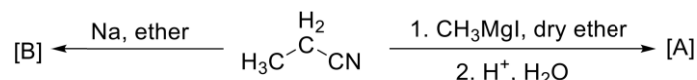


Question Set: Organonitrogen Compounds (CU, CEMA), for Sem-4, CC-4-8

2022 (CC-8)

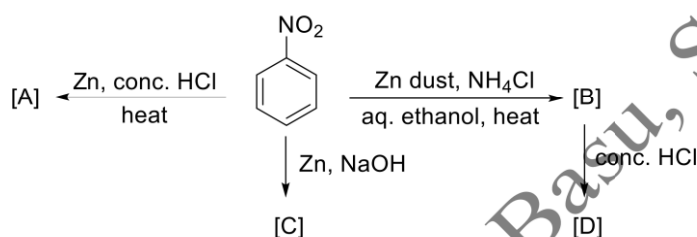
1. Phenol is directly converted into anisole on reaction with diazomethane but an aluminium alkoxide catalyst is required to convert ethanol to ethyl methyl ether with the same reagent. Explain. [Diazomethane] 1

2. Give the structures of A and B. [Organocyanide] 1



3. Provide the structures of the products obtained by diazo-coupling of benzenediazonium chloride with alkaline solution of β -naphthol and aniline separately. [Diazonium salts] 1

4. Identify A-D. Provide mechanism for conversion of B to D. [Aromatic nitro] 3



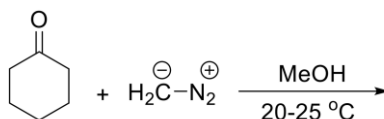
5. Primary and secondary nitroalkanes can take part in Nef carbonyl synthesis but tertiary nitroalkanes cannot. Explain. [Nitroalkanes] 2

6. Explain why anisole with a mixture of nitric acid and sulphuric acid gives *o*-nitroanisole in 31% yield whereas with $\text{HNO}_3\text{-Ac}_2\text{O}$ gives the same product in 71% yield. Provide a suitable mechanism to justify this observation. [Aromatic nitro] 3

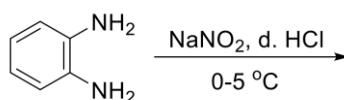
7. Show how a single reagent can be used to distinguish between primary, secondary and tertiary aromatic amines. (No mechanism needed.) [Aromatic amines] 2

8. Discuss the difficulties in synthesising $\text{Me}_3\text{C-NH}_2$ by Gabriel's phthalimide synthesis. Show how $\text{Me}_3\text{C-NH}_2$ can be synthesised from $\text{Me}_3\text{C-OH}$. [Aliphatic amines, Ritter] 3

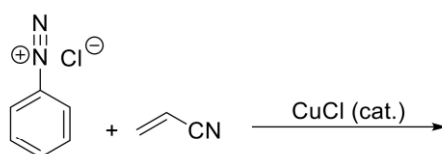
9. Predict the product(s) and provide the relevant mechanism. [Diazomethane, Tiffeneau-Demjanov] 2



10. Predict the product(s) and provide the relevant mechanism. [Aromatic amines] 2

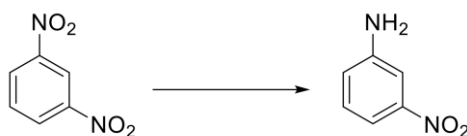


11. Predict the product(s) and provide the relevant mechanism. [Meerwein arylation] 1.5



2021 (CC-8)

12. Carry out the following conversion: [Aromatic nitro] 1

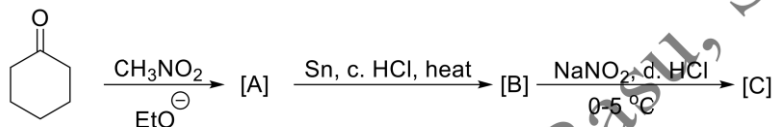


13. Suggest a reason for using excess mineral acid in diazotization. [Diazonium salts] 1

14. *p*-Toluidine reacts with benzenediazonium chloride to form a compound, which on boiling with H₂SO₄ gives four products (excluding nitrogen). Discuss. [Aromatic amines, diazonium salts] 3

15. Compare the reaction behaviour of aniline, *N*-methylaniline, and *N,N*-dimethylaniline towards NaNO₂ and dilute HCl. Explain the reactions. [Aromatic amines] 3

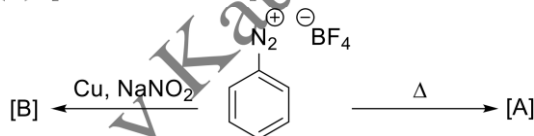
16. Suggest structures [A], [B] and [C]. Also suggest a mechanism of conversion from [B] to [C]. [Nitroalkanes, Tiffeneau-Demjanov] 3



17. Mention two chemical differences between RCN and RNC. [Organocyanides] 2

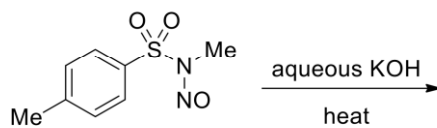
18. Alkyl halides give mainly cyanides with aqueous ethanolic KCN, but with AgCN, isocyanides become the major products. Account for these observations. [Organocyanides] 3

19. Give the structures of (A) and (B): [Diazonium salts] 1

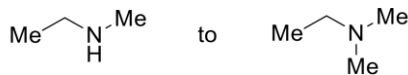


2019 (Third Paper)

20. Give the product of the following reaction with mechanism: [Diazomethane] 2

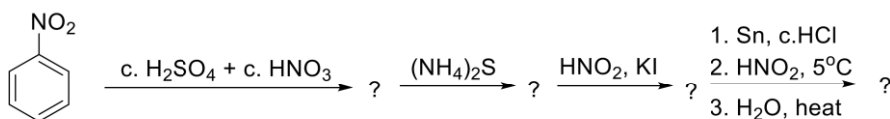


21. Explain, with mechanism, the process of converting



Can a quaternary ammonium salt be formed in this process? Give reasons supporting your answer. [Aliphatic amines] 3

22. Identify the missing compounds in the following scheme: [Aromatic amine] 2



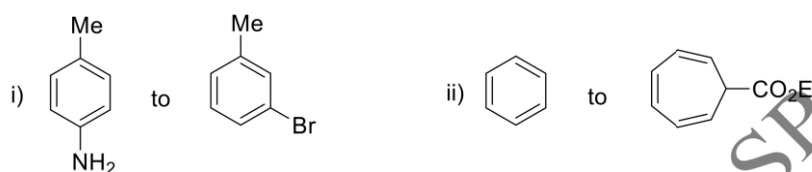
23. What happens when PhCH_2COCl is treated with CH_2N_2 and the resultant product is allowed to react with Ag_2O in water? Give mechanism of the second step of the reaction. [Diazomethane] 3

24. Why is β -naphthol used instead of α -naphthol in diazocoupling reaction with aromatic diazonium cation? Explain. [Aromatic amines, diazonium salts] 2

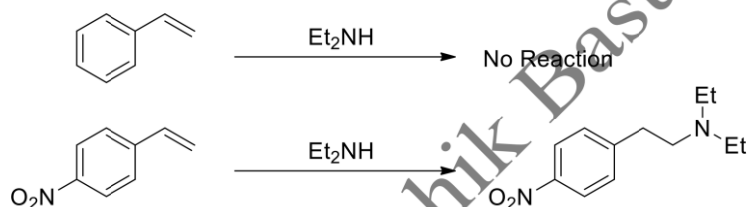
25. Show how to prepare 4-methyl-5-(*N,N*-dimethylamino)-3-pentanone by Mannich reaction. Give mechanism. [Aliphatic amine] 3

26. Why does 2,4,6-trinitrobenzenediazonium cation couple with mesitylene? Explain. [Diazonium salts] 2

27. Carry out the following conversions: [i) Aromatic amines, diazonium salts, ii) Diazoacetic esters] 3



28. Explain the following result: [Aliphatic amine] 2



2018 (Third Paper)

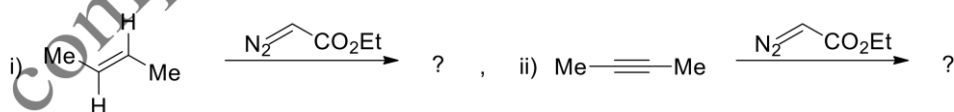
29. $\text{PhN}_2^+\text{Cl}^-$ couples with PhNMe_2 but not with $2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NMe}_2$. Explain. [Diazonium salts, aromatic amines] 2

30. Carry out the following conversions: 3

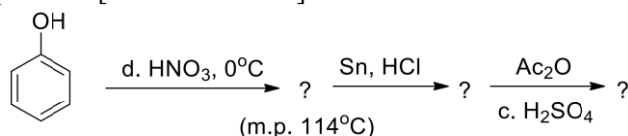
i) *p*-nitrotoluene to *m*-nitrotoluene, and ii) nitrobenzene to *m*-anisidine. [i) Diazonium salts, ii) Aromatic nitro] 3

31. Prepare *n*-butylamine by Gabriel synthesis. Why is the synthesis not a viable method for preparing – i) *t*-butylamine, and ii) neopentylamine? [Aromatic amines] 2

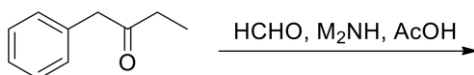
32. Write down the products of the following reactions: [Diazoacetic ester] 2



33. Identify the missing compounds in the following scheme. Also give the mechanism of the first step. Write the commercial name of the final product. [Aromatic amine] 3



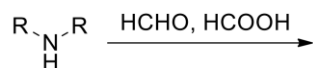
34. Predict the product with plausible mechanism: [Aliphatic amine] 2



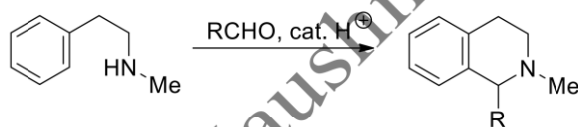
35. The diazo-coupling reaction with phenol should be carried out at pH 9. What will happen if this is carried out at pH > 10? Why is the diazo-coupling with aromatic tertiary amine is carried out at pH 5.6? [Diazonium salts] 3
36. Distinguish chemically between *N*-methylaniline and *N,N*-dimethylaniline. [Aromatic amine] 2

2017 (Third Paper)

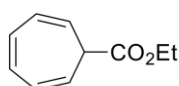
37. Predict the product with plausible mechanism: [Aliphatic amines] 2



38. Convert – i) aniline to 2,6-dichloroaniline, and ii) nitrobenzene to *p*-nitroaniline [i) Aromatic amine, ii) Aromatic nitro]. 3
39. Provide the products that form when NaNO₂, HCl is reacted with the following compounds separately: *N*-methylaniline, *N,N*-dimethylaniline, benzylamine and benzamide. [Aromatic amines, aliphatic amines] 2
40. How can you methylate phenol and methanol using diazomethane? Explain with mechanism. [Diazomethane] 3
41. How would you employ an enamine compound to synthesise 2,6-dimethylhexanone from 2-methylcyclohexanone? [Aliphatic amine] 2
42. What happens when nitrobenzene is reduced under acidic, basic and neutral conditions? [Aromatic nitro] 3
43. Using Mannich reaction as a guide, suggest a mechanism of the following reaction: [Aromatic amine] 2

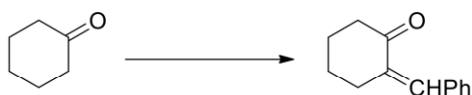


44. *p*-Toluidine reacts with benzenediazonium chloride in weakly acidic medium to form a compound which on boiling with d. H₂SO₄ forms four compounds excluding nitrogen. Discuss. [Aromatic amines, diazonium salts] 3
45. Carry out the conversion of benzene to the following compound in a single step with mechanism [Diazoacetic esters]. 2



2016 (Third Paper)

46. When *p*-chloroaniline is diazotised with NaNO₂ and HBr, the resulting diazonium salt solution couples with *N,N*-dimethylaniline to give 4-bromo-4'-dimethylamino azobenzene as the major product. Explain. [Aromatic amines] 3
47. How can you carry out the following conversion using an enamine as an intermediate and why is a cyclic amine used for this purpose? [Aliphatic amines] 3



48. Convert acetone to methyl vinyl ketone. [Mannich, Aliphatic amine] 2
49. Convert the following – i) nitrobenzene to 1,3,5-tribromobenzene (*s*-tribromobenzene), ii) *p*-nitrotoluene to *p*-aminobenzoic acid. [Aromatic nitro] 3

50. Provide the missing structures of the following scheme: [Aliphatic amine] 2

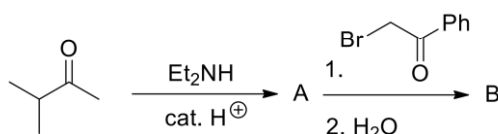


51. How can you prepare ethyl diazoacetate from glycine? Explain what happens when diazomethane is reacted with cyclopentanone. [Diazoacetic ester, diazomethane] 3

52. Distinguish chemically between a nitrile and an isonitrile. [Organocyanide, isocyanide] 2

2015 (Third Paper)

52. Identify A and B with mechanism: [Aliphatic amine] 3



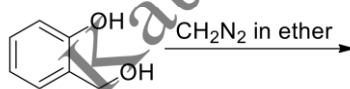
53. Convert *m*-dinitrobenzene to *m*-bromophenol. [Aromatic nitro] 2

54. Explain mechanistically the difference between the pattern of coupling of benzenediazonium cation with – i) aniline, and ii) *N,N*-dimethylaniline. [Aromatic amines] 3

55. Illustrate the use of diazomethane for conversion of both acyclic and cyclic ketones to respective higher homologues. Show possibilities of formation of other compounds. [Diazomethane] 3

56. Explain why diazoacetic ester is more stable than diazomethane. [Diazoacetic ester] 2

57. Predict the product and explain its formation: [Diazomethane] 2



2014 (Third Paper)

58. Convert aniline to 1,2,3-tribromobenzene. [Aromatic amine] 2

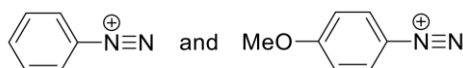
59. Alkaline hydrolysis of benzonitrile affords the salt of an acid but in presence of hydrogen peroxide, an amide is formed. Explain. [Organocyanide] 3

60. Write down Gabriel's phthalimide synthesis for EtNH₂. Why the primary amines like Et₃CCH₂NH₂ cannot be prepared by this method? [Aliphatic amines] 3

61. Phenol is converted to anisole using diazomethane, but aliphatic alcohols cannot be converted to the corresponding methyl ethers by the same method. Explain. [Diazomethane] 2

2013 (Third Paper)

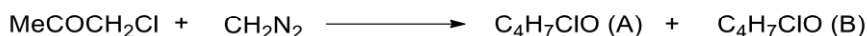
62. Between the following two diazonium cations, which one undergoes nucleophilic displacement of nitrogen at a faster rate? Explain. [Diazonium salts] 2



63. How can you prepare allyl cyanides and allyl isocyanides from allyl alcohol separately? [Organocyanides] 3

64. How can you convert aniline to *p*-dinitrobenzene? [Aromatic amines, diazonium salts] 2

65. In the following scheme, A is a ketone and B is an epoxide. Suggest their structures and mechanisms for their formation: [Diazomethane] 3



66. How can you separate a mixture of primary, secondary and tertiary aliphatic amines by the Hinsberg method? [Aliphatic amines] 3

2012 (Third Paper)

67. Tertiary amine of the type $\text{R}^1\text{R}^2\text{NCH}_3$ can be prepared using formaldehyde and formic acid as the reagent. Explain. [Aliphatic / aromatic amines] 2

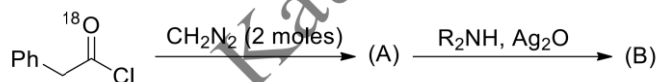
68. Explore the possibility of conversion of nitrobenzene to azobenzene and azoxybenzene. [Aromatic nitro] 2

2011 (Third Paper)

69. On reacting with KOH both A and B give the same product. Write the structure of the product and its stabilising feature. Explain the mechanistic feature, common in both cases, for the formation of the product. [Diazomethane] 4



70. Identify A and B in the following sequence. Explain why two molar equivalents of diazomethane is required for the first step of this reaction sequence: [Diazomethane] 3



2010 (Third Paper)

71. Write one method of synthesis of diazomethane. How is diazomethane dried? The strength of the ethereal solution of diazomethane can be estimated by reacting with *p*-nitrobenzoic acid – justify. [Diazomethane] 4

72. Why does 2-methyl-1-naphthol couple with benzenediazonium chloride but 1-methyl-2-naphthol fails to do so? [Diazonium salts] 1

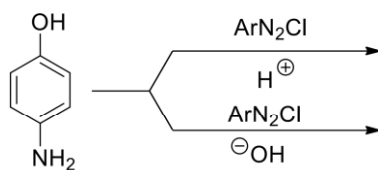
73. Suggest a route to obtain R-NH_2 from R-I (R is a primary alkyl group) without using any organometallic reagent. [Aliphatic amine] 1

74. How can you convert ArNH_2 exclusively to ArNHMe without any ArNMe_2 ? [Aromatic amines] 2

75. In Arndt-Eistert synthesis, two equivalents of diazomethane are required. Why? What happens if only one equivalent of diazomethane is used? [Diazomethane] 3

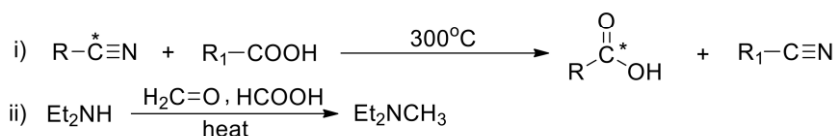
2009 (Third Paper)

76. Predict the products with plausible mechanism in each case: [Diazonium salts] 3



77. Suggest mechanisms for each of the following: [Organocyanide]

3

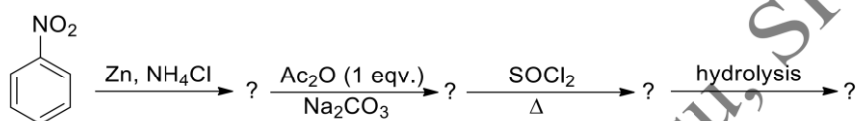


78. Convert cyanobenzene to *trans*-stilbene. [Organocyanide]

2

79. Identify the missing compounds and explain the following sequence of reactions: [Aromatic Nitro]

3



80. How can you chemically distinguish between each of the following pair: (i) Aliphatic nitro, ii) organocyanide]

i) 1-nitrobutane and 2-nitrobutane, ii) benzyl cyanide and benzyl isocyanide.

3

81. Predict the product and explain the following reactions: [i] diazoacetic ester, ii) aromatic nitro, iii) aliphatic nitro]

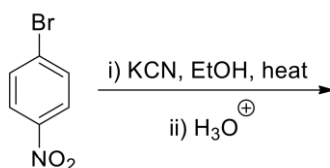
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2008 (Third Paper)

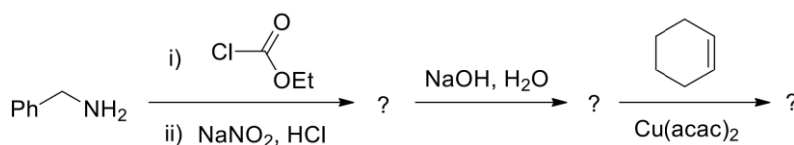
82. Predict the major product of the following reaction and write mechanism to show their formation: [Aromatic nitro]

2



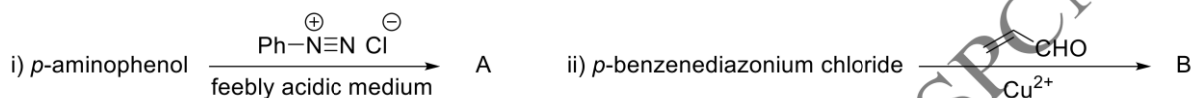
83. Complete the following reaction scheme (no mechanism is necessary): [Diazoalkane]

3



2005 (Third Paper)

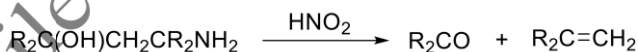
84. Illustrate the use diazomethane for – i) methylation of phenol, ii) synthesis of pyrazole, iii) conversion of RCO₂H to RCH₂CO₂H and iv) conversion of cyclopentanone to cyclohexanone. [Diazomethane] 6
85. Write how you can distinguish chemically between the members of each of the following pair – i) EtCN and EtNC, ii) CH₃CH₂CH₂NO₂ and (CH₃)₂CHNO₂. [Aliphatic nitro] 3
86. Give one important use of ethyl diazoacetate. (No mechanism needed.) [Diazoacetic ester] 1
87. Write the following conversions (mechanism not needed) – i) benzene to *m*-ethylaniline, ii) benzene to *p*-dinitrobenzene, iii) aniline to 1,6-dichloroaniline. [i) Aromatic nitro, ii) and iii) Aromatic amines] 6
87. Identify A and B and explain their formation. [Diazonium salts] 2+2

**2004 (Third Paper)**

88. Explain all the steps of von Richter reaction taking *p*-bromonitrobenzene as the starting material. [Aromatic nitro] 3
89. Explain mechanistically the difference to the pattern of coupling of benzenediazonium cation with – i) aniline, and ii) *N,N*-dimethylaniline. [Diazonium salts] 4
90. Carry out the following transformation: aniline to 1,3,5-tribromobenzene. [Aromatic amines] 2
91. Give the mechanism of the following transformation: [Diazomethane] 2



92. Carry out the following transformation: *p*-nitrotoluene to *m*-nitrotoluene. [Aromatic nitro] 2
93. Discuss the following reaction: [Aliphatic amines] 2

**2003 (Third Paper)**

94. Write how you can distinguish chemically between the members of the following pair: *N*-methylaniline and *N,N*-dimethylaniline. [Aromatic amines] 2
95. Carry out the following transformation - aniline to 2,6-dichloroaniline. [Aromatic amines] 2
96. Write the canonical forms of diazomethane and select the most contributing structure. [Diazomethane] 2
97. Which one of the following has the higher dipole moment – C₂H₅CN or C₂H₅NC? Explain. [Organocyanide] 2

2002 (Third Paper)

98. How would you distinguish between *o*-phenylenediamine and *m*-phenylenediamine? [Aromatic amines] 2
99. Illustrate the use of diazomethane in the homologation of carboxylic acid, heterocycle formation and ring expansion. [Diazomethane] 3

100. How are methyl nitrite and nitromethane prepared? How would you distinguish between them by chemical methods? [Aliphatic nitro] 3

101. Carry out the following transformation – i) aniline to 1,2,3-tribromobenzene, ii) *p*-nitrophenol to 1,2,4-trihydroxybenzene, iii) *N,N*-dimethylaniline to *p*-nitrosophenol. [i) Aromatic amines, ii) aromatic nitro, iii) aromatic amines] 6

2001 (Third Paper)

102. Explain what will happen when *o*-nitroaniline is boiled with concentrated aqueous sodium hydroxide solution. [Aromatic nitro] 2

103. Nitration of phenol in dilute aqueous nitric acid is more efficient in presence of a catalytic amount of sodium nitrite. [Aromatic nitro] 2

2000 (Third Paper)

104. Alkyl isocyanides fail to undergo hydrolysis under basic condition – explain. [Organocyanide] 1

105. Discuss the relative stability of the compounds in each of the following pairs – i) diazomethane and diazoacetic ester, ii) benzenediazonium chloride and *p*-methoxybenzenediazonium chloride. [i) Diazomethane, ii) diazonium salts] 4

106. Distinguish between PhCH_2NO_2 and *p*-nitrotoluene by a suitable chemical reaction. [Nitro compounds] 2

107. Predict with proper reasoning the most suitable condition for the coupling of benzenediazonium chloride with *p*-toluidine at 0 °C to obtain the best possible yield. Explain what will happen if the coupled product is heated with dilute sulfuric acid. [Diazonium salts] 5

2007 (Third Paper)

108. Convert: i) toluene to *m*-toluic acid, ii) nitrobenzene to *p*-acetaminophenol, iii) aniline to 2,4,6-trimethylnitrobenzene. [i), ii) Aromatic nitro, diazonium, iii) Aromatic amine] 6

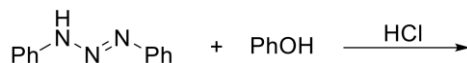
109. How would you prepare *N*-methylaniline from aniline? [Aromatic amine] 2

110. Give efficient methods for preparation for R_3CNH_2 and R_3CCN . [Aliphatic amine, organocyanide] 2

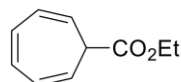
111. Give one use of diazomethane where it is used for ring expansion. [Diazomethane] 1

2006 (Third Paper)

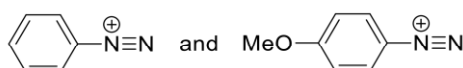
112. Give the products of the following reaction and explain: [Diazonium salts] 2



113. Show how the following molecule can be made from benzene in a single step. Give mechanism. [Diazoacetic ester] 1.5



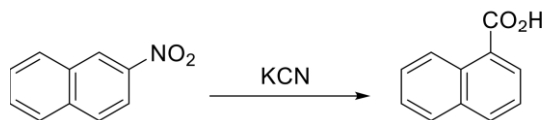
114. Between the following two diazonium cations, which one undergoes nucleophilic displacement of nitrogen at a faster rate? Explain. [Diazonium salts] 2



115. Write how the isomeric phenylenediamines are prepared in the laboratory. Write down their reactions with nitrous acid. [Aromatic amines] 3

116. Alkyl halides give mainly cyanides with aqueous ethanolic KCN, but with AgCN, isocyanides become the major products. Account for these observations. [Organocyanides] 3

117. Give mechanism of the following reaction: [Organocyanides] 3



118. *p*-Toluidine reacts with benzenediazonium chloride to form a compound, which on boiling with H₂SO₄ gives four products (excluding nitrogen). Identify the products and provide mechanism for their formation. [Aromatic amines, diazonium salts] 4

119. Predict the products with plausible mechanism in each of the following reactions: [i) Diazoalkane, ii) organocyanides] 4

