Quadrant II – Transcript and Related Materials

Programme: F.Y.B.Sc. (Chemistry)

Subject: Chemistry

Course Code: CHC 102 Section B

Course Title: Physical Chemistry and Organic Chemistry

Unit: 03- Alcohols

Module Name: Alcohols: Reactions

Module No: 13

Name of the Presenter: Ms. Anuja B. Naik

Notes

Transcript of the video

Hello students, I am Ms. Anuja Naik from Ganpat Parsekar College of Education, Harmal, Pernem Goa and I will be dealing with Aryl halides -Reactions (Chlorobenzene)-Nucleophilic Aromatic Substitution (replacement by -OH group).

The lecture deals with,

- **Reactions of Alcohols**
  - Reaction with sodium
  - Reaction with Hydrogen Halides (Lucas test)
  - Reaction with carboxylic acids (Esterification reaction)
  - Oxidation reactions with PCC, alk.$KMnO_4$, acidic dichromate, conc. HNO_3
  - Oppeneaur oxidation

So, at the end of the lecture, the student will be able to:

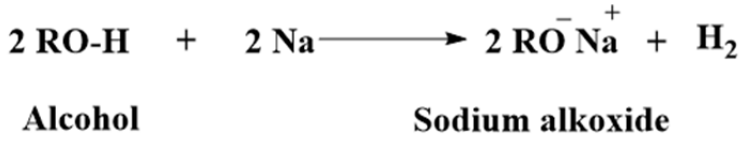
Learn different Reactions of Alcohols

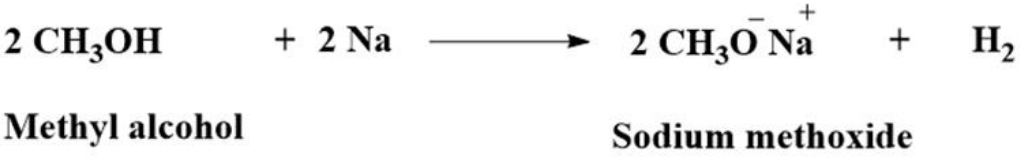
- Reaction with sodium

- Reaction with Hydrogen Halides (Lucas test)
- Reaction with carboxylic acids (Esterification reaction)
- Oxidation reactions with PCC, alk.$KMnO_4$, acidic dichromate, conc. HNO_3
- Oppeneaur oxidation

Reaction with sodium

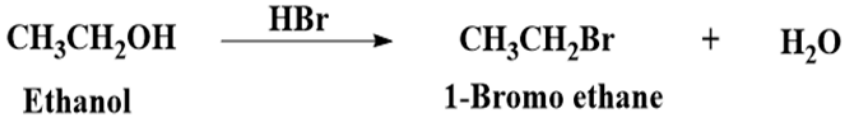
Alcohols react with Na to liberate hydrogen gas. The product formed is alkoxide.

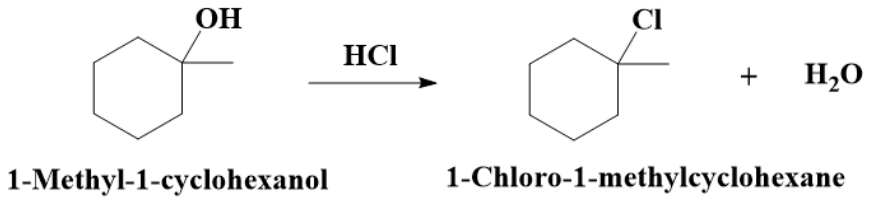


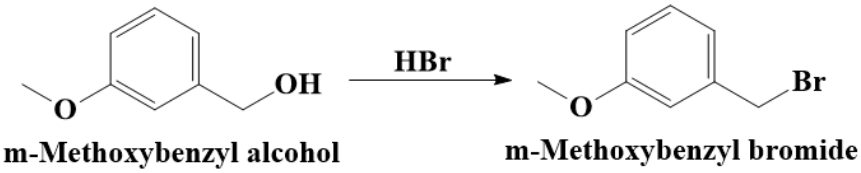


Next, Reaction with Hydrogen Halides (Lucas test)

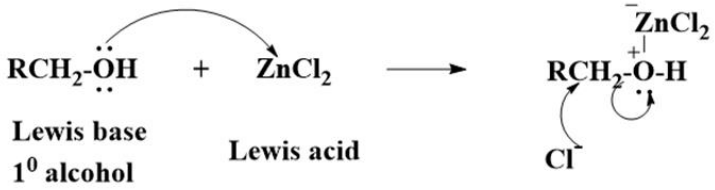
The reactions of alcohols with HX give 1^0, 2^0 and 3^0 alkyl halides. This is Nucleophilic substitution reaction. And More substituted alcohols react more rapidly with HX i.e. 3^0 alcohol react faster then 2^0 alcohol then 1^0 alcohol.

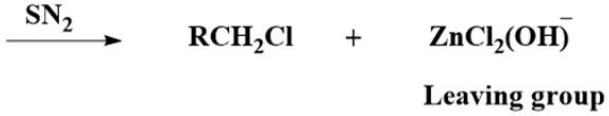






The reactivity of hydrogen halides increases with increasing acidity. HI is more reactive then HBr and HCl. Because Cl^- is a poorer nucleophile than Br^- or I^-, the reaction of 1^0 alcohols with HCl occurs only when an additional Lewis acid catalyst like $ZnCl_2$, is added. $ZnCl_2$ complexes with the O atom of the alcohol in a Lewis acid –base reaction, making a good leaving group and facilitating the SN_2 reaction.





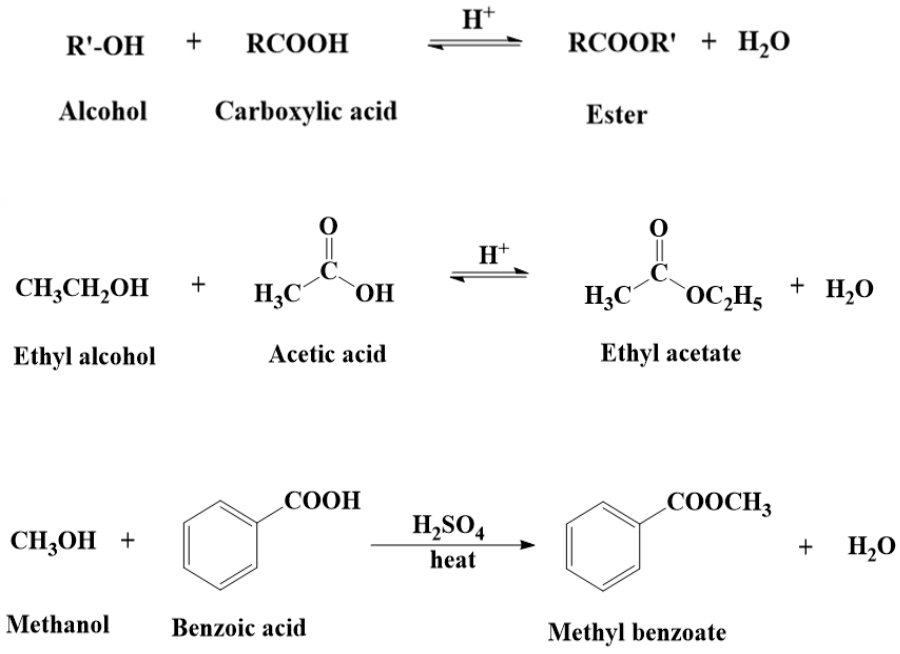
Lucas test This test helps to distinguish between primary, secondary and tertiary alcohols. In this test, alcohols are treated with a solution of HCl and $ZnCl_2$ (Lucas

reagent) to form alkyl halides, where $ZnCl_2$ serves as a catalyst. The alkyl chloride formed is insoluble which causes the solution to become cloudy before it separates as a distinct layer. The three types of alcohols undergo the reaction at different rates.

3^0 alcohols react with Lucas reagent rapidly. As a result cloudiness appears immediately. While 2^0 alcohols react with Lucas reagent slowly. As a result cloudiness appears in 5 minutes. While 1^0 alcohols react with Lucas reagent even more slowly. As a result solution remains clear.

Next, Reaction with carboxylic acids (Esterification reaction)

Alcohols react with carboxylic acids to form esters in the presence of conc.H_2SO_4 as a catalyst. Acid catalysed condensation of an alcohol and a carboxylic acid yields an ester and water. This reaction is known as Fischer esterification.



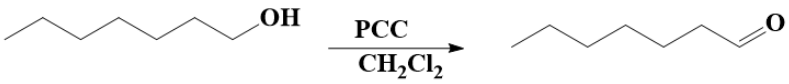
Next, Oxidation reactions

The oxidation of an alcohol involves the loss of one or more hydrogens (α-hydrogens) from the carbon bearing the –OH group. A primary alcohol contains

two α-hydrogens, and can either lose one of them to form an aldehyde or both of them to form a carboxylic acid. A secondary alcohol can lose its only α- hydrogen to form a ketone. A tertiary alcohol contains no α- hydrogens and is not oxidized.

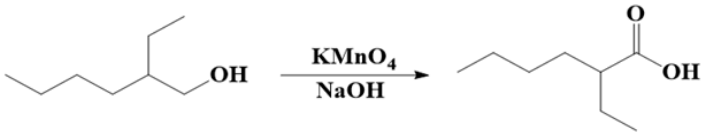
PCC is Pyridinium chlorochromate ($C_5H_6NCrO_3Cl$)**.** It is a soluble complex of chromium trioxide (CrO_3) and pyridine in dilute HCl.It is a mild oxidizing agent which oxidises primary alcohol to aldehyde. It does not oxidize the aldehyde to carboxylic acid.

Isobutyl alcohol **Isobutyraldehyde**

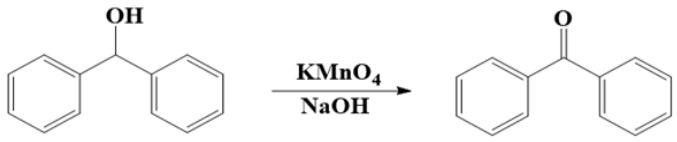


1-Heptanol **Heptanal**

Alkaline $KMnO_4$ It is a strong oxidising agent which oxidises primary alcohols to carboxylic acids and secondary alcohols to ketone. In the course of reaction, the purple Mn (VII) is reduced to Mn (IV), which precipitates as brown manganese dioxide (MnO_2).



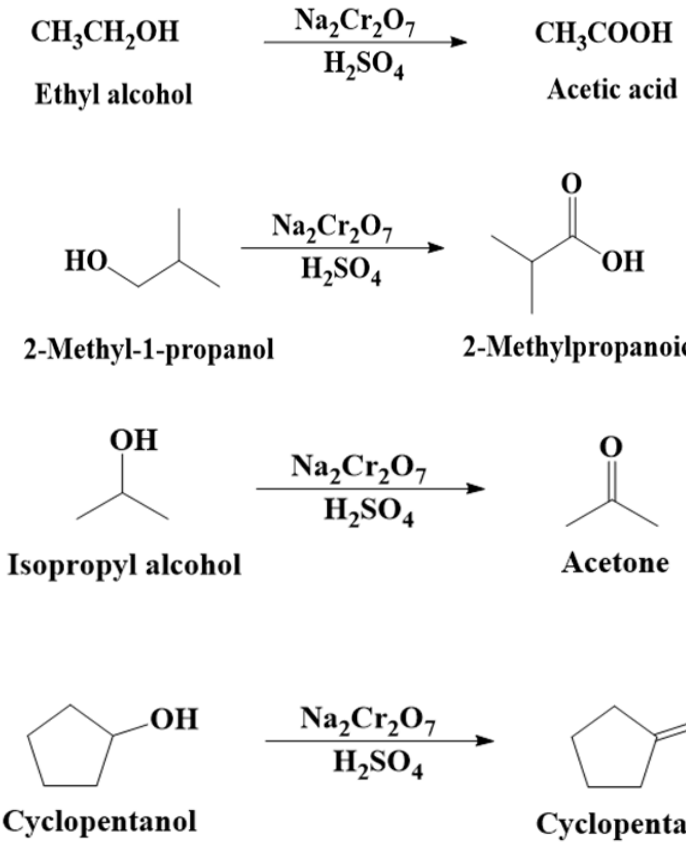
2-Ethyl-1-hexanol **2-Ethyl hexanoic acid**



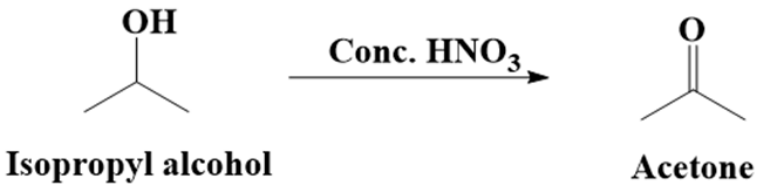
Diphenylmethanol **Diphenylmethanone**
(Benzophenone)

Acidic dichromate ($Na_2Cr_2O_7$ / H_2SO_4 , $K_2Cr_2O_7$ / H_2SO_4)

These are strong oxidising agents which oxidise primary alcohols to carboxylic acids and secondary alcohols to ketone.

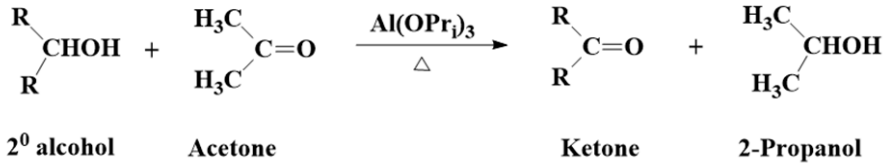


Conc. HNO_3 oxidises primary alcohols to carboxylic acids and secondary alcohols to ketone.

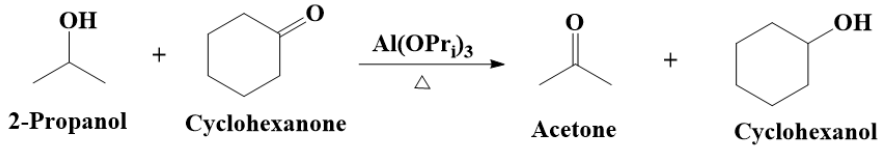


Oppenauer oxidation This is named after Rupert Viktor Oppenauer. This method selectively oxidises 2^0 alcohols to ketones. The alcohol is heated with Al-isopropoxide in the presence of a hydrogen acceptor like acetone or

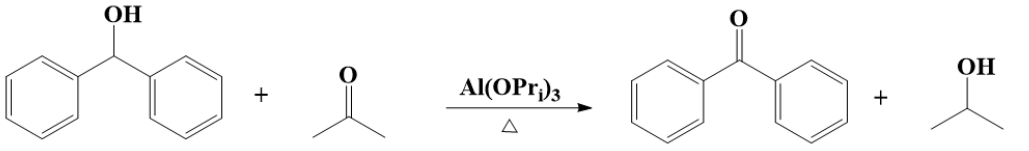
benzophenone. This oxidation is the reverse of Meerwein-Pondorf-Verley (MPV) reaction.



2^0 alcohol Acetone Ketone 2-Propanol



2-Propanol Cyclohexanone Acetone Cyclohexanol



Diphenylmethanol Acetone Benzophenone 2-Propanol

To summarise

- ✓ Reactions of alcohols with sodium give alkoxides and liberate hydrogen gas.
- ✓ Reactions of alcohols with HX give 1^0, 2^0 and 3^0 alkyl halides.
- ✓ Lucas test helps to distinguish between primary, secondary and tertiary alcohols.
- ✓ Alcohols react with carboxylic acids to form esters in the presence of conc.H_2SO_4 as a catalyst.
- ✓ PCC is a mild oxidizing agent and does not oxidize the aldehyde to carboxylic acid.

- ✓ Alkaline $KMnO_4$ and Acidic Dichromate ($Na_2Cr_2O_7$ / H_2SO_4 , $K_2Cr_2O_7$ / H_2SO_4) are strong oxidising agents which oxidise primary alcohols to carboxylic acids and secondary alcohols to ketone.
- ✓ Conc. HNO_3 oxidises primary alcohols to carboxylic acids and secondary alcohols to ketone.
- ✓ Oppenauer oxidation method selectively oxidises 2^0 alcohols to ketones in the presence of Al-isopropoxide and hydrogen acceptor like acetone or benzophenone.

Finally, these are the references.

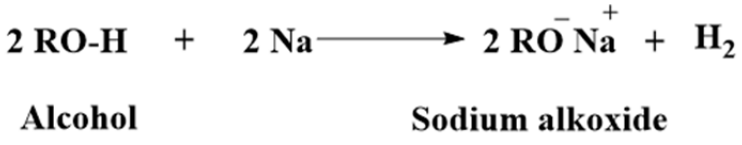
Thank you.

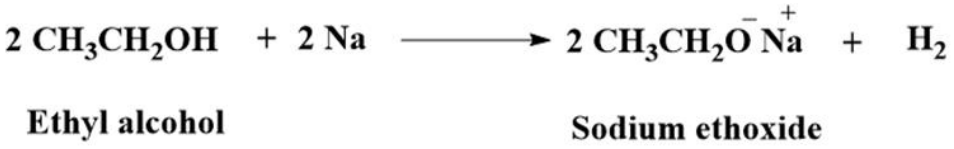
<u>Summary of the video (Abstract of the transcript)</u>

- **<u>Reactions of Alcohols</u>**
  - Reaction with sodium
  - Reaction with Hydrogen Halides (Lucas test)
  - Reaction with carboxylic acids (Esterification reaction)
  - Oxidation reactions with PCC, alk.$KMnO_4$, acidic dichromate, conc. HNO_3
  - Oppeneaur oxidation

- ✓ **<u>Reaction with sodium</u>**

- Alcohols react with Na to liberate hydrogen gas.
- The product formed is alkoxide.

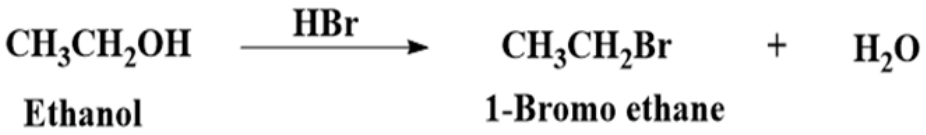


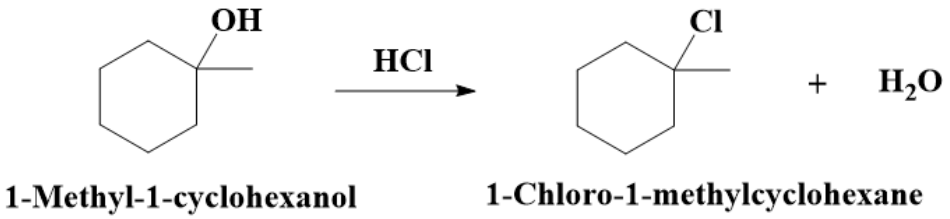


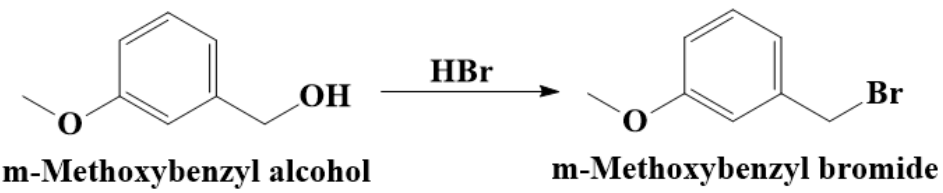
✓ **<u>Reaction with Hydrogen Halides (Lucas test)</u>**

- The reactions of alcohols with HX give 1^0, 2^0 and 3^0 alkyl halides.
- This is Nucleophilic substitution reaction.
- More substituted alcohols react more rapidly with HX.

$$3^0 \text{ alcohol} > 2^0 \text{ alcohol} > 1^0 \text{ alcohol}$$



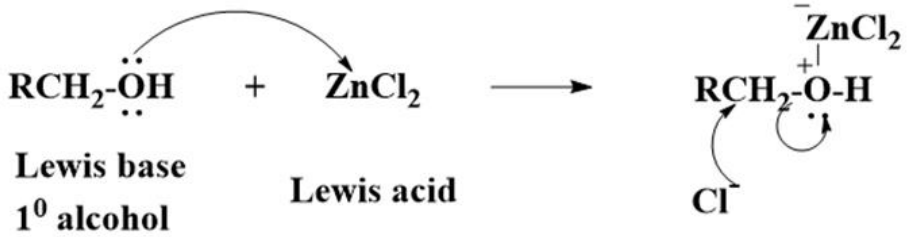


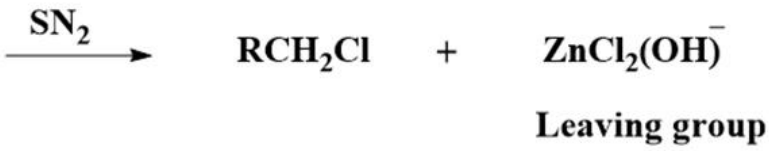


- The reactivity of hydrogen halides increases with increasing acidity.

$$HCl < HBr < HI$$

- Because Cl^- is a poorer nucleophile than Br^- or I^-, the reaction of 1^0 alcohols with HCl occurs only when an additional Lewis acid catalyst like $ZnCl_2$, is added.
- $ZnCl_2$ complexes with the O atom of the alcohol in a Lewis acid –base reaction, making a good leaving group and facilitating the SN_2 reaction.





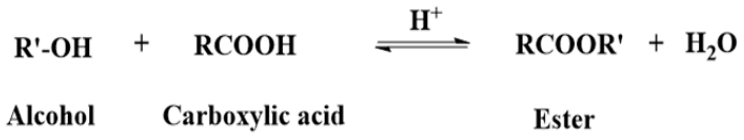
Lucas test

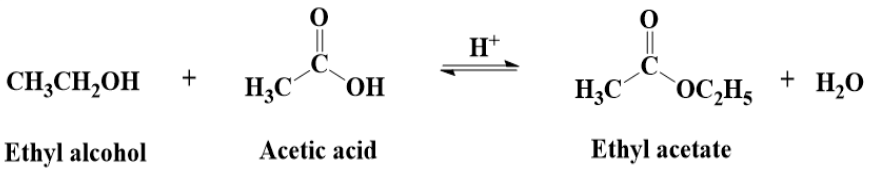
- This test helps to distinguish between primary, secondary and tertiary alcohols.
- In this test, alcohols are treated with a solution of HCl and $ZnCl_2$ (Lucas reagent) to form alkyl halides, where $ZnCl_2$ serves as a catalyst.
- The alkyl chloride formed is insoluble which causes the solution to become cloudy before it separates as a distinct layer.
- The three types of alcohols undergo the reaction at different rates.

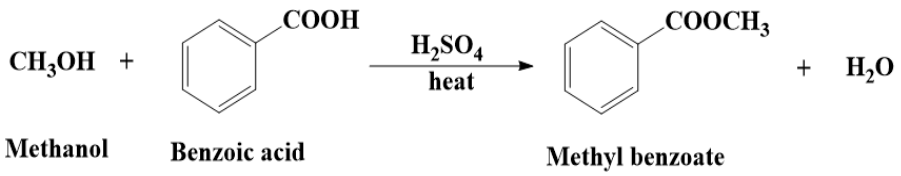
3^0 alcohols	2^0 alcohols	1^0 alcohols
React with Lucas reagent rapidly	React with Lucas reagent slowly	React with Lucas reagent even more slowly
Cloudiness appears immediately	Cloudiness appears in 5 minutes	Solution remains clear

✓ **Reaction with carboxylic acids (Esterification reaction)**

- Alcohols react with carboxylic acids to form esters in the presence of conc.H_2SO_4 as a catalyst.
- Acid catalysed condensation of an alcohol and a carboxylic acid yields an ester and water. This reaction is known as Fischer esterification.







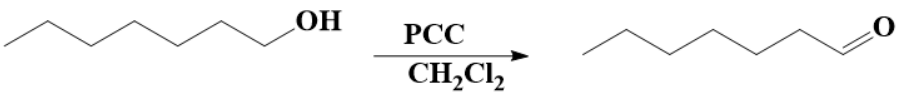
✓ **Oxidation reactions**

- The oxidation of an alcohol involves the loss of one or more hydrogens (α-hydrogens) from the carbon bearing the –OH group.
- A primary alcohol contains two α-hydrogens, and can either lose one of them to form an aldehyde or both of them to form a carboxylic acid.
- A secondary alcohol can lose its only α- hydrogen to form a ketone.
- A tertiary alcohol contains no α- hydrogens and is not oxidized.

a) PCC

- PCC is Pyridinium chlorochromate ($C_5H_6NCrO_3Cl$)
- It is a soluble complex of chromium trioxide (CrO_3) and pyridine in dilute HCl.
- It is a mild oxidizing agent which oxidises primary alcohol to aldehyde.It does not oxidize the aldehyde to carboxylic acid.

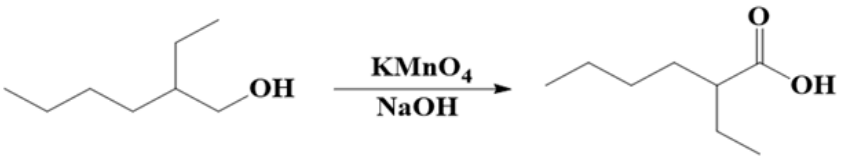
Isobutyl alcohol **Isobutyraldehyde**



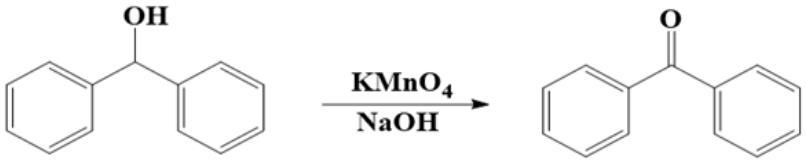
1-Heptanol **Heptanal**

b) Alkaline $KMnO_4$

- It is a strong oxidising agent which oxidises primary alcohols to carboxylic acids and secondary alcohols to ketone.
- In the course of reaction, the purple Mn (VII) is reduced to Mn (IV), which precipitates as brown manganese dioxide (MnO_2).



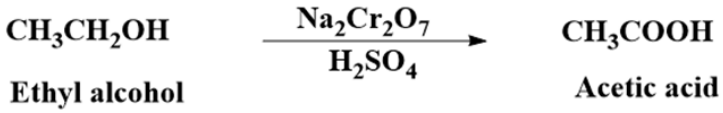
2-Ethyl-1-hexanol 2-Ethyl hexanoic acid



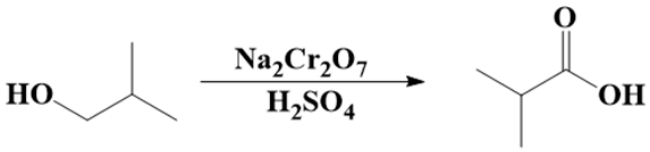
Diphenylmethanol Diphenylmethanone (Benzophenone)

c) Acidic dichromate ($Na_2Cr_2O_7$ / H_2SO_4 , $K_2Cr_2O_7$ / H_2SO_4)

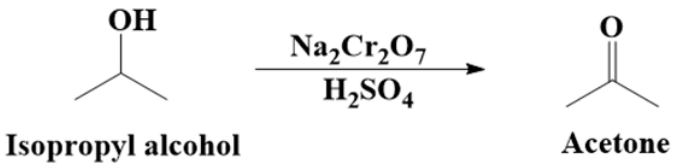
- These are strong oxidising agents which oxidise primary alcohols to carboxylic acids and secondary alcohols to ketone.



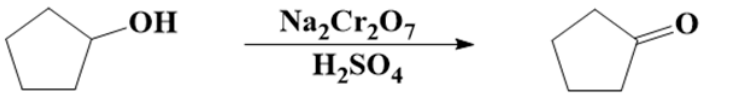
Ethyl alcohol Acetic acid



2-Methyl-1-propanol 2-Methylpropanoic acid



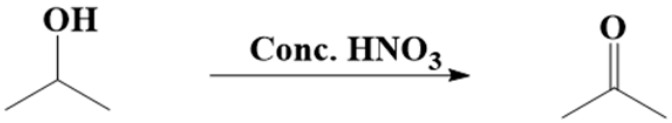
Isopropyl alcohol Acetone



Cyclopentanol Cyclopentanone

d) Conc. HNO_3

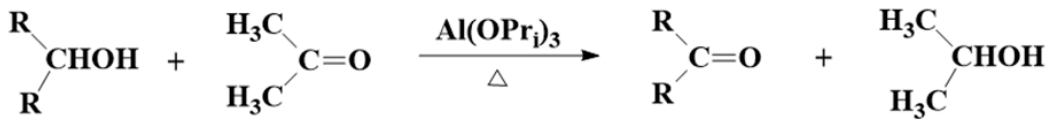
- Conc. HNO_3 oxidises primary alcohols to carboxylic acids and secondary alcohols to ketone.



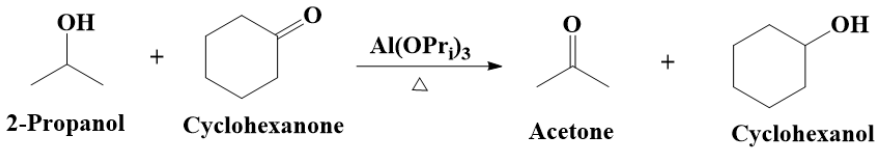
Isopropyl alcohol Acetone

e) Oppenauer oxidation

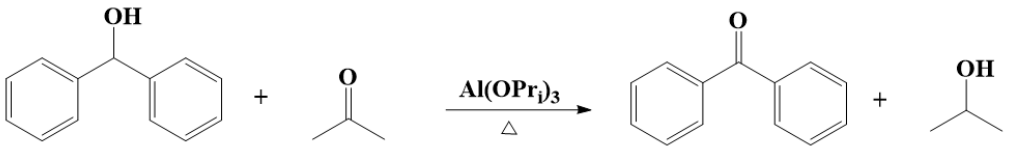
- This is named after Rupert Viktor Oppenauer.
- This method selectively oxidises 2^0 alcohols to ketones.
- The alcohol is heated with Al-isopropoxide in the presence of a hydrogen acceptor like acetone or benzophenone.
- This oxidation is the reverse of Meerwein-Pondorf-Verley (MPV) reaction.



2^0 alcohol Acetone Ketone 2-Propanol



2-Propanol + Cyclohexanone → Acetone + Cyclohexanol



Diphenylmethanol + Acetone → Benzophenone + 2-Propanol