

25

Organic Compounds Containing Nitrogen

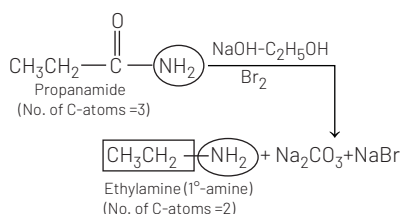
TOPIC 1

Aliphatic Amines

01 Reaction of propanamide with ethanolic sodium hydroxide and bromine will give [NEET (Oct.) 2020]

- (a) ethylamine (b) methylamine
(c) propylamine (d) aniline

Ans. (a)



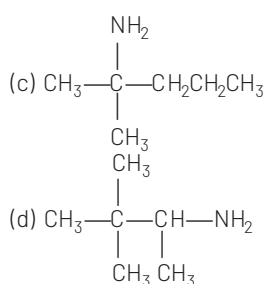
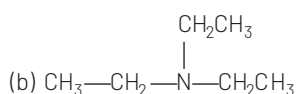
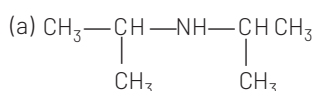
It is Hofmann bromamide reaction through which an acid amide degrades into an one carbon less primary (1°) amine.

Here, the carbon atom of the amide

group $\left(\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{NH}_2 \end{array} \right)$ gets decarboxylated

in the form of carbonate salt (Na_2CO_3).

02 The amine that reacts will Hinsberg's reagent to give an alkali insoluble product is [NEET (Odisha) 2019]

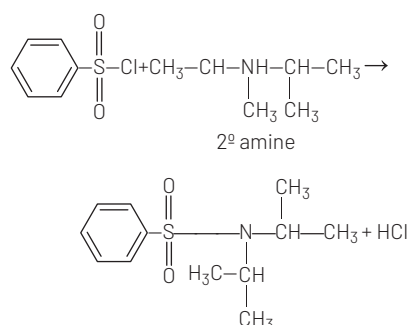


Ans. (a)

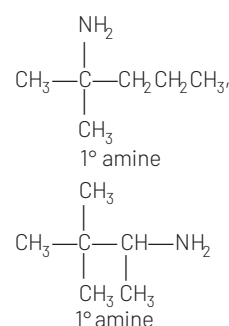
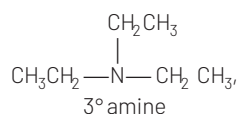
Secondary amines on reaction with Hinsberg's reagent (benzene sulphonyl chloride) forms N,N-dialkyl benzene sulphonamide.

The product formed is not acidic as no H-atom is attached to N thus it is insoluble in alkali.

The reaction of 2° amine given in option (a) takes place as follows:



On the other hand, 1° amines react with Hinsberg's reagent to yield N-alkyl benzene sulphonamide which is soluble in alkali and 3° amines do not react with $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$. The remaining options contain 1° and 3° amines.



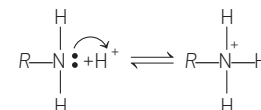
Thus, option (a) is correct.

03 The correct order of the basic strength of methyl substituted amines in aqueous solution is [NEET (National) 2019]

- (a) $(\text{CH}_3)_3\text{N} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_2\text{NH}$
(b) $(\text{CH}_3)_3\text{N} > (\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2$
(c) $\text{CH}_3\text{NH}_2 > (\text{CH}_3)_2\text{NH} > (\text{CH}_3)_3\text{N}$
(d) $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N}$

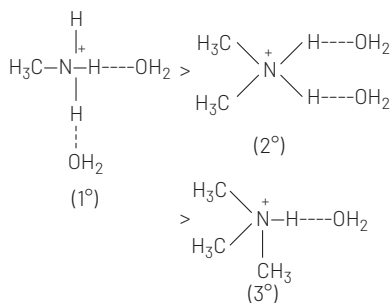
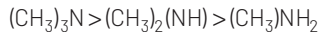
Ans. (d)

Basic strength of methyl substituted amines in aqueous solution depends upon the ease of formation of cation by accepting a proton from the acid.

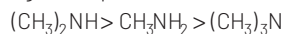


The basic strength can be decided by both inductive effect and solvation effect of alkyl group. In aqueous phase, the substituted NH_4^+ cations get stabilised not only by electron releasing effect of alkyl group (+I) but also by solvation with water molecules. Greater the size of ion, lesser will be solvation and less stabilised is the ion. The order is as follows:

Inductive effect



Strong +I-effect and hydrogen bonding favours higher basic strength of 2° amine. Thus, the correct order of basic strength in aqueous media will be

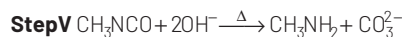
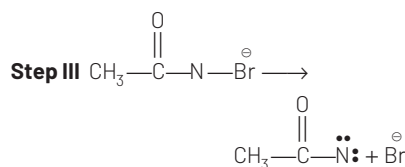
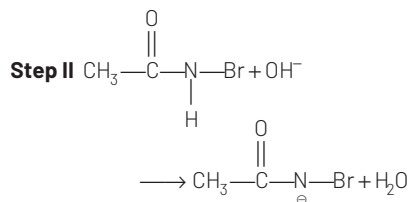
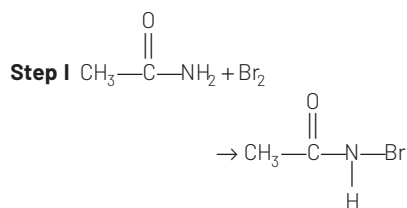
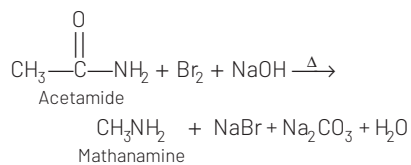


04 Which of the following reactions is appropriate for converting acetamide to methanamine? [NEET 2017]

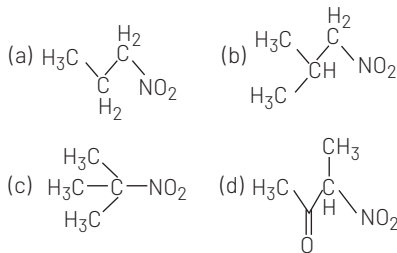
- (a) Carbylamine reaction
 (b) Hofmann hypobromamide reaction
 (c) Stephens reaction
 (d) Gabriels phthalimide synthesis

Ans. (b)

The conversion of amide with no substituent on nitrogen to an amine containing one carbon less by the action of alkaline hypobromide or bromine in presence of NaOH. It involves the migration of alkyl or aryl group with its electron pair to electron deficient N from adjacent carbon. The reaction involves the intermediates of isocyanate.



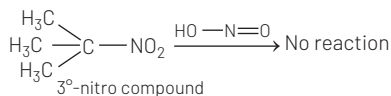
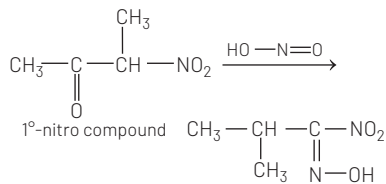
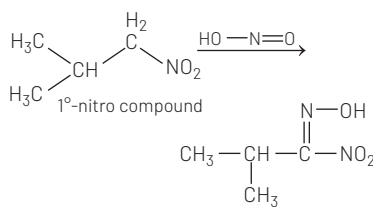
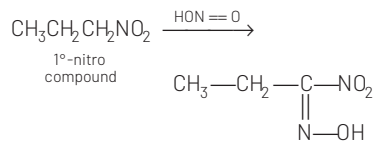
05 Which one of the following nitro-compounds does not react with nitrous acid? [NEET 2016, Phase II]



Ans. (c)

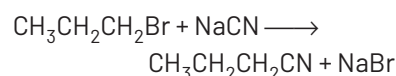
Key Idea 1° and 2° nitro compounds react with HNO_2 while 3°-nitro compound does not.

The reactions of given compounds with HNO_2 are as follow



Thus, option (c) is incorrect.

06 Consider the reaction

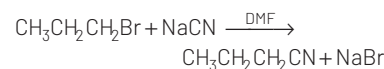


This reaction will be the fastest in

- (a) ethanol [NEET 2016, Phase II]
 (b) methanol
 (c) N,N'-dimethylformamide (DMF)
 (d) water

Ans. (c)

The given reaction follows $\text{S}_{\text{N}}2$ mechanism and $\text{S}_{\text{N}}2$ reactions are favoured in polar aprotic medium like DMSO, DMF... etc.



So, the correct option is (c).

07 Method by which aniline cannot be prepared is [CBSE AIPMT 2015]

- (a) hydrolysis phenyl isocyanide with acidic solution
 (b) degradation of benzamide with bromine in alkaline solution
 (c) reduction of nitrobenzene with H_2 / Pd in ethanol
 (d) potassium salt of phthalimide treated with chlorobenzene followed by the hydrolysis with aqueous NaOH solution

Ans. (d)

Due to resonance in chlorobenzene C—Cl bond acquires double bond character hence, C—Cl bond is inert towards nucleophile (phthalimide ion). Therefore aniline cannot be prepared.

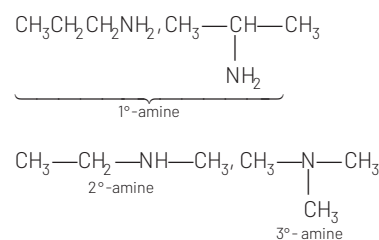
08 The number of structural isomers possible from the molecular formula $\text{C}_3\text{H}_9\text{N}$ is

[CBSE AIPMT 2015]

- (a) 4 (b) 5
 (c) 2 (d) 3

Ans. (d)

Structural isomers of $\text{C}_3\text{H}_9\text{N}$ are



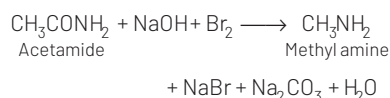
09 Acetamide is treated with the following reagents separately. Which one of these would yield methyl amine? [CBSE AIPMT 2010]

- (a) NaOH/Br₂
 (b) Sodalime
 (c) Hot conc. H₂SO₄
 (d) PCI₅

Ans. (a)

Key Idea The reagent which can convert —CONH₂ group into —NH₂ group is used for this reaction.

Among the given reagents only NaOH/Br₂ converts —CONH₂ group to —NH₂ group, thus it is used for converting acetamide to methyl amine. This reaction is called **Hoffmann bromamide reaction**, in which primary amides on treatment with Br₂ / NaOH form primary amines.

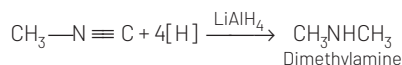


10 Which one of the following on reduction with LiAlH₄ yields a secondary amine?

[CBSE AIPMT 2007]


- (a) Methyl isocyanide
 (b) Acetamide
 (c) Methyl cyanide
 (d) Nitroethane

Ans. (a)



On catalytic reduction or with lithium aluminium hydride (LiAlH₄) or with nascent hydrogen, alkyl isocyanide yield 2° amine whereas cyanide gives 1° amine on reduction.

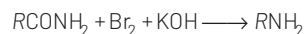
11 Intermediates formed during reaction of RCNH₂ with Br₂ and

KOH are  [CBSE AIPMT 2001]

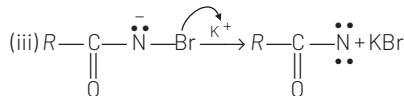
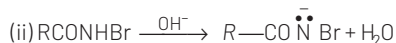
- (a) RCONHBr and RNCO
 (b) RNHCOBr and RNCO
 (c) RNHBr and RCONHBr
 (d) RCONBr₂

Ans. (a)

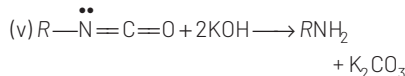
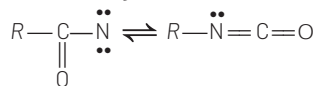
The reaction,



is known as Hofmann bromamide reaction. The mechanism of this reaction is given as :



(iv) On rearrangement



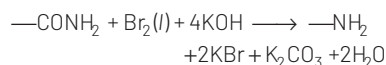
12 Amides can be converted into amines by a reaction named after

[CBSE AIPMT 1999]

- (a) Perkin (b) Claisen
 (c) Hofmann (d) Kekule

Ans. (c)

Amides can be converted into amines by Hofmann's bromamide reaction. This reaction is named after Hofmann. The reaction is as follow.



13 The decomposition of organic compounds, in the presence of oxygen and without the development of odoriferous substances, is called

[CBSE AIPMT 1999]

- (a) decay (b) N₂-fixation
 (c) nitrification (d) denitrification

Ans. (a)

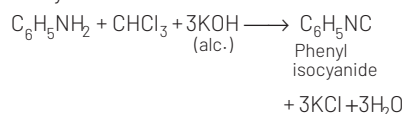
Decomposition of organic compounds in the presence of oxygen is generally called decay. The remaining three reactions takes place in the presence of bacteria.

14 Phenyl isocyanides are prepared from which of the following reaction? [CBSE AIPMT 1999]

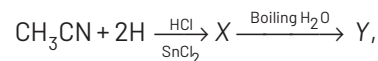
- (a) Rosenmund's reaction
 (b) Carbylamine reaction
 (c) Reimer-Tiemann reaction
 (d) Wurtz reaction

Ans. (b)

Both aliphatic and aromatic primary amines react with chloroform and alc. KOH to give isocyanides or carbylamines and the reaction is known as carbylamine reaction.



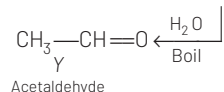
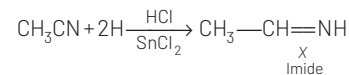
15 In the reaction,



the term Y is [CBSE AIPMT 1999]

- (a) acetone (b) ethanamine
 (c) acetaldehyde (d) dimethyl amine

Ans. (c)



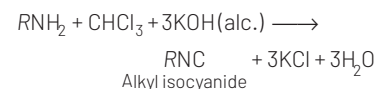
So, Y is acetaldehyde.

16 The compound obtained by heating a mixture of primary amine and chloroform with ethanolic potassium hydroxide (KOH) is

[CBSE AIPMT 1997]

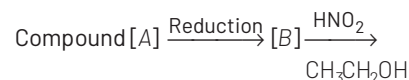
- (a) an alkyl isocyanide
 (b) an alkyl halide
 (c) an amide
 (d) an amide and nitro compound

Ans. (a)



This reaction is known as carbylamine test.(only 1° amine gives this reaction)

17 Consider the following sequence of reactions

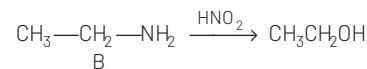
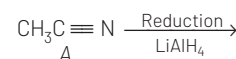


The compound [A] is

[CBSE AIPMT 1996]

- (a) CH₃CH₂CN (b) CH₃NO₂
 (c) CH₃CN (d) CH₃CN

Ans. (d)



1° amine (Ethanamine)

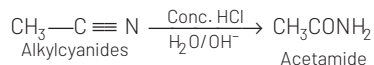
∴ A is CH₃CN.

18 Which is formed when acetonitrile is hydrolysed partially with cold conc. HCl? [CBSE AIPMT 1995]

- (a) Acetic acid (b) Acetamide
 (c) Methyl cyanide
 (d) Acetic anhydride

Ans. (b)

The partial hydrolysis of alkyl cyanides with cold conc. HCl or H₂SO₄ gives amides.



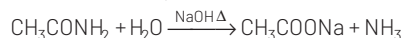
19 Acetamide and ethyl amine can be distinguished by reacting with

[CBSE AIPMT 1994]

- (a) aq. HCl and heat
- (b) aq. NaOH and heat
- (c) acidified KMnO₄
- (d) bromine water

Ans. (b)

When acetamide is heated with aq. NaOH it forms NH₃ gas but ethylamine cannot form NH₃.

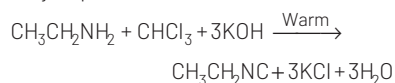


20 For carbylamine reaction, we need hot alc. KOH and [CBSE AIPMT 1992]

- (a) any primary amine and chloroform
- (b) chloroform and silver powder
- (c) a primary amine and an alkyl halide
- (d) a mono alkyl amine and trichloromethane

Ans. (a)

Aliphatic and aromatic primary amines when warmed with chloroform and an alcoholic solution of KOH, form isocyanide or carbylamine which has very unpleasant smell.



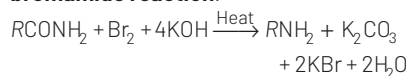
21 Indicate which nitrogen compound amongst the following would undergo Hofmann reaction?

[CBSE AIPMT 1989]

- (a) RCONHCH₃
- (b) RCOONH₄
- (c) RCONH₂
- (d) RCONHOH

Ans. (a)

When amides react with bromine in the presence of caustic alkali to form a primary amine carrying one carbon atom less than the parent amide, then the reaction is known as **Hofmann bromamide reaction**.



22 Mark the correct statement.

[CBSE AIPMT 1989]

- (a) Methyl amine is slightly acidic
- (b) Methyl amine is less basic than ammonia
- (c) Methyl amine is a stronger base than NH₃
- (d) Methyl amine forms salts with alkalis

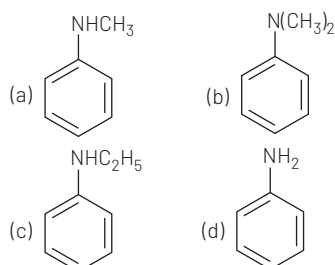
Ans. (a)

Methyl amine is a stronger base than NH₃. This is due to the reason that alkyl groups are electron releasing groups (+I-effect). As a result of which it increase the electron density on the nitrogen atom and therefore, they can donate electron pair more easily than ammonia.

TOPIC 2 Aromatic Amines

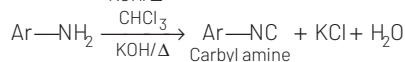
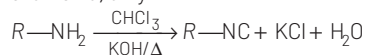
23 Which of the following amine will give the carbylamine test?

[NEET (Sep.) 2020]



Ans. (d)

Carbylamine test is responded by primary or 1°-amine (aliphatic or aromatic) only.



Options

- (a) Ph—NH—CH₃; 2° amine
- (b) Ph—N(CH₃)₂; 3° amine
- (c) Ph—NH—C₂H₅; 2° amine
- (d) Ph—NH₂; 1° amine (aniline)

It responds to carbylamine test.

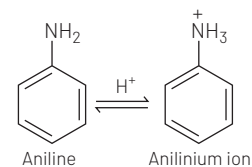
24 Nitration of aniline in strong acidic medium also gives *m*-nitroaniline because

[NEET 2018]

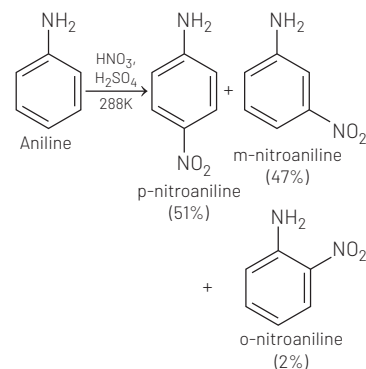
- (a) in absence of substituents nitro group always goes to *m*-position
- (b) in electrophilic substitution reactions amino group is meta directive
- (c) in spite of substituents nitro group always goes to only *m*-position
- (d) in acidic (strong) medium aniline is present as anilinium ion

Ans. (d)

In strongly acidic medium, aniline is protonated to form the anilinium ion.

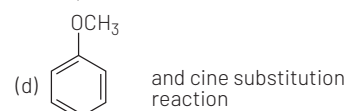
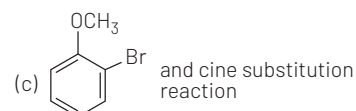
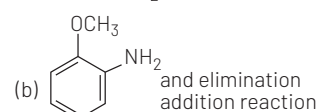
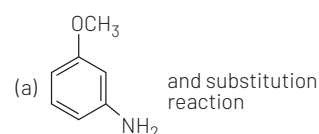
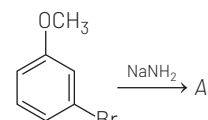


Since, anilinium ion so formed is *meta* directing, thus besides *ortho* and *para* derivatives, significant amount of *meta* derivative is also formed.

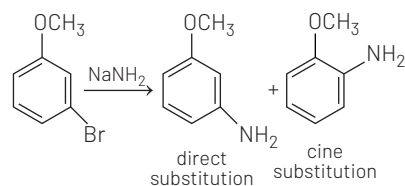


25 Identify A and predict the type of reactions.

[NEET 2017]

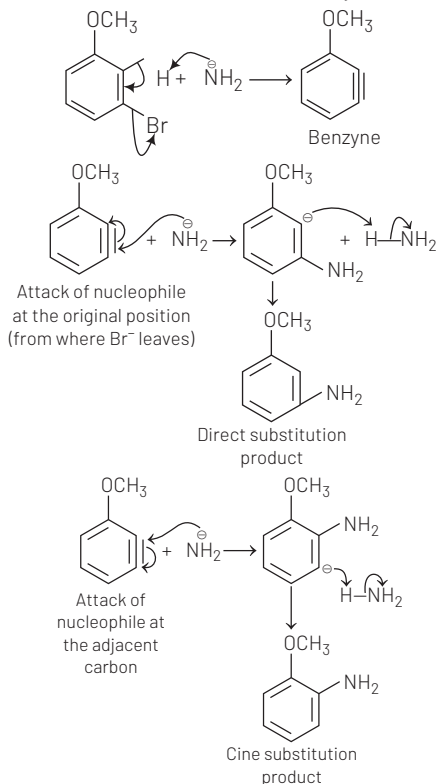


Ans. (a)

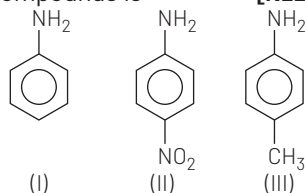


If nucleophile occupies same position of the leaving group, product is called **direct substitution product**.

If nucleophile occupies adjacent position of the leaving group, product is called **cine substitution product**. Intermediate formed in this reaction is benzyne.



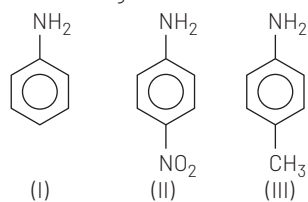
26 The correct increasing order of basic strength for the following compounds is [NEET 2017]



- (a) II < III < I
(b) III < I < II
(c) III < II < I
(d) II < I < III

Ans. (d)

Thinking process This type of problem can be solved by application of electron-withdrawing and electron donating group.



In III, —CH₃ group is an electron donating and *o/p* directing group which increase the electron density on benzene ring at *ortho* or *para* position while in II, —NO₂ group is an electron withdrawing group which decrease the electron density on benzene ring. Hence, the III is more basic than II.

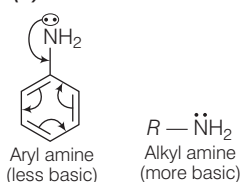
In I, there is no substituent attached, due to which I is more basic than II and less basic than III.

Therefore, the correct order of basic strength of above compounds is II < I < III.

27 The correct statement regarding the basicity of arylamines is [NEET 2016, Phase I]

- (a) Arylamines are generally more basic than alkylamines because the nitrogen lone-pair electrons are not delocalized by interaction with the aromatic ring π -electron system
- (b) Arylamines are generally more basic than alkylamines because of aryl group
- (c) Arylamines are generally more basic than alkylamines, because the nitrogen atom in arylamines is *sp*-hybridized
- (d) Arylamines are generally less basic than alkylamines because the nitrogen lone-pair electrons are delocalized by interaction with the aromatic ring π -electron system.

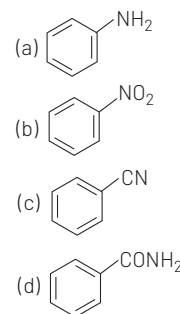
Ans. (d)



Due to delocalisation of lone pair of electrons of N-atom to the benzene ring, it loses its basicity and becomes less basic than alkyl amine.

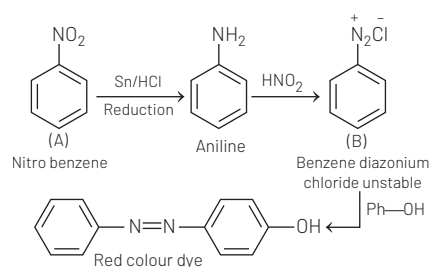
On the other hand, alkyl amine has free lone pair of electron as well as +I-effect of alkyl group increases electron density on N-atom enhancing its basic nature.

28 A given nitrogen-containing aromatic compound A reacts with Sn/HCl, followed by HNO₂ to give an unstable compound B. B, on treatment with phenol, forms a beautiful coloured compound C with the molecular formula C₁₂H₁₀N₂O. The structure of compound A is [NEET 2016, Phase II]

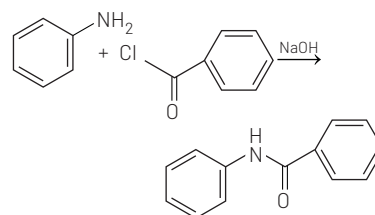


Ans. (b)

The complete road map of the reaction can be seen as



29 The following reaction,



Ans. (d)

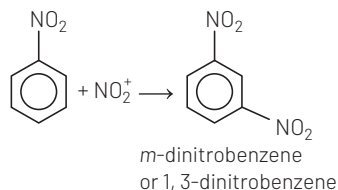
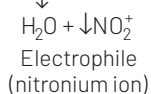
Schotten-Baumann reaction is a method to synthesise amides from amines and acid chlorides.

30 Nitrobenzene on reaction with conc. HNO₃/H₂SO₄ at 80-100°C forms which one of the following products? [NEET 2013]

- (a) 1, 2-dinitrobenzene
(b) 1, 3-dinitrobenzene
(c) 1, 4-dinitrobenzene
(d) 1, 2, 4-trinitrobenzene

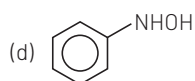
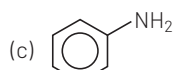
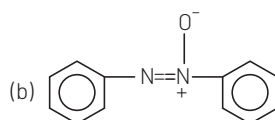
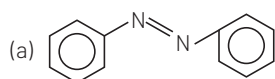
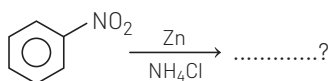
Ans. (b)

NO₂ group being electron withdrawing that's why it reduces the electron density at *ortho* and *para*-positions. Hence, as compare to *ortho* and *para* the *meta*-position is electron rich on which the electrophile (nitronium ion) can easily attacks during nitration.



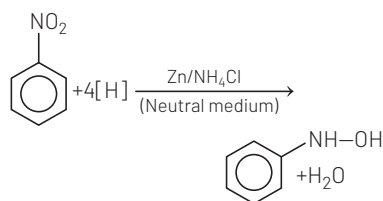
31 What is the product obtained in the following reaction?

[CBSE AIPMT 2011]



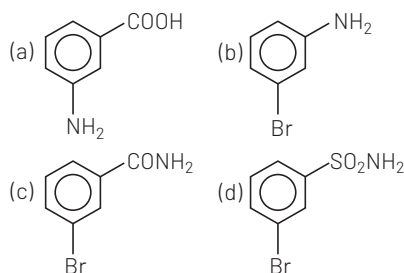
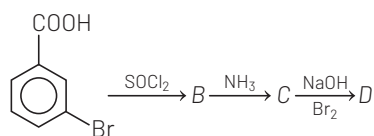
Ans. (d)

Reduction of nitrobenzene with Zn/ NH_4Cl (neutral medium) gives phenyl hydroxyamine.

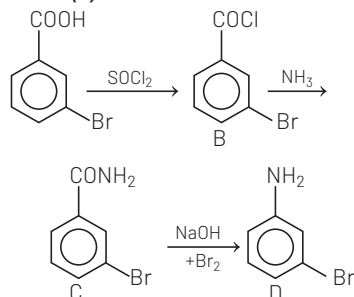


32 In a set of reactions, *m*-bromobenzoic acid gave a product *D*. Identify the product *D*.

[CBSE AIPMT 2011]



Ans. (b)



The conversion of 'C' to 'D' is an example of Hofmann bromamide degradation reaction.

33 Which of the following statements about primary amines is false?

[CBSE AIPMT 2010]

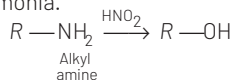
- (a) Alkyl amines are stronger bases than aryl amines
(b) Alkyl amines react with nitrous acid to produce alcohols
(c) Aryl amines react with nitrous acid to produce phenols
(d) Alkyl amines are stronger bases than ammonia

Ans. (c)

Key Idea (i) Presence of electron withdrawing substituent decreases the basicity while the presence of electron releasing substituent like, $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, etc. increases the acidity.

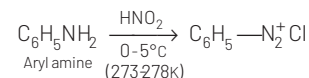
(ii) HNO_2 converts $-\text{NH}_2$ group of aliphatic amine into $-\text{OH}$ while that of aromatic amines into $-\text{N}=\text{NCl}$.

Since, phenyl group is an electron withdrawing group, it decreases the basicity. Alkyl group, on the other hand, being electron releasing, increases the basicity. Thus, alkyl amines are more basic as compared to aryl amines as well as ammonia.

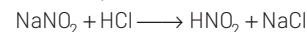


Thus, HNO_2 (nitrous acid) converts alkyl amines to alcohols.

But aryl amines react with nitrous acid to form diazonium salt.

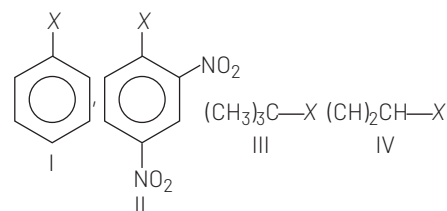


at $0-5^\circ\text{C}$ temperature



Thus, HNO_2 does not convert aryl amines into phenol.

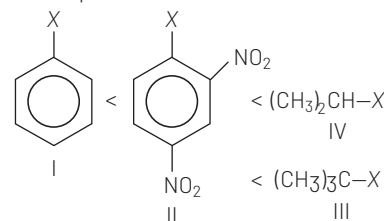
34 The correct order of increasing reactivity of C—X bond towards nucleophile in the following compounds is [CBSE AIPMT 2010]



- (a) $\text{I} < \text{II} < \text{IV} < \text{III}$ (b) $\text{II} < \text{III} < \text{I} < \text{IV}$
(c) $\text{IV} < \text{III} < \text{I} < \text{II}$ (d) $\text{III} < \text{II} < \text{I} < \text{IV}$

Ans. (a)

Key Idea Alkyl halides are more reactive towards nucleophilic substitution. Reactivity depends upon the stability of carbocation intermediate formed. Among the given halides, aryl halide ($\text{C}_6\text{H}_5\text{X}$) is least reactive towards nucleophile as in it the C—X bond acquires some double bond character due to resonance. Presence of electron withdrawing groups like $-\text{NO}_2$ at *ortho* and *para*-positions facilitates the nucleophilic displacement of $-\text{X}$ of aryl halide. Among alkyl halides, 3° halides are more reactive as compared to 2° halides due to the formation of more stable carbocation. Hence, the order of reactivity of C—X bond towards nucleophile is as follows:



35 Which of the following is more basic than aniline? [CBSE AIPMT 2006]

- (a) Diphenylamine (b) Triphenylamine
(c) *p*-nitroaniline (d) Benzylamine

Ans. (d)

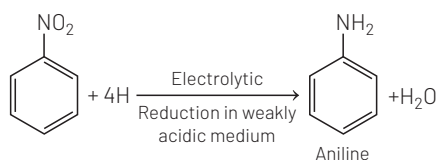
Benzylamine, $\text{C}_6\text{H}_5\text{CH}_2-\ddot{\text{N}}\text{H}_2$ is more basic than aniline because the benzyl group ($\text{C}_6\text{H}_5\text{CH}_2-$) is an electron donating group due to the $+I$ -effect. So, it is able to increase

the electron density of N of —NH_2 group. Thus, due to higher electron density, rate of donation of free pair of electron is increased, i.e. basic character is higher. Phenyl and nitro group are electron withdrawing groups, so they decrease the electron density on N of —NH_2 group. Hence, they are less basic than aniline.

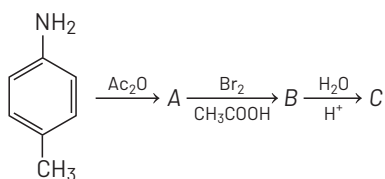
36 Electrolytic reduction of nitrobenzene in weakly acidic medium gives [CBSE AIPMT 2005]

- (a) aniline
 (b) nitrosobenzene
 (c) *N*-phenyl hydroxylamine
 (d) *p*-hydroxyaniline

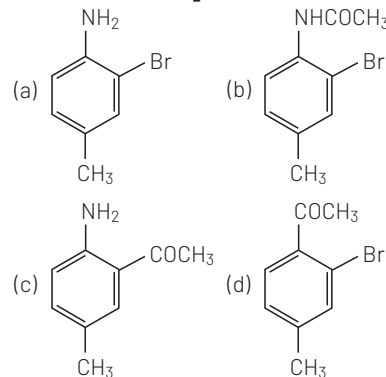
Ans. (a)



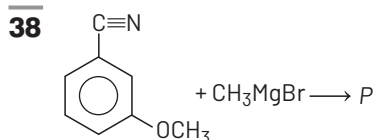
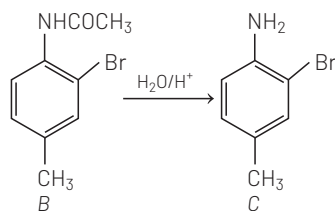
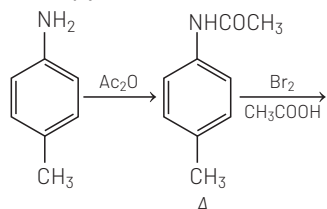
37 The final product *C*, obtained in this reaction



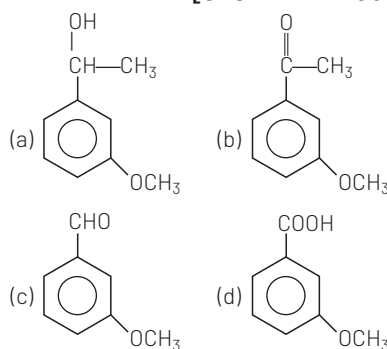
would be [CBSE AIPMT 2003]



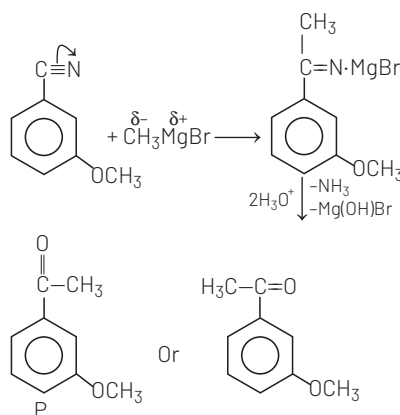
Ans. (a)



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



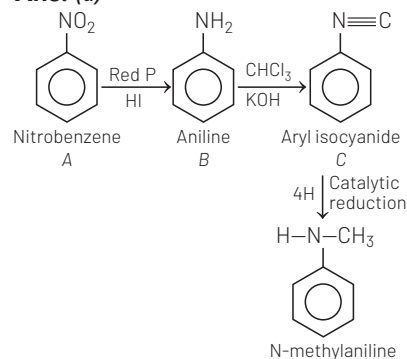
Ans. (b)



39 An organic compound *A* on reduction gives compound *B* which on reaction 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

Ans. (d)

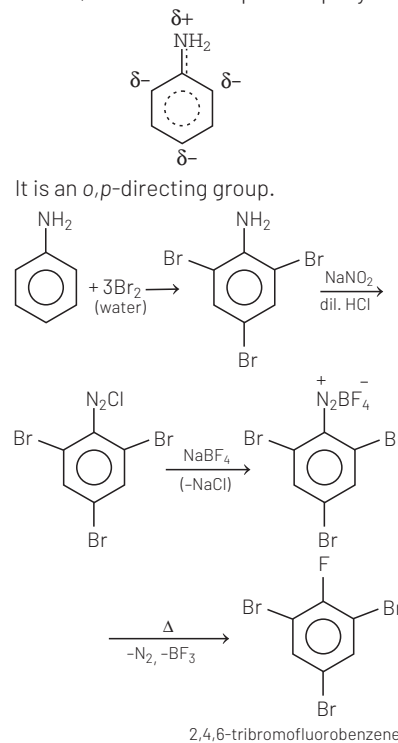


40 Aniline is reacted with bromine water and the resulting product is treated with an aqueous solution of sodium nitrite in presence of dilute hydrochloric acid. The compound so formed is converted into a tetrafluoroborate which is subsequently heated. The final product is [CBSE AIPMT 1998]

- (a) 1, 3, 5-tribromobenzene
 (b) *p*-bromofluorobenzene
 (c) *p*-bromoaniline
 (d) 2, 4, 6-tribromofluorobenzene

Ans. (d)

—NH_2 group is greatly activating group. Hence, reaction takes place rapidly.



2,4,6-tribromofluorobenzene

41 A reagent suitable for the determination of N-terminal residue of a peptide is
[CBSE AIPMT 1996]

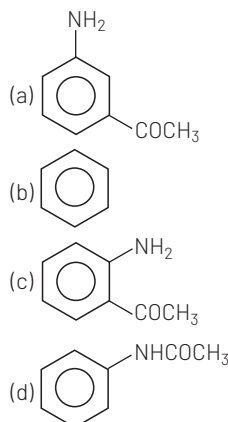
- (a) *p*-toluene sulphonyl chloride
(b) 2,4-dinitrophenyl hydrazine
(c) carboxypeptidase
(d) 2,4-dinitrofluorobenzene

Ans. (d)

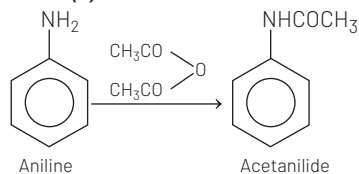
2,4-dinitrofluorobenzene is called Sanger's reagent. When this reagent reacts with amino group of peptide chain, it forms 2,4-dinitrophenyl derivatives which on hydrolysis form DNP derivatives of amino acids.

42 Aniline is an activated system for electrophilic substitution. The compound formed on heating aniline with acetic anhydride is

[CBSE AIPMT 1996]



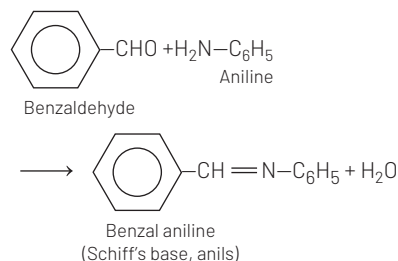
Ans. (d)



43 When aniline reacts with oil of bitter almonds ($\text{C}_6\text{H}_5\text{CHO}$) condensation takes place and benzal derivative is formed. This is known as [CBSE AIPMT 1995]

- (a) Millon's base
(b) Schiff's reagent
(c) Schiff's base
(d) Benedict's reagent

Ans. (d)



44 What is the decreasing order of basicity of 1°, 2° and 3° ethyl amines and ammonia?

[CBSE AIPMT 1994]

- (a) $\text{NH}_3 > \text{C}_2\text{H}_5\text{NH}_2 > (\text{C}_2\text{H}_5)_2\text{NH} > (\text{C}_2\text{H}_5)_3\text{N}$
(b) $(\text{C}_2\text{H}_5)_3\text{N} > (\text{C}_2\text{H}_5)_2\text{NH} > \text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3$
(c) $(\text{C}_2\text{H}_5)_2\text{NH} > \text{C}_2\text{H}_5\text{NH}_2 > (\text{C}_2\text{H}_5)_3\text{N} > \text{NH}_3$
(d) $(\text{C}_2\text{H}_5)_2\text{NH} > (\text{C}_2\text{H}_5)_3\text{N} > \text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3$

Ans. (d)

As the number of alkyl groups increases, the electron density on nitrogen atom also increases, so the basic character increases but 3° amines are less basic than 2° amines due to steric hindrance of 3° amines, so the correct order of basicity is

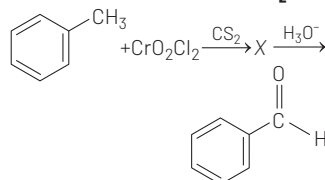
Ammonia $< 1^\circ < 3^\circ < 2^\circ$

$\text{NH}_3 < \text{C}_2\text{H}_5\text{NH}_2 < (\text{C}_2\text{H}_5)_3\text{N} < (\text{C}_2\text{H}_5)_2\text{NH}$

TOPIC 3

Diazonium Salts

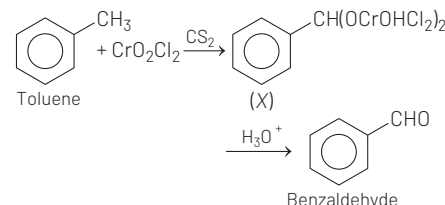
45 The intermediate compound 'X' in the following chemical reaction is [NEET 2021]



- (a)
- (b)
- (c)
- (d)

Ans. (a)

This is Etard reaction in which reaction of toluene with chromyl chloride in CCl_4 followed by hydrolysis gives benzaldehyde. Toluene reacts with chromyl chloride to form a precipitate called the Etard complex.

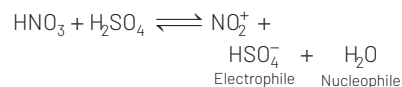


46 Consider the nitration of benzene using mixed conc. H_2SO_4 and HNO_3 . If a large amount of KHSO_4 is added to the mixture, the rate of nitration will be [NEET 2016, Phase I]

- (a) slower
(b) unchanged
(c) doubled
(d) faster

Ans. (d)

In the nitration of benzene in the presence of conc. H_2SO_4 and HNO_3 , nitrobenzene is formed.



If large amount of KHSO_4 is added to this mixture, more HSO_4^- ion furnishes and hence the concentration of NO_2^+ , i.e. electrophile decreases.

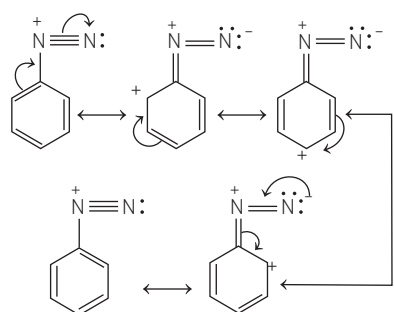
As concentration of electrophile decreases, rate of electrophilic aromatic reaction also decreases.

47 Which of the following will be most stable diazonium salt RN_2^+X^- ? [CBSE AIPMT 2014]

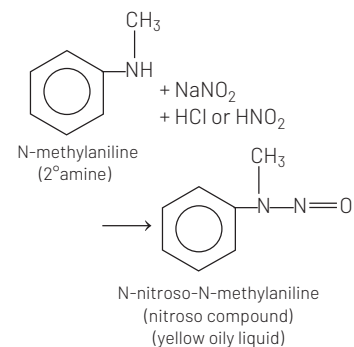
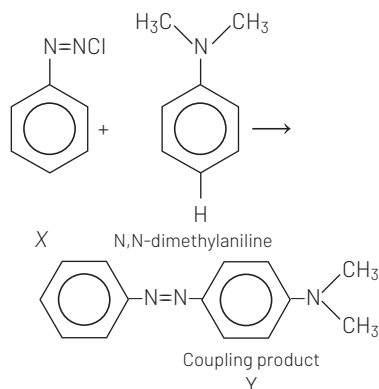
- (a) $\text{CH}_3\text{N}_2^+\text{X}^-$
(b) $\text{C}_6\text{H}_5\text{N}_2^+\text{X}^-$
(c) $\text{CH}_3\text{CH}_2\text{N}_2^+\text{X}^-$
(d) $\text{C}_6\text{H}_5\text{CH}_2\text{N}_2^+\text{X}^-$

Ans. (b)

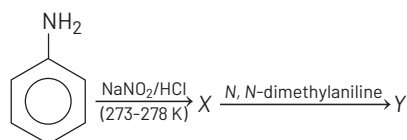
Diazonium salt containing aryl group directly linked to the nitrogen atom is most stable due to resonance stabilisation between the benzene nucleus and N-atom. Diazonium ion acts as an electrophile.



[Resonance structure of benzene diazonium ion]



- 48** Aniline in a set of the following reactions yielded a coloured product Y. [CBSE AIPMT 2010]

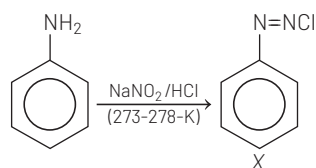


The structure of Y would be

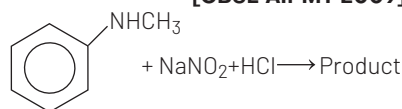
- (a)
- (b)
- (c)
- (d)

Ans. (a)

Key Idea NaNO_2/HCl causes diazotisation of $-\text{NH}_2$ group and the diazonium chloride gives a coupling product with active aryl nucleus.



- 49** Predict the product, [CBSE AIPMT 2009]

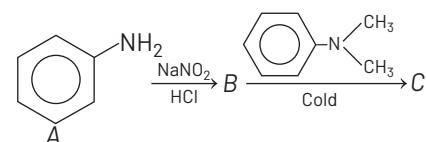


- (a)
- (b)
- (c)
- (d)

Ans. (a)

Both aliphatic and aromatic secondary amines react with $\text{NaNO}_2 + \text{HCl}$ or (HNO_2) to form N-nitrosamines which are insoluble in dilute mineral acids and separate out as neutral yellow oily compounds.

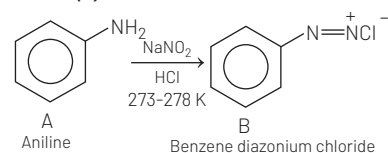
- 50** In a reaction of aniline a coloured product C was obtained.

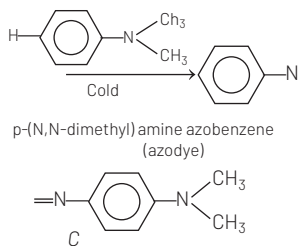


The structure of C would be [CBSE AIPMT 2008]

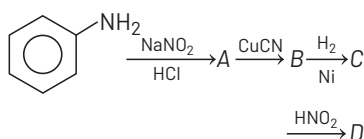
- (a)
- (b)
- (c)
- (d)

Ans. (d)





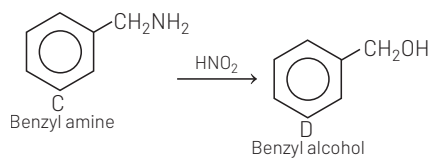
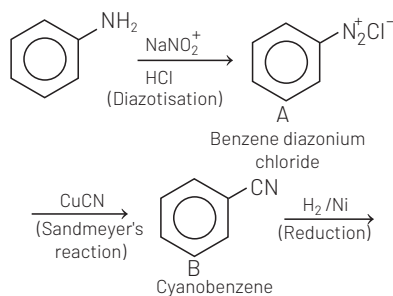
51 Aniline in a set of reactions yielded a product [CBSE AIPMT 2005]



The structure of the product D would be

- (a) $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$
- (b) $\text{C}_6\text{H}_5\text{NHCH}_2\text{CH}_3$
- (c) $\text{C}_6\text{H}_5\text{NHOH}$
- (d) $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$

Ans. (d)

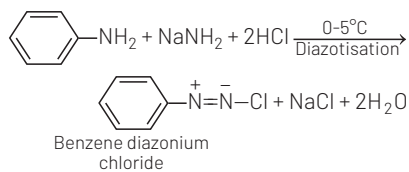


52 Aniline when diazotised in cold and then treated with dimethyl aniline, gives a coloured product. Its structure would be [CBSE AIPMT 2004]

- (a) $\text{CH}_3\text{NH}-\text{C}_6\text{H}_4-\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{NHCH}_3$
- (b) $\text{CH}_3-\text{C}_6\text{H}_4-\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{NH}_2$
- (c) $(\text{CH}_3)_2\text{N}-\text{C}_6\text{H}_4-\text{N}=\text{N}-\text{C}_6\text{H}_5$
- (d) $(\text{CH}_3)_2\text{N}-\text{C}_6\text{H}_4-\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{CH}_3$

Ans. (c)

Aniline on diazotisation in cold (at 0° to 5°C) gives benzene diazonium chloride.



This benzene diazonium chloride on coupling with dimethyl aniline gives a coloured product, i.e. p-(N,N-dimethyl) amino azobenzene (azo dye).