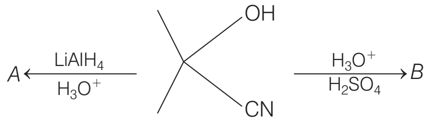
26

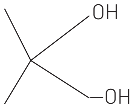
Organic Compounds Containing Nitrogen

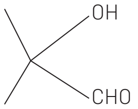
TOPIC 1

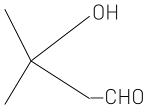
Aliphatic Amines

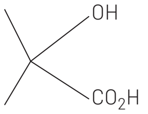
01 The major products A and B in the following set of reactions are **[2021, 31 Aug Shift-I]**

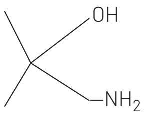


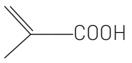
(a) A =


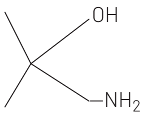
, B =


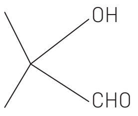
(b) A =


, B =


(c) A =


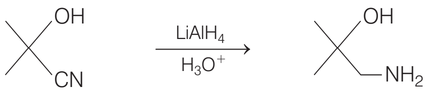
, B =


(d) A =


, B =


Ans. ***(c)***

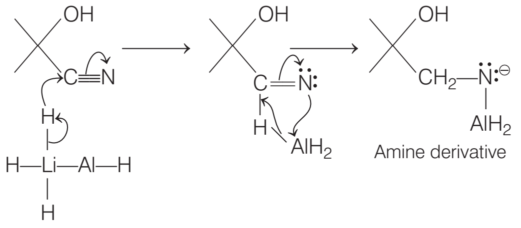
Nitriles can be converted to 1° amines by reaction with $LiAlH_4$.



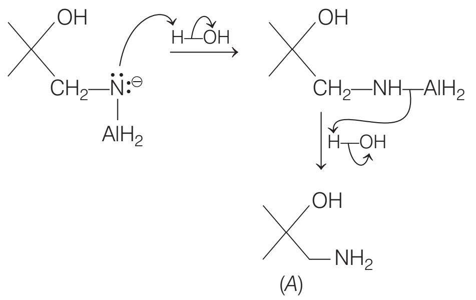
2-hydroxy-2-methyl propionitrile 1-amino-2-methylpropan-2-ol (A)

Mechanism

(i) Hydride nucleophile attacks the electrophilic carbon in nitrile to form imine anion.

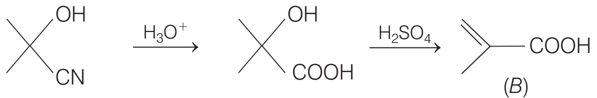


(ii) Hydrolysis of amine derivative.



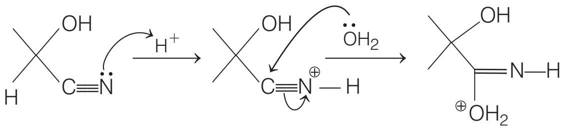
(A)

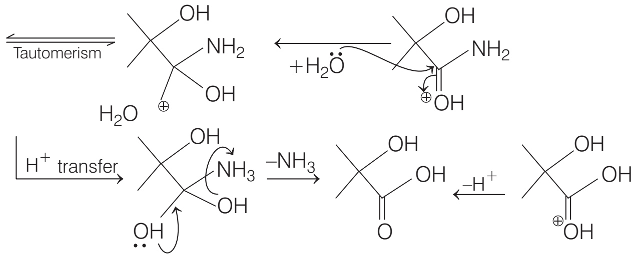
2-hydroxy-2-methyl propionitrile on acidic hydrolysis gives 2-hydroxy-2-methylpropionic acid.



2-hydroxy-2-methyl propionitrile 2-hydroxy-2-methyl propionic acid (B)

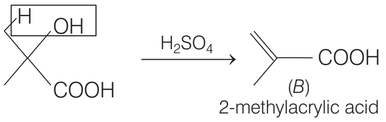
Mechanism



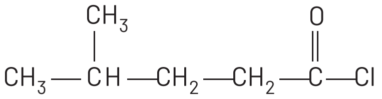


The last step of dehydration takes place in presence of H_2SO_4 to form 2-methylacrylic acid.

2-methylacrylic acid is the product (B).



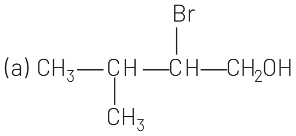
02 The major product of the following reaction is



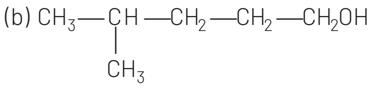
$CH_3-\underset{}{\overset{CH_3}{\overset{|}{CH}}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-Cl$

$\xrightarrow[\text{(iii) NaNO}_2\text{, HCl} \quad \text{(iv) H}_2\text{O}]{\text{(i) Alcoholic NH}_3 \quad \text{(ii) NaOH, Br}_2}$ Major product

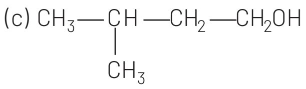
[2021, 27 Aug Shift-I]

(a) 

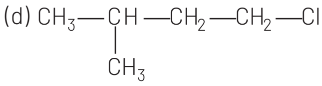
$CH_3-\underset{CH_3}{\underset{|}{CH}}-\overset{Br}{\overset{|}{CH}}-CH_2OH$

(b) 

$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_2-CH_2OH$

(c) 

$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_2OH$

(d) 

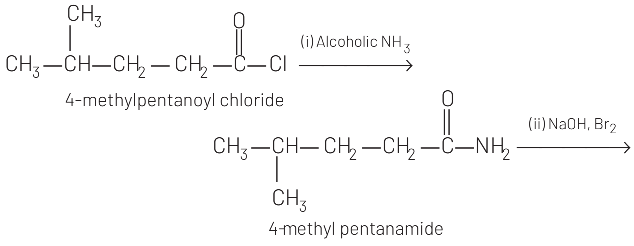
$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_2-Cl$

Ans. ***(c)***

In first step, ammonia reacts with ethanoyl chloride to give ethanamide and HCl. In the second step degradation of amide takes place that is known as Hoffmann's bromamide degradation reaction.

The third step is diazotisation, where an unstable diazonium salt is obtained, which further gives alcohol as a major product and alkene and alkyl halides.

The complete reaction is

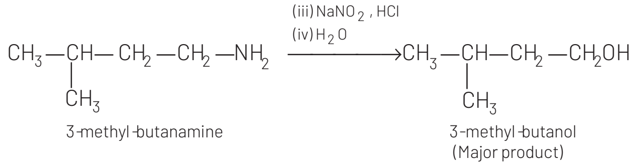


$CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{\text{(i) Alcoholic NH}_3}$

4-methylpentanoyl chloride

$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{\text{(ii) NaOH, Br}_2}$

4-methyl pentanamide



$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_2-NH_2 \xrightarrow{\text{(iii) NaNO}_2\text{, HCl} \quad \text{(iv) H}_2\text{O}} CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_2OH$

3-methyl-butanamine

3-methyl-butanol (Major product)

03 Which of the following is not a correct statement for primary aliphatic amines? **[2021, 27 Aug Shift-I]**

(a) The intermolecular association in primary amines is less than the intermolecular association in secondary amines.

(b) Primary amines on treating with nitrous acid solution form corresponding alcohols except methyl amine.

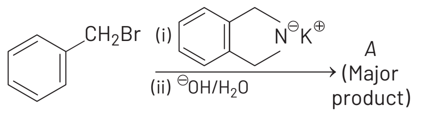
(c) Primary amines are less basic than the secondary amines.

(d) Primary amines can be prepared by the gabriel phthalimide synthesis.

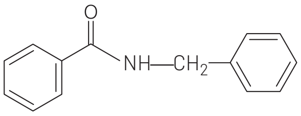
Ans. ***(a)***

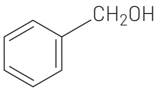
The intermolecular association is more in primary amines than in secondary amines as there is only one hydrogen atom available for formation of hydrogen bond in secondary amines, while primary amines has two hydrogen atoms. So, statement (a) is not correct.

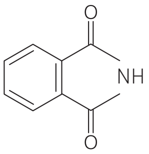
04 What is A in the following reaction?

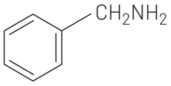


[2021, 27 July Shift-II]

(a) 

(b) 

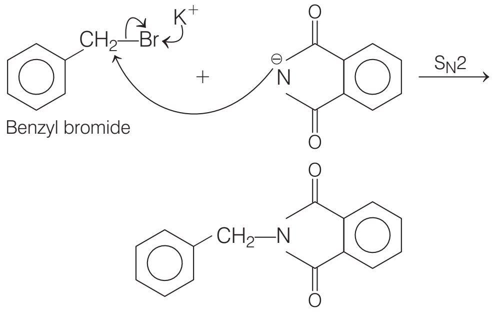
(c) 

(d) 

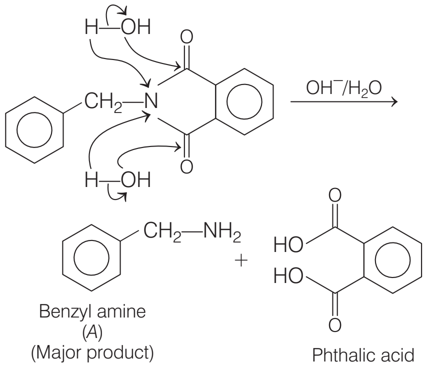
Ans. ***(d)***

Complete reaction is as follows :

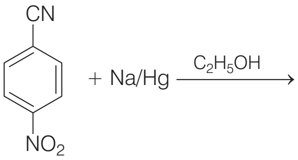
(i) Removal of Br^- and formation of C—N bond *via* S_N2 mechanism.

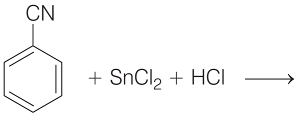


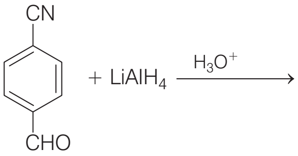
(ii) Hydrolysis process in basic medium Addition of OH^- ions for formation of phthalic acid and addition of H^+ ions for formation of benzyl amine.

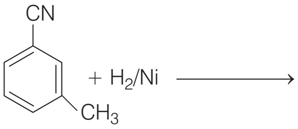


05 Which one of the products of the following reactions does not react with Hinsberg reagent to form sulphonamide? **[2021, 25 July Shift-I]**

(a) 

(b) 

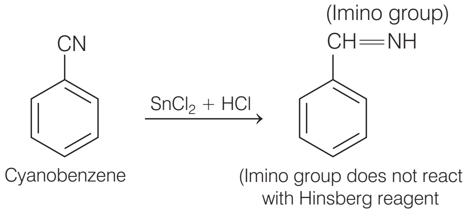
(c) 

(d) 

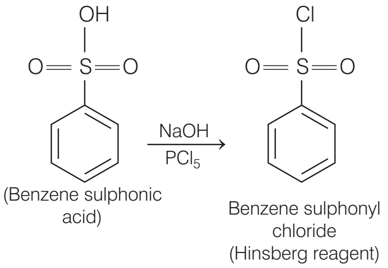
Ans. ***(b)***

Hinsberg reaction is a test for the detection of primary, secondary and tertiary amines. In this test, the amine is shaken well with Hinsberg reagent in the presence of aqueous alkali.

A reagent containing an aqueous sodium hydroxide solution and benzene sulphonyl chloride is added to a substrate. In reaction (b), imino group formed does not react with Hinsberg reagent.



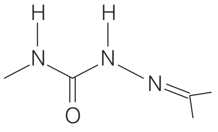
Product formed in all other reactions is a primary amine so, it gives Hinsberg reagent.



06 The number of nitrogen atoms in a semicarbazone molecule of acetone is .... **[2021, 20 July Shift-I]**

Ans. ***(3)***

Three nitrogen atoms are present as per structure below



Semicarbazone molecule of acetone

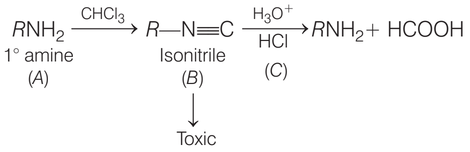
07 Compound *A* is converted to *B* on reaction with $CHCl_3$ and KOH. The compound *B* is toxic and can be decomposed by *C*. *A*, *B* and *C* respectively are **[2021, 20 July Shift-I]**

(a) primary amine, nitrile compound, conc. HCl
(b) secondary amine, isonitrile compound, conc. NaOH
(c) primary amine, isonitrile compound, conc. HCl
(d) secondary amine, nitrile compound, conc. NaOH

Ans. ***(c)***

Primary amine reacts in presence of chloroform gives isonitrile which is toxic in nature which further reacts in presence of HCl/H_3O^+ to give primary amine and acid.

Chemical reaction is as follows



$$\underset{\substack{1^\circ \text{ amine}\\(A)}}{RNH_2} \xrightarrow{CHCl_3} \underset{\substack{\text{Isonitrile}\\(B)\\\downarrow\\\text{Toxic}}}{R—N\equiv C} \xrightarrow[\substack{HCl\\(C)}]{H_3O^+} RNH_2 + HCOOH$$

Hence, *A*-primary amine, *B*-isonitrile compound and *C*-conc. HCl.

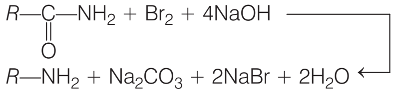
08 In the reaction of hypobromite with amide, the carbonyl carbon is lost as **[2021, 18 March Shift-II]**

(a) CO_3^{2-} (b) HCO_3^-
(c) CO_2 (d) CO

Ans. ***(a)***

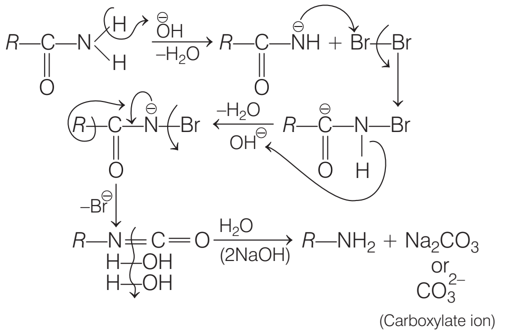
Hypobromite transforms the primary amide to carbonic acid which further loses carbonyl carbon as CO_3^{2-}, yielding the amine product.

Chemical reaction is as follows



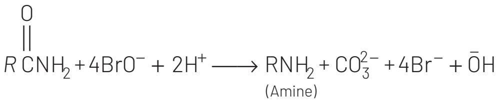
$$R—\underset{\underset{O}{\|}}{C}—NH_2 + Br_2 + 4NaOH \longrightarrow R—NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

Mechanism



Thus, the carbonyl carbon is lost as CO_3^{2-} in the given reaction.

The complete reaction in ionic form looks like.



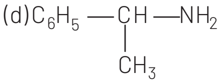
$$R\overset{\overset{O}{\|}}{C}NH_2 + 4BrO^- + 2H^+ \longrightarrow \underset{\text{(Amine)}}{RNH_2} + CO_3^{2-} + 4Br^- + \bar{O}H$$

09 An organic compound "*A*" on treatment with benzene sulphonyl chloride gives compound *B*. *B* is soluble in dil. NaOH solution. Compound *A* is **[2021, 18 March Shift-II]**

(a) $C_6H_5 — N —(CH_3)_2$

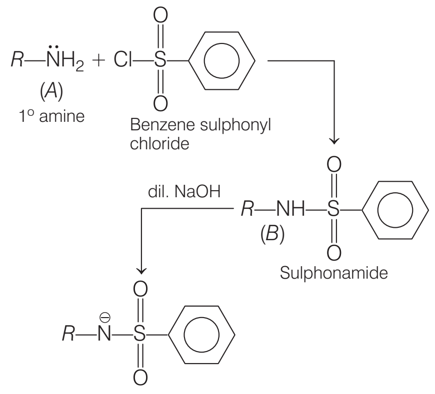
(b) $C_6H_5 —NHCH_2CH_3$

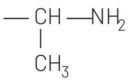
(c) $C_6H_5 —CH_2NHCH_3$

(d)  $C_6H_5 — \underset{\underset{CH_3}{|}}{CH} — NH_2$

Ans. ***(d)***

Hinsberg reagent (benzene sulphonyl chloride) with 1º amine gives sulphonamide product i.e. N-ethylbenzene sulphonamide and it is soluble in dil. NaOH.



Hence, *A* is 1° amine i.e.  $C_6H_5 — \underset{\underset{CH_3}{|}}{CH} — NH_2$

10 Primary, secondary and tertiary amines can be separated using **[2021, 17 March Shift-II]**

(a) *para*-toluene sulphonyl chloride

(b) chloroform and KOH

(c) benzene sulphonic acid

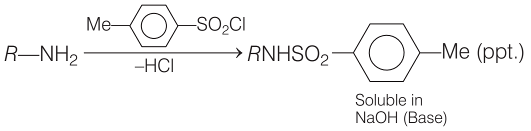
(d) acetyl amide

Ans. ***(a)***

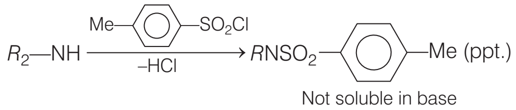
Primary, secondary and tertiary amines can be separated using *para*-toluene sulphonyl chloride. This test is known as Hinsberg test.

Reaction involved are as follows:

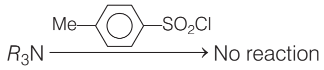
Primary (1°) amine Primary amines react with *para* toluene sulphonyl chloride to form a precipitate that is soluble in NaOH.



Secondary (2°) amine Secondary amines reacts with *para* toluene sulphonyl chloride to give a precipitate that is insoluble in NaOH.



Tertiary (3°) amine Tertiary amines do not react with *para* toluene.



11 Which of the following is least basic? **[2021, 16 March Shift-II]**

(a) $(CH_3CO)\ddot{N}HC_2H_5$

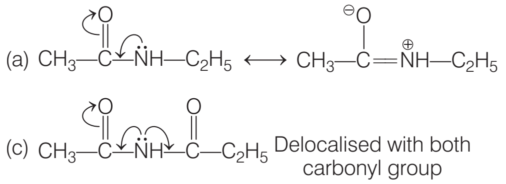
(b) $(C_2H_5)_3\ddot{N}$

(c) $(CH_3CO)_2\ddot{N}H$

(d) $(C_2H_5)_2\ddot{N}H$

Ans. ***(c)***

Basic nature is directly proportional to electron releasing tendency. If lone pair is delocalised, electron density decreases and basic strength decreases.



So, there is delocalisation of electron in both options (a) and (c). But it option (c) there is delocalisation of electron with both carbonyl group. Hence, it is weakest base.

There is a subtle interplay of the inductive effect, solvation effect and steric hinderance of the alkyl group, which decides the basic strength of alkyl amines in the aqueous state. The order of basic strength in case of ethyl substituted amines in aqueous solution is as follows

$$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$$

$\therefore (C_2H_5)_2\ddot{N}H$ is strong base.

12 Ammonolysis of alkyl halides followed by the treatment with NaOH solution can be used to prepare primary, secondary and tertiary amines. The purpose of NaOH in the reaction is **[2021, 16 March Shift-II]**

(a) to remove basic impurities

(b) to activate NH_3 used in the reaction

(c) to remove acidic impurities

(d) to increase the reactivity of alkyl halide

Ans. ***(c)***

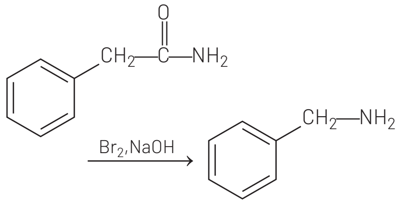
Ammonolysis of alkyl halides

$$R\text{–}X \xrightarrow[-HX]{NH_3} R\text{—}NH_2 \xrightarrow[-HX]{R\text{—}X} R_2NH \xrightarrow[-HX]{R\text{—}X} R_3N \xrightarrow{RX} R_4\overset{\oplus}{N}\overset{\ominus}{X}$$

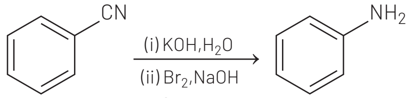
During the reaction HX (acid) is formed. Hence, we use NaOH to remove this acidic impurities.

13 Which of the following reaction does not involve Hoffmann bromamide degradation? **[2021, 16 March Shift-I]**

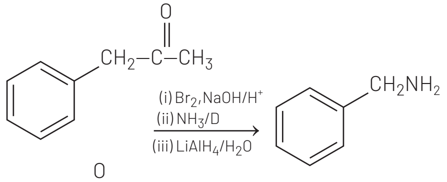
(a)



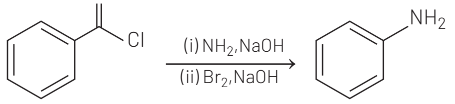
(b)



(c)

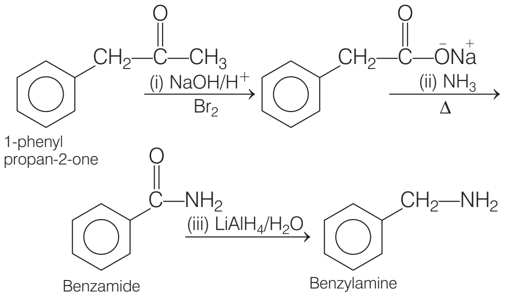


(d)

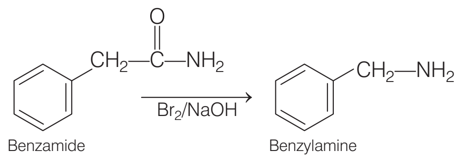


Ans. ***(c)***

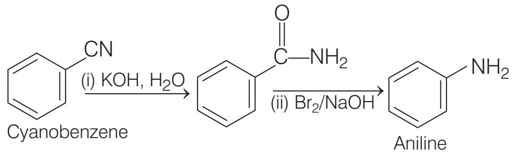
Methyl ketone gives haloform reaction to form carboxylic acid salt which on heating with NH_3 forms amide. Amide is reduced to amine by $LiAlH_4$.



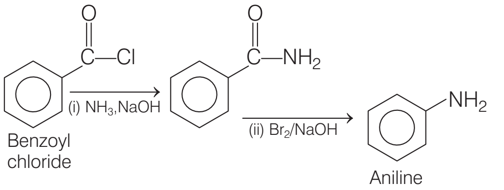
(a) Benzamide undergoes Hofmann bromamide degradation when treated with bromine and aqueous sodium hydroxide, to produces benzylamine.



(b) Benzene nitrile undergoes alkaline hydrolysis to form acidamide which further give Hofmann bromamide degradation.

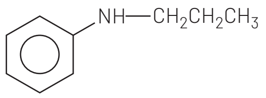


(d) Acid chloride undergoes nucleophilic substitution with NH_3 to form acid amide. Acid amide undergoes Hoffmann bromamide degradation.



14 An amine on reaction with benzene sulphonyl chloride produces a compound insoluble in alkaline solution. This amine can be prepared by ammonolysis of ethyl chloride. The correct structure of amine is **[2021, 26 Feb Shift-I]**

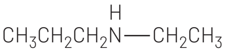
(a)



(b) $CH_3CH_2NH_2$

(c) $CH_3CH_2CH_2NHCH_3$

(d)



$CH_3CH_2CH_2\overset{H}{N}\text{—}CH_2CH_3$

Ans. ***(d)***

The amine on reaction with benzene sulphonyl chloride (Heisenberg reagent) produces a compound insoluble in alkali. It indicates the amine is a 2° amine. i.e. all options are possible except option (b) which is a 1° amine ($CH_3CH_2NH_2$).

As this 2° amine can be prepared by ammonolysis of ethyl chloride, the 2°-amine should have at least one ethyl (C_2H_5) group.

(a) $Ph\text{—}NH\text{—}CH_2CH_2CH_3$ does not have ethyl group.

(c) $CH_3CH_2CH_2\text{—}NH\text{—}CH_3$ does not have ethyl group.

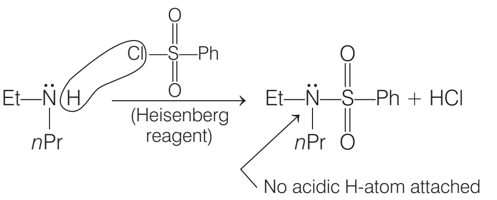
(d) $CH_3CH_2CH_2\text{—}NH\text{—}CH_2CH_3$ has one ethyl group.

So, option (d) is the correct answer.

Preparation $CH_3CH_2CH_2\text{—}NH\text{—}CH_2CH_3$ by ammonolysis of CH_3CH_2Cl

$$\underset{\substack{\text{Ethyl}\\\text{chloride}}}{CH_3CH_2Cl} \xrightarrow[-HCl]{NH_3} \underset{\substack{\text{Ethanamine}\\(1°)}}{CH_3CH_2\text{—}NH_2} \xrightarrow[(n\text{-propyl chloride})]{CH_3CH_2Cl} \underset{\substack{\text{1-(N-ethyl)-propanamine}\\(2°)}}{CH_3CH_2\text{—}NH\text{—}CH_2CH_2CH_3}$$

Heisenberg test of $CH_3CH_2\text{—}NH\text{—}CH_2CH_2CH_3$ or $Et\text{—}NH\text{—}n\text{Pr}$



No acidic H-atom attached with the nitrogen atom, hence, it is insoluble in alkali.

15 The most appropriate reagent for conversion of C_2H_5CN into $CH_3CH_2CH_2NH_2$ is **[2020, 5 Sep Shift-I]**

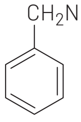
(a) $Na(CN)BH_3$ (b) $LiAlH_4$ (c) $NaBH_4$ (d) CaH_2

Ans. ***(b)***

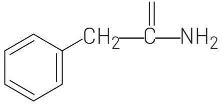
For the conversion of C_2H_5CN into $CH_3CH_2CH_2NH_2$, strong reducing agent is required among the given reducing agent. Strong reducing agent is $LiAlH_4$. It is the most appropriate reagent for this reduction.

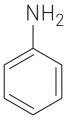
$$C_2H_5CN \xrightarrow{LiAlH_4} CH_3CH_2CH_2NH_2$$

16 Which of the following compounds can be prepared in good yield by Gabriel phthalimide synthesis? **[2020, 6 Sep Shift-II]**

(a) 

(b) $CH_3—CH_2—NHCH_3$

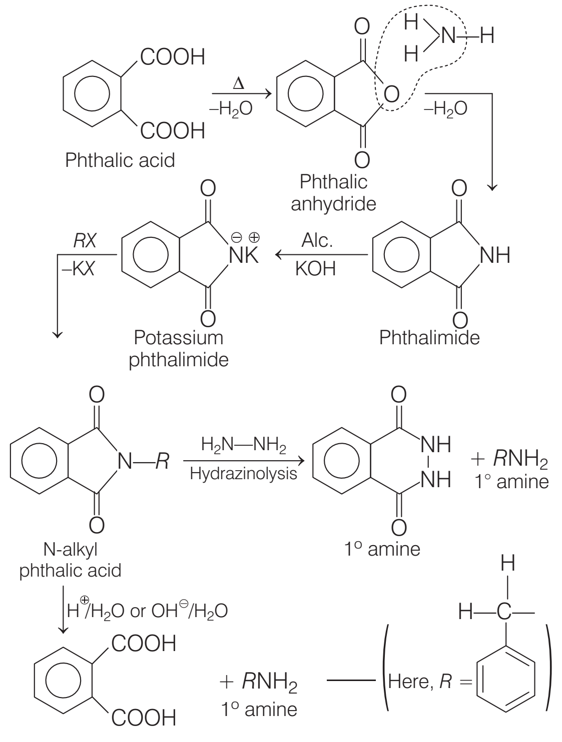
(c) 

(d) 

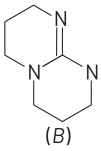
Ans. ***(a)***

Gabriel phthalimide synthesis is used for the preparation of 1° aliphatic amine and 1° aromatic amine.

Phthalimide on treatment with ethanolic KOH forms potassium salt of phthalimide which on heating with *RX* followed by either alkaline hydrolysis or hydrazinolysis with hydrazine $(H_2N \cdot NH_2)$ produces the corresponding 1° amine. 1° aromatic amine (except those containing EWG at *o*-and *p*-positions, e.g., $—NO_2$ group cannot be synthesised by this method because Ar*X* does not urdergo S_N reaction with anion formed by phthalimide.



17 The increasing order of pK_b for the following compounds will be :

$NH_2—CH—NH$, (*A*)


(*B*)
$CH_3—NH—CH_3$ (*C*)

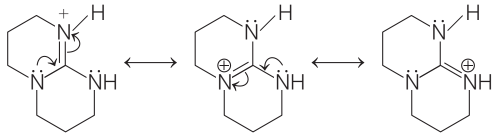
[2020, 7 Jan Shift-I]

(a) (*B*)<(*C*)<(*A*) (b) (*C*)<(*A*)<(*B*)

(c) (*A*)<(*B*)<(*C*) (d) (*B*)<(*A*)<(*C*)

Ans. ***(d)***

(*B*) is most basic because of high resonance stabilisation of its conjugate acid.



Among rest two compounds, $NH_2—CH=\ddot{N}H(A)$ has higher basicity than $CH_3—NH—CH_3\,(C)$ because conjugate acid of (*B*) is resonance stabilised but conjugate acid of (*C*) is not resonance stabilised at all.

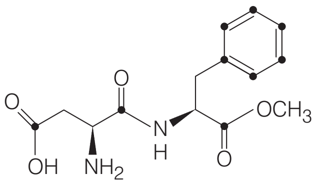
$$\ddot{N}H_2—CH=\overset{\oplus}{N}H_2 \longleftrightarrow \overset{\oplus}{N}H_2—CH=\ddot{N}H_2$$

Hence, the correct order of basicity of the given compounds is, $B > A > C$. Stronger is the base, smaller will be its pK_b value. Thus, the increasing order of pK_b values is $B < A < C$.

18 The number of sp^2-hybridised carbons present in "aspartame" is .... **[2020, 7 Jan Shift-II]**

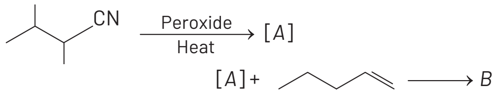
Ans. ***(9)***

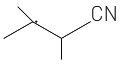
Structure of aspartame :

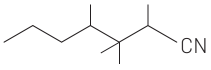


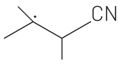
The 9 carbon atoms highlighted by the dark circle are sp^2-hybridised.

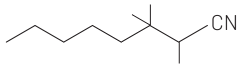
19 The major products *A* and *B* in the following reactions are : **[2020, 8 Jan Shift-I]**

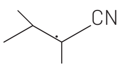


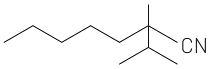
(a) $A =$ 

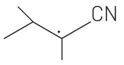
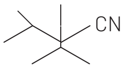
and $B =$ 

(b) $A =$ 

and $B =$ 

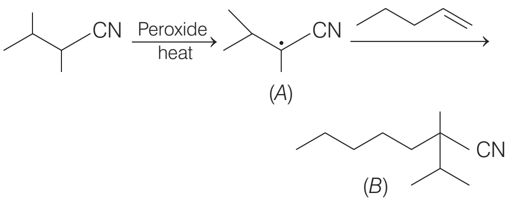
(c) $A =$ 

and $B =$ 

(d) $A =$  and $B =$ 

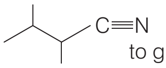
Ans. *(c)*

The reaction is given as follows :

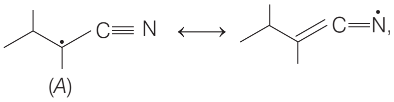


It can be proceed as :

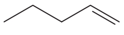
Peroxide on heating give radicals which abstract hydrogen from

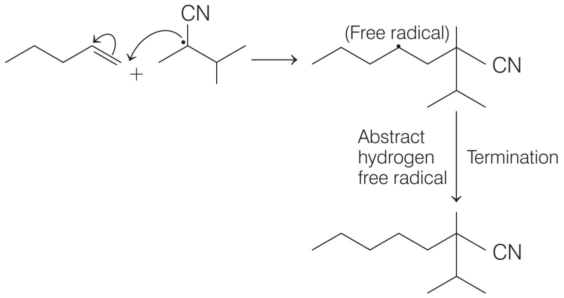


to give (*A*)



'*A*'which on addition to

 (Anti-Markownikoff's)



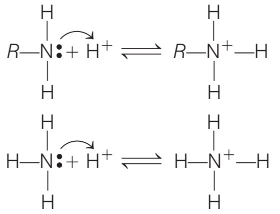
20 In the following compounds, the decreasing order of basic strength will be **[2019, 8 April Shift-I]**

(a) $C_2H_5NH_2 > NH_3 > (C_2H_5)_2NH$ (b) $(C_2H_5)_2NH > NH_3 > C_2H_5NH_2$

(c) $(C_2H_5)_2NH > C_2H_5NH_2 > NH_3$ (d) $NH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$

Ans. *(c)*

Basic strength can be compared by the reaction of an alkanamine and ammonia with proton.



$$R-\ddot{N}H_2 + H^+ \rightleftharpoons R-NH_3^+$$

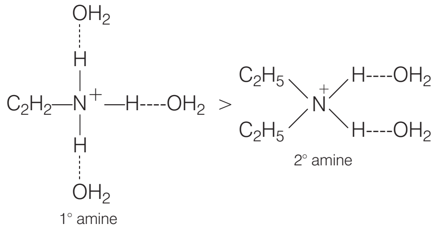
$$H-\ddot{N}H_2 + H^+ \rightleftharpoons H-NH_3^+$$

Basicity of an amine in aqueous solution depends upon the solubility of ammonium cation formed by accepting proton from water. The stability of ammonium cation depends upon the following factors.

(a) $+I$-effect (b) Steric effect (c) Solvation effect

In first case, on increasing the size of alkyl group $+I$ effect increases and the positive charge of ammonium cation gets dispersed more easily, Therefore, order of basicity is 2º amine > 1º amine > ammonia.

In second case, substituted ammonium cation is also stabilised by solvation with water molecules. Greater the size of ion, lesser will be the solvation and less stabilised is the ion.



Considering both steric and solvation effect, it can be concluded that greater the number of H-atoms on the N-atom, greater will be the H-bonding and hence more stable is the ammonium cation. But in case of $-C_2H_5$ group, $+I$-effect predominates over H-bonding. Therefore, order is 2° amine > 1° amine > ammonia, i.e. $(C_2H_5)_2NH > C_2H_5NH_2 > NH_3$.

21 Which of the following amines can be prepared by Gabriel phthalimide reaction? **[2019, 8 April Shift-I]**

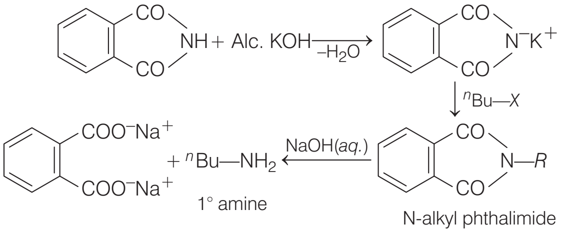
(a) *n* - butylamine (b) triethylamine

(c) *t*-butylamine (d) *neo* -pentylamine

Ans. *(a)*

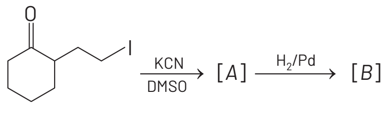
n- butylamine ($CH_3CH_2CH_2CH_2NH_2$) can be prepared by Gabriel phthalimide reaction. This method produces only primary amines without the traces of secondary or tertiary amines.

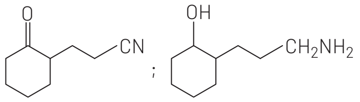
In this method, phthalimide is treated with ethanolic KOH, it forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis forms corresponding primary amines.

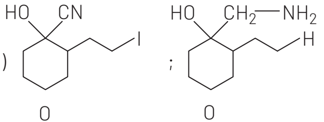


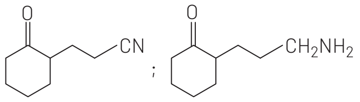
Triethylamine, *t*-butylamine and *neo*-pentylamine cannot be prepared by Gabriel phthalimide reaction.

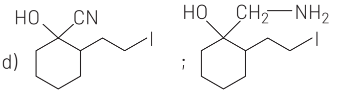
22 The major products *A* and *B* for the following reactions are, respectively **[2019, 9 April Shift-II]**



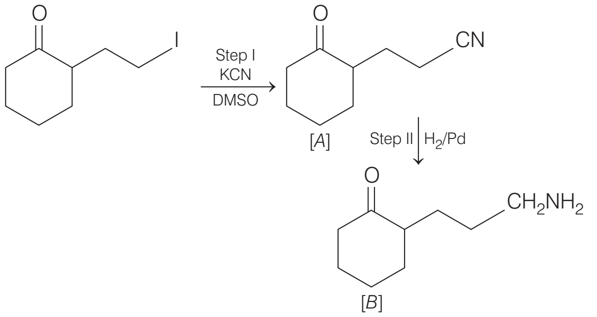
(a) 

(b) 

(c) 

(d) 

Ans. ***(c)***



Step I involves the nucleophilic substitution reaction in which I (Iodine) is substituted by —CN group.

In step II, H_2/Pd reagent is used for reduction process. Here, —CN group reduces itself to —CH_2NH_2.

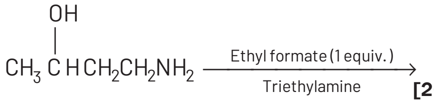
23 Hinsberg's reagent is **[2019, 9 April Shift-II]**

(a) $SOCl_2$ (b) C_6H_5COCl (c) $C_6H_5SO_2Cl$ (d) $(COCl)_2$

Ans. ***(c)***

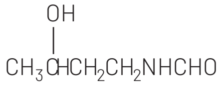
Hinsberg's reagent is $C_6H_5SO_2Cl$ (benzene sulphonyl chloride). This reagent is used to distinguish between primary, secondary and tertiary amines.

24 The major product of the following reaction is



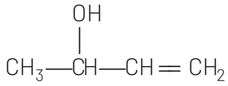
$$CH_3\overset{OH}{\overset{|}{C}}HCH_2CH_2NH_2 \xrightarrow[\text{Triethylamine}]{\text{Ethyl formate (1 equiv.)}}$$

[2019, 10 April Shift-I]

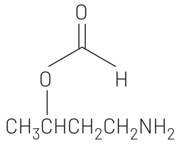
(a) 

$CH_3\overset{OH}{\overset{|}{C}}HCH_2CH_2NHCHO$

(b) $CH_3CH{=}CH{—}CH_2NH_2$

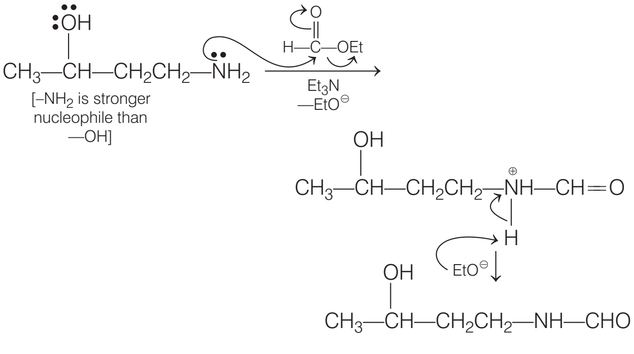
(c) 

$CH_3{—}\overset{OH}{\overset{|}{C}H}{—}CH{=}CH_2$

(d) 

Ans. ***(a)***

The mechanism of the given reaction is as follows :



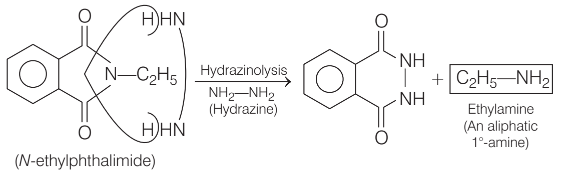
The basic mechanism of the reaction is acyl S_N2 because the nucleophile, $CH_3(OH)CH_2CH_2NH_2$ attacks the sp^2 carbon of the ester $(H—CO_2Et)$ and gets substituted.

25 Ethylamine $(C_2H_5NH_2)$ can be obtained from N-ethylphthalimide on treatment with **[2019, 10 April Shift-I]**

(a) $NaBH_4$ (b) NH_2NH_2
(c) H_2O (d) CaH_2

Ans. ***(b)***

The reaction for the production of ethylamine from *N*-ethylphthalimide can be takes place as follows:



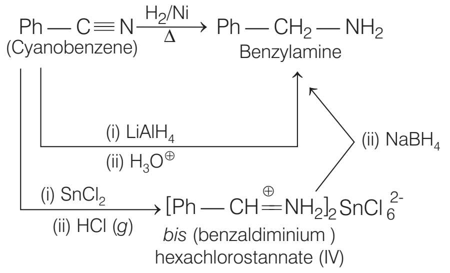
This reaction is the second step of Gabriel phthalimide synthesis for the preparation of aliphatic 1°-amines and amino acid. In this step concentrated alkali can also be used in place of hydrazine.

26 Which of the following is not a correct method of the preparation of benzylamine from cyanobenzene? **[2019, 10 April Shift-II]**

(a) H_2 / Ni
(b) (i) HCl/H_2O (ii) $NaBH_4$
(c) (i) $LiAlH_4$ (ii) H_3O^+
(d) (i) $SnCl_2$ + HCl(gas) (ii) $NaBH_4$

Ans. ***(b)***

The preparation of benzylamine from cyanobenzene using given reagents are as follows :



$$\underset{\text{}}{PhCN} \xrightarrow[-NH_4Cl]{HCl,\,H_2O} \underset{\text{Benzoic acid}}{PhCOOH} \xrightarrow{NaBH_4} \underset{\text{Benzyl alcohol}}{PhCH_2OH}$$

Thus, option (b) is incorrect.

27 The major product of following reaction is

$$R{—}C\equiv N \xrightarrow[\text{(ii)}\,H_2O]{\text{(i)}\,AlH(i\text{-}Bu)_2} ?$$

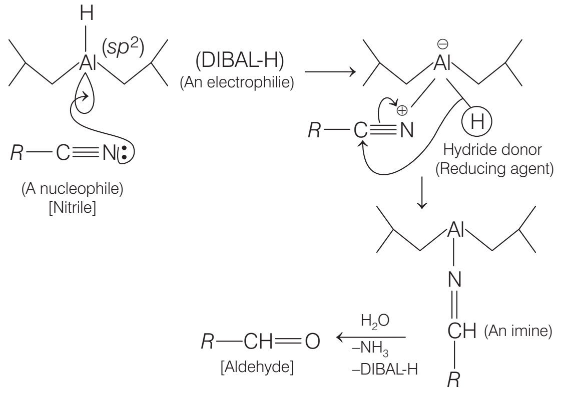
[2019, 9 Jan Shift-I]

(a) *R*CHO (b) *R*$CONH_2$
(c) *R*COOH (d) *R*CH_2NH_2

Ans. ***(a)***

Key Idea DIBAL-H is diisobutyl aluminium hydride, $[(CH_3)_2CHCH_2]_2AlH$. It is a selective reducing agent. It reduces carboxylic acids, carboxylic acid derivatives and nitriles into aldehydes. It is an electrophilic reducing agent.

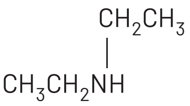
The mechanism of the reaction is as follows:



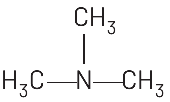
So, $R-\underset{\underset{\displaystyle O}{\|}}{C}H$ is the correct answer.

28 The increasing basicity order of the following compounds is

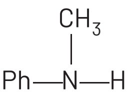
(A) $CH_3CH_2NH_2$

(B) 

$CH_3CH_2\overset{\overset{\displaystyle CH_2CH_3}{|}}{N}H$

(C) 

$H_3C—\overset{\overset{\displaystyle CH_3}{|}}{N}—CH_3$

(D) 

$Ph—\overset{\overset{\displaystyle CH_3}{|}}{N}—H$

[2019, 9 Jan Shift-II]

(a) $(D) < (C) < (B) < (A)$
(b) $(A) < (B) < (C) < (D)$
(c) $(A) < (B) < (D) < (C)$
(d) $(D) < (C) < (A) < (B)$

Ans. *(d)*

If we consider Lewis basicity (basicity in aprotic solvents or in vapour phase), the order of basicity will be.

$$\underbrace{D}_{2^\circ} < \underbrace{A}_{1^\circ} < \underbrace{B}_{2^\circ} < \underbrace{C}_{3^\circ}$$

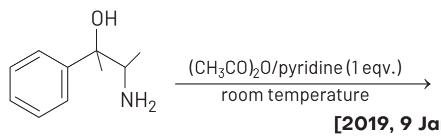
But, this order does not match with the options given. So, it has been asked on basicity of the amines in aqueous solution. When no phase is given, then basicity of amine is considered in aqueous solution as they are liquids.

In aqueous solution, basicity of 2°-amines (aliphatic) is maximum because, of the thermodynamic stability of its conjugate acid.

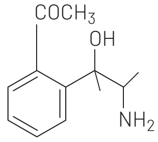
$$\underset{(B)}{Et_2NH} + H_2O \rightleftharpoons \underset{\text{Conjugate acid}}{Et_2\overset{\oplus}{N}H_2} + \overset{\ominus}{O}H$$

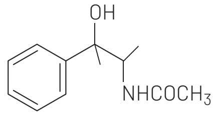
$Et_2\overset{\oplus}{N}H_2$ is a sterically symmetric tetrahedral ion as it contains equal number (two) of bulkier Et-group and small size H-atoms. Here, two H-atoms give additional stability through hydrogen bonding with H_2O (solvent) molecules.

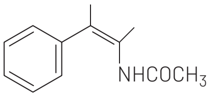
29 The major product obtained in the following reaction is

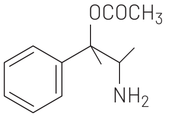


[2019, 9 Jan Shift-II]

(a) 

(b) 

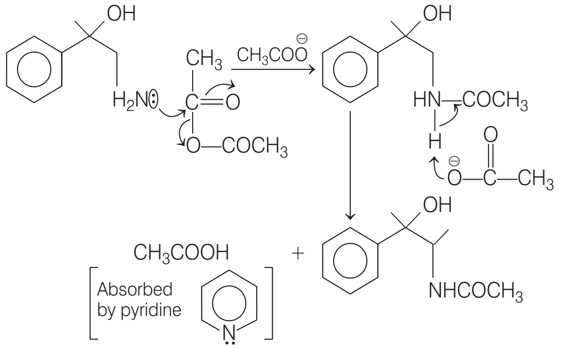
(c) 

(d) 

Ans. *(b)*

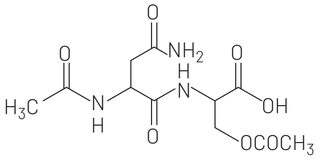
Rate of acetylation $—NH_2 > —OH$ because N-bases are stronger than O-bases. Size of N-atom is larger than O-atom and at the same time, N atom is less electronegative than O-atom.

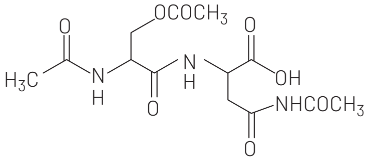
So, N-atom of the $—\ddot{N}H_2$ group can donate its lone pair of electrons (Lewis basicity) more easily than that of O atom of the $—\ddot{O}H$ group.

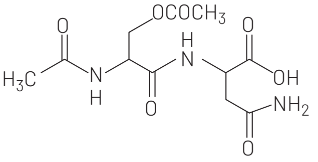


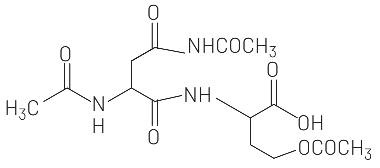
30 The correct structure of product '*P*' in the following reaction is Asn – Ser + $\underset{\text{(Excess)}}{(CH_3CO)_2O} \xrightarrow{NEt_3} P$

[2019, 10 Jan Shift-I]

(a) 

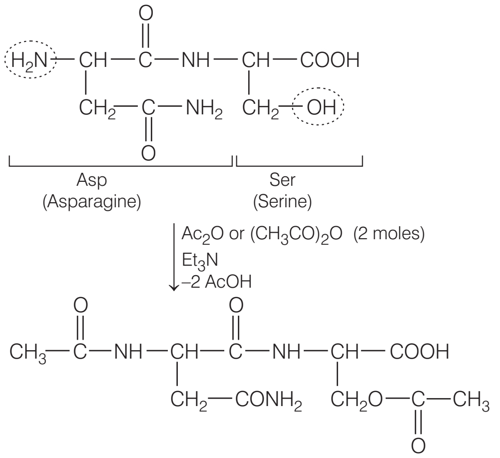
(b) 

(c) 

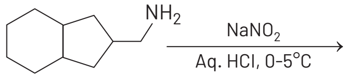
(d) 

Ans. ***(a)***

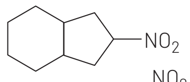
Acetylation by Ac_2O / Et_3N is possible with —NH_2 (1°-amine) and —OH(alcohol) groups only, but not with '—NH_2' part of $-\overset{O}{\overset{\|}{C}}-NH_2$ (amide) groups, because the *lp* of nitrogen in amide group is involved in resonance with >C=O part.

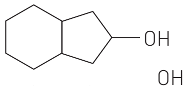


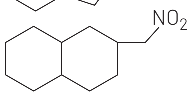
31 The major product formed in the reaction given below will be

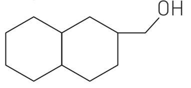


[2019, 10 Jan Shift-I]

(a) 

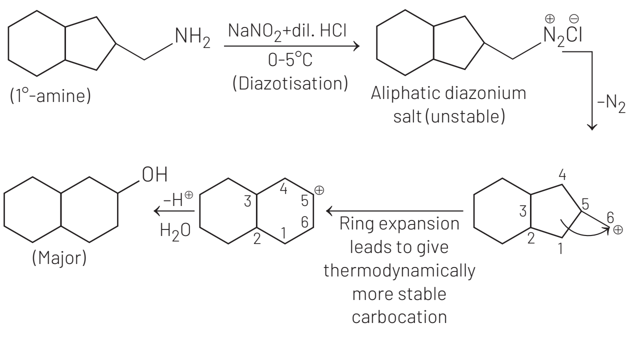
(b) 

(c) 

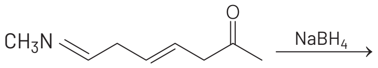
(d) 

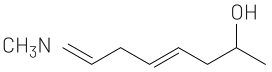
Ans. ***(*)***

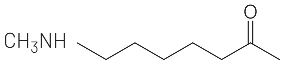
No option is the correct answer. Amines in presence of $NaNO_2$ + dil. HCl undergoes diazotisation. The diazotised product readily loses nitrogen gas with the formation of carbocation. The resulting carbocation rearranges itself to give the expanded ring.

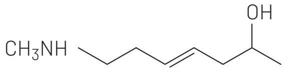


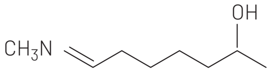
32 The major product of the following reaction is



(a) 

(b) 

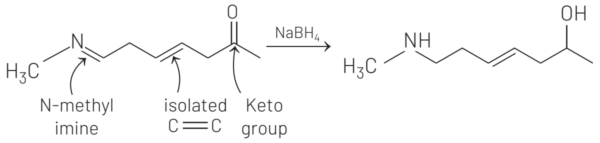
(c) 

(d) 

[2019, 10 Jan Shift-II]

Ans.*(c)*

$NaBH_4$ is a selective reducing agent. It can reduce >C=O group into alcohol, N-methyl imine group, Me—N == CH—into 2°-amine but cannot reduce an isolated C =C.

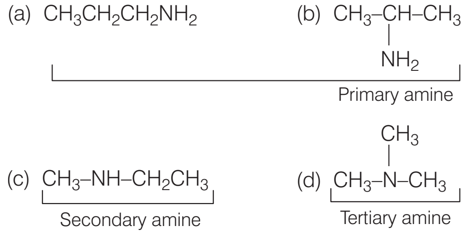


33 A compound '*X*' on treatment with Br_2 / NaOH, provided C_3H_9N, which gives positive carbylamine test. Compound '*X*' is **[2019, 11 Jan Shift-II]**

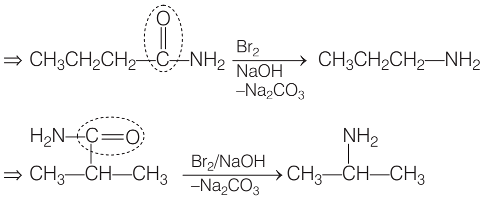
(a) $CH_3COCH_2NHCH_3$
(b) $CH_3CH_2CH_2CONH_2$
(c) $CH_3CON(CH_3)_2$
(d) $CH_3CH_2COCH_2NH_2$

Ans. ***(b)***

The molecular formula, C_3H_9N refers to four structural isomers of amines

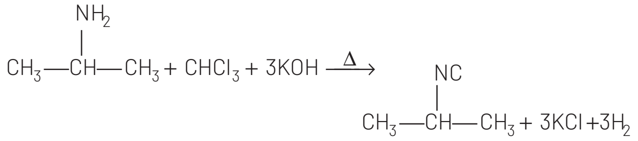


Here, only *a* and *b* (primary amines) can be prepared from their respective amides by Hoffmann bromamide (Br_2/NaOH) method and can give positive carbylamine test.



So, '*X*' can be $CH_3CH_2CH_2$—$CONH_2$ (a) or $CH_3CH(CONH_2)CH_3$ (b). Carbylamine test given by (a) and (b)

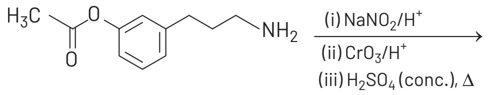
$$CH_3CH_2CH_2NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} CH_3(CH_2)_2NC + 3KCl + 3H_2$$



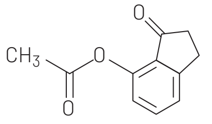
$$CH_3-\overset{NH_2}{\overset{|}{C}H}-CH_3 + CHCl_3 + 3KOH \xrightarrow{\Delta} CH_3-\overset{NC}{\overset{|}{C}H}-CH_3 + 3KCl + 3H_2$$

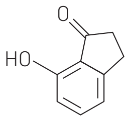
As (b) is not among the given options So, it is ruled out and compound (X) is $CH_3CH_2CH_2CONH_2$.

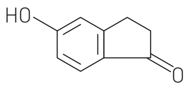
34 The major product of the following reaction is

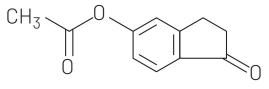


[JEE Main 2018]

(a)


(b)


(c)


(d)


Ans. ***(c)***

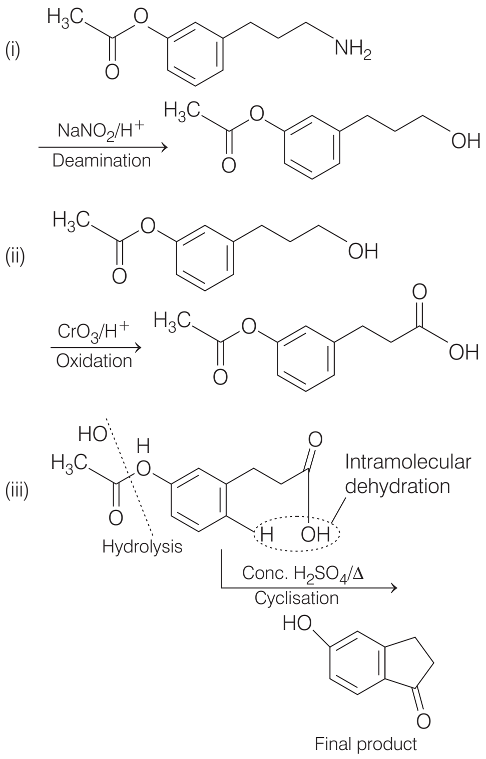
Key Idea The reaction involves:

A. Deamination in step (i)

B. Oxidation in step (ii)

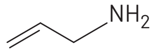
C. Hydroysis in step (iii)

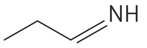
The complete pathway of reactions is as follows:

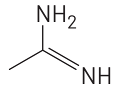


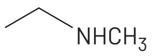
Thus, option (c) is the correct answer.

35 The increasing order of basicity of the following compounds is **[JEE Main 2018]**

I.


II.


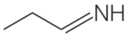
III.


IV.


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

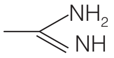
Ans. ***(d)***

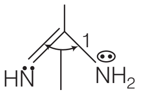
Among the given compounds the basic nature depends upon their tendency to donate electron pair.

Among the given compounds in  Nitrogen is sp^2-hybridised.

This marginally increases the electronegativity of nitrogen which in turn decreases the electron donation tendency of nitrogen.

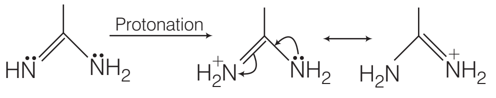
Thus making compound least basic.

Among the rest  is totally different from others as in this compound lone pair of one nitrogen are in conjugation with π bond i.e.

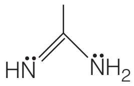


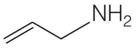
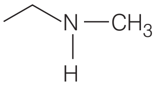
In conjugation

As a result of this conjugation the cation formed after protonation becomes resonance stabilised



Equivalent resonance

This equivalent resonance in cation makes  most basic among all.

Categorisation is very simple between rest two as  (primary amine) is less basic than  (secondary amine)

Hence, the correct order is

(II) < (I) < (IV) < (III)

i.e. option (c) is correct.

36 In the Hofmann-bromamide degradation reaction, the number of moles of NaOH and Br_2 used per mole of amine produced are **[JEE Main 2016]**

(a) four moles of NaOH and two moles of Br_2
(b) two moles of NaOH and two moles of Br_2
(c) four moles of NaOH and one mole of Br_2
(d) one mole of NaOH and one mole of Br_2

Ans. ***(c)***

Hofmann-bromamide degradation reaction is given as:

$$RCONH_2 + 4NaOH + Br_2 \longrightarrow \underset{(1^\circ\text{ amine})}{RNH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$

Hence, four moles of NaOH and one mole of Br_2 are used.

37 On heating an aliphatic primary amine with chloroform and ethanolic potassium hydroxide, the organic compound formed is **[JEE Main 2014]**

(a) an alkanol
(b) an alkanediol
(c) an alkyl cyanide
(d) an alkyl isocyanide

Ans. ***(d)***

Reaction of aliphatic primary amine with chloroform and ethanolic potassium hydroxide, leads to the formation of isocyanides/carbylamines. Thus, this reaction is called carbylamine reaction.

$$R\text{—}NH_2 + CHCl_3 + KOH \xrightarrow{\Delta} \underset{\text{Alkyl isocyanide}}{R\text{—}NC} + 3KCl + 3H_2O$$

38 Considering the basic strength of amines in aqueous solution, which one has the smallest pK_b value? **[JEE Main 2014]**

(a) $(CH_3)_2NH$ (b) CH_3NH_2
(c) $(CH_3)_3N$ (d) $C_6H_5NH_2$

Ans. ***(a)***

It is known that, $pK_b = -\log k_b$

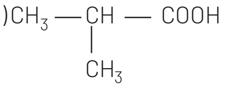
Thus, larger the value of k_b, smaller is the value of pK_b and hence, stronger is the base.

The order of basic strength of amines is as follows

$$(CH_3)_2\ddot{N}H > CH_3\ddot{N}H_2 (CH_3)_3\ddot{N} > C_6H_5\ddot{N}H_2$$

The basic strength of amines depends on the inductive effect as will as steric hinderance of alkyl groups. Hence, $(CH_3)_2\ddot{N}H$ [secondary amine] possess the smallest value of pK_b.

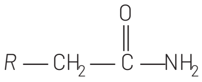
39 An organic compound A on reacting with NH_3 gives B. On heating B gives C. C in the presence of KOH reacts with Br_2 to give $CH_3CH_2NH_2$. A is **[JEE Main 2013]**

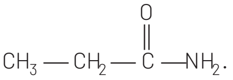
(a) 
$CH_3\text{—}\underset{\underset{CH_3}{|}}{CH}\text{—}COOH$
(b) $CH_3CH_2CH_2CH_2COOH$
(c) CH_3CH_2COOH (d) CH_3COOH

Ans. ***(c)***

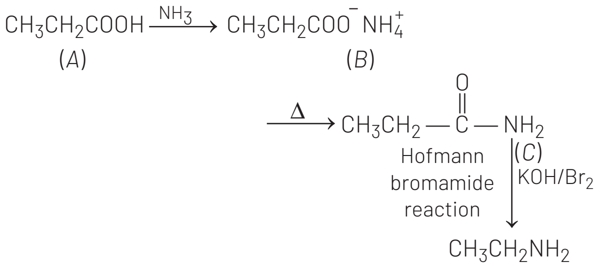
$$A \xrightarrow{NH_3} B \xrightarrow{\Delta} C \xrightarrow{KOH/Br_2} CH_3CH_2NH_2$$

The reaction of C with KOH/Br_2 to give amine is called Hofmann bromamide reaction. This reaction is give by acid amides only in which


$R\text{—}CH_2\text{—}\overset{\overset{O}{\|}}{C}\text{—}NH_2$ group undergoes rearrangement along with the loss of CO_2 molecule. Thus, the compound C must be acid amide with three carbon atoms. Hence, the compound C is


$CH_3\text{—}CH_2\text{—}\overset{\overset{O}{\|}}{C}\text{—}NH_2$.

Since, all the options shows that A is an acid and it forms acid amide on reaction with NH_3. Thus, acid must contain three carbon atoms. Hence, the compound A is CH_3CH_2COOH. The complete series of reaction can be represented as



40 A compound with molecular mass 180µ is acylated with CH_3COCl, to get a compound with molecular mass 390µ. The number of amino groups present per molecule of the former compound is **[JEE Main 2013]**

(a) 6 (b) 2 (c) 5 (d) 4

Ans. ***(c)***

During acetylation, one H atom with atomic mass 1 amu of —NH_2 group is replaced by an acetyl group CH_3CO [molecular mass = 434µ]. Thus,

$$\text{—}NH_2 + CH_3COCl \longrightarrow \text{—}NHCOCH_3 + HCl$$

The above equation suggests that, the acylation of each —NH_2 group increases the mass by 42µ [43 – 1]. If the molecular mass of the organic compound is 180µ while that of the acylated product is 390µ, then the increase in the mass due to acylation is given by

$$390 - 180 = 210\,\mu$$

Hence, the number of —NH_2 groups $= \dfrac{210\,\mu}{42\,\mu} = 5$

41 Which one of the following is the strongest base in aqueous solution ? **[AIEEE 2007]**

(a) Trimethylamine (b) Aniline
(c) Dimethylamine (d) Methylamine

Ans. ***(c)***

In aqueous solution, basicity order is

$$\underset{2^\circ}{\text{Dimethylamine}} > \underset{1^\circ}{\text{methylamine}} > \underset{3^\circ}{\text{trimethylamine}} > \text{aniline}$$

This order depends upon the inductive effect and steric hinderance of alkyl groups.

42 In the chemical reaction,

$CH_3CH_2NH_2 + CHCl_3 + 3KOH \longrightarrow (A) + (B) + 3H_2O$,

the compounds (A) and (B) are respectively **[AIEEE 2007]**

(a) C_2H_5CN and 3KCl
(b) $CH_3CH_2CONH_2$ and 3KCl
(c) C_2H_5NC and 3KCl
(d) C_2H_5NC and 3KCl

Ans. ***(c)***

$$\underset{(A)}{CH_3CH_2NH_2} + CHCl_3 + \underset{(alc)}{3KOH} \rightarrow \underset{(B)}{CH_3CH_2—N \overrightarrow{=} C} + 3KCl + 3H_2O$$

The above reaction is called carbylamine reaction in which isocyanides or carbylamines are produced.

43 Which one of the following methods is neither meant for the synthesis nor for separation of amines ? **[AIEEE 2005]**

(a) Curtius reaction
(b) Wurtz reaction
(c) Hofmann method
(d) Hinsberg method

Ans. ***(b)***

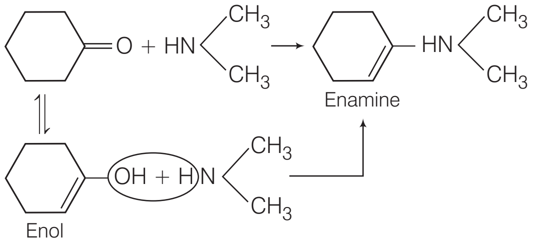
Wurtz reaction is used to prepare alkanes from alkyl halides.

$$2R—X + 2Na \xrightarrow{\text{Dry ether}} R—R + 2NaX$$

44 Reaction of cyclohexanone with dimethylamine in the presence of catalytic amount of an acid forms a compound. Water during the reaction is continuously removed. The compound formed is generally known as

(a) an amine
(b) an imine **[AIEEE 2005]**
(c) an enamine
(d) a Schiff 's base

Ans. ***(c)***



45 An organic compound having molecular mass 60 is found to contain C = 20%, H = 6.67% and N = 46.67% while rest is oxygen. On heating, it gives NH_3 alongwith a solid residue. The solid residue gives violet colour with alkaline copper sulphate solution. The compound is

(a) $CH_3CH_2CONH_2$
(b) $(NH_2)_2CO$ **[AIEEE 2005]**
(c) CH_3CONH_2
(d) CH_3NCO

Ans. ***(b)***

Element	Percentage	$\frac{\text{Percentage}}{\text{at. wt.}}$	Simple Ratio
C	20.0	$\frac{20.0}{12} = 1.66$	$\frac{1.66}{1.66} = 1$
H	6.67	$\frac{6.67}{1} = 6.67$	$\frac{6.67}{1.66} = 4$
N	46.67	$\frac{46.67}{14} = 3.33$	$\frac{3.33}{1.66} = 2$
O	26.66	$\frac{26.66}{16} = 1.66$	$\frac{1.66}{1.66} = 1$

Empirical formula = CH_4N_2O

Empirical formula weight = $12 + (4 \times 1) + (2 \times 14) + 16 = 60$

$$\therefore \quad n = \frac{\text{Mole formula weight}}{\text{Emp formula weight}} = \frac{60}{60} = 1$$

$\therefore$ Molecular formula = CH_4N_2O

Given compound gives biuret test, thus given compound is urea $(NH_2)_2CO$.

$$NH_2CONH_2 + HNHCONH_2 \xrightarrow{\Delta} \underset{\text{Biuret}}{NH_2CONHCONH_2} + NH_3$$

$$\Big\downarrow \text{ as } CuSO_4$$

Violet colour

46 The correct order of increasing basic nature for the bases NH_3, CH_3NH_2 and $(CH_3)_2NH$ is **[AIEEE 2003]**

(a) $CH_3NH_2 < NH_3 < (CH_3)_2NH$
(b) $(CH_3)_2NH < NH_3 < CH_3NH_2$
(c) $NH_3 < CH_3NH_2 < (CH_3)_2NH$
(d) $CH_3NH_2 < (CH_3)_2NH < NH_3$

Ans. ***(c)***

The basicity of an amine in aqueous solution primarily depends upon the stability of the ammonium cation or the conjugate acid formed by accepting the proton from water.

$$RNH_2 + H_2O \rightleftharpoons \underset{[\text{ammonium cation}]}{R\overset{+}{N}H_3} + OH^-$$

The stability of the ammonium cation depends upon

(i) $+I$ effect of alkyl groups
(ii) Extent of H-bonding with water molecules
(iii) Steric effects of the alkyl groups

On the basis of above factors, the basic strength of amine is as follows

$$(CH_3)_2NH > CH_3NH_2 > NH_3$$

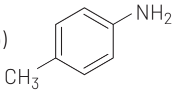
($+I$ effect of $—CH_3$ group predominates)

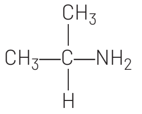
TOPIC 2

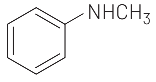
Aromatic Amines

47 Which one of the following gives the most stable diazonium salt ? **[2021, 01 Sep Shift-II]**

(a) $CH_3—CH_2—CH_2—NH_2$

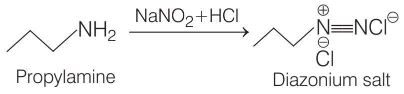
(b)


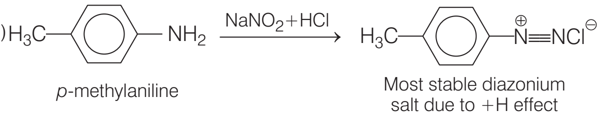
(c)

$$CH_3—\overset{CH_3}{\underset{H}{C}}—NH_2$$

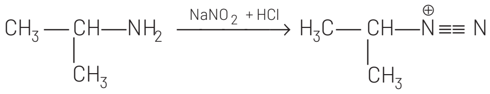
(d)


Ans. ***(b)***

Primary amines react with $NaNO_2$ and HCl to give diazonium salts.

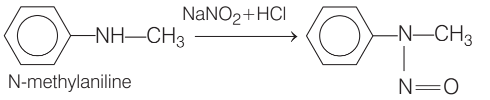
(a)


(b)


(c) 

$CH_3-\underset{CH_3}{CH}-NH_2 \xrightarrow{NaNO_2 + HCl} H_3C-\underset{CH_3}{CH}-\overset{\oplus}{N}\equiv N$

2-methylethanamine

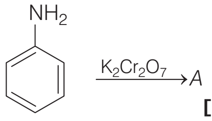
(d) 

N-alkyl nitroso amine

Diazonium salt is not formed rather N-alkylnitroso amine is formed as product.

∴ In option (b) the most stable diazonium salt is formed.

48 Identify *A* in the following reaction.

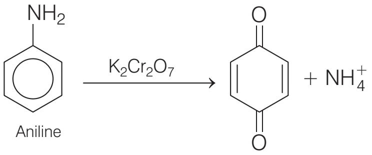


[2021, 01 Sep Shift-II]

Ans. *(a)*

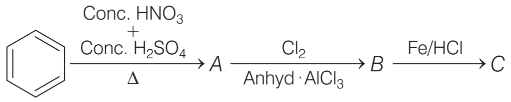
Aniline reacts with potassium dichromate ($K_2Cr_2O_7$) to form 1,4-benzoquinone as the product. The nascent oxygen produced from $K_2Cr_2O_7$ reacts with aniline to form 1,4-benzoquinone with the removal of NH_4^+ ion.

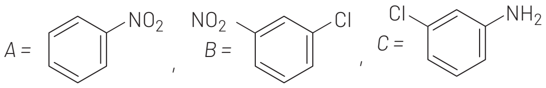
This reaction involves oxidation of aniline.

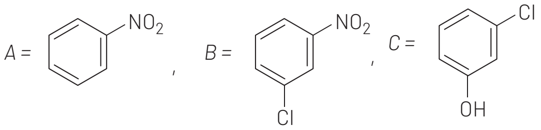


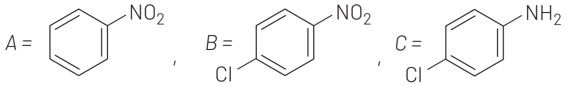
(A)
1,4-benzoquinone

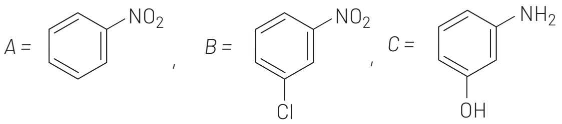
49 Identify correct *A*, *B* and *C* in the reaction sequence given below. **[2021, 31 Aug Shift-II]**



(a) 

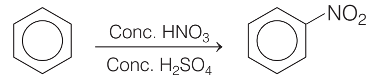
(b) 

(c) 

(d) 

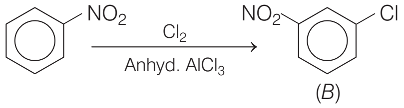
Ans. *(a)*

Benzene undergoes nitration on reaction with conc. HNO_3 and conc. H_2SO_4.

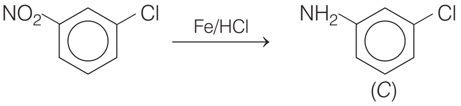


Benzene (A) Nitrobenzene

Nitrobenzene on reaction with Cl_2/ anhyd. $AlCl_3$ undergoes electrophilic substitution reaction to give 1-chloro-3-nitro benzene, which on reaction with Fe/HCl gives chloroaniline.

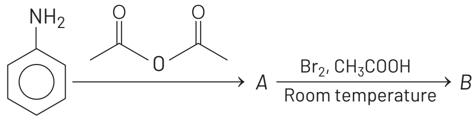


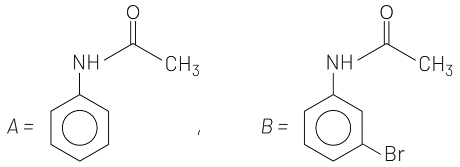
(B)
1-chloro-3-nitro benzene

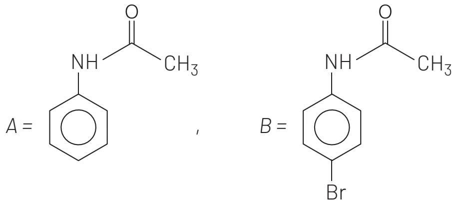


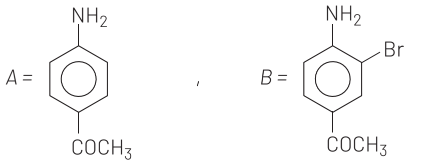
(C)
Chloroaniline

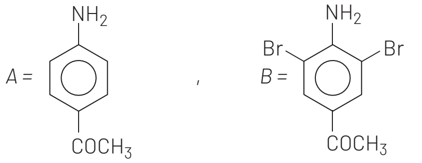
50 The major products *A* and *B* formed in the following reaction sequence are **[2021, 31 Aug Shift-II]**



(a) 

(b) 

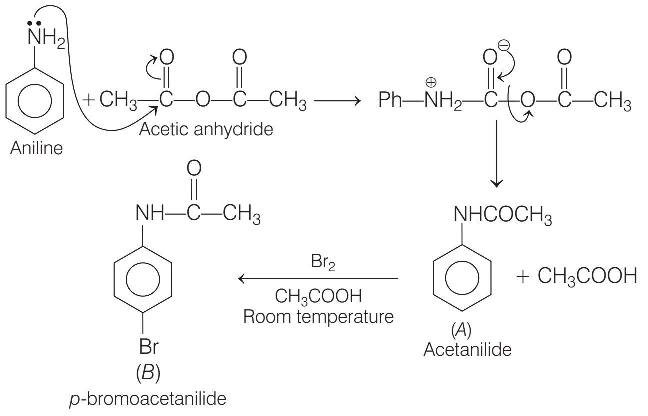
(c) 

(d) 

Ans. *(b)*

Aniline reacts with acetic anhydride to give acetanilide.

The acetic acid part is removed and N-acylation takes place by nucleophilic substitution reaction.



Acetanilide is brominated with bromine/acetic acid. As —$NHCOCH_3$ is *ortho/para* directing group (since lone pair on N activates the ring).

Bromine attached to *para* position is the major product losse.

51 The total number of reagents from those given below, that can convert nitrobenzene into aniline is .... (Integer answer) **[2021, 31 Aug Shift-I]**

I. Sn – HCl II. Sn – NH_4OH

III. Fe – HCl IV. Zn – HCl

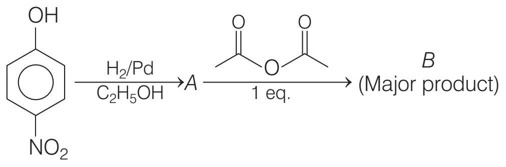
V. H_2 – Pd VI. H_2-Raney nickel

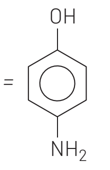
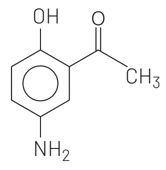
Ans. ***(5)***

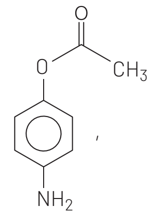
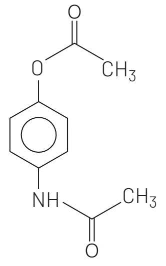
The nitrobenzene can be reduced to aniline *via* following reagents.

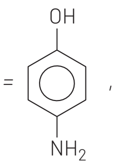
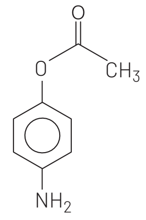
(I) Sn-HCl (V) H_2-Pd (III) Fe-HCl (VI) H_2 (Raney Ni)
(IV) Zn-HCl

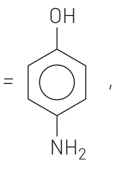
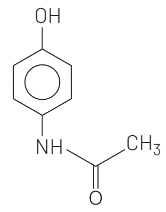
52 The correct structures of *A* and *B* formed in the following reactions are **[2021, 27 Aug Shift-II]**



(a) *A* =

, *B* =


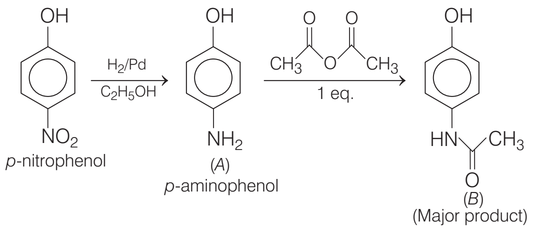
(b) *A* =

, *B* =


(c) *A* =

, *B* =


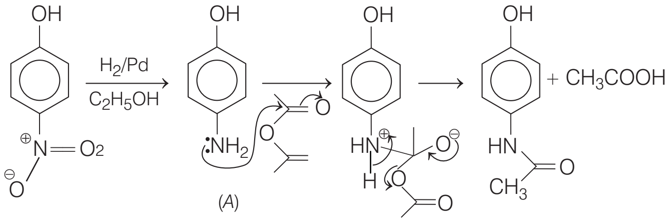
(d) *A* =

, *B* =


Ans. ***(d)***

Since, only one equivalent of acetic anhydride is present and – NH_2 group is more nucleophilic than –OH group due to lower electronegativity of nitrogen. So, it attacks at the carbonyl center of acetic anhydride forming the product *B*.



Mechanism



Therefore, the option (d) is correct.

53 Given below are two statements.

Statement I Aniline is less basic than acetamide.

Statement II In aniline, the lone pair of electrons on nitrogen atom is delocalised over benzene ring due to resonance and hence less available to a proton.

Choose the most appropriate option : **[2021, 27 July Shift-I]**

(a) Statement I is true but statement II is false.
(b) Statement I is false but statement II is true.
(c) Both statement I and statement II are true.
(d) Both statement I and statement II are false.

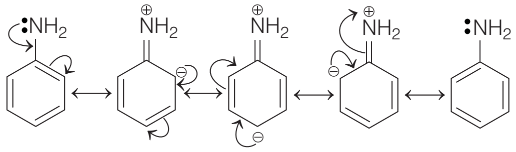
Ans. ***(b)***

Statement I is false but Statement II is true.

Aniline ($C_6H_5NH_2$) is more basic than acetamide (C_2H_5NO) because in acetamide lone pair of electron present on nitrogen is delocalised to more electronegative element, i.e. oxygen.

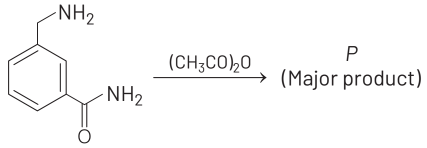
As lone pair of N in acetamide is in conjugation with C═O that is strong electron withdrawing than phenyl group, so lone pair of N is unavailable for proton, so it is less basic than aniline.

In aniline, lone pair of electrons on the N atom is delocalised over benzene ring.



Ph — $NH_2 > RCONH_2$ (Basic strength).

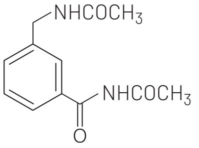
54



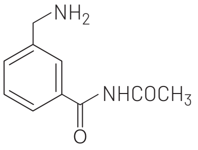
The major product in the above reaction is

[2021, 26 Aug Shift-II]

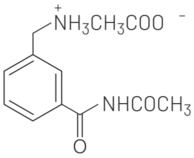
(a)



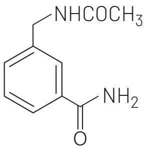
(b)



(c)

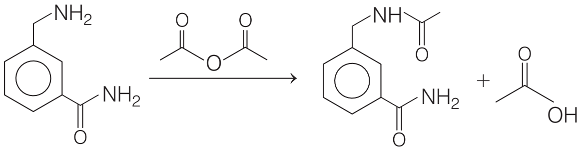


(d)



Ans. ***(d)***

Since — CH_2 — NH_2 is more basic, the resulting amide will fail to react further. Therefore, imide formation takes place at only one site (i.e. primary amine). The complete reaction is as follows :



55 Given below are two statements, one is labelled as : Assertion (A) and other is labelled as Reason (R).

Assertion (A) Gabriel phthalimide synthesis cannot be used to prepare aromatic primary amines.

Reason (R) Aryl halides do not undergo nucleophilic substitution reaction.

In the light of the above statements, choose the correct answer from the options given below

[2021, 22 July Shift-I]

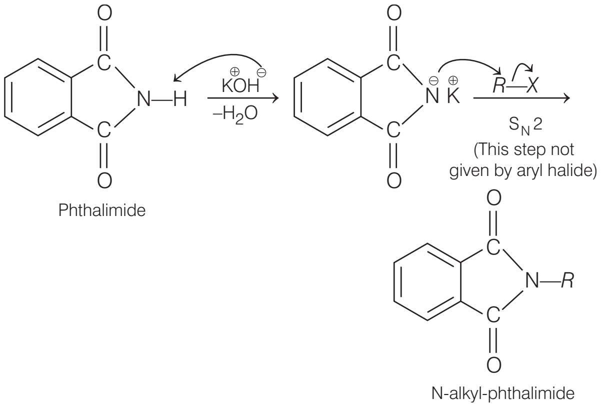
(a) Both (A) and (R) true but (R) is not the correct explanation of (A).
(b) (A) is false but (R) is true.
(c) Both (A) and (R) true and (R) is correct explanation of (A).
(d) (A) is true but (R) is false.

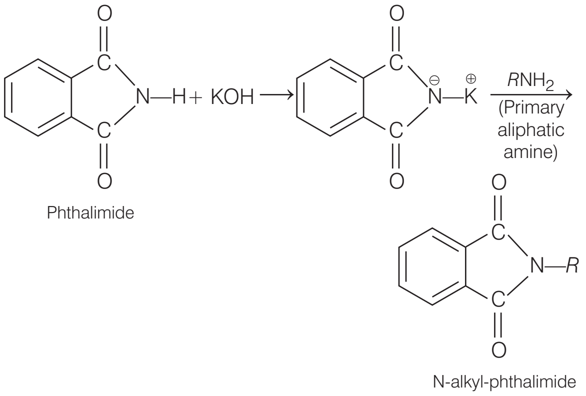
Ans. ***(c)***

Both (A) and (R) are true and (R) is correct explanation of (A). Aromatic halide does not give S_N2 reaction.

Gabriel pthalimide synthesis is used to form primary aliphatic amine, because aryl halides do not undergo nucleophilic substitution reaction.

Gabriel phthalimide reaction

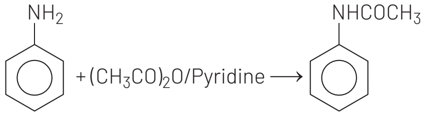




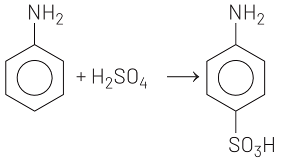
56 Which one of the following reactions does not occur?

[2021, 22 July Shift-II]

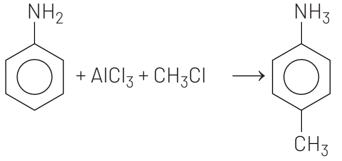
(a)



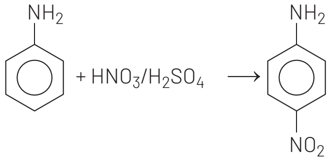
(b)



(c)



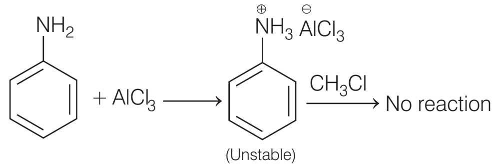
(d)



Ans. ***(c)***

Friedel-Craft reaction is not possible in highly activated ring, i.e. aniline because NH_2 group forms complex with Lewis acid and deactivate the ring.

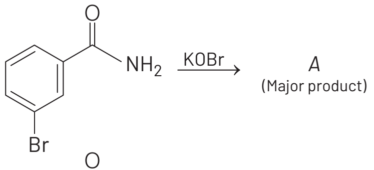
Chemical reaction is as follows :

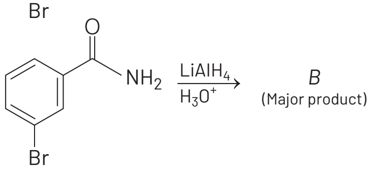


Due to lone pair of electrons on N, aniline is a strong Lewis base. So, an acid base reaction occur between aniline and $AlCl_3$ leading to anilinium salt formation.

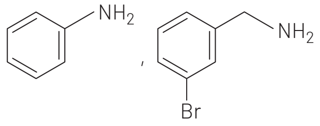
Since, $\overset{+}{N}H_3$ is a deactivating group and hence electrophilic substitution *via* Friedel-Craft alkylation does take place.

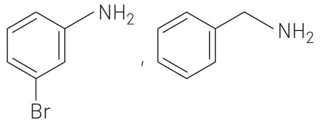
57

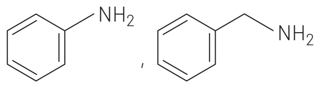


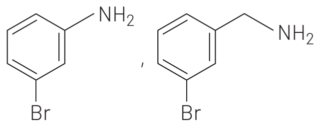


In the above reactions, products *A* and *B* respectively are **[2021, 20 July Shift-II]**

(a)


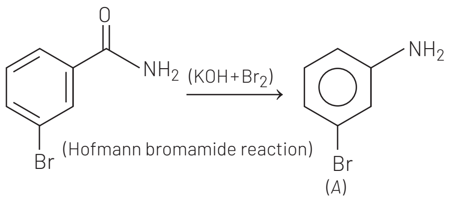
(b)


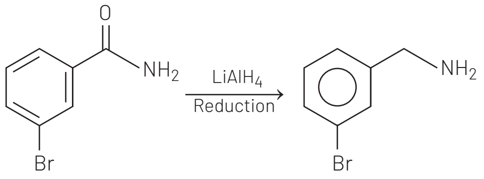
(c)


(d)


Ans. ***(d)***

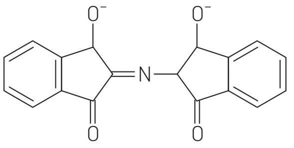
Hofmann reagent reduces amide to amine with one carbon less. This reaction is known as Hofmann bromamide reaction.

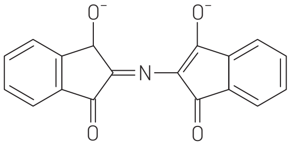


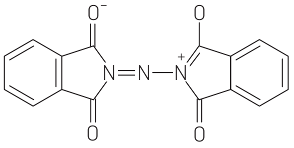


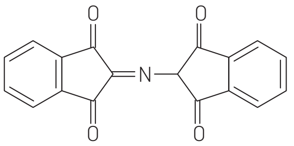
$LiAlH_4$ reduces amide to primary amine with same number of carbon atom.

58 The correct structure of Rhumann's Purple, the compound formed in the reaction of ninhydrin with proteins is **[2021, 20 July Shift-I]**

(a)


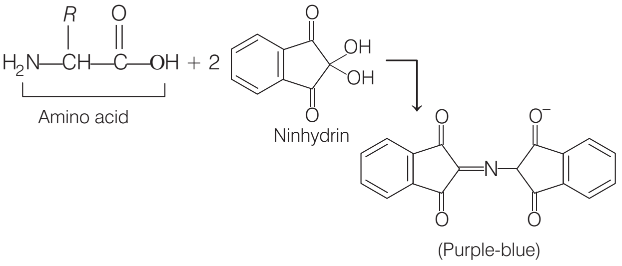
(b)


(c)


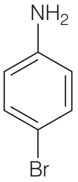
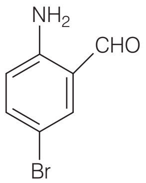
(d)


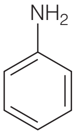
Ans. ***(d)***

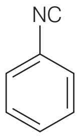
Rhumann's purple is confirmatory test for the presence of protein. The correct structure of Rhumann's Purple, the compound formed in the reaction of ninhydrin with proteins is an follows

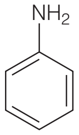


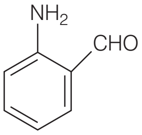
59 Hofmann bromamide degradation of benzamide gives product *A*, which upon heating with $CHCl_3$ and NaOH gives product *B*. The structures of *A* and *B* are **[2021, 17 March Shift-I]**

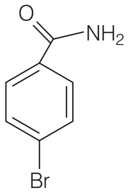
(a) *A* =

B =


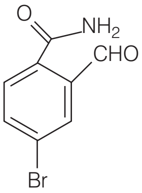
(b) $A =$ 

$B =$ 

(c) $A =$ 

$B =$ 

(d) $A =$ 

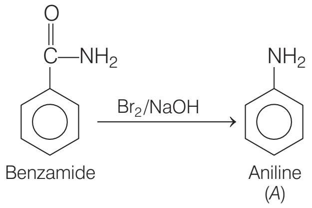
$B =$ 

Ans. ***(b)***

Hofmann bromamide degradation of benzamide gives product aniline (A), which upon heating with $CHCl_3$ and NaOH gives product benzene isocyanide (B), by carbylamine reaction.

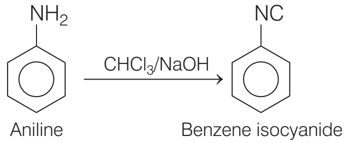
Hofmann bromamide degradation method is for preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide.

The amine formed contains one carbon less than that present in the amide.



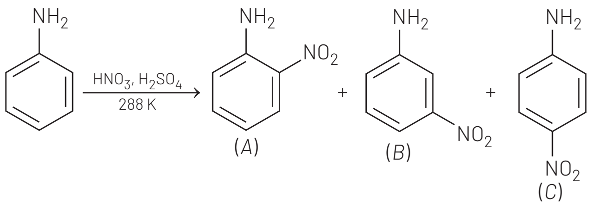
Hofmann bromamide reaction

Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances.



Carbylamine reaction

Note Secondary and tertiary amines do not show this reaction. This reaction is known as carbylamine reaction or isocyanide test and is used as a test for primary amines.

60 

Consider the given reaction, percentage yield of **[2021, 18 March Shift-II]**

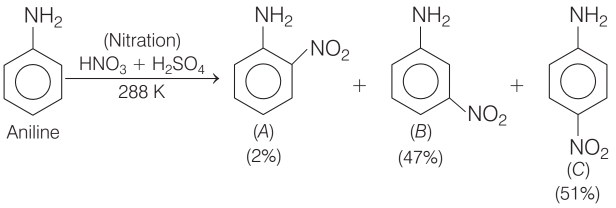
(a) $(C) > (A) > (B)$ (b) $(B) > (C) > (A)$

(c) $(A) > (C) > (B)$ (d) $(C) > (B) > (A)$

Ans. ***(d)***

During nitration of aniline, *meta*-nitroaniline is also formed as product due to formation of NH_3^+ group which is meta directing group under strongly acidic medium. The percentage of *p*, *m* and *o* product is 51%, 47% and 2%, respectively.

Reaction is as follows



% yield order is $C > B > A$.

61 A. phenyl methanamine B. N,N-dimethylaniline
C. N-methyl aniline D. Benzenamine

Choose the correct order of basic nature of the above amines. **[2021, 26 Feb Shift-II]**

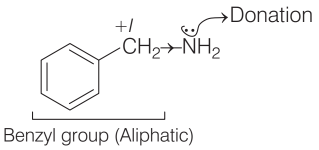
(a) A > C > B > D (b) D > C > B > A

(c) D > B > C > A (d) A > B > C > D

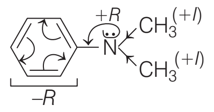
Ans. ***(d)***

In phenyl methanamine, the lone pair on nitrogen of —NH_2 group is localised and does not undergoes resonance as attached to sp^3-hybridised C-atom.

Phenyl methanamine or benzyl amine

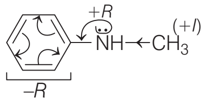


(B), (C) and (D) are aromatic amines in which lone pair of electrons of N-atoms goes in resonance
$(+R$ effect) with the benzene ring. So, Lewis basicity or donation of lone of electrons of these amines will be decreased in comparison to (A).

(B) 

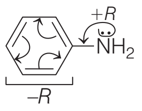
N, N-dimethyl aniline (3°-amine)

$+I$ effects of two —CH_3 groups are in compensation with $-R$-effect of the ring.

(C) 

N-methyl aniline (2°-amine)

$+I$ effect of one —CH_3 group is trying to compensate $-R$ effect of the ring.

(D) 

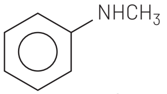
Benzenamine or aniline (1° amine)

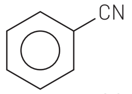
It has no $+I$-effect on N-atom to outweigh $-R$-effect of the ring.

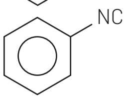
So, *A* is purely aliphatic 1°-amine. *B* is aromatic 3°-amine with more aliphatic nature (for two $-CH_3$ groups). *C* is aromatic 2°-amine with less aliphatic nature (for one $-CH_3$ group). *D* is purely aromatic 1°-amine.

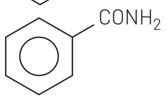
Hence basicity order is $A > B > C > D$.

62 Carbylamine test is used to detect the presence of primary amino group in an organic compound. Which of the following compound is formed when this test is performed with aniline? **[2021, 25 Feb Shift-II]**

(a) 

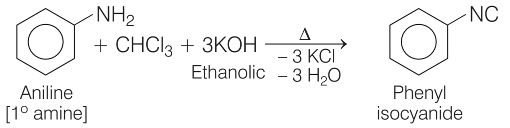
(b) 

(c) 

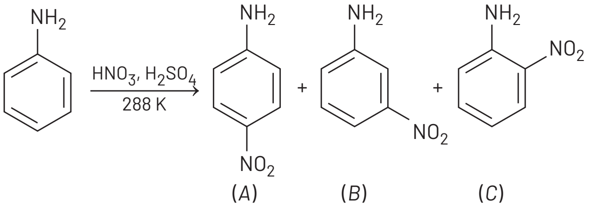
(d) 

Ans. ***(c)***

Aniline on carbylamine reaction produces a foul smelling gas, phenyl isocyanide (C_6H_5NC).



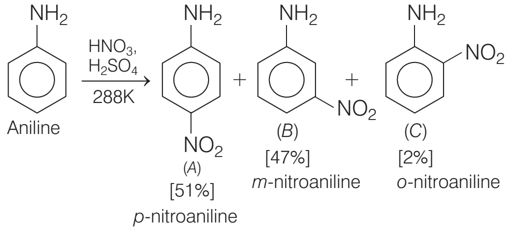
Carbylamine test is used to detect aliphatic and aromatic primary amines.

63 

Correct statement about the given chemical reaction is **[2021, 25 Feb Shift-II]**

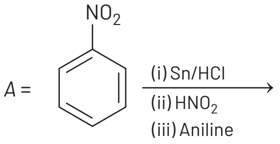
(a) $-\ddot{N}H_2$ group is *ortho* and *para* directing, so product (*B*) is not possible.
(b) reaction is possible and compound (*B*) will be the major product.
(c) the reaction will form sulphonated product instead of nitration.
(d) reaction is possible and compound (*A*) will be major product.

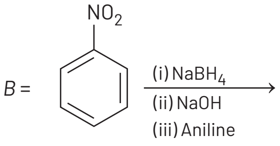
Ans. ***(d)***

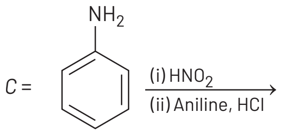


During nitration, in strongly acidic medium, aniline gets protonated to form the anilinium ion i.e, $(C_6H_5-\overset{\oplus}{N}H_3)$ which is *meta*-directing as $-\overset{\oplus}{N}H_3$ is an electron withdrawing $(-I)$ group. As a result, we get *meta*-nitro aniline (*B*) as the major product.

64 Which of the following reaction(s) will not give *p*-aminoazobenzene? **[2021, 25 Feb Shift-I]**



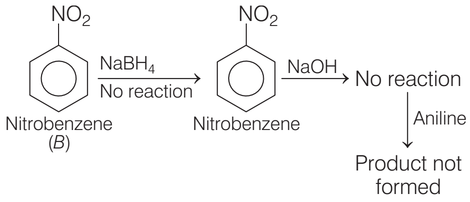




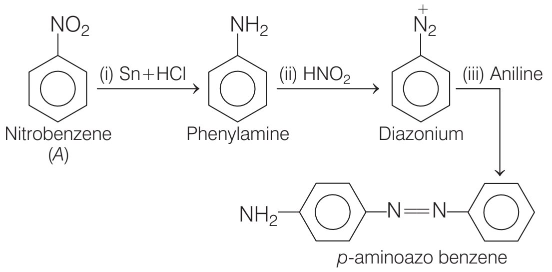
(a) *A* only
(b) *C* only
(c) *B* only
(d) *A* and *B*

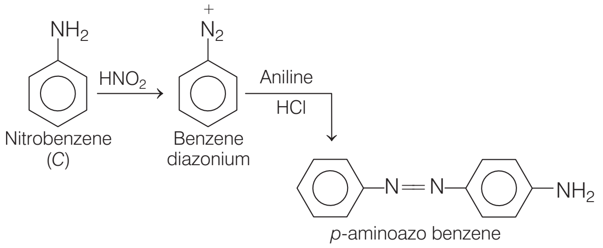
Ans. ***(c)***

Nitrobenzene in presence of $NaBH_4$, NaOH and aniline will not give *p*-amino azobenzene.



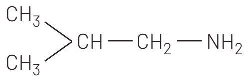
In case of (*A*) and (*C*), coupling reaction takes place as the medium is quite acidic follows



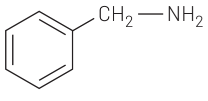


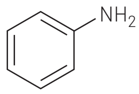
65 The total number of amines among the following which can be synthesised by Gabriel synthesis is ....

[2021, 24 Feb Shift-II]

(a) 
$(CH_3)_2CH—CH_2—NH_2$

(b) $CH_3CH_2NH_2$

(c) 

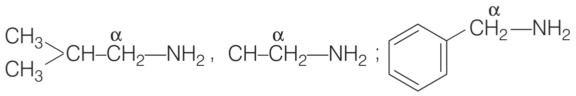
(d) 

Ans. ***(3)***

Gabriel phthalimide synthesis is used to prepare 1° aliphatic or alicyclic amine. Hence, amine which can be synthesised by Gabriel phthalimide synthesis method contains α-carbon.

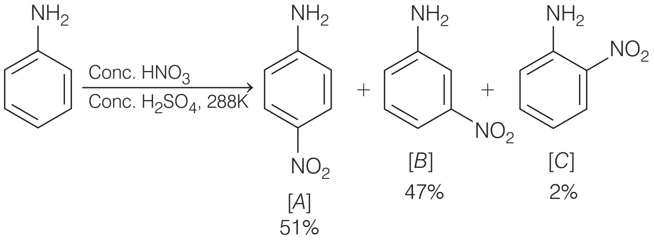
Aniline ($C_6H_5NH_2$) does not contain α -C cannot be prepared by Gabriel reaction.

Rest amines all contain α-C in its respective position, hence they can easily give Gabriel phthalimide reaction.



∴ Three amins out of given four anions can be prepared by Gabriel synthesis.

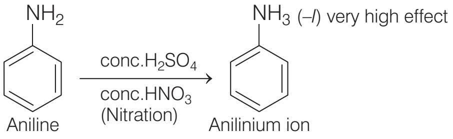
66 In the following reaction the reason why *meta*-nitro product also formed is **[2021, 24 Feb Shift-I]**



(a) $—NH_2$ group is highly *meta*-directive
(b) $—NO_2$ substitution always takes place at *meta*-position
(c) Formation of anilinium ion
(d) Low temperature

Ans. ***(c)***

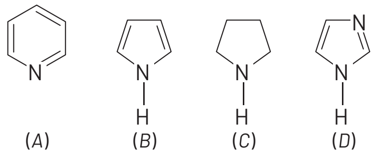
Aniline on protonation forms anilinium ion, which is *meta*-directing. So, a considerable amount of *meta* product is formed alongwith *o*-nitroaniline and *p*-nitroaniline.



Nitrating mixture is mixture of conc. HNO_3 and a conc. H_2SO_4. When aniline is reacted with nitrating mixture *ortho*, *meta* and *para* nitroanilines are obtained.

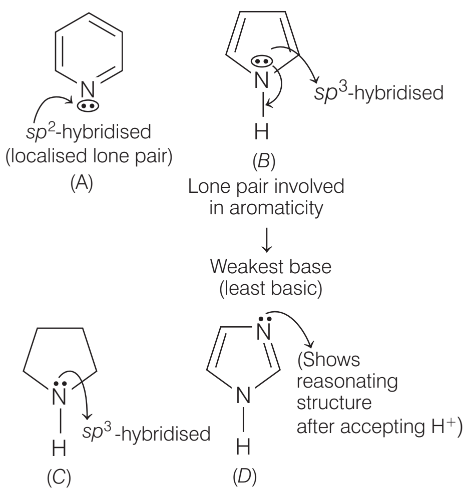
Aniline being basic in nature, reacts with acids to form anilinium ion which is *meta* directing.

67 The increasing order of basicity of the following compounds is **[2020, 5 Sep Shift-I]**

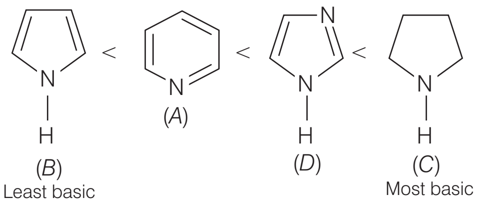


(a) $(A) < (B) < (C) < (D)$
(b) $(D) < (A) < (B) < (C)$
(c) $(B) < (A) < (D) < (C)$
(d) $(B) < (A) < (C) < (D)$

Ans. ***(c)***



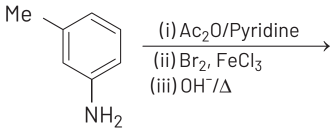
More free lone pair of electron for donation, hence most basic.

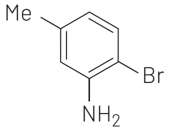


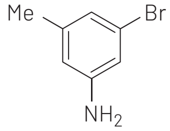
Hence, correct increasing order of basicity is

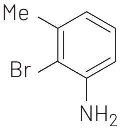
$$(B) < (A) < (D) < (C)$$

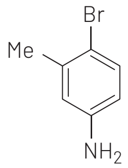
68 The final major product of the following reaction is **[2020, 5 Sep Shift-II]**



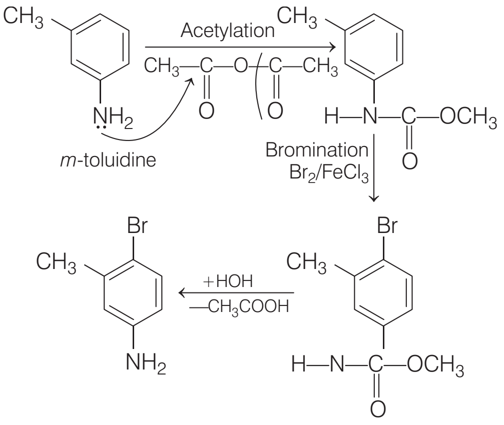
(a) 

(b) 

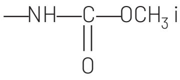
(c) 

(d) 

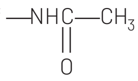
Ans. ***(d)***



The basic nature of *m*-toluidine is not greatly affected by the —CH_3 group.

 $-NH-\underset{\underset{O}{\|}}{C}-OCH_3$ is moderately activating

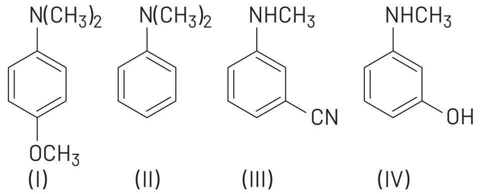
group, its activating nature overcome weak activating —CH_3 group.

Due to bulky nature of  $-NH\underset{\underset{O}{\|}}{C}-CH_3$ attack

happen *para* to —NHCO-CH_3.

Here, NH_2 group has been protected by forming its aceyl derivative and as such if does not interfere in the bromination.

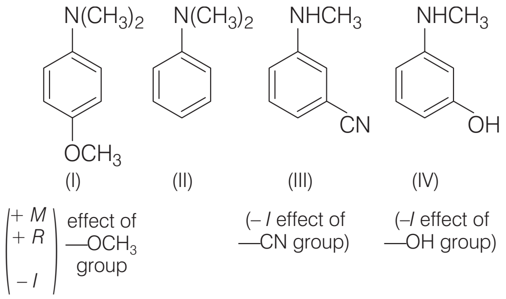
69 The increasing order of pK_b values of the following compounds is **[2020, 6 Sep Shift-I]**



(I) (II) (III) (IV)

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

Ans. ***(b)***



pK_b is inversely proportional to basic strength and as the electron density increases in the ring, K_b will increases and pK_a value decreases. Electron density within the ring is maximum in (I) thus it has least pK_b value. So, option (a), (c) and (d) are incorrect.

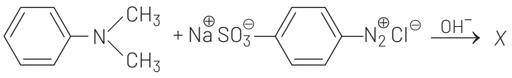
In (III) structure, —CN group attached at *meta*-position, thus electron density is less affected, so pK_b value is more than structure (IV).

Thus decreasing order for K_b is (I) > (II) > (IV) > (III)

∴ Order of pK_b : (III) > (IV) > (II) > (I).

Hence, the correct option is (b).

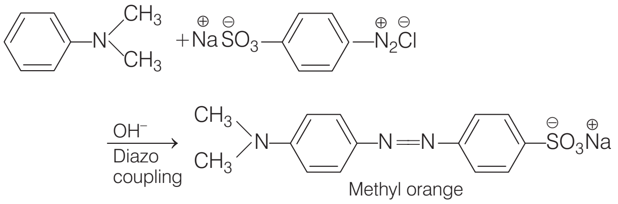
70 Consider the following reaction :



The product 'X' is used **[2020, 7 Jan Shift-I]**

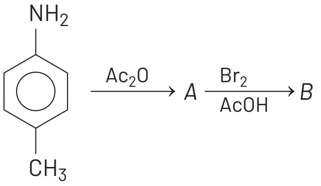
(a) in acid base titration as an indicator
(b) in protein estimation as an alternative to ninhydrin
(c) as food grade colourant
(d) in laboratory test for phenols

Ans. ***(a)***

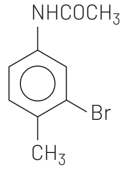


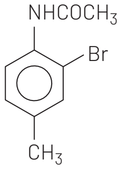
Methyl orange is used as an indicator in acid-base titration.

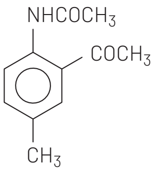
71 In the following reaction sequence,

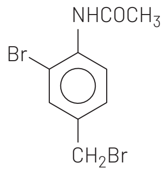


the major product *B* is: **[2020, 7 Jan Shift-II]**

(a) 

(b) 

(c) 

(d) 

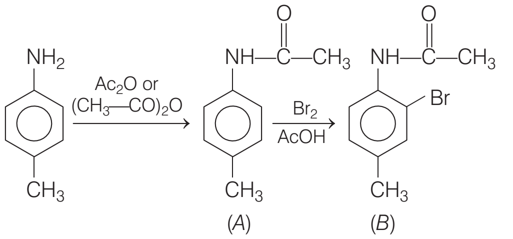
Ans. ***(b)***

The first step of the reaction is acylation.

In the second step of reaction, $-\ddot{N}H-\overset{O}{\overset{\|}{C}}-CH_3$ has $+R$ (or $+M$) effect, so it acts as *ortho/para*-directing group. But, since *para* position has CH_3 group, substitution at *ortho* takes place. $-CH_3$ has weak *ortho-/para-* directing effect due to hyperconjugation, but it is suppressed due to more predominant effect of

$-\ddot{N}H-\overset{O}{\overset{\|}{C}}-CH_3$.

Thus, the complete reaction is given as follows :



72 Kjeldahl's method cannot be used to estimate nitrogen for which of the following compounds? **[2020, 8 Jan Shift-II]**

(a) $C_6H_5NO_2$

(b) $NH_2-\overset{O}{\overset{\|}{C}}-NH_2$

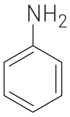
(c) $CH_3CH_2-C\equiv N$

(d) $C_6H_5NH_2$

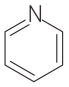
Ans. ***(a)***

Kjeldahl's method cannot be used for nitro compounds, diazo compounds and compounds with nitrogen in a ring, because these on reaction with H_2SO_4 do not give ammonium ion.

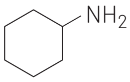
73 The decreasing order of basicity of the following amines is **[2020, 9 Jan Shift-II]**



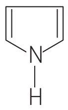
(I)



(II)



(III)



(IV)

(a) (III) > (I) > (II) > (IV)

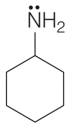
(b) (III) > (II) > (I) > (IV)

(c) (I) > (III) > (IV) > (II)

(d) (II) > (III) > (IV) > (I)

Ans. ***(b)***

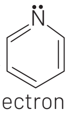
Among the given options, compound (III) has maximum basicity.

III. 

: No resonance or delocalisation of lone pair of electron on nitrogen.

The ring contains sp^3 carbon atoms that cause $+I$-effect.

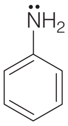
∴ More basic among options.

II. 

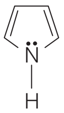
: No resonance or delocalisation of lone pair of electrons on nitrogen.

The ring contains sp^2 carbon atoms that have $-I$-effect, compared to sp^3 C-atoms.

∴ Less basic than compound III.

I. 

: Resonance or delocalisation of lone pair of electrons on benzene ring occur that decreases basicity.

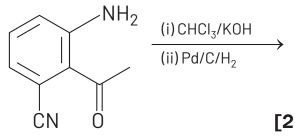
IV. 

: Strong resonance or delocalisation of lone pair of electron on nitrogen. The electron pair is a part of aromatic 6 electron system.

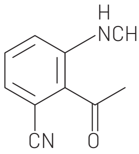
∴ Least basic among given options.

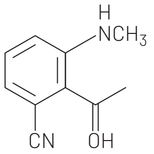
So, the correct order of basicity is III > II > I > IV

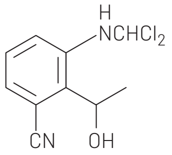
74 The major product obtained in the following reaction is

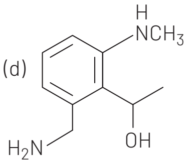


[2019, 8 April Shift-II]

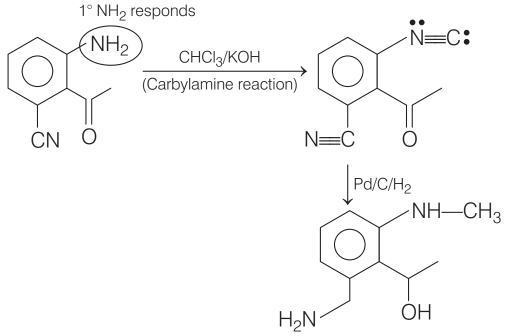
(a) 

(b) 

(c) 

(d) 

Ans. ***(d)***

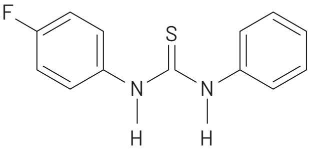


In step (i), 1° amine is converted into isocyanide, when reacts with $CHCl_3$ /KOH. This reaction is known as carbylamine reaction. This reaction is used to detect primary amine in a compound.

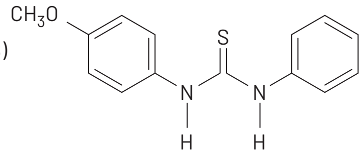
In step (ii), isocyanide is reduced to secondary amine and cyanide is reduced to primary amine, and carbonyl group to alcoholic group when treated with Pd/C/H_2.

75 The increasing order of the pK_b of the following compound is **[2019, 12 April Shift-I]**

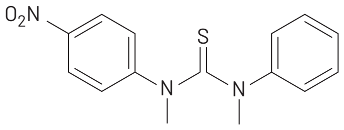
(A)



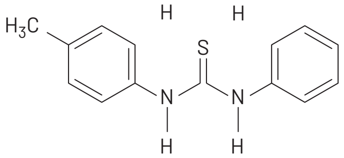
(B)



(C)



(D)



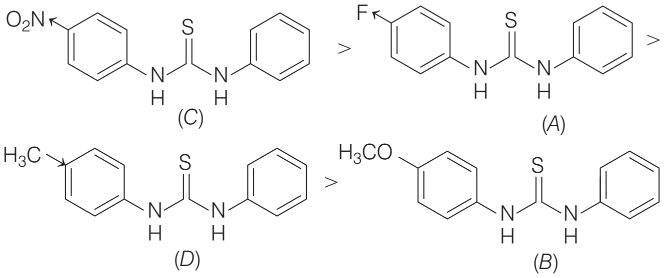
(a) (A) < (C) < (D) < (B)
(b) (C) < (A) < (D) < (B)
(c) (B) < (D) < (A) < (C)
(d) (B) < (D) < (C) < (A)

Ans. ***(c)***

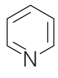
Key Idea pK_b value is defined as the minus logarithm of K_b. Smaller the value of pK_b, stronger is the base and *vice-versa*.

In the given options, $+R$ effect is shown by $-CH_3$ and $-OCH_3$ group ($-OCH_3 > -CH_3$). These group increases the electron density at *o* and *p*-positions. Groups such as $-F$ and $-NO_2$ shows $-R$-effect ($-NO_2 > -F$). These group decreases the electron density at *o* and *p*- positions.

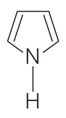
Increase in electron density at *p*-position makes the unshared electron pair of '*N*' more available and decrease in electron density at *p*-position makes the unshared electron pair of '*N*' less available. Compound containing $-OCH_3$ group act as strongest base and hence possess lowest value of pK_b. So, the correct increasing order of pK_b in the given compound is



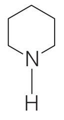
76 Arrange the following amines in the decreasing order of basicity : **[2019, 9 Jan Shift-I]**



(I)



(II)



(III)

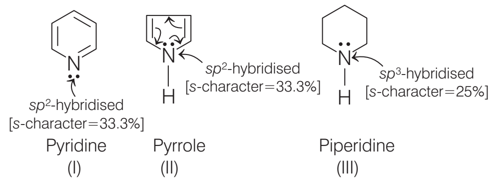
(a) I > II > III (b) III > II > I (c) I > III > II (d) III > I > II

Ans. ***(d)***

Key Idea Basicity ∝ Ease of donation of lone pair of electrons

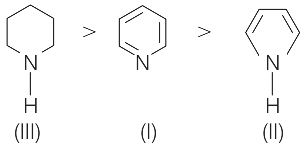
$$\propto \frac{1}{\%\text{ of s-character of N}} \propto \frac{1}{\text{Electronegativity of N}}$$

The % of *s*-character in the given amines are as follows:

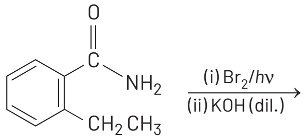


Therefore, piperidine (III) having minimum % s-character is most basic. Among the rest, pyridine (I) and pyrrole (II) the lone pair of electrons of N in pyrrole (II) is involved in delocalisation and follows $(4n+2)\ \pi$ aromatic $(n=1)$ system. So, the N-atom of pyrrole (II) will show least basicity.

Thus, the order of basicity is as follows:

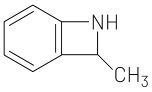


77 The major product of the following reaction is

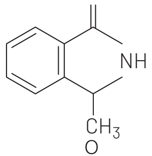


[2019, 9 Jan Shift-II]

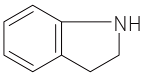
(a)



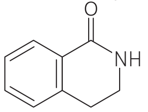
(b)



(c)

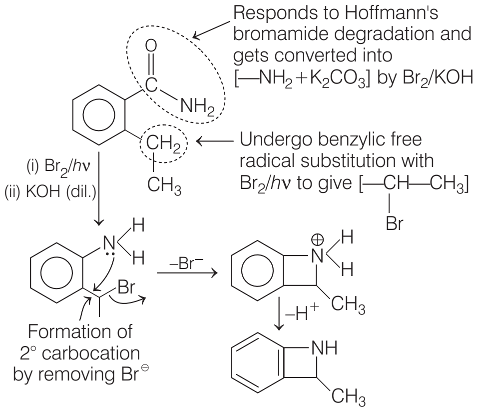


(d)

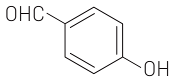


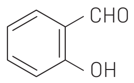
Ans. ***(a)***

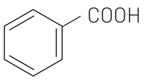
In the given reaction,

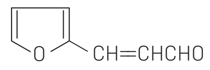


78 An aromatic compound '*A*' having molecular formula $C_7H_6O_2$ on treating with aqueous ammonia and heating forms compound '*B*'. The compound '*B*' on reaction with molecular bromine and potassium hydroxide provides compound '*C*' having molecular formula C_6H_7N. The structure of '*A*' is

(a) 

(b) 

(c) 

(d) 

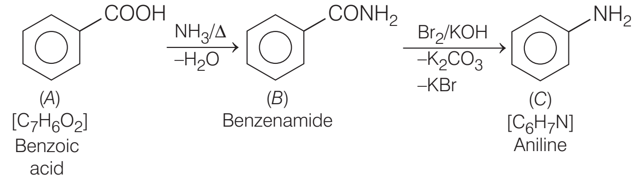
[2019, 10 Jan Shift-II]

Ans. ***(c)***

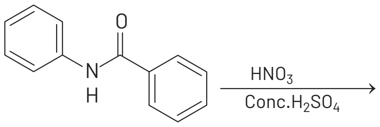
Using retro-synthesis, to get the required compounds, *A*, *B* and *C*.

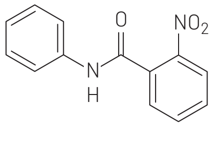
$$\underset{\substack{(C)\\ [1^\circ\text{-amine}]\\ (\text{No. of C}=6\\ 1\text{ carbon less})}}{C_6H_7N} \xleftarrow[\substack{\text{Hoffmann}\\ \text{bromamide}\\ \text{reaction}\\ (\text{step down})}]{\substack{Br_2\\ KOH}} \underset{\substack{[\text{An amide}]\\ (\text{No. of C}=7)}}{B} \xleftarrow{NH_3/D} \underset{\substack{[\text{Carboxylic acid}\\ C_7H_6O_2\,]}}{A}$$

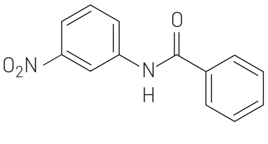
So, the reactions can be shown as:

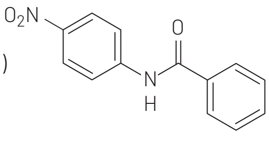


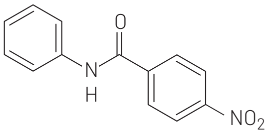
79 What will be the major product in the following mononitration reaction ?



(a) 

(c) 

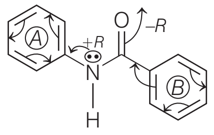
(b) 

(d) 

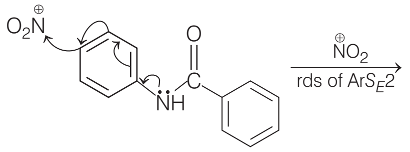
[2019, 10 Jan Shift-II]

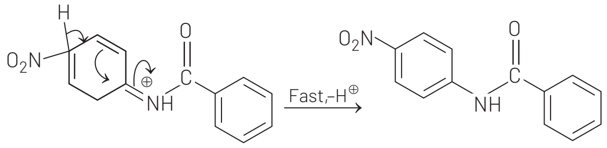
Ans. ***(b)***

Here, in mononitration the electrophile produced from mixed acid (HNO_3 + conc.H_2SO_4) is $\overset{+}{N}O_2$.

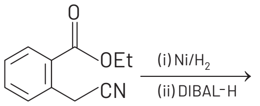


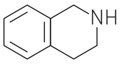
Ring-(*A*) is activated, i.e. becomes more nucleophilic by the + *R* effect of the $-\ddot{N}H-$ group and it becomes *o* / *p*-directing towards the electrophile, NO_2^+ in the ArS_E2 reaction. For mononitration, $\overset{\oplus}{N}O_2$ will preferably come at *p*-position, whereas the ring-(*B*) gets deactivated by −*R*- effect of the $-\overset{\overset{O}{\|}}{C}-$ group,

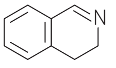


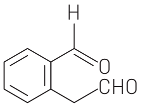


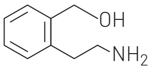
80 The major product of the following reaction is



(a) 

(b) 

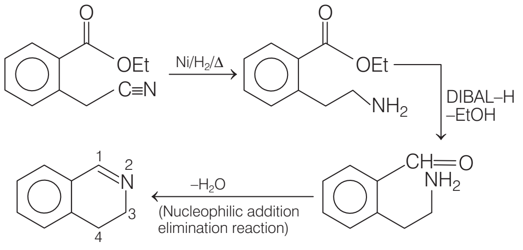
(c) 

(d) 

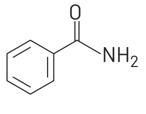
[2019, 11 Jan Shift-I]

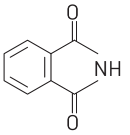
Ans. ***(b)***

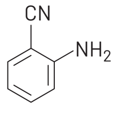
Ni/H_2 can reduce $-C\equiv N$ into $-CH_2-NH_2$ (1°-amine) but cannot reduce an ester group ($-CO_2Et$) whereas DIBAL-H, di-isobutylaluminium hydride, $[(CH_3)_2CH]_2AlH$ reduces the ester group ($-CO_2Et$) into $-CHO$ (an aldehyde) and C_2H_5OH.

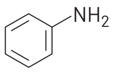


81 The increasing order of reactivity of the following compounds towards reaction with alkyl halides directly is **[2019, 12 Jan Shift-I]**


(A)


(B)


(C)

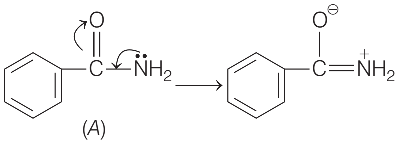

(D)

(a) $(A) < (C) < (D) < (B)$ (b) $(B) < (A) < (C) < (D)$
(c) $(B) < (A) < (D) < (C)$ (d) $(A) < (B) < (C) < (D)$

Ans. ***(b)***

The reaction of alkyl halide with amine or amides is a nucleophilic substitution reaction.

More nucleophilic nitrogen is more reactive with alkyl halide. Compound (A) is benzamide and lone pair of 'N' of it, is not available in this compound.

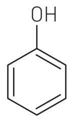


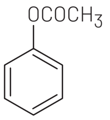
In compound (D), lone pair of 'N' are available but in compound (C), the lone pair of 'N' are not readily available due to the presence of electron withdrawing group (—CN) attach to benzene ring.

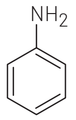
In compound (B), i.e. pthalimide, 'N' is not nucleophilic due to the presence of two polar groups attached to it that pulls lone pair towards them.

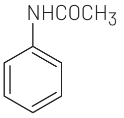
Hence, the correct order is : $(B) < (A) < (C) < (D)$.

82 Which of the following compounds will give significant amount of *meta*-product during mononitration reaction? **[JEE Main 2017]**

(a)


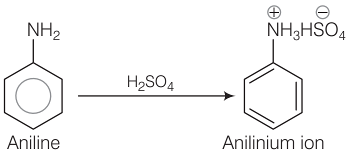
(b)


(c)


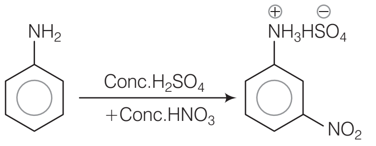
(d)


Ans. ***(c)***

Aniline in presence of nitrating mixture (conc. HNO_3 + conc. H_2SO_4) gives significance amount (≈ 47%) of meta-product because in presence of H_2SO_4 its protonation takes place and anilinium ion is formed.



Here, anilinium ion is strongly deactivating group and *meta*-directing in nature. So, it gives *meta*-nitration product.

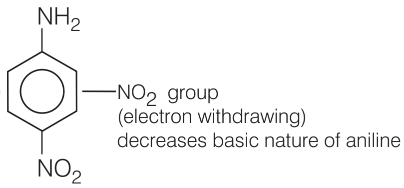


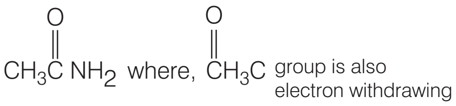
83 Amongst the following the most basic compound is **[AIEEE 2005]**

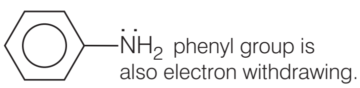
(a) *p*-nitroaniline (b) acetanilide
(c) aniline (d) benzylamine

Ans. ***(d)***

Basic nature of the compound is related to their tendency to donate their lone pair of electrons more readily. $-I$ effect [e^- withdrawing] exerting group decreases the basic strength while $+I$ effect [e^- donating] exerting group increases the basic strength of the compound.

(a)


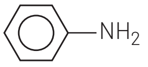
(b)

$CH_3\overset{O}{\overset{\|}{C}}\,NH_2$ where, $CH_3\overset{O}{\overset{\|}{C}}$ group is also electron withdrawing

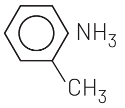
(c)


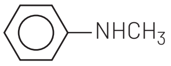
(d) Benzylamine ($C_6H_5CH_2NH_2$) contains alkyl group linked to amine, —NH_2 group. This alkyl group is + I effect [e^- donating] exerting group which increases the basicity of benzylamine.

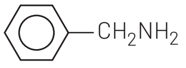
Thus, most basic compound is benzylamine.

84 Which of the following is the strongest base? **[AIEEE 2004]**

(a)


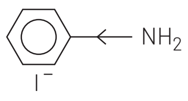
(b)


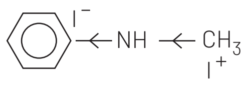
(c)


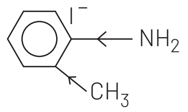
(d)


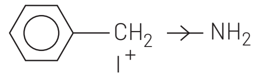
Ans. ***(d)***

CH_3—[an electron releasing $(+I)$ group] increases electron density at N-atom, hence basic nature is increased.

(a)


(b)


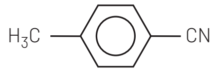
(c)


(d)


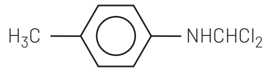
C_6H_5 decreases electron density at N-atom due to delocalisation of e^- of NH_2 with πe^- of benzene. Thus, basic nature is decreased.

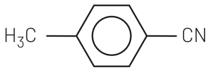
Hence, (d) is the strongest base.

85 The reaction of chloroform with alcoholic KOH and *p*-toluidine form **[AIEEE 2003]**

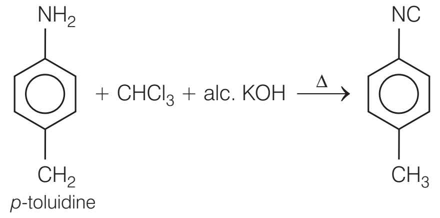
(a) 

(b) 

(c) 

(d) 

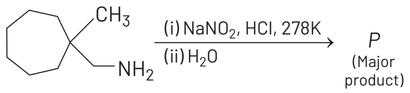
Ans. ***(c)***



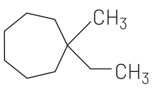
This is carbylamine reaction.

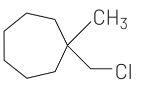
TOPIC 3
Diazonium Salts

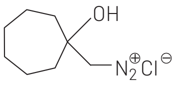
86 What is the major product *P* of the following reaction ?

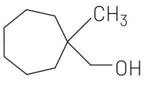


[2021, 25 July Shift-II]

(a) 

(b) 

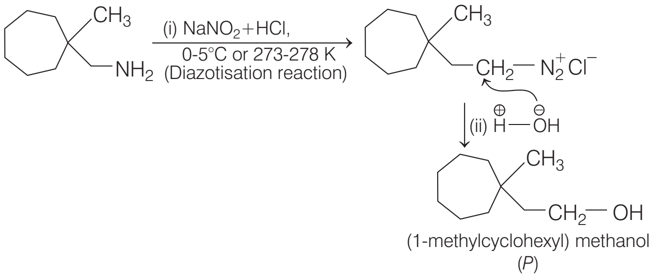
(c) 

(d) 

Ans. ***(d)***

In first step, $NaNO_2$, HCl is used for diazotisation reaction at 0-5°C. In last step, H_2O is used as a nucleophilic substitution of N_2 (leaving group).

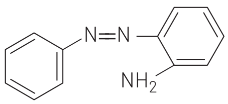
N_2 is best leaving group to form (1-methylcyclohexyl) methanol as major product.

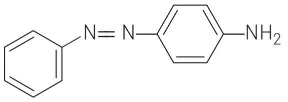


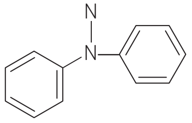
(1-methylcyclohexyl) methanol
(*P*)
(Major product)

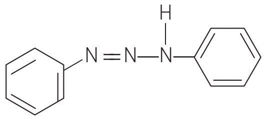
87 $C_6H_5NO_2 \xrightarrow{Sn + HCl} A \xrightarrow[H^+]{C_6H_5N_2^+Cl^-} P$ (Yellow coloured compound)

Consider the above reaction, the product *P* is **[2021, 25 July Shift-II]**

(a) 

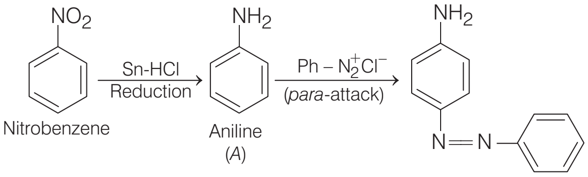
(b) 

(c) 

(d) 

Ans. ***(b)***

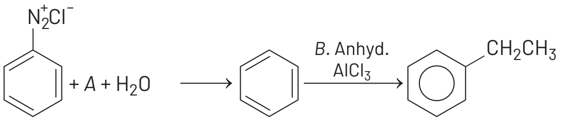
Sn — HCl is used for reduction of — NO_2 group into —NH_2 group. On next step, $PhN_2^+Cl^-$ is used to form yellow coloured azo dye with aniline. This is a coupling reaction.



p-aminoazobenzene
(*Y*-aminoazobenzene)

Due to its various resonating structures, there's an excess of electron or negative charge over *ortho* and *para* positions of the benzene ring than the *meta*-position. Thus, anilines are *o* and *p*-directing towards electrophilic substitution reactions.

88



(Major product)

In the chemical reactions given above *A* and *B* respectively are **[2021, 22 July Shift-II]**

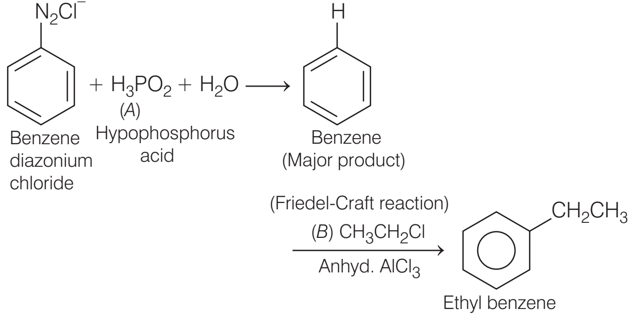
(a) H_3PO_2 and CH_3CH_2Cl
(b) CH_3CH_2OH and H_3PO_2
(c) H_3PO_2 and CH_3CH_2OH
(d) CH_3CH_2Cl and H_3PO_2

Ans. ***(a)***

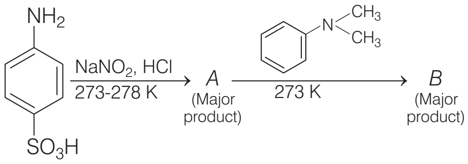
H_3PO_2 is compound A and CH_3CH_2Cl is compound *B*.

When benzene diazonium chloride reacts with H_3PO_2 (hypophosphorus acid) and water gives benzene (major product) which on reaction with ethyl chloride in presence of anhydrous $AlCl_3$ gives ethyl benzene.

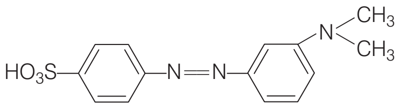
Chemical reaction is as follows ;

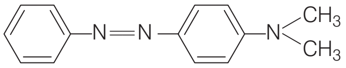


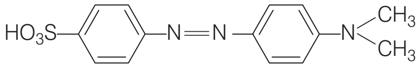
89

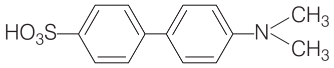


Consider the above reaction, compound *B* is **[2021, 20 July Shift-II]**

(a) 

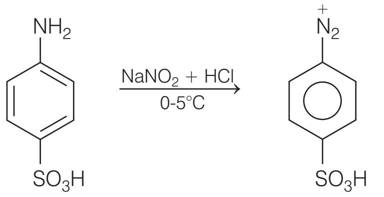
(b) 

(c) 

(d) 

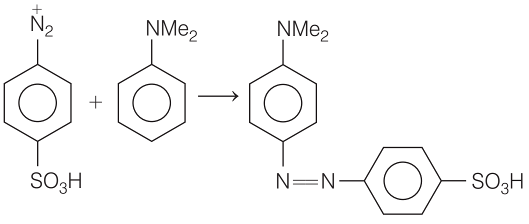
Ans. ***(c)***

Diazonium salt is formed on treating an amine with $NaNO_2$ / HCl at low temperature.

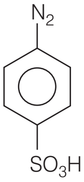


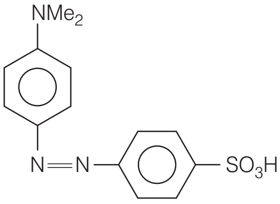
A (Major product)

Diazonium salt on treating with a N,N-dimethylaniline gives an azo compound. N, N-dimethyl aniline forms bond with N at *para*-position as amine group is a *o*, *p*-directing group.



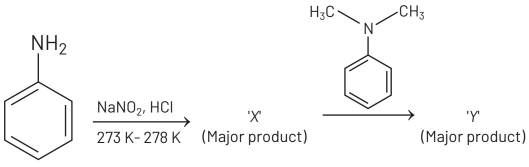
B (Major product)
(Azo compound)

Therefore, *A* is  *para*-diazosulphonic acid

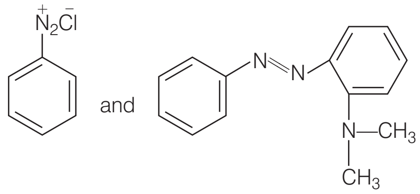
B is 

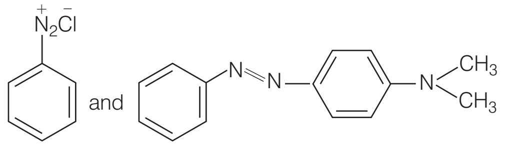
para (N,N-dimethylaminophenyl
Benzene sulphonic acid

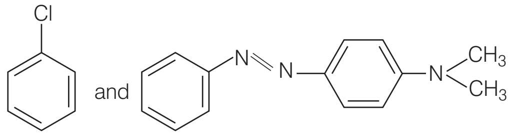
90

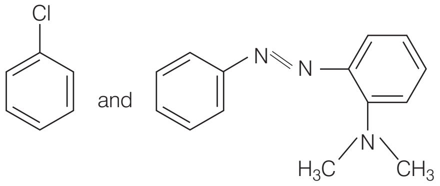


[2021, 18 March Shift-I]

(a) 

(b) 

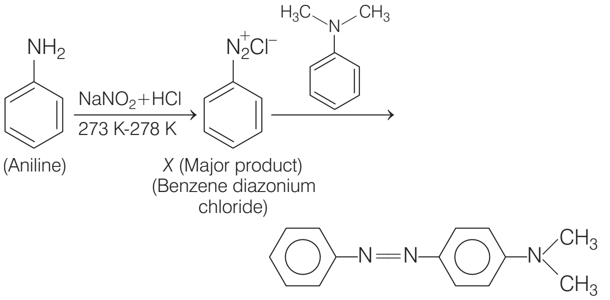
(c) 

(d) 

Ans. ***(b)***

Aniline reacts with sodium nitrite and HCl in cold condition to form benzene diazonium chloride (*X*) and on further reaction, it form azo dye (*Y*).

Chemical reactions are as follows

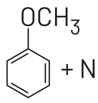


(Aniline)

X (Major product)
(Benzene diazonium
chloride)

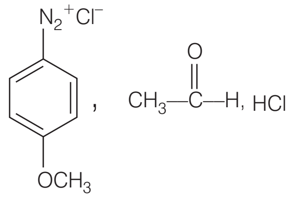
Y (Major product)
(Azo dye)

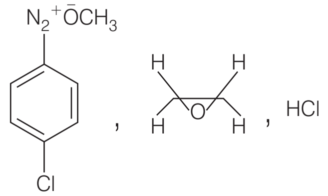
91

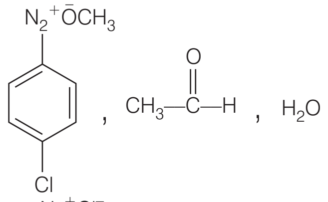
$C_7H_7N_2OCl + C_2H_5OH \longrightarrow$  $+ N_2 + X + Y$

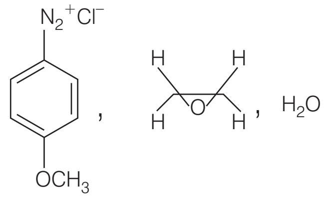
(*A*)

In the above reaction, the structural formula of (*A*), *X* and *Y* respectively are **[2021, 17 March Shift-II]**

(a) 

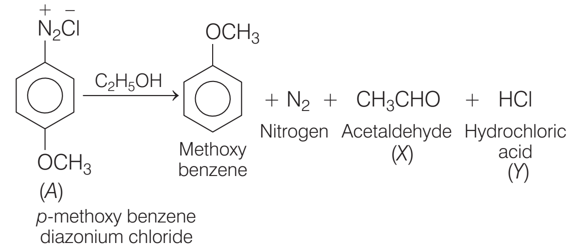
(b) 

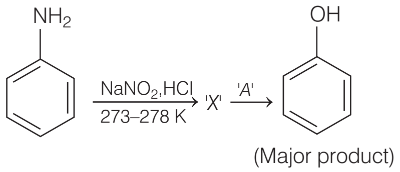
(c) 

(d) 

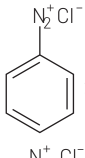
Ans. ***(a)***

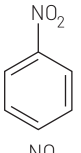
The structural formula of (*A*), *X* and *Y* are *p*-methoxy benzene diazonium chloride, acetaldehyde and hydrochloric acid respectively. Reaction involved are as follows

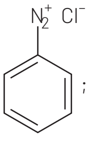


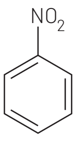
92 

In the above chemical reaction, intermediate *X* and reagent / condition *A* are **[2021, 16 March Shift-I]**

(a) X-  ; A -H_2O/NaOH

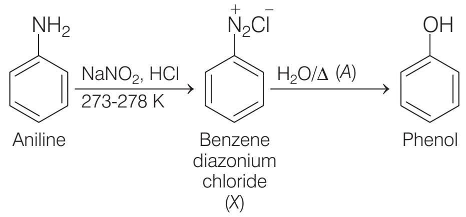
(b) X-  ; A -H_2O/Δ

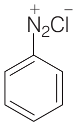
(c) X-  ; A -H_2O/Δ

(d) X-  ; A -H_2O/NaOH

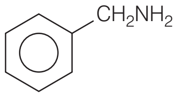
Ans. ***(c)***

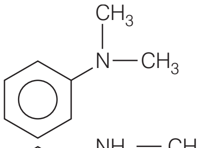
Aniline reacts with NaNO$_2$, HCl at 273-278 K to give benzene diazonium salt ($C_6H_5\overset{+}{N_2}\overset{-}{Cl} = X$) which on hydrolysis ($H_2O/\Delta$) gives phenol. Complete reaction is as follows

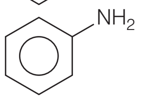


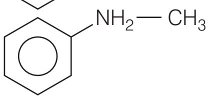
So, *X* =  and $A = H_2O/\Delta$

93 The diazonium salt of which of the following compounds will form a coloured dye on reaction with β-naphthol in NaOH ? **[2021, 24 Feb Shift-II]**

(a) 

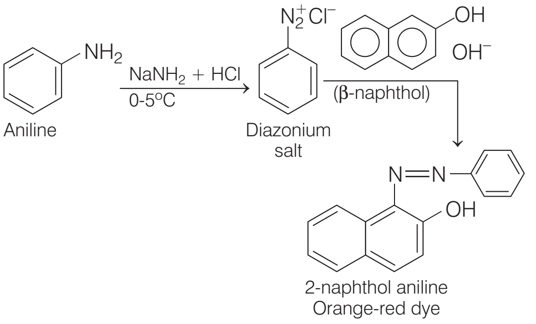
(b) 

(c) 

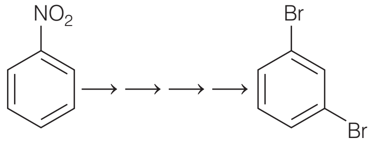
(d) 

Ans. ***(c)***

Initially aniline reacts with diazotisation reagent to form diazonium salt. Then β-naphthol react with salt and orange-red dye is obtained. So, diazonium salt of aniline is used to prepare orange-red dye.



94 What is the correct sequence of reagents used for converting nitrobenzene into *m*-dibromobenzene?



[2021, 24 Feb Shift-II]

(a) $\xrightarrow{NaNO_2} / \xrightarrow{HCl} / \xrightarrow{KBr} / \xrightarrow{H^+}$

(b) $\xrightarrow{Br_2/Fe} / \xrightarrow{Sn/HCl} / \xrightarrow{NaNO_2/HCl} / \xrightarrow{CuBr/HBr}$

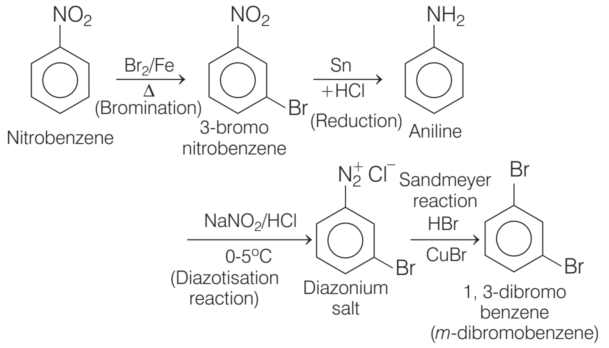
(c) $\xrightarrow{Sn/HCl} / \xrightarrow{KBr} / \xrightarrow{Br_2} / \xrightarrow{H^+}$

(d) $\xrightarrow{Sn/HCl} / \xrightarrow{Br_2} / \xrightarrow{NaNO_2} / \xrightarrow{NaBr}$

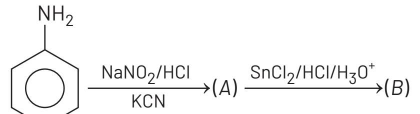
Ans. ***(b)***

In first step, NO_2 group is electron withdrawing group, it decreases the electron density in *meta* position and bromination occur in *meta* position. In second step, Sn/HCl used for reduction to convert —NO_2 to —NH_2 and form aniline. In next step, diazonium salt is formed and at last bromine replace $N_2^+Cl^-$ group to form 1, 3-dibromobenzene.

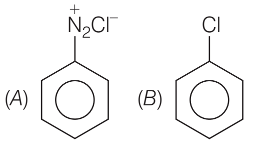
Complete reaction is as follows

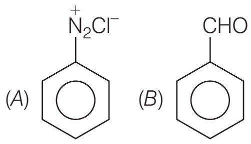


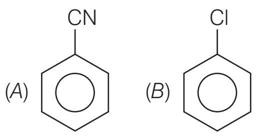
95 '*A*' and '*B*' in the following reaction are

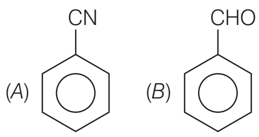


[2021, 24 Feb Shift-I]

(a)


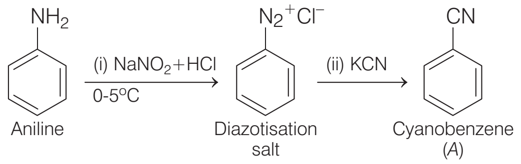
(b)


(c)


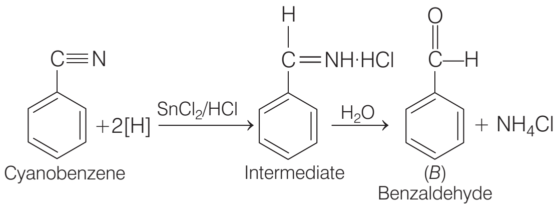
(d)


Ans. ***(d)***

Step 1 In step 1, $NaNO_2$ + HCl, 0-5°C used for diazotisation reaction. It will form diazonium salt. Further, it will react with KCN to form cyanobenzene.



Step 2 In step 2, $SnCl_2$ and HCl is a Stephen's reduction reagent. Cyanobenzene reduced to benzaldehyde by $SnCl_2$/HCl.



96 Three isomers A, B and C (molecular formula $C_8H_{11}N$) give the following results :

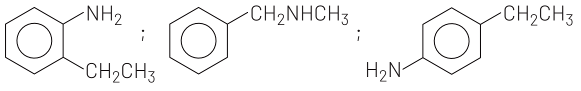
$$A \text{ and } C \xrightarrow{\text{Diazotisation}}$$

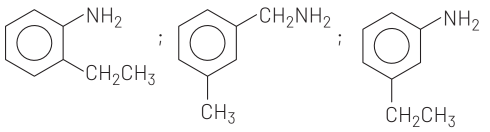
$$P+Q \xrightarrow[\text{(ii) Oxidation (KMnO}_4+\text{H}^+)]{\text{(i) Hydrolysis}} \begin{array}{c} R\,(\text{product of } A) \\ + \\ S\,(\text{product of } C) \end{array}$$

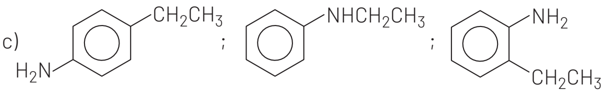
R has lower boiling point than S.

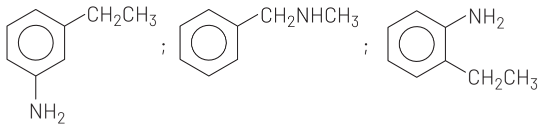
$$B \xrightarrow{C_6H_5SO_2Cl} \text{alkali-insoluble product.}$$

A, B and C, respectively are **[2020, 3 Sep Shift-II]**

(a)


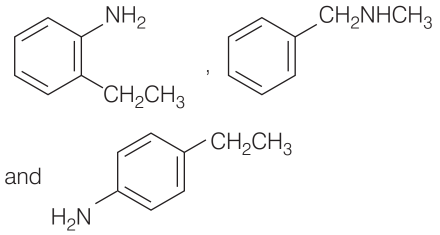
(b)


(c)


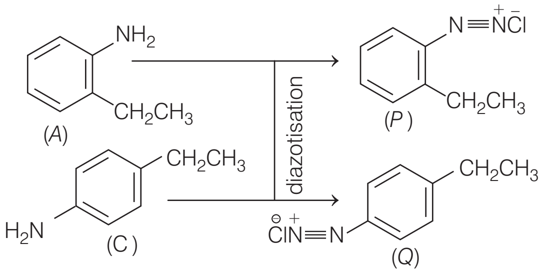
(d)


Ans. ***(a)***

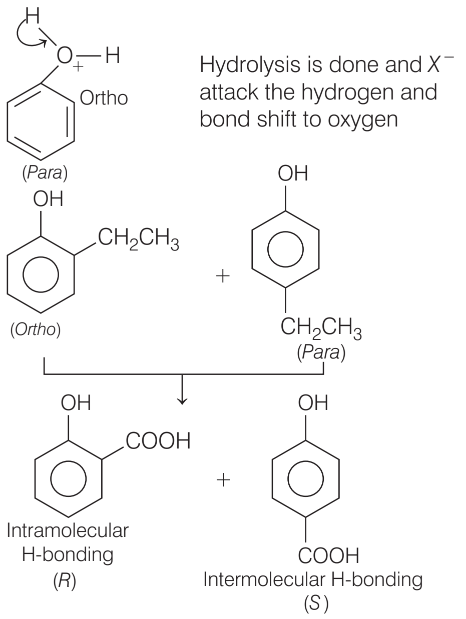
A, *B* and *C* respectively are



According to the question, *A* and *C* undergoes diazotisation to give *P* and *Q*. So, amine must be primary aromatic amine.



Which on hydrolysis followed by oxidation gives alcohol derivative.



Hydrolysis is done and X^- attack the hydrogen and bond shift to oxygen

Given, R has low boiling point than S. Intramolecular H-bond is weaker than intermolecular H-bond.

It means intramolecular H-bonding show low boiling point and here, R is *ortho* product and S is *para* product.

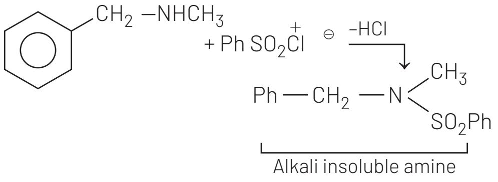
$$\text{Given, }(B)\xrightarrow{C_6H_5SO_2Cl}\text{alkali-insoluble product}$$

$C_6H_5SO_2Cl$ act as electrophile then B must be amine.

Secondary amine act as a nucleophile.

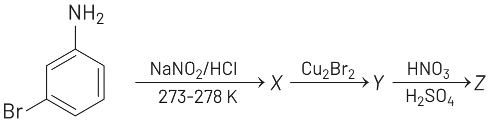
The $C_6H_5SO_2Cl$ act as electrophile and displace Cl.

In the given option (b), secondary amine is present in the reaction takes place as follows :

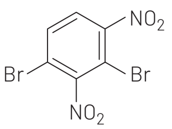


Primary and secondary amine forms poorly soluble ppt. on reaction with $PhSO_2Cl$.

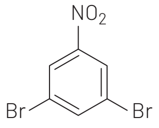
97 The major product Z obtained in the following reaction scheme is **[2020, 9 Jan Shift-I]**



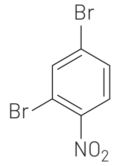
(a)



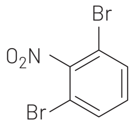
(b)



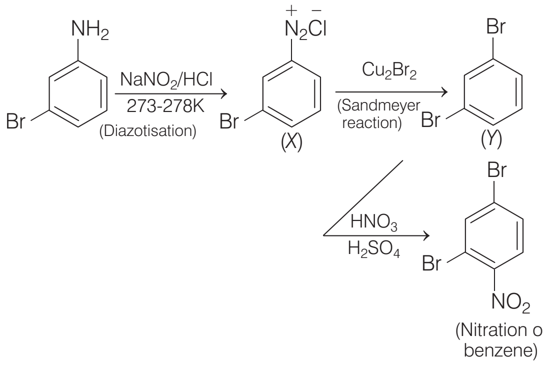
(c)



(d)



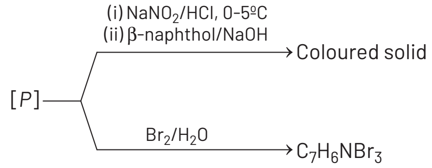
Ans. ***(c)***



Br is *o*, *p*-directing group.

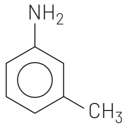
∴ NO_2 is attached at the *ortho* position of one of the Br atoms which is also *para* position with respect to the other Br atom.

98 Consider the following reactions :

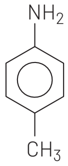


The compound [P] is **[2020, 9 Jan Shift-II]**

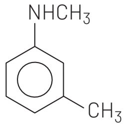
(a)



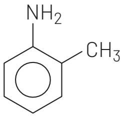
(b)



(c)

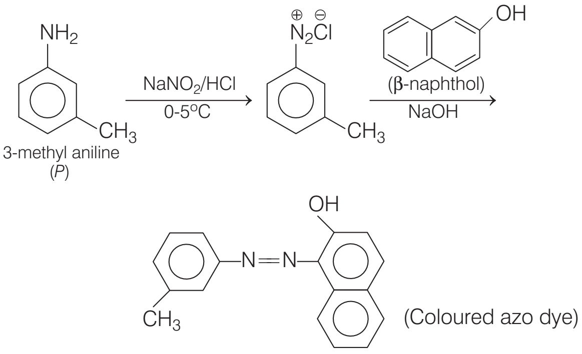


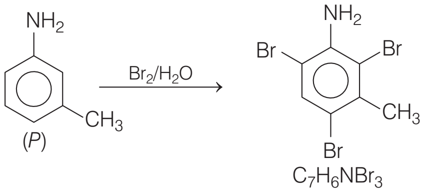
(d)



Ans. ***(a)***

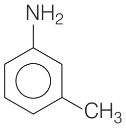
Compound [P] is 3-methylaniline.
Complete reaction is as follows :





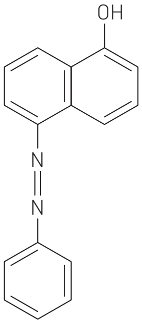
On comparing the formula $C_7H_6NBr_3$ with the formula of *m*-methylaniline (C_7H_9N), it is noticed that, three H atoms are substituted with three Br atoms (tribromination). To get a tribrominated product, all three activated positions of aniline (2 *ortho* and one *para*) must be free, where Br can come.

Then, it can be concluded that the methyl group must be at *meta*-position only.

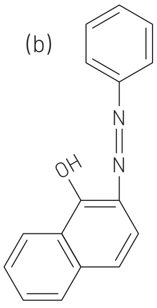


99 Coupling of benzene diazonium chloride with 1-naphthol in alkaline medium will give **[2019, 8 April Shift-I]**

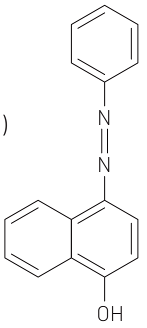
(a)



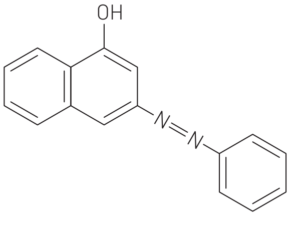
(b)



(c)

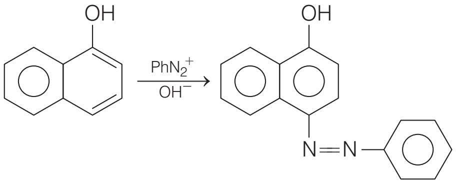


(d)



Ans. ***(c)***

Coupling of benzene diazonium chloride with 1-naphthol in alkaline medium will give the following coupling reaction.



In the presence of $\bar{O}H$ ion, $Ar\overset{+}{N}_2$ exists in equilibrium with an unionised compound (Ar — N = N — OH) and salts [ArN = N$^+$]$^-$ —$\overset{\ominus}{O}$H derived from it, which do not couple.

$$[Ar-N\equiv N]^+\overset{\ominus}{O}H \underset{H^+}{\overset{NaOH}{\rightleftharpoons}} \underset{\text{Does not couple}}{Ar-N=N-OH}$$

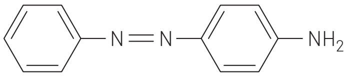
$$\underset{H^+}{\overset{NaOH}{\rightleftharpoons}} \underset{\text{Does not couple}}{Ar-N=N-\overset{-}{O}\overset{+}{Na}}$$

Following conditions are very useful for coupling reaction to take place.

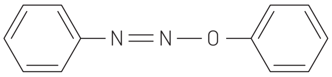
(a) The solution must be so alkaline that the concentration of diazonium ion is too low.
(b) It must not be so acidic that the concentration of free phenoxide ion is too low.

100 Aniline dissolved in dil. HCl is reacted with sodium nitrite at 0°C. This solution was added dropwise to a solution containing equimolar mixture of aniline and phenol in dil. HCl. The structure of the major product is **[2019, 9 April Shift-I]**

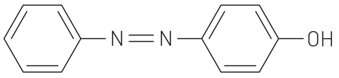
(a)



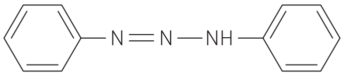
(b)



(c)

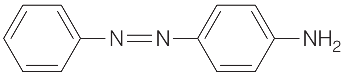


(d)



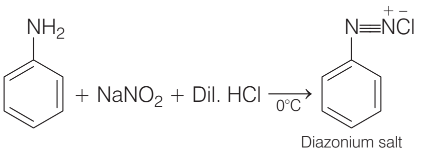
Ans. ***(a)***

Major product of the reaction is

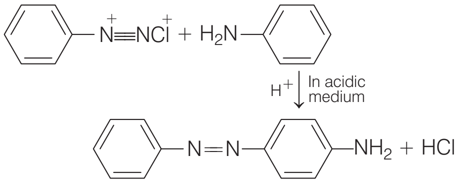


It is obtained by coupling reaction.

Reaction of aniline with dil. HCl and sodium nitrite at 0°C is shown below :



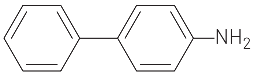
Diazonium salt formed when added to equimolar mixture of aniline and phenol in dil. HCl then aniline couples with diazonium salt. Reaction is as follows :

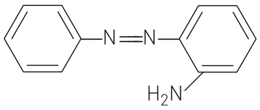


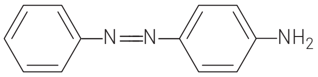
For an effective coupling, the solution must be so alkaline that the concentration of diazonium ion is too low. It must not be so acidic that the concentration of free amine or phenoxide ion is too low. That is why amines couple fastest in mild acidic solution and phenols couple fastest in mild alkaline solution.

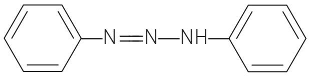
101 Benzene diazonium chloride on reaction with aniline in the presence of dilute hydrochloric acid gives

[2019, 12 April Shift-II]

(a) 

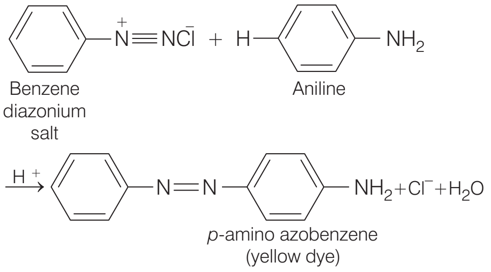
(b) 

(c) 

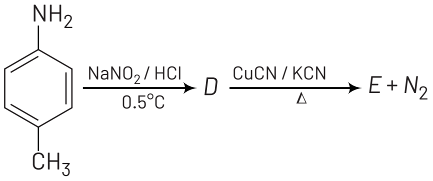
(d) 

Ans. ***(c)***

Benzene diazonium chloride on reaction with aniline in the presence of dilute hydrochloric acid undergoes coupling reaction and produces *p*-amino azobenzene. In this reaction, benzene diazonium chloride reacts with aniline in which aniline molecule at its *para*-position is coupled with diazonium salt to give *p*-amino azobenzene (yellow dye).

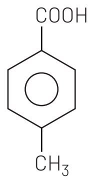


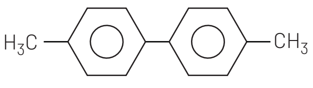
102 In the reaction,

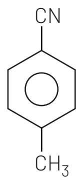


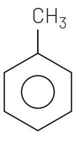
The product *E* is

[JEE Main 2015]

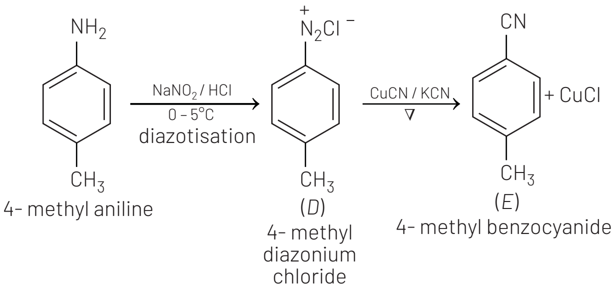
(a) 

(b) 

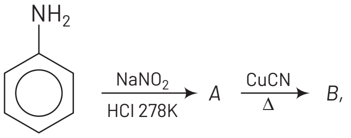
(c) 

(d) 

Ans. ***(c)***



103 In the chemical reaction,



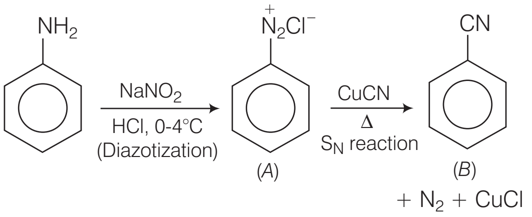
compounds *A* and *B* respectively are

[AIEEE 2011]

(a) fluorobenzene and phenol
(b) benzene diazonium chloride and benzonitrile
(c) nitrobenzene and chlorobenzene
(d) phenol and bromobenzene

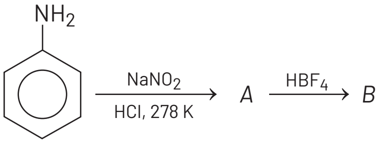
Ans. ***(b)***

Formation of *A* is by diazotisation and formation of *B* from *A* is by S_N reaction. Thus, the complete series of reaction is given by



104 In the chemical reaction,

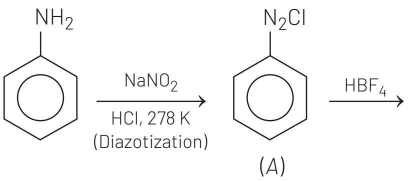
[AIEEE 2010]

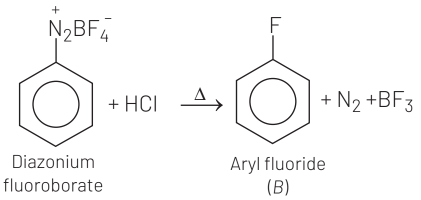


the compounds '*A*' and '*B*' respectively are

(a) nitrobenzene and fluorobenzene
(b) phenol and benzene
(c) benzene diazonium chloride and fluorobenzene
(d) nitrobenzene and chlorobenzene

Ans. ***(c)***



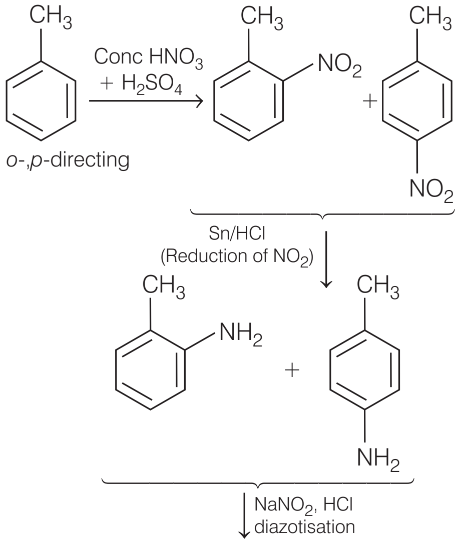


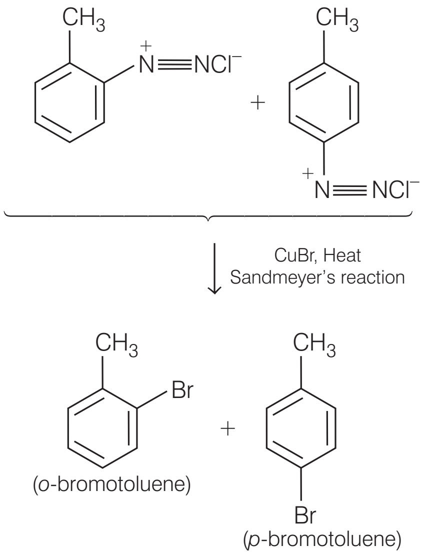
The reaction of diazonium chloride with fluoroboric acid (HBF_4) is called Balz-Schiemann reaction.

105 Toluene is nitrated and the resulting product is reduced with tin and hydrochloric acid. The product so obtained is diazotised and then heated with cuprous bromide. The reaction mixture so formed contains **[AIEEE 2008]**

(a) mixture of *o*-and *p*-bromotoluenes
(b) mixture of *o*-and *p*-dibromobenzenes
(c) mixture of *o*-and *p*-bromoanilines
(d) mixture of *o*-and *m*-bromotoluenes

Ans. ***(a)***





106 Fluorobenzene (C_6H_5F) can be synthesized in the laboratory **[AIEEE 2006]**

(a) by heating phenol with HF and KF
(b) from aniline by diazotisation followed by heating the diazonium salt with HBF_4
(c) by direct fluorination of benzene with F_2 gas
(d) by reacting bromobenzene with NaF solution

Ans. ***(b)***