: $Et^-\ (C_2H_6)$

Weak acid: $NH_3$

Strong acid: $Li^+$

Weak base: $NH_3$

(c) $C_2H_5OH \xrightarrow[NH_3]{HC≡CNa} C_2H_5O^-Na^+ + HC≡CH$

Strong acid: $Na^+$

Weak acid: $C_2H_5OH$

Strong base: $HC≡C^-$

Weak base: HC≡CH

(d) $NaH + CH_3OH \longrightarrow CH_3O^-Na + H_2$

Strong acid: $Na^+$

Weak acid: $CH_3OH$

Strong acid: $H^-$

Weak base: $H_2$

**Sol 10:** The following four types of electronic effects operates in covalent bonds

(a) Inductive effect

(b) Mesomeric and Resonance effect

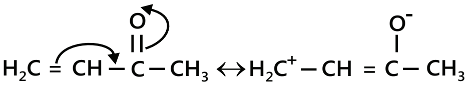
(c) Electronic effects

(d) Hyperconjugation

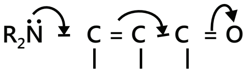
(a) Inductive Effect: In a covalent bond between the two dissimilar atoms, the electron pair forming the bond is never shared absolutely equally between the two atoms but is attracted a little more towards the more electronegative atom of the two.

E.g. $CH_3-\overset{\delta-}{\underset{\cdot\cdot}{\ddot{O}}}-\overset{\delta+}{H}$ $\qquad \overset{\delta+}{CH_3}-\overset{\delta-}{\underset{\cdot\cdot}{\ddot{Cl}}}:$

(b) Resonance & Mesomeric Effect: There are many organic molecules which cannot be represented by a single lewis structure. In turn, they are assigned more than one structure called canonical forms or contributing of resonating structures. The phenomenon exhibited by such compounds is called resonance. For example,



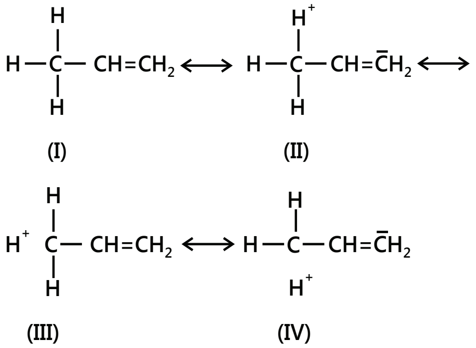
(c) Electromeric Effect: It is a temporary effect in which a shared pair of electron (p - electron pair) is completely transferred from a double bond or triple bond to one of the atoms joined by the bond at the requirement of attacking reagent.



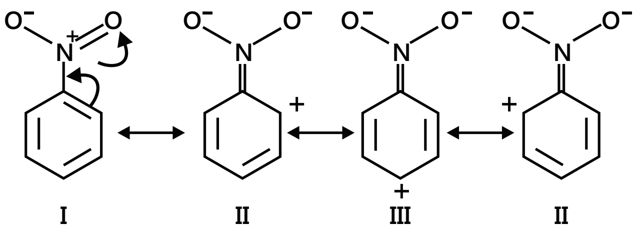
(d) Hyperconjugation: It is the delocalisation of sigma electron. Also known as sigma-pi conjugation or no bond resonance

Condition: Presence of –H with respect to double bond, triple bond carbon containing positive charge (in carbonium ion)

Example:



**Sol 11:** Resonance or mesomeric effect (on reaction rates, ionization equilibria, etc.) is attributed to a substituent due to the overlap of its p- or π-orbitals with the p- or π-orbitals of the rest of the molecular entity. There are many organic molecules which cannot be represented by a single lewis structure. In turn, they are assigned more than one structure called canonical forms or contributing of resonating structures. The phenomenon exhibited by such compounds is called resonance. For example, The nitro group, $-NO_2$, in nitrobenzene shows -M effect due to the delocalization of conjugated π electrons as shown below. Note that the electron density on the benzene ring is decreased particularly on ortho and para positions.



This is the reason for why nitro group deactivates the benzene ring towards the electrophilic substitution reaction.

**Sol 12:** The displacement of σ-electrons towards the multiple bond occurs when there are hydrogens on the α-carbon (which is adjacent to the multiple bond). This results in the polarization of the multiple bond. In the formalism that separates bonds into σ and π types, hyper conjugation is the interaction of σ-bonds (e.g. C–H, C–C, etc.) with a π network. This conjugation between electrons of single (H-C) bond with multiple bonds is called hyper conjugation.Hyperconjugation is a permanent effect whereas resonance effect is temporary.

Significance of hyperconjugation:

Bond Length: Like resonance, hyperconjugation also affects bond lengths because during the process the single bond in compound acquires some double bond character and vice-versa. E.g. C—C bond length in propene is 1.488 Å as compared to 1.334Å in ethylene .

Dipole moment : Since hyperconjugation causes the development of charges, it also affects the dipole moment of the molecule.

**Sol 13:** Free radical :These are neutral intermediates, formed due to homolytic cleavage of a single bond. Some common bonds which cleave to give free radicals in organic chemistry are shown: C-O, C-Cl, C-Br, C-I, C-C, C-H. Carbon free radicals are mainly generated by:

i. Photolysis (action of light) like acetone alpha cleavage

ii. Other radical initiator like allylic bromination by N-Bromosuccinimide (NBS)

**Carbocations:** Carbocations are formed from the heterolytic cleavage of a carbon-heteroatom.These are mainly generated by:

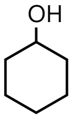
Formed due to heterolysis of a C-X bond (where X is more electronegative) and thus has a positive charge.

Planar in shape ($sp^2$ hybridized carbon), with empty p orbital perpendicular to the plane of the molecule.

Reactive towards electron rich species

**Carbanion:** These are intermediates also formed as a result of heterolysis, but here the electron pair from the bond is kept by the carbon atom.

- Formed due to heterolysis of a C-X bond (where X is less electronegative) and thus has a negative charge.
- Pyramidal is shape (sp3 hybridized) with the excess electrons placed in one sp3 hybrid orbital.
- Reactive towards positively charged (electron deficient species).

**Sol 14:** Cyclohexanol :  (a)

1-hexanol :  (b)

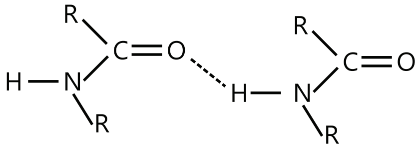
(a) Is more soluble than (b) due to greater extent of H-bonding due to its compact structure and less steric hindrance

**Sol 15:** 1,5 pentanediol :  (a)

1 pentanol :  (b)

(a) Is more soluble than (b) because of greater extent of H-bonding in (a) due to 2-OH groups compared with 1 in (b)

**Sol 16:** 1° and 2° amides tend to exist as dimer in solid and pure liquid state, because of H-bonding between them.



But this cannot happen in 3° amides as there is no hydrogen available for H-bonding

**Sol 17:**

**1. Addition Reactions:** The reactions in which the attacking reagent adds up to the substrate molecule is called a addition reaction.

E.g. $CH_2 = CH_2 + HBr \longrightarrow CH_3 - CH_2 - Br$

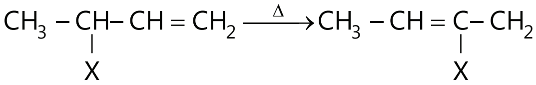
**2. Substitution Reaction:** The replacement of an atom ore a group from a molecule by different atom or group is known as substitution reaction

E.g. $CH_3OH + HBr \longrightarrow CH_3Br + H_2O$

**3. Elimination Reactions:** These reactions are the reverse of the addition reaction and involve the loss of atoms or group of atoms from a molecule to form a multiple linkage. Most commonly, loss of atoms or groups occurs from adjacent carbon atoms to yield an olefin.

$CH_3CH_2 \xrightarrow{\text{alc.KOH}} CH_2 = CH_2 + HCl$

**4. Rearrangement:** Rearrangement reactions involve either the migration of functional group to another position in the molecule containing a double bond or change the sequences of atoms forming the base carbon skeleton of the molecule to form a product with a new structure.

E.g. 

$CH_3 - \underset{X}{CH} - CH = CH_2 \xrightarrow{\Delta} CH_3 - CH = \underset{X}{C} - CH_2$

**Sol 18:**

(i) Homolytic cleavage is the breaking of a covalent bond in such a way that each fragment gets one of the shared electrons.

(ii) Heterolytic or ionic fission is the breaking of a covalent bond in such a way that one atom gets both of the shared electrons.

**Sol 19:** Electrophile: The species which carry +ve charge or are electron deficient are called electrophiles these species attack regions of high electron density in a molecule.

Two types

(i) Positively charged electrophile: $H^+$, $CH_3^+$

(ii) Netral electrophiles: $SO_3$, RCOCl

Nucleophiles: Those species which carry a negative cleavage / electron rich species or which have some pair of electrons are called nucleophiles. They attack regions of low electron density.

Two types

(i) Negatively charged: $Br^-$, $CH_3^-$

(ii) Neutral electrophiles: $NH_3$, ROH

**Sol 20: Free radical:** Photolysis (action of light) like acetone alpha cleavage.Other radical initiator like allylic bromination by N-Bromosuccinimide (NBS)

**Carbocations:** Formed due to heterolysis of a C-X bond (where X is more electronegative) and thus

**Carbanion:** Formed due to heterolysis of a C-X bond (where X is less electronegative) and thus has a negative charge.

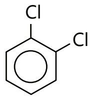
**Sol 21:** Carbanions will be more stable if they are attached to a group which withdraws go electrons (–I) .

Therefore, the more the –I effect of surrounding atoms, the more stable the carbanion will be

**Sol 22:** (a) p-dichlorobenzene 

has a dipole moment which make this compound non-polar and therefore, its solubility will be more in a polar solvent compared to a non-polar one. Now polarity of methyl alcohol ($CH_3OH$) > n-propyl alcohol

∴ Its solubility is more in n-propyl alcohol than methyl alcohol.

o-dichrolobenzene  has a non zero dipole moment and therefore its solubility will be more in a polar solvent.

(b) A: B $\longrightarrow A^{\ominus} + B^{\oplus}$

Heterolytic bond fission requires higher energy compared to homolytic bond fission as it involves separation of opposite charges which will be hindered by electrostatic force of attraction between ions.

If we study heterolytic cleavage step wise

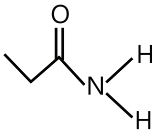
If is first homolytic cleavage and then

Ionisation of atom:

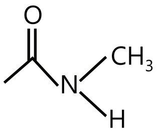
$$\begin{tikzcd} A - B \arrow[r] & A\cdot \arrow[d, "+e^-"] & + & \cdot B \arrow[d, "-e^-"] \\ & A^- & & B^+ \end{tikzcd}$$

$$\frac{w}{2E+410} = \frac{x}{\text{for } 195}$$

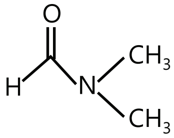
**Sol 23:** 4 isomers are possible



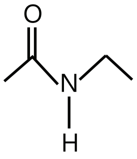
(i)



(ii)



(iii)



(iv)

Out of these four isomers, only (iii) cannot do hydrogen bonding and therefore exhibits different characteristics than the other three.

Name of (iii): Dimethyl formamide

**Sol 24:**

(i) Substitution reaction (also known as single displacement reaction or single replacement reaction) is a chemical reaction during which

one functional group in a chemical compound is replaced by another functional group.

(ii) An addition reaction, in organic chemistry, is in its simplest terms an organic reaction where two or more molecules combine to form a larger one (the adduct).

(iii) An elimination reaction is a type of organic reaction in which two substituents are removed from a molecule in either a one or two-step mechanism. The one-step mechanism is known as the E2 reaction, and the two-step mechanism is known as the E1 reaction.

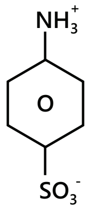
(iv) A rearrangement reaction is a broad class of organic reactions where the carbon skeleton of a molecule is rearranged to give a structural isomer of the original molecule.

(v) Isomerization: The chemical process by which a compound is transformed into any of its isomeric forms

(vi) Condensation: It is a chemical reaction in which two molecules or functional groups combine to form a large molecule, together with the loss of a small molecule.

(vii) Pericyclic: It is a chemical reaction where in the transition state of the molecule has a cyclic geometry, and the reaction progress in a concerted fashion.

**Sol 25:** Sulphanilic acid exists as Zwitter ion as :



In the presence of dil. NaOH the weakly acidic — $NH_3$ + group transfers its $H^+$ to $OH^-$ to form soluble salt P — $NH_2C_6H_4SO_3$ $-Na^+$. On the other hand, — $SO_3^+$ group is a very weak base and does not accept $H^+$ from dil HCl to form $NH_3C_6H_4SO_3H$ and therefore, it does not dissolve in dil HCl.

## Exercise 2

### Single Correct Choice Type

**Sol 1: (A)** Ph $S^-$ will attack C–Br bond (because carbocation formed from this carbon will have most stability due to conjugation with the ring) and from opposite side of Br

**Sol 2: (B)** I and III are stabilized by +M effect of O, I is further stabilized as it is tertiary carbocation.

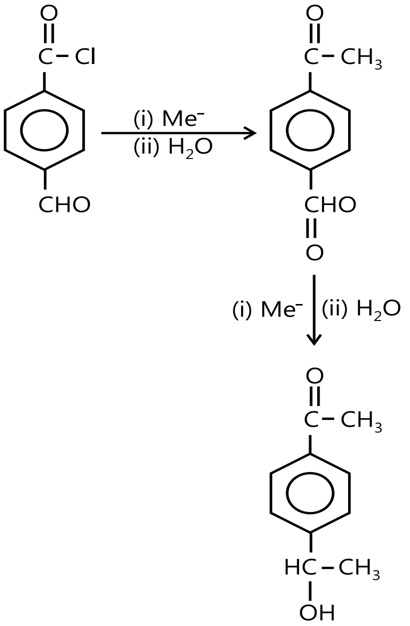
II is secondary carbocation

IV is primary carbocation.

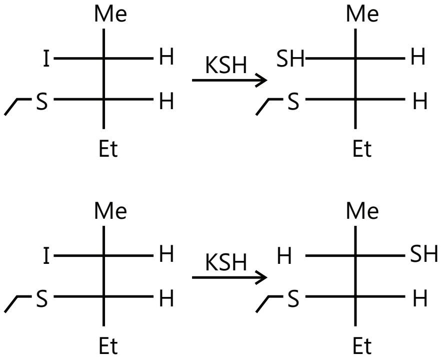
**Sol 3: (C)** In this structure O contains 10 valence electrons, which is not possible

**Sol 4: (B)** $BCl_3$ is an electrophile as B has only 6 valence electrons and needs electrons to complete its octet.

**Sol 5: (B)**



**Sol 6: (C)** Mechanism is same for both (nucleophilic substitution) , But products will be isomers

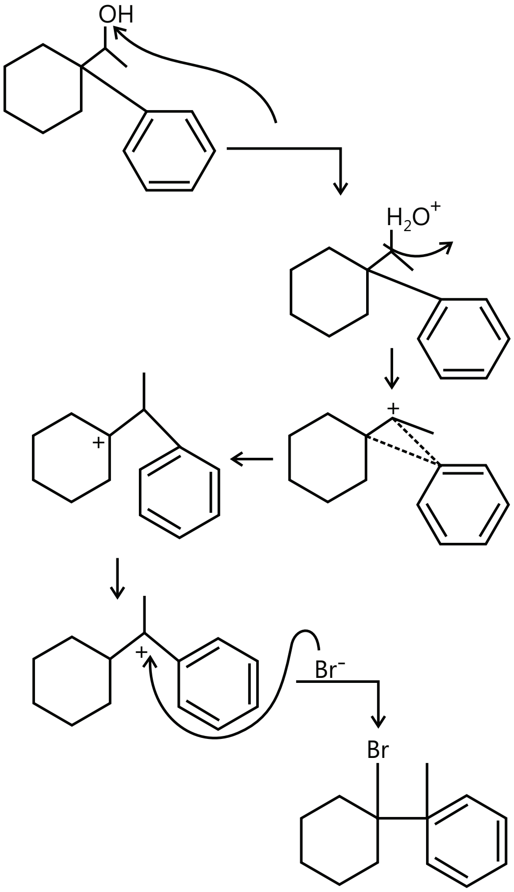


**Sol 7: (A)** (A) is antiaromatic (4 π electrons)

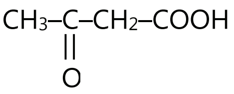
(B) is aromatic (6 π electrons)

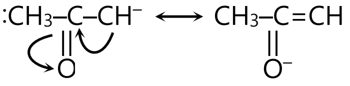
**Sol 8: (B)** –Cl group have –I effect which stabilizes the anion and it decreases with distance.

**Sol 9: (C)**



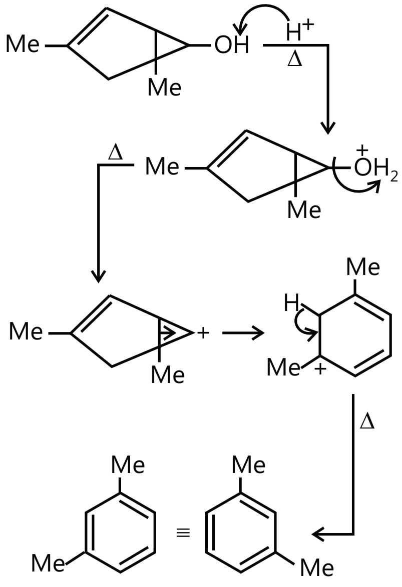
**Sol 10: (C)** $CCl_3$–CH (OH) $_2$ is most stable as it can form hydrogen bonding most effectively due to more –I effect of $CCl_3$– group

**Sol 11: (A)**  $CH_3-\underset{\underset{O}{\|}}{C}-CH_2-COOH$ has most reactivity as

the resulting carbanion:  $CH_3-\underset{\underset{O}{\|}}{C}-CH^- \longleftrightarrow CH_3-\underset{\underset{O^-}{\|}}{C}=CH$

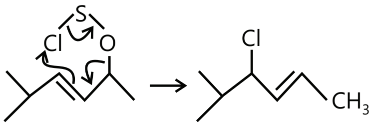
This is stabilized by resonance

**Sol 12: (B)**

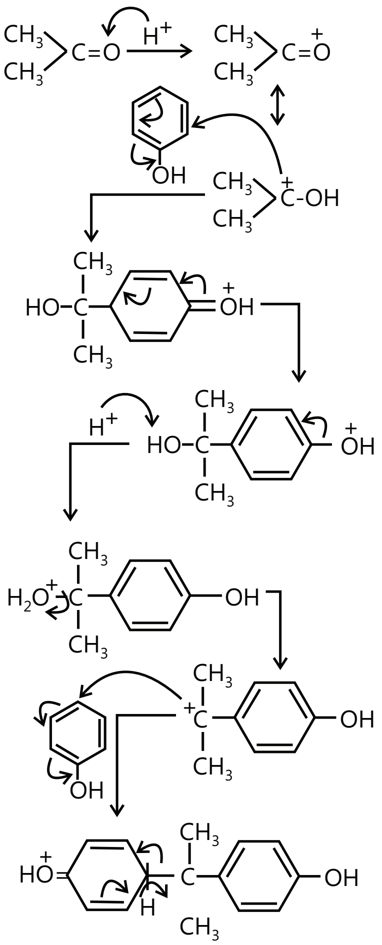


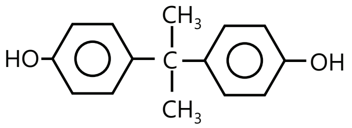
**Sol 13: (C)** n-propyl alcohol will dehydrate by E2 mechanism. Rest statements are correct)

**Sol 14: (A)**

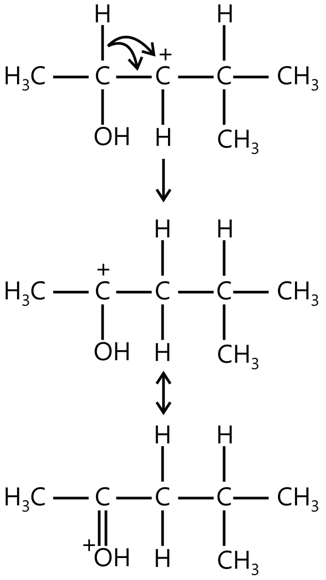


**Sol 15: (D)**



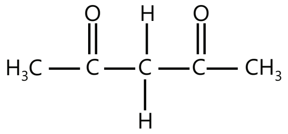


**Sol 16: (D)**

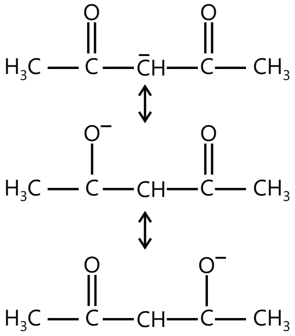


(This is very stable as it contains octet for all elements)

**Sol 17: (A)**



Enol ate form is



This structure is stabilised most by resonance

**Sol 18: (D)** (A) Triphyenylmethyl radical is more stable than trimethyl radical due to more conjugation (increasing stability) in the former.

(B) This trend is not always nessarily followed

(C) $^+CH_3$ is the least stable one as the positive charge needs to be dispersed to increase stability.

**Sol 19: (A)** Heat of hydrogenation of Benzene involves hydrogenation of 3 normal $\pi$ bonds – the resonance energy of benzene.

$\therefore$ Heat of hydrogenation of $3\pi$ bonds

= (49.8 + 36) K cal./mol = 85.8 k cal/mol

Heat of hydrogenation of cyclohexene involves.

Hydrogenation of 1 $\pi$ bonds, therefore,

Heat of hydrogenation = $\frac{85.8}{3}$ k cal/mole

= 28.6 k cal/mole

**Sol 20: (A)** + H effect 9 $\alpha$ – H in $(CH_3)_3$–$C^+$

### Multiple Correct Choice Type

**Sol 21: (A, B, C)** These are the characteristics of resonance structures

### Comprehension Type

### Paragraph 1

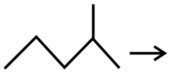
**Sol 22: (C)** Infinite orientations are possible and each orientation represents one conformation.

**Sol 23: (A)** Chair forms has least strain

**Sol 24: (A)** Conformation have very less difference in energy and are easily transformed into one another at room temperature.

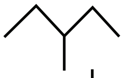
### Paragraph 2

**Sol 25: (C)** (A) :



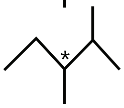
⟶ No chiral carbon

(B) :



: No chiral carbon

(A) :

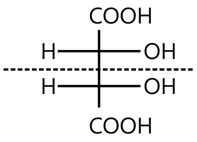


: * C is chiral

Making it optically active

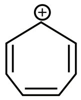
**Sol 26: (A)** d-glucose and $\ell$-glucose are enantionmers

**Sol 27: (B)** Meso compounds contain internal plane of symmetry which is only in C



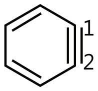
### Assertion Reasoning Type

**Sol 28: (A)** Tropylium cation:



This cation is aromatic and hence very stable due to resonance $(CH_3)_3C^+$ is stabilized only by +I effect

**Sol 29:** (A) Benzyne:



$C_1$ and $C_2$ are sp hybridized as $C_1$–$C_2$ is triple bond

**Sol 30: (C)** $PH_3$ is stronger nucleophile than $NH_3$ due to big size of P and increased polarisability

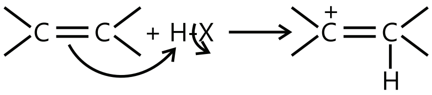
$PH_3$ is weak base than $NH_3$ as lone pair density is more in $NH_3$ due to its small size making it a better electron donor and hence better base

**Sol 31: (A)** R is the correct explanation for A

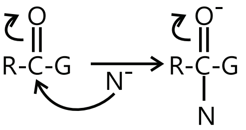
### Match the Columns

**Sol 32:** A → p, s ; B → q ; C → r ; D → q

**(A)** Carbocations are formed in E1 reaction and halagenation of alkenes

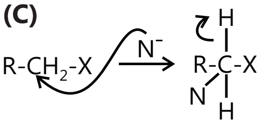


**(B)**



(Tetrahedral transition state)

**(C)**



(Pentavalent transition state)

**(D)** Carbonyl compounds undergo nucleophilic addition

**Sol 33:** A → p, r, s, t ; B → p, q, r, s, t ; C → p, r, s, t ; D → p, r, t

**(A)** Cannot undergo electrophillic addition as there is electron rich centre except benzene ring which does not undergo addition Nucleophilic addition can occur due to electron withdrawing effect of

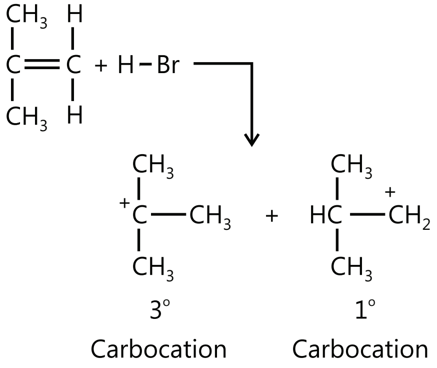
**(B)** It can undergo all reaction at different sites

**(C)** Cannot undergo electrophilic addition, no $\pi$ bonds which can be broken

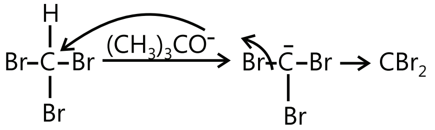
**(D)** Cannot undergo electrophilic addition reaction and elimination reaction

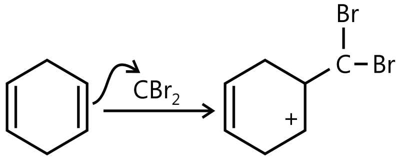
**Sol 34:** A → p, r; b → r, s; C → p, r; D → q, r

**(A)**



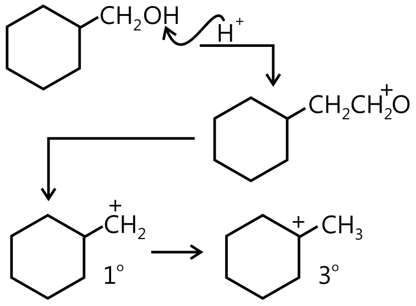
**(B)**



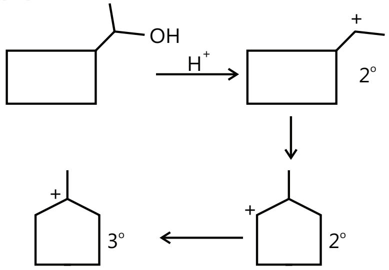


2° carbocation

**(C)**



**(D)**



**Sol 35:** A → p, r ; B → s ; C → p, s ; D → q, r, s

**(A)** Carbocations can undergo reaction with ethylene and rearrangement

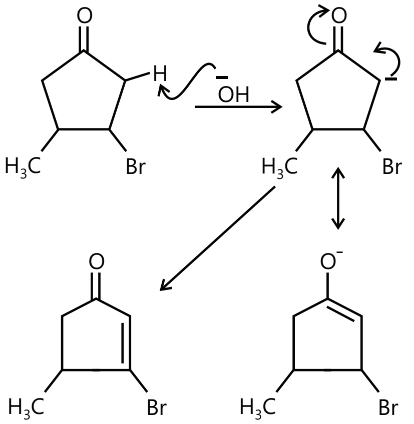
**(B)** Carbanions undergo disproport-ionation

**(C)** 2 carbenes can combine to form ethane. Carbenes can also react with ethylene

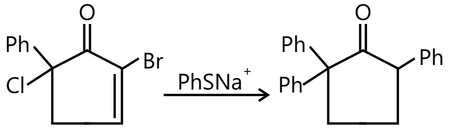
**(D)** Free radicals can combine and they also undergo rearrangement

**Sol 36:** A → t; B → p; C → r; D → q

**(A)** $E_1$ CB mechanism

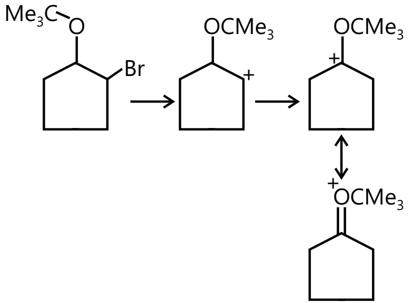


**(B)**



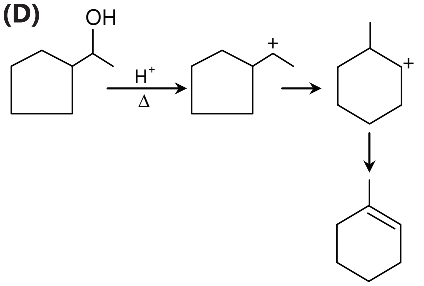
Will undergo E2 because of sterical hindrance and nucleophile PhS⁻

**(C)** Will undergo $S_N1$ due to stability of carbocation and weaker nucleophile



very stable

**(D)**



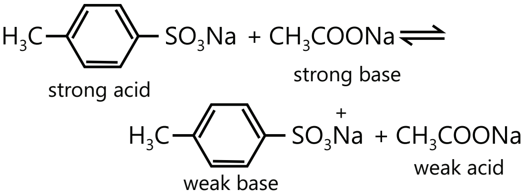
Can't undergo $E_{cb}$ as no acidic hydrogen.

## Previous Years' Questions

**Sol 1: (C)** $CH_2 = CH_2 - \overset{\oplus}{C}H = \overset{\ominus}{C}H - O - CH_3$

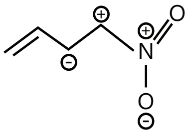
Lone pair of oxygen is not the part of this mode of delocalisation.

**Sol 2: (C)** A spontaneous neutralisation will occur between strong acid and strong base as



**Sol 3: (D)**

**Sol 4: (A)** The following structure has like charge on adjacent atoms, therefore, least stable.



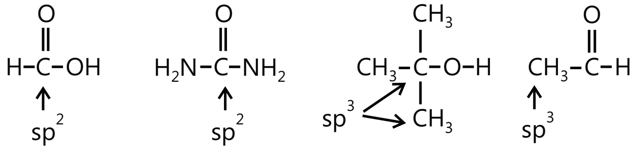
**Sol 5: (B, D)** Phenol is less acidic than a carboxylic acid (acetic acid). Nitro group from para position exert electron withdrawing resoance effect, increases acid strength. Therefore, phenol is less acidic than p-nitro phenol.

On the other hand, methoxy group from para postion, donate electrons by resonance effect, decreases acid strength of phenol. Also ethanol is weaker acid than phenol due to resonance stabilisation in phenoxide ion. Hence,

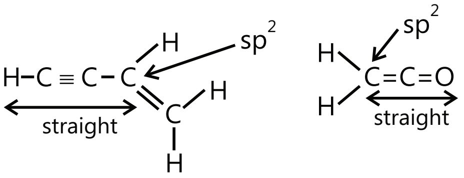
ethanol < p-methoxyphenol < phenol < p-nitrophenol < acetic acid

—increasing acid strength ⟶

**Sol 6: (C, D)**



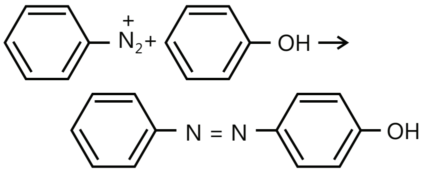
**Sol 7: (B, C)** In both (B) and (C), all the atoms are present in one single plane



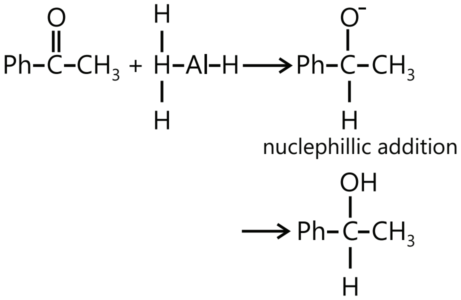
In (A) 1,3-butadiene, conformational change is possible between $C_2$–$C_3$ bond in which atoms will be present in more than one single plane.

In (D) allene, the terminals H–C–H planes are perpendicular to one another.

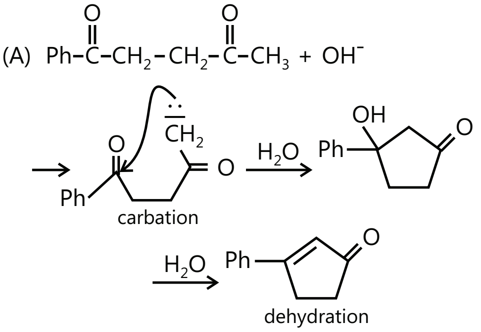
**Sol 8:** A → r, s ; B → t ; C → p, q ; D → r



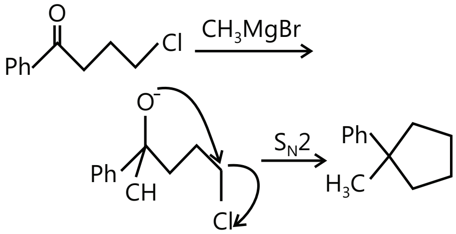
this is an example of electrophilic substitution at para position of phenol, giving a coupling product.



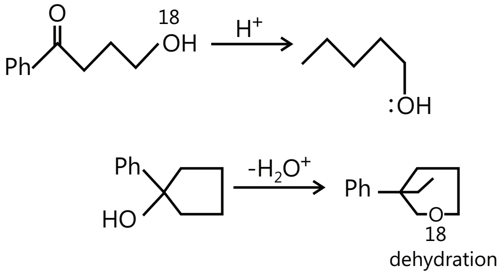
**Sol 9:** A → r,s,t ; B → p, s ; C → r, s ; D → q, r



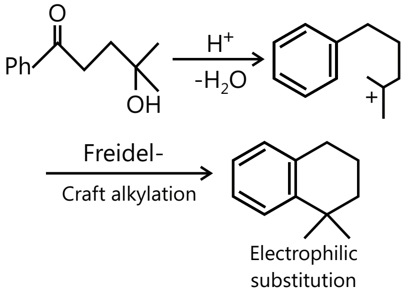
(B)



(C)



(D)



**Sol 10:** H–C≡C–H is more acid than $CH_2=CH_2$.

**Sol 11:** A → r; B → s; C → p; D → q

p-methoxy benzoic acid is the weakest and p-nitrobenzoic acid is the strongest acid among these acids. Chloro group has overall electron withdrawing effect on ring, therefore, increases acid strength of benzoic acid. Methyl group decreases acid strength of benzoic acid by +I effect. Therefore,

p-methylbenzoic acid $3.3 \times 10^{-5}$

benzoic acid $6.4 \times 10^{-5}$

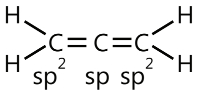
p-chlorobenzoic acid $10.2 \times 10^{-5}$

p-nitrobenzoic acid $36.2 \times 10^{-5}$

**Sol 12:** No. of hyper conjugative structure =6

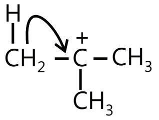
**Sol 13: (C)** The most acidic compound is ortho-hydroxy benzoic acid due to ortho effect.

**Sol 14: (B)**



(allene)

**Sol 15: (A)**

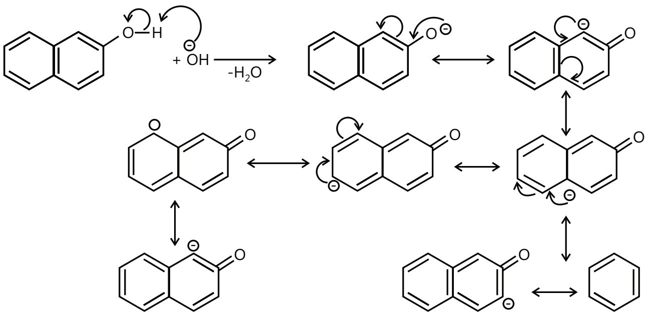


σ - p(empty) delocalisation

$CH_3-CH=CH_2$ (σ - π* electron) delocalisation

**Sol 16: (B)** With increase in branching boiling point decreases.

**Sol 17:**



**Sol 18: (A)**