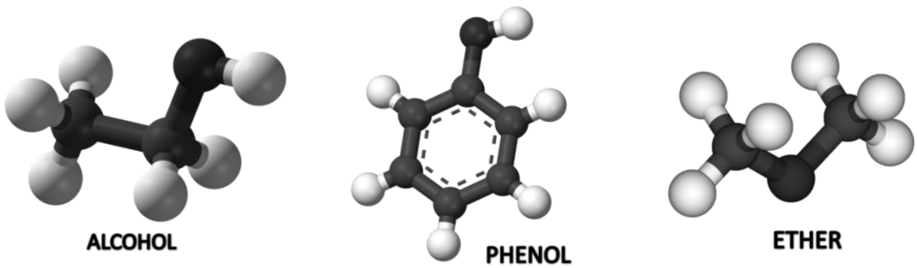
Chapter 5 Alcohols, Phenols and Ethers

Day – 1

Alcohols, Phenols and Ethers

Alcohols, phenols and ether are the basic compounds for the formation of detergents, antiseptics and fragrances, respectively. You have learnt that substitution of one or more hydrogen atom(s) from a hydrocarbon by another atom or a group of atoms result in the formation of an entirely new compound having altogether different properties and applications. Alcohols and phenols are formed when a hydrogen atom in a hydrocarbon, aliphatic and aromatic respectively, is replaced by –OH group. These classes of compounds find wide applications in industry as well as in day-to-day life. For instance, have you ever noticed that ordinary spirit used for polishing wooden furniture is chiefly a compound containing hydroxyl group, ethanol. The sugar we eat, the cotton used for fabrics, the paper we use for writing, are all made up of compounds containing –OH groups. Just think of life without paper; no note-books, news-paper, currency notes, cheques, certificates, etc. The magazines carrying beautiful photographs and interesting stories would disappear from our life. It would have been really a different world.



An alcohol contains one or more hydroxyl (OH) group(s) directly attached to carbon atoms, of an aliphatic system (CH_3OH) while a phenol contains –OH group(s) directly attached to carbon atoms(s) of an aromatic system (C_6H_5OH).

The substitution of a hydrogen atom in a hydrocarbon by an alkoxy or aryloxy group (R-O/Ar-O) yields another class of compounds known as 'ethers', for example, CH_3OCH_3 (dimethyl eather). You may also visualize ethers as compounds formed by substituting the hydrogen atom of hydroxyl group of an alcohol or phenol by an alkyl or aryl group.

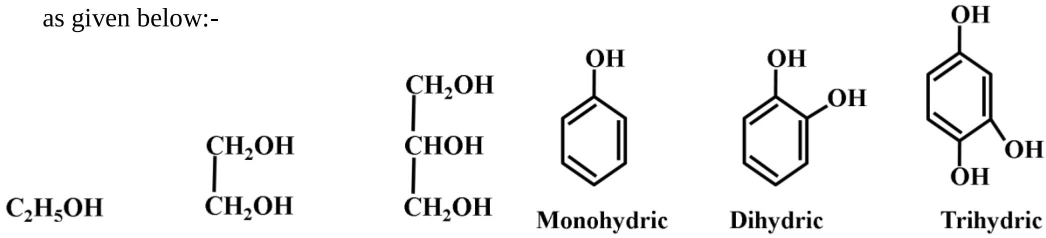
In this unit, we shall discuss the chemistry of three classes of compounds, namely — alcohols, phenols and ethers.

Classification

The classification of compounds makes their study systematic and hence simpler. Therefore, let us first learn how are alcohols, phenols and ethers classified.

Mono, Di, tri or Polyhydric Compounds

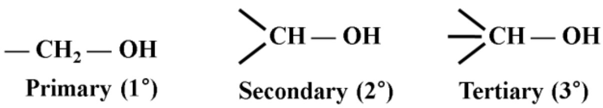
Alcohols and phenols may be classified as mono–, di–, tri– or polyhydric compounds depending on whether they contain one, two, three or many hydroxyl groups respectively in their structures as given below:-



Monohydric alcohols may be further classified according to the hybridization of the carbon atom to which the hydroxyl group is attached.

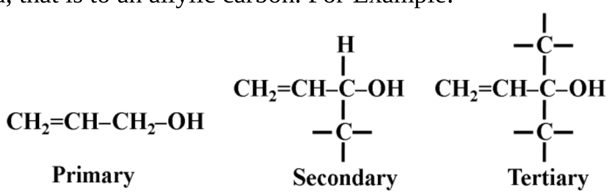
In this class of alcohols, the –OH group is attached to an sp^3 hybridised carbon atom of an alkyl group. They are further classified as follows:-

Primary, secondary and tertiary alcohols: In these three types of alcohols, the –OH group is attached to primary, secondary and tertiary carbon atom, respectively as depicted below:-

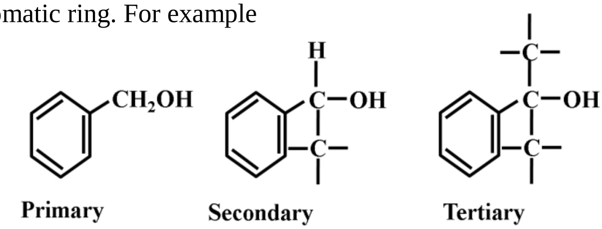


Allylic Alcohols

In these alcohols, the –OH group is attached to a sp^3 hybridised carbon next to the carbon-carbon double bond, that is to an allylic carbon. For Example:-

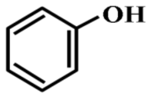


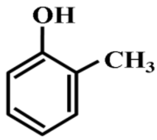
Benzylic alcohols: In these alcohols, the –OH group is attached to a sp^3 –hybridized carbon atom next to an aromatic ring. For example



(ii) Compounds containing C_{sp2} – OH bond: These alcohols contain —OH group bonded to a carbon-carbon double bond i.e., to a vinylic carbon or to an aryl carbon. These alcohols are also known as vinylic alcohols.

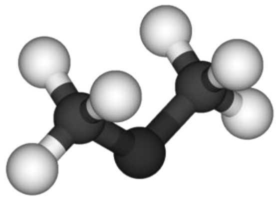
Vinylic alcohol: $CH_2 = CH – OH$





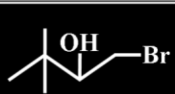
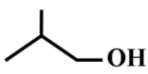
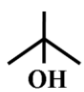
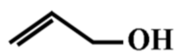
Ethers

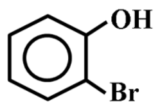
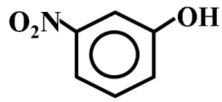
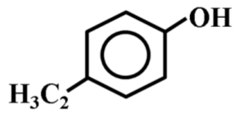
Ethers are classified as simple or symmetrical, if the alkyl or aryl groups attached to the oxygen atom are the same, and mixed or unsymmetrical, if the two groups are different. Diethyl ether, $C_2H_5OC_2H_5$, is a symmetrical ether whereas $C_2H_5OCH_3$ and $C_2H_5OC_6H_5$ are unsymmetrical ethers.

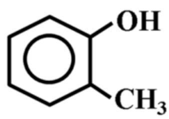
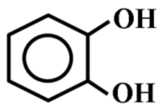
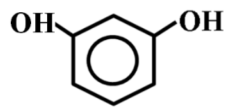


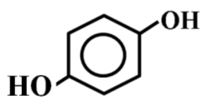
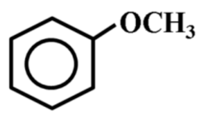
ETHER

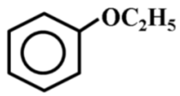
Nomenclature

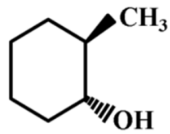
Structure			
Common Name		n-butanol	sec-butanol
IUPAC Name	1-bromo-3,3-dimethybutan-2-ol	Butan-1-ol	Butan-2-ol
Structure			
Common Name	Isopropyl alcohol	Tert-butanol	Vinyl Alcohol
IUPAC Name	2-methyl propan-1-ol	2-methyl propan-2-ol	Prop-2-ene-1-ol

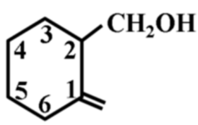
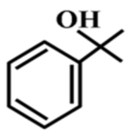
Structure			
Common Name	Ortho bromophenol	metanitrophenol	Pera ethylphenol
IUPAC Name	2-methyl phenol	3-nitrophenol	4-elhyplenol

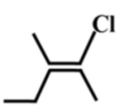
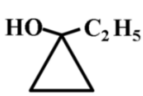
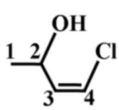
Structure			
Common Name	Ortho cresol	Catechol	Resorcinol
IUPAC Name	2-methyl phenol	Benzene-1,2-diol	Benzene-1,3-diol

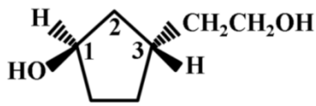
Structure		$CH_3 - O - CH_2CH_3$	
Common Name	Hydroquinone	Ethyl methyl ether	Anisole
IUPAC Name	Benzene-1,4-diol	Ethoxy Ethane	Mehtoxy benzene

Structure	$C_2H_5-O-C_2H_5$	
Common Name	Diehtyl ether	Phenetol
IUPAC Name	Ethoxy ethane	Ethoxy benzene

Structure	$C_6H_5-O-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_3$	
Common Name	Phenylisopentyl ether	
IUPAC Name	3-methyl butoxy benzene	(1R, 2R) 2-methyl cyclo hexenol

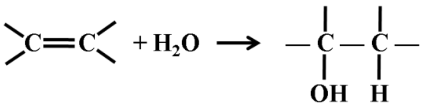
Structure		
Common Name		
IUPAC Name	2-(hydroxy methyl) cyclohexanone	2-phenylproan-2-ol

Structure			
Common Name			
IUPAC Name	(2E) -2-chloro-3-methylpent-2-ene	1-ethyl cyclopropan-1-ol	(3-Z)-4-chlorobut-3-en-2-ol

Structure	
Common Name	
IUPAC Name	(1R, 3S)-3-(2hydroxy) cyclopentanol

(1) Preparation of Alcohol

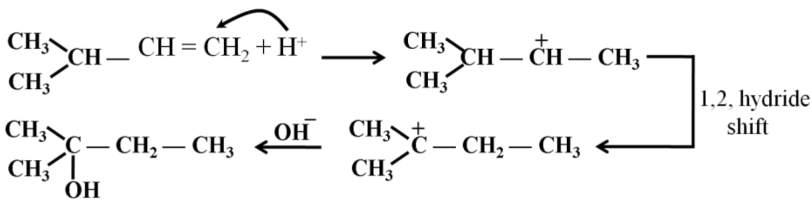
(A) Hydration of Alkenes



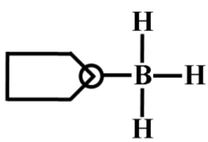
This is of three types

(a) Simple $H^+ + H_2O$

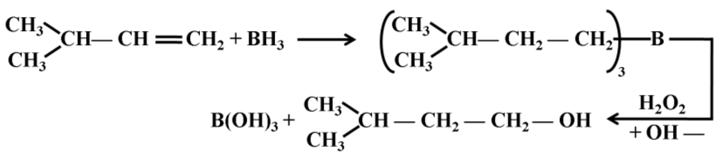
It will follow Markoni koff's addition, with 1-2 shift is its possible.



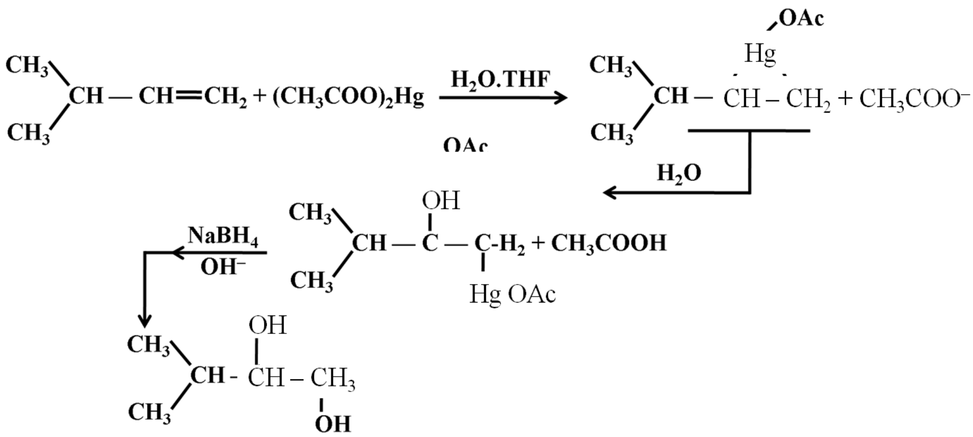
(b) Hydroboration-Oxidation:- This follow Anti Markoni koff's addition.

BH_3 in THF 

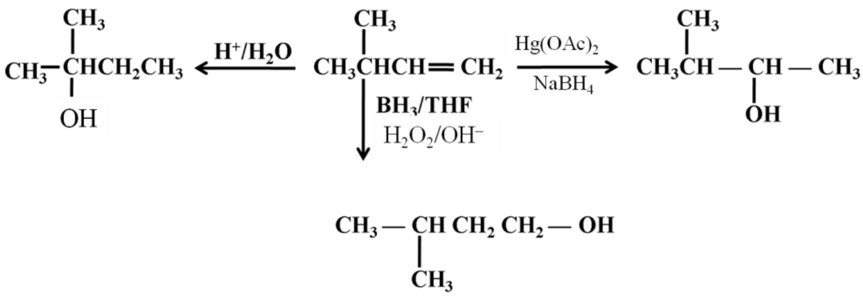
BH_3 is reactive and does not exist alone. It forms dimer B_2H_6



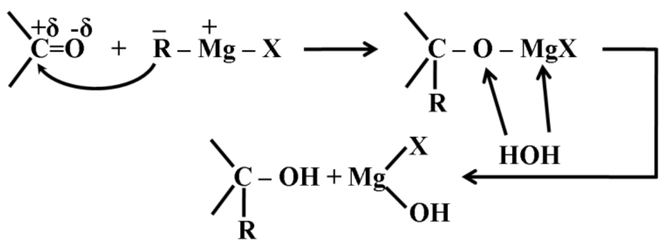
(c) Oxymercuration–demercuration:- Follows markoni koffs rule but there is no formation of carbocation therefore there is no 1-2 hydride, methyl or phenyl shift.



Summary of all three Rxn



(2) From Grignard's Reagent and Carbonyl Group



From formaldehyde (HCHO) we get → 1° alcohol

From other aldehydes we get → 2° alcohol

From ketones we get → 3° alcohol

(3) From Alkyl Halide

$$RX + OH^- \rightarrow ROH + X^-$$

Both SN^1 and SN^2 reactions

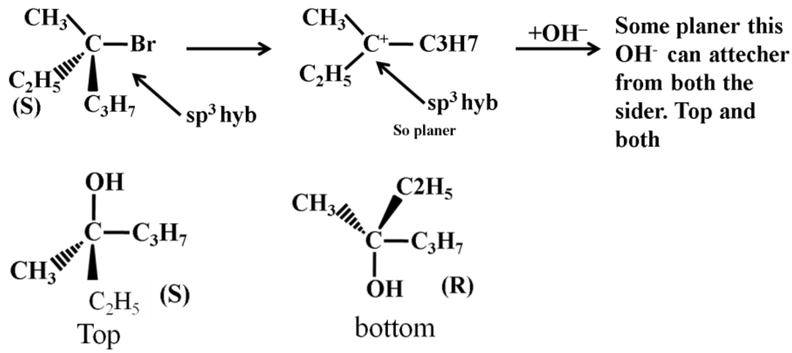
$$SN^1 :- \ RX \xrightarrow{\text{Slow}} R^+ + X^- \xrightarrow[\text{Fast}]{+OH^-} ROH + X^-$$

(1) Intermediate is carbocation so there can be 1-2 shift

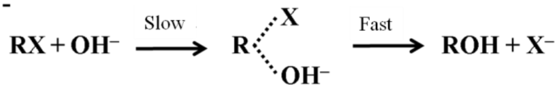
(2) Mainly 3° halides show this reaction

(3) Sterochemistry → mixture of inversion and retention

(4) two step reaction



SN² :-



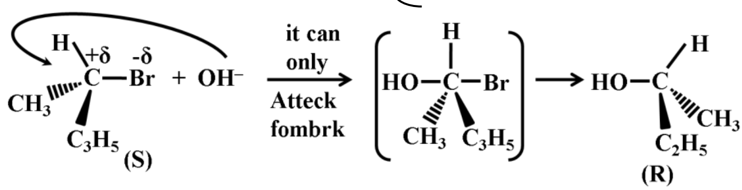
(1) No intermediate. (So no 1-2 shift)

(2) One step reaction

(3) Generally 1° halides show these

(4) Stereochemistry – only inversion

2° can show SN_1 for weak base and SN_2 for strong base



(4) Hydrolysis of Ethers

$$R - O - R' + H_2O \xrightarrow{H^+} ROH + R'OH$$

(5) Reduction of carbonyl group for 1° and 2° alcohol

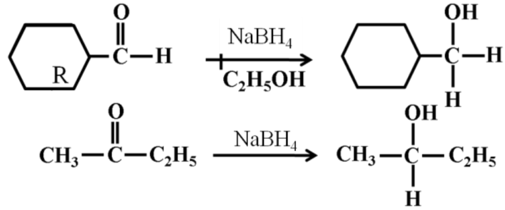
A use of sodium borohydride ($NaBH_4$)

$NaBH_4$ reduces Aldehydes to 1° alcohols and

Ketone to 2° alcohols

Solvent may be alcohol, ethers or water

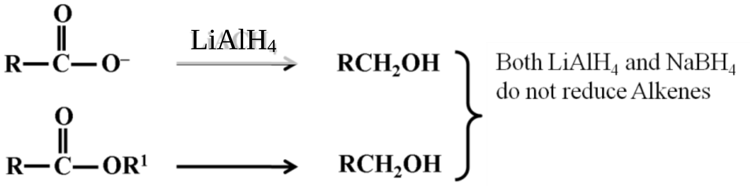
Ex:-



$NaBH_4$ is weal reducing agent. So it will not reduce carboxylic acid and esters

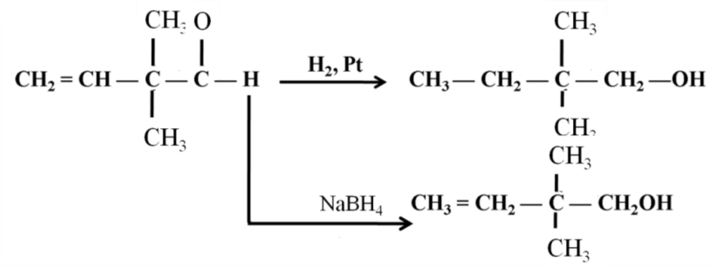
(B) Use of $LiAlH_4$

Strong reducing agent. Reduces aldehyde and ketones to alcohols. Also reduces acids and esters to alcohols.



(c) Reduction by catalytic Hydrogen

In presence of Reney's Nickel or Pt. hydrogen added changes C = O to C – OH. But this also reduces alkenes.



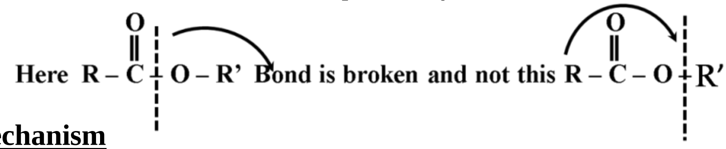
SOME Common Reducing Agents

Group	Product	$LiAlH_4$ (ether)	$NaBH_4$ (ether)	B_2H_6 (THF)	H_2/metal
–CHO	$-CH_2OH$	Yes	Yes	Yes	Yes
>C=O	>CH–OH	Yes	Yes	Yes	Yes
– COOH	$-CH_2OH$	Yes	Yes	Yes	Yes
$-C(=O)Cl$	$-CH_2OH$	Yes	Yes	No	Yes
$(CO)_2O$	RCH_2OH	Yes	No	Yes	Yes
$-C(=O)OR$	RCH_2OH	Yes	No	Yes	Yes
>C=C<	–C–C–	No	No	Yes	Yes

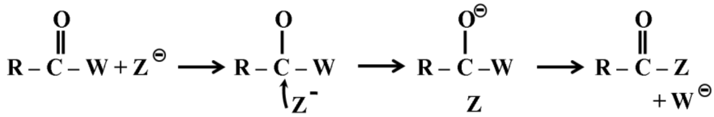
(6) Hydrolysis of Esters

$$RCOOR' + H_2O \xrightarrow{H^+ \text{ or } OH^-} RCOOH + R'OH$$

Alcohol is more volatile so can be separated by distillation



General Mechanism



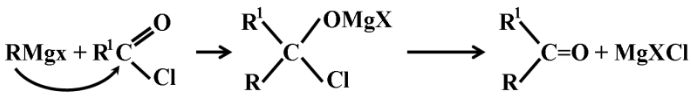
W can be OR' (ester); -Cl (Chloro); NH_2 (amide); -OH (alcohol); OOCR (anhydride)

Z⊖ - is a base.

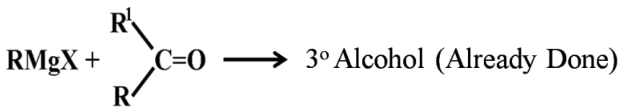
(7) From Acid and Acid Derivatives

(A) Reduction by $LiALH_4$ ($NaBH_4$ does not work)

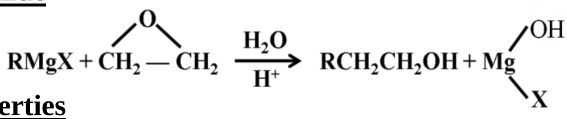
(B) Add of RMgX to give 3° Alc.



Also



(8) From Epoxide



Physical Properties

(1):- C_1 – C_{11} – Colourless liquid, lower members have smell

(2):- C_{12} and above – waxy solid – No smell

(3):- CH_3OH – Toxic C_2H_5OH – neuro-inhibitor

(4):- Less acidic than water and lighter than water

(5):- Highly soluble for lower no. But solubility decreases with increase in Carbon No.

(6):- b.p. ∝ carbon No.

(7):- 1° > 2° > 3° for b.p.

(8):- bp < carboxylic acid but greater than other molecules of similar size

Illustration

Find the order of b.p?

Solution

(i) Pentan-1-ol, butan-1-ol, butan-2-ol, ethanol, propen-1-ol; methanol

CH_3OH < C_2H_5OH < C_3H_7OH < butan-2-ol < butanol < pentanol

(ii) n-butane, butanol, 1chlopropane, ethoxy ether

n-butene < ethoxy ether < ether < butanol