Chemistry of Organic Compounds Containing Functional Group - I

Rijoy Kodiyan Jacob

July 23, 2020

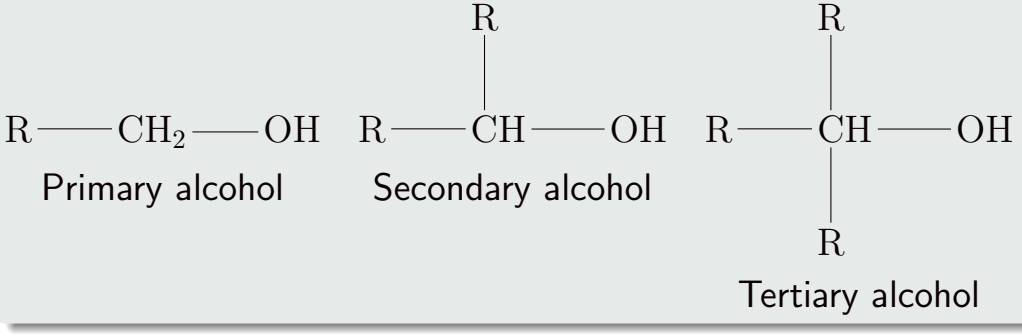
Syllabus

Halogen Compounds: Preparation of alkyl halides from alkanes and alkenes – Wurtz reaction and Fittig's reaction – Mechanism of SN1 and SN2 reactions of alkyl halides – Effect of substrate and stereochemistry.
Alcohols: Preparation from Grignard reagent – Preparation of ethanol from molasses – Wash, rectified spirit, absolute alcohol, denatured spirit, proof spirit and power alcohol (mention only) – Comparison of acidity of ethanol, isopropyl alcohol and tert-butyl alcohol

Syllabus - Contd...

– Haloform reaction and iodoform test – Luca's test – Chemistry of methanol poisoning – Harmful effects of ethanol in the human body. Phenols: Preparation from chlorobenzene – Comparison of acidity of phenol, p-nitrophenol and p-methoxyphenol – Preparation and uses of phenolphthalein

Alcohols have the general formula 'R-OH', where 'R' is an alkyl group. Depending upon the carbon atom carrying the '-OH' group is primary, secondary or tertiary, mono hydric alcohols are classified as primary, secondary and tertiary alohols.

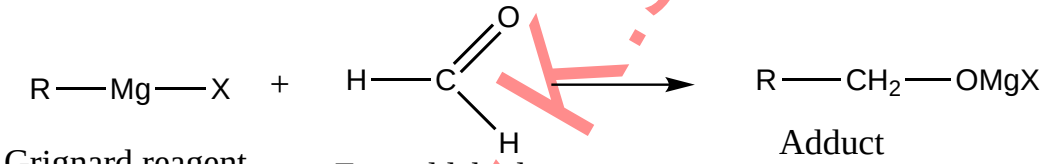


Preparation of Alcohols

Grignard reagents(alkyl magnesium halides) react with react with aldehydes and ketones to give adducts which on hydrolytic decomposition with dilute acid give alcohols.

Formation of Primary Alcohols

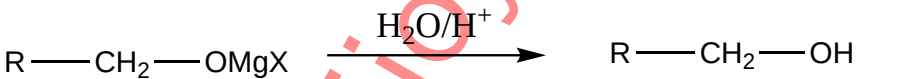
Formaldehyde react with Grignard reagents and followed by hydrolysis of the product formed gives a primary alcohol.



Grignard reagent

Formaldehyde

Adduct

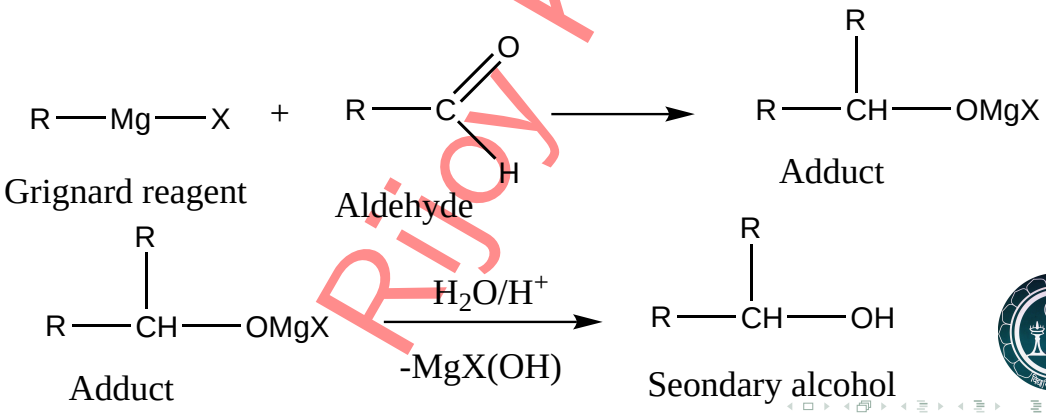


Adduct

Primary alcohol

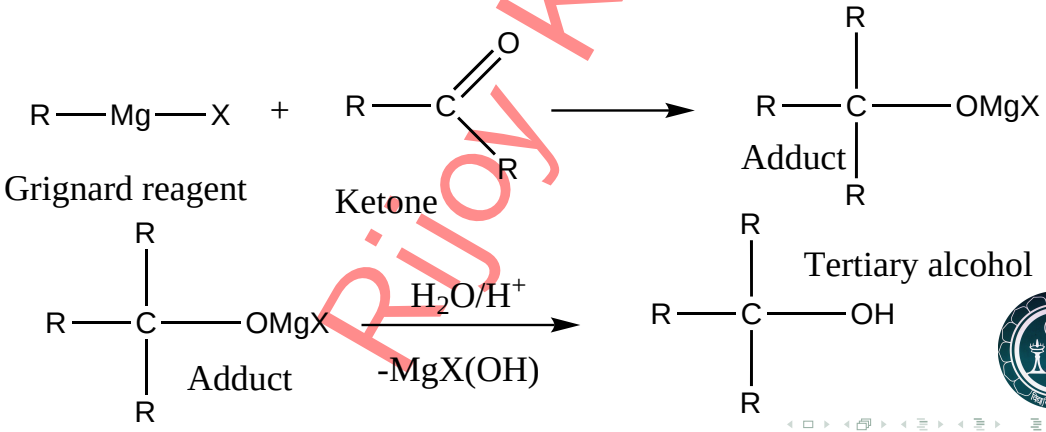
Preparation of Secondary Alcohol

Aldehydes other than formaldehyde react with Grignard reagent followed by hydrolysis give secondary alcohols.



Preparation of Tertiary Alcohols

Ketones react with Grignard reagents to give tertiary alcohols



Manufacture of Ethanol from Molasses

- Methanol is manufactured from **molasses** by fermentation process by the process of **fermentation**.

Fermentation

It is the process of breaking down complex organic molecules into simpler ones in the presence biological catalysts known as enzymes.

- Molasses is the mother liquor left after the crystallisation of cane sugar from sugar cane juice. It contains large amounts (≈40%) uncrystallisable cane sugar.
- Molasses Is diluted with water to get ≈10% solution of sugar.
- Yeast is added to it and it is kept at 303-308 K for 2-3 days.

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- The enzyme invertase present in yeast brings about the hydrolysis of sucrose (cane sugar) to glucose and fructose.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{Yeast}]{\text{Invertase}} C_6H_{12}O_6 + C_6H_{12}O_6$$

- The enzyme zymase present in yeast then brings about the conversion ol both glucose and fructose into ethanol.

$$C_6H_{12}O_6 \xrightarrow[\text{Zymaze}]{[O]} 2\ C_2H_5OH + 2\ CO_2$$

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Alcohol for industrial purposes is rendered unfit for drinking by adding some copper sulphate (to give it colour) and poisonous or nauseating substances like methanol, pyridine, etc. This process is called **denaturation** of alcohol and the sample thus obtained is called **denatured spirit.** Ethanol denatured with a small quantity of methanol (5%) is called **methylated spirit**.

Proof Spirit

- The term "Proof" with a prefix number is used for government documentation of the alcoholic content of distilled alcoholic beverages in certain countries.
- The term proof spirit is used to represent an alcohol-water mixture or a beverage containing a standard amount of alcohol.
- In US, it represents a mixture of alcohol and water containing 50 per cent alcohol by volume at 60^0F (-15.36^0) having al specific gravity 0.93353.

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Power Alcohol

Ethanol is used as an additive to the fuels for auto mobiles or other internal combustion engines in certain countries; ethanol thus used for the generation of power is referred to as **power alcohol**. Alcohol has a lower caloric value and hence the power output generated from alcohol is much less than that from conventional fossil fuels. However, it has a higher octane rating (better antiknock property) as compared to petroleum fuels and hence the addition of a small quantity of ethanol (say, 5%) to a petroleum fuel increases its octane rating.

Alcohols ae feebly acidic. The feeble acidity is illustrated with reaction with active metals like Na, K, etc.

$$\underset{\text{Alcohol}}{2\ \text{R-OH}} + 2\ \text{Na} \longrightarrow \underset{\text{Alkoxide}}{2\ \text{R-O}^{-}\text{Na}^{+}} + \text{H}_2$$

$$\underset{\text{Ethanol}}{2\ \text{CH}_3\text{-CH}_2\text{-OH}} + 2\ \text{Na} \longrightarrow \underset{\text{Sodium ethoxide}}{2\ \text{CH}_3\text{-CH}_2\text{-O}^{-}\text{Na}^{+}} + \text{H}_2$$

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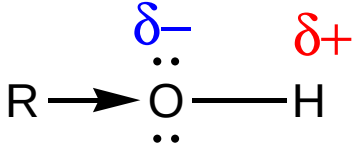
Ethanol → Sodium ethoxide

The acidic character is due to the polar nature of the 'O-H' bond. But due to the presence of electron releasing alkyl group makes it less polar and thereby makes alcohol weakly acidic.



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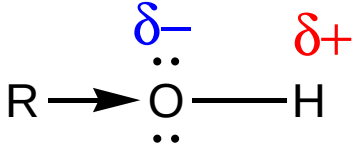
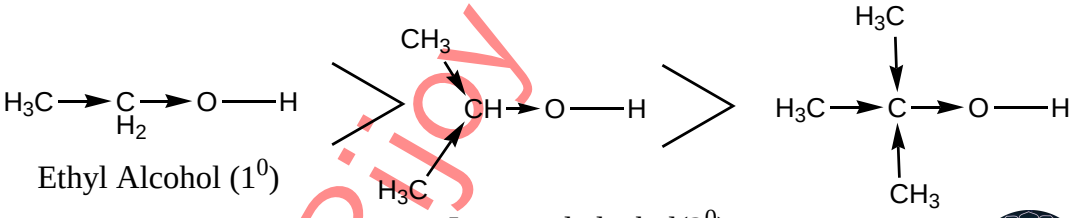


Order of Acidity os Alcohols

Acidity of alcohols decreases in the following order.



Haloform Reaction

Aldehydes and ketones containing '**CH_3-CO-**' group are oxidised by halogen and alkali(I_2 and alkali Br_2 and alkali or Cl_2 and alkali) to form haloform (chloroform, bromoform, or iodoform) and the salt of the carboxylic acid containing one carbon atom less than the parent carbonyl compound. The reaction is known as **haloform reaction**.

$$CH_3\text{-}CO\text{-}R + 3\ NaOX \xrightarrow{X_2/NaOH} CX_3\text{-}CO\text{-}R + NaX + H_2O$$

Trihalo derivative

$$CX_3\text{-}CO\text{-}R + NaOH \longrightarrow R\text{-}COONa + CHX_3$$

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Haloform

Any compound having '**CH_3-CO-**' and '**CH_3-CH-OH**'will get converted to haloform and salt of carboxylic acid.

Therefore all methylketones (R-CO-CH_3), and 1^0 and 2^0 alcohols like ethanol will give haloform test.

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$$CH_3\text{-}CHO + 3\ NaOCl \xrightarrow{Cl_2/NaOH} \underset{\text{Trichlorocetaldehyde}}{CCl_3\text{-}CHO} + NaCl + H_2O$$

$$CH_3\text{-}CHO + NaOH \xrightarrow{Cl_2/NaOH} \underset{\text{Chloroform}}{CHCl_3} + H\text{-}COO^{(-)}Na^{+} + H_2O$$

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Since Iodoform is highly recognisable, the reaction is used to distinguish compounds having '**CH_3-CO-**' group. This test is known as Iodoform test.

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$$CH_3\text{-}CHO + 3\ NaOI \xrightarrow{I_2/NaOH} \underset{\text{Triiodocetaldehyde}}{CI_3\text{-}CHO} + NaI + H_2O$$

$$CCl_3\text{-}CHO + NaOH \xrightarrow{I_2/NaOH} \underset{\text{Iodoform}}{CHI_3} + H\text{-}COO^{(-)}Na^{+} + H_2O$$

Reactions of alcohols with Halogen acids

Alcohols are converted into corresponding alkyl halides by the action of halogen acids particularly in presence of anhydrous $ZnCl_2$ and Con. H_2SO_4.

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The reaction of HCl requires Con. H_2SO_4, HBr and HI prepared in situ by reaction with NaBr +Con. H_2SO_4 and KI + 95% H_3PO_4 respectively.

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Chloroethane

$$CH_3\text{-}CH_2\text{-}OH + HBr \xrightarrow[\Delta]{NaBr/\ H_2SO_4} CH_3\text{-}CH_2\text{-}Br + H_2O$$

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Lucas Test

So 3^0 alcohols react readily with Con. HCl in presence of an. $ZnCl_2$ at room temperature, 2^0 alcohols require more time at room temperature or mild heating and 1^0 alcohols do not undergo reaction at room temperature and requires strong heating. This forms the basis of Lucas Test to distinguish 3^0, 2^0 and 1^0 alcohols.

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The time required by different alcohols to react with Lucas reagent to form the alkyl halide which is indicated by the formation of the turbidity is different.

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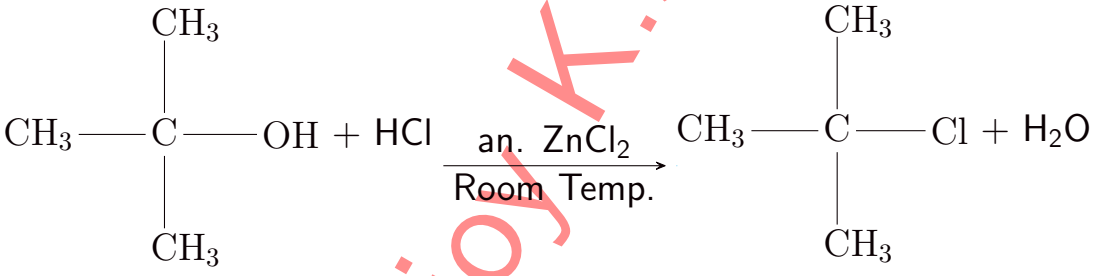
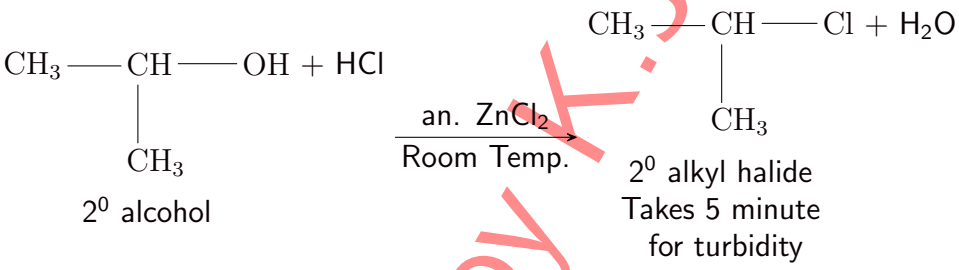


3^0 alcohol

3^0 alkyl halide


CH3 — CH — OH + HCl
CH3
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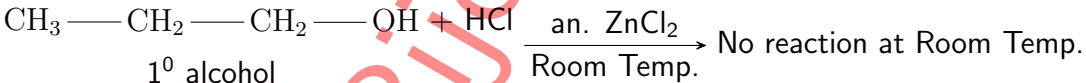
for turbidity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Harmful Effects of Ethanol in Human Body

- Consumption of alcohol causes serious damage to the human body. A few ill effects of alcohol on the various parts of human body are briefly mentioned here.
- Central nervous system: Alcohol depresses the central nervous system and thereby interferes with the brain's communication pathways, Causes changes in mood and behaviour as well as makes it harder to think clearly and move with coordination.
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- It impairs judgement and leads to accidents including vehicle crashes, falls, burns and drowning.
- It adversely affects normal thought processes and moral judgement, leading to a total disregard of the moral values which, in turn leads to sexual assaults and domestic violence.
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