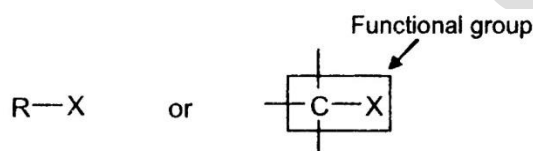


CHAPTER 5

ALKYL HALIDES AND AMINES

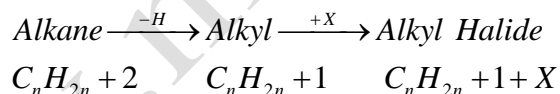
Alkyl halides are the halo derivatives of alkanes. When a hydrogen or many hydrogens of an alkane are replaced by halogens, the resulting compound is known as alkyl halide. Alkyl halides are compounds in which a halogen atom is attached to carbon. The compounds containing C, H and halogen are called alkyl halides. The functional group of these compounds is halide (-X).

Alkyl halides are represented by R-X, where R is an alkyl and X is functional group (halide).

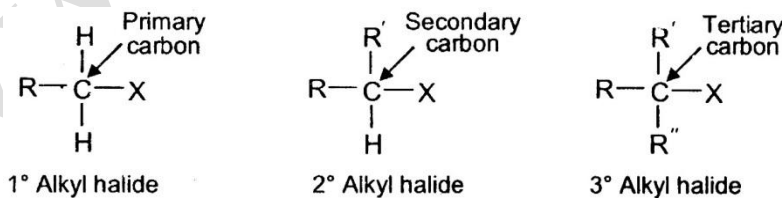


where R = alkyl group; X = Cl, Br, I, or F. The halogen atom bonded to carbon is the functional group of alkyl halides.

The general formula of alkyl halides is $C_nH_{2n+1}X$.



Types of alkyl halides: Alkyl halides are classified as *Primary* (1°), *Secondary* (2°), or *Tertiary* (3°), depending upon whether the X atom is attached to a primary, secondary, or a tertiary carbon.

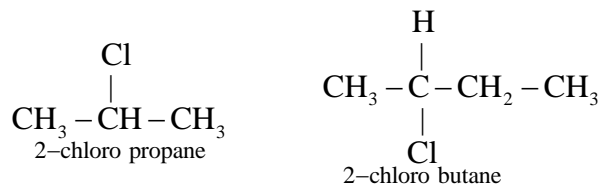


Primary alkyl halides: Alkyl halides in which halogen atom is directly attached to a primary carbon are called primary alkyl halides.

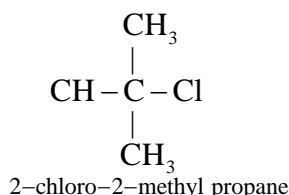
Example:



Secondary alkyl halides: The alkyl halides in which halogen atom is directly attached to a secondary carbon atom are called secondary alkyl halides.



Tertiary alkyl halides: Alkyl halides in which halogen atom is directly attached to tertiary carbon atom are called tertiary alkyl halides.

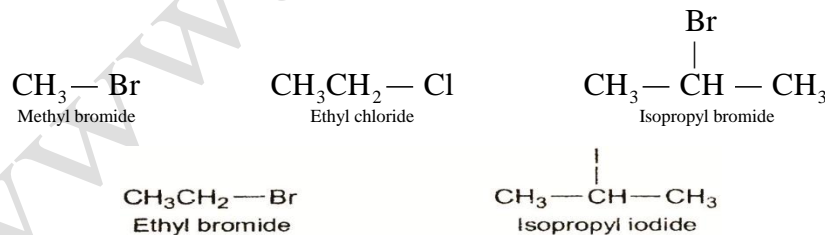


Alkyl halides are among the most useful organic compounds. They are frequently used to introduce alkyl groups into other molecules.

Nomenclature

Alkyl halides are named in two ways:

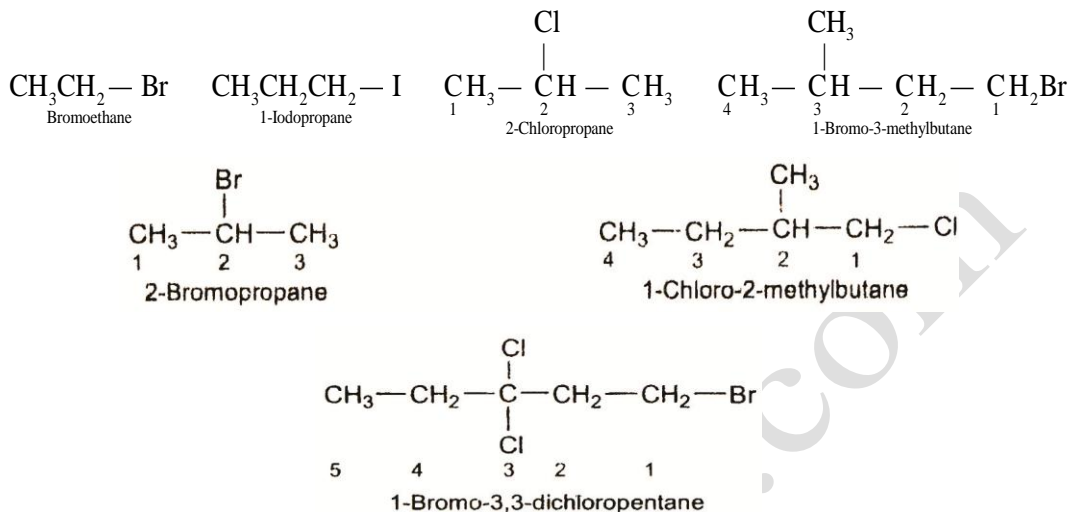
Common System: In this system the alkyl groups attached to the halogen atom is named first. This is then followed by an appropriate word *chloride*, *bromide*, iodide or *fluoride*. Notice that the common names of alkyl halides are two-word names. In case of primary, secondary and tertiary alkyl halides, the word *pri*, *sec*, and *ter* are written before the names of alkyl halides.



IUPAC System: The IUPAC names of alkyl halides are obtained by using the following rules:

- Select the longest carbon chain containing the halogen atom and name the alkyl halide as a derivative of the corresponding hydrocarbon.
- Number the chain so as to give the carbon carrying the halogen atom the *lowest* possible number.
- Indicate the position of the halogen atom by a number.
- Prefix the name of the alkane by the *fluoro-*, *chloro-*, *bromo-*, or *iodo-*.

- (e) Name other substituents and indicate their positions by numbers.
Notice that the IUPAC names of alkyl halides are one-word names.



Physical Properties

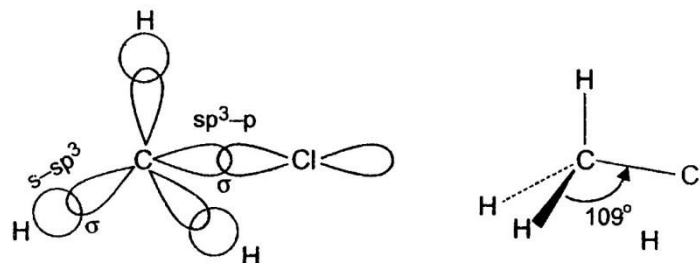
- (1) CH_3Cl , CH_3Br , CH_3F , and $\text{CH}_3\text{CH}_2\text{Cl}$ are gases at room temperature. Other alkyl halides up to C_{18} are colourless liquids. Those beyond C_{18} are colourless solids.
- (2) Alkyl halides are insoluble in water but soluble in organic solvents. The insolubility in water is due to their inability to form hydrogen bonds with water.
- (3) Alkyl bromides and iodides are denser than water. Alkyl chlorides and fluorides are lighter than water.
- (4) Alkyl halides have higher boiling points than alkanes of comparable molecular weight. For a given halogen atom, the boiling points of alkyl halides increase with the increase in the size of the alkyl group. For a given alkyl group, the boiling points of alkyl halides follow the order $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$.

Boiling Points of Some Alkyl Halides

Name	Structure	bp ^o C
Methyl chloride	CH_3Cl	-24 (gas)
Methyl bromide	CH_3Br	5 (gas)
Methyl iodide	CH_3I	43 (liquid)
Ethyl chloride	$\text{CH}_3\text{CH}_2\text{Cl}$	13 (gas)
Ethyl bromide	$\text{CH}_3\text{CH}_2\text{Br}$	38 (liquid)
Ethyl iodide	$\text{CH}_3\text{CH}_2\text{I}$	72 (liquid)

Structure

Let us consider methyl chloride (CH_3Cl) for illustrating the orbital make up of alkyl halides. In methyl chloride, the carbon atom is sp^3 hybridized. The chlorine atom has a half-filled p orbital in its valence shell. The C–Cl bond is formed by the overlap of an sp^3 orbital of carbon and the half-filled p_z orbital of chlorine atom. Each C–H bond is formed by the overlap of an sp^3 orbital of carbon and the s orbital of hydrogen. All bonds are σ bonds. The H–C–H and H–C–Cl bond angles are tetrahedral.

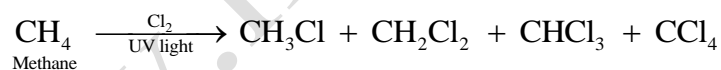


Orbital structure of Methyl chloride

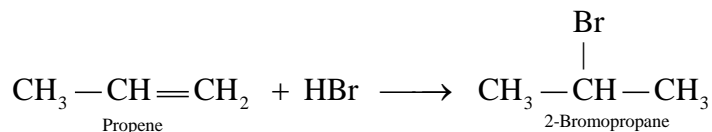
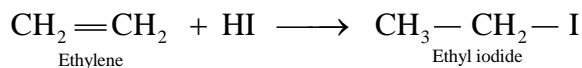
Methods of Preparation

Alkyl halides can be prepared by the following methods:

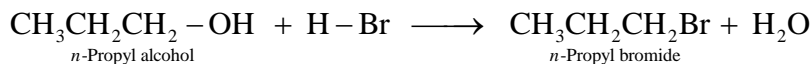
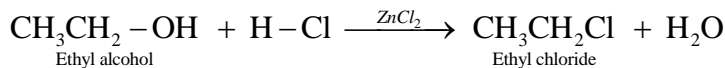
(1) **Halogenation of Alkanes:** Alkanes react with Cl_2 or Br_2 in the presence of UV light or at high temperature (400°C) to give alkyl halides along with polyhalogen derivatives.



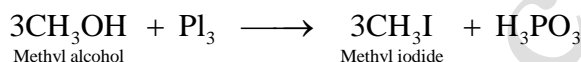
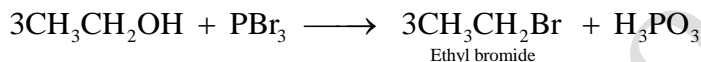
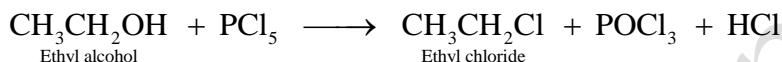
(2) **Addition of Halogen Acids to Alkenes:** Halogen acids (HCl , HBr , HI) add to alkenes to yield alkyl halides. The mode of addition follows *Markovnikov rule*, except for the addition of HBr in the presence of organic peroxides ($\text{R}-\text{O}-\text{O}-\text{R}$).



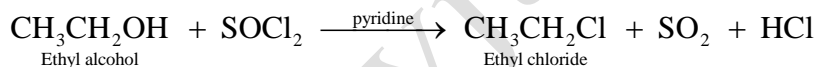
(3) **Action of Halogen Acids on Alcohols:** Alcohols react with HBr or HI to produce alkyl bromides or alkyl iodides. Alkyl chlorides are produced by the action of *dry* HCl in the presence of zinc chloride catalyst.



(4) Action of Phosphorus Halides on Alcohols: Alcohols react with phosphorus halides (PX_5 or PX_3) to form alkyl halides.



(5) Action of Thionyl Chloride on Alcohols: Alcohols react with thionyl chloride (SOCl_2) in the presence of pyridine to produce alkyl chlorides. Pyridine ($\text{C}_5\text{H}_5\text{N}$) absorbs hydrogen chloride as it is formed.



Reactivity of alkyl halides

The bond between carbon and halogen of alkyl halides is polar. The polarity is due to the higher electronegativity of halogen atom. Carbon atom has partial positive charge while the halogen bears partial negative charge. Alkyl halides are reactive due to the polar bond between C and X. Partial positive carbon atom of alkyl halide is a good and attractive target for the attack of nucleophile. Due to high reactivity of alkyl halides, these are widely used for the synthesis of a large number of organic compounds.

The reactivity of alkyl halides can be explained in three ways.

- 1. Polarity of the carbon halogen bond:** Greater the electronegativity of halogen atom, more polar will be the bond and hence its reactivity will be more. The reactivity order of alkyl halides on the basis of bond polarity is $\text{R-F} > \text{R-Cl} > \text{R-Br} > \text{R-I}$.
- 2. Strength of the carbon halogen bond:** Stronger the bond between carbon and halogen in alkyl halide, high will be its bond energy and less will be its reactivity. The reactivity order of alkyl halides on the basis of bond strength is $\text{R-I} > \text{R-Br} > \text{R-Cl} > \text{R-F}$.

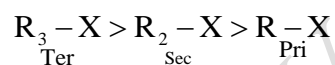
Thus the strength of carbon-halogen bond decreases from fluorine to iodine due

to their bond energies.

C-X Bond	Bond energy (kJ.mol ⁻¹)
C-F	467
C-Cl	346
C-Br	290
C-I	228

This shows that Iodo compounds are most reactive while Fluoro compounds are least reactive.

- 3. Nature of the alkyl group:** Smaller the alkyl group present more will be the polarity of the alkyl halide and more will be its reactivity. Alkyl group is an electron releasing group so greater the number of alkyl groups more will be the polarity of the alkyl halide and high will be the reactivity. Tertiary alkyl halides are more reactive than secondary which are more reactive than primary.



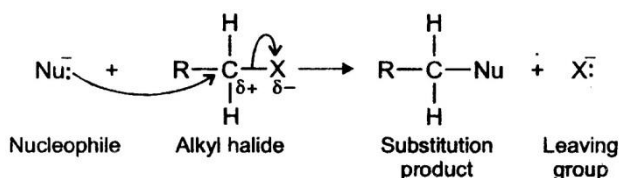
Experimental order of reactivity: Experimentally the bond energy of C-X decides the reactivity of alkyl halides and not the polarity of the bond. So the experimental order of the reactivity of alkyl halides is $R-I > R-Br > R-Cl > R-F$.

Chemical Properties

Alkyl halides are very reactive compounds. They undergo *substitution*, *elimination*, and *reduction* reactions. Alkyl halides also react with metals to form organometallic compounds.

1. Substitution Reactions

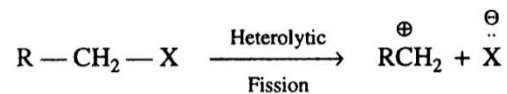
The carbon-halogen bond in alkyl halides is *polar* because of the high electronegativity of the halogen atom relative to carbon. The carbon atom is therefore a good target for attack by nucleophiles (electron rich species). In fact, the nucleophilic substitution reactions are the most common reactions of alkyl halides. These may be represented as:



Important concepts in aliphatic nucleophilic substitution reactions

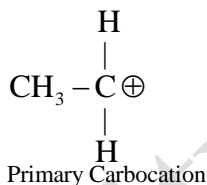
Carocations or carbonium ions: These are defined as the species in which the positive charge is carried by the carbon atom with six electrons in its valence shell. These are formed by the heterolytic fission in which an atom or group along with its

pair of electrons leaves the carbon. In heterolytic fission, the shared pair of electrons between two atoms goes to one atom only. When halogen atom detaches (as halide ion, X^-) from the carbon atom of an alkyl halide, the substrate is converted into a positively charged ion. This ion in which carbon atom bears positive charge is called carbonium ion.

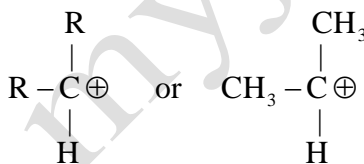


Types of carbocations: There are three types of carbocations.

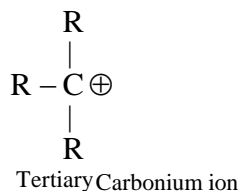
(i) **Primary Carbocation:** In primary carbocation the positive charge is on the primary carbon atom.



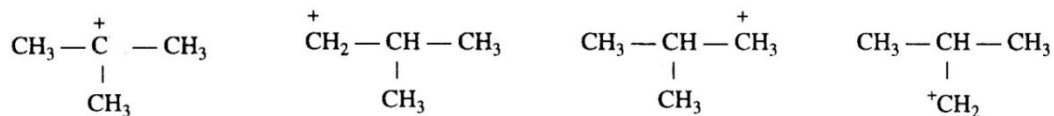
(ii) **Secondary Carbocation:** In secondary carbocation the positive charge is on the secondary carbon atom.



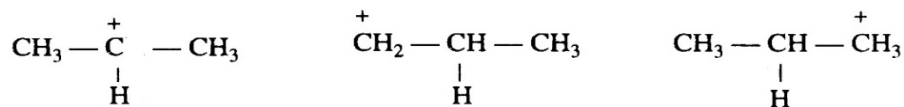
(iii) **Tertiary Carbocation:** In tertiary carbocation the positive charge is on the tertiary carbon atom.



Stability of the carbonium ion: The migration of hydrogen along with an electron pair to the positive centre takes place which results in the formation of more stable carbocation. This shifting is called hyperconjugation. Due to hyperconjugation a tertiary carbocation is more stable than secondary carbocation, which in turn is more stable than primary carbocation. Greater the number of resonance structures, greater is the stability. Tertiary carbocation will give the maximum number of resonance structures involving hydride shift, like



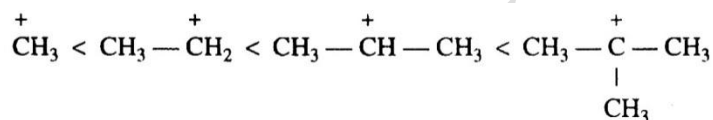
Secondary carbocation ion has less resonating structure so it is less stable than tertiary.



Primary carbocation and methyl carbocation are least stable due to two and single resonating structure.



The increasing order of stability of carbocations is:



This can further be confirmed from the bond dissociation energies of various alkyl halides.



As the bond dissociation energy of tertiary alkyl halide is low, it means that its formation is easy due to its greater stability. The bond dissociation energy of primary alkyl halide is high, as its formation is unfavourable due to its lesser stability.

Nucleophile: A reagent with an electron pair that tends to attack an electron-deficient centre is called a nucleophilic reagent or simply a nucleophile. It is electron rich specie. It donates a pair of electron in a chemical reaction. It is nucleus lover. It may be neutral molecule with lone pair of electron or may be negative ions. It is generally represented by $\bar{N} \ddot{u}$.

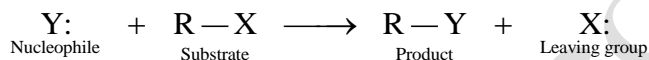
Base: Any neutral specie with a lone pair of electron or negatively charged ion can act both as a base and nucleophile, but a base has affinity for proton (hydrogen ion) while nucleophile has affinity for positively charged carbon atom. A base attacks the hydrogen atom in the elimination while a nucleophile attack carbon atom in the substitution reaction.

Substrate: An organic compound, like methyl chloride, that is attacked by a reagent is called a substrate. It is the molecule which undergoes nucleophilic substitution

reaction. In case of aliphatic nucleophilic substitution reaction alkyl halide acts as substrate.

Leaving group or nucleofuge: Part of the substrate that departs along with the electron pair, like chlorine in alkyl halide is called the leaving group. It is the group which is being replaced by the incoming nucleophile in the substitution reactions. It is also called nucleofuge.

Nucleophilic Substitution reactions: The reactions in which a part of a molecule is substituted by a nucleophile is called nucleophilic substitution and is denoted by S_N where S stands for substitution and N for nucleophilic. The nucleophilic substitution reactions are of a fairly broad nature and are generally represented as:



Alkyl halides are good substrates for nucleophilic substitution reactions because the halide ion is a good leaving group and therefore can be readily substituted by a nucleophile. Since the alkyl group at which the substitution takes place is generally aliphatic in nature, these reactions are commonly known as aliphatic nucleophilic substitution reactions. As a result of these reactions the alkyl group is attached to the nucleophile. Therefore, the nucleophile is said to be *alkylated*.

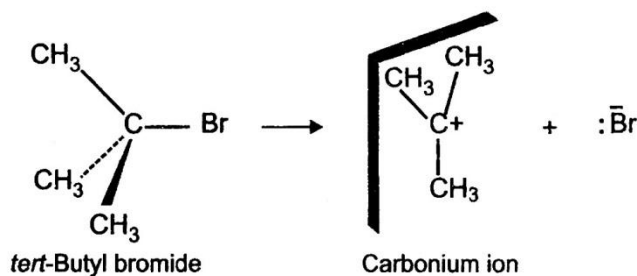
Sometimes, the solvent itself functions as a nucleophile; the reaction is then called solvolysis. Thus, a reaction in which water is used as a solvent and it also acts as a nucleophile, is called *hydrolysis* while a reaction involving methanol as a solvent and also as a nucleophile is known as *methanolysis*. *Ammonolysis* is the reaction in which ammonia acts as solvent as well as nucleophile.

Mechanism: *The mechanism of a reaction is the actual pathway through which the reaction proceeds, i.e., which bonds are broken, which are formed, and in what order; how many steps are involved and what is the relative rate of each step, etc.*

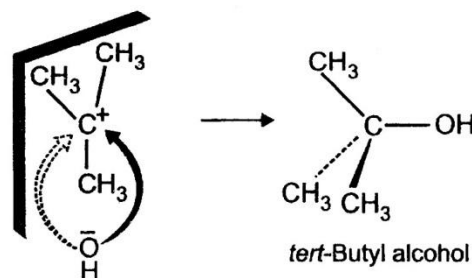
Alkyl halides can undergo nucleophilic substitution by two mechanisms S_N1 and S_N2 :

S_N1 Mechanism: The S_N1 is abbreviated from *substitution nucleophilic unimolecular*. It is a two step mechanism. Consider the hydrolysis of *tert*-butyl bromide with aqueous NaOH.

Step 1. It is a slow step which involves slow ionization of the substrate resulting in the formation of a carbocation. The alkyl halide ionizes to give a planar carbonium ion. The carbonium ion is planar because the central positively charged carbon atom is sp^2 hybridized.



Step 2. It is a fast step in which the nucleophile can attack the planar carbonium ion from either side to give the product.



Mostly the solvent itself acts as a nucleophile. The $\text{S}_{\text{N}}1$ reaction is therefore generally called *solvolysis*.

In this reaction the first step, which is the slow step, *i.e.*, the carbocation formation is the rate-determining step.

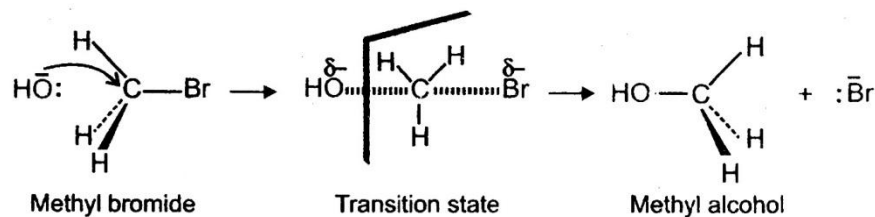
It is a *first-order* reaction, as the rate depends only on the concentration of the substrate.

$$\text{Rate} = k_1[(\text{CH}_3)_3\text{Cl}]$$

Since only one molecule, *i.e.*, the substrate is involved in the rate-determining step, this reaction is called a unimolecular reaction.

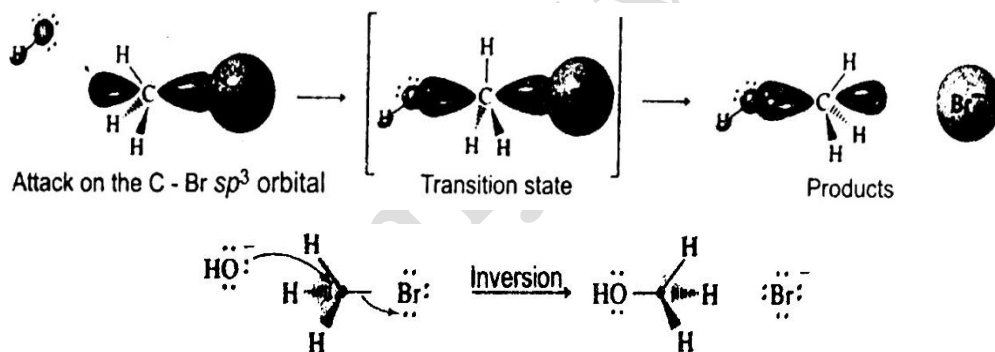
$\text{S}_{\text{N}}2$ Mechanism: $\text{S}_{\text{N}}2$ stands for *substitution nucleophilic bimolecular*. It is a single step mechanism. No carbonium ion is formed. In this mechanism, the attack of the nucleophile and the ejection of the halide ion take place simultaneously. In this mechanism the nucleophile attacks the substrate from the side opposite to the leaving group. *i.e.*, from the *backside* as the front side is blocked by the halogen atom. As the nucleophile starts making the bond with the central carbon atom of the substrate, the leaving group starts leaving it and in the transition state both the nucleophile and the leaving group are loosely bound to the carbon atom such that at no time the carbon atom has more than eight electrons in its outer shell. The extent of bond formation on one side is equal to the extent of bond breaking on the other side. Finally the bond between the leaving group and substrate is completely broken while the bond between the entering group and substrate is formed completely. The hybridization of the

central carbon atom changes from sp^3 in the substrate to sp^2 in the transition state and again to sp^3 in the product. Consider the example of the hydrolysis of methyl bromide by aqueous NaOH. The reaction and the transition state are shown in the figure.



Nucleophilic substitution by S_N2 mechanism

The S_N2 reaction takes place through nucleophilic attack on the back lobe of carbon's sp^3 hybrid orbital. This back-side attack inverts the carbon atom's tetrahedron, like the wind inverts an umbrella. Since the nucleophile attacks the substrate from the backside, inversion of configuration should take place.



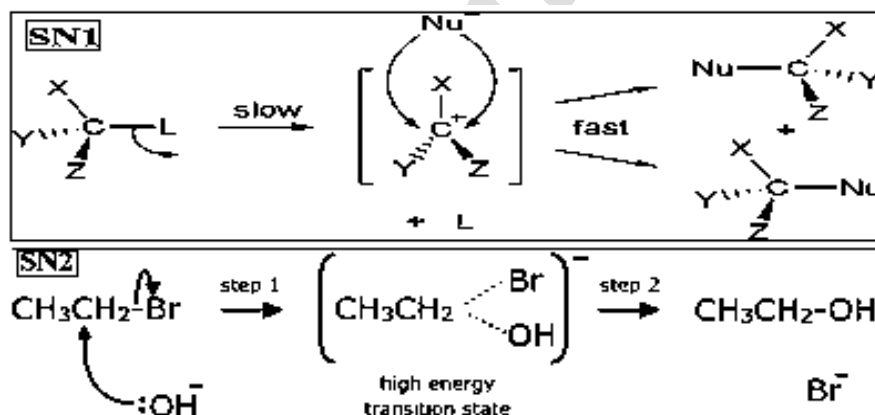
Since two molecules, *i.e.*, the nucleophile and the substrate, are involved in the rate-determining step, so this reaction is said to be *bimolecular*.

$$\text{Rate} = k_2[\text{CH}_3\text{I}][\text{OH}^-]$$

Remember that the primary alkyl halides undergo substitution by S_N2 mechanism. The tertiary alkyl halides undergo substitution by S_N1 mechanism. This is because the attack of the nucleophile on the crowded tertiary alkyl halide is quite difficult. The secondary alkyl halides may undergo nucleophilic substitution by either S_N1 or S_N2 mechanism depending on the solvent. S_N1 mechanism will predominate if an ionizing solvent is present. S_N2 mechanism will predominate in case of non-polar solvent.

Difference Between S_N1 and S_N2 Reactions

S_N1 Reactions	S_N2 Reactions
1. It is two-step mechanism.	1. It is one-step mechanism.
2. Rate depends only on concentration of alkyl halide.	2. Rate depends on concentration of alkyl halide and nucleophile.
3. It is unimolecular.	3. It is bimolecular.
4. Occurs in tertiary alkyl halides.	4. Occurs in primary alkyl halides.
5. Reaction is favoured by polar solvents.	5. Reaction is favoured by non-polar solvents.
6. Reaction can occur with weak nucleophile.	6. Reaction requires strong nucleophile.
7. It is first order reaction.	7. It is second order reaction.
8. Either side attack of the nucleophile.	8. Back side attack of the nucleophile.
9. Formation of carbonium ion.	9. Formation of transition state.
10. Retention of configuration.	10. Inversion of configuration.

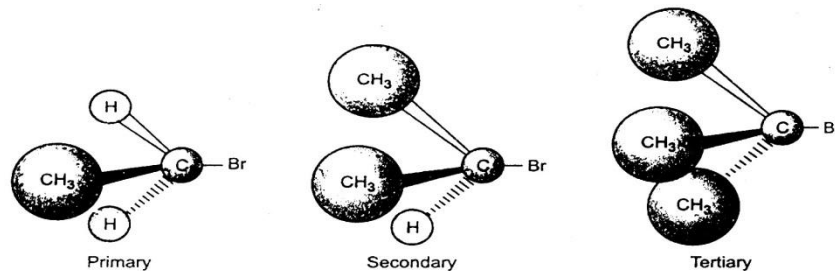


Factors affecting the rate of S_N1 and S_N2 mechanisms: The rate of S_N1 and S_N2 mechanisms, depends on the nature of the substrate, the nucleophile, the leaving group and the solvent.

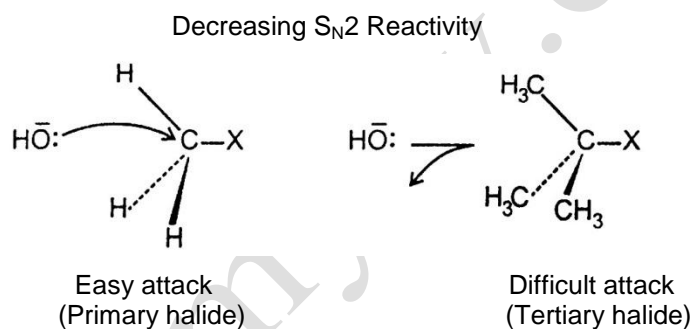
(i) Effect of the substrate: As in S_N1 mechanism there is the formation of a carbocation. The ease of formation of the carbocation depends on its stability. The greater the stability of the carbocation, the more rapidly it is formed. The order of stability of the carbocations is: Tertiary \gg Secondary $>$ Primary $>$ Methyl. So, the S_N1 reaction is more favourable for the tertiary substrates than for the secondary or primary substrates.

The S_N2 reactions proceed through a transition state. The alkyl groups

attached to the central carbon atom will make the transition state more over-crowded, and thus more unfavourable, than would do the hydrogen atoms. Also the approach of a nucleophile from the backside to a tertiary carbon atom is sterically more hindered than to a primary carbon atom. Thus, the S_N2 reactions are more favourable for the primary substrates and less favourable for the tertiary substrates.



Steric crowding in ethyl bromide, isopropyl bromide, and *t*-butyl bromide.



Generally, the primary substrates follow the S_N2 mechanism, whereas the tertiary substrates follow the S_N1 mechanism. The secondary substrates could proceed either by S_N1 or S_N2 or both mechanisms depending on the reaction conditions.

(ii) Effect of the nucleophile: Nucleophile is not involved in the rate-determining step of an S_N1 reaction. It is only the second step when the nucleophile combines with the intermediate carbocation to form the product. The rate of the S_N1 reaction is therefore not influenced by the nucleophile. In S_N1 reaction weak nucleophile is required not to attack the substrate in the presence of attached halide ion. In S_N2 mechanism, strong nucleophile is required to attack the substrate in the presence of attached halide.

(iii) Effect of the leaving group: In most of the nucleophilic substitution reactions alkyl halides are used as substrates in which halide ion acts as a leaving group. The ability of a group to act as a leaving group is usually inverse of its basicity; the weakest base is the best leaving group; (conjugate base of a strong acid is a weak base). Thus, among the halides, iodide is the best leaving group and fluoride the poorest.

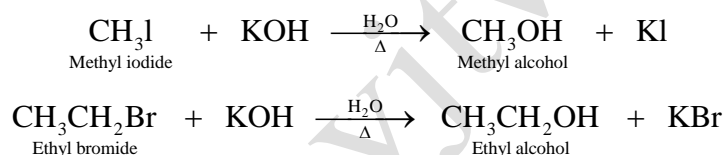
S_N1 reactions do not require powerful nucleophiles but do require good leaving group so that it may detach from the carbon easily and to form carbonium ion. On the other hand, S_N2 reactions which do require powerful nucleophiles, require bad leaving group so that it may not detach from the carbon before the nucleophilic attack.

(iv) Effect of the solvent: The nucleophilic substitution reactions are heterolytic processes that usually take place in solution. Reaction medium (solvent) can therefore play an important role in determining the mechanism and the rate of these reactions.

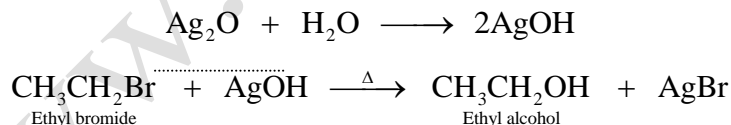
The polarity of a solvent, usually determined from its *dielectric constant*. *The greater the polarity of a solvent the greater its ability to stabilize a charged species, i.e., the greater its ionizing power.* The S_N1 reactions in which carbocations are formed in the rate-determining step are more favourable in polar solvents. In the S_N2 reactions non-polar solvent is required so that no carbonium ion may form.

Some important nucleophilic substitution reactions of alkyl halides

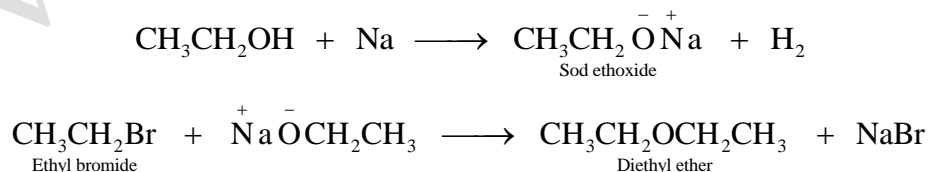
(1) Reaction with Aqueous KOH: Alkyl halides react with aqueous potassium hydroxide to form alcohols. The halogen atom is substituted by $-OH$ group.



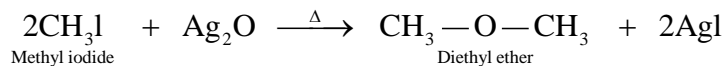
(2) Reaction with Moist Silver Oxide: Alkyl halides on treatment with a suspension of silver oxide in moist ether produce alcohols. Halogen atom is substituted by $-OH$ group.



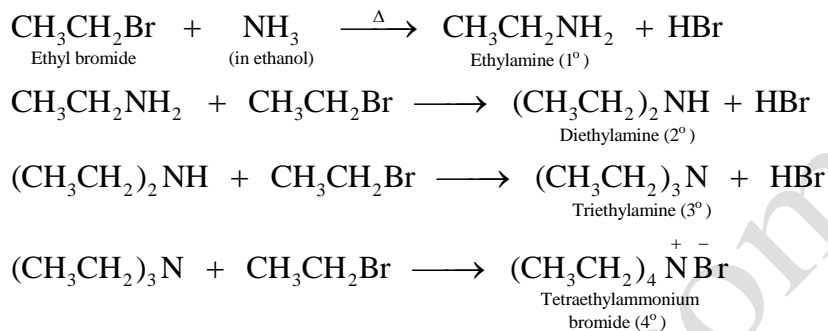
(3) Reaction with Sodium Alkoxides (Williamson Reaction): Alkyl halides react with sodium alkoxides (RONa) to form ethers. Sodium alkoxides are prepared by dissolving metallic sodium in excess of the appropriate alcohol. For example,



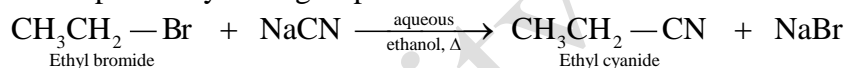
Ethers can also be produced by heating an alkyl halide with dry silver oxide.



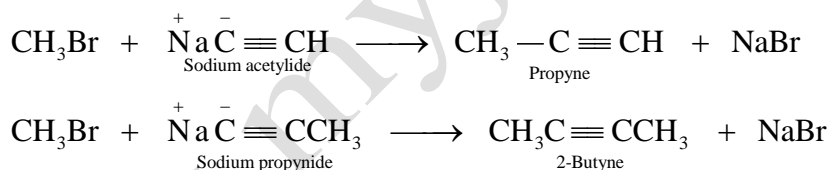
(4) Reaction with Ammonia (Hoffmann's Reaction): When an alkyl halide is heated with an alcoholic solution of ammonia in sealed tube, alkylation of ammonia takes place. A mixture of different classes of amines results.



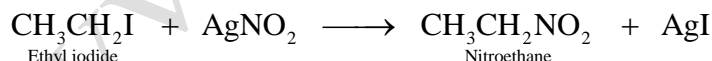
(5) Reaction with Sodium Cyanide: Alkyl halides react with sodium cyanide in a suitable solvent, (generally aqueous ethanol) to form alkyl cyanide or nitriles. Halogen atom is replaced by –CN group.



(6) Reaction with Acetylides: Alkyl halides react with sodium acetylides to form higher alkynes.



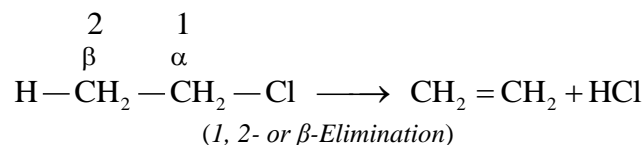
(7) Reaction with AgNO₂: Alkyl iodides react with silver nitrite to form nitroalkanes.



2. Elimination reactions

Alkyl halides undergo another very important type of reactions known as elimination reactions. The most common form of eliminations involves the loss of two atoms (or groups) from the adjacent carbon atoms of a molecule resulting in the formation of a multiple bond. These are the reverse of addition reactions. During elimination reactions two strong sigma bonds are broken down and a new weaker pi bond is formed. The saturated compounds are converted into unsaturated compounds. During elimination from alkyl halide, halogen and hydrogen is removed from the adjacent carbon atoms result in the formation of an alkene. The process is generally known as 1,2-elimination or β-elimination with reference to the relative positions of the two departing groups on the carbon skeleton. These reactions takes place in the

presence of a base.

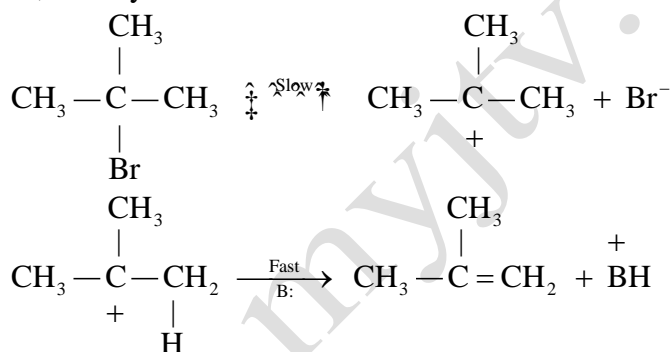


In the β -eliminations one group leaves along with the bonding electrons and is referred to as the leaving group (or *nucleofuge*); the other group leaves without electrons and most often is hydrogen. Elimination reaction may either proceed through E^1 or E^2 mechanisms.

E^1 mechanism: The E^1 stands for *elimination unimolecular* mechanism. Like S_N1 , it is a two-step mechanism.

Step-I: In this step the substrate undergoes slow ionization to form a carbocation.

Step-II: In this step the carbocation rapidly loses a proton from a β -carbon atom to a base, usually a solvent.



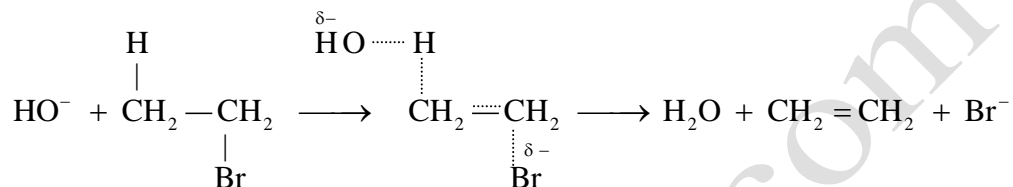
The E^1 reactions are unimolecular and only one molecule (substrate) is involved in the rate determining step (slow step). These reactions therefore follow first order kinetics. These reactions are generally followed by tertiary alkyl halides which are completed in two steps. In the first step the substrate ionizes slowly and a carbocation is formed. In the second step, the base removes hydrogen from the beta carbon of the carbocation as a proton and a double bond is formed between alpha and beta carbon atoms, the resulting product is an alkene.

The E^1 reaction is analogous to the S_N1 reaction. In fact, the first step, i.e., the rate-determining step of the E^1 reaction is exactly the same as that of the S_N1 reaction. Therefore, both reactions proceed at the same rate. It is the second step where the two reactions differ. In the E^1 reaction the solvent pulls off a β -proton from the intermediate carbocation to produce an alkene, whereas in the S_N1 reaction the solvent attacks at the positively charged carbon atom to form the substitution product.

The E^1 mechanism follows first-order kinetics, the rate depending on the concentration of the substrate only.



E² mechanism: E² stands for elimination bimolecular mechanism. It is a single step mechanism in which pulling off the proton from the β-carbon atom by a base and the departure of the leaving group are simultaneous. In the transition state of the reaction all the five atoms involved in its formation, i.e., the basic atom, the β-hydrogen, α- and β-carbons and the departing atom, lie in one plane, and the β-hydrogen and the leaving group are trans to each other.



Primary alkyl halides follow E² mechanism. The E² mechanism is analogous to the S_N2 mechanism. The difference between the two pathways is whether the reagent with an unshared electron pair attacks the hydrogen atom (acts as a base) or the carbon atom (acts as a nucleophile) of the substrate.

The E² reaction is bimolecular and follows second order kinetics. Two species (substrate and base) are involved in the rate determining step of these reactions.

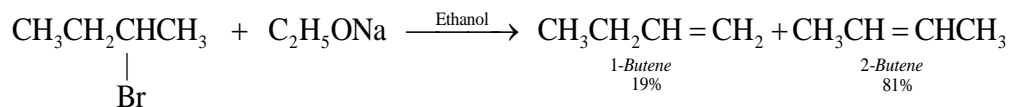


Difference between a base and a nucleophile

Any species (neutral or negatively charged) that carries a lone pair of electrons can function as both base and nucleophile. Whereas basicity is the affinity for proton, nucleophilicity is the ability to form bond to carbon atom. A base therefore attacks hydrogen atom in elimination reactions while a nucleophile attacks carbon atom in substitution reactions. Basicity is an equilibrium phenomenon and is a measure of the proportion of protons attached to the base at equilibrium, whereas nucleophilicity is a kinetic phenomenon and is a measure of the rate at which a nucleophile attacks the carbon atom.

Orientation of Double Bond

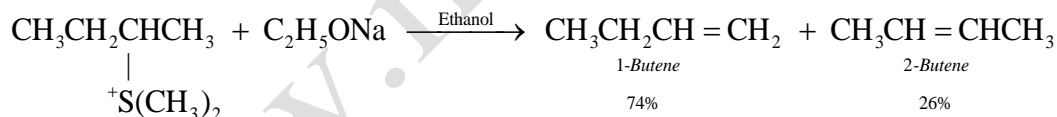
If a substrate has a β-hydrogen on only one carbon atom, there is no doubt about the position of the new double bond. For example, PhCH₂CH₂Br can give only PhCH=CH₂. However, many substrates have β-hydrogens at more than one position that can be lost in the elimination reaction and more than one olefinic products are possible. For example, the elimination of HBr from 2-bromobutane may lead either to 1-butene or 2-butene. In fact, a mixture of both alkenes is formed.



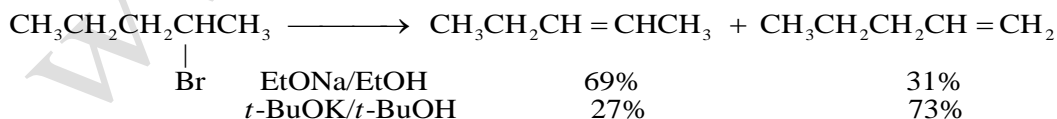
Which olefinic product dominates depends on various factors. In general, the alkene with greater number of alkyl groups attached to the double-bonded carbon atoms, is more stable. So, the double bond will preferably go in the direction as to produce the most highly substituted alkene. This is known as the **Saytzeff rule** and the product is called the *Saytzeff product*.

Saytzeff Rule: If the dehydrohalogenation of an alkyl halide can yield more than one alkene, then according to the *Saytzeff rule*, the main product is the most highly substituted alkene.

In the case of an E² reaction, the presence of a transβ-hydrogen is necessary. If such hydrogen is available at only one position then that is the direction of the double bond. However, if transβ-hydrogens are available at more than one position, two types of behaviour are observed depending on the structure of the substrate and the nature of the leaving group. If the substrate contains an uncharged leaving group (that comes off as a negative ion), the *Saytzeff rule* is generally followed, as in the case of E1 eliminations, no matter what the structure of the substrate is. However, if the substrate contains a charged leaving group like —⁺NR₃ or —⁺SR₂ (that comes off as a neutral molecule), the double bond will go mainly toward the least highly substituted carbon. This is known as the **Hofmann rule** and the product formed in this way is called the *Hofmann product*.



The Hofmann product appears to be formed due to steric reasons because the formation of a less-substituted alkene is favoured even when the leaving group is a halide, if a large base is used.



Factors affecting the rate of elimination reactions

The rates of elimination reactions depend on the following factors.

(i) **Effect of the substrate:** Like substitution reactions, the elimination reactions proceed by the E¹ mechanism when alkyl halides are tertiary, because in this case a stable carbonium ion is formed. When the substrate is primary, E² mechanism is followed. In the case of a secondary substrate the mechanism changes from E¹ to E²

depending on the reaction conditions. The E^2 mechanism also happens in tertiary alkyl halides. This is due to the reason that in E^2 reaction the base has to abstract a proton from a β -carbon atom where steric hindrance is normally not as significant as when the nucleophile directly attack the central carbon atom from which the leaving group departs in case of S_N2 reactions.

(ii) Effect of the base: In E^1 reaction the solvent itself acts as a base, external base is generally not required. When an external base is added, the reaction proceeds by E^2 mechanism. If a strong base is used, the reaction proceeds through E^2 even with a tertiary substrate. When the base is weak E^1 mechanism is observed with tertiary and, in some cases with secondary substrates. A strong base not only favours E^2 over E^1 but also favours elimination over substitution. Similarly if the solvent is a better base, E^1 will be the predominant pathway and if it is a better nucleophile, then S_N1 mechanism will predominate.

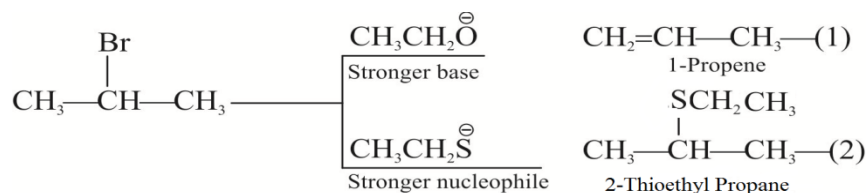
(iii) Effect of the leaving group: The role of the leaving group in the elimination reactions is similar to that in the substitution reactions. A better leaving group favours the E^1 mechanism because it makes ionization easier, whereas a poor leaving group favours the E^2 mechanism.

(iv) Effect of the solvent: The E^1 mechanism is favoured by polar solvent while in case of nonpolar solvent the reaction will tend to proceed by the E^2 mechanism. Elimination is favoured more than substitution by decreasing the solvent polarity. Thus, *alcoholic* KOH is used to carry out elimination while the more polar *aqueous* KOH is used in case of substitution.

(v) The effect of temperature: In elimination reactions greater changes in bonding are involved as compared to the substitution reactions. Therefore an increase in temperature will favour elimination more than substitution, whether the mechanism is unimolecular or bimolecular.

Substitution Verses Elimination

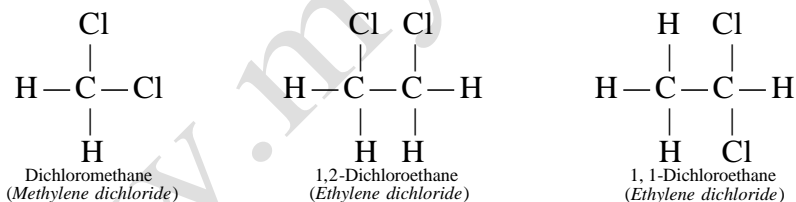
Consider the example of 2-bromopropane ($\text{CH}_3 - \overset{\text{Br}}{\underset{|}{\text{CH}}} - \text{CH}_3$). If we treat it with ethoxide ($\text{CH}_3\text{CH}_2\bar{\text{O}}$), 1-propene is formed. If we treat it with $\text{C}_2\text{H}_5\bar{\text{S}}$ (thioethyl or ethosulphide) then thioethyl propane is formed. The ethoxide ion caused hydrogen ion abstraction from the carbonium ion mean it played the role of a base and hence caused elimination reaction while the thioethyl/ethosulphide ion substitute the bromide and caused substitution reaction. Ethoxide is strong base compared to ethosulphide so it attacked the proton and caused elimination while ethosulphide is a strong nucleophile so it attacked the carbon atom and caused substitution.



If we treat the alkyl halide with strong base then it will undergo elimination reaction and alkenes will form. If the alkyl halide is treated with strong nucleophile then it will undergo substitution reaction. Along with nature of the base and the nucleophile the reaction also depends upon the nature of substrate. Crowding within the molecule of the substrate always favours elimination over substitution because due to steric hindrance the nucleophile cannot approach the alpha carbon atom of the substrate. The greater number of alkyl groups on the substrate favours elimination over substitution because these alkyl groups stabilize the alkene more than the substituted product.

Dihalogen derivatives

Dihalogen derivatives are compounds obtained by replacing two hydrogen atoms of a hydrocarbon by two halogen atoms. The presence of the identical halogen atoms is indicated by the prefix *di-* and position numbers. For example,



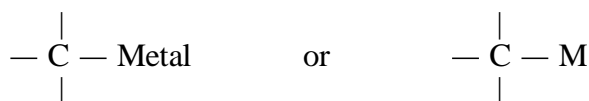
Vicinal Dihalide: If two halogen atoms are attached to *adjacent* carbons, the compound is referred to as a vicinal (*vic-*) Dihalide.

Geminal Dihalide: If two halogen atoms are attached to the *same* carbon, then it is known as a geminal (*gem-*) Dihalide.

Notice that in the above example, 1,2-dichloroethane is a *vic*-dihalide; 1,1-dichloroethane is a *gem*-dihalide.

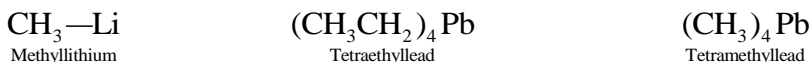
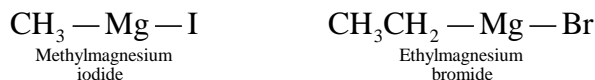
Organometallic compounds

Organometallic compounds are those compounds which contain at least one carbon-metal bond.



where M = Mg, Li, Pb, Zn, Na, Fe etc.

Organometallic compounds are named by simply adding the name of the metal to that of the organic group bonded to the metal. For example,



Several organometallic compounds are of great importance. Like cisplatin is used in chemotherapy and anticancer activities. Chlorophyll is capable of trapping energy from the sun to enhance the process of photosynthesis. Haemoglobin is capable of transporting oxygen.

Grignard Reagents, RMgX

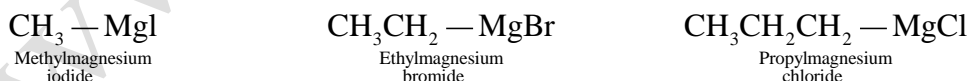
Alkyl magnesium halide and aryl magnesium halides are commonly known as Grignard reagents. These are organomagnesium halides. These are named after Victor Grignard who discovered them and developed their use as synthetic reagents. Due to this great achievement, Victor Grignard was awarded with Noble Prize in 1912. The Grignard reagents are highly reactive and used in the synthesis of alkanes, alcohols, aldehydes, ketones, and carboxylic acids. Due to its synthetic applications, Grignard reagent is also known as synthetic tool in the hands of an organic chemist. The general formula of Grignard reagent can be written as:



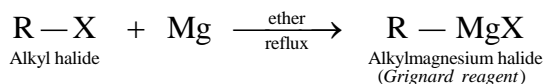
where R = Alkyl or aryl group

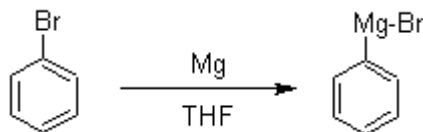
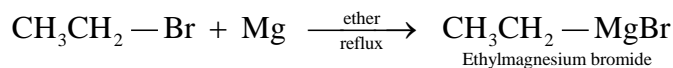
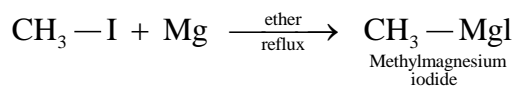
X = Cl, Br, or I

Examples are:

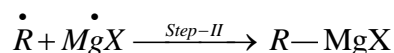
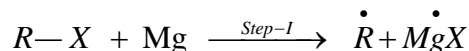


Preparation: Grignard reagents are prepared in the laboratory by the action of alkyl halides on magnesium metal in the presence of *dry ether*. Dry ether is pure anhydrous diethyl ether, $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$. Tetrahydrofuran (THF) can also be used in place of dry ether.



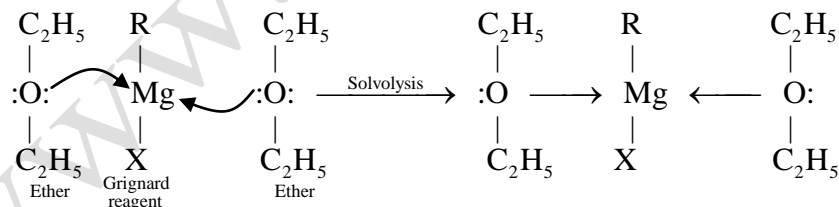


The above reaction takes place in two steps. In the first step alkyl halide reacts with magnesium and yields alkyl radical and magnesium halide radical. In the second step, the free radicals combine and form Grignard reagent.



Alkyl iodides are most reactive than the bromides, which are in turn more reactive than chlorides. Alkyl bromides are most suitable for the preparation of Grignard reagents.

In practice, a Grignard reagent is produced by dropping a solution of the alkyl halide in dry ether into the reaction flask containing magnesium ribbon suspended in dry ether. The ether solution of the Grignard reagent thus obtained is used immediately in the flask in which it is prepared. Diethyl ether plays two important roles: (a) It provides a medium for the reaction; and (b) It dissolves the Grignard reagent through *solvolysis* (reaction with solvent).



Grignard reagent cannot be isolated, its ethereal solution is used directly in the synthetic reactions.

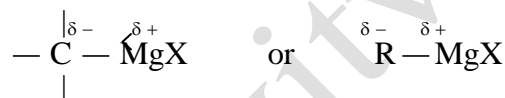
Precautions: Take the following precautions when preparing the Grignard reagents:

- (1) Make sure that there are no naked flames anywhere in the vicinity. Diethyl ether is inflammable. It catches fire very quickly.
- (2) Make sure that all reagents and apparatus are completely dry. The moisture or any other impurity will react with the Grignard reagent produced and prevent its formation.

The ease of formation of Grignard reagent depends upon the nature of both alkyl/aryl group and halide. Increasing size of the alkyl group makes the formation of Grignard reagent difficult. Increasing size of the halide makes the formation of Grignard reagent easy. Alkyl magnesium fluorides are not known. Alkyl iodides are expensive so alkyl bromides are usually used for the preparation of Grignard reagents.

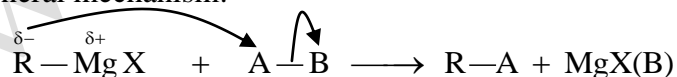
Physical Properties: Grignard reagents are non-volatile, colourless solids. These are seldom isolated in the free state on account of their explosive nature. Therefore, for synthetic purposes the Grignard reagents are always prepared and used in ether solution.

Reactivity of Grignard reagents: The C–Mg bond in Grignard reagents is covalent but highly polar. The carbon atom is more electronegative than magnesium. The electrons of the C–Mg bond are drawn towards the carbon atom. As a result, the carbon atom has a partial negative charge and the magnesium atom has a partial positive charge.

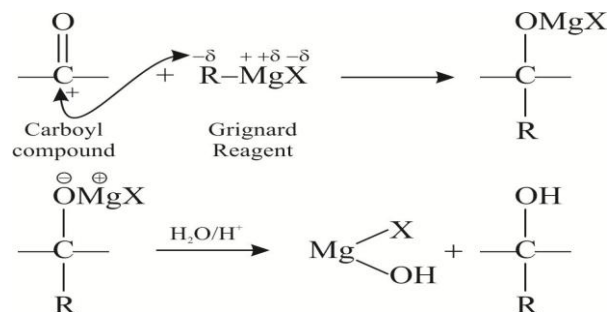


The alkyl groups in Grignard reagents being electron-rich can act as carbanions or nucleophiles. They would attack polarized molecules at points of low electron density. Thus the characteristic reactions of Grignard reagents are nucleophilic substitution and nucleophilic addition reactions. Grignard reagents are highly reactive compounds, these react with many organic and inorganic compounds to produce a large number of valuable products.

Nucleophilic Substitution: The Grignard reagents undergo substitution reactions by the following general mechanism:



Nucleophilic Addition: Carbonyl compounds are attacked by Grignard reagents to form addition products which on acid-hydrolysis yield alcohols, acids, esters, etc. Addition always proceeds such that the positive part of the Grignard reagent ($\text{MgX}^{\delta+}$) combines with the oxygen atom of the carbonyl group. The negative part ($\text{R}^{\delta-}$) of the Grignard reagent goes to the carbon atom of the carbonyl group.



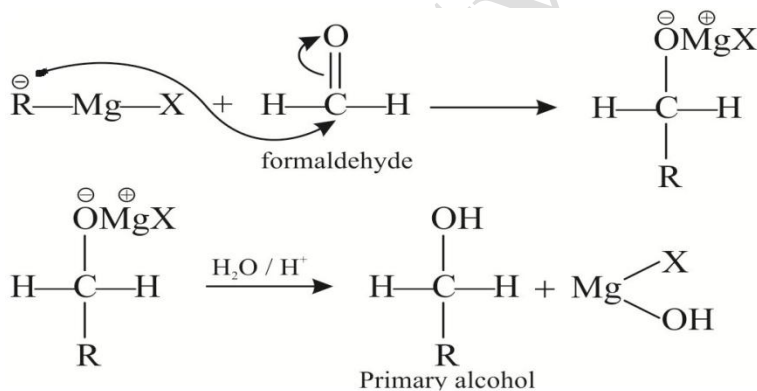
Grignard reagents react with a variety of compounds yielding almost the entire range of organic substances.

Synthetic applications of Grignard reagent/Chemical properties of G.R

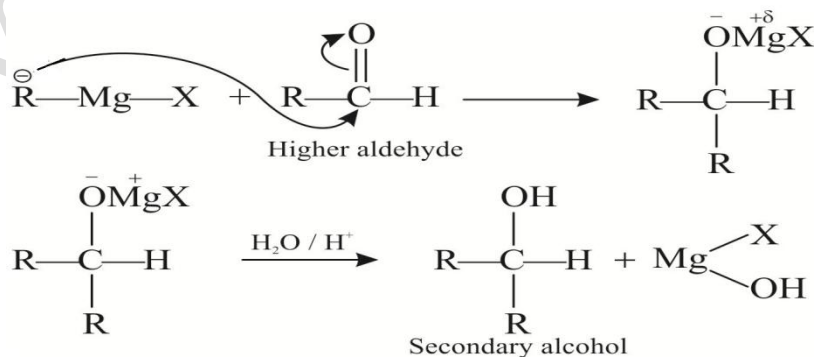
The following reactions illustrate the synthetic importance of Grignard reagents:

(1) **Reaction with Aldehydes:** Primary or secondary alcohols are obtained.

(a) **Formaldehyde** reacts with Grignard reagents to give addition products which on hydrolysis yield *primary alcohols*.



(b) **Acetaldehyde and higher aldehydes** react with Grignard reagents to give addition products which on hydrolysis yield *secondary alcohols*.

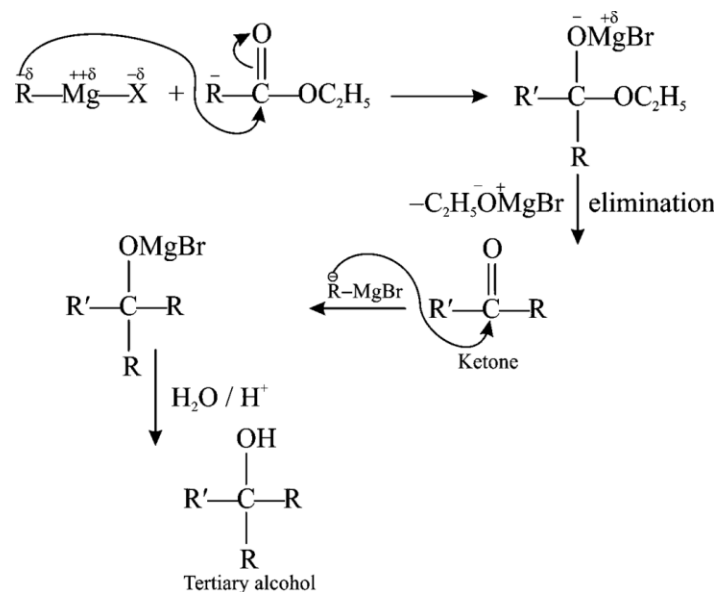


(2) **Reaction with Ketones:** Grignard reagents react with ketones to give addition

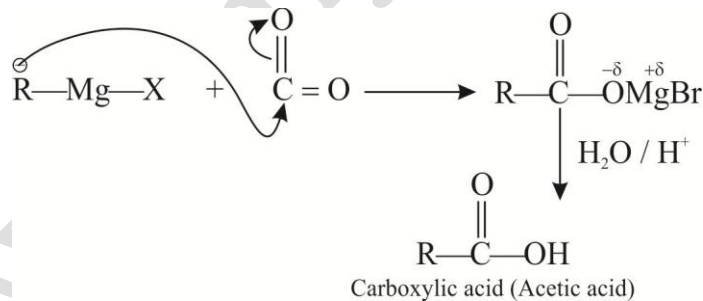
(b) **Reaction with Ethyl Acetate:** Two steps are involved:

Step 1. Ethyl acetate reacts with Grignard reagents to first form ketones.

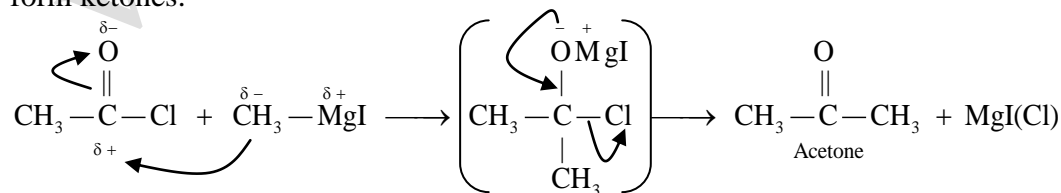
Step 2. The ketone then reacts with more of the Grignard reagent to give an addition product which on hydrolysis forms a tertiary alcohol.



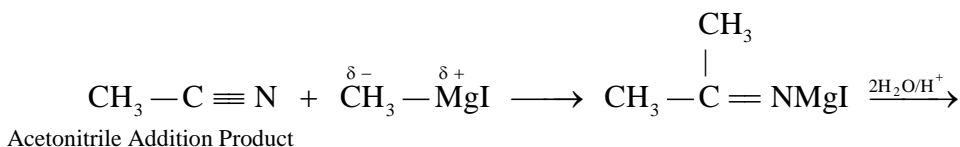
(4) **Reaction with Carbon Dioxide:** Grignard reagents react with carbon dioxide ($O=C=O$) to give addition products which on hydrolysis yield carboxylic acids.



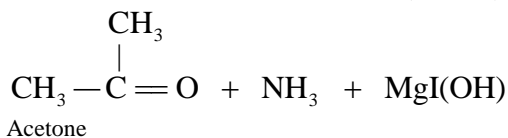
(5) **Reaction with Acid Chlorides:** Grignard reagents react with acid chlorides to form ketones.



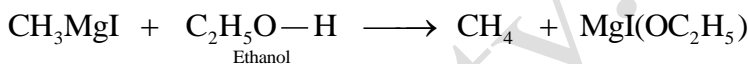
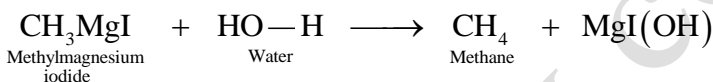
(6) **Reaction with Cyanides:** Grignard reagents react with cyanides to give addition products which on hydrolysis with dilute HCl yield ketones.



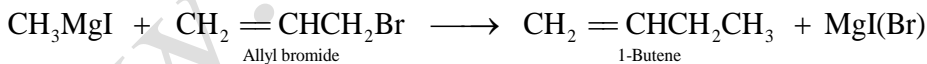
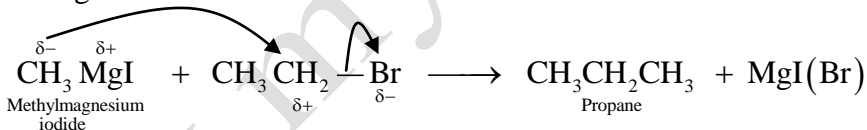
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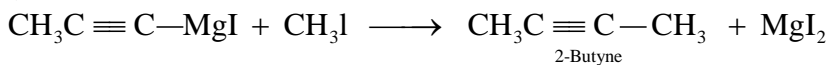
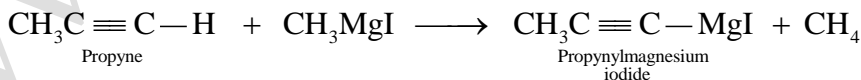
(7) Reaction with Compounds Containing Active Hydrogens: By active hydrogen we mean a hydrogen that is more acidic than that in alkanes. Thus compounds like water, alcohols, and amines which contain active hydrogens react with Grignard reagents to form alkanes.



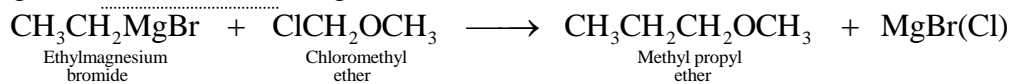
(8) Reaction with Alkyl Halides: Grignard reagents react with saturated alkyl halides to form higher alkanes or alkenes.



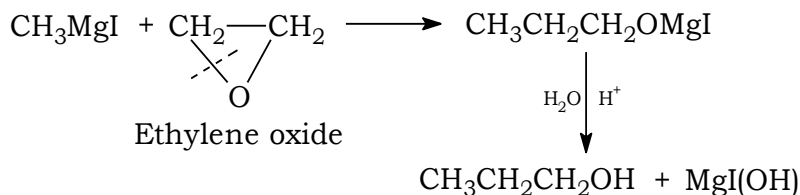
(9) Reaction with Alkynes: Terminal alkynes (1-alkynes) react with Grignard reagents to form alkynylmagnesium halides which on subsequent treatment with alkyl halides form higher alkynes.



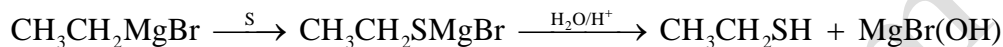
(10) Reaction with Lower Halogenated Ethers: Grignard reagents react with lower halogenated ethers to form higher ethers.



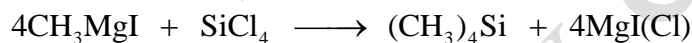
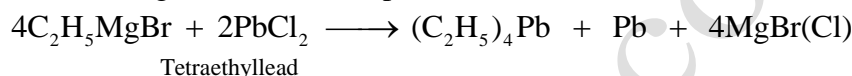
(11) Reaction with Ethylene Oxide: Grignard reagents react with ethylene oxide to give an addition product which on hydrolysis forms primary alcohols.



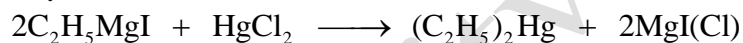
(12) Reaction with Sulphur: Sulphur reacts with a Grignard reagent to give a product which on hydrolysis gives the corresponding thioalcohol.



(13) Reactions with Inorganic Halides: Grignard reagents react with inorganic halides to form other organometallic compounds.



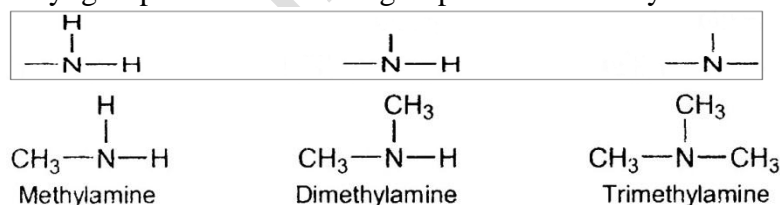
Tetramethylsilane



Diethylmercury

AMINES

Amines are important nitrogen containing organic compounds. Amines are derivatives of ammonia (NH_3) in which one or more hydrogen atoms have been replaced by alkyl groups. The functional groups of amines may be.

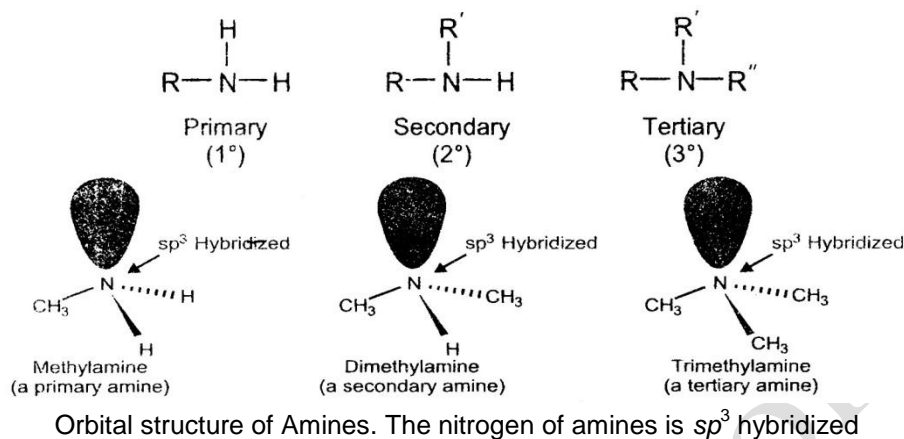


Amines are classified as Primary (1°), Secondary (2°), or Tertiary (3°), according to the number of alkyl groups attached to the nitrogen atom.

(i) Primary Amines: Amines in which only one alkyl group is directly attached to the nitrogen atom are known as primary amines.

(ii) Secondary Amines: Amines in which two alkyl groups are directly attached to the nitrogen atom are known as secondary amines.

(iii) Tertiary Amines: Amines in which three alkyl groups are directly attached to the nitrogen atom are known as tertiary amines.

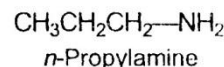
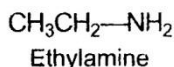
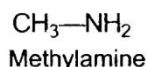


Nomenclature

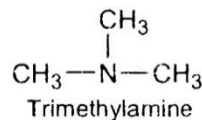
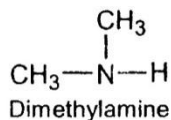
The following systems are applied in naming amines:

Common system

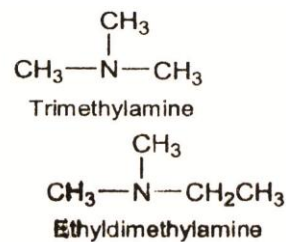
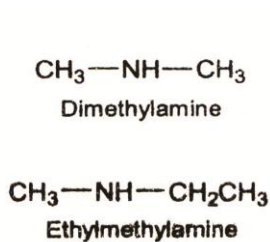
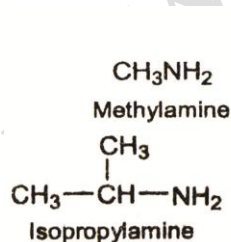
(1) Amines are named by naming the alkyl groups attached to the nitrogen atom followed by the ending-*amine*. Notice that the names are written as one word.



(2) When two or three identical alkyl groups are attached to the nitrogen atom, the prefix *di-* or *tri-* is added to the name of the amine.

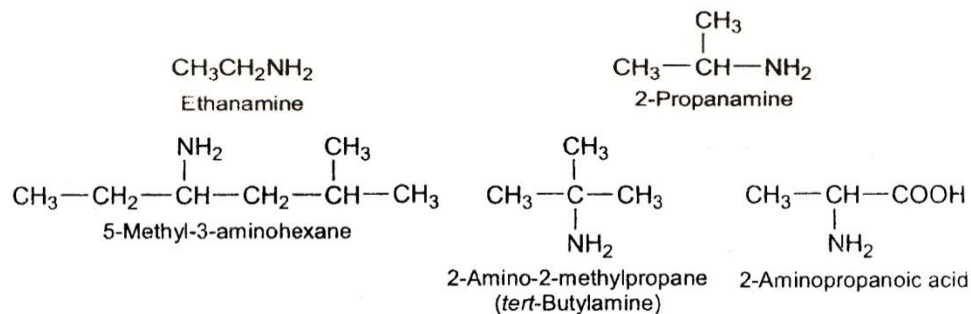


(3) When two or three different alkyl groups are attached to the nitrogen atom, they are named in alphabetical order.

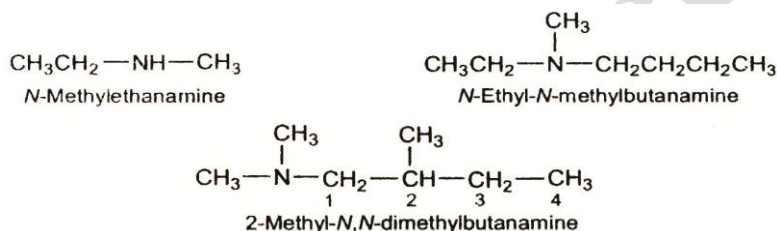


IUPAC System: If the name is too complex, the IUPAC system of nomenclature is used.

In this system the amino group ($-\text{NH}_2$) is considered as a substituent, and its position on the chain is indicated by the lowest possible number.



Secondary or tertiary amines are named as *N*-substituted derivatives of primary amines. The largest of the groups attached to nitrogen is chosen as the organic group of the primary amine. The remaining alkyl groups are named as substituents by using the prefix *N*- to indicate that they are attached to nitrogen.



For diamines, the final *-e* of the hydrocarbon name is retained.

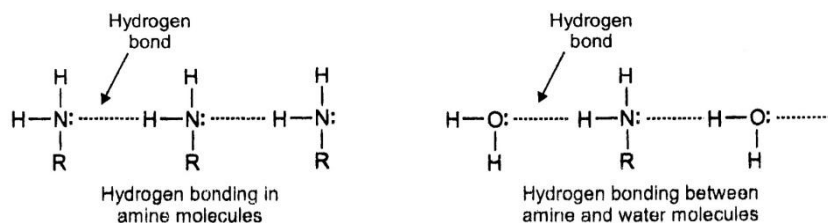


When it is necessary to name $-\text{NH}_2$ as a substituent, it is called the *amino* group.



Physical Properties

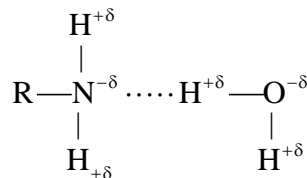
- (1) Lower amines are gases or low-boiling liquids at room temperature.
- (2) Amine possess characteristic ammonia-like smell.
- (3) Amines have higher boiling points than non-polar compounds of similar molecular weights. This is because amines, are polar compounds and form intermolecular hydrogen bonds. For example, ethylamine, $\text{C}_2\text{H}_5\text{NH}_2$, boils at $+17^\circ\text{C}$ and propane, C_3H_8 , at -42°C .



4. Amines are soluble in water. This is because they are capable of forming

hydrogen bonds with water. Amines are also soluble in benzene and ether.

All types of amines i.e. primary secondary and tertiary are soluble in water because of hydrogen bonding with water.

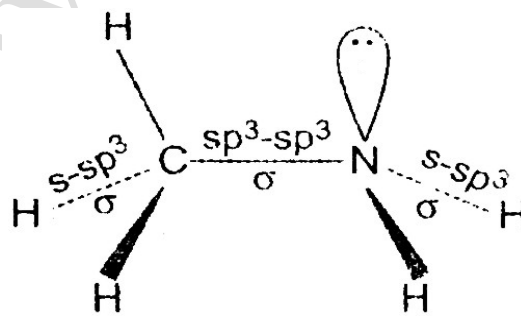


5. The boiling points of tertiary amines are lower than secondary and primary amines due to the absence of hydrogen bonding in tertiary amines.

Structure

Amines are the derivatives of ammonia, where one or more H atoms have been replaced by alkyl groups. Since ammonia molecule has trigonal pyramidal geometry, the resulting amines also have the same geometry and the R-N-H or R-N-R angle is close to the tetrahedral angle.

Let us consider methylamine (CH_3NH_2) for illustrating the orbital make up of amines. In methylamine both nitrogen and carbon are sp^3 hybridized. One of the sp^3 orbitals of nitrogen is completely filled and cannot take part in bond formation. The C-N σ bond in methylamine is formed by overlap of an sp^3 orbital of carbon and an sp^3 orbital of nitrogen. Each N-H σ bond is formed by the overlap of an sp^3 orbital of nitrogen and s orbital of hydrogen. Each C-H σ bond is formed by overlap of an sp^3 orbital of carbon and s orbital of hydrogen. All bond angles are approximately tetrahedral.

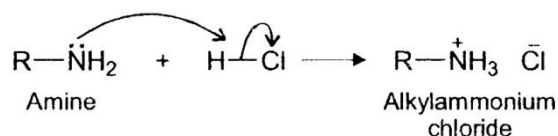


Structure of Methylamine

Basicity of amines

Amines are basic in nature. This is because they possess an unshared pair (lone pair) of electrons on nitrogen. This lone pair of electrons is available for the formations of a new bond with a proton or Lewis acids. Thus amines react with acids

to form salts.



Strong bases (*e.g.*, NaOH or KOH) completely ionizes in aqueous solution. Amines are weak bases. They are only partially ionized in aqueous solution and an equilibrium exists between the ionized and un-ionized forms.

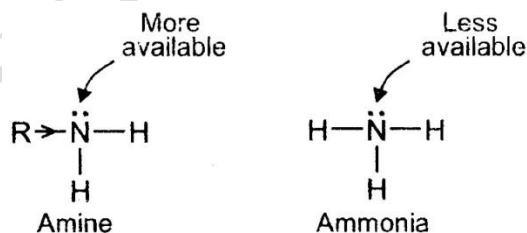


The extent of ionization is described by an equilibrium constant K_b , which is known as Basicity Constant. It is defined as the concentration of the products of ionization in moles per liter divided by the concentration of the un-ionized base.

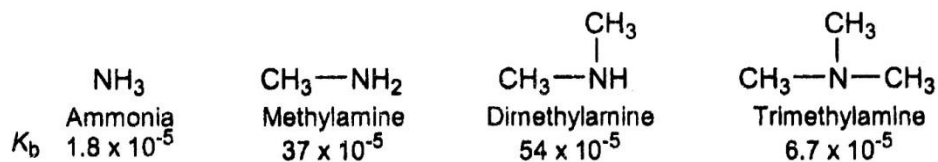
$$K_b = \frac{[\text{RNH}_3^+][\text{OH}^-]}{[\text{RNH}_2]}$$

The basicity constant describes the relative strength of a weak base. Stronger bases will have higher numerical values of basicity constants.

Aliphatic amines are stronger bases than ammonia. This is because the alkyl groups are electron-releasing. These increase the electron density around the nitrogen, thereby increasing the availability of the lone pair of electrons. The greater the number of electron-releasing alkyl groups, the greater the availability of nitrogen's lone pair and stronger the base will be.



Amines are more basic than ammonia because the electron release by alkyl groups increases lone-pair availability



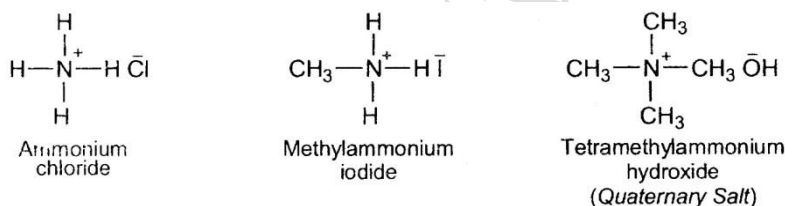
Notice that the dimethylamine is a stronger base than methylamine. However, trimethylamine is a weaker base than both dimethylamine and methylamine.

Although in trimethylamine the electron-density is further increased but *the steric crowding of three methyl groups makes the approach and bonding by a proton relatively difficult*. The electrons are there but the path is blocked therefore its basicity is low.

Haloalkyl amines are weaker bases than alkyl amines. In haloalkyl amines, the haloalkyl groups are electron withdrawing so will withdraw the electron density and the N of amine will be electron deficient so its basicity will be lower.

Salts of amines

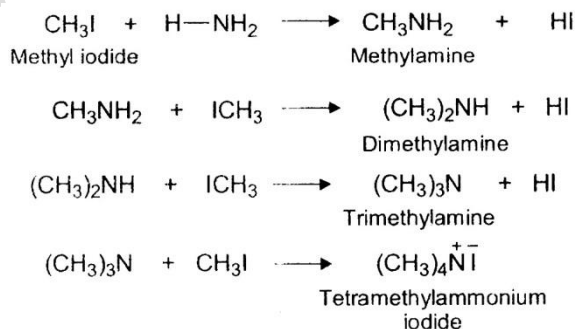
All amines are basic. These react with acids to form salts. The salts can be considered as being related to ammonium (NH_4^+) salts where the hydrogens of ammonium ion have been replaced by alkyl groups. When all four hydrogens of the ammonium ion have been replaced by alkyl groups, the compound is called Quarternary Ammonium Salt. The amine salts are named as substituted ammonium salts. The alkyl groups are named first, and are followed by the ending *-ammonium*. The name of the anion present in the salt is then written as a second word. For example,



Methods of preparation

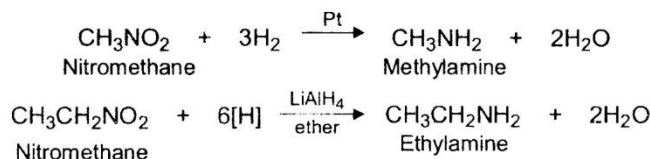
The general methods of preparation of amines may be classified as follows:

(1) Reaction of Alkyl Halides with Ammonia (Alkylation of ammonia): Amines can be prepared by heating an alkyl halide with alcoholic ammonia in a sealed tube. A mixture of primary, secondary, tertiary amines, and quarternary ammonium salt is obtained.

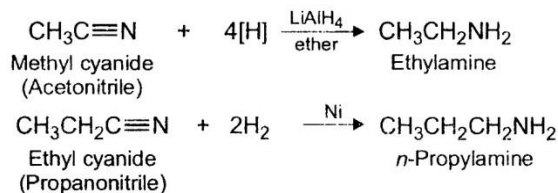


(2) Reduction of Nitroalkanes: Primary amines can be obtained by reduction of

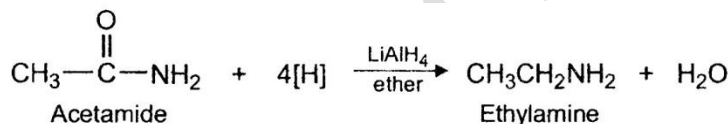
nitroalkanes with $\text{H}_2 + \text{Pt}$ (or Ni) or lithium aluminium hydride.



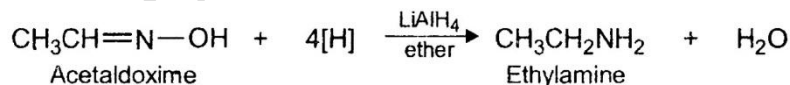
(3) Reduction of Nitriles: Primary amines can be prepared by reduction of nitriles (alkyl cyanides) with $\text{H}_2 + \text{Ni}$ or lithium aluminium hydride.



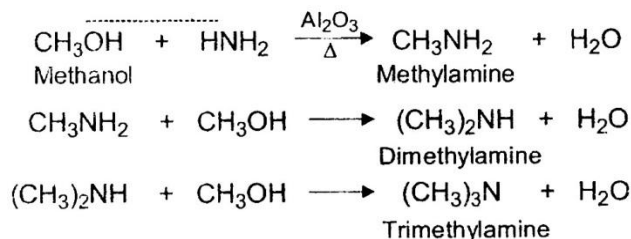
(4) Reduction of Amides: Primary amines can be obtained by reduction of simple amides with lithium aluminium hydride. Notice that the product contains the same number of carbons as the original amide.



(5) Reduction of Oximes: Primary amines may be obtained by reduction of oximes of aldehydes and ketones with lithium aluminium hydride. Other reducing agents which can be used in place of lithium aluminium hydride are: $\text{H}_2 + \text{Ni}$ and $\text{Na} + \text{C}_2\text{H}_5\text{OH}$.



(6) Reaction of Alcohols with Ammonia: Amines can be prepared by passing the vapours of alcohol and ammonia over heated alumina at 400°C . A mixture of primary, secondary, and tertiary amines is produced.

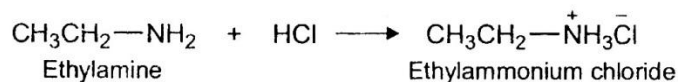


Chemical Properties

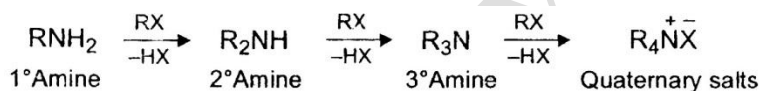
The main reactions of amines are due to the presence of the lone pair of

electrons on nitrogen. This lone pair of electrons is available for donation to electron-seeking (electron deficient/electrophilic) reagents. Amines are nucleophilic reagents. Greater the electron density over nitrogen or availability of lone pair of electrons more will be the reactivity of the amines. On this basis secondary amines are more reactive than primary and primary is more reactive than tertiary amines due to easy availability of lone pair over nitrogen atom.

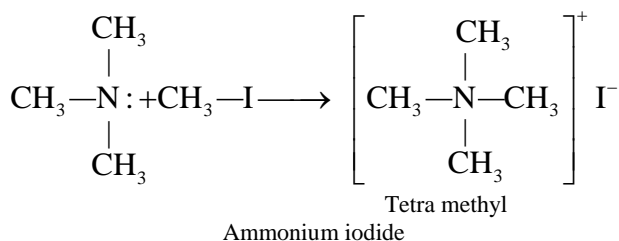
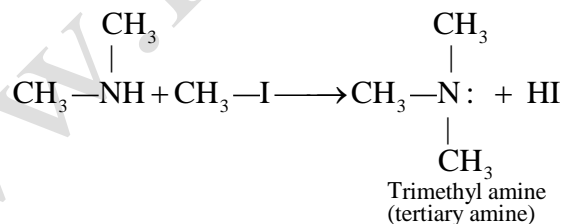
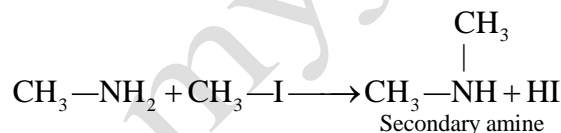
(1) Salt Formation: Amines are basic compounds. They react with mineral acids to form salts. For example,



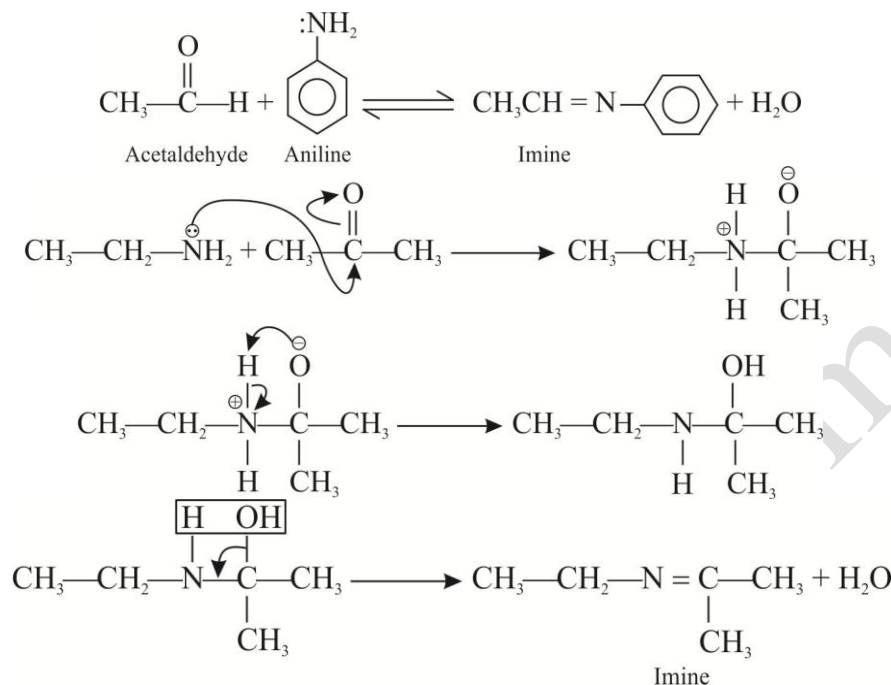
(2) Reaction with Alkyl Halides: When an amine is treated with an alkyl halide, hydrogen atoms of the N atom are successively replaced by alkyl groups. In the final step, the tertiary amine adds one molecule of the alkyl halide to yield a quaternary ammonium salt.



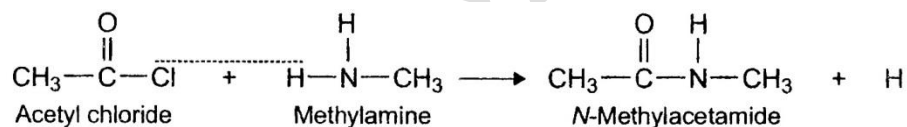
Or



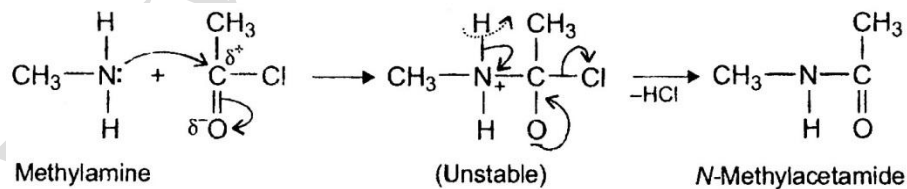
(3) Reaction with aldehydes and ketones (Schiff's Reaction): Primary amines react with aldehyde and ketone yield condensation products called Imines. These are also known as Schiff's bases.



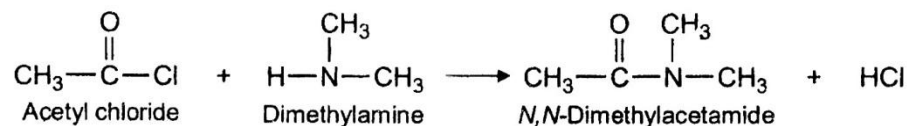
- (4) **Reaction with Acid Halides (Formation of amides):** (a) Primary amines react with acid chlorides or acid anhydrides to form *N*-substituted amides. For example,



Mechanism: The mechanism involves the nucleophilic attack by the amine on the electrophilic carbon.



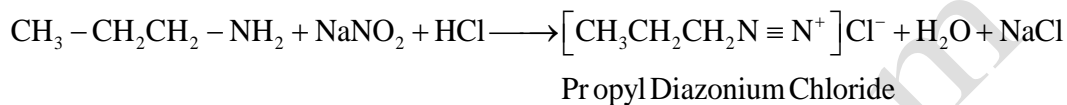
- (b) Secondary amines react with acid chloride to form *N,N*-disubstituted amides.



- (c) Tertiary amines do not react since they do not have a replaceable hydrogen on the nitrogen.

(5) **Formation of Diazonium Salts:** Diazonium salts are aromatic or aliphatic organic compounds containing $-N_2X$ group where X is halogen.

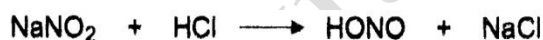
When primary aliphatic amines are treated with nitrous acids they yield highly unstable salts known as diazonium salt and the reaction is termed as diazotization. Nitrous acid is an unstable acid which is prepared in situ by the reaction of $NaNO_2$ and dil.HCl.



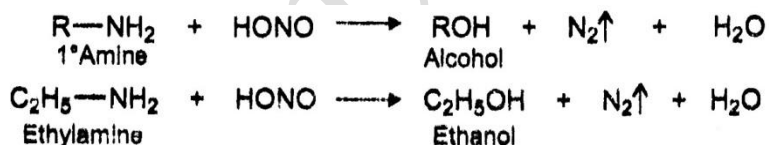
Diazonium salts are unstable and explosive in the solid state. These are used in the preparation of benzonitrile, phenol, iodobenzene, bromobenzene, chlorobenzene, aniline etc.

Testing of primary, secondary and tertiary amines

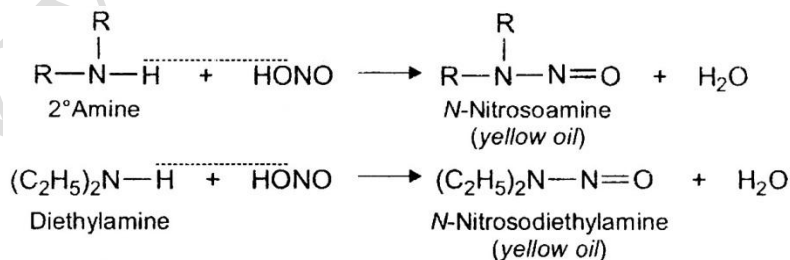
(I) **Nitrous acid test:** Nitrous acid (HONO) is an unstable substance and is therefore prepared *in situ* by the reaction of sodium nitrite and dilute HCl at $0^\circ C$.



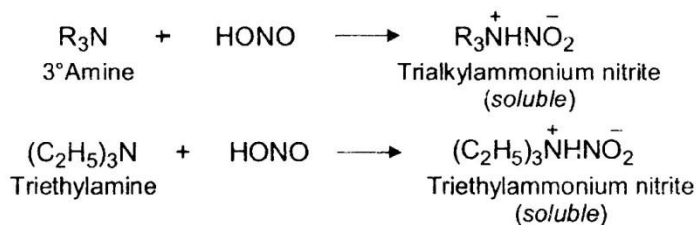
(a) Primary amines react with nitrous acid to form alcohols and nitrogen gas.



(b) Secondary amines react with nitrous acid to form *N*-nitrosoamines which are water-insoluble yellow oils.



(c) Tertiary amines react with nitrous acid to form trialkylammonium nitrate salts which are soluble in water.



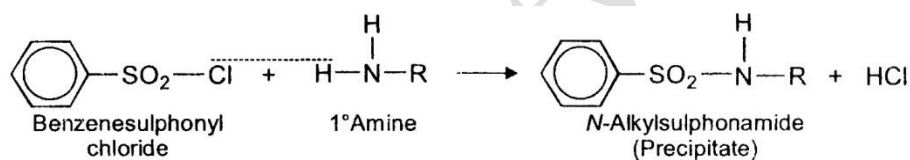
This reaction is used as the basis of a test to distinguish between primary, secondary, and tertiary amines. The test is known as the Nitrous Acid Test. To summarize this test:

(a) Primary amines react with nitrous acid to produce nitrogen gas (seen as bubbles).

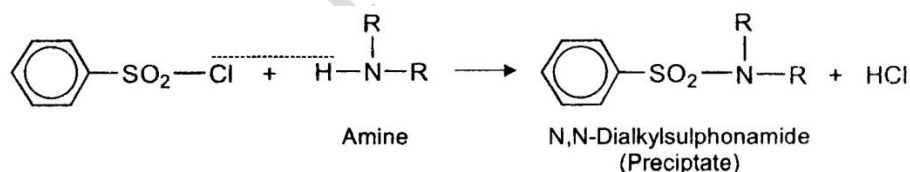
(b) Secondary amines react with nitrous acid to produce a yellow oily layer.

(c) Tertiary amines react with nitrous acid to form soluble nitrite salts. There is no visible sign of reaction.

(II) Hinsberg Test: (a) Primary amines react with benzenesulphonyl chloride to form *N*-alkyl benzenesulphonamide.

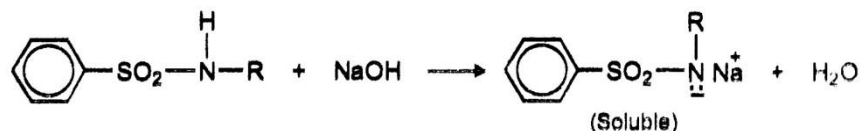


(b) Secondary amines react with benzenesulphonyl chloride to form *N,N*-dialkylbenzenesulphonamide.

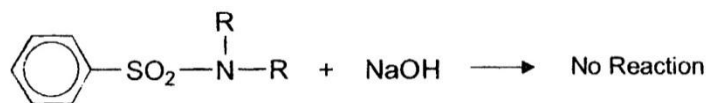


(c) Tertiary amines do not react since they do not possess a replaceable hydrogen.

The sulphonamides from primary amines still have a replaceable hydrogen on the nitrogen. This hydrogen is acidic. Thus sulphonamides from primary amines *dissolve in bases* to form soluble salts.



The sulphonamides from secondary amines do not have a replaceable hydrogen and so *do not dissolve in bases*.



These reactions are used in the basis of a test to distinguish between primary, secondary, and tertiary amines. The test is known as the Hinsberg Test. To summarize this test:

(a) Primary amines react with benzenesulphonyl chloride to form a precipitate that is *soluble* in NaOH solution.

(b) Secondary amines react with benzenesulphonyl chloride to give a precipitate that is *insoluble* in NaOH solution.

(c) Tertiary amines *do not react* with benzenesulphonyl chloride.

(III) Carbylamine Reaction: Primary amines react with chloroform and a solution of KOH in ethanol to form isocyanides (isonitriles or carbylamines). Secondary and tertiary amines do not give this reaction.



The isocyanides or carbylamines are evil-smelling and can be easily detected. This reaction is used to distinguish primary amines from secondary and tertiary amines.

EXERCISE

Q.1. Choose the correct option.

- (i) The reaction of CH_3MgI with acetone followed by hydrolysis gives.
- (a) ✓ ter-butanol (b) sec-butanol
(c) n-butanol (d) none of these
- (ii) Which one of the following Halide is most reactive towards nucleophilic substitution reaction?
- (a) $\text{C}_2\text{H}_5\text{Br}$ (b) ✓ $\text{C}_2\text{H}_5\text{I}$
(c) $\text{C}_2\text{H}_5\text{F}$ (d) $\text{C}_2\text{H}_5\text{Cl}$
- (iii) All electron deficient species are classified as.
- (a) Nucleophiles (b) ✓ Electrophiles
(c) Bases (d) All of these
- (iv) $\text{R-CH}_2\text{-X}$ is an example of

- (a)✓ Primary alkyl halide (b) Secondary alkyl halide
(c) Isopropyl halide (d) Both (a) and (b)
- (v) The carbon atom carrying positive charge and attached to three other atoms or groups is called.
(a)✓ Carbonium ion (b) Carbon ion
(c) Oxonium ion (d) Carbanion
- (vi) Grignard reagent can be represented by general formula
(a) R-Mg-N (b) R-Mg-O
(c) R-Mg-OH (d)✓ R-Mg-X
- (vii) The end product reaction of Grignard reagent with Ethyl acetate is
(a) primary alcohol (b) secondary alcohol
(c)✓ tertiary alcohol (d) none of these
- (viii) A electron pair donor is classified as
(a) Lewis acid (b)✓ Lewis base
(c) Bronsted acid (d) Bronsted base
- (ix) In primary alkyl halides the carbon atom to which the halo group is attached is in turn bonded directly to
(a)✓ one other carbon (b) two other carbons
(c) three other carbons (d) four other carbons

SHORT QUESTIONS


Q.2. Short Questions:

(1) What is the importance of Grignard reagent?

Ans: Due to the great importance of Grignard reagent it is called as synthetic tool in the hands of organic chemists. It is used in the preparation of the following compounds.

- | | |
|---------------------------|------------------------------|
| (1) Alkanes | (2) Alkenes |
| (3) Alkynes | (4) Aldehydes |
| (5) Ketones | (6) Carboxylic acids |
| (7) Alcohols | (8) TML (tetramethyl lead) |
| (9) TEL (tetraethyl lead) | (10) TMS (tetramethylsilane) |

(2) Compare nucleophilic substitution reaction and electrophilic substitution reaction.

Ans.	Nucleophilic Substitution Reactions	Electrophilic Substitution Reactions
	<ul style="list-style-type: none"> ★ Reactions in which a nucleophile is replaced by another nucleophile. ★ These are represented as SN reactions. ★ These are the characteristic reactions of aliphatic hydrocarbons i.e. alkyl halides and alcohols etc. ★ A strong nucleophile replaces a weak nucleophile. ★ Representation $\begin{array}{c} \\ -\text{C}-\text{X} + \text{Nu} \longrightarrow -\text{C}-\text{Nu} + \bar{\text{X}} \\ \qquad \qquad \qquad \end{array}$	<ul style="list-style-type: none"> ★ Reactions in which an electrophile is replaced by another electrophile. ★ These are represented as ES reactions. ★ These are the characteristic reactions of aromatic hydrocarbons. ★ A strong electrophile replaces a weak nucleophile. ★ Representation 
	<ul style="list-style-type: none"> ★ Depend on nature of the solvent. ★ No catalyst is required. ★ It may be single step or two steps reaction. ★ The intermediate carbocation formed is stabilized by hyperconjugation effect. 	<ul style="list-style-type: none"> ★ Does not depend on nature of the solvent. ★ Catalyst is required. ★ It is a three steps reaction. ★ The intermediate sigma complex formed is stabilized by resonance effect.

(3) Why tertiary carbocation is more stable?

Ans. Given in the theory.

(4) In reaction between chloroethane and aqueous sodium hydroxide identify the attacking nucleophile and atom in the chloroethane molecule being attacked.

Nucleophile: $\bar{\text{O}}\text{H}$ group of NaOH

Substrate = $\text{CH}_3-\boxed{\text{CH}_2}-\text{Cl}$

Atom attacked = $\bar{\text{O}}\text{H}$ ions will attack partial positively charged carbon atom attached to chlorine atom.

(i) Aldehydes

(ii) ketones

(iii) Esters

(iv) carbon dioxide

Ans. Given in the theory.

(5) How amines are prepared? Discuss its structure and basicity.

Ans. Given in the theory.

(6) Write down different reactions of amines.

Ans. Given in the theory.
