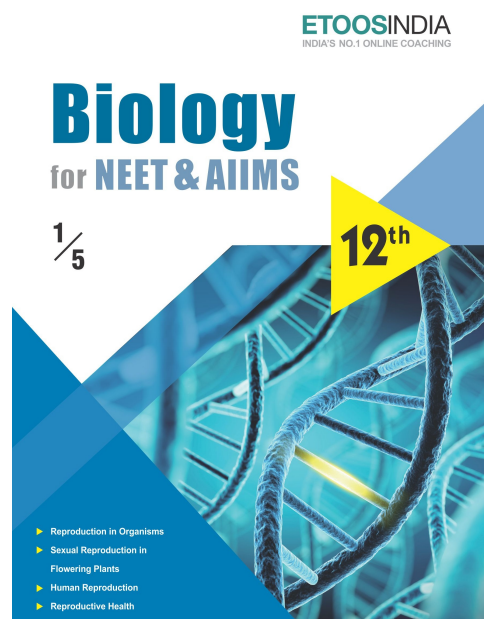
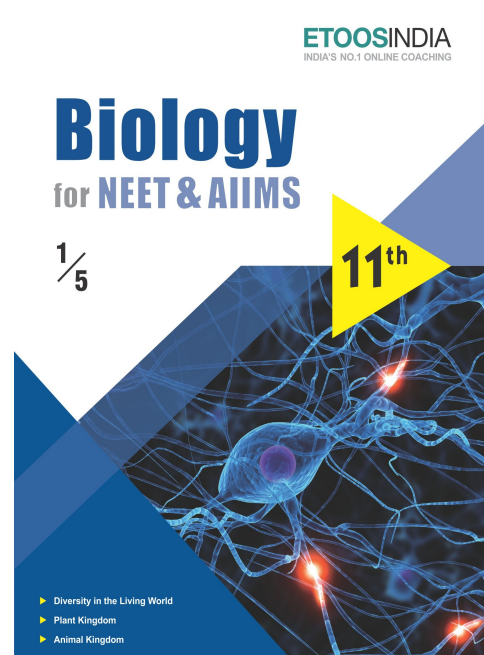
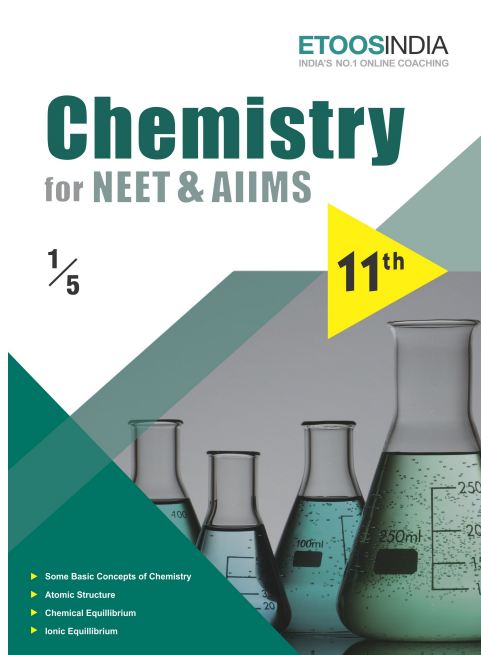
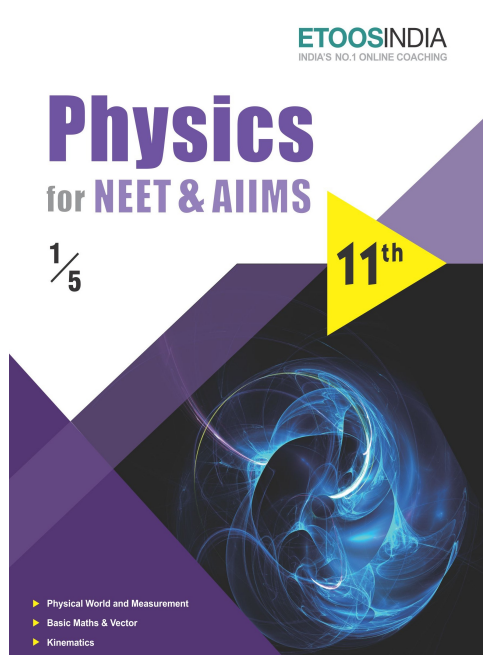


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For NEET & AIIMS**

NITROGEN AND ITS DERIVATIVES

Many years ago it was taught that plants and animals were composed of different materials: Plants, of a chemical substance of three elements- Carbon, Hydrogen and Oxygen; animals of one of four elements, nitrogen being added to the other three.

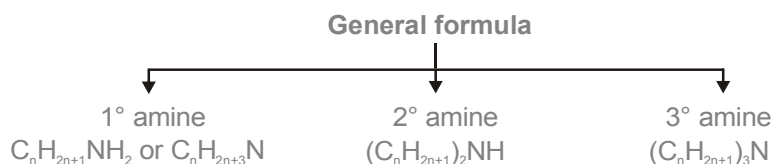
"ASA GRAY"

INTRODUCTION

Amines constitute an important class of organic compounds derived by replacing one or more hydrogen atoms of ammonia molecule by alkyl/aryl group(s). In nature, they occur among protein, vitamins, alkaloids and hormones. The chief commercial use of amines is as intermediates in the synthesis of medicines and fibres. Synthetic examples include polymers, dyestuffs and drugs. Two biologically active compounds, namely adrenaline and ephedrine, both containing secondary amino group, are used to increase blood pressure. Novocain, a synthetic amino compound, is used as an anaesthetic in dentistry. Benadryl, a well known antihistaminic drug also contains tertiary amino group. Quaternary ammonium salts are used as surfactants. Diazonium salts are intermediates in the preparation of a variety of aromatic compounds including dyes. In this Unit, you will learn about amines, cyanide, isocyanide and diazonium salts.

AMINES

Amines are derivatives of ammonia in which one or more hydrogen atoms are replaced by alkyl groups(s). Amines are classified as primary, secondary and tertiary depending on the number of alkyl groups attached to nitrogen atom.

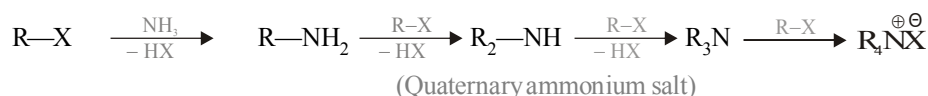


GENERAL METHOD OF PREPARATION :

(I) AMMONOLYSIS OF ALKYL HALIDES AND ALCOHOL :

(a) From Ammonolysis of alkyl halides [Hofmann's ammonolysis] :

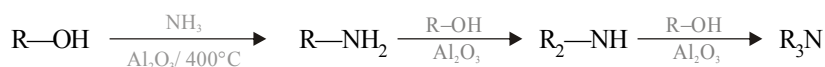
When an aqueous solution of ammonia is heated with alkyl halide all the three types of amines and quaternary ammonium salt are formed.



If ammonia is taken in excess, 1° amine is the main product.

(b) Ammonolysis of alcohols :

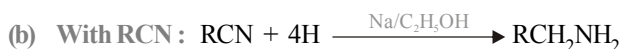
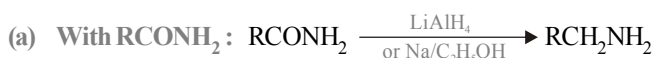
When ROH and NH₃ are passed over Al₂O₃ or ThO₂ at 350° C all the three types of amines are formed.



Note :

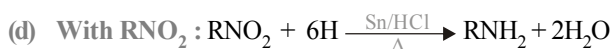
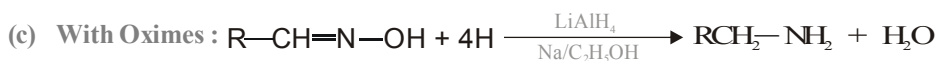
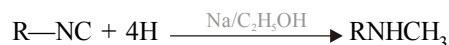
- (i) Quaternary ammonium hydroxide is not formed due to steric hindrance.
- (ii) If excess of ammonia is used, then main product will be primary amine.

(II) BY REDUCTION :



This reaction is called mendius reaction.

The reduction of alkyl isocyanides with sodium and ethanol gives secondary amines.



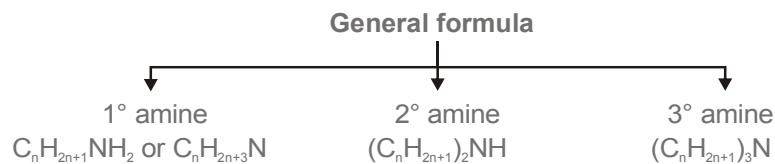
In lab method we use Sn/HCl while in industrial method we use Fe / HCl.

(III) BY HYDROLYSIS OF :

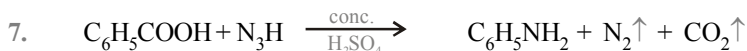
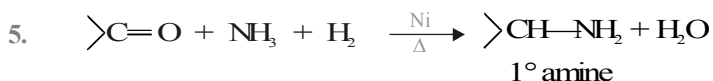
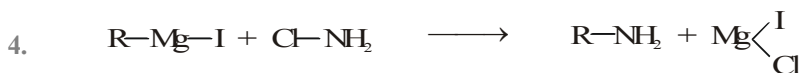
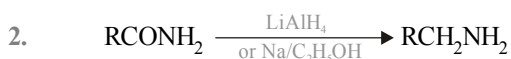
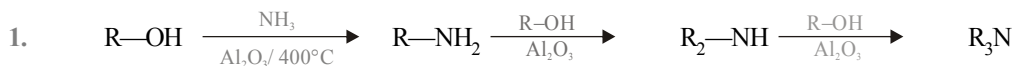
(a) R—NC : Alkyl isocyanide undergoes hydrolysis with mineral acid and forms alkyl amine.



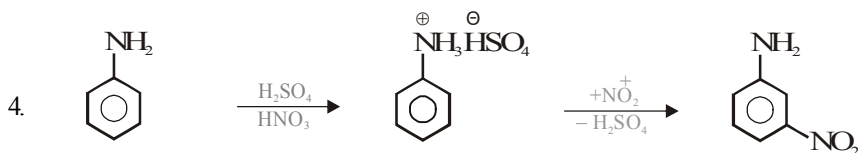
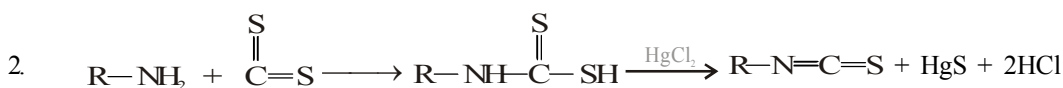
Etoos Tips & Formulas



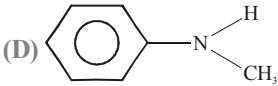
General method of preparation :



Chemical reaction :

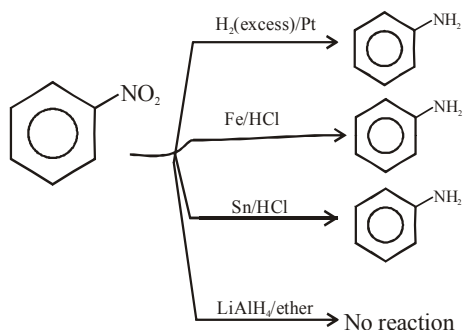


SOLVED EXAMPLE

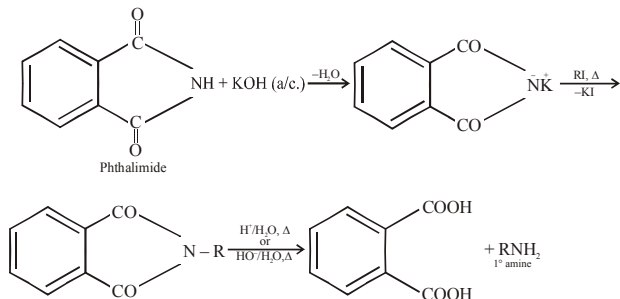
- Ex. 1 Amongst the following, the strongest base in aqueous medium is
- (A) CH_3NH_2 (B) NCCH_2NH_2 (C) $(\text{CH}_3)_2\text{NH}$ (D) $\text{C}_6\text{H}_5\text{NHCH}_3$
- Sol. (C) Compound Factors responsible for basic character are
 (A) CH_3-NH_2 Inductive effect (+I)
 (B) $\text{NC}-\text{CH}_2-\text{NH}_2$ Inductive effect (-I)
 (C) $(\text{CH}_3)_2\text{NH}$ Inductive effect (+I) and Solvation
 (D)  -I effect and resonance

Since, +I effect and solvation increases basic character while -I effect and resonance decreases basic character.

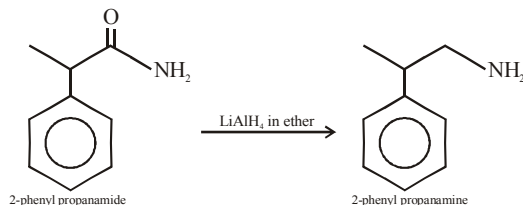
- Ex. 2 Which of the following reagents would not be a good choice for reducing an aryl nitro compound to an amine
- (A) $\text{H}_2(\text{excess})/\text{Pt}$ (B) LiAlH_4 in ether (C) Fe and HCl (D) Sn and HCl
- Sol. (B) Aryl nitro compound can't be converted into amine using LiAlH_4 in ether.



- Ex. 3 The source of nitrogen in Gabriel synthesis of amines is
- (A) Sodium azide, NaN_3 (B) Sodium nitrite, NaNO_2
 (C) Potassium cyanide, KCN (D) Potassium phthalimide $\text{C}_6\text{H}_4(\text{CO}_2)\text{N}^-\text{K}^+$
- Sol. (D) Source of nitrogen in Gabriel phthalimide synthesis is potassium phthalimide



- Ex. 4 The best reagent for converting 2-phenylpropanamide into 2-phenylpropanamine is
- (A) Excess H_2 (B) Br_2 in aqueous NaOH
 (C) Iodine in the presence of red phosphorus (D) LiAlH_4 in ether
- Sol. (D) The best reagent for converting 2-phenylpropanamide into 2-phenylpropanamine is LiAlH_4 in ether. Reaction is as given below



Exercise # 1

SINGLE OBJECTIVE

NEET LEVEL

- Cyanide ion is
(A) Nucleophilic
(B) Electrophilic
(C) Strongly acidic
(D) Non-reactive and neutral
- Compounds containing both amino and COOH groups are known as
(A) Diamines (B) Unknown
(C) Amino acids (D) Enzymes
- Which of the following is 1° amine
(A) Ethylene diamine (B) Dimethyl amine
(C) Trimethyl amine (D) N-methyl aniline
- C₃H₉N represents
(A) Primary amine (B) Secondary amine
(C) Tertiary amine (D) All of these
- $(\text{CH}_3)_2\text{C}(\text{NH}_2)\text{CH}_2\text{CO}\cdot\text{CH}_3$ is
(A) Diacetone (B) Acetoneamine
(C) Diacetoneamine (D) Aminoacetone
- Amides may be converted into amines by reaction named after
(A) Perkin (B) Claisen
(C) Hoffmann (D) Kolbe
- Reaction $\text{CH}_3\text{CONH}_2 \xrightarrow{\text{NaOBr}}$ gives
(A) CH₃Br (B) CH₄
(C) CH₃COBr (D) CH₃NH₂
- Acetamide is treated separately with the following reagents. Which would give methyl amine
(A) PCl₅ (B) NaOH + Br₂
(C) Sodalime (D) Hot conc. H₂SO₄
- The amine formed from an amide by means of bromine and alkali has
(A) Same number of C atoms as that of amide
(B) One less C atom than that of amide
(C) One more C atom than that of amide
(D) Two more C atoms than that of amide
- $\text{CH}_3\text{CN} \xrightarrow{\text{Na} + \text{C}_2\text{H}_5\text{OH}} \text{X}$
The compound X is
(A) CH₃CONH₂ (B) CH₃CH₂NH₂
(C) C₂H₆ (D) CH₃NHCH₃
- Ethylamine can be prepared by the action of bromine and caustic potash on
(A) Acetamide (B) Propionamide
(C) Formamide (D) Methyl cyanide
- Ethylamine can be obtained by the
(A) Action of NH₃ on ethyl iodide
(B) Actio of NH₃ on ethyl alcohol
(C) Both (A) and (B)
(D) None of these
- Aniline is usually purified by
(A) Steam distillation
(B) Simple distillation
(C) Vacuum distillation
(D) Extraction with a solvent
- Reduction of nitroalkanes yields
(A) Acid (B) Alcohol
(C) Amine (D) Diazo compounds
- Acetamide changes into methylamine by
(A) Hofmann bromamide reaction
(B) Hofmann reaction
(C) Friedel-Craft's reaction
(D) Hinsberg reaction
- When methyl iodide is heated with ammonia, the product obtained is
(A) Methylamine
(B) Dimethylamine
(C) Trimethylamine
(D) A mixture of the above three amines
- Acetanilide can be prepared from aniline and which of the following
(A) Ethanol (B) Acetaldehyde
(C) Acetone (D) Acetic anhydride
- Reduction of nitroalkanes in neutral medium (e.g. Zn / NH₄Cl) forms mainly
(A) R - NH₂ (B) R - NHOH
(C) R - N = N - Cl (D) All of these
- Nitrosobenzene can be prepared by oxidizing aniline from
(A) H₂SO₄ (B) H₂SO₅
(C) H₂SO₃ (D) K₂Cr₂O₇

Exercise # 2

SINGLE OBJECTIVE

AIIMS LEVEL

1. A secondary amine is
 - (A) An organic compound with two $-NH_2$ groups
 - (B) A compound with two carbon atoms and an $-NH_2$ group
 - (C) A compound with an $-NH_2$ group on the carbon atom in number 2 position
 - (D) A compound in which two of the hydrogens of $-NH_3$ have been replaced by organic groups
2. The structural formula of methyl aminomethane is
 - (A) $(CH_3)_2CHNH_2$
 - (B) $(CH_3)_3N$
 - (C) $(CH_3)_2NH$
 - (D) CH_3NH_2
3. Allyl isocyanide has
 - (A) 9 sigma bonds and 4 pi bonds
 - (B) 8 sigma bonds and 5 pi bonds
 - (C) 8 sigma bonds, 3 pi bonds and 4 non-bonding electrons
 - (D) 9 sigma bonds, 3 pi bonds and 2 non-bonding electrons
4. Reduction of nitroalkanes yields
 - (A) Acid
 - (B) Alcohol
 - (C) Amine
 - (D) Diazo compounds
5. Acetamide changes into methylamine by
 - (A) Hofmann bromamide reaction
 - (B) Hofmann reaction
 - (C) Friedel-Craft's reaction
 - (D) Hinsberg reaction
6. When methyl iodide is heated with ammonia, the product obtained is
 - (A) Methylamine
 - (B) Dimethylamine
 - (C) Trimethylamine
 - (D) A mixture of the above three amines
7. Acetanilide can be prepared from aniline and which of the following
 - (A) Ethanol
 - (B) Acetaldehyde
 - (C) Acetone
 - (D) Acetic anhydride
8. Reduction of nitroalkanes in neutral medium (e.g. Zn / NH_4Cl) forms mainly
 - (A) $R-NH_2$
 - (B) $R-NHOH$
 - (C) $R-N=N-Cl$
 - (D) All of these
9. Nitrosobenzene can be prepared by oxidizing aniline from
 - (A) H_2SO_4
 - (B) H_2SO_5
 - (C) H_2SO_3
 - (D) $K_2Cr_2O_7$
10. The Hinsberg's method is used for
 - (A) Preparation of primary amines
 - (B) Preparation of secondary amines
 - (C) Preparation of tertiary amines
 - (D) Separation of amine mixtures
11. Reaction of primary amines with aldehyde yields
 - (A) Amides
 - (B) Aldimines
 - (C) Nitriles
 - (D) Nitro compounds
12. When acetamide is treated with HNO_2 , the gas is evolved
 - (A) H_2
 - (B) O_2
 - (C) N_2
 - (D) CH_4
13. Nitrobenzene on nitration gives
 - (A) o-dinitrobenzene
 - (B) p-dinitrobenzene
 - (C) m-dinitrobenzene
 - (D) o- and p-nitrobenzene
14. Reduction of alkyl nitrites yields
 - (A) Alcohol
 - (B) Base
 - (C) Amine
 - (D) Acid
15. When primary amines are treated with HCl, the product obtained is
 - (A) An alcohol
 - (B) A cyanide
 - (C) An amide
 - (D) Ammonium salt
16. Which one is weakest base
 - (A) Ammonia
 - (B) Methylamine
 - (C) Dimethylamine
 - (D) Trimethylamine
17. Chloroform when treated with aniline and alcoholic KOH gives
 - (A) Phenyl cyanide
 - (B) Phenyl isocyanide
 - (C) Chlorobenzene
 - (D) Phenol
18. Which of following do not react with HNO_2
 - (A) Primary nitroalkanes
 - (B) Secondary nitroalkanes
 - (C) Tertiary nitroalkanes
 - (D) All of these
19. Primary amines can be distinguished from secondary and tertiary amines by reacting with
 - (A) Chloroform and alcoholic KOH
 - (B) Methyl iodide
 - (C) Chloroform alone
 - (D) Zinc dust

Exercise # 3

PART - 1

MATRIX MATCH COLUMN

1. Match each of the compounds in Column I with its characteristic reaction(s) in Column II.

Column - I

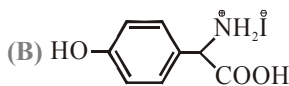
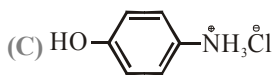
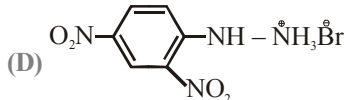
- (A) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$
 (B) $\text{CH}_3\text{CH}_2\text{OCOCH}_3$
 (C) $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2\text{OH}$
 (D) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$

Column - II

- (p) Reduction with Pd - C / H_2
 (q) Reduction with SnCl_2/HCl
 (r) Development of foul smell on treatment with chloroform and alcoholic KOH
 (s) Reduction with diisobutylaluminium hydride (DIBAL-H)
 (d) Alkaline hydrolysis

2. Match the entries in Column I with the correctly related entries in Column II.

Column - I

- (A) $\text{H}_2\text{N}-\overset{\ominus}{\text{N}}\text{H}_3\overset{\oplus}{\text{C}}\text{I}$
 (B) 
 (C) 
 (D) 

Column - II

- (p) sodium fusion extract of the compound gives Prussian blue colour with FeSO_4
 (q) gives positive FeCl_3 test
 (r) gives white precipitate with AgNO_3
 (s) reacts with aldehydes to form the corresponding

hydrozone derivative

3. Match the entries listed in Column I with appropriate entries listed in Column II.

Column - I

(Amines)

- (A) $\text{C}_2\text{H}_5\text{NH}_2$ and $\text{C}_6\text{H}_5\text{NH}_2$
 (B) $(\text{C}_2\text{H}_5)_3\text{N}$ and $(\text{C}_2\text{H}_5)_2\text{NH}$
 (C) $\text{C}_2\text{H}_5\text{NH}_2$ and $(\text{C}_2\text{H}_5)_3\text{N}$
 (D) $(\text{C}_2\text{H}_5)_3\text{N}$ and $\text{C}_6\text{H}_5\text{NH}_2$

Column - II

(Distinguish by)

- (p) Carbylamine test
 (q) Azo dye test
 (r) Hinsberg's reagent test
 (s) Liebermann nitroso reaction

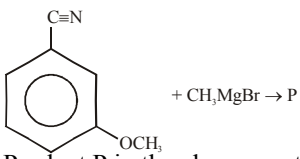
Exercise # 4

PART - 1

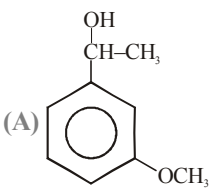
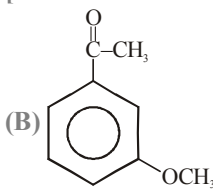
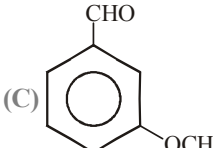
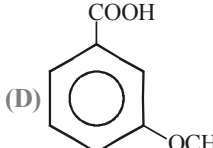
PREVIOUS YEAR (NEET/AIPMT)

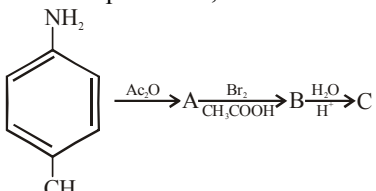
- An organic compound A on reduction gives compound B which on reduction with chloroform and potassium hydroxide forms C. The compound C on catalytic reduction gives N-methylaniline. The compound A is [CBSE AIPMT 2000]

(A) nitrobenzene (B) nitromethane
(C) methylamine (D) aniline
- Intermediates formed during reaction of RCNH_2 with Br_2 and KOH are [CBSE AIPMT 2001]

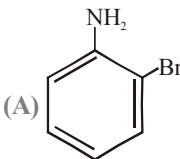
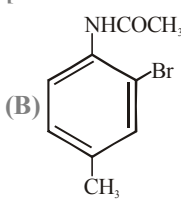
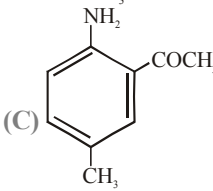
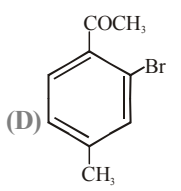
(A) RCONHBr and RNCO
(B) RNHCOBr and RNCO
(C) RNHBr and RCONHBr
(D) RCONBr_2
- 

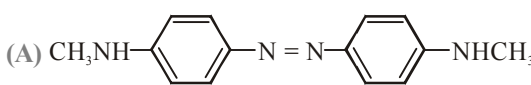
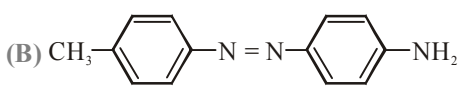
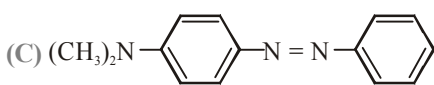
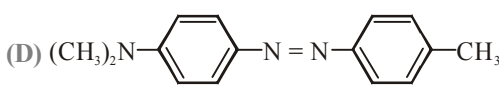
Product P in the above reaction is [CBSE AIPMT 2002]

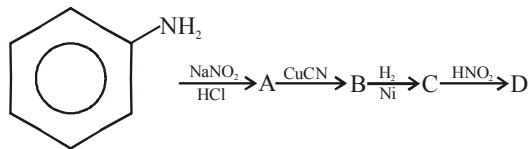
(A)  (B) 
(C)  (D) 
- The final product C, obtained in this reaction



Would be [CBSE AIPMT 2003]

(A)  (B) 
(C)  (D) 
- Aniline when diazotised in cold and then treated with dimethyl aniline, gives a coloured product. Its structure would be [CBSE AIPMT 2004]

(A) 
(B) 
(C) 
(D) 
- Aniline in a set of reactions yielded a product



The structure of the product D would be [CBSE AIPMT 2005]

(A) $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ (B) $\text{C}_6\text{H}_5\text{CH}_2\text{NHCH}_2\text{CH}_3$
(C) $\text{C}_6\text{H}_5\text{NHOH}$ (D) $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$
- Electrolytic reduction of nitrobenzene in weakly acidic medium gives [CBSE AIPMT 2005]

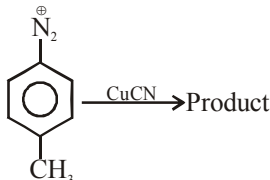
(A) aniline
(B) nitrosobenzene
(C) N-phenyl hydroxylamine
(D) p-hydroxyaniline
- Which of the following is more basic than aniline? [CBSE AIPMT 2006]

(A) Diphenylamine (B) Triphenylamine
(C) p-nitroaniline (D) Benzylamine
- Which one of the following on reduction with LiAlH_4 yields a secondary amine? [CBSE AIPMT 2007]


(A) Methyl isocyanide (B) Acetamide
(C) Methyl cyanide (D) Nitroethane
- Nitrobenzene on reaction with conc. $\text{HNO}_3/\text{H}_2\text{SO}_4$ at $80-100^\circ\text{C}$ forms which one of the following products? [NEET 2007]

(A) 1, 2-dinitrobenzene (B) 1, 3-dinitrobenzene
(C) 1, 4-dinitrobenzene (D) 1, 2, 4-trinitrobenzene

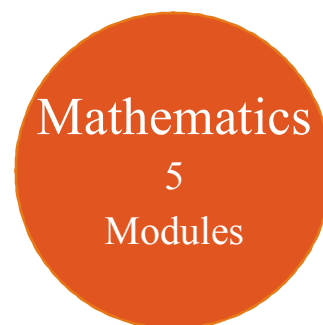
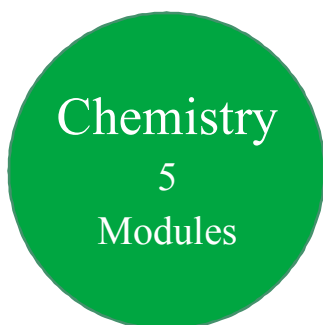
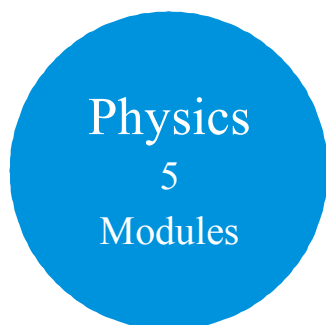
STRAIGHT OBJECTIVE TYPE

- Acetonitrile is:
 (A) C_2H_3CN (B) CH_3CN (C) CH_3COCN (D) $C_6H_5CH_2CN$
- In alkyl cyanide alkyl group attached with
 (A) C of CN group (B) N of CN group
 (C) Either C or N of CN group (D) Both C and N of CN group
- Number of isomeric primary amines obtained from $C_4H_{11}N$ are
 (A) 3 (B) 4 (C) 5 (D) 6
- 

The product is


- Ethyl amine on heating with CS_2 in presence of $HgCl_2$ forms
 (A) C_2H_5NCS (B) $(C_2H_5)_2S$ (C) $(C_2H_5)_2CS$ (D) $C_2H_5(CS)_2$
- Which of the following reacts with $NaNO_2 + HCl$ to give phenol
 (A) $C_6H_5CH_2NHCH_3$ (B) $(CH_3)_2NH$ (C) CH_3NH_2 (D) $C_6H_5NH_2$
- When chlorobenzene is treated with NH_3 in presence of Cu_2O in xylene at 570 K. The product obtained is
 (A) Benzylamine (B) Diazonium salt (C) Schiff's base (D) Aniline
- Nitrobenzene can be prepared from benzene by using a mixture of conc. HNO_3 and conc. H_2SO_4 . In the nitrating mixture, HNO_3 acts as a
 (A) Base (B) Acid (C) Catalyst (D) Reducing agent
- The rate determining step for the preparation of nitrobenzene from benzene is
 (A) Removal of NO_2^+ (B) Removal of NO_2^- (C) Formation of NO_2^+ (D) Formation of NO_2^-
- In this reaction
 $C_6H_5NH_2 + HCl + NaNO_2 \rightarrow X$. Product X is
 (A) Aniline hydrochloride (B) Nitro aniline
 (C) Benzenediazonium chloride (D) None of these
- The end product of the reactions is
 $C_2H_5NH_2 \xrightarrow{HNO_2} A \xrightarrow{PCl_5} B \xrightarrow{H.NH_2} C$
 (A) Ethyl cyanide (B) Ethyl amine (C) Methyl amine (D) Acetamide
- Primary and secondary amines are distinguished by
 (A) Br_2/KOH (B) $HClO_4$ (C) HNO_2 (D) NH_3

11th Class Modules Chapter Details



PHYSICS	CHEMISTRY	BIOLOGY
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