KARPAGAM ACADEMY OF HIGHER EDUCATION
DEPARTMENT OF CHEMISTRY

LECTURE PLAN

Name of the Staff	:	Dr. S.P. Rajendran
Department	:	Chemistry
Title of the Paper	:	Organic Chemistry-I (Basics and hydrocarbons)
Paper Code	:	19CHU103
Class	:	I-B.Sc-Chemistry
Year and Semester	:	I-Year (2019) and I-Semester
Total Hours	:	60 Hours

UNIT-I **HOURS REQUIRED-12**

S.No.	Lecture Hour	Topics to be Covered	Support Materials
1.	1	Basics of Organic Chemistry: Hybridization- Shapes of molecules.	T1:277-282 T2:31-33
2.	1	Electronic Displacements: Inductive and Electromeric effects.	T1:296-301 T2:59-60
3.	1	Resonance and mesomeric effects.	T1:291-296 T2:60-63
4.	1	Hyperconjugation and dipole moment	T1:301-306 T2:63-64
5.	1	Hydrogen bonding (Applications to be discussed with relevant topics).	T1:306-311 T2:36-38
6.	1	Homolytic and Heterolytic fission with suitable examples. Curly arrow rules-formal charges.	T1:319-320, 342-343 T2:57-58
7.	1 1	Electrophiles and Nucleophiles. Types, shape and relative stability of Carbocations.	T1:322-328 T2:64-69, 90
8.	1	Types, shape and relative stability of Carbanions.	T1:329-331 T2:69-72
9.	1	Types, shape and relative stability of Free radicals and Carbenes.	T1:331-338 T2:72-76, 81-86
10.	1	Introduction to types of organic reactions: Addition, Elimination and Substitution reactions.	T1:321-322 T2:55-56
11	1	Recapitulation and discussion of important questions.	

UNIT-II **HOURS REQUIRED -12**

S.No.	Lecture Hour	Topics to be Covered	Support Materials
1.	1	Stereochemistry: introduction	T1:391
2.	2	Fischer, Newmann and Sawhorse Projection formulae and their interconversions.	T1:391-392 T2:173-177
3	1	Geometrical isomerism: cis–trans, syn-anti and	T1:383-390 T2:230-233
4.	1	E/Z notations with C.I.P rules.	T1:383-390

			T2:230-233
5	1	Optical Isomerism: Optical Activity-Specific Rotation.	T1:358-359 T2:170-172
6	1	Chirality/Asymmetry and Enantiomers.	T1:359-364 T2:177-178
7	1	Molecules with two or more chiral-centres, Diastereoisomers-meso structures.	T1:363-364, 377-378 T2:186-190
8	1	Racemic mixture and their resolution.	T1:378-382 T2:179-181
9	1	Relative and absolute configuration: D/L designations. .	T1:365-367 T2:182-183
10.	1	Relative and absolute configuration: R/S designations.	T1:367-374 T2:183-186
11	1	Recapitulation and discussion of important questions	

UNIT-III **HOURS REQUIRED -12**

S.No.	Lecture Hour	Topics to be Covered	Support Materials
1	1	Chemistry of Aliphatic Hydrocarbons Carbon-Carbon sigma bonds:General methods of preparation, physical properties of alkanes.	T1:418 T1:418-425
2	1	Chemical properties of alkanes.	T2:141-151
3	1	Wurtz Reaction and Wurtz-Fittig Reaction. .	T1:418-419, 624
4	1	Free radical substitutions	T1:425-429 T2:148-154
5	1	Halogenation-relative reactivity and selectivity.	T1:437-442 T2:154-161
6	1	Cycloalkanes and Conformational Analysis: Conformational analysis of alkanes .	T1:393-395 T2:122-130
7	1	Relative stability and Energy diagrams	T1:393-395
8	1	Types of cycloalkanes and their relative stability-	T1:444-445, T2:206-207,
9	1	Baeyer strain theory:	T1;454-455 T2:212-215
10	1	Chair, Boat and Twist boat forms of cyclohexane with energy diagrams.	T1:396-400

11	1	Relative stability of mono substituted cycloalkanes.	T2:216-224
12	1	Recapitulation and discussion of important questions.	

UNIT-IV **HOURS REQUIRED -13**

S.No.	Lecture Hour	Topics to be Covered	Support Materials
1	1	Chemistry of Aliphatic Hydrocarbons Carbon-Carbon pi bonds: General methods of preparation, physical properties of alkenes,.	T1:466-468 T2:302-308
2	1	Chemical properties of alkenes	T1:466-468 T2:302-308
3	1	General methods of preparation, physical and chemical properties of alkynes.	T1:512-515 T2:415-419
4	1	Mechanism of E1, E2, E1cb reactions.	T1:471-474 T2:309-310,319-321 T2: 309-321
5	1	Saytzeff and Hofmann eliminations.	T1:468-469 T2:316-318
6	1	Electrophilic additions and their mechanisms (Markownikoff/ Anti Markownikoff addition).	T1:476-481 T2:345-348
7	1	Mechanism of oxymercuration-demercuration and hydroboration-oxidation.	T1:484-486 T2:364-367
8	1	Ozonolysis, reduction (catalytic and chemical), syn and anti-hydroxylation (oxidation).	T1:482-484 T2:374-377
9	1	1,2-and 1,4-addition reactions in conjugated dienes and Diels-Alder reaction.	T1:499-506 T2:401-406
10	1	Allylic and benzylicbromination and mechanism, e.g. propene, 1-butene, toluene and ethyl benzene.	T1: 488-489, 564-566 T2:384-388
11	1	Reactions of alkynes: Acidity, Electrophilic and Nucleophilic additions.	T1:515-521 T2:420-424
12	1	Hydration to form carbonyl compounds-Alkylation of terminal alkynes.	T1:521-524 T2:418-419
13	1	Recapitulation and discussion of important questions.	

UNIT-V **HOURS REQUIRED -11**

S.No.	Lecture Hour	Topics to be Covered	Support Materials
1	1	Aromatic Hydrocarbons Aromaticity: Hückel’s rule-	T2:253 T1:545-546 T2:253
2	1	aromatic character of arenes.	T1:312-313

3	1	Aromaticity of Cyclic carbocations/carbanions and heterocyclic compounds with suitable examples.	T1:546-549 T2:254-256
4	1	Electrophilic aromatic substitution: halogenation, Electrophilic aromatic substitution: nitration	T1:549-552, 554 T2:262-264
5	1	Electrophilic aromatic substitution: sulphonation.	T1:549-552, 554
6	1	Friedel-Craft's alkylation/acylation with their mechanism.	T1:552-553 T2:264-265
7	2	Directing effects of the groups.	T1:555-560 T2:265-268, 276-282
8	1	Recapitulation and discussion of important questions.	
9	1	Discussion of previous ESE question papers.	
10	1	Discussion of previous ESE question papers.	

Text books:

T1. Madan, R.L. (2015). *Chemistry for Degree Students.*New Delhi: S. Chand and Company Pvt, Ltd.

T2. Morrison, R. N. & Boyd, R. N. (1992).*Organic Chemistry*. New Delhi: Dorling Kindersley Pvt. Ltd. (Pearson Education).

UNIT-I

Syllabus

Basics of Organic Chemistry
Hybridization, Shapes of molecules
Electronic Displacements: Inductive, electromeric, resonance and mesomeric effects, hyperconjugation and dipole moment; Hydrogen bonding (Applications to be discussed with relevant topics) Homolytic and Heterolytic fission with suitable examples. Curly arrow rules, formal charges; Electrophiles and Nucleophiles; Types, shape and relative stability of Carbocations, Carbanions, Free radicals and Carbenes. Introduction to types of organic reactions: Addition, Elimination and Substitution reactions.

Hybridisation of orbitals

The electronic configuration of carbon is $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1$ as its atomic number is 6. As the bonds are formed by unpaired electrons, carbon should show a valency of 2. But, we observe that carbon shows tetravalency in its compounds like methane or carbon dioxide. This was explained by saying that the above mentioned configuration is the configuration in the ground state. During the formation of bonds with other atoms, some of the electrons in lower energy levels are excited to higher levels. Thus, in the case of carbon, one electron from 2s level is excited to empty $2p_z$ level**(Figure 1.1).**

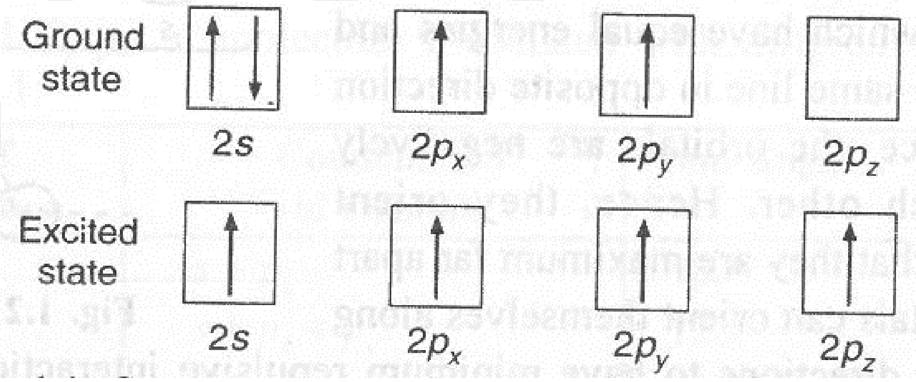


Figure 1.1. Ground and excited state configuration of carbon.

Now, there are 4 electrons which are unpaired. These four electrons will form four bonds by overlapping with the orbitals of other atoms. For example, they combine with four hydrogen atoms to form methane (CH_4).

However, there is one thing which is surprising. We find that in methane, all the C-H bonds have the same bond energy and all the angles H-C-H are the same, i.e., 109° 28’. Looking back at the orbitals, which participate in bonding, i.e., one s-orbital and three p-orbital which have different shapes and energies, we expect one of the bonds formed by s-orbital to be different from the three bonds formed by p-orbitals. Moreover, as the p-orbitals are inclined at an angle of 90° to each other, we expect the bond angles of 90° in methane also. But this actually is not so. To explain this anomaly, the concept of hybridization was introduced.

It is assumed that the 2s-orbital and three 2p-orbitals which are associated with different shapes and energies mix with each other and produce four equivalent types of orbitals with the same shape and energy and are oriented symmetrically in space. These are called hybrid or hybidised orbitals and this phenomenon is called hybridisation. These hybridised orbitals then overlap with the orbitals of other atoms to form bonds.

Thus, hybridisation is the process of mixing of orbitals of different shapes and energies, to produce orbitals of equivalent shape and energy oriented symmetrically with respect to one another.

This phenomenon explains satisfactorily why the bond energies and bond angles are equal in the case of methane and many other molecules.

Necessary conditions for hybridisation

There are certain conditions which must be satisfied before the orbitals hybridise to produce equivalent type of orbitals. These are:

i) The orbitals taking part in hybridisation should not differ too much in their energies. for example, 1s and 2p orbitals cannot hybridise. The participating orbitals must possess almost similar energies.
ii) As many hybrid orbitals will be obtained as the number of orbitals combining together.

iii) Whereas the paired orbitals do not take part in bonding, they can take part in hybridisation. In such a case, one of the positions in the geometrical shape is occupied by the loan pair of electrons. This happens in the case of ammonia and water molecules.

iv) It is not essential for all the unpaired orbitals to participate in hybridisation. Those unpaired orbitals which do not take part in hybridisation from π bonds by lateral overlapping.

Types of Hybridisation

Depending upon which atomic orbitals are combining together, we have different types of hybridisation, which are given below:

1**. sp or diagonal hybridisation**. This type of hybridisation occurs when one s orbital and one p orbital combine together to give two hybridised orbitals known as sphybridised orbitals which have equal energies and they are oriented along the same line in opposite direction at an angle of 180°. Since, the orbitals are negatively charged, they repel each other. Hence, they orient themselves in such a way that they are maximum far apart from each other. Two orbitals can orient themselves along the same line in opposite directions to have minimum repulsive interactions. The shapes of the hybridised orbitals in sphybridisation is given in **Figure 1.2**.

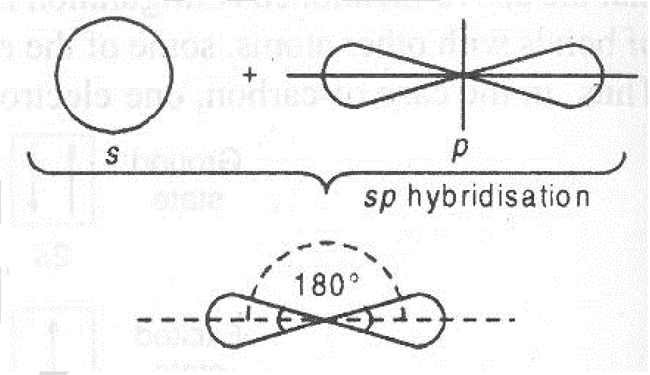


Figure 1.2.sp hybridization.

2**. sp^2 or trigonalhybridisation**. This type of hybridisation takes place when one s orbital and two 2p orbitals combine together to give three sp^{2}hybridised orbitals of equal energies. These hybrid orbitals are oriented at an angle of 120° in the same plane. The three orbitals point towards the corners of an equilateral triangle with the nucleus occupying the centre of the triangle. This is illustrated in **Figure 1.3.**

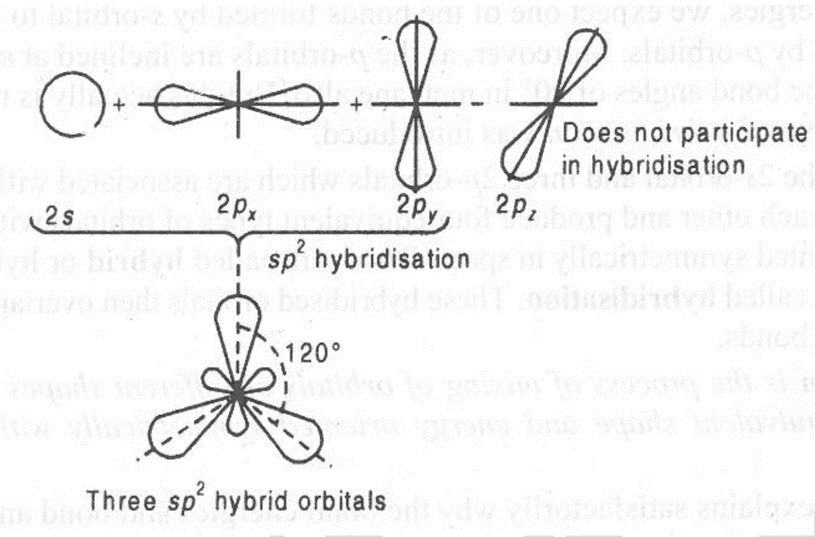


Figure 1.3.sp^2 hybridization.

3**. sp^3 or tetrahedral hybridisation**. When one s-orbital and three p orbitals combine together to produce equivalent type of orbitals, sp^3hybridisation takes place. Four sp^3hybridised orbitals are produced which have the same energy and shape and are oriented at an angle of 109°28' to one another. This is also known as tetrahedral hybridisation because the hybridised orbitals are pointing towards four corners of a tetrahedron with the nucleus occupying the centre of tetrahedron. In this position, the hybridised orbitals experience minimum repulsive forces. This is illustrated in **Figure1.4.**

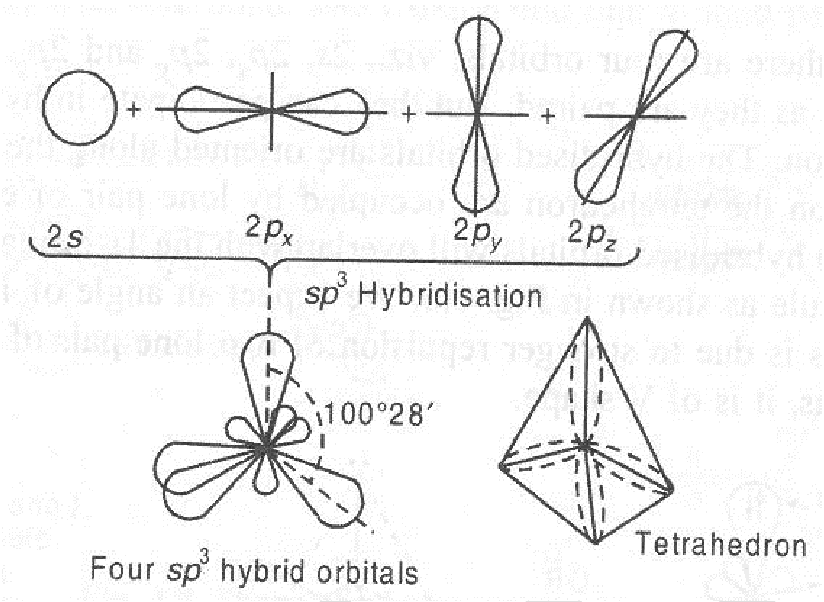


Figure1.4.sp^3 hybridization.

The geometry and shape of molecules associated with different types of hybridisation is summarised in **Table 1.1.**

S. No.	**Type of Hybridisation**	**Combination of Orbitals**	**Bond Angle**	**Geometry**
1.	sp	$s + p_x$	180°	Linear
2.	sp^2	$s + p_x + p_y$	120°	Trigonal
3.	sp^3	$s + p_x + p_y + p_z$	109°28'	Tetrahedral
4.	dsp^2	$d + s + p_x + p_y$	90°	**Square planer**
5.	sp^3d	$s + p_x + p_y + p_z + d$	90°, 120°	Trigonalbipyramidal
6.	sp^3d^2	$s + p_x + p_y + p_z + (2\times d)$	90°	Octahedral

SHAPES OF CERTAIN MOLECULES

1. Shape of methane molecule (CH_4)

Atomic number of carbon = 6. Electronic configuration of C in ground state = $1s^2\,2s^2\,2p_x^1\,2p_y^1$. Electronic configuration of C in excited state = $1s^2\,2s^2\,2p_x^1\,2p_y^1\,2p_z^1$.

There are four orbitals having unpaired electrons. These are 2s, $2p_x$,$2p_y$ and$2p_z$ orbitals. They will first hybridise. So, it is a case of sp^3hybridisation. Four hybridised orbitals are oriented tetrahedrally as shown in **Figure 1.5.**

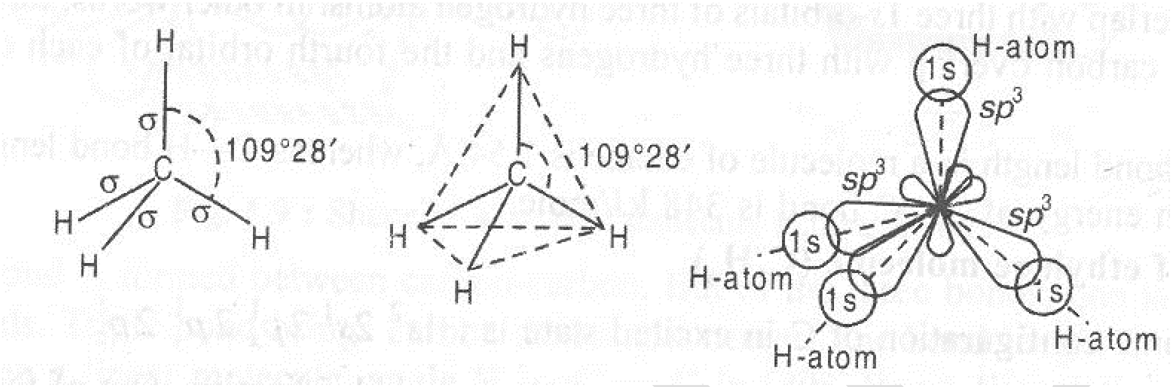


Figure 1.5. Shape of methane molecule.

All the four hybridised orbitals overlap with the 1s-orbital of four hydrogen atoms. All these overlappings take place along the internuclear axes. Hence, four carbon-hydrogen σ-bonds are formed. The angle <HCH is 109°28'.

2. Shape of ethylene molecule (C_2H_4)

The electronic configuration of C in excited state is: $1s^2\ 2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1$.
Here, all the four unpaired orbitals do not participate in hybridization. Out of four, only three orbitals viz., 2s, $2p_x$,and $2p_y$hybridise. The fourth one $2p_z$remains unhybridised. Hence, it is a case of sp^2hybridisation. The hybridised orbitals are oriented in the same plane at an angle of 120◦. We have two such carbons. One orbital of each carbon overlaps with each other to form a bond. Two orbitals of each carbon overlap with two 1s-orbitals of hydrogen to form four C-H σ-bonds. We are left with 2 unhybridised orbitals of two carbons which are oriented perpendicular to the plane of the rest of the molecule. They will overlap laterally giving rise to a weak π bond between carbon-carbon. Hence, there will be a double bond, one σ bond and one π bond between carbon-carbon **(Figure1.8).**

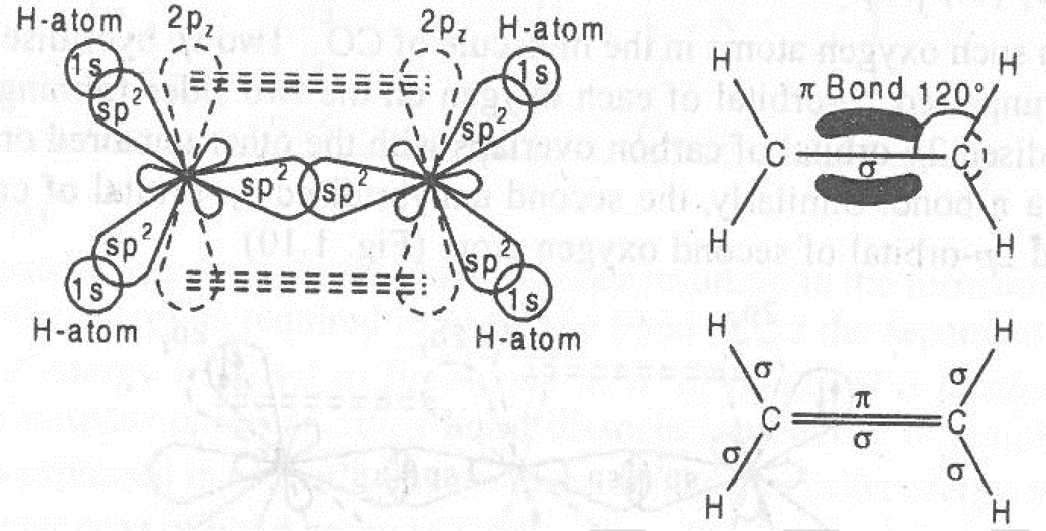


Figure 1. 8. Shape of ethylene molecule.

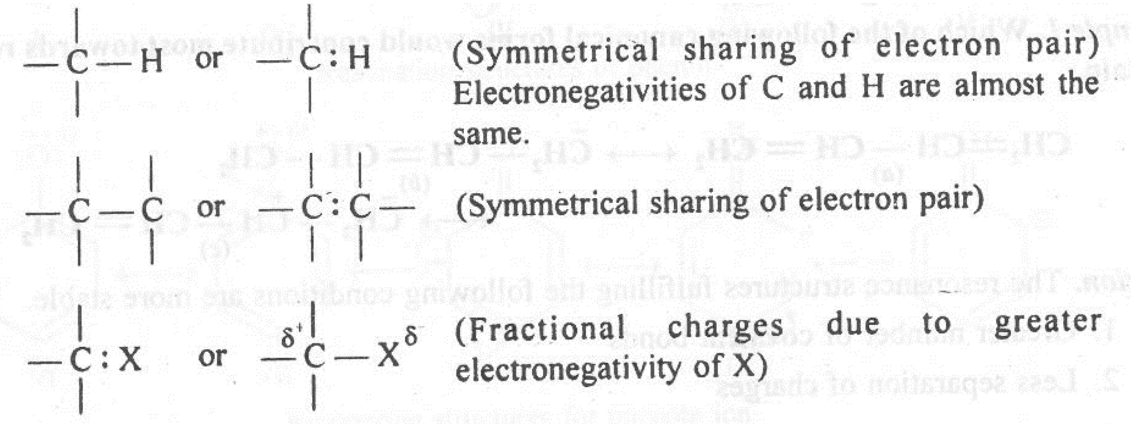
A double bond brings the carbon atoms together. Hence, the C=C bond length in C_2H_4 is shortened to 1.34 Å. The angle <HCH or <HCC is 120°, the trigonal angle. Bond dissociation energy of C=C bond is 614 KJ/mole.

ELECTRON DISPLACEMENT IN ORGANIC COMPOUNDS

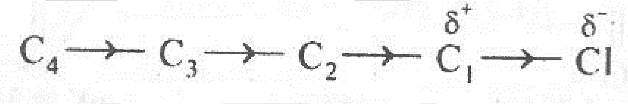
The behaviour of an organic compound is influenced by the electron displacement taking place in its covalent bonds. These displacements may be permanent or temporary which take place in presence of another species in the molecule. The acidity and basicity of organic compounds, their stability, their reactivity towards other substances, etc. can be predicted based on such electronic displacements.

Inductive Effect

This is a permanent effect operating in polar covalent bonds. The induction of a permanent dipole in a covalent bond between two unlike atoms of different electronegativities is called the inductive effect. The development of partial +ve and –ve charges is due to shift of the shared pair of electrons towards the more electronegative atom. This results is small fractional charges on the constituent atoms. When a carbon atom is bonded to a hydrogen (C–H) or another carbon (C–C) atom by a covalent bond as in alkanes, the sharing of electron-pair is symmetrical between them. Thus, no charges are induced on the atoms. However, when carbon is bonded to a halogen (X), charges are created.



The direction of displacement is shown by placing an arrow head midway along the line representing the sigma bond.



$$C_4 \rightarrow C_3 \rightarrow C_2 \rightarrow \overset{\delta^+}{C_1} \rightarrow \overset{\delta^-}{Cl}$$

The inductive effect of an atom or a group of atoms diminishes rapidly with distance. Infact, the inductive effect is almost negligible beyond two carbon atoms from the active atom or group.

Inductive effect does not involve actual transfer of electrons from one atom to another but simply helps in displacing them permanently.

Groups with – I effect:

NO_2> CN > F > COOH >Cl> Br > 1 > OCH_3> C_6H_6

Decreasing order of –I effect ⟶

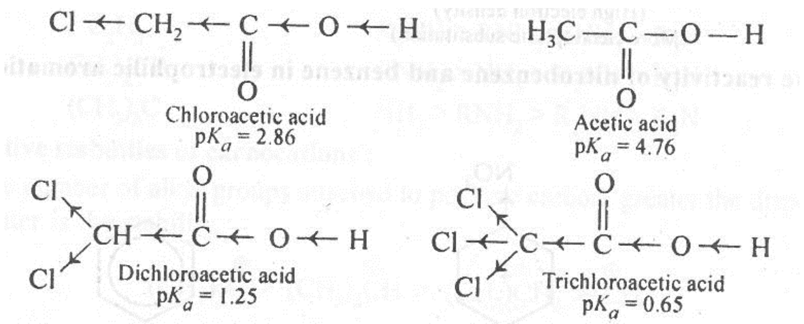
Groups with + I effect:

$(CH_3)_3C$ > $(CH_3)_2CH$ > C_2H_5> CH_3> - H

Decreasing order of +I effect ⟶

Applications

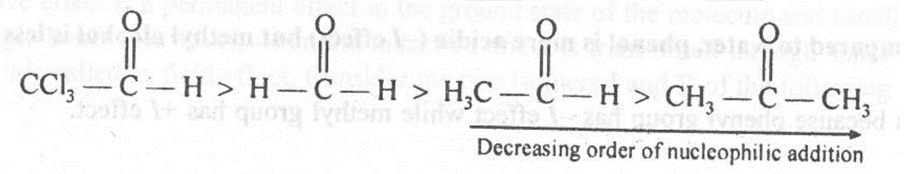
(i) (a) Acidity of acetic acid and halogen substituted acetic acid



The decreasing order of acid strength

$$Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH > CH_3COOH$$

On the other hand, electron withdrawing -I effect decreases electron availability on carbonyl carbon and therefore increases the rate of nucleophilic addition.



(ii) Strength of base: Base strength is defined as the tendency to donate an electron pair for sharing. Strength of a base can be explained on the basis of inductive effect.

(a) As compared to ammonia, methyl amine is more basic (+I effect) but aniline is less basic and diphenyl amine is a still weaker base (-I effect).

$$CH_3NH_2 > NH_3 > C_6H_5NH_2 > (C_6H_5)_2NH$$

(b) The decreasing order of base strength in alcohols from tertiary to primary is due to +I effect of alkyl groups.

$$(CH_3)_3COH > (CH_3)_2CHOH > CH_3CH_2OH > CH_3OH$$

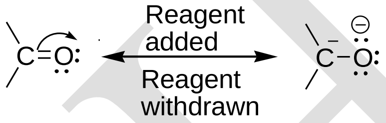
3^o 2^o 1^o methyl

(c) Greater the tendency to donate electron pair for coordination with proton, more is the basic nature, or more the negative charge on nitrogen atom (due to +I effect of alkyl group), higher is the basic strength.

ELECTROMERIC EFFECT

This is a temporary effect operating in unsaturated compounds only at the demand of a reagent. As soon as this attacking reagent is removed, the original condition is restored.

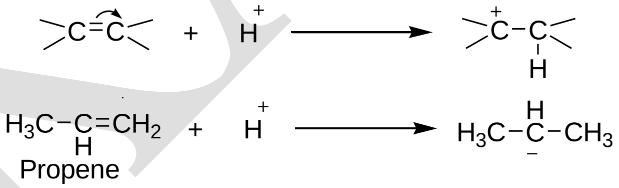
It involves the complete transfer of π electrons of multiple bonds, because π bonds are loosely held and are easily polarizable.



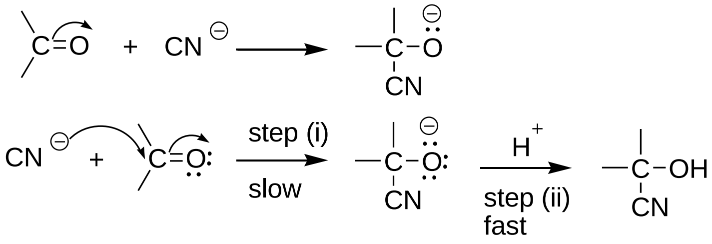
The complete transfer of shared pair of π-electrons of a multiple bond to the more electronegative atom of the bonded atoms at the requirement of an attacking reagent is called electromeric effect (E-effect)

When the transfer of π electrons takes place towards the attacking reagent (electrophile), the effect is called +E-effect.

For example,



When the transfer of electrons takes place away from the attacking reagent, the effect s called –E-effect. For example,



When the I– and E-effect occur together in a molecule, they may be supporting or opposing each other. When they are opposing, the E-effect generally dominates over I-effect.

Applications

(i) Electrophilic addition reactions of unsaturated compounds involve electromeric effect or the polarisation of the carbon-carbon double bond in the presence of attacking electrophiles like H^+.

(ii) Nucleophilic addition reactions of carbonyl compounds involve electromeric effect or polarisation through –E electromeric effect of the carbon–oxygen double bond in the presence of a nucleophile.

Comparison of Inductive and Electromeric Effects

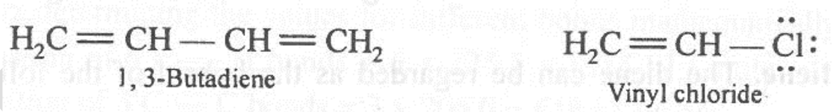
Inductive effect	Electromeric effect
1. It involves a permanent displacement of the electron pairs in the molecule.	It involves a temporary transference of the electron pair towards more electronegative atom in the molecule.
2. The displaced electron pair does not leave its molecular orbital. There is only a distortion in shape of the molecular orbital	The electron pair which gets transferred completely leaves its molecular orbital and takes up a new position.
3. The presence of the outside attacking reagent is not needed.	The presence of the outside attacking reagent is essential.
4. There is a partial separation of the charges.	There is a complete separation of the charges.
5. No ions are formed.	Ions are formed.
6. The presence of multiple bond is not essential.	The presence of multiple bond is essential.

Comparison of Resonance and Inductive Effects

Resonance effect	Inductive effect
1. It occurs in conjugated systems.	It occurs in saturated compounds.
2. It involves the transference of the π-electrons.	It involves the displacement of the σ-electron.
3. It involves delocalization of electrons.	It does not involve any delocalization of electrons.
4. It does not undergo any change in charge density with distance.	It decreases as we move from the atom involved in the initial polar bond.

RESONANCE EFFECT OR MESOMERIC EFFECT

If two double bonds in a molecule are separated by a single bond, they are said to be in conjugation and the molecule having such bonds are called conjugated molecules e.g., 1,3-butadiene.



$H_2C=CH-CH=CH_2$ 1, 3-Butadiene $\quad H_2C=CH-\ddot{\underset{..}{Cl}}:$ Vinyl chloride

Another example of conjugation is given by benzene which is a hexagonal ring of carbon atoms with three double bonds in the alternate positions. Alternatively, a **double** bond or a **triple** bond may also be in conjugation with a lone electron pair e.g., in vinyl chloride.

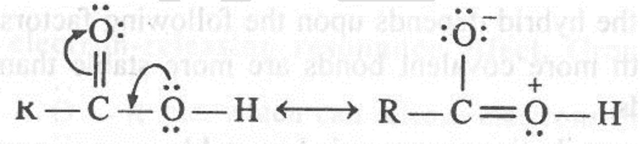
The conjugated molecules do not exhibit the character of pure double bond or triple bond, for example, benzene is expected to be highly reactive since it has three double bonds in the ring but is actually quite stable. In order to explain the difference in the expected and the actual behaviour of the conjugated molecules, Robinson and Ingold stated that such compounds exist in two or more forms none of which can explain all the properties of the molecule under investigation. They called this concept as **mesomerism** or **mesomeric effect**. Heisenberg studied the same mathematically and named it as resonance or resonance effect. According to the concept, If a compound having a certain molecular formula can be represented by different structural formulae which differ only in the arrangement of the electron pairs and not of the atoms, such like structures are called **resonating** or **contributing** or **canonical structures** and the phenomenon is known as resonance. The compound cannot be represented completely by any of the resonating or contributing structures but by a mixture of all of them which is called resonance hybrid (cannot be actually represented). Resonance is indicated by the sign ⟷ .

It may be noted that the various resonating or contributing structures do not actually exist i.e., they are all hypothetical structures. They have been given simply to explain certain properties of the compounds which cannot be otherwise explained.

Examples of Resonance

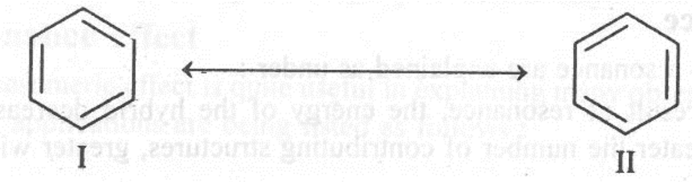
A common analogy of a resonance hybrid is that of a mule which is a hybrid of horse and donkey.

1. Monocarboxylic acid. The acidic character of monocarboxylic acid is explained with the help of resonance. The following contributing structures for the monocarboxylic acid are possible which differ in the position of the electron pairs.



As a result of resonance, the oxygen atom of the O-H group acquires a positive charge i.e., n draws the electrons pair towards itself resulting in the release of protons.

2. Benzene. Benzene is a hybrid of two equivalent contributing structures (I and II) which differ in the position of the π-electron pairs representing double bonds. These were suggested by Kekule.



Conditions of resonance

Wheland has suggested the following conditions for resonance

i) The resonance or the contributing structures must differ only in the position of the electron pairs and not of the atomic nuclei.

ii) The resonating structures must have the same number of paired and unpaired electrons.

iii) The energies of the various resonating structures must be either same or nearly the same.

iv) All the contributing or resonating structures do not contribute equally towards the hybrid. The equivalent structures have greater contribution. The contribution of any resonating structure towards the hybrid depends upon the following factors:

a) Structures with more covalent bonds are more stable than the structures with less covalent bonds.

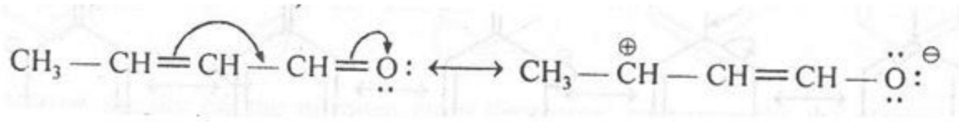
b) The charged contributing structure is less stable as compared to the structure without any charge.

c) Structure with negative charge on more electronegative atom is more stable than the structure with negative charge on less electronegative atom.

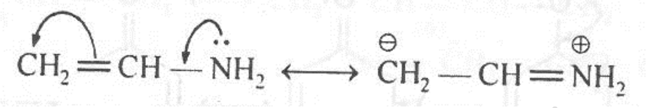
Types of resonance or mesomeric effect

Depending upon the nature of the functional group present adjacent to the multiple bond, the resonance effect (R) or mesomeric effects (M) are of two types:

(i) Groups having electron–withdrawing resonance effect. Groups such as –NO_2,>C=O, -CN, -COOH etc. tend to withdraw the electrons from the multiple bond through resonance and are said to have –M or –R effect. For example, in the following compound, the aldehyde group (–CH = O) has –R effect.



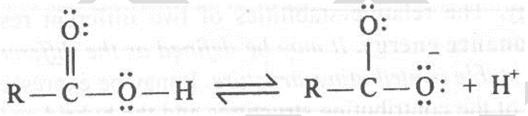
(ii) Groups having electron – releasing resonance effect. Group such as –NH_2, -NHR, -NR_2, -O–H, -O–R etc. which can release electrons through resonance are said to have + M or + R effect. For example, the amine group (-NH_2) in the following compound has + R effect.



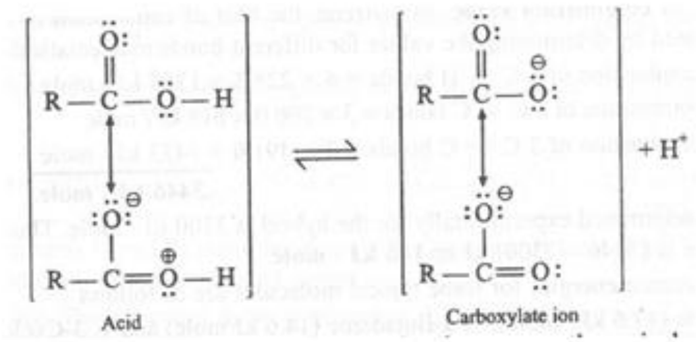
Applications of resonance effect

Resonance effect or mesomeric effect is quite useful in explaining many observations in organic compounds. A few typical applications are being listed as follows:

1. Explanation for the acidic character of carboxylic acid. The acidic character of carboxylic acid is due to release of H^+ ion in aqueous solution.



This is explained with the help of resonance. Both the acid the carboxylate ion are resonance stabilized as shown below:



While the contributing structures for the carboxylate ion are exactly equivalent, they are not so for the acid. Therefore, hybrid for the ion is more stable than for the acid. The acid changes to a more stable ion by releasing a proton and this account for the acidic character of carboxylic acid.

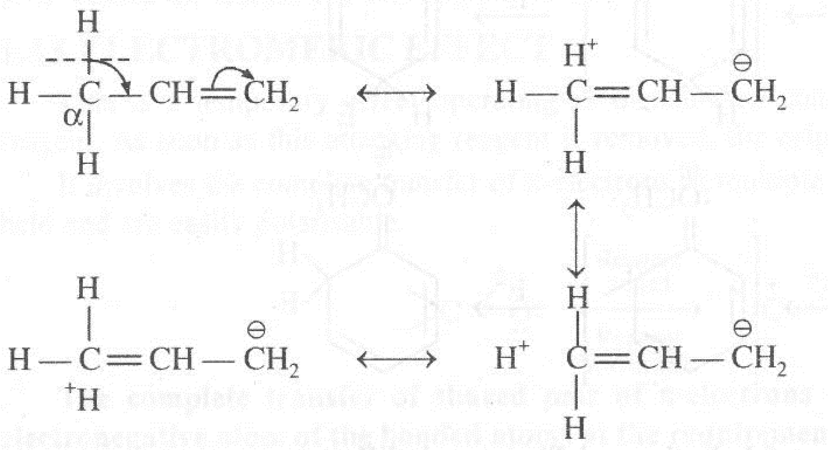
HYPERCONJUGATION OR NO BOND RESONANCE

In the study of inductive effect, we have observed that the alkyl group has +I effect and the order of +I effects of different alkyl groups follow the order:

$$-CH_3 < -C_2H_5 < -CH(CH_3)_2 < -C(CH_3)_3$$

But when the alkyl group is attached to an unsaturated system such as $-CH=CH_2$ group, the order of the inductive effect simply gets reversed. This anomaly in the electron releasing tendency of the alkyl groups is explained on the basis of **hyperconjugation**which was developed by Baker and Nathan. It is also called Baker-Nathan effect.

Explanation. According to the concept, if an alkyl group carrying at least one hydrogen is attached to an unsaturated carbon atom, it releases the electrons of the C–H bond towards the multiple bond. For example, in propene ($CH_3-CH=CH_2$), the following contributing structures are involved.

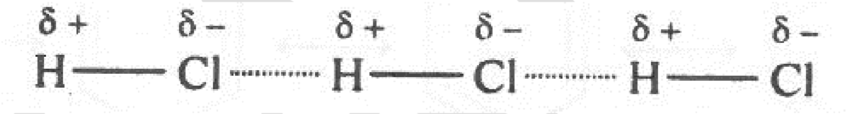


Since there is no bond between the α-carbon atom and one of the hydrogen atoms, the hyper conjugation is also called **no-bond resonance**. Now, hyperconjugation due to CH_3–group is expected to be more than due to CH_3CH_2 –group since the latter has only two hydrogen atoms attached to the α -carbon atom directly linked to the double bonded carbon atom. Therefore, the number of contributing structures for ethyl group will be less. Similarly, the electron releasing tendency in $(CH_3)_2CH$–group will be still less as it has only one hydrogen atom attached to the α-carbon atom and this tendency will be the least when the $(CH_3)_3C$–group is attached to the $CH=CH_2$ group. Thus, the order of the electron releasing tendency or inductive effect of the alkyl groups gets reversed because of the phenomenon of hyperconjugation.

THE HYDROGEN BOND

The compounds, in which hydrogen is attached to some electronegative atom, general exhibit unexpected properties like relatively high melting and boiling points, high solubility in water. The behavior is explained on the basis of a new concept termed as the hydrogen bond. The hydrogen bond an electrostatic force of attraction between a hydrogen atom attached to more electronegative atom and some other electronegative atom of the same or different molecule.

For example, in hydrogen chloride, hydrogen is attached to electro-negative atom of chlorine. The bond is a polar covalent bond. Hydrogen has partial positive charge and chlorine has partial negative charge. An electrostatic force of attraction is set up between hydrogen atom of one molecule and chlorine atom of other molecule.



$$\overset{\delta+}{H}-\overset{\delta-}{Cl}\cdots\cdots\overset{\delta+}{H}-\overset{\delta-}{Cl}\cdots\cdots\overset{\delta+}{H}-\overset{\delta-}{Cl}$$

The force of attraction is a hydrogen bond and is represented by a dotted line.

Thus, as a result of hydrogen bonding, & H-atom links the two electronegative atoms simultaneously, one by a covalent bond and the other by a hydrogen bond, it is said to form a hydrogen bridge.

Conditions for hydrogen bonding

The following conditions must be fulfilled for the formation of hydrogen bond:

(i) *The molecule must contain a highly electronegative atom linked to H-atom, Higher the electronegativity, greater is the polarization of the molecule.*

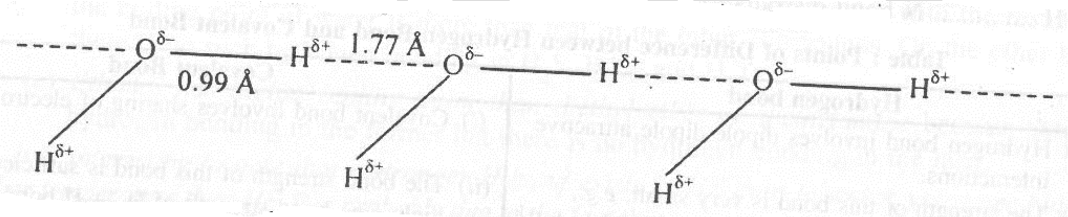
(ii) *The size of the electronegative atom should be small.* Smaller the size of the electronegative atom, greater is the electrostatic attraction.

Thus, only F, O and N atoms satisfy these conditions and form hydrogen bonds of high electronegativities.

Chlorine having the same electronegativity as that of nitrogen does not form hydrogen bond due to its large size.

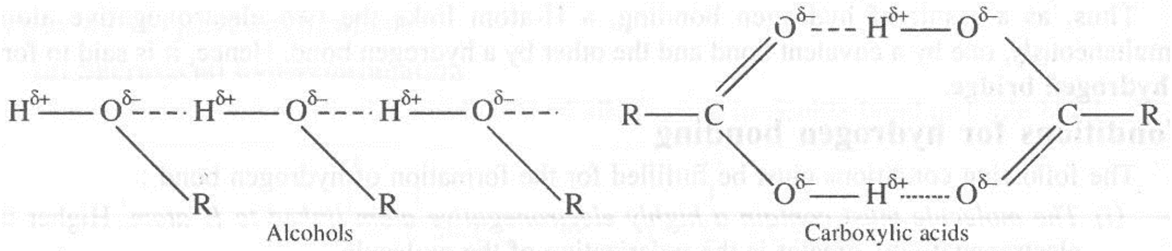
Examples of hydrogen bonding

(i) Water (H_2O): Water molecule contains highly electronegative oxygen atom linked to hydrogen atom. Due to large electronegativity difference, oxygen end of the molecule becomes negative, whereas the H-atom becomes positive. The negative end of one molecule attracts the positive end of the other and hydrogen bonding takes place as shown below:



Parameters of the two kinds of O – H bonds are also indicated.

(ii) **Alcohols (ROH) and carboxylic acids (RCOOH) :** Theses molecules contain the highly electronegative oxygen atom linked to H-atom and, hence, form associated molecules as follows :



In carboxylic acids, the hydrogen bonding causes association of two molecules only.

Strength of hydrogen bond

Hydrogen bond is a very weak bond. The strength of hydrogen bonds is intermediate between the weak van der Waals' forces and the strong covalent bonds. Thus, whereas the bond dissociation energy of a covalent bond is 209 – 418 kJ mol^{-1}, that for H-bond is only 12.6–41.8 kJ mol^{-1}. The dissociation energy of the H-bond depends upon the attraction of the shared pair of electrons and, hence, on the electronegativity of the atom. The bond energies in case of three elements are as follows:

H …………..F bond dissociation energy is 41.8 kJ mole $^{-1}$.
H ………… O bond dissociations energy is 29.3 mole^{-1}.
H ………… N bond dissociations energy is 12.6 mole^{-1}.

Table: Points of difference between Hydrogen bond and Covalent bond

Hydrogen bond	Covalent bond
(i) Hydrogen bond involves dipole-dipole attractive interactions.	(i) Covalent bond involves sharing of electrons.
(ii) The strength of this bond is very small, e.g., bond strength of H …. F bond is 41.8 kJ mol^{-1}	(ii) The bond strength of this bond is sufficiently high e.g., bond strength of H …. H bond is 433 kJ mol^{-1}
(iii) It is formed between a hydrogen atom and a highly electronegative atom such as F, O and N.	(iii) It is formed between two electronegative atoms which may be of the same element or of different elements.

Consequences of hydrogen bonding

(i) Dissociation: In aqueous solution, hydrogen fluoride dissociates to give the difluoride ion (HF_2^- instead of fluoride ion (F^-). This is due to H-bonding in HF. This explains the existence of KHF_2. On the other hand, the molecules of HCI, HBr and HI do not have H bonding (because C1 Br and I are not so highly electronegative). This explains the non-existence of compounds like $KHCl_2$,KHBr, or KHI_2.

(ii) Association: Carboxylic acids exist as dimers because of the hydrogen bonding. The molecular masses of such compounds are found to be double than those calculated from their simple formulae. For example molecular mass of acetic acid is found to be 120.

Types of hydrogen bonding

Hydrogen bonding is of two types:

(i) **Intermolecular hydrogen bonding:** When hydrogen bonding takes place between different molecules of the same or different compounds, it is called intermolecular hydrogen bonding Hydrogen fluoride, water, alcohols and solutions of alcohol or ammonia in water involve intermolecular hydrogen bonding.

(ii) **Intramolecular hydrogen bonding:** When hydrogen bonding takes place within a molecule, it is called intramolecular hydrogen bonding. It takes place in compounds containing two groups such that one group contains a H – atom linked to an electronegative atom and other group contains a highly electronegative atom linked to a lesser electronegative atom. The bond is formed between the H-atom of one group with the more electronegative atom of the other group. Intramolecular hydrogen bonding is involved in compounds like o-nitrophenol, o-nitrobenzaldehyde and salicylic acid.

Effects of intramolecular hydrogen bonding

The intramolecular hydrogen bonding prevents association of molecules causes a contraction of size of the molecules and, hence, decreases its surface area. Consequently, intramolecular hydrogen bonding results in lowering their melting and boiling points. It also decreases their solubility and increases their vapour pressure. Intramolecular hydrogen bonding produces results opposite to that of intermolecular hydrogen bonding.

HOMOLYTIC AND HETEROLYTIC BOND BREAKING (FISSION)

Consider a covalent bond between atoms A and B.

A : B or A - B

The cleavage (or breaking) of this bond can take place in three possible ways depending upon the relative electronegativities of A and B.

(*i*) $A:B \longrightarrow A\bullet + B\bullet$ (A• and B• of equal electronegativity)

(*ii*) $A:B \longrightarrow \overset{-}{A}\!: + \overset{+}{B}$ (A more electronegative than B)

(*iii*) $A:B \longrightarrow \overset{+}{A} + :\overset{-}{B}$ (B more electronegative than A)

The first type of cleavage is called homolytic fission or homolysis and leads to the formation of very reactive species called 'free radicals' (atoms or groups of atoms containing odd or unpaired electrons).

In homolytic fission the covalent bond breaks in such a way that each fragment carries one unpaired electron.

The second and third types of cleavage are called heterolytic fission and leads to the formation of ionic species. These ionic species are also very reactive and carry charges on carbon. Cationic species carrying positive charge on a carbon atom are called carbonium ions or carbocations. Anionic species carrying negative charge on carbon atom are called carbanions.

In heterolytic fission the covalent bond breaks in such a way that the pair of electrons stays on the more electronegative atom.

CURVED ARROW NOTATION

In the study of organic reaction mechanisms, we come across movement of electrons from one atom to the other. This movement of electron is represented with the help of curved arrows. This method is known as curved arrow notation. For example, when the atom B is more electronegative than atom A in the following compound. Then in the presence of a reagent, the flow of electrons that takes place may be represented with the help of curved arrows.

$$A{=}B \xrightarrow{\text{Reagent added}} \overset{\delta+}{A} - \overset{\delta-}{B}$$

Electronegativity plays an important role in knowing the direction of transfer of the shared pair of electron to one of the atoms.

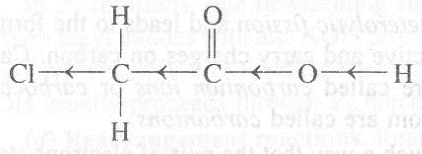
(i) In a carbonyl group, >C=O, present in aldehydes and ketones, the displacement is towards the oxygen atom which is represented by a curved arrow as under

DRAWING ELECTRON MOVEMENTS WITH ARROWS

There are instances in organic molecules where the separation of charges (complete +ve or –ve) does not take place. But, due to the presence of electron-attracting or electron repelling groups, some kind of polarization or movement of electrons takes place. We represent it with the help of arrows along he bonds. For example, in the molecule of ethyl chloride the arrows would be drawn as:

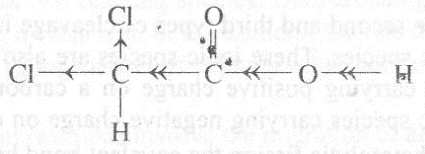
$$CH_3 \rightarrowtail CH_2 \rightarrowtail Cl$$

Presence of a halogen group in a carboxyl acid helps in the release of protons. This happens because the electron movement takes place in the direction of the halogen group. Greater the number of halogen groups, greater will be the charge movement away from the carboxylic group and towards the halogen groups. This can be illustrated as under.



$$Cl \longleftarrow \underset{H}{\overset{H}{C}} \longleftarrow \overset{O}{\overset{\|}{C}} \longleftarrow O \longleftarrow H$$

Chloroacetic acid



$$Cl \longleftarrow \underset{H}{\overset{Cl}{\overset{\uparrow}{C}}} \twoheadleftarrow \overset{O}{\overset{\|}{C}} \twoheadleftarrow O \twoheadleftarrow H$$

Dichloroacetic acid

HALF-HEADED AND DOUBLE HEADED ARROWS

In the complete conversion of a compound A to the compound B, we use half-headed arrow.

$$A \longrightarrow B$$

But when the conversion to B is not complete or it is reversible, we use the notation $\rightleftharpoons$ or $\longleftrightarrow$

$$A \rightleftharpoons B \quad \text{or} \quad A \longleftrightarrow B$$

The notation $\longleftrightarrow$ is also used to represent the resonating structures of a compound.

(i) Resonating structures of carbon dioxide are represented as under

$$\underset{\text{I}}{O=C=O} \longleftrightarrow \underset{\text{II}}{O^{-}-C\equiv \overset{+}{O}} \longleftrightarrow \underset{\text{III}}{\overset{+}{O}\equiv C-\overset{-}{O}}$$

TYPES OF REAGENTS – NUCLEOPHILES AND ELECTROPHILES

Nucleophilic reagents or nucleophiles

A nucleophilic reagent is a reagent with an atom having an unshared or lone pair of electrons. Such a reagent is in search of a point where it can share these electrons to form a bond. Nucleophiles are of two types.

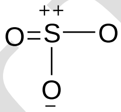
(i) Neutral nucleophiles. These are the nuclephiles which are neutral in charge. But they carry some unshared electrons which they like to share with some positive centre or electron deficient centre. Ammonia NH_3, water H_2O and alcohols R–O–H are examples of neutral nucleophiles.

(ii) Negative nucleophiles. These are the nucleophiles which carry negative charge. Examples of this type of nucleophiles are hydroxyl ions (OH^-), halide ion (X^-), alkoxide ion (RO^-) and cyanide ion (CN^-). Carbanions also come in the category of negative nucleophiles.

Electrophilic reagents or electrophiles

An electrophile is a reagent containing electron deficient atoms. Such species have a tendency to attach themselves to centres of high electron density. There are two types of electrophiles:

(i) Neutral electrophiles. These electrophiles do not carry any net charge. Lewis acids like $AlCl_3$, $FeCl_3$ and BF_3 belong to this category of electrophiles. Sulphonium ion (SO_3) carries no net charge, but it acts as an electrophile for sulphonation in benzene rings. This is because of its structure.

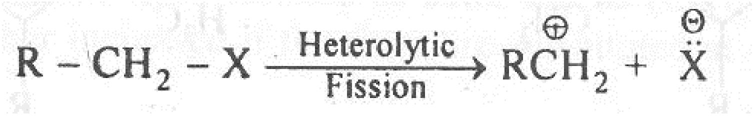


As the positive charge is concentrated and the negative charge is scattered, it acts as an electrophile. Substances like $SnCl_4$ which have vacant d-orbitals would like to accommodate electrons in them. Thus such substances also act as electrophiles.

(ii) Positive electrophiles. These electrophiles carry a net positive charge. Examples of this category of electrophiles are hydrogen ion (H^+), hydronium ion (H_3O^+), nitronium ion (NO_2^+), and chloronium ion (Cl^+). In the halogenation and nitration of aromatic systems, these electrophiles are involved.

CARBOCATIONS

These are defined as the species in which the positive charge is carried by the carbon atom with six electrons in its valence shell. These are formed by the heterolytic fission in which an atom or group along with its pair of electrons leaves the carbon. In heterolytic fission, the shared pair of electrons between two atoms goes to one atom only.



$$R-CH_2-X \xrightarrow[\text{Fission}]{\text{Heterolytic}} R\overset{\oplus}{C}H_2 + \overset{\ominus}{\ddot{X}}$$

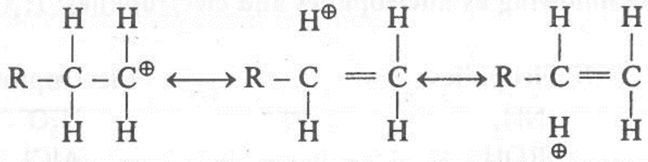
Stability of Carbocations

1. The order of stability among simple alkyl carbocations is tertiary>secondary > primary. In most of the reactions, primary and secondary carbocations get rearranged to tertiary carbocations. Both n-propyl fluoride and isopropyl fluoride form the same isopropyl cation(2^{o}carbocation). Similarly all the four butyl fluorides viz., n-, iso-, sec. and tertiary butyl fluorides form the same tert-butyl cation. There are two factors which determine the stability:

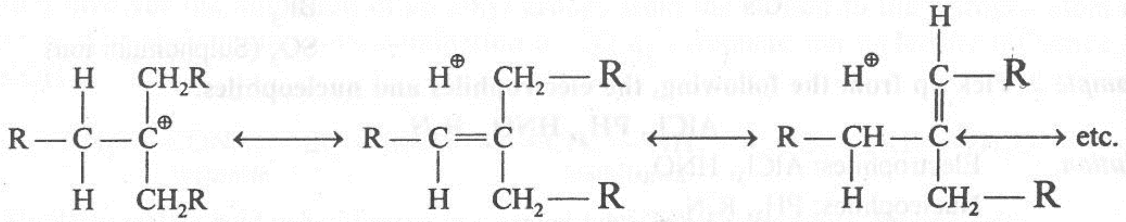
(i) Hyperconjugation or resonance.
(ii) Field effect or inductive effect of groups

Hyperconjugation

A large number of canonical forms can be written for tertiary carbocation compared to those for primary carbocation. Consider hyperconjugation in primary and tert-carbocation.



Hyperconjugation in primary carbocation



Hyperconjugation in tertiary cation

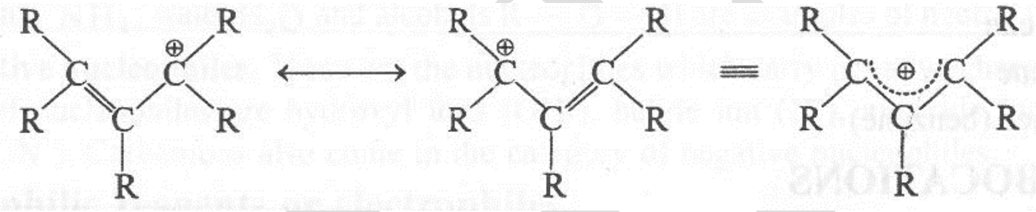
Greater the number of canonical forms, greater is the stability.

Field effect

1. Electron donating effect of alkyl groups increases the electron density around the +vely charged carbon. This result in reducing the magnitude of positive charge on it and thus the charge is delocalized on α–carbon. Dispersal of positive charge increases the stability. Of

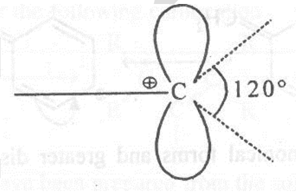
carbocation of all the simple cation, tert-butyl cation being most stable. Even tert-pentyl and tert-hexyl cations produce tert-butyl cation at high temperature. Lower alkanes like methane, ethane and propane when treated with super acid also yield tert-butyl cation as the main product. Salts of tert-butyl cation, like $(CH_3)_3C^+ SbF_3^-$ have been prepared from super acid solutions.

2. The stability of carbocation containing a conjugated double bond is usually greater due to increased delocalization by resonance. In such carbocations, the positive charge is dispersed on at least two carbon atoms. Consider the following carbocation.



Structure and reactions of carbocations

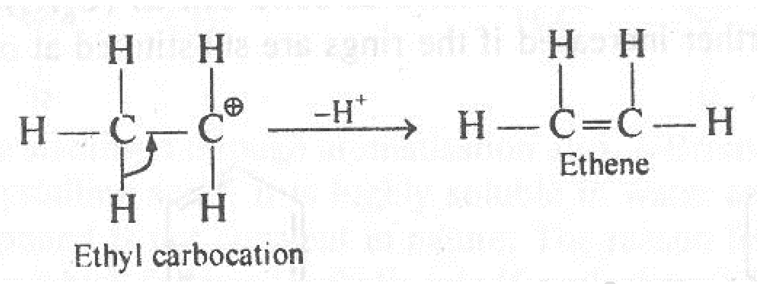
Structure: The carbon atom bearing the positive charge in a carbocation is sp^{2}hybridised. The three sp^2 hybrid orbitals are utillised in the formation of sigma bonds with three atoms or groups. The third unused p-orbital remains vacant. Thus, the carbocation is a flat species having all the three bonds in one plane with a bond angle of 120^o between them as shown below:



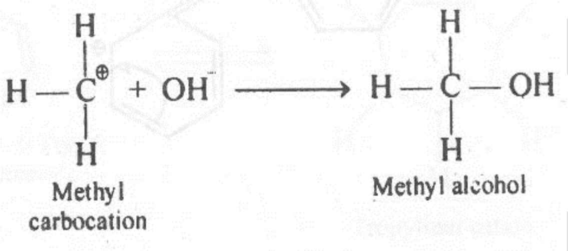
Reactions

Carbocations, which are short-lived species and very reactive give the following reactions:

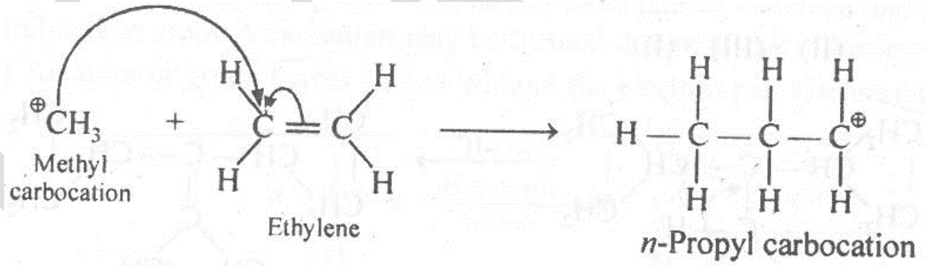
1. Proton loss. Carbocation may lose a proton to form an alkene. An ethyl carbocation loses a proton to form ethene.



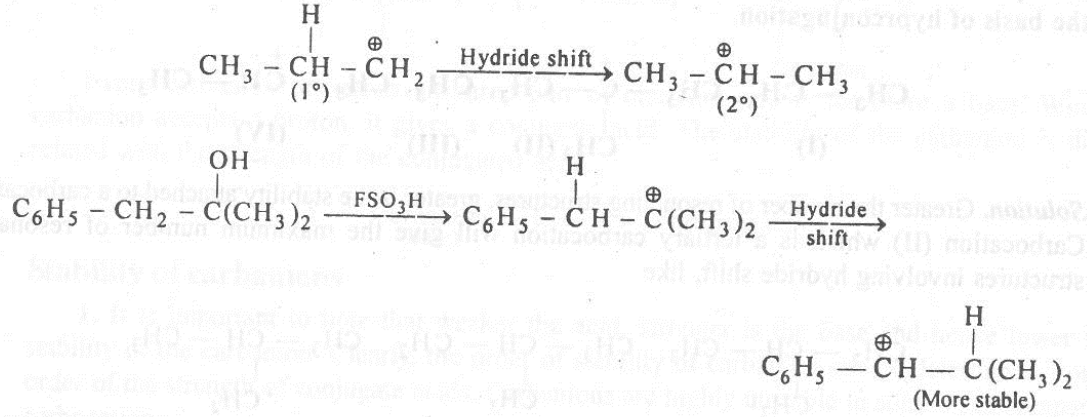
2. Combination with nucleophiles. Carbocations combine with nucleophiles to acquire a pair of electrons. For example, a highly reactive methyl carbocation with hydroxyl ion to form methyl alcohol.



3. Addition to alkene. A carbocation may add to an alkene to produce another carbocation possessing higher molecular weight.



4. Rearrangement. The migration of alkyl or aryl or hydrogen along with an electron pair to the positive centre takes place which results in the formation of more stable carbocation. Some examples are given below.



$$CH_3-\overset{H}{\underset{(1^\circ)}{CH}}-\overset{\oplus}{C}H_2 \xrightarrow{\text{Hydride shift}} CH_3-\underset{(2^\circ)}{\overset{\oplus}{C}H}-CH_3$$

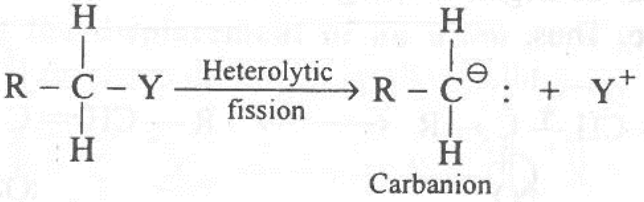
$$C_6H_5-CH_2-\overset{OH}{C}(CH_3)_2 \xrightarrow{FSO_3H} C_6H_5-\overset{H}{C}H-\overset{\oplus}{C}(CH_3)_2 \xrightarrow[\text{shift}]{\text{Hydride}} \underset{\text{(More stable)}}{C_6H_5-\overset{\oplus}{C}H-\overset{H}{C}(CH_3)_2}$$

Such a rearrangement takes place because a tertiary carbocation is more stable than secondary carbocation, which in turn is more stable then primary carbocation. Similarly, a carbocation attached to a phenyl group (benzene ring) is more stable than others.

CARBANIONS

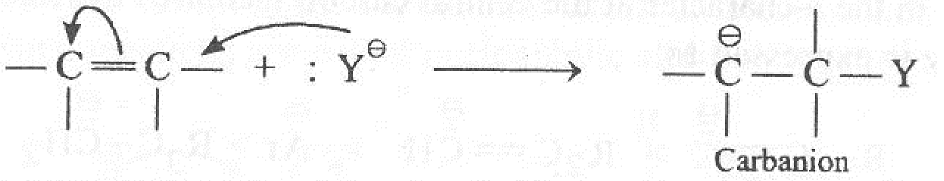
These are defined as the species with an unshared pair of electrons and a negative charge on the central carbon atom. A carbanion may be formed in one of the following ways:

(i) An atom or group leaves carbon without the electron pair (Heterolytic fission).



$$R-\overset{H}{\underset{H}{C}}-Y \xrightarrow[\text{fission}]{\text{Heterolytic}} \underset{\text{Carbanion}}{R-\overset{H}{\underset{H}{C}}^{\ominus}:} + Y^+$$

(ii) An anion adds to a carbon-carbon double or triple bond



$$-\overset{|}{\underset{|}{C}}=\underset{|}{C}- + :Y^{\ominus} \longrightarrow \underset{\text{Carbanion}}{-\overset{\ominus}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-Y}$$

Every carbanion possesses unshared pair of electrons and is therefore a base. When the carbanion accepts a proton, it gives a conjugate acid. The stability of the carbanion is directly related with the strength of the conjugate acid.

$$\underset{\text{(Base)}}{\text{Carbanion}} + H^+ \longrightarrow \text{Conjugate acid}$$

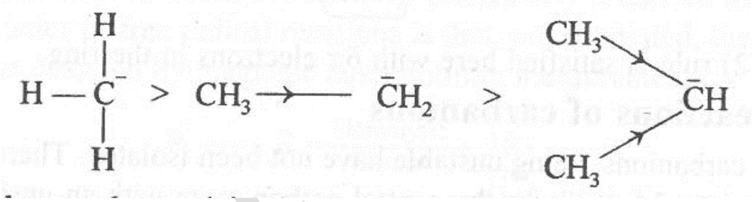
Stability of carbanions

1. It is important to note that weaker the acid, stronger is the base and hence lower is the stability of the carbanion. Clearly, the order of stability of carbanion can be determined from the order of the strength of conjugate acids. Carbanions are highly unstable in solution as compared to carbocations.

2. The order of stability of carbanions is:

Vinyl > Phenyl >Cyclopropyl> Ethyl > n-Propyl > Isobutyl

Also it has been found that the stability of carbanions decrease in the order methyl > primary-carbanion> secondary-carbanion.

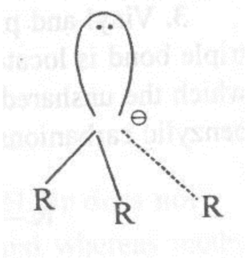


This stability order can be explained simply by the field effects. The presence of electron donating alkyl groups in secondary (isopropyl) carbanion results in greater localisation of negative charge on the central carbon atom and hence the stability falls. Cyclopropylcarbanion has greater stability due to greater s-character on the carbanionic carbon.

Structure and reactions of carbanions

Structure

The carbanions, being unstable have not been isolated. Therefore, their structure is not known with certainty. Most likely, the central carbon atom with an unshared pair of electrons (and negative charge) is sp^3hybridised. The three sp^3 hybrid orbitals are used in forming three sigma bonds with the other atoms. The fourth sp^3–orbital is occupied by a lone pair of electron. In fact, the structure of carbanion is quite similar to that of ammonia as shown in the Figure.

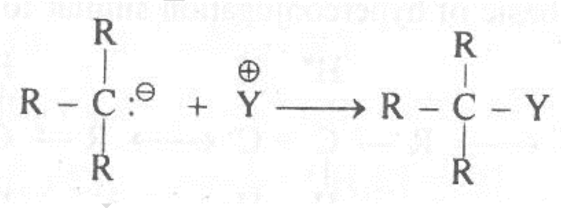


It different alkyl groups are attached to the central carbon, the carbanion will be chiral. Reactions in which such a carbanion is formed, give a product with retention of configuration. Carbanions which get stabilized by resonance involving the lone pair of electron and the π electrons of multiple bonds, should be planar as this is the necessary condition for resonance to take place.

Reactions

Some important reactions of carbanions are described below:

1. Reaction with positive species or electrophiles. A carbanion reacts with a proton or with another action.



$$R-\underset{R}{\overset{R}{C}}:^{\ominus} + \overset{\oplus}{Y} \longrightarrow R-\underset{R}{\overset{R}{C}}-Y$$

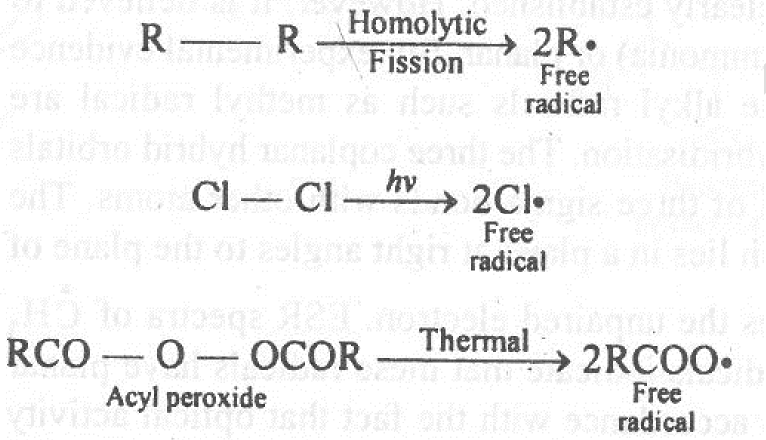
2.Rearrangement. In some cases, carbanions may rearrange to form more stable species. Consider the rearrangement in triphenylmethylcarbanion.

$$(C_6H_5)_3\,C-\overset{\ominus}{C}H_2 \longrightarrow (C_6H_5)_2\,\overset{\ominus}{\ddot{C}}-CH_2-C_6H_5$$

Here the two phenyl groups directly attached to the central carbon help in dispersing the negative charge.

FREE RADICALS

Free radicals are produced by the hemolytic fission of a covalent bond. These are odd electron neutral species which are formed by the hemolytic fission of a covalent bond. Free radicals are paramagnetic due to the presence of unpaired electron. Formation of free radicals is favoured by the presence of UV light, heat and organic peroxides. Reactions involving radicals widely occur in the gas phase. Such reactions also occur in solutions, particularly if carried in non-polar solvents. An important characteristics of free radical reactions is that, once initiated, they proceed very fast. The free radicals can be detected by magnetic susceptibility measurement.

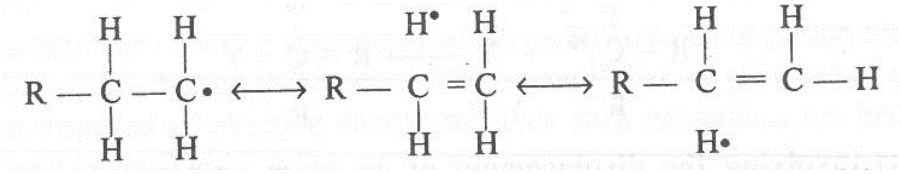


Stability of free radicals

1. Simplest alkyl free radicals are highly reactive like carbocations and carbanions. Their life time is extremely short in solution. The relative stability of simple alkyl radicals has the order:

$$\underset{3^\circ}{R_3\dot{C}} > \underset{2^\circ}{R_2\dot{C}H} > \underset{1^\circ}{R\dot{C}H_2} > \underset{\text{Methyl}}{\dot{C}H_3}$$

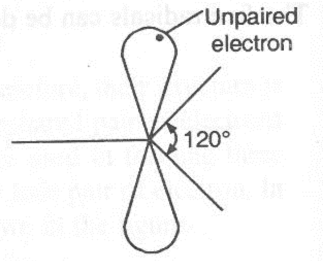
It can be explained on the basic of hyperconjucation similar to that in carbocations.



Greater the number of the resonating structures, greater is the stability of the free radical.

Structure and reaction of free radical

Structure. The state of hybridization of carbon atom having the unpaired electron is not clearly established. However, it is believed to be either pyramidal (like ammonia) or planar. But experimental evidence suggests strongly that the alkyl radicals such as methyl radical are actually planar with sp^2hybridisation. The three coplanar hybrid orbitals are used in the formation of three sigma bonds with other atoms. The unhybiridised orbital which lies in a plane at right angles to the plane of the hybrid orbitals, carriers the unpaired electron. ESR spectra of $^{\bullet}CH_3$ and other simple alkyl radicals indicate that these radicals have planar structure. This is also in accordance with the fact that optical activity is lost when a free radical is generated at an asymmetric carbon. As a general rule we can say that simple alkyl free radical prefer a planar or near planar shape. However, the free radicals in which the carbon is connected to atoms of high electronegativity prefer a pyramidal shape. The increase in electronegativity causes the deviation from the planar geometry.



Structure of a free radical

Reactions

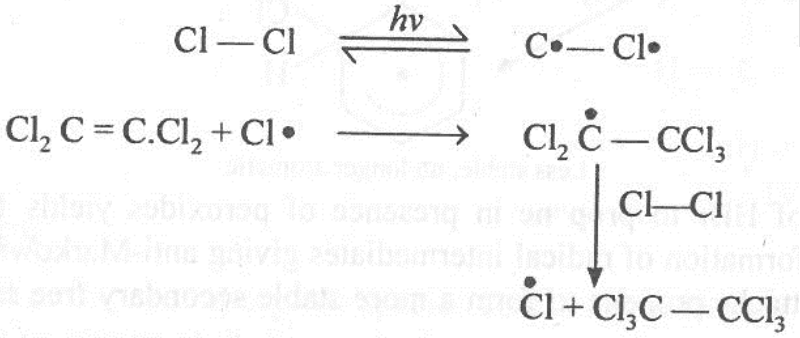
Some important reactions of free radicals are described below:

1. Halogenation of aliphatic hydrocarbons

$$Cl-Cl \xrightarrow{h\nu} 2Cl\bullet$$
$$CH_4 + Cl\bullet \longrightarrow CH_3\bullet + HCl$$
$$CH_3^{\square} + Cl_2 \longrightarrow CH_3Cl + Cl\square$$

In the presence of sunlight, chlorination of methane gives chloromethane, dichloromethane, chloroform and carbon tetrachloride.

2. Addition. Halogen addition to alkenes takes place with free radical mechanism. The addition of chlorine to tetrachloroethene is photochemicallycatalysed. A molecule of chlorine undergoes homolytic fission giving two chlorine radicals. Each radical is capable of initiating a reaction chain.



$$Cl-Cl \underset{}{\overset{h\nu}{\rightleftharpoons}} C\bullet-Cl\bullet$$

$$\begin{tikzcd}
Cl_2C=C.Cl_2+Cl\bullet \arrow[r] & Cl_2\dot{C}-CCl_3 \arrow[d, "Cl-Cl"] \\
 & \dot{C}l+Cl_3C-CCl_3
\end{tikzcd}$$

Cl$^\bullet$radical further adds to tetrachloroethene. This continues till the whole of tetrachloroethene has been converted into hexachloroethane. Chain termination occurs through radical-radical collision. The radical reactions are inhibited by the presence of oxygen. The reason is that the molecule of oxygen has two unpaired electrons and behaves as a biradical. This biradical combines with highly reactive radical intermediate and converts it to less reactive peroxy radical which is unable to propagate the chain reaction.

CARBENES

These are defined as the neutral organic species containing a divalent carbon atom having a sextet of electrons but no charge on it. For example,

(a) $:CH_2$ Methyl carbene

(ii) $:CCl_2$ Dichlorocarbene

Formation of carbenes

They can be generated by the following methods:

(i) By the action of UV light on diazomethane.

$$CH_2N_2 \longrightarrow \underset{\text{Methylene (Carbene)}}{:CH_2} + N_2$$

(ii) By the action of sodium ethoxide on chloroform.

$$\underset{\text{Chloroform}}{CHCl_3} + C_2H_5ONa \longrightarrow \underset{\text{Dichloro carbene}}{:CCl_2} + C_2H_5OH + NaCl$$

These are highly reactive species.

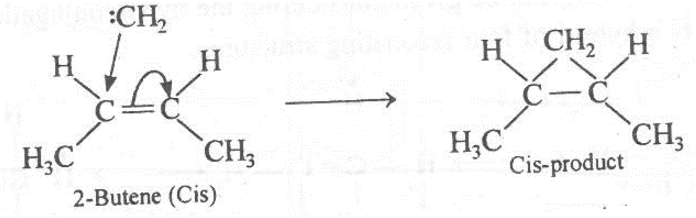
Stability

1. The two unbounded electrons of a carbene may be either paired or unpaired. When the two electrons on the carbon atom are paired, then it is called singlet carbene. In the triplet state, it is called a biradical as the two electrons on carbon atom are unpaired.

$$\underset{\text{Singlet methylene}}{H-\ddot{C}-H} \text{ or } \uparrow\downarrow CH_2 \qquad \underset{\text{Triplet methylene}}{H-\overset{\cdot}{\underset{\cdot}{C}}-H} \text{ or } \uparrow\uparrow CH_2$$

In the triplet state, carbene is relatively more stable as it has lower energy content.

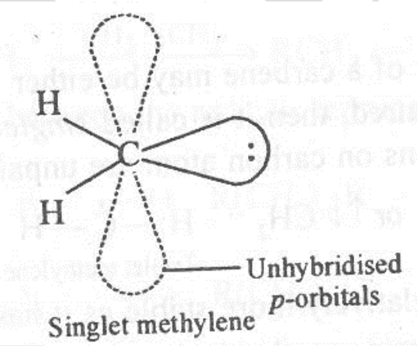
2. The singlet and the triplet species can be distinguished by the common addition reaction of carbene to double bond to form cyclopropane derivatives. The addition of singlet species to cis-butene forms a cis product. The reason is that the movement of two pairs of electrons occur either simultaneously or with one rapidly succeeding the other.



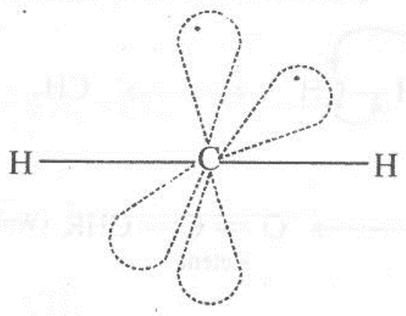
Structure and reactions of carbenes

Structure

The structures of two types of carbenes are different: Singlet carbene have their carbon in sp^2hybridised state. Of the three sp^2 hybrid orbitals, two are used in forming two single bonds with monovalent atoms or groups attached to carbon. The unshared pair of electrons is present in the third sp^2 hybrid orbital and the unhybridisedp-orbital is empty.

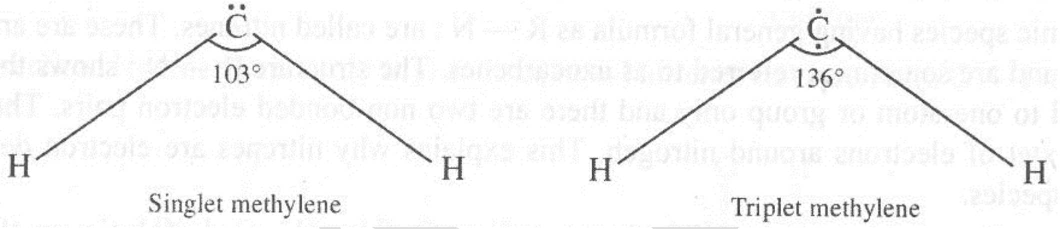


Triplet carbene has its carbon in sphybridised state. The two sp hybrid orbitals form two bonds with monovalent atoms or groups attached to carbon. The two unhybridised p-orbitals contain one electron each.



Triplet methylene

The structure of triplet methylene is revealed by ESR measurement since these species are biradicals. Its geometry is found to be bent with bond angle of about 136º. The electronic spectra of singlet methylene formed in flash photolysis of diazomethane tell that it is also bent and the bond angle is about 103º.

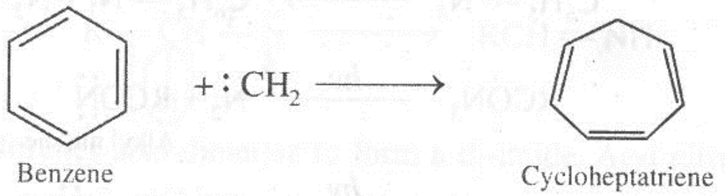


The bond angles in CCl_2 and CBr_2 are 100° and 114° respectively.

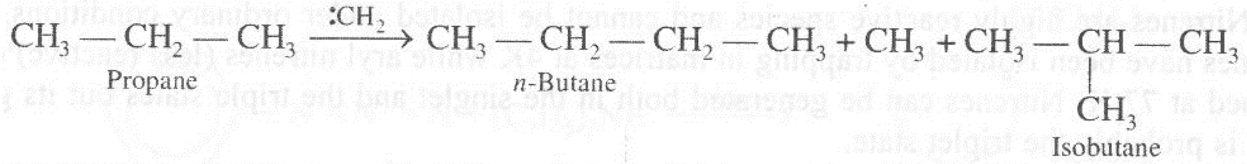
Reactions

Some important types of reactions of carbenes are described below:

1. Addition of carbon-carbon double bonds. The reaction of singlet and triplet methylene to 2-butene has been discussed above. Carbenes also add to aromatic systems and the intermediate products rearrange with ring enlargement reaction. Carbenes also show addition reactions to C=N bonds.



2. Addition reactions to alkanes. Methylene (:CH_2) reacts with ethaneto form propane. Propane adds methylene to yield n-butane and isobutane. This shows the greater reactivity of carbene.



$$\underset{\text{Propane}}{CH_3-CH_2-CH_3} \xrightarrow{:CH_2} \underset{n\text{-Butane}}{CH_3-CH_2-CH_2-CH_3} + CH_3 + \underset{\text{Isobutane}}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3}$$

The reaction of carbenes with higher alkanes yields a number of possible products. It shows that the addition of carbenes is not all selective. Dichlorocarbenes do not give reactions involving insertion.

TYPES OF ORGANIC REACTIONS

Organic reactions may be classified into four main types:

(a) Substitution reactions
(b) Addition reactions
(c) Elimination reactions
(d) Rearrangements.

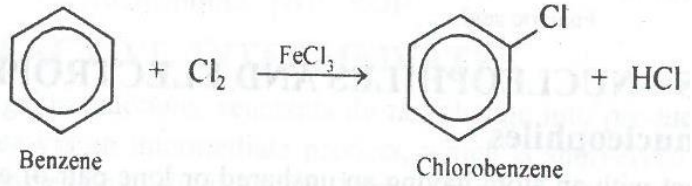
These are separately described as under.

(a) Substitution reactions. A substitution reaction is one in which a part of one molecule is replaced by other atom or group without causing a change in the rest of the molecule. Following are some examples of substitution reactions.

(*i*) $\underset{\text{Methane}}{CH_4} + Cl_2 \longrightarrow \underset{\text{Methyl chloride}}{CH_3Cl} + HCl$

(*ii*) $C_2H_5Br + KOH \longrightarrow C_2H_5OH + KBr$

(*iii*)



The substitution reactions may be brought about by free-radicals,nucleophilic or electrophilic reagents. Thus, there are free radical substitution reactions, nucleophilic substitution reactions and electrophilic substitution reactions.

(b) Addition reactions. When two molecules of same or different substances combine together giving rising to a new product, it is an addition reaction. Example of addition reactions are:

$$\underset{\text{Ethane}}{CH_2=CH_2} + Br_2 \longrightarrow \underset{\text{Ethylene dibromide}}{CH_2BrCH_2Br}$$

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + HCN \longrightarrow \underset{\text{Acetaldehyde cyanohydrin}}{CH_3CH(OH)CN}$$

Addition reactions could be brought about by free-radical, electrophilic or nucleophilicreagents.

As in the case of substitution, there are free radicals, electrophilic and nucleophilic substitution reactions.

(c) Elimination reactions. These reactions involve the removal of atoms or groups from a molecule to form a new compounds containing multiple bonds. Dehydrohalogenation of alkyl halides is a common example of this type reaction.

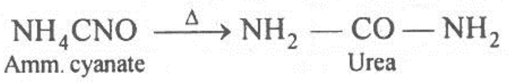
$$\underset{n\text{-Propyl chloride}}{CH_3-CH_2CH_2Cl} + KOH \xrightarrow{\text{Alc.}} \underset{\text{Propene}}{CH_3CH=CH_2} + KCl + H_2O$$

Elimination reactions are of two types. Bimolecular eliminations or E_2 reactions and monomolecular or E_1 elimination reactions.

In E_2 reactions, rate determining step involves two reacting species. Dehydrohalogenation of tertiary alkyl halides with alc. KOH proceeds by E_2 mechanism. In E_1 reactions the rate determining step involves only one reacting species. Dehydrohalogenation of primary alkyl halides with alc. KOH usually proceeds through E_1 mechanism.

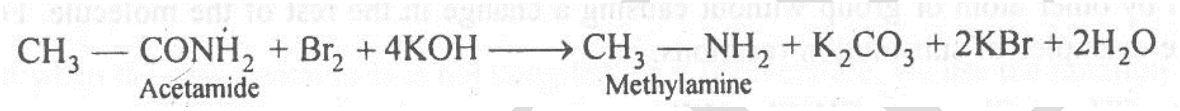
(d) Rearrangement reactions. Rearrangement reactions involve the migration of an atom or a group form one atom to the other within the same molecule.

It is interesting to note that the first organic compound, i.e., urea synthesized in the laboratory by Wohler actually involved a rearrangement reaction.



$$\underset{\text{Amm. cyanate}}{NH_4CNO} \xrightarrow{\Delta} \underset{\text{Urea}}{NH_2-CO-NH_2}$$

Another important example of such reactions is Hoffmann bromamide reaction. This reaction involves the migration of an alkyl groups from the carbon to the nitrogen atom of an amide with the simultaneous elimination of CO as carbonate ion under the influence of Br_2/KOH.



$$\underset{\text{Acetamide}}{CH_3-CONH_2} + Br_2 + 4KOH \longrightarrow \underset{\text{Methylamine}}{CH_3-NH_2} + K_2CO_3 + 2KBr + 2H_2O$$

Text books:

1. Madan, R.L. (2015). *Chemistry for Degree Students.*New Delhi: S. Chand and Company Pvt, Ltd.

2. Morrison, R. N. & Boyd, R. N. (1992). *Organic Chemistry*. New Delhi: Dorling Kindersley Pvt. Ltd. (Pearson Education).

POSSIBLE QUESTIONS

PART A(20 multiple choice questions)

Online Examinations

PART B(2 marks questions)

1. Define substitution reaction with a suitable example.
2. What are +I and –I effects? Illustrate with two examples in each case.
3. Define resonance energy.
4. Why phenol is a stronger acid than aliphatic alcohol?
5. Out of $(CH_3)_3C^+$ and $(CH_3)_2CH^+$ carbocations, which is more stable and why?

PART C(6 marks questions)

1. Give a brief account of inductive effect?
2. What are carbocation? Discuss the relative stability of primary, secondary and tertiary carbocation. Give one method of generation of carbocation. Discuss its structure.
3. Explain the hyperconjugation effect?
4. Explain why? With reasons.

(i) Carboxylic acid is stronger acid than phenol.
(ii) Ethyl amine is a stronger base than acetamide.
(iii) Ethyl amine is much more basic than aniline.

5. (i) Explain what do you understand by inductive effect?
   (ii) How does inductive effect help in explaining?
   (a) Relative acidic strengths of acetic acid and formic acid?
   (b) Relative basic strengths of primary, secondary and tertiary amines?
6. Write a note on hydrogen bonding.
7. Explain the stability, structure and reactions of carbanions.
8. (i) How will you distinguish between resonance and inductive effect?
   (ii) Explain the terms "Sacrificial hyperconjugation" and "Isovalenthyperconjugation", giving examples.
   (iii) Discuss the effect of hydrogen bonding on the boiling points and water solubility of organic compounds.
9. What is hybridisation? What are the distinguishing features of sp^3 and sp^2 orbitals? Explain with examples.
10. Discuss the stability, structure and reactions of free radicals.

KARPAGAM ACADEMY OF HIGHER EDUCATION

Class: I B.Sc Chemistry Course Name:Organic Chemistry-I (Basics and Hydrocarbon)

Course Code: 19CHU103 Unit: I Batch-2019-2022

S.No	Questions	Option 1	Option 2	Option 3	Option
1.	When the carbon atom is sp^2 hybridized in a compound, it is bonded to	2 other atoms	4 other atoms	3 other atoms	5 other
2.	What is bond angle between the hybrid orbital's in methane?	180°	120°	109.5°	115.5°
3.	What is the bond length of a carbon – carbon double bond?	1.20 Å	1.34 Å	1.54 Å	1.68 Å
4.	The carbon–carbon bond length is maximum in	ethylene	ethane	acetylene	benzen
5.	Compound in which carbons use only sp^2 hybrid orbitals for bond formation is	cyclohexane	cyclohexanol	1,3-butadiene	allene
6.	The H – C – C bond angle in ethane is	60°	109°28′	120°	118°28
7.	Which of the following hydrocarbons has the shortest C–C bond length?	ethylene	ethane	acetylene	benzen
8.	The H-C-H bond angle in ethylene is	60°	120°	90°	180°
9.	The unusually high boiling point of HF among the halogen acids is due to	hydrogen bond	covalent bond	ionic bond	coordir
10	The order of stability of carbonium ions is	tertiary > secondary > primary	secondary > tertiary > primary	primary > secondary > tertiary	primary tertiary second
11	Which of the following carbonium ions will be most stable?	methyl cation	ethyl cation	isopropyl cation	allylcat
12	Resonance structures of a molecule have	unequal arrangement of atoms	different arrangement of atoms	same number of paired electrons	differen of paire electror
13	The order of stability of carbanions is ‘	primary > secondary > tertiary	secondary > tertiary > primary	tertiary > secondary > primary	tertiary > secor
14	Which of the following compounds have planar molecules?	ethyl alcohol	methyl alcohol	diethyl ether	1,3- bu
15	In stable organic compounds, carbon will	2 bonds	4 bonds	3 bonds	5 bond

	always form				
16	Compound in which carbons use only sp^3 hybrid orbital's for bond formation is	$CH_3CH_2CH_3$	$CH_3C\equiv CH$	$CH_3CH=CH_2$	$CH_2=C$ $CH=C$
17	Ammonium ion is	nucleophile	electrophile	free radical	neutral
18	Reagents which have at least one unshared pair of electrons like $:NH_3$, H_2O or bear negative charge are called	electrophile	nucleophile	free radical	neutral
19	An alkyl free radical has planar structure with central carbon being	sp^1 hybridized	sp^2 hybridized	sp^3 hybridized	d^2sp^3 h
20	A singlet carbene has two electrons in	two different orbitals	in same orbitals	one of the orbitals	four dif orbitals
21	The decreasing order of stability of free radicals is	allyl> benzyl >tert. alkyl > prim. alkyl > sec-alkyl	Benzyl >tert. alkyl > sec-alkyl >allyl> prim. alkyl	Benzyl >allyl>tert. alkyl> sec. alkyl > prim. Alkyl	tert. alk Benzyl alkyl > prim. a
22	The decreasing order of stability of carbanion is	benzyl >diphenylmethyl>triphenylmethyl	Diphenylmethyl> Benzyl >triphenylmethyl	Triphenylmethyl>diphenylmethyl> benzyl	Tripher Benzyl >dipher
23	A carbanion has	sp^3 hybrid carbon	sp^2 hybrid carbon	d^2sp^3 hybrid carbon	sp hybr
24	Homolytic fission of a covalent bond results in the formation of	carbocations	carbanions	free radicals	neutrals
25	Triphenylmethyl free radical exists in	10 resonating forms	5 resonating forms	9 resonating forms	3 reson forms
26	Heterolytic fission results in the formation of	carbocations	carbanions	free radicals	carboca carbani
27	The least stable carbanion is	benzyl anion	trimethylmethanecarbanion	trichloromethanecarbanion	methyl
28	Which of the following is an electrophile?	CH_3O^-	$CH_3CH_2^+$	NH_3	CH_3CH
29	Which of the following statements is correct regarding nucleophiles?	they have an over–all positive charge	they have a lone–pair of electrons	they have an unpaired electron	they ha orbitals
30	Which of the following is not a nucleophile?	NH_3	HSO_3^-	$AlCl_3$	HO^-

31	Homolytic fission of C-C bond leads to the formation of	free radicals	carbonium ions	carbanions	nucloph
32	Which of the following is not an electrophile?	NH_3	Br^+	$AlCl_3$	NO_2^+
33	Which alkyl free radical is the most stable?	methyl	primary	secondary	tertiary
34	Which of the following is a nucleophile?	$AlCl_3$	H_3O^+	BF_3	CN^-
35	Which of the following is not a nucleophile?	CN^-	BF_3	CH_3O^-	NH_3
36	Which of the following ranges best represents the strength of a hydrogen bond?	5-10 kcals	60-80 kcals	80-100 kcals	100-12
37	Which of the following free radicals is most stable?	$R_3C^{\bullet}$	$R_2C^{\bullet}$	$RCH_2^{\bullet}$	$^{\bullet}CH_3$
38	Which of the following is the least stable carbanion?	cyclopropyl	vinyl	isobutyl	ethyl
39	Trichloroacetic acid is a strong acid because of	mesomeric effect	electromeric effect	hyperconjugative effect	inductiv
40	The hyperconjugative effect is the largest in		$^{+}C(CH_3)_3$	$^{+}CH(CH_3)_2$	
41	No bond resonance is another name for	hyperconjugative effect	electromeric effect	mesomeric effect	inductiv
42	Inductive effect is a	temporary effect	weak effect	strong effect	perman
43	The term no bond resonance refers to	inductive effect	mesomeric effect	hyperconjugative effect	electron effect
44	The electron displacement occurring in saturated compounds along a carbon chain is termed as	inductive effect	electromeric effect	steric effect	resonan
45	Inductive effect is represented by	single arrow head	double arrow head	reverse arrow head	equilibr head
46	Inductive effect is represented by arrow head pointing towards the more	electro positive atom	electro negative atom	neutral atom	hydrog
47	The atoms or groups having greater electron affinity than hydrogen are said to	+I effect	-I effect	+E effect	–E effe

48	The atoms or groups having lesser electron affinity than hydrogen are said to	+I effect	-I effect	+E effect	–E effe
49	Relative strength of various aliphatic monocarboxylic acids can be explained with the help of	inductive effect	electromeric effect	steric effect	resonar
50	The pKa value is lower indicate that	lower acid strength	greater acid strength	lower base strength	higher b strengtl
51	Formic acid is stronger than acetic acid due to	+I effect	–I effect	+E effect	–E effe
52	Chloroacetic acid is much stronger than acetic acid due to	+I effect	–I effect	+E effect	–E effe
53	The complete transfer of a shared pair of electrons in one of the atom joined by a double or triple bond at the requirement of attacking reagent is known as	inductive effect	electromeric effect	steric effect	resonar
54	The reaction of acetone with HCN is an example of	inductive effect	electromeric effect	steric effect	resonar
55	When several structures may be assumed to contribute to the true structure of a molecule then the molecule is referred as	resonance hybrid	conjugation	hyperconjugation	hybrid
56	Resonance effect is also known as	inductive effect	mesomeric effect	steric effect	electror effect
57	Aniline is a weaker base than the primary aliphatic amines due to	resonance effect	inductive effect	hyperconjugative effect	electror effect
58	The aliphatic alcohols are neutral whereas phenol is acidic due to	inductive effect	resonance effect	steric effect	electror effect
59	The phenoxide ion is stabilized by	inductive effect	steric effect	electromeric effect	resonar
60	The vinyl chloride is polar due to	resonance effect	inductive effect	electromeric effect	steric e

UNIT-II

Syllabus

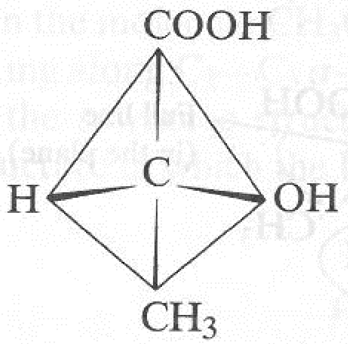
Stereochemistry

Fischer, Newmann and Sawhorse Projection formulae and their interconversions; Geometrical isomerism: cis–trans , syn-anti and E/Z notations with C.I.P rules.
Optical Isomerism: Optical Activity, Specific Rotation, Chirality/Asymmetry, Enantiomers, Molecules with two or more chiral-centres, Diastereoisomers, meso structures, Racemic mixture and their resolution. Relative and absolute configuration: D/L and R/S designations.

Projection structures of stereoisomers

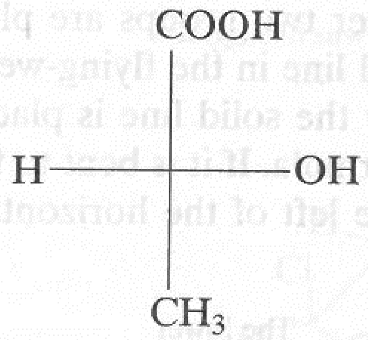
It is inconvenient to represent 3D-molecules in a paper or a board. So several 2D-formulas have been developed to represent the molecules having 3D-structures. For example,

1. **Fischer's projection of enantiomers.** This type of representation is done for chiral carbon. The chiral C-atom is assumed to be in plane of the paper or the board. The four bonds are shown by two vertical and two horizontal straight lines. The point of intersection of the two straight lines is accepted as the chiral C-atom. The two vertical bonds actually project below the plane of the paper and the two horizontal lines project above the plane.



Tetrahedral formula

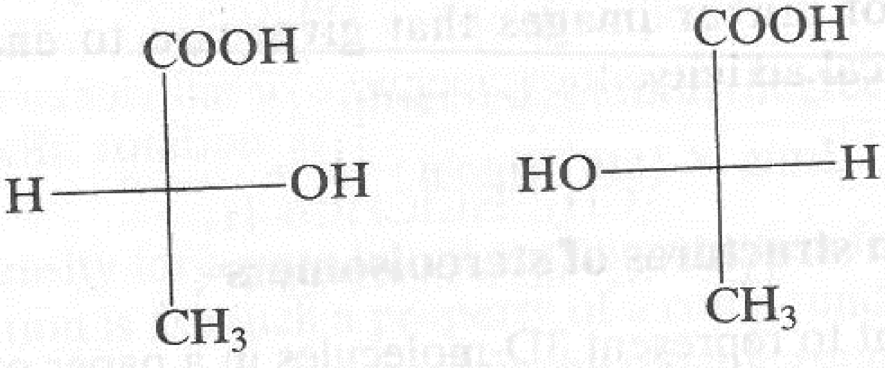
Chiral C-atom is in the plane of the paper, —COOH and CH_3 groups project below, and H and —OH project above the plane of the paper



Fischer's projection formula

For example, in the tetrahedral model shown above, if the chiral C-atom is in the plane, the groups -COOH and -CH_3 project below the plane, and the other two groups -OH and -H project above the plane. Therefore, in Fischer's projection formula, -COOH and -CH_3 groups are written in the vertical line and the groups -OH and -H in the horizontal line.

For the purpose of the comparison of the two Fisher's projection formulas, rotation or sliding of the structures in the plane of the paper is allowed, but no bond can be lifted from the plane of the paper. For example, the two Fischer's projection formulas written below are not superimposable if no bond is allowed to be lifted from the plane of the paper. So, these two are stereoisomers. Also, they are related as mirror images, therefore, these are enantiomers.



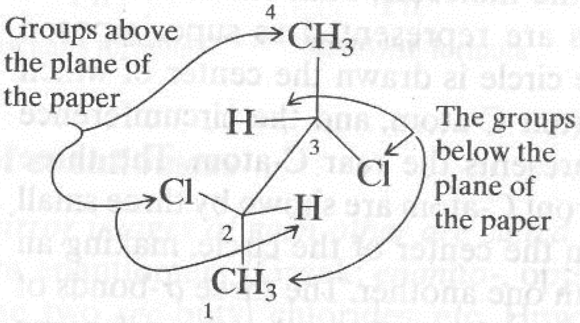
Enantiomers of lactic acid

As a rule, exchange of two groups in the Fischer's formula by odd number of times gives the structure of the enantiomer. But exchange of two groups by even number of times does not change the configuration.

2. Sawhorse projection. When it is necessary to know the spatial relation between two adjacent C-atoms, both chiral or achiral, sawhorse representation is quite convenient. In this projection, the two key C-atoms are joined by a diagonal line in the plane of the paper. The remaining bonds are shown by a smaller lines projected above and below the plane of the paper. There is a free rotation around the diagonal line either clockwise or anticlockwise.

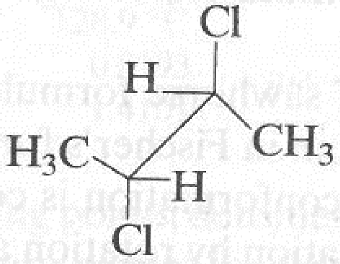
$\overset{1}{C}H_3\overset{2}{C}HCl\overset{3}{C}HCl\overset{4}{C}H_3$

Key atoms are C-2 and C-3

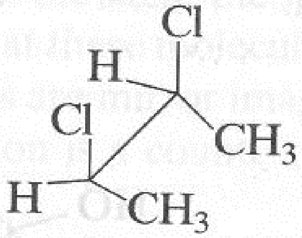


Sawhorse formula of the above compound

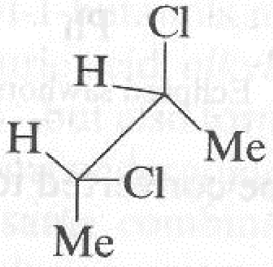
For example in the molecule $CH_3CHCl^{\cdot}CHClCH_3$, the two key atoms are C-2 and C-3. Looking along C_2-C_3 σ-bond and drawing the diagonal in the plane of the paper the sawhorse structure of the compound is written as shown above. The structure in which the bulky atoms or groups (Cl atoms in the case shown below) make a dihedral angle $\theta = 180°$, the sawhorse conformation of the compound is called the staggered conformation. Since the free rotation along the diagonal C_2-C_3 bond is allowed other conformation of the compound are also possible. For example, the conformation in which the dihedral angle θ between the two Cl atoms is equal to 0º, it is termed as the eclipsed sawhorse formula, and when θ is equal to 120º, the representation is known as the partially eclipsed sawhorse formula.



Staggered sawhorse formula
($\theta = 180°$)

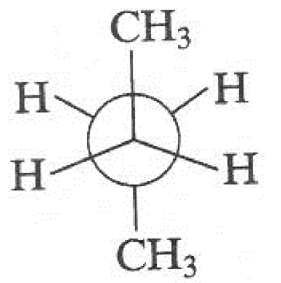


Eclipsed sawhorse formula
($\theta = 0°$)

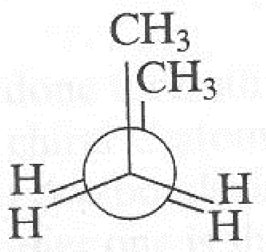


Partially eclipsed sawhorse formula
($\theta = 120°$)

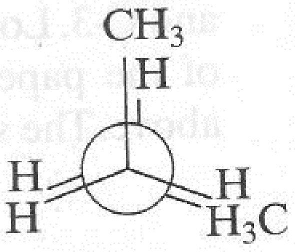
3. Newman projection formula. In this projection, the molecule is viewed along the bond that binds the two key C–atom of the molecule both chiral or achiral and these atoms are represented as superimposed circles. Only one circle is drawn the center of which represents the front C–atom and the circumference of the circle represents the front C–atom and the circumference of the circle represents the rear C–atom. The three σ-bonds of the front C–atom are shown by three small lines drawn from the center of the circle. Making an angle of 120° with one another. The three σ-bonds of the rear C–atom are drawn from the circumference of the circle. For example the staggered, eclipsed, gauche and partially eclipsed conformations of n–butane can be drawn as shown in the right.



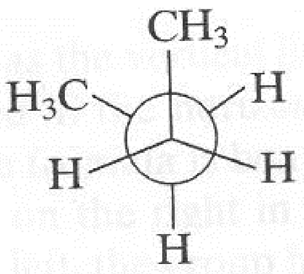
Staggered *n*-butane



Eclipsed *n*-butane



Partially eclipsed *n*-butane



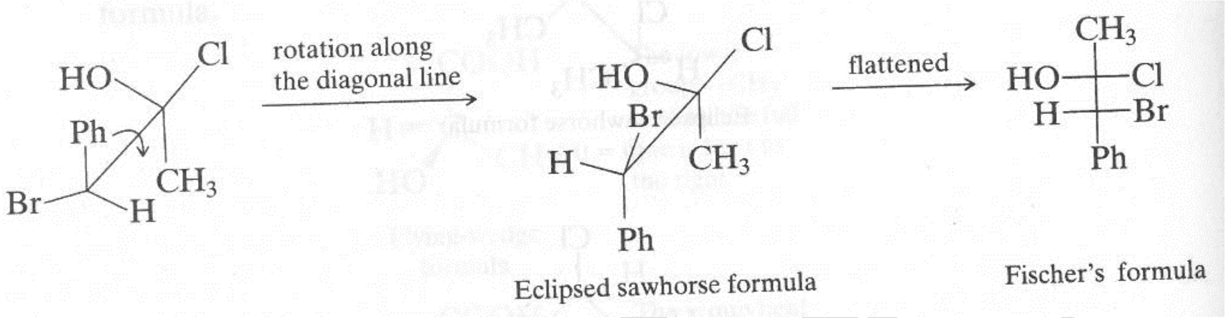
Gauche or skewed *n*-butane

Interconversion of projection formulas. Different projection formulas may be interconverted by following some simplified steps. For example, a sawhorse formula can be converted to a Fischer's formula following the steps mentioned below:

Step 1. The front C–atom of sawhorse formula is considered as the lowest chiral C–atom in Fischer's formula.

Step 2. The given sawhorse conformation is converted to an eclipsed sawhorse conformation by rotation along the diagonal line by the minimum number of degrees.

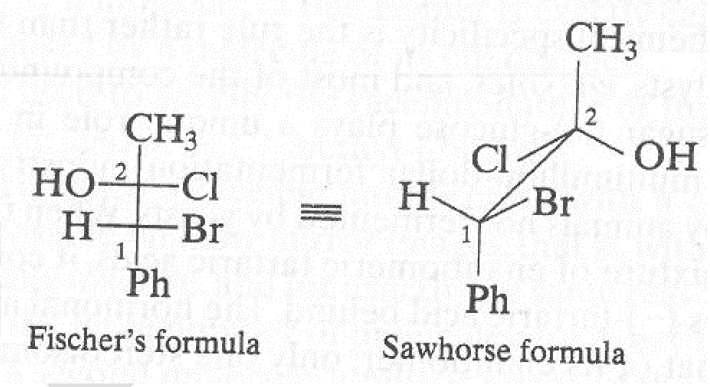
Step 3. The eclipsed sawhorse conformation so obtained after step 2 operation is now flattened to get the Fischer's projection formula. For example,



Similarly a Fischer's formula can be converted to a sawhorse formula by the following simplified steps:

Step 1. The lowest chiral C–atom of the Fischer's formula becomes the front C–atom of the sawhorse formula.

Step 2. The groups in Fischer's formula that are drawn in anti- or trans- orientation with respect to each other are drawn on the same side of the diagonal line in the sawhorse formula. For example,



GEOMETRICAL ISOMERISM

Two carbon atoms joined by a single bond (σ bond) are capable of free rotation around each other, but this rotation is hindered in case of compounds containing carbon-carbon double bond. According to molecular orbital theory, carbon atoms involved in double bond formation are sp^2 hybridised so that each carbon atom has three planar sp^2 hybridised orbitals and fourth *p* orbital having its lobes at right angles to the plane of sp^2 orbitals. The formation of π bond involves the overlapping of *p* orbitals. With the formation of a π bond between C-C along with a σ bond which already existing, there remains no possibility of rotation along C-C axis. Neither of the two doubly bonded carbon atoms can be rotated about double bond without destroying π orbital which requires large amount of energy. Thus at ordinary temperature, the rotation about a carbon-carbon double bond is restricted or hindered and gives rise to a kind of stereoisomerism known as *Geometrical isomerism.*

Geometrical isomerism, also known as *cis-trans* isomerism takes place in compounds containing carbon-carbon double bond in which each of the two doubly bonded carbon atoms is attached to two different atoms or groups. All the compound with general formula of the type $C_{AB} = C_{DE}$ or $C_{AB} = C_{AB}$ show geometric isomerism. If either of the two carbon atoms carries two identical groups as in $C_{AB} = C_{AA}$ or $C_{AB} = C_{DD,}$ the isomerism does not exist. *This isomerism is due to difference in the relative spatial arrangement of the atom or groups about the doubly bonded carbon atoms.*

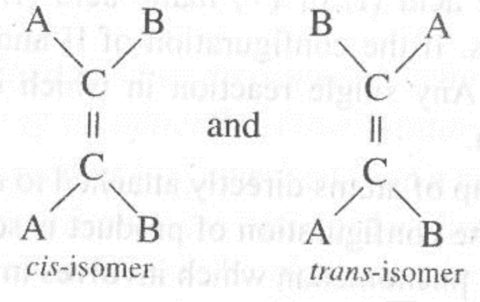
Conditions to be fulfilled by a compound to exhibit geometrical isomerism

For a compound to show geometrical isomerism the following conditions are necessary:

(i) The molecule must contain a carbon-carbon double bond about which there is no free rotation.

(ii) Each of the double bonded carbon atoms must be attached to two different atoms or groups.

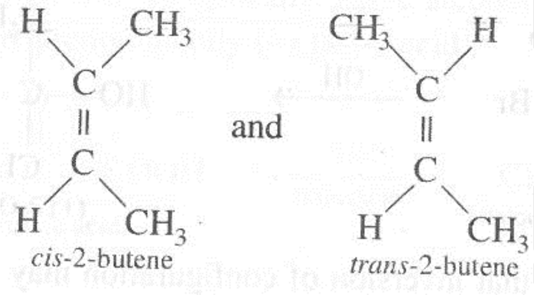
In case of compounds with formula of the type $C_{AB} = C_{AB}$: if two similar groups are on the same side of double bond, the isomer is known as a *cis-* and if two similar groups are on the opposite sides of the double bond the isomer is known as *trans-*such as:



cis-isomer *trans*-isomer

For example,

2-butane exists in two isomeric forms

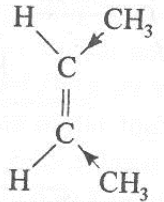


cis-2-butene *trans*-2-butene

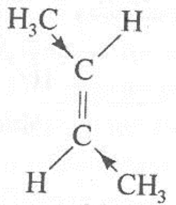
Determination of configuration of a geometrical isomer

Different methods available for determination of configuration of a geometrical isomer are described below:

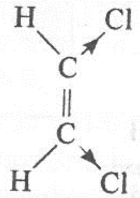
(*i*) From Dipole moments. Generally *cis*-isomer has greater dipole moment as compared to *trans*-isomer. In case of *cis*-the similar groups being on the same side, the electronic effects are additive, while in case of *trans*-isomer, the similar groups being on opposite side, the electronic effects cancel each other.



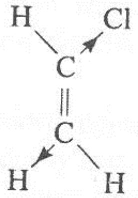
cis-2-butene
$\mu = 0.4$



trans-2-butene
$\mu = 0$



cis-2-Dichlorethene
$\mu = 1.85$



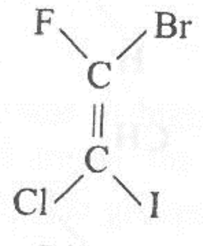
trans-1, 2-dichloroethen
$\mu = 0$

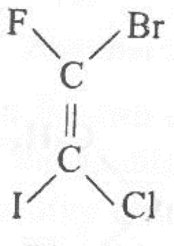
E and Z designations of geometrical isomers

The *cis* and *trans*-designated can be used only for the compounds in which two doubly bonded carbon atoms are having similar atoms or groups *e.g.*, of the type $C_{AB} = C_{AB}$. But, when the two doubly bonded carbon atoms are having different atoms or groups attached to them *e.g.*, of the type $C_{AB} = C_{DE}$; it is not possible to assign them *cis* or *trans* configurations. To overcome this difficulty, a more general system for designating the configuration of geometric isomers has been adopted. This system developed by *Cahn*, *Ingold* and *Prelog* originally for the absolute configuration of optical isomers is known as *E* and *S system* and is based on priority of attached groups. The atoms or groups attached to each carbon of the double bond, are assigned first and second priority. If the atoms or groups having higher priority attached to two carbons are on the same side of double bond the configuration is designated as Z (derived from German word *Zusammen* meaning together) and if the atoms or groups of higher priority are on the opposite side of the double bond, the configuration is designed as E (derived from German word –*entgegen* meaning across or opposite).

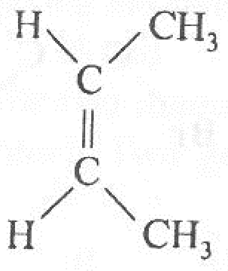
Priorities of atoms or groups are determined in the same way as for R & S configuration of optical isomers. At weights or atomic numbers of atoms directly linked with ethylenic carbon atoms are taken into consideration.

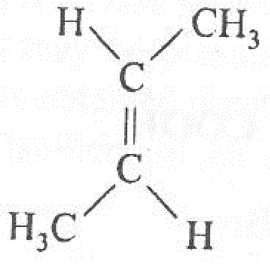
Let us consider an example in which two doubly bonded atoms are attached to four different halogens such as $C_{BrF} = C_{lCl}$. Since Br is having higher priority over F and l is having priority over Cl (due to their higher atomic numbers). The isomer in which Br and l are on the same side of double bond will be called Z and the isomer in which Br and l are on the opposite sides of double bond will be called E.


Z-isomer

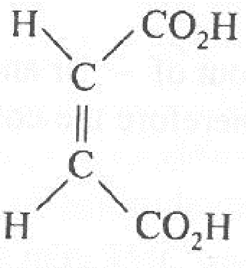

E-isomer

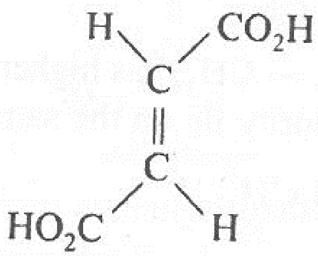
In the same way *cis* and *trans* isomers of 2-butene can be called Z and E-2-butenes respectively.





Similarly maleic acid can be specified as Z-isomer and fumaric acid E-isomer.

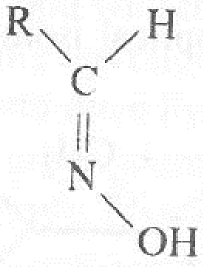

Maleic acid
(*Z*-isomer)

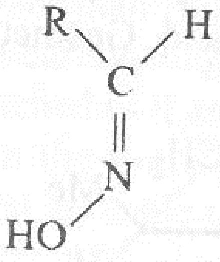

Fumaric acid
(*E*-isomer)

In determining the configuration, we have to select the group of higher priority on one carbon. Similarly we select the group of higher priority on the other carbon atom. If these two groups are on the same side of double bond, the configuration is Z, otherwise it is E.

Geometrical isomerism in oximes

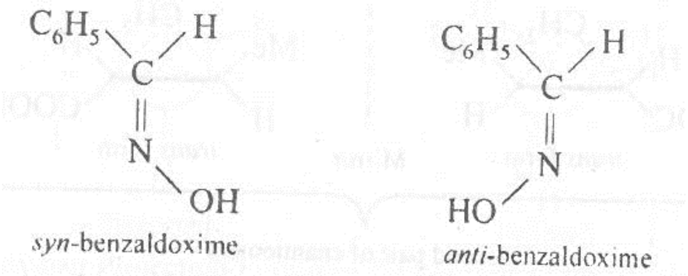
Oximes of aldehydes having the general formula R-CH=N-OH are capable of exhibiting geometrical isomerism as -H and -OH groups may be present on the same side or opposite sides of the double bond. The two stereoisomers thus obtained are named as *syn* (equivalent of *cis*) and anti (equivalent of *trans*). Two geometrical isomers of an aldoxime may be represented as:


syn-aldoxime

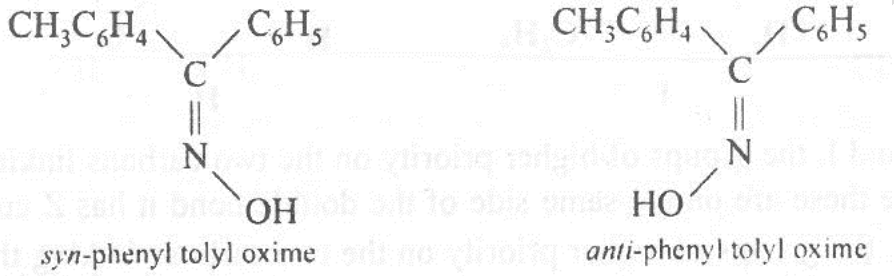

anti-aldoxime

Geometrical isomers of benzaldoxime have been actually isolated.

syn-benzaldoxime has m.p. 35°C while anti- benzaldoxime has m.p. 130°C. The two compounds may be shown as under:



Oximes of ketones (RR'C==NOH) can also show geometrical isomerism provide R and R' are not the same. Thus benzophenone oxime does not exhibit geometrical isomerism because the two groups attached to carbonyl carbon are the same. Phenyl tolyl ketoxime is known to exist in two geometrical forms.



OPTICAL ISOMERISM OR ENANTIOMERISM

Before taking up optical isomerism, let us understand the terms: plane polarized light, optical activity and specific rotation.

Plane polarized light

Ordinary light has vibrations taking place at right angles to the direction of propagation of light spread in all the possible planes. If we pass ordinary light through nicol, prism vibrations in all planes except one are cut off. Thus light coming out of nicol prism has vibrations only in one plane. Such a light is called *plane polairsed light.*

Optical activity

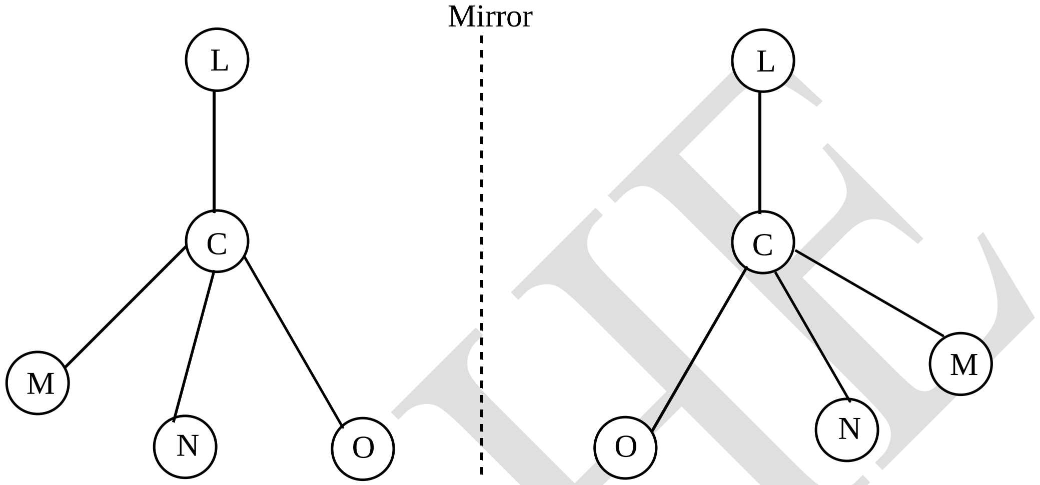
Behaviour of certain substances is strange. When a plane polarized light is passed through the solution of such substances, the light coming out of the solution is found to be in a different plane.

The plane of polarized light is rotated. *Such substances, which rotate the plane of plane polarized light when placed in its path are known as optically active substances* and the phenomenon is known as *optical activity.* The angle of rotation (α) of plane polarized light is known as *Optical rotation.* The substances which rotate the plane of polarized light to the clockwise or right direction are known as dextrorotatory or having positive (+) rotation and those which rotate the plane polarized light to the anticlockwise or left direction are known as *laevorotatory* or having negative (-) rotation. Substances which do not rotate the plane of polarized light are said to be optically inactive.

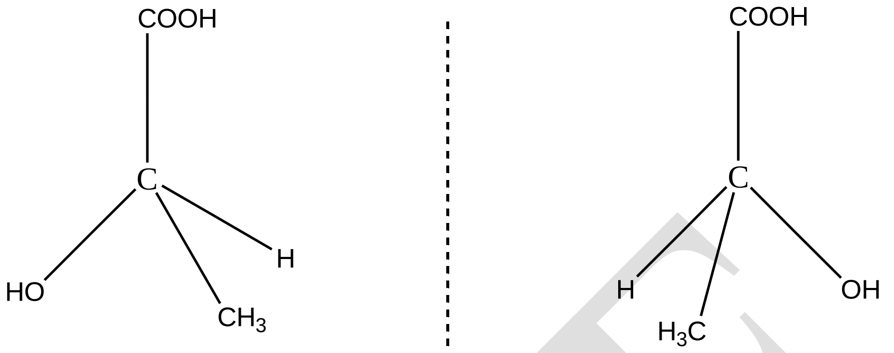
Louis Pasteur, while studying the crystallography of salts of tartaric acid made a peculiar observation. He observed that optically inactive sodium ammonium tartarate existed as a mixture of two different types of crystals which were mirror image of each other. With the help of a hand lens and a pair of forceps, he carefully separated the mixture into two different types of crystals. These crystals were mirror images of each other and were called enantiomorphs and the phenomenon as *enantiomorphism.* Although the original mixture was optically inactive, each type of crystals when dissolved in water, were found to be optically active. Moreover the specific rotations of the two solutions were exactly equal but of opposite sign *i.e.* one solution rotated the plane polarised light to the right or clockwise while the other to the left or anticlockwise and to the same extent. Two types of crystals or solutions were identical in all other physical and chemical properties. *Isomers which are non-superimposable mirror images of each other are called enantiomers.*

According to La Bell and Van't Holf the four valencies of a carbon atom are directed towards the four corners of a regular tetrahedron at the centre of which lies the carbon atom.

Consider a compound of formula C_{LMNO} having four different groups L, M, N and O attached to a carbon atom. This compound can be represented by two models which look like mirror images of each other.



It is important to note here that these two molecules cannot be superimposed on each other *i.e.* they will not coincide in all their parts. We may turn them in as many as we like but we find that though two groups of each may coincide, the other two do not. Hence these must represent two isomers of formula $C_{LMNO.}$ Lactic acid $CH_3CHOHCOOH$ and sec-Butyl chloride $C_2H_5CHClCH_3$ exist as two optically active isomers which are enantiomers, *i.e.* mirror images of each other. Mirror images of the two compounds are represented as above.



Enantiomers of Lactic acid

The carbon atom to which four different groups are attached, is known as *asymmetrical* or *chiral carbon atom* or *stereogenic centre.*

If two of the groups attached to carbon are same, we shall observe that it is possible to superimpose the mirror images on each other. Such a compound will not show optical isomerism or *enantiomerism.*

Hence non-superimposability of the mirror images is responsible and essential for the type of stereoisomerism known as enantiomerism.

The term optical isomerism is used for the existence of stereoisomers which differ in their behavior towards the plane polarised light. Thus enantiomeric molecules are always non-superimposable mirror images of each other. The non-superimposability of mirror images arises due to chiral or asymmetric nature of molecule. A molecule is said to chiral if it has no plane of symmetry and is therefore non-superimposable on its mirror image.

It may be concluded with the remarks that chirality is the fundamental condition of enantiomerism or optical isomerism.

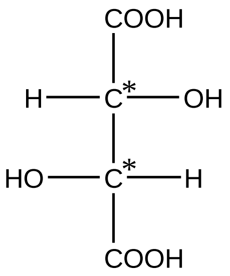
Chirality and dissymmetry

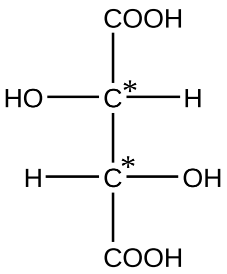
An object which is non-superimposable on its mirror image is called chiral object. And an object which is superimposable on its mirror image is called achiral object.

Achiral objects or molecules possess a plane of symmetry that can divide the molecule into two identical halves. Chiral objects or molecules do not possess a plane of symmetry that can divide the molecule into two identical halves. The **chirality** is also known as **dissymetry** while **achirality** is also known as **symmetry.**

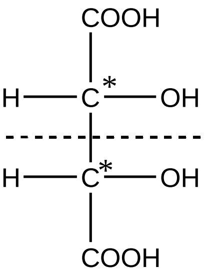
Thus chirality or dissymmetry is the property associated with certain compounds which do not have a plane of symmetry and are thus non-superimpossable on their mirror images. Dissymmetry is an essential condition for optical activity. In the study of enantiomers containing one chiral carbon atom, we find that they do not have a plane of symmetry and hence are dissymmetric in nature, for example, lactic acid, sec-butyl acid chloride etc. We can thus say that compounds a chiral carbon atom are optically active in nature.

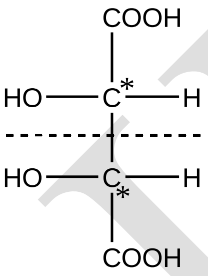
This is not true, however, for compounds with two or more chiral carbon atoms. Here, one or more isomers may be optically inactive in spite of the presence of chiral carbon atoms. Consider for example, the case of tartaric acid, CH(OH)COOHCH(OH)COOH. It has two chiral carbons (sterogenic centres) marked* and thus has four isomers as shown below.


I


II

I and II are optically active due to the absence of plane of symmetery


III


IV

III and IV are optically inactive due to the presence of plane of symmetery (shown by dotted line)

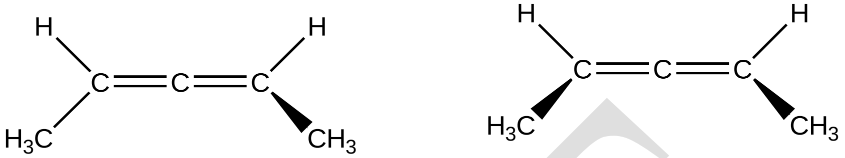
Isomers I and II are non-superimposable mirror images of each other, they are dissymmetric and optically active. But III and IV have a plane of symmetry. Therefore, they are symmetric and optically inactive in nature.

In other words, optical activity in organic compounds is due to the presence of dissymmetry and not due to chiral carbon atoms alone.

No. of optical isomers for a compound is given by 2^n where *n* is the number of chiral carbon atoms.

It may be noted that some organic compounds are optically active even though they do not contain chiral atom. For example,

Substituted allenes. Dienes with double bonds in adjacent positions are called allenes. Substituted allense may be represented as RCH=C=CHR. Pentane-2, 3-diene exists in two optically active forms. This is because the groups linked to one end carbon are in different plane than those linked to the other end carbon.



In allenes, the central carbon is *sp* hybridized, and the terminal carbons are sp^2 hybridized. The central carbon forms two *sp*- sp^2 σ bonds. The central carbon also has two *p* orbitals which are mutually perpendicular. These forms π bonds with the *p* orbitals on the other carbon atoms. As a result, the substituent at one end of the molecule are in a plane which is perpendicular to that of the substituent's at the other end, so that the compound exists in two forms which are non-superimposable mirror images and are optically active.

Properties of enantiomers

(*i*) They have identical physical properties but differ in direction of rotation of plane polarised light. Though the two enantiomers rotate the plane polarised light in opposite direction, the extent of rotation is the same.

(*ii*) They have identical chemical properties except towards optically active reagents. The rates of reaction of optically active reagents with two enantiomers differ and sometimes one of the enantiomers does not react at all.

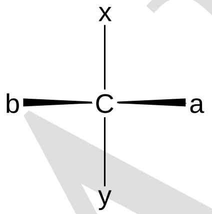
(*iii*) In biological system (-) or *l*-glucose is neither metabolized by animals nor fermented by yeast whereas (+) or *d*-glucose undergoes both these processes and plays an important role in animal metabolism and fermentation. Similarly mould *Penicillium glaucum* consumes only *d*-tartaric acid when fed with a mixture of equal quantities of *d- and l*-tartaric acid.

(*iv*) When equal amount of enantiomers are mixed together an optically inactive racemic modification denoted by (+) of *dl* is obtained.

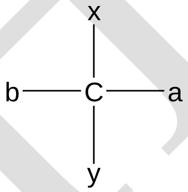
Fischer's projection formula for planar representation of three dimensional molecules.

Emil Fischer 1891 introduced a simple method for representing three dimensional molecule in one plane. It is known as *Fischer Projection formula.* Following point are to be observed for this purpose.

(*i*) The chiral molecule is imagined in such a way that two groups point towards the observer and two away from the observer. The groups pointing towards the observer are written along the horizontal line (shown by thick wedge-like bonds) and those pointing away are written along the vertical line. The central carbon is present at the crossing of the horizontal and vertical lines.



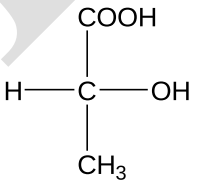
Flying wedge representation



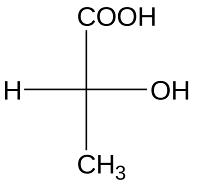
Normal representation

Thus if *a, b, x* and *y* are four groups attached to a carbon, the molecule will be represented by the projection formula as above. Here *a* and *b* groups point towards the observer (or above the plane) and groups *x* and *y* are away from the observer (or below the plane).

(*ii*) The longest chain of carbon atoms in the molecule should be represented along the vertical line. Lactic acid, therefore, according to the above conventions will be represented as

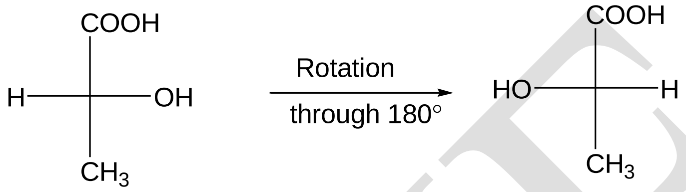


or



(*iii*) We can avoid writing carbon at the crossing of the vertical and horizontal lines. A crossing automatically means the presence of a carbon.

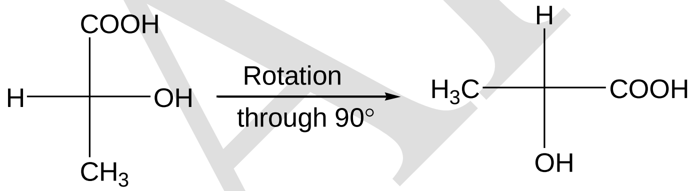
(*iv*) If necessary, planar formula may be imagined to be rotated from end to end without lifting it from the plane of the paper. Rotation by 180° in the plane of the paper does not create any change in the configuration of the molecule.



I (-) lactic acid II (-) lactic acid

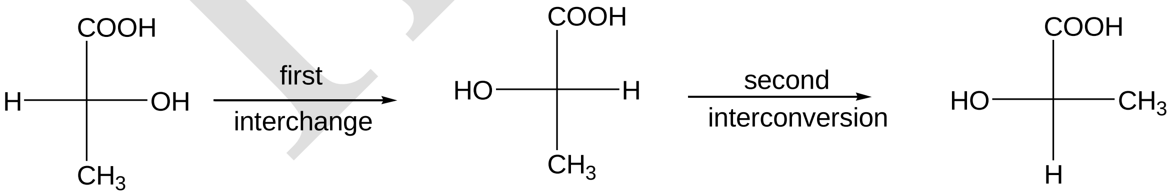
In the above rotation by 180°, II has been obtained from I. There has been no change in configuration of the molecule. I and II are in fact the same thing.

(*v*) Rotation by 90° or 270° brings about a change in configuration of the molecule. Consider the following rotation.



(-) lactic acid (+) lactic acid

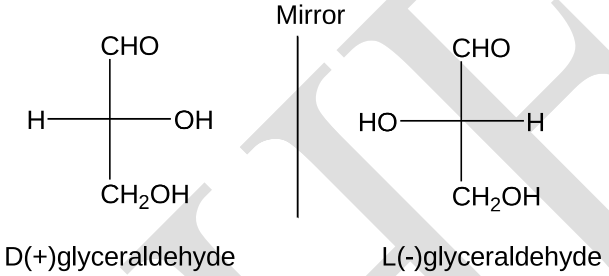
(*v*) If the positions of two groups across the chiral atom are interchanged, it leads to inversion of configuration. Two consecutive such changes neutralize the effect.



(-) lactic acid I (+) lactic acid II (-) lactic acid III

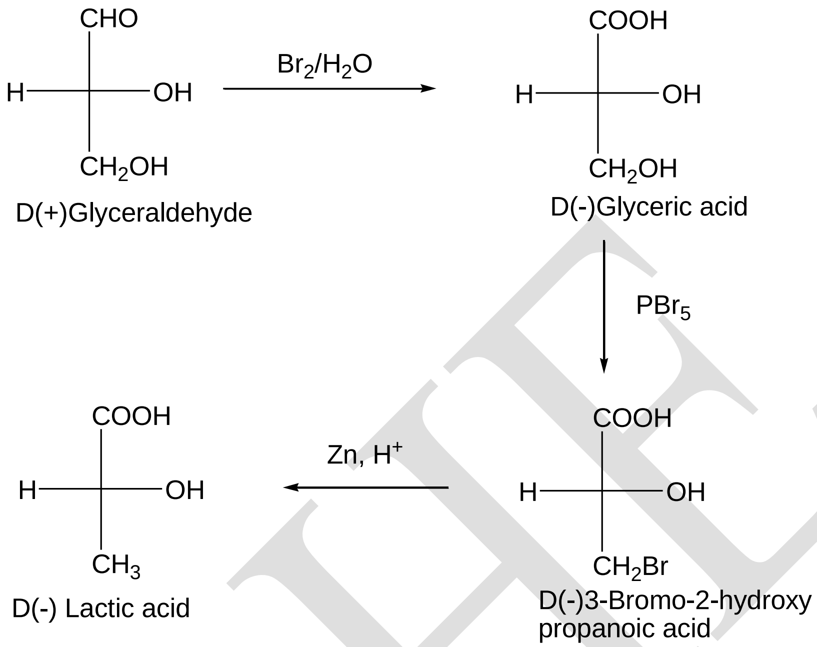
Absolute configuration of optical isomers

In the earlier days, as the modern techniques of finding out configuration were not available, structure III and I are the same because as per rule (iv) above, III on rotation through 180° will give I Fischer assigned the following configurations to the (+) and (-) enantiomers of glyceraldehydes arbitrarily and denoted them by capital letters D and L respectively. Small letters *d* and *l* represent sign of rotation, while capital letters D and L represent configuration.



The relative configuration of a number of other optically active compounds have been established by correlating them with D(+) or L (-) glyceraldehydes. All those optically active compounds, which are obtained from D(+) glyceraldehydes through a sequence of reactions *without breaking the bonds of asymmetric carbon atom,* are designated as D configuration irrespective of their sign of rotation and the other enantiomer as L configuration.

For example,



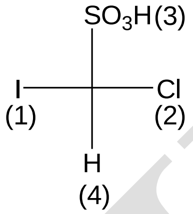
In all D configurations, -OH attached to asymmetric carbon atom is written on the right hand side of Fischer projection formula. Similarly, in all the L-configurations, -OH attached to the lowest asymmetric carbon atom is written on the left hand side in the Fischer's projection formula.

R and S Specification for the configuration of an optically active compound

Cahn, Ingold and Prelog developed a method which can be used to designate the configuration of all the molecules containing asymmetric carbon atom (chiral centre). This system is known as *Cahn-Ingold-Prelog system* or R and S system and involves two steps.

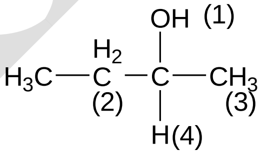
Step I. The four different atoms or groups of atoms attached to chiral carbon atom are assigned a sequence of priority according to the following set of sequence rules.

Sequence Rule 1. *If the four atoms, directly attached to asymmetric carbon atom, are all different, the priority depends on their atomic number. The atom of higher atomic number gets higher priority.* For example, in chloroiodomethane suphonic acid the priority sequence is I, Cl, SO_3H, H.



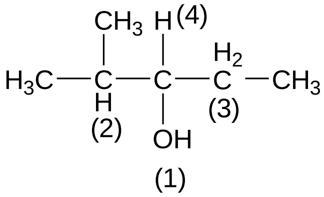
We consider the atom of the group which is directly linked to the central carbon.

Sequence Rule 2. *If Rule 1 fails to decide the relative priority of two group it is determined by similar comparison of next atoms in the group and so on.* In other words, if two atoms directly attached to chiral centre are same, the next atoms attached to each of these atoms, are compared. For example in 2-butanol two of the atoms directly attached to chiral centre are carbon themselves. To decide the priority between the two groups $-CH_3$ and $-CH_2CH_3$, we proceed like this. Methyl carbon is further linked to H, H and H. The sum of atomic numbers of three H is 3. The methylene carbon of the ethyl group is linked to two hdyrogens and one carbon directly. The sum of atomic numbers of two H and one C is 8. Thus ethyl group gets the priority over methyl. Hence the priority sequence is OH, C_2H_5, CH_3, H.



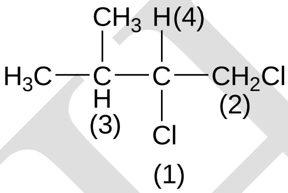
2-Butanol

In 2-methyl–3-penanol, the C, C, H of isopropyl gets priority over the C, H, H of ethyl, so the priority sequence is OH, isopropyl, ethyl, H.


$H_3C-CH(CH_3)-CH(OH)-CH_2-CH_3$

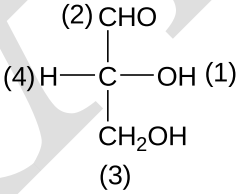
2-Methyl-3-pentanol

In 1, 2-dichloro-3-methylbutane the Cl, H, H of CH_2Cl gets priority over the C, C, H of isopropyl due to atomic number of Cl being higher than that of C. So the priority sequence is Cl, CH_2Cl , isopropyl, H.


$H_3C-CH(CH_3)-CH(Cl)-CH_2Cl$

1,2-Dichloro-3-methylbutane

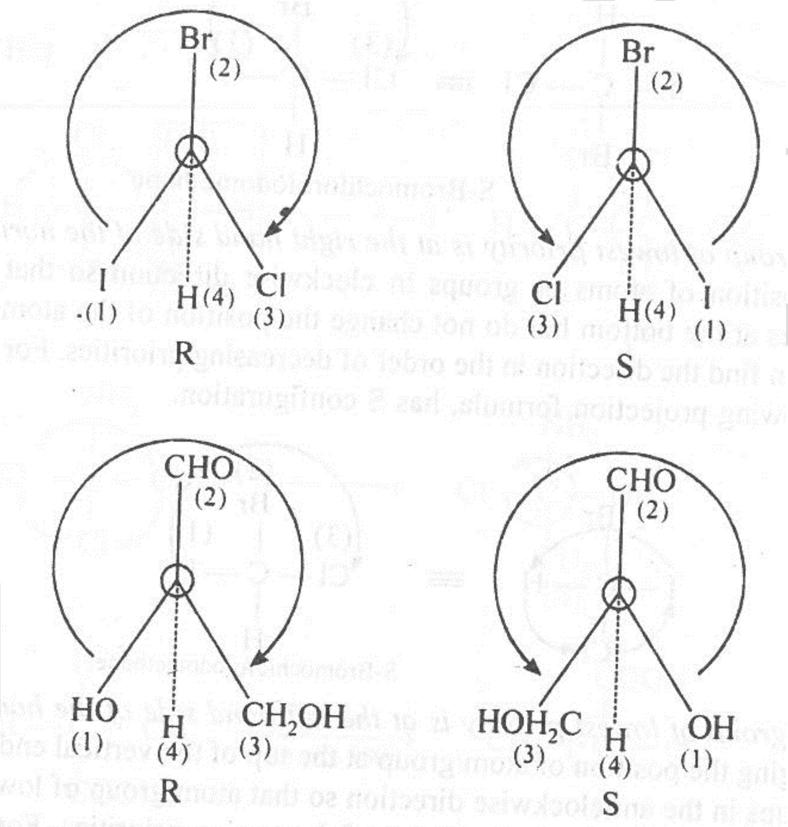
Sequence Rule 3. *A doubly or triply bonded atom is considered equivalent to two or three such atoms; but two or three atoms. If attached actually gets priority over doubly or triply bonded atom.* In glyceraldehydes, O, O, H of -CHO gets priority over the O, H, H of $-CH_2OH$: so the priority sequence is -OH, -CHO, $-CH_2OH$, - H.


$HOCH_2-CH(OH)-CHO$

Glyceraldehyde

Step II. After deciding the sequence of priority for four atoms or groups attached to asymmetric carbon atom; the molecule is visualized in such a way that the atom or group of lowest or last (*i.e.* fourth) priority is directed away from us, while the remaining three atoms or groups are pointing towards us. Now if on looking at these three groups (pointing towards us) in the order of their decreasing priority, our eye moves in clockwise direction, the configuration is specified as R (from Latin word *rectus* meaning right) and on the other hand if our eye moves in anticlockwise direction the configuration is specified as S (from Latin word *sinister* meaning left).

The following examples illustrate the above method for specification of configuration as R and S to molecules of compounds containing an asymmetric or chiral carbon atom.

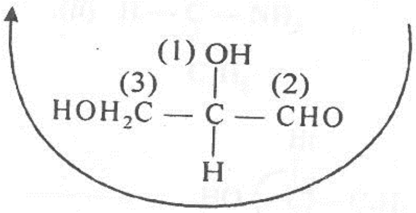


Configuration on the basis of projection formula

When a compound is represented by the Fischer projection formula, the configuration can be easily determined without constructing the model. To determine whether the eye travels clockwise or anticlockwise, we have to place the group of atom of the lowest priority at the bottom of the Fischer projection formula. The following four situations arise:

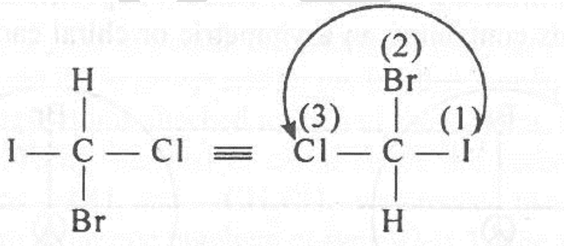
(i) *The atom/group of lowest priority is at the bottom.* In such a case, simply rotate the eye in the order of decreased priorities. The configuration is R if the eye travels in clockwise direction and S if the eye travels in *anticlockwise* direction.

For example, Glyceraldehyde, represented by the following projection formula has R configuration.



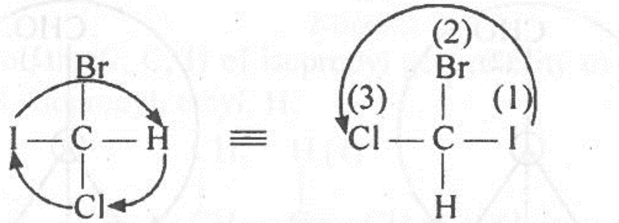
R—Glyceraldehyde

(*ii*) *The atom/group of lowest priority is at the top.* In such case, rotate the molecule by 180° so as to bring atom/group of lowest priority at the bottom. This can be done by reversing the position of all the atoms or groups. Then find the direction in the order of decreasing priorities. For example, the compound CHBrClI, represented by following projection formula, has S configuration.



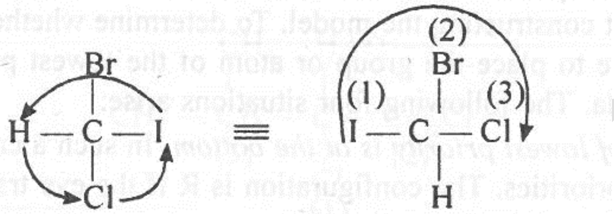
S-Bromochloroiodomethane

(*iii*) *The atom/group of lowest priority is at the right hand side of the horizontal line.* In such case, change the position of atoms or groups in clockwise direction so that atom/group of the lowest priority comes at the bottom but do not change the position of the atom/group at the top of the vertical end. Then find the direction in the order of decreasing priorities. For example, CHBrClI represented by following projection formula, has S configuration.



S-Bromochloroiodomethane

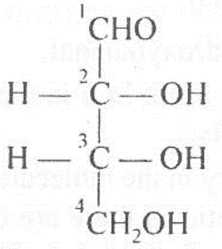
(*iv*) *The atom/group of lowest priority is at the left hand side of the horizontal line.* In such case, without changing the position of atom/group at the top of the vertical end, change the position of other atoms/groups in the anticlockwise direction so that atom/group of lowest priority comes at the bottom. Then find the direction in the order of decreasing priorities. For example CHBrClI represented by the following projection formula, has R configuration.



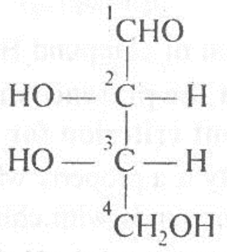
R-Bromochloroiodomethane

Configuration of compounds containing more than one chiral carbon

In such a case, firstly the configuration about each of the chiral carbon is specified and then with the help of numbers, the specification pertaining to the carbon atom of that number is written. Thus the configuration of isomers of 2, 3, 4-trihydroxybutanal are:



(2R, 3R)-2, 3, 4-Trihydroxy butanal
(A)

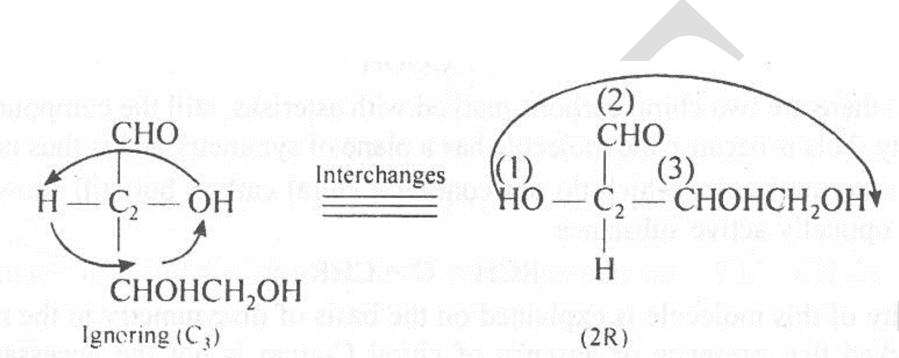


(2S, 3S)-2, 3, 4-Trihydroxy butanal
(B)

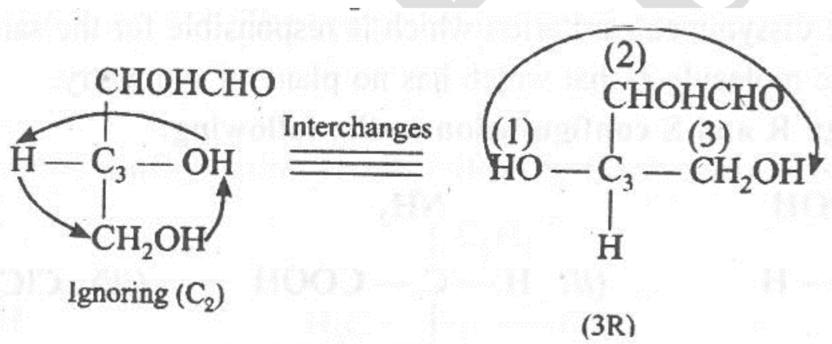
The configurations are explained as follows:

In the compound A above, sequence of groups attached to C_2 is OH, CHO, CHOH-CH_2OH and H.

Now in order to fix specification, first we consider C_2 and ignore C_3



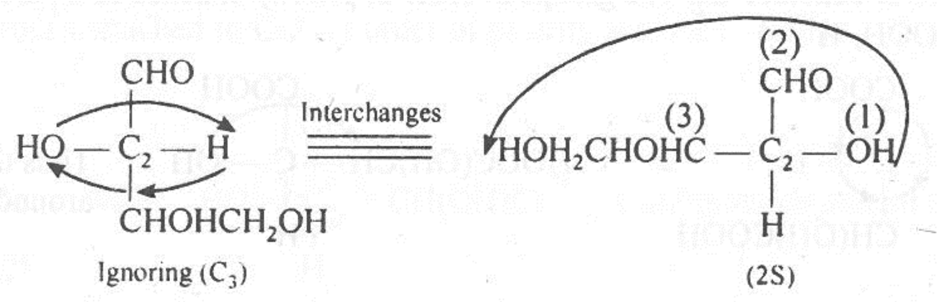
Similarly we consider C_3 and we ignore $C_{2.}$ Thus



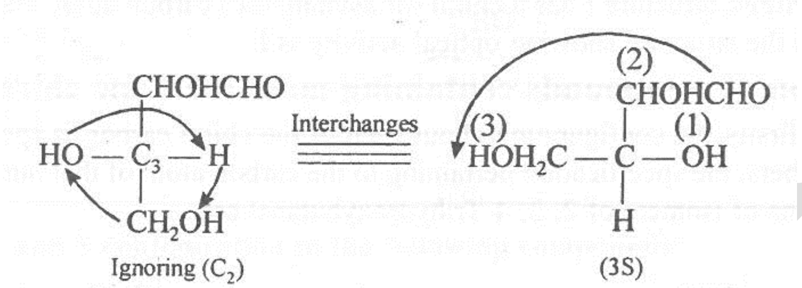
(Here the sequence of groups attached to C_3 is OH, CHOHCHO, CH_2OH and H.

Hence the configuration of compound A is (2R, 3R)-2, 3, 4- Trihydroxybutanal . Similarly the configuration of compound B can be derived as explained below:

For C_2:



For C_3:



Hence configuration of compound B is (2S, 3S)-2, 3, 4-Trihydroxybutanal.

Example 12. Prove that the presence or absence of chiral carbon atom in a molecule is not the necessary and sufficient criterion for existence of optical activity.

Solution: Optical activity is a property which is related to dissymmetry in the molecule. Dissymmetry occurs normally in compounds with chiral carbon atoms. But sometimes there are deviations.

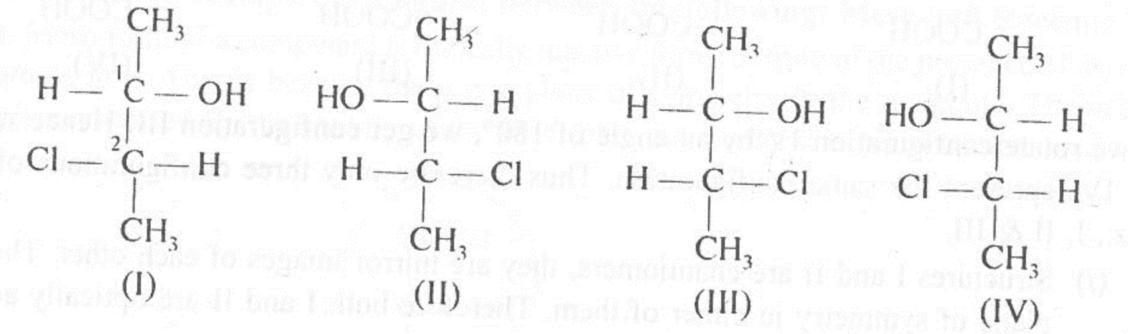
Racemic modifications

Racemic modification is the term used for a mixture of equal amounts of enantiomers. A racemic mixture is optically inactive because of external compensation. The optical activity caused by one enantiomer is neutralized by the activity of other enantiomer. The rotation for a racemic modification or mixture is ± or *dl*. A racemic mixture may also be denoted by the letters R and S. For example, RS-sec. butyl chloride.

When a chiral compound is synthesized from an achiral reactant, a racemic variety of products is obtained. For example, when propionic acid is brominated, α–bromopropionic acid (a chiral product) is obtained. The two enantiomers (+) and (-)α–bromopropionic acids are formed in equal quantities and the product is racemic mixture. It is optically inactive.

Optical isomerism (enantiomerism) in compounds having two dissimilar chiral carbon atoms

Two asymmetric carbon atoms are said to be dissimilar when atoms or groups attached to one asymmetric carbon atom are different from those attached to the other. Compounds of this type exist in 2^2 *i.e.*, 4 stereoisomers. For example 3-chloro-2-butanol is a compound with two dissimilar chiral carbons marked 1 and 2 and exists in the following four forms:

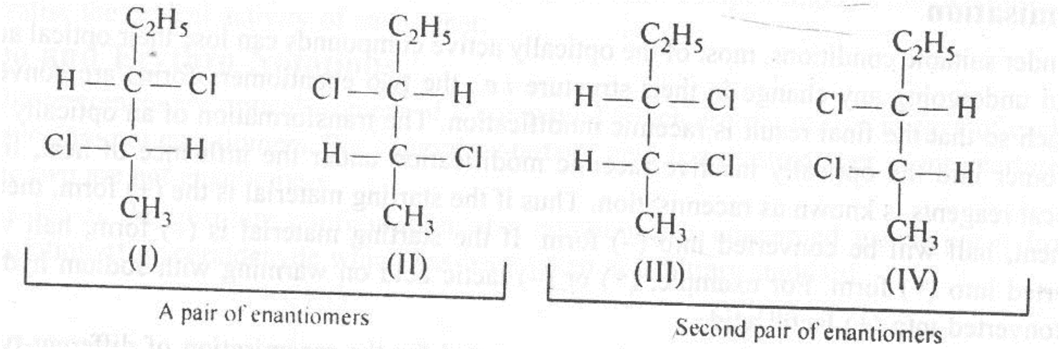


The structures I and II are non-superimposale mirror images, so these are a pair of enantiomers. Similarly structures III and IV are another pair of enantiomers. These two pairs of enantiomers give rise of two racemic modifications.

The structure I and III are neither enantiomers nor superimposable. Such types of stereoisomers are called *diastereomers.* Similarly I and IV, II and III, and II and IV, are the other pairs of diastereomers. *Diastereomers can be defined as those stereoisomers which are not mirror images of each other.*

Unlike enantiomers, distereomers have different physical properties and may rotate the plane of polarised light in the same or different directions and to different extent.

Another example of this type is 2, 3–dichloropentane.



Properties of Diastereomers

(1) They show similar, but not identical, chemical properties (as they contain the same functional groups). Rates of reactions of diastereomers with a given reagent are generally different.

(2) They have different physical properties like m.p. and b.p., densities, refractive indices, specific rotations, solubilities etc. in a given solvent.

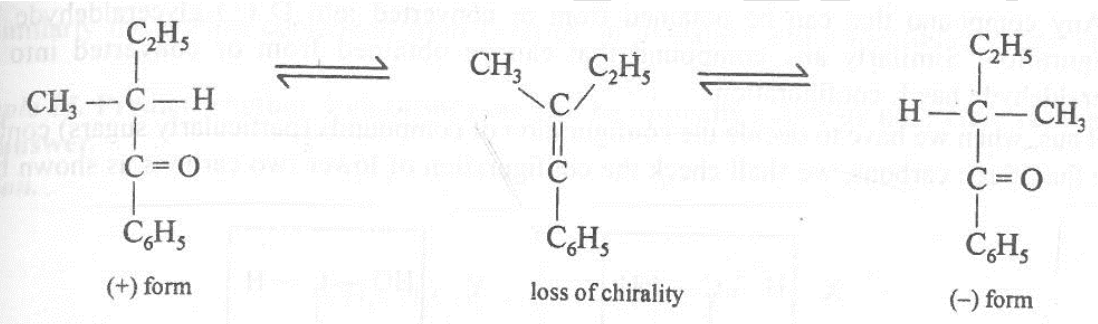
(3) They can be separated by techniques like fractional crystallization, fractional distillation and chromatography.

Racemisation

Under suitable conditions, most of the optically active compounds can lose their optical activity without undergoing any change in their structure *i.e.*, the two enantiomers forms are convertible into each so that the final result is racemic modification. The transformation of an optically active enantiomer into the optically inactive racemic modification under the influence of heat, light or chemical reagents is known as racemisation. Thus if the starting material is the

(-) form, then after treatment, half will be converted into (-) form. If the starting material is (-) form, half will be converted into (-) form. For example, (+) or (-) lactic acid on warming with sodium hydroxide gets converted into (±) lactic acid.

Though different mechanisms have been presented for the racemisation of different types of compounds in most of the cases it occurs via the formation of an intermediate which is no longer dissymmetric or chiral. For example, a ketone in which chiral carbon atom is joined to a hydrogen atom can undergo racemisation via the formation of enolic form by tautomeric change.



The intermediate enolic form, which is no longer chiral when reverts to the stable keto form, it is equally likely to produce (+) or (-) forms and thus racemisation takes place.

Such a mixture does not show any optical activity.

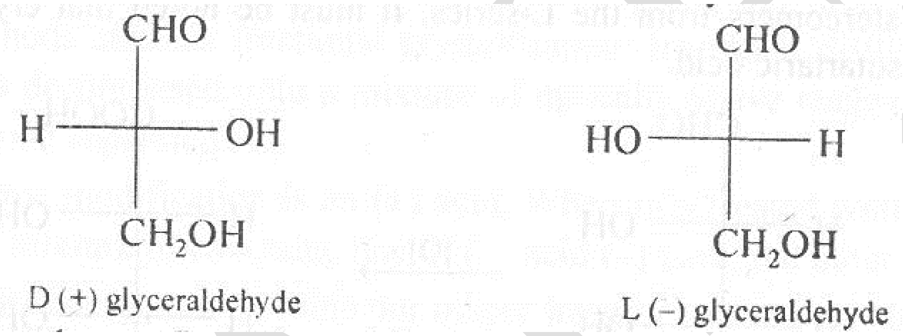
It may be mentioned that optical inactivity of the meso form is due to internal compensation as the activity of one part of the molecule is neutralised by that of the other part.

Optical inactivity of the racemic form is due to external compensation as the two forms *d*- and *l*-neutralise the optical activity of each other.

Threo and Erythro Notations

Diastereomers are optical isomers of a compound which are not mirror images of each other and hence are not enantiomers. For example *d*- tartaric acid is a diastereomer of mesotartaric acid. But the two are not enantiomers.

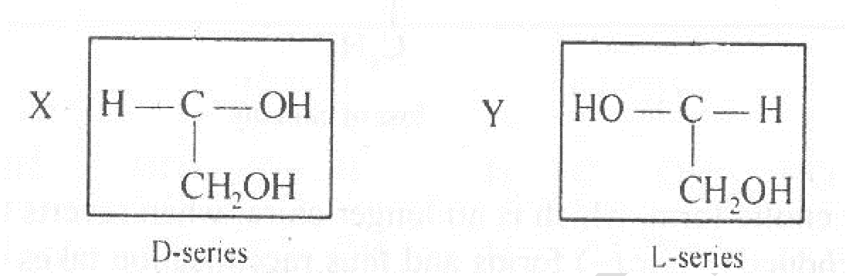
As for as the absolute configuration of a compound is concerned we derive it from the configuration of glyceraldehydes which has been taken as arbitrary standard.



D and L stand for the configuration while (+) and (-) signs denote the actual direction of rotation of plane polarised light. If H and OH are on LHS and RHS of central carbon, it denotes D configuration. If OH and H are on the same LHS and RHS of central carbon it denotes L configuration.

Any compound that can be obtained from or converted into D (+) glyceraldehydes has D configuration. Similarly any compound that can be obtained from or converted into L (-) glyceraldehydes has L configuration.

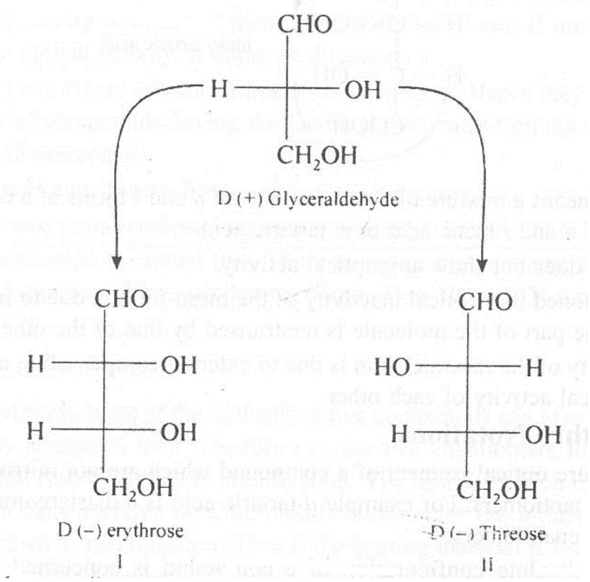
Thus, when we have to decide the configuration of compounds (particularly sugars) containing more than three carbons, we shall check the configuration of lower two carbons as shown below.



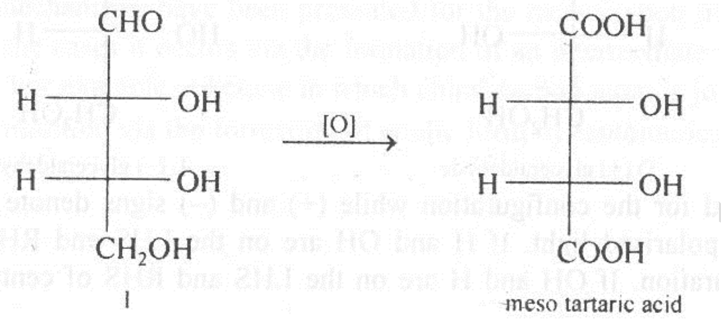
If the arrangement corresponds to X, the compound has D configuration. If the arrangement corresponds to Y, the compound belongs to L configuration.

Let us take the example of $CHO^{*}CH\ OH^{*}CHOH\ CH_2OH$. This contains two asymmetric carbon atoms marked with asterisks. There are four optical isomers possible, all of which are known.

If the H on the third carbon atom (from the bottom) is on the left hand side, the compound is *erythro*, while if the H on the third carbon atom is on the right hand side, the compound is *threo*. The structures of D-erythrose and D-threose which may be assumed to be obtained form D-glyceraldehyde are given below.



Compound I and II are diastereomers of each other from the D-series. Similarly there will be another pair of diastereomers from the L-series. It must be noted that erythro compound (I) on oxidation gives mesotartaric acid.



Similarly the erythro compound from L-series on oxidation will also produce meso tartaric acid.

Methods for the resolution of racemic mixtures

The separation of racemic modification into enantiomers is called resolution. Since the two enantiomers in a racemic mixture have identical physical and chemical properties, these cannot be separated by usual methods of fractional distillation or fractional crystallization. Special methods are adopted for their separation as given below.

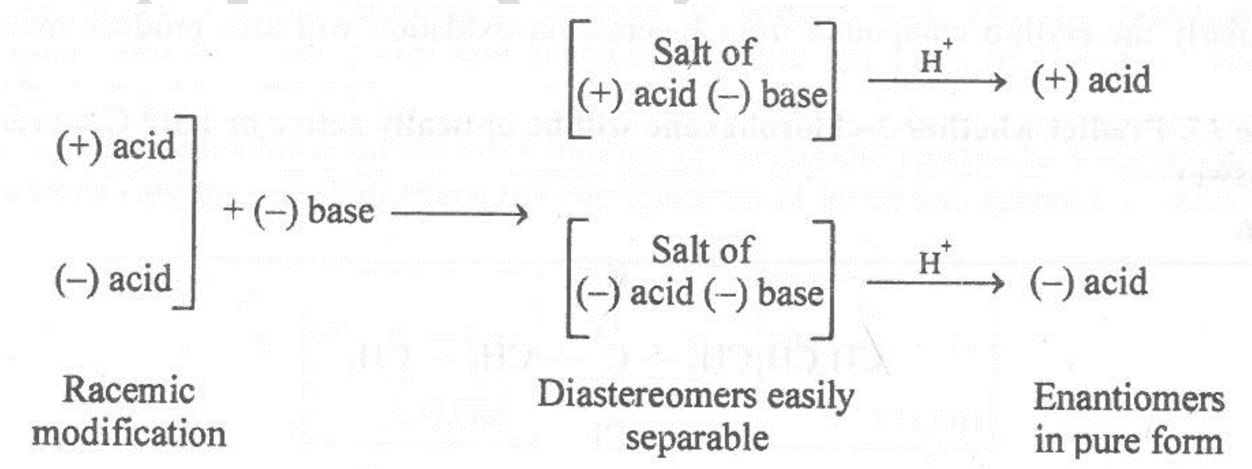
(*i*) **Mechanical separation.** This method was first adopted by Pasteur for separating the enantiomers of ammonium tartarate. When racemic modification is crystallized from a solution, two types of crystals are obtained. These are mirror images of each other consisting of (+) and (-) form which can be separated by hand picking with the help of a pair of tweezers and a powerful lens. This is a very laborious method and can be applied only to those compounds which give well defined distinguishable crystals of enantiomers.

(*ii*) **Biochemical method.** Certain micro-organisms grow in a racemic mixture, consuming only one of the enantiomers while leaving the other unaffected. Thus *Penicillium* *glaucum* when placed in (±) tartaric acid consume only (+) tartaric acid and leaves (-) tartaric acid unused. The major disadvantage of this method is that one of the enantiomers get destroyed.

(*iii*) **Chemical method.** This method is mostly used for the resolution of racemic modification. In this method the racemic modification is treated with an optically active reagent to get a pair of *diastereomers.* Since diastereomers differ in their physical properties, it is possible to separate them by physical methods such as fractional crystallization, fractional distillation etc. The pure diastereomers are the decomposed, into a mixture of optically active reagent and corresponding enantiomer, which can be separated.

Suppose the racemic modification is an (±) acid. When it is treated with an optically active, say (-) base, it gives a mixture of two salts, one of (+) acid (-) base, the other of (-) acid (-) base.

These salts are neither superimposable nor mirror images; so these are diastereomers having different physical properties and can be separated by fractional crystallization. After separation the optically active acids can be recovered in pure forms by adding a mineral acid.



The commonly used optically active bases for the purpose are naturally occurring alkaloids such as (-) brucine, (+) quinine, (-) strychnine and (+) cinchonine.

Similarly, the resolution of racemic bases can be carried out using a naturally occurring optically active such as (-)malic acid. Alcohols can be resolved in a similar way by ester formation using an optically active acid.

Text books:

1. Madan, R.L. (2015). *Chemistry for Degree Students*. New Delhi: S. Chand and Company Pvt, Ltd.

2. Morrison, R. N. & Boyd, R. N. (1992). *Organic Chemistry*. New Delhi: Dorling Kindersley Pvt. Ltd. (Pearson Education).

POSSIBLE QUESTIONS

PART A (20 multiple choice questions)

Online Examinations

PART B (2 marks questions)

1. What is chiral carbon atom?
2. Define specific rotation.
3. What is cracking? Give one example.
4. What do you understand by the term conformation?
5. What is meant by an enantiomer.
6. Why a Racemic mixture is optically inactive.
7. What are the conditions to exhibit optical activity

PART C (6 marks questions)

1. Explain with one example in each case
(i) R and S configuration (ii) E and Z notations (iii) Racemisation.

2. Explain the following terms:
(i) Polarised light (ii) Optical activity (iii) Requirement for a compound showing optical activity (iv) Two examples of optically active compounds.

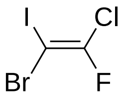
3. What are R and S configurations? State sequence rules with examples.

4. (i) Explain the term meso form with suitable examples.

(ii) Explain the properties of enantiomers.

5. Assign E and Z configuration to the following compounds:

(i)



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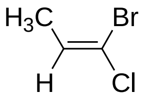

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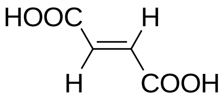

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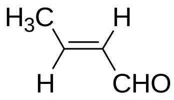


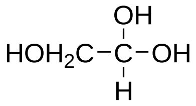
6. (i) What is optical activity? Give the stereoisomers of tartaric acid. How do you

account for the lack of optical activity in meso form and racemic mixtures?

(ii) What are the essential differences between enantiomers and diastereoisomers?

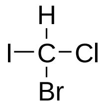
7. Assign R or S configuration for the following molecules:

(i)



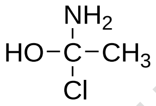
$HOH_2C-\underset{H}{\overset{OH}{C}}-OH$

(ii)



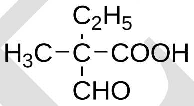
$I-\underset{Br}{\overset{H}{C}}-Cl$

(iii)



$HO-\underset{Cl}{\overset{NH_2}{C}}-CH_3$

(iv)



$H_3C-\underset{CHO}{\overset{C_2H_5}{C}}-COOH$

8. Explain the E and Z designations of geometrical isomers?

9. (i) Discuss the methods of resolution of a recemic mixture which illustrates the formation of diasteromers.

(ii) Distinguish between meso and racemic forms of tartaric acid.

10. (i) Explain the racemisation of optical isomers with suitable examples.

(ii) What is the most essential condition of compound to be optically active in nature?

KARPAGAM ACADEMY OF HIGHER EDUCATION

Class: III B.Sc Chemistry Course Name: Organic Chemistry I- Basics and Hydrocarbons

Course Code: 19CHU103 Unit: II Batch-2019-2022

S.No	Questions	opt1	opt2	opt3	opt4	Answer
1.	The isomers of a substance must have	same chemical properties	same molecular weight	same structural formula	same functional groups	same molecular weight
2.	Alkenes show geometrical isomerism due to:	asymmetry	rotation around a single bond	resonance	restricted rotation around a double bond	restricted rotation around a double bond
3.	Two compounds have the same composition and also have the same atoms attached to the same atoms, although with different orientations in space. These compounds are	identical	position isomers	structural isomers	stereoisomers	stereoisomers
4.	Compounds with the same molecular formula but different structural formulas are called	alkoxides	iso compounds	isomers	ortho compounds	isomers
5.	Optical isomerism is shown by	n-butyl chloride	sec-butyl chloride	tert–butyl chloride	isobutyl chloride	sec-butyl chloride
6.	Lactic acid, CH_3–CHOH–COOH, is a molecule which shows	geometrical isomerism	tautomerism	optical isomerism	metamerism	optical isomerism
7.	Consider (R)–and (S)-2-butanol. Which physical property distinguishes the two compounder?	melting point	solubility in common solvents	rotation of plane–polarized light	Infrared spectrum	rotation of plane–polarized light
8.	How many optical isomers are possible for lactic acid?	2	4	6	8	2
9.	Which of the following compounds is an optically active compound?	lactic acid	chloroform	acetic acid	ethanol	lactic acid
10.	Which of the following represents a racemic mixture?	75% (R)-2-butanol, 25% (S) -2-butanol	25% (R)-2-butanol, 75% (S) -2-butanol	50% (R)-2-butanol, 50% (S)-2 butanol	80% (R)-2-butanol, 20% (S) -2-butanol	50% (R)-2-butanol, 50% (S)-2 butanol
11.	Geometrical isomerism is shown by	lactic acid	maleic acid	1-butene	1,1-dichloroethylene	maleic acid

12.	It is possible to distinguish between optical isomers by	using chemical tests	mass spectrometry	IR spectroscopy	polarimetry	polarimetry
13.	Which of the following compounds will not show geometrical isomerism?	ethanol	maleic acid	fumaric acid	2-butene	ethanol
14.	R and S-2–butanols can be distinguished by the rotation of	ordinary light	polarised light	UV light	IR light	polarised light
15.	Lactic acid exhibits	optical isomerism	geometrical isomerism	linkage isomerism	cis-trans isomerism	optical isomerism
16.	Molecules containing n different asymmetric carbon atoms will have	2^n optically different forms	2^{n-1} optically different forms	2^{n-2} optically different forms	$2^{n-1/2}$ optically different forms	2^n optically different forms
17.	Mesotartaric acid has a	centre of symmetry	rotation-reflection symmetry	inversion of symmetry	plane of symmetry	plane of symmetry
18.	Separation of racemic modification into its enantiomorphs is called	diastereoisomer	resolution	inversion	rotomer	resolution
19.	A molecule that is not superimposable on its mirror image is	achiral	enantiomer	optically inactive	chiral	chiral
20.	Which of the following compounds exhibit geometrical isomerism?	1-pentene	2-methyl-2-pentene	2-pentene	2-methyl-2-butene	2-pentene
21.	Which equation is used to calculate the specific rotation. (Alpha represents the observed rotation)	alpha × cell length	alpha/(cell length × concentration)	(alpha × cell length)/concentration	alpha × cell length × concentration	alpha/(cell length × concentration)
22.	How many chiral centers are there in tartaric acid and how many different stereoisomers exist for this acid?	2 chiral centers; 2 isomers	2 chiral centers; 1 isomer	1 chiral center; 1 isomer	2 chiral centers; 3 isomers	2 chiral centers; 3 isomers
23.	A chiral molecule may be defined as one that is not super imposable on	mirror reflection	mirror rotation	mirror vibration	mirror image	mirror image
24.	A molecule is said to be chiral	if it contains plane of symmetry	if it contains centre of symmetry	if it cannot be superimposed on its mirror image	if it can be superimposed on its mirror image	if it cannot be superimposed on its mirror image
25.	Which of the statements is false regarding chiral molecules?	rotate the plane of polarized light	have cis and trans isomers	exist as enantiomers	can be detected with a polarimeter	have cis and trans isomers
26.	An optically active compounds	must contain atleast four	when in solution rotate the plane	must always contain as asymmetric carbon	in solution always give a	when in solution rotate the plane

		carbons	of polarized light	atom	negative reading in polarimeter	of polarized light
27.	Substance which rotate the plane polarized light are called as	optically active substance	optically inactive substance	isomers	enantiomers	optically active substance
28.	Substance which rotate the plane polarized light to the right are called	laevo rotatory	dextro rotatory	specific rotation	angle of rotation	dextro rotatory
29.	Plane-polarised light is affected by	identical molecules	all polymers	chiral molecules	all biomolecules	chiral molecules
30.	1,2-dichloroethane can exhibit	optical isomerism	tautomerism	functional group isomerism	geometrical isomerism	geometrical isomerism
31.	Optical isomers that are mirror images are called	tautomers	diastereomers	enantiomers	metamers	enantiomers
32.	Which of the following compounds show geometrical isomerism?	triethylamine	propene	diethylamine	2-butene	2-butene
33.	Lactic acid exists in	only one optically active form	three optically active forms	two optically active forms	four optically active forms	two optically active forms
34.	The isomer which rotates the plane of polarized light to the right is called	laevo rotatory	specific rotation	walden inversion	dextro rotatory	dextro rotatory
35.	Optical isomers that are not mirror images are called	diastereomers	enantiomers	metamers	meso compounds	diastereomers
36.	Tartaric acid can exist in	4 forms	3 forms	2 forms	only one form	4 forms
37.	Enantiomers have which of the following characteristics?	rotate ordinary light	have the same melting point	are superimposable mirror images	react with optically active molecules at the same rate	have the same melting point
38.	Which of the following statements is false about enantiomers?	rotate plane-polarised light	are superimposable mirror images	are nonsuperimposable mirror images	have the same melting point	are superimposable mirror images
39.	Tartaric acid contains	only one asymmetric carbon atoms	two asymmetric carbon atoms	three asymmetric carbon atoms	four asymmetric carbon atoms	two asymmetric carbon atoms
40.	The separation of a racemic mixture into its enantiomers is termed	racemisation	resolution	inversion	retention	resolution

41.	The process of producing a racemic modification starting with one of the pure enantiomers is termed as	racemisation	resolution	retention	inversion	racemisation
42.	What is the possible number of optical isomers for a compound containing 2 dissimilar asymmetric carbon atoms?	2	4	6	8	4
43.	The racemic mixture is	optically inactive	optically active	chiral	asymmetric	optically inactive
44.	What is the possible number of optical isomers for a compound containing n dissimilar asymmetric carbon atoms?	n2	2^n	n+1	n+2	2^n
45.	In the Cahn, Ingold and Prelog R, S nomenclature, what does the S represent?	sonorous	sinister	spatial	solid	sinister
46.	The R and S nomenclature also called as	Cahn, Ingold and Prelog notation	Cram's rule	E and Z notation	Prelog's rule	Cahn, Ingold and Prelog notation
47.	The R and S configuration of (-)-lactic acid is	R	S	E	Z	R
48.	The Cahn, Ingold and Prelog notation of (+)-tartaric acid is	S, S	S, S	R, R	R, S	R, R
49.	The R and S nomenclature is mainly based on	Prelog's rule	Cram's rule	Fajan's rule	sequence rule	sequence rule
50.	If the group of similar priority are one the opposite side of the π-plane the isomer is known as	E-isomer	Z-isomer	R-isomer	S-isomer	E-isomer
51.	What is the correct R, S ranking of the substituents?	hydrogen > methyl > ethyl > bromine	ethyl > methyl > hydrogen > bromine	bromine > ethyl > methyl > hydrogen	bromine > ethyl > hydrogen > methyl	bromine > ethyl > methyl > hydrogen
52.	The main condition for geometrical isomerism is	The molecule must have single bond	The molecule must have sigma bond	The molecule must have double bond	The molecule not has double bond	The molecule must have double bond
53.	The German word Zusammen meaning	Not same	opposite	across	together	together
54.	The German word Entgeqen meaning	not same	opposite	together	same	opposite
55.	Meso-tartaric acid is	sometimes optically active	always optically active	sometimes optically inactive	always optically inactive	always optically inactive

56.	Which of the following compounds will be optically active?	succinic acid	meso-tartaric acid	lactic acid	chloroacetic acid	lactic acid
57.	2-Butanol is optically active because it contains	an asymmetric carbon	a plane of symmetry	a hydroxyl group	a centre of symmetry	an asymmetric carbon
58.	Which of the following has the highest CIP priority?	$-CH(CH_3)_2$	$-CH_2CH_2CH_3$	$-CH_2CH=CH_2$	$-CH_2CH_2CH_2CH_3$	$-CH(CH_3)_2$
59.	Which one of the following compound cannot exhibit optical activity?	alanine	sucrose	1-butanol	2-butanol	1-butanol
60.	Which of the following compound contains diastereotopic protons?	ethyl chloride	1,2-dichloropropane	2-methyl-2-butene	1,2-dichloroethane	1,2-dichloropropane

UNIT-III

Syllabus

Chemistry of Aliphatic Hydrocarbons

Carbon-Carbon sigma bonds
General methods of preparation, physical and chemical properties of alkanes: Wurtz Reaction, Wurtz-Fittig Reactions, Free radical substitutions: Halogenation-relative reactivity and selectivity.
Cycloalkanes and Conformational Analysis
Conformational analysis of alkanes: Relative stability and Energy diagrams. Types of cycloalkanes and their relative stability, Baeyer strain theory: Chair, Boat and Twist boat forms of cyclohexane with energy diagrams; Relative stability of mono substituted cycloalkanes.

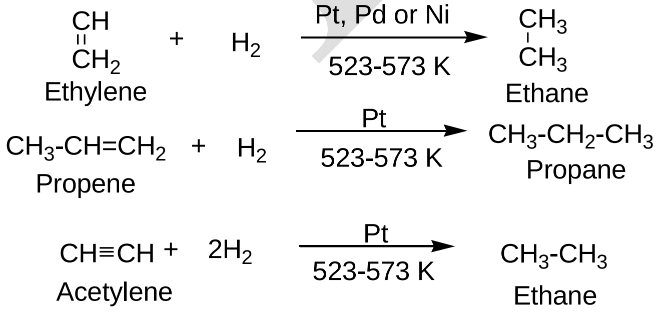
Sources of alkanes

Two main sources of alkanes are natural gas and petroleum. Both these substances are generally found together in underground deposits. Natural gas contains about 80%methane, 10%ethane, the rest being mixture of higher hydrocarbons. Petroleum contains hydrocarbons containing upto 40 carbon atoms.

General methods of Preparation of alkanes

Different methods of preparation of alkanes are given blow:

(1) Hydrogenation of unsaturated hydrocarbons (Sabatier-Senderen's reaction). A mixture of unsaturated hydrocarbons and hydrogen is passed our finely divided platinum,palladium or nickel at 523-573 k. Alkenes and alkynes are reduced to alkanes.



$$\underset{\text{Ethylene}}{CH=CH_2} + H_2 \xrightarrow[523\text{-}573\ K]{Pt,\ Pd\ or\ Ni} \underset{\text{Ethane}}{CH_3\text{-}CH_3}$$

$$\underset{\text{Propene}}{CH_3\text{-}CH=CH_2} + H_2 \xrightarrow[523\text{-}573\ K]{Pt} \underset{\text{Propane}}{CH_3\text{-}CH_2\text{-}CH_3}$$

$$\underset{\text{Acetylene}}{CH\equiv CH} + 2H_2 \xrightarrow[523\text{-}573\ K]{Pt} \underset{\text{Ethane}}{CH_3\text{-}CH_3}$$

(2) Reduction of alkyl halides. This may be done in different ways:

(i) Chemical reducing agents like zinc and acetic acid or hydrochloric acid, zinc-copper couple and alcohol; magnesium-amalgam and water etc., convert alkyl halides into alkanes.

$$\underset{\text{Alkyl halide}}{R\text{-}X} \quad + \quad 2[H] \xrightarrow[\text{Zn/Acetic acid}]{\text{Zn-Cu/alcohol}} \underset{\text{Alkane}}{R\text{-}H} + H\text{-}X$$

$$\underset{\text{Ethyl bromide}}{C_2H_5\text{-}Br} \quad + \quad 2[H] \xrightarrow[\text{Zn/Acetic acid}]{\text{Zn-Cu/alcohol}} \underset{\text{Ethane}}{C_2H_6} + HBr$$

(ii) Alkyl iodides are easily reduced by heating with concentrated HI at about 423 K in a seated tube.

$$R\text{-}I + HI \xrightarrow[\text{423 K}]{P} R\text{-}H + I_2$$

$$C_2H_5I + HI \xrightarrow[\text{423 K}]{P} C_2H_6 + I_2$$

(3)Wurtz reaction. It is the reaction of two molecules of alkyl halides (expect fluorides) with metallic sodium in dry ether to form **alkane**.For example,

$$\underset{\text{Ethyl bromide}}{CH_3CH_2\text{—}Br} + 2Na + \underset{\text{Ethyl bromide}}{Br\text{—}CH_2CH_3} \xrightarrow{\text{Dry ether}} \underset{\text{Butane (}n\text{-Butane)}}{CH_3CH_2CH_2CH_3} + 2NaBr$$

$$\text{In general,} \quad R\text{—}X + 2Na + X\text{—}R \xrightarrow{\text{Dry ether}} R\text{—}R + 2NaX$$

When a mixture of two **different** alkyl halides are used, a mixture of **three** alkanes in formed,as shown below:

$$CH_3\text{—}Br + 2Na + Br\text{—}CH_2CH_3 \xrightarrow{\text{Dry ether}} \underset{\text{Propane}}{CH_3CH_2CH_3} + 2NaBr$$

$$CH_3\text{—}Br + 2Na + Br\text{—}CH_3 \xrightarrow{\text{Dry ether}} \underset{\text{Ethane}}{CH_3CH_3} + 2NaBr$$

$$CH_3CH_2Br + 2Na + BrCH_2CH_3 \xrightarrow{\text{Dry ether}} \underset{\text{Butane}}{CH_3CH_2CH_2CH_3} + 2NaBr$$

The separation of such mixtures into individual alkanes may not always be easy.

Limitations: This reaction as a preparative method suffers from the following **limitations**:

1. It is suitable only for the preparation of alkanes containing **even** number of carbon atoms.
2. Halogen compounds containing other reactive functional groups like –OH and –COOH groups cannot be used.
3. It fails with **tert-alkyl halides**,due to steric effects.
4. Methane cannot be prepared by this method.

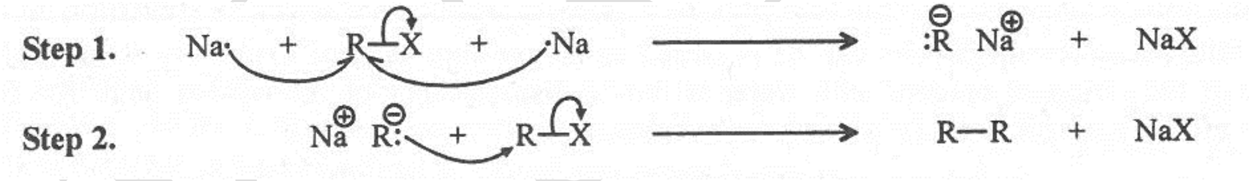
Importance: It is useful in **ascending the series** of organic compounds, because it leads to the **formation** of **new carbon-carbon**bond.For example,

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

$$CH_3Cl + 2Na + ClCH_3 \longrightarrow CH_3CH_3 + 2NaCl$$

Mechanism: The two possible mechanisms are outlined below:

(i)Ionic mechanism involving the formation of intermediate organosodium compound .The organosodium compound provides the nucleophilic alkyl **carbanion** to replace the halide ion from another molecule of alkyl halides, as shown below:



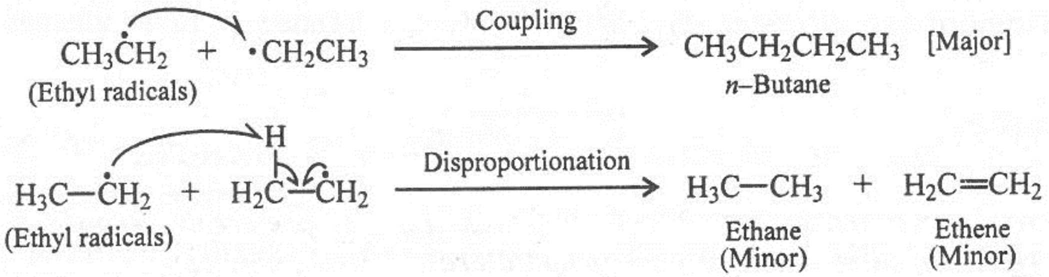
Grignard reagents,being less reactive than organosodium compounds, can react only with alkyl halides which are very reactive (e.g., benzyl halides, allyl halides) and this seems to support this mechanism.

(ii)Free radicalmechanism. Alkyl free radicals (**R$^\bullet$**) as reactive intermediates couple together,as shown below to form alkane.

$$R{-}X + Na \longrightarrow R\cdot + NaX$$

$$R\cdot + R\cdot \longrightarrow R{:}R \quad (R{-}R)$$

Formation of minor amount of **ethane** and **ethene**,besides n-butane,in reaction between ethyl halide and sodium **supports** this mechanism. Disproportionation of ethyl radical can explain this experimental fact.



(4) Wurtz-Fittig reaction. It consists in treating a mixture of an **aryl halide** and **alkyl halide** with sodium, using anhydrous ether as the reaction medium (cf. the Wurtz reaction). The yields are usually fair to good.

$$C_6H_5{-}X + 2Na + X{-}R \xrightarrow{\text{Dry ether}} C_6H_5{-}R + 2NaX$$

Small amount of side products are given by the self–coupling of phenyl and alkyl residues, as illustrated below:

$$C_6H_5{-}Br + 2Na + Br{-}CH_3 \xrightarrow{\text{Ether}} \underset{\text{Toluene}}{C_6H_5CH_3} + 2NaBr$$

$$C_6H_5{-}Br + 2Na + Br{-}C_6H_5 \xrightarrow{\text{Ether}} \underset{\text{Diphenyl}}{C_6H_5{-}C_6H_5} + 2NaBr$$

$$CH_3{-}Br + 2Na + Br{-}CH_3 \xrightarrow{\text{Ether}} \underset{\text{Ethane}}{CH_3{-}CH_3} + 2NaBr$$

Unlike Friedel-Crafts reaction,there is no rearrangement of the alkyl groups.**This method is,therefore, preferable to the Friedel-Crafts method when the alkyl group being introduced has a straight chain longer than two carbon chain.**

Mechanism. According to one view,it is believed to be a **free radical reaction**, as outlined below:

Step 1. Formation of free radicals:

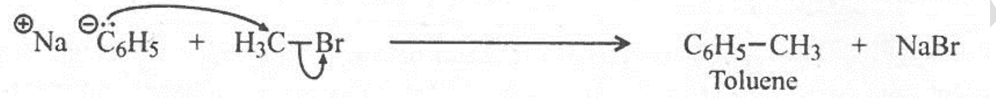
$$C_6H_5Br + Na \longrightarrow \cdot C_6H_5 + NaBr$$

$$CH_3Br + Na \longrightarrow \cdot CH_3 + NaBr$$

Step 2. Carbon–carbon coupling of free radicals:

$$C_6H_5\cdot + \cdot CH_3 \longrightarrow \underset{\text{Toluene}}{C_6H_5{-}CH_3}$$

According to another view, it involves the intermediate formation of organosodiumcompounds,say, $C_6H_5^-Na^+$ and $CH_3^-Na^+$followed by nucleophilic attack of these carbanions on the halides:



$$\overset{\oplus}{Na}\ \overset{\ominus}{C_6H_5} + H_3C{-}Br \longrightarrow \underset{\text{Toluene}}{C_6H_5{-}CH_3} + NaBr$$

(5) Corey-House synthesis. It is a better method than Wurtz reaction. An alkyl halide and a lithium dialkyl copper are reacted to give a higher hydrocarbon.

$$\underset{\text{Alkyl halide}}{R'-X} + \underset{\text{Lithium dialkyl copper}}{R_2CuLi} \longrightarrow \underset{\text{Alkane}}{R-R'} + R\text{-}Cu + LiX$$

(R and R' may be same or different)

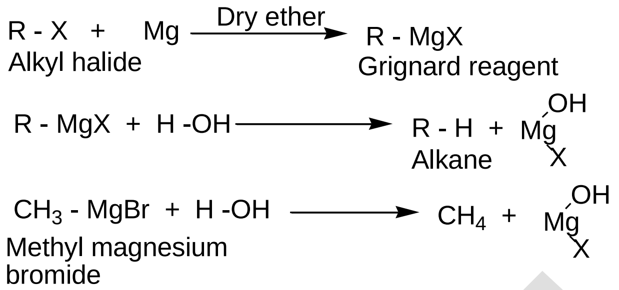
For example,

$$\underset{\text{n-Propyl bromide}}{CH_3CH_2CH_2Br} + \underset{\text{Lithium dimethyl copper}}{(CH_3)_2CuLi} \longrightarrow \underset{\text{n-Butane}}{CH_3CH_2CH_2CH_3} + \underset{\text{Methyl copper}}{CH_3Cu} + LiBr$$

A notable feature of this reaction is that it can be used for preparing symmetrical,unsymmetrical, straight-chain or branched-chain alkanes.

For a better yield of the product, the alkyl halide used should be primary whereas lithium dialkyl copper may be primary, secondary or tertiary.

(6) Indirect reduction of alkyl halides. Alkyl halides react with magnesium in dry ether to form alkyl magnesium halides (Grignard reagent). Decomposition of the Grignard reagent with water yield alkanes.



$$\underset{\text{Alkyl halide}}{R-X} + Mg \xrightarrow{\text{Dry ether}} \underset{\text{Grignard reagent}}{R-MgX}$$

$$R-MgX + H-OH \longrightarrow \underset{\text{Alkane}}{R-H} + Mg\genfrac{}{}{0pt}{}{OH}{X}$$

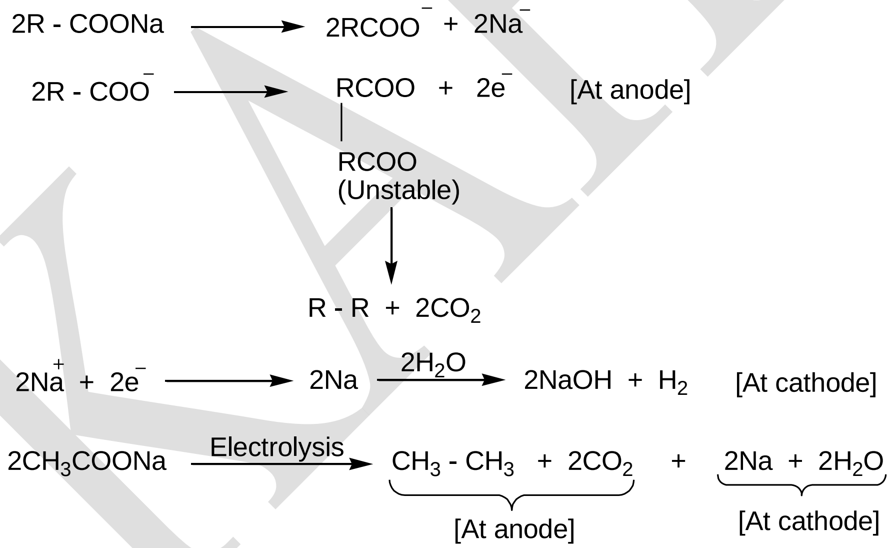
$$\underset{\text{Methyl magnesium bromide}}{CH_3-MgBr} + H-OH \longrightarrow CH_4 + Mg\genfrac{}{}{0pt}{}{OH}{X}$$

(7) Decarboxylation of carboxylic acid salt. Sodium salts of a fatty acid are heated with soda lime (NaOH + CaO) to form alkanes.

$$R-COONa + NaOH \xrightarrow{CaO} R-H + Na_2CO_3$$

$$\underset{\text{Sodium acetate}}{CH_3-COONa} + NaOH \xrightarrow{CaO} CH_4 + Na_2CO_3$$

(8) Kolbe's Electrolytic process. By the electrolysis of conc. Solution of sodium potassium salts of fatty acids, alkanes are obtained.



$$2R-COONa \longrightarrow 2RCOO^- + 2Na^-$$

$$2R-COO^- \longrightarrow \begin{array}{c} RCOO \\ | \\ RCOO \\ \text{(Unstable)} \\ \downarrow \\ R-R + 2CO_2 \end{array} + 2e^- \quad \text{[At anode]}$$

$$2Na^+ + 2e^- \longrightarrow 2Na \xrightarrow{2H_2O} 2NaOH + H_2 \quad \text{[At cathode]}$$

$$2CH_3COONa \xrightarrow{\text{Electrolysis}} \underbrace{CH_3-CH_3 + 2CO_2}_{\text{[At anode]}} + \underbrace{2Na + 2H_2O}_{\text{[At cathode]}}$$

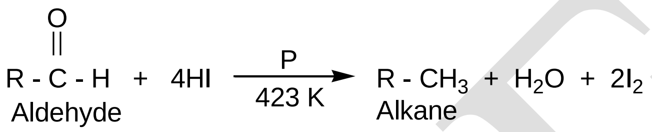
(8) By reduction of alcohols,aldehydes,ketones and acids. The reduction is carried out with the help of HI and P.

(i)

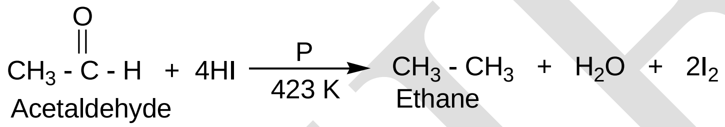
$$\underset{\text{Alcohol}}{R-OH} + 2HI \xrightarrow[423\ K]{P} R-H + H_2O + I_2$$

$$\underset{\text{Ethyl alcohol}}{C_2H_5-OH} + 2HI \xrightarrow[423\ K]{P} \underset{\text{Ethane}}{C_2H_6} + H_2O + I_2$$

(ii)

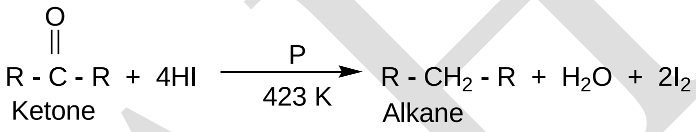


$$\underset{\text{Aldehyde}}{R-\overset{O}{\overset{\|}{C}}-H} + 4HI \xrightarrow[423\ K]{P} \underset{\text{Alkane}}{R-CH_3} + H_2O + 2I_2$$

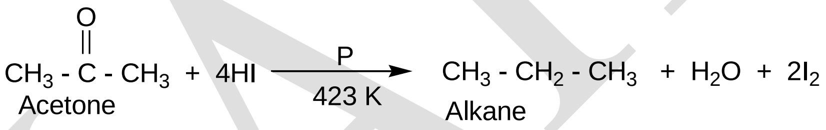


$$\underset{\text{Acetaldehyde}}{CH_3-\overset{O}{\overset{\|}{C}}-H} + 4HI \xrightarrow[423\ K]{P} \underset{\text{Ethane}}{CH_3-CH_3} + H_2O + 2I_2$$

(iii)

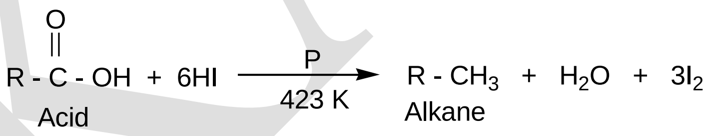


$$\underset{\text{Ketone}}{R-\overset{O}{\overset{\|}{C}}-R} + 4HI \xrightarrow[423\ K]{P} \underset{\text{Alkane}}{R-CH_2-R} + H_2O + 2I_2$$



$$\underset{\text{Acetone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3} + 4HI \xrightarrow[423\ K]{P} \underset{\text{Alkane}}{CH_3-CH_2-CH_3} + H_2O + 2I_2$$

(iv)



$$\underset{\text{Acid}}{R-\overset{O}{\overset{\|}{C}}-OH} + 6HI \xrightarrow[423\ K]{P} \underset{\text{Alkane}}{R-CH_3} + H_2O + 3I_2$$

$$\underset{\text{Formic acid}}{H-COOH} + 6HI \xrightarrow[423\ K]{P} CH_4 + 2H_2O + 3I_2$$

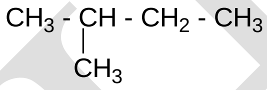
$$CH_3-COOH + 6HI \xrightarrow[423\ K]{P} CH_3-CH_3 + 2H_2O + 3I_2$$

PHYSICAL PROPERTIES OF ALKANES

1. Solubility. Alkanes being non-polar in nature are insoluble in water but soluble in non polar solvents like ether,benzene, ect. Solubility decreases with increase in molecular size.

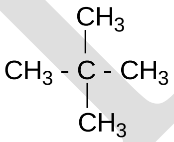
2. Boiling point. As alkanes are non-polar molecules, they have only weak van der Waals' forces operating between them. Van der Waals' forces of attraction depend upon the molecular size and increase with in molecular size. Among the chain isomers of a compound, the branched chain isomer has lower boiling point compared to straight-chain isomer. For example, the boiling points of three isomeric pentanes are given below:

$CH_3CH_2CH_2CH_2CH_3$
n- Pentane
(b.p = 309 K)



$CH_3-CH(CH_3)-CH_2-CH_3$

Isopentane
(b.p = 301 K)



$CH_3-C(CH_3)_2-CH_3$

Neopentane
(b.p = 281 K)

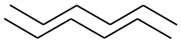
Explanation. The boiling point of a substance depends upon the force of attraction between the molecules. Force of attraction between the molecules depends upon the area of contact between them. Area of contact and force of attraction will be maximum for straight chain compound. As branching increases, the area of contact decreases. Consequently, the force of attraction and boiling point will decrease.

3. Melting point. Alkanes show lower melting point because of absence of charge. Melting point is expected to increase with increase in molecular size. This is found to be true but the increase is not uniform.

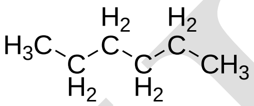
Alkanes	Melting Point (K)
C_3H_8	85.9
n-C_4H_{10}	138
n-C_5H_{12}	143.3
n-C_6H_{14}	179

We find that increase in melting point is relatively more in going from odd-carbon to even-carbon alkane compared to when we move from even-carbon to odd-carbon alkane.

Explanation. It may be realised that in even-carbon alkanes (e.g. C_6H_{14}) the packing of molecules can take place to a greater extent, resulting in greater attraction force and hence greater melting points. This is not so with odd-carbon alkanes.

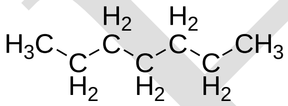


Representation of two
chain of n-C_6H_{14}
(greater attractive forces)



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

n-hexane



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

n-heptane

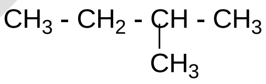
Example 1. Write the structural formula of n-pentane. isopentane and neopentane. Which of these has highest boiling point and way?

Solution:

Structural formula of pentanes

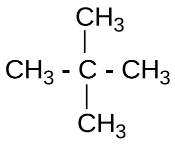
$CH_3 - CH_2 - CH_2 - CH_2 - CH_3$

n-pentane



$CH_3 - CH_2 - \underset{CH_3}{\underset{|}{CH}} - CH_3$

Isopentane



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

Neopentane

Highest boiling point. Of thethree pentanes, n-pentane has the highest boiling point.

Explanation. All the three pentanes are non-polar compounds having only weak intermolecular forces of attraction (van der Wall's forces). The molecular weights of the three isomers are naturally the same but they have different surface areas. As the surface area of n-pentane is large than those of the other two, it has strongest intermolecular forces of attraction. Therefore it has highest boiling point followed by iso- and neopentanes.

CHEMICAL PROPERTISE OF ALKANES

Chemical properties of alkanes are described as under:

1. Halogenation. Displacement or substitution of hydrogen atom by halogens is known as halogenation. Methane on treatment with chlorine in the presence of diffused sunlight or by heating the reaction mixture to 523-673 K gives chloromethane.

$$CH_4 + Cl_2 \xrightarrow[\text{or 523-673 K}]{\text{Sunlight}} \underset{\text{Chloromethane}}{CH_3Cl} + HCl$$

The reaction doses not stop here. Chloromethane is further chlorinated to dichloromethane.Dichloromethane is chlorinated to trichloromethane is finally chlorinated to tetrachloromethane. This sequence of reactions to gives blow.

$$CH_3Cl + Cl_2 \longrightarrow \underset{\text{Dichloromethane}}{CH_2Cl_2} + HCl$$

$$CH_2Cl_2 + Cl_2 \longrightarrow \underset{\text{Trichloromethane}}{CHCl_3} + HCl$$

$$CHCl_3 + Cl_2 \longrightarrow \underset{\text{Tetrachloromethane}}{CCl_4} + HCl$$

Bromination of alkanes, takes place in similar manner but less readily. Direct iodination of these is not possible as the reaction is reversible.

$$R - H + I_2 \rightleftharpoons R - I - HI$$

However, iodination can be carried out in the presence of oxidising agent such as iodic acid (HIO_3), which destroys the hydrogen iodide as soon as it is formed and so drives the reaction to the right.

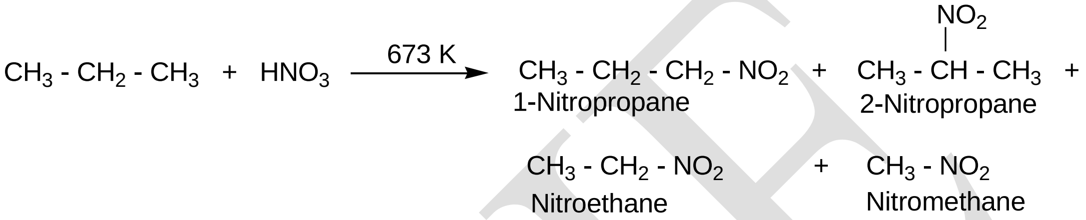
$$5HI + 4HIO_3 \longrightarrow 3I_2 + 3H_2O$$

Direct fluorination is usually explosive and brings about repture of C–C and C–H bonds leading to a mixture of products. However, fluorination of alkanes can be carried out by diluting fluorine with an inert gas such as nitrogen.

2. Nitration. It is a process in which hydrogen atom of alkane is replaced by nitro group ($-NO_2$). Alkanes undergo nitration when treated with fuming HNO_3 in the vapour phase between 423-748 K. For example,

$$CH_3 - H + HO - NO_2 \longrightarrow \underset{\text{Nitro methane}}{CH_3 - NO_2} + H_2O$$

Higher alkanes on nitration give a mixture of all possible mono derivatives. For example,



$$CH_3 - CH_2 - CH_3 + HNO_3 \xrightarrow{673\text{ K}} \underset{\text{1-Nitropropane}}{CH_3 - CH_2 - CH_2 - NO_2} + \underset{\text{2-Nitropropane}}{CH_3 - \overset{\overset{NO_2}{|}}{CH} - CH_3} + \underset{\text{Nitroethane}}{CH_3 - CH_2 - NO_2} + \underset{\text{Nitromethane}}{CH_3 - NO_2}$$

3. Sulphonation. It is a process in which hydrogen atom of alkane is replaced by sulphonic acid group ($-SO_3H$). Sulphonation of hexane and higher members may be carried out by treating the alkanes with oleum (fuming sulphuric acid). For example,

$$\underset{\text{n-Hexane}}{C_6H_{13} - H} + HO - SO_3H \xrightarrow{\triangle} \underset{\text{n-Hexane sulphonic acid}}{C_6H_{13} - SO_3H} + H_2O$$

4. Oxidation. *(i) Combustion.* Alkanes burn readily in excess of air or oxygen to form CO_2 and H_2O. This process is called combustion and is accompanied by the evolution of a large amount of heat. For example,

$$C_nH_{2n+2} + O_2 \xrightarrow{\triangle} nCO_2 + (n+1)\,H_2O + \text{Heat}$$

$$CH_4 + 2O_2 \xrightarrow{\triangle} CO_2 + 2H_2O + 890\text{ KJ}$$

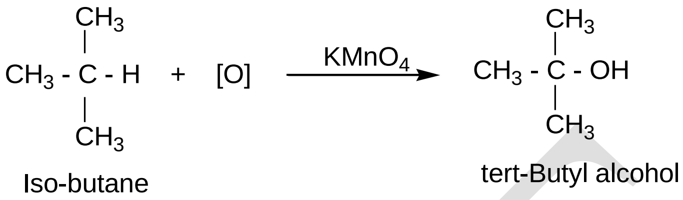
Alkanes are, therefore, used as fuels in the form of kerosene oil, gasoline, LPG.

(ii) Catalytic oxidation. When alkanes are heated in a limited supply of air or oxygen at high pressure and in the pressure of suitable catalyst, they are oxidized to alcohols, aldehydes or fatty acids. For example,

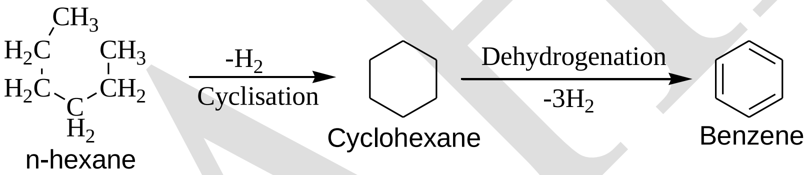
$$2CH_4 + O_2 \xrightarrow[\text{Cu Tube}]{523\text{ K, 100 Atm}} 2\,CH_3OH$$

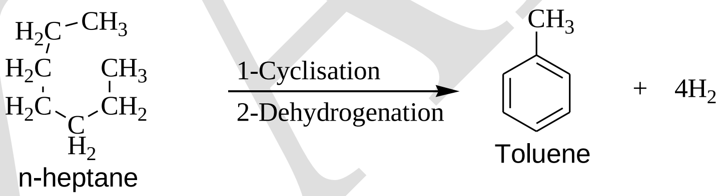
$$CH_4 + O_2 \xrightarrow[Mo_2O_3]{673\text{ K, 200 Atm}} HCHO + H_2O$$

(iii) Alkanes containing tertiary hydrogens can be oxidised by such reagents to form alcohols. For example,



5. Aromatisation. When alkanes containing six or more carbon atoms are heated to high temperature (773 K) under high pressure and in the presence and in the presence of a catalyst (oxide of chromium, vanadium, molybdenum supported on alumina), they are converted into aromatic hydrocarbons. The process involves cyclisation, isomerisation and is known as aromatisation. For example,





6. Thermal decomposition or pyrolysis or cracking. The process of decompositionof bigger molecules into a number of simpler molecules by the action of heat is called *pyrolysis* or *cracking*. This process involves the breaking of C − C and C – H bonds leading to the formation of lower alkanes and alkanes. For example,

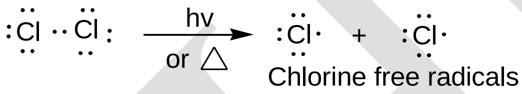
$$CH_3\text{-}CH_2\text{-}CH_3 \xrightarrow{733\ K} \underset{\text{Ethylene}}{CH_2 = CH_2} + \underset{\text{Methane}}{CH_4} \quad \text{or} \quad \underset{\text{Propene}}{CH_3 - CH = CH_2} + H_2$$

MECHANISM OF HALOGENATION OF ALKANE

The halogenation of alkanes occurs by a free radical mechanism. It involves three steps: (a) Chain initiation, (b) Chain propagation, (c) Chain termination. Mechanism of halogenation is explained by considering the chlorination of methane.

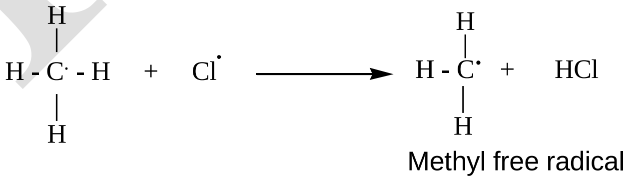
(a) Chain Initiation. When a mixture of CH_4 and Cl_2 is heated or subjected to diffused sunlight, Cl_2 absorbs energy and undergoes homolytic fission producing chlorine free radicals. One molecule gives rise to two radicals.

Step (1)



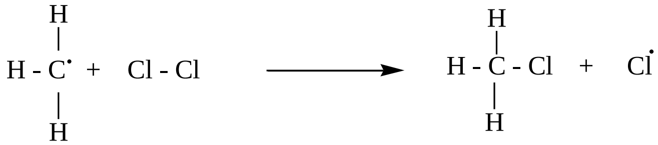
(b) Chain propagation. The chlorine free radical produced above collides with a molecule of methane forming hydrogen chloride and a methyl free-radical. The methyl free-radical in turn reacts with a molecule of chlorine forming methyl chloride and chlorine free-radical. The newly formed chlorine radical can react with another molecule of methane as in step (2) generating methyl free-radical and hydrogen chloride. The methyl free-radical can again repeat step (3) and so on. Thus the sequence of reactions in steps (2) and (3) is repeated over and over again and thus the chain is propagated. In other words, a single photon of light initially absorbed by chlorine can bring about the conversion of a large number of molecules of methane into methyl chloride.

Step (2)



$$\mathrm{H-\overset{H}{\underset{H}{C}}-H} + \mathrm{Cl}^{\cdot} \longrightarrow \mathrm{H-\overset{H}{\underset{H}{C}}^{\cdot}} + \mathrm{HCl}$$

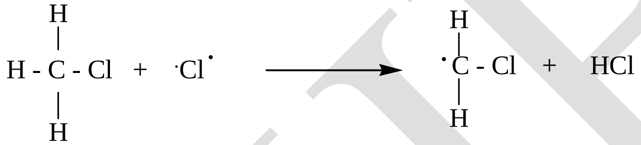
Step (3)



$$\mathrm{H{-}\overset{H}{\underset{H}{|}}\!\!\!\overset{\bullet}{C} + Cl{-}Cl \longrightarrow H{-}\overset{H}{\underset{H}{C}}{-}Cl + Cl^{\bullet}}$$

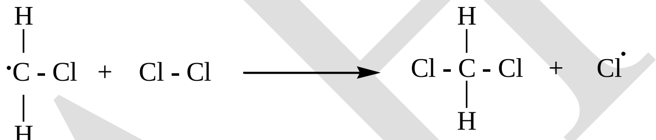
However, the above reaction does not stop at methyl chloride stage but proceeds further till all the H-atoms of methane are replaced by chlorine atoms giving a mixture of mono-, di-, tri- and tetra- chloromethane

Step (4)



$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}Cl + {}^{\bullet}Cl^{\bullet} \longrightarrow {}^{\bullet}\overset{H}{\underset{H}{C}}{-}Cl + HCl}$$

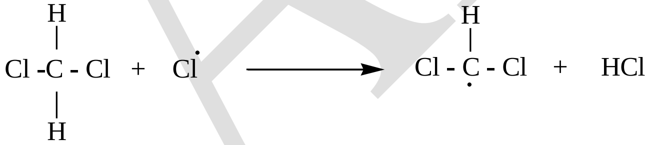
Step (5)



$$\mathrm{{}^{\bullet}\overset{H}{\underset{H}{C}}{-}Cl + Cl{-}Cl \longrightarrow Cl{-}\overset{H}{\underset{H}{C}}{-}Cl + Cl^{\bullet}}$$

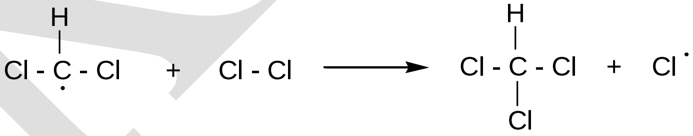
Methyledine chloride

Step (6)



$$\mathrm{Cl{-}\overset{H}{\underset{H}{C}}{-}Cl + Cl^{\bullet} \longrightarrow Cl{-}\overset{H}{\underset{\bullet}{C}}{-}Cl + HCl}$$

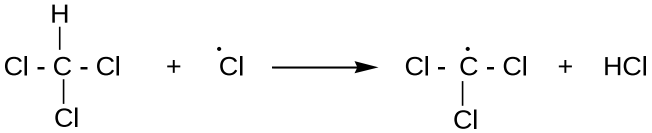
Step (7)



$$\mathrm{Cl{-}\overset{H}{\underset{\bullet}{C}}{-}Cl + Cl{-}Cl \longrightarrow Cl{-}\overset{H}{\underset{Cl}{C}}{-}Cl + Cl^{\bullet}}$$

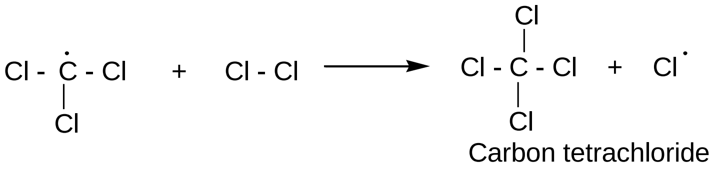
Chloroform

Step (8)



$$\mathrm{Cl{-}\overset{H}{\underset{Cl}{C}}{-}Cl + {}^{\bullet}Cl \longrightarrow Cl{-}\overset{\bullet}{\underset{Cl}{C}}{-}Cl + HCl}$$

Step (9)



$$\mathrm{Cl-\overset{\bullet}{\underset{Cl}{C}}-Cl} + \mathrm{Cl-Cl} \longrightarrow \mathrm{Cl-\overset{Cl}{\underset{Cl}{C}}-Cl} + \mathrm{Cl^{\cdot}}$$

Carbon tetrachloride

Chain termination

The chain reactions mentioned above, however, come to an end if the free radicals combine amongst themselves to from neutral molecules. Some of the chain terminating steps are:

$$^{\cdot}Cl + {}^{\cdot}Cl \longrightarrow Cl - Cl$$

$$^{\cdot}CH_3 + {}^{\cdot}Cl \longrightarrow CH_3 - Cl$$

$$^{\cdot}CH_3 + {}^{\cdot}CH_3 \longrightarrow CH_3 - CH_3$$

Evidence in support of free radical mechanism of halogenations of alkanes

The following points support the free radical mechanism:

(i) Reaction does not take place in dark at room temperature but requires energy in the form of heat or light. This is due to the fact that the chain initiation step (1) is endothermic and hence needs large amount of energy to break the Cl-Cl bond into radicals.

(ii) The reaction has a high quantum yield *i.e.*, many thousand molecules of methyl chloride (or alkyl halide in general) are formed for each photon of light absorbed. This fact can be explained on the basis of chain propagation steps (2) and (3).

(iii) Oxygen acts as an inhibitor. This is due to the fact oxygen combines with the alkyl free radicals to form peroxyalkyl radical ($R-O-O^{\bullet}$). This radical is much less reactive than alkyl free radical ($R^{\bullet}$) to continue the chain. As a result, the halogenation of alkyl in the presence of oxygen is slowed down or stopped. Thus the role of inhibitors like oxygen in this reaction gives support to the above mechanism.

(iv) If the above mechanism actually involves free radicals as reactive intermediate, then the addition of substances which are source of free radicals should initiate the reaction even in the dark at room temperature or much below 523 K. This has actually been found to be so. Thus chlorination of methane can be carried out in the dark at room temperature in the presence of small amount of benzoyl peroxide.

$$\underset{\text{Bezoyl peroxide}}{C_6H_5CO - O - O - COC_6H_5} \xrightarrow[298\text{ K}]{\text{dark}} \underset{\text{Benzoyl free radical}}{C_6H_5 - CO - \ddot{\underset{..}{O}}\cdot}$$

$$C_6H_5 - CO - \ddot{\underset{..}{O}}\cdot \longrightarrow \underset{\text{Phenyl free radical}}{\dot{C_6H_5}} + CO_2$$

$$\dot{C_6H_5} + Cl - Cl \longrightarrow C_6H_5 - Cl + Cl^{\cdot}$$

Once, the chlorine free radicals are produced the reaction can take place in the manner explained above.

(v) Chlorination of methane takes place at 423 K in dark in the presence of a little $(C_2H_5)_4$ Pb (Tetraethyl lead). Tetraethyl lead yields free radicals, when heated to 423 K.

$$(C_2H_5)_4Pb \xrightarrow[\text{dark}]{423\text{ K}} 4C_2\dot{H_5} + Pb$$

The ethyl free radical then reacts with chlorine molecule forming ethyl chloride and chlorine free radical.

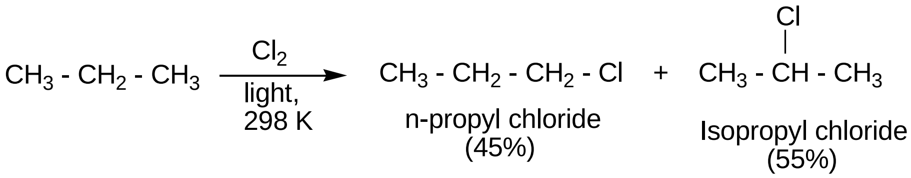
$$^{\cdot}C_2H_5 + Cl - Cl \longrightarrow C_2H_5 - Cl + Cl^{\cdot}$$

The chlorine free radical thus formed brings about chlorination of methane as explained above.

Chlorination and bromination of propane, butane and isobutane

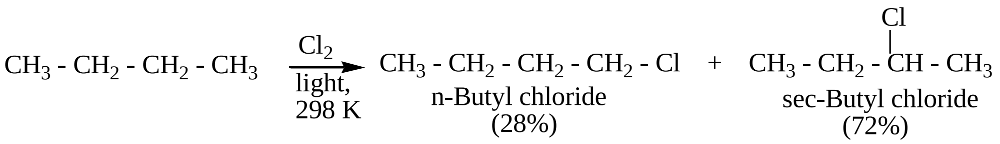
Halogenation of alkane containing more than one type (primary, secondary, tertiary) of halogens, gives a mixture of isomeric products. For example, chlorination of propane, butane and isobutane gives the following products in the proportion given below each.

(i)



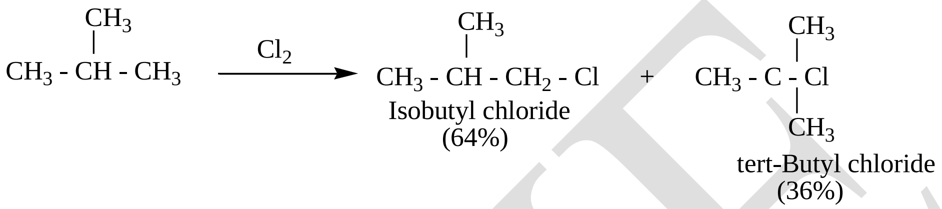
$$CH_3 - CH_2 - CH_3 \xrightarrow[\text{light, } 298\text{ K}]{Cl_2} \underset{\substack{\text{n-propyl chloride}\\(45\%)}}{CH_3 - CH_2 - CH_2 - Cl} + \underset{\substack{\text{Isopropyl chloride}\\(55\%)}}{CH_3 - \overset{\overset{Cl}{|}}{CH} - CH_3}$$

(ii)



$$CH_3-CH_2-CH_2-CH_3 \xrightarrow[\text{light, 298 K}]{Cl_2} \underset{\substack{\text{n-Butyl chloride}\\(28\%)}}{CH_3-CH_2-CH_2-CH_2-Cl} + \underset{\substack{\text{sec-Butyl chloride}\\(72\%)}}{CH_3-CH_2-\overset{\overset{Cl}{|}}{C}H-CH_3}$$

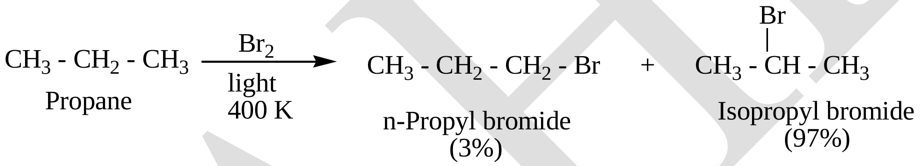
(iii)



$$CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_3 \xrightarrow{Cl_2} \underset{\substack{\text{Isobutyl chloride}\\(64\%)}}{CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2-Cl} + \underset{\substack{\text{tert-Butyl chloride}\\(36\%)}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Cl}$$

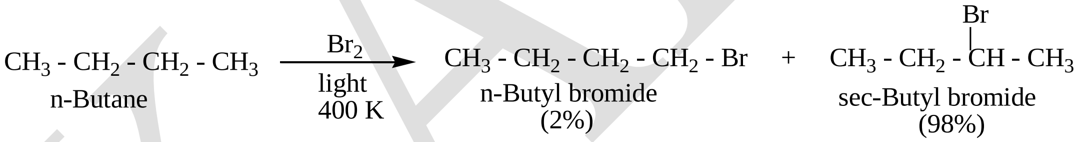
Bromination gives the corresponding bromides but in different proportions:

(iv)



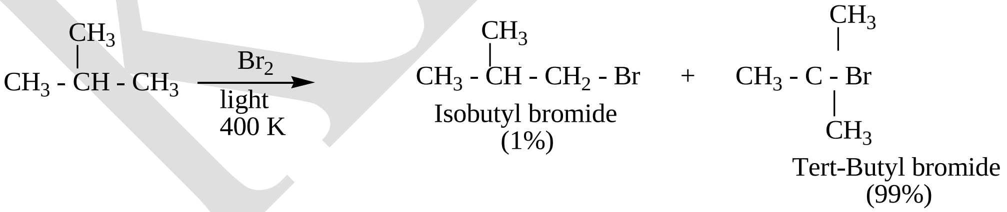
$$\underset{\text{Propane}}{CH_3-CH_2-CH_3} \xrightarrow[\text{light, 400 K}]{Br_2} \underset{\substack{\text{n-Propyl bromide}\\(3\%)}}{CH_3-CH_2-CH_2-Br} + \underset{\substack{\text{Isopropyl bromide}\\(97\%)}}{CH_3-\overset{\overset{Br}{|}}{C}H-CH_3}$$

(v)



$$\underset{\text{n-Butane}}{CH_3-CH_2-CH_2-CH_3} \xrightarrow[\text{light, 400 K}]{Br_2} \underset{\substack{\text{n-Butyl bromide}\\(2\%)}}{CH_3-CH_2-CH_2-CH_2-Br} + \underset{\substack{\text{sec-Butyl bromide}\\(98\%)}}{CH_3-CH_2-\overset{\overset{Br}{|}}{C}H-CH_3}$$

(vi)

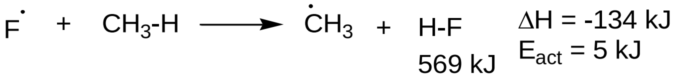


$$CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_3 \xrightarrow[\text{light, 400 K}]{Br_2} \underset{\substack{\text{Isobutyl bromide}\\(1\%)}}{CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2-Br} + \underset{\substack{\text{Tert-Butyl bromide}\\(99\%)}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Br}$$

The result give above shows that the relative amounts of the different isomeric products differ largely depending upon the halogen used. It is also important to note that the bromination, in contrast to chlorination, leads to the formation of only one of the possible isomeric products. This is reflected in the percentages like 97%, 98% and 99% for one of the products in each reaction. Thus bromine atom is more selective in the site of attack than chlorine.

ACTIVATION ENERGY

Consider the reaction



$$F^{\bullet} + CH_3\text{-}H \longrightarrow \overset{\bullet}{C}H_3 + \underset{569\ kJ}{H\text{-}F} \qquad \begin{array}{l}\Delta H = -134\ kJ \\ E_{act} = 5\ kJ\end{array}$$

For a reaction to occur, collision between reactant molecules is a must. Thus the above mentioned reaction takes place only if the collision between a chlorine atom and a methane molecule takes place. But all the collisions are not effective. For a collision to be effective, the reactant molecules must be associated with a certain minimum amount of energy called threshold energy. The number of such molecules constitutes only a small fraction of total numberof molecules or most of the molecules have kinetic energy lower than the threshold energy. Thus, in order that the reaction should occur the molecules must be raised to higher energy level, i.e., they must be activated before they react to form the products. The additional amount of energy which the reactant molecules having energy less than threshold energy must acquire so that their collisions result in chemical reaction is called activation energy.

In the above mentioned exothermic reaction we expect that the energy released in the formation of H-F bond (569kJ /mole) appears to be sufficient to break the weaker C….H bond of methane (435kJ /mole) .however, it is not so. Clearly, the bond breaking and bond-making are not perfectly synchronized, and the energy released through bond formation is not completely available for bond breaking. In other words, certain minimum amount of energy (5kJ /mole as shown experimentally) must be supplied to initiate the reaction. This is the activation energy for the reaction.

There is another aspect which must be kept in mind. In addition to the adequate energy (kinetic energy) which the colliding molecules possess at the time of collision, they must be properly oriented before the collision can be really effective in causing the reaction. The number of properly oriented collisions in a reaction is quite small is compared to the total number of collisions.

Thus in the above mentioned example, the methane molecule must be oriented in such a way that it presents a hydrogen atom to the full force of the impact. In this case, only about one collision in eight is properly oriented.

In general, in collisions, sufficient energy (E_{act}) and proper orientation are essential for a reaction to take place.

As the reaction proceeds, changes in the potential energy takes place and these energy changes are shown in **Figure 3.1.**

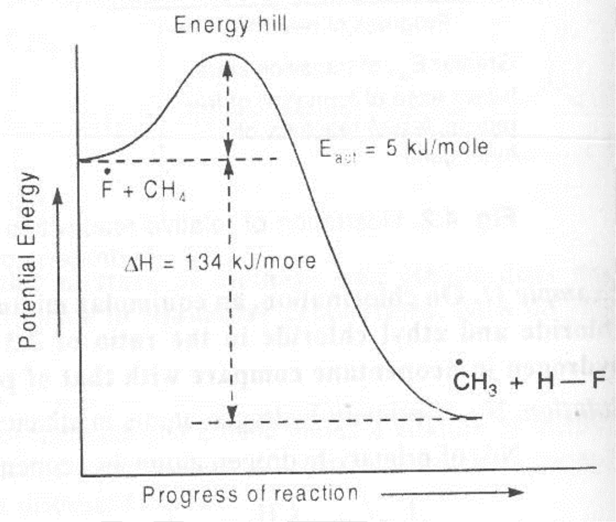


Figure 3.1. Concept of activation energy.

The potential energy of methane molecule and fluorine atom is shown on the left and that of the methyl free radical ($^{\bullet}CH_3$) and hydrogen fluoride on the right. As the reaction begins, the kinetic energy of the reactants (due to their motion) is changed into potential energy side. During the descent, the potential is changed back into kinetic energy till we reach the level of the products ($^{\bullet}CH_3$ and HF).As the potential energy of the product is less than that of the reactants; there must be a corresponding increase in kinetic energy.In other words,the molecules of the products ($^{\bullet}CH_3$ and HF) move faster than the molecules of the reactants (CH_4 and $^{\bullet}F$) so there would be rise in temperature or heat will be evolved. The height of the hill top or energy hill (in kJ /mole) above the level of the reactant is the energy of activation (5kJ /mole).

RELATIVE REACTIVITIES OF HALOGENS IN THE HALOGENATIONS OF ALKANES

The magnitude of E_{act} determines the rate of a reaction. Reactions with low E_{act} proceed at faster rate than the one with a high E_{act} at the same temperature. This relationship between the rate of a reaction and the magnitude of the energy of activation can be explained with the help of halogenation of methane as follows:

$$CH_4 + X_2 \xrightarrow[(X_2 = F_2, Cl_2, Br_2, I_2)]{} CH_3 - X + HX$$

The rate determining step here is the abstraction of hydrogen by halogen atom .i.e., how fast methyl radical is formed.

$$CH_4 + X^{\cdot} \longrightarrow CH_3^{\cdot} + HX$$

Formation of CH_3 radical in chain propagation step is difficult but once formed it gets readily converted into the alkyl halide.

Thus, the overall rate of halogenation of methane depends upon how fast the methyl radical is formed which, in turn, depend on the E_{act} for the formation of methyl radical. Thus,

$$F^{\cdot} + \underset{435\ KJ}{CH_3 - H} \longrightarrow \underset{569\ KJ}{H - F} + {}^{\cdot}CH_3 \qquad \begin{array}{l} H = -134\ kJ \\ E_{act} = 5\ kJ \end{array}$$

$$Cl^{\cdot} + \underset{435\ KJ}{CH_3 - H} \longrightarrow \underset{431\ KJ}{H - Cl} + {}^{\cdot}CH_3 \qquad \begin{array}{l} H = +4\ kJ \\ E_{act} = 17\ kJ \end{array}$$

$$Br^{\cdot} + \underset{435\ KJ}{CH_3 - H} \longrightarrow \underset{368\ KJ}{H - Br} + {}^{\cdot}CH_3 \qquad \begin{array}{l} H = +67\ kJ \\ E_{act} = 78\ kJ \end{array}$$

$$I^{\cdot} + CH_3 - H \longrightarrow \underset{297\ KJ}{H - I} + {}^{\cdot}CH_3 \qquad \begin{array}{l} H = +138\ kJ \\ \text{Eact} = 138\ kJ \end{array}$$

Potential energy diagrams for the above mentioned reactions are given in **Figure 3.2.**

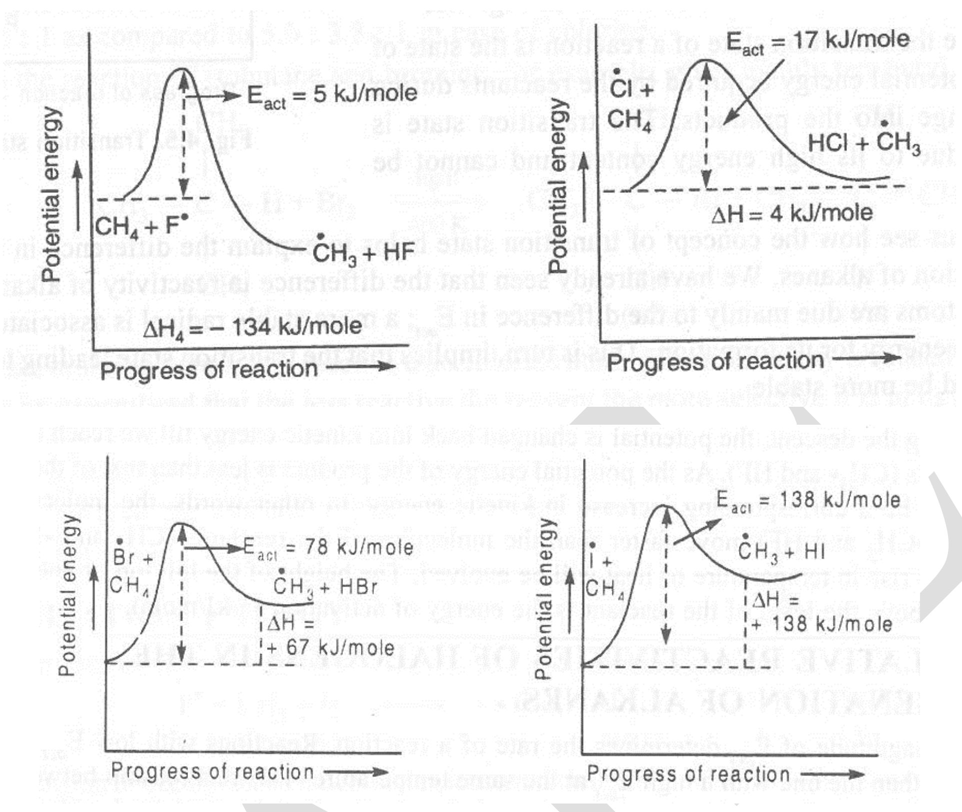


Figure 3.2. Potential energy diagrams.

It is clear decreasing order of E_{act} for chain propagation step is:

Iodination >Bromination> Chlorination > fluorination

Hence order of halogenation should be:

Fluorination > Chlorination >Bromination> Iodination

This order is in conformity with the observed order of halogenation reactivity of F_2, Cl_2, Br_2 and I_2 in halogenation of methane in particular and alkanes in general.

EFFECT OF ACTIVATION ENERGY ON THE STRUCTURE OF TRANSITION STATE IN HALOGENATION OF ALKANES

For a collision to be effective collision, the reactant molecules must be associated with a certain amount of energy called threshold energy. Thus, they also have to cross an energy barrier (hill top) between the reactants and products before reaction can be accomplished. The top of the energy hill (energy barrier) represents an intermediate structure called the transition state. The transition state corresponds to a particular arrangement of atoms of reacting species as they are converted from reactants into product. It represents a configuration in which old bonds are partially broken and new bonds are partially formed. The activation energy (E_{act}) is the difference in energy content between the transition state and reactants, as shown in**Figure 3.3.**

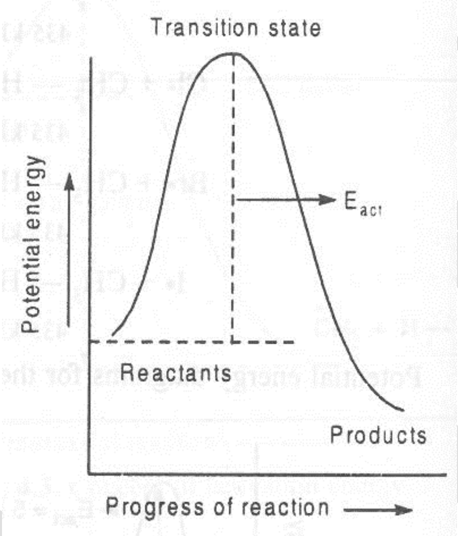
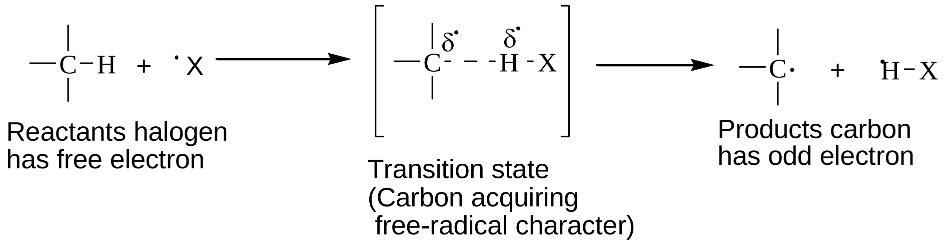


Figure 3.3. Transition state.

Hence the transition state of a reaction is the state of highest potential energy acquired by the reactants during their change into the products. The transition state is unstable due to its high energy content and cannot be isolated.

Let us see how the concept of transition state helps to explain the difference in the rates or halogenations of alkanes, We have already seen that the difference in reactivity of alkanes towards of alkanes towards halogen atoms are due mainly to the difference in E_{act} a more stable radical is associated with low activation energy for its formation. This is turn, implies that the transition state leading to its formation would be more stable.

The transition state for the abstraction of hydrogen atom from an alkane may be represented as follows:



The C−H bond is party broken and H−X bond is party formed(**Figure 3.4**). Depending upon the extent to which the C−H bond is broken, the alkyl group is associated with the character of free radical it will form. Factors that stabilise the resulting free radical (delocalisation of the odd electron) tend to stabilize the nascent free radical in the transition sate.

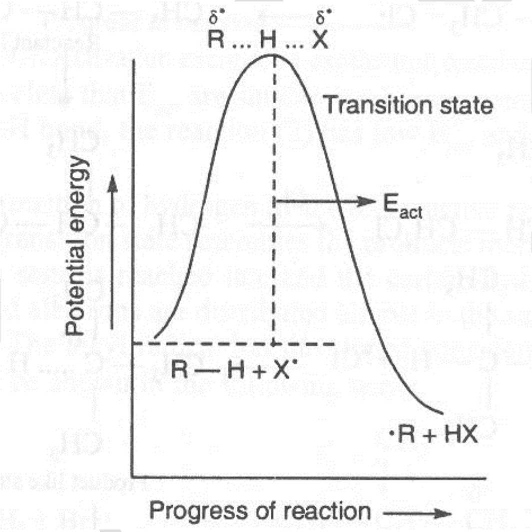
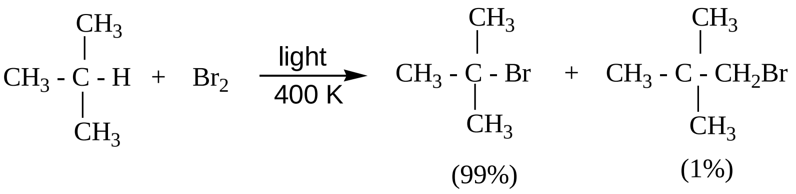


Figure 3.4. Transition state in halogenation of alkane.

REACTIVITY AND SELECTIVITY OF HALOGENS TOWARDS ALKANES

Bromine is less reactive towards alkanes than chlorine but bromine is more selective than chlorine. The relative rates of substitution by bromine per hydrogen atom (3°, 2°,1° hydrogen) are 1600: 82: 1 as compared to 5.0: 3.8 : 1 in case of chlorine.

Thus the reaction of isobutane and bromine, for example, gives mainly tert-butyl bromide.

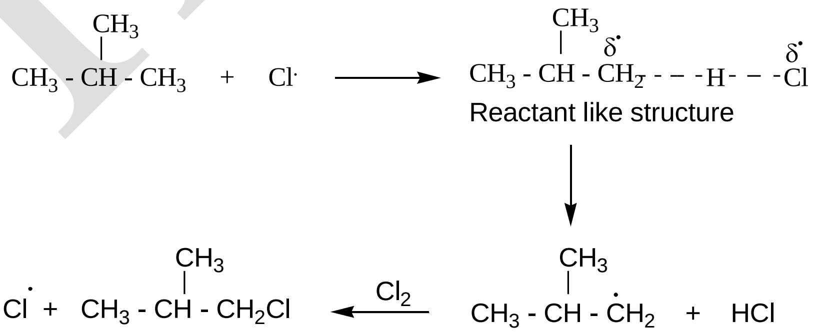


$$CH_3\text{ - }\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\text{ - }H + Br_2 \xrightarrow[400\ K]{light} \underset{(99\%)}{CH_3\text{ - }\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\text{ - }Br} + \underset{(1\%)}{CH_3\text{ - }\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\text{ - }CH_2Br}$$

Further, bromine atom is less reactive than chlorine atom. Thus, selectivity is related to reactivity and it can be generalised that the less reactive the reagent the more selective it is in its attack under a set of similar reaction. The greater selectivity of bromine can be explained in terms of transition state theory. According to a postulate made by Professor G.S. Hammond the structure of transition state of endothermic step (with high value of E_{act}) of a reaction resembles the products of that step more than it does the reactants. The structure of transition state of exothermic state with low value of E_{act} of a reaction resembles the reactant of that step more than it does the products.

This principle can be explained with the help of potential energy diagrams for the chlorination and bromination of isobutene.

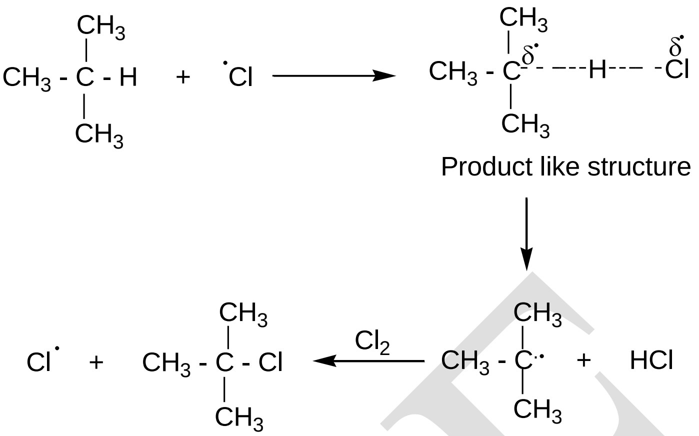
The abstraction of hydrogen by the highly reactive chlorine atom is exothermic and has low E_{act}. According to the above postulate, the transition state resembles the reactants more than it does the products. In other words, the transition state is reached early and the carbon–hydrogen bond is slightly stretched. Atoms and electrons are distributed almost in the same way as in the reactants; carbon is still tetrahedral. The alkyl radical has developed very little free radical character. The transition state for the hydrogen (1ºand 3º) abstraction steps may be shown as follows:



$$CH_3\text{ - }\overset{\displaystyle CH_3}{CH}\text{ - }CH_3 + Cl^{\cdot} \longrightarrow CH_3\text{ - }\overset{\displaystyle CH_3}{CH}\text{ - }\overset{\delta^{\cdot}}{CH_2}\text{ - - - }H\text{ - - - }\overset{\delta^{\cdot}}{Cl}$$

Reactant like structure

$$\dot{Cl} + CH_3\text{ - }\overset{\displaystyle CH_3}{CH}\text{ - }CH_2Cl \xleftarrow{Cl_2} CH_3\text{ - }\overset{\displaystyle CH_3}{CH}\text{ - }\dot{C}H_2 + HCl$$



The transition state in both cases resembles the reactants. Since the reactants in both the cases are the same and the same type of C-H bonds are broken (primary or tertiary), it has a relatively small influence on the relative rates of the reactions. The two reactions proceed with similar (but not identical) rates because their respective activation energies are similar**(Figure3.5)**.

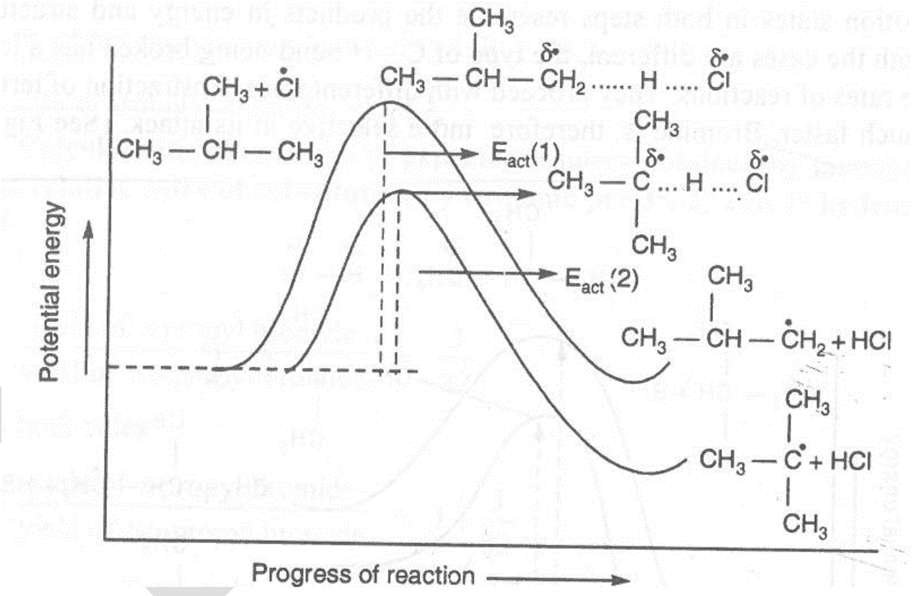
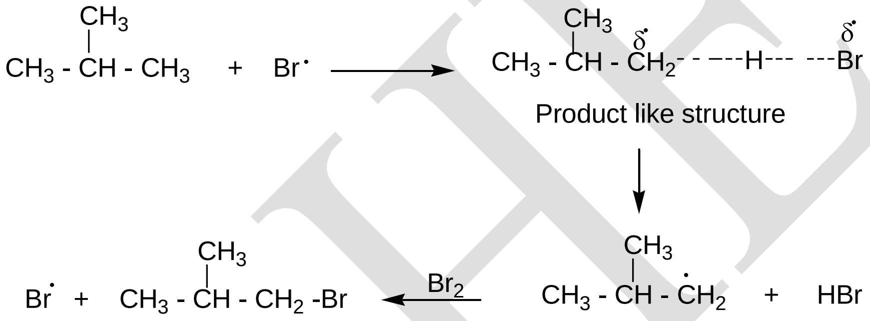


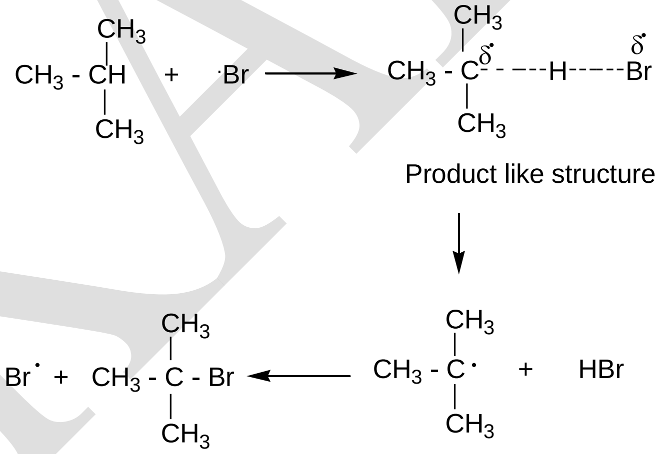
Figure 3.5. Activation energies in exothermic reactions.

In the above diagram it is a clear that E_{act} are similar, but because tertiary C-H bond is broken more easily than primary C-H bond, the reaction (2) has low E_{act} and proceeds comparatively at faster rate.

On the other hand, the abstraction of hydrogen by the less reactive bromine atom is endothermic and has a very high E_{act}. The transition state resembles the products more than it does the reactants. In other words, the transition state is reached late and the carbon-hydrogen bond is broken to a considerable extent. Atoms and electrons are distributed almost in the same way as in the products; the carbon is almost trigonal. The alkyl radical has developed considerable free radical character.

The transition states may be shown in the following ways:





The transition states in both steps resemble the products in energy and structure. Since the products in both the cases are different, the type of C-H bond being broken has a lot of influence on the relative rates of reactions. They proceed with different rates. Abstraction of tertiary hydrogen takes place much faster. Bromine is, therefore, more selective in its attack**(Figure 3.6).**

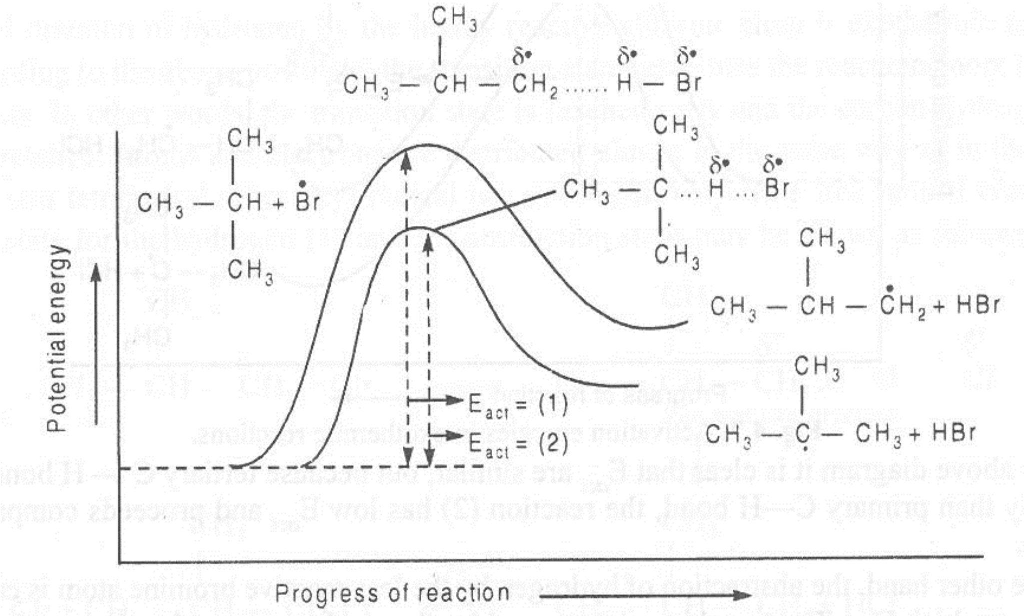
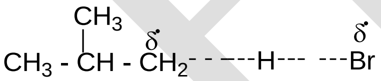


Figure 3.6. Activation energies in endothermic reactions.



$$CH_3-\overset{\overset{CH_3}{|}}{C}H-\overset{\delta\bullet}{C}H_2\text{-----}H\text{---}\ \text{---}\overset{\delta\bullet}{Br}$$

It is clear from the diagram that transition state for reaction (1) resembles a less stable primary radical while the transition state for reaction (2) resembles a more stable radical. The E_{act} for reaction (2) is much lower than that for reaction (1). The product contains mostly tert-butyl bromide.

CONFORMATIONAL ISOMERISM

Carbon–carbon single bond in alkanes is a sigma bond formed by the overlapping of sp^3 hybrid atomic orbitals along the inter-nuclear axis. The electron distribution in such a bond is symmetrical around internuclear axis; so that free rotation of one carbon against the other is possible without breaking sigma or single covalent bond. Consequently such compound can have different arrangements of atoms in space, which can be converted into one another simply by rotation around single bond, without breaking it. These different arrangements are known as *Conformational isomers of rotational isomers or Conformers.* Since the potential energy barrier for their inter-conversion is very low, it is not possible to isolate them at room temperature. At least 60-85kJ/mole must be the energy difference between two conformers to make them isolatable at room temperature.

Hence, conformations can be defined as different arrangements of the atoms which can be converted into one another by rotation around single bonds.

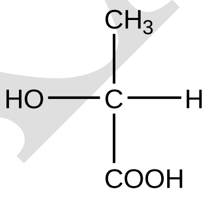
Difference between conformation and configuration

Conformation

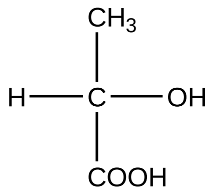
Structures contains different arrangement of atoms of a molecule in space which can arise by rotation about a single bond are called *conformers*. For example ethane exists in different conformations called staggered, eclipsed and skew conformations. The energy difference between different conformers is rather small. This phenomenon is called conformation. The property of conformation is also exhibited by *n*-butane, cyclohexane, stilbene dichloride.

Configuration

Structure of a compound differencing in the arrangement of atoms or groups around a particular atom in space are called *Configurations*. Enantiomers, distereomers and geometrical isomers come under this category. For example *d*-and *l*-lactic acids are configurations of lactic acid.

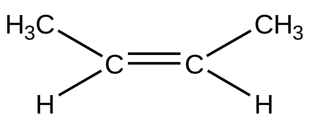


d-lactic acid

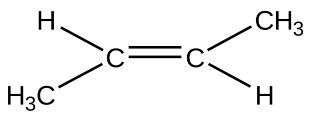


l-lactic acid

cis and trans butenes are configuration of butane.



cis-2-butene



trans-2-butene

Factors affecting relative stability of conformations

The following factors play a vital role in the stability of conformations.

1.Angle strain. Every atom has the tendency to have the bond angles that match those of its bonding orbitals. If there is any deviation from this normal bond angle, the molecule suffers from *angle strain*. Conformations suffering from angle strain are found to be less stable.

2.Torsional strain. There is a tendency on the part of two carbons linked to each other to have their bonds staggered. That is why the staggered form of any molecule likesethane,*n*-butane is most stable. As the bonds of two connected carbons move towards eclipsed state, a *torsional strain* is set up in the molecule thus raising its energy. Thus the staggered conformations have the least and eclipsed the highest torsional strain. The energy required to rotate the molecule around the carbon-carbon bond is called *torsional energy*.

3.Steric strain (van der Waals' strain). Groups attached to two linked carbons can interact in different ways depending upon their size and polarity. These interactions can be attractive or repulsive. If the distance between the groups or atoms is just equal to the sum of their van der Waals' radii, there will be attractive interactions between them. And if these atom or groups are brought closer than this distance, there will be repulsions leading to *van der Waals'strain or steric strain* in the molecule.

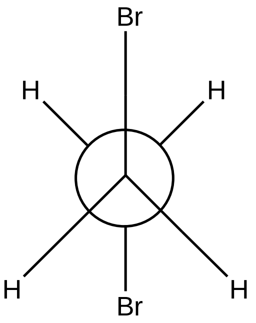
4. Dipole-dipole interactions. Atoms or groups attached to bonded carbons orient or position themselves to have favourable dipole-dipole interactions. It will be their tendency to have maximum dipole-dipole attractions. Hydrogen bond is a particular case of powerful dipole-dipole attractions.

The stability of a conformer is determined by the net effect of all the above factors.

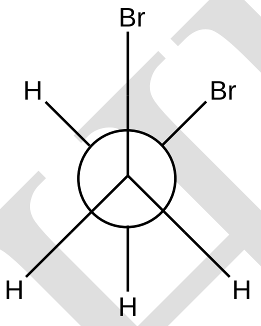
Conformations and change in dipole-moment of 1, 2-dibromomethane with temperature

The conformations of 1, 2 dibromoethane have been extensively studied by dipole-moment measurement. The conformations are depicted as under.

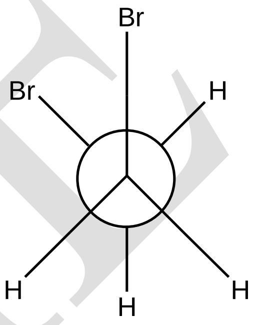
In the liquid state, the percentage of anti forms is 65 corresponding to conformational free energy of 3.5 kJ mol^{-1} in favour of *anti*.



anti



gauche

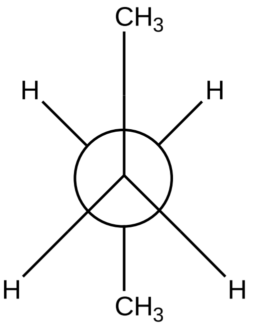


gauche

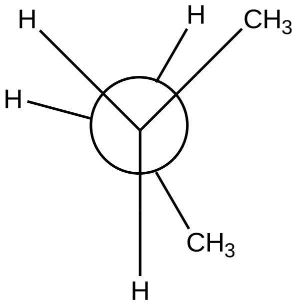
Stability of *anti*-form is due to combined effects of steric factor and dipole-dipole interactions. It goes in favour of formations of *anti* conformer. Dipole movement increases with increase of temperature.

Conformations of butane

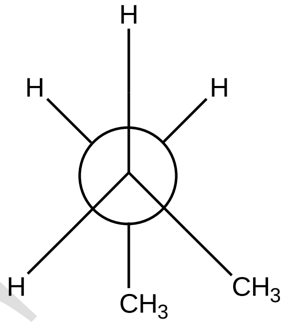
n-butane is an alkane with four carbon atoms, which can be considered to e derived from ethane by replacing one hydrogen on each carbon with a methyl group. If we consider the rotation about the central carbon-carbon bond (C_2-C_2), the situation is somewhat similar to ethane, but *n*-butane has more than one staggered and eclipsed conformations (unlike ethane which has only one staggered and one eclipsed conformation). Newman Projection formulae for various staggered and eclipsed conformations of *n*-butane are as given below.



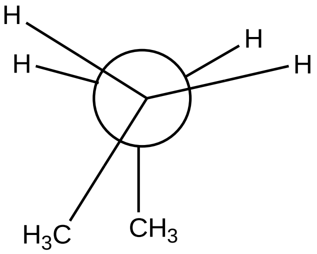
Completely staggered
or anti form
I



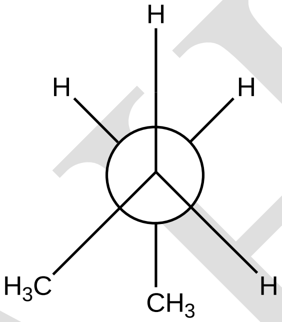
Partially eclipsed
form
II



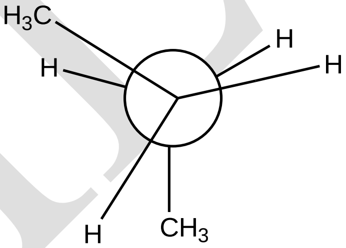
Partially eclipsed or gauche
form or skew form
III



Completely
eclipsed form
IV



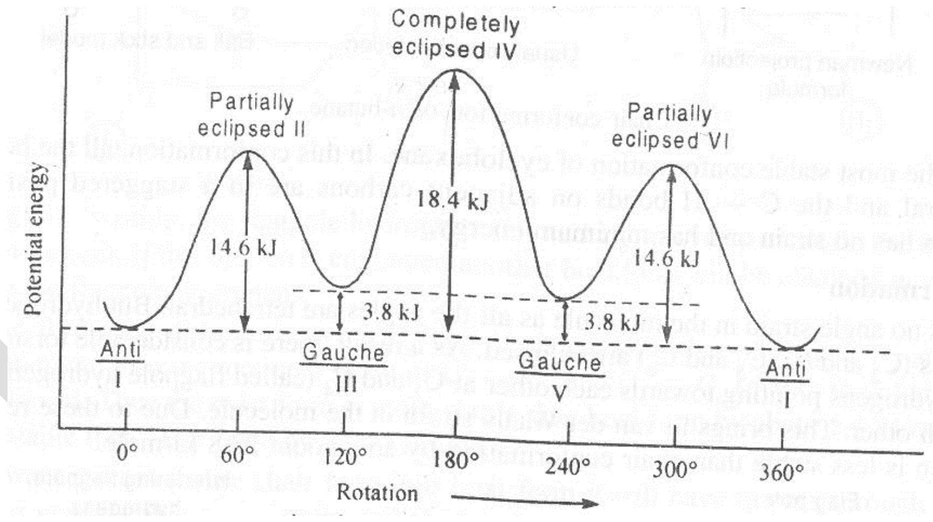
Partially staggered
or gauche
V



Partially
eclipsed form
VI

The *completely staggered* conformation, (I) also known as *anti* form, is having the methyl groups as far apart as possible. Let us see how these forms have been obtained. Let us start from structure I. Holding the back carbon (represented by circle) fixed along with its groups. H, -H and -CH_3 rotate the front carbon (shown by a dot) in clockwise direction by an angle of 60°. Groups attached to it will also move. *Partially eclipsed* form (II) is obtained. In this conformation (II), methyl group of one carbon is at the back of hydrogen of the other carbon. Further rotation of 60° leads of a *partially staggered* conformation (III), also known as *gauche* form, in which the two methyl groups are at an angle of 60°. Rotation by another 60° gives rise to a *fully eclipsed* form (IV) having two methyl groups at the back of each other. Further rotation of 60°, again leads to *partially staggered or gauche* form (V) having methyl groups at an angle of 60° (as in III) Still further rotation of 60° leads to *partially eclipsed* form (VI), having methyl group of one carbon at the back of hydrogen of the other (as in II). If a further rotation of 60° is operated (completing the rotation of 360°), again form I is obtained. Of course, there will be an infinite number of other conformations in between these six conformations (I to VI). (*Gauche* form is also known as skew form).

Out of these six conformations, the *completely staggered or anti conformation* (I) is most stable and *partially staggered* or *gauche* conformation (III or V) is slightly less stable: the energy difference being only 3.8 kJ/mole. On the other hand the completely eclipsed conformation (IV) is least stable and partially eclipsed conformation (II or VI) is slightly more stable, again the energy difference being 3.8 kJ/mole(This is due to presence of steric strain between two methyl groups). The energy difference between most stable conformation (I) and least stable conformation (IV) is about 18.4 kJ/mole while that between I and II (or VI) is about 14.6 kJ/mole..

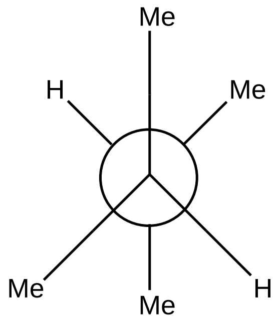


Rotational or torsional energy of n-butane.

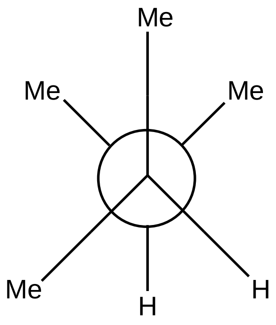
Thus at ordinary temperature, *n*-butane molecule exists predominantly in *anti* form with some *gauche* forms.

Conformational enantiomers of 2, 3-Dimethylbutane and 2,2,3-Trimethylbutane

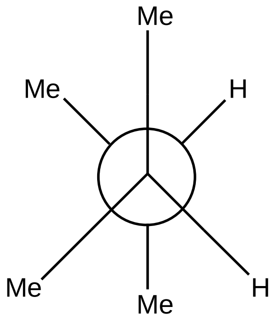
Conformational isomers of 2,3-Dimethylbutane



I



II

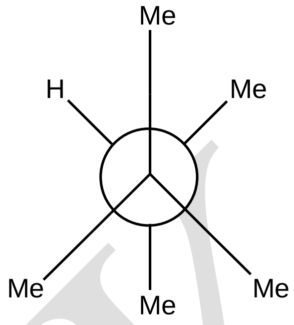


III

Structure I is supposed to have maximum stability of these three isomers, II and III are conformational enantiomers (mirror-images) also. This can e visualized after rotation of III as a whole.

Conformational isomers of 2, 2, 3-Trimethylbutane

All these structures have the same stability and the compound may be assumed to occur in one conformation only.



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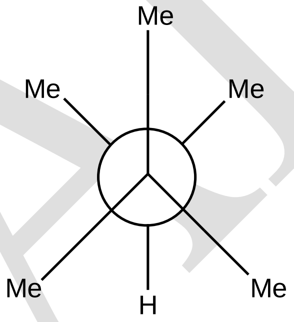
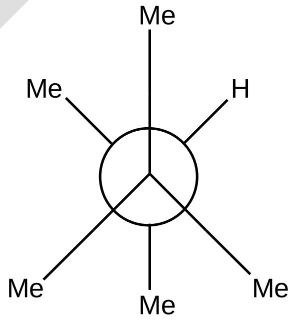


II



III

BAEYER STRAIN THEORY

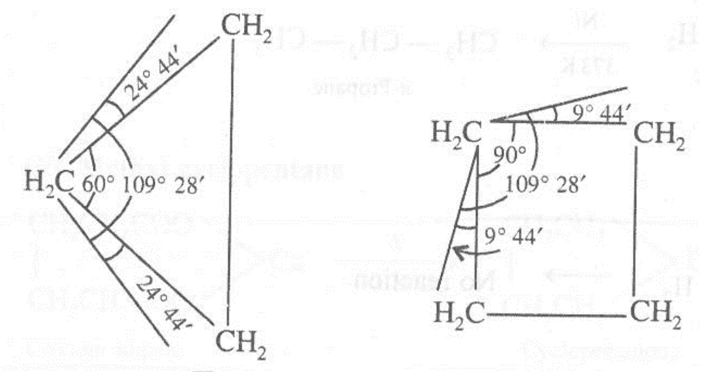
According to Le Bel and vant Hoff, the four valencies of a carbon atom are directed towards the corners of a regular tetrahedron and hence the angle between any two valencies (any two bonds) is 109°28'. Baeyer held that any departure from this position leads to a strain in the molecule resulting in the decrease of the stability of the molecule.

In the light of this concept Baeyer gave a theory which is known as Baeyer's Strain Theory. The main points of the theory are given below:

(*i*) *The carbon atoms constituting the rings lie in the same plane. Hence bond angles between the adjacent carbon atoms of the ring no longer remain 109°28'. Different rings have different values of this angle.* For example, the cyclopropane ring is a triangle having C-C-C angle of 60° only.

(*ii*) *Any deviation, positive or negative from the normal tetrahedral bond angle of 109°28'during the formation of a ring creates a strain in the molecule which makes the molecule unstable.*

(*iii*) *The larger* (*more*) *the deviation from the normal angle, the greater is the strain and thus lesser is the stability. However, it should e noted that the sign of deviation does not make any difference.*



Baeyer worked out the deviation from normal angle or what can be called *angle strain* involved in the formation of cycloalkanes of various ring sizes. For instance the C-C-C angle of a cyclopropane ring is 60° because each carbon atom occupies a corner of an equilateral triangle. This shows that the angle strain in cyclopropane would be ½ (109°28'-60°) = 24°44'. In the same way C-C-C angle in cyclobutane would be 90° because each carbon atom is situated at the corner of the square. The angle strain in cyclobutane is ½ (109°28'-90°) = 9°44'. The angle of strain for cycloalkanes calculated for various ring sizes are given in following table.

Table 3.1. Angle strains in various cycloalkanes

Compound	*C- C-C Angle*	*Angle strain*
Cyclopropane, C_3H_6	60°	½ (109°28'-60°) = + 24°44'
Cyclobutane, C_4H_8	90°	½ (109°28'-90°) = + 9° 44'
Cyclopentane, C_5H_{10}	108°	½ (109°28'-108°) = + 0°44'
Cyclohexane, C_6H_{12}	120°	½ (109°28'-120°) = - 5°16'
Cycloheptane, C_7H_{14}	128°35'	½ (109°28'-128°34°) = -9°33'
Cyclooctane, C_8H_{16}	134°	½ (109°28'-135°) = -14°46'

It is clear from the above data that angle strain decreases as we move from cyclopropane to cyclopentane. This predicts case of formation and stability of the compound from cyclopropane to cyclopentane. This is actually found to be so.

However the stability of cyclohexane and higher members cannot be explained by the angle strain values. According to angle strains, cyclohexane and higher members should be quite unstable as there is a lot of strain in the molecule. But this is not true. Actually cyclohexane and higher members are not planar molecules. Different carbon atoms in such molecules lie in different planes, thereby relieving the strain.

Example 2. Giving examples of first three cycloalkanes, explain the relationship of relative stabilities with the heat of combustion.

Solution:

Relationship of relative stability with heat of combustion

Size of the ring	*Heat of combustion per -CH_2 group kJ mol^{-1}*	*Size of ring*	*Heat of combustion per -CH_2 group kJ mol^{-1}*
3	697	6	658.5
4	686	7	662.3
5	664	8	663.6

Heat of combustion per CH_2 group of open chain alkanes = 658.0 kJ mol^{-1}.

Heat of combustion may be defined as the quantity of heat evolved when one mole of the compound is burnt in excess of air.

Heat of combustion per CH_2 group gives a fair idea of the relative stabilities of cycloalkanes. If the heat of combustion is large, the compound contains more energy and is therefore less stable.

With this principle, let us examine the stabilities of cyclopropane, cyclobutane and cyclopentane. Heat of combustion of cyclopropane is 697 kJ mol^{-1}. It is 39 kJ more than that of open chain alkane. Thus it is less stable than the open chain alkane by this amount.

In the case of cyclobutane, the heat of combustion is more by and amount 28kJ as compared to open-chain alkane. Thus cyclobutane is less stable than open chain alkanes but it is more stable than cyclopropane. Cyclopentane having heat of combustion 664kJ is more stable than cyclobutane. The relative stability of first three members of cycloalkanes in decreasing order is given as under.

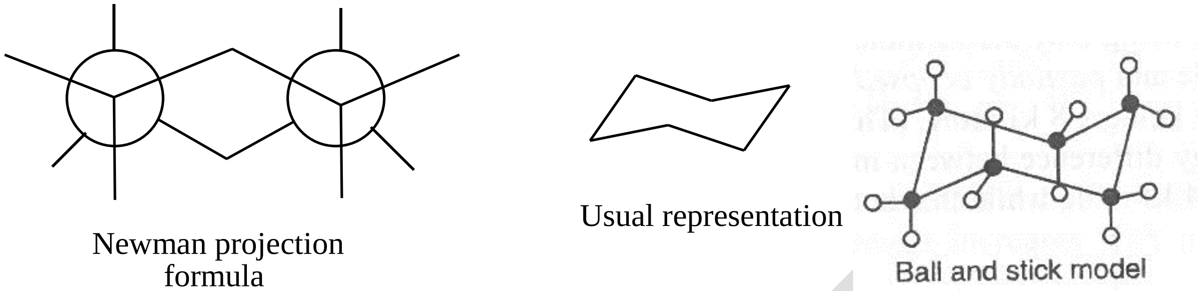
Cyclopentane>Cyclobutane>Cyclopropane

On having a look at the heat of combustion of cyclohexane and higher members, we observe that the values do not differ much. Thus higher members are expected to display almost uniform stability which is confirmed by their reactions.

Conformations of cyclohexane

Chair conformation

Chair conformation of cyclohexane is represented below:


Newman projection formula

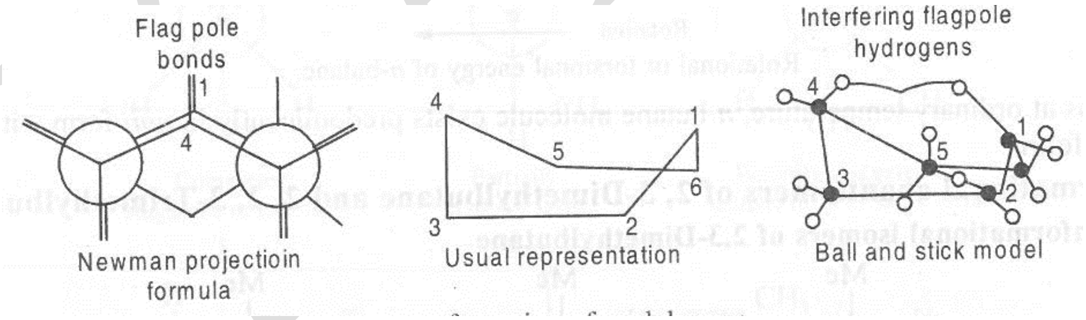
Usual representation

Chair conformation of cyclohexane

This is the most stable conformation of cyclohexane. In this conformation, all the bond angles are tetrahedral and the C-H bonds on adjacent carbons are in a staggered position. This conformation has no strain and has minimum energy.

Boat conformation

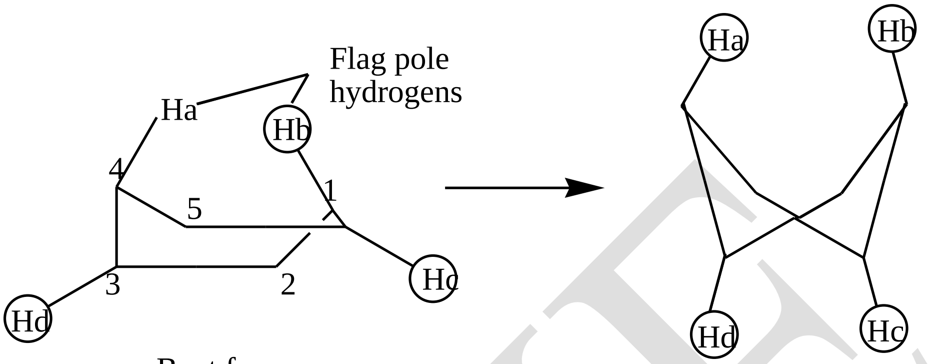
There is no angle strain in the molecule as all the angles are tetrahedral. But hydrogens on four carbon atoms (C_2 and $C_{3,}$ C_5 and C_6) are eclipsed. As a result, there is considerable torsional strain. Also, two hydrogens pointing towards each other at C_1 and C_4 (called flagpole hydrogens) are very close to each other. This brings in van der Waals strain in the molecule. Due to these reasons boat conformation is less stable than chair conformation by an amount 28.8 kJ/mole.



Boat conformation of cyclohexane

Twist conformation of cyclohexane. Sequence of changes in going from chair form to boat form.

Besides chair and boat conformation, cyclohexane can have several other possible conformations. Consider model of boat conformation of cyclohexane. Hold C_2-C_3 bond in one hand and C_5- C_6 in the other and twist the model so that C_2 and C_5 come upwards and C_3 and C_6 go downwards. We will get another conformation known as *twist form* or *skew boat* form.



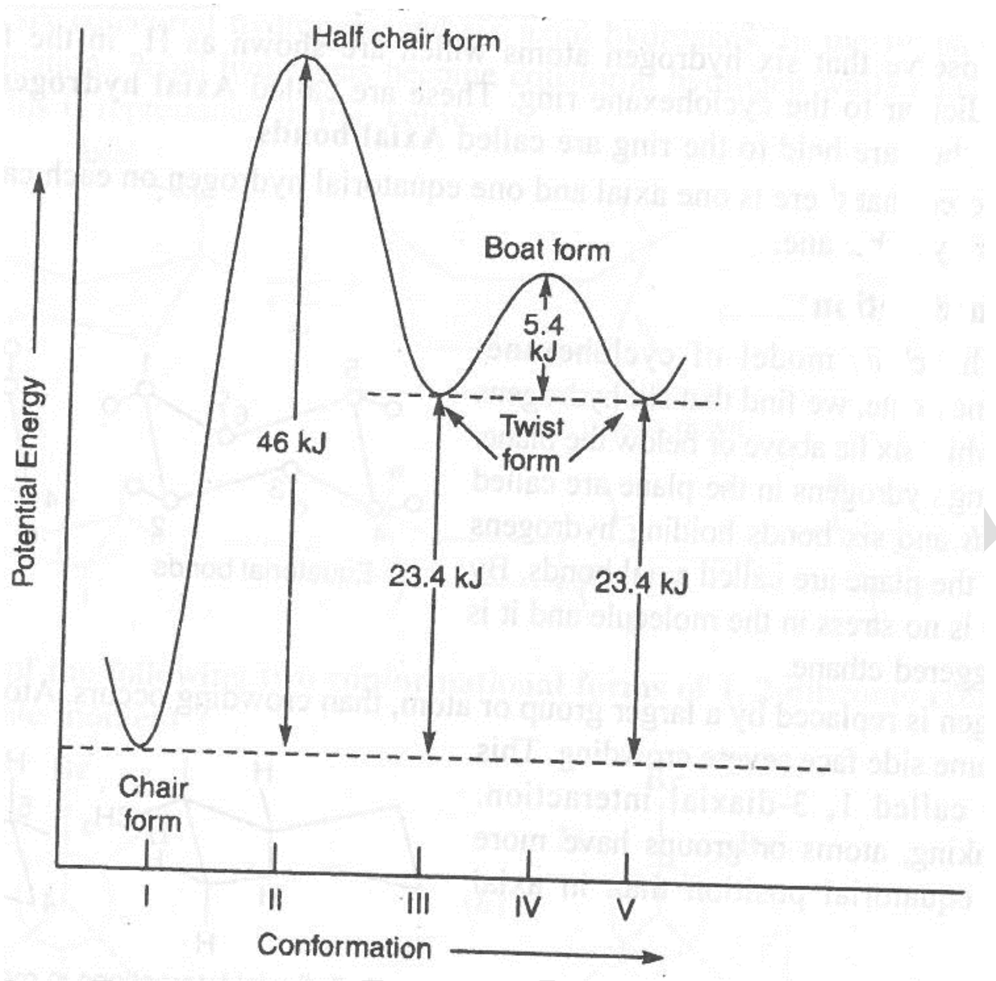
Boat form

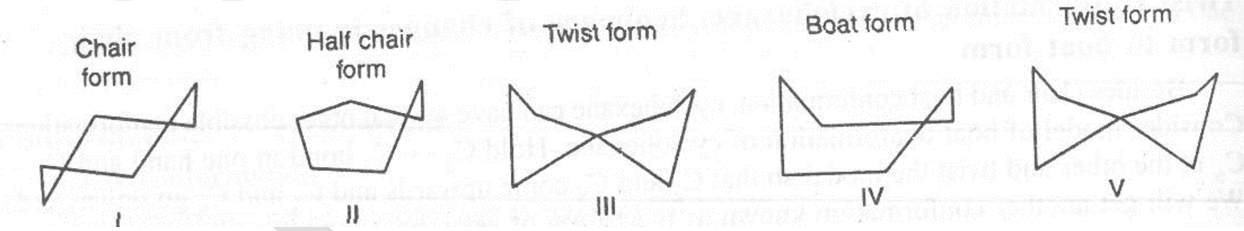
Twist form

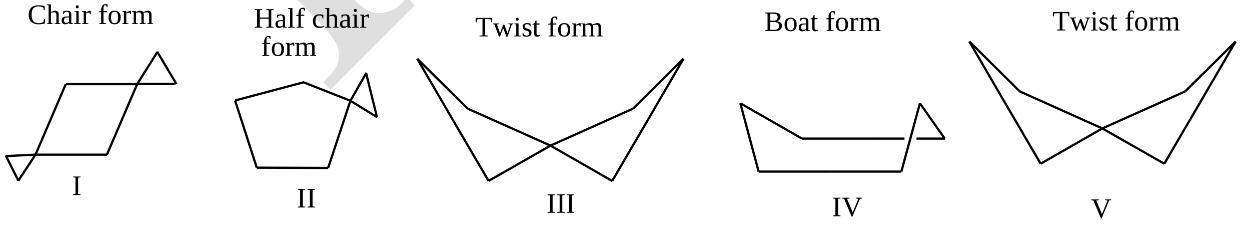
During this twisting, the flagpole hydrogens (H_a and H_b) move apart while the hydrogensH_c and $H_d$move closer. If this motion is continued another boat from will be obtained in which H_c and H_d become the flagpole hydrogens.

In twist forms the distance between H_a and H_b is equal to that of H_c and H_d and the steric strain is minimum; also the torsional strain of C_2-C_3 and C_2-C_6(due to their being eclipsed) is partly relieved. Thus the twist form is more stable than boat form by about 5.4 kJ/mole, but it is much less stable than chair form by 23.4 kJ/mole.

If we want to convert the chair form into boat form it will have to pass through a half chair form having considerable angle strain and torsional strain. The energy difference between chair form and half chair form being about 11kcal/mole, half chair form is quite unstable.







Equatorial and axial bonds in cyclohexane

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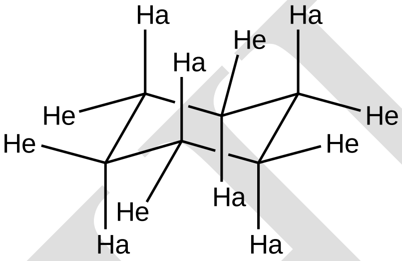
Consider the structure of chair form of cyclohexane as given below:

Although, the cyclohexane ring is not planar completely, but for approximation, we can take it a planar. Consider the position of various hydrogensin the chair conformation. There are two distinct kinds of hydrogens, six of the hydrogenswhich are marked H_e are almost oriented within the plane of cyclohexane ring. These are called **Equatorial hydrogen atoms.** The bonds by which these are held to the ring are called **Equatorial bonds.**



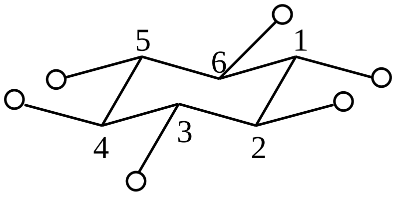
Equatorial and axial bonds in cyclohexane.

We again observe that six hydrogen atoms which are shown as $H_a$in the figure above are oriented perpendicular to the cyclohexane ring. These are called **Axial hydrogen atoms** and the bonds by which they are held to the ring are called **Axial bonds.**

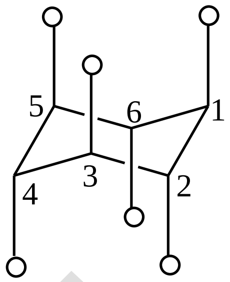
It may be noted that there is one axial and one equatorial hydrogen on each carbon in the chair conformation of cyclohexane.

1,3-diaxial interaction

Consider the chair model of cyclohexane. Looking at the molecule, we find that six hydrogens lie in the plane while six lie above or below the plane. Six bonds holding hydrogens in the plane are called *equatorial bonds* and six bonds holding hydrogens above or below the plane are called axial bonds. By and large, there is no stress in the molecule and it is stable as staggered ethane.



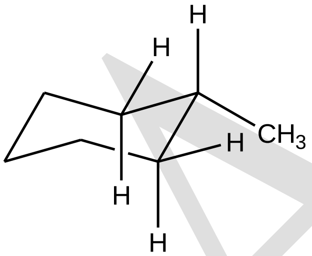
Equatorial bonds

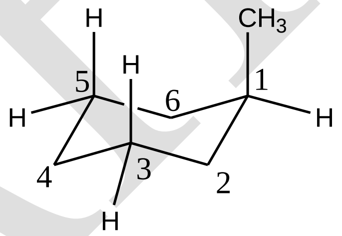


Axial bonds

If a hydrogen is replaced by a larger group or atom, than crowding occurs. Atoms linked by axial bonds on the same side face severe crowding. This interaction is called 1, 3-diaxial interaction. Generally speaking, atoms or groups have more free space in equatorial position than in axial position.

There are two possible chair conformations of methyl cyclohexane, one with -CH_3 in equatorial position and the other with -CH_3 in axial position.



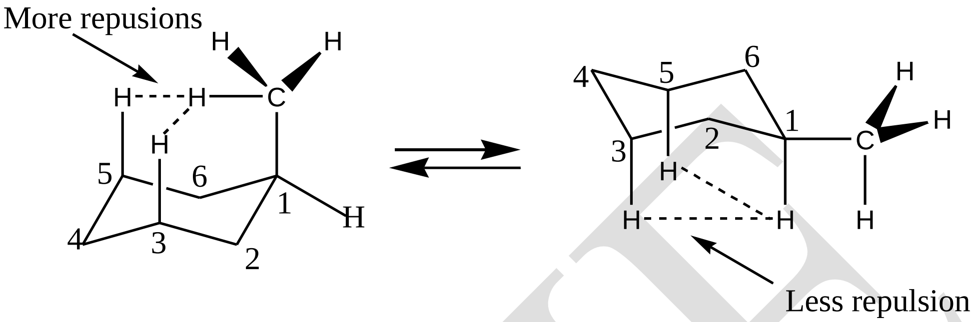


It is observed that -CH_3 equatorial position faces less crowding by hydrogens compared to -CH_3 in the axial position. Methyl group in the axial position is approached more closely by axial hydrogens on C-3 and C-5. This is called *1, 3-diaxial interaction.*

Conformations of substituted cyclohexanes

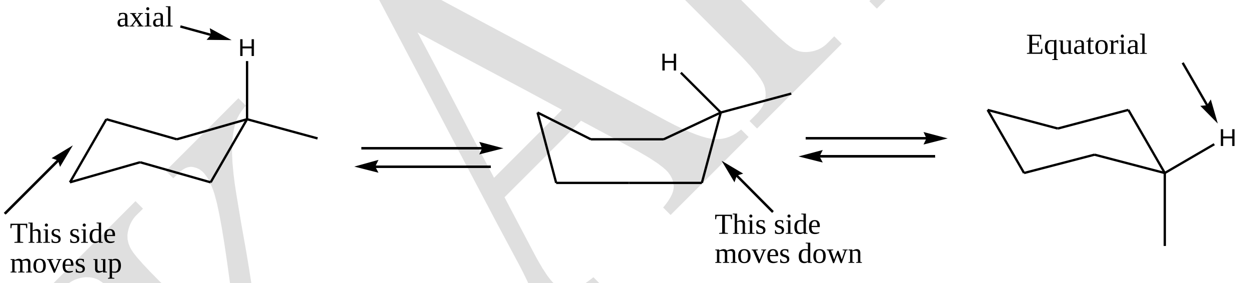
A methyl group is bulkier than a hydrogen atom. When the methyl group in methyl cyclohexane is in the axial position, they methyl group and the axial hydrogens of the ring repel each other. These interactions are called **Axial-Axial Interactions.** When the methyl group is in the equatorial position, the repulsions are minimum. Thus, the energy of the conformation with equatorial methyl group is lower. At room temperature, about 95% methylcyclohexane molecules are in the conformations in which the methyl group is equatorial.

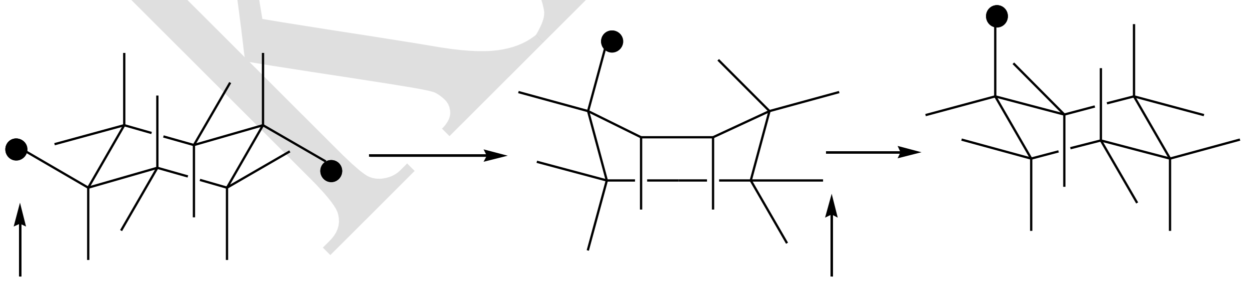
The bulkier the group, the greater is the energy difference between equatorial and axial conformations. In other words, a cyclohexane ring with a bulky substituent (e.g., *t*-Butyl group) is more likely to have that group in the equatorial position.



Conversion of Axial Bonds to Equatorial Bonds and Vice Versa

Each of the six carbon atoms of cyclohexane has one equatorial one axial hydrogen atom. Thus, there are six equatorial hydrogens and six axial hydrogens. In the flipping and reflipping between conformations, axial hydrogens become equatorial hydrogen while equatorial hydrogens become axial. This is represented in Fig. below:-





Text books:

1. Madan, R.L. (2015). *Chemistry for Degree Students.*New Delhi: S. Chand and Company Pvt, Ltd.
2. Morrison, R. N. & Boyd, R. N. (1992). *Organic Chemistry*. New Delhi: Dorling Kindersley Pvt. Ltd. (Pearson Education).

POSSIBLE QUESTIONS

PART A(20 multiple choice questions)

Online Examinations

PART B(2 marks questions)

1. What is Corey-House synthesis?
2. What is Sabatier-Senderen's reaction?
3. What is cracking? Give one example.
4. What do you understand by the term conformation?
5. What are two main conformations of cyclohexane? How will you represent them?

PART C(6 marks questions)

1. Give the main features of Baeyer's strain theory? Why does this theory fail to account for the stability of cyclohexane?
2. (i) Corey-House reaction is better method for preparing alkanes than Wurtz reaction. Explain why?
   (ii) Write the mechanism of reduction of alkyl halide to alkane by zinc and acetic acid.
3. Write notes on: (i) Wurtz reaction (ii) Wurtz-Fittig reaction.
4. What do you understand by the following: (i) Chair conformation (ii) Boat conformation (iii) Twist boat conformation?
5. Write short notes on: (i) Pyrolysis of alkanes (ii) Aromatisation of alkanes (iii) Controlled oxidation of alkanes.
6. (i) Why is chair conformation of cyclohexane more stable than the boat conformation?
   (ii) Explain the difference between the terms conformation and configuration by taking suitable examples.
7. Give the mechanism of halogenation of methane and give three evidences in support of mechanism.
8. Discuss the brief the factors which influence the relative stabilities of the conformations.

9. (i) “The boiling points of isomeric alkanes decreases with the increases in the branching of the chain” Explain.

   (ii) Give two methods for the preparation of alkanes.

10. (i) Draw the structure of the chair form of cyclohexane depicting the axial and equatorial bonds.

    (ii) Give a brief account of 1,3-diaxial interactions.

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Class: I B.Sc Chemistry Course Name:Organic Chemistry-I (Basics and Hydrocarbon)
Course Code: 19CHU103 Unit: III Batch-2019-2022

S.No	Questions	opt1	opt2	opt3	opt4	Answer
1.	Halogenation of methane in the presence of sunlight follows	ionic mechanism	free radical mechanism	cationic mechanism	anionic mechanism	free radical mechanism
2.	Methane reacts with chlorine in presence of sunlight to form methyl chloride. This reaction is governed by	electrophilic substitution	nucleophilic substitution	free radical substitution	addition reaction	free radical substitution
3.	n-Butane has several conformations given below. Which one out of these is most stable?	eclipsed	gauche	fully eclipsed	anti form	anti form
4.	Which one form of cyclohexane is most stable?	chair	half chair	boat	twist boat	chair
5.	In cyclopropane angel strain is minimized by the formation of banana bond by raising internal angle to 140˚ . This concept is known as	Sachse-Mohr theory	Baeyer strain theory	Coulson-Moffits concept	Huckel theory	Coulson-Moffits concept
6.	The most stable and preferred conformation of cyclopentene is	planar conformation	chair conformation	envelope conformation	boat conformation	envelope conformation
7.	Hydrogenation of alkene with H_2 in the presence of nickel at 200ºC is known as	Wurtz reaction	Sabatier-senderen's reaction	Corey House synthesis	Kolbe's reaction	Sabatier-senderen's reaction
8.	What are the products if methyl bromide and ethyl bromide react with sodium in dry ether	ethane	ethane and propane	butane	propane, ethane and butane	propane, ethane and butane
9.	Corey- House synthesis of alkane is governed by	electrophilic substitution	free radical substitution	nucleophilic substitution	ionic substitution	nucleophilic substitution
10.	Kolbe's electrolysis for the synthesis of alkane involve	ionic mechanism	free radical mechanism	both free radical and ionic mechanism	elimination mechanism	both free radical and ionic mechanism
11.	The boiling point of isopentane is	lower than n-pentane	higher than n-pentane	equal to n-pentane	higher than neopentane	lower than n-pentane
12.	The correct order of ease of abstraction of	pri. H > sec.	tert. H > sec.	sec. H >pri. H	tert. H >pri. H >sec.	tert. H > sec. H

	different classes of hydrogen in halogenations is	H >tert. H	H >pri. H	>tert. H	H	>pri. H
13.	Nitration of alkane is governed by	electrophilic substitution	nucleophilic substitution	free radical substitution	ionic substitution	free radical substitution
14.	The decreasing order of halogenations of alkane will be	fluorination > chlorination >bromination	chlorination >bromination> fluorination	bromination> chlorination > fluorination	bromination> fluorination > chlorination	fluorination > chlorination >bromination
15.	Select the correct decreasing order of energy of activation in halogenations of alkanes	fluorination > chlorination >bromination	chlorination >bromination> fluorination	bromination> chlorination > fluorination	bromination> fluorination > chlorination	bromination> chlorination > fluorination
16.	Hexane when heated at 500°C gives lower alkanes and alkenes. This reaction is known as	isomerisation	aromatization	pyrolysis	catalytic reforming	pyrolysis
17.	If the decreasing order of E_{act} of hydrogen abstraction in the series methyl > prim. > sec . > tertiary, the rate of reaction will be	ter. > sec. > prim. > methyl	prim. >sec. >tert> methyl	tert. >prim. > sec. > methyl	sec. >prim .>tert. > methyl	ter. > sec. > prim. > methyl
18.	Hydrocarbons are	insoluble in water	compound of carbon and hydrogen	insoluble in water and compound of carbon and hydrogen	soluble in water	insoluble in water and compound of carbon and hydrogen
19.	A tertiary carbon is bonded directly to	2 hydrogens	3 carbons	2 carbons	4 carbons	3 carbons
20.	Alkanes are	water soluble	polar	relatively un-reactive compared with many other types of organic compounds	more acidic	relatively un-reactive compared with many other types of organic compounds
21.	Hydrocarbons are	composed of carbon and hydrogen	composed of carbon ,hydrogen ,and oxygen	composed of carbon and oxygen	composed of carbon and nitrogen	composed of carbon and hydrogen

22.	Which of the following statement is false about propane?	all bond angles are 109.5°	each carbon is sp^{3}hybridised	the compound is combustible	the compound undergoes polymerization to give polypropylene	the compound undergoes polymerization to give polypropylene
23.	Generally, as the amount of branching among alkane isomers increases, the	boiling point increases	boiling point decreases	number of tertiary and quaternary carbon decreases	number of primary carbons decreases	boiling point decreases
24.	What type of an alkyl group is isobutyl group?	primary	secondary	tertiary	Quaternary	primary
25.	How many monochlorinated isomers would result from the reaction of chlorine with n-butane in the presence of UV light?	2	4	6	8	2
26.	A compound of formula C_3H_8 does not react with bromine in Cl_4 in the dark. The compound could be	alkane	cycloalkane	alkene	Cycloalkane	alkane
27.	Which halogen does not react appreciably with methane in a free–radical substitution reaction ?	chlorine	bromine	iodine	Fluorine	iodine
28.	Which compound could be most cleanly made by free-radical chlorination of an alkane?	1-chloropentane	1-chloro-3-methylbutane	1-chloro-2-methylbutane	1-chloro-2,2-dimethylpropane	1-chloro-2,2-dimethylpropane
29.	Which of the cycloalkanes is not expected to have ring strain?	Cyclopropane	cyclobutane	cycloheptane	Cyclopentane	cycloheptane
30.	Most stable conformation of cyclohexane is the	Haworth form	boat form	Newmann form	chair form	chair form

31.	The chlorination of methane may yield chloromethane, dichloromethane, trichloromethane and tetrachloromethane. What measure ensures that chloromethane is the principal product analysis?	use excess chlorine	use high pressure	use low temperature and low pressure	use excess methane	use excess methane
32.	What percentage of cyclohexane molecule is estimated to be in the boat form at any given time?	over 99%	between 90% and 99%	approximately 50%	less than 1%	less than 1%
33.	Which of the following cycloalkanes is most reactive?	cyclopropane	cyclohexane	cyclobutane	Cycloheptane	cyclopropane
34.	Which of the following statements is wrong about cyclohexane?	It is a saturated cyclic hydrocarbon	All C-C-C bond angle are 109° 28´	It is very unstable and strained compound	It can exist in two conformations designated as boat and chair forms	It is very unstable and strained compound
35.	Which occurs when methane is combined with fluorine in the presence of light?	explosive exothermic reaction	slow endothermic reaction	fast exothermic reaction	no reaction	explosive exothermic reaction
36.	Which sequence correctly describes the steps involved in a free radical chain reaction?	initiation, propagation, termination	propagation, initiation, termination	initiation, termination, propagation	propagation, termination, initiation	initiation, propagation, termination
37.	The most stable conformation of 1-methyl cyclohexane is	methyl group in axial position	methyl group in equatorial position	equilibrium condition	methyl group in axial and equatorial position	methyl group in equatorial position
38.	The compound which can exist in chiral form, amongst the following is	methyl cyclohexane	1-methyl cyclohexene	3- methyl pentane	3- methyl hexane	methyl cyclohexane
39.	Which pair of structures represents conformational isomers?	isopentane and neopentane	hexane and cyclohexane	eclipsed and staggered ethane	hexane and cyclohexane	eclipsed and staggered ethane
40.	When methyl group in the axial position in methyl cyclohexane the molecule has	one n-butane gauche interaction	no n-butane gauche interaction	two n-butane gauche interaction	three -butane gauche interaction	two n-butane gauche interaction
41.	In the boat conformation of cyclohexane, the most destabilizing interaction is	eclipsing	1,3-diaxial	1,3-diequatorial	flagpole-flagpole	flagpole-flagpole
42.	In sawhorse projection, a fully eclipsed form	60°	90°	180°	360°	180°

	can be transformed to anti-staggered form by a rotation of					
43.	The Newmann projections of chair form of cyclohexane reveal that those are	six butane gauche interaction	no butane gauche interaction	four butane gauche interaction	eight butane gauche interaction	six butane gauche interaction
44.	Which statement is false?	many alkanes are soluble in water	all alkanes have a lower density than water	at room temperature some alkanes are liquids, some solids, some gases	all alkanes burn	many alkanes are soluble in water
45.	As the molecular weight of alkanes increases, how do the boiling point and melting point change?	boiling point increases; melting point decreases	boiling point decreases; melting point decreases	boiling point increases; melting point decreases	boiling point increases; melting point increases sequentially for alkanes over four carbons	boiling point increases; melting point increases sequentially for alkanes over four carbons
46.	How does the melting point of propane and ethane compare?	the melting point of propane is greater	the melting point of ethane is greater	the melting points are within 5°C of one another	no relationship exists among these alkenes and their melting points	the melting point of ethane is greater
47.	The branching of alkanes that produce symmetrical structures?	raises the boiling point; raises the melting point	raises the boiling point; lowers the melting point.	lowers the boiling point; lowers the melting point	lowers the boiling point; raises the melting point	raises the boiling point; raises the melting point
48.	Hoe do the boiling points of butane, propane, and ethane compare?	the boiling point of ethane is greatest	the boiling point of butane is greatest	the boiling point of propane is greatest	there is no relationship among these three alkanes and their boiling points	the boiling point of butane is greatest
49.	Which of the following alkanes will have the highest boiling point?	n-octane	isopentane	n-butane	Neopentane	n-octane
50.	Which of the following alkanes will have the lowest boiling point?	n-heptane	isopentane	n-hexane	Neopentane	neopentane

51.	Methane can be prepared by	the reaction of iodomethane with sodium in dry ether	the reaction of methanol with concentrated H_2SO_4	the reaction of sodium methanoate with soda-lime	the reaction of sodium ethanoate with soda-lime	the reaction of sodium ethanoate with soda-lime
52.	Which of the following reactions can be used to prepare alkanes?	Corey-House synthesis	Williamson synthesis	Friedel-Crafts reactions	Wittig reaction	Corey-House synthesis
53.	Kolbe's electrolysis of sodium butyrate ($CH_3CH_2CH_2COO^- Na^+$) gives	$C_8 H_{16}$	$C_6 H_{14}$	$C_8 H_{18}$	$C_6 H_{12}$	$C_6 H_{14}$
54.	Which of the following classes of compounds is unreactive toward sulphuric acid?	alkanes	alcohols	alkenes	Alkynes	alkanes
55.	Which of the following compounds does not dissolve in concentrated H_2SO_4 on warming?	n-hexane	diethyl ether	1-butene	aniline	n-hexane
56.	Why is the halogenation of alkanes considered a chain reaction?	it occurs quickly	it occurs without the generation of intermediates	each step generates the reactive intermediate that causes the next step to occur	the reaction allows long chain of halogenated alkanes to be formed	each step generates the reactive intermediate that causes the next step to occur
57.	The chlorination of methane to give CCl_4 is an example of	an electrophilic addition	a free-radical substitution	a nucleophilic addition	an electrophilic substitution	a free-radical substitution
58.	In the chlorination of alkanes, the first step in which chlorine free radicals are produced is called	initiation	activation	propagation	deactivation	initiation
59.	Chlorination of an alkane as compared to bromination proceeds	at a slower rate	at a faster rate	with equal rates	with equal or different rate depending upon the source of alkane	at a faster rate
60.	The thermal decomposition of alkanes in the absence of air is called	combustion	oxidation	cracking	Hydrogenation	cracking

UNIT-IV

Syllabus

Chemistry of Aliphatic Hydrocarbons

Carbon-Carbon pi bonds:
General methods of preparation, physical and chemical properties of alkenes and alkynes, Mechanism of E1, E2, E1cb reactions. Saytzeff and Hofmann eliminations. Electrophilic additions and their mechanisms (Markownikoff/ Anti Markownikoff addition), mechanism of oxymercuration-demercuration, hydroboration- oxidation, ozonolysis, reduction (catalytic and chemical), syn and anti-hydroxylation(oxidation). 1,2-and 1,4-addition reactions in conjugated dienes and Diels-Alder reaction; Allylic and benzylic bromination and mechanism, e.g. propene, 1-butene, toluene, ethyl benzene.
Reactions of alkynes: Acidity, Electrophilic and Nucleophilic additions. Hydration to form carbonyl compounds, Alkylation of terminal alkynes.

ALKENES

NOMENCLATURE OF ALKENES

Alkenes are unsaturated hydrocarbons having the general formula C_nH_{2n}. They contain two hydrogen atoms less than required to form alkenes with the same number of carbon atoms. This is made possible by introducing a double bond between two carbon atoms. This symbolises unsaturation in the compound. Examples of alkenes are ethylene and propylene.

Nomenclature

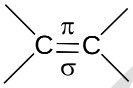
Nomenclature of alkenes is explained in the form of table below:

S. No.	Structure	Common name	IUPAC name
1.	$CH_2=CH_2$	Ethylene	Ethene
2.	$CH_3CH=CH_2$	Propylene	Propene
3.	$CH_3CH_2CH=CH_2$	β-Butylene	But-1-ene
4.	$CH_3CH=CHCH_3$	α-Butylene	But-2-ene
5.	$(CH_3)_2C=CH_2$	Isobutylene	2-Methylpropene

HINDERED ROTATION AROUND DOUBLE BOND

The lack of freedom of rotation of the bonded atoms around a carbon-carbon double bond is known as hindered rotation.

Explanation: A double bond is constituted of a σ bond and a π bond between two carbon atoms.



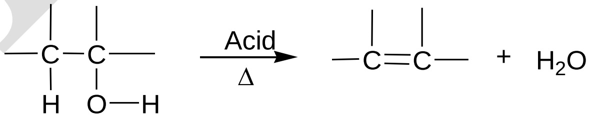
It is thus associated with greater bond dissociation energy compared to a single bond. Bond length is also shorter compared to a single bond. It is therefore much more difficult to break a double bond.

Rotation round a double bond would involve breaking the double bond which requires a large amount of energy. Hence rotation around the double bonds is difficult.

METHODS OF PREPARATION OF ALKENES

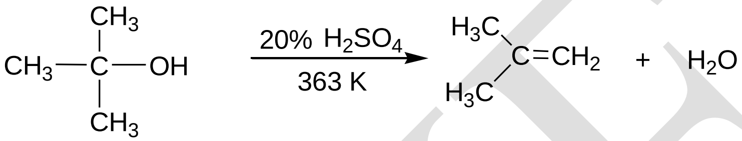
By Dehydration of Alcohols

An alcohol is converted into an alkene by dehydration. Dehydration is brought about by the use of an acid say conc. H_2SO_4 and application of heat. It involves heating the alcohol with conc. H_2SO_4 and application of heat. It involves heating the alcohol with H_2SO_4 or by passing the vapours of alcohol over alumina Al_2O_3 at 623-673 K.



1. $CH_3CH_2OH \xrightarrow[433\text{-}443\ K]{H_2SO_4} CH_2{=}CH_2 + H_2O$
Ethylene

2. $CH_3CH_2{-}CH_2{-}CH_2OH \xrightarrow[413K]{H_2SO_4} CH_3{-}CH{=}CH{-}CH_3$
Butan-1-ol — But-2-ene (Major product)

3.


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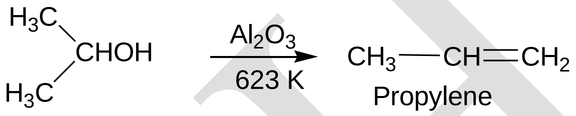
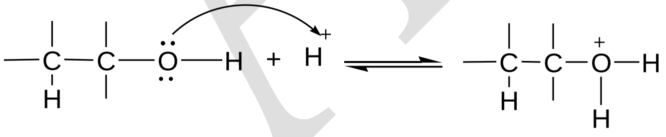
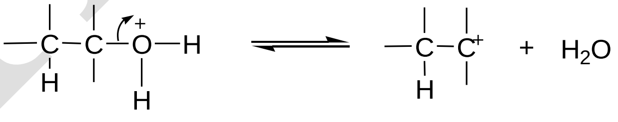


Mechanism of dehydration of alcohols. The mechanism of dehydration of alcohols is given schematically below:

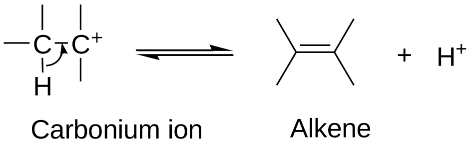
1. Attachment of proton to the alcoholic oxygen



2. Removal of water molecule



3. Removal of proton

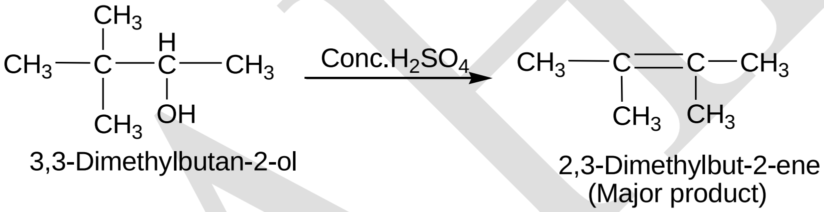


*For those alcohols that yield volatile olefins, the reaction can always be driven to completion by distillation off the olefin as it formed.

Alkyl shift and hydrogen shift

Sometimes it is found that the alkene obtained by dehydration of alcohols does not fit in the mechanism.

For example,



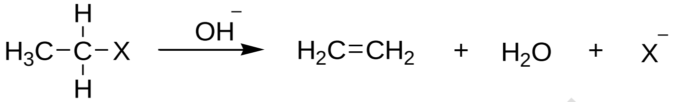
This can be explained by considering a rearrangement of carbonium ions. A carbonium ion can arrange to form a more stable carbonium ion.

Thus we see that the carbonium ion which is intermediate product in the dehydration of alcohol changes to a more stable carbonium ion by shifting of alkyl group from one position to another. If the alkyl group shifts to the neighbouring carbon atom, it is called **1,2 alkyl shift**.

Somethings a hydride ion shifts from the neighbouring carbon to the carbonium ion, there by producing a more stable carbonium ion. This is called **1,2 hydride shift**.

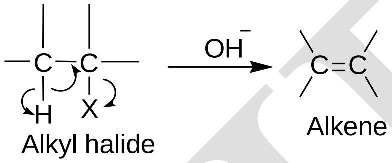
Preparation of alkenes by dehydrohalogenation of alkyl halides

Alkyl halides can form alkenes by the loss of molecule of hydrogen halide under the influence of a base catalyst (alcoholic potash). The reaction is known as dehydrohalogenation of alkyl halides. It involves the removal of the halogen atom together with the hydrogen atom from the adjacent carbon atom.



$$H_3C-CH_2-X \xrightarrow{OH^-} H_2C{=}CH_2 + H_2O + X^-$$

Mechanism of reaction (E_2 mechanism)



Orientation in dehydrohalogenation. In some cases, this reaction yields a single product (alkene) and in other cases yields a mixture of alkenes. For example, out of 1-chlorobutane and 2-chlorobutane the former yields only but-1-ene while the latter gives but-1-ene and but-2-ene. Thus the preferred product is the alkene that has the greater number of alkyl groups attached to the doubly bonded carbon atoms. In other words, the ease of formation of alkene has the following order:

$$R_2C = CR_2 > R_2C = CHR > R_2C = CH_2 > RCH = CHR > RCH = CH_2 > CH_2 = CH_2$$

This order is based on heat of hydrogenation values.

Hence in dehydrogenation, the more stable the alkene more easily it is formed.

In the dehydrohalogenation of alkyl halide to form alkene, the preferred product is the alkene which is more highly alkylated at the doubly bound carbon atoms. This is another statement of Staytzeff Rule.

Reactivity of alkyl halides in dehydrohalogenation. The decreasing order of reactivity of alkyl halides in this reaction is:

Tert–Alkyl halides > Sec–Alkyl halides > Primary Alkyl halides
(3^{o}) (2^{o}) (1^{o})

As we move from primary to secondary and from secondary to tertiary halides, the structure becomes more branched at carbon atom bearing the halogen .This increased branching has two results. (i) The number of hydrogen atoms available for attack by base is more and thus there is greater probability towards elimination, (ii) it leads to the formation of more highly branched (hence more stable) alkene hence more stable transmission state and low E_{act}.

As a result of these two factors, the decreasing order of reactivity of alkyl halides for dehydrohalogenation is:

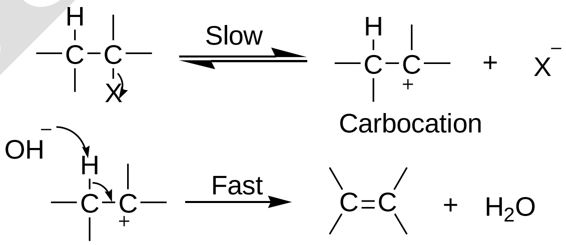
$3^{o} > 2^{o} > 1^{o}$

The mechanism discussed above is called E_2 type of mechanism of dehydrohalogenation.

Mechanism of Dehydrohalogenation (E_1 mechanism)

Some secondary and tertiary alkyl halides undergo halogenations in solution of low base concentration by a different mechanism called E_1 mechanism (E for elimination; 1 for unimolecular). *This mechanism operates through a two step process in which the rate determining step involves only one molecule.* It is believed that in the first step, which is a slow and rate determining step, the alkyl halides dissociates into halide ion and carbocation. In the second step which is a fast one, the carbocation loses a proton to the OH^- ion to form the alkene.

The complete mechanism is as shown below:



In certain alkyl halides (say 3°), there can be slight variation in the mechanistic approach as the carbon cation initially formed undergoes real arrangements to from the more stable carbocation and thus yields highly branched alkenes as the chief product of the reaction.

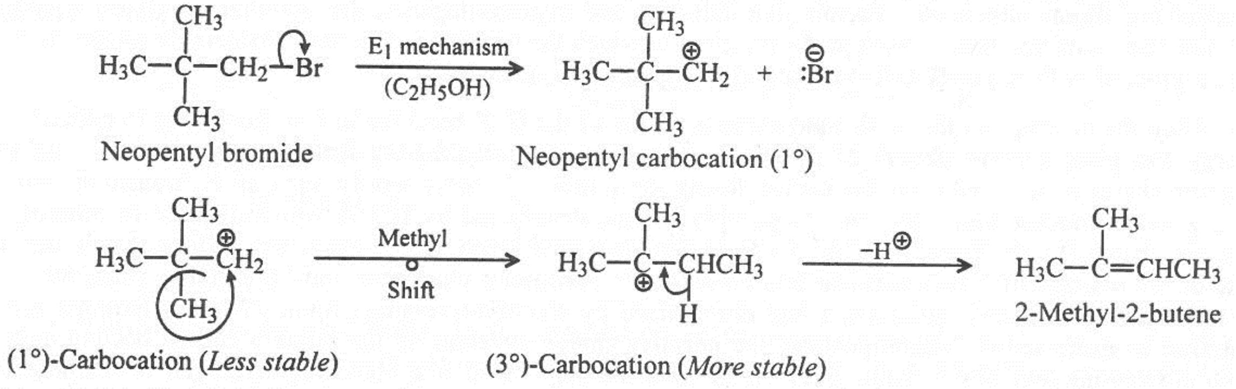
For a given alkyl group, the order of reactivity of different alkyl halides is RI > RBr > RCl > RF. For the same halogen atom, the order of reactivity is: Tertiary alkyl halide > Secondary alkyl halide > Primary alkyl halides. We thus observe that the order of reactivity of alkyl halides in both E_1 and E_2 types of reactions is the same. It is tertiary > secondary > primary.

Evidence in support of E_1 mechanism. It is supported by the following evidence:

1. Effect of structure on the reactivity of alkyl halides. The rate of an E_1 reaction should be, and actually is, influenced largely by electronic factors and not by steric factors. Electron release or withdrawal through electronic factors stabilize or destabilize the cationic intermediate in the usual way, and the following order of reactivity of alkyl halides is observed in E_1 reactions:

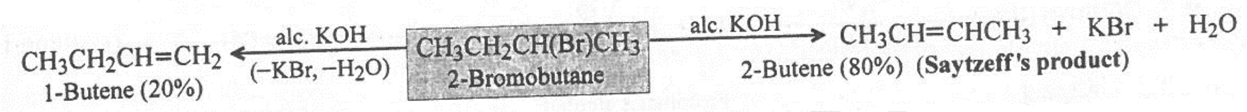
Allyl, Benzyl > Tertiary >secondary > Primary > Methyl halides

2. Rearrangements. E_1 reactions should be, and actually are, susceptible to rearrangements, wherever the cationic intermediate permits. For examples,



Saytzeff elimination

Dehydrohalogenation generally proceeds in such a way that the **more stable** (the highly substituted) alkene is the dominant product (**Saytzeff elimination**). For example,



$$\underset{\text{1-Butene (20\%)}}{CH_3CH_2CH=CH_2} \xleftarrow[(-KBr,\ -H_2O)]{\text{alc. KOH}} \boxed{\underset{\text{2-Bromobutane}}{CH_3CH_2CH(Br)CH_3}} \xrightarrow{\text{alc. KOH}} \underset{\text{2-Butene (80\%)}}{CH_3CH=CHCH_3} + KBr + H_2O$$

(Saytzeff's product)

While the Saytzeff rule will be discussed later, let us define here the rule, emphasize its limitations and also the way it differs from the rule governing **Hofmann elimination**. According to **Saytzeff rule**, “an elimination reaction usually gives the most stable alkene product (**Saytzeff product**), commonly the most highly substituted alkene”. However, Saytzeff rule does not apply always, especially with a bulky base (e.g., potassium tertiary butoxide) or bulky leaving group .An elimination reaction that gives the Saytzeff product is known as **Saytzeff elimination**. In contrast, **Hofmann elimination** leads to the **least** highly substituted alkene (**Hofmann product**).

Relative reactivities of alkyl halides. The **decreasing order** of reactivity of alkyl halide is:

tert-Alkyl halides > **sec**-Alkyl halides > **primary**–Alkyl halides

The branching around carbon carrying the halogen increases as we move along the series from primary to tertiary alkyl halides .The **greater** the **branching**, the **greater** is the number of **hydrogens** which would be **available for attack** by the **base**, hence, the more favourable probability factor for elimination. The more branched alkyl halide (say ,a tert-halide) leads to the formation of a more highly branched (hence ,more stable) alkene (Saytzeff product).

Among different halides, the decreasing order of reactivity due to halogen is:

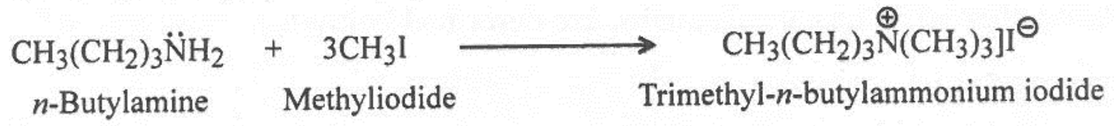
Iodide > Bromide > Chloride

Hofmann elimination

Alkenes are also produced in a number of important organic reactions such as **Hofmann elimination, Cope elimination, Wittig** reaction, pyrolysis of esters and xanthates, cracking of natural gas/ petroleum, etc.While we shall deal with all these reactions in detail at other places, we shall consider here briefly only Hofmann elimination .This reaction is specially important in being an important tool for ascertaining the structure of unknown bases containing nitrogen (say, alkaloids occurring in nature). Let us illustrate this important reaction by taking a simple base, n-butylamine.

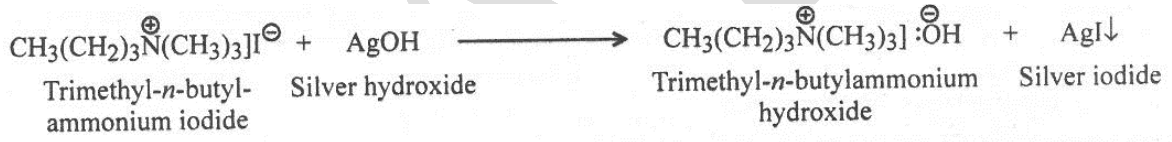
The **Hofmann elimination** (also known as **Hofmann's Exhaustive Methylation)** can be applied to this amine in the following steps:

(i) n-Butylamine is methylated exhaustively by the interaction with methyl iodide to get the quaternary ammonium salt trimethyl n-butylammonium iodide).



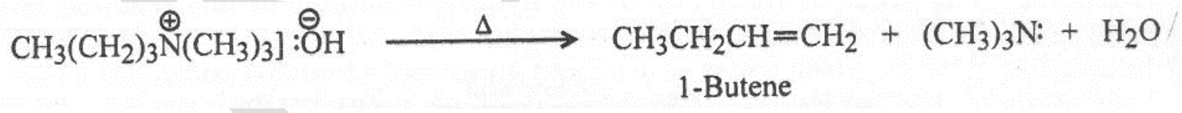
$$\underset{n\text{-Butylamine}}{CH_3(CH_2)_3\ddot{N}H_2} + \underset{\text{Methyliodide}}{3CH_3I} \longrightarrow \underset{\text{Trimethyl-}n\text{-butylammonium iodide}}{CH_3(CH_2)_3\overset{\oplus}{N}(CH_3)_3]I^{\ominus}}$$

(ii) The quaternary ammonium salt obtained is step (i) is treated with AgOH when AgI precipitates out and a halogen free solid quaternary ammonium hydroxide forms.



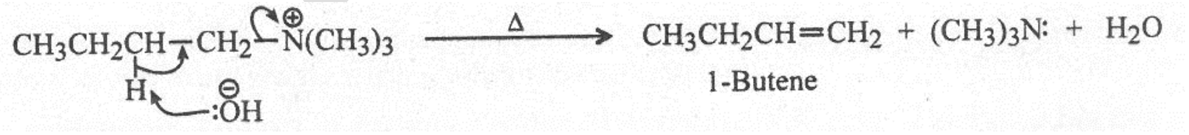
$$\underset{\text{Trimethyl-}n\text{-butyl-ammonium iodide}}{CH_3(CH_2)_3\overset{\oplus}{N}(CH_3)_3]I^{\ominus}} + \underset{\text{Silver hydroxide}}{AgOH} \longrightarrow \underset{\text{Trimethyl-}n\text{-butylammonium hydroxide}}{CH_3(CH_2)_3\overset{\oplus}{N}(CH_3)_3]\ :\overset{\ominus}{\ddot{O}}H} + \underset{\text{Silver iodide}}{AgI\downarrow}$$

(iii) The quaternary ammonium hydroxide obtained in step (ii) is heated strongly, it decomposes to form tertiary amine $(CH_3)_3$ N:, an alkene (1-butene) and water.



$$CH_3(CH_2)_3\overset{\oplus}{N}(CH_3)_3]\ :\overset{\ominus}{\ddot{O}}H \xrightarrow{\Delta} \underset{\text{1-Butene}}{CH_3CH_2CH{=}CH_2} + (CH_3)_3N: + H_2O$$

The step (iii) is a typical nucleophilic–β–elimination, as shown below:

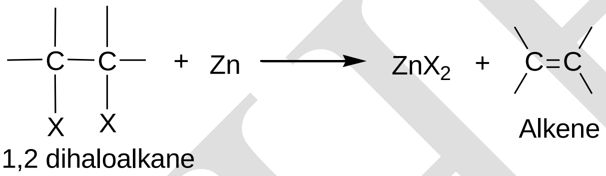


$$CH_3CH_2\underset{H}{CH}-CH_2-\overset{\oplus}{N}(CH_3)_3 \quad :\overset{\ominus}{\ddot{O}}H \xrightarrow{\Delta} \underset{\text{1-Butene}}{CH_3CH_2CH{=}CH_2} + (CH_3)_3N: + H_2O$$

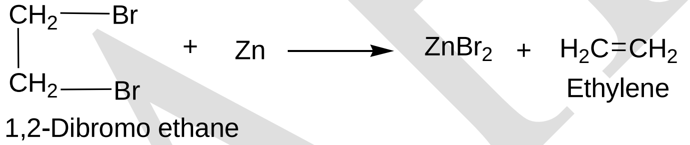
This elimination reaction is a general reaction applicable to all type of amines of varied structures. If the parent amine is an unknown nitrogenous base, we can identify the alkene formed in step (iii) and work backward to deduce the structure of the parent amine.

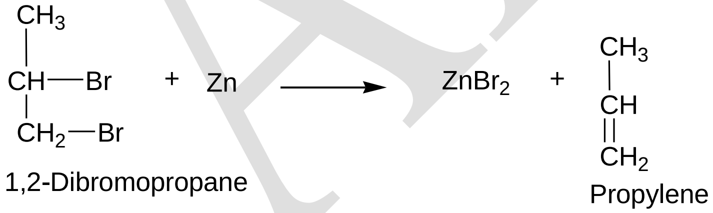
Preparation of alkenes by dehalogenation of dihalides

Dehalogenation of 1,2 dihaloalkanes (*vic*-dihalides) involves the treatment to the *vic*-dihalides with reactive metals like Zn in acetic acid and it yields the corresponding alkenes.

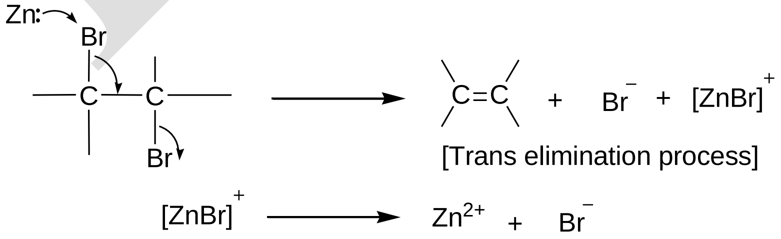


For example:





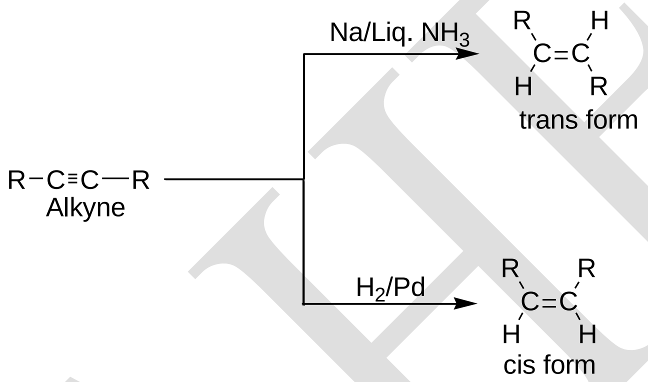
Mechanism: The divalent Zn metal possesses a pair of electrons in its outermost shell and therefore it acts as a nucleophile, Br⁻ are formed in the reaction solution and the reaction can be represented by a concerted process.



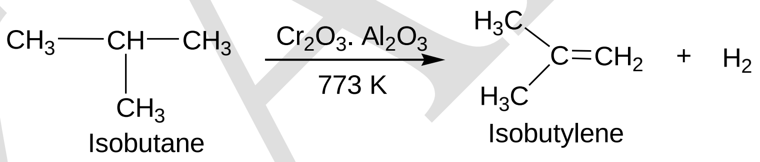
Preparation of alkenes by (i) reduction of alkynes and (ii) dehydrogeanation of alkanes

(i) Alkenes can be prepared by the partial reduction of alkynes using metallic sodium or lithium in liquid ammonia, or by using a calculated quantity of hydrogen over palladium catalyst.

Reduction with sodium in liquid ammonia yields trans alkene, whereas cis alkene results from H_2 in the presence of Pd.



(ii) Dehydrogenation of alkanes. It involves the passing of the alkane in the vapour phase over a bed of catalysts (oxides of chromium and aluminium).

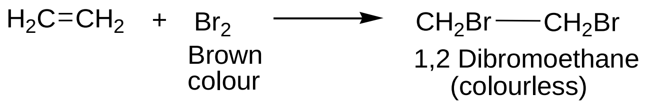


PROPERTIES OF ALKENES

Addition reaction

Addition of halogens

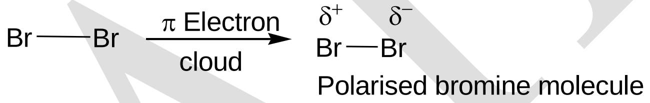
Alkenes add a molecule of halogen to form alkyl halides.


$$H_2C{=}CH_2 + \underset{\text{Brown colour}}{Br_2} \longrightarrow \underset{\text{1,2 Dibromoethane (colourless)}}{CH_2Br{-}CH_2Br}$$

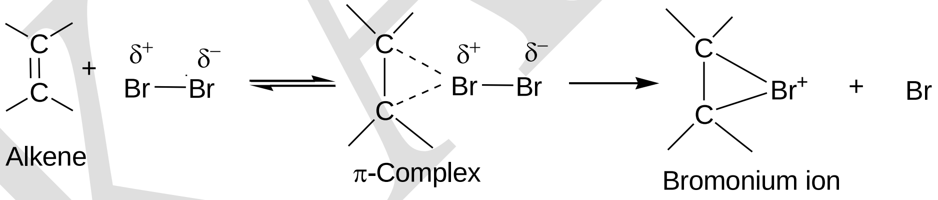
On adding bromine water to a compound containing a double bond, brown colour due to bromine disappears.

Mechanism of halogenations

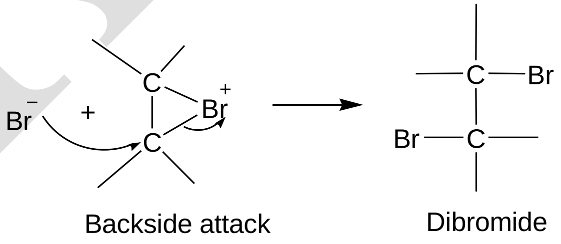
Halogenation of an alkene takes place by electrophilic addition mechanism. A halogen molecule (Cl_2, Br_2 or I_2) is non polar in nature. But when this molecule approaches the alkene molecule, the π bonds have the effect of polarising the halogen molecule. The positive end of the polarised halogen molecule is attached to one ethylenic carbon atom with simultaneous attachment of the negative end to the second ethylenic carbon atom forming a halonium ion, with the release of halide ion. The halide ion then attacks the halonium ion from the backside to steric hindrance, thus giving rise to a dihalides. The steps of the mechanism are shown under, taking the example of bromination.



Step 1



Step 2



Evidence to prove that addition of halogen to an alkene proceeds through halonium ion and through carbonium ion (carbocation).

Addition of halogen to an alkene proceeds through the formation of a halonium ion and not through a carbonium ion. This can be proved like this:

It is observed that the halogenation of alkenes gives rise to products that are optically active. This phenomenon can be explained by halonium ion mechanism and not by carbonium ion mechanism.

In halonium ion mechanism, the halide (in the second step) attacks from the back of halonium ion, giving rise to trans dihalide product.

In carbonium ion mechanism, the halide can attack from both sides of the carbonium ion (as it is flat in shape), giving rise to both cis and trans isomer.

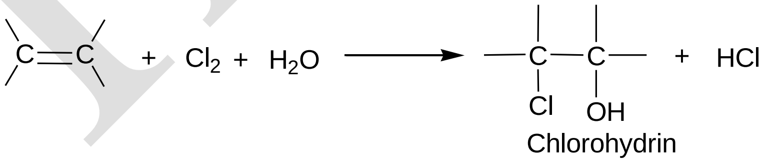
Trans product obtained from halonium ion mechanism explains optical activity of the actual product obtained.

If we assume the carbonium ion mechanism, the mixture of cis and trans products will give as a racemic modification which will have no net optical activity. This is against the observations. Practically, we get an optically active compound.

Reaction of alkenes with halogens in the presence of water

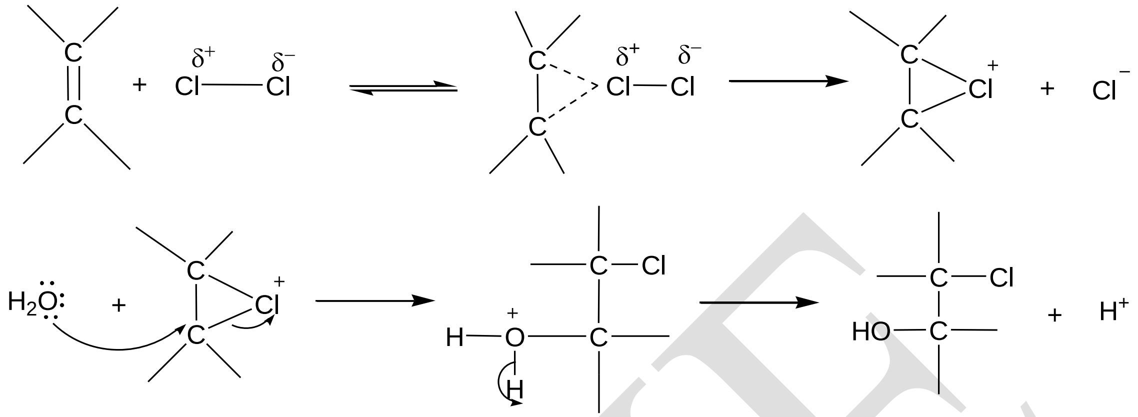
Alkenes react with halogens in the presence of water to form halohydrins.

For example:



Mechanism of the reaction

The reaction takes place through the intermediate formation of a halonium ion as shown below:

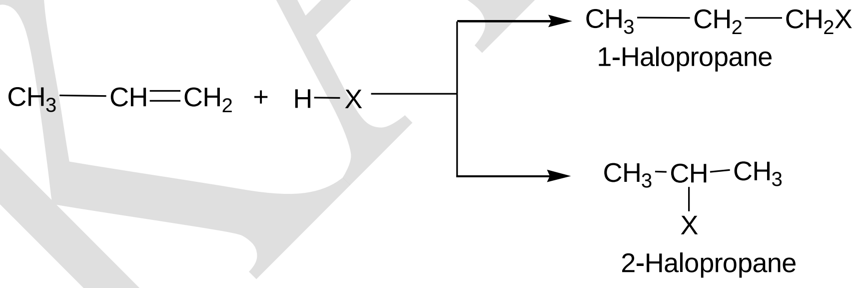


Addition of an unsymmetrical molecule over a double bond. Markownikoff's rule

When olefins are treated with hydrogen halides either in the gas phase or in an inert non ionizing solvent (pentane), addition occurs to form alkyl halides.

$$\underset{\text{Ethylene}}{H_2C=CH_2} + HX \longrightarrow \underset{\text{Ethyl halide}}{H_3C-CH_2X}$$

With propylene (CH_3-$CH=CH_2$), the next higher homologue, the addition of HX yields two products (1-halopropane and 2-halopropane).



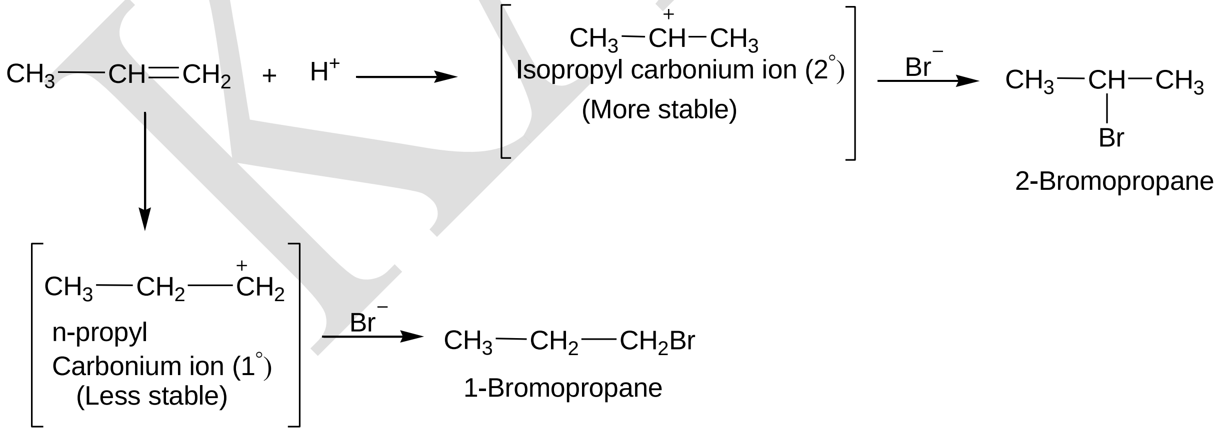
However, in actual practice 2-halopropane is exclusively obtained.

The exclusively formation of the above product is in accordance with Markownikoff's rule which governs the addition of unsymmetrical reagents to unsymmetrical alkenes. *It states that the ionic addition of unsymmetrical reagents to unsymmetrical olefins proceeds in such a* *way that the more positive part of the reagent, becomes attached to the carbon atom with larger number of hydrogen atoms.*

When the hydrogen halides or water is added, hydrogen atoms constitutes the more positive part or in other words, the hydrogen atom becomes attached to the olefinic carbon atom which carries the larger number of hydrogen atoms, for example:

Theoretical explanation of the orientation of addition to olefins is related to the relative stability of carbonium ions. We known that relative stability of carbonium ions are: tertiary > secondary > primary > CH_3^+. If there is the probability of more than one carbonium ions being formed, the addition of electrophile yields the more stable one.

That is why 2-bromopropane is exclusively formed by the addition of HBr to propylene (an unsymmetrical alkene) and not 1-bromopropane because secondary isopropyl carbonium ion is more stable than primary n-propyl carbonium ion.



Thus the modern statement of Markownikoff's rule is:

In the ionic addition of an unsymmetrical reagent to a double bond, the positive portion of the adding reagent becomes attached to the carbon atom of the double bond so as to yield the more stable carbonium ion.

Anti–Markownikoff's addition peroxide effect (Kharasch Effect)

If has been observed that the addition of H-Br to propylene in the presence of peroxides ,yields predominantly 1-bromopropane, that is the reagent ads onto the olefins under these conditions in manner contrary to Markownikoff's rule thus suggesting a change in the mechanism.

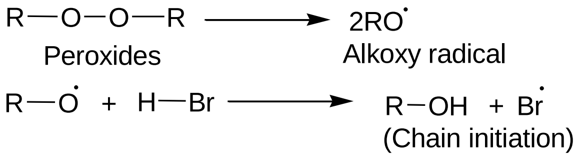
This change in the orientation of addition due to presence of peroxides is known as the peroxide effect.

Here the change in the mode of addition of the reagent is due to change from an ionic mechanism to a free radical mechanism. Markownikoff's addition requires the initiation by H^+. Anti-Markownikoff's addition requires initiation by ($Br^\bullet$). Each species attacks the olefin molecule at the center of the highest electron density to yield the most stable intermediate carbonium ion or free radical.

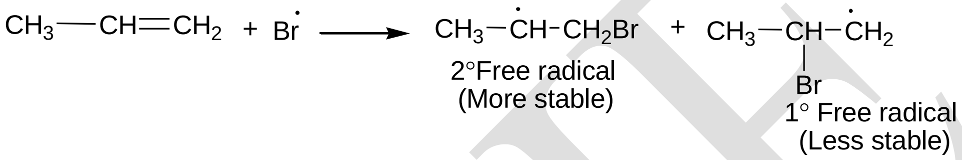
Mechanism of addition of HBr to propylene in the presence of peroxides

It involves the following steps:

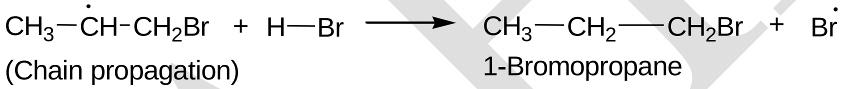
(i) Chain initiation step. The reaction is initiated by the alkoxy radical produced by the hemolytic fission of peroxides, which abstracts an atom of hydrogen from HBr generating bromine free radicals ($Br^\bullet$).



(ii) Chain propagation step. The Br• then attacks the propylene molecule to give a more stable secondary radical addition species:



The secondary radical then reacts with another H – Br molecule to yield the product, and anther Br• which can further propagate the reaction:



This mechanism is supported by the fact that small amount of peroxide can influence addition to large number of molecules of an alkene and a small amount of an inhibitor such as hydroquinone or diphenyl amine can prevent this change.

Peroxide oxide effect or Anti-Markownikoff's rule (or Kharasch effect) is observed in the addition of H–Br and not H–Cl or H–I.

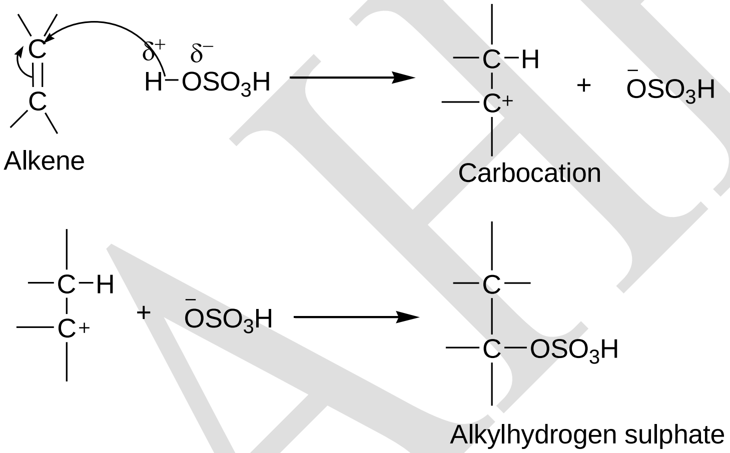
In case of HCl, it is probably due to the fact that H–Cl bond (430 kJ/mol) is stronger than H–Br bond (368 kJ/mol) and is not broken homolytically by the free radicals generated by peroxides. As such free radical addition of HCl to alkenes is not possible. In case of HI, H–I bond (297 kJ/mol) is no doubt weaker than H–Br bond and can be broken easily. But the iodine atoms (I•) thus formed readily combine amongst themselves to form iodine molecules rather than add to the olefins.

Addition of (i) Sulphuric acid and (ii) water to an alkene

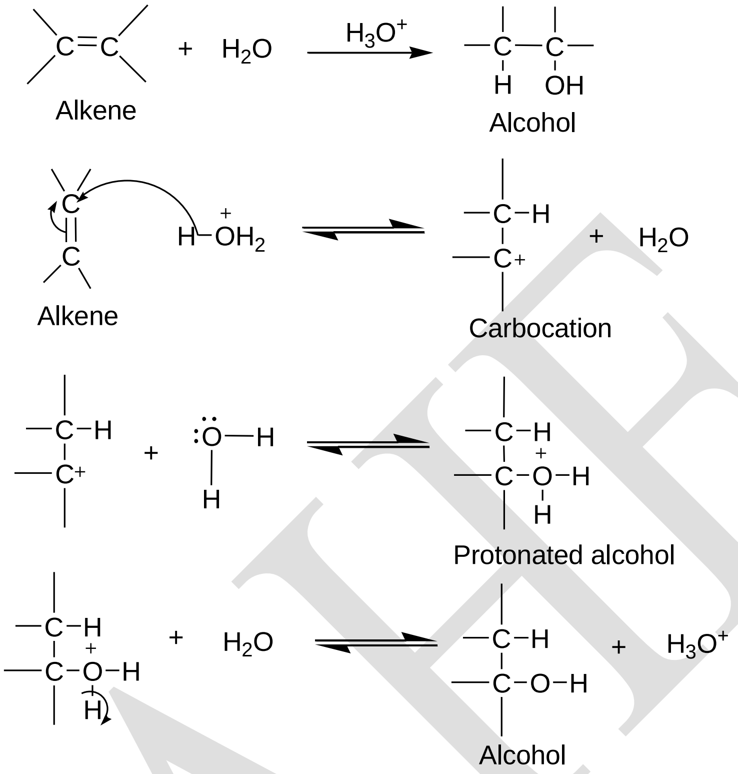
Sulphuric acid adds to an alkene to form alkyl hydrogen sulphate while water adds in the presence of an acid to form alcohol.

Mechanism of addition of (i) sulphuric acid and (ii) water to an alkene

(i) Mechanism of addition of sulphuric acid to alkene. It is a two step electrophilic addition reaction which takes place as follows:



(ii) Mechanism of addition of water to an alkene. Alkenes react on water in the presence of an acid form alcohols.

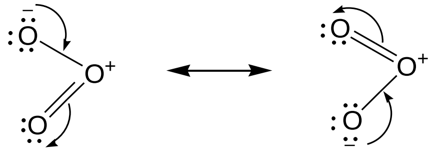


Ozonolysis

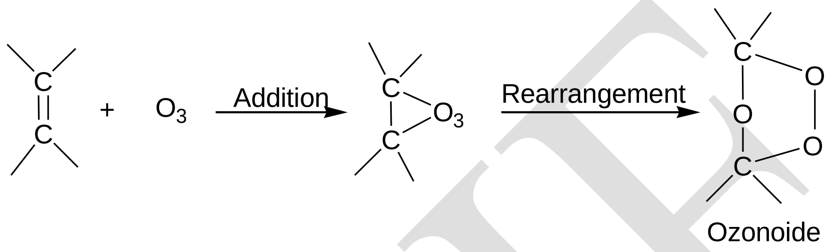
Ozone undergoes a reaction with olefins in an inert solvent at low temperature to yield unstable addition compounds called ‘ozonides’. These ozonides are not easily isolated and yield carbonyl compounds on further treatment either with boiling water and Zn or zinc and acetic acid. This overall reaction is called as Ozonolysis.

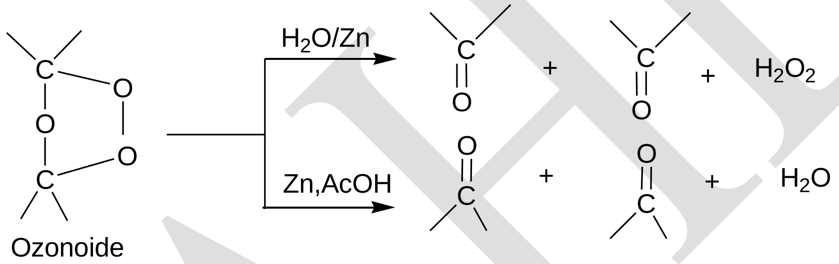
Ozonolysis is a very useful reaction for illucidating the structures of olefinic compounds.

Ozone has a dipolar resonance structure with a bond angle of about 120º.



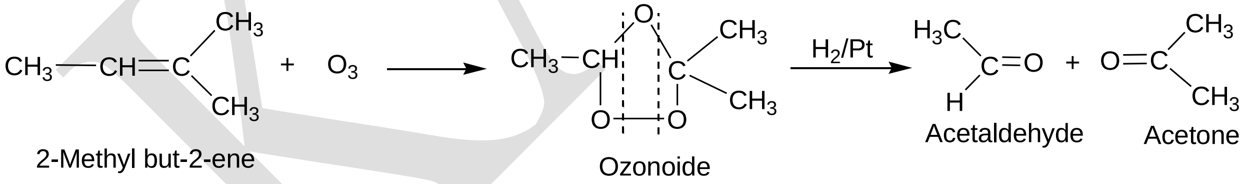
The central atom (oxygen) is relatively electron deficient and thus can act as an electrophile for attack on the π electrons of the olefins. The final structure of the ozonide has been shown to have a structure resulting from the complete rupture of the carbon-carbon double bond.





The important thing to note about ozonides is that the *carbon-carbon bond has been broken*.

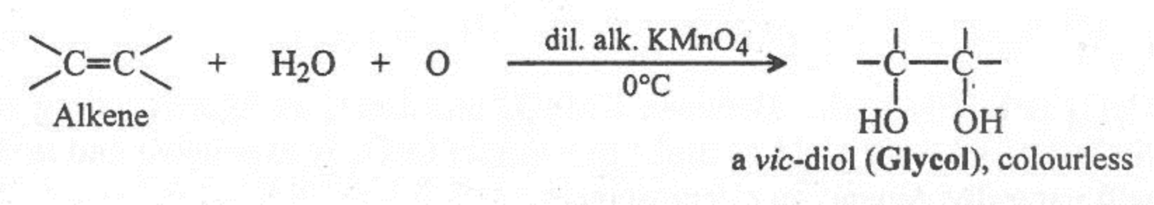
For example:



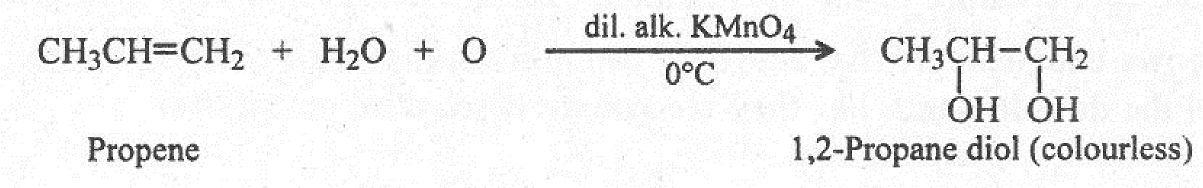
By identifying the products of ozonolysis, it is possible to locate the double bond in alkene.

Hydroxylation

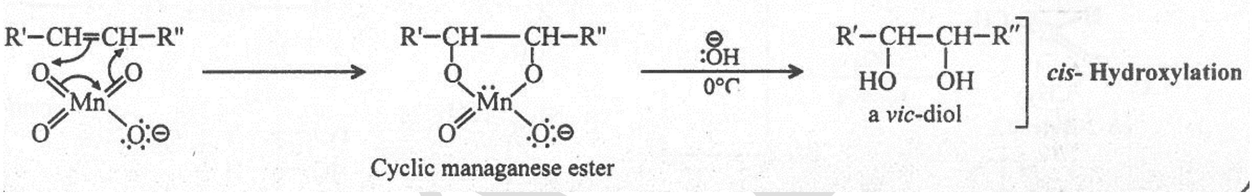
(a) Dilute alkaline potassium permanganate at low temperature, leads to the formation of vicinal diols (glycols).



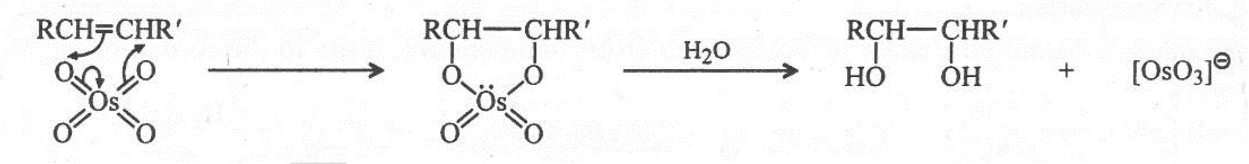
For example,



Mechanism: It involves the intermediate formation of a cyclic manganese ester through electrophilic addition, as shown below:



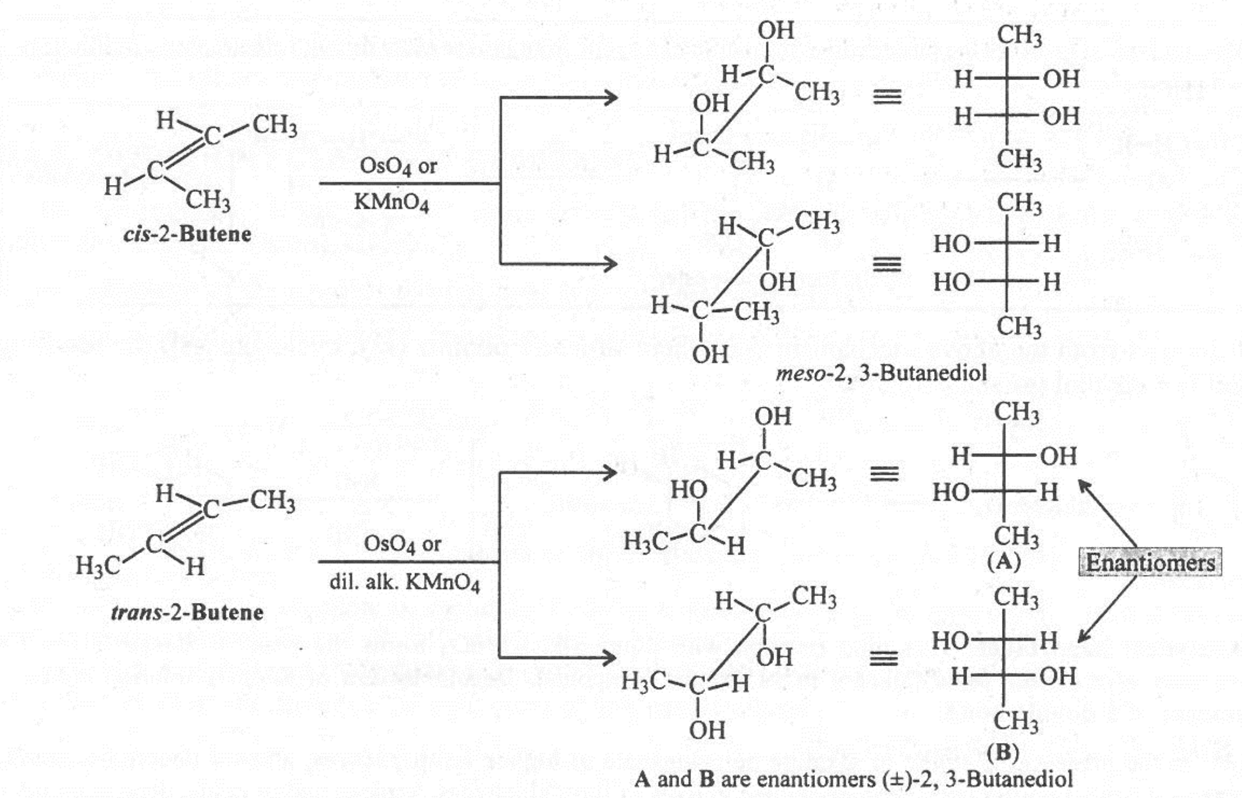
(c) Reaction with Osmium tetraoxide: This leads to the hydroxylation of the double bond of the alkene at room temperature. This reaction also proceeds through the intermediate formation of a cyclic **osmate ester** (a one–step concerted attack) as shown below, to form eventually cis-hydroxylation product (syn-hydroxylation).



Caution: OsO_4 is highly toxic. Between $KMnO_4$ and OsO_4 as hydroxylating reagent $KMnO_4$ is **cheaper** and safer but gives poor yield of diol. In contract OsO_4 is expensive and toxic but gives better yields. Choice will naturally depend on circumstances.

Because of the cyclic nature of the intermediate osmate ester, cycloalkene also give **cis-** 1,2-**diols**.

Figure below shows conclusively that action of osmium tetraoxide or $KMnO_4$ on alkenes leads to **cis –hydroxylation** of the **double bond** ,i.e., they are **syn stereoselective** oxidations.



cis-Hydroxylation of 2-Butenes with osmium tetraoxide or potassium permanganate.

Hydroboration-Oxidation. It involves two steps, namely **hydroboration** and **oxidation**.

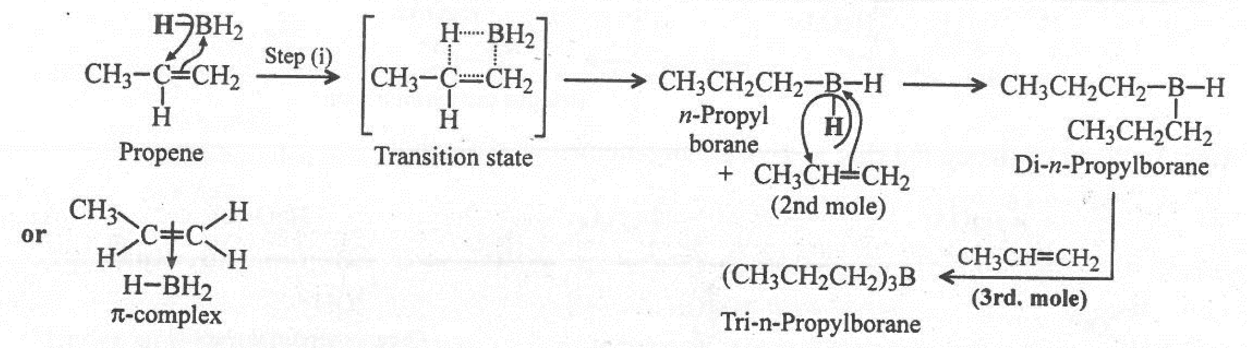
(i) Hydroboration. Borane (BH_3) forms a stable complex with cyclic ether like tetrahydrofuran (THF) [a Lewis-acid base complex], is commercially available as a solution of BH_3 in THF, and is used as such in this reaction called hydroboration addition of H and B to an alkene. For example,

$$(a)\ BH_3 \xrightarrow[\text{(1st mol)}]{CH_2{=}CH_2} CH_3CH_2BH_2 \xrightarrow[\text{(2nd mol)}]{CH_2{=}CH_2} (CH_3CH_2)_2BH \xrightarrow[\text{(3rd mol)}]{CH_2{=}CH_2} (CH_3CH_2)_3B$$

Similarly,

$$(b)\ 3CH_3CH{=}CH_2 + BH_3 \longrightarrow \underset{\text{Tri-}n\text{-propylborane}}{(CH_3CH_2CH_2)_3B}$$

Mechanism: Hydroboration does not involve a **free carbocation** intermediate. Actually there is a simultaneous addition of hydrogen and boron to alkene via π-complex to form a **four centred transition state** in which boron is attached to the least hindered i.e., least substituted carbon of the double bond (as shown below). Where structure permits, it shows stereoselectivity.

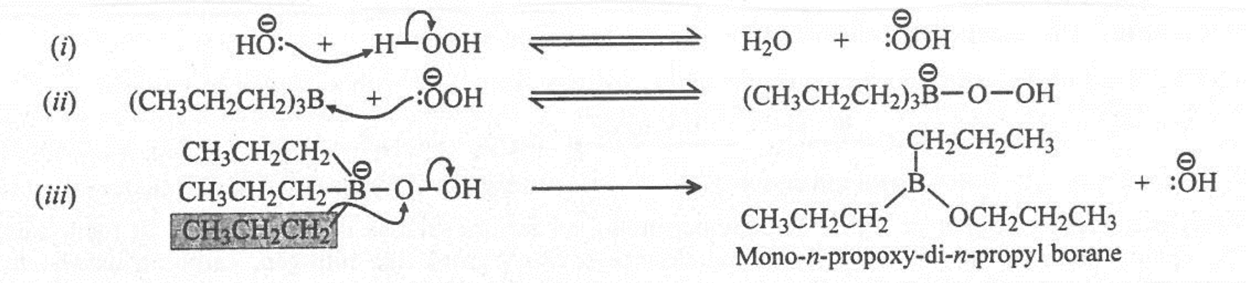


As the transition state is approached, the carbon which is losing the π-electrons becomes increasingly electron-deficient, and it tends to take up the nearby hydrogen (shown in thick type), together, with its electron pair held to born. Boron with sextet of electrons is itself electron-deficient but as it gains the π electrons, it is increasingly willing to release hydrogen along with its electron pair. This four centred mechanism is supported by the fact that hydroboration is a cis addition (both B and H add to the same face). Whereas hydrogen adds without electrons in ordinary electrophilic addition, it adds here with electrons (hydride ion) in hydroboration. It is, therefore, natural to expect that addition in hydroboration should be **anti-Markovnikov**, and this is actually so. It may be noted that the rate of addition of borane to alkenes decrease with the increase in the alkyl substituents on the double bond, as expected from its four centred transition state mechanism.

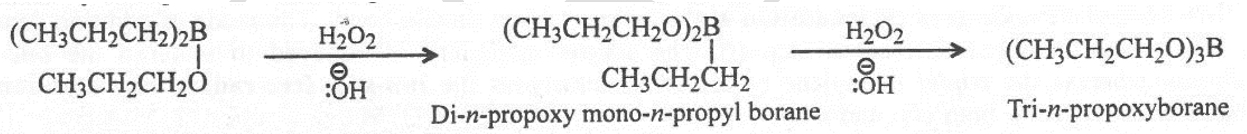
(ii) Oxidation of trialkylboranes. Trialkyboranes are generally not isolated. They are directly oxidized to alcohols by hydrogen peroxide in aqueous sodium hydroxide.

$$\underset{\text{Tri-}n\text{-propylborane}}{(CH_3CH_2CH_2)_3B} + 3H_2O_2 + 3NaOH \longrightarrow \underset{\text{1-Propanol}}{3CH_3CH_2CH_2OH} + \underset{\text{Sodium borate}}{Na_3BO_3} + 3H_2O$$

Mechanism: The oxidation of alkylboranes proceeds in following steps:



Similarly mono-n-propoxy-di-n-propylborane can react with excess alkaline hydrogen peroxide to form successively di-n-propoxy-mono-n-propylborane and tri-n-propoxyborane:



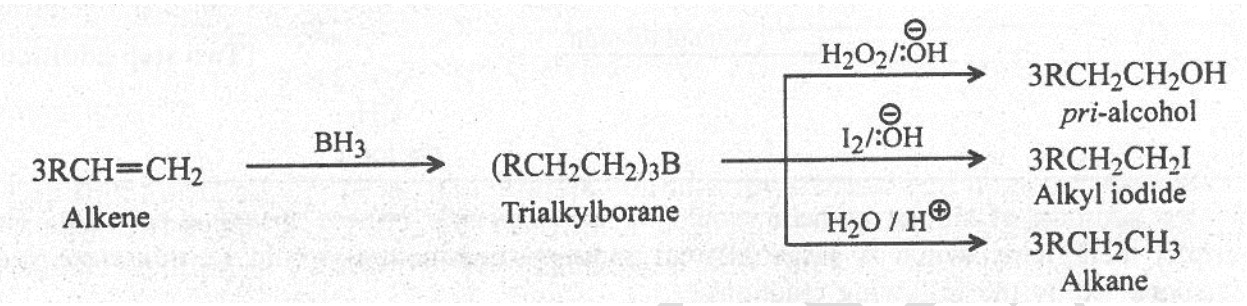
$$\underset{CH_3CH_2CH_2O}{(CH_3CH_2CH_2)_2B} \xrightarrow[:\overset{\ominus}{O}H]{H_2O_2} \underset{\text{Di-}n\text{-propoxy mono-}n\text{-propyl borane}}{\underset{CH_3CH_2CH_2}{(CH_3CH_2CH_2O)_2B}} \xrightarrow[:\overset{\ominus}{O}H]{H_2O_2} \underset{\text{Tri-}n\text{-propoxyborane}}{(CH_3CH_2CH_2O)_3B}$$

The tri-n-propoxyborane can then be hydrolysed to n-propyl alcohol (1-Propanol).

$$\underset{\text{Tri-}n\text{-propoxyborane}}{(CH_3CH_2CH_2O)_3B} \xrightarrow{3H_2O} \underset{\text{1-Propanol}}{3\ CH_3CH_2CH_2OH} + H_3BO_3$$

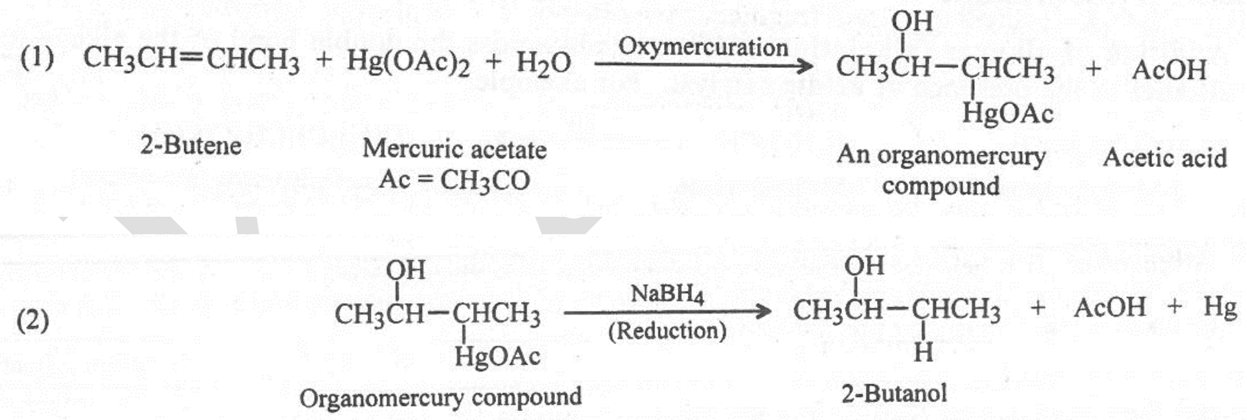
It may be noted that the net result of this hydroboration-oxidation of alkenes is the **anti-Markovnikov** addition of water to alkenes (cf. the Markovnikov addition observed in the direct hydration or the indirect hydration of alkenes via sulphuric acid addition).

Application: The hydroboration has immense utility as alkyl boranes undergo a variety of useful transformations to yield **anti-Markovnikov** products. For example,

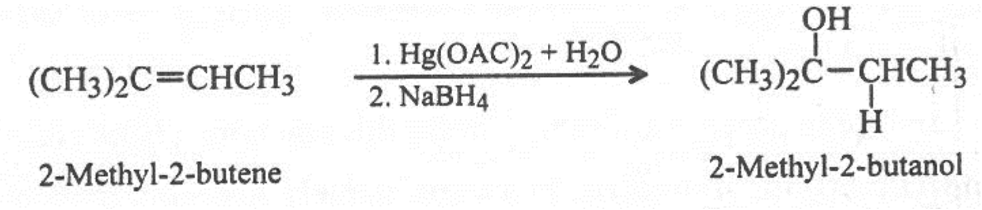


Hydration by oxymercuration-demercuration

This reaction involves two steps namely oxymercuration and demercuration. The alkene is treated with mercuric acetate in the oxymercuration step to form an organomercury compound which is than reduced by sodium borohydride ($NaBH_4$) in the demercuration step to replace HgOAc by H and give the final product alcohol, as shown below:

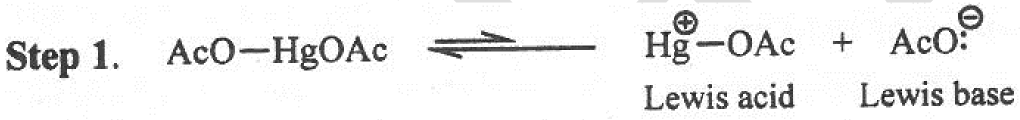


When the alkene is step (1) is unsymmetrical, the HgOAc gets attached to less substituted carbon of the alkene and the –OH of water gets attached to the more substituted carbon in trans fashion. Thus, the step (1) is regioselective. For example,



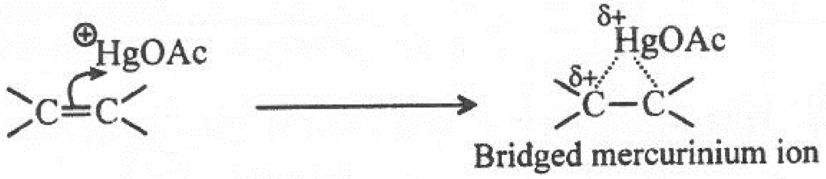
The net result of th is reaction is the **Markovnikov addition** of water to an alkene. Since this reaction proceeds without rearrangement, it is likely that in this reaction of free carbocation intermediate is formed. From this evidence, it is clear that the **oxymercuration-demercuration** is a stereoselective reaction where structure permits. In the light of these facts, the following mechanism has been proposed for this reaction.

Mechanism: The oxymercuration part of this reaction involves the following steps:

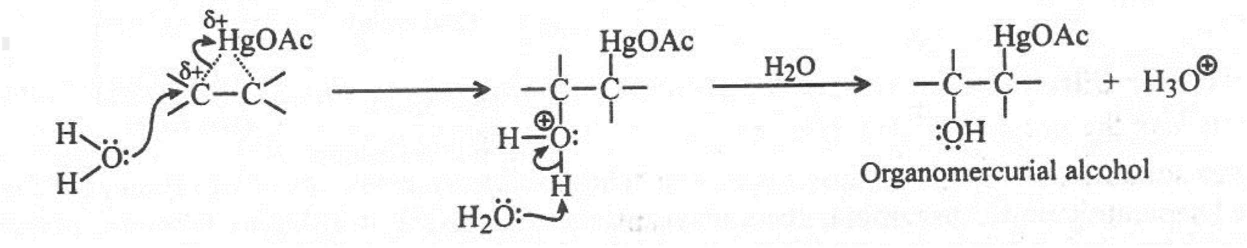


It is just a dissociation of mercuric acetate into a Lewis acid, Hg $^{\ominus}$ (OAc), and Lewis base, AcO $^{\bigcirc}$.

Step 2. The electrophilic attack on the carbon-carbon double bond by the Lewis acid formed in step 1, to give a bridged mercurinium ion.

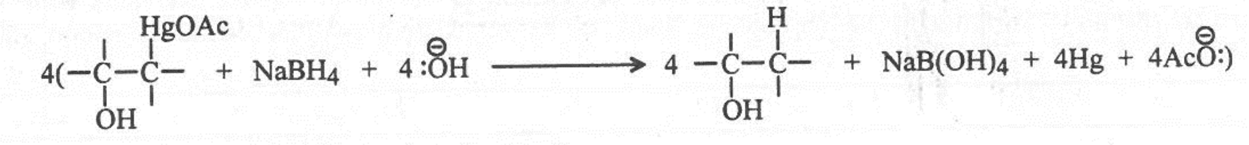


Step 3. Water opens up the ring to give the organomercurial alcohol.



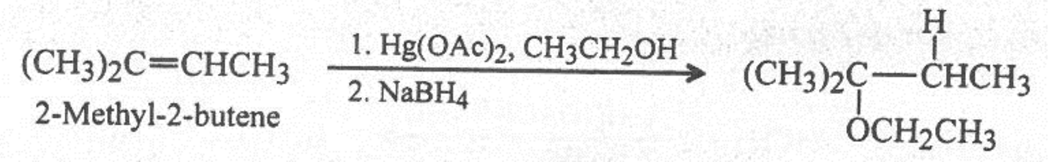
Attack by H_2O on the mercurinium ion in this step takes place from the opposite side of the ring so that the hydroxyl group and mercury atom add from the opposite sides of the ring. In other words, this a case of **anti-addition**.

Step 4. This step pertains to the demercuraiton stage of this reaction. The reducing agent $NaBH_4$ simply replaces the mercuric acetate fragment by hydrogen to give alcohol.



In conclusion, it may be pointed out that the **Markovnikov hydration** of the double bond by oxymercuration-demercuration is better than all available methods and needs relatively milder conditions. Of course, the downside of this method is that organomercurial compounds are highly toxic. Extreme care has to be taken while employing this method.

In passing, it may be stated that when mercuration is carried out in an alcohol solvent rather than water and then treated with $NaBH_4$, the net result is addition of –OR and -H. This is an example of **alkoxymercuration-demercuraiton**, used in the preparation/synthesis of ethers. For example,



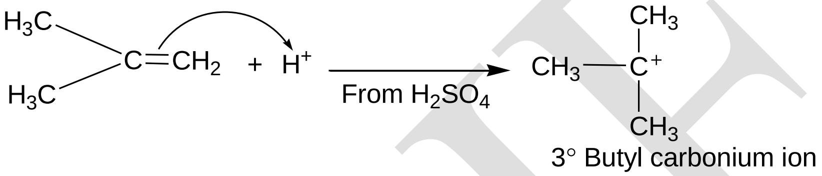
It would be a good exercise to propose a mechanism for this reaction. (Hint: Similar to hydration).

Alkylation of alkenes

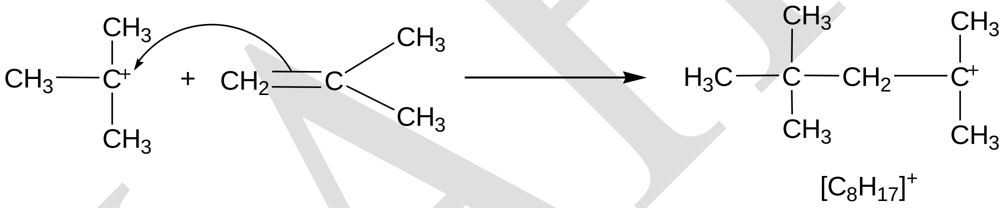
Isobutylene may be converted into iso-octane by the addition of isobutane in the presence of H_2SO_4 as a catalyst. This process is known as '*alkylation*' and is of industrial importance as it is extensively used in oil refineries in the production of high grade motor fuels.

The probable route adopted may be shown taking place as:

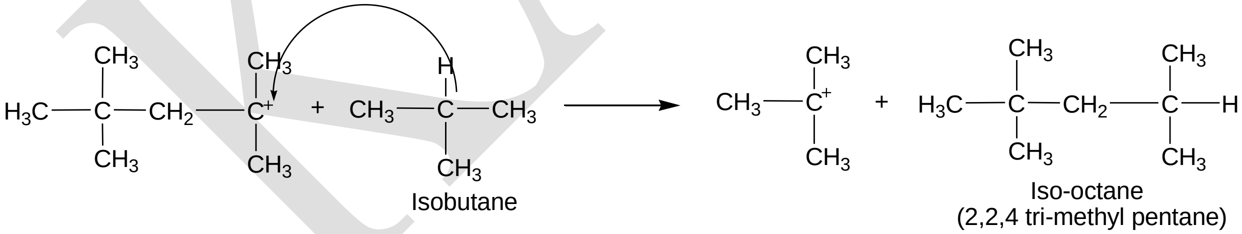
Initiation



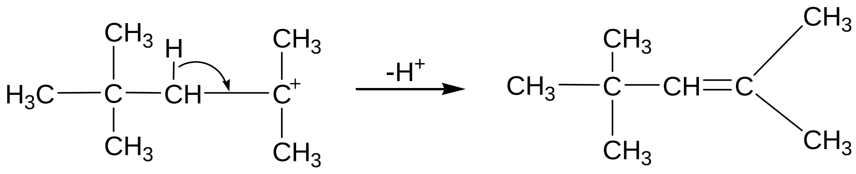
Propagation. There are two propagation steps. In the first step; addition of 3º butyl carbonium ion with isobutylene to form a new carbonium ion ($^+C_8H_{17}$) takes place.



In the second step this new carbocation then abstracts a hydride ion from iso-butane to form isooctane and a new 3º butyl carbonium ion.

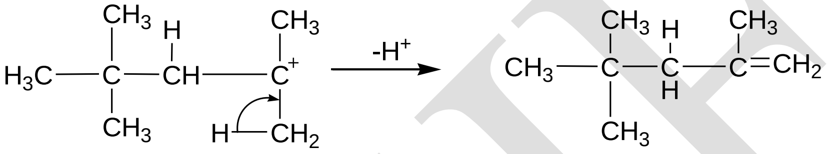


Termination. It involves the loss of a proton from the carbonium ions to form an alkene.



2,4,4- Trimethylpent-2-ene
(Higher %)
(A)

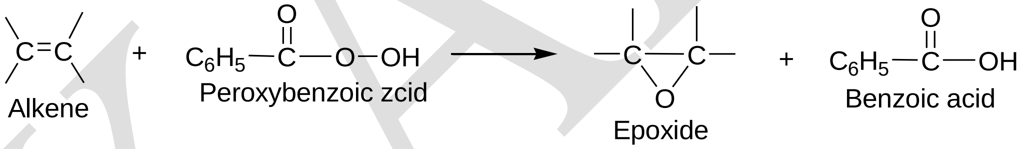
(Or)



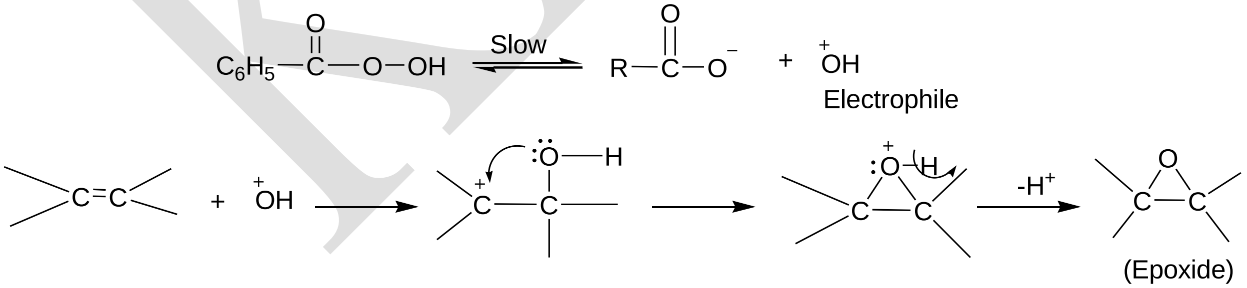
2,4,4- Trimethylpent-1-ene
(B)

Epoxidation reaction

When an alkene is treated with peroxybenzoic acid, an epoxide is formed. This reaction is called epoxidation reaction.

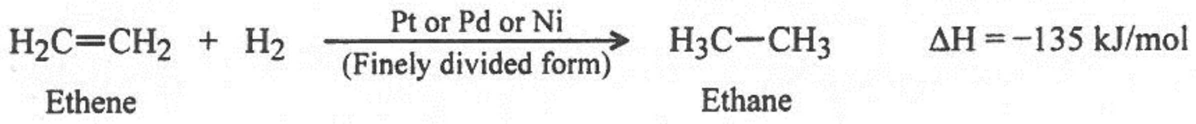


Mechanism of the reaction



Reduction (Catalytic hydrogenation)

Addition of hydrogen across the double bond in an alkene to form corresponding alkane takes place only in the presence of finely divided metals (hence large surface area) platinum or palladium or nickel. The overall reaction is known as **catalytic hydrogenation** of alkene. For example,



$$\underset{\text{Ethene}}{H_2C{=}CH_2} + H_2 \xrightarrow[\text{(Finely divided form)}]{\text{Pt or Pd or Ni}} \underset{\text{Ethane}}{H_3C{-}CH_3} \qquad \Delta H = -135\ \text{kJ/mol}$$

Analytical importance: Catalytic hydrogenation of alkenes is usually qualitative. The process is used to determine the number of carbon-carbon double bond/triple bonds in an organic compound (one mole per double bond or two moles per triple bond).

The catalyst mentioned above are heterogeneous catalysis, i.e., they are used in a phase different from the reaction solution. Recently, homogeneous catalysis, such as Wilkinson's catalyst consisting of rhodium or ruthenium phosphines, have been developed.

DIENES

Introduction

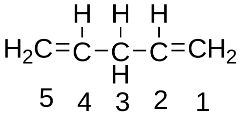
Hydrocarbons containing two double bonds are called dienes. These are also called alkadienes. General formula for such compounds is C_nH_{2n-2}. These compounds are isomeric with alkynes which also have the same general formula. But there are striking differences between the two classes of compounds.

Dienes are classified into three types depending upon the location of double bonds.

(a) Isolated dienes (b) Cumulated dienes (c) Conjugated dienes

(a) Isolated dienes. The dienes in which the double bonds are separated by more than one single bond are isolated dienes.

For example:



$H_2C=\overset{H}{C}-\underset{H}{\overset{H}{C}}-\overset{H}{C}=CH_2$ 1,4 -pentadiene

5 4 3 2 1

$H_2C=CH-H_2C-H_2C-CH=CH_2$ 1,5-pentadiene

6 5 4 3 2 1

(b)Cumulated dienes. These dienes contain the grouping >C=C=C< and are characterized by the presence of at least one carbon atom joined to both the neighbouring C-atoms by double bonds.

For example,

$H_2C=C=CH_2$ allene or 1,2-propadiene

$H_3C-CH=C=CH_2$ 1,2-butadiene

(c) Conjugated dienes. In these dienes, a single bond intervenes two double bonds or in other words, they have an arrangement of alternate single and double bonds.

For example,

$H_2C=CH-CH=CH_2$ 1,3 butadiene

β-carotene which is found in carrots and green leaves, contains a system of eleven conjugate double bonds.

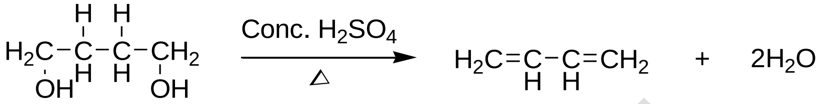
METHODS OF FORMATION OF 1,3–BUTADIENE

Methods of preparation of 1,3–butadiene are given as under.

(i) **Dehydrogenation of alkenes.** 1, 3–butadiene is prepared on an industrial scale by passing the vapours of n-butane over heated Cr_2O_3 and Al_2O_3 catalysts.

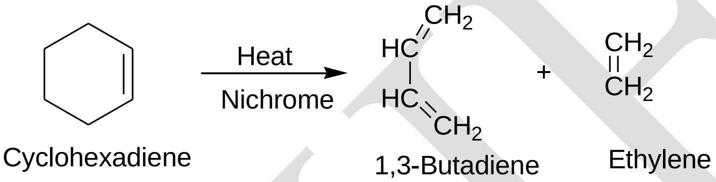
$$\underset{\text{n-butane}}{CH_3-CH_2-CH_2-CH_3} \xrightarrow[Cr_2O_3,\ Al_2O_3]{\text{Heat}} \underset{\text{1,3-butadiene}}{CH_2=CH-CH=CH_2} + 2H_2O$$

(ii) **Dehydration of diols.** 1, 3 –butadiene can be prepared by the dehydration of butane 1,4-diol (or butane-1,3-diol) in the presence of H_2SO_4 or phosphoric acid.



$$\underset{OH}{H_2C}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\underset{OH}{CH_2} \xrightarrow[\triangle]{\text{Conc. } H_2SO_4} H_2C=\underset{H}{C}-\underset{H}{C}=CH_2 \quad + \quad 2H_2O$$

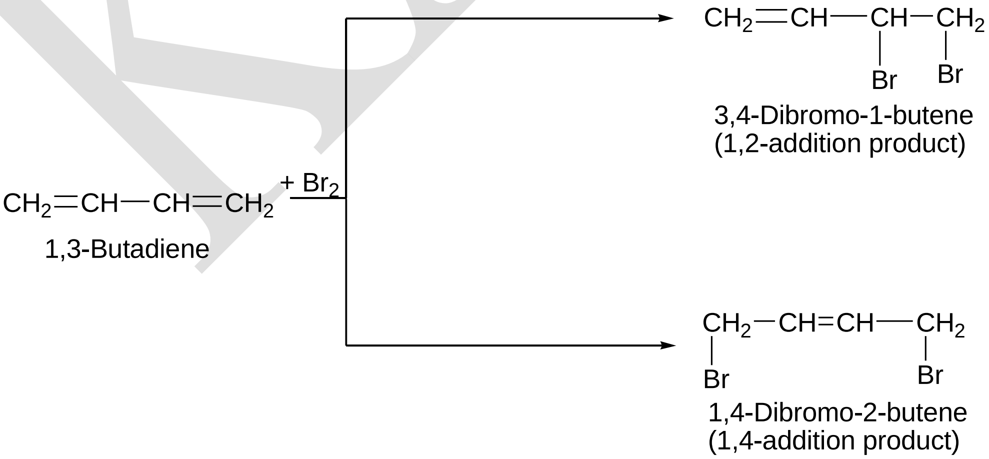
(iii) **Pyrolysis of Cycloalkenes.** When the vapours of cyclohexene are passed over heated Nichrome (Ni – Cr – Fe) alloy, 1, 3–butadiene results.



PROPERTIES OF 1,3 –BUTADIENE

Addition of Br_2 to 1,3 – butadiene

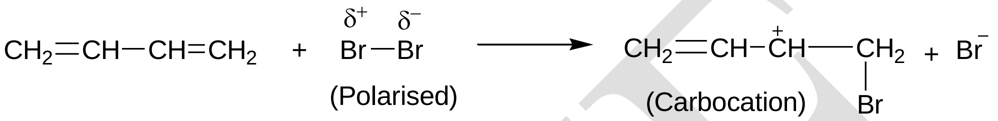
When one mole of the addendum such as Br_2 is added to a conjugated diene, the resulting product obtained is a mixture of 1, 2 and 1, 4–addition products. Such an addition is known as 1,2 – and 1,4–addition to conjugated dienes. Consider the addition of 1 mole of Br_2 to 1,3 -butadiene.



In order to understand the occurrence of 1,2– and 1,4 –addition reactions, the mechanism of the above reaction is discussed.

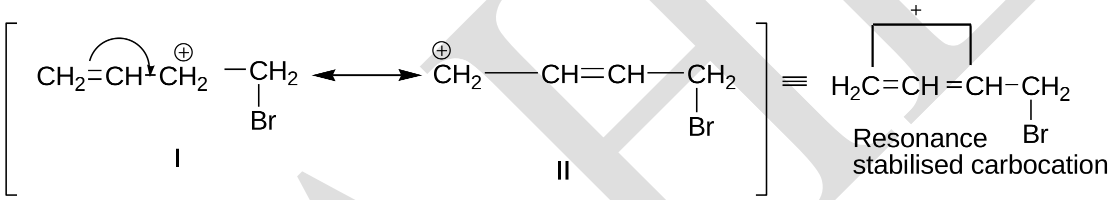
Mechanism. It involves two steps:

(i) Formation of carbocation.

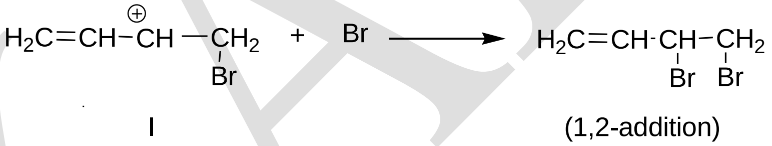


$$CH_2=CH-CH=CH_2 + \overset{\delta^+}{Br}-\overset{\delta^-}{Br} \longrightarrow CH_2=CH-\overset{+}{C}H-\underset{Br}{CH_2} + Br^-$$

The above intermediate carbocation is allylic in nature and hence can be considered to be a resonance hybrid of two equivalent resonating structures I and II.

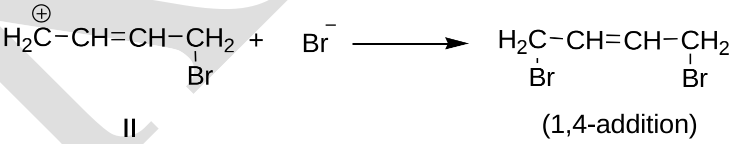


(ii) **Combination of bromide with carbocation.**



$$H_2C=CH-\overset{\oplus}{CH}-\underset{Br}{CH_2} + Br \longrightarrow H_2C=CH-\underset{Br}{CH}-\underset{Br}{CH_2}$$

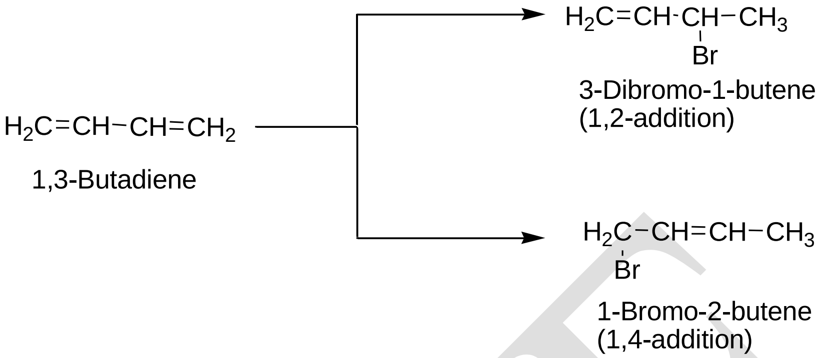
Bromide ion combines with carbocation I and II to form 1,2 and 1,4 addition products respectively.



$$\overset{\oplus}{H_2C}-CH=CH-\underset{Br}{CH_2} + Br^- \longrightarrow \underset{Br}{H_2C}-CH=CH-\underset{Br}{CH_2}$$

Addition of HBr to 1,3–butadiene

Addition of HBr to 1,3 – butadiene gives a mixture of 1,2 and 1,4 addition products as given below:

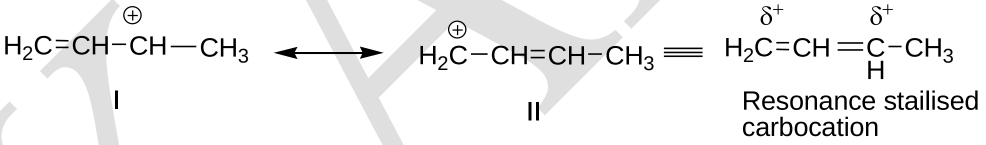


This can be explained in terms of the mechanism which assumes the formation of carbocations I and II.

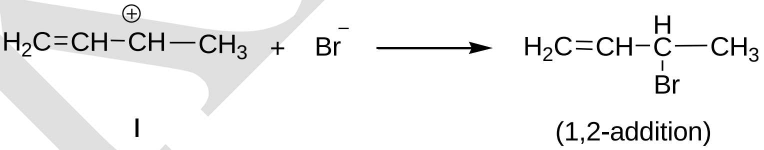
Mechanism

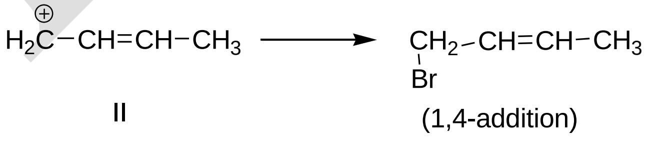
(i)

The above carbocation is a resonance hybrid of the following two equivalent structures (I and II).



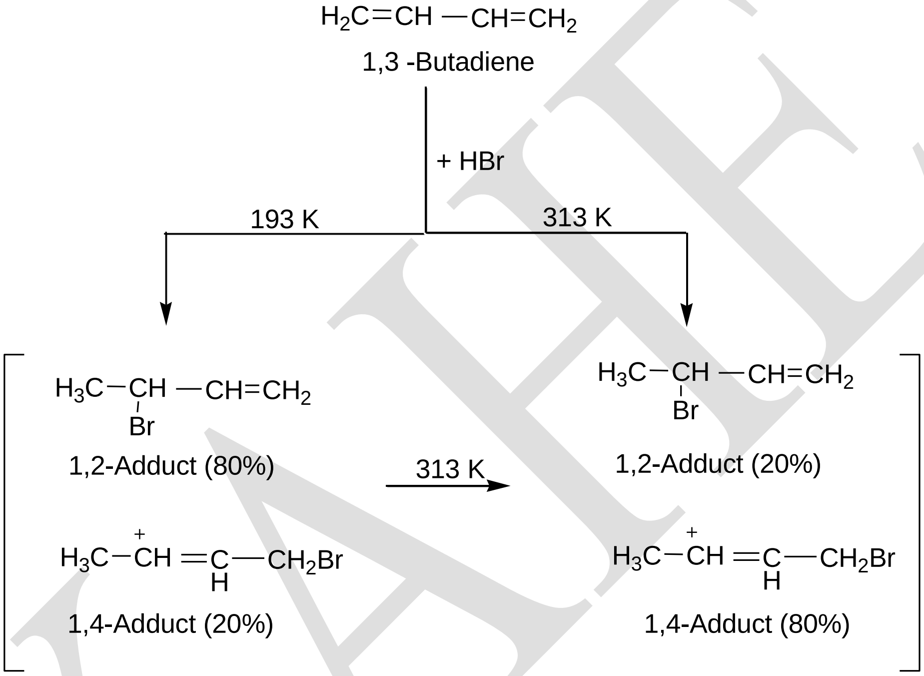
(ii) Carbocations I and II react with bromide to give 1,2 and 1,4 products respectively.





Effect of temperature on 1, 2 and 1, 4- addition to conjugated dienes

It has been observed that temperature has a marked effect on the proportions in which 1,2 and 1,4 products are obtained as a result of electrophilic additions to conjugated dienes. For example:



The observations can be summed up as follows:

(a) At 193 K, a mixture containing 80% of the 1,2-product and 20% of the 1,4 product is obtained .

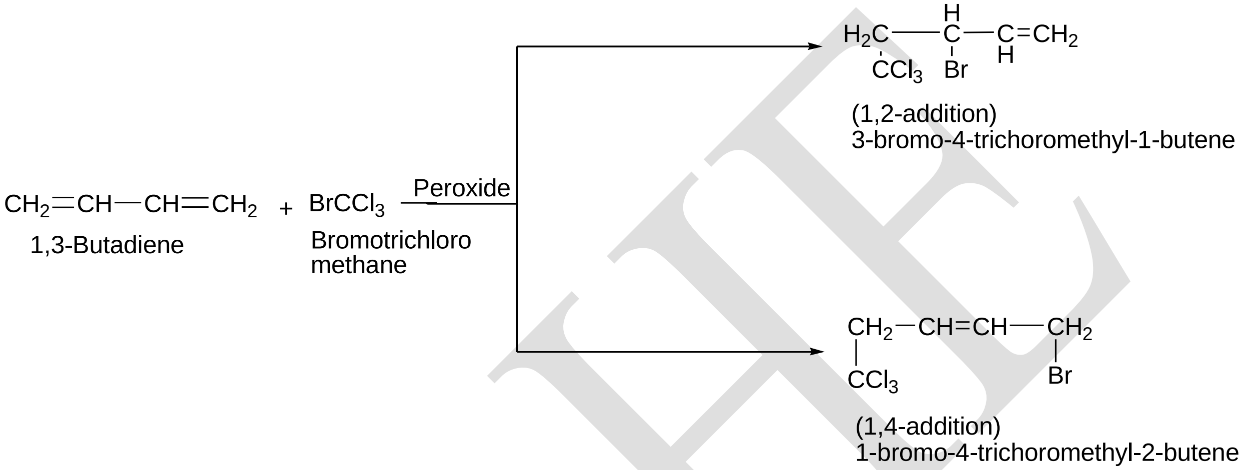
(b) Reaction at 313 K yields a mixture containing 80% of the 1,4 –product 20% of the 1,2-product.

(c) At intermediate temperatures, mixtures of intermediate compositions are obtained.

(d) Although each isomer is quite stable at low temperatures, prolonged heating of either 1,2 product or 1,4 product yields the same mixture.

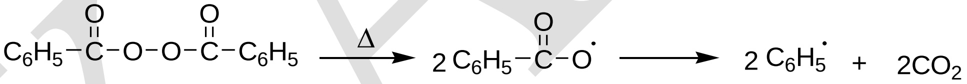
Free-radical addition in butadiene

When $BrCCl_3$ is added to 1,3- butadiene in the presence of some organic peroxide, a mixture containing 1,2- and 1,4- addition products is obtained.



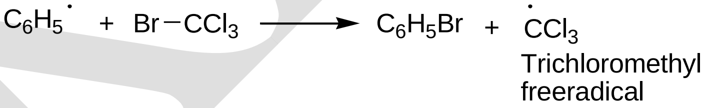
Mechanism. The above reaction is assumed to occur by a free radical mechanism as illustrated below:

(i)



$$C_6H_5-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-C_6H_5 \xrightarrow{\Delta} 2\,C_6H_5-\overset{O}{\overset{\|}{C}}-\dot{O} \longrightarrow 2\,C_6H_5^{\bullet} + 2CO_2$$

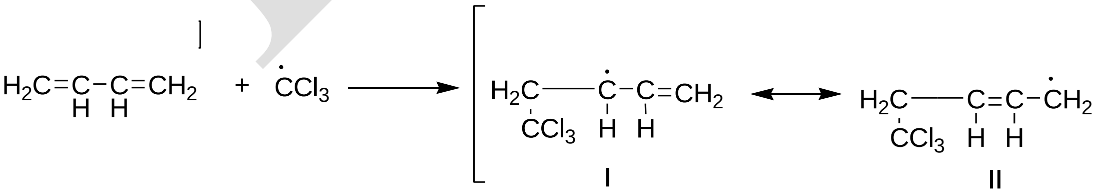
(ii)



$$C_6H_5^{\bullet} + Br-CCl_3 \longrightarrow C_6H_5Br + \dot{C}Cl_3$$

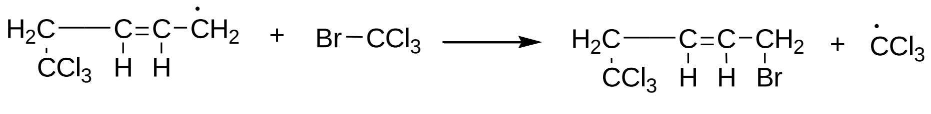
Trichloromethyl freeradical

(iii)



$$H_2C=CH-CH=CH_2 + \dot{C}Cl_3 \longrightarrow \left[\underset{\text{I}}{H_2C(CCl_3)-\dot{C}H-CH=CH_2} \longleftrightarrow \underset{\text{II}}{H_2C(CCl_3)-CH=CH-\dot{C}H_2} \right]$$

(iv)



$$\underset{CCl_3}{H_2C}-\underset{H}{C}=\underset{H}{C}-\dot{C}H_2 + Br-CCl_3 \longrightarrow \underset{CCl_3}{H_2C}-\underset{H}{C}=\underset{H}{C}-\underset{Br}{C}H_2 + \dot{C}Cl_3$$

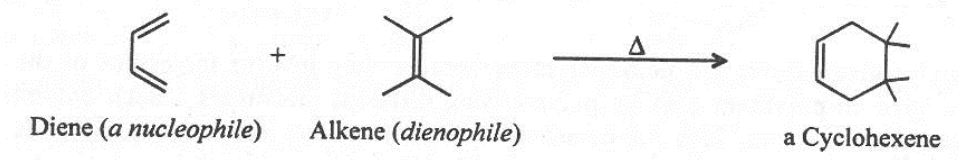
1,4-product

The newly formed ${}^{\bullet}CCl_3$ free radical propagates the chain reaction.

DIELS-ALDER REACTION

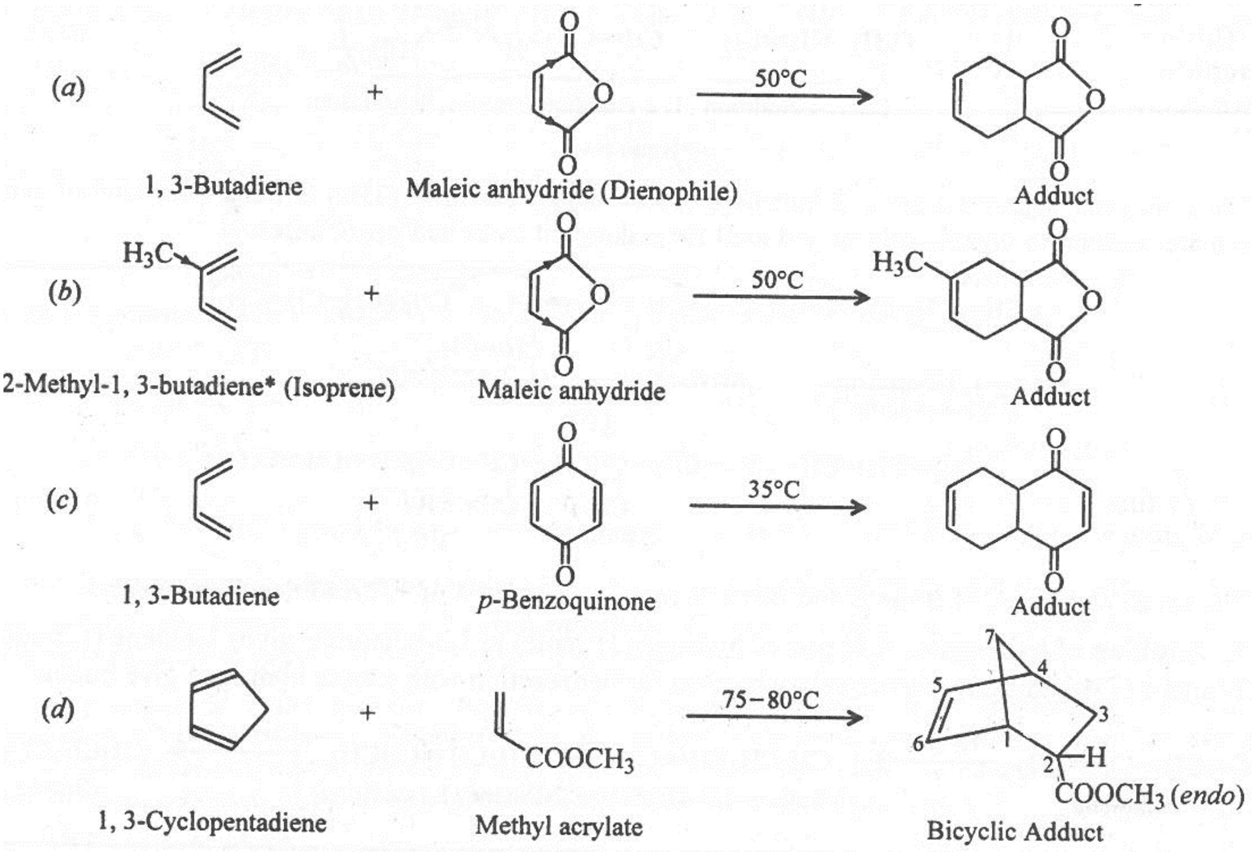
GENERAL DESCRIPTION

This reaction is known after the name of its discoverers **Otto Diels** and **Kurt Alder**. It involves the addition of conjugated dienes to an alkene or an alkyne to form a six membered cycloalkane. The alkene or alkyne taking part in this reaction is known as a **dienophile** (diene loving). For example,



Since, this reaction involves the interaction of four π-electrons from the diene with two π-electrons of the dienophile to form a ring, this reaction is called a **(4+2) cycloaddition reaction**. Simple alkenes or alkynes are poor dienophiles. One or more electron withdrawing substituents (see below) enhance the reactivity of dienophiles. It is also regarded as **nucleophile-electrophile** reaction because the diene being electron rich is a **nucleophile** and the dienophile being electron poor is an **electrophile.**

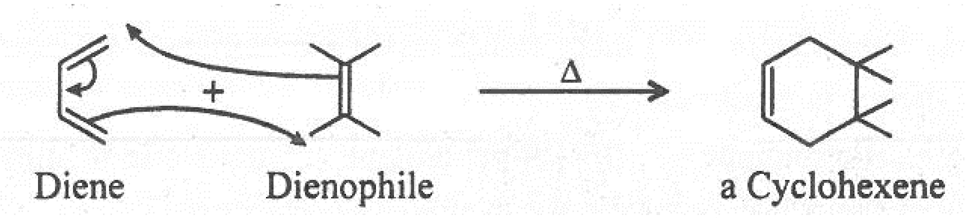
Dienophiles containing electron withdrawing substituents such as -C=O, -COOH, -COOR, C≡N, $-NO_2$ etc., are more reactive in this reaction. On the other hand **electron releasing** substituents like alkyl and alkoxy groups when present on a diene increases the reactivity of this reaction. For example,



The stereochemical preference for the electron-withdrawing substituents to go into the endo position in the adduct of the **Diels-Alder** reaction is called, the **endo rule** or Alder Endo Rule. It may be noted that the endo rule is applicable to other types of Diels-Alder reactions also.

MECHANISM

It is a one-step concerted mechanism, with three pairs of electrons moving simultaneously. The net result of this reaction is the formation of one new π bond and two new σ bonds, as shown below.



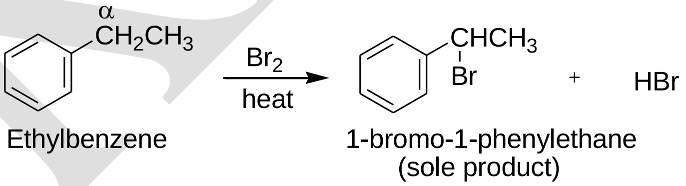
It must be emphasized at this point that the mechanism of Diels-Alder reaction suggested above is rather simplistic. It is actually more complex than this so called electron-pushsing mechanism given above. This reaction essentially involves overlap of orbitals of one molecule with orbitals of the other, and during this interaction of orbitals it is important that the **conservation of orbital symmetry** is ensured.

IMPORTANCE

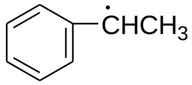
Diels-Alder reaction is a powerful synthetic tool in organic chemistry. It is one of the best ways to make cyclohexenes with diverse functional groups and controlled stereochemistry.

SIDE CHAIN HALOGENATION ONLY AT CARBON DIRECTLY ATTACHED TO BENZENE RING

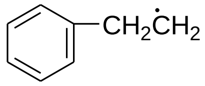
Side-chain halogenation in alkylbenzenes occurs preferentially at position α-to the aromatic nucleus. For example,



Explanation for the dominant α-substitution. Since the side-chain halogenation of alkylbenzenes is a free-radical substitution chain reaction, it would involve radical intermediate. For example,

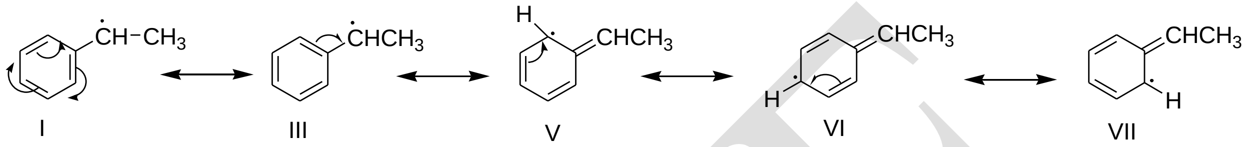


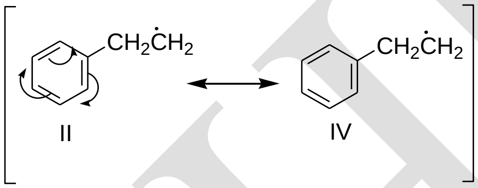
I



II

Each of these radicals is resonance–stabilized as shown below:





Only two structure

Further, three additional contributing structure (V, VI and VII) can be written for the resonance hybrid of I, but no such contributing structures are possible for II.

The radical I, a **benzylic radical**, is thus a resonance hybrid of I, III, V, VI and VII, but the alternative radical II is hybrid of only two structures II and IV. The **benzylic radical I should, therefore, be more stable than the radical II**, and hence I should, therefore be more stable than the radical II, and hence I should be formed more readily than II. In other words, abstraction of benzylic hydrogens should be preferred in such substitution reactions.

ALKYNES

NOMENCLATURE OF ALKYNES

Alkynes are unsaturated hydrocarbons having general formula C_nH_{2n-2}. Such compounds are more unsaturated than alkenes. This is because alkynes contain a triple bond in a molecule. One triple bond is equivalent to two double bonds. First member of this series is acetylene C_2H_2 with two carbon atoms.

Nomenclature of alkynes, according to common system and IUPAC system is given below:

S. No.	Structure	Common name	IUPAC name
1.	$HC{\equiv}CH$	Acetylene	Ethyne
2.	$H_3CC{\equiv}CH$	Methyl acetylene	Propyne
3.	$H_3CH_2CC{\equiv}CH$	Ethyl acetylene	But-1-yne
4.	$H_3CC{\equiv}CCH_3$	Dimethyl acetylene	But-2-yne
5.	$H_3CH_2CC{\equiv}CCH_3$	Ethyl methyl acetylene	Pent-2-yne

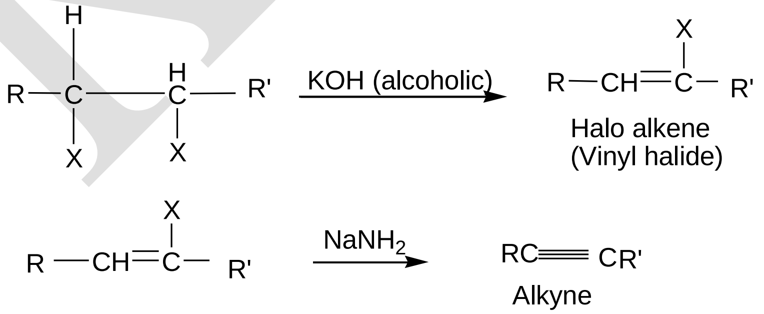
PREPARATION OF ALKYNES

Methods of Preparation of Alkynes are described as under

(i) Dehydrohalogenation of vicinal dihalides.

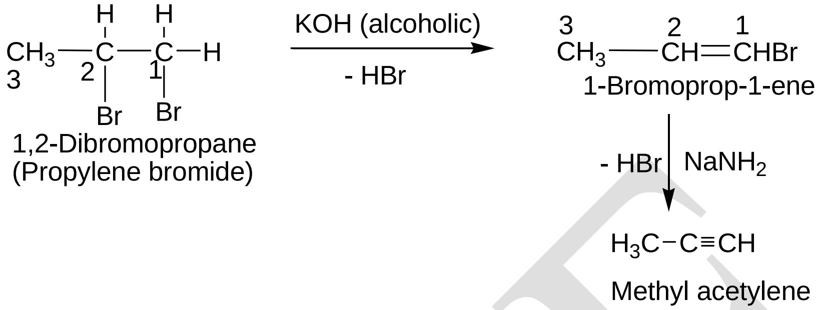
When 1,2-dihaloalkane is heated with alcoholic potash, it undergoes dehydrohalogenation, yielding an alkyne. The reaction takes place in two stages involving the intermediate formation of vinyl halide (haloalkene).

The second stage of reaction generally requires a strong base (sodium amide).



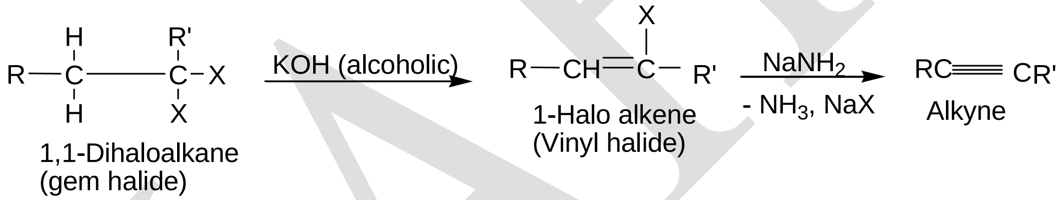
X = Cl, Br or I. R, R' may be H or alkyl group

For example,



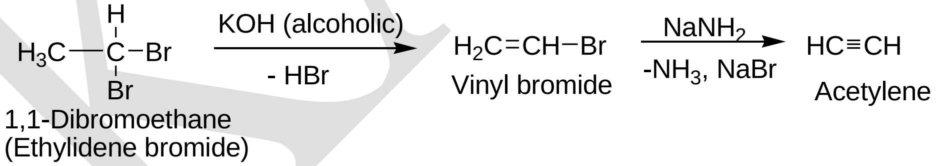
From Gem dihalide. When 1,1- dihaloalkane is heated with alcoholic potash or sodium amide, it undergoes dehydrohalogenation yielding an alkyne. The reaction proceeds in two stages involving the intermediate formation of haloalkene.

The sequence of the reactions is similar to that in dehydrohalogenation of vic., dihalides.

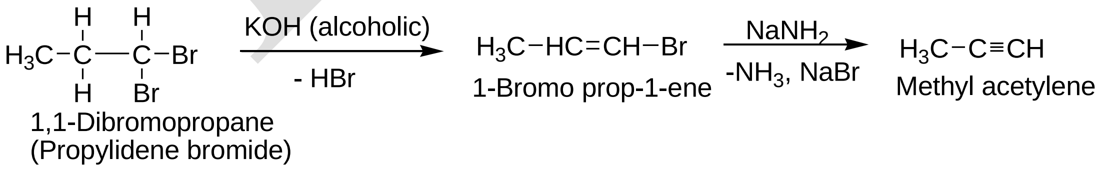


For example,

(a)

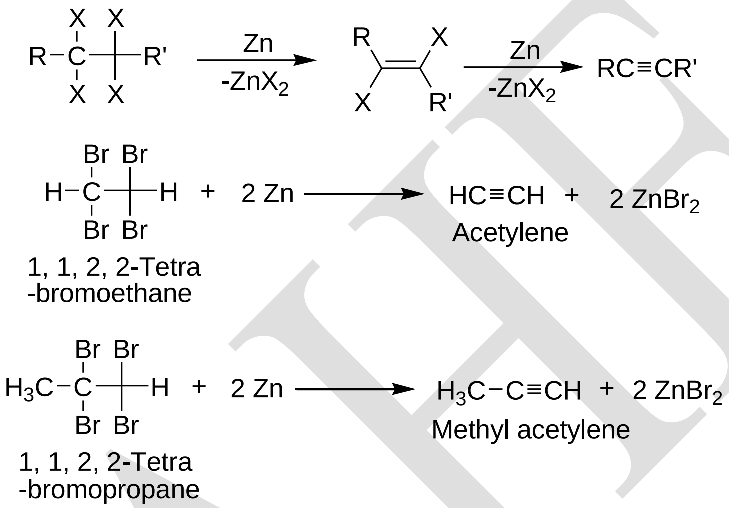


(b)



(i) Dehalogenation of Tetra halides

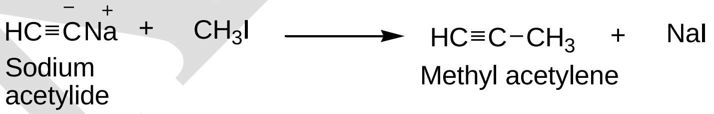
Dehalogenation of tetra halides (1, 1, 2, 2-tetra haloalkanes) is carried out by passing their vapours over heated zinc and it results in the formation of alkyne.



(iii) Action of Acetylides on Alkyl Halides

The metallic acetylides yield higher alkynes by reacting with alkyl halides. It is a very good method of converting lower alkynes into higher alkynes.

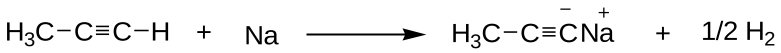
For example,



$$HC{\equiv}\overset{-}{C}\overset{+}{Na} + CH_3I \longrightarrow HC{\equiv}C{-}CH_3 + NaI$$

Sodium acetylide   Methyl acetylene

Acetylides used in the reaction are obtained from alkynes with terminal triple bond ($-C{\equiv}C{-}H$) by the action of sodium or sodium amide.



$$H_3C{-}C{\equiv}C{-}H + Na \longrightarrow H_3C{-}C{\equiv}\overset{-}{C}\overset{+}{Na} + 1/2\ H_2$$

(iv) **Hydrolysis of Calcium Carbides**

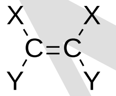
Acetylene is prepared by the hydrolysis of calcium carbide. The latter is obtained by heating lime stone with coke at 2000ºC in an electric furnace.

$$CaCO_3 + 3C \xrightarrow{2000°C} CaC_2 + CO_2 + CO$$

$$CaC_2 + 2\,H_2O \longrightarrow CH\equiv CH + Ca(OH)_2$$

Alkynes do not exhibit geometrical isomerism

The carbon atoms involved in the formation of triple covalent bond in alkynes are sp Hybridised. As a result, alkynes have linear structure. Each triply bonded carbon atom is further linked to only one atom or group of atoms. Hence inspite of hindered rotations, the possibility of different relative spatial arrangement of the groups does not arise. Thus, alkynes do not exhibit geometrical isomerism. This type of isomerism is possible when there are at least two groups attached to one carbon.



Geometrical isomerism possible

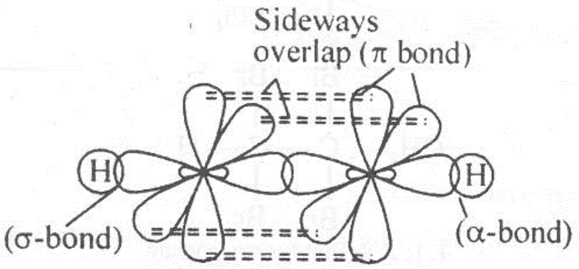
$X-C\equiv C-X$

or Y
Geometrical isomerism not possible

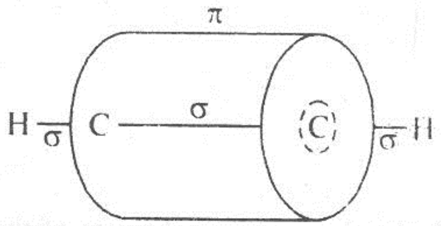
Orbital structure of acetylene

In acetylene molecule both the carbon atoms are sp hybridised. One of the sp hybridised orbitals of carbon overlaps along internuclear axis with similar orbital of the carbon atom to form C-C, σ –bond. The second sp orbital of each carbon atom overlaps along internuclear axis with half filled 1s orbital of hydrogen atom to form C-H, σ–bond each. Since sp orbitals of each carbon atom lie along a straight line and overlapping of these orbitals takes place along their internuclear axis, all the four atoms of acetylene lie along the single straight line. Thus, acetylene is a linear molecule.

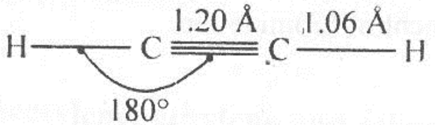
Each carbon atom is still left with two unhybridised p-orbitals which are perpendicular to each other as well as to the plane of carbon and hydrogen atoms. Each of these hybridised orbitals of one carbon atom overlaps sideways with similar orbitals of the other carbon atom to form two π-bonds. There is overlapping between these two π electron clouds. As a result, the four lobes of two π-bonds merge to form a single electron cloud which is cylindrically symmetrical about the internuclear axis.



Orbital picture of acetylene



Cylindrical π electron cloud



Acetylene molecule (shape and size)

The carbon-carbon triple bond is made up of one strong σ-bond and two weak π-bonds.

Bond parameters. The various bond lengths and energies for the molecule of acetylene are given below:

(i) C≡C bond length = 1.20 Å

(ii) C−H bond length = 1.06 Å

(iii) H−C−C bond length = 180°

(iv) C≡C bond dissociation energy = 830 kJ mol^{-1}

(v) C−H bond dissociation energy = 522 kJ mol^{-1}

CHEMICAL REACTIONS OF ALKYNES

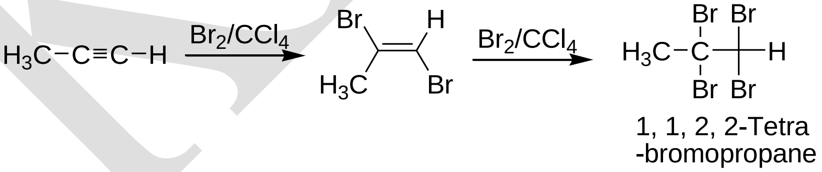
Addition Reactions

Alkynes are less reactive than alkenes towards electrophilic addition reactions. Following factors are responsible for this:

(i) Cylindrical π-electron cloud. In alkynes, the four lobes of two π-bonds merge to form a single electron cloud which is cylindrically symmetrical about the internuclear axis and occupies a big volume. Thus, electron density per unit volume becomes low. Due to decrease in electron density, π-electrons are less available to an electrophile. Hence alkynes are less reactive than alkenes towards electrophilic addition reactions.

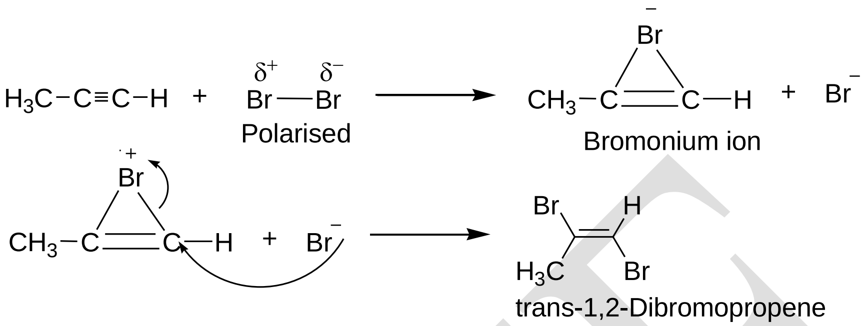
(ii) sp-Hybridisation of carbon. The carbon atoms in alkynes are sp-hybridised while in alkenes are sp^2 hybridised. Greater the s character of an orbital, the more closely the electrons in that orbital are held by the nucleus. Thus л electrons in alkynes are more strongly held by the carbon atoms than in case of alkenes and are less easily available for reactions with electrophiles. Thus makes alkynes less reactive than alkenes in electrophilic reactions.

Bromine readily adds to propyne first forming trans-1,2-dibromopropene and then 1, 1, 2, 2-tetrabromopropane.



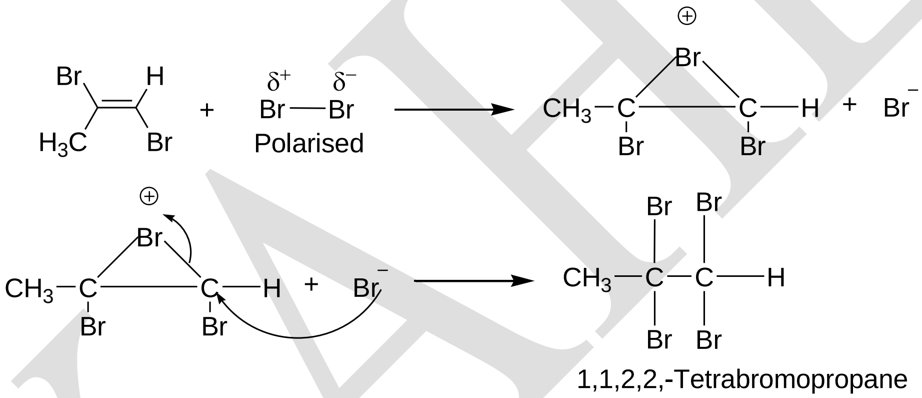
Mechanism. The mechanism of the reaction involves electrophilic addition. It takes place in two steps. This is known as halonium ion mechanism of addition. Bromine (or any halogen) gets polarised under the influence of π-electrons. Bromonium ion (Br^+) adds first forming a bridge bond, followed by the attachment of bromide ion.

First step



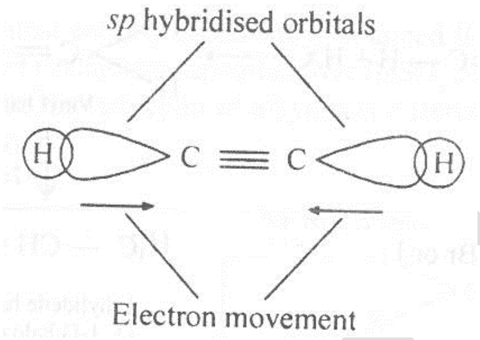
This sequence is repeated in the addition of another bromine molecule.

Second step



Acidic nature of acetylenic protons

In acetylene and terminal alkynes, the hydrogen atom is attached to a sp hybridised carbon which is more electronegative because of increase in s-character. Due to greater electronegativity of the sp hybridised carbon, the electron pair of C-H bond gets displaced more towards carbon and this helps in the release of proton by the strong bases. Consequently acetylene and terminal alkynes behave as acids.



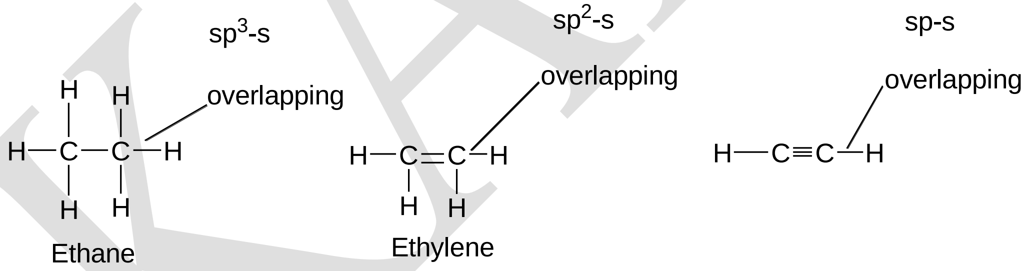
Following reactions illustrate the acidic nature of 1-alkynes:

$$\underset{\text{Acetylene}}{2\,HC{\equiv}C{-}H} + 2\,Na \longrightarrow \underset{\text{Sodium acetylide}}{2\,HC{\equiv}\overset{-}{C}\,\overset{+}{Na}} + H_2$$

$$\underset{\text{Propyne}}{H_3C{-}C{\equiv}C{-}H} + NaNH_2 \longrightarrow \underset{\text{Sodium methyl acetylide}}{H_3C{-}C{\equiv}\overset{-}{C}\,\overset{+}{Na}} + NH_3$$

Comparison of acidic strength of acetylene, ethylene and ethane

Strength of an acid depends upon the ease with which it can lose a proton. This will depend upon the type of bonding between carbon and hydrogen.



(i) In the case of ethane, C-H bond involves overlapping of sp^3 hybrid orbital of carbon and s-orbital of H.

(ii) In case of ethylene, overlapping is between sp^2 hybrid orbital of carbon and s-orbital of H.

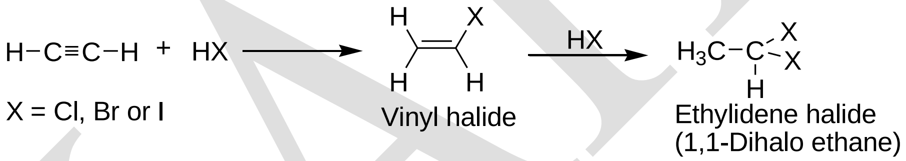
(iii) In case of acetylene, overlapping in C-H bond is between sp hybrid orbital of carbon and s-orbital of hydrogen, s-orbital has greater electron density compared to a p-orbital, which can be explained in terms of their shape . Out of sp^3, sp^2 and sp hybrid orbitals, the sp orbital has the greatest s-character followed by sp^2 and sp^3. Thus carbon atom possessing sp hybrid orbital will have maximum electronegativity followed by carbon having sp^2 hybrid orbitals and then followed by carbon having sp^3 hybrid orbitals.

In view of this, the hydrogen atom in acetylene will be replaceable with maximum ease followed by that in ethylene and ethane. Hence acidic strength decreases in the order.

acetylene > ethylene > ethane

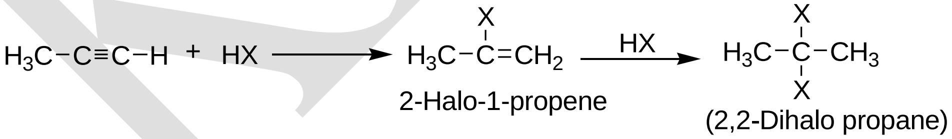
Addition of halogen acids on alkynes

Treatment of alkynes with halogen acid initially yields vinyl halides and finally alkylidene halides. Combination with second molecule takes place in accordance with Markownikoff's rule.

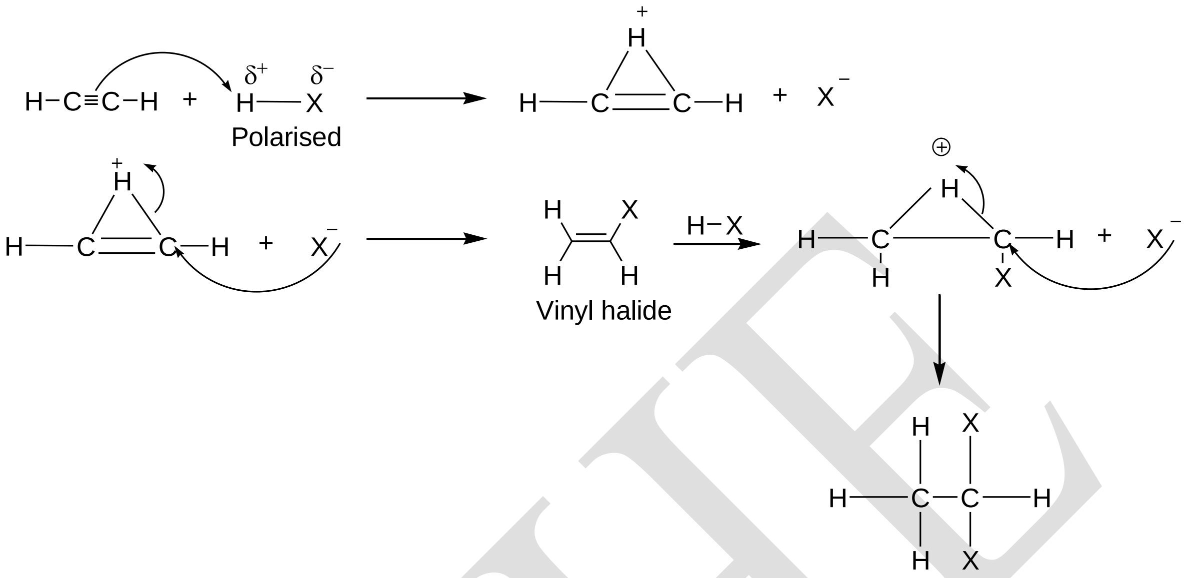


In case of propyne (unsymmetrical alkyne), the first molecule of HX adds according to Markownikoff's rule.

For example,



Mechanism of the reaction is depicted below:

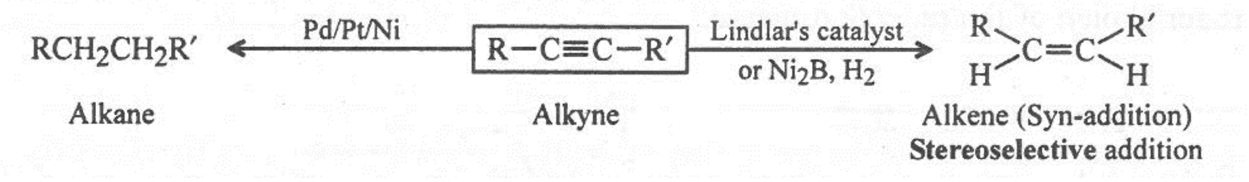


REDUCTION REACTIONS

These can be performed catalytically or chemically as described below:

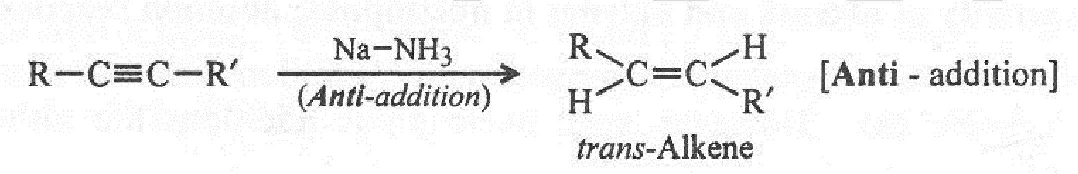
(1) Catalytic reduction. Alkynes can be hydrogenated catalytically first to alkenes and then to alkanes. Direct reduction to alkanes can be achieved by hydrogen in the presence of finely divided Nickel or Pd or Pt. However, reduction to the alkenes stage can be achieved if alkynes are hydrogenated in the presence of **Lindlar's catalyst** (Palladium supported over $CaCO_3$ or $BaSO_4$, but partially poisoned by lead acetate, quinoline, etc.,) or **Nickel boride catalyst** (Nickel borid (Ni_2B) catalyst is better than Lindlar's catalyst in that it is more easily made and often gives better yields) (also known as P-2 catalyst).

For example,

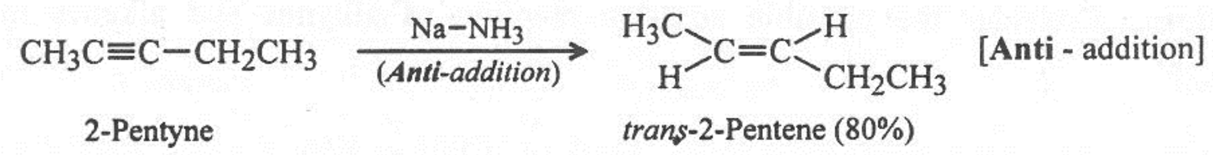


The mechanism of catalytic reduction (hydrogenation) of alkynes is similar to that of the catalytic hydrogenation of alkenes. The faceof a π -bond contacts the solid catalyst and catalyst weakens the π-bond, allowing two hydrogen atoms to add. This simultaneous addition of two hydrogen atoms on the same face of the alkyne ensures **syn-stereochemistry**. Thus, partial hydrogenation of an alkyne with Lindlar's catalyst or the Ni_2B catalyst is a stereoselective and leads almost exclusively to a cis-alkene.

(2) Chemical reduction (Metal-Ammonia reduction): It is stereoselective reaction involving reduction of an alkyne with **Sodium or Lithium in liquid ammonia**. It gives predominantly a trans alkene, as shown below:



For example,



Since, **Birch** used this reduction procedure extensively, Na-NH_3 reduction came to be known as **Birch reduction** also.

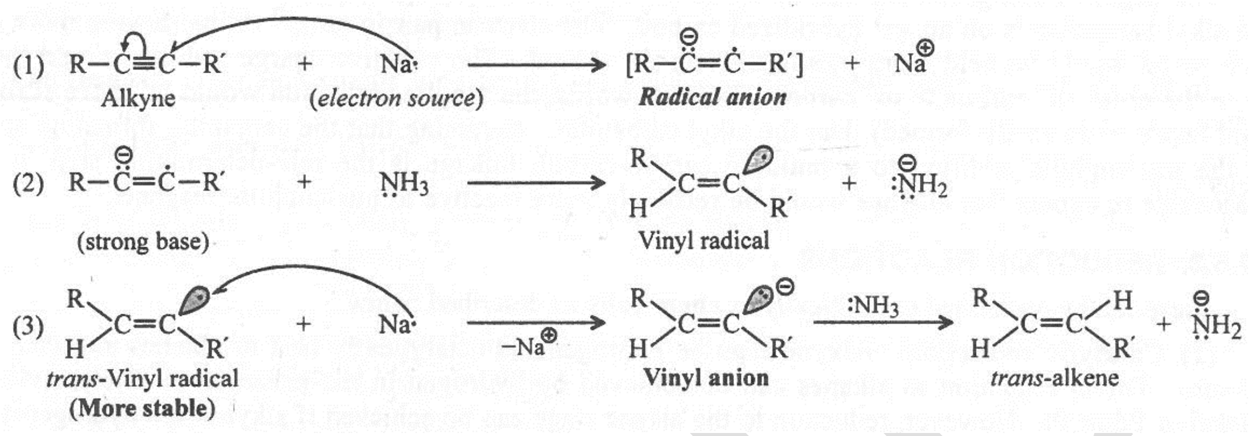
Dry ice (solid carbon dioxide) is often used to keep the NH_3 gas in a liquid stat. As sodium dissolves in liquid ammonia, it gives up electrons and produces a deep blue colour.

$$Na + NH_3 \longrightarrow NH_3 \cdot e^{\ominus} + Na^{\oplus}$$

(Deep blue solution)

The electrons solved in this manner actually reduce the alkyne.

Mechanism: This is illustrated below in the sodium-ammonia reduction of an alkyne.



The first electron from Na goes into an antibonding π-orbital (step 1) to form **radical anion** (strong base). Ammonia acting as an acid protonates the radical anion give vinyl radical (step 2). This takes another electron from Na to form vinyl anion (strong base). Followed by protonation by ammonia to give trans alkene, trans addition is favoured due to **greater stability** of trans–vinyl radical formed in step 2 than cis vinyl radical (alkyl groups intrans configuration are father apart).

Thus we see that catalytically and chemical (metal-ammonia) reductions of an alkyne are complementary. By the proper choice of the reduction method, we can reduce an alkene to either cis-alkene or a trans-alkene.

Addition of HCN

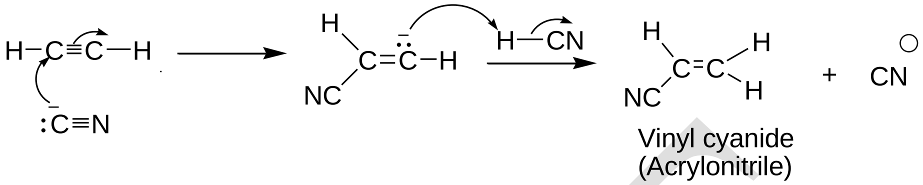
Acetylene reacts with hydrogen cyanide in the presence of barium cyanide yielding vinyl chloride (acrylonitrile).

$$H-C\equiv C-H \quad + \quad HCN \xrightarrow{Ba^{++}} H_2C=CH-CN$$

Vinyl cyanide
(acrylonitrile)

Acrylonitrile is used in the manufacture of Buna N.

The probable mechanism of the reaction is depicted below:

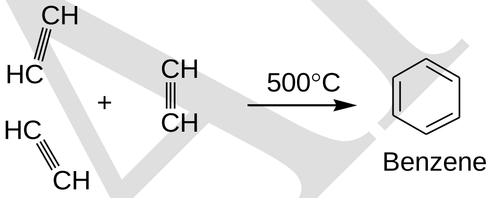


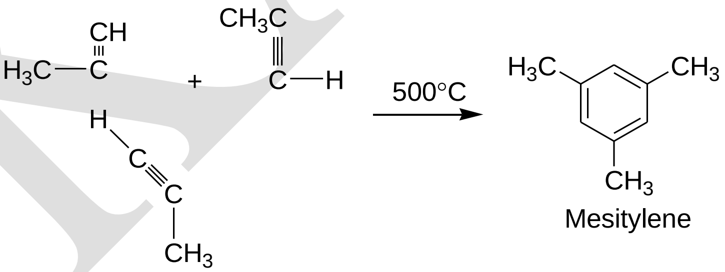
Polymerisation

Acetylene and propyne undergo polymerization in two different ways depending upon the experimental conditions.

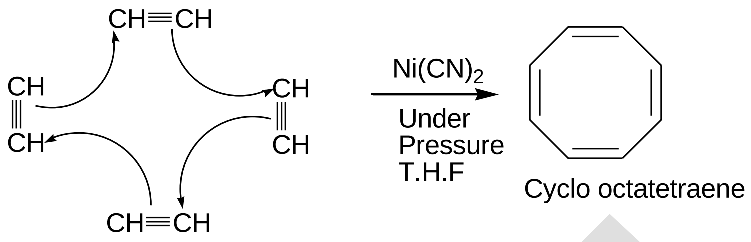
Cyclic polymerization

Acetylene and methyl acetylene when passed through red hot iron tube, polymerize to form benzene and mesitylene respectively.



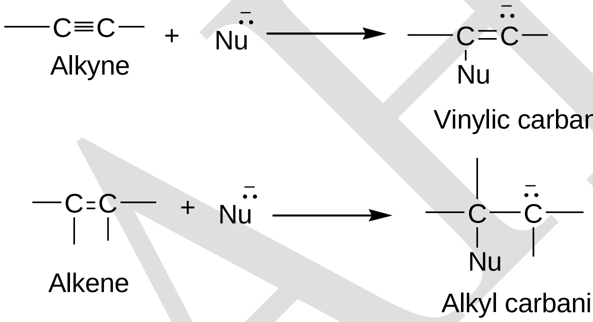


Acetylene when passed through tetrahydrofuran (THF) under high pressure and in the presence of catalyst $Ni(CN)_2$ tetamerises to form cyclo octatetraene.



Nucleophilic Addition reactions

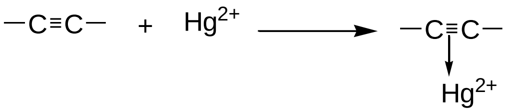
Alkynes undergo nucleophilic addition reactions because of the greater stability of the resulting carbanion formed by the attack of nucleophilie. Thus, consider the possible formation of carbanions formed by the attack of nucleophilie, $\ddot{Nu}$



In vinylic carbanion, the negative charge can be dissipated more easily by the electronegative sp^2 hybridised carbon. In other words, vinylic carbanion is more stable than the alkyl carbanion. Since the rate determining step involves the formation of carbanion, it is clear that alkynes are more susceptible to nucleophilic attack than alkynes.

Mechanism of nucleophilic addition to alkynes

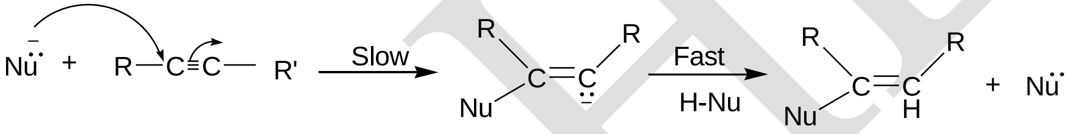
It is observed that such reactions are generally catalysed by the presence of heavy metal salts such as those of mercury and barium .This suggests that metal ions form some sort of complex with alkyne by co-coordinating with the electrons of the pie (π) bonds as shown below:



This complex formation decreases the electron density around the triply bonded carbon atoms and thus helps in the attack by the nucleophilic reagent.

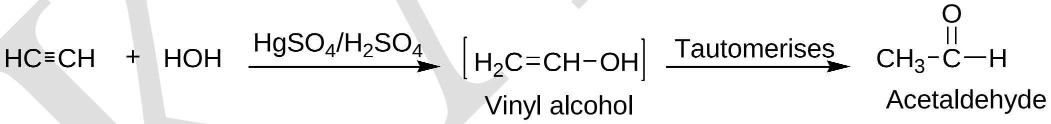
Like electrophilic addition reactions, nucleophilic addition also takes place in two steps.

In the first step, the nucleophilic attacks the alkyne to form a vinyl carbanion. In the second step, the carbanion takes up a proton to form the final product. The complete mechanism may be depicted as follows:

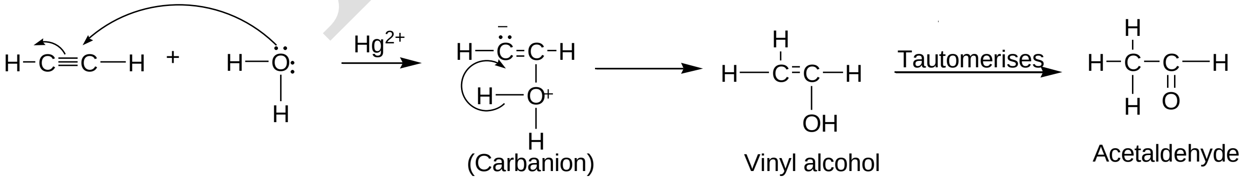


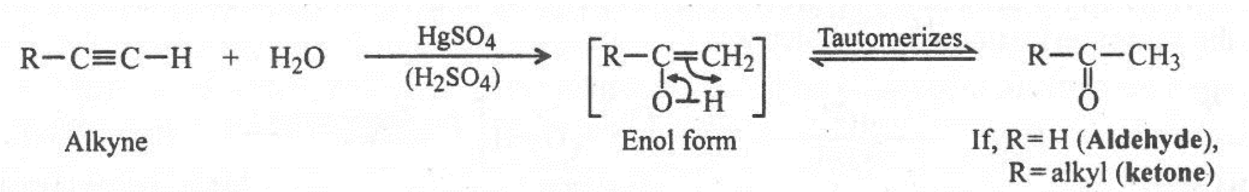
Reaction with dilute sulphuric acid in the presence of mercuric sulphate

When treated with dil. H_2SO_4 in the presence of mercuric sulphate, acetylene gets hydrated to form first an enol which readily tautomerises to form acetaldehyde.

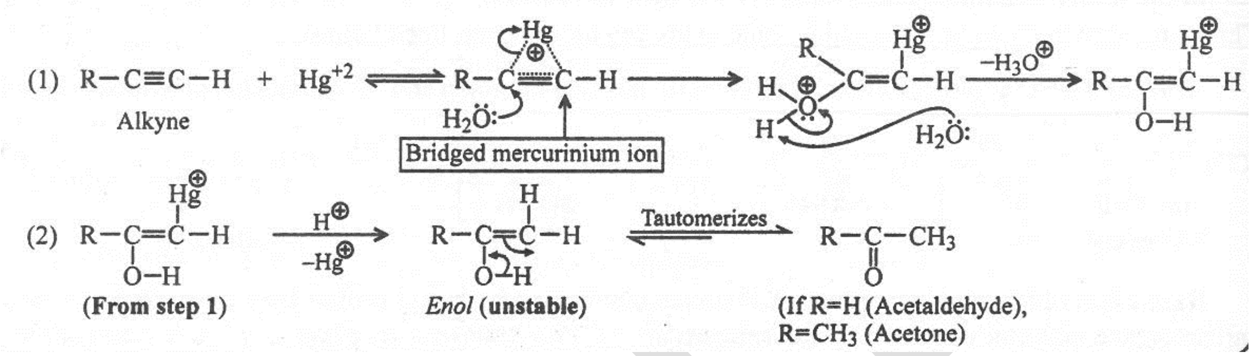


Mechanism. The mechanism involves the nucleophilic attack of water molecule on acetylene to form a carbanion which changes into vinyl alcohol. Since vinyl alcohol is unstable, it tautomerises to form stable aldehyde.





Mechanism: This nucleophilic addition involves the formation of bridged mercurinium ion intermediate with mercuric ions, as shown below.



Text books:

1. Madan, R.L. (2015). *Chemistry for Degree Students.* New Delhi: S. Chand and Company Pvt, Ltd.

2. Morrison, R. N. & Boyd, R. N. (1992). *Organic Chemistry*. New Delhi: Dorling Kindersley Pvt. Ltd. (Pearson Education).

POSSIBLE QUESTIONS

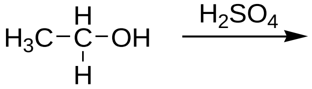
PART A (20 Multiple choice questions)

Online Examinations

PART B (2 marks questions)

1. Define Saytzeff elimination.
2. What is Baeyer's test? Give the reaction.
3. What do you understand by term cycloaddition?

4. Complete the following reaction and discuss its mechanism.



$$H_3C-\underset{H}{\overset{H}{C}}-OH \xrightarrow{H_2SO_4}$$

5. Explain the mechanism of the following reaction.

$$HC\equiv CH \xrightarrow[HgSO_4]{\text{dilute } H_2SO_4}$$

PART C (6 marks questions)

1. What is Markownikoff's rule? Illustrate with suitable examples.
2. (i) Give the mechanism of allylic substitution in alkenes.
   (ii) What do you know about Simmon-Smith reagent?
3. What do you understand by term hydroboration-oxidation? Discuss its mechanism and application.
4. Give the mechanism of 1,2 and 1,4 addition reactions to 1,3-butadiene. What is the effect of temperatures to the addition of HBr to 1,3-butadiene?
5. (i) Why is chair conformation of cyclohexane more stable than the boat conformation?
   (ii) Explain the difference between the terms conformation and configuration by taking suitable examples.
6. (i) Write a short note on Diels-Alder reaction.
   (ii) What is the product of ozonolysis of 2-butyene?
7. (i) Discuss the E1 mechanism of dehydrohalogenation of alkyl halides.

(ii) Write the reaction for the hydroxylation of alkene with osmium tetroxide.

8. (i) How will you explain the acidic nature of C-H bond in acetylene?

(ii) Discuss keto-enoltautomerism with reference to the products of reaction of acetylene with water in the presence of $HgSO_4$ and H_2SO_4.

9. Acidic hydration of propene yields 2-propanol while the hydroboration-oxidation gives 1-propanol. Explain.

10. (i) How will you justify that the addition of halogens to alkenes is of ionic nature?

(ii) What happens when 1,3-butadiene is treated with $BrCCl_3$in the presence of peroxide?

KARPAGAM ACADEMY OF HIGHER EDUCATION

Class: I B.Sc Chemistry Course Name:Organic Chemistry-I (Basics and Hydrocarbon)

Course Code: 19CHU103 Unit: IV Batch-2019-2022

S.No	Questions	opt1	opt2	opt3	opt4	Answer
1.	Chlorination of an alkane as compared to bromination proceeds	at a slower rate	at a faster rate	with equal rates	with equal or different rate depending upon the source of alkane	at a faster rate
2.	The thermal decomposition of alkanes in the absence of air is called	combustion	oxidation	cracking	Hydrogenation	cracking
3.	Alkene undergo addition reactions with halogen and haloacids by the mechanism of	electrophilic substitution	nucleophilic substitution	free radical substitution	Elimination	electrophilic substitution
4.	Addition of HBr to an unsymmetric alkene in the presence peroxide in governed by	nucleophilic addition	free radical addition	electrophilic addition	nucleophilic substitution	free radical addition
5.	1-Pentyne when heated with alc. KOH gives the major product	2-pentyne	1,3-pentadiene	1,2-pentadiene	1,4- pentadiene	2-pentyne
6.	1,3-Butadiene reacts with ethylene to form cyclohexane. This reaction is known as	cyclopropane	4 + 2 cycloaddition	aromatization	2 + 2 cycloaddition	4 + 2 cycloaddition
7.	Out of the following alkenes which one is the most stable?	cis-2-Butene	trans-2-butene	propene	Ethane	trans-2-butene
8.	Dehydrohalogenation of 2-bromobutane with alc. KOH gives mainly	1-butene	2-butene	2-methyl propene	2-butanol	2-butene
9.	Reduction of $R-C\equiv C-R'$ with sodium in liquid ammonia gives	cis-alkene	trans-alkene	both cis& trans-alkene	Alkane	trans-alkene
10.	The major product of addition of HCl to 3,3-dimethyl-1-butene is	2-chloro-2, 3-dimethyl butane	3-chloro-2,2-dimethyl butane	3-chloro-2,2-dimethylbutane	1-chloro-2,2-dimethylbutane	2-chloro-2, 3-dimethyl butane
11.	Which one among the following haloacids shows anti-	HCl	HBr	HI	HF	HBr

	Markovnikovaddition to an asymmetric alkene in the presence of peroxides?					
12.	Addition of hypochlorous acid to propene gives	1-chloro-2-propanol	2-chloro-1-propanol	both compounds	Propene	1-chloro-2-propanol
13.	2-Butene on hydroboration followed by treatment with alkaline H_2O_2 gives	1-butanol	2-butanol	butanal	butan-2-one	2-butanol
14.	trans-2-Butene reacts with diazomethane in liquid phase in the presence of U.V. light to give	cis-1,2-dimethyl cyclopropane	trans-1,2 –dimethylcyclopropane	trans-1,2-dimethyl cyclobutane	cis-1,2-dimethyl cyclobutane	trans-1,2 –dimethylcyclopropane
15.	Baeyer’s reagent used to detect double bond in alkene is	dilutealk. $KMnO_4$	aqueous $KMnO_4$	acid $KMnO_4$	acid $K_2Cr_2O_7$	dilutealk. $KMnO_4$
16.	Hydroxylation of an alkene by peroxytrifluoroacetic acid followed by boiling with water gives-	cis-alkanediol	trans–alkanediol	both cis-and trans –alkanediols	cis vicinal diol	trans–alkanediol
17.	Which one of the following reagent is known as simmon-smith reagent?	Pd/C	Na-liq. NH3	alk. $KMnO_4$	ICH_2ZnI	ICH_2ZnI
18.	An alkene hydrogenation reaction is normally catalyzed by	acid	hydrogen	metal	solvent	metal
19.	The reagent NBS is used for	preparing Gilman reagent	preparing Grignard reagent	preparing alkenes out of alkyl halides	bromination of allylic positions	bromination of allylic positions
20.	Addition of HBr to 1,3-butadiene above 40ºC gives mainly	3-bromo-1-butene	1-bromo-2-butene	2-bromo-1-butene	3-bromo-1-butane	1-bromo-2-butene
21.	Addition of bromine (1mole) to 1,3-butadiene at 60ºC gives mainly	cis-1, 4-dibromo-2-butene	3,4-dibromo-1-butene	trans-1,4-dibromo-2-butene	meso-1, 4-dibromo-2-butene	trans-1,4-dibromo-2-butene
22.	Electron withdrawing substituent in dienophile in Diels –Alder reaction	favour cyclization	disfavour cyclization	does not effect cyclization	no cyclization	favour cyclization
23.	Which reagents/conditions are not used for dehydration reactions?	concentrated sulfuric acid	concentrated phosphoric acid	phosphorus oxychloride	KOH/ethanol	KOH/ethanol
24.	Which substrates cannot be reduced with lithium aluminium hydride, LAH?	alkenes	ketones	esters	Aldehydes	alkenes
25.	The first step in the mechanism for	attachment of	a carbocation	protonation of	no reaction takes	protonation of an

	electrophilic addition of HBr to an alkene is	the bromide to the most substituted carbon	rearrangement	an alkene carbon to yield a carbocation	place	alkene carbon to yield a carbocation
26.	Diels-Alder reaction takes place in an	endo adduct	exo adduct	meso adduct	exo and endo adduct	endo adduct
27.	Which addition product of 1,3-butadiene is thermodynamically more stable ?	1,2	1,3	1,4	1,2 and 1,3	1,4
28.	The decreasing order of acidity of ethane, ethylene and acetylene is	ethane >ethene>ethyne	ethyne>ethene> ethane	ethene>ethyne> ethane	ethyne> ethane >ethane	ethyne>ethene> ethane
29.	Hydroboration oxidation of 2-butyne with BH_3-H_2O_2 and alkali gives	2-butanone	2-butanol	1-butanol	Butanal	2-butanone
30.	1-Pentyne when heated with alc.KOH gives the major product	1, 2-Pentadiene	2-pentyne	1, 3-pentadiene	2-pentanone	2-pentyne
31.	Which of the following is the most acidic?	ethane	ethene	ethyne	Ammonia	ethyne
32.	The hydration of acetylene requires strong acid catalysis. Which catalyst gives the best results?	sulfuric acid	mercuric sulphate	sulfuric acid and magnesium sulphate	sulfuric acid and mercuric sulphate	sulfuric acid and mercuric sulphate
33.	2-Butyne adds two molecules of hypochlorous acid to form	2-butanone	3,3-dichloro-2-butanone	butanal	2,3-butanediol	3,3-dichloro-2-butanone
34.	Propyne adds a molecule of water in the presence of H_2SO_4 and Hg^{+2} to give	acetone	propanal	1-propanol	2-propanol	acetone
35.	Ethylbenzene on bromination gives mainly	1-bromo-1-phenyl ethane	1-bromo-2-phenyl ethane	2-bromo-2-phenyl ethane	mixture of 1-bromo-2-phenyl ethane and 2-bromo-2-phenyl ethane	1-bromo-1-phenyl ethane
36.	Which one is more selective in side chain halogenations of ethyl benzene?	fluorine	chlorine	bromine	iodine	bromine
37.	Chlorination of toluene in the presence of sunlight is governed by	free radical mechanism	ionic mechanism	cationic mechanism	anionic mechanism	free radical mechanism

38.	Cyclohexanol can be converted into cyclohexene by heating with	Zn (Hg) and HCI	conc.H_2SO_4	$SOCl_2$	H_2 and Ni	conc.H_2SO_4
39.	Reaction of alkene with diborane is called	hydroxylation	hydration	hydroboration	Reduction	hydroboration
40.	Cummulateddiene is called	allene	1,3-butadiene	1,4-pentadiene	1,5-pentadiene	allene
41.	In Diels Alder reaction, diene reacts with	dipole	azomethineylide	azomethineylide	Dienophile	dienophile
42.	Markovnikov's addition of HBr is not applicable to	propene	1-butene	1-pentene	2-butene	2-butene
43.	Which of following compounds will react most readily with bromine in CCl_4?	$CH_3CH_2CH_3$	$(CH_3)_3CH$	$CH_3CH=CH_2$	$(CH_3)_4C$	$CH_3CH=CH_2$
44.	Ethylene reacts with HI to give	iodoethane	2,2-diiodoethane	1,3-diiodopropane	Methyliodide	iodoethane
45.	2-Butene reacts with HBr to give	1-bromobutane	2,3-dibromobutane	2-bromobutane	2,3-dibromobutene	2-bromobutane
46.	2-Methylpropene reacts with HBr to give	tert-butyl bromide	isobutane	n-butyl bromide	tert-butane	tert-butyl bromide
47.	Which of the following alkenes reacts with HBr in the presence of a peroxide to give anti Markovnikov's product?	1-butene	2,3- dimethyl-2-butane	2-butene	3-hexene	1-butene
48.	In the addition of HX to a double bond, the hydrogen goes to the carbon that already has more hydrogen's, is a statement of	Hund's rule	Markovnikov's rule	Huckel rule	Saytzeff rule	Markovnikov's rule
49.	In the reaction of $CH_3CH_2CH=CH_2$ with HCl, the H of the HCl will become attached to Which carbon?	C-1	C-2	C-3	C-4	C-1
50.	The disappearance of the purple colour of $KMnO_4$ in its reaction with alkene is known as	Markovnikov test	Grignard test	Baeyer test	Wurtz test	Baeyer test

51.	Which of the following reagents will react with propene?	hot alkaline $KMnO_4$	sodium metal	cold dilute HNO_3	$LiAIH_4$	hot alkaline $KMnO_4$
52.	Which of the following will give a negative test when treated with bromine in carbon tetrachloride?	butane	2-butene	1,3-butadiene	3-butyne	butane
53.	Which of the following compounds on hydrolysis gives acetylene?	CaC_2	Mg_2C_3	Al_4C_3	Cu_2Cl_2	CaC_2
54.	Which alkyne yields propanoic acid as the only product upon treatment with ozone followed by hydrolysis ?	1-butyne	2-hexyne	1-pentyne	3-hexyne	3-hexyne
55.	Lindlar's Catalyst is	$LiAlH_4$	Pd /$BaSO_4$ in quinoline	NH_2NH_2	HCl / $ZnCl_2$	Pd /$BaSO_4$ in quinoline
56.	A triple bond consists of	2 sigma bonds and 1 pi bond	2 sigma bonds	1 sigma bonds and 2 pi bonds	3 pi bonds	1 sigma bonds and 2 pi bonds
57.	Propyne reacts with aqueous H_2SO_4 in the presence of $HgSO_4$ to form	acetone	proponol-1	acetaldehyde	propan-2-ol	acetone
58.	1-Butyne can be distinguished from 2–butyne by using	potassium permanganate	bromine in CCl_4	tollen's reagent	chlorine in CCl_4	tollen's reagent
59.	Toluene on chlorination in the presence of sunlight undergoes	side-chain substitution	ring substitution	electrophilic substitution	nucleophilic substitution	side-chain substitution
60.	Side chain substitution takes place through	cationic mechanism	free radical mechanism	anionic mechanism	ionic mechanism	free radical mechanism
61.	Toluene reacts with bromine in the presence of UV light to give.	m-bromotoluene	benzyl bromide	o-bromotoluene	benzoyl bromide	benzyl bromide

UNIT-V

Syllabus

Aromaticity

Aromaticity: Hückel's rule, aromatic character of arenes, cyclic carbocations/carbanions and heterocyclic compounds with suitable examples. Electrophilic aromatic substitution: halogenation, nitration, sulphonation and Friedel-Craft's alkylation/acylation with their mechanism. Directing effects of the groups.

AROMATICITY

Organic compounds which resemble benzene in their chemical behaviour are called aromatic compounds. They exhibit certain characteristic properties which are quite different from those of aliphatic and alicylic compounds. These characteristic properties are collectively referred to as **aromaticity or aromatic character**.

Characteristics.

(i) Although their molecular formulae suggest a high degree of unsaturation, yet they do not respond to tests characteristic of unsaturated compounds. Thus, aromatic compounds fail to decolorise an aqueous solution of potassium permanganate (Baeyer's test).

(ii) They undergo readily certain electrophilic substitution reactions such as nitration, halogenation, sulphonation, Friedel-Crafts alkylation and acylation, etc.

(iii) Their molecules are flat or nearly flat as shown by physical methods such as X-ray and electron diffraction methods.

(iv) They are associated with high thermodynamic stability as is indicated by their low heats of combustion and hydrogenation.

Aromatic compound was naturally thought that compounds showing aromaticity contain at least one benzene ring. However, this notion soon proved wrong. Today, we know compounds which contain no benzene ring and yet they show aromatic character or aromaticity. Such compounds are called **nonbenzenoid aromatic compounds** to distinguish them from the usual

benzenoid aromatic compounds containing one or more benzene rings. More recently, we have term such as **antiaromatic compounds** or **nonaromatic compounds** also. We propose to discuss these term/concepts in some detail in the following subsection, and then consider what the latest picture we have about the **aromaticity** of organic compounds.

AROMATIC, ANTIAROMATIC AND NON AROMATIC COMPOUNDS

For a compound to be aromatic, it must meet following criteria:

1. It must be cyclic compound with some number of conjugated π bonds.
2. Each atom in the ring must have an unhybridized p orbital (the ring atoms or usually sp^2 hybridized).
3. The unhybridized p orbital must overlap to form a continuous ring of parallel orbitals. The structure must be planar or nearly planar for an effective overlap to occur.
4. The delocalization of the π electrons over the ring must decrease the electronic energy.

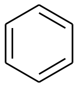
The criterion (4) above is crucial. If the delocalization of π electrons over the ring **increases electronic energy**, the compound would be **antiaromatic** even if it meets the criteria 1 through 3. When a cyclic compound does not have a continuous, overlapping ring of p orbitals, it cannot be aromatic or antiaromatic. It is said to be **nonaromatic** or **aliphatic**. **It electronic energy is similar to that of its open-chain counterpart**.

When we use this approach, we take a linear chain of **sp^2 hybridized atom** that carrier the same number of π electrons as our cyclic compound. Imagine that we have removed two hydrogen atoms from the ends of this chain to form a ring. If this ring has lower π electron energy then the open chain the ring is said to be **aromatic**. If the **ring** and **chain** have the same π electron energy, than the ring is said to be **nonaromatic**. If the ring as **greater π electron energy then the open chain**, the ring is said to be **antiaromatic**.

It may be pointed out the classical criteria such as **resistance to addition** (e.g., failure to decolorise a solution of bromine in carbon tetrachloride or an alkaline potassium permanganate solution as in Bayer test), reaction typical of π bonds and occurrence of substitution reactions characteristic of benzene seem to be unnecessary in today's context. Once a compound meets the essential criteria listed above, the compound would automatically show these reactions also. These classical criteria for aromatic character have not, therefore, been included here.

Examples:

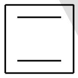
(i) **Benzene**. The Kekule' structure of benzene (cyclohexatriene) meets all the criteria of an aromatic compound listed above. Since it has **lower** energy than that of its open-chain counterpart **1, 3, 5-hexatriene**, it is more stable than the open-chain counterpart. Therefore, benzene or its Kekule' structure (cyclohexatriene) should be, and actually is, **aromatic** (see below).



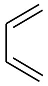
Benzene (Cyclohexatriene)
More stable (**Aromatic**)

1, 3, 5-Hexatriene
Less stable (**non aromatic**)

(ii) **Cyclocbutadiene**. It meets the first three criteria listed above, but delocalization of the π electrons **increase** its electronic energy. It is, therefore, less stable than it open-chain counterpart, **1, 3-butadiene**. So, cyclobutadiene should be, and actually is, **antiaromatic** (see below).

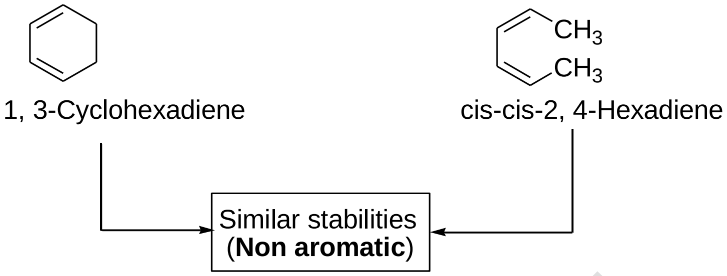


Cyclobutadiene
Less stable (**Antiaromatic**)



1, 3-Butadiene
More stable

(iii) **1, 3-Cyclohexdiene**. Since it does not have a continuous overlapping ring of p orbitals as required under criterion (3) listed above, it cannot be aromatic or antiaromatic. Its electronic energy is similar to that of its open-chain counterpart cis, cis-2, 4-hexadiene. In other words, it is about as stable as its open-chain counterpart. 1,3-Cyclohexadiene, therefore, should be, and is, **non aromatic** (see below).



HUCKEL'S RULE

Erich Huckel, a German chemical physicist, proposed this rule in early 1930s. Based on certain quantum mechanical calculations. This rule enables us to predict whether a given system is aromatic or antiaromatic. Huckel's rule is applicable only if the system meets the following pre-requisite:

1. A cyclic structure.
2. An unhybridized p orbital on each atom of the ring.
3. A planar or nearly planar structure so that there is a continuous or nearly continuous overlap of all p orbitals of the ring.

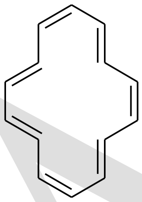
Once the compound/system fulfills these pre requisites, Huckel's rule applies. **Huckel's Rule** states that if the number of π electrons in the system is (4n + 2), the system is **aromatic**, and if it is (4n), the system is **antiaromatic** or **nonaromatic**, where **n is a positive integer** (0, 1, 2, 3, 4, - - -). Thus, common aromatic system have 2, 6, 10 - - - - π electrons and antiaromatic and nonaromatic systems have 4, 8, 12, - - - - π electrons. Benzene and cyclobutadiene, for example, fulfill all the three pre-requisites cited above. Whereas benzene with six π electrons is a (4n + 2) system, cyclobutadiene with four π electrons is a (4n) system. Therefore, benzene should be **aromatic** and cyclobutadiene should be **antiaromatic,** according to Huckel's rule. This is actually so.

APPLICATION OF HUCKEL'S RULE

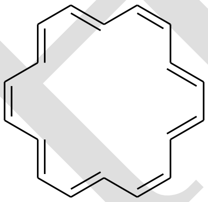
Huckel's rule has been applied to a wide variety of systems. The important results of these studies are summarised here.

A. **Large Ring Hydrocarbons (Annulenes)**. This study has led to three kinds of results, and these are described under the following subheads:

(a) **Those which are aromatic**: [14]-Annulene and [18]-annulene are (4n + 2) systems. They can attain planar structures. Therefore, these annulenes should be, and actually are, aromatic, as predicted by Huckel's rule. [18]- Annulene has, in fact, resonance energy of about 100 kcal/mol.

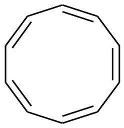


[14] Annulene

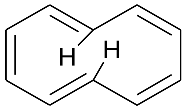


[18] Annulene

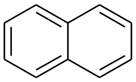
(b) **Those which are nonaromatic**: All-cis [10]-annulene, a (4n + 2) system, is expected to be aromatic, but it **cannot attain planarity** due to excessive **angle strain**. Therefore, all-cis [10]- annulene is **nonaromatic** despite being a (4n + 2) system. Even [10]-annulene with two trans double bonds cannot assume a planarity because the two hydrogens interfere with each other. Therefore, [10]-annulene with two trans double bonds also is nonaromatic. It is interesting that when these interfering hydrogens (show in antic) are removed, the resulting hydrocarbon (naphthalene) is planar an aromatic.



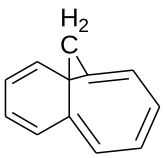
[10] Annulene
all cis non-planar
(Nonaromatic)



[10] Annulene
Two trans double bond
non-planar **(Nonaromatic)**



Naphthalene
(aromatic)



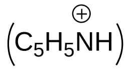
Bicyclo [4, 4, 1]
undeca-1, 3, 5, 7, 9-pentaene
(aromatic)

An unusual hydrocarbon (bicycle[4,4,1] undeca-1,3,5,7,9-pentaene) has been prepared in which two interior hydrogens have been replaced by a bridging methylene (-CH_2) group. This hydrocarbon cannot have completely coplanar π system, but **enough cyclic overlap occurs to give aromatic character.**

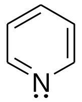
(c) **Those which behave like polyalkenes**: Cyclooctatetraene, which is rarely named as an annulene, is considered here along with the usual annulene such as [12]-and [16] annulene for want of a better place.

B. **Heterocyclic compounds**. Hitherto, we have applied Huckel's rule to only hydrocarbons. Let us now apply Huckel's rule to heterocyclic compounds with rings containing sp^2 hybrizides atoms other then carbon (say, N, O and S).

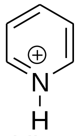
(a) **Pyridine**: It is a nitrogen analogue of benzene in which one of the (C-H) units of benzene has been replaced by nitrogen with a nonbonding pair of electron. These nonbonding electrons on nitrogen are in an sp^2 hybrid orbital in the plane of the ring. They are perpendicular to the π system and do not overlap with it. Pyridine is thus a planar molecule with six delocalized electrons (sextet) in its π system and the nonbonding electrons on N are not interacting with the π electrons of the ring. Pyridine, therefore, should be and actually is, **aromatic** (resonance energy ≈ 125 kJ/mol) in character. Since pyridine is basic, it can be protonated to give a pyridinium ion



$\left(C_5H_5\overset{\oplus}{N}H\right)$. Since the additional proton on N has no effect on the electrons of the aromatic sextet, pyridinium ion also should be, and actually is, still aromatic. It may be noted that both pyridine and pyridinium ion meet Huckel's criteria of aromaticity also (monocyclic, planar, a 2p orbital on each atom of the ring and the sextet of electron in the π system). Thus, **the aromaticity of pyridine and pyridinium ion is in accord with Huckel's rule**.

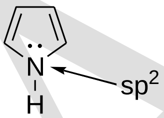


Pyridine
(**aromatic**)

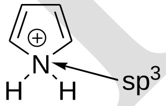


Pyridinum ion
(**aromatic**)

(b) **Pyrrole, Furan and Thiophene**: In pyrrole, N atom is sp^2 hybridized and its unhybridized p orbital overlaps the p orbitals of carbons to form a continuous ring. Unlike the lone pair of electrons on pyridine N, the lone pair of pyrrole N occupies the p orbital and these electrons take part in the π bonding system. These two electrons, together with the four π electrons of the two double bonds, complete the **aromatic sextet**. Thus, pyrrole should be, and is **aromatic** (resonance energy ≈ 88 kJ/mol) as per Huckel's rule. Pyrrole is a much weaker base than pyridine because of the structure of the protonated pyrrole (pyrrole N has to become sp^3 hybridized to abstract a proton and this eliminates the unhybridized p orbital needed for aromaticiy). Therefore, **protonated pyrrole**, unlike protonated pyridine, should be, and is, **nonaromatic**.

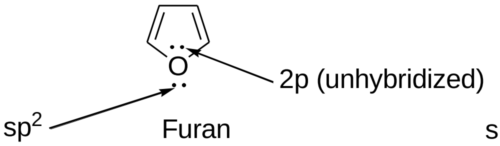


Pyrrole
(**aromatic**)

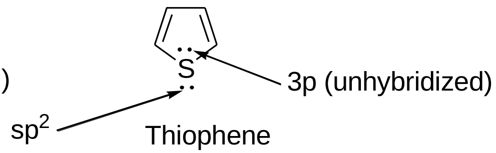


Protonated pyrrole
(**nonaromatic**)

In furan one lone pair of electrons of the hetero atom (O) lies in the unhybridized 2p orbital and is a part of the π system whereas the other lone pair in an sp^2 hybrid perpendicular to the p orbitals and is not a part of the π system. Thiophene with S having two lone pairs of electrons is similar, expect that S uses an unhybridized 3p orbital to overlap with the 2p orbitals on cations. Thus, furan and thiophene, with their aromatic sextets should be, and actually are **aromatic** (resonance energies of 67 kJ/mol and 177 kJ/mol respectively). This is in accord with Huckel's rule too.

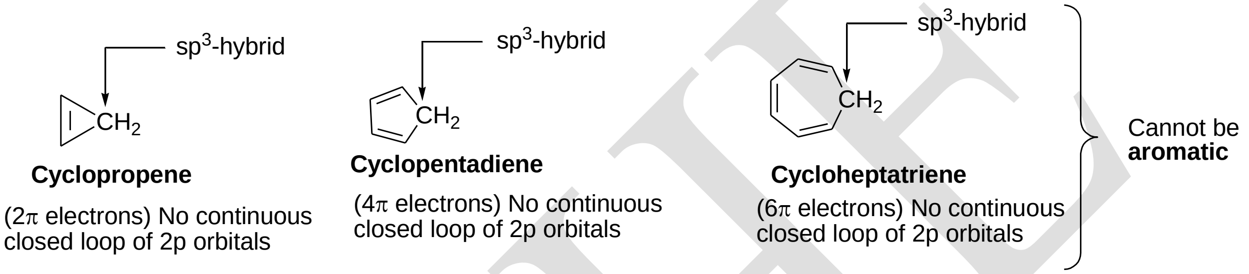


Furan
(**aromatic**)



Thiophene
(**aromatic**)

C. **Ions** : If we recall the hydrocarbons to which Huckel's rule has been applied so far, we find that all those hydrocarbon (aromatic as well as antiaromatic) were monocyclic unsaturated hydrocarbons having an even number of carbon atoms. A neutral monocyclic unsaturated hydrocarbon with a odd number of carbon atoms in the ring must necessarily have at least one methylene ($-CH_2-$) group in the ring, but such molecules cannot be aromatic because they cannot have a continuous **closed loop of 2p orbitals**. For example,



Cyclopropene

(2π electrons) No continuous closed loop of 2p orbitals

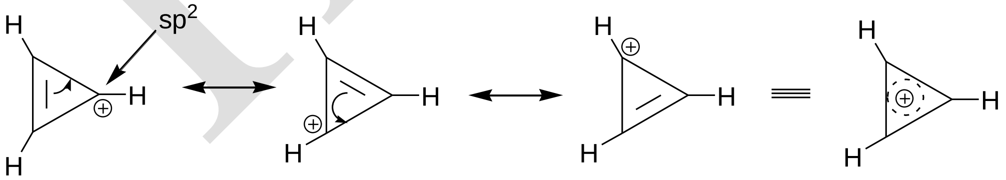
Cyclopentadiene

(4π electrons) No continuous closed loop of 2p orbitals

Cycloheptatriene

(6π electrons) No continuous closed loop of 2p orbitals

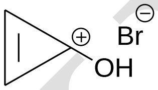
(a) **Cyclopropene versus cyclopropenyl cation**: Cyclopropene has two π electrons [a typical Huckel number under Huckel's $(4n + 2)$ rule for aromaticity, where $n = 0$, i.e., $4(0) + 2 = 2$. Apparently, cyclopropene can be aromatic, but it lacks a continuous closed ring of 2p oritals and this makes Huckel's rule unternabel in the case of cyclopropene. Howere, if we convert cyclopropene into cyclopropyl cation, we create an sp^2 hybridized carbon with an empty 2p orbital. In that case, the overlap of p orbitals becomes continuous. Therefore, cyclopropyl cation, unlike cyclopropene, should be **aromatic** in accordance with Huckel's rule. Further, cyclopropenyl cation is a resonance hybrid of **three equivalent** contributing structures, as shown below:



I II III

Resonance hydrid of cyclopropenyl cation continuous closed loop of 2p orbitals can be aromatic.

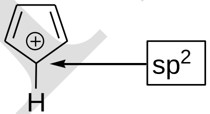
The following experimental fact also furnished proof for the aromatic stabilization of cyclopropenyl cation. Stable **cyclopropenium salts** such as cyclopropenyl hexachloroantimonate and hydroxyl-bromide have been prepared by R. Breslow (1967). Presence of **three** equivalent protons in cyclopropenyl cation also confirms the structure of this **non-benzenoied aromatic** ring system.



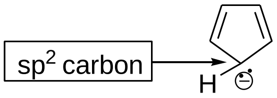
Hydroxycyclopropenyl
bromide: stable

Thus, cyclopropenyl cation meets all the requirements of Huckel’s rule for aromaticity. In addition, its aromaticity is supported by experimental evidence cited above. Therefore, **cyclopropenyl cation, unlike cyclopropene, is aromatic**.

(c) **Cyclopentadienyl cation versus Cyclopentadienyl anion**: The cyclic, planar and conjugated cyclopentadienyl cation with four π electrons is a (4n) system under Huckel’s rule. Therefore, **cyclopentadienyl cation** should be expected to be **antiaromatic**. That it is actually so is confirmed by the fact that cyclopentadienyl cation, unlike cyclopropenyl cation, fails to form a stable salt regardless of the fact that it can be shown as a resonance hybrid of five equivalent contributing structures.



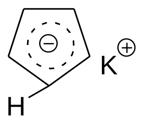
Huckel number-(4)
Cyclopentadienyl cation
(antiaromatic)



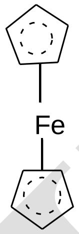
Huckel number-(6)

Resonance-stabilized
Cyclopentadienyl anion
(aromatic)

Cyclopentadienyl anion (also called cyclopentadienide ion) has sp^2 carbon and has two electrons in its unhybridised 2p orbital. This anion, with a sextet of electrons (n = 1), is a (4n + 2) system and meets all the criteria of Huckel rule for aromaticity. Therefore, cyclopentadienyl anion should be, actually is, **aromatic**. The aromaticity of this anion is further confirmed by the experimental observations that cyclopentadienide ion (i) forms a stable potassium cyclopentadienide salt and (ii) **ferrocene** (a stable orange solid, m.p. 173ºC) is dicyclopentadienide iron.

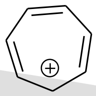


Potassium salt

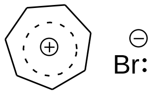


Ferrocene (stable)m.p.173^{o} C
undergose electrophilic aromatic substitution reactions (**aromatic**)

(d) **Cycloheptatrienyl cation (tropylium ion)**: It contains an sp^2 hybridized carbon with an empty 2p orbital. Thus, cycloheptatrienyl cation is planar, has a sextet of π electrons, forms a continuous ring of p orbitals, and is a resonance hybrid of seven equivalent contributing structures. In other words, cycloheptatrienyl cation meets all the Huckel requirements for aromaticity. Therefore, cycloheptatrienyl cation should be, and actually is, **aromatic**. Its aromaticity is further supported by existence of stable tropylium salts such as tropylium bromide and hydroxy tropyium chloride.



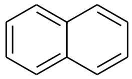
Cycloheptatrienyl cation or tropylium ion
(6 π electrons)

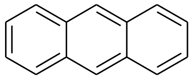


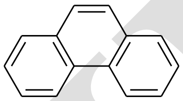
Tropylium bromide
(stable, an aromatic ion)

D. **Polycyclic compounds**: Strictly speaking, Huckel's rule for aromaticity and antiaromaticity is applicable to monocyclic systems only. However, certain polycyclic systems have also responded positively to this rule for aromaticity and antiaromaticity, though the rule has to be modified slightly sometimes.

(a) **Polynuclear hydrocarbons**: Naphthalene (I), anthracene (II) and phenanthrene (III) have 10, 14 and 14 π electrons respectively (the typical Huckel numbers for aromaticity). They also shown chemistry typical of benzene. These polynuclear hydrocarbons, should be, and are, **aromatic** even on the basis of Huckel's rule. This conclusion is supported by the resonance energy data of these ring systems. Compared with benzene (150 kJ/mol); Naphthalene, Anthracene and phenanthrene have shown resonance energies per benzene ring of 127 kJ, 117 kJ and 128kJ/mol respectively.


Naphthalene (I)
10 π electrons stable
similar to benzene


Anthracene (II)
14 π electrons stable
similar to benzene


Phenanthrene (III)
14 π electrons stable
similar to benzene

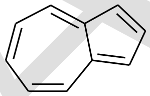

Benzene (IV)
6 π electrons
stable

All **aromatic**
compound

(b) **Azulene**: It has 10 pi electrons (a typical Huckel number, when n = 2). So, it should be, and actually is, aromatic even by **Huckel rule**. Its aromaticity is further confirmed by-

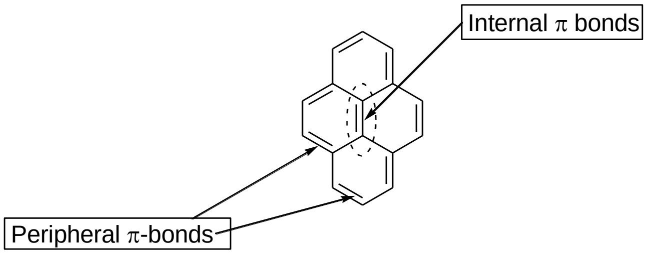
(i) Its existence as an intensely blue stable solid, m. p. 99ºC,

(ii) Its chemistry being similar to that of benzene despite the absence of benzene ring in it.

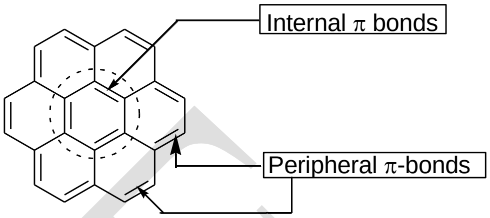

Azulene
10 π electrons stable
similar to benzene

Thus, **azulene is a non-benzenoid aromatic compound**.

(c) **Pyrene and related hydrocarbons**: Since pyrene with 16 pi electrons is a 4n system, it should be expected to be an antiaromatic compound under the Huckel's rule (where n = 4). Experimentally, it behaves like a typical aromatic compound. To account for this anomaly, Huckel's rule was modified slightly. The modified Huckel's rule states that "in polycyclic systems, Huckel's rule is applicable only to **the peripheral π electrons** of the compound". Pyrene has only 14 peripheral π electrons (a typical Huckel number for aromaticity, where n= 3). With the modified Huckel's rule, pyrene also falls in line with **aromatic**, rather than antiaromatic, compounds. This prediction was confirmed when V. Boekelheide (University of Oregon synthesized trans-15,16-dimethyldihydropyrene and showed that it is aromatic).



Pyrene 16 π electron (**14**-Peripheral) with one Kekule' structure behave like **aromatic** compounds satisfies Modified Huckel Rule, the internal double bond enclosed in a dotted circle.



Coronene 24 π electrons(**18**-Peripheral) with one Kekule' structure behave like **aromatic** compounds satisfies Modified Huckel Rule, the internal double bond enclosed in a dotted circle.

Similarly, coronene, with 24 π electrons but only 18 peripheral π electrons, should be expected to show aromaticity according to the modified Huckel's rule and it is actually so.

Thus, we see that Huckel's rule gives a fairly reliable guideline to determine if a given cyclic compound is **aromatic or antiaromatic**. Strictly speaking, Huckel's rule is applicable only to monocyclic compounds. However, the modified Huckel rule accounts for aromaticity of complex polycyclic compounds such as pyrene and coronone also. In conclusion, it must be stressed that an aromatic compound does not have at least a benzene ring always. **Non-benzenoide aromatic compounds/ions** are also known today.

GENERAL MECHANISM OF ELECTROPHILIC SUBSTUTION IN BENZENE

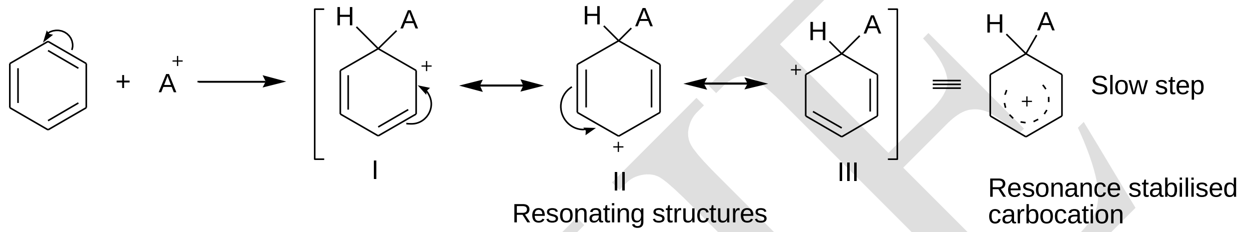
Electrophilic substitution reactions are initiated by substances which are either electrophilic themselves or which generate some electrophilic species. General mechanism involves the following sequence of steps:

(I) Generation of electrophile. To start with, there is preliminary reaction which generates an electrophile.

$$A + B \longrightarrow \overset{\oplus}{A} + \overset{\ominus}{B}$$

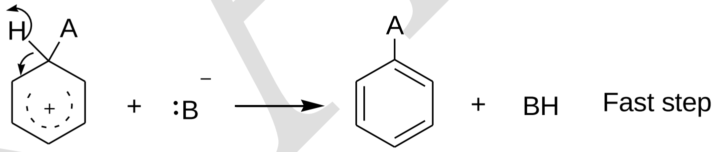
Electrophile

(II) Formation of intermediate carbocation (carbonium ion). The electrophile attacks the π electron cloud of the benzene ring and thus brings about an electronic displacement. This result in the formation of **intermediate carbocation** which is resonance stabilized as shown below:



During the formation of the carbocation, the aromaticity of the benzene ring is destroyed. Consequently, the formation of the carbocation is slow and hence is the **rate determining step**.

(III) Abstraction of a proton from the carbocation. The base present in the reaction mixture abstracts the proton from the carbocation to form the final product. Since the aromatic character of the benzene ring is restored, this step is **fast** and hence is not the rate determining step.

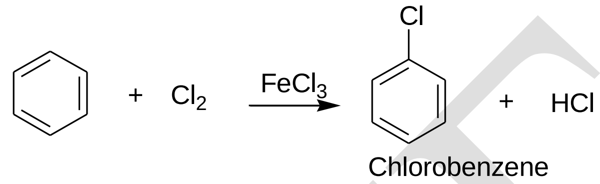


Electrophilic substitution

Benzene has a tendency to give electrophillic substitution reactions because of the π-electron cloud above and below benzene ring. In these reactions, a hydrogen atom of benzene is substituted by $–NO_2$, -X (halogens), $-SO_3H$, -R (alkyl) or –COR group, under different conditions and by taking a suitable electrophile. Such reactions are called electrophilic substitution reactions.

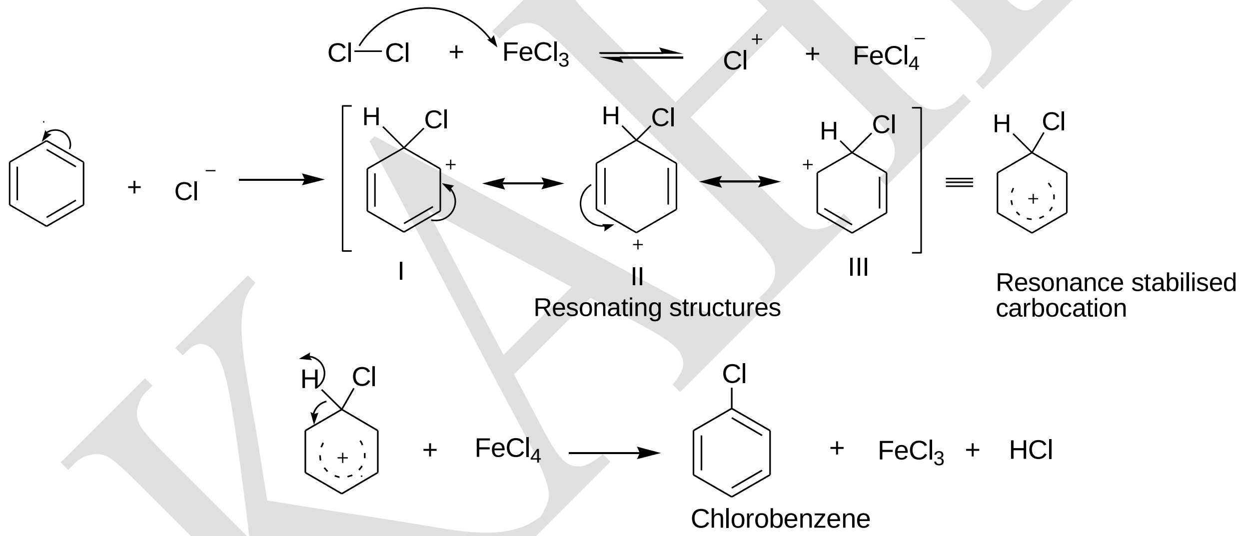
Halogenation of Benzene

Halogenation of benzene and other aromatic hydrocarbons can be brought about by treating with halogens in the presence of Lewis acids such as ferric halides, anhydrous aluminium chloride. Chlorination of benzene is considered below:



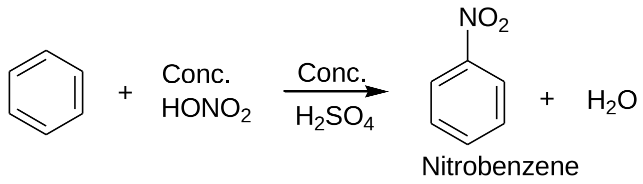
Mechanism: Various steps involved in the reaction are as follows:

(I) Generation of electrophile



Nitration

This reaction involves the treatment of an aromatic compound with a mixture of nitric acid and sulphuric acid. For example:

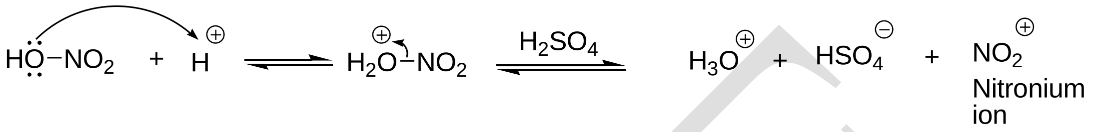


Mechanism. The various steps in the nitration of benzene can be outlined as below:

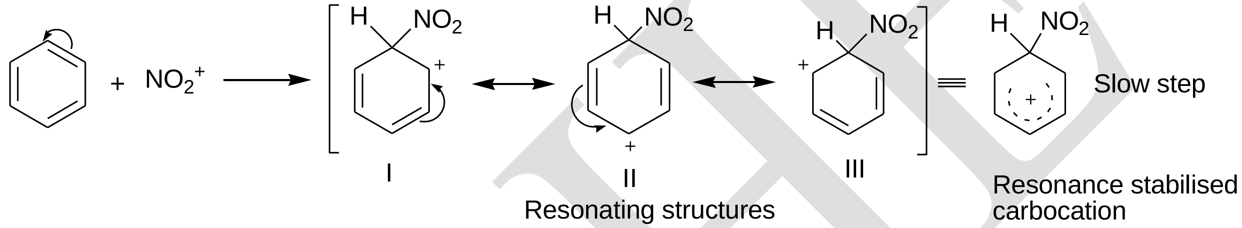
(I) Generation of electrophile

$$HONO_2 + 2H_2SO_4 \rightleftharpoons \underset{\text{Nitronium ion}}{NO_2^+} + H_3O^+ + 2HSO_4^-$$

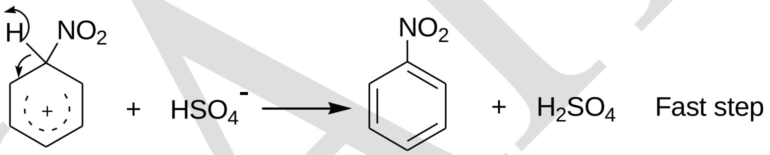
$$H_2SO_4 \rightleftharpoons H^{\oplus} + HSO_4^{\ominus}$$



(II) Formation of carbocation

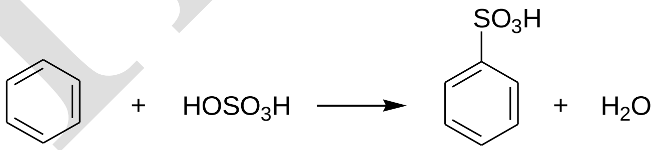


(III) Abstraction of proton from the carbocation

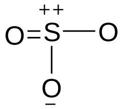


Sulphonation of Benzene

The sulphonation of an aromatic compound can be brought about by the action of conc. H_2SO_4 or oleum. For example:



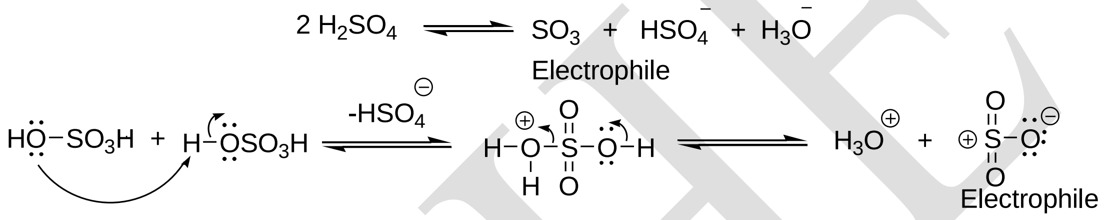
Mechanism: The attacking electrophilic reagent in this reaction is believed to be sulphur trioxide which is present as such in oleum or may be formed by the dissociation of sulphuric acid. The electrophilic nature of SO_3 molecule is due to the presence of electron deficient sulphur atom.



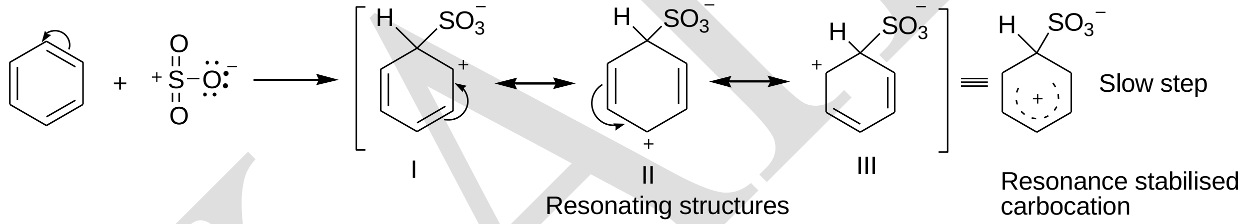
As the positive charge is concentrated on sulphur and negative charges are scattered on two oxygens, SO_3 molecule acts as electrophile.

The complete mechanism for this reaction may be outlined as follows:

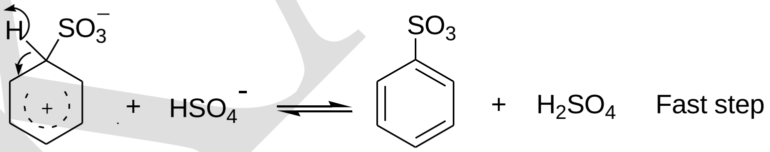
(I) Generation of electrophile



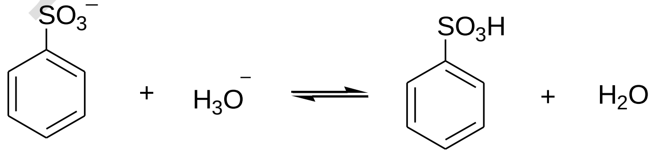
(II) Formation of carbocation



(III) Abstraction of proton from the carbocation

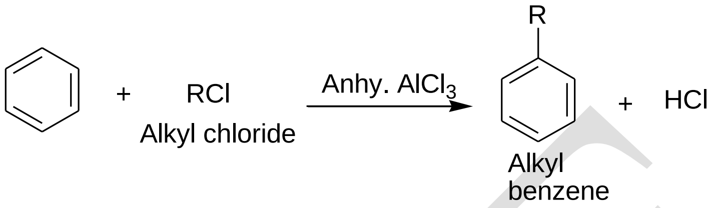


(IV) Formation of the final product



Friedel-Crafts Alkylation of Benzene

The reaction consists in treating benzene or substituted benzenes with an alkyl halide in the presence of small amounts of Lewis acids ($AlCl_3$, BF_3, $FeCl_3$, etc..,). It leads to the direct introduction of an alkyl group into the benzene ring.

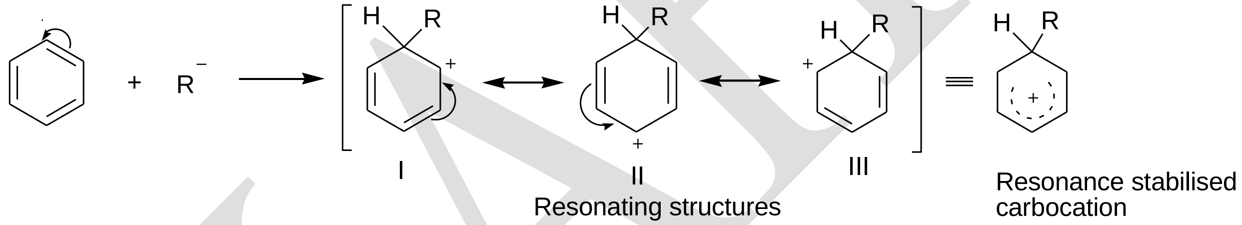


Mechanism: The reaction is believed to take place through the following steps:

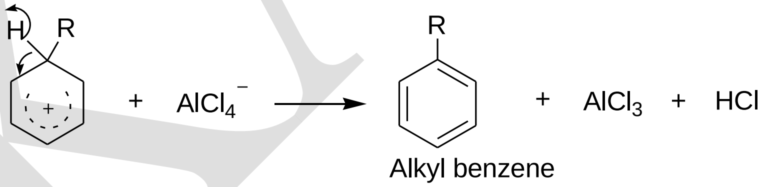
(I) Generation of electrophile

$$R-Cl + AlCl_3 \rightleftharpoons \underset{\text{Electrophile}}{\overset{+}{R}} + AlCl_4^-$$

(II) Formation of carbocation

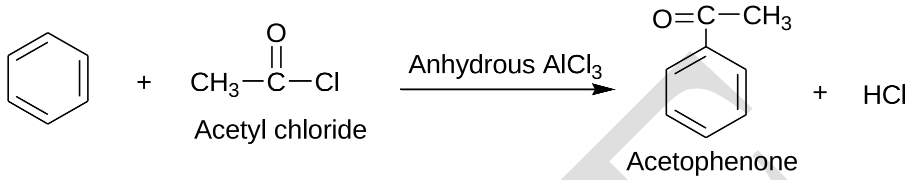


(III) Abstraction of proton from the carbocation



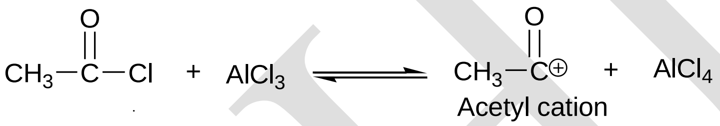
Friedel-Craft's Acylation of Benzene

When benzene is treated with acetyl chloride in the presence of anhydrous aluminium chloride, the formation of acetophenone takes place. This reaction is known as Friedel-Craft's acylation.

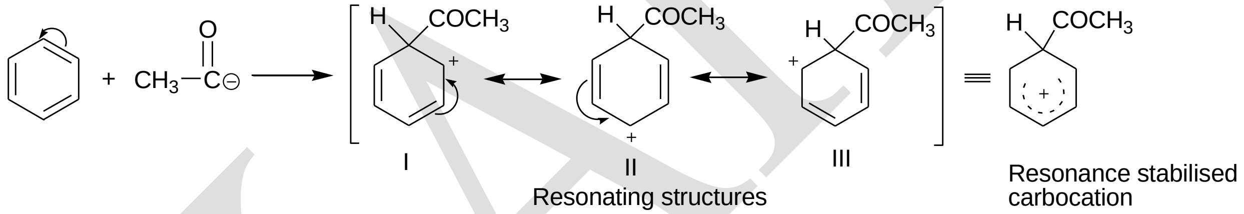


Mechanism: The most probable mechanism of the above reaction is discussed as under:

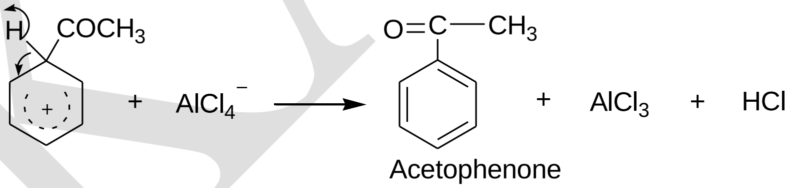
(I) Generation of electrophile



(II) Formation of carbocation



(III) Abstraction of proton from the carbocation



EFFECT OF SUBSTITUENTS ON ORIENTATION AND REACTIVITY OF BENZENE RING

It has been observed that substituents already attached to the benzene ring not only govern the orientation of further substitution but also affect the reactivity of benzene ring. It is discussed in brief as below:

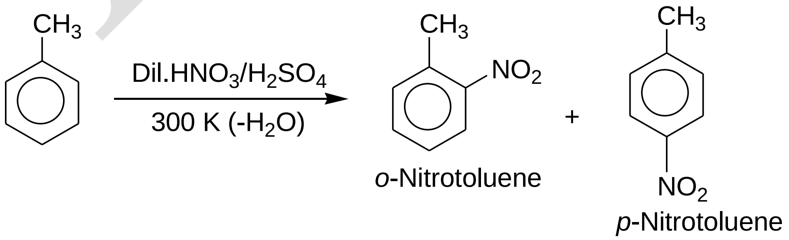
(I) Effect of substitution on orientation. As stated above, the nature of the group already attached to benzene ring determines the position of the incoming group. In general, groups have been classified into two categories:

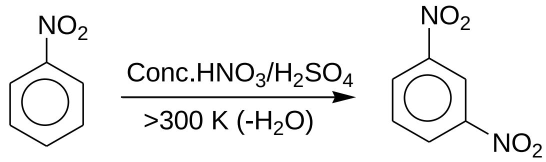
(a) Ortho-para directing groups. The groups which direct the incoming group towards ortho and para positions are called ortho–para directing groups. Groups such as –R, -C_6H_5, -OH, SH, -OR, -NH_2, -NHR, -NR_2, -Cl, -Br, -I, etc. are all ortho-para directing group.

(b) Meta directing groups. The groups which direct the incoming groups towards meta position are called meta directing groups. Groups such as –COOH, -CHO, -CN, -NO_2, COR, -SO_3H, etc., are all meta directing groups.

It may be mentioned that groups which contain double or triple bond are usually meta directing while those which do not contain multiple bonds are ortho-para directing. However, there are certain exceptions to this rule.

(II) Effect of substituents on reactivity. Reactivity of the benzene ring in electrophilic substitution reactions depends upon the tendency of the substituent group already present in the benzene ring to release or withdraw electrons. A group that release electrons activates benzene ring while the one which draws electrons deactivates the benzene ring. It is found that except halogens all ortho-para directing groups activate the ring and all meta directing groups deactivate the ring towards further electrophilic substitution. Thus, nitration of toluene can be carried out at room temperature, while that of nitrobenzene requires more drastic conditions. This is illustrated as below:

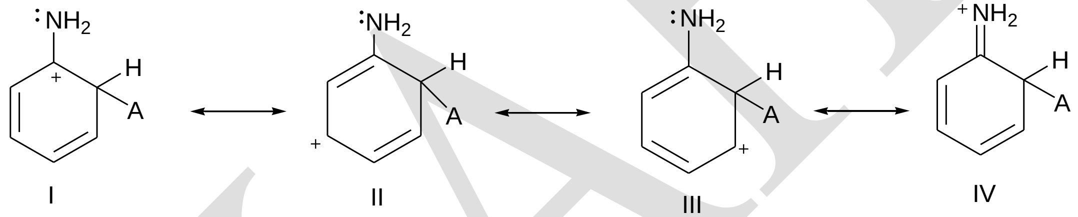




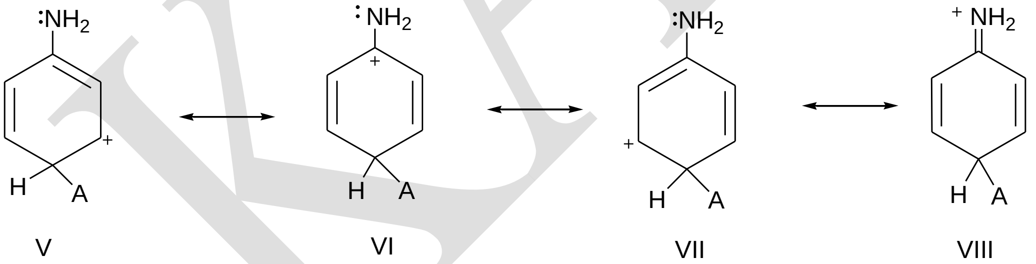
m-Dinitrobenzene

Electron Interpretation of the Ortho-para Directing Influence of Amino group

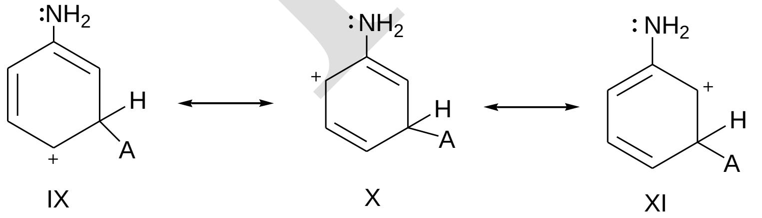
Amino group exerts electron withdrawing (-I) and electron releasing (+M) effects. Of the two opposing effects, the resonance effect dominates and the overall behaviour of $–NH_2$ group can be explained by assuming that nitrogen can share more than a pair of electrons with the benzene ring and can accommodate a positive charge. Thus, consider the case of further electrophilic substitution in aniline. The various resonating structures of the carbocations formed by ortho, para and meta attack are given below:



Ortho attack



Para attack



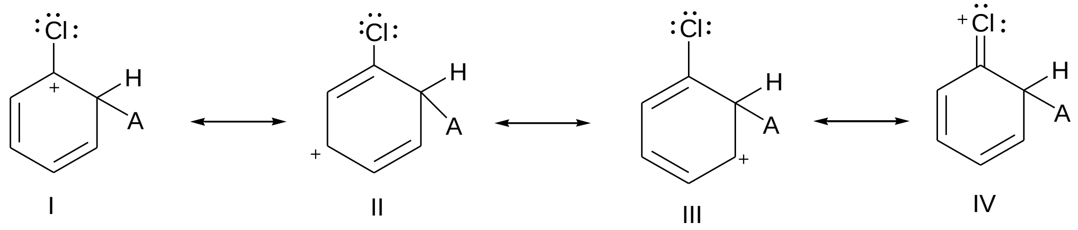
Meta attack

The intermediate carbocation resulting from ortho as well as para attack is a resonance hybrid of four structures while the one formed by meta attack is a resonance hybrid of three structures. Further, in structures IV and VIII, the positive charge is carried by nitrogen. These structures are more stable since in every atom (except hydrogen) has a complete octet of electrons in them. No such structure is, however, possible in case of meta attack. It is, therefore, clear that the resonance hybrid carbocations resulting from ortho and para attack are more stable than the carbocation formed by attack at the meta position. Consequently, further electrophilic substitution in aniline occurs faster at the ortho and para positions than at the meta position. In other words $–NH_2$ group is an ortho and para detecting group.

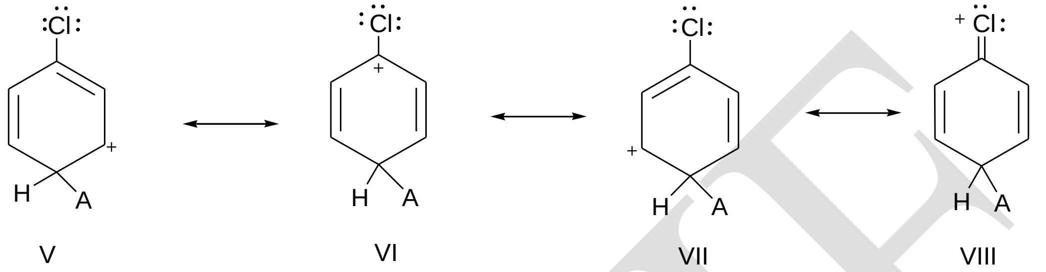
Ortho- Para Directing Influence of Halogens

Halogens exert electron withdrawing (-I) and electron releasing (+M) effects. Due to high electronegativities of halogens, the inductive effect predominates over the mesomeric effect and thus the overall behaviour of halogens is electron withdrawing. In other words, halogens act as deactivators for further substitution.

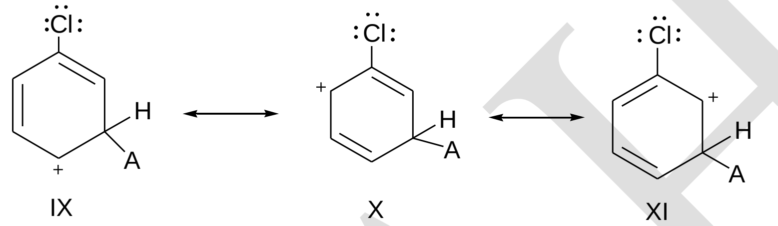
In order to account for their ortho and para directing nature, it has been assumed that halogens can share more than one pair of electrons with the benzene ring and can accommodate positive charge. Thus, consider the case of further electrophilic substitution in chlorobenzene. The various resonating structures of the carbocation formed by ortho, para and meta attack are given below:



Ortho attack



Para attack



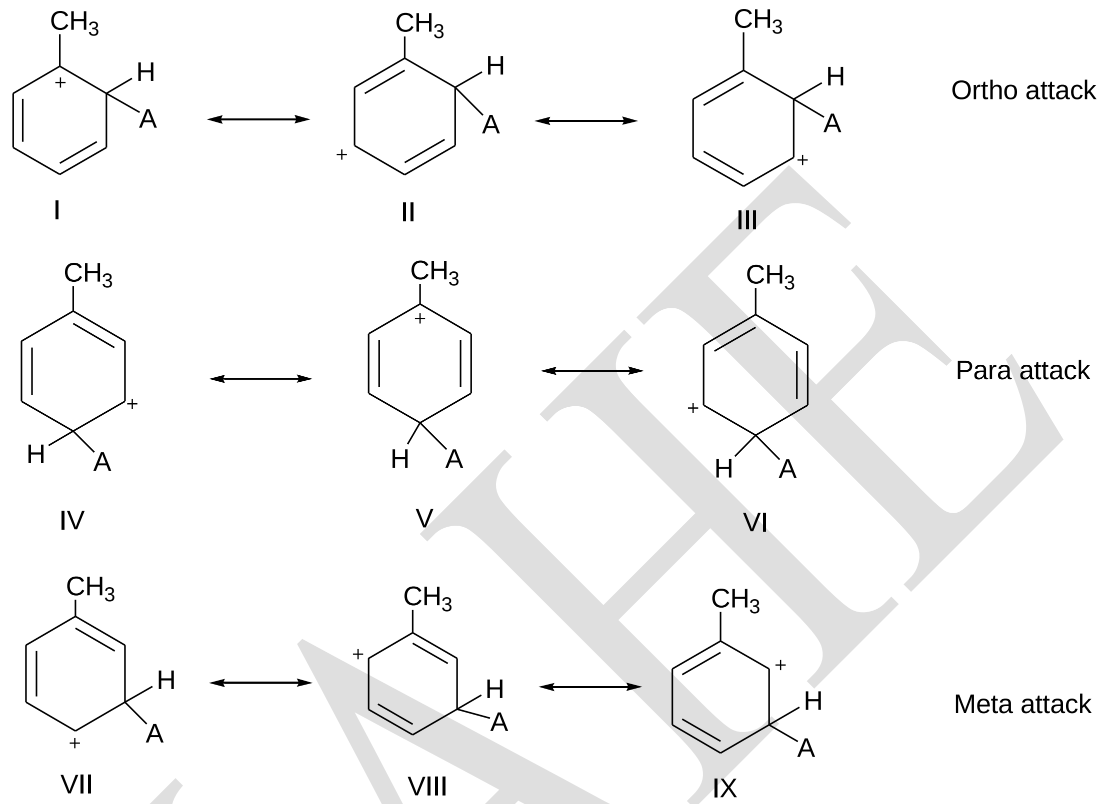
Meta attack

It is clear that the intermediate carbocation resulting from ortho as well as para attack is a resonance hybrid of four structures while the one formed by meta attack is a resonance hybrid of three structures. Structures (I) and (VI) are highly unstable since in these the positive charge is carried by that carbon which is linked to electron withdrawing chlorine atom. However in structures (IV) and (VIII), the positive charge is carried by chlorine. These structures are extra stable since in every atom (except hydrogen) has a complete octet of electrons in them. No such structure is, however, possible in case of meta attack. Thus, the resonance hybrid carbocations resulting from ortho and parra directing. The same is true for other halogens. It may thus be concluded that in case of halogens, the reactivity is controlled by the stronger inductive effect and the orientation is determined by mesomeric effect.

Ortho and Para Directing Influence of Alkyl Groups

Alkyl groups exert electron releasing inductive effect (+I effect). Consider the case of further electrophilic substitution in toluene which contains an electron releasing methyl group.

The various resonating structures of the carbocations by ortho, para and meta attack are given below:

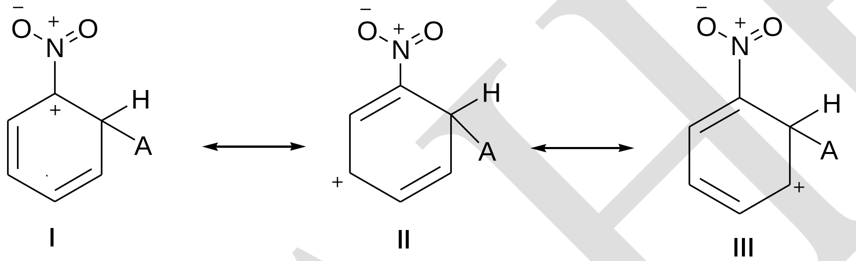


We find in each case, the intermediate is a resonance hybrid of three structures. In structures (I) and (V), the positive charge is located on the carbon atom to which electrons releasing methyl group is attached. Therefore, the positive charge on such a carbon is highly dispersed and thus the corresponding structures (I) and (V) are more stable than all other structures. No such structure is however, possible in case of meta attack. Hence the resonance hybrid carbocations resulting from ortho and para attack are more stable than the one formed by attack at the meta position. Therefore further elecrtophilic substitution in toluene occurs faster at the ortho and para positions than at the meta position. In other words, methyl group is an ortho and para directing group. Other alkyl groups behave similarly.

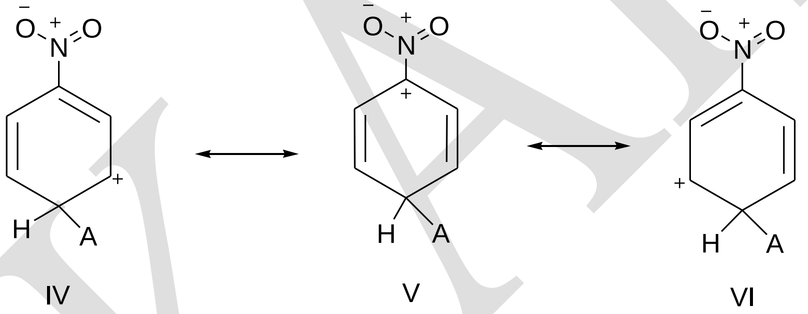
Deactivating and Meta Directing Nature of Nitro Group towards Electrophilic Aromatic substitution.

Nitro group is electron withdrawing in nature. In this case, the electron withdrawal occurs through electron withdrawing effect (-I effect) as well as electron withdrawing resonance effect (-M effect). Due to its electron withdrawing character, nitro group deactivates the benzene ring towards further electrophilic substitution.

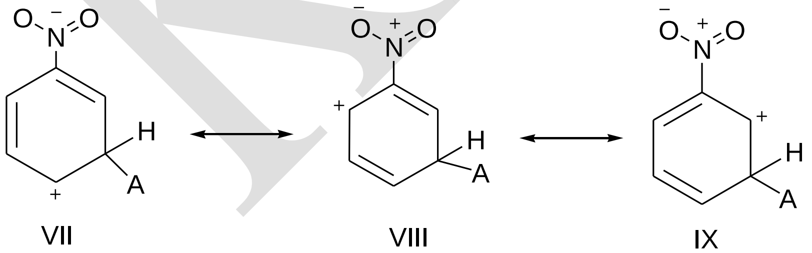
Let us examine the directing influence of $-NO_2$ group by considering electrophilic substitution in nitrobenzene. The various resonating structures of the carbocations formed by ortho, para and meta attack are given below.



Ortho attack



Para attack



Meta attack

In the contributing structures (I) and (V) , the positive charge is located on that carbon atom which is directly linked to electron withdrawing nitro group. Although $-NO_2$ group withdraws electrons from all positions, it does so most from the carbon directly attached to it. Hence this carbon atom, already made positive by nitro group has little tendency to accommodate the positive charge of the carbocation. Consequently structures (I) and (V) are unstable and their contribution towards stabilization of the carbocation is almost negligible. Thus carbocations formed by ortho and para attack are virtually resonance hybrids of only two structures while the one formed by meta attack is a resonance hybrid of three structures. Therefore the resonance hybrid carbocation resulting from meta attack is more stable than the carbocations resulting from ortho and para attack. Consequently, further electrophilic substitution takes place at the meta position. Thus, nitro group is meta directing.

Text books:

1. Madan, R.L. (2015). *Chemistry for Degree Students*. New Delhi: S. Chand and Company Pvt, Ltd.

2. Morrison, R. N. & Boyd, R. N. (1992). *Organic Chemistry*. New Delhi: Dorling Kindersley Pvt. Ltd. (Pearson Education).

POSSIBLE QUESTIONS

PART A (20 Multiple choice questions)

Online Examinations

PART B (2 marks questions)

1. State Huckel's rule for aromaticity?
2. What is aromaticity?
3. Explain why pyrrole is an aromatic compound?
4. "Nitration of benzene takes place more readily than nitrobenzene."Justify this statement.
5. Toluene is nitrated more readily than benzene. Explain why?

PART C (6 marks questions)

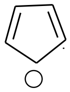
1. (i) Methyl group attached to benzene ring has no lone pair of electrons but is still ortho and para directing in nature. Explain why.

(ii) Chlorine deactivates the benzene ring yet it is ortho and para directing in nature. Explain.

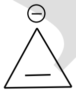
2. Which of the following have aromatic character and why?

(i)

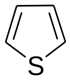
(ii)



(iii)



(iv)



3. Define the terms: Aromatic, Non-Aromatic and Anti-Aromatic compounds and classify the following into these:

(i) Cyclopropenyl anion (ii) Naphthalene (iii) Cyclooctatetraene.

4. (i) Give the mechanism of sulphonation of benzene.

(ii) Write a short note on annulenes.

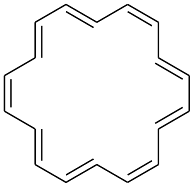
5. (i) Explain why $-NH_2$group when attached to benzene ring is ortho and para directing in nature.

(ii) Why is it easier to introduce a nitro group at ortho and para positions in phenol than in toluene?

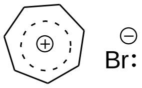
6. (i) Halogens are electron withdrawing in nature but they are ortho and para directing in benzene. Explain.

   (ii) Out of toluene and nitrobenzene, which will be nitrated more easily?

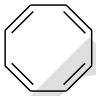
7. Which of the following compounds would show aromatic character?



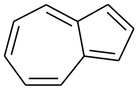
[18] Annulene



Tropylium bromide



Cyclooctatetraene



Azulene

8. Discuss the mechanism of electrophilic substitution in benzene.
9. (i) Explain the mechanism of nitration of benzene.

   (ii) Explain why nitration of chlorobenzene gives ortho and parachloronitrobenzene but the chlorination of nitrobenzene gives metachloronitrobenzene.

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Class: I B.Sc Chemistry Course Name:Organic Chemistry-I (Basics and Hydrocarbon)

Course Code: 19CHU103 Unit: V Batch-2019-2022

S.No	Questions	Optional 1	Optional 2	Optional 3	Optional 4	Answer
1.	The conversion of acetylene into aldehyde is effected by	$Hg(OAC)_2/H_2O$	H_2O/H^+	$HgSO_2/H_2O$	$HgSO_4/H_2O$	$HgSO_4/H_2O$
2.	Huckel rule of aromaticity is	4n	4n + 2	4n + 4	n + 2	4n + 2
3.	Which is the following will be aromatic?	cyclopropenylcation	cyclopropenyl anion	1,3-cyclobutadiene	cyclopropene	cyclopropenylcation
4.	Which one of the following is a nonbenzenoid aromatic compound?	pyrrole	benzene	naphthalene	anthracene	pyrrole
5.	Which one of the following is antiaromatic?	pyrrole	1,3-cyclobutadiene	azulene	[14]-annulene	1,3-cyclobutadiene
6.	Cyclopropenylcation is	benzenoid aromatic	non-benzenoid aromatic	antiaromatic	non-aromatic	non-benzenoid aromatic
7.	Pyrrole is having only two π-bonds yet it is an aromatic compound. This can be explained by	Huckel rule	nonbenzenoid system	aromatic sextet theory	Bredt's rule	aromatic sextet theory
8.	Cyclo-octatetraene has alternate double bonds are considered as	aromatic	anti aromatic	non aromatic	non-benzenoide aromatic	non aromatic
9.	Pyrene has 16 π-electrons yet it is considered to be an aromatic compound due to	Ten peripheral π electron	14 peripheral π electron	Two internal π-electron	eighteen peripheral π electron	14 peripheral π electron
10.	Which one of the following statement is false for substituted benzene?	When both groups are o- & p-directing, the more powerful group controls orientation	When both groups are m-directing, it is difficult to introduce a third group	When both groups direct differently, the meta directing group takes precedence over o- & p	When both groups occupy meta positions, there is usually no substitution between two groups.	When both groups direct differently, the meta directing group takes precedence over o- & p
11.	Sulphonation of benzene is a	reversible reaction	irreversible reaction	equilibrium reaction	forward reaction	reversible reaction
12.	Rate of sulphonation in deutrated	no deuterium effect	deuterium effect	secondary kinetic	steric effect	deuterium effect

	benzene is slow and reversible. This indicates			isotopic effect		
13.	Which compound has three double bonds but does not undergo addition reactions readily.	acetylene	benzene	naphthalene	anthracene	benzene
14.	In Friedel Crafts alkylation reaction, the electrophile is a	carbonium ion	free radical	carbanion	negative charge	carbonium ion
15.	An aromatic molecule must obey	Hund’s rule	Markovnikov’s rule	Huckel rule	Saytzeff rule	Huckel rule
16.	Sulphonation of benzene, the attacking species is	H^+	SO_2	SO_3	HSO4-	SO_3
17.	Benzene reacts with benzoyl chloride in the presence of anhydrous aluminium chloride to form	benzyl chloride	benzaldehyde	benzal chloride	benzophenone	benzophenone
18.	Benzene undergoes Friedel-Crafts reaction with isopropyl alcohol in the presence of H_2SO_4 catalyst to give	n- Propylbenzene	benzophenone	isopropylbenzene	nothing happens	isopropylbenzene
19.	The conversion of benzene into 1-ethylbenzene is effected by	$LiAlH_4$	$AlCl_3$	Na	KOH	$AlCl_3$
20.	Butadiene is	aromatic	non-aromatic	anti-aromatic	homo-aromatic	non-aromatic
21.	Which of the following compounds is aromatic?	1,3-cyclobutdiene	cyclooctatetraene	pyridine	1,3-cyclohexadiene	pyridine
22.	Benzene undergoes substitution reaction more readily then addition reaction because	it has cyclic structure	it has three double bonds	it has six hydrogen atom	there is delocalisation of electrons	there is delocalisation of electrons
23.	Which of the following compounds undergoes nitration most easily?	benzene	toluene	nitrobenzene	benzoic acid	toluene
24.	Which compound undergoes substitution slower than benzene?	phenol	acetanilide	fluorobenzene	Anisole	fluorobenzene

25.	Which of the following will undergo substitution in the ortho and para positions rather than in the meta, position?	nitrobenzene	benzoic acid	acetanilide	benzaldehyde	acetanilide
26.	Compared to benzene, nitration of toluene takes place at	same rate	faster rate	slower rate	unpredictable	faster rate
27.	Which of the following contains a 5-membered ring found with 7-membered ring?	azulene	annulene	ferrocene	Syndone	azulene
28.	Which of the following is called a sandwich compound?	Ferrocene	azulene	annulene	naphthalene	Ferrocene
29.	Huckel’s rule is called as	$4n\pi$ rule	$(4n+1)\pi$ rule	$(4n+2)\pi$ rule	$(2n+2)\pi$ rule	$(4n+2)\pi$ rule
30.	Cyclopentadienyl anion is	aromatic	non aromatic	anti aromatic	not aromatic	aromatic
31.	Which is having lower degree of aromaticity?	pyridine	furan	thiophene	Pyrrole	furan
32.	An example for heteroaromatic compound is	cyclopentadienyl anion	pyridine	[14] annulene	tropylium ion	pyridine
33.	Cyclopentadiene is	aromatic	non aromatic	anti aromatic	homoaromatic	non aromatic
34.	Ferrocene is an	cyclopentadienyl iron	dicyclopentadienyl iron	tricyclopentadienyl iron	cyclohexadienyl iron	dicyclopentadienyl iron
35.	Azulene is a	aromatic compound	aliphatic compound	heterocyclic compound	non-benzenoid aromatic compound	non-benzenoid aromatic compound
36.	A cyclic compound that does not have a continuous, overlapping ring of p orbital is said to be	anti-aromatic compound	non-aromatic compound	aromatic compound	heterocyclic compound	non-aromatic compound
37.	Non-aromatic compound is also called as	heterocyclic compound	aliphatic compound	benzenoid compound	non-benzenoid compound	aliphatic compound
38.	Which of the following is aromatic?	pyran	pyrlium ion	cyclobutadiene	cyclopetadienylcation	pyrlium ion
39.	The corresponding anion of cyclopetadienyl is	aromatic	non aromatic	antiaromatic	straight chain compound	aromatic
40.	The example for non-aromatic compound is	benzene	ferrocenes	fulvenes	1,3-cyclohexadiene	1,3-cyclohexadiene
41.	Ferrocene is readily under does	aliphatic electrophilic	aromatic electrophilic	aliphatic nucleophilic substitution reactions	aromatic nucleophilic substitution reactions	aromatic electrophilic

		substitution reactions	substitution reactions			substitution reactions
42.	Conjugated monocyclic polyenes are	azulenes	fulvenes	annulenes	Ferrocenes	annulenes
43.	Azulene is aromatic due to	charge separated structures	both rings are aromatic	both rings having 6π electrons	two Kekule structures	charge separated structures
44.	Cycloheptatriene loses a hydride ion to form a carbonium ion is called	tropylium anion	cyclopentadienyl anion	tropyliumcation	tropylium radical	tropyliumcation
45.	The number double bonds in tropyliumcation is	two	three	four	One	three
46.	Cyclopentadiene is much more acidic than cycloheptatriene is due to	the conjugate base of cycloheptatriene is aromatic	the conjugate base of cyclopentadiene is anti-aromatic	the conjugate base of cycloheptatriene is non-aromatic	the conjugate base of cyclopentadiene is aromatic	the conjugate base of cyclopentadiene is aromatic
47.	The system contain 4n electrons are predicated to be	Sandwich compound	ionic compound	fused ring compound	anti-aromatic compound	anti-aromatic compound
48.	Acetophenone can be obtained by the Friedel-Crafts acylation of benzene with	CH_3COCl and $AlCl_3$	$Ac_2O$and $AlCl_3$	CH_3COCl and HCl	CH_3Cl and $AlCl_3$	CH_3COCl and $AlCl_3$
49.	Toluene can be obtained by the Friedel-Crafts acylation of benzene with	CH_3COCl and $AlCl_3$	$Ac_2O$and $AlCl_3$	CH_3COCl and HCl	CH_3Cl and $AlCl_3$	CH_3Cl and $AlCl_3$
50.	For alkylation commonly used reagents are alkyl halides and commonly used catalyst is	HCl	$AlCl_3$	$ZnCl_2$	H_2SO_4	$AlCl_3$
51.	The pyridine molecule is failure for	Kolbe reaction	Friedel-Crafts reaction	Reimer-Tiemann reaction	Hofmann-Martius reaction	Friedel-Crafts reaction
52.	Which is called nitrating mixture?	conc. HNO_3	aqua regia	conc. HNO_3 and conc. H_2SO_4	conc. H_2SO_4	conc. HNO_3 and conc. H_2SO_4
53.	What is the attacking species in nitration?	NO	NO_2	NO^+	NO_2^+	NO_2^+
54.	The catalyst employed in Friedel-Craft s reaction is	$AgCl_3$	$AlCl_3$	$FeCl_3$	NaCl	$AlCl_3$
55.	Typical substitution reaction in aromatic hydrocarbons are	electrophilic	nucleophilic	free radical	photochemical	electrophilic
56.	Name the reaction which is used	halogenation	Friedel-Craft’s	sulphonation	nitration	Friedel-Craft’s

	to prepare styrene from benzene		reaction			reaction
57.	Nitration takes place very easily in	benzene	toluene	naphthalene	anthracene	toluene
58.	Ethyl benzene is obtained from benzene in	nitration	halogenation	sulphonation	Friedel-Craft's reaction	Friedel-Craft's reaction
59.	In an electrophilic substitution reaction, the attacking species attacks	an electron-poor carbon	a neutral carbon	a tertiary carbon	an electron rich carbon	an electron rich carbon
60.	The halogenations of benzene requires	very high temperature	a catalyst	a polar solvent	a non-polar solvent	a catalyst
61.	In the Friedel-Crafts alkylation of benzene, the attacking species is	$AlCl_3$	R^-	R^+	RX	R^+