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SENIOR SIX TERM 3

TOPIC 1/2: Organic Chemistry III

Topic competency: The learner analyses the chemical properties, industrial applications, and environmental impacts of amines and polymers, evaluates their social and ecological implications, and proposes innovations and sustainable solutions for addressing challenges in their use and disposal.

Amines

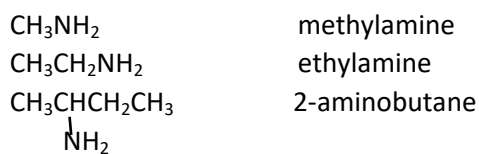
These are organic derivatives of ammonia

Classification of amines

According to the number of alkyl groups attached to the nitrogen atom

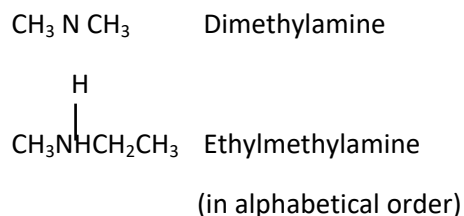
- (a) Primary amines: have only one alkyl group attached to a nitrogen atom. i.e. RNH_2

Examples



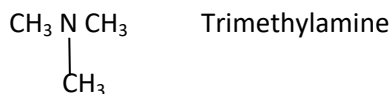
- (b) Secondary amines: have two alkyl groups attached to a nitrogen atom, R_2NH

Examples



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(c) Tertiary amine: have 3 alkyl groups on the nitrogen atom i.e, R_3N , where R is an alkyl group.



Physical properties of amines

1. Boiling and melting points

- (a) Amines are polar compounds and therefore have higher melting and boiling points than non-polar compounds of similar molecular mass due to dipole-dipole intermolecular forces or hydrogen bonding,
- (b) Primary and secondary amines have higher melting points and boiling points than tertiary amines because tertiary amine do not form intermolecular hydrogen bonds
- (c) Primary amines have higher melting and boiling points than secondary amines because they form many hydrogen bonds per molecule.

2. Solubility

Amines are soluble in water because they can form hydrogen bonds with water but the solubility decrease with alkyl chain length. Generally, primary amines are more soluble than secondary amines than tertiary amines because they form many hydrogen bonds in water.

3. Basicity of amines

Like ammonia, amines dissolve in water to form alkaline solution.



The strength of the alkaline solution is measured by the function K_b

$$K_b = \frac{[RN^+H_3][OH^-]}{[RNH_2]}$$

The higher the K_b the stronger the base or the higher the hydroxyl ion concentrations.

The ability to form alkaline solution, by amines, is due to the presence of a lone pair of electron on the nitrogen atom.

- (i) Groups (such as alkyl groups) that donate electrons increase the electron density of the lone pair on the nitrogen atom. This increases the ability of alkylamine to attract a proton from water to release hydroxide ions.

Thus, secondary amines are stronger bases than primary amines than ammonia because secondary amine has two electron donating groups, primary amines has one, whereas, amines have none.

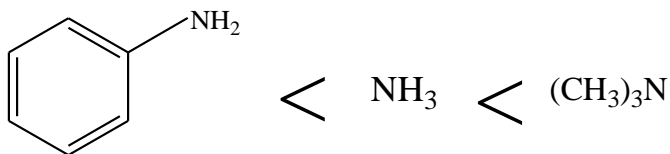
However, tertiary amines are weaker bases than either secondary or primary amines because their iminium ions are poorly solvated or hydrated or are unstable.

- (ii) Groups that withdraw electrons from nitrogen atoms like phenyl group, make amines weaker bases because they reduce the ability of the lone pair of electron on the nitrogen atom and its ability to attract a proton from water.

Example 1

Explain the following observations

- (i) The basic strength of the following amine is in order.



Solution

Trimethylamine is a stronger base than ammonia because the methyl groups donate electrons to the nitrogen atom. This increases the density of lone pair of electron on the nitrogen atom on trimethylamine and its ability to attract a proton from water and form hydroxyl ions.

Phenylamine is a weaker base than ammonia because the phenyl group pulls electrons from the nitrogen atom. The reduction of electron density of lone pair on the nitrogen atom reduces the ability of the lone pair to attract a proton from water and form hydroxyl group.

- (ii) The boiling points of the following amines are

<chem>CH3CH2CH2NH2</chem>	= 66.8°C
<chem>CH3CH2NHCH3</chem>	= 45.4°C
<chem>(CH3)3CN</chem>	= 7.70C

Solutions

Propylamine has the highest boiling point because it has two hydrogen atoms on the nitrogen atom which form many intermolecular hydrogen bonding. The hydrogen bonds necessitate high temperature to break; hence high boiling point.

Ethylmethanamine has one hydrogen bond on the nitrogen atom and thus forms fewer hydrogen bonds leading to lower boiling point.

Trimethylamine lacks a hydrogen atom on a nitrogen atom and is incapable of forming intermolecular hydrogen bonds leading to the lowest boiling point.

(iii) The acid constants K_a for the following amines are:

Amine	K_a (mol dm^{-3})
$(\text{CH}_3)_3\text{N}$	9.70
$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$	10.67

Solution

Trimethylamine $(\text{CH}_3)_3\text{N}$ is a weaker base than propylamine because it forms unstable aqueous ammonium ions

Chemical properties

1. They react with acids to form salts

Example

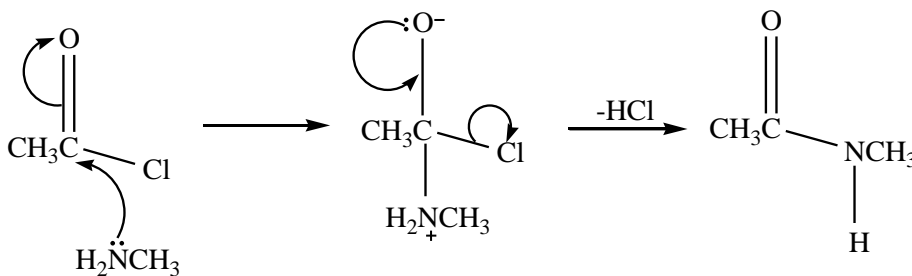


2. Primary and secondary amines react with alkanoyl halides to form amides

Example 2

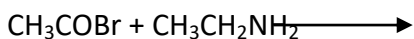


Mechanism



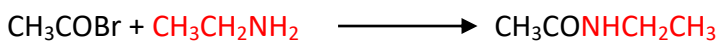
Trial 1

Complete and write a mechanism

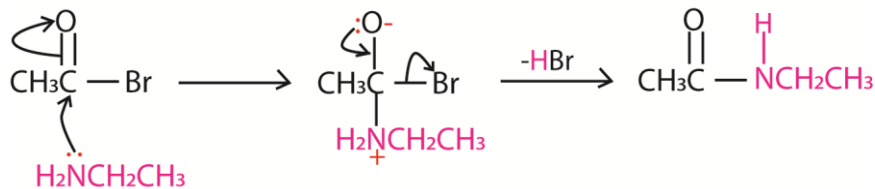


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Solution

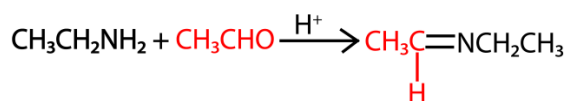


Mechanism

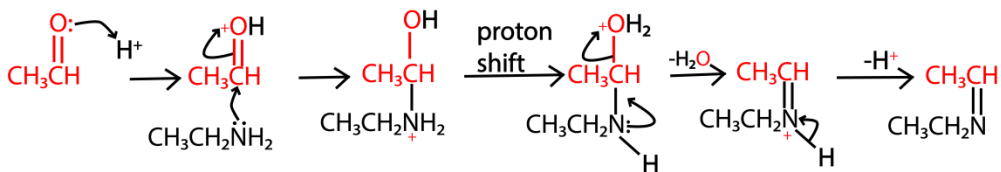


3. Primary amines undergo condensation reaction with carbonyl compounds between pH 4 -5 to form **imines**. At lower pH the **amine is protonated** as well making it a weaker nucleophile.

Example 3

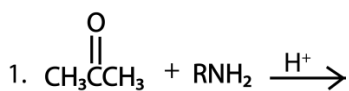


MECHANISM

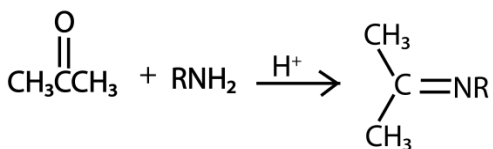


Exercise 2

Complete the following equations and write appropriate mechanism.



Solution



Mechanism

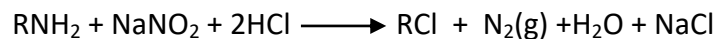
Distinguishing between primary, secondary and tertiary amines

A. Reagent: nitrous acid (NaNO_2 , HCl ($0-5^\circ\text{C}$))

Observations

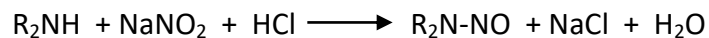
(i) Primary amine: effervescence

Equation



(ii) Secondary amines: yellow oil liquid

Equation



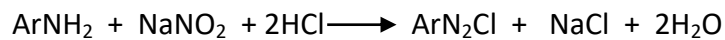
(iii) Tertiary amines: no observable change due to the formation of soluble diazonium salts

Equation

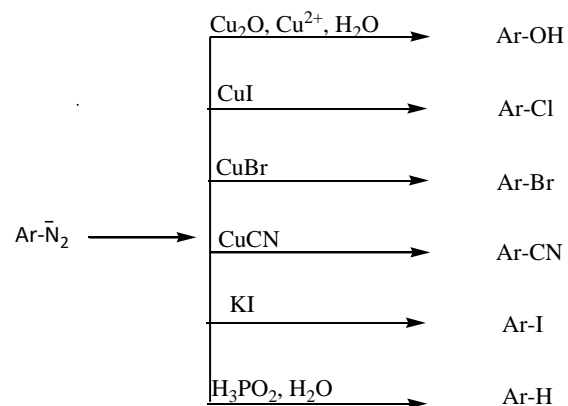


(iv) Aromatic amine: no observable change due to the formation of soluble diazonium salts

Equation



Reaction of aromatic diazonium salts



B. The Hinsberg test

Procedure: a mixture of small amount of the amine and benzenesulfonyl chloride is shaken with potassium hydroxide, time allowed for the reaction to take place and then the mixture is acidified.

Primary amine: forms a colorless solution with potassium hydroxide, forming a precipitate when the mixture is acidified.

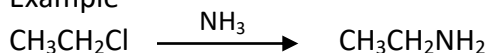
Secondary amine: forms a precipitate with potassium hydroxide insoluble when the mixture is acidified

Tertiary amine: no observable change

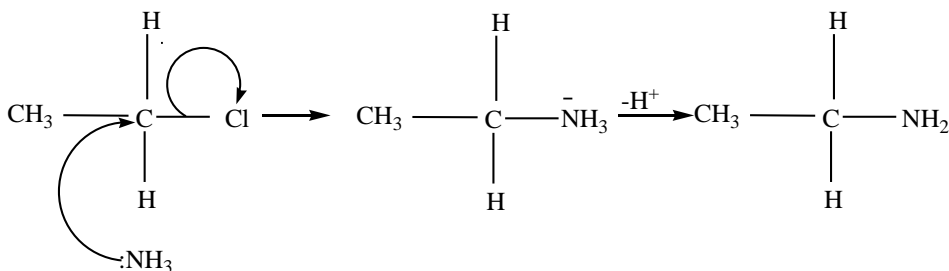
Preparation of amines

1. Reaction of alkyl halides with ammonia

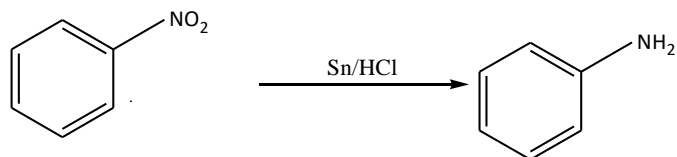
Example



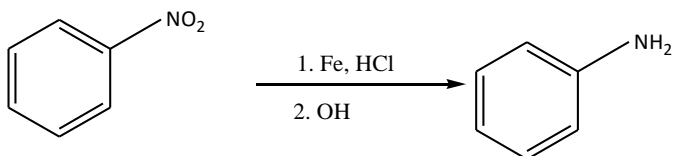
Mechanism



2. By reduction of nitroalkane

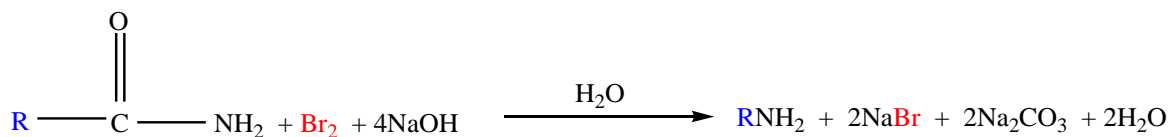


Or

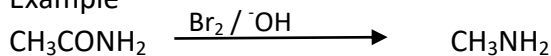


3. By Hofmann degradation

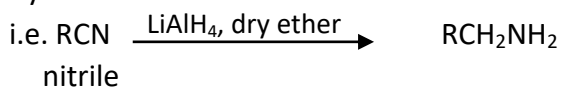
Amides with no substituent on the nitrogen atom react with solution of bromine or chlorine in sodium hydroxide to yield amines.



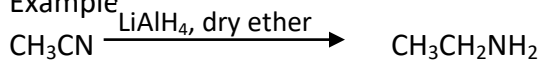
Example



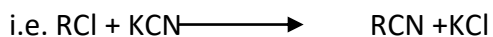
4. By reduction of nitriles



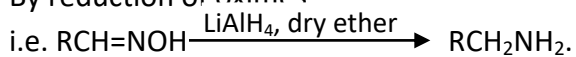
Example



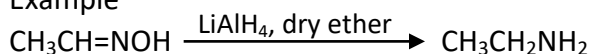
Nitrile can be obtained by reacting alkyl halides with potassium cyanide.



5. By reduction of oximes



Example



Polymerization

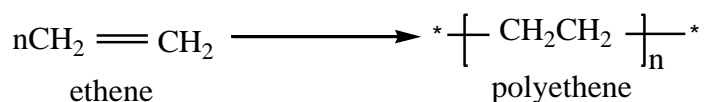
A polymer is a high molecular mass species consisting of a regular repeating units or chemically similar units, linked by primary covalent bonds.

Polymerization is the process by which high molecular mass species are formed many chemically similar units called monomers.

Types of polymerization.

1. Addition polymerization: monomers add one to each other to form polymers without loss of any molecule.

- a. Alkenes undergo addition polymerization to form polyalkenes

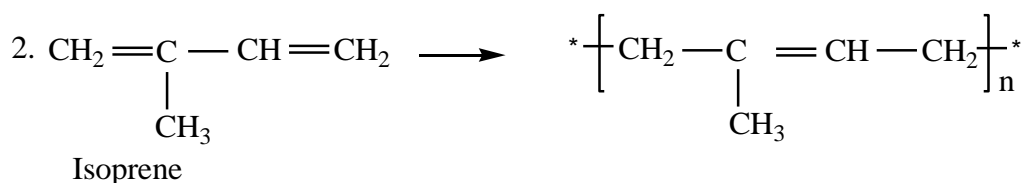
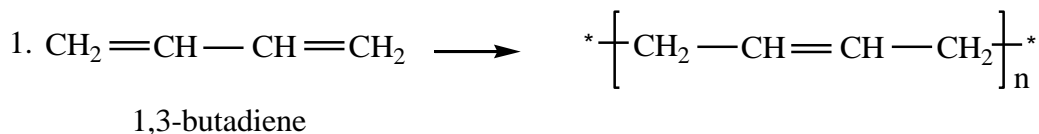


Other common polyalkenes are:

Monomer	Structure	Name of the polymer
Vinyl monomers		
Propene	$\text{CH}_3\text{CH}=\text{CH}_2$	Polypropene
Vinylchloride	$\text{CH}_2=\text{CHCl}$	Polyvinylchloride (PVC)
Vinylacetate	$\text{CH}_2=\text{CHOCOCH}_3$	Polyvinylacetate
Styrene	$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_5$	Polystyrene
acrylonitrile	$\text{CH}_2=\text{CHCN}$	Polyacrylonitrile
Acrylic monomers		
Acrylic acid	$\text{CH}_2=\text{CHCOOH}$	Polyacrylic acid
Methylacrylate	$\text{CH}_2=\text{CHCOOCH}_3$	Polymethylacrylate
butylacrylate	$\text{CH}_2=\text{CHCOOC}_4\text{H}_9$	Polybutylacrylate
Methacrylic acid	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOH}$	Polymethacrylic acid
Methylmethacrylate	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3$	Polymethylmethacrylate
Ethylmethacrylate	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_2\text{H}_5$	Polyethylmethacrylate
Acrylamide	$\text{CH}_2=\text{CHCONH}_2$	Polyacrylamide

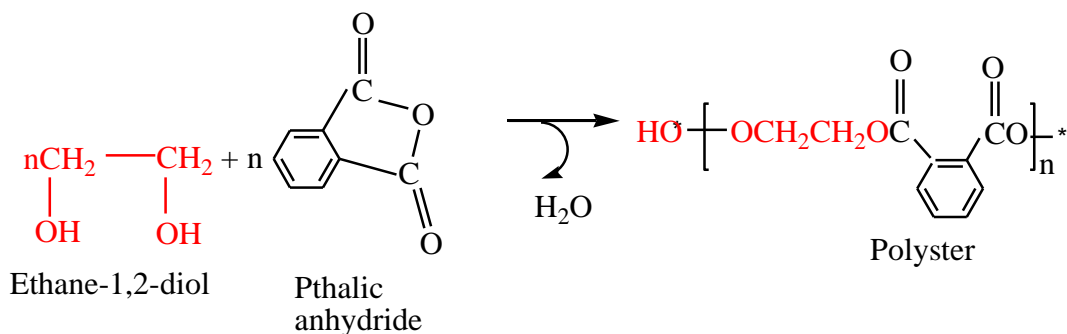
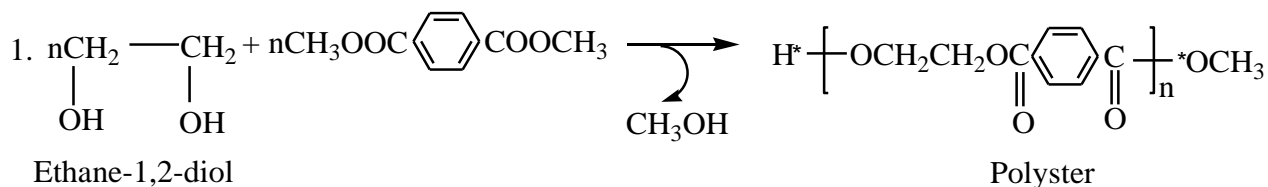
b. Conjugated dienes undergo addition polymerization to form polydienes.

Examples

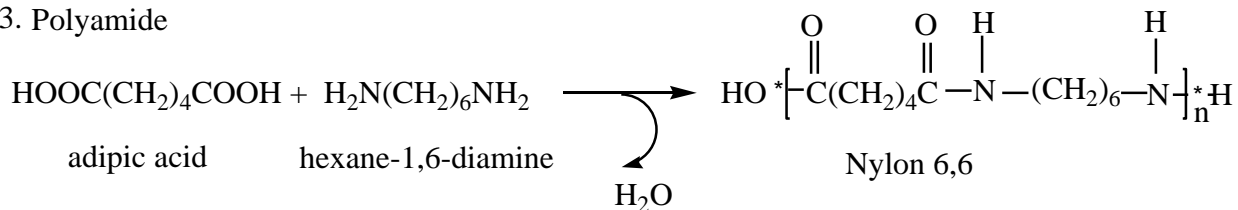


2. Condensation polymerization is formation of big molecules called polymers from small molecules called monomers accompanied by loss of small molecules such as water, ammonia e.t.c

Examples



3. Polyamide



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Thermoplastic and thermosetting polymers

Thermoplastic polymers are polymers that soften and can be remolded on heating, e.g. polyethene.

Thermosetting polymers are polymers that cannot be remolded on heating. E.g. phenolic and epoxy resins.

Thank you
Dr. Bbosa Science