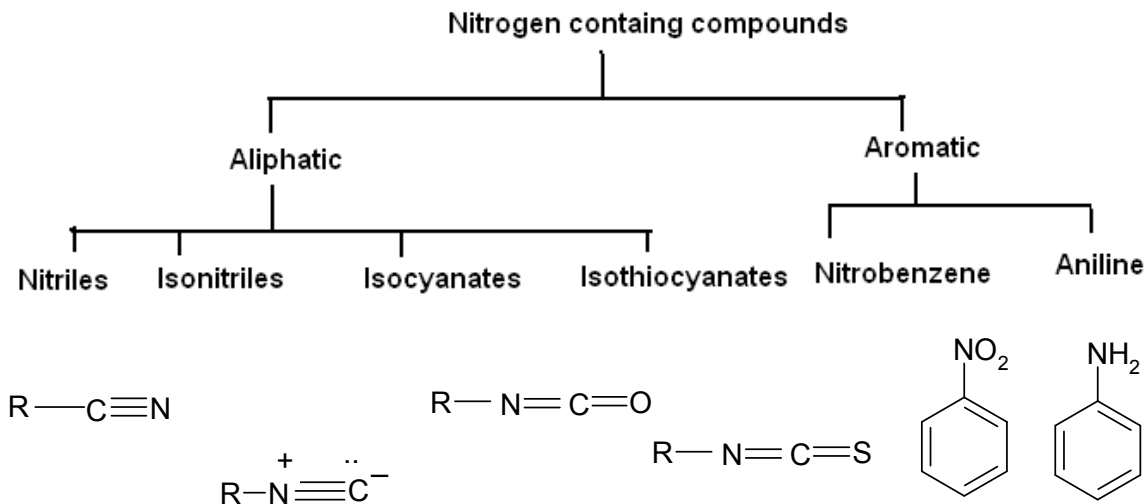


Unit 6: Nitrogen containing compounds - - - - - [10 lectures]



**Aliphatic - Nitrogen containing compounds**

**6.1 Nitriles :**

Introduction. Method of preparations of alkanenitriles i) haloalkane ii) From alkali salts of sulphonic acid iii) From aldoxime iv) From Grignard reagent

Chemical properties – i) Hydrolysis ii) Reduction iii) Addition of hydrogen halide iv) Reaction with Grignard reagent.

**1. Nitriles:**

Nomenclature: three methods as cyanide, common name and IUPAC

Cyanide: the alkyl group attached to the CN group is mentioned before “cyanide”.

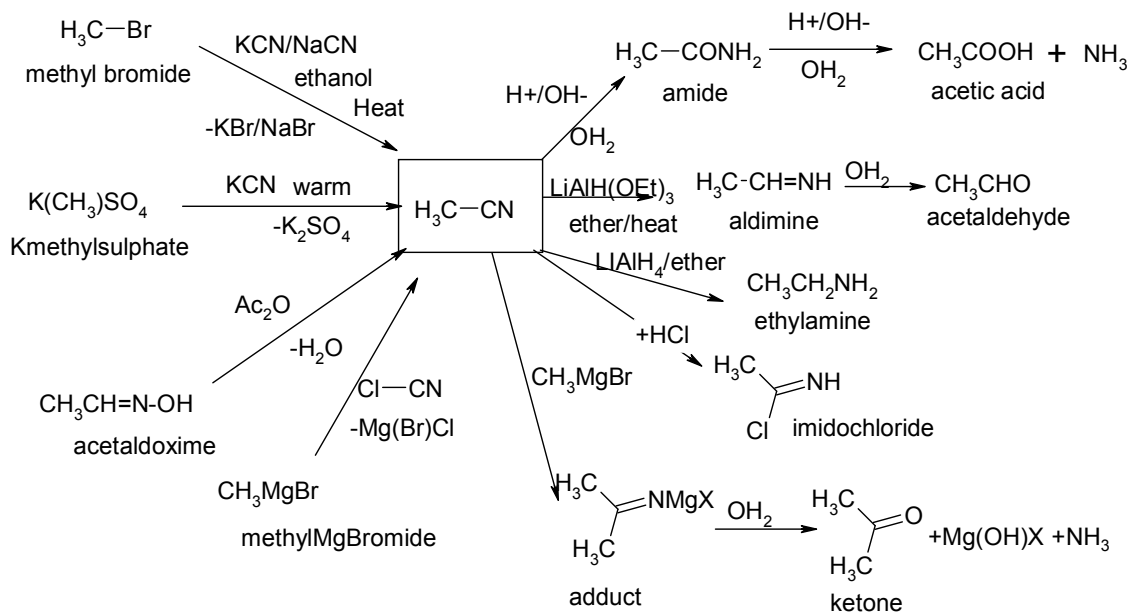
common name: “ic acid” from the name of the acid formed after hydrolysis is replaced by “onitrile”

IUPAC: The name of the parent alkane (with CN carbon) is followed by “nitrile”

Formula	Cyanide method	Common name	IUPAC name
CH <sub>3</sub> CN	methyl cyanide	Acetonitrile	Ethane nitrile
CH <sub>3</sub> CH <sub>2</sub> CN	Ethyl cyanide	propionitrile	Propane nitrile
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CN	Propyl cyanide	Butyronitrile	Butane nitrile
CH <sub>3</sub> CH(CH <sub>3</sub> )CN	Isopropyl cyanide	Isobutyronitrile	2-methyl propane nitrile

### Chemistry of Acetonitrile:

#### Chemistry of acetonitrile



#### 6.2 Isonitriles :

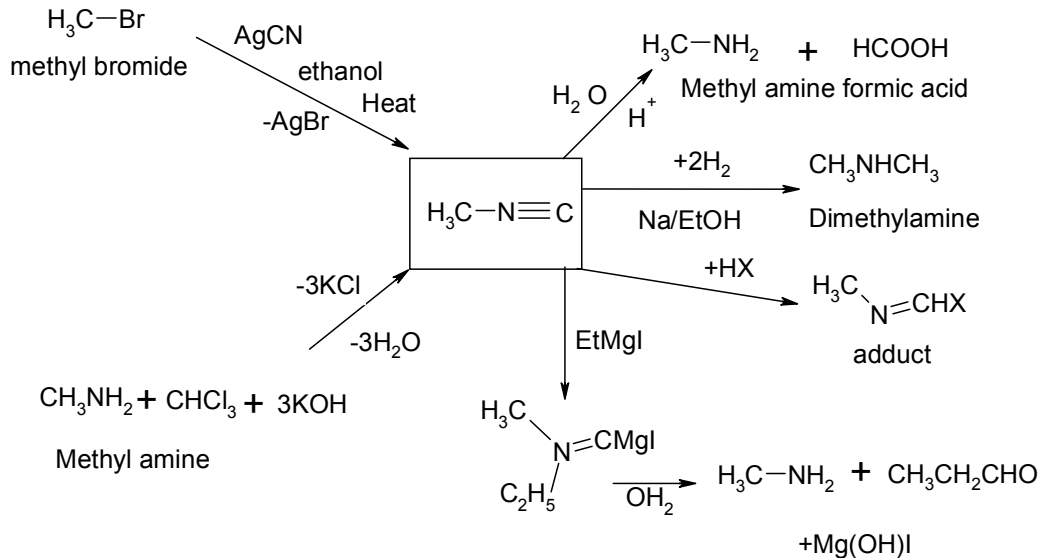
Introduction. Method of preparations of alkaneisonitriles i) From haloalkane ii) From amine, Chemical properties – i) Hydrolysis ii) Reduction iii) Addition of hydrogen halide iv) Reaction with Grignard reagent.

#### 2. Isonitriles:

Structural isomer of nitriles, derivatives of hydrogen isocyanide [H-N≡C]

formula	Common name	IUPAC name
CH <sub>3</sub> NC	methyl isocyanide	Methyl carbylamine
CH <sub>3</sub> CH <sub>2</sub> NC	Ethyl isocyanide	Ethyl carbylamine
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> NC	Propyl isocyanide	Propyl carbylamine

Chemistry of methyl isocyanide



6.3 Isocyanates :

Introduction. Method of preparations of methylisocyanate from potassium cyanate and from phosgene.

Chemical properties – i) Hydrolysis ii) Reaction with alcohol & phenol. iii) Reaction with  $\text{NH}_3$  iv) Trimerization.

3. Isocyanates:

Organic compounds with gr.  $-\text{N}=\text{C}=\text{O}$  are isocyanates, derivatives of isocyanic acid ( $\text{H}-\text{N}=\text{C}=\text{O}$ ) eg. Methyl isocyanate [MIC].

Nomenclature: Common name: alkyl isocyanate

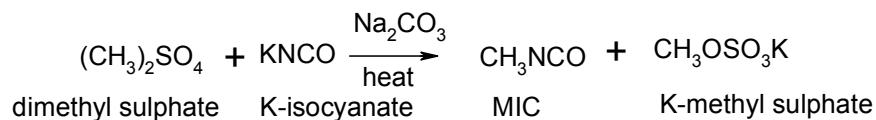
IUPAC: isocyanato alkane/alkyl carboxylamine

$\text{CH}_3-\text{N}=\text{C}=\text{O}$  methyl isocyanate/ isocyano methane/ methyl carboxylamine/MIC

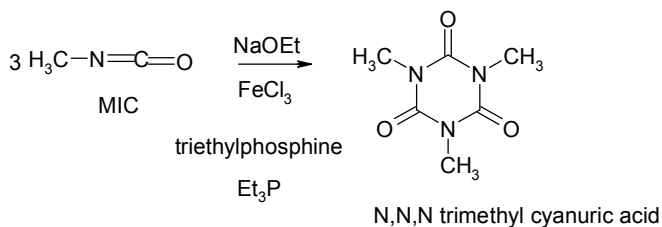
Chemistry of MIC

**Methods of preparation:**

- From DMS (Potassium cyanate): dimethyl sulphate heated in presence of  $\text{Na}_2\text{CO}_3$  with  $\text{KCNO}$







#### 6.4 Isothiocyanates :

Introduction. Method of preparations of methylisothiocyanate From Hoffmann's mustard oil test and from sulphur and isonitrile

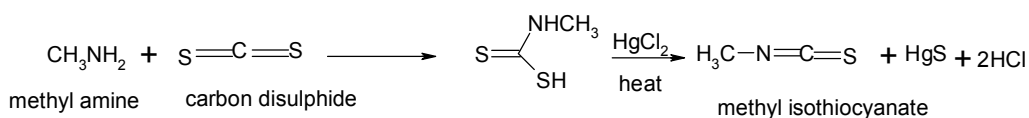
Chemical properties – i) Hydrolysis ii) Halogenation iii) Reaction with amines.

#### 4. Isothiocyanates:

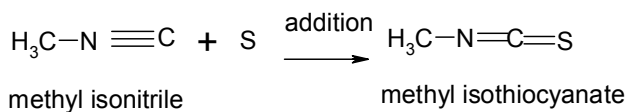
R-N=C=S are considered to be derivatives of isothiocyanic acid H-N=C=S (mustard oil)

Methods of formation:

1. From Hoffmann's mustard oil reaction:

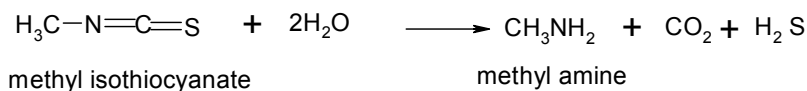


2. From sulphur and isonitrile:

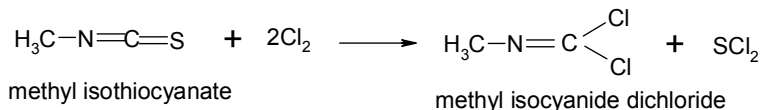


Chemical reactions:

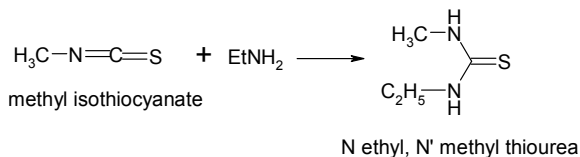
1. Hydrolysis:



2. Halogenation:



3. Reaction with ammonia/amine:



## Aromatic - Nitrogen containing compounds

### 6.5 Introduction – Groups activating and deactivating Benzene ring.

### 6.6 Mechanism of electrophilic substitution reactions with respect to halogenation of nitrobenzene & aniline

### 6.7 Mechanism of nucleophilic substitution reactions with respect to alkylation of nitrobenzene & aniline.

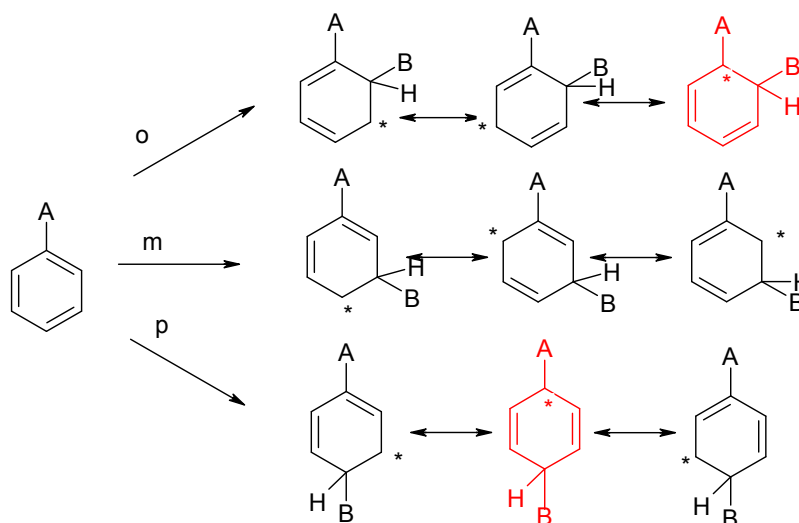
**Groups activating and deactivating Benzene ring:** Mono substituted benzene when undergoes further substitution the mechanism of the reaction [electrophilic or nucleophilic] and the nature of the 1st substituent decide the rate of the reaction and the orientation of the second group in the benzene ring. The group already present in the ring if increases the rate of second substitution, is called activating group and the group which decreases the rate of second substitution is called deactivating group. This is evident from the following example:

Eg.

1. **NH<sub>2</sub> group present in aniline** being electron donating group, stabilizes +ve charge on the ring so, favours electrophilic attack, **halogenations is fast** and **O/P halo derivative** is obtained. Whereas, it doesnot favour nucleophilic attack and hence, **alkylation occurs slow** resulting in **m-alkyl derivative**.
2. **NO<sub>2</sub> group present in nitrobenzene** being electron attracting group, stabilizes -ve charge on the ring so, favours nucleophilic attack, **alkylation is fast** and **O/P alkyl derivative** is obtained. Whereas, it doesnot favour electrophilic attack and hence, **halogenations occurs slow** resulting in **m- halo derivative**.

During the **halogenation** and **alkylation of nitrobenzene & aniline**, orientation of the second substituent is decided by the first substituent present in the ring.

The following diagram represents general mechanism of the both reactions:



A= first Gr. B=second Gr.      = +ve or -ve charge

the structure in red is highly stabilized when the charge is +ve and the Gr.A is electron donating and vice versa. , whereas the structures in red are highly destabilized when the charge is -ve and Gr. A is electron withdrawing.

A	Nature	B	mechanism	charge	Rate of reaction	of product
NH <sub>2</sub>	electron donating	Cl	Electrophilic	+ ve	fast	o/p
		R	Nucleophilic	-ve	slow	m
NO <sub>2</sub>	Electron attracting	Cl	Electrophilic	+ ve	slow	m
		R	Nucleophilic	-ve	fast	o/p