GENERAL CHEMISTRY-I

Unit-V: Colloids and Macromolecules

A colloid is a mixture that has particles ranging between 1 and 1000 nanometers in diameter, yet is still able to remain evenly distributed throughout the solution. These are also known as colloidal dispersions because the substances remain dispersed and do not settle to the bottom of the container.

In chemistry, a colloid is a phase separated mixture in which one substance of microscopically dispersed insoluble or soluble particles is suspended throughout another substance.

Types of Colloids

- Sol is a colloidal suspension with solid particles in a liquid.
- Emulsion is between two liquids.
- Foam is formed when many gas particles are trapped in a liquid or solid.
- Aerosol contains small particles of liquid or solid dispersed in a gas.

Preparation of Colloids

Colloids can be prepared by a variety of techniques involving physical, chemical as well as some dispersion methods. However, there are two principal ways of preparation of colloids:

- Dispersion of large particles or droplets to the colloidal dimensions by milling, spraying, or application of shear (e.g. shaking, mixing, or high shear mixing).
- Condensation of small dissolved molecules into larger colloidal particles by precipitation, condensation, or redox reactions. Such processes are used in the preparation of colloidal silica or gold.

Chemical Methods of Preparation of Colloids

Hydrophilic or Lyophobic colloidal solutions can be prepared by various chemical techniques such as:

- **Double Decomposition Technique:** When hydrogen sulphide is passed through a solution of arsenious oxide in distilled water, we get a colloidal solution of arsenious chloride.

$$As_2O_3 + 3H_2S \rightarrow As_2S_3 + 3H_2O$$

- **Oxidation Technique:** A colloidal solution of Sulphur is made to pass through an aqueous solution of sulphur dioxide. It can also be obtained by passing the gas through a solution of an oxidization agent such as bromine water as well as nitric acid.

$$SO_2 + 2H_2S \rightarrow 2H_2O + 3S$$

$$H_2S + [O] \rightarrow H_2O + S$$

- **Reduction Technique:** Another technique of preparing colloidal solutions of metals such as silver, gold as well as platinum involves the use of reducing agent for reduction of the salt solutions of these metals. Example of reducing agent include stannous chloride.
- **Hydrolysis Technique:** It involves the use of boiling water to obtain a reduced solution of ferric chloride.

$$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3\,HCl$$

Purification of Colloidal Solution

The following methods are commonly used for the purification of colloidal solutions.

Dialysis

- The process of separating the particles of colloid from those of crystalloid, by means of diffusion through a suitable membrane is called dialysis.
- It's principle is based upon the fact that colloidal particles can not pass through a parchment or cellophane membrane while the ions of the electrolyte can pass through it.
- The impurities slowly diffused out of the bag leaving behind pure colloidal solution
- The distilled water is changed frequently to avoid accumulation of the crystalloids otherwise they may start diffusing back into the bag.
- Dialysis can be used for removing HCl from the ferric hydroxide sol.

Electrodialysis

- The ordinary process of dialysis is slow.
- To increase the process of purification, the dialysis is carried out by applying electric field. This process is called electrodialysis.
- The important application of electrodialysis process in the artificial kidney machine used for the purification of blood of the patients whose kidneys have failed to work. The artificial kidney machine works on the principle of dialysis.

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Ultra – filtration

- Sol particles directly pass through ordinary filter paper because their pores are larger (more than 1μ or $1000\,m\mu$) than the size of sol particles (less than $200\,m\mu$).
- If the pores of the ordinary filter paper are made smaller by soaking the filter paper in a solution of gelatin of colloidion and subsequently hardened by soaking in formaldehyde, the treated filter paper may retain colloidal particles and allow the true solution particles to escape. Such filter paper is known as ultra - filter and the process of separating colloids by using ultra – filters is known as ultra – filtration.

Ultra – centrifugation

- The sol particles are prevented from setting out under the action of gravity by kinetic impacts of the molecules of the medium.
- The setting force can be enhanced by using high speed centrifugal machines having 15,000 or more revolutions per minute. Such machines are known as ultra– centrifuges.

Stability of Colloids

The stability of a colloidal system is defined by particles remaining suspended in solution at equilibrium.Stability is hindered by aggregation and sedimentation phenomena, which are driven by the colloid's tendency to reduce surface energy. Reducing the interfacial tension will stabilize the colloidal system by reducing this driving force. Aggregation is due to the sum of the interaction forces between particles. If attractive forces prevail over the repulsive ones particles aggregate in clusters.Electrostatic stabilization and steric stabilization are the two main mechanisms for stabilization against aggregation.

Electrostatic stabilization is based on the mutual repulsion of like electrical charges. In general, different phases have different charge affinities, so that an electrical double layer forms at any interface. Small particle sizes lead to enormous surface areas, and this effect is greatly amplified in colloids. In a stable colloid, mass of a dispersed phase is so low that its buoyancy or kinetic energy is too weak to overcome the electrostatic repulsion between charged layers of the dispersing phase. The electrostatic repulsion between suspended colloidal particles is most readily quantified in terms of the zeta potential, a measurable quantity describing electrical potential at the slipping plane in an electrical double layer.

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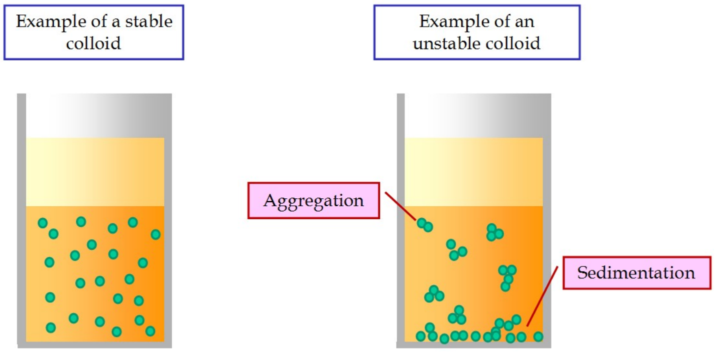
Steric stabilization consists in covering the particles in polymers which prevents the particle to get close in the range of attractive forces.



Gold Number

The Gold Number is the minimum weight (in milligrams) of a protective colloid required to prevent the coagulation of 10 ml of a standard hydro gold sol when 1 ml of a 10% sodium chloride solution is added to it.

The coagulation of gold sol results in an increase in particle size, indicated by a colour change from red to blue or purple. The higher the gold number, the lower the protective power of the colloid, because a greater amount of colloid is required to prevent coagulation. The gold numbers of some colloids are given below.

Protective Colloid	**Gold Number**
Gelatin	0.005-.01
Haemoglobin	0.03-0.07
Egg Albumin	0.15-0.25
Potato Starch	20-25
Gum arabic	0.15-0.25
Caseinate	0.01-0.02
Sodium Oleate	1-5
Dextrin	125-150

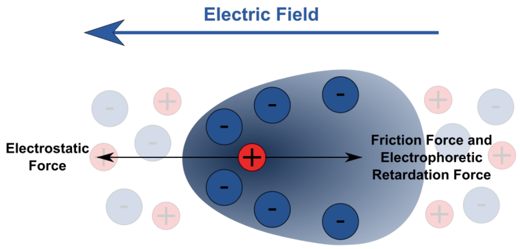
Properties of Colloids

Electrical properties

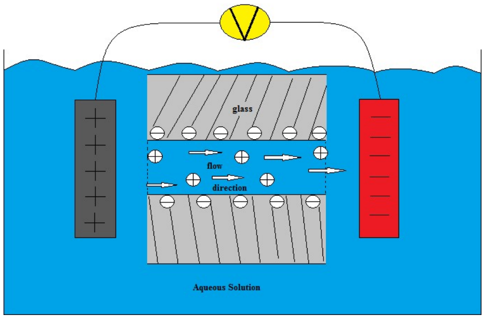
Electrical double layer theory: In this theory, charge is imparted to the particles by placing ions which are adsorbed preferentially at immovable points which for the first layer. The second layer consists of diffused mobile ions. The charge present on both the layers is equal. This two-layer arrangement leads to a development of potential called **zeta or Electrokinetic**

potential. As a result of this potential developed across the particles, under the influence of electric field these particles move.

Electrophoresis: It is a process in which an electric field is been applied to a colloidal solution which is responsible for the movement of colloidal particles. Depending upon the accumulation near the electrodes the charge of the particles can be predicted. The charge of the particles is positive if the particles get collected near a negative electrode and vice versa.



Electro-osmosis: It is a process in which the dispersing medium of the colloidal solution is brought under the influence of electric field and the particles are arrested.



Optical properties

Tyndall's effect is defined as the phenomenon in which light is scattered by the colloidal particles. The light is been absorbed by the particles present in the solution. Once the light is been absorbed a part of the light gets scattered in all the directions. The result of scattering exhibits this effect.

Kinetic properties

During the observation of the colloidal dispersion under an ultra-microscope, it is clearly seen that the particles are in a continuous movement in the solution. This random zigzag movement of the particles in the colloidal solution is called Brownian effect. This movement is mainly due to the unique bombardment of the molecules present in the dispersed medium on the colloidal particles.

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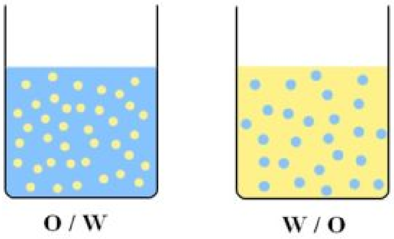
Emulsions

An emulsion is a type of colloid formed by combining two liquids that normally don't mix. In an emulsion, one liquid contains a dispersion of the other liquid. Common examples of emulsions include egg yolk, butter, and mayonnaise. The process of mixing liquids to form an emulsion is called emulsification.

Types of Emulsions



Emulsions can exist as "oil in water" or " water in oil" of emulsions. The type of emulsion depends upon the properties of the dispersed phase and continuous phase. If the oil phase is dispersed in a continuous aqueous phase the emulsion is known as "oil in water". If the aqueous phase is the dispersed phase and the oil phase is the continuous phase, then its known as "water in oil"

Whether an emulsion of oil and water turns into a "water-in-oil" emulsion or an "oil-in-water" emulsion depends on the volume fraction of both phases and the type of emulsifier used to emulsify them.

Preparation of Emulsions

The methods commonly used to prepare emulsions can be divided into two categories

A) Trituration Method

This method consists of dry gum method and wet gum method.

Dry Gum Method

In this method the oil is first triturated with gum with a little amount of water to form the primary emulsion. The trituration is continued till a characteristic 'clicking' sound is heard and a thick white cream is formed. Once the primary emulsion is formed, the remaining quantity of water is slowly added to form the final emulsion. 4:2:1 formula 4 parts (volumes) of oil 2 parts of water 1 part of gum.

Wet Gum Method

Wet Gum Method As the name implies, in this method first gum and water are triturated together to form a mucilage. The required quantity of oil is then added gradually in small proportions with thorough trituration to form the primary emulsion. Once the primary emulsion has been formed remaining quantity of water is added to make the final emulsion. 4:2:1 formula 4 parts (volumes) of oil 2 parts of water 1 part of gum.

Bottle Method

This method is employed for preparing emulsions containing volatile and other non-viscous oils. Both dry gum and wet gum methods can be employed for the preparation. ¬ As volatile oils have a low viscosity as compared to fixed oils, they require comparatively large quantity of gum for emulsification. ¬ In this method, oil or water is first shaken thoroughly and vigorously with the calculated amount of gum. Once this has emulsified completely, the second liquid (either oil or water) is then added all at once and the bottle is again shaken vigorously to form the primary emulsion. More of water is added in small portions with constant agitation after each addition to produce the final volume.

Properties of Emulsion

- Emulsions show all the characteristic properties of colloidal solution such as Brownian movement, Tyndall effect, electrophoresis etc.
- These are coagulated by the addition of electrolytes containing polyvalent metal ions indicating the negative charge on the globules.
- The size of the dispersed particles in emulsions in larger than those in the sols. It ranges from 1000 Å to 10,000 Å. However, the size is smaller than the particles in suspensioins.
- Emulsions can be converted into two separate liquids by heating, centrifuging, freezing etc. This process is also known as demulsification.

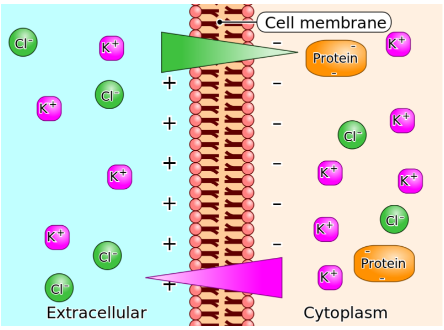
Applications of Emulsions

- Concentration of ores in metallurgy
- In medicine (Emulsion water-in-oil type)
- Cleansing action of soaps.
- Milk, which is an important constituent of our diet an emulsion of fat in water.

- Digestion of fats in intestine is through emulsification**.**

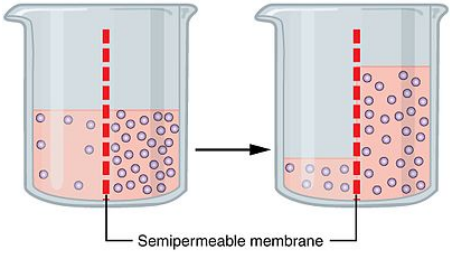
Donnan Membrane Equilibrium

The Gibbs–Donnan effect (also known as the Donnan's effect, Donnan law, Donnan equilibrium, or Gibbs–Donnan equilibrium) is a name for the behaviour of charged particles near a semi-permeable membrane that sometimes fail to distribute evenly across the two sides of the membrane.



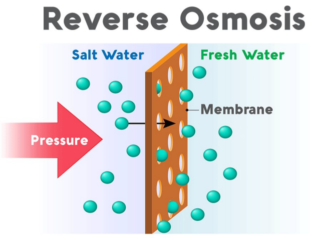
Osmosis

Osmosis is the spontaneous net movement of solvent molecules through a selectively permeable membrane into a region of higher solute concentration, in the direction that tends to equalize the solute concentrations on the two sides.



Reverse osmosis (RO)

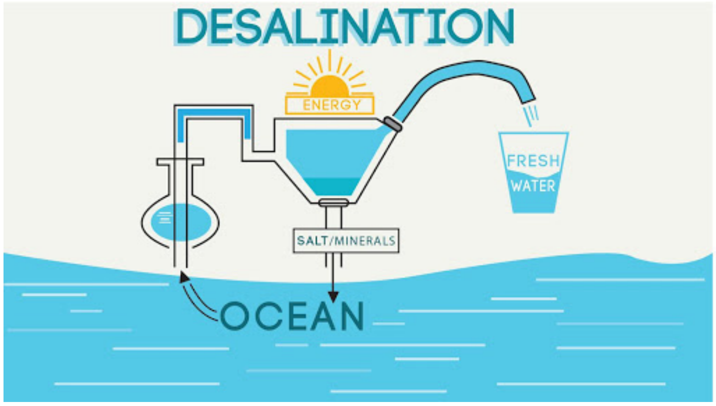
Reverse osmosis (RO) is a water purification process that uses a partially permeable membrane to remove ions, unwanted molecules and larger particles from drinking water. In reverse osmosis, an applied pressure is used to overcome osmotic pressure, a colligative property that is driven by chemical potential differences of the solvent, a thermodynamic parameter. Reverse osmosis can remove many types of dissolved and suspended chemical species as well as biological ones (principally bacteria) from water, and is used in both industrial processes and the production of potable water.



Desalination

Desalination is a process that takes away mineral components from saline water. More generally, desalination refers to the removal of salts and minerals from a target substance, as in soil desalination, which is an issue for agriculture.

Saltwater is desalinated to produce water suitable for human consumption or irrigation. The by-product of the desalination process is brine. Desalination is used on many seagoing ships and submarines. Most of the modern interest in desalination is focused on cost-effective provision of fresh water for human use. Along with recycled wastewater, it is one of the few rainfall-independent water sources.



Macromolecules

Macromolecules are large molecules composed of thousands of covalently connected atoms. Carbohydrates, lipids, proteins, and nucleic acids are all macromolecules. Macromolecules are formed by many monomers linking together, forming a polymer.

A macromolecule is a very large molecule, such as protein, commonly composed of the polymerization of smaller subunits called monomers. They are typically composed of thousands of atoms or more. A substance that is composed of monomers is called a polymer. The most common macromolecules in biochemistry are biopolymers (nucleic acids, proteins, and carbohydrates) and large non-polymeric molecules (such

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as lipids and macrocycles), synthetic fibers as well as experimental materials such as carbon nanotubes.

Molecular Weight of Macromolecule

Macromolecules are composed of much larger numbers of atoms than ordinary molecules. For example, a molecule of polyethylene, a plastic material, may consist of as many as 2,500 methylene groups, each composed of two hydrogen atoms and one carbon atom. The corresponding molecular weight of such a molecule is on the order of 35,000. Insulin, a protein hormone present in the pancreas and responsible for regulation of blood-sugar levels, has a molecular unit derived from 51 amino acids (by themselves molecules containing carbon, hydrogen, oxygen, nitrogen, and sometimes sulfur). The exact molecular weight of insulin from cattle has been determined to be 5,734.

Determination of Molecular Weight by Osmotic Pressure

Osmometry is used to determine the molecular mass, which depends on colligative properties, meaning that the number of dissolved molecules is the only factor that alters the properties of a solution. In addition, boiling point elevation, osmotic pressure, freezing point depression, and vapor pressure reduction are based on colligative properties.

There are two principal methods of osmometry that are suitable for determining average molecular weights of polymers: membrane and vapor pressure osmometry. While the first one is suitable for molecular weights between 50000 and 2 million (g mol^{-1}), the second one is applicable for 'short' polymeric chains below 40000 g mol^{-1}. Both methods deliver the absolute value of the number average molecular weight (M_n).

In the first case, a solution of a polymer and the pure solvent are placed in compartments separated by a semipermeable membrane. The membrane allows diffusion of small solvent molecules, but restricts the larger polymer chains to one compartment only. Hence, a net diffusion of solvent takes place from the solvent side to the solution side until sufficient hydrostatic pressure develops that prevents further diffusion. This hydrostatic pressure is the osmotic pressure, which is related to molecular weight by the van't Hoff equation extrapolated to zero concentration:

$$\pi/C_{C=0} = RT/Mn + A_2C$$

where π is the osmotic pressure, C the concentration of polymer (g l^{-1}), T the temperature (K), R the gas constant, and A_2 the second virial coefficient (solvent dependent).

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A plot of π/C versus C is a straight line of slope A_2, and y-intercept equal to RT/M_n. The permeability of the membrane to low molecular weight chains renders membrane osmometry useful for polymer molecular weights greater than 50000, while inaccuracy in the measurement of very small osmotic pressures sets the upper limit at 2 million.

The second method is based on the vapor pressure difference of pure solvent and a polymer solution. A sample of the solution and pure solvent are introduced into a temperature-controlled measuring chamber, which is saturated with solvent vapor. Since the vapor pressure of the solution is lower than that of the solvent, solvent vapor condenses on the solution sample causing its temperature to rise. This temperature difference (ΔT) can be measured for different concentrations (C) of the polymer solution and $1/M_n$ can be calculated according to the following formula:

$\Delta T/KC = 1/Mn + A_2C$

K is a measuring constant determined for a given solvent and temperature with an organic substance (e.g., benzoin) with exactly known molecular weight. A plot of ($\Delta T/KC$) versus C delivers $1/M_n$ as the y-axis intercept (slope A_2).

Determination of Molecular Weight by Light Scattering Method

Static light scattering is a technique in physical chemistry that measures the intensity of the scattered light to obtain the average molecular weight M_w of a macromolecule like a polymer or a protein in solution.

A light scattering instrument composed of many detectors placed at various angles, all the detectors need to respond the same way. Usually detectors will have slightly different quantum efficiency, different gains and are looking at different geometrical scattering volumes. In this case a normalization of the detectors is absolutely needed. To normalize the detectors, a measurement of a pure solvent is made first. Then an isotropic scatterer is added to the solvent. Since isotropic scatterers scatter the same intensity at any angle, the detector efficiency and gain can be normalized with this procedure. It is convenient to normalize all the detectors to the 90° angle detector.

Molecular Weight Determination by Light-scattering Method

One of the most used methods to characterize the molecular weight is light scattering method. When polarizable particles are placed in the oscillating electric field of a beam of light, the light scattering occurs. Light scattering method depends on the light, when the light is passing through polymer solution, it is measure by loses energy because of absorption, conversion to heat and scattering. The intensity of scattered light relies on the concentration, size and polarizability that is proportionality constant which depends on the molecular weight. Figure shows light scattering off a particle in solution.

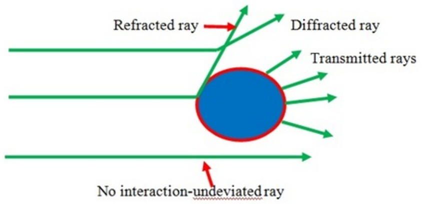

Figure: Modes of scattering of light in solution.

A schematic laser light-scattering is shown in Figure. A major problem of light scattering is to prepare perfectly clear solutions. This problem is usually accomplished by ultra-centrifugation. A solution should be as possible as clear and dust free to determine absolute molecular weight of polymer. The advantages of this method, it doesn't need calibration to obtain absolute molecular weight and it can give information about shape and M_w information. Also, it can be performed rapidly with less amount of sample and absolute determinations of the molecular weight can be measured. The weaknesses of the method is high price and most times it requires difficult clarification of the solutions.

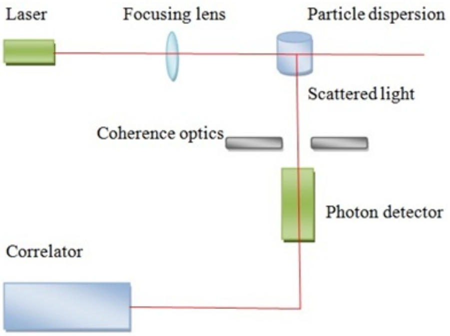

Figure: Schematic representation of light scattering.

The weight average molecular weight value of scattering polymers in solution related to their light scattering properties, where K is the wave vector. C is solution concentration, R(θ) is the reduced Rayleigh ratio, P(θ) the particle scattering function, θ is the scattering angle, A is the osmotic virial coefficients, where n_0 solvent refractive index, λ the light wavelength and N_a Avagadro's number. The particle scattering function, where R_z is the radius of gyration.

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$$KC/R(\theta) = 1/M_W(P(\theta) + 2A_2C + 3A_3C_2 + ...)$$

$$K = 2\pi^2 n^2_0(dn/dC)^2/Na\lambda^2$$

$$1/(P(\theta)) = 1+16\pi^2 n^2_0(R^2_z)\sin^2(\theta/2)3\lambda^2$$

Weight average molecular weight of a polymer is found from extrapolation of data in the form of a Zimm plot. Experiments are performed at several angles and at least at 4 different concentrations. The straight line extrapolations provides M_w.

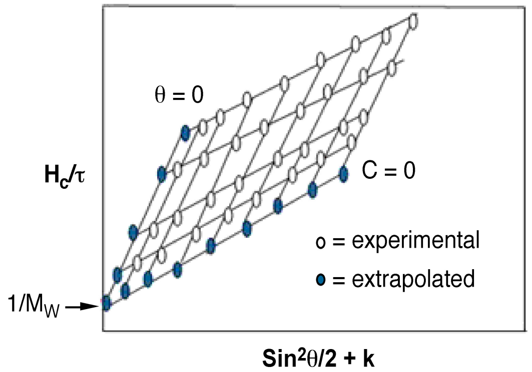

Figure: EA typical Zimm plot of light scattering data.

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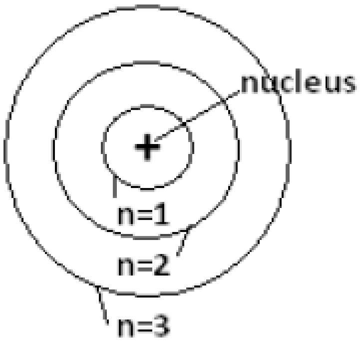
UNIT - I

Periodic table and periodic properties

Quantum Numbers

The most prominent system of nomenclature spawned from the molecular orbital theory of Friedrich Hund and Robert S. Mulliken, which incorporates Bohr energy levels as well as observations about electron spin. This model describes electrons using four quantum numbers: energy (n), angular momentum (ℓ), magnetic moment (m_ℓ), and spin (m_s). It is also the common nomenclature in the classical description of nuclear particle states (e.g. protons and neutrons).



The Principal Quantum Number (n)

The first quantum number describes the electron shell, or energy level, of an atom. The value of n ranges from 1 to the shell containing the outermost electron of that atom. For example, in caesium (Cs), the outermost valence electron is in the shell with energy level 6, so an electron in caesium can have an n value from 1 to 6. For particles in a time-independent potential, per the Schrödinger equation, it also labels the *n*th eigenvalue of Hamiltonian (H) (i.e. the energy E with the contribution due to angular momentum, the term involving J2, left out). This number therefore has a dependence only on the distance between the electron and the nucleus (i.e. the radial coordinate r). The average distance increases with *n*, thus quantum states with different principal quantum numbers are said to belong to different shells.

The Azimuthal Quantum Number (*l*)

The second quantum number, known as the angular or orbital quantum number, describes the subshell and gives the magnitude of the orbital angular momentum through the relation. In chemistry and spectroscopy, ℓ = 0 is called an s orbital, ℓ = 1 a p orbital, ℓ = 2 a d orbital, and

$\ell = 3$ an f orbital. The value of ℓ ranges from 0 to $n - 1$ because the first p orbital ($\ell = 1$) appears in the second electron shell ($n = 2$), the first d orbital ($\ell = 2$) appears in the third shell ($n = 3$), and so on. In chemistry, this quantum number is very important since it specifies the shape of an atomic orbital and strongly influences chemical bonds and bond angles.

The Magnetic Quantum Number (m)

The magnetic quantum number describes the energy levels available within a subshell and yields the projection of the orbital angular momentum along a specified axis. The values of $m\ell$ range from − to ℓ, with integer steps between them. The s subshell ($\ell = 0$) contains one orbital, and therefore the $m\ell$ of an electron in an s subshell will always be 0. The p subshell ($\ell = 1$) contains three orbitals (in some systems depicted as three “dumbbell-shaped” clouds), so the $m\ell$ of an electron in a p subshell will be −1, 0, or 1. The d subshell ($\ell = 2$) contains five orbitals, with m_ℓ values of −2, −1, 0, 1, and 2. The value of the m_ℓ quantum number is associated with the orbital orientation.

The Spin Projection Quantum Number(s)

The fourth quantum number describes the spin (intrinsic angular momentum) of the electron within that orbital and gives the projection of the spin angular momentum (s) along the specified axis. Analogously, the values of m_s range from $-s$ to s, where s is the spin quantum number, an intrinsic property of particles. An electron has spin $s = ½$, consequently m_s will be ±, corresponding with spin and opposite spin. Each electron in any individual orbital must have different spins because of the Pauli exclusion principle, therefore an orbital never contains more than two electrons.

For example, the quantum numbers of electrons from a magnesium atom are listed below. Remember that each list of numbers corresponds to (n, l, m_l, m_s).

Two s electrons: (1, 0, 0, +½) (1, 0, 0, -½)

Two s electrons: (2, 0, 0, +½) (2, 0, 0, -½)

Six p electrons: (2, 1, -1, +½) (2, 1, -1, -½) (2, 1, 0, +½) (2, 1, 0, -½) (2, 1, 1, +½) (2, 1, 1, -½)

Two s electrons: (3, 0, 0, +½) (3, 0, 0, -½)

Pauli Exclusion Principle

Pauli Exclusion Principle states that in a single atom no two electrons will have an identical set or the same quantum numbers (n, l, m_l, and m_s). To put it in simple terms, every electron should have or be in its own unique state (singlet state). There are two salient rules that the Pauli Exclusion Principle follows:

- Only two electrons can occupy the same orbital.
- The two electrons that are present in the same orbital must have opposite spins or it should be antiparallel.

However, Pauli Exclusion Principle does not only apply to electrons. It applies to other particles of half-integer spin such as fermions. It is not relevant for particles with an integer spin such as bosons which have symmetric wave functions. Moreover, bosons can share or have the same quantum states, unlike fermions. As far as the nomenclature goes, fermions are named after the Fermi–Dirac statistical distribution that they follow. Bosons, on the other hand, get their name from the Bose-Einstein distribution function.

Formulation of the Principle

An Austrian physicist named Wolfgang Pauli formulated the principle in the year 1925. With this principle, he basically described the behavior of the electrons. Later in the year 1940, he expanded on the principle to cover all fermions under his spin-statistics theorem. Meanwhile, fermions that are described by the principle include elementary particles such as quarks, electrons, neutrinos, and baryons.

Wolfgang Pauli was also awarded the Nobel Prize in the year 1945 for the discovery of the Pauli Exclusion Principle and his overall contribution in the field of quantum mechanics. He was even nominated by Albert Einstein for the award.

Pauli Exclusion Principle in Chemistry

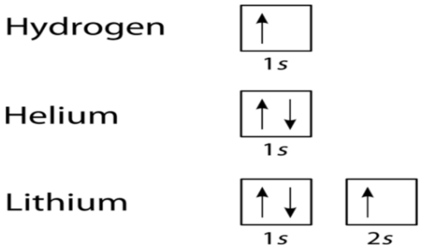
In chemistry, the law is mainly used to explain or determine the electron shell structure of atoms and predict which atoms are likely to donate electrons. How does the principle work or where does it apply? Well, if we look at the atoms whenever it gains a new electron or electrons it usually moves to the lowest energy state or it shifts to the outermost shell. If the state has one electron then it can either be spin-up or spin down. Now, if we consider the Pauli exclusion principle if there are two electrons in a state, then each of the electrons will have spin-up or spin down-state but not the same.

Pauli Exclusion Principle Example

We can take a neutral helium atom as a common Pauli Exclusion Principle example. The atom has 2 bound electrons and they occupy the outermost shell with opposite spins. Here, we will find that the two electrons are in the 1s subshell where $n = 1$, $l = 0$, and $m_l = 0$.

Their spin moments will also be different. One will be $m_s = -1/2$ and the other will be $+1/2$. If we draw a diagram then the subshell of the helium atom will be represented with 1 “up” electron and 1 “down” electron. In essence, 1s subshell will consist of two electrons, which have opposite spins.

Similarly, if we take Hydrogen it will have 1s subshell with 1 “up” electron ($1s_1$). Lithium will have the helium core (1s2) and then one more “up” electron ($2s_1$). What we are trying to depict here is that the electron configuration of the orbitals is written in this manner.



From the above example, we can further deduce that successive larger elements will have shells of successively higher energy. The number of electrons in the outermost shell is also directly related to the different chemical properties that elements possess. Elements with the same number of electrons in the outermost shell will have similar properties.

Importance and Applications Of Pauli Exclusion Principle

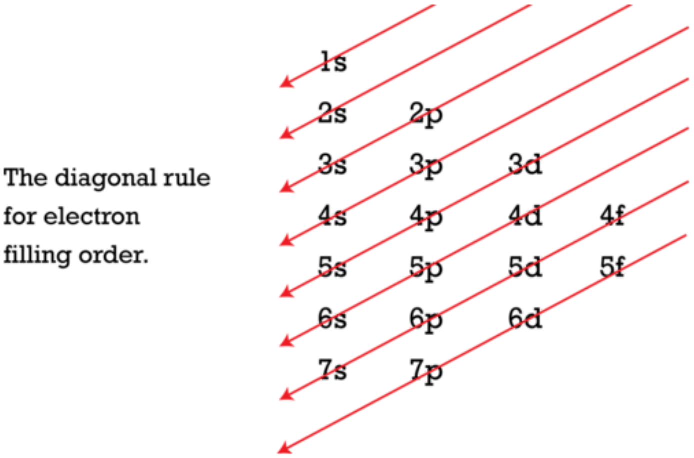
- The Pauli Exclusion Principle helps to explain a wide variety of physical phenomena.
- It helps in describing the various chemical elements and how they participate in forming chemical bonds.

- The periodic table can also be defined with the help of this principle.
- Apart from chemistry, the principle is a fundamental principle in quantum mechanics which is mainly studied in physics.
- It is also used in astrophysics.

Aufbau principle

You may consider an atom as being "built up" from a naked nucleus by gradually adding to it one electron after another, until all the electrons it will hold have been added. Much as one fills up a container with liquid from the bottom up, the orbitals of an atom are filled from the lowest energy orbitals to the highest energy orbitals.

Orbitals with the lowest principal quantum number (n) have the lowest energy and will fill up first, in smaller atoms. Larger atoms with more subshells will seem to fill "out of order", as the other factors influencing orbital energy become important. Within a shell, there may be several orbitals with the same principal quantum number. In that case, more specific rules must be applied. For example, the three p orbitals of a given shell all occur at the same energy level. So, how are they filled up? Answer: all the three p orbitals have same energy so while filling the p orbitals we can fill any one of the Px, Py or Pz first. It is a convention that we chose to fill Px first, then Py and then Pz for our simplicity. Hence you can opt for filling these three orbitals from right to left also. Aufbau principle state that “atomic orbitals are filled with electrons in order of increasing energy level”



The Aufbau principle is illustrated in the diagram by following each red arrow in order from top to bottom: 1s1s, 2s2s, 2p2p, 3s3s, etc.

Hunds Rule of Maximum Multiplicity

Hunds Rule of Maximum Multiplicity rule states that for a given electron configuration, the term with maximum multiplicity falls lowest in energy. According to this rule electron pairing in p, d and f orbitals cannot occur until each orbital of a given subshell contains one electron each or is singly occupied.

State Hund’s Rule

It states that:

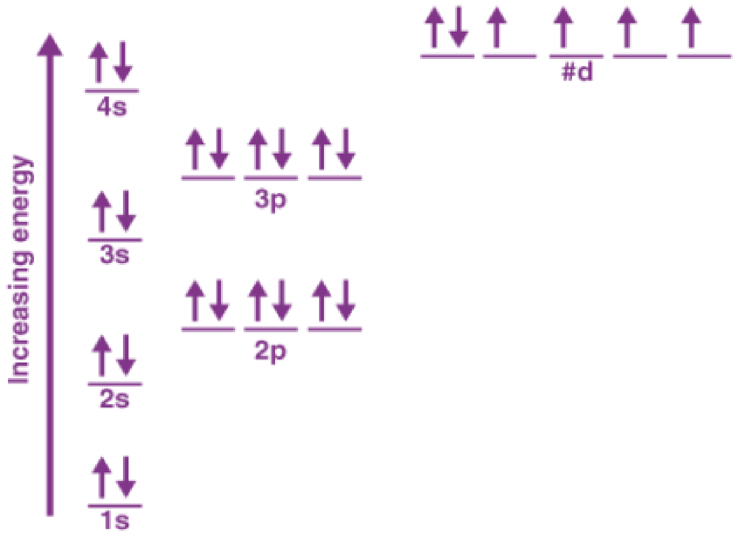
1. In a sublevel, each orbital is singly occupied before it is doubly occupied.

2. The electrons present in singly occupied orbitals possess identical spin.

The electrons enter an empty orbital before pairing up. The electrons repel each other as they are negatively charged. The electrons do not share orbitals to reduce repulsion.

When we consider the second rule, the spins of unpaired electrons in singly occupied orbitals are the same. The initial electrons spin in the sub-level decides what the spin of the other electrons would be. For instance, a carbon atom’s electron configuration would be $1s^2 2s^2 2p^2$. The same orbital will be occupied by the two 2s electrons although different orbitals will be occupied by the two 2p electrons in reference to Hund’s rule.

Electron Configuration



Electron Configuration

The above image helps in understanding the electronic configuration and its purpose. The valence shells of two atoms that come in contact with each other will interact first. When valence shells are not full then the atom is least stable. The chemical characteristics of an element are largely dependent on the valence electrons. Similar chemical characteristics can be seen in elements that have similar valence numbers.

The stability can also be predicted by the electron configuration. When all the orbitals of an atom are full it is most stable. The orbitals that have full energy level are the most stable, for example, noble gases. These type of elements do not react with other elements.

Hund’s rule of maximum multiplicity

The rule states that, for a stated electron configuration, the greatest value of spin multiplicity has the lowest energy term. It says if two or more than two orbitals having the same amount of energy are unoccupied then the electrons will start occupying them individually before they fill them in pairs. It is a rule which depends on the observation of atomic spectra, which is helpful in predicting the ground state of a molecule or an atom with one or more than one open electronic shells. This rule was discovered in the year 1925 by Friedrich Hund.

Uses of Hund’s Rule:

It has wide applications in the following –

It is majorly used in atomic chemistry, quantum chemistry, and spectroscopy, etc.

Stability of half filled and completely filled orbitals:

The exactly half filled and completely filled orbitals have greater stability than other partially filled configurations in degenerate orbitals. This can be explained on the basis of symmetry and exchange energy. For example chromium has the electronic configuration of $[Ar]3d^5$ 4s1 and not $[Ar]3d^4$ $4s^2$ due to the symmetrical distribution and exchange energies of d electrons.

Symmetrical distribution of electron:

Symmetry leads to stability. The half filled and fully filled configurations have symmetrical distribution of electrons (Figure 2) and hence they are more stable than the unsymmetrical configurations.

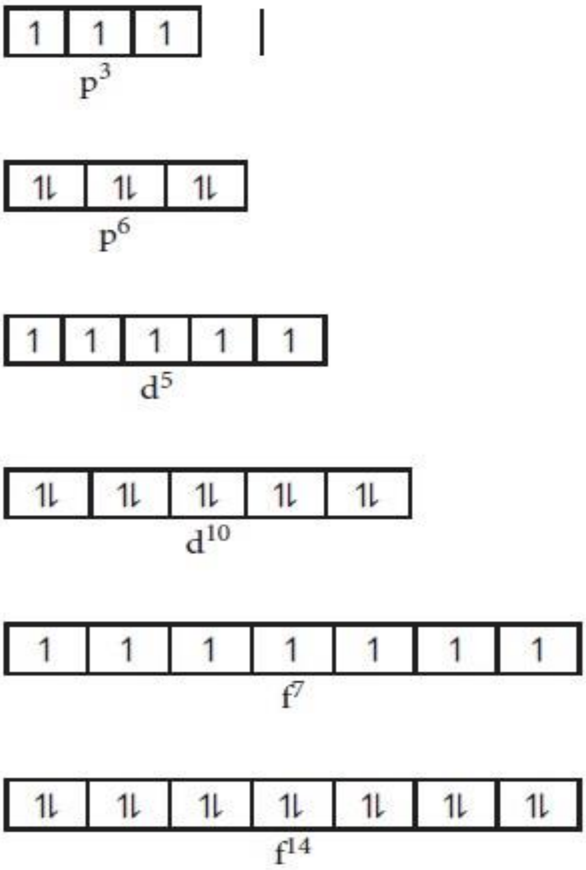


Figure 2. Half filled and fully filled p, d and f orbitals

The degenerate orbitals such as px, py and pz have equal energies and their orientation in space are different as shown in Figure 2.14. Due to this symmetrical distribution, the shielding of one electron on the other is relatively small and hence the electrons are attracted more strongly by the nucleus and it increases the stability.

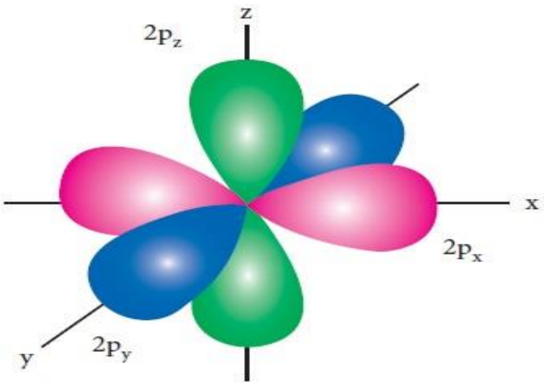
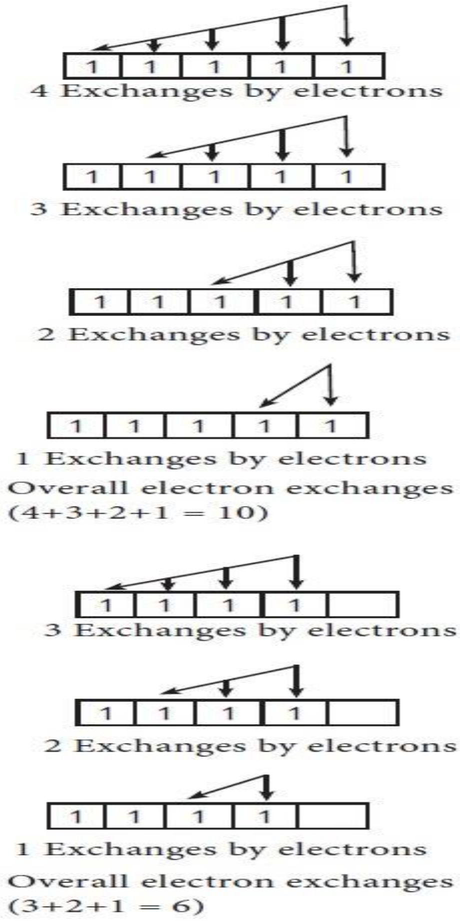


Figure 2.14 Shape of the degenerate p orbitals.

Exchange energy:

If two or more electrons with the same pinare presenting degenerate orbitals, there is a possibility for exchanging their positions. During exchange process the energy is released and the released energy is called exchange energy. If more number of exchanges are possible, more exchange energy is released. More number of exchanges are possible only in case of half filled and fully filled configurations.

For example, in chromium the electronic configuration is [Ar] 3d5 4s1. The 3d orbital is half filled and there are ten possible exchanges as shown in Figure 2.15. On the other hand only six exchanges are possible for [Ar]3d4 4s2 configuration. Hence, exchange energy for the half filled configuration is more. This increases the stability of half filled 3d orbitals.

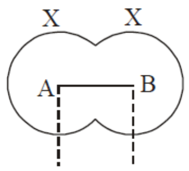


Possible exchanges in Chromium d orbitals: a) for d^5 configuration b) for d^4 configuration

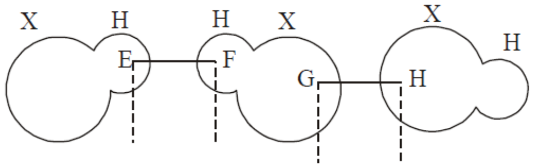
The exchange energy is the basis for Hund's rule, which allows maximum multiplicity, that is electron pairing is possible only when all the degenerate orbitals contain one electron each.

Variation of Atomic Volume

Atomic size: It refers to the distance between the centres of the nucleus of the atom to the outermost shell containing electrons. Since absolute value of the atomic size cannot be determined, it is usually expressed in terms of the following operational definitions.



$1/2\ AB = r_{covalent}$
(of element X)



$1/2\ EF = r_{\text{van der Waals}}$ of hydrogen in HX molecule
$1/2\ GH = r_{\text{van der Waals}}$ of X in HX molecule

$$r_n = \frac{n^2 a_0}{Z^*}$$

Covalentradius. It is defined as one-half of the distance between the nuclei of two covalently bonded atoms of the same element in a molecule.

$$d_{A-A} = r_A + r_A \quad \text{or} \qquad 2r_A$$

$$r_A = \frac{d_{A-A}}{2}$$

Single Bond Covalent Radius, SBCR- (a) For Homolatomic molecules

For hetrodiatomic molecules while electronegativityis approx same.

$$\mathbf{d_{A-B} = r_A + r_B}$$

For heteronuclear diatomic molecule. A–B, while difference between the electronegativity values of Atom A and atom B is relatively larger, (X_A and X_B) are the electron negativity in Pauling Scale.

$$d_{A-B} = r_A + r_B - 0.09\ |(X_A - X_B)|\ \text{[Bond length or radius expressed in Å]}$$

Where X_A and X_B is electronegativity values of high electronegative element A and less electronegative element B, respectively. This formula was given by **Stevenson** & **Schomaker**.

Covalent radius is slightly smaller than actual radius.

Van derWaals' radius. It is defined as one-half of the distance between the nuclei of two non-bonded isolated atoms or two adjacent atoms belonging to two neighboring molecules of an element in the solid state. By definition, van derWaals' radius of an element is always larger than its covalent radius.

Variation of atomic radii :

(i) Across the period atomic radii decreases

(ii) Where we move from 17th group to 18th atomic radii increases the period decreases

Atomic Radii

Atomic radii are useful for determining many aspects of chemistry such as various physical and chemical properties. The periodic table greatly assists in determining atomic radius and presents a number of trends.

Definition

Atomic radius is generally stated as being the total distance from an atom's nucleus to the outermost orbital of electron. In simpler terms, it can be defined as something similar to the radius of a circle, where the center of the circle is the nucleus and the outer edge of the circle is the outermost orbital of electron. As you begin to move across or down the periodic table, trends emerge that help explain how atomic radii change.

The effective nuclear charge (Zeff) of an atom is the net positive charge felt by the valence electron. Some positive charge is shielded by the core electrons therefore the total positive charge is not felt by the valence electron. A detailed description of shielding and effective nuclear charge can be found here. Zeff greatly affects the atomic size of an atom. So as the Zeff decreases, the atomic radius will grow as a result because there is more screening of the electrons from the nucleus, which decreases the attraction between the nucleus and the electron. Since Zeff decreases going down a group and right to left across the periodic table, the atomic radius will *increase* going down a group and right to left across the periodic table.

Types of Radius

Determining the atomic radii is rather difficult because there is an uncertainty in the position of the outermost electron – we do not know exactly where the electron is. This phenomenon can be explained by the Heisenberg Uncertainty Principle. To get a precise measurement of the radius, but still not an entirely correct measurement, we determine the radius based on the distance between the nuclei of two bonded atoms. The radii of atoms are therefore determined by the bonds they form. An atom will have different radii depending on the bond it forms; so there is no fixed radius of an atom.

Covalent Radius

When a covalent bond is present between two atoms, the covalent radius can be determined. When two atoms of the same element are covalently bonded, the radius of each atom will be half the distance between the two nuclei because they equally attract the electrons. The distance between two nuclei will give the diameter of an atom, but you want the radius which is half the diameter.

The covalent radius depicted below in Figure 1 will be the same for both atoms because they are of the same element as shown by X.

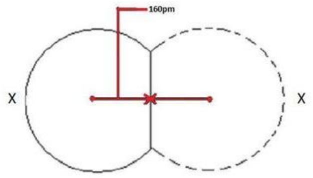


Fig.1 Covalent radii

Ionic Radius

The ionic radius is the radius of an atom forming ionic bond or an ion. The radius of each atom in an ionic bond will be different than that in a covalent bond. This is an important concept. The reason for the variability in radius is due to the fact that the atoms in an ionic bond are of greatly different size. One of the atoms is a cation, which is smaller in size, and the other atom is an anion which is a lot larger in size. So in order to account for this difference, one most get the total distance between the two nuclei and divide the distance according to atomic size. The bigger the atomic size, the larger radius it will have. This is depicted in Figure 2 as shown below where the cation is displayed on the left as X+, and clearly has a smaller radius than the anion, which is depicted as Y- on the right.

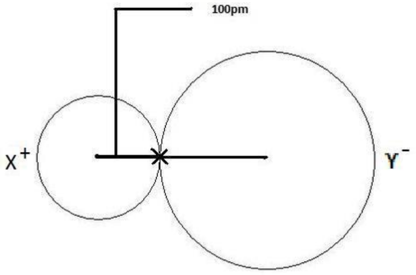


Fig. 2 *Ionic radii*

- The cation, which is an ion with a positive charge, by definition has fewer electrons than protons. The loss in an electron will consequently result in a change in atomic radii in comparison to the neutral atom of interest (no charge).

- The loss of an electron means that there are now more protons than electrons in the atom, which is stated above. This will cause a *decrease* in atomic size because there are now fewer electrons for the protons to pull towards the nucleus and will result in a stronger pull of the electrons towards the nucleus. It will also decrease because there are now less electrons in the outer shell, which will decrease the radius size.
- An analogy to this can be of a magnet and a metallic object. If ten magnets and ten metallic objects represent a neutral atom where the magnets are protons and the metallic objects are electrons, then removing one metallic object, which is like removing an electron, will cause the magnet to pull the metallic objects closer because of a decrease in number of the metallic objects. This can similarly be said about the protons pulling the electrons closer to the nucleus, which as a result *decreases* atomic size.

Figure 3 below depicts this process. A neutral atom X is shown here to have a bond length of 180 pm and then the cation X^+ is smaller with a bond length of 100 pm.

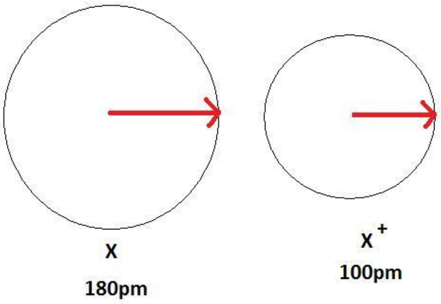


Fig. 3: The ionic radius decreases for the generation of positive ions.

An anion, on the other hand, will be bigger in size than that of the atom it was made from because of a gain of an electron. This can be seen in the Figure 4 below. The gain of an electron adds more electrons to the outermost shell which *increases* the radius because there are now more electrons further away from the nucleus and there are more electrons to pull towards the nucleus so the pull becomes slightly weaker than of the neutral atom and causes an *increase* in atomic radius.

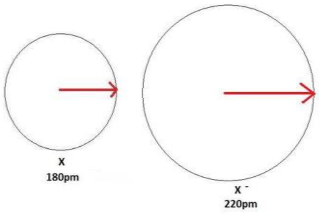


Fig. 4: The ionic radius increases for the generation of negative ions

IONISATION POTENTIAL

The energy required to remove the most loosely bound electron from the outermost orbit of one mole of isolated gaseous atoms of an element, is called **ionisationpotential (IP)**.This ionization is an endergonic or energy-absorbing process.

An electron cannot be removed directly from an atom in solid state. For this purpose, the solid state is converted to gaseous state and the energy required for this is called **sublimation energy**.

$$A \xrightarrow{I^{st}\ IP} A^{+1} \xrightarrow{II^{nd}\ IP} A^{+2} \xrightarrow{III^{rd}\ IP} A^{+3}$$

The energyrequired to remove one electron froma neutral gaseous atomto convert it to monopositive cation, is called first ionisation potential (I^{st} IP).The energy required to convert a monopositive cation toa diapositive cation is called second ionisation potential (II^{nd} IP) of an atom

I^{st} IP < II^{nd} IP < III^{rd} IP because as the electrons go out of the atom, the ionic size goes on decreasing and the amount of positive charge goes on increasing.

Factors Affecting Ionisation Potential

(i) Atomic size:

When the size of an atom is very large the electron of the outermost orbit bound to the nucleus by weaker attractive forces. Such an electron will be readily removed from the atom. Therefore, The value of ionisation potential will be low.

$$\boxed{\text{Ionisation potential} \propto \frac{1}{\text{atomic size}}}$$

(ii) Effective Nuclear Charge:

Atomic size decreases with increase in effective nuclear charge because, higher the effective nuclear charge stronger will be the attraction of the nucleus towards the electron of the outermost orbit and higher will be the ionisation potential

$$\boxed{\text{Ionisation potential} \propto \text{Effective nuclear charge}}$$

(iii) Shielding Effect:

The electrons of internal orbits repel the electrons of the electron of the outermost orbit due to which the attraction of the nucleus towards the electron of the outermost orbit decreases and thus atomic size increases and the value of ionisation potential decreases.

$$\boxed{\text{Ionisation potential} \propto \frac{1}{\text{shielding effect}}}$$

(iv) Stability of half filled and fully filled orbitals :

The atoms whose orbitals are half-filled (p^3, d^5, f^7) or fully-filled (s^2 , p^6 , d^{10} , f^{14}) have greater stability than the others. Therefore, they required greater energy to for removing out electron. However stability of fully filled orbitals is greater than that of the half filled orbitals

$$\boxed{\text{I.P. of fully} - \text{filled orbitals} > \text{I.P. of half} - \text{filled orbitals}}$$

(V) Penetration power : In any atom the *s* orbital is nearer to the nucleus in comparison to *p*, *d* and *f* orbitals. Therefore, greater energy is required to remove out electron from s orbital than from*p*, *d* and *f* orbitals. Thus the decreasing order of ionisation potential of *s*, *p*, *d* and *f* orbitals is as follows $s > p > d > f$

$$\boxed{\text{Ionisation potential} \propto \text{penetration power}}$$

Periodic Table & Ionisation Potential

(a) In aPeriod : The value of Ionisation potential normally increase ongoing from left to right in a period, because effective nuclear charge increases and atomic size decreases.

Exceptions:

- In second period ionisation potential of Be is greater than that of B, and in the third period ionization potential of Mg is greater than that of Al due to high stability of fully filled orbitals.
- In second period ionisation potential of Nis greater than O and in the third period ionisation potential of P is greater than that of S, due to stability of half filled orbitals.
- The increasing order of the values of ionisation potential of the second period elements is Li < B < Be < C < O < N < F < Ne

  The increasing order of the values of ionisation potential of the third period elements is Na <Al < Mg < Si < S < P < Cl <Ar

Inner Transition Elements: The size of inner transition elements is greater than that of d block elements. Therefore the value of ionisation potential of f block elements is smaller than that of d block elements and due to almost constant atomic size of f block elements in a period the value of their ionization potential remains more constant than that of d block elements.

In a Group

- The value of ionisation potential normallydecreases on going fromtop to bottomin a group because both atomic size and shielding effect increase.

Exception:

- The value of ionisation potential remains almost constant from Al to Ga in the IIIA group.
  (B>Al, Ga > In)
  $IP_1(Sn) < IP_1(Pb)$
  $IP_1(In) < IP_1(Tl)$
- In the periodic table the element having highest value of ionisation potential is He.
- The values of ionisation potential of noble gases are extremely high, because the orbitals of outermost orbit are fully-filled (ns^2, np^6) and provide great stability.
- In a period, the element having least value of ionisation potential is an alkalimetal (group IA) and that having highest value is inert gas (Group 0)

Applications of Ionisation Potential

- The elements having high values of ionisation potential have low reactivity, e.g. inert gases.
- The value of ionisation potential decreases more ongoing from top to bottom in a group in comparison to a period. Therefore, reactivity of metal increases and the atom forms a cation by loss of electron.

$$\text{Ionisation potential} \propto \frac{1}{\text{Reactivity of metal}}$$

- The elements having low value of ionisation potential readily lose electron and thus behave as strong reducing agents.

$$\text{Ionisation potential} \propto \frac{1}{\text{Reactivity of metal}}$$

- The elements having low value of ionization potential readily lose electron and thus exhibit greater metallic property.

$$\text{Ionisation potential} \propto \frac{1}{\text{Metallic property}}$$

- The elements having low value of ionisation potential readily lose electron and thus have basic property.

$$\text{Ionisation potential} \propto \frac{1}{\text{Basic property}}$$

ELECTRON AFFINITY (EA)

The energy released on adding up one mole of electron to one mole of neutral atom(A) in its gaseous state to form an anion (A–) is called **electron affinity** of that atom. In general, **electron affinity** is associated with an exothermic process.

$$A(g) + e^- \rightarrow A^-(g)\ , \quad \Delta H_{eg} = -E_n$$

When one electron adds up to a neutral atom, it gets converted to a unit negative ion and energy is released. On adding one more electron to themononegative anion, there is repulsion between the negatively charged electron and anion. In order to counteract the repulsive forces, energy has to be provided to the system. Therefore, the value of the second electron affinity is positive.

$$A^-(g) + e^- \rightarrow A^{-2}(g)\ , \Delta H_{eg} = +E_n \quad \Delta H_{eg} : \text{Electron gain enthalpy}$$

Factors Affecting Electron Affinity

- **Effective Nuclear charge:** When effective nuclear charge is more, then the atomic size less. Hence EA increases.

$$\boxed{\text{Electron affinity} \propto \text{Effective nuclear charge}}$$

- **Atomic Size or Atomic Radius:** When the size or radius of an atom increases, the electron entering the outermost orbit is more weakly attracted by the nucleus and the value of electron affinity is lower.

$$\boxed{\text{Electron affinity} \propto \frac{1}{\text{Atomic size}}}$$

- **Shielding Effect:** Shielding effect is directly proportional to atomic size and atomic size is inversely proportional to electron affinity.

$$\boxed{\text{Electron affinity} \propto \frac{1}{\text{Shielding effect}}}$$

- **Stability of Fully-Filled and Half-Filled Orbitals :**

  The stability of the configuration having fully-filled orbitals (p^6, d^{10}, f^{14}) and half filled orbital (p^3, d^5, f^7) is relatively higher than that of other configurations.

- **Periodic Table and Electron Affinity:**

  In a period, atomic size decreases with increase in effective nuclear charge and hence increases in electron affinity.

ELECTRONEGATIVITY ALONG PERIODS AND GROUPS

- The measure of the capacity or tendency of an atom to attract the shared pair of electrons of the covalent bond towards itself is called **electronegativity** of that atom.
- Electronegativity is a relative value that indicates the tendency of an atom to attract shared electrons more than the other atom bonded to it. Therefore it does not have any unit. Pauling was the first scientist to put forward the concept of electronegativity.
- The numerical value of electro negativity of an atom depends on its ionisation potential and electron affinity values.

Factors Affecting Electronegativity

- **Atomic size –** Electronegativity of a bonded atom decreases with increase in its size.

$$\boxed{\text{Electronegativity} \propto \frac{1}{\text{Atomic size}}}$$

In a Group

- The values of electron affinity normally decrease ongoing from top to bottom in a group because the atomic size increases which decreases the actual force of attraction by the nucleus.

Exceptions (E.A. 2nd period p-block element < E.A. 3rd period p-block element)

- The value of electron affinity of Fis lower than that of Cl, because the size of Fis very small and compact And the charge density is high on the surface. Therefore, the incoming electron experiences more repulsion in comparison to Cl .That is why the value of electron affinity of Cl is highest in the periodic table.
- The values of electron affinity of alkali metals and alkaline earth metals can be regarded as zero, because they do not have tendency to form anions by accepting electron.

Pauling Electronegativity

Linus Pauling described electronegativity as “the power of an atom in a molecule to attract electrons to it.”[1] Basically, the electronegativity of an atom is a relative value of that atom's ability to attract election density toward itself when it bonds to another atom. The higher the electronegativity of an element, the more that atom will attempt to pull electrons towards it and away from any atom it bonds to. The main properties of an atom dictate it's electronegativity are its atomic number as well as its atomic radius. The trend for electronegativity is to increase as you move from left to right and bottom to top across the periodic table. This means that the most electronegative atom is Fluorine and the least electronegative is Francium.

There are a few different 'types' of electronegativity which differ only in their definitions and the system by which they assign values for electronegativity. For example, there is Mulliken electronegativity which is defined as "the average of the ionization energy and electron affinity of an atom, which as we will see, differs slightly from Pauling's definition of electronegativity.

Pauling Electronegativity

Linus Pauling was the original scientist to describe the phenomena of electronegativity. The best way to describe his method is to look at a hypothetical molecule that we will call XY. By comparing the measured X-Y bond energy with the theoretical X-Y bond energy (computed as the average of the X-X bond energy and the Y-Y bond energy), we can describe the relative affinities of these two atoms with respect to each other.

$$\Delta \text{ Bond Energies} = (\text{X-Y})_{\text{measured}} - (\text{X-Y})_{\text{expected}}$$

If the electonegativities of X and y are the same, then we would expect the measured bond energy to equal the theoretical (expected) bond energy and therefore the Δ bond energies would be zero. If the electronegativities of these atoms are not the same, we would see a polar molecule where one atom would start to pull electron density toward itself, causing it to become partially negative.

By doing some careful experiments and calculations, Pauling came up with a slightly more sophisticated equation for the relative electronegativities of two atoms in a molecule: $EN(X) - EN(Y) = 0.102\ (\Delta^{1/2})$.[1] In that equation, the factor 0.102 is simply a conversion factor between kJ and eV to keep the units consistent with bond energies.

By assigning a value of 4.0 to Fluorine (the most electronegative element), Pauling was able to set up relative values for all of the elements. This was when he first noticed the trend that the electronegativity of an atom was determined by it's position on the periodic table and that the electronegativity tended to increase as you moved left to right and bottom to top along the table. The range of values for Pauling's scale of electronegativity ranges from Fluorine (most electronegative = 4.0) to Francium (least electronegative = 0.7).[2] Furthermore, if the electronegativity difference between two atoms is very large, then the bond type tends to be more ionic, however if the difference in electronegativity is small then it is a nonpolar covalent bond.

Classification of elements

s-block elements.

Elements of groups 1 and 2 including He in which the last electron enters the s-orbital of the valence shell are called s-block elements. There are only 14 s-block elements in the periodic table.

p-block elements.

Elements of groups 13–18 in which the last electron enters the p-orbitals of the valence shell are called p-block elements.

d-block elements.

There are three complete series and one incomplete series of d-block elements. These are: 1st or 3dtransition series which contains ten elements which atomic numbers 21–30 ($_{21}$Sc – $_{30}$Zn). 2nd or 4d-transition series which contains ten elements with atomic numbers 39 – 48 ($_{39}$Y – $_{48}$Cd). 3rd or 5d transition series which also contains ten elements which atomic numbers 57 and 72 – 80 ($_{57}$La, $_{72}$Hf – $_{80}$Hg).

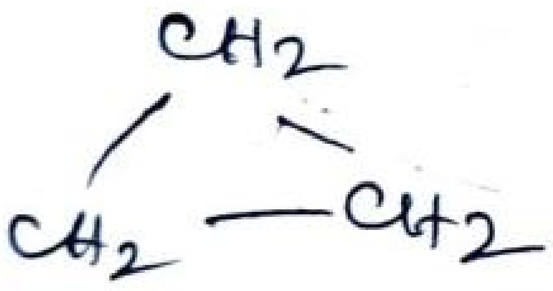
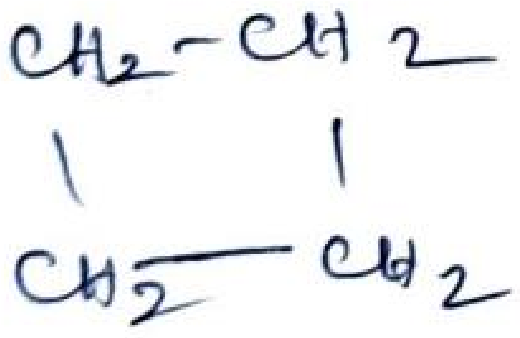
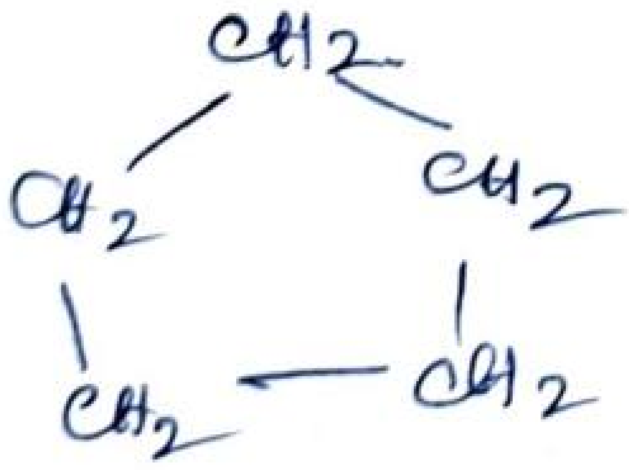
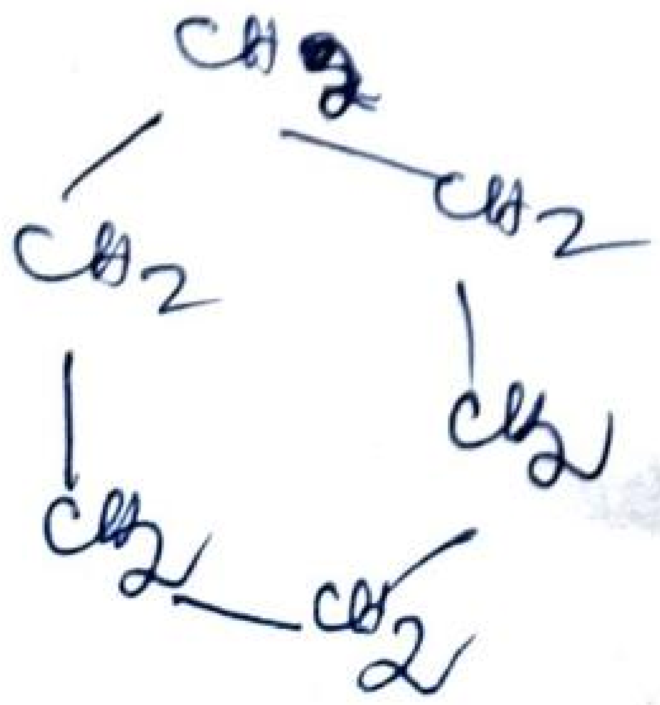
4th or 6d transition series which is incomplete at present and contains only nine elements. These are 89Ac, 104Rf, 105Ha, Unh (Unnihexium, Z = 106), 107Ns (Neilsobohrium), 108Hs (Hassium), 109Mt (Meitherium), Uun (Ununnilium, Z = 110) and Uud (Unundium, Z = 112) or Ekamercury. The element, Z = 111 has not been discovered so far. Thus, in all there are 39 d-block elements.

Cyclo alkanes

cycloalkanes are cyclic compounds containing closed hydrocarbon chains. They are also called alicyclic compounds and resemble alkanes in many respects. eg: cyclo propane, cyclobutane etc. They can be expressed by a general formula $(CH_2)_n$ where n is 3,4,5....

Nomenclature

Common and IUPAC System of nomenclature of cyclo alkanes are given below.

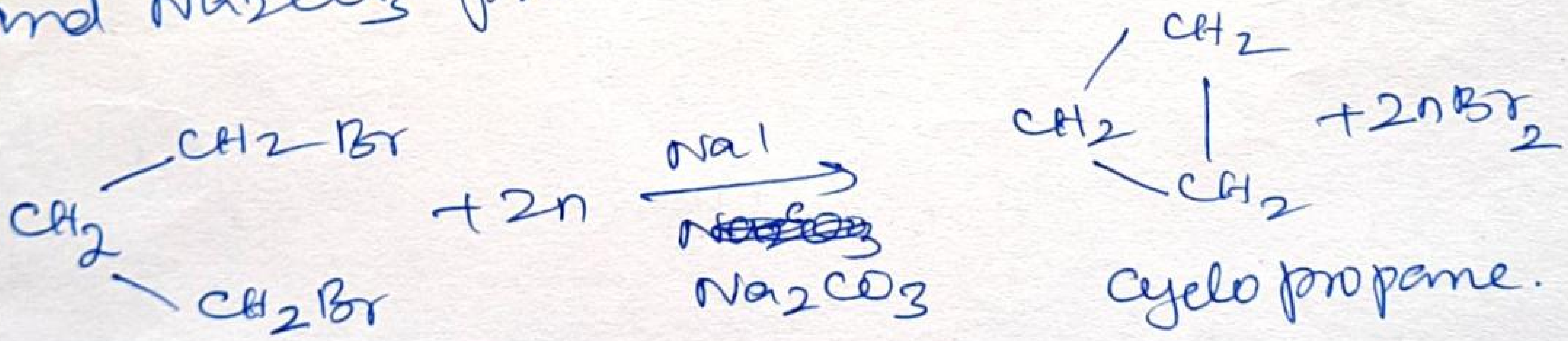
Compound	Common name	IUPAC name.
	Trimethylene	cyclo propane
	Tetramethylene	cyclobutane
	Pentamethylene	cyclo pentane
	Hexamethylene	cyclohexane.

For the sake of simplicity, cyclopropane, cyclobutane, cyclopentane and cyclohexane are represented by the following geometrical figures:

Preparation:

1. **Freund's method:** (From ω-dihalides)

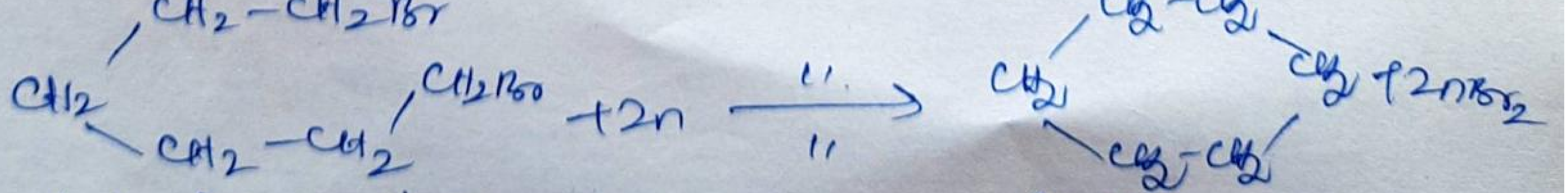
Dichloro or dibromo alkanes having terminal halogen atom when treated with Sodium or zinc in the presence of catalyst NaI and Na_2CO_3 produce cycloalkane.



1,3-dibromopropane

1,4-dibromobutane

cyclobutane



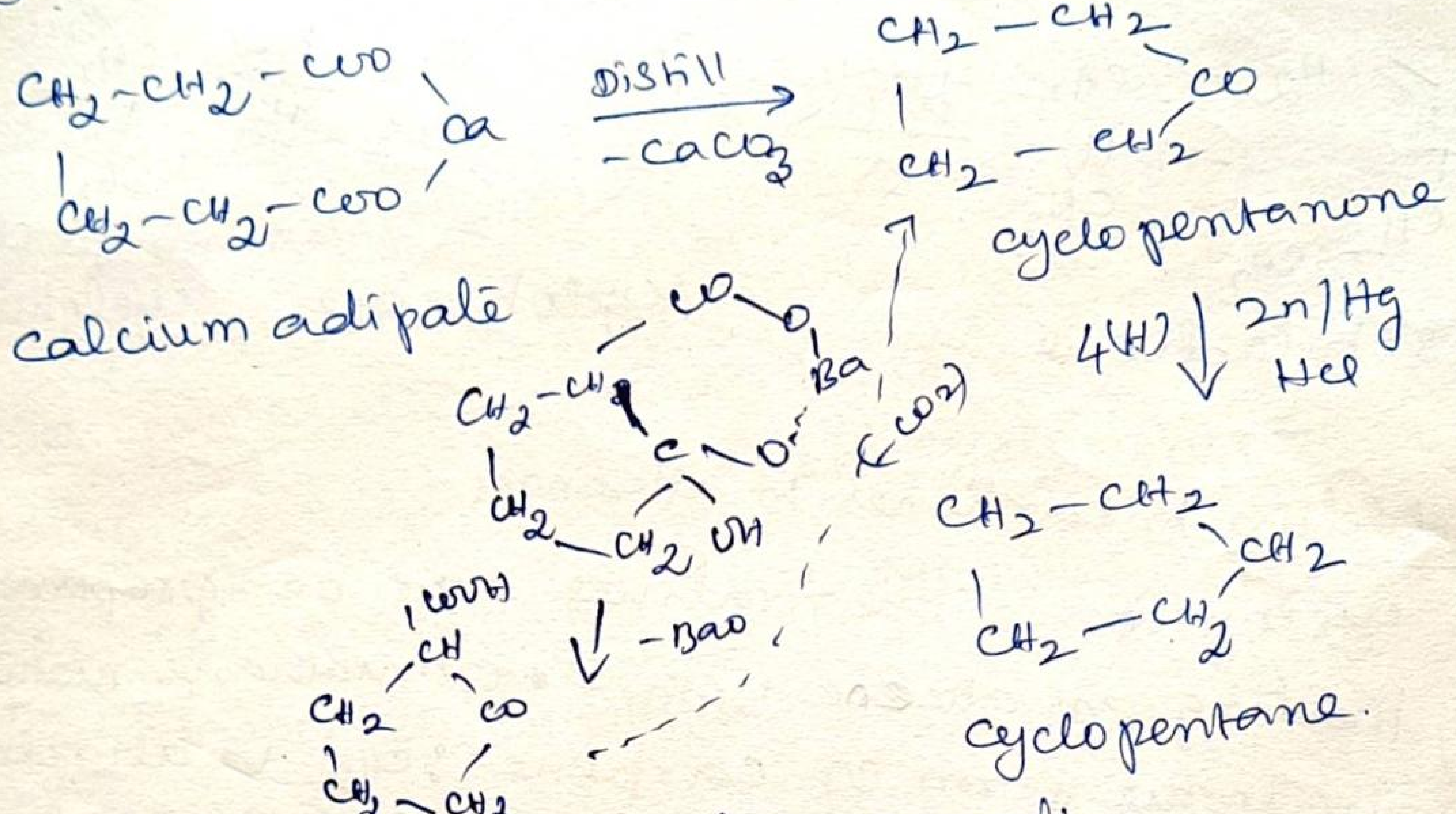
1,6-dibromohexane

cyclo hexane.

2 **Wislicenus** method:

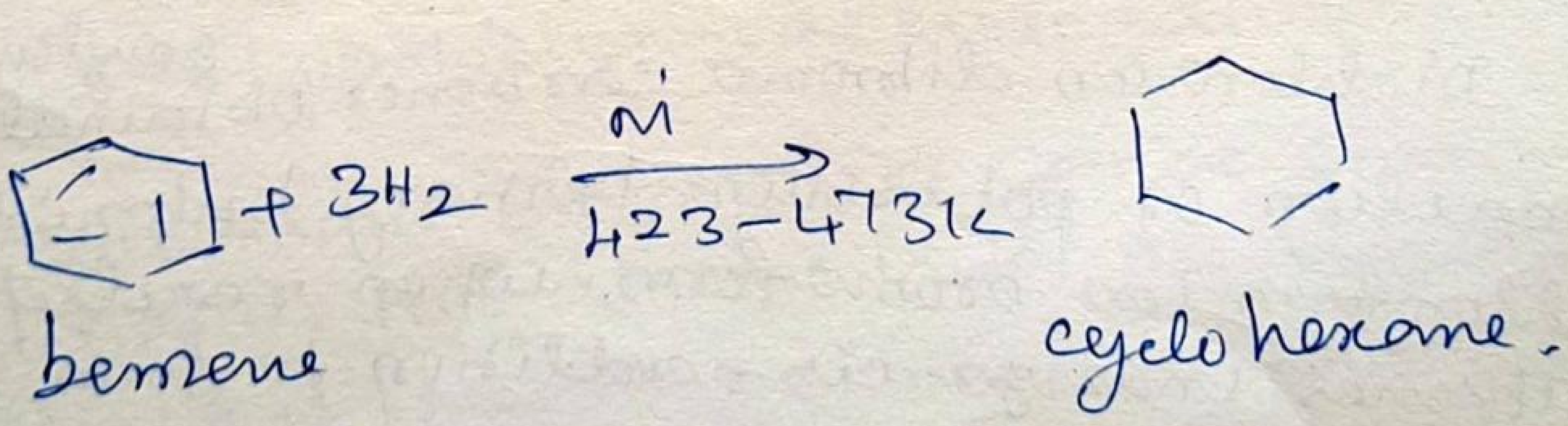
From calcium (or) barium salt of dicarboxylic acid.

When a calcium (or) barium salt of a dicarboxylic acid is distilled. ketone is obtained is subjected to clemmenson reduction, giving the cyclo alkane as illustrated by the following reaction.



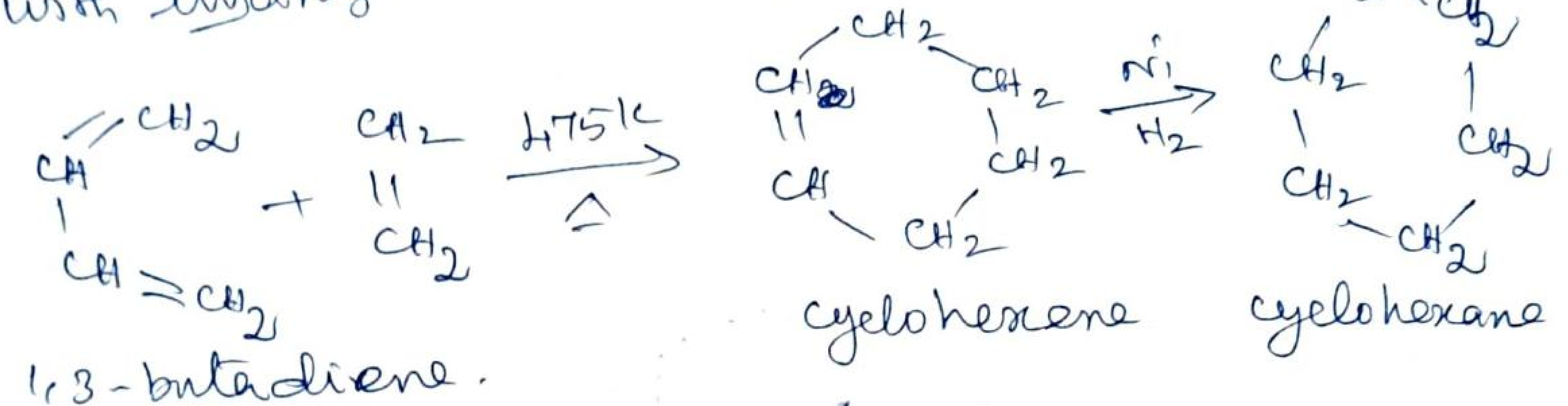
3. **Reduction** of aromatic compd:

cyclohexane and its derivatives can be prepared by passing hydrogen gas through benzene (or) its derivatives, in the presence of Ni at 423-473K temperature.



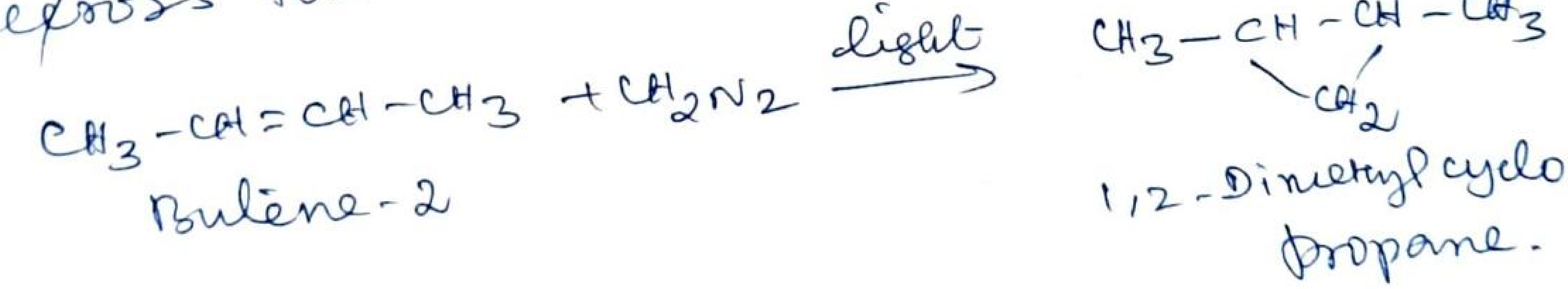
4. **Diel's-Alder addition:**

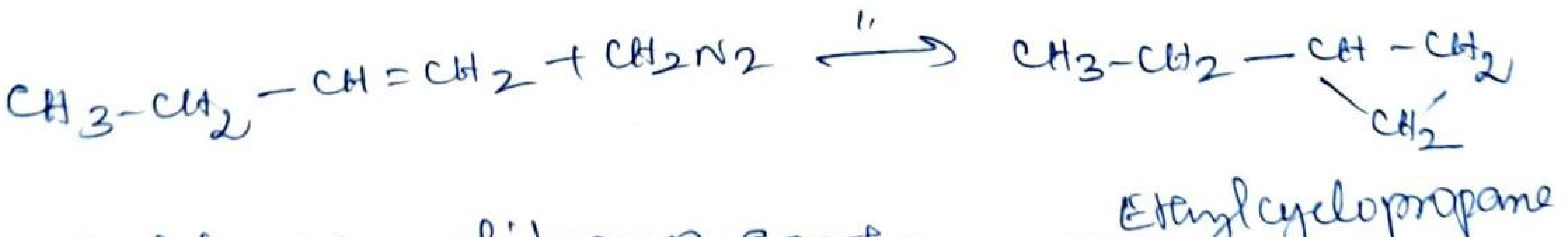
Two unsaturated compds can be combined to produce a cycloalkane. When a mixture of 1,3-butadiene and ethylene is heated to 475K cyclo-hexene is obtained. It can be reduced with hydrogen to yield cyclohexane.



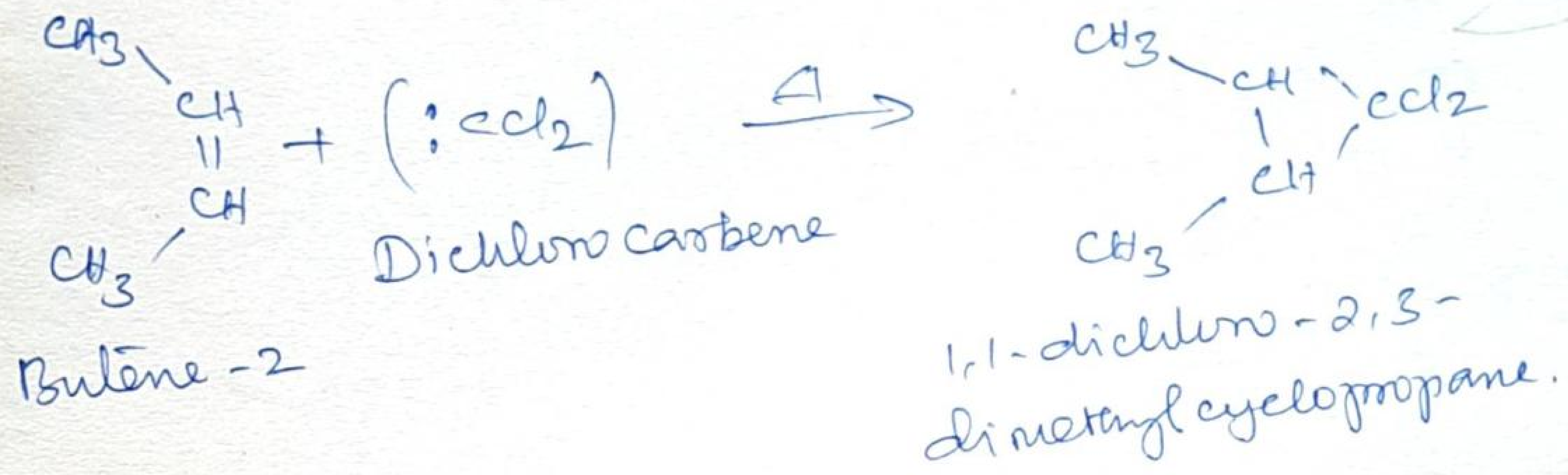
5. **Addition to carbenes to alkenes:**

cyclopropane derivatives can be prepared by treating an alkene with diazomethane. methylene group in the form of carbene $:CH_2$ is attached across the double bond in the alkene molecules.



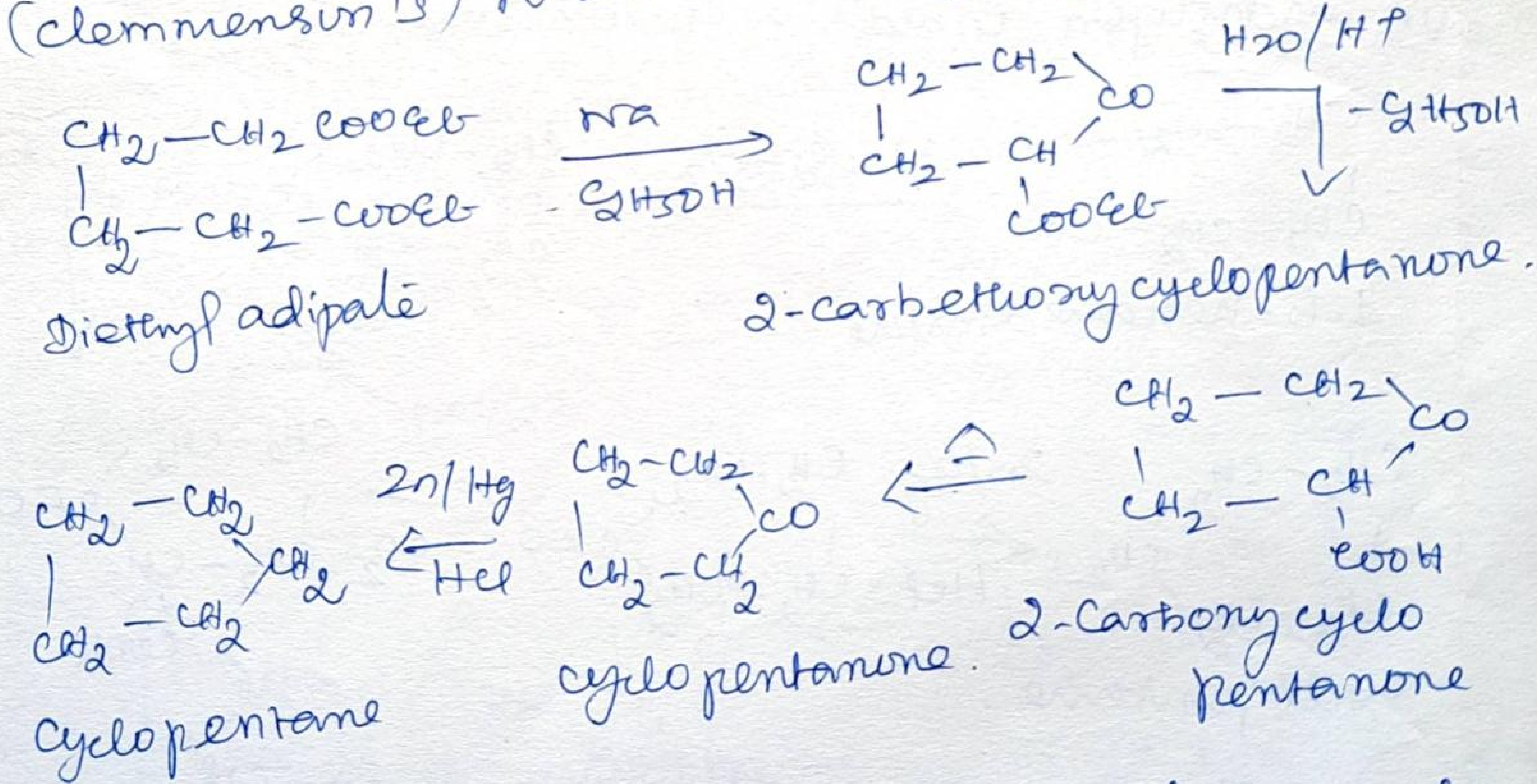


Dichloro (or) dibromo carbenes obtained by the reaction of potassium tertiary butoxide and chloroform (or) bromoform when reacted with alkenes undergo cis-addition to form alicyclics.



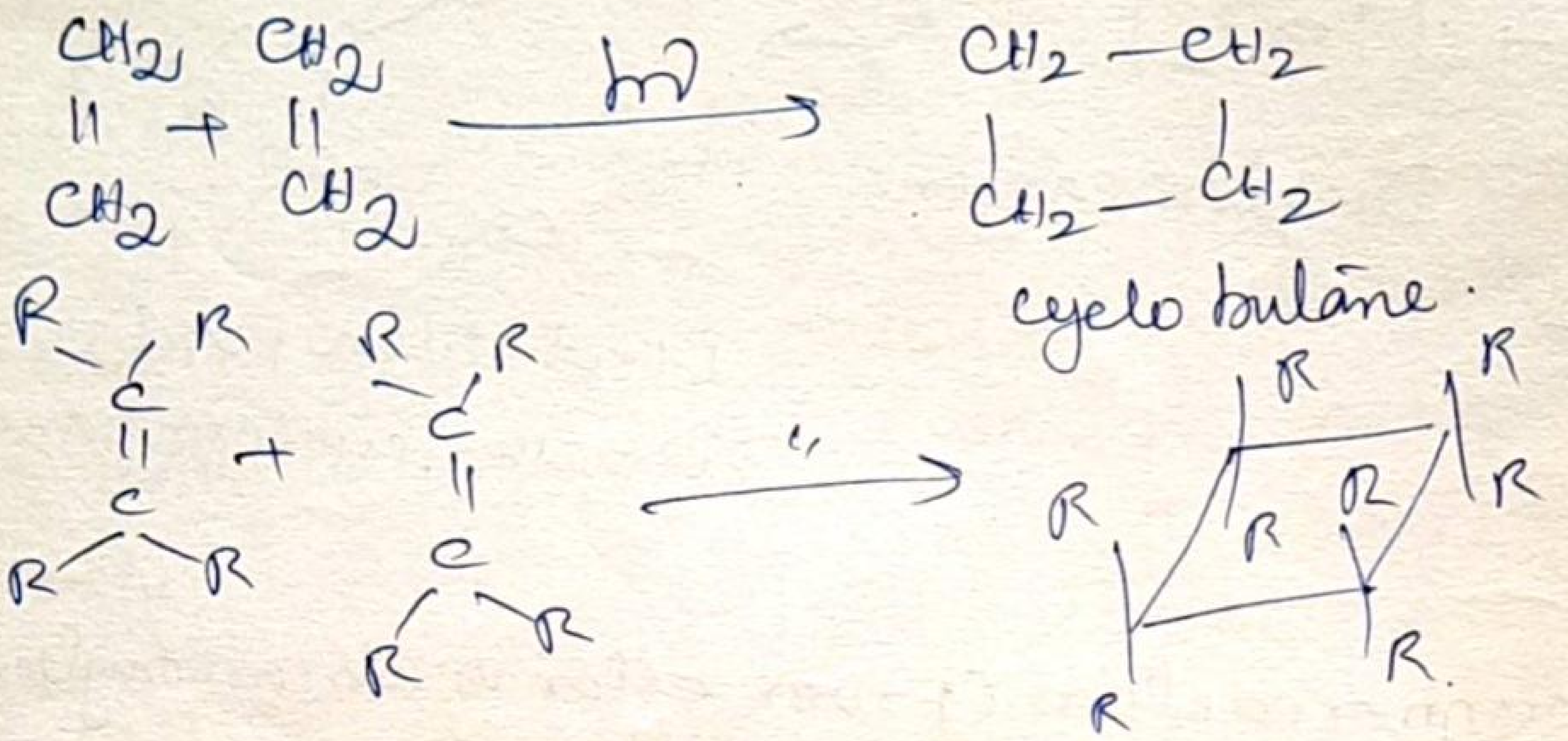
6. Dieckmann reaction (From ester of dicarbonylic acid)

Cyclopentane can be obtained when an ester of adipic acid is treated with sodium on sodium ethoxide. Intramolecular change produces cyclic ketone. Ketone is reduced (clemmenson's) to obtained cyclopentane.



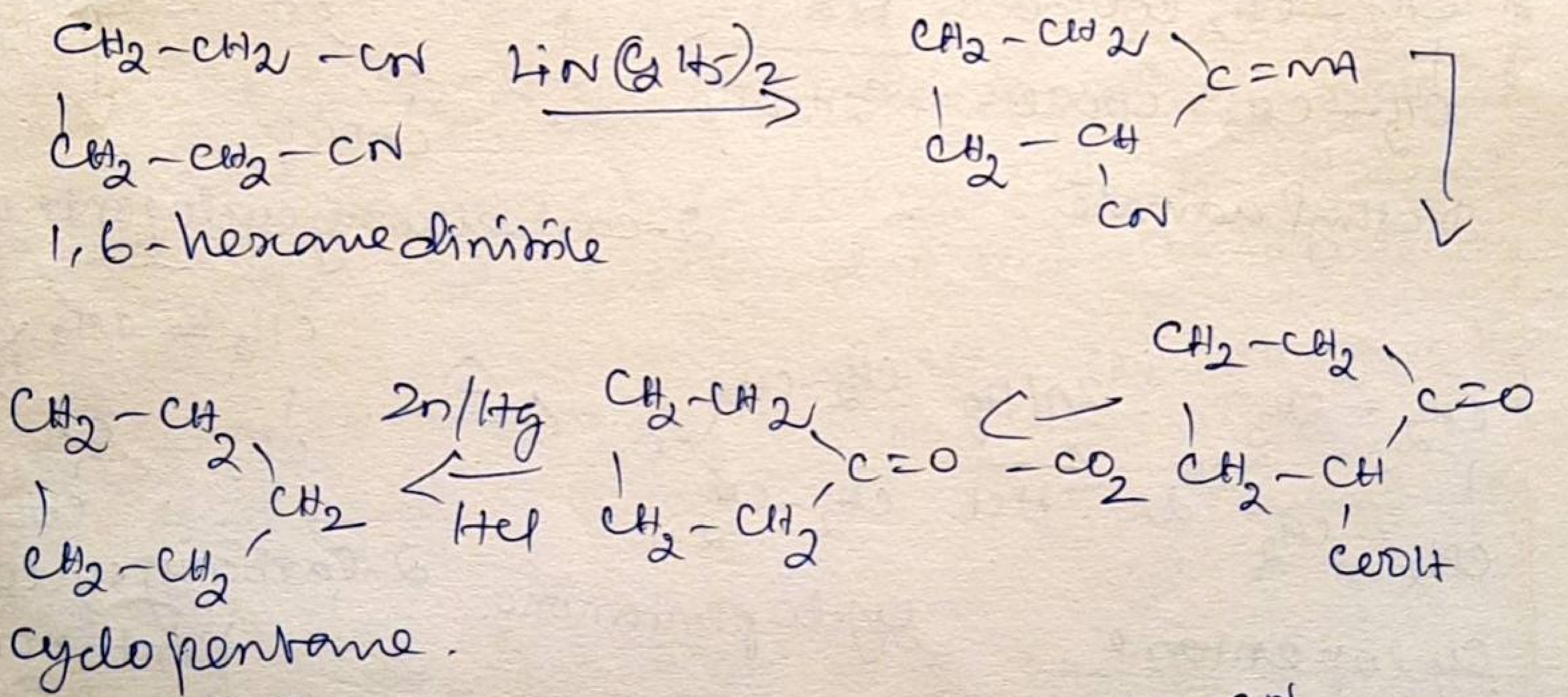
7) By [2+2] photochemical cycloaddition reaction

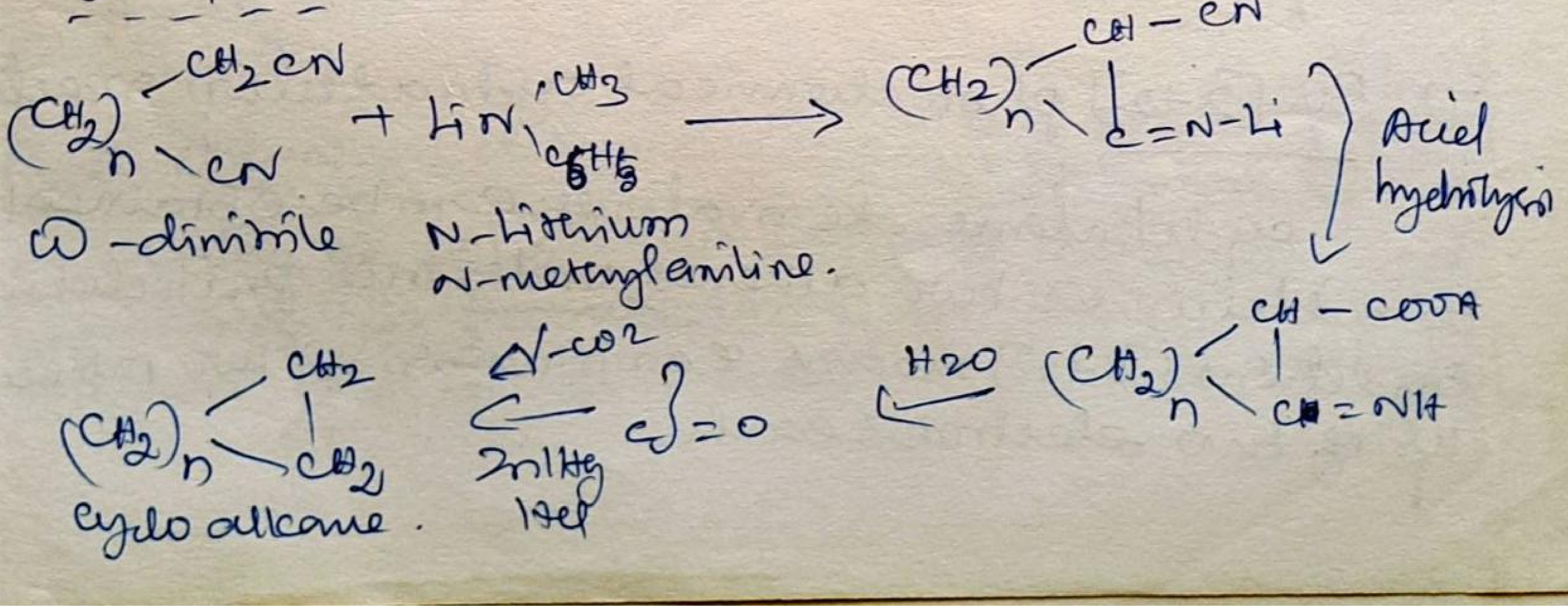
Cyclobutane derivatives can be obtained by addition of two alkenes under the photochemical conditions [2+2] means combination of two molecule using two electrons each.



8. Thorpe - Ziegler reaction (Thorpe)

A dinitrile is treated with LiN$(C_2H_5)_2$ in a large volume of benzene or toluene as solvent. A cyclic imino compd is obtained which on hydrolysis yields a cyclo ketone





Properties

Physical

1) The first two members i.e. cyclo propane, cyclo butane are gases at room temperature while higher cycloalkanes are colourless liquids having pleasant odours.

(2) Their bp, mp, and sp. gr. shows a gradual increases with the increase in molecular weight as shown in.

S.No	Name	formula	Bp°c	mp°c	sp. gr	Heat of Combustion
1	cyclopropane	C_3H_6	−35	−127	—	499.9
2	" butane		+12	−90	0.704	655.6
3	" pentane		49	−94	0.764	793.5
4	" hexane		81	+7	0.793	944.4
5	" heptane	C_7H_{14}	117	−12	0.825	1108.1
6	" octane		148	11.5	0.830	1268.8
7	" nonane		172	11	0.845	1429.2
8	" decane.	$C_{10}H_{20}$	201	9.6	—	1586.0

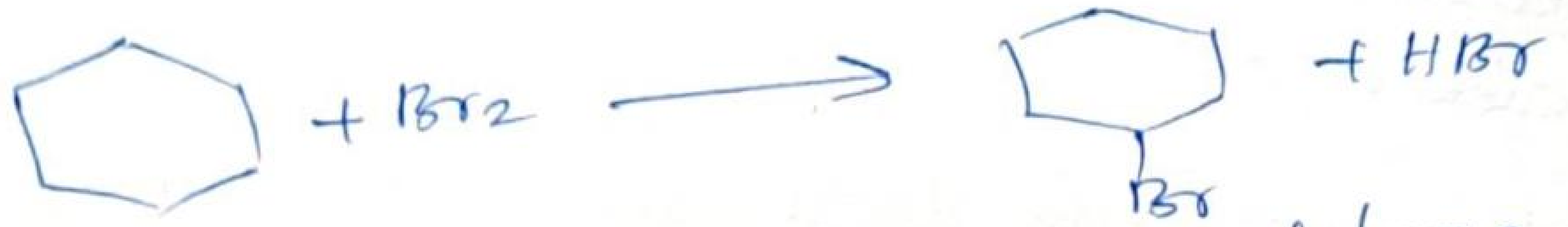
3. They are insoluble in water but soluble in ether alcohol etc.

4. This heats of combustion follow an irregular pattern revealing that cyclohexane & cyclopentane systems are more stable while cyclopropane & cyclo butane systems are less stable. This has been explain on the basis of bayer strain theory.

Chemical properties

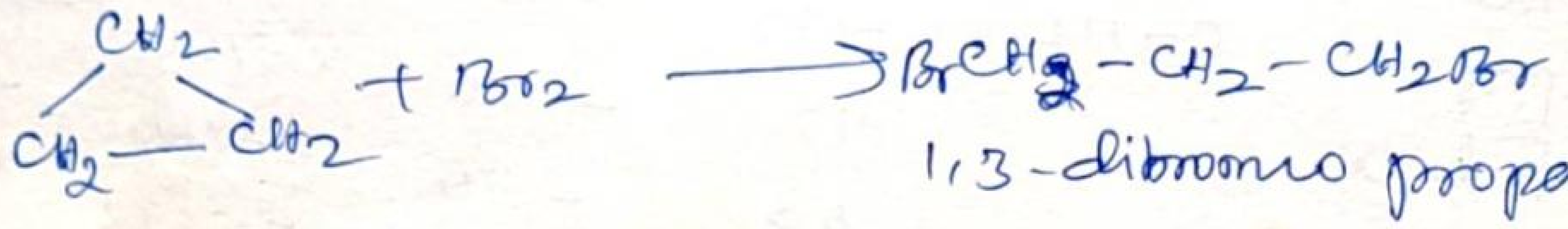
1. Reaction with halogen:

~~Halogens chlorine~~ Generally cycloalkanes undergo free radical substitution with halogen at high temperature or in the presence of light

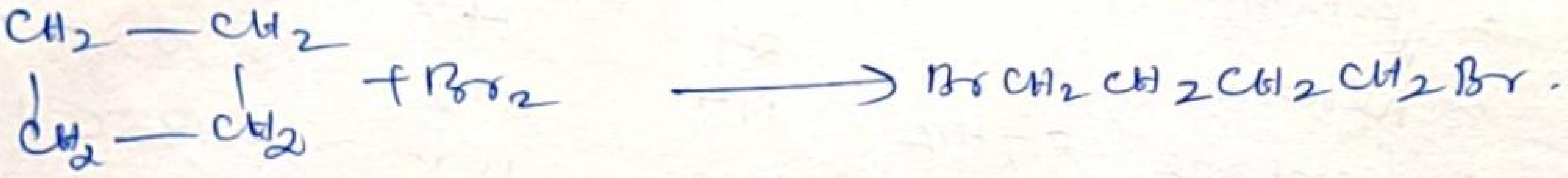


Bromo cyclohexane

whereas in the case of cyclopropane, It react with bromine & chlorine to give addition products with ring fission.

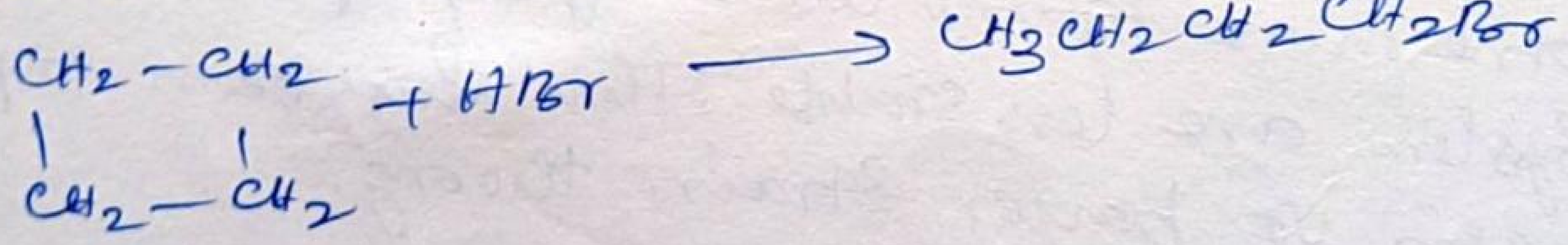


1,3-dibromo propane.



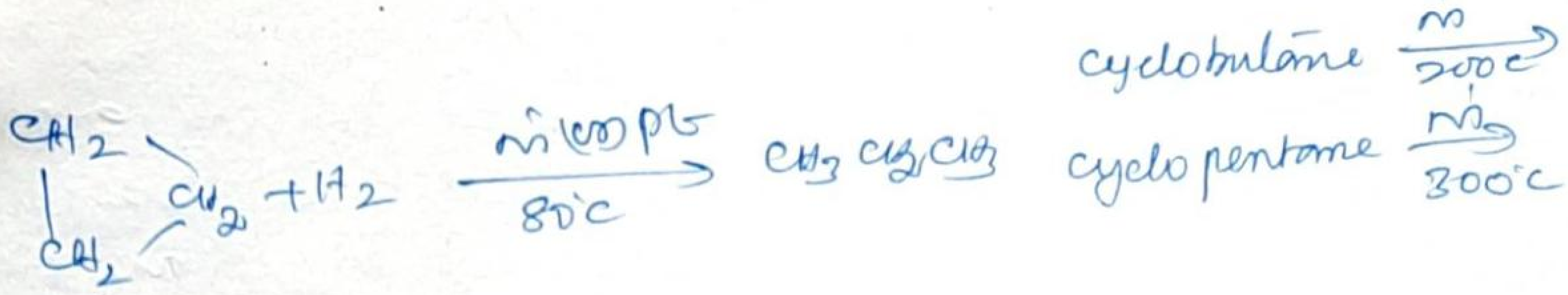
2. Reaction with halogen acids

Lower members cyclopropane and cyclobutane react with halogen acid like HCl HBr etc. to form addition products. whereas Higher cycloalkane do not react with ~~HCl~~ easily



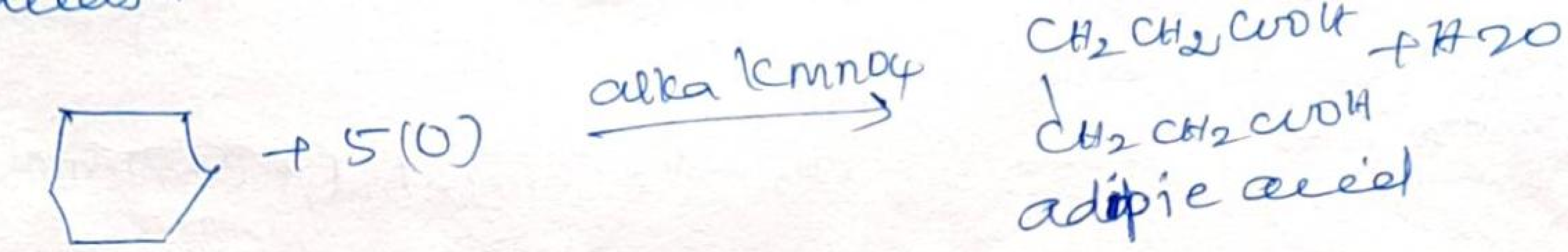
3. Reaction with Hydrogen.

When heated with Hydrogen in the presence of nickel cyclopropane & cyclobutane gives addition product whereas higher members do not give this reaction.



4. Oxidation.

Cycloalkane are resistant to oxidation by cold aqueous $KMnO_4$ (or ozone. However they are readily oxidized by alkaline $KMnO_4$ to dicarboxylic acids.



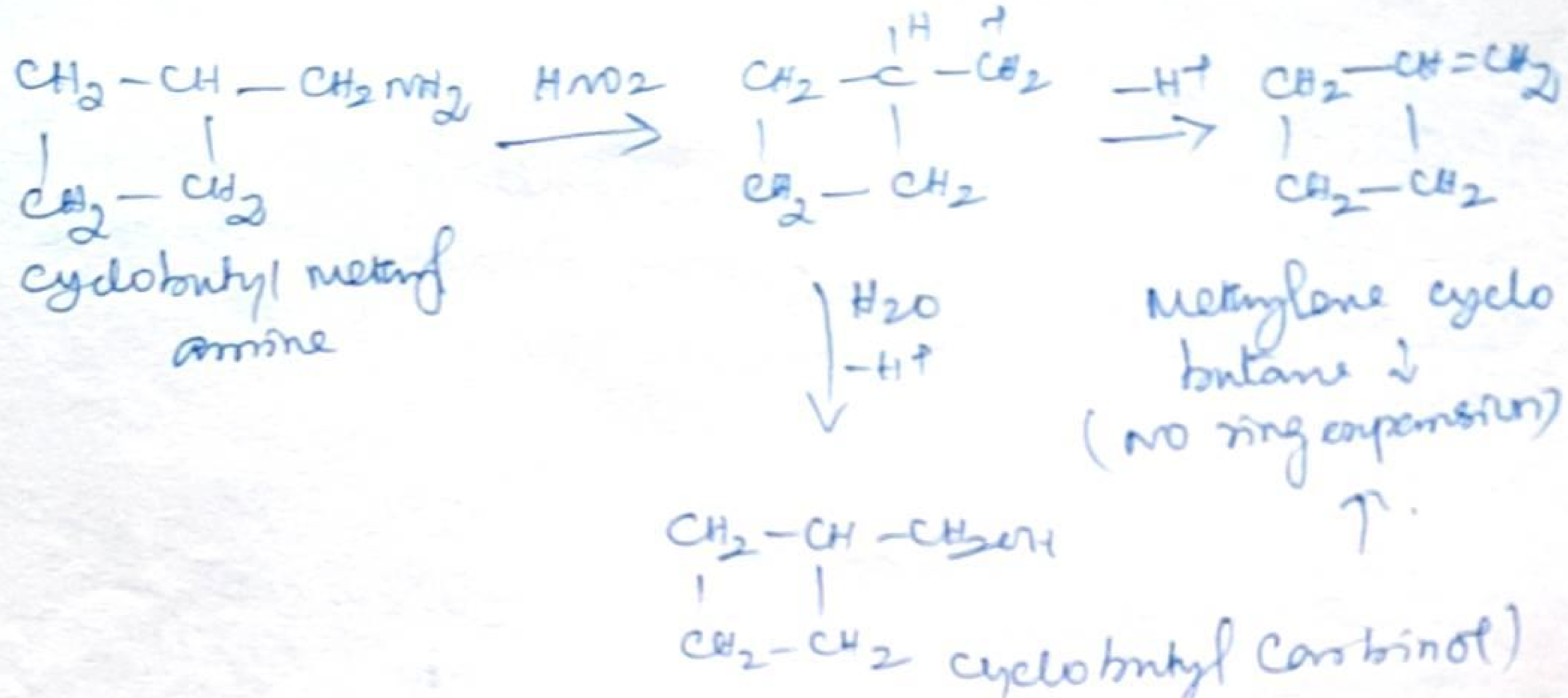
5. Rearrangement: (Demjanov)

~~[illegible] features of cycloalkane~~
~~[illegible]~~.

This is a convenient method of expanding and contracting alicyclic ring systems through the formation of carbocation intermediate. This is achieved by deamination of alicyclic amines with nitrous acid. The carbocation may ~~undergo~~ undergo reaction such as addition of nucleophile, elimination of a proton and rearrangement to a more stable carbocation.

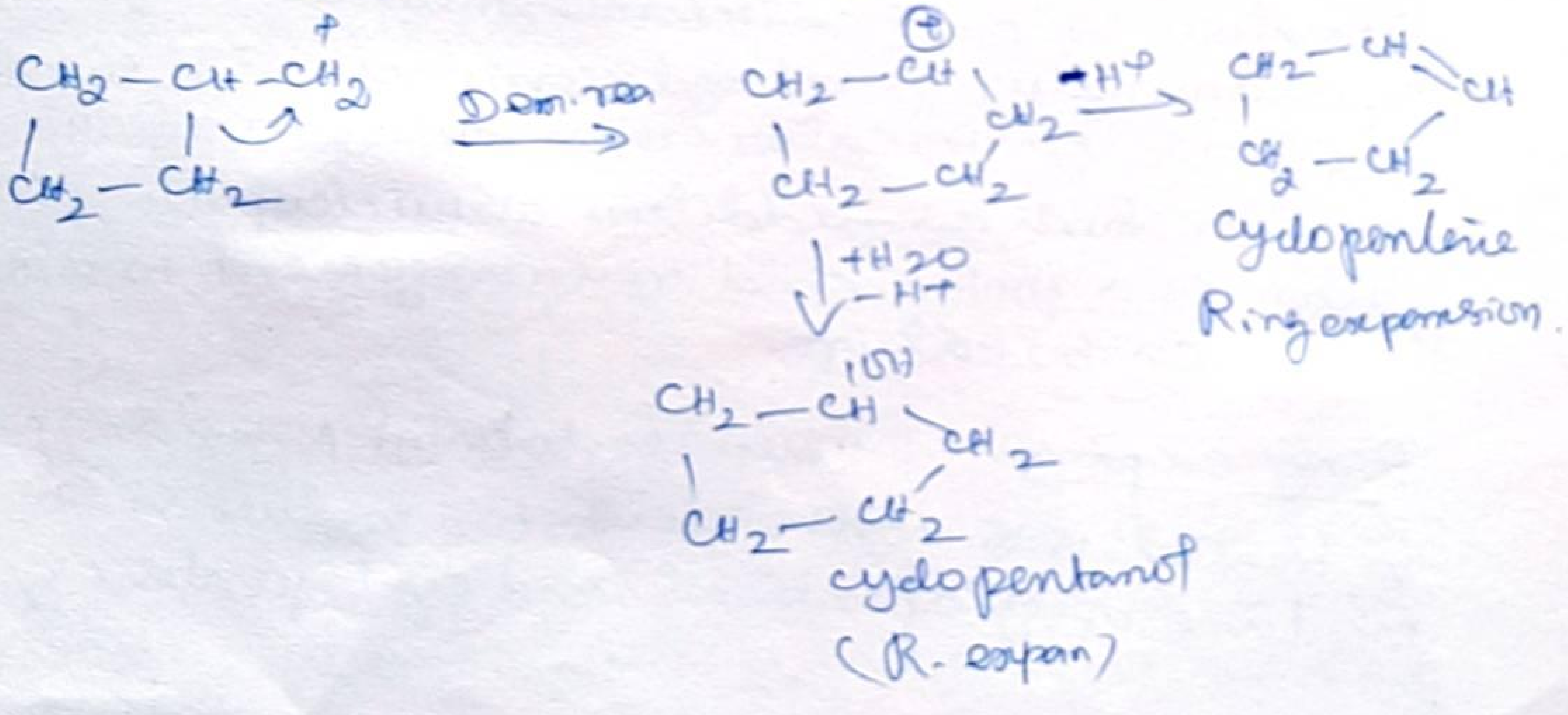
Ring expansion: when cyclobutyl methylamine is treated with nitrous acid the product is a mixture of cyclopentanol and cyclopentene.

Both these products are formed by ring expansion In addition to this cyclo carbinol and Methylene cyclobutane are formed where there is no ring expansion. The series of reaction are given below.

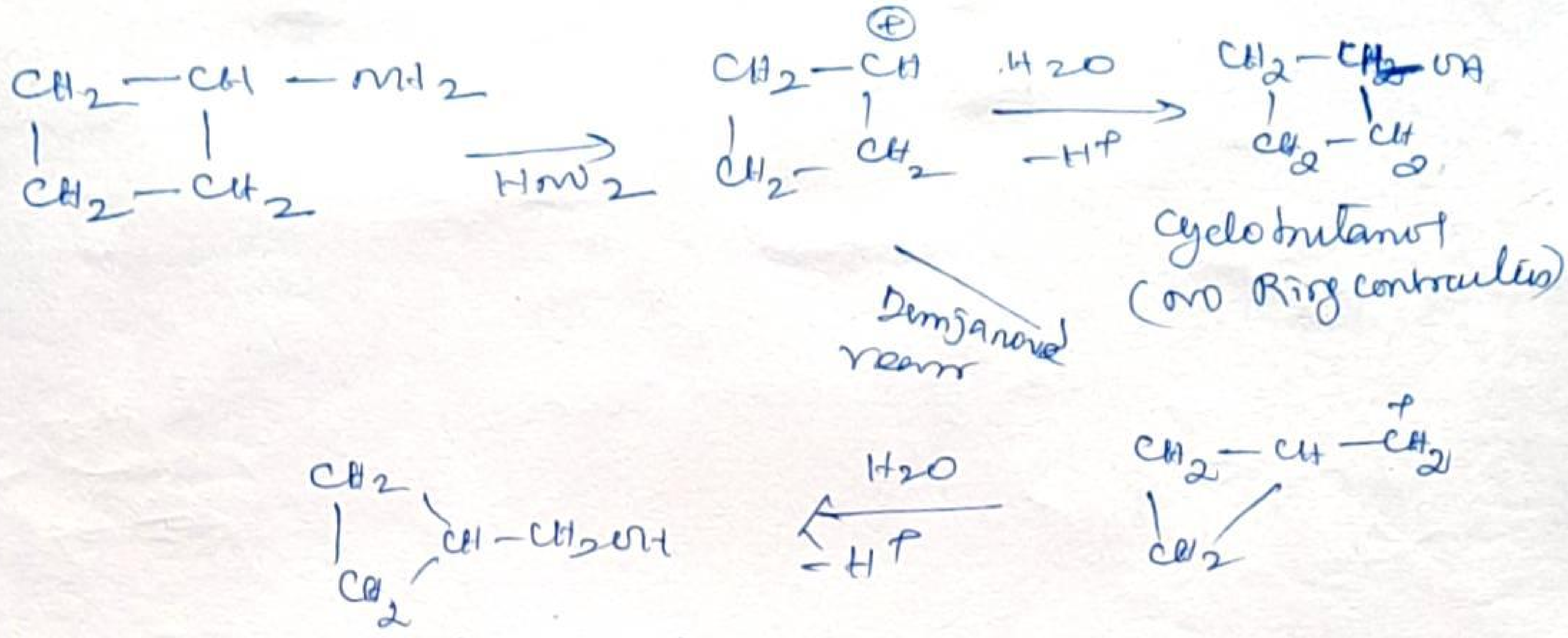


The above changes rearrangement of carbo-cation has not taken place.

If the carbocation rearrange itself to a more stable secondary carbocation, it is accompanied by ring expansion as shown below. This is called Demjanov rearrangement.



Ring Contraction: This ring contraction of the cyclobutyl amine gives cyclopropyl carbinol by Demjanov rearrangement. In addition to this cyclobutanol is also formed without any ring contraction. This reaction involved are shown below.



cyclopropyl carbinol.

If Demjanove rearrangement the ring contraction takes place when the carbocation intermediate has a positive charge on the alicyclic carbon atom. IIIly ring expansion takes place when the carbocation has a positive charge on the carbon atom α to the ~~edge~~ alicyclic ring.

DIENES OR DIOLEFINS

Dienes (or) Diolefins are bifunctional compd having two carbon-carbon double bonds in the molecule. The general formula of such hydrocarbon is C_nH_{2n-2} which is same as that of alkynes. They are known as alkadienes

The properties of compound containing two double bonds may be similar (or) different from alkenes depending upon the position of these double bonds in the molecule. They are divided into three main class.

1. Dienes with cumulated double bonds (or) Allenes:

In cumulated dienes the double bond are attached to same carbon atom. These are also known as allenes.

$>C=C=C<$ (or) $CH_2=C=CH_2$ Allene

2. Dienes with isolated double bonds:

In these dienes the double bonds are separated from each other by at least two single bonds.

$>C=CH-CH_2-CH=C<$ (or) $CH_2=CH-CH_2-CH=CH_2$
1,4-pentadiene

The isolated double bonds in dienes behave like independent double bonds. They only difference betn the alkenes and dienes is that in dienes the reaction of alkenes or double bonds are given twice because of the presence of two such linkages.

3. Dienes with conjugated doubles bonds:

When the double and single bonds are present alternately in the molecule, the compound is said to have conjugated double bonds.

$>C=CH-CH=C<$; $CH_2=CH-CH=CH_2$; $CH_3-CH=CH-CH=CH_2$
1,3-butadiene ; 1,3-pentadiene

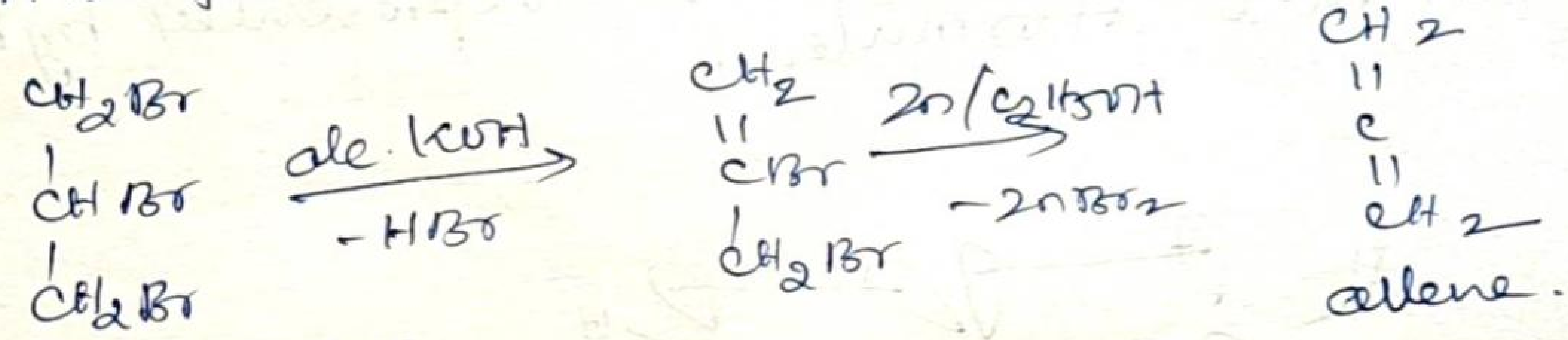
The properties of conjugated dienes are different from those of cumulated (or) isolated dienes

The compound containing three, four (or) many double bond are termed as trienes, tetraenes, polyenes respectively and the above classification may be extended to them as well. The IUPAC system they are named by replacing the 'ane' of the corresponding alkane by "diene", 'tetraene' and polyene depending upon the number of double bonds in the molecule and locates are used to indicate the position of the double bonds.

ALLENES

Allene (or) propadiene is the parent compd of series of diene with cumulated double bonds

1. From Trichloropropane: Trichloro (or) Tribromo propane on treatment with alcoholic potassium hydroxide and then with zinc and alcohol results in the formation of allene.



$$\begin{matrix} CH_2Br \\ | \\ CHBr \\ | \\ CH_2Br \end{matrix} \xrightarrow[-HBr]{alc.\ KOH} \begin{matrix} CH_2 \\ \| \\ CBr \\ | \\ CH_2Br \end{matrix} \xrightarrow[-ZnBr_2]{Zn/C_2H_5OH} \begin{matrix} CH_2 \\ \| \\ C \\ \| \\ CH_2 \end{matrix}$$

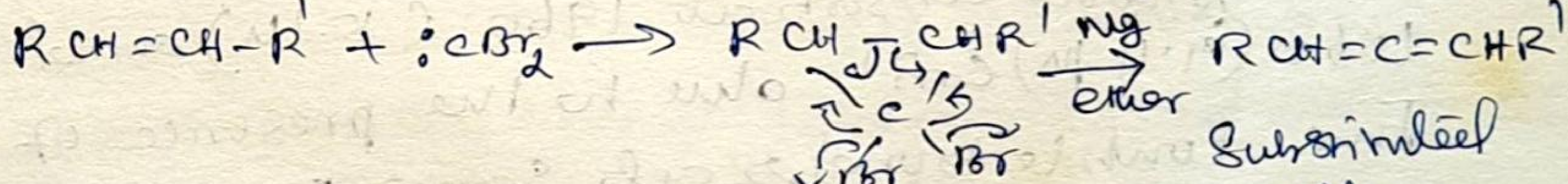
allene.

1,2,3-tribromo propane.

2. From olefins: A general method for preparing allenes is to treat an alkene with bromoform and pot. t-butoxide, followed by ~~reduction~~ reaction with magnesium in ether.

$$CHBr_3 + (CH_3)_3COK \longrightarrow :CBr_2 + (CH_3)_3COH + KBr.$$

Dibromocarbene.
(Transitory intermediate)



$$RCH=CH-R' + :CBr_2 \longrightarrow \underset{\underset{Br\ \ Br}{C}}{RCH-CHR'} \xrightarrow[ether]{Mg} RCH=C=CHR'$$

Substituted allene.

Allene are highly reactive and readily undergo rearrangement to form acetylene derivatives. For examples allene on reaction with sodium gives sodium methyl acetylides.

$$CH_2=C=CH_2 \xrightarrow[ether]{Na} CH_3C\equiv CNa$$

Sod. methyl acetylide.

~~Allene~~

The formula of allene suggests that the central carbon atom is in sp hybridized state and therefore the two double bonds and the terminal methylene groups must lie at right angles to each other in different planes. The other two carbon atoms involved in double bonds are in sp^2 hybridized state. Allenes may therefore be represented by the given M.O formula.

M.O representation of allene.

If the allene is suitably substituted (as (abC=C=Cab) because of its peculiar structure, it will exist in two enantiomorphic forms and exhibit optical activity.

Allene absorb at 1960 (5.1 μ) and 1060 (9.4 μ) cm^{-1} due to the presence of two double bonds at same carbon in IR region.

Conjugated Dienes

The Simplest Conjugated dienes is buta-diene (or 1,3-butadiene). It has been observed that butadiene and other conjugated dienes shows remarkable differences in the physical and chemical properties. when compared with isolated dienes. In general They are more reactive and more stable than corresponding isolated dienes. Another important member of the series is isoprene (or 2 methyl butadiene.

Preparation

1) Dehydration of 1,2; 1,3 and 1,4 diols:

Butanediols when passed over heated acid catalyst eliminates two molecules of water to give butadiene

$$\underset{OH}{CH_2}-CH_2-CH_2-\underset{OH}{CH_2} \xrightarrow[-2H_2O]{H_3PO_4/270^\circ C} \underset{1,3\text{-butadiene}}{CH_2=CH-CH=CH_2}$$

2. Dehydrogenation of alkanes (or) alkenes:

n-butane (or) butene when passed over heated chromic oxide gives butadiene

$$CH_3-CH_2-CH_2-CH_3 \xrightarrow[-H_2]{Cr_2O_3/\Delta} \underset{2\text{-butene}}{CH_3-CH=CH-CH_3}$$

$$\xrightarrow[-H_2]{Cr_2O_3/\Delta} \underset{1,3\text{-butadiene}}{CH_2=CH-CH=CH_2}$$

$$CH_3-CH_2-CH=CH_2 \xrightarrow[-H_2]{''} CH_2=CH-CH=CH_2$$

Isopentane (2-methylbutane) or iso-pentylene (3-methyl-1-~~pexen~~ pentene) gives isoprene.

$$\underset{\text{2-methyl butane}}{(CH_3)_2CHCH_2CH_3} \xrightarrow[-H_2]{Cr_2O_3/\Delta} \underset{\text{isoprene}}{CH_2=\overset{CH_3}{\overset{|}{C}}-CH=CH_2}$$

$CH_3-\overset{CH_3}{\overset{|}{CH}}-CH=CH_2$ isopentylene or

3. By passing Ethyl alcohol and acetaldehyde over heated catalyst: The catalyst is Silica gel and tantalum oxide

$$C_2H_5OH + CH_3CHO \xrightarrow{\Delta} CH_2=CH-CH=CH_2$$

4. By decomposition of cyclohexene.
cyclohexene when passed over heated nickel chromium catalyst gives butadiene.

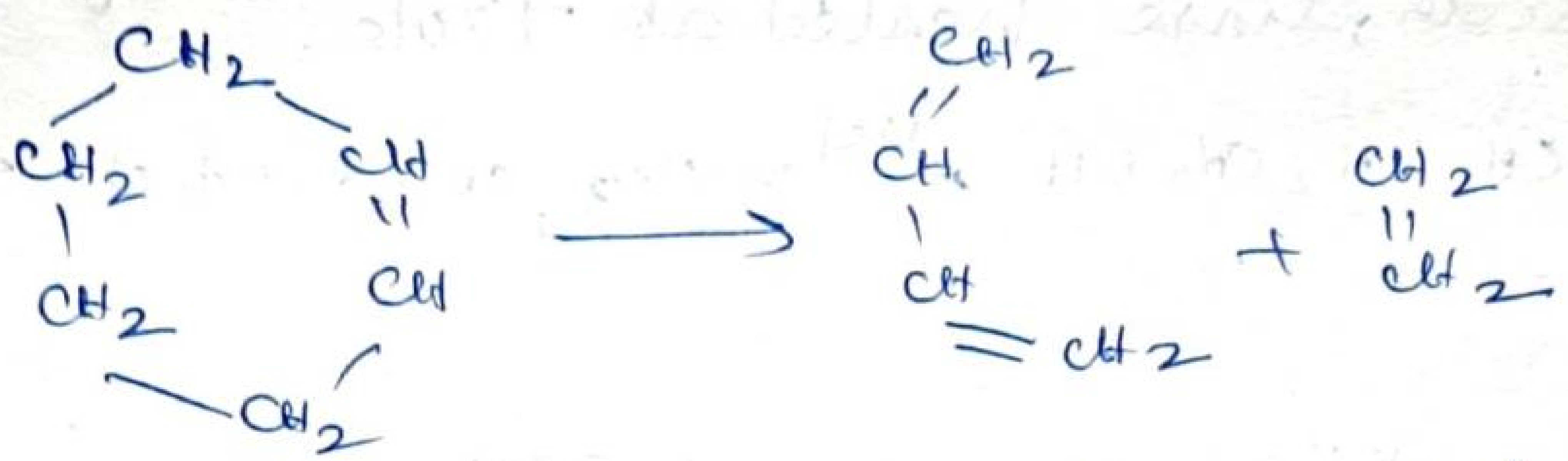
$$C_6H_{10} \xrightarrow{Ni/Cr} \underset{\text{Butadiene}}{CH_2=CH-CH=CH_2} + \underset{\text{Ethene}}{CH_2=CH_2}$$

Properties.

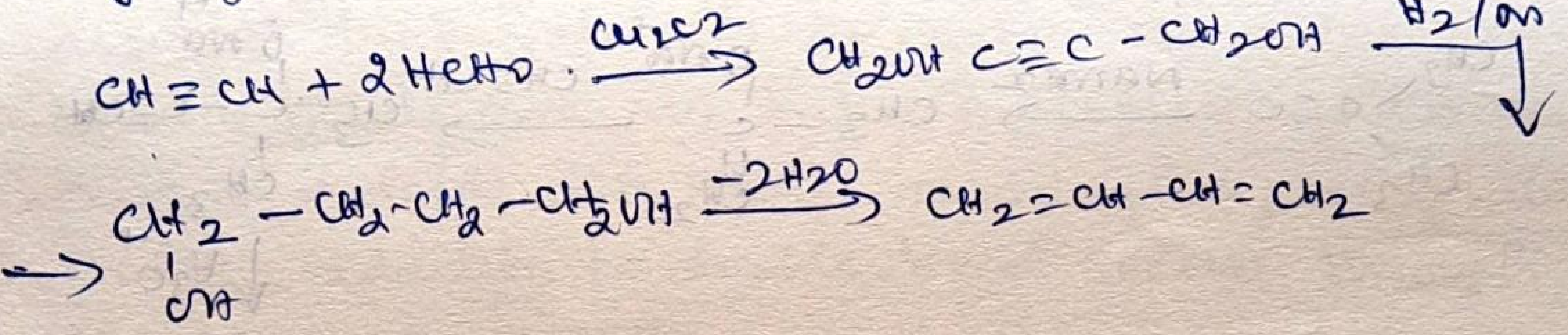
Physical: Butadiene is a gas at room temp (bp -2.6°c) whereas isoprene is a liquid (bp 30°c). The heat of combustion and hydrogenation of butadiene and isoprene are lower than the expected value.

The bond distance of carbon atoms in butadiene are neither those of pure single nor of pure double bond and they have intermediate value. Thus C_1 to C_2 or C_3 to C_4 bond length is 1.35A° and C_2 and C_4 bond length is 1.47A°

1. Butadiene may be prepared in 65-70% yield by passing cyclohexene over a heated nichrome wire



2. By passing a mixture of acetylene and formaldehyde over copper acetylide (catalyst) followed by catalytic hydrogenation of the intermediate product butynediol



$$CH \equiv CH + 2HCHO \xrightarrow{Cu_2C_2} CH_2OH\,C \equiv C - CH_2OH \xrightarrow{H_2/Ni}$$

$$\rightarrow \underset{OH}{CH_2} - CH_2 - CH_2 - CH_2OH \xrightarrow{-2H_2O} CH_2 = CH - CH = CH_2$$

ALKYNES

Alkynes are unsaturated hydrocarbons having the general formula C_nH_{2n-2}. Such Compounds are more unsaturated than alkenes. This is because alkynes contains 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. The triple bond implies the sharing of three pairs of e^- betn two carbon atoms and is often called as the acetylenic (or) alkynie linkage.

Nomenclature

1. The Common name system.

The Common name of the first member of the Series (C_2H_2) is acetylene. This name has been adopted even in IUPAC system. The common name of the alkynes do not bear any relationship and are based on the names of related compounds for example.

Formula	Common name.
$C_2H_2(CH\equiv CH)$	Acetylene
$C_3H_4(CH_3C\equiv CH)$	Allylene
$C_3H_8(CH_3C\equiv C-CH_3)$	Crotonylene

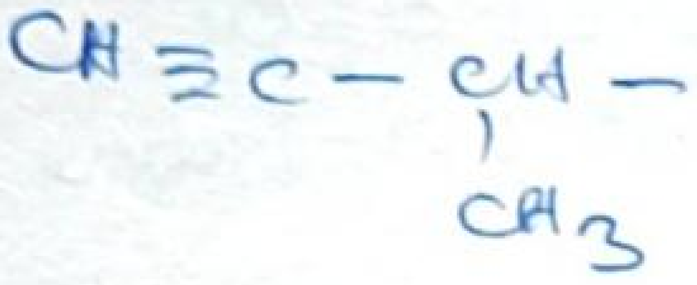
However, except acetylene other names are no longer used.

2. Acetylene derivatives System

Acetylene is considered to be the parent member of the alkynes Series and all other alkynes are named as alkyl derivatives of acetylene.

$CH\equiv C-$ Ethynyl $CH\equiv C-CH_2-$ 2-propynyl

$CH_3C\equiv C-$ propynyl $C_2H_5-C\equiv C-$ Butynyl


$CH\equiv C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-$ 2(1-methyl) propynyl.

If the molecules contains more than one triple bond the suffix 'ane' of the alkanes is replaced by 'adiyne' 'atriyne' etc. depending on the number of triple bond. Compd having many triple bonds are known as "alkapolynes" The position of triple bonds are indicated by the number of carbon atoms preceding these bonds for example.

$\overset{4}{C}H\equiv\overset{3}{C}-\overset{2}{C}\equiv\overset{1}{C}H$

1,3-butadiyne (Diacetylene)

$\overset{2}{CH}\equiv C-CH_2CH_2-C\equiv\overset{1}{C}H$

1;5 hexadiyne (Dipropargyl)

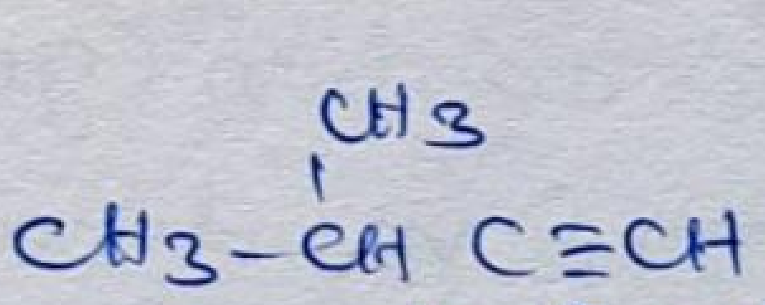
Isomerism

Ethyne and propyne donot exhibit any type of isomerism. Other alkynes exhibit various types of isomerism.

1. **Chain isomerism**: It is due to difference in the type of carbon skeleton in chain for example C_5H_8

$CH_3-CH_2-CH_2\,C\equiv CH$

1-pentyne (Straight chain)


$CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}\,C\equiv CH$

3-methyl-1-butyne
(branched chain)

2. **Position isomerism**: Butyne, pentyne etc exhibit isomerism due to the various structure which may be changing the position of triple bond.

$CH_3-CH_2-C\equiv CH$
1-butyne

$CH_3-C\equiv C-CH_3$
2-butyne.

$CH_3-CH_2CH_2C\equiv CH$
1-pentyne

$CH_3CH_2C\equiv CCH_3$
2-pentyne

$$CH_3-\overset{\overset{CH_3}{|}}{CH}C\equiv CH$$
3 metyl-1-butyne.

3. Functional isomerism. Alkynes are isomeric with dienes. Thus C_4H_6 represents butyne and butadiene

$CH_3-CH_2-C\equiv CH$
1-butyne

$CH_2=CHCH=CH_2$
1,3-butadiene

All these isomers are known. However the alkynes do not exhibit geometrical isomerism because of linearity of the molecule around the triple bond.

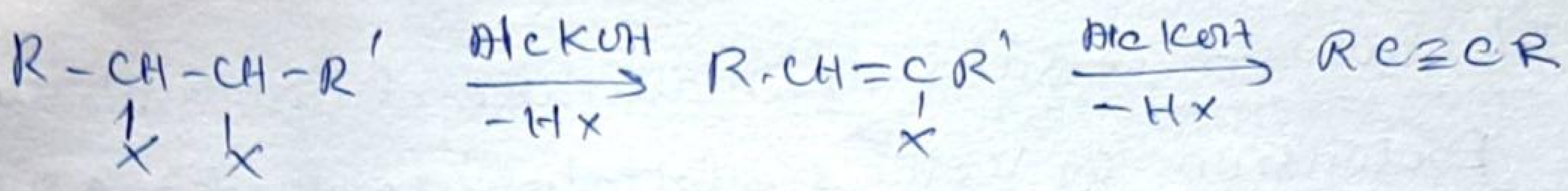
Butyne exists in two isomeric forms. pentyne exists in three isomeric forms.

Preparation

1. Dehydrohalogenation of Dihalides:

When dihaloalkanes are treated with excess of alcoholic KOH alkynes are formed by the elimination of two moles of halogen acids. Dihaloalkanes (or) alkyl dihalides may have two halogen attached at the same carbon (gem-dihalides) (or) at adjacent carbon atoms (vic-dihalides).

I) From vic-dihalides : The vic-dihalides on treatment with alcoholic KOH (or) sodamide gives alkyne. This reaction occurs in two stages first an olefinic halides is formed on subsequent elimination of a hydrogen halides yields an alkyne.



$$\underset{X}{R-CH}-\underset{X}{CH}-R' \xrightarrow[-HX]{Alc\ KOH} R\cdot CH=\underset{X}{C}R' \xrightarrow[-HX]{Alc\ KOH} RC\equiv CR$$

$$CH_2Br-CH_2Br \xrightarrow[\text{''}]{\text{''}} \underset{\text{vinyl bromide}}{CH_2=CHBr} \xrightarrow[\text{''}]{\text{''}} \underset{\text{Acetylene.}}{CH\equiv CH}$$

$$CH_3-CHBr\,CH_2Br \xrightarrow[\text{''}]{\text{''}} \underset{\text{1-bromo-1-propene}}{CH_3-CH=CH_2Br} \xrightarrow[-HX]{NaNH_2} \underset{\text{propyne.}}{CH_3C\equiv CH}$$

ii) <u>From gem-Dihalides</u>: The reaction of gem-dihalides with strong bases like alcoholic potash to gives alkynes.

$$R-CH_2CHX_2 \xrightarrow[-XH]{alc\cdot KOH} R-CH=CHX \xrightarrow[-HX]{Alc\cdot KOH} RC\equiv CH.$$

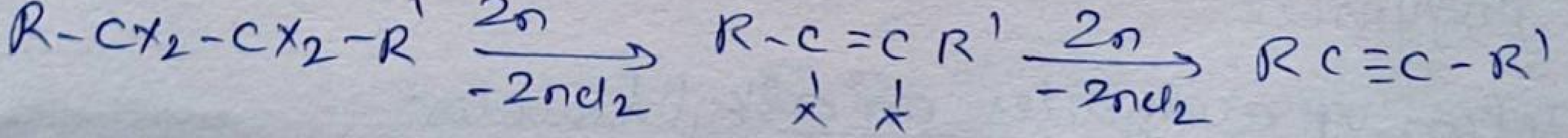
$$CH_3CHBr_2 \xrightarrow[\text{''}]{\text{''}} CH_2=CHBr \xrightarrow[\text{''}]{\text{''}} CH\equiv CH.$$

Ethylidene bromide

$$CH_3\,CBr_2\,CH_3 \xrightarrow[\text{''}]{\text{''}} CH_3C\equiv CH.$$

As both vic-and gem dihalides are ~~red~~ readily obtained by the treatment of alkenes with halogen and of aldehyde or ketones with pcl5 respectively,

2. <u>Dehalogenation of Tetrahalides</u>: Tetrahalo alkanes on treatment with active metals like zinc, magnesium etc. form alkynes.



$$R-CX_2-CX_2-R' \xrightarrow[-ZnCl_2]{Zn} R-\underset{X}{C}=\underset{X}{C}R' \xrightarrow[-ZnCl_2]{Zn} RC\equiv C-R'$$

$$CHBr_2-CHBr_2+2Zn \longrightarrow CH\equiv CH+2ZnBr_2$$

$$CH_3CBr_2CHBr_2+2Zn \longrightarrow CH_3C\equiv CH+2ZnBr_2$$

properties

1. Acetylene is a colourless gas, bp -84°c and has an ethereal smell when pure.

2. It is sparingly soluble in water but readily soluble in acetone

3. when Compressed con liquified acetylene is explosive but its solution under pressure (10atm) in acetone absorbed on some suitable porous material can be handled with safety.

4. Acetylene burns with a luminous smoky flame (due to heigh carbon content) and hence is used for lighting purposes.

5. It is also used in oxy-acetylene blow-pipe, a temp above 3000°c being reached.

6. Acetylene is used for the preparation of a large number of compounds. eg. CH_3CHO, CH_3CH_2OH, acetic acid etc.

Chemical properties

1. Addition Reaction

Alkynes combine with hydrogen gas in presence of Suitable catalysts like finely divided Ni, Pt, (or) Pd Initially alkenes are formed which then take up another molecule of hydrogen to form alkanes.

$$\underset{\text{Alkyne}}{R-C\equiv CH} \xrightarrow[\Delta]{Ni|H_2} \underset{\text{Alkene}}{RCH=CH_2} \xrightarrow{Ni|H_2} \underset{\text{alkane}}{RCH_2CH_3}$$

$$\underset{\text{Acetylene}}{CH\equiv CH} \xrightarrow[\text{''}]{\text{''}} \underset{\text{Ethene}}{CH_2=CH_2} \xrightarrow[\text{''}]{\text{''}} \underset{\text{Ethane}}{CH_3-CH_3}$$

$$\underset{\text{propyne}}{CH_3-C\equiv CH} \xrightarrow[\text{''}]{\text{''}} CH_3CH=CH_2 \xrightarrow[\text{''}]{\text{''}} \underset{\text{propane}}{CH_3-CH_2-CH_3}$$

If the lindlar's catalyst (palladium heavy metal| quinoline) is used the hydrogenation does not proceeds beyond the alkene stage

$$CH_3C\equiv CH \xrightarrow[\text{Lindlar's catalyst}]{H_2} \underset{\text{propene}}{CH_3-CH=CH_2}$$

2. Addition of Halogen

Alkynes are react with one or two mole of halogens to giving dihalides and tetrahalides respectively. Cl_2 and Br_2 add readily to the triple bond while Iodine react rather slowly. (catalyst light (or) metallic halides)

$$CH\equiv CH + Cl_2 \longrightarrow \underset{\text{1,2-dichloro ethene}}{CHCl=CHCl} \xrightarrow{Cl_2} \underset{\text{1,1,2,2-tetrachloro ethane}}{\underset{Cl_2}{CH}-\underset{Cl_2}{CH}}$$

$$CH_3-C\equiv CH + Br_2 \xrightarrow[\text{''}]{\text{''}} CH_3-\underset{Br}{C}=CHBr \xrightarrow[\text{''}]{\text{''}} CH_3-CBr_2-CHBr_2$$

Acetylene reacts with dilute bromine water to form dibromide but with liquid bromine and in absence of solvent tetrabromide is formed.

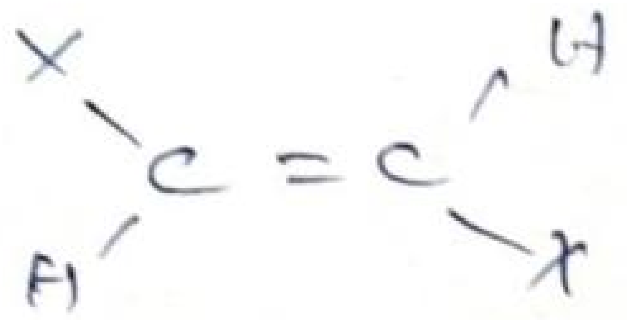
Acetylene adds on iodine with difficult but if reaction is carried out in ethanolic solution, Acetylene di iodide is obtained.

$$CH\equiv CH + I_2 \xrightarrow{C_2H_5OH} CHI=CHI$$

1,2- Di iodoethane.

The alkenes formed by the addition of halogen to alkynes are generally trans isomers because the addition is stereo selective.

$CH\equiv CH + X_2 \longrightarrow$



3. Addition of halogen acids.

The addition of halogen acids and other unsymmetrical reagents to alkynes occur in according to Markownikov's rule. The addition of the halogen acid can take place in the dark but is catalysed by light or metallic halides.

$$CH\equiv CH + HCl \longrightarrow CH_2=CHCl \xrightarrow{HCl} CH_3-CHCl_2$$

$$R-C\equiv CH + HCl \longrightarrow R-\underset{X}{\underset{|}{C}}=CH_2 \xrightarrow{HX} R-\underset{X_2}{C}-CH_3$$

when Acetylene is passed in dil HCl at 65°C in presence of Hg^{2+} as catalyst vinyl chloride is formed.

$$CH\equiv CH + HCl \xrightarrow{Hg^{2+}} CH_2=CHCl$$

In presence of peroxides anti-Markownikov product is obtained.

$$CH_3-C\equiv CH + HBr \xrightarrow{Peroxide} CH_3-CH=CHBr \xrightarrow{HBr} CH_3\underset{Br}{\underset{|}{CH}}-\underset{2}{CHBr}$$

The order of reactivity of the halogen acids is HI > HBr > HCl > HF.

4. Addition of hypohalous acid

Allkynes when passed in hypochlorous (or hypobromous acid yield haloaldehyde (or halo ketones. With acetylene dichloroacetaldehyde formed is partially oxidised to dichloro acetic acid by hypo chlorous acid.

$$R-C\equiv CH \xrightarrow{HOX} ROHC=CHX \xrightarrow{HOX} R(OH)_2C\cdot CHX_2 \xrightarrow{-H_2O} RCOCHX_2$$

α-dihaloketone.

$$CH\equiv CH + HOCl \longrightarrow HOCH=CHCl \xrightarrow{HOCl} (OH)_2CH\,CHCl_2 \xrightarrow[-H_2O]{} CHCl_2\cdot CHO$$

dichloroacetaldelyde.

$$CH_3C\equiv CH + HOBr \longrightarrow CH_3-\underset{OH}{C}=CHBr \xrightarrow{HOBr} CH_3-(OH)_2C\cdot CHBr_2 \xrightarrow{-H_2O} CH_3COCHBr_2$$

1,1-dibromo acetone.

5. Addition of water

Allkynes react with water in presence of $H_2SO_4/HgSO_4$ to yield carbonyl compound unlike alkene. The addition of water to alkyne initially yields a hydroxy alkene in which hydroxy group is on double bonded carbon atom. These compd is immediately rearrange to form a more stable carbonyl (or keto form.

$$R-C\equiv CH + H_2O \xrightarrow[H_2SO_4]{Hg/H_2SO_4} R-\overset{OH}{C}=CH_2 \longrightarrow R-\underset{O}{\overset{}{\underset{\|}{C}}}-CH_3$$

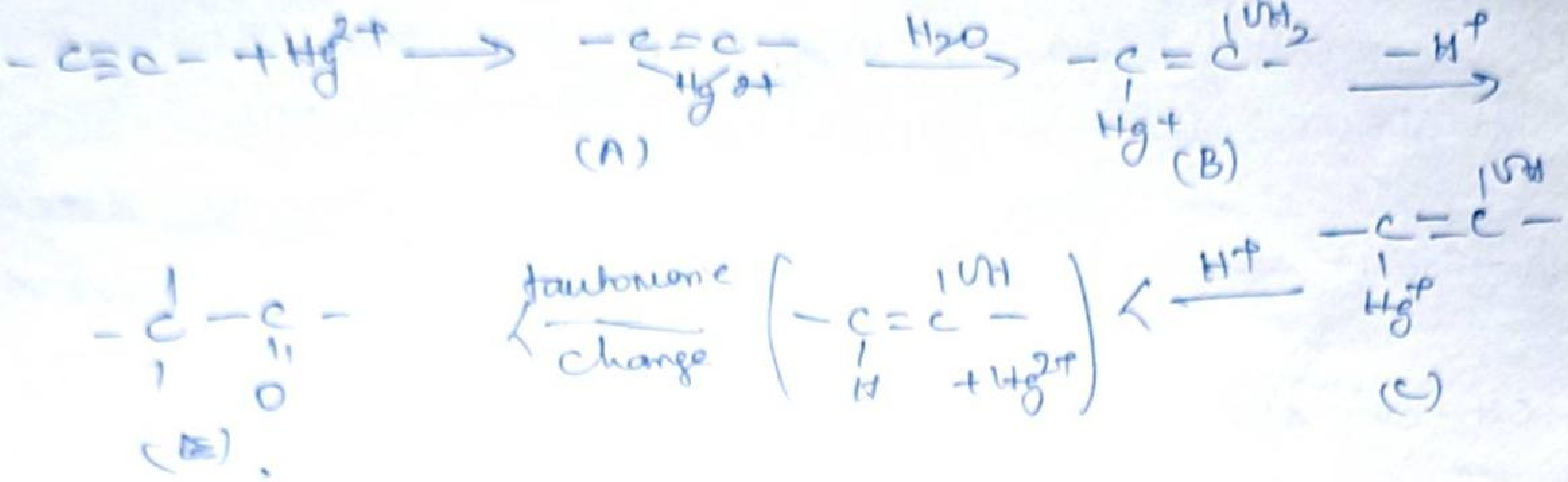
unstable

$$CH\equiv CH + H_2O \xrightarrow[''\ ]{''} \underset{OH}{CH}=CH_2 \longrightarrow CH_3CHO$$

$$CH_3-C\equiv CH + H_2O \xrightarrow[''\ ]{''} CH_3-COH=CH_2 \longrightarrow CH_3-\underset{O}{\underset{\|}{C}}-CH_3$$

Mechanism

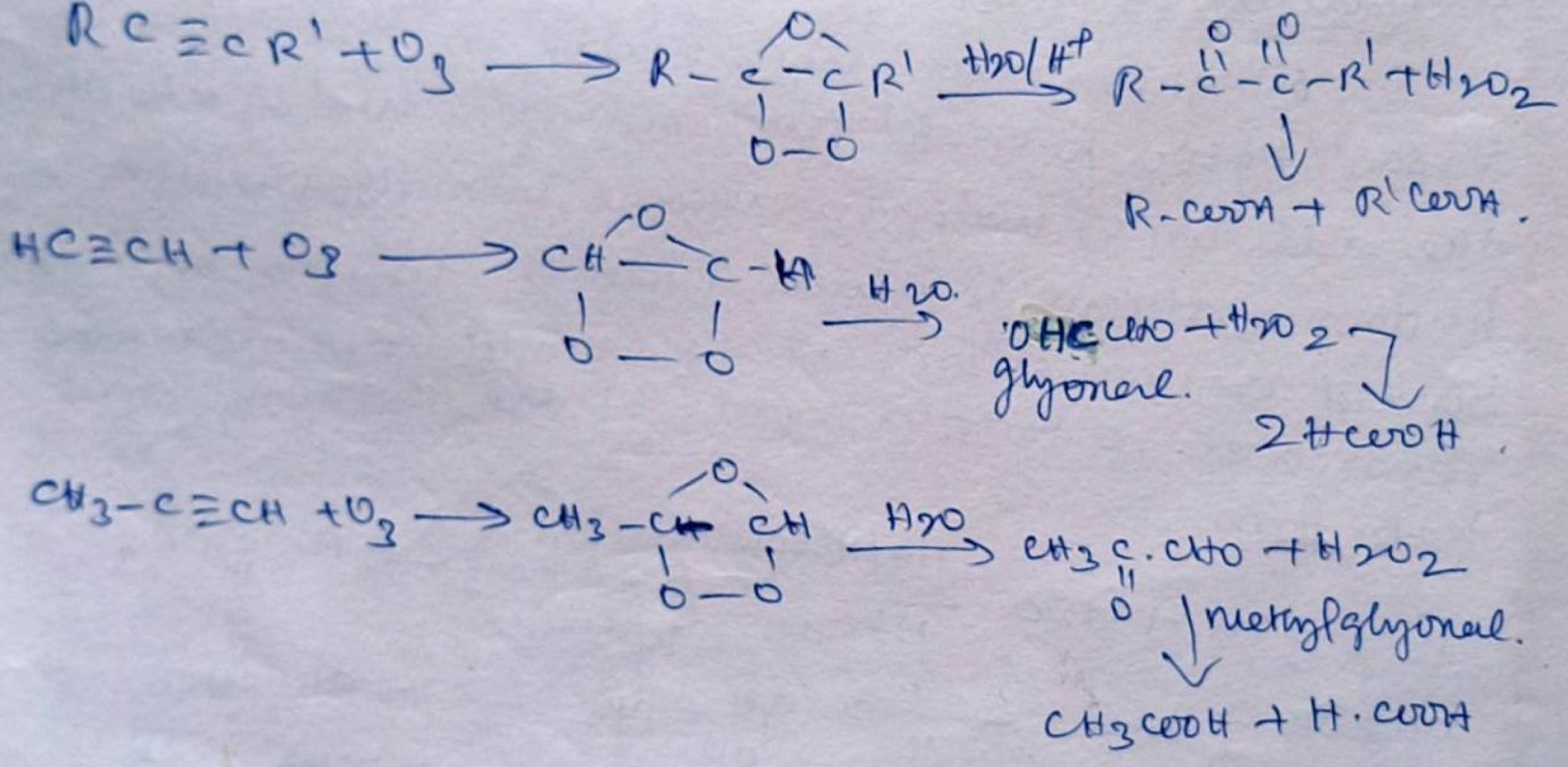
The first step is the formation of the complex (A) involving Hg^{2+}. water then attacks the complex (A) in SN_2 type process to give the intermediate (B) which forms (C) losing a proton. Hydrolysis of (C) gives (D) which after a tautomeric change forms (E) the carbonyl compound.



$$-C\equiv C- + Hg^{2+} \longrightarrow \underset{Hg^{2+}}{-C=C-}\ (A) \xrightarrow{H_2O} -\underset{Hg^{+}}{C}=\overset{\overset{+}{O}H_2}{C}-\ (B) \xrightarrow{-H^{+}} -\underset{Hg^{+}}{C}=\overset{\overset{+}{O}H}{C}-\ (C) \xrightarrow{H^{+}} \left(-\underset{H}{C}=\overset{\overset{+}{O}H}{C}- + Hg^{2+}\right) \xrightarrow[\text{change}]{\text{tautomeric}} -\underset{|}{\overset{|}{C}}-\underset{\overset{\|}{O}}{C}-\ (E).$$

Addition of ozone and ozonolysis

With ozone alkynes forms ozonide, which are decomposed by water to form diketones and H_2O_2. Diketones are oxidised by hydrogen peroxide to carboxylic acid by the cleavage of carbon-carbon bonds.



Acetylene is exceptional as it gives glyoxal as well as formic acid. Since oxidation is very much slower with alkynes as compared to alkenes, a triple bond is left intact in enynes by choosing a suitable oxidising agent.

$$R'C\equiv C(CH_2)_n CH=CH R'' \xrightarrow[\text{Acetic acid}]{CrO_3} R'C\equiv C.(CH_2)_n COOH + R''COOH$$

7. <u>Addition of carboxylic acid</u> and their derivatives.

Alkynes are treated with carboxylic acid in the presence of catalyst like Mercuric oxide (or) boron trifluoride etc. to give vinyl esters.

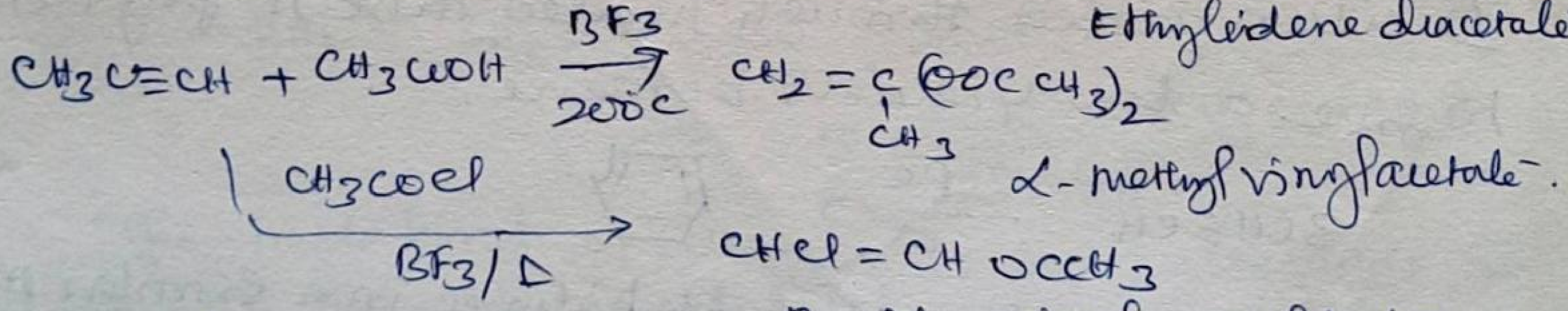
$$R-C\equiv CH + R'COOH \xrightarrow{BF_3} RC(OOCR')=CH_2 \text{ (or) } CH_2=CRCOOCR'$$

vinyl esters.

When acetylene is passed into warm acetic acid in presence of mercuric ion as catalyst vinyl acetate and ethylidene diacetate are formed.

$$CH\equiv CH + CH_3COOH \xrightarrow{Hg^{2+}} \underset{\text{vinyl acetate}}{CH_2=CH\,OOC\,CH_3} \xrightarrow{CH_3COOH} CH_3CH(OOCCH_3)_2$$

Ethylidene diacetate



$$CH_3C\equiv CH + CH_3COOH \xrightarrow[200°C]{BF_3} CH_2=\underset{CH_3}{C}(OOCCH_3)_2$$

α-methyl vinyl acetate.

$$CH_3C\equiv CH \xrightarrow[BF_3/\Delta]{CH_3COCl} CHCl=CH\,OCCH_3$$

β-chloro vinyl methyl ketone.

8 <u>Addition of HCN</u> and NH_3

Hydrogen cyanide react with acetylene in presence of cuprous chloride in HCl to form vinyl cyanide (or) acrylonitrile.

$CH\equiv CH + HCN \xrightarrow[HCl,\ \Delta]{Cu_2Cl_2} CH_2=CHCN$
vinyl cyanide.

$R\cdot C\equiv CH + HCN \xrightarrow[\text{"}]{\text{"}} R\cdot \underset{CN}{C}=CH_2$ (substituted acrylonitrile)

Ammonia adds in presence of Al_2O_3 at a temp of 300-350°c to give nitrile.

$HC\equiv CH + NH_3 \xrightarrow[\Delta]{Al_2O_3} CH_3C\equiv N + H_2$

$RC\equiv CH + NH_3 \xrightarrow[\text{"}]{\text{"}} RCH_2C\equiv N + H_2$

9 Addition of alcohols

Alkynes add to alcohol ~~when passed~~ in the presence of small amount of CH_3OK at 160-200°c under the pressure to give Methyl vinyl ether is formed

$CH\equiv CH + CH_3\bar{O} \longrightarrow \bar{C}H=CHOCH_3 \xrightarrow{CH_3OH} CH_2=CHOCH_3 + CH_3\bar{O}$

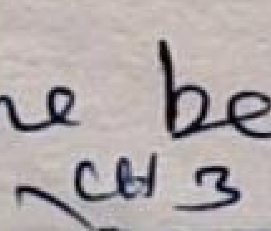
$CH\equiv CH + C_2H_5OH \xrightarrow{NaOH} CH_2=CHOC_2H_5$

10 Self-addition (or) polymerisation

Alkynes polymerize to give cyclic (or) linear polymers depending upon the temperature and catalyst used.

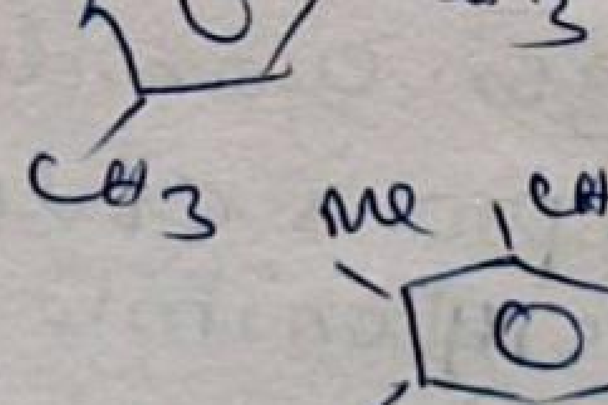
1) when passed through heated tube it polymerises to give a low yield of benzene.

$3CH\equiv CH \xrightarrow[\Delta]{Fe}$



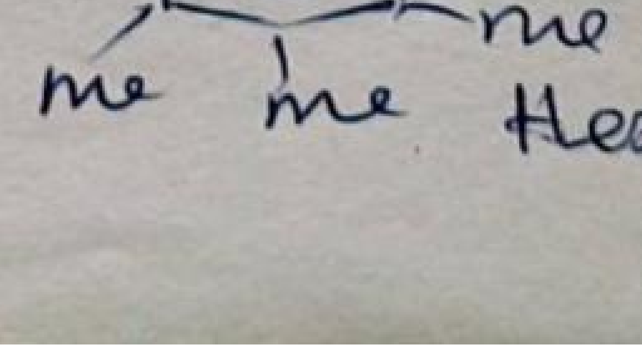
(ii) Homologues of acetylene behave in a similar manner.

$3CH_3C\equiv CH \xrightarrow[\Delta]{H_2SO_4}$



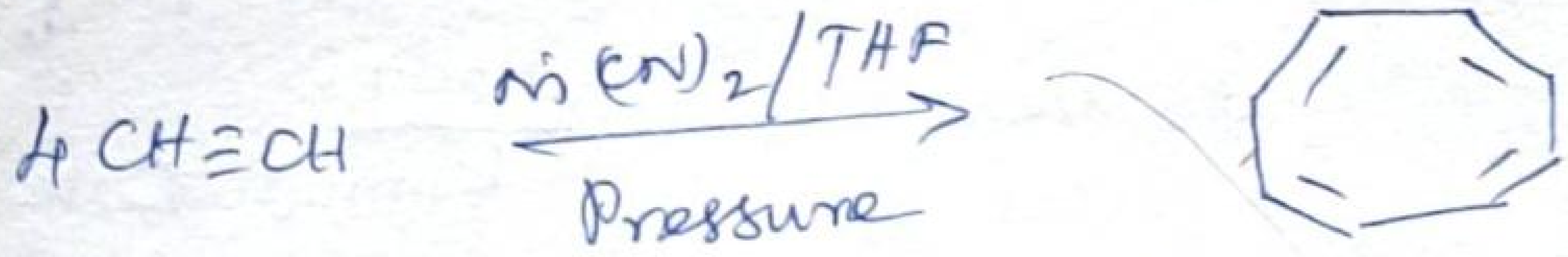
mesitylene

$3\ CH_3C\equiv CCH_3 \xrightarrow[\text{"}]{\text{"}}$



Hexamethyl benzene.

III) Under pressure and in presence of catalyst acetylene polymerises to cyclo octatetraene



IV) Acetylene undergoes linear polymerization when passed in a solution of cuprous chloride in NH4Cl.

$$2\,CH\equiv CH \xrightarrow[NH_4Cl]{Cu_2Cl_2} \underset{\text{Vinylacetylene}}{CH_2=CH-C\equiv CH} \xrightarrow[NH_4Cl]{Cu_2Cl_2} \underset{C_2H_2}{}$$

(1-butene-3yne)

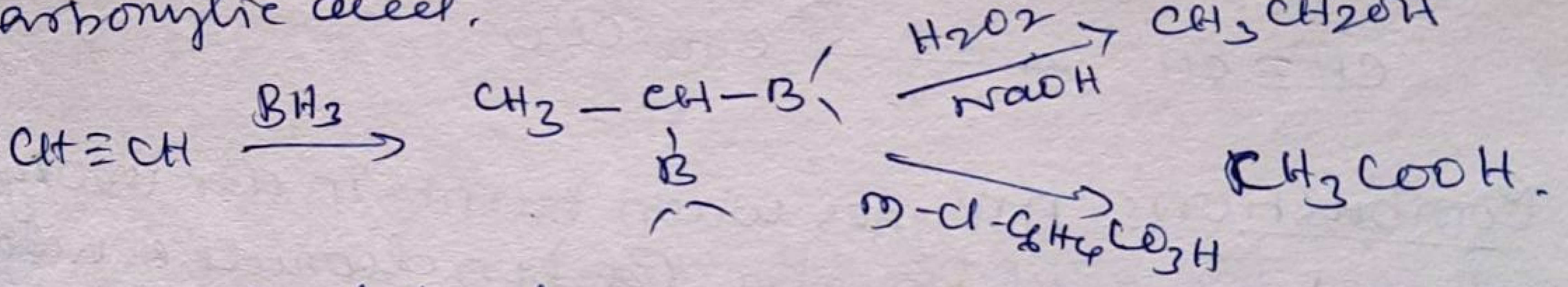
$$CH_2=CH-C\equiv C-CH=CH_2$$

Divinylacetylene

(1,5-hexadiene-3-yne)

Oxidation reaction

I) Hydroboration-oxidation. This reaction between terminal alkynes and BH_3 produce 1,1-diboro compound which on oxidation with ($NaOH-H_2O_2$) gives primary alcohol and when oxidised with m-chloroperbenzoic acid give carboxylic acid.



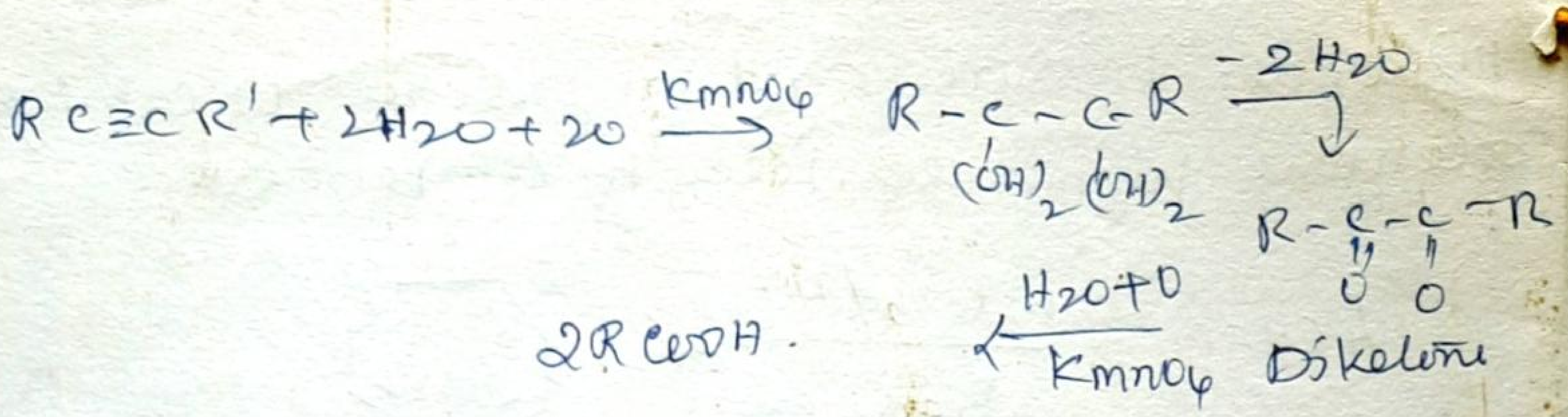
$$CH\equiv CH \xrightarrow{BH_3} CH_3-\underset{B}{CH}-B \xrightarrow[NaOH]{H_2O_2} CH_3CH_2OH$$

$$\xrightarrow{m\text{-}Cl\text{-}C_6H_4CO_3H} CH_3COOH.$$

The triple bond of alkynes is less susceptible to oxidation than the double bond of alkenes. different oxidation product with different reagents.

II) Oxidation with Strong alkaline $KMnO_4$

Alkynes on oxidation with Strong alkaline $KMnO_4$ gives carboxylic acid Containing lesser number of Carbon atoms.



$$RC\equiv CR' + 2H_2O + 2O \xrightarrow{KMnO_4} R-\underset{(OH)_2}{C}-\underset{(OH)_2}{C}-R \xrightarrow{-2H_2O} R-\underset{\|\atop O}{C}-\underset{\|\atop O}{C}-R$$

Diketone

$$\xleftarrow[KMnO_4]{H_2O+O} 2RCOOH.$$

$$CH_3-C\equiv CH + 2H_2O + O \xrightarrow{KMnO_4} CH_3COCHO \xrightarrow[KMnO_4]{H_2O+O} CH_3COOH + HCOOH$$

Methyl glyoxal

$$CH\equiv CH + 2H_2O + 2O \xrightarrow[\text{''}]{\text{''}} CHO-CHO \xrightarrow[KMnO_4]{2(O)} COOH\cdot COOH.$$

Oxalic acid

iii) Oxidation with acidic $K_2Cr_2O_7$

On treatment with acidic $K_2Cr_2O_7$ alkynes give Carboxylic acid

$$RC\equiv CH + H_2O + O \xrightarrow[H^+]{K_2Cr_2O_7} R-C(OH)=CHOH \rightarrow RCH_2COOH$$

$$CH\equiv CH + H_2O + O \xrightarrow[\text{''}]{\text{''}} CH_3COOH.$$

(IV) Oxidation with SeO_2 : Selenium dioxide alkynes to give diketone

$$R-C\equiv C-R \xrightarrow[SeO_2]{2(O)} RCO\cdot COR$$

$$CH\equiv CH \xrightarrow[\text{''}]{\text{''}} CHO\cdot CHO$$

(V) Combustion: Alkynes when burnt in air or oxygen produce heat and evolve Carbon dioxide & water.

$$C_nH_{2n-2} + \frac{3n-1}{2}O_2 \longrightarrow nCO_2 + (n-1)H_2O$$

$$2CH\equiv CH + 5O_2 \longrightarrow 4CO_2 + 2H_2O + 312\,kcal.$$

This reaction is used industrially for welding when acetylene is burnt with oxygen. (Oxy acetylene flame).

ALKENES

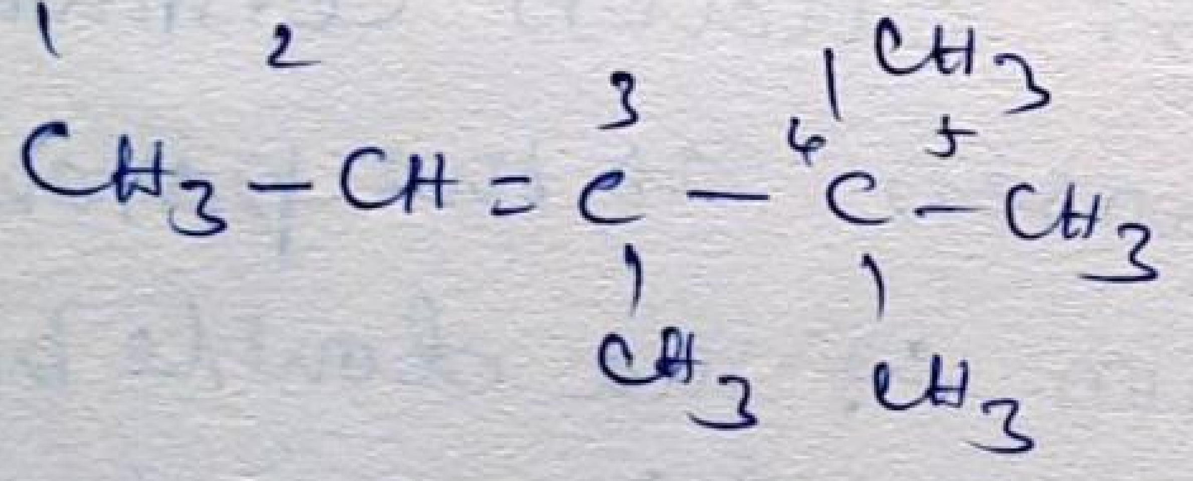
Alkenes are unsaturated hydrocarbon having the general formula C_nH_{2n}. They contains two hydrogen atom less than required to form alkane with the same number of carbon atom. This is made possible by introducing a double bond between two carbon atoms. This symbolises unsaturation in the compound examples: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

Nomenclature:-

1. The olefins are named after the corresponding paraffins by changing the suffix -ane into -ylene in the trivial system; and into -ene in the IUPAC system. Thus the series is named as alkylene (or) alkene.
2. The longest carbon chain containing the double bond is chosen as the parent alkene and the position of the double bond and side chain indicated by number.
3. The lowest possible number is given to the double bond and the side chain are indicated accordingly.
4. Complicated alkene cannot be named by the trivial system ~~but~~ they are always named according to the IUPAC system.

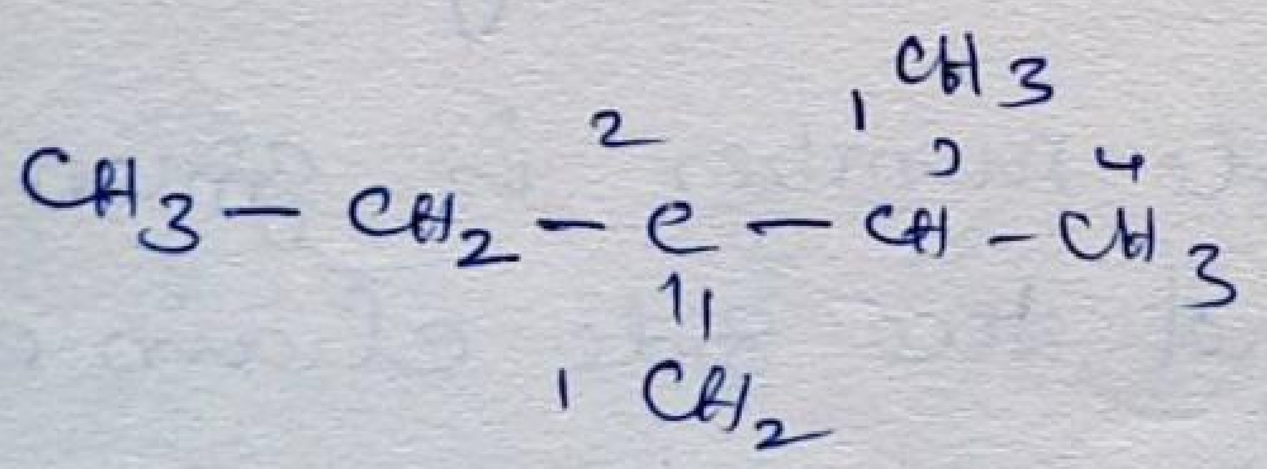
formula	Corresponding paraffin.	Common name	IUPAC name.
C_nH_{2n}	C_nH_{2n+2} (alkane)	Alkylene	Alkene
CH_2	CH_4 (methane)	Methylene	Methene.
$CH_2=CH_2$	C_2H_6 (Ethane)	Ethylene	Ethene
$CH_3CH=CH_2$	C_3H_8 (propane)	Propylene	propene
$CH_3CH_2CH=CH_2$	C_4H_{10} (butane)	α-butylene (or) 1-butylene	1-butene
$CH_3CH=CH-CH_3$	C_4H_{10} (butane)	β-Butylene (or) 2-butene	2-butene

The number indicated the position of the double bond is placed before the name. example.



$$\overset{1}{CH_3}-\overset{2}{CH}=\underset{CH_3}{\overset{3}{C}}-\underset{CH_3}{\overset{CH_3}{\overset{4}{C}}}-\overset{5}{CH_3}$$

3,4,4-Trimethyl 2-pentene



$$CH_3-CH_2-\underset{\overset{1}{CH_2}}{\underset{\|}{\overset{2}{C}}}-\overset{CH_3}{\overset{3}{CH}}-\overset{4}{CH_3}$$

2-ethyl-3-methyl-1-butene.

Preperation

1- Dehydration of alcohols:

Alcohol when dehydrated in the presence of catalyst gives alkene. The best procedure is to pass the vapour of alcohol overheated alumina

$$CH_3CH_2OH \xrightarrow[433-443K]{H_2SO_4} \underset{ethylene}{CH_2=CH_2} + H_2O$$

$$CH_3-CH_2CH_2CH_2OH \xrightarrow[413K]{''} \underset{But-2-ene\ (major)}{CH_3CH=CH-CH_3}$$

$$RCH_2CH_2OH \xrightarrow[350-450^\circ C]{Al_2O_3} R-CH=CH_2 + H_2O$$

Other substance like P_2O_5, H_3PO_4 are also used for dehydration.

2 By the action of alcoholic potash on alkyl halides:

Alkyl halides on treatment with alcoholic KOH gives alkene.

$$R-CH_2CH_2-X \xrightarrow[KOH]{alcoholic} R-CH=CH_2 + KX + H_2O$$

$$CH_3CH_2Br \xrightarrow[''] {''} CH_2=CH_2 + KBr + H_2O$$

The order of reactivity of dehydro halogenation is given as follows

$$3^\circ > 2^\circ > 1^\circ$$

Chemical properties

1. Addition Reaction. (Addition of hydrogen)

The alkene when heated with hydrogen gas in presence of catalyst like Ni [Sabatier - Senderen reduction) Pt, Pd etc. gives alkane.

$$R-CH=CH_2 + H_2 \xrightarrow[200-300^\circ C]{Ni} R.CH_2CH_3$$

$$CH_3-CH=CH_2 + H_2 \xrightarrow[200 C]{Ni} CH_3CH_2CH_3$$

2. Addition of halogen:

Alkene react with halogen to form dihalogen derivatives by an addition reaction. the order of reactivity of halogens for a given alkene is Cl > Br > I.

$$R-CH=CH_2 + X_2 \longrightarrow R-\underset{X}{\underset{|}{CH}}-CH_2X.$$

Vic dihalides

$$CH_2=CH_2 + Cl_2 \longrightarrow CH_2Cl \cdot CH_2Cl$$

ethylene dichloride
or
1,2 dichloro ethane.

$$CH_3-CH=CH_2+Br_2 \longrightarrow CH_3-CHBr-CH_2Br$$

1,2-dibromo propene.

Mechanism

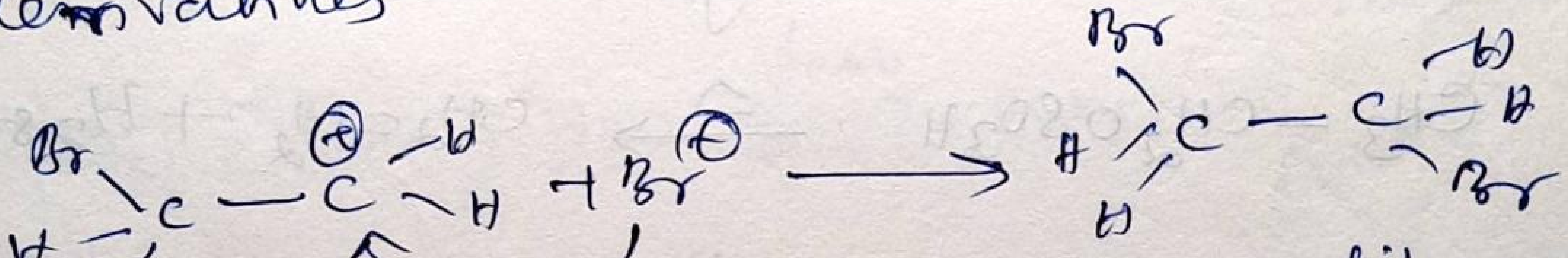
1. The Br_2 molecules ionises into bromonium ion and bromide ion

$$Br_2 \longrightarrow Br^+ \text{(Electrophilic)} + Br^- \text{(nucleophilic)}$$

2. The positive bromonium ion Br^+ attack the double bond to form a carbonium ion

Carbonium ion

3 step: The negative bromide ion Br^- attacks the carbonium ion to form the dibromo derivatives



1,2-dibromo ethane.

Addition of sulphuric acid

Ethylene is readily absorbed by concentrated sulphuric acid and still better by fuming sulphuric acid to produce ethyl hydrogen sulphate

$$CH_2=CH_2 + HO\,SO_2OH \longrightarrow \overset{+}{C}H_2-CH_3 + \overset{-}{O}SO_2OH$$

$$\downarrow$$

$$CH_3CH_2O\,SO_2OH$$

Ethyl hydrogen sulphate gives ethylene when heated to 430-440K while ethanol is obtained on boiling it with water.

$$CH_3-CH_2OSO_3H \xrightarrow{\Delta} CH_2=CH_2 + H_2SO_4$$

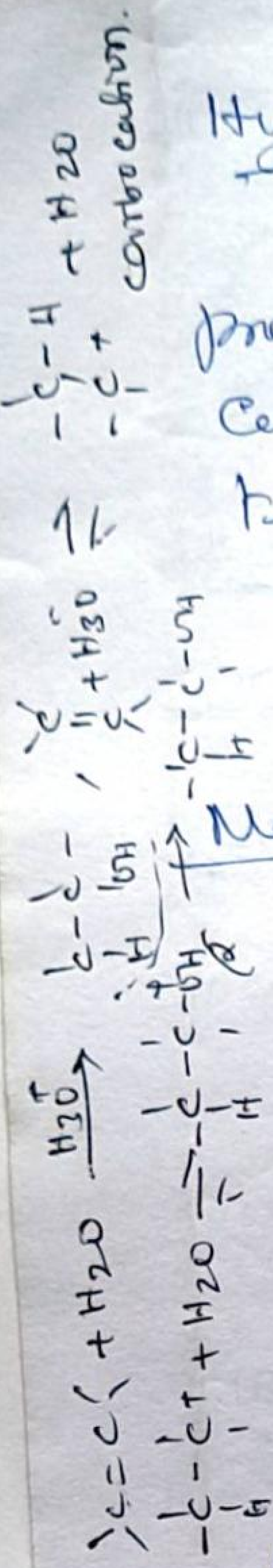
$$CH_3CH_2OSO_3H \xrightarrow{H_2O} C_2H_5-OH + H_2SO_4$$

This reaction is used for the seperation of ethylene from gaseous mixture and production of ethyl alcohol from ethylene.

addition of sulphuric to higher alkene also takes place according to the Markownikoff's rule.

$CH_3-CH=CH_2 + HSO_3H \longrightarrow CH_3-\overset{+}{C}H-CH_3 + \bar{O}SO_2OH$

$CH_3-\overset{+}{C}H-CH_3 + \bar{O}SO_3H \longrightarrow (CH_3)_2CHOSO_3H$
isopropyl hydrogen sulphate



Hydration of olefins

Olefin is treated with water in the presence of dilute acid to gives the corresponding alcohol. eg: Isobutylene gives tert-butyl alcohol in dilute solution.

$$(CH_3)_2C=CH_2 + H_2O \xrightarrow{H^+} (CH_3)_3COH.$$

Mechanism.

$$(CH_3)_2C=CH_2 + H-\overset{+}{O}H_2 \underset{}{\overset{slow}{\rightleftharpoons}} (CH_3)_2\overset{+}{C}-CH_3 + H_2O$$
carbocation.

$$(CH_3)_2\overset{+}{C}-CH_3 + H_2O \overset{fast}{\rightleftharpoons} (CH_3)_2-\underset{\overset{+}{O}H_2}{C}-CH_3$$

$$(CH_3)_2\underset{\overset{+}{O}H_2}{C}-CH_3 \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} (CH_3)_2-\underset{OH}{C}-CH_3 \text{ (or) } (CH_3)_3COH.$$

Combustion

Alkenes burns with a luminous flame giving carbon dioxide and water vapour and with air or oxygen form explosive mixture.

$$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O.$$

Hydroboration

alkene reacted with ~~borane~~ borane (diborane) to yield alkyl borane (R_3B) which on oxidation with H_2O_2 give alcohols.

B_2H_6 \ or $(BH_3)_2 \xrightarrow{CH_2=CH_2} (CH_3CH_2)BH_2 \xrightarrow{C_2H_4}$

$(CH_3CH_2)_3B \xleftarrow{C_2H_4} (CH_3CH_2)_2BH$

Trimethyl borane.

$(CH_3CH_2)_3B + H_2O_2 \xrightarrow{OH^-} 3\,CH_3CH_2OH + H_3BO_3$

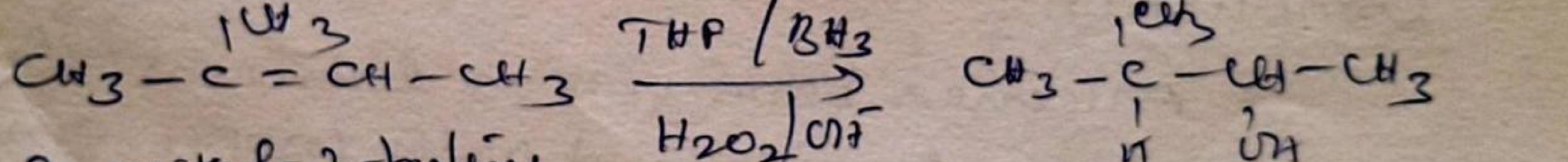
This above reaction followed anti markovnikoff rule.

$3\,CH_3CH=CH_2 \xrightarrow{(BH_3).2} 3(CH_3CH_2CH_2)_3B \xrightarrow[-H_3BO_3]{H_2O_2/NaOH}$

$3-CH_2CH_2CH_2OH$

1-propanol.

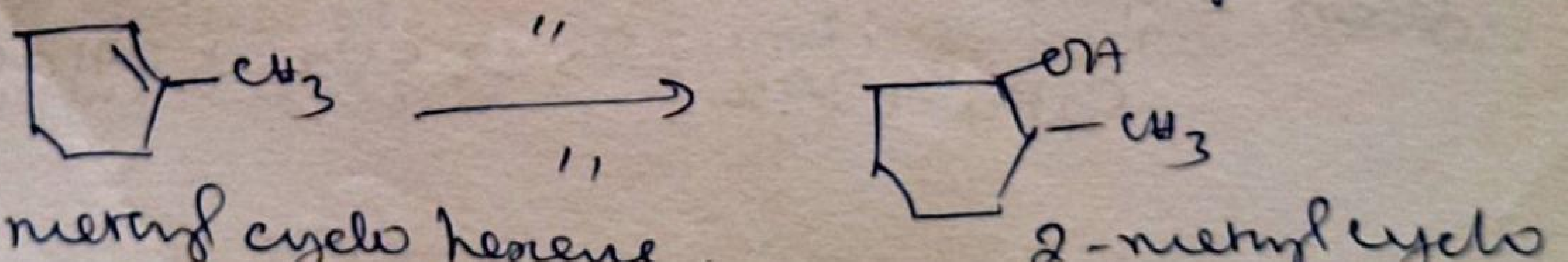
Other example.



$CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_3 \xrightarrow[H_2O_2/OH^-]{THF/BH_3} CH_3-\underset{H}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\underset{OH}{\underset{|}{CH}}-CH_3$

2-methyl-2-butene

3-methyl-2-butanol

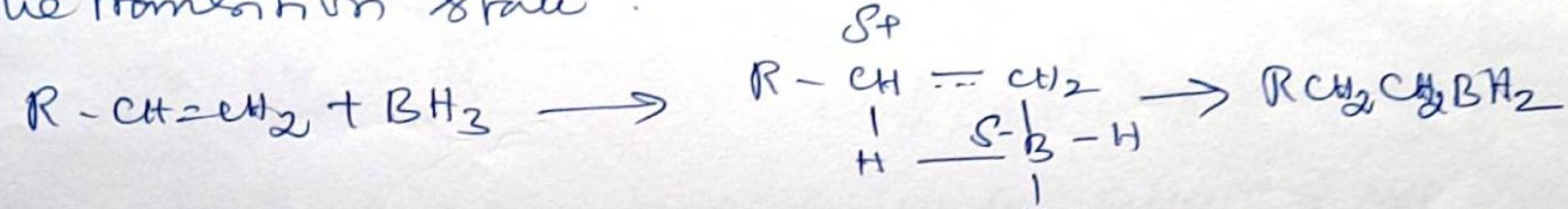


1-methyl cyclo hexene.

2-methyl cyclo hexanol.

Mechanism

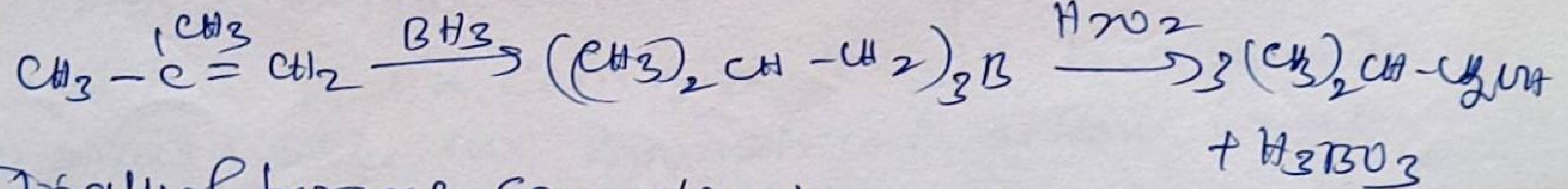
Boron has only four ē in BH_3 hence it acts as an electrophile. It seeks πē of the double bond betn two carbon atoms of alkene. when it approach alkene it starts attaching itself to carbon with negative charge but in the meantime the other carbon atom constituting the double bonds starts getting a (+) charge on losing πē. with positive charge develops this carbon begins to take charge of the hydrogen of BH_3 which is near it. Boron which has gained πē is willing to part ~~whi~~ with this hydrogen to acidic carbon atom. and developed the transition state.



$$R-CH=CH_2 + BH_3 \longrightarrow \overset{\delta+}{R-CH}=CH_2 \cdots \overset{\delta-}{B}H_2 \cdots H \longrightarrow RCH_2CH_2BH_2$$

This process goes on till trialkyl borane is formed.

Trialkyl borane are useful because they can be oxidized to alcohol by using alkaline solution of H_2O_2



$$CH_3-\overset{CH_3}{C}=CH_2 \xrightarrow{BH_3} ((CH_3)_2CH-CH_2)_3B \xrightarrow{H_2O_2} 3(CH_3)_2CH-CH_2OH + H_3BO_3$$

Trialkyl borane can also be used to get alkanes or aldehyde

$$(RCH_2CH_2)_3B \xrightarrow[\Delta]{CH_3COOH} R-CH_2CH_3$$

$$(R(CH_2CH_2)_3B \xrightarrow[\Delta]{H_2Cr_2O_7} RCH_2-CHO$$

Addition of halogen acid

Alkene react with halogen acid (HCl, HBr, HI) to form alkyl halide.

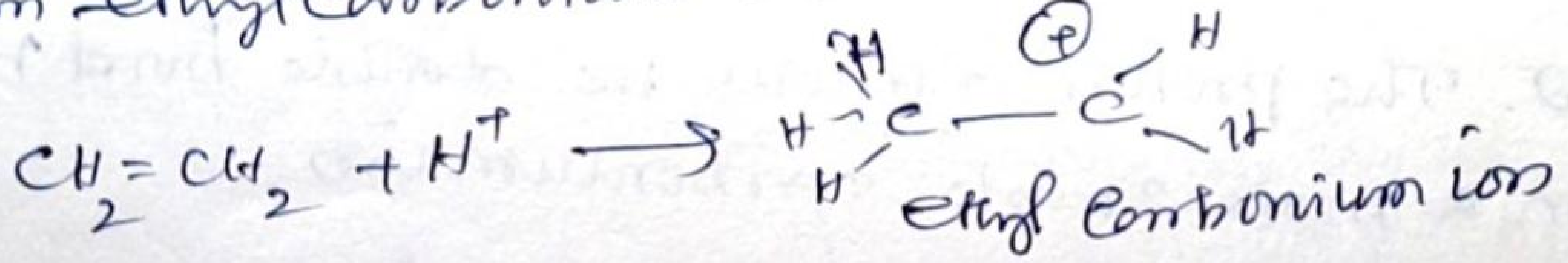
$$CH_2=CH_2 + HBr \longrightarrow CH_3-CH_2Br$$

Mechanism

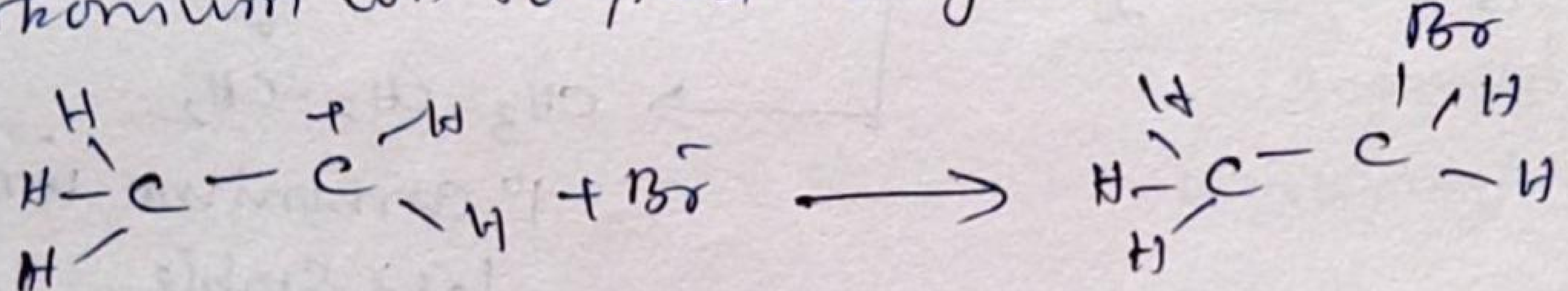
Step 1. HBr ionises to give a proton and a bromide ion

$$H-Br \longrightarrow H^{\oplus} + Br^{\ominus}$$

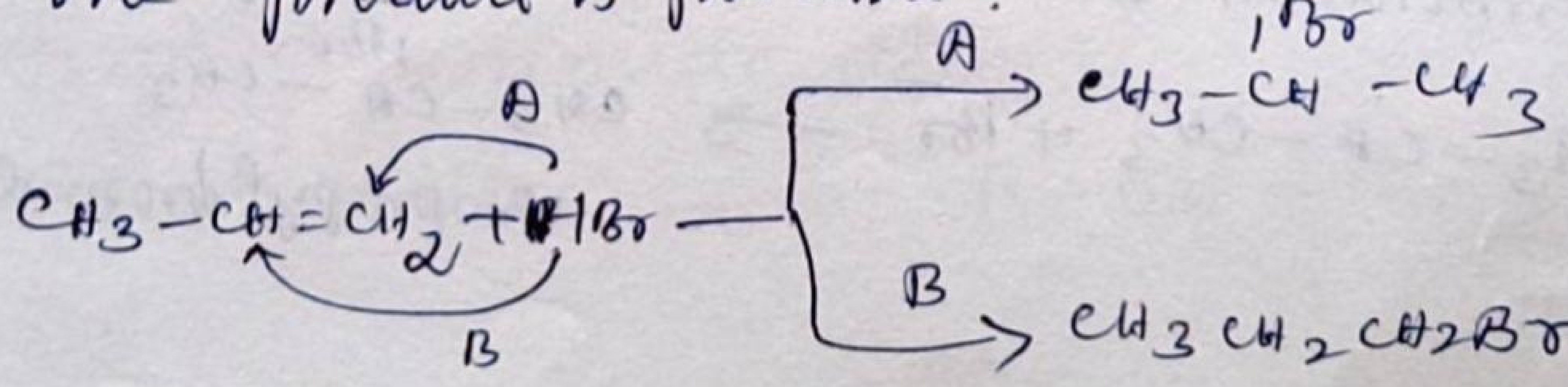
Step 2: The proton attacks the double bond to form ethyl carbonium ion



Step 3: The negative bromide ion Br⁻ attacks the carbonium ion to yield ethyl bromide.



However, the alkene is unsymmetrical, the addition of HX can give rise to two isomeric product while the symmetrical alkene we get only one product is possible.



Markownikoff's rule

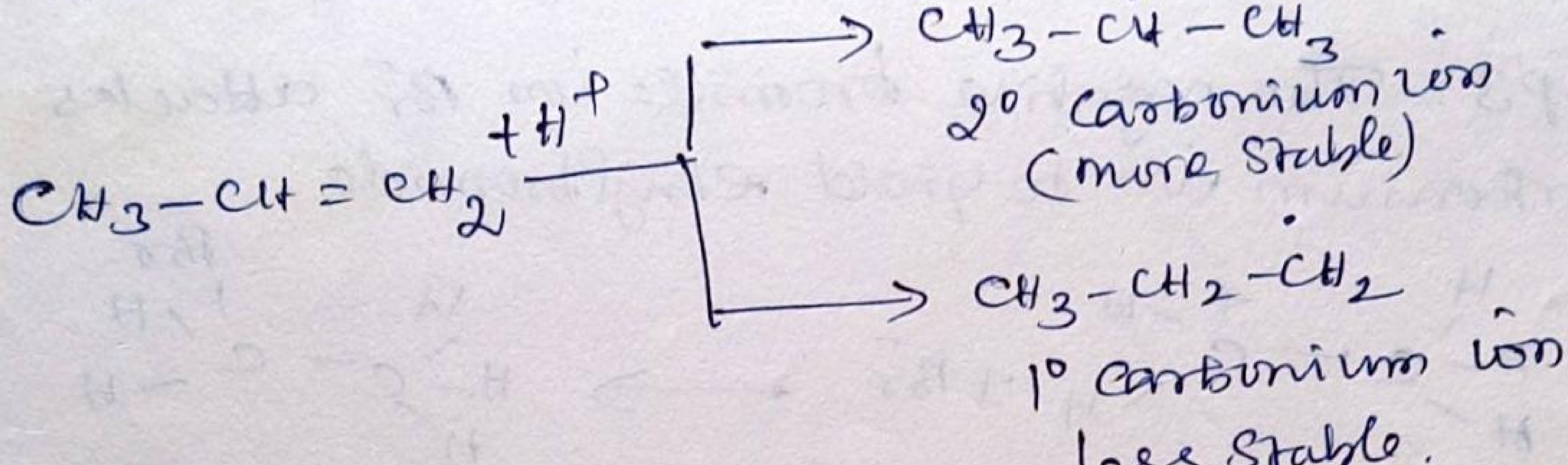
when addition accross an unsymmetrical ethylenic bond (= bond) takes place, the negative part of the attacking reagent goes to the carbon atom containing the least number of hydrogen atoms.

Mechanism

Step 1. HBr ionises to gives a proton and a bromide ion.

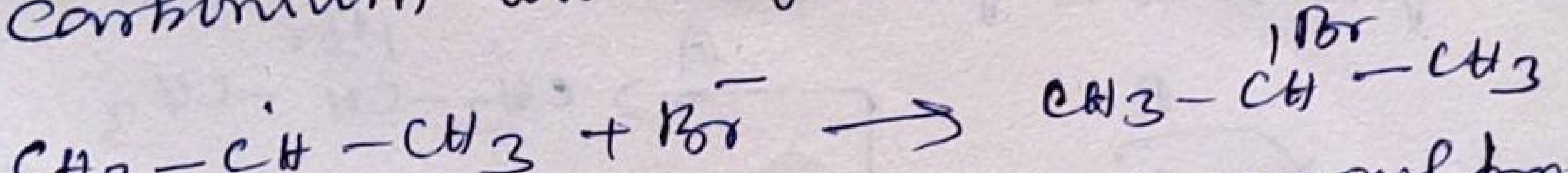
$$HBr \longrightarrow H^+ + Br^-$$

Step 2: The proton attacks the double bond to form a more stable carbonium ion.



3° carbonium ion is more stable then 2° carbonium ion and more stable them 1° carbonium ion.

Step 3. The bromide ion attacks the more stable 2° carbonium ion to gives the major products.



$$CH_3-\overset{+}{C}H-CH_3 + Br^- \longrightarrow CH_3-\overset{Br}{CH}-CH_3$$

isopropyl bromide.

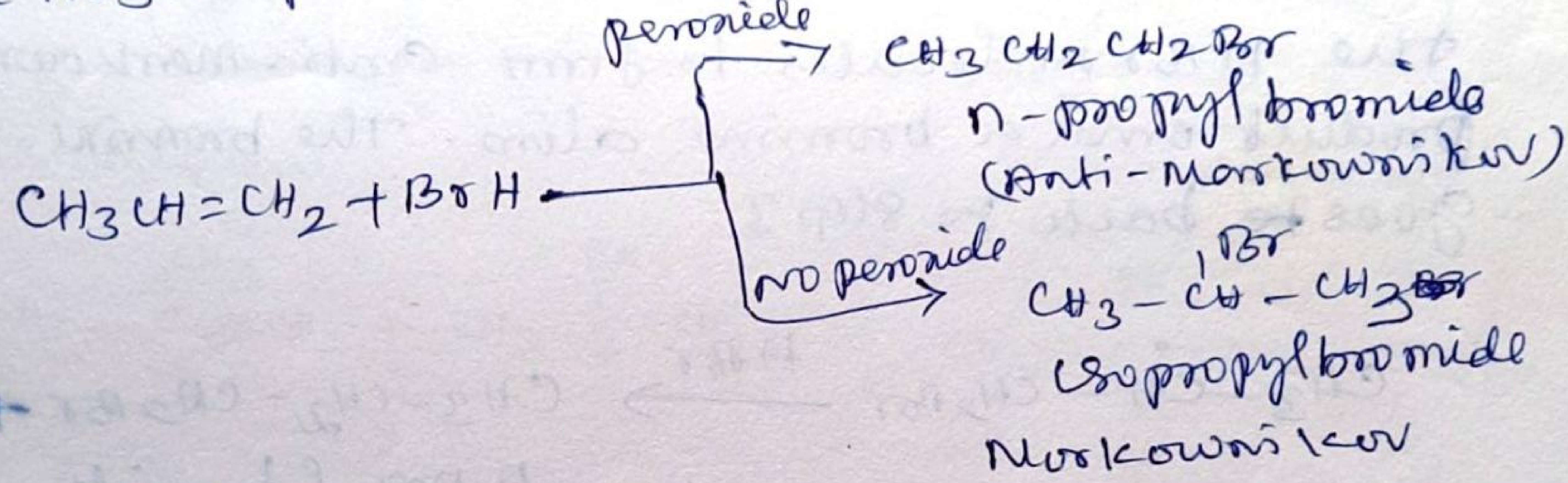
Peroxide [Karasch . m.s)

The addition of HBr to unsymmetrical alkene in the presence of organic peroxide (ROOR)

When the addition across on unsymmetrical ethylenic bond (= bond) takes place in the presence of peroxide, the positive part of the attacking reagent goes to the carbon atom with the lesser number of hydrogen atoms.

For examples.

When propylene react with HBr in the presence of a peroxide the major product is n-propyl bromide where as in the absence of a peroxide the major product is isopropyl bromide.



Mechanism

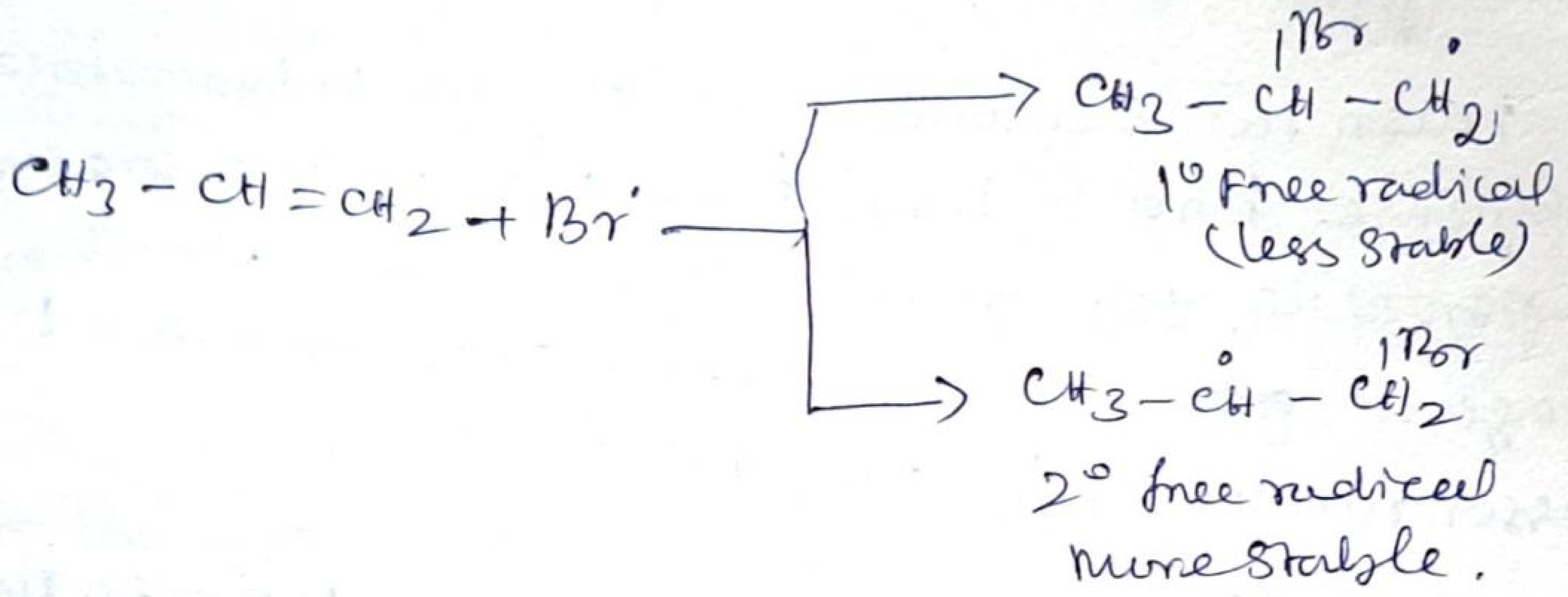
Step 1 Peroxide dissociates to give alkoxy free radicals

$$R-O-O-R \xrightarrow{\Delta} 2R\dot{O}$$

Step 2: the alkoxy free radical attacks HBr to form a bromide atom.

$$R-\dot{O} + HBr \longrightarrow R-OH + \dot{Br}$$

Step 3. The bromine atom can attack propylene to give a 1° free radical and sec. free radical.



$$CH_3-CH=CH_2+Br^{\cdot} \rightarrow CH_3-\overset{|Br}{CH}-\dot{C}H_2$$

1° free radical (less stable)

$$\rightarrow CH_3-\dot{C}H-\overset{|Br}{CH_2}$$

2° free radical more stable.

The order of stability of free radical is $3^\circ > 2^\circ > 1^\circ$.

Step 4: The more stable free radical attack the HBr molecules to from anti-Markowni kov product and a bromine atom. The bromine atom goes ~~to~~ back to step 3.

$$CH_3-\dot{C}H-CH_2Br \xrightarrow{HBr} CH_3-CH_2-CH_2Br + Br^{\cdot}$$

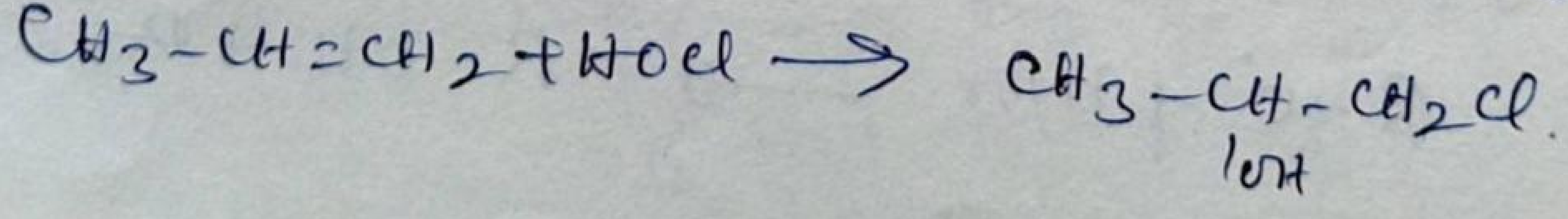
n-propyl bromide

Addition of hypohalous acids

Alkene react with ~~hydro acids~~ HOCl to gives halohydrin.

$$CH_2=CH_2+\overset{-}{HO}\overset{+}{Cl} \longrightarrow CH_2OH-CH_2Cl$$

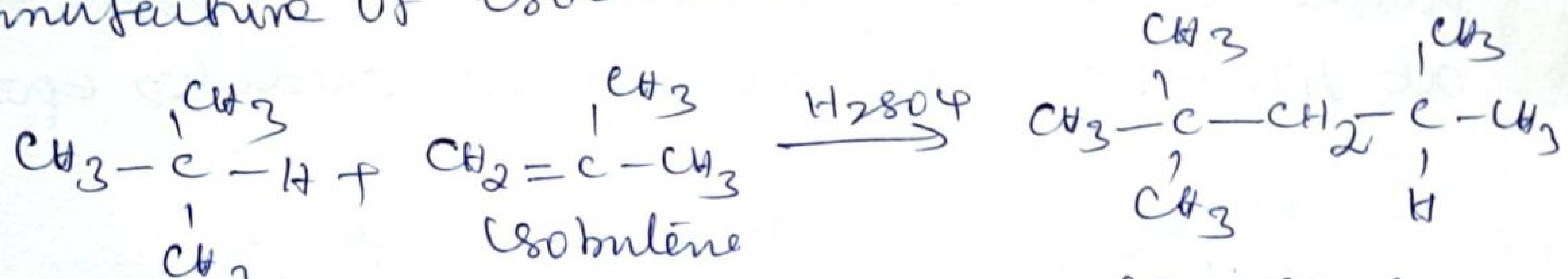
ethylene chlorohydrin.



$$CH_3-CH=CH_2+HOCl \longrightarrow CH_3-\underset{|OH}{CH}-CH_2Cl$$

Alkylation

Some alkane add to alkene in the presence of H_2SO_4 (or) HF. This reaction is used in the Manufacture of isooctane.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-H + CH_2=\overset{CH_3}{C}-CH_3 \xrightarrow{H_2SO_4} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{H}{\overset{CH_3}{C}}-CH_3$$

Isobutene

isooctane.
(or)
2,2,4-Trimethyl pentane

Mechanism

Alkylation takes place by electrophilic Mechanism as given below.

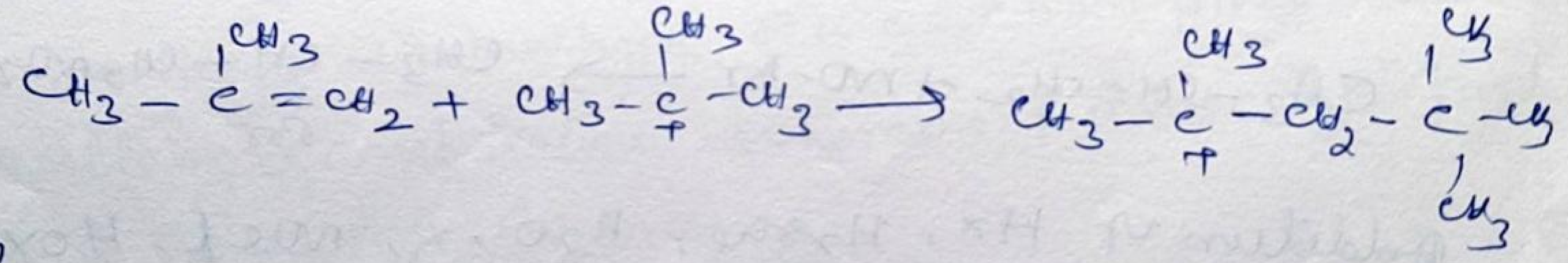
I) Isobutene Accepts H^+ to provide ter-butyl carbocation

$$CH_3-\overset{CH_3}{C}=CH_2 + H^+ \longrightarrow CH_3-\underset{+}{\overset{CH_3}{C}}-CH_3$$

Isobutylene

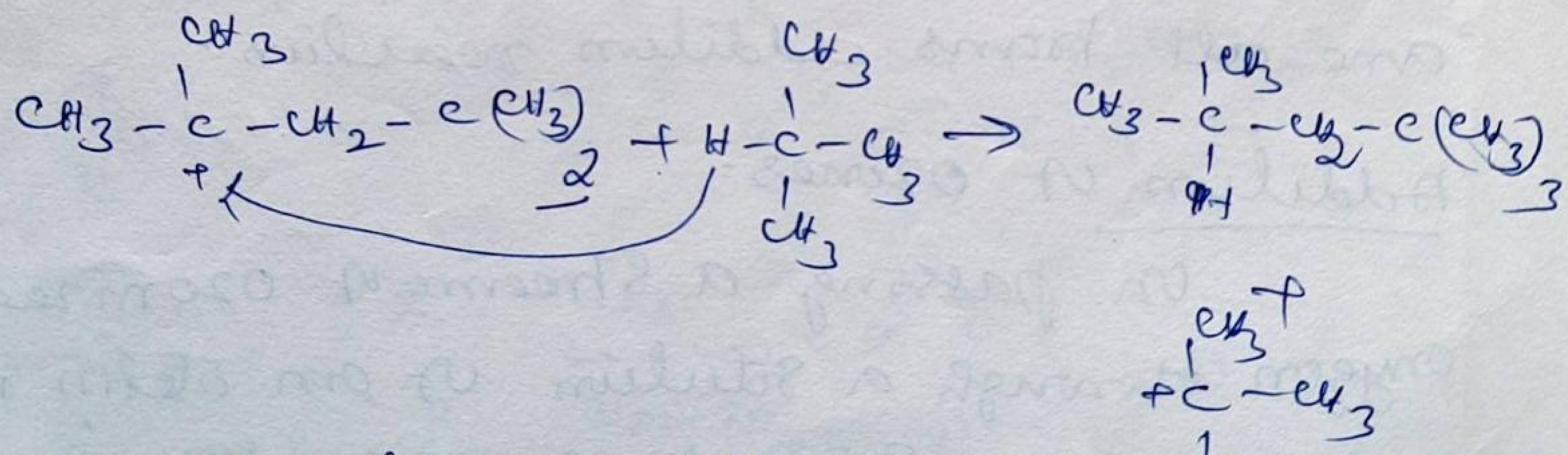
3° carbonium ion

II)



$$CH_3-\overset{CH_3}{C}=CH_2 + CH_3-\underset{+}{\overset{CH_3}{C}}-CH_3 \longrightarrow CH_3-\underset{+}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

(III)



$$CH_3-\underset{+}{\overset{CH_3}{C}}-CH_2-C(CH_3)_3 + H-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \longrightarrow CH_3-\underset{H}{\overset{CH_3}{C}}-CH_2-C(CH_3)_3$$

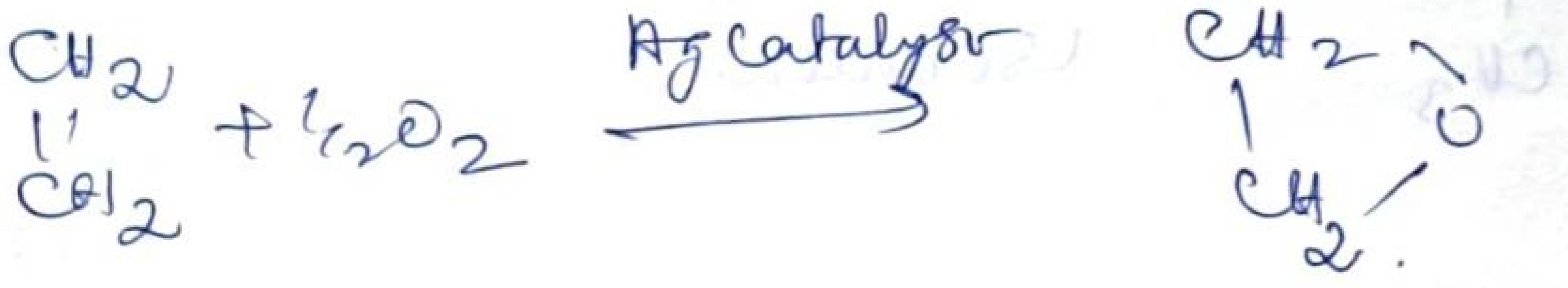
$$\overset{+}{}\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

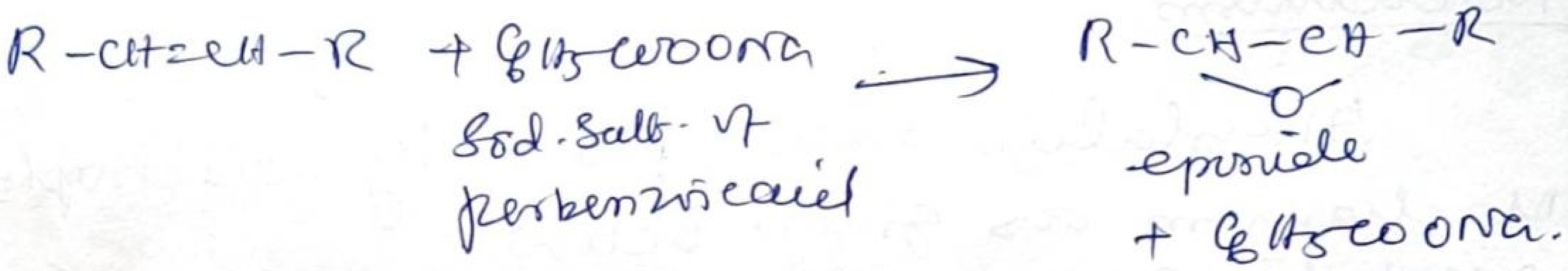
(II) the carbocation goes to site of the to add up to isobutene

(III) The carbocation formed in step (II) abstract a hydride ion from isobutene

Addition of oxygen.

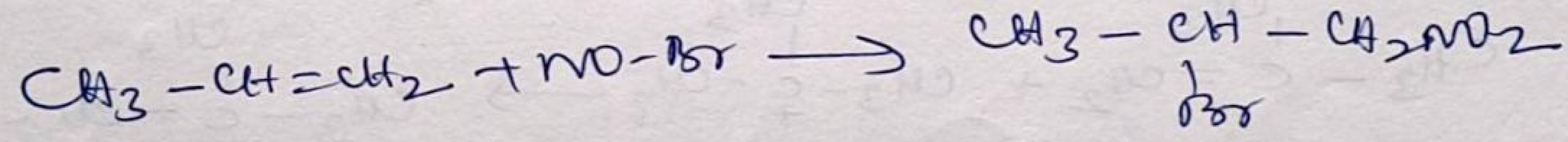
Lower alkene when mixed with air and passed under the pressure over a silver catalyst at 470 – 670K to give alkene oxide (or) epoxide





Addition of nitrosyl chloride.

$CH_2=CH_2 + NOCl \longrightarrow ClCH_2-CH_2NO$

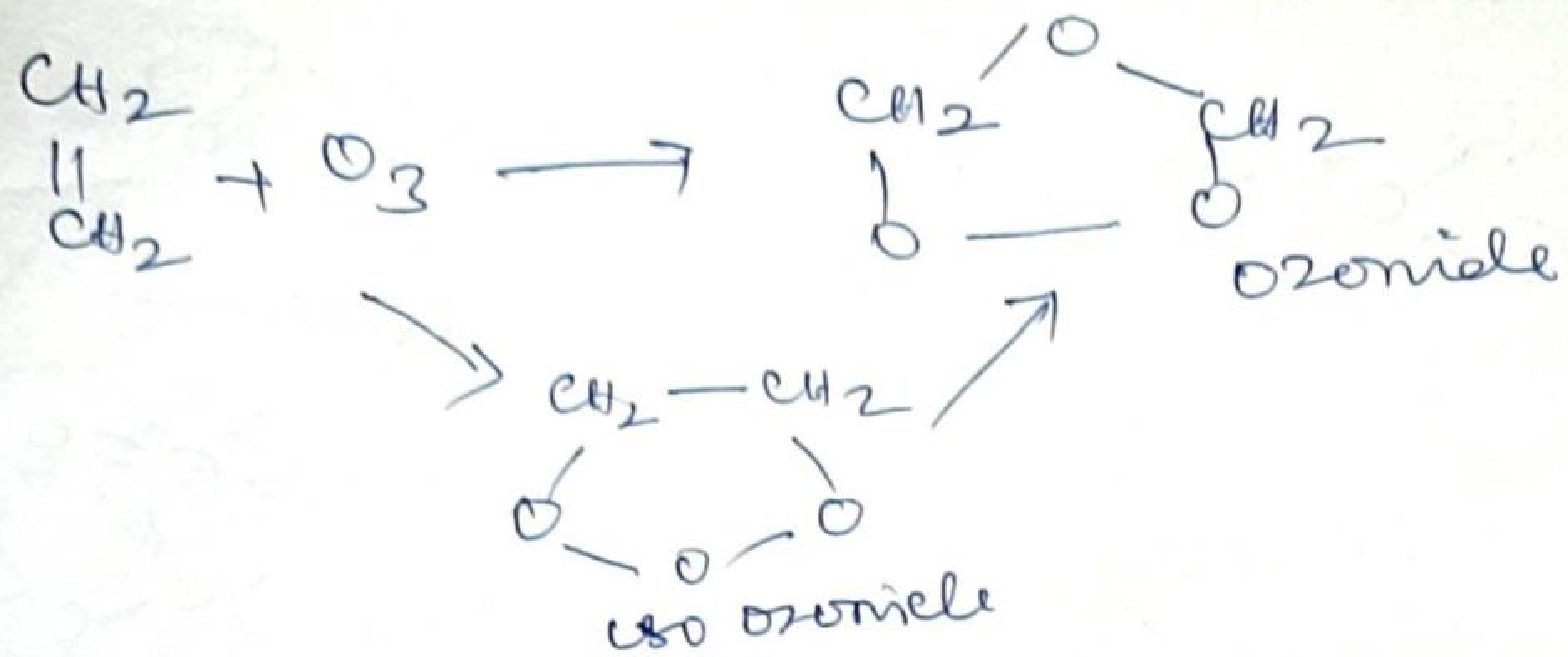


$CH_3-CH=CH_2 + NO-Br \longrightarrow CH_3-\underset{Br}{CH}-CH_2NO_2$

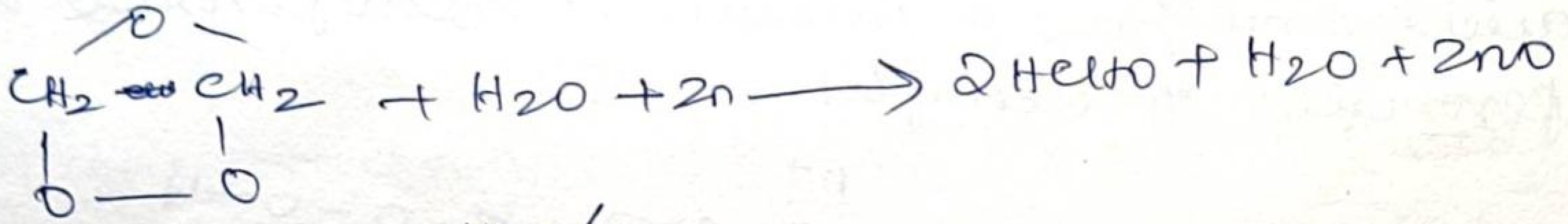
Addition of HX, H_2SO_4, H_2O, X_2, NOCl, HOX are all trans addition reaction.

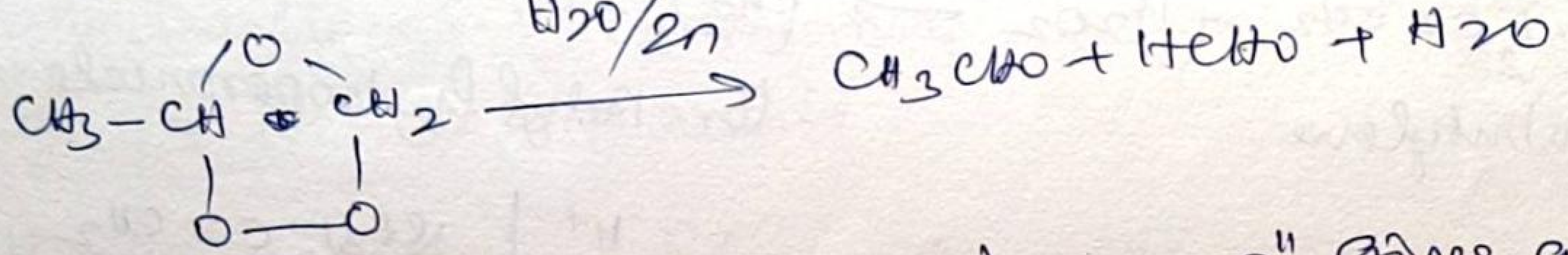
Addition of ozones.

On passing a stream of ozonized oxygen through a solution of an olefin in an organic solvent an ozonide is obtained.

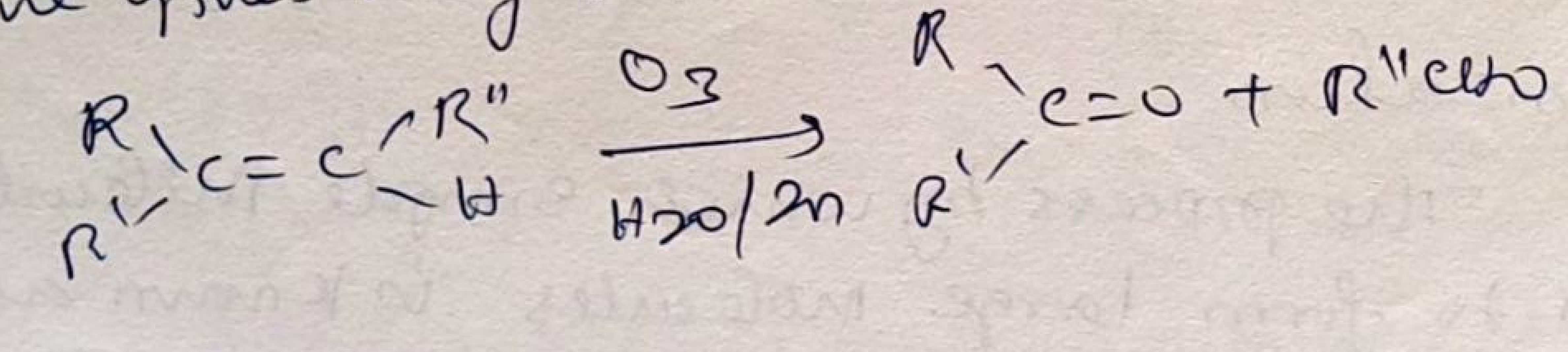


The ozonide are explosive and on reduction with hydrogen in the presence of catalyst (Pt/Pd) (or) on boiling with water containing trace of zinc dust. Split into give aldehyde (or) ketone.

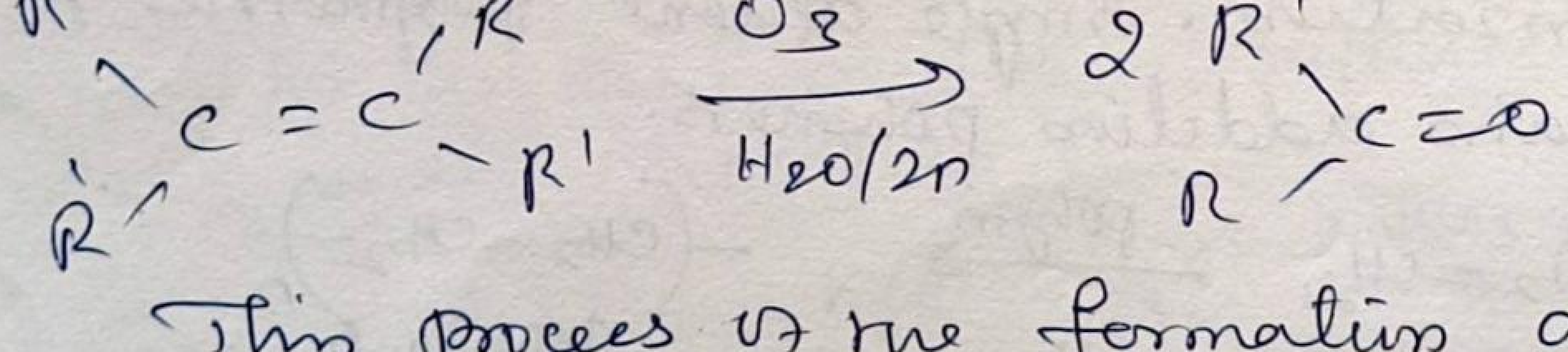




An alkene of the type RR'C=CHR'' gives a mixture of aldehyde and ketone. Whereas RR'C=CRR' type alkene gives only ketone.



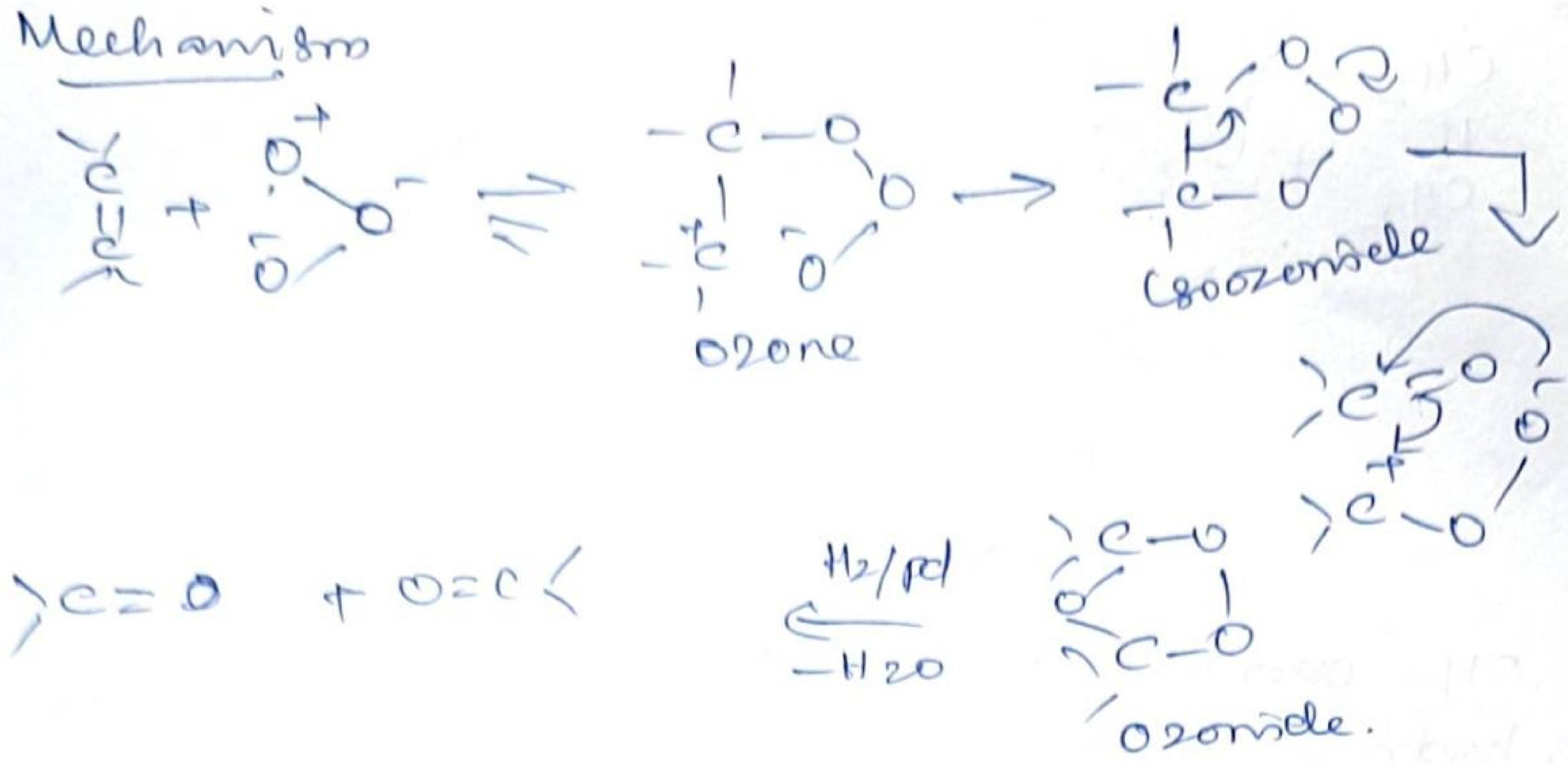
$$RR'C{=}CR''H \xrightarrow[H_2O/Zn]{O_3} RR'C{=}O + R''CHO$$



$$RR'C{=}CRR' \xrightarrow[H_2O/Zn]{O_3} 2\,RR'C{=}O$$

This process of the formation of ozonide and its decomposition to give carbonyl compds. is known as ozonolysis.

Mechanism



Addition of Hydrogen peroxide

The addition H_2O_2 to alkene is catalysed by acids and gives a mixture of hydroperoxide and peroxides for examples.

$(CH_3)_2C=CH_2 + H_2O_2 \xrightarrow{H^+} (CH_3)_3-C-O-O-H$

isobutylene — Ter-Butyl hydroperoxide

$\Big\downarrow H^+ \; (CH_3)_2C=CH_2$

$(CH_3)_3C-O-O-C-(CH_3)_3$

Ter-Butyl peroxide

Polymerization:

The process by which simple molecule join together to form large molecules is known as polymerization. Simple alkene polymerize to form long chain addition polymers.

$n\,CH_2=CH_2 \xrightarrow{polym} -(CH_2-CH_2-)_n$ polyethylene.

$n-CH_3CH=CH_2 \xrightarrow{''} -(\underset{CH_3}{CH}-CH_2-)_n$ polypropylene.

Oxidation with mild oxidizing agent:

When alkenes are treated with mild oxidizing agent like dilute 1% alkaline $KMnO_4$ ~~baye~~ (Baeyer's reagent) in low temp hydroxylation occurs resulting in the formation of dihydroxy compd known as ~~vicinal~~ vicinol glycol. The pink color of the $KMnO_4$ is discharged during the reaction. This reaction used for the test of unsaturated molecule.

$$R-CH=CH_2+H_2O+O \xrightarrow{dil.\ KMnO_4} R-\underset{OH}{CH}-\underset{OH}{CH_2}$$

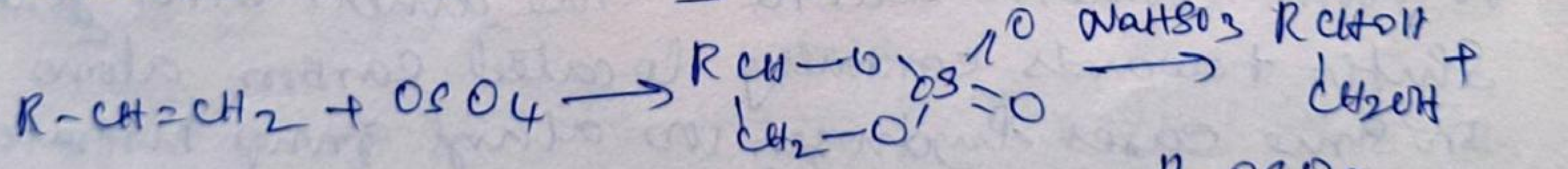
Alkene reacts with i) cold dilute $KMnO_4$ to gives glycol. whereas ii) Hot $KMnO_4$ (hot conc $KMnO_4$) gives ketone or acids.

i) $$\underset{CH_2}{\overset{CH_2}{\|}} + KMnO_4 \xrightarrow{H_2O} \underset{OH}{CH_2}-\underset{OH}{CH_2}$$

ii) $$CH_3-CH=CH_2 \xrightarrow[hot\ KMnO_4]{(O)} CH_3COOH + CO_2 + H_2O$$

$$CH_3-\overset{CH_3}{C}=\overset{H}{C}-CH_3 \xrightarrow[{''}]{''} CH_3-\overset{CH_3}{C}=O + CH_3COOH.$$

glycol are also formed when osmium tetroxide is added to the olefin and then refluxed with alcoholic ~~NaHSO3~~ $NaHSO_3$ solution.



$$R-CH=CH_2 + OsO_4 \longrightarrow \begin{matrix} RCH-O \\ CH_2-O \end{matrix}\!\!>Os\!\!<\begin{matrix}O\\O\end{matrix} \xrightarrow{NaHSO_3} \begin{matrix} RCHOH \\ CH_2OH \end{matrix} +$$

H_2OsO_2

~~Os~~ Osmic acid

Oxidation with HIO_4 (or) Lead tetraacetate (LTA)

Alkene are oxidised with HIO_4 to gives alcohol ~~and~~ which is subsequently oxidised to aldehyde (or) ketone.

$$(CH_3)_2C=CH_2 + H_2O \xrightarrow[LTA]{HIO_4} (CH_3)_2C\,OH\,CH_2OH \xrightarrow[LTA]{HIO_4} (CH_3)_2C=O + HCHO$$

Isobutylene

Oxidation with acidic $K_2Cr_2O_7$ (or) $KMnO_4$

Alkene when oxidised with acidic $KMnO_4$ (or) acidic $K_2Cr_2O_7$ first give glycol which are further oxidised to aldehyde, ketones and acids.

$$CH_3-CH=CH_2 + H_2O + O \xrightarrow[KMnO_4]{Acid} CH_3\underset{OH}{CH}-\underset{OH}{CH_2} \xrightarrow{KMnO_4} CH_3CHO + HCHO$$

$$CH_3CHO \xrightarrow{O} CH_3COOH \qquad HCHO \xrightarrow{O} HCOOH$$

$$(CH_3)_2C=CH_2 \xrightarrow[KMnO_4\ acid]{H_2O/O} (CH_3)_2C\,OH-\underset{OH}{CH_2} \xrightarrow{K_2Cr_2O_7} (CH_3)_2CO + HCHO$$

$$HCHO \xrightarrow{O} HCOOH.$$

Isomerization reaction

When alkene are heated in the presence of a catalyst (or) alone, they undergo isomerization to form isomeric alkene. The double bond generally shift towards centrally located carbon atoms In some cases hydrogen (or) alkyl group migrate to form a branched chain alkene.

$$CH_3-CH_2-CH_2-CH=CH_2 \xrightarrow[200-300^\circ C]{Al_2(SO_4)_3} CH_3-CH_2\,CH=CH-CH_3$$

1-pentene

2-pentene

$$(CH_3)_2CH\;CH=CH_2 \xrightarrow[\text{''}]{\text{''}} (CH_3)_2C=CH-CH_3$$

3-methyl-1-butene

2-methyl-2-butene

$$CH_3-CH=CH-CH_3 \xrightarrow[\text{''}]{\text{''}} (CH_3)_2C=CH_2$$

2-butene

2-methyl-1-propene.

GENERAL CHEMISTRY-I

Unit-V: Colloids and Macromolecules

A colloid is a mixture that has particles ranging between 1 and 1000 nanometers in diameter, yet is still able to remain evenly distributed throughout the solution. These are also known as colloidal dispersions because the substances remain dispersed and do not settle to the bottom of the container.

In chemistry, a colloid is a phase separated mixture in which one substance of microscopically dispersed insoluble or soluble particles is suspended throughout another substance.

Types of Colloids

- Sol is a colloidal suspension with solid particles in a liquid.
- Emulsion is between two liquids.
- Foam is formed when many gas particles are trapped in a liquid or solid.
- Aerosol contains small particles of liquid or solid dispersed in a gas.

Preparation of Colloids

Colloids can be prepared by a variety of techniques involving physical, chemical as well as some dispersion methods. However, there are two principal ways of preparation of colloids:

- Dispersion of large particles or droplets to the colloidal dimensions by milling, spraying, or application of shear (e.g. shaking, mixing, or high shear mixing).
- Condensation of small dissolved molecules into larger colloidal particles by precipitation, condensation, or redox reactions. Such processes are used in the preparation of colloidal silica or gold.

Chemical Methods of Preparation of Colloids

Hydrophilic or Lyophobic colloidal solutions can be prepared by various chemical techniques such as:

- **Double Decomposition Technique:** When hydrogen sulphide is passed through a solution of arsenious oxide in distilled water, we get a colloidal solution of arsenious chloride.

$$As_2O_3 + 3H_2S \rightarrow As_2S_3 + 3H_2O$$

- **Oxidation Technique:** A colloidal solution of Sulphur is made to pass through an aqueous solution of sulphur dioxide. It can also be obtained by passing the gas through a solution of an oxidization agent such as bromine water as well as nitric acid.

$$SO_2 + 2H_2S \rightarrow 2H_2O + 3S$$

$$H_2S + [O] \rightarrow H_2O + S$$

- **Reduction Technique:** Another technique of preparing colloidal solutions of metals such as silver, gold as well as platinum involves the use of reducing agent for reduction of the salt solutions of these metals. Example of reducing agent include stannous chloride.
- **Hydrolysis Technique:** It involves the use of boiling water to obtain a reduced solution of ferric chloride.

$$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3\ HCl$$

Purification of Colloidal Solution

The following methods are commonly used for the purification of colloidal solutions.

Dialysis

- The process of separating the particles of colloid from those of crystalloid, by means of diffusion through a suitable membrane is called dialysis.
- It's principle is based upon the fact that colloidal particles can not pass through a parchment or cellophane membrane while the ions of the electrolyte can pass through it.
- The impurities slowly diffused out of the bag leaving behind pure colloidal solution
- The distilled water is changed frequently to avoid accumulation of the crystalloids otherwise they may start diffusing back into the bag.
- Dialysis can be used for removing HCl from the ferric hydroxide sol.

Electrodialysis

- The ordinary process of dialysis is slow.
- To increase the process of purification, the dialysis is carried out by applying electric field. This process is called electrodialysis.
- The important application of electrodialysis process in the artificial kidney machine used for the purification of blood of the patients whose kidneys have failed to work. The artificial kidney machine works on the principle of dialysis.

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Ultra – filtration

- Sol particles directly pass through ordinary filter paper because their pores are larger (more than 1μ or $1000\,m\mu$) than the size of sol particles (less than $200\,m\mu$).
- If the pores of the ordinary filter paper are made smaller by soaking the filter paper in a solution of gelatin of colloidion and subsequently hardened by soaking in formaldehyde, the treated filter paper may retain colloidal particles and allow the true solution particles to escape. Such filter paper is known as ultra - filter and the process of separating colloids by using ultra – filters is known as ultra – filtration.

Ultra – centrifugation

- The sol particles are prevented from setting out under the action of gravity by kinetic impacts of the molecules of the medium.
- The setting force can be enhanced by using high speed centrifugal machines having 15,000 or more revolutions per minute. Such machines are known as ultra–centrifuges.

Stability of Colloids

The stability of a colloidal system is defined by particles remaining suspended in solution at equilibrium.Stability is hindered by aggregation and sedimentation phenomena, which are driven by the colloid's tendency to reduce surface energy. Reducing the interfacial tension will stabilize the colloidal system by reducing this driving force. Aggregation is due to the sum of the interaction forces between particles. If attractive forces prevail over the repulsive ones particles aggregate in clusters.Electrostatic stabilization and steric stabilization are the two main mechanisms for stabilization against aggregation.

Electrostatic stabilization is based on the mutual repulsion of like electrical charges. In general, different phases have different charge affinities, so that an electrical double layer forms at any interface. Small particle sizes lead to enormous surface areas, and this effect is greatly amplified in colloids. In a stable colloid, mass of a dispersed phase is so low that its buoyancy or kinetic energy is too weak to overcome the electrostatic repulsion between charged layers of the dispersing phase. The electrostatic repulsion between suspended colloidal particles is most readily quantified in terms of the zeta potential, a measurable quantity describing electrical potential at the slipping plane in an electrical double layer.

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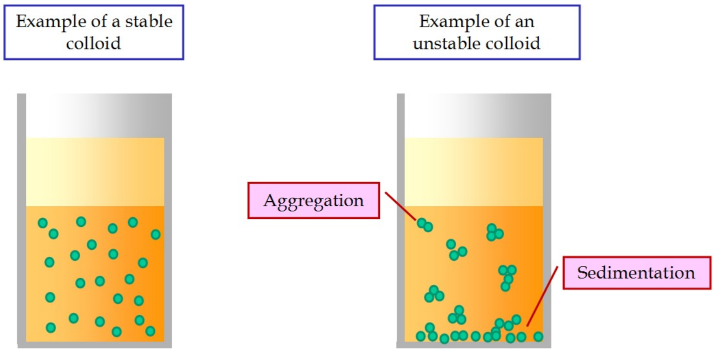
Steric stabilization consists in covering the particles in polymers which prevents the particle to get close in the range of attractive forces.



Gold Number

The Gold Number is the minimum weight (in milligrams) of a protective colloid required to prevent the coagulation of 10 ml of a standard hydro gold sol when 1 ml of a 10% sodium chloride solution is added to it.

The coagulation of gold sol results in an increase in particle size, indicated by a colour change from red to blue or purple. The higher the gold number, the lower the protective power of the colloid, because a greater amount of colloid is required to prevent coagulation. The gold numbers of some colloids are given below.

Protective Colloid	**Gold Number**
Gelatin	0.005-.01
Haemoglobin	0.03-0.07
Egg Albumin	0.15-0.25
Potato Starch	20-25
Gum arabic	0.15-0.25
Caseinate	0.01-0.02
Sodium Oleate	1-5
Dextrin	125-150

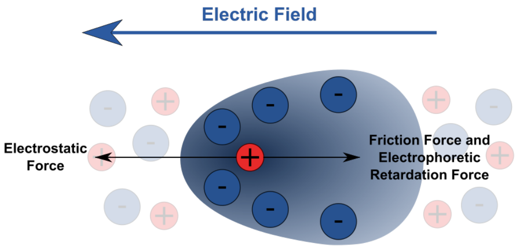
Properties of Colloids

Electrical properties

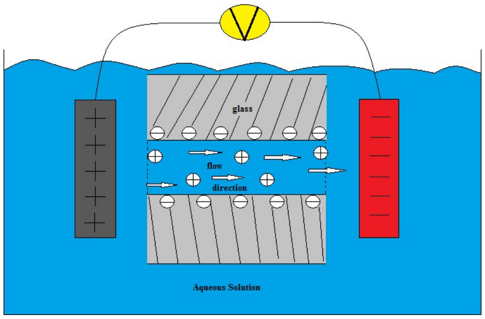
Electrical double layer theory: In this theory, charge is imparted to the particles by placing ions which are adsorbed preferentially at immovable points which for the first layer. The second layer consists of diffused mobile ions. The charge present on both the layers is equal. This two-layer arrangement leads to a development of potential called **zeta or Electrokinetic**

potential. As a result of this potential developed across the particles, under the influence of electric field these particles move.

Electrophoresis: It is a process in which an electric field is been applied to a colloidal solution which is responsible for the movement of colloidal particles. Depending upon the accumulation near the electrodes the charge of the particles can be predicted. The charge of the particles is positive if the particles get collected near a negative electrode and vice versa.



Electro-osmosis: It is a process in which the dispersing medium of the colloidal solution is brought under the influence of electric field and the particles are arrested.



Optical properties

Tyndall's effect is defined as the phenomenon in which light is scattered by the colloidal particles. The light is been absorbed by the particles present in the solution. Once the light is been absorbed a part of the light gets scattered in all the directions. The result of scattering exhibits this effect.

Kinetic properties

During the observation of the colloidal dispersion under an ultra-microscope, it is clearly seen that the particles are in a continuous movement in the solution. This random zigzag movement of the particles in the colloidal solution is called Brownian effect. This movement is mainly due to the unique bombardment of the molecules present in the dispersed medium on the colloidal particles.

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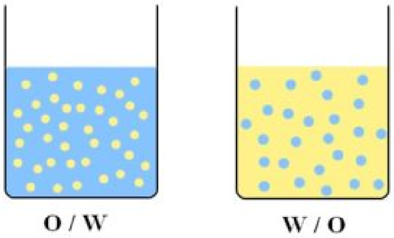
Emulsions

An emulsion is a type of colloid formed by combining two liquids that normally don't mix. In an emulsion, one liquid contains a dispersion of the other liquid. Common examples of emulsions include egg yolk, butter, and mayonnaise. The process of mixing liquids to form an emulsion is called emulsification.

Types of Emulsions



Emulsions can exist as “oil in water” or ” water in oil” of emulsions. The type of emulsion depends upon the properties of the dispersed phase and continuous phase. If the oil phase is dispersed in a continuous aqueous phase the emulsion is known as “oil in water”. If the aqueous phase is the dispersed phase and the oil phase is the continuous phase, then its known as “water in oil”

Whether an emulsion of oil and water turns into a “water-in-oil” emulsion or an “oil-in-water” emulsion depends on the volume fraction of both phases and the type of emulsifier used to emulsify them.

Preparation of Emulsions

The methods commonly used to prepare emulsions can be divided into two categories

A) Trituration Method

This method consists of dry gum method and wet gum method.

Dry Gum Method

In this method the oil is first triturated with gum with a little amount of water to form the primary emulsion. The trituration is continued till a characteristic ‘clicking’ sound is heard and a thick white cream is formed. Once the primary emulsion is formed, the remaining quantity of water is slowly added to form the final emulsion. 4:2:1 formula 4 parts (volumes) of oil 2 parts of water 1 part of gum.

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Wet Gum Method

Wet Gum Method As the name implies, in this method first gum and water are triturated together to form a mucilage. The required quantity of oil is then added gradually in small proportions with thorough trituration to form the primary emulsion. Once the primary emulsion has been formed remaining quantity of water is added to make the final emulsion. 4:2:1 formula 4 parts (volumes) of oil 2 parts of water 1 part of gum.

Bottle Method

This method is employed for preparing emulsions containing volatile and other non-viscous oils. Both dry gum and wet gum methods can be employed for the preparation. ¬ As volatile oils have a low viscosity as compared to fixed oils, they require comparatively large quantity of gum for emulsification. ¬ In this method, oil or water is first shaken thoroughly and vigorously with the calculated amount of gum. Once this has emulsified completely, the second liquid (either oil or water) is then added all at once and the bottle is again shaken vigorously to form the primary emulsion. More of water is added in small portions with constant agitation after each addition to produce the final volume.

Properties of Emulsion

- Emulsions show all the characteristic properties of colloidal solution such as Brownian movement, Tyndall effect, electrophoresis etc.
- These are coagulated by the addition of electrolytes containing polyvalent metal ions indicating the negative charge on the globules.
- The size of the dispersed particles in emulsions in larger than those in the sols. It ranges from 1000 Å to 10,000 Å. However, the size is smaller than the particles in suspensioins.
- Emulsions can be converted into two separate liquids by heating, centrifuging, freezing etc. This process is also known as demulsification.

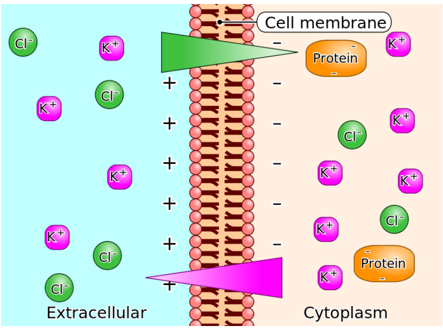
Applications of Emulsions

- Concentration of ores in metallurgy
- In medicine (Emulsion water-in-oil type)
- Cleansing action of soaps.
- Milk, which is an important constituent of our diet an emulsion of fat in water.

- Digestion of fats in intestine is through emulsification**.**

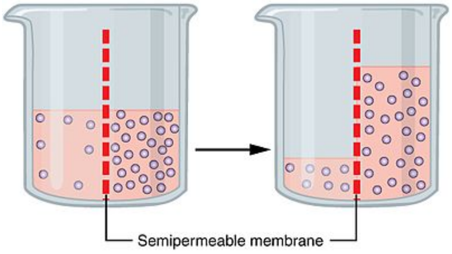
Donnan Membrane Equilibrium

The Gibbs–Donnan effect (also known as the Donnan's effect, Donnan law, Donnan equilibrium, or Gibbs–Donnan equilibrium) is a name for the behaviour of charged particles near a semi-permeable membrane that sometimes fail to distribute evenly across the two sides of the membrane.



Osmosis

Osmosis is the spontaneous net movement of solvent molecules through a selectively permeable membrane into a region of higher solute concentration, in the direction that tends to equalize the solute concentrations on the two sides.



Reverse osmosis (RO)

Reverse osmosis (RO) is a water purification process that uses a partially permeable membrane to remove ions, unwanted molecules and larger particles from drinking water. In reverse osmosis, an applied pressure is used to overcome osmotic pressure, a colligative property that is driven by chemical potential differences of the solvent, a thermodynamic parameter. Reverse osmosis can remove many types of dissolved and suspended chemical species as well as biological ones (principally bacteria) from water, and is used in both industrial processes and the production of potable water.

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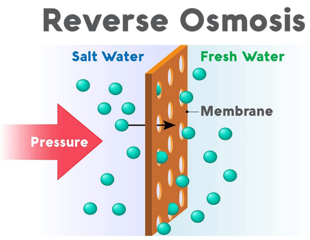
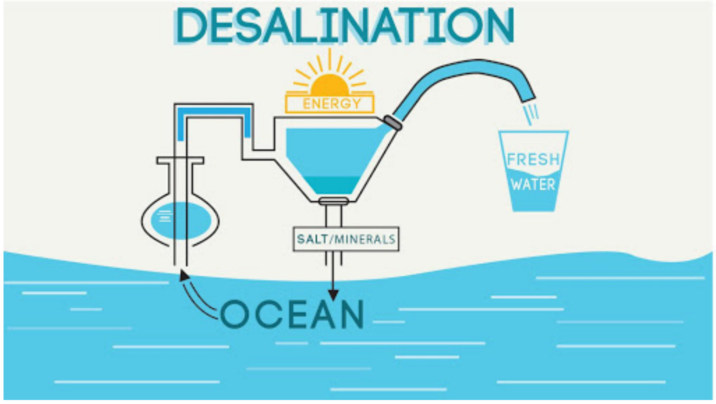


Desalination

Desalination is a process that takes away mineral components from saline water. More generally, desalination refers to the removal of salts and minerals from a target substance, as in soil desalination, which is an issue for agriculture.

Saltwater is desalinated to produce water suitable for human consumption or irrigation. The by-product of the desalination process is brine. Desalination is used on many seagoing ships and submarines. Most of the modern interest in desalination is focused on cost-effective provision of fresh water for human use. Along with recycled wastewater, it is one of the few rainfall-independent water sources.



Macromolecules

Macromolecules are large molecules composed of thousands of covalently connected atoms. Carbohydrates, lipids, proteins, and nucleic acids are all macromolecules. Macromolecules are formed by many monomers linking together, forming a polymer.

A macromolecule is a very large molecule, such as protein, commonly composed of the polymerization of smaller subunits called monomers. They are typically composed of thousands of atoms or more. A substance that is composed of monomers is called a polymer. The most common macromolecules in biochemistry are biopolymers (nucleic acids, proteins, and carbohydrates) and large non-polymeric molecules (such as lipids and macrocycles), synthetic fibers as well as experimental materials such as carbon nanotubes.

Molecular Weight of Macromolecule

Macromolecules are composed of much larger numbers of atoms than ordinary molecules. For example, a molecule of polyethylene, a plastic material, may consist of as many as 2,500 methylene groups, each composed of two hydrogen atoms and one carbon atom. The corresponding molecular weight of such a molecule is on the order of 35,000. Insulin, a protein hormone present in the pancreas and responsible for regulation of blood-sugar levels, has a molecular unit derived from 51 amino acids (by themselves molecules containing carbon, hydrogen, oxygen, nitrogen, and sometimes sulfur). The exact molecular weight of insulin from cattle has been determined to be 5,734.

Determination of Molecular Weight by Osmotic Pressure

Osmometry is used to determine the molecular mass, which depends on colligative properties, meaning that the number of dissolved molecules is the only factor that alters the properties of a solution. In addition, boiling point elevation, osmotic pressure, freezing point depression, and vapor pressure reduction are based on colligative properties.

There are two principal methods of osmometry that are suitable for determining average molecular weights of polymers: membrane and vapor pressure osmometry. While the first one is suitable for molecular weights between 50000 and 2 million (g mol^{-1}), the second one is applicable for 'short' polymeric chains below 40000 g mol^{-1}. Both methods deliver the absolute value of the number average molecular weight (M_n).

In the first case, a solution of a polymer and the pure solvent are placed in compartments separated by a semipermeable membrane. The membrane allows diffusion of small solvent molecules, but restricts the larger polymer chains to one compartment only. Hence, a net diffusion of solvent takes place from the solvent side to the solution side until sufficient hydrostatic pressure develops that prevents further diffusion. This hydrostatic pressure is the osmotic pressure, which is related to molecular weight by the van't Hoff equation extrapolated to zero concentration:

$$\pi/C_{C=0} = RT/Mn + A_2C$$

where π is the osmotic pressure, C the concentration of polymer (g l^{-1}), T the temperature (K), R the gas constant, and A_2 the second virial coefficient (solvent dependent).

A plot of π/C versus C is a straight line of slope A_2, and y-intercept equal to RT/M_n. The permeability of the membrane to low molecular weight chains renders membrane osmometry useful for polymer molecular weights greater than 50000, while inaccuracy in the measurement of very small osmotic pressures sets the upper limit at 2 million.

The second method is based on the vapor pressure difference of pure solvent and a polymer solution. A sample of the solution and pure solvent are introduced into a temperature-controlled measuring chamber, which is saturated with solvent vapor. Since the vapor pressure of the solution is lower than that of the solvent, solvent vapor condenses on the solution sample causing its temperature to rise. This temperature difference (ΔT) can be measured for different concentrations (C) of the polymer solution and $1/M_n$ can be calculated according to the following formula:

$\Delta T/KC = 1/Mn + A_2C$

K is a measuring constant determined for a given solvent and temperature with an organic substance (e.g., benzoin) with exactly known molecular weight. A plot of ($\Delta T/KC$) versus C delivers $1/M_n$ as the y-axis intercept (slope A_2).

Determination of Molecular Weight by Light Scattering Method

Static light scattering is a technique in physical chemistry that measures the intensity of the scattered light to obtain the average molecular weight M_w of a macromolecule like a polymer or a protein in solution.

A light scattering instrument composed of many detectors placed at various angles, all the detectors need to respond the same way. Usually detectors will have slightly different quantum efficiency, different gains and are looking at different geometrical scattering volumes. In this case a normalization of the detectors is absolutely needed. To normalize the detectors, a measurement of a pure solvent is made first. Then an isotropic scatterer is added to the solvent. Since isotropic scatterers scatter the same intensity at any angle, the detector efficiency and gain can be normalized with this procedure. It is convenient to normalize all the detectors to the 90° angle detector.

Molecular Weight Determination by Light-scattering Method

One of the most used methods to characterize the molecular weight is light scattering method. When polarizable particles are placed in the oscillating electric field of a beam of light, the light scattering occurs. Light scattering method depends on the light, when the light is passing through polymer solution, it is measure by loses energy because of absorption, conversion to heat and scattering. The intensity of scattered light relies on the concentration, size and polarizability that is proportionality constant which depends on the molecular weight. Figure shows light scattering off a particle in solution.

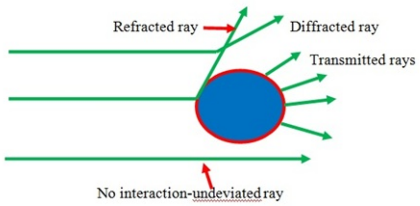


Figure: Modes of scattering of light in solution.

A schematic laser light-scattering is shown in Figure. A major problem of light scattering is to prepare perfectly clear solutions. This problem is usually accomplished by ultra-centrifugation. A solution should be as possible as clear and dust free to determine absolute molecular weight of polymer. The advantages of this method, it doesn't need calibration to obtain absolute molecular weight and it can give information about shape and M_w information. Also, it can be performed rapidly with less amount of sample and absolute determinations of the molecular weight can be measured. The weaknesses of the method is high price and most times it requires difficult clarification of the solutions.

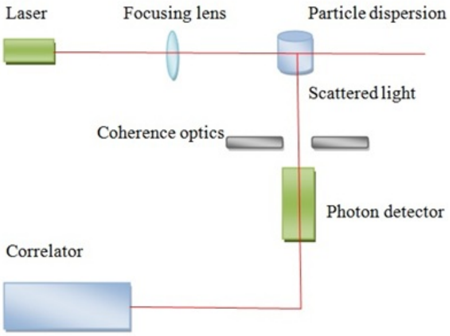


Figure: Schematic representation of light scattering.

The weight average molecular weight value of scattering polymers in solution related to their light scattering properties, where K is the wave vector. C is solution concentration, R(θ) is the reduced Rayleigh ratio, P(θ) the particle scattering function, θ is the scattering angle, A is the osmotic virial coefficients, where n_0 solvent refractive index, λ the light wavelength and N_a Avagadro's number. The particle scattering function, where R_z is the radius of gyration.

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$$KC/R(\theta) = 1/M_W(P(\theta) + 2A_2C + 3A_3C_2 + ...)$$

$$K = 2\pi^2 n^2{}_0(dn/dC)^2/Na\lambda^2$$

$$1/(P(\theta)) = 1+16\pi^2 n^2{}_0(R^2{}_z)\sin^2(\theta/2)3\lambda^2$$

Weight average molecular weight of a polymer is found from extrapolation of data in the form of a Zimm plot. Experiments are performed at several angles and at least at 4 different concentrations. The straight line extrapolations provides M_w.

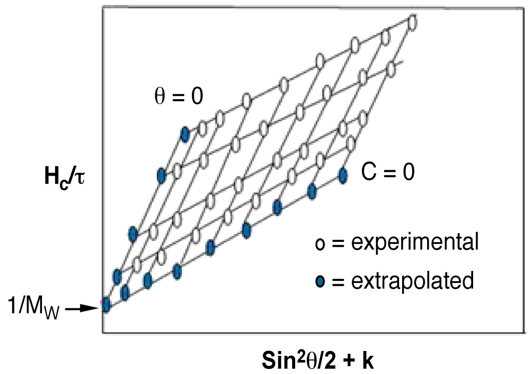

Figure: EA typical Zimm plot of light scattering data.

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UNIT - III

Basic concepts in organic chemistry

Catenation :

All organic compounds contain carbon. The compounds of carbon are far more numerous than the known compounds of all the other elements put together. This is because that carbon has the power to combine with other carbon atoms to form long chains. This property is not shown to such an extent by any other element.

Definition :

The property of carbon to form long chains by combining with other carbon atoms is known as catenation.

E.g, CH_3-CH_3, $CH_3-CH_2-CH_3$, $CH_3-CH_2-CH_2-CH_3$
Ethane Propane Butane

Orbital Overlap :

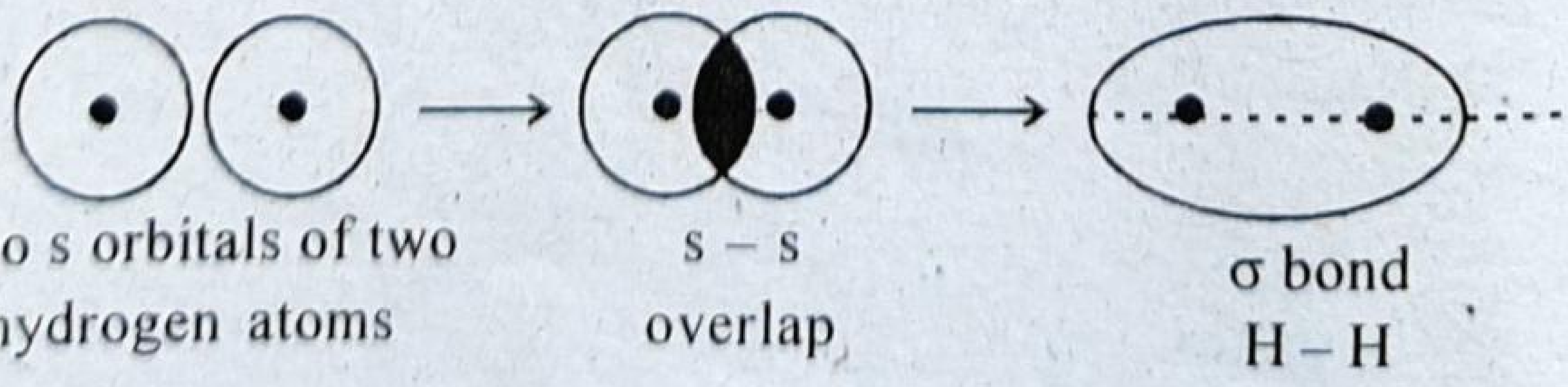
Organic compounds contain covalent bonds. A covalent bond is formed by the sharing of a pair of electrons between two atoms. For this purpose the two atoms must be so located that on orbital of one of the combining atoms overlaps with the orbital of the other atom ; each combining orbital containing one electron. The strength of the chemical bond is proportional to the extent overlapping of the orbitals.

Types of orbital overlapping :

i. s - s Overlapping :

If one s - orbital of an atom overlaps with one s - orbital of another atom to form a covalent bond, it is called s-s overlapping

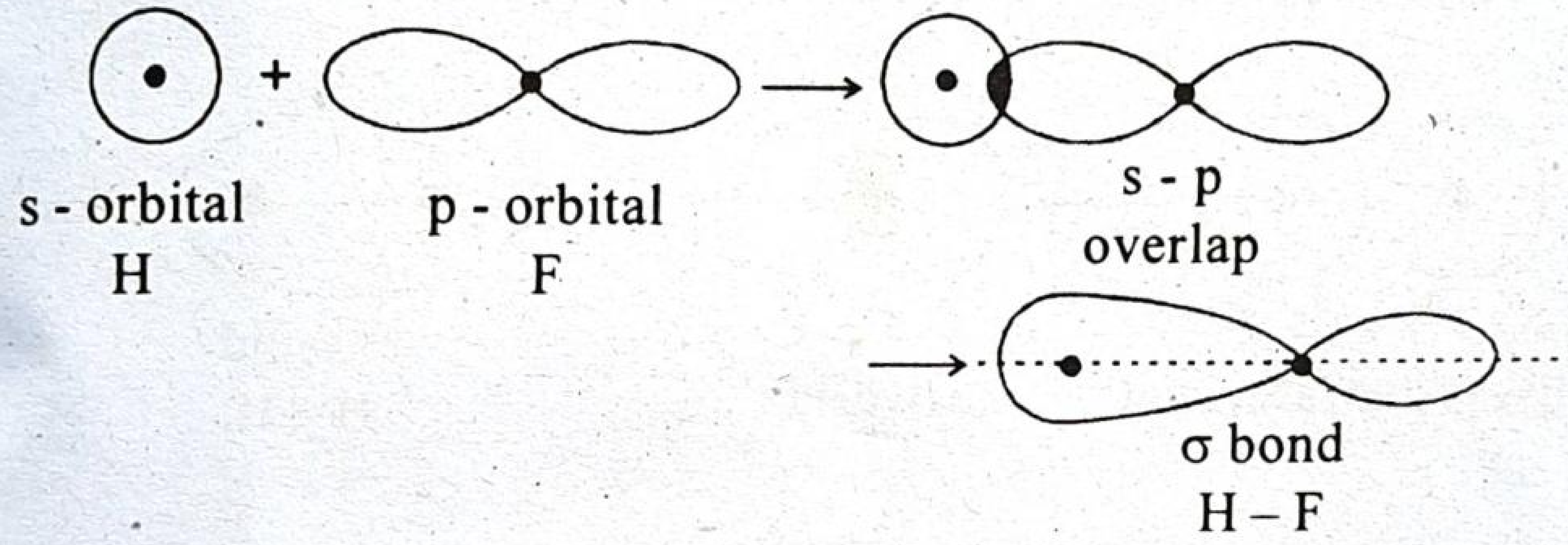
Eg., A molecule of hydrogen is formed by the overlapping of one 1s orbital of a hydrogen atom with one 1s orbital of another hydrogen atom.



ii. s - p Overlapping :

If one s - orbital of an atom overlaps with one p - orbital of another atom to form a covalent bond, it is called s – p overlapping.

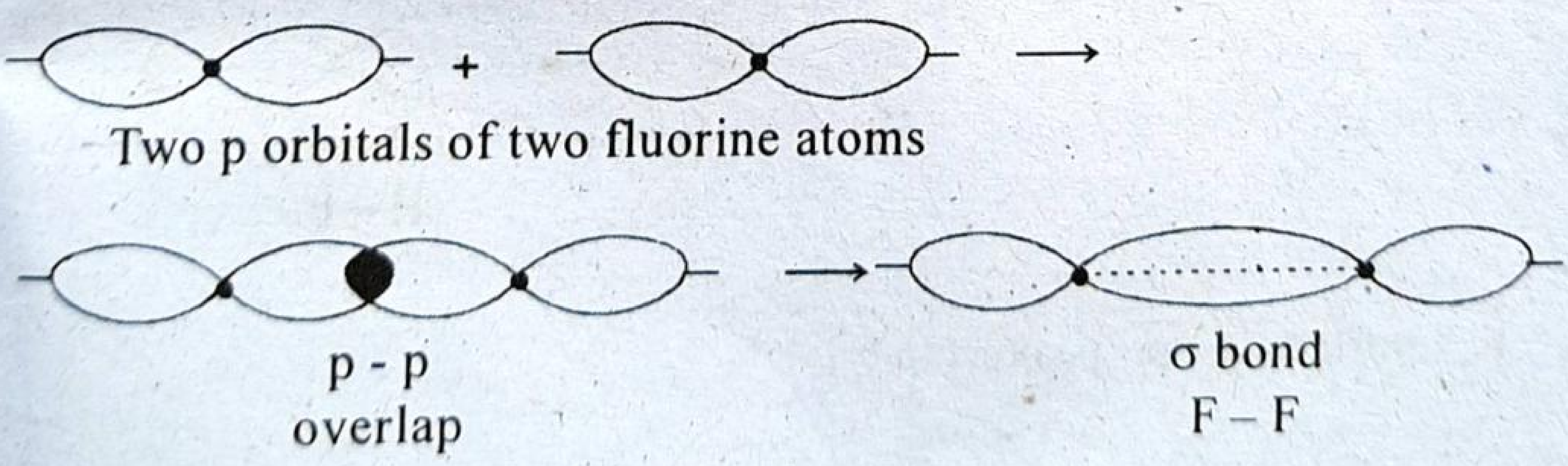
Eg., A molecule of hydrogen fluoride is formed by the overlapping of one s - orbital of a hydrogen atom with one p -orbital of fluroine atom.



iii. p - p Overlapping :

If one p -orbital of an atom overlaps with one p - orbital of another atom to form a covalent bond then it is called p - p overlapping

Eg., A molecule of fluorine is formed by the overlapping of one 2p orbital of a fluorine atom with one 2p orbital of another fluorine atom.



σ - bond and π - bonds

σ - bond :

When two bonding orbitals overlap to form a molecular orbital (MO), which is symmetrically distributed about the nuclear axis (the line joining the nuclei of the two atoms) then the bond so formed is called a sigma bond.

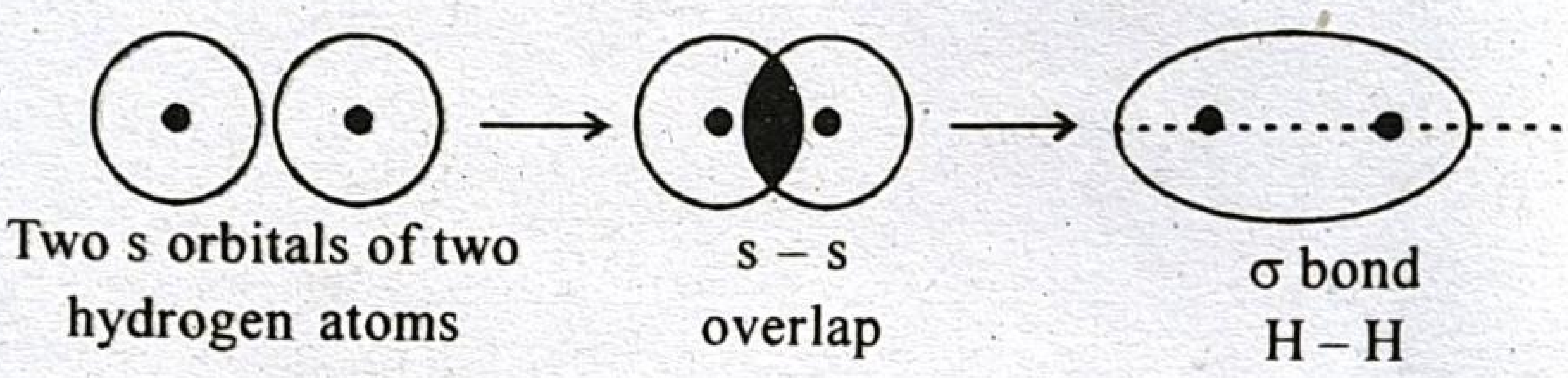
Sigma bonds are formed as the result of the orbital overlaps of

i. s - orbital of one atom and s - orbital of the other ;

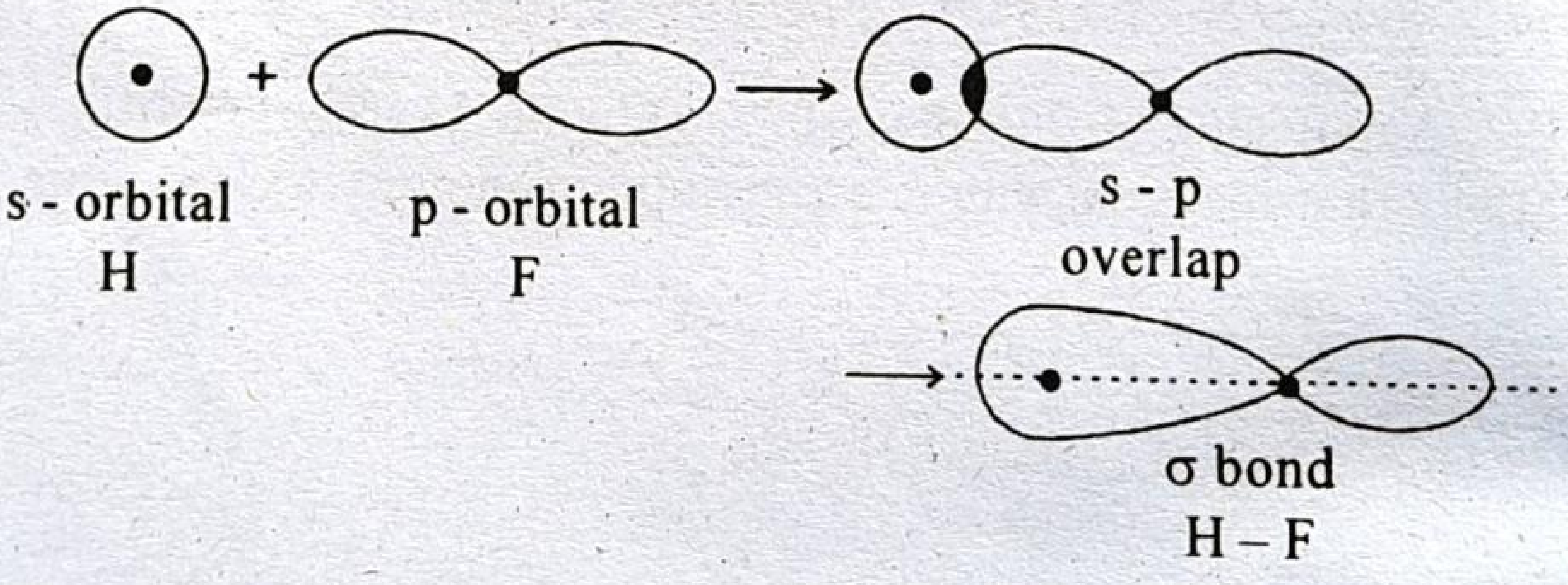
ii. s - orbital of one atom and p - orbital of the other ;

iii. p - orbital of one atom and p - orbtial of the other (in a linear fashion).

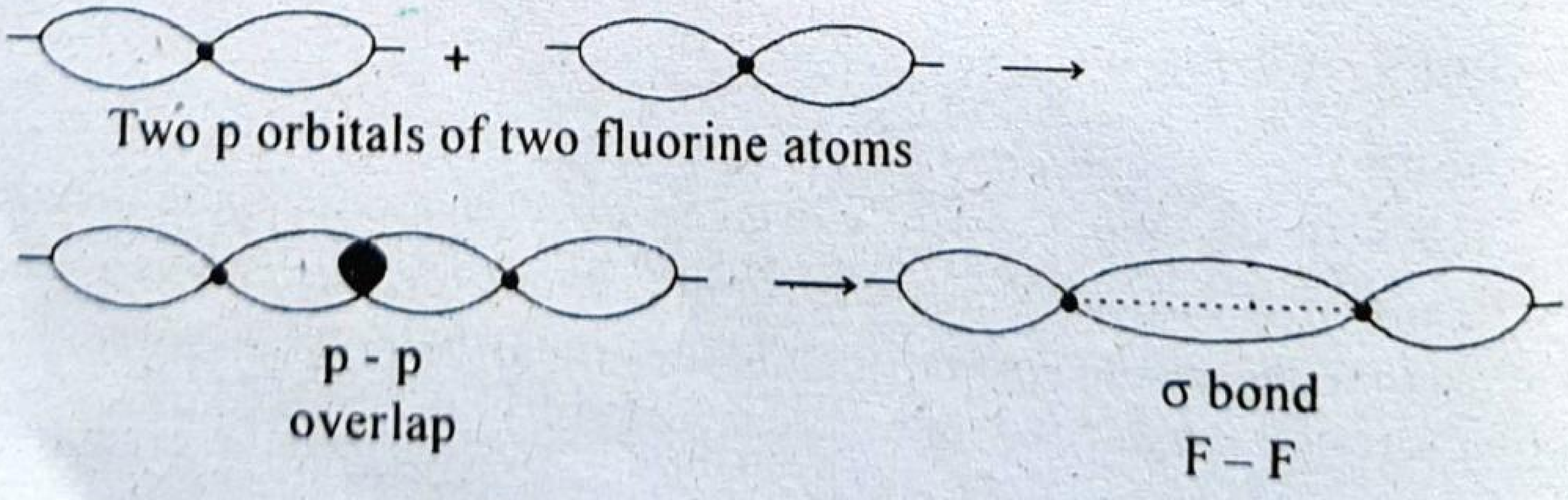
Eg., i. H_2 - molecule ; s -s overlap



ii. HF - molecule ; s - p overlap



iii. F_2 - molecule ; p - p overlap



In practice a single horizontal line is used to indicate a sigma bond

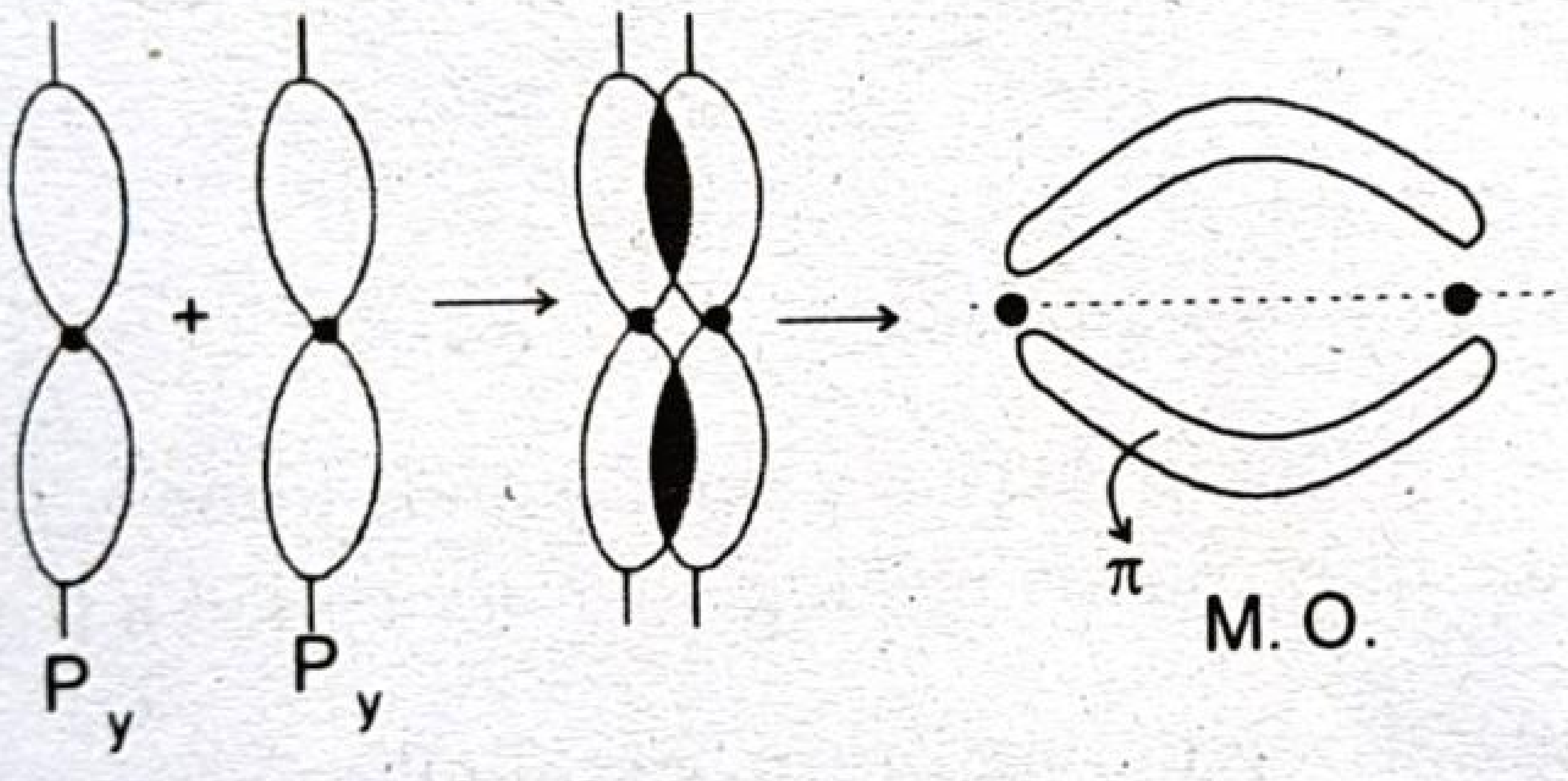
Eg.

H–H	H–F	F–F
Hydrogen	Hydrogen fluoride	Fluorine

π - bond :

When two p - orbitals overlap in a sidewise fashion or laterally to form a molecular orbital (MO), then, the bond so formed is called a π - bond.

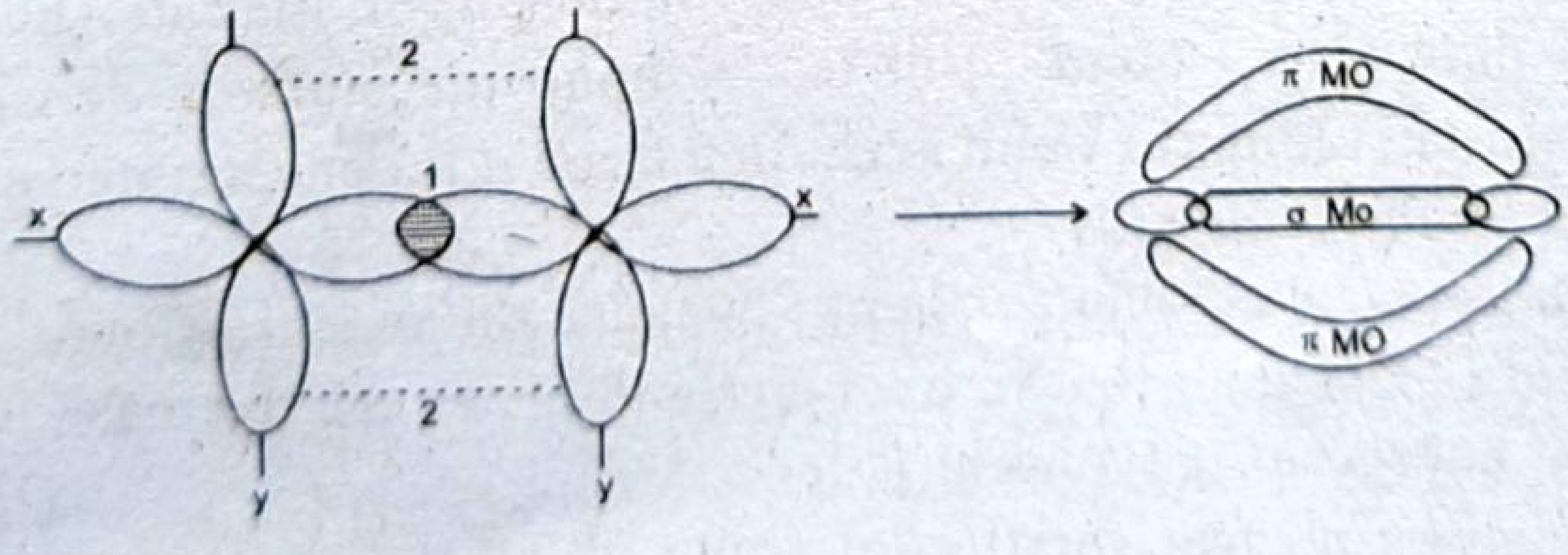
For a lateral overlap, the two *p* - orbitals must be held parallel.



The MO thus formed lies above and below the nuclear axis.

Examples of molecules involving one or more π bonds :

i. ***O_2 - Molecule***



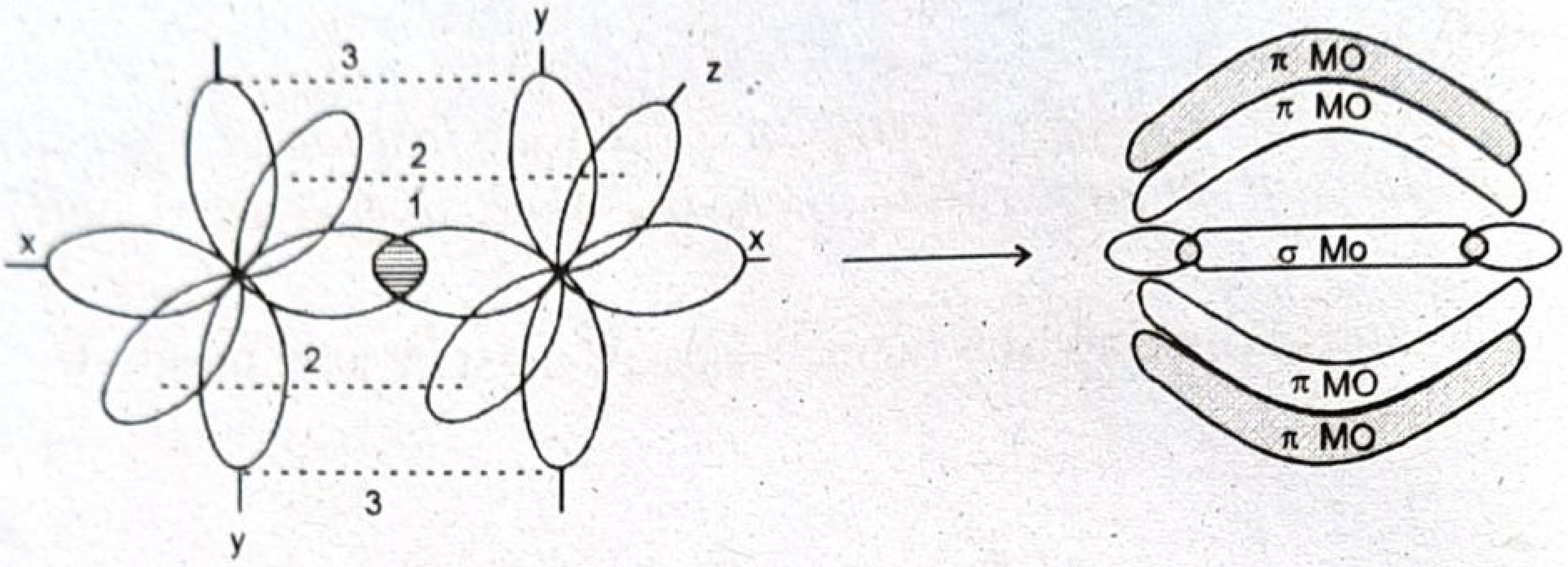
1. Head on overlap - σ bond;
2. Sidewise (lateral) overlap - π bond; A = Axis of the molecule.

Thus in oxygen molecule there are two bonds: one σ - bond and one π - bond. Both of there together are called a double bond.

In practice two horizontal lines are used to indicate a double bond.

Eg., $O=O$
Oxygen

ii. N_2 Molecule



1 Head on overlap - σ bond;
2 and 3 Lateral overlaps - two π bonds.

Thus in nitrogen molecule there are three bonds : one σ - bond and two π - bonds. All the three bonds put together are called a triple bond.

In practice three horizental lines are used to indicate a triple bond.

Eg., $N \equiv N$
Nitrogen

Differences between σ - bond and π - bonds :

i. The π - bond has an increased electron density in the inter-nuclear region than in σ - bond. But in σ - bond the electron density is concentrated along the bond axis. In π bond it is concentrated above and below the bond axis.

ii. π - bond is weaker than σ - bond; because the extent of overlap in π - bond is less than that in σ - bond and hence the decrease in the internal energy of the system is less.

iii. There can be no free rotation of atoms about the nuclear axis in a π - bond; because during rotation, the coplanarity of the overlapping *p*-orbitals would disappear. So the extent of *p-p* overlapping decreases. The energy of the system would increase. Thus the rotation about the bond axis of a π - bond would be restricted, because, work will have to be done for the same. Because of this restricted rotation, many π - bonded compounds exhibit *cis - trans* isomerism.

HYBRIDISATION

We have also seen the shapes of orbitals and formation of various types of bonds, but these concepts are not enough to explain the observed shapes of various molecules. So, to account for the shapes of various molecules the concept of ***hybridisation*** was introduced.

The tetra valency of carbon is explained as follows :

It is assumed that, at the time of bond formation the carbon atom attains an excited state. In the excited state, the two 2s electrons are unpaired and one of them is promoted to the vacant 2*p*, orbital.

Carbon	2s	$2p_x$	$2p_y$	$2p_z$
Ground state	↑↓	↑	↑	
Excited state	↑	↑	↑	↑

Now the tetra-valency of carbon has been accounted for, by proposing an excited state structure for carbon atom with four unpaired electrons. The four unpaired electrons are not identical. There is one s - electron and three *p* - electrons. The explain the equivalent nature of the four bonds of carbon in its saturated compounds a new concept called hybridisation has been proposed.

According to this concept, the atomic orbitals of an atom which lie close to one another in energy, tend to merge or mix and then re-distribute their energy and shape to produce an equivalent number of new orbitals which are idential in all respects called hybridised orbitals.

Definition :

Hybridisation is the concept of mixing or merger of orbitals of an atom having nearly equal energies, to produce entirely new orbitals, which are equal in number to the mixing orbitals. The hybridised new orbitals will have equal energies; identical shapes and are symmetrically placed in space.

Conditions for hybridisation of atomic orbitals :

1. The orbitals of an isolated, single atom only could undergo hybridisation.
2. The hybridising orbitals must differ only slightly in their energy content.

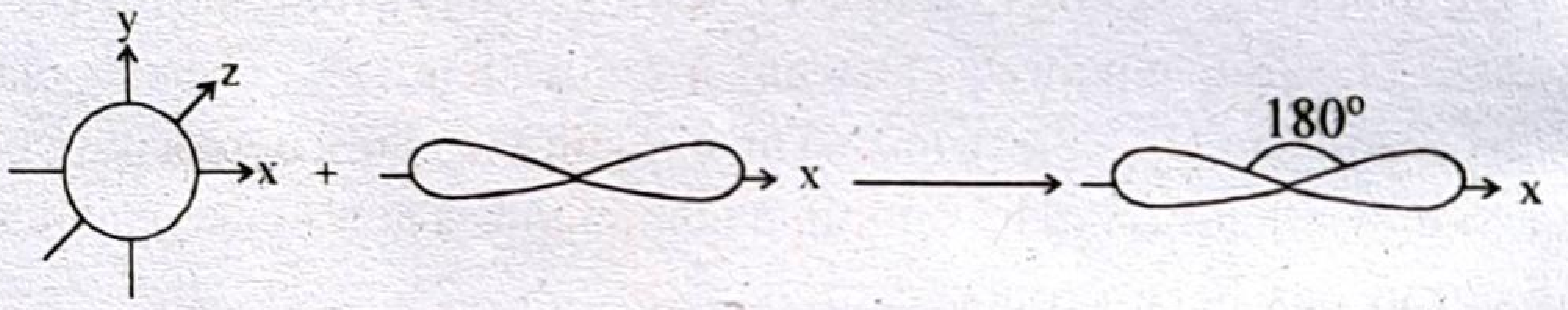
Characteristics of hybrid orbitals :

1. The number of hybridised orbitals is equal to the number of pure atomic orbitals which mix up.
2. A hybrid orbital can have only two electrons as the pure atomic orbitals. The two electrons must have opposite spins.
3. The electron waves in hybrid orbitals repel each other. So they tend to be as far away as possible.
4. The hybrid orbitals distribute themselves in such a way that they assume the direction o the dominating orbitals.

Modes of hybridisation and shapes of hybrid orbitals :

1. *sp - hybridisation :*

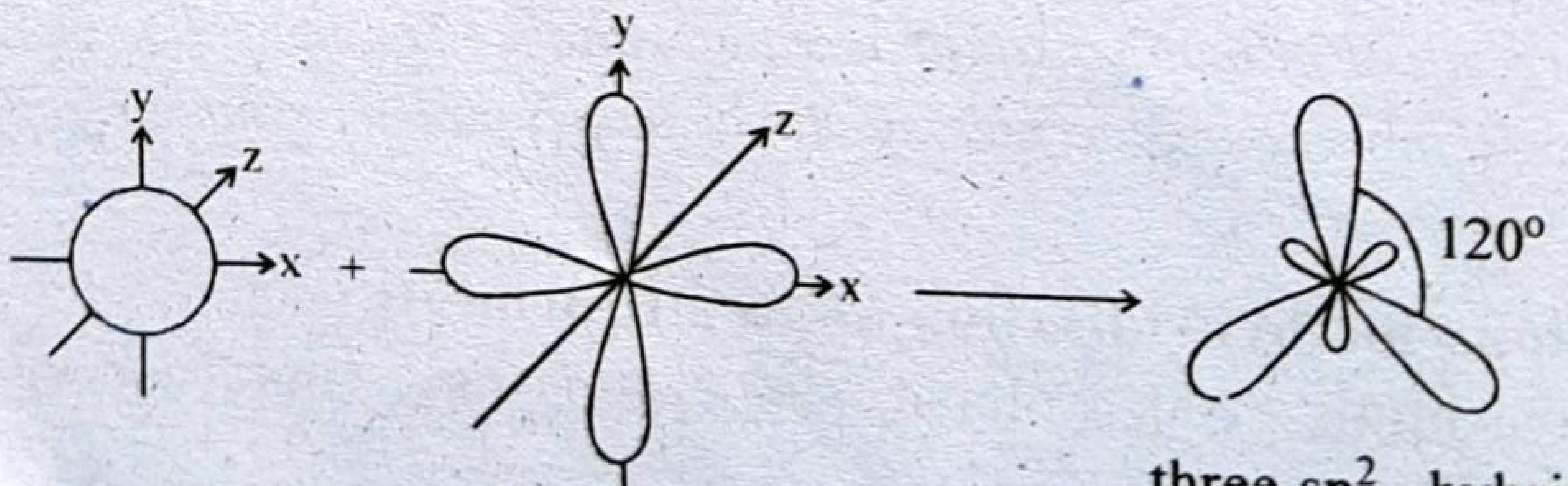
One s and one p orbitals mix and give ***two*** *identical hybrid orbitals. This is known as sp hybridisation.* These hybrid orbitals are co-linear. The bond angle is 180°. E.g., $BeCl_2$.



one s - orbital   one p - orbital   two sp - hybrid orbitals

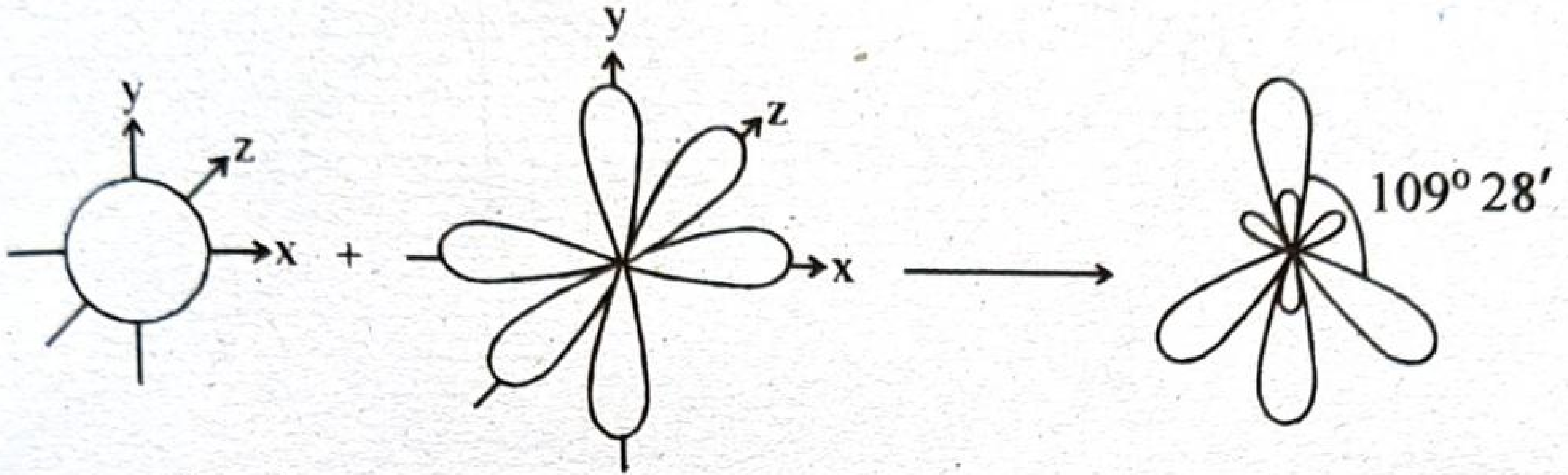
2. *sp^2 - hybridisation :*

One s orbital and two p orbitals mix and give ***three*** *identical hybrid orbitals. This is known as sp^2 hybridisation.* These hybrid orbitals lie in the same plane. The shape is plane tri angular. The bond angle is 120°. E.g., Ethylene



one s - orbital   two p - orbitals   three sp^2 - hybrid orbitals

3. ***sp^3* - hybridisation :** *One s orbital and three p orbitals mix and give four indentical orbitals. This is known as sp^3 hybridisation.* The four hybrid orbitals are oriented towards the four corners of a regular tetrahedron. The bond angle is 109° 28′. E.g., : Methane



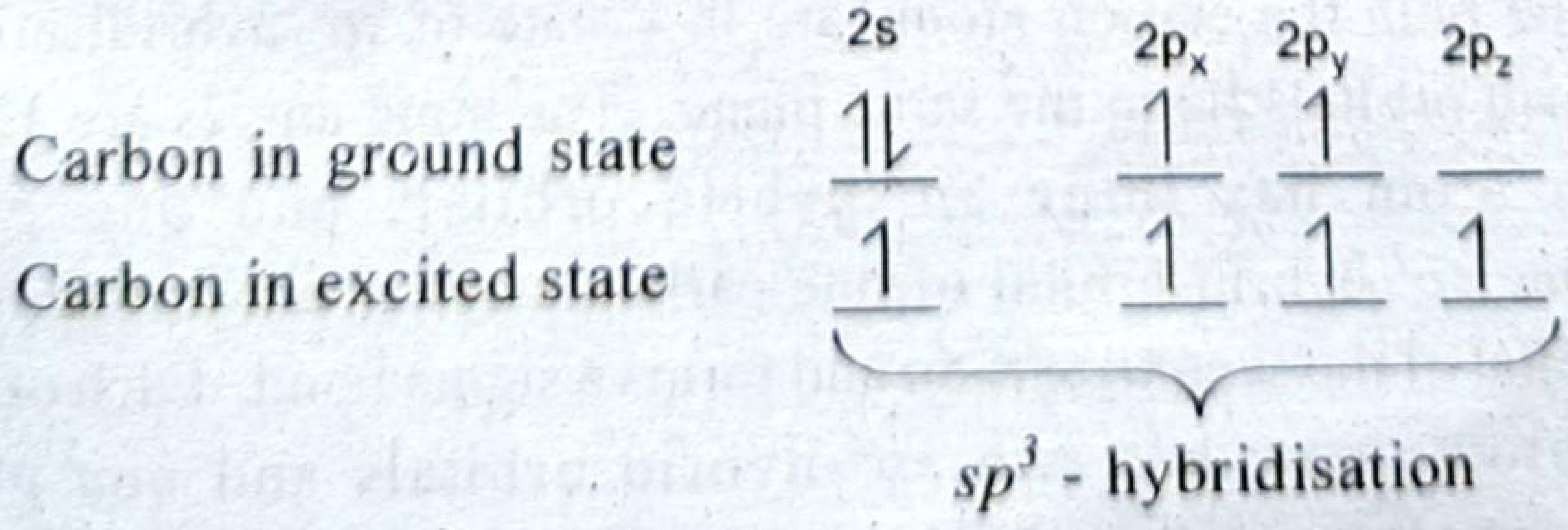
one s - orbital three p - orbital four sp^3 - hybrid obitals

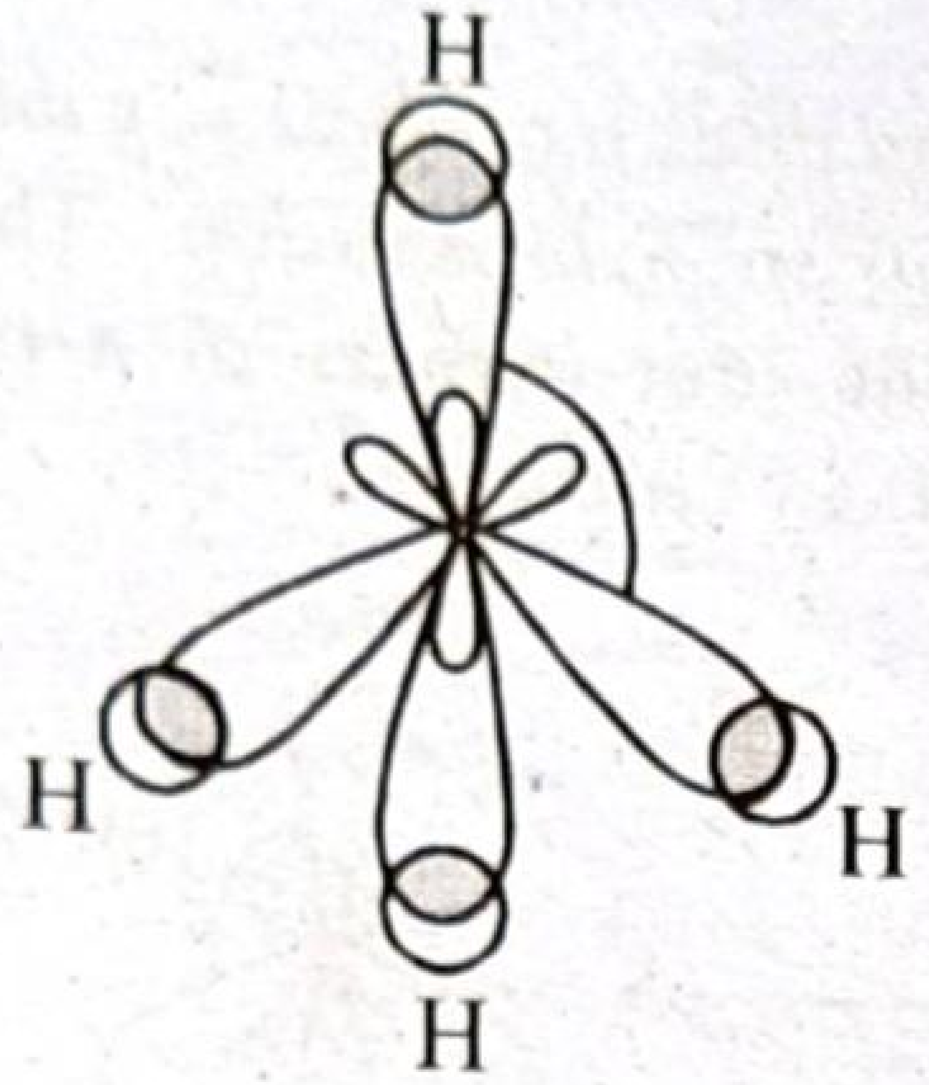
Geometry of molecules

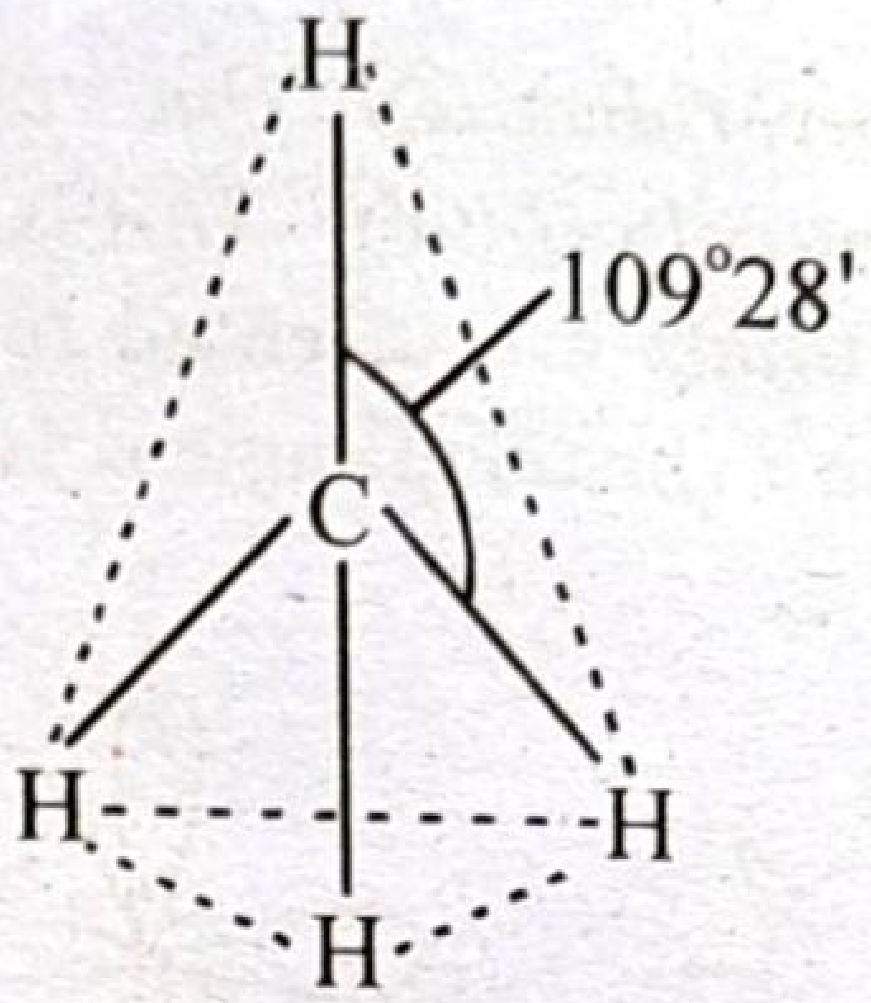
1. Methane

In methane the carbon atom is in a state of *sp^3* hybridisation. One 2s orbital and three 2p orbitals of carbon hybridise and give four *sp^3* hybridised orbitals. There are four electrons in the valency shell of carbon. Each occupies one *sp^3* hybridised orbital. Thus there are four single unpaired electrons in each of the four *sp^3* hybrid orbitals.

1s orbitals of four hydrogen atoms overlap with four *sp^3* hybrid orbitals of carbon and give four sigma bonds. i.e., there are four bonded pairs of electrons around carbon in methane. As per **VSEPR** theory, only if they are arranged tetrahedrally the bonded pairs will be as far apart as possible. That is why the methane molecules assumes a **tretrahedral shape** H–C bond angle is 109° 28′.

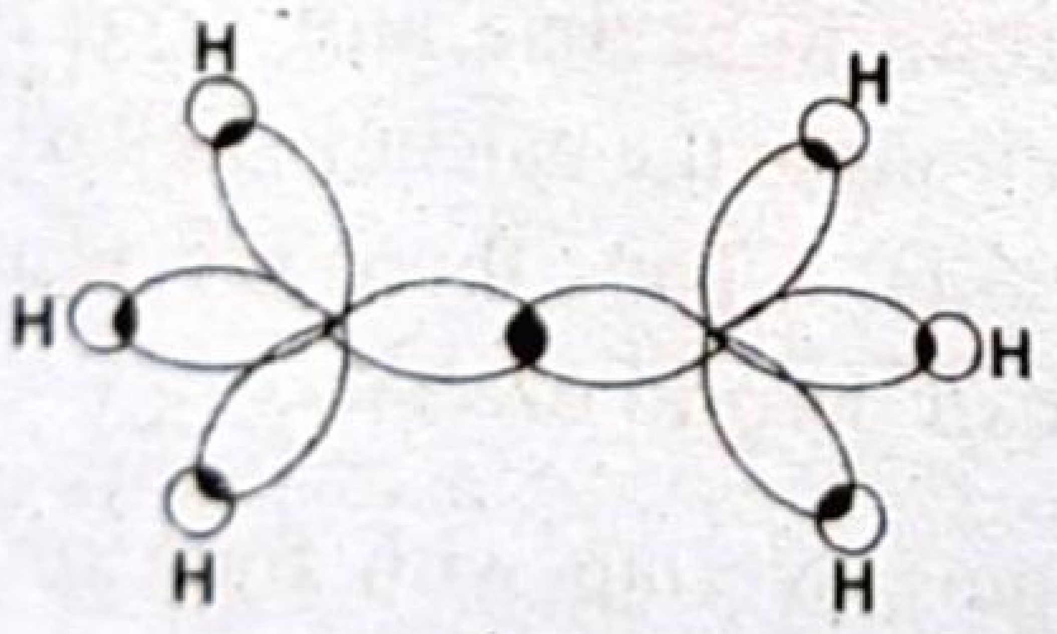


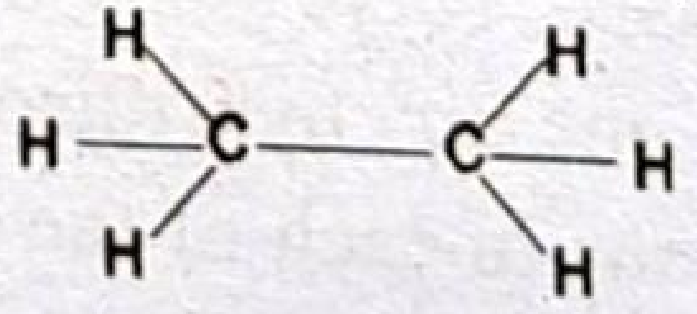




2. Ethane

In ethane, both the carbon atoms are in a state of sp^3 hybridisation. One sp^3 hybrid orbital of one carbon atom overlaps with one sp^3 hybrid orbital of the secone carbon atom and forms a sigma bond. Each of the two carbon atoms now have three sp^3 hybrid orbitals left. Each of these overlap with 1s orbitals of three hydrogen atoms and form three s - sp^3sigma bonds.



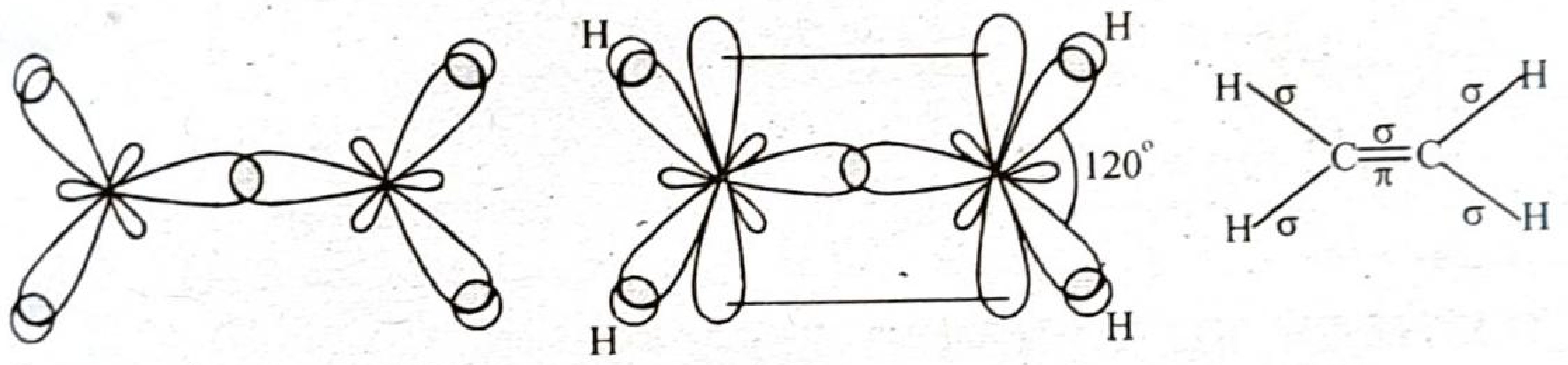


Thus there are totally seven sigma bonds in ethane (One C-C *sigma bond* and six *C-H sigma bonds.)*

3. Ethylene

In ethylene both the carbon atoms are in a state of sp^2-hybridisation. These sp^2-hybrid orbitals lie in the same plane. The bond angles are 120°. Each carbon atom has three sp^2-hybrid orbitals and one pure *p* - orbital. One sp^2-hybrid orbital of one carbon atom overlaps with one sp^2- hybrid orbital of the second carbon and forms a sigma bond. Each of the two carbon atoms now has two sp^2-hybrid orbitals and one pure *p* - orbital left. The two sp^2- hybrid orbitals on each of the two carbon atoms overlap with the 1s orbital orbitals on each carbon atom overlap in a side wise fashion and form a π - bond. The electron cloud of the π - bond lies above and below the C–C sigma bond. Thus in ethylene the following bonds are present.

Type of bond	Name of bond	Number of bond
C-C	σ	1
C-H	σ	4
C-C	π	1



Ethylene has a double bond in it. The double bond in ethylene contains one σ - bond one π - bond. The shape of the molecule is **trigonal planar.**

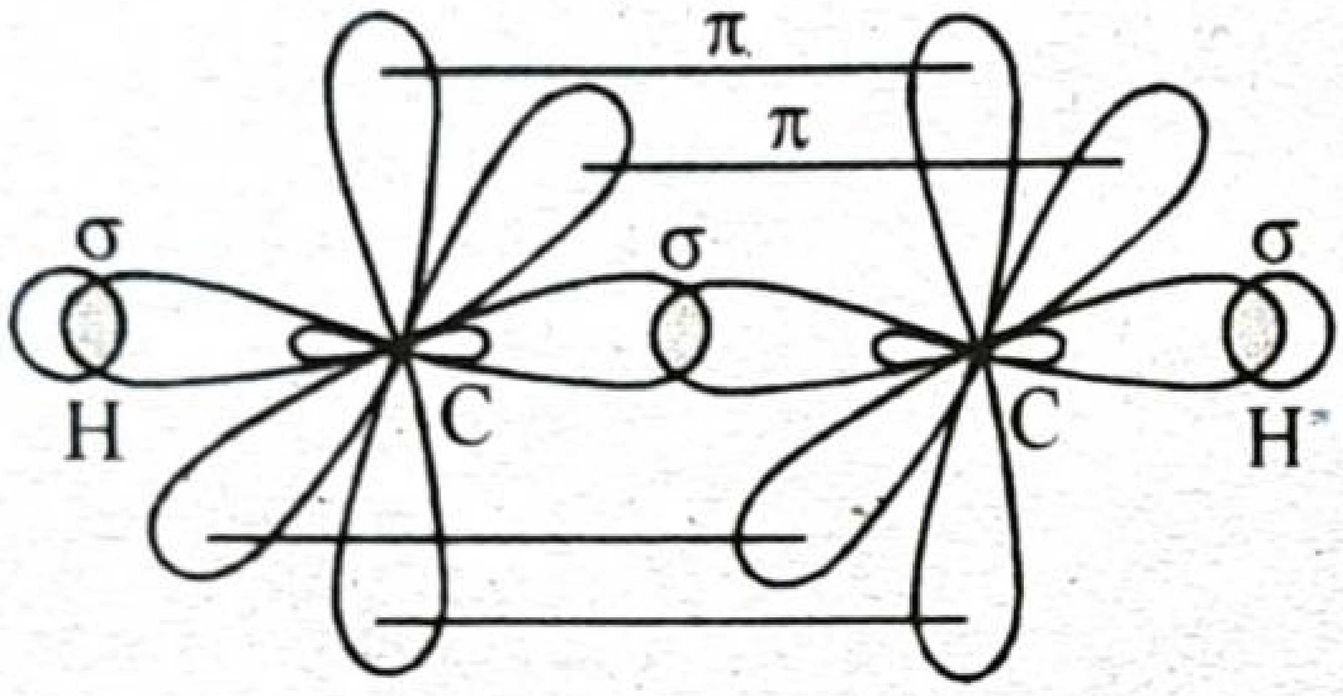
4. Acetylene

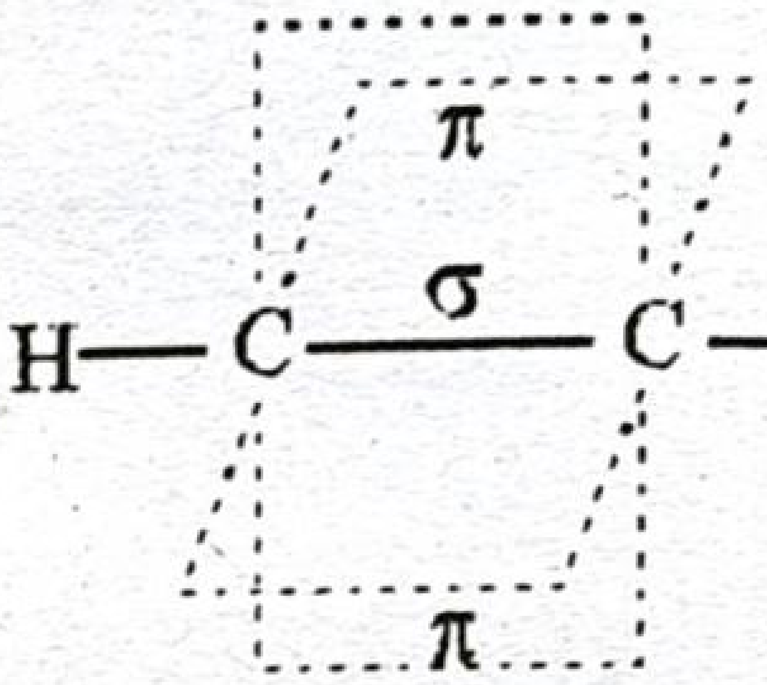
In acetylene both the carbon atoms are in a state of *sp* - hybridisation. These *sp* - hybrid orbitals are co-linear. The bond angle is 180°. Each carbon atom has two *sp* - hybrid orbitals and two pure *p* - orbitals. One *sp* - hybrid orbital of one carbon atom overlaps with one *sp* - hybrid orbital of the second carbon atom and forms a σ - bond. Each of the two carbon atoms now have one *sp* - hybrid orbital and two pure *p* - orbitals left. The hybrid *sp* - orbital on each of the two carbon atoms overlaps with 1s orbital of the hydrogen atom and forms *s* - *sp* sigma bond. The two pure *p* - orbitals on each carbon atom overlap in a sidewise fashion and form two π - bonds. The electron clouds of the π - bonds lie above and below the C – C sigma bond. These two π - bonds are in two planes which are perpendicular, to each other. Each of the π - bonds is perpendicular the following bonds are as well.

Thus in acetylene the following bonds are present :

Type of bond	Name of bond	Number of bond
C - C	σ	1
C - H	σ	2
C - C	π	2

We say acetylene has a triple bond in it. The triple bond in acetylene contains one σ - bond and 2π - bonds. The shape of the molecule is **linear**.





(or)

H– C ≡ C –H

ELECTRON DISPLACEMENT EFFECTS

1. Inductive Effect

When a hydrogen atom is attached to a carbon atom (C – H) by a covalent bond, the shared pair of electron is symmetrically placed between them. If instead of hydrogen atom we have a substituent X having higher electronegativity, then the shared pair of electrons in the C – X bond will move towards X. On the other hand, if a substituent Y having lower electronegativity is attached to carbon as C – Y then the shared pair of electrons in the C – Y bond will move towards C. Thus if the electronegativity values of the atoms forming a bond are different, the bond is said to be polarised.

Let us consider a chain of carbon atoms with a chlorine atom linked to the end carbon atom such as $- C_4 - C_3 - C_2 - C_1 - Cl$. Due to greater electronegativity of chlorine, the electron pair shared between C_1 and Cl is displaced towards the chlorine atom. As a result of this, chlorine acquires a small negative charge while C_1 becomes slightly positively charged as shown below :

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

The positively charged C_1 attracts the electron pair shared between C_1 and C_2.

The positively charged C_1 attracts the electron pair shared between C_1 and C_2. The shared pair of electron moves slightly towards C_2. Thus C_2 gets a slight positive charge. But the charge on C_2 is smaller than that on C_1. The positive charge on C_2 in turn attracts the electron pair between C_2 and C_3. This effect falls rapidly as we move away from C_1.

This process of electron shift along a chain of atoms due to the presence of a polar bond in the molecule is called **inductive effect.** It is represented as

$$C_4 \rightarrow C_3 \rightarrow C_2 \rightarrow C_1 \rightarrow Cl$$

The inductive effect is a permanent effect. When the substitutent X attached to the carbon atom is electron attracting it develops a negative charge on X and the effect is called negative inductive effect or **- I effect.** The following groups cause-I effect. They are given in the order of their decreasing effect.

$$NO_2 > F > COOH > Cl > Br > I > OH > C_6H_5$$

If the substitutent Y attached to the carbon atom is electron repelling, it develops a positive charge on Y and the effect is called positive inductive effect or + **I effect.** The following groups cause + I effect. They are given in the order of their decreasing effect.

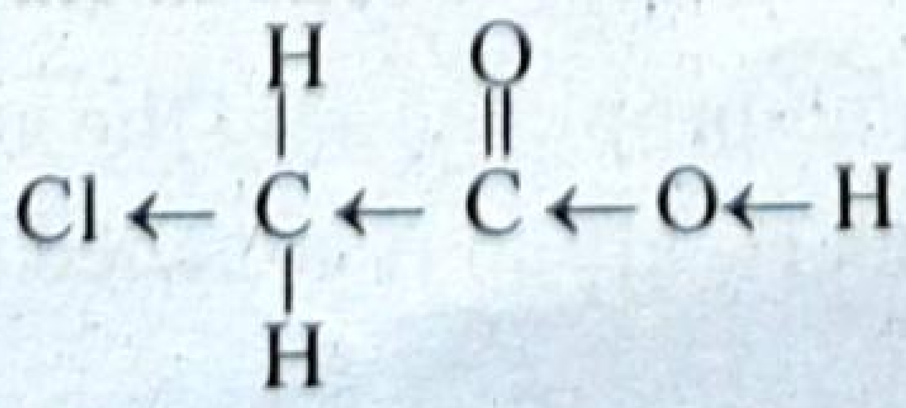
$$(CH_3)_3C -> (CH_3)_2\,CH -> CH_3\,CH_2 -> CH_3-$$

Inductive effect and properties of organic compounds :

1. *Why monochloro acetic acid is more acidic than acetic acid?:* We know that acetic acid is a weak mono basic acid. It ionises as follows :

$$CH_3\,COOH \rightleftharpoons CH_3\,COO^- + H^+$$

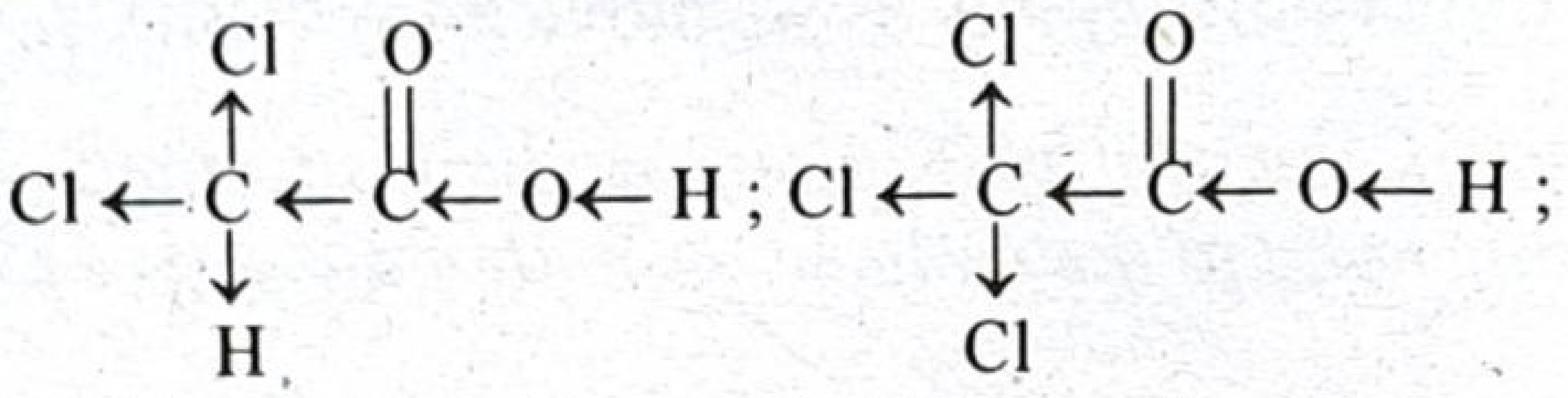
The strength of the acid is a measure of the ease with which H^- ion leaves from COOH. If one of the hydrogen atoms of methyl group is replaced by a chlorine atom, the following situation arises. The chlorine atom is electron withdrawing. The electron pair between carbon and chlorine moves towards chlorine. In turn the electron pair between C and CO moves towards carbon and so on. Thus the –I effect prevails in the chloroacetic acid molecule as shown below:



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

This makes the separation of hydrogen atom as ion easier. Thus chloroacetic acid is stronger than acetic acid.

In a similar manner we can show that dichloroacetic acid is stronger than chloroacetic acid and trichloroacetic acid is stronger than dichloroacetic acid.



$$Cl \leftarrow \overset{\overset{Cl}{\uparrow}}{\underset{\underset{H}{\downarrow}}{C}} \leftarrow \overset{\overset{O}{\|}}{C} \leftarrow O \leftarrow H \; ; \; Cl \leftarrow \overset{\overset{Cl}{\uparrow}}{\underset{\underset{Cl}{\downarrow}}{C}} \leftarrow \overset{\overset{O}{\|}}{C} \leftarrow O \leftarrow H \; ;$$

Dichloroacetic acid Trichloroacetic acid

In dichloroacetic acid there are two chloro group with - I effect and in trichloroacetic acid there are three chloro groups with - I effect. Thus the separation of hydrogen atom as ion becomes progressively easier as we move from mono to di to trichloroacetic acids. Thus their acid strengths increase in the order.

Monochloroacetic acid <dichloroacetic acid < trichloroacetic acid.

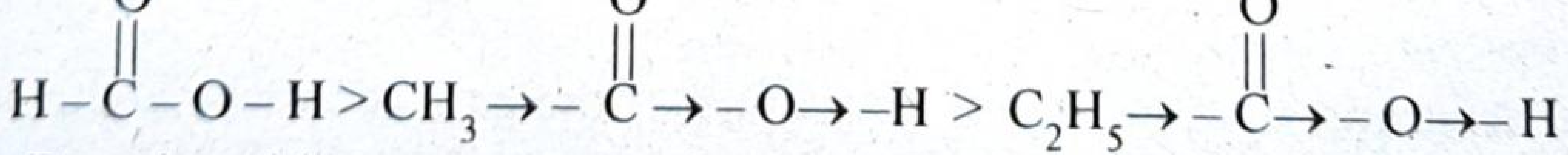
2. *Why α - Chloropropitonic acid is stronger than β-chloropropionic acid?*

$$CH_3 - CHCl - COOH > CH_2Cl - CH_2 - COOH$$

α - Chloropropionic acid > β - Chloropropionic acid

This is because inductive effect decreases with distance. In *b*-chloropropionic acid the chloro group with - I effect is two carbons away from the COOH group while in *s*-chloropropionic acid it is one carbon away. So the chloro group in *b*-choloropropionic acid has only less electron withdrawing effect. So it is weaker.

3. *Strengths of aliphatic acids :* They, decrease in the following order.



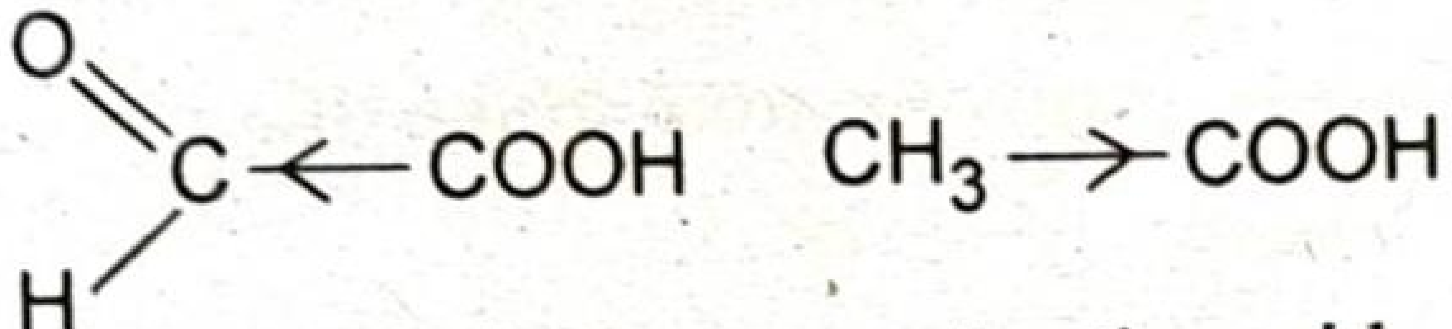
$$H - \overset{\overset{O}{\|}}{C} - O - H > CH_3 \rightarrow - \overset{\overset{O}{\|}}{C} \rightarrow - O \rightarrow - H > C_2H_5 \rightarrow - \overset{\overset{O}{\|}}{C} \rightarrow - O \rightarrow - H$$

Formic acid Acetic acid Propionic acid

Reason : In formic acid the COOH group is attached to H while in acetic acid it is attached to CH_3. We know CH_3 group has + I effect. This pushes electrons towards H. This strengthens OH bond. i.e., removal of H as H^+ becomes difficult. This effect is absent in formic acid.

Between acetic acid and propionic acid the stronger is acetic acid. It is because in acetic acid a CH_3 group is attached to COOH. In propionic acid a C_2H_5 group is attached to COOH. C_2H_5 is bulkier than CH_3. So it has more + I effect than CH_3. Thus it pushes electrons towards the OH bond more forcibly than CH_3. So it becomes more difficult for H to leave as H+ from propionic acid than from acetic acid.

4. *Glyoxalic acid is stronger than acetic acid :*



Glyoxalic acid Acetic acid

This is because CHO groups is a strong – I group. This facilitates H to leave as H^+. But in acetic acid the CH_3 group is a +I group. This pushes electrons towards the OH bond making it difficult to part with H^+.

2.Inductomeric Effect

The extent of inductive effect can be influenced temporarily by the approach of a charged ion. This happens prior to a reaction.

Thus –I effect will be increased at the approach of a negatively charged ion and +I effect will be increased at the approach of a positively charged ion. This is known as polarisability effect. It is a temporary effect. It is brought into play only in the presence of charaged attacking reagent.

In methyl iodide there is a small permanent displacement of electrons, in the C – I bond towards the iodine atom.

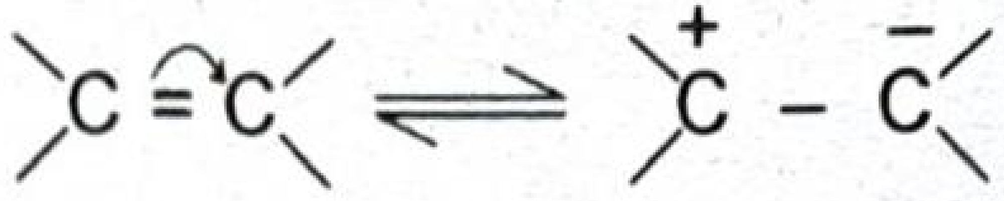
It is due to the electron repelling character of the CH_3 group when an OH^- ion approaches the carbon atom its electrical field repels the electrons of the C - I bond still further towards the iodine atom. This increases the electron displacement already present.

Thus a polarisability effect operates through the inductive mechanism, This is called inductomeric effect. It is represented in the same way as an inductive effect, e.g., $CH_3 \rightarrow -I$.

However this does not have an important role in organic reactions. It assists the displacement of electrons in inductive effect.

3. Electrometric Effect

In a molecule in which two atoms are linked together by a double bond, one of the pairs of electrons forming a bond may move to one of the atoms. The other pair continues to form a covalent bond between the two atoms. When the compound containing the double bond (or triple bond) is exposed to electrophilic regent, this change occurs. There is a complete transfer of a pair of electrons from one atom to the other as shown bellow:



The atom that takes the electron pair becomes negatively charged and the other positively charged. This is purely a temporary effect and remains in the presence of electrophilic reagent. As soon as the attaking reagent is removed, the polarised molecule comes back to the original state.

The electrometric effect is a temporary effect which involves the complete transfer of a shared paid of electrons of multiple bond, to one of the bonded atoms, under the influence of an electrophilic reagent.

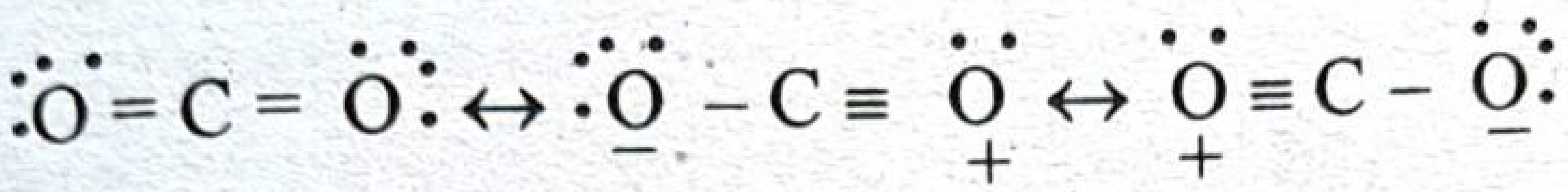
The electromeric effect is usually denoted as E effect. If both inductive and electromeric effects occur together, these may assist or oppose eath other. In case they are opposed to each other, the electromeric effect generally predominates the inductive effect.

Differences between inductive and electromeric effects

	Inductive effect	**Electromeric effect**
1. Nature of electron displacement	Partial-along a Sigma bond	Complete Movement of a pair π electrons to one of the two atoms bond by a double bond.
2. Charge	Respective atoms attain partial negative and positive charges.	Respective atoms attain a full positive and negative charges.
3. Nature of effect	Permanent	Temporary
4. When occurs	Even in the absence of an electrophile	Only in the presence of elecltrophile
5. Prodominancy	Less	More

4. Mesomeric Effect or Resonance Effect

A molecule containing multiple bond may be represented by several electronic formula. For example, carbondioxide has the following electronic arrangements.



$$:\ddot{O}=C=\ddot{O}: \leftrightarrow :\overset{..}{\underset{-}{\ddot{O}}}-C\equiv \underset{+}{\ddot{O}} \leftrightarrow \underset{+}{\ddot{O}}\equiv C-\underset{-}{\ddot{O}}:$$

But the actual condition of the molecule is in between these three structures. This type of effect is known as mesomeric effect or resonance effect. It is represented by the symbol M or R respectively.

If a molecule can be assigned two or more structural formulae, each of which can explain most but not all the properties of the compound, the actual structure lies in between the various possible structures. This phenomenon is called measomerism or resonance. [Ingold called this phenomenon mesomerism based on chemical grounds. Heisenberg called it resonance based on theoretical background. (Resonance is the name that is widely used).

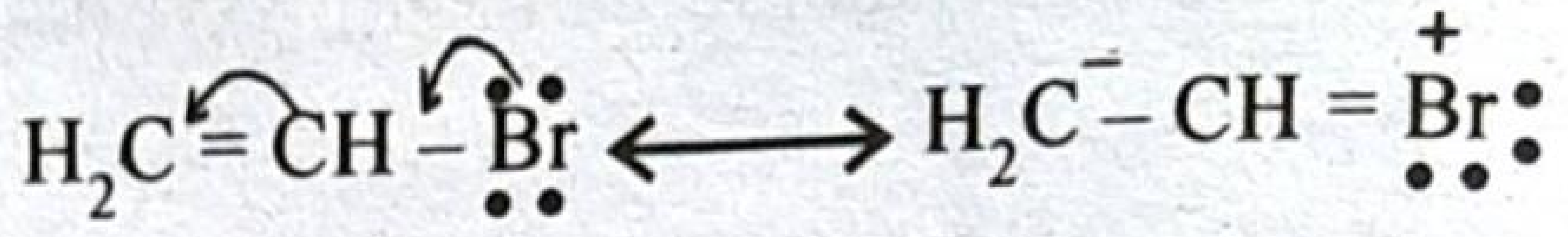
The effects arising out of the presence of mesomerism or resonance is called mesomeric or resonance effect respectively.

The various possible structures are called **canonical structures.** The actual structure is called resonance hybrid. The canonical structures are represented by putting double headed arrow (⟷) in between them. The resonance hybrid is not a mixture of the various structures. It is an entirely new and individual structure which is in between the several canonical structures.

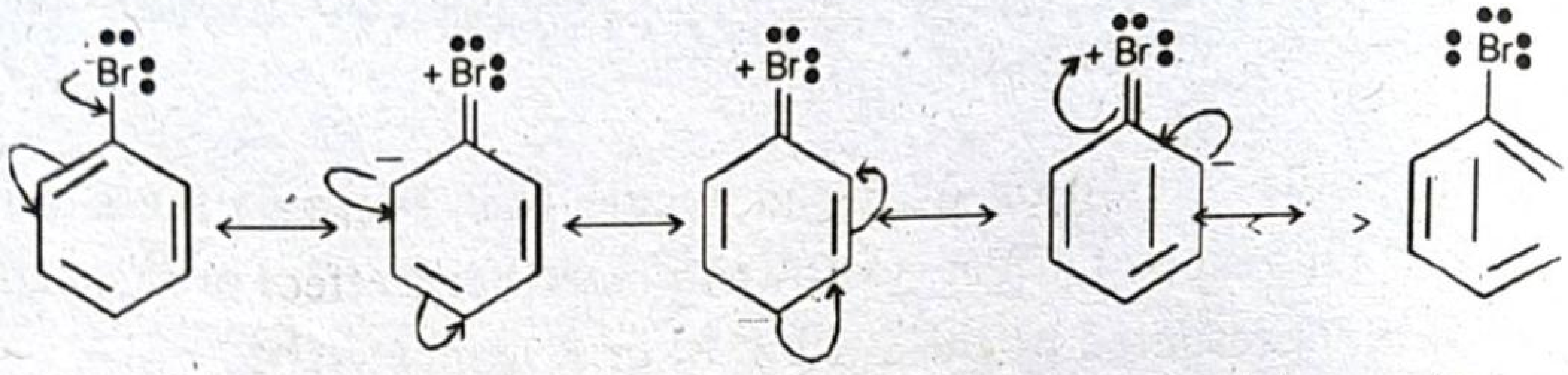
The mesomeric effect, like the inductive effect, may be + or – and is denoted by + M or – M. A group of atoms is said to have + M effect, when the direction of electron displacement is away from it. Such groups have lone pairs of electrons. – OH, – OR, – NH_2 and – SR groups have + M effect. A group of atoms is said to have - M effect, when the direction of election displacedment is towards it. $>C=O$, $-NO_2$, – CN and $-SO_3H$ groups have – M effect.

The +M effect of halogen atom brings a double bond character between the halogen and the carbon atom attached to the halogen. Because of the double bond character, the halogen is held firmly. Thus the halogen atom in vinyl halides and aryl halides are less reactive than alkyl halides.

CH_3-CH_2-Br



$H_2C=CH-\ddot{Br}: \longleftrightarrow H_2\bar{C}-CH=\overset{+}{Br}:$



(The halogen in alkyl halide cannot have resonance and hence it cannot have double bond character. So It can be easily hydrolysed).

Differences between inductive and mesomeric effects

	Inductive effect	Mesomeric effect
1. Nature of electron displacement	σ-electrons-along a single bond-transmitted though the chain-decreases as the the distance.	π -electrons-negative charge flows towards on side of the molecule-effect is uniform.
2. Charge	Respective atoms attain partial negative and positive charges.	Charge separation is complete.
3. Relation with stability of the molecule.	None	Stabilises the molecule
4. Effect on bond length	None	Affected.
5. Effect on colour	Nil	Causes perceptible Colour.

Conditions for mesomerism or Resonance :

1. The contributing structures must be reasonably stable.
2. The number of electrons in each contributing structure must be the same.
3. All the contributing structures should have the same or nearly the same amount of energy.

4. When the contributing structures differ in energy contents, i.e., relative stabilities, the more stable structure makes greater contribution towards the resonance hybrid.
5. The various contributing structures should differ from each other only in the positions of electrons. The relative arrangement of atoms must be the same.

Resonance energy :

The energy of a resonance hybrid is always less than any one of the contributing structures. The difference between the energy of the most stable contributing structure and that of the resonance hybrid is known as the resonance energy or delocalisation energy.

A resonance hybrid i.e., the actual molecule is always more stable than any one of the contributing structures. Because of this fact we say that the compound is stabilised by resonance.

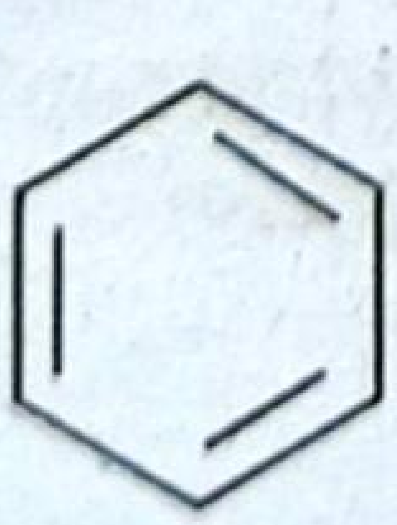
Example :

The enthalpy of formation of benzene calculated from bond energy values is – 5384.1 kJ mole^{-1}. The experimental value of enthalpy of formation of benzene is – 5535.1 kJ mole^{-1}. This is called the *resonance energy of benzene.* We say benzene is stabilised by resonance to an extent of 151 kJ/mole.

Effects of resonance :

1. *Stability :*

The compounds which exhibit resonance are more stable than their contributing structures. E.g., Though there are three double bonds in the contributing structures of benzene I and II, it behaves as a saturated compound. It does not undergo addition reactions instead undergoes only substitution reactions. The resonance energy is a measure of the stability caused by resonance.



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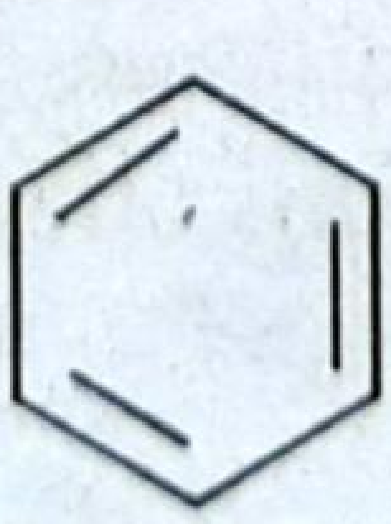


II

2. ***Bond lengths :***

The bond lengths in a resonance hybrid are different from those in the contributing structures. E.g., The contributing structures of benzene suggest that there are three C – C and three C = C bonds. Actually in benzene all the six carbon-carbon bond lengths are the same. Their lengths are in between those of C – C and C = C bonds.

3. ***Dipole moments :***

The observed dipole moments are different from the values expected from the contributing structures.

4. ***Colour :***

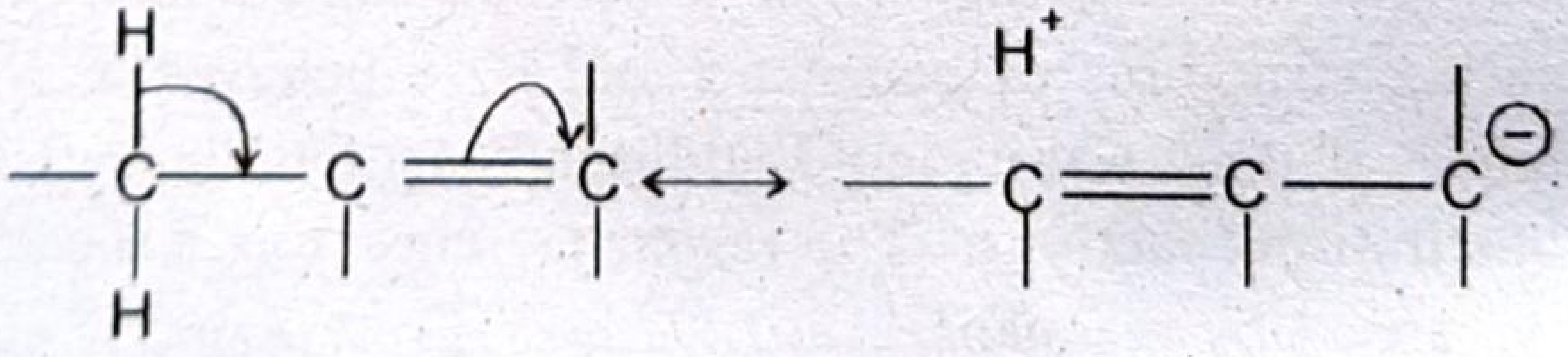
The colour of organic compounds is a consequence of resonance. E.g., Dyes. When the number of contributing structures increase, the intensity of the colour also increases.

5. Hyperconjugation

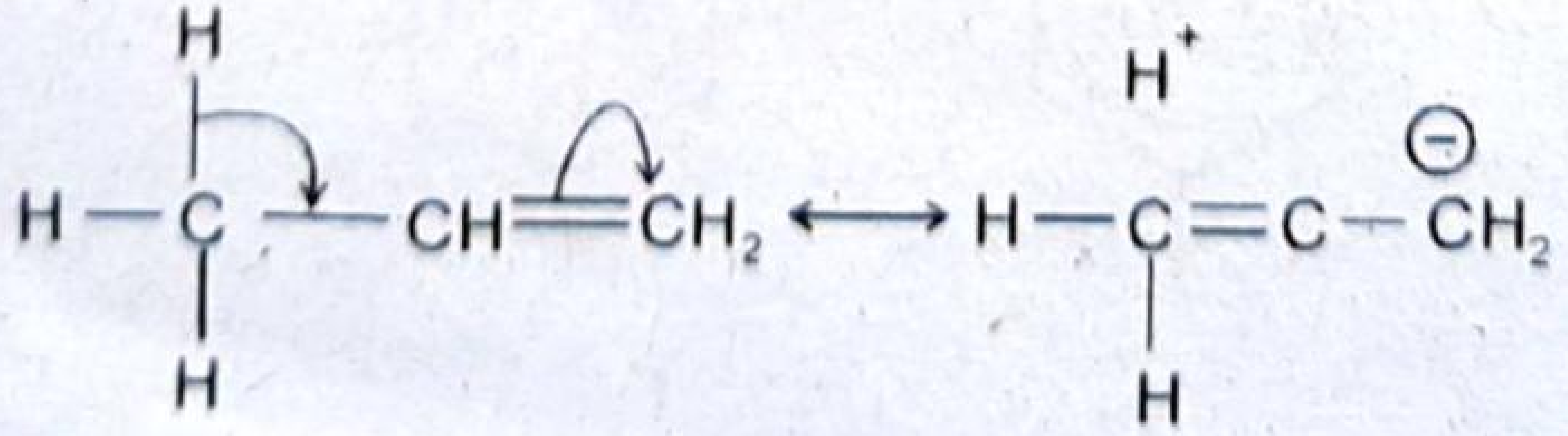
The resonance involving the delocalisation of σ electrons in conjugation with the π - electrons of an adjacent double bond is called hyperconjugation.

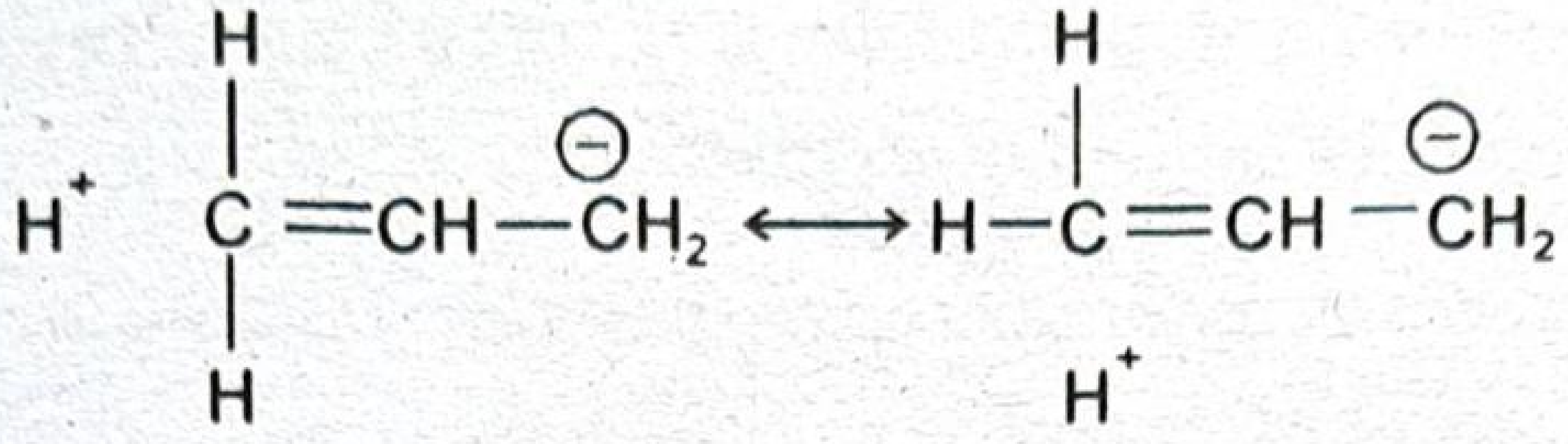
Explanation :

The hyperconjugative effect operates in a system containing a C – H bond directly attached to a double bond. In other words, the hyperconjugative effect takes place through the interaction of σ electrons of the carbon - hydrogen bond with π - electrons of the double bond. In hyperconjugation the electron displacement takes place towards the double bond as shown below.



The three C– H bonds of methyl group in the propylene molecule contribute to this effect as follows.



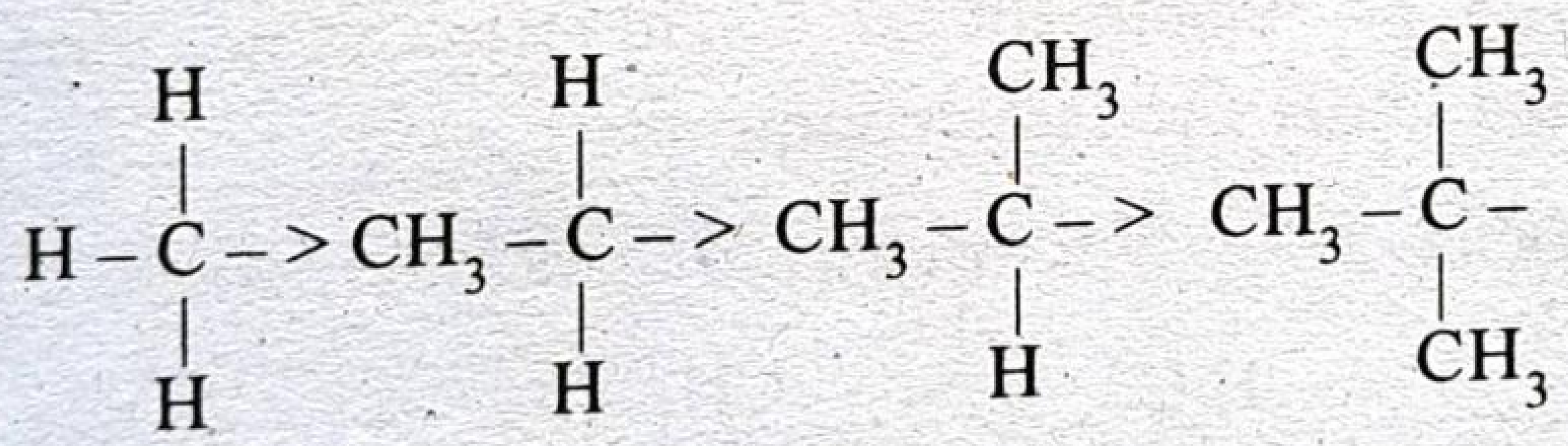


$$H^{+}\quad \underset{H}{\overset{H}{C}}{=}CH{-}\overset{\ominus}{C}H_2 \longleftrightarrow H{-}\underset{H^{+}}{\overset{H}{C}}{=}CH{-}\overset{\ominus}{C}H_2$$

While discussing inductive effect, it was pointed out that the inductive effect of the alkyl group is in the order.

tertiary > secondary > primary

This order is reversed when an unsaturated system (C=C) is attached with the alkyl group. As we have seen just now, the σ–electron from the C-H bonds at the α–carbon the unsaturated system gives the no bond resonance. As the number of C-H bonds are greater, greater would be the hyperconjugative effect. Thus methyl group (3 C-H bonds) has the maximum hyperconjugative effect. Ethyl group (2 C-H bonds) has lesser effect. Isopropyl group (1 C-H bond) has the least effect. Tertiary butyl group (0 C-H bond) has no hyperconjugative effect at all.



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

Methyl Ethyl Isopropyl Tert-butyl

Hyperconjugation is a temporary effect. In the canonical forms, there is no bond between carbon and hydrogen. The proton in such hyperconjugative form does not move any distance away than its normal bonding distance to carbon. This type of resonance is different from tautomerism where the proton moves from one position to another. Hyperconjugation can also be regarded as an overlap of σ–orbital of the C – H bond with the π–orbital of the carbon-carbon double bond. This is analogous to the π–π orbital overlap in resonance. Hyperconjugation can also be regarded as a second order resonance.

Hyperconjugation is also called **Baker-Nathan effect** or **No bond Resonance.**

6. Steric Effect :

The presence of a bulky group or groups near a reaction site in a compound makes it behave in a peculiar way.

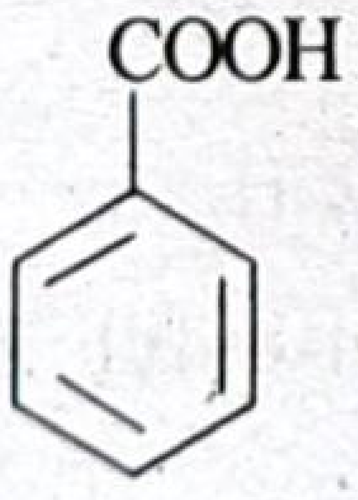
The effects of size of substituents and their spatial arrangement in compound are called steric effects.

Steric effects may affect the speed and mechanism of a reaction. When the steric effect slows down a reaction, it is called **steric hindrance** when it speeds up a reaction, it is called **steric acceleration.**

In aromatic compounds the properties of *ortho* substituted compounds differ considerably from those of the *meta* or *para isomers*. In *ortho* substituted compounds the attack of the reagent at the reaction centre is hindered by the bulky groups present in the *ortho* positions. These effects are also known as *ortho effects* or *proximity effects*.

Examples :

i. Benzoic acid (I) reacts with methanol and hydrogen chloride to form methyl benzoate; but 2, 6 - dimethylbenzoic acid (II) does not form the corresponding product under the same conditions.



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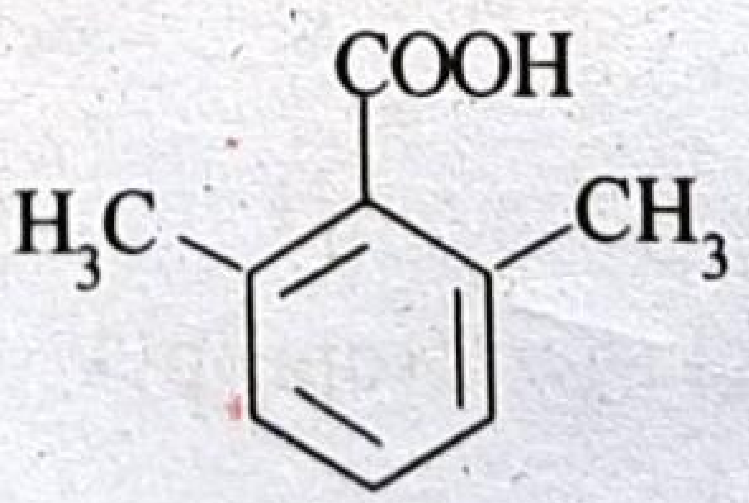

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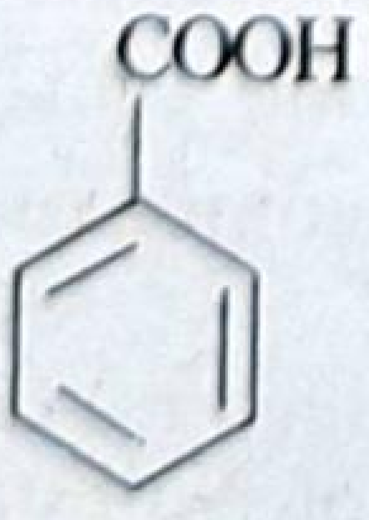
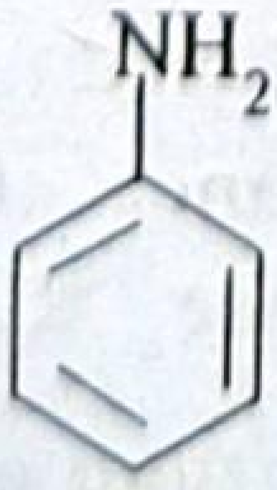
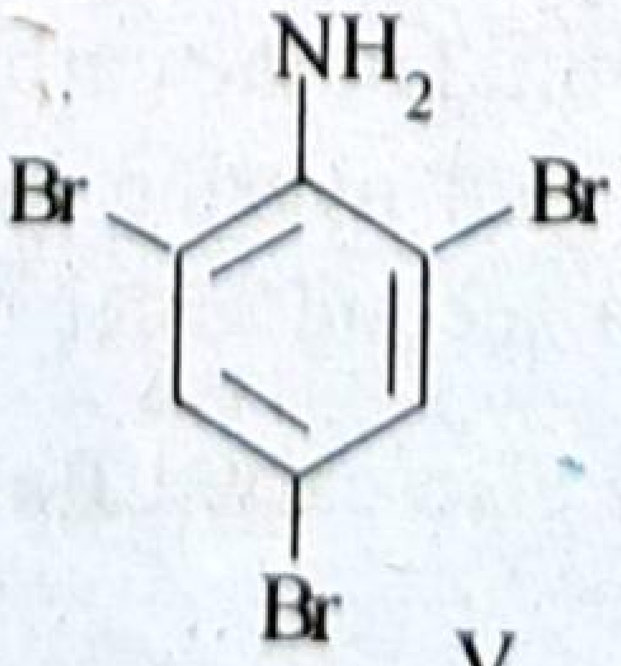
ii. Benzaldehyde (III) reacts with aniline (IV) to form an anil but not with s-tribromoaniline (V).



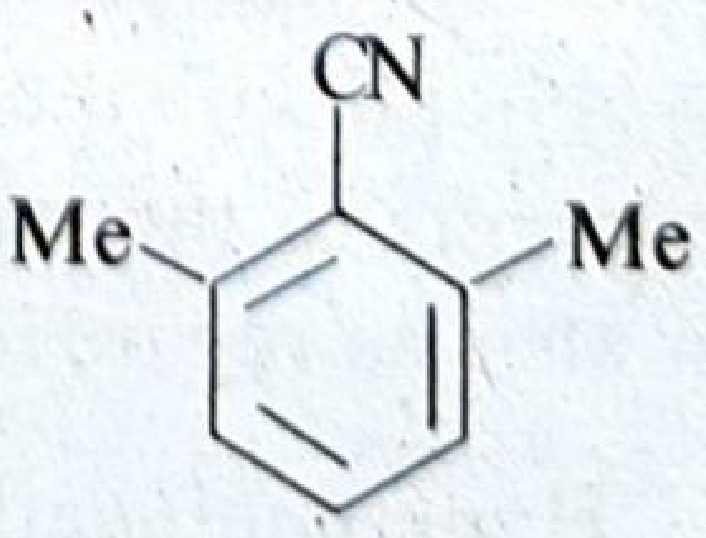
III



IV



V

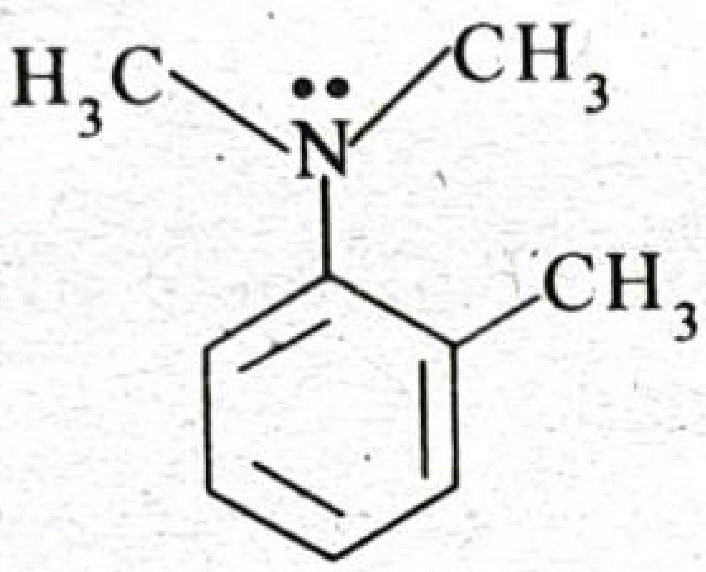


VI

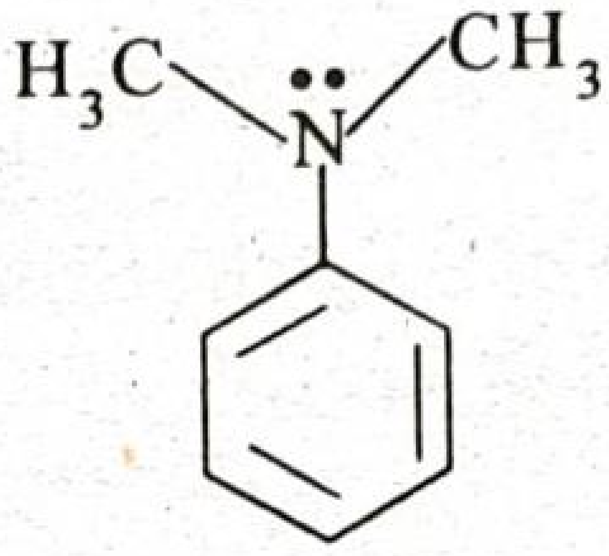
iii. Phenyl cyanide undergoes hydrolysis where as 2,6 - dimethyl phenyl cyanide (VI) does not.

In all these cases, the *ortho* groups mechanically interfere with the reactions of the functional groups, viz., carboxyl, amino and cyano groups. The *ortho* groups tend to shield the reacting groups from the attacking reagent.

iv. N, N-dimethyl o-toluidine (VII) is more basic than N, N- dimethylaniline VIII.



VII



VIII

Reason :

The extra stailisation due to resonance is less in VII than in VIII, because of steric hindrance the lone pair of electrons over the nitrogen is more readily available in VII. So it is more basic.

Cleavage of bonds :

Organic compounds generally contain covalent bonds. During reactions, existing covalent bonds are broken and new covalent bonds are formed. A covalent bond is formed by sharing of two electrons between two atoms. The breaking or cleavage of bonds occurs in two ways. They are

i. Homolytic fission of carbon - carbon bonds
ii. Heterolytic fission of carbon - carbon bonds.

Homolytic Fission :

If the covalently bonded two carbon atoms take away one electron each of the bonding pair of electrons during the fission of the carbon - carbon bond, then the fission is symmetrical. This is called homolytic fission.

$$\overset{\curvearrowleft\curvearrowright}{A{:}B} \longrightarrow A^{\bullet} + B^{\bullet}$$

The two fragements produced during homolytic fission contain one electron each and they are called free redicals.

Free radicals are unstable. They react at once with other free radicals or molecules, forming stable molecules or new free radicals respectively. The free radicals are neutral. Their extreme reactivity is due to the tendency of the singal electron to 'pair up' with another available single electron.

Compounds undergo homilytic fission on heating or by irradiation with light of suitable energy.

Example : Substitution reactions of alkanes proceed through homolytic fission of carbon - carbon bonds.

Reaction : Methane + Chlorine ⟶ Methyl chloride + Hydrogens hloride

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

Mechanism : $Cl : Cl \longrightarrow 2Cl^{\bullet}$

$$Cl + CH_4 \longrightarrow CH_3Cl + H^{\bullet}$$

Such reactions will be chain reactions.

Heterolytic fission :

When a covalent bond breaks in such a way that both the bonding electrons are taken away by one of the two bonded atoms, then the fission is known as heterolytic fission.

$$\overset{\curvearrowleft}{A:}B \longrightarrow A:^{-} + B^{+}$$

$$A\overset{\curvearrowright}{:B} \longrightarrow A^{+} + B:^{-}$$

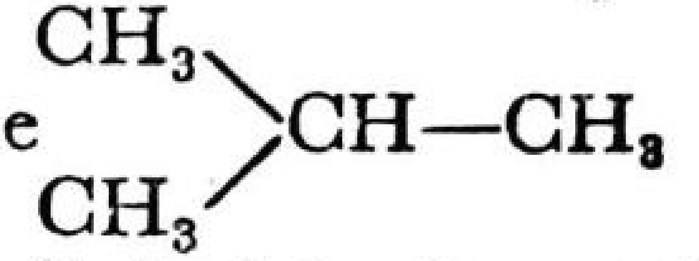
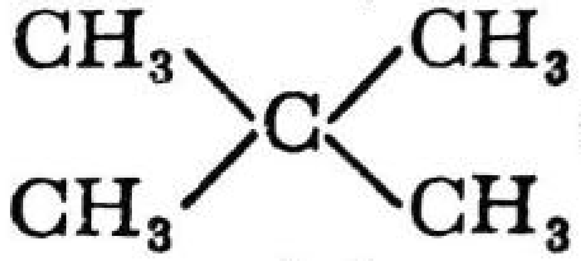
Thus heterolytic fission yields one positively charged ion and one negatively charged ion. Which of the two atoms A or B that will become the negatively charged ion? This depends ont eh electronegativity of A and B. That atom, which is more electronegative, will become the negatively charged ion.

PART II—ORGANIC COMPOUNDS

13

Alkanes or Paraffins

1. Nomenclature of the Paraffins. The class name for saturated aliphatic hydrocarbons is alkanes or paraffins. The paraffins are represented by the general formula C_nH_{2n+2} and are given this name because they are quite non-reactive. The name comes from the Latin words *parum* (=little) and *affinis* (affinity). There are at least three systems in use for naming paraffins and in all the three, the class suffix remains *-ane*.

(*i*) In the **trivial system** of nomenclature, the straight-chain paraffins are termed *normal* usually abbreviated to *n-*; those with a branched-chain like  $(CH_3)_2CH{-}CH_3$ (containing a tertiary carbon atom—one directly linked to three other carbon atoms) are termed *iso* whereas others containing a quaternary carbon atom (attached to four other carbon atoms), *e.g.*,  $(CH_3)_2C(CH_3)_2$ are called *neo.*

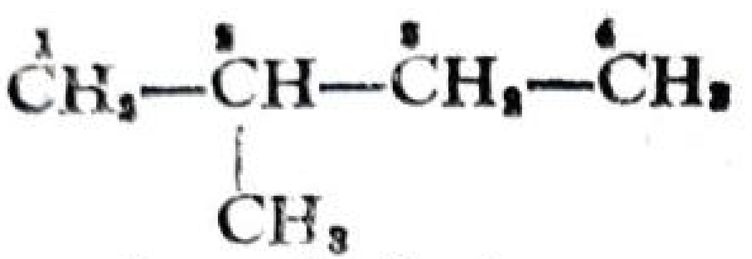
The first four paraffins have special names which are related to their history; from the fifth paraffin onwards, the names follow the Latin or Greek numerals which indicate the number of carbon atoms in the molecule as given below:

Formula	*Name*	*Formula*	*Name*
CH_4	Methane	C_9H_{20}	Nonane
C_2H_6	Ethane	$C_{10}H_{22}$	Decane
C_3H_8	Propane	$C_{12}H_{26}$	Dodecane
C_4H_{10}	Butane	$C_{20}H_{42}$	Eicosane
C_5H_{12}	Pentane	$C_{30}H_{62}$	Triacontane
C_6H_{14}	Hexane	$C_{50}H_{102}$	Pentacontane
C_7H_{16}	Heptane	$C_{70}H_{142}$	Heptacontane
C_8H_{18}	Octane	$C_{80}H_{162}$	Octaneontane

The univalent radicals which are formed by the removal of one hydrogen atom of the paraffins are termed alkyl groups or radicals.

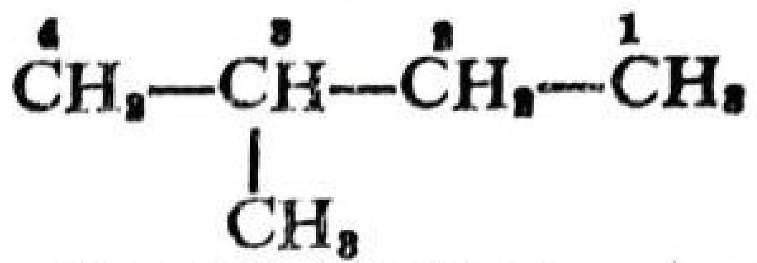
(*ii*) According to another system, branched-chain paraffins are named as substituted methanes. The most highly branched carbon atom is termed the methane parent and the alkyl groups attached to this carbon atom are named in alphabetical order. Thus every name indicates the structure of the compound.

(*iii*) In the **IUPAC system**, the longest possible straight chain is selected and the paraffin is named as the derivative of this alkane. *The carbon atoms constituting the straight chain are so numbered that the numbers, used to indicate the positions of side-chains, are the lowest possible.* Various groups present are arranged alphabetically. For example,



$$\overset{1}{C}H_3-\underset{\underset{CH_3}{|}}{\overset{2}{C}H}-\overset{3}{C}H_2-\overset{4}{C}H_3$$

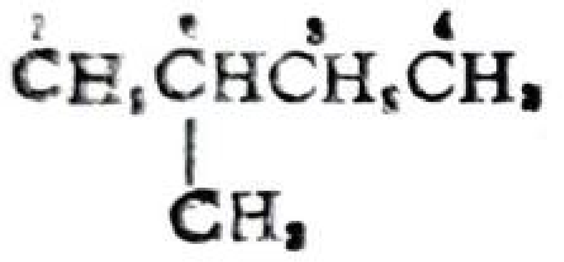
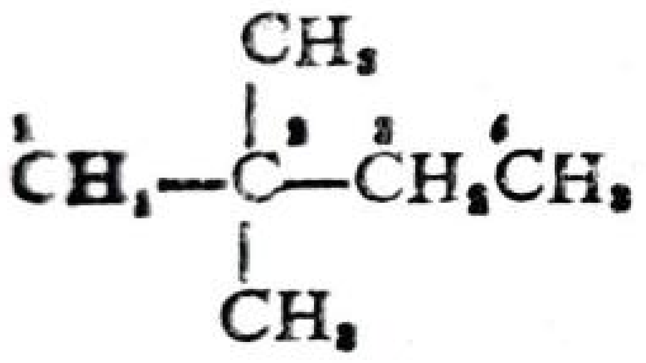
2-methylbutane
(Right)



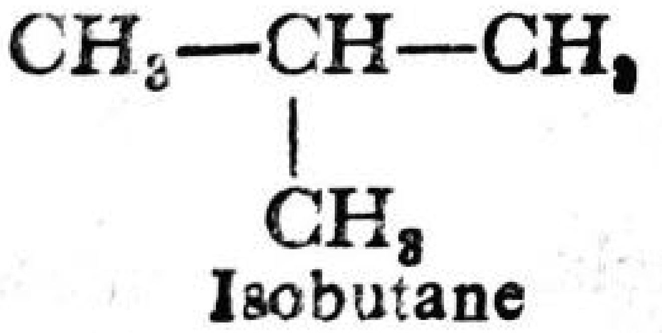
$$\overset{4}{C}H_3-\underset{\underset{CH_3}{|}}{\overset{3}{C}H}-\overset{2}{C}H_2-\overset{1}{C}H_3$$

3-methylbutane
(Wrong)

A few examples of the three systems of nomenclature are given below :

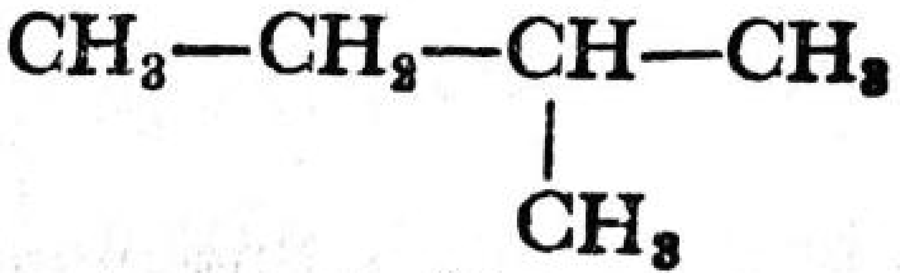
Formula	*I System*	*II System*	*III System*
$CH_3CH_2CH_2CH_3$	*n*-butane		butane
 $\overset{1}{C}H_3\underset{\underset{CH_3}{\vert}}{\overset{2}{C}H}\overset{3}{C}H_2\overset{4}{C}H_3$	Isopentane	dimethylethylmethane	2-methylbutane
 $\overset{1}{C}H_3-\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{\overset{2}{C}}}-\overset{3}{C}H_2\overset{4}{C}H_3$	Neohexane	trimethylethylmethane	2, 2-dimethylbutane

Four branched alkanes have trivial names recognized in the 1957 IUPAC Rules. These are :



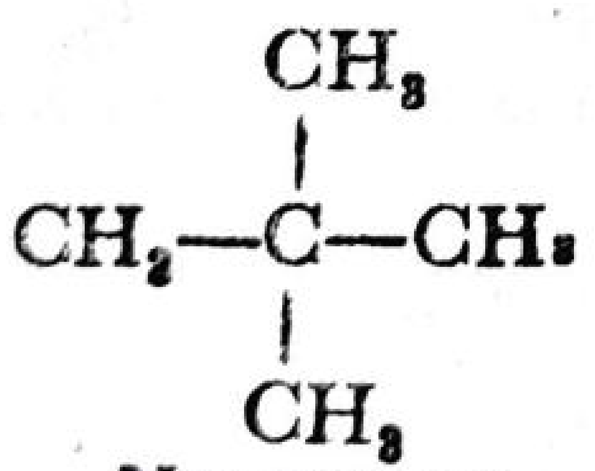
$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

Isobutane



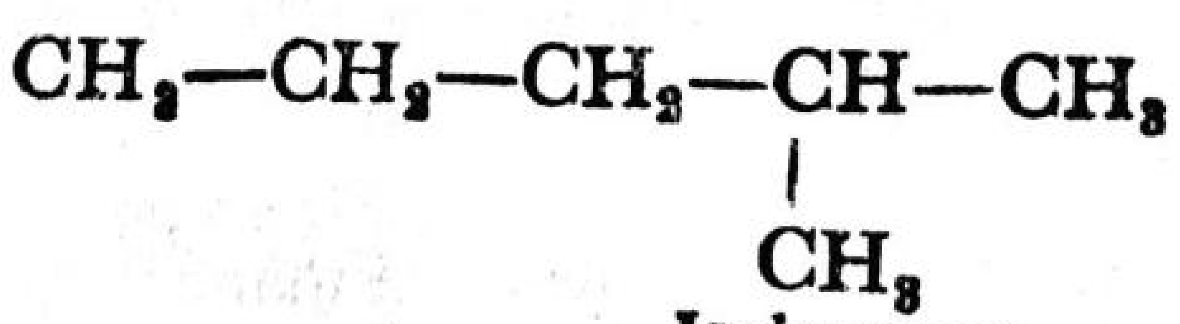
$$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

Isopentane



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

Neopentane



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

Isohexane

These names are, however, to be used only for the unsubstituted alkanes.

2. Occurrence. The most important source of alkanes is petroleum or the natural gas associated with it. Fuel gases obtained from coal, *e.g.*, coal gas, etc., contain these hydrocarbons in small amounts. Methane is formed during the decay of plants or animal tissues.

3. General Methods of Preparation. One of the characteristics of a homologous series is that its various homologues can be prepared by similar methods. This gives rise to the general methods of preparation of a particular homologous series. The gederal methods of preparation of the paraffins are given below :

(*i*) *By heating a mixture of the anlydrous sodium salt of a fatty acid with soda lime** ($NaOH + CaO$).

$$\underset{\text{Sodium salt of the fatty acid}}{RCOONa} + \underset{\text{Soda lime}}{NaOH} \xrightarrow[\Delta]{CaO} \underset{\text{Paraffin}}{RH} + Na_2CO_3$$

$$\underset{\text{Sodium acetate}}{CH_3COONa} + NaOH \xrightarrow[\Delta]{CaO} \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

For the lower homologues the yield is good but it is poor for the higher ones. The process of elimination of carbon dioxide from a carboxylic acid is known as *decarboxylation.*

(*ii*) *By reducing alkyl halides* (*dissolved in acetic acid*), by dissolving metals, *e.g.*, zinc and acetic acid or hydrochloric acid, zinc and sodium hydroxide, *zinc-copper couple,*† *or aluminium amalgam and ethanol*, etc. It is believed that the reduction is due to electron transfer from the metal to the substrate.

$$\underset{\text{from Zn/Cu couple}}{Zn} \rightarrow Zn^{2+} + \underset{\text{electron}}{2e^-}$$

$$RX + e^- \rightarrow X^- + R^{\cdot} \xrightarrow{e^-} R^- :$$

$$R^- : + C_2H_5OH \rightarrow R{-}H + C_2H_5O^-$$

Alkyl halide may also be reduced catalytically by using palladium as catalyst (*catalytic hydrogenolysis*).

$$RI + H_2 \longrightarrow RH + HI$$

Iodides are conveniently reduced by heating with concentrated hydriodic acid (57% HI) at 420K under pressure in a sealed tube.

$$RI + HI \longrightarrow RH + I_2$$

Primary and secondary alkyl halides may conveniendy be reduced with lithium aluminium hydride, $LiAlH_4$.

$$4RX + LiAlH_4 \longrightarrow 4RH + LiAlX_4$$

(*iii*) *By treating alkyl halide* (*preferably the bromide or iodide*) *solution in dry ether with metallic sodium* (**Wurtz Synthesis**—1854). Two molecules of the alkyl halide react with two atoms of sodium

---

* Soda lime is obtained by saturating lime with caustic soda solution and drying the product. Lime serves to dilute the strong action of caustic soda. It also does not etch glass like caustic soda. CaO stands for soda lime here.

The delta symbol (△) indicates the application of heat.

† Zinc-copper couple consists of pieces of zinc coated with copper obtained by immersing zinc pieces in copper sulphate solution. It is a valuable reducing agent. Similarly, aluminium amalgam is obtained by dipping small pieces of aluminium foil in mercuric chloride solution. The couple or the amalgam obtained is washed thoroughly with water and then with alcohol.

to yield a hydrocarbon containing double the number of carbon atoms present in the alkyl halide.

$$\underset{\substack{\text{Alkyl halide}\\\text{First molecule}}}{RX} + 2Na + \underset{\substack{\text{Alkyl halide}\\\text{second molecule}}}{XR} \longrightarrow \underset{\text{Paraffin}}{R—R} + 2NaX$$

e.g., $$\underset{\substack{\text{Methyl}\\\text{iodide}}}{CH_3I} + 2Na + \underset{\substack{\text{Methyl}\\\text{iodide}}}{ICH_3} \longrightarrow \underset{\text{Ethane}}{CH_3—CH_3} + 2NaI$$

If instead of one alkyl halide, a mixture of two different alkyl halides (say, CH_3I and C_2H_5I) is taken, we get a mixture of three hydrocarbons: propane, ethane and butane.

$$\underset{\substack{\text{Methyl}\\\text{iodide}}}{CH_3I} + 2Na + \underset{\substack{\text{Ethyl}\\\text{iodide}}}{IC_2H_5} \longrightarrow \underset{\text{Propane}}{CH_3—C_2H_5} + 2NaI$$

Two molecules of CH_3I will react to give C_2H_6 (ethane) as given above and two molecules of ethyl iodide will react to gixe butane.

This reaction has been found to give good yield for paraffins of high molecular mass containing even number of carbon atoms. With tertiary alkyl halides the reaction generally fails. *Methane cannot be prepared by this method.*

Mechanism of the Reaction. A free radical mechanism has been suggested for the Wurtz reaction which is given below :

$$C_2H_5—I + Na \longrightarrow \underset{\text{Free radical}}{C_2H_5^{\cdot}} + NaI$$

$$C_2H_5^{\cdot} + C_2H_5^{\cdot} \longrightarrow \underset{n\text{-butane}}{C_2H_5—C_2H_5}$$

Free radicals can also undergo *disproportionation*, *i.e.*, one radical can gain hydrogen at the expense of the other which loses hydrogen, *e.g.*,

$$C_2H_5^{\cdot} + C_2H_5^{\cdot} \longrightarrow \underset{\text{Ethane}}{C_2H_6} + \underset{\text{Ethylene}}{C_2H_4}$$

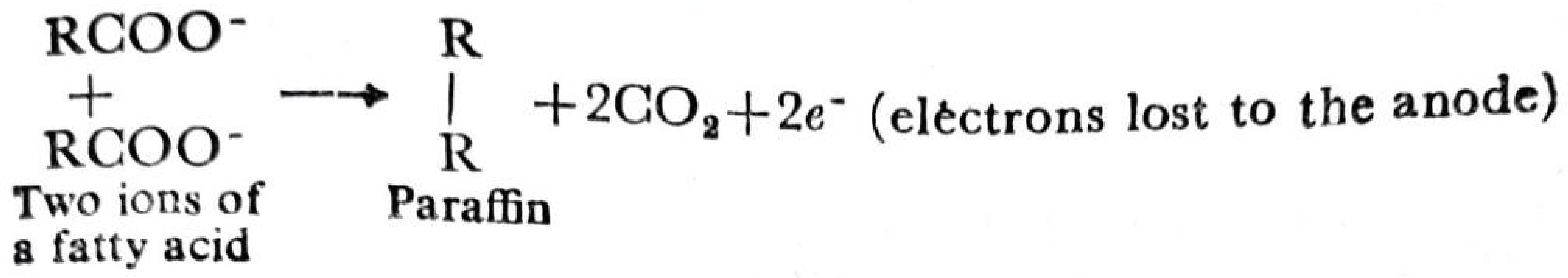
A superior method for coupling of two alkyl halides is the **Corey-House Synthesis.**

$$\text{RMgX or RLi} \xrightarrow[(ii)\ R'X]{(i)\ CuX} R—R'$$

(where R is a primary, secondary or tertiary alkyl group while R' is a primary alkyl group.

(iv) *By the electrolysis of a concentrated aqueous solution of the sodium or potassium salt of a fatty acid* (**Kolbe's electrolytic reaction**).

At anode :



$$\underset{\text{Two ions of a fatty acid}}{\begin{array}{c}RCOO^-\\+\\RCOO^-\end{array}} \longrightarrow \underset{\text{Paraffin}}{\begin{array}{c}R\\|\\R\end{array}} + 2CO_2 + 2e^- \text{ (electrons lost to the anode)}$$

At cathode :

$$2H_2O + 2e^- \longrightarrow 2OH^- + H_2\uparrow \text{ (electrons accepted from cathode)}$$

The yields are good if only a single substance is electrolysed *Methane cannot be prepared by this method.*

Mechanism of the Reaction. The exact mechanism of the reaction is not clear but is believed to involve *free radicals.* For example, formation of *n*-butane, ethane, ethylene and ethyl propionate from electrolysis of sodium propionate solution is explained as follows :

$$C_2H_5COONa \rightleftharpoons C_2H_5COO^- + Na^+$$

$$\underset{\text{Propionate ion}}{C_2H_5COO^-} \longrightarrow \underset{\text{Free propionate radical}}{C_2H_5COO^\cdot} + \underset{\text{given to anode}}{\text{One electron}}$$

Free propionate radical further breaks up into the ethyl radical and carbon dioxide (*Fragmentation*).

$$C_2H_5COO^\cdot \longrightarrow C_2H_5^\cdot + CO_2$$

Free ethyl radicals then give

(*a*) *n*-butane, by combination; $2C_2H_5^\cdot \longrightarrow C_2H_5{-}C_2H_5$,

(*b*) ethane and ethylene; by disproportionation

$$C_2H_5^\cdot + C_2H_5^\cdot \longrightarrow C_2H_6 + C_2H_4, \text{ and}$$

(*c*) ethyl propionate; by combination with free propionate radical.

$$C_2H_5COO^\cdot + C_2H_5^\cdot \longrightarrow C_2H_5COOC_2H_5$$

(v) *By heating an alcohol ROH, or a carbonyl compound (aldehyde, or ketone) with excess of concentrated hydriodic acid at high temperatures under pressure in a sealed tube. The reduction is usually carried out in the presence of a small amount of red phosphorus which regenerates the hydriodic acid from the iodine formed.*

$$\underset{\text{Alcohol}}{ROH} + 2HI \xrightarrow{\text{Red P, 420K}} \underset{\text{Paraffin}}{RH} + H_2O + I_2$$

$$CH_3.CO.CH_3 + 4HI \xrightarrow{\text{Red P, 420K}} CH_3.CH_2.CH_3 + 2I_2 + H_2O$$

$$RCOOH + 6HI \xrightarrow{\text{Red P, 470K}} RCH_3 + 2H_2O + 3I_2$$

Carbonyl compounds (preferably ketones) may also be reduced with zinc amalgam and concentrated hydrochloric acid. This reaction is called the **Clemmensen reduction.**

$$\mathrm{RCOR} \xrightarrow{e^-\,;\,H^+} \mathrm{RCH_2R}$$

The yield of this reduction is very good for higher alkanes.

(*vi*) *By hydrogenation of unsaturated hydrocarbons in the presence of finely-divided nickel at 570K*—(**Sabatier and Senderens Reaction**).

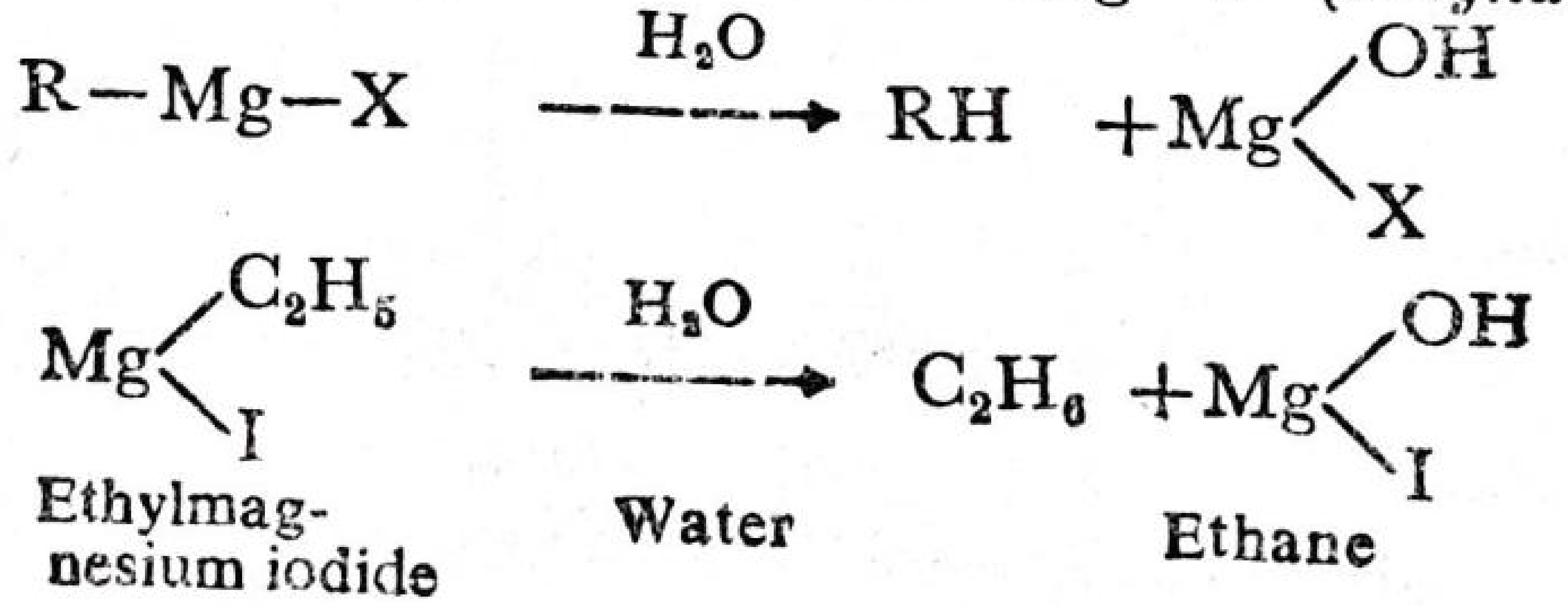
$$\underset{\text{Olefin}}{C_nH_{2n}} + H_2 \xrightarrow{\text{Ni 570K}} \underset{\text{Paraffin}}{C_nH_{2n+2}}$$

$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + H_2 \xrightarrow{\text{Ni, 570K}} \underset{\text{Ethane}}{CH_3{-}CH_3}$$

$$\underset{\text{Acetylene}}{CH{\equiv}CH} + 2H_2 \xrightarrow{\text{Ni, 570K}} \underset{\text{Ethane}}{CH_3{-}CH_3}$$

(*vii*) *By the action of water on Grignard reagent (Alkylmagnesium halides). An alkyl halide (preferably an iodide) is heated with dry magnesium powder in dry ether and the Grignard reagent so obtained is then decomposed by water.*

$$\mathrm{RI} + \mathrm{Mg} \xrightarrow{\text{Dry ether}} \mathrm{R{-}Mg{-}I} \quad \textit{(Grignard reagent)}$$



$$\mathrm{R{-}Mg{-}X} \xrightarrow{H_2O} \mathrm{RH} + \mathrm{Mg}\begin{cases} \mathrm{OH} \\ \mathrm{X} \end{cases}$$

$$\underset{\substack{\text{Ethylmag-}\\\text{nesium iodide}}}{\mathrm{Mg}\begin{cases} C_2H_5 \\ \mathrm{I} \end{cases}} \xrightarrow[\text{Water}]{H_2O} \underset{\text{Ethane}}{C_2H_6} + \mathrm{Mg}\begin{cases} \mathrm{OH} \\ \mathrm{I} \end{cases}$$

(*viii*) Long-chain alkanes can be prepared by coupling alkylboranes (*see page 2·29*) in the presence of $AgNO_3$ containing NaOH at 300K. For example,

$$\underset{\text{1-Pentene}}{6CH_3(CH_2)_2CH{=}CH_2} \xrightarrow{2B_2H_6} \underset{\text{Pentylborane}}{[2CH_3(CH_2)_3CH_2{-}]_3B}$$

$$\xrightarrow[\text{NaOH}]{AgNO_3} \underset{\text{Decane}}{3CH_3(CH_2)_3CH_2{-}CH_2(CH_2)_3CH_3}$$

4. General Physical Properties of the Paraffins. The paraffins from C_1 to C_4 are colourless and odourless gases while C_5 to C_{18} are colourless and odourless liquids. The higher paraffins are solids. They are insoluble in polar solvents like water, but are soluble in non-polar solvents, *e.g.*, various organic solvents like alcohol, ether and benzene. Their solubility decreases with increase in their molecular weights. Other physical constants (*e.g.*, melting points, boiling points, density, etc.) show a regular gradation. This, however, holds good only for the normal paraffins.

The boiling points and melting points increase with increase in the number of carbon atoms in a paraffin because the intermolecular forces increase as the molecule gets bigger. The boiling point increases by 20-30K for each carbon added to the chain. (See Fig. 13·1.). The increase in melting point, however, is not so regular. This is because intermolecular forces in a crystal depend not only upon the size of the molecules but also upon how well they fit in to the crystal lattice. They are all less dense than water (highest density about 0·8).

In the case of isomeric paraffins, the normal **paraffin always has the highest b.p. and m.p.** Generally, the greater the branching **in a paraffin, the lower is the boiling point.**

Name	M.P.	B.P.	Name	M.P.	B.P.
Methane	89K	111·6K	Isobutane	114K	261 K
Ethane	101K	184·7K	*n*-Pentane	143·8K	309 K
Propane	83·1K	228·5K	Isopentane	113K	301·1K
n-Butane	134·7K	272·45K	Neopentane	253K	282·5K

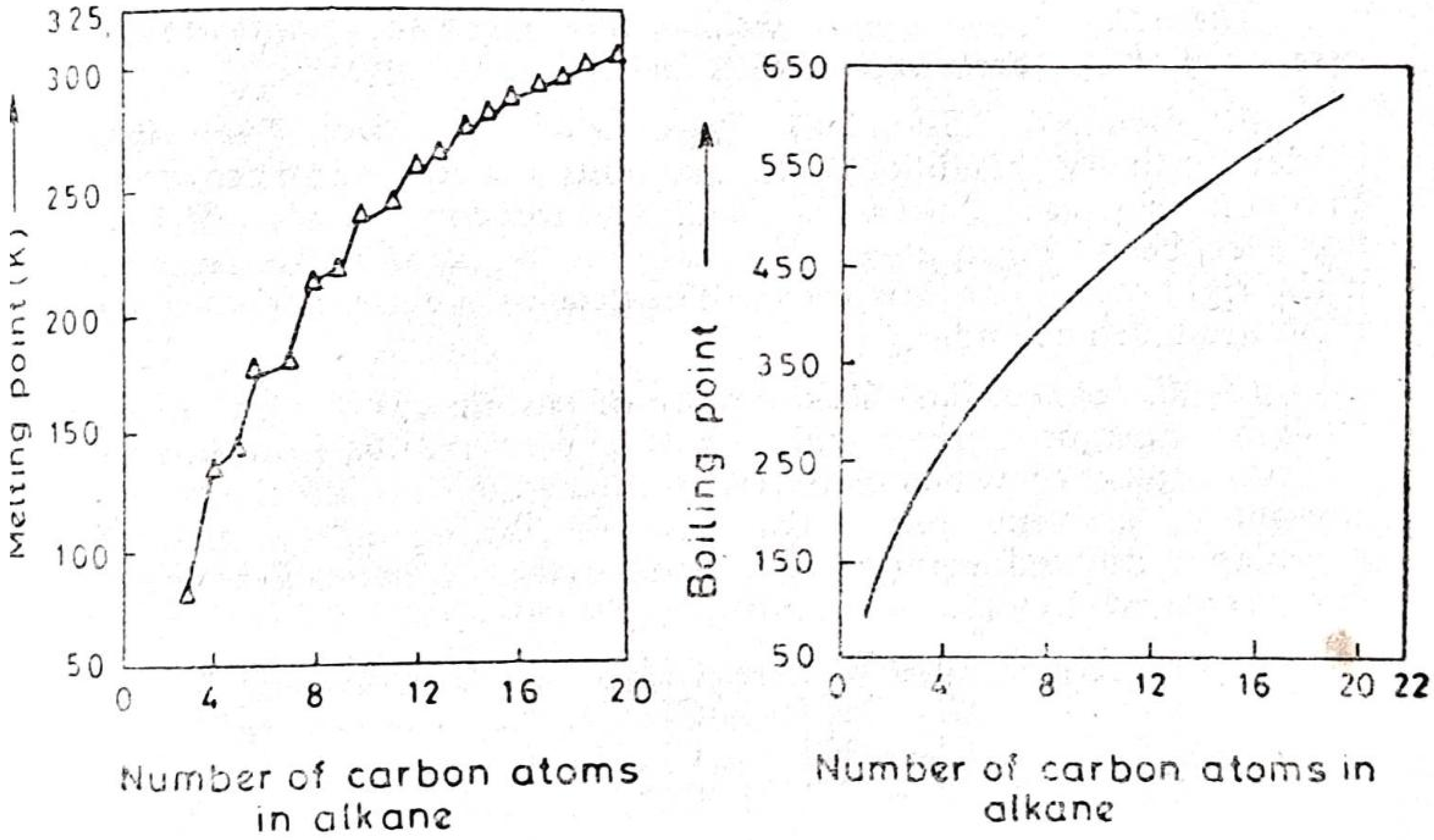
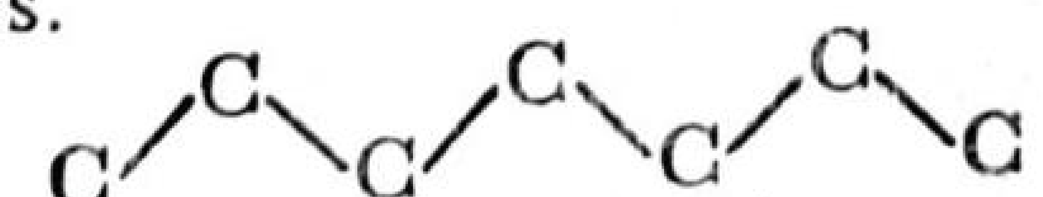
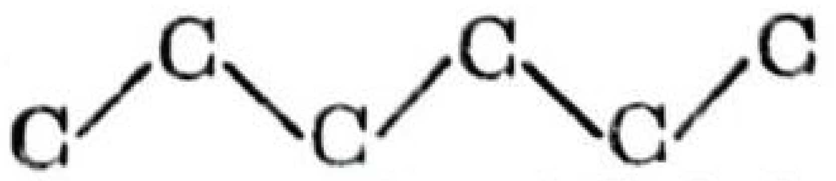


Fig. 13.1 Variation of boiling point and melting point with structure.

Alkanes with even number of carbon atoms have higher m.p. than the next lower and next higher alkanes having odd number of carbon atoms. This is probably due to the fact that alkanes with an odd number of carbon atoms have their end carbon atoms on the same side of the molecule and the even-numbered carbon atom alkanes have their end carbon atoms on opposite side of the molecules.



Odd-numbered C-chain



Even-numbered C-chain

Therefore alkanes with even number of carbon atoms pack in a way so as to permit greater intermolecular attraction and, therefore, they have slightly higher melting points.

5. IR Spectrum of Paraffins. The position of IR absorption region of CH group (stretch) in alkanes depends on the nature of carbon atom (whether primary, secondary or tertiary). Various regions of absorption in alkanes are given below.

C—H *Stretching absorption frequencies* :

$-CH_3$ 2975—2950 and 2885—2860 cm^{-1} (*m*)
$>CH_2$ 2944—2915 and 2870—2845 cm^{-1} (*m*)
$>\!\!-CH$ 2900—2880 cm^{-1} (*w*)

C—H *Deformation absorption frequencies* :

$-CH_3$ 1470—1435 (*m*) and 1385—1370 cm^{-1} (*m*)
$>CH_2$ 1480—1440 cm^{-1} (*m*)

Skeletal vibrations :

iso, Me_2CH- 1175—1165 cm^{-1} (*s*)
neo, Me_3C- 1255—1245 cm^{-1} (*s*)

The letters s, w and m in the brackets given above indicate the essence of sharp, weak and medium intensity absorptions.

6. General Chemical Properties of the Paraffins. Under ordinary conditions, the paraffins are quite inert towards common reagents such as acids, alkalis and oxidising agents. It has, however, been shown in recent years that the paraffins are reactive if the right conditions are used. The general reactions shown by them are given as under.

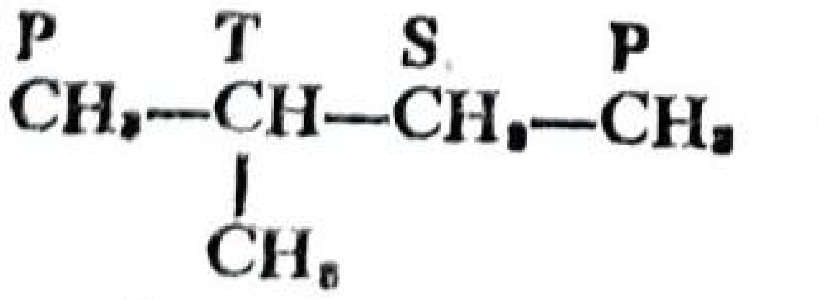
(1) **Halogenation.** Chlorination of paraffins is brought about by light, heat, or catalysts (called *halogen carriers, e.g.*, iron filings) and the extent to which chlorination occurs depends largely on the amount of chlorine used. For example, during chlorination of methane in diffused sunlight, the four hydrogen atoms are successively replaced by chlorine atoms.

*

$$\begin{array}{llll}
CH_4 + Cl_2 \rightarrow HCl + CH_3Cl & (\textit{methyl chloride}) \\
CH_3Cl + Cl_2 \rightarrow HCl + CH_2Cl_2 & (\textit{methylene chloride}) \\
CH_2Cl_2 + Cl_2 \rightarrow HCl + CHCl_3 & (\textit{chloroform}) \\
CHCl_3 + Cl_2 \rightarrow HCl + CCl_4 & (\textit{carbon tetrachloride})
\end{array}$$

---

* Hydrogen atoms attached to primary, secondary and tertiary carbon atoms are known as primary, secondary and tertiary hydrogen atoms, respectively. A carbon atom is termed primary, secondary or tertiary according as it is attached to one, two or three other carbon atoms. For example, in the isopentane given below :



$$\overset{P}{CH_3}-\underset{\underset{CH_3}{|}}{\overset{T}{CH}}-\overset{S}{CH_2}-\overset{P}{CH_3}$$

Isopentane

there are three primary carbon atoms, one secondary carbon atom and one tertiary carbon atom. In this compound there are nine primary hydrogen atoms attached to three primary carbon atoms. Similarly there are two secondary hydrogen atoms attached to one secondary carbon atom and one tertiary hydrogen atom attached to the tertiary carbon atom.

This type of replacement reaction is known as **substitution.** *In a substitution reaction, an atom or a group present in a compound is replaced by another without the compound undergoing any change in its structure.* The products thus obtained are called *substitution products.*

In higher members mixtures of all possible isomeric monochlorides are obtained. According to *Markownikoff* (1875) the *order of substitution is tertiary hydrogen ⊳ secondary hydrogen ⊳ primary hydrogen**.

Bromination is similar but the reaction is not so vigorous as chlorination. With iodine the reaction is reversible.

$$CH_4 + I_2 \rightleftharpoons CH_3I + HI$$

Iodination is, therefore, carried out in the presence of an oxidising agent such as iodic acid, nitric acid, mercuric oxide, etc., which destroys the hydriodic acid as it is formed.

$$5HI + HIO_3 \rightarrow 3I_2 + 3H_2O$$

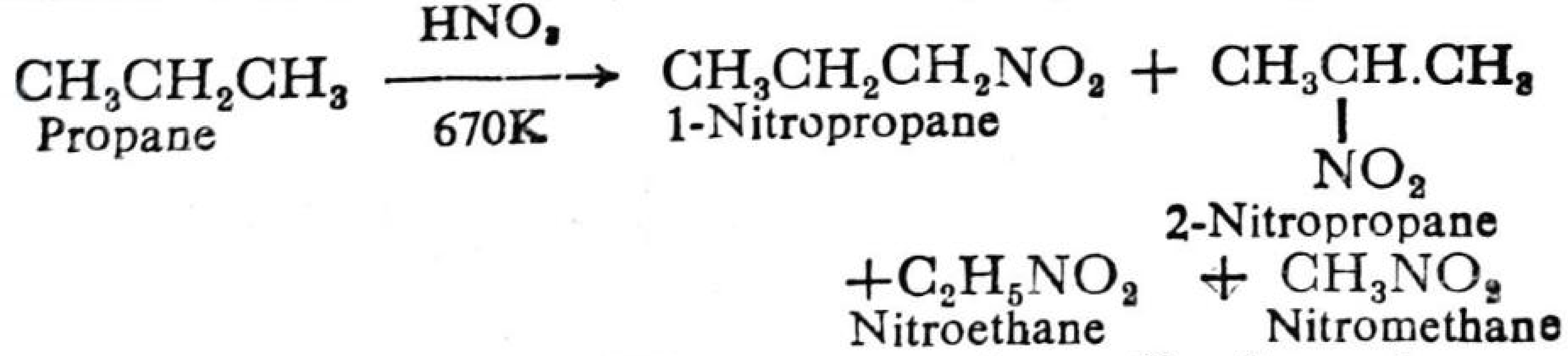
Direct fluorination is usually explosive (*cf.* chlorination of methane in bright sunlight which is also explosive).

$$CH_4 + 2F_2 \rightarrow C + 4HF$$
$$CH_4 + 2Cl_2 \rightarrow C + 4HCl$$

Mechanism of Halogenation (*See Part I, Chapter 10*)

Halogenation of paraffins is an oxidative process. Oxidation involves complete or relative loss of electrons by an atom. Before halogenation, the electron pair constituting the C—H bond is nearly equally shared between the two atoms. After halogenation, the electron pair of the C—X bond is nearer the halogen atom. The carbon atom has thus lost some share in the electron pair and is said to be oxidised.

(2) **Nitration.** Paraffins react with nitric acid under certain conditions when a hydrogen atom is replaced by the *nitro group,* NO_2 and the process is termed *nitration.* Nitration is carried out in vapour phase between 420-720K when a mixture of all possible mononitro derivatives (obtained direct or after *chain fission*) is obtained. For example, by nitration of propane, we get



$$\underset{\text{Propane}}{CH_3CH_2CH_3} \xrightarrow[670K]{HNO_3} \underset{\text{1-Nitropropane}}{CH_3CH_2CH_2NO_2} + \underset{\text{2-Nitropropane}}{CH_3\underset{\displaystyle NO_2}{\underset{|}{C}}H.CH_3}$$
$$+ \underset{\text{Nitroethane}}{C_2H_5NO_2} + \underset{\text{Nitromethane}}{CH_3NO_2}$$

(3) **Sulphonation.** When a normal paraffin from hexane onwards is treated with oleum, a hydrogen atom is replaced by a sulphonic acid group, $—SO_3H$. This process of replacement is known as *sulphonation.* The ease of replacement of hydrogen atoms is tertiary ⊳ secondary ⊳ primary (*cf.* halogenation and nitration). For example, sulphonation of isobutane yields 2-methyl-2-propanesulphonic acid.

$$\underset{\text{Isobutane}}{(CH_3)_3CH} + \underset{\text{Oleum or fuming sulphuric acid } (H_2SO_4+SO_3)}{HO.SO_3H} \rightarrow \underset{\text{2-Methyl-2-propane-sulphonic acid}}{(CH_3)_3C.SO_3H} + H_2O$$

(4) **Oxidation.** (*a*) COMBUSTION. Paraffins readily burn with a non-luminous flame in excess of air or oxygen to give carbon dioxide and water. They form explosive mixture with air or oxygen.

$$CH_4+2O_2 \rightarrow CO_2+2H_2O$$
$$2C_2H_6+7O_2 \rightarrow 4CO_2+6H_2O$$

(*b*) OXIDISING AGENTS, *e.g.*, alkaline potassium permanganate, readily oxidise a *tertiary* hydrogen to a hydroxyl group. For instance, isobutane gives *tert*-butyl alcohol when oxidised.

$$\underset{\text{Isobutane}}{(CH_3)_3CH}+[O] \xrightarrow{KMnO_4} \underset{\textit{tert}\text{-Butyl alcohol}}{(CH_3)_3COH}$$

A tertiary carbon atom is relatively easily oxidized because the alkyl groups are weakly electronegative as compared to hydrogen and possess a relatively low attraction for electrons. Thus the electron density about a tertiary carbon atom is relatively high which, therefore, accounts for its relatively easier oxidation.

(*c*) CATALYTIC OXIDATION of methane gives methanol, CH_3OH and formaldehyde, HCHO whereas that of higher homologues (C_{16}—) produces long-chain fatty acids.

(*i*) When a mixture of methane and dioxygen in the ratio 9 : 1 is compressed to 100 atmospheres and passed through copper tubes at 470K, methane is oxidised to methanol.

$$2CH_4+O_2 \rightarrow \underset{\text{Methanol}}{2CH_3OH}$$

(*ii*) When methane mixed with oxygen is passed over a heated catalyst, *e.g.*, molybdenum oxide, it is oxidised to methanal.

$$CH_4 + O_2 \longrightarrow \underset{\text{Formaldehyde}}{HCHO} + H_2O$$

(*iii*) $$\underset{\text{Higher alkane}}{2RCH_3} + \underset{\text{From air}}{3O_2} \xrightarrow[\text{acetate}\ 370\text{-}430K]{\text{Manganese}} \underset{\text{Higher fatty acid}}{2RCOOH} + 2H_2O$$

(*d*) SLOW COMBUSTION. Recently it has been found that when methane or ethane is treated with oxygen at high pressure and comparatively low temperature, the hydrogen atoms change to (OH) groups successively. The end products in this reaction are CO_2+H_2O.

$$\begin{tikzcd}
\underset{\text{Methane}}{CH_4} \arrow[r, "O"] & \underset{\text{Methanol}}{CH_3OH} \arrow[r, "O"] & CH_2(OH)_2 \arrow[r, "-H_2O"] & \underset{\text{Formaldehyde}}{HCHO} \arrow[d, "O"] \\
 & & CO_2+H_2O & \underset{\text{Formic acid}}{HCOOH} \arrow[l, "O"']
\end{tikzcd}$$

(5) **Thermal Decomposition, Pyrolysis or Cracking.** When vapours of higher paraffins are passed through a hot metal tube (770-970K), they break up to yield smaller molecules and this process is called cracking. For example, on cracking propane, the possible products are :

$$\underset{\text{Propene}}{C_3H_6} + H_2 \longleftarrow \underset{\text{Propane}}{C_3H_8} \longrightarrow \underset{\text{Methane}}{CH_4} + \underset{\text{Ethylene}}{C_2H_4} \rightarrow 2CH_4+C$$

Large quantities of high-boiling fractions of petroleum are converted into low-boiling gasoline by cracking.

Propene and hydrogen are produced from propane as a result of fission of C—H linkages whereas methane and ethylene are obtained due to the fission of C—C linkages.

In the case of higher alkanes, fission of C—C linkages occurs more readily. The presence of catalysts (like oxides of chromium, vanadium and molybdenum), however, accelerates the fission of C—H linkages. Pyrolysis in the presence of catalysts is used in the manufacture of alkenes.

The exact **mechanism of cracking** is still obscure. However, out of the many mechanisms suggested, the one *involving free radicals is* highly favoured by experts. For example, in the cracking of propane,

$$\underset{\text{Propane}}{CH_3CH_2CH_3} \rightarrow CH_3CH_2{-}\dot{C}H_2 + H^{\cdot} \longrightarrow CH_3CH{=}CH_2 + H_2$$

$$\downarrow$$

$$\underset{\text{(Free radicals)}}{CH_3{-}CH_2^{\cdot} + CH_3^{\cdot}} \xrightarrow{\text{Disproportionation}} \underset{\text{Ethylene}}{CH_2{=}CH_2} + \underset{\text{Methane}}{CH_4}$$

Problem 13·1. (*a*) Why are alkanes inert ?

(*b*) Why do the C—C bonds rather than the C—H bonds break during pyrolysis of alkanes ?

(*c*) Although combustion of alkenes is an exothermic process, yet they burn only at high temperatures. Explain why.

[**Hints** (*a*) A reactive site in a molecule has usually one or more unshared pairs of electrons, a polar bond, an electron-deficient atom or an atom in which the octet can expand. Alkanes have no such reactive site and are, therefore, inert. Further alkanes contain only sigma bonds which require high energy to break.

(*b*) Bond dissociation energy of C—C bond ($\Delta H = +347$ kJ mol^{-1}) is lower than that of C—H bond ($\Delta H = +415$ kJ mol^{-1})

(*c*) Energy of activation (ΔH) being very high, the reaction is very slow at room temperature.

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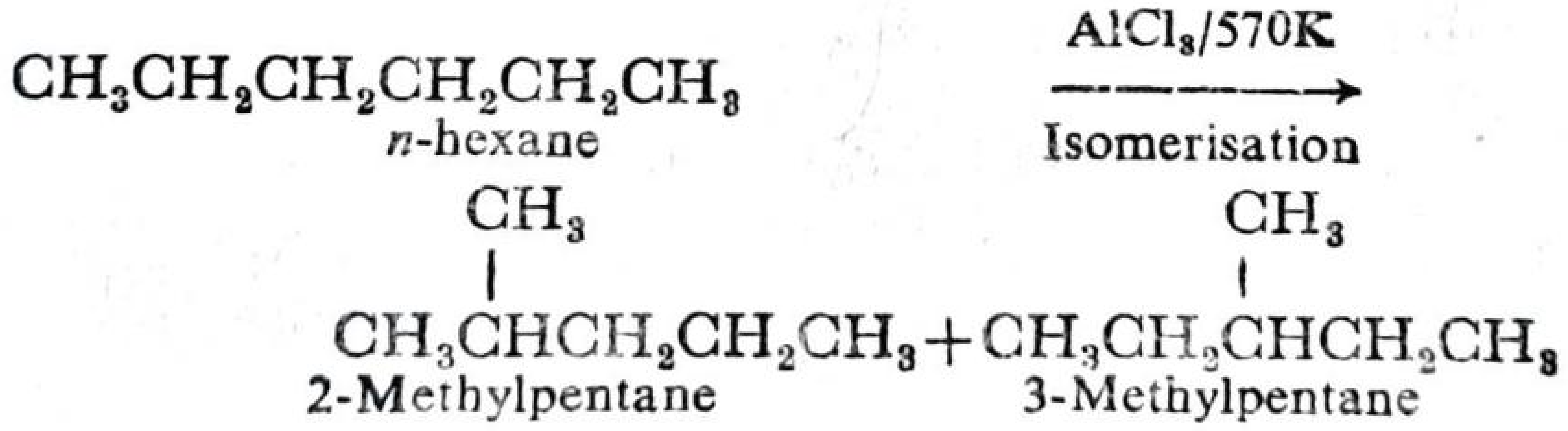
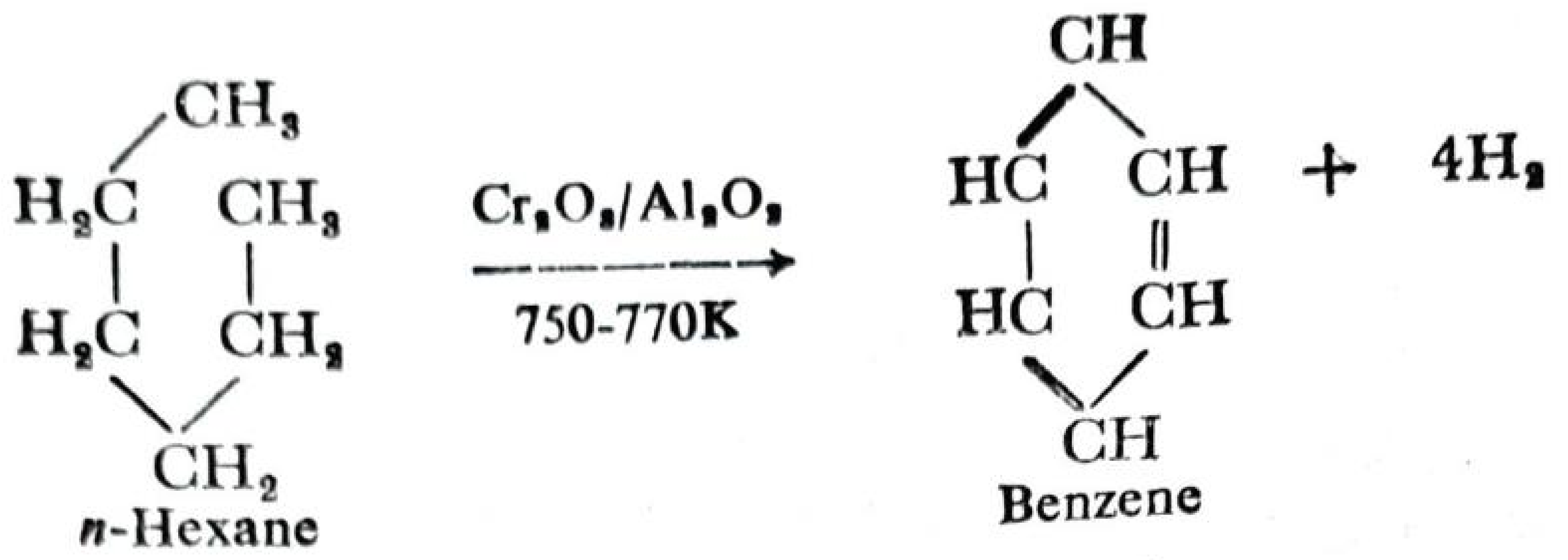
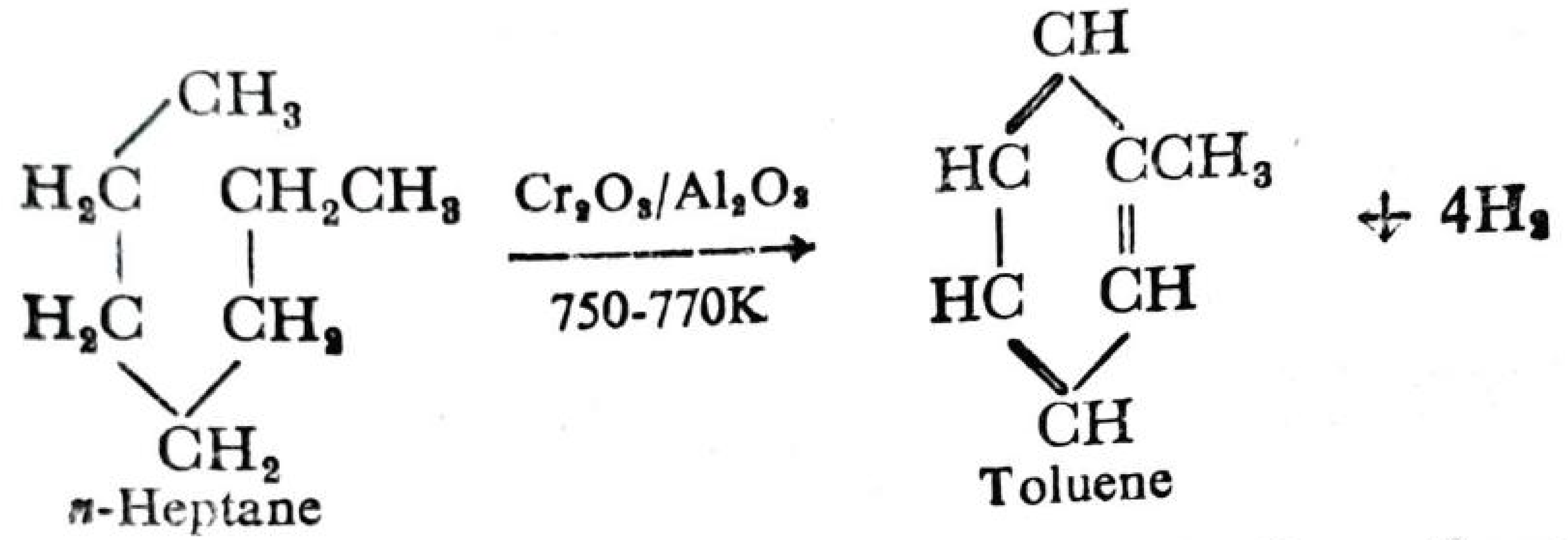
(6) **Isomerisation.** *n*-Alkanes when heated with aluminium chloride at 570K isomerise to give branched-chain alkanes. For example,



$$\underset{n\text{-hexane}}{CH_3CH_2CH_2CH_2CH_2CH_3} \xrightarrow[\text{Isomerisation}]{AlCl_3/570K} \underset{\text{2-Methylpentane}}{CH_3\overset{\overset{CH_3}{|}}{C}HCH_2CH_2CH_3} + \underset{\text{3-Methylpentane}}{CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_3}$$

(7) **Aromatisation.** Paraffins containing six or more carbon atoms when heated under pressure in presence of suitable catalysts get cyclised to give aromatic compounds. For example, *n*-hexane when passed under pressure over a heated catalyst (chromic oxide carried on an alumina support) at 750-770K gives benzene and hydrogen is set free.





7. Thermodynamics and Kinetics of the Reactions of Methane with Halogens. The order of reactivity of halogens in the substitution reaction is

Fluorination > Chlorination > Bromination > Iodination

The relative reactivity of one substance towards another is measured by the rate at which these two substances react. Fluorine is most reactive and if special precautions are not taken, fluorination of methane is explosive. Chlorination can be easily controlled, bromination is slow and direct iodination is very difficult.

Mechanism of chlorination of methane has been discussed in Chapter 10 of Part I. Assuming that the mechanism for fluorination, bromination and iodination are the same as for the chlorination of methane, we can account for the order of reactivity of the halogens on the basis of thermodynamic quantities ΔH and E_{act} for the various steps involved in halogenation in each case.

Fluorination	ΔH (kJ mol^{-1})	E_{act} (kJ mol^{-1})
(*i*) $F_2 \rightarrow 2F^{\cdot}$	$+159{\cdot}1$	$+159{\cdot}1$
(*ii*) $F^{\cdot} + CH_4 \rightarrow HF + CH_3^{\cdot}$	$-133{\cdot}9$	$+5{\cdot}1$
(*iii*) $CH_3^{\cdot} + F_2 \rightarrow CH_3F + F^{\cdot}$	$-292{\cdot}9$	small

Overall $\Delta H = -426{\cdot}8$

The chain-initiating step (*i*) in fluorination is highly endothermic and has, therefore, a high energy of activation ($= +159{\cdot}1$ kJ mol^{-1}). If rates of reactions were dependent only on this step, fluorine would be very unreactive. One chain-initiating step is followed by thousands of chain propagation steps [(*ii*) and (*iii*)] which in fluorination have very small energies of activation. As a result, the high activation energy of step (*i*) is not an impediment to the fluorination reaction.

If a chain reaction has to proceed, the chain-propagating steps must necessarily have low energies of activation. If it is not so, the highly reactive intermediates (free radicals) will be consumed by the chain-terminating steps before the chain progresses very far.

Overall heat of reaction, ΔH for fluorination is very large. As the reaction proceeds, heat of reaction accumulates in the reaction medium raising its temperature thereby. At higher temperatures there will be more chain-initiating steps and thus additional chains will be formed.

These two factors, *viz.* (*i*) the low energy of activation for the chain-propagating steps and (*ii*) the large overall heat of reaction (ΔH), account for the high reactivity and explosive violence with which fluorine reacts with methane.

Chlorination	ΔH (kJ mol^{-1})	E_{act} (kJ mol^{-1})
(*i*) $Cl_2 \rightarrow 2Cl^{\cdot}$	+242·7	+242·7
(*ii*) $Cl^{\cdot} + CH_4 \rightarrow HCl + CH_3^{\cdot}$	+4·2	+15·9
(*iii*) $CH_3^{\cdot} + Cl_2 \rightarrow CH_3Cl + Cl^{\cdot}$	−106·7	small

Overall $\Delta H = -102{\cdot}5$

On the basis of thermodynamic quantities ΔH and E_{act}, we can explain why fluorination is more rapid as compared to chlorination as follows :

(*i*) Higher energy of activation of the first chain-propagating step in chlorination ($E_{act} = +15{\cdot}9$ kJ mol^{-1}) as compared to that of the corresponding step in fluorination ($E_{act} = +5{\cdot}1$ kJ mol^{-1}).

(*ii*) Greater energy required for the chain-initiating step in chlorination ($E_{act} = +242{\cdot}7$ kJ mol^{-1} as compared to much lower $E_{act} = +159{\cdot}1$ kJ mol^{-1} for fluorination) also has some effect.

(*iii*) Most important role is played by the much greater overall heat of reaction in fluorination ($\Delta H = -426{\cdot}8$ kJ mol^{-1} as compared to $-102{\cdot}5$ kJ mol^{-1} for chlorination).

Bromination	ΔH (kJ mol^{-1})	E_{act} (kJ/mol^{-1})
(*i*) $Br_2 \rightarrow 2Br^{\cdot}$	+192·5	+192·5
(*ii*) $Br^{\cdot} + CH_4 \rightarrow HBr + CH_3^{\cdot}$	+69	+77·8
(*iii*) $CH_3^{\cdot} + Br_2 \rightarrow CH_3Br + Br^{\cdot}$	−100·4	small

Overall $\Delta H = -31{\cdot}4$

First chain-propagating step in bromination has a very high energy of activation ($E_{act} = +77{\cdot}8$ kJ mol^{-1} in contrast to $+15{\cdot}9$ kJ mol^{-1} for chlorination). In comparison to chlorine bromine is, therefore, much less reactive towards methane.

Iodination	ΔH (kJ mol^{-1})	E_{act} (kJmol^{-1})
(*i*) $I_2 \rightarrow 2I^{\cdot}$	+150·7	+150·7
(*ii*) $I^{\cdot} + CH_4 \rightarrow HI + CH_3^{\cdot}$	+129·7	+140·2
(*iii*) $CH_3^{\cdot} + I_2 \rightarrow CH_3I + I^{\cdot}$	−83·7	small

Overall $\Delta H = +46{\cdot}0$

First chain-propagating step in iodination has much higher energy of activation even when compared to bromination (+140·2.

Reaction in polar solvents proceed through heterolytic fission.

Example : Alkylhalide + OH^- Alcohol + X^-

$$R - X + OH^- \longrightarrow R - OH + X^-$$

Mechanism

$$R\overset{\curvearrowright}{-}X \longrightarrow R^+ + X^-$$

$$R^+ + OH^- \longrightarrow ROH$$

Reaction intermediates

Reaction intermediate is a discrete species that is formed during the conversion of reactants into products in a reaction. These can be detected or even isolated.

There are three types of reaction intermediates (i) radicals (ii) carbocations or carbonium ions and (iii) carban ions.

Free radicals

Homolytic fission of bonds produces species called radicals. Radicals have unpaired electron.

E.g., $R_3C - X \longrightarrow \underset{\text{Radicals}}{R_3C^\bullet} + X^\bullet$

Methods of formation :

a. Photochemical fission :

When electromagnetic radiation falls on amolecule, it is absorbed by the molecule causing bond fission. E.g., Acetone, etc., undergo such photochemical fission.

$$H_3C - CO - CH_3 \longrightarrow H_3C^\bullet + {}^\bullet CO - CH_3\ CO + {}^\bullet CH_3$$

b. Thermal fission :

Organic compounds on pyrolysis give radicals

E.g.,

i. $\underset{\text{Leadtetraethyl}}{Pb(C_2H_5)_4} \longrightarrow Pb + \underset{\text{Ethylradical}}{4C_2H_5^\bullet}$

ii. $CH_3-N=N-CH_3 \longrightarrow 2CH_3^{\bullet} + N_2$

Azo Methane — Methyl radical

iii. $C_6H_5\,COOOCOC_6H_5 \longrightarrow 2C_6H_5COO^{\bullet}$

Benzoyl peroxide — Benzoate radical

$\longrightarrow 2C_6H_5^{\bullet} + 2CO_2$

Pheny radical

iv. $(CH_3)_3COOC(CH_3)_3 \longrightarrow 2(CH_3)_3CO^{\bullet}$

Di - tert - butyl peroxide

$\longrightarrow 2CH_3^{\bullet} + 2(CH_3)_3CO$

e. ***Oxidation or reduction reactions :***

E.g., In Kolbe's reaction, an aqueous solution of the alkali salt of a fatty acid is electrolysed when alkanes are formed.

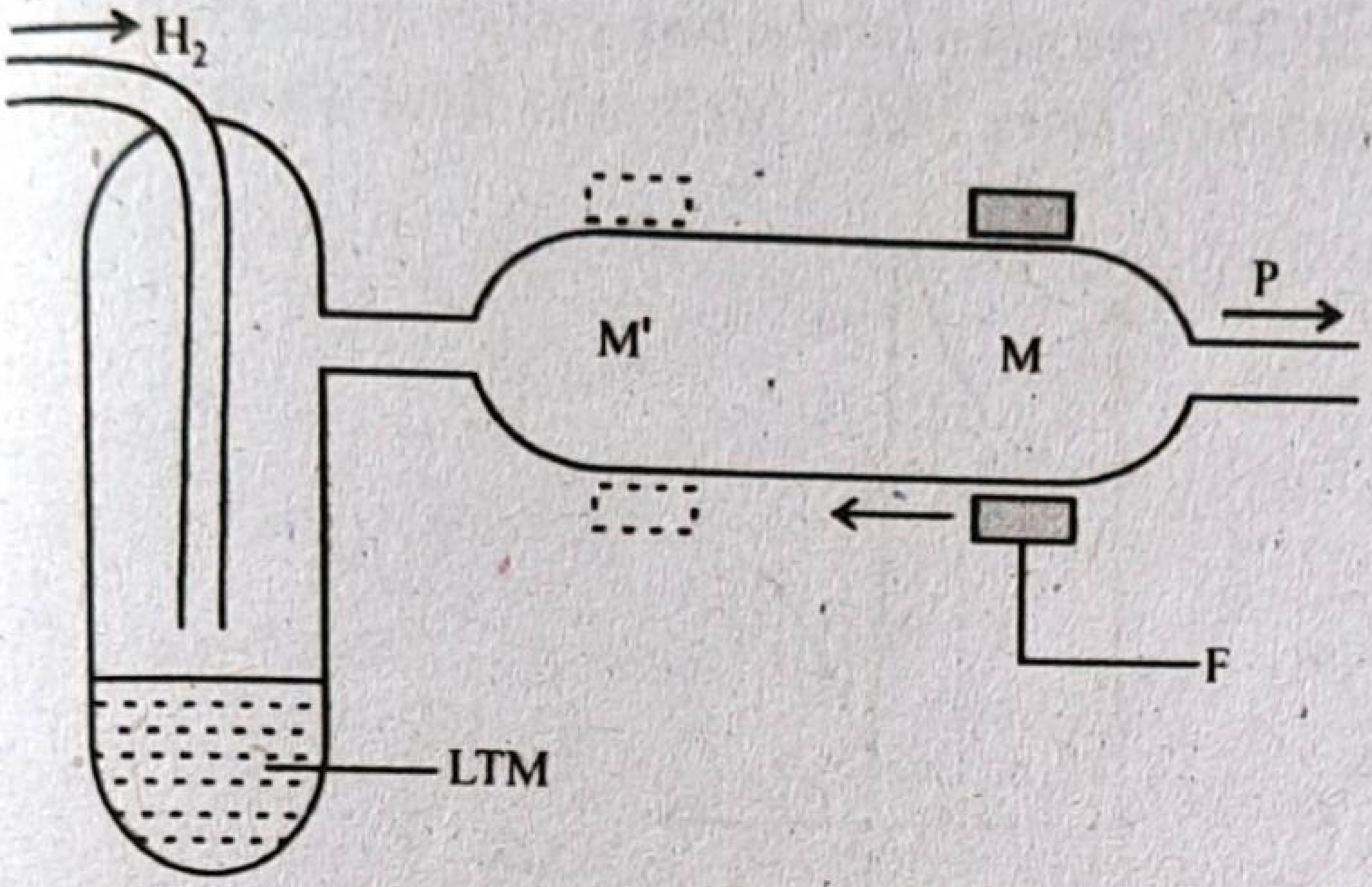
$$2RCOONa \rightleftharpoons 2Na^{+} + 2RCOO^{-} \xrightarrow[\text{At anode}]{-2e^{-}} 2RCOO^{\bullet} \xrightarrow{-2CO_2} 2R^{\bullet}$$

Detection :

i. ***Paneth mirro technique :***

The presence of the methyl radicals from the thermal decomposition of lead tetramethyl has been detected by this technique. The apparatus used is shown is Figure.

Lead tetramethyl is a volatile liquid. The apparatus is evacuated. H_2 gas a 1 mm pressure is passed over the liquid. It mixes with the vapours of lead tetramethyl and carries it through the tube. The gases are sucked by a pump at the other end. A furnace F is first placed at position M and the mixture is heated. After sometimes a lead mirror is deposited at M. Now the furnace is moved to M′. A new mirror is deposited at M′. The original mirror at M slowly disappears.



LTM = Lead Tetramethyl, M = and M′ = Mirrors,
P = To Pump, F = Furance

This phenomenon is explained as follows : First lead tetramethyl decomposes on heating to form lead and free methyl radicals. The lead is deposited as a mirror at M. The methyl radicals are carried away by H_2. When the furnace is moved to M′, decomposition takes place at M′.

$$Pb(CH_3)_4 \longrightarrow \underset{\text{Mirror}}{Pb} + 4CH_3^{\bullet}$$

So, the mirror is formed at M′. The methyl radicals on their way to the pump recombine with lead at M. So the mirror at M disappears.

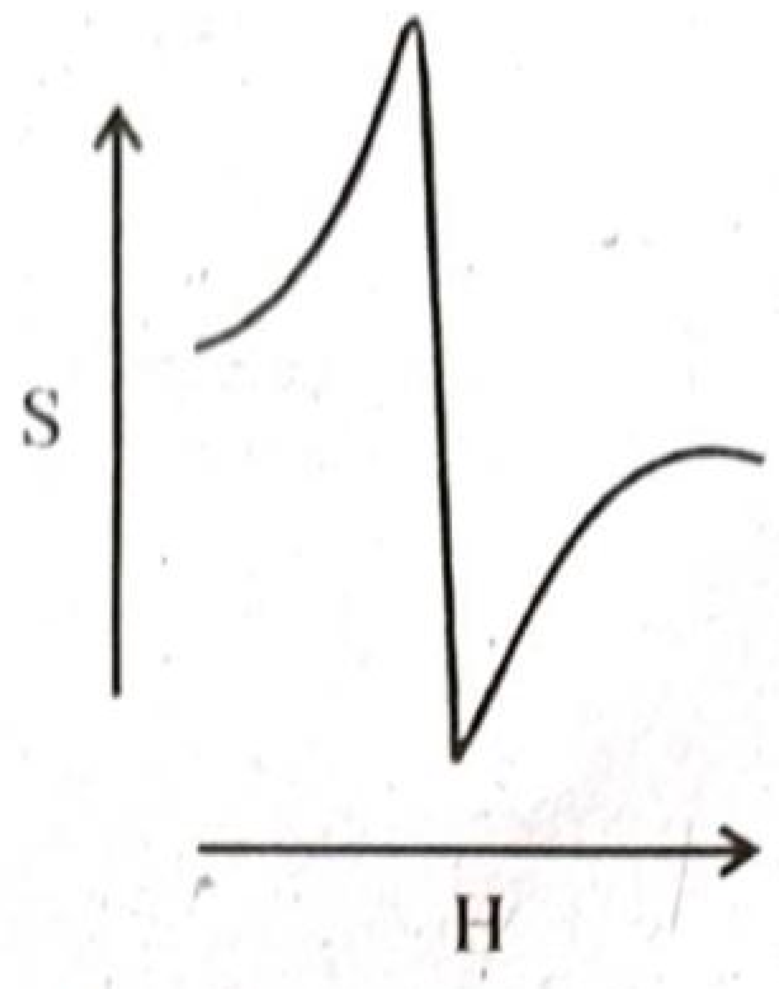
$$Pb + 4CH_3^{\bullet} \longrightarrow Pb\,(CH_3)_4$$

The technique is used to detect radicals.

ii. From electron spin resonance spectroscopy :

Because of the presence of an unpaired electron, radicals may be detected by means of electron spin resonance spectroscopy. The sample is placed in e.s.r. spectrometer where a plot of the first derivative of the curve of absorption against magnetic field is recorded. The specturm will be as shown in figure.

The sensitivity of e.s.r. spectroscopy for detection of radicals is high. A concentration of 10^{-12} M of radicals can be detected. Identification of simple hydrocabon radicals is possible by the analysis of the fine structure in their spectra. If there are n interacting protons in the radical, there will be (n +1) resonance, lines (E.g., Methyl radical shows four resonance lines).



S = Signal, H = Magnetic Field

iii. From paramagnetic susceptibility measurements :

Because of the presence of an unpaired electron, radicals may be detected by means of magnetic susceptibility measurements. Such measurements help us to detect the extent to which a substance exists in the form of radical.

Radical reactions :

a. Combination :

Radicals may undergo dimerisation. Two different radicals combine on colliding with each other.

$$Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl_2$$

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

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

Free radical substitution reactions follow this type only. Most of the free radical substitution reactions are chain reactions.

b. Disproportionation :

This involve transfer of hydrogen between two radicals. This is energetically more fovourable since it involves fission of one bond and formation of new bonds.

E.g., $\underset{\text{Two ethyl radicals}}{2CH_3 - CH_2^{\bullet}} \longrightarrow \underset{\text{Ethane}}{CH_3 - CH_3} + \underset{\text{Ethylene}}{CH_2 = CH_2}$

c. ***Abstraction :***

Radicals may abstract an atom (usually a hydrogen atom) from a saturated organic compound.

E.g, $$\underset{\text{Methyl radical}}{CH_3^\bullet} + \underset{\text{Ethane}}{H-C_2H_5} \longrightarrow \underset{\text{Methane}}{CH_4} + \underset{\text{Ethyl radical}}{C_2H_5^\bullet}$$

$$Cl^\bullet + H-CH_3 \longrightarrow HCl + CH_3^\bullet$$

In general the reaction will proceed if the energy of the X – H bond is greater than the energy of the H – R bond because in that case products are more stable than the starting materials.

$$X^\bullet + H-R \longrightarrow XH + R^\bullet$$

d. ***Addition to multiple bonds :***

Radicals add to other molecules having a multiple bond producing, new free radicals.

E.g., $$\underset{\text{Propylene}}{CH_3-CH-CH_2} + \underset{\text{radical}}{Br^\bullet} \longrightarrow \underset{\text{Another radical}}{CH_3-{}^\bullet CH-CH_2Br}$$

e. ***Fragmentation :***

Certain radicals undergo fission resulting in the formation of a new radical and a non radical fragment.

E.g., i. $$\underset{\text{Benzoate radical}}{C_2H_5-COO^\bullet} \longrightarrow \underset{\text{Phenyl radical}}{C_6H_5^\bullet} + CO_2$$

ii. $$\underset{\text{Propionate radical}}{C_2H_5-COO^\bullet} \longrightarrow \underset{\text{Ethyl radical}}{C_2H_5^\bullet} + CO_2$$

Stability of Free radicals

When an alkane dissociates into radicals ($R-H \rightarrow R^\bullet + H^\bullet$) energy equal to its bond dissociation energyhas to be supplied to it. This increases the potential energy of the radical.

Smaller the bond dissociation energy, greater the case with which the free radical is formed and less will be its potential energy making it more stable.

Bond dissociation energies of some radicals are as follows :

$$\underset{\text{Methane}}{CH_3-H} \longrightarrow \underset{\text{Methyl radical}}{CH_3^\bullet} + H^\bullet \qquad ; \Delta H = 435.1\ \text{kJ}$$

$$\underset{\text{Ethane}}{CH_3-CH_2-H} \longrightarrow \underset{\substack{\text{Ethyl radical}\\ \text{(Primary radical)}}}{CH_3-CH_2^\bullet} + H^\bullet \qquad ; \Delta H = 411\text{kJ}$$

$$\underset{\text{Propane}}{(CH_3)_2CH-H} \longrightarrow \underset{\substack{\text{Isopropyl radical}\\ \text{(Secondary radical)}}}{(CH_3)_2CH^\bullet} + H^\bullet \qquad ; \Delta H = 395.5\ \text{kJ}$$

$$\underset{\text{Isobutane}}{(CH_3)_3CH} \longrightarrow \underset{\substack{\text{Tert. butyl radical}\\ \text{(Tertiary radical)}}}{(CH_3)_3C^\bullet} + H^\bullet \qquad ; \Delta H = 380.7\ \text{kJ}$$

In the above series, dissociation energy decreases and hence potential energy decreases as we pass from $CH_3^\bullet$ to $(CH_3)_3C^\bullet$ radical. With decrease in potential energy the stability of the radical increases. Hence stability of the radicals increase from $CH_3^\bullet$ to $(CH_3)_3C^\bullet$.

Thus we see that their relative stabilities are in the order

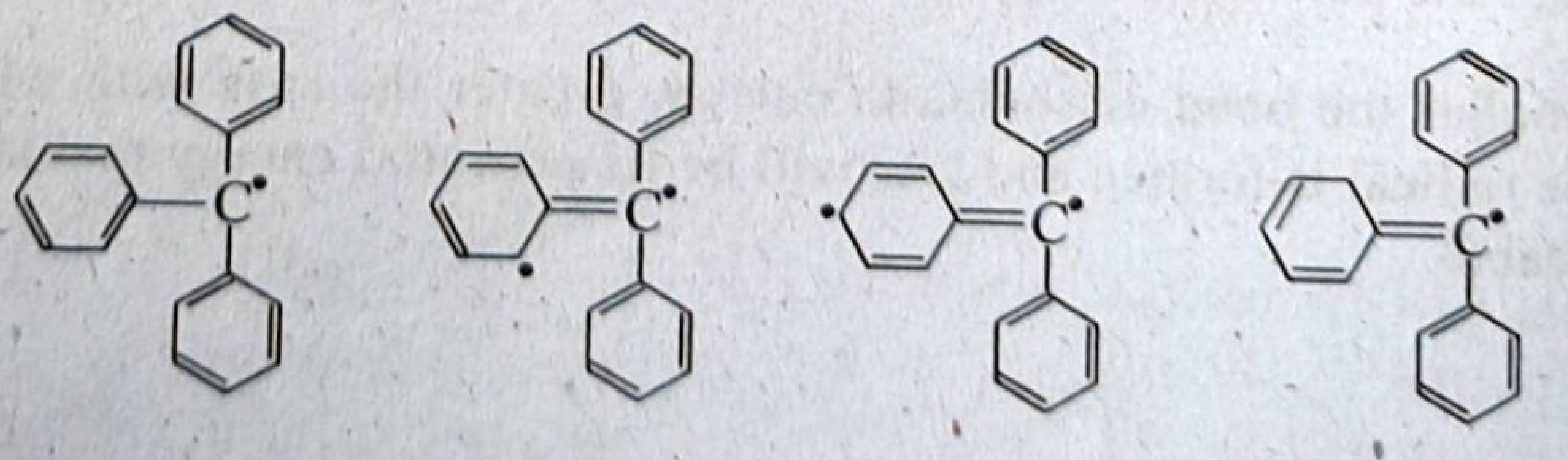
$$\underset{\text{Tert. butyl}}{(CH_3)_3C^\bullet} > \underset{\text{Isopropyl}}{(CH_3)_2CH^\bullet} > \underset{\text{Ethyl}}{CH_3-CH_2^\bullet} > \underset{\text{Methyl}}{CH_3^\bullet}$$

In general the stability of radicals is in the following order.

tertiary > secondary > primary > emthyl

The case of formation is also of the same order. That is, the more stable the free radical, more easily it is formed.

The stability of the radicals many also be attributed to resonance.



etc.

The stability of triphenyl radical is attributed to resonance. A large number of resonating structures contribute to the resonance hybrid.

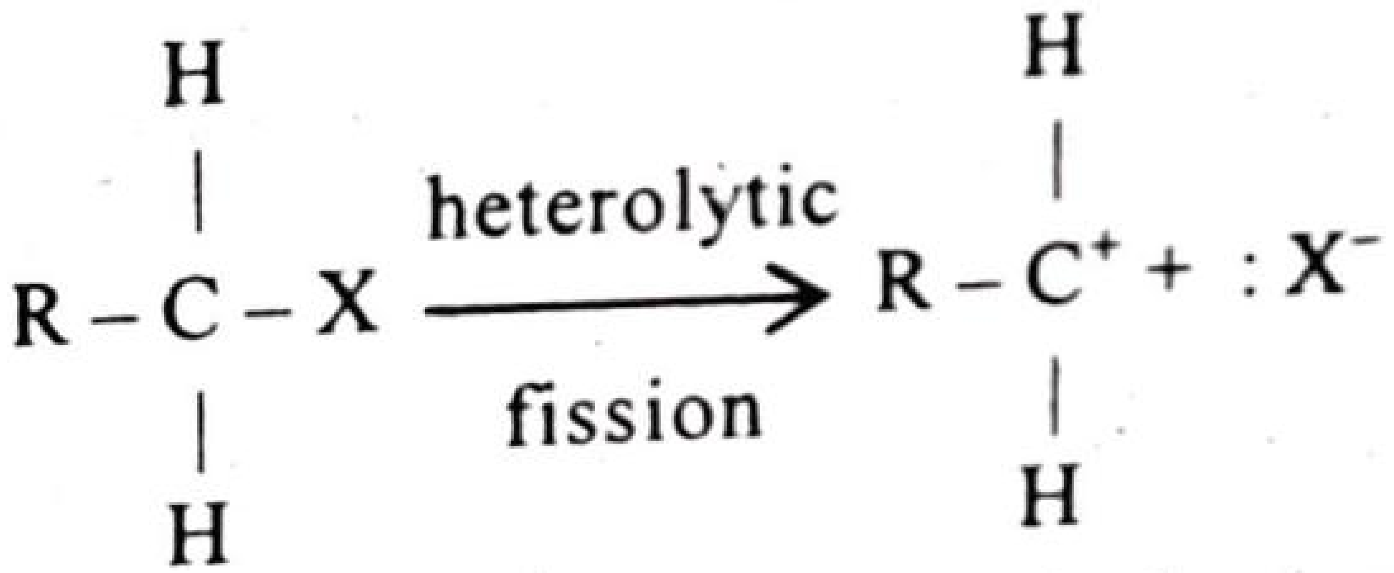
Carbocation (Carbonium ions)

Definition :

When R^+ is a positive group in which the carbon atom carrier a positive charge, i.e., lacks a pair of electrons in its valency shell, the group is known as carbocation.

Explanation with examples :

Let us take the example of heterolytic fissionof C – X bond present in an organic compound. If X has greater electronegativity than the carbon atom then X takes the bonding pair of electrons along with it, during the fission. Correspondingly, an ion with a positive charge on C is got.



$$\mathrm{R-\overset{H}{\underset{H}{C}}-X \xrightarrow[\text{fission}]{\text{heterolytic}} R-\overset{H}{\underset{H}{C^+}} + :X^-}$$

Such an ion containing a positively charged carbon centreis called a carbocation or carbonium ion. E.g., CH_3 – methyl carbocation :

$CH_3 - {}^+CH_2$ - Ethyl carbocation.

Methods of formation

1. ***By heterolysis :***

$$\underset{\text{t - butyl halide}}{(CH_3)_3\,CX} \longrightarrow \underset{\text{t - butyl cation}}{(CH_3)_3C^+} + X^-$$

2. By protonation of alkenes

$$CH_2 = CH_2 \xrightarrow{H^+} {}^+CH_2 - CH^3$$

3. By protonation of alcohal

$$R - O - H \xrightarrow{H^+} R{-}^+OH_2 \xrightarrow{-H_2O} \underset{\text{Alkyl cation}}{R^+}$$

4. By decomposition of certain compounds like benzene diazonium chloride.

$$C_6H_5N_2Cl \xrightarrow{-Cl^-} C_6H_5N_2^+ \xrightarrow{-N_2} \underset{\text{Phenyl cation}}{C_6H_5^+}$$

Reactions of carbocations :

Carbocations very reactive reaction intermediates. This is because the carbocation contains a positively charged carbon atom which has only six electrons in the outer most shell. Such a species has a marked tendency to complete the octer. So a carbocation combines readily with any susbtance that can donate a pair of electrons, (nucleophiles) to complete the octet.

After the carbocations are formed they react further and get stabilised as follows.

1. ***Elmination of porton :***

A carbonium ion may lose a proton and become an alkene. The proton is lost from an α - carbon atom.

$$\text{E.g., Ethyl alcohol} \xrightarrow[160-170^\circ C]{\text{Cond. } H_2SO_4} \text{Ethylene}$$

Mechanism :

$$C_2H_5OH + H^+ \xrightarrow{H_2SO_4} C_2H_5OH_2^+ \xrightarrow{-H_2O^+} C_2H_5^+ \xrightarrow{-H^+} CH_2=CH_2$$

2. ***Combination with nucleophile :***

A carbonium ion may combine, with a nucleophile.

$$\text{E.g, Teritiary butyl bromide} \xrightarrow{KOH} \text{Tertiary butyl alcohol}$$

Mchanism :

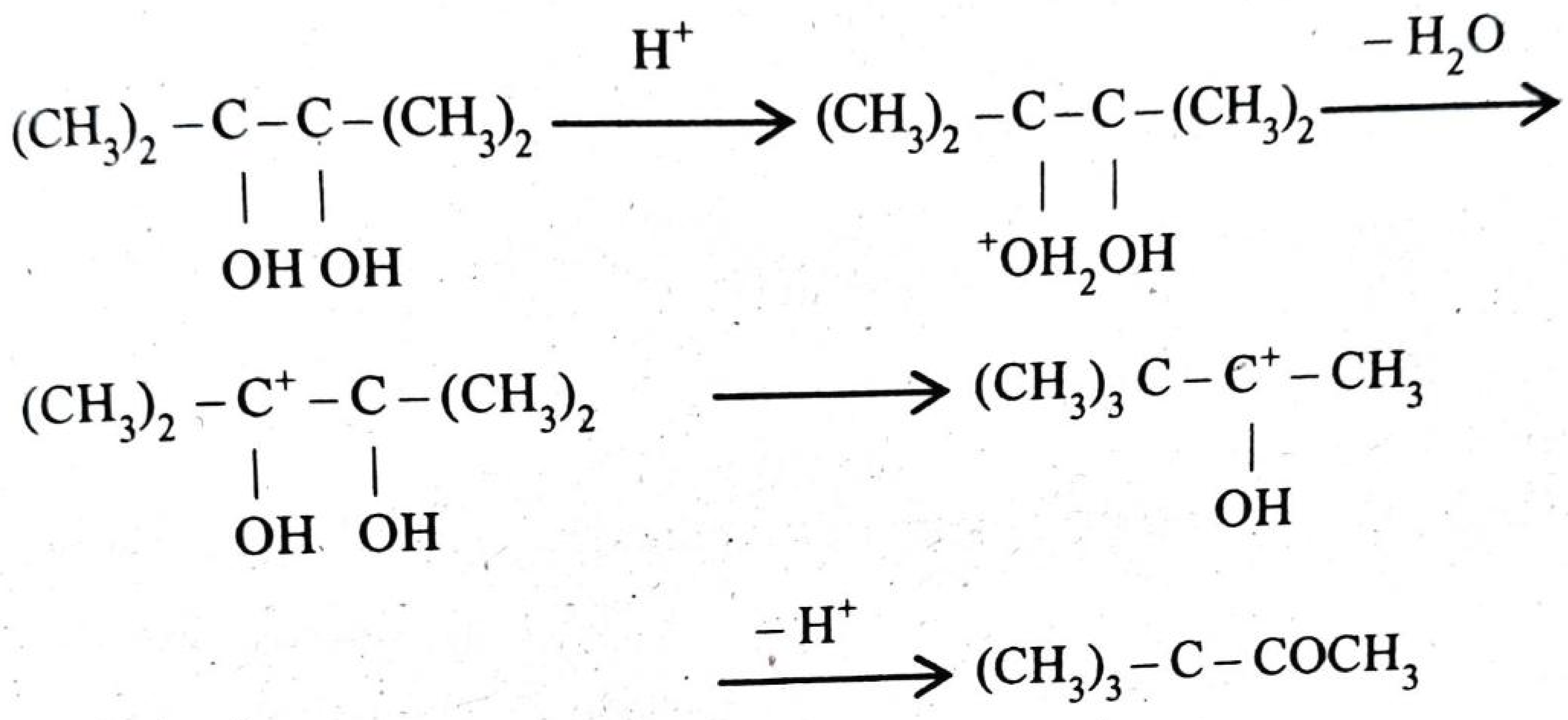
$$Me_3CBr \xrightarrow{-Br^-} Me_3C^+ \xrightarrow{OH^-} Me_3COH$$

3. ***Molecular rearragement :***

A carbonium ion may undergo molecular rearrangement.

E.g., Pinacol (Tetramethyl) dihydroxyethane $\xrightarrow{H^+}$ Pinacolone (Trimethyl acetone)

Mechanism



$$(CH_3)_2-\underset{OH}{\underset{|}{C}}-\underset{OH}{\underset{|}{C}}-(CH_3)_2 \xrightarrow{H^+} (CH_3)_2-\underset{^+OH_2}{\underset{|}{C}}-\underset{OH}{\underset{|}{C}}-(CH_3)_2 \xrightarrow{-H_2O}$$

$$(CH_3)_2-\underset{OH}{\underset{|}{C^+}}-\underset{OH}{\underset{|}{C}}-(CH_3)_2 \longrightarrow (CH_3)_3C-\underset{OH}{\underset{|}{C^+}}-CH_3$$

$$\xrightarrow{-H^+} (CH_3)_3-C-COCH_3$$

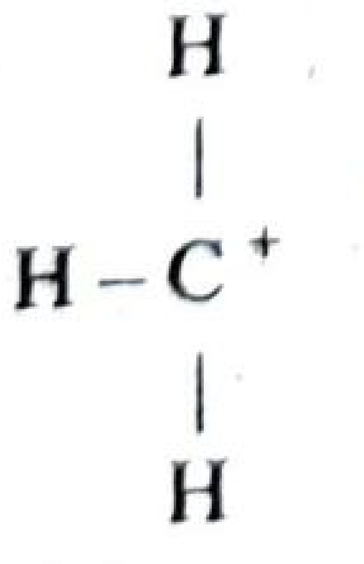
This rearragement is known as pinacol - pinacolone rearrangement.

Stability of carbocations :

i. Electron donating subtituents increase the stability of carbonium ions and electron with drawing substitutents decrease the stability of carbonium ions.

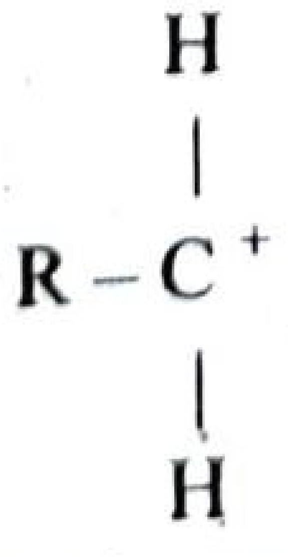
If alkyl groups are attached to the positively charged carbon atom, they have an electron releasing effect (+ I effect). so alkyl groups reduce the positive charge of the carbon atom to which they are attached. Thus alkyl groups stabilise carbonium ions.

Carbocations are classified into primary, secondary and tertiary carbocations.



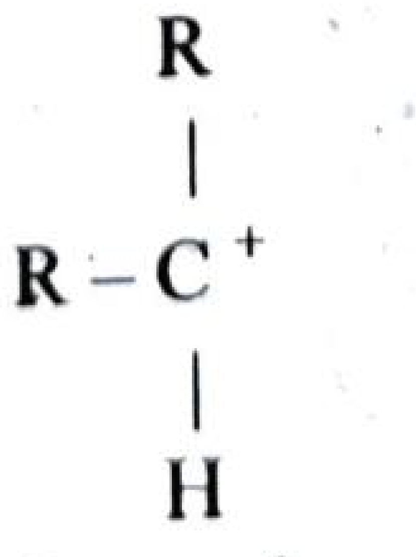
$$H-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C^+}}}}$$

Primary



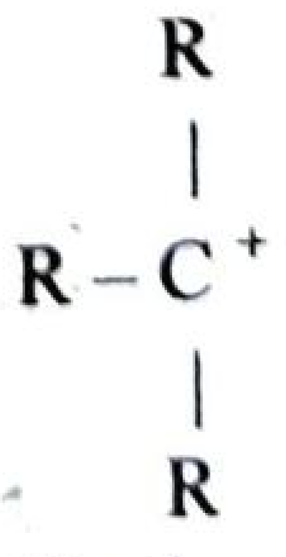
$$R-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C^+}}}}$$

Primary



$$R-\underset{H}{\underset{|}{\overset{R}{\overset{|}{C^+}}}}$$

Secondary



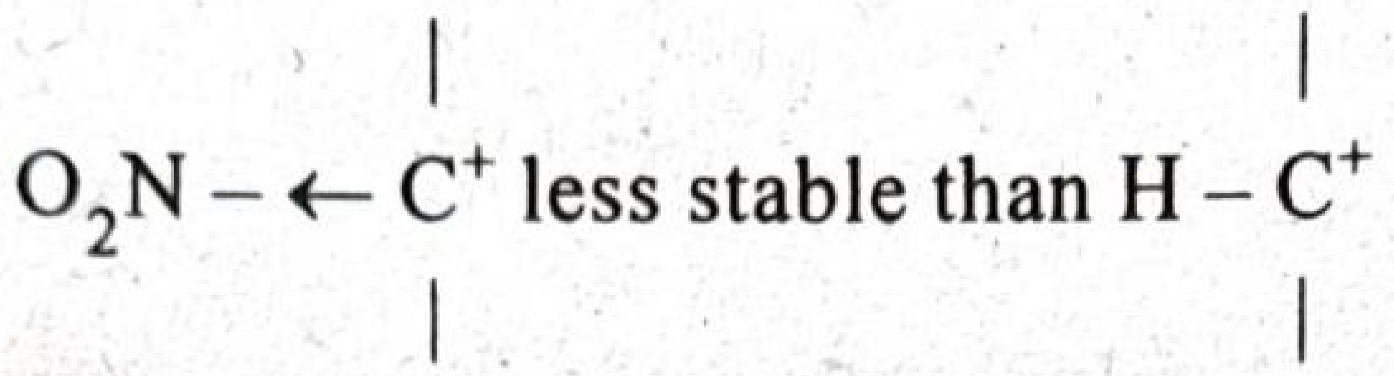
$$R-\underset{R}{\underset{|}{\overset{R}{\overset{|}{C^+}}}}$$

Tertiary

A tertiary carbonium ion has there alkyl groups. So it is more stable than a secondary carbonium ion with two alkyl groups. A secondary carbonium ion is more stable a primary carbonium ion with only one alkyl group. Methyl carbonium ion has no methyl group. So it is the least stable carbonium ion. Thus the stability of carbonium ions decreases inthe following order :

tertiary > secondary > primary > methyl

ii. The stability of carbonium ions is reduced by electron attracting groups like $-NO_2 > C = O$ etc., If they are attached to the carbon containing the positive charge.

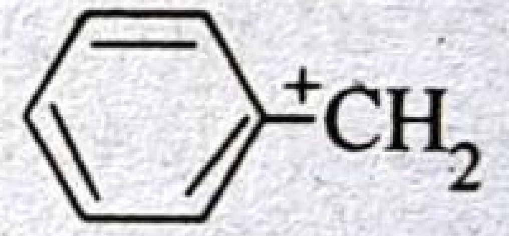


$$O_2N - \leftarrow \overset{|}{\underset{|}{C^+}} \text{ less stable than } H - \overset{|}{\underset{|}{C^+}}$$

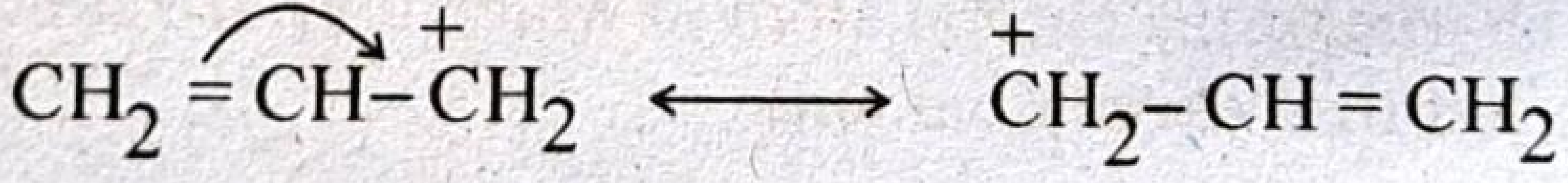
iii. Carbonium ion becomes stabilised if the positively charged atom is attached to another group which delocalise the positive charge by resonane.

E.g., The order of stability of the following carbonium ions is as shown below :

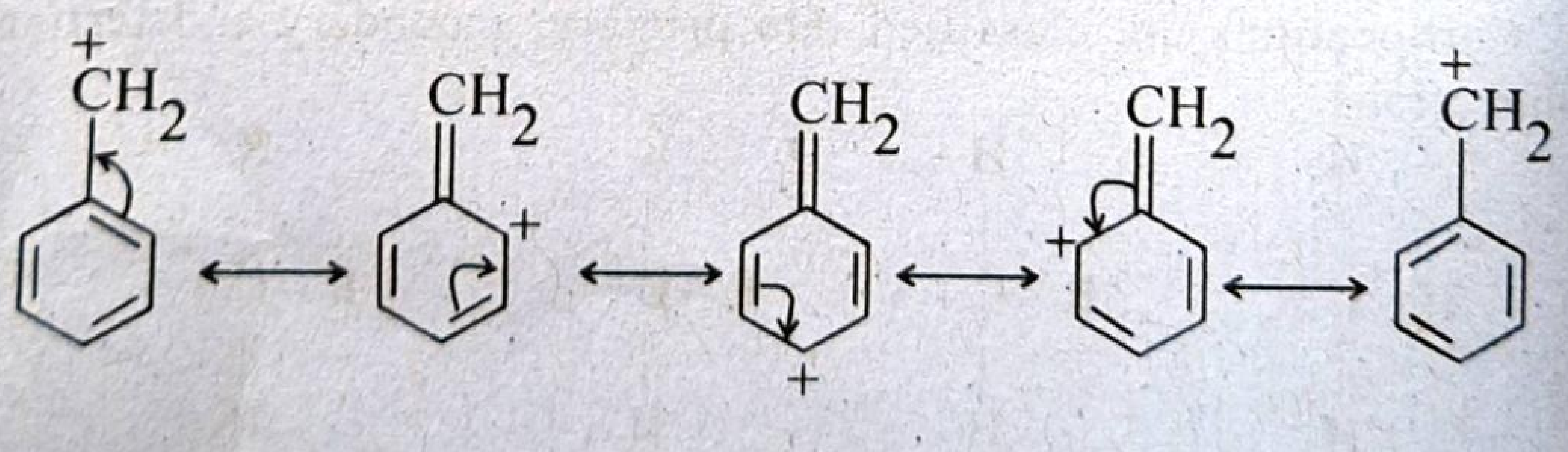
propyl < allyl < benyl

$CH_3CH_2{}^+CH_2 < CH_2 = CH - {}^+CH_2 <$ 

In propyl carbonium ion, resonance is not possible. In allyl carbonium ion there are two canonical structure possible. So it is more stable then propyl carbonium ion. In benzyl carbonium ion there are five canonical structures possible.



$$CH_2 = CH - \overset{+}{C}H_2 \longleftrightarrow \overset{+}{C}H_2 - CH = CH_2$$



Hence, if is the most stable of the three carbonium ions. Resonance becomes possible because the carbonium ion carbon is in an sp^2 hybridisd state and hence is flat. It has an unhybridised p orbital which is perpendicular to the plane of the molecule. So the pi electron of the benzene ring easily undergo resonance with the carbonium ion and stabilise it.

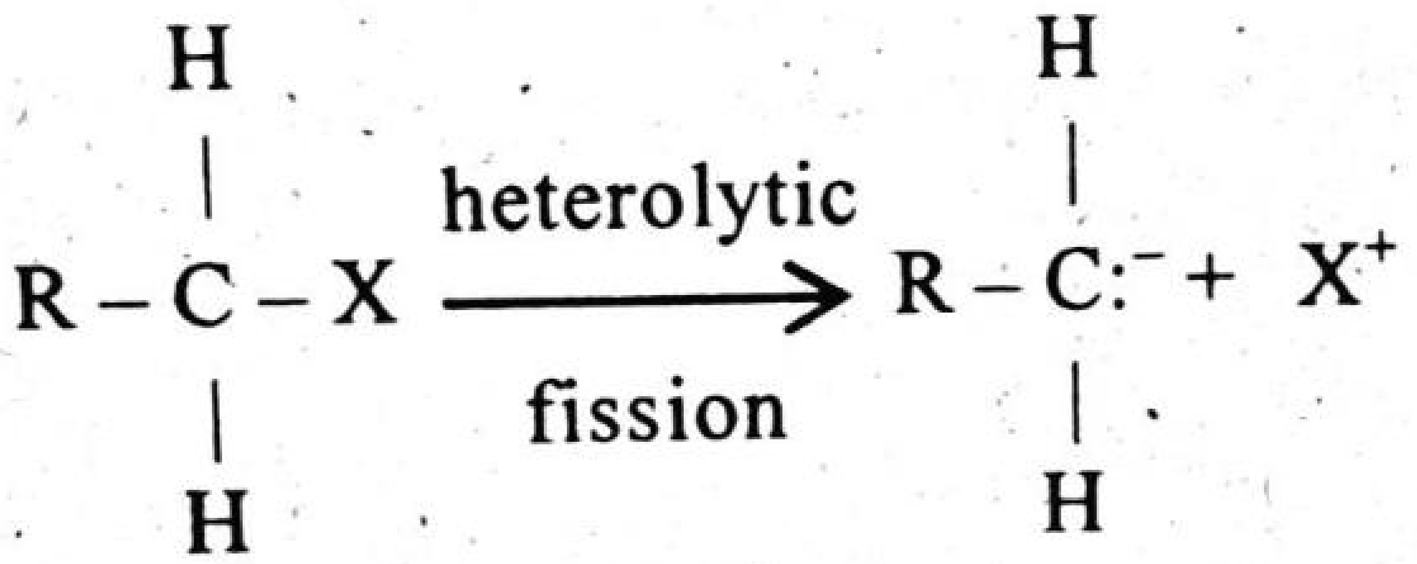
Carbanions

Definition :

When R**:** is a negative group in which the carbon atom carries the negative charge, i.e., has an unshared pair of electrons, the group is known as carbanion.

Explanation with examples :

Let us take the example of heterolytic fission of a C – X bond present in an organic compound. If C has greater electronegativity than X, than C takes the bonding pair of electrons along with it during the fission. Correspondingly an ion with a negative charge on C is got.

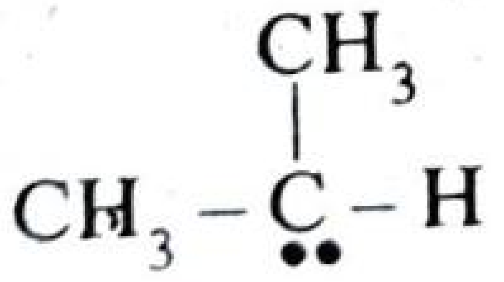


$$R-\underset{\displaystyle H}{\overset{\displaystyle H}{C}}-X \xrightarrow[\text{fission}]{\text{heterolytic}} R-\underset{\displaystyle H}{\overset{\displaystyle H}{C}}{:}^- + X^+$$

Carbanion

Such an ion containg a negatively charged carbon centre is called carbanion.

E.g., $CH_3 - \ddot{C}H_2$ Ethyl carbanion



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

Iso propyl carbanion

Methods of formation :

i. By removal of an atom or group

$$Ph_3C-H + Na^+\ddot{N}H_2 \longrightarrow PH_3C^-Na^+ + NH_3$$

ii. By decarboxylation

$$R-COO^- \longrightarrow R:^- + CO_2$$

Reactions of carbanions :

They are very reactive intermediates. They readily combine with any species which takes up a pair of electrons (electrophiles).

After carbanions are formed they react further and are stabilised as follows :

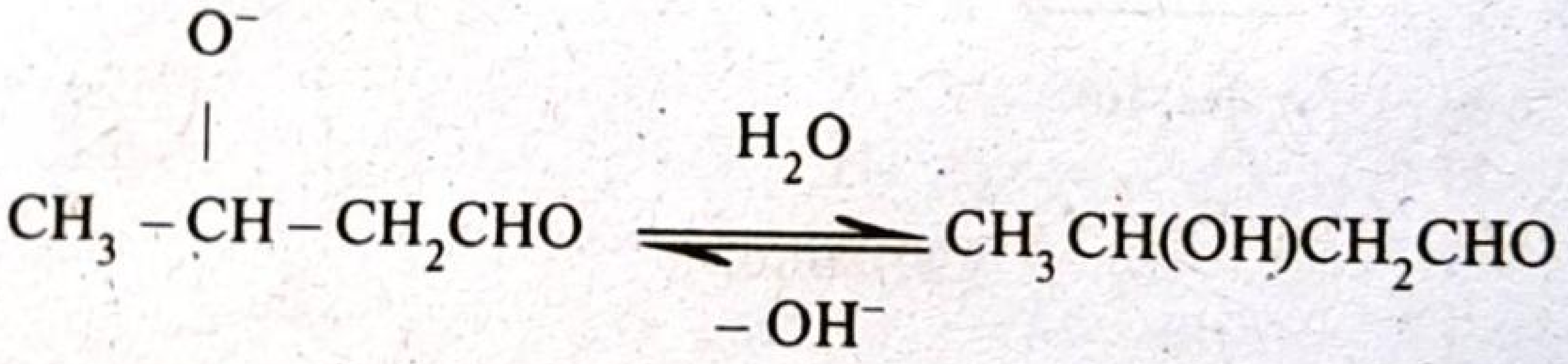
1. Addition reactions

Carbanion + Carbonyl group of an aldehyde or ketone ⟶ Product

$$\text{E.g., Acetaldehyde} \xrightarrow{-OH^-} \text{Aldol}$$

Mechanism

$$CH_3CHO \underset{H_2O}{\overset{OH^-}{\rightleftharpoons}} :CH_2CHO \overset{CH_3CHO}{\rightleftharpoons}$$

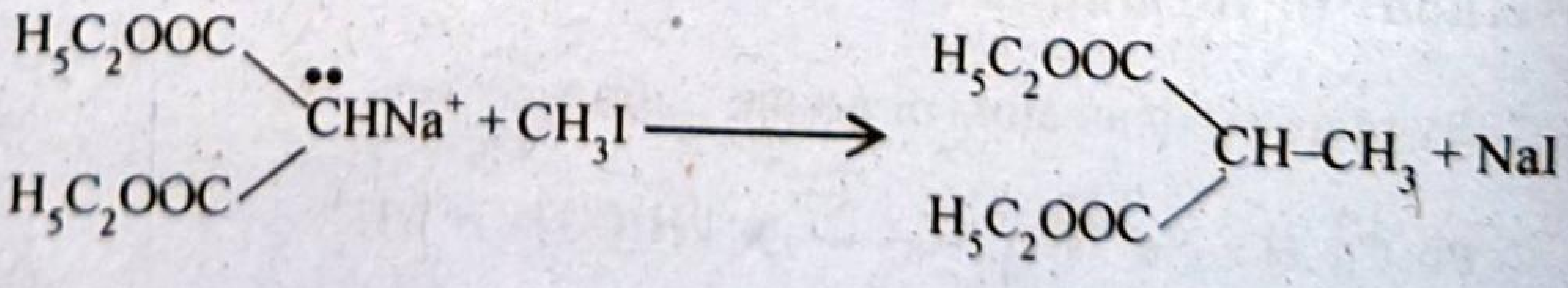


$$CH_3-\overset{\overset{O^-}{|}}{C}H-CH_2CHO \underset{-OH^-}{\overset{H_2O}{\rightleftharpoons}} CH_3CH(OH)CH_2CHO$$

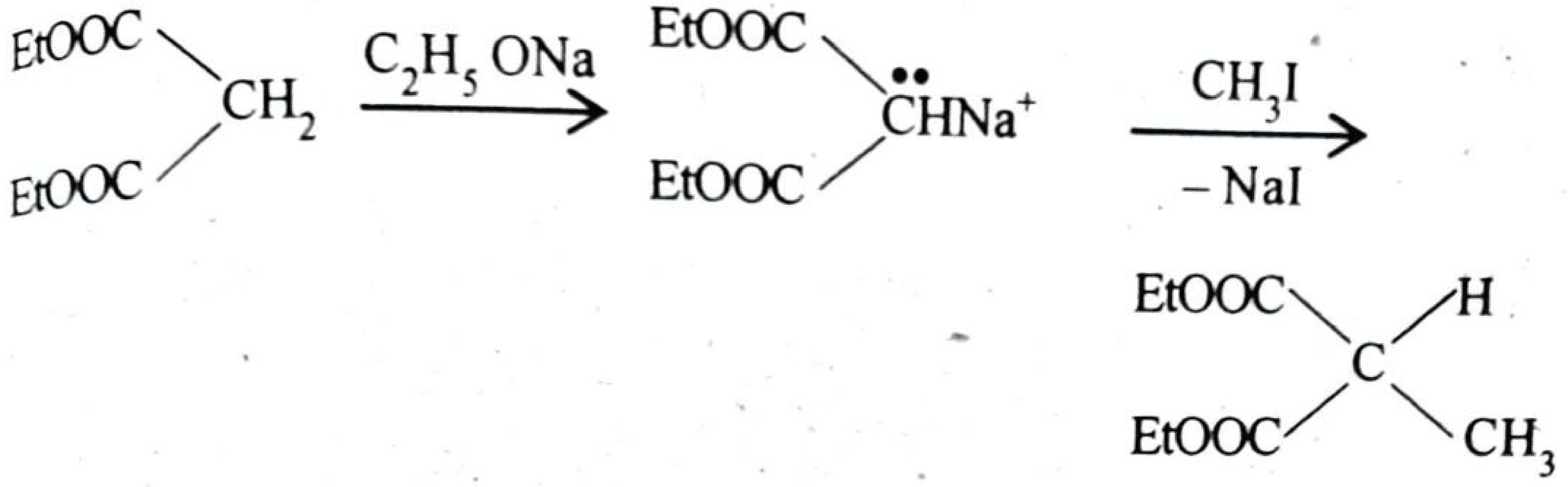
A number of the condensation reactions like Clasien condensation, Perkin condensation are also good examples of addition reactions of carbanions.

2. Substitution reactions :

Sodium salt of malonic ester + alkyl halide alkyl substituted malonic ester.



Mechanism :



The synthetic applications of malonic ester acetoacetic ester and cyanoacetic ester are based on the fact that carbanions are easily formed from the esters.

Stability of carbanions :

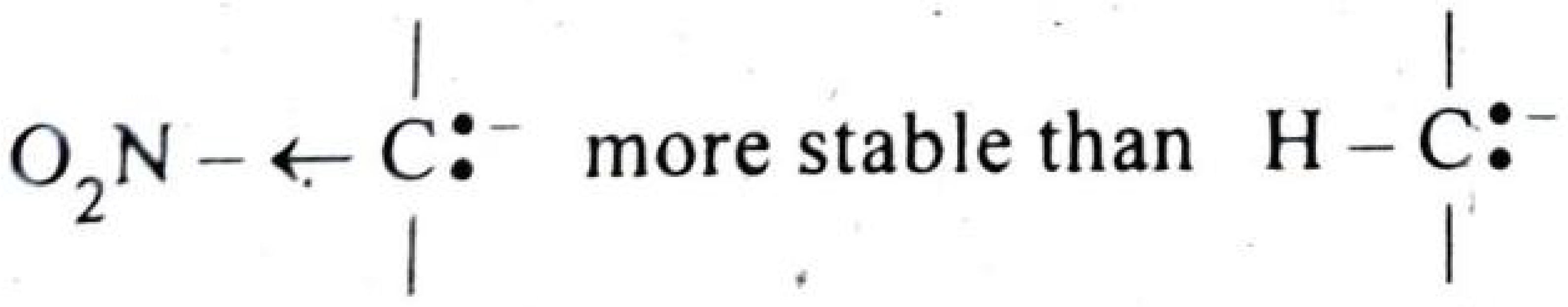
i. Electron donating substitutents decrease the stability of carbanions and electron with drawing substitutents increase the stability of carbanions.

If alkyl groups are attached to the negatively charged carbon atom, they have an electron releasing effect (+I effect). So alkyl groups increase the negative charge of the carbon atom to which they are attached. Thus alkyl groups decrease the stability of carbanions.

A tertiary carbanion, has three alkyl groups. So it is less stable than a secondary carbanion, with two alkyl groups. A secondary carbanion, in turn is less stable than a primary carbanion with only one alkyl group. Methyl carbanion has no methyl groups. So it is the most stable carbanion. Thus the stability of carbanions decrease in the following order.

Methyl > Primary > Secondary > Tertiary

ii. The stability of carbanions is increased by electron attracting groups like $-NO_2$ $>C=O$ etc., if they are attached to the carbon containing the negative charge.

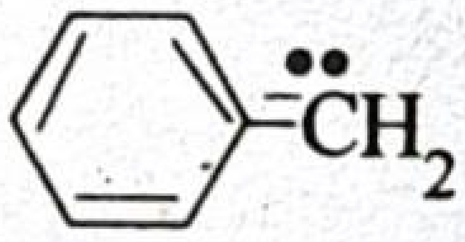


$$O_2N - \leftarrow \overset{|}{\underset{|}{C}}{:}^{-} \text{ more stable than } H - \overset{|}{\underset{|}{C}}{:}^{-}$$

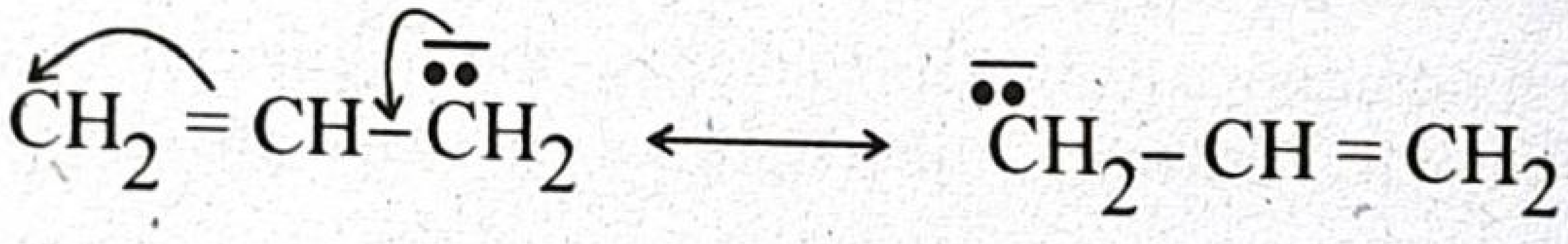
iii. Carbanions becomes stabilised if the negatively charged atom is attached to another group which delocalises the negative charge by resonance.

E.g., The order of stability of the following carbanions is as follows.

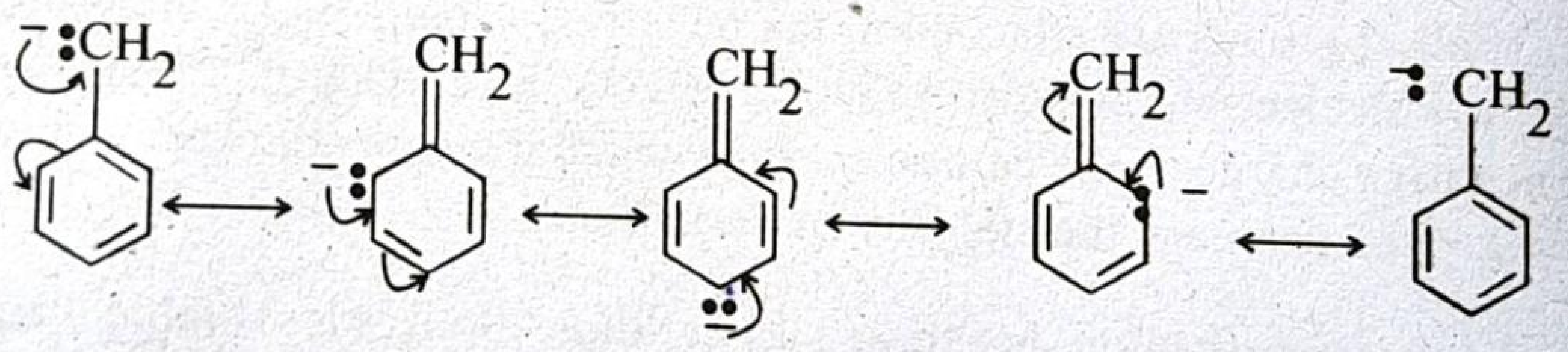
propyl < allyl < benyl

$CH_3CH_2\overset{\bullet\bullet}{^-C}H_2 < CH_2=CH-\overset{\bullet\bullet}{^-C}H_2 <$ 

In propyl carbanion, resonance is not possible. In allyl carbanion, there are two canonical structures possible. So it is more stable than propyl carbanion. In banzyl carbanion five canonical structures are possible. Hence it is the most stable of the three carbanions.



$$CH_2=CH-\overset{\bullet\bullet}{\bar{C}}H_2 \longleftrightarrow \overset{\bullet\bullet}{\bar{C}}H_2-CH=CH_2$$



Resonance becomes possible because the carbanion carbon is in an sp^2 hybridised state and hence it is flat. It has an unhybridised p orbital which is prependicular to the plane of the molecule. So the pi electrons of the benzene ring easily undergo resonance with the electrons on the carbanion and stabilise it.

Carbenes :

Carbenes are neutral species having a carbon atom with two bonds and two electrons.

$-\ddot{C}-$ From example : Methylene ($H_2C:$)

Carbenes are highly reactive. They act as strong electrophiles because they can accept a pair of electrons to complete their outer shell.

Fromation :

Carbenes may be generated in a number of ways :

1. By reaction of chloroform in the presence of a strong alkali on alkoxides.

$$CHCl_3 + R\bar{O}\colon \xrightarrow{OH^-} ROH + Cl_3\bar{C}\colon$$

$$Cl_3\bar{C}\colon \longrightarrow Cl_2C\colon + \bar{Cl}\colon$$

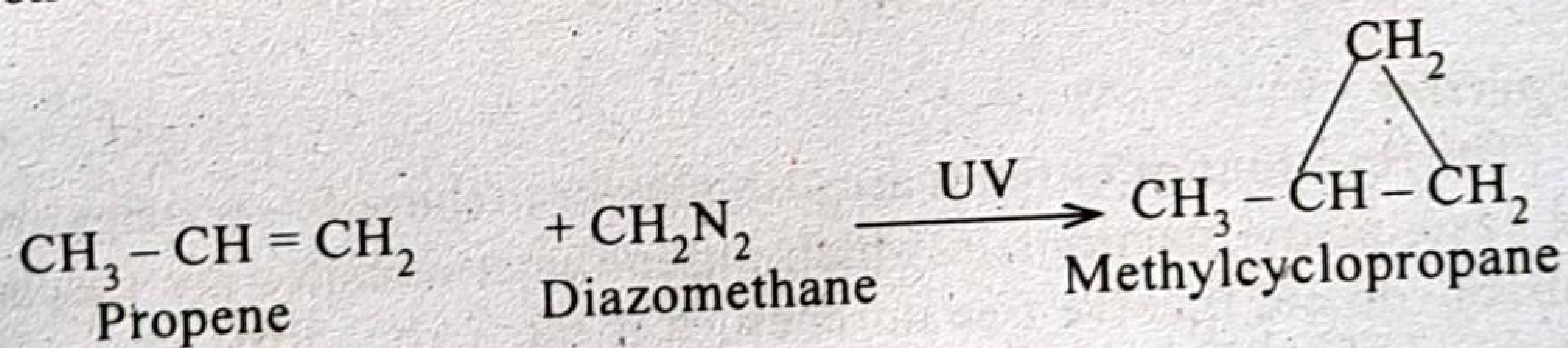
2. By decomposition of diazomethane or ketene in the presence of UV light.

$$\underset{\text{Diazomethane}}{H_2C=\overset{+}{N}=\bar{N}} \xrightarrow{UV} H_2C\colon + N_2$$

$$\underset{\text{Ketene}}{H_2C=C=O} \xrightarrow{UV} H_2C\colon + CO$$

Reactions :

An important reaction of carbenes is their addition to a carbon - carbon double bond to form a cyclopropane derivative.



Nitrenes :

Nitrenes, R–N are the nitrogen analogs of carbenes. Nitrenes are too reactive for isolation under ordinary conditions. Alkyl nitrenes have been isolateld by trapping in matrices at 4K, while aryl nitrenes, which are less reactive, can be trappepd at 77K. The ground state of NH and probably of most nitrenes, is a triple, though nitrenes can be generated in both triplet and singlet states.

In additions of EtOOC – N to C = C double bonds two species are involved.

$R-\underline{\overline{N}}$ $\qquad$ $R-\underset{\bullet}{N}\bullet$

Singlet $\qquad$ Triplet

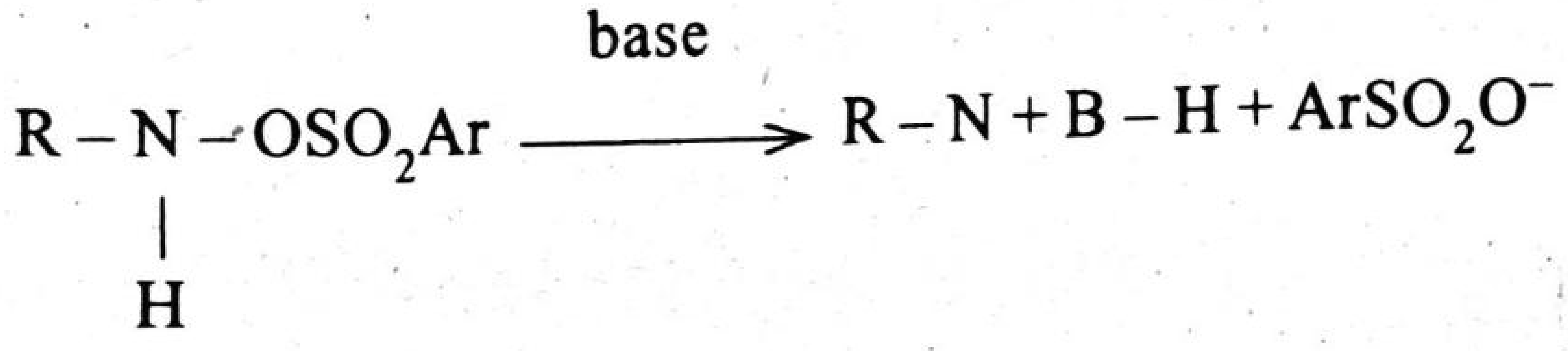
One of which adds stereospecifically and the other not. By analogy with Skell's proposal involving carbenes these are taken to be singlet and triplet species, respectively.

Formation :

The two principal means of generating nitrenes are analogous to those used to form carbenes.

1. *Elimination :*

When sulphonyl derivatives in presence of a base undergo elimination to form nitrene.



$$R-\underset{\underset{H}{|}}{N}-OSO_2Ar \xrightarrow{\text{base}} R-N+B-H+ArSO_2O^-$$

2. *Breakdown of certain double bond compounds :*

The most common method of forming nitrenes is photolytic or thermal decomposition of azides.

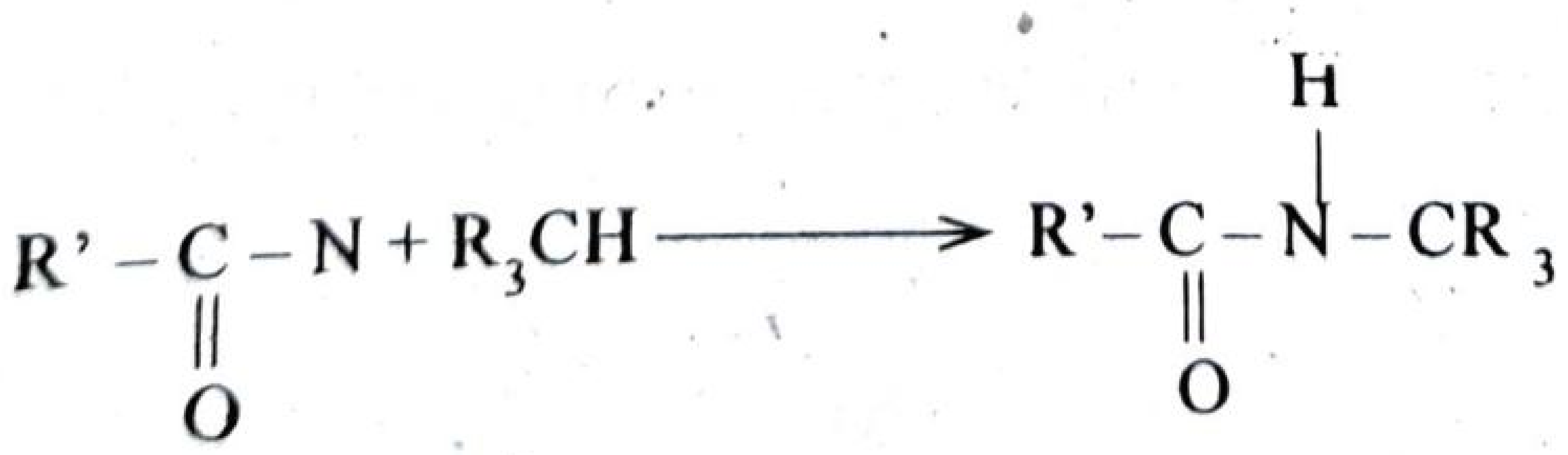
$$\underset{\text{azides}}{R-N=\overset{+}{N}=\overline{N}} \xrightarrow{\Delta} R-N + N_2$$

Properties :

The reactions of nitrenes are also similar to those fo carbenes. As in that case, many reactions in which nitrene intermediates are suspected probably do not involve free nitrenes. It is often very difficult to obtain proof in any given case that a free nitrene is or is not an intermediate.

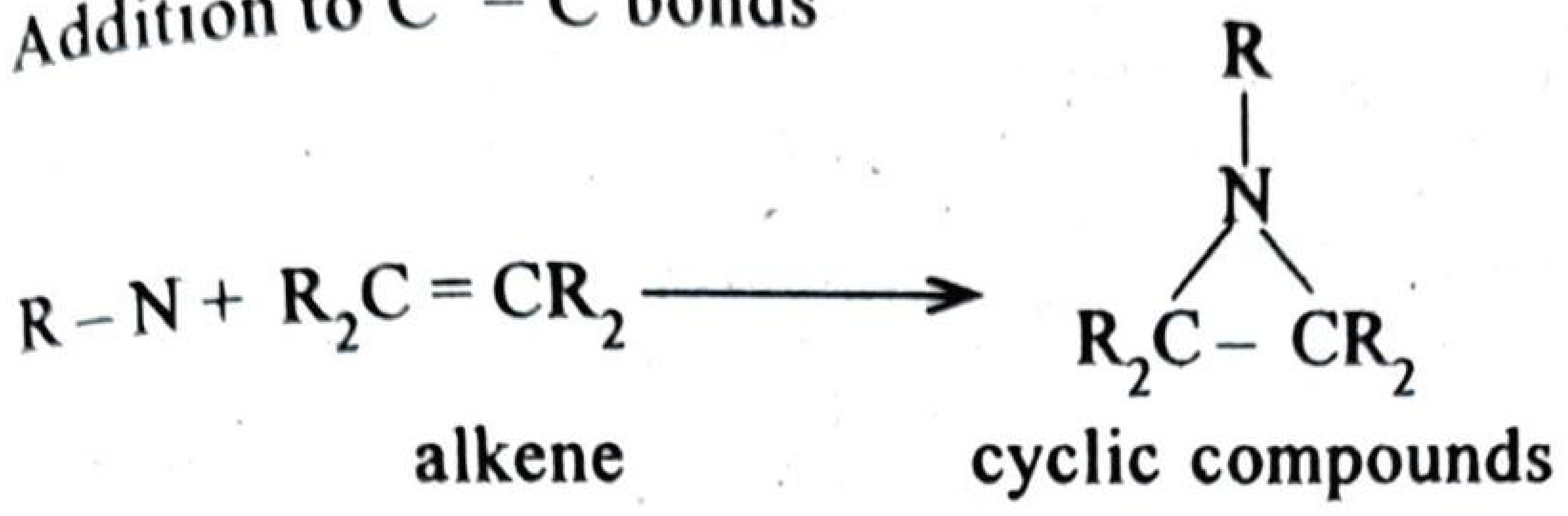
1. *Insertion :*

Nitrenes, especially acyl nitrenes and sulfonyl nitrenes, can inert into C – H and certain other bonds, e.g.,



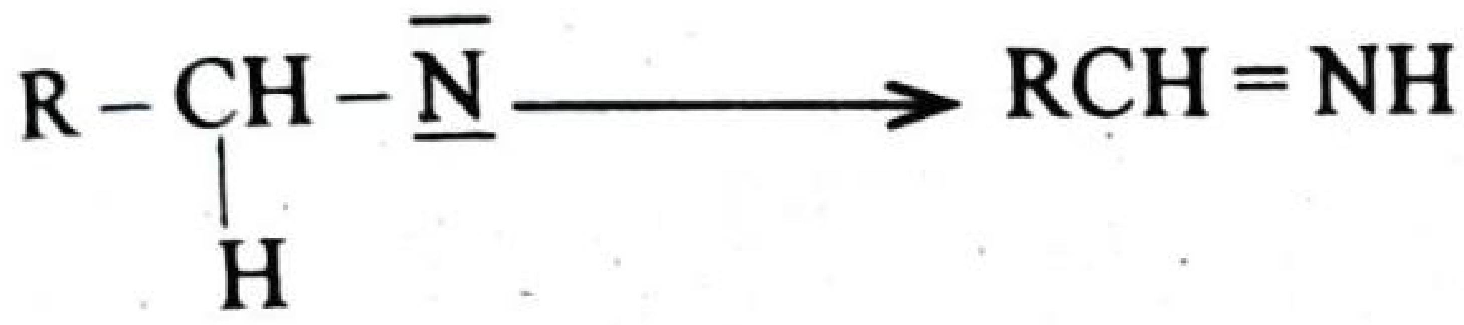
$$R'-\underset{\underset{O}{\|}}{C}-N+R_3CH \longrightarrow R'-\underset{\underset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-CR_3$$

2. *Carbon - Carbon double bonds :*
Addition to C = C bonds



3. *Rearrangements :*

Alkyl nitrenes do not generally give either of the two preceding reactions because rearrangement is more rapid. e.g,



$$R-\underset{\displaystyle H}{\underset{|}{C}}H-\overline{\underline{N}} \longrightarrow RCH=NH$$

Such arrangements are so rapid that it is usually difficult to exclude the possiblility that a free nitrene was never present at all i.e., that migration takes place at the same time that the nitrene is formed.

4. *Abstraction e.g.,*

$$R-N+R-H \longrightarrow R-\dot{\underline{N}}-H+R$$

5. *Dimerization :*

One of the principal reactions of NH is dimerization to dimide N_2H_2. Azobenzenes are often obtained in reactions where aryl nitrenes are implicated.

$$2Ar-N \longrightarrow Ar-N=N-Ar$$

It would thus seem that dimerization is more important for nitrenes than it is for carbenes, but again it has not been proved that free nitrenes are actually involved.

Arynes (or) Benzynes :

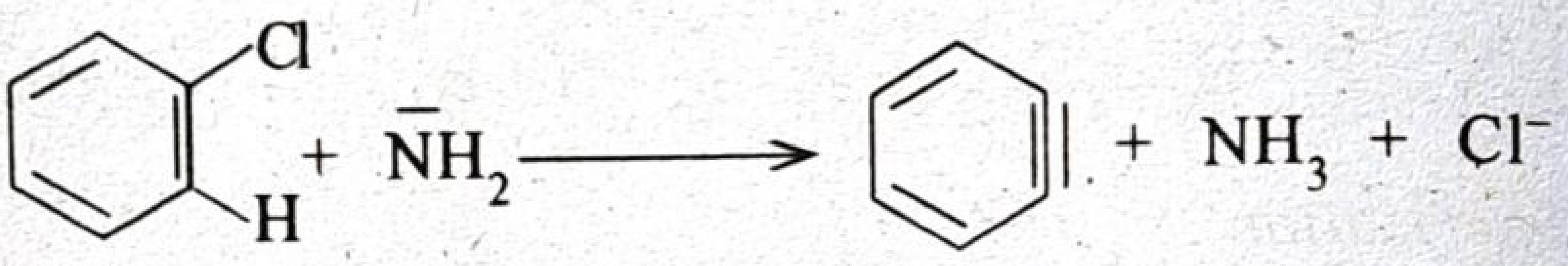
Arynes are also called benzynes. Benzynes are very reactive intermediates and they are not isolated under ordinary conditions. Benzyne has been isolated in an argon matrix at 8K, where its IR spectram could be observed.

I Benzene II

The presence of extra pair of electrons does not affect the aromaticity of ring. The original sextet still functions as a closed ring and the two additional electrons are merely located in a π - orbital that covers only two carbons. The benzyne intermediate is stablished by the **resonance**.

Formation : When chloro benzene is treated with potassium amide two types of amines (a) and (b) are obtained. This can be explained only by the formation of benzyne intermediate. This reaction involves the following two steps.

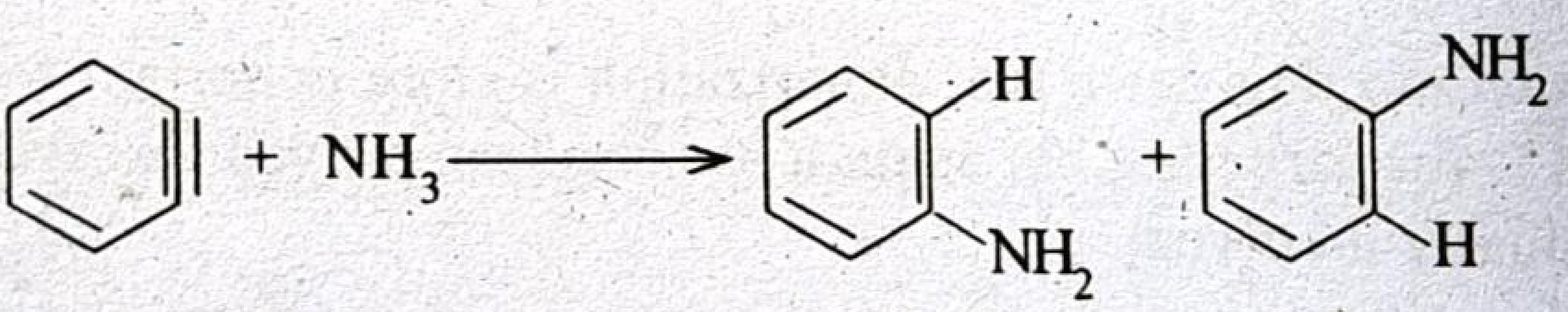
Step - I :



chloro benzene

Benzyne

Step - II :



(a) (b)

amines

The symmetrical benzyne intermediate can be attached by the NH_3 at either of the two positions forming the products (a) and (b).

THERMODYNAMICS AND KINETIC ASPECTS

Hammond's postulates

The precise structure of an unstable intermediate is far better understood than the transition state. It is helpful to regard an intermediate as a model for the transition state which reflects on the rate of a reaction. Thus the transition state may have some character of the intermediate formed in a reaction. The Hammond postulate states that the structure of the transition state for a reaction step is closer to that of the species to which it is closer in energy. The application of Hammond postulate to explain pregio selectiving of bromination versus chlorination.

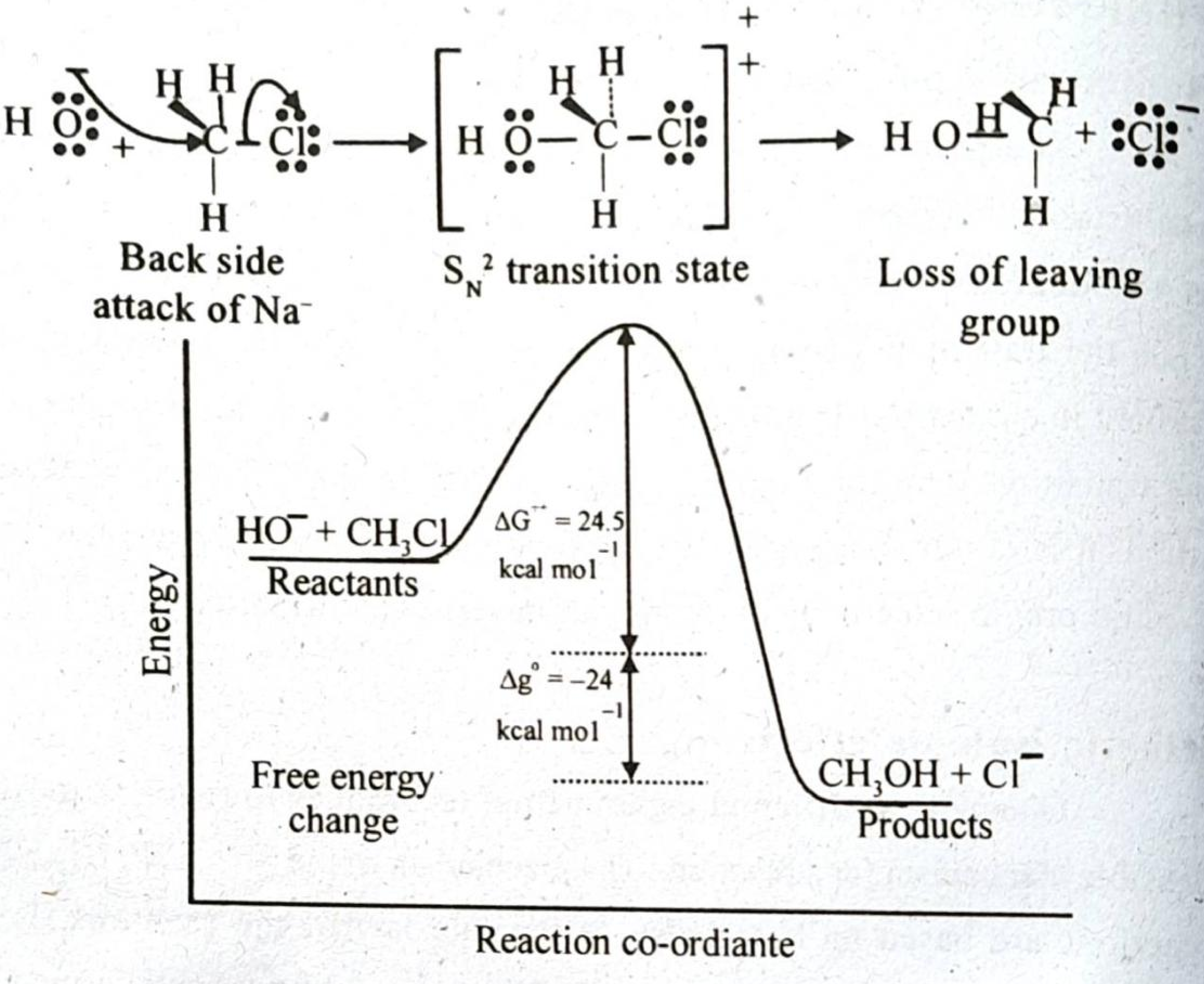
Kinetic isotopic effects

Chemist use different experimental techniques to reach at most possible mechanism for a reaction. The mechanism of the SN^1, SN^2, E1, E2 reactions are based on knowledge of the rate law of the reaction.The relative reactivity of the reactants and the structure of the products formed. Another powerful experimental evidence to investigate the mechanism of a reaction is the deuterium kinetic isotope effect. The ratio of the rate constant observed for a related compound in which one or more of the hydrogens are replaced by deuterium an isotope of hydrogen.

$$\text{Deuterium kinetic isotopic effect} = \frac{KH}{KD} = \frac{\text{Rate of H contain reason}}{\text{Rate constant for D-containing reactor}}$$

Energy profile diagrams

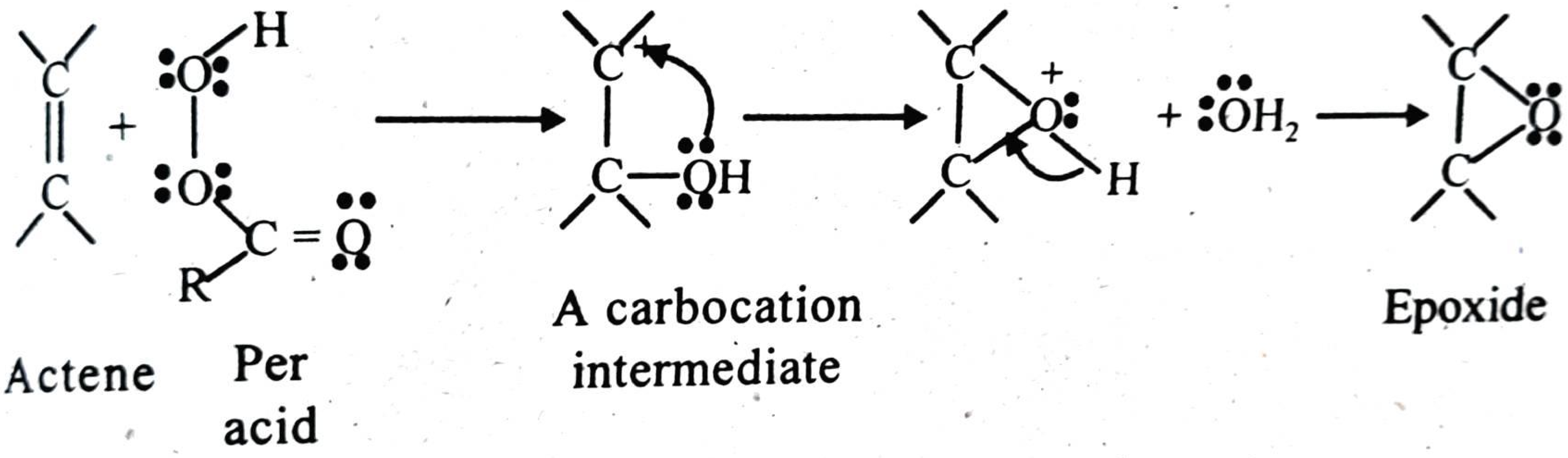
Organic chemistry generally represents the course of a reaction through an energy profile diagram. The interpretation of simple SN^2 is grown in figure.



A potential energy diagram for the reaction of methyl chloride with hydroxide. The energy profile diagram is applied to the concept of transition state and activation energy. This is useful energy profile diagram for one step reaction without intermediate. For the reaction to occur, free energy of activation ΔG_T^+ must be added. The vertical axis of the energy profile depicts the total free energy of all the species involved the reaction. The horizontal axis is called the reaction co-ordinates which reflect the progress of the reaction.

Product analysis

A mechanism proposed for a reaction must account for all products as well as for their relative properties. Olefinic double bond react with per acids to give epoxies and the reaction is an electrophilic attack on the olefin. Electron releasing group in the olefin and electron is an electrophilic attack on the olefin.



Crossover experiments

Intra or intermolecular name of a rearrangement can often be demonstrated by carrying out the reaction on a mixture and then the anlysing products. For example Hoffmann reaction.

$$RCONH_2 \longrightarrow RNH_2$$