**Electronic Displacements**

**Electron Delocalization:**

Electron **delocalization**effects play a crucial role in the stabilization of the intermediate and the product of a reaction. Dispersal of a charge or electron density stabilizes a species. On the other hand, **localization**of a charge or electron density increases the reactivity of a species. The dispersal or delocalization of electron density in a species may take place by the following four important ways ―

1. Inductive effect or transmission effect (Effect),
2. Electromeric effect,
3. Resonance effect, and
4. Hyperconjugative effect.

**Inductive effect or transmission effect (- Effect)**:

This is an electron delocalization effect in a chain of a- bond of the species where two - bonded atoms differ considerably in their electronegativities. For example, in the - bonded chain given below ―



The terminal - atom is much electronegative than the atom to which it is attached. - atom pulls the -bonded electron pair of the bond toward itself, which makes the - atom fractionally . This - atom now is more electronegative than the next - atom of the chain to which it is attached. So, it pulls the -bonded electron pair of the Cβ― Cα― Cl bond toward itself making the - atomfractionally. This means that the electron pulling effect of - atom is transmitted through the chain of - atoms. But this transmission is rapidly diminishing with the distance and can practically be ignored beyond atom of a chain.



The inductive effect is shown by an arrow drawn at the middle of the - bond with the arrowhead pointing to the more electronegative atom. Further, it is a permanent effect, and it operates in the ground energy state of the molecule. Thus, in the-effect, the bonded - electron pair is permanently shifted to the more electronegative side, yet the electron pair remains in the BMO. This means that due to the -effect the - bond is not cleaved, but weakened.

If a group or atom withdraws electron density toward itself, thereby decreasing electron density at the - end by inductive effect, then such groups or atoms are denoted by  groups and effect as an -effect. For example, groups are the  groups.

The groups or atoms that release electron (donating) from them to the - end are termed as  groups and effect as  effect. For example,groups, etc., are groups.



**Electromeric effect**:

It is a temporary effect displayed mostly by multiple bonded groups in the presence of a reagent. Unlike the  effect, in an electromeric effect the bonded pair of electrons, usually - electrons are permanently shifted to the more electronegative side, giving a charge-separated structure. This means, such an effect is operative only in the excited state of the molecule. It always acts in the direction in which the reaction involving the multiple bonds is enhanced. The effect is temporary because it disappears when the reagent is withdrawn. For example, in carbonyl function,



**Delocalization: Delocalized Chemical Bond: Resonance effect:**

There are many compounds for which a single Lewis structure is not sufficient for an adequate description. These compounds usually contain one or more bonding orbitals that are not restricted to two atoms, but are spread out over three or more and such bonding is said to be delocalized.

Thus because of the presence of delocalized orbitals we will have several possible Lewis structures (called canonical forms) for the same molecule, and the actual structure of the molecule is taken to be a weighted average of these. The representation of a real structure as a weighted average of two or more canonical forms is called **resonance**, indicated by a double – headed arrow.

**For example**: (1) Benzene is a resonance hybrid of the following five structures (canonical forms)



All resonance structures can be well explained by considering molecular orbital method quantitatively.



Since each C – atom being connected to other three atoms (2C & 1H), uses sp2 orbitals to form σ – bonds, so all the 12 – atoms are in the same plane. Each C – atom has a p – orbital (containing 1 - electron) remaining and each other can overlap equally with two adjacent p – orbitals. This overlap of σ – orbitals results 6 – new orbitals viz. 3 – bonding π – orbitals and 3 – antibonding π – orbitals (π\*) and we will have the following orbital diagram of benzene.



Since because of delocalization of orbitals we have more than one possible resonance structures, hence the energy of the actual molecule is obviously less than that of any one Lewis structure, since otherwise it would have one of those structures. The difference in energy between the actual molecule and the Lewis structure of lowest energy is call the **resonance energy**.

**Molecular Structure that Exhibit Delocalization**:

There are three main types of (molecules) structures that exhibit delocalization:

1. **Double (or triple) bonds in conjugation:**

For example, benzene, but the simplest one is butadiene. For butadiene, in the resonance picture, following structures are considered to contribute:



And in the molecular orbital picture is ―



Similar delocalization is found in other conjugated systems such as:



1. **Double (or triple) bonds in conjugation with a p – orbital on an adjacent atom:**

Examples of these types of delocalization are —

1. Canonical forms of vinyl chlorides: In this case, overlap between unfilled orbitals and a filled orbital takes place



1. System containing an atom that has an unshared electron pair and that is directly attached to a multiple bond can also show this type of delocalization. Common examples of this type are: carbonate radical, allylic carbanions, etc.



1. Hyperconjugation: This is also a special type of delocalization

**Question**: Write the canonical structure for 2 – vinylbut – 1, 3 – diene.

Solution:



**Rules for Resonance: Condition for Resonance:**

Following conditions must be fulfilled in order to write the possible canonical forms for a compound containing delocalized bonds for the actual molecule:

1. All the canonical forms must be bona fide Lewis structure. For example, none of them may have a C – atom with 5 bonds
2. The relative position of the nuclei must be the same in all the structures. This means that all we are doing when we draw the various canonical forms in putting the electrons in indifferent ways. For example, as in chlorobenzene —



1. All the atoms taking part in the resonance, i.e. covered by the delocalized electrons, must lie in a plane to have maximum overlap of the p – orbitals
2. All the canonical forms must have the same number of unpaired and paired electrons. For example, is not a valid canonical form for butadiene.
3. The energy of the actual molecule is lower than that of any form. Therefore, delocalization is a stabilizing phenomenon.
4. All the canonical forms do not contribute equally to the true molecule. Each form contributes in proportion to its stability, the most stable form contributing most. For example, for ethylene the formhas such an energy compared tothat it essentially does not contribute at all.

**Factors that decides the relative Stabilities of Canonical Forms**:

It is not always easy to decide relative stabilities of imaginary structures; the chemist is often guided by intuition (i.e. qualitative method for weighting canonical forms). However, the following rules may be helpful:

1. Structures with more covalent bonds are ordinarily more stable than those with fewer. For example, stability order of —



1. Stability is decreased by an increase in charge separation. Structures with formal charges are less stable than uncharged structures. Structures with more than two formal charges are usually contributes very little. An especially unfavourable type of structure is one with two like charges on adjacent atoms.
2. Structures that carry a charge on a more electronegative atom are more stable than those in which the charge is on a less electronegative atom. Thus structure (1) is less stable than (2) given below.



Similarly, charges are best carried on atoms of low electronegativities.

Similarly, considering the carbonyl functionalities,



Again, in the benzene molecule,



**Hyperconjugation: No Bond Resonance**:

In resonance or other delocalization only π - electrons are involved, but hyperconjugation is a special type of delocalization that involves the σ – electrons. When a C – atom attached to **at least** one hydrogen is attached to an unsaturated atom or one with an unshared orbital (e.g. ), then we can draw the following forms of canonical form:



In which there is no bond at all between the C & H, and hence the name no bond resonance, popularly known as **hyperconjugation**.

Actually, hyperconjugation may be regarded as an overlap of the σ – orbital of the C — H bond and the - orbital of the bond, analogous to the orbital overlap of delocalization.

**Application of Hyperconjugation**:

1. Stability of toluene:



1. The dipole-moment of the following gas phase compounds PhCH3, PhC2H5, PhCH(CH3)2, and PhC(CH3)3 are respectively 0.37, 0.58, 0.65 & 0.70D.

**Explanation**: The order of electron release patterns of simple alkyl groups connected to an unsaturated system is:

* The above electron releasing order is due to the gradual decrease in the number of hyperconjugative structure. Hence, we have the above- value order.

1. Stability of carbocation & free radicals is



Since stability increases with increasing hyperconjugative structure, hence we have the above order. As for- we have 9 (nine) hyperconjugative structure, whereas for and for methyl none.

**Tautomerism:**

The term tautomerism represents a rapid equilibrium between mixtures of two or more structurally distinct compounds having same molecular formula. Individual members are termed as **tautomers**. In most cases, the rapid equilibrium between the tautomers takes place due to a shift of **proton**from one atom of the molecule to another.

**Keto – Enol Tautomerism**:

This is the most common form of tautomerism that exist between a carbonyl compound containing an α – H atom and its enol form, i.e.



In simple cases (= H, alkyl, OR, etc.) the equilibrium lies well to left, i.e. enol forms are less stable than the keto – form. This can be explained as —

The relative stabilities of keto – and enol – form can be accounted from the bond enthalpies data. The keto –form differ from the enol – form in possessing a C — H, a C — C, & a C = C bond; where the enol – has a C = C, a C — O and an O — H bond.

The approximate sum of the first three (i.e. keto – form) = 359 k cal mol –1 or 1500 k Jmol –1

And for the 2nd three = 347 k cal mol –1 or 1452 k Jmol –1

Thus keto – form is thermodynamically more stable by about 12k cal mol –1 or 50 k Jmol –1 and further, the enol – form cannot normally be isolated.

However, in some certain cases enol – forms predominant over the keto – form. Following are the three main types of the more stable enols:

(1) Molecules in which the enolic double bond is in conjugation with another double bond —



For example: Acetoacetic ester, its enol form is stabilized by internal H – bonding, which is absent in keto form:



**Similarly**, for

(2) Molecules that contain two or three bulky aryl groups — For example: 2, 2 – dimesitylethenol for which 95% enol at equilibrium:



**This observed % composition can be explained as**:

Because of steric repulsion of two bulky mesityl group keto – form is unstable than enol form. Moreover, in enol – form the two aryl groups are at about 1200 apart (), but in keto – form they must move closer together (). [Such compounds are often called Fusion – type enols]

(3) Highly fluorinated enols are more stable compared to its corresponding keto – form —

For example:



Thus, at room temperature form is very stable owing to the electron withdrawing power of - atom.

**The extent of enolization is greatly affected by solvent, conc. and temperature. For example,**

Acetoacetic ester has an enol – content of 0.4 % in water and 19.8 % in toluene.

**Explanation**:

**Acetoacetic ester exhibits keto – enol tautomerism:**



In aqueous medium, water forms H – bonding with carbonyl O – atom and making this group less available for internal H – bonding with enolic – OH group and thus, reduces the concentration of the enol – form. This effect is found to be absent in toluene medium.



**Other types of Proton – shift Tautomerism**:

Other than the most common keto – enol tautomerism, following are the some (only four) other types of Proton – shift tautomerism are observed in organic compounds:

1. **Phenol – Keto tautomerism**:



**Lewis Acids & Bases: Hard & Soft Acids & Bases (HSAB): —**

Compounds with an available pair of electrons, either unshared or in a - orbital are called **Lewis base**(). In contrast, any species with a vacant orbital is called a **Lewis acid**(). In a Lewis acid–base reaction the unshared pair of the base forms a covalent bond with the vacant orbital of the acid, as represented by the general equation given below, in which changes are not shown, since they may differ.

**A specific example is**—

**[**:

When a Lewis acid combines with a base to give an ion in which the central atom has a higher than normal valence, the resulting salt is called an “**ate complex**”. For example,

Ate complexes are analogous to the formed when a Lewis base expands its valence. For example,

The facility with which an acid – base reaction takes place depends on the strengths of the acid and the base. But it also depends on quite another quantity, called the **hardness or softness**of the acid or base. Hard and soft acids and bases have the following characteristics: —

**Soft Bases:**The donor atoms are of low electronegativity and high polarizability and are easy to oxidise. They hold their valence electrons loosely. For example:

**Hard Bases:**The donor atoms are of high electronegativity and low polarizability and are hard to oxidise. They hold their valence electrons tightly. For example:

**Soft Acids:**The acceptor atoms are small, have low  charge, and contain unshared pairs of electrons () in their valence shells. They have high polarizability and low electronegativity. For example:

**HardAcids:**The acceptor atoms are small, high charge, and do not contain unshared pairs in their valence shells. They have low polarizability and high electronegativity. For example:(hydrogen bonding molecules).

Quantitatively, the hardness and softness of acids and bases is given by —

Here is the absolute hardness and is the half of the difference betweenthe ionization potential, andthe electronegativity. The **softness**“”, is the reciprocal of.

Once acids and bases have been classified as hard or soft, a **simple rule** can be given: **Hard acids prefer to bond to Hard bases and Soft acids prefer to bond to Soft base** (the HSAB principle). The rule has nothing to do with acid or base strength but merely says that the product A — B will have extra stability if both A & B are hard or if both are soft. Another **rule is that** soft Lewis acid and soft Lewis base tend to form a covalent bond, while a hard acid and a hard base tend to bond ionically.

One application of the 1st rule given above is found in complexes between alkenes or aromatic compounds and metal ions. For example,

Since alkenes and aromatic rings are soft bases and should prefer to form complexes with soft acids. Thus,complexes are common, but the complexes ofare rare. Chromium complexes are also common, but in such complexes theis in a low or zero oxidation state (which softens it) or attached to other soft ligands.

**In another application, considering the reaction** —

The HSAB principle predicts that the equilibrium should lie to the right because the acid should have a greater affinity for the hard basethan for the soft base. Indeed, the esters are easily cleaved byor hydrolysed by dilute base (is also a hard base).

**HOMO – LUMO Concept:**

MO’s are constructed from individual AO’s, which are of two types viz.

1. One associated with lower energy called bonding MO and
2. One associated with higher energy called antibonding MO.

Total number of AO’s and MO’s are always equal and MO’s electronic configuration is same as for AO’s i.e. follows Aufbau, Pauli and Hund’s’ rule. A general MO energy level diagram involving only s & p atomic orbitals is as shown below.

From the MO energy level diagram, the Highest Occupied Molecular Orbital (**HOMO**) is the MO that, according to building – up principle, is occupied last. The Lowest Unoccupied Molecular Orbital (**LUMO**) is the next higher MO. For example,

1. For, 

HOMO is  and LUMO is 

1. For, 

HOMO is  and LUMO is 

1. For, 

HOMO is  and LUMO is, and so on.

HOMO and LUMO are called Frontier orbitals, as these only involves during a chemical transformation. For example,

For cycloaddition reaction, the reaction will be allowed only when all overlaps between highest – occupied molecular orbitals (HOMO) of reactant and the LUMO of the other are such that a  lobe overlaps only with another  lobe and a  lobe only with another  lobe.

For example, [4 + 2] – Cycloaddition Reactions:



In [4s + 2s] – cycloaddition, the four π - MO’s of the conjugated diene is obtained by LCAO, and have the following symmetries:



The ground-state π - electronic configuration of butadiene is. Therefore, the ground state HOMO is  which possesses the symmetry as shown. The LUMO of ethylene is the MO – which has the symmetry as:

Now,



Therefore, supra – supra interaction is symmetry as well as geometry allowed in the ground state, i.e. [4s+ 2s] – cycloaddition is a thermally allowed process (Δ – allowed).

The same can also be shown by taking the LUMO of butadiene, which is  and HOMO of ethylene, which is π - MO.



\*\*\*\*\*\*\*\*\*\*\*

**Reaction Path:**

**Homolytic & Heterolytic Bond Cleavage:**

A **heterolytic** bond cleavage or fission is that in which the shared electron pair of the sigma – bond is not shared equally during fission by thecovalently bonded atoms, and thus results in the formation of a cation and an anion. For example,



The ease of heterolysis depends on the nature of the leaving group, as well as on the stability of the anion and cation. For example,

The order of ease of hydrolysis of some *t* – butyl compounds is —

The above mentioned order is due to the fact that the corresponding acid strength follows the following order —

This order indicated that the chloride ion () is better leaving group than acetate ion () and acetate ion as better than that of hydroxide ion ().

If the bonding electron pair is shared equally during fission, the process is termed as **homolytic** bond fission, and results in the formation of two free radicals. For example,



The process occurs on heating to moderate temperature to those compounds that either contain an intrinsically weak bond, such as O — O, or that no dissociation, liberated a particularly strongly bonded molecule, such as . Peroxides illustrate the former class. For example,





Certain – compounds illustrates the latter. For example,



**General Path of a Reaction:**

From reactants to products or intermediate is not take place directly but through an unstable, highly energetic **transition state**(TS). Reactions in which bond making and bond breaking occurs at the same time i.e. simultaneously are known as **concerted** reactions. For example,



To undergo reactions, the reactants must first have adequate energy to collide and they orient in a favourable condition for reaction. Proper collision and orientation is an important factor in determining the probability of reaction. The system is then must have sufficient energy to break the bonds undergoing change.

The configuration of reactants in which all the stringent requirements for an effective collision are met is commonly known as the **TS or activated complex**, a hypothetical description of the atoms at the **point of highest energy** along with the reaction pathway. TS’s can’t be isolated but can be detected their presence. For example, the complete process for the above shown reaction can be represented as shown below.



**Energy Profile Diagram & Activation Energy:**

The graphical representation of energy – structure relations for a reaction is known as energy profile diagram. Here energy is plotted along the vertical axis, and the reaction coordinate (i.e. change in geometry) along the horizontal axis.

The energy profile diagram shows that energy must be added to the reactants in order to attain the transition state. This energy, the difference between the average free energy of the reactants and of the TS, is known as the **free energy of activation**. The termgoverns the rate of a chemical reaction. Typical organic reactions have activation energies of 10– 50 kcalmol-1 (40 – 200 kJmol-1).

Actually, experimentally we determine the **Arrhenius activation energy**, for a reaction, which relates the **enthalpy of activation**, by the equation —



Again, the enthalpies of reaction are related to free energies of activation,by the equation —





Here is the entropy of activation of the reaction.

In many cases the value ofis an acceptable approximation of.

The energy profile diagram for a single step concerted reaction such as hydroxylation of primary alkyl halide is as shown in the figure.

**Energy Profile Diagram for Multistep Reactions:**

The reactions that involve more than one step to yield the products from the reactants are known as multistep reactions. For example, nucleophilic substitution of chloride by hydroxyl group in tertiary halo-alkanes like 2 – chloro – methylpropane (*t* - butylchloride) is a two-step reaction.

**Step I:** Heterolytic cleavage of C — Cl bond to form an stable carbocation intermediate,

**Step II:** Reaction of the energetic carbocation intermediate with water, the nucleophile to yield the product,

The figure shows the energy profile diagram for a 2 – step reaction.

  
**Kinetically Controlled & Thermodynamically Controlled Reactions:**

In most reactions which can proceed by two or more pathways each of which gives different sets of products, the products isolated are those derived from the pathway of lowest free energy of activation, regardless of whether this path results in the greatest decrease in the free energy of the system. These reactions are described as being kinetically controlled.

If, however, the reaction conditions are suitable for equilibrium to be established between the reactants and the kinetically controlled products, a different set of products, formed more slowly but corresponding to a lower free energy for the system, can in some instances be isolated. Such reactions are described as being thermodynamically controlled.



For example, considering the sulphonation (by concentrated H2SO4) of naphthalene, for which two monosulphonated products are in principle obtainable.



The 1 – derivative is formed the faster of the two but the 2 – derivative is thermodynamically the more stable (at least in part because of the repulsive forces between the sulphonic acid group and the H – atom, shown in the 1 - isomer). The situation can be represented schematically as in the figure given below:

At low temperature (800C), sulphonation at the 1 – position occurs fairly rapidly whereas that the 2 – position is very slow. The free energy of activation () for the desulphonation of the 1 – sulphonic acid is such that in these conditions this product is essentially isolated. At higher temperature (1600C), desulphonation of the 1 – sulphonic acid becomes important and equilibrium is fairly rapidly established between this product and the reactants. The rate of formation of the 2 – sulphonic acid is now also greater, so that gradually most of the naphthalene is converted into the 2 – derivative and this becomes the major product.



**One more example**: **Addition of to 1, 3 – butadiene gives both the 1, 2 – and 1, 4 – addition products.**

**Kinetic control or rate control reaction**&**equilibrium controlled or thermodynamically control reaction**.[Solomon Page 606]

Electrophilic addition of or  to 1, 3 – butadiene (or any conjugated diene) to give both 3 – chlorobut – 1 – ene and 1 – chlorobut – 2 – ene by 1, 2 – and 1, 4 – addition respectively.



Formation of these two products can be explained through the formation of a resonance stabilized allylic cation.



This reaction is temperature dependent as shown below:



Thus, at low temperature, 1, 2 – addition occurs exclusively but at high temperature, 1, 4 – addition occurs exclusively. Again, when the mixture formed at low temperature () is brought to the high temperature, the relative amounts of the two products changes. The new reaction mixture eventually contains the same proportion of products given by the reaction carried out at high temperature ().

It can also be shown that at higher temperature and in the presence of , the 1, 2 – addition product rearranges to the 1, 4 – addition product and that an equilibrium exists between them:



Because this equilibrium favours the 1, 4 – addition product, that product must be more stable.

Thus, the reaction of with 1, 3 – butadiene provides an example, which can be explained by both relative rate of competing reaction and relative stabilities of the final product. At low temperature, the relative amount of the product formed is explained by the relative rates at which the two addition occurs; 1, 2 – addition occurs faster, so it is the major product. At high temperature, the relative amounts of the products are determined by the position of equilibrium. The 1, 4 – addition product is the more stable, so it is the major product.

Since, 1, 2 – addition at low temperature is governed by the relative rates of the product formation is called the **kinetic control or rate control reaction**. On the other hand, 1, 4 – addition at high temperature is governed by the position of equilibrium, so it is called **equilibrium controlled or thermodynamically control reaction**.

**Organic Transformations —**

Depending upon the operational representation of organic reactions, these are broadly of 3 – types:

1. Addition,
2. Elimination, and
3. Substitution.

**Addition Reactions:**Addition reaction takes place with compounds that are **unsaturated**. Compounds with carbon – carbon double bond and triple bond and carbon – oxygen double bonds are the most common structural types which undergo addition reactions. For example,

1. Bromination or halogenation of alkene:



1. Catalytic hydrogenation:



1. Hydration:



1. Hydrohalogenation:



**Elimination Reactions:**Here atoms are removed from a molecule to form products with multiple bonds or, in some cases rings. When the atoms or groups removed from adjacent atoms of the C – skeleton, then these are called 1, 2 – elimination reactions. For example,

1. **Dehydration**: Dehydration implies loss of water molecule, usually from alcohol. The process is usually promoted by heat and strongly acidic conditions. Thus,



1. **Dehydrohalogenation**: These reactions are promoted by heat and strong basic reaction conditions. Thus,



Many dehydration and dehydrohalogenation reactions usually generate a mixture of isomeric alkenes, where one predominates over the other (**Saytzeff rule**). For example,



**Substitution Reactions:**

A substitution reaction occurs when an atom or group supplied by the reagent replaces an atom or group of the reactant molecule. Substitution can take place at saturated or unsaturated carbon atoms. For example,



**Stereochemical Effects — on Reactants, TS, Intermediate & Products:**

Thereare two types of stereochemical control reactions —

1. **Stereospecific**— Here stereochemically different starting materials give stereochemically different products and
2. **Stereoselective**—Here same starting materials give two or more stereoisomeric products, one is formed in predominance.

Let us consider the stereochemical factors controlling reactivity for the stereospecificity and stereoselectivity of reactions for (a) acyclic and (b) cyclic compounds.

**Acyclic Compounds: —**

1. **SN2 Reactions**: These are **stereospecific**, involving inversion of configuration at the reaction centre. Thus,



If inversion of configuration is not possible, SN2 – displacement do not occur. For example,



Thus, here the incoming nucleophile approaches from the opposite direction of the departing group.

1. **SN1 Reactions**:These reactions are not **stereospecific**, because the intermediate carbocation is coplanar and can be attracted by the nucleophile from both sides to give a mixture two possible products. Thus,



Inpractice, the product usually contains more of the enantiomer in which the original configuration has been inverted. This can be explained as —

Path (a) in the above scheme of the SN1 reaction leads to the major product, because it is believed that the carbocation and  formed, they exist as an ion – pair for a short time during which  shields the side of the C – atom to which it was attached so that the incoming nucleophile more easily approaches from the other side.

1. **E2 Elimination**:The stereo – electronic requirement for E2 is that the four atoms that take part in the elimination should be attain a coplanar arrangement. Of the two possibilities (***syn* – and *anti* –**), elimination occurs much more rapidly in the *anti* – periplanar conformation:



For example, Elimination of , induced byions, from the diastereomers of . Reaction occurs through the anti – conformations I & II respectively, former (I) diastereomer gives specifically () – alkene and the latter (II) gives specifically ()– alkene:





Similarly, elimination of Br2, induced by, gives specifically – 2 – butane from meso – 2, 3 – dibromo butane and specifically  – 2 – butane from () – and () – 2, 3 – dibromo butane.



The above reactions are stereospecific, and as the rate of formation of  – product is greater in each case than that of the  – product.

**Stereoselective E2 – Reaction: -**

Base induced elimination of from 1, 2 – diphenyl – 1 – chloroethane can occur through each of two  – conformations to give  – and  – stilbene respectively, the latter in predominance.



1. **Pyrolytic Elimination**: Here elimination occurs only on heating directlythrough cyclic TS, i.e. in the absence of an added reagent and here, the eliminated groups are always in  –position. For example, pyrolysis of xanthate ester,



1. **E1 Elimination**:E1 – eliminations are not stereospecific, because the intermediate carbocation can undergo rotation about the bonds to the trivalent C – atom before a portion is eliminated. For example,



1. **Electrophilic Addition to Alkene**: Here, – addition occurs exclusively,if the electrophile forms a strongly bridged intermediate cation, and also when it forms a less strongly bridged cation provided that there is no aryl – conjugated substituent. Again,  – addition predominates in the addition of to alkenes with no aryl – substituent, whereas  –addition is predominant with aryl conjugated alkenes. For example,

Addition of to alkene is stereospecific; only  – adduct is formed, as shown for the reaction ofwith  – and  – 2 – butene,





Selectivity decreases if an aryl group is attached to the double bond, for example, in 1 – phenylprop – 1 ene, PhCH = CHCH3 the ratio of  – adduct is 15: 85. This is due to the stabilization of the  charge of the intermediate by its delocalization with the aromatic ring, which reduces the effectiveness of bridging and allows rotation to occur. For example,



Exactly in the same manner (as in addition of Br2 as shown above) Cl2 – also gives the anti – adduct. Addition of HX is also anti —



But when an aryl group is present, the syn – adduct is predominant,



1. **Molecular Addition to Alkene**: These are concerted reactions and yield  – product. For example, Diels – Alder reaction,



Similarly, hydroxylation of alkene by OsO4, & KMnO4, catalytic hydrogenation, reduction by diimide, formation of alcohol via bydroboration, etc. are characteristic  –addition.

**Cis – Hydroxylation by OsO4**:



**Cis – Hydroxylation by KMnO4**:



**Catalytic Hydrogenation**:



**Reduction by Diimide**:



1. **Addition to Alkynes**: Electrophilic addition gives mainly  – products. For example,



Nucleophilic addition also occurs in the  – manner. For example,



1. **Intramolecular Rearrangement**:For electrophilic rearrangement type, there are three stereochemical properties:
   1. Migrating group retains its configuration,
   2. Inversion of configuration at the migrating origin and
   3. Inversion of configuration at the migration terminus.

**Example of (a)** is the Hofmann rearrangement; here an asymmetric alkyl group migrates:



**Mechanism**:



**Example of (b)** is rare.

**The third property is shown in Pinacol type reaction**. For example,



**Similarly**,



1. **Neighbouring Group Participation**: Participation by neighbouring groups can result not only in an enhancement of the rate of reaction but also in the alteration of the normal stereochemical course. This is particularly significant in substitution. For example,

**(1)** The optically active 3 – bromo – 2 – butanol (I) reacts with HBr to give (±) – 2, 3 – dibromobutane, whereas the diastereomeric (II) form gives meso – 2, 3 – dibromobutane. If the reaction occurred through ‘open’ carbocations, each compound would give a mixture of (±) – and meso – products. However, the neighbouring Br – atom fixes the stereochemistry of the intermediate ion, i.e. anti – addition occurs.





**(2)** Participation of phenyl group in the solvolysis of the diastereomeric toluene–p–sulphonates I & II in acetic acid (AcOH),



**Cyclic Compounds: — [Cyclohexane System]**

1. **Equilibria**: Monosubstituted cyclohexanes exists as equilibrium system in which axially and equatorially substituted compounds interconvert rapidly through the flipping of the ring, although equatorially substituted compounds predominate because of no 1, 3 – diaxial interaction.



Disubstituted and more complex cyclohexanes can exist in stereoisomeric forms which are not normally inter-convertible, whether or not the ring is able to flip. For example,

1. ***Cis* – and *Trans* – menthane** exist as separate compounds even though ring flipping occurs in each case;



1. ***Cis* – and *Trans* – decalin** exist as separate compounds because ring flipping cannot occur to inter-convert the two;



1. Under certain conditions, depending upon the structural situations inter-conversion occurs in the stereoisomers of cyclohexane system. For example,

Introduction of a carbonyl group in menthane gives cis – and trans – isomers which are inter-convertible in both acidic and basic conditions: the trans – isomer, having both alkyl groups equatorial predominates.



In acidic conditions, interconversion occurs through the enol tautomer of the ketone and, in basic conditions, through the enolate.

1. Interconversion can also be brought about if the ring system readily undergoes ring opening and ring closure. The best known example is the glucose:

α –D – Glucose and β – D – glucose are inter-converted fairly rapidly in solution through the open chain tautomer. The β – form predominates (α : β ≈ 2 : 1) because all the substituents are in equatorial positions.



When crystalline α – D – glucose is dissolved in water, the initial rotation of the solution corresponding to, falls gradually to an equilibrium value of (the β – form has ). This phenomenon is known as mutarotation.

1. **Substitution**: Equatorially and axially substituted conformational isomers normally react at different rates. Which isomers reacts faster depends on whether the steric requirements of the TS are less or greater than those of the reacts.

**Example of 1st case:**

Considering thesolvolysis of – and trans – isomers of 4t – butylcyclohexyltoluene – *p* – sulphonate, the cis – isomer is less stable, but the TS differ less in stability because the substituents has become somewhat removed from the ring system:



From the figure, it is clear that the activation energy should be smaller for the cis – compound then the TS. In practice, solvolysis of the cis – isomer is faster by a factor of about 3 and is described as being sterically assisted.



**Example of 2ndcase:**

Considering the hydrolysis of cis – and trans – isomers of 4t – butylcyclohexylethyl-mehanoate: Here, cis – compound is again less stable, but since the difference in the stabilities of the transition state is greater than that of the reactants, because the addition of the hydroxide ion further increases the molecular crowding. Consequently, the trans – isomer reacts more rapidly, by a factor of about 20.



**Generally**, if the TS is associated with a decrease in steric crowding, the axial substituent will react faster, whereas if it is associated with an increase in crowding, the equatorial substituent will react faster.

1. **E2 Eliminations**: The stereo-electronic requirement for an E2 – elimination is a periplanar arrangement, preferably anti, of the atoms involved. The requirement can affect both rates and products. For example —

Neo-menthyl chloride undergoes base catalysed dehydrochlorination readily, giving the expected 3 – menthane (Saytzeff rule); reaction occurs through the favoured conformation in which both alkyl groups are equatorial. The stereoisomeric menthyl chloride, on the other hand, reacts at only  the rate and gives 2 – menthane; elimination occurs through the unfavourable conformation in which the three substituents are axial and in which the proton for Saytzeff elimination is not in the necessary anti position.



1. **Electrophilic Addition to Alkene**:Addition which occurs via bridged ions to give anti products from diaxial compounds which, if ring flipping is possible, can convert predominantly into the di – equatorial products.



1. **Intramolecular Reactions**: The stereochemical requirement for the intramolecular reaction is the anti conformation that can lead to different behaviours. For example —

Treatment of trans – 2 – aminocyclohexanol with nitrous acid gives only cyclopentane-carbaldehyde, by rearrangement,



But, the cis – isomer gives a mixture of ring contracted aldehyde and cyclohexanone. Here, alternative anti – conformations are available for rearrangement, one involving ring contraction and the other hydride migration:



A slightly different situation holds for cis – and trans – 2 – chlorocyclohexanol. The oxyanion formed by the trans – isomer with base is suitably sited to displace chloride ion intramolecularly by backside attack; reaction occurs rapidly to give the epoxides. The cis – isomer cannot achieve the necessary conformation for displacement and instead a slower reaction occurs in which a hydride ion migrates to give cyclohexanone.

