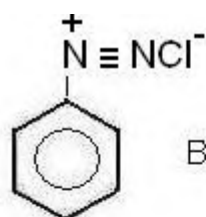


DIAZONIUM SALTS

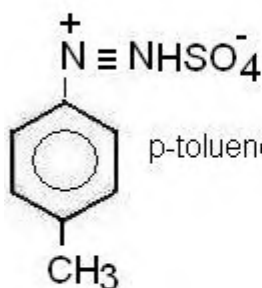
The diazonium salts have general formula $R^+N_2X^-$ where R stands for aryl and X^- ion may Cl^- , Br^- , HSO_4^- , BF_4^- etc

NOMENCLATURE

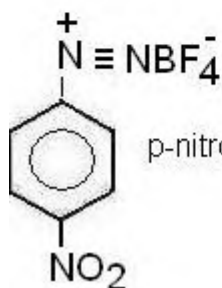
Arenediazonium salts are named by adding the suffix diazonium to the name of parent aromatic hydrocarbon Example:



Benzenediazonium chloride



p-toluenediazonium hydrogen sulphate

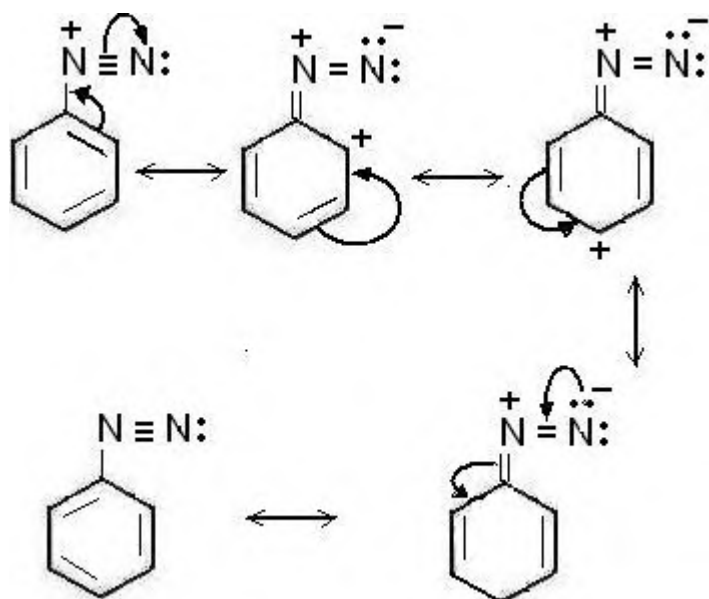


p-nitrobenzene diazonium fluoborate

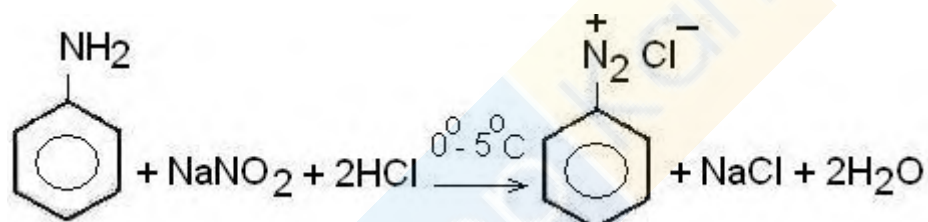
STABILITY OF DIAZONIUM SALT

Aryldiazonium salts are stable because of dispersal of positive charge over benzene ring due to resonating structures.

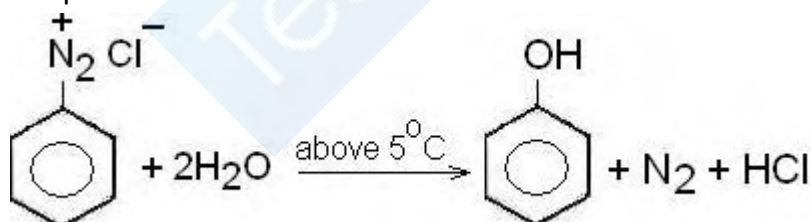
Diazonium salts and Nitro



PREPARATION OF ARENEDIAZONIUM CHLORIDE

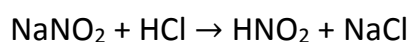


- This process of converting an aromatic primary amine into diazonium salt is called diazotization
- Diazotisation should be carried out at low temperature since at higher temperature benzenediazonium salt reacts with water to form phenol.

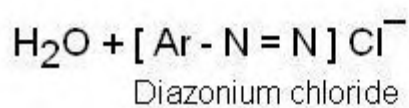
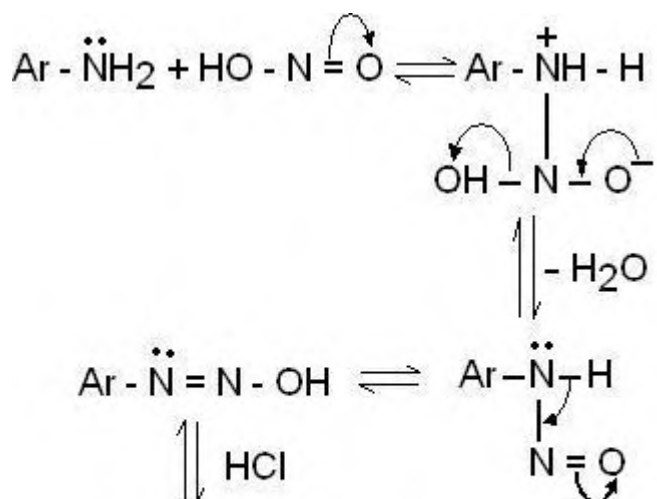


- Aromatic amines substituted with electron withdrawing groups require more concentrated acids than unsubstituted amines because of their weak basic character

Mechanism



Diazonium salts and Nitro



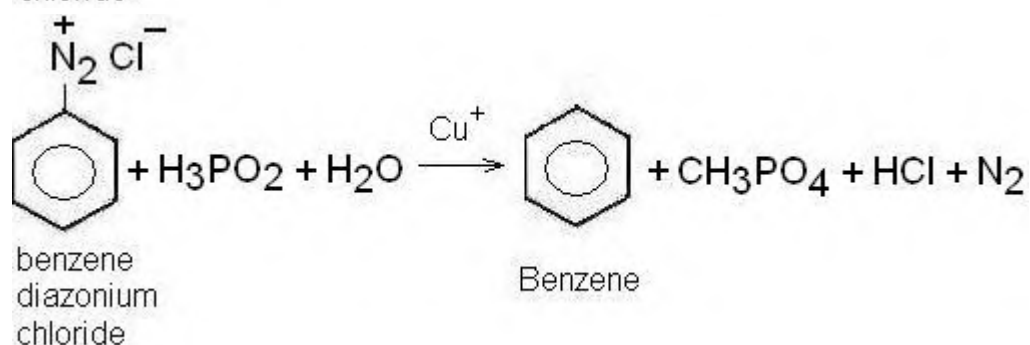
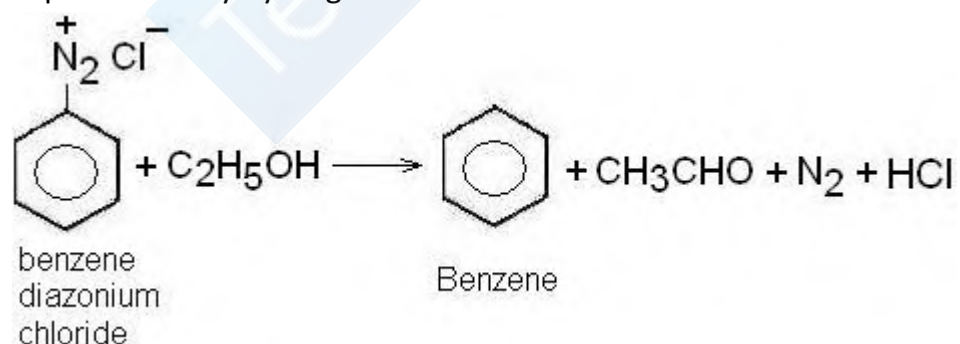
PHYSICAL PROPERTIES

- Aryl diazonium salts are colourless crystalline solids which turn brown when come in contact with air
- They are highly soluble in water but sparingly soluble in ethanol and insoluble in ether
- They are unstable and decomposes easily when dry

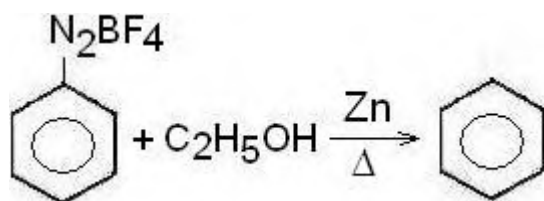
CHEMICAL PROPERTIES

A) Replacement reactions: The reactions in which the diazonium group (-N₂X) as a whole is replaced by monovalent atom or group

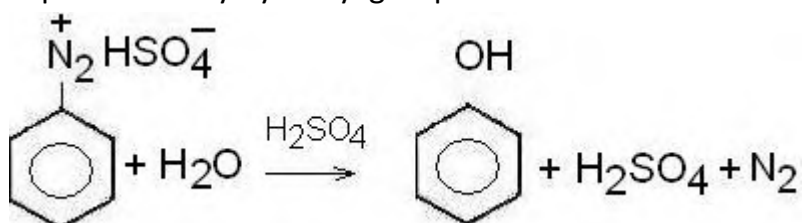
1. Replacement by hydrogen



Diazonium salts and Nitro



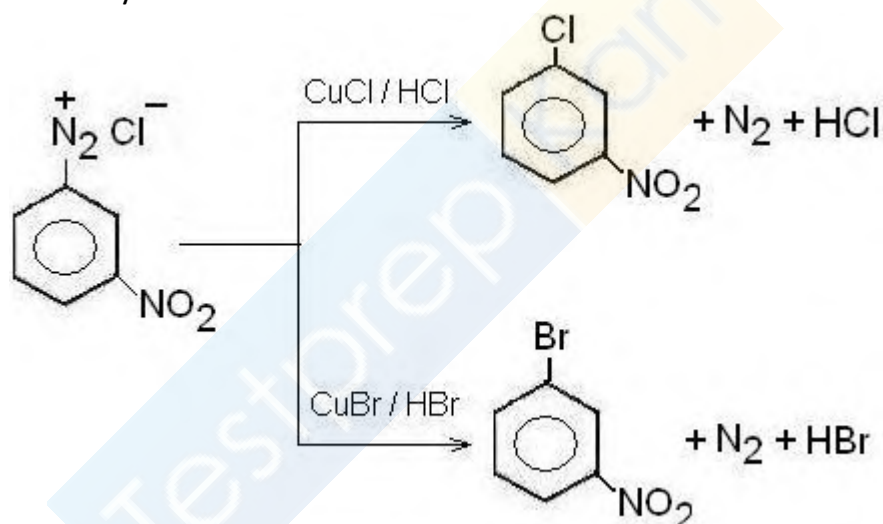
2. Replacement by hydroxyl group



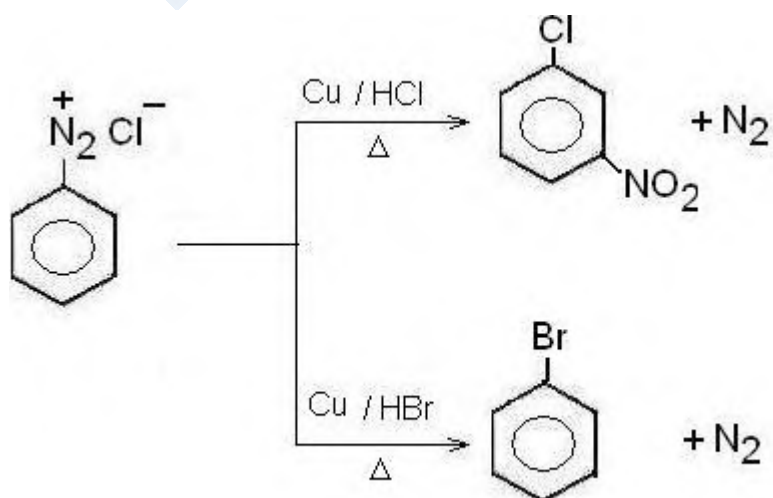
Highly acidic conditions avoid chances of coupling reaction between phenol and diazonium salt

3. Replacement by halogen

(i) Sandmeyer reaction

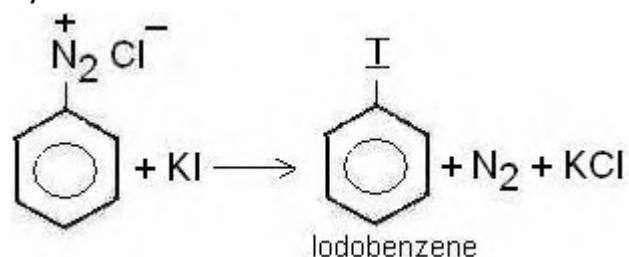


(ii) Gattermann reaction

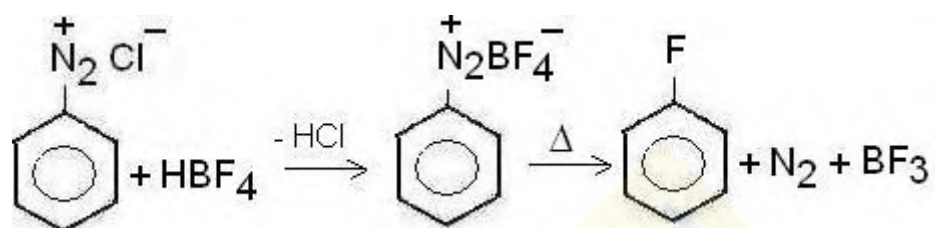


Diazonium salts and Nitro

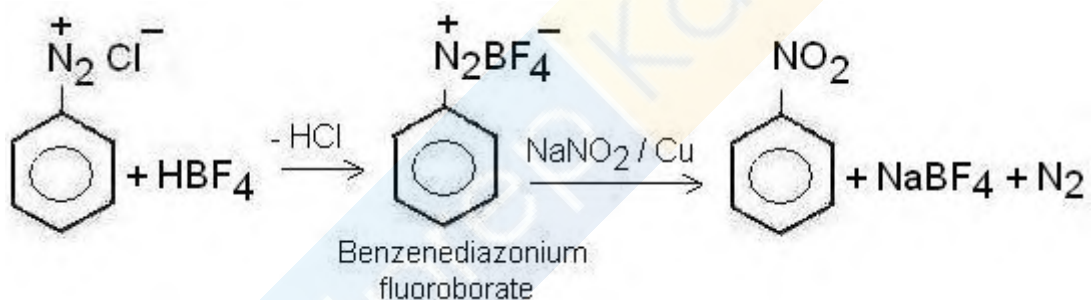
(iii) Replacement by iodine



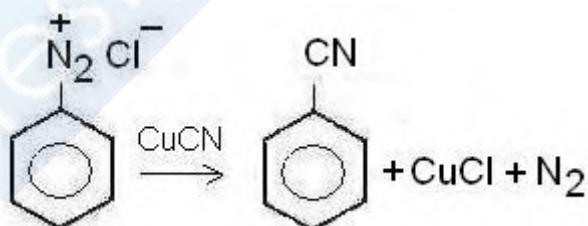
(iv) Replacement by fluorine (Balz –Schiemann reaction)



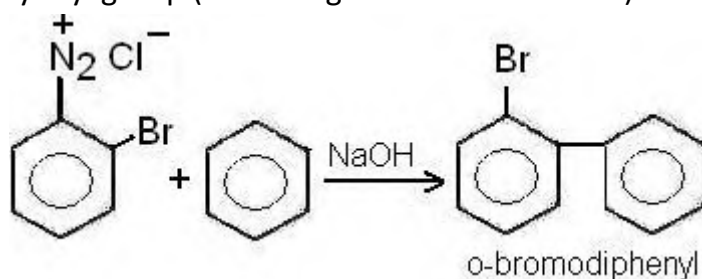
4. Replacement by (-NO₂) group



5. Replacement by cyano (-CN) group



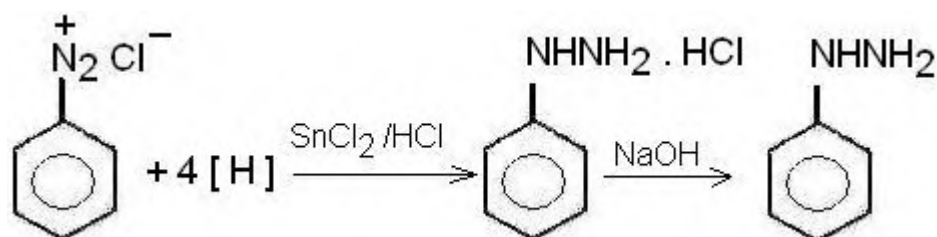
6. Replacement by aryl group (Gomberg Bachmann reaction)



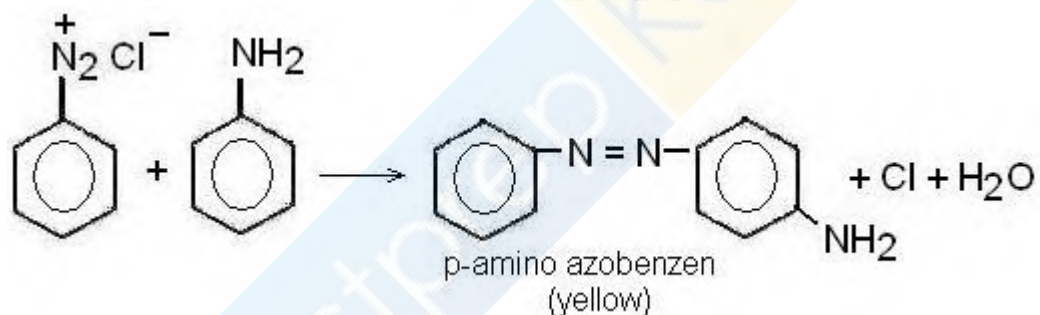
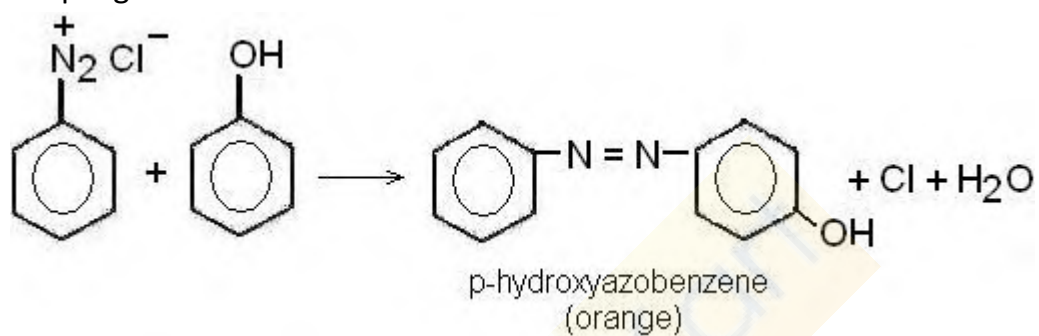
Diazonium salts and Nitro

B) Coupling reactions: The reactions in which both the nitrogen atoms are retained and only halogen is replaced

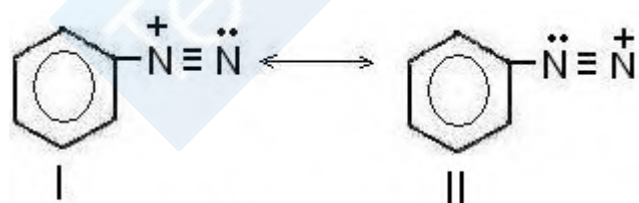
1. Reduction



2. Coupling reaction

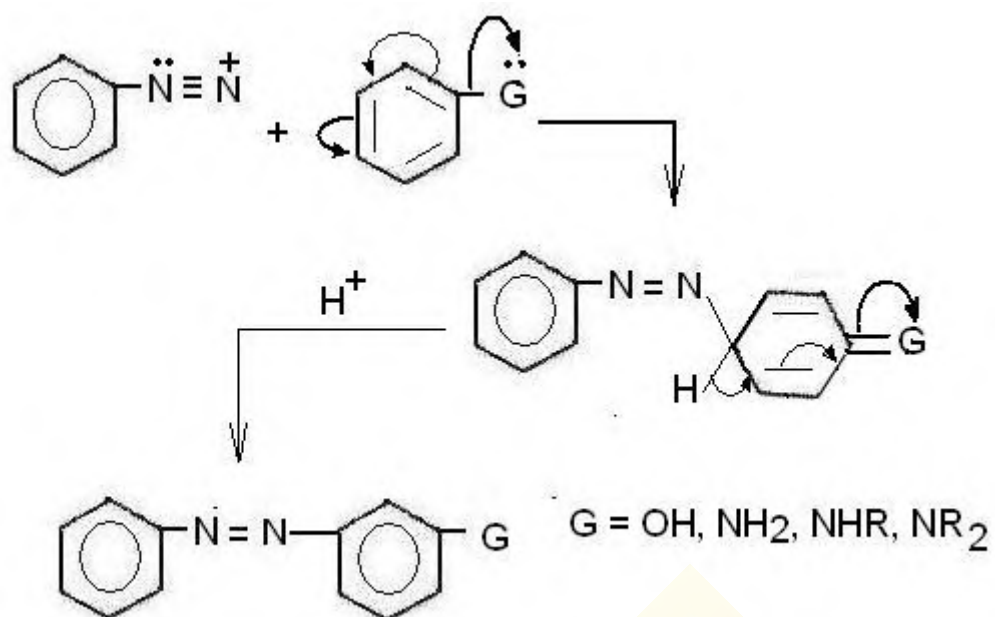


Mechanism



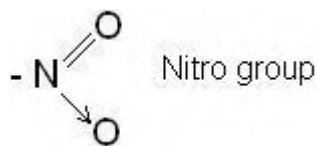
Diazonium ion

Diazonium salts and Nitro

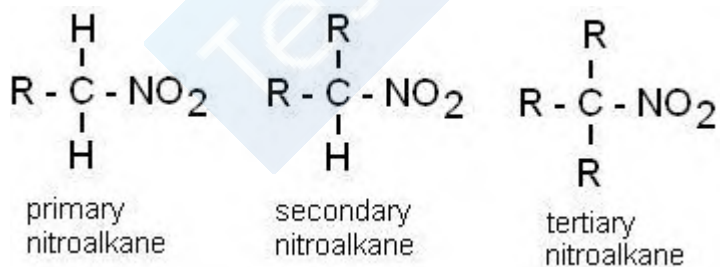


NITRO COMPOUNDS

- When nitro group is attached to an alkyl group the compounds are known as nitro-alkanes and nitro group attached to aryl group are known as nitroarenes

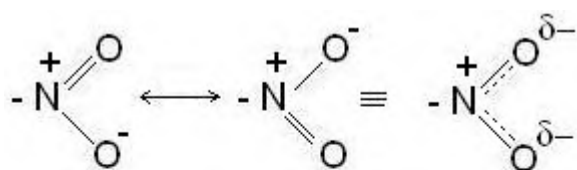


- Nitro compounds are classified as primary, secondary and tertiary depending upon whether the nitro group is attached to a primary, secondary or tertiary carbon respectively

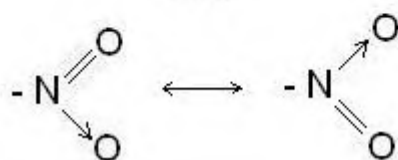


Diazonium salts and Nitro

STRUCTURE OF $-\text{NO}_2$ GROUP

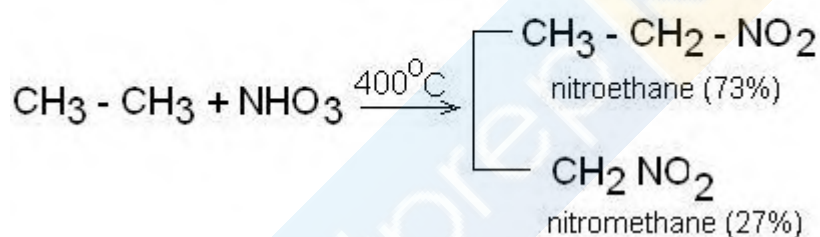
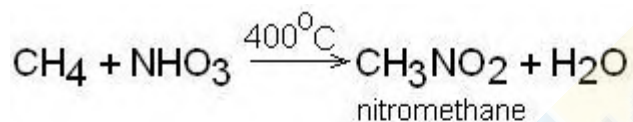


OR

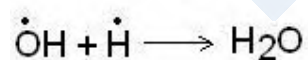


PREPARATION OF NITRO COMPOUNDS

1. Nitration

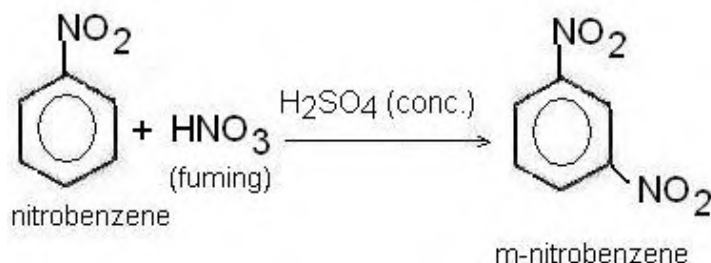
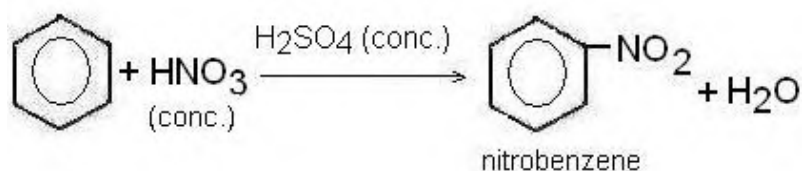


Mechanism

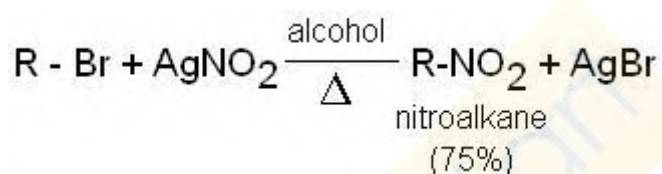


Ease of substitution follows the order tertiary > secondary > primary

Diazonium salts and Nitro



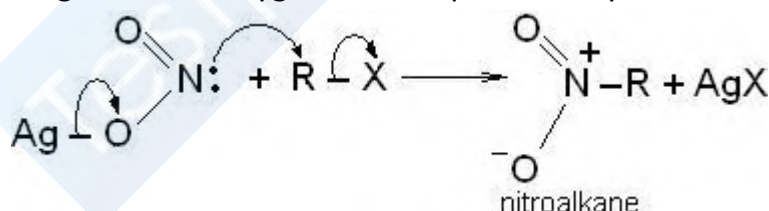
2. From alkyl halides



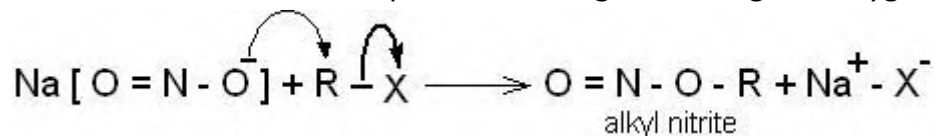
- If we use sodium nitrate (NaNO_2) in place of AgNO_2 in the above reaction, then alkyl nitrite is obtained as major yield

Reason

Nitrite ion is an ambident nucleophile. Silver nitrite being covalent compound attacks electrophilic carbon of alkyl halide through a lone pair. Since nitrogen is less electronegative than oxygen, its lone pair is easily available for bonding.



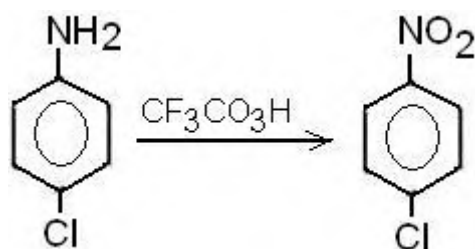
But sodium nitrite is an ionic compound with negative charge on oxygen



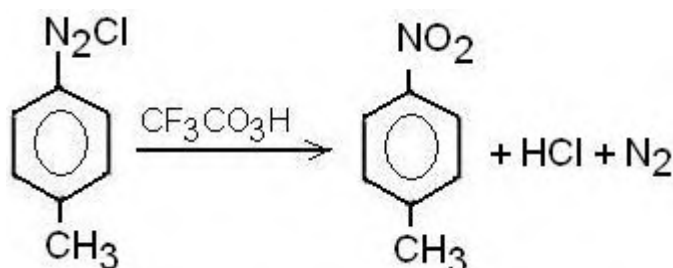
- Order of reactivity of alkyl halides towards **nitroalkane** formation is
Primary > secondary > tertiary
- Order of reactivity of alkyl halides towards **nitrite** formation is
Tertiary > secondary > primary

Diazonium salts and Nitro

3. Oxidation of aromatic amine



4. From diazonium salts

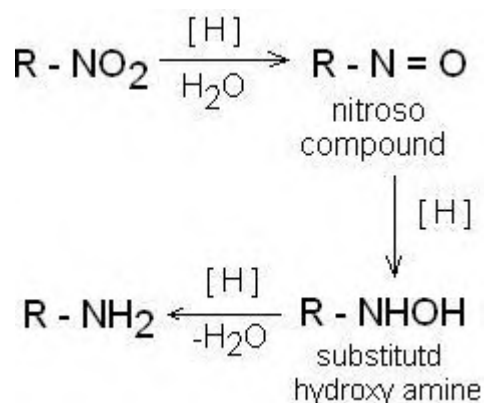


PHYSICAL PROPERTIES

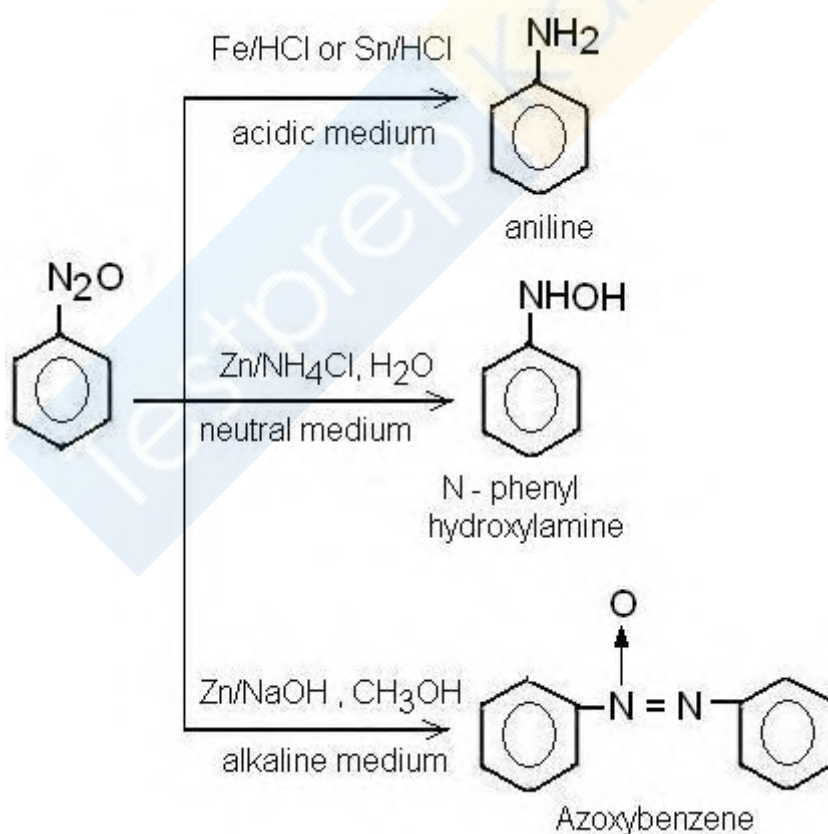
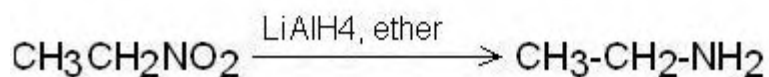
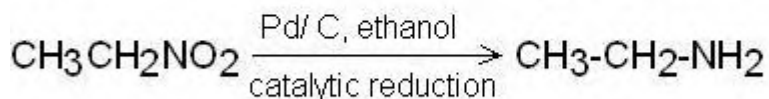
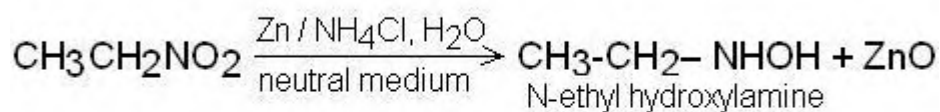
- Nitroalkanes are colourless, pleasant smelling liquids, whereas nitroarenes are pale yellow crystalline solids except nitrobenzene. Which is pale yellow liquid with an odour of bitter almond
- Both nitroalkanes and nitroarenes are insoluble in water but fairly soluble in organic solvents
- Being highly polar in nature, nitroalkanes and nitroarenes possess strong dipole-dipole interactions
Hence they have much higher boiling points than hydrocarbons of comparable molecular masses

CHEMICAL PROPERTIES

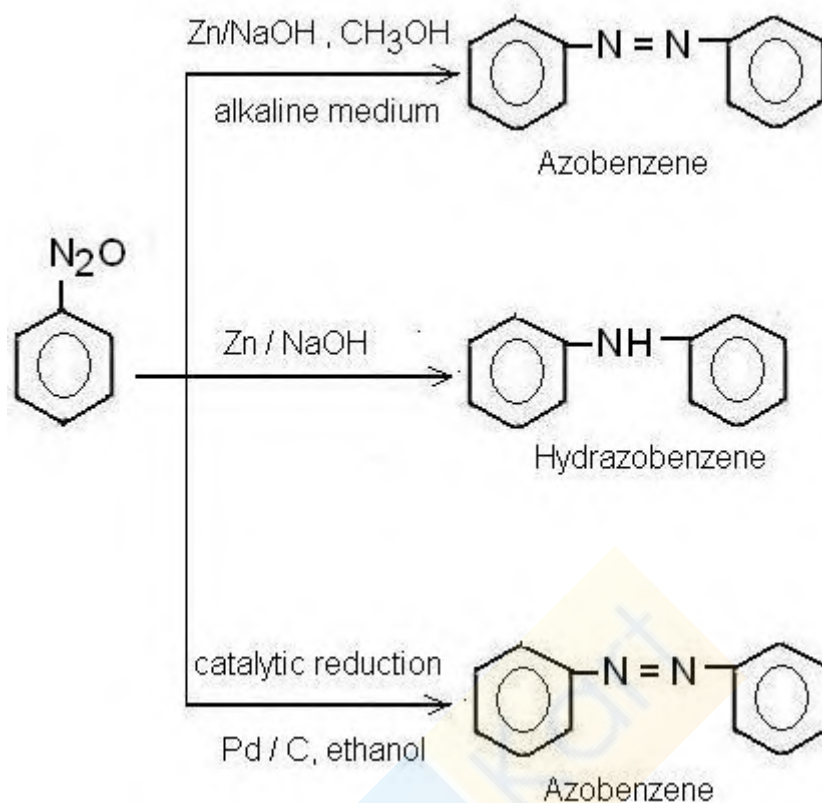
1. Reduction



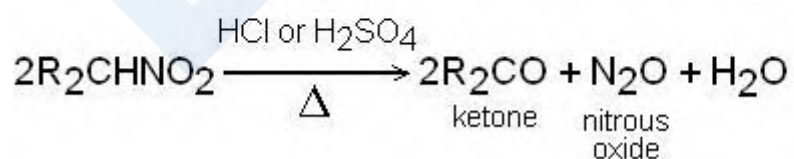
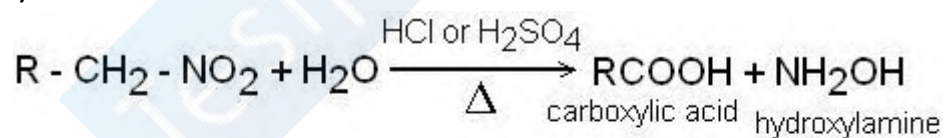
Diazonium salts and Nitro



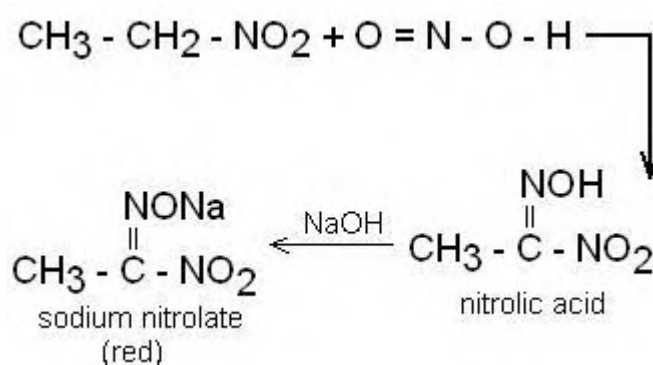
Diazonium salts and Nitro



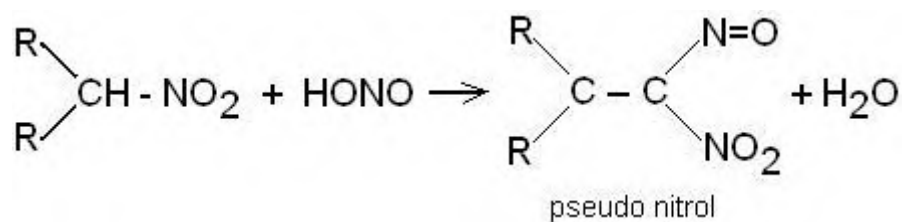
2. Hydrolysis



3. Reaction with nitrous acid



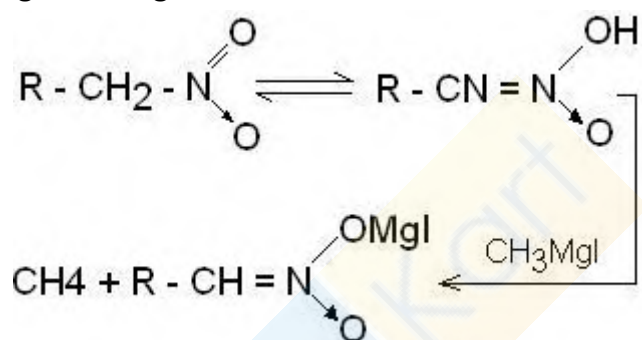
Diazonium salts and Nitro



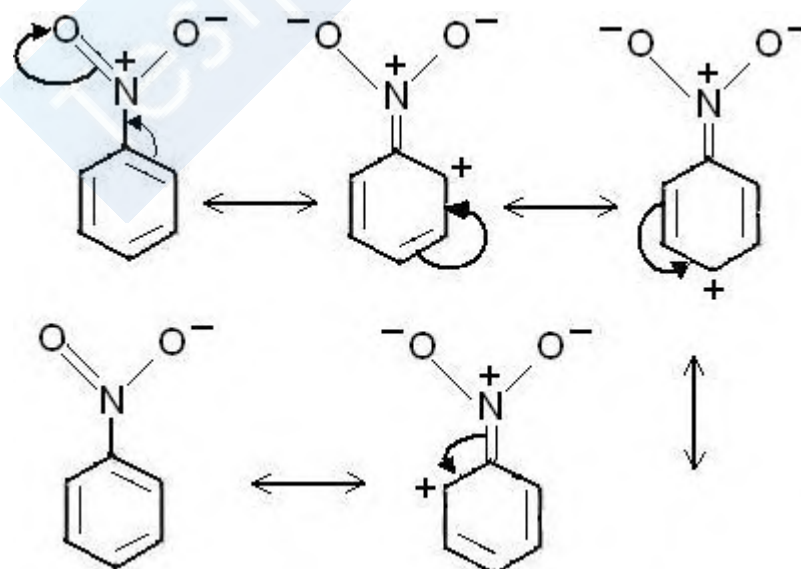
Tertiary nitroalkanes do not react with HNO₂, as they lack α-hydrogen atom

This is also known as Victor Meyer's test for distinction of 1°, 2° and 3° nitroalkanes

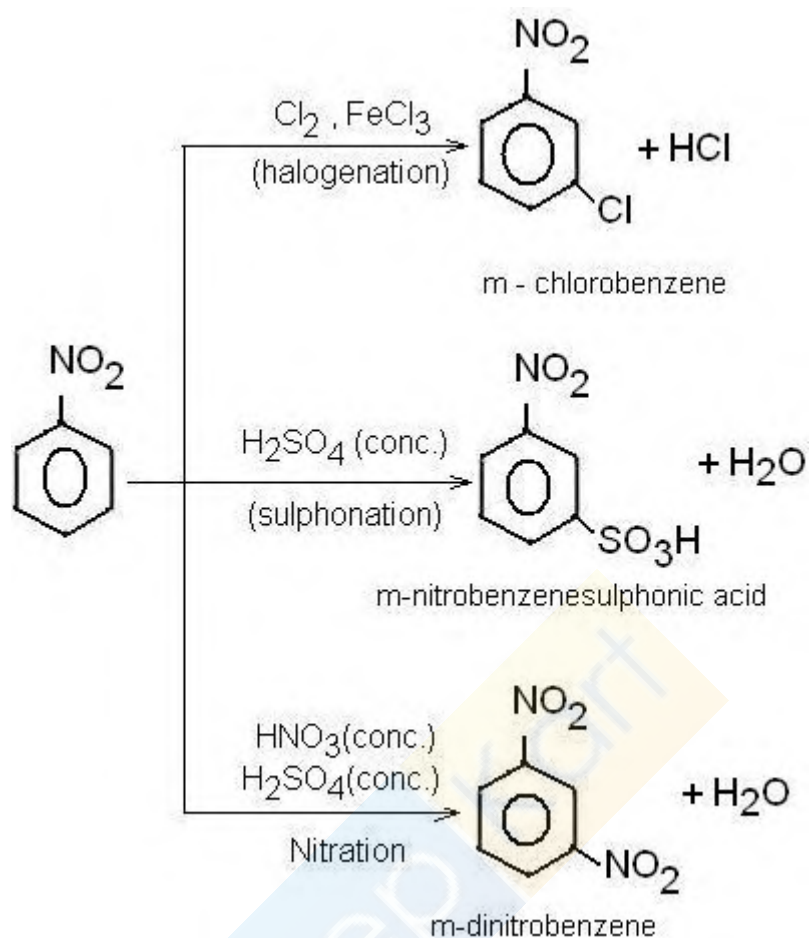
4. Reaction with Grignard reagent.



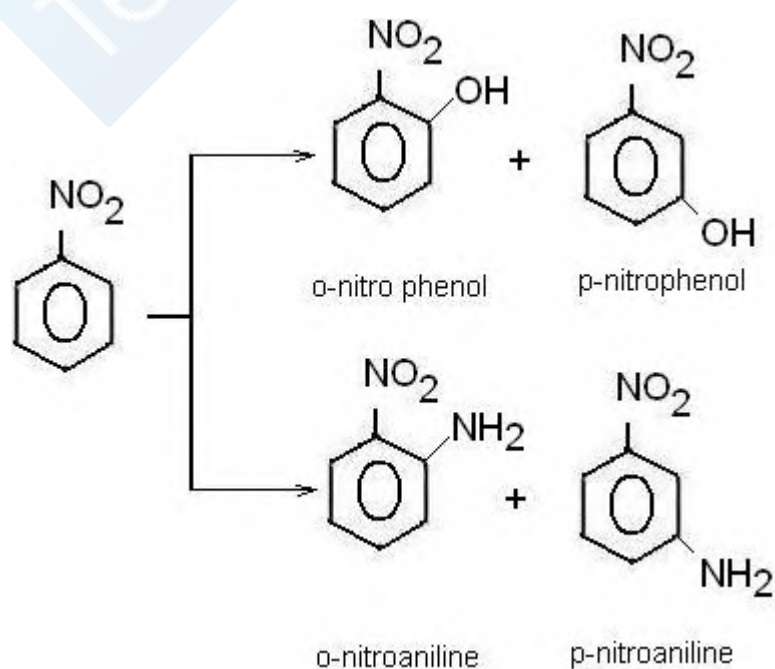
5. Electrophilic substitution reaction



Diazonium salts and Nitro

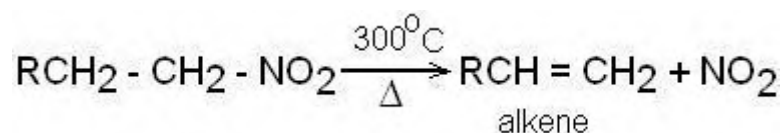


6. Nucleophilic substitution reaction

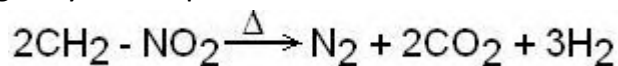


Diazonium salts and Nitro

7. Action of heat

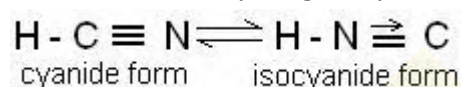


On strong heating they decompose with violence



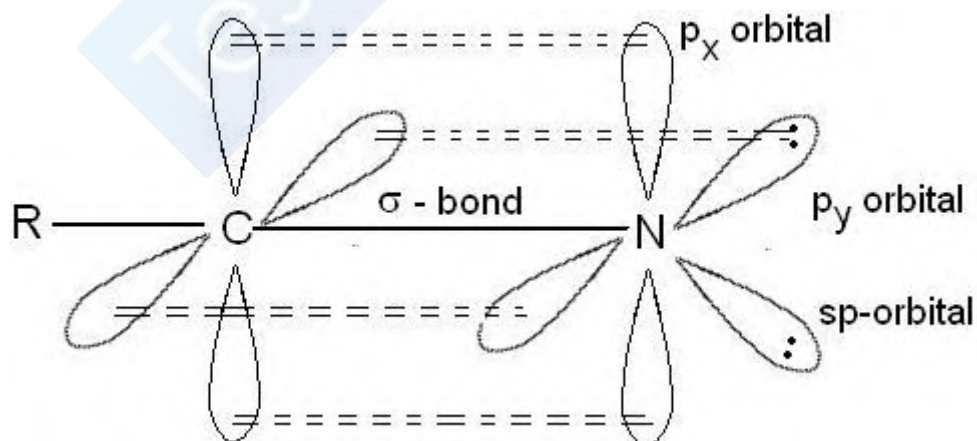
CYANIDES AND ISOCYANIDES

- Cyanides and isocyanides are isomeric to each other and are considered as derivative of two tautomeric forms of hydrogen cyanides



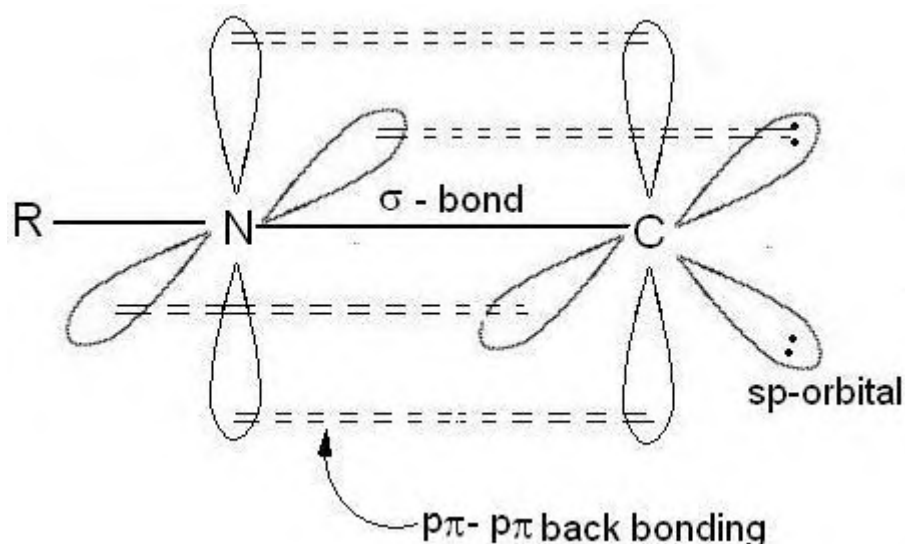
- CN can attach either through carbon or nitrogen atom. Such a group which has more than one attacking sites is known as ambident group

STRUCTURE OF -CN or -NC group



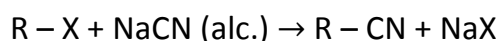
ORBITAL STRUCTURE OF ALKYL CYANIDES

Diazonium salts and Nitro



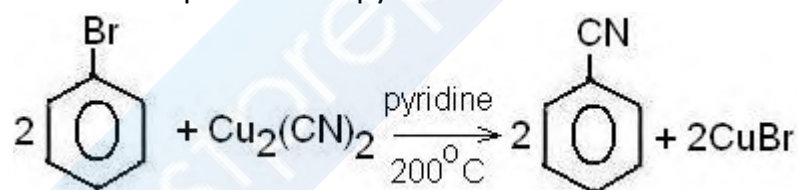
GENERAL METHOD OF PREPARATION OF CYANIDES

1. From alkyl halide

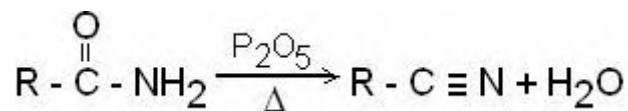


Aryl cyanides cannot be prepared by this method, since Ar-X bond is not easy to be cleaved by CN^-

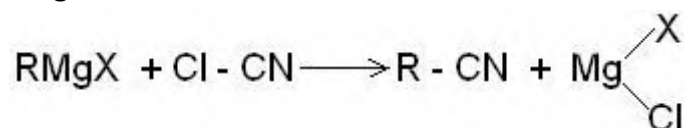
For preparing aryl cyanides, aryl halides are heated with anhydrous cuprous cyanide at 200°C in the presence of pyridine.



2. From acid amides

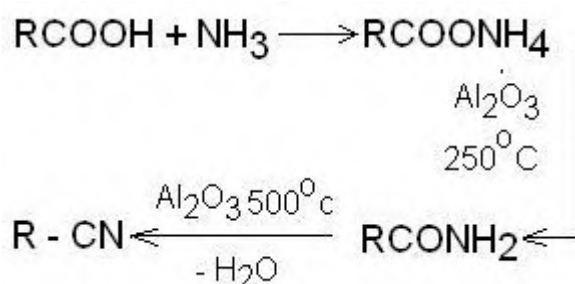


3. From Grignard reagent

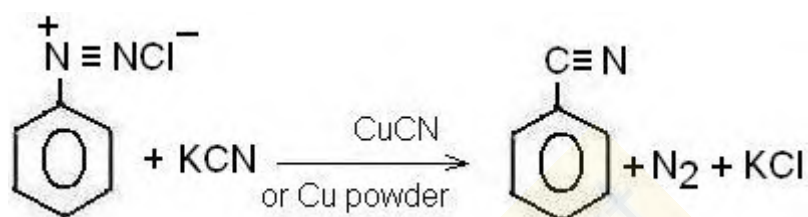


Diazonium salts and Nitro

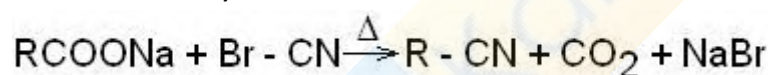
4. From carboxylic acid



5. From arene diazonium salts



6. From sodium salt of carboxylic acid

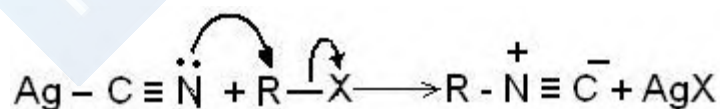


GENERAL METHOD OF PREPARATION OF ISOCYANIDES

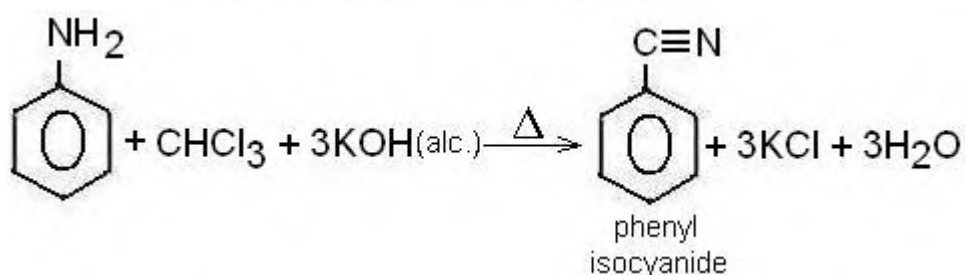
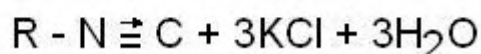
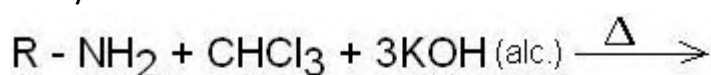
1. From alkyl halides



- AgCN is covalent in nature. Only nitrogen atom has lone pair of electrons available for nucleophilic attack, thus attack takes place mainly through nitrogen atom leading to formation of isocyanide along with small amount of cyanide

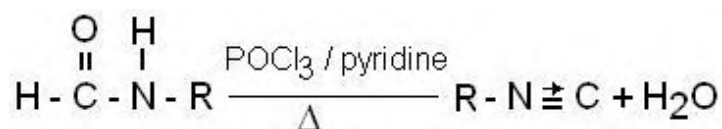


2. Carbylamine reaction



Diazonium salts and Nitro

3. From N-alkyl formamides



PHYSICAL PROPERTIES OF CYANIDES AND ISOCYANIDES

1. Physical state and smell:

Lower members of alkyl cyanides and isocyanides are colourless liquids whereas higher members are crystalline solids

Alkyl cyanides are pleasant smelling, while alkyl isocyanides have extremely unpleasant smell

2. Solubility

Lower member of alkyl cyanide are sparingly soluble in water due to intermolecular hydrogen bonding, but the solubility decreases with increase of molecular weight

However isocyanides (both alkyl and aryl) and aryl cyanides are insoluble in water. All members of cyanides and isocyanides are fairly soluble in organic solvents

3. Boiling points

Both $-\text{CN}$ and $-\text{NC}$ group are polar in nature hence they possess strong intermolecular dipole-dipole interaction

As a result of which they have higher boiling point than that of alkyl halides or hydrocarbons of comparable molecular mass

However boiling points of alkyl isocyanides are lower than that of alkyl cyanides since $-\text{NC}$ group is less polar than $-\text{CN}$ group

CHEMICAL PROPERTIES OF CYANIDES AND ISOCYANIDES

(A) Chemical reactions shown by cyanides only

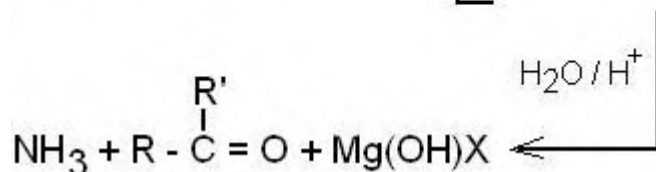
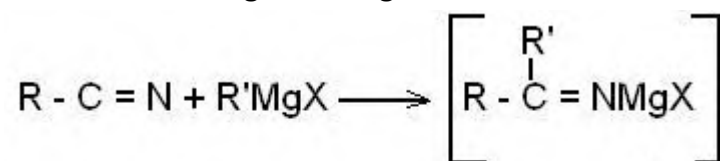
(1) Basic nature of cyanides

In spite of the presence of unshared pair of electrons on nitrogen atom, the nitriles or cyanides are not enough basic to form salt with aqueous acids

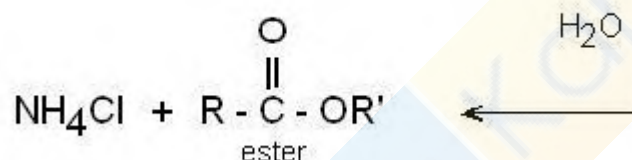
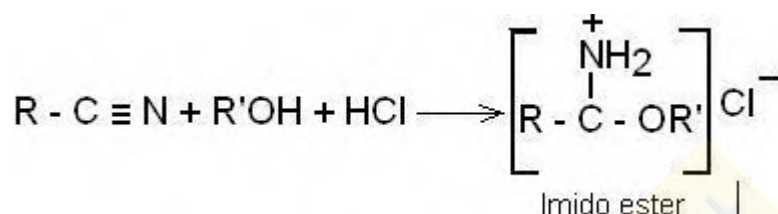
Because in nitriles, nitrogen atom is sp -hybridised and hence highly electronegative. Electron pair present in sp -orbitals are less easily available for donation and hence nitriles behave as weak base, weaker than amines and ammonia.

Diazonium salts and Nitro

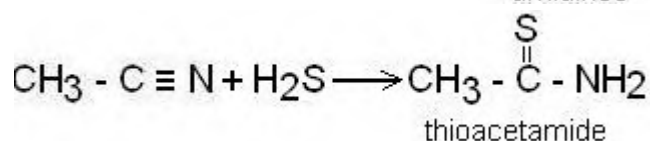
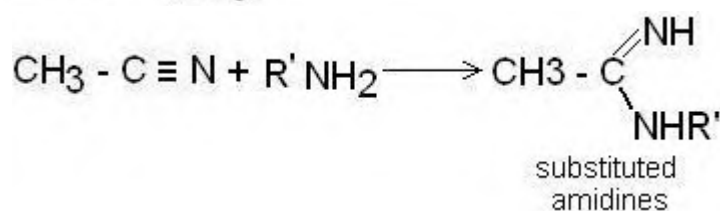
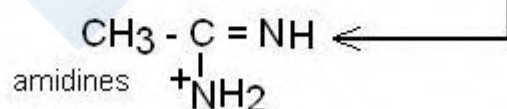
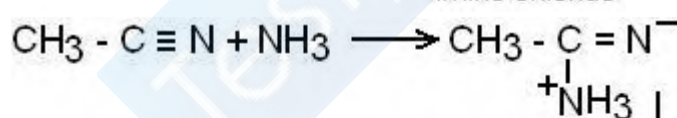
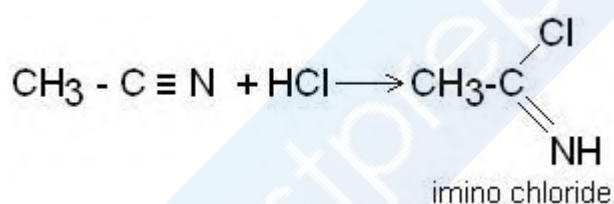
(2) Reaction with Grignard reagent



(3) Reaction with alcohol



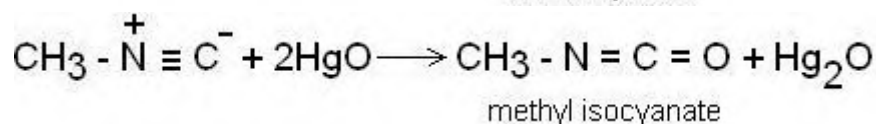
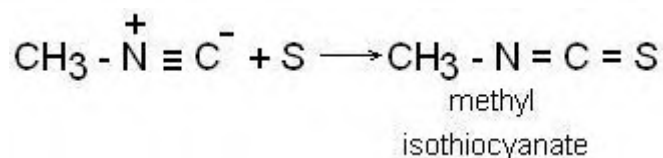
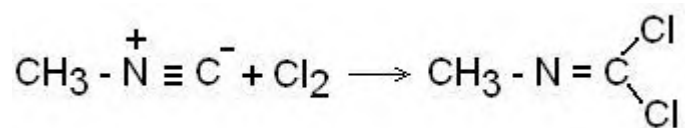
(4) Addition reactions



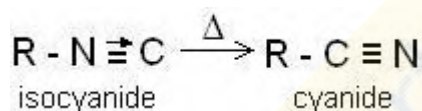
Diazonium salts and Nitro

(B) Chemical reaction shown by isocyanides only

(1)



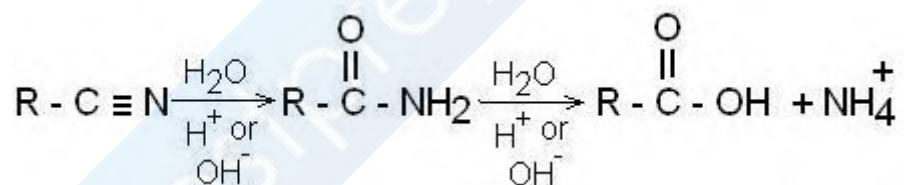
(2) Action of heat



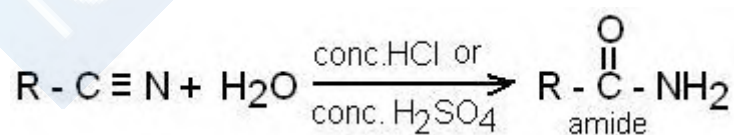
(C) Reaction shown by both cyanides and isocyanides

(1) Hydrolysis

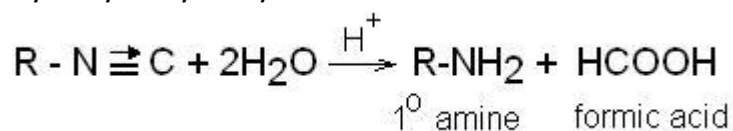
(a) Hydrolysis of cyanides: complete hydrolysis



Partial hydrolysis



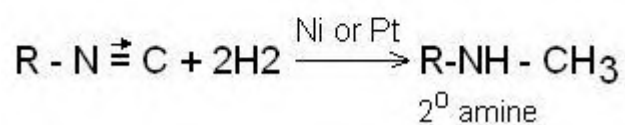
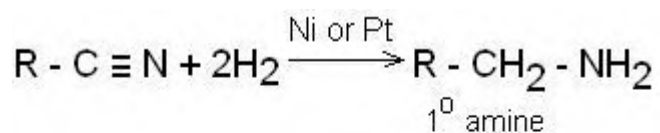
(b) Hydrolysis by isocyanide.



(2) Reduction

(a) Complete reduction

Diazonium salts and Nitro



(b) Partial reduction

