Ch-2

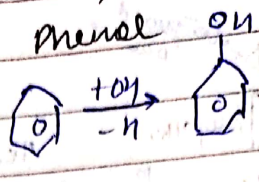
Date

# Alcohol, Phenol & Ethers

**Alcohol**

$R-H \xrightarrow[-H]{+OH} R-OH$

**Phenol**



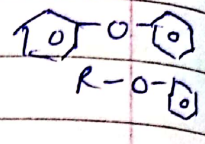
**Ether**

$R-O-R'$

Alkoxy grp [-OR]

Aryloxy grp [-O-Ar]

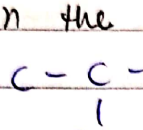
$R-OR$



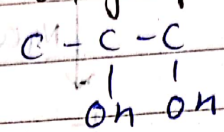
$R-O-Ar$

* Classifications [Alcohols]

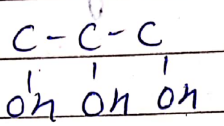
On the Basis of no. of -OH group.



Monohydric

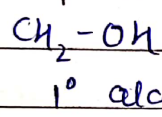


Dihydric

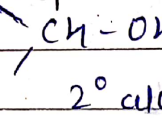


Trihydric

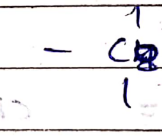
- Compounds containing $C_{sp^3} - OH$ Bond :



1° alcohol

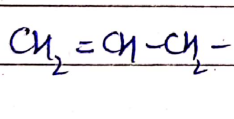


2° alcohol

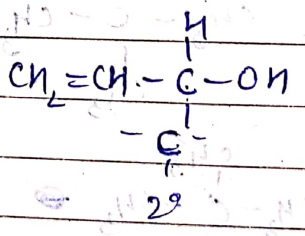


3° alcohol

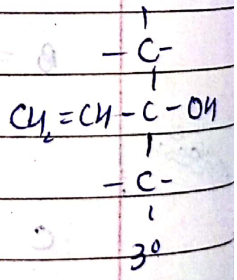
- Allylic alcohols : → Double bonded carbon से Next carbon पे OH हो



1°

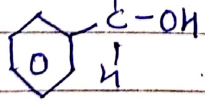


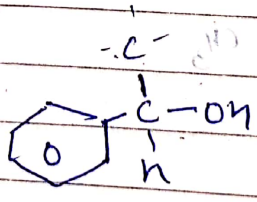
2°

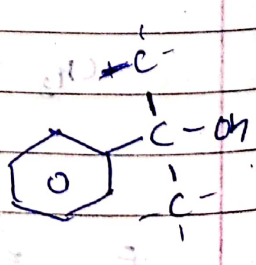


3°

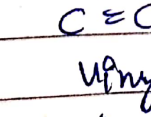
- Benzylic alcohols :



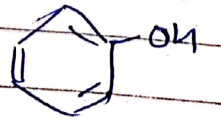




- Compounds containing $C_{sp^2} - OH$ Bond : [OH directly double bond से जुड़ा हो]

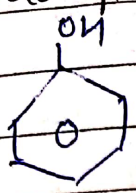


Vinylic Alcohol

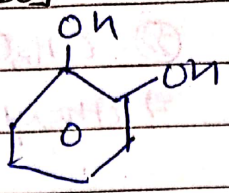


Aryl Alcohol or Phenol

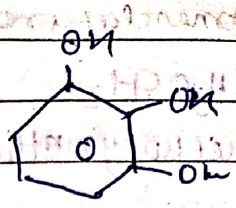
* Classification [Phenol]



Monohydric Phenol



Dihydric Phenol



Trihydric Phenol

* Classification [Ethers]

$R-O-R'$

Symmetrical

$CH_3-O-CH_3$

$C_2H_5-O-C_2H_5$

Unsymmetrical.

$CH_3-O-C_2H_5$

$CH_3-O-C_3H_7$

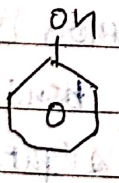
Simple ether

$C_2H_5-O-C_2H_5$

Mixed ether

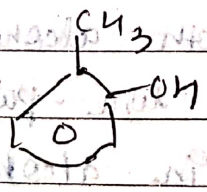
$CH_3-O-$ 

* Common & IUPAC name.



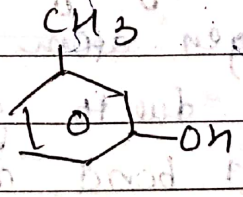
Common name: Phenol

IUPAC name: Phenol



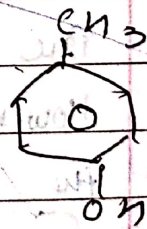
O-cresol

2-Methylphenol



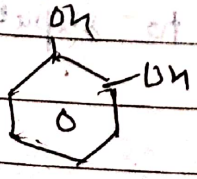
m-Cresol

3-methyl phenol



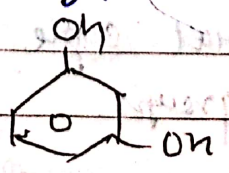
p-cresol

4-methyl phe



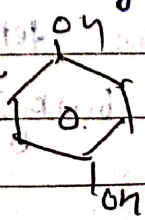
Common name: Catechol

IUPAC name: Benzene-1,2-diol



Resorcinol

Benzene-1,3-diol



Hydroquinone or quinol

Benzene-1,4-diol

* Nomenclature of ether.

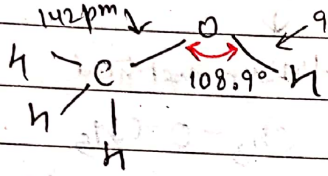
(1) $CH_3OCH_3$ → Methoxymethane

(2) $C_2H_5OC_2H_5$ → Ethoxyethane

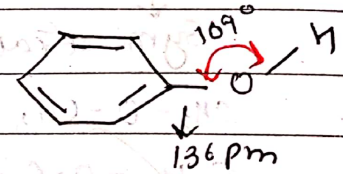
(3) $CH_3OCH_2CH_2CH_3$ → 1-Methoxypropane

(4) $C_6H_5OCH_2CH_3$ → Ethoxy Benzene.

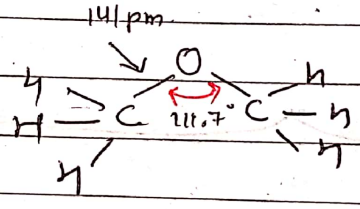
* Structures of functional groups:




Methanol.




Phenol




Methoxymethane.

Q. Why is the C-OH bond angle in alcohols slightly less than the tetrahedral angle whereas the C-O-C bond angle in ether is slightly greater?

Ans The oxygen atom in both alcohols & ethers is $sp^3$-hybridised. However, due to greater lone-pair than bond pair repulsion the C-OH bond angle in alcohols is slightly lower [109°] than the normal tetrahedral angle of 109°-28'. However, in ether C-O-C bond angle is slightly greater [110°] than tetrahedral angle due to repulsion b/w the two bulky R-groups.

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## Preparation of Alcohols

### (1) From alkenes

i) By acid catalysed hydration: [Direct hydration].

ii) Alkenes react with water in the presence of acid as catalyst.

iii) In case of unsymmetrical alkene, the addition take place in acc. to Markovnikov's rule.

iv) Reagent used [$H_2O$ / $H^+$]

$$CH_2=CH_2 + \underset{H^+/OH^-}{H_2O} \xrightleftharpoons{H^+} CH_2(OH)-CH_2$$

$$CH_3-CH=CH_2 + \underset{H^+/OH^-}{H_2O} \xrightleftharpoons{H^+} CH_3-\underset{OH}{CH}-CH_3$$

Propan-2-ol.

### (2) ~~Hydroboration~~ : [~~Oxo process~~]

Mechanism:

Step-I Protonation of alkene to form carbocation by electrophilic attack of $H_3O^+$

$$H_2O + H^+ \longrightarrow H_3O^+$$

$$>C=C< + H-\overset{H}{\overset{|}{O}}-H \longrightarrow -\overset{|}{C}-\overset{+}{C}< + H_2O$$

Step II Nucleophilic attack of water on carbocation.

$$-\overset{|}{C}-\overset{+}{C}< + H_2\ddot{O} \longrightarrow -\overset{|}{C}-\overset{|}{C}-\overset{+}{O}-H$$

Step III Deprotonation to form an alcohol.

$$-\overset{|}{C}-\overset{|}{C}-\overset{+}{O}-H + H_2\ddot{O} \longrightarrow H-\overset{|}{C}-\overset{|}{C}-OH + H_3O^+$$

Advantage: Alcohol is obtained in excellent yield.

Follows Anti-M.R.

ii) By hydroboration-oxidation (anti-Markovnikov hydration)

Diborane $(BH_3)_2$ reacts with alkenes to give trialkyl boranes as addition products. This is oxidised to alcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide

$$CH_3-CH=CH_2 + (H-BH_2)_2 \xrightarrow[\#OH^-]{H_2O,\ H_2O_2} CH_3-\underset{H}{CH}-\underset{OH}{CH_2} + B(\ldots)$$

Propan-1-ol

$$CH_3-CH_2-\overset{CH_3}{\overset{|}{C}}=CH_2 \xrightarrow[H_2O_2,\ OH^-]{B_2H_6} CH_3-CH_2-\underset{OH}{\overset{CH_3}{\overset{|}{\underset{|}{CH}}}}-CH_2$$

② From carbonyl compounds:

(i) By reduction of aldehydes & ketones:

- $RCHO + H_2 \xrightarrow{Pd} RCH_2OH$

Methanal — 1° alcohol.

eg: $CH_3CHO + H_2 \xrightarrow{Pd} CH_3CH_2OH$

$CH_3-\underset{O}{\overset{\|}{C}}-H + H_2 \longrightarrow CH_3CH_2OH$

a) Reduction of aldehyde give 1° alcohol.

- $RCOR' \xrightarrow[\text{Sodium borohydride}]{NaBH_4}$ (weak R.A) $R-\underset{OH}{CH}-R'$

$CH_3-\underset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{NaBH_4} CH_3-\underset{OH}{CH}-CH_3$

2° alcohol

b) Reduction of ketone give 2° alcohol.

(ii) By reduction of carboxylic acid & esters:

$$R-\underset{O}{\overset{\|}{C}}-OH \xrightarrow[H_2O]{LiAlH_4\ (\text{strong R.A})} RCH_2OH$$

1° alcohol

a) COOH acid reduced to 1° OH in excellent yield by Lithium aluminium hydride, very strong reducing agent.

- $RC(=O)-OR' \xrightarrow[\text{catalyst}]{H_2} RCH_2OH + R'OH$

=) $NaBH_4$ reagent is not used for reduction of ester.

(3) From Grignard reagents.

$C=O + R-MgX \longrightarrow -C(R)-O-MgX \xrightarrow{H_2O} RCH_2OH + Mg(OH)X$

- Overall rxns using different aldehydes & ketones:

- $HCHO + RMgX \longrightarrow RCH_2OMgX \xrightarrow{H_2O} RCH_2OH + Mg(OH)X$
  Methanal — 1° alcohol

- $RCHO + R'MgX \longrightarrow R-CH(R')-OMgX \xrightarrow{H_2O} R-CH(R')-OH + Mg(OH)X$
  Ethanal — 2° alcohol

- $RCOR + R'MgX \longrightarrow R-C(R')(R)-OMgX \xrightarrow{H_2O} R-C(R')(R)-OH + Mg(OH)X$
  (Propanone) Ketone — 3° alcohol

Note:

Formaldehyde / methanal $\xrightarrow[H_2O]{RMgX}$ 1° alcohol.

Other aldehyde $\xrightarrow[H_2O]{RMgX}$ 2° alcohol.

Ketone $\xrightarrow[H_2O]{RMgX}$ 3° alcohol.

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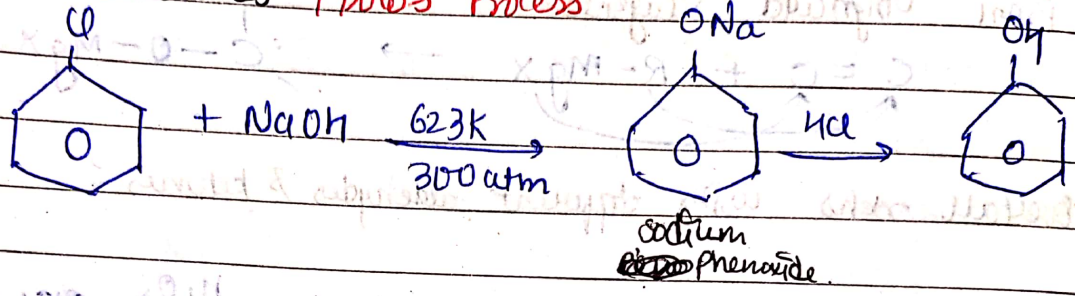
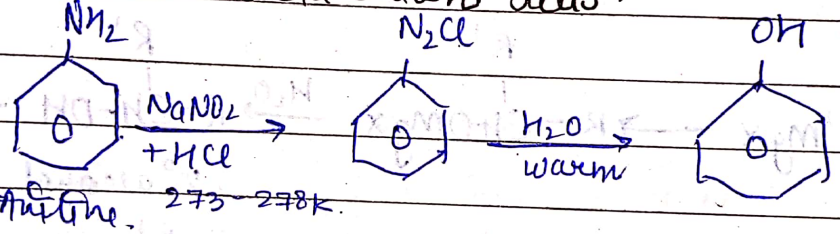
## Preparation of phenol

- Phenol is also k/a carbolic acid.
- Phenol was first isolated in the early 19th century from coal tar.

### (1) From haloarenes / Dow's Process




### (2) From Benzene diazonium salts.

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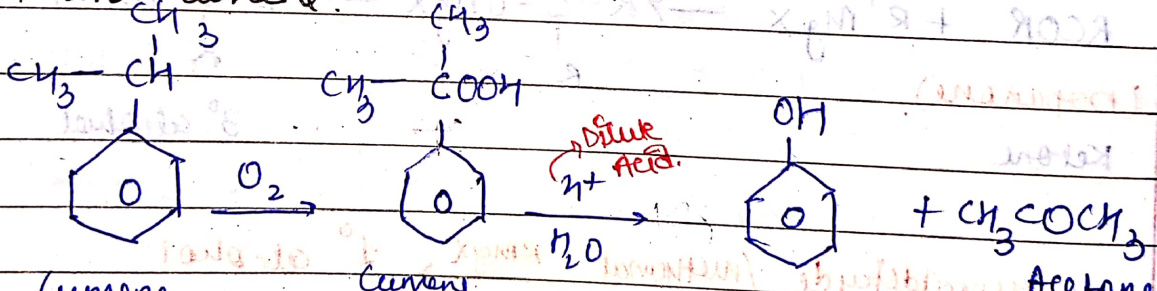
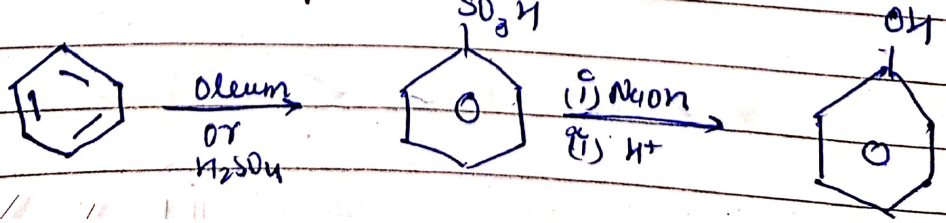
### (3) From Cumene.




- Acetone, a by-product of this rxn, is also obtained in large quantities by this method.

### (4) From benzenesulphonic acid.



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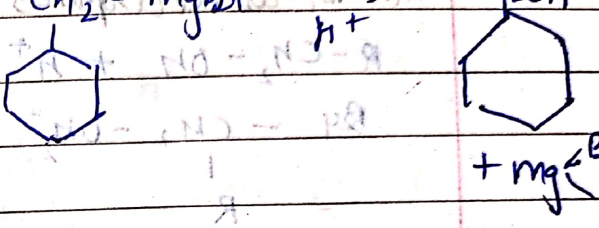
Intext Q.4] (i) $4CHO + CH_3-\underset{\underset{CH_3}{|}}{CH}-MgBr \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-O-MgBr \xrightarrow{H_2O} CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2OH + Mg\langle_{OH}^{Br}$

(ii) $4CHO +$  $\xrightarrow{H_2O,\ H^+}$ 

* Physical Properties of Alcohol
- Lower Alcohols [ethanol & methanol] are sweet smelling liquids & colourless
- higher alcohols are odourless, colourless, waxy solids
- Due to formation of intermolecular H-bonding with $H_2O$ molecules alcohols are highly soluble in water when present in any proportion
- Boiling points of alcohols are greater than alkyl halides or corresponding ethers due to presence of intermolecular H-bonding in alcohols.

$$B.P \propto Mol.\ Mass \propto Size$$

$$B.P \propto \frac{1}{Branching}$$

eg: $C_2H_5OH > CH_3OCH_3$ or $C_2H_5X$

- Increasing order of B.P

Hydrocarbon < ether < aldehyde < ketone < Alcohol < Acid

* Chemical Reaction of Alcohols

• Alcohols as nucleophiles.

(i) $R-\ddot{O}-H + \overset{|}{\underset{|}{-C}}- \longrightarrow R-\overset{H}{O}-\overset{|}{\underset{|}{C}}- \longrightarrow R-O-\overset{|}{\underset{|}{C}}- + H^+$

(ii) The bond b/w C=O is broken when they react as electrophiles

• Alcohol as electrophiles

$$R-CH_2-OH + H^+ \longrightarrow R-CH_2-OH_2$$

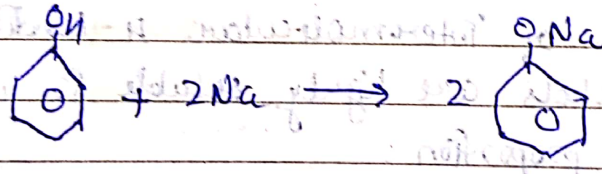
$$Br^- + CH_2(R)-OH_2^+ \longrightarrow Br-CH_2(R) + H_2O$$

(2) Rxn involving cleavage of O-H Bond.

(1) Acidity of alcohols & phenols.

(i) Rxn with metals:

$$2R-O-H + 2Na \longrightarrow 2R-O-Na + H_2$$




Alcohol & Phenols are acidic in nature.

(ii) Acidity of alcohols:

• The acidic character of alcohols is due to the polar nature of O-H bond.

• An electron donating group [$-CH_3$, $-C_2H_5$] decrease the acidic strength by increasing electron density on oxygen which tend to decrease the polarity of O-H bond.

$$R-CH_2OH > \underset{R}{\overset{R}{\diagdown}}CHOH > \underset{R}{\overset{R}{\diagdown}}C-OH$$

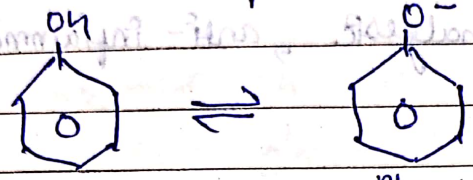
1° 2° 3°

• There are 3 $e^-$ donating group which ↑ $e^-$ density on oxygen & ↓ the polarity on OH Bond than ↓ acidic character.

- Polarity ↑ Acidic character ↑
- withdrawing group present ; Acid character ↑

(iii) Acidity of phenols:

- Phenol act as good acid because after losing proton phenoxide ion is formed which resonance stabilised.




Phenoxide ion.

- Phenol is more acidic than alcohol because its ring is e⁻ withdrawing which stabilised the resonance.
- In phenols, the presence of electron withdrawing group such as [$NO_2$, CN, -COOH] increases the acidic strength of phenol.
- This effect is more when such a group is present at ortho & para positions.
- The e⁻ releasing groups such as alkyl group decrease the acidic strength.
- For eg: Cresols are less acidic than phenol.

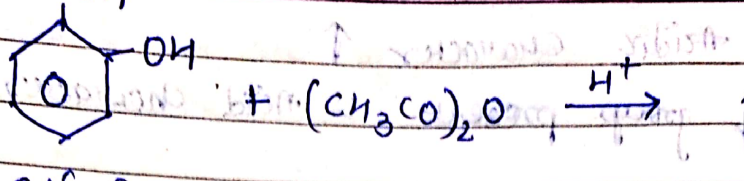
(2) Esterification.

$$Ar/R\text{-}OH + R'\text{-}COOH \underset{\text{enzyme}}{\overset{H^+}{\rightleftharpoons}} R\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}R' + H_2O$$

$$R\text{-}OH + (R'CO)_2O \overset{H^+}{\rightleftharpoons} R\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH + R\overset{O}{\overset{\|}{C}}\text{-}OR$$

$$R/ArOH + R'COCl \xrightarrow[\text{Neutralise}]{\text{Pyridine}} R/ArOCOR' + HCl$$

Imp



Salicylic acid

Acetylsalicylic Acid [Aspirin] → Painkiller.

⇒ Aspirin possesses analgesic, anti-inflammatory & antipyretic properties.

(b) Rxns involving cleavage of carbon-oxygen [C-O] bond in alcohols

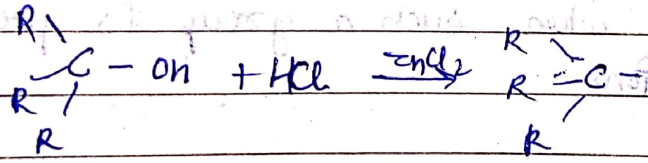
① Rxn with hydrogen halides:

$$R\text{-}OH + HX \longrightarrow R\text{-}X + H_2O$$

⇒ Lucas Test → [HCl + $ZnCl_2$] → Lucas Reagent

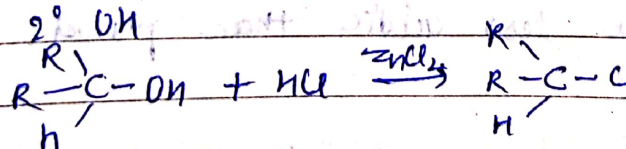
⇒ Reactivity order: 3° > 2° > 1°

3° OH



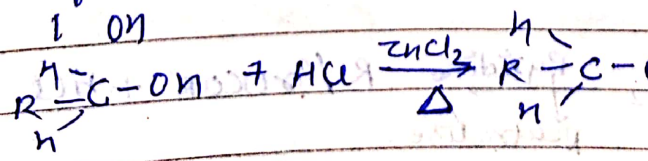
- Turbidity appears immediately.

2° OH



- Turbidity appears in 5 min

1° OH



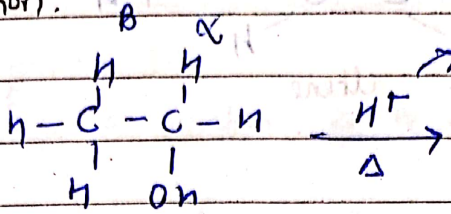
- Turbidity appear on heating only.

OR

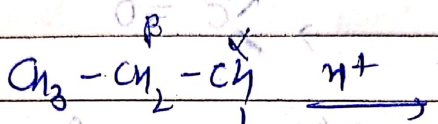
Do not appear.

eg: $C_2H_5-OH + SOCl_2 \longrightarrow C_2H_5-Cl + HCl + SO_2$

2) Dehydration.




$$CH_2=CH_2 + H_2O$$



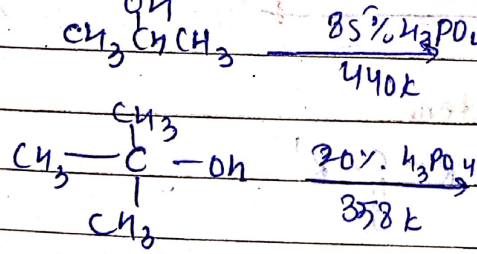

$$CH_3-CH=CH + H_2O$$

$3^\circ > 2^\circ > 1^\circ$ ⇒ Reactivity order

Ethanol undergoes dehydration by heating it with concentrated $H_2SO_4$ at [443 k]

$$C_2H_5OH \xrightarrow[443k]{H_2SO_4} CH_2=CH_2 + H_2O$$

$2^\circ$ & $3^\circ$ alcohols are dehydrate under milder condition.

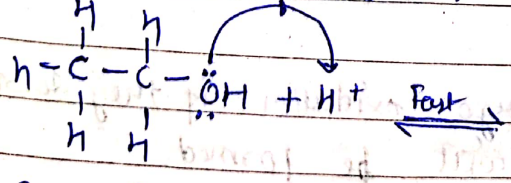



$$CH_3-CH=CH_2 + H_2O$$

$$CH_3-C(=CH_2)-CH_3 + H_2O$$

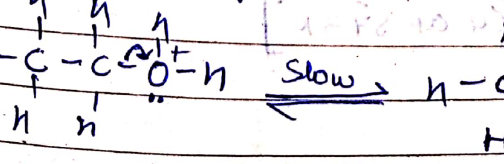
* Mechanism

Step I. Protonation of alcohol.




Protonated alcohol

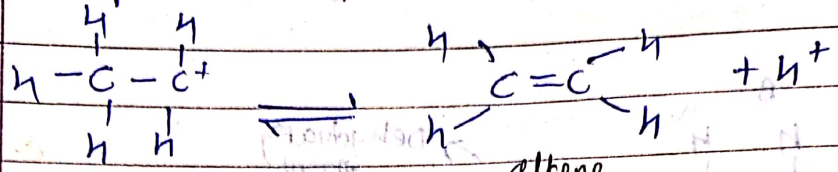
Step II. Formation of carbocation. [Slowest, rate determining step]




$$+ H_2O$$

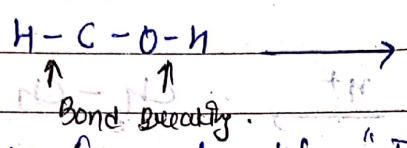
Strong O.A : $KMnO_4$, $K_2Cr_2O_7$ Weak O.A : $CrO_3$, PCC, Cu/573K

Step III. Deprotonation / elimination of proton



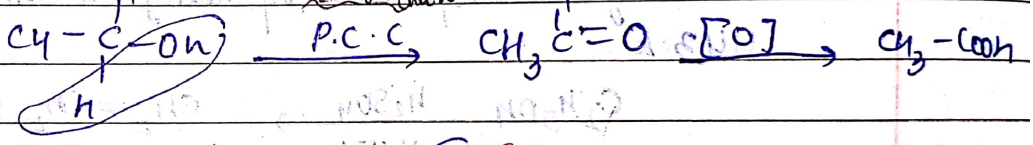
alkene.

3) Oxidation



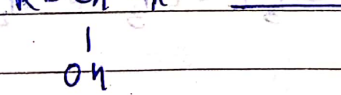

- This rxn is also k/a "Dehydrogenation" because it involves loss of dihydrogen from an alcohol molecule.

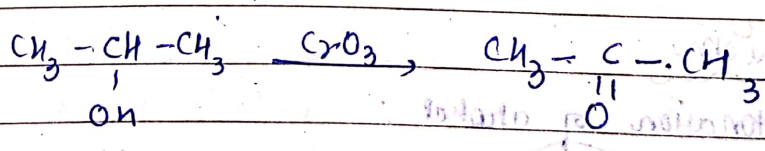
- 1° Alcohol $\xrightarrow{\text{oxidation}}$ Aldehyde $\xrightarrow{\text{oxidation}}$ Carboxylic acid

eg: 


* strong oxidising agent such as (acidified $KMnO_4$) are used for getting (COOH and directly)

- 2° Alcohol $\xrightarrow{\text{oxidation}}$ Ketone

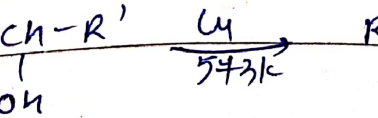


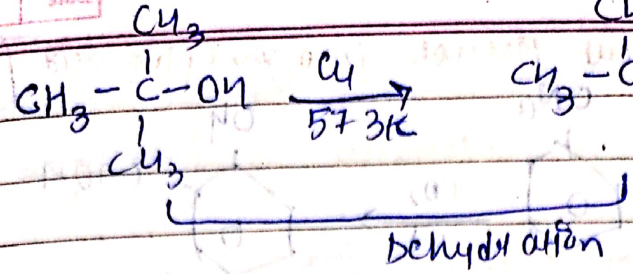
eg: 

- 3° Alcohol do not undergo oxidation if they do so β elimination will happen & alkene will be formed.

* Dehydrogenation [if Cu at 573K]

- $RCH_2OH \xrightarrow[573K]{Cu} RCHO$

- 

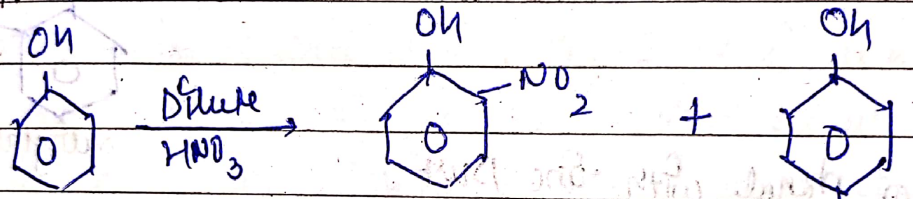


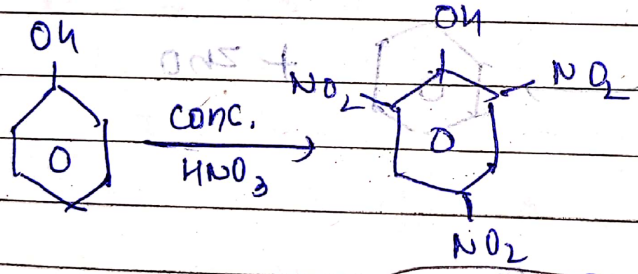

7) Because it is 3° carbon so dehydrogenation will not occur also

c) Rxns. of phenols [ortho & para directing]

1) Electrophilic substitution.

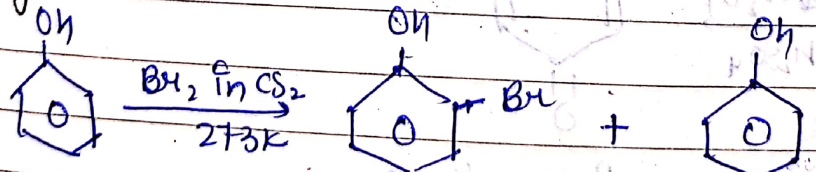
i) Nitration:

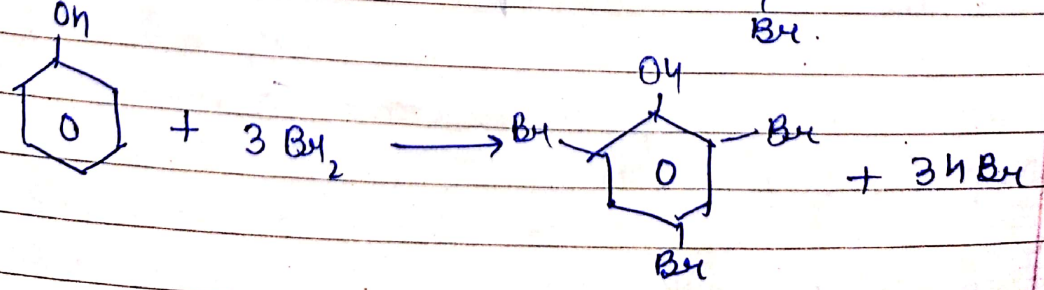



Picric acid.

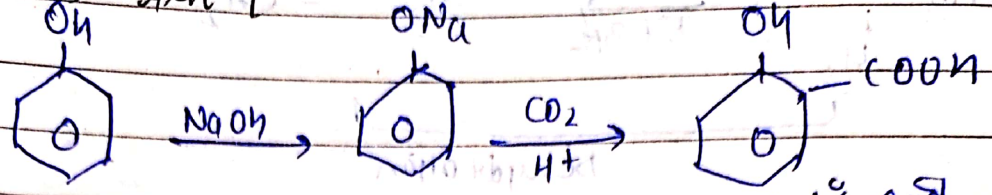
ii) Halogenation:



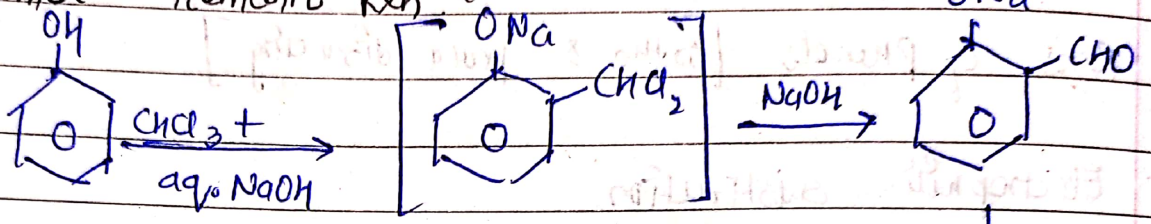

White precipitate.

2) Kolbe's Rxn [Convert Phenol into salicylic acid]



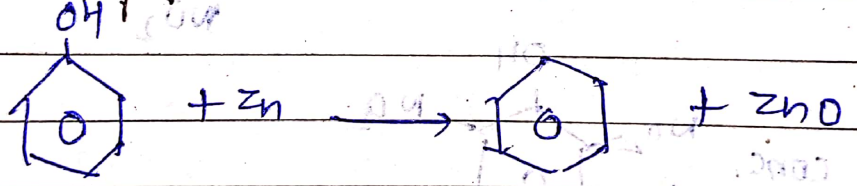

Salicylic acid

3) Reimer - Tiemann Rxn [Convert Phenol into salicylaldehyde]

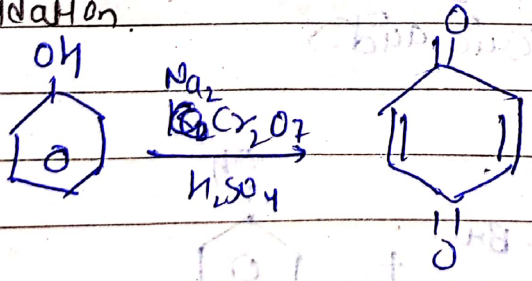



Salicylaldehyde

4) Rxn of phenol with zinc dust




5) Oxidation




Benzoquinone

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* Preparation of Ethers-

1) By dehydration of alcohols

$CH_3CH_2-OH \xrightarrow[443K]{H_2SO_4} CH_2=CH_2$

$CH_3CH_2-OH \xrightarrow[413K]{H_2SO_4} C_2H_5OC_2H_5$ — used as anaesthetic

Diethyl ether.

2) Williamson synthesis. [Follow SN2 mechanism]

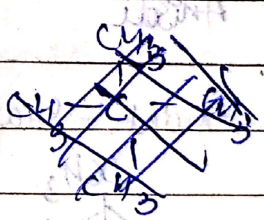
$R-X + RONa \longrightarrow R-O-R + NaX$

⇒ Alkyl halide should be 1°, if 2° or 3° alkyl halide is taken then alkene will be the major product.

⇒ If 2° or 3° alkyl halide is taken then elimination competes over substitution

eg: $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-ONa + CH_3-Br \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-CH_3 + NaBr$

Alkyl halide

If 2° or 3° alkyl halide eg: $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br + CH_3-O-Na \longrightarrow$  $+ NaBr$

$CH_3-C(CH_3)=CH_2$

* Physical Properties.

- First 2 members of the ether family, i.e. diethyl ether & dimethyl ether are solid rest are liquids & some aromatic ethers are solid.
- Ethers have a lower B.P's than their corresponding isomeric alcohol as they do not form H-bond like alcohols. For eg: $C_2H_5OH > CH_3-O-CH_3$

- Ethers are partially soluble in $H_2O$ because of formation of H-bonds with water

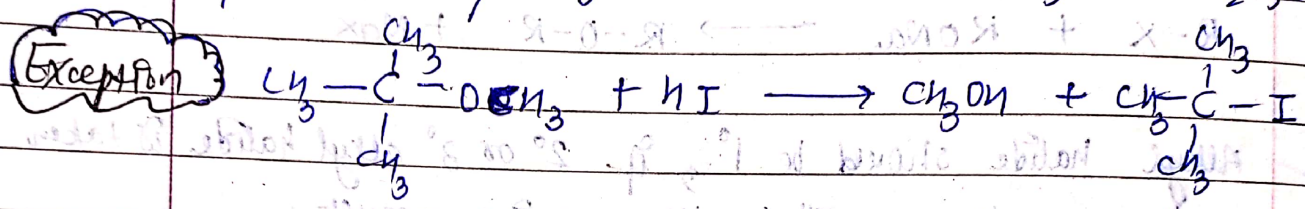
* Chemical Rxns.

(1) Cleavage of C-O bond in ethers.

$$R-O-R + HX \longrightarrow RX + R-OH$$
$$R-OH + HX \longrightarrow R-X + H_2O$$

eg: $C_2H_5-O-C_2H_5 + H-Br \longrightarrow C_2H_5-OH + C_2H_5Br$

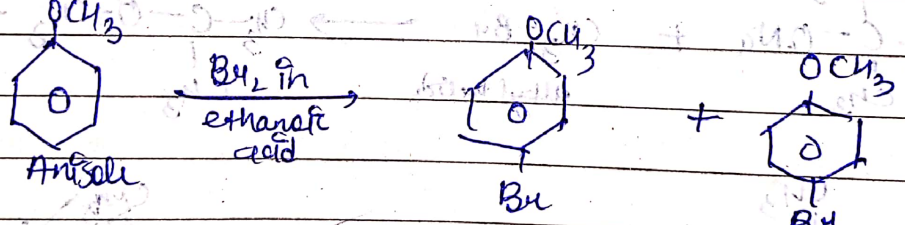
Exception:



Reactivity order of hydrogen halide: $HI > HBr > HCl$

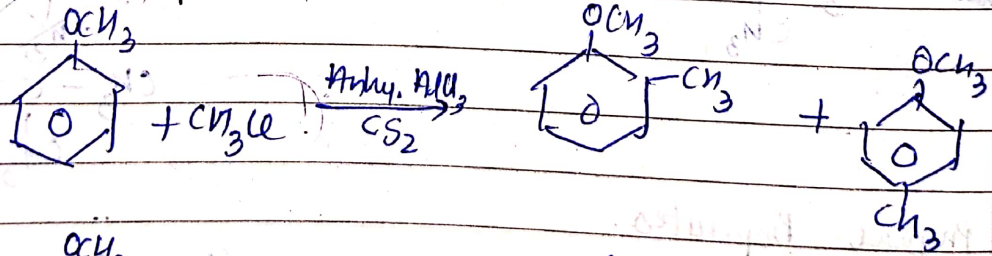
(2) Electrophilic substitution.

(i) Halogenation

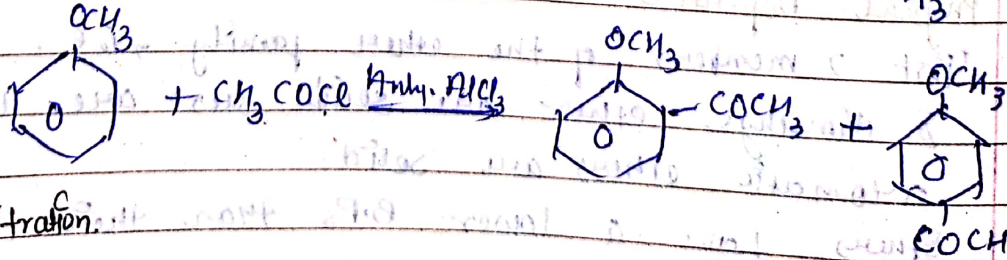



(ii) Friedal - Craft

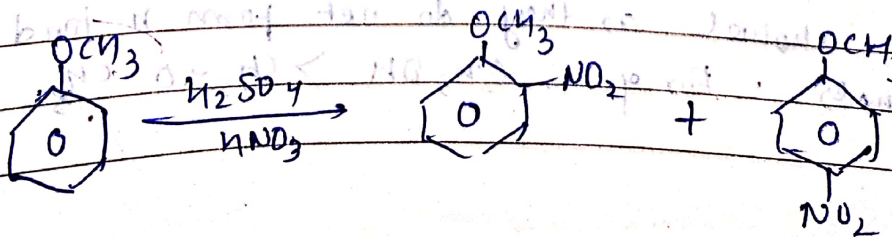
Alkylation




Acetylation




(iii) Nitration.



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* Some commercially important Alcohols.

① Methanol [$CH_3OH$]

- Also called "wood spirit"
- Earlier method: Produced by destructive distillation of wood.
- Modern method: Prepared by catalytic hydrogenation of CO [carbon monoxide] with $H_2$ at high pressure & temp. in presence of $ZnO - Cr_2O_3$ catalyst.

$$CO + 2H_2 \xrightarrow[573K - 673K]{ZnO - Cr_2O_3,\ 200-300\ atm} CH_3OH$$

- Properties
  - Colourless liquid boils at 373K.
  - Highly poisonous — even small quantity can cause blindness, large quantity can cause death.
- Uses:
  - Used as solvents in paints & varnishes
  - Chiefly used for making formaldehyde.

② Ethanol [$C_2H_5OH$]

- Preparation [commercial]
  - Obtained by fermentation of sugars
  - source of sugars: molasses, sugarcane, grapes, fruits.
  - steps:

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{\text{zymase}} 2C_2H_5OH + 2CO_2$$

- Fermentation conditions.
  - Anaerobic [absence of air].
  - Stops when alcohol concentration exceeds 14% because the zymase enzyme is inhibited.

⇒ If air enters, ethanol gets oxidized to acetic acid, spoiling alcoholic drinks.

Note: In wine making, grapes supply both sugars & yeast [present on outer skin]. On crushing, fermentation begins naturally.

• Properties:

⇒ colourless liquid, B.P = 351K.

⇒ Miscible in water.

• Uses:

⇒ Solvent in paint industry & for organic compounds preparation.

⇒ Used in medicines, tinctures, perfumes.

⇒ Alcoholic beverages.

⇒ Fuel [eg → gasohol].

• Denatured Alcohol.

⇒ Pure ethanol is made unfit for drinking by mixing $CuSO_4$ [for colour] & pyridine [for bad smell].

⇒ This process is called denaturation of alcohol.

• Modern preparation:

⇒ Nowadays, ethanol is also prepared industrially by hydration of ethene [$C_2H_4$]

$$C_2H_4 + H_2O \xrightarrow[H_3PO_4]{\text{catalyst}} C_2H_5OH$$