

CHAPTER 17
ALKYL HALIDES AND
AMINES

After completing this lesson, you will be able to:

- name alkyl halides using IUPAC system.
- Discuss the and reactivity of RX.
- Describe the preparation of RX by the reaction of alcohols with WC, SQC12 and by radical halogenations of alkanes.
- Describe the mechanism and types of nucleophilic substitution reaction (Understanding)
- Describe the and types of elimination reactions.
- Describe the preparation and reactivity of Grignard's Reagents.
- Discuss chemistry of Grignard's reagent by the addition of aldehyde, ketones, ester and carbon dioxide.
- Discuss and basicity of amines. Describe the preparation amines by alkylation of ammonia to RX and reduction of nitriles, nitro and functional groups.
- Discuss reactivity of amines.
- Describe chemistry of amines by alkylation of amines with RX, reaction with ketones preparations of amides and diazonium salts.

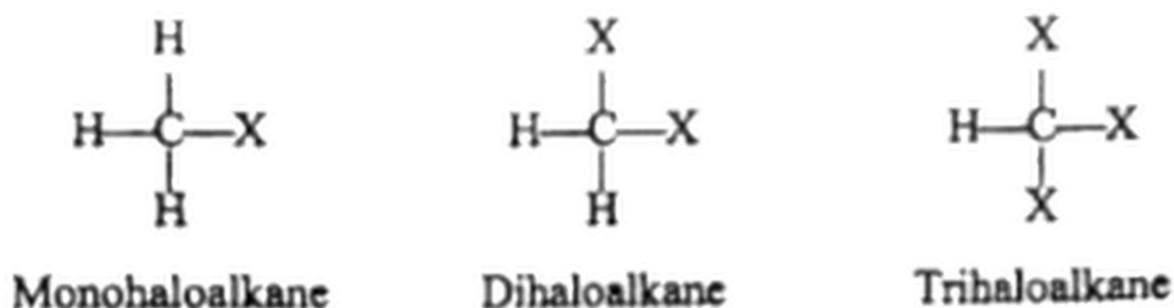
Q1. What are alkyl Halides? Explain with examples.

Answer

"Alkyl halides are the compounds in which one hydrogen atom of Alkanes has been replaced by one halogen atom. They are also known as halogen derivatives."

Types:

They may be Mono, di, tri or poly haloalkanes depending upon the number of halogen atoms present in the molecule. Monohaloalkanes are called alkyl halides having general formula R-X.

**Classification of Alkyl Halides:**

Alkyl halides are classified into primary, secondary and tertiary alkyls halides.

i) Primary Alkyl Halides:

"Alkyl halide in which halogen atom is attached with primary carbon are called primary halides. Carbon atom attached to one or no carbon atom is called primary C - atom."



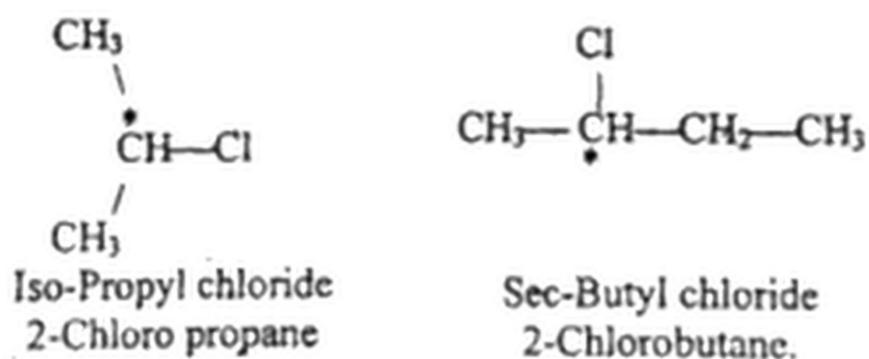
($\overset{\cdot}{\text{C}}$ is a primary carbon atom)

ii) Secondary Alkyl Halides:

"Alkyl halide in which halogen atom is attached with a secondary carbon atom is called secondary alkyl halide."

Secondary C-atom:

"C-atom, attached to two C-atoms simultaneously is called secondary C-atom."



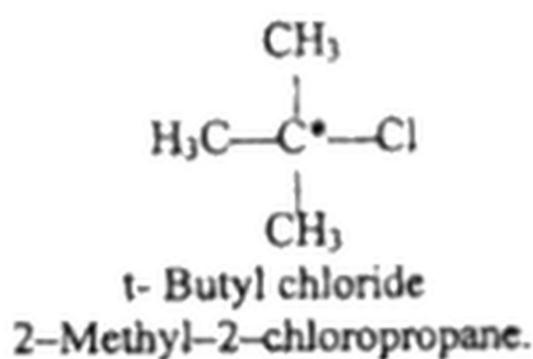
(C^\bullet is the secondary carbon atom)

iii) Tertiary Alkyl Halides:

"Alkyl halides, in which halogen atom is attached to a tertiary carbon is called tertiary alkyl halide".

Tertiary C-atom

"C-atom, attached to three C-atoms simultaneously is called tertiary C-atom".



(C^\bullet is tertiary carbon atom)

Nomenclature of Alkyl halides

Alkyl halides are named according to the following systems:

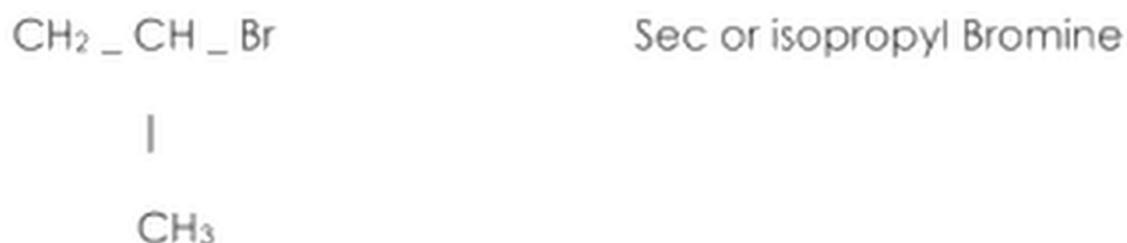
- i) Common System of naming.
- ii) IUPAC System of naming.

I) Common System of Naming:

This method consists in first writing the name of alkyl group to which halogen atom is attached and then writing the name of halide ion, e.g.,



For secondary alkyl halides, the prefix sec _ and for tertiary alkyl halides, the prefix ter_ to t_ is added before the name of alkyl halides, e.g.,



When all the carbons of alkyl group of primary alkyl halides are in a straight chain, the prefix n- is used before the name which indicates 'normal'. e.g,



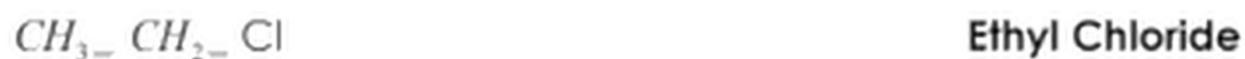
II) IUPAC System of naming.

According to this system alkyl halides are named as derivatives of alkanes. The following rules are observed for this purpose:

- i) The longest chain bearing halogen is selected as parent hydrocarbon.
- ii) Prefix 'halo' i.e., chloro for Cl, Bromo for Br, etc, is used before the name of hydrocarbon.
- iii) Positional numbers are used to indicate halogen and other substituent by the usual methods,



The names given below are also accepted by the IUPAC





Q2. Give Physical Properties of Alkyl Halides

Answer

1) The polar bond creates a molecular dipole that raises the melting points and boiling points compared to alkanes.

Structure:

- The alkyl halide functional group consists of an sp^3 hybridized C atom bonded to a halogen, X, via a σ bond.
- The carbon halogen is typically quite polar due to the electronegativity and polarizability of the halogen.

Q3. Give preparations of alkyl halides.

Answer

1) Reaction of Alcohols with Hydrogen Halides

Alcohols may be converted to the corresponding alkyl halides by the action of halogen acid in the presence of $ZnCl_2$, which acts as a catalyst.



2) Reaction of Alcohols with other Halogenating agents (SOCl_2 , PX_3)

- a) Alcohols reacts with thionyl chloride in pyridine as a solvent to give alkyl chlorides.

This is the best method because HCl, and SO₂ escape leaving behind the pure product.



b) Phosphorous or phosphorous pentahalides react with alcohols to form alkyl halides.



3) Halogenation of Alkanes

By the action of chlorine or bromine, alkanes are converted into alkyl halides. This reaction takes place in the presence of diffused sunlight or ultraviolet light.



This method does not give pure alkyl halides. Halogen derivatives containing two or more halogen atoms are also formed along with alkyl halides.

The detail mechanism of this reaction has already been discussed in section 16.3.2.

Reactivity of Alkyl Halides

There are two main factors which control the reactivity of alkyl halides:

- i) Bond polarity of C-X bond
- ii) Bond energy of C-X bond

1) Bond Polarity

The molecule of alkyl halide is polarized due to the greater electronegativity of halogens as compared to C.

Atom	Electronegativity	Atom	Electronegativity
F	4.0	I	2.5
Cl	3.0	H	2.1
Br	2.8	C	2.5

Hence carbon acquires partial positive whereas halogens acquires partial negative charge. Halogen becomes nucleophilic in character, which can be replaced by another nucleophile.

2) Bond Energy

Experiments have shown that the bond energy of C-X bond is the main factor which decides the reactivity of alkyl halides, and not the polarity of the molecule.

A study of bond energies of C-X bond shows that C-F bond is the strongest. So, the overall order of reactivity of alkyl halides is:



In fact, the C-F bond is so strong that alkyl fluorides do not react under ordinary conditions.

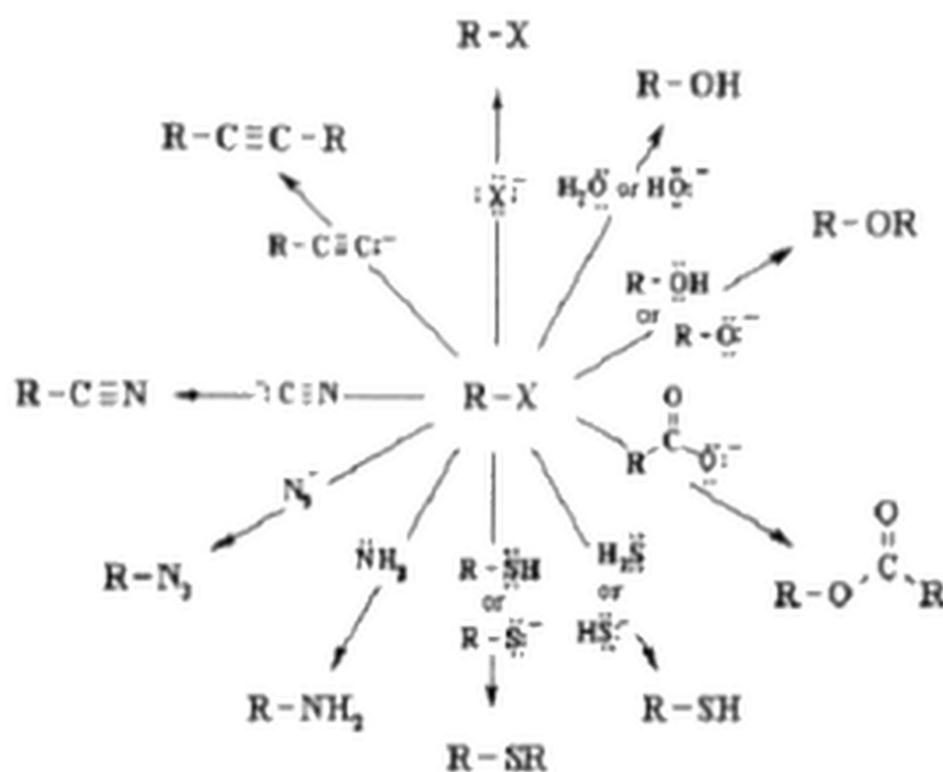
Q4. Give nucleophilic substitution reactions of alkyl halides.

Answer

- 1) Alkyl chlorides, bromides and iodides are good substrates for substitution reactions.
- 2) A variety of nucleophiles can be used to generate a range of new functional groups.
- 3) The following diagram reflects some of the more important reactions you may encounter.

- 4) For practice, make sure you can draw the mechanisms that lead to these products.

Reactions



Nucleophilic Substitution Reactions

General Introduction What does the term nucleophilic substitution imply?

- **A nucleophile** is electron rich species that will react with an electron poor species
- **A substitution** implies that one group replaces another.

Nucleophilic substitution reactions occur when an rich species, the nucleophile, reacts at an electrophilic C atom attached to an electronegative group (important), the leaving group, that can be displaced as shown by the general scheme:



The electrophilic C can be recognized by looking for the polar sigma bond due to the presence of an electronegative substituent (esp. C-Cl, C-Br, C-I and C-O)

Nucleophilic substitution reactions are an important class of reactions that allow the interconversion of functional groups.

Of particular importance are the reactions of alkyl halides (R-X) and alcohols (R-OH). For alcohols, the range of substitution reactions possible can be increased by utilizing the tosylates (R-OTs), an alternative method of converting the -OH to a better leaving group.

Overall a nucleophilic substitution can be represented as follows:



There are two fundamental events in a nucleophilic substitution reaction:

- 1) formation of the new σ bond to the nucleophile
- 2) breaking of the σ bond to the leaving group

Depending on the relative timing of these events, two different mechanisms are possible:

- Bond breaking to form a carbocation precedes the formation of the new bond: $\text{S}_{\text{N}}1$ reaction
- Simultaneous bond formation and bond breaking: $\text{S}_{\text{N}}2$ reaction

CARBOCATIONS AND THEIR STABILITY

Stability:

The general stability order of simple alkyl carbocations is: (most stable) $3^\circ > 2^\circ > 1^\circ > \text{methyl}$ (least stable)



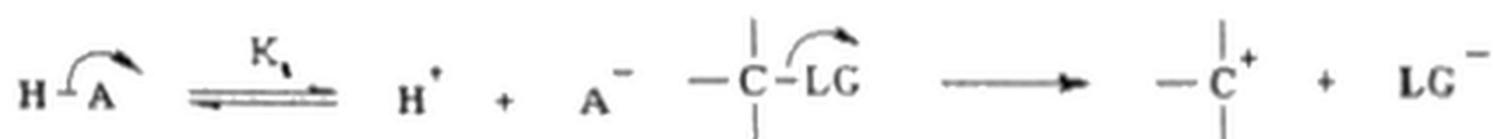
Answer**Substrate Molecule:**

The alkyl halide molecule on which a nucleophile attacks is called a substrate molecule.

Leaving Group (LG):

Leaving group is also a nucleophile. It departs with an unshared pair of electrons. The incoming nucleophile must be stronger than the departing one, Cl⁻, Br⁻, I⁻, HS₀₄⁻ are good leaving groups. Poor leaving groups are OH⁻, OR and NH₂⁻, Iodide ion is a good nucleophile as well as a good leaving group.

What do we mean by this? First, we should write the chemical equations for the two processes:



These two equations represent Bronsted acid dissociation and loss of a leaving group in a S_N1 type reaction. Note the similarity of the two equations: both show heterolytic cleavage of a σ bond to create an anion and a cation.

For acidity, the more stable A⁻ is, then the more the equilibrium will favor dissociation, and release of protons meaning that HA is more acidic.

For the leaving group, the more stable LG⁻ is, the more it favors "leaving".

Hence factors that stabilize A⁻ also apply to the stabilization of a LG⁻.

Type equation here. Here is a table classifying some common leaving groups that we will eventually meet Excellent

Excellent	TsO, NH ₃
Very Good	I, H ₂ O

Good	Br
Fair	Cl
Poor	F
Very Poor	HO, NH ₂ , RO

But water itself, H₂O, is a good leaving group, since it is the conjugate base of H₃O⁺ which

Q7. Give S_N1 Reaction mechanism.

Answer

S_N1 Mechanism

"It is substitution nucleophilic unimolecular two step reaction."

Explanation:

The substrate R-X first ionizes reversibly into R⁺ and X⁻ ions.



Then the carbonium ion combines with the attacking nucleophile to form product.



Since only one molecule is undergoing a change in covalency in rate determining step, this two-step nucleophilic substitution reaction is unimolecular and is called S_N1 reaction. The brief mechanistic picture of S_N1 reaction based upon the following evidences:

1) Kinetic Evidence:

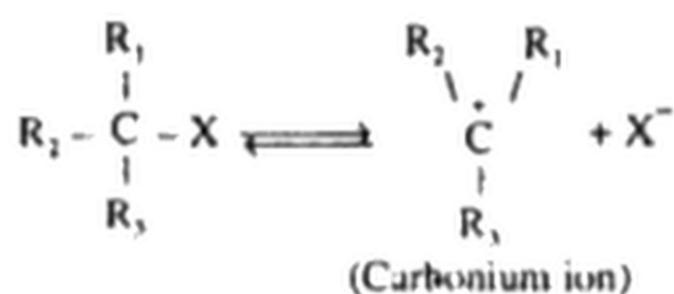
The rate of an S_N1 reaction depends upon the concentration of alkyl halide only. The change in concentration of attacking nucleophile has no effect on the rate

$$\text{Rate} = k[\text{R-X}]$$

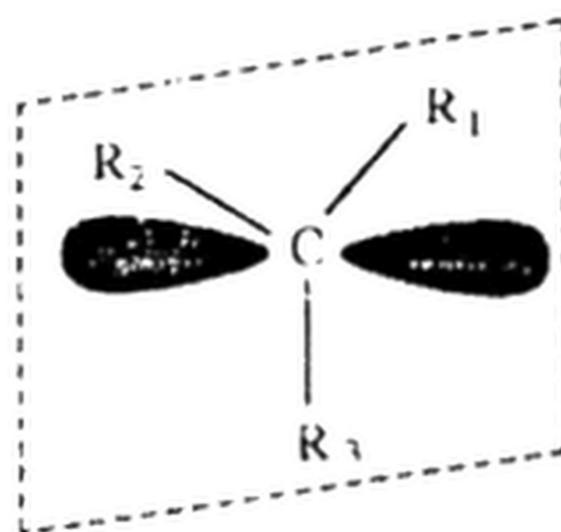
It is because the nucleophile combines with the carbonium ion in the second step. For the same reason, the rate of an S_N1 reaction does not depend on the nature of attacking nucleophile.

2) Stereo Chemical Evidence:

Experiments have shown that S_N1 reaction occur with partial racemization. The extent of partial racemization depends upon several factors including stability of carbonium ion.

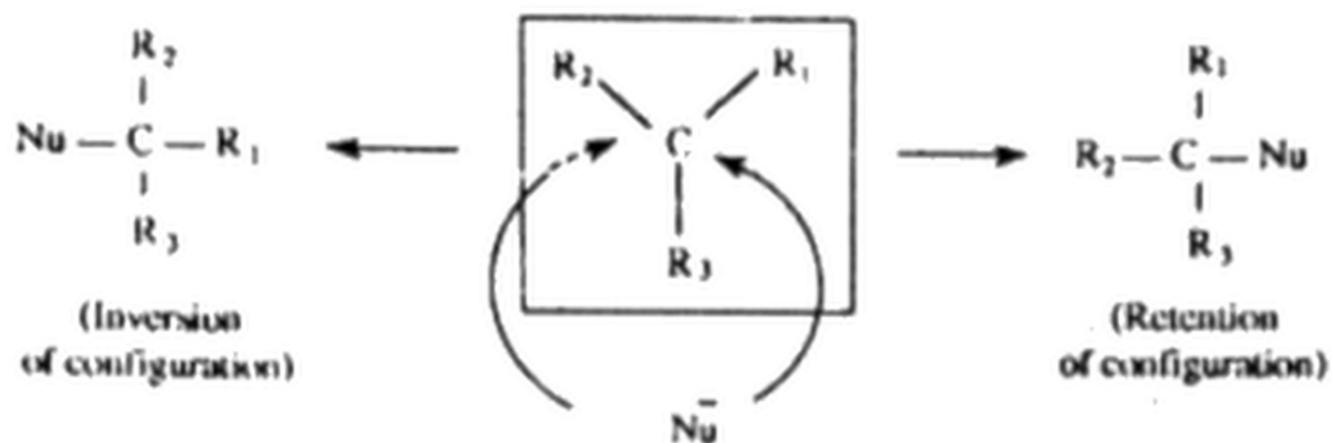


The carbon atom of carbonium ion is sp² hybridized and carries one empty p-orbital. The nucleophile can attach itself to the p-orbital either on the right or on the left side of carbon with equal ease. The expected product is a racemic mixture. However, the partial racemization suggests a different way of attachment, e.g., in case of unstable carbonium ion, the attack of nucleophile is greater from the side



opposite to that of leaving group. Thus, the side of carbon atom to which the leaving group is attached is somewhat shielded from the attack of nucleophile. The attack of nucleophile occurs more often

on the side opposite to the side to which leaving group is attached, leading to partial inversion of configuration



Therefore, the product has some optical activity.

Step 1: slow loss of the leaving group, to generate a carbocation intermediate



Step 2: rapid attack of a nucleophile on the electrophilic carbocation to form a new σ bond



Q8. Give SN2 Reaction Mechanism.

Answer

"It is substitution nucleophilic bimolecular reaction. It occurs in one step".

Explanation:

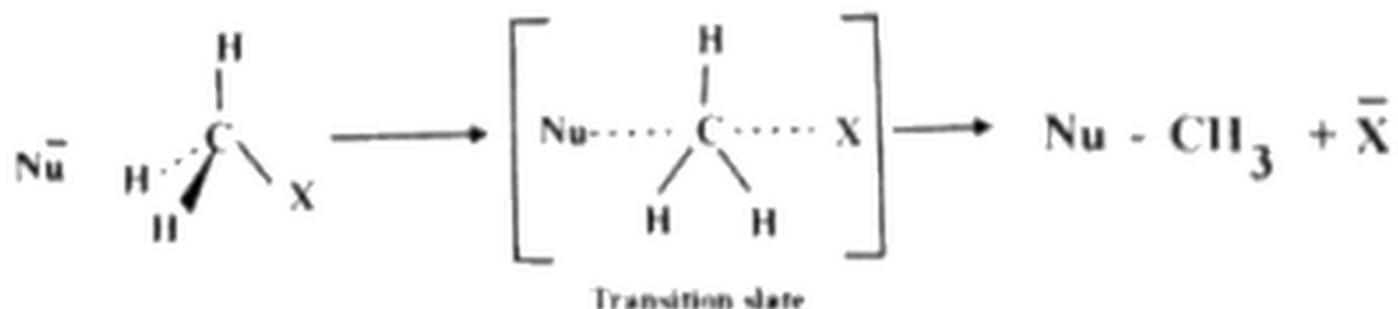
Consider the reaction:



(Nucleophile)

Mechanism:

The attack of nucleophile on carbon and the departure of the halide ion take place simultaneously in single step,



This is rate determining step because the bond breaking and bond making processes occur simultaneously. Since two molecules are undergoing change in covalency in rate determining step. It is a bimolecular nucleophilic substitution reaction which is taking place in one step. This mechanistic picture is based upon the following evidences.

1) Kinetic Evidence:

The rate of an SN2 reaction depends upon the concentration of nucleophile as well as the concentration of alkyl halide. The rate expression for the reaction

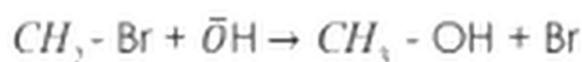


can be written as

$$\text{Rate} = [\text{Nu}][\text{R-X}]$$

Where k = specific rate constant.

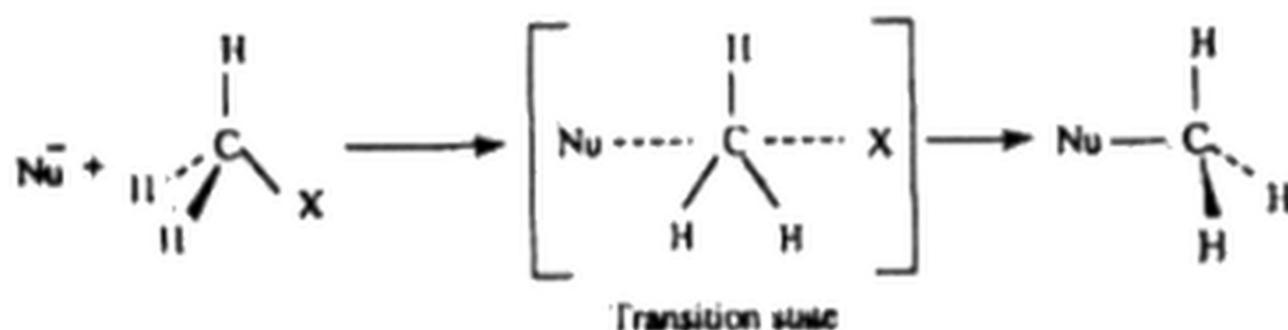
This means that the rate of reaction will be double if the concentration of any of the two is double e.g., the rate of hydrogen.



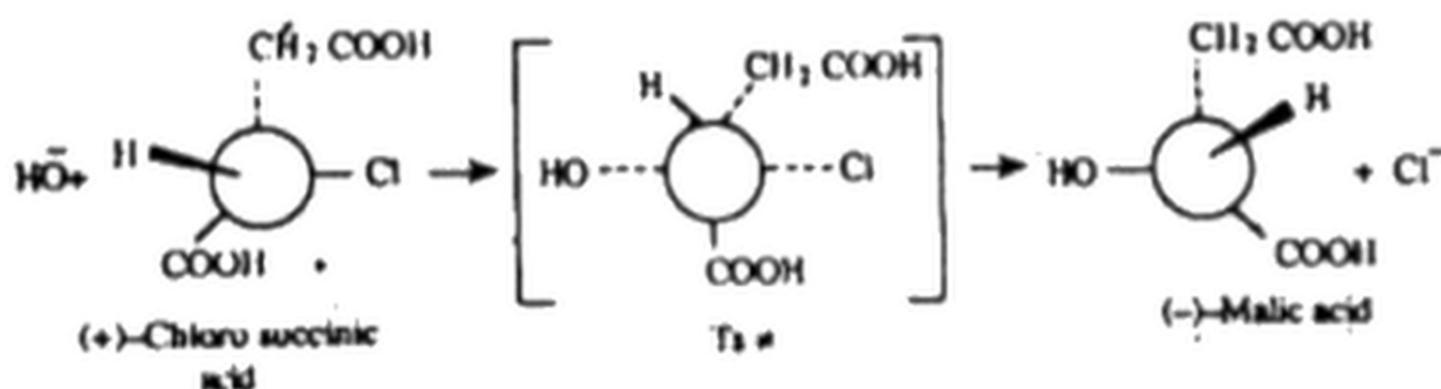
Increases when either OH or CH₃-Br is increased.

2) Stereo Chemical Evidence:

A bimolecular nucleophilic substitution always occurs with inversion of configuration. The carbon atom in transition state is sp^2 -hybridized and is planar. The attacking nucleophile and the leaving groups are present in the transition state on opposite sides of electrophilic carbon atom.



In methyl chloride, we cannot prove the inversion of configuration because it is optically inactive. However, the reaction of a hydroxide ion with chloro succinic acid is found to occur with inversion of configuration.



Comparison of S_N1 and S_N2 Mechanism

Sr. No.	S_N1	Sr.	S_N2
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(1)	It is a two step mechanism.	(1)	It is a single step mechanism.
(2)	First step is slow one and second is fast.	(2)	It has only one step and that is slow.
(3)	It is a unimolecular reaction.	(3)	It is a bimolecular reaction.
(4)	It is favoured in polar solvents.	(4)	It is favoured in non-polar solvents.
(5)	Mostly tertiary alkyl halides give this reaction.	(5)	Mostly primary alkyl halides give this reaction.
(6)	50 % is inversion and 50% retention of configuration takes place.	(6)	100% inversion of configuration takes place.

Q9. What are Elimination Reactions?

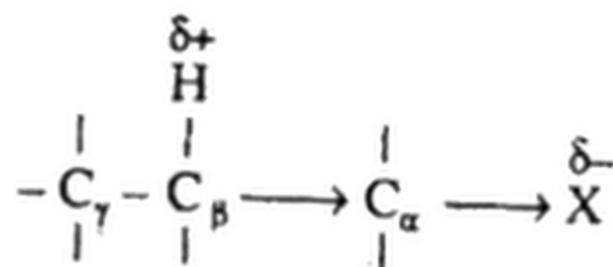
Answer

Definition of Elimination Reaction:

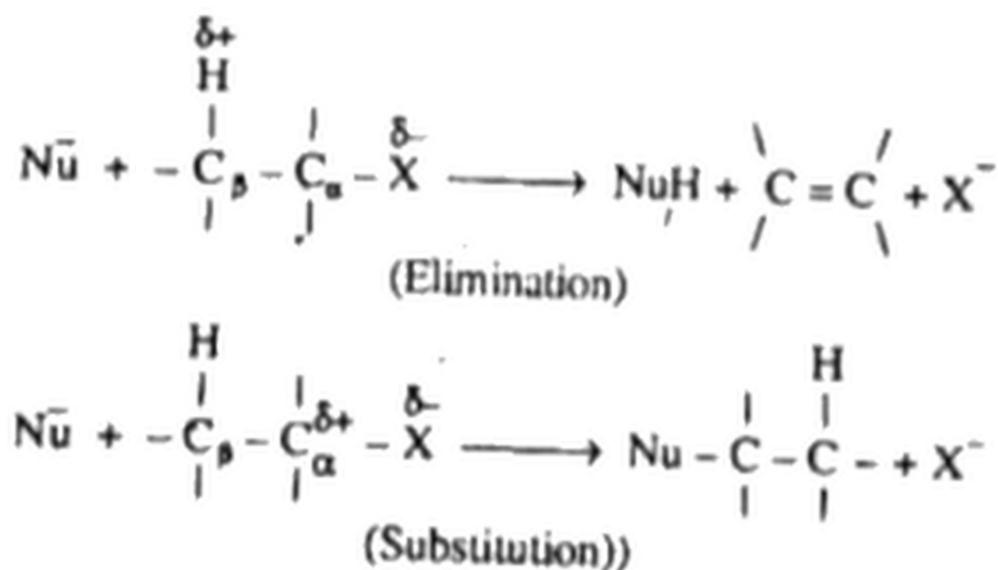
"The chemical reaction in which two groups are eliminated from two adjacent atoms is called elimination reaction". Since β -hydrogen is necessary for eliminations, it is also called P-elimination.

Explanation:

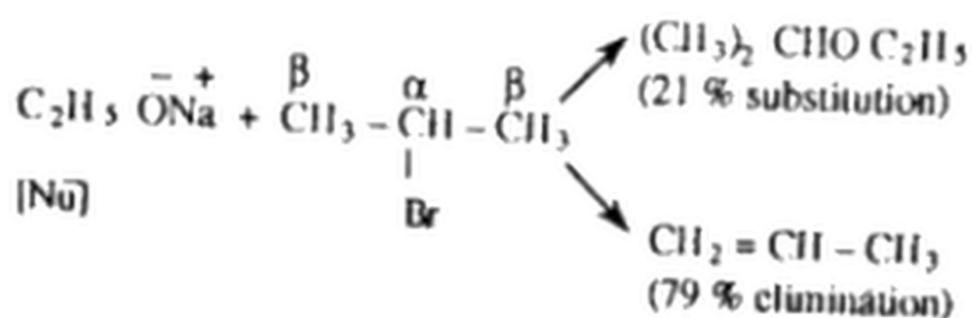
P-hydrogen atom in alkyl halides is slightly acidic due to electron withdrawing effect of halogen.



The attacking nucleophile can either attack α -carbon to give substitution product or hydrogen to give elimination reaction.



Strong bases such as OH⁻, OR⁻, NH₂⁻ cause elimination in preferences to substitution. Highly polarizable nucleophile and weak bases such as I⁻, RS⁻ etc. give substitution reactions.

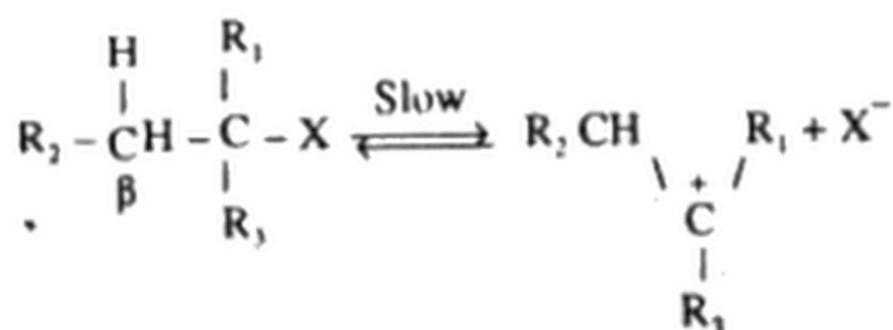


El Mechanism

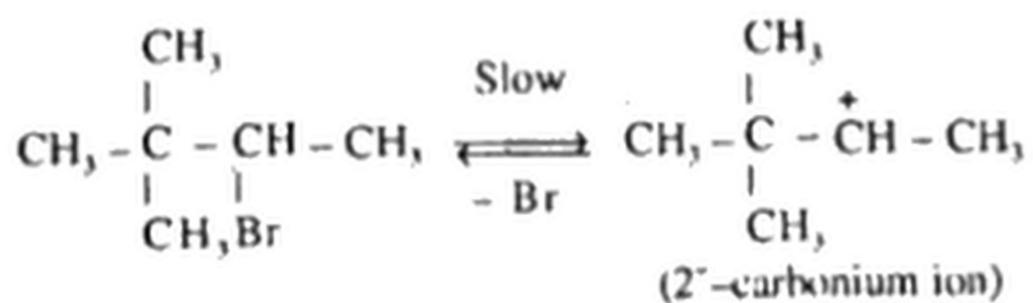
"It is unimolecular two step elimination reactions."

Explanation:

The substrate undergoes slow ionization in the first step to form carbonium ion,



In the second step the solvent or base pulls off a P-hydrogen

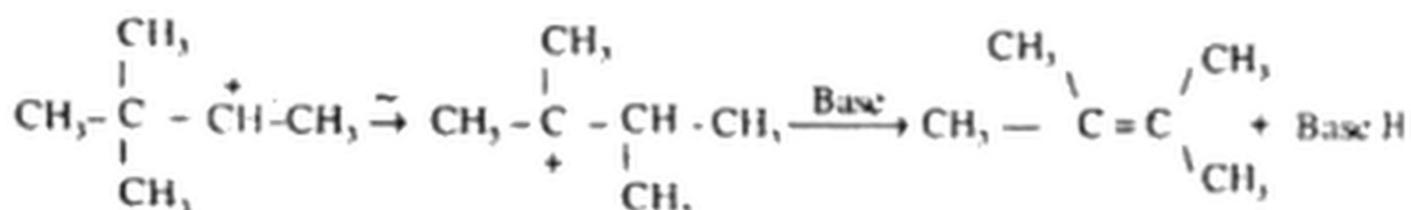
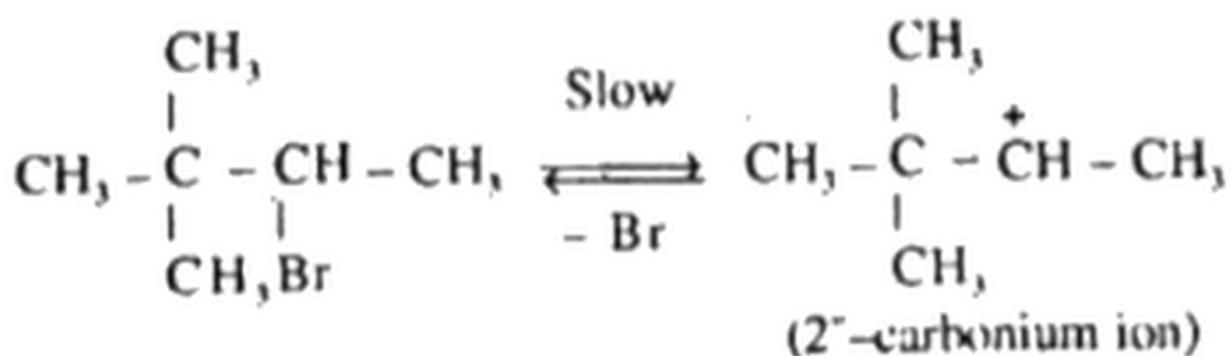


Since only one molecule is undergoing a change in the rate determining step, i.e., first step, this is two step unimolecular elimination reactions.

The E1-mechanism has been supported by the study of the reaction. It follows first order kinetics, in which rate of reaction depends only on the concentration of substrate.

$$\text{Rate} = k[\text{R-X}]$$

The presence of carbonium ion as an intermediate has been indicated by the presence of more than one kind of elimination products. A relatively less stable carbonium ion rearranges to give a more stable carbonium ion before giving the elimination product.

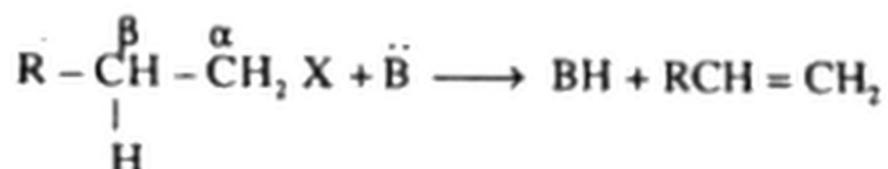


E2 mechanism

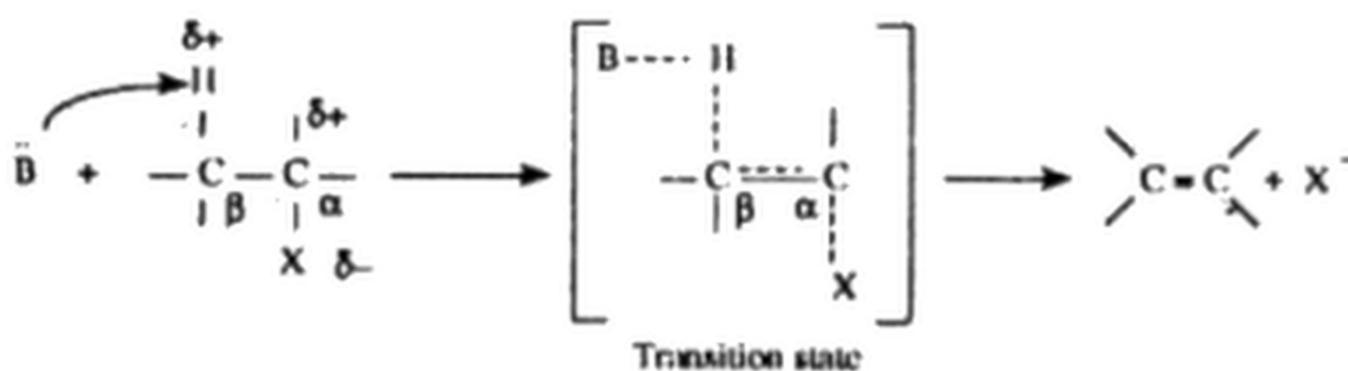
"It is bimolecular one step elimination reaction".

Explanation:

Consider the reaction,



The attacking base removes a proton from the β -carbon simultaneously with the formation of double bond between C_α and C_β and the loss of halide ions.

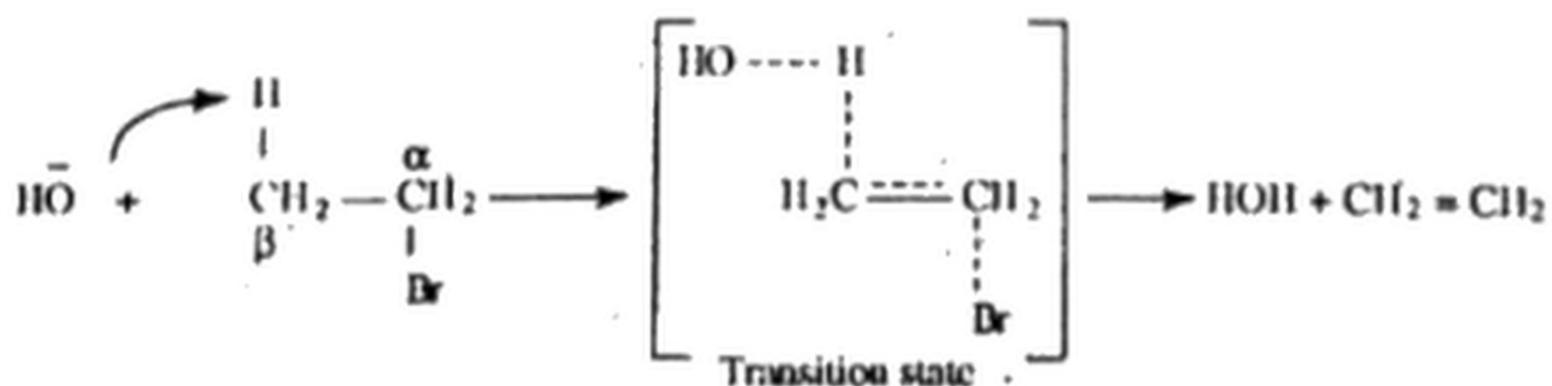


This is rate determining step because bond breaking and bond making processes are taking place simultaneously.

Since two molecules are undergoing a change in transition state, it is a bimolecular one step elimination reaction. Thus, E2 is a one step process in which both the substrate and the base participate. The observed rate law the E2-reaction is

$$\text{Rate} = k[\text{R-X}] [\text{B}]$$

The rate of E2-reaction depends upon the concentration of substrate and the base e.g., for the reaction



The rate of reaction follows second order kinetics

$$\text{Rate} = k [\text{CH}_3, \text{CH}_2 \text{ Br}] [\text{OH}^-]$$

Q10. Give a Comparison of Substitution & Elimination Reactions.

Answer

Though substitution and elimination reaction lead to different products, there is always a competition between them because of close resemblance in their mechanism.

Since substitution is more favorable energetically it is the dominant reaction in the substitution-elimination reaction.

Elimination occurs only in the presence of B-H where substitution reactions do not require this condition to be satisfied.

The following factors help to compare these two path ways:

i) Structure of Substrate:

Crowding within the substrate favors elimination over substitute because the approach of the nucleophile to a-carbon is difficult for substitution. However, the elimination is favorable because the removal of B-H atom by base from tertiary planar carbonium ion is easy, e.g.,



(elimination = 12%)

CH₃

\



/

CH₃

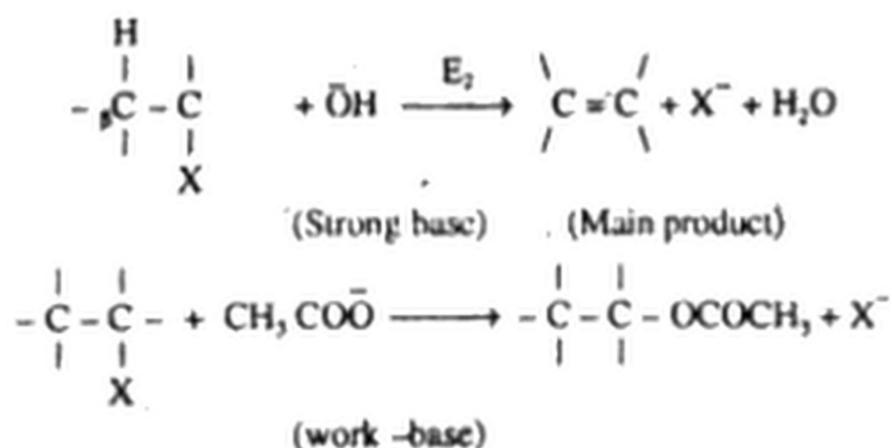
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CH₃

Subst. 39% (elimination = 61%)

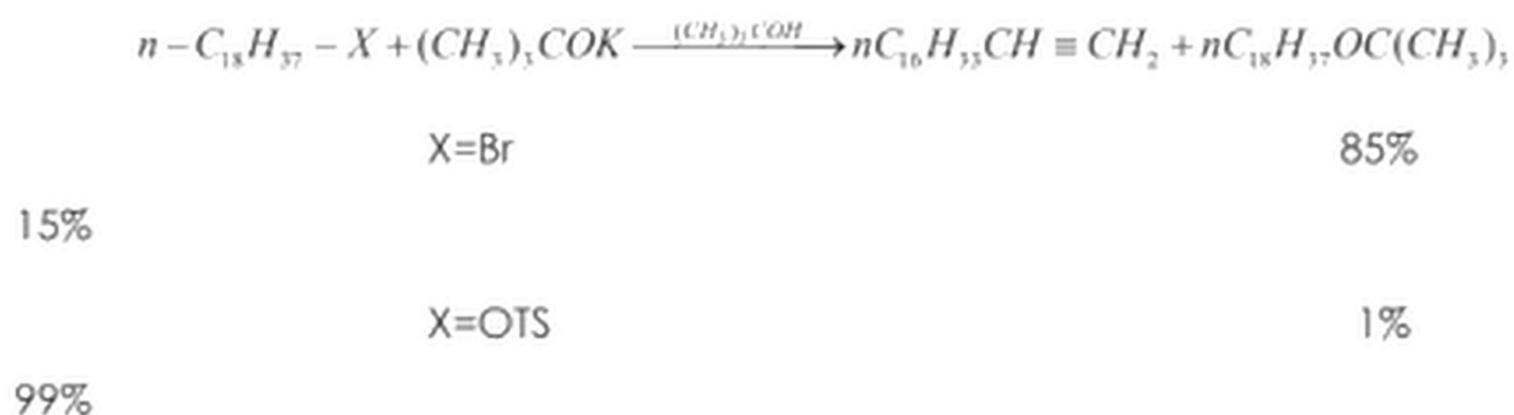
ii) Nature of Base:

When the electron pair donor is a strong base, e.g., OH, OR etc., the dominant reaction is E2 and SN2 reaction is a side reaction. However, when the nucleophile is a weak base like X⁻, RS⁻, etc., The main reaction will be substitution and E2 will be minor side reaction.



iii) the nature of Leaving Group:

The role of leaving groups in Elimination reactions is similar to that in substitution reactions. In unimolecular reactions it does not affect the mechanism because both the elimination and substitution products are decided with carbonium ion. However, in the bimolecular reactions the nature of product greatly depends upon the nature of leaving group, e.g.,



iv) Nature of Solvent

Elimination is favored more than substitution by decreasing the solvent polarity. Thus, alcoholic KOH affects elimination while more polar aqueous KOH is used for substitution. E1 is favored by polar solvents like S_N1 reaction. In non-polar solvents, the reaction will follow E2-mechanism.

v) Effect of Temperature

An increase in temperature will favor more than substitution, because substitution reaction involves less reorganization of bonds as compared to eliminations, e.g.,



at 25°C 17% 83%

at 65°C 36% 64%



I

Br

at 45°C 53%

47%

at 100°C 64%

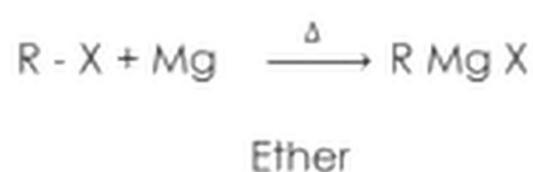
36%

Q11. What are Organ metallic Compounds (Grignard's Reagents)? Give their preparation & Reactions.

Answer

Preparation of Grignard's Reagents

Magnesium metal cut into small pieces is added to a solution in of an alkyl halide or awl halide in only dry ether. The reaction mixture is heated with electric heater in a round bottom flask fitted with condenser and other arrangement to avoid the contact of moisture or oxygen.



Alkyl bromides are generally used in the preparation of Grignard's reagents because of their intermediate reactivity. When alkyl halides are used, the solvent is either the high boiling solvent such as tetrahydrofuran is employed when less reactive aryl halides are used. Alkyl magnesium halides are not isolated but are used as ethereal layers.

Reactivity of Grignard's Reagent

Organometallic compounds are nucleophilic because of the partial negative charge on the carbon of the alkyl group

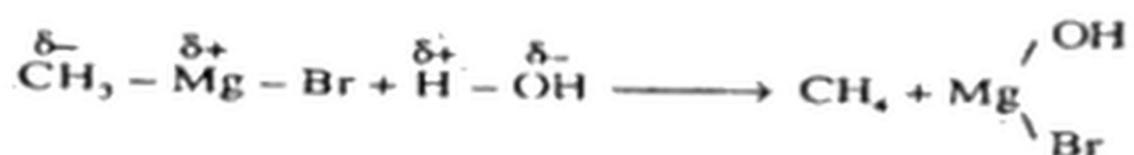


Carbon atom being more electronegative than metals such as Mg, Li etc., the alkyl

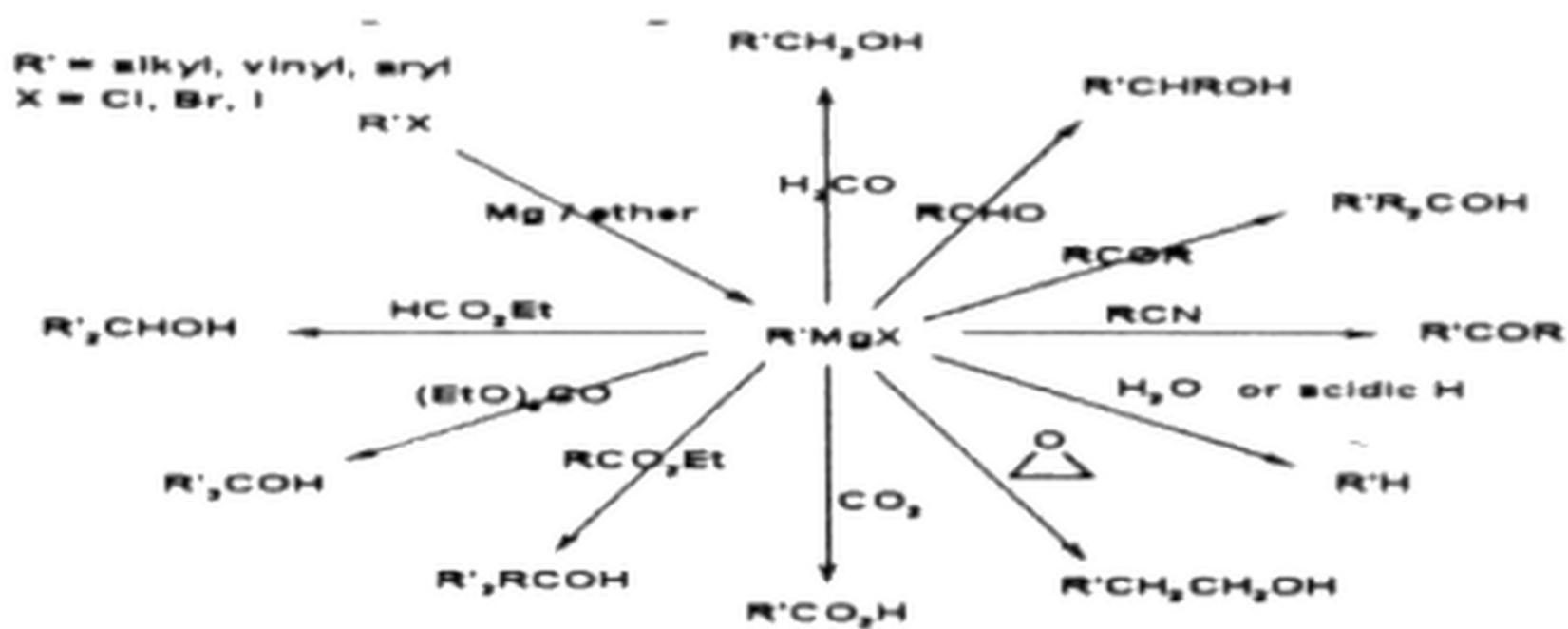
group as a whole bears a partial negative charge and organometallic compounds act as a source of nucleophile, e.g.,



The following reaction supports the electrophilic character of organometallic compounds:



Reactions of Grignard's Reagents



Typical work-up for these reactions:
 1. Dilute aqueous acid or
 2. Aqueous ammonium chloride

1) With Aldehydes and Ketones

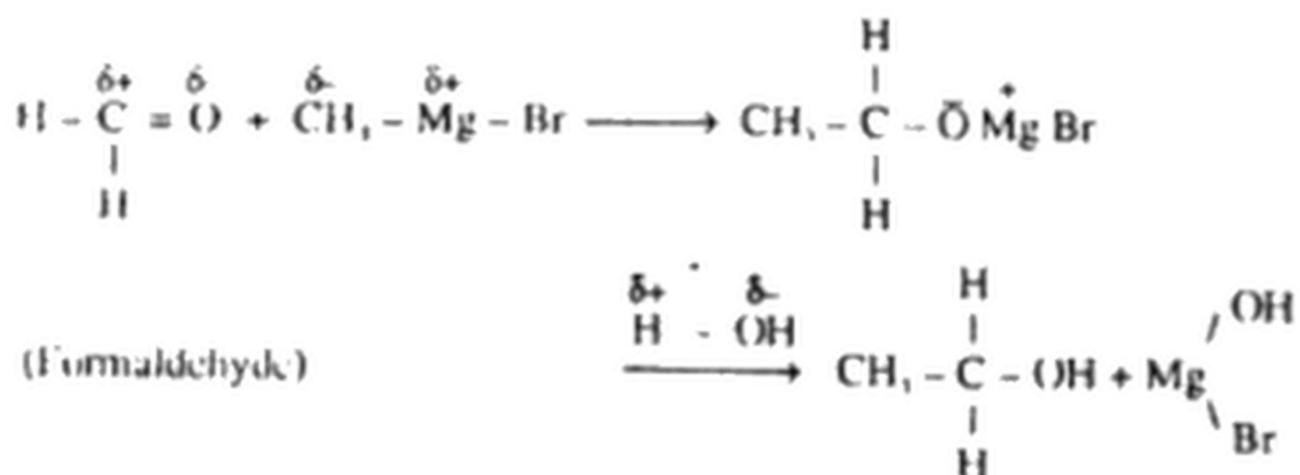
This is done in following three steps to produce primary, secondary and tertiary alcohols. These reactions are carried in the presence of ether followed by H_3O^+ . First two reactions are with aldehydes while third belongs to ketones.

Classification of Monohydric Alcohols:

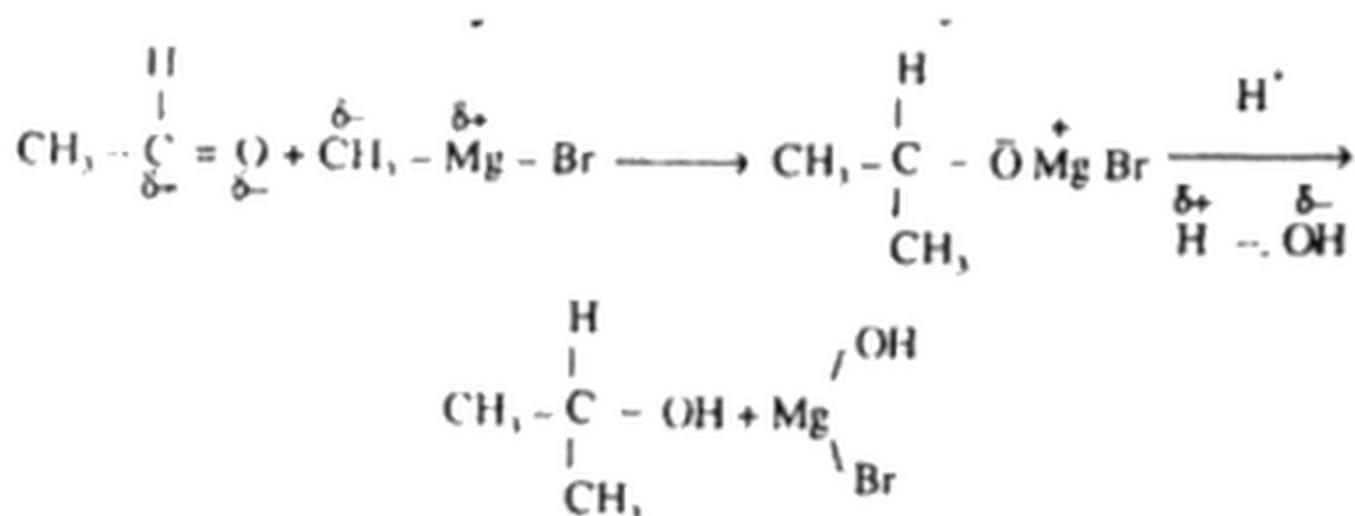
Monohydric alcohols are classified into the following three families:

- i) Primary alcohols
- ii) Secondary alcohols
- iii) Tertiary alcohols

i) Reaction with Methanol (Aldehyde) to form primary alcohol



ii) Reaction with Ethanal (Aldehyde) to form secondary alcohol



2) With Esters



Reaction type: Nucleophilic Acyl Substitution then Nucleophilic Addition

Elaboration:

- i) Carboxylic esters, $\text{R}'\text{CO}_2\text{R}''$, react with 2 equivalents of organolithium or Grignard reagents to give tertiary alcohols.
- ii) The tertiary alcohol contains 2 identical alkyl groups (see R)
- iii) The reaction proceeds via a ketone intermediate which then reacts with the second equivalent of the organometallic reagent.

iv) Since the ketone is more reactive than the ester, the reaction cannot be used as a preparation of ketones.

REACTION OF RLi or RMgX WITH AN ESTER

Step 1:

The nucleophilic C in the organometallic reagent adds to the electrophilic C in the polar carbonyl group of the ester. Electrons from the C=O move to the electronegative O creating an intermediate metal alkoxide complex.

Step 2:

The tetrahedral intermediate collapses and displaces Cl⁻; the alcohol portion of the ester as a leaving group, this produces a ketone as an intermediate.

Step 3:

The nucleophilic C in the organometallic reagent adds electrophilic to the electrophilic C in the polar carbonyl group of the ketone. Electrons from the C=O move to the electronegative O creating an intermediate metal alkoxide complex.

Step 4:

This is the work-up step, a simple acid/base reaction. Protonation of the alkoxide oxygen creates the alcohol product from the intermediate complex.

3) With CO₂ (Carbonation of Grignard Reagents, RMgX) Nucleophilic Addition of Rmgx to Carbon Dioxide

Step 1:

The nucleophilic C in the Grignard reagent adds to the electrophilic C in the polar carbonyl group, electrons from the C=O move to the electronegative O creating an intermediate magnesium carboxylate complex.

Step 2:

This is the work-up step, a simple acid/base reaction. Protonation of the carboxylate oxygen creates the carboxylic acid product from the intermediate complex.

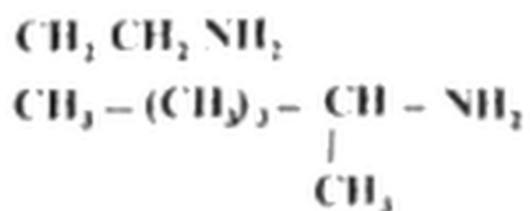
Q12. What are amines? Give their Nomenclature preparation & properties.

Answer

Nomenclature of Amines:

1) Common System of Naming

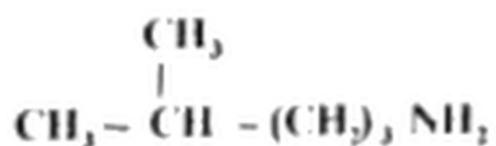
The common names of amines are written by adding the suffix-amine to the name of alkyl or aryl radicals.



Ethyl amine

Sec-hexyl amine

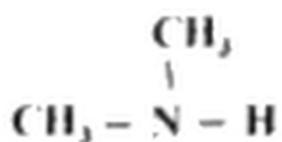
(a primary amine,
sec-indicates secondary group)



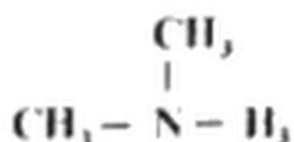
Iso-hexyl amine

a primary amine

(Iso-represents radical)



Dimethyl amine (a sec-amine)



Trimethyl amine (a ter-amine)

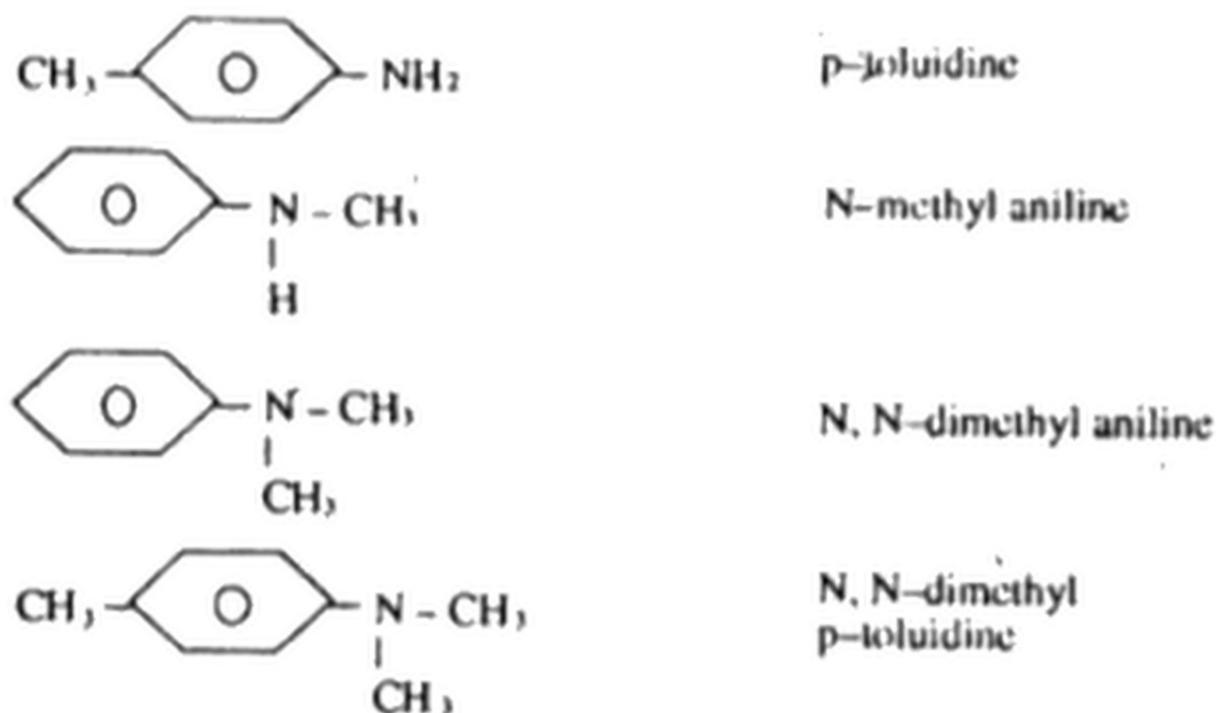


Pyridine (a ter-amine)



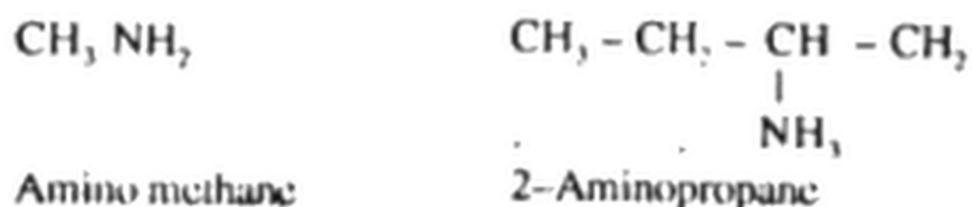
Piperidine

Aniline, $C_6H_5NH_2$ containing methyl group on the ring is called Toluidine. If there is some alkyl group substituted in $-NH_2$ its name is represented by writing N-(alkyl group). It indicates that alkyl group is located on N-atom and not on the ring. If there are two substituents on N, it is repeated twice.

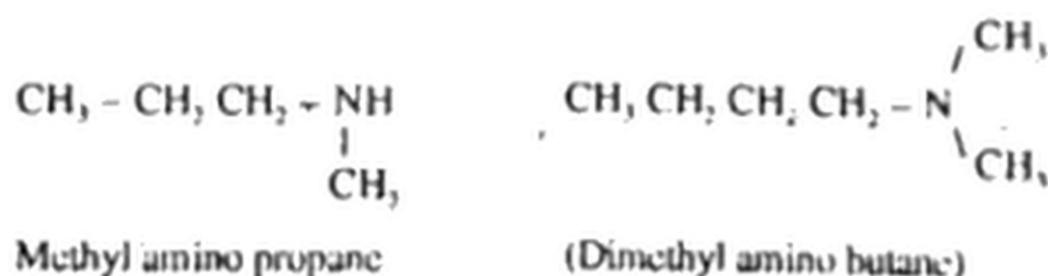


2) IUPAC System of Naming

In this system amino group is indicated by a prefix-amino followed by name of hydrocarbons, the position of amino group is indicated by a number obtained by numbering the chain of hydrocarbon.



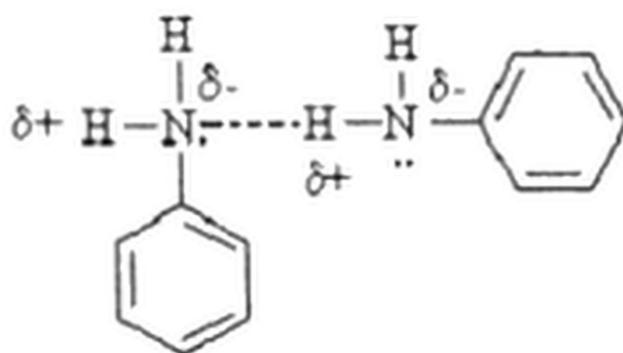
Secondary and tertiary amines are named by using a compound prefix that includes the names of all but the largest alkyl group.



Physical Properties:

The polar nature of the N-H bond (due to the electronegativity difference of the two atoms) results in the formation of hydrogen bonds with other amine molecules, see below, or other H-bonding systems (e.g. water). The implications of this are:

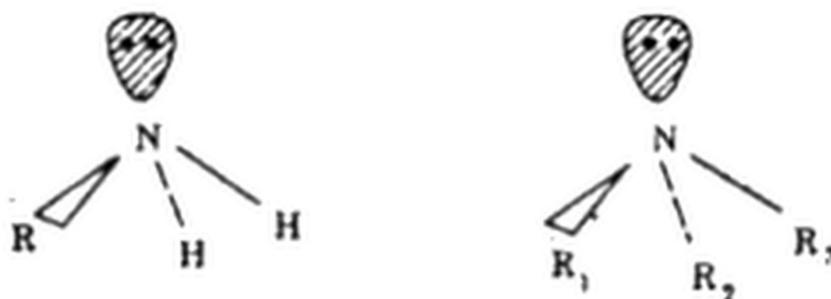
- high melting and boiling points compared to analogous alkanes
- high solubility in aqueous media



intermolecular H-bonding in amines

Structure:

In amines, nitrogen atom is sp^3 -hybridized and has nearly tetrahedral structure. It forms three sigma bonds with its three sp^3 -hybrid orbitals while the fourth non-bonding sp^3 hybrid carries a pair electron



(Such tertiary amine is optically active)

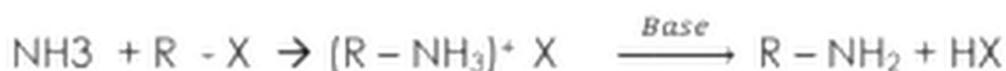
The non-bonding electron pair is extremely important in explaining the chemical behavior of amines because it is responsible for the basic and nucleophilic properties of these compounds. An amine with three different groups is optically active.

Basicity of amines:

Amines may act as bases towards acids and as Nucleophiles towards electrophile. They are more basic than alcohols and ethers and they are also more nucleophilic, e.g., ether does not react whereas at the same temperature amines gives addition product with CH_3I ,

**Preparation of Amines****1) Alkylation of Ammonia by Alkyl Halides**

When an alcoholic or aqueous solution of ammonia is heated with an alkyl halide, a mixture of prim-, sec-, ter- amines and a quaternary ammonium salt is obtained. The reaction occurs with nucleophilic displacement of halide by ammonia of amines,



This reaction is further alkylation, e.g., accompanies by the following reactions



|

H



|

H

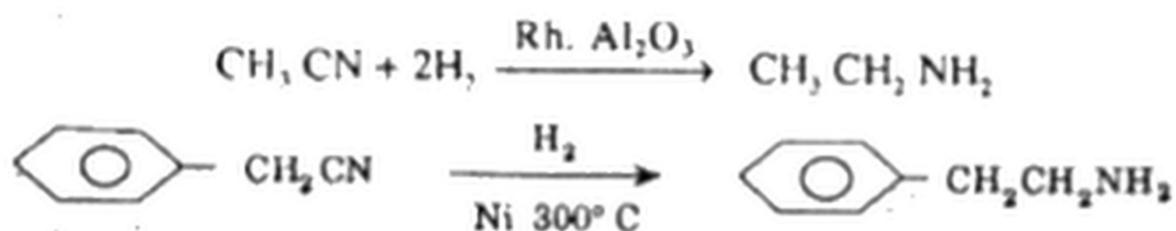


At the end of the reaction, addition of strong alkali such as KOH liberates free amines from their salts but the quaternary salt is unaffected. The three amines are separated by fractional distillation. Over alkylation can be avoided by using excess of ammonia but the yield is low.

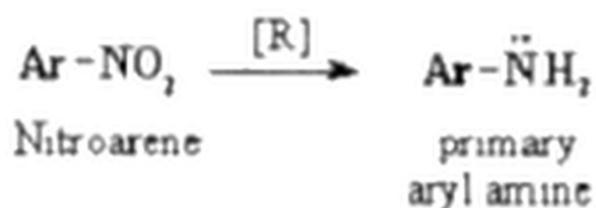
2) Reductions of nitrogen containing functional groups:

1) Reduction of Nitriles

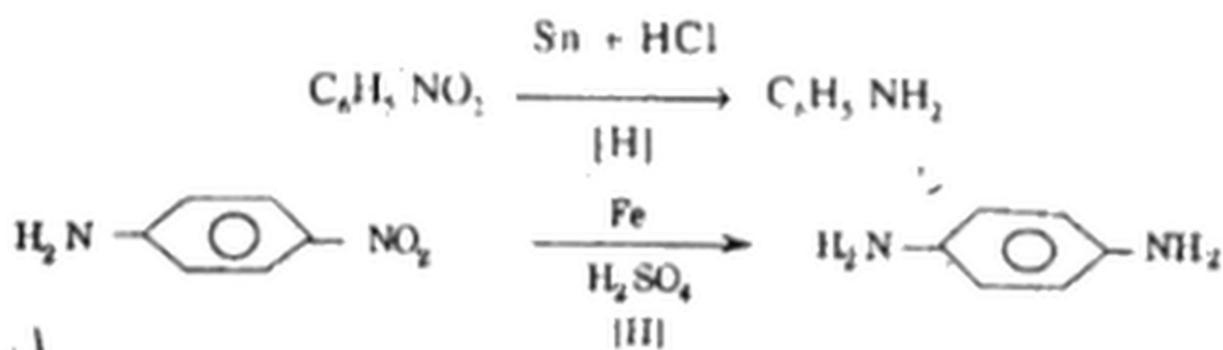
Reduction of alkyl or aryl nitriles gives primary amines. The reduction may be brought about by LiAlH_4 , or sodium in ethanol. Catalytic hydrogen with Rh-Al₂O₃, Pt or Raney nickel may also be employed to get primary amines



ii) Reduction of Nitro Compounds



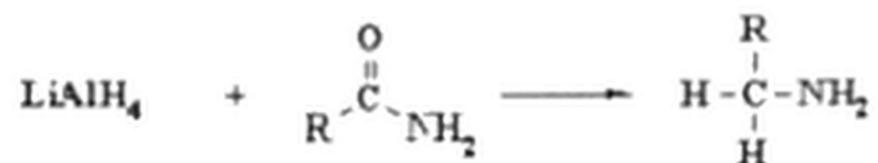
Nitro compounds on catalytic or chemical reduction produce primary amines



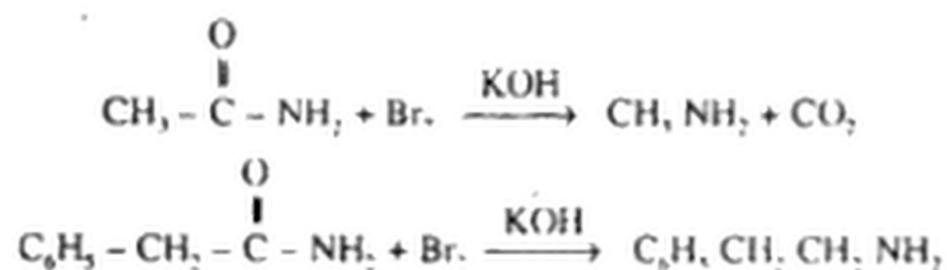
- Nitroarenes can be reduced to primary aryl amines (see scheme).

- Typical reducing agents include, Fe / H⁺, Sn / H⁺ or catalytic hydrogenation (e.g. H₂ /

Reduction of Amides



An amide on treatment with Bromine in the presence of KOH yields primary amines. The reaction occurs through rearrangement.



Reactivity:

Amines are basic and Nucleophiles because of non-bonding pair of electrons on nitrogen. The relative availability of this pair of electrons and the relative stability of corresponding ammonium ion is responsible of basicity of different amines. Consider the following reactions.

The strength of a base is expressed in terms of p_{kb}, i.e.

$$\text{p}k_b = -\log k_b$$

For ammonia and methyl amine, the p_{kb} values are

$$\text{p}k_{\text{NH}_3} = 4.76 \quad ; \quad \text{p}k_{\text{CH}_3\text{NH}_2} = 3.38$$

Since p_kNH₃ < p_kCH₃NH₂ methyl amine is a stronger base than ammonia. It can be explained as under:

In ammonia, the pair of electrons by s-orbitals of hydrogen atoms whereas in CH₃NH₂, sp³-orbital of carbon pushes electrons towards nitrogen.

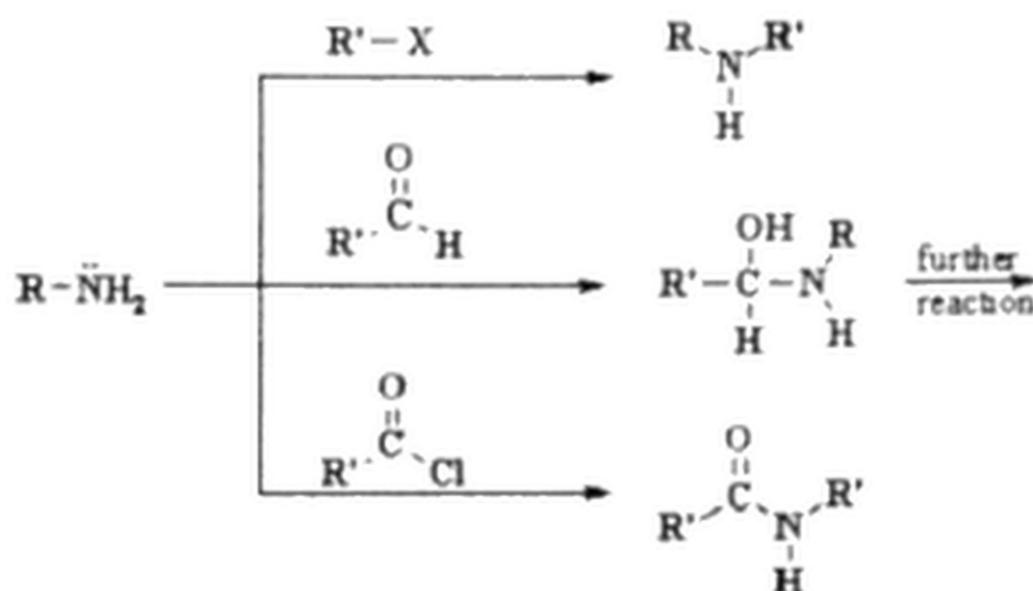
Therefore, the pair of electrons on nitrogen is relatively more available in methyl amine than in ammonia. The methyl ammonium ion, CH_3NH_3^+ is stabilized due to electron donating inductive effect of the methyl group. On the other hand, NH_4^+ ion is not stabilized by hydrogen atoms. Both these factors favor methylamine to a stronger base than ammonia.

Higher members show deviation to these arguments. It is because the stabilization of a positive ion also depends upon the extent of solvation, hydrogen bonding and resonance stabilization. Moreover, the availability of non-bonding pair of electrons is also affected by steric factor in addition to these aspects

REACTIONS OF AMINES

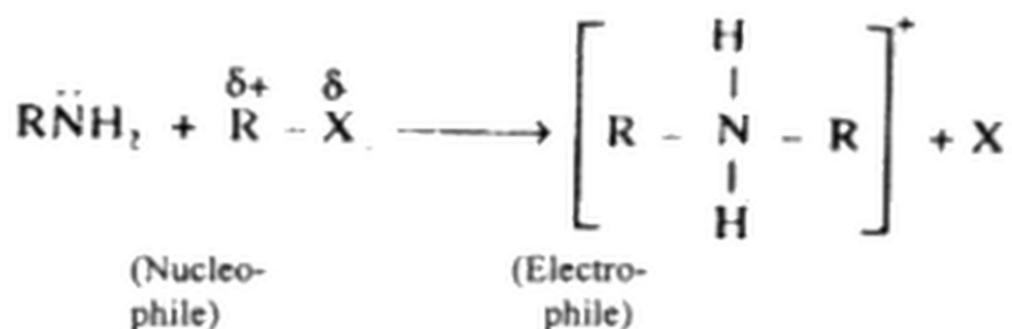
The important organic reactions of amines (nucleophiles) are with the common electrophiles:

- Alkyl halides via nucleophilic substitution
- Aldehydes or ketones via nucleophilic addition
- Carboxylic acid derivatives, especially acid chlorides or anhydrides, via nucleophilic acyl substitution.



Alkylation of Amine by Alkyl Halides

"The alkylation of alkyl is called alkylation". It produces sec- or tertiary amine,"



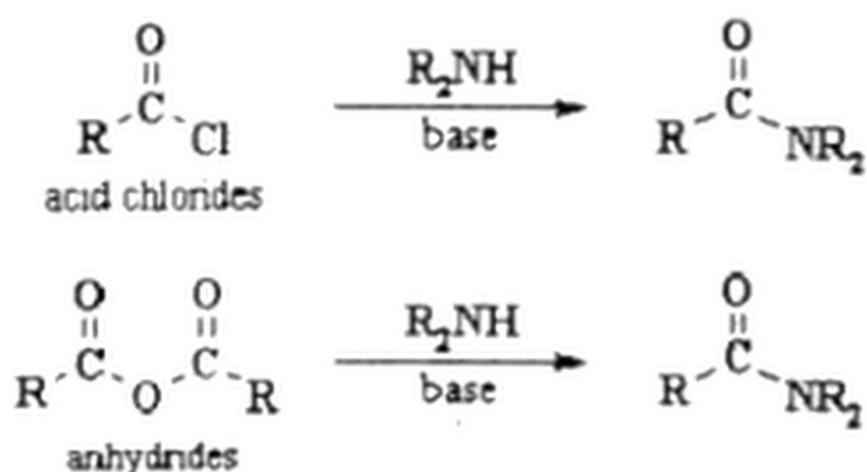
R_2NH_2^+ loses a proton with a base to give a free amine.

2) Reactions of Primary Amines with Aldehydes and Ketones

Aldehydes and ketones react with primary amines to form Schiff's base, e.g.,



3) Preparation of Amides

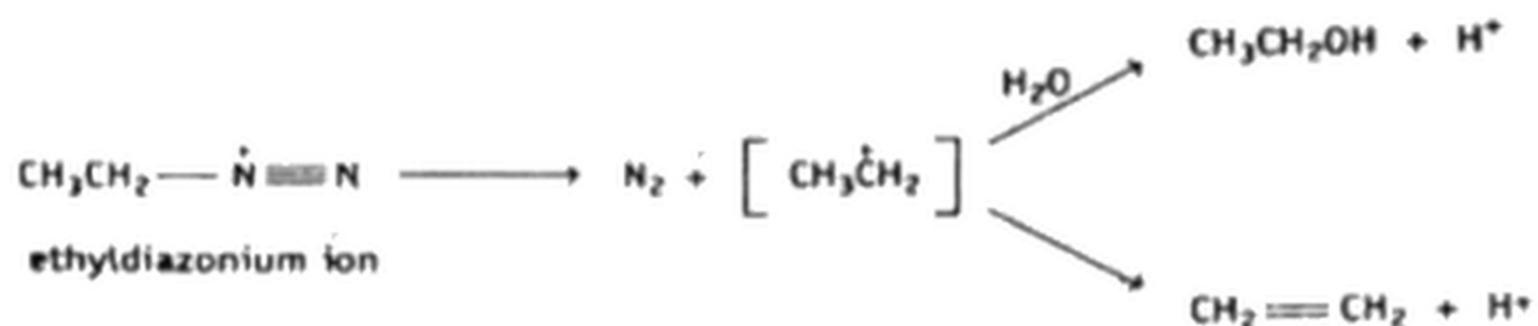


4) Preparation of Diazonium Salts

When amines react with nitrous acid, diazonium compounds are formed.



The diazonium group, group is rather unstable. In the case of the ethyldiazonium ion, it decomposes at once:



When the group is attached to a benzene ring, though, the ion is stabilized to some extent by the delocalized electron of the ring. The benzene diazonium ion is therefore much more stable than its aliphatic counterparts. Nevertheless, it decomposes readily above 10°C.

Primary amines, **R-NH₂** or **ArNH₂**, undergo nucleophilic addition with aldehydes or ketones to give **carbinolamines** which then dehydrate to give substituted **imines**.

