CONCEPT
MAP

ISOMERISM

Class XI

The concept of isomerism illustrates the fundamental importance of molecular structure and shape in organic chemistry and the isomers play a vital role in biological processes.

Isomerism

Structural Isomerism

Same molecular formula and different bond pattern *i.e.*, different arrangement of atoms or groups of atoms within the molecules.

Chain Isomerism

Due to different arrangements of carbon atoms leading to linear and branched chains *e.g.*,

$H_3C-CH_2-CH_2-CH_3$, $H_3C-\overset{CH_3}{\overset{|}{C}H}-CH_3$

Butane　　*iso*-Butane

Position Isomerism

Due to different positions of side chains, substituents, functional groups, double bonds, triple bonds, etc. on the parent chain *e.g.*,

$H_2C=CH-CH_2-CH_3$, $H_3C-CH=CH-CH_3$

But-1-ene　　But-2-ene

Functional Isomerism

Due to presence of different functional groups. *e.g.*,

H_3C-CH_2-OH, $H_3C-O-CH_3$

Ethyl alcohol　　Dimethyl ether

Metamerism

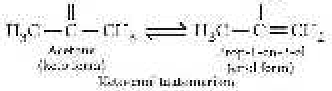
Arises when different alkyl groups are attached to the same functional group *e.g.*,

$H_3C-CH_2-O-CH_2-CH_3$　$H_3C-O-CH_2-CH_2-CH_3$

Diethyl ether or Ethoxyethane　　Methyl propyl ether or 1-Methoxypropane

Tautomerism

Tautomers have different functional groups and exist in dynamic equilibrium with each other due to a rapid interconversion from one form to another and the phenomenon is known as tautomerism. It is also called as *desmotropism* or *kryptotropism* or *prototropy* or *allelo-tropism* *e.g.*,



$H_3C-\overset{O}{\overset{||}{C}}-CH_3 \rightleftharpoons H_3C-\overset{OH}{\overset{|}{C}}=CH_2$

Acetone (keto form)　　Prop-1-en-2-ol (enol form)

Keto-enol tautomerism

Nitromethane (nitro-form)　　(aci-form)

Nitro-aci tautomerism

Diastereoisomers

- Chiral molecules having different arrangement of groups or atoms at one or more (but not all) of the equivalent stereocentres.
- They are not mirror images and are non-superimposable.

Stereoisomerism

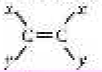
Same molecular formula and bond pattern but different arrangement of atoms or groups of atoms in space.

Geometrical Isomerism

Same structural formula but differ in the spatial arrangement of atoms or groups of atoms about double bond (C=C, C=N or N=N).

Cis

Similar groups on the same side of the double bond



Trans

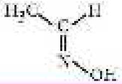
Similar groups on the different sides of the double bond

Syn

Two substituents (usually alkyl and hydroxyl) on the same side of the plane.

Anti

Two substituents (usually alkyl and hydroxyl) on the opposite side of the plane.

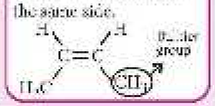


E

E is assigned to an isomer in which high priority atoms or groups are on the opposite sides.

Z

Z is assigned to an isomer in which high priority atoms or groups are on the same side.



Optical Isomerism

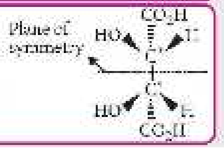
Same molecular formula but differing only in the behaviour towards polarised light are called optical isomers and the phenomenon is called optical isomerism.

Enantiomers

- Chiral molecules with one or more stereocentres.
- Non-superimposable mirror images.
- No symmetry elements.

Meso Compounds

- Molecules with multiple stereocentres.
- Internal plane of symmetry thus, optically inactive.



CONCEPT
MAP

REACTIVE INTERMEDIATES

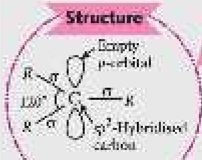
Class XI

Intermediates which are short-lived species generated during conversion of reactants to products in a chemical reaction. They play an important role in various organic synthesis as well as in biological world.

Carbocation ($-\overset{|}{\underset{|}{C}}^{+}$)

Carbon species carrying +ve charge on carbon having only six electrons in its valence shell.

Structure



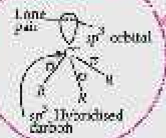
Stability

- More the number of alkyl/aryl groups present, greater is the stability.
- Electron donating groups increase the stability whereas electron withdrawing groups decrease the stability.
- The decreasing order of the stabilities of carbocations :
  $(Ph)_3\overset{+}{C} \approx (R)_2\overset{+}{C}-CH=CH_2 > (Ph)_2\overset{+}{C}H \approx R\overset{+}{C}HCH=CH_2 > R_3\overset{+}{C} > Ph\overset{+}{C}H_2 >$
  $(R)_2\overset{+}{C}H > \overset{+}{C}H_2CH=CH_2 > R\overset{+}{C}H_2 > \overset{+}{C}H_3 > \overset{+}{C}H=CH_2 > \overset{+}{Ph}$ or $\overset{+}{Ar}$

Carbanion ($-\overset{|}{\underset{|}{\bar{C}}}$)

Carbon species carrying –ve charge on carbon having eight electrons in its valence shell.

Structure



Stability

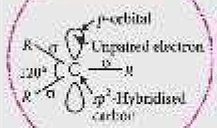
- More the number of alkyl groups present, lower is the stability.
- Electron withdrawing groups increase stability whereas electron donating groups decrease stability.
- The order of stability of carbanions :
  $(C_6H_5)_2CH^- > (C_6H_5)_3\bar{C} > C_6H_5\bar{C}H_2 >$ allyl $> \bar{C}H_3 >$
  1°alkyl > 2°alkyl > 3°alkyl

Note : Carbanions are sp^3-hybridised with pyramidal geometry. Due to steric hindrance of three phenyl (Ph–) groups, and to acquire pyramidal geometry, lots of energy is required due to which Ph_3C^- is less stable than Ph_2CH^-.

Free Radical ($-\overset{|}{\underset{|}{\dot{C}}}$)

Atom or a group of atoms having odd or unpaired electron having seven electrons in its valence shell. They are highly unstable, electrically neutral and short-lived species.

Structure



Stability

- More the number of alkyl groups present, greater is the stability.
- Allyl and benzyl free radicals are more stable than alkyl free radicals due to resonance effect.
- Greater the number of phenyl groups, more stable is the free radical.
- The order of the stability of free radicals is
  $(C_6H_5)_3\dot{C} > (C_6H_5)_2\dot{C}H > C_6H_5\dot{C}H_2 > CH_2=CH\dot{C}H_2 >$
  3°alkyl > 2°alkyl > 1°alkyl > $\dot{C}H_3 > CH_2=\dot{C}H > HC=\dot{C}$

Carbene (:CH_2)

Neutral, divalent carbon species in which two non-bonding electrons are present along with two bonding pairs (i.e; having sextet of electrons).

Singlet

sp^2-hybridised (bent), diamagnetic.

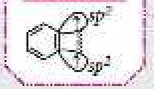
Electrophile

Triplet

sp hybridised (linear), paramagnetic

Diradical (more stable)

Benzyne

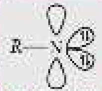


An additional bond is formed between two neighbouring carbon atoms by side ways overlapping of two sp^2-orbitals. The new bond orbital lies along with side of the ring and has little interaction with the π-electron cloud lying above and below the ring. This sideways overlapping is weak and thus, makes the benzyne more reactive.

Nitrenes or Imidogens ($R-\ddot{N}$)

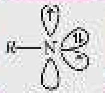
Neutral, univalent nitrogen species in which nitrogen has a sextet of electrons. They are highly reactive and act as strong electrophiles

Singlet



Electrophile

Triplet



Diradical