16.2 Aromatic Amines (Aniline)

Learning outcomes

After the lesson, learners should be able to:

- Show preparation of aniline from nitrobenzene and phenol.
- State the physical properties of aromatic amine.
- Explain the chemical properties of aromatic amines
  - i.e., basicity of aniline, comparison of the basic nature of aniline with aliphatic amines and ammonia,
  - alkylation,
  - acylation,
  - diazotization,
  - carbylamines,
  - coupling reaction and
  - electrophilic substitution (Nitration, sulphonation, and bromination).
- State important uses of aniline.

Preparation

1. From nitrobenzene (studied in Nitrobenzene)

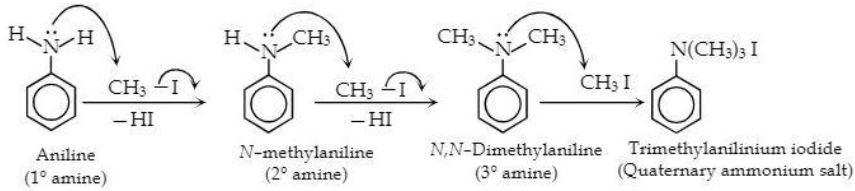
2. From Phenol (studied in properties of Phenols)

Physical Properties

1. colorless liquid with an unpleasant odor and very sensitive to oxidation, so it rapidly becomes brown when exposed to air.
2. B pt 184^0C and Mpt 6.2^0C.
3. Sparingly soluble in water but readily soluble in organic solvents.

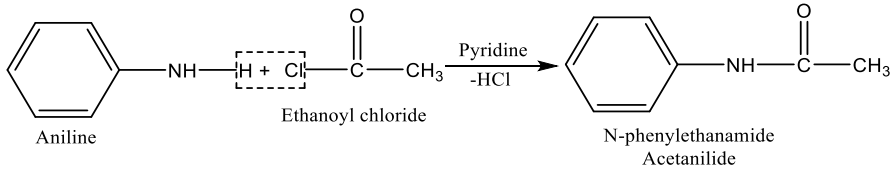
Chemical Properties

1. Alkylation



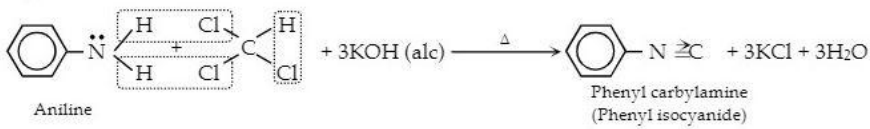
1. Give the action of Aniline upon methyl iodide. 1
2. Starting from Aniline, how would you obtain N-methylaniline? 1

2. Acylation



3. How is acetanilide prepared from Aniline? 1

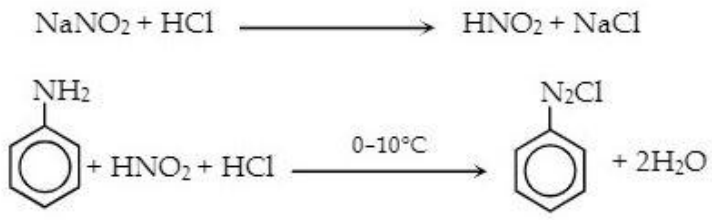
3. Carbyl amine reaction *(test of 1^0amine and chloroform)*



4. Give the action of Aniline upon $CHCl_3$/alc.KOH. 1
5. Give an example of a carbyl amine reaction. 1
6. What happens when Aniline is warmed with Chloroform and Ethanolic potassium hydroxide? 1
7. How would you convert Aniline into Phenyl isocyanide? 1
8. How does Aniline react with chloroform? 1
9. Give the action of Chloroform upon aniline in the presence of aqueous NaOH. 1.5

1. A nitrogen-containing compound, on heating with $CHCl_3$ and alcoholic KOH, evolved very bad-smelling vapours. The compound is
   a. Aniline b. N-methyl aniline
   c. Nitrobenzene d. Benzamide

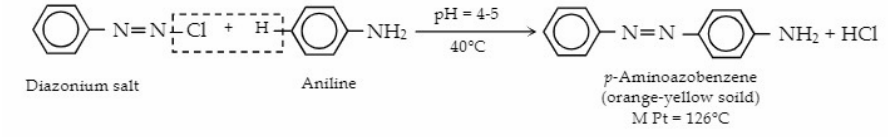
4. Diazotization



Aniline Benzene diazonium chloride

2. Give the action of Aniline upon $NaNO_2$/HCl under ice-cold conditions. 1
3. How does Aniline react with $NaNO_2$+HCl at low temperature? 1
4. How would you convert Aniline into benzene diazonium chloride? 1
5. Mention one example of Diazotization reaction. 2
6. How would you convert Aniline into phenol? 1
7. How is phenol prepared from Aniline? 1.5

11. Coupling reaction

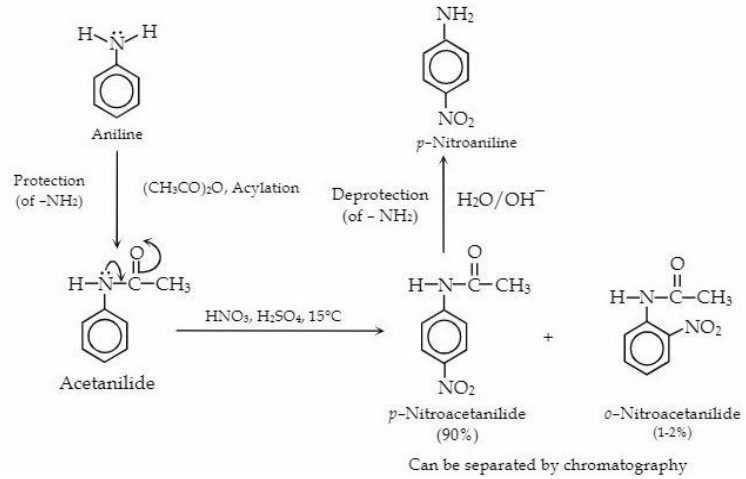


8. Define and give an example of a coupling reaction. 1
9. How does Aniline react with benzene diazonium chloride? 1

Aromatic electrophilic substitution

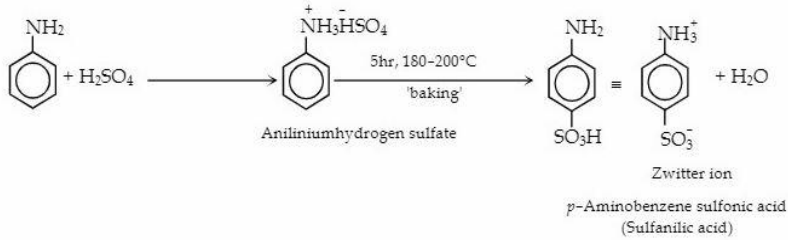
1. Nitration

Aniline cannot be nitrated directly with conc. HNO_3 and conc. H_2SO_4 because $-NH_2$ group in such cases gets oxidized into $-NO_2$ group.



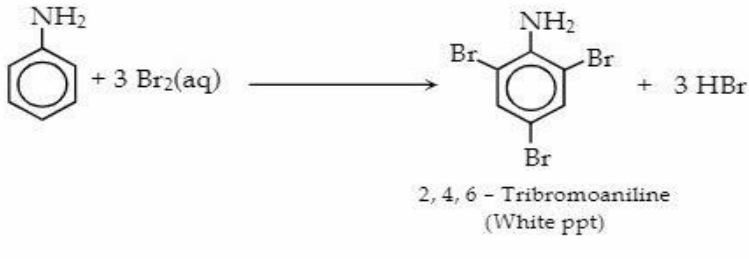
10. Why is the $-NH_2$ group of Aniline protected before nitration? 2
11. Starting from Aniline, how would you obtain o-nitroaniline? 1

2. Sulphonation



12. How would you convert Aniline into Sulphanilic acid? 1

3. Bromination



13. Explain why the amino group of Aniline is ortho-para directing? 1
14. Give the action of Aniline upon aq. Br_2. 1
15. How does Aniline react with aqueous bromine? 1
16. What happens when Aniline is shaken with aq. Br_2? 1

12. Aniline, when reacted with bromine water, gives
    a. o-bromoaniline
    b. p-bromoaniline
    c. m-bromoaniline
    d. 2,4,6-tribromoaniline

Basic nature (study in detail from the book)

All amines are basic in nature due to the presence of a lone pair of electrons on the nitrogen atom. They are stronger bases than water and are therefore protonated by water in their aqueous solutions.

$$RNH_2 + H_2O \rightleftharpoons RNH_3^+ + OH^-$$

Aminoalkane — Alkyl ammonium ion

The basicity constant can be expressed as;

$$K_b = K_{eq} \times [H_2O] = \frac{[RNH3+][OH-]}{[RNH2]}$$

Following order of basicity is observed by the basicity constant of the different amines.

N-methylaminomethane > Aminomethane >

N,N-dimethylaminomethane > Ammonia

Aminomethane > Aminoethane > Aminopropane

a. Aliphatic amines are more basic than ammonia
b. Aromatic amines are less basic than ammonia
c. Basic strength of 1^0, 2^0, and 3^0 amines
    i) Hydration effect
    ii) Inductive effect
    iii) Steric effect
d. Effect of the substituent on the basicity of aniline

17. Which of the following has the most basic character? Explain.

a) NH_3 b) $(CH_3)_2NH$ c) CH_3NH_2 d) $C_6H_5NH_2$ **2**

Ans: $(CH_3)_2NH > CH_3NH_2 > NH_3 > C_6H_5NH_2$

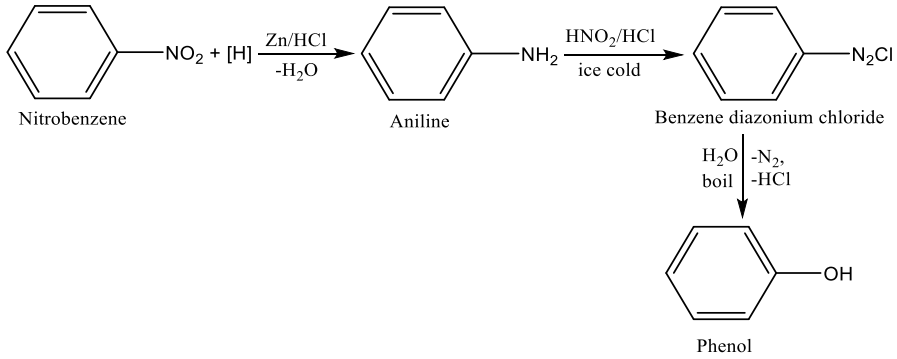
18. Why is amine more acidic (basic) than ammonia? 2
19. Why is an aliphatic amine more basic than Aniline? 2
20. Explain why Aniline is a weaker base than aliphatic amine? 1
21. Why is Aniline less basic than Methylamine? 1
22. Why is Methanamine more basic than Aniline? 2

(study in detail from the book)

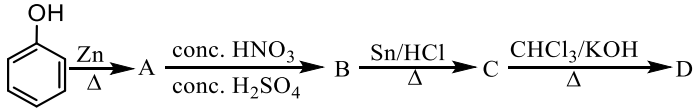
23. The most basic amine among the following is
    e. Dimethylamine
    f. Aniline
    g. Trimethylamine
    h. Ethylamine
24. The order of basic strength of 1^0 amine, 2^0 amine, 3^0 amine, and ammonia is
    i. $3^0 > 2^0 > 1^0$ > ammonia
    j. $2^0 > 1^0 > 3^0$ > ammonia
    k. $2^0 > 3^0 > 1^0$ > ammonia
    l. $3^0 > 1^0 > 2^0$ > ammonia
25. Which one of the following is most basic in nature?
    m. NH_3 c. CH_3NH_2
    n. $(CH_3)_2NH$ d. $C_6H_5NH_2$
26. Which of the following is most basic in nature?
    o. RNH_2 c. $C_6H_5NH_2$
    p. $(CH_3)_2NH$ d. $C_6H_5NH_2$

Conversions

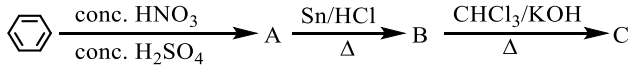
27. How is Nitrobenzene converted to Phenol? 1



28. Identify A, B, C, and D in the following sequence of reactions.



29. Write the structures of organic compounds A, B, C, and D in the following sequence of reactions.



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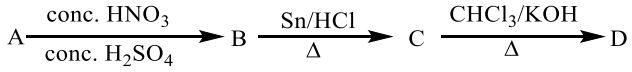
30. How will you carry out the following conversions:
    Aniline to chlorobenzene 2
31. A list of compounds is given as follows:
    p-aminoazobenzene, benzenediazonium chloride, aniline, nitrobenzene, phenol and benzene
    From the above list of compounds, prepare a sequence of reaction chain with suitable conditions and reagents? 5
32. Identify A, B, C, D, and E in the following reaction sequences.



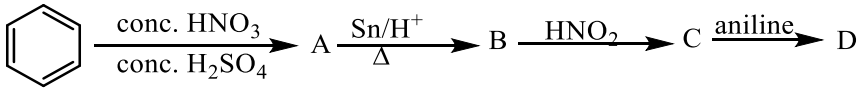
Compound A can be obtained by heating phenol in the presence of Zn-dust. *5*

33. A list of compounds is given as follows

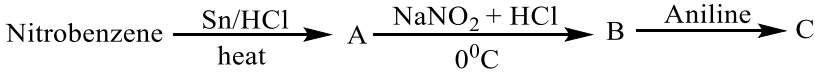
p-hydroxyazobenzene, $C_6H_5NO_2$, $C_6H_5N_2Cl$, C_6H_6, $C_6H_5NH_2$

From the list of above compounds, prepare a sequence of reaction chain, with suitable conditions and reactions. 5

34. Write the structures of organic compounds A, B, C, and D in the following sequence of reactions.



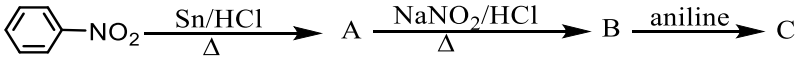
35. Identify A B, and C in the following reaction sequence



36. 5 Convert Nitrobenzene to p-aminoazobenzene.

2

37. Consider the following reaction:



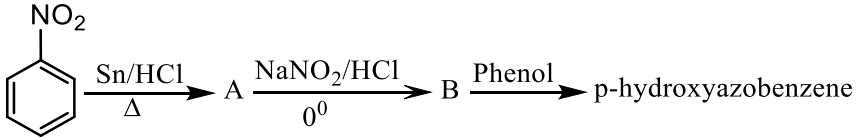
Identify compounds A, B, and C and write the reaction involved. *4*

38. An aromatic compound A on reduction yields parent hydrocarbon B. B on nitration gives C. *C* on reduction in acidic solution gives *D*. On coupling with diazonium salt, D gives diazoaminobenzene. Give names for A, B, C, and D. Write the chemical reaction involved.

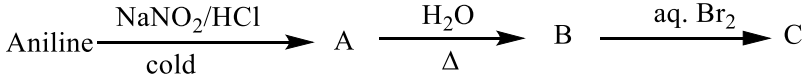
5

39. How is nitrobenzene converted to p-hydroxyazobenzene? 3

Hint:

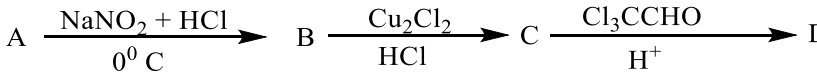


40. Identify A, B, C, and D in the following reaction sequence.



What happens when A is treated with phenol in alkaline conditions? 4

41. Identify the major products A, B, C, and D in the following reaction sequence.



The compound C undergoes reduction with $LiAlH_4$ to give Benzene.

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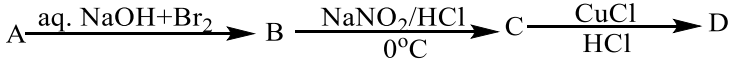
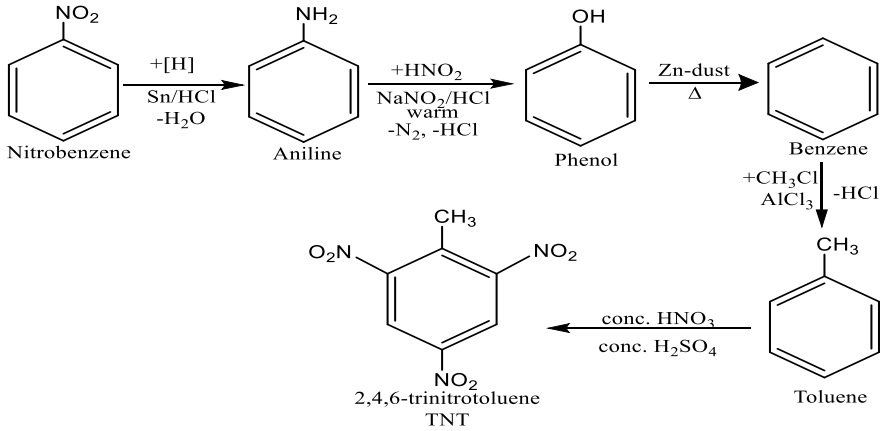
42. Identify the major products A, B, C, and D in the following reaction sequence.



The compound D, if heated with chloral in the presence of acid, gives DDT. 4

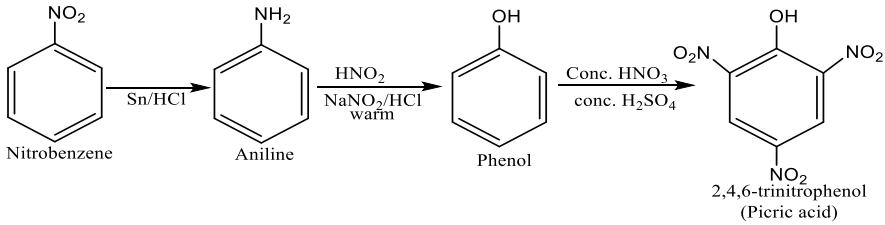
43. Starting with nitrobenzene, how would you prepare TNT?

1



44. Starting from Nitrobenzene, how would you obtain Picric acid?

2

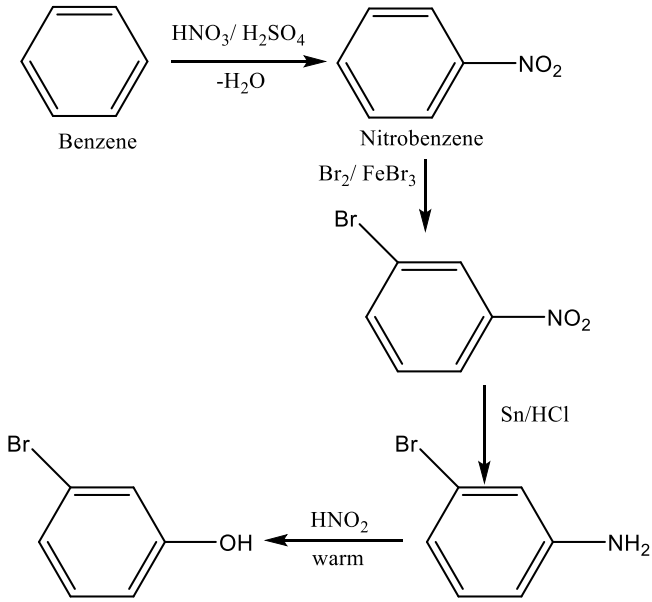


45. Starting from Aniline, how would you obtain picric acid?

1

46. Convert Benzene to m-bromophenol.

2.5



47. Look at the different organic compounds given below.

A = $C_6H_5NH_2$ B = C_6H_5OH C= C_6H_5CHO

D = C_6H_6 E = $C_6H_5CH_3$ F = $C_6H_5N_2Cl$

Make a correct reaction sequence of the above compounds with the proper reagent and conditions.

48. What happens when aniline is warmed with benzaldehyde? 1

49. *Convert Benzaldehyde to aniline and vice versa. 5*

*****This is not a complete note. It is to guide you. It is recommended to study the prescribed textbooks along with this material. *****