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DIAZONIUM SALTS

The diazonium salts have general formula $R^+N_2X^-$ where R stands for aryl and X⁻ ion may Cl⁻, Br⁻, HSO₄⁻, BF₄⁻ etc

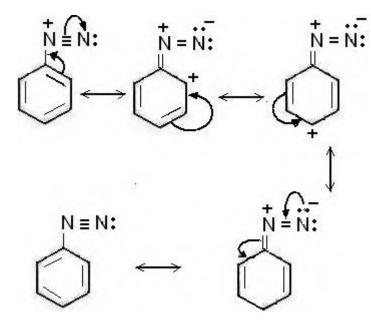
NOMENCLATURE

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

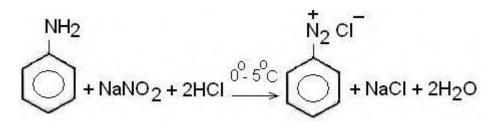


STABILITY OF DIAZONIUM SALT

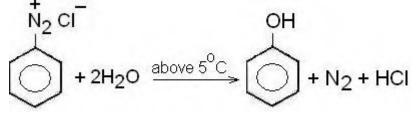
Aryldiazonium salts are stable because of dispersal of positive charge over benzene ring due to resonating structures.



PREPARATION OF ARENEDIAZONIUM CHLORIDE



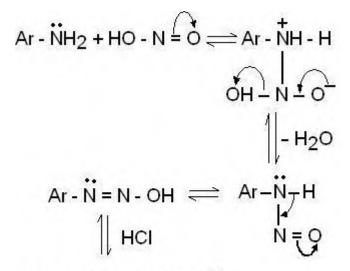
- This process of converting an aromatic primary amile into diazonium salt is called diazotization
- Diazotisation should be carried out at low temperature since at higher temperature benzenediazonium salt reacts with water to form phenol.



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

 $NaNO_2 + HCI \rightarrow HNO_2 + NaCI$

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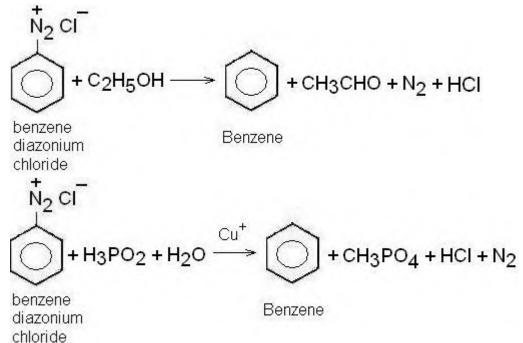
H₂O + [Ar - N = N] Cl Diazonium chloride

PHYSICAL PROPERTIES

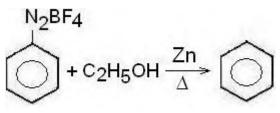
- Aryl diazonium salts are colourless crystalline solids which turn brown when come in contact with air
- They are highly soluble in water but sparingly soluble in ethanol and insoluble in ether
- They are unstable and decomposes easily when dry

CHEMICAL PROPERTIES

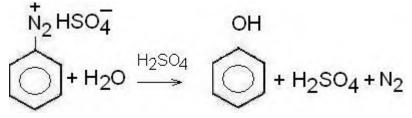
- A) Replacement reactions: The reactions in which the diazonium group ($-N_2X$) as a whole is replaced by monovalent atom or group
- 1. Replacement by hydrogen



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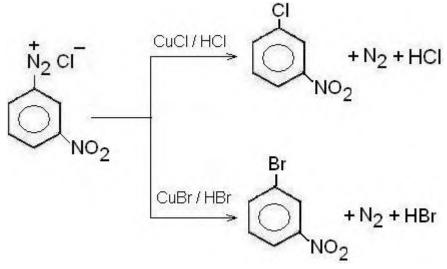


2. Replacement by hydroxyl group

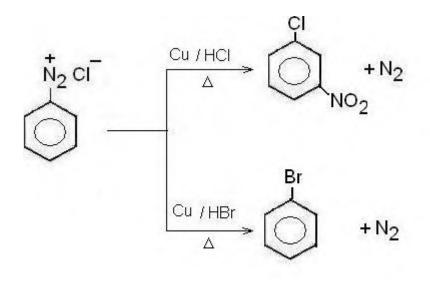


Highly acidic conditions avoid chances of coupling reaction between phenol and diazonium salt

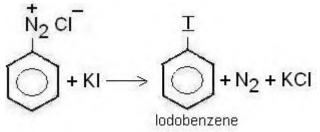
- 3. Replacement by halogen
 - (i) Sandmeyer reaction



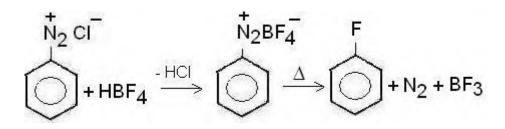
(ii) Gattermann reaction



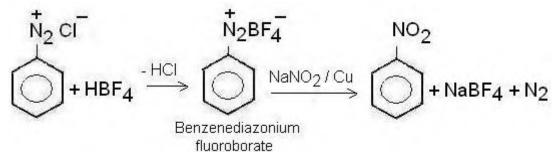
(iii) Replacement by iodine



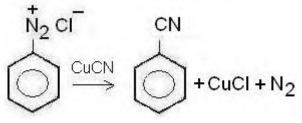
(iv) Replacement by fluorine (Balz – Schiemann reaction)



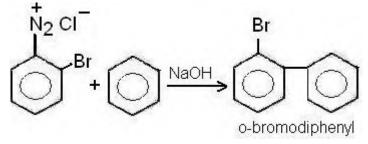
4. Replacement by (-NO₂) group



5. Replacement by cyano (-CN) group

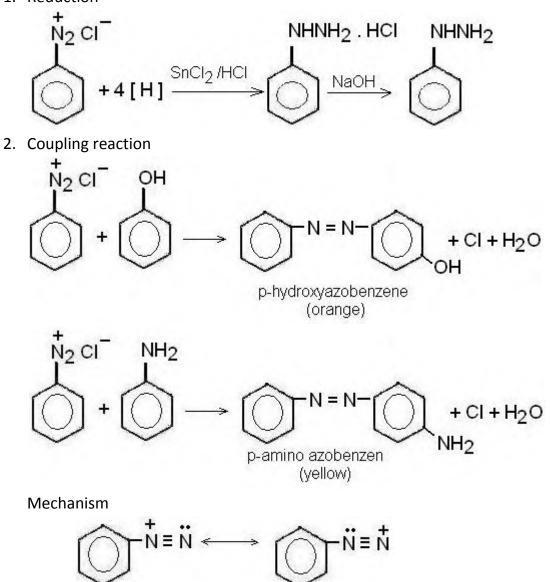


6. Replacement by aryl group (Gomberg Bachmann reaction)

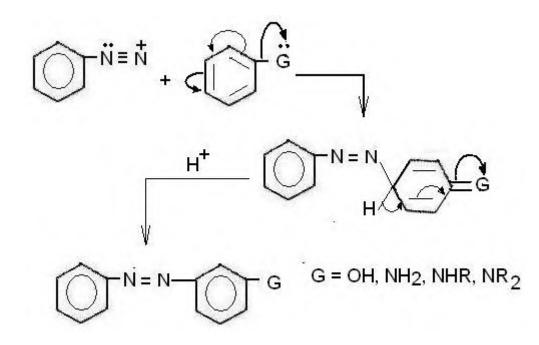


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- B) Coupling reactions: The reactions in which both the nitrogen atoms are retained and only halogen is replaced
- 1. Reduction



Diazonium ion



NITRO COMPOUNDS

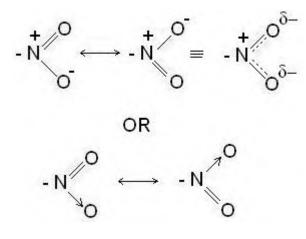
• When nitro group is attached to an alkyl group the compounds are known as nitro-alkanes and nitro group attached to aryl group are known as nitroarenes

- N Nitro group

 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

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STRUCTURE OF -- NO₂ GROUP



PREPARATION OF NITRO COMPOUNDS

1. Nitration

$$CH_4 + NHO_3 \xrightarrow{400^{\circ}C} CH_3NO_2 + H_2O$$

$$CH_3 - CH_3 + NHO_3 \xrightarrow{400^{\circ}C} CH_3 - CH_2 - NO_2$$

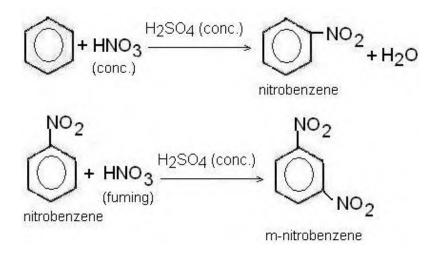
$$nitroethane (73\%)$$

$$CH_2 NO_2$$

nitromethane (27%)

Ease of substitution follows the order tertiary > secondary > primary

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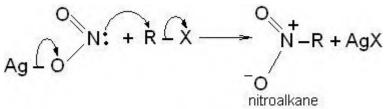


2. From alkyl halides

R - Br + AgNO₂
$$\frac{\text{alcohol}}{\Delta}$$
 R-NO₂ + AgBr
nitroalkane
(75%)

 If we use sodium nitrate (NaNO₂) in place of AgNO₂ in the above reaction, then alkyl nitrite is obtained as major yield Reason

Nitrite ion is an ambidient 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.



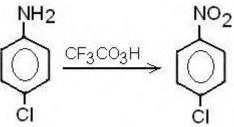
But sodium nitrite is an ionic compound with negative charge on oxygen

Na
$$[O = N - O] + R - X \longrightarrow O = N - O - R + Na^+ - X$$

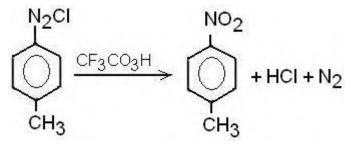
- Order of reactivity of alkyl halides towards **nitroalkane** formation is Primary > secondary > tertiary
- Order of reactivity of alkyl halides towards nitrite formation is Tertiary > secondary > primary

Diazonium salts and Nitro compounds

3. Oxidation of aromatic amine



4. From diazonium salts

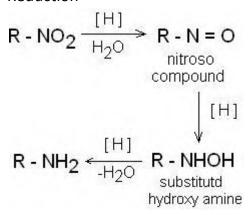


PHYSICAL PROPERTIES

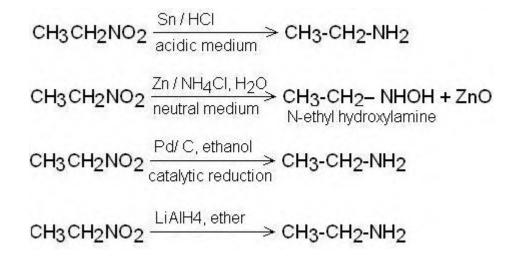
- Nitroalkanes are colourless, pleasant smelling liquids, whereas nitroarenes are pale yellow crystalline solids except nitrobenzene. Which is pale yellow liquid with an odour of bitter almond
- Both nitroalkanes and nitroarenes are insoluble in water but fairly soluble in organic solvents
- Being highly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

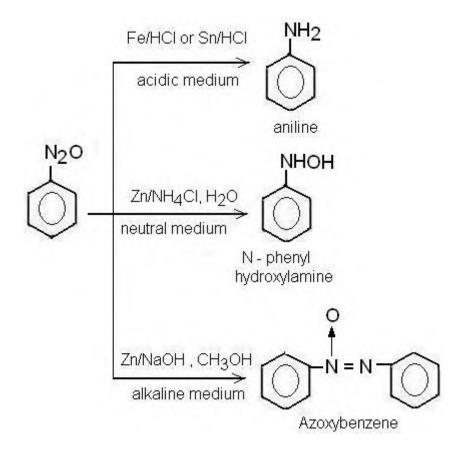
CHEMICAL PROPERTIES

1. Reduction



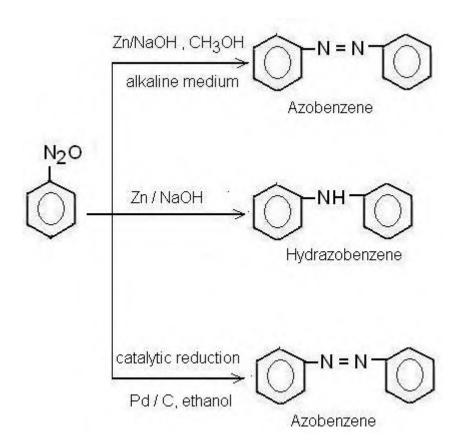
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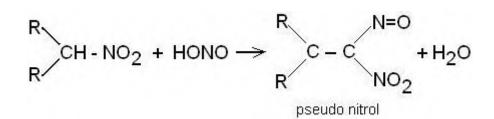
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Diazonium salts and Nitro compounds



2. Hydrolysis

 $\begin{array}{c} \text{HCI or } \text{H}_2\text{SO}_4 \\ \hline \text{A} \\ \text{Carboxylic acid} \\ \text{hydroxylamine} \end{array} \end{array}$ $2R_2CHNO_2 \xrightarrow{HCl \text{ or } H_2SO_4} 2R_2CO + N_2O + H_2O$ ketone nitrous oxide 3. Reaction with nitrous acid CH3 - CH2 - NO2 + O = N - O - H -NOH NONa NaOH CH3 - C - NO2 CH3 - C - NO2 nitrolic acid sodium nitrolate (red)



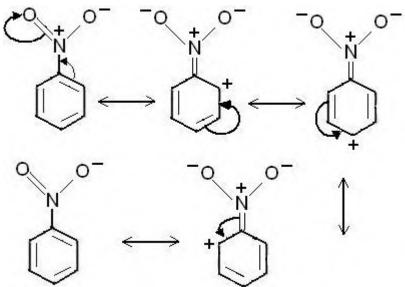
Tertiary nitroalkanes do not react with HNO₂, as they lack α -hydrogen atom

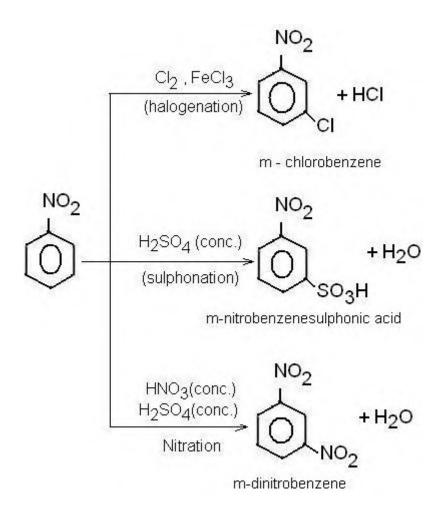
This is also known as Victor Meyer's test for distinction of 1°, 2° and 3° nitroalkanes

4. Reaction with Grignard reagent.

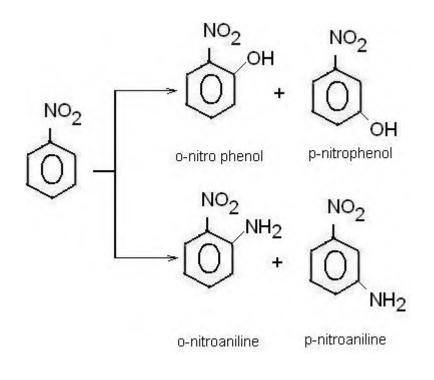
$$R - CH_2 - N \stackrel{O}{\underset{O}{\longrightarrow}} R - CN = N \stackrel{OH}{\underset{O}{\longrightarrow}} R - CH = N \stackrel{OH$$

5. Electrophilic substitution reaction





6. Nucleophilic substitution reaction



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7. Action of heat

$$RCH_2 - CH_2 - NO_2 \xrightarrow{300^{\circ}C} RCH = CH_2 + NO_2$$

alkene

On strong heating they decompose with violence

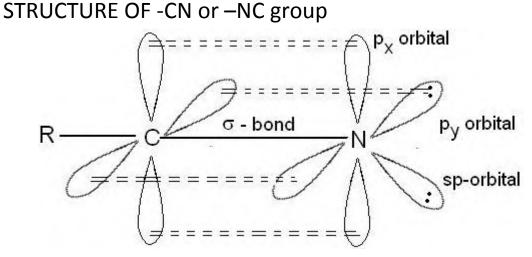
$$2CH_2 - NO_2 \xrightarrow{\Delta} N_2 + 2CO_2 + 3H_2$$

CYANIDES AND ISOCYANIDES

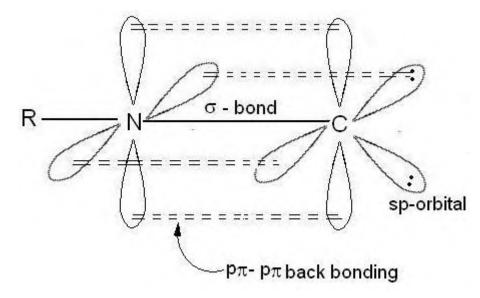
• Cyanides and isocyanides are isomeric to each other and are considered as derivative of two tautomeric forms of hydrogen cyanides

 $\begin{array}{c} \mathsf{H} - \mathsf{C} \equiv \mathsf{N} \rightleftharpoons \mathsf{H} - \mathsf{N} \geqq \mathsf{C} \\ \text{cyanide form} & \text{isocyanide form} \end{array}$

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



ORBITAL STRUCTURE OF ALKYL CYANIDES



GENERAL METHOD OF PREPARATION OF CYANIDES

1. From alkyl halide

 $R - X + NaCN (alc.) \rightarrow R - CN + NaX$

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.

$$2 \bigcirc Pr + Cu_2(CN)_2 \xrightarrow{\text{pyridine}}{200^{\circ}C} 2 \bigcirc Pr + 2CuBr$$

2. From acid amides

$$R - C = NH_2 \xrightarrow{P_2O_5} R - C \equiv N + H_2O$$

3. From Grignard reagent

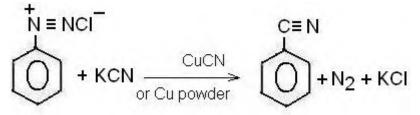
$$RMgX + CI - CN \longrightarrow R - CN + Mg$$

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4. From carboxylic acid

 $\begin{array}{c} \text{RCOOH + NH}_{3} \longrightarrow \text{RCOONH}_{4} \\ & \stackrel{\text{Al}_{2}O_{3}}{250^{\circ}\text{C}} \\ \text{R-CN} \xleftarrow{} & \stackrel{\text{Al}_{2}O_{3}500^{\circ}\text{c}}{-H_{2}O} \\ \end{array}$

5. From arene diazonium salts



6. From sodium salt of carboxylic acid

RCOONa + Br - CN
$$\xrightarrow{\Delta}$$
R - CN + CO₂ + NaBr

GENERAL METHOD OF PREPARATION OF ISOCYANIDES

1. From alkyl halides

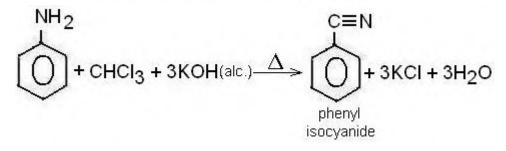
 AgCN is covalent in nature. Only nitrogen atom has lone pair of electrons available for nucleophilic attack, thus attack takes place mainly through nitrogen atom leading to formation of isocyanide along with small amount of cyanide

$$Ag - C \equiv N + R - X \rightarrow R - N \equiv C + AgX$$

2. Carbylamine reaction

R - NH₂ + CHCl₃ + 3KOH (alc.)
$$\xrightarrow{\Delta}$$

$$R - N \stackrel{*}{=} C + 3KCI + 3H_2O$$



3. From N-alkyl formamides

$$\mathbf{H} = \mathbf{H}$$

H - C - N - R $\frac{\mathsf{POCl}_3 / \mathsf{pyridine}}{\Delta}$ R - N \leq C + H₂O

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 –CN and –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 ioscyanides are lower than that of alkyl cyanides since –NC group is less polar than –CN group

CHEMICAL PROPERTIES OF CYANIDES AND ISOCYANIDES

- (A) Chemical reactions shown by cyanides only
 - (1) Basic nature of cyanides

Inspite 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.

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(2) Reaction with Grignard reagent R' R-C=NMgX R - C = N + R'MgXH₂0/H⁺ $NH_3 + R - C = O + Mg(OH)X =$ (3) Reaction with alcohol NH₂ $R - C \equiv N + R'OH + HCI$ R -C - OR Imido ester H₂O 0 NH4CI + R-C-OR' ester (4) Addition reactions $CH_3 - C \equiv N + HCI -$ →CH3imino chloride $CH_3 - C \equiv N + NH_3 \longrightarrow CH_3 - C = N$ NH3 $CH_3 - C = NH \in$ amidines NH $CH_3 - C \equiv N + R' NH_2 -$ >CH3 HR' substituted amidines $CH_3 - C \equiv N + H_2S \longrightarrow CH_3 - C = NH_2$

thioacetamide

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(B) Chemical reaction shown by isocyanides only

1

(1)

$$CH_3 - N \equiv C + S \longrightarrow CH_3 - N = C = S$$

methyl

isothiocyanate

$$CH_3 - N \equiv C + 2HgO \longrightarrow CH_3 - N = C = O + Hg_2O$$

methyl isocyanate

(2) Action oh heat

$$\begin{array}{c} \mathbf{R} - \mathbf{N} \stackrel{\bullet}{=} \mathbf{C} \stackrel{\Delta}{\longrightarrow} \mathbf{R} - \mathbf{C} \equiv \mathbf{N} \\ \text{isocyanide} \\ \text{cyanide} \end{array}$$

- (C) Reaction shown by both cyanides and isocyanides
- (1) Hydrolysis

(a) Hydrolysis of cyanides: complete hydrolysis

$$R - C \equiv N \xrightarrow[H^+ \text{ or } O]{H^+ \text{ or }} R - C - NH_2 \xrightarrow[H^+ \text{ or } O]{H^+ \text{ or }} R - C - OH + NH_4$$

Partial hydrolysis

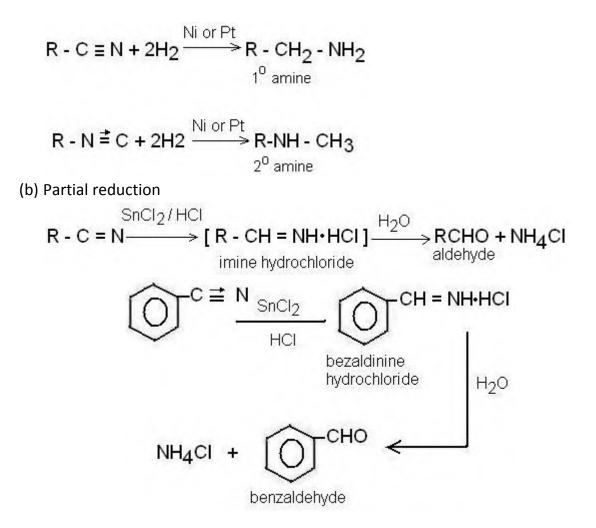
$$R - C \equiv N + H_2O \xrightarrow[conc.HCl or]{Conc.HCl or} R - C - NH_2$$

(b) Hydrolysis by isocyanide.

(2) Reduction

(a) Complete reduction

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