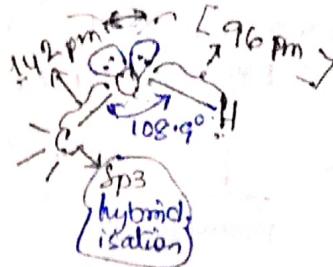


18/7/10

Alcohol, Phenols, Ethers

Hydroxyl derivatives
of aliphatic hydrocarbons.
General formula - $C_nH_{2n+1}OH$



Classification of alcohols

Aliphatic alcohols

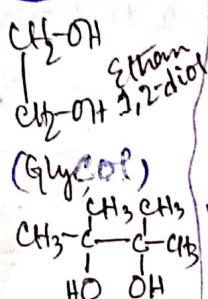
Monohydric alcohols

Alcohols having only one $-OH$ group

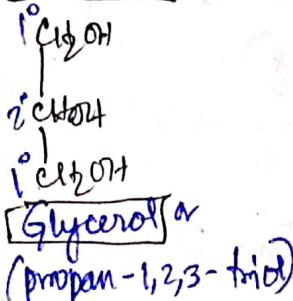
- 1° alcohol
- 2° alcohol
- 3° alcohol

Dihydric alcohols

Alcohols having at least 2 $-OH$ groups.



Trihydric alcohols



When C of C-OH bond is sp^3 hybridised

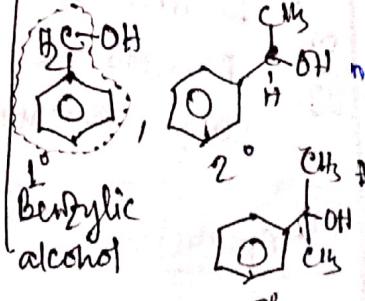
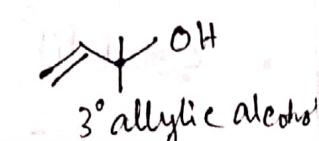
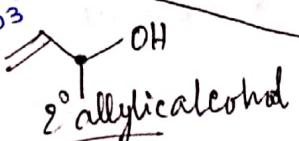
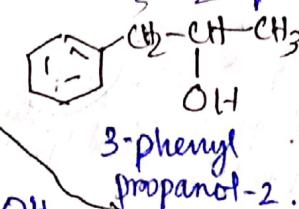
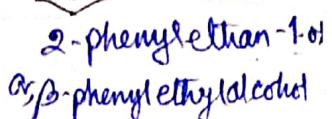
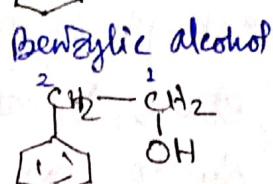
- $\begin{array}{c} CH_3-CH_2-OH \\ | \\ SP^3 \quad SP^3 \end{array}$ (1° alcohol)
- $\begin{array}{c} CH_3-CH(OH)-CH_3 \\ | \\ CH_3 \end{array}$ (2° alcohol)
- $\begin{array}{c} CH_3-CH(OH)-CH_3 \\ | \\ CH_3 \end{array}$ (3° alcohol)

Allylic alcohol: $\begin{array}{c} CH_2=CH-CH_2-OH \\ | \\ SP^3 \end{array}$

When C of C-OH bond is sp^2 hybridised

- Vinyllic alcohol: $\begin{array}{c} CH_2=CH-OH \\ | \\ SP^2 \end{array}$
- Aryllic alcohol: $\begin{array}{c} OH \\ | \\ SP^2 \end{array}$ Phenol

Aromatic alcohols



Difference between 1°, 2° and 3° alcohols in terms of structure
→ Done above.

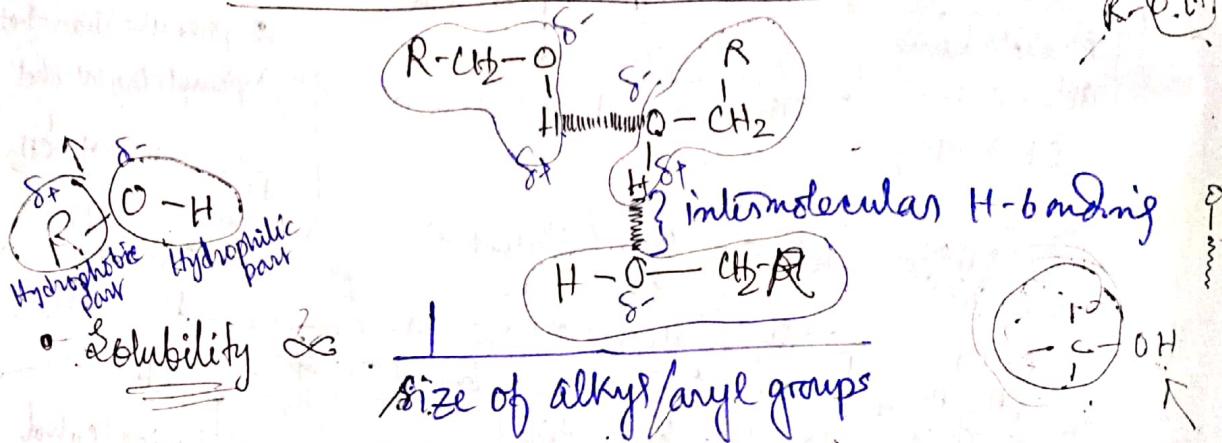
Physical properties of alcohols

B.p.t of ethers are comparable to those of hydrocarbons.

B.p.t. \propto no. of C-atoms (Due to increase in the amount of VanderWaals force of interaction)

B.p.t $\propto \frac{1}{\text{Branching}}$ (1° > 2° > 3°) as much the extent of branching increases the molecule gets a spherical shape due to surface tension which the VanderWaals force decreases as well as b.p.t. decreases.

B.p.t of alcohols & phenols are higher than that of hydrocarbons, ethers, haloalkanes, haloarenes of comparable molecular masses due to intermolecular H-bond formation.



Solubility \propto Branching of alcohols (3° > 2° > 1°)

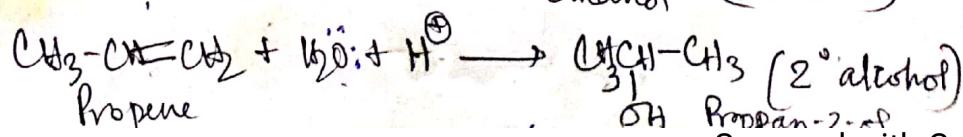
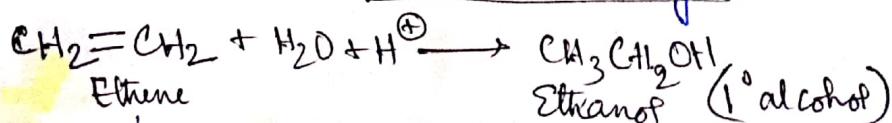
Soluble in water due to formation of intermolecular H-bonding.

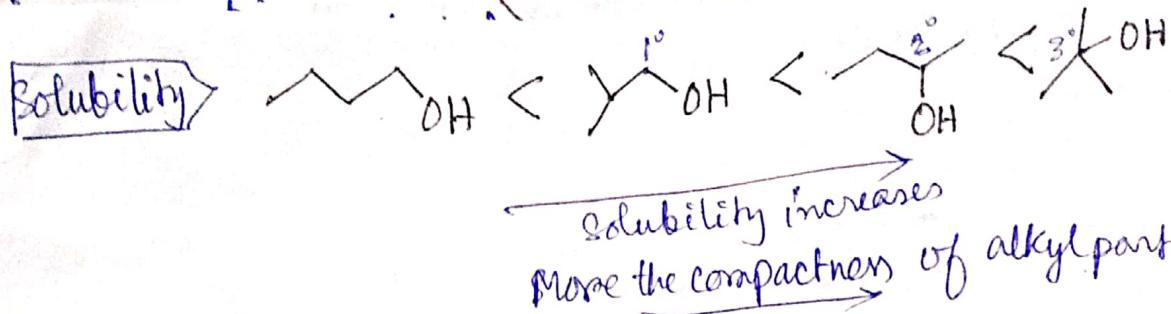
Phenols are less soluble than alcohols due to presence of large hydrocarbon part (benzene ring).

Preparation of alcohols

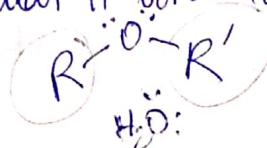
METHODS OF PREPARATION :-

Hydration of Alkenes By Direct Addition of water at low temp and high pressure in presence of mineral acids as catalyst.



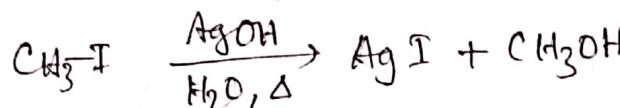
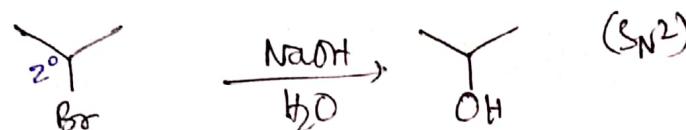
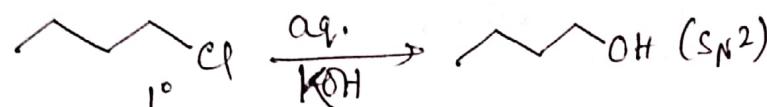


- Alcohols can form intermolecular H-bonds but ethers can't.

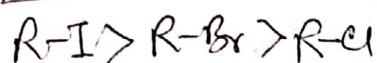


Prepn of Alcohols

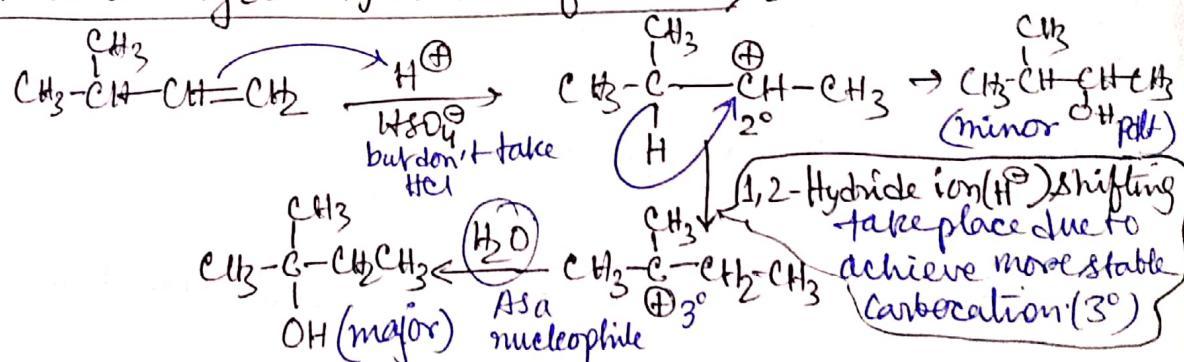
1) Hydrolysis of Alkyl Halides:



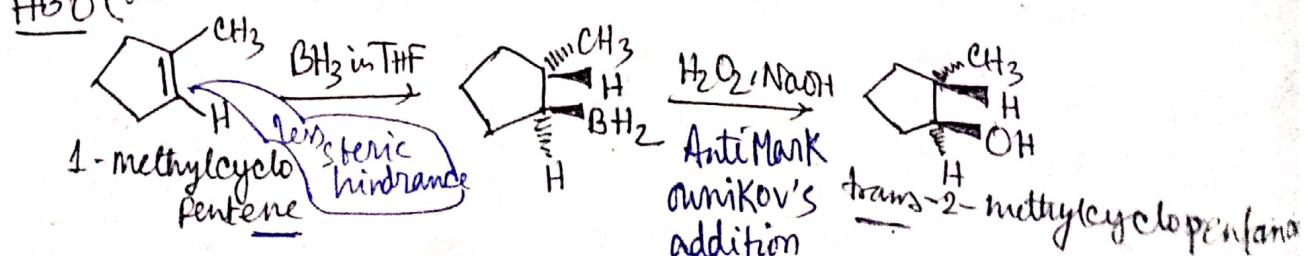
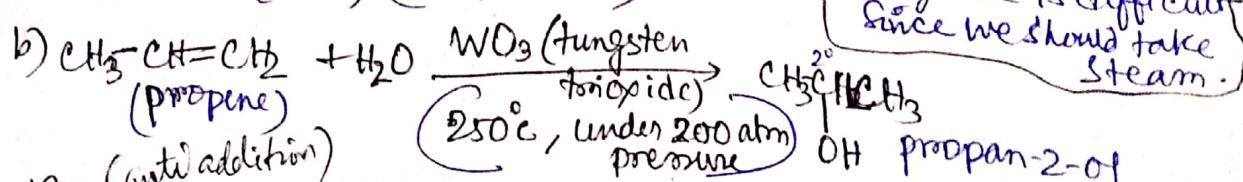
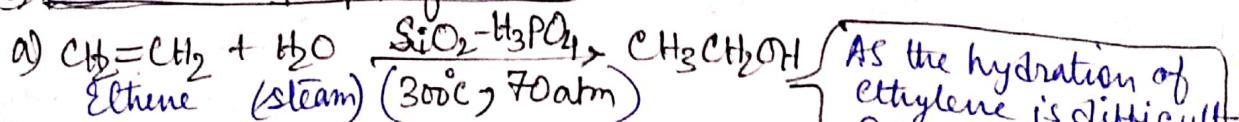
Reactivity of halides :-



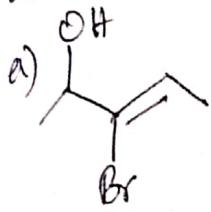
2) Acid catalyzed hydration of Alkenes:



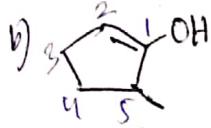
3) Industrial prepn. of alcohol



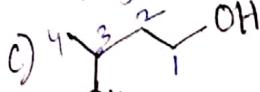
Give IUPAC names for these structures :-



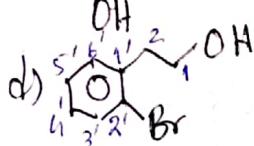
3-Bromo-2-hydroxy
Pent-3-ene



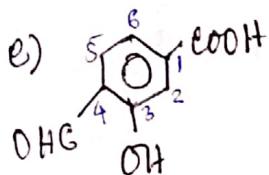
5-Methyl Cyclopent-1-enol



Butane-1,3-diol



2-(2'-Bromo-phenyl)ethanol



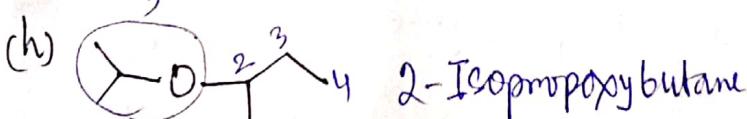
4-formyl-3-hydroxy benzoic acid



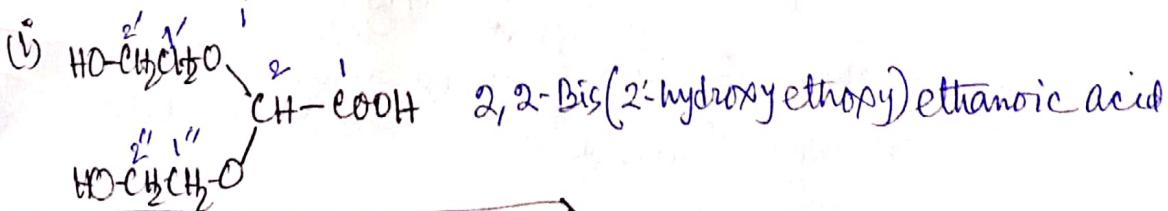
Methoxy ethane



2-Methoxy propane



2-Isopropoxybutane



2,2-Bis(2-hydroxyethyl)ethanoic acid

Some common Cyclic Ethers



Oxacyclopropane or
oxirane (ethylene oxide)



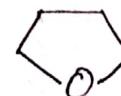
1,4-Dioxacyclohexane
(1,4-dioxane)



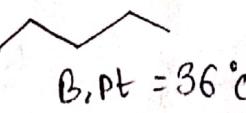
ether B.Pt = 34.6°C



Oxacyclobutane
or oxetane



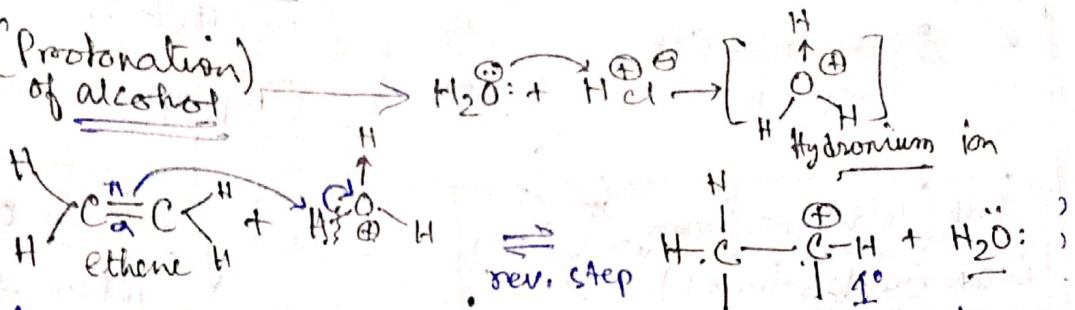
Oxacyclopentane
(tetrahydrofuran
or THF)



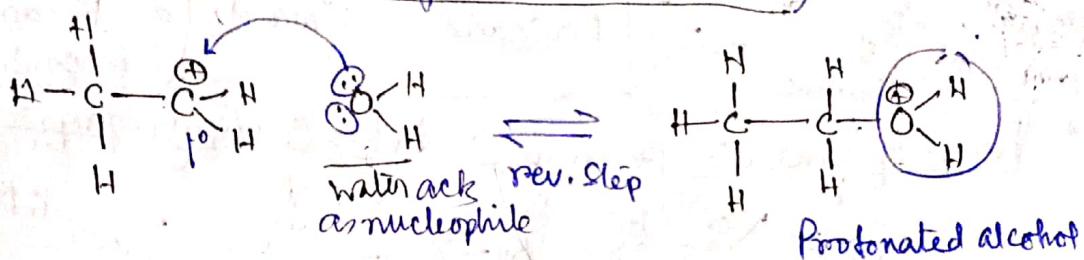
CH_3OH		78.3°C	97.2°C
		117.7°C	
		108°C	
		82.3°C	

Mechanism The acid catalyst hydration of alkenes involves three steps:

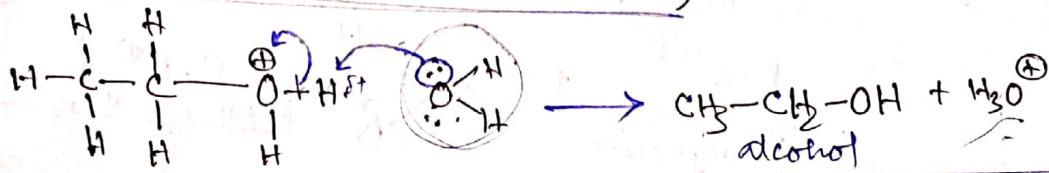
Step 1: (Protonation of alcohol)



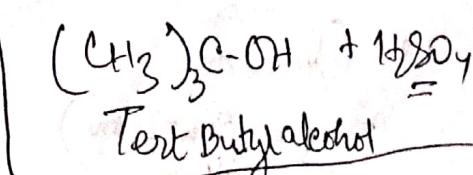
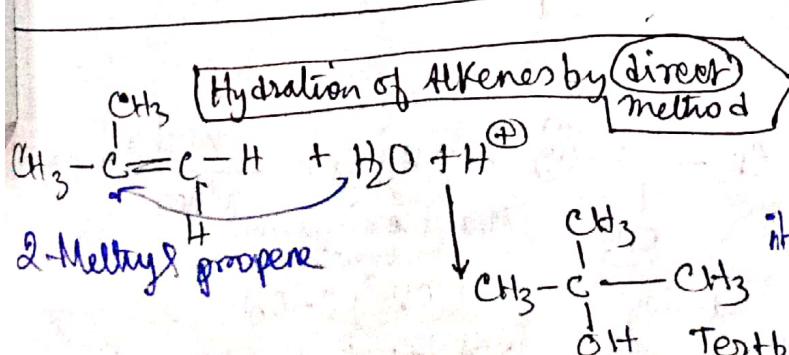
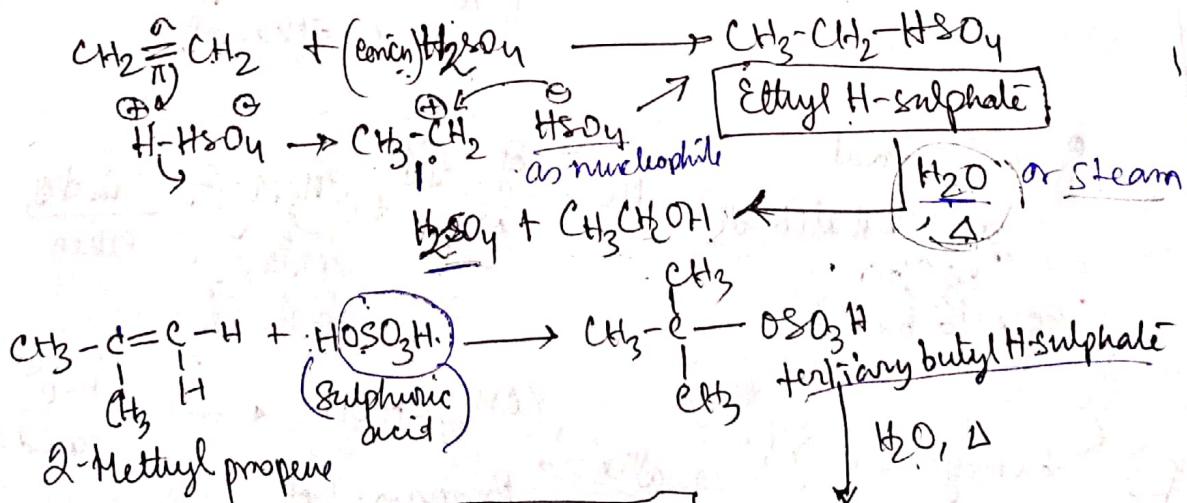
Step 2: (Nucleophilic attack of water on carbocation)



Step 3: (Deprotonation to form an alcohol)

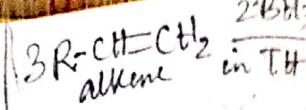
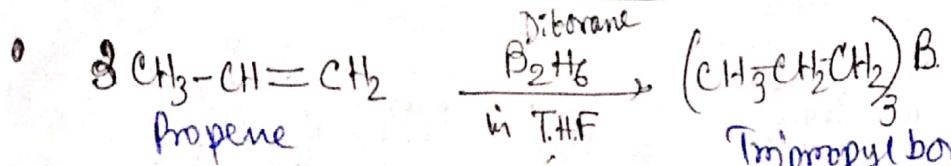


By indirect method in which alkenes are passed through concentrated H_2SO_4 to form alkyl hydrogen sulphate, followed by hydrolysis of alkyl hydrogen sulphate with steam.



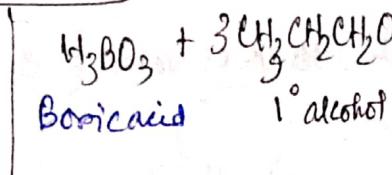
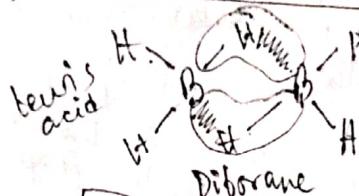
it obeys Markovnikoff's rule of addition

Hydroboration Oxidation (HBO)



Tripropyl
Borane
in
alkaline
medium
 $\text{R}-\text{C}_6\text{H}_5$

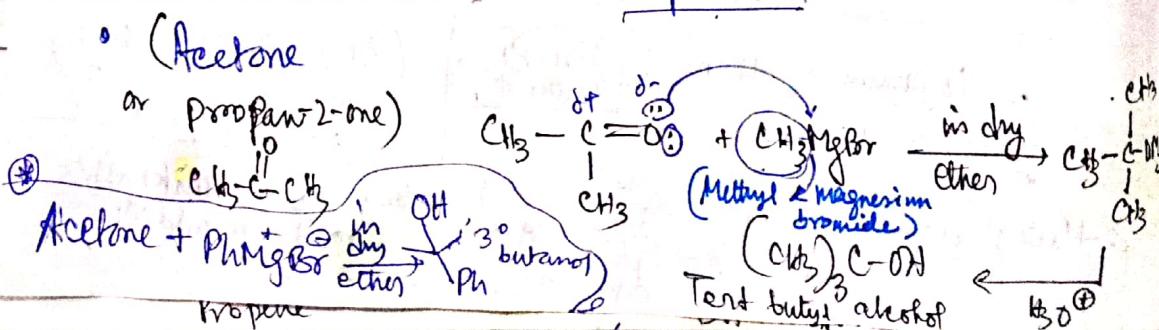
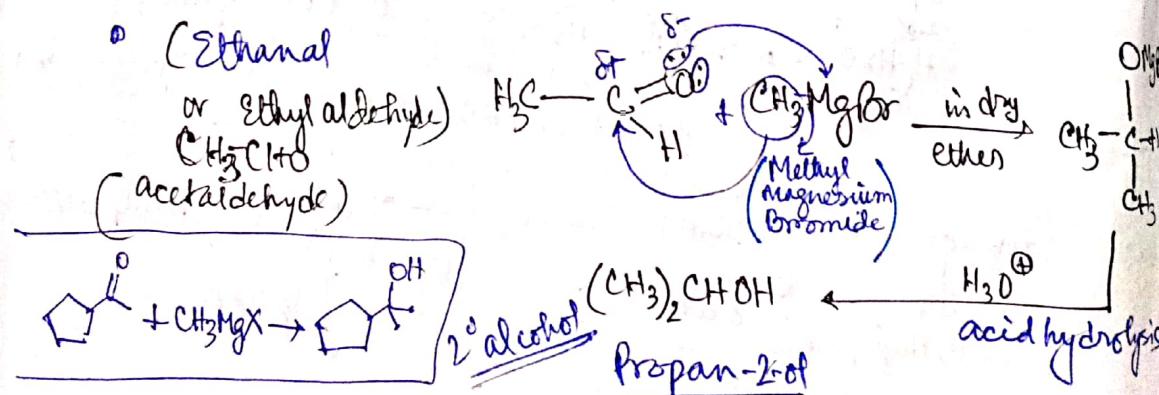
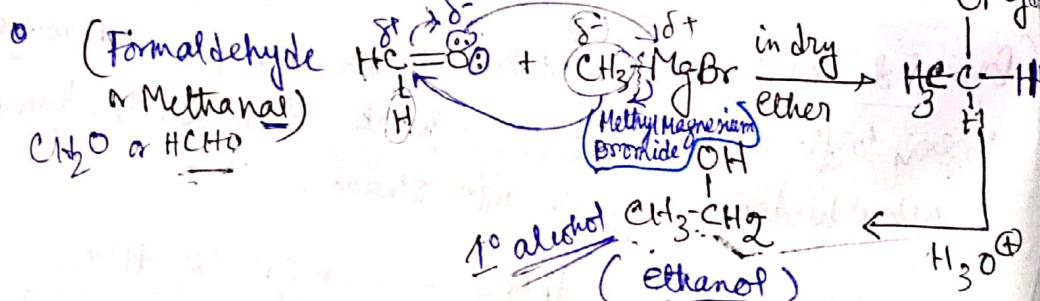
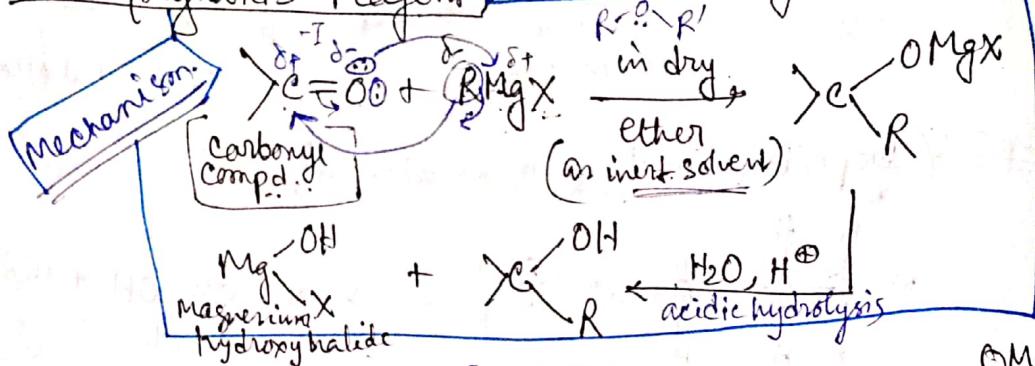
THF (Tetrahydrofuran is an inert solvent)

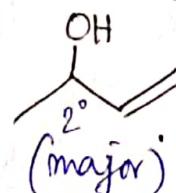
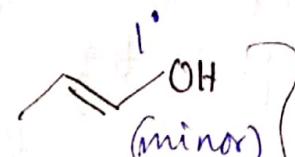
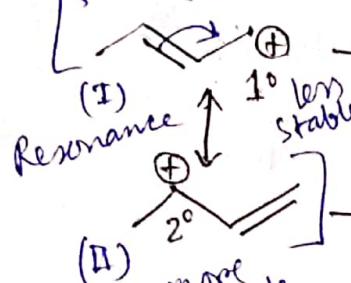
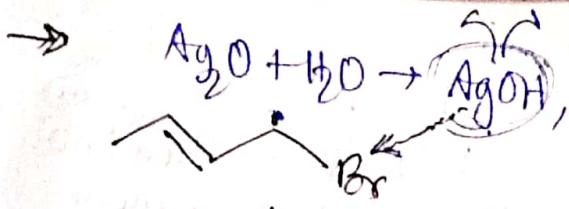


H_2O_2 in OH^- alkaline medium

Obeys AntiMarkovnikoff's addition rule or Kharas or Peroxide effect

From Grignard's reagent \rightarrow From Carbonyl - prepn. of alcohol





Dihydroxylation synthesis
of 1,2-diols from alkenes

Syn Dihydroxylation

$(\text{OsO}_4, \text{H}_2\text{O}_2)$

or

alkene $\xrightarrow[\text{KMnO}_4, \text{OH}^-]{\text{H}_2\text{O}_2}$

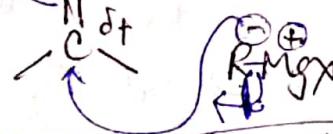
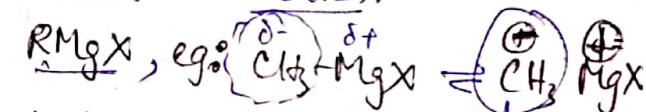
(cold, dilute) (Syn dihyd)
-hydroxylation

Preparation of Alcohols - From Carbonyl

- Using Grignard Reagent with Aldehydes & Ketones.

C-metal

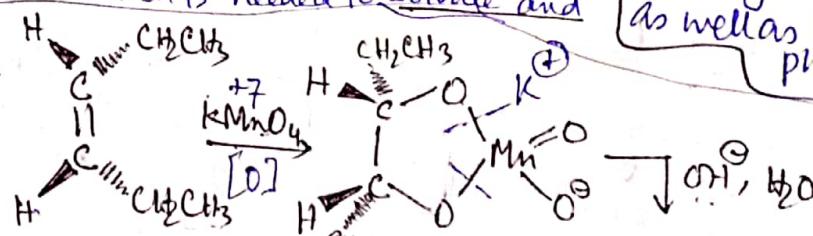
$\text{R-X} \xrightarrow[\text{alkyl halide}]{\text{Mg in dry ether}}$



This rxn is always carried out in a dry (anhydrous) ether solvent which is needed to solvate and

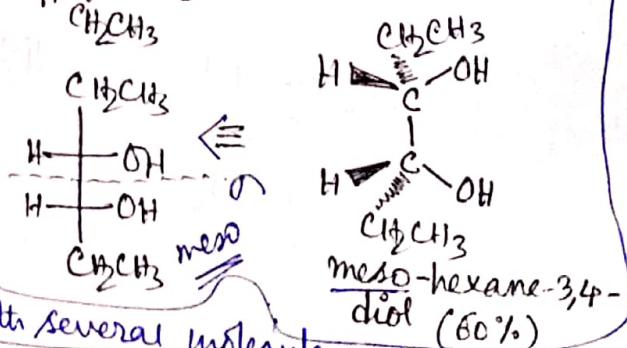
Strong base as well as Nucleophile

Dihydroxylation



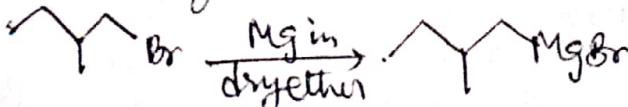
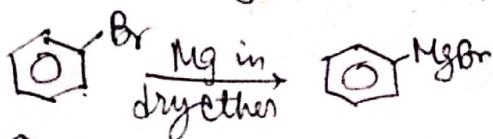
Stabilize the Grignard reagent

as it forms. Although we write the grignard reagent as R-MgX the actual species in solution usually contains two, three or four of these units associated together with several molecules of the ether solvent.



Grignard reagents may be made from 1°, 2° and 3° alkyl halides as well as from vinyl and aryl halides. Alkyl iodides are the most reactive halides, followed by bromides and chlorides. Alkyl fluorides generally don't react.

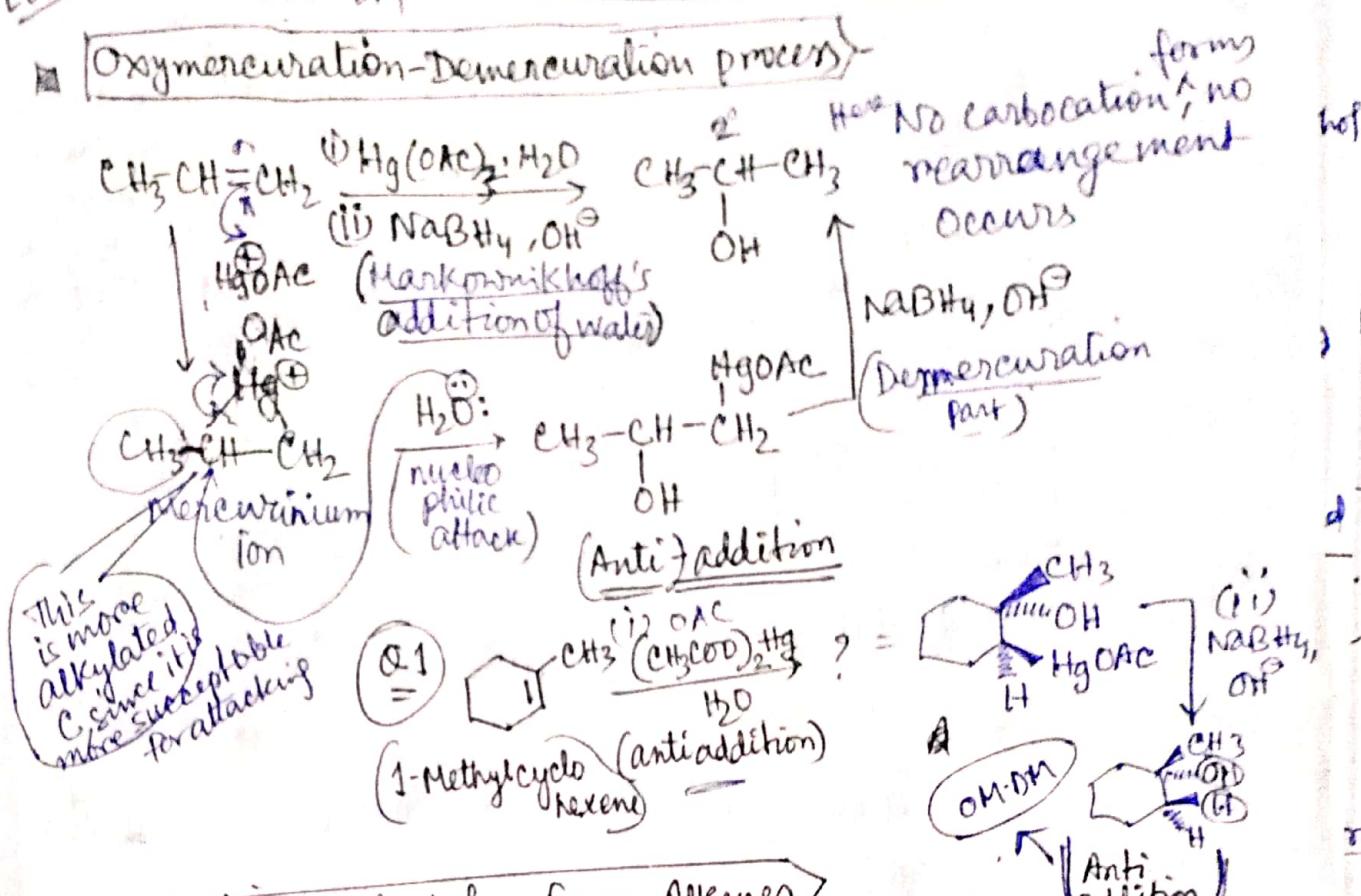
reactivity: $\text{R-I} > \text{R-Br} > \text{R-Cl} > \text{R-F}$



Lunit

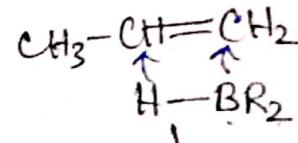
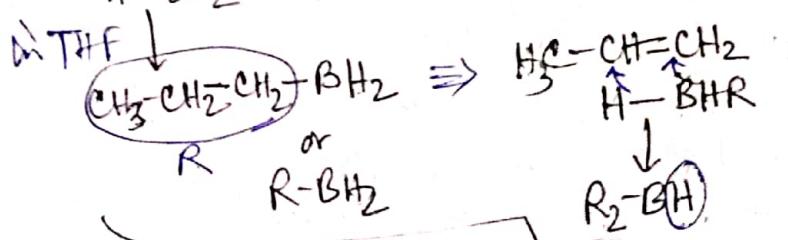
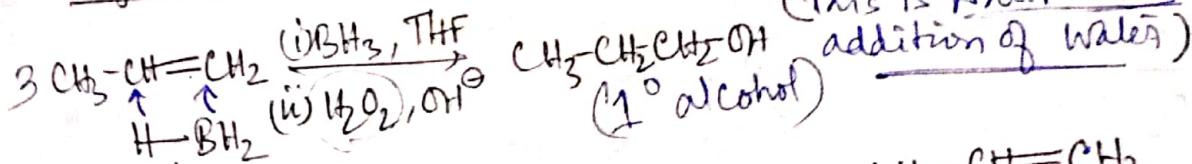
OM-DM

Oxymmercuration-Demercuration process



Preparation of Alcohols - from Alkenes

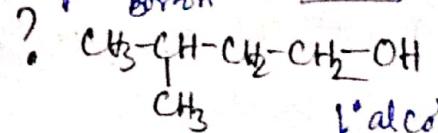
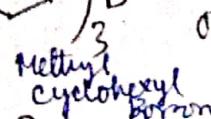
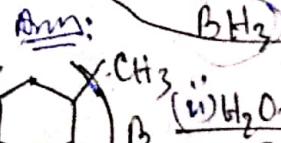
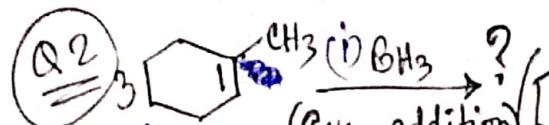
Hydroboration Oxidation process: $\text{C=C} \xrightarrow{\text{(i) } \text{BH}_3, \text{THF}}$ $\text{C}(\text{H})(\text{R})-\text{CH}_2\text{OH}$ (This is Anti-Markownikoff addition of water)



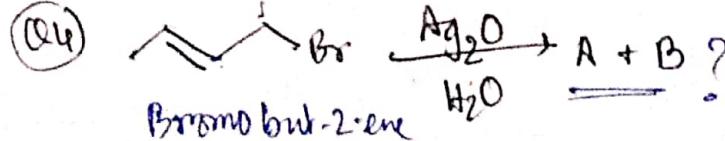
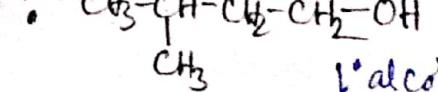
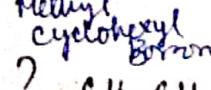
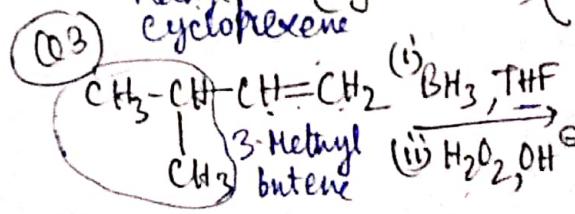
R_3B
Trialkylborane

$3\text{ROH} + \xleftarrow{\text{H}_2\text{O}_2}$ in OH^- , alkali medium

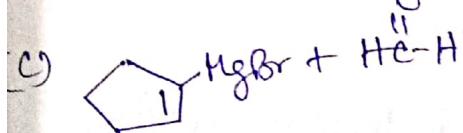
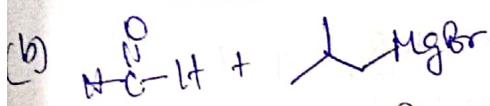
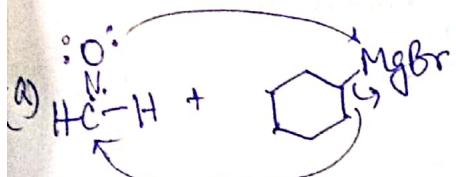
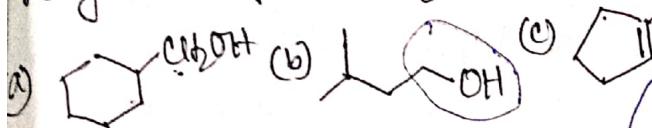
BH_3



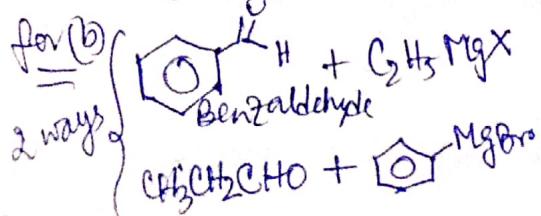
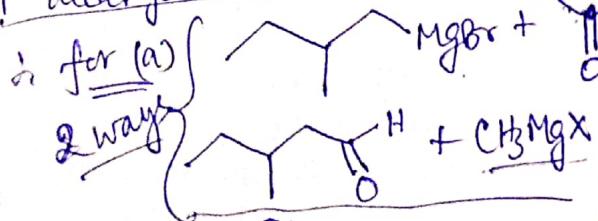
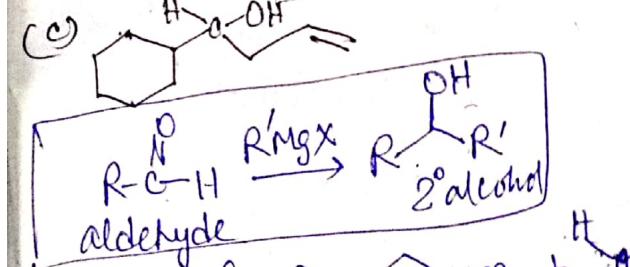
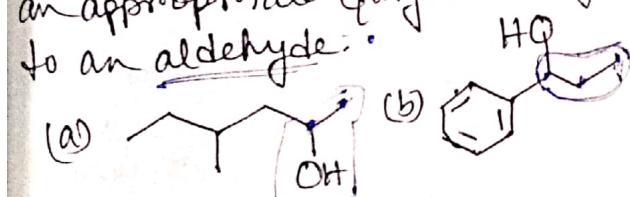
1° alcohol



Show how you would synthesize the following primary alcohols by adding an appropriate Grignard reagent to formaldehyde (HCHO)



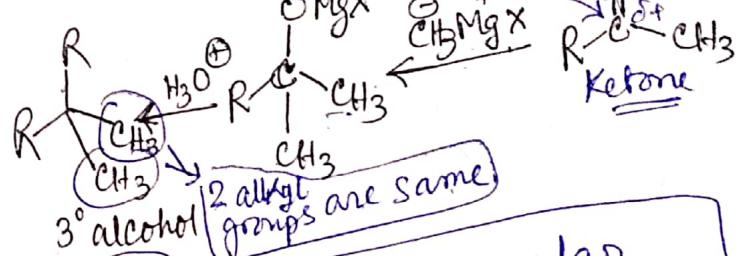
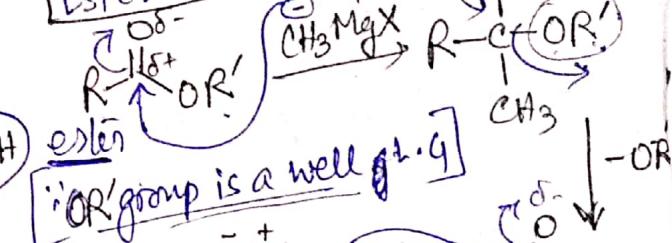
Q2 Show two ways you could synthesise each of the following secondary alcohols by adding an appropriate Grignard reagent to an aldehyde.



Prepn. of Alcohols - from Carbonyl and Reagent with

Using Grignard Reagent (cont.)

ESTERAS



where

$$Z = -OR(\underline{\text{ester}})$$

$Z \equiv X$ (acyl halide)

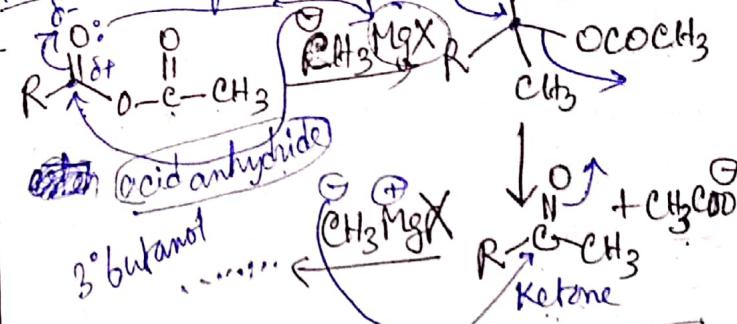
$\text{Z} \Rightarrow (\text{dehydrating agent})$

α -Z = -OCOR (anhydride)

Map of equiv. of RMgX

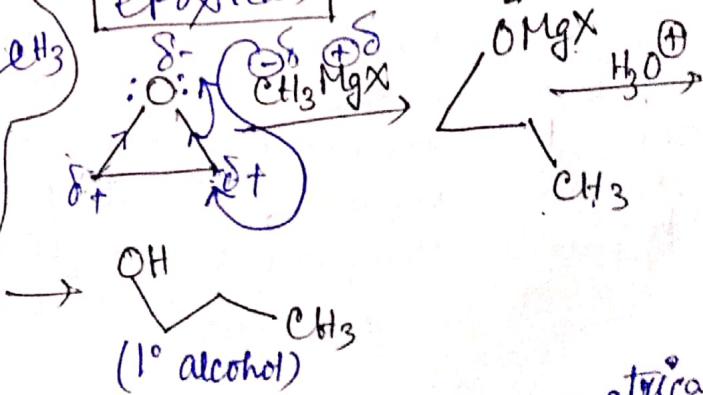
Here AS 2 equiv. of

70: 0 H₂MgX₂

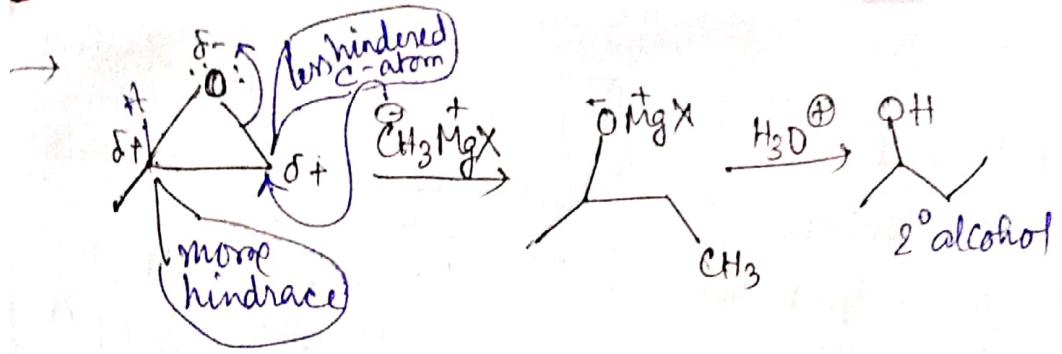


Using Grignard Reagent with Carboxylates

Epoxy

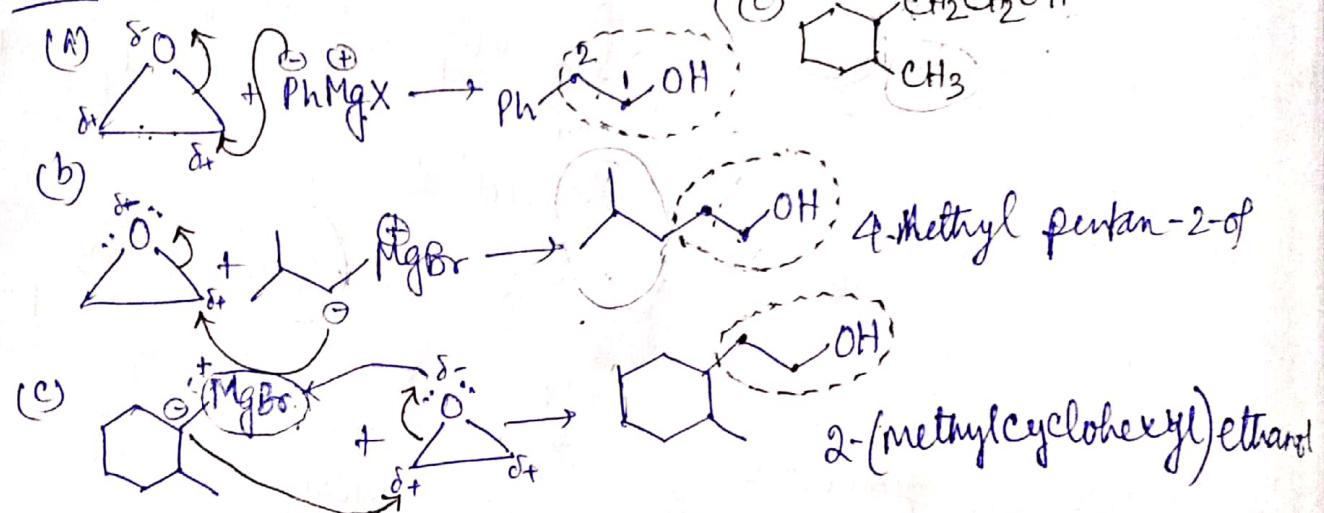


(1° alcohol)
But in case of unsymmetrical epoxides then —

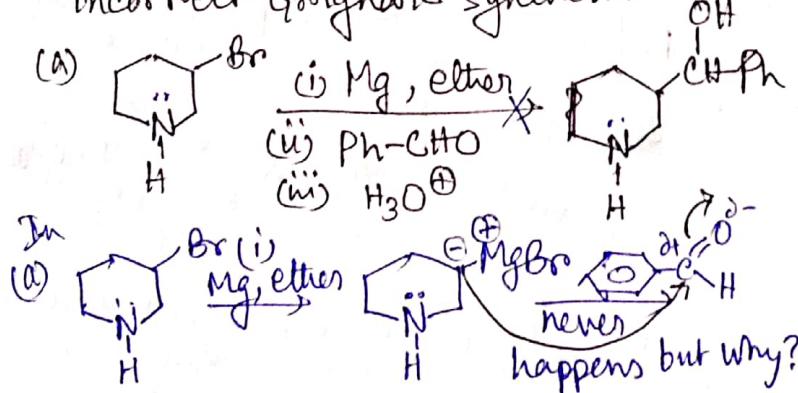


Q3 Show how you would synthesize the following alcohols by adding Grignard reagents to ethylene oxide.

Solution:



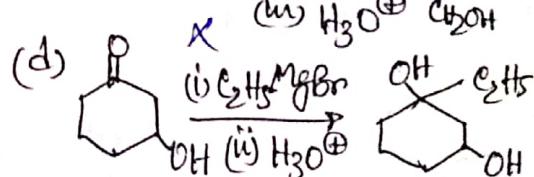
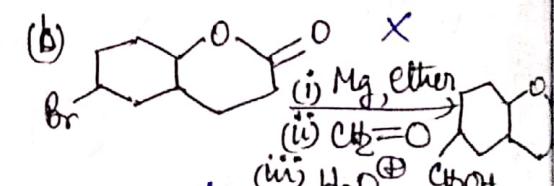
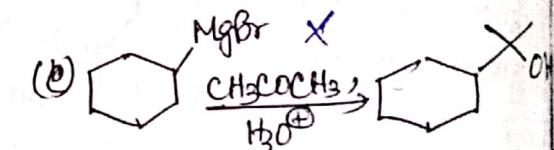
Q4 Point out the flaws in the following incorrect Grignard synthesis.



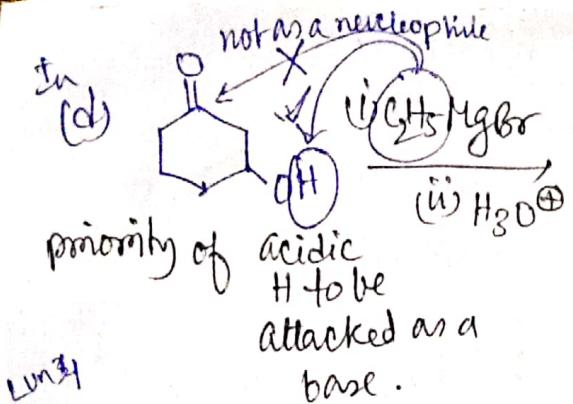
As here the acidic H-atom presents so →

then what will we have to do? — & we shall remove the acidic H, by replacing it with Methyl group then we can get the given compd in the product side.

In (c), H_3O^+ has to be reacted at 2nd step not in the 1st step.

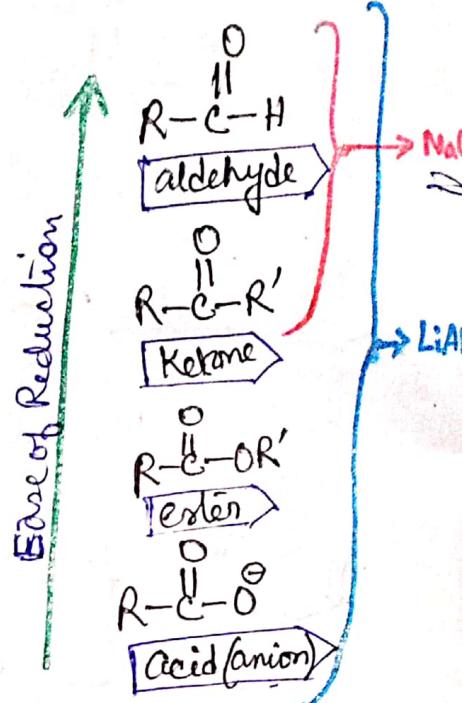
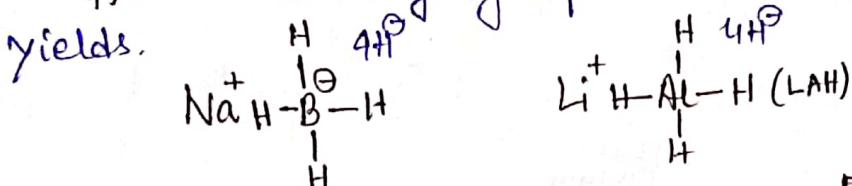


In (b), in lactone or cyclic ester a nucleophilic attack site presents. so RMgX will attack inside the molecule rather than outside $>\text{C}=\text{O}$ carbonyl compd.

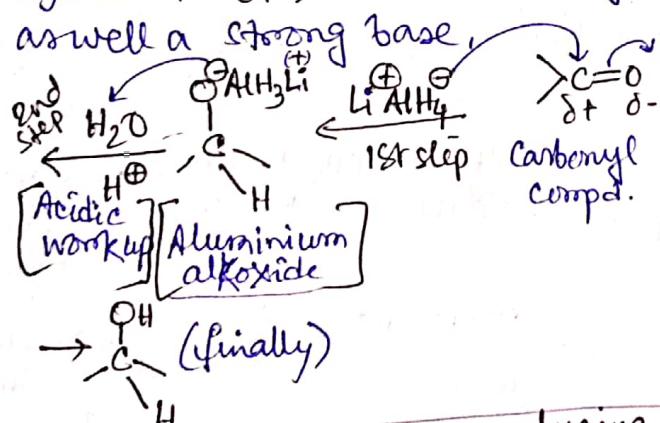


Reduction of Carbonyl group - prep'n of Alcohol

The two most useful hydride reagents, sodium borohydride (NaBH_4) and lithium aluminium hydride (LiAlH_4) reduce carbonyl groups in excellent yields.



Hydride ion (H^-) is both a strong nucleophile as well as a strong base.



Q. Which is the stronger reducing agent among LiAlH_4 and NaBH_4 and why?

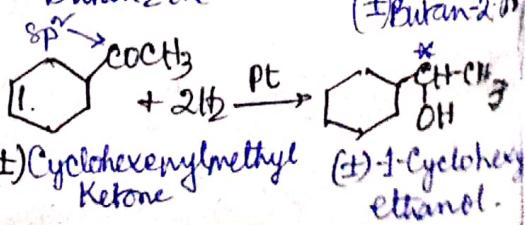
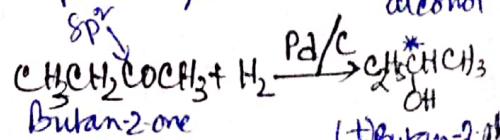
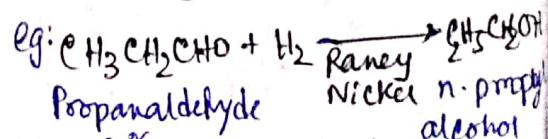
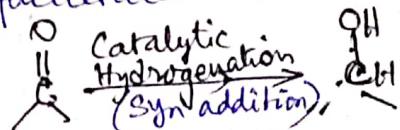
Aluminium is less electronegative than boron, so more of \rightarrow ve charge in the AlH_4^- ion is borne by the H-atoms. Therefore (LAH) is much stronger reducing agent & it is much more difficult to work with than NaBH_4 . LAH reacts

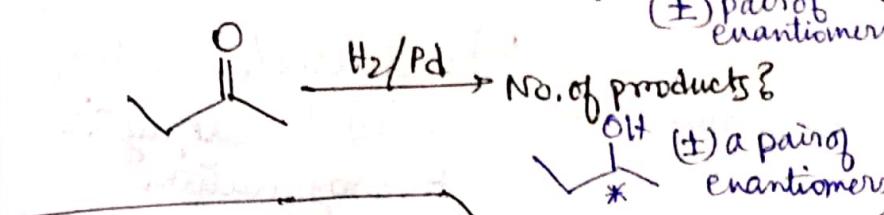
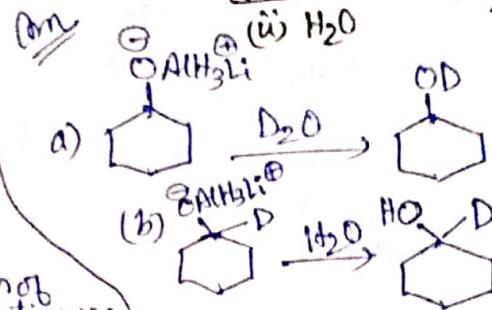
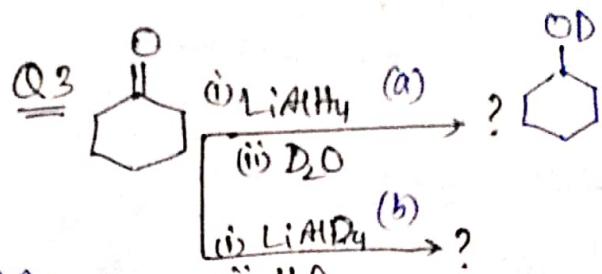
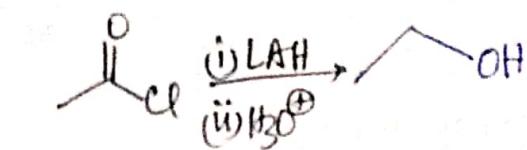
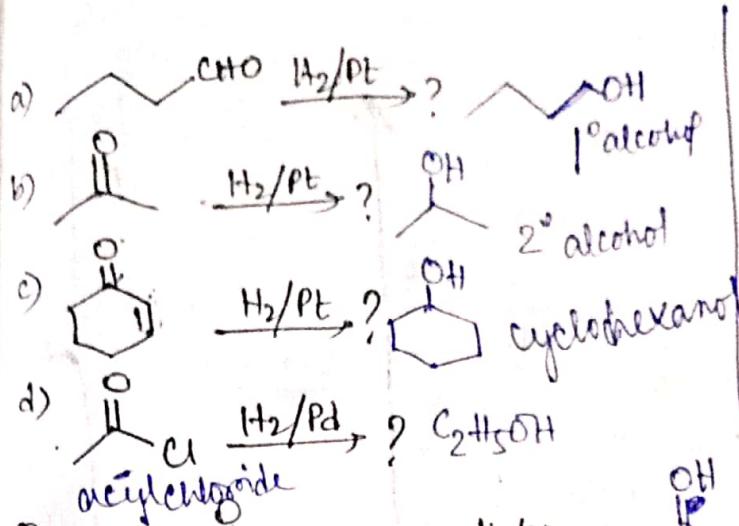
explosively with water and alcohols, liberating H_2 gas & sometimes starting fire. NaBH_4 reacts slowly with alcohols & with water as long as the pH is high (basic). NaBH_4 is a convenient and highly selective reducing agent.

Reduction of Carbonyl Compds by Catalytic Hydrogenation

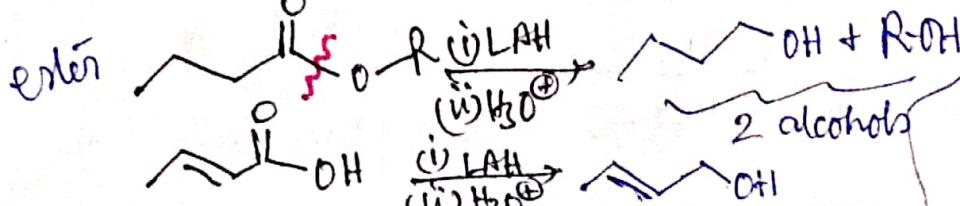
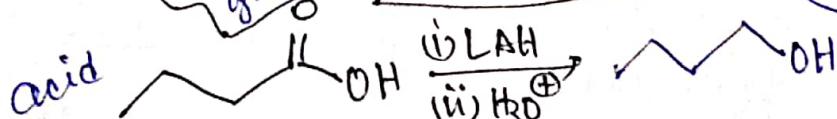
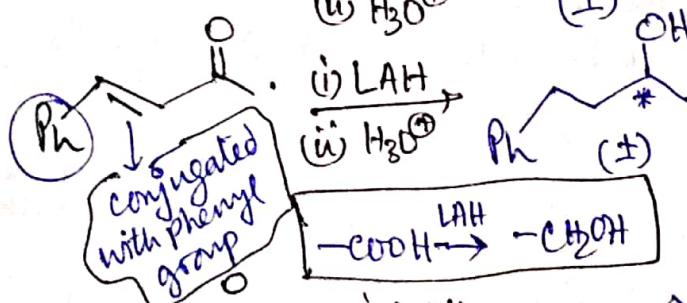
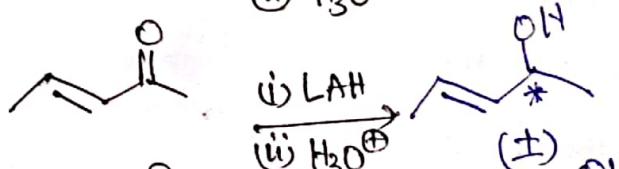
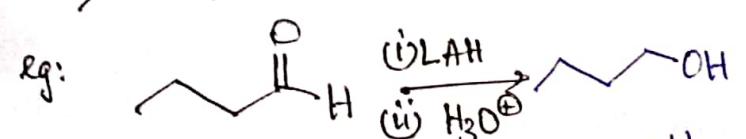
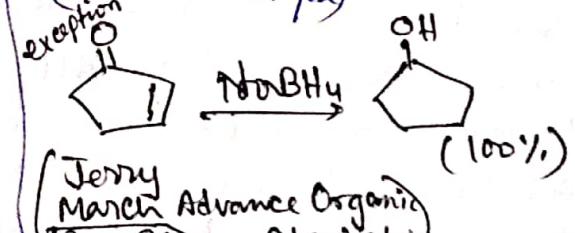
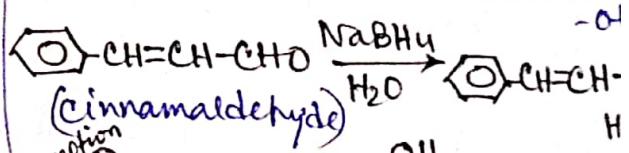
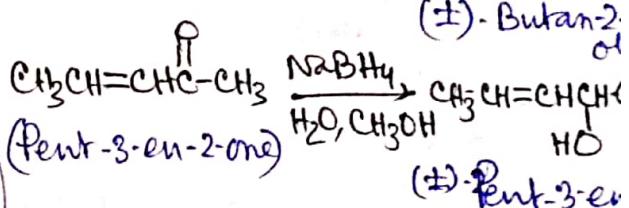
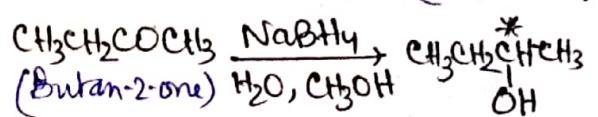
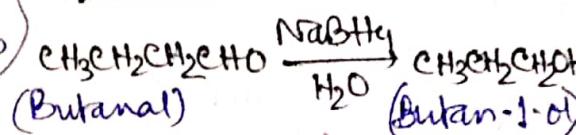
Reagents :- H_2/Pt or H_2/Pd or $\text{H}_2/\text{Ni}, \Delta$

- PtO_2 (Adam's catalyst)
- The reduction takes place at the surface of the catalyst which adsorbs both H_2 & the organic compd & facilitates their contact.





Reduction with $NaBH_4$



Unit-11: Alcohols, Phenols & Ethers

A. How to Convert? :-

1. Propene \rightarrow Propanal, 2. $\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{OH}$, 3. $\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{OH}$,
4. Cumene \rightarrow Phenol, 5. Phenol \rightarrow Salol, 6. Phenol \rightarrow Picric Acid ($\text{C}_6\text{H}_5\text{O}_2\text{NO}_2$)
7.  \rightarrow , 8. $\text{RCH}_2\text{OH} \rightarrow \text{R}-\text{C}(=\text{O})\text{NHOH}$, 9. $\text{CH}\equiv\text{CH} \rightarrow \text{CH}_3\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_3$
10. Propanol \rightarrow Propanal, 11.  \rightarrow , 12. Ethanol \rightarrow 1-Butanal.
13. Ethanol \rightarrow Di Ethylether, 14. Di Ethylether \rightarrow Ethane, 15. $\text{HCHO} \rightarrow \text{CH}_3\text{OH}$,
16.  \rightarrow , 17.  \rightarrow , 18. 1-Propanol \rightarrow 2-Propanol, 19. $\text{CH}_2=\text{CH}_2 \rightarrow \text{CH}_3\text{OH}$,
20.  \rightarrow , 21.  $\xrightarrow{\text{SO}_3\text{Na}}$ , 22.  \rightarrow , 23.  \rightarrow 
24. $\text{CH}_3\text{Br} \rightarrow (\text{CH}_3)_2\text{C}-\text{OH}$, 25.  $\xrightarrow{\text{BrP}}$ , 26.  \rightarrow , 27.  \rightarrow 
28. $\text{CH}_3\text{CH}_2\text{NH}_2 \rightarrow \text{CH}_3\text{CH}_2\text{OH}$, 29.  $\xrightarrow{\text{BrP}}$, 30. $\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CH}_2-\text{O}-\text{CH}_3$.

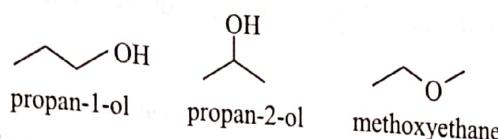
B. Mention the Product:-

1. $\text{CH}_3\text{COOCCH}_3 \xrightarrow[\text{C}_2\text{H}_5\text{OH}]{\text{Na}} ? + ?$, 2.  $\xrightarrow[\text{ii. dil. HCl}]{\text{i. } \text{CH}_3\text{CH}_2\text{NaOH}} ? + ?$, 3.  $\xrightarrow[\text{AlCl}_3 + \text{CS}_2]{\text{CH}_3\text{COCl}} ? + ?$,
4. $\text{CH}_3-\text{O}-\text{C}(\text{CH}_3)_3 \xrightarrow{\text{HI}} ? + ?$, 5. $\text{CH}_3-\overset{\text{OH}}{\underset{\text{CH}_3}{\text{C}}}=\text{CH}_2 \xrightarrow[\text{300}^\circ\text{C}]{\text{Cu}} ?$, 6. $\text{CH}_3\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_3 \xrightarrow{\text{O}_2} ?$,
7. $\text{CH}_3\text{CH}_2\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_3 \xrightarrow[\text{D}_2\text{O}]{\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+} ? + ?$, 8. $\text{CH}_3\text{OH} \xrightarrow[\text{P/I}_2]{\text{P/I}_2} ?$, 9. $\text{CH}_3\text{OH} \xrightarrow[\text{NaOH}(\text{aq})]{\text{(CH}_3\text{CO})_2\text{S}_6\text{O}_4} ?$, 10. $\text{CH}_3\text{OH} \xrightarrow[\text{Fe}]{\text{H}_3\text{PO}_4} ?$, 11.  $\xrightarrow[\text{H}_2\text{O}]{\text{CH}_3\text{COOH}} ?$,
12.  $\xrightarrow[\text{aq. NaOH}]{\text{CH}_3\text{COCl}} ?$, 13.  $\xrightarrow[\text{t-BuOH}]{\text{Na/NH}_3(\text{l})} ?$, 14.  $\xrightarrow[\Delta]{\text{SO}_3\text{Na}} ?$, 15.  $\xrightarrow[\text{H}_2\text{O}]{\text{NaOH}} ?$,
16.  $\xrightarrow[\text{Ether}]{\text{CH}_2=\text{CH}_2} ?$, 17.  $\xrightarrow[\text{Ether}]{\text{NaH, CH}_3\text{I}} ?$, 18.  $\xrightarrow[\Delta]{\text{conc. H}_2\text{SO}_4} ?$, 19.  $\xrightarrow[\Delta]{\text{HNO}_3} ?$, 20.  $\xrightarrow[\Delta]{\text{O}_2} ?$, 21. $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow[\text{CuO}]{\text{PCC}} ?$, 22.  $\xrightarrow[\text{H}_2\text{SO}_4, \text{D}_2\text{O}]{\text{CH}_3\text{MgBr}} ?$, 23.  $\xrightarrow[\text{H}_2\text{O}]{\text{H}_3\text{O}^+} ?$,
24. $\text{CH}_3\text{MgBr} \xrightarrow[\text{dry Ether}]{\text{CH}_3\text{OH}} ?$, 25.  $\xrightarrow[\text{conc. H}_2\text{SO}_4]{\text{KBr} + \text{KBrO}_3} ?$, 26.  $\xrightarrow[\text{H}_2\text{O}]{\text{Na}} ?$, 27.  $\xrightarrow[\text{H}_2\text{O}]{\text{CH}_2\text{I}_2} ?$,
28.  $\xrightarrow[\Delta]{\text{conc. H}_2\text{SO}_4} ?$, 29. $\xrightarrow[\Delta]{\text{Cl}_2(\text{1 mol})} ?$, 30. $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow[\text{H}_2\text{O}, \Delta]{\text{Ca(OCl)Cl}} ?$,
31. $\xrightarrow{\text{H}_2} ? + ?$, 32. $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 \xrightarrow[\text{H}_2\text{O}]{\text{HBr}} ?$, 33. $\xrightarrow[\text{H}_2\text{O}]{\text{C}_2\text{H}_5\text{ONa}} ?$, 34. $(\text{CH}_3\text{CO})_2\text{O} \xrightarrow[\text{Pyridine}]{\text{C}_2\text{H}_5\text{OH}} ? + ?$, 35. $\xrightarrow[\Delta]{\text{C}_2\text{H}_2\text{O}_2} ?$, 36. $\xrightarrow[\text{conc. H}_2\text{SO}_4]{\text{CH}_3\text{COOH}} ?$,
37. $\xrightarrow[\text{H}_2\text{O}]{\text{NaOH}} ? + ?$, 38. $\text{C}_2\text{H}_5\text{OH} \xrightarrow[\Delta]{\text{Cu}} ?$, 39. $\xrightarrow[\text{H}_2\text{O}]{\text{NaNO}_2} ?$, 40. $\text{CH}_3-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{CH}}}=\text{CH}_2 \xrightarrow{\text{H}^+} ? + ?$, 41. $\text{CH}_3\text{OH} \xrightarrow[\Delta]{\text{Cu}} ?$, 42. $\text{CH}_3\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_3 \xrightarrow[\text{Anh. ZnCl}_2]{\text{CH}_3\text{COCl}} ?$, 43. $(\text{CH}_3)_2\text{C}-\text{CH}=\text{CH}_2 \xrightarrow[\Delta]{\text{H}_2\text{O}^+} ?$ (Major), 44.  $\xrightarrow{\text{H}^+} ?$

	glycol	ethane-1,2-diol
	glycerol	propane-1,2,3-triol
	benzyl alcohol	phenylmethanol

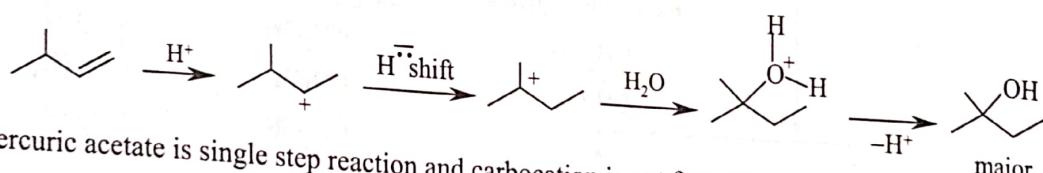
Isomerism

The alkanols with general molecular formula $[C_nH_{2n+2}O]$ exhibits chain, position, functional and metamerism. Since degree of unsaturation is zero, they exhibit optical isomerism but fail to form geometrical isomers. The alkoxyalkanes (ethers) are functional isomers of alkanols (alcohols). The organic compounds with molecular formula C_3H_8O form three isomers representing alkanols and alkoxyalkanes.

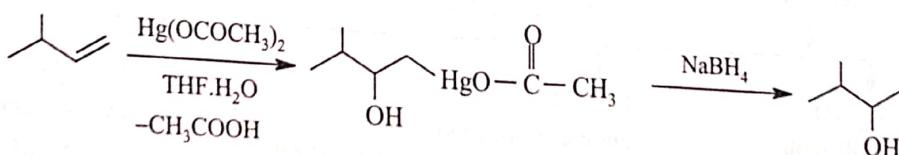


General methods of preparations

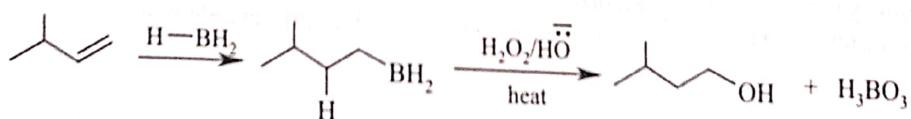
During acid catalysed hydration, carbocation intermediate is formed which rearranges to stable carbocation before the attack of nucleophile.



Addition of mercuric acetate is single step reaction and carbocation is not formed.



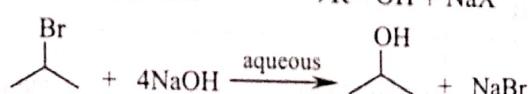
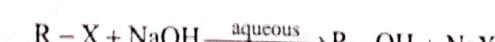
The oxymercuration followed by reduction gives alcohol which represents Markownikoff product without rearrangement. The addition of boronhydride to multiple bond of alkene is concerted reaction and yields product corresponding to anti-Markownikoff addition of H_2O .



The oxymercuration and hydroboration of alkene are *stereospecific*.

From alkylhalides

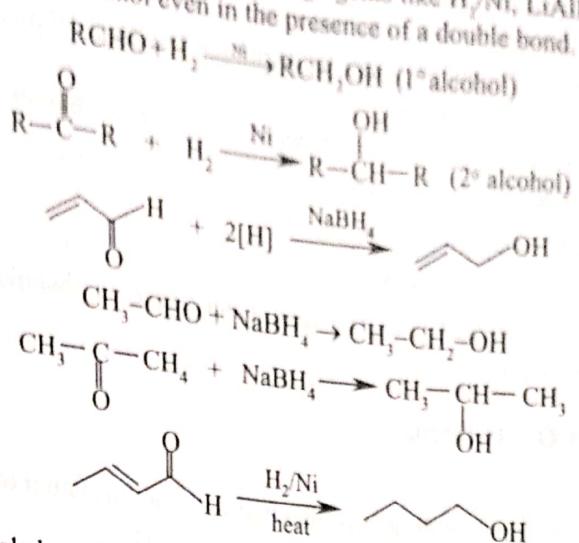
The hydrolysis of alkylhalides give alcohols.



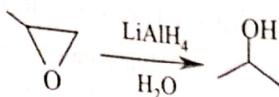
To avoid dehydrohalogenation of $R-X$, mild base like moist silver oxide or aqueous K_2CO_3 is used. The ease of hydrolysis of alkyl halides: $R-I > R-Br > R-Cl$ and $3^\circ R-X > 2^\circ R-X > 1^\circ R-X$.

From carbonyl compounds

Aldehydes or ketones are reduced to alcohol by using reducing agents like H_2/Ni , $LiAlH_4$, $NaBH_4$, $Na/\text{alcohol}$ etc. $NaBH_4$ selectively reduces the carbonyl group to alcohol even in the presence of a double bond.

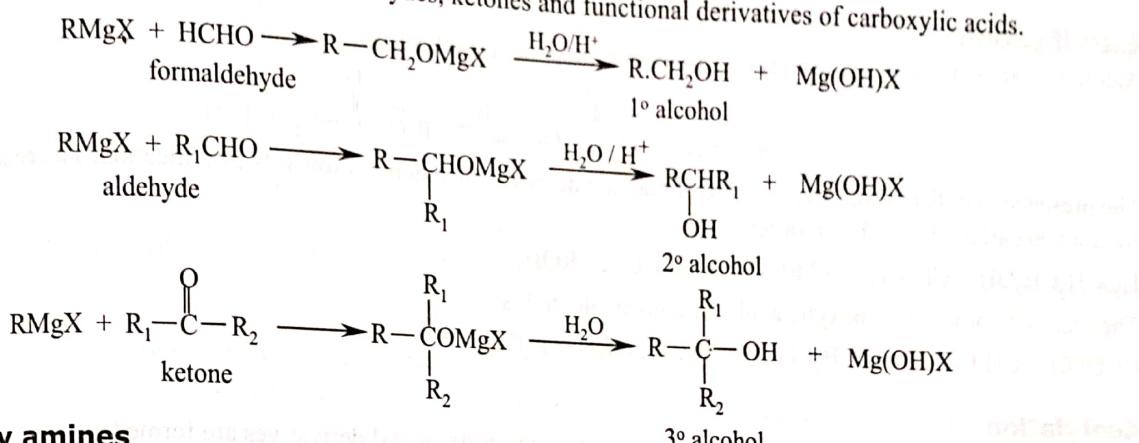


The epoxides are reduced to alcohols by using $LiAlH_4$. Hydride (H^-) selectively attacks on less sterically hindered carbon of epoxides.



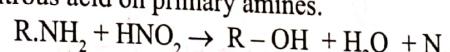
From Grignard reagent

Alcohols are prepared by Grignard addition to aldehydes, ketones and functional derivatives of carboxylic acids.



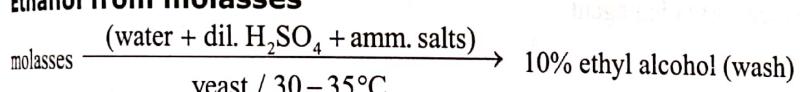
From Primary amines

Alcohols are obtained by the action of nitrous acid on primary amines.

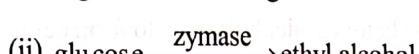


Methylamine does not give methyl alcohol when treated with HNO_2 . It gives CH_3OCH_3 and CH_3ONO .

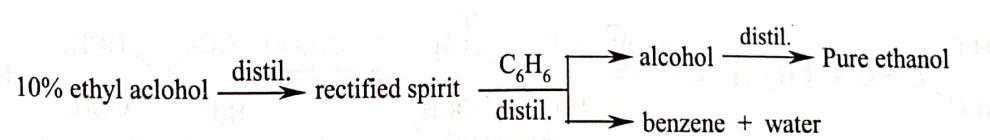
Ethanol from molasses



Fermentation takes place in two stages (i) sugar $\xrightarrow{\text{invertase}}$ glucose



Concentration



General Characteristics

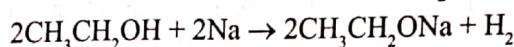
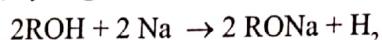
- Due to hydrogen bonding, alcohols have higher boiling points and melting points than alkanes, alkenes, alkynes, alkyl halides, ethers and amines of comparable molecular masses.
- Lower alcohols (upto C-4) are soluble in water due to hydrogen bonding. Higher alcohols are soluble in all organic solvents. They are soluble in concentrated H_2SO_4 .
- Alcohols have pK_a values greater than pK_a value of water (15.7) except methanol as they are weaker than water. The acidity of alcohol greatly depends on substituents.

Alcohol:	CH_3OH	CH_3CH_2OH	$CICH_2CH_2OH$	Cl_3CCH_2OH	H_2O
pK_a	15.5	15.9	14.3	12.4	15.7

Hydration energy of conjugate acid of methanol is greater than water hence, methanol is slightly stronger than water. The electron withdrawing group increases acidity.

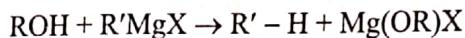
Reaction due to cleavage of O – H bond**Reaction with metals**

When alcohols are treated with sodium metal, hydrogen is liberated with the formation of sodium alkoxide

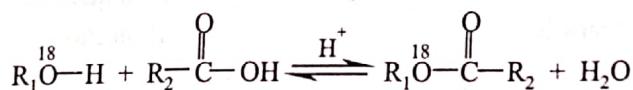


The order of reactivity of alcohols with metals is in order: $CH_3OH > 1^\circ ROH > 2^\circ ROH > 3^\circ ROH$

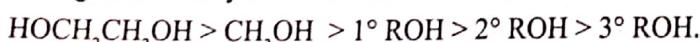
This reaction accounts acidic character of alcohols. The following neutralization reaction also accounts for acidic property.

**Esterification**

Alcohols react with carboxylic acids to form esters under acid catalysis



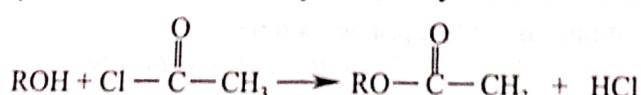
The presence of bulky groups near the site of reaction decrease the reactivity towards esterification. The reactivity of alcohols for a given carboxylic acid is in order:



The reactivity order of carboxylic acids for a given alcohol is:

**Acetylation**

When alcohols are treated with acetyl chloride or acetic anhydride, acetyl derivatives are formed.

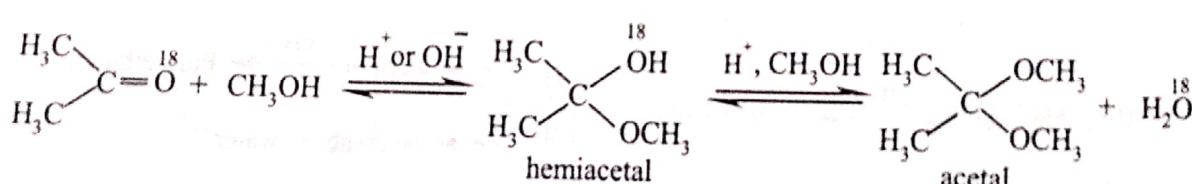
**Reaction with tosyl chloride (TsCl)**

Tosyl chloride is p-tolene sulphonyl chloride called tosylating agent.



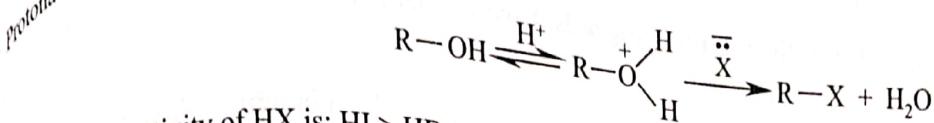
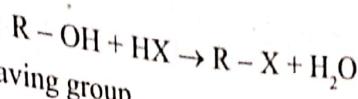
The tosate ($Ts\ddot{O}$) group is better leaving group and cleavage of C – O bond readily takes place during substitution and elimination reactions.

Hemiacetal/Acetal formation: With aldehydes/ ketones, alcohols react to form hemiacetal first and then acetal. This is shown for the reaction between methanol and acetone.



reactions due to cleavage of C – O bond (S_N reactions)

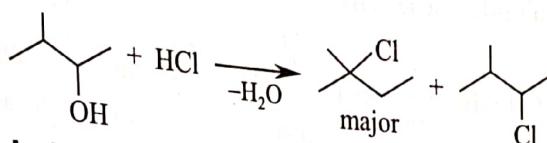
reaction with hydrogen halides



The order of reactivity of HX is: HI > HBr > HCl > HF for a given alcohol.

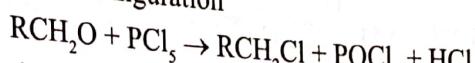
Primary (1°) alcohols follow S_N2 path, hence rearrangement does not take place.

Secondary (2°) and tertiary (3°) alcohols follow S_N1 mechanism, carbocation is formed and rearrangement is favoured to form more stable carbocation.

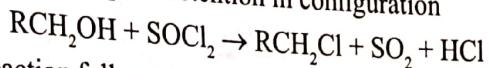


Reactions with phosphorus halides and thionyl chloride

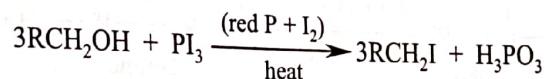
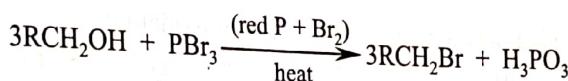
Reaction with PCl_5 proceeds with inversion in configuration



Reaction with thionyl chloride proceed with complete retention in configuration



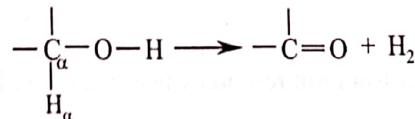
In presence of base like pyridine, this reaction follows S_N2 path. The best reagent for converting an alcohol to an alkyl halide is thionyl chloride as gaseous products SO_2 and HCl are formed.



These reactions follow S_N2 path. Reaction with PBr_3 , $(\text{P} + \text{I}_2)$ and SOCl_2 yield 1° alkyl halide which are not possible with Lucas reagent ($\text{ZnCl}_2 + \text{conc. HCl}$)

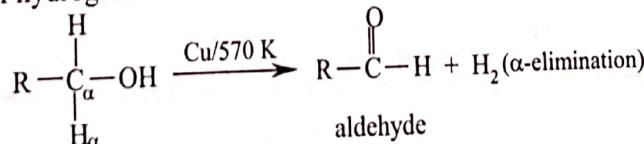
Reactions involving cleavage of $\text{C}-\text{H}_\alpha$ bond

The oxidation of alcohols involves the formation of carbonyl group ($\text{C} = \text{O}$) with the cleavage of $\text{O} - \text{H}$ and $\text{C} - \text{H}_\alpha$ bonds of $-\text{CHOH}-$ group.

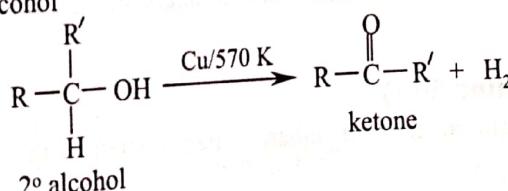


Dehydrogenation

When vapours of a primary or a secondary alcohol are passed over preheated copper metal at 570 K an aldehyde or a ketone is formed with the elimination of hydrogen. This reaction is called dehydrogenation.

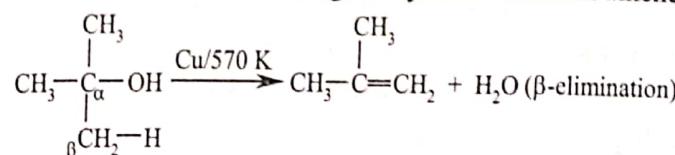


1° alcohol



2° alcohol

The tertiary alcohols under similar reaction conditions undergo dehydration to form alkenes.

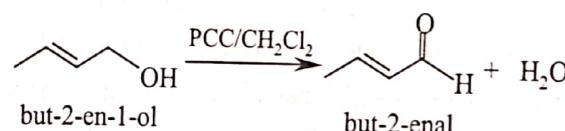
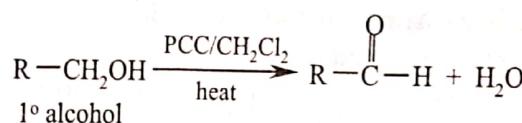
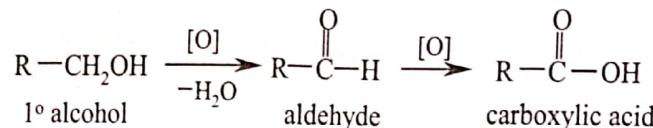


Lesser the steric hindrance on α -carbon, greater is the reactivity towards dehydrogenation.

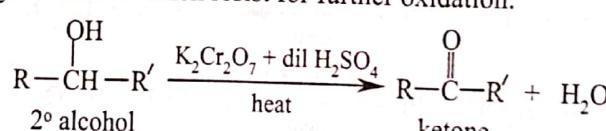
Oxidation

Depending on the oxidising agent used, a primary alcohol is oxidised to an aldehyde which in turn oxidised to a carboxylic acid. Strong oxidising agents such as acidified potassium dichromate or acidified potassium permanganate oxidise primary alcohols to carboxylic acids.

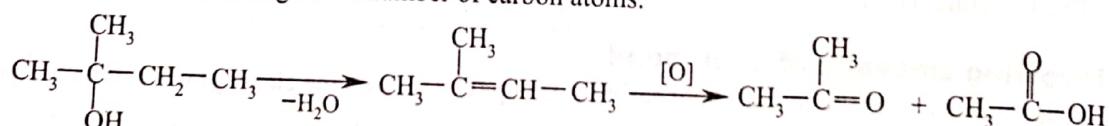
The primary alcohol on oxidation gives monocarboxylic acid containing same number of carbon atoms. The pyridinium chlorochromate (PCC) in methylene chloride is a selective oxidant, which oxidises primary alcohols to aldehydes.



Secondary alcohols on oxidation give ketones which resist for further oxidation.

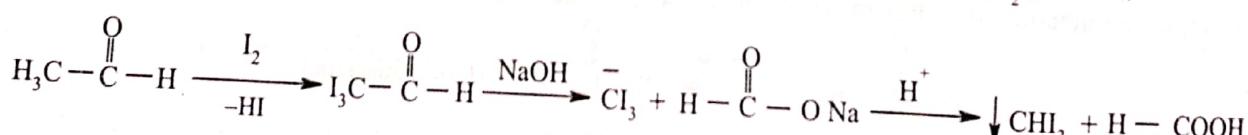
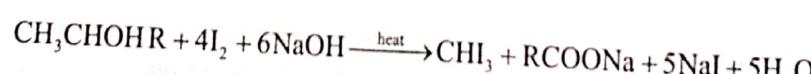


The tertiary alcohols (3°) are resistant to oxidation. However, under the specified conditions these alcohols give a mixture of ketone and carboxylic acid containing lesser number of carbon atoms.



Iodoform reaction

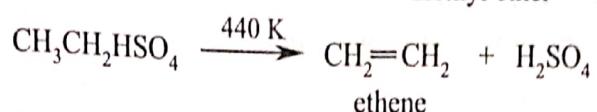
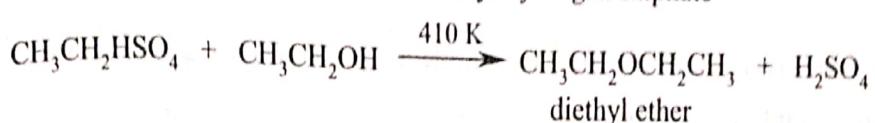
Methyl carbinols ($\text{CH}_3-\text{CHOH}-\text{R}$) undergo haloform reaction when treated with alkali and a halogen. This is shown with ethanol reacting with iodine and NaOH.



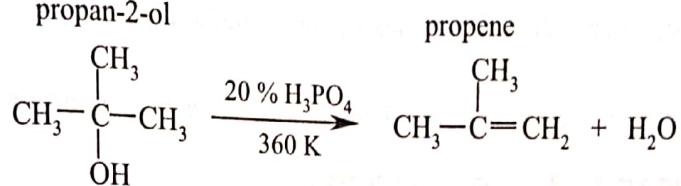
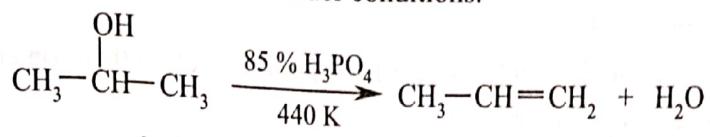
Iodoform is obtained as a yellow precipitate and this reaction is a diagnostic test for the presence of methyl carbinol unit in an alcohol.

Dehydration reaction (β - Elimination)

Alcohols undergo dehydration to form alkenes or ethers when heated with dehydrating agents like concentrated H_2SO_4 or H_3PO_4 .



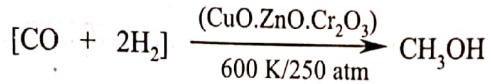
tary and tertiary alcohols are dehydrated under milder conditions.



The formation of alkenes from alcohols by dehydration represents β -elimination reactions.

The formula for methyl alcohol is CH_3OH .

Methanol (CH_3OH) is called wood spirit as it was obtained by the destructive distillation of wood. It is manufactured by passing a mixture of carbon monoxide and hydrogen over a preheated catalyst 600 K under pressure.



Water gas [$\text{CO} + \text{H}_2$] is source for carbon monoxide and hydrogen.

Uses of Methanol

It is used,

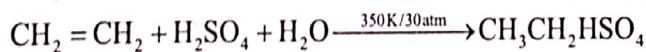
as a solvent for oils, fats and varnishes.

- (i) as a solvent.
 - (ii) as a fuel (a fuel substitute). A 20% mixture of methyl alcohol and gasoline is a good motor fuel.
 - (iii) as an antifreeze for automobile radiators.
 - (iv) to denature (render unfit for drinking) industrial alcohol. It acts as a poison causing blindness and even death.
 - (v) in the preparation of dyes, medicines and perfumes. Methyl salicylate and methyl anthranilate are used in perfumery.

Ethanol (ethyl alcohol) $\text{CH}_3\text{CH}_2\text{OH}$

In many countries including USA, ethanol is manufactured from ethene. However, in India, ethanol is mainly obtained by fermentation of molasses.

Ethene is passed into concentrated sulphuric acid at 350 K and 30 atm, ethylhydrogen sulphate is formed.



Hydrolysis of ethylhydrogen sulphate gives ethanol and sulphuric acid.



Fractional distillation of aqueous solution yields *rectified spirit*.

Rectified spirit

Rectified spirit Rectified spirit is an *azeotropic* (constant boiling) mixture of 95.5% ethyl alcohol and 4.5% water. Such a mixture cannot be further concentrated by fractional distillation.

Absolute alcohol Absolute alcohol is 100% ethyl alcohol. In order to get absolute alcohol the rectified spirit is refluxed with calcium oxide for six hours. It is allowed to stand overnight and distilled with calcium.

Power alcohol: A mixture of absolute alcohol and petrol roughly in the ratio 20 : 80 is used as fuel in internal combustion engine is called power alcohol.

Uses of Ethanol

Ethanol is one of the most extensively used organic compounds. Its main uses are given below. It is used as a substitute for petrol in internal combustion engines.

- as a solvent for paints, oils, perfumes, dyes, varnishes, gums, etc.
- as an alcoholic beverage.
- as a preservative for biological specimens.
- as an antifreeze for automobile radiators.
- as a low freezing F.P.-11.0° and mobile fluid in scientific apparatus such as thermometers and spirit level.
- in the manufacture of terylene and polythene.
- as a solvent for pharmaceutical preparation and a constituent of medicines.
- in hospitals as an antiseptic.
- in the manufacture of acetaldehyde, acetic acid, ethyl halides, ethyl acetate, chloroform, iodoform, etc.

Tests to distinguish between 1° 2° and 3° alcohols

Test	Observation	Inference
Lucas Test Alcohol + anhy. $ZnCl_2$ + conc. HCl	Immediate turbidity Turbidity in five minutes No turbidity.	3° alcohol 2° alcohol 1° alcohol
Dichromate Test Alcohol + $K_2Cr_2O_7$ + dil. H_2SO_4	Orange solution turns green no change in colour	1° or 2° alcohol 3° alcohol

Colour change associated in dichromate test forms the basis for **breathanalyser test** to detect intoxication.

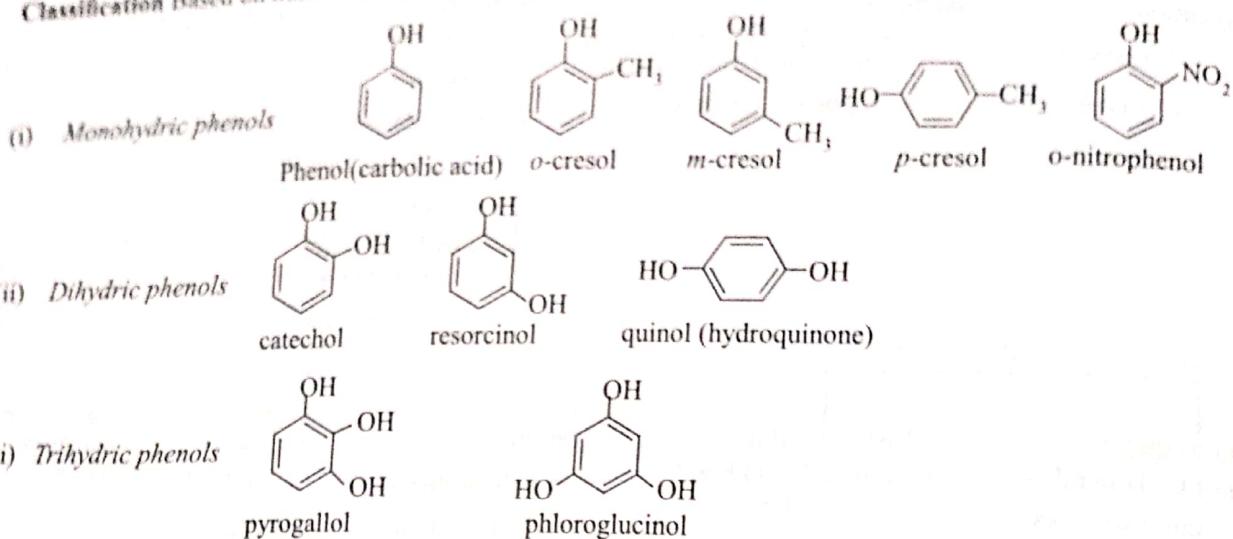
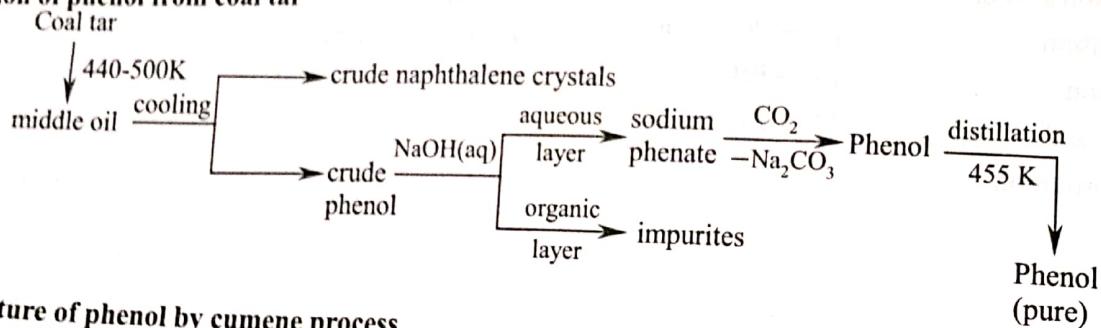
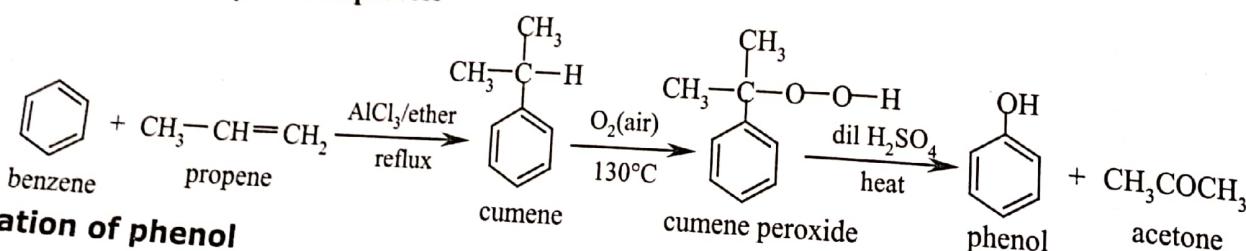
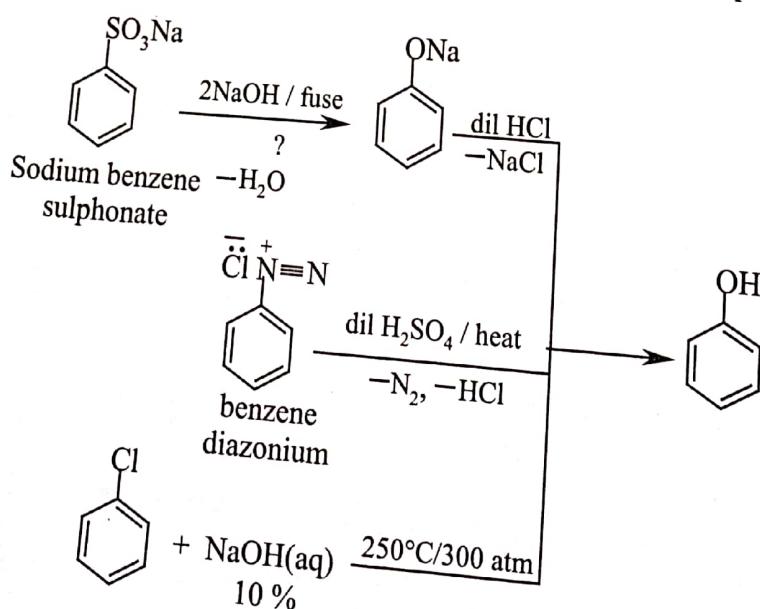
Victor Mayer Test

Test	1° alcohol	2° alcohol	3° alcohol
alcohol + $(P + I_2)$, resulting iodoalkane is treated with $AgNO_2$ solution followed by HNO_2	CH_3CH_2OH $\downarrow (P + I_2)$ CH_3CH_2I $\downarrow AgNO_2$ $CH_3-CH_2-NO_2$ $\downarrow O=NOH$ $CH_3-C(=O)-NO_2$ \parallel $N-OH$ nitrolic acid (blue solution) $\downarrow NaOH$ $-H_2O$ $CH_3-C(=O)-NO_2$ \parallel $N-ONa$ red solution	$CH_3-CH(OH)CH_3$ $\downarrow (R + I_2)$ $CH_3-CH(I)CH_3$ $\downarrow HO-NO_2$ CH $CH_3-CH(=O)NO_2$ $\downarrow HO-N=O$ $CH_3-C(=O)-NO_2$ \parallel $N=O$ blue solution $\downarrow NaOH$ No change in colour	$CH_3-C(CH_3)_2OH$ $\downarrow (P + I_2)$ $CH_3-C(CH_3)_2I$ $\downarrow AgNO_2$ $CH_3-C(CH_3)_2NO_2$ $\downarrow HO-NO$ No reaction (colourless solution)

PHENOLS

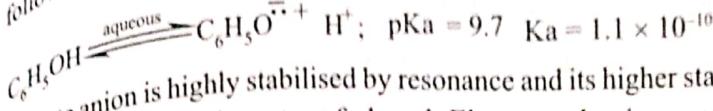
The hydroxy derivatives of aromatic hydrocarbons in which $-OH$ groups is/are bonded to benzene ring (aromatic ring system) are called phenols.

Classification Based on number of $-OH$ groups present in a molecule, they are classified as follows.

**Isolation of phenol from coal tar****Manufacture of phenol by cumene process****Preparation of phenol**

Physical characteristics of phenol Phenols form intermolecular hydrogen bonding and their boiling points are much higher than hydrocarbons of comparable molecular mass. (m.p. = 43°C ; b.p. = 182°) Its miscibility temperature is 67°C. It is highly corrosive.

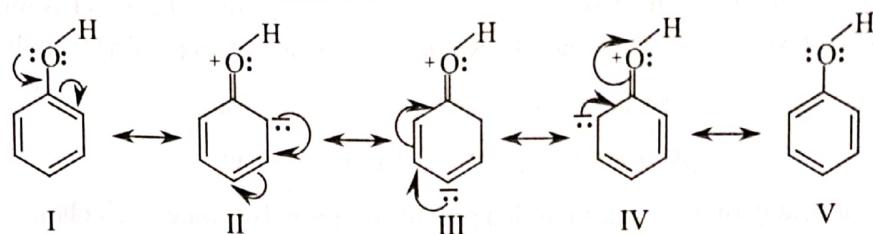
Acidic character Phenol containing 5% water is called carbolic acid. In aqueous medium, phenol molecules ionise and the following ionic equilibrium is established.



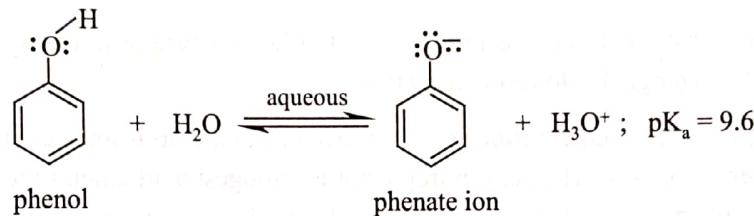
Phenate anion is highly stabilised by resonance and its higher stability over phenol is the driving force for the ionisation which accounts for acidic character of phenol. Electron releasing groups like $-\text{CH}_3$, $-\text{OR}$, $-\text{NHCOCH}_3$, $-\text{NH}_2$ etc. on benzene ring decrease the acidity while electron withdrawing groups such as $-\text{NO}_2$, $-\text{CN}$, $-\text{CHO}$, $-\text{COOR}$, $-\text{COOH}$, $-\text{X}$ etc., increase the acidity of phenol. It neutralises NaOH solution but does not decompose bicarbonates or carbonates as its acidity is less than carbonic acid ($\text{pK}_a = 6.8$).

Explanation for acidity of phenols

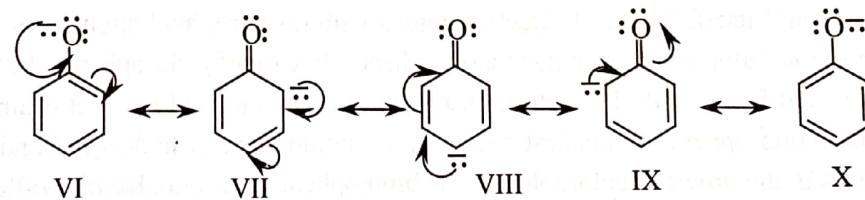
Phenols are stronger acids than alcohols but much weaker than carboxylic acids. In aqueous solution following ionic equilibrium is established. Phenol molecule is considered as resonance hybrid of following resonance structures.



As a result of resonance, oxygen atom acquires a partial positive charge (II - IV). This weakens the bond and facilitates the release of proton.



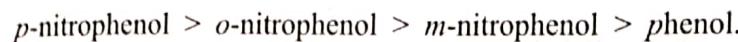
Phenate ion is stabilised by delocalisation of negative charge which is evident from the following resonance structure (VI-X).



Thus, both phenol and phenate ion are stabilised by resonance. But phenate ion is more resonance stabilised than phenol as delocalisation of negative charge alone takes place in phenate ion (VI-X) where as resonance structures of phenol possess less stable polar structures (II - IV). Thus, higher stability of phenate ion is the driving force for the ionisation of phenol in polar solvents like water and accounts for acidic character by releasing proton.

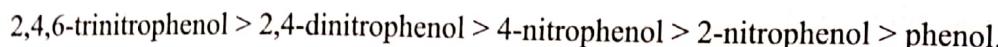
Effect of substituents on the acidity of phenols: As discussed above, the acidity of phenol is due to the greater resonance stabilisation of the phenate ion relative to phenol. Therefore, a substituent which stabilises phenate ion by delocalising negative charge will tend to increase the acidity of phenols. Conversely, a substituent which destabilises phenate ion by intensifying negative charge on oxygen atom will decrease the acidity of phenols.

Electron withdrawing groups such as $-NO_2$, $-CN$, $-CHO$, $-COOR$, $-X$ (halogen) etc., stabilise the phenate ions by dispersing the negative charge by resonance and $-I$ effects. Higher the stability of conjugate base (phenate ion) greater is the acidity. Thus, electron withdrawing groups increase the acidity of phenol. The magnitude of resonance stabilisation of phenate ion is much higher than $-I$ effect hence, the effect is more pronounced at *ortho* (*o*)- and *para* (*p*)- positions than at *meta* (*m*)- position as substituent as this position does not participate in resonance. Thus, acid strength of nitrophenols decreases in the order.



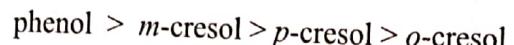
$$pK_a = 7.15 \quad 7.23 \quad 8.40 \quad 9.60$$

The intramolecular hydrogen bonding in *o*-nitrophenol makes loss of proton more difficult hence, it is less acidic than *p*-nitrophenol. Acidity of phenols increases with increase in the number of electron withdrawing groups, the decreasing order of acidity of a few phenols is as follows:



$$pK_a = 0.74 \quad 1.4 \quad 7.15 \quad 7.23 \quad 9.60$$

The electron releasing groups like $-R$ (alkyl), $-RO$ (alkoxy), etc., destabilise conjugate base (phenate ion) by intensifying the negative charge at oxygen atom and decrease the acidic strength of phenols. The effect is more pronounced at *o*- and *p*- positions than at *m*- position with respect to group. Thus acid strength of cresols (methylphenols) decreases in the order,

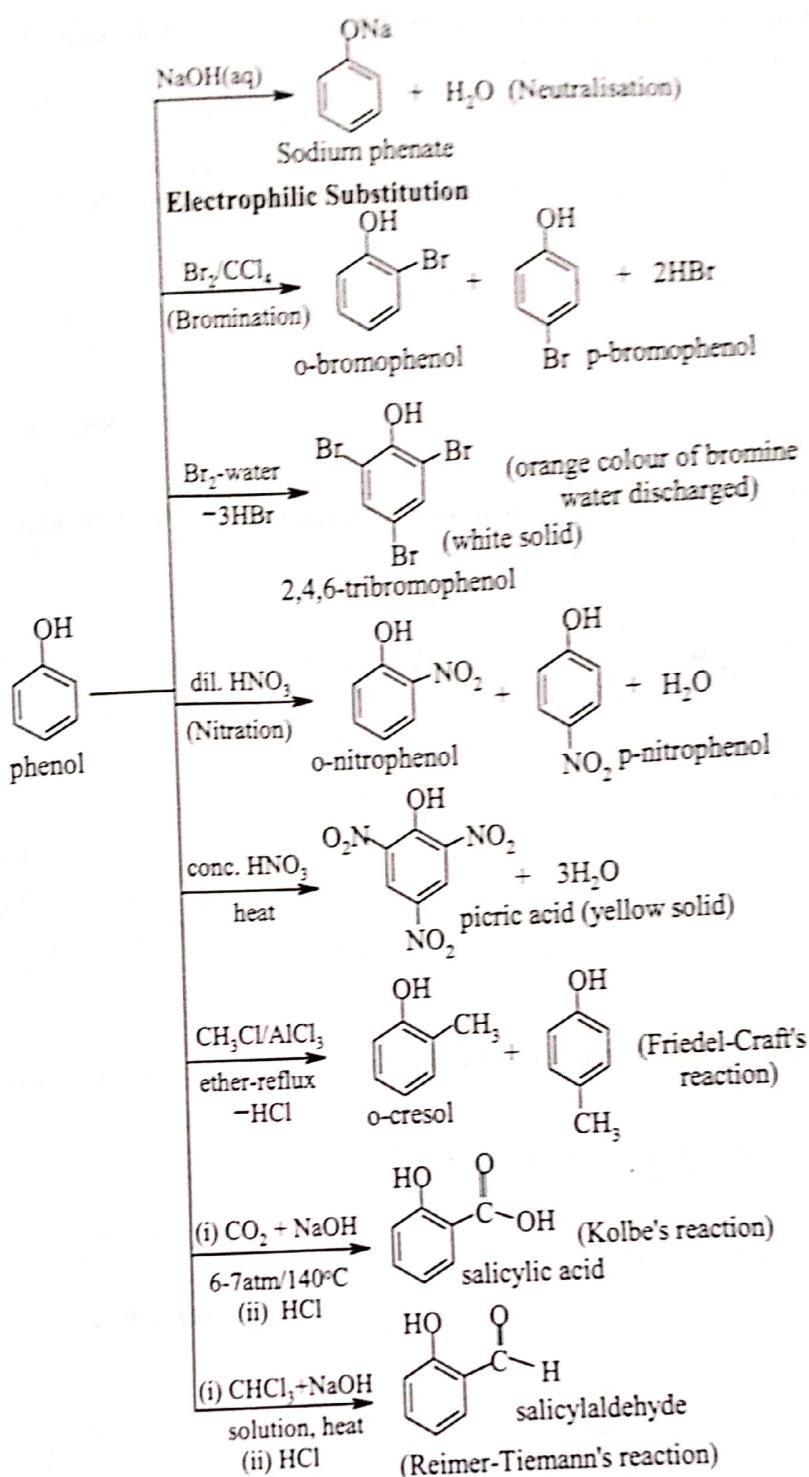


$$pK_a = 9.60 \quad 10.05 \quad 10.14 \quad 10.30$$

- In conclusion order of acidity of water, alcohols and phenols is : phenols > water > alcohol.
- The electron withdrawing substituents such as nitro group at *ortho* and *para* positions stabilise corresponding phenate ion by mesomeric effect.
- The electron withdrawing substituents such as nitro group at *ortho* and *para* positions stabilise corresponding phenate ion by delocalizing negative charge due to resonance effect.
- The structure (III) is highly stable and contributes to a maximum extent to resonance hybrid. Higher the stability of a conjugate base, stronger is the acid. Hence, *p*-nitrophenol is strongest acid among the nitrophenols. Intramolecular hydrogen bond in *o*-nitrophenol decreases the ionization, hence less acidic than *p*-nitrophenol. The substituent at *meta*-position does not take part in resonance, hence, *m*-nitrophenol is weaker acid than *o*-nitrophenol.

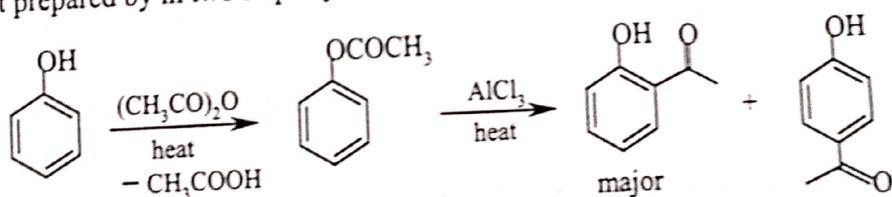
In case of halophenols, $-I$ effect predominates over $+R$ effect, therefore, all halophenols except *o*- and *p*-fluorophenols are more acidic than phenol itself. Since, $-I$ effect decreases with distance, acid strength of halophenols decrease in the order *o*-halophenol > *m*-halophenol > *p*-halophenol > phenol. In case of *p*-fluorophenol, because of almost identical size of 2p-orbitals of C and F, $+R$ and $-I$ effects almost balance each other and hence it is almost as acidic as phenol. Amongst halophenols, *o*-fluorophenol is weakest due to strong intramolecular hydrogen bonding. Thus, the acidity of *o*-halophenols decreases in the order: *o*-chlorophenol > *o*-bromophenol > *o*-iodophenol > *o*-fluorophenol. Higher the electron withdrawing ability of a group, greater is the acidic strength. Decreasing order of acidity of a few substituted phenols is *p*-nitrophenol > *p*-cyanophenol > *p*-chlorophenol > phenol. Higher the electron releasing ability weaker is the phenols. It is illustrated by following order of acid strength $-methoxyphenol < p\text{-methylphenol} < \text{phenol.}$

Reactions of phenol



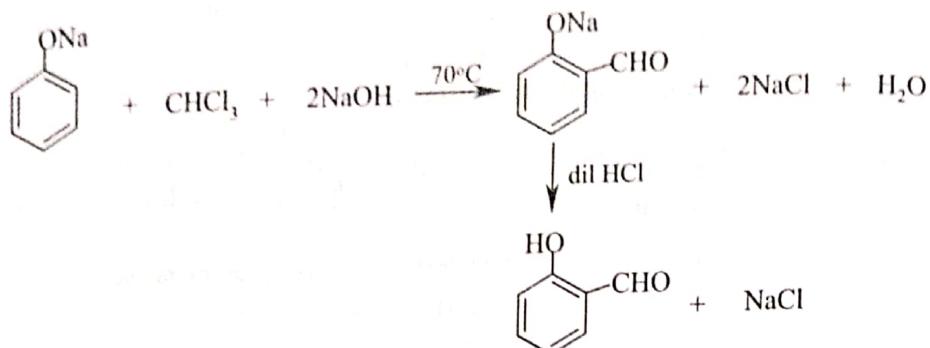
Friedel crafts alkylation with RX and AlCl_3 gives poor yield of alkylated product as AlCl_3 coordinates with oxygen of phenol and deactivate benzene ring for S_E reactions.

Phenolic ketones are best prepared by in two steps by means of *Fries rearrangement*.

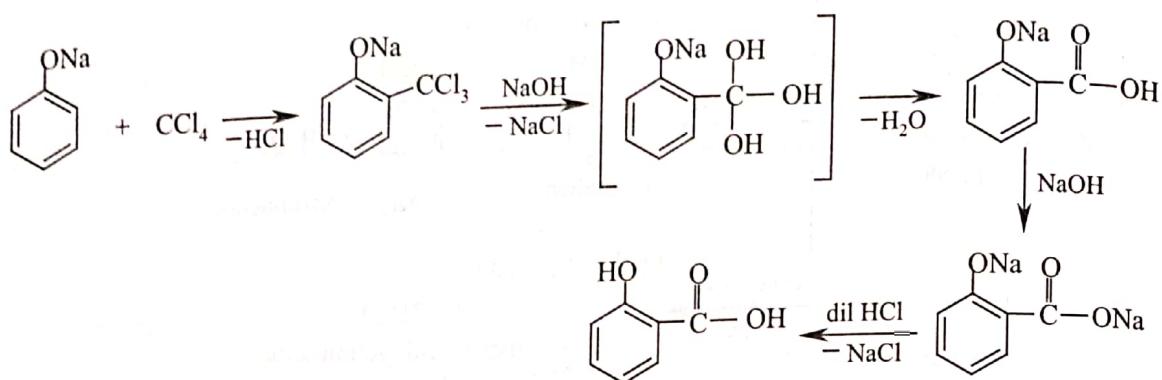


Reimer-Tiemann reaction

When sodium phenate is heated with chloroform in presence of aqueous sodium hydroxide followed by acidification it gives salicylaldehyde. This reaction is called *Reimer Tiemann reaction*.



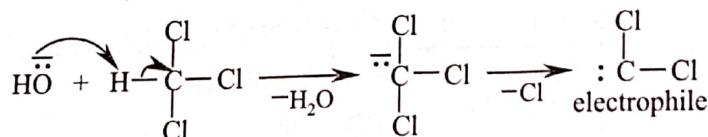
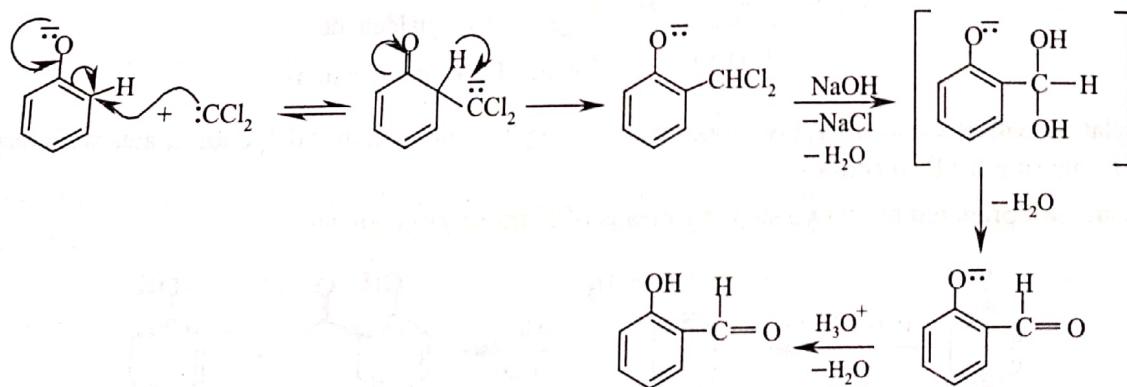
If carbon tetrachloride is used in place of chloroform, the reaction terminates with the formation of salicylic acid.

**Mechanism**

This reaction is an electrophilic substitution reaction which involves attack of dichlorocarbene (electrophile) on sodium phenate ion.

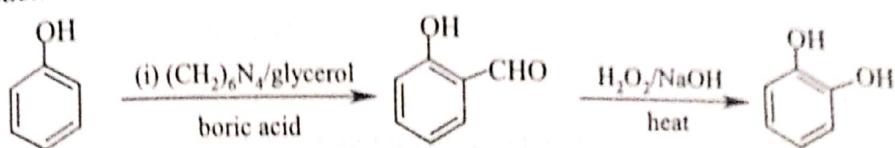
Formation of dichlorocarbene

In alkaline medium chloroform molecule yields dichlorocarbene.

*Attack of electrophile*

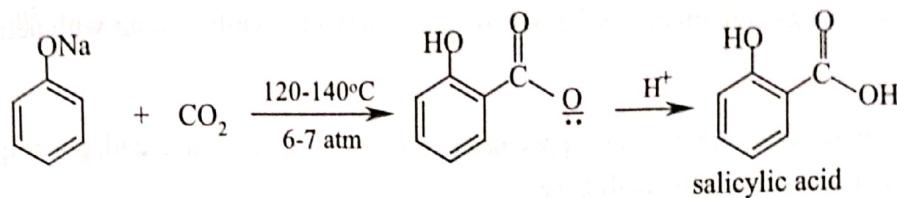
Small amount *p*-hydroxybenzaldehyde is also formed. At higher temperature, formation of *para* isomer is favoured.

Duff reaction
Salicylaldehyde is also prepared by heating phenol with hexamethylenetetramine (urotropin), glycerol and boric acid. This reaction is called Duff reaction.



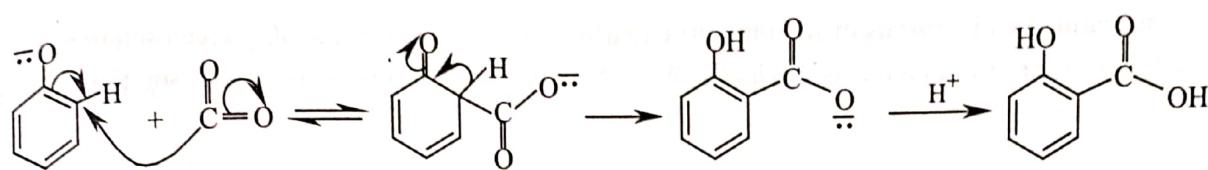
Kolbe's reaction

When sodium phenate is heated with carbondioxide (weak electrophile) at 130-140°C under 6-7 atm pressure gives sodium salicylate. This reaction is called Kolbe's reaction.



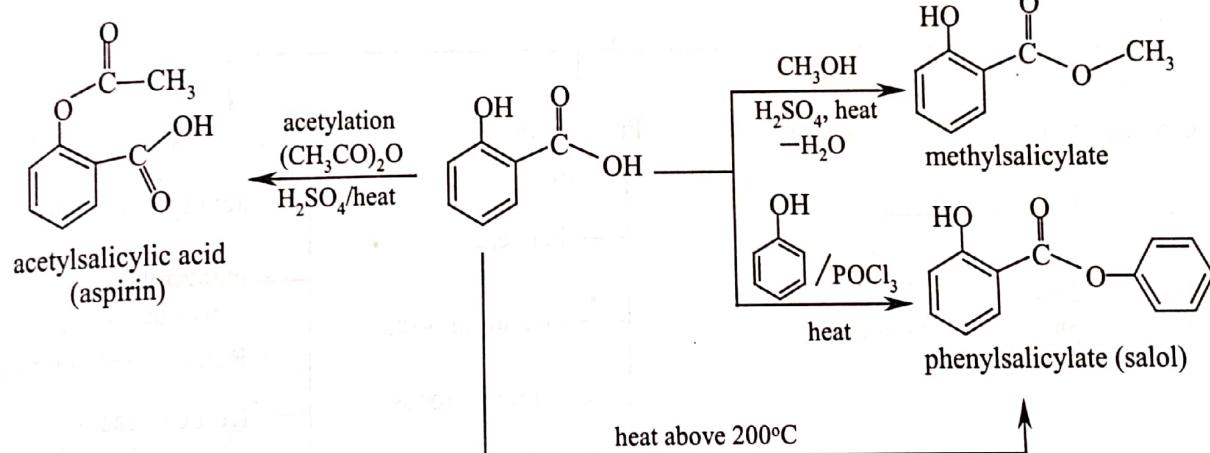
Mechanism

It involves attack of CO₂ which is a weak electrophile.



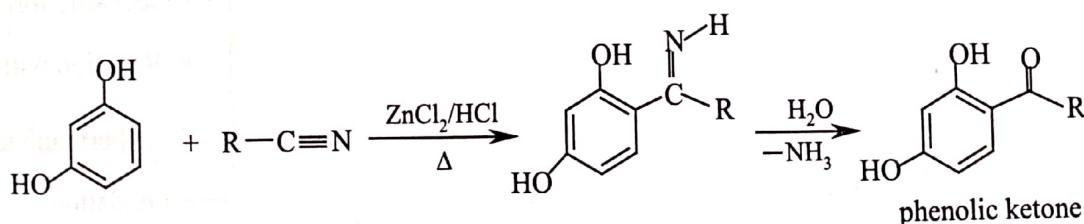
At high temperature (above 150°C) formation of p-hydroxybenzaldehyde is favoured.

Salicylic acid is an important derivative of phenol which is used for synthesis of *aspirin*, *salol* and methyl salicylate (*oil of winter green*)



Houben Hoesch reaction

When polyhydric phenols in which -OH groups are *meta* to one another are treated with alkyl nitrile in presence of anhydrous zinc chloride and hydrogen chloride, phenolic ketones are formed. The reaction is called Houben Hoesch reaction.



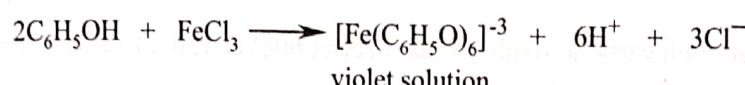
Uses

Used in manufacture of bakelite, cyclohexanol, salol, methyl salicylate, aspirin, phenacetin (drugs). 2,4-dichlorophenoxyacetic acid (weed killer), chloroxylenol (antiseptic) picric acid, (explosive).

Tests for phenol

Reaction with ferric chloride

When phenol is treated with neutral ferric chloride, red or violet solution is formed.



Aliphatic or aromatic compounds containing *enol* group ($\text{C}=\text{C}-\text{OH}$) give violet colour with neutral ferric chloride.

Phthalein reaction

When phenol is heated with phthaleic anhydride in presence of concentrated sulphuric acid, phenolphthalein is formed which gives pink solution when neutralized with alkali/base.

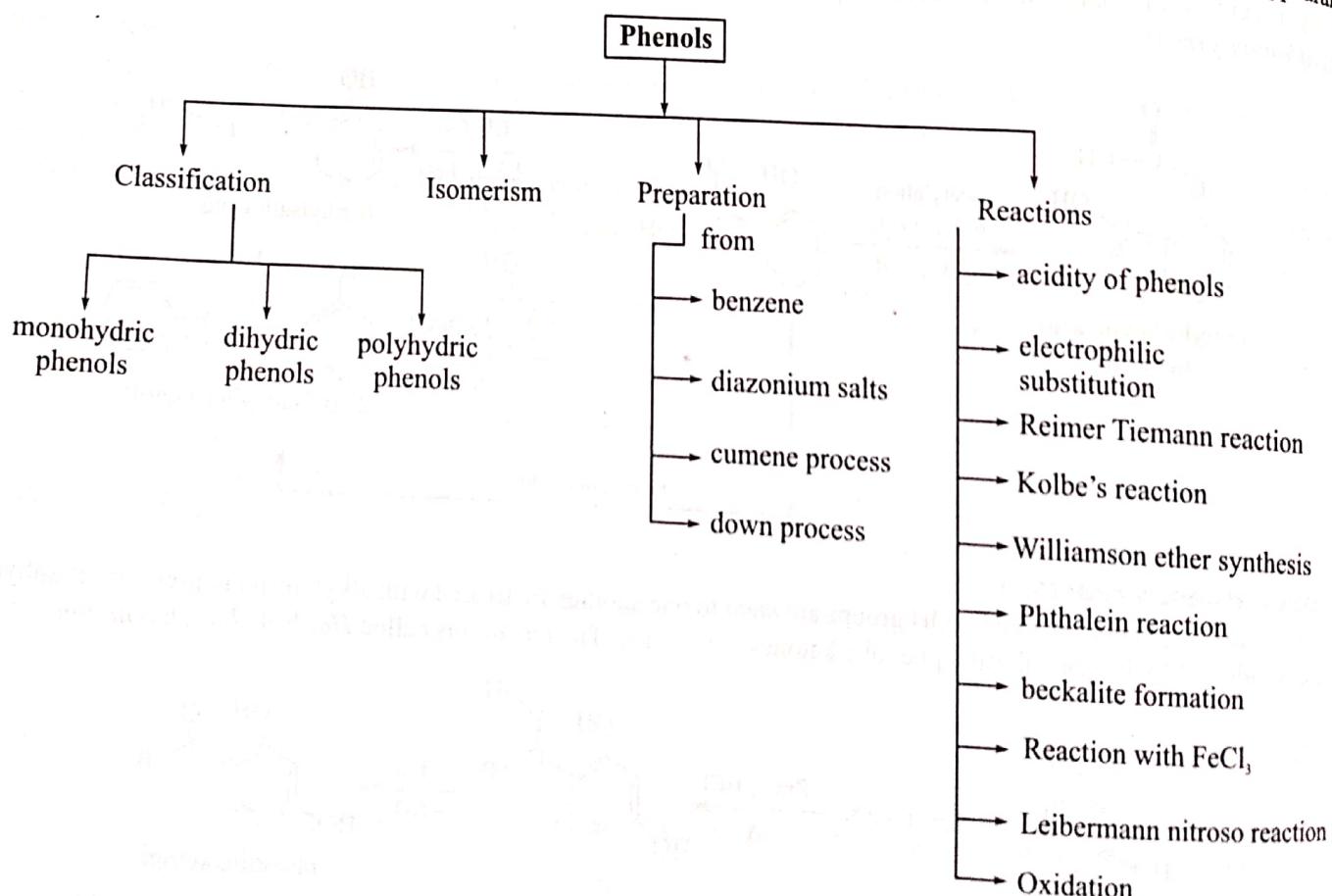
Condensation of resorcinol with phthaleic anhydride in presence of concentrated H_2SO_4 gives *fluorescein*.

Liebermann's nitroso reaction

When phenol is warmed with crystals of sodium nitrite (NaNO_2) and concentrated H_2SO_4 , green solution is formed. When this is poured into water, a red colour is produced. When it is treated with excess of NaOH solution, a blue solution is formed.

Bromine water test

When phenol is treated with excess of bromine water, white solid of 2,4,6-tribromophenol is separated with the disappearance of orange colour of bromine water.

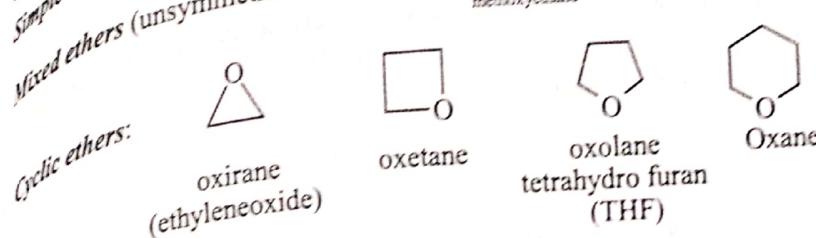


Ethers

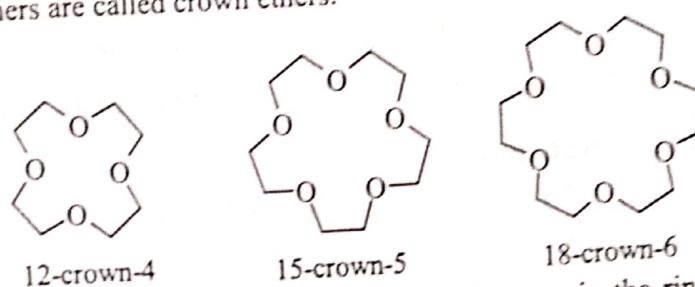
The organic compounds containing C—O—C unit are called ethers. The general formula of open chain aliphatic ethers is R—O—R' (R and R' are alkyl groups).

Simple ethers (symmetrical ethers): (R = R') CH₃—O—CH₃, CH₃CH₂—O—CH₂CH₃

Mixed ethers (unsymmetrical ethers): CH₃CH₂OCH₃



Crown ethers: The cyclic polyethers are called crown ethers.



Crown ethers are named as x-crown-y where x is the total number of atoms in the ring and y, is the number of oxygen atoms. Crown ethers are used to transport ionic compounds into organic phase (phase transfer catalyst). 18-Crown-6, the host transports potassium ion, the guest from aqueous solution to the organic phase. Oxygen in the crown ether coordinated with the metal cation is engulfed in the cavity of the host. The cavity size of 18-crown-6 is perfect for K⁺ and 12-crown-4 for Li⁺ and 15-crown-5 for Na⁺.

Isomerism in ethers

Functional isomerism: Ethers are functional isomers of monohydric alcohols. Examples: CH₃OCH₃ and C₂H₅OH.

Metamerism: Ethers with four or more carbons can show metamerism (alkyl groups flanking the oxygen are different).

Examples: CH₃CH₂OCH₂CH₃ and CH₃OCH₂CH₂CH₃.

Chain isomerism: The isomers differ in the arrangement of carbon atoms in parent chain.

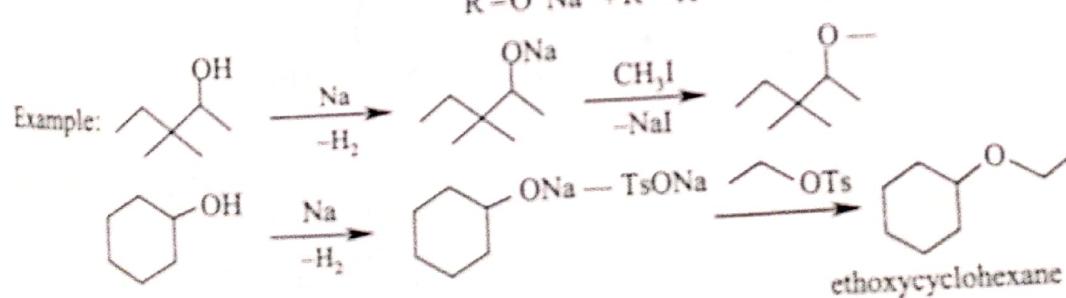
Examples: CH₃—O—CH₂CH₂CH₃ and (CH₃)₂CHOCH₃.

Preparation of Ethers**From alkyl halide (haloalkanes)**

By heating alkyl halides with dry silver oxide

**Williamson ether synthesis**

This method involves the attack of an alkoxide ion electron deficient carbon atom of primary haloalkanes or tosylate. In case of secondary or a tertiary halides, the elimination reaction predominates over substitution.



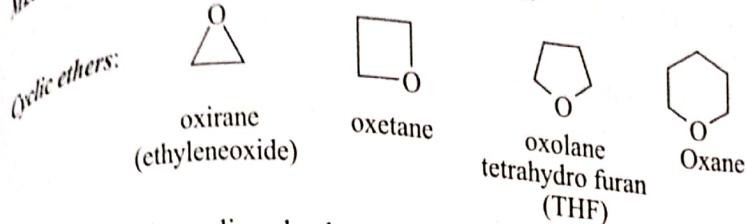
Ethers

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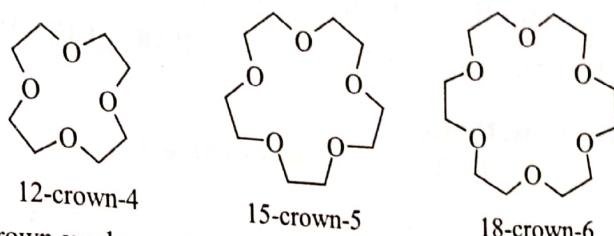
Simple ethers (symmetrical ethers): (R = R') CH₃-O-CH₃, CH₃CH₂-O-CH₂CH₃

Mixed ethers (unsymmetrical ethers): CH₃CH₂OCH₃

methoxymethane
methoxyethane



Crown ethers: The cyclic polyethers are called crown ethers.



Crown ethers are named as x-crown-y where x is the total number of atoms in the ring and y, is the number of oxygen atoms. Crown ethers are used to transport ionic compounds into organic phase (phase transfer catalyst). 18-Crown-6, the host transports potassium ion, the guest from aqueous solution to the organic phase. Oxygen in the crown ether coordinated with the metal cation is engulfed in the cavity of the host. The cavity size of 18-crown-6 is perfect for K⁺ and 12-crown-4 for Li⁺ and 15-crown-5 for Na⁺.

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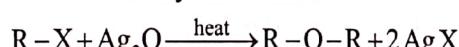
Examples: CH₃CH₂OCH₂CH₃ and CH₃OCH₂CH₂CH₃.

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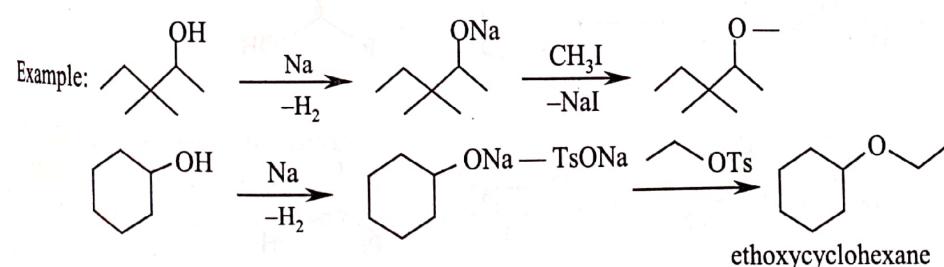
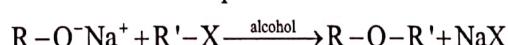
Examples: CH₃-O-CH₂CH₂CH₃ and (CH₃)₂CHOCH₃.

Preparation of Ethers**From alkyl halide (haloalkanes)**

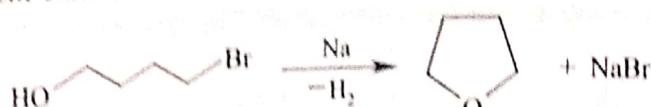
By heating alkyl halides with dry silver oxide

**Williamson ether synthesis**

This method involves the attack of an alkoxide ion electron deficient carbon atom of primary haloalkanes or tosylate. In case of secondary or a tertiary halides, the elimination reaction predominates over substitution.



Intramolecular reaction yields cyclic ethers.

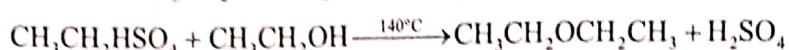
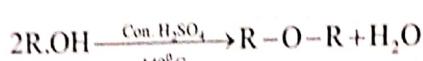


This ether cannot be prepared using sodium ethanoate and t-butyl chloride. Tertiary and secondary alkyl halides tend to undergo elimination in the presence of an alkoxide ion.

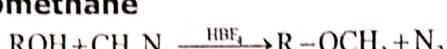
Alkyl aryl ethers can be prepared using alkyl halide and sodium phenoxide.

From alcohol

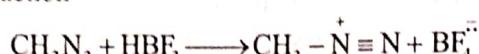
The dehydration of alcohols gives ethers.



Reaction of alcohols and diazomethane

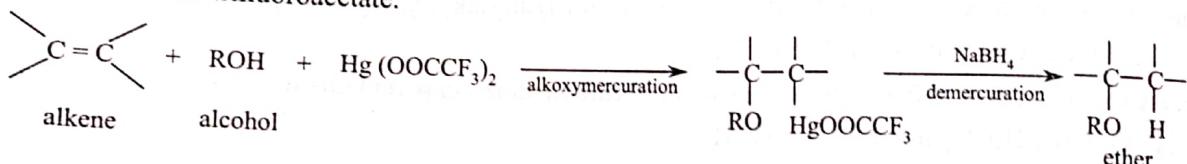


HBF_4 acts as an acid and catalyses the reaction

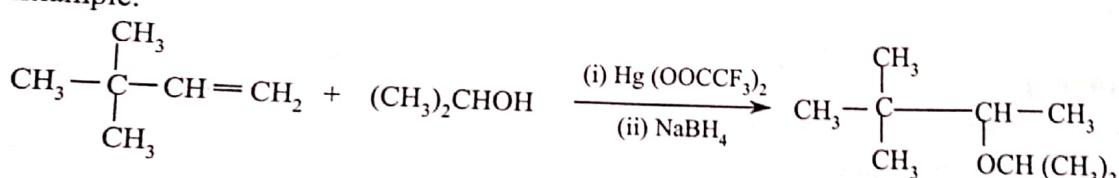


By Alkoxymercuration – demercuration

It is one of the best methods for preparing ethers. Some of the advantages of this method are speed, convenience, high yield, virtual absence of rearrangement and no competing elimination reaction. It involves a reaction between an alkene and alcohol in the presence of mercuric trifluoroacetate.

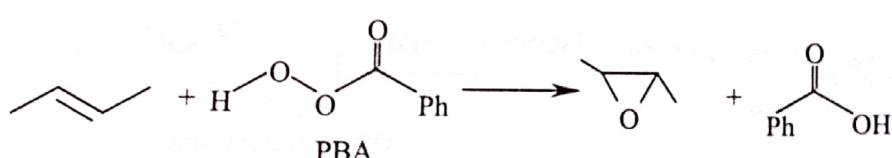
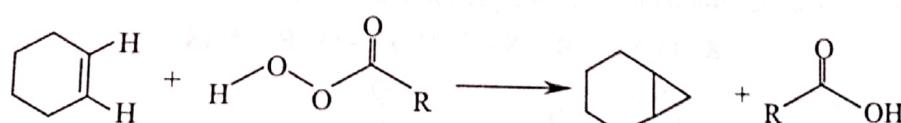


Example:



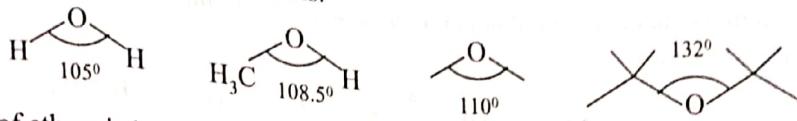
3-isopropoxy-2, 2-dimethylbutane

Oxiranes (epoxides) are formed by the action of per acids such as perbenzoic acid (PBA), peracetic acid (PAA) etc. The epoxidation is concerted reaction (S_N2) which involves attack of π electrons on oxygen atom of OH group.



General Characteristics

Like water, the oxygen atom of ethers is sp^3 hybridised. In ethers, van der Waals strain involving alkyl groups causes bond angle at oxygen to be greater than alcohols.

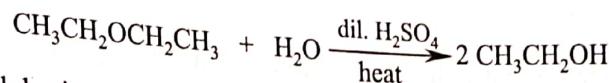
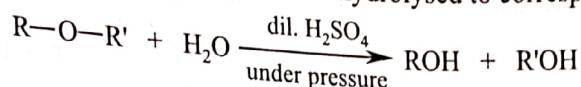


The dipole moment of ethers is less than alcohols ($\mu = 1.18$ D).
point of ether is less than the com-

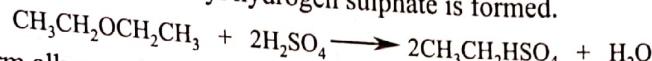
The boiling point of ether is less than the corresponding functional isomer alcohol.

The bond
Reaction due to cleavage of C-O bond
Catalysis

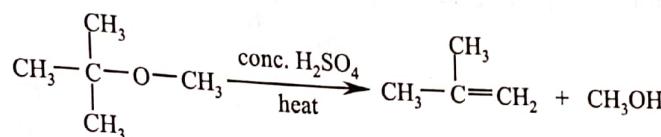
When heated with dilute sulphuric acid under pressure, ethers are hydrolysed to corresponding alcohols.



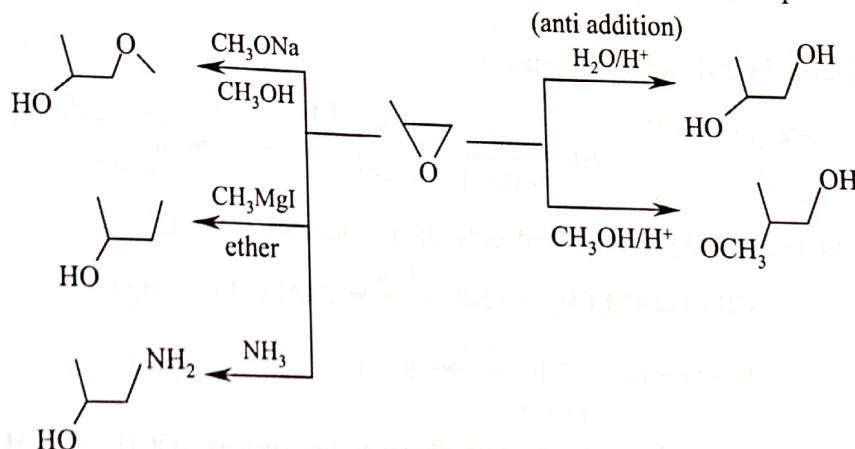
When heated with concentrated sulphuric acid, alkyl hydrogen sulphate is formed.



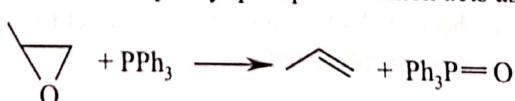
Secondary and tertiary ethers form alkenes



Acid catalysed hydrolysis of unsymmetrical epoxide (oxirane) favours the formation of stable carbocation followed by attack of nucleophile. The nucleophile attacks on less sterically hindered carbon of unsymmetrical epoxides in basic medium.



Oxiranes can be reduced to alkene by the action of triphenyl phosphene which acts as nucleophile.

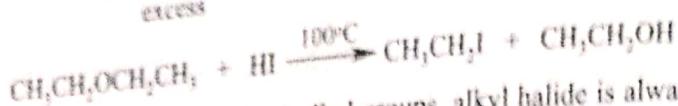
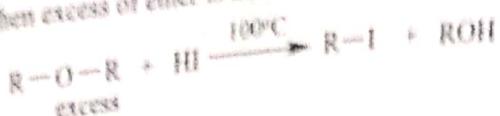


Action of hydroiodic acid

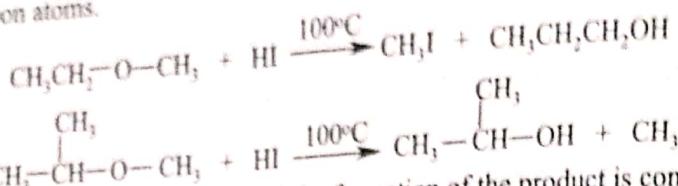
Ethers are readily attacked by concentrated HI and decomposed into alkyl iodide ($R-I$). This reaction involves the cleavage of C-O bond and the product formed depends on the temperature of the reaction and molar ratio of reactants.

11.10 Chemistry

Alkyl iodide and alkanol are formed when excess of ether is heated with hydroiodic acid at 100°C.

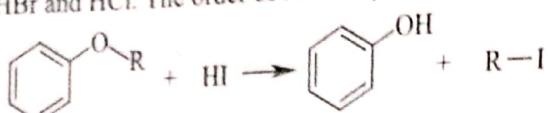


In case of mixed ethers containing primary (or secondary) alkyl groups, alkyl halide is always formed from an alkyl group containing less number of carbon atoms.

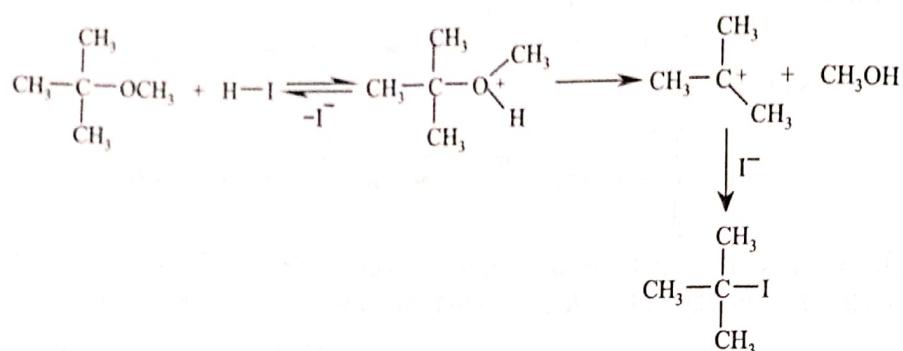


The cleavage of such ethers occurs by S_N2 mechanism and the formation of the product is controlled by steric factor. In case of aromatic ethers, phenol and alkyl iodide are formed.

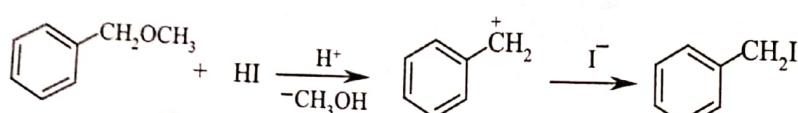
Similar reactions are observed with HBr and HCl. The order of reactivity of hydrogen halides is $\text{HI} > \text{HBr} > \text{HCl}$.



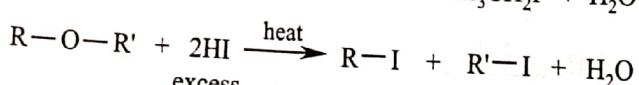
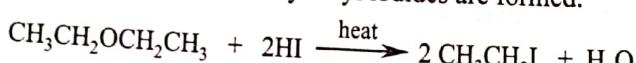
If one of the alkyl group is tertiary, the alkyl halide is formed from tertiary alkyl group as the reaction follows S_N1 mechanism.



In case of benzyl methyl ether, benzyl iodide is formed.



When ethers are heated with excess of hydroiodic acid, only alkyl iodides are formed.

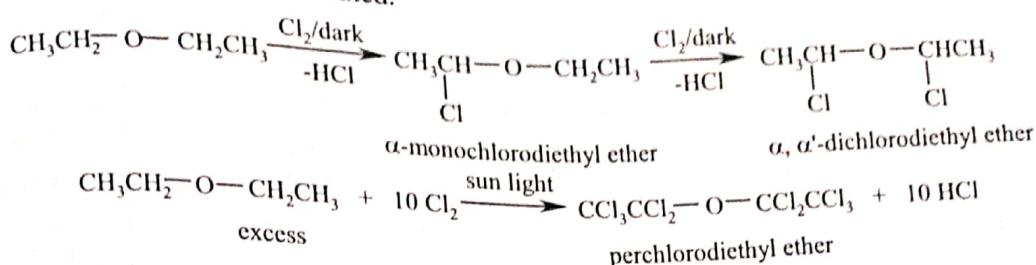


This reaction forms basis of *Zeisel method* for estimation of alkoxy groups such as $-\text{OCH}_3$, $-\text{OCH}_2\text{CH}_3$, etc. $\text{ROR} + 2\text{HI} \rightarrow 2\text{RI} + \text{H}_2\text{O}$. The alkyl iodide formed is absorbed in alcoholic AgNO_3 solution to form silver iodide. From the mass of silver iodide formed, the number of alkoxy group per molecule may be calculated.

Ester formation
With acid anhydrides or acid chloride in the presence of anhydrous zinc chloride, ethers form ester.
 $(\text{C}_2\text{H}_5)_2\text{O} + \text{CH}_3\text{COCl} \xrightarrow{\text{anhy. ZnCl}_2} \text{CH}_3\text{COOC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{Cl}$
 $(\text{C}_2\text{H}_5)_2\text{O} + (\text{CH}_3\text{CO})_2\text{O} \xrightarrow{\text{anhy. ZnCl}_2} 2\text{CH}_3\text{COOC}_2\text{H}_5$

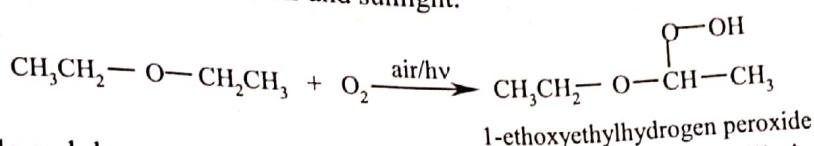
Halogenation

Ethers undergo substitution reactions at alkyl group when treated with chlorine or bromine in absence of sunlight to form halogenated ethers. Highly reactive hydrogen atoms at α -carbon get substituted readily. However, in presence of sunlight all the hydrogen atoms of diethyl ether are substituted.



Formation of peroxides

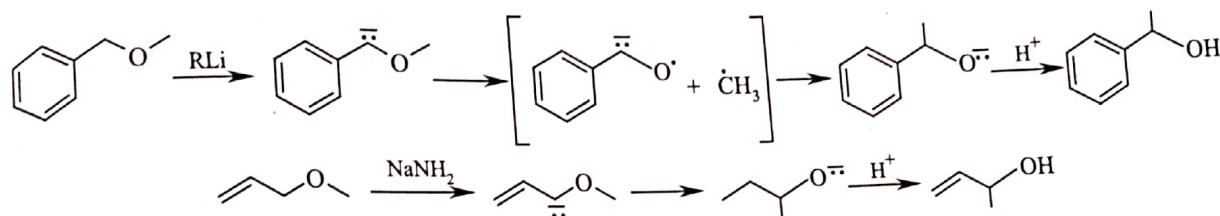
Ethers are oxidized to peroxides when exposed to air and sunlight.



These peroxides are unstable and decompose violently at high temperatures. During distillation of old sample of ether, the peroxides are removed by treating with a freshly prepared solution of ferrous sulphate.

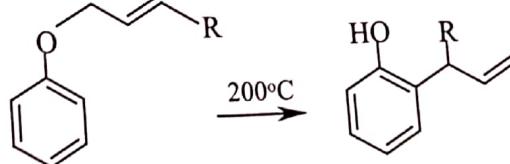
Wittig's rearrangement

The base catalysed rearrangement of allyl alkyl ethers or benzyl alkyl ethers into corresponding alcohols is called Wittig's rearrangement. Strong bases like RLi , NaNH_2 etc., are employed. This rearrangement takes place by free radical mechanism.

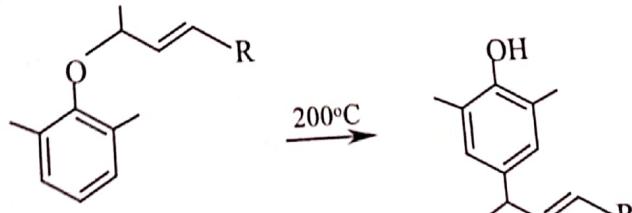


Claisen rearrangement

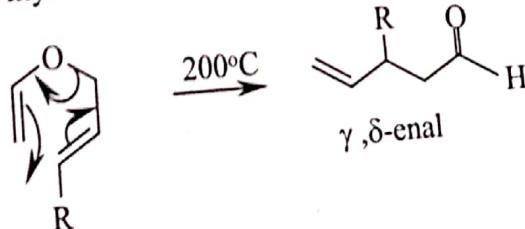
When allyl phenyl ethers are heated at 200°C the corresponding *o*-allylphenols are formed. This rearrangement is called Claisen rearrangement.



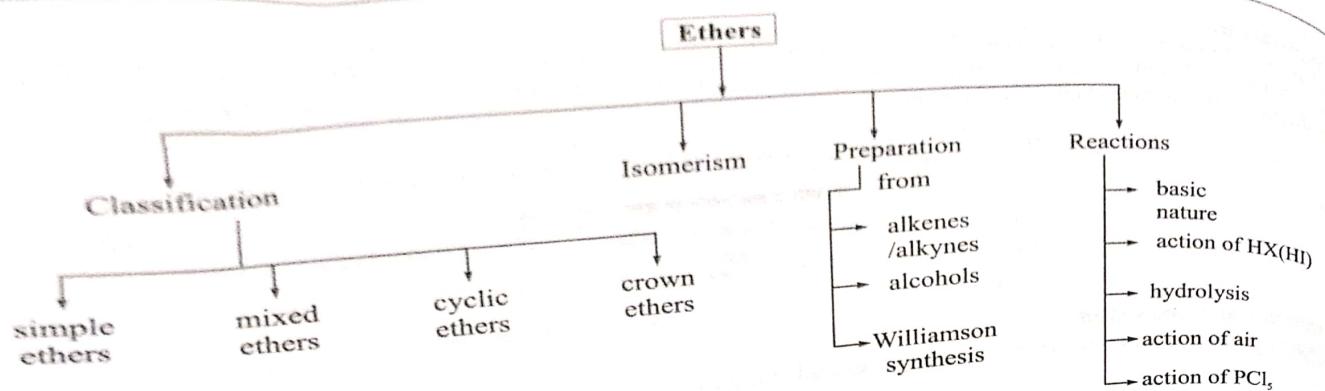
If both *ortho* positions are substituted, then rearrangement occurs at *para* position.



This rearrangement is also given by allyl vinyl ethers leading to the formation of γ, δ -enones.



11.22 Chemistry



Methods to determine the number of hydroxyl groups in a polyhydric alcohol.

Let molecular mass of organic compound having -OH group is a gm. On acylation the molecular mass of product is b gm. Then number of -OH groups in given compound will be given as -

$$\text{Number of } -\text{OH} \text{ groups} = \frac{\text{Molecular mass of the product} - \text{Molecular mass of reactant}}{12}$$

This 12 is increase in mass of product on acylation of one -OH group.
 $\text{-NH}_2 + \text{CH}_3\text{COCl} \rightarrow \text{NH}_3\text{COCH}_3 + \text{HCl}$

There is also an alternate method to determine the no. of -OH groups.

Let W g of acyl derivatives of polyhydric alcohol is taken. It is hydrolysed by V ml (excess) of standard alkali. Unused alkali is titrated with standard acid. This is done to get the weight of used alkali (a gm). Now suppose one molecule contains n number of OH groups and molecular mass of alcohol be M g.

Now if W g of acyl derivatives utilizes a g of KOH

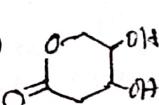
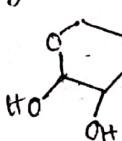
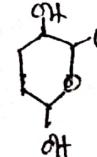
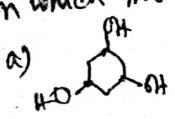
Hence $(M+42n)$ g of it will utilize $(M+42n)a/56$ g of KOH i.e. $56n$

Thus an expression can be obtained W like -

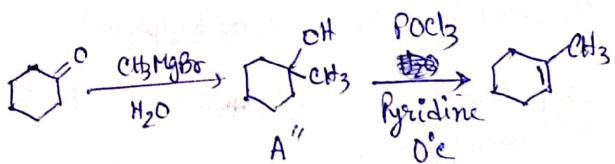
$$\frac{a}{W}(M+42n) = 56n$$

This expression will give the value of n no. of -OH groups present in the given compound.

In which molecule, cleavage by HIO_4 is not observed?



In other words acylation of each NH group increases the mass by $42 - 1 = 41$ amu.

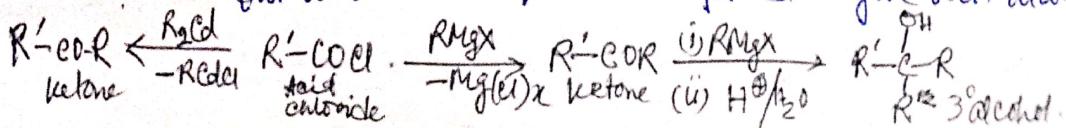


Explain why

dialkylcadmium is considered superior to Grignard reagent for the preparation of a ketone from an acid chloride?

Dialkylcadmium are less reactive than Grignard reagents towards nucleophile addition reactions because Cd is less electropositive than Mg. Dialkylcadmium react with the more reactive acid chlorides to give ketones but don't react further.

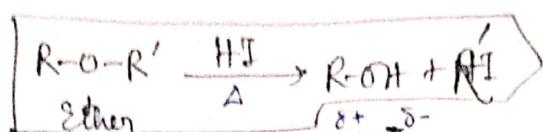
In contrast, Grignard reagents being more reactive not only react with the acid chlorides but also with the ketones so formed to give tert-alcohols.



Classification of Polymers

①

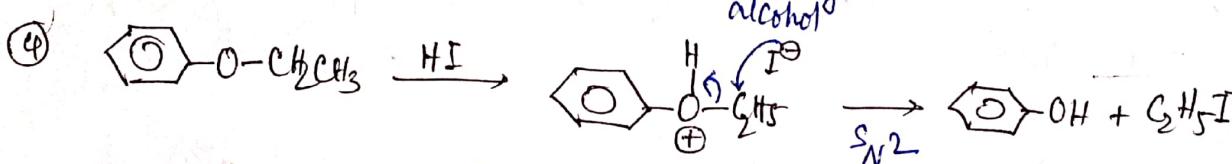
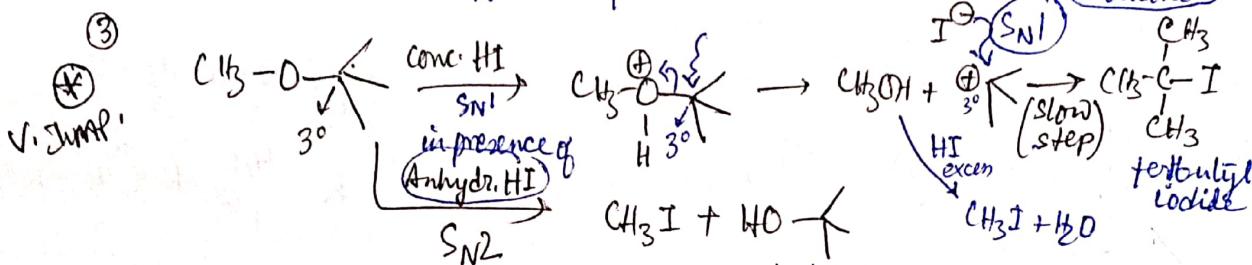
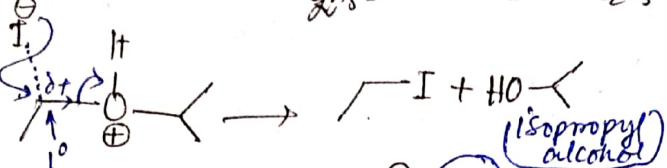
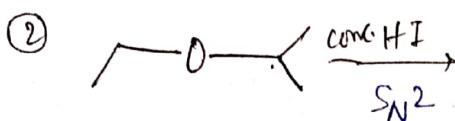
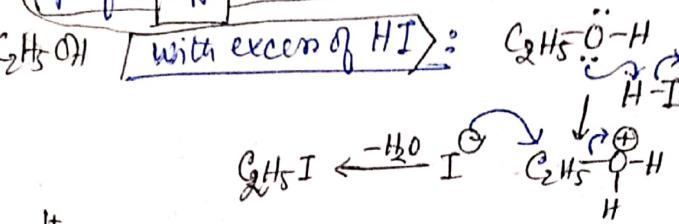
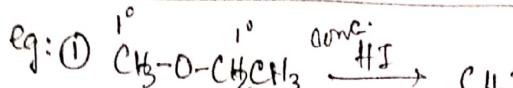
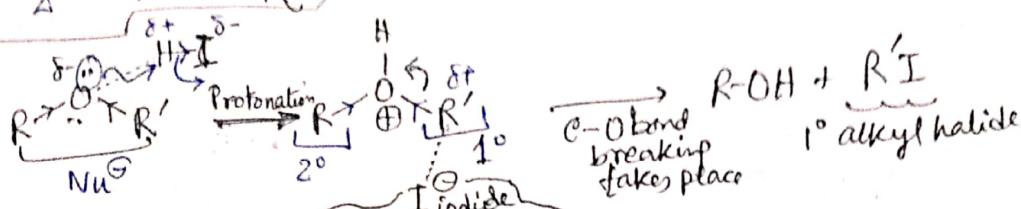
Rxn of Ethers with concn HI



* S_N^2

* S_N^1 (3° /Resonance stability)

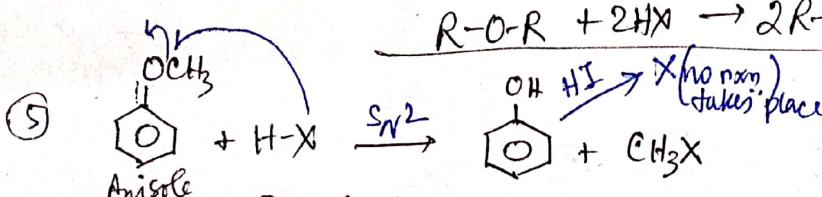
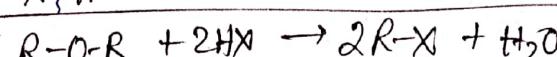
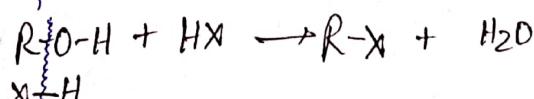
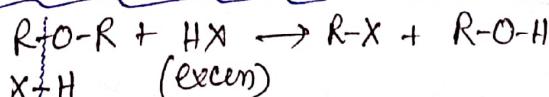
Mechanism



$R-O-R'$; C-O bond cleavage chemical Rxn

least reactive functional group

① Ether rxn with HX: \rightarrow (Temp. must be high)



Reactivity order of HX towards ether is $\text{HI} > \text{HBr} > \text{HCl}$

