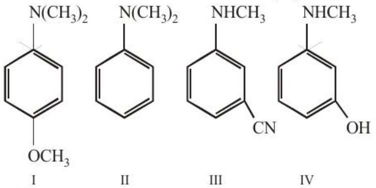
27

Amines

TOPIC 1 Aliphatic and Aromatic Amines

1. The increasing order of pK_b values of the following compounds is : **[Sep. 06, 2020 (I)]**

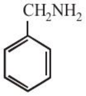


(a) II < IV < III < I (b) I < II < IV < III

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

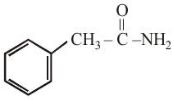
2. Which of the following compounds can be prepared in good yield by Gabriel phthalimide synthesis? **[Sep. 06, 2020 (II)]**

(a)

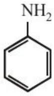


(b) $CH_3-CH_2-NHCH_3$

(c)



(d)

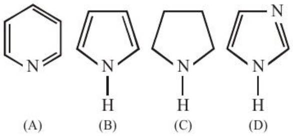


3. The most appropriate reagent for conversion of C_2H_5CN into $CH_3CH_2CH_2NH_2$ is : **[Sep. 05, 2020 (I)]**

(a) $NaBH_4$ (b) CaH_2

(c) $LiAlH_4$ (d) $Na(CN)BH_3$

4. The increasing order of basicity of the following compounds is: **[Sep. 05, 2020 (I)]**



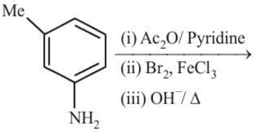
(a) (A) < (B) < (C) < (D)

(b) (B) < (A) < (D) < (C)

(c) (D) < (A) < (B) < (C)

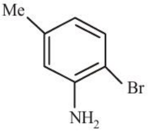
(d) (B) < (A) < (C) < (D)

5. The final major product of the following reaction is :

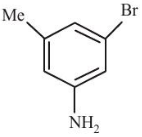


[Sep. 05, 2020 (II)]

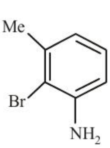
(a)



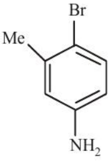
(b)



(c)



(d)



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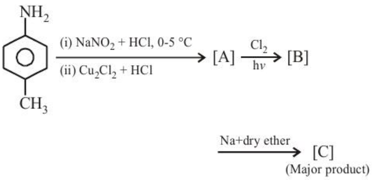
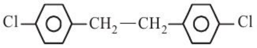
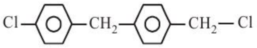
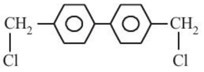
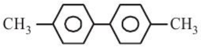
6. In the following reaction sequence, [C] is : **[Sep. 04, 2020 (II)]**



(a) 

(b) 

(c) 

(d) 

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

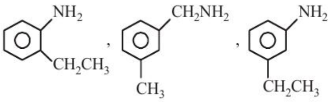
A and C $\xrightarrow{\text{Diazotization}}$ P + Q $\xrightarrow[\text{(ii) Oxidation } (KMnO_4 + H^+)]{\text{(i) Hydrolysis}}$

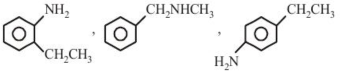
R (product of A) + S (product of C)

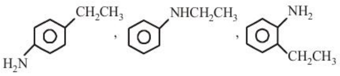
R has lower boiling point than S

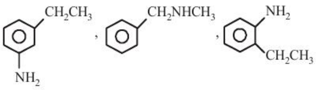
B $\xrightarrow{C_6H_5SO_2Cl}$ alkali-insoluble product

A, B and C, respectively are : **[Sep. 03, 2020 (II)]**

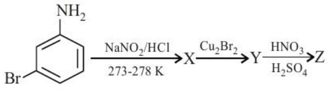
(a) 

(b) 

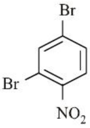
(c) 

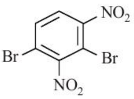
(d) 

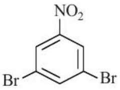
8. The major product Z obtained in the following reaction scheme is: **[Jan. 09, 2020 (I)]**



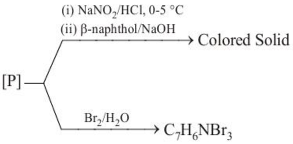
(a) 

(b) 

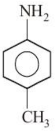
(c) 

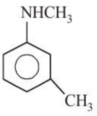
(d) 

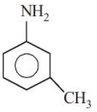
9. Consider the following reactions,

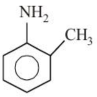


The compound [P] is: **[Jan. 09, 2020 (II)]**

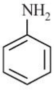
(a) 

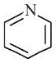
(b) 

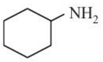
(c) 

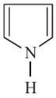
(d) 

10. The decreasing order of basicity of the following amines is: **[Jan. 09, 2020 (II)]**


(A)


(B)


(C)


(D)

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

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

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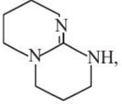
11. The increasing order of pK_b for the following compounds will be: **[Jan. 07, 2020 (I)]**

$NH_2-CH=NH,$

(A)



(B)

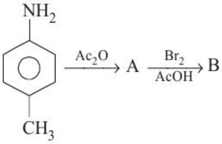
CH_3NHCH_3

(C)

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

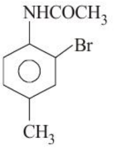
(c) (C) < (A) < (B) (d) (B) < (A) < (C)

12. In the following reaction sequence,

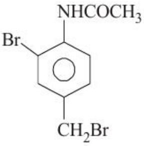


the major product B is: **[Jan. 07, 2020 (II)]**

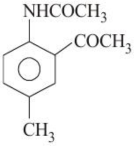
(a)



(b)



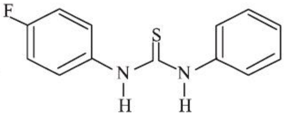
(c)



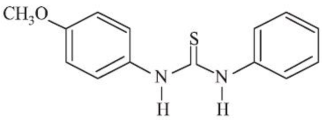
(d)

13. The increasing order of the pK_b of the following compounds is : **[April 12, 2019 (I)]**

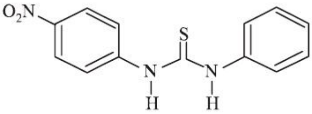
(A)



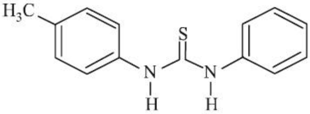
(B)



(C)



(D)



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

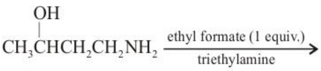
(c) (B) < (D) < (A) < (C) (d) (B) < (D) < (C) < (A)

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

(a) NH_2NH_2 (b) CaH_2

(c) $NaBH_4$ (d) H_2O

15. The major product of the following reaction is: **[April 10, 2019 (I)]**



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

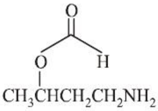
(a)

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

(b)

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

(c)



(d) $CH_3CH=CH-CH_2NH_2$

16. Which of the following is NOT a correct method of the preparation of benzylamine from cyanobenzene ? **[April 10, 2019 (II)]**

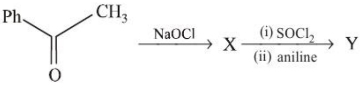
(a) H_2/Ni

(b) (i) $LiAlH_4$ (ii) H_3O^+

(c) (i) $SnCl_2$ + HCl(gas) (ii) $NaBH_4$

(d) (i) HCl/H_2O (ii) $NaBH_4$

17. The major product 'Y' in the following reaction is: **[April 10, 2019 (II)]**



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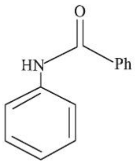
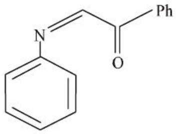
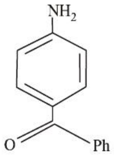
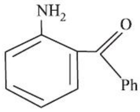
(a)


(b)


(c)


(d)


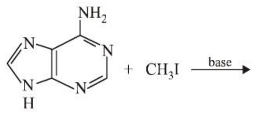
18. Hinsberg's reagent is: **[April 9, 2019 (II)]**
(a) C_6H_5COCl (b) $SOCl_2$
(c) $C_6H_5SO_2Cl$ (d) $(COCl)_2$

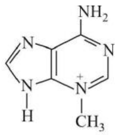
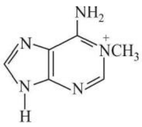
19. Which of the following amines can be prepared by Gabriel phthalimide reaction ? **[April 8, 2019 (I)]**
(a) *n*-butylamine (b) triethylamine
(c) *t*-butylamine (d) neo-pentylamine

20. In the following compounds, the decreasing order of basic strength will be: **[April 8, 2019 (I)]**
(a) $C_2H_5NH_2 > NH_3 > (C_2H_5)_2NH$
(b) $(C_2H_5)_2NH > NH_3 > C_2H_5NH_2$
(c) $(C_2H_5)_2NH > C_2H_5NH_2 > NH_3$
(d) $NH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$

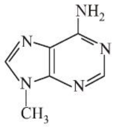
21. Polysubstitution is a major drawback in : **[April 8, 2019 (II)]**
(a) Friedel Craft's alkylation
(b) Reimer Tiemann reaction
(c) Acetylation of aniline
(d) Friedel Craft's acylation

22. The major product in the following reaction is: **[April 8, 2019 (II)]**

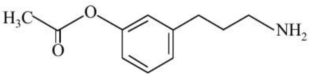


(a)

(b)


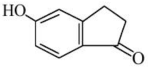
(c)

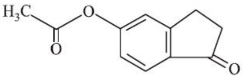
(d)


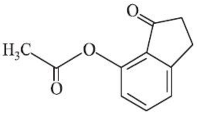
23. The major product of the following reaction is : **[Jan. 12, 2019 (II)]**

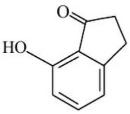


$\xrightarrow{\text{(i)NaNO}_2/\text{H}^+}$
(ii) CrO_3/H^+
(iii) H_2SO_4 (conc.), Δ

(a)


(b)


(c)


(d)


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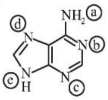
24. In the following compound,



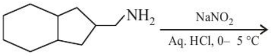
the favourable site/s for protonation is/are :

[Jan. 11, 2019 (II)]

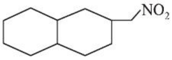
(a) (a) and (e) (b) (b), (c) and (d)

(c) (a) and (d) (d) (a)

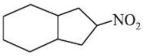
25. The major product formed in the reaction given below will be: **[Jan. 10, 2019 (I)]**



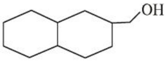
(a)



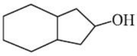
(b)



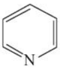
(c)



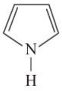
(d)



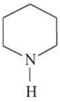
26. Arrange the following amines in the decreasing order of basicity : **[Jan. 9, 2019 (I)]**



I



II

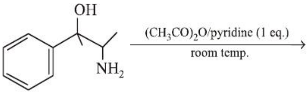


III

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

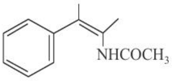
(c) III > II > I (d) I > III > II

27. The major product obtained in the following reaction is:

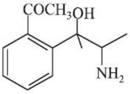


[Jan. 9, 2019 (II)]

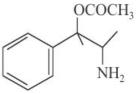
(a)



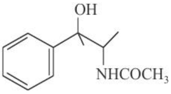
(b)



(c)



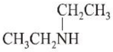
(d)



28. The increasing basicity order of the following compounds is: **[Jan. 9, 2019 (II)]**

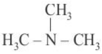
(A) $CH_3CH_2NH_2$

(B)



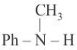
$CH_3CH_2\overset{CH_2CH_3}{\overset{|}{N}}H$

(C)



$H_3C-\overset{CH_3}{\overset{|}{N}}-CH_3$

(D)

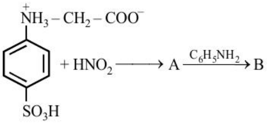


$Ph-\overset{CH_3}{\overset{|}{N}}-H$

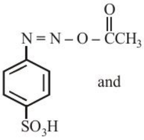
(a) (D) < (C) < (B) < (A) (b) (D) < (C) < (A) < (B)

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

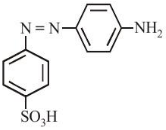
29. Products A and B formed in the following reactions are respectively : **[Online April 16, 2018]**



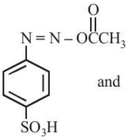
(a)



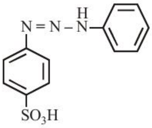
and



(b)



and



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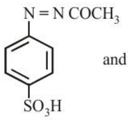
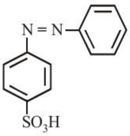
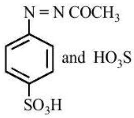
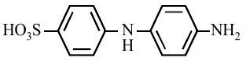
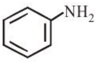
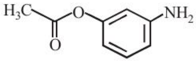
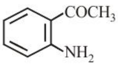
(c)  and 

(d)  and 

30. The increasing order of diazotisation of the following compounds is: **[Online April 15, 2018 (II)]**

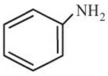
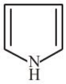
(A)  (B) 

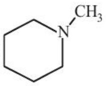
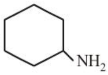
(C) 

(D) 

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

31. Among the following compounds, the increasing order of their basic strength is : **[Online April 9, 2017]**

(I)  (II) 

(III)  (IV) 

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

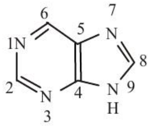
32. In the Hofmann bromamide degradation reaction, the number of moles of NaOH and Br_2 used per mole of amine produced are : **[2016]**

(a) Two moles of NaOH and two moles of Br_2.
(b) Four moles of NaOH and one mole of Br_2.
(c) One mole of NaOH and one mole of Br_2.
(d) Four moles of NaOH and two moles of Br_2.

33. The test to distinguish primary, secondary and tertiary amines is : **[Online April 9, 2016]**

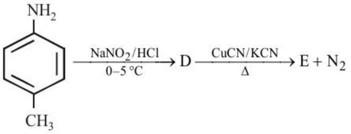
(a) Sandmeyer's reaction (b) Carbylamine reaction
(c) Mustard oil test (d) $C_6H_5SO_2Cl$

34. The "N" which does not contribute to the basicity for the compound is : **[Online April 10, 2016]**

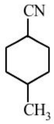
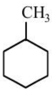


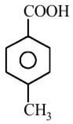
(a) N9 (b) N3 (c) N1 (d) N7

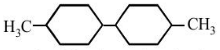
35. In the reaction



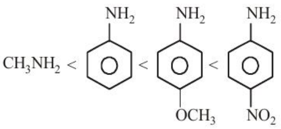
the product E is : **[2015]**

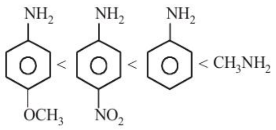
(a)  (b) 

(c) 

(d) 

36. Arrange the following amines in the order of increasing basicity. **[Online April 10, 2015]**

(a) 

(b) 

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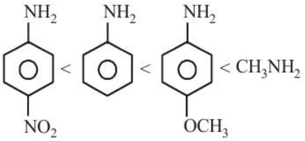
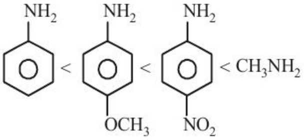
(c) 

(d) 

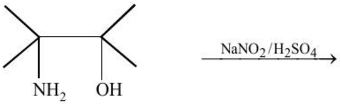
37. On heating an aliphatic primary amine with chloroform and ethanolic potassium hydroxide, the organic compound formed is: **[2014]**

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

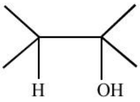
38. Considering the basic strength of amines in aqueous solution, which one has the smallest pK_b value? **[2014]**

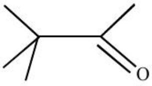
(a) $(CH_3)_2NH$ (b) CH_3NH_2
(c) $(CH_3)_3N$ (d) $C_6H_5NH_2$

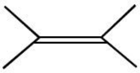
39. The major product of the reaction

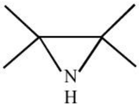


[Online April 9, 2014]

(a) 

(b) 

(c) 

(d) 

40. The final product formed when methyl amine is treated with $NaNO_2$ and HCl is: **[Online April 19, 2014]**

(a) Diazomethane (b) Methylalcohol
(c) Methylcyanide (d) Nitromethane

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

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

42. The order of basicity of amines in gaseous state is: **[Online April 23, 2013]**

(a) $1° > 2° > 3° > NH_3$ (b) $3° > 2° > NH_3 > 1°$
(c) $3° > 2° > 1° > NH_3$ (d) $NH_3 > 1° > 2° > 3°$

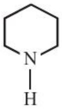
43. Carbylamine forms from aliphatic or aromatic primary amine via which of the following intermediates? **[Online April 25, 2013]**

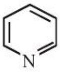
(a) Carbanion (b) Carbene
(c) Carbocation (d) Carbon radical

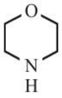
44. The most basic compound among the following is **[2005, Online May 7, 2012]**

(a) Acetanilide (b) Benzylamine
(c) *p*-Nitro aniline (d) Aniline

45. The order of basicity of the compounds


(I)


(II)

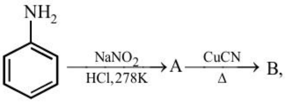

(III)


(IV)

is **[Online May 19, 2012; Online May 26, 2012]**

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

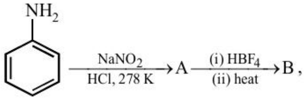
46. In the chemical reactions: **[2011RS]**



the compounds A and B respectively are:

(a) Benzene diazonium chloride and benzonitrile
(b) Nitrobenzene and chlorobenzene
(c) Phenol and bromobenzene
(d) Fluorobenzene and phenol

47. In the chemical reactions,



the compounds 'A' and 'B' respectively are **[2010]**

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

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

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

49. In the chemical reaction,

$CH_3CH_2NH_2 + CHCl_3 + 3KOH \rightarrow$
$(A) + (B) + 3H_2O$, the compounds (A) and (B) are respectively **[2007]**

(a) C_2H_5NC and 3KCl
(b) C_2H_5CN and 3KCl
(c) $CH_3CH_2CONH_2$ and 3KCl
(d) C_2H_5NC and K_2CO_3.

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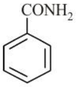
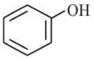
50. Which one of the following methods is neither meant for the synthesis nor for separation of amines? **[2005]**
(a) Curtius reaction (b) Wurtz reaction
(c) Hofmann method (d) Hinsberg method

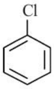
51. The correct order of increasing basic nature for the bases NH_3, CH_3NH_2 and $(CH_3)_2NH$ is **[2003]**
(a) $(CH_3)_2NH < NH_3 < CH_3NH_2$
(b) $NH_3 < CH_3NH_2 < (CH_3)_2NH$
(c) $CH_3NH_2 < (CH_3)_2NH < NH_3$
(d) $CH_3NH_2 < NH_3 < (CH_3)_2NH$

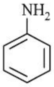
TOPIC 2 Amides, Cyanides and Isocyanides

52. Which of these will produce the highest yield in Friedel Crafts reaction? **[Jan. 09, 2020 (I)]**

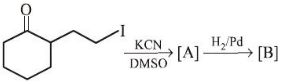
(a) 

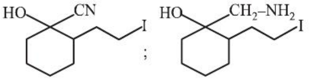
(b) 

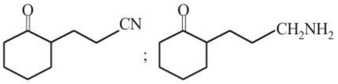
(c) 

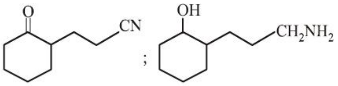
(d) 

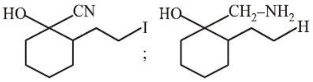
53. The major products A and B for the following reactions are, respectively: **[April 9, 2019 (II)]**



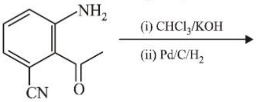
(a) 

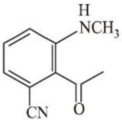
(b) 

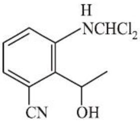
(c) 

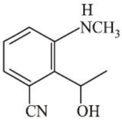
(d) 

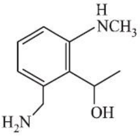
54. The major product obtained in the following reaction is : **[April 8, 2019 (II)]**



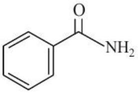
(a) 

(b) 

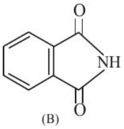
(c) 

(d) 

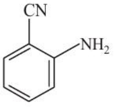
55. The increasing order of reactivity of the following compound towards reaction with alkyl halides directly is: **[Jan. 12, 2019 (I)]**



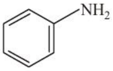
(A)



(B)



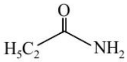
(C)

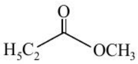


(D)

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

56. The increasing order of the reactivity of the following with $LiAlH_4$ is : **[Jan. 12, 2019 (II)]**

(A) 
$H_5C_2-\overset{O}{\overset{\|}{C}}-NH_2$

(B) 
$H_5C_2-\overset{O}{\overset{\|}{C}}-OCH_3$

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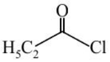
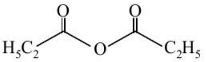
(C) 

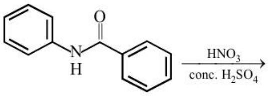
(D) 

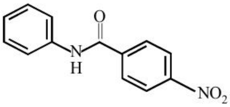
(a) (B) < (A) < (C) < (D) (b) (B) < (A) < (D) < (C)
(c) (A) < (B) < (D) < (C) (d) (A) < (B) < (C) < (D)

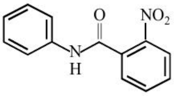
57. A compound 'X' on treatment with Br_2/NaOH, provided C_3H_9N, which gives positive carbylamine test. Compound 'X' is : **[Jan. 11, 2019 (II)]**

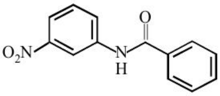
(a) $CH_3COCH_2NHCH_3$ (b) $CH_3CH_2COCH_2NH_2$
(c) $CH_3CH_2CH_2CONH_2$ (d) $CH_3CON(CH_3)_2$

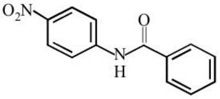
58. What will be the major product in the following mononitration reaction? **[Jan. 10, 2019 (II)]**



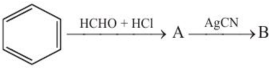
(a) 

(b) 

(c) 

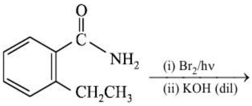
(d) 

59. The compounds A and B in the following reaction are, respectively : **[Jan. 9, 2019 (I)]**

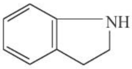


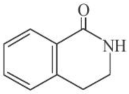
(a) A = Benzyl alcohol, B = Benzyl cyanide
(b) A = Benzyl chloride, B = Benzyl cyanide
(c) A = Benzyl alcohol, B = Benzyl isocyanide
(d) A = Benzyl chloride, B = Benzyl isocyanide

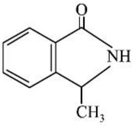
60. The major product of the following reaction is:

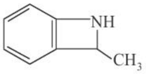


[Jan. 9, 2019 (II)]

(a) 

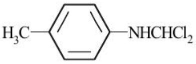
(b) 

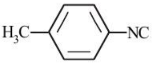
(c) 

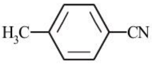
(d) 

61. The reaction of chloroform with alcoholic KOH and p-toluidine forms **[2003]**

(a) 

(b) 

(c) 

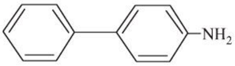
(d) 

62. Ethyl isocyanide on hydrolysis in acidic medium generates **[2003]**
(a) propanoic acid and ammonium salt
(b) ethanoic acid and ammonium salt
(c) methylamine salt and ethanoic acid
(d) ethylamine salt and methanoic acid

63. When a primary amine reacts with chloroform in ethanolic KOH then the product is **[2002]**
(a) an isocyanide (b) an aldehyde
(c) a cyanide (d) an alcohol.

TOPIC 3 Nitrocompounds, Alkyl Nitrites and Diazonium Salts

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

(a) 

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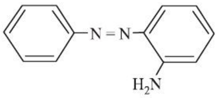
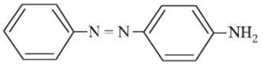
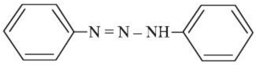
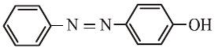
EBD_8345

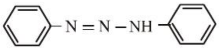
(b)


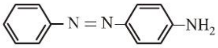
(c)


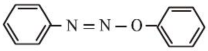
(d)


65. Aniline dissolved in dilute HCl is reacted with sodium nitrate 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: **[April 9, 2019 (I)]**

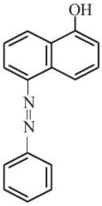
(a)


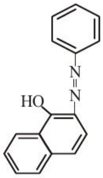
(b)


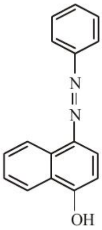
(c)


(d)


66. Coupling of benzene diazonium chloride with 1-naphthol in alkaline medium will give : **[April 8, 2019 (I)]**

(a)


(b)


(c)


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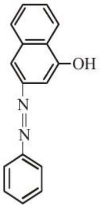
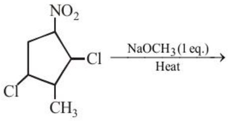
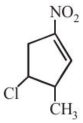
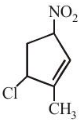


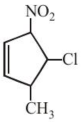
67. The major product formed in the following reaction is:

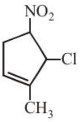


[Online April 15, 2018 (II)]

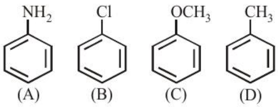
(a)


(b)


(c)


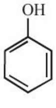
(d)


68. The increasing order of nitration of the following compounds is : **[Online April 15, 2018 (I)]**

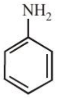


(a) (A) < (B) < (D) < (C) (b) (A) < (B) < (C) < (D)
(c) (B) < (A) < (C) < (D) (d) (B) < (A) < (D) < (C)

69. Which of the following compounds will form significant amount of meta product during mono-nitration reaction ? **[2017]**

(a)


(b)


(c)


(d)


70. Fluorination of an aromatic ring is easily accomplished by treating a diazonium salt with HBF_4. Which of the following conditions is correct about this reaction?
[Online April 10, 2016]

(a) NaF/Cu (b) Cu_2O/H_2O
(c) Only heat (d) $NaNO_2/Cu$

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71. Complete reduction of benzene-diazonium chloride with Zn/HCl gives: **[Online April 11, 2014]**

(a) Aniline (b) Phenylhydrazine

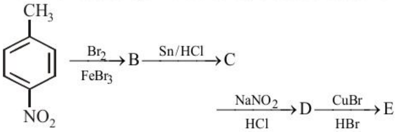
(c) Azobenzene (d) Hydrazobenzene

72. Conversion of benzene diazonium chloride to chlorobenzene is an example of which of the following reactions? **[Online April 12, 2014]**

(a) Claisen (b) Friedel-craft

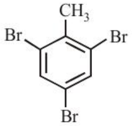
(c) Sandmeyer (d) Wurtz

73. In a set of reactions *p*-nitrotoluene yielded a product E.

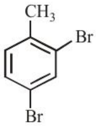


The product E would be: **[Online April 19, 2014]**

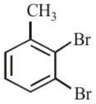
(a)



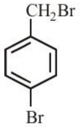
(b)



(c)



(d)



74. The conversion of benzene diazonium chloride to bromobenzene can be accomplished by

(a) Reimer-Tiemann reaction **[Online May 12, 2012]**

(b) Friedel-Crafts reaction

(c) Gattermann reaction

(d) Azo-Coupling reaction

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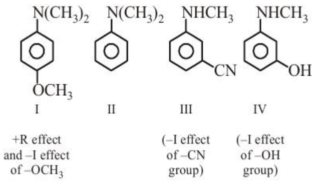
Hints & Solutions

1. **(b)**



– OCH$_3$ group increases electron density of ring at *o*- and *p*- position making (I) most basic. (III) is least basic due to –I effect of –CN group at meta position.
Since, –I effect of –CN > –I effect of –OH group.
Hence, correct basic strength will follow the order

$$I > II > IV > III$$

$$\text{Basic strength} \propto \frac{1}{pK_b \text{ value}}$$

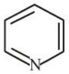
Order of K_b value is, I < II < IV < III.

2. **(a)** Gabriel phthalimide synthesis gives 1° amine in good yield.

3. **(c)** $CH_3CH_2-C\equiv N \xrightarrow{LiAlH_4} CH_3CH_3-CH_2-NH_2$

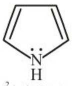
NaBH$_4$ does not reduce R–CN.

4. **(b)** (A)



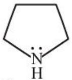
sp^2 hyb. N atom
(localised L.P.)

(B)



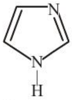
sp^2 hyb. N atom
(delocalised L.P.)

(C)



sp^3 hyb. N atom
(localised L.P.)

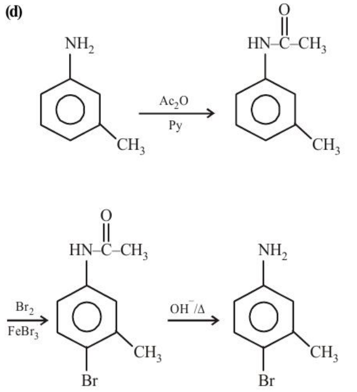
(D)



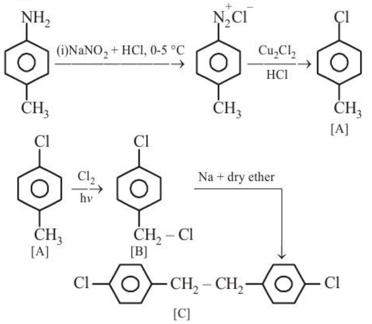
sp^2 hyb. N atom
(localised L.P. with partial negative ch.)

Thus, increasing order of basicity is
(B) < (A) < (D) < (C).

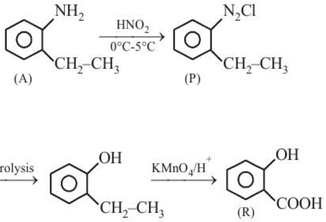
5. **(d)**



6. **(a)**



7. **(b)**



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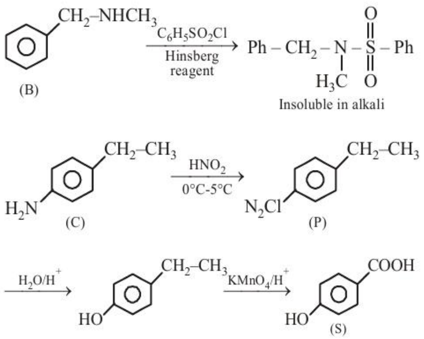
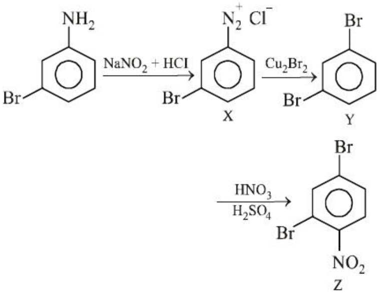
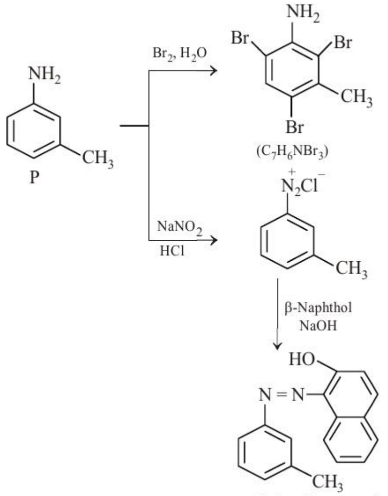


8. **(b)**



9. **(c)**



Coloured compounds

10. (d) Basic strength of amines depends upon availability of lone pair of electrons. Aliphatic amines are more basic than aromatic amines.

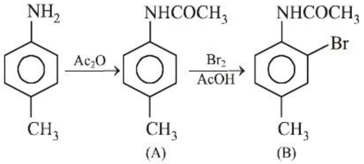
11. **(d)** Conjugate acid of guanadine(B) is resonance stabilised and have 2 resonance structure.

Similarly conjugate acid of (A) is also resonance stabilised and have one resonance structure. (C) does not exhibit resonance structure.

therefore the basic order is, k_b : (B) > (A) > (C)

∴ pk_b : (B) < (A) < (C)

12. **(a)**

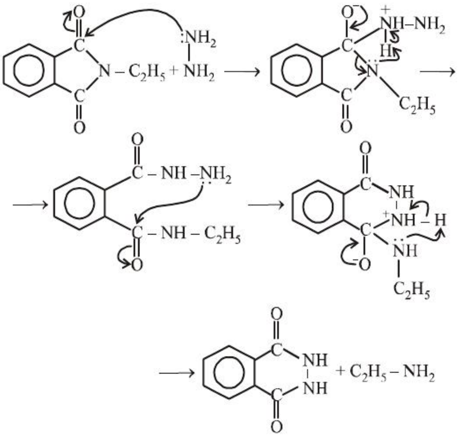


13. **(c)** Electron withdrawing group attached to benzene ring will reduce the basic strength and increase pK_b, while electron donating group decreases pK_b.

Therefore the correct increasing order of pK_b is

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

14. **(a)** N-Ethyl phthalimide on treatment with $NH_2–NH_2$ gives ethylamine.



In place of NH_2NH_2 we can also use H_2O in presence of H^+ or OH^- as a catalyst.

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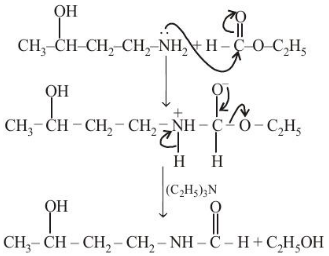
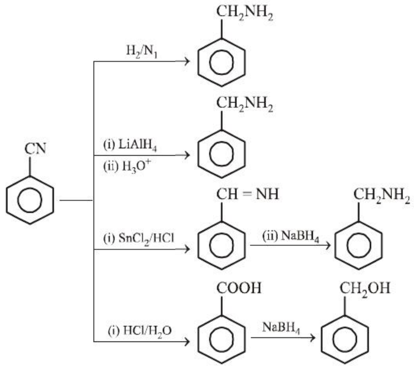
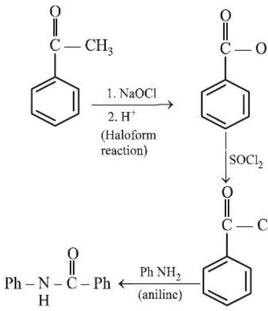
15. **(b)**



16. **(d)**

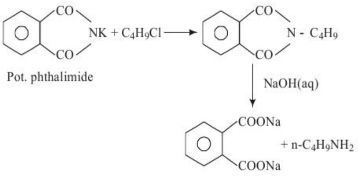


17. **(a)**



18. **(c)** Hinsberg's reagent is benzenesulphonyl chloride ($C_6H_5SO_2Cl$). It is used for detection of primary, secondary and tertiary amines.

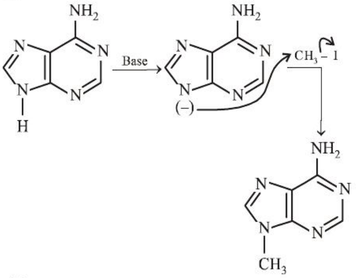
19. **(a)** Primary amines are prepared by Gabriel phthalimide synthesis



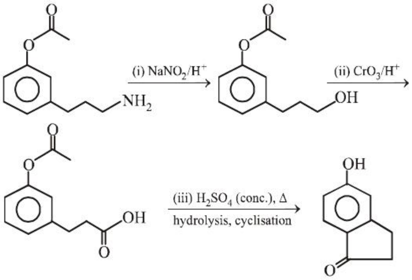
20. **(c)** $\underset{\text{Two +I gp.}}{(C_2H_5)_2NH} > \underset{\text{one + I gp.}}{C_2H_5NH_2} > \underset{\text{No + I gp.}}{NH_4}$

21. **(a)** Polysubstitution is a major drawback in Friedel Craft's alkylation because the introduced alkyl group is activating and gives polyalkylated product.

22. **(d)**



23. **(a)**



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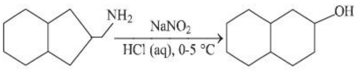
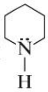
24. **(b)** Higher the electronegativity ($sp^2 > sp^3$) of an atom, more will be its capacity to take proton. Thus N labelled as (b, (c) and (d) are better protonated than the N at (a) and (e).

25. **(N)**

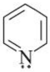


26. **(b)** Compound, III



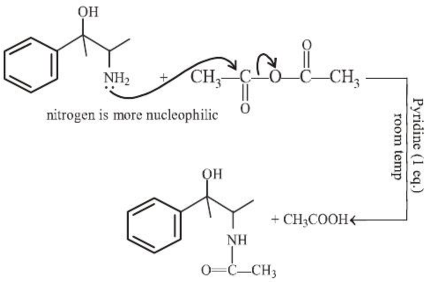
is most basic as the lone pair of nitrogen is easily available for the donation.

In case of compound (I)



lone pair is not involved in resonance but nitrogen atom is sp^2 hybridsed, whereas in compound II the lone pair of nitrogen is involved in aromaticity which makes it least basic.

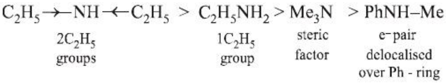
27. **(4)** – NH_2 is a stronger base than – OH, hence 1 equation of acetic anhydride will acetylate only – NH_2 group. Reaction involved:



28. **(2)**

		pK_b
(A)	$EtNH_2$	3.29
(B)	$(Et)_2NH$	3.00
(C)	Me_3N	4.22
(D)	Ph – NH – Me	4.7

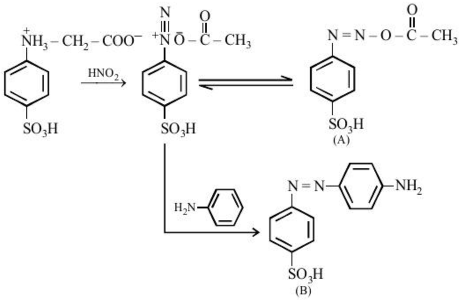
So, order of basic strength is:



$$\underset{\substack{2C_2H_5\\\text{groups}}}{C_2H_5\rightarrow NH\leftarrow C_2H_5} > \underset{\substack{1C_2H_5\\\text{group}}}{C_2H_5NH_2} > \underset{\substack{\text{steric}\\\text{factor}}}{Me_3N} > \underset{\substack{\text{e-pair}\\\text{delocalised}\\\text{over Ph - ring}}}{PhNH{-}Me}$$

(B) > (A) > (C) > (D)

29. **(a)**

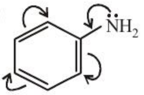


30. **(d)** Aromatic diazonium salts are more stable than aliphatic diazonium salts. The higher stability of aryl diazonium salts is due to resonance. Electron donating substituents increase electron density on benzene ring. Hereby they increase the stability of diazonium salts. Electron withdrawing substituents decrease electron density on benzene ring. Hereby they decrease the stability of diazonium salts. $-COCH_3$ group is electron withdrawing and hence, diazonium salts from (D) is less stable than that from (B). Although $-O-COCH_3$ is electron donating substituent, but it is present in meta position. Hence, it will not have significant effect on stability.

Therefore the increasing order of diazotisation is

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

31. **(c)** (a)



+ R effect

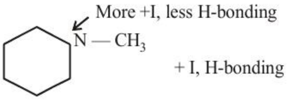
the lone pair of electron is less easily available for protonation.

(b)

+ R effect

the lone pair of electron is not available for proton.

(c)



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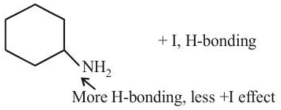
+I more preferred than H-bonding, is due to steric hindrance to H-bonding in 1° amine.

(d)



Unstable Thus, the correct order is

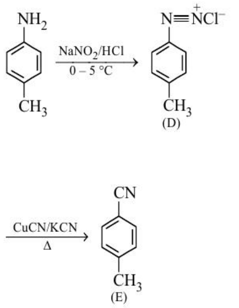
$$(I) < (II) < (IV) < (III)$$

32. **(b)** $RCONH_2 + Br_2 + 4NaOH \longrightarrow R–NH_2 + K_2CO_3 + 2NaBr + 2H_2O$

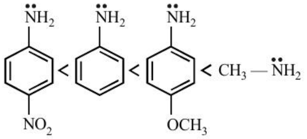
33. **(d)** Primary, secondary and tertiary amines are distinguished by Hinsberg reagent test. The Hinsberg reagent is an alternative name for benzene sulphonyl chloride ($C_6H_5SO_2Cl$).

34. **(a)** Lone pair of N is involved in aromaticity.

35. **(a)**



36. **(c)** Aliphatic amines are more basic than aromatic amines thus methylamine is most basic. Electron donating groups increase the basicity whereas electron withdrawing groups decrease the basicity of the aromatic amines. Thus *p*-methoxyaniline is more basic than aniline which is further more basic than *p*-nitroaniline.



37. **(d)** $R-CH_2-NH_2 + CHCl_3 + 3KOH\ (alc) \xrightarrow{\text{(Carbyl amine reaction)}} \underset{\text{Alkyl isocyanide}}{R-CH_2-NC} + 3KCl + 3H_2O$

38. **(a)** Arylamines are less basic than alkyl amines and even ammonia. This is due to resonance. In aryl amines the lone pair of electrons on N is partly shared with the ring and is thus less available for sharing with a proton.

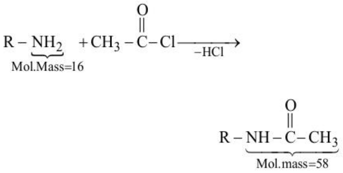
In alkylamines, the electron releasing alkyl group increases the electron density on nitrogen atom and thus also increases the ability of amine for protonation. Hence more the no. of alkyl groups higher should be the basicity of amine. But a slight discrepancy occurs in case of trimethyl amines due to steric effect. Hence the correct order is

$$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > C_6H_5NH_2$$

39. **(b)**

40. **(b)** $CH_3NH_2 + HNO_2 \longrightarrow CH_3OH + N_2 + H_2O$

41. **(b)**



$$R-\underbrace{NH_2}_{\text{Mol.Mass=16}} + CH_3-\overset{\overset{O}{\|}}{C}-Cl \xrightarrow[-HCl]{} R-\underbrace{NH-\overset{\overset{O}{\|}}{C}-CH_3}_{\text{Mol.mass=58}}$$

Now since the molecular mass increases by 42 unit as a result of the reaction of one mole of CH_3COCl with one-NH_2 group and the given increase in mass is (390 – 180) 210. Hence the number of $-NH_2$ groups = 210/42 = 5.

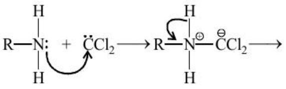
42. **(c)** The correct order of relative basicity of amines in the gas phase is $3° > 2° > 1° > NH_3$

The alkyl group releases electron and thus, tends to disperse the positive charge of the alkyl ammonium ion and therefore stabilises it. Since, NH_4^+ (from NH_3) has no such alkyl group, it is not stabilised to such an extent as alkylammonium ion.

43. **(b)** $RNH_2 + CHCl_3 + 3KOH \longrightarrow RNC + 3KCl + 3H_2O$

Mechanism

$$CHCl_3 \xrightarrow[\alpha\ \text{elimination}]{OH^-/\Delta} \underset{\text{Dichlorocarbene}}{\ddot{C}Cl_2}$$



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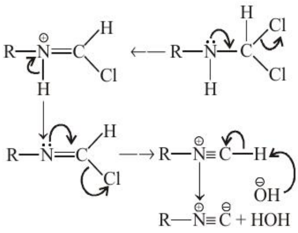
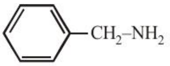
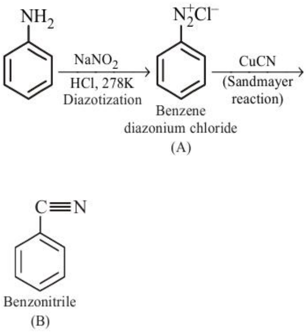


44. **(b)**  compound is most basic due to presence of localized lone pair of electron on nitrogen atom while other compounds have delocalized lone pair of electron.

45. **(b)** The order of basicity is I > III > II > IV
The lone pair of electrons on N is more readily available for protonation in I and III than in II. III contains an oxygen atom which has – I effect due to which it is less basic than I. In compound IV lone pair of e⁻s on N–atom is contributed towards the aromatic sextet formation and hence it is not at all available for protonation.

46. **(a)** 

47. **(c)** $\underset{1^\circ \text{ Aromatic amine}}{ArNH_2} + NaNO_2 + 2HX \xrightarrow{\text{cold}} \underset{\text{Arene diazonium salt}}{Ar—N\equiv N^+X^-} + NaX + 2H_2O$

The diazonium group can be replaced by fluorine by treating the diazonium salt with fluoroboric acid (HBF_4). The precipitated diazonium fluoroborate is isolated, dried and heated until decomposition occurs to yield the aryl fluoride. This reaction is known as **Balz-Schiemann reaction.**

$$Ar—N_2^+X^- \xrightarrow{HBF_4} Ar—N_2^+BF_4^- \downarrow$$

$$\xrightarrow{\text{heat}} Ar—F + BF_3 + N_2$$

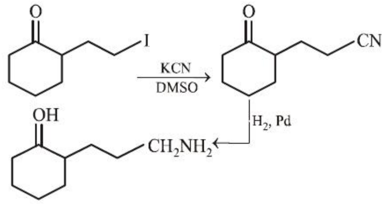
48. **(d) Note:** Aromatic amines (e.g. aniline) are less basic than aliphatic amines due to delocalisation of electrons. Among aliphatic amines the order of basicity in aq. solution is 2° > 1° > 3°. The electron density is decreased in 3° amine due to crowding of alkyl group over N atom which makes the approach and bonding by a proton relatively difficult. Therefore the basicity decreases.
∴ The correct order of basic strength is
Dimethylamine > Methyl amine > Trimethyl amine > Aniline.

49. **(a)** This is carbylamine reaction.
$CH_3CH_2NH_2 + CHCl_3 + 3KOH$
$\longrightarrow C_2H_5NC + 3KCl + 3H_2O$

50. **(b)** Wurtz reaction is used for the preparation of hydrocarbons from alkyl halides.
$RX + 2Na + XR \longrightarrow R-R + 2NaX$

51. **(b)** The alkyl groups are electron releasing (+ I) groups, thus increase the electron density around the nitrogen thereby increasing the availability of the lone pair of electrons to proton or Lewis acid and making the amine more basic. Hence more the number of alkyl groups, more basic is the amine. Therefore, the correct order is
$NH_3 < CH_3NH_2 < (CH_3)_2NH$

52. **(c)** Aniline and phenol form complex with lewis acid. Chlorobenzene produces highest yield in Friedel craft reaction among the given options.

53. **(c)** 

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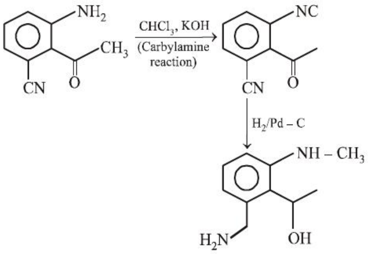
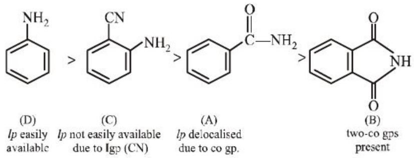
54. (d)



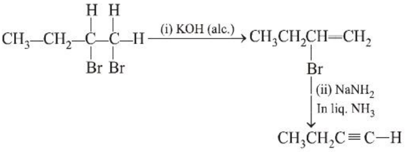
55. (a)



56. (c) The reactivity order of carboxylic acid derivatives depends on the electrophilicity of the carbonyl carbon and leaving tendency of the leaving group.
Leaving ability of the four groups is

$-Cl > -COOC_2H_5 > -OCH_3 > -NH_2$.

Therefore, reactivity order towards $LiAlH_4$ is



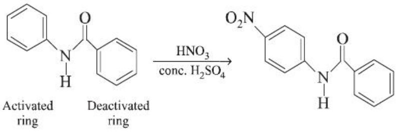
$$CH_3-CH_2-\underset{Br}{\overset{H}{C}}-\underset{Br}{\overset{H}{C}}-H \xrightarrow{\text{(i) KOH (alc.)}} CH_3CH_2\underset{Br}{CH}=CH_2 \xrightarrow[\text{In liq. } NH_3]{\text{(ii) } NaNH_2} CH_3CH_2C\equiv C-H$$

57. (c)

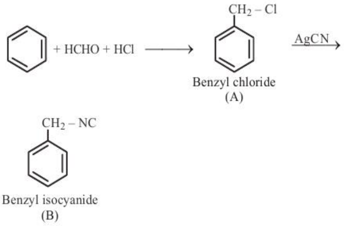
$$\underset{(X)}{CH_3CH_2CH_2CONH_2} \xrightarrow[\text{(Hofmann rearrangement)}]{Br_2/NaOH} \underset{(C_3H_9N)}{CH_3CH_2CH_2NH_2}$$

$$\xrightarrow[\text{KOH (Carbylamine reaction)}]{CHCl_3} CH_3CH_2CH_2NC$$

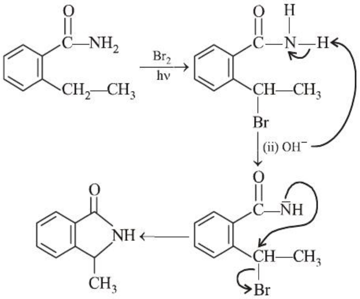
58. (d) In the given nitration reaction, major product will be formed as per the activating group, –NH part of $-NH-\overset{O}{\overset{\|}{C}}-$ is activating, while $-\overset{O}{\overset{\|}{C}}-$ part is deactivating group.



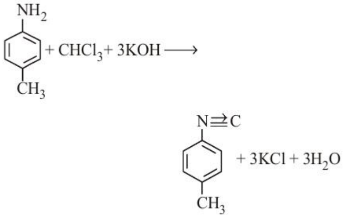
59. (d)



60. (3) Reaction involved for the given reaction:



61. (c)



62. (d) Ethyl isocyanide on hydrolysis form primary amines.

$$CH_3CH_2N\equiv C + H_2O \xrightarrow{H^+} CH_3CH_2NH_2 + HCOOH$$

63. (a) $C_2H_5NH_2 + CHCl_3 + 3KOH$

$$\longrightarrow \underset{\text{(Ethyl isocyanide)}}{C_2H_5N \equiv C} + 3KCl + 3HCl$$

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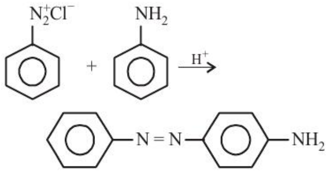
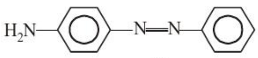
64. **(c)**

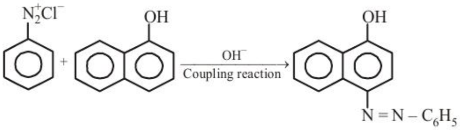


65. **(c)** In acidic medium, benzene diazonium chloride reacts with aniline (a basic compound) forming a_{30} dye (c).



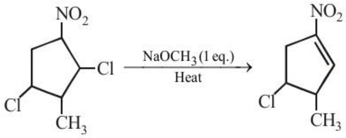
(c)

66. **(c)**



67. **(a)** Note : In the given reaction a molecule of HCl is lost and C = C double bond is formed. Thus it is dehydrohalogenation reaction.

Nitro group is electron withdrawing group. Hence increases the acidity of H atom (attached to C atom bearing nitro group) which is removed easily. Further the newly formed double bond is in conjugation with nitro group.



68. **(a)** In the given substituted benzene rings, the substitutents methoxy ($-OCH_3$) and amino ($-NH_2$) are strongly activating groups, while methyl ($-CH_3$) is weakly activating and chloro ($-Cl$) is a deactivating group towards electrophilic aromatic substituation reaction.

Since among methyl and methoxy group, methoxy group is more reactive than methyl group, (c) is more reactive than (d). Although amino group is strongly activating group, it gets protonated in presence of acid to form anilinium ion ($-\overset{+}{N}H_3$) which is strongly deactivating. Hence, (a) is less reactive than (c) and (d).

Chloro group is also deactivating group but less deactivating than ($-\overset{+}{N}H_3$). Thus order is (a) < (b) < (d) < (c).

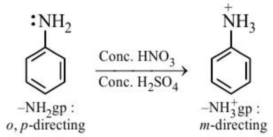
Note:

The activating groups increases the electron density on benzene ring and thus increases the rate of electrophilic aromatic substitution reaction. The deactivating groups decreases the electron density on benzene ring and thus decreases the rate of electrophilic aromatic substitution reaction.

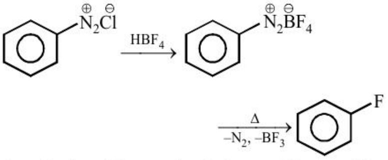
69. **(c)** Nitration takes place in presence of conc.

HNO_3 + conc. H_2SO_4.

In strongly acidic medium, amine is converted into anilinium ion ($-NH_3^+$); substitution is thus controlled not by $-NH_2$ group but by $-NH_3^+$ group which, because of its positive charge, directs the entering group to the meta-position instead of ortho- and para.

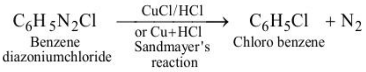


70. **(c)**



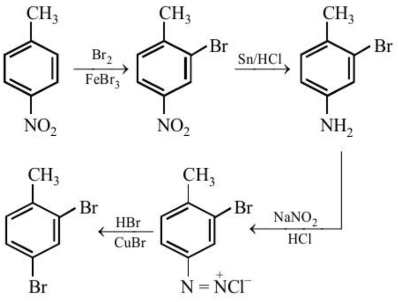
71. **(a)** On reduction with Zn and HCl, $C_6H_5N_2Cl$ forms aniline as the main product.

72. **(c)**

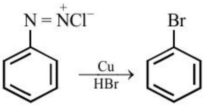


$$\underset{\text{Benzene diazoniumchloride}}{C_6H_5N_2Cl} \xrightarrow[\text{or Cu+HCl Sandmayer's reaction}]{CuCl/HCl} \underset{\text{Chloro benzene}}{C_6H_5Cl} + N_2$$

73. **(b)**



74. **(c)** Diazonium salts react with copper powder and hydrogen bromide to form bromobenzene. This reaction is known as **Gattermann reaction.**



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