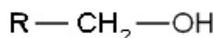


# Alcohols and phenols

**Alcohols** are non-aromatic hydroxy derivatives of hydrocarbons, whereas **phenols** contain a hydroxyl functional group bonded directly to the benzene ring. According to the position of the -OH group in the aliphatic chain, alcohols are distinguished as primary, secondary and tertiary.

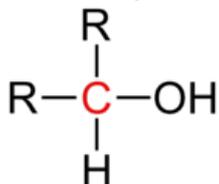
## Alcohols

### Primary alcohols



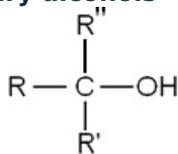
The -OH group is bonded to the primary carbon (i.e. the carbon bonded to only one alkyl group).

### Secondary alcohols



- The -OH group is bonded to the secondary carbon (i.e. the carbon bonded to the two alkyl groups).

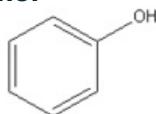
### Tertiary alcohols



-The OH group is bonded to a tertiary carbon (i.e. a carbon bonded to three alkyl groups).

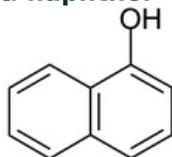
## Examples of phenols

### Phenol



-OH group is bonded directly to the benzene core

### $\alpha$ -naphthol



-OH group is bound directly to the naphthalene nucleus

**A number of reactions are typical for these substances. For the purposes of the practical exercises, we will focus only on the oxidation reactions of alcohols and the azo-copulation reactions of phenols.**

## Alcohol oxidation

- Primary alcohols are oxidised to aldehydes and further to carboxylic acids by suitable oxidising agents
- secondary to ketones
- tertiary are not oxidised without breaking the carbon skeleton

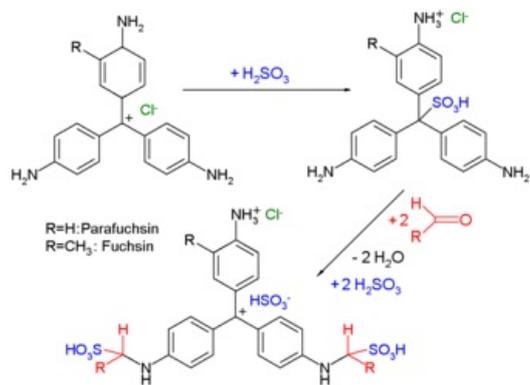
Of the phenols, only compounds with two -OH groups in the o- and p- positions are oxidised to form quinones.

A suitable oxidizing agent is, for example, a chrome-sulfur mixture, i.e. an orange-colored dichromate (i.e., a Cr 6+ compound ) with sulfuric acid, which is reduced to green chromium sulfate (Cr 3+ ) by reaction with a primary or secondary alcohol.

An example is the oxidation of methanol and formaldehyde



If we want to distinguish between primary and secondary alcohols, we will use the different properties of their oxidation products, i.e. aldehydes and ketones. Aldehydes are reduced by Tollens' , Fehling 's or Benedict's reagent (see below). However, the most sensitive reaction, which does not require the production of a large amount of aldehyde and is therefore suitable for the determination of the aldehyde formed, is the reaction with Schiff's reagent.



Schiff's reagent mechanism

Schiff's reagent is an aqueous solution of the violet-red dye fuchsin to which bisulfite or sulfite is added. Hydrogen sulphite is adducted to the central carbon atom, thereby disrupting the quinoid structure that conditions the colour. A colorless fuchsin sulfuric acid solution is formed. After adding even a small amount of aldehyde, sulfuric acid is released from the bond to fuchsin, which binds to the aldehyde group with a stronger bond. In the fuchsin molecule, the quinoid structure is restored and the solution turns violet-red again.

Differentiation of primary and secondary alcohols by oxidation with a chromium-sulfur mixture and reaction with Schiff's reagent

The reaction is carried out in the apparatus shown in the figure. The mixture of alcohol and chromic sulfuric acid is carefully heated. The resulting aldehyde / ketone is introduced into a tube with Schiff's reagent, which turns purple in the presence of aldehyde.

The reaction with Schiff's reagent is also widely used in histology in the so-called PAS reaction (Periodic Acid - Schiff) for the detection of glycogen and other polysaccharides in tissues. The principle is the oxidation of carbohydrates with *periodic acid* to aldehydes, which then react with Schiff's reagent to produce a purple-red coloration.

### Oxidation of alcohols in the body

Ethanol is a component of many alcoholic beverages, pharmaceuticals, and is also produced spontaneously in the digestive tract to a small extent. In the body it is metabolised mainly by the liver, with small amounts of unmetabolised alcohol excreted through the lungs, kidneys and skin. The main system of hepatic metabolism of ethanol is oxidation in the cytoplasm of hepatocytes. In the first step, ethanol is oxidised to acetaldehyde by the enzyme alcohol dehydrogenase (ADH, EC 1.1.1.1). The activity of this enzyme is genetically determined and may explain the different individual susceptibility to alcohol. Acetaldehyde is converted by aldehyde dehydrogenases (ALDH, e.g. EC 1.2.1.3) to the final acetate, which is further metabolised to acetyl-CoA.

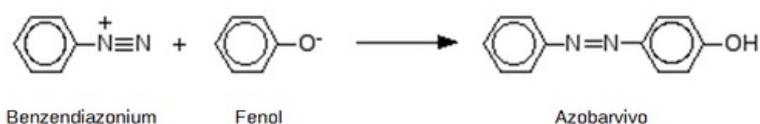
Unlike ethanol, methanol is highly toxic to humans even in small doses. Ingestion of 10 ml can cause irreversible damage to the optic nerve and blindness; a dose of around 30 ml is fatal. The cause of methanol's high toxicity is its oxidation using the same enzymatic systems as ethanol. ADH converts methanol to toxic formaldehyde and this is converted to form formic acid by ALDH, causing hypoxia at the cellular level and metabolic acidosis. The antidote for methanol poisoning is ethanol, a competitive inhibitor of ADH, which prevents the formation of toxic metabolites and allows methanol to be eliminated by the kidneys.

### Azo-coupling reactions of phenols

Arendiazonium salts are formed by the reaction of aromatic amines with sodium nitrite.

The N≡N<sup>+</sup> group is then the basis for the formation of a nitrogen bridge that links the arendiazonium salt to the phenolic compound in an acidic environment. The result is the formation of a coloured azo compound, i.e. a substance with benzene nuclei linked by an N=N bridge.

The simplest azocoupling reaction is the formation of an azo dye by the reaction of an arendiazonium salt with a phenol. A yellow dye is formed, referred to as aniline yellow or sudane yellow R.



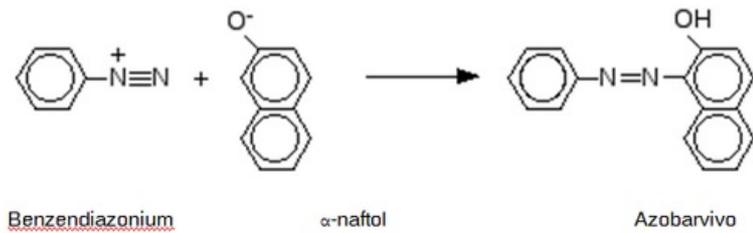
Benzendiazonium

Fenol

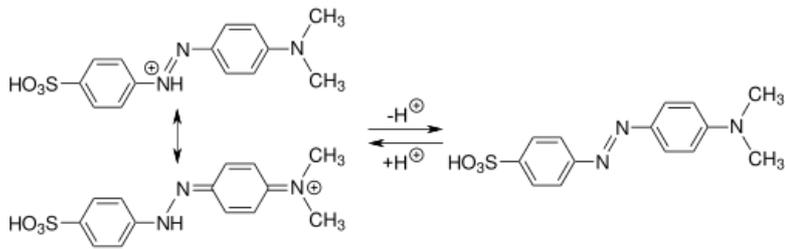
Azobarvivo

Azo compounds are characterized by differently rich  $\pi$  electron bonding systems. When white light passes through this system, some wavelengths are absorbed by the electron system and the resulting colour is actually made up of the unabsorbed wavelengths. This gives rise to a whole range of coloured compounds that can be used in analytical spectrophotometric determinations in biochemistry (bile dyes) or in industry for the production of dyes (diazo dyes).

Another example of an azocoupling reaction is the formation of an orange azo dye by an azocoupling reaction with  $\alpha$ -naphthol.



Even a relatively small change in the structure of an azo dye can result in a different absorption of wavelengths by the substance in question, and thus the colour we perceive. This is used, for example, in the determination of pH. For example, methyl orange exists in two forms depending on the pH:



## References

### Source

Leníček M.: Organika I