



MINISTRY OF EDUCATION,
YOUTH AND SPORTS



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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 $-\text{N}\equiv\text{N}^+$ ion

Azocompounds = compounds with $-\text{N}=\text{N}-$

AMINES

Classification and naming:

- Primary: one hydrogen atom of ammonia is substituted by an or group, $\text{R}-\text{NH}_2$

CH_3NH_2			
		ethanamine	
			1-aminopropane
	Phenylamine		

- Secondary: H atoms substituted by alkyl or aryl groups: $\text{R}_1-\text{NH}-\text{R}_2$
- Tertiary: hydrogen atoms are substituted by alkyl or aryl groups: $\text{R}_1\text{R}_2\text{R}_3\text{N}$

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

$(\text{CH}_3)_2\text{NH}$		
		N-methylethanamine
	Diethylamine	
$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{NH}_2$		
	Triethylamine	
		N-ethyl-N-methylethanamine

1. Write all the structures with a molecular formula $\text{C}_3\text{H}_9\text{N}$, name them and classify them as primary, secondary or tertiary.

Putrescine and cadaverine are toxic naturally occurring 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



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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	$-6^\circ C$	$C_2H_5NH_2$	$16.6^\circ C$	$C_3H_7NH_2$	$48^\circ C$
$(CH_3)_2NH$	$7^\circ C$	$(CH_3)_3N$	$3^\circ C$	$NH_2(CH_2)_2NH_2$	$116^\circ C$

4. *Discuss the following:*

- A boiling point is increasing from methylamine to propylamine.*
- Dimethylamine has a higher boiling point than methylamine.*
- Trimethylamine has a lower boiling point than dimethylamine.*
- $NH_2(CH_2)_2NH_2$ ($M_R = 60$) has much higher b.p. than propylamine ($M_R = 59$).*
- 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

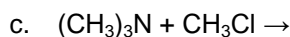
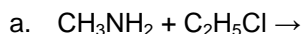
1. Reactions with acids \rightarrow ammonium salts

- $CH_3NH_2 + HCl \rightarrow$
- $C_6H_5NH_2 + HBr \rightarrow$
- $C_2H_5NH_2 + H_2SO_4 \rightarrow$
- $(CH_3)_3N + HCl \rightarrow$

5. *Estimate the state of matter and the solubility of ammonium salts.*

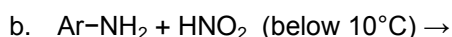
6. *The basicity increases as follows: $C_6H_5NH_2 \rightarrow NH_3 \rightarrow C_2H_5NH_2$. Try to explain it.*

2. Reactions with halogenocompounds = alkylation



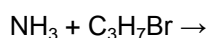
Tetraalkylammonium salts with one long carbon chain, e.g. $\text{CH}_3(\text{CH})_{14}\text{CH}_2\text{N}^+(\text{CH}_3)_3\text{Cl}^-$ act as as polar (.....) head interacts with, the long non-polar carbon part interacts with The polar part is said to be hydro..... while the non-polar is said to be hydro.....

3. Reactions with nitrous acid = diazotation \rightarrow diazonium salts



Preparation of amines

1. Ammonia + haloalkanes

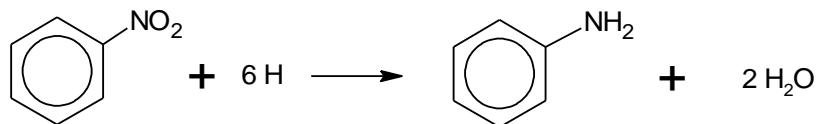


7. *What is the reaction mechanism of this reaction?*

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: $\text{Sn} + \text{HCl}$, $\text{Fe} + \text{HCl}$, $\text{Fe} + \text{steam}$ (industrial manufacture of aniline)

NITROCOMPOUNDS

= compounds containing group

Occurrence and properties:

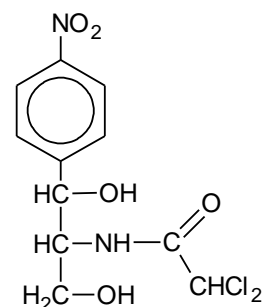
rarely in nature, e.g. pheromone



or some antibiotics, e.g. chloramphenicol



1. What type of stereoisomerism is possible for the formula of chloramphenicol?
2. How many stereoisomers 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.: $NO_2^\cdot + CH_4 \rightarrow$
 $CH_3^\cdot + HNO_3 \rightarrow$
 $CH_4 + \dots \rightarrow$
 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:

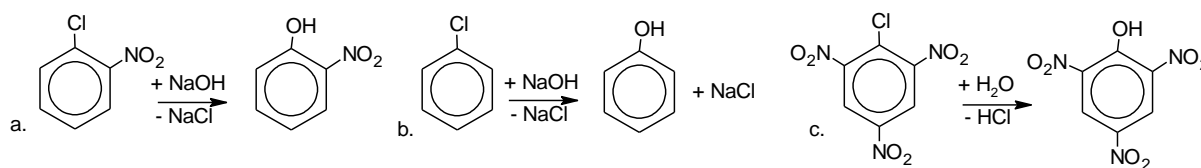
Reactions

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 $-\text{NO}_2$ group.



Uses of nitrocompounds

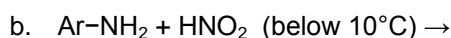
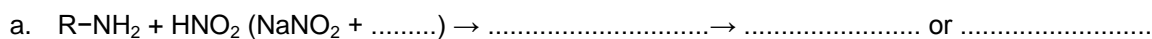
- Perfumes production (artificial musk)
- Insecticides
-
-

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

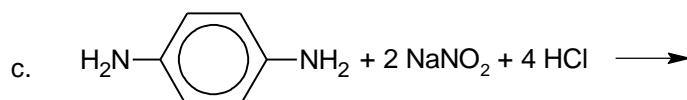
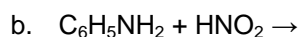
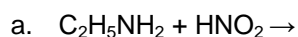
DIAZONIUM COMPOUNDS (SALTS)

= compounds with the functional group

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



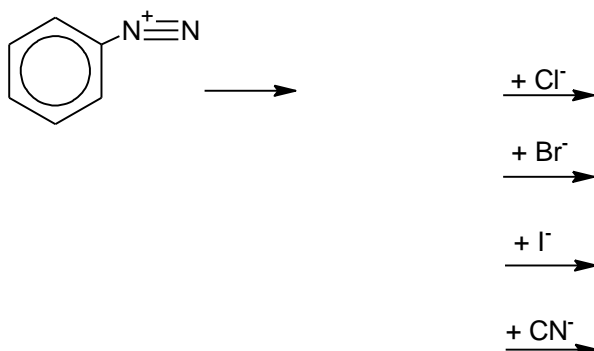
1. Write the formulae of the organic products of the following reactions:



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 $24.4 \text{ dm}^3 \cdot \text{mol}^{-1}$). Find the molar mass of this amine and suggest its molecular formula.

Reactions

1. Substitution

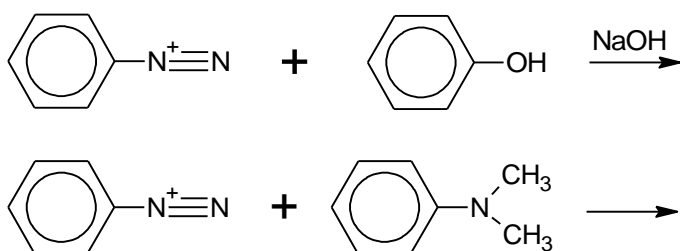


The reactions take place in the presence of catalyst.

2. Coupling

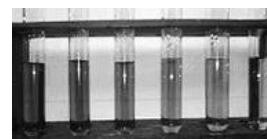
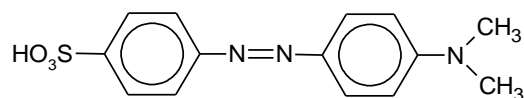
Diazonium ion acts as a weak *nucleophile/electrophile/free radical*. It may react with the derivatives of arenes containing electron *withdrawing/donating* groups, e.g.

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



The products are substances with $-\text{N}=\text{N}-$ 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