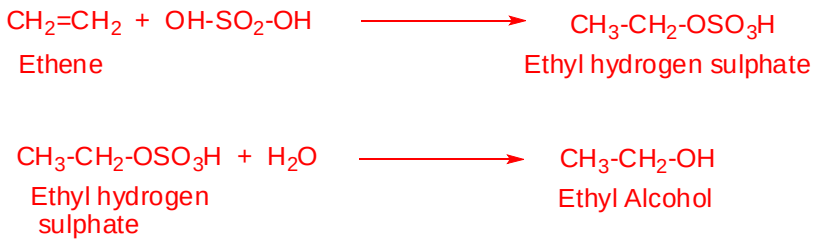
# HANDOUT

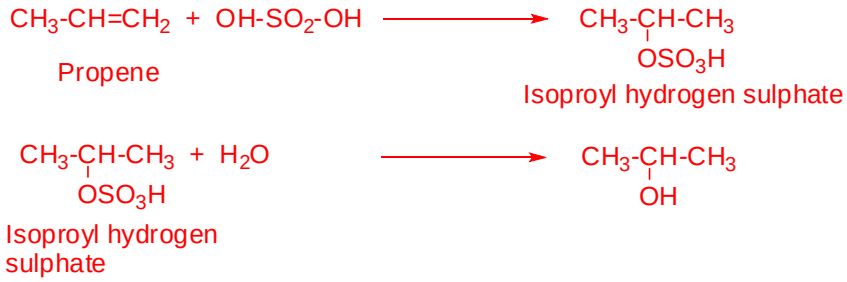
## Preparation and Properties of Alcohols

## Methods of preparation of alcohols

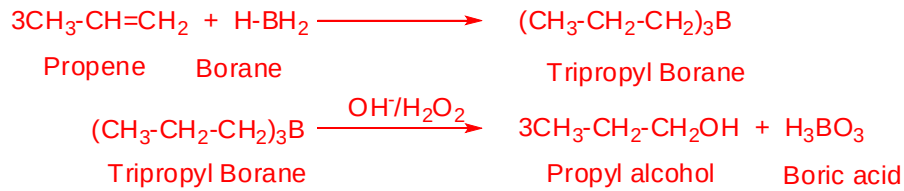
**1) Hydration of Alkenes:** Alkenes on treatment with concentrated sulphuric acid and followed by subsequent hydrolysis of intermediate (alkyl hydrogen sulphates) alcohols are produced. This is one of the best method and basic method for producing alcohols on large scale in industries.




Propene under these conditions produces isopropyl alcohol.




Addition of sulphuric acid follows the **Markovnikov** rule. In primary alcohols only ethyl alcohol can be prepared from this method. Majority of primary alcohols can be prepared by **hydroboration–oxidation** of alkene.

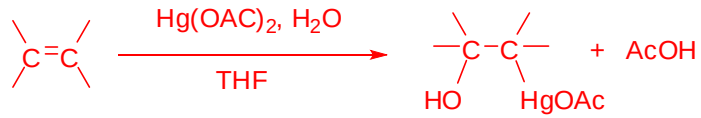



Hydroboration follows **anti-markovnikov** rule.

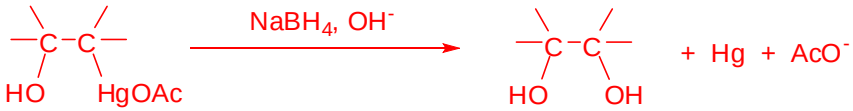
**2) Oxymercuuration-Demercuration:** Alkenes on reaction with mercuric acetate in a mixture of water and tetrahydrofuron producing (hydroxyalkyl)mercuric compounds. These

((hydroxyalkyl)mercuric compounds) on reduction with sodium borohydride and water gives alcohols.

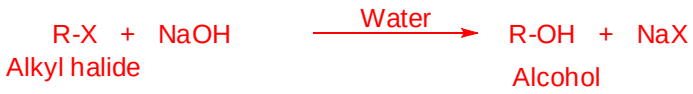
**Oxymercuuration:** In first step mercuric acetate add to the double bond.

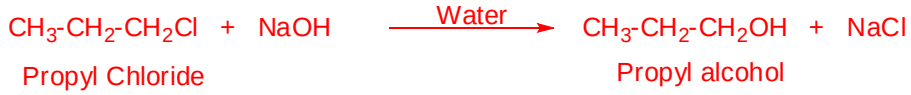



**Demercuration:** In second step acetoxymercuric group undergoes reduction and it is replaced with hydrogen. Addition of -H and –OH takes place according to the markovnikov regioselectivity rule.

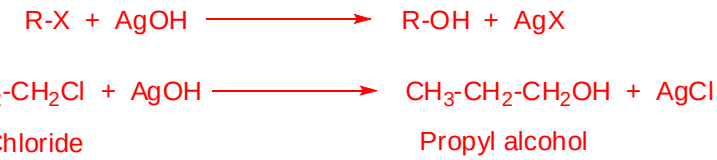



**3) Hydrolysis of Alkyl halides:** Alcohols can be prepared by the addition of dilute aqueous solution of sodium or potassium hydroxide to alkyl halides.




Alkyl halides under these conditions may undergo **dehydrohalogenation** giving alkenes. Mild alkali like moist silver oxide or aqueous potassium carbonate is used to get more yield.

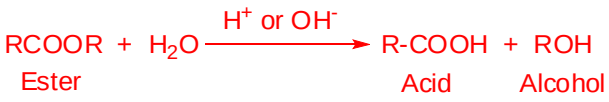



Reactivity order of alkyl halides:

RI > RBr > RI

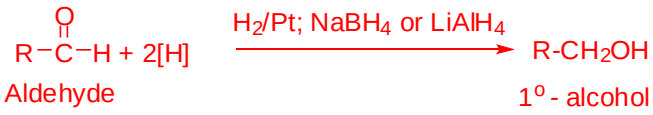
This method is not used frequently due to less abundance of alkyl halides.

**4) Hydrolysis of carboxylic esters:** Alcohols can be prepared by the addition of dilute solution of an alkali or mineral acid to ester.

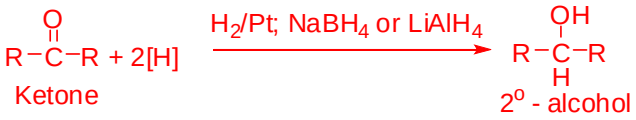



**5) Reduction of carbonyl compounds:** Carbonyl compounds, carboxylic acids, esters on reduction with appropriate reducing agents, alcohols can be prepared.

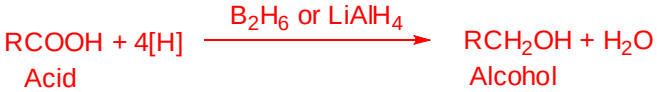
a)Reduction of aldehydes



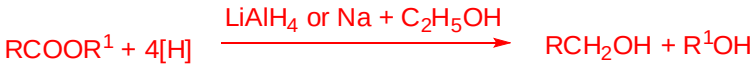

b) Reduction of ketones




c) Reduction of carboxylic acids

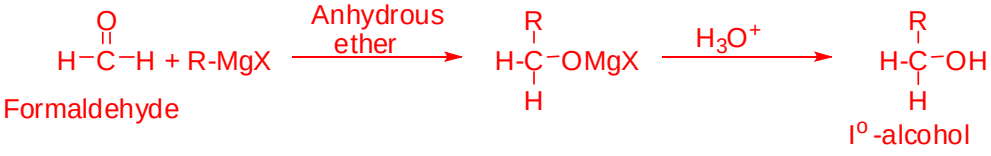



d) Reduction of esters

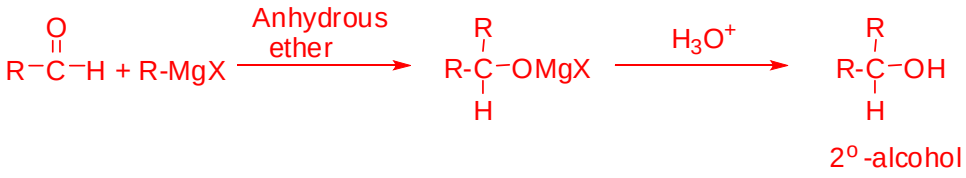



**6) From Grignard reagent (**RMgX):

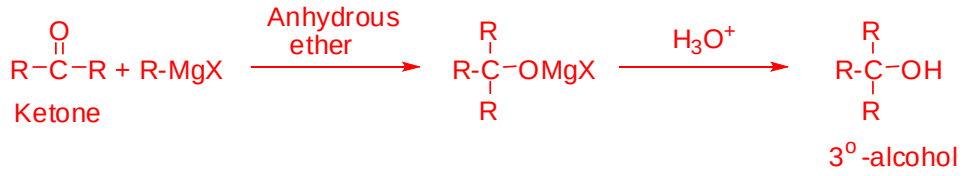
**Preparation of primary alcohol:** Formaldehyde on reaction with Grignard reagent in presence of anhydrous ether forms addition product, which on hydrolysis with dilute acid forms 1°-alcohol.



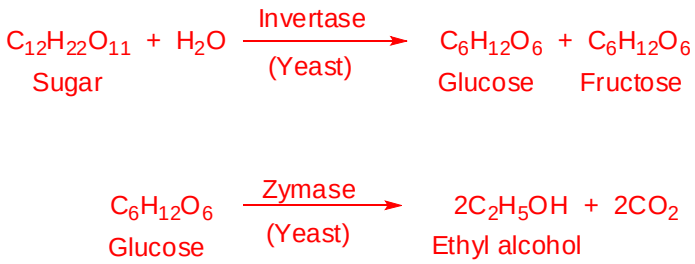

**Preparation of secondary alcohol:** Except formaldehyde any other aldehydes on reaction with Grignard reagent in presence of anhydrous ether forms addition product, which on hydrolysis with dilute acid forms 2°-alcohol.




**Preparation of tertiary alcohol:** Ketone on reaction with Grignard reagent in presence of anhydrous ether forms addition product, which on hydrolysis with dilute acid forms 3°-alcohol.



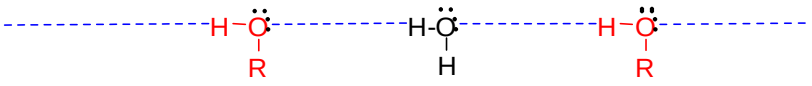

**7) Fermentation of carbohydrates:** Molasses on fermentation in the presence of yeast produces ethyl alcohol. Molasses is the mother liquor left after the crystallization of sugar.




## Physical properties:

**1) State:** Lower alcohols are colorless volatile liquids while higher alcohols are solids. Methyl alcohol is a nerve poison, very small intake also causes blindness.

**2) Solubility:** Lower alcohols are soluble in water, solubility of alcohols in water is due to the hydrogen bonding. Solubility of alcohols decreases with increase in molar mass.



Among the isomeric alcohols, ***n*-butyl alcohol** is least soluble while ***ter*-butyl alcohol** is extremely soluble because solubility increases with decrease in surface area.

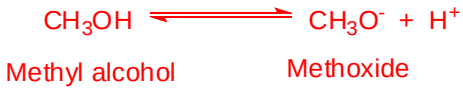
**3) Boiling points:** Alcohols have higher boiling points compared to alkanes because of hydrogen bonding existing between alcohol and water molecules.

## Chemical Properties: Chemical properties of alcohols can be studied in three ways

1. Reactions involving cleavage of O-H bond
2. Reactions involving cleavage of C-O bond
3. Reactions involving unshared electrons of oxygen.

## Reactions involving cleavage of O-H bond:

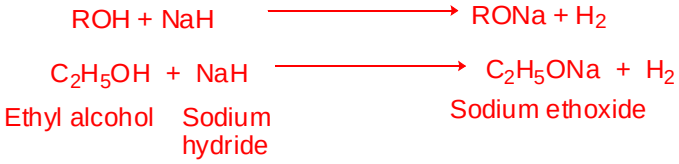
**1. Acidic nature:** Alcohols behave as weak acids. Alcohols acidic strength is less than that of water.

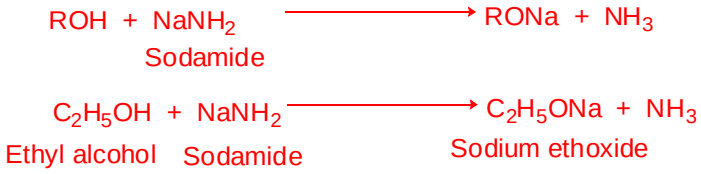

**2) Action with alkali metals:** Alcohol reacts with alkali metals and liberates hydrogen.



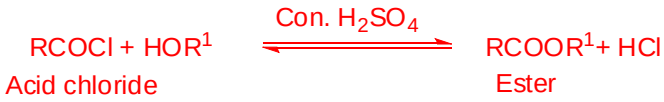
**3) Action with metal hydrides:** Alcohols form metal alkoxide on reaction with metal hydrides.



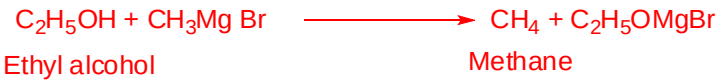

Metal amides also form metal alkoxide on reaction with alcohols.



4) **Esterfication:** Esters are formed when alcohols react with acid chlorides.

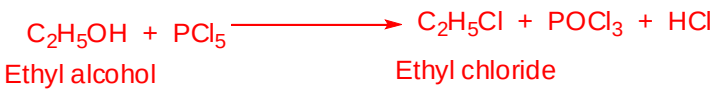


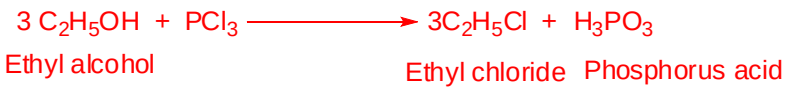

**5) Reaction with Grignard reagent:** Alcohols form alkanes on reaction with Grignard reagent.




## Reactions involving cleavage of C-O bond

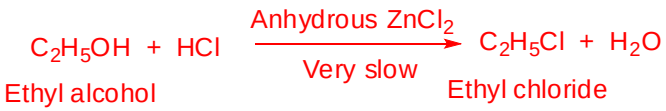
**1) Action with phosphorus halides:** Alcohols form alkyl halides on reaction with phosphorus halides**.**

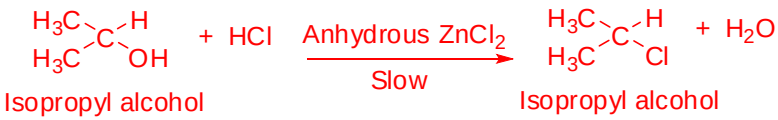


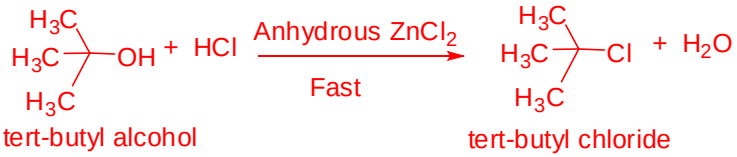




**2) Action with thionyl chloride:** Alcohols on reaction with thionyl chloride in the presence of pyridine produces alkyl halides.


**3) Reaction with Lucas reagent:** A solution of **zinc chloride in con. HCl** is known as **Lucas reagent**. Alcohols form alkyl halides and water on reaction with Lucas reagent.



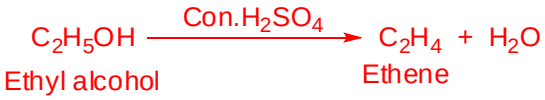



Order of reactivity of alcohols towards Lucas reagent:

$$3^o > 2^o > 1^o$$

**4) Dehydration** : Alcohols on dehydration gives alkenes.

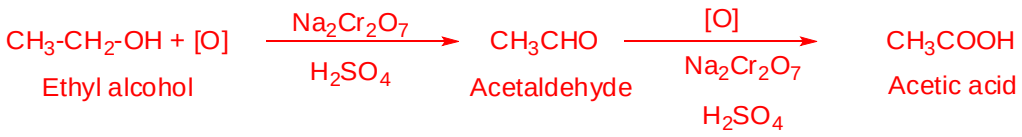



Order of reactivity of alcohols towards dehydration to form alkene:

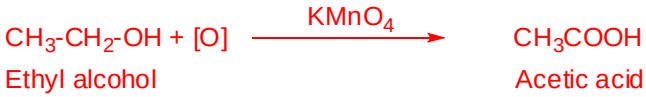
$$3^o > 2^o > 1^o$$

**5) Oxidation:** Oxidation product of alcohols depend upon the nature of alcohol, that is, whether the alcohol is primary, secondary or tertiary.

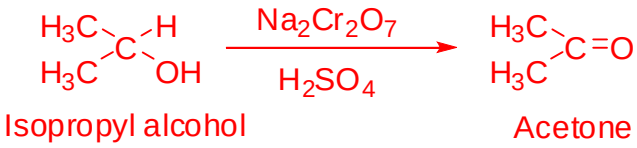
**Oxidation of 1º alcohol:** Primary alcohol on oxidation with sodium dichromate and sulphuric acid first produces aldehyde and finally converts to the carboxylic acid. Both aldehyde and acid contain same number of carbon atoms as the parent alcohol.



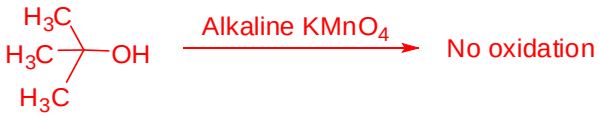

Potassium permanganate oxidizes primary alcohol to carboxylic acid. Ex:



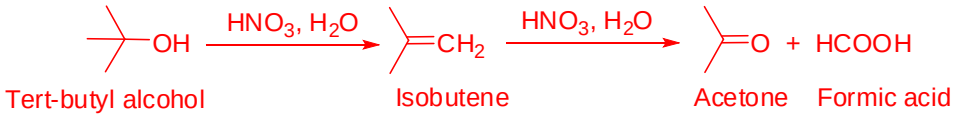

**Oxidation of 2º alcohol:** Secondary alcohol on oxidation with sodium dichromate and sulphuric acid forms ketone with same number of carbon atoms.




**Oxidation of 3º alcohol:** Tertiary alcohols are resistant to oxidation in alkaline $KMnO_4$.

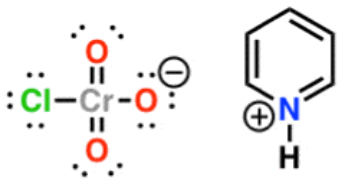



However, on drastic oxidation with acid oxidising agents tertiary alcohols gives mixture of ketone and carboxylic acid.

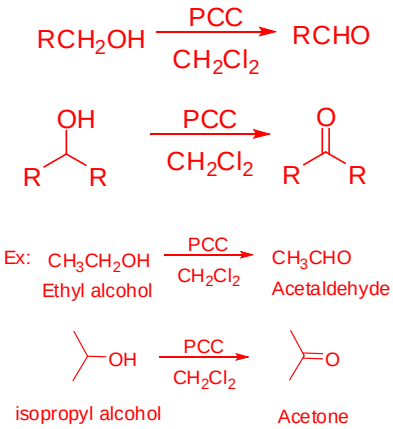



Formic acid is further oxidised to $CO_2$ and $H_2O$, whereas ketone is oxidised to mixture of acids.

**Oxidation with PCC**: Pyridinium chlorochromate (PCC) is a yellow-orange solid, it oxidizes alcohols to carbonyl compounds.

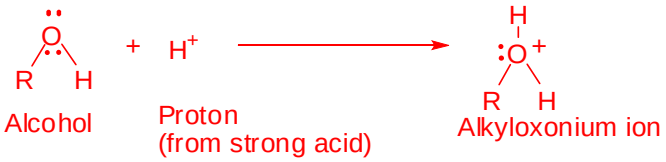



**PCC**
**(Pyridinium chlorochromate)**

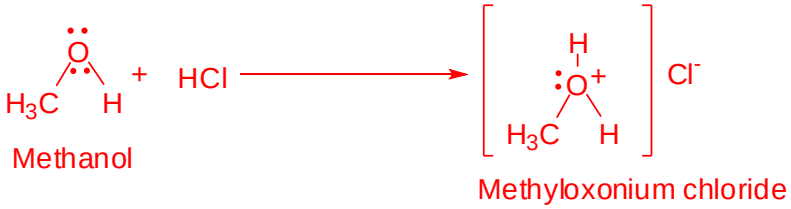



## Reactions involving unshared electrons of oxygen

**Formation of alkyloxonium salts:** Since oxygen atom of **alcohol** has two lone pairs of electrons, alcohols act as bases.




Methyloxonium chloride is formed by passing HCl gas through methyl alcohol.



## List of Reference Books:

1) Organic Chemistry (English, Paperback, 10th edition) by T W Graham Solomons, John Wiley and Sons Ltd.

2) Organic Chemistry (English, Paperback, 7th edition) by Paula Y Bruice, Pearson Education.

3) Organic Chemistry (English, Paperback, 3rd edition) by Janice Gorzynski Smith, McGraw-Hill.

4) Organic Chemistry (English, Paperback, 2nd edition) by Jonathan Clayden, Nick Greeves and Stuart Warren, Oxford University Press.

**Web Links:**

1. https://byjus.com/chemistry/physical-chemical-properties-of-alcohols/
2. https://youtu.be/DhwgNaRwscQ
3. https://youtu.be/jmiCWSwcaKY
4. https://youtu.be/Aa1CMokCch4

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