Types of reactions in organic chemistry

Types of reactions

In accordance to transmitted molecules:

- redox reactions (transmission of electrons)
- acid-base reactions (transmission of protons)
- reactions of decomposition of networks of crystal ions (transmission of ions)
- complexity reactions (transmission of molecules and ions)

Practical part

1. Reactions of oxidation
2. Reactions of reduction
3. Reactions of condensation
4. Reactions of substitution
5. Reactions of elimination
6. Reactions of esterification
7. Characteristic reaction to determine hydroxyl groups in aromatic molecules and in aliphatic molecules

Redox reactions

Processes where the exchange of electrons between oxidizing and reducing substrance occurs.

In result atoms of elements involved in these reactions change their degree of oxidation.

Redox reactions

OXIDATION is based on **giving** electrons by atoms or groups of atoms (deelectronisation)

OXIDATES are atoms, ions or molecules that have the ability to **accept** electrons, that is, to take them away from other atoms, causing them to oxidize, themselves are **reduced** (the oxidation rate decreases during the reaction)

REDUCTION is based on **accepting** electrons (electronisation)

REDUCTORS are atoms, ions or molecules that have the ability to **give** electrons to atoms, ions or molecules causing their reduction, themselves **oxidize** (the oxidation rate increases during the reaction)

I. Reactions of oxidation – based on the example of various organic compounds

Oxidation of primary alcohol (ethanol and methanol)

1. Oxidation of primary alcohol (ethanol and methanol)

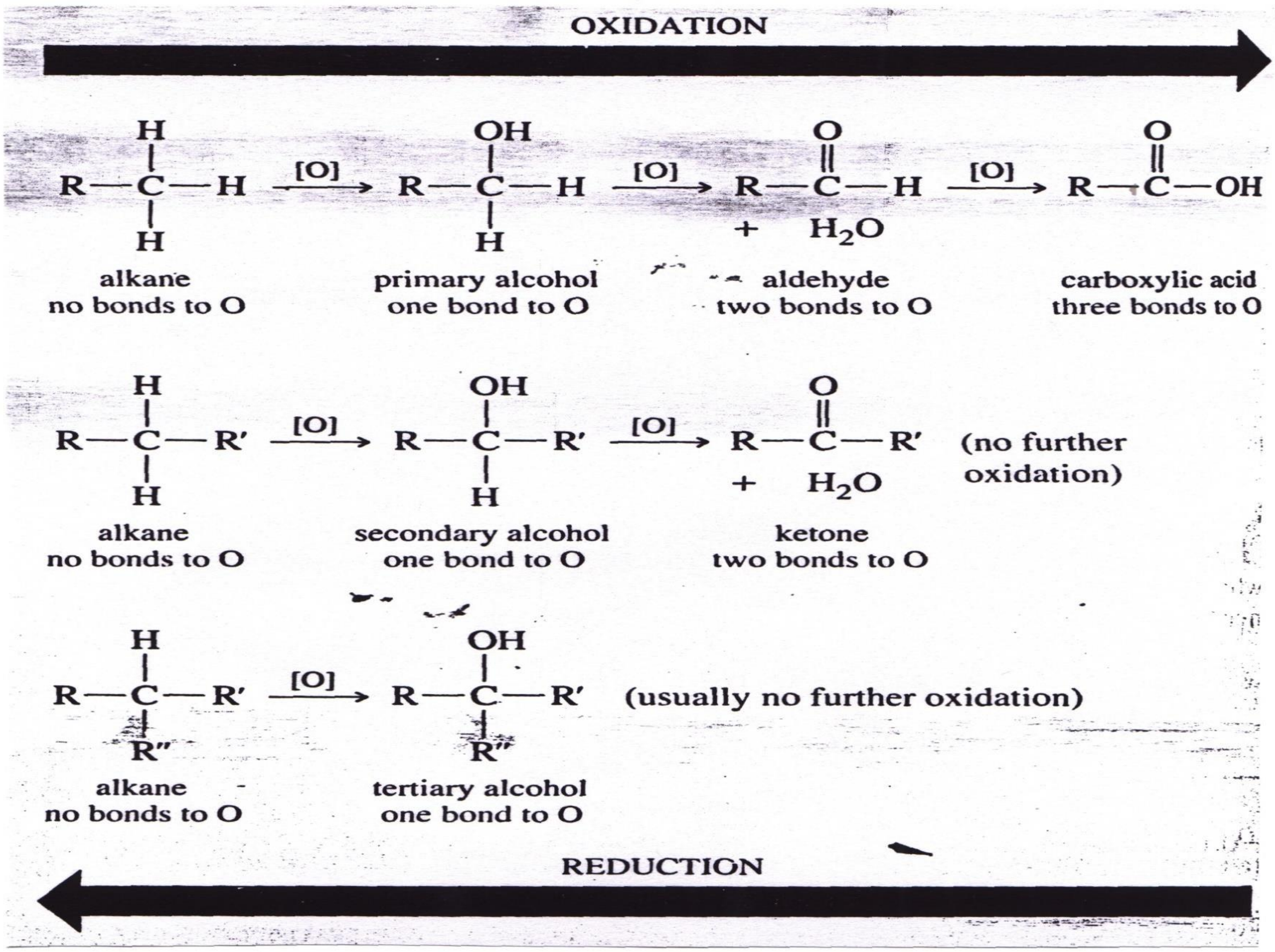
Mark two tubes as 1 and 2. Add to them 1 cm^3 of 5% $K_2Cr_2O_7$ solution and 0.5 cm^3 of 20% H_2SO_4 solution. Next, add 1 cm^3 of ethanol to tube 1, and 1 cm^3 methanol to tube 2. Mix the solutions, wait two minutes and then, warm them over the burner. Observe the change of colour.

In these reactions, alcohol is oxidised and aldehydes are formed (acetaldehyde, formaldehyde), and chrome is reduced – therefore, the tint of solution change from yellow to green or brown. The reaction follows the scheme:

$$3\ R\text{-}CH_2OH + K_2Cr_2O_7 + 8\ H_2SO_4 \rightarrow 3\ R\text{-}CHO + Cr_2(SO_4)_3 + K_2SO_4 + 7\ H_2O$$

The solutions from tube 1and 2 will be used in next experiment!

Redox reactions in organic chemistry



Oxidation of aldehyde using Tollens reagent

a) preparation of Tollens reagent

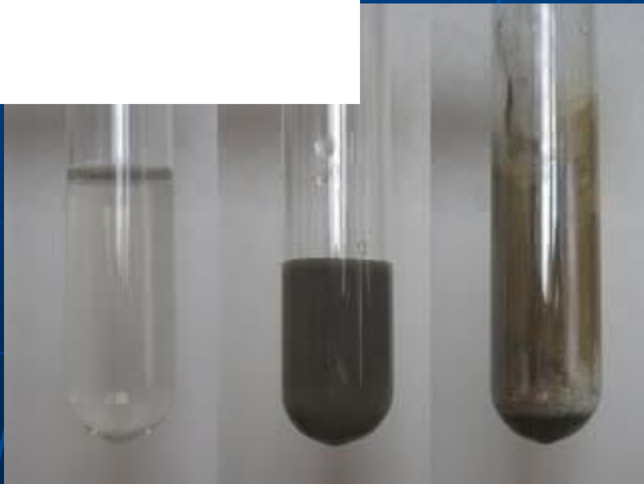
Pipette 1 cm^3 of 0.1M $AgNO_3$ into a tube and add by drops the solution of 2M $NH_3 \cdot H_2O$ stirring the tube until the primary formed white precipitate of Ag_2O disolves.

b) methanol and/or ethanol oxidation using Tollens reagent

Pipette 0.5 cm^3 of fresh Tollens reagent and 0.1 cm^3 of 20% NaOH solution. To one tube, add 0.1 cm^3 of content of tube 1 from previous experiment, as the source of acetaldehyde, and 0.1 cm^3 of tube 2 to other tube, as the source of formaldehyde.

In both tubes, aldehydes are oxidised to adequate acid, and silver ions are reduced to metallic silver which precipitates on the internal walls of tube producing a mirror. The reaction follows the scheme:

$$\text{R-CHO} + Ag_2O \rightarrow \text{R-COOH} + 2\ Ag\downarrow$$



Oxidation of formic acid to carbon dioxide

Add 1 cm^3 of acetic acid solution and 1 cm^3 of concentrated H_2SO_4 to glass tube and next, add drop by drop $KMnO_4$ solution. Observe the discolouration of the solution.

During this reaction, manganese is reduced, and acetic acid is oxidised to CO_2:

$$5\ HCOOH + 2\ KMnO_4 + 3\ H_2SO_4 \rightarrow 5\ CO_2 + 2\ MnSO_4 + K_2SO_4 + 8\ H_2O$$

$$C^{+III} \rightarrow C^{+IV}$$

$$Mn^{+7} \rightarrow Mn^{+2}$$

Oxidation of oxalic acid to carbon dioxide

Add 1 cm³ of oxalic acid solution and a few drops of concentrated H_2SO_4 into a tube, heat over the burner and add drop by drop $KMnO_4$ solution. Observe that the solution is discoloured and bubbles of CO_2 are formed. In this reaction, manganese is reduced, and oxalic acid is oxidised to CO_2:

$$5\ (COOH)_2 + 2\ KMnO_4 + 3\ H_2SO_4 \rightarrow 10\ CO_2 + 2\ MnSO_4 + K_2SO_4 + 8\ H_2O$$

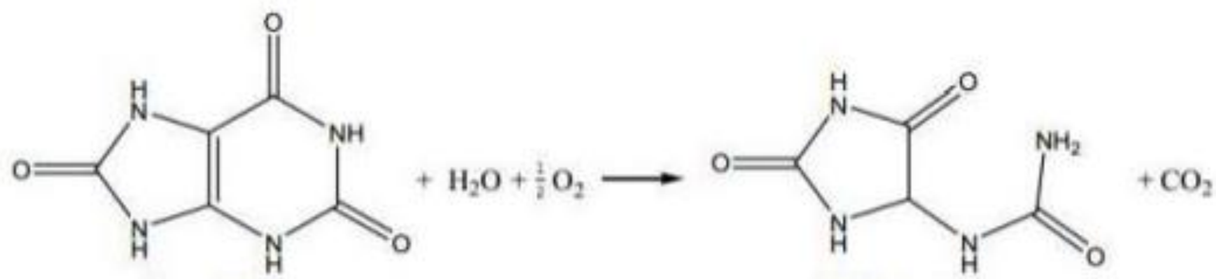
Oxidation of hydroxy acids on the example of lactic acid

Add a few drops of lactic acid solution { $CH_3CH(OH)COOH$ } and 1 cm^3 of 1 mol/dm^3 H_2SO_4 solution to a tube, and then by drops the $KMnO_4$ solution. Manganese is reduced, and lactic acid is oxidised to CO_2 and acetaldehyde { CH_3CHO }:

$$8\ CH_3CH(OH)COOH + 2\ KMnO_4 + 3\ H_2SO_4 \rightarrow 8\ CO_2 + 2\ MnSO_4 + K_2SO_4 + 8\ CH_3CHO + 8\ H_2O$$

Oxidation of ring compounds on the example of uric acid

Disolve some crystals of uric acid in 1 cm^3 of 0.1 mol/dm^3 NaOH solution in a tube, and then add drop by drop $KMnO_4$ solution. The solution is discoloured, manganese is reduced, and lactic acid is oxidised to CO_2 and allantoin.



uric acid   allantoin

Enzyme *Rasburicase*: It is a recombinant version of urate oxidase (oxidises uric acid to allantoin) produced by a genetically modifies *Saccharomyces cerevisiae*.

II. Reactions of reduction

Reducing properties of aldehydes – on the example of formaldehyde reaction with potassium permanganate

Add 1 cm^3 of formaldehyde solution, 2 cm^3 of $KMnO_4$ solution and 1 cm^3 of 1 M H_2SO_4, and heat the solution in a tube. The solution discolours. Manganese is reduced, and formaldehyde is oxidised to formic acid.

$$5\ HCHO + 2\ KMnO_4 + 3\ H_2SO_4 \rightarrow 5\ HCOOH + 2\ MnSO_4 + K_2SO_4 + 3\ H_2O$$

Reducing properties of aldehydes on the example of formaldehyde using Fehling reaction

Pipette 1 cm^3 of Fehling I and 1 cm^3 of Fehling II solutions* into a tube, and add a few drops of formaldehyde solution. Heat the tube over the burner. The orange or red precipitate of cooper oxide is formed.

$$HCHO + 2\ Cu(OH)_2 \rightarrow HCOOH + Cu_2O\downarrow + 2\ H_2O$$

*Fehling I – it is $CuSO_4$ solution, Fehling II it is the base solution of sodium-potassium tartrate

III. Reactions of condensation

Type of chemical reaction when two substrates combine to form a single, bigger molecule of the main product and smaller co-product, which is mostly water.

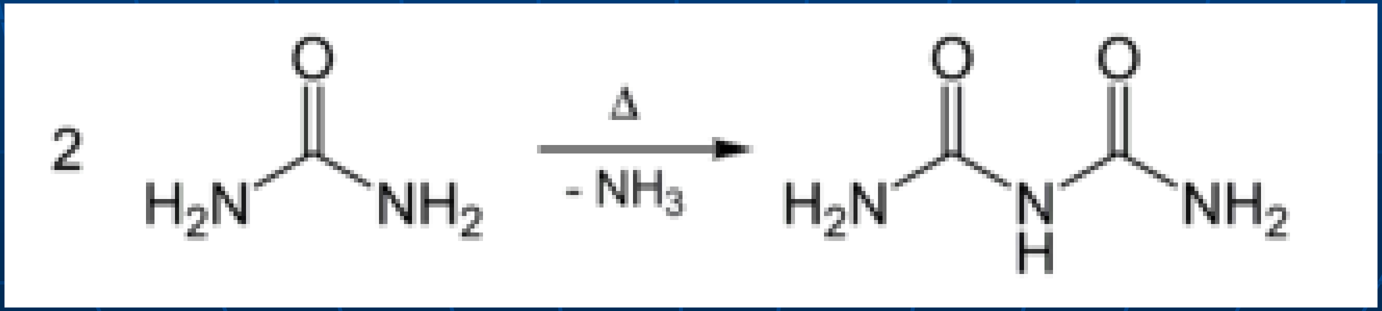
Example: **esterification**

III. Reactions of condensation

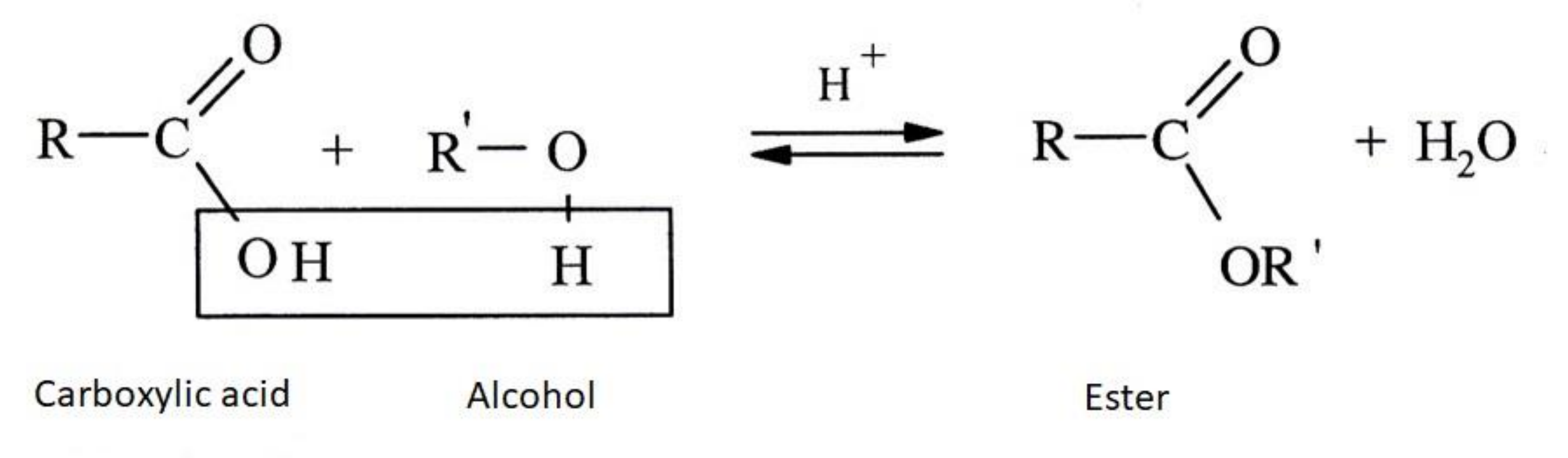
Esterification reaction:

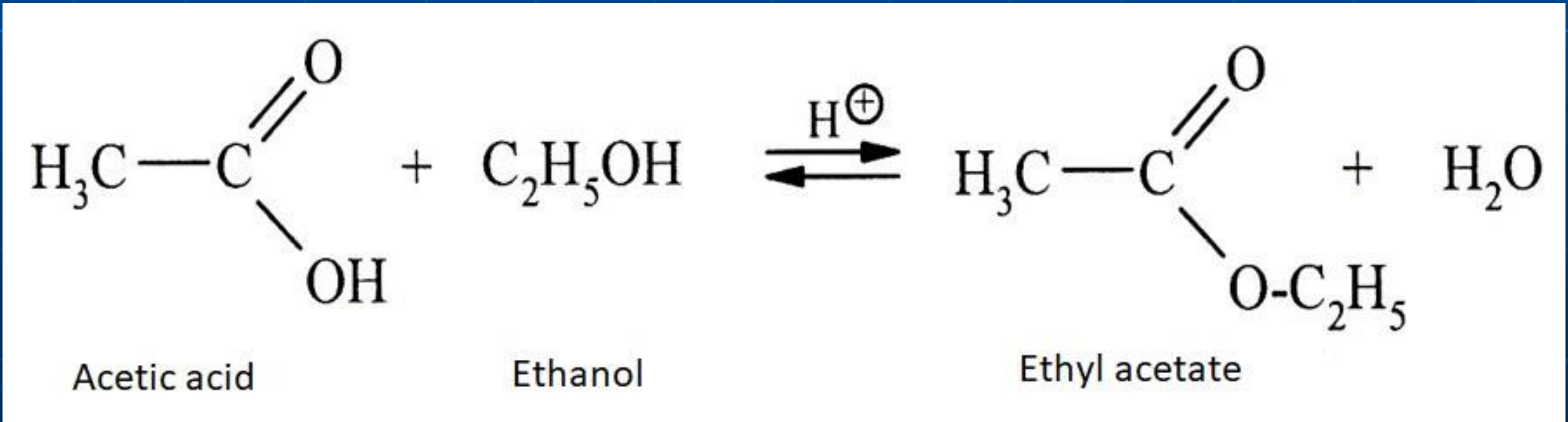
- reaction of organic or inorganic acid with alcohol
- reaction of acid chlorides with alcohol
- reaction of acid anhydrides with alcohol

Other example of esterification – obtaining biuret:

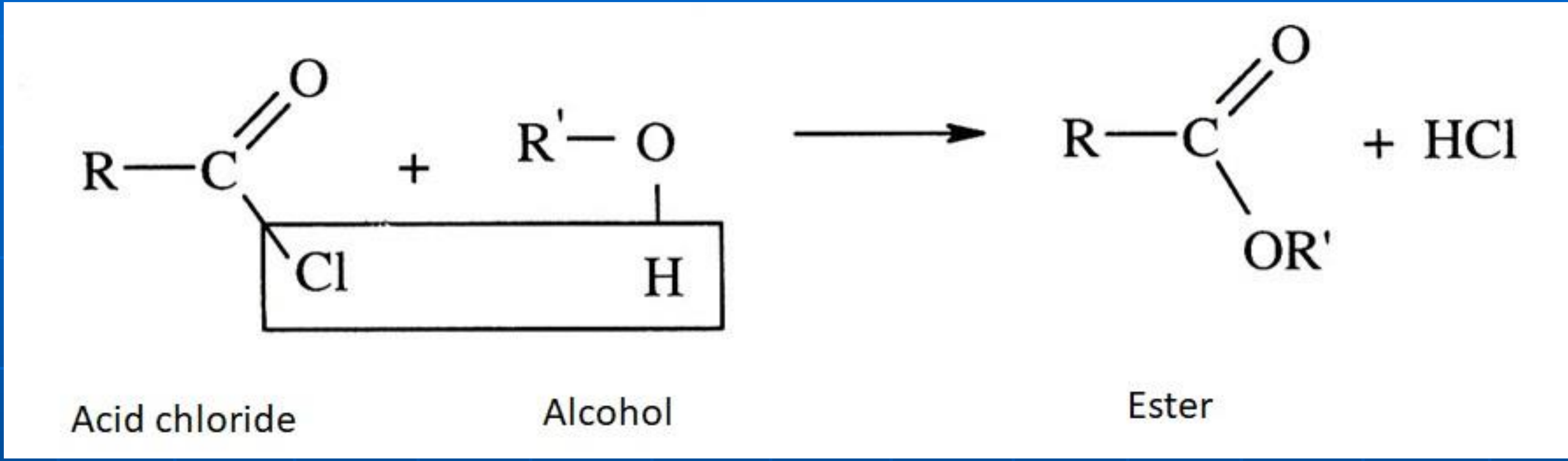


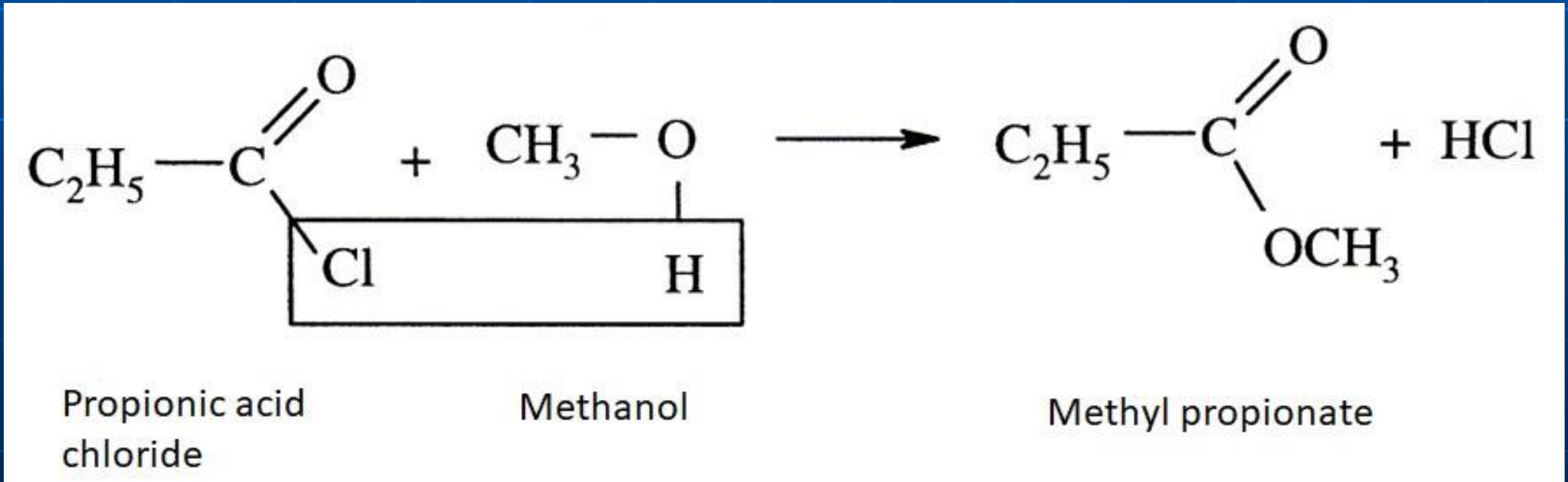
Reaction of organic acid with alcohol



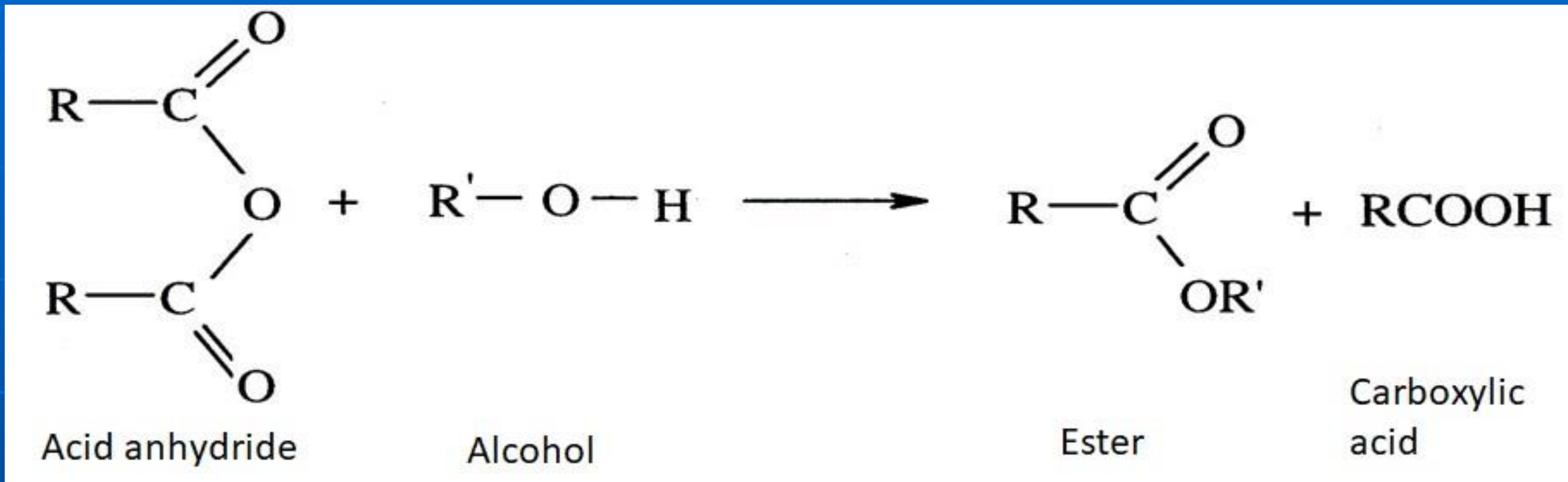


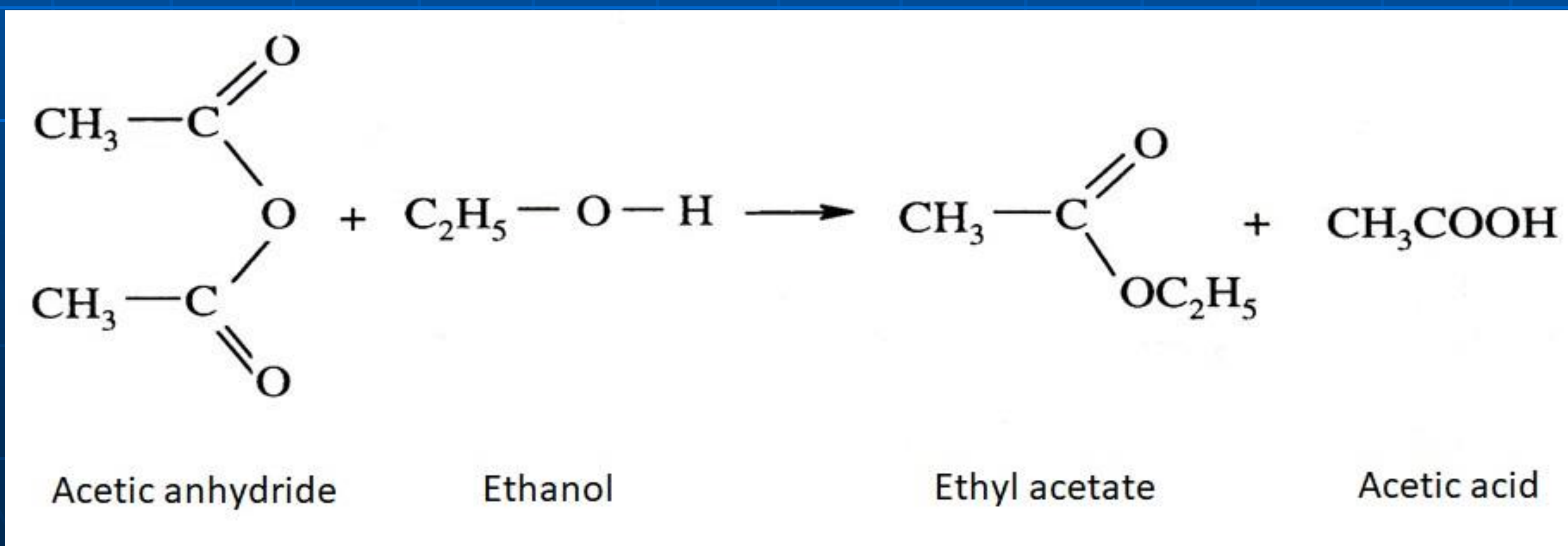
Reaction of acid chlorides with alcohol





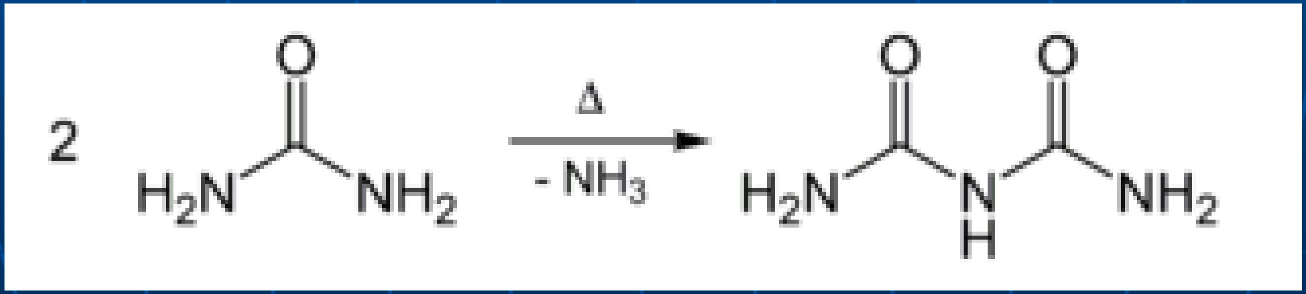
Reaction of acid anhydrides with alcohol





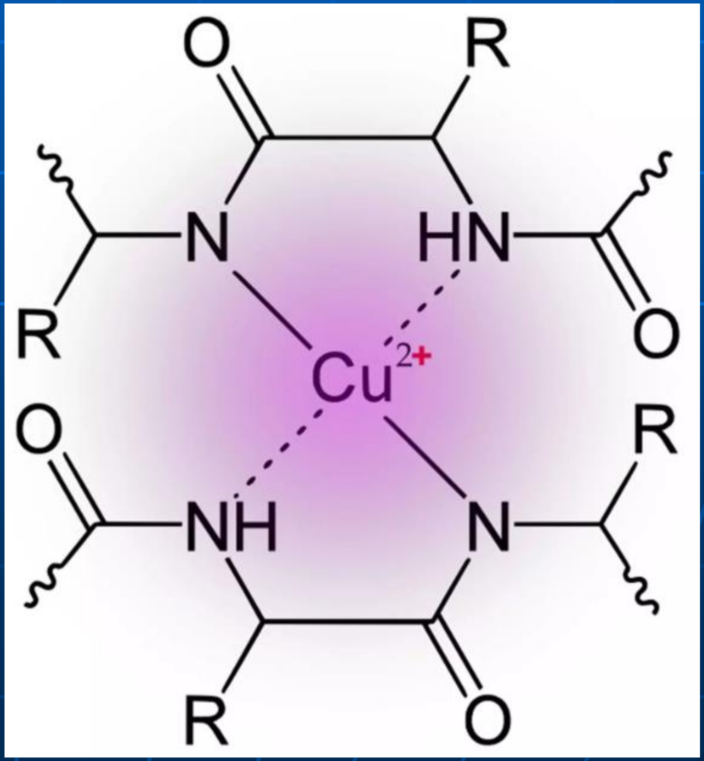
Biuret formation and its detection with biuret reaction

Heat up about 1 g of urea in dry tube until the crystals of urea dissolve. Wait until it cools. Dissolve the clotted mass in 5 cm^3 of distilled water and add 1 cm^3 of 2 mol/dm^3 NaOH. Filter the obtained solution if it is turbid. Add drop by drop 1% $CuSO_4$ solution until red-purple colour occurs. This colour is characteristic for complex of peptide bond with copper which is present in biuret reagent.



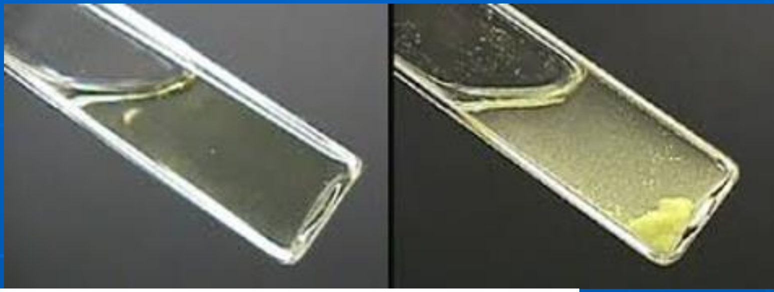
Biuret reaction

Is used to detect the presence of peptide bonds (at least two) by use of copper(II) sulphate (VI)



IV. Reactions of substitution

Preparation of iodoform



Principles of determination

Yellow iodoform is produced and precipitated during the heating up the mixture of ethanol and iodine in basic solution. It is multi-step reaction, in which atoms of hydrogen are substituted by iodine. The summary equation of this reaction:

$$CH_3CH_2OH + 4\ I_2 + 6\ NaOH \rightarrow CHI_3\downarrow + 5\ NaI + H\text{-}C{=}O + 5\ H_2O$$

It is one of the most sensitive reactions for the detection of ethanol in small quantities.

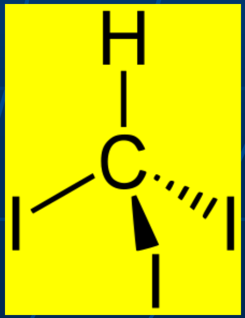
Procedure

Mix in a tube 1 cm^3 of ethanol with 2 cm^3 of 5% solution of iodine in IK and add drop by drop the solution of 2 mol/dm^3 NaOH until discolouration. Heat it over the burner until the solution has light yellow tint. At the outlet of the tube, the characteristic smell of iodoform is noticeable. After cooling the tube, the precipitate of iodoform crystals can be formed.

Iodoform

Iodoform is used as an antiseptic. However, the substance does not have antiseptic properties, bacteria can even develop in it!

Only after contact with the tissue, especially with the serous or purulent secretion, slowly undergoes gradual decomposition, releasing **free iodine**, which combines the protoplasm of microbial cells, denaturates the protein, also acting oxidatively. Therefore, it has a long-lasting bactericidal effect.

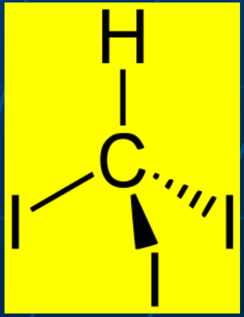


Iodoform

In addition, iodoform has a:

- local anaesthetic effect,
- inhibits bleeding,
- drying,
- stimulates granulation processes.

The disadvantage of the compound is an intense, unpleasant odor and high toxicity, especially for the central nervous system. Consumed accidentally per os is poisonous.



Iodoform

The current use of iodoform in treatment compared to the historical one is much smaller.

The compound is used in dentistry in the form of dental pastes for root canal fillings also in dermatology and sometimes in gynecology (vaginitis purulenta) and urology (urethritis).

Occasionally, it can be used in laryngology (ether solutions) and other branches of treatment.

V. Reactions of elimination

The type of reaction in which atoms or groups of atoms are eliminated, without adding any other groups of atoms in place of the removed. When a compound loses elements, it forms a new pi bond.

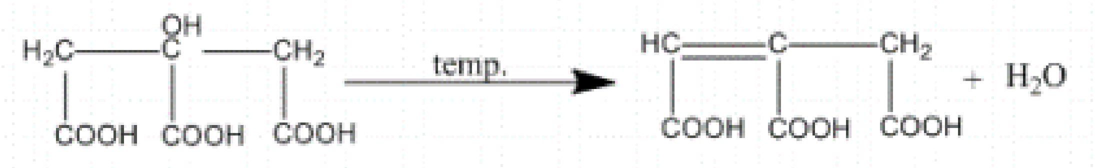
In the result, the compound can become cyclic or can form the double/triple bond.

V. Reactions of elimination

Formation and detection of product of citric acid dehydration (aconic acid)

Principles of determination

Citric acid in high temperature loses the water molecule and transforms into aconic acid. This reaction occurs in Krebs cycle.



Procedure

Heat a few crystals of citric acid in dry tube over the burner. At the outlet of the tube, the smoke of aconic acid occurs, and characteristic, unpleasant smell is noticeable.

VI. Reactions of esterification

Formation of ethyl acetate and ethyl formate

Principles of determination

Ethanol can react with acetic acid and/or formic acid. The results of these reaction are esters: ethyl acetate and/or ethyl formate:

$$CH_3CH_2OH + CH_3COOH \rightarrow CH_3COOCH_2CH_3 + H_2O$$

$$CH_3CH_2OH + HCOOH \rightarrow HCOOCH_2CH_3 + H_2O$$

a) formation of ethyl acetate

Mix 1 cm^3 of ethanol with 1 cm^3 of concentrated acetic acid in a tube. Add 5 drops of concentrated sulphuric acid. Heat the tube over the burner until boiling. Alcohol and acid are esterified. Smell carefully the vapours of ethyl acetate which has a nice, fruity smell.

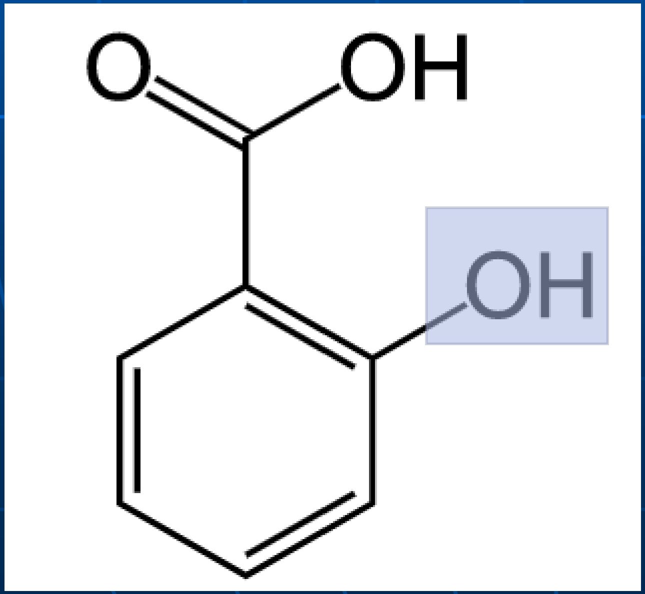
b) formation of ethyl formate

Mix 1 cm^3 of ethanol with 1 cm^3 of concentrated formic acid in a tube. Add 5 drops of concentrated sulphuric acid. Heat the tube over the burner until boiling. Smell carefully the vapours of ethyl formate which remains the smell of rum.

VII. Characteristic reaction to determine hydroxyl groups in aromatic molecules and in aliphatic molecules, in which the hydroxyl groups are located near each other

1. Detection of free hydroxyl groups in salicylic acid

Dissolve a few crystals of salicylic acid in 1 cm^3 of distilled water by warming them in a tube. After cooling, add one drop of $FeCl_3$ solution. Complex compound having red-purple colour is formed.



Salicylic acid

Salicylic acid (from latin *Salix* - willow), is an aromatic hydroxy carboxylic acid with the general formula $C_6H_4(OH)COOH$.

The most important use of salicylic acid is the production of:

- **acetylsalicylic acid (aspirin)** – nonsteroidal anti-inflammatory drug (NSAID), cylooxygenase inhibitor. Used for reduce pain, fever, and as an antithromboric factor (reduces formation of blood clots).
- **p-aminosalicylic acid** – formerly used for the treatment of tuberculosis infections (especially drug resistant).

Salicylic acid

Salicylic acid itself is used in medicine as a disinfectant (eg. in the form of salicylic alcohol) and keratolytic.

Salicylic acid salts – salicylates also have significant importance in medicine.

This acid was formerly used as a food preservative, however, due to its toxic action at higher concentrations, it has now been replaced by sodium benzoate and potassium nitrate.

It can be also used as a sympathetic ink.

2. Detection of free hydroxyl groups in aliphatic compounds

Take three tubes and mark them as A, B and C. Fill them in with 0.5 cm^3 of 1% $CuSO_4$ and 0.2 cm^3 of 1 mol/dm^3 NaOH solution. Next, add 0.5 cm^3 of ethanol to tube A, 0.5 cm^3 of glycerol to tube B, and 0.5 cm^3 of tartaric acid to tube C. Note the observed results in the table below:

Probe	Examined compound	Observed result
A	Ethanol	
B	Glycerol	
C	Tartaric acid	

Try to write the equations of these reactions. Explain the results of the experiment.