Experiment 10: *Reaction of Functional Group - II*
Aldehydes, Ketones, and Alcohols

Lab of general and organic chemistry, chem0303003

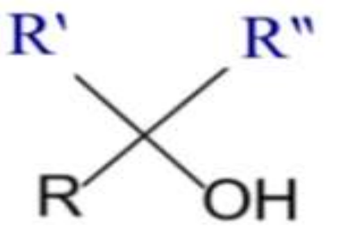
Prof Arab Qaseer 17 December 2022

Objectives:

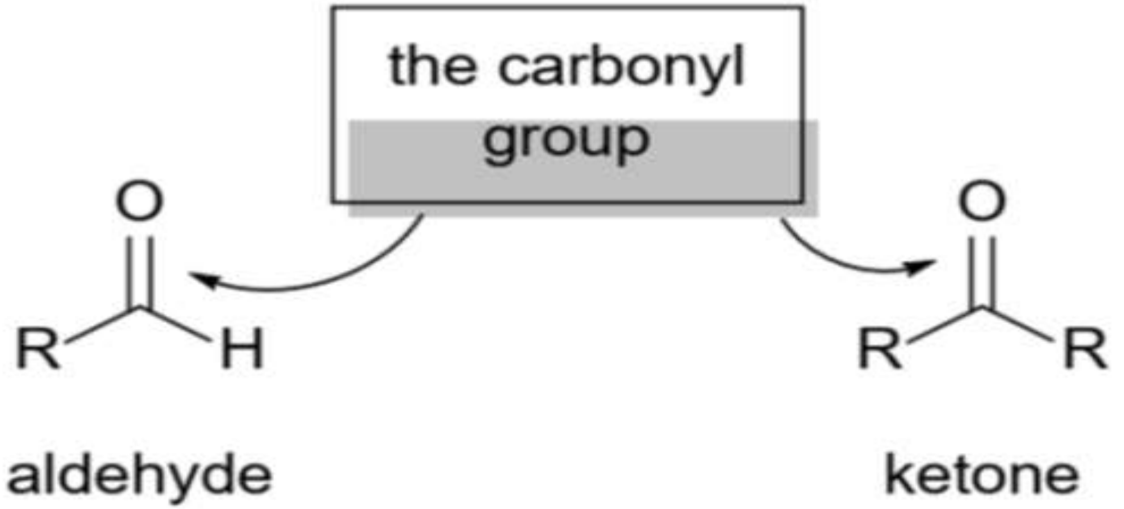
- To learn to recognize the aldehydes, ketones, and alcohols.
- To learn the major chemical reactions of aldehydes, ketones, and alcohols.
- To distinguish aldehydes, ketones, and alcohols by their chemical reactions and reactivity.

Introduction

In this experiment, you will be asked to identify an unknown liquid, which will be either an alcohol, aldehyde, or ketone. Identification will be accomplished by carrying out chemical tests, called classification tests, preparing a solid derivative of the unknown and determining its melting point (MP), making careful observations.



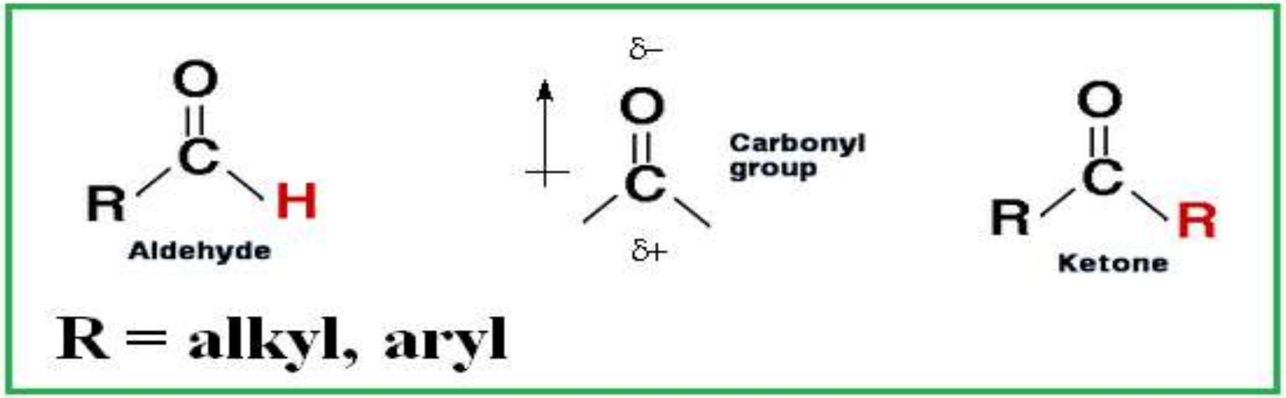
R = H, alkyl
R' = H; alkyl
R" = H; alkyl
alcohol



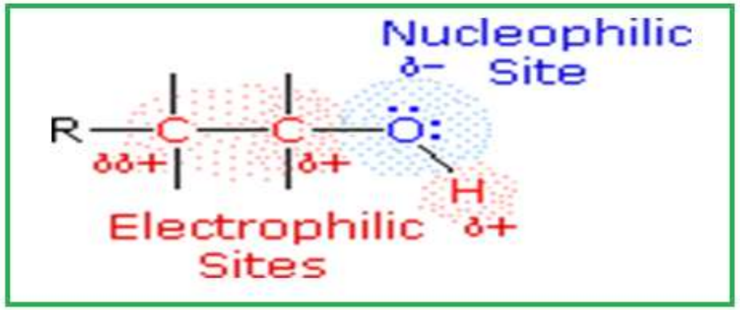
Introduction

- Aldehydes and ketones are both characterized by the carbonyl group, C=O.
- Aldehydes have at least one hydrogen bonded to the carbonyl carbon whereas in ketones, both bonds are to alkyl or aryl groups.
- Carbon of the carbonyl group is sp^2 hybridized, and the C=O bond is polar.

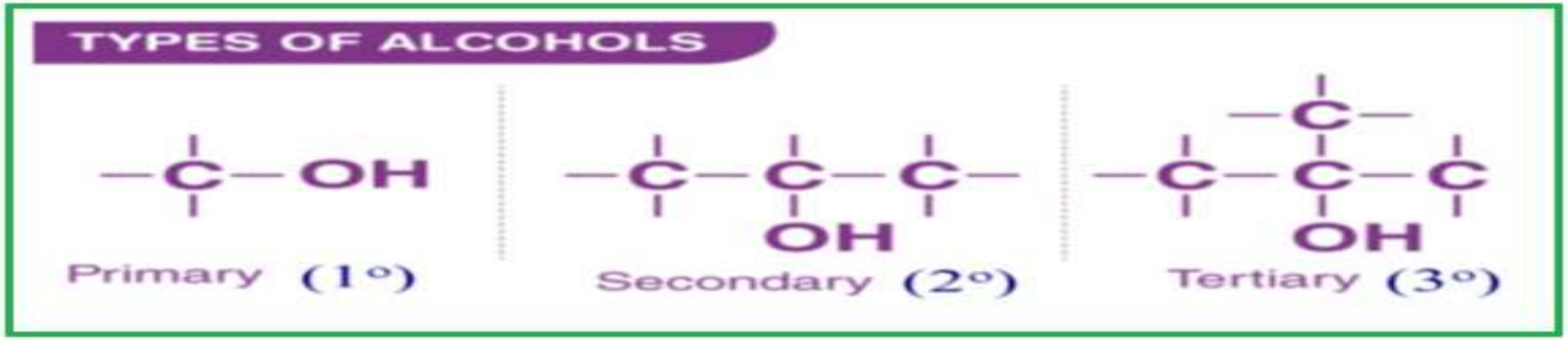
- Two types of chemical behavior will be tested. First, in both aldehydes and ketones, the carbonyl group reacts well with many reagents to form derivatives. Secondly, aldehydes are readily oxidized by mild oxidizing agents that do not react with ketones.
- Several tests that work for methyl ketones will also be tried.



- Structurally, alcohols have a hydroxy group bonded saturated carbon.



- The reactions of alcohols involve the <u>polar carbon– oxygen and oxygen – hydrogen bonds.</u>
- Alcohols are classified as <u>primary, secondary, or tertiary</u>, and their rates of reaction frequently vary depending on the structure.



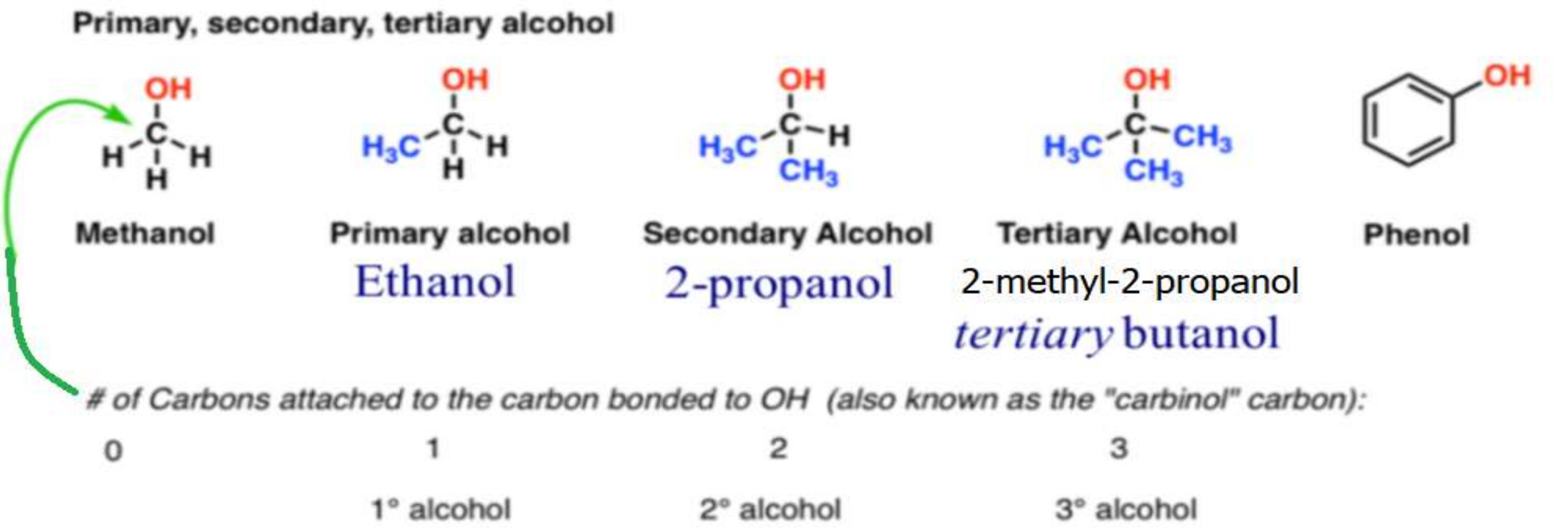
- In **chemistry**, a **nucleophile is a chemical species that forms bonds by donating an electron pair**. All molecules and ions with a free pair of electrons or at least one pi bond can act as nucleophiles. Because nucleophiles donate electrons, they are Lewis bases.

- **Electrophiles are electron-deficient species that are attracted to an electron-rich center. Electrophiles react by accepting an electron pair in order to form a bond to a nucleophile including the interactions of a proton and a base**

Nomenclature

Alcohols:

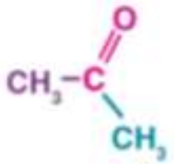
In the IUPAC system, alcohols are named by changing the ending of the parent alkane name to *-ol.* Alcohols are classified according to the number of carbon atoms attached to the carbon atom that is attached to the OH group.



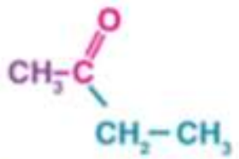
Nomenclature (التسمية)

Ketones:

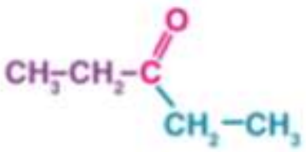
- The longest chain containing the carbonyl group gives the stem; ending *one*
- If substituents are present number from the end of the chain so the carbonyl group has the lowest possible number.
- There are non-systematic names for the common aldehydes and ketones.



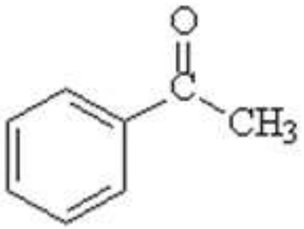
propanone
(acetone)



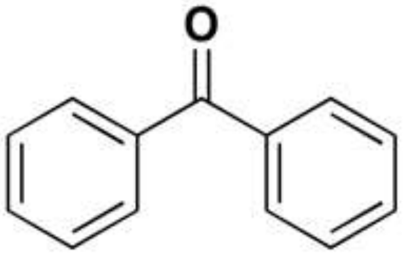
butanone



3-pentanone



acetophenone
(methyl phenyl ketone)

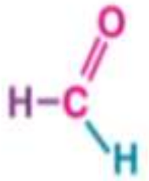


benzophenone
(diphenyl ketone)

Nomenclature

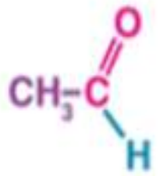
Aldehydes:

- The longest chain containing the CHO group gives the stem; **ending *al***
- If substituents are present, start the numbering from the aldehyde group - C1



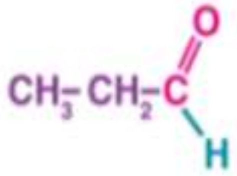
Methanal

formaldehyde



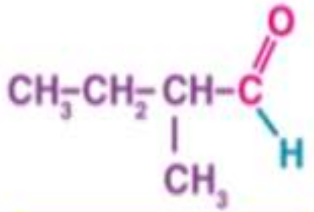
Ethanal

acetaldehyde

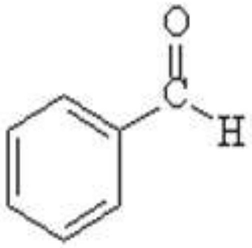


Propanal

propionaldehyde



2-Methylbutanal



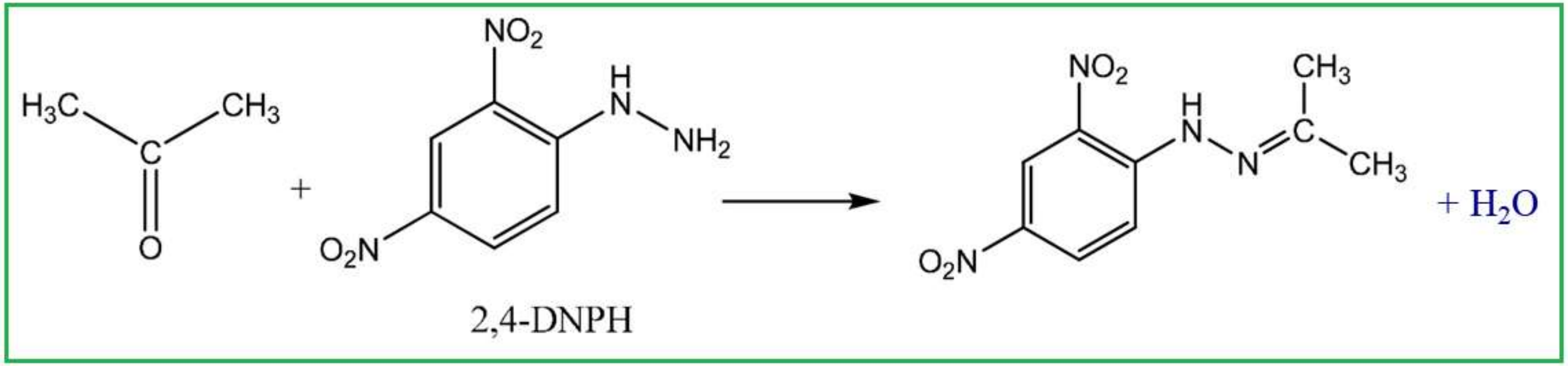
benzaldehyde

Reactions of Aldehydes and Ketones

1. 2,4-Dinitrophenylhydrazine (2,4-DNP)

This orange–red solution of 2,4-DNPH in H_2SO_4 produces an immediate precipitate with most aldehydes and ketones called 2,4-dinitrophenylhydrazone derivatives, colored **yellow to deep red**.

Example:



https://youtu.be/sYKPlpf0upA

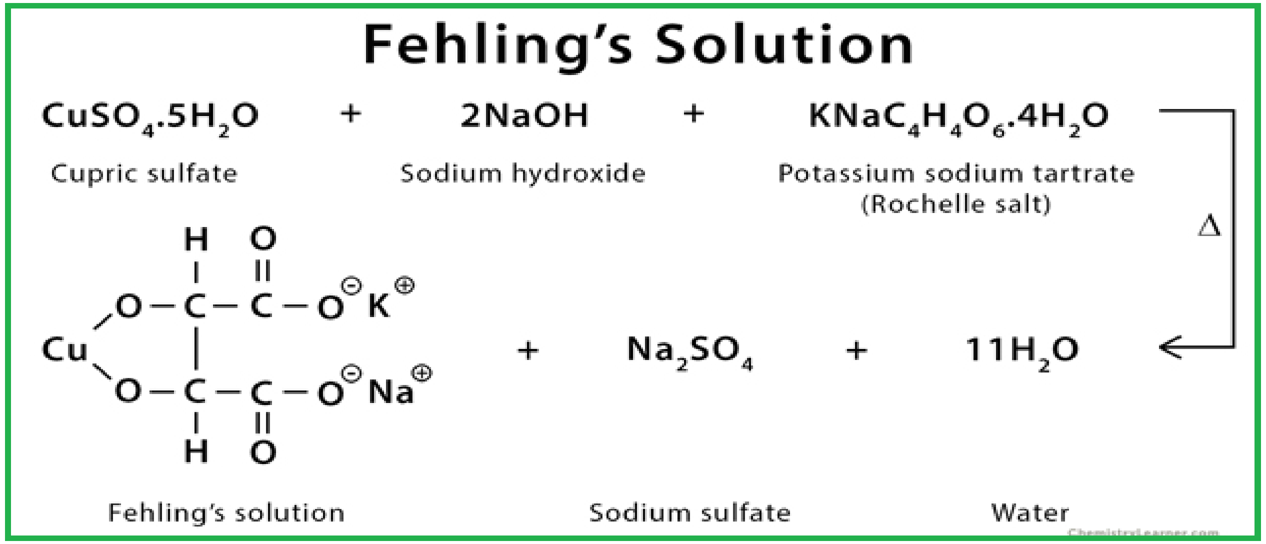
2,4-DNP test with aldehyde and ketone

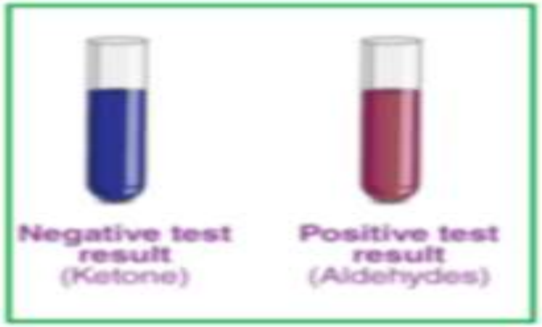
2. Fehling's Test (اختبار فيلينج)

- Fehling's solution of is an alkaline solution of sodium tartrate, in which copper(II) ion is soluble because of complex formation.
- Fehling's is a very mild oxidizing agent, oxidize aldehydes but not much else.

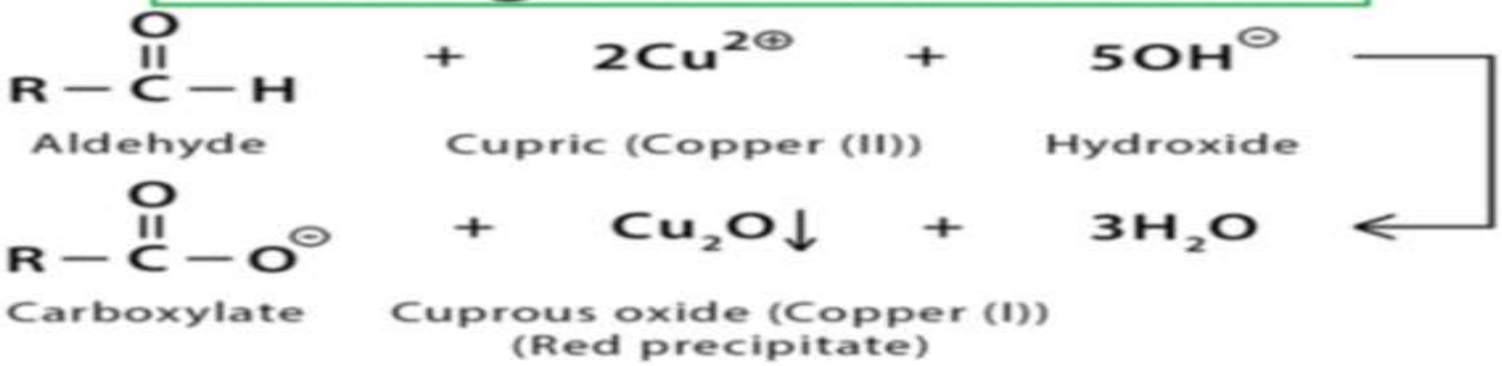
Prep. Notes

- **Fehling I** consists of 7 g of hydrated copper(II) sulfate dissolved in 100 mL of dist. water.
- **Fehling II** is made by dissolving 35 g of potassium sodium tartrate and 10 g of sodium hydroxide in 100 mL of dist. water.
- **Fehling's reagent:** Equal volumes of Fehling I and Fehling II are mixed to form a deep blue solution.

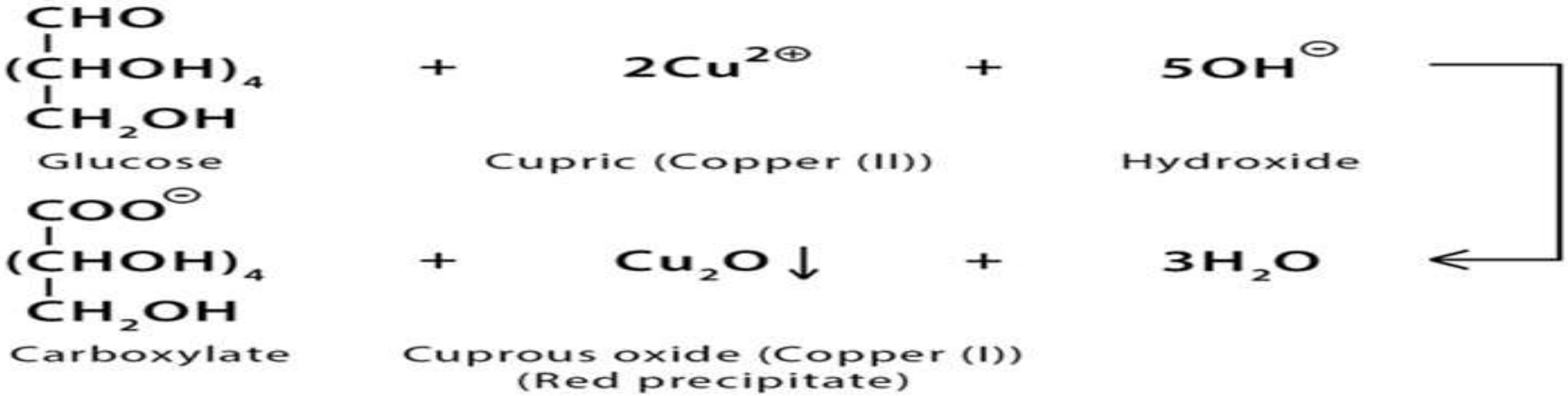




Fehling's Test Reaction



Fehling's Test for Glucose



https://youtu.be/yjLB_ntM324

Fehling's Test with Sugar (Glucose and Sucrose)

3. Tollens' Test

- Tollens' test, also known as silver-mirror test (اختبار المرآة الفضية), is a **qualitative laboratory test used to distinguish between an aldehyde and a ketone.** It exploits the fact that aldehydes are readily oxidized, whereas ketones are not.
- Tollens' test uses a reagent known as Tollens' reagent, which is a colorless, basic, aqueous solution containing silver ions coordinated to ammonia $[Ag(NH_3)_2^+]$. It is prepared using a two steps procedure:
- **Step 1:** Aqueous silver nitrate is mixed with aqueous sodium hydroxide.

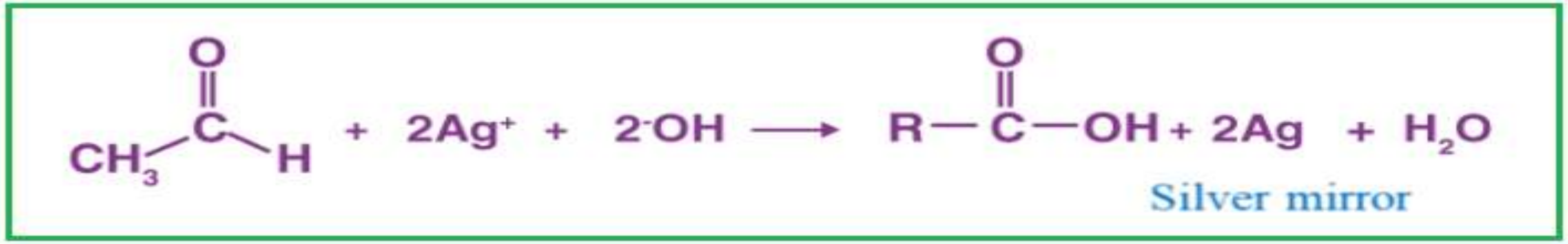
$$AgNO_3 + NaOH \rightarrow AgOH + NaNO_3$$

$$2AgOH \rightarrow Ag_2O + H_2O$$

- **Step 2:** Aqueous ammonia is added drop-wise until the precipitated silver oxide completely dissolves.

$$Ag_2O + 4NH_3 + H_2O \rightarrow 2[Ag(NH_3)_2]^+ + 2OH^-$$

Tollens' reagent oxidizes an aldehyde into the corresponding carboxylic acid.



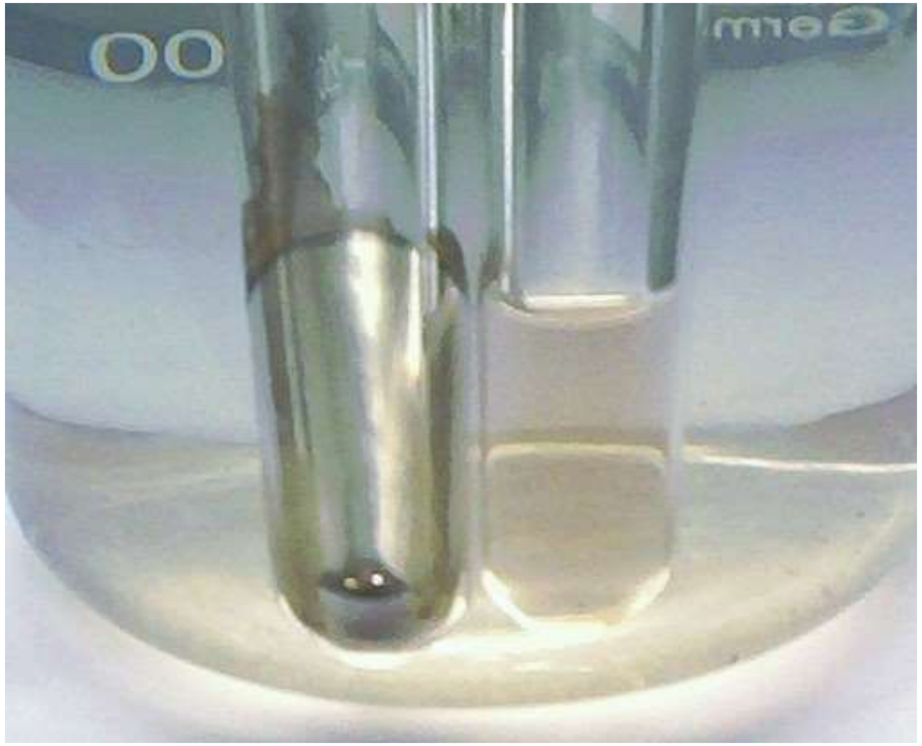


Figure 1: Tollens' test for aldehyde: left side positive (silver mirror), right side negative

Ketones are not oxidized by Tollens’ reagent, so the treatment of a ketone with Tollens’ reagent in a glass test tube does not result in a silver mirror (Figure 1; right).

https://youtu.be/CMCVpE8p8yo
Tollens’ Test for aldehyde

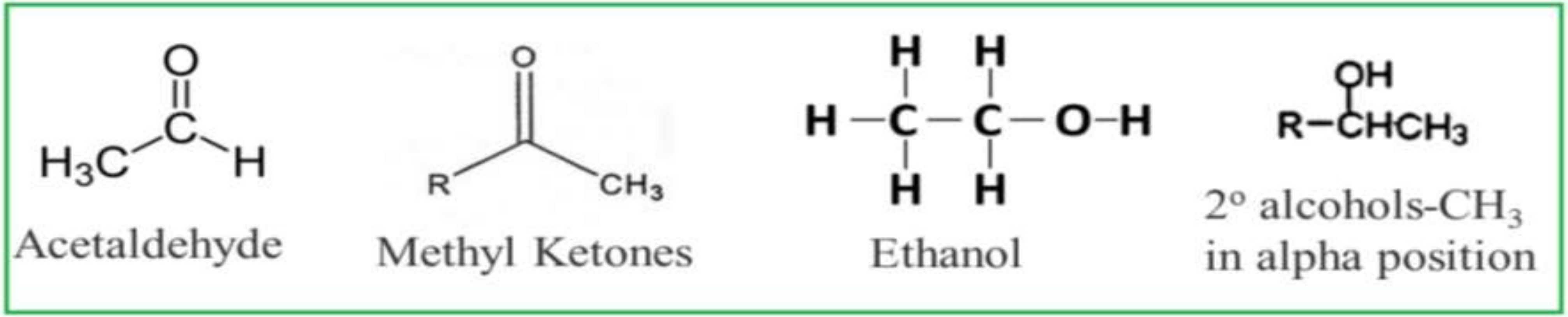
4. Iodoform Test

Iodoform test is used to check the presence of carbonyl compounds with the structure R-CO-CH_3 or alcohols with the structure R-CH(OH)-CH_3 to give a yellow ppt (CHI_3).

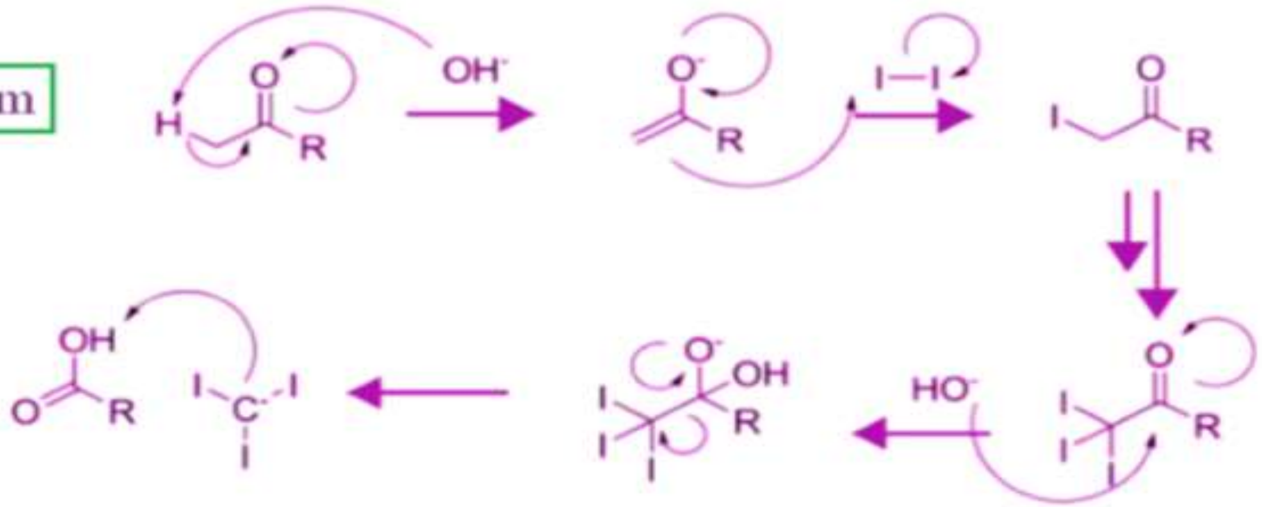
Iodoform Test Description

When Iodine and sodium hydroxide are added to a compound that contains either a methyl ketone or a secondary alcohol with a methyl group in the alpha position, a pale-yellow precipitate of iodoform or triiodomethane is formed. It can be used to identify aldehydes or ketones. If an aldehyde gives a positive iodoform test, then it must be acetaldehyde since it is the only aldehyde with a $CH_3C=O$ group. Given below are a few example reactions for positive iodoform tests.

Compounds That Give Positive Iodoform Test



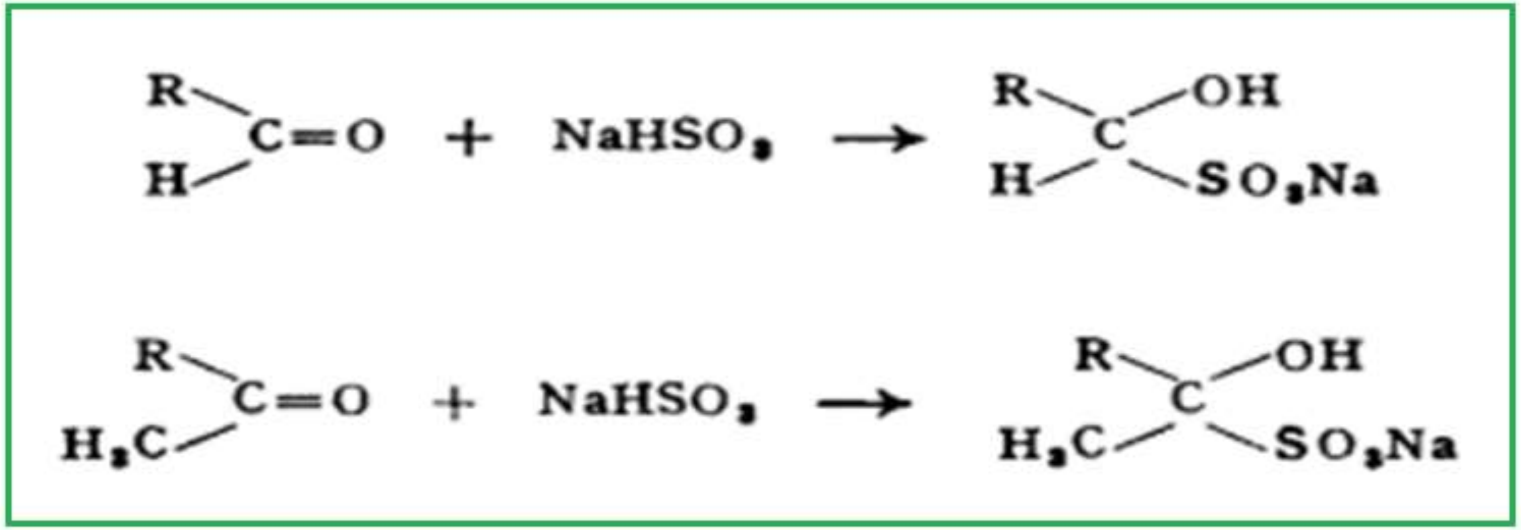
Mechanism

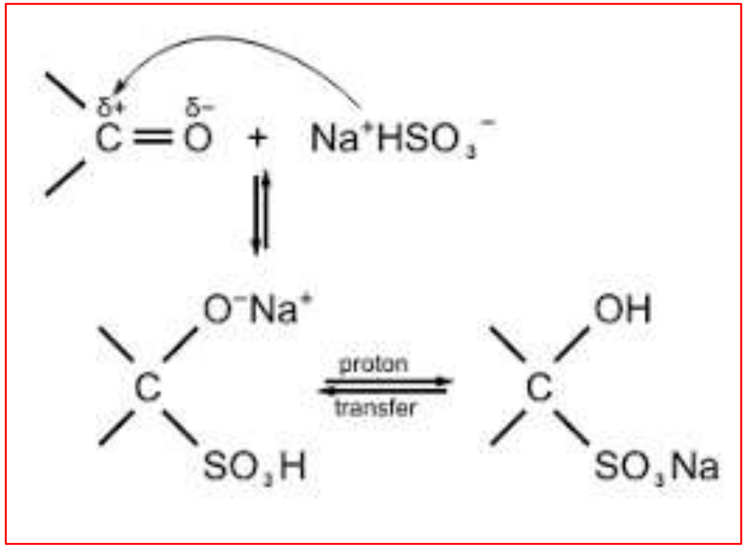


https://youtu.be/mcfOXuYPn6U
Iodoform Test

5. Sodium Bisulfite Test

Sodium bisulfite adds to aldehydes and methyl ketones to give crystalline addition products.





https://youtu.be/Lzg_ZJ9E7C4
https://youtu.be/QOMOyfzvLSs
Sodium bisulfite Test of aldehyde and ketone

6. Lucas Test

Lucas test is used to differentiate and categorize primary, secondary and tertiary alcohols using a solution of anhydrous zinc chloride in concentrated hydrochloric acid. This solution is commonly referred to as the Lucas reagent.

What is the Lucas Test?

Primary, Secondary and Tertiary Alcohols are classified based on their reactivity with the Lucas reagent. The reaction that occurs in the **Lucas test can be seen as a nucleophilic substitution reaction**. In this reaction, the Chloride in the zinc-chloride bond is replaced with a hydroxyl group originating from the given alcohol. The reaction displays the difference in reactivity of the different types of alcohol as well as the difference in the ease at which corresponding carbocations of the alcohols are formed. **For example, primary alcohols do not react readily at room temperature with the added Lucas reagent whereas tertiary alcohols react immediately.** The observation of a change where the **clear and colorless** characteristic of the solution changes to a **turbid, cloudy, and hazy** one implies that a chloroalkane has formed. This observation is a positive indication for the Lucas test.

Primary, Secondary, and Tertiary alcohols react with the Lucas reagent to form the **chloroalkane at different rates.** **Tertiary alcohols react the fastest** due to the fact that organic chloride has relatively low solubility in the aqueous mixture.

Alcohols are soluble in Lucas reagent, but the alkyl halides which form from the reaction are not soluble. Therefore, two layers form in the reaction medium. How the layers separate can indicate the type of reaction as shown below.

Tertiary alcohol $R_3COH + HCl \xrightarrow{ZnCl_2} R_3CCl + H_2O$

(The layers separate immediately)

Secondary alcohol $R_2CHOH + HCl \xrightarrow{ZnCl_2} R_2CHCl + H_2O$

(The layers separate within 1-5 minutes)

Primary alcohol $RCH_2OH + HCl \xrightarrow{ZnCl_2}$ No reaction / Slow reaction

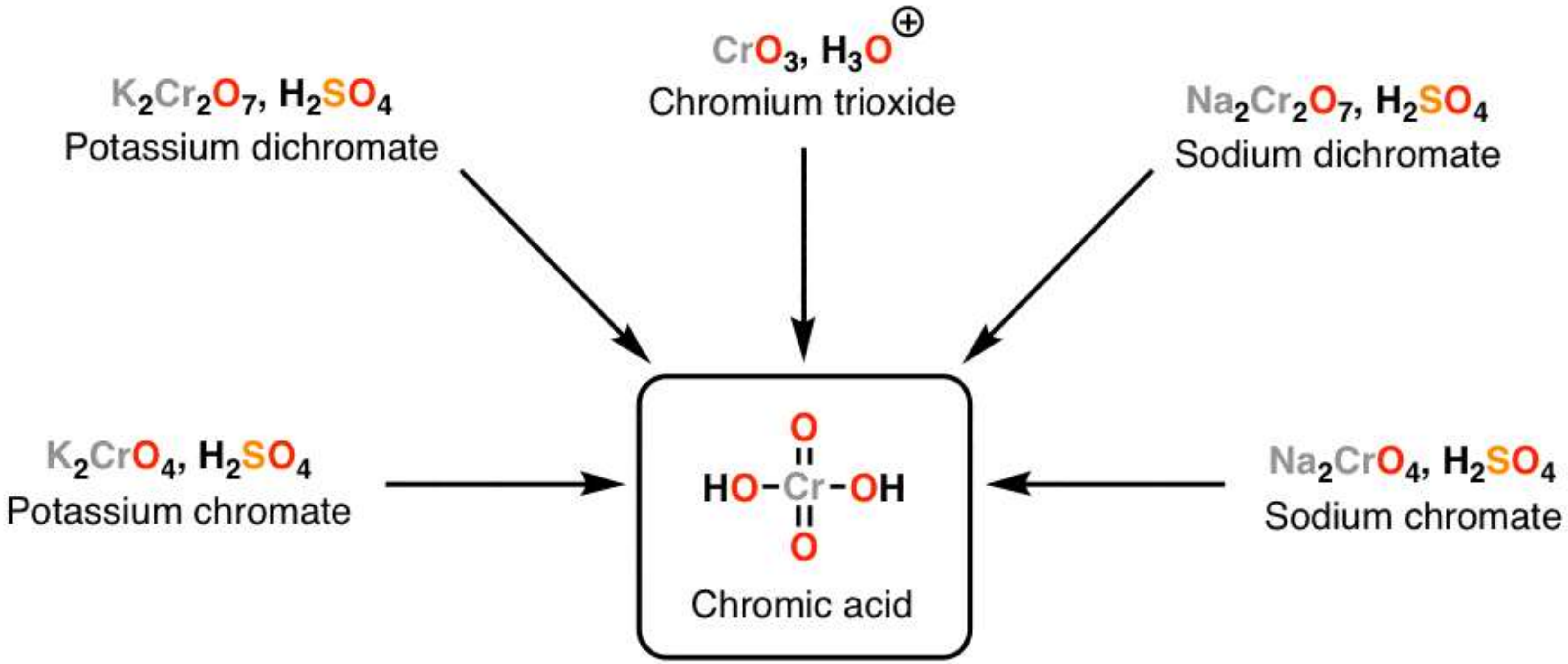
(The layers do not separate)

https://youtu.be/ZuAKxcxdDF8

Lucas Test for 1^o-, 2^o-, and 3^o - alcohols

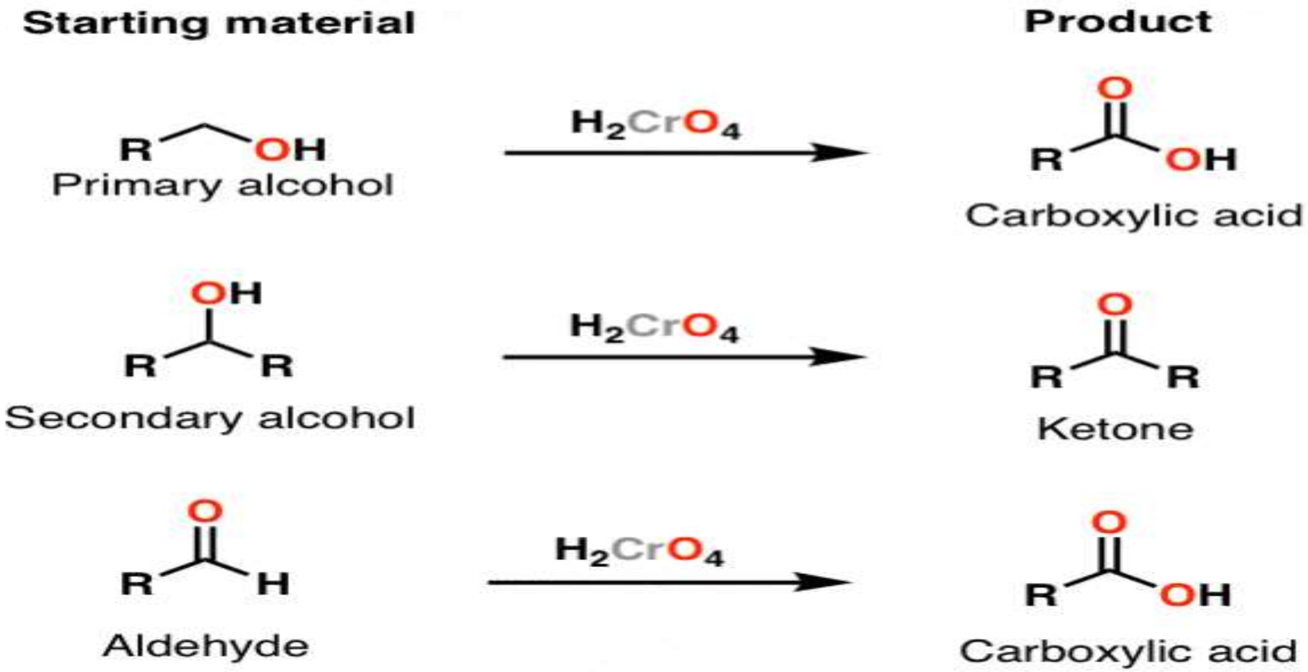
6. Chromic Anhydride – Oxidation of Alcohols

Chromic acid (H_2CrO_4) is often made “in situ” (that is, in the reaction flask) through the addition of acid to sources of chromium (such chromate salts) as shown below:



Chromic acid, H_2CrO_4, is a strong acid and a reagent for oxidizing alcohols to ketones and carboxylic acids.

Chromic acid is oxidized primary alcohols to aldehydes and then to carboxylic acids. Secondary alcohols are readily oxidized to ketones Tertiary alcohols are not readily oxidized.



https://youtu.be/aoCH-xZdvIo

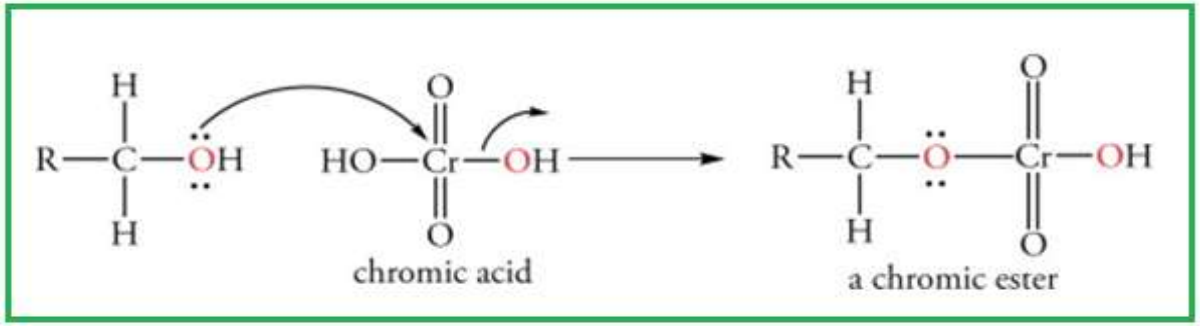
Oxidation of alcohols by $K_2Cr_2O_7$

https://youtu.be/HPEBc8ywUhA

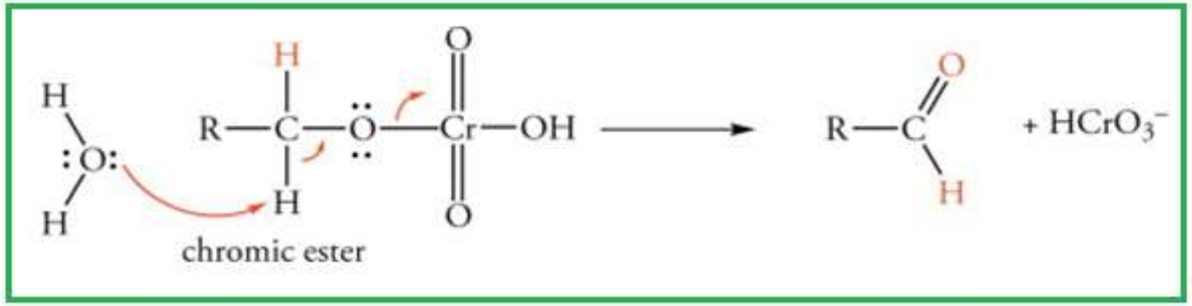
Lucas test & oxidation of alcohol by chromic acid

Mechanism

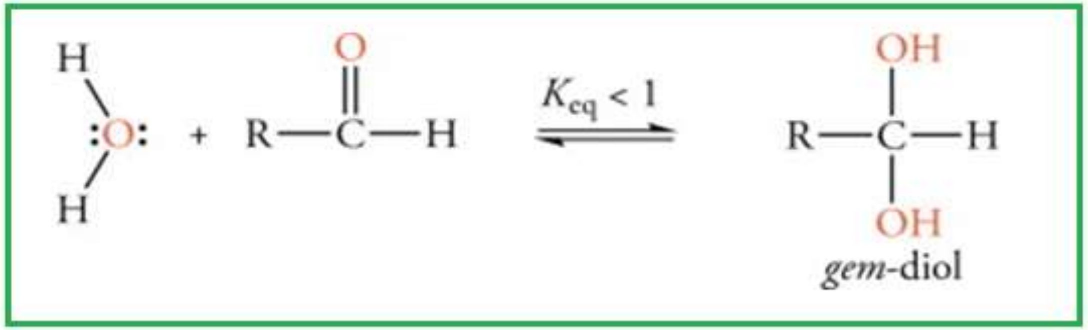
1. Chromic acid (H_2CrO_4) reacts with alcohols to form a chromic ester in which the alcohol oxygen atom bridges the carbon and chromium atoms.



2. Water extracts a hydrogen atom from the alcohol carbon, the electron pair in the C—H bond acts as a nucleophile, and the O—Cr bond in the chromic ester breaks to form a carbon–carbon double bond.



3. In an aqueous acid solution, chromic acid converts aldehydes to carboxylic acids.



4. The *gem*-diol is an alcohol. One of its hydroxyl groups is oxidized by way of a chromic half-ester in the same manner as alcohols giving carboxylic acid.