Semester-I

19BTCE103 **Chemistry –I** **4H-4C**

Instruction Hours/week: L:3 T:1 P:0 **Marks:** Internal**:40** External**:60** Total**:100**

End Semester Exam:3 Hours

Course Objective

- To understand the terminologies of quantum theory of chemical systems.
- To study about various chemical bonding
- To understand the stereochemistry of molecules.
- To understand the thermodynamic functions.
- To comprehend the basic organic chemistry and to synthesis simple drug.

Course Outcomes

1. Appreciate quantum theory of chemical systems.
2. Appreciate aliphatic chemistry
3. Describe the concepts of stereochemistry
4. Write simple mechanisms
5. To synthesis of organic molecules
6. Integrate the chemical principles in the projects undertaken in field of engineering and technology

UNIT I - Introduction to quantum theory for chemical systems:

Schrodinger equation, Applications to Hydrogen atom, Atomic orbitals, many electron atoms

UNIT II - Chemical bonding in molecules:

MO theory, Structure, bonding and energy levels of bonding and shapes of many atom molecules, Coordination Chemistry, Electronic spectra and magnetic properties of complexes with relevance to bio-inorganic chemistry, organometallic chemistry

UNIT III - Introduction to Stereochemistry:

Stereodescriptors – R, S, E, Z.Enantiomers and Diastereomers.Racemates and their resolution.Conformations of cyclic and acyclic systems.

UNIT IV - Reactivity of organic molecules:

Factors influencing acidity, basicity, and nucleophilicity of molecules, kinetic vs. thermodynamic control of reactions

UNIT V - Strategies for synthesis of organic compounds:

Reactive intermediates substitution, elimination, rearrangement, kinetic and thermodynamic aspects, role of solvents

SUGGESTED READINGS:

1. B. H. Mahan, (2010) University chemistry, Pearson Education.
2. K. P. C. Volhardt and N. E. Schore, 5th Edition, (2014) Organic Chemistry: Structure and Function, W.H. Freeman,
3. B. L. Tembe, Kamaluddin and M. S. Krishnan, (2009) Engineering Chemistry (NPTEL Web-book)
4. Robert Neilson Boyd, SaibalKanti Robert Thornton Morrison, (2012) Organic Chemistry, Pearson, 7th edition
5. Michael B. Smith and Jerry March, (2006) Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, Wiely..
6. Arun Bahl and BS Bahl, (2014) Advanced Organic Chemistry, S Chand.

KARPAGAM ACADEMY OF HIGHER EDUCATION

(*Deemed to be University*)
(*Established under section 3 of the UGC Act, 1956*)
COIMBATORE – 641021

CHEMISTRY –I

19BTCE103

LECTURE PLAN

TOTAL HOURS: 55

UNIT-I

Introduction to quantum theory for chemical systems

S.No	Topics	Hours
1.	Introduction to quantum theory	2
2.	Schrodinger equation	1
3.	Schrodinger equation-Particle in one dimensional box	1
4.	Schrodinger equation -Particle in three dimensional box	1
5.	Tutorial	1
6.	Applications to Hydrogen atom	2
7.	Atomic orbitals	1
8.	Many electron atoms	1
9.	Tutorial	1
	Total hours	9+2

UNIT-II

Chemical bonding in molecules

S.No	Topics	Hours
1.	Introduction to chemical bonding	1
2.	Molecular Orbital theory	1
3.	Structure, bonding and energy levels of bonding	1
4.	Shapes of many atom molecules	1
5.	Tutorial	1
6.	Coordination Chemistry	1
7.	Electronic spectra of complexes	1
8.	Magnetic properties of complexes	1
9.	Bio-inorganic chemistry	1
10.	Organometallic chemistry	1
11.	Tutorial	1
	Total hours	9+2

UNIT-III

Introduction to Stereochemistry

S.No	Topics	Hours
1.	Introduction to Stereochemistry	1
2.	Stereodescriptors	1
3.	R, S, E, Z notations	1
4.	Enantiomers and Diastereomers	2
5.	Tutorial	1
6.	Racemates	1
7.	Resolution of Racemates	1
8.	Conformations of cyclic systems	1
9.	Conformations of acyclic systems	1
10.	Tutorial	1
	Total hours	9+2

UNIT-IV

Reactivity of organic molecules

S.No	Topics	Hours
1.	Introduction to reactivity of organic molecules	1
2.	Factors influencing acidity	2
3.	Factors influencing basicity	2
4.	Factors influencing nucleophilicity	2
5.	Tutorial	1
6.	Kinetics of reactions	1
7.	Thermodynamic control of reactions	1
8.	Tutorial	1
	Total hours	9+2

UNIT-V

Strategies for synthesis of organic compounds

S.No	Topics	Hours
1.	Introduction to synthesis of organic compounds	1
2.	Reactive intermediates	1
3.	Substitution reactions	1
4.	Elimination reactions	1
5.	Rearrangement reactions	1
6.	Tutorial	1
7.	kinetic and thermodynamic aspects	2
8.	Role of solvents in reactions	2
9.	Tutorial	1
	Total hours	9+2

SUGGESTED READINGS

1. B. H. Mahan, (2010) University Chemistry, Pearson Education.
2. K. P. C. Volhardt and N. E. Schore, 5th Edition, (2014) Organic Chemistry: Structure and Function, W.H. Freeman,
3. B. L. Tembe, Kamaluddin and M. S. Krishnan, (2009) Engineering Chemistry (NPTEL Web-book)
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5. Michael B. Smith and Jerry March, (2006) Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, Wiely..
6. Arun Bahl and BS Bahl, (2014) Advanced Organic Chemistry, S Chand.
7. P C Jain & Monica Jain, (2015) Engineering Chemistry, Dhanpat Rai Publishing Company.

STAFF HoD

Classical Mechanics and Quantum Mechanics

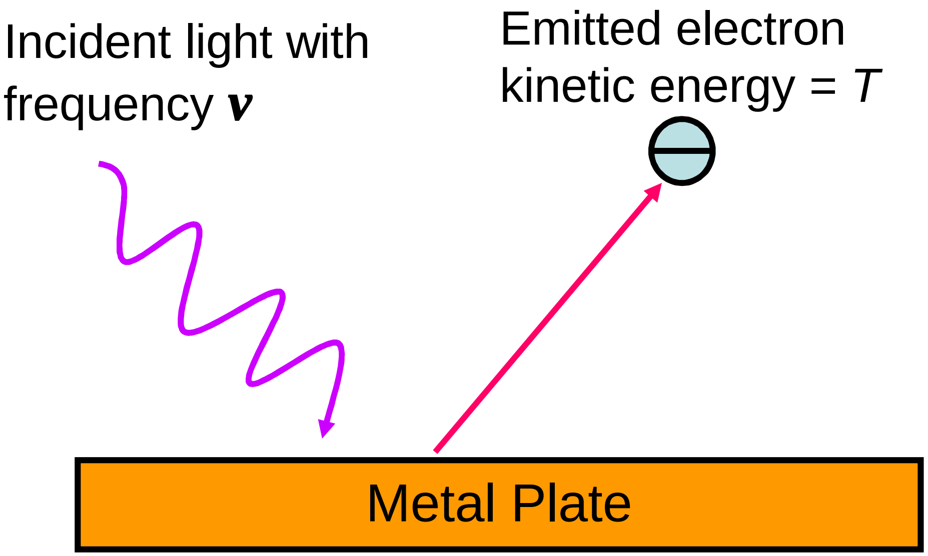
Mechanics: the study of the behavior of physical bodies when subjected to forces or displacements

Classical Mechanics: describing the motion of macroscopic objects.

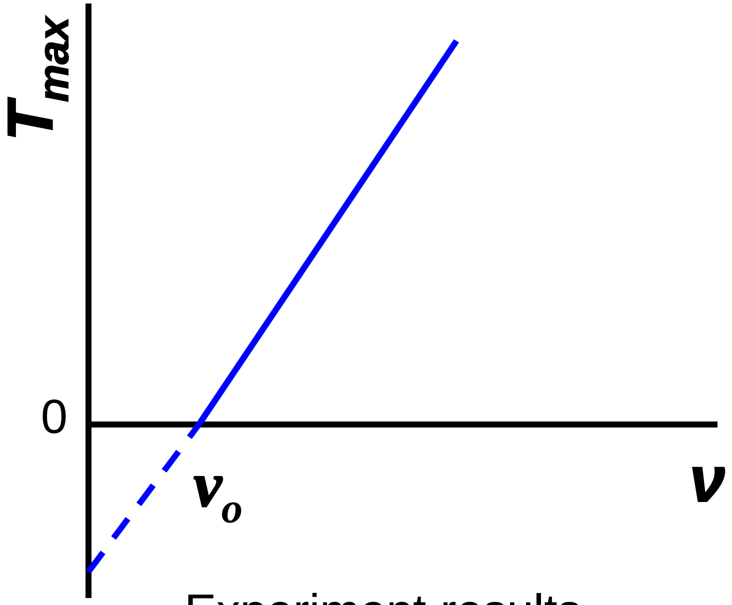
Macroscopic: measurable or observable by naked eyes

Quantum Mechanics: describing behavior of systems at atomic length scales and smaller .

Photoelectric Effect



The photoelectric effect (year1887 by Hertz)



Experiment results

- Inconsistency with classical light theory

According to the classical wave theory, maximum kinetic energy of the photoelectron is only dependent on the incident intensity of the light, and independent on the light frequency; however, experimental results show that the kinetic energy of the photoelectron is dependent on the light frequency.

Concept of “energy quanta”

Energy Quanta

- Photoelectric experiment results suggest that the energy in light wave is contained in discrete energy packets, which are called energy quanta or photon
- The wave behaviors like particles. The particle is photon

Planck's constant: $h = 6.625\times10^{-34}$ J-s

Photon energy = $h\nu$

Work function of the metal material = $h\nu_o$

Maximum kinetic energy of a photoelectron: $T_{max} = h(\nu - \nu_o)$

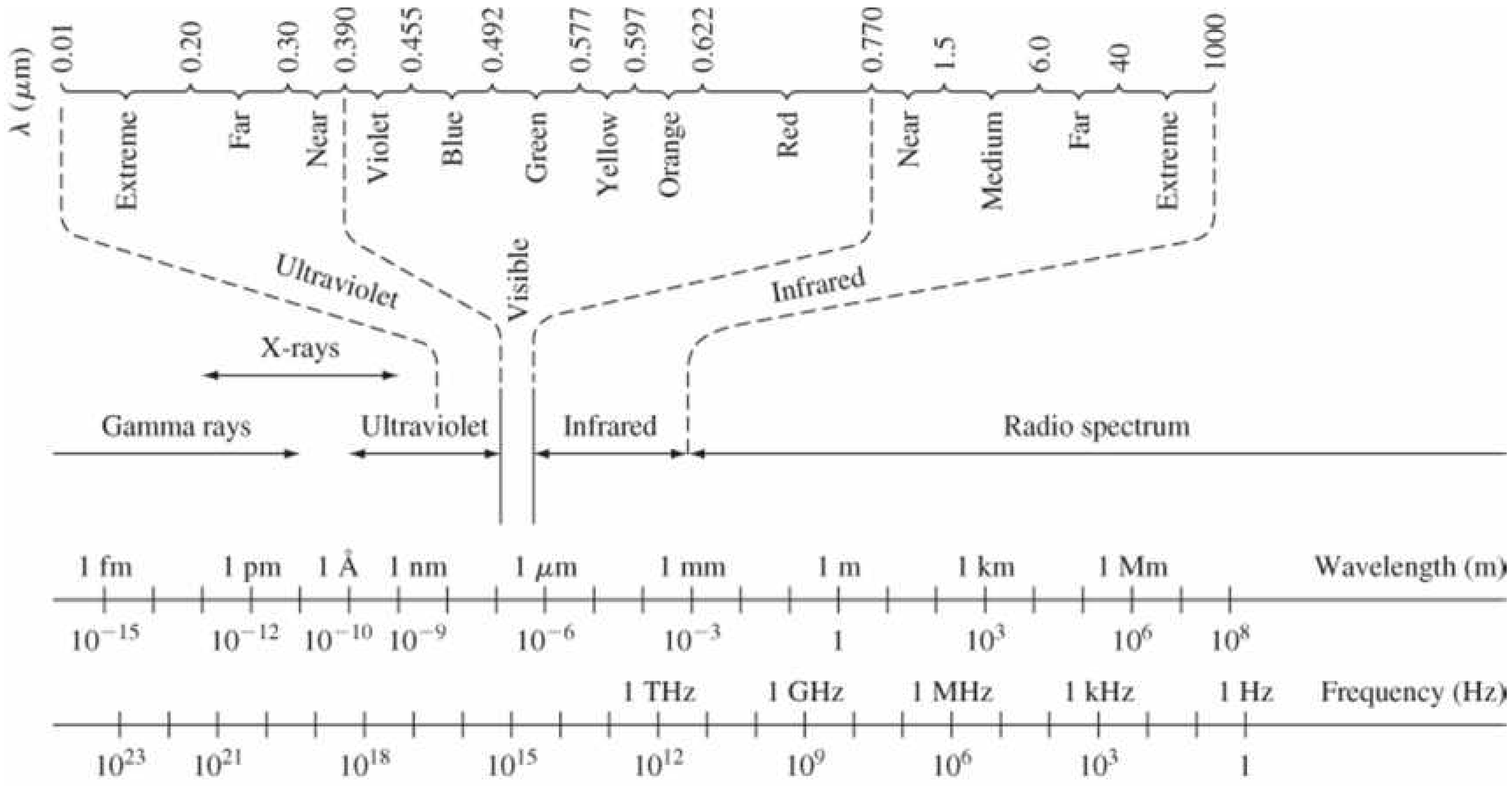
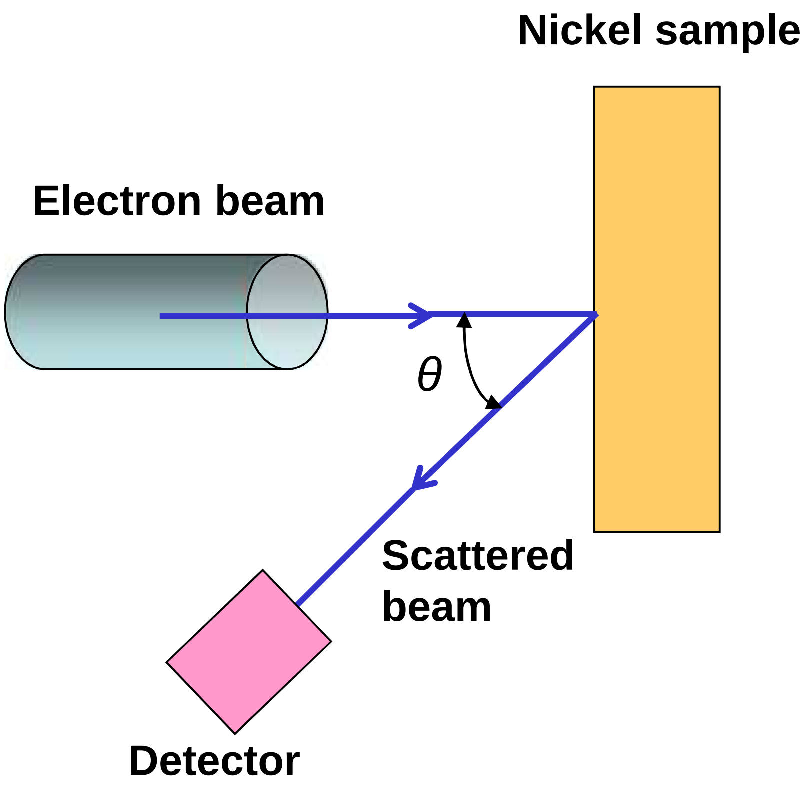
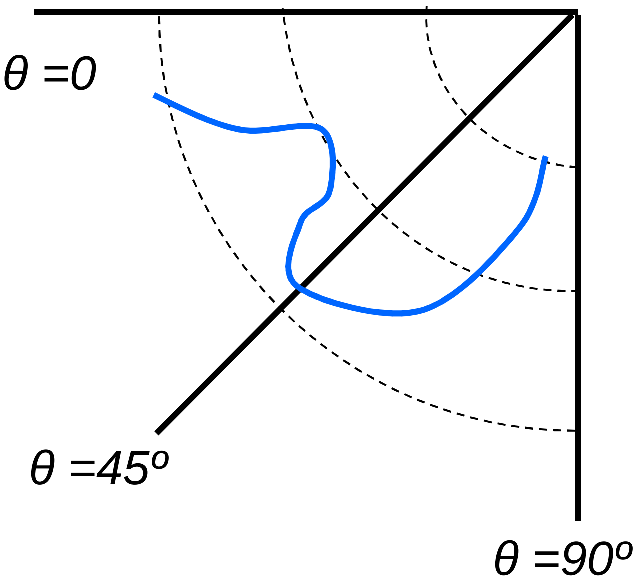


Figure 2.4 | The electromagnetic frequency spectrum.

Electron’s Wave Behavior





Davisson-Germer experiment (1927)

Electron as a particle has wave-like behavior

Wave-Particle Duality

Particle-like wave behavior
(example, photoelectric effect)

Wave-like particle behavior
(example, Davisson-Germer experiment)

Wave-particle duality

Mathematical descriptions:

The momentum of a photon is: $p = \frac{h}{a}$

The wavelength of a particle is: $a = \frac{h}{p}$

λ is called the *de Broglie wavelength*

The Uncertainty Principle

The Heisenberg Uncertainty Principle (year 1927):

- It is impossible to simultaneously describe with absolute accuracy the position and momentum of a particle

$$\Delta p \, \Delta x \geq \hbar$$

- It is impossible to simultaneously describe with absolute accuracy the energy of a particle and the instant of time the particle has this energy

$$\Delta E \, \Delta t \geq \hbar$$

The Heisenberg uncertainty principle applies to electrons and states that we can not determine the exact position of an electron. Instead, we could determine the probability of finding an electron at a particular position.

Schrödinger’s Wave Equation

One dimensional Schrödinger’s Wave Equation:

$$\frac{-\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2}+V(x)\Psi(x,t)=j\hbar\frac{\partial\Psi(x,t)}{\partial t}$$

$\Psi(x,t):$ Wave function

$|\Psi(x,t)|^2 dx$, the probability to find a particle in (x, $x+dx$) at time t

$|\Psi(x,t)|^2$, the probability density at location x and time t

$V(x):$ Potential function

$m:$ Mass of the particle

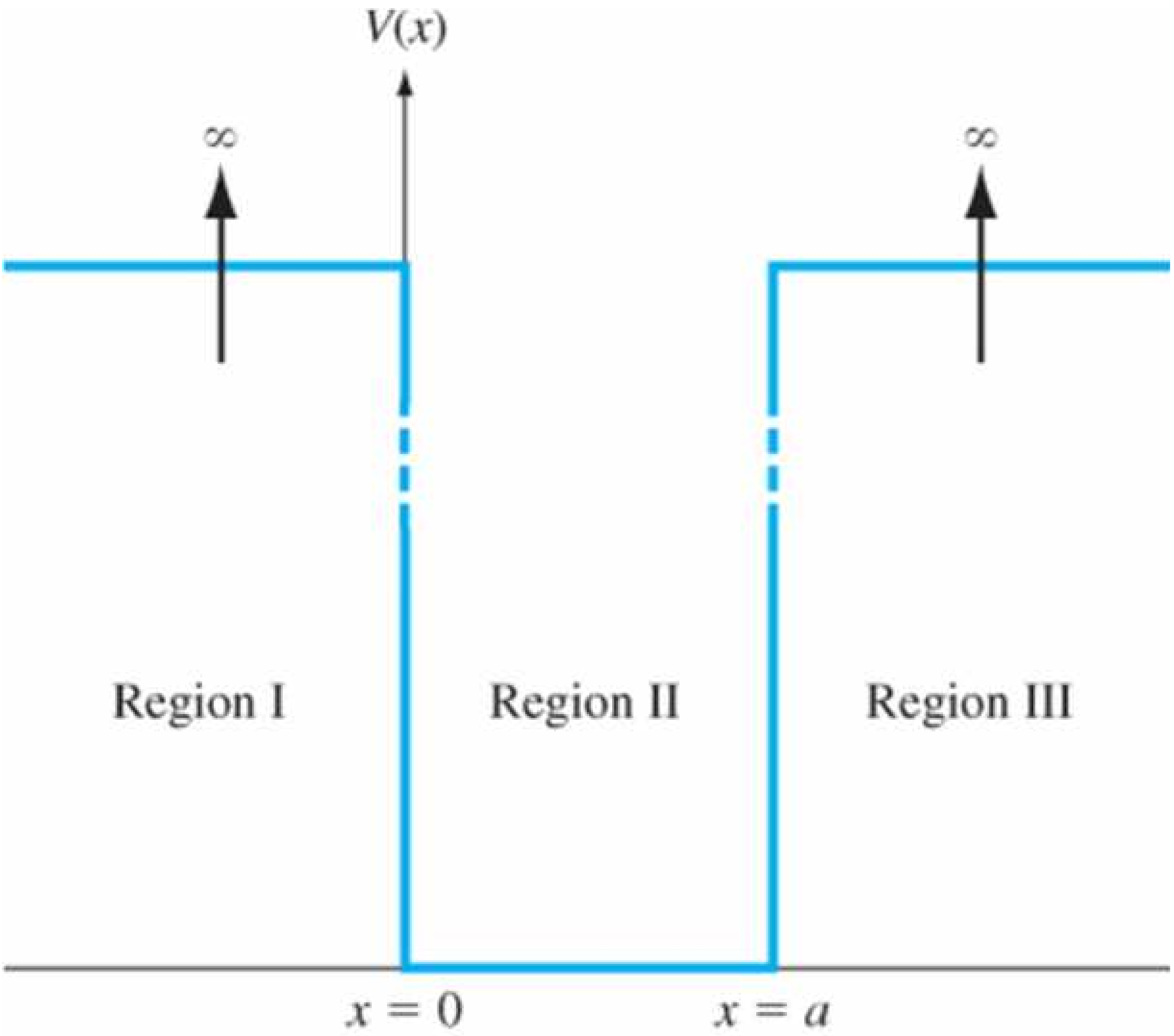


Figure 2.6 | Potential function of the infinite potential well.

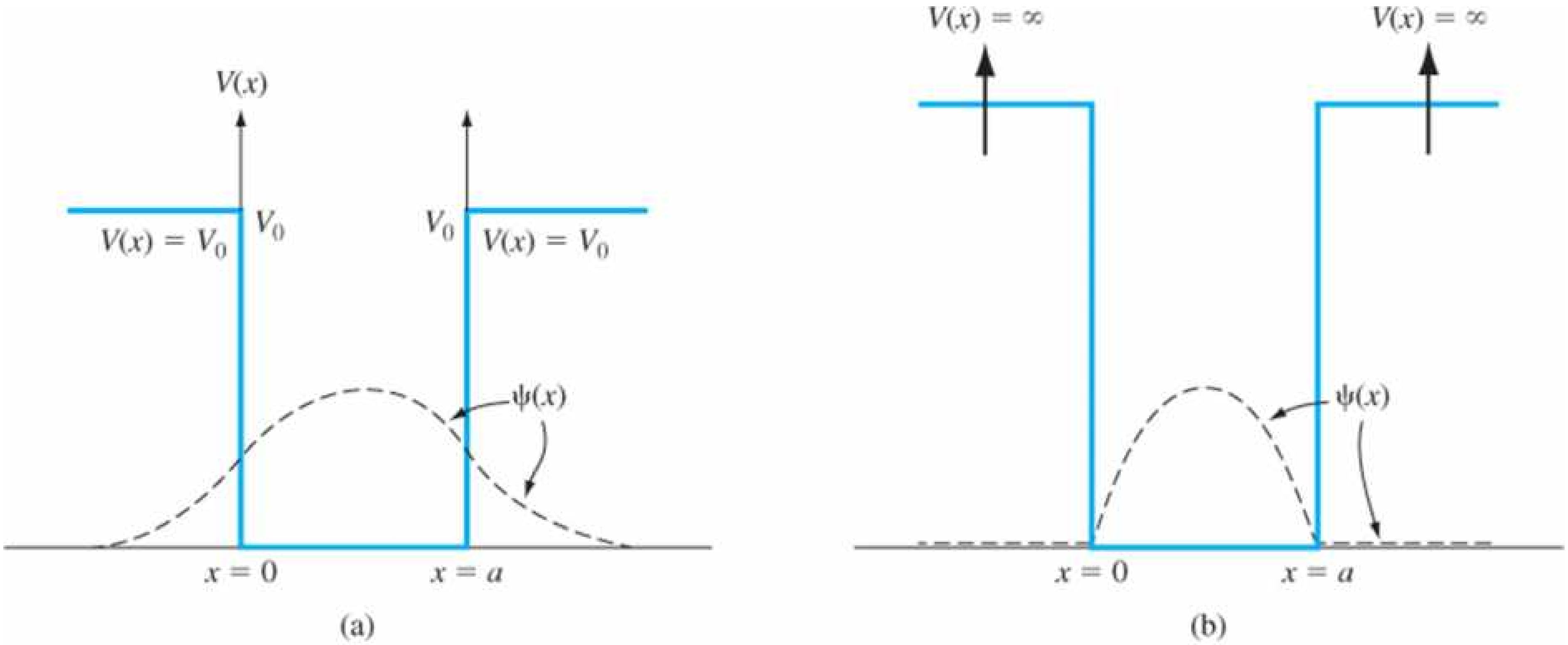


Figure 2.5 | Potential functions and corresponding wave function solutions for the case (a) when the potential function is finite everywhere and (b) when the potential function is infinite in some regions.

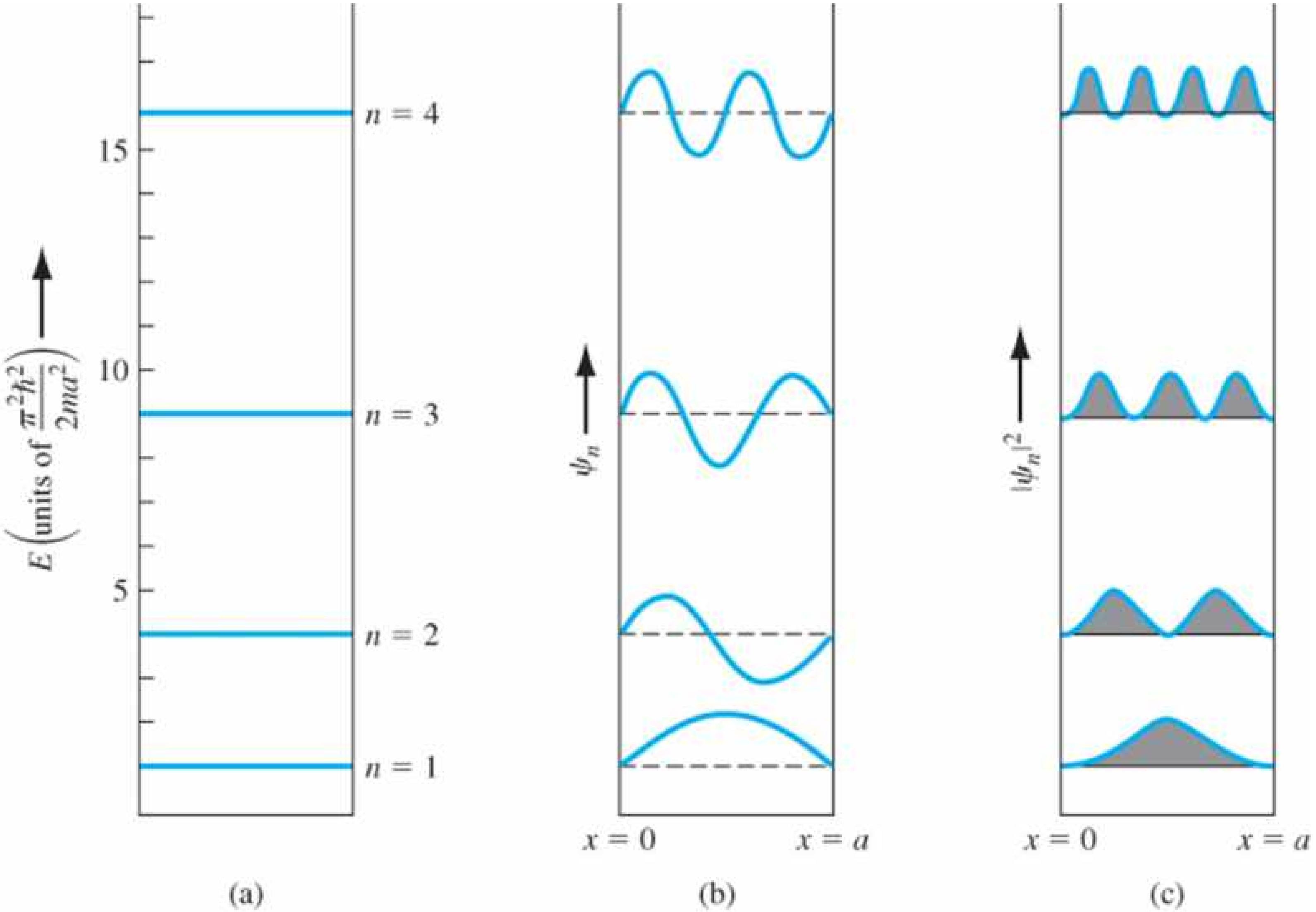


Figure 2.7 | Particle in an infinite potential well: (a) four lowest discrete energy levels, (b) corresponding wave functions, and (c) corresponding probability functions. *(From Pierret [10].)*

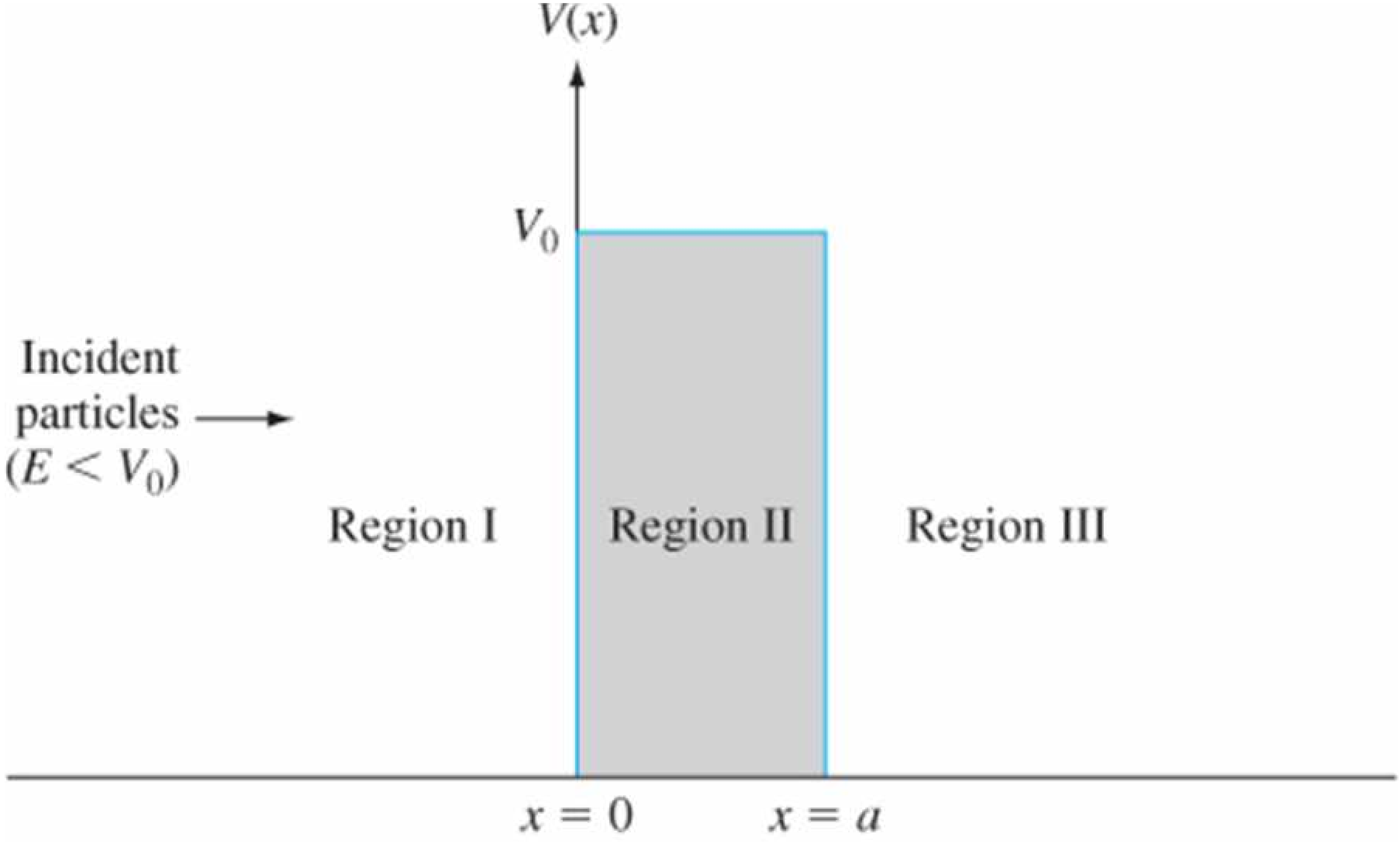
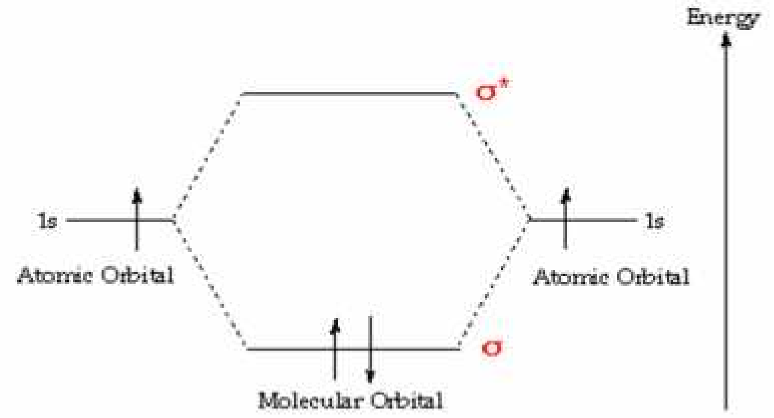


Figure 2.9 | The potential barrier function.

MOLECULAR ORBITAL THEORY

The molecular orbital theory is a method developed at the beginning of the twentieth century by F. Hund and R. S. Mulliken to describe the structure and properties of different molecules.

Molecular orbital theory approximates the molecular orbitals as linear combinations of atomic orbitals which can be illustrated as follows.



Linear Combination of Atomic Orbitals (LCAO)

Molecular orbitals can generally be expressed through a linear combination of atomic orbitals (abbreviated to LCAO). These LCAOs are useful in the estimation of the formation of these orbitals in the bonding between the atoms that make up a molecule.

The Schrodinger equation used to describe the electron behavior for molecular orbitals can be written in a method similar to that for atomic orbitals.

It is an approximate method for representing molecular orbitals. It's more of a superimposition method where constructive interference of two atomic wave function produces a bonding molecular orbital whereas destructive interference produces non-bonding molecular orbital.

Conditions for Linear Combination of Atomic Orbitals

The conditions that are required for the linear combination of atomic orbitals are as follows:

Same Energy of Combining Orbitals

The atomic orbitals combining to form molecular orbitals should have comparable energy. This means that 2p orbital of an atom can combine with another 2p orbital of another atom but 1s and 2p cannot combine together as they have appreciable energy difference.

Same Symmetry about Molecular Axis

The combining atoms should have the same symmetry around the molecular axis for proper combination, otherwise, the electron density will be sparse. For e.g. all the sub-orbitals of 2p have same energy but still, 2pz orbital of an atom can only combine with a 2pz orbital of another atom but cannot combine with 2px and 2py orbital as they have a different axis of symmetry. In general, the z-axis is considered as the molecular axis of symmetry.

Proper Overlap between Atomic Orbitals

The two atomic orbitals will combine to form molecular orbital if the overlap is proper. Greater the extent of overlap of orbitals, greater will be the nuclear density between the nuclei of the two atoms.

The condition can be understood by two simple requirements. For the formation of proper molecular orbital, proper energy and orientation are required. For proper energy, the two atomic orbitals should have the same energy and for the proper orientation, the atomic orbitals should have proper overlap and the same molecular axis of symmetry.

What are Molecular Orbitals?

The space in a molecule in which the probability of finding an electron is maximum can be calculated using the molecular orbital function. Molecular orbitals are basically mathematical functions that describe the wave nature of electrons in a given molecule.

These orbitals can be constructed via the combination of hybridized orbitals or atomic orbitals from each atom belonging to the specific molecule. Molecular orbitals provide a great model via the molecular orbital theory to demonstrate the bonding of molecules.

Types of Molecular Orbitals

According to the molecular orbital theory, there exist three primary types of molecular orbitals that are formed from the linear combination of atomic orbitals. These orbitals are detailed below.

Anti Bonding Molecular Orbitals

The electron density is concentrated behind the nuclei of the two bonding atoms in anti-bonding molecular orbitals. This results in the nuclei of the two atoms being pulled away from each other. These kinds of orbitals weaken the bond between two atoms.

Non-Bonding Molecular Orbitals

In the case of non-bonding molecular orbitals, due to a complete lack of symmetry in the compatibility of two bonding atomic orbitals, the molecular orbitals formed have no positive or negative interactions with each other. These types of orbitals do not affect the bond between the two atoms.

Features of Molecular Orbital Theory

- The atomic orbitals overlap to form new orbitals called **molecular orbitals.** When two atomic orbitals overlap they lose their identity and form new orbitals called **molecular orbitals.**
- The electrons in the molecules are filled in the new energy states called the Molecular orbitals similar to the electrons in an atom being filled in an energy state called atomic orbitals.
- The probability of finding the electronic distribution in a molecule around its group of nuclei is given by the molecular orbital.
- The two combining atomic orbitals should possess energies of comparable value and similar orientation. For example, 1s can combine with 1s and not with 2s.
- The number of molecular orbitals formed is equal to the number of atomic orbitals combining.

- The shape of molecular orbitals formed depends upon the shape of the combining atomic orbitals.

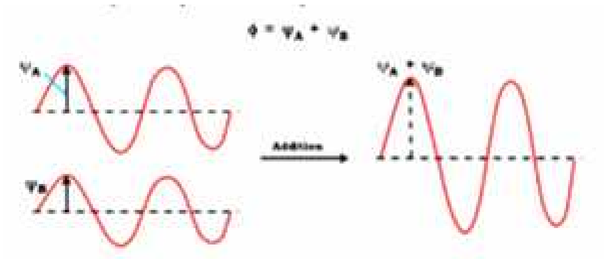
According to the Molecular Orbital Theory, the filling of orbitals takes place according to the following rules:

- Aufbau's principle: Molecular orbitals are filled in the increasing order of energy levels.
- Pauli's exclusion principle: In an atom or a molecule, no two electrons can have the same set of four quantum numbers.
- Hund's rule of maximum multiplicity: Pairing of electrons doesn't take place until all the atomic or molecular orbitals are singly occupied.

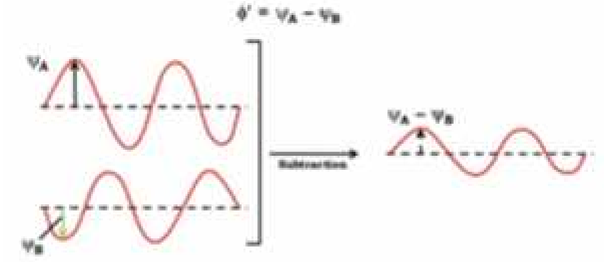
Formation of Molecular Orbitals

An atomic orbital is an electron wave; the waves of the two atomic orbitals may be in phase or out of phase. Suppose Ψ_A and Ψ_B represent the amplitude of the electron wave of the atomic orbitals of the two atoms A and B.

Case 1: When the two waves are in phase so that they add up and amplitude of the wave is
$\Phi = \Psi_A + \Psi_B$



Case 2: when the two waves are out of phase, the waves are subtracted from each other so that the amplitude of the new wave is $\Phi' = \Psi_A - \Psi_B$



Characteristics of Bonding Molecular Orbitals

- The probability of finding the electron in the internuclear region of the bonding molecular orbital is greater than that of combining atomic orbitals.
- The electrons present in the bonding molecular orbital result in the attraction between the two atoms.
- The bonding molecular orbital has lower energy as a result of attraction and hence has greater stability than that of the combining atomic orbitals.
- They are formed by the additive effect of the atomic orbitals so that the amplitude of the new wave is given by $\Phi = \Psi_A + \Psi_B$
- They are represented by σ, π, and δ.

Characteristics of Anti-bonding Molecular Orbitals

- The probability of finding the electron in the internuclear region decreases in the anti-bonding molecular orbitals.
- The electrons present in the anti-bonding molecular orbital result in the repulsion between the two atoms.
- The anti-bonding molecular orbitals have higher energy because of the repulsive forces and lower stability.
- They are formed by the subtractive effect of the atomic orbitals. The amplitude of the new wave is given by $\Phi\,' = \Psi_A - \Psi_B$
- They are represented by σ^*, π^*, δ^*

Antibonding Orbitals Higher in Energy

The energy levels of bonding molecular orbitals are always lower than those of anti-bonding molecular orbitals. This is because the electrons in the orbital are attracted by the nuclei in the case of bonding molecular orbitals whereas the nuclei repel each other in the case of the anti-bonding molecular orbitals.

The lowering of the energy of bonding molecular orbital than the combining atomic orbital is called **stabilization energy** and similarly increase in energy of the anti-bonding molecular orbitals is called **destabilization energy**.

Difference between Bonding and Antibonding Molecular Orbitals

Molecular Orbital Theory	
Bonding Molecular Orbitals	**Anti-Bonding Molecular Orbitals**
Molecular orbitals formed by the additive effect of the atomic orbitals is called bonding molecular orbitals	Molecular orbitals formed by the subtractive effect of atomic is called anti-bonding molecular orbitals
Probability of finding the electrons is more in the case of bonding molecular orbitals	Probability of finding electrons is less in antibonding molecular orbitals. There is also a node between the anti-bonding molecular orbital between two nuclei where the electron density is zero.
These are formed by the combination of + and + and – with – part of the electron waves	These are formed by the overlap of + with – part.
The electron density, in the bonding molecular orbital in the internuclear region, is high. As a result, the nuclei are shielded from each other and hence the repulsion is very less.	The electron density in the antibonding molecular orbital in the internuclear region is very low and so the nuclei are directly exposed to each other. Therefore the nuclei are less shielded from each other.
The bonding molecular orbitals are represented by σ, π, δ.	The corresponding anti-bonding molecular orbitals are represented by $\sigma*$, $\pi*$, $\delta*$.

VBT (VALENCE BOND THEORY)

The Valence Bond Theory was developed in order to explain chemical bonding using the method of quantum mechanics. This theory primarily focuses on the formation of individual bonds from the atomic orbitals of the participating atoms during the formation of a molecule.

The Lewis approach to chemical bonding failed to shed light on the formation of chemical bonds. Also, valence shell electron pair repulsion theory (or VSEPR theory) had limited applications (and also failed in predicting the geometry corresponding to complex molecules).

In order to address these issues, the valence bond theory was put forth by the German physicists Walter Heinrich Heitler and Fritz Wolfgang London. The Schrodinger wave equation was also used to explain the formation of a covalent bond between two hydrogen atoms. The chemical bonding of two hydrogen atoms as per the valence bond theory is illustrated below.

Valence Bond Theory (VBT)

This theory focuses on the concepts of electronic configuration, atomic orbitals (and their overlapping) and the hybridization of these atomic orbitals. Chemical bonds are formed from the overlapping of atomic orbitals wherein the electrons are localized in the corresponding bond region.

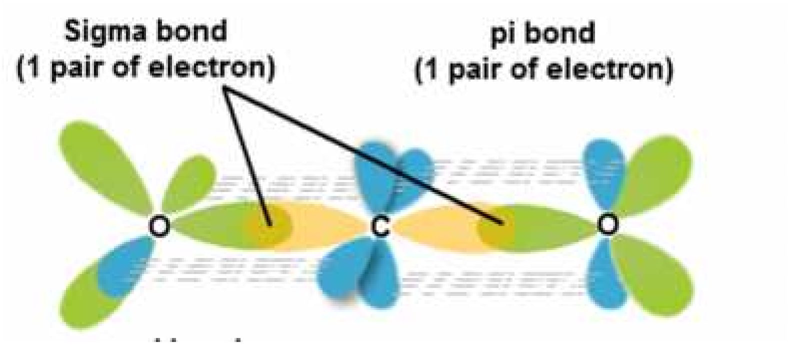
The valence bond theory also goes on to explain the electronic structure of the molecules formed by this overlapping of atomic orbitals. It also emphasizes that the nucleus of one atom in a molecule is attracted to the electrons of the other atoms.

Postulates of Valence Bond Theory

The important postulates of the valence bond theory are listed below.

- Covalent bonds are formed when two valence orbitals (half filled) belonging to two different atoms overlap on each other. The electron density in the area between the two bonding atoms increases as a result of this overlapping, thereby increasing the stability of the resulting molecule.
- The presence of many unpaired electrons in the valence shell of an atom enables it to form multiple bonds with other atoms. The paired electrons present in the valence shell do not take participate in the formation of chemical bonds as per the valence bond theory.
- Covalent chemical bonds are directional and are also parallel to the region corresponding to the atomic orbitals that are overlapping.
- Sigma bonds and pi bonds differ in the pattern that the atomic orbitals overlap in, i.e. pi bonds are formed from sidewise overlapping whereas the overlapping along the axis containing the nuclei of the two atoms leads to the formation of sigma bonds.

The formation of sigma and pi bonds is illustrated below.



It can be noted that sigma bonds involve the head-to-head overlapping of atomic orbitals whereas pi bonds involve parallel overlapping.

Applications and Limitations of VBT

The maximum overlap condition which is described by the valence bond theory can explain the formation of covalent bonds in several molecules. This is one of its most important applications. For example, the difference in the length and strength of the chemical bonds in H2 and F2 molecules can be explained by the difference in the overlapping orbitals in these molecules.

The covalent bond in an HF molecule is formed from the overlap of the 1s orbital of the hydrogen atom and a 2p orbital belonging to the fluorine atom, which is explained by the valence bond theory.

Limitations of Valence Bond Theory

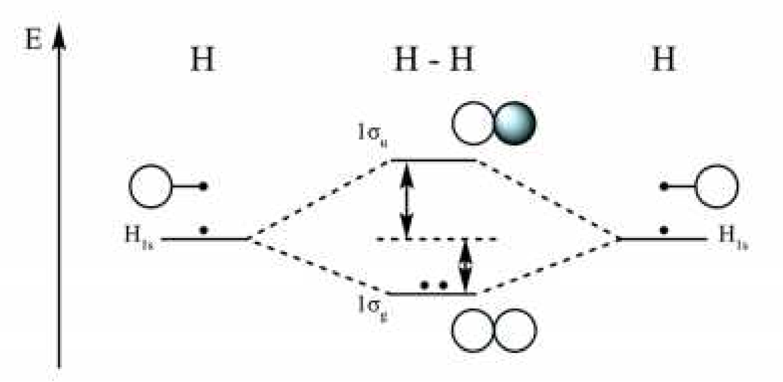
The shortcomings of the valence bond theory include:

- Failure to explain the tetravalency exhibited by carbon
- No insight offered on the energies of the electrons.
- The theory assumes that electrons are localized in specific areas.

Thus, the limitations and the applications of the valence bond theory are discussed.

Diatomic molecules

Molecules formed upon the bonding of two same elements are known as homonuclear diatomic molecules. For example dihydrogen (H_2), dinitrogen (N_2), etc. In this article, we will study the formation of these diatomic molecules, their stability, and other characteristics.



Some common diatomic molecules:

1. **Hydrogen molecule (H_2):** Dihydrogen molecule belongs to the family of diatomic molecules, which consists of two hydrogen atoms bonded to each other by a covalent bond. According to the atomic number of hydrogen, it has only one electron in its 1s orbital. The electronic configuration of H_2 molecule is given as:
   H_2: $(\sigma 1s)^2$
   Bond order = = = 1
   Due to the absence of unpaired electrons in the hydrogen molecule, it is diamagnetic in nature.

2. **Lithium molecule (Li_2):** Lithium molecule belongs to the family of diatomic molecules, which consists of two lithium atoms, bonded to each other by a covalent bond. The electronic configuration of Li_2 molecule is given as:
   Li_2: $(\sigma 1s)^2\ (\sigma^*1s)^2\ (\sigma 2s)^2$
   Bond order == 1
   Thus the Li_2 molecule is stable and is diamagnetic in nature due to the absence of unpaired electrons.

3. **Carbon molecule (C_2):** Carbon molecule belongs to the family of diatomic molecules, which consists of two carbon atoms, bonded to each other by a covalent bond. The electronic configuration of the Carbon molecule is given as,
   C_2 :$(\sigma 1s)^2\ (\sigma^*1s)^2(\sigma 2s)^2\ (\sigma\ ^*2s)^2\ (\pi 2p^2{}_x = \pi\ 2p^2{}_y)$
   Bond order = = 2
   Due to the absence of unpaired electrons, C_2 is diamagnetic in nature. Furthermore, due to the presence of four electrons in pi bonding orbitals, the double bond in C_2 consists of both pi bonds.

4. **Oxygen molecule (O_2):** Oxygen molecule belongs to the family of diatomic molecules, which consists of two oxygen atoms, bonded to each other by a covalent bond.The

electronic configuration of the Oxygen molecule is given as,
O_2: $(\sigma 1s)^2$ $(\sigma^*1s)^2$ $(\sigma 2s)^2$ $(\sigma\ {*2s})^2$ $(\sigma 2p_z)^{\,2}$ $(\pi 2p^2{}_x = \pi\ 2p^2{}_y)$ $(\pi^*2p^1{}_x = \pi^*2p^1{}_y)$
Bond order = = 2.
Due to the presence of one unpaired electron, O_2molecule should be paramagnetic.

5. **Helium molecule (He_2):** According to the atomic number of helium, it has two electrons in 1s.The electronic configuration of the helium molecule according to molecular orbital theory is given as:
   He_2: $(\sigma 1s)^2$ $(\sigma^*1s)^2$
   Bond order == 0.
   Thus, He_2 molecule is unstable and does not exist.

CHEMICAL BONDING

Chemical Bonding refers to the formation of a chemical bond between two or more atoms, molecules, or ions to give rise to a chemical compound. These chemical bonds are what keep the atoms together in the resulting compound.

The attractive force which holds various constituents (atom, ions, etc.) together and stabilizes them by the overall loss of energy is known as chemical bonding. Therefore, it can be understood that chemical compounds are reliant on the strength of the chemical bonds between its constituents; The stronger the bonding between the constituents, the more stable the resulting compound would be. The attractive force that binds two atoms together is known as the chemical bond.

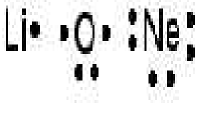
Important Theories on Chemical Bonding

Albrecht Kössel and Gilbert Lewis were the first to explain the formation of chemical bonds successfully in the year 1916. They explained chemical bonding on the basis of the inertness of noble gases.

Lewis Theory of Chemical Bonding

- An atom can be viewed as a positively charged ‘Kernel’ (the nucleus plus the inner electrons) and the outer shell.
- The outer shell can accommodate a maximum of eight electrons only.
- The eight electrons present in the outer shell occupy the corners of a cube which surround the ‘Kernel’.
- The atoms having octet configuration, i.e. 8 electrons in the outermost shell, thus symbolize a stable configuration.
- Atoms can achieve this stable configuration by forming chemical bonds with other atoms. This chemical bond can be formed either by gaining or losing an electron(s) (NaCl, $MgCl_2$) or in some cases due to the sharing of an electron (F_2).
- Only the electrons present in the outer shell, also known as the valence electrons take part in the formation of chemical bonds. Gilbert Lewis used specific notations better known as Lewis symbols to represent these valence electrons.
- Generally, the valency of an element is either equal to the number of dots in the corresponding Lewis symbol or 8 minus the number of dots (or valence electrons).

Lewis symbols for lithium (1 electron), oxygen (6 electrons), neon (8 electrons) are given below:



Here, the number of dots that surround the respective symbol represents the number of valence electrons in that atom.

Kossel's theory of Chemical Bonding

- Noble gases separate the highly electronegative halogens and the highly electropositive alkali metals.
- Halogens can form negatively charged ions by gaining an electron. Whereas alkali metals can form positively charged ions by losing an electron.
- These negatively charged ions and positively charged ions have a noble gas configuration that is 8 electrons in the outermost shell. The general electronic configuration of noble gases (except helium) is given by ns^2np^6.
- As unlike charges attract each other these unlike charged particles are held together by a strong force of electrostatic attraction existing between them. For example, $MgCl_2$, the magnesium ion, and chlorine ions are held together by force of electrostatic attraction. This kind of chemical bonding existing between two unlike charged particles is known as an electrovalent bond.

Explanation of Kossel Lewis Approach

In 1916 Kossel and Lewis succeeded in giving a successful explanation based upon the concept of an electronic configuration of noble gases about why atoms combine to form molecules. Atoms of noble gases have little or no tendency to combine with each other or with atoms of other elements. This means that these atoms must be having stable electronic configurations.

Due to the stable configuration, the noble gas atoms neither have any tendency to gain or lose electrons and, therefore, their combining capacity or valency is zero. They are so inert that they even do not form diatomic molecules and exist as monoatomic gaseous atoms.

Types of Chemical Bonds

When substances participate in chemical bonding and yield compounds, the stability of the resulting compound can be gauged by the type of chemical bonds it contains.

The type of chemical bonds formed vary in strength and properties. There are 5 primary types of chemical bonds which are formed by atoms or molecules to yield compounds. These types of chemical bonds include:

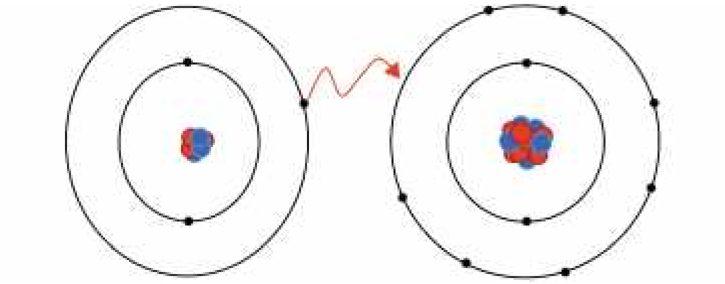
- Ionic Bonds
- Covalent Bonds
- Coordinate Covalent Bonds
- Hydrogen Bonds
- Van der Waals bond

These types of bonds in chemical bonding are formed from the loss, gain, or sharing of electrons between two atoms/molecules.

Ionic Bonding

Ionic bonding is a type of chemical bonding which involves a transfer of electrons from one atom or molecule to another. Here, an atom loses an electron which is in turn gained by another atom. When such an electron transfer takes place, one of the atoms develops a negative charge and is now called the anion.

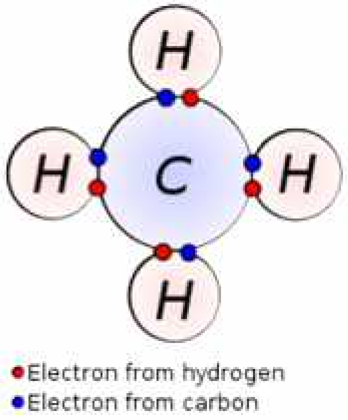
The other atom develops a positive charge and is called the cation. The ionic bond gains strength from the difference in charge between the two atoms, i.e. the greater the charge disparity between the cation and the anion, the stronger the ionic bond.



Types of Chemical Bonds – Ionic bonding

Covalent Bonding

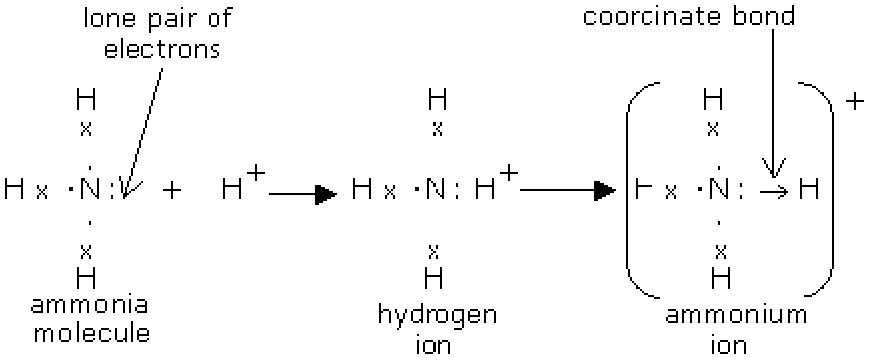
A covalent bond indicates the sharing of electrons between atoms. Compounds that contain carbon (also called organic compounds) commonly exhibit this type of chemical bonding. The pair of electrons which are shared by the two atoms now extend around the nuclei of atoms, leading to the creation of a molecule.

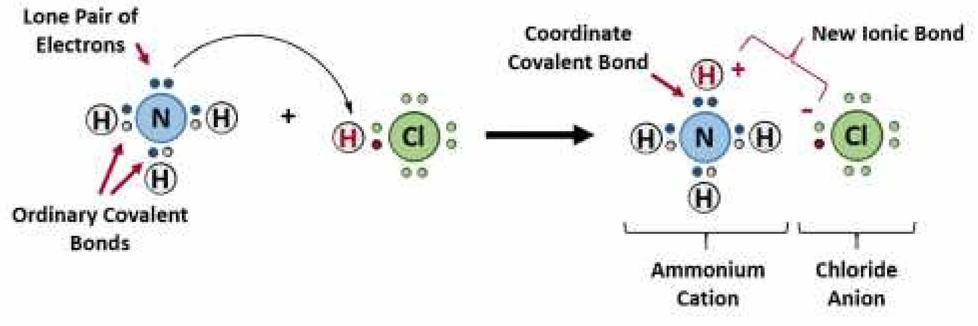


Covalent Bonding

Coordinate Covalent Bonding

A **coordinate bond** (also called a dative **covalent bond**) is a **covalent bond** (a shared pair of electrons) in which both electrons come from the same atom. A **covalent bond** is formed by two atoms sharing a pair of electrons. The atoms are held together because the electron pair is attracted by both of the nuclei.

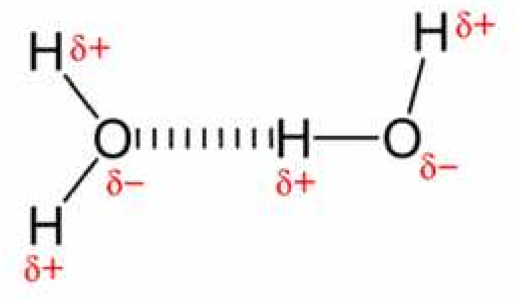




Hydrogen Bonding

Compared to ionic and covalent bonding, Hydrogen bonding is a weaker form of chemical bonding. It is a type of polar covalent bonding between oxygen and hydrogen wherein the hydrogen develops a partial positive charge. This implies that the electrons are pulled closer to the more electronegative oxygen atom.

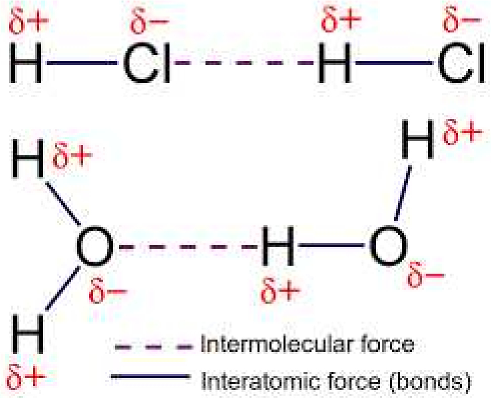
This creates a tendency for the hydrogen to be attracted towards the negative charges of any neighbouring atom. This type of chemical bonding is called a hydrogen bond and is responsible for many of the properties exhibited by water.



Hydrogen Bonding

Van der Waals bond

Hydrogen **bonding** is the third **type** of **van der Waals**' forces. It is exactly the same as dipole-dipole interaction, it just gets a special name. A hydrogen **bond** is a dipole dipole interaction that occurs between any molecule with a **bond** between a hydrogen atom and any of oxygen/fluorine/nitrogen.



Hybridization is defined as the concept of mixing two atomic orbitals with the same energy levels to give a degenerated new type of orbitals. This intermixing is based on quantum mechanics. The atomic orbitals of the same energy level can only take part in hybridization and both full filled and half-filled orbitals can also take part in this process provided they have equal energy.

During the process of hybridization, the atomic orbitals of similar energy are mixed together such as the mixing of two ‘s’ orbitals or two ‘p’ orbital’s or mixing of an ‘s’ orbital with a ‘p’ orbital or ‘s’ orbital with a ‘d’ orbital.

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What is Hybridization?

Redistribution of the energy of orbitals of individual atoms to give orbitals of equivalent energy happens when two atomic orbitals combine together to form hybrid orbital in a molecule.

This process is called **hybridization**. The new orbitals thus formed are known as **hybrid orbitals.**

⇒ Also Read

- Chemical Bonding
- Molecular Orbital Theory

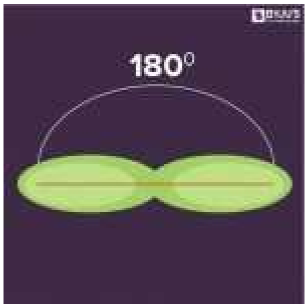
Types of Hybridization

Based on the types of orbitals involved in mixing, the hybridization can be classified as sp3, sp2, sp, sp3d, sp3d2, sp3d3. Let us now discuss the various types of hybridization along with their examples.

sp Hybridization

sp hybridization is observed when one s and one p orbital in the same main shell of an atom mix to form two new equivalent orbitals. The new orbitals formed are called **sp hybridized orbitals.** It forms linear molecules with an angle of 180°

- This type of hybridization involves the mixing of one ‘s’ orbital and one ‘p’ orbital of equal energy to give a new hybrid orbital known as an sp hybridized orbital.
- sp hybridization is also called diagonal hybridization.
- Each sp hybridized orbital has an equal amount of s and p character, i.e., 50% s and p character.



Examples of sp Hybridization:

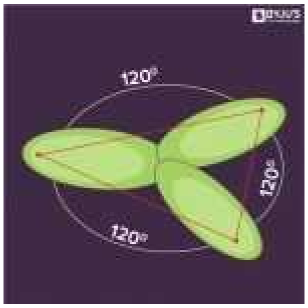
- All compounds of beryllium like BeF_2, BeH_2, $BeCl_2$
- All compounds of carbon-containing triple Bond like C_2H_2.

sp^2 Hybridization

sp^2 hybridisation is observed when one s and two p orbitals of the same shell of an atom mix to form 3 equivalent orbital. The new orbitals formed are called **sp^2 hybrid orbitals.**

- sp^2 hybridization is also called trigonal hybridization.

- It involves mixing of one ‘s’ orbital and two ‘p’ orbital’s of equal energy to give a new hybrid orbital known as sp^2.
- A mixture of s and p orbital formed in trigonal symmetry and is maintained at 120^0.
- All the three hybrid orbitals remain in one plane and make an angle of 120° with one another. Each of the hybrid orbitals formed has 33.33% s character and 66.66% ‘p’ character.
- The molecules in which the central atom is linked to 3 atoms and is sp2 hybridized have a triangular planar shape.



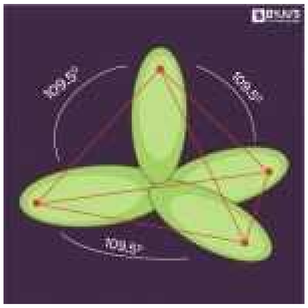
Examples of sp^2 Hybridization

- All the compounds of Boron i.e. BF_3, BH_3
- All the compounds of carbon containing a carbon-carbon double bond, Ethylene (C_2H_4)

sp^3 Hybridization

When one ‘s’ orbital and 3 ‘p’ orbitals belonging to the same shell of an atom mix together to form four new equivalent orbital, the type of hybridization is called a **tetrahedral hybridization or sp^3**. The new orbitals formed are called **sp^3 hybrid orbitals.**

- These are directed towards the four corners of a regular tetrahedron and make an angle of 109°28’ with one another.
- The angle between the sp3 hybrid orbitals is 109.28^0
- Each sp^3 hybrid orbital has 25% s character and 75% p character.
- Example of sp^3 hybridization: ethane (C_2H_6), methane.



sp^{3}d Hybridization

sp^3d hybridization involves the mixing of 3p orbitals and 1d orbital to form 5 sp3d hybridized orbitals of equal energy. They have trigonal bipyramidal geometry.

- The mixture of s, p and d orbital forms trigonal bipyramidal symmetry.
- Three hybrid orbitals lie in the horizontal plane inclined at an angle of 120° to each other known as the equatorial orbitals.
- The remaining two orbitals lie in the vertical plane at 90 degrees plane of the equatorial orbitals known as axial orbitals.
- **Example:** Hybridization in Phosphorus pentachloride (PCl_5)

sp^3d^2 Hybridization

- sp3d2 hybridization has 1s, 3p and 2d orbitals, that undergo intermixing to form 6 identical sp3d2 hybrid orbitals.
- These 6 orbitals are directed towards the corners of an octahedron.
- They are inclined at an angle of 90 degrees to one another.

Key Features of Hybridization

- Atomic orbitals with equal energies undergo hybridization.
- The number of hybrid orbitals formed is equal to the number of atomic orbitals mixing.
- It is not necessary that all the half-filled orbitals must participate in hybridization. Even completely filled orbitals with slightly different energies can also participate.
- Hybridization happens only during the bond formation and not in an isolated gaseous atom.
- The shape of the molecule can be predicted if hybridization of the molecule is known.
- The bigger lobe of the hybrid orbital always has a positive sign while the smaller lobe on the opposite side has a negative sign.

Try This: Give the hybridization states of each of the carbon atom in the given molecule.

- $H_2C = CH – CN$
- $HC \equiv C - C \equiv CH$
- $H_2C = C = C = CH_2$

VSEPR Theory is used to predict the shape of the molecules from the electron pairs that surround the central atoms of the molecule. The theory was first presented by Sidgwick and Powell in 1940. VSEPR theory is based on the assumption that the molecule will take a shape such that electronic repulsion in the valence shell of that atom is minimized.

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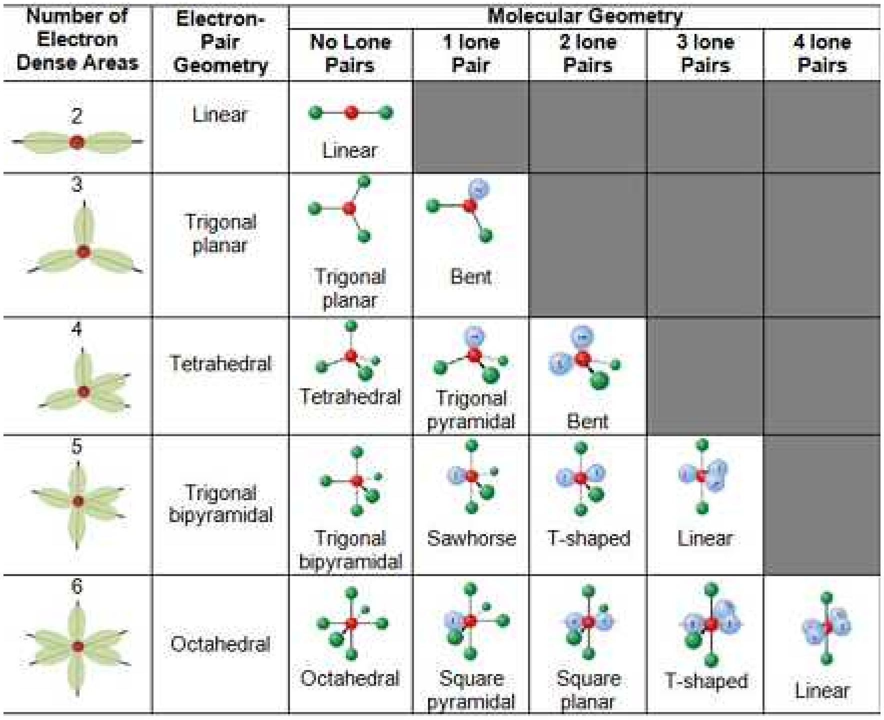
What is VSEPR Theory?

The Valence Shell Electron Pair Repulsion Theory abbreviated as VSEPR theory is based on the premise that there is a repulsion between the pairs of valence electrons in all atoms, and the atoms will always tend to arrange themselves in a manner in which this electron pair repulsion is minimalized. This arrangement of the atom determines the geometry of the resulting molecule.

The different geometries that molecules can assume keeping with VSEPR theory can be seen in the illustration provided below.



Number of Electron Dense Areas	Electron-Pair Geometry	Molecular Geometry				
		No Lone Pairs	1 lone Pair	2 lone Pairs	3 lone Pairs	4 lone Pairs
2	Linear	Linear				
3	Trigonal planar	Trigonal planar	Bent			
4	Tetrahedral	Tetrahedral	Trigonal pyramidal	Bent		
5	Trigonal bipyramidal	Trigonal bipyramidal	Sawhorse	T-shaped	Linear	
6	Octahedral	Octahedral	Square pyramidal	Square planar	T-shaped	Linear

VSEPR Theory – Different Geometries that Molecules can Assume

The two primary founders of the VSEPR theory are Ronald Nyholm and Ronald Gillespie. This theory is also known as the Gillespie-Nyholm theory to honour these chemists.

Also Read

- Chemical Bonding
- Covalent Bond
- Hydrogen Bonding
- Hybridization
- Molecular Orbital Theory

According to the VSEPR theory, the repulsion between two electrons is caused by the Pauli exclusion principle that has greater importance than electrostatic repulsion in the determination of molecular geometry.

Postulates of VSEPR Theory:

The postulates of the VSEPR theory are listed below

- In polyatomic molecules (i.e. molecules made up of three or more atoms), one of the constituent atoms is identified as the central atom to which all other atoms belonging to the molecule are linked.
- The total number of valence shell electron pairs decides the shape of the molecule.
- The electron pairs have a tendency to orient themselves in a way that minimizes the electron-electron repulsion between them and maximizes the distance between them.
- The valence shell can be thought of as a sphere wherein the electron pairs are localized on the surface in such a way that the distance between them is maximized.
- Should the central atom of the molecule be surrounded by bond pairs of electrons, then, the asymmetrically shaped molecule can be expected.
- Should the central atom be surrounded by both lone pairs and bond pairs of electrons, the molecule would tend to have a distorted shape.
- The VSEPR theory can be applied to each resonance structure of a molecule.
- The strength of the repulsion is strongest in two lone pairs and weakest in two bond pairs.
- If electron pairs around the central atom are closer to each other, they will repel each other. This results in an increase in the energy of the molecules.
- If the electron pairs lie far from each other, the repulsions between them will be less and eventually, the energy of the molecule will be low.

Limitations of VSEPR Theory:

Some significant limitations of the VSEPR theory include:

- This theory fails to explain isoelectronic species (i.e. elements having the same number of electrons). The species may vary in shapes despite having the same number of electrons.

- The VSEPR theory does not shed any light on the compounds of transition metals. The structure of several such compounds cannot be correctly described by this theory. This is because the VSEPR theory does not take into account the associated sizes of the substituent groups and the lone pairs that are inactive.
- Another limitation of VSEPR theory is that it predicts that halides of group 2 elements will have a linear structure, whereas their actual structure is a bent one.

Predicting the Shapes of Molecules:

The following steps must be followed in order to decide the shape of a molecule.

- The least electronegative atom must be selected as the central atom (since this atom has the highest ability to share its electrons with the other atoms belonging to the molecule).
- The total number of electrons belonging to the outermost shell of the central atom must be counted.
- The total number of electrons belonging to other atoms and used in bonds with the central atom must be counted.
- These two values must be added in order to obtain the valence shell electron pair number or the VSEP number.

What is VSEP Number?

The VSEP number describes the shape of the molecule, as described in the table provided below.

VSEP Number	**Shape of the Molecule**
2	Linear
3	Trigonal Planar
4	Tetrahedral
5	Trigonal Bipyramidal
6	Octahedral
7	Pentagonal Bipyramidal

Each of these corresponding shapes can also be found in the illustration provided earlier. However, the VSEPR theory cannot be used to obtain the exact bond angles between the atoms in a molecule.

Now, we will discuss each shape in detail:

Linear Shape of Molecule:

- In this type of molecule, we find two places in the valence shell of the central atom.
- They should be arranged in such a manner such that repulsion can be minimized (pointing in the opposite direction).
- **Example:** BeF_2

Trigonal Planar Shape of Molecule:

- In this type of molecule, we find three molecules attached to a central atom.
- They are arranged in such a manner such that repulsion between the electrons can be minimized (toward the corners of an equilateral triangle).
- **Example:** BF_3

Tetrahedral Shape of Molecule:

- In two-dimensional molecules, atoms lie in the same plane and if we place these conditions on methane, we will get a square planar geometry in which the bond angle between H-C-H is 90^0.
- Now, if we consider all these conditions for a three-dimensional molecule, we will get a tetrahedral molecule in which the bond angle between H-C-H is $109^0$28' (toward the corners of an equilateral triangle) CH_4

Trigonal Bipyramid Shape of Molecule:

- Let's take an example of PF_5. Here, repulsion can be minimized by even distribution of electrons towards the corner of a trigonal pyramid. In trigonal bipyramid, three positions lie along the equator of the molecule. The two positions lie along an axis perpendicular to the equatorial plane.

How can the VSEPR Theory be used to Predict the Shapes of Molecules?

The strength of the repulsion between a lone pair and a bond pair of electrons lies in between the repulsion between two lone pairs and between two bond pairs. The order of repulsion between electron pairs as follows:

Lone Pair- lone pair > Lone Pair- bond- pair > Bond Pair- bond pair.

1. Total number of electron pairs around the central atom = ½ (number of valence electrons of central atom + number of atoms linked to central atom by single bonds)

- For negative ions, add the number of electrons equal to the units of negative charge on the ions to the valence electrons of the central atom.
- For positive ions, subtract the number of electrons equal to the units of positive charge on the ion from the valence electrons of the central atom.

2. The number of Bond pair = Total number of atoms linked to central atom by single bonds.

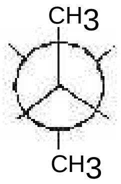
3. Number of lone pairs = Total number of electron – No of shared pair

The electron pairs around the central atom repel each another and move so far apart from each another that there are no greater repulsions between them. This results in the molecule having minimum energy and maximum stability.

- The shape of a molecule with only two atoms is always linear.
- For molecules with three or more atoms, one of the atoms is called the central atom and other atoms are attached to the central atom.
- If the central atom is linked to similar atoms and is surrounded by bond pairs of electrons only, the repulsions between them are similar as a result the shape of the molecule is symmetrical and the molecule is said to have regular geometry.
- If the central atom is linked to different atoms or is surrounded by bond pair as well as a lone pair of electrons, the repulsion between them is similar. As a result, the shape of the molecule has an irregular or distorted geometry.
- The exact shape of the molecule depends upon the total number of electron pairs present around the central atom.

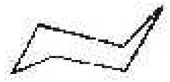
1) Anti conformation :

For example, anti conformation of butane, two methyl groups at an angle of 180° to each other.



2) Chair conformation :

Staggered conformation of cyclohexane that has no angle strain or torsional strain and is therefore lowest energy conformation.



3) Chiral molecule :

A molecule that is not superimposable on its mirror image. Chiral molecules have handedness and are capable of exisiting as a pair of enantiomers.

4) Chirality :

The property of having handedness.

5) Configuration :

The particular arrangement of atoms or groups in space that is characteristic of a given stereoisomer.

6) Conformation :

A particular temporary orientation of a molecule that results from rotations about its single bond.

7) Conformational analysis :

An analysis of the energy changes that a molecule undergoes as its groups undergo rotations(sometimes only partial) about the single bonds that join them.

8) Conformer :

A particular staggered conformation of a molecule.

9) Dextrorotatory :

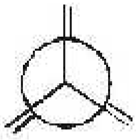
A compound that rotates plane palarised light clockwise.

10) Diastereomers :

Stereoisomers that are not mirror image of each other.

11) Eclipsed conformation :

A temporary orientation of grups around two atoms joined by a single bond such that the groups directly oppose each other.



12) Gauche conformation :

A gauche conformation of butane, for example, in which methyl groups at an angle of 60° to each other.

13) Isomers :

Different molecules that have the same molecular formula.

14) Mutarotation :

The spontaneous change that takes place in the optical rotation of α & β anomers of a sugar when they are dissoved in water. The optical rotations of the sugars change until they reach the same value.

15) Plane polarised light :

Ordinary light in which the oscillations of the electrical field occur only in one plane.

16) Racemic form (recemic mixture) :

An equimolar mixture of enantiomers. A racemic form is optically inactive.

17) Meso compound :

An optically inactive compound whose molecules are achiral even though they contain tetrahedral atoms with four different attached groups.

18) Optically active compounds :

A compound that rotates the plane of polarisation of plane polarised light.

19) Periplaner :

A conformation in which vicinal groups lie in the same plane.

20) <u>Staggered conformation</u> :

A temporary orientation of groups around two atoms joined by a single bond such that the bonds of the back atom exactly bisect the angles formed by the bonds of the front atom in Newman projection formula.

21) <u>Resolution</u> :

The process by which the enantiomers of the racemic forms are separated.

22) <u>Rotamers</u> :

Rotamers are extreme conformations.

23) <u>Homomers</u> :

Identical representation of same compound.

STEROISOMERISM

Stereochemistry deals with the study of arrangement of atoms of a molecule in three diamension space.

Stereoisomers are the compounds that have same molecular formula and mode of attachment between atoms but differ in arrangement of atoms in space. This phenomenon is called stereoisomerism. Stereoisomerism is of three types :

1) Conformational isomerism
2) Optical isomerism
3) Geometrical isomerism.

CONFORMATION ISOMERISM

Groups bonded only by a sigma bond (i.e.by a single bond) can undergo rotation about that bond with respect to each other. That is, these groups are not fixed in a single position, but are relatively free to rotate about the single bond connecting them. The different structures which result by rotation about a sigma bond are called as conformations.

Conformational stereoisomers interconvert easily at room temperature through rotation about single bond.

A single conformation cannot be physically separated from one another.

METHODS OF REPRESENTING CONFORMATIONS

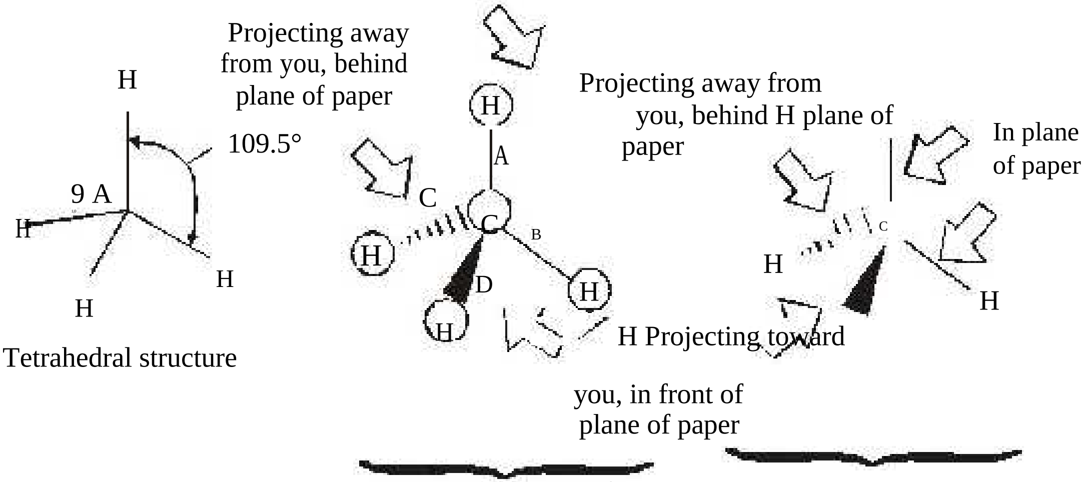
Three diamensional figures cannot be properly represented on a two diamensional surface like that of paper. Hence various projectional formulae have been suggested for drawing conformations. Four of them are discussed below:

1) Dotted line wedge formula :

Dotted line wedge formula is a shorthand notation used to simplify three diamensional drawing. In this method the molecule is seen from the side of C – C bond.

1) Dashed lines show the bonds that go backward away from the reader.
2) Thick lines are used to show bonds that come forward, towards the reader.
3) The normal lines represent bonds within the plane of the paper.

A plane drawn through the H-C-H bonds of bonds A and B.



Tetrahedral structure

Representations of the three-dimensional structure

Though tadious, it is the best method of representation.

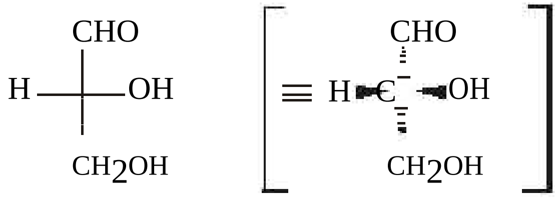
2) **Fischer projection** :

Fischer projection is a standard way to project three diamensional configuration of each carbon onto a plane surface. The projection looks like a cross with a chiral carbon at the point where the lines cross.

The Fischer projection can be written in the following way:

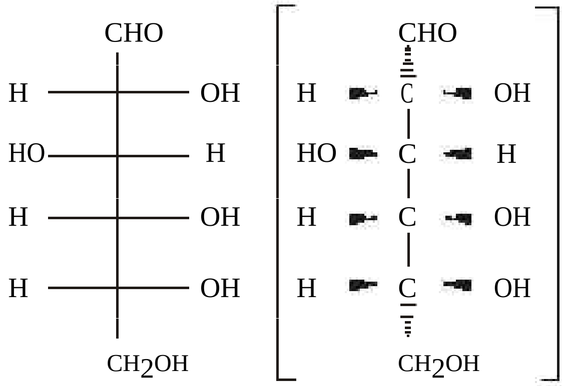
If a molecule has a single chiral centre e.g.-D-glyceraldehyde, the carbon chain is drawn vertical with the most oxidised atom at the top. Then mentally flatten the structure at each chiral centre onto a plane surface.

The horizontal lines at the chiral center represent bonds that project forward. The vertical lines at the chiral center actually represent bonds which project in the rear.



$$\begin{array}{ccc} & CHO & \\ H & + & OH \\ & CH_2OH & \end{array} \quad \left[\equiv \begin{array}{ccc} & CHO & \\ H & C & OH \\ & CH_2OH & \end{array} \right]$$

Fischer formulae can be used for two or more chiral centres with,conventionally, the longest carbon chain vertical, the bonds to top and bottom atom or groups go back, and all the atoms or groups to one side or the other come forward.



Fischer formula for the open chain form of D-glucose

Fischer projection formulae is convenient method for representing acyclic compounds with one or more chiral centres.

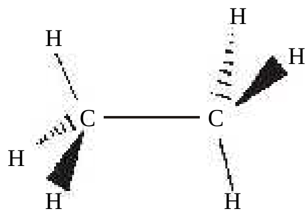
3) <u>Newman Projection</u> :

Newman's projections are a way of drawing conformation.

To draw this formula we have to look along C–C bond from the front.

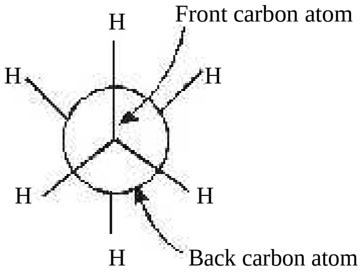
The front carbon with its three substituents is denoted by inverted Y.

The back carbon is represented by a circle with three bonds pointing out from its periphery.



Three-dimensional projection formula

≡



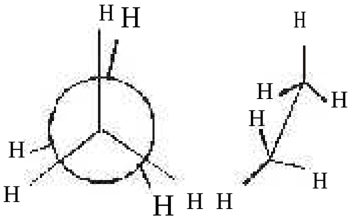
Newman projection formula

4) <u>Saw horse formula</u> :

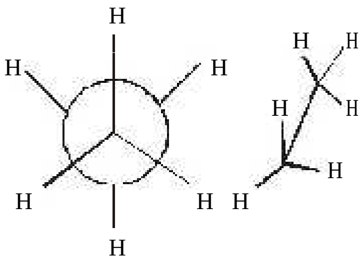
Sawhorse formula is the perspective formula which is used to specify a conformation.

In sawhorse representation, the C–C bond is viewed side ways due to which the C – C bond can be seen unlike in Newman projection.

Newman projection Sawhorse projection



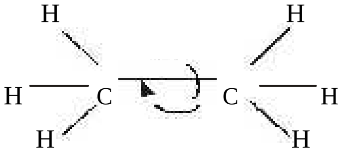
The eclipsed conformation



The staggered conformation

CONFORMATIONS OF ETHANE

The two methyl groups in ethane are not fixed in a single positon. They are free to rotate about the single bond connecting the two carbon atoms. The various structures which result by rotation about a single bond are called as conformations.



An infinite number of different conformations could result from rotations of the CH_3 groups about the carbon – carbon sigma bond since the dihedral angle between the hydrogen atoms on the front and back carbon’s can have an infinite number of values.

The two extreme conformations of ethane are

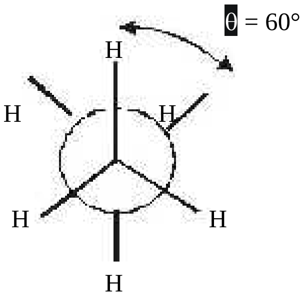
1)Staggered Conformation.

2)Eclipsed Conformation.

There are innumerable number of conformations in between these two extreme forms called as skew conformations.

1)STAGGERED CONFORMATION

In the staggered conformation, dihedral angle (θ) i.e. the angle between C-H bonds on the front carbon atom and the C-H bonds on the back carbon in the Newman projection, is 60°.



Staggered

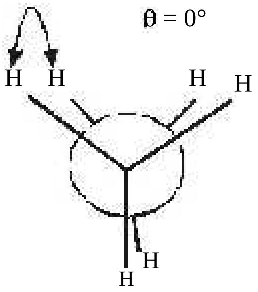
Stability :

The staggered conformation allows the maximum possible separation of the electron pairs of the six carbon-hydrogen bonds thereby minimizing the repulsive interactions between bonding pairs of electrons and therefore it has lowest energy.

2) <u>Eclipsed Conformation</u> :

The conformation of ethane with the dihedral angle of 0° is called eclipsed conformation.

Newman projection of eclipsed conformation shows the hydrogen atoms on the back carbon to be hidden (eclipsed) by those on the front carbon.



Eclipsed

<u>Stability</u> :

In the eclipsed conformation, the electron pairs of the six carbon-hydrogen bonds are closest and therefore eclipsing leads to steric repulsion of hydrogen atoms that are not directly bonded. These non bonded interactions raises the energy of eclipsed conformation by about 3 kcal/mol. It is of highest energy and has the least stability.

3) <u>Skew Conformation</u> :

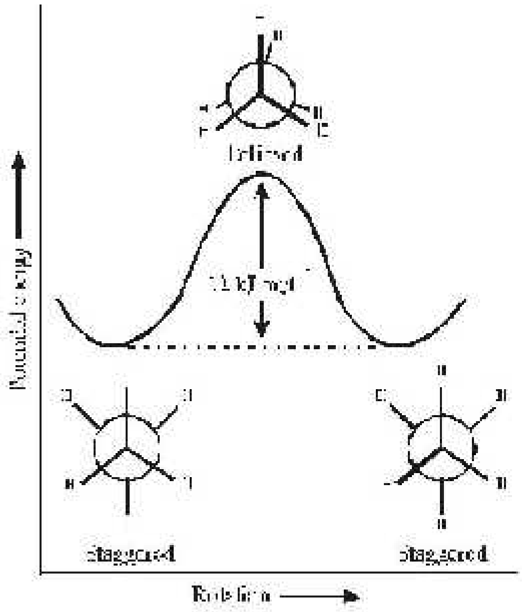
Any conformation of ethane that is not precisely staggered nor eclipsed is called as skew Conformation.

Stability :

In any Skew conformation of ethane, electron pairs of the cabon-hydrogen bonds are not so far as in staggered conformation nor so close as in eclipsed conformation and therefore it is more stable than eclipsed conformation and less stable than staggered conformation.

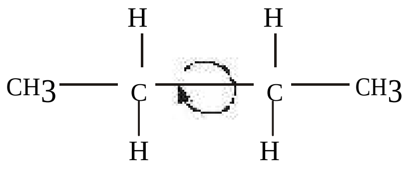
TORSIONAL ENERGY

When ethane rotate towards eclipsed conformation, its potential energy increases which leads to resistance to rotation. The resistance to twisting is called as torsional strain and 3 kcal/ mole energy needed is called torsional energy. The torsional energy of ethane in lowest in staggered conformation. In the eclipsed conformation, the molecule is about 3 kcal/mol higher in energy. This barrier is easily overcome at room temperature and the molecules rotate constantly.



CONFORMATIONS OF BUTANE

Focussing our attention on the middle C–C bond in butane, we see a molecule similar to ethane but with a methyl group replacing one hydrogen on each carbon.



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

Due to the presence of the two methyl groups, two new point are encountered here

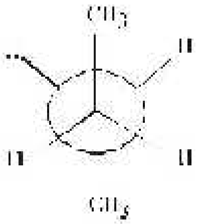
1) There are several staggered and eclipsed conformations.
2) van der Waals repulsion besides torsional strain plays important role in conformational stabilities.

Various conformations of butane are discussed below :

1) ANTI CONFORMATION :

In anti conformation there is 180° dihedral angle between the largest groups.

In anti conformation of butane, the dihedral angle between two methyl groups is 180°.



I

An anti conformation

Stability :

The anti conformation does not have torsional strain because

a) the groups are staggered

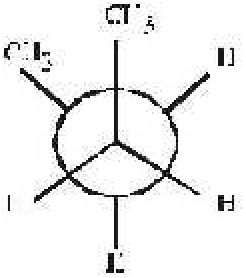
b) two methyl grups are far apart from each other.

Therefore anti conformation is the most stable.

2) GAUCHE CONFORMATION

A conformation with a 60^0 dihedral angle between the largest groups is called gauche conformation.

In the gauche conformation of butane, two methyl groups are 60^0 apart.



III

A gauche conformation

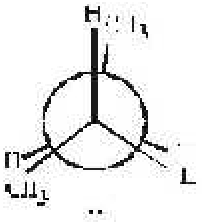
Stability :

In the gauche conformation, the methyl groups are close enough to each other that the van der Waals forces between them are repulsive.

This repulsion causes the gauche conformation to have approximately 3.8 kJ/mol energy more than the anti conformation.

3) PARTLY ECLIPSED CONFORMATION :

Eclipsed conformation of butane in which dihedral angle between two methyl groups is 120^0 is known as partly eclipsed conformation.



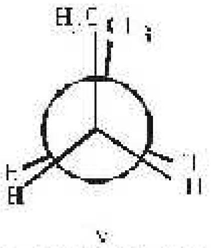
An eclipsed conformation

Stability :

Partly eclipsed conformation has torsional strain. It also has additional van der Waals repulsions arising from the eclipsed methyl groups and hydrogen atoms. These repulsions cause partly eclipsed conformation to have energy 16 kJ/mol than the anti conformation.

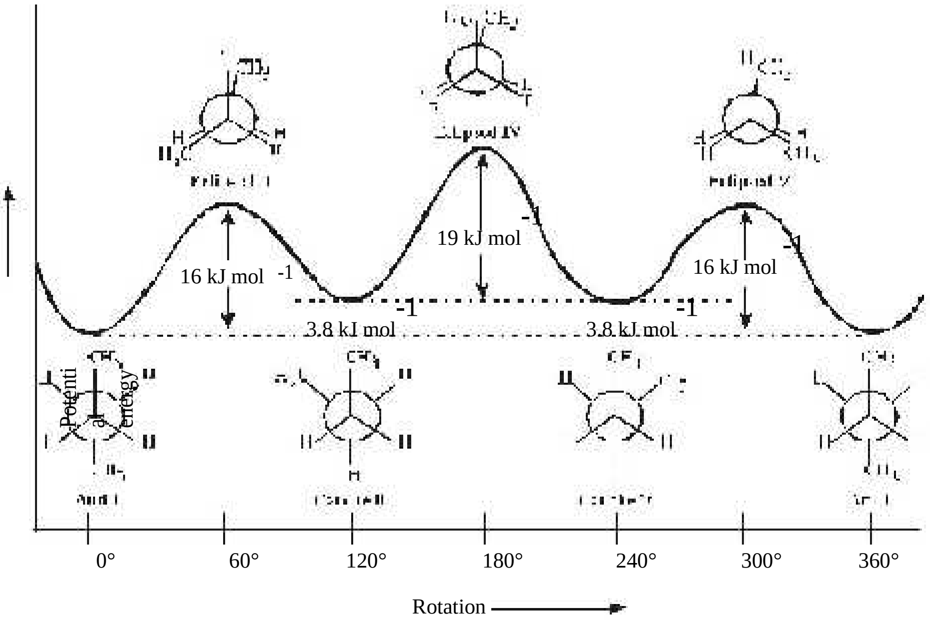
4) FULLY ECLIPSED CONFORMATION

The conformation in which the methyl groups are pointed in the same direction (dihedral angle = 0^0) is called fully eclipsed conformation.



Stability :

Fully eclipsed conformation has the greatest energy and thus least stability of all because, in addition to torsional strain, there is added large van der Waal's repulsive forces between the eclipsed methyl groups.



CONFORMATIONS OF CYCLOHEXANE

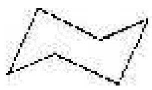
Existance of an innumerable number of conformers in the case of cyclohexane as happens in the case of ethane or butane is not possible. The number of conformers in the case of cyclohexane are limited due to the presence of ring structure which is rigid.

Various conformations of cyclohexane are discussed below:

1) <u>CHAIR CONFORMATION</u> :

The chair conformation is free from angle strain since each angle is 109^0 28'.

In chair form all the C-H bonds are in staggered condition and thus it is free of torsional strain. Thus the potential energy of chair form is minimum.



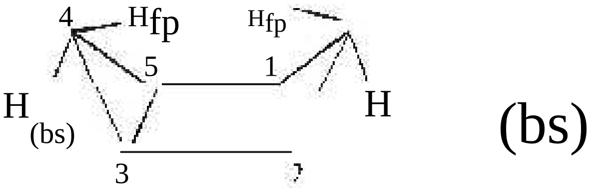
Chair (most stable)

2) <u>BOAT CONFORMATION</u> :

The Boat conformation is free from the angle strain since each angle is 109^0 28'.

Two flagpole hydrogen atoms in the boat conformation lie only 1.83 A^0 and thus there is steric repulsion between them. Morover C_2 and C_6 are eclipsing C_3 and C_5 to which there is bond eclipsing strain.

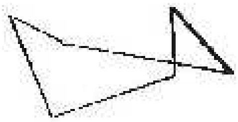
The strain energy calculations indicate that the boat conformation is about 6.4 kcal/mol higher in energy than the chair conformation.



Boat (Less stable)

3) Skew boat conformation :

When the two flagpole bonds in the boat conformation are moved apart, one gets a twist or skew boat conformation.



Twist boat (Stable)

In the skew boat conformation, the flag pole hydrogens are thrown apart.

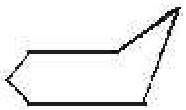
In the first conformer C_2 and C_5 and in the second twist form C_3 and C_6 have gone down. Thus there is less strain in twist conformer than in the boat as there is less of hydrogen eclipsing and flagpole interactions.

According to Hendrickson, the twist form contains 1.6 kcal/mol less energy than the boat form.

The strain energy calculations indicate that the skew boat conformation is about 5 kcal/mol higher in energy than the chair conformation.

4) Half chair conformation :

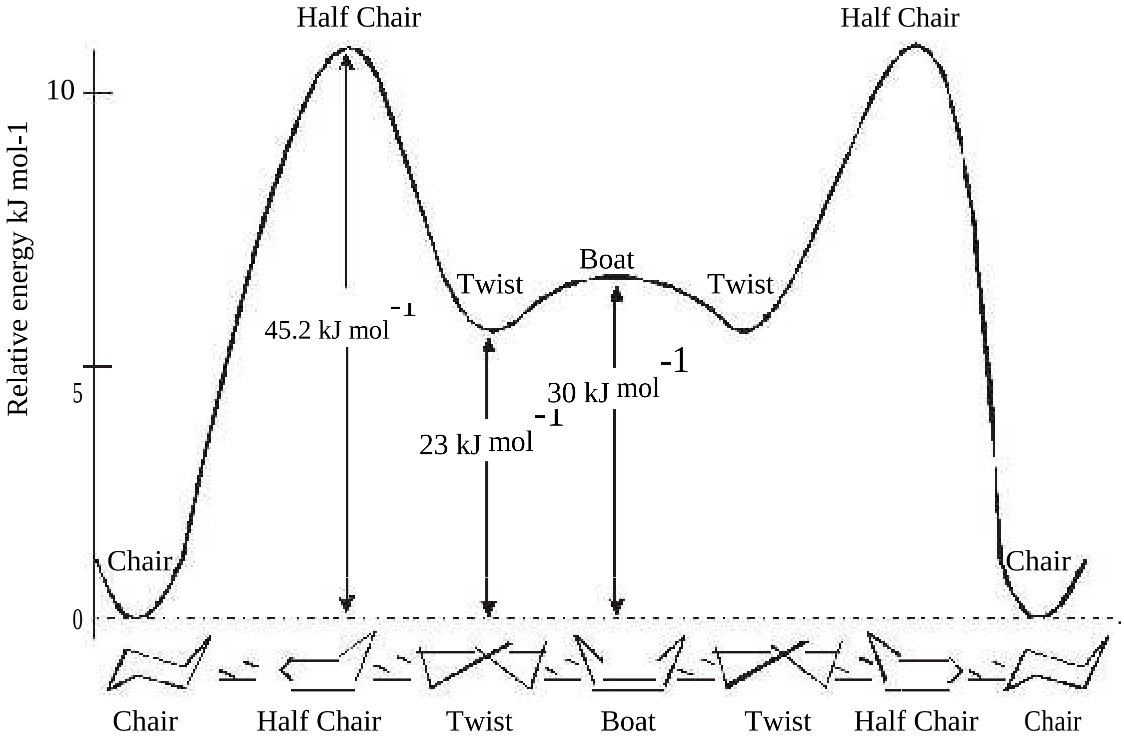
A transition state conformer between the chair and twist forms is supposed to exist. This is known as half chair conformer. This has a high strain. It has about 11 k cal/mole energy than the chair form and is least stable.



Halt chair (List stable)

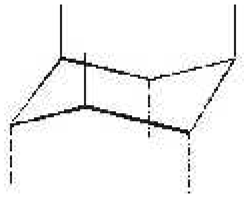
We can summarise the relative stabilities of the various conformations of cyclohexane as :

chair > twist / skew boat > boat > half chair

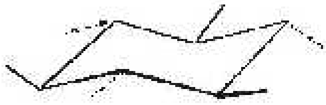


AXIAL AND EQUATORIAL BONDS IN CYCLOHEXANE

The bonds which are parallel to the three fold axis of symmetry of the chair are known as axial bonds and those which extend outward from the ring are known as equatorial bonds.



axial bonds



Equatorial bonds

Each carbon atom of cyclohexane has one axial bond and one equatorial bond.

CONFORMATIONS OF MONOSUBSTITUTED CYCLOHEXANE DERIVATIVES

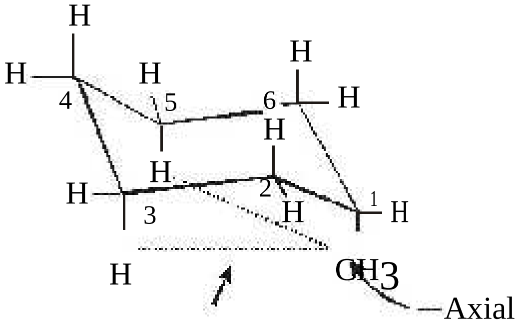
In the case of cyclohexane derivatives when one hydrogen atom is replaced by a larger group or atom then the two chair forms are obtained in case of this mono substituted derivative. The two isomeric chair forms difer in the position of substituent. In one isomer, the substituent is axially located whereas in the other, the substituent is equatorially located.

The stabilities of both the forms are different. Let us consider the case of methyl cyclohexane. This molecule can have two isomeric chair forms whose stabilities would be different. The two isomeric chair forms are

1) Axial isomer, 2) Equatorial isomer.

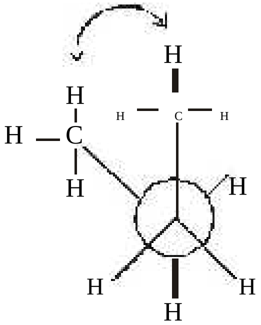
1) <u>Axial Isomer</u> :

In the axial conformer the methyl group is located at axial position. In this conformer, the methyl group is so close to the two axial hydrogens on the same side of the molecule (attached to C-3 and C-5 atoms) that the van der Waals forces between them are repulsive. This type of steric strain, because it arises from an interaction between axial groups on carbon atoms that have 1,3-relation, is called as a 1,3-diaxial interaction.



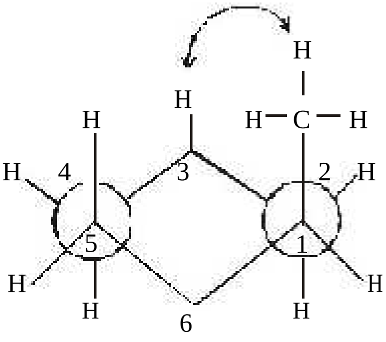
1,3–diaxial methyl-hydrogen interaction is about 0.9 kcal/mole

The strain caused by a 1,3-diaxial interaction in methyl cyclohexane is the same as the strain caused by the close proximity of the hydrogen atoms of methyl groups in the gauche form of butane. These gauche interactions in the gauche butane causes gauche butane to be less stable than anti-butane by 3.8 kJ/mol.



Gauche-Butane

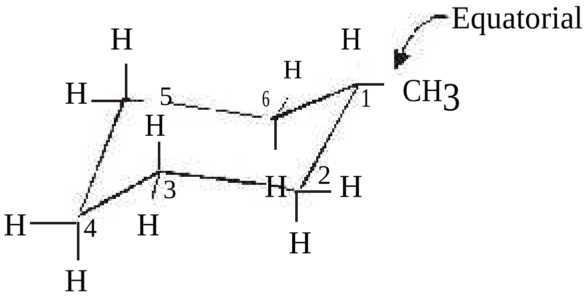
(3.8 kJ mol^{-1} steric strain)

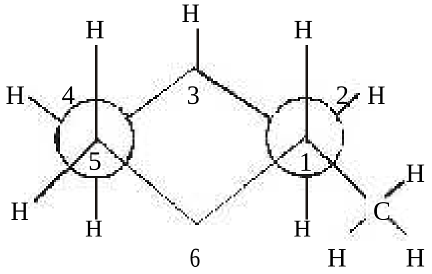


Axial methylcyclohexane
(two gauche interactions =
7.6 kJ mol^{-1} steric strain)

2) **Equatorial Isomer** :

In the equatorial isomer, the methyl group is placed at equatorial position. In the equatorial conformer the methyl group extends into space away from the rest of molecule because of which its hydrogen atoms are far away It is free from diaxial interactions because equatorial methyl group is anti to C-3 and C-5.





Equatorial methycyclohexane

STABILITY :

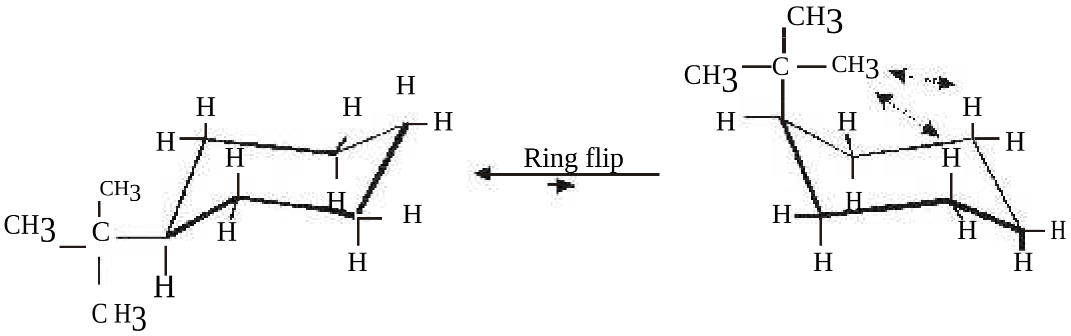
Equatorial conformer is more stable than axial conformer.

MAGNITUDE OF 1,3-DIAXIAL INTERACTION

The magnitude of the 1,3-axial interactions varies with different substituents. The energy difference between the axial and equatorial conformers can be larger or smaller depending on the substituent on the ring.

Conformational free energy :

The energy difference between conformers is known as conformational free energy or A value. The important aspect of conformational analysis is that the two diastereomeric chair forms are not of equal free energy and therefore are differently populated. In other words we can say that the different monosubstitued cyclohexane derivatives display different conformational preferances due to difference in energies of axial and equatorial conformers.



Equatorial tert-butylcyclohexane Axial tert-butylcyclohexane

There is a direct relationship between difference in energy, called the free energy (ΔG^0) and the equilibrium constant (Keq) associated with a given equilibrium in solution

ΔG^0 = difference in free energy = RT ln keq
where R = gas constant (0.00199 kcal/mole)
T = absolute temperature at which the equilibrium is measured.

The product of R, T and the natural logarithm of keq gives ΔG^0 i.e. the free energy difference between the two conformers in kcal/mol.

ΔG^0 is usually negative is the difference of free energy between the equatorial and axial conformer and ΔG^0 is known as conformational free energy of the substituent.

For substituted cyclohexane, it is conventional to specify the value of - ΔG^0 for the equilibrium:

$$\text{axial} \rightleftharpoons \text{equatorial}$$

ΔG^0 will be negative when the equitorial conformation is more stable than the axial. The value of ΔG^0 is positive for the case of substituent groups which favour the equatorial position.

The larger the ΔG^0, the greater is the preferance for the equatorial position.

Conformational free energies of substituent groups

Conformational free energy values for many substituent groups on cyclohexane ring are determined by NMR spectroscopy. Conformational free energy values are measured at low temperatures. It is believed that these values do not vary much at room temperature.

Conformational free energies (– Δ G°) for Substituent Groups

Substituent	**– Δ G° (kcal/mole)**
$–F$	0.24-0.28
$–Cl$	0.53
$–Br$	0.48
$–I$	0.47
$–CH_3$	1.8
$–CH_2CH_3$	1.8
$–CH(CH_3)_2$	2.1
$–C(CH_3)_3$	>4.5
$–CH{=}CH_2$	1.7
$–C_6H_5$	2.9
$–CN$	0.15-0.25
$–O_2CCH_3$	0.71
$–CO_2H$	1.35
$–CO_2C_2H_5$	1.1-1.2
–OH (aprotic solvents)	0.52
–OH (protic solvents)	0.87
$–OCH_3$	0.60
$–NO_2$	1.16
$–HgBr$	0

Relationship Between Free-Energy Difference and Isomer Percentage for Isomers at Equilibrium at 25°C.

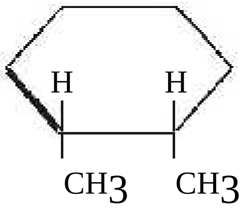
Free-Energy Difference, $\Delta G°$ (kJ mol^{-1})	More Stable Isomer (%)	Less Stable Isomer (%)
0	50	50
1.7	67	33
2.7	75	25
3.4	80	20
4.0	83	17
5.9	91	9
7.5	95	5
11	99	1
17	99.9	0.1
23	99.99	0.01

DISUBSTITUTED CYCLOHEXANE

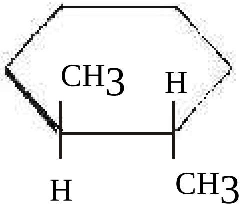
The presence of two substituents on the ring of a cyclohexane allows for the possibility of cis-trans isomerism. Geometrical isomerism in various disubstituted cyclohexane is discussed below,

1,2- disubstituted cyclohexane :

The planar representation of the cis and trans isomers of 1,2- disubstituted cyclohexane is as follows:-



Cis -1,2-Dimethylcyclohexane

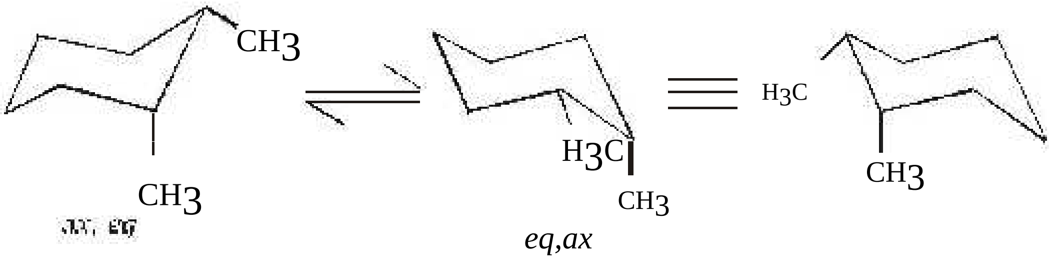


Trans-1,2-Dimethylcyclohexane

CIS FORM :

The cis isomer has two identical e,a- and a,e- conformations.

Consider cis-1,2- dimethyl cyclohexane, the two conformations are



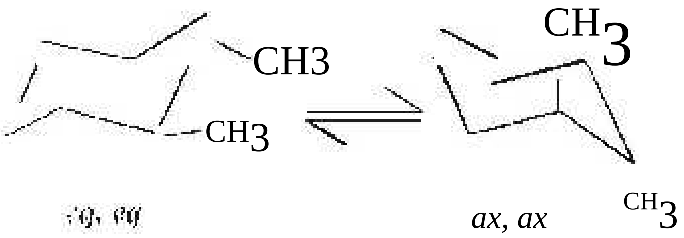
Cis - isomer

cis conformation has three butane gauche interactions.

TRANS FORM :

There are two possible chair conformations of trans-1,2- disubstituted cyclohexane. In one conformation, both the groups are axial; in the other both are equatorial.

The two chair conformations of 1,2- dimethyl cyclohexane are

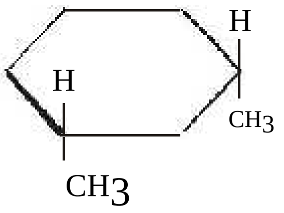


Trans-isomer (one enantiomer)

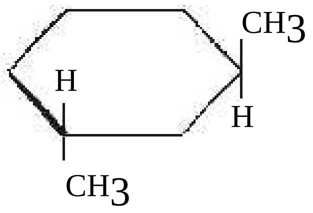
The diaxial form of trans-isomer in the case of 1,2- dimethyl cyclohexane has four butane gauche interactions whereas the diequatorial form has only one, that between the methyl groups. Thus, in the case of 1,2- dimethyl cyclohexane, the diequitorial trans isomer is more stable than the cis isomer by about 1.8 kcal/mole.

1.3 - disubstituted cyclohexane

1,3- disubstituted cyclohexane exist in diastereomeric cis and trans forms whose planar representation is as follows



Cis-1,3-Dimethylcyclohexane

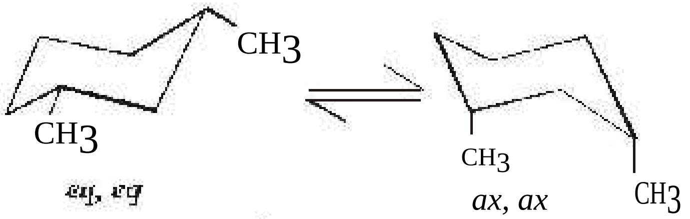


Trans-1,3-Dimethylcyclohexane

<u>CIS FORM :</u>

There are two possible conformations of CIS form. In one conformation, both the groups are axial whereas in the other, both are equatorial.

The two possible conformations of cis-1,3- dimethyl cyclohexane are given below.



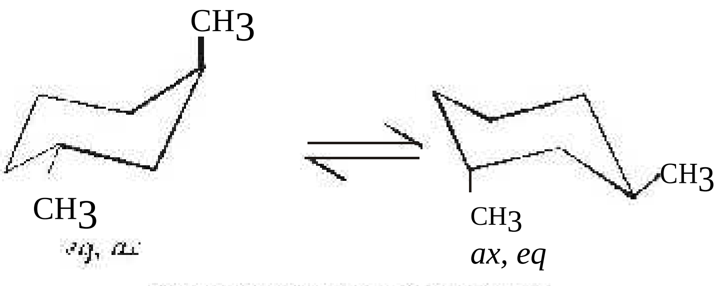
Cis-isomer

The diequatorial form of cis-1,3-dimethyl cyclohexane is more stable than the diaxial conformation by about 5.4 kcal/mole. Thus diequatorial form is most preferred one.

<u>TRANS FORM</u> :

The trans isomer has two identical e,a and a, e conformations.

Consider trans-1,3- dimethyl cyclohexane with identical conformations.



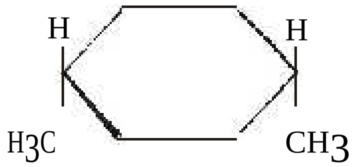
Trans-isomer (one enantiomer)

The trans isomer of 1,3- dimethyl cyclohexane has two butane gauche interactions.

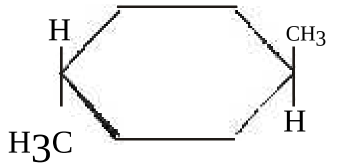
Thus the cis isomer is more stable by about 1.8 kcal/mole than the trans isomer.

1.4 disubstituted cyclohexane :

The planar representation of the cis-trans isomers of 1,4- disubstituted cyclohexane is as follows



Cis-1,4-Dimethylcyclohexane

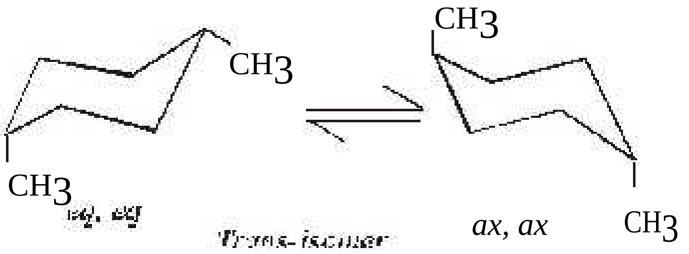


Trans-1,4-Dimethylcyclohexane

CIS FORM :

The cis isomer has two identical e,a and a,e conformation.

Consider the two identical conformations of cis-1,4- dimethyl cyclohexane.

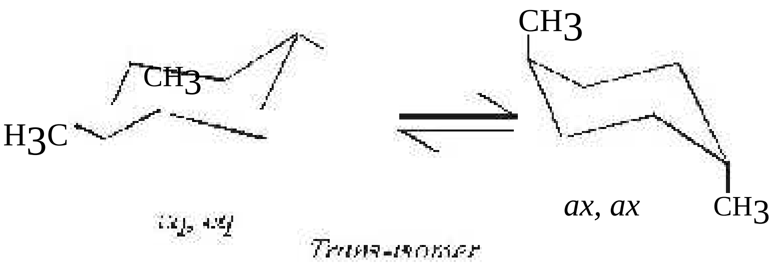


TRANS FORM :

There are two possible conformations of trans form of 1,4- disubstituted cyclohexane,

In one conformation both the groups are axial; in other both are equatorial.

Consider the two conformations of trans-1,4- dimethyl cyclohexane.



The diequatorial conformation is more stable than diaxial conformation and it represents the structure of at least 99% of the molecules at equilibrium. The diaxial conformation has four gauche interactions.

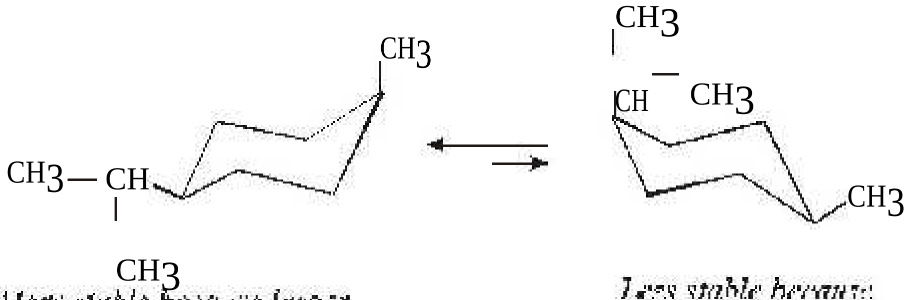
Conformations and Energies of the Dimethylcyclohexanes

Isomer	Conformation	No. of gauche interactions	Interaction kcal./mole
	e,a		
cis-1,2	⇅	3	2.7
	a,e		
	e,e	1	0.9
trans-1,2	⇅		
	a,a	4	3.6
	a,a	4	5.4
cis-1,3	⇅		
	e,e	0	0
	e,a		
trans-1,3	⇅	2	1.8
	a,e		
	e,a		
cis-1,4	⇅	2	1.8
	a,e		
	e,e	0	0
trans-1,4	⇅		
	a,a	4	3.6

PROBLEM :

a) Write structural formulas for the two chair conformations of cis-1-isopropyl-4-methyl cyclohexane. b) Are these two conformations equivalent ? c) If not, which would be more stable? d) Which would be the preferred conformation at equilibrium?

SOLUTION :



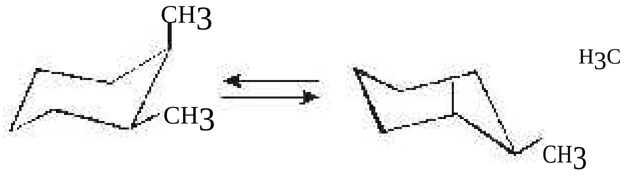
More stable because larger group is equatorial

Less stable because larger group is axial

PROBLEM :

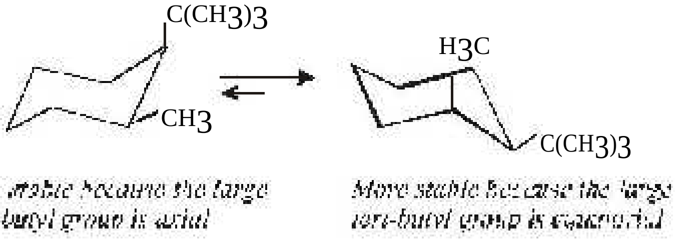
a) Write the two conformations of cis-1,2-dimethylcyclohexane. b) Would these two conformations have equal potential energy? c) What about the two conformations of cis-1-terta-butyl-2-methylcyclohexane? d) Would the two conformations of trans-1,2-dimethylcyclohexane have the same potential energy?

a)

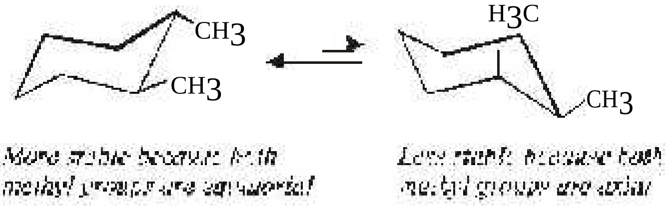


b) Yes

c)

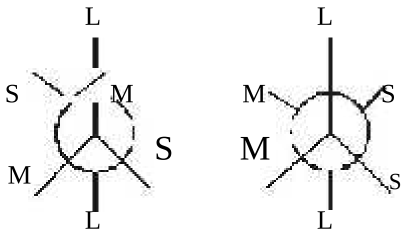


d)



CONFORMATIONAL EFFECTS ON STABILITY

The free energies of acyclic diastereoisomers usually differ. Generally meso forms are more stable than d l pairs. This is illustrated by considering meso isomer and its active diastereo isomer in their most stable conformations.



Meso Active

Most stable conformation of meso and active isomers

L denotes the largest substituent, M the medium sized substituent, and S the small substituent in the two isomers.

The gauche interactions observed in the meso form are 2L-
M+2L-S+2M-S+2L-M+2L-S.

The gauche interactions observed in the active form are
2M-S+2L-S+M-M+S-S.

The difference between the two forms is 2M-S-(M-M+S-S).

In general, the crossed steric interactions between two groups of unequal size are less than the sum of interactions between the groups of like size i.e.(M-M+S-S)> 2M-S, provided that interactions are purely steric in origin.

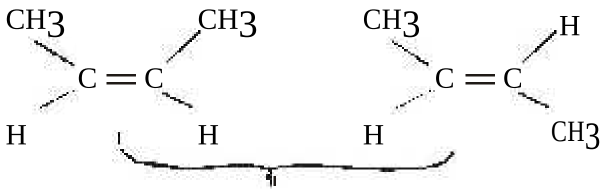
Thus it is follows from the above discussion that meso isomer is more stable than the active isomer.

GEOMETRICAL ISOMERISM

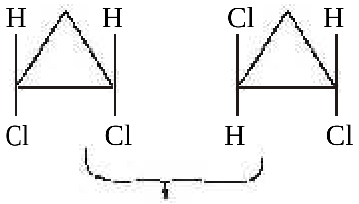
Geometrical isomerism is another type of stereoisomerism arising out of different spatial arrangement of groups attached to double bonds or rings in which stereoisomers are not readily interconvertible.

GEOMETRICAL ISOMERS :

Geometrical isomers are stereoisomers which differ in spatial arrangement of atoms or groups attached to double bonds or rings and this phenomenon is known as geometrical isomerism.



Geometrical isomers



Geometrical isomers

RESTRICTED ROTATION AND THE DOUBLE BOND

Substituents attached to the C = C can’t rotate freely since there is large energy barrier to rotation associated with the groups joined by a double bond.

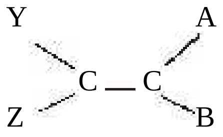
REASON FOR HINDERED ROTATION :

The C = C double bond consist of a π bond and a σ bond; it is difficult to rotate the substituents 180^0, since the π bond must be broken, a reaction which requires about 264 kJ/mol of energy. Such a rotation will seldom happen at room temperature. The inability of an olefinic double bond to rotate at room temperature is called hindered rotation.

GEOMETRIC ISOMERISM IN OLEFINS

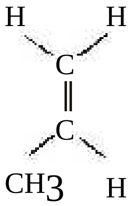
There is hindered rotation about any carbon-carbon double bond but not all show geometric isomerism. Geometric isomerism is only observed when there is a certain relationship among the groups attached to the doubly bonded carbons.

The requirement for geometric isomerism is shown in following olefin.

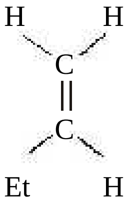


The requirement for geometric isomerism is A and B must be different groups, as must Y and Z; However, either A or B can be same as Y or Z.

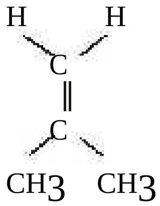
Thus, on this basis, we find that propylene, 1-butene and isobutylene do not show isomerism.



Propylene



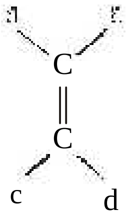
1-Butene



Isobutylene

No geometric isomerism

Geometric isomerism can’t exist if either carbon carries two identical groups.



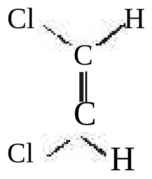
No isomerism

CIS-TRANS ISOMERS

The prefixes cis and trans work well to specify the geometric isomers.

• CIS ISOMER :

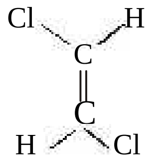
The geometric isomer in which similar groups are present on the same side of the double bond is refererd as cis isomer.



Cis-1,2-dichloroethene

• TRANS ISOMER :

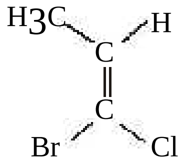
The geometric isomer in which similar groups are present on the opposite side of the double bond is referred as trans isomer.

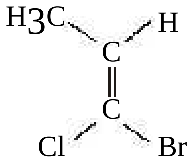


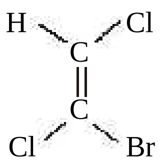
trans-1,2-dichloroethene

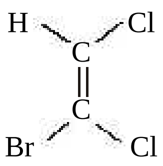
DRAWBACKS OF CIS-TRANS NOMENCLATURE

Cis-trans nomenclature fails to specify the configurations of following compounds.







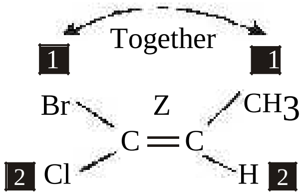


E-Z SYSTEM OF NOMENCLATURE

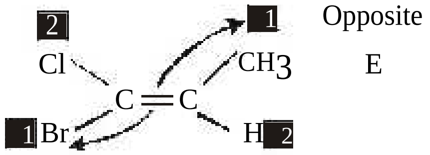
E-Z system of nomenclature for geometric isomers have been developed after Cahn-Ingold-Prelog convention for chiral carbon atoms.

In order to assign E-Z nomenclature to geometric isomer :

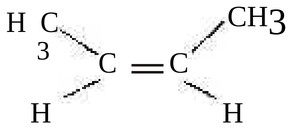
1) The two groups attached to each carbon of the double bond are arranged in order of priority.
2) If the two groups of highest priority are together on the same side of the double bond then the configuration is called as the Z isomer.
3) If the two groups of highest priority are on the opposite sides of the double bond then the configuration is called as the E isomer.



(Z)-1-bromo-1-chloropropene



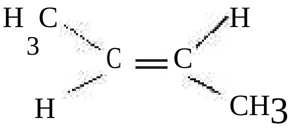
(E)-1-bromo-1-chloropropene



(Z)-2-Butene

$CH_3 > H$

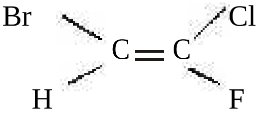
$CH_3 > H$



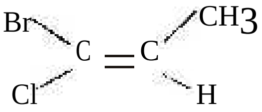
(E)-2-Butene

$CH_3 > F$

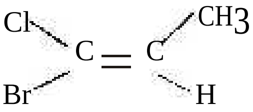
$CH_3 > H$



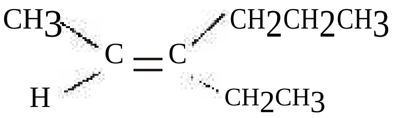
Z



(I)

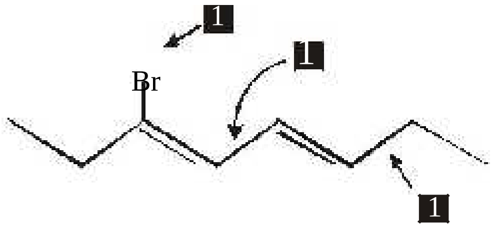


(II)



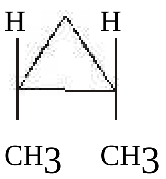
(III)

When an alkene has more than one double bond, the stereochemistry about each double bond can be specified with E and Z nomenclature.

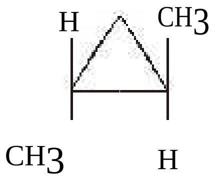


3-bromo-(3Z,5E)-octadiene

The E-Z nomenclature can also be used to designate cyclic compounds. When the two higher priority groups are on the same side of the ring then the compound is called as Z isomer and when these groups are on opposite sides of the ring, the compound is called as E isomer.

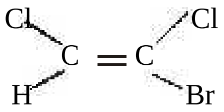


Z-1,2-dimethylcyclopropane

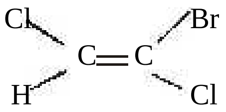


E-1,2-dimethylcyclopropane

The Z or E isomers are not necessarily always the ones which would be called cis or trans isomers respectively under the old nomenclature because E and Z nomenclature depends on the priorities of the groups attached to the unsaturated carbon atoms.



Cl > H
Br > Cl



(E)-1-Bromo-1,2-dichloroethene
(cis-1-bromo-1,2-dichloroethene)

(Z)-1-Bromo-1,2-dichloroethene
(trans-1-bromo-1,2-dichloroethene)

OLEFINS AND CHIRALITY

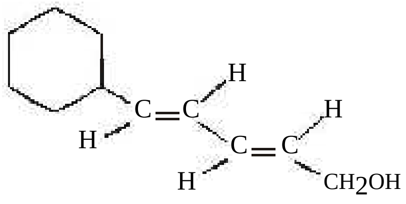
The compounds which show cis-trans isomerism with one double bond are not chiral because the four groups are in one plane.

When the compound contains odd number of cumulative double bond (three,five,etc) then orbital overlap causes the four groups to occupy one plane and hence cis-trans isomerism is observed in such compounds.

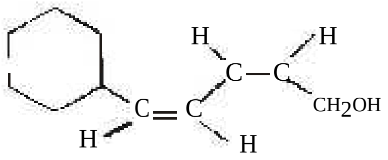
When the compound contains even number of cumulative double bonds and when the both sides are disymmetric then optical activity is possible in such compounds.

MULTIPLE DOUBLE BONDS :

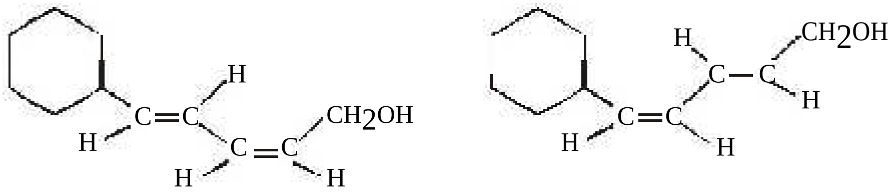
If a molecule has more than one double bond, each substituted properly so as to give geometrical isomerism, then the number of possible geometric isomers of it will be **2^n**. Thus four geometric isomers should exist if there are two such double bonds. The four isomers of 5-cyclohexyl-2,4-pentadien-1-0] are shown below; these are designated as trans-trans,cis-cis-,trans-cis,and cis-trans.



Trans-trans



Cis-cis



Trans-cis

Cis-trans

Geometric isomers of 5-cyclohexyl-2,4-pentadien-1-0 l

Vitamin A has five double bonds thus the total number of possible isomers is 2^5=32.

PROPERTIES OF GEOMETRICAL ISOMERS

A pair of geometric isomers can be referred as diastereomers. Thus as far as chemical and physical properties are concerned, geometric isomers show the same relationship to each other as do the other diastereomers.

Chemical Properties :

The chemical properties of geometrical isomers are not identical, however, since their structures are neither identical nor mirror images; they react with the same reagents, but at different rates.(Under certain conditions-especially in biological systems-geometrical isomers can very widely in their chemical behaviour).

Physical Properties :

Geometrical isomers have different physical properties such as melting points, boiling points, refractive indices, solubilities, densities etc.

They can be distinguished from each other on the basis of their physical properties. On the basis of the differences in physical properties they can be separated.

INTERCONVRSION OF GEOMETRICAL ISOMERS

The most straight forward way of interconverting geometrical isomers is by heating. The cis and trans isomers can be interconverted at higher temperatures or by irradiation with light of suitable wavelength.

The interconversion of isomers involves the breaking of the π bond of the carbon-carbon double bond followed by rotation about the carbon-carbon σ bond and subsequent reformation of a new π bond.

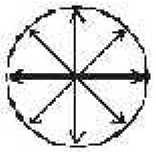
OPTICAL ISOMERISM

ORDINARY AND PLANE POLARIZED LIGHT

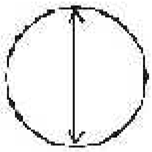
The nature of light is such that no purely verbal description can adeqately represent all of its properties. However one of the oldest and most successful attempts at a description of this phenomenon treats light as a form of energy which is transmitted in waves.

When an ordinary light is passed through a Nicol prism, it is converted into plane polarized light. Plane polarized light can be defined as the light whose waves vibrate in one direction (plane).

When ordinary light from a source with an infinite number of planes is passed through a Nicol prism, only a single plane is allowed to emerge.



Ordinary light



Plane polarized light

OPTICAL ACTIVITY

Certain substances have ability to rotate the plane of polarized light are called as optically active compounds and this phenomenon of rotating the plane of polarized light is called optically activity.

If the substance does not rotate the plane of polarized light, it is considered to be optically inactive.

DEXTRO AND LAEVO ROTATORY SUBSTANCES

Optically active compound may rotate the plane of polarized light to the right or to the left.

The substances which rotate the plane of plane polarized light to the right are called as dextrorotatory and are designated as d or (+).

The substances which rotate the plane of plane polarized light to the left are called as laevorotatory and are designated as l (–).

SPECIFIC ROTATION

The presence of optical activity, its direction and extent of rotation is measured by an instrument called polarimeter.

The optical activity of a compound is reported as its specific rotation.

OPTICAL ROTATION :

If polarized light is allowed to pass through a solution of an optically active compound then the single plane of polarized light will be rotated. The rotated light is then allowed to pass through a second prism. This prism is rotated until the plane of light is again vertical. The angle that the second prism must be moved to bring the light back to vertical is called as optical rotation(α).

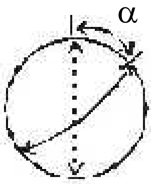


Diagram : Rotation of a plane of polarized light by an optically active organic molecule. The dotted line indicates the original plane of light and α the degree of rotation from original plane.

Optical rotation is a function of concentration,sample thickness, temperature,wavelength of polarised light etc.

SPECIFIC ROTATION:-[α **]** : Specific rotation is the number of degrees of rotation of the plane polarized light to the wavelength of the sodium D line (5890 A^0) when passed through a solution of concentration 1gm/ml in a 1-decimeter tube.

Optical rotation is usually recorded in terms of specific rotation.

The equation to determine specific rotation [α] is

$$[\alpha] = \frac{\alpha}{C.l}$$

Where [α]=specific rotation.

α = observed rotation.

C = the concentration of the solution in gms/ml of solution. l

= the length of the tube in decimeters (1dm=10cm).

The specific rotation depends on the temperature and the wavelength of light that is employed and hence specific rotations are reported so as to incorporate these quantities. A specific rotation might be given as follows:

$$[\alpha]^{25}_{0} = +312.^\circ$$

This means that the D line of a sodium lamp was used for the light, that a temperature of 25^{0}C was maintained and that a sample containing 1.00g/ml of the optically active substance, in a 1 dm tube, produced a rotation of 3.12^0 in a clockwise direction.

The specific rotation is considered as another physical constant like melting point, boiling point, or density.

PROBLEMS ON SPECIFIC ROTATION

1) The concentration of cholesterol dissolved in $CHCl_3$ is 6.15 gms per 100 ml. of solution.

A) A portion of this solution in a 5 cm polarimeter tube causes an observed rotation of -1.2^0. Calculate the specific rotation of cholesterol.

B) Predict the observed rotation if the same solution were placed in a 10 cm. tube. Solution :

A] -39^0

B] -2.4°

2) An aqueous solution of pure compound of concentration 0.10 g/ml had observed rotation -30^0 in a 1.0-dm tube at 589.6 nm and 25^{0}C. Determine the specific rotation. Solution : -300^0

CAUSE OF OPTICAL ACTIVITY

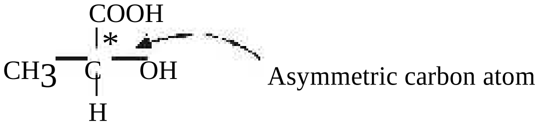
1] The theory of Van’t Hoff and Le Bel:-

By 1874,over a dozen examples of optically active organic molecules were known. In every case at least one carbon in the molecule had four different groups attached to it.

Van’t Haff and Le Bel related the phenomenon of optical rotaton to the presence of asymmetrically substituted carbon atoms (chiral carbon atoms) in the molecules.

Chiral Carbon:-

If the carbon atom is attached to four different groups or atoms, it is called chiral carbon.



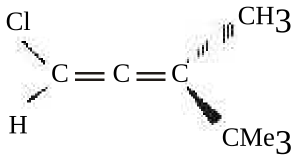
$$CH_3-\overset{\text{COOH}}{\underset{\text{H}}{\overset{|*}{\underset{|}{C}}}}-OH$$

Asymmetric carbon atom

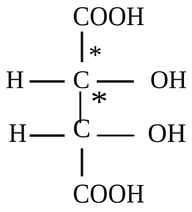
In the case of organic compounds, the presence of chiral carbon is most probable cause of optical activity.

They also realised that there could exist optically active compounds having no asymmetric atoms.

They also observed that many compounds were optically inactive though they contained two or more asymmetric carbon atoms.



Optically active though doesnt contains asymmetric carbon atoms



Optically inactive though contains two asymmetric carbon atoms

Thus the concept of asymmetric carbon atoms could not explain satisfactorily the cause of optical activity.

The theory of Van’t Hoff and Le Bel States that,for a molecule or a crystal to be optically active,it’s mirror image must be non superimposable. Whereas a molecule with superimposable mirror image is optically inactive.

NON SUPERIMPOSABLE MIRROR IMAGE

An object or molecule or crystal can be superimposable on its mirror image when it has any one of the following elements of symmetry :

1)Plane of Symmetry

2)Centre of Symmetry

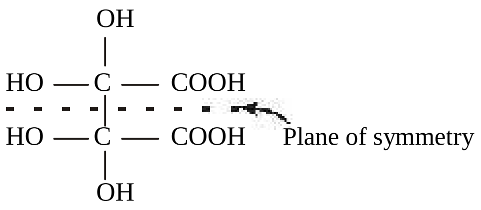
3)Alternating axis of Symmetry

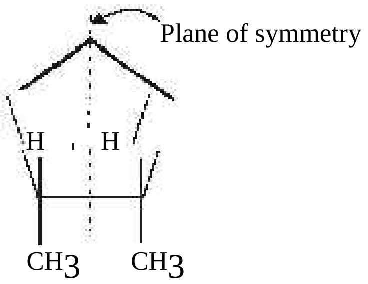
1) Plane of Symmetry :

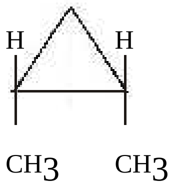
A molecule is said to possess as plane of symmetry when an imaginary plane passing through the centre of molecule can divide it into two parts such that one is the exact mirror image of the other.

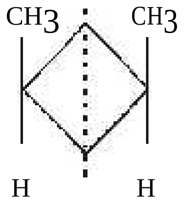
If a molecule has plane of symmetry then the molecule and its mirror image are superimposable and hence molecule is optically inactive or achiral.

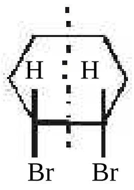
Few molecules with plane of symmetry are shown below :

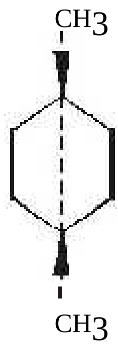












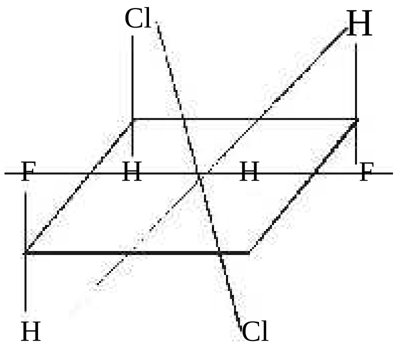
2) Centre of Symmetry :

It is an imaginary point in the molecule from which the similar groups are at equidistant.

Generally centre of symmetry is observed in the even membered rings.

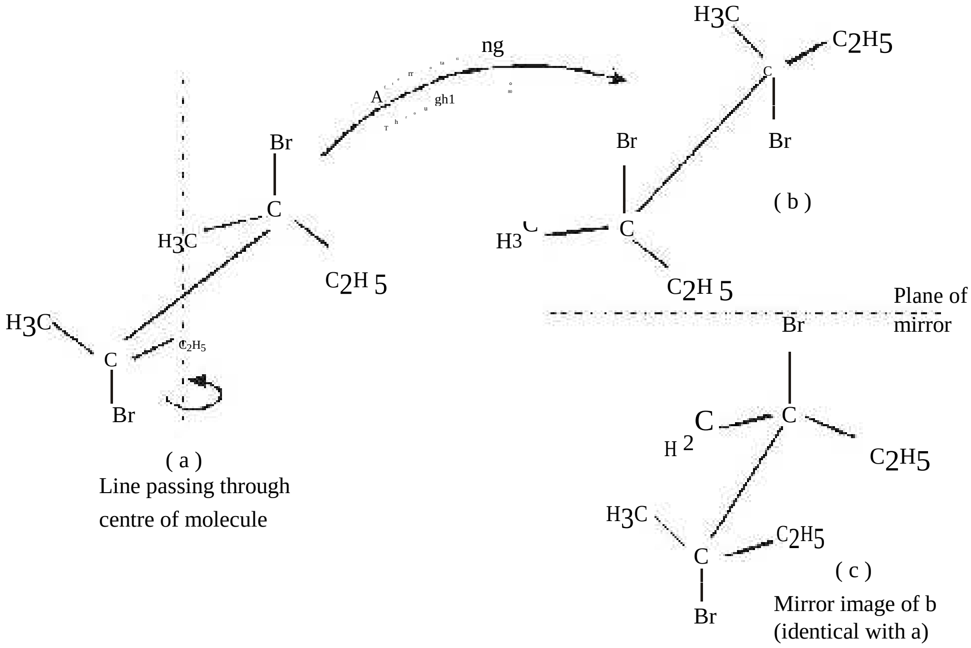
The compounds having centre of symmetry are optically inactive or achiral.

Following isomer of 1,3-dichloro -2,4- difluoro cyclo butane has a centre of Symmetry:



3) Alternating axis of Symmetry :-

It is a line about which the crystal may be rotated so that it represents the same appearance more than once during a complete revolution.



Alternating axis of symmetry
Many compounds which posses alternating axis of symmetry are achiral.

A molecule is said to have alternating axis symmetry,if an identical structure results when it is rotated around the axis by an angle of $2\pi/n$ (n=number of fold of Symmetry) and then reflected across the plane perpendicular to the axis. For example, 3, 4-dibromo-3, 4-dimethyl hexane has alternating axis of symmetry.

Many compounds which possess alternating axis of symmetry are achiral.

Thus a molecule that has a plane of symmetry,a center of symmetry and an alternating axis of symmetry is superimposable on its mirror image and is optically inactive and a molecule that has no element of symmetry is not superimposable with its mirror image and is optically active.

CONDITION OF OPTICAL ACTIVITY

A chiral molecule has a center of chirality within it and it consist of a suitable atom substituted in a way so as to be non superimposable on its mirror image. Thus chirality is the property of a molecule of being non superimposable on its mirror image. The most common feature which gives chirality to the molecule is a chiral centre but not always. We can say that many but not all molecules that contain chiral centre are chiral and many but not all chiral molecules contain chiral centre.

Chirality is necessary and sufficient condition for exhibiting optical activity.

The optical activity of sodium bromate, sodium iodate, quartz is lost when their lattice structure is destroyed by melting or dissolving in water. This indicates that chirality is in the lattice structure.

Many organic compounds show optical activity even in solid, liquid, vapour or in solution form. This indicates that chirality is inherent in the molecule. Hence, they show optical activity even if their physical state is changed. That is they have molecular chirality.

ASYMMETRIC AND DISSYMMETRIC MOLECULES

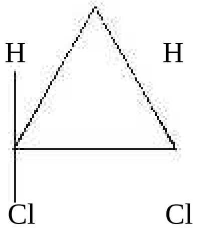
A disymmetric molecule lacks those elements of symmetry which preclude a mirror image relationship, whereas asymmetric molecule has no elements of symmetry at all.

Disymmetric and asymmetric molecules are usually optically active.

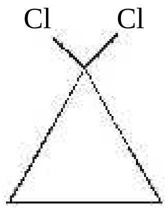
(A molecule having none of the elements of symmetry which preclude a mirror image relationship or having only an axis of symmetry is not superimposable with its mirror image and is called disymmetric.)

DETERMINING WHETHER A MOLECULE IS CHIRAL OR NOT

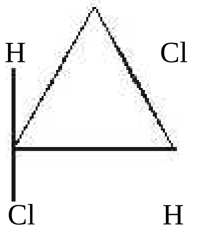
A foolproof method to determine whether a molecule is chiral or not, is to construct molecular models of the molecule and its mirror image relationship and look if these pass the test of superimposition. The chiral molecules are those in which object is non super imposable on its mirror image.



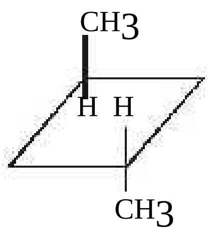
Achiral or Meso compound because contains plane of symmetry



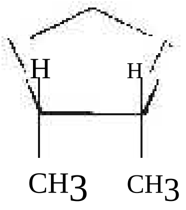
Achiral because contains plane of symmetry



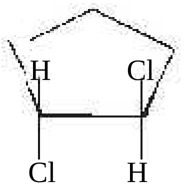
Chiral because has non superimposible mirror image



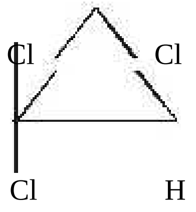
Achiral because has plane of symmetry.



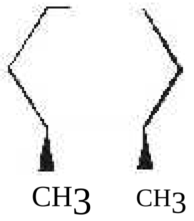
Achiral because has plane of symmetry



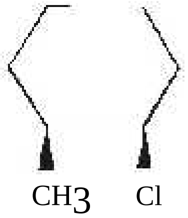
Chiral because has non superimposible mirror image



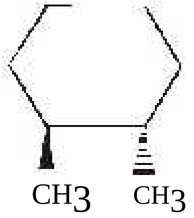
Chiral because has non superimposable mirror image



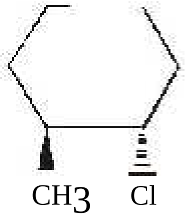
Achiral (Plane of symmetry)



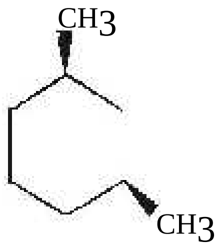
Chiral



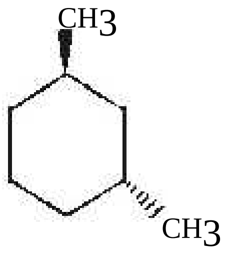
Chiral



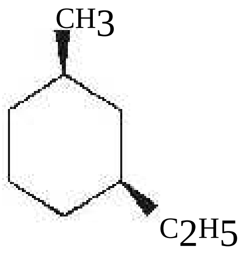
Chiral



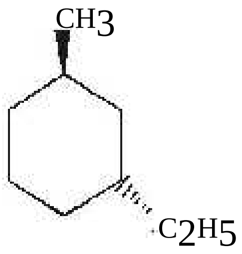
Achiral (Plane of symmetry)



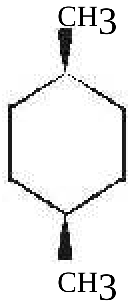
Chiral



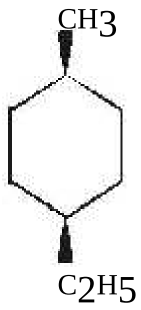
Chiral



Chiral



Achiral



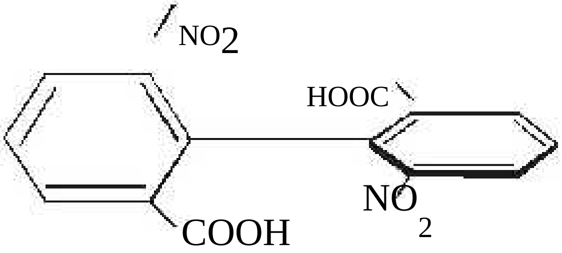
Achiral

CHIRAL COMPOUND WITHOUT CHIRAL CENTRE

The presence or absence of chiral centre is no criteria for chirality. Many compounds are chiral though they do not contain chiral centre. Some of such compounds are listed below :

1) BIPHENYLS :

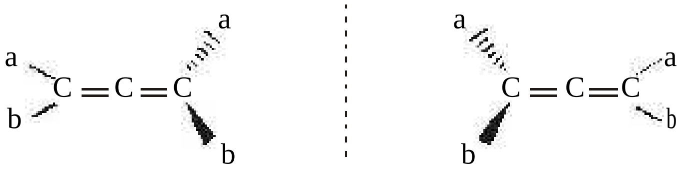
Properly substituted biphenyls are chiral. Their chirality is due to restricted rotation about the central bond (atropisomerism). Biphenyls with heavy groups in the ortho positions when substituted suitably can’t rotate freely about the central bond because of steric hinerance. In biphenyls, two rings are in perpendicular planes. Biphenyls are chiral provided both sides are dissymmetric. Introduction of bulky o-substitutents would prevent free rotation of the nuclei about the coaxis and at the same time produce a coaxial twist. Hence the two benzene rings cannot be coplanar due to impingement of the o-substituents and thus biphenyls become dissymmetric.



2) ALLENES :

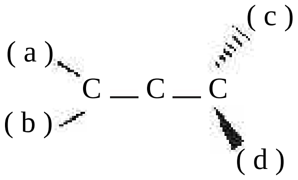
Suitably substituted allenes are chiral provided both the sides are dissymmetric.

Following types of allenes will be dissymmetric provided that a≠ b.



Enantiomeric allenes

Molecular dissymmetry is possible because the groups at one end of the allene molecule lie in a plane at right angles to those at the other end.

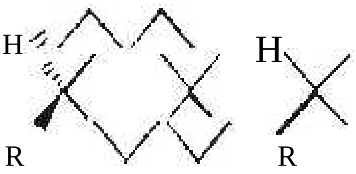


3) SPIRANES :

Suitably substituted spiranes are chiral provided both sides are dissymmetric.

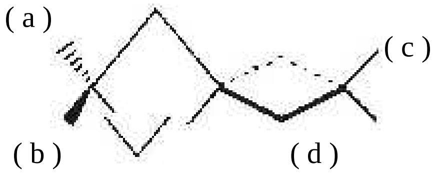
In spiranes, the two rings are orthogonal as a consequence,groups attached to the ends of the system lie in planes which are mutually perpendicular.

Dissymmetric spiranes are obtained by attaching unequal substituents at each end of the system.



H ≠ R

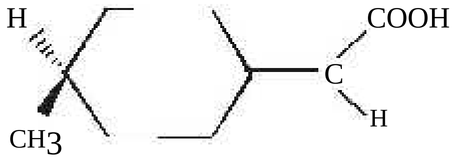
dissymetric spiranes



4) METHYLENE CYCLOALKANES :

Substituted methylene cycloalkanes are chiral provided both sides are dissymmetric.

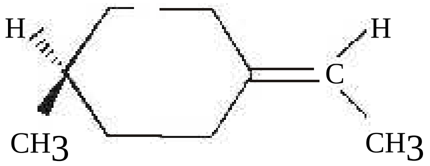
4-Methyl cyclohexyliden acetic acid was the first chiral compound of this type that was reported.

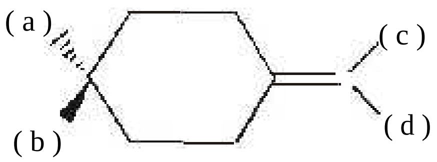


4-Methyl cyclohexyliden acetic acid

This substituted methylenecyclohexane is dissymmetric because the groups attached to the double bond lie in a plane at right angle to those attached to the 4-position of ring.

Another example of dissymmetric methylene cyclohexane is show below:-

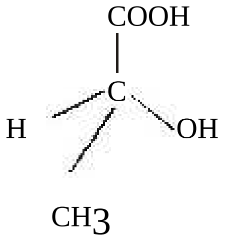




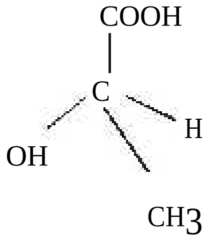
OPTICAL ISOMERS

The stereoisomers which are otherwise same but differ in their action towards the plane polarised light are called optical isomers and this phenomenon is called optical isomerism.

Eg:- d-lactic acid and] - Lactic acid are optical isomers.



d-lactic acid
[α] = +2.24°



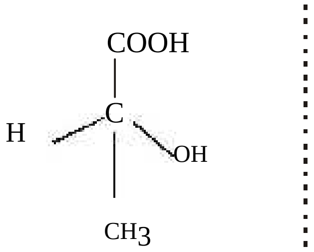
] - lactic acid
[α] = –2.24°

Similarly d-tartaric acid and] -tartaric acid are optical isomers.

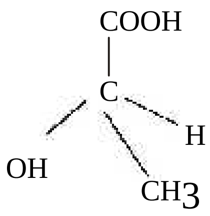
ENANTIOMERS

Stereoisomers that are mirror images of each other are called as enantiomers.

Eg:- d-lactic and] -lactic acid are enantiomers.



d-lactic acid



] - lactic acid

PROPERTIES OF ENANTIOMERS

1)Enantiomers have identical physical properties such as boiling point, refractive index, relative density etc but differ each other in their action on plane polarized light. If one of the enantiomer rotate the plane of plane polarized light to the right, the other will rotate to the left. However the extent of rotation is same.

Eg- The properties of two 2-methyl-1-butanols are shown below :

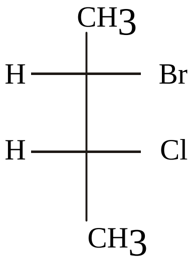
Property	**(+)-2-Methyl-1-butanol**	**(–)-2-Methyl-1-butanol**
Specific rotation	+5.90°	–5.90°
Boiling point	128.9°C	128.9°C
Relative density	0.8193	0.8193
Refractive index	1.4107	1.4107

2) Enantiomers have same chemical properties except the fact that they differ in the rate of reaction with the other optically active reagents (chiral probes).

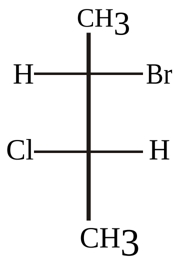
DIASTEREOISOMERS

Stereoisomers that are not mirror images of each other are called diastereoisomers.

e.g. :



(I)



(II)

(I) and (II) are diastereomers.

PROPERTIES OF DIASTEREOMERS

1)Diastereoisomers have different physical properties :

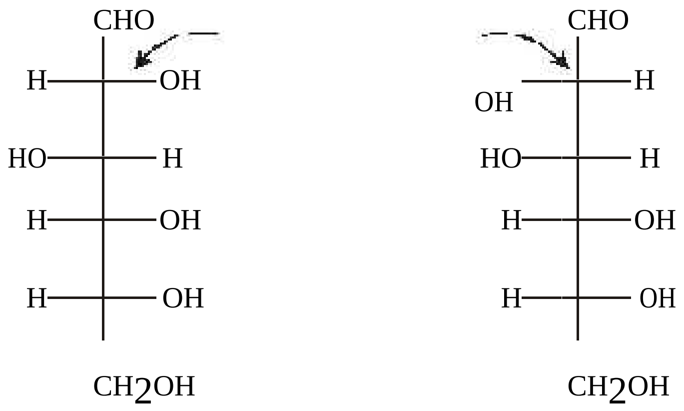
Diastereomers have different physical properties like melting points,boiling points,solubilities in a given solvent,densities,refractive indexes etc. Diastereomers differ in specific rotaton;they may have the same or opposite signs of rotation, or some may be inactive.

2)Diastereoisomers have different chemical properties.

EPIMERS AND ANOMERS

Several sugars are closely related to each other and differ only by the stereochemistry at a single carbon atom. Sugars which differ only by the stereochemistry at a single carbon atom are called epimers. The carbon atom where the two sugars differ is generally stated and when it is not stated it is assumed to be C-2.

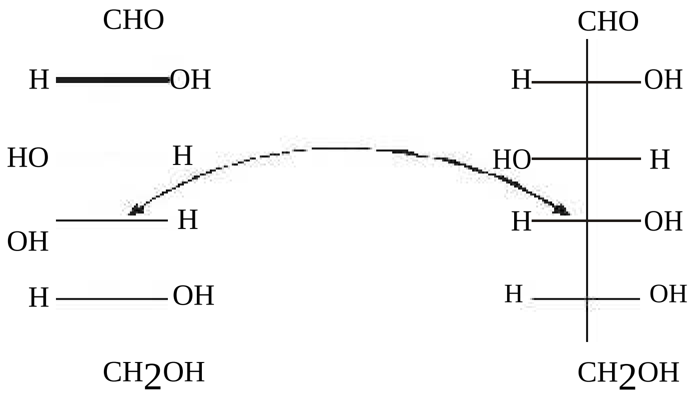
Eg- D(+)- glucose and D(+) – mannose are C-2 epimers.



D (+) - glucose D (+) – mannose

C–2 Epimers

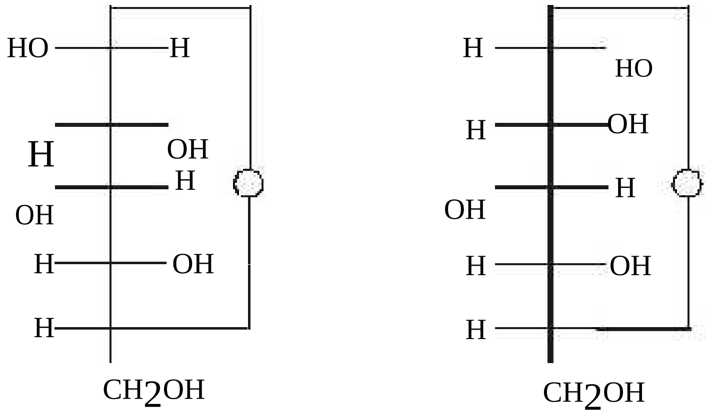
Similarly D-glucose and D-Galactose are C-4 epimers.



C-4 Epimers

Anomers :

Glucose and other hexoses exist as an equilibrium mixture with their cyclic hemiacetal isomers in which the latter strongly predominates. The carbonyl carbon turns into a new stereocenter on cylcization. Thus glucose has two cyclic forms which differ only in the stereochemistry at C-1 and the hemiacetal carbon is called as the anomeric carbon. Such isomers are called as anomers. The two anomers are commonly differentiated by the Greek letters α and β and thus in the case of glucose these diastereomers are termed α -D-glucose and β -D- glucose.



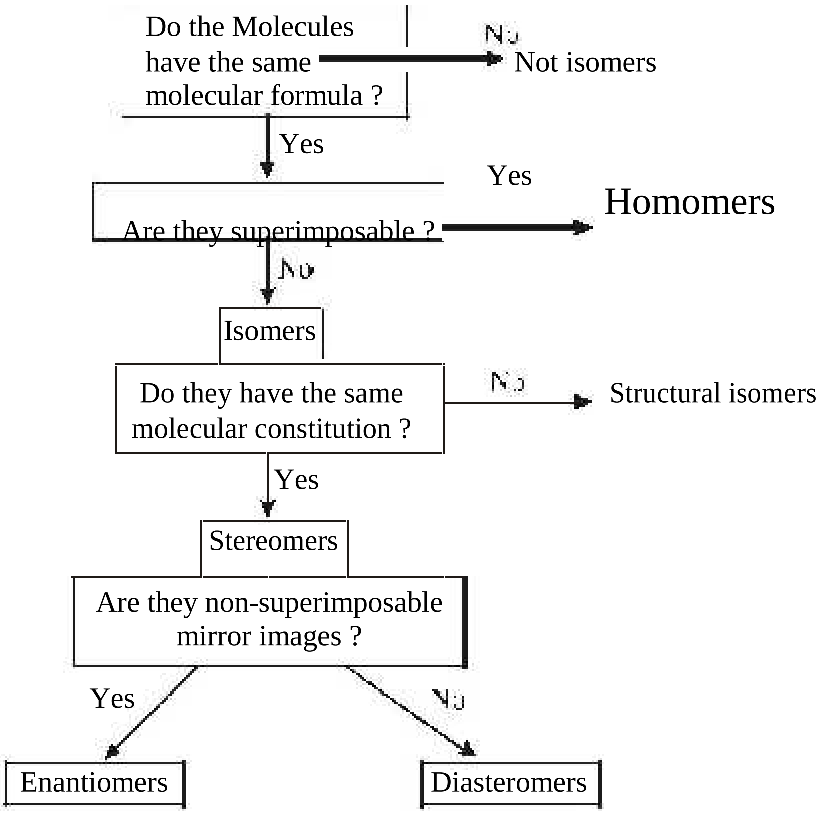
β -D-Glucose α -D-Glucose

Anomers

STUDY AID

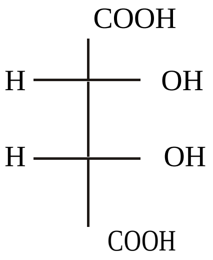
An approach to the classification of Isomers :

We can classify isomers by asking and answering a series of a questions :

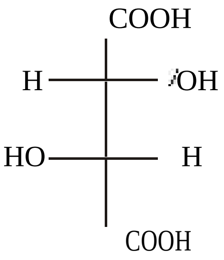


SOME SOLVED PROBLEMS

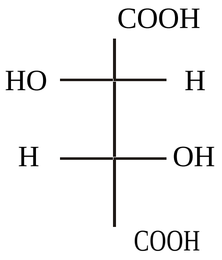
1) Find out the enantiomeric pair amongst following compounds.



(A)



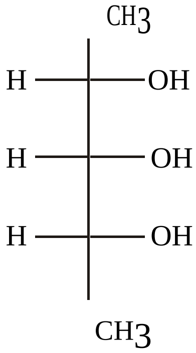
(B)



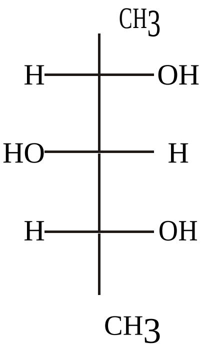
(C)

Solution : B and C are enantiomeric pair.

2) Find out relationship between i and ii.



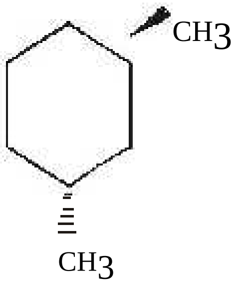
(i)



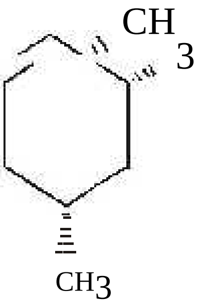
(ii)

Solution : i and ii are diastereomers.

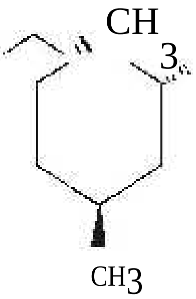
3) Choose the correct relation of (ii) and (iii) with (i).



(i)



(ii)

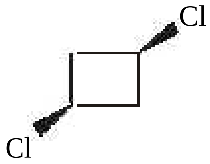


(iii)

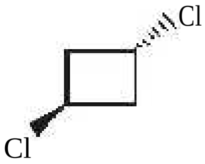
Solution : Compound (ii) is a diastereomer of (i) whereas (iii) is enantiomer of (i).

4) Identify the relationship between following pairs of structures.

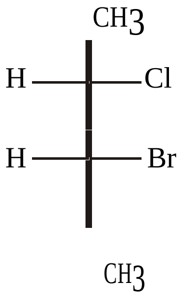
a)



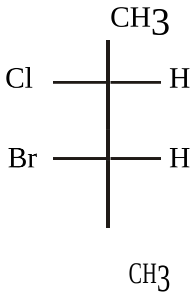
And



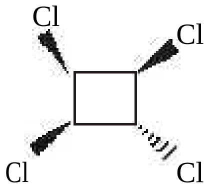
b)



And



c)



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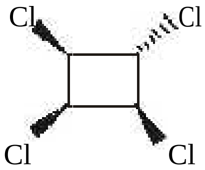

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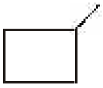

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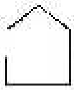

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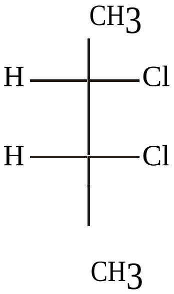

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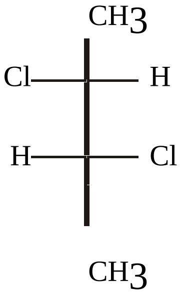


Solution :

a) Diastereomers

b) Enantiomers

c) Same

d) Constitutional isomers

e) Diastereomers

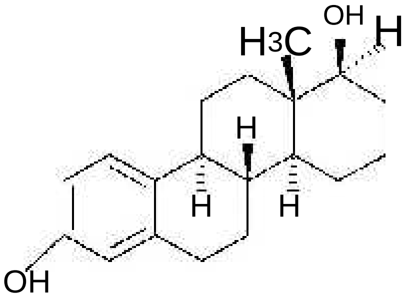
DETERMINING NUMBER OF STEREOISOMERS

According to van't Hoff's rule, the maximum number of optical isomers for a molecule having plural centres of asymmetry is 2^n, where n is the number of asymmetric carbons.

Eg- D-Glucose whose structure can be abbreviated as $HOCH_2 – (CHOH)_4 – CHO$ has four asymmetric carbon atoms and therefore there are 2^4 or 16 isomers of this structure. One of these is D-Glucose and one of the remaining 15 is its mirror image,L-glucose and remaining 14 isomers of D-Glucose are diastereomers.

SOLVED EXAMPLES

1)How many stereoisomers are possible for cholesterol.

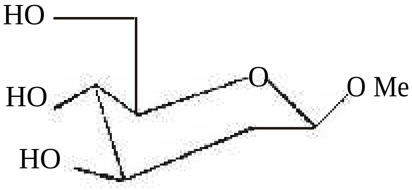


Solution : Number of stereoisomers $=2^8=256$.

2)Menthol has three asymmetric centres. How many epimers and diastereoisomers are possible for it?

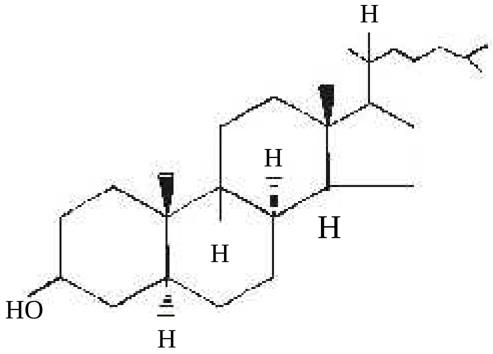
Solution : 3 Epimers and 6 diastereoisomers.

3)Methyl-D-glusoside has five asymmetric centres how many epimers(E) and diastereoisomer(D) are possible for this molecule?



Solution : 5 Epimers and 30 Diastereoisomers.

4)Natural cholesterol on hydrogenation affords cholestanol as one of the products



Cholestanol

As this compound has nine asymmetric centres, it can exists as 2^9 i.e. 512 possible isomers. The number of diastereomers of cholestanol are Solution : 510.

RACEMIC MIXTURE

Racemic modification or mixture is defined as a mixture containing equimolar quantities of a pair of enantiomers. It is represented as, (±) or dl.

When a pair of enantiomers is mixed in equal molar proportion, the resulting mixture do not show optical activity and it is called racemic mixture.

The optical inactivity is because, the right hand rotation (+) by dextro component is nullified by equal left hand rotation (–) by laevo component, since they are present in equal proportion. This type of compensation is called external compensation.

RESOLUTION

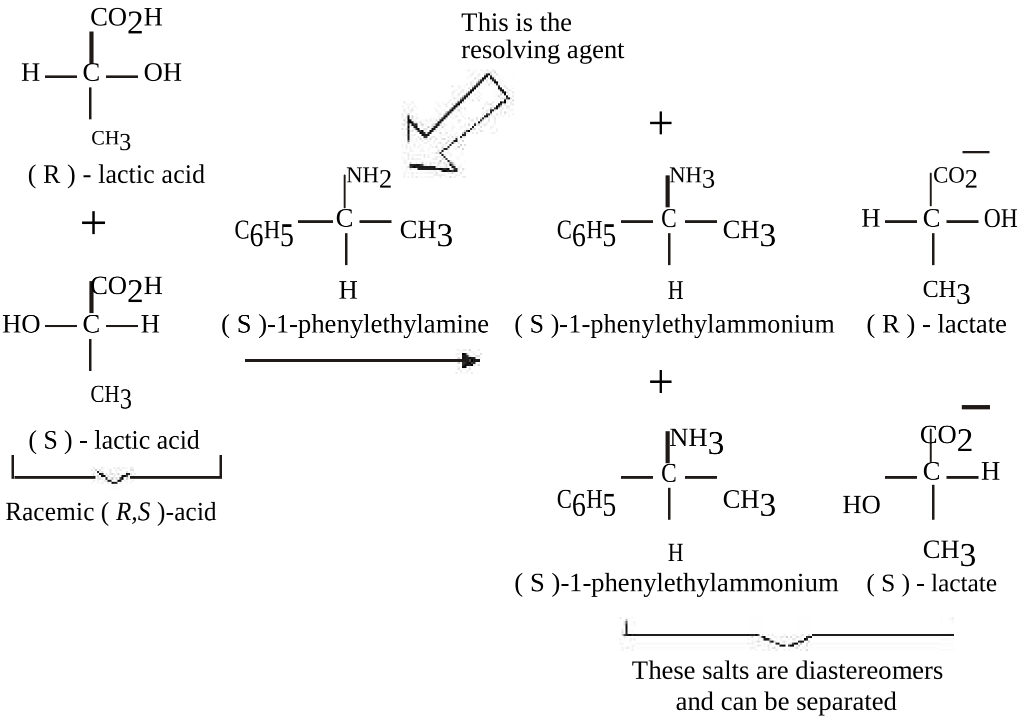
The separation of enantiomers from a racemic mixture is called as resolution. Since enantiomers have almost similar physical and chemical properties, it is difficult to separate them from racemic mixture.

METHODS OF RESOLUTION

Various methods of resolution are discussed below.

1) USING CHIRAL PROBE :

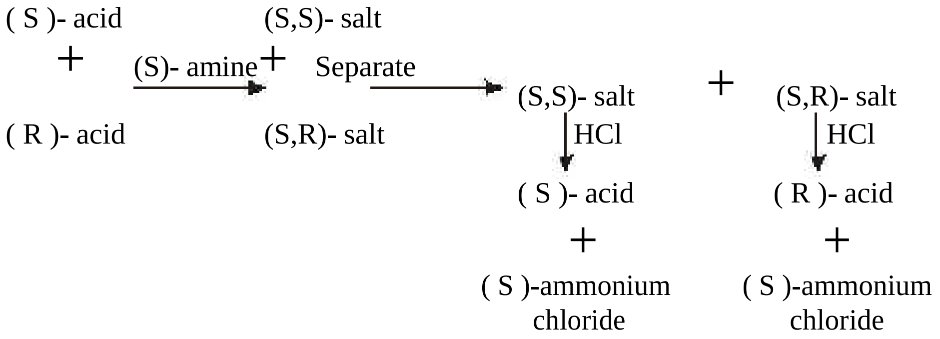
Resolution is carried out by converting the mixture of enantiomers (recemic mixture) into a mixture of diastereomers by using chiral compound called as resolving agent. Since the resulting products will be diastereomeric, these can be separated. Separated diastereomers are converted back to enantiomers.



a) Resolution of Acids and Bases :

Acid-base reactions are often used to resolve racemic acids and bases.

A racemic acid reacts with optically active base to form diastereomeric salts which can be separated. Separated diastereomeric salts are then converted back into enantiomers.

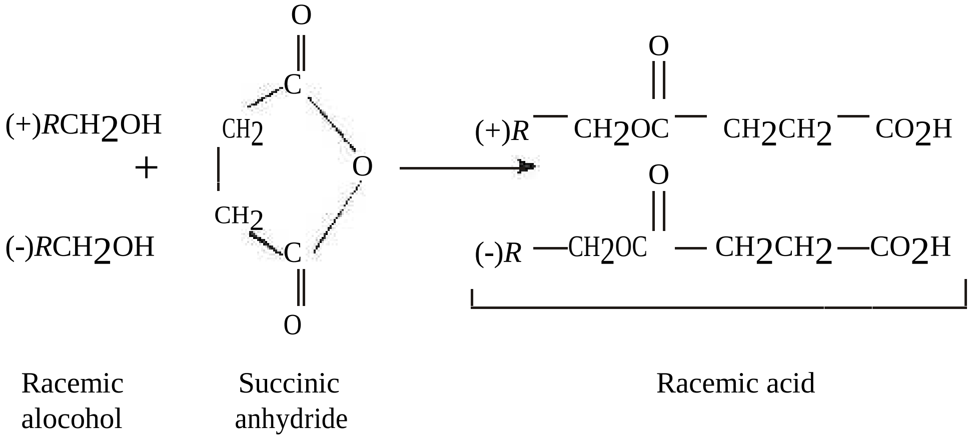


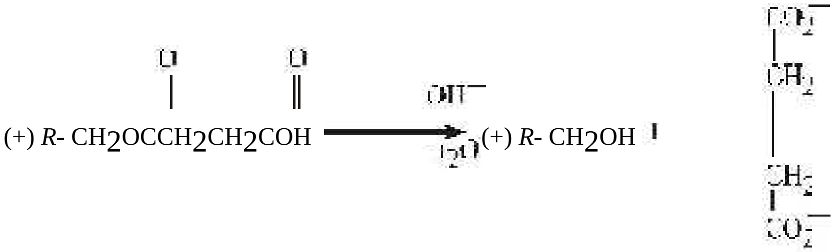
The resolution of the racemic form of an organic acid

Similaraly, a racemic base reacts with optically active acid to form diastereomeric salts which can be separated. Separated diastereomeric salts are then converted back into enantiomers by conventional methods.

b) Resolution of other compounds :

Racemic compounds which are neither acids nor bases are often resolved by first attaching an acidic handle. Consider an example of racemic alcohol. A racemic alcohol reacts with cyclic anhydride to form both an ester and an acid. The racemic acid thus produced is separated via diastereomeric salts and converted back to the enantiomeric acids. The acidic handle is then removed by hydrolysis of the ester group and the separated alcohol enantiomers are obtained.





Various naturally occuring alkaloids (optically active) are available for the resolution of racemic acids. Common examples are strychnine, brucine, morphine, ephedrine, cinchonine, quinine, quinidine. One of the most important synthetic basic resolving agent is α -phenyl ethyl amine. Among the acids which are used in the resolution of racemic bases are camphoric acid, camphor-10-sulphonic acid, methyoxy acetic acid and pyrrolidine-5-carboxylic acid

2) CHROMATOGRAPHIC TECHNIQUES

The resolution by using chromatography depends on the difference in the rates of reaction of the two enantiomers with the chiral probe material on the column packing.

The method involves preparation of column of solid optically active compounds like tartaric acid, sucrose etc. The enantiomeric components of the racemic mixture form diastereomeric complexes with the chiral material used on column. (one enantiomer passes through the chromatographic column faster than the other due to varied rate with the chiral material).

The racemic mandelic acid has been resolved by column chromatography on starch.

Racemic p- phenylenebisiminocamphor has been resolved on lactose column.

Racemic Troger’s base has been resolved on lactose column.

3) ENZYMATIC RESOLUTION

Enzymes are complex optically active protenoid catalysts which are produced by living organism. A fundamental property of enzymatic reactions is high degree of stereoselectivity due to the asymmetric nature of enzymes. Enzymes show different rates of reaction with the two enantiomers. For example, a certain bacterium digest only one enantiomer and not the other. This method has limiting value since one of the enantiomer is destroyed during resolution.

E.g. : Penicillium glaucum destroys ammonium (+) tartarate more rapidly than the (-) tartarate in a dilute solution of ammonium (±) tartartes.

Racemic ∝-amino acids are resolved by using swine kidney acylase.

4) MECHANICAL SEPARATION

Enantiomers of very few substances can be crystallised into asymmetric crystals.

Since the appearance of these crystals are different, a trained crystallographer can separate them with tweezers.

The method was first time used by Pasteur. The mechanical separation is an attractive method for effective resolution. However, difficulties arise due to the fact that very few substances can be crystallised into asymmetric crystals. Sodium ammonium tartarate is one of this rare group of compounds, and even in this case the crystalization must be carried out below 27^0C.

5) DIFFERENTIAL REACTIVITY

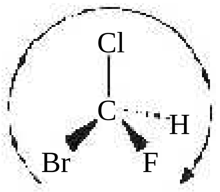
Since enantiomers react with chiral compounds at different rates, it may be possible to effect a partial separation by stopping the reaction before it goes to completion.

R & S NOMENCLATURE

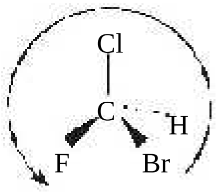
The R, S convention is governed by three rules which are quite logical and easy to remember; these rules set a priority sequence for the four substituents, A, B, D, E, about an asymmetric carbon.

Rule-1 : The priorities assigned to the four substituents on an asymmetric carbon depend upon the atomic number of the attached atom. Greater the atomic number of atom, greater is the priority. [For example, the halogens have the priority I > Br > Cl > F ; other obvious priorities would be Cl > O > N > C.]

Let us now consider the configurational assignment for bromochlorofluoromethane, which has the atomic priorities Br > Cl > F > H. Visualize the molecule in such a way that the atom with lowest priority projects behind the paper ; the remaining three substituents are arranged in order of priority either clockwise or counterclockwise as follows



Clockwise
(R) configuration

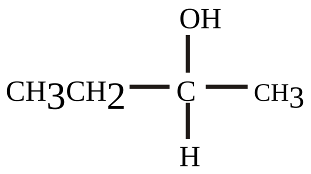


Counterclockwise
(S) configuration

The clockwise direction is assigned the R configuration (Latin: rectus, right) and the counterclockwise direction is assigned the S configuration (Latin: sinister, left).

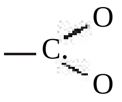
Rule–2 : When two or more substiuents on the asymmetric carbon have atoms with the same atomic number, then Rule 2 applies; precedence is given to the substituent with the highest atomic number in the second atom from the asymmetric center.

For example, with sec-butyl alcohol, two of the adjacent atoms are C. However, the C of $-CH_2-CH_3$ is bonded to C, whereas the C of $-CH_3$ is bonded only to H; therefore, $-CH_2-CH_3$ takes priority order for sec-buty1 alcohol is $OH > C_2H_5 > CH_3 > H$.



$CH_3CH_2-C(OH)(H)-CH_3$

sec-Butyl alcohol

Rule–3 : If the second atom from the asymmetric center has an identical atomic number in two groups, then the total of the atomic numbers attached to the first carbon are considered. With this rule a double bond, -C=A, is treated as $-CA_2$; for example, -C=O would be treated as 

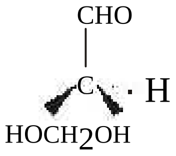
Similarly a triple bond, $C \equiv A$, would be treated as $-CA_3$.

With this rule, the carboxy1 (-COOH) with combined atomic numbers of 48 would take precedence over an aldehyde (-CH=O) with combined atomic numbers of 33; similarly -CH=O would take precedence over $-CH_2OH$ (combined atomic numbers = 18). Thus in the case of glyceraldehyde, the priorities are

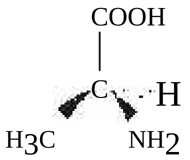
$$-OH > -CH{=}O > CH_2OH > H.$$

The phenyl substituent is treated as $-C-C_3$ with combined atomic numbers of 36; thus phenyl would take priority over isopropy1, $-CH(CH_3)_2$, with combined atomic numbers of 25.

By applying these rules to some common substituents, one obtains the following sequence (group of highest priority first): I, Br, Cl, SO_2R, SOR, SR, SH, F, OCOR, OR, OH, NO_2, NHCOR, NR_2, NHR, NH_2, CCI_3, COCI, CO_2R, $CONH_2$, COR, CHO, CR_2OH, CHOHR, CH_2OH, CR_3, C_6H_5, CHR_2, CH_2R, CH_3, D, H.

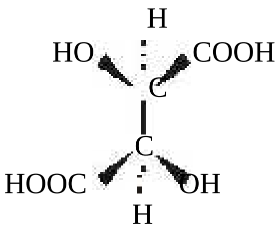


R-Glyceraldehyde

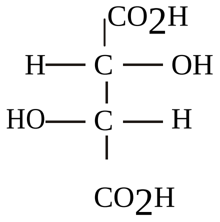


S - Alanine

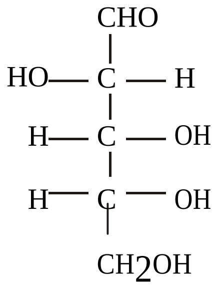
If more than one asymmetric carbon is present, then each configuration is specified, along with the position number of the asymmetric carbon.



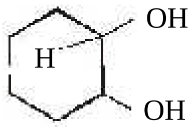
2(*R*), (*R*)-Tartaric acid



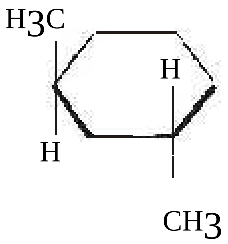
2(R), 3(R)-Dihydroxy succinic acid



2(S), 3(R), 4(R), 5-Tetrahydroxy- pentanal



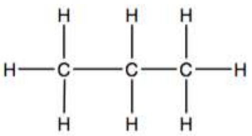
Cyclohexanediol-1(R), 2(S) or meso-cyclohexanediol-1,2

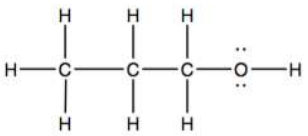


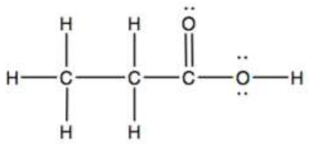
1(S),3(S)-Dimethyl cyclohexane

Factors Influencing Reactivity of Organic Reactions

Electronic factors that influence organic reactions include the **inductive effect**, **electromeric effect**, **resonance effects**, mesomeric effects and **hyperconjugation**. These electronic factors involve organic molecules, most of which are made from a combination of the following six elements: carbon, hydrogen, nitrogen, oxygen, phosphorus, and sulfur (known collectively as CHNOPS). Yet, the limited number of building blocks does not prevent organic compounds from taking on diverse properties in their physical characteristics and chemical reactivity. The subtle differentiation of various compounds in organic chemistry is essential for the biological functions of the molecules and creates a wide variety of reactions.


Propane (C_3H_8)


Propanol (C_3H_8O)


Propanoic Acid ($C_3H_6O_2$)

Part of this variety in organic chemistry stems from differences in electron behavior when elements other than carbon and hydrogen participate in molecular bonds. For example, the three compounds pictured above have similar formula units and structures, but react very differently from one another because of these electronic factors. Varying electronegativity can cause *delocalization effects*, where the electron cloud for a given bond expands to more than two atoms within the molecule.

Contents

Polarity of Organic Molecules

Partial polarity within a molecule leads to electron transfer among the atoms in a molecule, leading to different behavior than what would be expected in a non-polar version of the compound, where no sections were electron-rich or electron-deficient.

Saturated hydrocarbons are nonreactive because there is no polarity in C-C bond and practically no polarity in C-H bonds. Carbon and hydrogen are almost identical in electronegativity, so the electrons involved in a bond between the two atoms are equally attracted to each nucleus and spend roughly the same amount of time orbiting one as the other.

Electron density is evenly distributed between the two atoms in a non-polar bond, which prevents charged species from attacking or altering the bond. In contrast, charged species (electrophiles and nucleophiles) react with polar organic molecules because there is an imbalance in electron density or polarity.

Elements with higher electronegativity, including oxygen and the halide group, can change the electron density around an organic molecule and make the molecule more reactive.

Electronic effects complicate chemical reactions, and they can stabilize a molecule, make a compound less volatile, make a molecule more likely to react in a desired fashion, or affect the acidity or basicity. Understanding the factors involved in electronic imbalance is vital for understanding the underlying mechanisms of a chemical reaction, predicting the products of a reaction and predicting organic molecules' behavior.

Examples of Electronic Effects

1. The Inductive Effect
2. Resonance
3. The Mesomeric Effect
4. Electromeric Effect
5. Hyperconjugation

Inductive Effect

The **inductive effect** is a permanent state of polarization. The electron density in a σ bond between two unlike atoms is not uniform. The electron density is more dense toward the more electronegative of the two atoms.

The inductive effect is a distance-dependent phenomenon:

The atom XX above acquires a slightly negative charge ($\delta-$), and the carbon atom a slightly positive charge ($\delta+$), which means the bond is polarized:

$$C^{\delta\delta\delta\delta^+} \longrightarrow C^{\delta\delta\delta^+} \longrightarrow C^{\delta\delta^+} \longrightarrow C^{\delta^+} \longrightarrow X^{\delta^-}$$

$$C^{\delta\delta\delta\delta^-} \longleftarrow C^{\delta\delta\delta^-} \longleftarrow C^{\delta\delta^-} \longleftarrow C^{\delta^-} \longleftarrow Y^{\delta^+}$$

If the electronegative atom XX is connected to a chain of carbon atoms, then the positive charge is relayed to the other carbon atoms. $C1$, with its positive δ charge, exerts a pull on the electrons of$C2$, but the pull is weaker than it is between XX on $C1$. The effect rapidly dies out and is usually not significant after the 2nd carbon atom, or at most the 3rd.

The inductive effect is permanent, but relatively weak, and can be easily overshadowed by the electronic effects discussed later.

There are two categories of inductive effects: the electron-withdrawing (-I effect) and the electron-releasing (+I effect). The latter is also called the *electron-donating effect.* In the image above, XX is electron-withdrawing and YY is electron-donating.

-I effect:

The -I effect is seen around a more electronegative atom or group, and electron density is higher there than elsewhere in the molecule. Electron-withdrawing groups include halogen, nitro ($-NO_2$), cyano ($-CN$), carboxy($-COOH$), ester ($-COOR$), and aryloxy ($-OAr$).

+I effect:

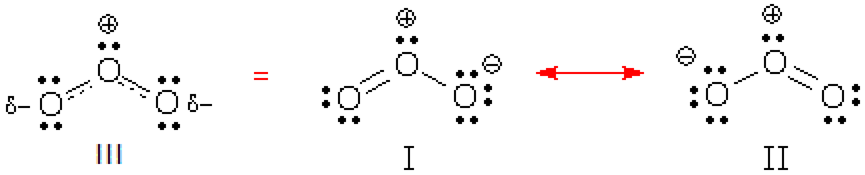
The +I effect is observed among the less electronegative atoms of the molecule by electron-releasing (or electron-donating) groups. The alkyl groups are usually considered electron-releasing (or electron-donating) groups.

Resonance

Sometimes, there are several correct Lewis structures for a given molecule. Ozone (O_3) is one example. The compound is a chain of three oxygen atoms, and minimizing the charges while giving each atom an octet of electrons requires that the central oxygen atom form a single bond with one terminal oxygen and a double bond with the other terminal oxygen.

When drawing the Lewis structure, the choice of placement for the double bond is arbitrary, and either choice is equally correct. The multiple correct ways of drawing the Lewis structure are called the **resonance forms**.

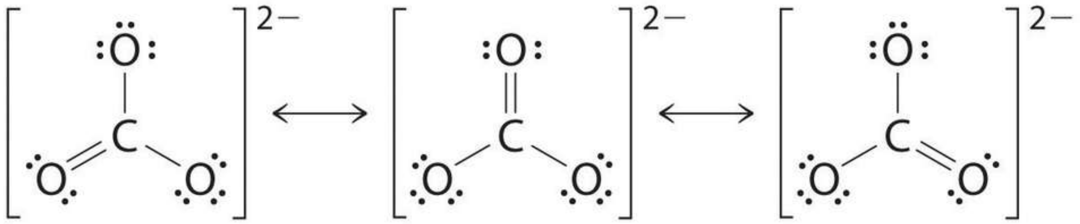
Based on the resonance forms, a beginning chemistry student might wonder if ozone has bonds of two different lengths, since single bonds are generally longer than double bonds. However, the ozone molecule is perfectly symmetrical, with bonds that are the same length. None of the resonance forms represent the true structure of the molecule. Rather, the negative charge of the electrons that would form a double bond are **delocalized**, or distributed evenly across the three oxygen atoms. The true structure is a composite, with bonds shorter than what would be expected for single bonds, but longer than the expected double bonds.

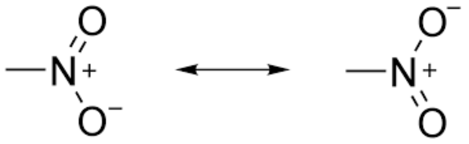


The resonance hybrid for ozone is found by identifying the multiple resonance structures for the molecule.

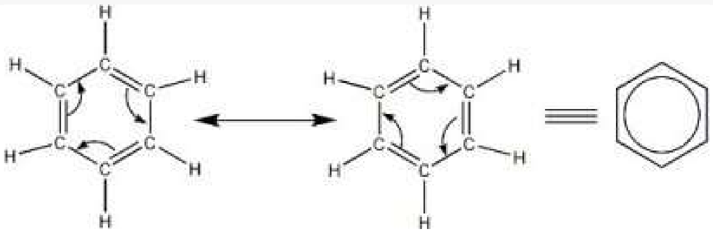
Thus for O_3 the two structures (I and II) shown above constitute the canonical structures or resonance structures and their hybrid (*i.e.* the III structure) represents the structure of O_3 more accurately. Resonance is represented by a double-headed arrow between the resonance structures, as illustrated above.

(1)





(2)



The resonance hybrid is more stable than its canonical forms, i.e. the actual compound (hybrid) is at a lower energy state than its canonical forms. Resonance stability increases with increased number of resonance structures.

The difference in the experimental and calculated energies is the amount of energy by which the compound is stable. This difference is known as resonance energy or delocalization energy.

All resonance structures are not equivalent. The following rules help determine whether or not a resonance structure will contribute significantly to the hybrid structure.

Rules of Resonance

Rule 1: The most significant resonance contributor has the greatest number of full octets (or if applicable, expanded octets).

Rule 2: The most significant resonance contributor has the fewest atoms with formal charges.

Rule 3: If formal charges cannot be avoided, the most significant resonance contributor has the negative formal charges on the most electronegative atoms, and the positive formal charges on the least electronegative atoms.

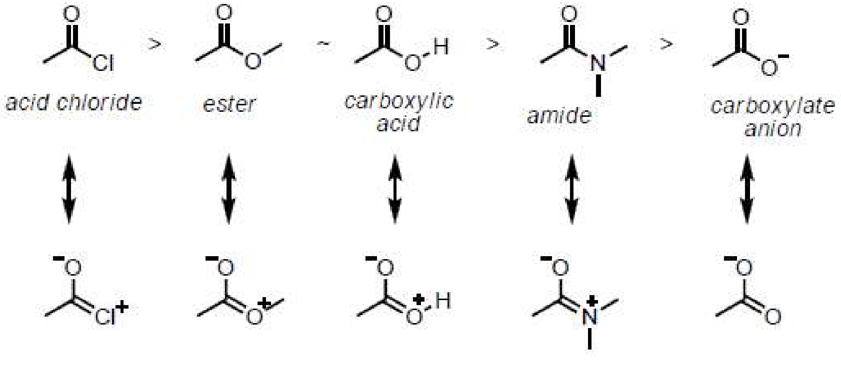
Rule 4: The most significant resonance contributor has the greatest number of covalent bonds.

Rule 5: If a pi bond is present, the most significant resonance contributor has this pi bond between atoms of the same row of the periodic table (usually carbon pi bonded to boron, carbon, nitrogen, oxygen, or fluorine).

Rule 6: Aromatic resonance contributors are more significant than resonance contributors that are not aromatic.

Mesomeric Effect

The permanent polarization of a group conjugated with a π bond or a set of alternate π bonds is transmitted through the π electrons of the system, resulting in a different distribution of electrons in the unsaturated chain. This kind of electron distribution in unsaturated compounds conjugated with electron-releasing or withdrawing groups or atoms is called **mesomeric effect**.



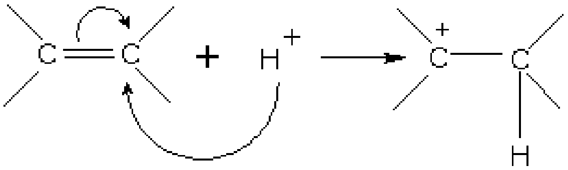
As shown above, a polarity is induced in compounds due to transfer of electrons through π bonds. This effect is a consequence of resonance and is seen in compounds that contain a double bond that is separated from another double bond or a lone pair of electrons by a single bond.

Electromeric Effect

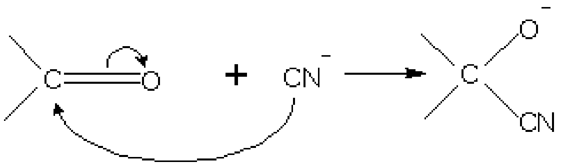
The **electromeric effect** is an intramolecular movement of electrons from a pi bond to another atom in the molecule due to attack by a reagent. It is temporary and reversible.

There are two distinct types of electromeric effects:

(i) Positive Electromeric Effect (+E effect): In this effect the \pi$\pi$-electrons of the multiple **bond** are transferred to that atom to which the reagent gets attached. For example:

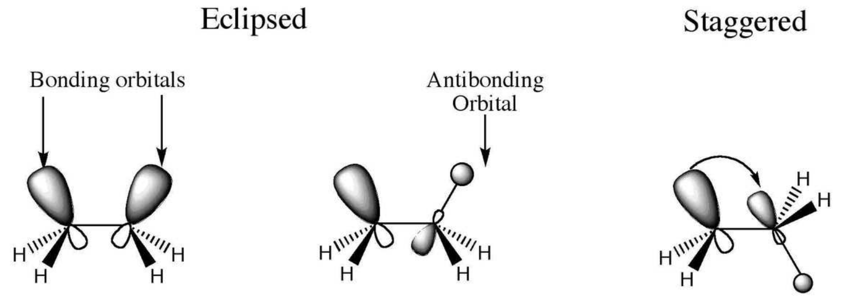


(ii) Negative Electromeric Effect (-E effect): In this effect the \pi$\pi$-electrons of the multiple bomd are transferred to that atom to which the attacking reagents do not get attached. For example:



Hyperconjugation

Hyperconjugation helps explain the stability of alkyl radicals. It involves the delocalization of σ-electrons belonging to the C-H bond of the alkyl group attaching to an atom with an unshared p orbital. The more the hyperconjugative hydrogen, the more is the stability.



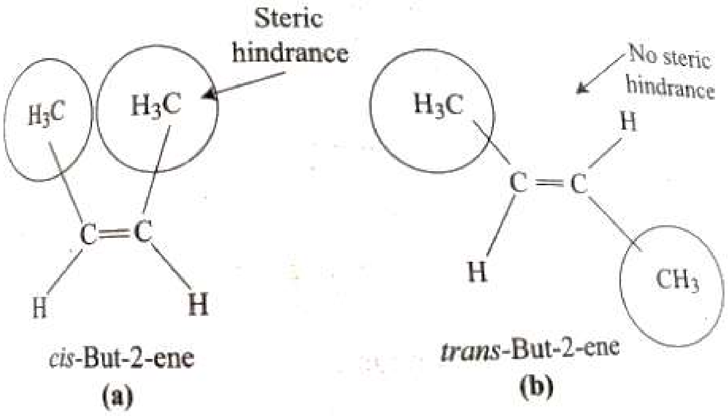
Pauli Exchange (repulsive)

Weakened Hyperconjugation

Strengthened Hyperconjugation (attractive)

Steric Effect

The structure and reactivity of many compounds in organic chemistry are greatly dictated by the presence of bulky groups or constituents in the molecule. This is called **steric hindrance**. It arises because of **inter-electronic repulsions** due to spatial crowding amongst bulky groups. Using steric factors, we can conclude that trans-2-butene is more stable than cis-2-butene.



Steric Hindrance in Organic Chemistry

Hydrogen bonding

Hydrogen bond or hydrogen bonding is a type of weak force that results in the formation of dipole-dipole interaction between a hydrogen atom and an electronegative atom that is strongly bonded to another electronegative atom. The bond or bonds are mostly strong in comparison to normal dipole-dipole and dispersion forces. However, they are weak compared to true covalent or ionic bonds.

In a molecule, when a hydrogen atom is linked to a highly electronegative atom, it attracts the shared pair of electrons more and so this end of the molecules becomes slightly negative while the other end becomes slightly positive. The negative end of one molecule attracts the positive end of the other and as a result, a weak bond is formed between them. This bond is called the **hydrogen bond.**

As a result of hydrogen bonding, a hydrogen atom links the two electronegative atoms simultaneously, one by a covalent bond and the other by a hydrogen bond. The conditions for hydrogen bonding are:

1. The molecule must contain a highly electronegative atom linked to the hydrogen atom. The higher the electronegativity more is the polarization of the molecule.
2. The size of the electronegative atom should be small. The smaller the size, the greater is the electrostatic attraction.

Strength of the Hydrogen bond

The hydrogen bond is a weak bond. The strength of hydrogen bond is in-between the weak van der Waals forces and the strong covalent bonds.

The dissociation energy of the hydrogen bond depends upon the attraction of the shared pair of electrons and hence on the electronegativity of the atom.

Properties of Hydrogen Bonding

- **Solubility:** Lower alcohols are soluble in water because of the hydrogen bonding which can take place between water and alcohol molecule.
- **Volatility:** As the compounds involving hydrogen bonding between different molecules have a higher boiling point, so they are less volatile.
- **Viscosity and surface tension:** The substances which contain hydrogen bonding exists as an associated molecule. So their flow becomes comparatively difficult. They have higher viscosity and high surface tension.
- **The lower density of ice than water:** In the case of solid ice, the hydrogen bonding gives rise to a cage-like structure of water molecules. As a matter of fact, each water molecule is linked tetrahedral to four water molecules. The molecules are not as closely packed as they are in a liquid state. When ice melts, this case like structure collapses and the molecules come closer to each other. Thus for the same mass of water, the volume decreases and density increases. Therefore, ice has a lower density than water at 273 K. That is why ice floats**.**

Types of Hydrogen Bonding

There are two types of H bonds, and it is classified as the following:

- Intermolecular Hydrogen Bonding
- Intramolecular Hydrogen Bonding

Intermolecular Hydrogen Bonding

When hydrogen bonding takes place between different molecules of the same or different compounds, it is called **intermolecular hydrogen bonding.**

For example – hydrogen bonding in water, alcohol, ammonia etc.

Intramolecular Hydrogen Bonding

The hydrogen bonding which takes place within a molecule itself is called **intramolecular hydrogen bonding.**

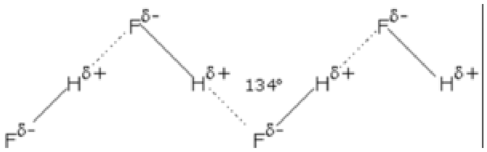
It takes place in compounds containing two groups such that one group contains hydrogen atom linked to an electronegative atom and the other group contains a highly electronegative atom linked to a lesser electronegative atom of the other group.

The bond is formed between the hydrogen atoms of one group with the more electronegative atom of the other group

Examples of Hydrogen Bonding

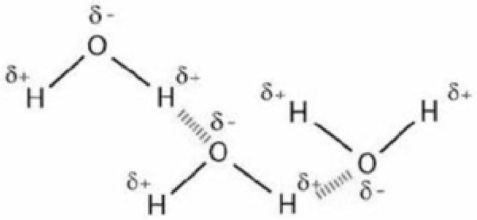
Hydrogen Bonding in Hydrogen fluoride

Fluorine having the highest value of electronegativity forms the strongest hydrogen bond.



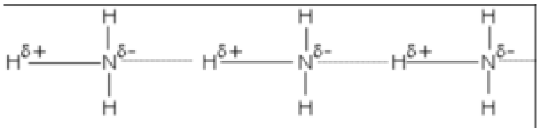
Hydrogen Bonding in Water

A water molecule contains a highly electronegative oxygen atom linked to the hydrogen atom. Oxygen atom attracts the shared pair of electrons more and this end of the molecule becomes negative whereas the hydrogen atoms become positive.



Hydrogen Bonding in Ammonia

It contains highly electronegative atom nitrogen linked to hydrogen atoms.

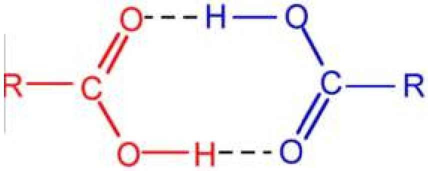


Hydrogen Bonding in Alcohols and Carboxylic acid

Alcohol is a type of an organic molecule which contains an -OH group. Normally, if any molecule which contains the hydrogen atom is connected to either oxygen or nitrogen directly, then hydrogen bonding is easily formed.

$$\cdots\overset{R}{O}\text{-H}\cdots\overset{H}{O}\text{-H}\cdots\overset{R}{O}\text{-H}\cdots\overset{H}{O}\text{-H}\cdots$$

Hydrogen Bonding in Alcohols



Hydrogen Bonding in Carboxylic acid

Hydrogen Bonding in Polymers

Hydrogen bonding is an important factor in determining the 3D structures and properties that are acquired by synthetic and natural proteins. Hydrogen bonds also play an important role in defining the structure of cellulose as well as derived polymers such as cotton or flax.

CHAPTER 6

Organic Reactions and Their Mechanisms

6-1 SUBSTITUTION REACTION

In a substitution reaction, a functional group in a particular chemical compound is replaced by another group.

Reagent	Substrate	Reactive intermediate	Type of organic substitution
Nucleophilic	Aliphatic	Carbocation	Aliphatic nucleophilic substitution
Electrophilic	Aromatic	Carbanion	Aromatic electrophilic substitution
		Free radical	Free radical substitution

- ➢ The electrophilic and nucleophilic substitution reactions are of prime importance.
- ➢ Detailed understanding of a reaction type helps to predict the product outcome in a reaction. It also is helpful for optimizing a reaction with regard to variables such as temperature and choice of solvent.

I. ALIPHATIC NUCLEOPHILIC SUBSTITUTION

A. General description

$$R\text{—}L + Nu: \rightarrow R\text{—}Nu + L:$$

☞ Nucleophilic substitution reactions can carry out at a *saturated aliphatic carbon* or at other *unsaturated carbon* centre.

☞ Charge type:

Type a $R-I + OH^{-} \longrightarrow R-OH + I^{-}$

Type b $R-I + NMe_3 \longrightarrow R-\overset{+}{N}Me_3 + I^{-}$

Type c $R-\overset{+}{N}Me_3 + OH^{-} \longrightarrow R-OH + NMe_3$

Type d $R-\overset{+}{N}Me_3 + H_2S \longrightarrow R-\overset{+}{S}H_2 + NMe_3$

All necleophiles are Lewis bases.

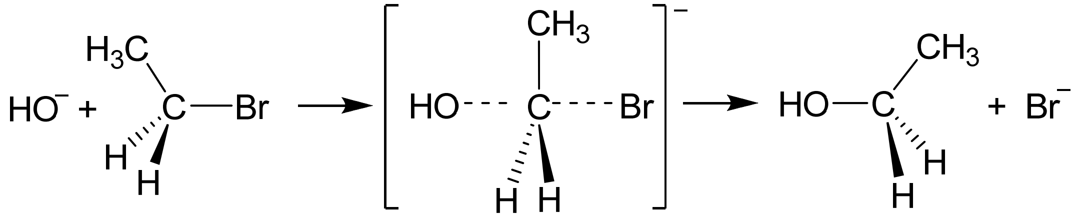
Solvolysis: solvent used as a necleophile.

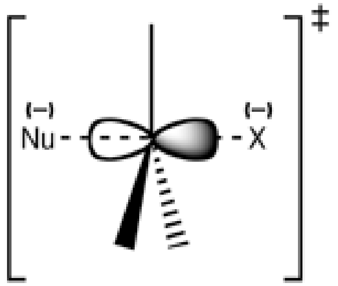
Alkylattion: nucleophilic substitution at an alkyl carbon.

Acylation: nucleophilic substitution at an acyl carbon.

B. NUCLEOPHILIC SUBSTITUTION MECHANISMS AT SATURATED CARBON CENTRES

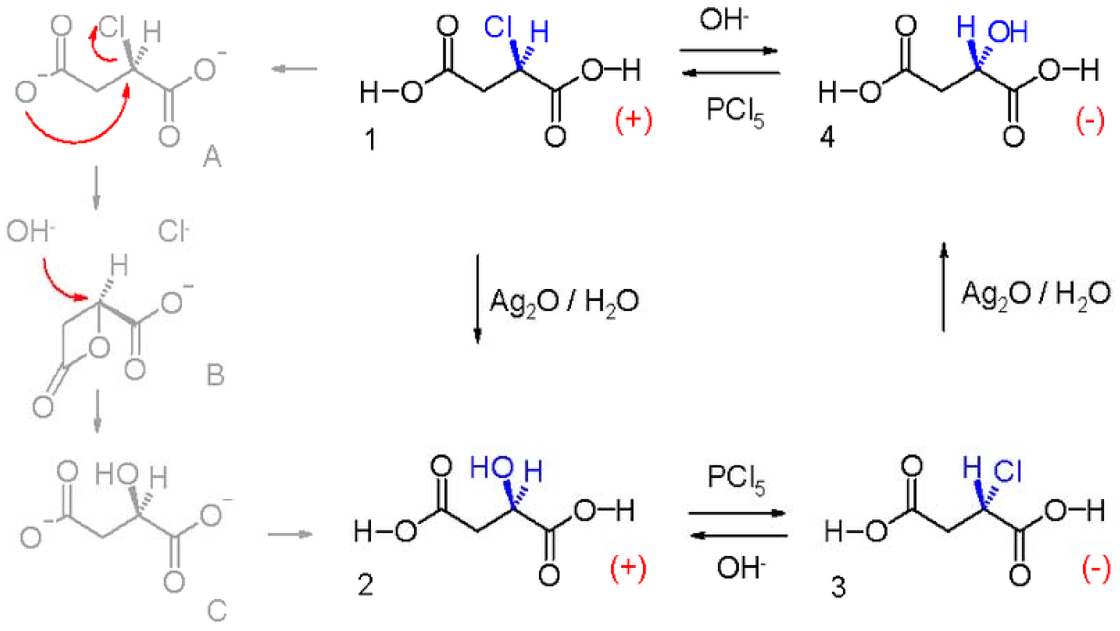
- Bimolecular Nucleophilic Substitution (S_N2)





Structure of the S_N2 transition state

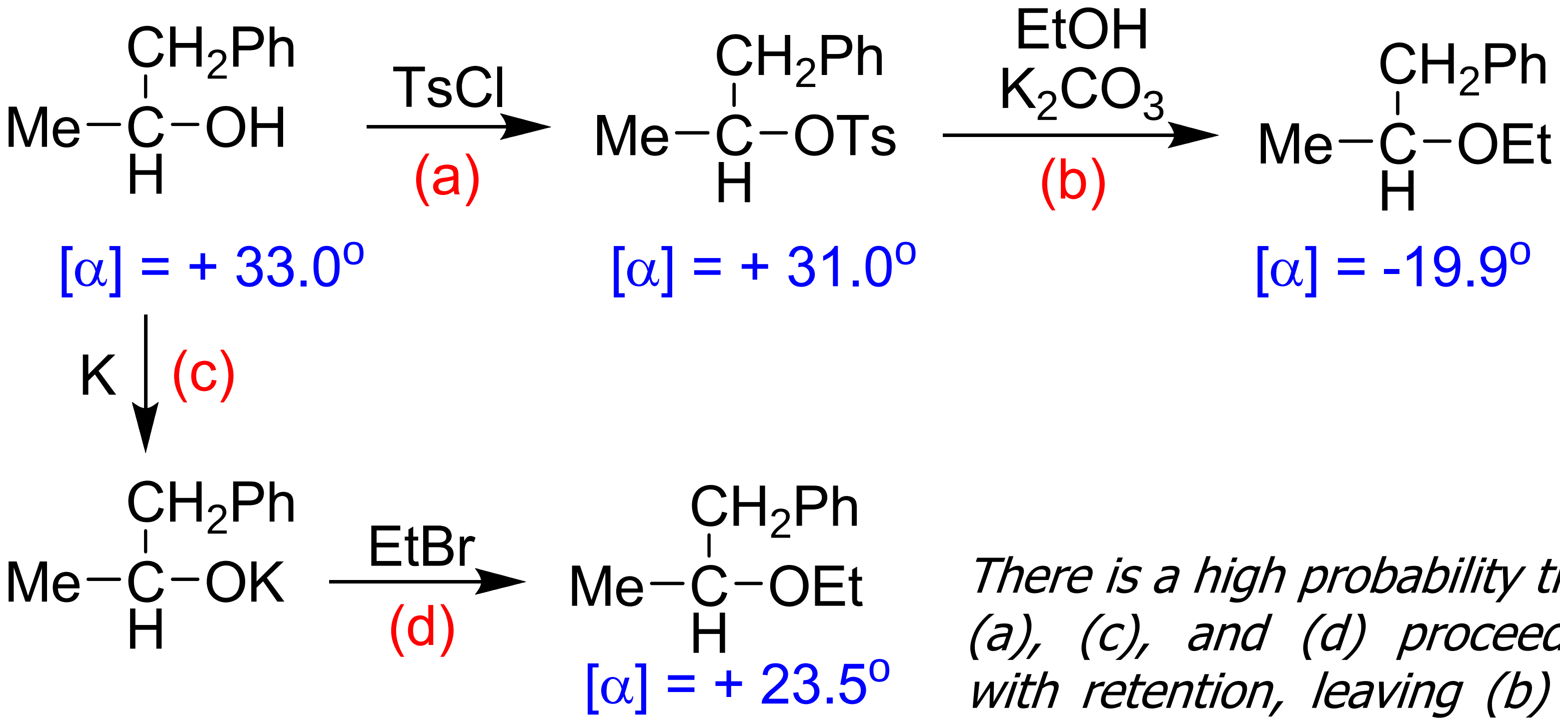
☞ The kinetic evidence: Rate = k [RX][Nu]



☞ Walden inversion:

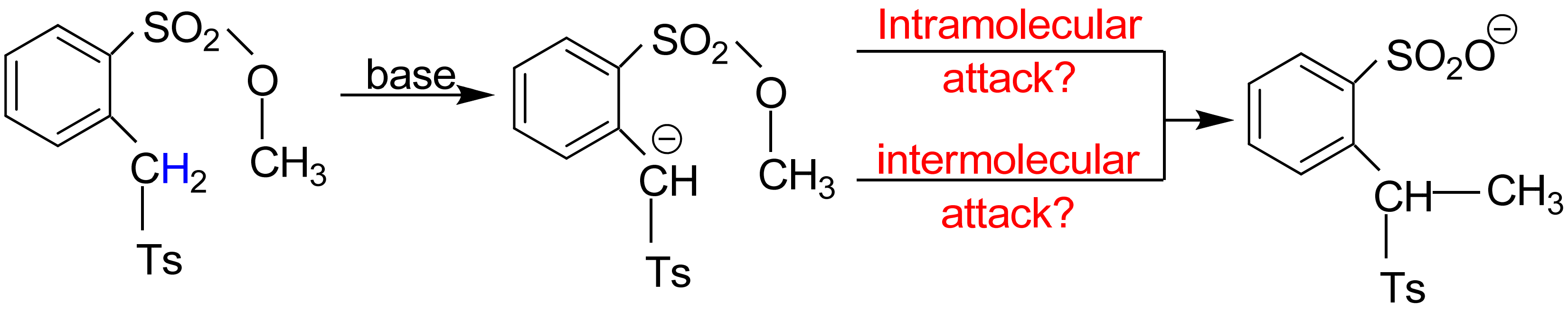
(+)-chlorosuccinic acid **1** was converted to (+) malic acid **2** by action of Ag_2O in water with retention of configuration, in the next step the OH was replaced by Cl to **3** by reaction with PCl_5.

Philips (1923)



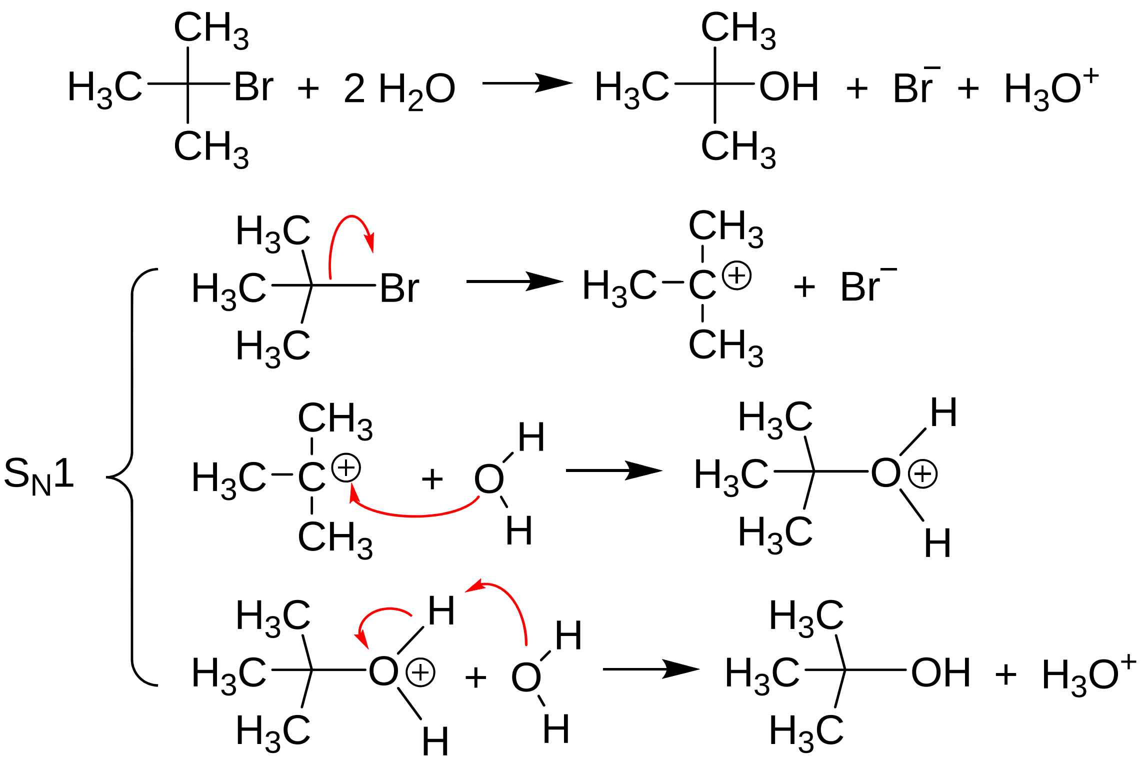
There is a high probability that (a), (c), and (d) proceeded with retention, leaving (b) as the inversion.

ESCHENMOSER ET AL.



- The negatively charged carbon attacks the methyl group of another molecule rather than the nearby one in the same molecule, that is, the reaction is intermolecular and not intramolecular. The transition state in an SN2 reaction must be linear.

Unimolecular Nucleophilic Substitution (S_N1)



$$(CH_3)_3C{-}Br + 2\,H_2O \longrightarrow (CH_3)_3C{-}OH + Br^- + H_3O^+$$

☞ Reaction kinetics:

rate = k[RX]

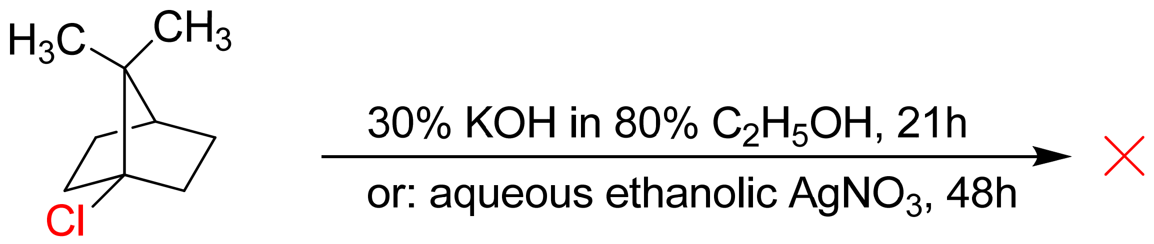
Ionization of the substrate is the rate-determining step.

t-BuCl → t-Bu$^+$ + Cl$^-$

630 kJ/mol (in gas phase)
84 kJ/mol (in water)

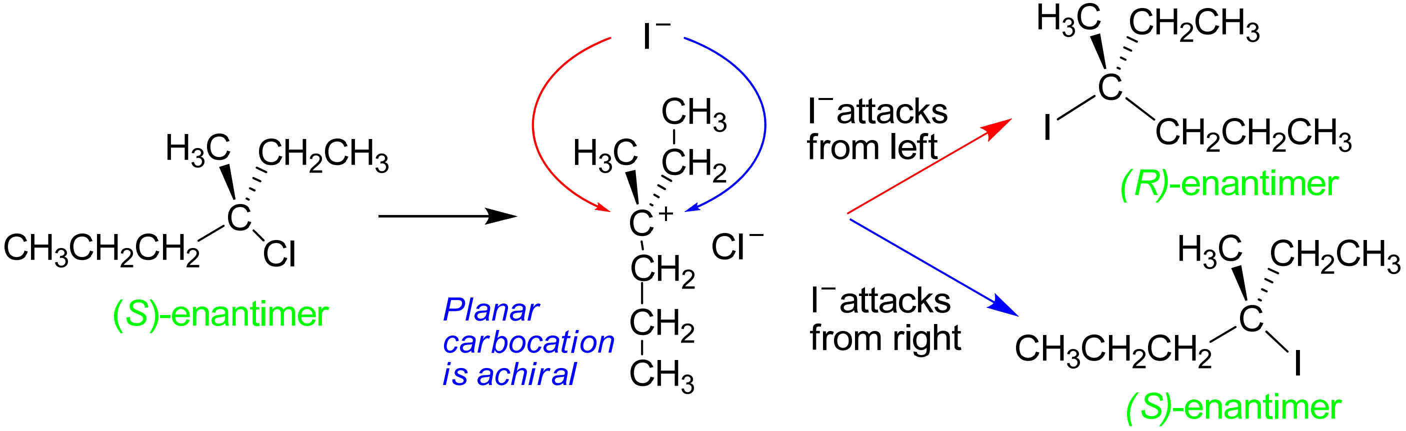
☞ Salt effect and common-ion effect: An increase in ionic strength of the solution usually increases the rate of an S_N1 reaction. A common ion will depress the S_N1 rate.

☞ **Steric factor:** The reactions run under SN1 conditions fail or proceed very slowly at the bridgehead position of [2,2,1](norbornyl) systems.

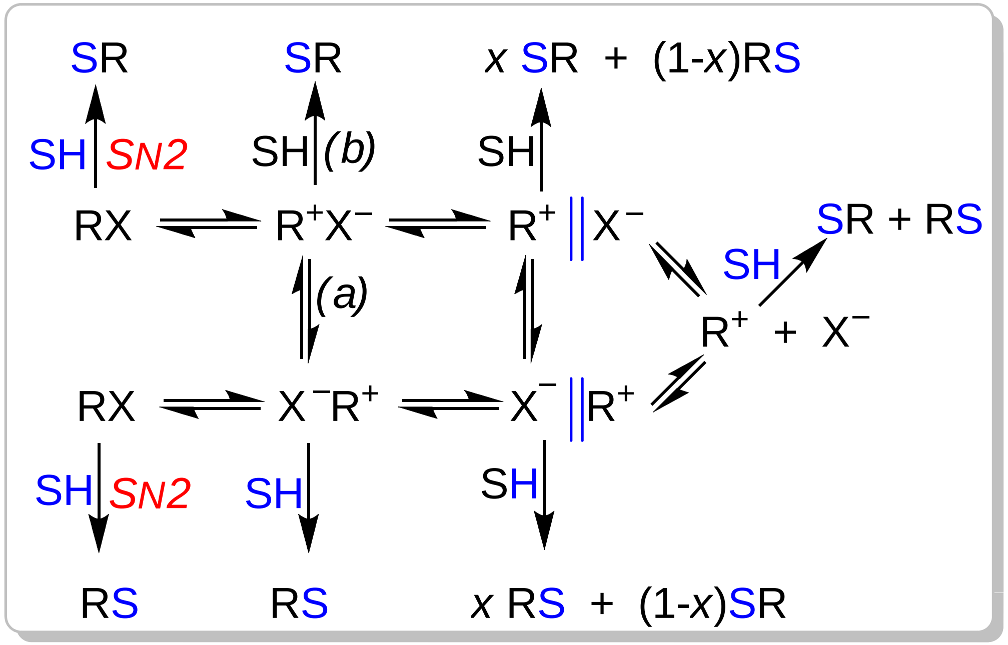


1-chloroapocamphane

- **Stereochemistry:** An excess of inversion is usually observed, as the leaving group can remain in proximity to the carbocation intermediate for a short time and block nucleophilic attack.



➢ Ion Pairs in the SN1 Mechanism



A complete picture of the possibilities for solvolysis in a solvent SH (ignoring the possibilities of elimination or rearrangement). RS and SR represent enantiomers; *x* = some fraction.

i. SN2 process: a complete inversion

ii. Intimate ion pair R^+X^-: total inversion if *(a)* does not take place or to a combination of inversion and racemization if there is competition between *(a)* and *(b)*.

iii. Solvent-separated $R^+ \| X^-$: more racemization (perhaps total)

iv. Free R^+: complete racemization

v. The difference: SN1 and SN2 mechanisms is in the timing of the steps.

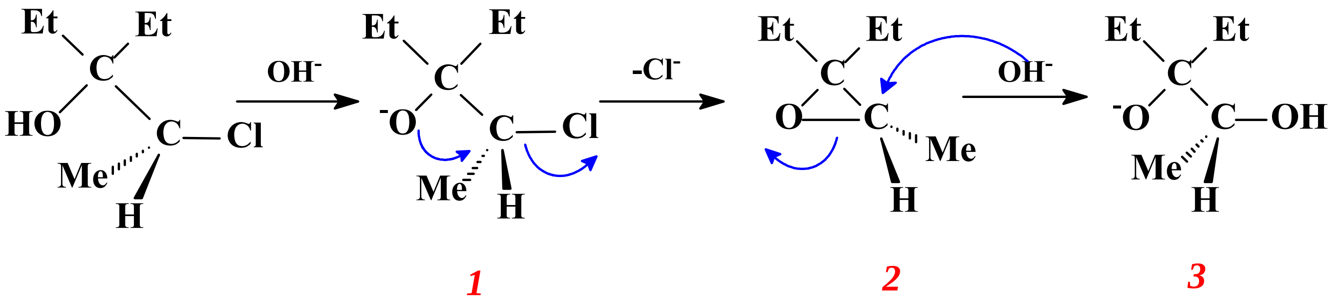
- **The Neighboring-Group Mechanism**

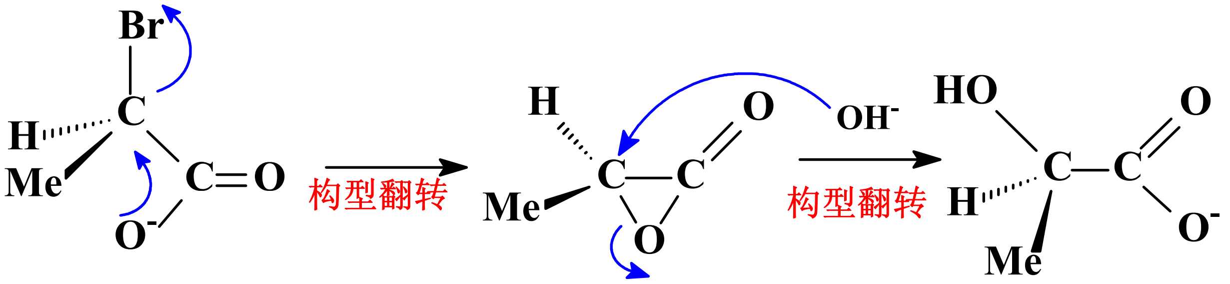
OBSERVATION with certain substrates:

i. The rate of reaction is greater than expected,

ii. The configuration at a chiral carbon is retained and not inverted or racemerized.

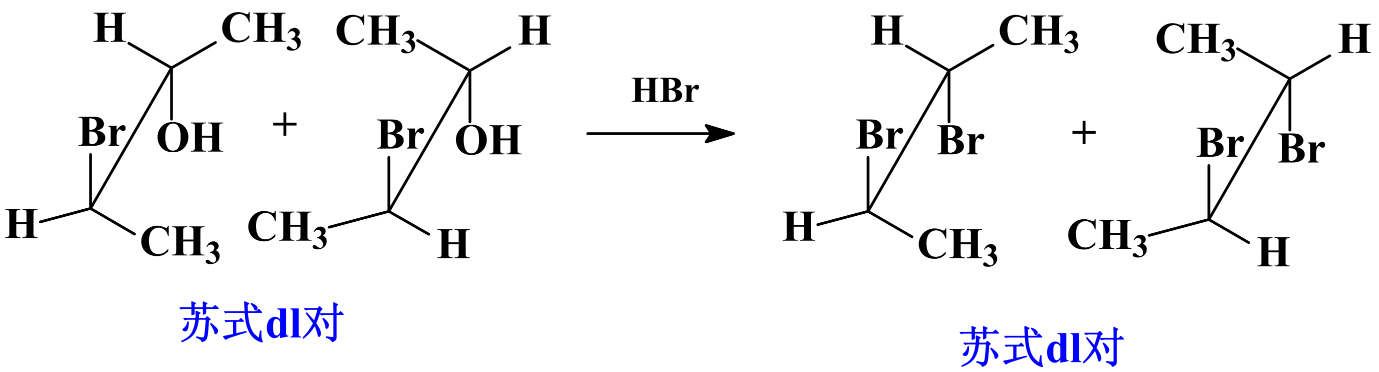
The *neighboring-group mechanism* consists essentially of two S_N2 substitutions, each causing an inversion so that the net result is retention of configuration.

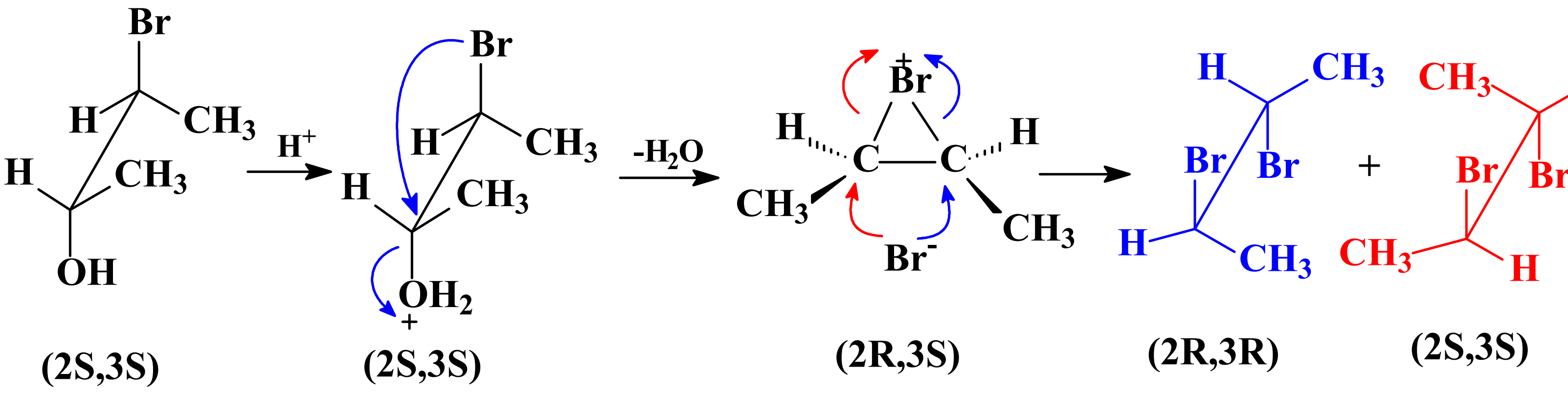


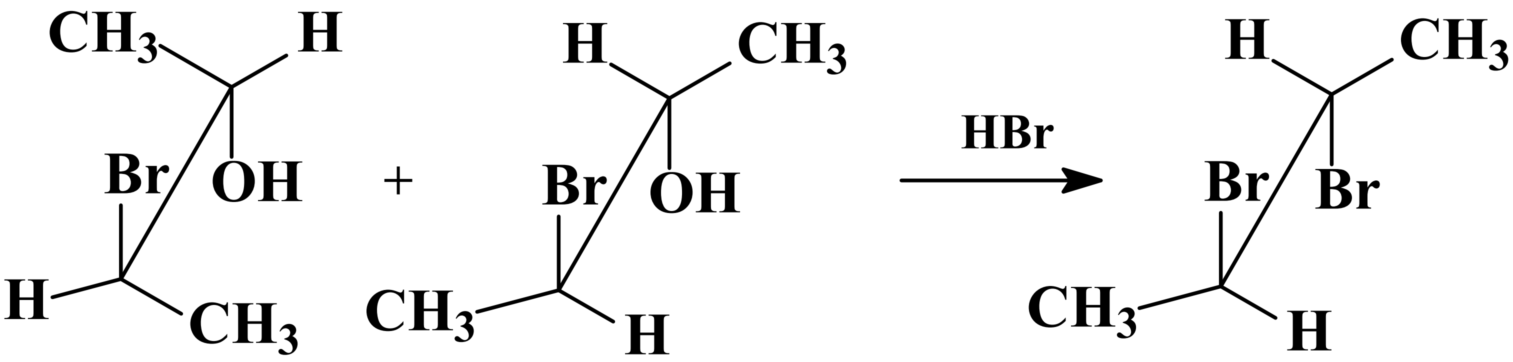


EVIDENCE:

(i) Configurational retention. Note that both products are optically inactive and so cannot be told apart by differences in rotation. The *meso* and *dl* dibromides have different boiling points and indexes of refraction and were identified by these properties.

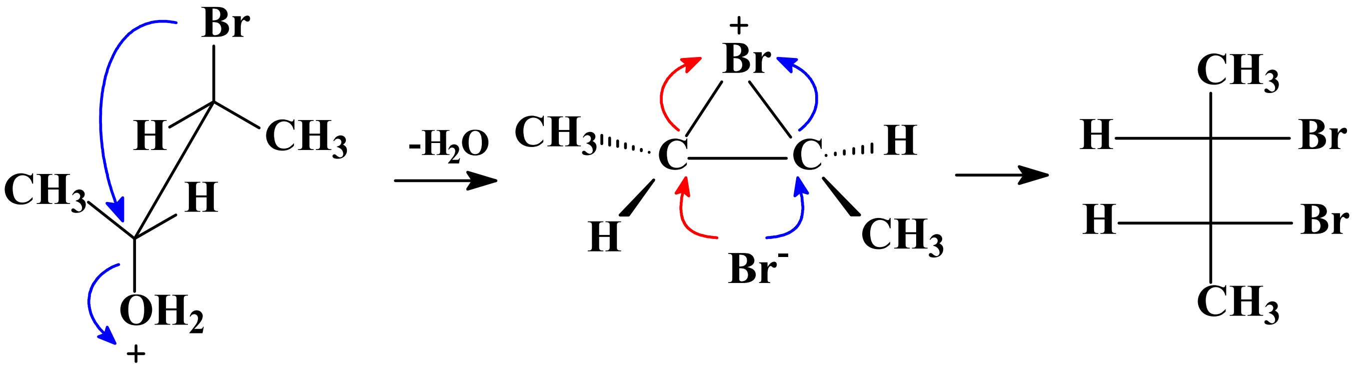






赤式dl对

赤式meso

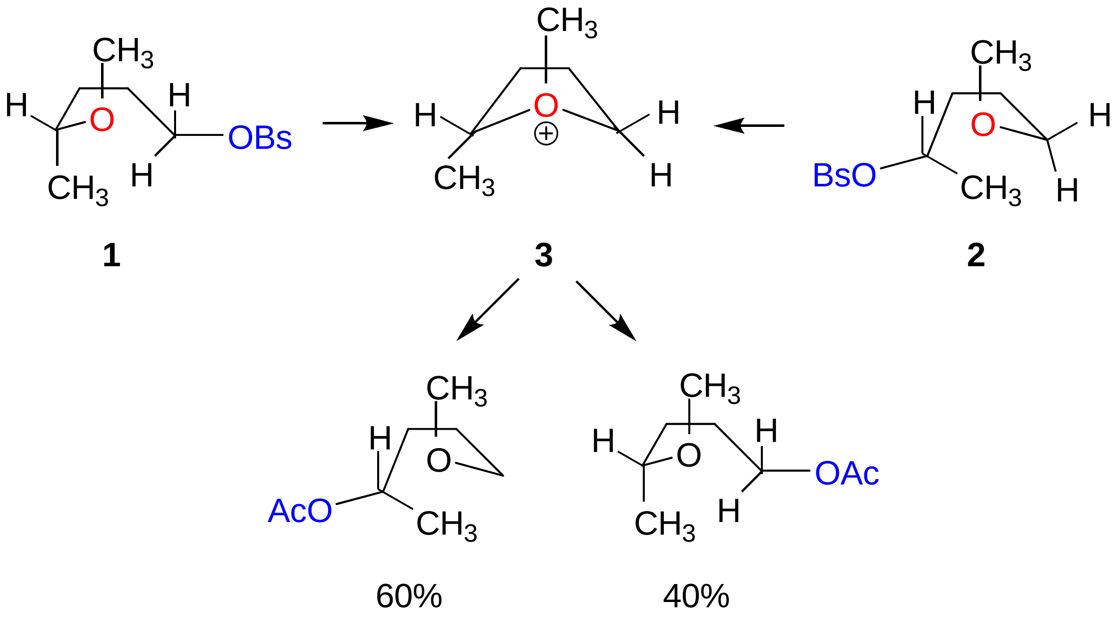


(2R,3S)

(2S,3S)

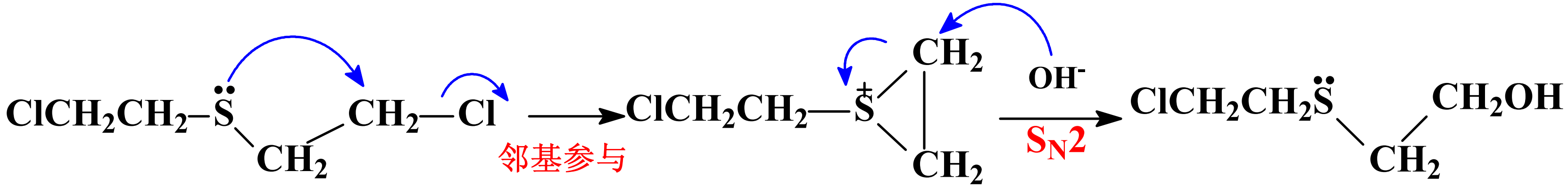
meso

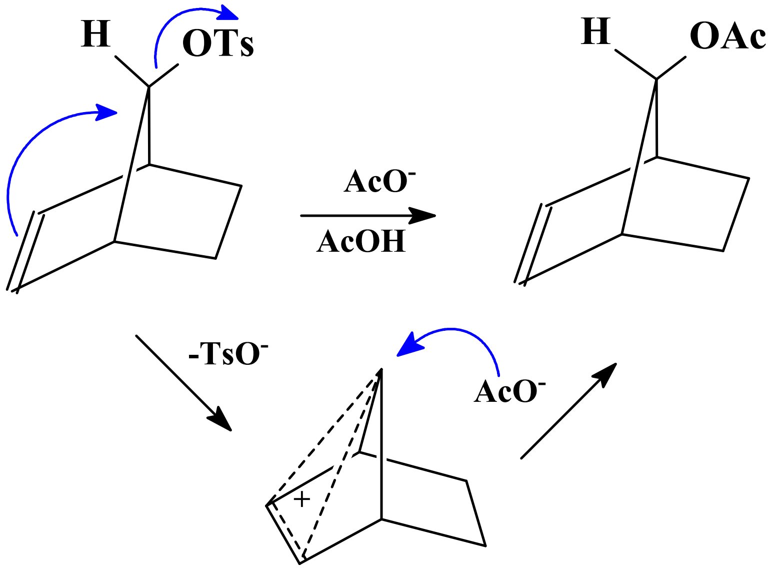
(iii) Acetolysis of both 4-methoxy-pentyl brosylate **1** and 5-methoxy-2-pentyl brosylate **2**: the same mixture of products. In this case the intermediate **3** is common to both substrates.

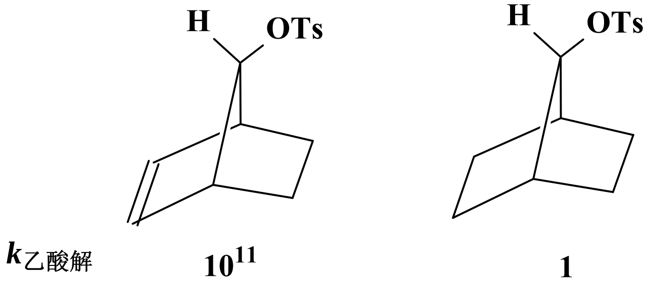


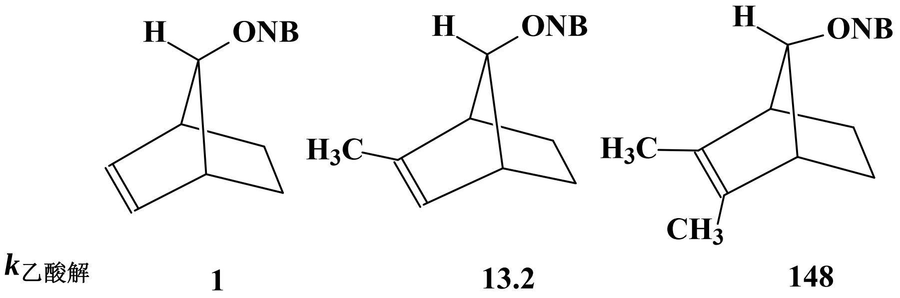
☞ Important neighboring groups: COO$^-$, COOR, COAr, OCOR, OR, OH, O$^-$, NH_2, NHR, NR_2, NHCOR, SH, SR, S$^-$, I, Br, Cl.

☞ The effectiveness: I > Br > Cl.

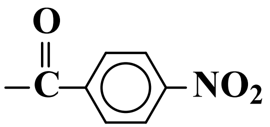

ClCH₂CH₂–S
CH₂
CH₂—Cl
邻基参与
ClCH₂CH₂—S⁺
CH₂
CH₂
OH⁻
S_N2
ClCH₂CH₂S
CH₂OH
CH₂


H
OTs
AcO⁻
AcOH
H
OAc
-TsO⁻
+
AcO⁻


H
OTs
H
OTs
k乙酸解
10¹¹
1

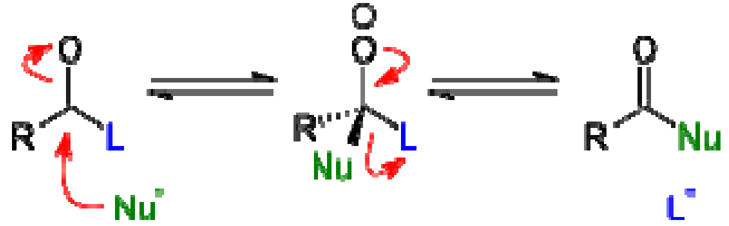

H
ONB
H
ONB
H₃C
H
ONB
H₃C
CH₃
k乙酸解
1
13.2
148

NB：

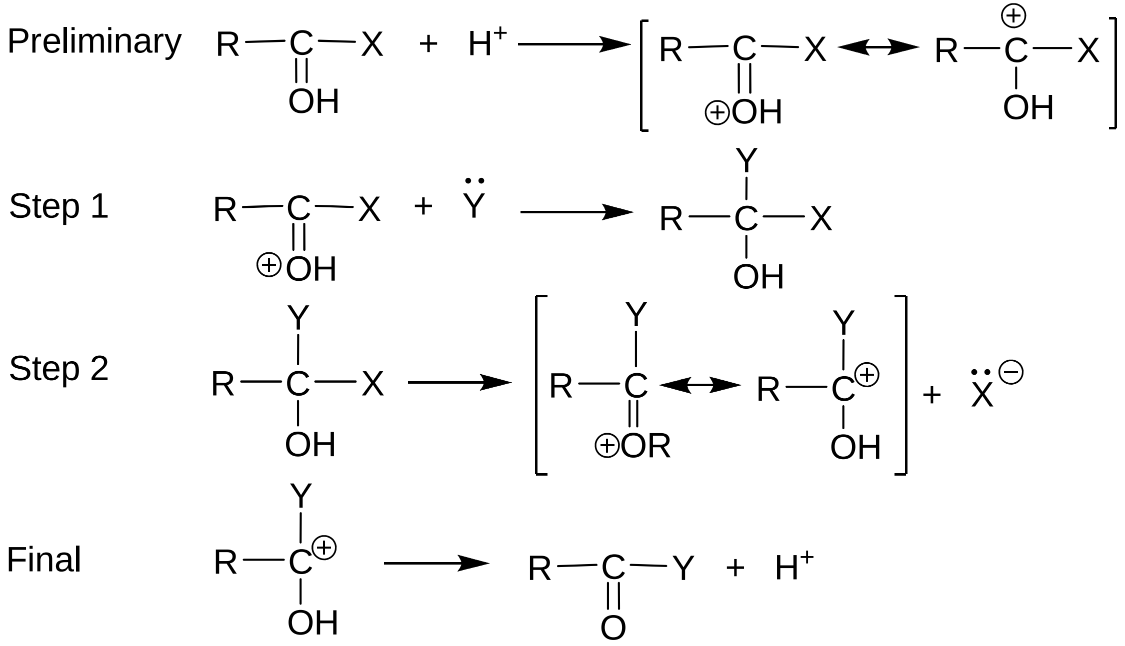

O
C
NO₂

C. NUCLEOPHILIC SUBSTITUTION AT AN ALIPHATIC TRIGONAL CARBON. THE TETRAHEDRAL MECHANISM

Acyl substitution is basically a two-step nucleophilic addition and elimination reaction. Both reaction steps are reversible reactions.



When reactions are carried out in acid solution, there may also be a preliminary and a final step.



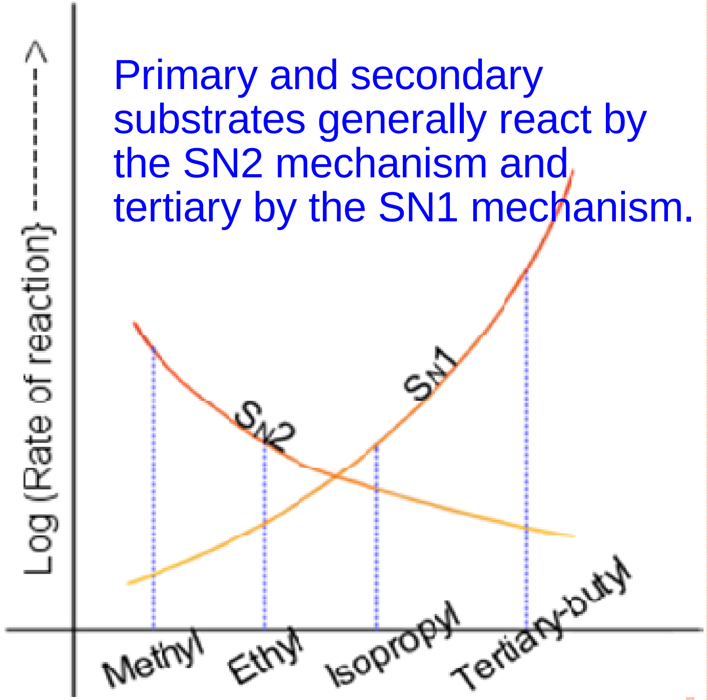
D. **Reactivity**

- **The Effect of Substrate Structure**

➢ For the SN2 mechanism, branching at either the α or the β carbon decreases the rate.

Table 1. Average relative SN2 rates for some alkyl substrates

R	Relative rate	R	Relative rate
Methyl	30	Isobutyl	0.03
Ethyl	1	Neopentyl	10^{-5}
Propyl	0.4	Ally	10
Butyl	0.4	Benzyl	120
Isopropyl	0.025		



Primary and secondary substrates generally react by the SN2 mechanism and tertiary by the SN1 mechanism.

➢ Elimination is always a possible side reaction of nucleophilic substitutions of tertiary substrates (wherever a hydrogen is present).

- Substrates of the type RCOX are usually much *more* reactive than the corresponding RCH_2X. The mechanism here is always the tetrahedral one. Explanation:

i. The carbonyl carbon has a sizable partial positive charge.

ii. In an SN1 reaction a σ bond must break in the rate-determining step, which requires more energy than the shift of a pair of π electrons, which is what happens in a tetrahedral mechanism.

iii. A trigonal carbon offers less steric hindrance to a nucleophile than a tetrahedral carbon.

- Unsturation at the β-carbon.

Table 2. Relative rates for the SN1 reaction between ROTs and ethanol at 25°C

CH_3CH_2-	0.26	$PhCH_2-$	100
$(CH_3)_2CH-$	0.69	Ph_2CH-	~ 10^5
$CH_2=CHCH_2-$	8.6	Ph_3C-	~ 10^{10}

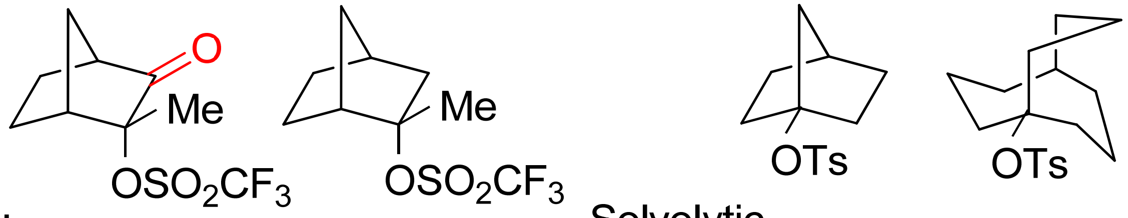
NOTE

☞ In general, SN1 rates at allylic substrate are increased by any substituent in the 1 or 3 position that can stabilized the carbocation by resonance or hyperconjugation. Among these are alkyl, aryl, and halo groups.

☞ SN2 rates for allylic and benzylic systems are also increased (See Tab.1), probably owing to resonance possibilities in the transition state.

- α-Substitution — resonance effect, field effect

ZCH_2X	SN1 relative rate
Z = RO, RS or R_2N–	Very rapid
Z = RCO, HCO, ROCO, NH_2CO, NC, F_3C	Decreased compared to CH_3X



Relative rate: 1 $10^{7.3}$

Solvolytic rate (*k*) $4x10^{-17}$/s $3x10^{6}$/s

Table 3. List of groups in approximately descending order of reactivity toward SN1 and SN2 reactions. (Z = RCO, HCO, ROCO, NC, or a similar group)

SN1 reactivity		SN2 reactivity	
Ar_3CX	RCHDX	Ar_3CX	R_3CX
Ar_2CHX	$RCHDCH_2X$	Ar_2CHX	ZCH_2CH_2X
$ROCH_2X$, $RSCH_2X$, R_2NCH_2X	C=CX	$ArCH_2X$	R_3CCH_2X
R_3CX	ZCH_2X	ZCH_2X	C=CX
$C{=}CCH_2X$	ZCH_2CH_2X	$C{=}CCH_2X$	ArX
R_2CHX	ArX	RCH_2X ~ RCHDX ~ $RCHDCH_2X$	Bridgehead-X
RCH_2X ~ R_3CCH_2X	[2,2,1]bridgehead-X	R_2CHX	

- **The Effect of the Attacking Nucleophile**

➢ SN1 rate: are independent of the identity of the nucleophile, since it does not appear in the rate-determining step.

➢ For SN2 reactions in solution there are four principles that govern the effect of the nucleophile on the rate.

i. A nucleophile with a negative charge > its conjugate acid. $OH^- > H_2O$, $NH_2^- > NH_3$

ii. In comparing nucleophiles whose attacking atom is in the same row of the periodic table, nucleophilicity is approximately in order of basicity. $NH_2^- > RO^- > OH^- > R_2NH > ArO^- > NH_3 > C_6H_5N > F^- > H_2O > ClO_4^-$; $R_3C^- > R_2N^- > RO^- > F^-$.

iii. Going down the periodic table, nucleophilicity increases, though basicity decreases. $I^- > Br^- > Cl^- > F^-$ (solvation, HSAB principle)

iv. The freer the nucleophile, the greater the rate.

Ex.: The rate of nucleophilic attack by $(EtOOC)_2CBu^-Na^+$ in benzene was increased by the addition of 1,2-dimethoxyethane.

NOTE:

i. The four rules given above do not always hold. One reason is that steric influences often play a part.

Basicity: $Me_3CO^- > OH^-$ or OEt^-
Nucleophilicity: $Me_3CO^- < OH^-$ or OEt^-

ii. Nucleophilicity order for SN2 mechanism (in protonic solvents):

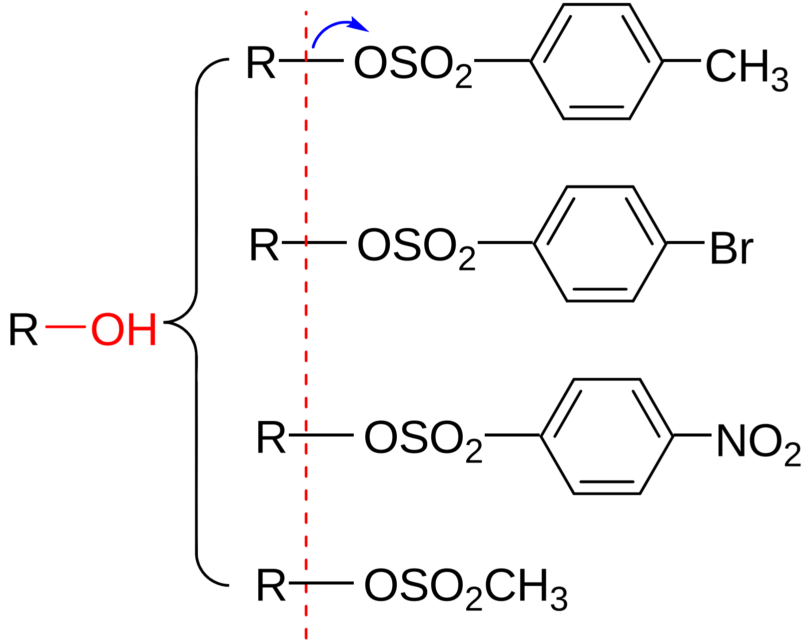
$RS^- > Ar^- > I^- > CN^- > OH^- > N_3^- > Br^- > ArO^- > Cl^- > C_6H_5N > {}^-OAc > H_2O$.

iii. For substitution at a carbonyl carbon, the nucleophilicity order is not the same as it is at a saturated carbon, but follows the basicity order more closely.

$EtO^- > MeO^- > OH^- > ArO^- > N_3^- > F^- > H_2O > Br^- \sim I^-$

- **The Effect of the Leaving Group**

➢ At a saturated carbon. The leaving group comes off more easily the more stable it is as a free entity. This is usually inverse to its basicity, and the best leaving groups are the weakest bases. Thus iodide is the best leaving group among the halides and fluoride the poorest.



ROTs
p-Toluenesulfonates, Tosylates

ROBs
p-Bromobenzenesulfonates, Brosylates

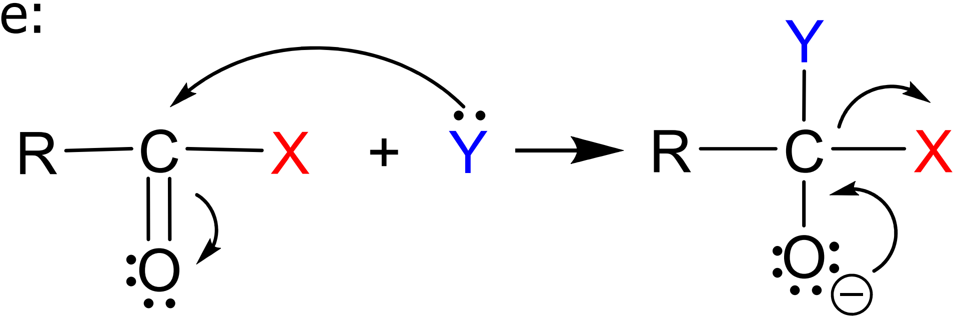
RONs
p-Nitrobenzenesulfonates, Nosylates

ROMs
Methanesulfonates, Mesylates

- **At a carbonyl carbon.** In the tetrahedral mechanism at a carbonyl carbon, the bond between the substrate and leaving group is still intact during the slow step. Nevertheless, the nature of the leaving group still affects the reactivity in two ways:

i. The greater the electron-withdrawing character of X, the greater the partial positive charge on carbonyl carbon and the more rapid the attack by a nucleophile.

ii. The nature of the leaving group affects the position of equilibrium. There is competition between X and Y as to which group leave:



$RCOCl > RCOOCOR' > RCOOAr > RCOOR' > RCONH_2 > RCOO^-$.

• The Effect of the Reaction Medium

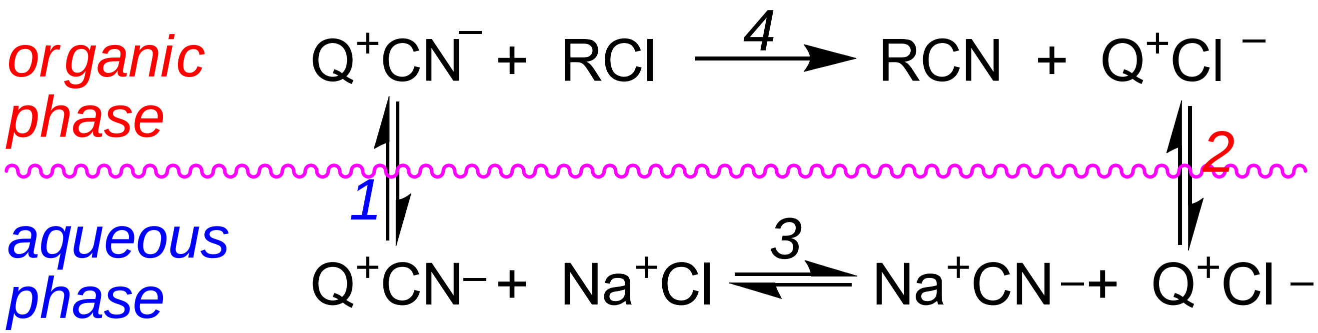
Table 3. Transition states for SN1 and for SN2 reactions of the four charge types

Reactants and transition states	Charge in the transition state relative to starting materials	How an increase in solvent polarity affects the rate
Type a $RX + Y^- \rightarrow Y^{\delta-}\cdots R\cdots X^{\delta-}$	Dispersed	Small decrease
Type b $RX + Y \rightarrow Y^{\delta+}\cdots R\cdots X^{\delta-}$	Increased	Large increase
Type c $RX^+ + Y^- \rightarrow Y^{\delta-}\cdots R\cdots X^{\delta+}$	Decreased	Large decrease
Type d $RX^+ + Y \rightarrow Y^{\delta+}\cdots R\cdots X^{\delta+}$	Dispersed	Small decrease
$RX \rightarrow R^{\delta+}\cdots X^{\delta+}$	Increased	Large increase
$RX^+ \rightarrow R^{\delta+}\cdots X^{\delta+}$	Dispersed	Small decrease

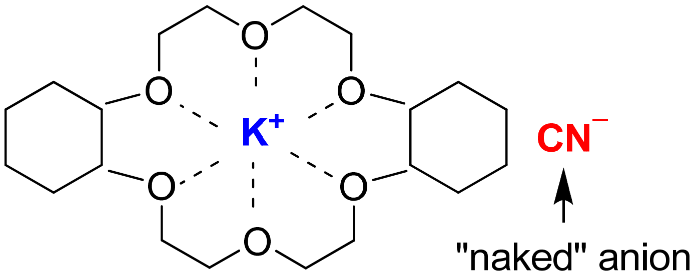
- When there is a greater charge in the transition state than in the starting compound, the more polar the solvent, the faster the reaction.
- Even for solvents with about the same polarity, there is a difference between protonic and aprotonic solvents. In *type a* and *b*, TS solvation: polar aprotonic solvents > prontonic solvents.
- It is quite possible for the same reaction to go by the SN1 in one solvent and the SN2 in another. (see: *J. Am. Chem. Soc.* 1961, 83, 618)

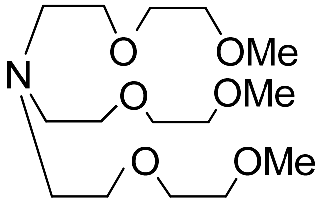
- **Phase Transfer Catalysis**

A difficulty that occasionally arises when carrying out nucleophilic substitution reactions is that the reactants do not mix.



$Q^+ = R_4N^+$ or R_4P^+

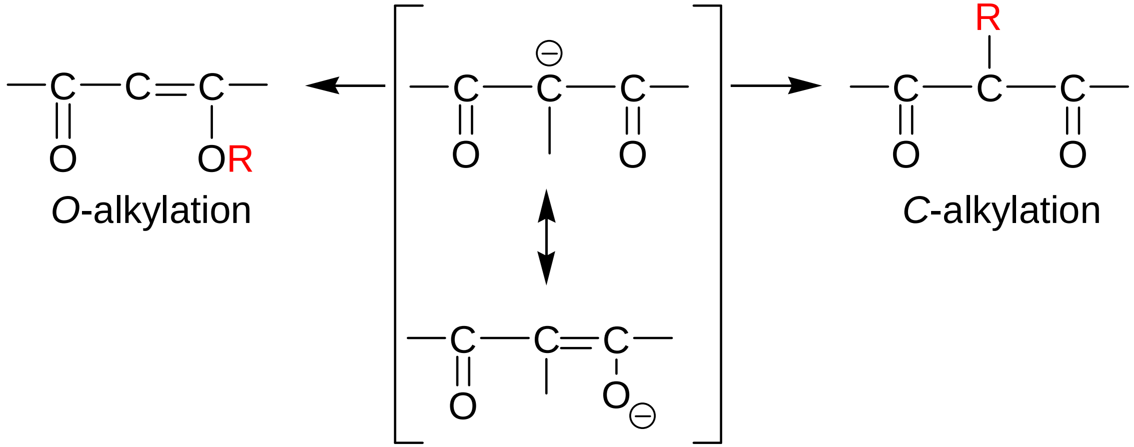


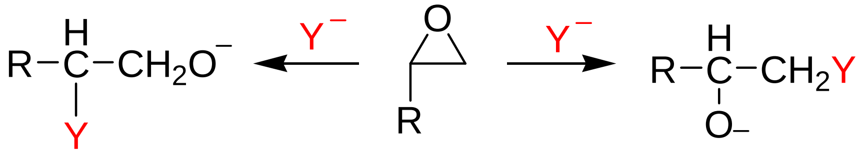


- **Ambident Nucleophiles / Substrates. Regioselectivity**

➢ Ambident nucleophiles: Some nucleophiles have a pair of electrons on each of two or more atoms, or canonical forms can be drawn in which two or more atoms bear an unshared pair.

➢ Ambident substrates: Some substrates (e.g., 1,3-dichlrorbutane) can be attacked at two or more positions.

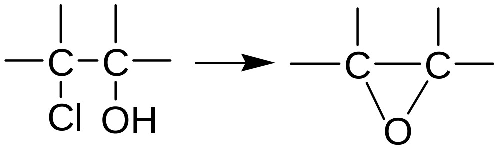




E. Reactions

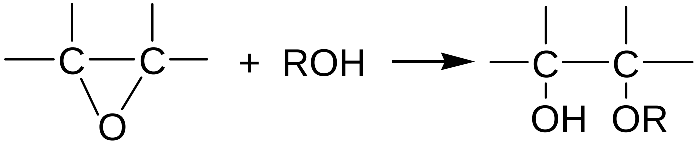
$RX + OH^- \longrightarrow ROH$

$RX + OR'^- \longrightarrow ROR'$



$R{-}OSO2OR'' + OR' \longrightarrow ROR'$

$2\ ROH \longrightarrow ROR$



$R_3O^+ + R'OH \longrightarrow ROR'$

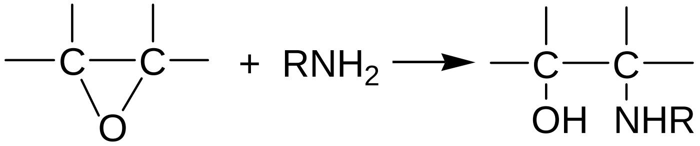
$RX + R'COO^- \longrightarrow R'COOR$

$RX + OOH^- \longrightarrow ROOH$

$RX + R'_2NH \longrightarrow RR'_2N$

$RX + R'_3N \longrightarrow RR'_3N^+X^-$

$RX + R'CONH^- \longrightarrow RNHCOR'$



$RCOX + H_2O \longrightarrow RCO_2H$

$RCOOCOR' + H_2O \longrightarrow RCO_2H + R'CO_2H$

$RCO_2R' + H_2O \longrightarrow RCO_2H + R'OH$

$RCONR' + H_2O \longrightarrow RCO_2H + R'_2NH$ (R = H, alkyl, aryl)

$RCOX + R'OH \longrightarrow RCO_2R'$

$RCOOCOR + R'OH \longrightarrow RCO_2R'$

$RCOOH + R''OH \longrightarrow RCO_2R'' + R'OH$

$RCOX + R'COO^- \longrightarrow RCOOCOR'$

$RCOX + H_2O_2 \longrightarrow RCO_3H$

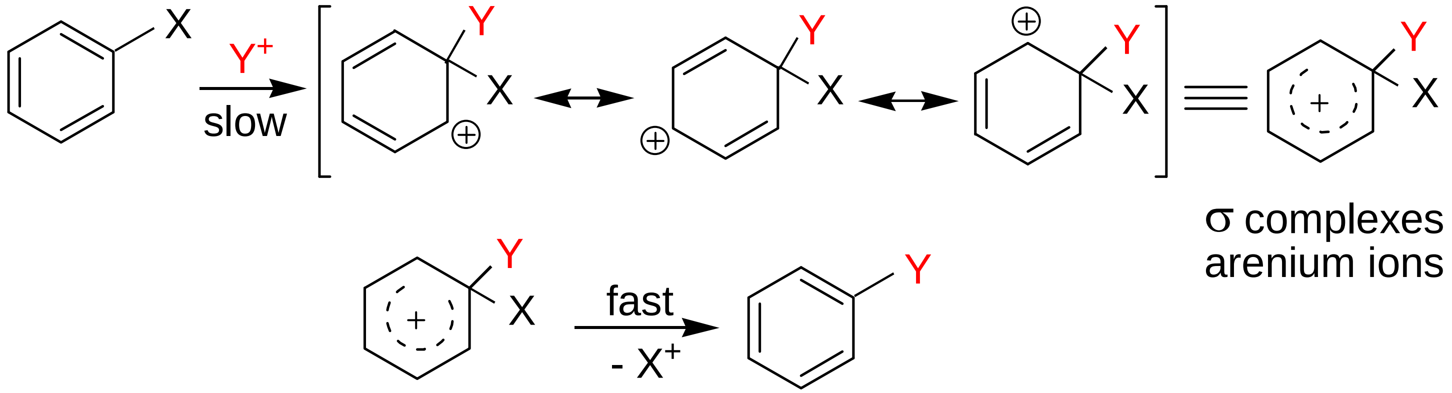
II. Aromatic Electrophilic Substitution

◆ Most substitution at an aliphatic carbon are nucleophilic. In aromatic systems the situation is reversed, because the high electron density at the aromatic ring attracts positive species and not negative ones. In electrophilic substitutions the attacking species is a positive ion or the positive end of a dipole or induced dipole. The leaving group must necessarily depart without its electron pair.

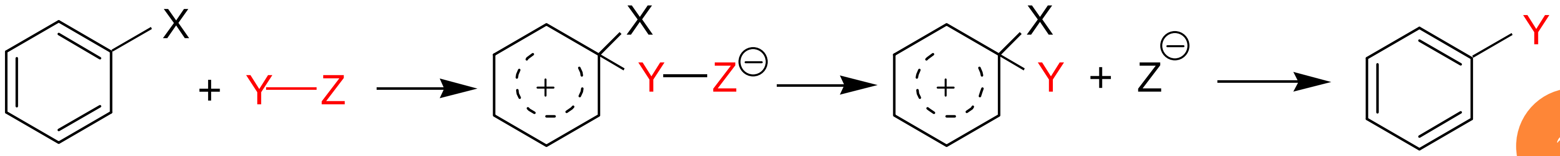
◆ In nucleophilic substitutions, the chief leaving groups are those best able to carry the unshared pair: Br－, H_2O, OTs－, etc., that is, the weakest bases. In electrophilic substitutions the most important leaving groups are those that can best exist without the pair of electrons necessary to fill the outer shell, that is, the weakest Lewis acids. The most common leaving group in electrophilic aromatic substitutions is the proton (H^+).

A. The Arenium Ion Mechanism

- In the arenium ion mechanism the attacking species may be produced in various ways, but what happens to the aromatic ring is basically the same in all cases. For this reason most attention in the study of this mechanism centers around the identity of the attacking entity and how it is produced.



σ complexes
arenium ions



The attacking species
is not an ion but a dipole.

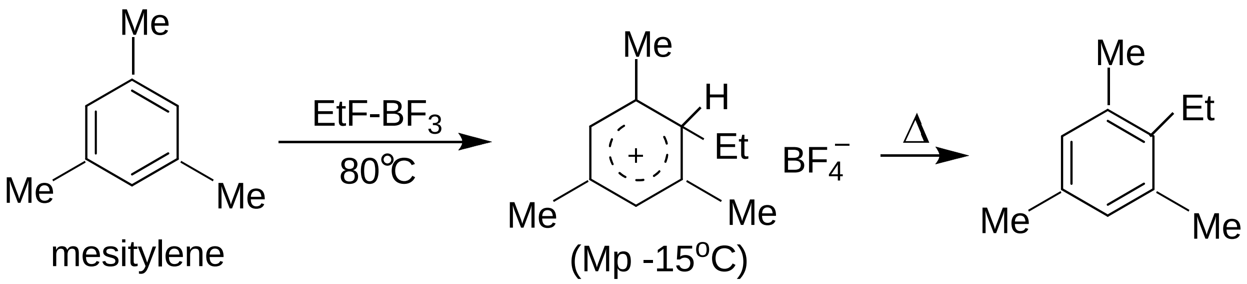
➢ **Evidence:**

i. No isotope effects

If the hydrogen ion departs before the arrival of the electrophile or if the arrival and departure are simultaneous, there should be a substantial isotope effect (i.e., deuterated substrates should undergo substitution more slowly than nondeuterated compounds) because, in each case, the C—H bond is broken in the rate-determining step.

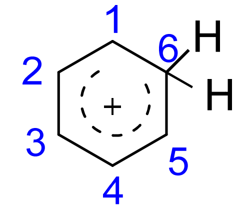
However, in the arenium ion mechanism, the C—H bond is not broken in the rate-determining step, so no isotope effect should be found.

ii. Isolation of arenium ion intermediates



mesitylene

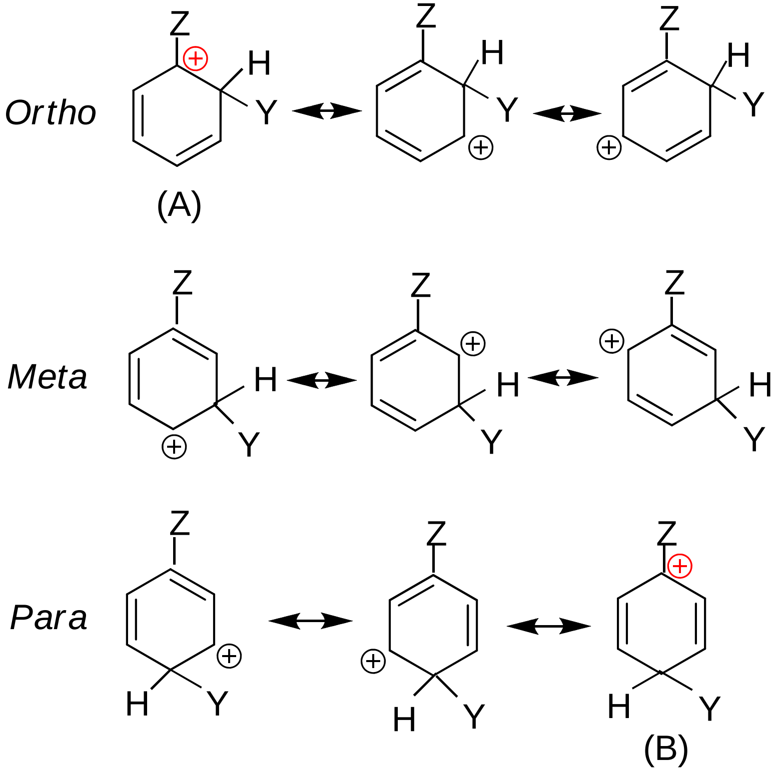
(Mp -15°C)



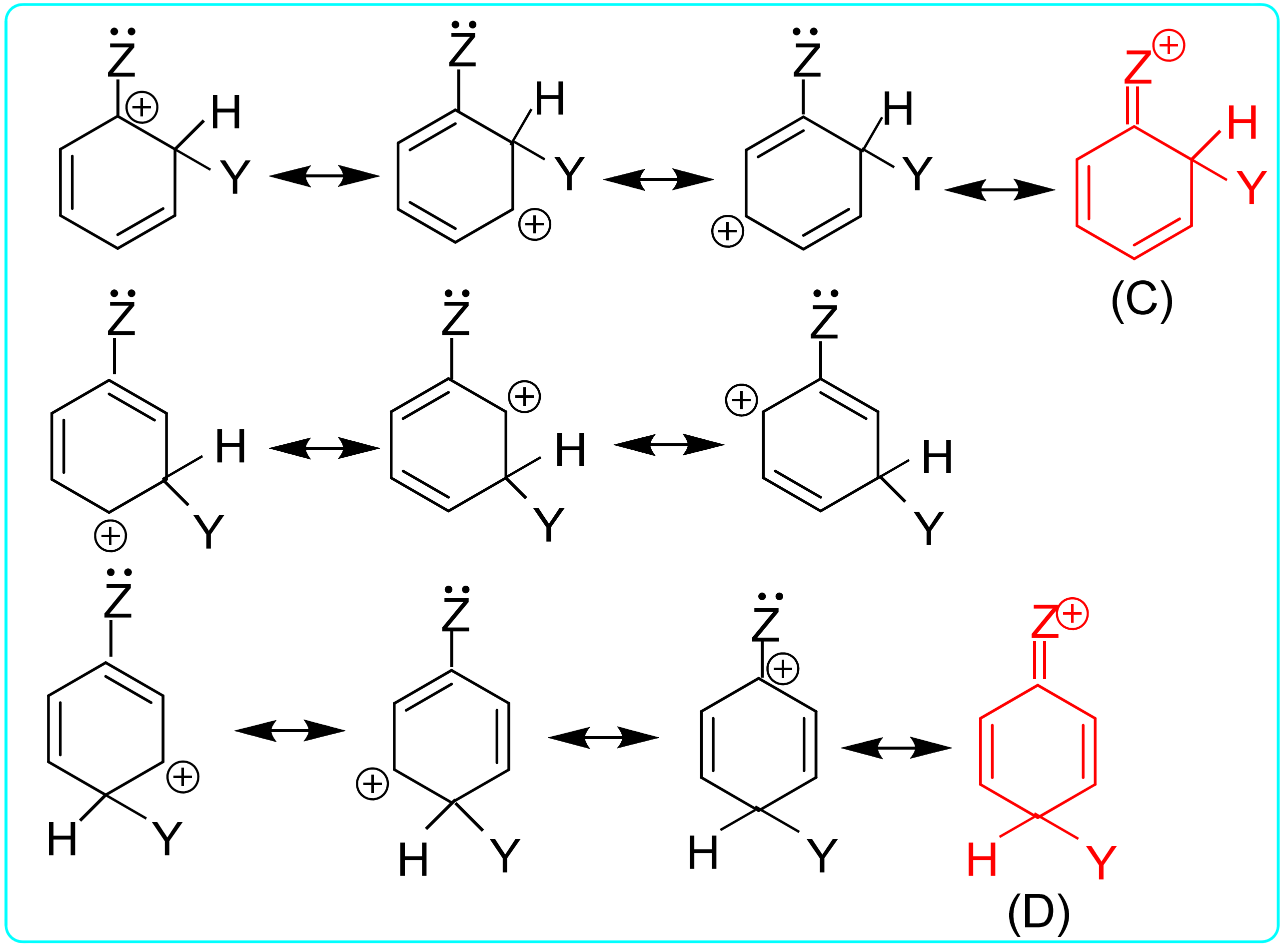
Benzenonium ion in HF-SbF$_5$-SO$_2$ClF-SO$_2$F$_2$ at -134°C

B. Orientation and Reactivity

➢ Monosubstituted Benzene Rings



- Any group Z that has an electron donating field effect should stabilize all three ions.
- Electron-withdrawing groups will increase the positive charge on the ring, and destabilize the arenium ion.
- Field effects should taper off with distance and are strongest at the carbon connected to the group Z. +*I* groups should stabilize all three ions but mostly the ortho and para



Some substituents have a pair of electrons (usually unshared) that may be contributed toward the ring. Not only to direct ortho and para, but also to activate these positions for electrophilic attack

Three Types of Groups:

i. Groups that contain an unshared pair of electrons on the atom connected to the ring.

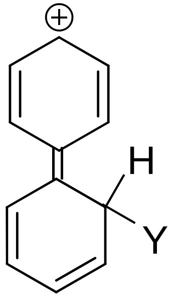
O^-, NR_2, NHR, NH_2, OH, OR, NHCOR, OCOR, SR, the four halogens, and SH (except for the case of thiophenols electrophiles usually attack the sulfur rather than the ring).
☞ Cl, Br, and I deactivate the ring, but they direct ortho-para.

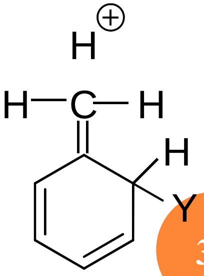
ii. Groups that lack an unshared pair on the atom connected to the ring and that are –*I*.

Approximate deactivating ability: $NR_3^+ > NO_2 > CF_3 > CN > SO_3H > CHO > COR > COOH > COOR > CONH_2 > CCl_3 > NH_3^+$.
☞ The NH_3^+ group is an anomaly, since this group directs *para* about as much as or a little more than it directs *meta*.

iii. Groups that lack an unshared pair on the atom connected to the ring and that are *ortho-para*-directing.

–R, –Ar, –COO⁻ groups, which active the ring.


(E)

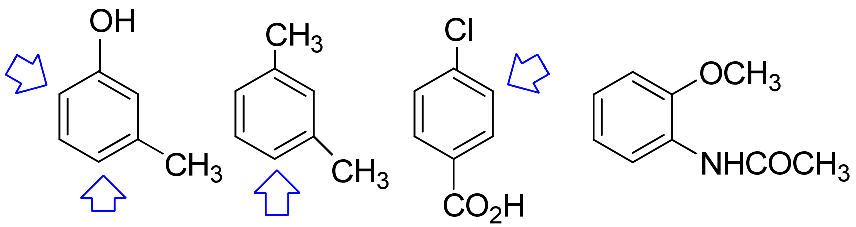

(F)

➢ Orientation in Benzene Rings with More than One Substituent

Generalization

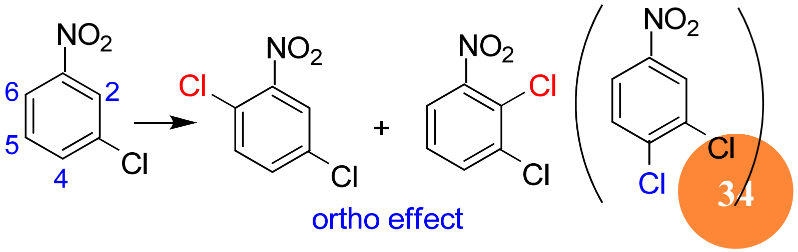
i. If a strong activating group competes with a weaker one or with a deactivating group, the former controls.

Directing order: NH_2, OH, NR_2, O^- > OR, OCOR, NHCOR >, R, Ar > halogen > *meta*-directing groups.



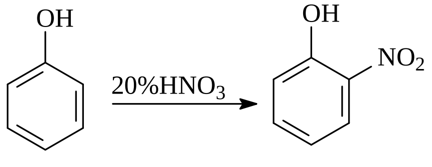
ii. All other things being equal, a third group is least likely to enter between two groups in the *meta* relationship (steric hindrance).

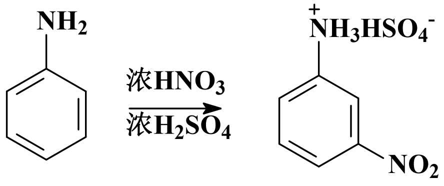
iii. When a *meta*-directing group is *meta* to an *ortho-para*-directing group, the incoming group primarily goes *ortho* to the *meta*-directing group rather than *para*.



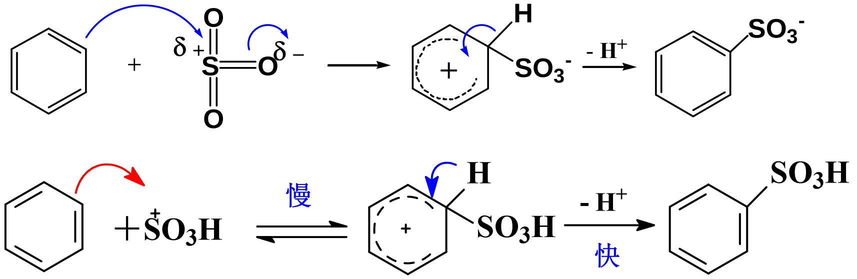
Reactions

Nitration



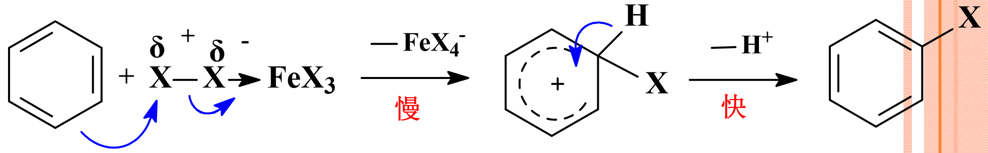


Sulfonation



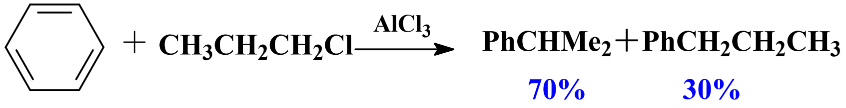
Halogenation

$$X_2 + FeX_3 \rightleftharpoons \overset{\delta+}{X}—\overset{\delta-}{X}\rightarrow FeX_3$$

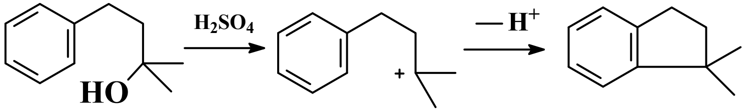


Fridel-Crafts Reactions

$$R—Cl + AlCl_3 \rightleftharpoons \overset{\delta+}{R}\text{--}\overset{\delta-}{Cl}\text{--}AlCl_3 \rightleftharpoons R^+ + AlCl_4^-$$



$$CH_3CH_2CH_2Cl + AlCl_3 \xrightarrow{-AlCl_4^-} CH_3CH_2\overset{+}{C}H_2 \rightleftharpoons CH_3\overset{+}{C}HCH_3$$



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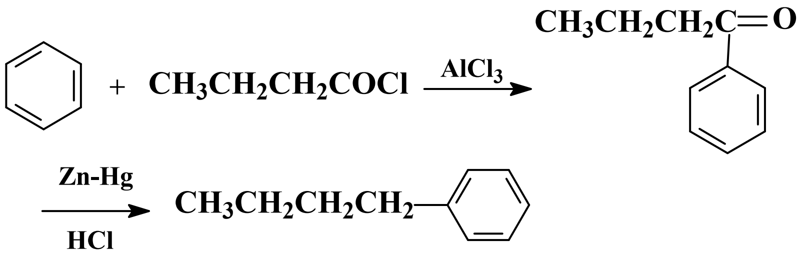
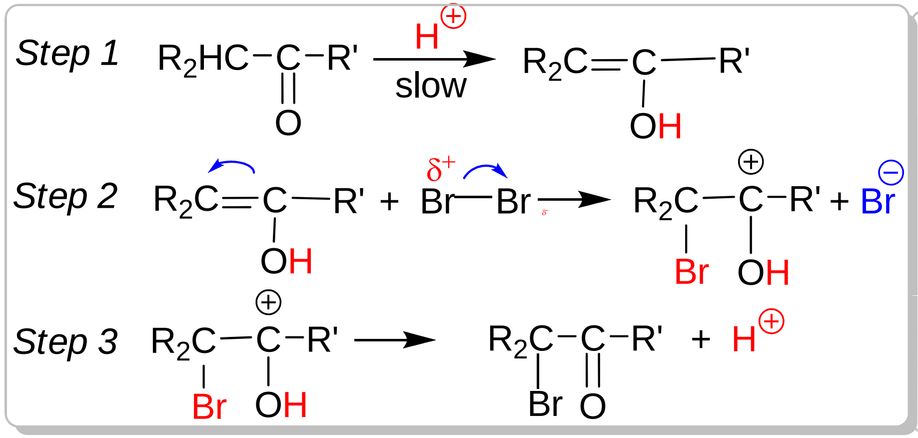


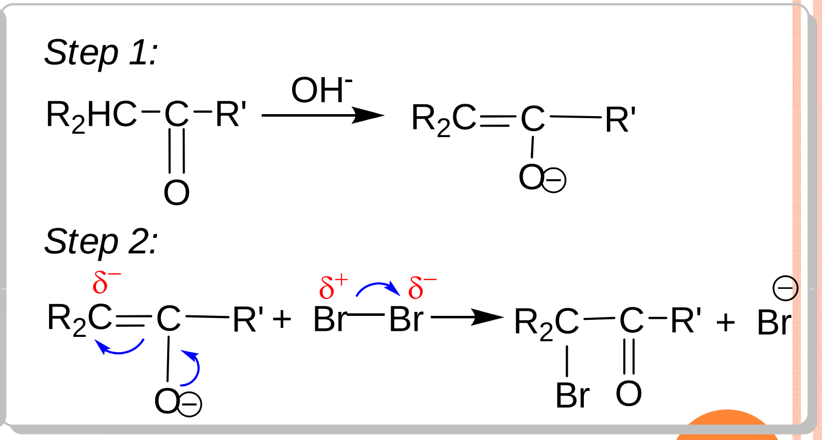
III. Aliphatic Electrophilic Substitution

MECHANISMS

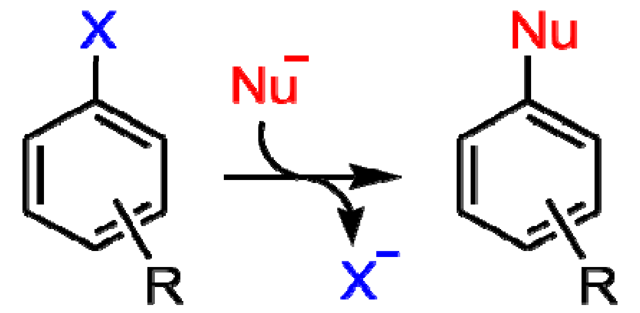
Aliphatic electrophilic substitution can be distinguish unimolecular (SE1) and bimolecular (SE2). The bimolecular mechanisms are analogous to the SN2 mechanism in that the new bond forms as the old one breaks.

Halogenation of Aldehydes and Ketones:





IV. Aromatic Nucleophilic Substitution



X = halogen etc. Nu = nucleophile

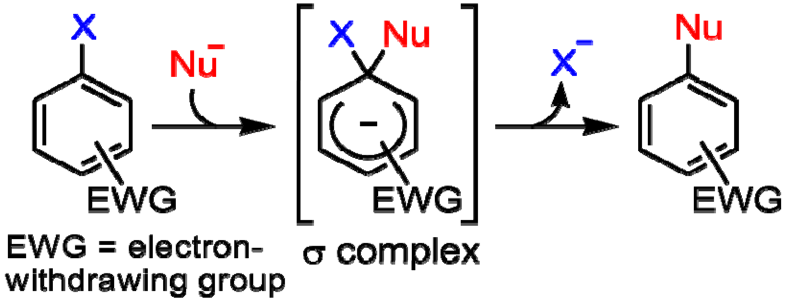
i. Reactions activated by electron-withdrawing groups *ortho* and *para* to the leaving group;

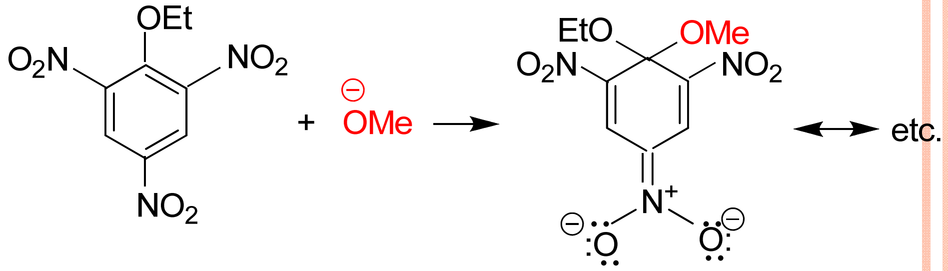
ii. Reactions catalyzed by very strong bases and proceeding through aryne intermediates; 苯炔

iii. Reactions initiated by electron donor;

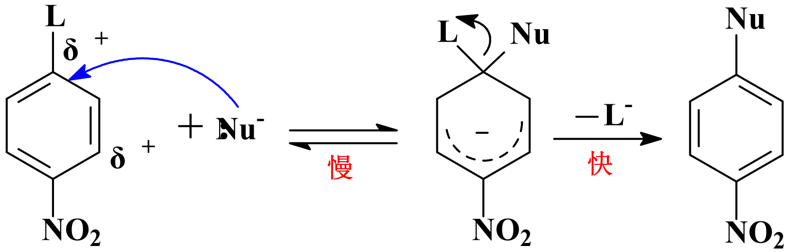
iv. Reactions in which the nitrogen of a diazonium salt is replaced by a nucleophile. 重氮盐

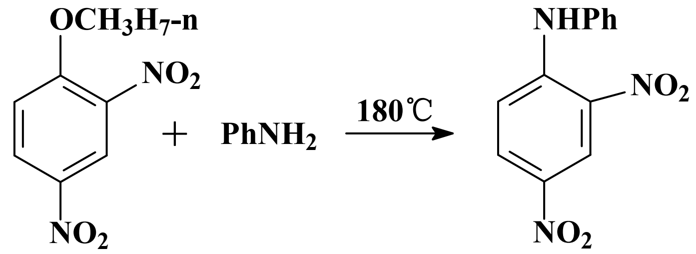
- the S_NAr (addition-elimination) mechanism



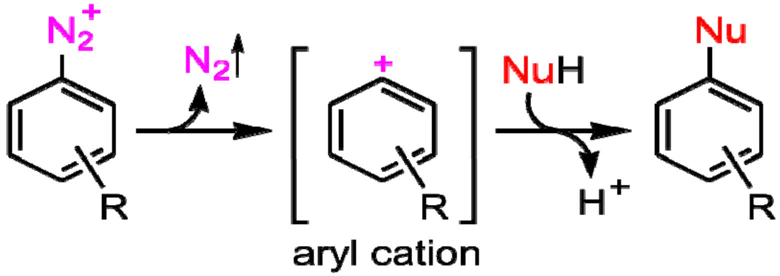


Meisenheimer-Jackson salt
1902

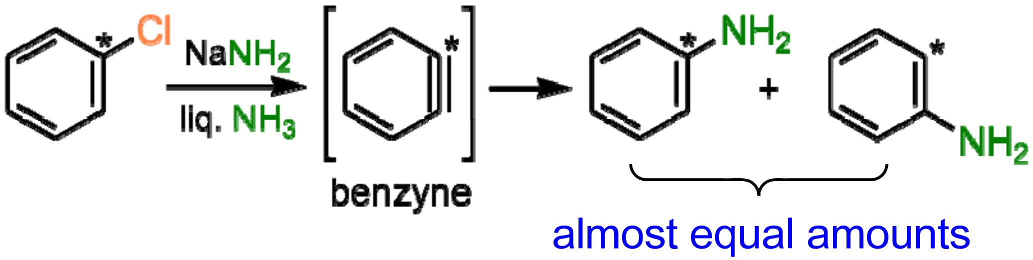


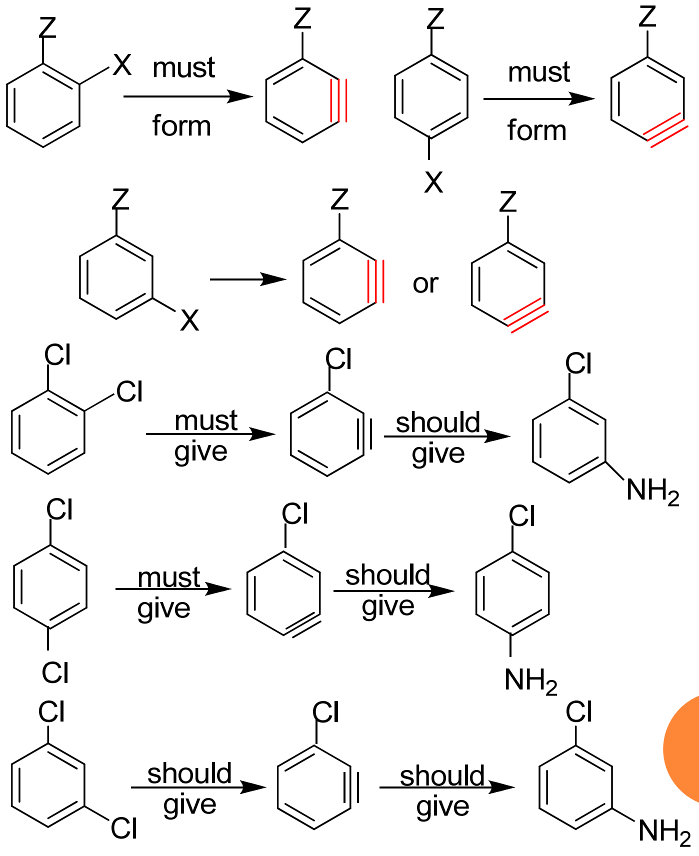


- the aromatic S_N1 mechanism



The Benzyne Mechanism





Two factors affect the positions of the incoming group:

i. The direction in which the aryne forms.

ii. The aryne, once formed, can be attacked by two positions. The favored position for nucleophilic attack is the one that leads to the more stable carbanion intermediate, and this in turn also depends on the field effect of Z.

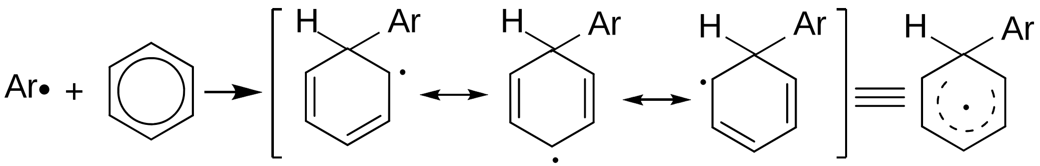
VI. Free-Radical Substitution

Some general characteristics:

1. Reactions are fairly similar whether they are occurring in the vapor or liquid phase, though solvation of free radicals in solution does cause some differences.
2. They are largely unaffected by the presence of acids or bases or by changes in the polarity of solvents, except that nonpolar solvents may suppress competing ionic reactions.
3. They are initiated or accelerated by typical free-radical sources, such as the peroxides referred to, or by light.
4. Their rates are decreased or the reactions are suppressed entirely by substrates that scavenge free radicals, e.g., nitric oxide, molecular oxygen, or benzoquinone. These substances are called inhibitors.

➢ Mechanisms at an Aromatic Substrate

In the first step, the radical attracts the ring in much the same way as would an electrophile or a nucleophile:



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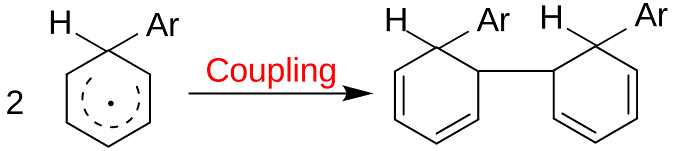

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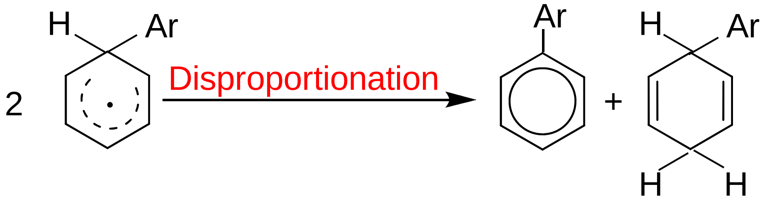

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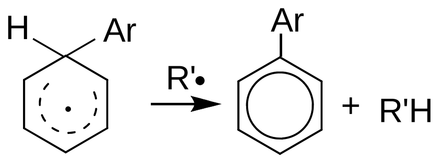

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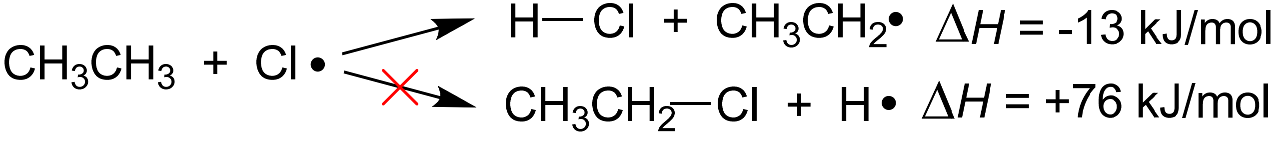
➢ REACTIVITY IN ALIPHATIC SUBSTRATES

In a chain reaction, the step that determines what the product will be is most often an abstraction step. What is abstracted by a radical is nearly always univalent, it is hydrogen or halogen for organic compounds.



$$CH_3CH_3 + Cl\bullet \rightarrow H{-}Cl + CH_3CH_2\bullet \quad \Delta H = -13\ \text{kJ/mol}$$

$$CH_3CH_3 + Cl\bullet \not\rightarrow CH_3CH_2{-}Cl + H\bullet \quad \Delta H = +76\ \text{kJ/mol}$$

i. A univalent atom is much more exposed to attack by the incoming radical;
ii. In many cases abstraction of a univalent atom is energetically more favored.

Table 5. Relative susceptibility to attack by Cl· of promary, secondary, and tertiary hydrogen in the gas phase

Temp. / °C	Primary	Secondary	Tertiary
100	1	4.3	7.0
600	1	2.1	2.6

Temperature ↑ selectivity ↓

Table 6. Relative substitution rates

	CH_3H	CH_3CH_2–H	$(CH_3)_2CH$–H	$(CH_3)_3C$–H	$PhCH_2$–H	Ph_2CH–H	Ph_3C–H
Br·	0.0007	1	220	19400	64000	1.1×10^6	6.4×10^6
Cl·	0.004	1	4.3	6.0	1.3	2.6	9.5

Compounds containing electron-withdrawing substituents

	CH_3 —	CH_2 — COOH
CH_3·	1	7.8
Cl·	1	0.03

Electrophilic radical: halogen atoms
Nucleophilic radical: Me•, t-butyl, benzyl, cyclopropyl

☞ When the substrate molecule contains a double bond, treatment with chlorine or bromine leads to addition rather than substitution.

☞ Vinylic hydrogens are practically never abstracted, allylic hydrogens are greatly preferred to other position of the molecule.

➢ REACTIVITY IN AROMATIC SUBSTRATES

Generalizations:

i. All substituents increase reactivity at *ortho* and *para* positions over that of benzene. There is no great difference between electron-donating and electron-withdrawing groups.

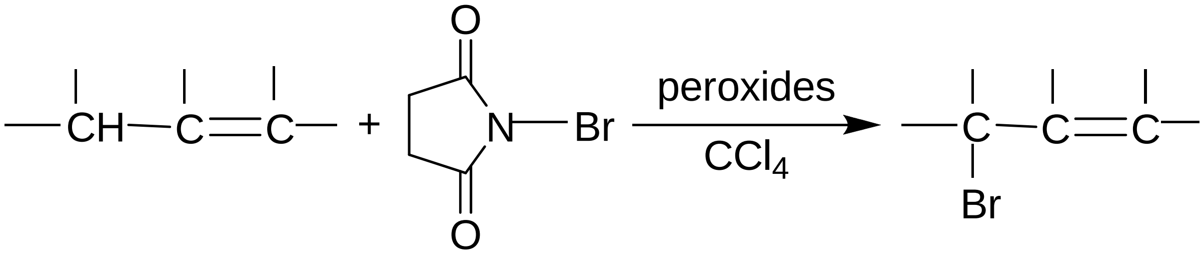
ii. Reactivity at *meta* positions is usually similar to that of benzene, perhaps slightly higher or lower. This fact, coupled with the preceding one, means that all substituents are activating and *ortho-para*-directing; none are deactivating or (chiefly) meta-directing.

iii. Reactivity at *ortho* position is usually somewhat greater than at *para* positions, except where a large group decreases *ortho* reactivity for steric reasons.

REACTIONS

Allylic Halogenation

Olefins can be halogenated in the allylic position by a number of reagents, of which N-bromosuccinimide (NBS) is by far the most common.



NBS (Wohl-Ziegler bromination)

Coupling of Alkynes

$$2\ R-C\equiv C-H \xrightarrow[\text{pyridine}]{CuX_2} R-C\equiv C-C\equiv C-R$$

The mechanism of the reaction probably begins with loss of a proton, then carbanion becomes oxidized to the radical.

6-2 Addition to Multiple Bonds

There are basically four ways in which addition to a double or triple bond can take place.

◆ **A two-step process**, with initial attack by a **nucleophile**, an **electrophile**, or a **radical**, and then second step consists of combination of the resulting intermediate with, respectively, a positive species, a negative species, or a neutral entity.

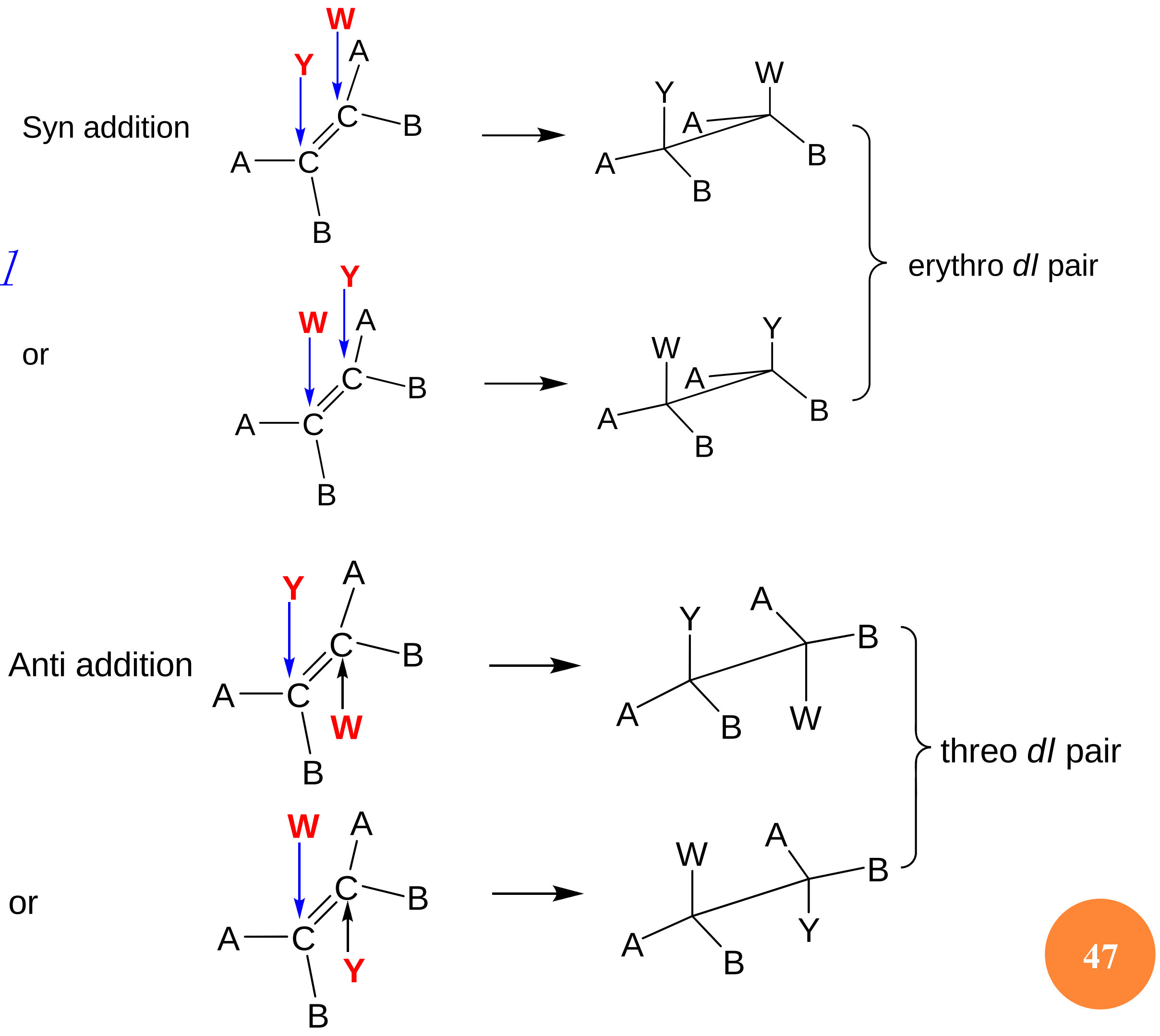
◆ **A one-step mechanism**, attack at the two carbon atoms of the double or triple bond is simultaneous.

Which of the four mechanisms is operating in any given case is determined by the nature of the substrate, the reagent, and the reaction conditions.

I. Stereochemistry

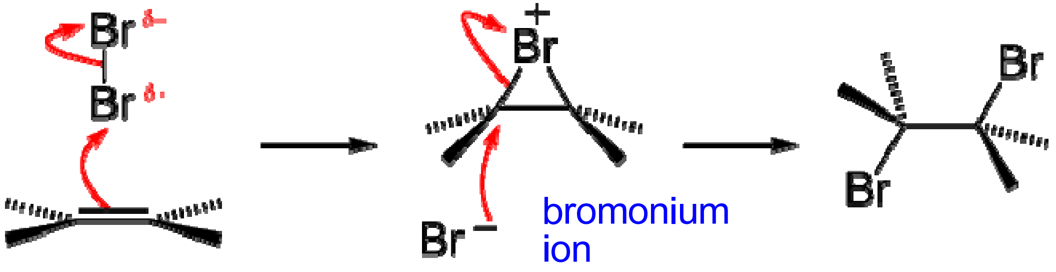
◆ Syn addition→ the erythro *dl* pair

◆ Anti addition → the threo *dl* pair

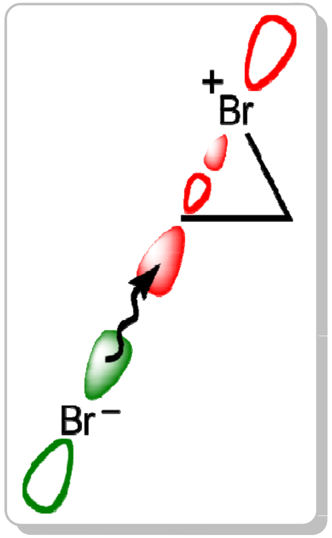


II. Electrophilic Addition

There is much evidence that when the attack is by Br^+ (or a carrier of it), the bromonium ion is often an intermediate and the addition is anti.



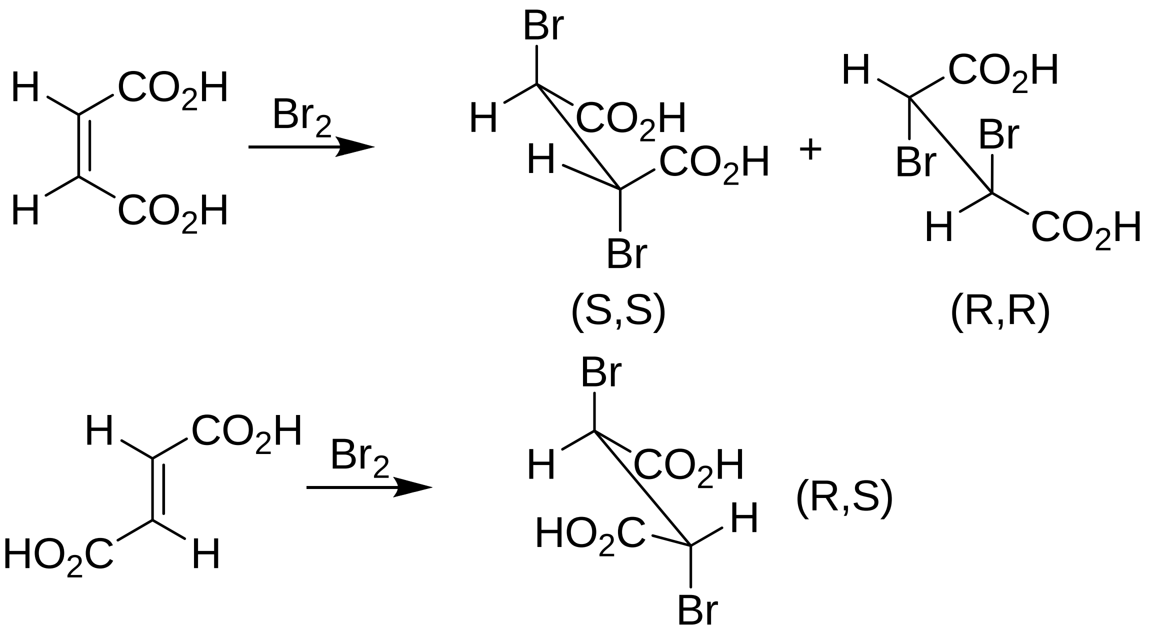
The atom is electrophilic at this time and attacks the negatively charged, high energy π-bond portion of the alkene's C=C bond. It forms for an instant a single σ-bond to *both* of the carbon atoms involved.

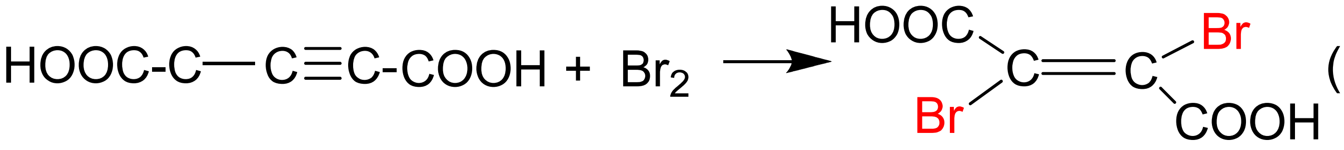


A bromide ion attacks the C–Br σ^* antibonding molecular orbital of a bromonium ion.

The two halogens add in an anti addition fashion, and when the alkene is part of a cycle the dibromide adopts the trans configuration.

- Brominations of maleic acid and fumaric acid: stereospecific *trans*-addition:




$HOOC\text{-}C{-}C{\equiv}C\text{-}COOH + Br_2 \longrightarrow$

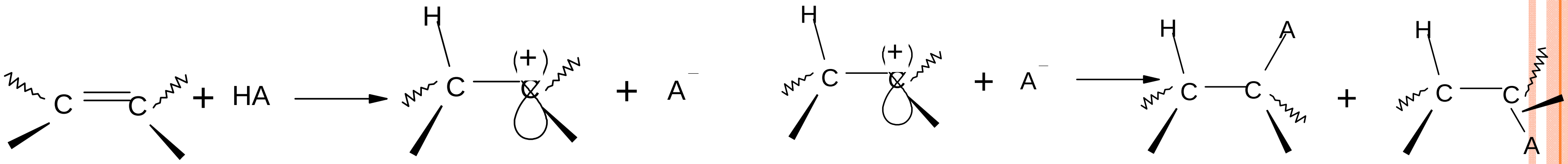
(70% trans)

When the electrophile is a proton:

i. The reaction is general-acid, implying rate-determining proton transfer from the acid to the double bond.

ii. The existence of alkyl substituent effects.

iii. Open carbocations are prone to rearrange.

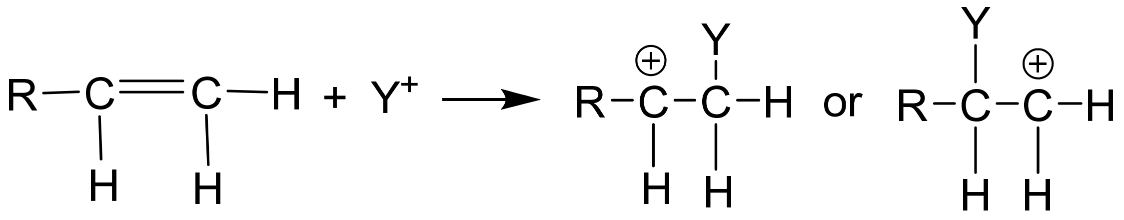


The Reactivity Toward Electrophilic Addition:

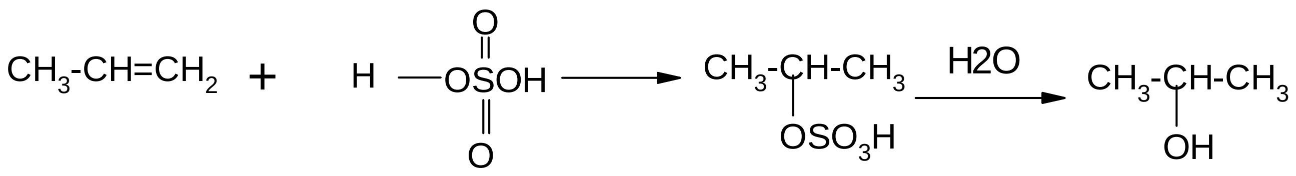
$CCl_3CH=CH_2 < CHCl_2CH=CH_2 < CH_2ClCH=CH_2 < CH_3CH=CH_2$

$(CH_3)_2C=C(CH_3)_2 > (CH_3)_2C=CHCH_3 > (CH_3)_2C=CH_2 > CH_3CH=CH_2 > CH_2=CH_2$

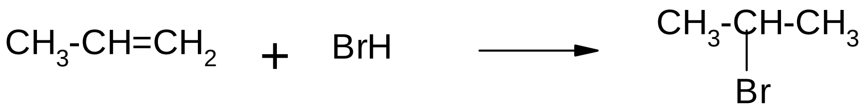
➢ **Orientation — Markovnikov's rule:** For electrophilic attack, the positive portion of the reagent goes to the side of the double or triple bond that has more hydrogens.



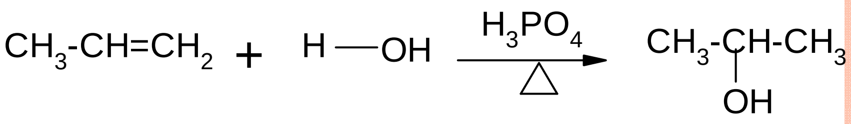
$$R-CH=CH-H + Y^+ \longrightarrow R-\overset{\oplus}{C}H-CH(Y)-H \text{ or } R-CH(Y)-\overset{\oplus}{C}H-H$$



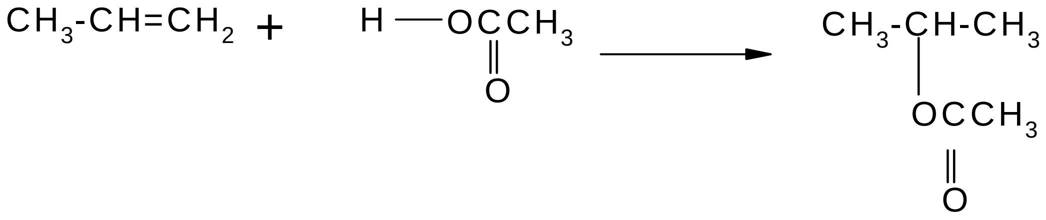
$$CH_3\text{-}CH{=}CH_2 + H\text{—}OSO_2OH \longrightarrow CH_3\text{-}CH(OSO_3H)\text{-}CH_3 \xrightarrow{H2O} CH_3\text{-}CH(OH)\text{-}CH_3$$



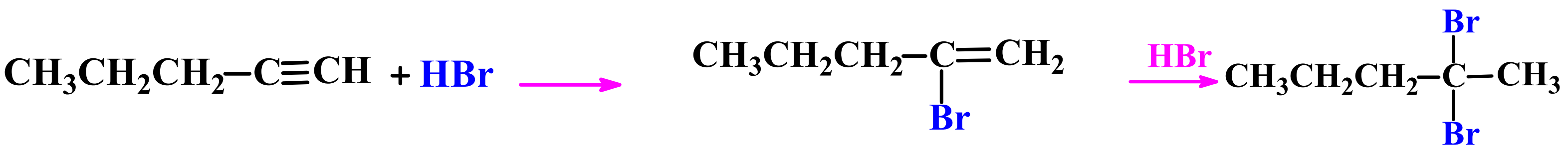
$$CH_3\text{-}CH{=}CH_2 + BrH \longrightarrow CH_3\text{-}CH(Br)\text{-}CH_3$$



$$CH_3\text{-}CH{=}CH_2 + H\text{—}OH \xrightarrow[\triangle]{H_3PO_4} CH_3\text{-}CH(OH)\text{-}CH_3$$

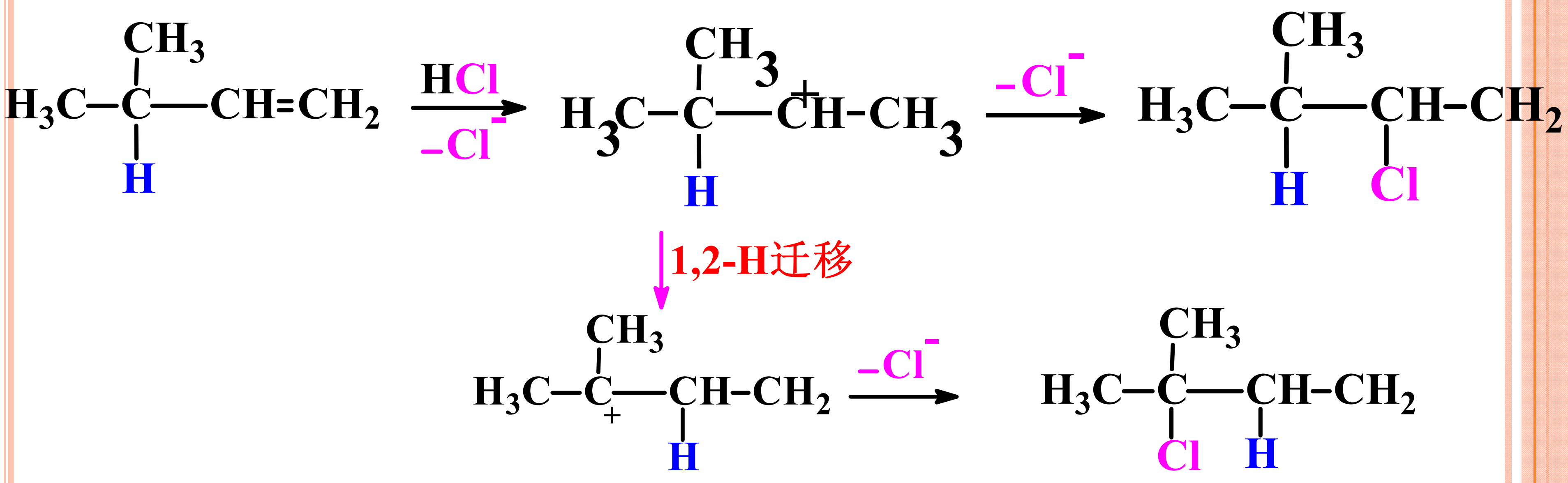


$$CH_3\text{-}CH{=}CH_2 + H\text{—}OC(=O)CH_3 \longrightarrow CH_3\text{-}CH(OC(=O)CH_3)\text{-}CH_3$$



$$CH_3CH_2CH_2\text{—}C{\equiv}CH + HBr \longrightarrow CH_3CH_2CH_2\text{—}C(Br){=}CH_2 \xrightarrow{HBr} CH_3CH_2CH_2\text{—}C(Br)_2\text{—}CH_3$$

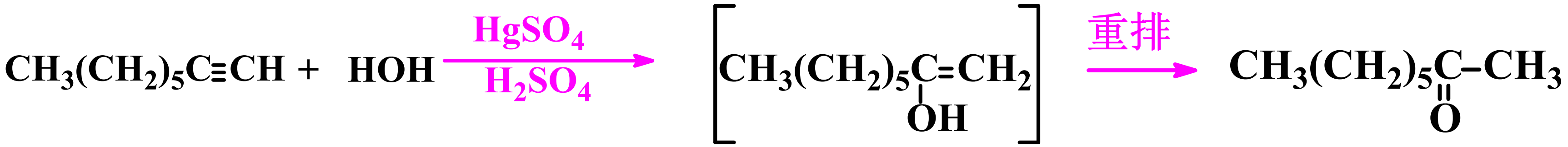
➢Rearrangement



$$H_3C-\underset{H}{\overset{CH_3}{C}}-CH=CH_2 \xrightarrow[-Cl^-]{HCl} H_3C-\underset{H}{\overset{CH_3}{C}}-\overset{+}{C}H-CH_3 \xrightarrow{-Cl^-} H_3C-\underset{H}{\overset{CH_3}{C}}-\underset{Cl}{CH}-CH_2$$

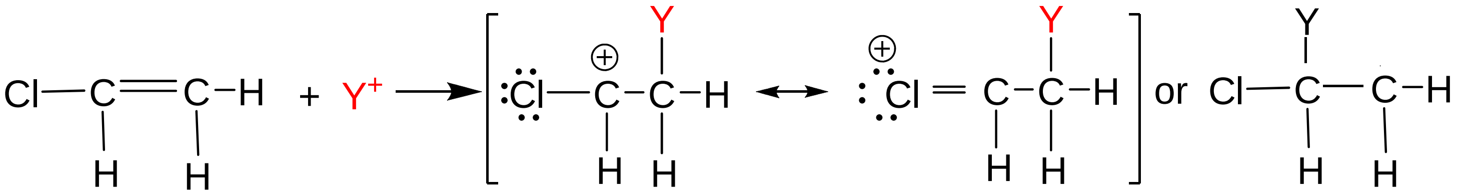
1,2-H迁移

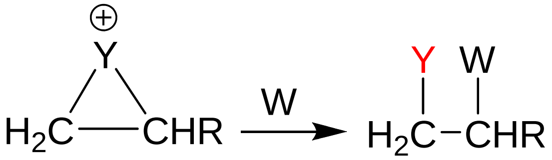
$$H_3C-\underset{+}{\overset{CH_3}{C}}-\underset{H}{CH}-CH_2 \xrightarrow{-Cl^-} H_3C-\underset{Cl}{\overset{CH_3}{C}}-\underset{H}{CH}-CH_2$$



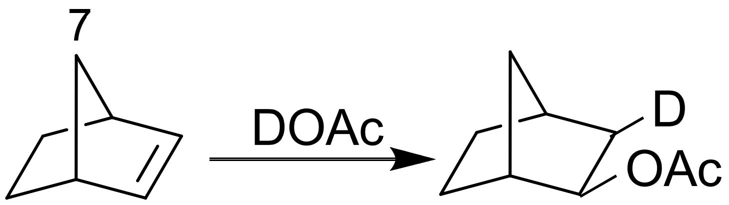
$$CH_3(CH_2)_5C\equiv CH + HOH \xrightarrow[H_2SO_4]{HgSO_4} \left[CH_3(CH_2)_5\underset{OH}{C}=CH_2\right] \xrightarrow{\text{重排}} CH_3(CH_2)_5\underset{O}{\underset{\|}{C}}-CH_3$$

☞ Markovnikov's rule also applies for halogen substituents or the case where bromonium ions or other three-membered rings are intermediates.



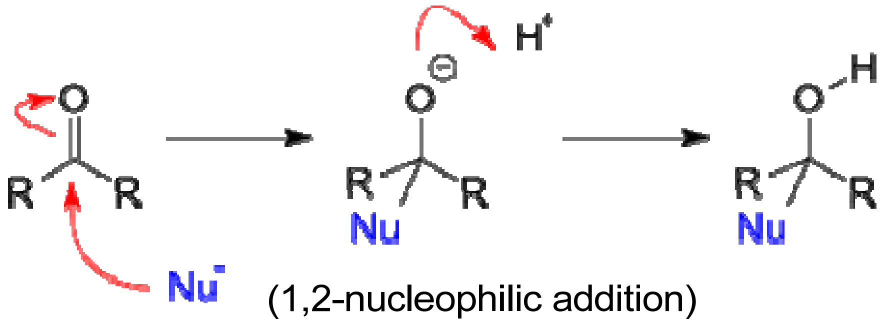


- **Stereochemical Orientation** Many electrophilic additions to norbornene and similar strained bicycloalkenes are syn addition, in these cases attack is always from the exo side. unless the exo side is blocked by substituents in the 7 position, in which case endo attack may predominate.



III. NUCLEOPHILIC ADDITION

A. Addition to Carbon-Hetero Multiple bonds

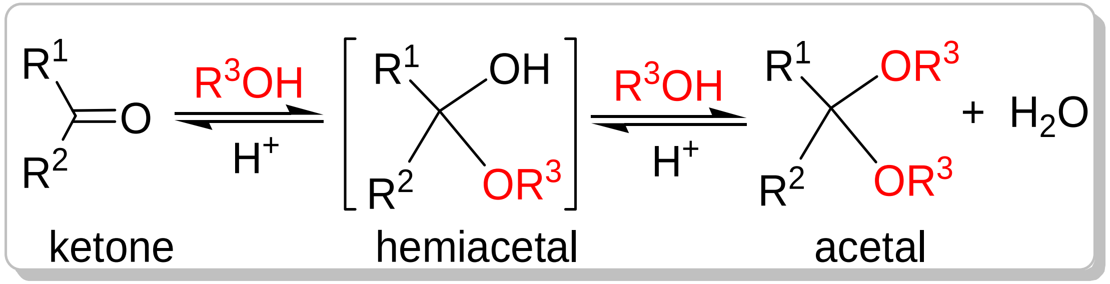


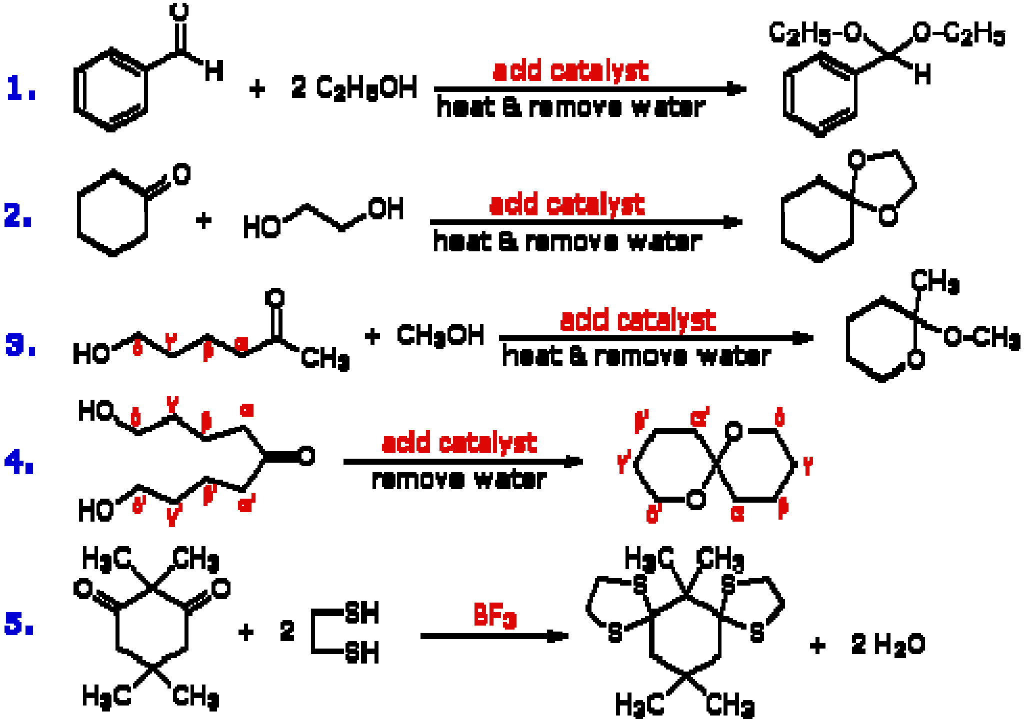
(1,2-nucleophilic addition)

➢ With a carbonyl compound electrophiles, the Nu can be:

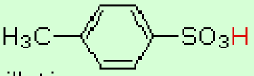
- an alcohol in Acetalisation
- an amine in Mannich reaction
- a ylides in Wittig reaction
- an enolate ion an Aldol reaction
- a hydride in reduction
- an organometallic nucleophile (RMgX) in the Grignard reaction

Acetalisation



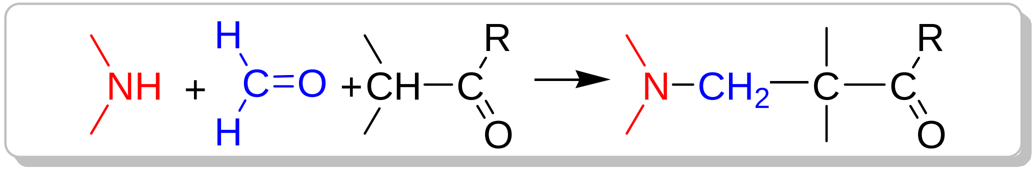


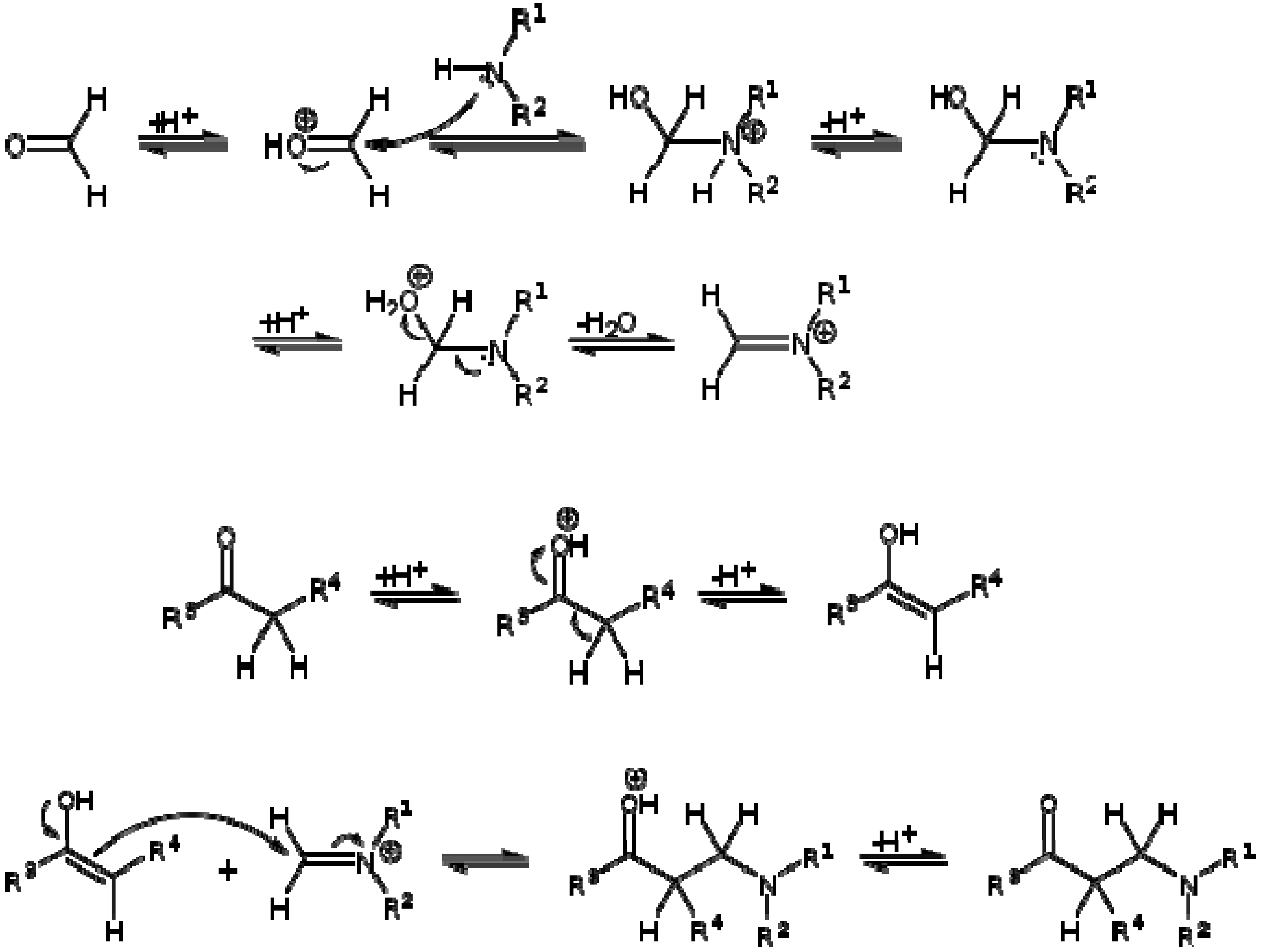
The acid often used to catalyze acetal formation is p-toluenesulfonic acid



Toluene is usually the solvent, and water is removed azeotropically by distillation

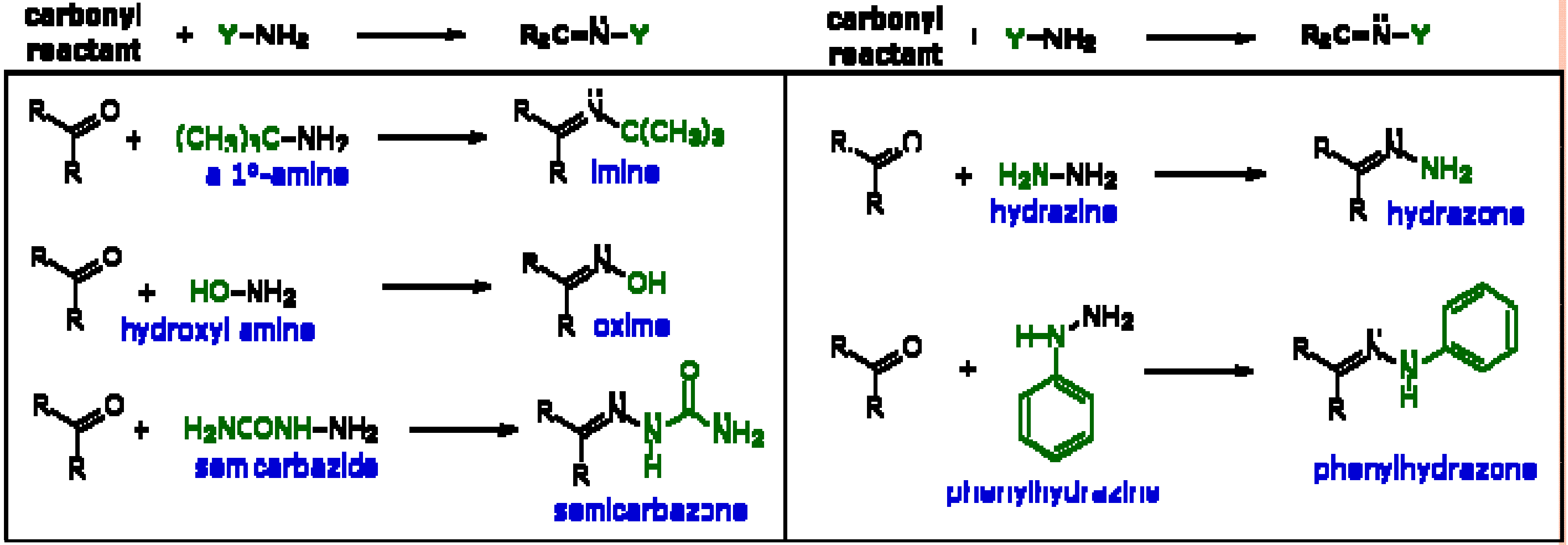
Mannich reaction



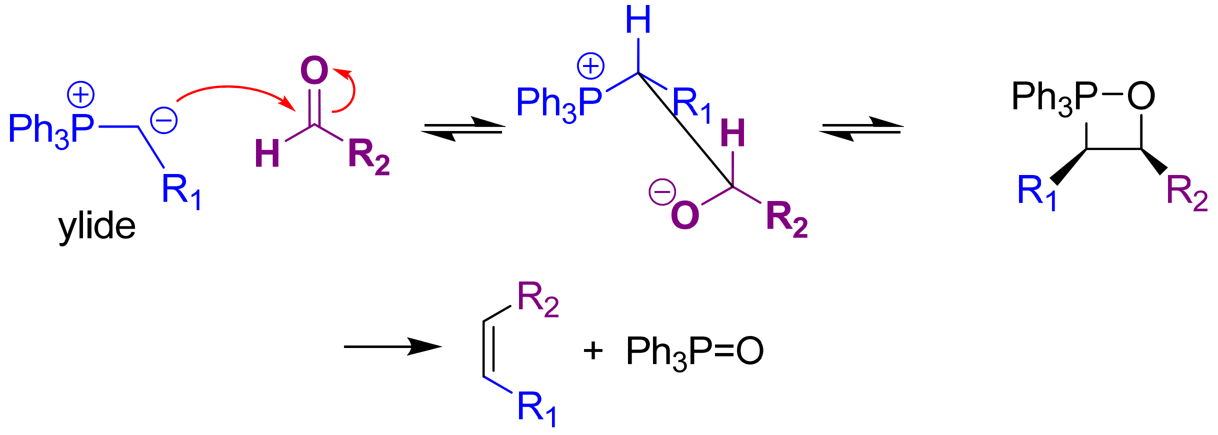


Schiff base

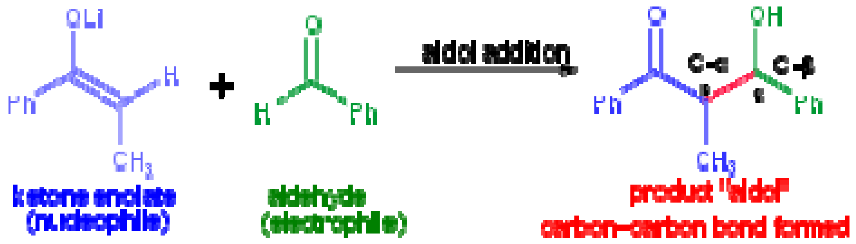
$$R_2C{=}O \quad + \quad R'NH_2 \rightleftharpoons R'NH\text{-}(R_2)C\text{-}O\text{-}H \rightleftharpoons R_2C{=}NR' \quad + \quad H_2O$$

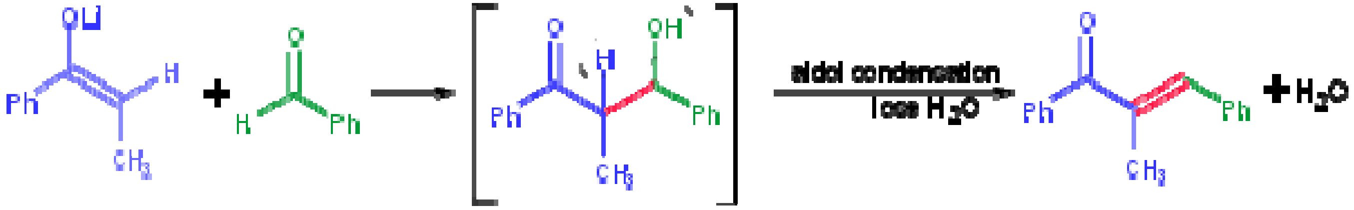


Wittig reaction

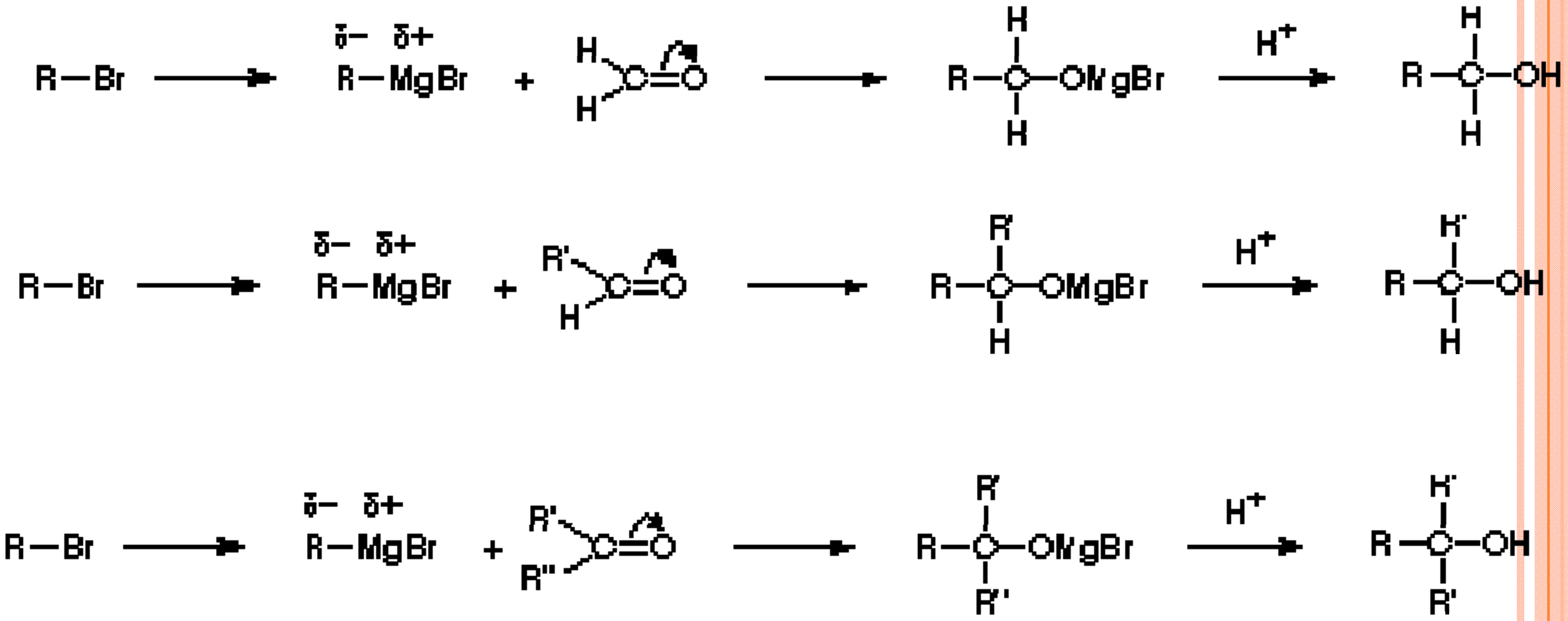


Aldol reaction



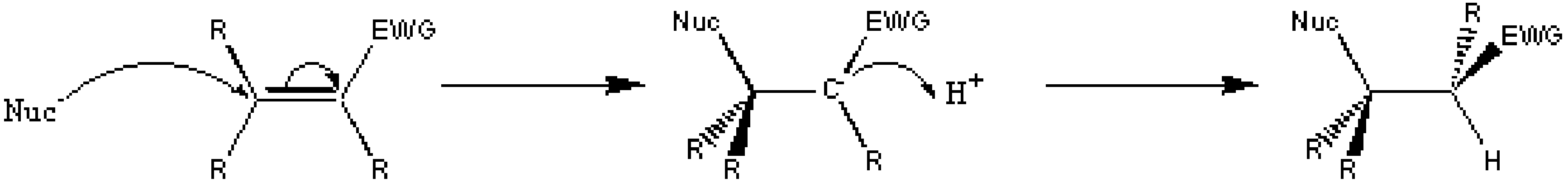


Grignard reaction

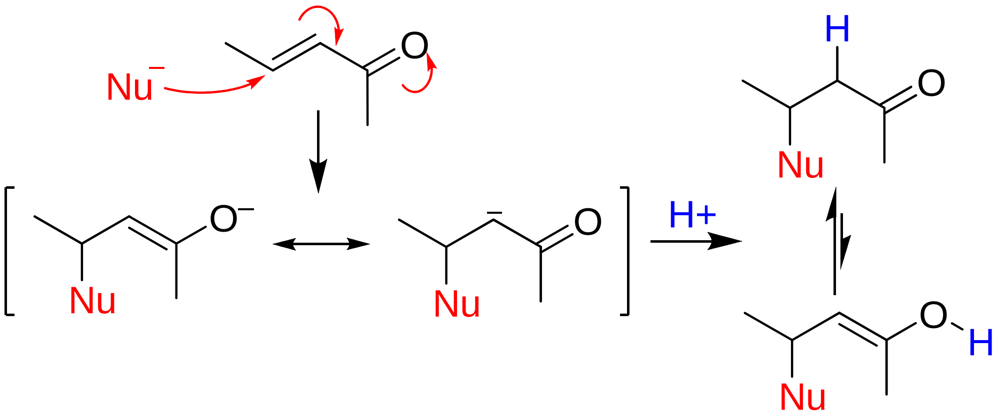


B. Addition to Carbon-Carbon Double Bonds

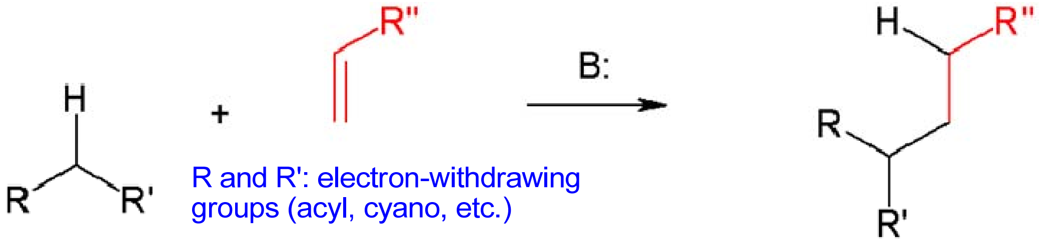
Ordinary alkenes are not susceptible to a nucleophilic attack (apolar bond).



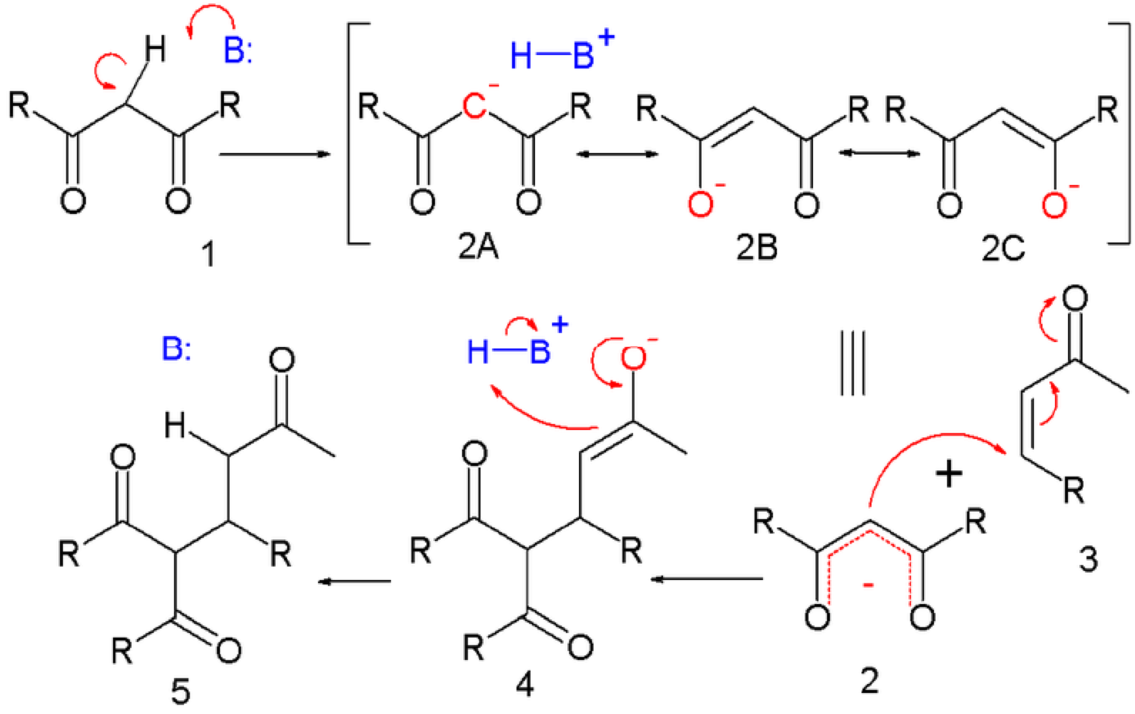
- Nucleophilic conjugate addition:



Michael reaction (1,4-addition)

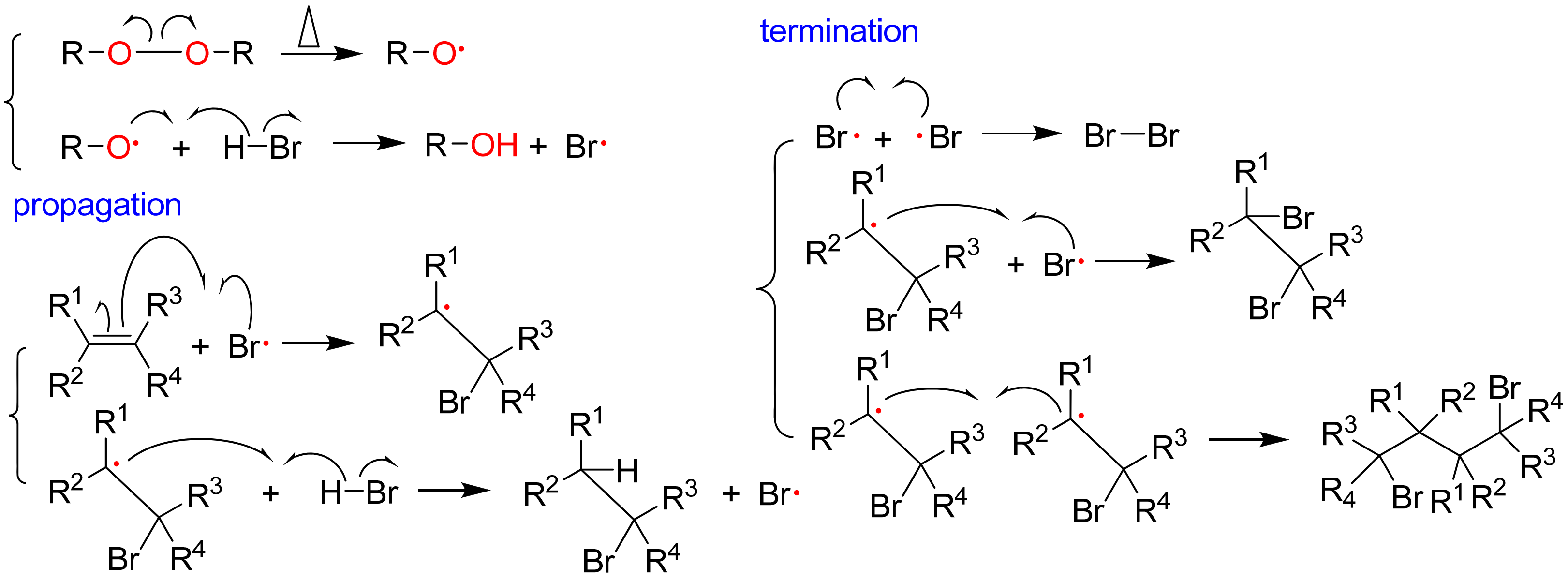


R and R': electron-withdrawing groups (acyl, cyano, etc.)



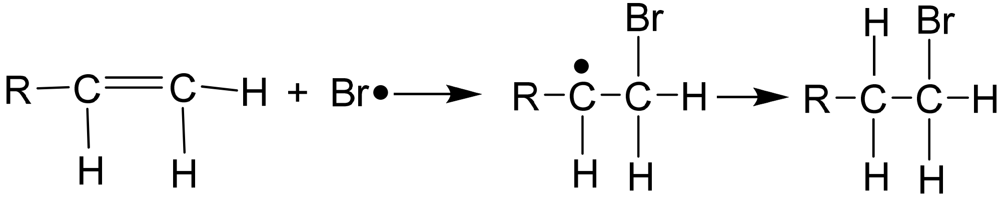
IV. FREE-RADICAL ADDITION

initiation



propagation

termination



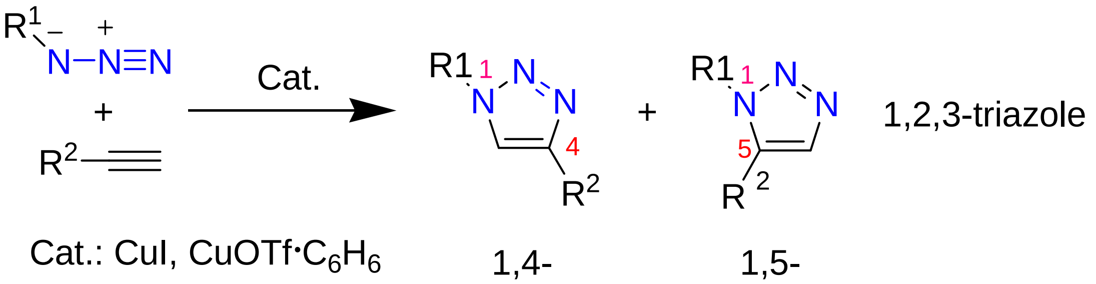
preferentially formed intermediate

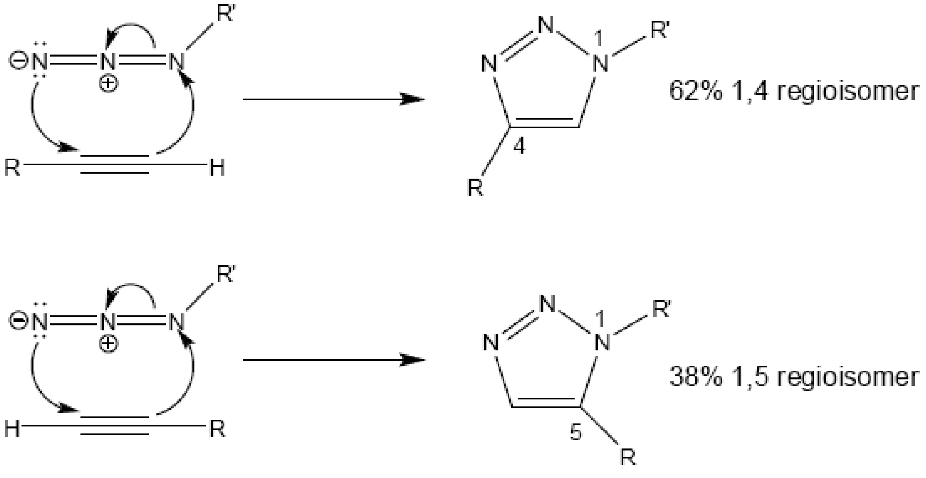
product

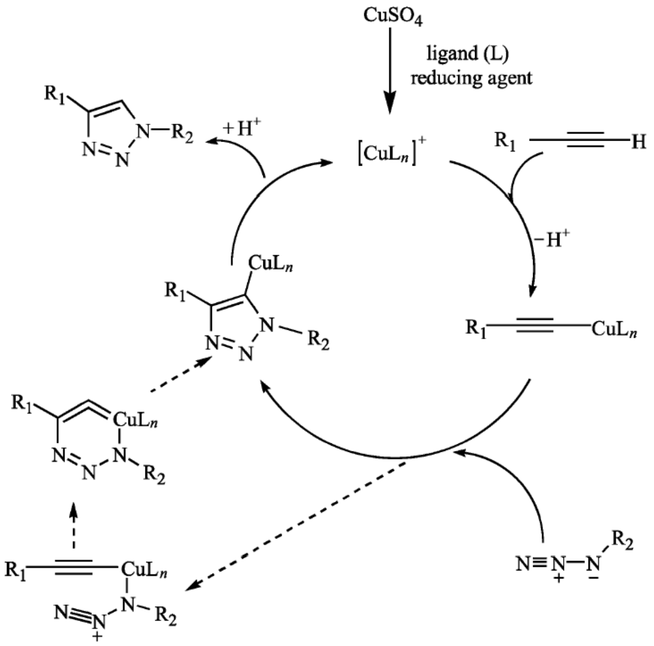
The main effect seems to be steric.

V. CYCLOADDITION: CLICK CHEMISTRY

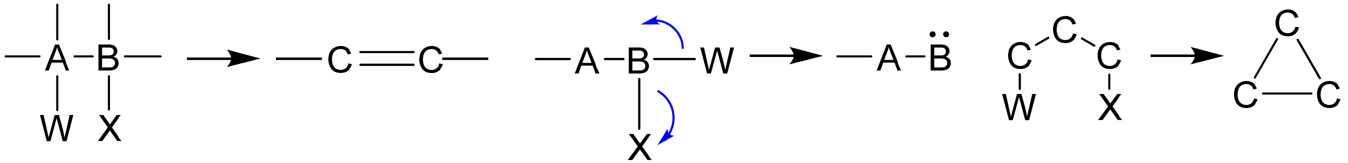
- The Huisgen 1,3-dipolar cycloaddition using a Cu(I) catalyst at room temperature — the “cream of the crop” of click reactions.





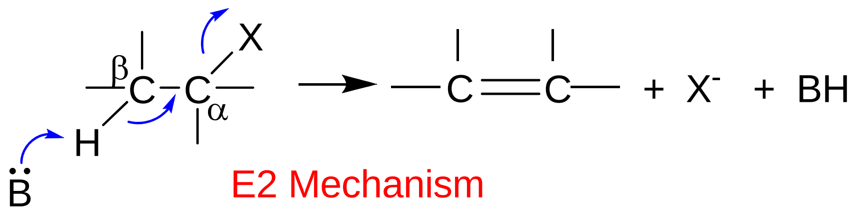


6-3 Elimination Reactions

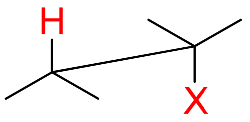


β-elimination α-elimination γ -elimination

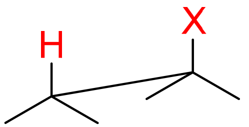
I. E2 and E1 Mechanism



E2 Mechanism



(a) anti-periplanar



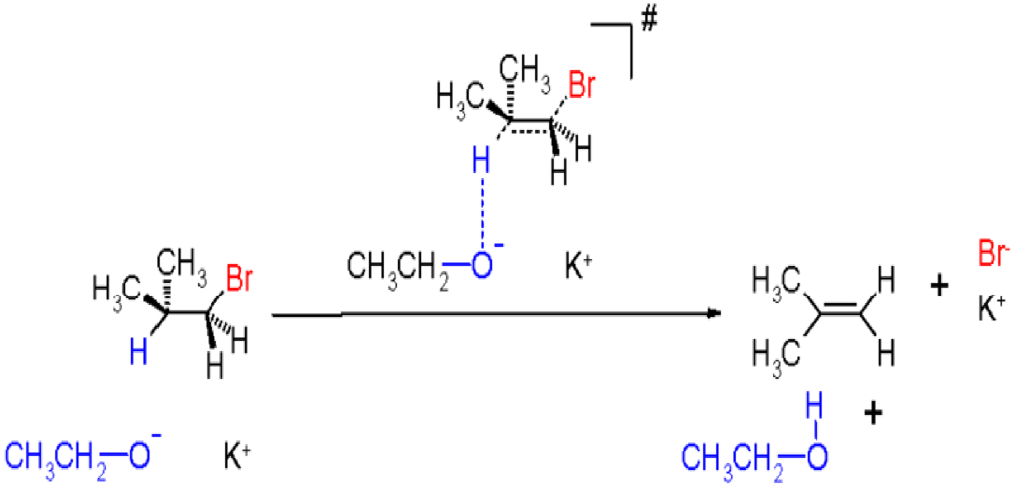
(b) syn-periplanar

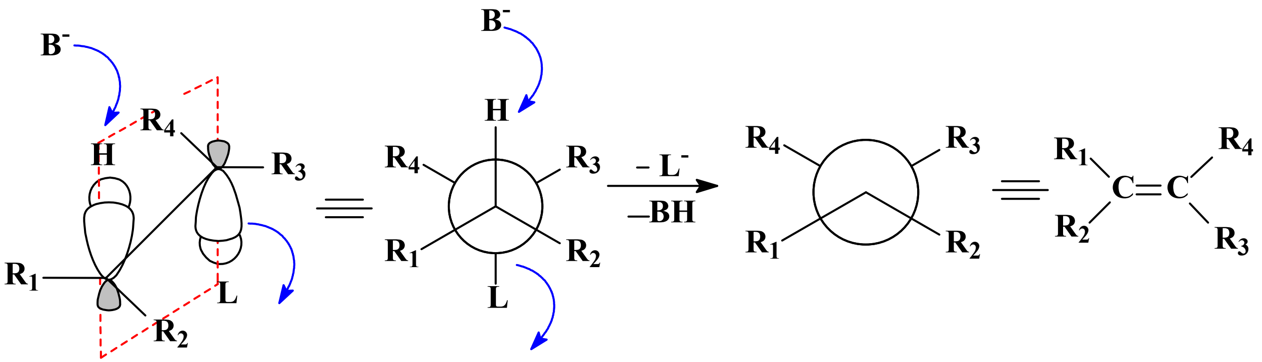
i. The proper second-order kinetics;

ii. An isotope effect: $k_D/k_H = 3\sim8$;

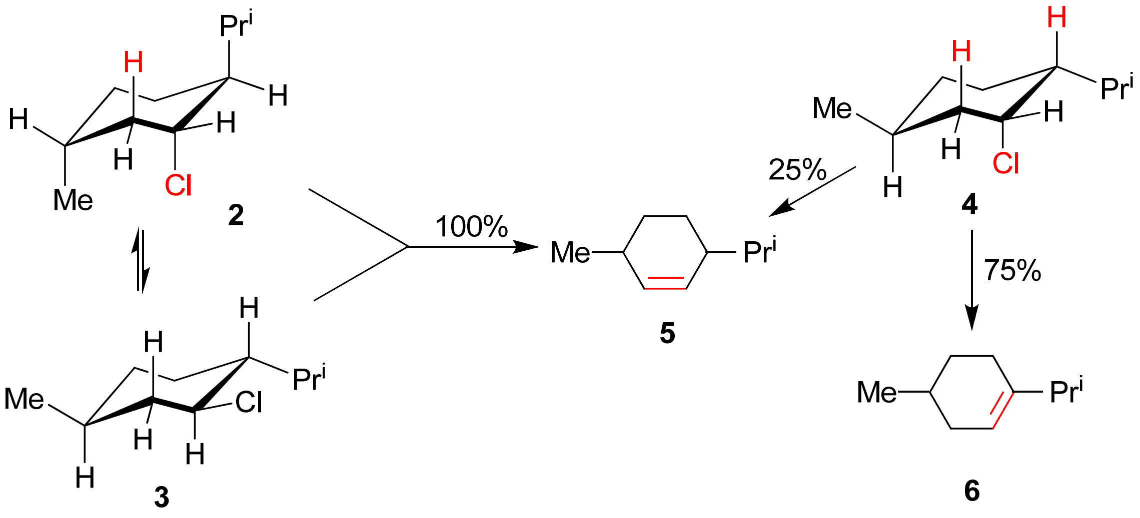
iii. Stereochemistry — the E2 mechanism is stereospecific: the five atoms involved (including the base) in the transition state must be in one plane.

- *Anti* elimination is usually greatly favored over *syn* elimination, probably because **a** is a staggered conformation and the molecule requires less energy to reach this transition state than it does to reach the eclipsed transition state **b**.





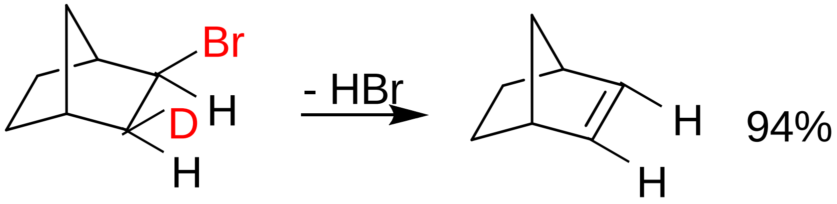
For a six-membered ring, anti-periplanarity of the leaving groups requires that they be diaxial even if this is the conformation of higher energy.

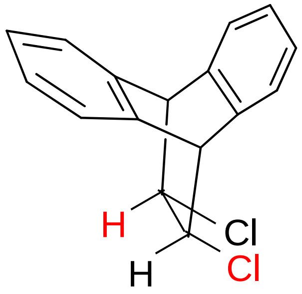


	Relative rate	Product
cis-HOOCCH=CClCOOH	1	HOOC−C≡C−COOH
trans-HOOCCH=CClCOOH	50	

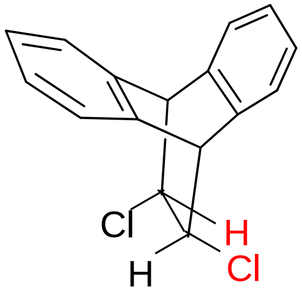
syn-Elimination

The deuterated norbornyl bromide





cis-isomer



trans-isomer

cis-isomer: HCl elimination is much slower than from corresponding nonbridged compounds.

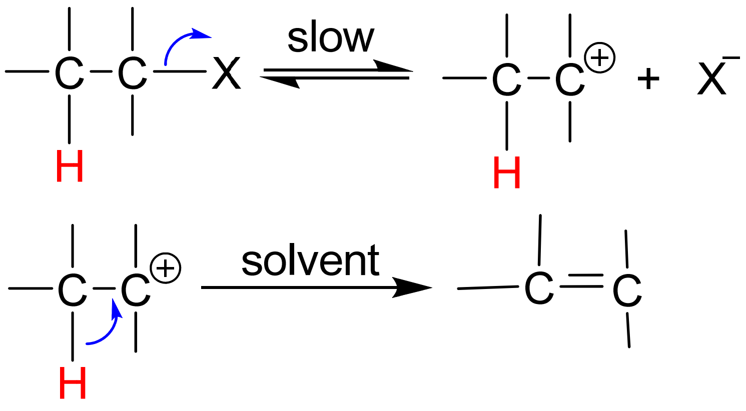
trans-isomer: Syn elimination can take place (dihedral angle about 0°); reached about eight times faster than cis-isomer.

a) Anti elimination requires a dihedral angle of 180°. When this angle cannot be achieved, anti elimination is greatly slowed or prevented entirely.

b) Anti elimination is generally favored in the E2 mechanism, but that steric (inability to form the anti-periplanar transition state), conformational, ion-pairing, and other factors cause syn elimination to intervene (and even predominate) in some cases.

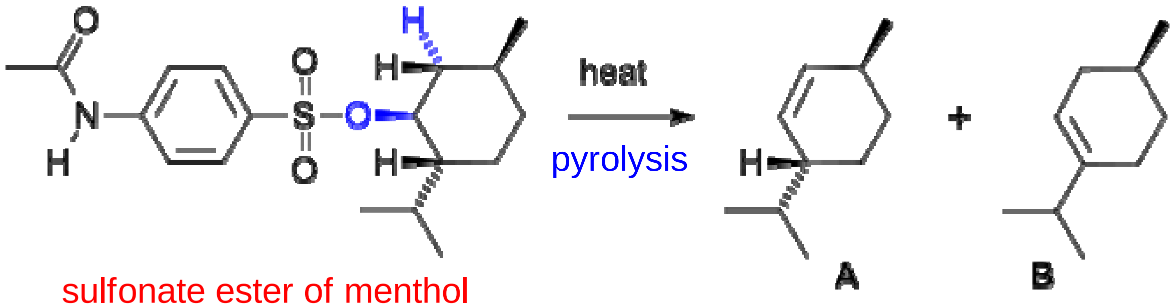
The E1 Mechanism

The E1 mechanism is a two-step process, ionization of the substrate to give a carbocation that rapidly loses a β proton to a base, usually the solvent:



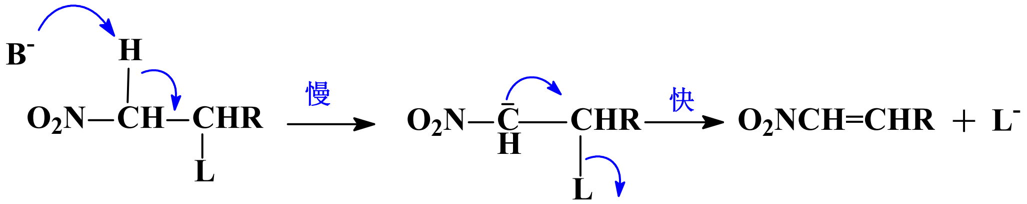
i. Tertiary and some secondary substituted alkyl halides.
ii. First order kinetics
iii. Reaction mostly occurs in complete absence of base or presence of only a weak base
iv. E1 are in competition with S_N1
v. No deuterium isotope effect
vi. No antiperiplanar requirement:

Example 1:

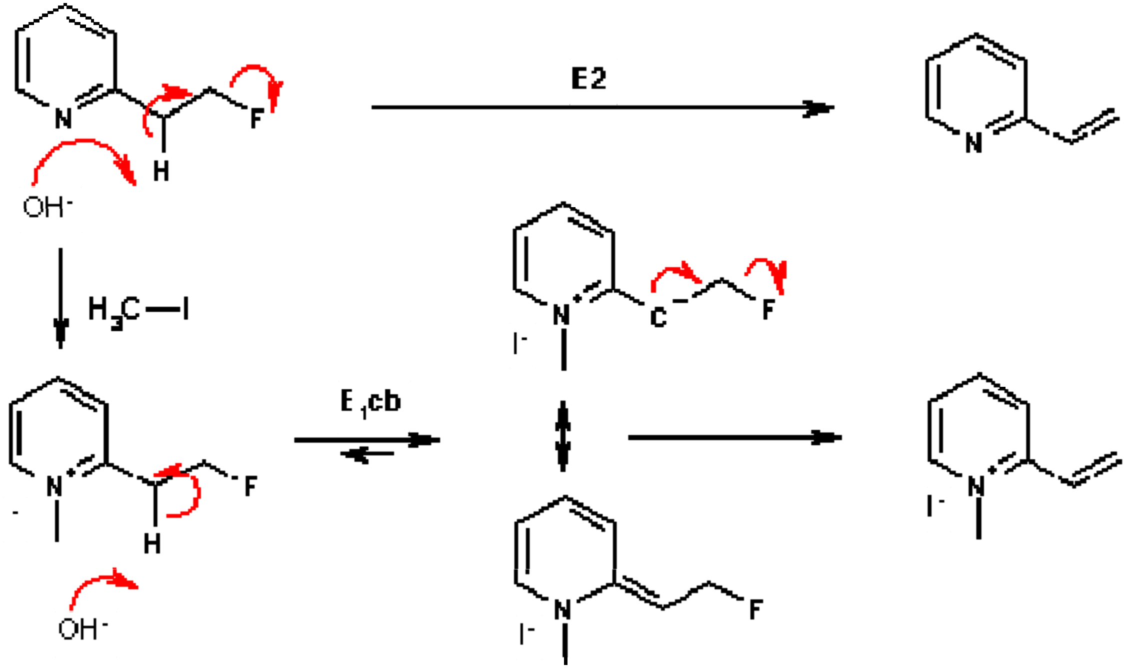


sulfonate ester of menthol

II. E1cB MECHANISM (CARBANION MECHANISM)

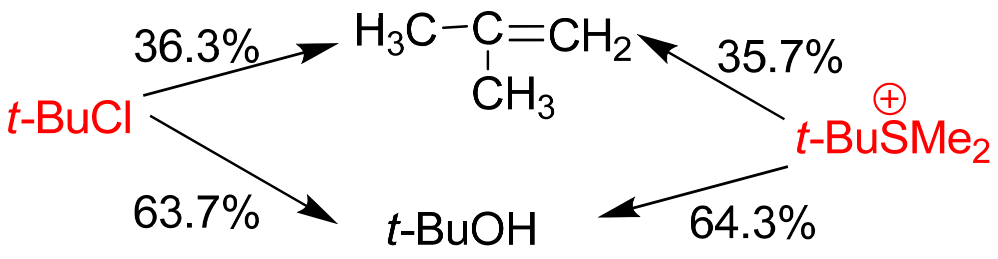


$$B^- \quad O_2N-\underset{\textstyle H\ \text{(above)}}{CH}-\underset{\textstyle L}{CHR} \xrightarrow{慢} O_2N-\underset{H}{\bar{C}}-\underset{L}{CHR} \xrightarrow{快} O_2NCH{=}CHR + L^-$$



The E1cB reaction mechanism. Dehydration of 1-methyl-2-(2-fluoroethyl)pyridinium iodide).

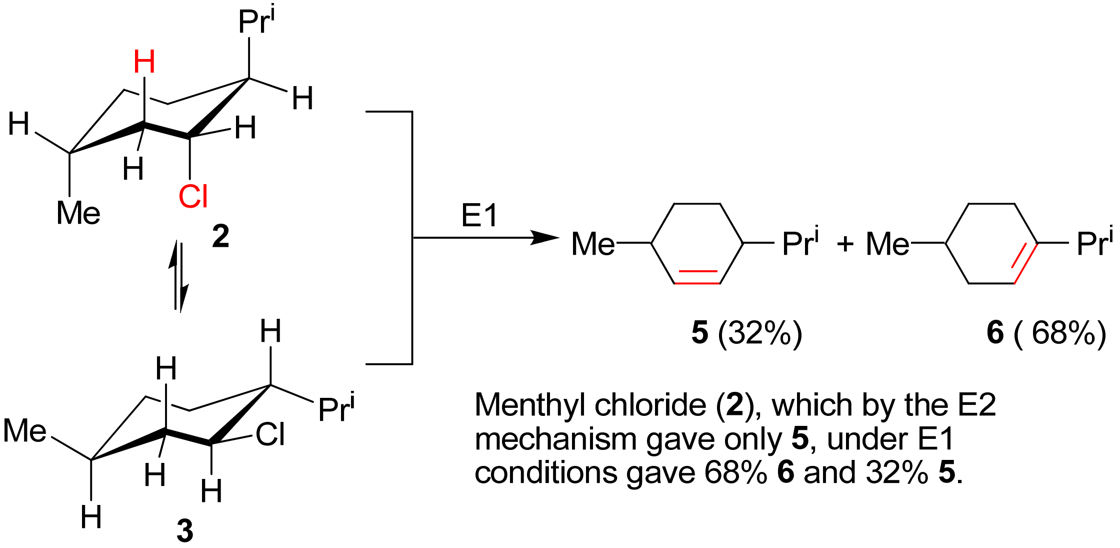
Example 2.



Solvolysis at 65.3°C in 80% aqueous ethanol.

If this reaction had taken place by a second-order mechanism, the nucleophile would not be excepted to have the same ratio of preference for attack at the β hydrogen compared to attack at a *neutral* chloride as for attack at the β hydrogen compared to attack at a *positive* SMe_2 group.

Example 3.



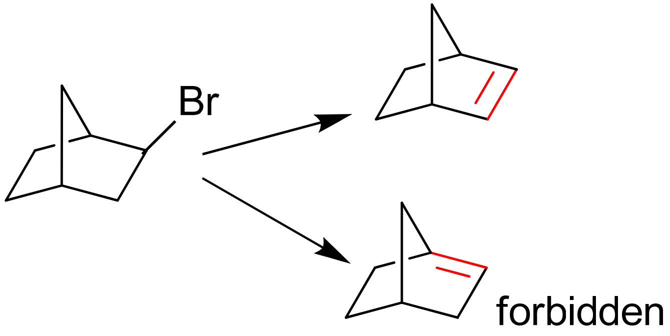
5 (32%)

6 (68%)

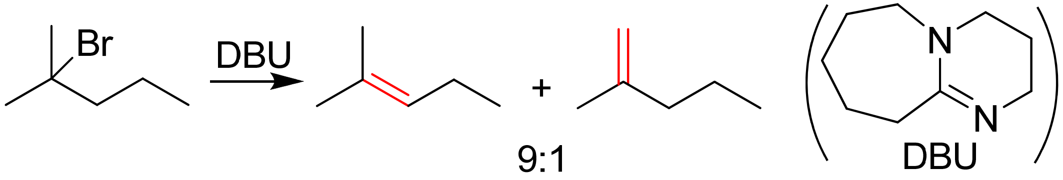
Menthyl chloride (**2**), which by the E2 mechanism gave only **5**, under E1 conditions gave 68% **6** and 32% **5**.

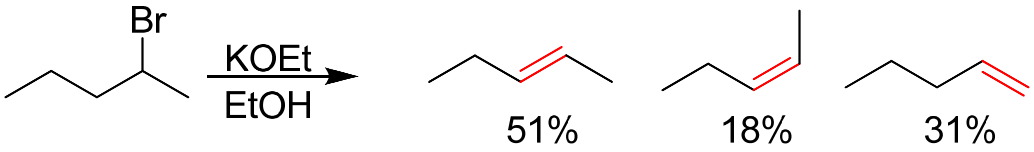
III. Orientation of the Double Bond

i. No matter what the mechanism, a double bond does not go to a bridgehead carbon unless the ring sizes are large enough (Bredt's rule).

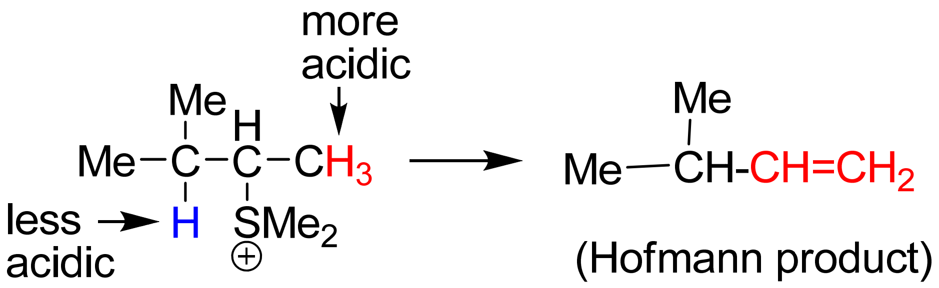


ii. Zaitsev's rule: the double bond goes mainly toward the most highly substituted carbon.





iii. Elimination from compounds with charged nucleofuges, e.g., NR_3^+, SR_2^+ (those that come off as neutral mlecules), follow Hofmann's rule if the substrate is acyclic: *the double bond goes mainly toward the least highly substituted carbon*, but Zaitsev's rule if the leaving group is attached to a six-membered ring.



iv. No matter what the mechanism, if there is a double bond (C=C or C=O) or an aromatic ring already in the molecule that can be in conjugation with the new double bond, the conjugated product usually predominates, sometimes even when the stereochemistry is unfavorable.

IV. REACTIVITY

- Factors influencing the elimination reactivity:
- Substrate structure
- The attacking base
- The leaving group
- The medium
- Elimination Reaction *vs* Nucleophilic Substitution:

Substitution generally predominates and elimination occurs only during precise circumstances. Generally, elimination is favored over substitution when

- steric hindrance increases
- basicity increases
- temperature increases
- the steric bulk of the base increases ($KOBu^t$)
- the nucleophile is poor.

Competition between E and Sn

Steric hindrance

$$CH_3(CH_2)_{15}CH_2CH_2Br \xrightarrow[\text{回流}]{RO^-,\ ROH} CH_3(CH_2)_{15}CH{=}CH_2 + CH_3(CH_2)_{15}CH_2CH_2OR$$

CH_3O^-, CH_3OH	~1% (E2)	99%(S_N2)
Me_3CO^-, Me_3COH	~85%(E2)	~15%(S_N2)

Basicity

$$CH_3COO^- + (CH_3)_2CHBr \longrightarrow CH_3COOCH(CH_3)_2 + Br^-$$

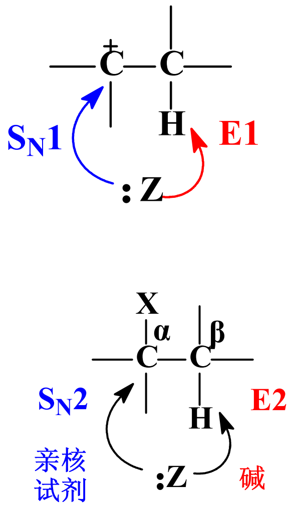
$$C_2H_5O^- + (CH_3)_2CHBr \longrightarrow CH_3CH_2O{-}CH(CH_3)_2 + CH_2{=}CHCH_3$$

碱性　$C_2H_5O^- > CH_3COO^-$	21%	79%

Temperature

$$(CH_3)C{-}Br + C_2H_5ONa \xrightarrow{C_2H_5OH} Me_3C{-}OEt + CH_2{=}CMe_2$$

25℃	9%（S_N1）	91%（E1+E2）
55℃	0%	100%(E1+E2)

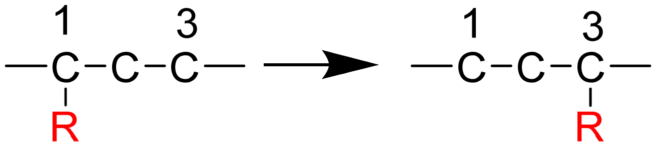


1°RX　　2°　RX　　3°　RX $\longrightarrow$

E2比例增加，S_N2比例降低

6-4 Rearrangement Reaction

In a rearrangement reaction a group moves from one atom to another in the same molecule. Most are migrations from an atom to an adjacent one (called 1,2 shift), but some are over longer distances.

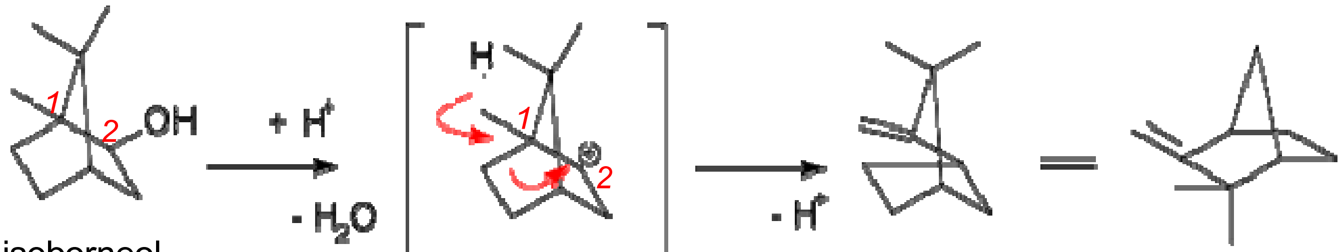


- A rearrangement is not well represented by simple and discrete electron transfers. The actual mechanism of alkyl groups moving probably involves transfer of the moving alkyl group fluidly along a bond, not ionic bond-breaking and forming.
- Some key rearrangement reactions:
  - 1,2-rearrangements
  - pericyclic reactions
  - olefin metathesis

- **Wagner-Meerwein rearrangement**

A Wagner-Meerwein rearrangement is a class of carbocation 1,2-rearrangement reactions in which a hydrogen, alkyl or aryl group migrates from one carbon to a neighboring carbon.

The rearrangement was first discovered in bicyclic terpenes:

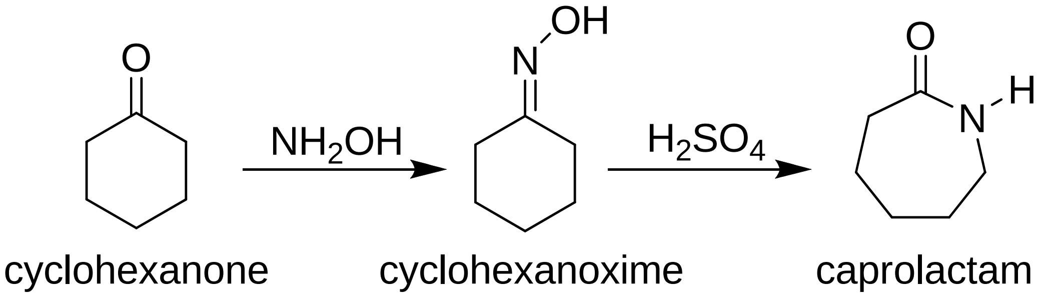


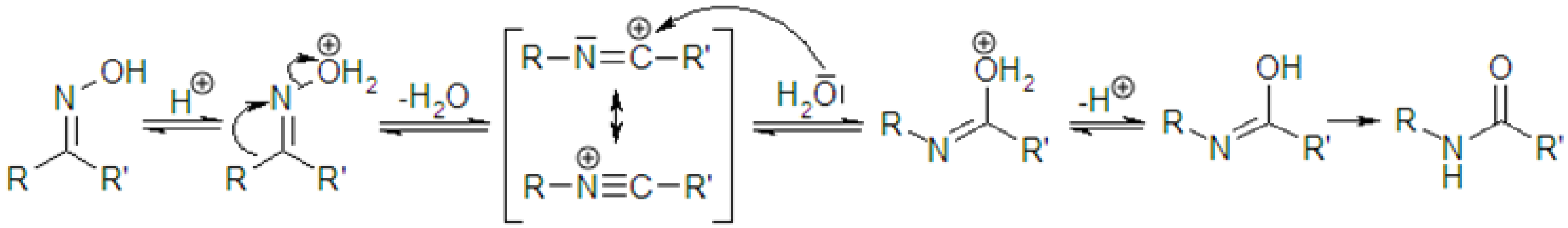
isoborneol

- **Beckmann rearrangement**

This is an acid-catalyzed rearrangement of an oxime to an amide. Cyclic oximes yield lactams.

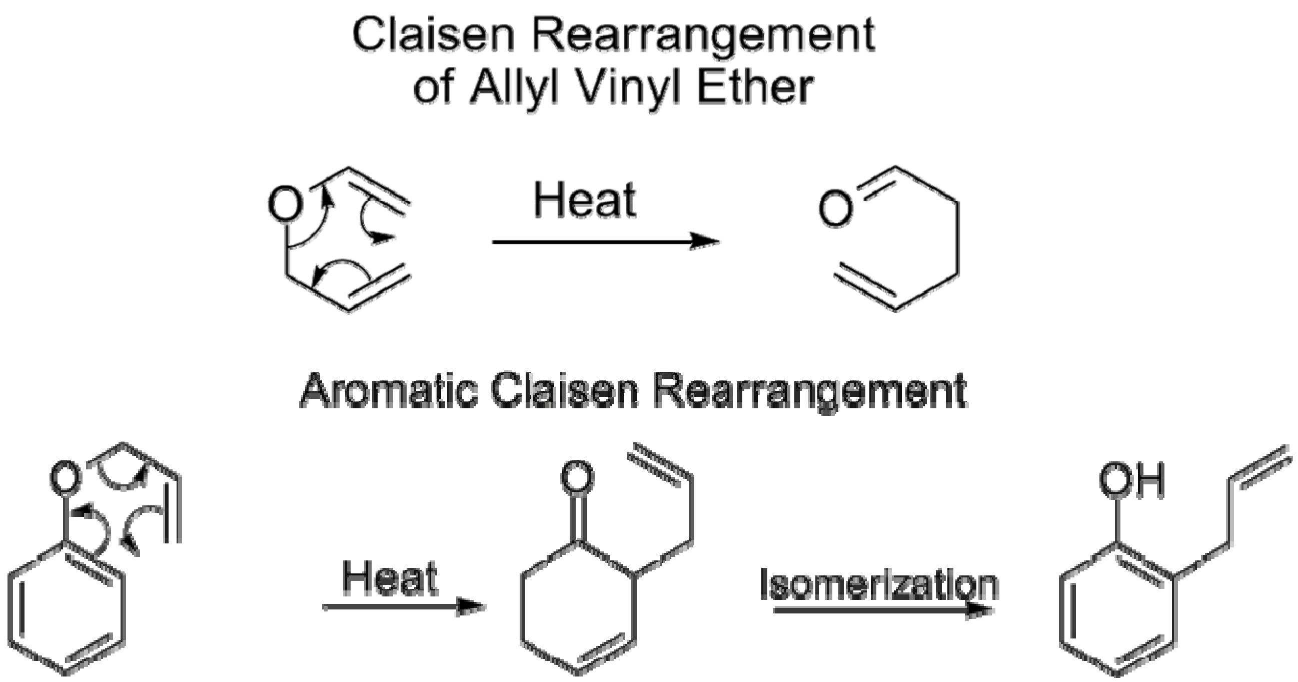
The mechanism is generally believed to consist of an alkyl migration with expulsion of the hydroxyl group to form a nitrilium ion followed by hydrolysis:





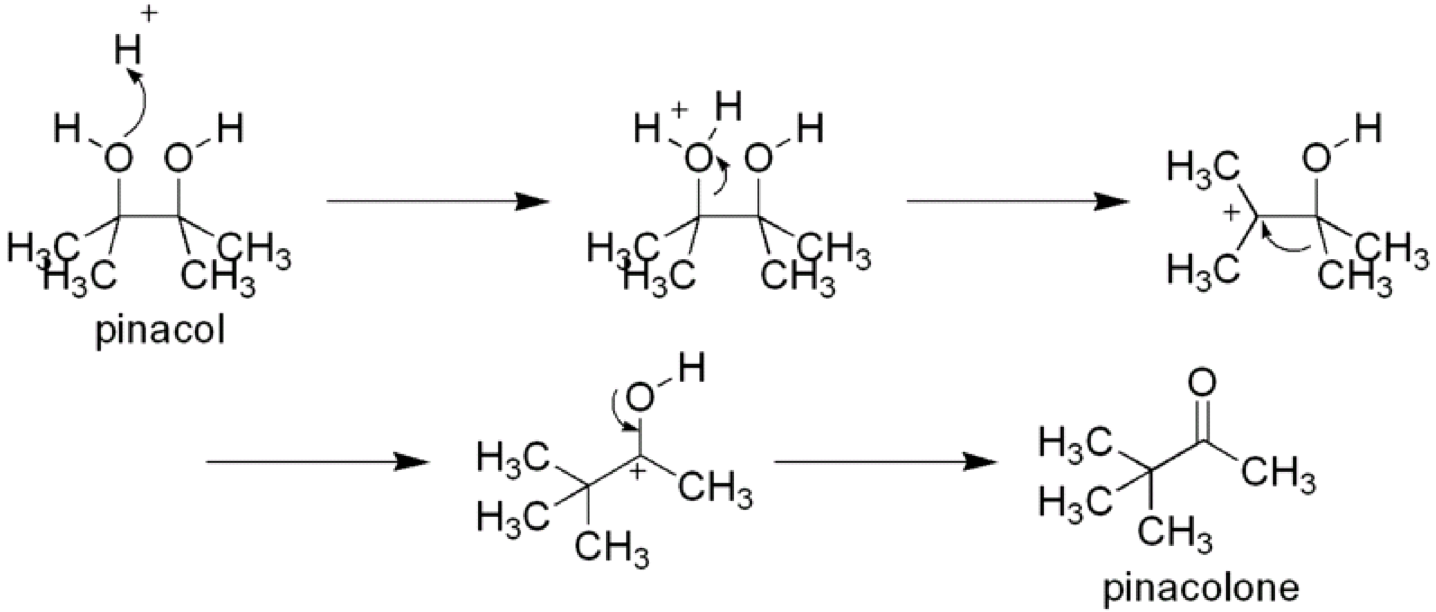
Claisen rearrangement

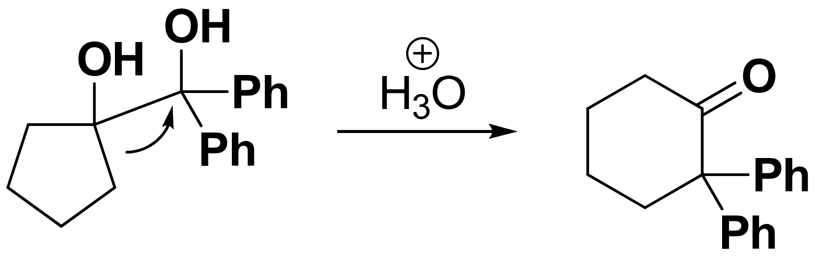
The Claisen rearrangement is a powerful carbon-carbon bond-forming chemical reaction. The heating of an allyl vinyl ether will initiate a [3,3] rearrangement to give a γ, δ-unsaturated carbonyl.


Claisen Rearrangement of Allyl Vinyl Ether

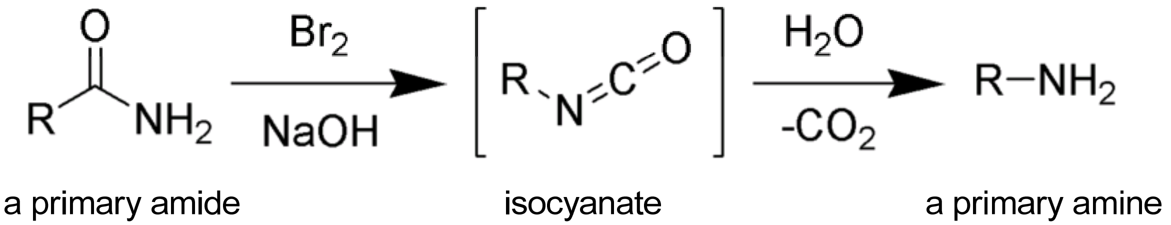
Aromatic Claisen Rearrangement

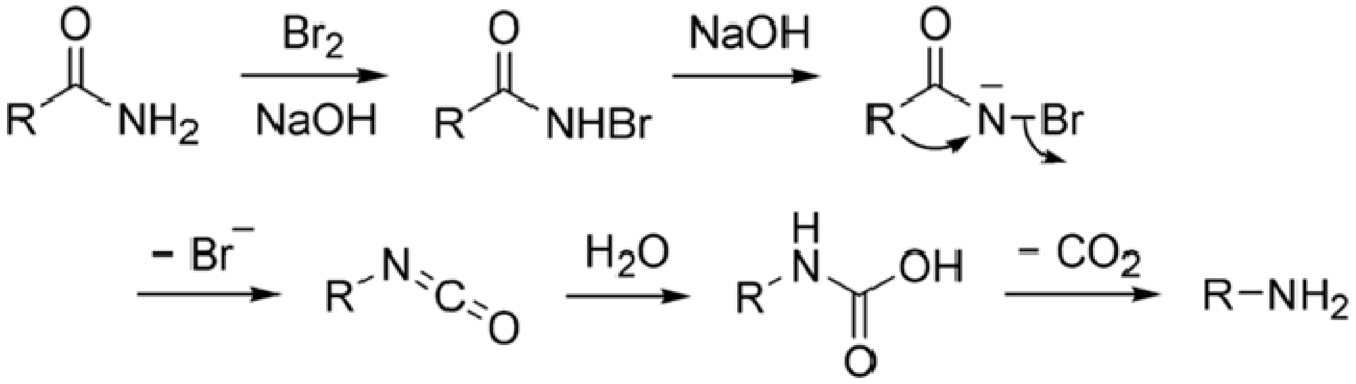
Pinacol Rearrangement

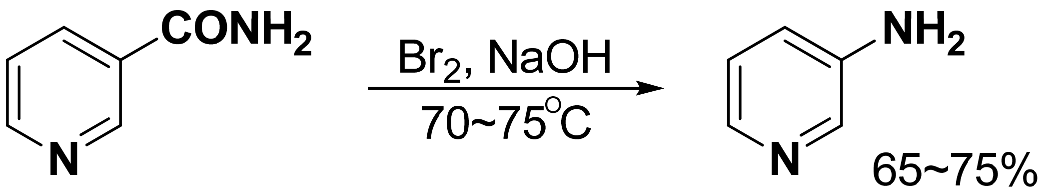




Hofmann rearrangement



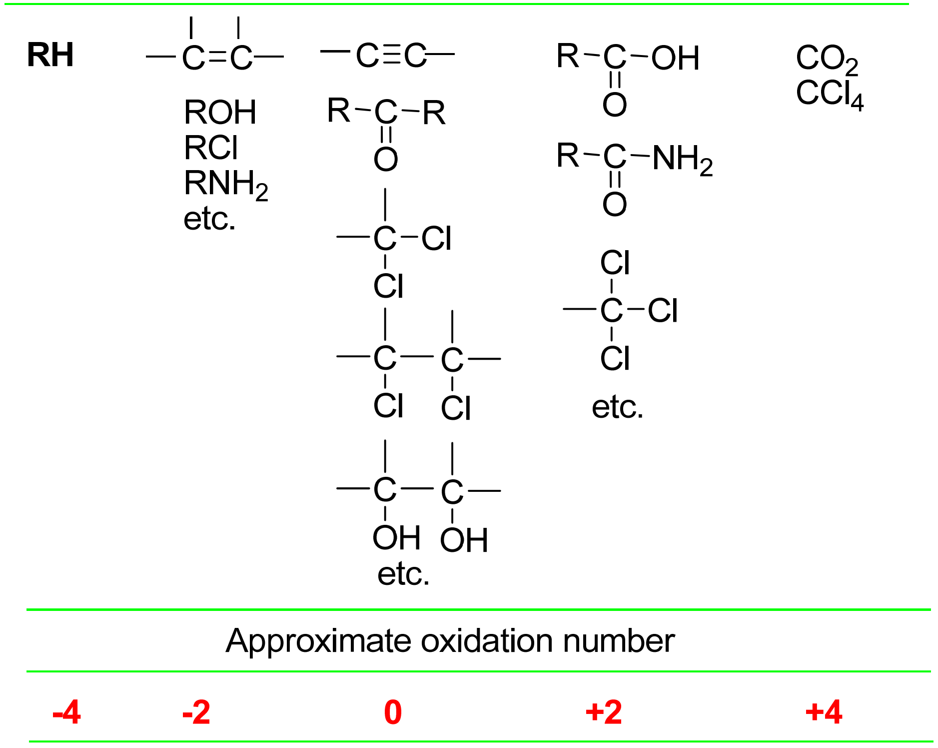




6-5 Organic Redox Reaction

In organic chemistry oxidations and reductions are different from ordinary redox reactions because many reactions carry the name but do not actually involve electron transfer in the electrochemical sense of the word.

- Categories or simple functional groups arranged according to oxidation state

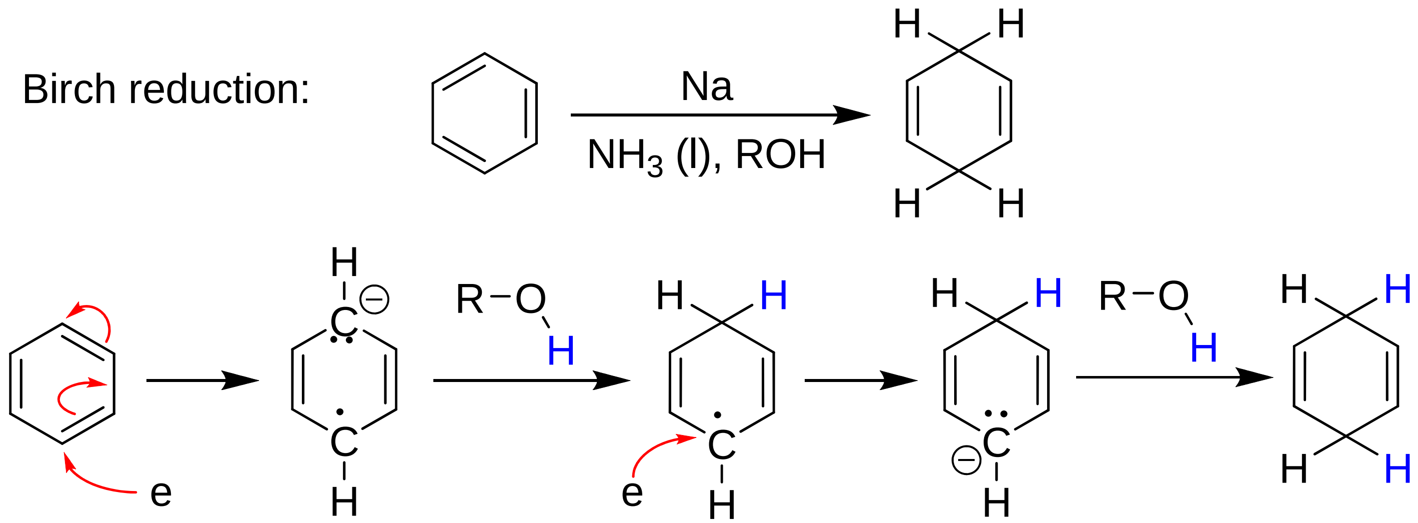


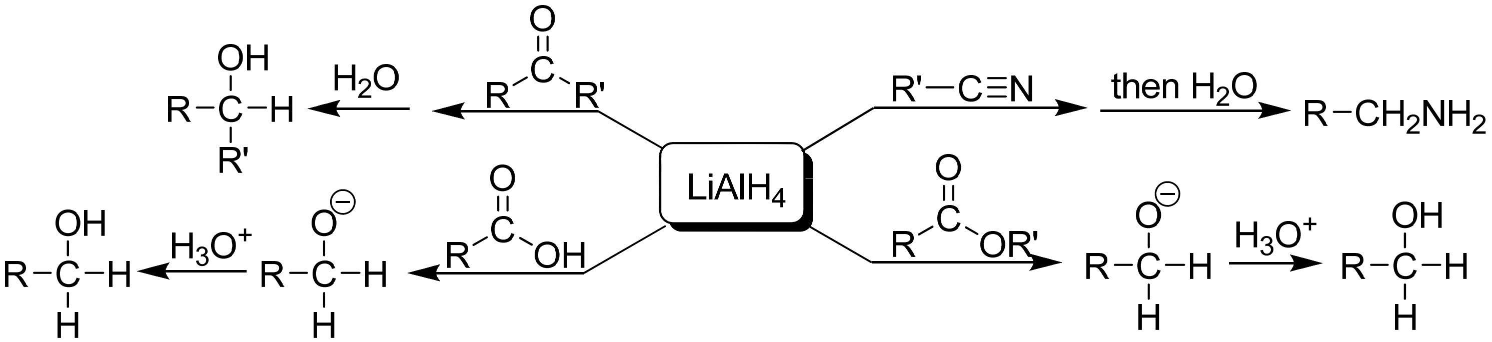
I. Organic reductions

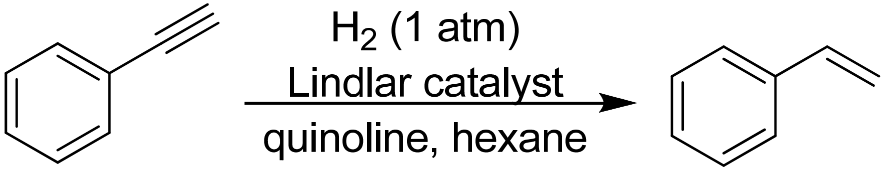
Several reaction mechanisms exist for organic reductions:

- Direct electron transfer in Birch reduction
- Hydride transfer in reductions, $LiAlH_4$
- Hydrogen reduction with a catalyst such as Lindlar catalyst
- Disproportionation reaction such as the Cannizzaro reaction

Birch reduction:

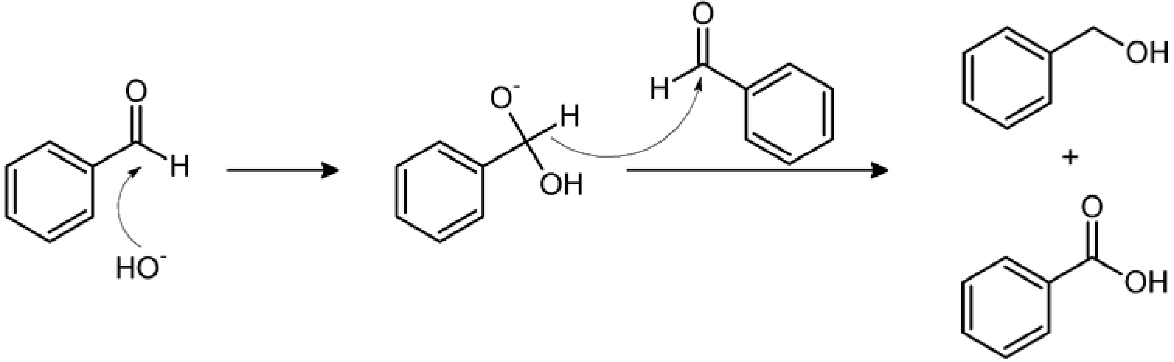






A Lindlar catalyst: consists of palladium deposited on calcium carbonate and treated with various forms of lead.

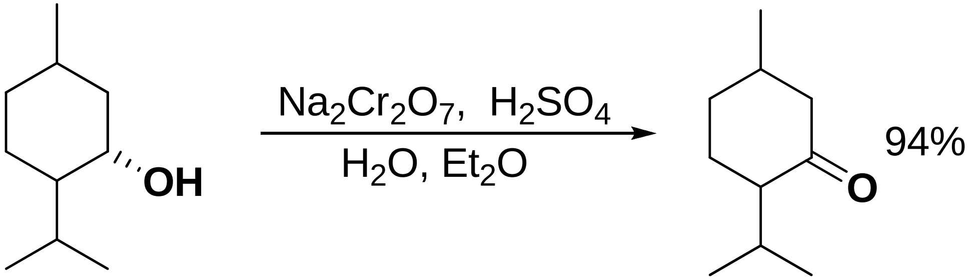
Cannizzaro reaction



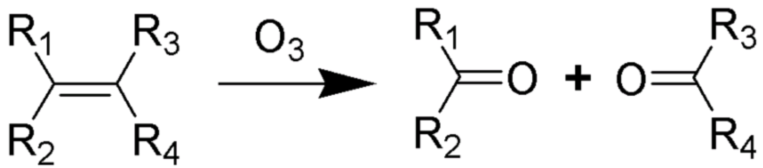
II. ORGANIC OXIDATIONS

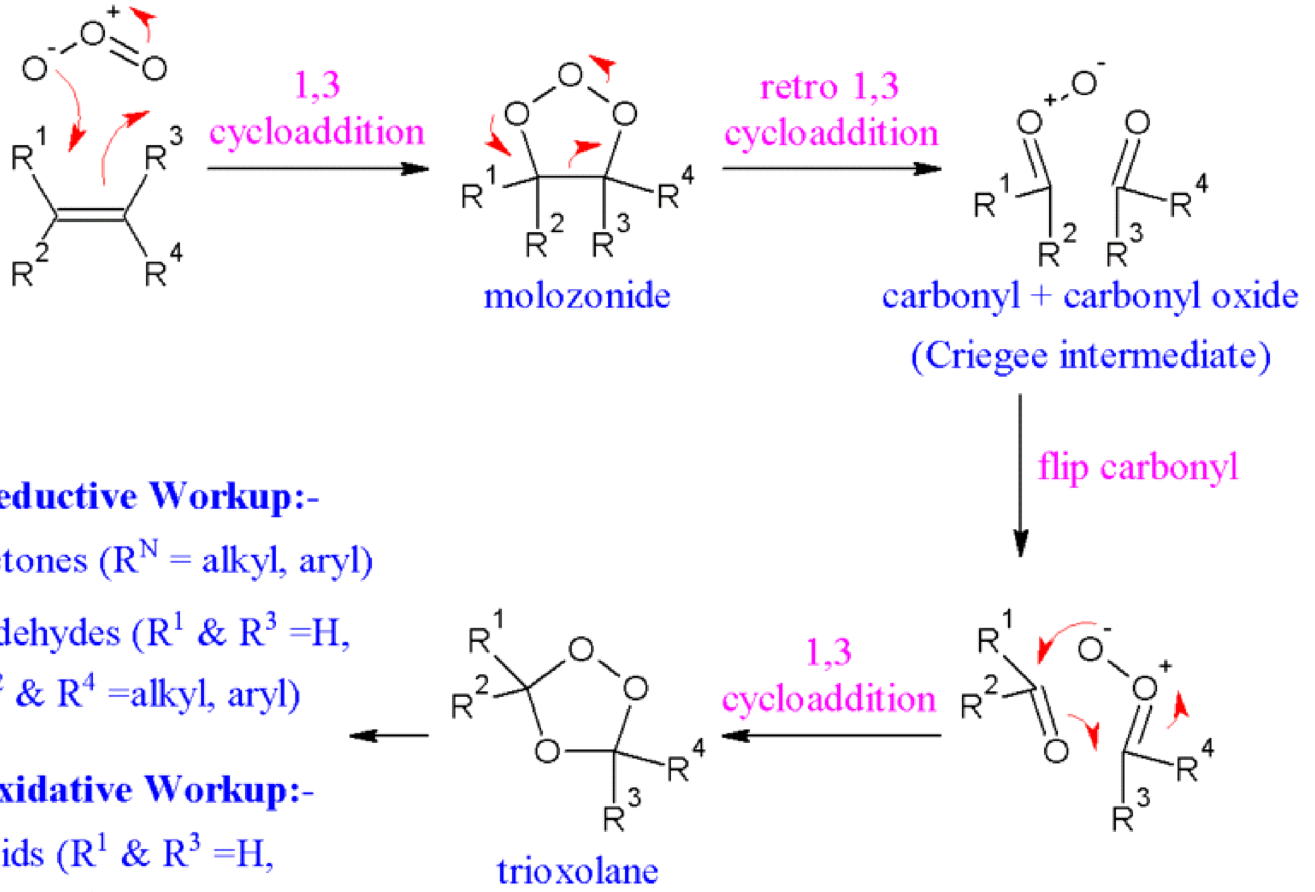
Several reaction mechanisms exist for organic oxidations:

- Single electron transfer;
- Oxidations through ester intermediates with chromic acid;
- Hydrogen atom transfer as in Free radical halogenation;
- Oxidation with oxygen (combustion);
- Oxidation involving ozone (O_3) in ozonolysis;
- Oxidations involving an elimination reaction mechanism such as the Swern oxidation;
- oxidation by nitroso radicals, fremy's salt or TEMPO.



Ozonolysis




1,3 cycloaddition

molozonide

retro 1,3 cycloaddition

carbonyl + carbonyl oxide (Criegee intermediate)

flip carbonyl

1,3 cycloaddition

trioxolane

Reductive Workup:-

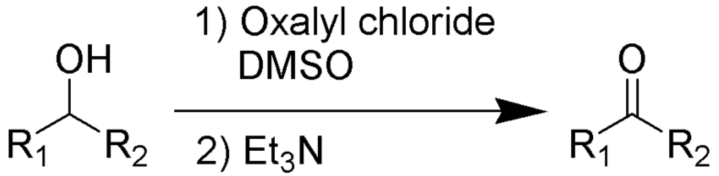
ketones (R^N = alkyl, aryl)

aldehydes (R^1 & R^3 =H, R^2 & R^4 =alkyl, aryl)

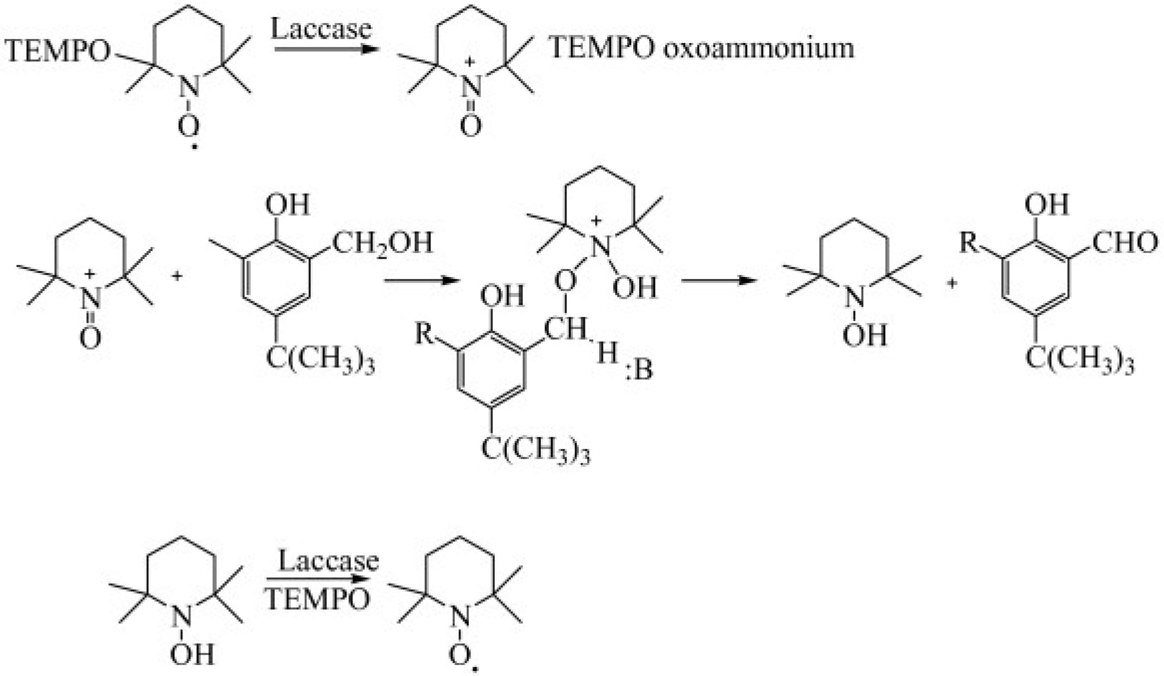
Oxidative Workup:-

acids (R^1 & R^3 =H, R^2 & R^4 =alkyl, aryl)

Swern oxidation



Oxidation by TEMPO



Questions	opt1	opt2	opt3	opt4	**Answer**
Which of the following is known as the Schrodinger equation?	$E = h^{o}$	$E = mc^2$	h=p	^H Ã = EÃ	**^H Ã = EÃ**
For the hydrogen atom, which of the following orbitals has the lowest energy?	4s	4p	4d	They all have the same energy	**They all have the same energy**
Number of lobes in fifth d-orbital are	1	2	3	4	**2**
Size of 2s-orbital as compared to 1s-orbital is	large	small	medium	very large	**large**
Planck proposed that energy travels in	discontinuous manner	continuous manner	slow manner	general manner	**discontinuous manner**
Energy is absorbed by body in form of	photons	quantas	waves	energy	**photons**
Size of s-orbital increases when value of principal quantum number	Decreases	increases	remains constant	fluctuates	**increases**
The s-orbital does not show preference to any direction because	It is the smallest orbital	It is present in every atom	It is spherically symmetric	It is the first orbital	**It is spherically symmetric**
The p-orbital is in the shape of a	Sphere	Dumbbell	Pear-shaped lobe	No shape	**Dumbbell**
Schrodinger's equation described the	complement of the wave function	behavior of "matter" waves	motion of light	procedure for splitting an atom	**behavior of "matter" waves**
Which subatomic particles contribute to the mass number of an atom?	protons and neutrons	protons and electrons	neutrons and electrons	protons, neutrons, and electrons	**protons and neutrons**
Where are the neutrons located in an atom?	outside the nucleus	the electron cloud	they are not found in an atom	inside the nucleus	**inside the nucleus**
What is the shape of the s orbital?	dumbbell	spherical	flower	flat	**spherical**
What is the shape of a p orbitatl?	peanut	spherical	flower	flat	**peanut**

What is the shape of the d orbitals?	peanut	spherical	flower or four leaf clover	flat	**flower or four leaf clover**
What quantum number describes the energy level and size of an orbital?	l	m	s	n	**n**
What quantum number describes the spin of the electron?	l	m	s	n	**s**
What quantum number describes the orientation of the orbital and tells how many orbitals exist in an a sublebvel?	l	m	s	n	**m**
if n = 2, then "l" can equal	1	2	3	0 and 1	**0 and 1**
How many elelctrons can occupy any one orbital?	2	4	6	8	**2**
Using 2nsquare calculate how many elelctrons could occupy the 6th energy level of an atom.	6	36	24	72	**72**
How many orbitals are there in the "d" sublevel?	1	3	5	7	**5**
The "ml" quantum number describes the ______ of the electron.	energy level and size of the energy level	orbital or sublevel or shape	orientation of the orbital	spin of the electrons in the first level	**orientation of the orbital**
The smallest particle of an element or matter	Proton	Atom	Electron	Electron Cloud	**Atom**
The central part of an atom that is made up of neutrons and protons	Protons	Neutrons	Nucleus	Reactivity	**Nucleus**
The region around the nucleus where the electrons may be found.	Electron Cloud	Reactivity	Neutron	Atom	**Electron Cloud**
Positivley charged particle located in the nucleus of an atom.	Electrons	Protons	Subatomic Particles	Neutrons	**Protons**
Negatively charged particle found outside the nucleus of an atom	Electrons	Protons	Subatomic Particles	Neutrons	**Electrons**
What are the maximum number of electrons that go on the first 3 energy levels?	2,4,16	2,8,18	4,8,12	3,4,6	**2,8,18**

What are valence electrons?	electrons on the first orbital always	nucleus	the outermost shell	the number of electrons on the outermost orbital	**the number of electrons on the outermost orbital**
Which particles make up the nucleus of an atom?	protons and neutrons	electrons and protons	electrons, protons, and neutrons	electrons and neutrons	**protons and neutrons**
Max Planck’s great discovery was that radiation energy is emitted in packets that he called what?	wave function	photon	quanta	gamma ray	**quanta**
In the Heisenberg uncertainty principle, which two measurable properties of a particle cannot be observed precisely at the same time?	Energy and torque	Size and speed	Position and momentum	Spin and color	**Position and momentum**
Niels Bohr used quantum mechanics to describe which element?	Zinc	Hydrogen	Carbon	Helium	**Hydrogen**
The square of a particle’s wave function describes the probability of what about the particle?	That it will decay	That it is at a particular place	That it has a specific spin	That it will disappear	**That it is at a particular place**
In quantum mechanics, the angular momentum of a particle is called what?	spin	swirl	rotation	orbital	**spin**
Magnetic quantum number is also called	1st quantum number	2nd quantum number	3rd quantum number	4th quantum number	**3rd quantum number**
Value of 'm' depends upon values of	s	l	d	f	**l**
Sub shell which is not sub-divided into any other orbital is termed as	p-sub shell	s-sub shell	d-sub shell	f-sub shell	**s-sub shell**
Region around nucleus which can be filled with one or two electrons is knows as	field	axis	zone	atomic orbital	**atomic orbital**
Electronic configuration of atom which possess lowest energy is most	stable	unstable	transitional	ductile	**stable**

The uncertainty principle was enunciated by	Einstein	Heisenberg	Rutherford	Pauli	**Heisenberg**
The position and velocity of a small particle like electron cannot be simultaneously determined.? This statement is	Heisenberg uncertainty principle	Principle of de Broglie's wave nature of electron	Pauli's exclusion principle	Aufbau's principle	**Heisenberg uncertainty principle**
Simultaneous determination of exact position and momentum of an electron is	Possible	Impossible	Sometimes possible sometimes impossible	always Possible	**Impossible**
Uncertainty principle gave the concept of	Probability	An orbital	Physical meaning of Ψ	Physical meaning of Ψ2	**Probability**
Which quantum number is not related with Schrodinger equation	Principal	Azimuthal	Magnetic	Spin	**Spin**
Orbital is	Space around the nucleus where the probability of finding the electron is maximum	Circular path around the nucleus in which the electron revolves	Amplitude of electrons wave	square of electrons wave	**Space around the nucleus where the probability of finding the electron is maximum**
The electronic energy levels of the hydrogen atom in the Bohr?s theory are called	Rydberg levels	Orbits	Ground states	Orbitals	**Orbits**
The energy of a photon is calculated by	E=hν	h=Eν	h=ν/E	E=h/ν	**E=hν**
Electron occupies the available orbital singly before pairing in any one orbital occurs, it is	Pauli's exclusion principle	Hund's Rule	Heisenberg's principle	Prout's hypothesis	**Hund's Rule**

Questions	opt1	opt2	opt3	opt4	**Answer**
When two atomic orbitals combine they form	One molecular orbital	two molecular orbital	three molecular orbital	four molecular orbital	**two molecular orbital**
In a double bond connecting two atoms, there is a sharing of	2 electrons	1 electron	4 electrons	All electrons	**4 electrons**
π bond is formed	By overlapping of atomic orbitals on the axis of nuclei	By mutual sharing of pi electron	By sidewise overlapping of half filled p-orbitals	By overlapping of s-orbitals with p-orbitals	**By sidewise overlapping of half filled p-orbitals**
In a sigma bond	Sidewise as well as end to end overlap of orbitals take place	Sidewise overlap of orbitals takes place	End to end overlap of orbitals takes place	No overlapping	**End to end overlap of orbitals takes place**
Which of the following is not correct	A sigma bond is weaker than π bond	A sigma bond is stronger than π bond	A double bond is stronger than a single bond	A double bond is shorter than a single bond	**A sigma bond is weaker than π bond**
Bond created by overlapping of one modified orbit on another orbit is known as	Sigma bond (σ-bond)	Pi bond (π-bond)	Covalent bond	Dative bond	**Sigma bond (σ-bond)**
The paramagnetic nature of oxygen molecule is best explained on the basis of	Valence bond theory	Resonance	Molecular orbital theory	Hybridization	**Molecular orbital theory**
Complete transfer of one or more electrons between atoms constitutes in forming	ionic bond	covalent bond	co-ordinate	dative bond	**ionic bond**

The bond order of NO molecule is	1	2	2.5	3	**2.5**
Molecular orbital theory was developed mainly by	Pauling	Pauling and Slater	Mulliken	Thomson	**Pauling and Slater**
Paramagnetism is exhibited by molecules	Not attracted into a magnetic field	Containing only paired electrons	Carrying a positive charge	Containing unpaired electrons	**Containing unpaired electrons**
The difference in energy between the molecular orbital formed and the combining atomic orbitals is called	Bond energy	Activation energy	Stabilization energy	Destabilization energy	**Stabilization energy**
With increasing bond order, stability of a bond	Remains unalte	Decreases	Increases	None of these	**Increases**
The total number of electron that takes part in forming bonds in N2	2	4	6	10	**6**
Which molecule is linear	NO_2	ClO_2	CO_2	H_2S	**CO_2**
Compound formed by sp3d hybridization will have structure	Planar	Pyramidal	Angular	Trigonal bipyramidal	**Trigonal bipyramidal**
Octahedral molecular shape exists in .... hybridisation	sp3d	$sp3d_2$	sp3d3	sp	**$sp3d_2$**
Shape of methane molecule is	Tetrahedral	Pyramidal	Octahedral	square planer	**Tetrahedral**
Which species do not have sp3hybridization	Ammonia	Methane	Water	Carbon dioxide	**Carbon dioxide**
As compared to pure atomic orbitals, hybrid orbitals have	Low energy	Same energy	High energy	None of these	**Low energy**
The number of unpaired electrons in O2 molecule is	0	1	2	3	**2**
When two pairs of electrons are shared, bond is	Single covalent bond	Double covalent bond	Dative bond	Triple bond	**Double covalent bond**
Carbon atoms in diamond are bonded to each other in a configuration	Tetrahedral	Planar	Linear	Octahedral	**Tetrahedral**
Hybridisation involves	Addition of an electron pair	Mixing up of atomic orbitals	Removal of an electron pair	Separation of orbitals	**Mixing up of atomic orbitals**

The geometry of sulphur trioxide molecule is	Tetrahedral	Trigonal plana	Pyramidal	Square planar	**Trigonal planar**
The shapes of BCl3,PCl3 and ICl3molecules are all	Triangular	Pyramidal	T−shaped	Linear	**Triangular**
sp3 hybridization leads to which shape of the molecule	Tetrahedron	Octahedron	Planar	Linear	**Tetrahedron**
In sp hybridisation, shape is	Tetrahedron	Octahedron	Planar	Linear	**Linear**
The geometry of the molecule with sp3d2 hybridised central atom is	Tetrahedral	Planar	Linear	Octahedral	**Octahedral**
sp3d2 hybrid orbitals are	Tetrahedral	Planar	Linear	Octahedral	**Octahedral**
The trigonal bipyramidal geometry results from the hybridisation	dsp3	dsp2	d2sp3	d3sp2	**dsp3**
The valency of carbon is four. On what principle it can be explained in a better way	Resonance	Hybridization	Electron transfer	cannot be explained	**Hybridization**
Hybridization is due to the overlapping of	Orbitals of different energy levels	Orbitals of different energy content	Orbitals of same energy content	atoms	**Orbitals of same energy content**
The d-orbital involved in sp3d hybridisation is	d x2−y2	dxy	dz2	dzx	**d x2−y2**
The coordination number of a metal in coordination compounds is	Same as primary valency	Sum of primary and secondary valencies	Same as secondary valency	difference of primary and secondary	**Same as secondary valency**
A group of atoms can function as a ligand only when	It is a small molecule	It has an unshared electron pair	It is a negatively charged ion	It is a positively charged ion	**It has an unshared electron pair**

The coordination number of a central metal atom in a complex is determined by	The number of ligands around a metal ion bonded by sigma and pi-bonds both.	The number around a metal ion bonded by pi-bonds	The number of ligands around a metal ion bonded by sigma bonds	The number of only anionic ligands bonded to the metal ion	**The number of ligands around a metal ion bonded by sigma bonds**
That ion or molecule which forms a complex compound with transitional metal ion is called	Recipient	Ligand	Coordinate io	No special na	**Ligand**
Generally, a group of atoms can function as a ligand if	They are positively charged ions	They are free radicals	They are either neutral molecules or negatively charged ions	They have no charge	**They are either neutral molecules or negatively charged ions**
Ligands, in complex compounds	Accept e−-pair	Donate e−-pair	Neither accept nor donate e−-pair	All of these happen	**Donate e−-pair**
The number of neutral molecules or negative groups attached to the central metal atom in a complex ion is called	Atomic number	Effective atomic number	Coordination number	Primary valency	**Coordination number**
In complex compounds, metal ligand bond is	Coordinate bon	Hydrogen bon	Ionic bond	Covalent bond	**Coordinate bond**
A molecule which contains unpaired electrons is	carbon monoxide	Molecular nitrogen	Molecular oxygen	Hydrogen pe	**Molecular oxygen**

According to VSEPR theory, the most probable shape of the molecule having 4 electron pairs in the outer shell of the central atom is	Tetrahedral	Planar	Linear	Octahedral	**Tetrahedral**
Which type of overlapping results the formation of a π bond	Axial overlapping of s−s orbitals	Lateral overlapping of p−p orbitals	Axial overlapping of p−p orbitals	Axial overlapping of s−p orbitals	**Lateral overlapping of p−p orbitals**
Coordination compounds have great importance in biological systems. In this context which of the following statements is incorrect	Cyanocobalamin is B_{12} and contains cobalt.	Haemoglobin is the red pigment of blood and contains iron.	Chlorophylls are green pigments in plants and contains calcium.	Carboxypepticase-A is an enzyme and contains zinc.	**Chlorophylls are green pigments in plants and contains calcium.**
In the case of small cuts, bleeding is stopped by applying potash alum. Here alum acts as	Fungicide	Disinfectant	Germicide	Coagulating agent	**Coagulating agent**
The complex used as an anticancer agent is	trans −$[Co(NH_3)_3Cl_3]$	cis−$[PtCl_2(NH_3)_2]$	cis−$K_2[PtCl_2Br_2]$	Na_2CO_3	**cis−$[PtCl_2(NH_3)_2]$**
Which of the following is not an organometallic compound	Ethyl magnesium bromide	Tetraethyl lead	Sodium ethoxide	Trimethyl aluminium	**Sodium ethoxide**
What is the use of tetraethyl lead	As a catalyst in addition reaction of alkenes	As a catalyst in polymerization reaction of alkenes	For reducing knocking	For creating knocking	**For reducing knocking**

Questions	opt1	opt2	opt3	opt4	**Answer**
Compounds which have different arrangements of atoms in space while having same atoms bonded to each other are said to have	position isomerism	functional group isomerism	chain isomerism	stereoisomerism	**stereoisomerism**
Which of the following can make difference in optical isomers?	heat	temperature	polarized light	pressure	**polarized light**
Choose the incorrect option regarding Isomerism:	They differ in both physical and chemical properties	They have the different molecular formula	There are two types of Isomerism : Structural and Stereo Isomerism	Geometric and optical isomerism are two types of Stereo Isomerism	**They have the different molecular formula**
Isomerism that arises out of the difference in spatial arrangement of atoms or groups about the doubly bonded carbon atoms are called?	Structural Isomerism	Stereo Isomerism	Geometrical Isomerism	Optical Isomerism	**Geometrical Isomerism**
Isomers with similar groups on the same side are called as	” trans” isomers	” cis” isomers	” R” isomers	” S” isomers	**” trans” isomers**
Which among the following correctly defines Diastereomer	These have same magnitude but different signs of optical rotation	Nonsuperimposable object mirror relationship	These differ in all physical properties	Separation is very difficult	**These differ in all physical properties**

Which of the following is the definition for enatiomerism?	A pair of stereoisomers each of which has two chirality centres	A pair of stereoisomers that are not mirror images of one another	A pair of stereoisomers that are non-superimposable mirror images of one another	Any pair of stereoisomers	**A pair of stereoisomers that are non-superimposable mirror images of one another**
Which of the following statements is not true regarding pairs of enantiomers	They have identical boiling points	They rotate plane polarized light in opposite directions	They react at identical rates with chiral reagents	They have identical melting points	**They rotate plane polarized light in opposite directions**
Which of the following statements regarding optical rotation is not true	All R enantiomers are dextrorotatory	All (+) enantiomers are laevorotatory	All (-) enantiomers rotate plane polarized light in a counter clockwise direction	(+) and (-) enantiomers rotate plane polarized light in opposite directions	**All (-) enantiomers rotate plane polarized light in a counter clockwise direction**
Which of the following notations is not used to distinguish between pairs of enantiomers?	R and S	E and Z	+ and –	D and L	**E and Z**

Which among the following is true about enantiomerism?	Assignments of R and S labels and (+) and (–) labels are not connected	The labels R and S refer to different conformers	The labels (+) and (–) are used to distinguish enantiomers	The specific rotation of enantiomers is equal and opposite	**The labels R and S refer to different conformers**
Which of the following is true of any (S)-enantiomerism?	It rotates plane-polarized light to the right	It rotates plane-polarized light to the left	It is a racemic form	It is the mirror image of the corresponding (R)-enantiomer	**It is the mirror image of the corresponding (R)-enantiomer**
Which of the following is not true of enantiomers?They have the same:	boiling point	melting point	specific rotation	density	**specific rotation**
In the absence of specific data, it can only be said that (R)–2–bromopentane is which of the following?	dextrorotatory (+)	levorotatory (–)	optically inactive	analogous in absolute configuration to (R)–2–chloropentane	**analogous in absolute configuration to (R)–2–chloropentane**
Which statement about a chiral compound A is incorrect?	A racemate contains equal amounts of (+)-A and (–)-A	If A is resolved, it is separated into its enantiomers	(+)-A can also be labelled R-A, because (+) means the same as R	(+)-A and (–)-A will rotate polarized light equally but in opposite directions	**(+)-A can also be labelled R-A, because (+) means the same as R**

Which of the following is the definition of chirality?	The superimposability of an object on its mirror image	A molecule with a mirror image	The non-superimposability an object on its mirror image	A molecule that has a carbon atom with four different substituents	**The non-superimposability an object on its mirror image**
Which of the following is the definition of a pair of diastereomers?	A pair of stereoisomers each of which has two chirality centers	Any pair of stereoisomers	A pair of stereoisomers that are non-superimposable mirror images of one another	A pair of stereoisomers that are not mirror images of one another	**A pair of stereoisomers that are not mirror images of one another**
Which of the following can exist as diastereomers?	Lactic acid	1-Butene	2-Butene	Ethane	**2-Butene**
Polarimeter works on the principle of which of the following?	polarisation of light	change of the electrical conductivity of solution with composition	change of angle of refraction with composition	change of electrical conductivity of solution with temperature	**polarisation of light**
What does a polarimeter measure?	Polarity of the substance	Angle of rotation of an optical active compound	Concentration of the substance	pH of the substance	**Angle of rotation of an optical active compound**
Which of the following groups has the highest priority according to the Cahn-Ingold-Prelog sequence rules?	CH_3	CH_2Cl	CH_2OH	CHO	**CH_2Cl**

What are Stereoisomer?	Isomers having same molecular formula and same configuration	Isomers having same molecular formula but different configuration	Isomers having different molecular formula but same configuration	Isomers having different molecular formula and different configuration	**Isomers having same molecular formula but different configuration**
What are diastereomers?	Molecules with non-superimposable mirror images	Molecules with superimposable mirror images	Molecules which do not have non-superimposable mirror images	same molecules	**Molecules which do not have non-superimposable mirror images**
Choose the correct option from the following.	A group gets priority if its atomic number is high	When atoms attached to a double bond have same atomic number, the first atoms are considered	A group gets priority if its atomic number is low	Lone pair gets more priority and is ranked above hydrogen	**A group gets priority if its atomic number is high**
Conformations are different arrangements of atoms that can be converted into one another by rotation about	Covalent bond	Double bond	Single bond	Triple bond	**Single bond**
The energy required to rotate n-butane molecule about the carbon-carbon bond is called	Rotational ener	Torsional energy	Enantiomeric energy	Potential energy	**Torsional energy**

The rotation about the (C2 – C3) carbon-carbon bond of n-butane requires the energy of about	100 kJ/mol	50 kJ/mol	10 kJ/mol	3 kJ/mol	**3 kJ/mol**
The infinity of intermediate conformations are called	Skew conformations	Staggered conformations	Eclipsed conformations	Gauche	**Skew conformations**
The potential energy of n-butane is minimum for	Skew conformations	Staggered conformations	Eclipsed conformations	Gauche	**Staggered conformations**
The potential energy of n-butane is maximum for	Skew conformations	Staggered conformations	Eclipsed conformations	Gauche	**Eclipsed conformations**
The relative instability of any of the intermediate skew conformations is due to	Lateral strain	Shear strain	Longitudinal strain	Torsional stra	**Torsional str**
In gauche conformations, the methyl groups are	60 degree apart	90 degree apart	180 degree apart	360 degree apart	**60 degree apart**
Gauche conformation is less stable due to	Hydrogen bonding	Covalent bonding	Vander Waal's repulsion	Torsional strain	**Vander Waal's repulsion**
Select the incorrect statement from the following option.	Racemic modification is an equimolar mixture of dextrorotatory and levorotatory isomers	Meso compounds contains more than one chiral carbon centre	Meso compounds are externally compensated	Racemic mixture is designated as dl-pair	**Meso compounds are externally compensated**
The number of configurational isomers of molecules having (n) different chiral carbons is	2n	2 power n	2 power n-1	2 power n+1	**2 power n**

The isomers which can be inter converted through rotation around a single bond are:	conformers	diastereomers	enantiomers	positional isomers	**conformers**
An isomer of ethanol is:	methanol	diethyl ether	acetone	dimethyl ether	**dimethyl ether**
optical isomeerism arise from the presence of	an assymetric carbon atom	a centre of symmetry	a line of symmetry	angle of symmetry	**an assymetric carbon atom**
Optically active molecules which rotate plane-polarized light in a counterclockwise direction are said to be	levorotary	of R configuration	dextrorotary	of S configuration	**levorotary**
What is the relationship between 1-butene and cis-2-butene?	unrelated compounds	constitutional isomers	enantiomers	diastereomers	**constitutional isomers**
What is the relationship between trans-2-butene and cis-2-butene?	unrelated compounds	constitutional isomers	enantiomers	diastereomers	**diastereomers**
Which of the following physical properties differ for each of a pair of enantiomers?	solubility in ethanol	direction of rotation of plane-polarized light	boiling point and melting point	index of refraction	**direction of rotation of plane-polarized light**
An optically active compound is composed of 75% of the (R) enantiomer and 25% of the (S) enantiomer. The enantiomeric excess (ee) is equal to	87.5%.	75%.	50%.	37.5%.	**50%.**

Which of the following statements is TRUE?	To be diastereomers, a pair of molecules must have 2 or more chiral centers.	To be diastereomers, a pair of molecules must have at least 1 chiral center.	To be diastereomers, a pair of molecules must be stereoisomers.	To be diastereomers, a pair of molecules must be a racemate.	**To be diastereomers, a pair of molecules must be stereoisomers.**
Which of the following may be separated by ordinary physical methods?	a pair of identical molecules	a pair of enantiomers	a pair of diastereomers	a pair of identical atoms	**a pair of diastereomers**
optical isomerism arise from the presence of	asymmetric carbon	centre of symmetry	line of symmetry	double bond	**asymmetric carbon**
Isomers have essentially identical	Structural formula	Chemical properties	Molecular formula	Physical properties	**Molecular formula**
In ethane and cyclohexane which one of the following pairs of conformations are more stable	Eclipsed and chair conformations	Staggered and chair conformations	Staggered and boat conformations	Eclipsed and boat conformations	**Staggered and chair conformations**
Compounds with same molecular formula but different structural formulae are called	Isomers	Isotopes	Isobars	Isoelectronic	**Isomers**
Which statement is true for cyclohexane	It has two possible isomers	It has three conformations	Boat conformation is most stable	Chair and boat conformations differ in energy by 44 kJ/mol	**Chair and boat conformations differ in energy by 44 kJ/mol**

rain

Questions	opt1	opt2	opt3	opt4	**Answer**
According to the Lewis definition, a base is a(n)	Proton donor.	Electron pair donor	Hydroxide ion donor.	Electron pair acceptor	**Electron pair donor**
Which one of the following is a true statement?	The stronger the acid, the larger is its pKa.	The conjugate base of a strong acid is a strong base	Acid-base reactions always favor the formation of the stronger acid and the stronger base.	Strong acids can have negative pKa values.	**Strong acids can have negative pKa values.**
Which of the following is more acidic alcohol?	Phenol	Cyclohexanol	Methanol	Ethanol	**Phenol**
Electronegativity is defined as the power of an atom in a molecule to	Repel electrons towards itself	Attract electrons towards itself	Expand itself	not related	**Attract electrons towards itself**
Which of the following is a permanent electron displacement effect?	inductomeric	Electromeric	Inductive	tautomeric	**Inductive**
Which of the following is a temporary effect brought into play at the requirement of attacking reagent?	inductomeric	Electromeric	Inductive	mesomeric	**Electromeric**
Select the correct statement from the following option.	Conjugate effect is stronger than (-I) effect	Conjugate effect is weaker than (-I) effect	Conjugate effect is same as (-I) effect	no relation	**Conjugate effect is stronger than (-I) effect**
When the complete transfer of π-electrons take place away from the atom at the requirement of attacking agent, it is called	(-E) effect	(+E) effect	(-I) effect	(+I) effect	**(+E) effect**
The positively charged and electron deficient compounds which have a tendency to form a bond by accepting the electron pair are known as	Electrophiles	Nucleophiles	Homophiles	Heterophiles	**Electrophiles**
Which of the following is an example of lewis base?	$ZnCl_2$	BF_3	NH_3	$FeCl_2$	**NH_3**

Which of the following is an incorrect statement about the nucleophiles?	They are electron rich	They possess an empty orbital to receive the electron pair	They attack on electron deficient centres	Examples are: OH–, NH3, H2O etc	**They possess an empty orbital to receive the electron pair**
Those groups which are electron repelling and have lesser electron attracting power than hydrogen show	(-E) effect	(+E) effect	(-I) effect	(+I) effect	**(+I) effect**
In mesomeric effect, the electrons are transferred from	A multiple bond to an atom	A multiple bond to a single covalent bond	An atom with lone pair to the adjacent single covalent bond	All of the mentioned	**All of the mentioned**
Which of the following is a resonance effect?	inductomeric	Electromeric	Inductive	mesomeric	**mesomeric**
he phenomenon in which 2 or more structures, involving identical position of atoms can be written for a particular molecule, is called	Conjugation	Resonance	Hyper conjugation	Vibration	**Resonance**
Select the incorrect option from the following option.	Resonating structures have a real existence	The actual structure lies between various possible resonating structures	Resonating structures are useful as they allow us to describe molecules	benzene has Resonating structures	**Resonating structures have a real existence**

The resonance energy is defined as difference in energy between	Two consecutive resonating structures	Resonance hybrid and most unstable resonating structure	Resonance hybrid and most stable resonating structure	First and last resonating structures	**Resonance hybrid and most stable resonating structure**
Which of the following is not an application of mesomeric effect?	Dipole moment	Strength of acids and bases	Bond length	Vibration	**Vibration**
Select the correct statement from the following option.	Benzene ring have two different types of bond length for single and double bonds	All the bond length in benzene ring is equal due to hyperconjugation	All the bond length in benzene ring is equal due to resonance	All the bond length in benzene ring is not equal	**All the bond length in benzene ring is equal due to resonance**
Greater the number of resonating structures for a given intermediate,	Less will be its stability	More will be its stability	It will not effect its stability	no relation	**More will be its stability**
Phenyl group show	(-E) effect	(+E) effect	(-M) effect	(+I) effect	**(-M) effect**
On which factor the rate constant of a reaction does not depend upon?	temperature	activation ener	catalyst	concentration of reactants and products	**concentration of reactants and products**
The rate of reaction, A + B Products, is given by the equation, r = k[A][B]. If B is taken in excess, what would be the order of reaction?	2	0	1	unpredictable	**1**

Which of the following is not true about nucleophile?	donates an electron pair to an electrophile to form a chemical bond	all molecules or ions with a free pair of electrons or at least one pi bond can act as nucleophiles	nucleophile are Lewis acids by definition	a nucleophile becomes attracted to a full or partial positive charge	**nucleophile are Lewis acids by definition**
A substance which increases rate of reaction but itself remain chemically unchanged is called a	substrate	enzyme	reactant	product	**enzyme**
If proportion of particles with energy is greater than activation energy, reaction will	slow down	speed up	remains constant	end up	**slow down**
Order of reaction can be identified by plotting graphs of	reaction	concentration	pH value	both reaction and concentration	**both reaction and concentration**
Identify the false statement regarding resonance	As the number of charges increases, the resonance forms gets more significant	Zero charge of resonance is the most significant one	Atoms with full octet resonance form are more stable when compared with the one with unfilled octet	Resonance is unstable in case of unfilled octet of nitrogen atom	**As the number of charges increases, the resonance forms gets more significant**

Identify the correct sequence with respect to Inductive effects	CF3`> CH2F`> CHF2`> CF3`	CF3`> CHF2`> CH2F`> CH3`	CH3`> CH2F`> CHF2`> CF3`	CH3`> CHF2`> CH2F`v CF3`	**CF3`> CHF2`> CH2F`> CH3`**
Select the incorrect statement:	A resonance may sometimes cause sp3 atoms to become sp2 hybridized	Delocalizing one lone pair causes aromaticity	One lone pair will be counted as two pi electrons according to Huckel's equation	Two sigma bonds make up a double bond	**Two sigma bonds make up a double bond**
Resonance structure of molecule does not have	Identical arrangement of atoms	Nearly the same energy content	The same number of paired electrons	Identical bonding	**Identical bonding**
All bonds in benzene are equal due to	Tautomerism	Inductive effect	Resonance	Isomerism	**Resonance**
Aromatic properties of benzene are not proved by	Aromatic sextet theory	Resonance theory	Molecular orbital theory	bohrs theory	**bohrs theory**
Benzene is unreactive because	It has double bonds	It has carbon-carbon single bond	Carbon are sp2 hybridised	π electrons are delocalised	**π electrons are delocalised**
Carboxylic acids are easily ionised. The main reason of this statement	Absence of a-hydrogen	Resonance stabilisation of carboxylate ion	Reactivity of a-hydrogen	Hydrogen bond	**Resonance stabilisation of carboxylate ion**
′C−C′ bond length in benzene lies between single and double bond. The reason is	Resonance	Isomerism	Metamerism	Inductive effect	**Resonance**

Credit for the ring structure of benzene goes to	Wholer	Faraday	Kekule	Baeyer	**Kekule**
Which of the following is observed in ethylene molecule	Electromeric effect	Inductive effect	Homolytic fission	Resonance	**Electromeric effect**
Orbital interaction between the sigma bonds of a substitutent group and a neighbouring pi orbital is known as	Conjugation	Resonance	Hyper conjugation	Vibration	**Hyper conjugation**
Select incorrect statement	Homolytic fission results in the formation of free radicals	Heterolytic fission results in the formation of Lewis acid and Lewis base	Completion of the octet provides a major driving force for the Lewis acid-base reaction	Steric bulky group increases nucleophilicity.	**Steric bulky group increases nucleophilicity.**
Which of the following is through space-effects on polarizability due to electronegativity differences?	Field effect	Resonance effect	Inductive Ef	Polarizability	**Field effect**
Which of the following occurs as a result of electronegativity differences?	Field effect	Resonance effect	Inductive Ef	Polarizability	**Inductive E**
Which of the following involves the actual movement of electrons through a pie-bond system?	Field effect	Resonance effect	Inductive Ef	Polarizability	**Resonance effect**
The movement of electrons through a conjugated system allows for charges to be dispersed over several atoms. This phenomenon is	Localization	Delocalization	Polarization	Depolarization	**Delocalization**
Sigma-bonding electrons, especially those from C-H bonds can be donated in a process known as	Polarization	Depolarization	conjugation	Hyper conjugation	**Hyper conjugation**
relative basic strength of amines does not depend on	steric effect	Inductive effect	mesomeric effect	stabilisation of cation by hydration	**mesomeric effect**

Which statement is correct about the inductive effect?	It operates through σ-bonds.	Its range is limited to one bond.	It operates through space.	It operates through π-bonds.	**It operates through σ-bonds.**
Which statement is correct about the field effect?	Its range is limited to one bond.	It operates through space.	It operates through σ-bonds.	It operates through π-bonds.	**It operates through space.**
Which of the following best describes the enthalpy change of a reaction	The difference between the energy of bond formation and bond cleavage	The energy consumed when chemical bonds are broken	The energy released when chemical bonds are broken	The increase in disorder of a system as a reaction proceeds	**the difference between the energy of bond formation and bond cleavage**
Enthalpy is represented by the symbol	K	H	S	U	**H**

ffect

Questions	opt1	opt2	opt3	opt4	**Answer**
Which intermediate carbocation is more stable in pinacole -pinacolone rearrangement?	primary	secondary	tertiary	quarternary	**tertiary**
Which of the following statements is correct for alkyl halide?	Alkyl halide will always show SN1 mechanism	As branching at carbon increases, E1 mechanism is favoured as compared to SN1 mechanism	In unimolecular reaction, increasing the temperature donot favours E1 mechanism	In most unimolecular reactions of alkyl halide E1 reaction is favoured over SN1 reaction	**As branching at carbon increases, E1 mechanism is favoured as compared to SN1 mechanism**
Which of the following statement is correct?	E2 is a concerted reaction in which bonds break and new bonds form at the same time in a single step	Order of reactivity of alkyl halides towards E2 dehydrohalogenation is found to be 3o > 2o> 1o	In E2 elimination different stereoisomer (diastereomer) converts into different stereo product	All of the mentioned	**All of the mentioned**
Formation of a single product from two reactant molecules is known as	addition reaction	elimination reaction	substitution reaction	oxidation	**addition reaction**
Reaction in which replacement of one atom or group of atoms are involved is termed as	addition reaction	elimination reaction	substitution reaction	oxidation	**substitution reaction**
Breakdown of any molecule with water (H2O in any reaction is	addition reaction	elimination reaction	substitution reaction	hydrolysis	**hydrolysis**

Stablization of a carbocation by alkyl groups involves hyperconjugation between:	a filled C-H sigma bond with a vacant p*-orbital	a vacant sigma*-orbital with the vacant p-orbital	a filled C-H sigma-bond with a vacant p-orbital	a filled C-H sigma-bond with a filled p-orbital	**a filled C-H sigma-bond with a vacant p-orbital**
Which of the following will react with an alkene to give a product in a single step?	NBS, H_2O, DMSO	carbene	H_3O	Cl_2	**carbene**
Which of the following statements concerning a carbocation is not true?	the hybridization is sp^2.	the geometry is trigonal planar.	they are stabilized by hyperconjugation.	they cannot be observed, isolated or trapped.	**they cannot be observed, isolated or trapped.**
Choose the correct one which will react faster in the SN2 nucleophilic substitution reaction	$CH_2-CH=CH_2=Br$	$CH_2 = CH-CH_2 – Br$	$CH_2 = CH-CH_2 = Br$	$CH= CH_2 – CH_2 – Br$	**$CH_2 = CH-CH_2 – Br$**
What will be the reactivity of chlorobenzene in an electrophilic substitution reaction with benzene?	Reacts very slowly than benzene	Reacts in the same way as benzene	Reacts faster than benzene	Does not react with benzene	**Reacts very slowly than benzene**
Primary alcohols undergo what reaction to form alkenes?	Elimination	Oxidation	Reduction	Hydrolysis	**Elimination**
In a free radical reaction, free radicals are formed at	initiation step	propagation step	termination step	both initiation step and propagation step	**both initiation step and propagation step**
An acceptor of pair of electron is termed as	nucleophile	electrophile	carbocation	anion	**electrophile**
Covalent bonds can be break by	homolytic fission	heterolytic fission	homolytic fusion	both homo and heterolytic fission	**both homo and heterolytic fission**

Formation of radicals which attack reactants molecules generate more free radicals. This step is a	initiation step	propagation step	termination step	elimination step	**propagation step**
Organic solvents are	polar solvents	non-polar solvents	donors of Hydrogen ions	formed through sigma bonds	**non-polar solvents**
Most of organic solvents are	strong electroly	non-electrolyte	weak electrol	poor insulators	**non-electroly**
Organic solvents do not include	alcohol	water	petrol	tetra chloromethane	**water**
In exothermic reactions, final energy content of products	is lower than the energy contents of the reactants	is higher than the energy contents of the reactants	does not depend upon the energy content of the reactants	forms highly stable compounds	**is lower than the energy contents of the reactants**
Incorrect statement is: An exothermic reaction,	forms a compound which gives out heat while being formed	contains products that are very stable	resulting in overall enthalpy change zero	gives overall negative enthalpy.	**contains products that are very stable**

Exothermic reactions take place when	energy given out in making bonds is less than the energy taken in for breaking bonds	energy given out in making bonds is more than the energy taken in for breaking bonds	energy given out in making bonds is equal to the energy taken in for breaking bonds	the final energy content of products is lower	**energy given out in making bonds is more than the energy taken in for breaking bonds**
Exothermic reactions does not include	upon heating, hydrogen results in water	neutralization of acids and alkalis	respiration	breaking of chemical bond	**breaking of chemical bond**
In which of the following species the central C-atom is negatively charged	Carbanion	Carbonium ion	Carbocation	Free radical	**Carbanion**
Which of the following free radicals is most stable	Primary	Methyl	Secondary	Tertiary	**Tertiary**
Which of the following contains three pairs of electrons	Carbocation	Carbanion	Free radical	Primary	**Carbocation**
Which of the following carbanion is most stable	Primary	Methyl	Secondary	Tertiary	**Methyl**
Among the given cations, the most stable carbonium ion is	sec-butyl	ter-butyl	n-butyl	quat-butyl	**ter-butyl**
Which of the following intermediate have the complete octet around the carbon atom	Carbonium ion	Carbene	Carbanion	Free radical	**Carbanion**
Which is the most stable carbocation	iso-propyl	Triphenylmethyl cation	Ethyl cation	π propyl cation	**Triphenylmethyl cation**
To which of the following four types does this reaction belong $B^- + R-A \rightarrow B-R + A^-$	Unimolecular electrophilic substitution	Bimolecular electrophilic substitution	Unimolecular nucleophilic substitution	Bimolecular nucleophilic substitution	**Bimolecular nucleophilic substitution**

An alkyl halide may be converted into an alcohol by	Elimination	Addition	Substitution	Dehydrohalogenation	**Substitution**
Dehydrohalogenation of an alkyl halide is a/an	Nucleophilic substitution reaction	Elimination reaction	Both nucleophilic substitution and elimination reaction	Rearrangement	**Elimination reaction**
Conversion of CH_4 to CH_3Cl is	Electrophilic substitution	Free radical addition	Nucleophilic substitution	Free radical substittion	**Free radical substittion**
$(CH_3)_3CBr + H_2O \rightarrow (CH_3)_3COH + HBr$ is an example of	Elimination reaction	Free radical substitution	Nucleophilic substitution	Electrophilic substitution	**Nucleophilic substitution**
The electrophile in the nitration of benzene is	NO_2+	CO_2	NO	CO	**NO_2+**
The following compound will undergo electrophilic substitution more readily than benzene	Nitrobenzene	Benzoic acid	Benzaldehyde	Phenol	**Phenol**
Elimination of bromine from 2-bromobutane results in the formation of	Equimolar mixture of 1 and 2-butene	Predominantly 2-butene	Predominantly 1-butene		**Predominantly 2-butene**
Bromination of alkanes involves	Carbanion	Carbonium ion	Carbocation	Free radical	**Free radical**

Which of the following statements regarding the E1 mechanism is wrong?	Reactions by the E1 mechanism are unimolecular in the rate-determining step.	Reactions by the E1 mechanism are generally first order.	Reactions by the E1 mechanism usually occur in one step.	Reactions by the E1 mechanism are multi-step reactions.	**Reactions by the E1 mechanism usually occur in one step.**
Which of the following statements regarding the E2 mechanism is wrong?	Reactions by the E2 mechanism are always bimolecular.	Reactions by the E2 mechanism are generally second order.	Reactions by the E2 mechanism usually occur in one step.	Reactions by the E2 mechanism usually occur in two steps.	**Reactions by the E2 mechanism usually occur in two steps.**
Which of the following statements regarding mechanisms of elimination reaction is wrong?	The E1 mechanism does not require a base.	The E2 mechanism generally occurs under highly basic conditions.	The E2 mechanism is stereospecific.	The E1cB mechanism is usually unimolecular	**The E1 mechanism does not require a base.**
The reaction rate of an Sn1 reaction is	k[electrophile]	k[nucleophile][electrophile]	Zero order	second order	**k[electrophil**
In an E2 reaction, the beta hydrogen is ______ to the leaving group.	adjacent	anti	attached	gauche	
The stereochemistry of an Sn2 reaction results in	a cis/trans product depending on the antiperiplanar nature of the substrate	a complete stereochemical inversion	a racemic mixture of products	the most highly substituted alkene	**a complete stereochemical inversion**

Dehydration of alcohols is an example of a(n) _____ mechanism.	E1 or E2	rearrangement	SN1	SN2	**E1 or E2**
Saytzeff rule states that the major product is	the most substituted alkene	the less substituted alkene	with more hydrogens	with the most neutrons	**the most substituted alkene**
The stereochemistry of an Sn1 reaction results in	a cis/trans product depending on the antiperiplanar nature of the substrate	a complete stereochemical inversion	a racemic mixture of products	the most highly substituted alkene	**a racemic mixture of products**
The rate of an Sn2 reaction is	0	1	2	-1	**2**
The rate of an Sn1 reaction is	0	1	2	-1	**1**

yte

e]