

B.Sc. GE-II (Chemistry) I Year

Chemistry- Chemical Energetics, Equilibria and Functional Organic Chemistry

Unit 6

Alcohols, Phenols, Ether, aldehydes and Ketones

### Alcohols

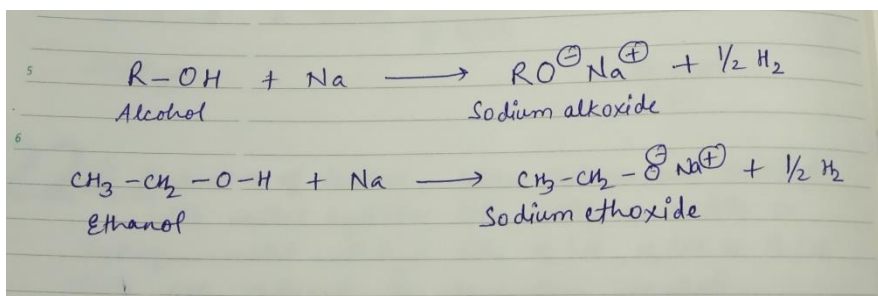
Reactions of Alcohols

Acidity of Alcohols

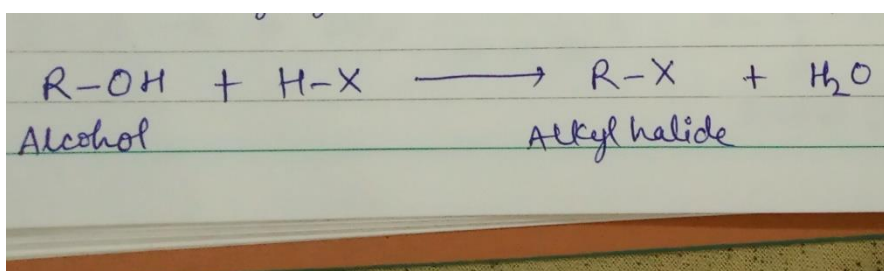
In alcohols a H-atom attached to electronegative O-atom which makes the O – H bond polar due to which the proton can be liberated easily. Therefore, Alcohols acts as a weak acids and forms alkoxides with active metals and liberates hydrogen gas. The ionization constant is  $10^{-18}$  which is less than that of water ( $10^{-14}$ ) thus, alcohols are weaker acids than the water.

1) Reaction with Sodium:

With sodium metal alcohol reacts to form alkoxides.



2) Reaction with hydrogen halides (HX): Alcohols reacts with hydrogen halides to form alkyl halides.



The reaction takes place through  $S_N1$  mechanism except for methanol and  $1^\circ$  alcohols.

Order of reactivity of alcohols:  $3^\circ > 2^\circ > 1^\circ$

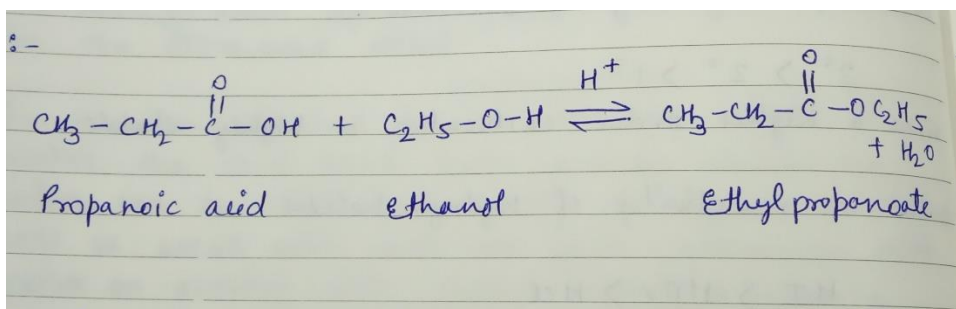
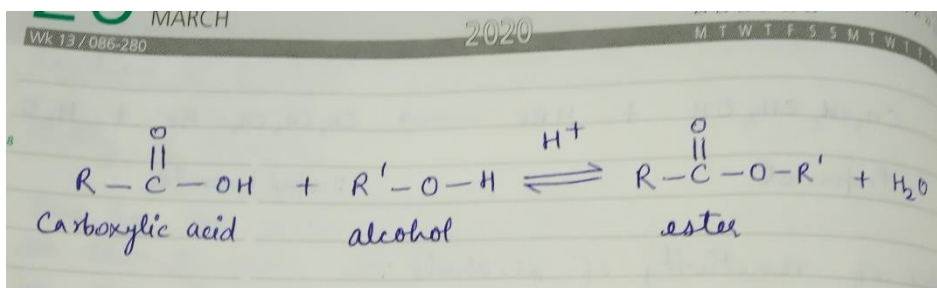
Order of reactivity of hydrogen halides:  $\text{HI} > \text{HBr} > \text{HCl}$

Lucas test: A solution of anhydrous zinc chloride and concentrated hydrochloric acid is called Lucas reagent. This reagent is used to distinguish  $3^\circ$ ,  $2^\circ$  and  $1^\circ$  alcohols. When alcohols are added to the solution of Lucas reagent in 1:1 ratio and the resulting mixture is shaken an insoluble alkyl halide is formed. This insoluble alkyl halide forms at a different speed with  $3^\circ$ ,  $2^\circ$  and  $1^\circ$  alcohols, thus this reaction can be used to distinguish them.

A  $3^\circ$  alcohol on reaction with Lucas reagent forms the respective alkyl halide immediately to form turbidity.  $2^\circ$  alcohols react in some time to form turbidity and  $1^\circ$  alcohols give no turbidity.

### 3) Esterification:

When alcohols react with carboxylic acids in the presence of concentrated sulphuric acid they give esters.



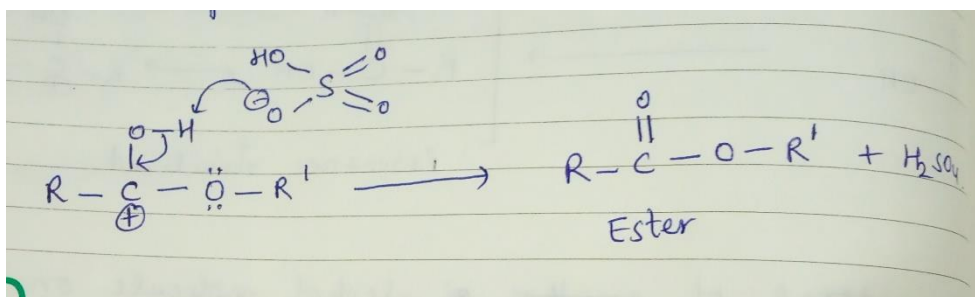
Mechanism:

It takes place in the following steps:

Step 1: In the first step the carboxylic acid takes a proton from the sulphuric acid.

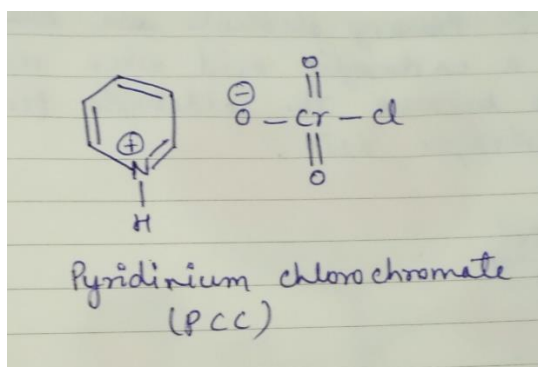


Step 5: Abstraction of proton from the above formed molecule by hydrogen sulphate ion gives the product.

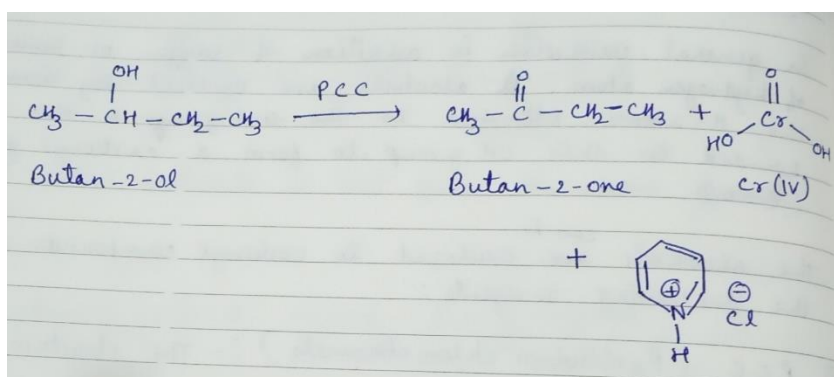


4) Oxidation of alcohols: In general, oxidation is addition of oxygen or removal of hydrogen atoms. Alcohols are oxidized by removing the H-atoms attached to the – OH group and to the C – atom bonded to this – OH group to form a carbonyl compound. The alcohols can be oxidized to carbonyl compounds by the following reagents:

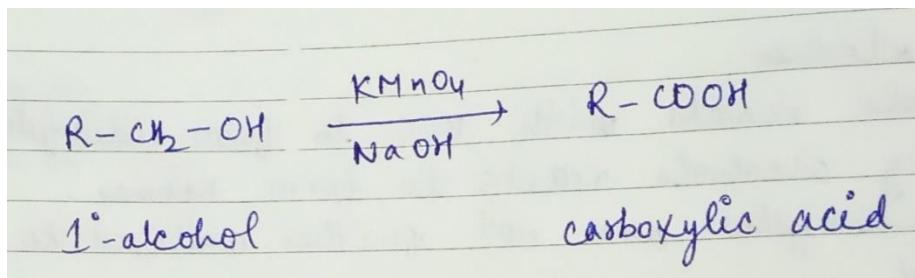
(a) PCC (Pyridinium chlorochromate): The structure of PCC is shown below:



Primary alcohol reacts with PCC to form aldehydes which is not further oxidized to carboxylic acids and secondary alcohol forms ketones on reaction with PCC.



(b) Alkaline  $\text{KMnO}_4$ : Primary alcohols form carboxylic acids when reacted with alkaline  $\text{KMnO}_4$  since the aldehyde formed quickly oxidizes to carboxylic acid.



Secondary alcohols are oxidized to ketones on reaction with alkaline  $\text{KMnO}_4$  since the ketone has no  $\alpha$  hydrogens so it is not oxidized further.

