SIMONA POPA

ORGANIC DYES

STUDENT BOOK

Editura POLITEHNICA

Colecţia “MANUALUL STUDENTULUI”

ORGANIC DYES

STUDENT BOOK

În industria chimică organică coloranţii reprezintă una din cele mai importante clase de produse. Cartea tratează problematica transformării materiilor prime din sinteza organică în intermediari aromatici utilizaţi la sinteza de coloranţi, fiind foarte utilă în pregatirea viitorilor ingineri care vor lucra în acest domeniu.

Referent ştiinţific: Prof. dr. ing. Gheorghe ILIA

Sinteza coloranţilor organici a cunoscut în timp o dezvoltare şi o perfecţionare continuă. Prezentul manual tratează probleme generale legate de obţinerea coloranţilor dovedindu-se potrivit atât studenţilor cât şi inginerilor interesaţi de acest domeniu. Bibliografia selectivă prezentată poate fi consultată în vederea completării cunoştinţelor.

Referent ştiinţific: Şef lucr. dr. ing. Sorina BORAN

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FOREWORD

This book is intended to be a teaching material for students and for those who want to learn general aspects of the organic dyes synthesis.

The book has two main chapters. The firs one deals with the transformation of the raw materials into organic intermediates via the well-known reactions, covering the aspects of the orientation in the substitution reactions. There may be found some synthesis schemes for various aromatic intermediates. Notes on the relationship between the structure and the color of organic compounds, mutual influence of auxocrome groups and factors that influence color are also presented.

The second chapter reffers to the main dye class, the azo dyes. The diazotization and the coupling reactions are presented, whith their mechanisms. Factors that influence the coupling reaction are highlighted. Different classes of azo dyes are described.

In this way, I would like to thank the late professor Romulus Palea, from whom I received the first notions about organic dyes, and who was a good pedagogue, making me love this discipline since my student years. I would also like to thank Professor Ioan Boc, from whom I had a lot to learn, both in terms of the Dyes discipline and in terms of human relations. At the same time, I would like to thank the late Professor Alfa Xenia Lupea, who always guided me, whenever I needed, giving me the most competent advice, and the late Professor Ioan Macarie, with whom I have collaborated for severeal years and from whom I have learned a lot in this fabulous field of dyes. Last but not least, I would like to thank Professor Gheorghe Ilia, Dr. Nicoleta Pleşu, Professor Sorina Boran, Professor Sabina Niţu, Dr. Marilena Rădulescu-Grad, Professor Marius Milea, Professor Radu Lazău and Professor Giannin Moşoarcă for their professionalism and friendship, and from whom I learned a lot.

Dr. Simona Popa

CHAPTER 1. GENERAL NOTIONS REGARDING ORGANIC DYES SYNTHESIS

1.1. Transformation of raw materials into aromatic intermediates used in dye synthesis

In order to synthesize an aromatic intermediate, several variants can be used, differentiated between them by the nature of the chemical processes and their succession. The choice of the optimal variant depends on the conversion of the raw material and its transformation efficiency into a useful product. Three groups of transformation methods are known, namely:

1. Substitution reactions of hydrogen atoms in the aromatic hydrocarbon with reactive groups (sulfonation, nitration, halogenation);

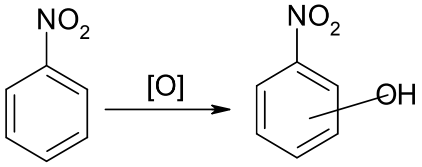
2. Transformation or replacement reactions of existing substituents (reduction of the NO_2 group to NH_2; replacement of the sulfonic group with other substituents: OH, OCH_3, NH_2, Cl; replacement of halogen with other substituents: OH, OCH_3, NH_2; replacement of the OH group with NH_2 and vice versa, alkylation, acylation, arylation of the OH or NH_2 group; diazotization of the NH_2 group; replacement of the diazo group with other substituents: OH, Hal, CN, H; reduction of nitrogen-free groups);

3. Reactions that modify the hydrocarbon skeleton by increasing or decreasing the number of carbon atoms in the cycle (condensation, oxidation, transposition).

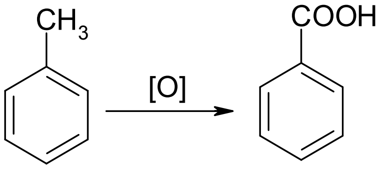
There may be cases in which reactions from group 1 and 2 occur simultaneously: the reduction of the nitro group to nitrates with sulfites can also lead to the formation of the amino group and the entry of the sulfonic group to the nucleus.

Oxidation is a particular case, which is part of all three reaction groups, presented above:

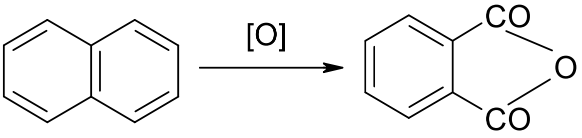
1. A substituent can be introduced in the nucleus:



2. An existing substitute can be modified:



3. The hydrocarbon skeleton can be modified:



The transformations from the first group determine the positions of the substituents not only on the product obtained, but also on its derivatives, obtained by the other two reaction groups. At the same time, the reactions from the first group are related to those of the two and three groups: sulfonation provides raw materials for alkaline melts - the formation of the oxy group; chlorination gives products, which can then be converted, by replacement of halogen, into amino- or hydroxy-derivatives.

The place of a substituent introduced into the molecule by the methods of the first group is preserved even after their modification or replacement by the methods of the second group.

1.1.1. Orientation of substitutes in substitution reactions to aromatic nuclei

The mutual influence of atoms in organic compounds influences the distribution of electrical charges in molecules. The explanation of the delimitation of charges, according to the electronic theory, can be done by using the notions of inductive and electromeric effects.

The inductive effect is related to the position of the pair of electrons that form the covalent bond. If the two atoms that form the bond are identical, they remain electrically neutral; and if they have different nuclear charges, the pair of electrons that form the covalent bond can be moved to one or the other of the atoms.

The direction of travel takes place according to the following criteria:

a) It is made towards the atom with higher positive nuclear charge, *ie* towards the atom of the element belonging to a superior group from the periodic system;
b) If atoms belong to the same group, the movement is made to the atom with lower atomic weight, with smaller volume (so the electrons are more strongly attracted to the nucleus)

Following these displacements, one atom will be charged with a positive charge fraction and the other with a negative one. This kind of electron displacement also occurs when a neutral atom is bonded to one that carries a charge through a covalent bond, such as ammonium ion (NR_3^+), or an atom joined by a semi-polar bond, as in the nitrogen atom of the nitro- group.

If there are chains of carbon atoms in a compound, an electrons movement along the chain develops, which decreases in intensity as it moves away from the atom that cause this shift. In benzene, however, due to the conjugation effect of the double bonds, the decrease in intensity of the inductive effect is small, practically all carbon atoms of the nucleus have the same charge, except the carbon atom directly bonded to the substituent, at which the charge is slightly higher.

The electromer effect occurs in the presence of double or triple bonds as well as in the case of the existence of non-participating pairs of electrons of atoms that are bonded to atoms that form multiple bonds. In the case of benzene, all bonds are equivalent.

Depending on the orientation ability in the aromatic nucleus, two types of substituents may exist. *First order substituents* - which are atoms or groups of atoms that orient the new substituents in the *ortho* and *para* positions (Hal, OH, OAlc, OAc, NH_2, NHR, NR_2, N=N, primary, secondary or tertiary Alc, CH_2Cl, CH_2ONO_2, CH_2SO_3H, CH_2NH_2, CH_2CN, CH_2COOH, CH = CH-COOH, CH=CH-NO_2, C_6H_5, etc. *Second order substituents* - which are groups that orient the new substituents in the *meta* position (NO_2, SO_3H, SO_2R in sulfones, CHO,

COOH, COOR, $CONH_2$, COR, CO-COOH, CN, CCl_3, N^+H_2X, N^+HX_2, SCN, etc.

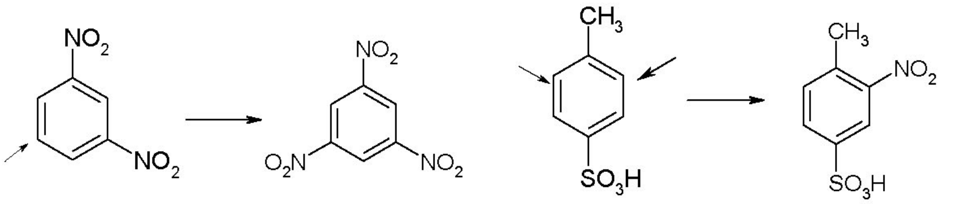
When there are first-order substituents in the benzene ring, the second substitution is easier than in the unsubstituted benzene, while the second-order substituents make subsequent substitution much more difficult. *The exception to the rule is halogens*: the large difference between the charges of the carbon and chlorine atoms leads to a high value of the inductive effect, which exceeds the value of the electromer effect. That is why all the carbon atoms in the nucleus remain positively charged, however the charge of the atoms in the *ortho* and *para* positions is lower due to the electromer effects.

Empirical rule regarding the orientation given by various substituents: If in the benzene derivative C_6H_5–XYn, the atom X bound to the aromatic nucleus has a valence less than 4, the group XYn orients in *o* and *p* (NH_2, OH); and if the valence is greater than 4, orients in *m* (NO_2, SO_3). At a valence equal to 4, orients in position *m*, if Y is an atom or a "negative" group (element from group V and from the upper groups of the periodic table: Hal, O, N - for example, CCl_3, CN, COOH) or if X carries a positive charge (S^+R_2, N^+H_3).

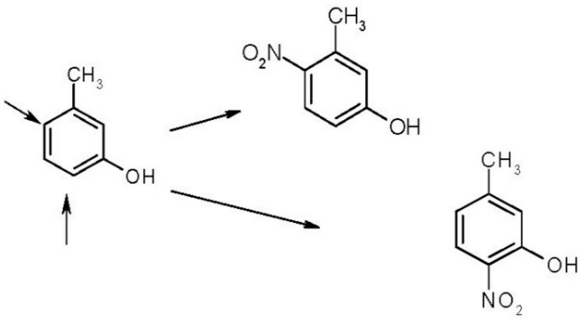
Substitutes can be ranked according to the power of orientation as follows:

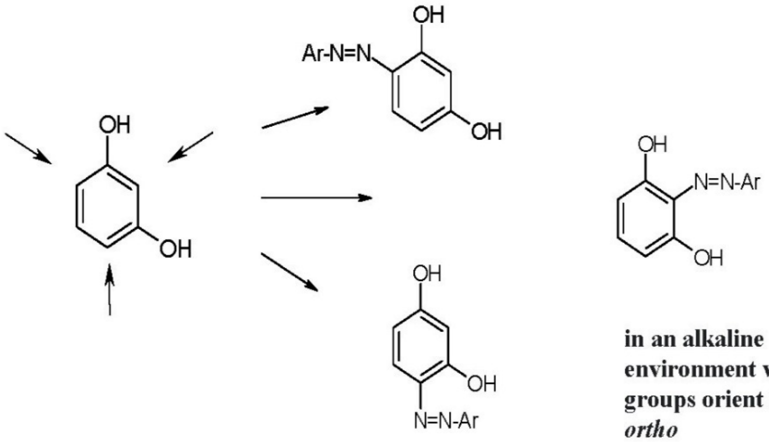
- For positions *o* and *p*: OH> NH_2> Cl> I> Br> CH_3
- For positions of *m*: COOH> SO_3H> NO_2

If there are two substituents in the benzene nucleus, both exert their orientation influence in the case of subsequent substitutions. Thus, if they are of the second order and are placed in the *meta* position or if they are in the *para* position and belong to different orientation groups, they determine the orientation of the third substituent only in a certain position, thus resulting in a single isomer.



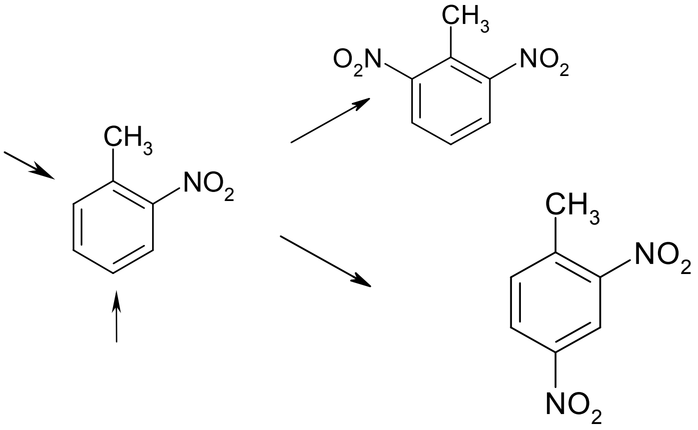
On the other hand, *meta*-disubstituted derivatives containing first-order substituents can give up to three isomers:



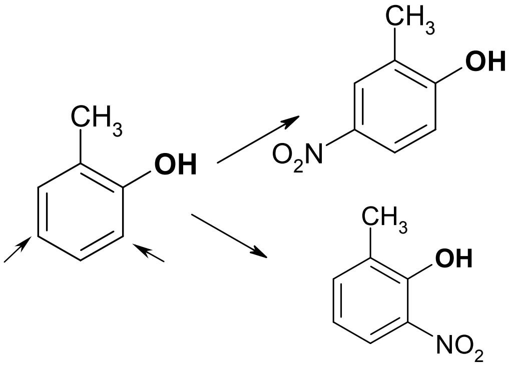


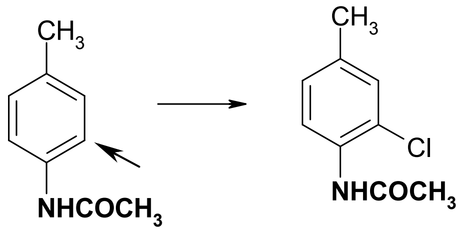
in an alkaline environment when both groups orient in the *ortho*

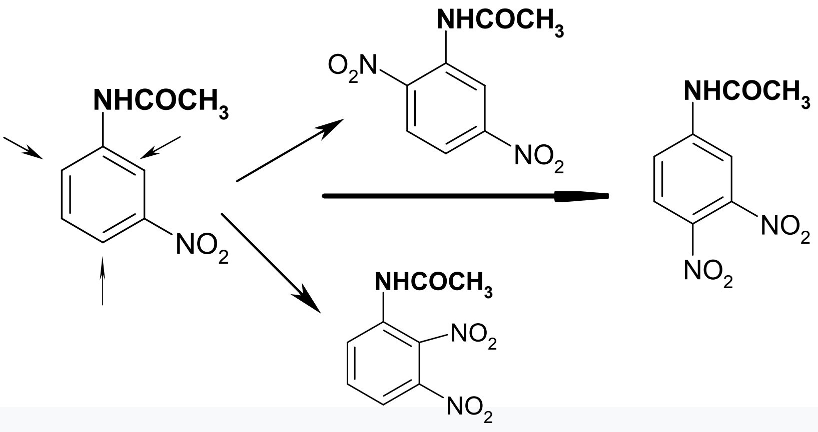
Ortho-disubstituted derivatives with substituents of different order give two isomers:



If there are two identical substituents in the *ortho* and *para* positions relative to each other or two different substituents in the *meta* position, the orientation influence competes, obtaining mixtures in which those formed due to the substituent with the highest orientation power predominate. These schemes are presented below:

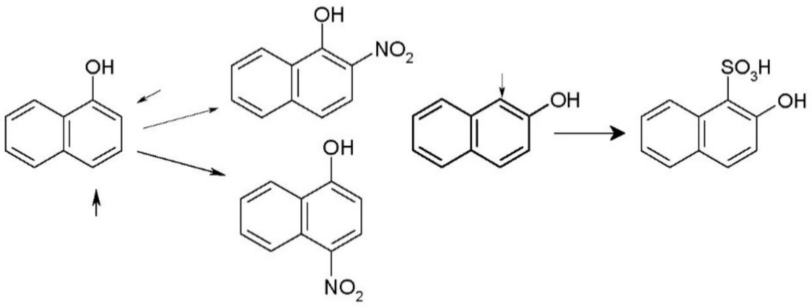




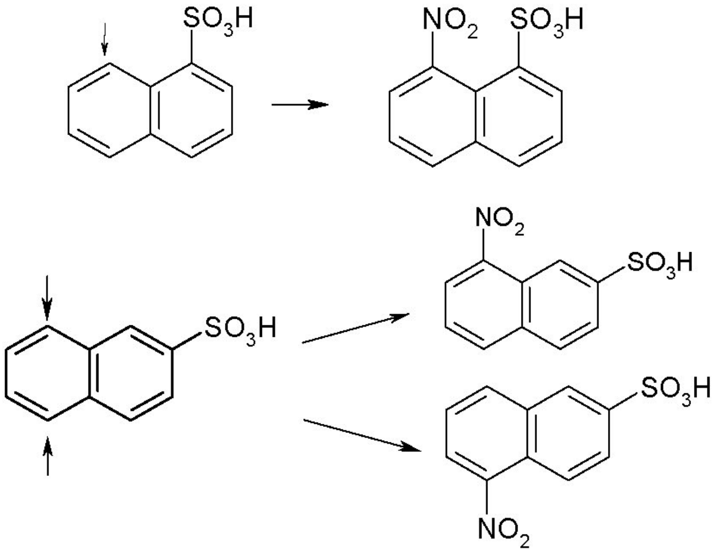


In the case of compounds with condensed aromatic nuclei (naphthalene, anthraquinone), the rules of orientation are more complicated. The number of possible isomers is higher and their separation is more difficult.

If there are first-order substituents in the nucleus of these compounds, the second substituent enters the nucleus containing the group whose orientation effect predominates, the orientation effect being similar to the benzene case. Thus, the second substitution of naphthalene, which had the first substituent in position 1, will take place in the *ortho* or *para* position relative to it, and if the first substituent is in position 2, isomers 1,2 are formed and not 2.3.



If there are second-order substituents in the nucleus, the new substituent will enter the unsubstituted nucleus, in positions favorable to substitution (α positions for naphthalene).



General rules of substitution for naphthalene and anthraquinone nuclei are presented below.

• First order substituents orient in the positions corresponding to the possible naphtho-quinones (quinogenic positions): 1,2; 1.4; 2,3-less often. If at one of the nuclei all the reactive positions are occupied, the new substituent enters the other nucleus, also in the corresponding quinogenic positions: 1.5; 1.7 (or 2.8); 2.6. Deviations from these rules may occur due to reactivities of α positions.

• Second order substituents orient the second substituent in non-kinogenic positions, especially in the unsubstituted nucleus. Due to the high reactivity of the α positions, however, substitutions can also take place in the quinogenic positions, thus obtaining more isomers than in the case of the existence of a first-order substituent, isomer form: 2.8 (1.7); 2.6; 2.5; (1.6); 2.7 - this being the main product of the reaction.

• In the case of anthrachinone, the marginal nuclei are identical and resemble two benzene nuclei substituted ortho with second-order substituents. Consequently, the guideline for introducing a new substituent is similar to that for benzene. So it would be expected to obtain both isomers (α and β), but in reality the replacement of anthraquinone is done according to special rules. Thus, only the β isomer is obtained by sulfonation, while α-derivatives are obtained by nitration or chlorination. The two nuclei of anthraquinone react independently, so substituting one does not decrease the reactivity of the other, usually the obtaining of disubstituted anthraquinone derivatives is much more easily than in the case of benzene or naphthalene.

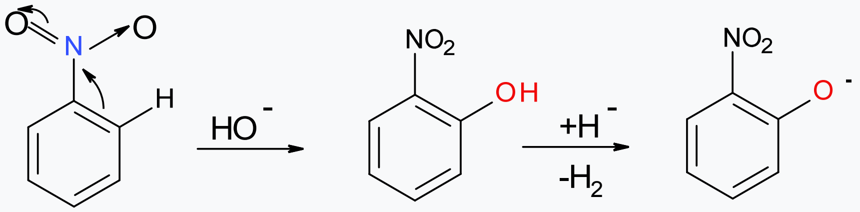
1.1.2. Factors that influence the substitution reaction

- The nature of the existing substituent in the molecule;
- The place occupied by the substituent in the molecule;
- The reactivity of α positions to naphthalene; the orientation influence of the substituent;
- The nature of the reactive agent, which can also generate secondary reactions;
- The polarity of the reactive agent;
- The non-equivalence of benzene nuclei in the case of naphthalene (one approaches a more stable aromatic structure, and the other a more reactive diene structure);

- In anthraquinone substitution is done according to special rules, the marginal nuclei being identical and resembling two *ortho*-substituted benzene nuclei with second-order substituents. The two benzene nuclei react independently and do not change each other's reactivity.

1.1.3. Nucleophilic substitution

The nucleophilic substitution of the aromatic nucleus is made with an agent that carries a negative charge, so it is a nucleophilic agent, and its attack will take place in the positive positions. In this case the first order substitutes will orient the new substituent in the *meta* position, while the second order ones will orient in *ortho* and *para*.



Replacement of a substituent in the molecule of an aromatic compound with another substituent usually occurs by nucleophilic attack by a nucleophilic agent, which, due to the non-participating electrons in the molecule, has an affinity for the low-density carbon atom, to which the substituent to be replaced is attached.

Examples of such nucleophilic substitutions are alkylation of aromatic amines, substitution of sulfonic group with hydroxyl (alkaline fusion), substitution of chlorine with OH, OR, OAr, NH_2, NHR, SO_3H, CN, etc., ammonolysis of hydroxy derivatives and amino hydrolysis -derivatives.

1.2. The main types of reactions related to the transformation of raw materials into aromatic intermediates

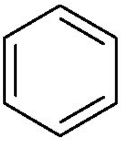
1.2.1. Raw materials used in the synthesis of aromatic intermediates

In the synthesis of aromatic intermediates, coal tar and oil are the main raw materials. Coke oven gas may also be used.

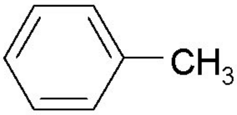
They contain the following important components for organic chemical industry:

- ***Benzene and its counterparts:***

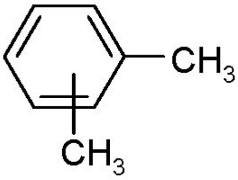
benzene C_6H_6



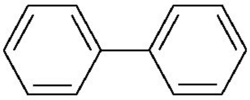
toluene $C_6H_5\text{-}CH_3$



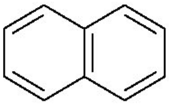
orto-,meta-, para- xylenes $C_6H_4(CH_3)_2$



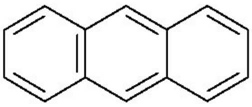
biphenyl $C_{12}H_{10}$



naphthalene $C_{10}H_8$

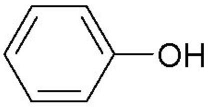
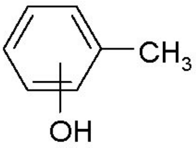
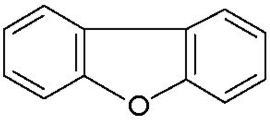
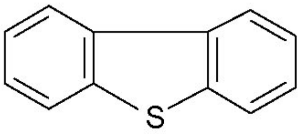
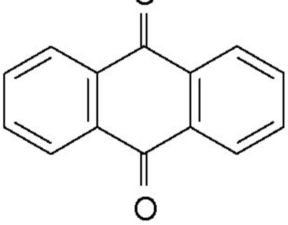


anthracene



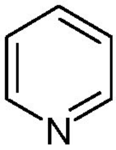
$C_{14}H_{10}$

- ***aromatic hydrocarbons having oxygen and sulfur in the molecule***

phenol	C_6H_5OH	
orto-,meta-, para-cresol	$C_6H_4(CH_3)OH$	
diphenilene-oxide	$C_{12}H_8O$	
diphenilene-sulfide	$C_{12}H_8S$	
anthraquinone	$C_{14}H_8O_2$	

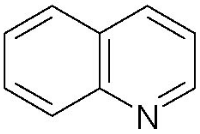
- ***aromatic hydrocarbons having nitrogen in the molecule***

pyridina C_5H_5N

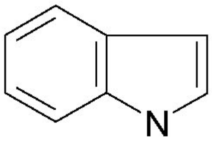


quinoline C_9H_7N

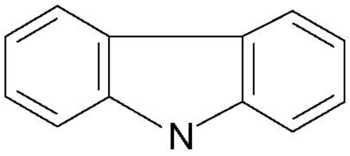
α,β-benzo-pyridine



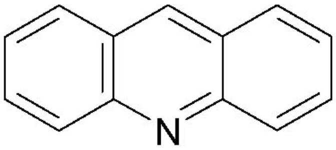
indole C_8H_7N



carbazole $C_{12}H_9N$



acridine $C_{13}H_9N$



1.2.2. Sulfonation

The sulfonation process is one of the fundamental processes of great importance in the organic synthesis industry. Sulfonation ensures on the one hand the solubilization of organic compounds in water, and on the other hand, aryl-sulfonic acids are raw materials in the synthesis of various intermediates by substituting the sulfonic group.

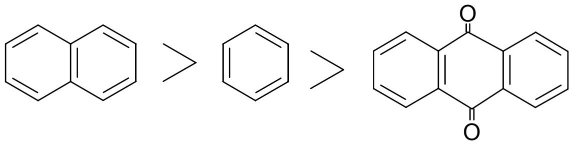
The synthesis of aryl-sulfonic acids uses a wide range of sulfonated agents. Concentrated sulfuric acid of 96-98% or sulfuric acid monohydrate of 100% concentration is usually used as the sulfonating agent.

The lower reactivity of some aromatic substrates requires the use as sulfonating agent of oleum sulfuric acid containing dissolved SO_3. In practice, SO_3 sulfonation processes have recently been introduced, respectively in the processes that require milder conditions, adduced by SO_3-Pyridine or SO_3 - tertiary bases -SO_3 - (CH_3) $2N$-C_6H_5. In exceptional cases, sodium bisulphite and sodium sulphite may be used as sulfonating agents.

Among the factors that play an important role in sulfonation processes, the following can be mentioned:

1) The nature of the aromatic substrate subjected to the sulfonation process.

The nature of the raw material used in the sulfonation processes decisively influences their substitution capacity. Thus, the higher the availability of electrons in an aromatic substrate, the easier the sulfonation rate. Thus, naphthalene is sulfonated more easily than benzene, and anthraquinone is harder than these are, as presented below:



2) Sulfonation agent concentration.

Aromatic substrates with increased reactivity require the use of concentrated sulfuric acid. Sulfonation processes performed on less reactive substrates, such as anthraquinones, require the use of oleum sulfuric acid as a mandatory condition.

With the advancement of the sulfonation process, the reaction capacity of the sulfonant decreases due to the decrease of its concentration following the formation of water as a by-product (dilution of the sulfonant).

Consequently, in order to ensure a more advanced transformation of the raw material, it is necessary to use the excess sulfonating agent.

3) Temperature

As the temperature increases, the reaction rate increases as well. Since the sulfonation processes are accompanied by side reactions, with the rise of the temperature, side reactions are also obtained. That is why for each intermediary it is necessary to choose the optimal working temperature.

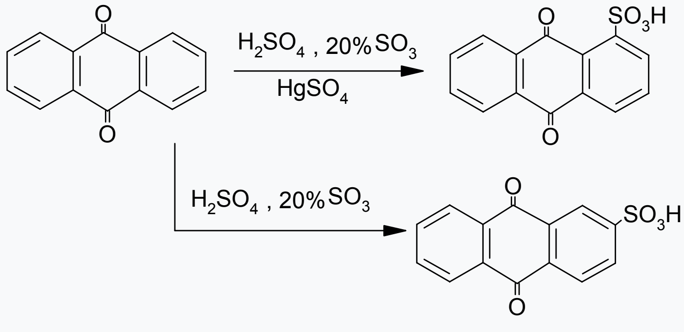
In the naphthalene series, the temperature also influences the sulfonation position. Thus, at a temperature of about 40ºC, the sulfonation takes place in α position, and at temperatures higher than 160ºC, it takes place in β position.

4) Sulfonation time

The prolongation of the period of improvement of the sulfonation process leads to a more rational use of the sulfonating agent, by decreasing its limit concentration with sulfonating effect. The increase of the process improvement period also has undesirable side effects due to the appearance of parasitic products, respectively due to the danger of isomerization or polysulfonation.

5) Catalysts

Most sulfonation processes take place in the absence of catalysts. The exception to the rule is anthraquinone sulfonation, where the presence of mercury sulphate catalysts determines the orientation in the α position, rather then in the β.



6) Stirring

Stirring is known to be an indispensable factor in any process in which various chemical transformations are perfected. During the sulfonation process, there may be situations in which the aromatic substrate is not miscible with sulfuric acid and it is logical that stirring is necessary in this case.

Stirring also ensures the most intimate contact of the reactants, which allows on the one hand the increase of the sulfonation rate and on the other hand the uniform uptake of the reaction heat, given the strong exothermic character of the sulfonation process, avoiding local overheating.

1.2.3. Nitration

Nitration is the process of introducing the nitro- (NO_2-) group into the molecule of aromatic substrates, by substituting a hydrogen atom.

Nitroderivatives are important intermediates in the organic synthesis industry because they are raw materials in the synthesis of aromatic amines and high-boiling solvents, such as nitrobenzene with m.p. higher than 200°C.

Depending on the nature of the nitrating agent, several variants of the synthesis of aromatic nitroderivatives are known. Thus, we can distinguish the following:

1) Nitration with nitrating acid, which is a variable mixture of sulfuric acid, nitric acid and water
2) Nitration with concentrated nitric acid
3) Nitration with nitric acid in the presence of organic solvents
4) Nitration with nitrogen oxides
5) Nitration with salts of nitric acid (sodium nitrate)
6) Indirect nitration processes: which involve prior sulfonation of aromatic compounds, followed by substitution of the sulfonic group by treatment with nitric acid, respectively there is the possibility of nitrosation of aromatic compounds followed by oxidation of the nitroso group to the nitro group.

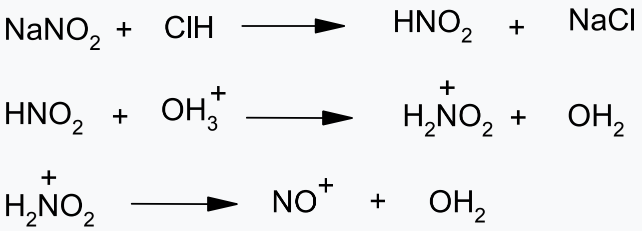
According to the general equation, one mole of water is obtained for each mole of nitroderivative, which influences the reaction capacity of nitric acid, forming the nitrate ion, which has no nitrating character.

$$HNO_3 + H_2O \rightleftharpoons OH_3^+ + NO_3^-$$

In order to ensure the complete transformation of nitric acid into the main product, it is necessary to bind the water resulting from the process. The most important variant of nitration is made with the help of the nitrating mixture, in which sulfuric acid binds the water formed and ensures the almost complete transformation of nitric acid into nitrate product, thus increasing the yield of the reaction. There is the possibility of performing the nitration process in the presence of water acceptors, such as acetic anhydride, but this is uneconomical.

Although not of a general nature, *nitrosation* is important for obtaining intermediates that are not accessible by other processes. In nitrosation processes, the active species is nitric acid, which is extremely unstable at ambient temperature. Therefore, nitrosation processes require the production of nitric acid during the reaction, by treating sodium nitrite with a mineral acid.

The active species in the nitrosation processes (the reaction mechanism being SE) is the *nitrosyl ion*, which results according to the following sequence of reactions: sodium nitrite, by treatment with hydrochloric acid is transformed into nitric acid, which in the acid medium forms the *nitrosacid ion*, which decomposes into *nitrosyl ion* and water.



$$NaNO_2 + ClH \longrightarrow HNO_2 + NaCl$$

$$HNO_2 + OH_3^+ \longrightarrow H_2\overset{+}{N}O_2 + OH_2$$

$$H_2\overset{+}{N}O_2 \longrightarrow NO^+ + OH_2$$

nitrosacid ion *nitrosyl ion*

Unlike nitronium ion ($NO2^+$) it is a very weak electrophile, although it has a positive charge. Therefore, in order for the nitrosation process to take place, it is mandatory that the aromatic substrate to have an increased reactivity. So only very active substrates with increased electron density, such as phenols and amines, participate in the nitrosation processes. By nitrosation unit products are obtained, and by oxidation nitroso-derivatives can be transformed into nitro-derivatives.

Among the factors that play an important role in nitration processes, the following can be mentioned:

1) The amount and concentration of nitric acid

Depending on the aromatic substrate, the concentration of nitric acid can vary widely. As most processes are carried out in the presence of sulfuric acid with a dehydrating effect, the amount of nitric acid that is contained in the nitrating mixture represents a few percent (2-5%) in excess of what is theoretically necessary. The exception is the nitration of anthraquinone, when the excess nitric acid must be 20% of what is theoretically necessary.

2) The nature of the aromatic substrate

The reaction capacity of aromatic compounds is directly influenced by the availability of electrons. The higher the electron density, the faster the rate of transformation into nitrate products.

Given that the nitronium ion is a very strong electrophilic, nitration processes take place at high speeds, so in substrates with high reactivity, the conditions are relatively mild (nitrating mixtures are used in which the amount of water varies between 10-25%).

Thus, the nature of the substituents in the structure of the aromatic compound significantly influences the reaction capacity. A first-order substituent activates the nitration processes and directs the substitution in the *ortho*- and *para*- positions (and even in the *meta*- to a lesser extent), and the second-order substituents delay the nitration processes, demanding more energetic conditions, regarding the concentration of the nitrating agent (the nitrating mixture). As the reactivity decreases, so does the amount of water in the nitrating mixture.

3) Temperature

As the temperature increases, the reaction rate increases. It is logical that this will also increase the speed of the side reactions.

Nitration is a process that has the peculiarity that it leads to secondary phenomena by which the number of polynitrate or even explosive derivatives increases therefore the nitration process must take place at low temperatures.

In substrates with increased reactivity the temperature is about 20^oC, in normal ones between $20\text{-}100^oC$, and in those with low reactivity at temperatures above 100^oC (in anthraquinone, for example).

4) Stirring

Stirring is a very important parameter in any process in the organic industry, as it ensures on the one hand the increase of the reaction rate and on the other hand determines the elimination of the reaction heat, given the strong exothermic character of the nitration processes.

The stirring at the same time ensures the increase of the reaction rate to obtain the main product and thus delimits the explosion dangers of the polynitrate derivatives.

The role of sulfuric acid in the nitrating mixture

Sulfuric acid in the nitrating mixture plays a multiple role, influencing the yield of nitrate products. The most important attributions of sulfuric acid are:

1- Sulfuric acid ensures the generation of nitronium ions and the acceptance of the proton by the bisulfite ion
2- In the presence of sulfuric acid a series of aromatic substrates dissolve, ensuring the development of the nitration process in homogeneous conditions
3- The high caloric value of sulfuric acid determines the takeover of the reaction heat, taking into account the strong exothermic character of the nitration processes
4- In the presence of sulfuric acid there is the possibility of protecting the amino group in the form of sulfate, given the strong oxidizing character of nitric acid
5- The mixture of sulfuric acid and nitric acid is less corrosive on steels than nitric acid alone.

Separation of nitrate products

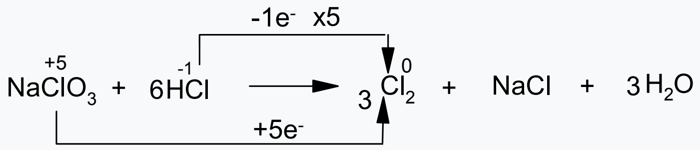
The steps of separating the aromatic nitroderivatives do not pose particular problems, given the poor solubilization of most nitrate intermediates in dilute acids.

Liquid nitroderivatives (nitrobenzene) are separated by simple decantation, followed by washing the crude product with aqueous and alkaline solutions to remove acidity. The solid nitroderivatives are separated by simply diluting the nitromass with water, when their precipitation or crystallization takes place. Nitro-aryl-sulfonic acids are isolated by diluting the reaction mass, followed by salting with sodium chloride, when precipitation of the sodium salt of the respective intermediates takes place. The final purification takes place by rectifying the nitroderivatives with a low boiling point or by recrystallization from organic solvents to solid ones.

1.2.4. Halogenation

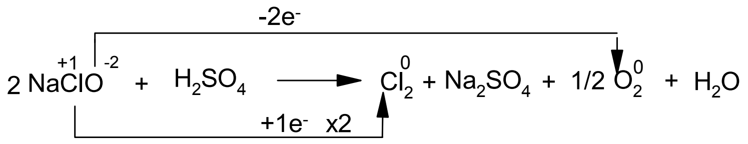
Halogen-aromatic derivatives are an important category of intermediates in the organic synthesis industry. Halogen atoms can be easily substituted with other groups, allowing a diversification of the classes of organic compounds, on the one hand, and on the other hand, the obtained poly-halogen-aromatic derivatives are solvents with high boiling points (chlor-benzene, dichlor-benzene, etc.). The relatively low cost of chlorine has led to the widespread use of chlorinated aromatic derivatives.

In the organic industry, the usual chlorinating agent is chlorine gas. There are also exceptional cases, when the use of less active halogenating agents is claimed, in which chlorine is generated as a result of chemical transformations. For example, by treating sodium chlorate with hydrochloric acid:



$$Na\overset{+5}{Cl}O_3 + 6H\overset{-1}{Cl} \longrightarrow 3\overset{0}{Cl_2} + NaCl + 3H_2O$$

Or by treating sodium hypochlorite with sulfuric acid:



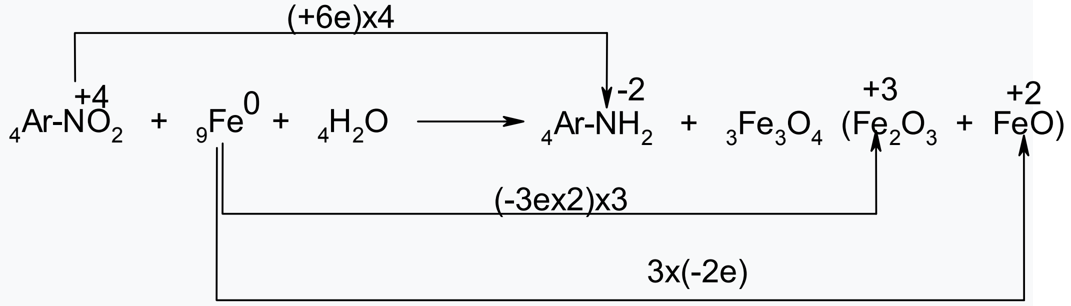
$$2\,Na\overset{+1}{Cl}\overset{-2}{O} + H_2SO_4 \longrightarrow \overset{0}{Cl_2} + Na_2SO_4 + 1/2\,\overset{0}{O_2} + H_2O$$

The chlorination with chlor-amides is a very gentle process.

1.2.5. Reduction

By reducing aromatic nitro-derivatives, amines are formed, which are intermediates of major importance in the organic synthesis industry. The process takes place under the influence of atomic hydrogen resulted from the interaction between water and metal surfaces, respectively under the influence of molecular hydrogen in the presence of catalysts.

The metal acts as an electron supplier, and hydrogen is generated by water. The general equation is actually a redox process.



Depending on the technological conditions in the reduction process, different intermediates may result. The decisive role in influencing the process is the pH of the environment.

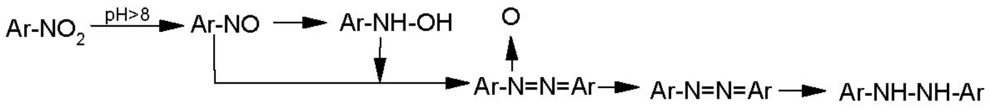
Thus, if the reduction of the aromatic nitro-derivatives takes place at a pH < 5, a nitroso-aromatic compound is formed in the first phase, which is then transformed into the aromatic hydroxyl-amine and finally into the aromatic amine.

$$\text{Ar-NO}_2 \xrightarrow{\text{pH<5}} \text{Ar-NO} \longrightarrow \text{Ar-NH-OH} \longrightarrow \text{Ar-NH}_2$$

If working at pH = 7 the nitroso-aromatic compound is obtained and in the end only hydroxylamine is reached.

$$\text{Ar-NO}_2 \xrightarrow{\text{pH=7}} \text{Ar-NO} \longrightarrow \text{Ar-NH-OH}$$

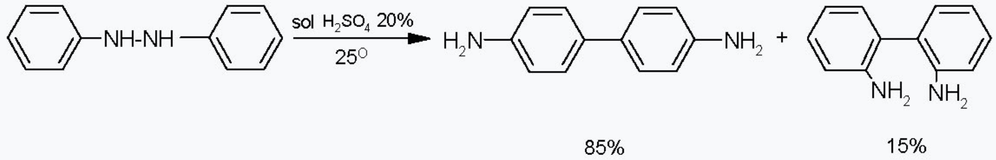
If the reduction performes at a pH > 8 the nitroso-derivatives are obtained and from the hydroxyl-amines resulting from them may lead to the formation of azo-derivative and finally hydrazo-derivative can be removed.



The process of reducing nitro-derivatives is performed with metals under different technological conditions. For example, the reduction of nitro-benzene with iron in the presence of mineral acid, hydrochloric acid was observed before the twentieth century. It was found that during the process, the amount of hydrochloric acid is below the required stoichiometric quantity, which led to the idea that the process is actually catalyzed by the iron salts ($FeCl_2$) resulting in the first stage of the process. It was later established that the processes of reduction of nitro-derivatives in weakly acidic medium is catalyzed by different electrolytes: $FeCl_2$, NH_4Cl, $(NH_4)_2SO_4$, NaCl (less often) etc.

$$Fe + {}_2HCl \longrightarrow FeCl_2 + {}_2H$$

Hydrazo-aromatic derivatives in the presence of mineral acids undergo the *transposition* process, resulting in *benzidine derivatives*. The process takes place at relatively low concentrations of mineral acid (20% sulfuric acid, 15-20% hydrochloric acid) and not too high temperatures. Hydrazo-benzene, at 25°C, in the presence of 20% sulfuric acid solution is converted to 85% benzidine and other by-products.



1.2.6. Amination

Amination or ammonolysis of organic compounds is the indirect process for the synthesis of aromatic amines. Amination occurs by the substitution of atoms or groups of atoms in the molecule of aromatic intermediates.

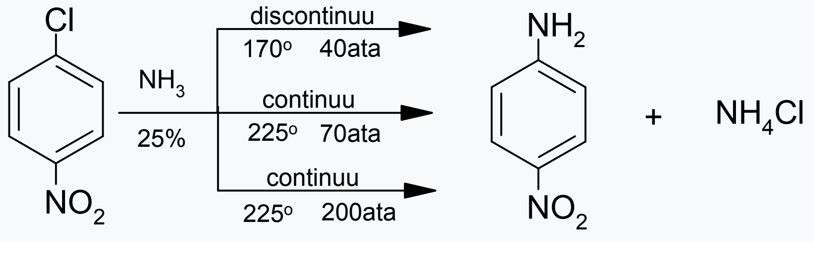
Ammonolysis processes are differentiated by the technological conditions and the nature of the raw materials from which they start. Aromatic amine synthesis variants are classified according to the nature of the raw materials used in the process in: amination of halogenated derivatives, hydroxylated derivatives, aryl-sulfonic acids, or there are also special amination processes.

The amination agent is ammonia, which can act in the gaseous state, less often in the form of a liquid, using solutions of 20-30% concentrations. In ammoniacal solutions, ammonia is physically bound and only in very small amounts in the form of ammonium hydroxide. In ammonolysis processes ammonia can be replaced by aliphatic or aromatic amines:

$$\text{Ar-X} + \text{NH}_3 \longrightarrow \text{Ar-NH}_2 + \text{HX}$$
$$\text{Ar-X} + \text{H}_2\text{N-R} \longrightarrow \text{Ar-NH-R} + \text{HX}$$
$$\text{Ar-X} + \text{H}_2\text{N-Ar'} \longrightarrow \text{Ar-NH-Ar'} + \text{HX}$$

The amination processes take place at high temperatures, conditions that determine the volatilization of ammonia and the appearance of a pressure corresponding to the temperature at which the process takes place. At high pressures and temperatures there is a danger of ammonia diffusion, which can lead to undesirable phenomena.

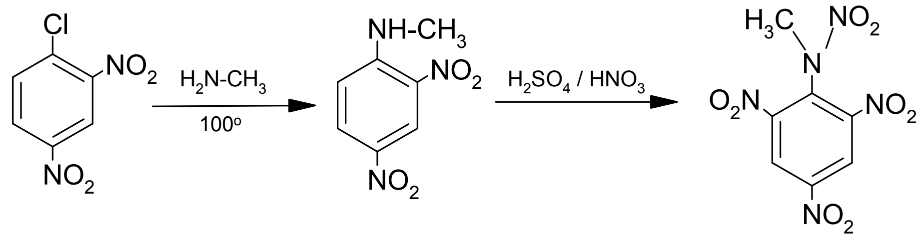
Of major importance is the amination of nitro-chlorine-aromatic derivatives. *p*-Nitro-aniline is obtained by amination of *p*-nitro-chloro-benzene in various embodiments. Discontinuous processes take place in milder conditions, and continuous ones in energetic ones. Thus, if working with 25% ammonia solution, *p*-nitro-aniline is obtained under the following conditions: in a batch process, at 170°C and 40°C; in continuous process at 225°C and 70°C; or in a continuous process, but in tubular reactors, at 225°C and 200°C:



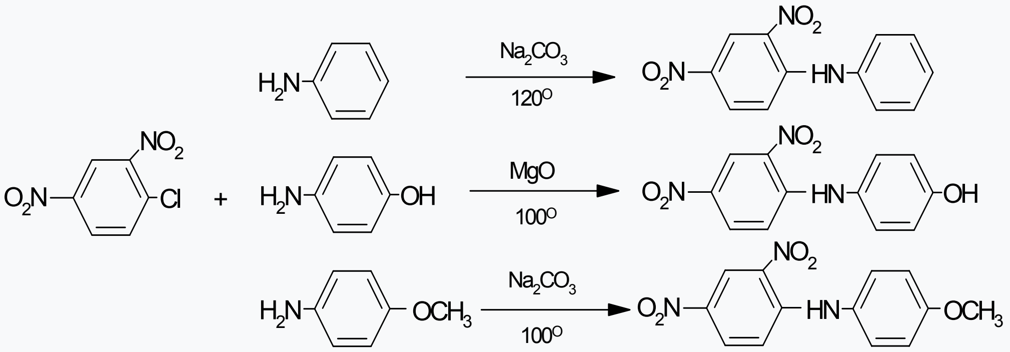
Regardless of the production process, the separation of *p*-nitro-aniline follows, the final yield being greater than 95%, at a purity in the useful product of 99%.

Alkyl- and aryl-amination of halogenated derivatives

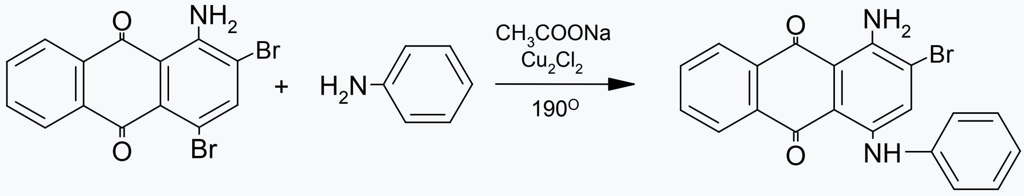
In the process of alkylation and arylation it is preferred to use raw materials with increased reactivity. Of importance is the alkyl amination of dinitro-chloro-benzene, which takes place at 100ºC with methyl amine, forming 2,4-dinitro-phenyl-methyl-amine, which in the presence of a nitrating mixture (sulfuric acid and nitric acid) nitrates to the secondary amine:



Under conditions of not too high temperatures, around 100ºC, with various inorganic salts (carbonates, oxides) various aryl-amine intermediates of aromatic halogen derivatives may be formed.

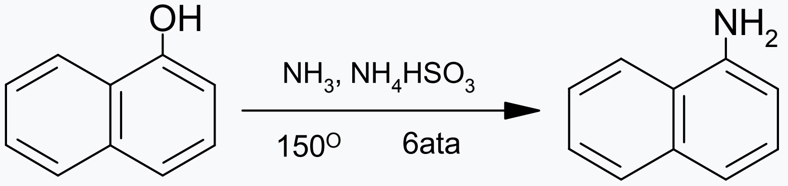


Halogenated anthraquinone derivatives can also be subjected to aryl-amination reactions, but in this case the working temperatures are higher:



Amination of hydroxylated derivatives

Ammonolysis of phenols is a fundamental process of importance in the organic synthesis industry. The amination of aromatic hydroxy derivatives and the reverse process of hydrolysis of aromatic amines are fundamental indirect processes of substituting a group of atoms in the molecule of aromatic compounds. The process takes place in difficult conditions and is suitable for application in the naphthalene and anthraquinone series. The amination agent is ammonia in the form of a 25-30% solution, accompanied by the presence of ammonium salts: chloride, carbonate, but especially bisulfite, which can play also a catalytic role.



1.2.7. Hydroxylation

Phenols, naphthols and aromatic amines are intermediates of particular importance in the organic synthesis industry. Phenols are raw materials in the pharmaceutical industry, dyes, detergents; phenol is the raw material for the synthesis of relon-type synthetic fibers. A wide range of phenol synthesis has been developed, which ensures a high degree of profitability.

The classification of the processes for the synthesis of aromatic hydroxy-derivatives is made according to the initial materials from which they are obtained. Hydroxylation processes are performed by substituting an atom or groups of atoms from the structure of aromatic compounds. The following synthesis variants are distinguished:

1) Alkaline melting of sulfonates:

$$Ar\text{-}SO_3Na + 2NaOH \longrightarrow Ar\text{-}ONa + Na_2SO_3 + H_2O$$

2) Hydrolysis of aromatic amines:

$$Ar\text{-}NH_2 + H_2O \rightleftharpoons Ar\text{-}OH + NH_3$$

3) Hydrolysis of halogenated aromatic derivatives:

$$Ar\text{-}Cl + NaOH \longrightarrow Ar\text{-}OH + NaCl$$

4) Specific processes for phenol synthesis

Factors that influence hydroxylation process

1- *The nature of the aromatic substrate*. The hydroxylation capacity of aromatic compounds is directly influenced by the aromatic system to which the aryl-sulfonic acid belongs. Thus, benzene-sulfonic acids have a lower reactivity in hydroxylation processes than naphthalene-sulfonic and anthraquinone-sulfonic acids, respectively. The lower reaction capacity results in the use of more drastic reaction conditions, expressed by increasing the alkali concentration and temperature. First-order substituents slow down the hydroxylation process, unlike second-order substituents, which facilitate (activate) it. For each aryl-sulfonic intermediate, the temperature and the alkali concentration are established at optimal values, which will ensure a higher reaction yield.

2- *Alkali concentration*. The reactivity of the aromatic substrate directly influences the concentration of the hydroxylating agent. The low hydroxylation capacity of aryl-sulfonic acids requires very high concentrations of hydroxides and molten alkalis, respectively. Aryl-sulfonic substrates with increased reactivity use alkali solutions of different concentrations, depending on their reactivity. Anthraquinone sulfonic acids, for example, which have an increased reactivity, require the use of less reactive alkaline agents, such as calcium or magnesium hydroxides.

3- *Temperature*. The hydroxylation processes are carried out at relatively low speeds, consequently, to ensure optimal conditions, high temperatures are used, above 150^{o}C, up to 330-350^{o}C. Depending on the reactivity of the aromatic substrates, the temperatures are extremely varied, but they cannot exceed certain values, even if the reaction rate would increase, because oxidation processes of organic compounds can occur.

4- *Stirring*. Being perfected in melt or concentrated solution of alkaline hydroxides, the hydroxylation processes take place at a very high viscosity of the medium. Consequently, it is necessary, as a mandatory condition, to stir the reaction mass intensely, in order to favor the energy exchange, avoiding agglomerations and overheating, and therefore unwanted side reactions or even ignition of the reaction mass.

5- *The presence of impurities*. In the process of separating aryl-sulfonic acids, one of the steps that usually occurs is the neutralization of sulfomas. Under these conditions, in the process of separating the salts of aryl-sulfonic acids, relative amounts of inorganic salts (NaCl, KCl) are also included. Their presence in the composition of the matter through it adversely affects the hydroxylation process. Inorganic salts cause agglomeration of the reaction mass, favoring local overheating and the occurrence of side reactions. In the process of separation of aryl-sulfonic acids, the aim is to reduce the presence of inorganic salts as much as possible, so it is necessary to monitor the technological parameters.

1.2.8. Alkylation, arilation and acilation of aromatic amines and phenols

The formation of C-N and C-O bonds falls into the category of alkylation, arylation and acylation processes of aromatic amines and phenols or naphthols. Alkylation of aromatic amines gives a wide range of intermediates which are secondary, tertiary or quaternary ammonium aliphatic-aromatic amines. Alkylation of phenols gives aliphatic-aromatic ethers. Mixtures of alkyl-aryl aminated products are usually obtained in the alkylation processes of aromatic amines, depending on the technological conditions and the amine-alkylating agent molar ratio.

A wide range of *alkylating agents* are used in alkylation processes, of which the following can be mentioned:

1- aliphatic alcohols: methanole, ethanol

2- aliphatic halogenated derivatives: chlor-methane, chlor-ethane, bromo-methane, iodine-methane, benzyl chloride

3- alkyl sulfates: dimethyl sulfate, diethyl sulfate

4- aliphatic ethers: dimethyl ether, diethyl ether

5- special agents: aldehydes, chloroacetic acid, ethylene oxide, hydrochloride, methyl acrylate

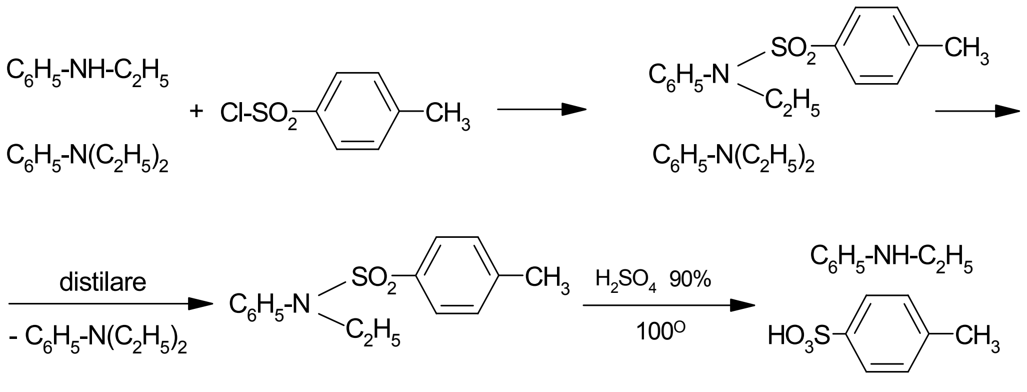
In the alkylation processes of the primary aromatic amines, mixtures of secondary and tertiary amines are usually obtained.

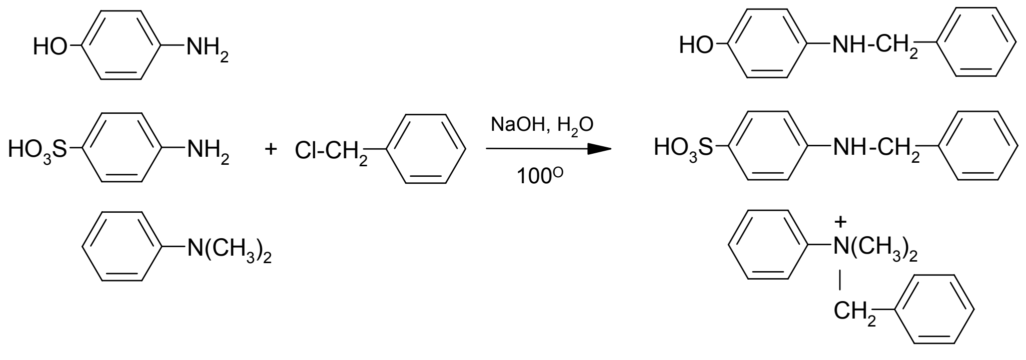
The schematic equations presented below exemplify some of these rections that use different alkylating agents:

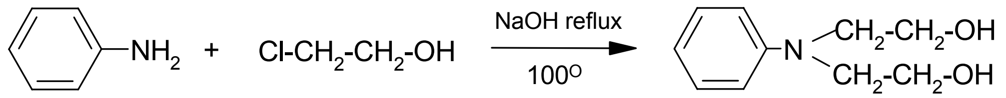
$$Ar\text{-}NH_2 \xrightarrow[-H_2O]{R\text{-}OH} Ar\text{-}NHR \xrightarrow[-H_2O]{R\text{-}OH} Ar\text{-}NR_2$$

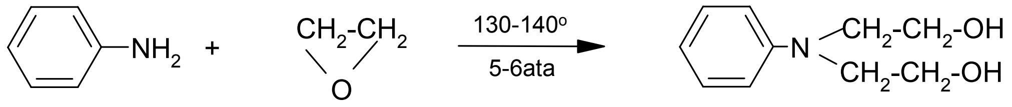
$$C_6H_5\text{-}NH_2 + \underset{\text{exces}}{HO\text{-}CH_3} \xrightarrow[230^{o}\quad 30\text{ata}]{H_2SO_4} C_6H_5\text{-}N(CH_3)_2 + {}_2H_2O$$

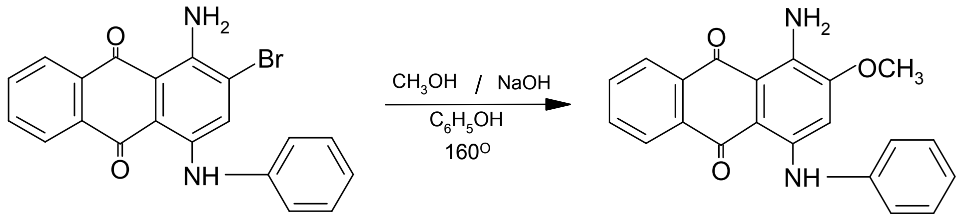
$$C_6H_5\text{-}NH_2 + HO\text{-}C_2H_5 \xrightarrow[190^{o}\quad 20\text{ata}]{HCl} \underset{62\%}{C_6H_5\text{-}NH\text{-}C_2H_5} +_2 \underset{38\%}{C_6H_5\text{-}N(C_2H_5)_2}$$



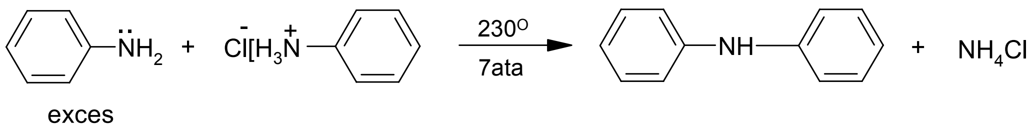


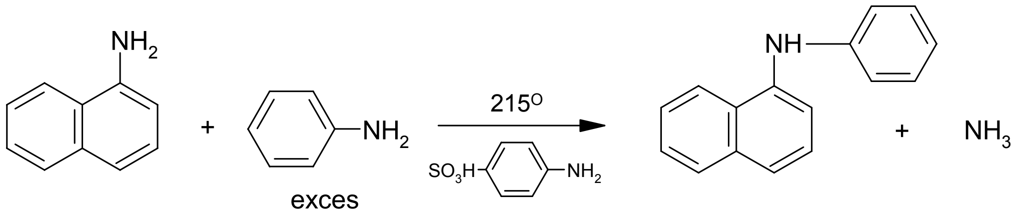


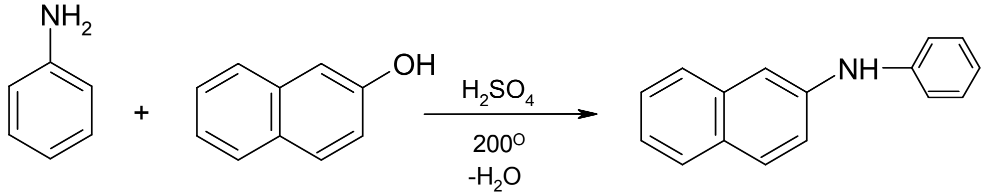




Unlike alkylation processes, *arylation processes* result in unitary products, respectively secondary aromatic amines. Aryl amines, in particular aniline, toluidine, anisidines and phenols (resorcinol, 2-naphthol), are used as arylating agents. Arylation processes with the help of aromatic amines are catalyzed by mineral or organic acids hydrochloric acid, sulfuric acid, benzene-sulfonic acid, toluene-sulfonic acid, etc. Some of these reactions are presented below:







By *acylation* is meant the replacement of the hydrogen atom of the amine group by an acyl residue which may be organic or inorganic. The acylation process pursues two main purposes, namely:

- on the one hand, by acylation, amides are obtained which allow the protection of the amino group in oxidative processes, such as nitrations, halogenations or oxidations. After the completion of the respective step, the amides are hydrolyzed, restoring the primary amine group.

- and on the other hand, amides or sulfon-amides are intermediates or finished products in the organic synthesis industry.

By transforming the amine group, a greater stability of the products is ensured at the oxidative phenomena that can intervene in the processing and use of the respective products.

Acylating agents. A wide range of reactants is used in the acylation processes, among which we can mention:

1) organic acids: formic acid, acetic acid, oxalic acid, 2-hydroxy-3-naphthoic acid

2) anhydrides of organic or inorganic acids: acetic anhydride, less frequently benzoic or phthalic anhydride, sulfur trioxide, carbon sulphide

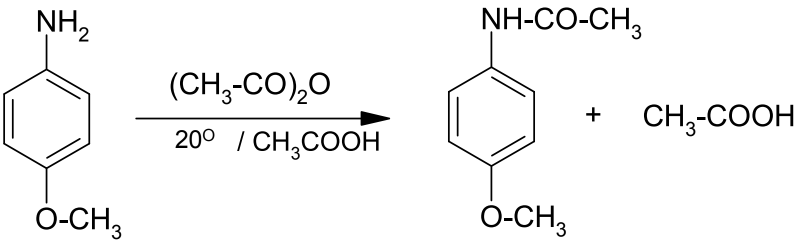
3) acid chlorides: acetyl chloride, benzoyl chloride, isophthalic and phthalic acid chlorides, phosgene (Cl_2CO), cyanuryl chloride (trichloro-triazine), benzene-sulfo-chloride, toluene-sulfo-chloride

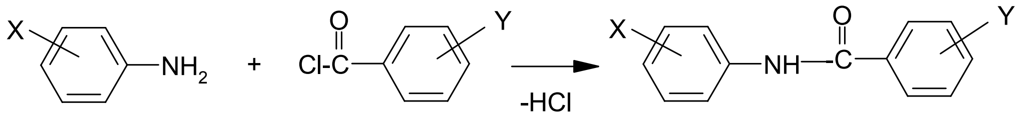
4) esters: ethyl ester of acetyl-acetic acid

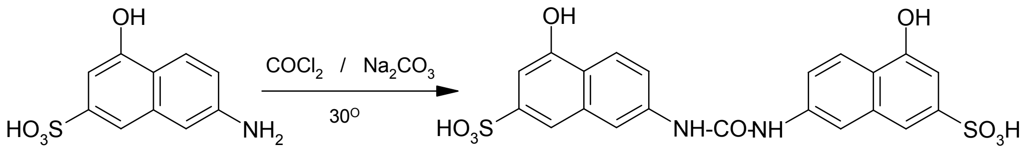
5) ketene ($CH_2 = C = O$), dicetene.

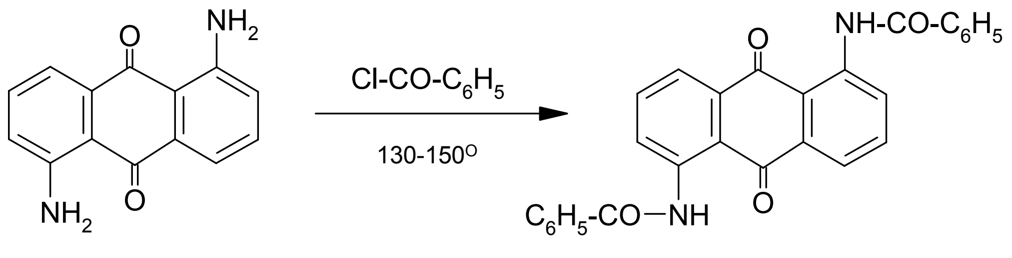
Examples:

$$C_6H_5\text{-}NH_2 + R\text{-}COOH \rightleftharpoons C_6H_5\text{-}NH\text{-}CO\text{-}R + H_2O$$



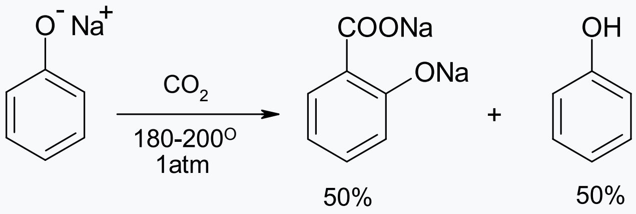


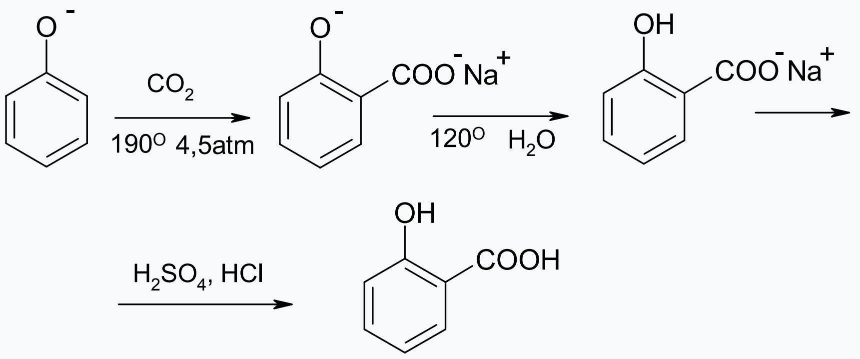


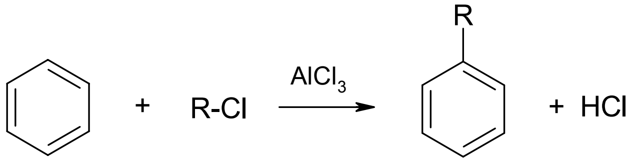


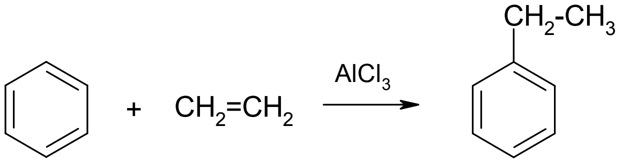
1.2.9. Condensation

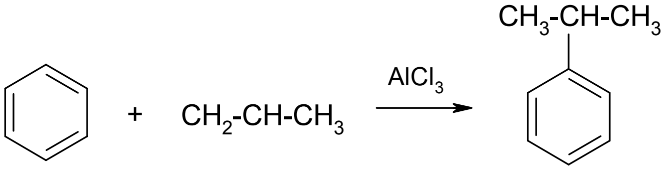
The notion of condensation includes the reactions of the formation of new C-C bonds, although there is a tendency to extend the notion to the formation of C-N or C-O bonds, which would cause some confusion. In the organic synthesis industry there are numerous condensation processes in which new C-C bonds are formed. For the fine organic industry, the carboxylation processes of alkaline phenoxides and the Friedel-Crafts processes are of major importance. Some examples of the condensation reactions are presented in the following:

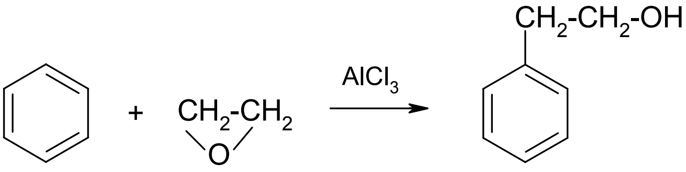


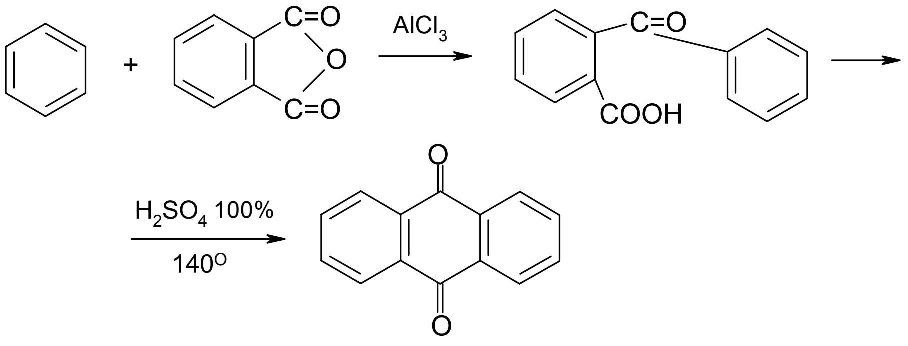












1.2.10. Oxydation

In the organic synthesis industry a wide range of intermediates obtained by the oxidation processes of various compounds are used. The variety of raw materials, respectively of oxidizing agents does not allow the evaluation of a general equation in which to fit most of the oxidative processes.

The classification of the oxidation processes of the aromatic compounds takes into account the technological conditions in which the various oxidative processes are perfected, respectively the nature of the oxidizing agents or the presence or not of the catalysts. Oxidation processes are classified into:

1) Liquid phase oxidation processes:
a) Oxidation processes with the help of chemical agents
b) Oxidation processes with the help of air in the presence of catalysts
2) Oxidation processes in the gas phase:
a) Oxidation processes with the help of air in the absence of catalysts
b) Oxidation processes with the help of air in the presence of catalysts

Regarding the nature of oxidizing agents, they can be classified into:

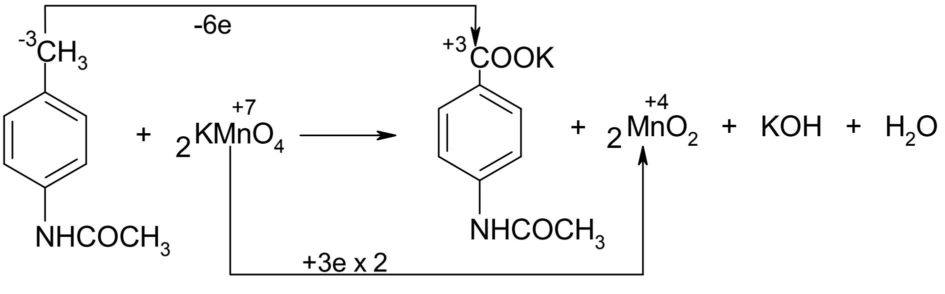
1) Chemical oxidizing agents: $KMnO_4$, $Na_2Cr_2O_7$, $K_2Cr_2O_7$, $NaClO_4$, HNO_3, NaClO, H_2SO_4, MnO_2, H_2O_2

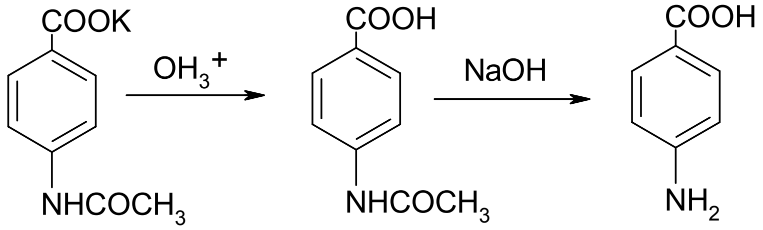
2) Oxygen from the air.

Of the chemical agents, potassium permanganate is one of the most important. It can participate in oxidation processes in alkaline, neutral or acidic environments.

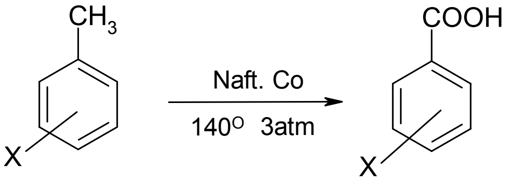
$$KMnO_4 + H_2O \longrightarrow MnO_2 + KOH + O$$

Based on this process, *p*-amino-benzoic acid is obtained. The starting material is introduced into an aqueous solution in the presence of potassium permanganate at the boiling point of that solution. The equations of the reactions that take place are the following:





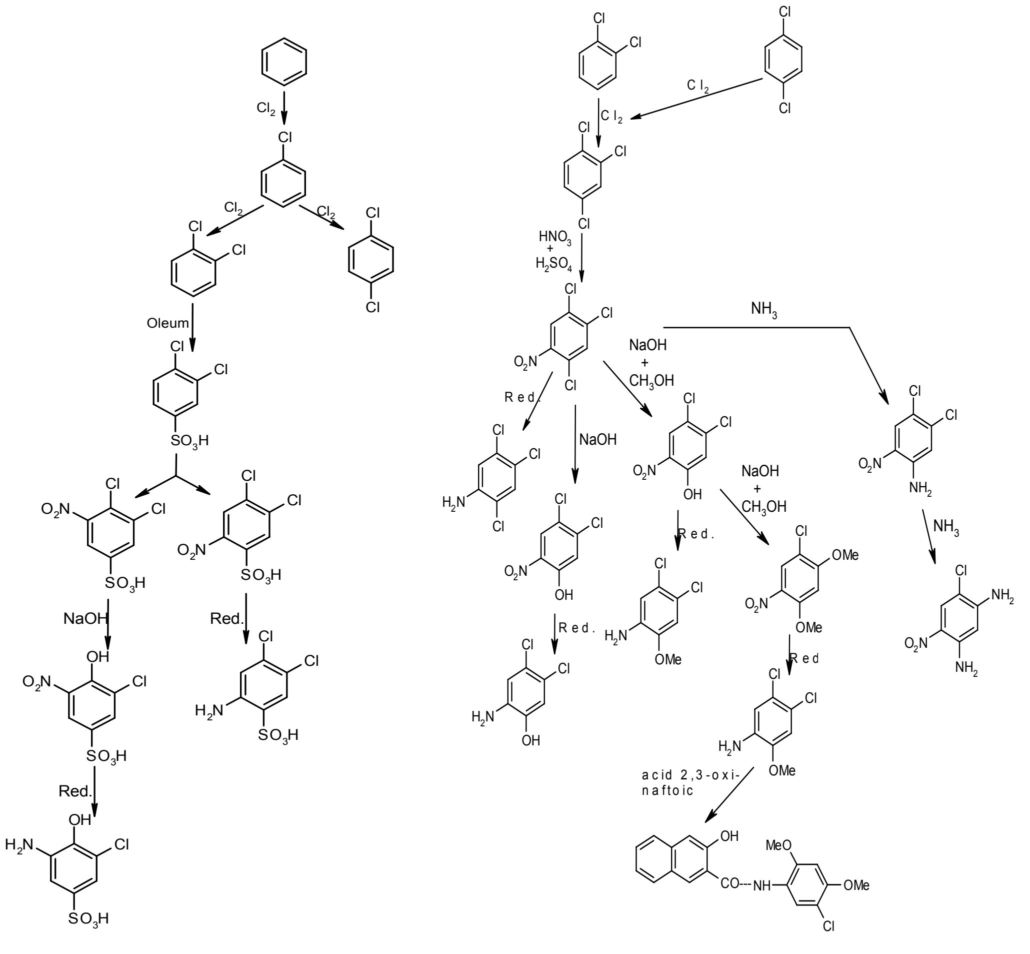
Oxidation processes in the presence of air take place at high temperatures (140 - 250°C) at pressures of 3-4 atm or even 40atm, in the presence of catalysts. Some of the reactions that can take place based on this procedure are presented below:



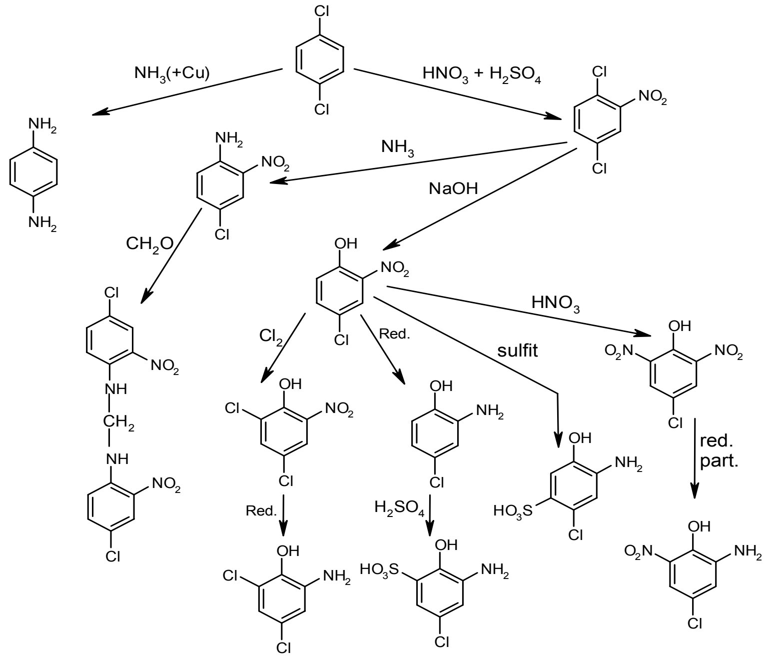
1.3. Synthesis schemes for various aromatic intermediates

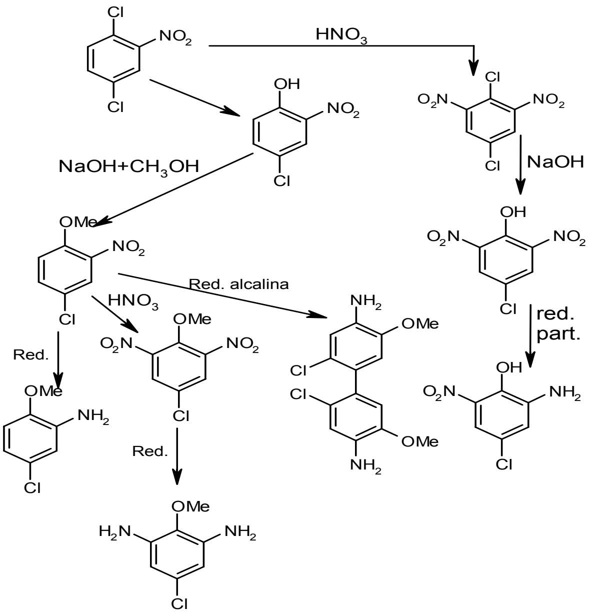
Using the information presented in the main organic synthesis processes, a number of aromatic intermediates may be obtained. Obtaining methods of some of the most important intermediates for the organic dyes synthesis are presented in the following schemes.

Synthesis schemes for *o*- and *p*-dichlor-benzenes (1)

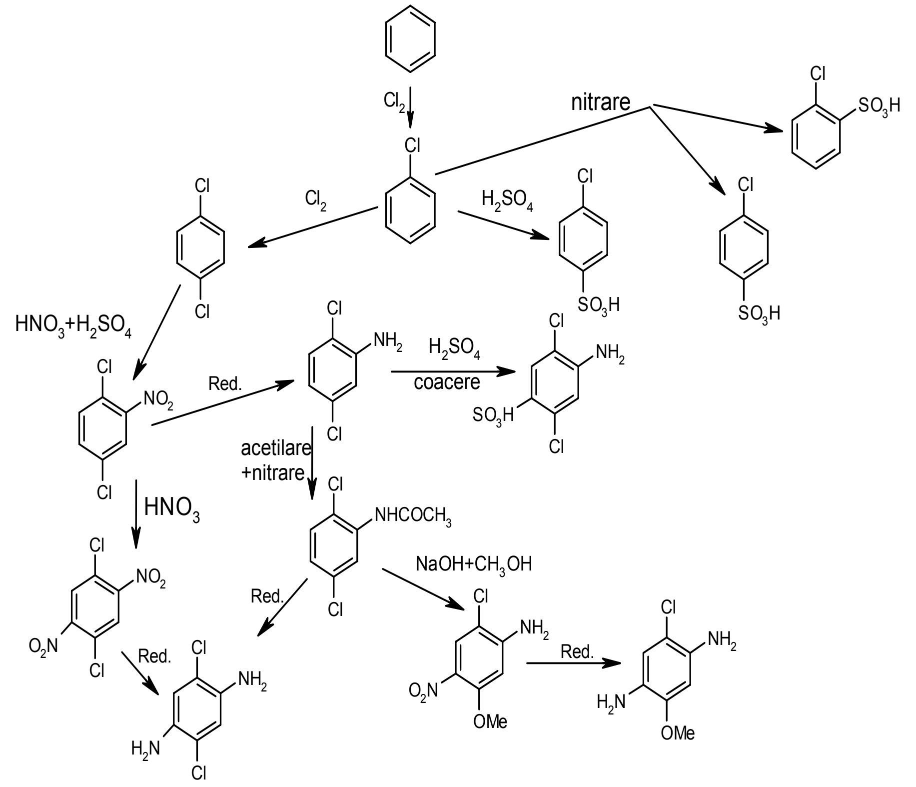


Synthesis schemes for *o*- and *p*-dichlor-benzenes (2)

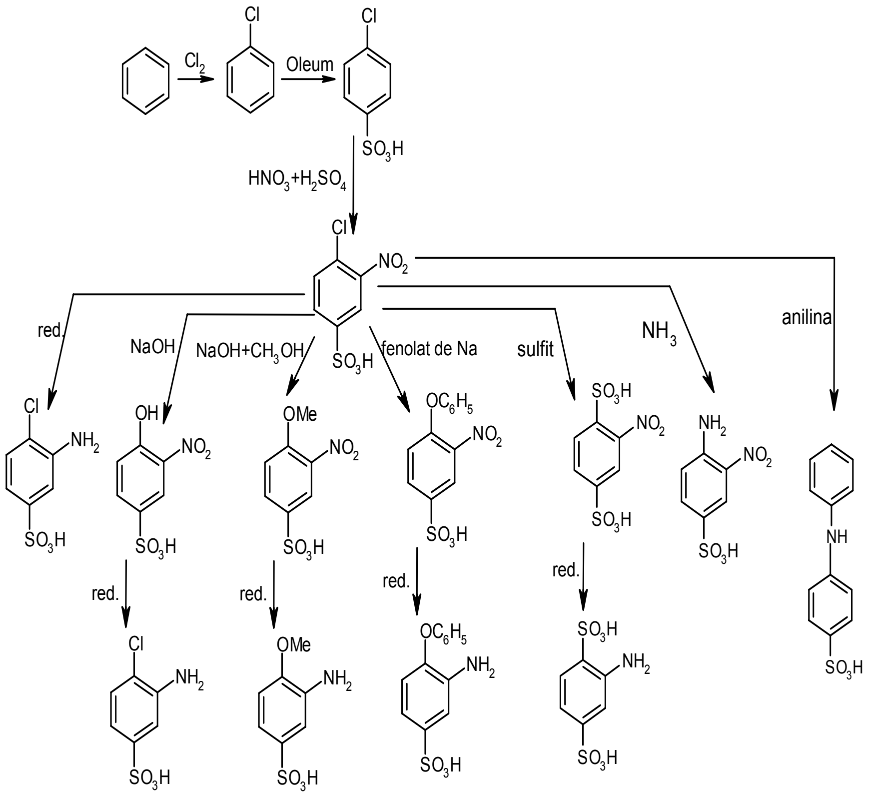




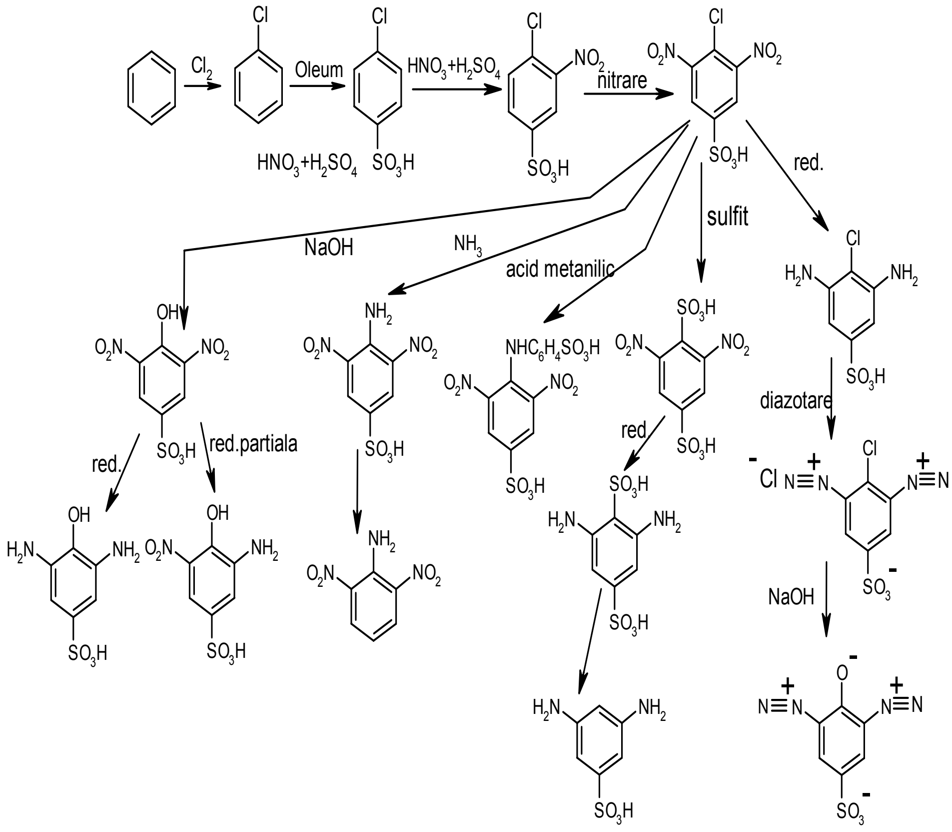
Synthesis schemes for *o*- and *p*-dichlor-benzenes (3)



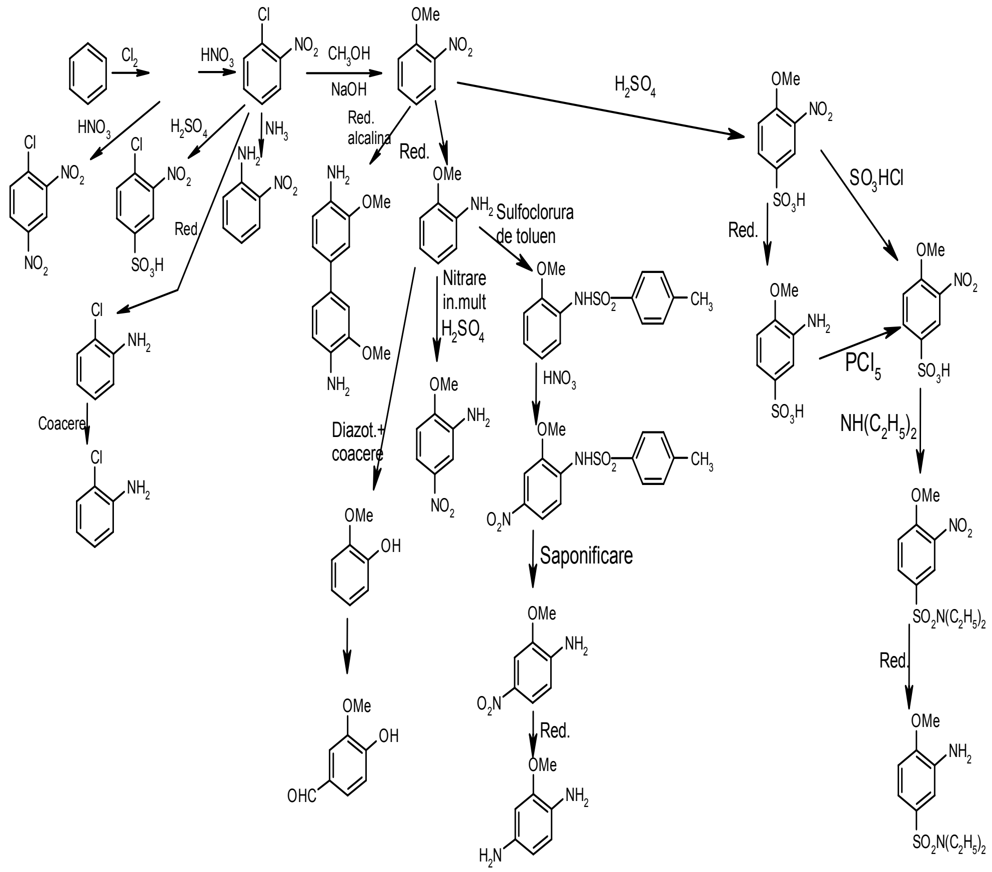
Synthesis schemes for hydrochlene-*p*-sulphonic acid derivatives (1)



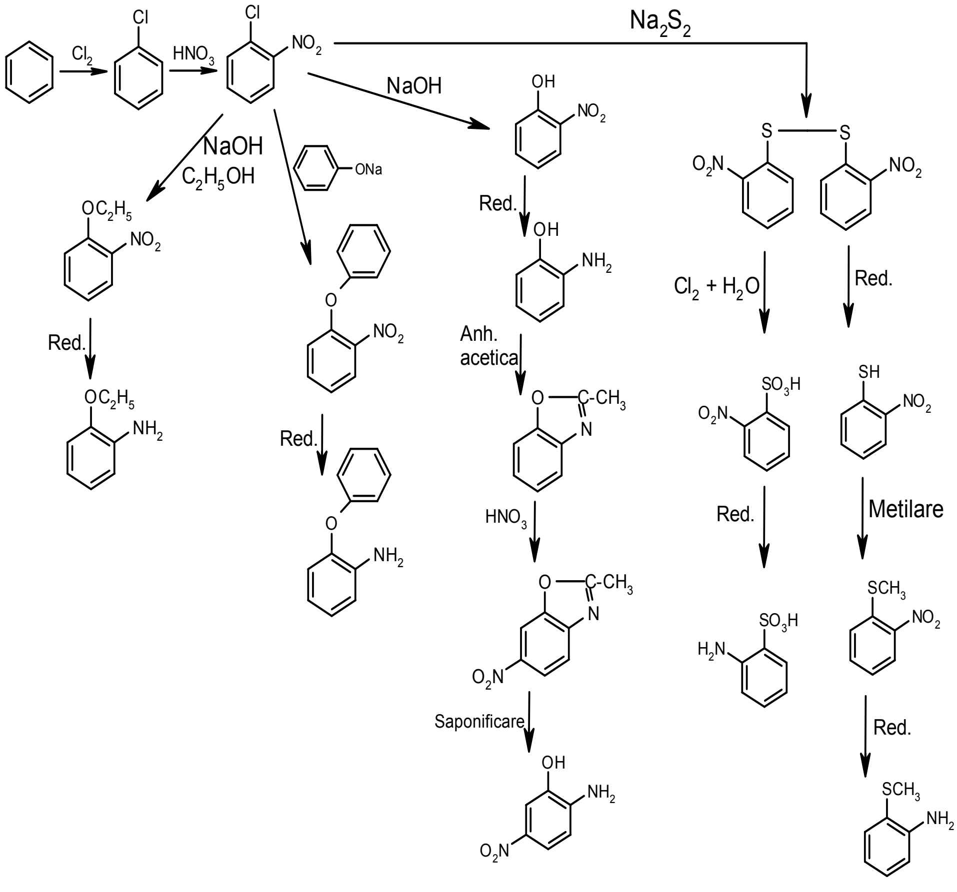
Synthesis schemes for hydrochlene-*p*-sulphonic acid derivatives (2)



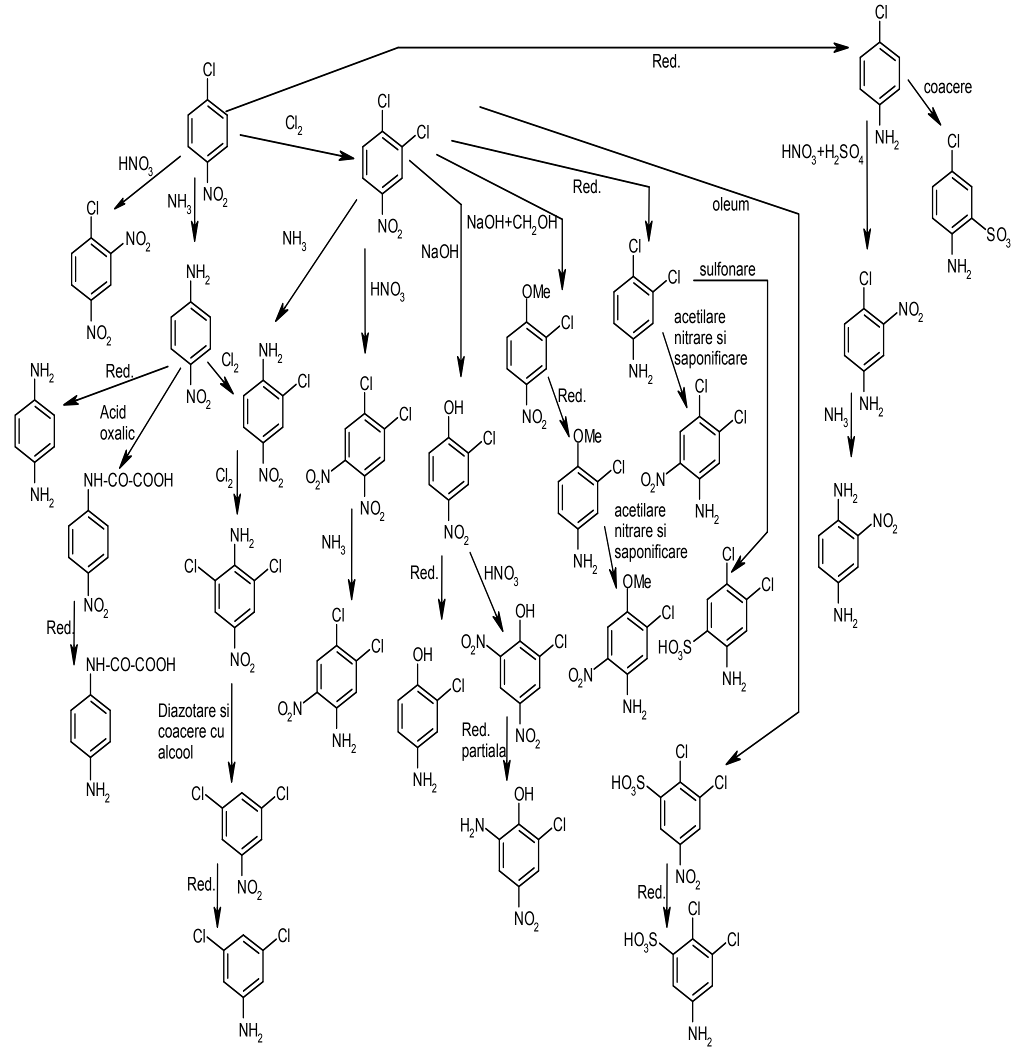
Synthesis schemes for *o*-nitro chlorine-benzene derivatives (1)



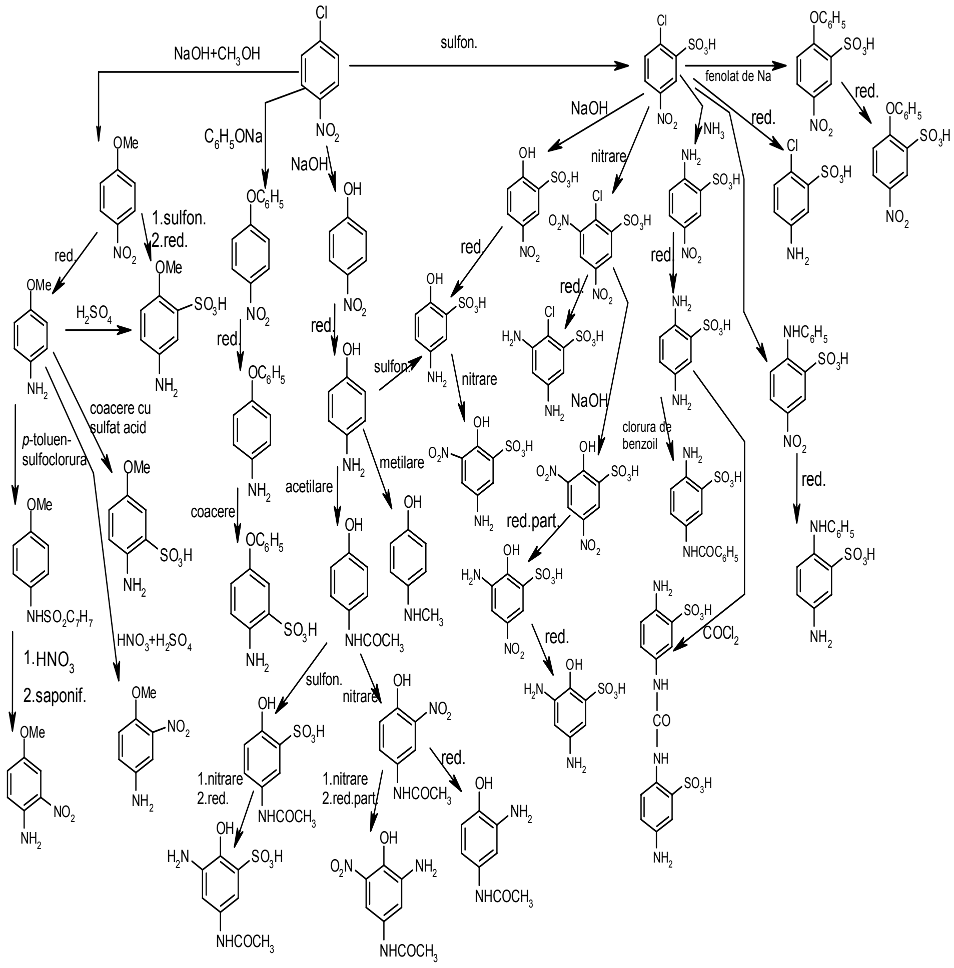
Synthesis schemes for *o*-nitro chlorine-benzene derivatives (2)



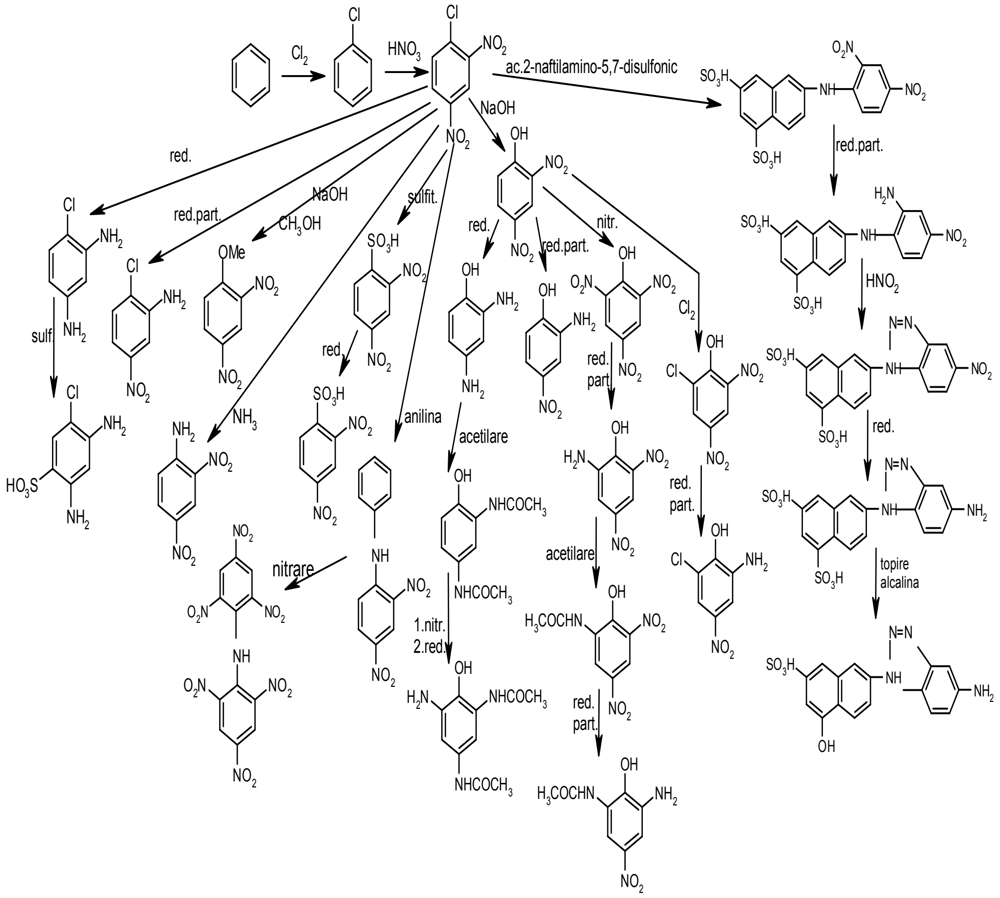
Synthesis schemes for *p*-nitro chlorine-benzene derivatives (1)



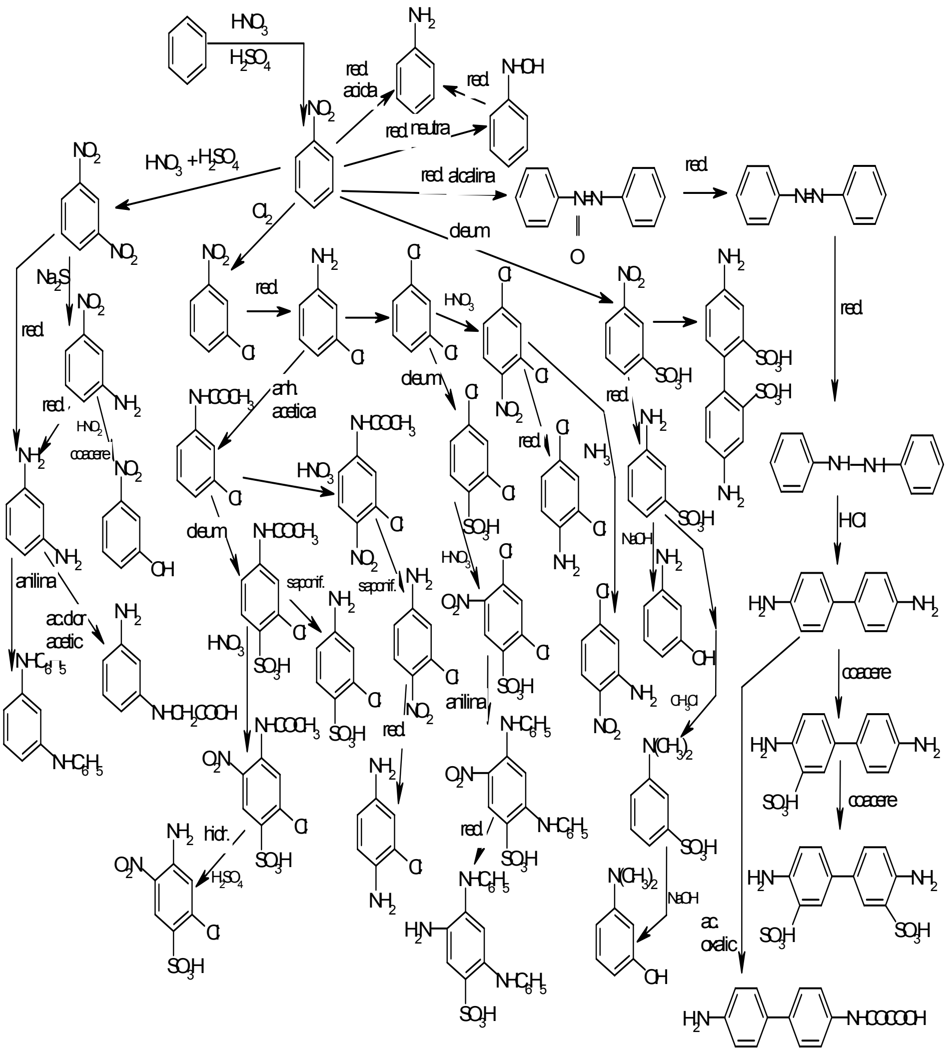
Synthesis schemes for *p*-nitro chlorine-benzene derivatives (2)



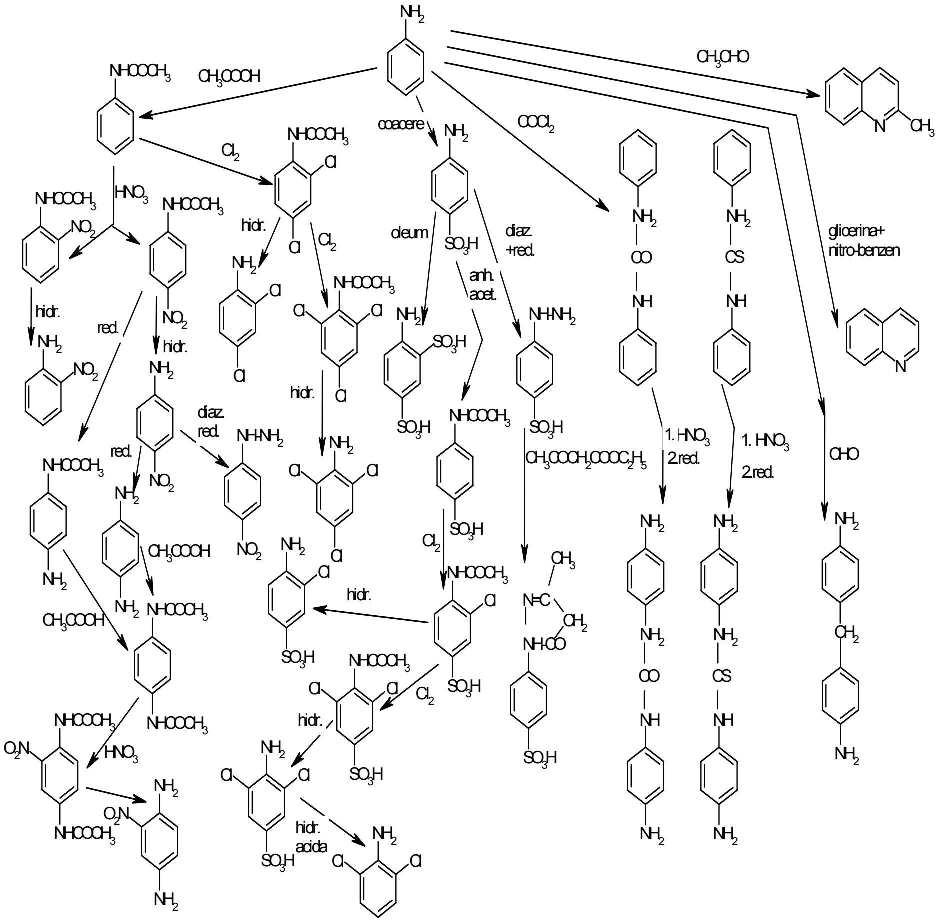
Synthesis schemes for 2,4-dinitro chlorine-benzene derivatives



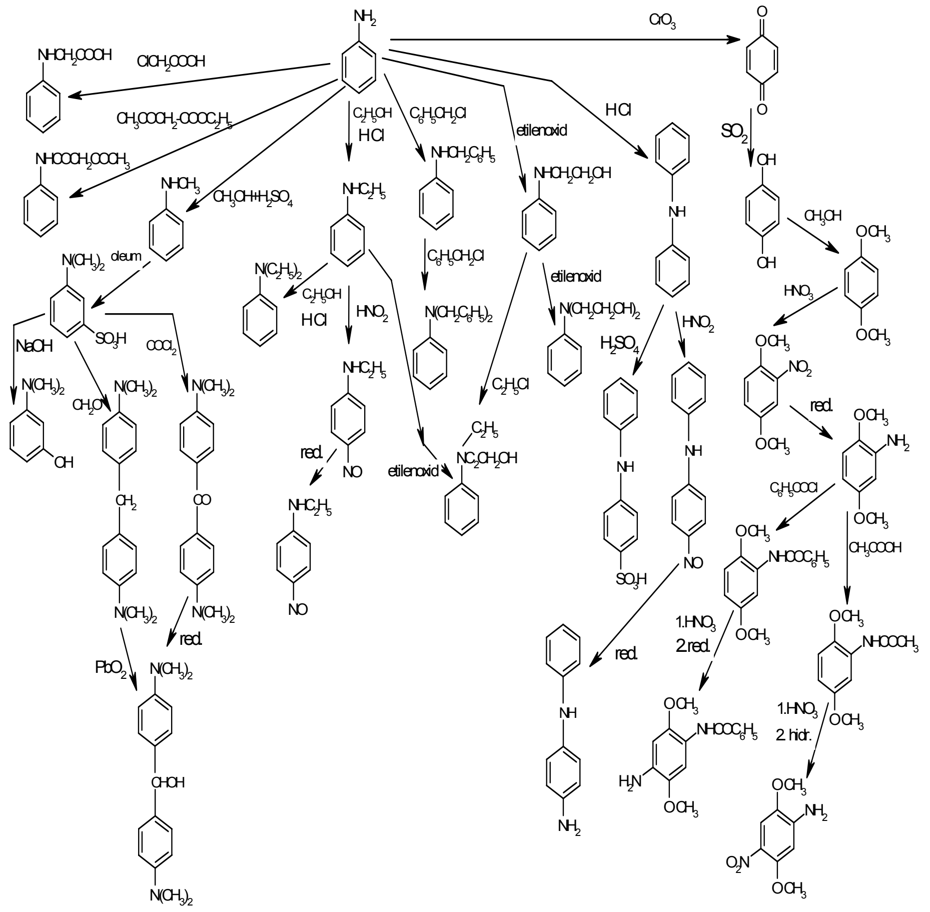
Synthesis schemes for nitro-benzene derivatives



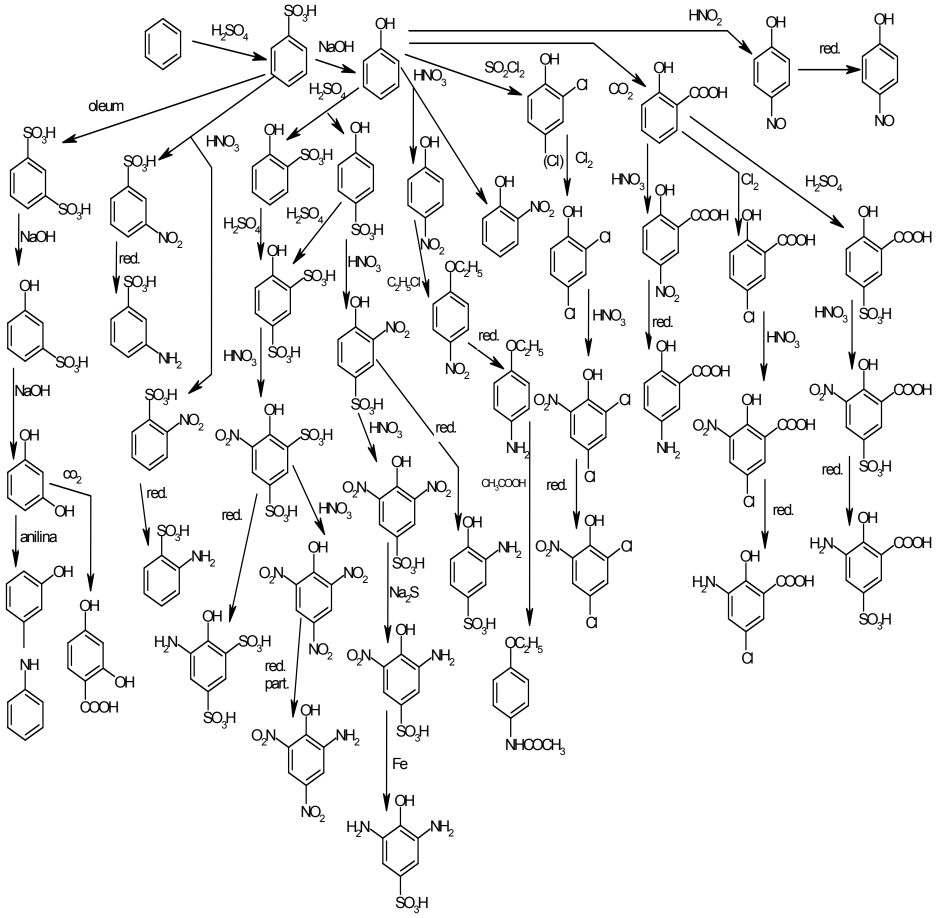
Synthesis schemes for aniline derivatives (1)



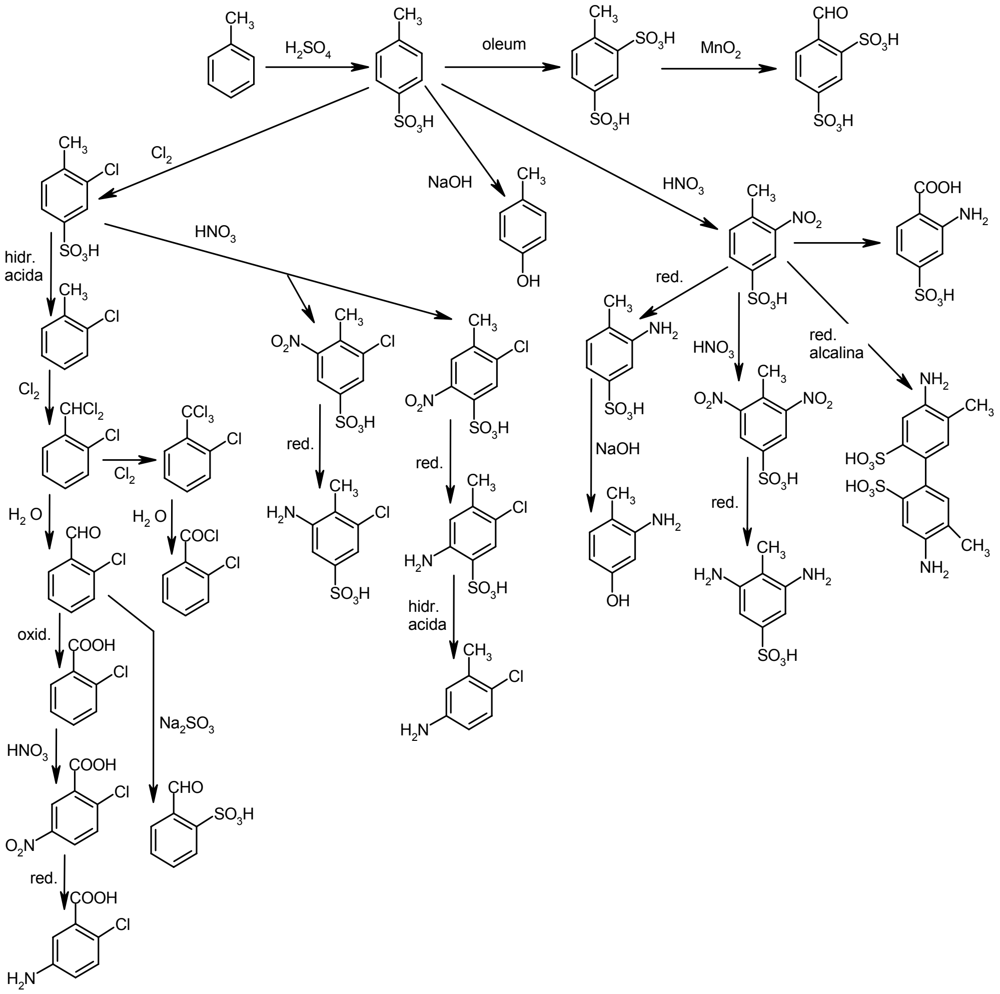
Synthesis schemes for aniline derivatives (2)



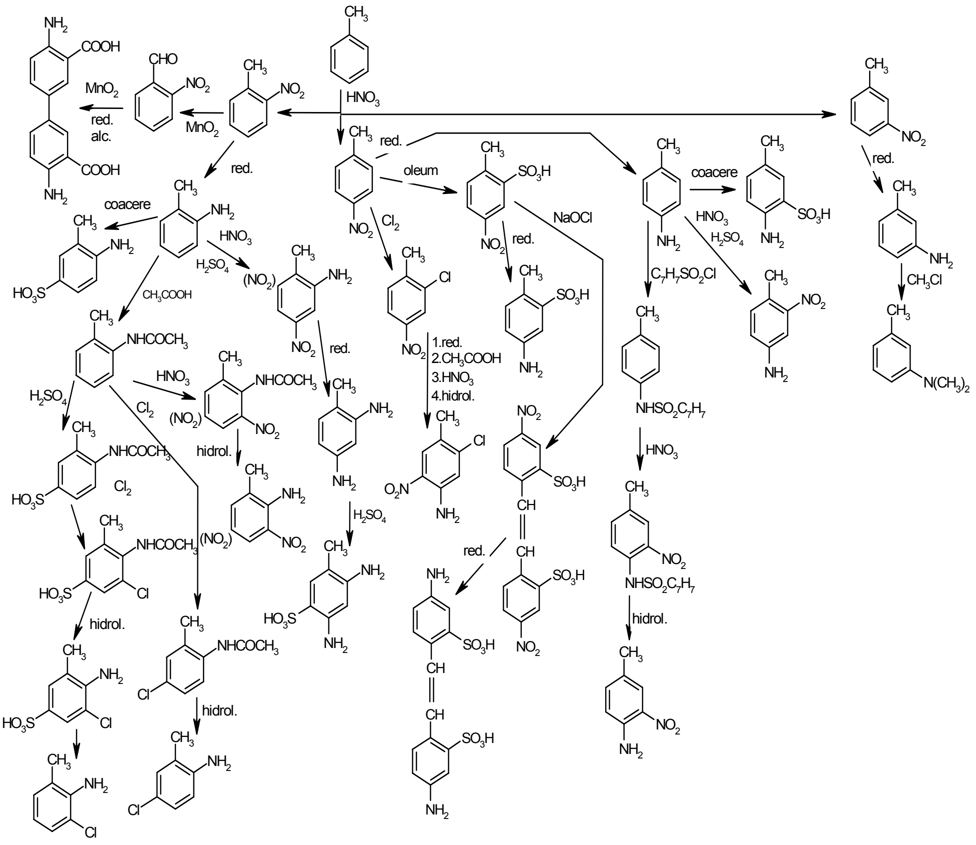
Synthesis schemes for benzensulphonic acid and phenol derivatives



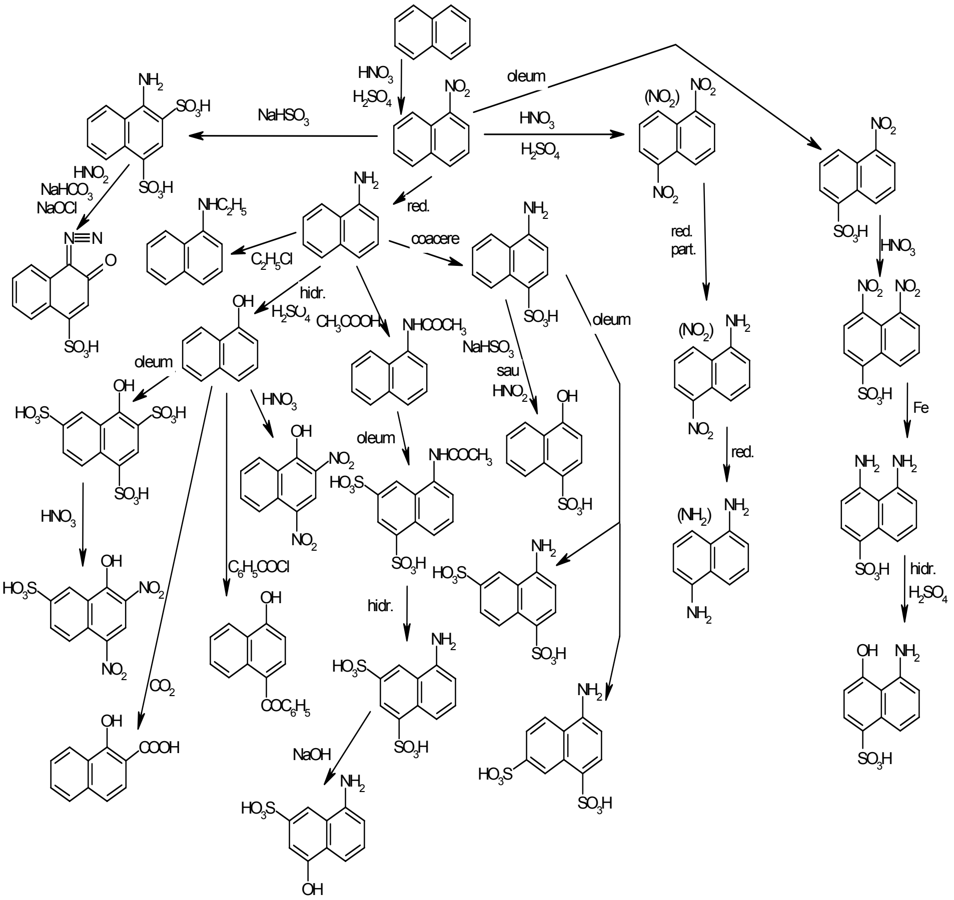
Synthesis schemes for toluen derivatives (1)



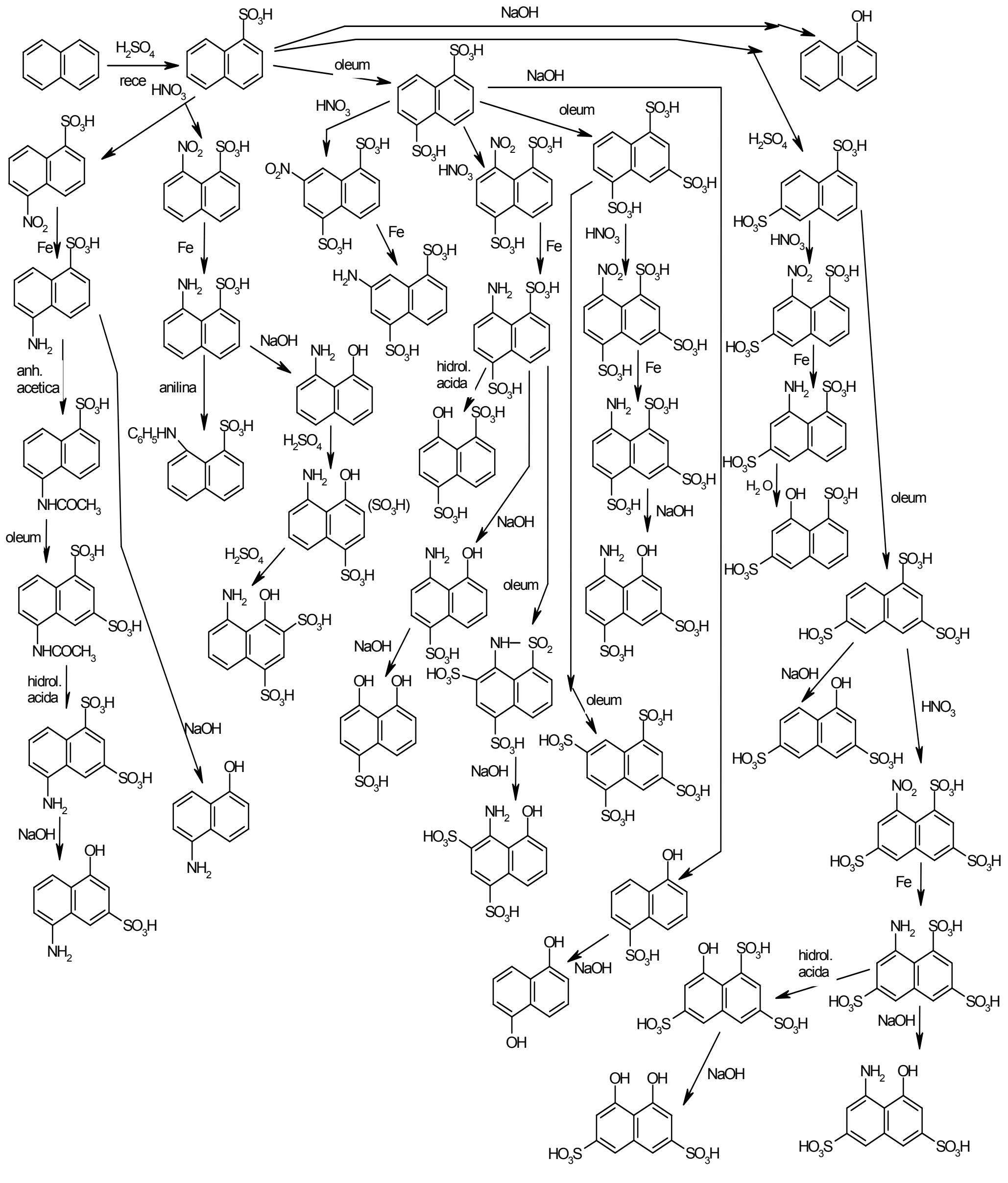
Synthesis schemes for toluen derivatives (2)



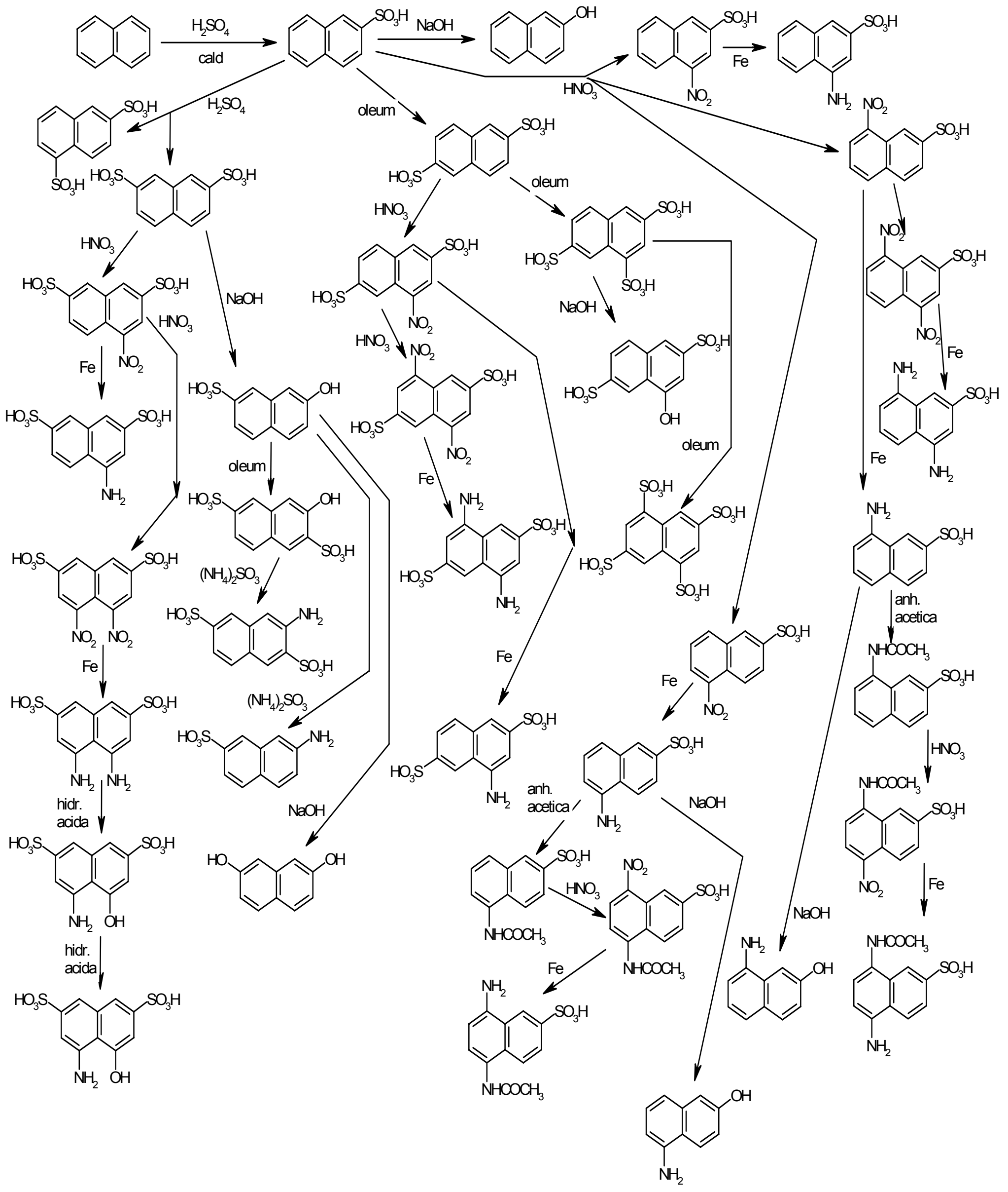
Synthesis schemes for α-nitro-naftaline derivatives



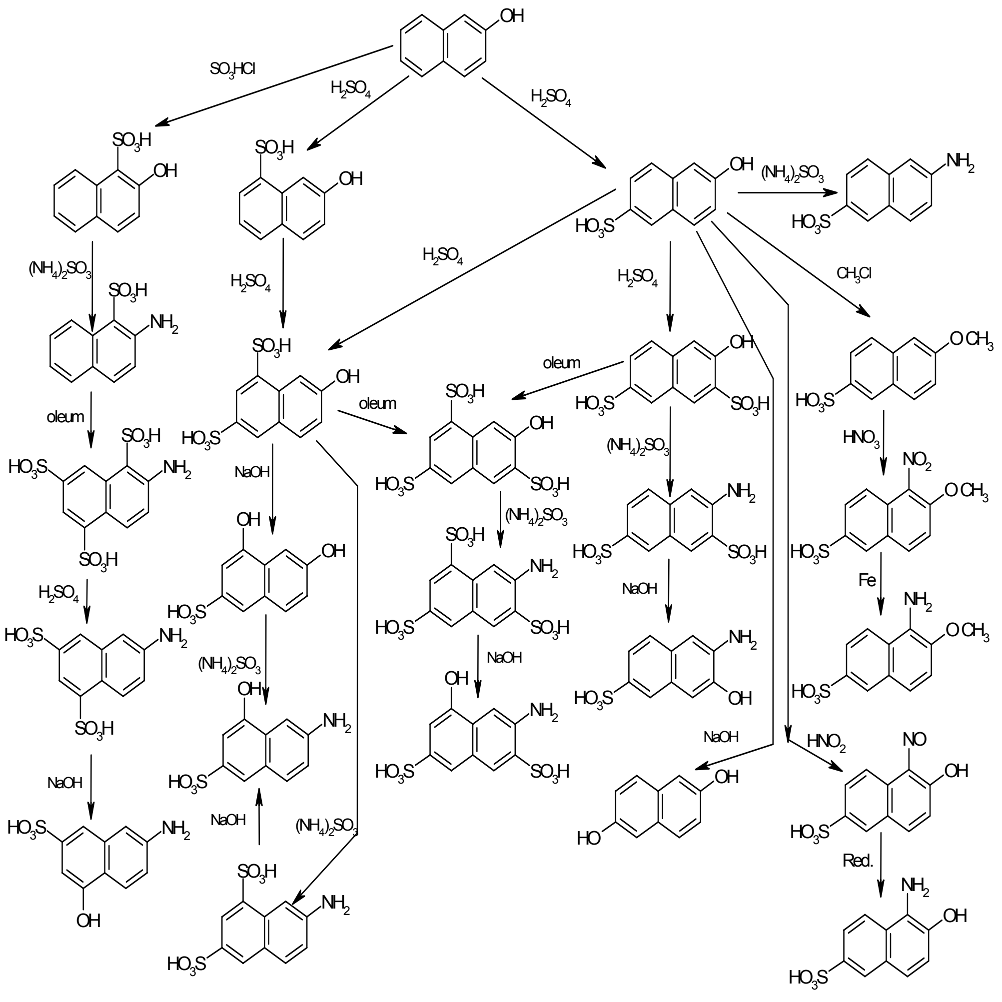
Synthesis schemes for α- and β-naftalin-sulphonic acid derivatives (1)



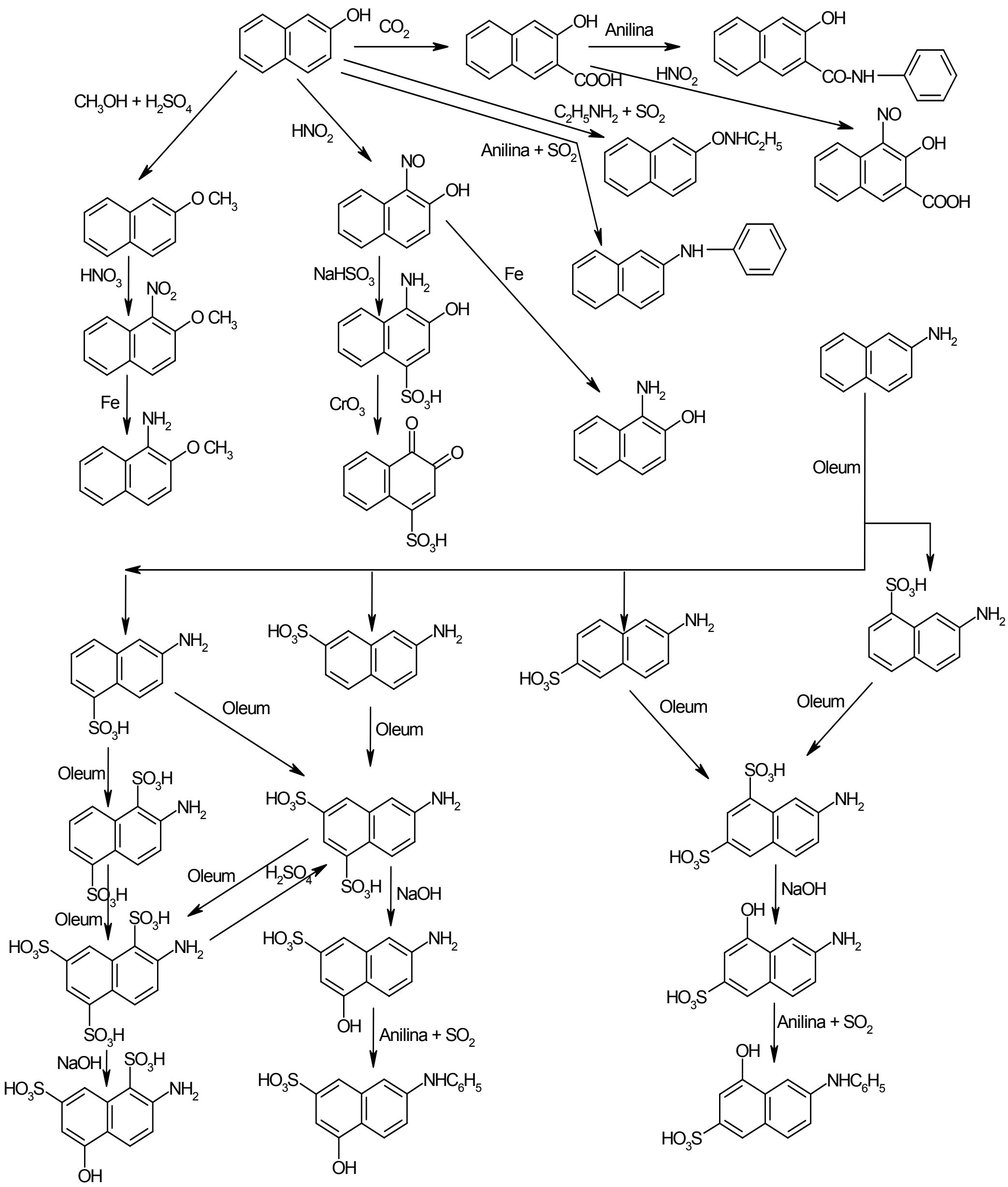
Synthesis schemes for α- and β-naftalin-sulphonic acid derivatives (2)



Synthesis schemes for β-naftol derivatives (1)



Synthesis schemes for β-naftol derivatives (2)



1.4. Notes on the relationship between the structure and the color of organic compounds

The notion of color is based on physical, chemical, physiological and psychological processes. The visible range, for the human eye, of the electromagnetic spectrum is between 380 nm and 780 nm. Light may or may not be completely absorbed or may only be partially absorbed by solid, liquid or gaseous bodies.

These bodies can reflect light that is not absorbed. The human eye perceives light that is emitted by a light source or is reflected by bodies. Thus, light with wavelengths between 380 nm and 780 nm initiates photochemical reactions, as do other series of interdependent reactions. Through a transfer of information between the eyes and the brain, the phenomenon of color perception occurs.

If the electromagnetic radiation, whose distribution of energy in the visible range corresponds to the sunlight on earth, reaches a solid body that reflects all the light diffusely, that body appears to the human eye as white. If the body absorbs all the radiation, it will appear black. If it absorbs evenly over the range of 380 nm to 780 nm, it will appear gray.

The colors white, black and gray are called achromatic colors, being uniformly absorbed throughout the visible range of the spectrum. Instead, bodies that have chrome colors have one or more bands, i.e. one or more maxima and minima in the spectrum. If an absorption band is between 400-430 nm, that part of the light will be absorbed and the rest reflected, the body appearing to the eye to be yellow.

The eye cannot distinguish, due to physiological imperfections, between these types of light absorption. For a qualitative and quantitative study of colored substances it becomes necessary to know the absorption spectra, which allow to ascertain the effective mechanism of color appearance.

Two or more dyes with different absorption spectra are mixed they give a less bright color than in the case of one dye of the desired shade. The mixture is called a *subtractive mixture* (the removal of the unwanted components). If the light emitted by several sources forms white light, the color combination represents an *additive mixture*.

For the perception of color by the human eye the position of the absorption maximum in relation to the wavelength and shape of the band (narrow band = pure nuance) are important:

For the industrial application of a dye the position of the absorption band in the spectrum and the absorption intensity in relation to the concentration reprezent important aspects. The dependence is given by the Lambert-Beer law:

$$\log\frac{I_0}{I} = E = \varepsilon \cdot d \cdot c \qquad (1.4.1.)$$

where: I_0 – incident intensity; I – emergent intensity; ε - molar absorbtion coefficient, l/mol·cm; d - the length of the path taken by the absorbent species, cm; c - concentration, mol/l

For industrial dyes, the value of the absorption coefficient, ε, has values between 104 and a little more than 105 (l / mol · cm). Dyes with ε greater than 105 are efficient and economical (such as triarylmethane dyes), compared to anthraquinone dyes that have low absorbtion coefficients (8000 - 18 000), being therefore more expensive, not only because of the intermediates from which they are obtained.

Changes in the position and intensity of the absorption band are shown in the figure 1.1.

Thus, by moving the absorption maximum to longer wavelengths, a bathochrome, color-closing effect is obtained, and moving to smaller wavelengths leads to a hypsochrome, color-opening effect. The location of the absorption intensity at higher values, so at higher values of the absorption coefficient determines a hyperchromic effect, and towards lower values of this coefficient, a hypsochromic effect.

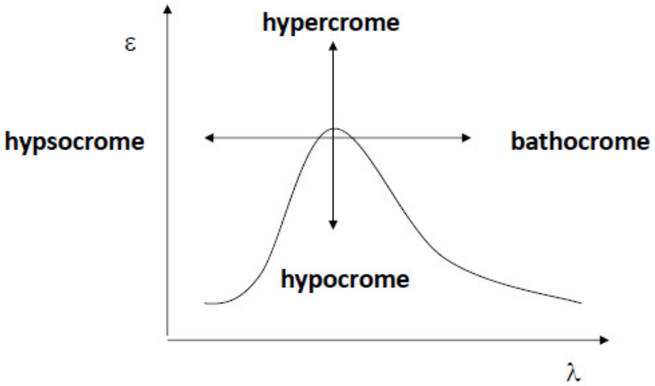


Fig. 1.1. Changes in the position and intensity of the absorption band

1.4.1. Mutual influence of auxocrome and anti-achocrome groups

The relationship between the structure and color of organic compounds is based on the study of the mutual interferences of atoms and the bonds between organic molecules. Colored substances are unsaturated combinations (by suppressing unsaturation the color disappears), the presence of unsaturated groups (C = C; C = O; N = N; N = O), called chromophore groups, generates color.

Grafting on the chromogenic system of specific groups, called auxochrome groups, causes the color to close, intensify, and the compound becomes a dye, and absorbs light in the visible range of the spectrum. The most important auxochrome groups are: NH_2 and OH and their derivatives: OH <OCH_3 <O- <NH_2 <$N(CH_3)_2$ <$NH(C_6H_5)$. The presence in the system of some groups that allow the participation of free electrons in the conjugation of the whole polyene system (NO_2, CN, CO, NO, N = N, etc.), called anti-auxochrome groups, determines the increase of the bathochrome effect: CN <SO_3R <COOH < $COOCH_3$ <CHO <NO_2. A decisive role in increasing the bathochrome effect is played by the nature and number of auxochrome and anti-auxochrome groups.

1.4.2. Factors that influence color

- The symmetry of the molecule determines the uniform distribution of energy on the whole molecule - hypsochrome effect.
- Transformation into salt determines the higher mobility of electrons - bathochrome effect.

- By blocking the electrons of the amine group, the conjugation can no longer take place - hypsochrome effect.

- The influence of solvents on the tautomeric equilibria or on the change of the association degree of the molecules in the dye, or by its polarity and the polarization capacity of the dye molecule – solvatochromia.

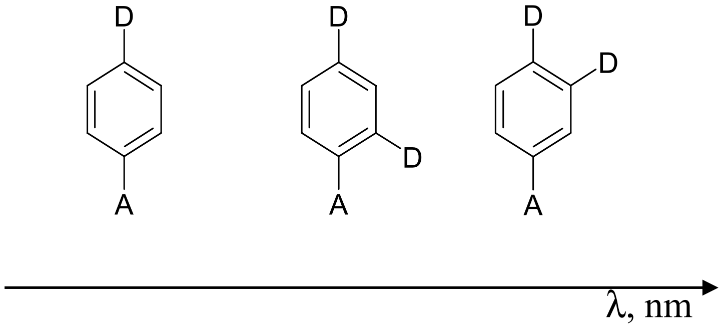
- Position of the substituents in the molecule, if coplanarity is prevented - hypsochrome effect.

1.4.3. The influence of the position of substitutes on the spectrum of organic compounds

For disubstituted benzene derivatives and quinone dyes of technological importance in the anthraquinone and quinacridonic series, qualitative rules based on the chemical classification of substituents may be applied.

Thus, the spectra of the three isomers of nitrophenol, cyanophenol and nitro-N-dimethylaniline (*o, m, p*), i.e. benzene derivatives with a donor group (D) and an acceptor group (A) cannot be interpreted simply, only on the basis of mesomeric structures, because *ortho*- and *meta*-compounds absorb light in a similar way throughout wavelengths greater than 220 nm, while *para*-isomers are displaced hypsochrome.

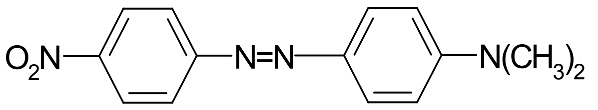
By introducing a new donor group, the absorption strips move batochrome, depending on the position of the new substituent, as in the example presented below:



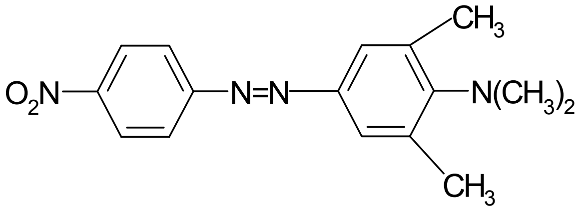
By preventing the coplanarity of the molecule, due to the steric effects of the substituents, the conjugation is interrupted, the effect on the spectrum being hypsochrome.

Thus, the -$N(CH_3)_2$ group is coplanar with the benzene nucleus on which it is grafted. However, if an -CH_3 group is introduced in the *ortho*- position with respect to the amine group, the coplanarity is disturbed due to the fact that the -CH_3 group is voluminous. As a result, the absorption would be shifted to shorter wavelengths (hypsochrome effect).

An example could be the absorption in methanol of *p*-nitro-*p*'-(N,N)-dimethylamino-azo-benzene, which has a maximum wavelength of 474 nm. If in the *o*'- positions with respect to the amine group there is a methyl group, the λmax will be at 423 nm.



λmax = 474 nm

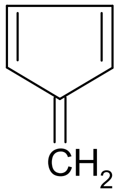


λmax = 423 nm

1.4.4. Characterization of chromophores

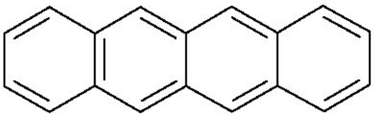
Saturated aliphatic groups absorb only in the range of small wavelengths (~ 125nm) in UV, these substances being thus transparent. They are used as solvents for colored substances in order to determine their absorption spectra.

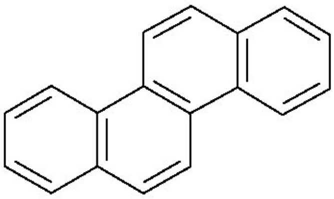
The ethylene group causes a shift of the absorption to longer wavelengths (~ 180nm). If the number of ethylene groups increases, there is no significant shift to longer wavelengths, only the absorbtion coefficient becomes higher; thus, in the presence of two groups, the absorbtion coefficient doubles from 10,000 to 20,000. Conversely, if there is conjugation between the ethylene groups, the effect is significantly bathochromic. Thus, butadiene absorbs at 217nm, and the accumulation of conjugated double bonds causes an even more intense bathochrome effect. Each additional conjugate double bond causes a displacement of 30-50nm, so that, in the present case of 4 conjugate bonds, the visible range of the spectrum is reached. If the conjugated double bonds are in a cycle, the bathochrome effect increases. If the double bonds are crossed, as in the case of the fulven, the visual field of the spectrum is reached, this being yellow (it is the simplest colored hydrocarbon):



Compounds derived from fulven, by substitutions to the CH_2 group, are orange and even red. Hydrocarbons with larger cycles have darker colors, so cyclo-octa-tetraene is yellow and azulenes are blue.

Benzene group and polynuclear aromatic hydrocarbons have characteristic absorbers, which differ from those of aliphatic compounds. In the case of benzene, the absorption maximum is in the region of 250-270nm, similar to the linear triene, but it is composed of several maxima. However, the absorption coefficient is much lower (210 for the highest maximum at 250nm). This occurs due to cyclization, which makes the molecule perfectly symmetrical, the π electrons being evenly distributed over the entire molecule; the excitation energy in this case being higher. In polynuclear aromatic hydrocarbons, such as naphthalene, phenanthrene, anthracene, two main bands of benzene appear, shifted to longer wavelengths. This occurs due to condensation, which promotes the mobility of π electrons that contribute to conjugation. Linear condensation of aromatic hydrocarbons causes a bathochromic effect on angular conjugation. Thus, naphthaene is yellow, absorbing in the visible region, while chrysanthemum is colorless:

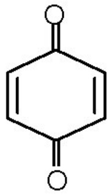

naftacen


crysene

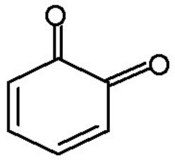
Biphenyl and polyphenyls absorb at shorter wavelengths. Thus, biphenyl has λmax at 215nm. This is because the existence of a chain between aromatic nuclei does not favor the mobility of π electrons between the two nuclei. The absorption coefficient is higher than the existence of a single aromatic nucleus, being about 18,600, which can be interpreted as the whole molecule behaves like a single chromophore, different from that of the benzene molecule.

The quinone group is very important for light absorption in the visible region of the spectrum, due to the presence of double cross-links. Thus, *p*-quinone is yellow and *o*-quinone is red:

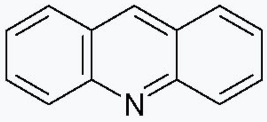
p-quinona



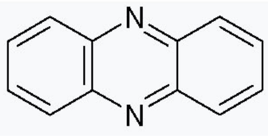
o-quinona



Similar to quinone systems, which are color generators, can be considered the following:

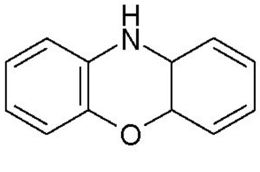


acridines

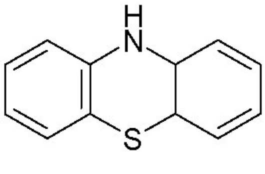


phenazines

phenoxazines



phentiazines



The *carbonyl* group appears in the structure of colored compounds. Acetone has a maximum absorption at 279nm with ε of 14. Alkyl groups cause a weak bathochrome effect, however, by cyclization, the band moves to the visible. Aldehydes and ketones have similar spectra. By conjugation, two carbonyl groups lose their individuality, behaving like two conjugated double bonds, the absorption maximum being shifted to the visible region of the spectrum. By increasing the number of carbonyl groups, a strong bathochrome effect is produced. Thus, tri-keto-pentane is orange-red.

The *nitroso* group is one of the most powerful chromophores when bound to a carbon atom. The aliphatic nitroso-derivatives are blue, and the aromatic ones, due to the conjugation with the benzene nucleus, are green, due to the shift towards red of the absorption band. In the case of nitroso-benzene, the two bands of chromophores appear distinctly: the benzene nucleus and the nitroso group.

The *azo* group is a very important chromophore, from which a whole range of organic dyes develops. In the case of aliphatic compounds, such as azo-methane, the maximum absorption of the azo group is at 330nm with a ε_{max} of 10, and at azo-benzene λmax it is at 450nm with an ε_{max} of 650. In addition to these maxima, the maxima appears in the first case at 230nm and at 330nm, and in the second at 228nm with ε_{max} of 2400 - of the phenyl groups conjugated with the azo group.

The existence of two different chromophores, separated from each other, for example by a group $-CH_2-$, determines the appearance of two maxima in the spectrum of the respective compound, corresponding to the two groups. However, if the two groups are conjugated, they keep their individuality, but they influence each other, determining the displacement of the respective maxima at longer wavelengths - the effect being bathochrome:

$CH_3\text{-}CO\text{-}CH{=}C(CH_3)_2$

$\lambda_{max} = 327nm$; $\varepsilon_{max} = 40$
(acetona = 237nm)
$\lambda_{max} = 239nm$; $\varepsilon_{max} = 12600$
(olefine = 185nm)

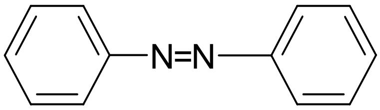
1.5. Classification of dyes

Dyes are characterized by the property of absorbing visible light (360-760nm), thus appearing colored. Given the multitude of synthesized dyes, it seemed necessary to classify them. In a first way they can be divided into inorganic and organic dyes, each of these groups being able to be subdivided into natural and synthetic compounds. There are dyes of natural origin that are currently produced synthetically.

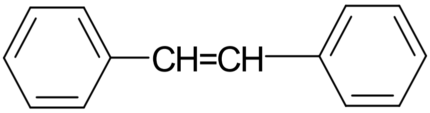
An important division is made into dyes and pigments. Although there is not much difference in the name, the pigments being considered a species of dyes, they are characterized by the fact that they are not soluble in the environment in which they are applied on the substrate, additional compounds being used for their application (such as a polymer). On the other hand, the dyes are soluble or partially soluble in the medium from which they are applied to the substrate, having some affinity for it.

Organic dyes can be also divided into several types:

- *Type of polyene combinations* - conjugated polyene chains with even number of atoms, which have auxochrome and antiauxochrome groups grafted. Examples: azo-benzene and stilbene:



azo-benzene



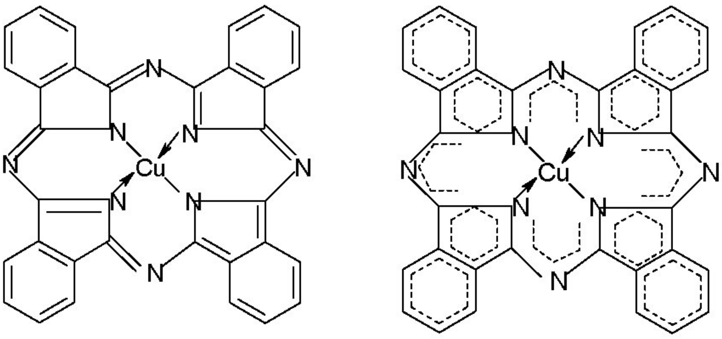
stilbene

- *Type of aromatic and phthalocyanine combinations*:

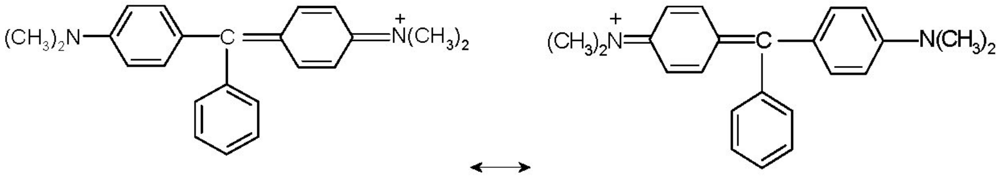
- aromatic combinations derived from:

benzene - (250-270nm): λmax = 235nm, ε_{max} = 10
naphthalene - 275 nm;
anthracene - 330nm;
naphthacene - 460nm (yellow);
pentacen - 580nm (indigo-blue)

- phthalocyanine combinations - tetra-benzo-porphyrin compounds, having the basic structure:



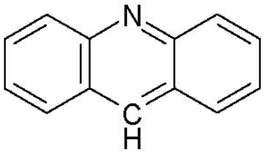
- merichinoid combinations - polyene compounds with odd number of atoms on which auxochrome and antiauxochrome groups are grafted. The electrons are evenly distributed, and the state of the molecule is intermediate between the benzoid and the quinoid:



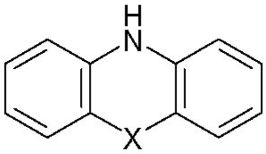
Green colour compound

Among this category the following may be mentioned:

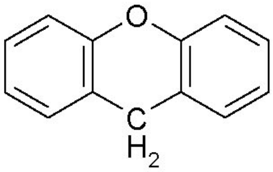
acridines



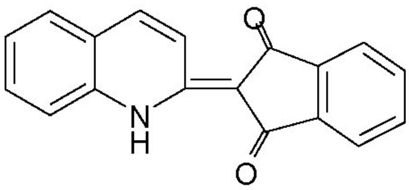
azines



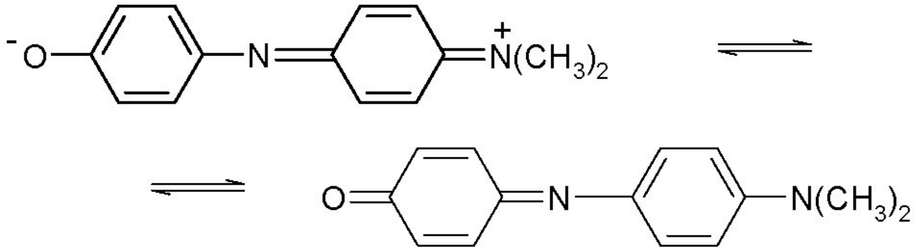
xantenes



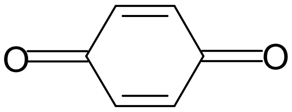
quinolines



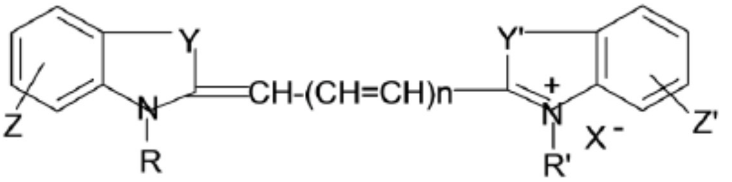
dyes such as indo-phenols and ind-amines



- quinone combinations, such as benzoquinone:



- polymethetic combinations



X - rest acid

Y, Y' - CH=CH - chinolina S - benz-tiazol Se - benz-selenazol O - benz-oxazol $C(CH_3)_2$ - 3,3'-dimetil-indol-enina

R,R' - Alc, Ar,Ar-Alc

n - 0, 1, 2, 3, 4

Z,Z' - diversi substituenti

Depending on the type of electronic excitation at light absorption, the dyes can be absorbent, fluorescent or energy transfer; light energy can be dissipated respectively by: internal conversion, fluorescence or by the interpenetration of intersystems.

By field of application: on textiles and similar substrates, and functional dyes - for lasers, liquid crystals, solar energy conversion, for the photographic industry, in reproduction technology, in biochemistry, analytical chemistry, medicine, food industry, etc.

Depending on the color, the dyes can be yellow, orange, red, purple, blue, green, brown and black.

In COLOR INDEX - (CI) - Catalog of dyes indexing - they are divided into dyes: acid, mordant, basic, dispersion, natural dyes and pigments, for food, for skin, direct dyes, sulfur, bath, printing reagents, diazonium azo components, azo coupling components, azo compositions, oxidation bases, optical bleaches, intermediates, developing and reducing agents.

Identification name: for example for indantrone:

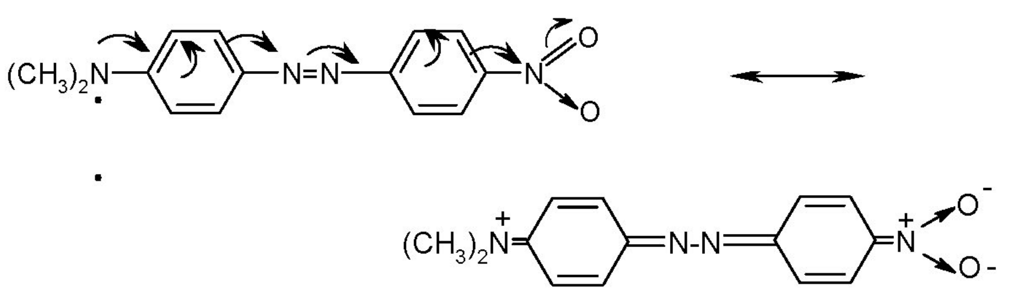
CI Blue bathtub 4 = generic name

CI 69 800 = name of constitution

Trade names (35): Indanthren Blue RS, Cibanone Blue RSN, Caledon Blue XRN, Nikonthren Blue RSN - depending on the manufacturer.

CHAPTER 2. AZO DYES

Azo dyes are conjugated polyene systems, with even number of carbon atoms, generally with even number of atoms, at the edges of which are the auxochrome and antiauxochrome groups, achieving a mutual influence, which results in light absorption in the visible region of spectrum.



Characteristic bands in the spectrum: 450 nm - azo chromophore N = N conjugated with benzene nuclei; 325 nm - benzene nuclei conjugated with the azo chromophore; 228 nm absorption of N atoms.

There are three basic processes for obtaining azo dyes, namely:

1. Diazotization of primary aromatic amines, followed by coupling with a suitable coupler
2. Condensation of aromatic nitro-derivatives with aromatic amines
3. Oxidation of primary aromatic amines

2.1. Diazotization of primary aromatic amines, followed by coupling with an appropriate couplant

2.1.1. Diazotization

The diazotization reaction consists in the transformation of the amine group into a diazo group, according to the general equation:

$$\text{Ar-NH}_2 + \text{HNO}_2 + \text{HX} \longrightarrow \text{Ar-}\overset{+}{\text{N}}\equiv\text{N]X}^- + {}_2\text{H}_2\text{O}$$

Due to the instability of nitric acid, sodium nitrite is actually used in the reaction:

$$Ar\text{-}NH_2 + NaNO_2 + {}_2HCl \longrightarrow Ar\text{-}\overset{+}{N}\equiv N]Cl^- + NaCl + {}_2H_2O$$

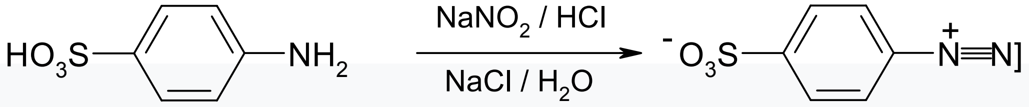
Which involves the action of nitric acid generated *in situ* from sodium nitrite and hydrochloric acid. There is a need to use two moles of HCl, one for the generation of nitric acid and the other for the formation of diazonium salt in the form of chloride.

Aromatic amines form slightly water-soluble salts with hydrochloric acid, which is why an aqueous HCl medium is used in diazotization for the solubilization of amines, although some diazotization is also performed on crystallized amines, which are insoluble in aqueous medium.

$$Ar\text{-}NH_2 + HX \rightleftharpoons Ar\text{-}\overset{+}{N}H_3]\ X^-$$

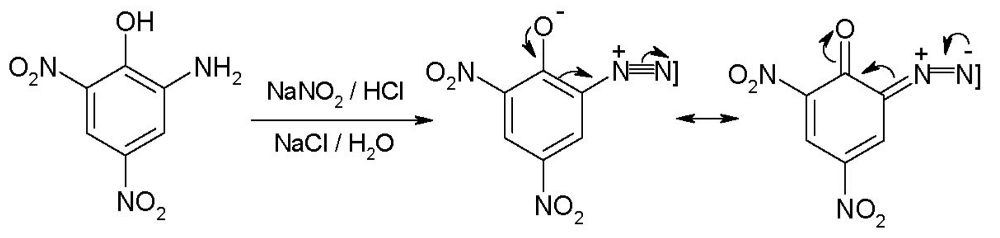
The diazotization reaction can also be performed in sulfuric acid medium, especially for amines with low basicity.

When diazotizing free amino-sulfonic or amino-carboxylic acids, only one mole of HCl is needed for one mole of aromatic amine, because the sulfonic and carboxylic groups allow the formation of an internal salt by intramolecular compensation. E.g:



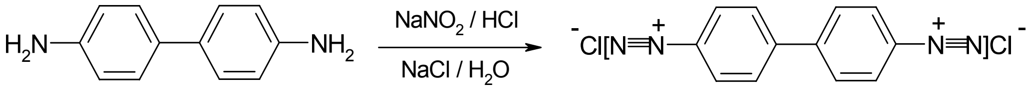
The product as such is insoluble in water, but the presence of several sulfonic groups ensures the solubilization of the disoderivatives.

By diazotization amino-phenols and amino-naphthols, diazo oxides with intramolecular ionic compensation are obtained, which confer stability to the diazoderivatives, as may be seen from the reaction presented below:



picraminic acid diazo-oxide quinone-diazo-derivative

Diazotization of diamines occurs in a single amino group, if they are in *ortho* or *para* positions relative to each other (hence mono-diazotization). The basicity of the non-nitrogenous amine is too small to be nitrogenized under normal conditions (the basicity of an amine is a measure of the tendency of the non-participating electron pair of the nitrogen atom to fix a proton). However, if desired, diazotization reactions in concentrated sulfuric acid, nitrosyl-sulfuric acid medium may be used, or diamines may be pre-converted to sulfamic acids, followed by diazotization under normal conditions. Instead, *meta*-diamines can be diazotized to both groups, forming *meta-bis*-diazo derivatives. Benzidine can be diazotized simultaneously in both amino groups.



Mono-diazotization can also be performed if working in acetic acid medium, using the required stoichiometric amount of sodium nitrite.

2.1.2. Mechanism of the diazotization reaction

The process is an N-nitrosation of the primary aromatic amines, followed by a prototropic transposition into diazo hydrate, which in the acidic environment now removes a molecule of water:

$$\text{Ar-NH}_2 \xrightarrow[\text{lent}]{\text{X-NO}} \text{Ar-NH-NO} \xrightarrow[\text{rapid}]{\text{transp.}} \text{Ar-N=N-OH} \xrightarrow[\substack{-H_2O \\ \text{rapid}}]{H^+} \text{Ar-}\overset{+}{N}\equiv N]A^-$$

Although aromatic amines protonate in acidic medium, the active species in the diazotization process is the free amine. The diazotization reaction is an electrophilic substitution …in the first step, an N-nitrosation of the electrophilic agent on the amine group.

Active species are formed as a result of pre-equilibria:

$$HNO_2 + H^+ \longrightarrow \overset{+}{H_2NO_2} \quad \text{nitrosacid ion}$$

$$_2HNO_2 \rightleftharpoons ON\text{-}\overset{+}{H_2O} + NO_2^- \rightleftharpoons N_2O_3 + H_2O$$

$$N_2O_3 \rightleftharpoons NO^+ + NO_2^-$$

$$\overset{+}{H_2NO_2} \longrightarrow NO^+ + H_2O \quad \text{nitrosyl ion}$$

Active species to be considered, in descending order of reactivity:

$$NO^+ > \overset{+}{H_2NO_2} > ON\text{-}Br > ON\text{-}Cl > ON\text{-}ON_2 > HNO_2$$

2.1.3. Factors that influence the diazotization process

1- *Solvent*: diazotization is performed in aqueous medium, but sometimes in organic solvent medium, which ensures a better solubilization. Diazotization in alcoholic environment or in the presence of acetic acid allows to obtain purer diazoderivatives. The low basicity of some amines recommends the use of a mixture of acetic acid and sulfuric acid as a solvent.

2- *Amount of nitrite*: it is possible to work with a necessary stoichiometric amount of nitrite (or with a small excess of 1-5% to complete the reaction), in the form of an aqueous solution of 20-40%. The addition speed is of particular importance for obtaining the desired yield and the purity required for the product. Excess nitrite can negatively influence the next coupling step, by nitrosating some components (in phenols, secondary or tertiary amines) or by partial diazotization of the primary amines. For this reason, excess nitric acid is removed by adding urea or sulfamic acid:

$$_2HNO_2 + NH_2\text{-}CO\text{-}NH_2 \longrightarrow CO_2\uparrow + {}_2N_2\uparrow + {}_3H_2O$$

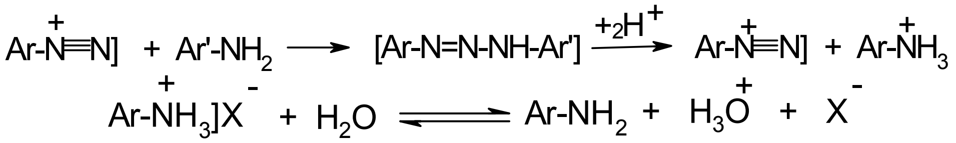
$$HNO_2 + H_2N\text{-}SO_3H \longrightarrow H_2SO_4 + N_2\uparrow + H_2O$$

3- *Amine concentration*: it is usually n / 2, but can vary between 2n and n / 5. Under these conditions the reaction time is 10 minutes, but at high dilutions and less basic amines, it can be extended to one hour or more.

4- *Temperature*: with the increase of the temperature, the reaction rate increases, both of the main reaction and of the secondary reactions, of decomposition of diazonium salts. Therefore, the reactions are conducted at temperatures between 0-10ºC. In the case of amines with lower solubility, the temperature can be raised to 30-60ºC. For the most important amines, the optimal working temperature was established experimentally.

5- *Nature of the substituents*: the primary aromatic amine acts through the non-participating electron pair of the nitrogen atom as a nucleophilic agent. Any change in the density of electrons to nitrogen influences the reaction rate, *ie*, the electron donor substituents (CH_3, OCH_3, etc.) increase the speed, and the electron attractants (NO_2, SO_3H, COOH, etc.) decrease the speed. These effects are more pronounced when the substituents are in positions conjugated to the amino group. If the substituents decrease the basicity of the amine - undesirable effect - the reaction rate also decreases.

6- *Mineral acid*: ensures the solubilization of the amine, reacts with sodium nitrite, releasing nitric acid, allows the formation of diazonium salt, prevents the formation of diazonium salts with non-nitrogenous amines:



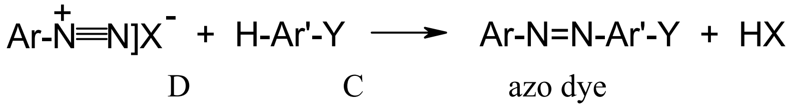
$$Ar\text{-}\overset{+}{N}\equiv N] + Ar'\text{-}NH_2 \longrightarrow [Ar\text{-}N{=}N\text{-}NH\text{-}Ar'] \xrightarrow{+2H^+} Ar\text{-}\overset{+}{N}\equiv N] + Ar\text{-}\overset{+}{N}H_3$$

$$Ar\text{-}\overset{+}{N}H_3]\overset{-}{X} + H_2O \rightleftharpoons Ar\text{-}NH_2 + H_3\overset{+}{O} + \overset{-}{X}$$

The pH produces two opposite effects: on the one hand, increasing the acidity decreases the concentration of free amine needed for diazotization, so the reaction rate decreases, on the other hand, increasing the acidity, more and more strongly active agents (nitrosation) are formed, which increases the reaction rate. Therefore, depending on the basicity of the amine, we work as follows: less basic amine - in concentrated acids (pH <1); more basic amine - in dilute acids (pH = 1-3).

2.1.4. Azo-coupling raction

It is the reaction between a diazotated component -D- (diazonium salts of primary aromatic amines) and a suitable coupling component -C- (phenols, naphthols, aromatic amines, aliphatic ketone combinations with active methylene, heterocyclic compounds, etc.), with formation of azo dyes:



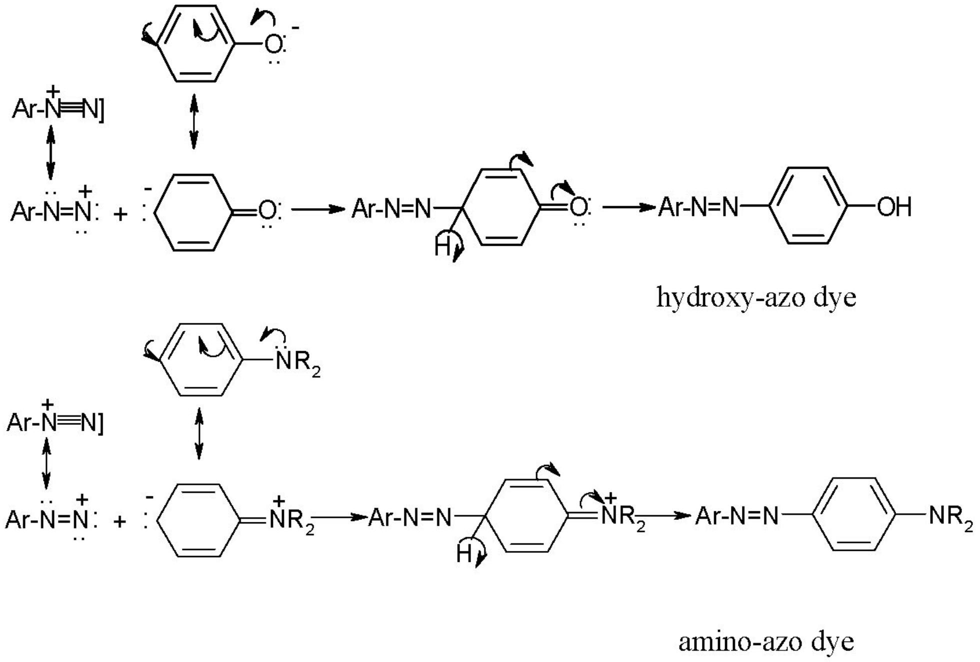
$$Ar\text{-}\overset{+}{N}{\equiv}N]X^- + H\text{-}Ar'\text{-}Y \longrightarrow Ar\text{-}N{=}N\text{-}Ar'\text{-}Y + HX$$

D C azo dye

2.1.5. Coupling reaction mechanism

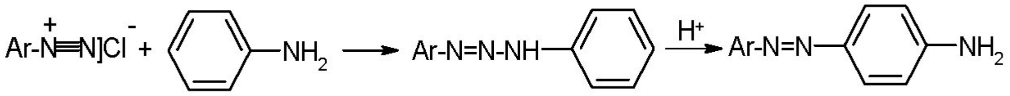
The coupling reaction takes place after an electrophilic substitution (SE) mechanism, in which the electrophilic agent is the diazonium salt ion, and the nucleophilic reactant is the coupling component having a favorable position with increased electron density.

Active components:



The coupling of phenols is done in alkaline medium, and of amines in weakly acidic medium, especially in the *para* position.

Primary and secondary amines can give decoupling reactions to amine nitrogen, forming di-azo-amino compounds, which in the mineral acid environment undergo intramolecular transpositions, resulting in *para*-amino-azo products:

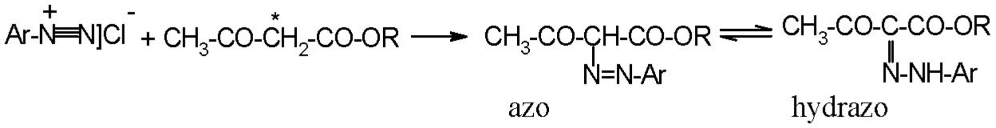


Modifications of primary amino groups by acetylation or benzoylation lead to amines that can no longer be coupled under normal conditions. By sulfonation of the amino groups, the coupling possibilities are similar to those of phenols. By acidic or alkaline saponification the animate group is restored.

$$\mathrm{Ar'\text{-}NH_2 + HCHO + NaHSO_3 \longrightarrow Ar'\text{-}NH\text{-}CH_2SO_3Na + H_2O}$$

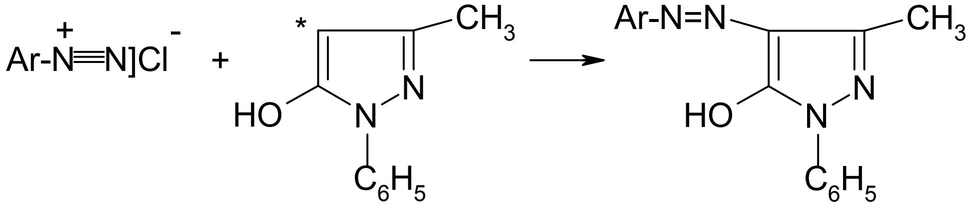
$$\mathrm{Ar\text{-}\overset{+}{N}{\equiv}N]Cl^- + Ar'\text{-}NH\text{-}CH_2SO_3Na \longrightarrow Ar\text{-}N{=}N\text{-}Ar'\text{-}NH\text{-}CH_2SO_3Na}$$

Coupling of ketone compounds with active methylene is done similarly to that of phenols



$$\mathrm{Ar\text{-}\overset{+}{N}{\equiv}N]Cl^- + CH_3\text{-}CO\text{-}\overset{*}{C}H_2\text{-}CO\text{-}OR \longrightarrow \underset{\text{azo}}{CH_3\text{-}CO\text{-}\underset{|}{\overset{}{C}}H(N{=}N\text{-}Ar)\text{-}CO\text{-}OR} \rightleftharpoons \underset{\text{hydrazo}}{CH_3\text{-}CO\text{-}C({=}N\text{-}NH\text{-}Ar)\text{-}CO\text{-}OR}}$$

and coupling to a heterocycle occurs similarly, for example to 1,3,5-phenyl-methyl-pyrazolone (1,3,5-FMP):



1,3,5-FMP

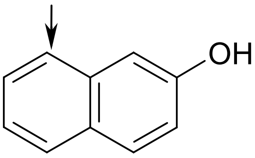
2.1.6. Coupling reaction orientation

The orientation of the coupling reaction is in line with the general rules for the orientation of substitution reactions.

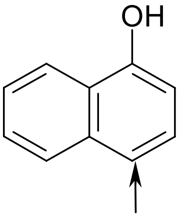
1) In the benzene series: the coupling is done in the *para* position with respect to OH, NH_2, NR_2, or in the *ortho*, but never in the *meta*. The labile substituents (COOH, SO_3H) can be removed;

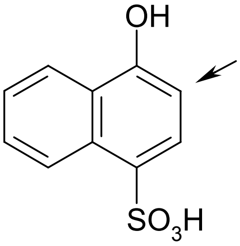
2) In the naphthalene series: the orientation of the coupling depends on the position of the OH and NH_2 groups.

- β-hydroxyl compounds orient in position 1 (α)

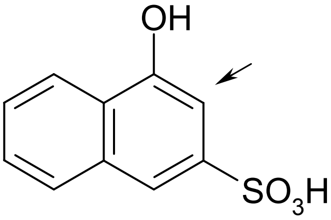


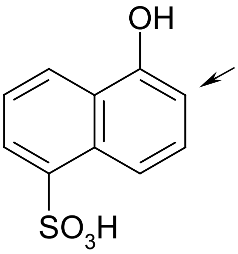
- the α-hydroxyl compounds orient in position 4 or in 2





- if there is an SO_3H group in 3 or 5 positions the coupling is done in the position 2

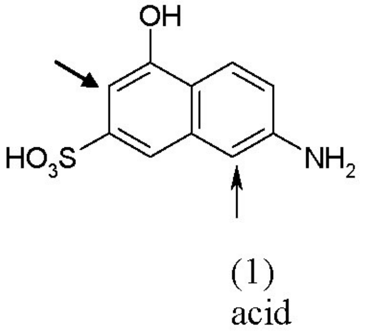




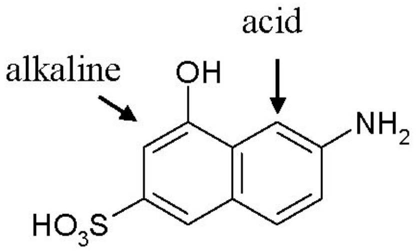
2.1.7. Factors that influence the coupling reaction

1) *nature of the coupling component*: aromatic compounds or an unsaturated chain with conjugated double bonds, on which OH or NH_2 groups are grafted, which polarize the compound anionically. In the benzene series:

phenols couple more easily than amines, and pyrazolonic derivatives behave similar to phenols; In the naphthalene series the coupling is easier if the OH and NH_2 groups are in favorable alternate positions (so they act in the same direction). This can be illustrated by the special coupling behavior of acid I and γ acid. Acid I in acidic medium produces the coupling oriented by the NH_2 group, and in basic medium, the one oriented by the OH group. There is the possibility of successive coupling, namely, first in acidic medium, then in basic medium, thus obtaining *dis*-azo dyes:

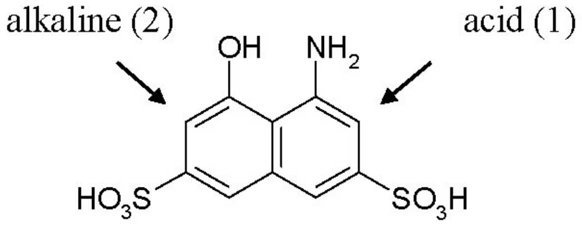


Acid I –
mono- şi dis-azo dyes



Acid γ –
only mono-azo dyes

H-acid can couple in both available positions, forming *dis*-azo dyes, first in acidic medium, then in basic medium:



2) *temperature*: increasing the temperature favors the coupling reaction, but at the same time increases the rate of the decomposition reaction of azo-derivatives. That is why it is worked at low temperatures, in alkaline solutions at <15ºC, and in acidic solutions at <10ºC.

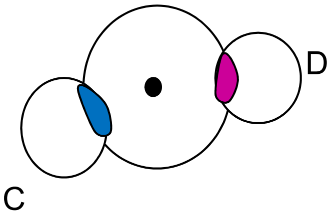
3) *pH* influences the coupling reaction by influencing the concentrations of the active forms it generates. The optimal pH for different components was determined experimentally. As a general rule, the first coupling is done at low pH, the second at high pH.

2.1.8. The control of the diazotizing and coupling processes

Diazotization: a certain acidity is maintained, checked during the reaction with Congo Red paper (blue in acid medium). The end of diazotization is made with iodized starch paper, which in the presence of nitric acid gives a blue color, according to the reaction:

$${}_{2}\mathrm{KI} + {}_{2}\mathrm{HNO_2} + {}_{2}\mathrm{HCl} \longrightarrow \mathrm{I_2} + {}_{2}\mathrm{KCl} + {}_{2}\mathrm{NO} + {}_{2}\mathrm{H_2O}$$

Coupling: A drop of solution is placed on the filter paper and a drop of a coupling component other than the one being worked on is placed next to it. If color appears at the intersection of the halos, there is still an uncoupled diazotant and the reaction must be continued, if no color appears, a drop of a diazotization component (other than the one being worked with) is placed on the filter paper. If color occurs, it means that the entire diazotization component has been consumed and is already in excess. Thus the coupling reaction is complete.



2.2. Classification of azo dyes

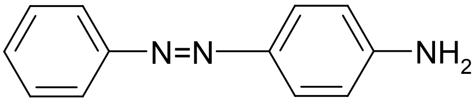
The classification of the azo dyes can be done according to different criteria.

2.2.1. Depending on the structure

D – represents the diazotization component; C – represents the coupling component

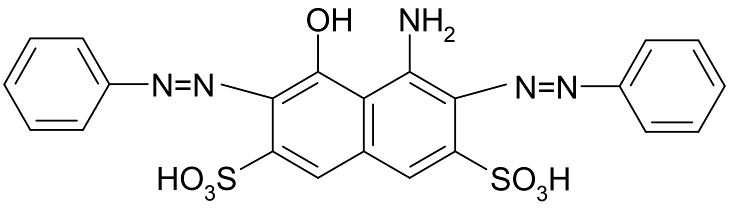
mono-azoic dyes:

$$D \longrightarrow C$$



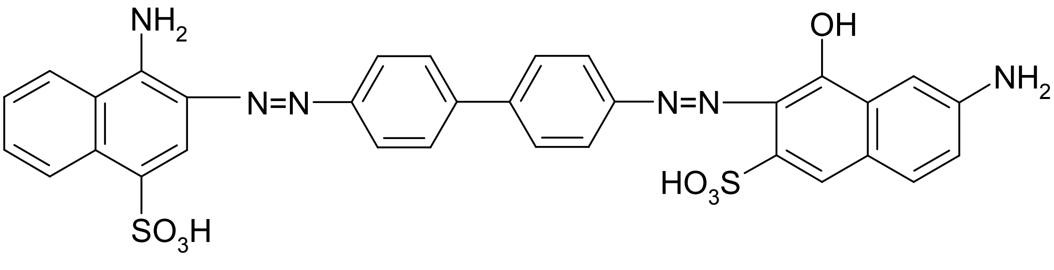
dis-azoic dyes:
primary

$$D1 \longrightarrow C \longleftarrow D2$$



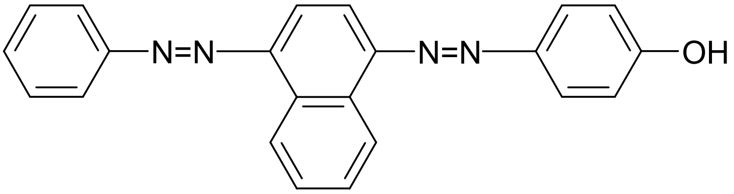
secondary

$$C1 \longleftarrow D \longrightarrow C2$$



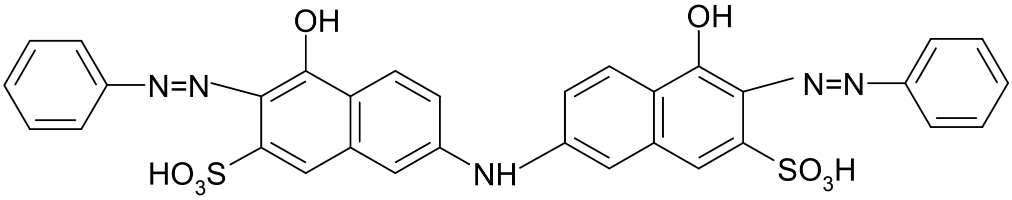
secondary in the chain

$$\left[\, D1 \xrightarrow{1} C1 \,\right] \xrightarrow{2} C2$$



poli-azoic dyes – that contain three ore more azoic bonds.

If the coupling part is a symetric component: Z – X – Z ; (X = NH, NHCONH) the following types of dyes may be obtained:



2.2.2. Depending to the tinctorial properies

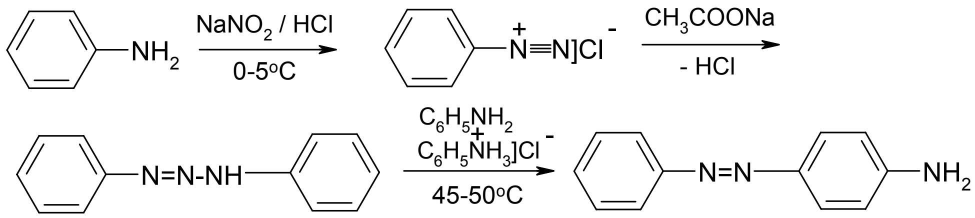
Depending on their dyeing properties, dyes can be divided into the following categories: acids, basic (amino-azoic), with mordant, direct (substantive), developing (ice), dispersing, azo-varnishes and azopigments, without sulfonic or carboxylic groups, complexable, cationic and reactive.

2.2.3. Types of azo dyes

2.2.3.1. Azo dyes without sulfonic or carboxylic groups

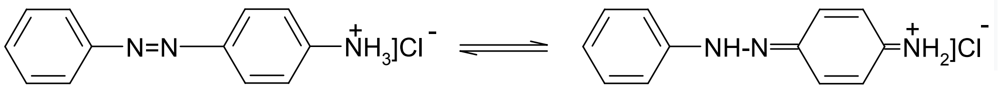
These dyes contain free or modified amino- or hydroxyl-groups in their structure; they do not contain acid or solubilizing groups, so they are insoluble in water. This category includes amino-azo and hydroxy-azo dyes with simple structure, azo dispersion dyes and pigments and azo development dyes (ice).

Amino-azo dyes are basic in nature due to the presence of amino groups likely to form salts with acids (HCl, H_2SO_4, CH_3COOH, etc.), which are soluble in water. They are soluble in oils and fats. The simplest dye in this series is aniline yellow - *p*-amino-azo-benzene, which is obtained by coupling aniline diazotate with aniline in an acid medium (buffering with CH_3COONa), when diazo-amino-benzene results in the first phase, which then undergoes transposition by heating to 45-50°C in *p*-amino-azo-benzene:



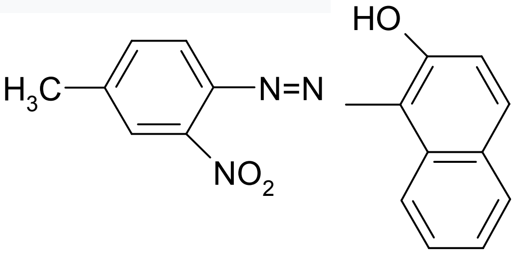
At present, this product is no longer used as such, it being used as an intermediate for the synthesis of *dis*-azo dyes, *p*-phenylene-diamine, etc.

Amino-azo dyes show the phenomenon of chromosomerism, so *p*-amino-azo-benzene hydrochloride can exist in two forms, one benzoid (yellow-red) and another quinoid (blue-gray), which is more stable.

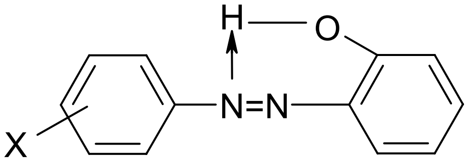


Sulfonated derivatives change color depending on pH, and can be used as indicators.

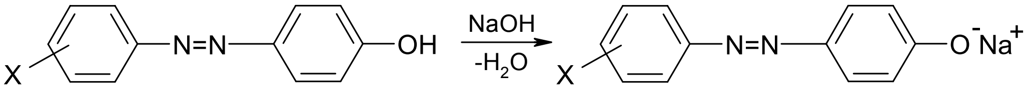
Hydroxy-azo dyes are generally mono-azo compounds, insoluble in water, having the character of pigments. As diazotization components, the most used are aniline, *o*-toluidine, *m*-xylidine, *p*-nitro-aniline; and as coupling components naphthols, FMP (phenyl-methyl-pyrazolones). Some hydroxy-azo dyes are non-toxic and can be used in cosmetics. Thus, toluidine red is obtained from 3-nitro-4-amino-toluene, diazotated and then coupled with 2-naphthol.



The behavior towards the alkalis is different for the *ortho*- compounds from the *para*- ones, namely the *ortho*- ones do not react with the alkaline hydroxides, so they do not change their color due to the formation of a hydrogen bond between the hydroxy group and the azo group,



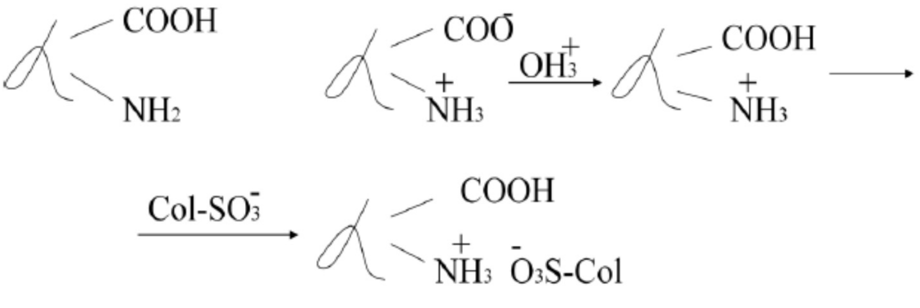
while the *para*- ones retain their acid character, reacting with alkalis and changing color in a bathochrome sense. The salts obtained (phenolates) are much less soluble in water.



Therefore, this must be taken into account when obtaining hydroxy-azo pigments, so that all have the OH group in the *ortho*-position with respect to the azo group.

2.2.3.2. Acid azo dyes

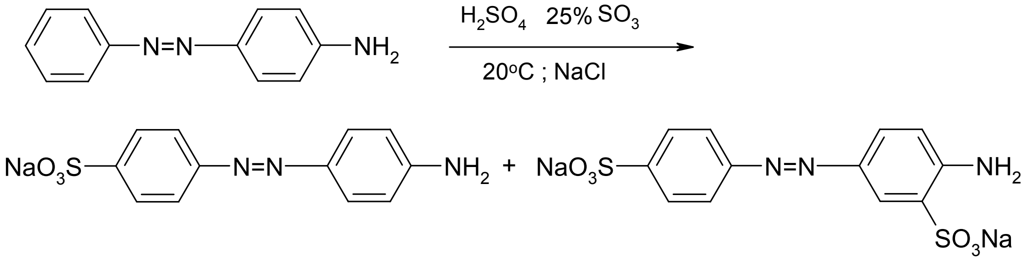
In the structure of the azo chromophore, in addition to other substituents, there are also acid groups (SO_3H, COOH) that ensure the water solubility of these dyes and their fixation on protein fibers.



Electrovalent bonds are formed between the dye and the support, which ensure increased resistance to various treatments. Tinctorially, these dyes are colored anions that dye wool or silk from acidic, salt-forming fleets. They can be mono-azo, *dis*-azo, *tris*-azo or *poly*-azo dyes.

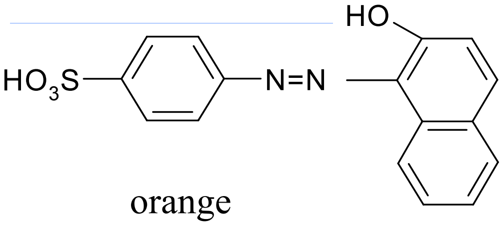
Monoazo acid dyes have relatively simple structures, containing amino or hydroxyl groups, or both. They are used to dye the protein and polyamide fibers, as indicators, to obtain colored varnishes and even as food dyes. The presence of sulfonic groups can be on the diazotization or on the coupling component ore on both. Aniline-sulfonic acids are frequently used as diazotization components, and naphthols, naphtho-sulfonic acids, etc. are frequently used as coupling components.

Amino-mono-azoic acid dyes. By sulfonation with oleum with 25% SO3 of p-amino-azo-benzene at 20°C a mixture of yellow products is obtained.

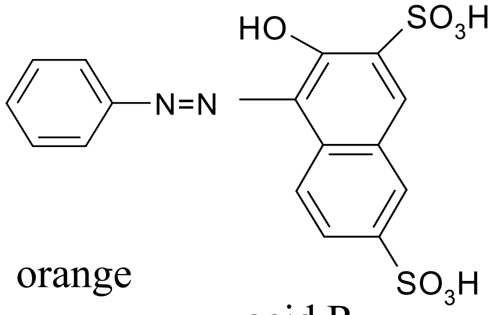


The sequences of reactions is as follows: the first sulfonic group enters the *para*-position relative to the azo group, after which the second sulfonic group enters in the other nucleus. Their separation is based on the difference in solubility of sodium salts, the compound with two sulfonic groups being more soluble. These products dye wool in yellow, with medium resistance to light and washing, and can also be used to obtain other azo dyes.

Acidic hydroxy-monoazo dyes can also be divided into several categories, depending on the position of the sulfonic group, either at the diazotant, or at the coupling, or at both components.

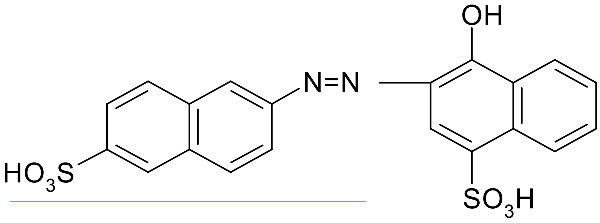


orange



orange

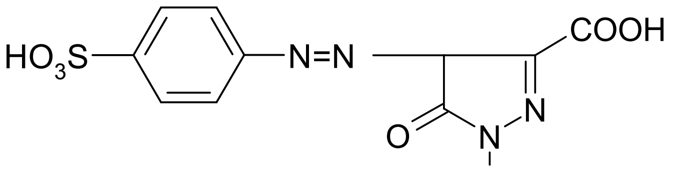
acid R

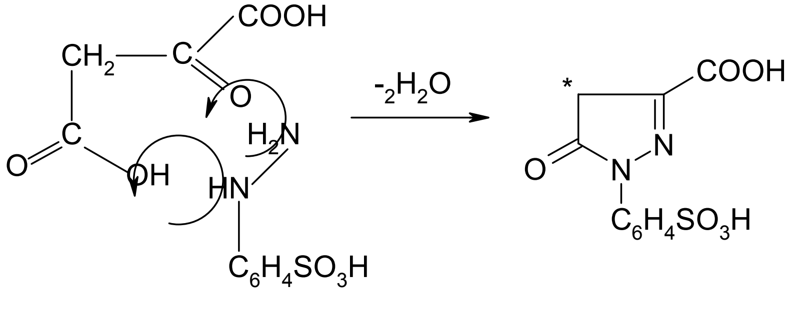


red

ac.Brönner ac.Nevile-Winther

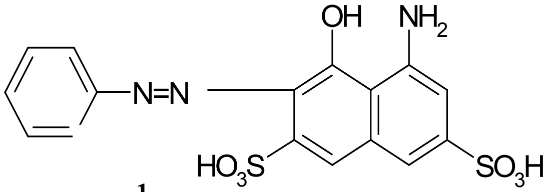
Some hydroxy-monoazo acidic dyes can form Ba or Ca salts hardly soluble in water and organic solvents, which can be used in a finely divided state as pigments, by coupling as Na salts and then precipitating as Ca or Ba salts, by the addition of $BaCl_2$ or $CaCl_2$. Important in this series are the varnishes that use as couplers: 2-naphthol and its derivatives (R acid, Schaffer acid, BON acid), with Nevile-Winther acid, azurinic acid, FMP and its derivatives, etc. It has been found that products derived from 2-naphthol and its derivatives, which contain a sulfonic or carboxylic group in the *ortho* to the azo bond, form high quality varnishes. A number of hydroxy-monoazo dyes can be used to color food if they are non-toxic and can be very well purified. An example of this kind is tartrazine (yellow):



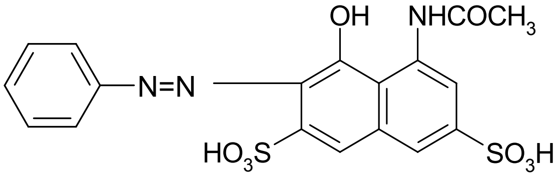


Food dyes contain in each component from which they are originated at least one sulfonic group, so that after their reduction in the body results amino acids, harmless, not amines that are toxic.

Monozoic acid dyes containing hydroxy- and amino- groups are derivatives of amino-naphthol-sulfonic acids, which may have an acylated or arylated amino group.

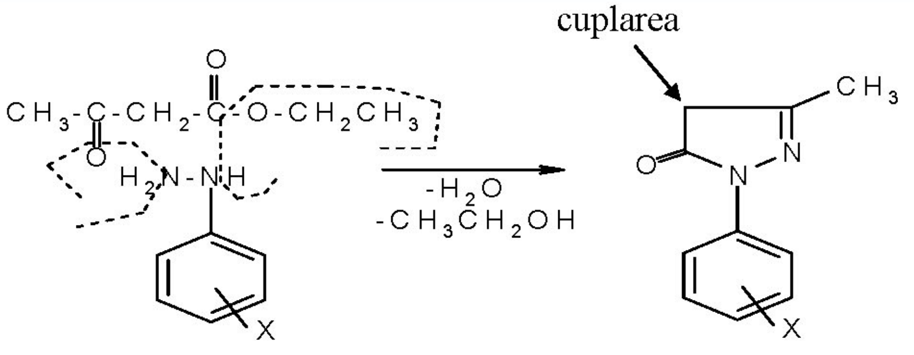


red



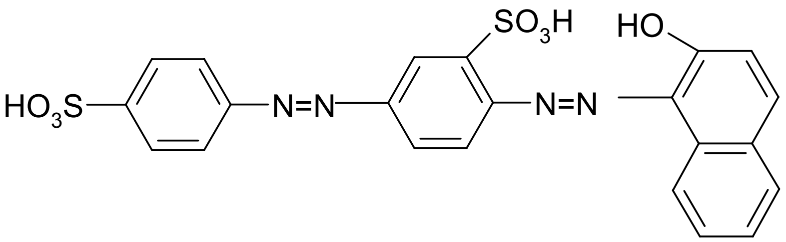
red

Pyrazolonic acid azo dyes have the basic structural feature of using pyrazolone as a coupling component and substituted derivatives to the aromatic ring. They are coupling components specific to light shades (yellow). Synthesis of pyrazolone intermediates takes place by condensation of phenyl hydrazines with acetyl-acetic acid ethyl ester:



Acid dis-azo dyes. Improving the resistance to various treatments and light is ensured by increasing the molecule of the chromophore system. Also by extending the conjugation, the displacement of the absorption to longer wavelengths is ensured, which determines the obtaining of darker shades (towards blue or even black). The synthesis of *dis*-azo dyes is performed in different ways, using the possibility of successive diazotization and coupling, respectively by using the diazonium salts of diamines and the coupling in two positions of the compounds with increased reactivity.

The first *dis*-azoic acid dye was the Biebrich Ecarlat, which is obtained by coupling diazotated *p*-amino-azobenzene-disulfonic acid with 2-naphthol.

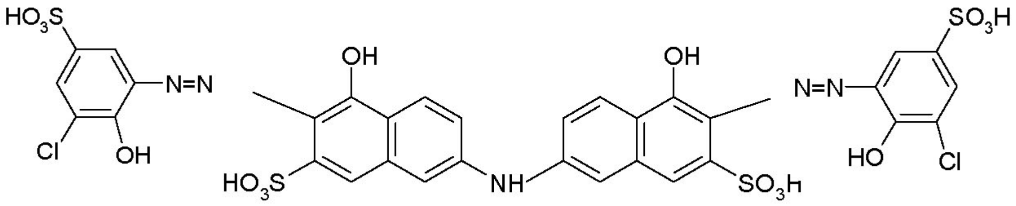


If a naphthalene derivative is used as a central component, dark dyes are obtained, and even black ones.

An important category of dyes is obtained from bifunctional components, such as *H acid*, and which are formed according to the general scheme presented below:

$$D_1 \longrightarrow C \longleftarrow D_2$$

Di-I acid is one of the intermediates often used for the synthesis of such dyes, it can give by suitable couplings both symmetrical and asymmetrical dyes:

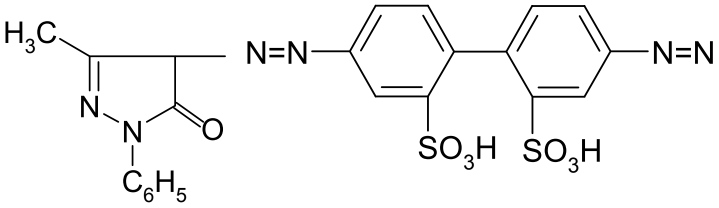


di-I acid

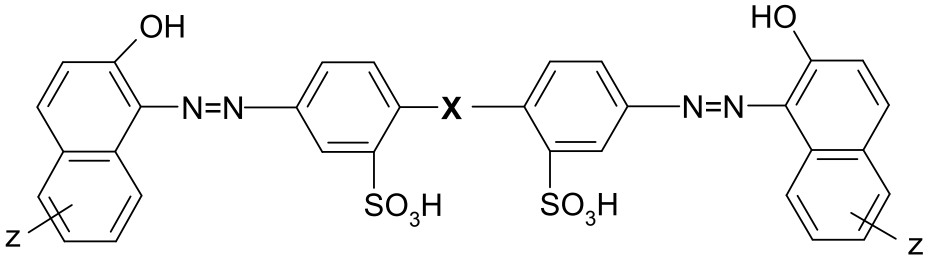
Diazotants with two possibilities of diazotization and then coupling with two corresponding couplers can be used to obtain *dis*-azo dyes, as in the scheme presented below:

$$C_1 \longrightarrow D \longleftarrow C_2$$

Benzidine and its derivatives are compounds very often used as diazotants for this purpose, and symmetrical and asymmetrical dyes can be obtained.



Oher similar dyes have the general structure:



where: X = CH_2; O; S; NH

Tris-azo and *tetrakis*-azo dyes require difficult synthesis conditions, have low purity, and are only used for dyeing leather.

2.2.3.3. Complex acid azo dyes (named also as dyes with mordant)

By treating the dyes with metal salts the light resistances and wet treatments are improved by the formation of particularly stable complexes. The structure of the dye must allow the formation of these complexes, by means of functional groups, with the metal, which has the free 3d substrate to form covalent or covalently coordinative bonds with the respective functional groups. The bonds are formed by substituting the hydrogen atom for the OH or COOH groups, or through the non-participating electrons of the functional groups or the azo bridge. By complexing, rings of 5-6 atoms are obtained, which are very stable, called chelating combinations. The higher the number of cycles, the better the stability and implicitly the resistance of the paints. Depending on the ratio of metal ion: dye, complexes can be obtained: 1: 1; 1: 2; 2: 3, etc. The metal ions that participate in the formation of the complex can be: Cr^{3+}; Co^{3+}; Cu^{2+}; Ca^{2+}; Fe^{3+}. Several variants of application of complexable acid dyes are known, namely:

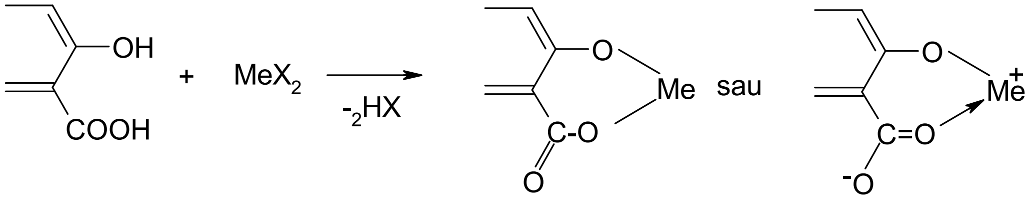
1. Pre-fixing the mordant on the material, followed by applying the dye
2. Dyeing the material, followed by complexation with metal salts
3. Simultaneous dyeing and complexation with metal salts of the material
4. Dyeing the fibers with preformed complex type dyes

Depending on the position of the complex with respect to the azo chromophore, the following are distinguished:

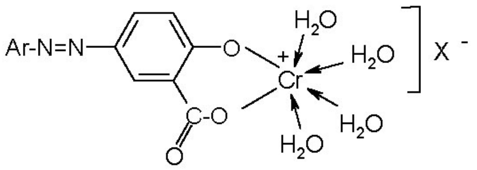
a) Dyes with a system of external complexes - in which the azo group does not participate in the formation of cycles

b) Dyes with a system of internal complexes - in which the azo group participates in the formation of cycles

In dyes with an external complex structure, salicylic acid plays an important role as a coupling component.

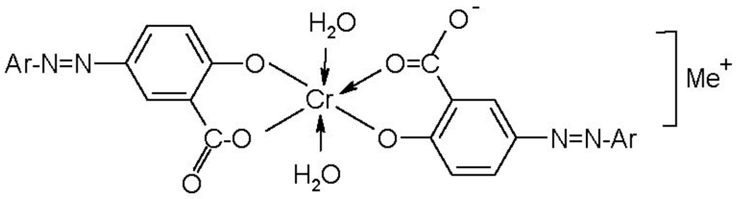


Examples of structures having complex 1:1



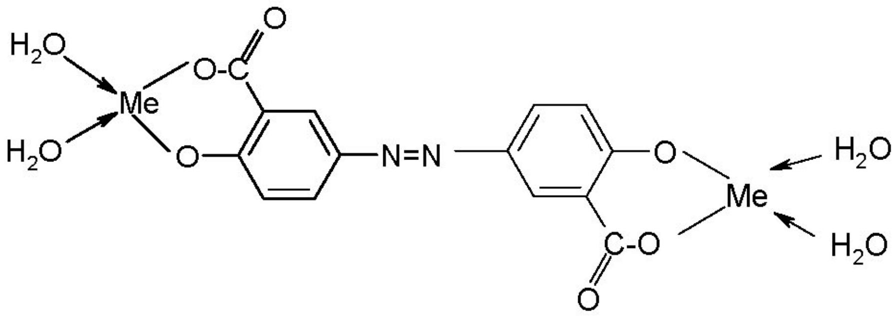
$X = HSO_4^-$; Cl^-

complex 1:2

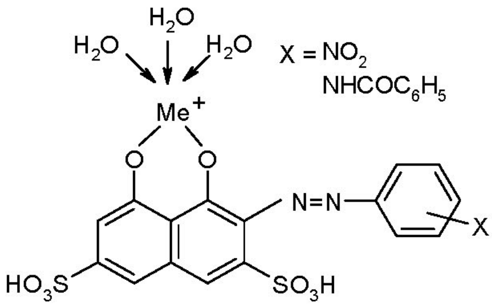


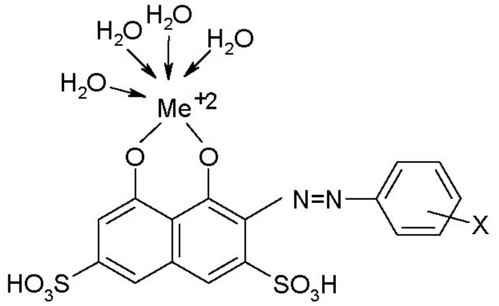
$Me = H^+$; Na^+

complex 2:1

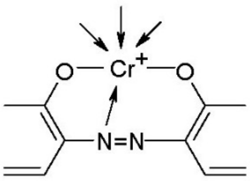


Another important intermediate in the synthesis of dyes of this type is the chromotropic acid, which can give red monoazo products, which by complexation change to purple-blue.

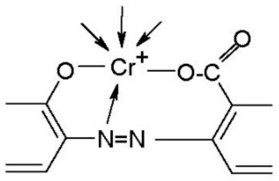




In acid dyes with the structure of internal complexes, the azo group participates in the formation of complexes through a covalent-coordinating bond of one of the nitrogen atoms. These dyes have an *o, o'*-di-hydroxy azo structure, or are derived therefrom by replacing an OH group with a COOH, NH_2, OCH_2COOH. Depending on the *metal : chromophore ratio*, there may be



1:1



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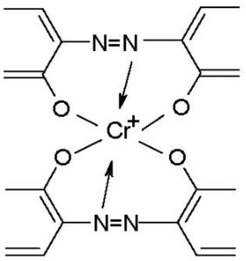

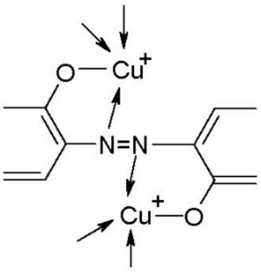

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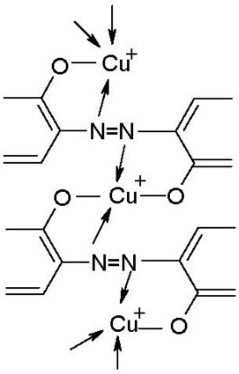


3:2

The diazotizing components are o-amino-phenols, respectively, o-amino-naphthols; and as coupling components: 2-naphthol, R-acid, G-acid, H-acid, γ-acid, I-acid, resorcinol, FMP, salicylic acid, m-phenylene-diamine, etc.

2.2.3.4. Direct azo dyes (named also as substantive dyes)

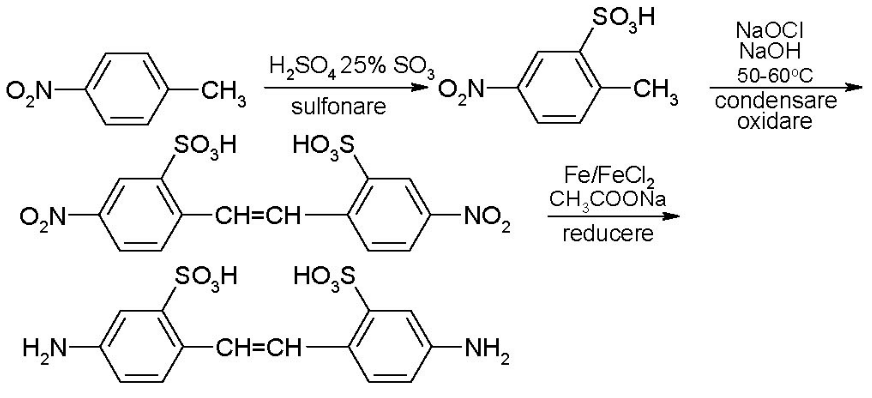
This class of dyes is used for dyeing cellulosic materials. *Substantivity* is the property of the dye to bind directly to the fiber, and it depends on the structure of the dyes and their physical and chemical properties. The dyes show the coplanarity of the extended conjugate system, and contain at least two azo groups, in addition to solubilizing groups, as well as a mobile electronic system. The classes to which these products belong are azo-benzene (benzene nuclei bound in 1.4, and naphthalene nuclei in 1.4; 1.5; 2.6); azo-stilbene; azo-urea and with triazine residue.

In the case of *direct poly-azo dyes* in the chain, as the molecule grows, so does the substantivity and the bathochrome effect. As central coupling components 1-naphthyl-amine; 2-ethoxy-1-naphthylamine; Cléve acids; *p*-xylidine; *m*-toluidine; etc. are used.

Azo direct dyes containing a free primary NH_2 group can increase their chain by diazotization on the textile material, followed by coupling with FMP, 2-naphthol, etc ., or by coupling (if there is a free coupling position) with the diazonium salt of 4-nitroaniline. In this way, the washing resistance is increased.

Benzidine direct dyes can be symmetrical or asymmetrical, and colors from yellow to black.

Stybene direct dyes use as a basic raw material for their synthesis two important intermediates: 4,4'-dinitro-stilben-disulfonic acid (DNSDS) and 4,4'-diamino-stilben-disulfonic acid (DASDS), which are obtained from p-nitro-toluene after the following sequence of reactions:

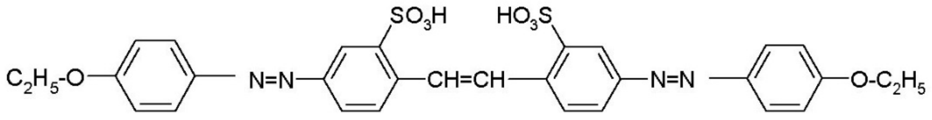


DNSDS

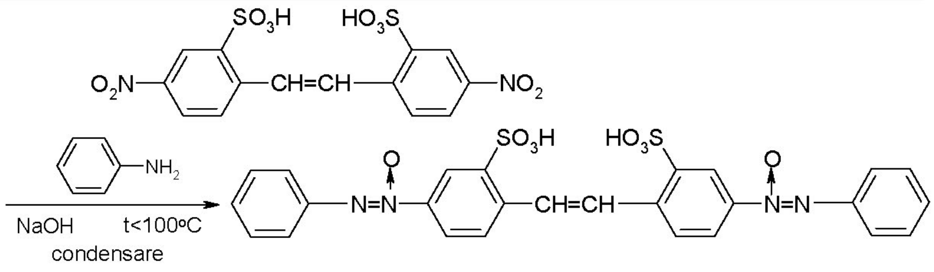
DASDS

Stilbene dyes are obtained by the following synthetic methods:

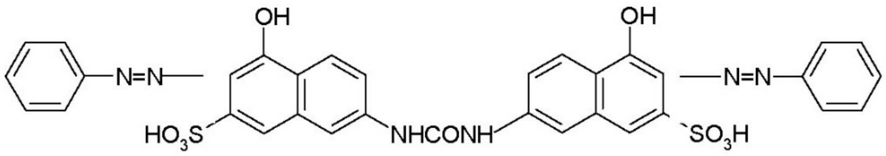
1- DASDS acid diazotization and coupling with various components



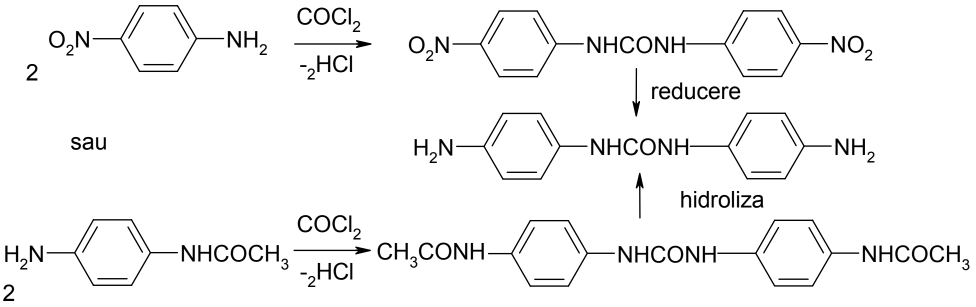
2- Condensation of DNSDS acid with different aromatic amines or amino-monoazo dyes, in aqueous NaOH solutions, at temperatures below 100°C.



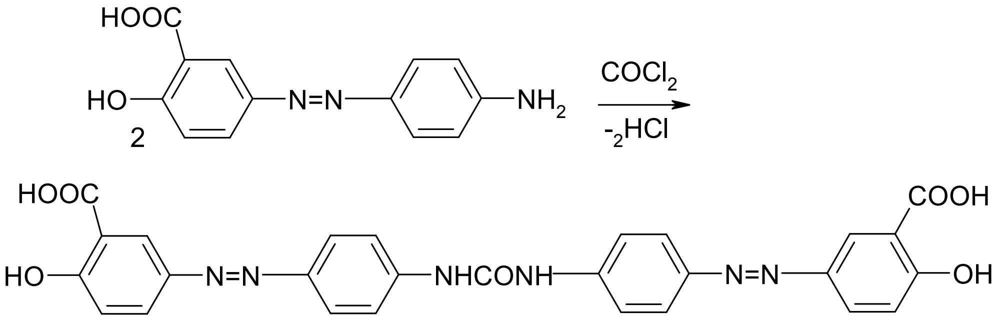
Azo-urea dyes give superiority to the products. They can come from either a urea coupler (eg: carbonyl di-I acid):



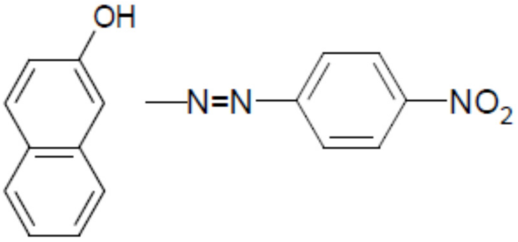
or by using a urea diazotant, *ie* by synthesizing di-amino-carb-anilides, which can be done by phosgening a nitro-aniline, followed by reducing the nitro group, or by phosgening an amino-acet-anilide, followed by hydrolysis of the group acetyl-amino:



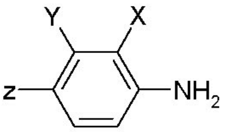
Another method of synthesis is by phosgenation of acidic amino-azo dyes:



Development dyes (named also as ice azo dyes) are obtained by developing the dye directly on the fiber. Their characteristic is the fact that they do not present solubilizing groups in the structure. The dyed material is impregnated with a coupling component (usually a naphthol), then developed by coupling with a diazotized amine directly on the fiber. The material thus dyed is washed to remove the dye fixed on the surface and washed in alkaline solution to obtain bright shades. The most famous ice dye is Para Red:



Diazotable amines used in the synthesis of the development dyes are of the type:



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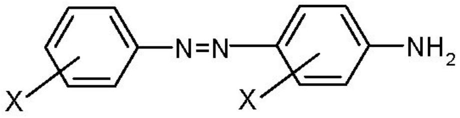
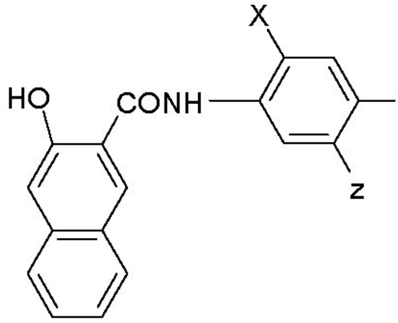


X,Y,Z = H, CH_3, OCH_3, Cl, NO_2

and naphthols or nitrogen are used as coupling components:



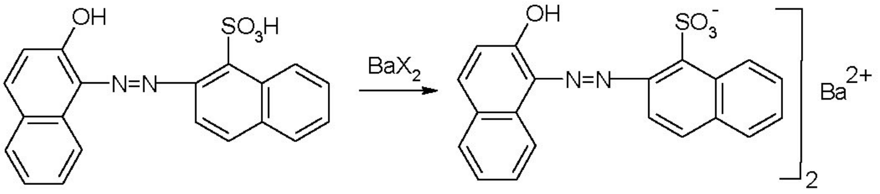
$X = H, CH_3, OCH_3$
$Y,Z = H, OCH_3, Cl$
etc.

2.2.3.5. Azovarnishes and azopigments

Azovarnishes are water-insoluble salts of soluble dyes, suspended on various supports. Varnishes can be obtained by transforming soluble azo dyes into insoluble products, by various methods:

1- Treatment of azo dyes with inorganic salts:

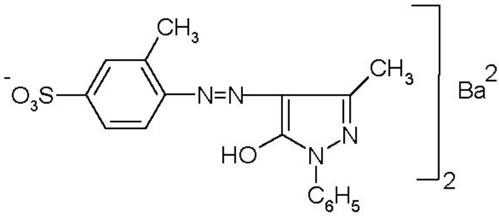
red



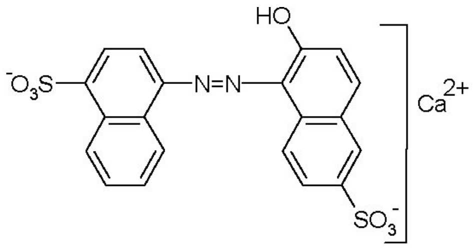
2- Transformation of basic azo dyes into salts of more complex acids (gallic, silicic), insoluble products
3- Treatment of complex dyes with salts that cause their precipitation (with mordants)

After obtaining the varnish, it is mixed with inert or active substances, which represent the support of the varnish, which has the role of diluting the concentrated precipitate by a fine dispersion of it. As inert substances are used kaolin, talc, etc.; and as active substances $Al(OH)_3$; $BaSO_4$; etc. Because the varnish is insoluble in water, in order to ensure a homogeneous mixture, it is suspended, together with the support, in water.

Dyes must meet a number of conditions in order to be used to obtaining varnishes, that are water resistant, or resistant to alkalis and oil, to have a high coverage and the fineness of the particles must ensure a good coverage of the surfaces on which it is applied. Azovarnishes are used to color oil paints and natural soils. Starting from any azo dye, varnishes can be obtained by treatment with salts of Ba^{2+}, Sr^{2+}, Ca^{2+}. Examples of such varnish products are presented bellow:



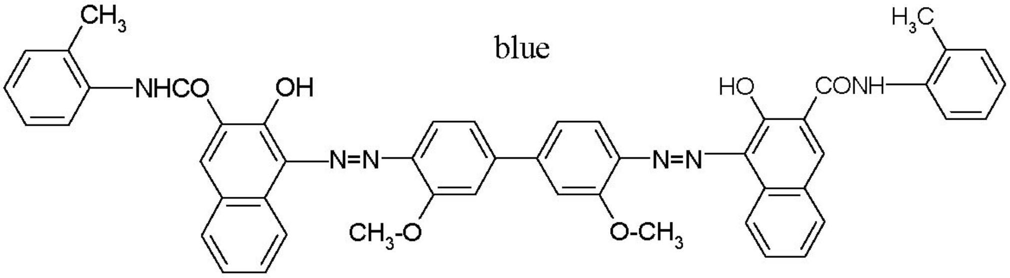
yellow



red

Azopigments are also water-insoluble products, but without sulfonic or carboxylic (solubilizing) groups. As coupling components the following may be used: naphthols, acetyl-acetic acid anilides, etc.; and as diazotants: nitro- or chloro-nitro-anilines.

An example of an azopigment is this blue one:



blue

REFERENCES

1 Floru L., Tărăbăşanu C., Palea R., *Chimia şi tehnologia intermediarilor aromatici şi a coloranţilor organici*, Editura Didactică şi Pedagogică, Bucureşti, 1980.

2 Floru L., Langfeld H.W., Tărăbăşanu-Mihăilă C., *Coloranţi azoici*, Editura Tehnică Bucureşti, 1981.

3 Griffiths J., *Colour and Constitution of Organic Molecules*, Academic Press, London, 1976.

4 Popa S., Jurcău D., Jurcău C., Pleşu N., *Pigmenţi organici. vol.I. Pigmenţii şi culoarea*, Editura Orizonturi Universitare, Timişoara, 2005.

5 Popa S., Jurcău D., Pleşu N., ş.a., *Pigmenţi organici. vol.II. Structură, proprietăţi şi utilizări*, Editura Eurostampa, Timişoara, 2008.

6 Griffiths J., *Deveopments in the Chemistry and Technology of Organic Dyes*, Blackwell Scientific Publications, Oxford, 1984.

7 Lewis P. A., *Organic Pigments*, Federation Series on Coatings Technology, Federation of Societies for Coatings Technology, Blue Bell, Luisville, PA, 1988.

8 Fabian J., *Light Absorbtion of Organic Colorants*, Springer-Verlag, Berlin, 1980.

9 Zollinger H., *Color Chemistry*, VCH, Cambridge, 1987.

10 Rys P., Zollinger H., *Fundamentals of the Chemistry and Application of Dyes*, Wiley Interscience, London, 1972.

11 Fierz-David H.E., Blangey L., *Grundlegende Operationen der Farben Chemie*, edition 4, Verlag von Julius Springer, Wien, 1938.

12 Moser F. H., Thomas A. L., *Phtalocyanines*, CRC Press Inc., Boca Raton, Florida, 1983.

13 Grad M. E., *Contribuţii la sinteza unor coloranţi direcţi nebenzidinici*, Teză de Doctorat, Editura Politehnica, 2009.

14 Lewis P.A. (ed.), *Pigment Handbook*, 2nd edition, vol.1-3, J.Wiley & Sons, New York, 1988.

15 Christie R. M., Color *Chemistry*, Royal Society of Chemistry, London, 2001.

16 Color Index, 3rd edition, The Society of Dyers and Colourists, Bradford, 1971.

17 Venkataraman K., Iyer V. N., *The Chemistry of Synthetic Dyes*, ed. by Venkataraman K., Academic Press, London, 1971.
18 Chiriţă A., *Produse auxiliare şi coloranţi pentru industria pielăriei*, Editura Tehnică, Bucureşti, 1988.
19 Bacaloglu R., Csunderlik C., Cotarcă L., Glatt H. H., *Structura şi proprietăţile compuşilor organici*, vol.1-2, EdituraTehnică, Bucureşti, 1985.
20 Balaban A. T., Banciu M., Pogany I., *Aplicaţii ale metodelor fizice în chimia organică*, Editura Stiinţifică şi Enciclopedică, Bucureşti, 1983.
21 Neniţescu C. D., *Chimie organică*, vol.1-2, ediţia a VII-a, Editura Didactică şi Pedagogică, Bucureşti, 1973.
22 Popa S., *Theory and practice in the teaching of organic colorants to chemical engineering students*, *J. of Educational Sciences*, 2014, 2, 35-42, https://rse.uvt.ro/pdf/2014/NR2/tot2_2014.5.pdf.

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