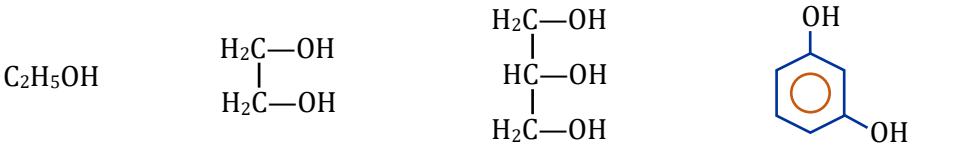
03 Alcohols, Phenols and Ethers

Alcohols and Phenols are formed when a hydrogen atom in a hydrocarbon, aliphatic and aromatic respectively, is replaced by –OH group.

Classification of Alcohols and Phenols :

Alcohols and Phenols may be classified as mono, di, tri or polyhydric depending on whether they contain one, two, three or more hydroxyl groups respectively in their structures.



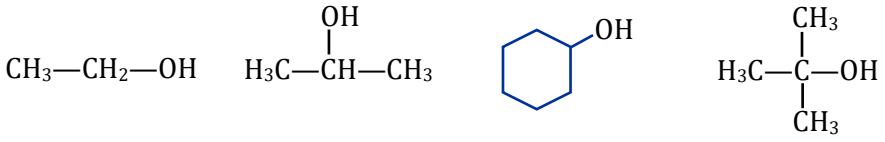
Ethanol (Monohydric) | **Ethane-1,2-diol (Dihydric)** | **Propane-1,2,3-triol (Trihydric)** | **Benzene-1,3-diol (Dihydric)**

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

(A) Compounds containing sp^3 C–OH bond :

(a) Primary, secondary and tertiary alcohols

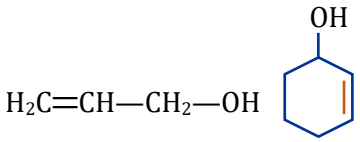
In these three types of alcohols, the –OH group is attached to primary, secondary and tertiary carbon atom, respectively.



Primary (1°) alcohol | **Secondary (2°) alcohol** | **Secondary (2°) alcohol** | **Tertiary (3°) alcohol**

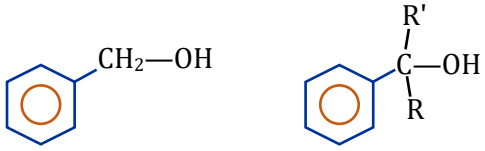
(b) Allylic alcohols

These are the compounds in which the –OH group is bonded to a sp^3 hybridised carbon atom next to carbon-carbon double bond.



(c) Benzylic alcohols

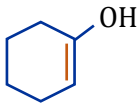
These are the compounds in which the –OH group is bonded to an sp^3 hybridised carbon atom next to an aromatic ring.



(B) Compounds containing sp^2 C–OH bond :

Vinylic alcohols

These are the compounds in which the –OH group is bonded to sp^2 hybridised carbon atom of a carbon-carbon double bond.

$H_2C{=}CH{-}OH$ 

BEGINNER'S BOX-1

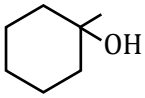
1. Which of the following is an allylic alcohol?

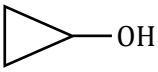
(1) $CH_2{=}CHCH_2OCH_3$ (2) $HOCH{=}CHCH_2CH_3$

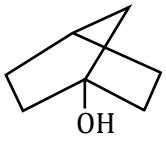
(3) $CH_3CH{=}CHCH_2OH$ (4) $CH_2{=}CHCH_2CH_2OH$

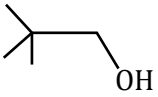
CAE095

2. Identify which of the following compound is 2° alcohol ?

(1) 

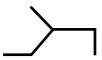
(2) 

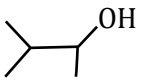
(3) 

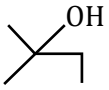
(4) 

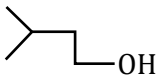
CAE096

3. Identify 1° alcohol having chiral carbon also

(1) 

(2) 

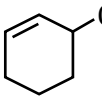
(3) 

(4) 

CAE097

4. True statement for vinylic alcohol is/are

(1) It may be 3° Alcohol (2) No resonance of lone pair of oxygen

(3) It is enol form (4) 

is vinylic alcohol

CAE098

Methods of Preparation of Alcohols :

(1) From alkenes :

(a) By acidic hydration

$$R{-}CH{=}CH_2 + H_2O \xrightarrow{\overset{\oplus}{H}} R{-}\underset{OH}{CH}{-}\underset{H}{CH_2}$$

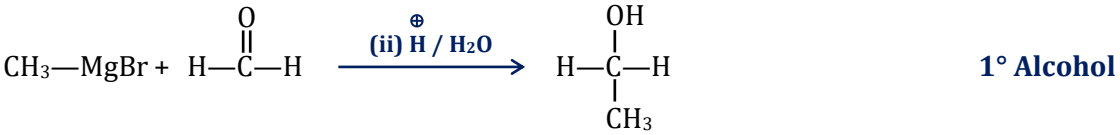
(b) By hydroboration oxidation

$$R{-}CH{=}CH_2 \xrightarrow[(ii)\ H_2O_2/\overset{\ominus}{O}H]{(i)\ BH_3/THF} R{-}\underset{H}{CH}{-}\underset{OH}{CH_2}$$

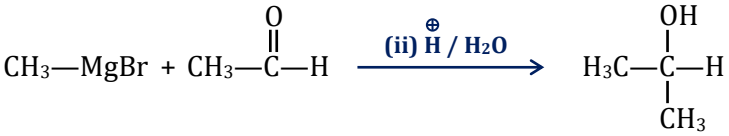
(c) By oxymercuration demercuration

$$R{-}CH{=}CH_2 \xrightarrow[(ii)\ NaBH_4\ /\ \overset{\ominus}{O}H]{(i)\ Hg(OAc)_2,\ H_2O} R{-}\underset{OH}{CH}{-}\underset{H}{CH_2}$$

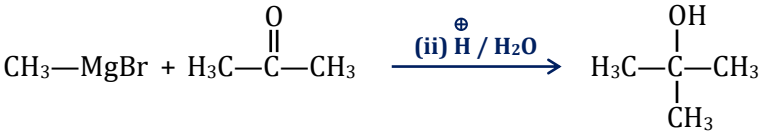
(2) By reaction of Grignard reagent with aldehydes and ketones :



1° Alcohol



2° Alcohol



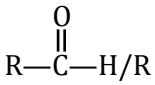
3° Alcohol

(3) By reduction using $LiAlH_4$, $NaBH_4$ and H_2/metal catalyst :

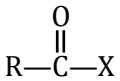
$LiAlH_4$ / Lithium Aluminium Hydride (LAH): It reduces all functional groups containing polar π bonds.

LAH reacts explosively with water and alcohols liberating hydrogen gas. Ether is commonly used as solvent for LAH reductions.

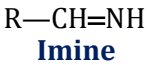
$NaBH_4$ / Sodium Borohydride: It reduces only 4 functional groups



Aldehyde / Ketone



Acid halide

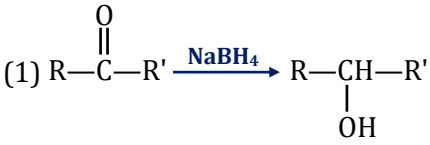


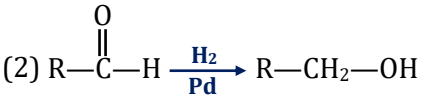
Imine

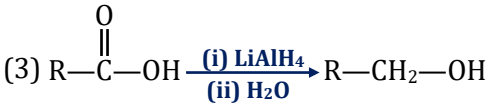
Sodium borohydride can be used in water as well as alcohol solvents

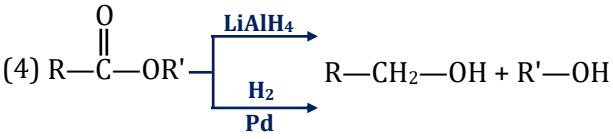
H_2 / metal catalyst

It reduces all polar as well as non-polar π bond containing functional groups.



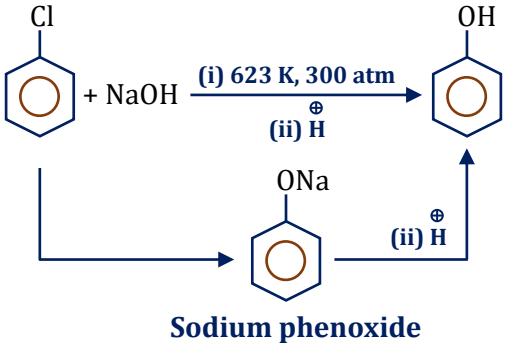






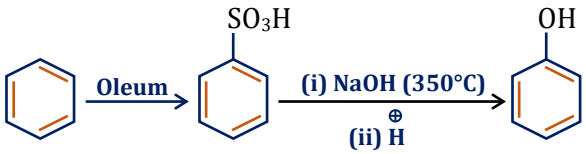
Methods of Preparation of Phenols :

1. From haloarenes :

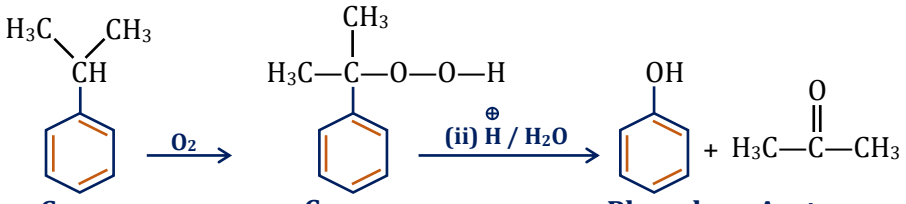


Sodium phenoxide

2. From benzene sulphonic acid :



3. From cumene (Industrial preparation of phenol) :



Cumene (Isopropyl benzene) | **Cumene hydroperoxide** | **Phenol** | **Acetone**

BEGINNER'S BOX-2

1. When acetone reacts with Grignard reagent followed by hydrolysis, it gives :

(1) 1°–alcohol (2) 2°–alcohol (3) 3°–alcohol (4) Methyl alcohol

CAE099

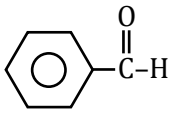
2. For the reduction of aldehydes and ketones into alcohol the reagent which can be used is/are :

(1) H_2 in presence of Ni, Pt or Pd (2) $NaBH_4$

(3) $LiAlH_4$ (4) All of these

CAE100

3. Which of the following compound when reacts with CH_3 Mg Br formation of 3° alcohol take place?

(1) $H-\overset{\overset{O}{\|}}{C}-H$ (2) $CH_3-\overset{\overset{O}{\|}}{C}-H$ (3) $CH_3-\overset{\overset{O}{\|}}{C}-Ph$ (4) 

CAE101

4. Which reaction gives 3° Alcohol ?

(1) $CH_3-CH_2-CHO + CH_3MgBr \xrightarrow{H_2O} ?$

(2) $CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2 + BH_3 \longrightarrow A \xrightarrow[\bar{O}H]{H_2O_2} ?$

(3) $CH_3-\underset{\underset{O}{\|}}{C}-O-CH_3 + 2CH_3MgBr \xrightarrow{H_2O} ?$

(4) $CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_3 + NaBH_4 \xrightarrow{H_2O} ?$

CAE102

5. Reaction between chlorobenzene and NaOH at 300°C followed by acidification gives ?

(1) Phenol (2) Sodium Phenoxide (3) Benzene (4) No reaction

CAE103

Physical Properties :

Boiling point:

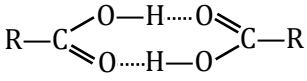
Generally,

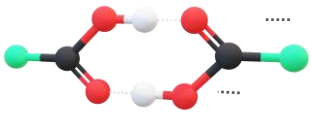
Carboxylic acids > Alcohols > Ketones > Aldehydes > Ether > Alkane

(For similar molecular mass)

	Acetic Acid	Propan-1-ol	Acetone	Propanal	Methoxy ethane	n-Butane
B.P.	391 K	370 K	329 K	322 K	281 K	273 K
Molecular Mass	60	60	58	58	60	58

Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses. This is due to more extensive association of carboxylic acids molecules through intermolecular hydrogen bonding. The H bonds are not broken completely even in vapour phase. In fact most carboxylic acids exist as a dimer in vapour phase or in aprotic solvent.





Boiling point of alcohols

Boiling Point $\propto$ Intermolecular forces of attraction

$\propto$ Molecular weight

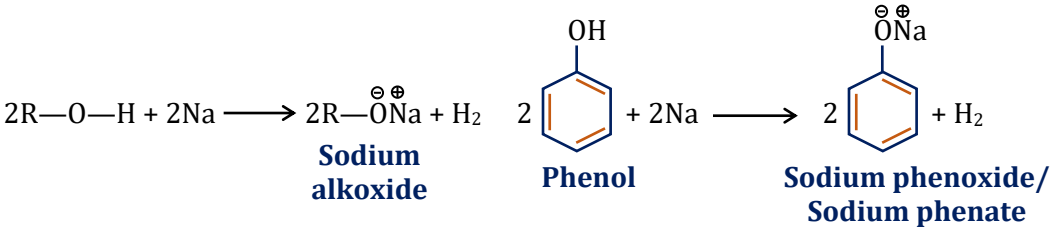
$\propto \frac{1}{\text{Branching}}$ (If molecular weight is same)

Chemical Reactions of Alcohols :

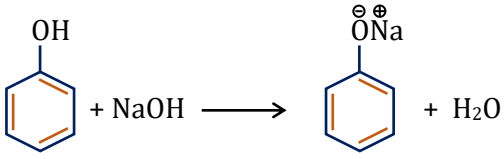
Reactions involving cleavage of O–H bond :

(1) Reaction with metals

Alcohols and phenols react with active metals such as sodium, potassium and aluminium to yield corresponding alkoxides/phenoxides and hydrogen.

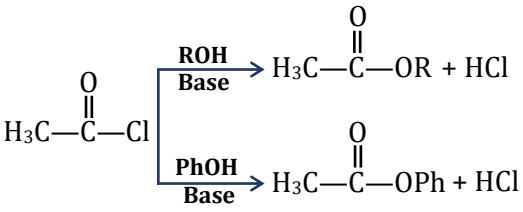


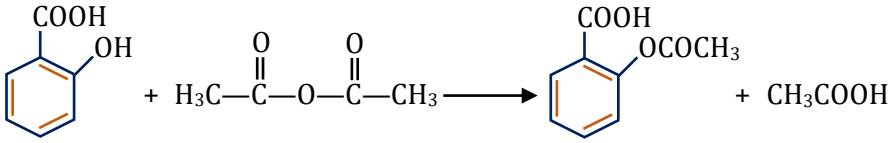
Phenols also react with aqueous sodium hydroxide to form sodium phenoxides.



(2) Esterification reaction

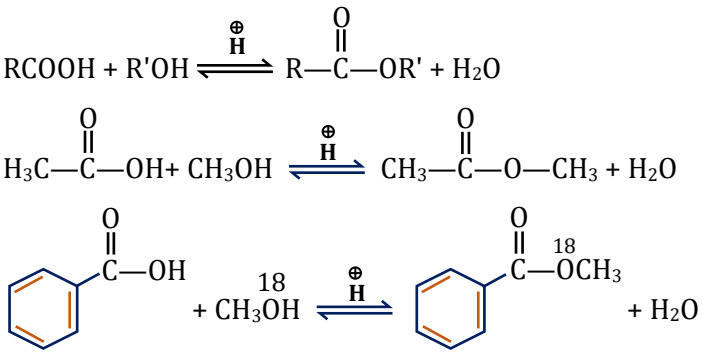
Alcohols and phenols react with acid chlorides, acid anhydrides and carboxylic acids to form esters.





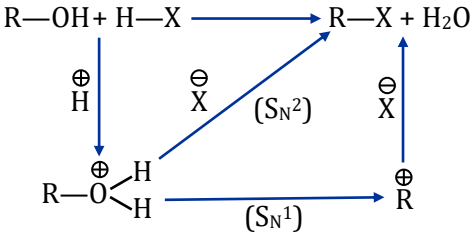
2-Hydroxybenzoic acid (Salicylic acid) **Acetylsalicylic acid (Aspirin)**

Carboxylic acids react with alcohols or phenols in the presence of an acid (conc.H_2SO_4 or dry HCl) to form esters. This method is called Fischer esterification.



Reactions involving cleavage of C–O bond :

(1) Reaction with conc. H–X

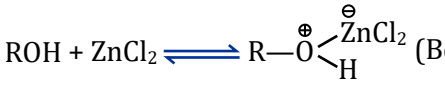


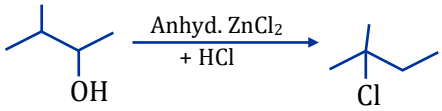
Note: Generally, CH_3OH and 1° alcohol $-S_N2$
2°, 3°, allylic, benzylic alcohol $-S_N1$

Important Points

1. Rate of reaction: H-I > H-Br > H-Cl > H-F
2. The reactivity order of alcohols towards H–X $\propto$ Stability of carbocation

Note: Reaction of ROH with conc. HCl takes place directly only if the alcohol is highly reactive.
The function of $ZnCl_2$ is similar to that of H^+


(Better leaving group than H_2O)



Lucas Test

It is a test mainly used to distinguish between primary, secondary and tertiary alcohols.

$$\underset{(1°,2°,3°)}{R—OH + HCl} \xrightarrow[+ HCl]{\text{Anhyd. } ZnCl_2} \underset{\text{(turbidity)}}{RCl}$$

3° alcohol – Immediate turbidity

2° alcohol – 5 minutes

1° alcohol – No turbidity at room temperature

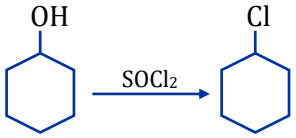
On heating – 30 minutes

Note: If 3° or more stable than 3° carbocation is formed then immediately turbidity is observed.

(2) Reaction with $SOCl_2$

$$R—OH + \underset{\text{(thionyl chloride)}}{SOCl_2} \longrightarrow R—Cl + SO_2 + HCl$$

One of the best methods for preparation of alkyl chloride as side product are gases.



(3) Reaction with PX_3

$$3R—OH + PX_3 \longrightarrow 3R—X + H_3PO_3$$

Reagents: PCl_3 / PBr_3 / Red P + Br_2 / Red P + I_2

(4) Reaction with PCl_5

$$R—OH + PCl_5 \longrightarrow R—Cl + POCl_3 + HCl$$

(5) Acidic dehydration of Alcohol

Acidic dehydration of alcohol is an example of elimination(E1) reaction

Reagents used:

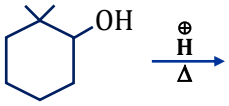
(1) Conc. H_2SO_4/Δ (2) Conc. H_3PO_4/Δ (3) $KHSO_4/\Delta$ (4) H^+/Δ

$$H_3C—CH_2—OH \xrightarrow[170°C]{\text{Conc. } H_2SO_4} H_2C=CH_2 + H_2O$$

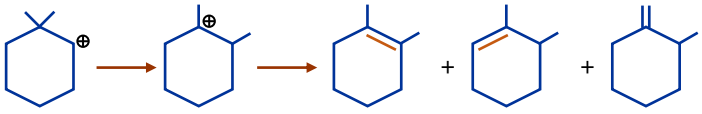
Note: Dehydration of alcohols is favoured at high temperature.

1. Dehydration of alcohols is an acid catalysed reaction.
2. Carbocation intermediate is formed. So rearrangement is possible.
3. Rate of dehydration $\propto$ Stability of carbocation

Illustration 1

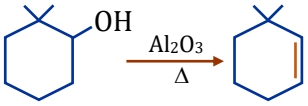


Solution:

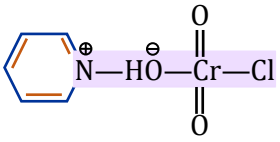
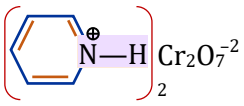


(Major)

Note: Al_2O_3 and P_2O_5 can also be used as dehydrating agents but no carbocation is formed.



Oxidation Reaction of Alcohols :

	Strong oxidising agents		Mild oxidising agents
(1)	$KMnO_4/\overset{\oplus}{H}$	(1)	Cu/300° C
(2)	$K_2Cr_2O_7/\overset{\oplus}{H}$	(2)	CrO_3/acetone or anhydrous CrO_3
(3)	H_2CrO_4 ($CrO_3 + H_2O$)	(3)	PCC (CrO_3/Pyridine/HCl + CH_2Cl_2)  (Pyridinium chlorochromate)
(4)	CrO_3 + aq. H_2SO_4 + acetone (Jone's regent)	(4)	Collin's reagent (CrO_3/pyridine + CH_2Cl_2)
		(5)	PDC (Pyridinium dichromate) 
	Function 1° alcohol – Carboxylic Acid 2° alcohol – Ketone 3° alcohol – No reaction		Function 1° alcohol – Aldehyde 2° alcohol – Ketone 3° alcohol – No reaction (except Cu/300°C)

	PCC	PDC	Cu/300°C	$KMnO_4/\overset{\oplus}{H}$	$K_2Cr_2O_7/\overset{\oplus}{H}$
$H_3C—CH_2–OH$	$H_3C—\overset{\overset{O}{\|\|}}{C}—H$	$H_3C—\overset{\overset{O}{\|\|}}{C}—H$	$H_3C—\overset{\overset{O}{\|\|}}{C}—H$	$H_3C—\overset{\overset{O}{\|\|}}{C}—OH$	$H_3C—\overset{\overset{O}{\|\|}}{C}—OH$
$H_3C—\underset{\underset{CH_3}{\|}}{CH}—OH$	$H_3C—\overset{\overset{O}{\|\|}}{C}—CH_3$	$H_3C—\overset{\overset{O}{\|\|}}{C}—CH_3$	$H_3C—\overset{\overset{O}{\|\|}}{C}—CH_3$	$H_3C—\overset{\overset{O}{\|\|}}{C}—CH_3$	$H_3C—\overset{\overset{O}{\|\|}}{C}—CH_3$
$H_3C—\underset{\underset{CH_3}{\|}}{\overset{\overset{CH_3}{\|}}{C}}—OH$	X	X	$H_2C=\underset{\underset{CH_3}{\|}}{C}—CH_3$	X	X

BEGINNER'S BOX-3

1. Which of the following reactions of alkanols does not involve C–O bond breaking

(1) $CH_3CH_2OH + SOCl_2$ (2) $CH_3CH(OH)CH_3 + PBr_3$

(3) $CH_3CH_2OH + CH_3COOH$ (4) $ROH + HX$

CAE104

2. Which of the following alkanols is most soluble in water

(1) 1–Butanol (2) 2–Butanol (3) Isobutyl alcohol (4) t–Butyl alcohol

CAE105

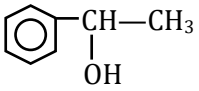
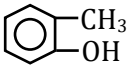
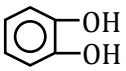
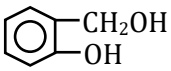
3. $CH_3CH_2CH_2–OH \xrightarrow{PCl_3} A \xrightarrow{Alc.KOH} B \xrightarrow{H_3O^{\oplus}} C$

Find product 'C' is

(1) $CH_3CH=CH_2$ (2) $CH_3—\underset{\underset{OH}{|}}{CH}—CH_3$ (3) $CH_3—\underset{\underset{Cl}{|}}{CH}—CH_3$ (4) $CH_3CH_2CH_2–Cl$

CAE106

4. Which of the following compounds does not show phenolic properties :-

(1)  (2)  (3)  (4) 

CAE107

5. The number of dihydric phenols possible with the molecular formula $C_6H_6O_2$ is :-

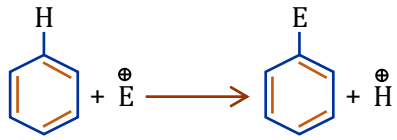
(1) 2 (2) 3 (3) 4 (4) 5

CAE108

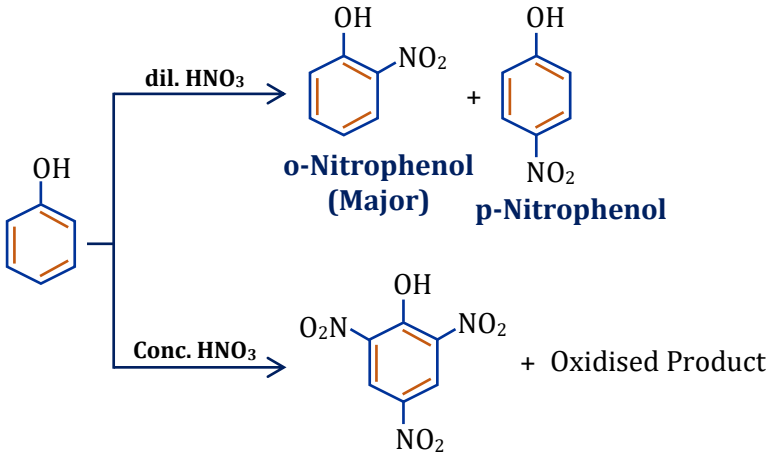
Chemical Reactions of Phenols :

1. Electrophilic Substitution Reaction (ESR) :

ESR is characteristic reaction of benzene and its derivatives.

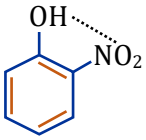


(a) Nitration of Phenol

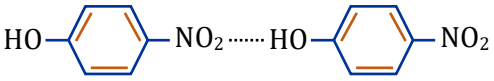


2,4,6-Trinitrophenol
(Picric acid)

Note: o-Nitrophenol and p-nitrophenol can be separated using steam distillation as o-nitrophenol is more volatile than p-nitrophenol due to intramolecular H-bonding.



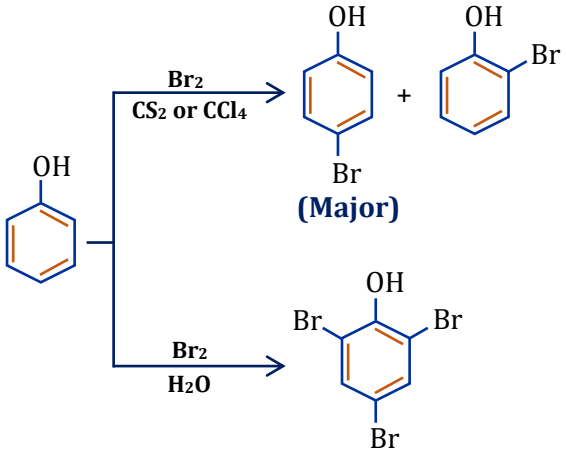
Intramolecular H-Bond



Intermolecular H-Bond

(b) Halogenation of Phenol

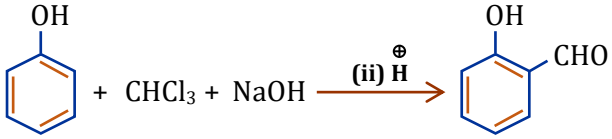
On treating phenol with bromine different reaction products are formed under different experimental conditions.



2,4,6-Tribromophenol
(White ppt.)

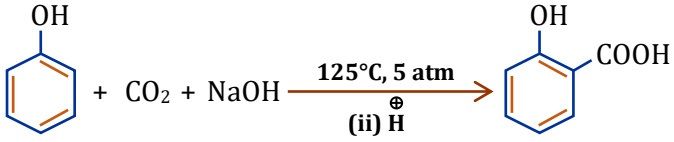
(c) Reimer-Tieman Reaction

On treating phenol with chloroform in the presence of a base (Ex. NaOH etc.) a –CHO group is introduced at ortho position in benzene ring.



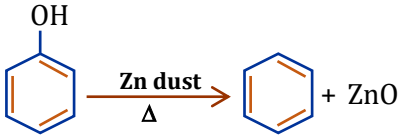
2-Hydroxybenzaldehyde
(Salicylaldehyde)
(Major)

(d) Kolbe's reaction / Kolbe schmidt reaction



2-Hydroxybenzoic acid
(Salicylic acid)
(Major)

2. Reaction of Phenol with zinc dust :



3. Oxidation reaction of Phenol :

p-Benzoquinone

Neutral $FeCl_3$ test

Aqueous solution of phenol reacts with neutral $FeCl_3$ to form a violet coloured complex. This reaction is used as a test of phenolic group.

$$6C_6H_5OH + FeCl_3 \longrightarrow [Fe(OC_6H_5)_6]^{-3} + 3HCl + 3\overset{\oplus}{H}$$

(violet)

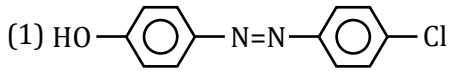
BEGINNER'S BOX-4

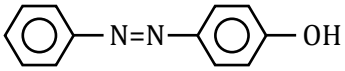
1. Reimer–Tieman formylation reaction involves addition of :-

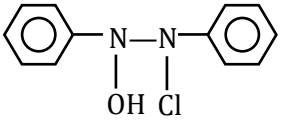
(1) Chloroform on phenoxide ion
(2) Trichloromethyl carbanion on phenoxide ion
(3) Dichlorocarbene on phenoxide ion
(4) Hydroxide ion on phenol

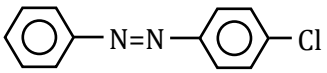
CAE109

2. Phenol reacts with benzenediazonium chloride solution to form a compound of the structure :-

(1) 

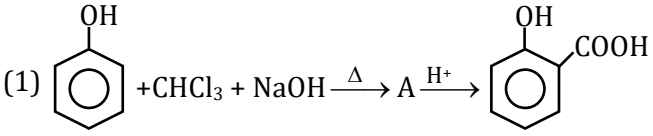
(2) 

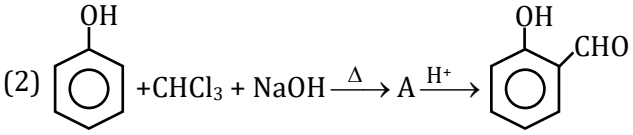
(3) 

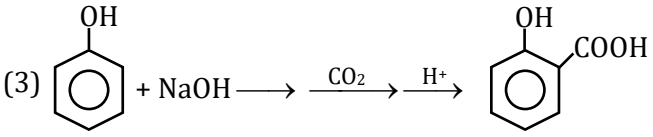
(4) 

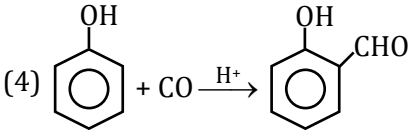
CAE110

3. Which is Kolbe-Schmitt reaction ?

(1) 

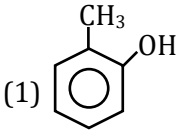
(2) 

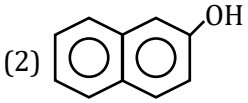
(3) 

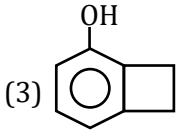
(4) 

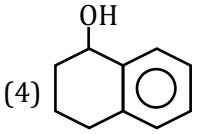
CAE111

4. Which does not give violet colour with neutral $FeCl_3$?

(1) 

(2) 

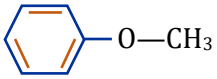
(3) 

(4) 

CAE112

Ethers :

Ethers

Symmetrical/Simple	Unsymmetrical/Mixed
R—O—R	R—O—R' (R≠R')
$CH_3—O—CH_3$	$CH_3—O—CH_2—CH_3$
$CH_3—CH_2—O—CH_2—CH_3$	

Method of Preparation of Ethers :

(1) Williamson continuous etherification process (S_N2) :

$$H_3C—CH_2—OH + \text{conc. } H_2SO_4 \xrightarrow{140°C} C_2H_5—O—C_2H_5$$

Diethyl ether

This method is suitable for the preparation of symmetrical ethers having primary alkyl group only.

$$H_3C—CH_2—OH + \text{conc. } H_2SO_4 \xrightarrow{140°C} C_2H_5—O—C_2H_5$$

Diethyl ether

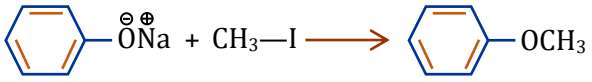
$$\xrightarrow{170°C} H_2C=CH_2$$

Ethene

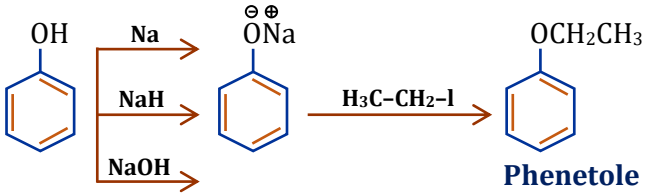
(2) Williamson synthesis :

$$R—\overset{\ominus\oplus}{O}Na + R'—X \longrightarrow R—O—R' + NaX$$

Sodium alkoxide **Must be 1° (or methyl)**



Sodium phenoxide **Anisole (methoxybenzene)**



Phenetole (ethoxybenzene)

BEGINNER'S BOX-5

1. The Williamson synthesis involves :-

(1) A nucleophilic addition
(2) An electrophilic substitution
(3) S_N2 displacement
(4) S_N1 displacement

CAE113

2. In the Williamson synthesis of ethers given by the general equation –

$R—X + R'O^{\ominus}Na^{\oplus} \longrightarrow R—O—R'$ the yield from

R—X follows the sequence :-

(1) $CH_3X > 1° > 2° > 3°$
(2) $CH_3X < 1° < 2° < 3°$
(3) $CH_3X < 1° < 2° > 3°$
(4) $CH_3X > 1° < 2° < 3°$

CAE114

3. Which of the following ether can not be prepared by Williamson's method ?

(1) Di tert butyl ether (2) Ethyl methyl ether

(3) Anisole (4) All

CAE115

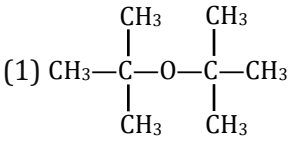
4. $CH_3–CH_2–OH + Ph–CH_2–OH \xrightarrow[140°C]{H^{\oplus}}$ Which product is not obtained?

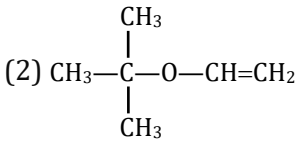
(1) $CH_3–CH_2–OCH_2–CH_3$ (2) $Ph–CH_2–OCH_2–Ph$

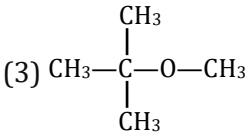
(3) $Ph–CH_2–O–CH_2–CH_3$ (4) $Ph–CH_2–O–CH_2–O–CH_3$

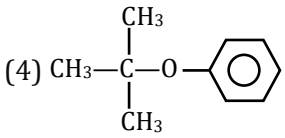
CAE116

5. Which can be obtained by Williamson ether synthesis in good yield ?

(1) 

(2) 

(3) 

(4) 

CAE117

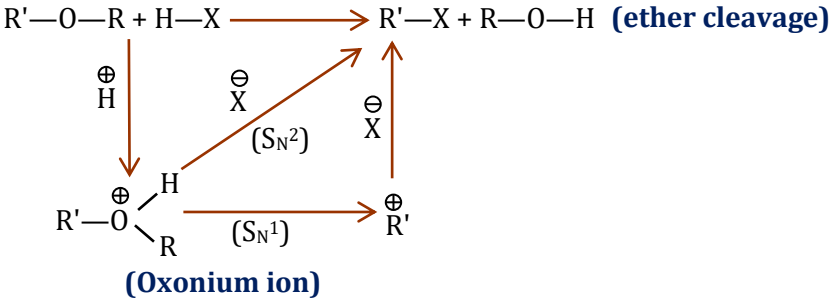
6. Which of the following is a simple ether/symmetrical ether ?

(1) CH_3OCH_3 (2) $C_2H_5OCH_3$ (3) $C_6H_5OCH_3$ (4) $C_6H_5OC_2H_5$

CAE118

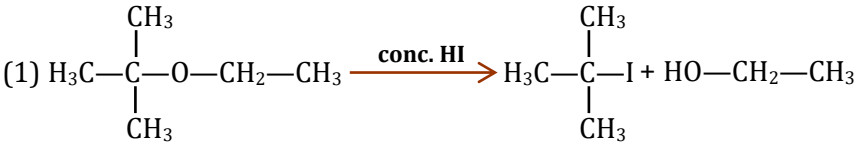
Chemical Reaction of Ethers :

(1) Reaction of ether with conc. H-X (Ziesel's method) :

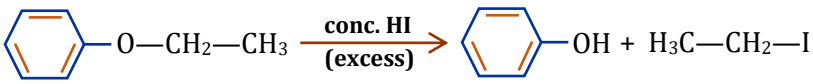


(Oxonium ion)

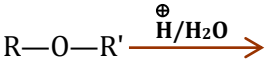
If any one of R or R' forms 3° or more stable carbocation then reaction follows S_N1 mechanism.

(1) 

(2) 

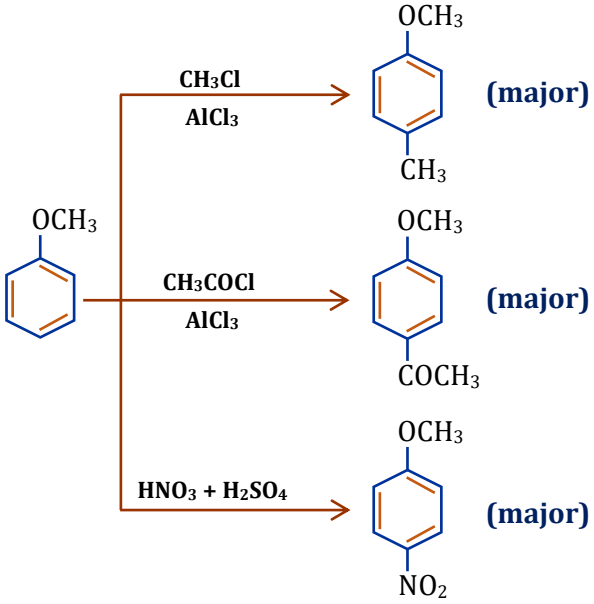
(3) 

(2) Reaction of ether with H^+/H_2O (Acidic hydrolysis) :



(Always S_N1)

(3) Electrophilic substitution reaction :



BEGINNER'S BOX-6

1. With conc. HBr, ethyl phenyl ether yields :

(1) Phenol and ethyl bromide
(2) Bromobenzene and ethanol
(3) Phenol and ethane
(4) Bromobenzene and ethane

CAE119

2. In the given reaction

$C_6H_5—O—CH_2—CH_3 \xrightarrow{\text{Excess HI}/\Delta}$ [X] + [Y]

[X] and [Y] will respectively be :

(1) C_6H_5I and CH_3CH_2I
(2) C_6H_5OH and $CH_3–CH_2–I$
(3) C_6H_5I and CH_3CH_2OH
(4) C_6H_5OH and $CH_2=CH_2$

CAE120

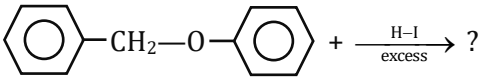
3. In the given reaction

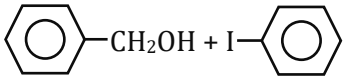
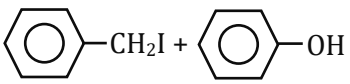
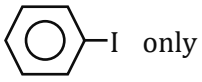
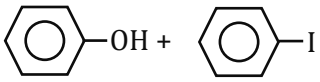
$CH_3—CH_2—CH_2—O—CH_2—CH_3 \xrightarrow{HI}$ [X] & [Y]

[X] and [Y] will respectively be :

(1) $CH_3CH_2CH_2OH$ and CH_3CH_2I
(2) $CH_3CH_2CH_2I$ and CH_3CH_2OH
(3) $CH_3CH_2CH_2I$ and $CH_2=CH_2$
(4) $CH_3–CH=CH_2$ and $CH_2=CH_2$

CAE121

4.  ?

(1) 
(2) 
(3)  only
(4) 

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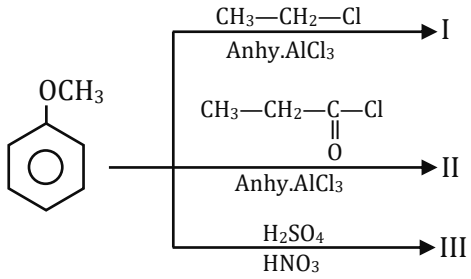
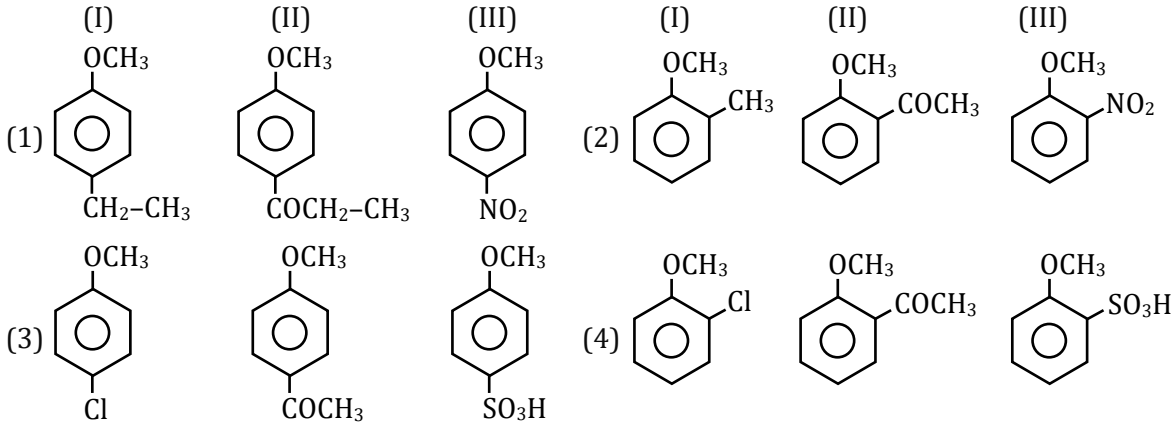
5. Identify the major product formed in the given reaction and choose the correct option from the codes given below :-





CAE123

BEGINNER'S BOX — ANSWER KEY

BEGINNER'S BOX-1	**Que.**	1	2	3	4			
	Ans.	**3**	**2**	**1**	**3**			
BEGINNER'S BOX-2	**Que.**	1	2	3	4	5		
	Ans.	**3**	**4**	**3**	**3**	**1**		
BEGINNER'S BOX-3	**Que.**	1	2	3	4	5		
	Ans.	**3**	**4**	**2**	**1**	**2**		
BEGINNER'S BOX-4	**Que.**	1	2	3	4			
	Ans.	**3**	**2**	**3**	**4**			
BEGINNER'S BOX-5	**Que.**	1	2	3	4	5	6	
	Ans.	**3**	**1**	**1**	**4**	**3**	**1**	
BEGINNER'S BOX-6	**Que.**	1	2	3	4	5		
	Ans.	**1**	**2**	**1**	**2**	**1**		