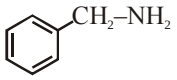
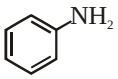
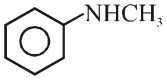
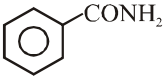
AMINES

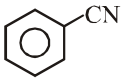
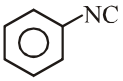
1. The total number of amines among the following which can be synthesized by Gabriel synthesis is _____.

(A) $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH–CH_2–NH_2$ (B) $CH_3CH_2NH_2$

(C)  (D) 

2. 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?

(1)  (2) 

(3)  (4) 

3. An amine on reaction with benzenesulphonyl chloride produces a compound insoluble in alkaline solution. This amine can be prepared by ammonolysis of ethyl chloride. The correct structure of amine is :

(1) 

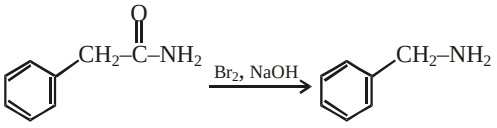
(2) $CH_3CH_2NH_2$

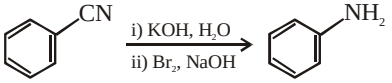
(3) $CH_3CH_2CH_2NHCH_3$

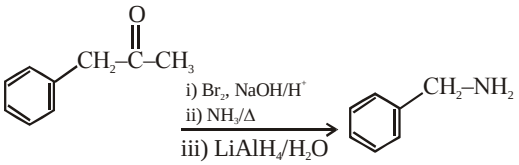
(4) $CH_3CH_2CH_2\underset{\underset{H}{|}}{N}-CH_2CH_3$

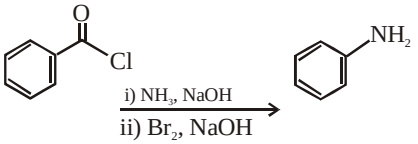
4. 1.86 g of aniline completely reacts to form acetanilide. 10% of the product is lost during purification. Amount of acetanilide obtained after purification (in g) is _____ $\times 10^{-2}$.

5. Which of the following reaction DOES NOT involve Hoffmann Bromamide degradation ?

(1) 

(2) 

(3) 

(4) 

6. 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 :

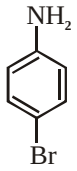
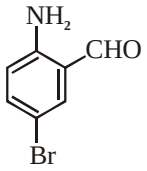
(1) to remove basic impurities

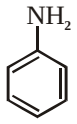
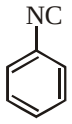
(2) to activate NH_3 used in the reaction

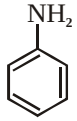
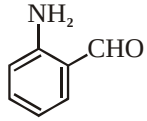
(3) to remove acidic impurities

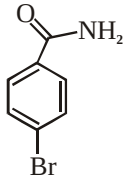
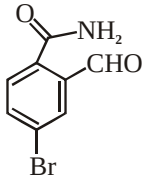
(4) to increase the reactivity of alkyl halide

7. Hoffmann bromomide degradation of benzamide gives product A, which upon heating with $CHCl_3$ and NaOH gives product B. The structures of A and B are :

(1) A -  B - 

(2) A -  B - 

(3) A -  B - 

(4) A -  B - 

8. Which of the following reaction is an example of ammonolysis?

(1) $C_6H_5COCl + C_6H_5NH_2 \longrightarrow C_6H_5CONHC_6H_5$

(2) $C_6H_5CH_2CN \xrightarrow{[H]} C_6H_5CH_2CH_2NH_2$

(3) $C_6H_5NH_2 \xrightarrow{HCl} C_6H_5\overset{+}{N}H_3Cl^-$

(4) $C_6H_5CH_2Cl + NH_3 \longrightarrow C_6H_5CH_2NH_2$

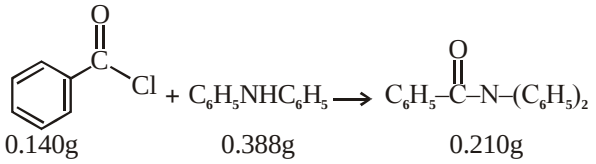
9. Primary, secondary and tertiary amines can be separated using :-

(1) Para-Toluene sulphonyl chloride

(2) Chloroform and KOH

(3) Benzene sulphonic acid

(4) Acetyl amide

10. 

0.140g 0.388g 0.210g

Consider the above reaction. The percentage yield of amide product is _____. (Round off to the Nearest Integer).

(Given : Atomic mass : C : 12.0 u, H : 1.0u, N : 14.0 u, O : 16.0 u, Cl : 35.5 u)

11. A reaction of 0.1 mole of Benzylamine with bromomethane gave 23 g of Benzyl trimethyl ammonium bromide. The number of moles of bromomethane consumed in this reaction are $n \times 10^{-1}$, when n = _____. (Round off to the Nearest Integer).

(Given : Atomic masses : C : 12.0 u, H : 1.0 u, N : 14.0 u, Br : 80.0 u]

12. In the reaction of hypobromite with amide, the carbonyl carbon is lost as :

(1) CO_3^{2-} (2) HCO_3^- (3) CO_2 (4) CO

13. An organic compound "A" on treatment with benzene sulphonyl chloride gives compound B. B is soluble in dil. NaOH solution. Compound A is :

(1) C_6H_5–N–$(CH_3)_2$ (2) C_6H_5–$NHCH_2CH_3$

(3) C_6H_5–CH_2 $NHCH_3$ (4) C_6H_5–CH(–CH_3)–NH_2

14. 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 :

(1) primary amine, nitrile compound, conc. HCl

(2) secondary amine, isonitrile compound, conc. NaOH

(3) primary amine, isonitrile compound, conc. HCl

(4) secondary amine, nitrile compound, conc. NaOH

15. 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:

(1) Both **(A)** and **(R)** true but **(R)** is not the correct explanation of **(A)**.

(2) **(A)** is false but **(R)** is true.

(3) Both **(A)** and **(R)** true and **(R)** is correct explanation of **(A)**.

(4) **(A)** is true but **(R)** is false.

16. Which one of the following compounds will liberate CO_2, when treated with $NaHCO_3$?

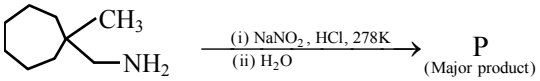
(1) $(CH_3)_3\overset{\oplus}{N}H\overset{\ominus}{Cl}$

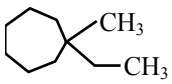
(2) $(CH_3)_4\overset{\oplus\ominus}{N}OH$

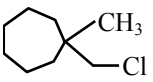
(3) $CH_3 - \overset{O}{\overset{\|}{C}} - NH_2$

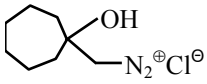
(4) CH_3NH_2

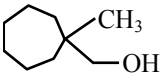
17. What is the major product "P" of the following reaction ?



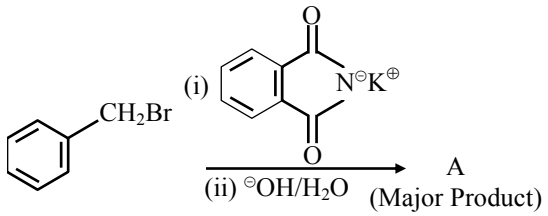
(1) 

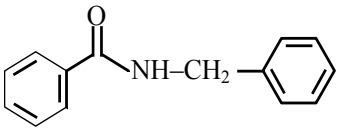
(2) 

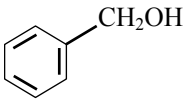
(3) 

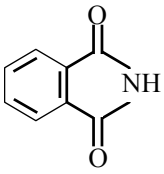
(4) 

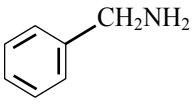
18. What is A in the following reaction ?

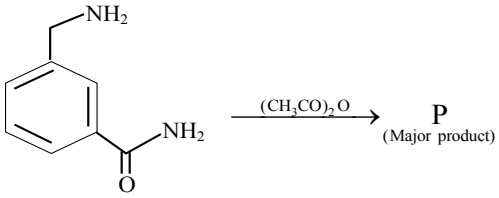


(1) 

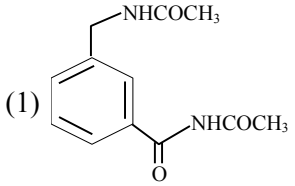
(2) 

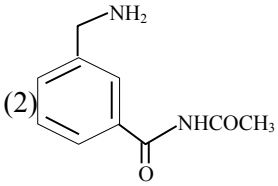
(3) 

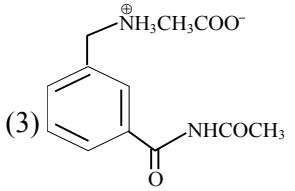
(4) 

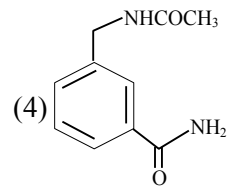
19. 

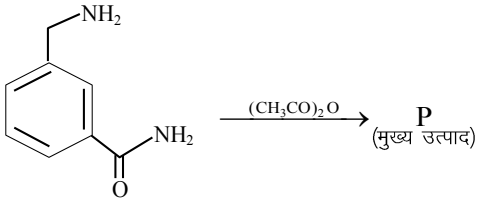
The major product in the above reaction is :

(1) 

(2) 

(3) 

(4) 



20. Which of the following is **not** a correct statement for primary aliphatic amines?

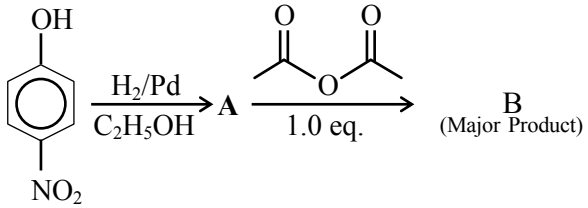
(1) The intermolecular association in primary amines is less than the intermolecular association in secondary amines.

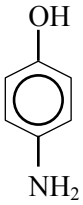
(2) Primary amines on treating with nitrous acid solution form corresponding alcohols except methyl amine.

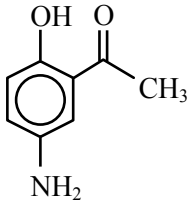
(3) Primary amines are less basic than the secondary amines.

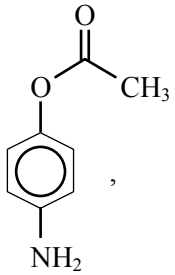
(4) Primary amines can be prepared by the Gabriel phthalimide synthesis.

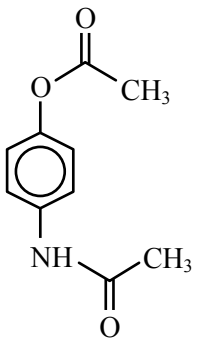
21. The correct structures of **A** and **B** formed in the following reactions are :

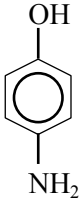


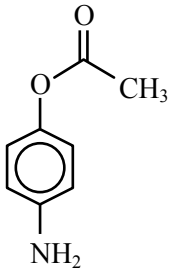
(1) **A** : 

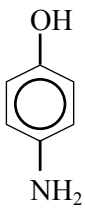
, **B** : 

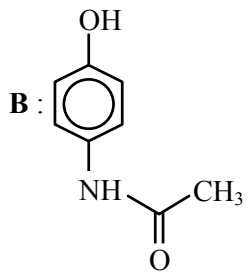
(2) **A** : 

, **B** : 

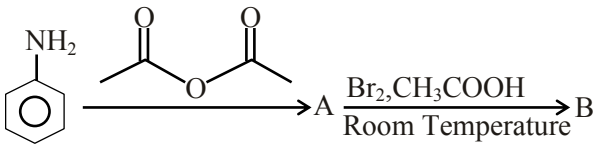
(3) **A** : 

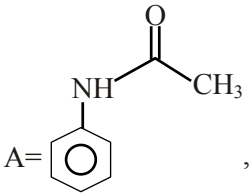
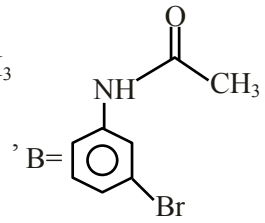
, **B** : 

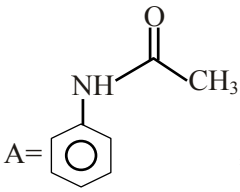
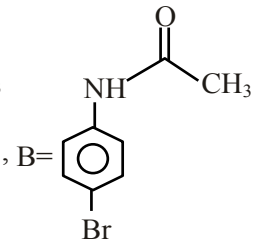
(4) **A** : 

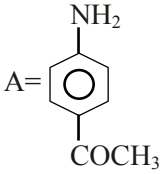
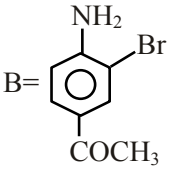
, **B** : 

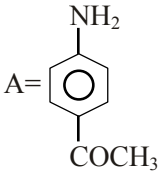
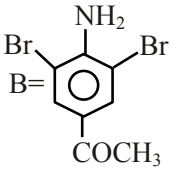
22. The major products A and B formed in the following reaction sequence are :



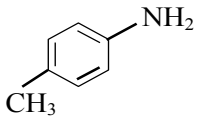
(1)  , 

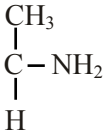
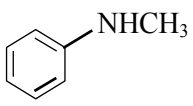
(2)  , 

(3)  , 

(4)  , 

23. Which one of the following gives the most stable Diazonium salt ?

(1) $CH_3–CH_2–CH_2–NH_2$ (2) 

(3)  (4) 

SOLUTION

1. Official Ans. by NTA (3)

Sol. Gabriel phthalimide synthesis is used to prepare 1° aliphatic/alicyclic amine in common.

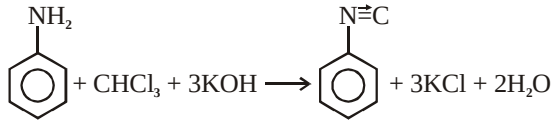
Hence amine which can synthesised by Gabriel phthalimide synthesis method is :

(A) $Me_2CH–CH_2–NH_2$ (B) $CH_3CH_2NH_2$

(C) $Ph–CH_2–NH_2$

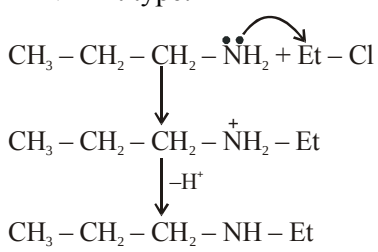
2. Official Ans. by NTA (4)

Sol. CARBYL amine given by 1° amine



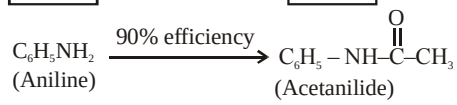
3. Official Ans. by NTA (4)

Sol. It has to be 2° amine because on reaction with benzene sulphonylchloride it gives water in soluble product. As it is formed by ammonolysis of ethylchloride, so it has to be R–NH–Et type.



4. Official Ans. by NTA (243)

Sol. $\boxed{M = 98}$ $\boxed{M = 135}$



Given 1.86 g

$\Rightarrow$ 1 mol $C_6H_5NH_2$ give 1 mol $C_6H_5NHCCH_3$ (O)

$\therefore$ moles of $C_6H_5NH_2$ = moles of $C_6H_5NHCCH_3$ (O)

$$\Rightarrow \frac{1.86}{93} = \frac{W_{acetanilide}}{135}$$

$$\Rightarrow W_{acelanilide} = \frac{1.86\times135}{93}g = 2.70g$$

But efficiency of reaction is 90% only

$$\therefore \text{Mass of acetanilide produced} = 2.70\times\frac{90}{100}g$$

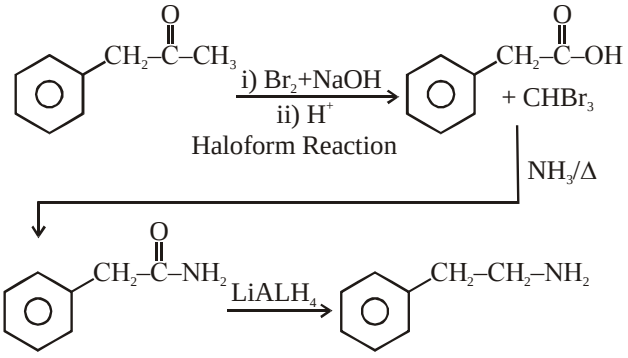
$= 2.43$ g

$= 243 \times 10^{-2}$g

$\Rightarrow x = 243$

5. Official Ans. by NTA (3)

Sol.

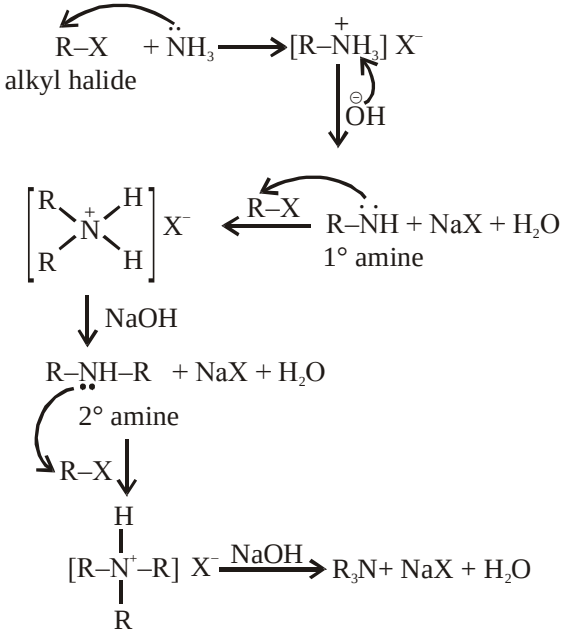


$\Rightarrow$ This reaction does not involve haffmann bromanide degradation.

$\Rightarrow$ Rest all options involve haffmann bromamide degradation during the reaction of Br_2+NaOH with amide.

6. Official Ans. by NTA (3)

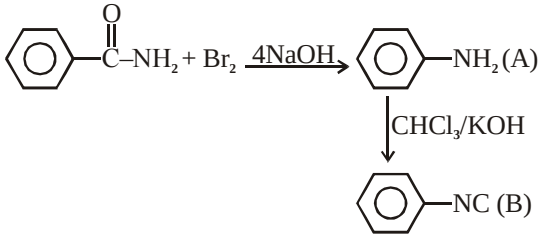
Sol.



So the purpose of NaOH in the above reactions in to remove acidic impurities.

7. Official Ans. by NTA (2)

Sol. Hoffmann bromamide degradation reaction :



Carbylamine reaction :

8. Official Ans. by NTA (4)

Sol. The process of cleavage of the C–X bond by Ammonia molecule is known as ammonolysis.

Ex : $R–CH_2–Cl + \ddot{N}H_3 \longrightarrow R–CH_2–NH_2$

9. Official Ans. by NTA (1)

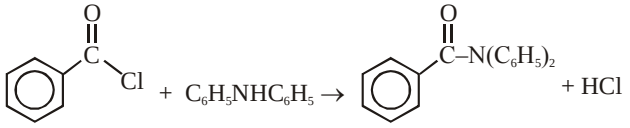
Sol. Primary amines react with Para Toluene sulfonyl chloride to form a precipitate that is soluble in NaOH.

Secondary amines reacts with para toluene sulfonyl chloride to give a precipitate that is insoluble in NaOH.

Tertiary amines do not react with para toluen.

10. Official Ans. by NTA (77)

Sol.



1 mole	1 mole	1 mole
= 140.5 gm	= 169 gm	= 273 gm

$\therefore$ 0.140 gm $\quad \frac{169}{140.5}\times 0.140$

L.R. $= 0.168 \text{ gm} < 0.388 \text{ gm}$

excess

$\therefore$ Theoretical amount of given product formed

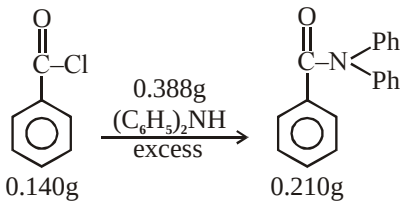
$$= \frac{273}{140.5}\times 0.140 = 0.272\text{gm}$$

But its actual amount formed is 0.210 gm.

Hence, the percentage yield of product.

$$= \frac{0.210}{0.272}\times 100 = 77.20 \approx 77$$

OR



Mole of $Ph - CoCl = \frac{0.140}{140} = 10^{-3}$mol

Mole of $Ph–\overset{\overset{O}{\|}}{C}–N(Ph)_2$, that should be obtained by mol-mol analysis = 10^{-3} mol.

Theoritical mass of product

$= 10^{-3} \times 273 = 273 \times 10^{-3}$g

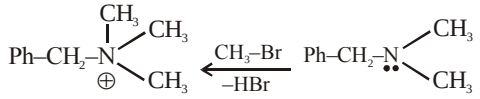
Observed mass of product = 210×10^{-3}g

$$\%\text{yield of product} = \frac{210\times 10^{-3}}{273\times 10^{-3}}\times 100 = 76.9\% = 77$$

11. Official Ans. by NTA (3)

Sol. $Ph–CH_2–NH_2 \xrightarrow[-HBr]{CH_3–Br} Ph–CH_2–\ddot{N}H–CH_3$

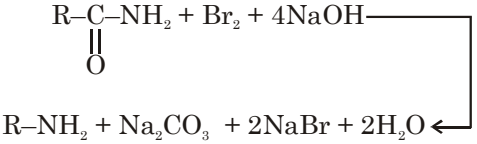
$\xrightarrow{-HBr}$ (with $CH_3–Br$)



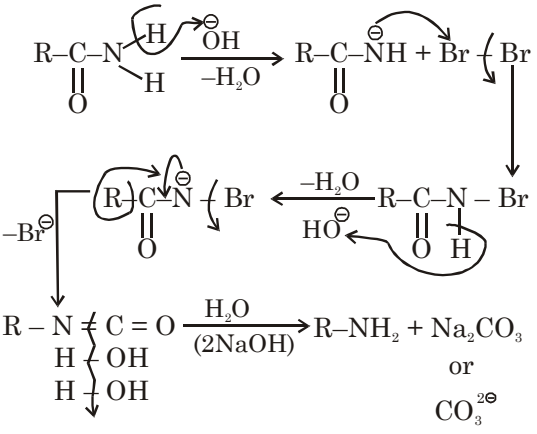
no of moles = 3

12. Official Ans. by NTA (1)

Sol.

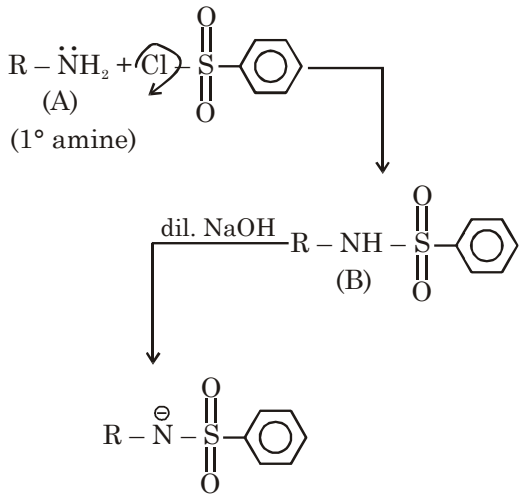


Mechanism



13. Official Ans. by NTA (4)

Sol. Hinsberg reagent (Benzene sulphonyl chloride) gives reaction product with 1° amine and it is soluble in dil. NaOH.



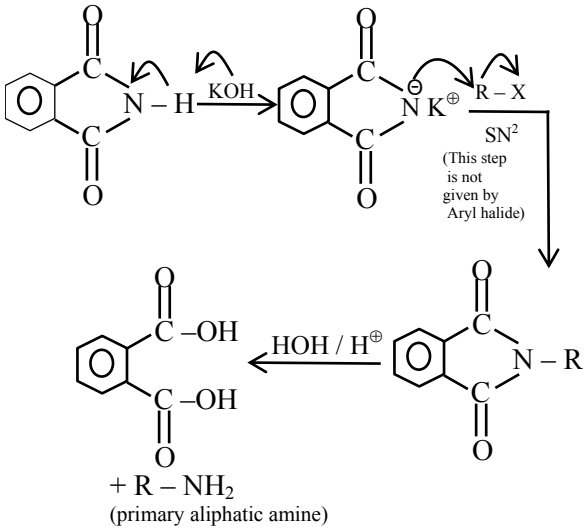
14. Official Ans. by NTA (3)

Sol. $R–NH_2 \xrightarrow{CHCl_3} R–N\equiv C \xrightarrow[(HCl)]{H_3O^{\oplus}} R\text{-}NH_2 + HCOOH$

1° amine (A) (Isonitrile) (B) (C)

15. Official Ans. by NTA (3)

Sol. Gabriel pthalamide synthesis



16. Official Ans. by NTA (1)

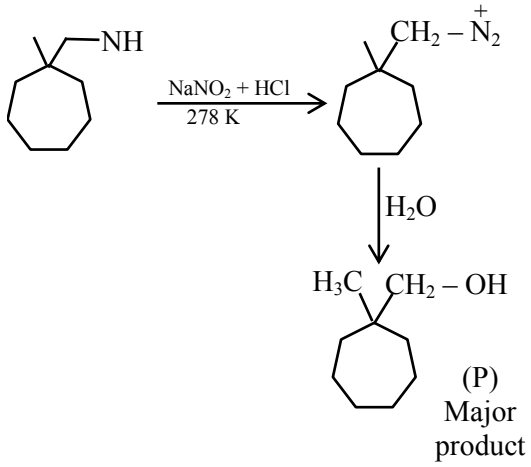
Sol. $(CH_3)_3\overset{\oplus}{N}H\overset{\ominus}{Cl} + NaHCO_3 \longrightarrow H_2CO_3 + (CH_3)_3N + NaCl$

$\downarrow$

$CO_2 + H_2O$

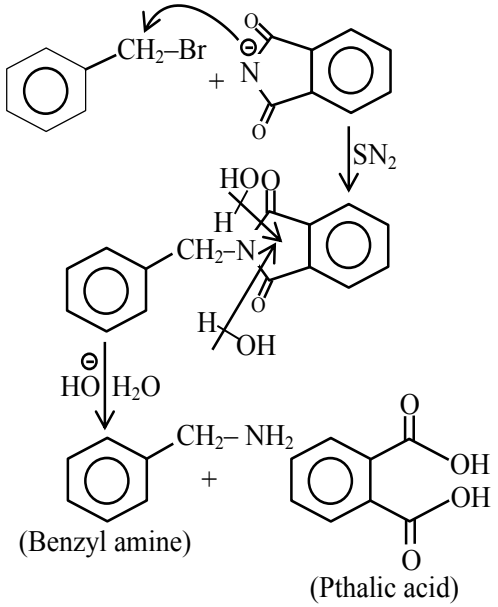
17. Official Ans. by NTA (4)

Sol.



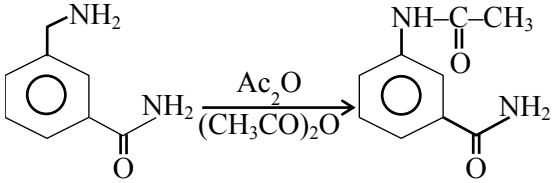
18. Official Ans. by NTA (4)

Sol.



19. Official Ans. by NTA (4)

Sol.

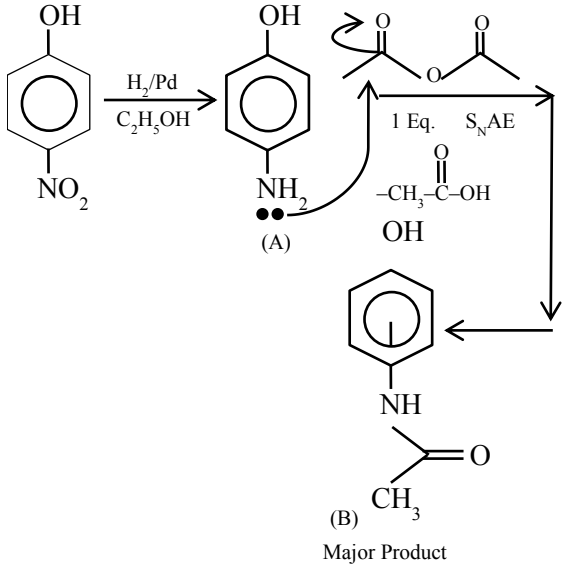


20. Official Ans. by NTA (1)

Sol. The intermolecular association is more prominent in case of primary amines as compared to secondary, due to the availability of two hydrogen atom.

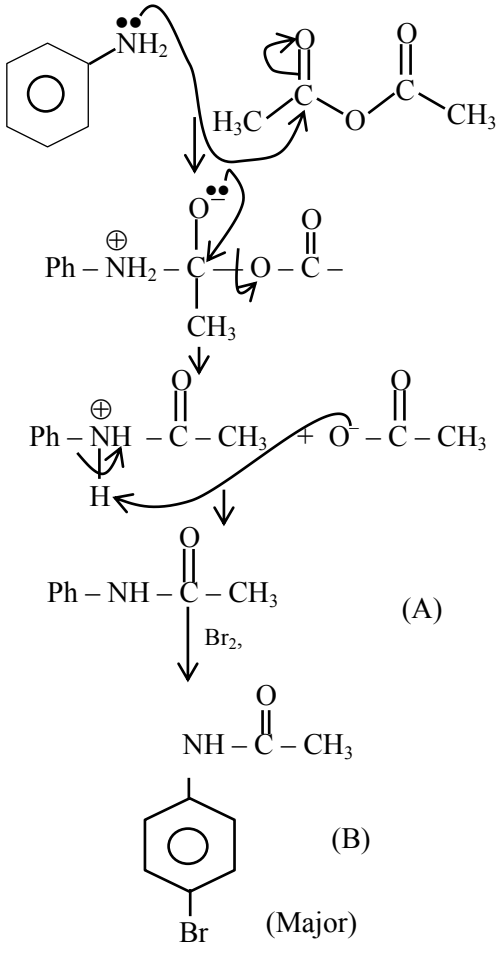
21. Official Ans. by NTA (4)

Sol.



22. Official Ans. by NTA (2)

Sol.



23. Official Ans. by NTA (2)

Sol. (1) $NH_2 \xrightarrow{NaNO_2+HCl} N\equiv N^+$

(2) H_3C–Ph–$NH_2 \xrightarrow{NaNO_2+HCl}$ Ph(H_3C)–$N\equiv N^+$ (Most stable) +H-effect

(3) $CH_3-CH(CH_3)-NH_2 \xrightarrow{NaNO_2+HCl} H_3C-CH(CH_3)-N\equiv N^+$

(4) Ph–NH–$CH_3 \xrightarrow{NaNO_2+HCl}$ Diazonium salt not form

Ph–NH–$CH_3 \xrightarrow{NaNO_2+HC}$ Ph–N(CH_3)–N=O (N, alkyl nitroso amine)