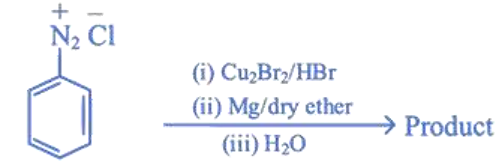
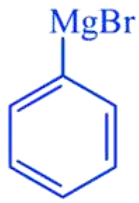
Amines

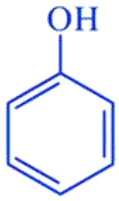
1. Identify the product in the following reaction: **(2023)**



(a) 

(b) 

(c) 

(d) 

2. Which of the following reaction will NOT give primary amine as the product? **(2023)**

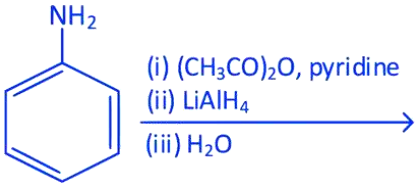
(a) $CH_3CN \xrightarrow[(ii)\ H_3O^{\oplus}]{(i)\ LiAlH_4}$ Product

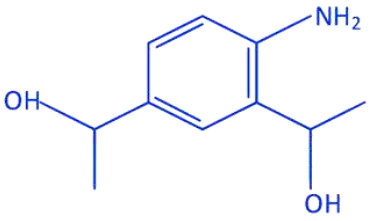
(b) $CH_3NC \xrightarrow[(ii)\ H_3O^{\oplus}]{(i)\ LiAlH_4}$ Product

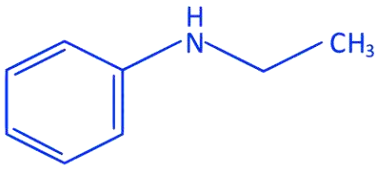
(c) $CH_3CONH_2 \xrightarrow[(ii)\ H_3O^{\oplus}]{(i)\ LiAlH_4}$ Product

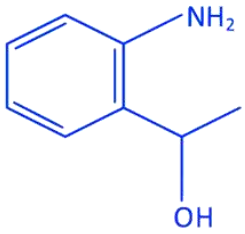
(d) $CH_3CONH_3 \xrightarrow{Br_2/KOH}$ Procuct

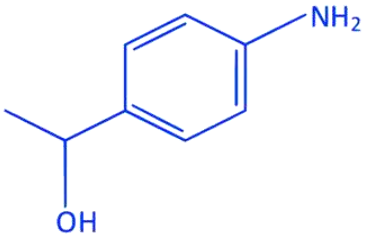
3. The product formed from the following reaction sequence is: **(2022)**



(a) 

(b) 

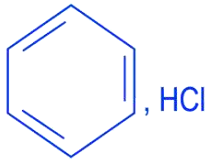
(c) 

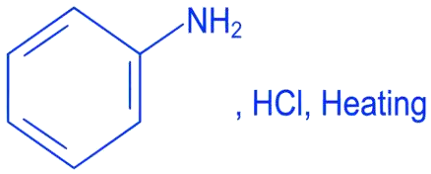
(d) 

4. Which of the following sequence of reactions is suitable to synthesize chlorobenzene? **(2022)**

(a) Benzene, Cl_2, anhydrous $FeCl_3$

(b) Phenol, $NaNO_2$, HCl, CuCl

(c) 

(d) 

5. Given below are two statements.

Statement I: Primary aliphatic amines react with HNO_2 to give unstable diazonium salts.

Statement II: Primary aromatic amines react with HNO_2 to form diazonium salts which are stable even above 300 K.

In the light of the above statements, choose the most appropriate answer from the options given below. **(2022)**

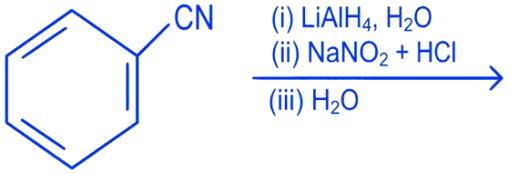
(a) Both Statement I and Statement II are correct.

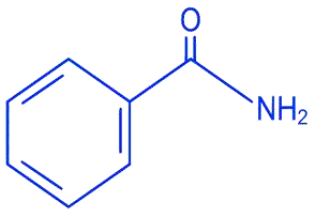
(b) Both Statement I and Statement II are incorrect.

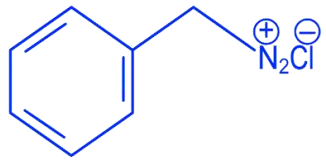
(c) Statement I is correct but Statement II is incorrect.

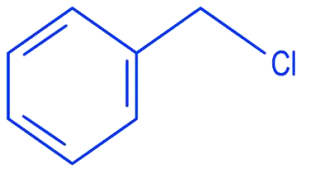
(d) Statement I is incorrect but Statement II is correct.

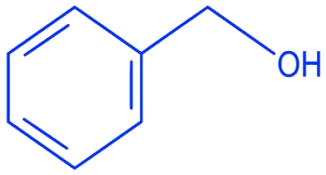
6. The product formed from the following reaction sequence is **(2022)**



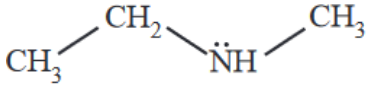
(a) 

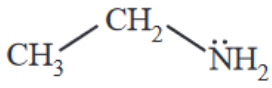
(b) 

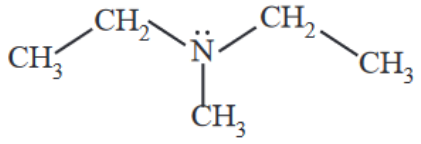
(c) 

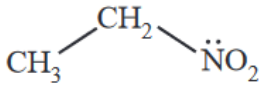
(d) 

7. Identify the compound that will react with Hinsberg's reagent to give a solid which dissolves in alkali. **(2021)**

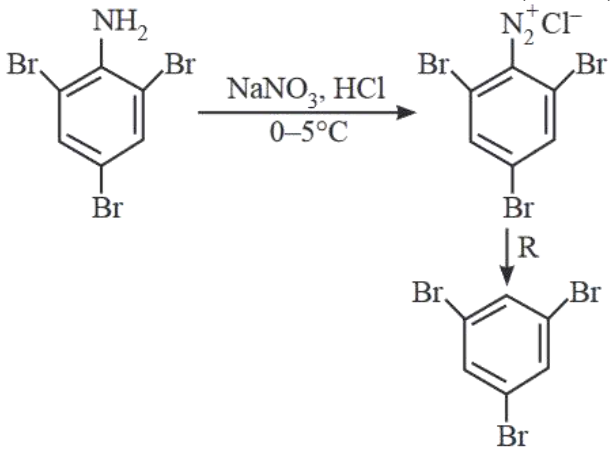
(a) 

(b) 

(c) 

(d) 

8. The reagent 'R' in the given sequence of chemical reaction is: **(2021)**



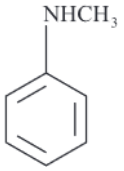
(a) CH_3CH_2OH

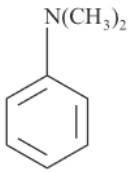
(b) HI

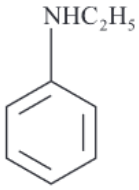
(c) CuCN/KCN

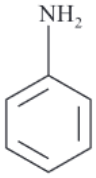
(d) H_2O

9. Which of the following amine will give the carbylamine test? **(2020)**

(a) 

(b) 

(c) 

(d) 

10. Reaction of propenamide with ethanolic sodium hydroxide and bromine will give **(2020 Covid Re-NEET)**

(a) Methylamine

(b) Propylamine

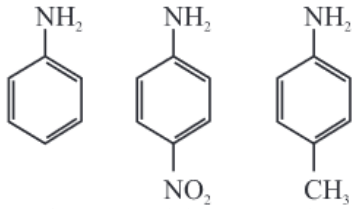
(c) Aniline

(d) Ethylamine

11. The correct order of the basic strength of methyl substituted amines in aqueous solution is: **(2019)**
    (a) $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N$
    (b) $(CH_3)_3N > CH_3NH_2 > (CH_3)_2NH$
    (c) $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2$
    (d) $CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$

12. Nitration of aniline in strong acidic medium also gives m-nitroaniline because: **(2018)**
    (a) Inspite of substituents nitro group always goes to only m-position.
    (b) In electrophilic substitution reactions, amino group is meta directive.
    (c) In acidic (strong) medium, aniline is present as anilinium ion.
    (d) Inabsence of substituents nitro group always goes tom-position.

13. The correct increasing order of basic strength for the following compounds is: **(2017-Delhi)**

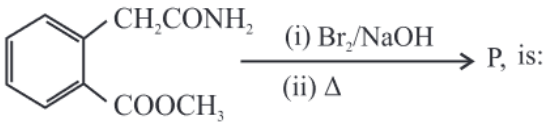


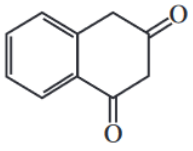
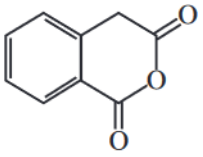
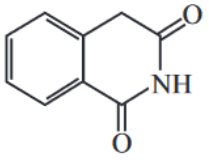
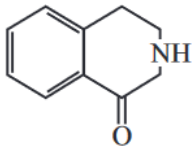
    (a) II < I < III
    (b) II < III < I
    (c) III < I < II
    (d) III < II < I

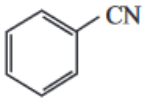
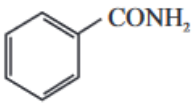
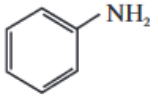
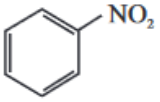
14. Which of the following reactions is appropriate for converting acetamide to methanamine? **(2017-Gujarat)**
    (a) Gabriel phthalimide synthesis
    (b) Carbylamine reaction
    (c) Hoffman bromamide reaction
    (d) Stephens reaction

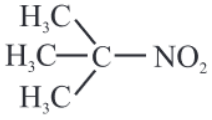
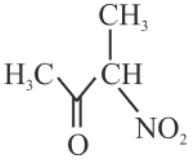
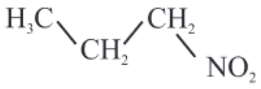
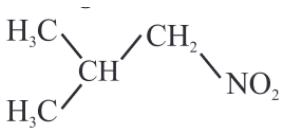
15. The reaction: $ArN_2Cl \xrightarrow{Cu/HCl} ArCl + N_2$ is known as: **(2017-Gujarat)**
    (a) Balz Schiemann reaction
    (b) Sandmeyers reaction
    (c) Finkelstein reaction
    (d) Gattermann reaction

16. The product (P) of the following reaction **(2017-Gujarat)**



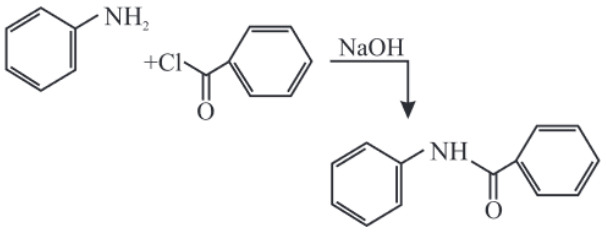
    (a) 
    (b) 
    (c) 
    (d) 

17. A given nitrogen-containing aromatic compound A reacts with Sn/HCl, followed by HNO_2 to give an unstable compound B. B, on treatment with phenol, forms a beautiful coloured compound C with the molecular formula $C_{12}H_{10}N_2O$. The structure of compound A is: **(2016-II)**
    (a) 
    (b) 
    (c) 
    (d) 

18. Which one of the following nitro-compounds does not react with nitrous acid? **(2016-II)**
    (a) 
    (b) 
    (c) 
    (d) 

19. The correct statement regarding the basicity of arylamines is: **(2016-I)**
    (a) Arylamines are generally more basic than alkylamines, because the nitrogen atom in arylamines is sp-hybridised.
    (b) Arylamines are generally less basic than alkylamines because the nitrogen lone pair electrons are delocalized by interaction with the aromatic ring π electrons system.
    (c) Arylamines are generally more basic than alkylamines because the nitrogen lone pair electrons are not delocalised by interaction with the aromatic ring π electron system.
    (d) Arylamines are generally more basic than alkylamines because of aryl group

20. The following reaction

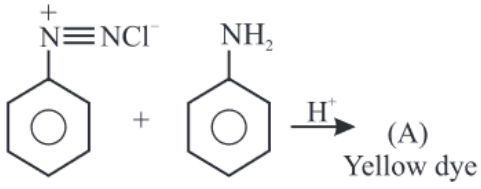


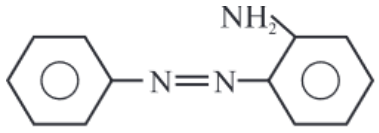
is known by the name: **(2015 Re)**
    (a) Schotten-Baumen reaction
    (b) Friedel-Craft's reaction
    (c) Perkin's reaction
    (d) Acetylation reaction

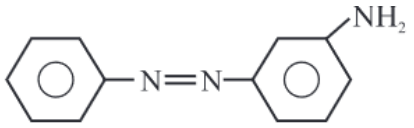
21. Method by which Aniline cannot be prepared is: **(2015 Re)**
    (a) Potassium salt of phthalimide treated with chlorobenzene followed by hydrolysis with aqueous NaOH solution
    (b) Hydrolysis of phenylisocyanide with acidic solution
    (c) Degradation of benzamide with bromine in alkaline solution
    (d) Reduction of nitrobenzene with H_2/Pd in ethanol

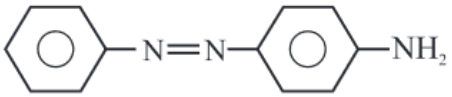
22. The electrolytic reduction of nitrobenzene in strongly acidic medium produces **(2015)**
    (a) Azobenzene
    (b) Aniline
    (c) p-aminophenol
    (d) Azoxybenzene

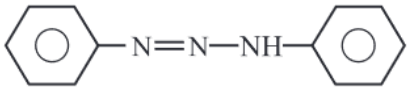
23. In the following reaction, the product (A) is: **(2014)**



(a) 

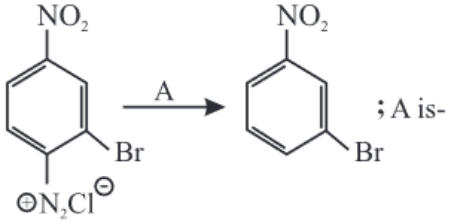
(b) 

(c) 

(d) 

24. Which of the following will be most stable diazonium salt $RN_2{}^+X^-$? **(2014)**
    (a) $C_6H_5N_2{}^+X^-$
    (b) $CH_3CH_2N_2{}^+X^-$
    (c) $C_6H_5CH_2N_2{}^+H^-$
    (d) $CH_3N_2{}^+X^-$

25. In the reaction: **(2013)**



; A is-
    (a) $HgSO_4/H_2SO_4$
    (b) Cu_2Cl_2
    (c) H_3PO_2 and H_2O
    (d) H^+/H_2O

Answer Key

S1. Ans. (a)

S2. Ans. (b)

S3. Ans. (b)

S4. Ans. (a)

S5. Ans. (c)

S6. Ans. (d)

S7. Ans. (b)

S8. Ans. (a)

S9. Ans. (d)

S10. Ans. (d)

S11. Ans. (a)

S12. Ans. (c)

S13. Ans. (a)

S14. Ans. (c)

S15. Ans. (d)

S16. Ans. (d)

S17. Ans. (d)

S18. Ans. (a)

S19. Ans. (b)

S20. Ans. (a)

S21. Ans. (a)

S22. Ans. (c)

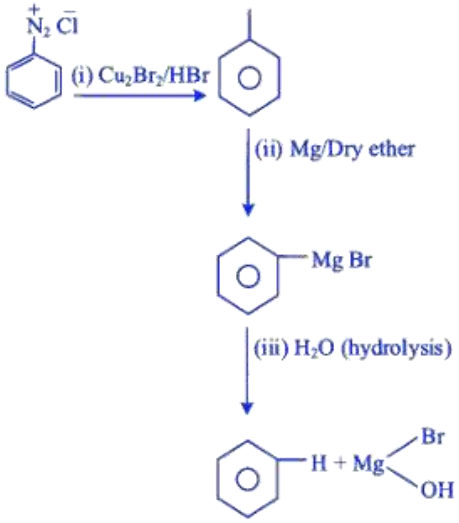
S23. Ans. (c)

S24. Ans. (a)

S25. Ans. (c)

Solutions

S1. Ans.(a)



S2. Ans.(b)

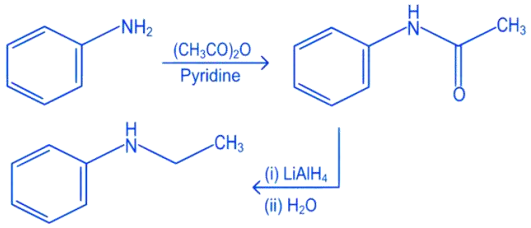
(1) $CH_3–CN \xrightarrow[(ii)\ H_3O^{\oplus}]{(i)\ LiAlH_4} CH_3–CH_2–NH_2$ 1° Amine

(2) $CH_3NC \xrightarrow[(ii)\ H_3O^{\oplus}]{(i)\ LiAlH_4} CH_3–NH–CH_3$ 2° Amine

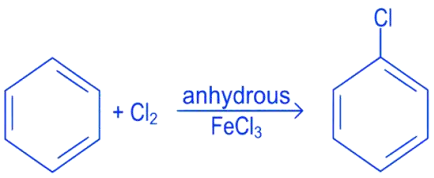
(3) $CH_3–\overset{O}{\overset{\|}{C}}–NH_2 \xrightarrow[(ii)\ H_3O^{\oplus}]{(i)\ LiAlH_4} CH_3–CH_2–NH_2$ 1° Amine

(4) $CH_3–\overset{O}{\overset{\|}{C}}–NH_2 \xrightarrow{Br_2+OH^-} CH_3–NH_2$ 1° Amine

S3. Ans.(b)



S4. Ans.(a)



Benzene reacts with chlorine in presence of anhydrous $FeCl_3$ to give chlorobenzene.

S5. Ans.(c)

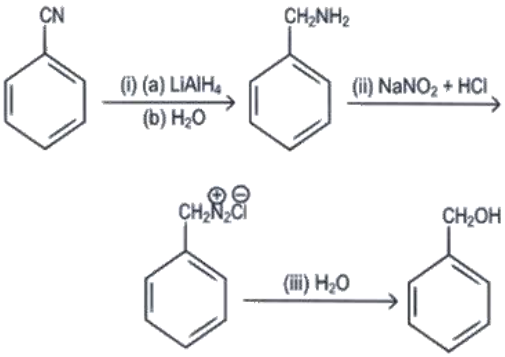
Primary aliphatic amines react with HNO_2 and give unstable diazonium salt which turns into alcohol

$R–NH_2 + HNO_2 \longrightarrow [R–N_2^+–Cl^-] \xrightarrow{H_2O} ROH + N_2 + HCl$

Primary aromatic amines reacts with HNO_2 and give stable diazonium salt which are stable at 273 to 278 K.

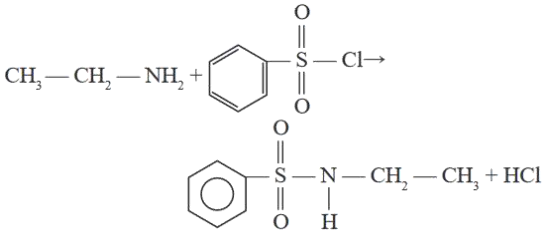
$C_6H_5 – NH_2 + HNO_2 \xrightarrow{273-278\ K} C_6H_5N_2^+Cl^-$

S6. Ans.(d)



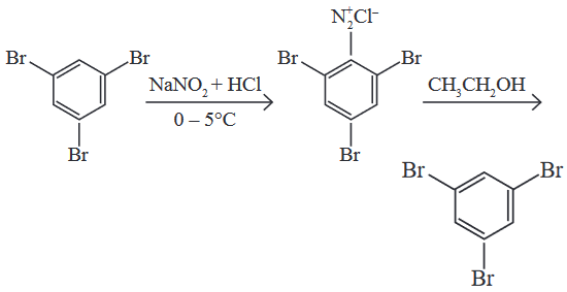
S7. Ans.(b)

1° amines react with Hingberg's reagent to give a solid, which dissolve in alkali.



Soluble in alkali

S8. Ans.(a)



$R – CH_3 – CH_2OH$

Certain mild reducing agents like hypophosphorus acid or ethanol reduce diazonium salts to arene and themselves get oxidized to phosphorous acid and ethanal respectively.

S9. Ans.(d)

S10. Ans.(d)

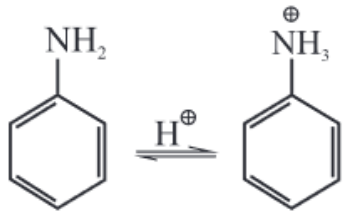
S11. Ans.(a)

In aqueous solution, electron donating inductive effect, solvation effect (H-bonding) and steric hindrance all together will affect basic strength of substituted amines

Basic character will be

$$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N$$
$$2^\circ \qquad 1^\circ \qquad 3^\circ$$

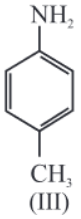
S12. Ans.(c)



Anilinium ion

$-\overset{\oplus}{N}H_3$ is m-directing, hence besides para (51%) and ortho (2%), meta product (47%) is also formed in significant yield.

S13. Ans.(a)



Is more basic as compared to other two because CH_3 is a donating group which increases the basic strength of the group.

S14. Ans.(c)

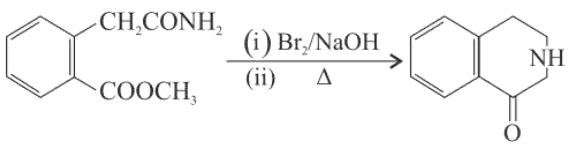
Hoffmann bromamide reaction

$$R-\overset{\overset{O}{\|}}{C}-NH_2 + Br_2 + 4NaOH \rightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

Hoffmann developed a method for preparation of primary amines by treating an amide with bromine in an aqueous or ethanoic solution, of sodium hydroxide. In this degradation reaction, migration of an alkyl or aryl group takes place from carbonyl carbon of the amide to the nitrogen atom. The amide so formed contains one carbon less than that present in the amide.

S15. Ans.(d)

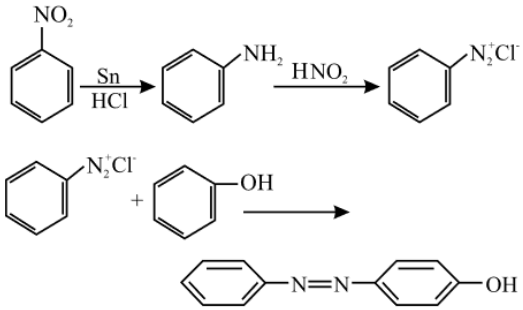
S16. Ans.(d)



Hoffmann bromamide reaction

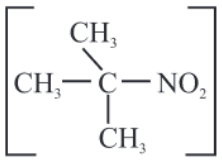
S17. Ans.(d)

Compound A must be $-NO_2$ containing compound:



S18. Ans.(a)

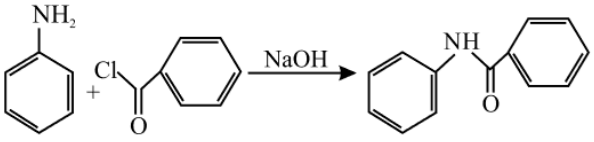
3° - NO_2 compounds do not react with HNO2 (nitrous acid) because of absence of α-H.



S19. Ans.(b)

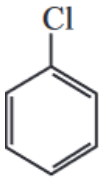
Arylamines are less basic than alkylamines as N on the benzene ring is in conjugation. Where its lone pair of electron are delocalized and partial-π-bond character is present thus making it unavailable for incoming electrophile, whereas in alkylamines such a process is not present and also –I effect increases the basic character on N.

S20. Ans.(a)



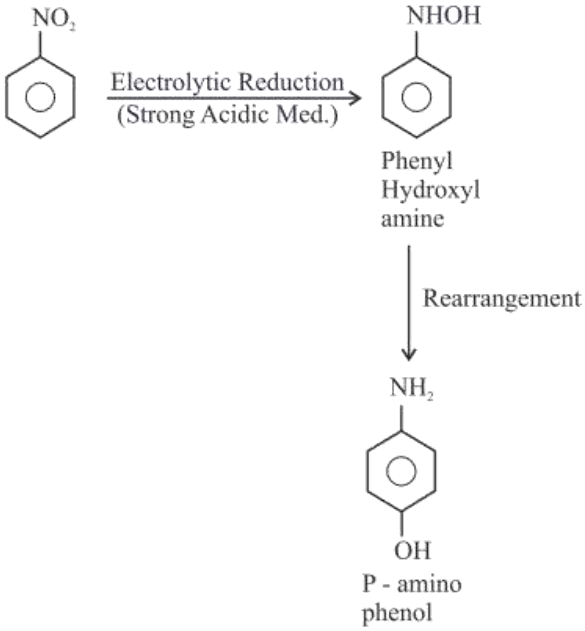
Synthesis of amides from amines from acyl halides or anhydrides in the presence of a base is known as Schotten-Baumen reaction.

S21. Ans.(a)

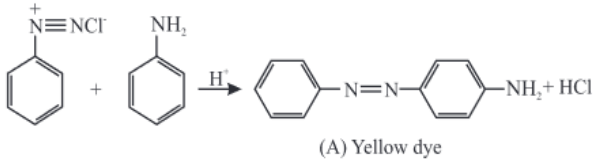


will not undergo nucleophilic substitution under normal conditions.

S22. Ans.(c)



S23. Ans.(c)



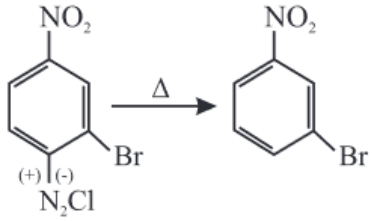
(A) Yellow dye

S24. Ans.(a)

Diazonium salt is most stabilized as the (–) charge on halogen is resonance stabilized.

In the rest options, stabilization is only because of +R & +I effect.

S25. Ans.(c)



For removal of diazonium (ion) H_3PO_2 & H_2O are used as reducing agents.