B.Sc. Applied Physical Sciences (Chemistry) I Year (Industrial Chemistry)

Chemistry- Thermodynamics, Equilibria and Functional Group Organic Chemistry

Section B Organic Chemistry-2

Unit 6

Alcohols, Phenols, Ether, aldehydes and Ketones

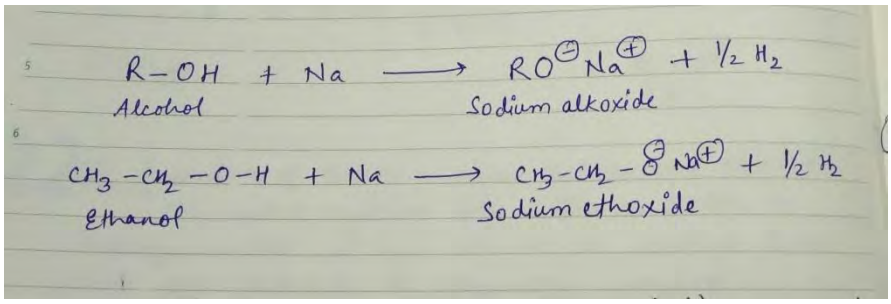
Alcohols

Reactions of Alcohols

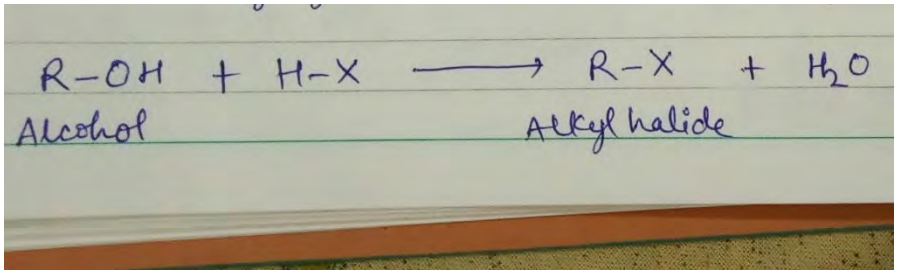
Acidity of Alcohols

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.



References: Organic Chemistry, R.T. Morrison, R.N. Boyd and S.K. Bhattacharjee, Pearson, 7th Edition and advance Organic Chemistry, Bahl and Bahl, S.Chand & Company Ltd.

The reaction takes place through S_N1 mechanism except for methanol and 1° alcohols.

Order of reactivity of alcohols: 3° > 2° > 1°

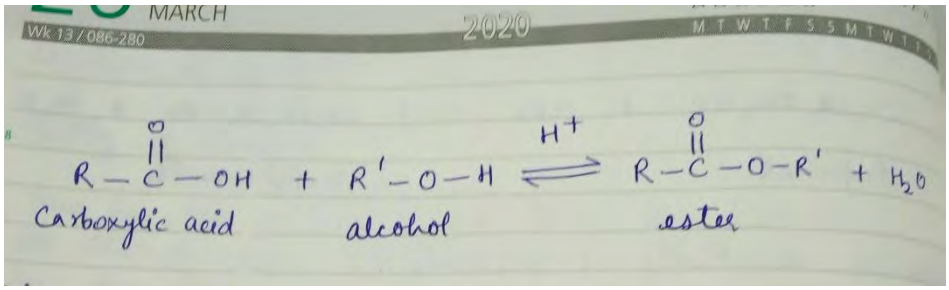
Order of reactivity of hydrogen halides: HI > HBr > HCl

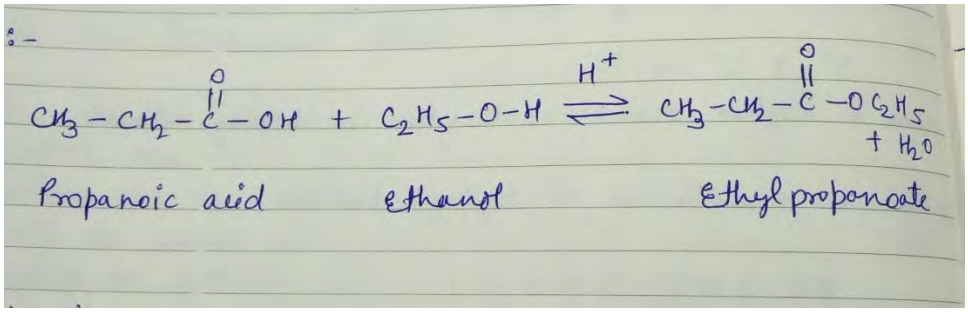
Lucas test: A solution of anhydrous zinc chloride and concentrated hydrochloric acid is called Lucas reagent. This reagent is used to distinguish 3°, 2° and 1° alcohols. When alcohols are added to the solution of Lucas reagent in 1:1 ratio and the resulting mixture is shaken an insoluble alkyl halide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

A 3° alcohol on reaction with Lucas reagent forms the respective alkyl halide immediately to form turbidity. 2° alcohols react in some time to form turbidity and 1° 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.

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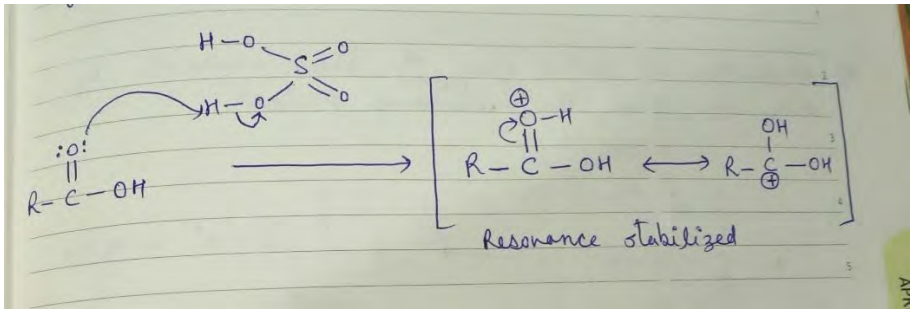
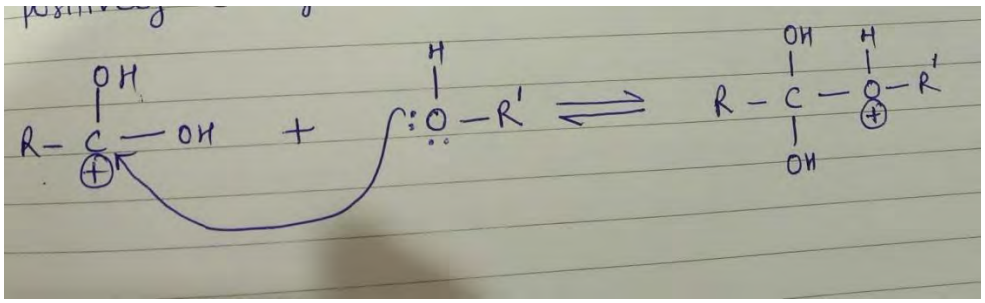
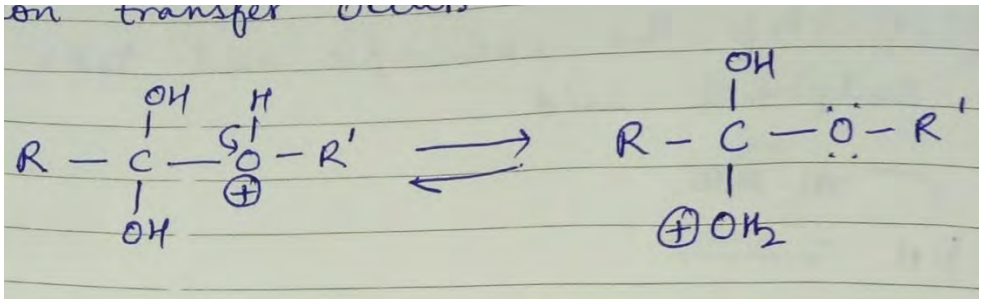


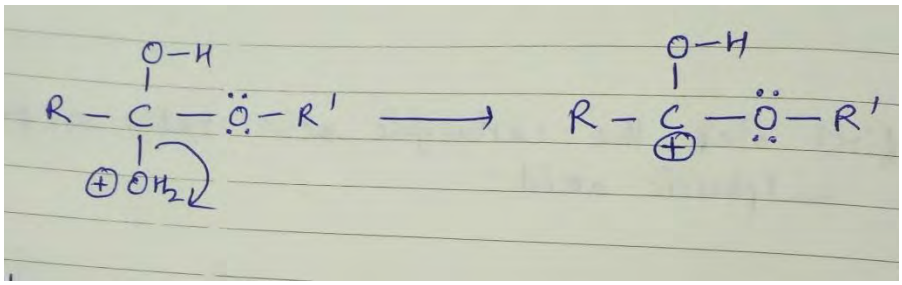
Step 2: The attack of alcohol molecule on the positively charged C-atom formed above takes place.



Step 3: Proton transfer occurs as follows:



Step 4: A water molecule is lost from the above formed ion.



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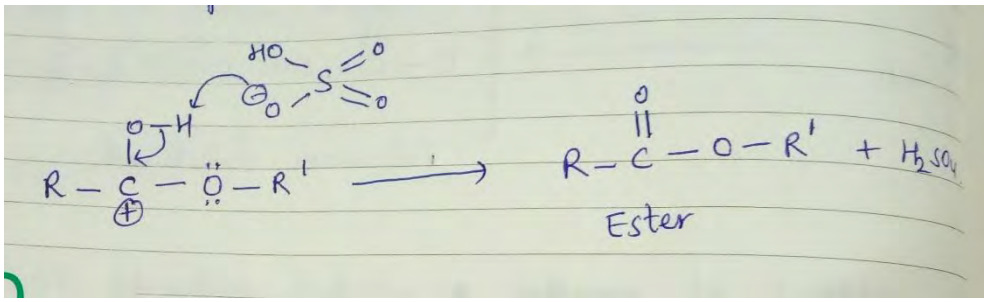
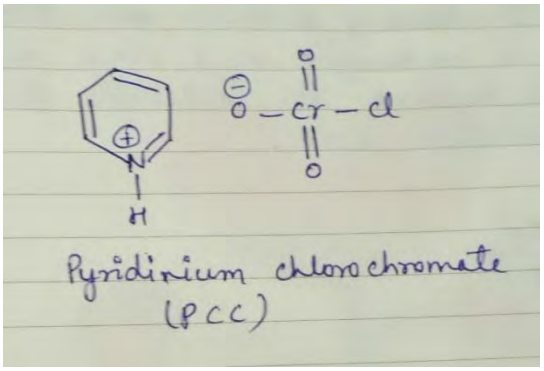
Step 5: Abstraction of proton from the above formed molecule by hydrogen sulphate ion gives the product.

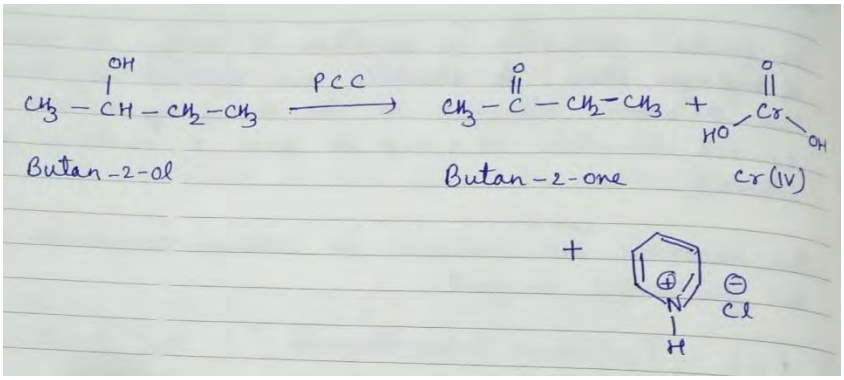


4) Oxidation of alcohols: In general, oxidation is addition of oxygen or removal of hydrogen atoms. Alcohols are oxidized by removing the H-atoms attached to the – OH group and to the C – atom bonded to this – OH group to form a carbonyl compound. The alcohols can be oxidized to carbonyl compounds by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



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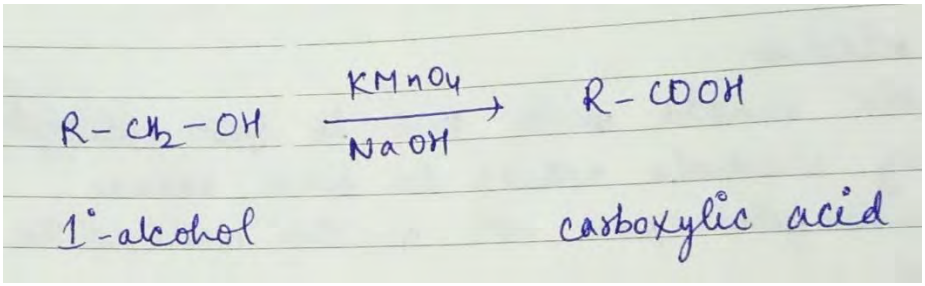
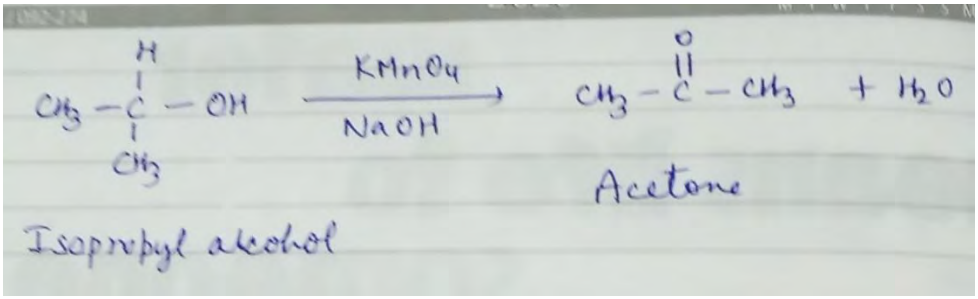
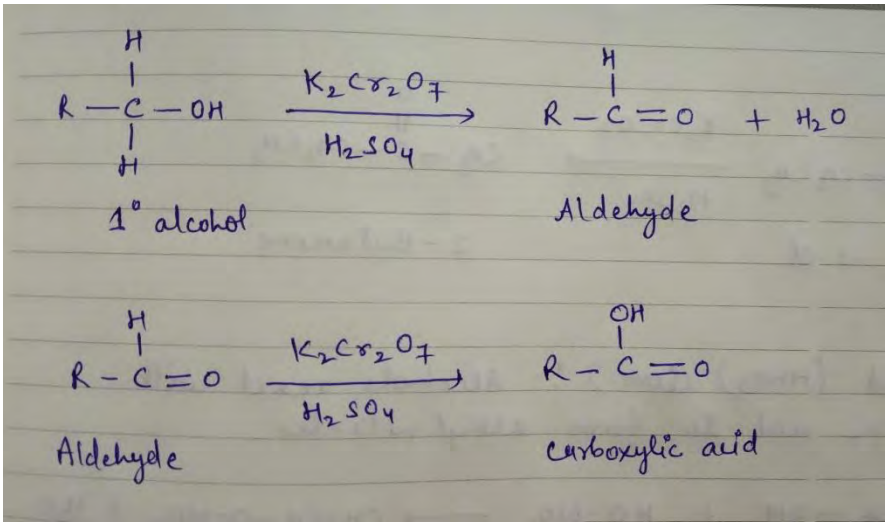
(b) Alkaline $KMnO_4$: Primary alcohols forms carboxylic acids when reacted with alkaline $KMnO_4$ since the aldehyde formed quickly oxidizes to carboxylic acid.



Secondary alcohols are oxidized to ketones on reaction with alkaline $KMnO_4$ since the ketone has no alpha hydrogens so it is not oxidized further.



(c) Potassium dichromate ($K_2Cr_2O_7$): When a primary alcohol is reacted with and sulphuric acid it converts firstly into an aldehyde and then quickly oxidizes to a carboxylic acid because the aldehyde has a H-atom attached to the carbonyl group (C = O). The number of C – atoms remains same as that of parent compound.



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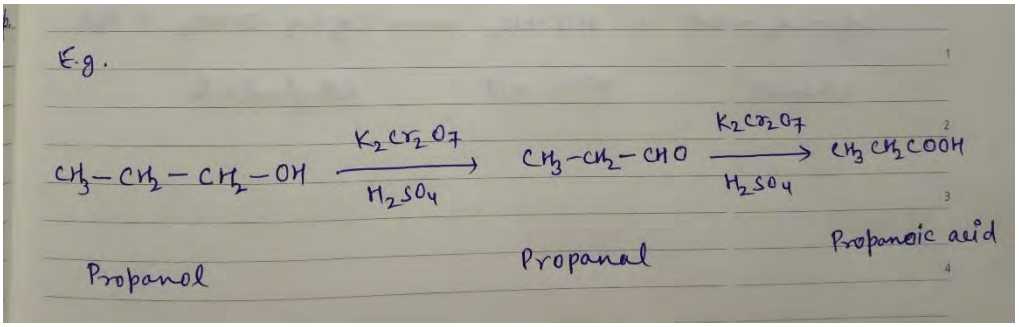
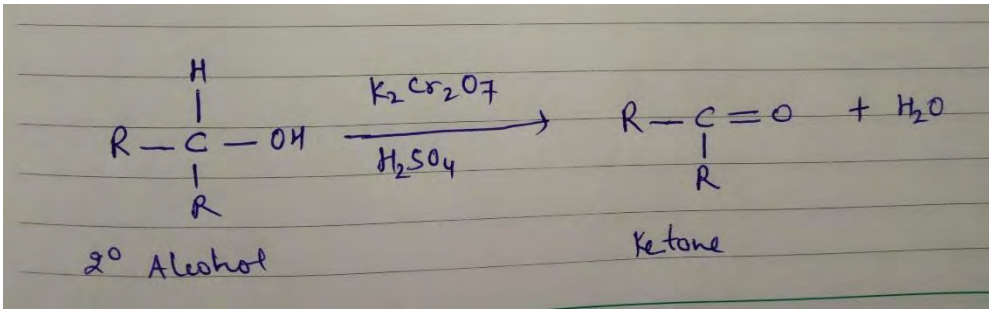
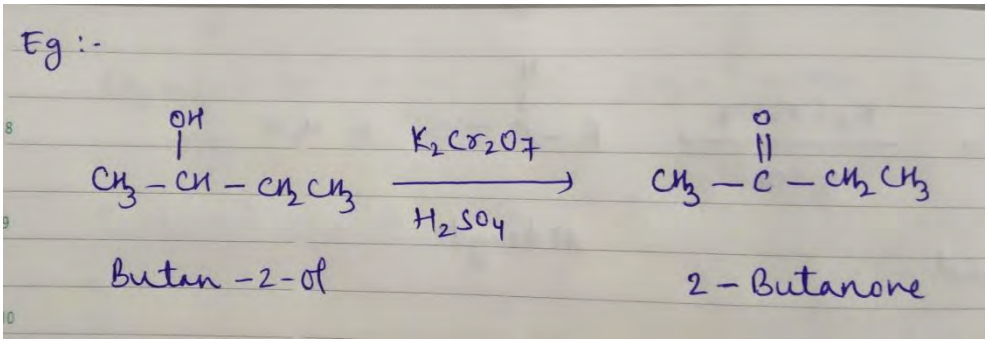
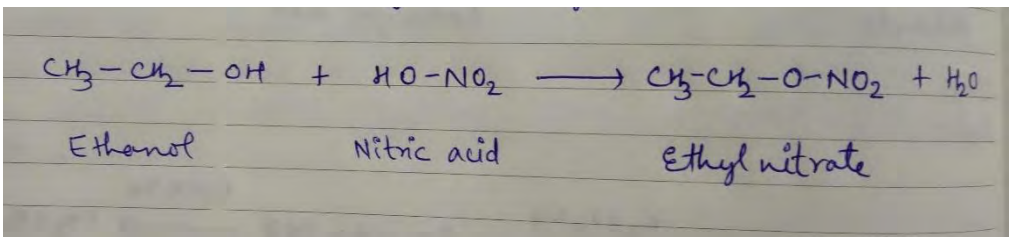


When Secondary alcohol is treated with potassium dichromate and sulphuric acid it is converted into a ketone having the same number of carbon atoms as that of parent compound. Since in a ketone no H-atom is present on the carbonyl carbon therefore, it is not further oxidized.





(d) Concentrated Nitric acid (HNO_3): Alcohols react with nitric acid to form alkyl nitrates.



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