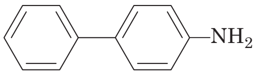
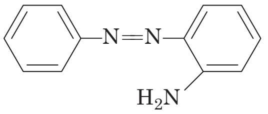
29

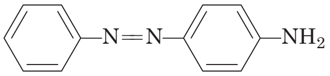
Aromatic Compounds Containing Nitrogen

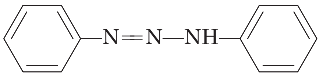
Objective Questions I (Only one correct option)

1. Benzene diazonium chloride on reaction with aniline in the presence of dilute hydrochloric acid gives **(2019 Main, 12 April II)**

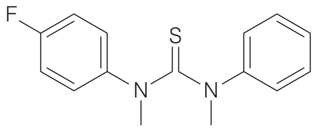
(a) 

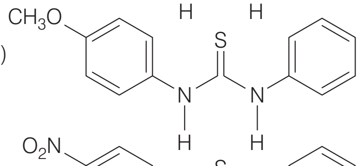
(b) 

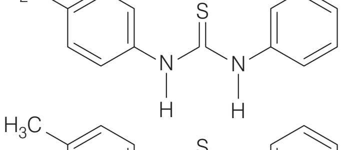
(c) 

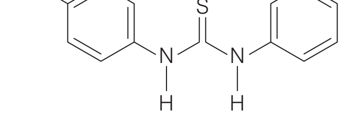
(d) 

2. The increasing order of the pK_b of the following compound is

(A) 

(B) 

(C) 

(D) 

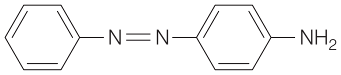
(2019 Main, 12 April I)

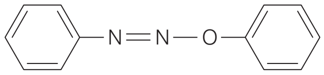
(a) (A) < (C) < (D) < (B)
(b) (C) < (A) < (D) < (B)
(c) (B) < (D) < (A) < (C)
(d) (B) < (D) < (C) < (A)

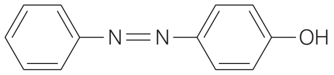
3. Which of the following is not a correct method of the preparation of benzylamine from cyanobenzene?

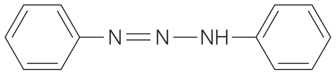
(a) H_2 / Ni **(2019 Main, 10 April II)**
(b) (i) HCl/ H_2O (ii) $NaBH_4$
(c) (i) $LiAlH_4$ (ii) H_3O^+
(d) (i) $SnCl_2 + HCl$(gas) (ii) $NaBH_4$

4. 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 Main, 9 April I)**

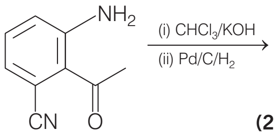
(a) 

(b) 

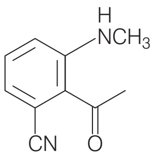
(c) 

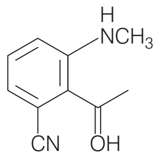
(d) 

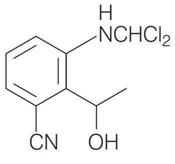
5. The major product obtained in the following reaction is

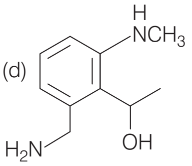


(2019 Main, 8 April II)

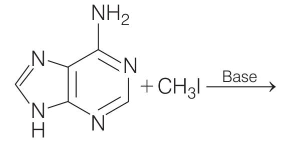
(a) 

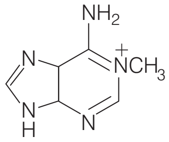
(b) 

(c) 

(d) 

6. The major product in the following reaction is **(2019 Main, 8 April II)**



(a)


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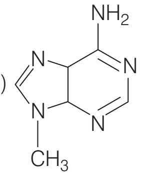

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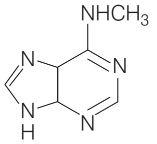

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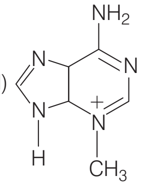

7. Coupling of benzene diazonium chloride with 1-naphthol in alkaline medium will give **(2019 Main, 8 April I)**

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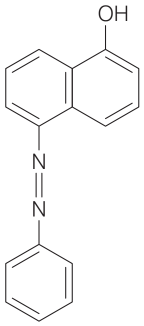

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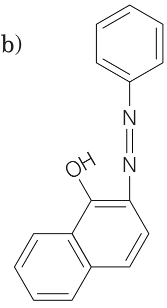
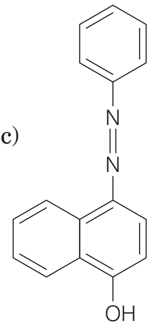


(c)


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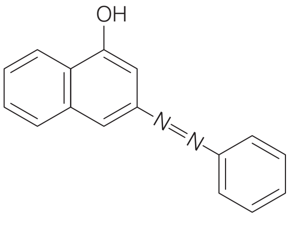
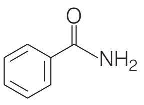
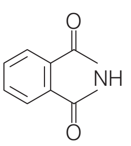
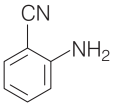
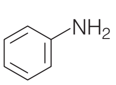


8. The increasing order of reactivity of the following compounds towards reaction with alkyl halides directly is **(2019 Main, 12 Jan I)**


(A)

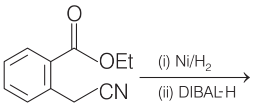

(B)

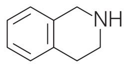

(C)


(D)

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

9. The major product of the following reaction is **(2019 Main, 11 Jan I)**



(a)


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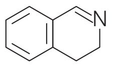

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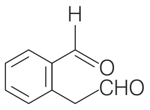

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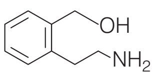
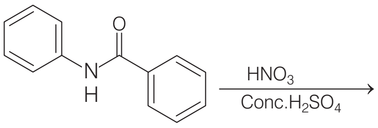
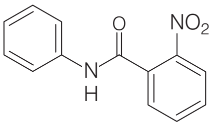
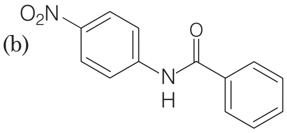
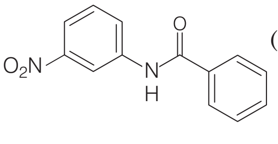


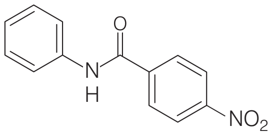
10. What will be the major product in the following mononitration reaction ? **(2019 Main, 10 Jan II)**



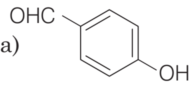
(a)


(b)


(c)


(d)


11. 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 **(2019 Main, 10 Jan II)**

(a)


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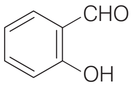
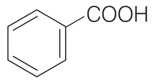
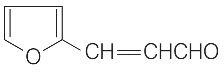
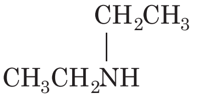


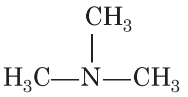
(c)


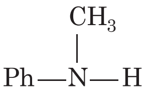
(d)


12. The increasing basicity order of the following compounds is

(A) $CH_3CH_2NH_2$

(B)

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

(C)

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

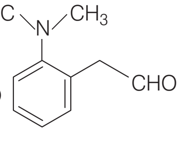
(D)

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

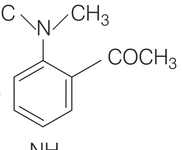
(a) (D) < (C) < (B) < (A)
(b) (A) < (B) < (C) < (D)
(c) (A) < (B) < (D) < (C)
(d) (D) < (C) < (A) < (B) **(2019 Main, 9 Jan II)**

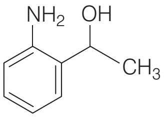
13. The tests performed on compound *X* and their inferences are :

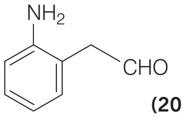
	Test	Inference
(a)	2, 4- DNP test	Coloured precipitate
(b)	Iodoform test	Yellow precipitate
(c)	Azo-dye test	No dye formation

Compound '*X*' is

(a) 

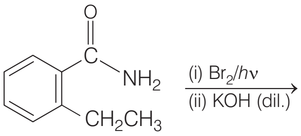
(b) 

(c) 

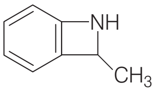
(d) 

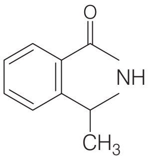
(2019 Main, 9 Jan II)

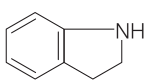
14. The major product of the following reaction is

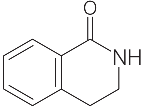


(2019 Main, 9 Jan II)

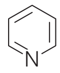
(a) 

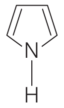
(b) 

(c) 

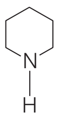
(d) 

15. Arrange the following amines in the decreasing order of basicity: **(2019 Main, 9 Jan I)**


(I)



(II)



(III)

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

16. The correct decreasing order for acid strength is **(2019 Main, 9 Jan I)**

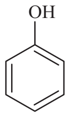
(a) $FCH_2COOH > NCCH_2COOH$
$> NO_2CH_2COOH > ClCH_2COOH$

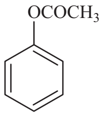
(b) $CNCH_2COOH > O_2NCH_2COOH$
$> FCH_2COOH > ClCH_2COOH$

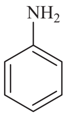
(c) $NO_2CH_2COOH > NCCH_2COOH$
$> FCH_2COOH > ClCH_2COOH$

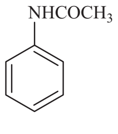
(d) $NO_2CH_2COOH > FCH_2COOH$
$> CNCH_2COOH > ClCH_2COOH$

17. Which of the following compounds will give significant amount of *meta*-product during mononitration reaction? **(2017 Main)**

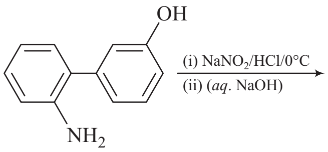
(a) 

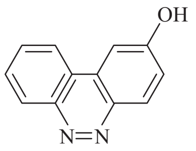
(b) 

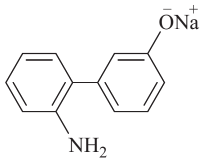
(c) 

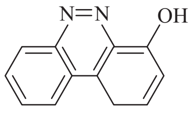
(d) 

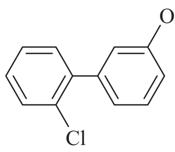
18. The major product of the following reaction is **(2017 Adv.)**



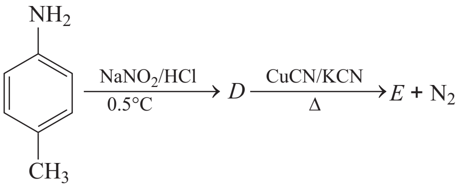
(a) 

(b) 

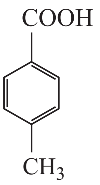
(c) 

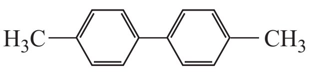
(d) 

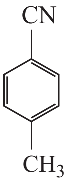
19. In the reaction,

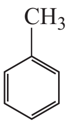


The product *E* is **(2015 Main)**

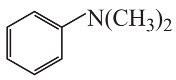
(a) 

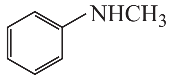
(b) 

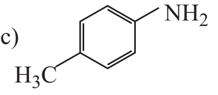
(c) 

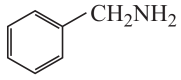
(d) 

20. Amongst the compounds given, the one that would form a brilliant coloured dye on treatment with $NaNO_2$ in dil. HCl followed by addition to an alkaline solution of β-naphthol is

(a) 

(b) 

(c) 

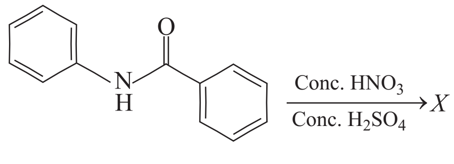
(d) 

(2011)

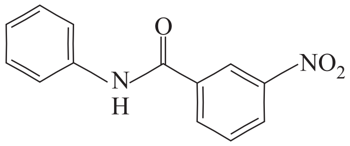
21. The species having pyramidal shape is **(2010)**

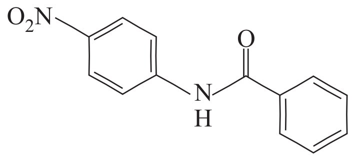
(a) SO_3 (b) BrF_3 (c) SiO_3^{2-} (d) OSF_2

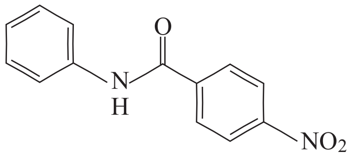
22. In the following reaction,

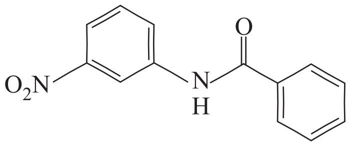


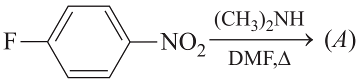
The structure of the major product X is **(2007, 3M)**

(a) 

(b) 

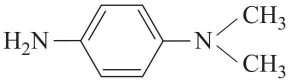
(c) 

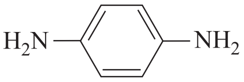
(d) 

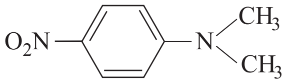
23. 

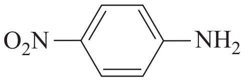
$\xrightarrow[\text{(iii) } H_2/Ni]{\text{(i) Fe/HCl (ii) } NaNO_2/HCl/0°C}$ (B), B is

(2003, 1 M)

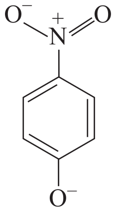
(a) 

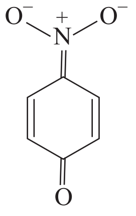
(b) 

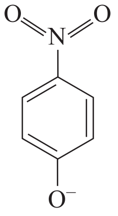
(c) 

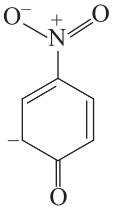
(d) 

24. The most unlikely representation of resonance structures of *p*-nitrophenoxide ion is **(1999, 2M)**

(a) 

(b) 

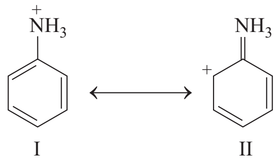
(c) 

(d) 

25. Benzene diazonium chloride on reaction with phenol in weakly basic medium gives **(1998, 2M)**

(a) diphenyl ether
(b) *p*-hydroxy azobenzene
(c) chlorobenzene
(d) benzene

26. Examine the following two structures of anilinium ion and choose the correct statement from the ones given below : **(1993, 1M)**



(a) II is not an acceptable canonical structure because carbonium ions are less stable than ammonium ions
(b) II is not an acceptable canonical structure because it is non-aromatic
(c) II is not an acceptable canonical structure because the nitrogen has 10 valence electrons
(d) II is an acceptable canonical structure

27. Chlorobenzene can be prepared by reacting aniline with **(1984, 1M)**

(a) hydrochloric acid
(b) cuprous chloride
(c) chlorine in the presence of anhyd $AlCl_3$
(d) nitrous acid followed by heating with cuprous chloride

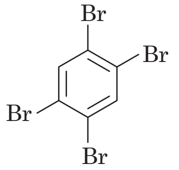
Objective Questions II

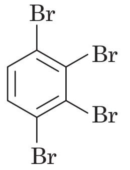
(One or more than one correct option)

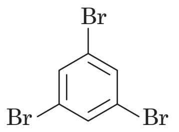
28. Aniline reacts with mixed acid (conc. HNO_3 and conc. H_2SO_4) at 288 K to give P (51%),Q (47%) and R (2%). The major product(s) of the following sequence is (are)

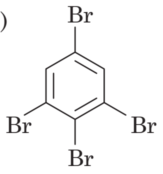
$$R \xrightarrow[\text{(3) } H_3O^+ \text{ (4) } NaNO_2,\ HCl/273\text{-}278\text{ K (5) EtOH, } \Delta]{\text{(1) } Ac_2O,\text{ pyridine (2) } Br_2,\ CH_3CO_2H} S \xrightarrow[\text{(3) } NaNO_2,\ HCl/273\text{-}278\text{ K (4) } H_3PO_2]{\text{(1) Sn/HCl (2) } Br_2/H_2O\text{ (excess)}}$$

Major product(s) **(2018 Adv.)**

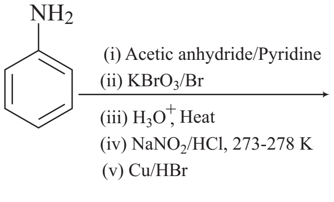
(a) 

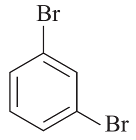
(b) 

(c) 

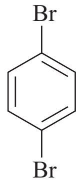
(d) 

29. The product(s) of the following reaction sequence is (are) **(2017, Adv.)**

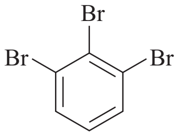




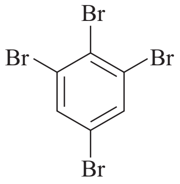
(a)



(b)

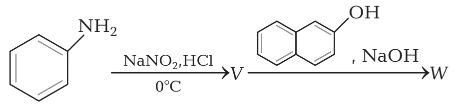


(c)

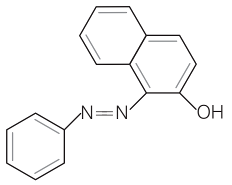


(d)

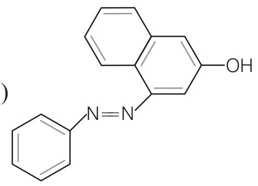
30. In the following reactions, the major product W is **(2015 Adv.)**



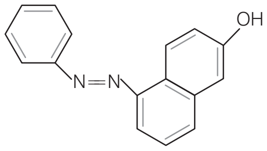
(a)



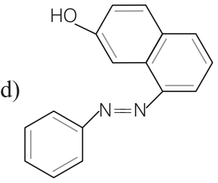
(b)



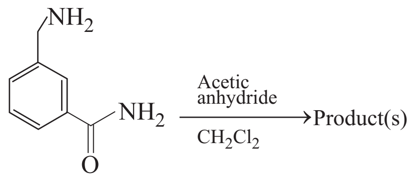
(c)



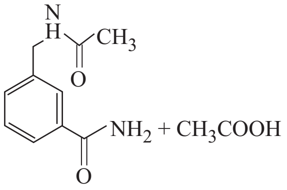
(d)



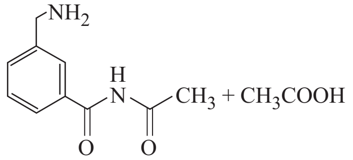
31. In the reaction shown below, the major product(s) formed is/are **(2014 Adv.)**



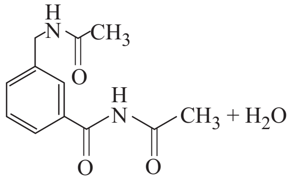
(a)



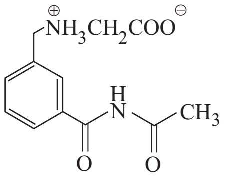
(b)



(c)



(d)



32. *p*-chloroaniline and anilinium hydrochloride can be distinguished by **(1998, 2M)**

(a) Sandmeyer reaction (b) $NaHCO_3$

(c) $AgNO_3$ (d) Carbylamine test

33. When nitrobenzene is treated with Br_2 in the presence of $FeBr_3$, the major product formed is *m*-bromonitrobenzene. Statements which are related to obtain the *m*-isomer, are **(1992, 1M)**

(a) the electron density on *meta* carbon is more than that on *ortho* and *para* positions

(b) the intermediate carbonium ion formed after initial attack of Br^+ at the *meta* position is less destabilised

(c) loss of aromaticity when Br^+ attacks at the *ortho* and *para* positions and not at *meta* position

(d) easier loss of H^+ to regain aromaticity from *meta* position than from *ortho* and *para* positions

Assertion and Reason

Read the following questions and answer as per the direction given below :

(a) Statement I is correct; Statement II is correct; Statement II is the correct explanation of Statement I.

(b) Statement I is correct; Statement II is correct; Statement II is not the correct explanation of Statement I.

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

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

34. **Statement I** Aniline on reaction with $NaNO_2/HCl$ at 0°C followed by coupling with β-naphthol gives a dark blue coloured precipitate.

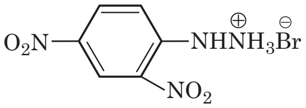
Statement II The colour of the compound formed in the reaction of aniline with $NaNO_2/HCl$ at 0°C followed by coupling with β-naphthol is due to the extended conjugation **(2008, 3M)**

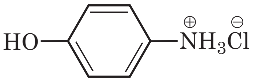
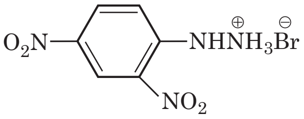
35. **Statement I** In strongly acidic solution, aniline becomes more reactive towards electrophilic reagents.

Statement II The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on nitrogen is no longer available for resonance. **(2001, 1M)**

Match the Column

36. Match the compounds in Column I with their characteristic test(s)/reaction(s) given in Column II. **(2008, 6M)**

	Column I		Column II
(A)	$H_2N—\overset{\oplus}{N}H_3\,\overset{\ominus}{Cl}$	(p)	Sodium fusion extract of the compound gives Prussian blue colour with $FeSO_4$
(B)		(q)	Gives positive $FeCl_3$ test

	Column I		Column II
(C)		(r)	Gives white precipitate with $AgNO_3$
(D)		(s)	Reacts with aldehydes to form the corresponding hydrazone derivative

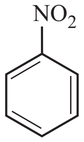
Fill in the Blanks

37. The high melting point and insolubility in organic solvents of sulphanilic acid are due to its…… structure. **(1994, 1M)**

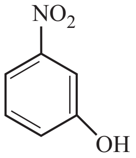
38. In an acidic medium, ……… behaves as the strongest base. (nitrobenzene, aniline, phenol) **(1981, 1M)**

Subjective Questions

39. Convert

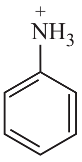


to

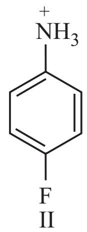


in not more than four steps. Also mention the reaction conditions and temperature. **(2004, 4M)**

40. Which of the following is more acidic and why?



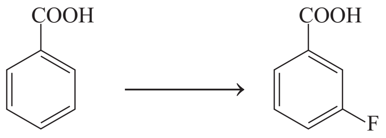
I



II

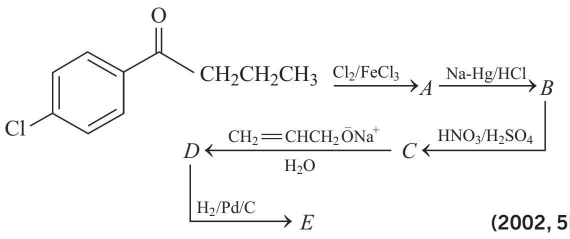
(2004, 2M)

41. Convert (in not more than 3 steps) : **(2003, 2M)**



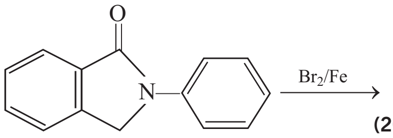
42. There is a solution of *p*-hydroxybenzoic acid and *p*-amino benzoic acid. Discuss one method by which we can separate them and also write down the confirmatory test of the functional group present. **(2003, 4M)**

43. Write structures of the products *A*, *B*, *C*, *D* and *E* in the following scheme



(2002, 5M)

44. What would be the major product in the following reaction?

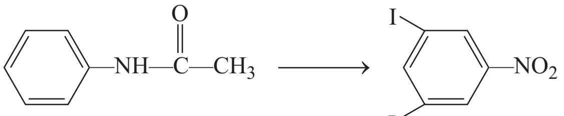


(2000, Main, 1M)

45. How would you bring about the following conversion (in 3 steps)?

Aniline ⟶ Benzylamine **(2000, 3M)**

46. Complete the following reactions with appropriate reagents



(1994, 4M)

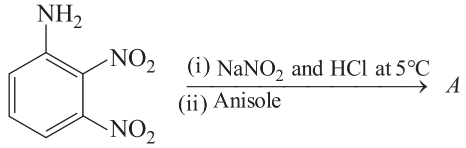
47. Following reaction gives two products. Write the structures of the products.

$$CH_3CONHC_6H_5 \xrightarrow{Br_2/Fe}$$

(1998, 2M)

48. Write the structure of foul smelling compound obtained when aniline is treated with chloroform in the presence of KOH. **(1996, 1M)**

49. Complete the following with appropriate structure:



(1995, 1M)

50. How will you bring about the following conversions?

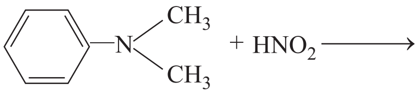
"Benzamide from nitrobenzene" **(1994, 2M)**

51. How will you bring about the following conversions?

"4-nitrobenzaldehyde from benzene" **(1994, 2M)**

52. Outline a synthesis of *p*-bromonitrobenzene from benzene in two steps. **(1993, 2M)**

53. Write the structure of the major organic product expected from the following reaction.

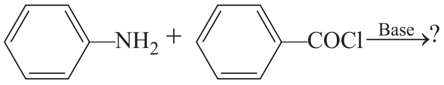


(1992, 1M)

54. How will you bring about the following conversion?

"4-nitro aniline to 1, 2, 3-tribromobenzene." **(1990, 2M)**

55. Complete the following with appropriate structures: **(1986, 1M)**



56. How would you convert aniline into chlorobenzene? **(1985, 1M)**

57. State the conditions under which the following preparation is carried out. "Aniline from benzene" **(1983, 1M)**

58. State the equation for the preparation of following compound.

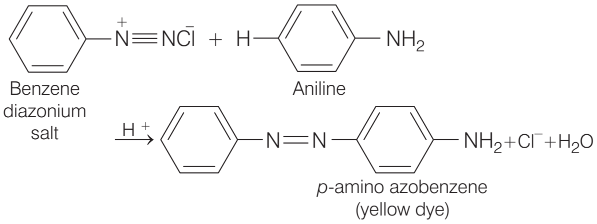
Chlorobenzene from aniline (in 2 steps). **(1982, 1M)**

Answers

1. (c) **2.** (c) **3.** (b) **4.** (a)
5. (d) **6.** (*) **7.** (c) **8.** (b)
9. (b) **10.** (b) **11.** (c) **12.** (d)
13. (b) **14.** (a) **15.** (d) **16.** (c)
17. (c) **18.** (a) **19.** (c) **20.** (c)
21. (d) **22.** (b) **23.** (a) **24.** (c)
25. (b) **26.** (c) **27.** (d) **28.** (d)
29. (b) **30.** (a) **31.** (a) **32.** (c,d)
33. (a,b) **34.** (d) **35.** (d)
36. A → r, s B → p, q C → p, q, r D → p
37. zwitter ionic **38.** Aniline

Hints & Solutions

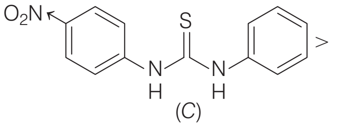
1. Benzene diazonium chloride on reaction with aniline in the presence of dilute hydrochloric acid undergoes coupling reaction and produces *p*-amino azobenzene. In this reaction, benzene diazonium chloride reacts with aniline in which aniline molecule at its *para*-position is coupled with diazonium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



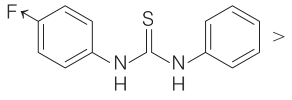
2. **Key Idea** pK_b value is defined as the minus lagarithm of K_b smallar the value of pK_b stronger is the base and *vice-versa*.

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.

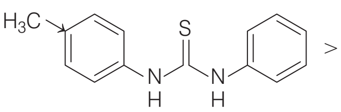
Increase in electron density at *p*-position makes the unshared electron pair of '*N*' more available and decrease in electron density at *p*-position makes the unshared electron pair of '*N*' less available. Compound containing —OCH_3 group act as strongest base and hence possess lowest value of pK_b.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



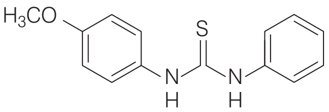
(*C*)



(*A*)

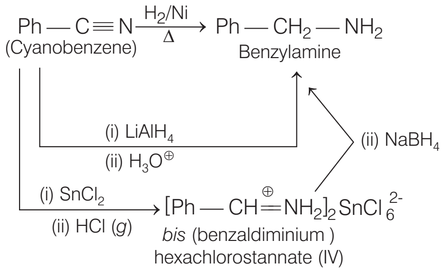


(*D*)



(*B*)

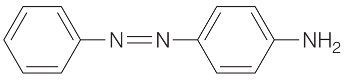
3. The preparation of benzylamine from cyanobenzene using given reagents are as follows :



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

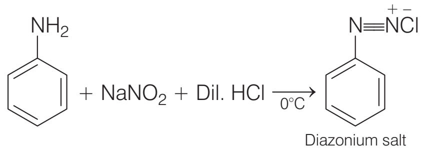
Thus, option (b) is incorrect.

4. Major product of the reaction is

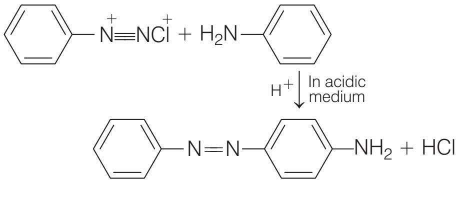


It is obtained by coupling reaction.

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

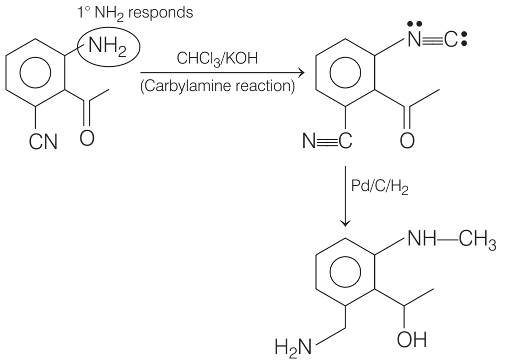


Diazonium salt formed when added to equimolar mixture of aniline and phenol in dil. HCl then aniline couples with diazonium salt. Reaction is as follows :



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.

5.

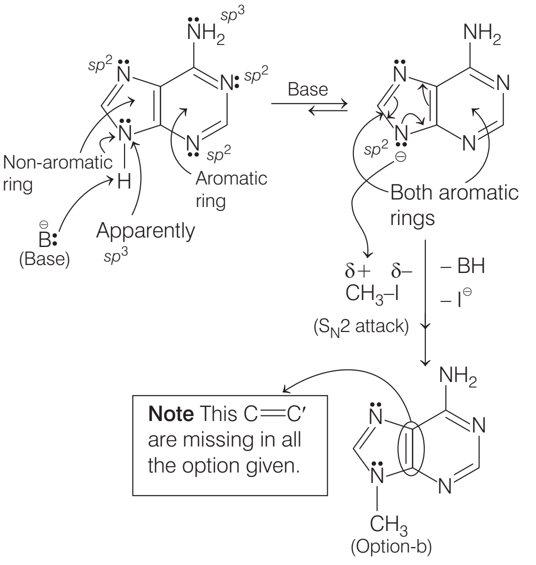


In step (i), 1° amine is converted into isocyanide, when reacts with $CHCl_3$ / KOH. This reaction is known as carbylamine reaction. This reaction is used to detect primary amine in a compound.

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 $Pd/C/H_2$.

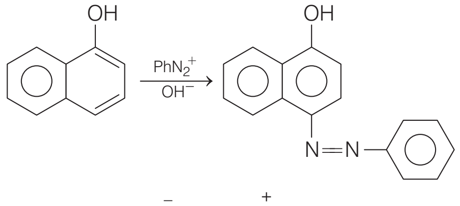
6. N is more electronegative than '*C*'. So, H of $\overset{\delta-}{N}$—$\overset{\delta+}{H}$ bond is more acidic than that of C—H bond in the ring.

Again, *sp*^{2}-N is more electronegative ($s\% = 33.3$) than *sp*^{3}-N ($s\% = 25$) of the —NH_2 group.



Note This C═C′ are missing in all the option given.

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



In the presence of $\overset{-}{O}H$ 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.

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

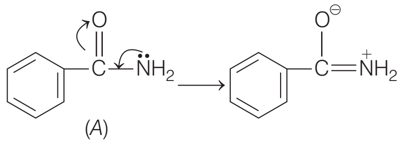
$$\underset{H^+}{\overset{NaOH}{\rightleftharpoons}} \underset{\text{Does not couple}}{Ar - N = N - \overset{-}{O}\overset{+}{Na}}$$

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.

8. 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.

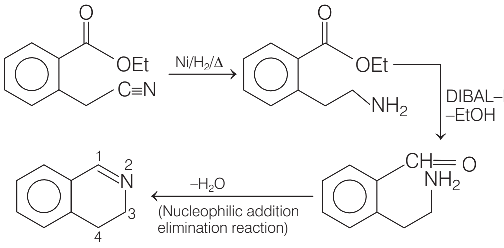


In compound (*D*), lone pair of 'N' are available but in compound (*C*), the lone pair of 'N' are not readily available due to the presence of electron withdrawing group (—CN) attach to benzene ring.

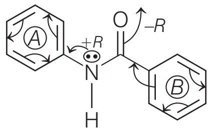
In compound (*B*), i.e. pthalimide, 'N' is not nucleophilic due to the presence of two polar groups attached to it that pulls lone pair towards them. Hence, the correct order is:

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

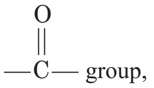
9. Ni/H_2 can reduce —C ≡ N into —CH_2—NH_2 (1°-amine) but cannot reduce an ester group (—CO_2Et) whereas DIBAL-H, di-isobutylaluminium hydride, $[(CH_3)_2CH]_2AlH$ reduces the ester group (—CO_2Et) into —CHO (an aldehyde) and C_2H_5OH.



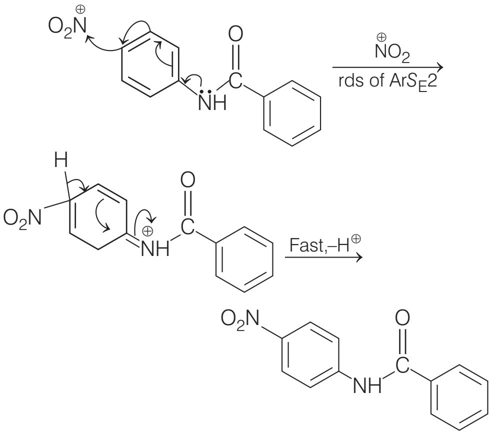
10. Here, in mononitration the electrophile produced from mixed acid (HNO_3 + conc.H_2SO_4) is $\overset{+}{N}O_2$.



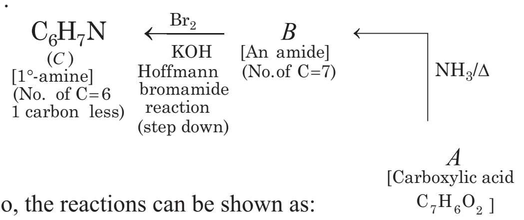
Ring-(*A*) is activated, i.e. becomes more nucleophilic by the + *R* effect of the —$\ddot{N}$H— group and it becomes *o* / *p*-directing towards the electrophile, NO_2^+ in the ArS_E2 reaction. For mononitration, $\overset{\oplus}{N}O_2$ will preferably come at *p*-position, whereas the ring-(B) gets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



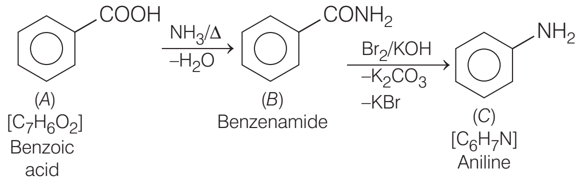
$\overset{\overset{\displaystyle O}{\|}}{—C—}$ group,



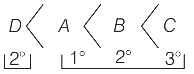
11. Using retro-synthesis, to get the required compounds, A, B and C.



So, the reactions can be shown as:



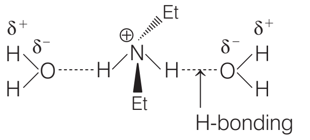
12. If we consider Lewis basicity (basicity in aprotic solvents or in vapour phase), the order of basicity will be.



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.

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

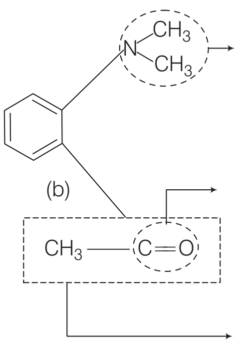
$Et_2\overset{\oplus}{N}H_2$ is a sterically symmetric tetrahedral ion as it contains equal number (two) of bulkier Et-group and small size H-atoms. Here, two H-atoms give additional stability through hydrogen bonding with H_2O (solvent) molecules.



Aromatic amines (D) are always weaker bases than aliphatic amines, because of the conjugation of lp of electrons of N (+ R-effect) with the benzene ring.

So, the correct order is (D) < (C) < (A) < (B).

13.



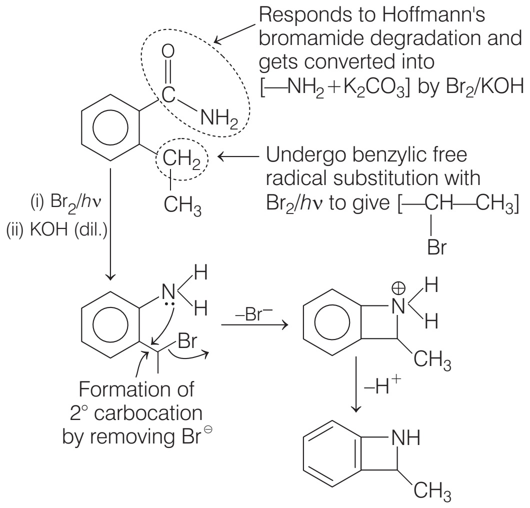
It is a 3°-amino group (—NMe_2) though aromatic which will not respond to diazotisation ($NaNO_2$ + dil. HCl/5°C). So, formation of diazonium ion and its further reaction with alkaline phenol or β-napthol at 5-10°C to produce a precipitate of azo-dye will not take place.

It is a keto group $>C{=}O$ and so it responds to 2, 4-DNP test with Brady's reagent (2, 4-dinitrophenyl hydrazine) to give a reddish orange precipitate.

It is a keto-methyl group $\overset{\overset{\displaystyle O}{\|}}{—C—}CH_3$ and hence, it responds to iodoform test to give a yellow precipitate of iodoform (CHI_3).

Compound (c) is an alcohol and does not give positive 2, 4-DNP test. Hence, eliminated (a) and (d) does not have —CH_3CO group and does not give idoform test. Hence, eliminated.

14. In the given reaction,



Responds to Hoffmann's bromamide degradation and gets converted into [—NH_2+K_2CO_3] by Br_2/KOH

Undergo benzylic free radical substitution with $Br_2/h\nu$ to give [$\underset{\underset{\displaystyle Br}{|}}{—CH—}CH_3$]

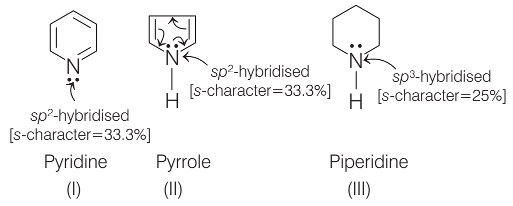
Formation of 2° carbocation by removing $Br^\ominus$

15. **Key Idea**

Basicity ∝ Ease of donation of lone pair of electrons

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

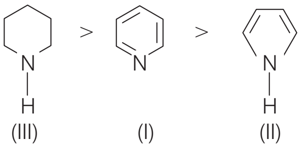
The % of s-character in the given amines are as follows:



Pyridine (I)
Pyrrole (II)
Piperidine (III)

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:



16. All the given compounds are α-monosubstituted acetic acid derivatives and the α-substitutions have been made by strong $-I$ groups/atoms. More powerful the $-I$ group, stronger will be the acid.

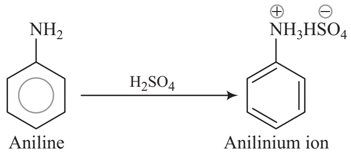
$-I$ power of different groups is as follows :

$$—NO_2 > —CN > —F > —Cl.$$

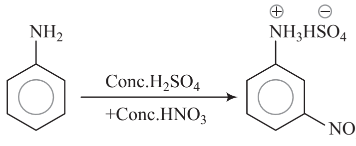
Thus, the correct decreasing order for acid strength is:

$$NO_2CH_2COOH > NCCH_2COOH > FCH_2COOH > ClCH_2COOH.$$

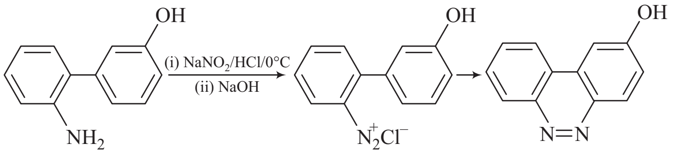
17. Aniline in presence of nitrating mixture (conc. HNO_3 + conc. H_2SO_4) gives significance amount (≈ 47%) of meta-product because in presence of H_2SO_4 its protonation takes place and anilinium ion is formed.



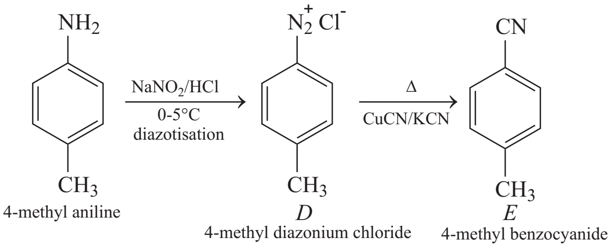
Here, anilinium ion is strongly deactivating group and *meta*-directing in nature. So, it gives *meta*-nitration product.



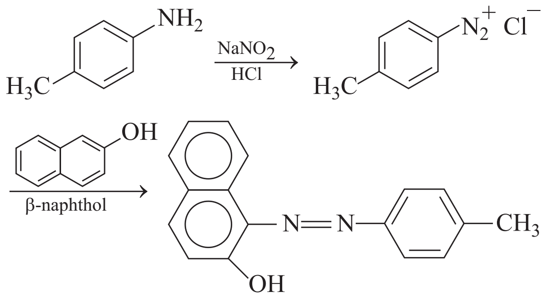
18. *Diazo* coupling occur at *para*-position of phenol.



19.



20. As we know, benzenediazonium salt forms brilliant coloured dye with β-naphthol, the compound under consideration must be *p*-toluidine (c) as it is a primary aromatic amine. Primary aromatic amine, on treatment with $NaNO_2$ in dil. HCl forms the corresponding diazonium chloride salt.



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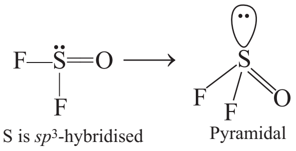
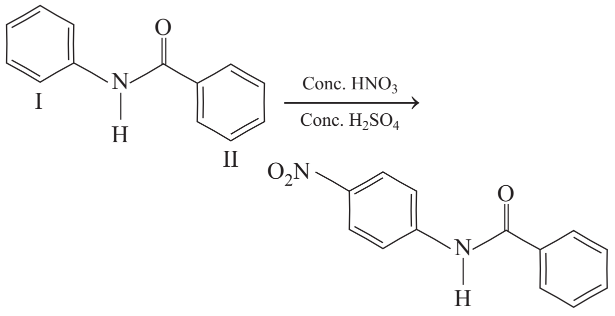


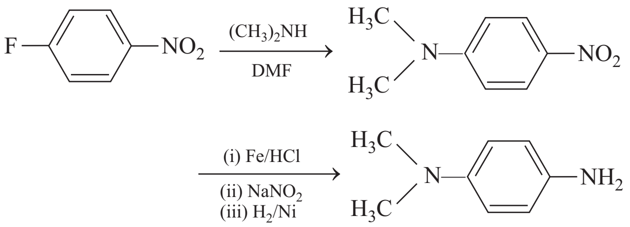
SO_3 is planar (S is sp^2-hybridised), BrF_3 is T-shaped and SiO_3^{2-} is planar (Si is sp^2-hybridised).

22.



Ring-I is activated while ring-II is deactivated towards electrophilic aromatic substitution reaction.

23.



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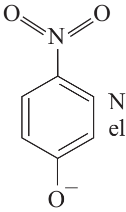
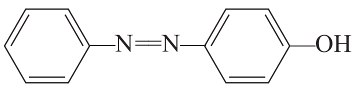


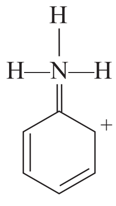
Nitrogen has five bonds and 10 valence electrons, not an acceptable resonance structure.

25. $C_6H_5\overset{+}{N_2}Cl^- + C_6H_5OH \longrightarrow$



p-hydroxy azobenzene

26. In structure II, nitrogen is associated with five bonds and 10 valence electrons, hence not acceptable.

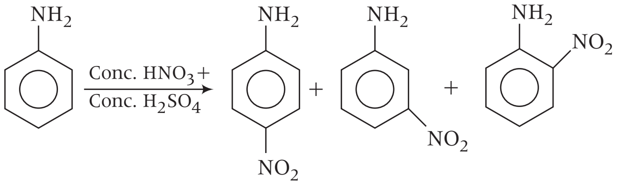


N-has five bonds
and 10 valence electrons

27. $C_6H_5NH_2 + HNO_2 \longrightarrow C_6H_5N_2OH \xrightarrow{CuCl} C_6H_5—Cl$

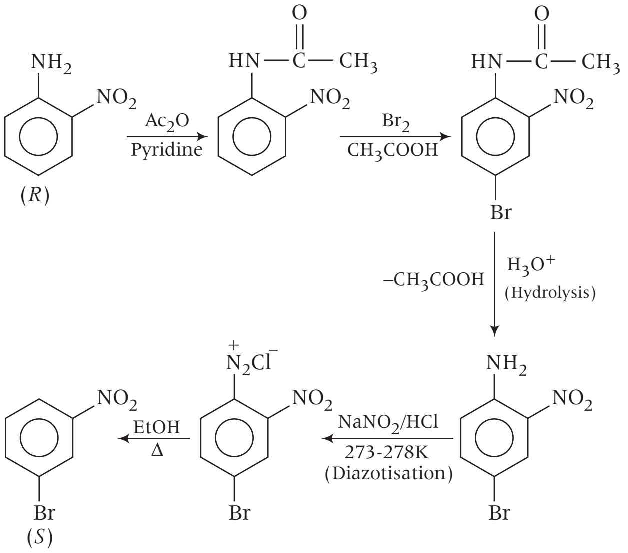
28. Given, Aniline $\xrightarrow[\text{Conc. } H_2SO_4]{\text{Conc. } HNO_3+} \underset{(51\%)}{P} + \underset{(47\%)}{Q} + \underset{(2\%)}{R}$

Then P, Q and R will be



P (51%) Q (47%) R (2%)

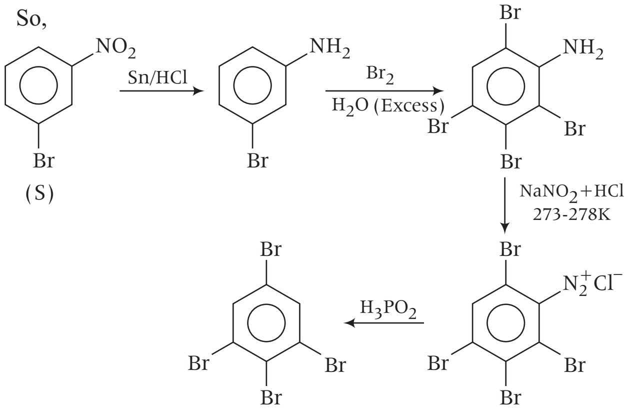
Its given $R \xrightarrow[\substack{\text{(iii) } H_3O^+ \\ \text{(iv) } NaNO_2,\ HCl/273\text{-}278\ K \\ \text{(v) EtOH, } \Delta}]{\substack{\text{(i) } Ac_2O,\ \text{Pyridine} \\ \text{(ii) } Br_2,\ CH_3COOH}} S$



Now from S to major products its given.

$$S \xrightarrow[\substack{\text{(iii) } NaNO_2,\ HCl/273\text{-}278K \\ \text{(iv) } H_3PO_2}]{\substack{\text{(i) Sn/ HCl} \\ \text{(ii) } Br_2/H_2O \text{ (Excess)}}} \text{Major product}$$

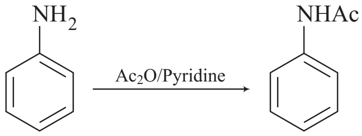
So,



Major product
1, 3, 4, 5-tetrabromobenzene

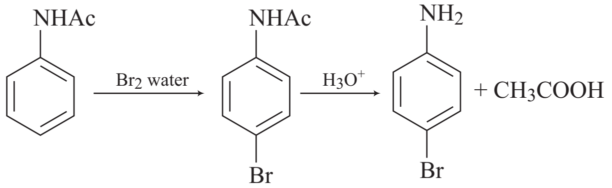
Hence, only (d) is the correct answer.

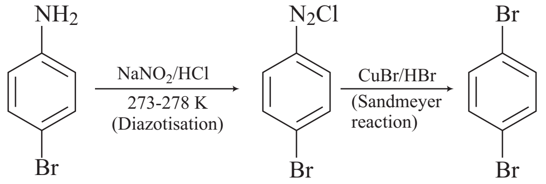
29.



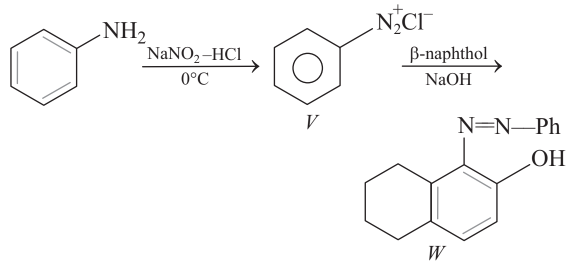
$KBrO_3 + HBr \longrightarrow Br_2$

Ac is CH_3CO (acetyl), it protects —NH_2 group from being oxidised.





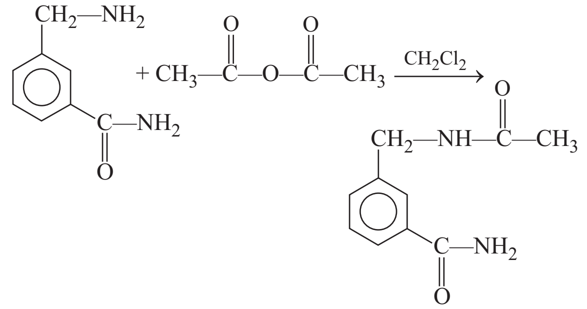
30.

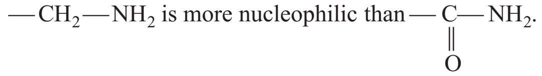


31. **PLAN** This problem includes concept of acetylation reaction and regioselectivity of chemical reaction.

Regioselectivity means which group will react selectivity in the presence of two or more than two functional groups. Here, among two functional group —NH_2 and —$CONH_2$,

NH_2 is more nucleophilic, hence NH_2 group will undergo reaction faster than $CONH_2$.





$$—CH_2—NH_2 \text{ is more nucleophilic than} —\underset{\underset{O}{\|}}{C}— NH_2.$$

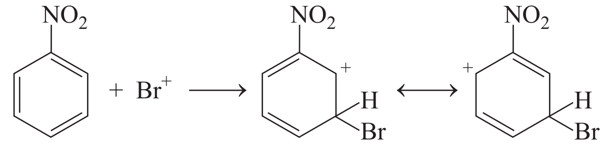
Hence, correct choice is (a).

32. $\underset{\text{anilinium hydrochloride}}{(C_6H_5\overset{+}{N}H_3Cl^-)} + AgNO_3 \longrightarrow \underset{\text{precipitate}}{AgCl\downarrow}$

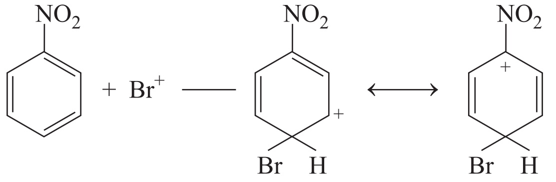
No such precipitate is formed with *p*-chloroaniline.

Also, carbylamine test will not be given by anilinium hydrochloride but *p*-chloroaniline give this test.

33. Nitro group withdraws electrons more from *ortho*/*para* position than from *meta* position. Also the σ-complex formed from *meta* attack is less destabilised than from *ortho*/*para* positions.



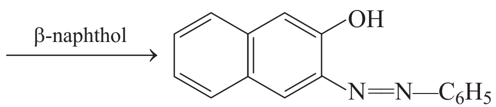
Nitro group not destabilising the positive charge by resonance.



Nitro group destabilises the positive charge directly by resonance, less stable σ-complex.

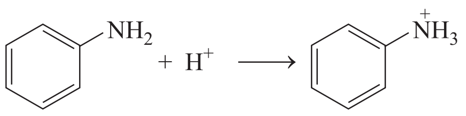
Similar phenomenon is observed with *ortho* attack.

34. $C_6H_5NH_2 + NaNO_2 / HCl \xrightarrow{0°C} C_6H_5\overset{+}{N_2}Cl^-$



coloured dye

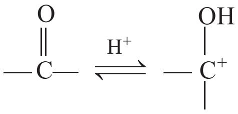
35. In strongly acidic medium, aniline is fully protonated, becomes deactivated for S_EAr reaction.



Lone pair on nitrogen is not available for resonance. Positive charge makes the group strongly electron withdrawing.

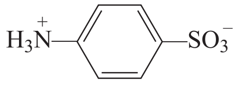
36. Sodium fusion extract gives Prussian blue colouration, nitrogen and carbon both present in the compound. Phenolic group and salt of carboxylic acid gives $FeCl_3$ test.

Chloride salt gives white precipitate of AgCl on treatment with $AgNO_3$. Hydrazone formation occur effectively at pH = 4.5. The reaction proceeds in that condition only when H^+ concentration is just sufficient to activate the following enolisation.



As H^+ concentration rises sufficiently, a large number of molecules of hydrazine gets converted into hydrazinium ion which is not nucleophilic and reaction becomes impossible. Further low concentration of H^+ (in the case of 2,4-dinitrophenyl hydrazinium bromide) is not effective to proceed elimination.

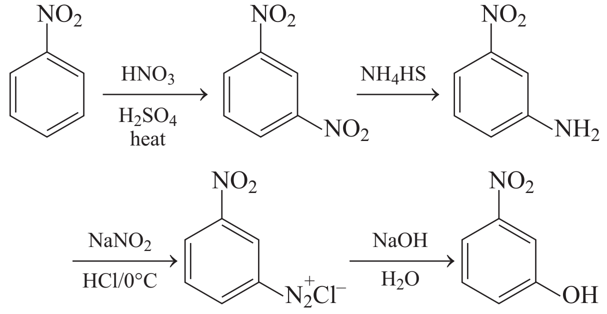
37. **Zwitter ionic**



sulphanilic acid

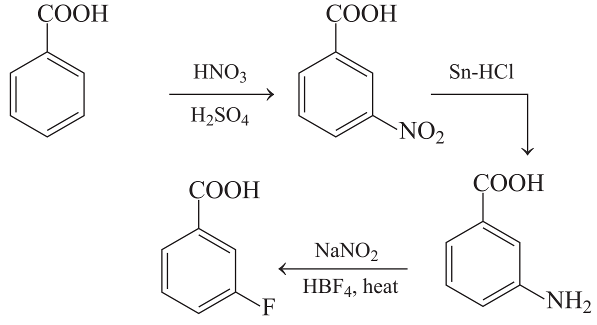
38. **Aniline** It is a stronger base than either phenol or nitrobenzene.

39.



40. II is more acidic due to – *I* effect of F.

41.



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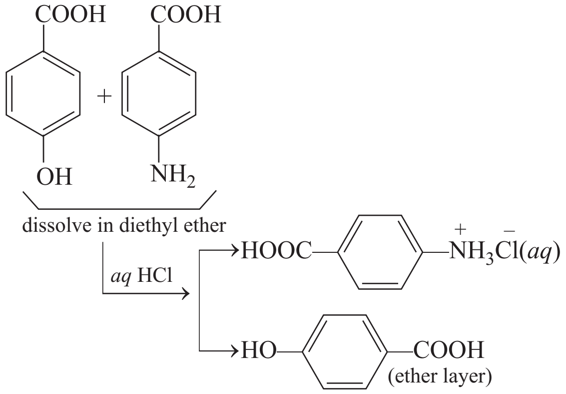

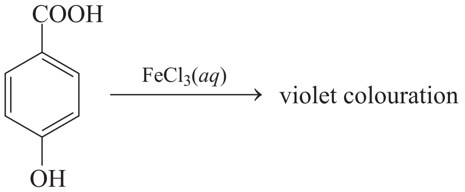

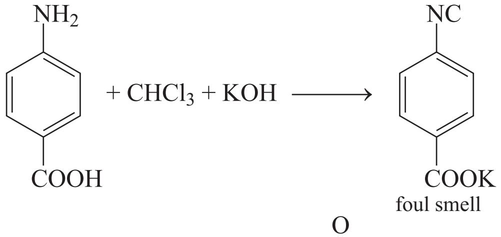

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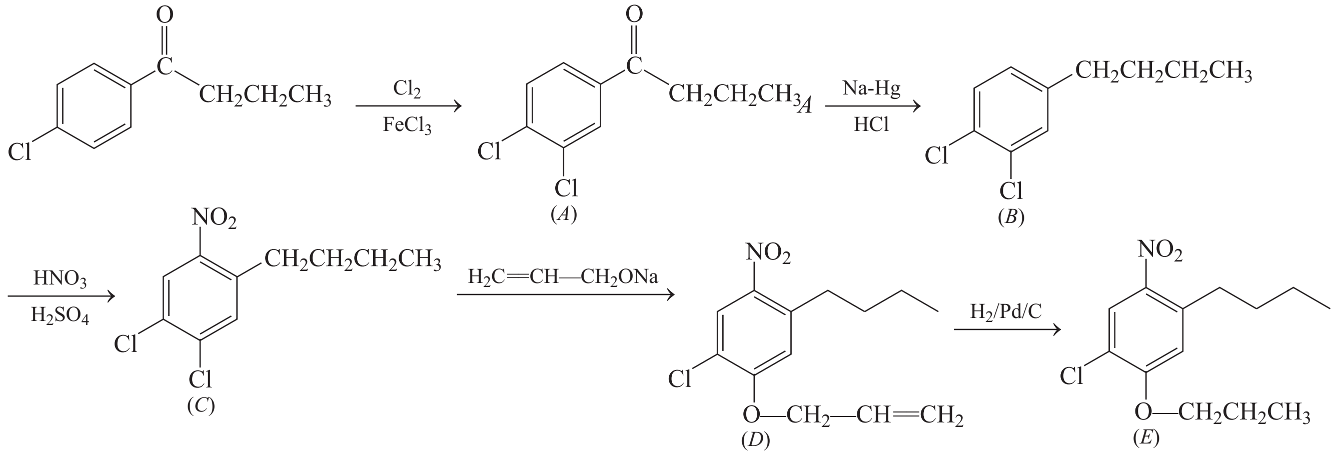

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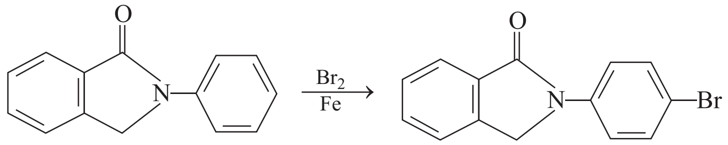
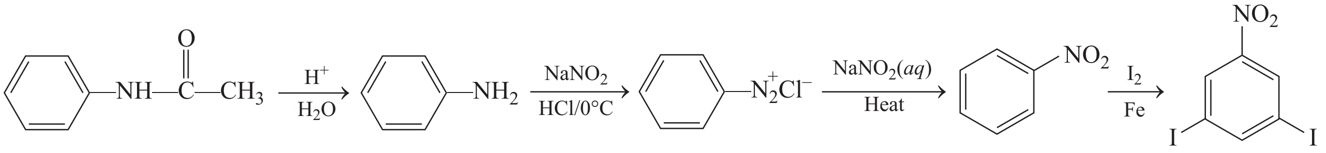


45. $C_6H_5NH_2 \xrightarrow[HCl/0°C]{NaNO_2} C_6H_5\overset{+}{N}_2Cl^- \xrightarrow{CuCN} C_6H_5—CN \xrightarrow{LiAlH_4} C_6H_5—CH_2NH_2$

46.



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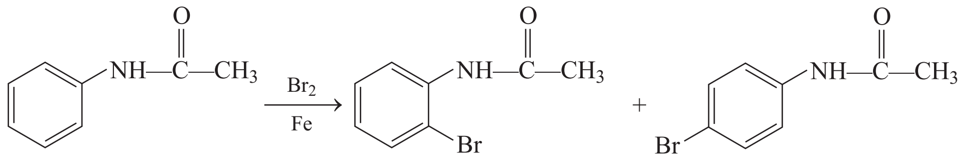
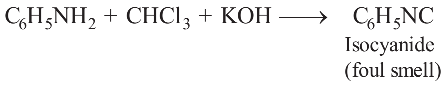
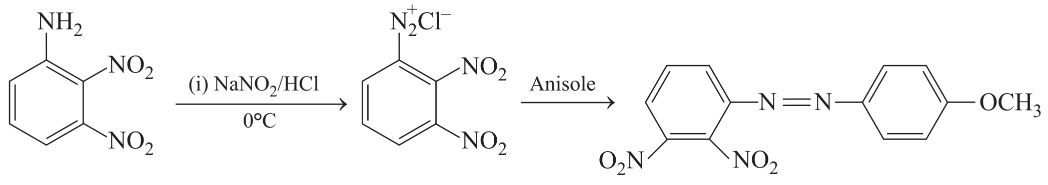


48.

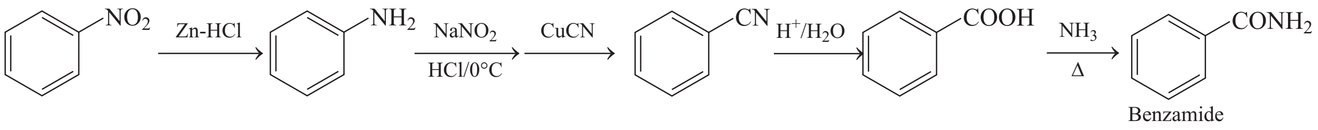


$C_6H_5NH_2 + CHCl_3 + KOH \longrightarrow \underset{\substack{\text{Isocyanide} \\ \text{(foul smell)}}}{C_6H_5NC}$

49.



50.



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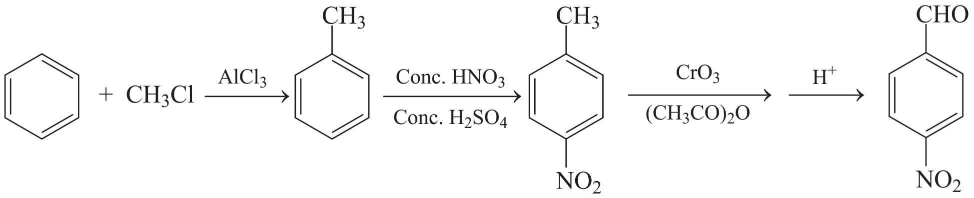

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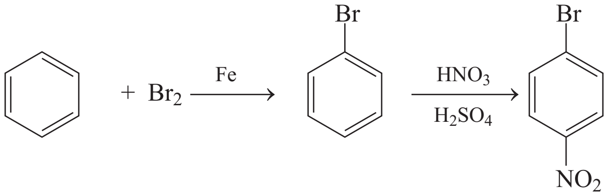
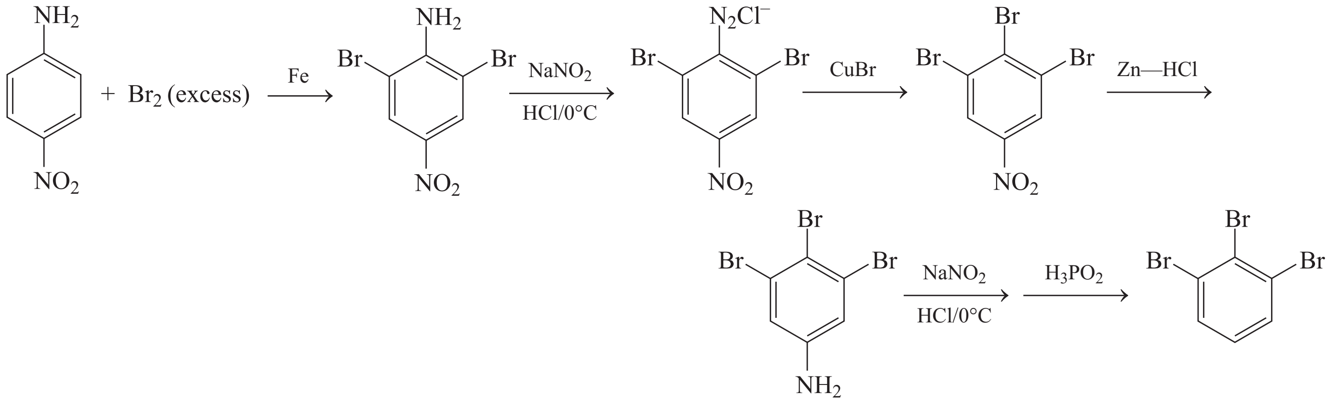


53. No reaction. Tertiary amine does not react with nitrous acid.

54.



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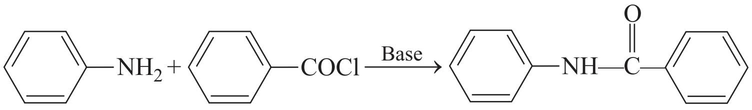

56. $C_6H_5—NH_2 \xrightarrow[0°C]{NaNO_2/HCl} C_6H_5\overset{+}{N_2}Cl^- \xrightarrow[Heat]{CuCl} C_6H_5—Cl$

57. $C_6H_6 + \text{Conc. } HNO_3 / \text{Conc.} H_2SO_4 \longrightarrow C_6H_5—NO_2 \xrightarrow{Zn-HCl} \underset{\text{Aniline}}{C_6H_5—NH_2}$

58. $C_6H_5NH_2 + NaNO_2 \xrightarrow[0°C]{HCl} C_6H_5\overset{+}{N_2}Cl^- \xrightarrow[Heat]{CuCl} C_6H_5—Cl$