

Alcohols

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ALCOHOLS

- Alcohols are organic compounds having general formula ROH as R is alkyl group which may be CH_3- , C_2H_5- , C_3H_7- etc.
- Alcohols are also called as hydroxy derivatives of alkanes, in which $-\text{OH}$ group is bounded to a saturated carbon atom and that carbon may be a part of common alkyl group or be part of more complex molecule such as cholesterol that would be discussed in classification of Alcohols.

Physical Properties of Alcohols

- Lower alcohols are generally colorless, toxic liquid with a specific smell and burning taste.
- Readily soluble in water via H-bonding and this solubility decreases in higher alcohols.
- Alcohols have high M.P and B.P than their respective alkanes due to hydrogen bonding.

Classification of Alcohols

1. Alcohols are classified on the basis of number of OH groups as monohydric and polyhydric etc. Polyhydric are those which contain two or more OH groups e.g. CH_3OH ,
 $\text{OH-CH}_2\text{-CH}_2\text{-OH}$
 - ▣ Monohydric Alcohols are further classified as primary, secondary and tertiary alcohols depending upon the type of carbon with which hydroxyl group is attached.
2. Alcohols are also classified as 1, 2 or 3 degree alcohols depending upon the number of carbon atoms bonded to the alcohol carbon. For example ethanol, 2-Propanol and 2-methyl-2-Propanol are denoted as 1, 2 and 3 degree alcohols.

Methods of preparation of alcohols

1. Hydrolysis of halo alkanes:

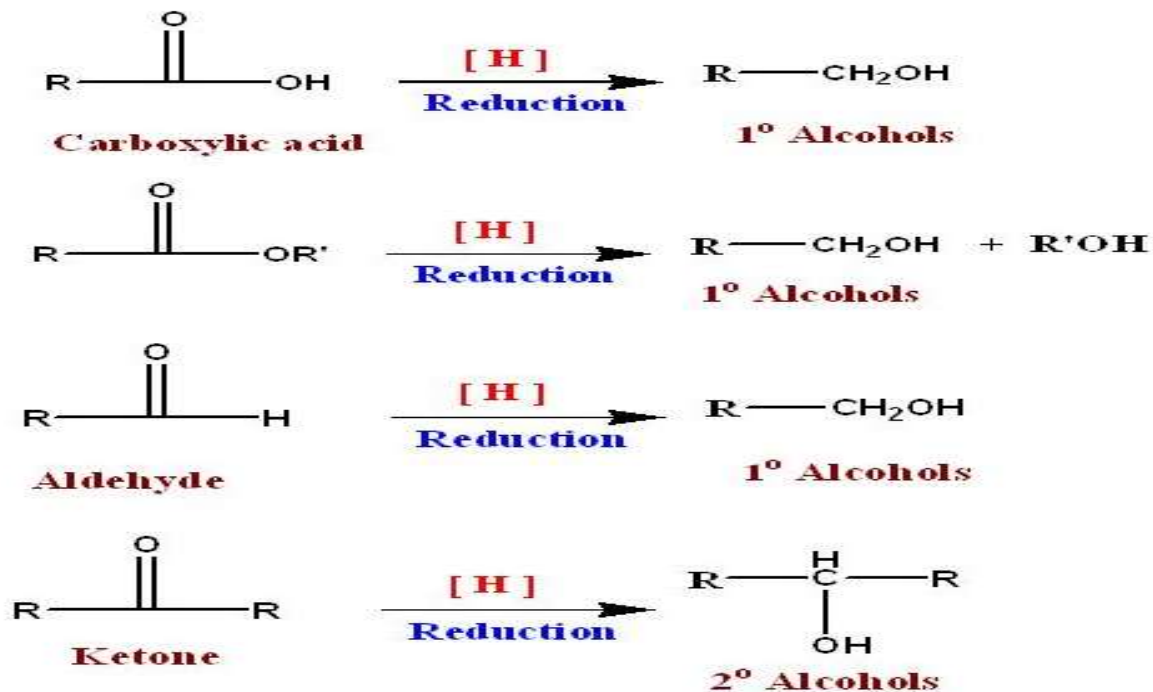
- Halo alkanes are converted into alcohols when treated with NaOH, KOH or Ca(OH)₂. primary and secondary alcohols are formed by primary and secondary halo alkanes.
- This is a type of nucleophilic substitution reaction (SN). This reaction is useful only with reactants that do not undergo E2 elimination readily.
- $$\text{R-X} + \text{KOH}_{\text{aq}} \rightarrow \text{R-OH} + \text{KX}$$

2 . Reduction of carbonyl compounds:

Carbonyl compound can be reduced to alcohols.

Aldehydes give primary alcohols and ketone give secondary alcohols by using catalytic hydrogenation or either in the presence of reducing agent lithium aluminum hydride, LiAlH_4 .

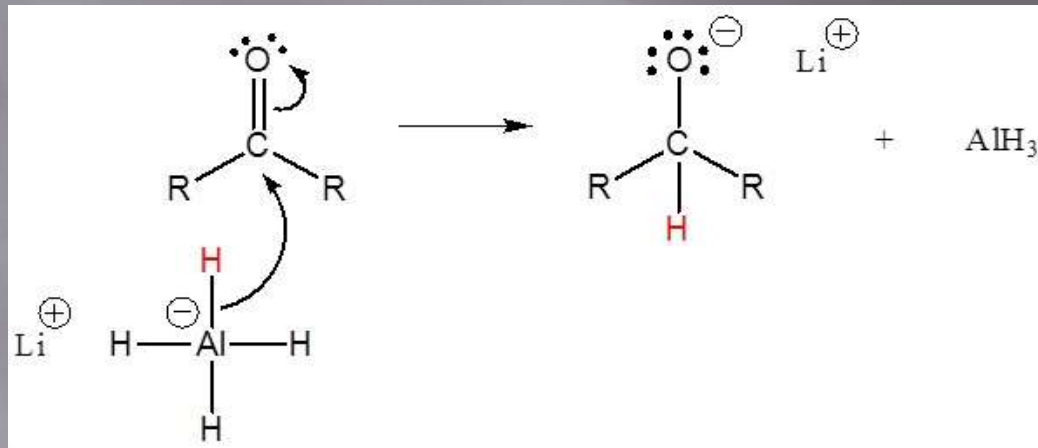
Carboxylic acid and ester also yield primary alcohols on reduction with hydride reagents such as LiAlH_4 and sodium borohydride NaBH_4



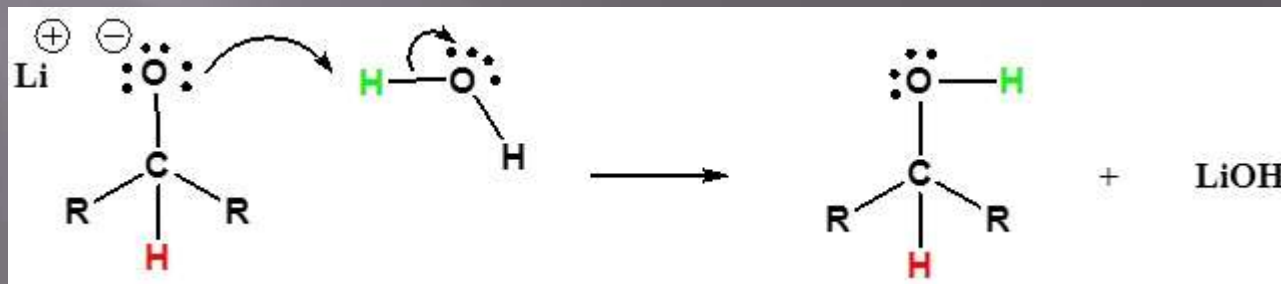
Mechanism

This mechanism is for a LiAlH_4 reduction. The mechanism for a NaBH_4 reduction is the same except methanol is the proton source used in the second step.

1) Nucleophilic attack by the hydride anion



2) The alkoxide is protonated



3 . Hydration of alkenes:

Hydration i.e. addition of H⁺ and OH⁻–double bond to give alcohols. This is an electrophilic addition of H₂O to the alkene. Alcohols can be prepared by adding water to an alkene in the presence of a strong acid H₂SO₄.

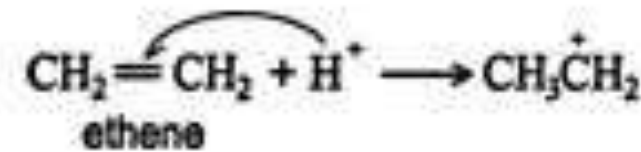
Because these reactions follow Markovnikov's rule, the product of the reaction is often a highly substituted 2^o or 3^o alcohol.



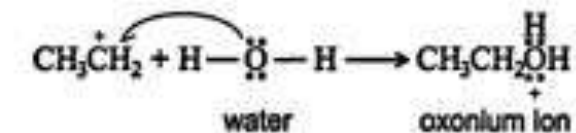
MECHANISM:

- The mechanism for the addition of water to ethene.

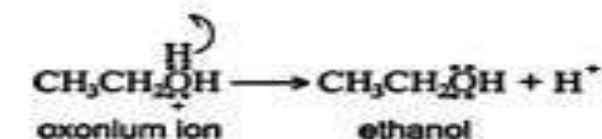
1. The hydrogen ion is attracted to the π bond, which breaks to form a σ bond with one of the double bonded carbons. The second carbon of the original double-bonded carbons becomes a carbocation.



2. An acid-base reaction occurs between the water molecule and the carbocation, forming an oxonium ion.

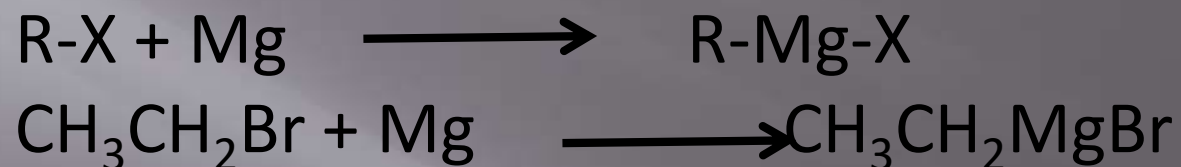


3. The oxonium ion stabilizes by losing a hydrogen ion, with the resulting formation of an alcohol.



4 . From Grignard reagents:

Grignard reagents are derivatives of alkyl halides belonging to class of organo-metallic compounds. These were firstly prepared by **Victor Grignard** in 1900.



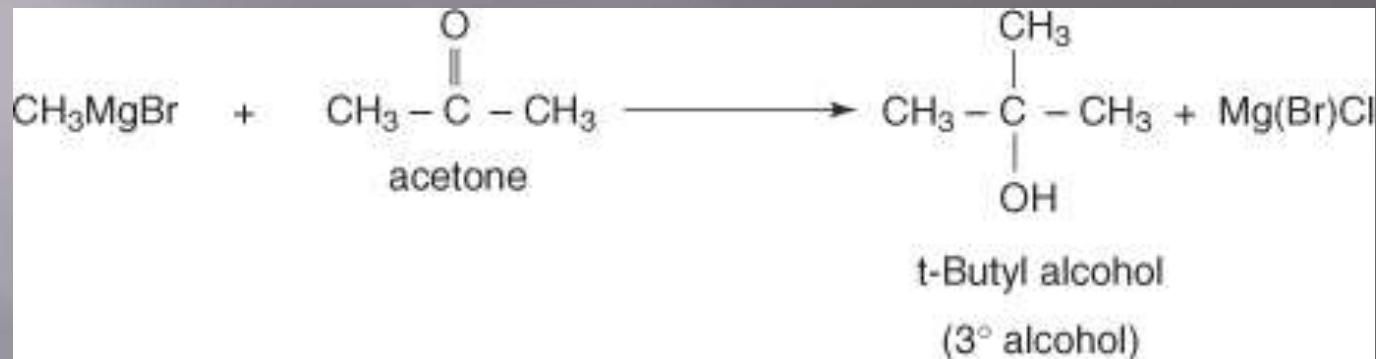
By reaction with aldehydes & ketones:

i) To produce a primary alcohol, the Grignard reagent is reacted with formaldehyde.



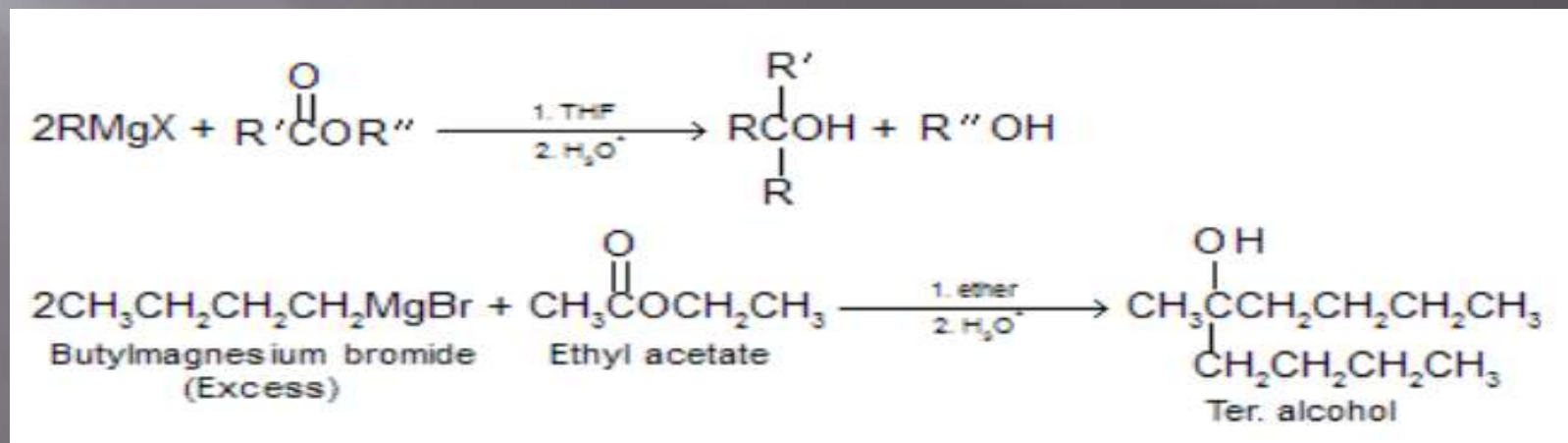
ii) Reacting a Grignard reagent with any other aldehyde will lead to a secondary alcohols

iii) Reacting a Grignard reagent with a ketone will generate a tertiary alcohol.

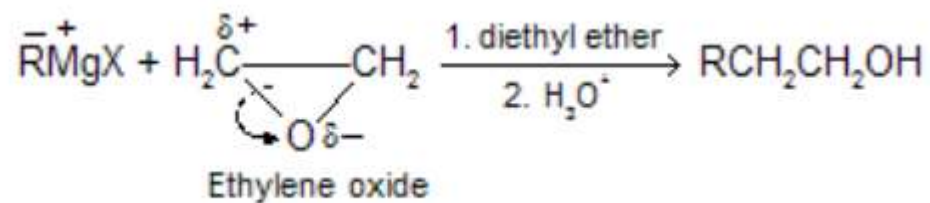


iv) **By reaction with esters:**

Produces tertiary alcohols in which two of the substituent on the hydroxyl-bearing carbon are derived from the Grignard reagent.



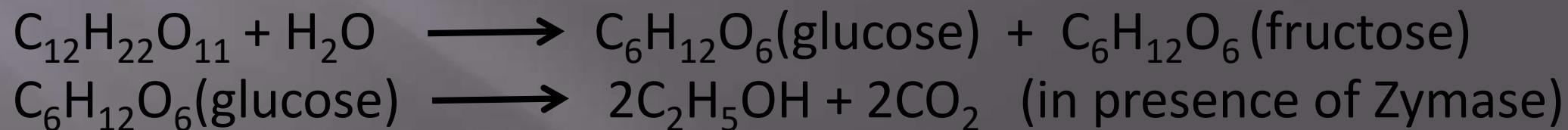
v) **By reaction with epoxides:** Grignard reagents react with epoxide to yield primary alcohols containing two or more carbon atoms.



vi) **Fermentation:**

Ethanol is prepared on a large scale using fermentation process. It involves breaking down large molecules into simpler ones using enzymes. Usually, yeast is added as a source of enzymes. Yeast converts the reactant glucose or fructose into ethanol and carbon dioxide in presence of zymase enzyme.

From molasses (in presence of Invertase/yeast)



vii From Carbon monoxide and water

Formerly alcohol like methanol by distillation of wood due to which it was called as wood spirit. Now commonly it is prepared from CO and H₂ or water in the presence of ZnO and Cr₂O₃ at 450°C temperature and 200atm pressure.



viii Oxymercuration and Demercuration of Alkenes

Alkenes react with mercuric acetate in the presence of water and tetrahydrofuran to produce alkyl mercuric compounds as a product.



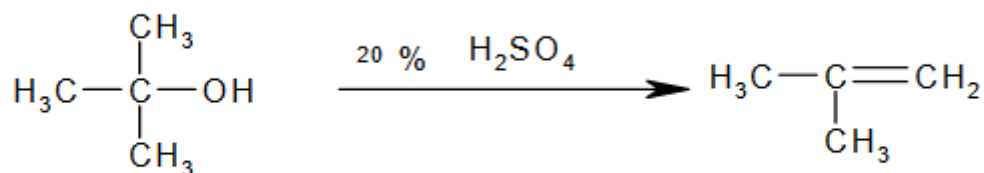
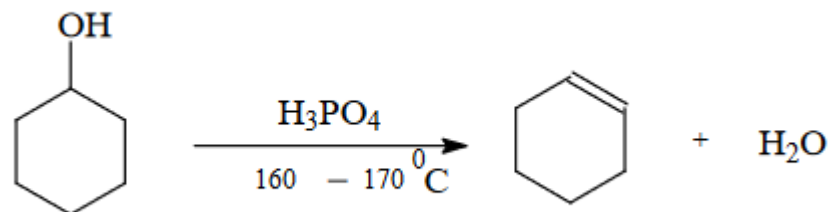
ix Catalytic Oxidation of Alkane

Catalytic oxidation of alkanes is used in industry to prepare higher fatty acids used in soap and vegetable oil industries.



Secondary alcohols are dehydrated under milder conditions.

Tertiary alcohols dehydrate under even milder conditions.



The main function of the acid is to transform the poor leaving group —OH into the very good leaving group OH_2^+ . The order of the relative ease of dehydration of alcohols is: $3 > 2 > 1$. Tertiary carbocations are most stable and therefore are easier to form than secondary and primary carbocations; tertiary alcohols are the easiest to dehydrate.

The order of stability of the carbocations is:

