# ORGANIC NITROGEN COMPOUNDS

**Amines** = derivatives of ammonia $NH_3$

**Nitrocompounds** = compounds containing $NO_2$ group (derived from $HNO_3$)

**Nitrosocompounds** = compounds containing NO group (derived from $HNO_2$)

**Diazonium salts** = ionic compounds containing $–N{\equiv}N^+$ ion

**Azocompounds** = compounds with –N=N−

## AMINES

**Classification and naming:**

- Primary: one hydrogen atom of ammonia is substituted by an ..... or ..... group, $R{-}NH_2$

| | | | |
|---|---|---|---|
| $CH_3NH_2$ | | | |
| | | ethanamine | |
| | | | 1-aminopropane |
| | Phenylamine | | |

- Secondary: ..... H atoms substituted by ..... alkyl or aryl groups: $R_1{-}NH{-}R_2$
- Tertiary: ..... hydrogen atoms are substituted by alkyl or aryl groups: $R_1R_2R_3N$

  Both secondary and tertiary amines are considered as derivatives of primary amines. Primary alkene is the one with the biggest alkyl group.

| | | |
|---|---|---|
| $(CH_3)_2NH$ | | |
| | | N−methylethanamine |
| | Diethylamine | |
| $CH_3CH(CH_3)CH_2NH_2$ | | |
| | Triethylamine | |
| | | N-ethyl-N-methylethanamine |

1. *Write all the structures with a molecular formula $C_3H_9N$, name them and classify them as primary, secondary or tertiary.*

Putrescine and cadaverine are toxic naturally occuring amines causing the bad smell of decaying animal flesh. They are formed there by the action of bacteria on aminoacids.

2. *If 0.1 g of putrescine is completely burnt, the combustion products are: 0.2 g of $CO_2$, 0.1227 g of water and 25.45 $cm^3$ of nitrogen gas (measured at s.t.p.). Find the empirical formula of putrescine. Find its molecular formula knowing that the relative formula mass of putrescine is*

*88 and suggest its structural formula. Suggest the formula of cadaverine knowing that its relative formula mass is 14 more than that of putrescine.*

3. *Revise the physical and chemical properties of ammonia:*
   Ammonia is a *gas/liquid* with a *pleasant/bad* smell. Its boiling point is affected by ..... ..... It also causes a *high/low* solubility in water. Ammonia is a weak ..... due to its ability to ..... $H^+$. This is enabled by the presence of a ..... electron ..... on the nitrogen atom.

**Physical properties**

Lower amines have similar properties to ammonia.

Boiling points of amines are affected by both ..... forces and ..... bonding.

| Amine | b.p. | Amine | b.p. | amine | b.p. |
|---|---|---|---|---|---|
| $CH_3NH_2$ | −6°C | $C_2H_5NH_2$ | 16.6°C | $C_3H_7NH_2$ | 48°C |
| $(CH_3)_2NH$ | 7°C | $(CH_3)_3N$ | 3°C | $NH_2(CH_2)_2NH_2$ | 116°C |

4. *Discuss the following:*
   a. *A boiling point is increasing from methylamine to propylamine.*
   b. *Dimethylamine has a higher boiling point than methylamine.*
   c. *Trimethylamine has a lower boiling point than dimethylamine.*
   d. *$NH_2(CH_2)_2NH_2$ ($M_R$= 60) has much higher b.p. than propylamine ($M_R$= 59).*
   e. *All amines from the table (including trimethylamine) are soluble in water.*

Lower amines have a smell resembling the smell of ....., higher amines have a more ..... smell.

**Chemical properties**

1. Reactions with acids → ammonium salts
   a. $CH_3NH_2 + HCl \rightarrow$
   b. $C_6H_5NH_2 + HBr \rightarrow$
   c. $C_2H_5NH_2 + H_2SO_4 \rightarrow$
   d. $(CH_3)_3N + HCl \rightarrow$
5. *Estimate the state of matter and the solubility of ammonium salts.*
6. *The basicity increases as follows: $C_6H_5NH_2 \rightarrow NH_3 \rightarrow C_2H_5NH_2$. Try to explain it.*

2. Reactions with halogenocompounds = alkylation

   a. $CH_3NH_2 + C_2H_5Cl \rightarrow$

   b. $(C_2H_5)_2NH + CH_3Cl \rightarrow$

   c. $(CH_3)_3N + CH_3Cl \rightarrow$

   Tetraalkylammonium salts with one long carbon chain, e.g. $CH_3(CH)_{14}CH_2N^+(CH_3)_3Cl^-$ act as ..... as polar (.....) head interacts with ..... , the long non-polar carbon part interacts with ..... The polar part is said to be hydro..... while the non-polar is said to be hydro.....

3. Reactions with nitrous acid = diazotation → diazonium salts

   a. $R{-}NH_2 + HNO_2$ ($NaNO_2$ + .....) → .....→ ..... or .....

   b. $Ar{-}NH_2 + HNO_2$ (below 10°C) →

**Preparation of amines**

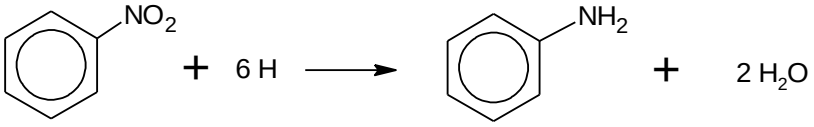
1. Ammonia + haloalkanes

   $NH_3 + C_3H_7Br \rightarrow$

   7. *What is the reaction mechanism of this reaction?*
   8. *What may be other products of this reaction? Suggest a way to separate them.*

   9. *Suggest why this kind of reaction is not suitable for making aniline (phenylamine).*

2. Reduction of nitrocompounds – especially for making aromatic amines




Reducing agents: Sn + HCl, Fe + HCl, Fe + steam (industrial manufacture of aniline)

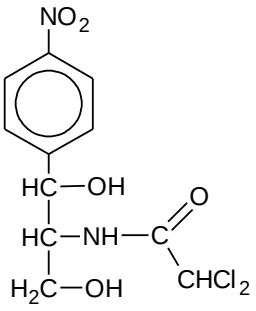
**NITROCOMPOUNDS**

= compounds containing ..... group


**Occurrence and properties:**

rarely in nature, e.g. ..... pheromone  or some antibiotics, e.g. chloramphenicol

1. *What type of stereoisomerism is possible for the formula of chloramphenicol?*
2. *How many stereoisomer exist for chloramphenicol?*
3. *What is the natural origin of antibiotics?*
4. *What is the risk connected with using antibiotics?*




Most nitrocompounds are toxic (mainly aromatic) and ....., e.g. TNT. They are colourless or ..... They have a characteristic smell reminiscent of bitter .....

**Preparation of:**

Aliphatic nitrocompounds

- $R{-}X + NO_2^- \rightarrow$
5. *What is the name of $NO_2^-$ ion and what is the reaction mechanism of the reaction above?*

- $R{-}H + HNO_3$ (contains $N_2O_4$) $\rightarrow$
  1. .....: $N_2O_4 \rightarrow 2\ NO_2\cdot$
  2. .....: $NO_2\cdot + CH_4 \rightarrow$

     $CH_3\cdot + HNO_3 \rightarrow$

     $CH_4 +$ ..... $\rightarrow$
  3. .....: .....

6. *What is the reaction mechanism of the reaction above? Name the steps and fill what is missing.*
7. *Write an equation of a nitration of ethane.*

Aromatic nitrocompounds

8. *Write down the equation of the nitration of*

a. *benzene (1:1)*

b. *phenol (excess of $HNO_3$)*

**The nature of $-NO_2$ group:**

**Reactions**

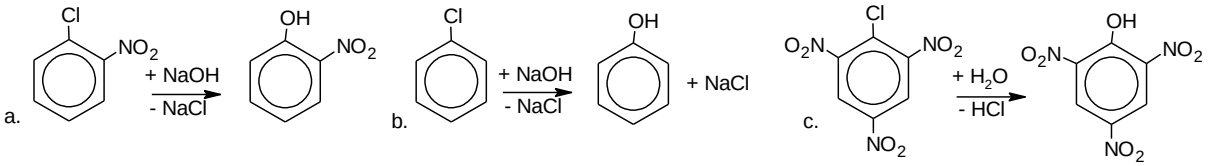
1. Reduction

2. Substitution on a benzene ring of nitrobenzene

9. *Write the formula of the product of chlorination of nitrobenzene. What is the necessary condition for this reaction?*

10. *What is the product of nitration of chlorobenzene?*

11. *Substitution of chlorine by OH group in 1-chloro-2-nitrobenzene (a.) takes place more easily than that in chlorobenzene (b.). The easiest is the substitution in 1-chloro-2,4,6-trinitrobenzene(c.). Explain it knowing the nature of $-NO_2$ group.*




**Uses of nitrocompounds**

- Perfumes production (artificial musk)
- Insecticides
-
-

12. *Find in the text about nitrocompounds two more their uses.*

**DIAZONIUM COMPOUNDS (SALTS)**

= compounds with the functional group .....

They are made by a reaction between amines and nitric(III) (.....) acid .....

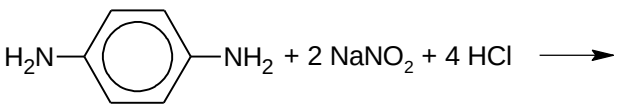
a. $R{-}NH_2 + HNO_2$ ($NaNO_2$ + .....) → .....→ ..... or .....

b. $Ar{-}NH_2 + HNO_2$ (below 10°C) →

1. *Write the formulae of the organic products of the following reactions:*

   a. $C_2H_5NH_2 + HNO_2 \rightarrow$

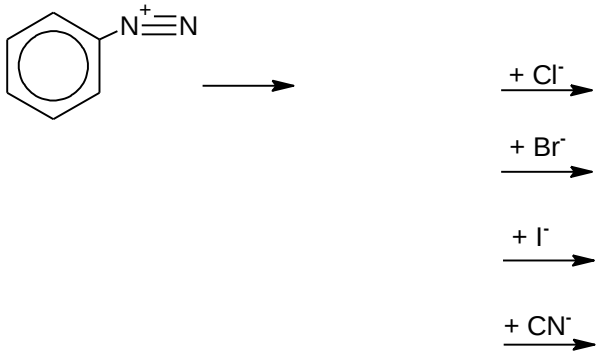
   b. $C_6H_5NH_2 + HNO_2 \rightarrow$

   c.  + 2 $NaNO_2$ + 4 HCl ⟶

2. *0.15 g of a primary amine $R{-}NH_2$ reacted with nitrous acid producing 62 $cm^3$ of nitrogen gas at 20°C ($V_m$ for this temperature is 24.4 $dm^3 \cdot mol^{-1}$). Find the molar mass of this amine and suggest its molecular formula.*

**Reactions**

1. Substitution

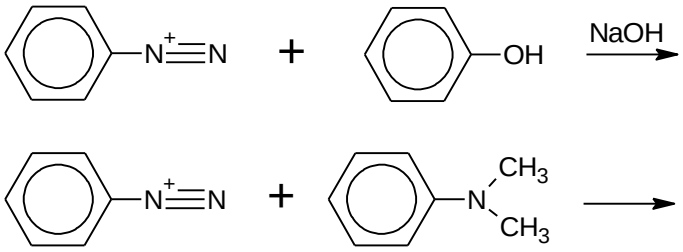



The reactions take place in the presence of ..... catalyst.

2. Coupling

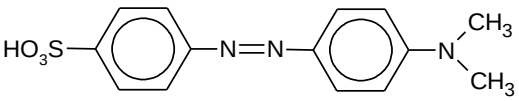
Diazonium ion acts as a weak *nucleophile/electrophile/free radical*. It may react with the derivatives of arenes containing electron *withdrawing/donating* groups, e.g.

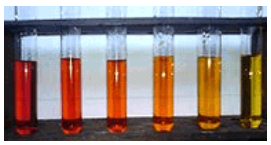
These groups direct the diazonium ion mainly to the position ..... If it is already occupied then to the position .....




The products are substances with –N=N− group = ..... They are colourful substances used e.g. as acid-base indicators or as dyes for colouring food, cosmetics, petrol, cloths, ...

3. *Methylorange is an acid base indicator, red in an acid and yellow in an alkali.Suggest the reactants needed for its preparation knowing the structure is*



Azo compounds derived from naphthalene may be green, blue or black