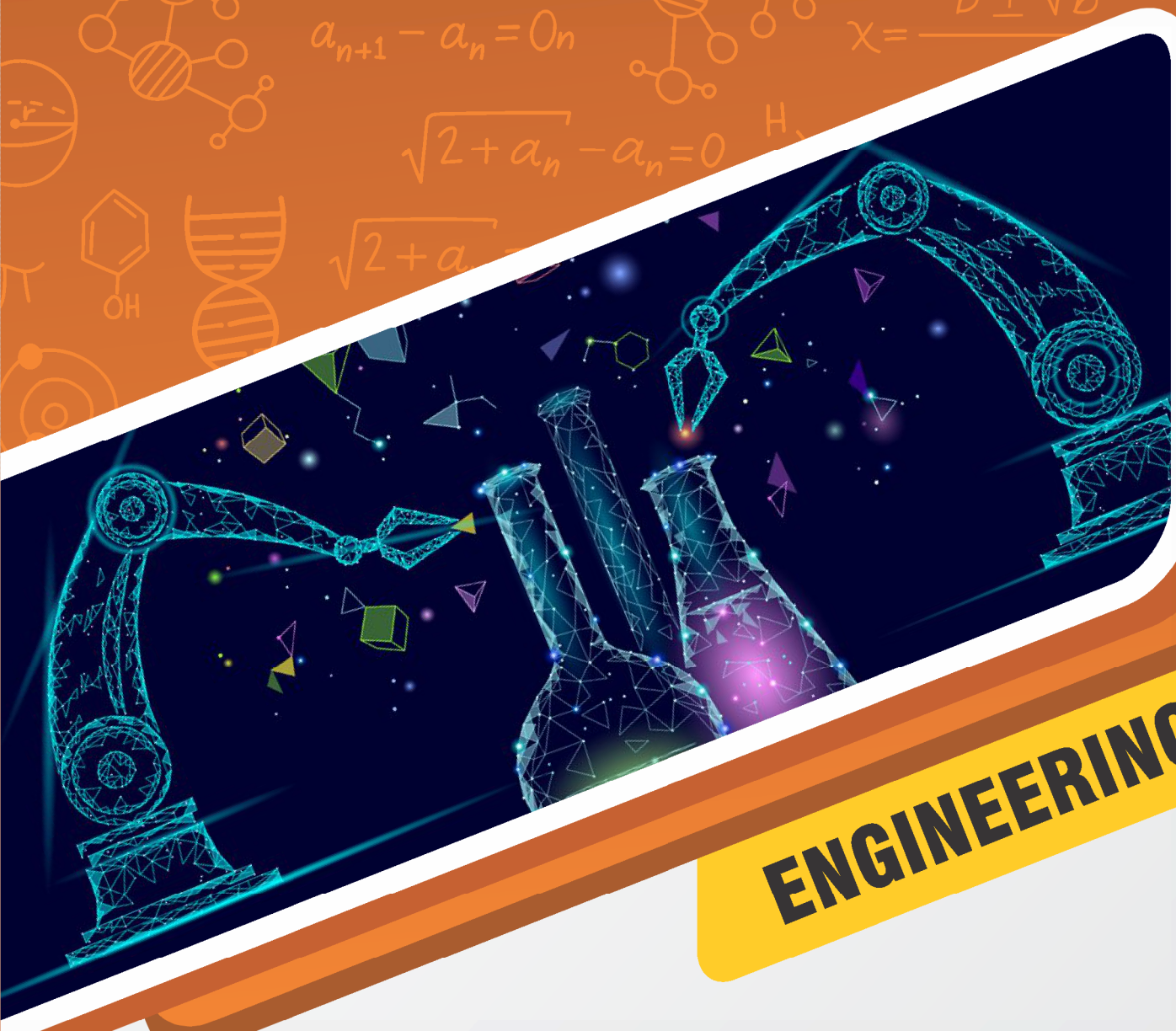
CHEMISTRY



ENGINEERING

ALCOHOL & ETHER

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ALCOHOL & ETHER

CONTENT

ALCOHOL

INTRODUCTION

(a) These are the organic compounds in which –OH group is directly attached with carbon.
(b) These are hydroxy derivatives of alkanes and mono alkyl derivatives of water.
(c) Their general formula is $C_nH_{2n+1}OH$ or $C_nH_{2n+2}O$.
(d) The hybridisation state of carbon is sp^3.
(e) Geometry is tetra hedral.
(f) In these compounds C-O bond length is 1.42 Å.
(g) These are of following types, depending upon the no. of OH groups.
  (i) Monohydric alcohol : Contains one –OH group only, eg.C_2H_5OH
  (ii) Dihydric alcohol : Contains two –OH groups. eg. glycol
  (iii) Trihydric alcohol : Contains three –OH groups eg. glycerol
  (iv) Polyhydric alcohol : Contains more than three - OH groups. eg, sorbitol, manitol.
(h) Alcohol shows chain, position & functional group isomerism. If chiral carbon atom is present, they shows optical isomerism.

METHODS OF PREPARATION

From Alkyl halides :

Alkyl halides reacts with aq. KOH/aq. AgOH or H_2O and forms alcohol.

$$R–CH_2–X + K–OH\ (aq.) \longrightarrow R–CH_2OH + KX$$

$$R–\underset{\displaystyle R}{\overset{\displaystyle R}{\underset{|}{\overset{|}{CH}}}}–X + AgOH\ (aq.) \longrightarrow R–\underset{\displaystyle R}{\overset{\displaystyle R}{\underset{|}{\overset{|}{CH}}}}–OH + AgX$$

$$R–\underset{\displaystyle R}{\overset{\displaystyle R}{\underset{|}{\overset{|}{C}}}}–X + H–OH \longrightarrow R–\underset{\displaystyle R}{\overset{\displaystyle R}{\underset{|}{\overset{|}{C}}}}–OH + HX$$

From Alkenes :

Hydration – Alkenes are catalytically hydrated by dilute mineral acid solution.

$$CH_2 = CH_2 + H_2O \xrightarrow{\text{dil } H_2SO_4} CH_3CH_2OH$$

$$R–CH = CH_2 + H_2O \xrightarrow{\text{dil } H_2SO_4} R–\underset{\displaystyle OH}{\underset{|}{CH}}–CH_3$$

Oxymercuration – demercuration :

Alkenes react with mercuric acetate in the presence of water to give hydroxymercurial compounds, which on reduction yield alcohols. (Markovnikov addition)

$$>C = C< + H_2O + Hg(OAc)_2 \longrightarrow \underset{\displaystyle OH\ Hg\ O\ Ac}{\underset{|}{\overset{|}{–C–C–}}} \xrightarrow{NaBH_4} \underset{\displaystyle OH\ H}{\underset{|}{\overset{|}{–C–C–}}}$$

Mercuric acetate Alcohol

Hydroboration – Oxidation :

(Anti–Markownikov orientation)

$$>C=C< + \frac{1}{2}(BH_3)_2 \longrightarrow B\left(>C-\underset{H}{\overset{|}{C}}<\right)$$

Alkene Diborane Tri alkyl borane

$$\xrightarrow[OH^-]{H_2O_2} -\underset{H}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}- + B(OH)_3$$

By Reduction of Carbonyl compounds :-

$$R-\underset{\underset{O}{\|}}{C}-H + 2H \xrightarrow{LiAlH_4/Na+C_2H_5OH} R-CH_2OH$$

1° alcohol

$$R-\underset{\underset{O}{\|}}{C}-R + 2H \xrightarrow{LiAlH_4/Na+C_2H_5OH} R-\underset{OH}{\overset{|}{CH}}-R$$

2° alcohol

Note :

(i) We cannot obtain 3° alcohol from this method

(ii) If we use NaH as reductant then the process is called as '**Darzen's process**'.

By Reduction of Acid & its derivatives :

$$R-\underset{\underset{O}{\|}}{C}-OH + 4H \xrightarrow{LiAlH_4} RCH_2OH$$

$$R-\underset{\underset{O}{\|}}{C}-X + 4H \xrightarrow{LiAlH_4} R\,CH_2OH + HX$$

$$R-\underset{\underset{O}{\|}}{C}-OR' + 4H \xrightarrow{LiAlH_4} RCH_2OH + R'OH$$

$$RCOOCOR + 8H \xrightarrow{LiAlH_4} 2\,RCH_2OH + H_2O$$

Important Note :- Acid amide does not form alcohol on reduction. It forms primary amine.

From Grignard reagent :

With oxygen : –

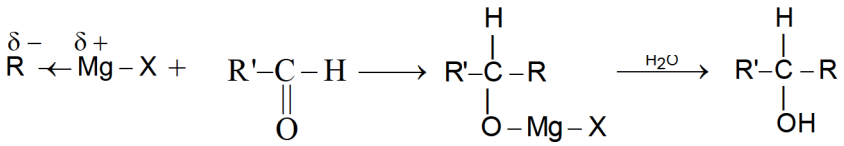
Grignard reagent forms alcohol of same no. of carbon atoms as in Grignard reagent.

$$2R-Mg-X + O_2 \xrightarrow[Al_2O_3]{\Delta} 2R-O-Mg-X \xrightarrow{2HOH} 2ROH + 2\,Mg(X)OH$$

With ethylene oxide :

$$R^{\delta-}\leftarrow Mg^{\delta+}-X + \underset{\delta-}{\overset{\delta+}{CH_2}}-\underset{O}{\overset{\delta+}{CH_2}} \longrightarrow R-CH_2-CH_2-O-Mg-X \xrightarrow{H_2O} R-CH_2-CH_2OH + Mg(X)OH$$

[Alcohol with two carbon more than Grignard reagent]

With carbonyl compounds : 

Note :

(i) If R' = H , Product will be 1° alcohol.

(ii) If R' = R, Product will be 2° alcohol.

(iii) If carbonyl compound is ketone, product will be 3° alcohol.

(iv) It is the best method for preparation of alcohol because we can prepare every type of alcohols.

From Primary amines :-

$R–NH_2 + HNO_2 \xrightarrow{HCl} R–OH + N_2 + H_2O.$

But it is not a good method for preparation of alcohol because a number of by products are formed in this reaction like alkyl chloride, alkyl nitrite, alkene and ether.

Note : In this reaction if we take ethyl amine then main product will be ethanol while if we take methyl amine, then main product will be dimethyl ether.

PHYSICAL PROPERTIES

(a) Alcohols are colourless with specific smell liquid. They are soluble is water due to H-bonding. These are partially soluble in organic solvents.

(b) They are liquid in nature up to 12-carbon.

(c) Melting point and Boiling point α molecular mass $\alpha \frac{1}{\text{No. of branches}}$

(d) Boiling point of alcohols are higher than equivalent ethers. It is due to H-bonding.

(e) Alcohols are poisonous in nature also. Poisonous character increase with increment in molecular weight or branching. Ethanol is exception, which is non-poisonous in nature. It is most useful organic solvent.

(f) Methanol causes blindness.

(g) Isopropyl alcohol is called as rubbing alcohol.

(h) Cholesterol is also an example of complex alcohol which is called notorious alcohol because it causes heart attack.

(i) Viscous nature of alcohol is directly proportional to H-bonding or number of -OH groups. That is why we can say alcohol is less viscous than glycerol & manitol is more viscous than glycerol.

(j) Ethanol is liquid while glucose is solid. It is due to more H-bonding in glucose.

CHEMICAL PROPERTIES

Chemical reactions of alcohols are classified in the following three types :-

(i) Reaction of H atom of –OH group of Alcohols

(ii) Reaction of OH group of Alcohols

(iii) General reaction of Alcohols.