Alcohol, Phenol & Ether

Alcohols

Alcohols are hydroxy derivatives of alkanes or alkyl derivatives of water with a general formula R–OH.

Types of Alcohols

Alcohols are of following types:

Monohydric alcohols:

These are alcohols with only one –OH group. Their general formula is C_nH_{2n+1} OH.

They are further divided in following types:

Primary alcohol (1°) RCH_2OH, for example, CH_3OH methyl alcohol (Methanol).

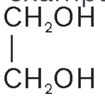
Secondary alcohol (2°) R_2CHOH, for example, $(CH_3)_2CHOH$ isopropyl alcohol (Propan-2-ol).

Tertiary alcohol (3°) R_3COH, for example, $(CH_3)_3COH$–tertiary butyl alcohol (2-Methyl-propan-2-ol).

Dihydric alcohols:

Alcohols that have two –OH groups.

For example, glycol, Propan 1, 2 diol

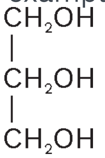


$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array}$$

Trihydric alcohols:

Alcohols that having three –OH groups.

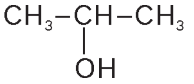
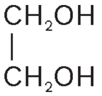
For example, glycerol



$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \\ | \\ CH_2OH \end{array}$$

Nomenclature of Alcohols

Alcohols are named as alkanol as below.

$CH_3–CH_2–CH_2OH$	Propanol
 $$\begin{array}{l} CH_3–CH–CH_3 \\ \quad\quad\;\; | \\ \quad\quad\; OH \end{array}$$	Propan-2-ol
$(CH_3)_3COH$	2-Methyl-propan-2-ol
 $$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array}$$	Ethan-1, 2-diol

Concept Ladder

All alcohols mainly can be divided into two broad categories, (i) aliphatic alcohols; (ii) aromatic alcohols.

Rack your Brain

What are alcohols and how are they classifie?

Previous Year's Questions

Which of the following compounds can be used as antifreeze in automobile radiators?

[AIPMT-2012]

(1) Methyl alcohol
(2) Glycol
(3) Nitrophenol
(4) Ethyl alcohol

Isomerism Shown by Alcohols

Alcohol may show chain, position and functional isomerism.

For example,

1. Butan-1-ol and 2-Methylpropan-1-ol are chain isomers.

2. Propan-1-ol and Popan-2-ol are position isomers.

3. Benzyl alcohol and Anisole are functional isomers.

Rack your Brain

Draw the isomeric structure of all isomeric alcohol of molecular formula $C_5H_{12}O$.

General Methods of Preparation

Alcohols are mainly prepared by following methods:

From alkanes (R–H): (Only by tertiary alkanes)

$$R_3C-H \xrightarrow{KMnO_4/OH^-} R_3C-OH$$

$$\underset{\substack{\text{2–methyl}\\\text{propane}}}{(CH_3)_3C-H} \xrightarrow{KMnO_4/OH^-} \underset{\substack{\text{Tertiary butyl alcohol}\\\text{(2–methylpropan–2–ol)}}}{(CH_3)_3C-OH}$$

- Here pink colour of $KMnO_4$ disappears as the reaction proceeds forward.

From haloalkanes (R–X):

Alkyl halides on hydrolysis by aqueous alkali like NaOH, KOH or moist Ag_2O, give alcohols by substitution reaction as follows:

$$R-X+AgOH(aq)\text{ or }KOH(aq) \longrightarrow R-OH+AgX\text{ or }KX$$

$$CH_3Br+AgOH(aq)\text{ or }KOH(aq) \longrightarrow CH_3OH+AgBr\text{ or }KBr$$

- This method is suitable only for the production of primary alcohols as secondary alkyl halides give a mixture of alcohol and alkene. Tertiary alkyl halides give only alkenes.

For example,

$$\underset{\substack{\text{Iso–proylbromide}\\\text{(2°–halide)}}}{(CH_3)_2CHBr} \xrightarrow{KOH\ (aq)} \underset{\text{Isopropylalcohol}}{(CH_3)_2\,CHOH} + \underset{\text{Propene}}{CH_3-CH=CH_2} + KBr + H_2O$$

Previous Year's Questions

How many isomers of $C_5H_{11}OH$ will be primary alcohols?

[AIPMT]

(1) 5 (2) 4

(3) 2 (4) 3

From ether (R–O–R):

Ethers, on hydrolysis by dilute acids, produce alcohols.

$$R-O-R+H.OH\xrightarrow{dil.H_2SO_4,\Delta}2R-OH$$

For example,

$$\underset{\text{Dimethyl ether}}{CH_3-O-CH_3}+H.OH\xrightarrow{dil.H_2SO_4,\Delta}\underset{\text{Methanol}}{2CH_3-OH}$$

- If alkyl groups are different, two types of alcohols will be formed. For example,

$$\underset{\text{Ethylproyl ether}}{C_2H_5-O-C_3H_7}+H_2O\xrightarrow{dil.H_2SO_4,\Delta}\underset{\text{Ethanol}}{C_2H_5-OH}+\underset{\text{Propyl alcohol}}{C_3H_7OH}$$

Concept Ladder

Addition of grignard reagent followed by hydrolysis with dil. HCl gives, following compounds;

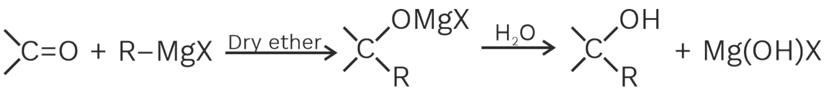
(i) HCHO → 1° alcohols

(ii) Aldehydes (except HCHO) → 2° alcohols

(iii) Ketone & Esters → 3° alcohols

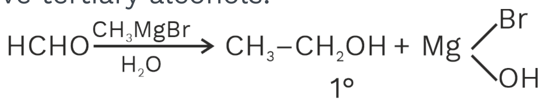
From grignard reagent:

Preparation of primary, secondary and tertiary alcohols using Grignard reagent is the ideal method Grignard reagent reacts with carbonyl compounds to form an intermediate compound, which on hydrolysis, gives alcohol.

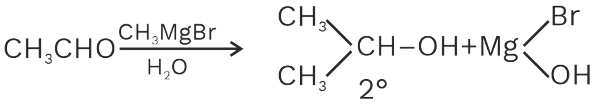


$$>C=O+R-MgX\xrightarrow{\text{Dry ether}}>C<^{OMgX}_{R}\xrightarrow{H_2O}>C<^{OH}_{R}+Mg(OH)X$$

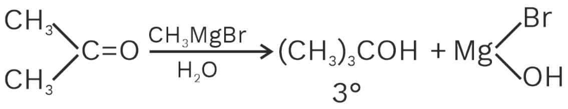
- Formaldehyde when reacted with Grignard reagent gives primary alcohol while the other aldehydes give secondary alcohols. Ketones give tertiary alcohols.



$$HCHO\xrightarrow[H_2O]{CH_3MgBr}\underset{1^\circ}{CH_3-CH_2OH}+Mg<^{Br}_{OH}$$



$$CH_3CHO\xrightarrow[H_2O]{CH_3MgBr}\underset{2^\circ}{(CH_3)_2CH-OH}+Mg<^{Br}_{OH}$$



$$(CH_3)_2C=O\xrightarrow[H_2O]{CH_3MgBr}\underset{3^\circ}{(CH_3)_3COH}+Mg<^{Br}_{OH}$$

Previous Year's Questions

Ethylene oxide when treated with Grignard reagent yields

[AIPMT]

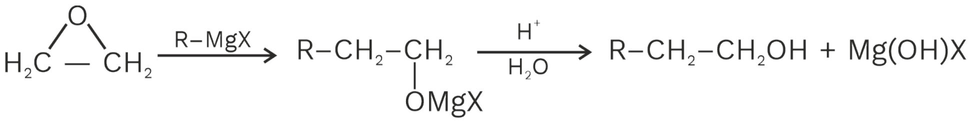
(1) primary alcohols

(2) secondary alcohols

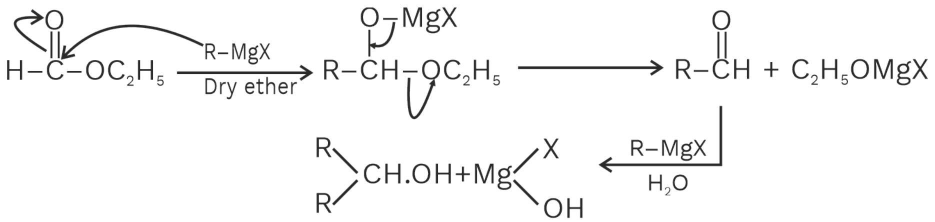
(3) tertiary alcohols

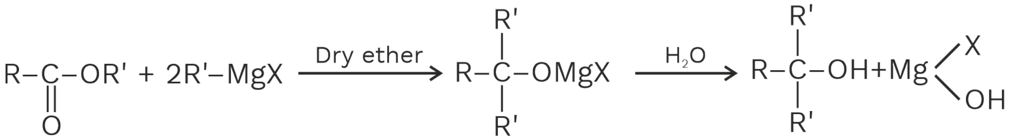
(4) cyclopropyl alcohol

Grignard reagent also reacts with oxirane (Epoxy ethane) to give alcohol as follows:



Grignard reagent on reaction with Ethyl formate gives 2°-alcohols and with other esters give 3°-alcohols as follows.





By the reduction of carbonyl compound (R–CHO and R–CO–R):

Carbonyl compounds on reduction by reducing agents like $LiAlH_4$, $NaBH_4$, Zn/HCl or H_2/Ni, produce alcohols.

- Aldehydes on reduction, give primary alcohols as shown:

$$R-CHO + H_2 \xrightarrow[\text{or LiAlH}_4]{\text{Ni}} \underset{\text{Primary alcohol}}{R-CH_2OH}$$

For example,

$$\underset{\text{Ethanal}}{CH_3CHO} + H_2 \xrightarrow[\text{or Na/C}_2\text{H}_5\text{OH}]{\text{Ni}} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

- Ketones on reduction, give secondary alcohols.

$$R-CO-R' + H_2 \xrightarrow[\text{or LiAlH}_4]{\text{Ni}} R_2CHOH$$

For example,

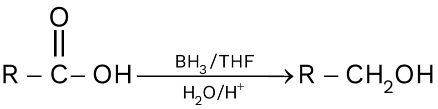
$$\underset{\text{Propan-2-one}}{CH_3-CO-CH_3} + H_2 \xrightarrow[\text{or LiAlH}_4]{\text{Ni}} \underset{\text{Propan-2-ol}}{(CH_3)_2CHOH}$$

Concept Ladder

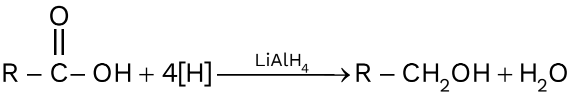
The reduction of carbonyl compound by addition of H_2 in presence of catalyst such as finely divided platinum, palladium, nickel or ruthenium.

By the reduction of acids and acid derivatives (R–COOH, R–COX, R–COOR):

These undergo reduction into alcohols with the help of reducing agents like $LiAlH_4$ B_2H_6/T.H.F or $NaBH_4$ as follows:



$$R-\overset{\overset{\large O}{||}}{C}-OH\xrightarrow[H_2O/H^+]{BH_3/THF}R-CH_2OH$$

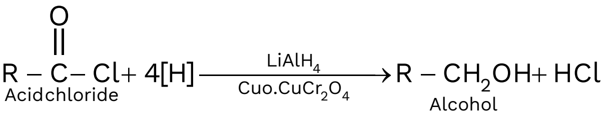


$$R-\overset{\overset{\large O}{||}}{C}-OH+4[H]\xrightarrow{LiAlH_4}R-CH_2OH+H_2O$$

Here, R may be H, CH_3, C_2H_5 etc.

For example

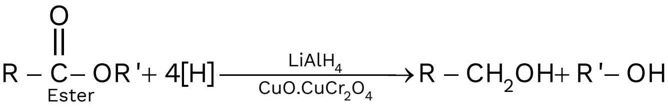
$$\underset{\text{Ethanol}}{CH_3COOH+4[H]\xrightarrow{LiAlH_4}CH_3CH_2OH+H_3O}$$



$$\underset{\text{Acidchloride}}{R-\overset{\overset{\large O}{||}}{C}-Cl}+4[H]\xrightarrow[Cuo.CuCr_2O_4]{LiAlH_4}\underset{\text{Alcohol}}{R-CH_2OH}+HCl$$

For example,

$$\underset{\text{Acetyl chloride}}{CH_3COCl}+4[H]\xrightarrow{LiAlH_4}CH_3CH_2OH+HCl$$



$$\underset{\text{Ester}}{R-\overset{\overset{\large O}{||}}{C}-OR'}+4[H]\xrightarrow[CuO.CuCr_2O_4]{LiAlH_4}R-CH_2OH+R'-OH$$

For example,

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5}+4[H]\xrightarrow{LiAlH_4}2C_2H_5OH$$

In case a $\rangle C=O$ group is also present along with –COOH or –COOR groups and we use $NaBH_4$ then reduction occurs at $\rangle C=O$ group mainly.

Concept Ladder

The reduction of aldehydes, ketones and esters with sodium and alcohol is commonly known as Bouveault-Blanc reduction.

Rack your Brain

Why diborane does not easily reduce functional groups such as ester, nitro, halo etc but reduce the carboxylic acids?

Previous Year's Questions

What is formed when a primary alcohol undergoes catalytic dehydrogenation?

[AIPMT]

(1) Aldehyde (2) Ketone

(3) Alkene (4) Acid

From primary amines:

Primary amines react with nitrous acid ($NaNO_2$ + HCl) to give alcohols

$$R{-}CH_2NH_2 + HNO_2 \longrightarrow R{-}CH_2OH + N_2 + H_2O$$

Example,

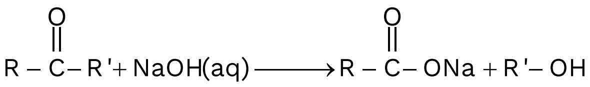
(I) $CH_3NH_2 + HNO_2 \longrightarrow CH_3OH + N_2 + H_2O$

(II) $(CH_3)_2\ CHNH_2 + HNO_2 \longrightarrow (CH_3)_2CHOH + N_2 + H_2O$

It is not a good method for 1°-alcohols as alkenes and R–X are also formed here with R–OH.

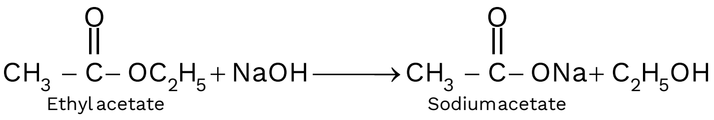
By hydrolysis of esters:

Esters on hydrolysis by dilute acid or alkali, gives alcohol as follows:

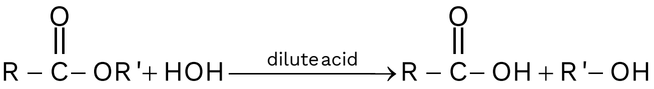


$$R-\overset{\overset{\large O}{||}}{C}-R' + NaOH(aq) \longrightarrow R-\overset{\overset{\large O}{||}}{C}-ONa + R'-OH$$

Example,

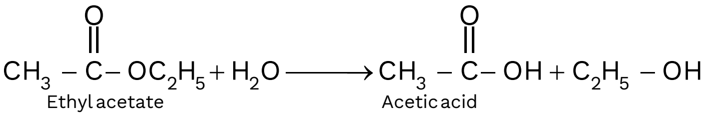


$$\underset{\text{Ethyl acetate}}{CH_3-\overset{\overset{\large O}{||}}{C}-OC_2H_5} + NaOH \longrightarrow \underset{\text{Sodium acetate}}{CH_3-\overset{\overset{\large O}{||}}{C}-ONa} + C_2H_5OH$$



$$R-\overset{\overset{\large O}{||}}{C}-OR' + HOH \xrightarrow{\text{dilute acid}} R-\overset{\overset{\large O}{||}}{C}-OH + R'-OH$$

Example,



$$\underset{\text{Ethyl acetate}}{CH_3-\overset{\overset{\large O}{||}}{C}-OC_2H_5} + H_2O \longrightarrow \underset{\text{Acetic acid}}{CH_3-\overset{\overset{\large O}{||}}{C}-OH} + C_2H_5-OH$$

Industrial preparation:

Alkenes undergo hydrolysis to form alcohols by following Markovnikov's addition.

Concept Ladder

When two or more hydroxyl groups are attached to the same carbon atom, the compound is usually unstable. The compound loses a water molecule and is converted into a stable compound.

Rack your Brain

Why amide do not add Grignard reagents to form ketones?

Previous Year's Questions

In the following sequence of reactions

$CH_3Br \xrightarrow{KCN} A \xrightarrow{H_3O^+} B \xrightarrow[\text{ether}]{LiAlH_4} C$

the end product (C) is

[AIPMT-2012]

(1) acetone (2) methane

(3) acetaldehdye (4) ethyl alcohol

Indirect hydrolysis:

Here alkenes are hydrolyzed by dilute acid like H_2SO_4 into alcohols as follows:

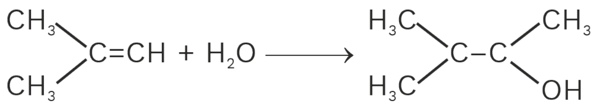
$$\underset{\text{Propene}}{CH_3-CH=CH_2} + H_2SO_4 \longrightarrow CH_3-CH_2-CH_2\,H.SO_4 \xrightarrow{H.OH} \underset{\text{Propanol}}{CH_3-CH_2-CH_2OH} + H_2SO_4$$

Direct hydrolysis:

It occurs according to Markovnikov's rule and here rearrangement occurs in case of less stable carbocation.

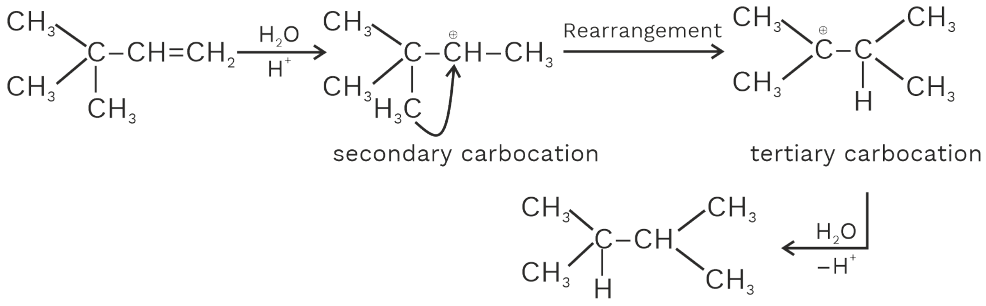
Example,

$$R-CH=CH_2 + H.OH \xrightarrow{dil.H_2SO_4} R-CHOH-CH_3$$



Isobutene

t-Butyl alcohol



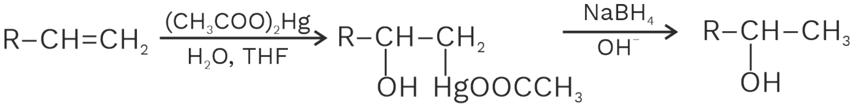
2, 3-Dimethylbutan-2-ol

Rack your Brain

What is the final product when carboxylic acid and esters are reduced by BH_3?

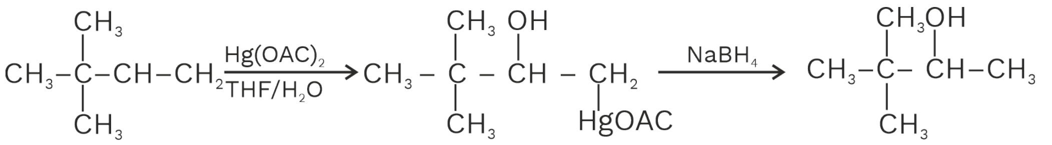
Oximercuration and demercuration of alkenes:

Alkenes undergo oximercuration by mercuric acetate in presence of tetrahydrofuran (THF) and water followed by reduction by $NaBH_4$ (demercuration) to give alcohols according to Markovnikov's rule. Here no rearrangement is made if C^+ is less stable.



$$R-CH=CH_2 \xrightarrow[H_2O,\ THF]{(CH_3COO)_2Hg} R-\underset{OH}{\underset{|}{CH}}-\underset{HgOOCCH_3}{\underset{|}{CH_2}} \xrightarrow[OH^-]{NaBH_4} R-\underset{OH}{\underset{|}{CH}}-CH_3$$

R may be H, CH_3, C_2H_5 etc.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH-CH_2 \xrightarrow[THF/H_2O]{Hg(OAC)_2} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{OH}{CH}-\underset{HgOAC}{CH_2} \xrightarrow{NaBH_4} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{OH}{CH}-CH_3$$

3, 3 Dimethyl butan-2-ol

Oxo process:

Here aldehyde is formed when an alkene in presence of cobalt carbonyl, is treated with CO and H, which on reduction with Ni or Zn-Cu gives alcohol. It is called carbonylation hydroformylation.

Example,

$$R-HC=CH_2 + CO + H_2 \xrightarrow[\substack{\text{High temperature} \\ \text{High pressure}}]{[Co(CO)_4]_2} R-CH_2-CH_2-CHO \xrightarrow{H_2/Ni} R-CH_2-CH_2-CH_2-OH$$

Some specifc preparations

Methyl Alcohol (CH_3OH)

$$CH_4 + O_2 \xrightarrow[\Delta,200\,atm\,300°C]{Cu-tube} CH_3OH$$

$$\underbrace{CO + H_2}_{\text{Water gas}} + H_2 \xrightarrow[\Delta]{\text{oxides of Cu,Zn}} CH_3OH$$

- The fractional distillation of pyroligneous acid (obtained by distillation of wood) gives CH_3OH.
- Pyroligneous acid has 0.1%–0.5% CH_3COCH_3 (56°C), 1%–3% CH_3OH (64°C), 6%–10% CH_3COOH.
- Acetic acid can be removed in the form of calcium acetate precipitate when pyroligneous acid is treated with calcium hydroxide. The liquor having acetone and methyl alcohol on fractional distillation gives methyl alcohol as acetone is removed first as it is more volatile than methylalcohol.

Previous Year's Questions

Methanol is industrially prepared by

[AIPMT]

(1) oxidation of CH_4 by steam at 900°C
(2) reduction of HCHO using $LiAlH_4$
(3) reduction HCHO with a solution of NaOH
(4) reduction of CO using H_2 and $ZnO-Cr_2O_3$

Synthesis using sugar:

The formation of ethanol is processed by fermentation of sugars present in molasses. The molasses with an initial sugar content of around 20 % is diluted to nearly 10 to 20 % of its original volume by adding H2O. Small amount of conc. H2SO4 and yeast is then added. The solution is fermented for 2 to 3 days and 298 K to produce ethanol as shown below:

$$\underset{\text{Sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{in yeast}]{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow[\text{in yeast}]{\text{Zymase}} 2C_2H_5OH + 2CO_2 \uparrow$$

Concept Ladder

Alcoholic beverges are prepared from different starting materials like molasses, barley, grape and other fruit juices by alcoholic fermentation.

Synthiesis using starch:

Starchy substances are treated with steam and malt (a source of diastase) to prepare ethyl alcohol as shown below:

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\text{diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}} \xrightarrow[\text{Maltase}]{H_2O\text{ yeast}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow[\text{in yeast}]{\text{Zymase}} 2C_2H_5OH + 2CO_2 \uparrow$$

Physical Properties of Alcohol

- Lower alcohols (ethanol, methanol) are sweet smelling liquids and colourless.
- Higher alcohols are odourless, colourless, waxy solids.
- Due to formation of intermolecular H-bonding with H2O 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.
  For example, $C_2H_5OH > CH_3OCH_3$ or C_2H_5X

Previous Year's Questions

Ethanol and dimethyl ether form a pair of functional isomers. The boiling point of ethanol is higher than that of dimethyl ether, due to the presence of

[AIPMT]

(1) H-bonding in ethanol
(2) H-bonding in dimethyl ether
(3) CH_3 group in ethanol
(4) CH_3 group in dimethyl ether

Chemical Properties of Alcohols

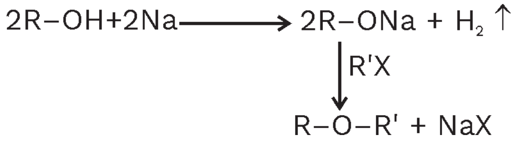
Alcohols give the following type of reactions:

Reactions with cleavage of O–H bond:

The acidic nature of alcohols is exhibited by these reactions. They do not give H^+ in aq. solution as they are less acidic than water.

Reaction with metals:

Alcohols reacts with alkali metals like Na and K for the formation of metal alkoxides which further react with haloalkanes to form ethers.



$$\begin{tikzcd} 2R{-}OH{+}2Na \arrow[r] & 2R{-}ONa + H_2\uparrow \arrow[d, "R'X"] \\ & R{-}O{-}R' + NaX \end{tikzcd}$$

Example,

$$2CH_3-OH+2Na \longrightarrow \underset{\text{Sodiummethoxide}}{2CH_3-ONa}+H_2\uparrow$$

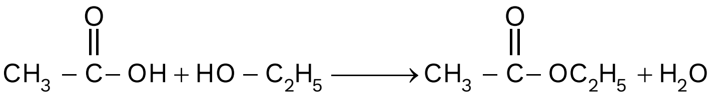
$$CH_3ONa+C_2H_5Cl \longrightarrow \underset{\text{Methylethylether}}{CH_3-O-C_2H_5}+NaCl$$

Ester formation:

Esters are formed when alcohols reacts with acids and acid derivatives as follows:

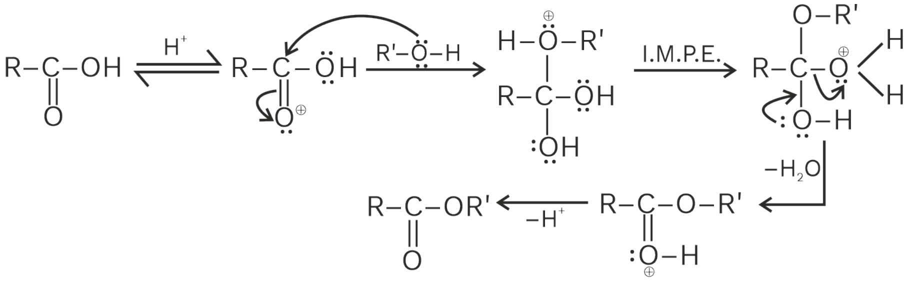
$$R'-OH+R-COOH \xrightarrow{\text{dil.acid}} R-COOR'+H_2O$$

Example,



$$CH_3-\overset{\overset{O}{\|}}{C}-OH+HO-C_2H_5 \longrightarrow \underset{\text{Ethylacetate}}{CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5}+H_2O$$

Mechanism:



Concept Ladder

Boiling point ∝ Molecular weight or surface area.

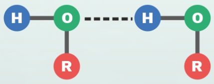
$CH_3CH_2CH_2CH_2OH >$
$(CH_3)_2CHOH > (CH_3)_3COH >$
$CH_3\ CH_2\ CH_2OH$

Rack your Brain

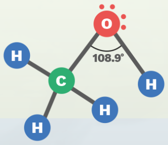
C—O bond is weaker in the case of tertiary alcohols. Why?

ALCOHOLS

BOILING POINT



Existence of Intermolecular Hydrogen bonding results in higher boiling point than hydrocarbons .



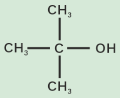
Oxygen acts as nucleophile due to the presence of lone pairs

SOLUBILITY

Alcohols are soluble in water due to the presence of Hydrogen Bonds

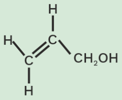
NOMENCLATURE

- Name the longest carbon chain that contains the carbon atom bearing the -OH group . Drop the final -e from the alkane name, and add the suffix -ol.
- Number the longest carbon chain starting at the end nearest the -OH group , and use the appropriate number, if necessary, to indicate the position of the -OH group.
- Name the substituents, and give their numbers as for an alkane or alkane.



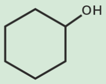
IUPAC Name
2- Methyl-2 Propanol

Common Name
t- Butyl alcohol



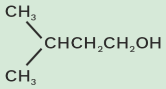
IUPAC Name
2- propen -1-ol

Common Name
Allyl alcohol



IUPAC Name
Cyclohexanol

Common Name
Cyclohexanol alcohal

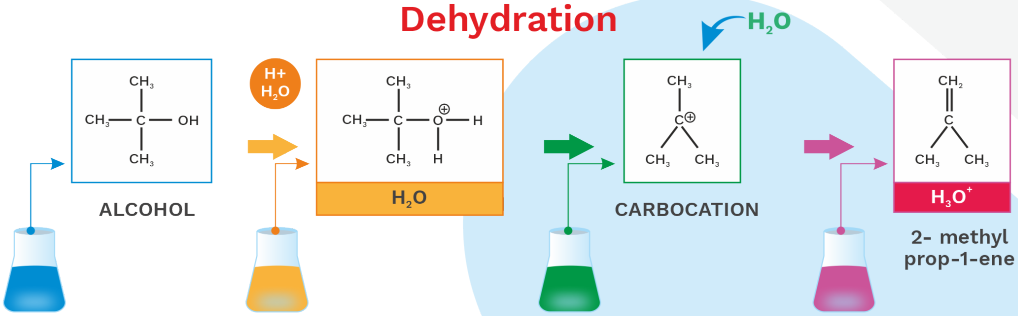


IUPAC Name
3- Methyl-1-butanol

Common Name
Isoamyl alcohol

CHEMICAL REACTIVITY

Dehydration



Formation of carbocation is RDS here . So always try to make a stable carbocation by rearrangement .

Here –OH is removed from R–COOH and 'H' is removed from R–OH. In it R–OH acts as a nucleophile.

Reactivity order:

(1) $HCOOH > CH_3COOH > C_2H_5COOH$

(2) $CH_3OH > C_2H_5OH > C_3H_7OH >$

Reaction with Grignard reagent:

Alkanes are formed on reacting alcohols with Grignard reagent.

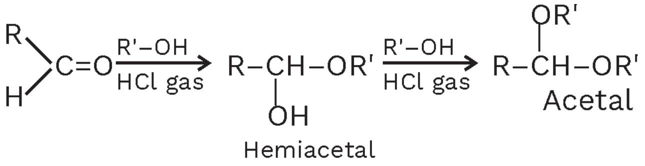
$$R - OH + R'MgX \longrightarrow R'H + R - OMgX$$

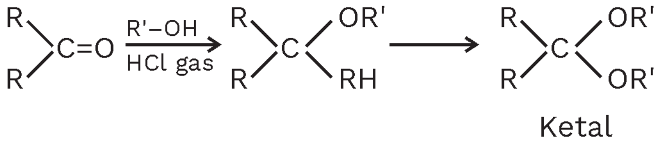
For example,

$$C_2H_5 - OH + CH_3MgBr \longrightarrow CH_4 + C_2H_5 - OMgBr$$

Reaction with Carbonyl Compounds:

An alcohol reacts with a carbonyl compound for formation of Ketal or acetal as follows:





Reaction Due to–OH Group (Cleavage of C–OH type)

Reaction With HX:

Here, alkyl halide is formed when alcohol reacts with HX. (S_N1 Reaction Mainly)

$$R - OH + HX \xrightarrow{Anhy.ZnCl_2} R - X + H_2O$$

$$C_2H_5OH + HBr \xrightarrow{Anhy.ZnCl_2} C_2H_5Br + H_2O$$

Concept Ladder

In O—H cleavage, the order of reactivity is, Primary > Secondary > Tertiary and in C—O cleavage, the order of reactivity is, Tertiary > Secondary > Primary.

Rack your Brain

Explain that Methanol is more acidic in nature then Tert. alcohol?

Previous Year's Questions

HBr reacts fastest with **[AIPMT]**

(1) 2-Methylpropan-1-ol
(2) Methylpropan-2-ol
(3) propan-2-ol
(4) propan-1-ol

- For this case the reactivity order of alcohols is tertiary > secondary > primary.
- For this case the reactivity order of HX is HI > HBr > HCl > HF

Reaction with PX_5, PX_3, $SOCl_2$:

$$R-OH + PX_5 \xrightarrow{\Delta} \underset{\text{Major}}{R-X} + POX_3 + HX$$

For example,

$$C_2H_5-OH + PCl_5 \xrightarrow{\Delta} C_2H_5Cl + POCl_3 + HCl$$

$$3R-OH + PX_3 \xrightarrow{\Delta} 3R-X + H_3PO_3$$

For example,

$$3C_2H_5-OH + PCl_3 \xrightarrow{\Delta} 3C_2H_5Cl + H_3PO_3$$

$$R-OH + SOCl_2 \xrightarrow{\text{Pyridine}} R-Cl + SO_2 + HCl$$

$$C_2H_5-OH + SOCl_2 \xrightarrow{\text{Pyridine}} C_2H_5Cl + SO_2 + HCl$$

- Here pyridine refluxes the gaseous byproducts HCl and SO_2. This method is known as **Dorzen's method**.
- An alcohol cannot give such reactions with Cl_2 or S_2Cl_2.

Reaction with NH_3:

When an alcohol reacts with NH4 over heated alumina, a primary amine is obtained along with 2° and 3° amines.

$$R-OH + NH_3 \xrightarrow[350^\circ C]{\Delta Al_2O_3} R-NH_2 + H_2O$$

$$R-NH_2 \xrightarrow[-H_2O]{R-OH} \underset{2^\circ}{R_2NH} \xrightarrow[-H_2O]{R-OH} \underset{3^\circ}{R_3N}$$

Example,

$$C_2H_5OH + NH_3 \xrightarrow[350^\circ C]{\Delta Al_2O_3} C_2H_5NH_2 + H_2O$$

Concept Ladder

Anhydrous $ZnCl_2$ is the catalyst as well as the dehydrating agent and it also prevents the accurance of its reverse reaction.

Rack your Brain

Explain that most substituted alcohol usually react more rapidly with HX?

Previous Year's Questions

Ethyl alcohol is industrially prepared form ethylene by **[AIPMT]**

(1) Permanganate oxidation
(2) Catalytic reduction
(3) Absorbing in H_2SO_4 followed by hydrolysis
(4) Fermentation

Reaction of R–OH:

Complete alcohol molecule is involved in these reaction.

Dehydration:

Alcohols can be dehydrated into ethers or alkenes depending upon the temperature, amount of alcohol and nature of the dehydrating agent used.

Some common dehydrating agents are conc. H_3PO_4, conc. H_2SO_4, Al_2O_3 etc.

(1) Ether is formed for excess of alcohols, H_2SO_4 is the dehydrating agent and the temperature is 140°C.

$$R-OH + H_2SO_4 \xrightarrow{100°-110°C} RHSO_4 + H_2O$$

$$RSHO_4 + R-OH \xrightarrow{140°C} R-O-R + H_2SO_4$$

For example,

$$C_2H_5-OH + H_2SO_4 \xrightarrow{100°-110°C} \underset{\text{Ethyl hydrogensulphate}}{C_2H_5HSO_4} + H_2O$$

$$C_2H_5HSO_4 + C_2H_5-OH \xrightarrow{140°C} \underset{\text{Diethyether}}{C_2H_5-O-C_2H_5} + H_2SO_4$$

(2) An alkene is formed for excessive H_2SO_4 at 170°C.

$$C_2H_5-OH + H_2SO_4 \xrightarrow{100°-110°C} \underset{\text{Ethyl hydrogen sulphate}}{C_2H_5HSO_4} + H_2O$$

$$C_2H_5HSO_4 \xrightarrow{170°C} \underset{\text{Ethene}}{C_2H_4} + H_2SO_4$$

$$CH_3-OH + H_2SO_4 \xrightarrow{100°-110°C} \underset{\text{Methyl hydrogen sulphate}}{CH_3HSO_4} + H_2O$$

- Here β-carbon atom having less no. of H atom removes β-hydrogen atom, to give a more stable alkene as a major product, in accordance with Saytzeff rule.

Concept Ladder

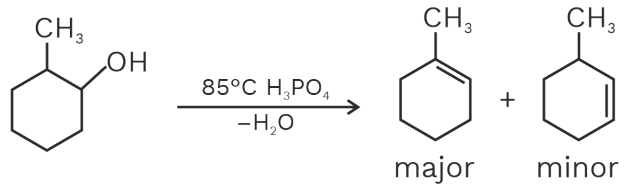
$POCl_3$/Pyridine, Al_2O_3/Δ, P_2O_5/Δ etc., are also used for the dehydration of alcohol without any rearrangement, Saytzeff alkenes are obtained as major product from these reagents.

Rack your Brain

Write the correct sequence of rate of dehydration for 1°, 2° and 3° alcohols?

Example,

$$CH_3{-}CH_2{-}CHOH{-}CH_3 \xrightarrow{\text{conc. } H_2SO_4} \underset{\text{But-2-ene}}{CH_3{-}CH{=}CH{-}CH_3}$$



(3) When on heated alumina (Al_2O_3), vapours of alcohol are passed over, following changes occur:

At 250°C ether is formed

$$R-OH+R-OH \xrightarrow[250°C]{Al_2O_3} R-O-R+H_2O$$

Example,

$$2C_2H_5OH \xrightarrow[250°C]{Al_2O_3} C_2H_5-O-C_2H_5+H_2O$$

- Three different types of ethers are formed When both the alcohols are different.

Rack your Brain

What is the product form when 3° alcohol react in the presence of Cu and 300°C?

Example,

$$CH_3OH+C_2H_5OH \xrightarrow[250°C]{Al_2O_3} CH_3-O-CH_3+C_2H_5-O-C_2H_5+CH_3-O-C_2H_5+H_2O$$

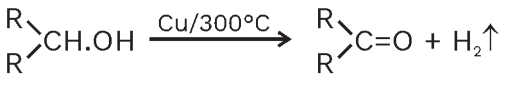
At 350°C alkene is formed

$$C_2H_5OH \xrightarrow[250°C]{Al_2O_3} C_2H_4+H_2O$$

Dehydrogenation (Cu/300°C):

It is a test for the detection of all three alcohols i.e. primary, secondary and tertiary as they give different products at 300°C on reaction with copper.

$$R{-}CH_2OH \xrightarrow{Cu/300°C} \underset{\text{Aldehyde}}{R{-}CHO} + H_2\uparrow$$



$$R_2CH.OH \xrightarrow{Cu/300°C} R_2C{=}O + H_2\uparrow$$

Ketone

Previous Year's Questions

$HOCH_2.CH_2OH$ on heating with periodic acid gives

[AIPMT]

(1) 2HCOOH (2) OHCCHO

(3) $2H_2C{=}O$ (4) $2CO_2$

Oxidation:

It is a test which gives different products on oxidation of different alcohols as primary secondary & tertiary alcohols.

(a) Primary alcohols on oxidation with $K_2Cr_2O_7$ or $KMnO_4$ give acids which have the same number of carbon atoms, as the parent alcohol.

$$R-CH_2OH \xrightarrow[-H_2O]{[O]\text{acidic}KMnO_4} R-CHO$$

$$RCHO \xrightarrow{[O]\text{acidic}KMnO_4} \underset{\text{Acid}}{R-COOH}$$

Concept Ladder

The oxidation of alcohol to carbonyl compound is typically carried out with Cr^{+6} oxidants, which are reduced to Cr^{3+} products.

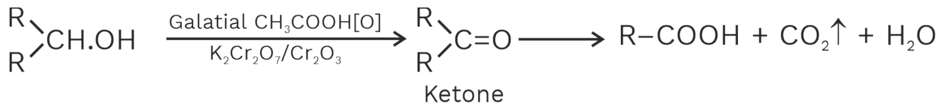
$$CH_3CH_2OH \xrightarrow[-H_2O]{[O]\text{acidic}KMnO_4} CH_3-CHO \xrightarrow{[O]\text{acidic}KMnO_4} \underset{\text{Acetic acid}}{CH_3COOH}$$

The colour of the solution disappears on proceeding oxidation reaction which is imparted by the oxidizing agent.

Rack your Brain

Explain why 3° alcohols cannot be oxidised?

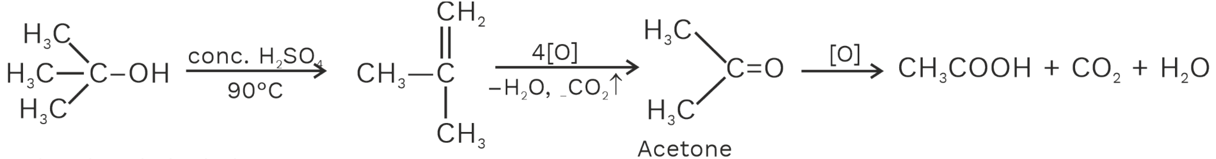
(b) Ketones are formed when secondary alcohols are oxidized, which on further oxidation give acids with one carbon atom less than the parent alcohol, under drastic conditions by strong oxidizing agents like HNO_3.



$$(CH_3)_2CHOH \xrightarrow[K_2Cr_2O_7/Cr_2O_3]{\text{Galatial } CH_3COOH} CH_3-CO-CH_3 \longrightarrow CH_3COOH + CO_2 + H_2O$$

Isoproyl alcohol

(c) Like in previous point, tertiary alcohols cannot undergo oxidation by mild oxidizing agents. However, they forms an acid with two carbon atom less than the parent alcohol by oxidizing under drastic conditions by strong oxidizing agents.



Tertiary butyl alcohol

Test For Primary, Secondary and Tertiary Alcohols

Lucas Method:

A mixture of conc. hydrochloric acid and anhydrous zinc chloride is called as Lucas reagent.

- The reactivity of alcohols towards Lucas reagent follows the order: tertiary > secondary > primary.

Rack your Brain

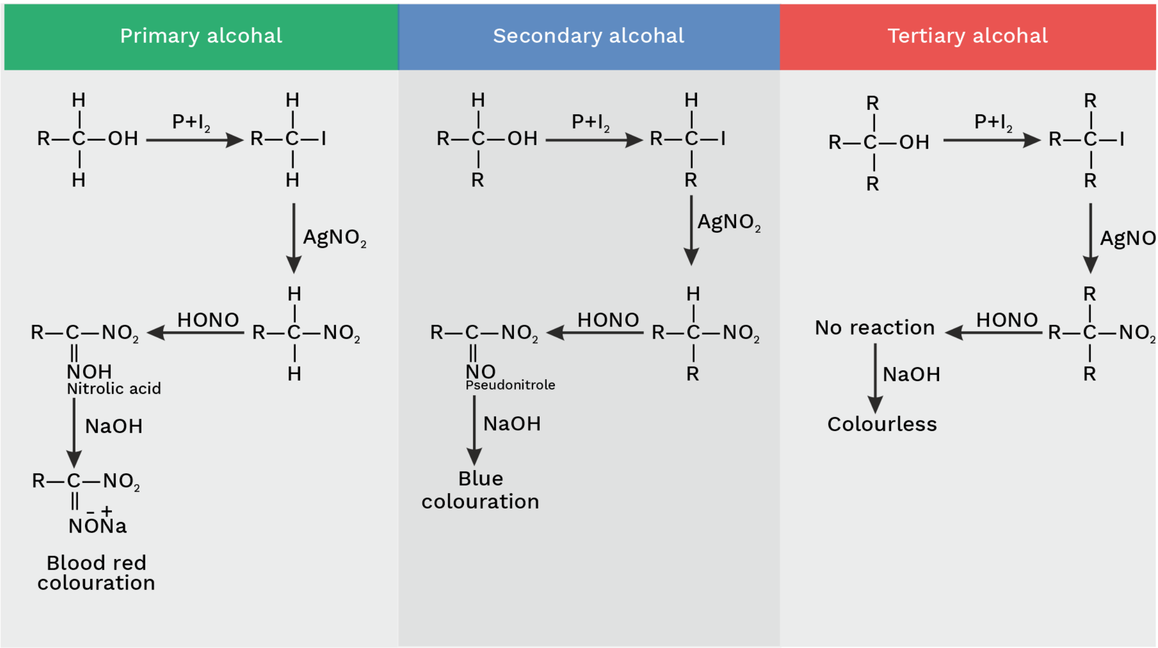
The benzyl and allyl alcohol reacts as rapidly as tertiary alcohols with Lucas reagent. Why?

- $\underset{\text{Primary alcohol}}{R-CH_2OH} \xrightarrow{\text{Lucas reagent}}$ No reaction in cold conditions
- $\underset{\text{Secondary alcohol}}{R_2CH_2OH} \xrightarrow{\text{Lucas reagent}}$ Formation of ppt. after 5–10 minutes.
- $\underset{\text{Tertiary alcohol}}{R_3C.OH} \xrightarrow{\text{Lucas reagent}}$ An oily layer (turbidity) is formed at once in cold

e.g., $(CH_3)COH \xrightarrow{\text{Lucas reagent}} \underset{3^\circ\text{–butylchloride (white ppt.)}}{(CH_3)_3C.Cl}$

Victor Mayer method:

Here, all three primary, secondary & tertiary alcohols give different colours on undergoing a set of reactions.

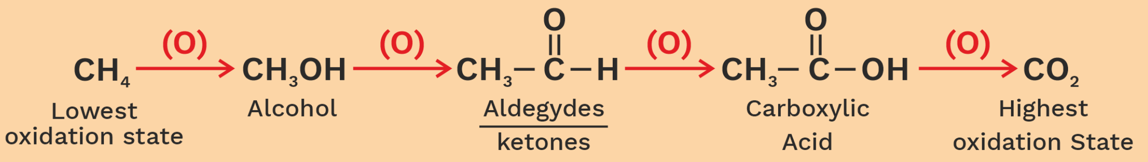


How To

Alcohol Prepare

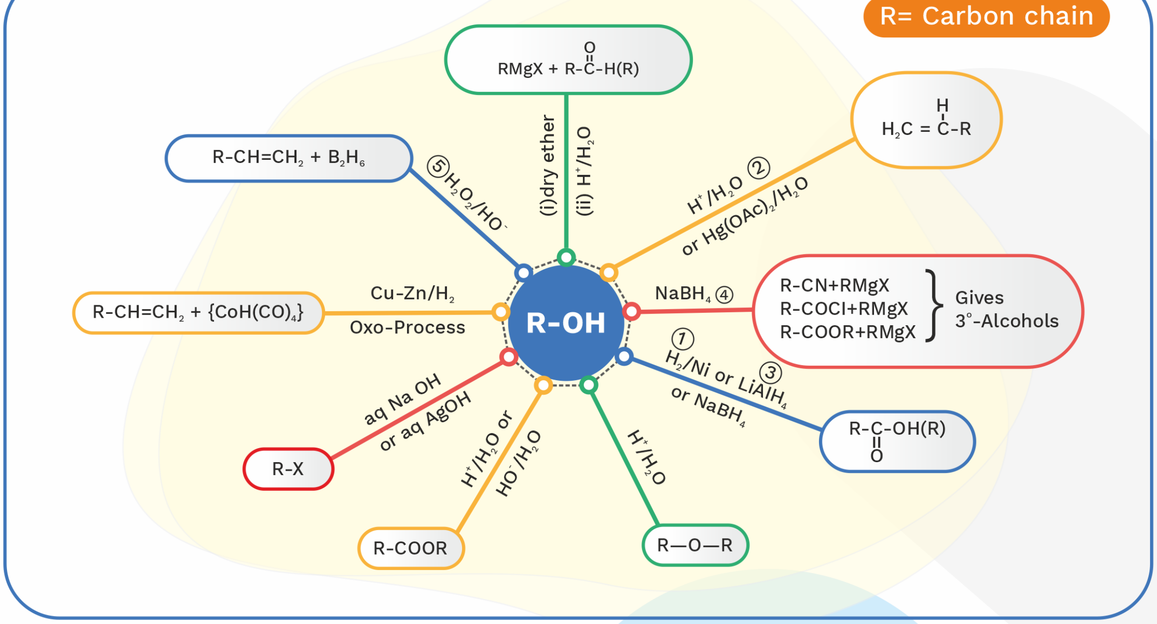
You need to have some basic information

HIERARCHY OF OXIDATION



$$CH_4 \xrightarrow{(O)} CH_3OH \xrightarrow{(O)} CH_3-\overset{\overset{\displaystyle O}{\parallel}}{C}-H \xrightarrow{(O)} CH_3-\overset{\overset{\displaystyle O}{\parallel}}{C}-OH \xrightarrow{(O)} CO_2$$

Ways to do it



Notes

- H$_2$/Ni reduces all reducible groups including olefinic bonds.
- Reaction proceeds via carbocation, rearrangement may accompany
- LIAIH$_4$ does not reduce olefinic bonds.
- .
- Anti-Markownikoff's hydration takes place.

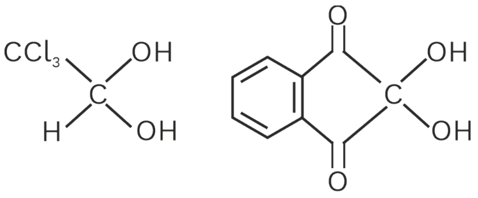
Catalytic Hydrogenation

$$\text{(Aldehyde) } R-\overset{\overset{\displaystyle O}{|}}{C}-H \xrightarrow[Pt]{H_2} \overset{1^{\circ}\text{ Alcohol}}{RCH_2OH} \ \overset{\text{Hydride}}{+\ H:^-}$$

$$\text{(Ketone) } R-\overset{\overset{\displaystyle O}{|}}{C}-R \xrightarrow[Pt]{H_2} \overset{2^{\circ}\text{ Alcohol}}{RCH_2OH} \ \overset{\text{Hydride}}{+\ H:^-}$$

Some Facts about Alcohols

- Alcohols show position, chain and functional isomerism, For ex. CH_3OCH_3 and C_2H_5OH are functional isomers.
- R–OH + ceric ammonium nitrate Red colour
- CH_3OH is called wood sprit or carbinol. (60% CH_3OH).
- Ethanol is also known as **grain alcohol**.
- 100% ethanol is **absolute alcohol**.
- **Power alcohol** is 20% ethanol + 80% gasoline. It is used as fuel in motor vehicles.
- Rectified spirit is 95.47% ethanol + 4.53%
- water.
- Isopropyl alcohol is also known as **rubbing alcohol**.
- Commercial ethanol is deleberately made unfit for human consumption as liquor by mixing it with methanol or petrol. (Denatured or methylated sprit.)
- Tendency of alcohols to form H-bonds: primary > secondary > tertiary.
- Order of R–OH to form ester with inorganic acids follows the order: tertiary > secondary > primary.
- A mixture of 95.57% C2H5OH and 4.43% water boils at constant temp., i.e., an azeotropic mixture.
- $\underset{C_2H_5OH}{\text{Wine}} \xrightarrow[\text{open}]{\text{oxidation}} \underset{CH_3COOH}{\text{Sour}}$
- Both the hydrates shown below are stable due to intramolecular H-bonding and electron withdrawing groups.



Concept Ladder

Reactivity of alcohols towards ester formation with organic acids follows the order: primary > secondary > tertiary.

Rack your Brain

Why methanol does not give the iodoform test?

Previous Year's Questions

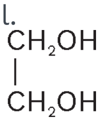
Lucas reagent is

[AIPMT]

(1) conc. HCl and anhydrous $ZnCl_2$
(2) conc. HNO_3 and hydrous $ZnCl_2$
(3) conc. HCl and hydrous $ZnCl_2$
(4) conc. HNO_3 and anhydrous $ZnCl_2$

Ethylene Glycol

Ethane 1, 2 diol or ethylene glycol is a dihydric alcohol.

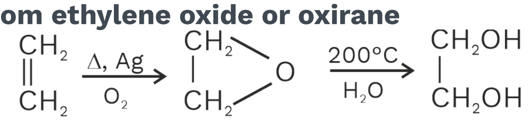


$$\begin{array}{c}CH_2OH\\ |\\ CH_2OH\end{array}$$

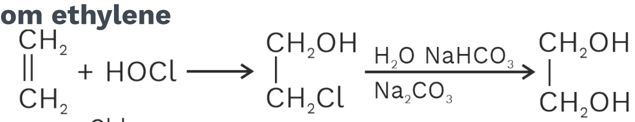
Methods of preparation:

Ethane-1, 2-diol is prepared by the following methods:

From ethylene oxide or oxirane



From ethylene

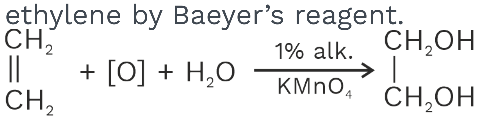


$$\begin{array}{c}CH_2\\ \|\\ CH_2\end{array} + HOCl \longrightarrow \begin{array}{c}CH_2OH\\ |\\ CH_2Cl\end{array} \xrightarrow[Na_2CO_3]{H_2O\ NaHCO_3} \begin{array}{c}CH_2OH\\ |\\ CH_2OH\end{array}$$

Chlorous acid

Glycol

- Ethylene glycol is formed on hydroxylation of ethylene by Baeyer's reagent.



$$\begin{array}{c}CH_2\\ \|\\ CH_2\end{array} + [O] + H_2O \xrightarrow[KMnO_4]{1\%\ alk.} \begin{array}{c}CH_2OH\\ |\\ CH_2OH\end{array}$$

Previous Year's Questions

Which of hte following is correct?

[AIPMT]

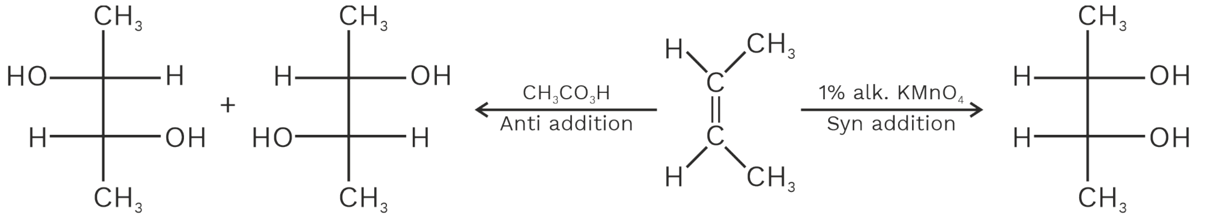
(1) On reduction, any aldehyde gives secondary alcohol.

(2) Reaction of vegatable oil with H_2SO_4 gives glycerine.

(3) Alcoholic iodine with NaOH gives iodoform.

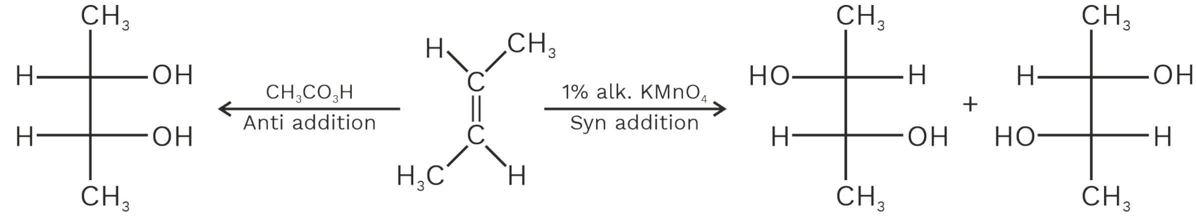
(4) Sucrose on reaction with NaCl gives invert

Prileschaiev Reaction



(Racemic mixture)
Butan-2,3-diol

meso butan-2,3-diol

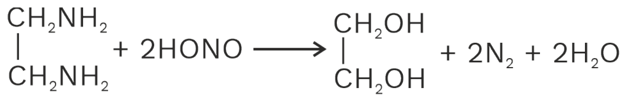


meso butan-2,3-diol

(Racemic mixture)
Butan-2,3-diol

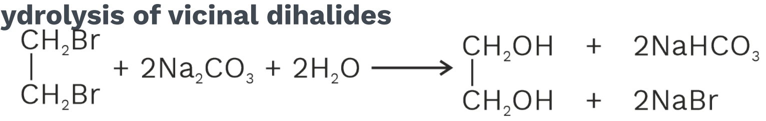
From ethylene diammine:

Glycol is formed when ethylene diammine reacts with nitrous acid.



$$\begin{array}{l}CH_2NH_2\\ |\\ CH_2NH_2\end{array} + 2HONO \longrightarrow \begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array} + 2N_2 + 2H_2O$$

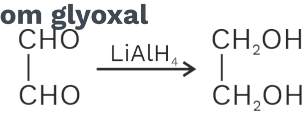
By hydrolysis of vicinal dihalides



$$\begin{array}{l}CH_2Br\\ |\\ CH_2Br\end{array} + 2Na_2CO_3 + 2H_2O \longrightarrow \begin{array}{lcl}CH_2OH & + & 2NaHCO_3\\ | & & \\ CH_2OH & + & 2NaBr\end{array}$$

1, 2-dibromoethane

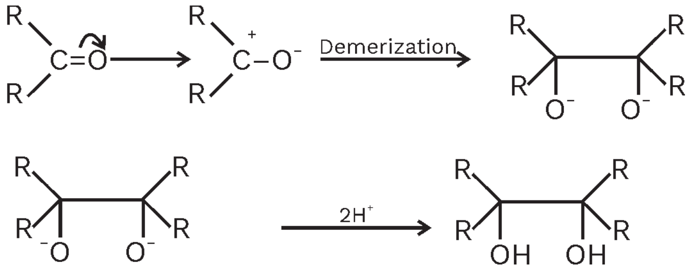
From glyoxal



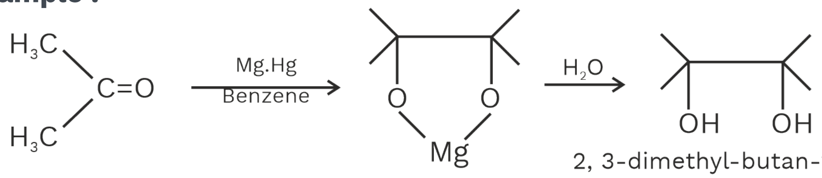
$$\begin{array}{l}CHO\\ |\\ CHO\end{array} \xrightarrow{LiAlH_4} \begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array}$$

From ketones

Ketones can be converted into diols as follows:



Example :



2, 3-dimethyl-butan-2, 3-diol

Concept Ladder

Ethyl glycol has high boiling point due to presence of intermolecular hydrogen bonding.

Physical properties of ethylene glycol

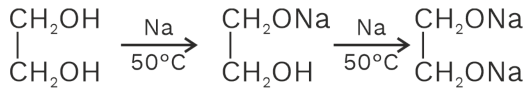
- Ethylene glycol is a clear, sweet, slightly viscous liquid.
- It is soluble in ethanol and water.
- The B.P. of glycol is 470 K.
- Ethylene glycol is highly poisonous; animals or humans that drink the solution become very ill and may die.

Rack your Brain

In glycol molecule has two alcoholic groups present but those are not equally reactive. Why?

Chemical properties of ethylene glycol

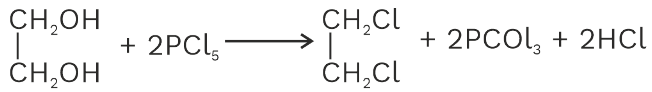
Reaction with sodium



$$\begin{array}{l}CH_2OH\\|\\CH_2OH\end{array}\xrightarrow[50°C]{Na}\begin{array}{l}CH_2ONa\\|\\CH_2OH\end{array}\xrightarrow[50°C]{Na}\begin{array}{l}CH_2ONa\\|\\CH_2ONa\end{array}$$

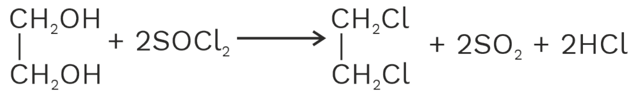
Disodium glycolate
(Dialkoxide)

Reaction with PCl_5 or $SOCl_2$



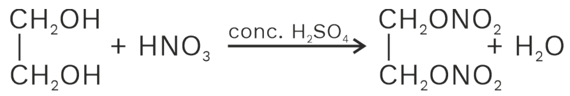
$$\begin{array}{l}CH_2OH\\|\\CH_2OH\end{array}+2PCl_5\longrightarrow\begin{array}{l}CH_2Cl\\|\\CH_2Cl\end{array}+2PCOl_3+2HCl$$

1, 2-Dichloroethane



$$\begin{array}{l}CH_2OH\\|\\CH_2OH\end{array}+2SOCl_2\longrightarrow\begin{array}{l}CH_2Cl\\|\\CH_2Cl\end{array}+2SO_2+2HCl$$

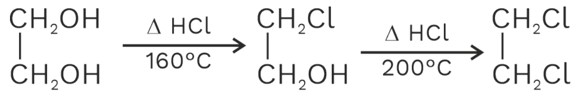
Reaction with HNO_3 (Nitration)



$$\begin{array}{l}CH_2OH\\|\\CH_2OH\end{array}+HNO_3\xrightarrow{conc.\ H_2SO_4}\begin{array}{l}CH_2ONO_2\\|\\CH_2ONO_2\end{array}+H_2O$$

Ethlenedinitrate

Reaction with HCl



$$\begin{array}{l}CH_2OH\\|\\CH_2OH\end{array}\xrightarrow[160°C]{\Delta\ HCl}\begin{array}{l}CH_2Cl\\|\\CH_2OH\end{array}\xrightarrow[200°C]{\Delta\ HCl}\begin{array}{l}CH_2Cl\\|\\CH_2Cl\end{array}$$

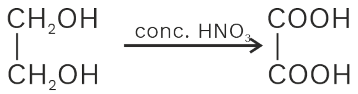
1, 2-Dichloroethane

Oxidation:

Glycol on oxidation by different reagents gives different products.

For example,

- Glycol gives oxalic acid on reacting with HNO_3.



$$\begin{array}{l}CH_2OH\\|\\CH_2OH\end{array}\xrightarrow{conc.\ HNO_3}\begin{array}{l}COOH\\|\\COOH\end{array}$$

Oxalic acid

Concept Ladder

The two OH– groups present in the glycol molecule are not equally reactive, one group always completely reacts before the other is attacked.

Rack your Brain

Write the product formed when ethylene glycol reacts with PBr_3?

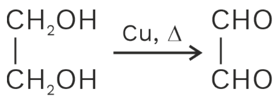
Previous Year's Questions

Ethylene oxide when treated with Grignard reagent yields

[AIPMT]

(1) primary alcohol
(2) secondary alcohol
(3) tertiary alcohol
(4) cyclopropyl alcohol

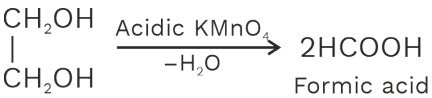
- Glycol is formed when glycol reacts with copper.



$$\begin{array}{l}CH_2OH\\|\\CH_2OH\end{array} \xrightarrow{Cu,\ \Delta} \begin{array}{l}CHO\\|\\CHO\end{array}$$

Glyoxal

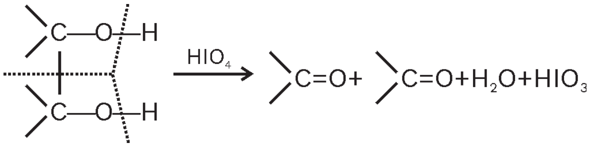
- Formic acid is formed when glycol reacts with acidic $KMnO_4$.



$$\begin{array}{l}CH_2OH\\|\\CH_2OH\end{array} \xrightarrow[-H_2O]{\text{Acidic } KMnO_4} \underset{\text{Formic acid}}{2HCOOH}$$

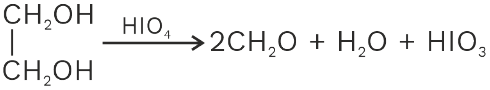
Oxidation By Periodic Acid (HIO_4):

When 1,2 di-ols are oxidised by $(CH_3OCO)_4Pb$ or HIO_4 1, 2 glycol splitting occurs to give aldehydes or ketones or both.

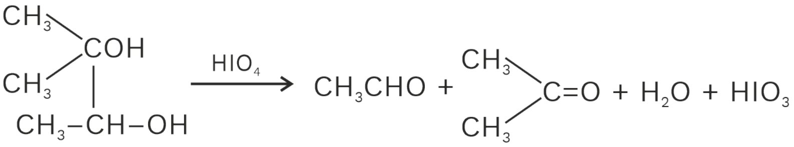


$$\begin{array}{l}>C-O-H\\ \ \ |\\>C-O-H\end{array} \xrightarrow{HIO_4} >C=O + >C=O + H_2O + HIO_3$$

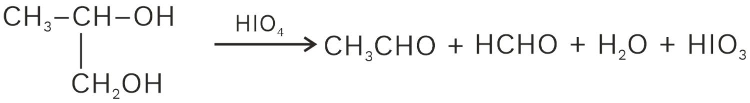
e.g.,



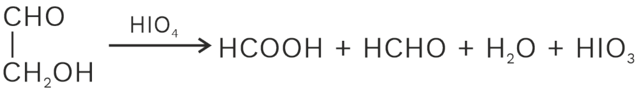
$$\begin{array}{l}CH_2OH\\|\\CH_2OH\end{array} \xrightarrow{HIO_4} 2CH_2O + H_2O + HIO_3$$



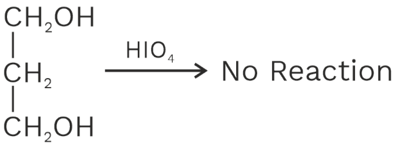
$$\begin{array}{l}CH_3\diagdown\\ \quad\ \ COH\\CH_3\diagup\ \ |\\ \ \ CH_3-CH-OH\end{array} \xrightarrow{HIO_4} CH_3CHO + \begin{array}{l}CH_3\diagdown\\ \qquad\ C=O\\CH_3\diagup\end{array} + H_2O + HIO_3$$



$$\begin{array}{l}CH_3-CH-OH\\ \qquad\ \ |\\ \qquad CH_2OH\end{array} \xrightarrow{HIO_4} CH_3CHO + HCHO + H_2O + HIO_3$$



$$\begin{array}{l}CHO\\|\\CH_2OH\end{array} \xrightarrow{HIO_4} HCOOH + HCHO + H_2O + HIO_3$$



$$\begin{array}{l}CH_2OH\\|\\CH_2\\|\\CH_2OH\end{array} \xrightarrow{HIO_4} \text{No Reaction}$$

Concept Ladder

Ethylene glycol is used as an antifreeze under the name preston in car radiators.

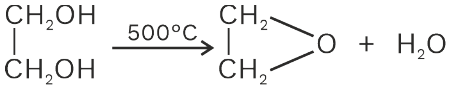
Rack your Brain

Why $(CH_2OH)_2CH_2$ does not react with HIO_4 to give prodct?

Dehydration:

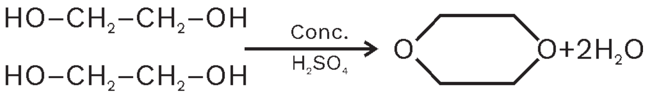
Different producta can be formed by dehydration of glycol as given below:

- At 500°C



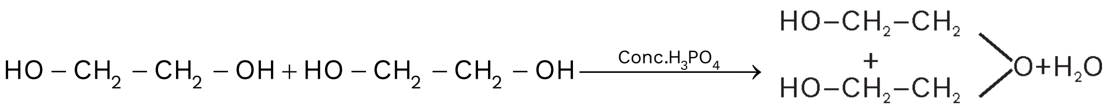
Oxirane

- Glycol reacts with concentrated sulphuric acid to yield 1,4-dioxane.



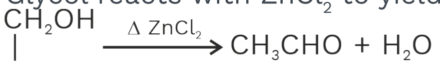
Dioxane

- Glycol reacts with boric acid to yield diethylene glycol.



Diethylene Glycol

- Glycol reacts with $ZnCl_2$ to yield ethanal.



$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} \xrightarrow{\Delta\ ZnCl_2} CH_3CHO + H_2O$$

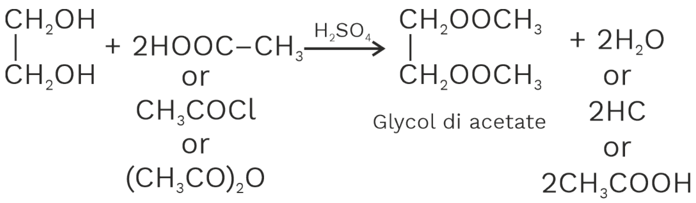
Ethanal

Rack your Brain

How will you convert methyl alcohol in to ethyl alcohol?

Acetylation:

Glycol on acetylation by acetic anhydride or acetic acid or acetyl chloride gives glycol di acetate.



$$\begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array} + \begin{array}{c}2HOOC-CH_3\\ \text{or}\\ CH_3COCl\\ \text{or}\\ (CH_3CO)_2O\end{array} \xrightarrow{H_2SO_4} \begin{array}{l}CH_2OOCH_3\\ |\\ CH_2OOCH_3\end{array} + \begin{array}{c}2H_2O\\ \text{or}\\ 2HC\\ \text{or}\\ 2CH_3COOH\end{array}$$

Glycol di acetate

Previous Year's Questions

Which one of the following will not form a yellow precipitate on heating with an alkalin solution of iodine?

[AIPMT]

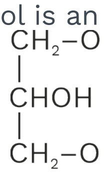
(1) $CH_3CH(OH)CH_3$
(2) $CH_3CH_2CH(OH)CH_3$
(3) CH_3OH
(4) CH_3CH_2OH

Uses of ethylene glycol

1. In manufacturing dioxane and Dacron.
2. As a solvent and as a preservative.
3. As an anti-freeze in automobile radiators.
4. As an explosive in the form of dinitrate.
5. As a cooling agent in aeroplanes.

Glycerol or Glycerine

Glycerol is an example of **trihydric alcohol.**



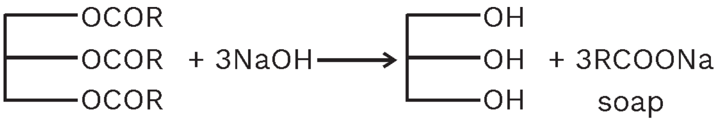
$$\begin{array}{l} CH_2{-}O \\ | \\ CHOH \\ | \\ CH_2{-}O \end{array}$$

Method of preparation of glycerol:

Glycerol is prepared as follows:

By saponifcation:

The process by which oils and fats are hydrolyzed to give glycerol and salt of higher fatty acids, is known as **saponifcation**.

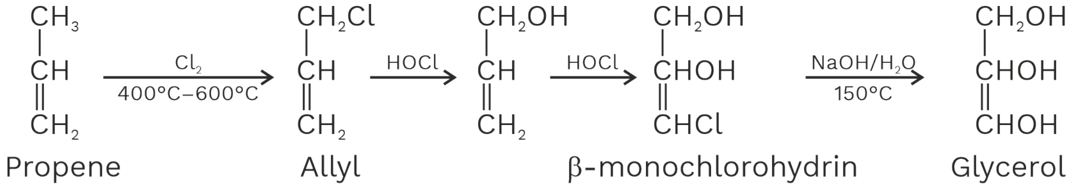


Fat or oil

Here, R may be: $C_{17}H_{33}$ (Olein), $C_{17}H_{35}$ (Steric), $C_{15}H_{31}$ (Palmitis)

From propene:

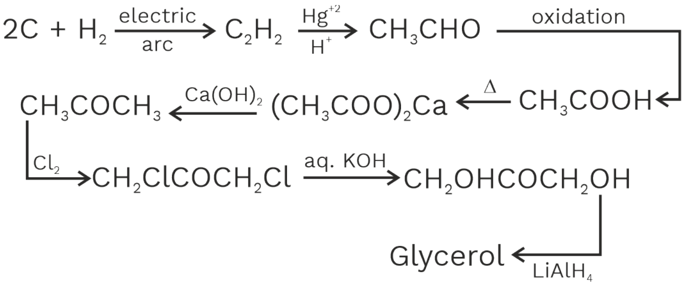
By propene, glycerol can also formed as follows:



Propene Allyl chloride β-monochlorohydrin Glycerol

Synthesis of glycerol:

Glycerol is synthesized by the following method:



Concept Ladder

Glycerol may be considered as derivative of propane, obtained by replacement of three hydrogen atoms from different carbon atoms by three hydroxyl groups.

Rack your Brain

Explain how glycerol can be prepared from fats and oils?

Previous Year's Questions

Reaction of $(CH_2)_2O$ with RMgX leads to the formation of **[AIPMT]**

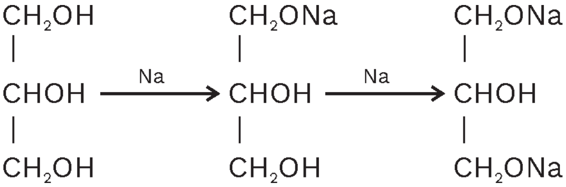
(1) RCH_2CH_2OH
(2) $RCHOHCH_3$
(3) $RCHOHR$
(4) R_2CHCH_2OH

Physical properties of Glycerol

- Due to presence of greater extent of H-bonding in glycerol, it becomes more viscous than other alcohols.
- Similarly due to greater extent of hydrogen
- Bonding, glycerol has highest boiling point
- Among alcohols (290°C).
- Glycerol is soluble in water and is a colourless
- oily liquid.
- Glycerol is hygroscopic in nature.

Chemical properties of Glycerol

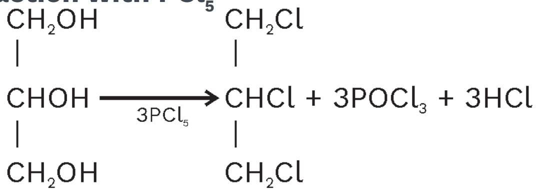
Reaction with sodium



$$\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \xrightarrow{Na} \begin{array}{c} CH_2ONa \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \xrightarrow{Na} \begin{array}{c} CH_2ONa \\ | \\ CHOH \\ | \\ CH_2ONa \end{array}$$

- Due to non acidic nature of hydrogen, reaction at β-carbon atom does not take place.

Reaction with PCl_5

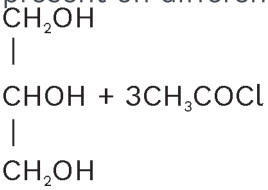


$$\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \xrightarrow[3PCl_5]{} \begin{array}{l} CH_2Cl \\ | \\ CHCl + 3POCl_3 + 3HCl \\ | \\ CH_2Cl \end{array}$$

(1, 2, 3-trichloropropane)

Acetylation by CH_3COCl or $(CH_3CO)_2O$

- Here the formation of glycerol triacetate confirms that glycerol has 3 –OH groups present on different carbon atoms.



$$\begin{array}{l} CH_2OH \\ | \\ CHOH + 3CH_3COCl \\ | \\ CH_2OH \end{array}$$

- If $(CH_3CO)_2O$ is used in place of HCl, acetic acid is formed.

Concept Ladder

Acrolein on reduction with $LiAlH_4$ gives allyl alcohol, which on treatment with Baeyer's reagent gives glycerol.

Rack your Brain

How much glycerol is formed when alcoholic fermentation of sugar takes place?

Previous Year’s Questions

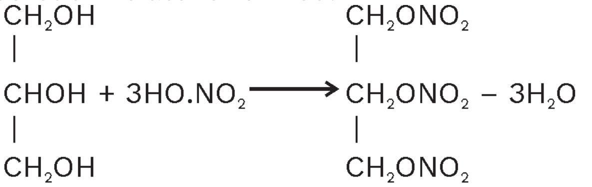
Which one of the following on oxidatnio gives a ketone?

[AIPMT]

(1) Primary alcohol
(2) Secondary alcohol
(3) Tertiary alcohol
(4) All of these

Reaction with HNO_3:

On adding glycerol, concentrated nitric acid and concentrated sulphuric acid in the proportion of 1 : 3 : 5 respectively and also on heating, glycerol trinitrate is formed.



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3HO.NO_2 \longrightarrow \begin{array}{l} CH_2ONO_2 \\ | \\ CH_2ONO_2 \\ | \\ CH_2ONO_2 \end{array} - 3H_2O$$

Glycerol trinitrate (TNG)
(Noble's oil)

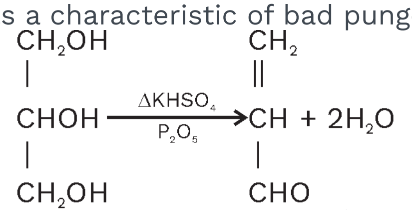
- Glycerol trinitrate is a poisonous, yellow in colour, oily liquid and causes headache.
- It releases large volume of gases on explosion.

$$\text{Glycerol trinitrate} \longrightarrow 12CO_2 + 10H_2O + 6N_2 + O_2$$

- When absorbed on kieselguhr, it becomes a safer explosive. In this form, it is called dynamite.
- Cordite-like explosives and blasting-gelatin can also be prepared from glycerol trinitrate.

Dehydration:

Glycerol on heated with dehydrating agents like P2O5 or $KHSO_4$, acrolein is obtained which has a characteristic of bad pungent odour.



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \xrightarrow[P_2O_5]{\Delta KHSO_4} \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CHO \end{array} + 2H_2O$$

Acrolein (prop-2-en-1-al)

Reaction with Oxalic acid:

Different products are formed under different conditions.

- Formic acid is formed at 110°C with excess of oxalic acid.

Concept Ladder

Nitroglycerine is also a medicine for heart patients as vasodilator, it releases large volume of gases and occupy 10,900 times the volume of nitroglycerine.

Rack your Brain

Write the chemical name of Nobel's oil?

Previous Year's Questions

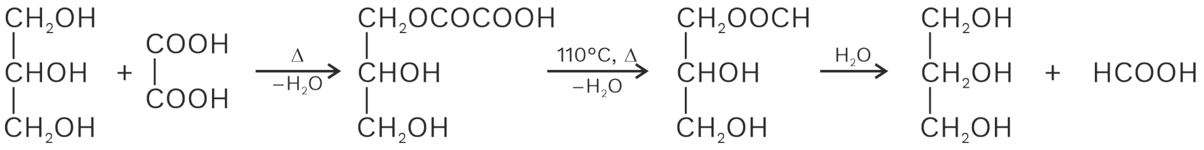
In the folowing sequence of reaction

$$CH_3Br \xrightarrow{KCN} A \xrightarrow{H_3O^+} B \xrightarrow[\text{ether}]{LiAlH_4} C$$

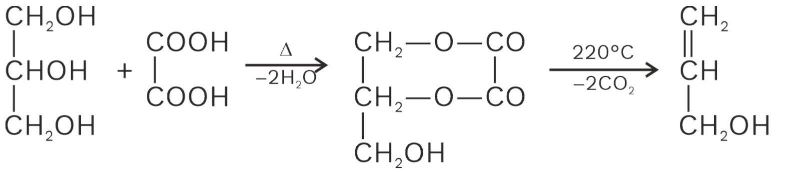
the end product (C) is

[AIPMT-2012]

(1) acetone (2) methane
(3) acetaldehyde (4) ethyl alcohol

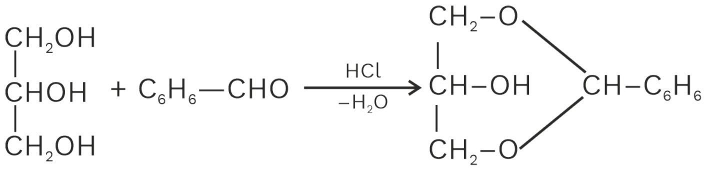


- It is a lab method to prepare formic acid and it can be formed in a good amount.
- Allyl alcohol is formed, at 220°C.



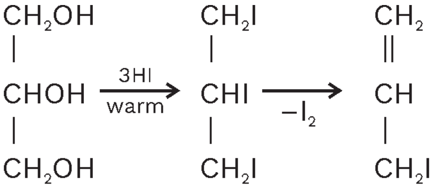
Reaction with benzaldehyde:

Acetals are fromed on reacting glycerol with benzaldehyde.



Reaction with HI :

- Allyl iodide is formed by warming glycerol with a small amount of HI.



- 2-iodopropane is formed, when HI is in excess reaction proceeds further.

Concept Ladder

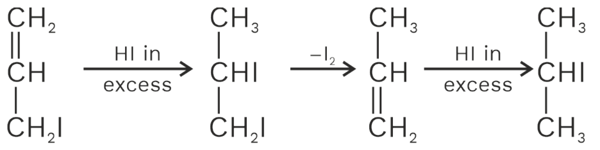
A mixture of glyceryl trinitrate and cellulose nitrate (gun cotton) is known as Blasting gelatin.

Previous Year's Questions

When vapours of a secondary alcohol is passed over heated copper at 573 K, the product formed is

[NEET-2019]

(1) a carboxylic acid
(2) an aldehyde
(3) a ketone
(4) an alkene



$$\begin{array}{c}CH_2\\ \|\\ CH\\ |\\ CH_2I\end{array} \xrightarrow[\text{excess}]{\text{HI in}} \begin{array}{c}CH_3\\ |\\ CHI\\ |\\ CH_2I\end{array} \xrightarrow{-I_2} \begin{array}{c}CH_3\\ |\\ CH\\ \|\\ CH_2\end{array} \xrightarrow[\text{excess}]{\text{HI in}} \begin{array}{c}CH_3\\ |\\ CHI\\ |\\ CH_3\end{array}$$

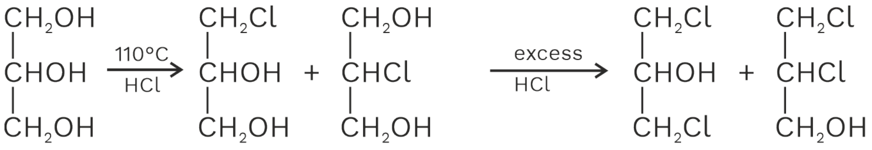
Allyl iodide 2-Iodopropane

Reaction with HCl or HBr :

When HCl is passed through glycerol at 110oC, both α and β glycerol monochlorohydrins are formed. If the HCl gas is passed for sufcient time, glycerol-α, α’-dichlorohydrin and glycerol α, β-dichlorohydrin are formed.

Rack your Brain

Write reaction used in formation of glceric acid and tartonic acid?



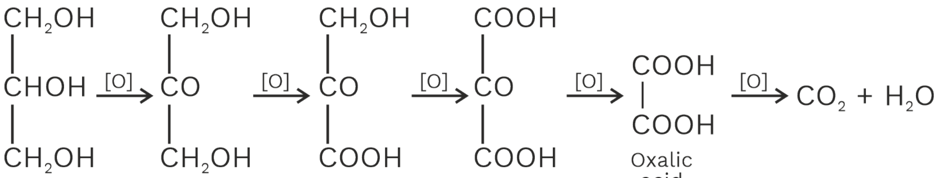
$$\begin{array}{c}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array} \xrightarrow[\text{HCl}]{110°C} \begin{array}{c}CH_2Cl\\ |\\ CHOH\\ |\\ CH_2OH\end{array} + \begin{array}{c}CH_2OH\\ |\\ CHCl\\ |\\ CH_2OH\end{array} \xrightarrow[\text{HCl}]{\text{excess}} \begin{array}{c}CH_2Cl\\ |\\ CHOH\\ |\\ CH_2Cl\end{array} + \begin{array}{c}CH_2Cl\\ |\\ CHCl\\ |\\ CH_2OH\end{array}$$

α-Glycerol β-Monochlorohydrine α (56%) β (44%)

34% 66%

Oxidation :

Depending on the nature of oxidizing agent, glycerol gives different products.



$$\begin{array}{c}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array} \xrightarrow{[O]} \begin{array}{c}CH_2OH\\ |\\ CO\\ |\\ CH_2OH\end{array} \xrightarrow{[O]} \begin{array}{c}CH_2OH\\ |\\ CO\\ |\\ COOH\end{array} \xrightarrow{[O]} \begin{array}{c}COOH\\ |\\ CO\\ |\\ COOH\end{array} \xrightarrow{[O]} \begin{array}{c}COOH\\ |\\ COOH\end{array} \xrightarrow{[O]} CO_2 + H_2O$$

Dihydroxy acetone Hydroxy pyruvic acid Mesoxalic acid Oxalic acid

Different Oxidizing Agents

- Dilute nitric acid oxidizes glyceric acid from glycerol.
- Concentrated nitric acid oxidizes glycerol to tartonic acid and glyceric acid.
- $Bi(NO_3)_3$ reacts with glycerol to give meso oxalic acid.
- Fenton’s reagent (H_2O_2 + $FeSO_4$) or Br_2/H_2O in the presence of Na_2CO_3 oxidises a mixture of dihydroxy acetone (or glyerose) and glyceraldehyde from glycerol.
- Solid $KMnO_4$ oxidizes glycerol into oxalic acid and carbon oxide. This reaction is explosive.

Previous Year’s Questions

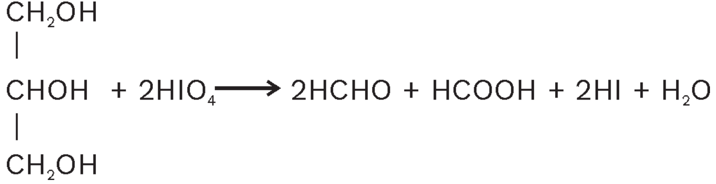
When glycerol is treated with excess of HI, it produces

[AIPMT]

(1) 2-iodopropane
(2) allyl iodide
(3) propene
(4) glycerol triiodide

Reaction with HiO_4 :

Formaldehyde and formic acid are formed by glycerol which undergoes oxidative cleavage by HIO_4 (periodic acid).



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 2HIO_4 \longrightarrow 2HCHO + HCOOH + 2HI + H_2O$$

Tests of glycerol

Acrolein test

$$\text{Glycerol} \xrightarrow{KHSO_4} \text{Acrolein} \xrightarrow{\text{Tollen's reagent}} \underset{\text{(Black precipitate)}}{\text{Silver mirror}}$$

Dunstan test

$$\text{A drop of HPH} + \text{5ml borax} \longrightarrow \text{Pink colour} \xrightarrow[\text{Drops}]{\text{Glycerol}} \text{No Pink colour}$$

$$\text{Phenol} + \text{Glycerol} + \text{conc.}H_2SO_4 \xrightarrow[130^\circ C]{\Delta} \text{Red colour}$$

Uses of glycerol

Glycerol finds its application in various field as listed below:

- It is used as sweetening agent in beverages, confectionary & medicines being non-toxic in nature.
- It is used as lubricant in watches.
- It is used as a preservative
- In the preparation of printing inks, non-drying inks and stamp pad inks.
- In the manufacture of synthetic fibres and plastics.
- In the preparation of good quality soap, vanishing creams, hand lotions, tooth pastes and shaving creams.
- Dynamite is a mixture of Kieselguhr and glycerol.

Rack your Brain

Which colour is produced on addition of ammonium hydroxide to the equimolar mixture of phenol and glycerol?

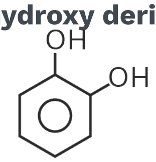
Previous Year's Questions

Reaction between acetone and methyl magnesium chloride followed by hydrolysis will give **[NEET-2020]**

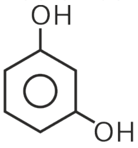
(1) iso-propyl alcohol
(2) sec-butyl alcohol
(3) tert-butyl alcohol
(4) iso-butyl alcohol

Phenols

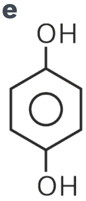
Dihydroxy derivatives of benzene



Catechol



Resorcinol



Hydroquinone

Phenol or Carbolic Acid

- Phenol is a hydroxy derivative of benzene and, hence, is known as hydroxybenzene.
- Runge discovered Phenol during coal tar distillation in the middle oil fraction.
- Phenol is antiseptic, acidic, and can also be used as a disinfectant.
- It is insoluble in aqueous NaHCO3 but soluble in aq. NaOH and KOH, while benzoic acid, are
- soluble in KOH, NaOH and aq. $NaHCO_3$.
- On reacting with aq. $FeCl_3$, it forms a violet coloured product $(C_6H_5O)_3Fe$.

Methods of Preparation

From middle oil fraction of coal tar distillation:

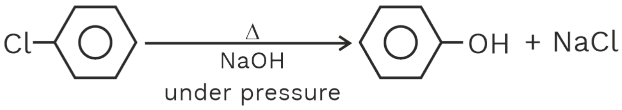
The middle oil fraction mostly contains naphthalene (neutral) and phenol (acidic). The mixture is dissolved in sodium hydroxide, in which Naphthalene is insoluble and phenol is soluble.

The aqueous solution on acidifcation gives phenol.

Lab method

$$C_6H_5SO_3H \xrightarrow[\text{Fuse}]{\text{NaOH}} C_6H_5SO_3Na \xrightarrow[\Delta]{\text{NaOH}} C_6H_5OH + Na_2CO_3$$

Commercial process or Dow's method



Definition

When OH group is attached at benzene ring, the compound formed is named as **Phenol**.

Rack your Brain

Draw structure of 2, 6-dimethyl phenol?

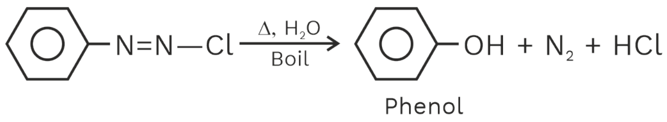
Previous Year's Questions

Reaction of phenol with chloroform in presence of dilute sodium hydroxide finally introduces which one of the following functional groups?

[NEET-2015]

(1) —COOH (2) $—CHCl_2$
(3) —CHO (4) $—CH_2Cl$

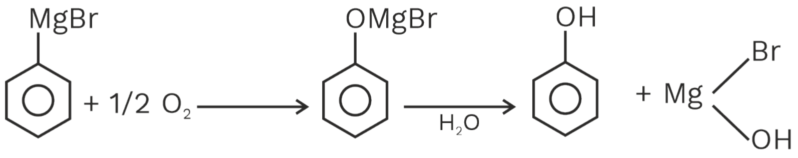
From benzene diazonium chloride



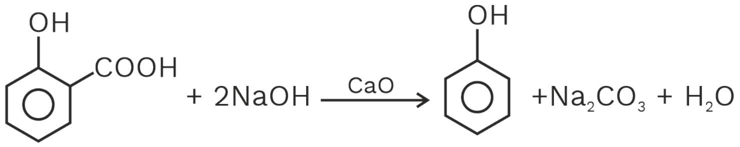
Rack your Brain

What is the position of OH on the carbonyl group in Dakin reaction?

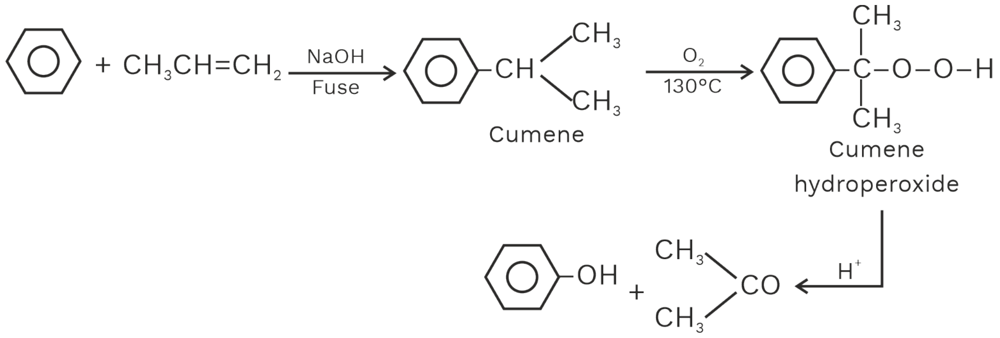
From grignard reagent



From salicylic acid



Industrial method (From cumene)



Physical Properties of Phenol

1. It is a deliquescent, crystalline solid with melting point and boiling point of 42°C and 182°C respectively.

2. Due to presence of H-bonding it is soluble in water.

3. Phenol attains a pink colour on exposure to light and air.

Chemical Properties of Phenol

Electrophilic subsitution:

It is easier and takes place at a higher rate than in benzene the –OH group in phenol is highly ring activating .

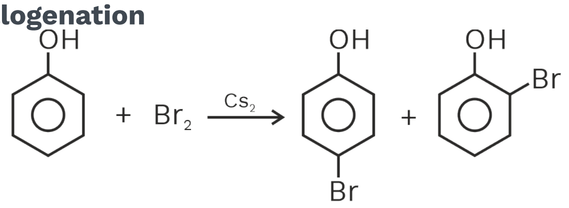
Previous Year's Questions

Which of the following will not be soluble in sodium hydrogen carbonate?

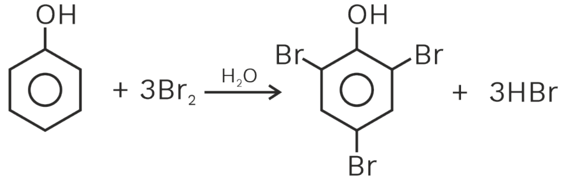
[NEET-2014]

(1) 2,4,6-Trinitrophenol
(2) Benzoic acid
(3) o-Nitrophenol
(4) Benzenesulphonic acid

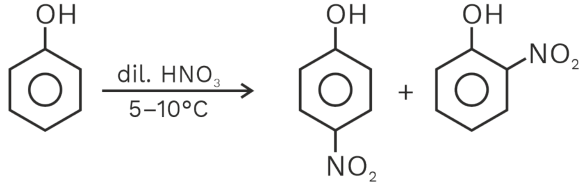
Halogenation



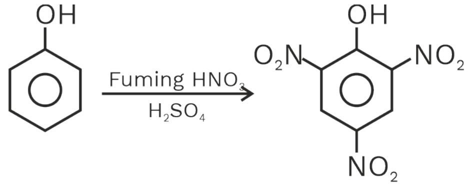
o- and p-bromophenol



2,4,6-Tribromo phenol



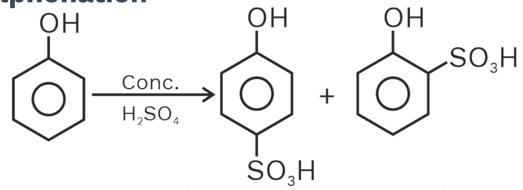
Nitration



2, 4, 6-tri nitro phenol
(Picric acid) (explosive)

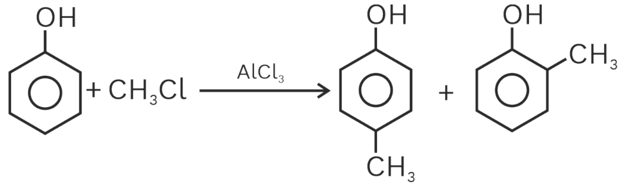
- A mixture of para and ortho nitrophenol, can be separated by steam distillation because of chelation, o-nitrophenol is volatile in steam.

Sulphonation



o, p-hydroxybenzene sulphonic acid

Freidal–Craft reaction



o- and p-cresol

Concept Ladder

Friedal Crafts reactions are a set of reactions developed in 1877, to attach substituent, to an aromatic ring. These are of two types alkylation reactions and acylation reactions.

Rack your Brain

Write reaction invovled when phenol react wtih dilute nitric acid at low temperature (290K) to give a mixture of ortho and para nitro phenols?

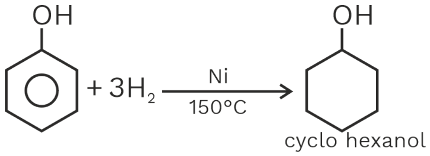
Previous Year's Questions

Phenol is heated with $CHCl_3$ and aqueous KOH when salicylaldehyde is produced. this reaction is known as

[AIPMT]

(1) Rosenmund's reaction
(2) Reimer-Tiemann reaction
(3) Friedel-Crafts reaction
(4) Sommelet reaction

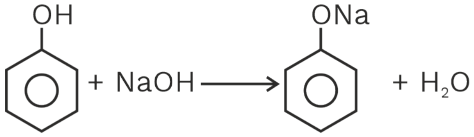
Reduction



cyclo hexanol

Reaction due to OH group

1. Salt formation

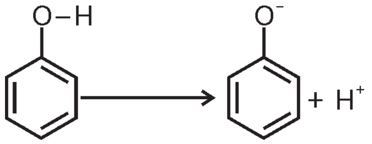


Concept Ladder

Phenol is more acidic than alcohol because phenoxide ion is more stable than the alkoxide ion present in alcohol.

2. Acidic nature:

Due to the formation of phenoxide ion (resonance stablised) phenol is weakly acidic in nature.



Phenoxide or Phenolate ion

3. Ether formation

$$C_6H_5OH + CH_2N_2 \longrightarrow \underset{\text{Anisole}}{C_6H_5OCH_3} + N_2$$

$$C_6H_5ONa + ClCH_3 \longrightarrow C_6H_5OCH_3 + NaCl$$

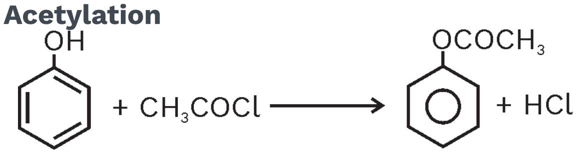
$$C_6H_5OH + (CH_3)_2SO_4 \xrightarrow{KOH} C_6H_5OCH_3 + CH_3HSO_6$$

$$C_6H_5OH + (C_2H_5)SO_4 \xrightarrow{KOH} \underset{\text{(phenatol)}}{C_6H_5OC_2H_5} + C_2H_5HSO_4$$

Rack your Brain

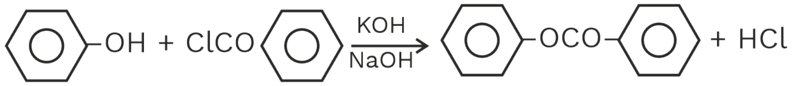
Write process for conversion of o- and p-hydroxy ketones from phenolic ester in presence of anhydrous $AlCl_3$?

4. Acetylation



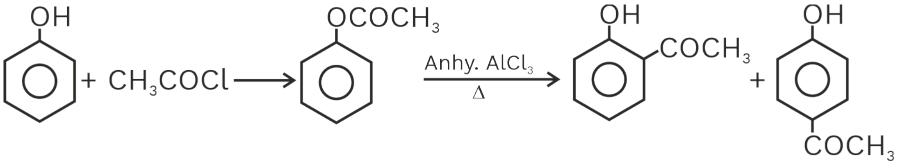
Phenyl Acetate

5. Benzoylation (Schotten – Baumann reaction)



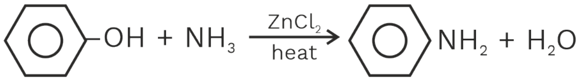
phenyl Benzoate

6. Fries migration

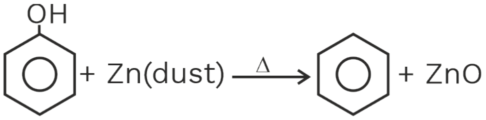


o- and p-hydroxy acetophenol

7. With Ammonia



8. Reduction



9. With P_2S_5

$$5C_6H_5OH + P_2S_5 \longrightarrow 5C_6H_5SH + P_2O_5$$

Previous Year's Questions

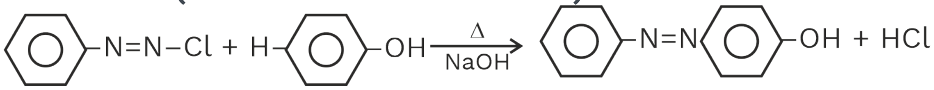
Which one of the following compounds will be most readily attacked by an electrophile?

[AIPMT]

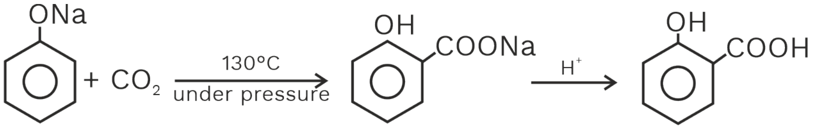
(1) Chlorobenzene
(2) Benzene
(3) Phenol
(4) Toluene

Other reactions

1. With B.D.A.C. (Benzene diazonium chloride)

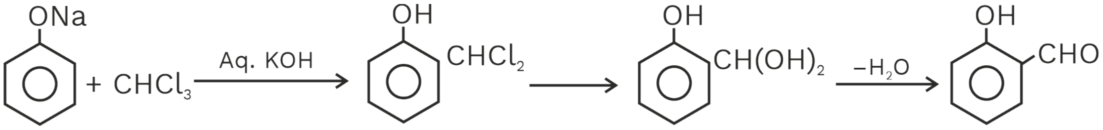


2. Kolbe's reaction



salicylic acid

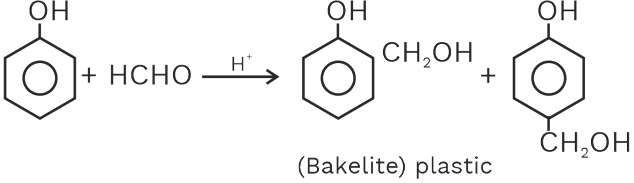
3. Reimer Tiemann Reaction



Salicyladehyde

4. Condensation with formaldehyde:

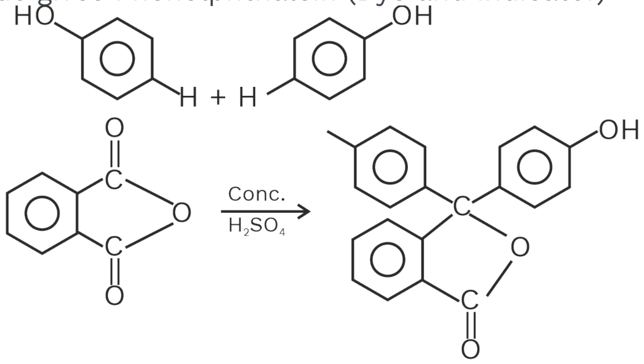
Phenol on condensation with HCHO gives Bakelite (Resin)



(Bakelite) plastic
thermosetting plastic

5. Condensation with Phthalic anhydride:

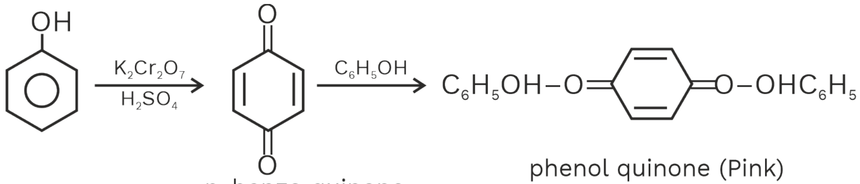
Phenol on condensation with phthalic anhydride gives Phenolphthalein (Dye and indicator)



Phenolphthalein (indicator)

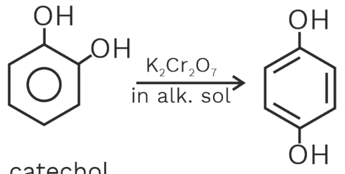
6. Oxidation:

Phenol on oxidation by different oxidants gives different products as follows:



p-benzo quinone

phenol quinone (Pink)



catechol

quinoline
or
Hydroquinone

- Both are antioxidants free radicals inhibitors usde in photography as developes because of strong reducing agent.

Test of Phenol

1. $C_6H_5OH \xrightarrow{FeCl_3}$ Violet colour product$(C_6H_5O)_3Fe$

2. Liebermann's Nitroso Reaction

$$C_6H_5OH \xrightarrow[\text{in excess of } H_2O_2]{NaNO_2} \text{Red} \xrightarrow[\text{Excess colouration}]{NaOH} \text{Blue colouration}$$

3. Phenol gives a blue coloured product on treacting with ammonia and sodium hypochlorite.

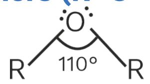
Concept Ladder

Oxidation of phenol with chromic acid produces a conjugate diketone known as benzoquinone.

Rack your Brain

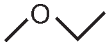
Name the reaction used in the treatment of phenol with chloroform in the presence of aqueous base?

Ethers (R–O–R)



- These are aryl or dialkyl derivatives of water, having a general formula $C_nH_{2n+2}O$.
- In simple ethers, both the aryl or alkyl groups
- are same.
- For ex. $C_6H_5-O-C_6H_5$, $C_2H_5-O-C_2H_5$,
- In mixed ethers, the two aryl or alkyl groups
- are different.

For example,

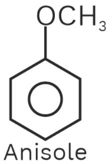


Methyl-ethyl ether, $CH_3-O-C_6H_5$

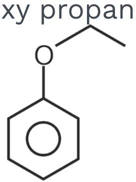
Nomenclature of Ethers

Ethers are named as alkoxy alkane. For example

$C_2H_5-O-C_2H_5$,	$CH_3-O-CH_2-CH_2-CH_3$
Ethoxy ethane	Methoxy propane



Anisole
(methoxy benzene)



Phenetole
(1-ethoxy benzene)

$CH_3-CH_2-O-CH_2CH(CH_3)_2$
Ethoxy 2-methyl propane

Isomerism Shown by Ethers

- Ethers are functional isomers of ethers and alcohols themselves show metamerism.

For example,

$C_2H_5-O-C_2H_5$ and $CH_3-O-CH_2-CH_2-CH_3$ are metamers.

$C_6H_5-CH_2-OH$ and $C_6H_5-O-CH_3$ are functional isomers.

Methods of Preparation

Williumson synthesis:

It is the best method for preparation of all type of ethers, i.e. simple, aromatic or mixed.

- Here for ether formation, alkyl halides in presence of magnesium, are treated with sodium alkoxide.

Definition

Ethers are a class of compounds which contain one divalent oxygen atom bonded to two monovalent alkyl groups (same or different).

Rack your Brain

Explain why ethers are dipolar in nature?t

Previous Year's Questions

The heating of phenyl methyl ether with HI produces

[NEET-2017]

(1) iodobenzene (2) phenol
(3) benzene (4) ethyl chloride

- The attack on R–X by R–O⁻, occurs from the rear side, i.e. it involves S_N2 mechanism.

Mechanism

$$R-X+R'-ONa \xrightarrow{\Delta, Mg} R'-O-R+NaX$$

$$R-OH+Na \longrightarrow R-ONa+H^+$$

$$R-ONa \longrightarrow R-O^- + Na^+$$

$$R-O^- + R'-X \xrightarrow{\Delta} \underset{\text{Unstable transition state}}{(R-O\cdots R'-X)} \xrightarrow{X} R'-O-R+Br^-$$

Concept Ladder

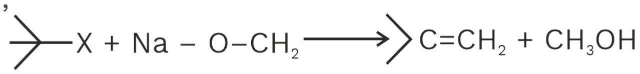
Williamson's ether synthesis reaction of alkyl halide with an alkoxide ion is still considered to be one of the best ways to synthesize an ether.

Example,

$$\underset{\text{Sodium ethoxide}}{C_2H_5-ONa}+C_2H_5Br \xrightarrow{\Delta, Mg} \underset{\text{Diethyl ether}}{C_2H_5-O-C_2H_5}+NaBr$$

- In case of tertiary halides, there is formation of an alkene takes place.

Ex.,



Rack your Brain

Write the order of dehydration of alcohols in the formation of ethers?

From R–X:

When an aryl or alkyl halide is treated with dry silver oxide, ether is formed as follows:

$$2\ R-X+Ag_2O \longrightarrow R-O-R+2\ AgX$$

Examples,

$$2C_2H_5Br+\text{dry } Ag_2O \xrightarrow{\Delta} C_2H_5-O-C_2H_5+2AgBr$$

$$CH_3Br+C_2H_5Br+Ag_2O \xrightarrow{\Delta} CH_3-O-CH_3+C_2H_5-O-C_2H_5+CH_3-O-C_2H_5$$

From alcohols:

Alcohols on dehydration, give ethers, depending upon the amount of alcohol used and the temperature condition employed.

(a) By dehydration of alcohols using concentrated sulphuric acid at 140°C, ethers are formed as follows:

Previous Year's Questions

Ethyl chloride is converted into diethyl ether by

[AIPMT]

(1) Perkins reaction
(2) Grignard reaction
(3) Wurtz synthesis
(4) Williamson's synthesis

$$R-OH+H_2SO_4\xrightarrow{\Delta}R-HSO_4+H_2O$$

$$R-HSO_4+R-OH\xrightarrow[140°C]{\Delta}R-O-R+H_2SO_4\,(1)$$

$$C_2H_5-OH+H_2SO_4\xrightarrow{\Delta}C_2H_5-HSO_4+H_2O$$

$$C_2H_5-HSO_4+C_2H_5-OH\xrightarrow[140°C]{\Delta}C_2H_5-O-C_2H_5+H_2SO_4$$

(b) At 250°C when vapours of an alcohol are passed over alumina or thoria, an ether is formed.

$$R-OH+R-OH\xrightarrow[250°C]{Al_2O_3}R-O-R+H_2O$$

Example,

$$C_2H_5-OH+C_2H_5-OH\xrightarrow[250°C]{Al_2O_3}\underset{\text{Diethyl ether}}{C_2H_5-O-C_2H_5}+H_2O$$

- Three different types of ether are formed, by using two different alcohols

Concept Ladder

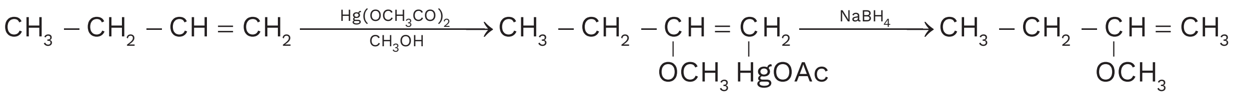
Higher members can be prepared by the action of Grignard reagents on lower halogenate ethers.

$$R-OH+R'-OH\xrightarrow[250°C]{Al_2O_3}R-O-R+R'-O-R'+R-O-R'+H_2O$$

By alkoxy mercuration-demercuration:

By the help of trifluoro mercuricacetate (mercuration) followed by reduction with NaBH4 (demercuration), alkenes undergo alkoxylation with alcohols.

According to Markovnikov's rule, addition can takes place here as follows:
Example,



$$CH_3-CH_2-CH=CH_2\xrightarrow[CH_3OH]{Hg(OCH_3CO)_2}CH_3-CH_2-\underset{OCH_3}{CH}-\underset{HgOAc}{CH_2}\xrightarrow{NaBH_4}CH_3-CH_2-\underset{OCH_3}{CH}=CH_3$$

Previous Year's Questions

Which one of the following compounds is resistant to nucleophilic attack by hydroxyl ions?

[AIPMT]

(1) Diethyl ether (2) Acetonitrile
(3) Acetamide (4) Methyl acetate

From grignard reagent

$$R-O-CH_2X+X'Mg-R'\longrightarrow R-O-CH_2-R'+X-Mg-X'$$

$$C_2H_5-O-CH_2Cl+Br=Mg-C_2H_5\longrightarrow\underset{\text{Methoxy propane}}{C_2H_5-O-CH_2-CH_2-CH_3}+MgBrCl$$

Synthesis of methoxy ethers:

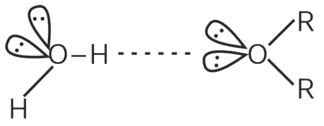
For formation of methoxy ethers, alcohol is treated with diazomethane.

$$R-OH+CH_2N_2 \xrightarrow{HBF_4} R-OCH_3+N_2$$

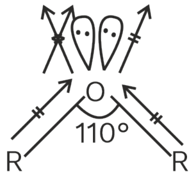
Diazomethane

Physical Properties of Ethers

- First 2 members of the ether family, i.e. diethyl ether and dimethyl ether are solids rest are liquids. Some aromatic ethers are solid.
- Ethers have a lower B.P.s than their corresponding isomeric alcohols, as they do not from H-bond like alcohols. For example, $C_2H_5OH > CH_3-O-CH_3$.
- Ethers are partially soluble in water beacause of formation of H-bonds with water as shown below:



- Ethers are weak Bronsted bases or Lewis bases, as the central atom O, has 2 lone pair of electrons to donate and it can accept H^+ ion also.
- Because of presence of lone pair of electrons on O atom, ethers have some value of dipole moment.



Concept Ladder

Ethers are lighter than water. Lower ethers are highly volatile and very inflammable.

Rack your Brain

The boiling point of ethers are close to the boiling point of ________.

Previous Year's Questions

The compound which does not react with sodium is

[AIPMT]

(1) CH_3COOH
(2) $CH_3CHOHCH_3$
(3) C_2H_5OH
(4) CH_3OCH_3

ETHERS

Ethers are a class of organic compounds that contain an oxygen between two alkyl or aryl groups. They have the formula R-O-R', where R and R' are alkyl groups. These compounds are used in dye, perfumes, oils, waxes and industrial use. Ethers are named as alkoxyalkanes.

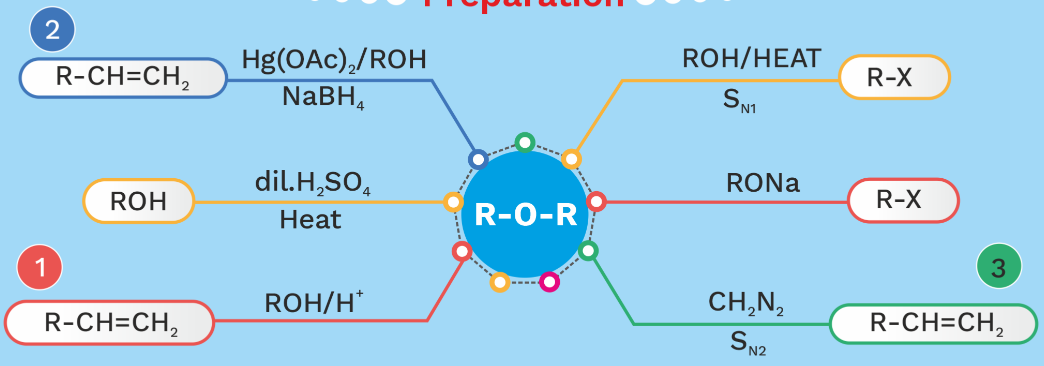
Nomenclature Of Ethers

Ethers are compounds having two alkyl or aryl groups bonded to an oxygen atom, as in the formula R,-O-R, The ether functional group does not have a characteristic IUPAC nomenclature suffix, so it is necessary to designate it as a substituent. To do so the common alkoxy substituents are given names derived from their alkyl component (below)

ALKYL GROUP	NAME	ALKOXY GROUP	NAME
CH_3^-	Methyl	CH_3O-	Methoxy
$CH_3CH_{2^-}$	Ethyl	$CH_3CH_2O^-$	Ethoxy
$(CH_3)_2CH^-$	Isopropyl	$(CH_3)_2CH^-$	Isopropoxy
$(CH_3)_3C^-$	Tert-Butyl	$(CH_3)_3CO^-$	Tert-Butoxy
$C_6H_5^-$	Phenyl	$C_6H_5O^-$	Phenoxy

Ethers can be named by naming each of the two carbon groups as a separate word followed by a space and the word ether. The - OR group can also be named as a substituent using the group name, alkoxy.

Preparation

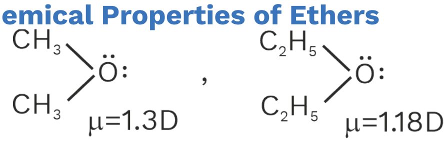


1 Procees via carbocation intermediate, rearrangement may take place.

2 Do not procees via carbocation intermediate, rearrangement is avoided.

3 Gives methyl ether ($RCH_2CH_2OCH_3$)

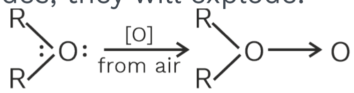
Chemical Properties of Ethers

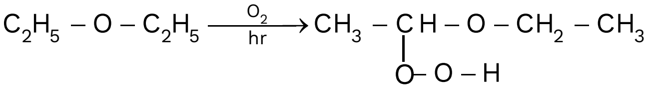


Ethers have inertness like alkanes. In normal conditions they are stable towards bases, hydrogenation, dil.acids etc. This is because of the fact that (—O—) does not have any a five site like –OH group.

Peroxide formation:

In the presence of light and ether can form peroxides. On heating these peroxides hydro peroxides, they will explode.





$$C_2H_5-O-C_2H_5 \xrightarrow[hr]{O_2} CH_3-\underset{\displaystyle O-O-H}{\underset{|}{C}}H-O-CH_2-CH_3$$

ethoxy ethyl hydroperoxide

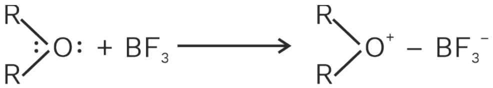
It is a free radical reaction occuring at adjacent C-atom to O-atom.

- When a small volume of ether is shaked with aq. KI solution, if peroxide is present the colour of the solution disappears.
- By washing ether with $FeSO_4$ solution followed by addition of KCNS it can be made free from peroxide ion.

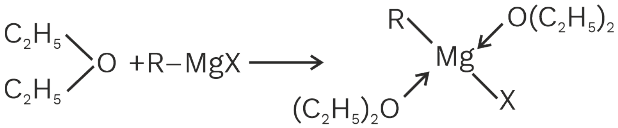
$$Fe^{+2} \xrightarrow[\text{oxide}]{\text{Per}} Fe^{3+} \xrightarrow{3CNS^-} \underset{\text{Blood Red colour}}{Fe(CNS)_3}$$

Reaction with lewis acids:

Ether are bases hence they can react with Lewis acids to form an adduct as follows:



Stable complexes



Grignard Reagent

Concept Ladder

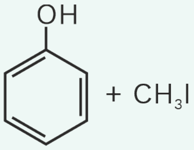
With strong oxidising agents like acid dichromate, ethers are oxidised to aldehydes and then to acetic acid.

Previous Year's Questions

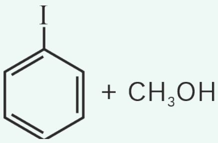
Anisole on cleavage with HI gives

[NEET-2020]

(1)



(2)



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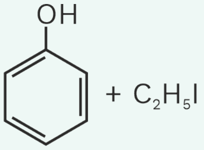
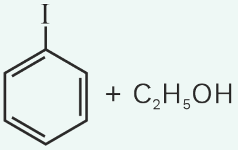


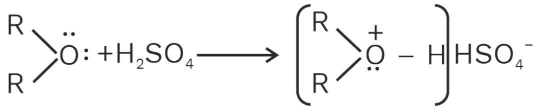
(4)



Formation of oxonium salts:

Ethers being lewis bases (due to 2 lp electrons) Can easily react with cold concentrated inarganic acids to form stable oxonium salts.

Di alkyl oxonium halide



Di alkyl oxonium hydrogen sulphate

Reaction with sulphuric acid

With dilute sulphuric acid:

When ethers are heated with dil. H2SO4, give alcohols. For two type of alcohols are to be formed, mixed ethers are used.

$$R-O-R+H-OH\xrightarrow{dil.H_2SO_4}2R-OH$$

Examples,

$$C_2H_5-O-C_2H_5+H-OH\xrightarrow{dil.H_2SO_4}2C_2H_5-OH$$

$$R-O-R'+H-OH\xrightarrow{dil.H_2SO_4}R-OH+R'-OH$$

Examples,

$$CH_3-O-C_2H_5+H-OH\xrightarrow{dil.H_2SO_4}CH_3-OH+C_2H_5-OH$$

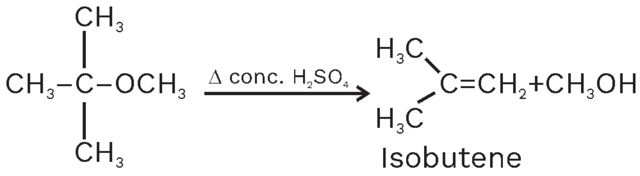
If temp. is kept low, oxonium salt is formed.

$$C_2H_5OC_2H_5+H_2SO_4\longrightarrow[(C_2H_5)_2OH]^+HSO_4^-$$

With hot and conc. H_2SO_4:

The products alkene and alcohols are formed as ethers undergo elimination and is mainly given by secondary and tertiary ethers.

Example,



Methyl tertiary butyl ether

Rack your Brain

Ethers are relatively inert, justify.

Concept Ladder

Ethers can form coordination complexes with Lewis acids like BF_3, $AlCl_3$, etc. As the ether are Lewis bases, they easily coordinate to form complexes known as etherates.

Rack your Brain

Explain how formation of peroxide in ethers can be prevented?

Reaction with halogen acids:

Ethers can be cleaved when treated with HBr or HI as follows:

$$R-O-R+H-X \xrightarrow[\text{dil.\&cold}]{} R-X+R-OH$$

$$R-OR+2H-X \xrightarrow[\text{Hot\&amount}]{\Delta} 2R-X+H_2O$$

- The order of reactivity for halogen acids are as follows: HI > HBr > HCl.

$$C_2H_5-OC_2H_5+\underset{\text{cold}}{HI} \xrightarrow{\Delta} C_2H_5OH+C_2H_5I$$

$$C_2H_5-OC_2H_5+\underset{\text{Hot}}{2HI} \xrightarrow{\Delta} 2C_2H_5I+H_2O$$

- When a mixed ether is used in above reaction, X– is taken with smaller alkyl group.

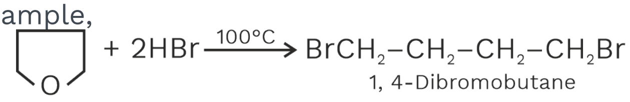
Example,

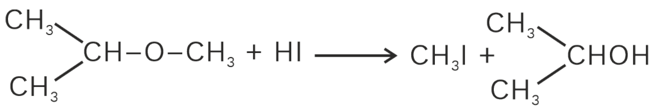
$$\underset{\text{Anisole}}{C_6H_5-OCH_3}+HI \xrightarrow{\Delta} C_6H_5-OH+CH_3I$$

$$CH_3I \xrightarrow{AgNO_3} \underset{\text{Yellow ppt}}{AgI}$$

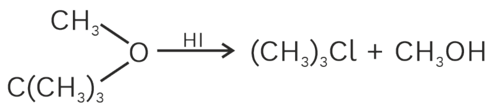
- The above method is known as **Zeisel method**. It is used to find the no. of alkoxy groups in an ether.
- Cyclic ethers can be cleaved by increasing the temperature to 100°C by heating.

Example,





$$(CH_3)_2CH-O-CH_3+HI \longrightarrow CH_3I+(CH_3)_2CHOH$$



$$CH_3-O-C(CH_3)_3 \xrightarrow{HI} (CH_3)_3CI+CH_3OH$$

Here, because of formation of a stable tertiary carbocation, I– is reacted with a large alkyl group.

Concept Ladder

In reaction with HI, if cold and dilute HI solution is treated with ether, alcohols are formed while in hot and concentrated HI, alkyl halides are formed.

Rack your Brain

Explain why conc. HF cannot be used to cleave ether?

Previous Year's Questions

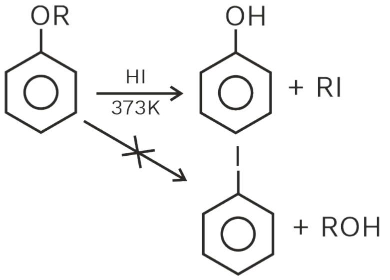
Among the following ethers, which one will produce methyl alcohol on treatment with hot concentrated HI?

[NEET-2013]

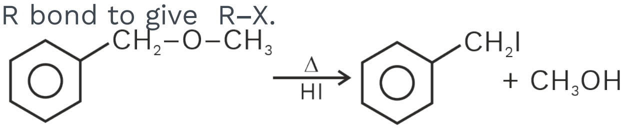
(1) $(CH_3)_3COCH_3$
(2) $(CH_3)_2CH_2OCH_3$
(3) $CH_3CH_2CH_2OCH_3$
(4) $CH_3CH_2(CH_3)CHOCH_3$

When this reaction is carried out with anhyd. HI in ether, the reaction forms are as follows:

$$(CH_3)_3C-OCH_3 \xrightarrow[ether]{HI} CH_3I + (CH_3)_3COH$$



As protonation of C_6H_5OR gives . Here, $C_6H_5-\underset{\substack{| \\ H}}{\overset{+}{O}}-R$ bond is weaker than C_6H_5–O bond because of presence of resonance and double bond character in O–C_6H_5. It means X– attacks on weak O–R bond to give R–X.



Acylation by R–COCl or $(R–CO)_2O$:

Esters are formed when ethers are treated with acid anhydrides or acid chlorides in presence of anhyd. $ZnCl_2$. A mixture of esters is formed by using a mixed ether as a reactant.

Concept Ladder

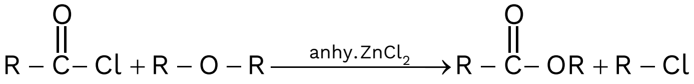
If mixture of two alcohols is subjected to dehydration with Al_2O_3 at 250°C or conc. H_2SO_4 at 140°C, then unsymmetrical ethers can not be obtained buty we get mixture of three ethers.

Previous Year's Questions

The compound that is most difficult to protonate is **[NEET-2019]**

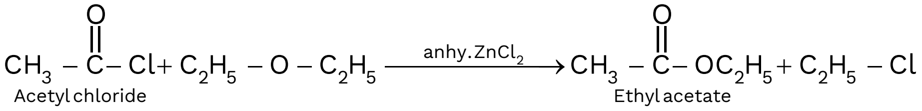
(1) PH—O—H (2) H—O—H

(3) H_3C—O—H (4) $H_3C—O—CH_3$

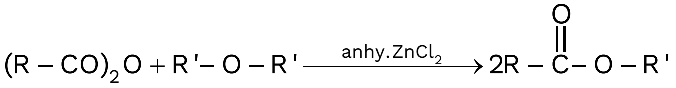


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + R-O-R \xrightarrow{anhy.ZnCl_2} R-\overset{\overset{\displaystyle O}{\|}}{C}-OR + R-Cl$$

Example,

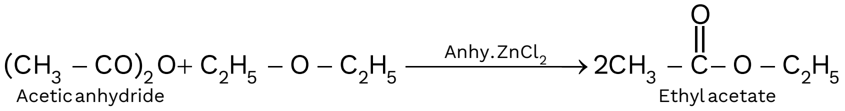


$$\underset{\text{Acetyl chloride}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-Cl} + C_2H_5-O-C_2H_5 \xrightarrow{anhy.ZnCl_2} \underset{\text{Ethyl acetate}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OC_2H_5} + C_2H_5-Cl$$



$$(R-CO)_2O + R'-O-R' \xrightarrow{anhy.ZnCl_2} 2R-\overset{\overset{\displaystyle O}{\|}}{C}-O-R'$$

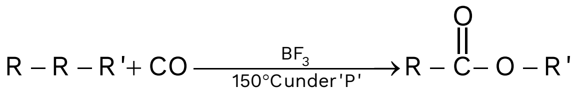
Example,



$$\underset{\text{Acetic anhydride}}{(CH_3-CO)_2O} + C_2H_5-O-C_2H_5 \xrightarrow{Anhy.ZnCl_2} \underset{\text{Ethyl acetate}}{2CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-C_2H_5}$$

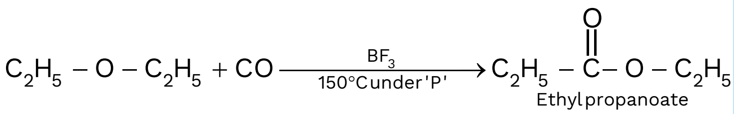
Reaction with carbon monoxide:

Ethers reacts with CO to form esters as follows:



$$R-R-R'+CO \xrightarrow[150^\circ C\text{ under }'P']{BF_3} R-\overset{O}{\overset{\|}{C}}-O-R'$$

Example,



$$C_2H_5-O-C_2H_5+CO \xrightarrow[150^\circ C\text{ under }'P']{BF_3} \underset{\text{Ethyl propanoate}}{C_2H_5-\overset{O}{\overset{\|}{C}}-O-C_2H_5}$$

Reaction with PCl_5

$$R-O-R+PCl_5 \xrightarrow{\Delta} 2R-Cl+2POCl_3$$

$$C_2H_5-O-C_2H_5+PCl_5 \xrightarrow{\Delta} 2C_2H_5-Cl+2POCl_3$$

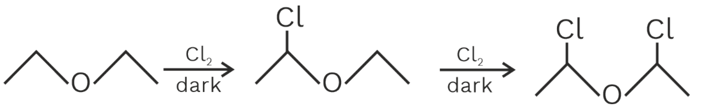
$$R-O-R'+PCl_5 \xrightarrow{\Delta} R-Cl+R'-Cl+2POCl_3$$

Example,

$$CH_3-O-C_2H_5+PCl_5 \xrightarrow{\Delta} CH_3-Cl+C_2H_5-Cl+2POCl_3$$

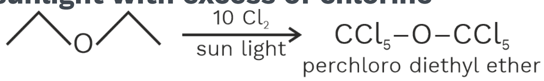
Halogenation:

The reaction of ethers with chlorine are as follows: In dark



1, 1'-Dichloro ethyl ethe

In sunlight with excess of chlorine



perchloro diethyl ether

Dehydration of ether

$$C_2H_5-O-C_2H_5 \xrightarrow[360^\circ C]{Al_2O_3} 2CH_2=CH_2+H_2O$$

Concept Ladder

A small amount of sulphuric acid is sufficient for the conversion of large amounts of alcohol to ether, this method is termed as continuous etherification process and pure ether colected at 34-35°C is called absolute etther.

Previous Year's Questions

Which one is formed when sodium phenoxide is heated with ethyl iodide?

[AIPMT]

(1) Phenetole
(2) Ethyl phenyl alcohol
(3) Phenol
(4) None of these

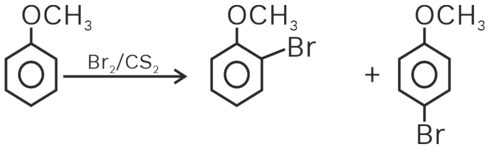
Electrophilic substitution reaction of aromatic ether

Aromatic ethers like anisole give reactions like halogenation, nitration.

Concept Ladder

Aromatic ethers are relatively less reactive towards electrophilic ring substitution than phenols.

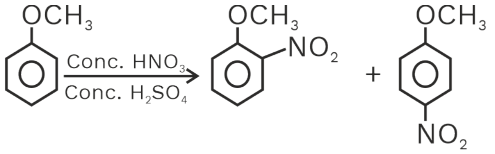
Bromination



(31%) ortho bromoanisole

(67%) para bromoanisole

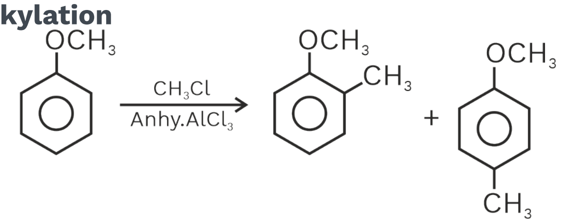
Nitration



(31%) ortho nitroanisole

(67%) para nitroanisole

Alkylation

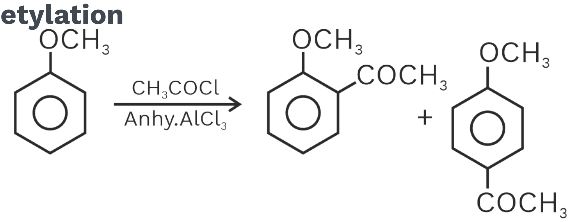


o, p-methyl-anisol

Rack your Brain

Draw resonating structures of alkoxybenzene.

Acetylation



o, p-methoxy acetophenone

Uses of Ethers

- Ethers are used as anesthetic agents and solvents.
- Dr William Mortan discovers the anesthetic nature of ethers.
- It is used as a reaction medium in the reduction reactions of LiAlH$_4$.
- It is used in the prepration organo metallic compounds like R–MgX.
- Polyethers (carbo–waxes) are highly solube in water beacause of multiple H-bond formation with it.
- R–X can be replaced by R–OSO$_2$R’ in Williamson synthesis.

Q.1 Name the factors responsible for the solubility of alcohols in water.

A.1 For the solubility of alcohols in water the responsible factors are :
(I) Hydrogen bonds
(II) Size of the alkyl or aryl groups
(III) The molecular mass of the Alcohols.

Q.2 What is denatured alcohol?

A.2 By mixing alcohol with some copper sulfate and pyridine, that are used for drinking are made unfit for human consumption, which gives the colour and a foul smell to the liquid respectively. This is called denatured alcohol.

Q.3 Out of 2-chloroethanol and ethanol which is more acidic and why?

A.3 Due to the presence of chlorine (an electron-withdrawing group), 2-chloroethanol becomes more acidic. This results in a negative inductive effect and thus, the electron density in the –O-H bond decreases. It stabilizes the alkoxide ion and therefore, 2-chloroethanol can easily release a proton.

Q.4 Suggest a reagent for conversion of ethanol to ethanal.

A.4 Pyridinium chlorochromate (PCC) can be used as reagents. The above conversion shows the oxidation of primary alcohol to an aldehyde.

Q.5 Suggest a reagent for conversion of ethanol to ethanoic acid.

A.5 For the above conversion acidified $KMnO_4$ can be used as a reagent. The above conversion shows the oxidation of primary alcohol to a carboxylic acid.

Q.6 Out of o-nitrophenol and p-nitrophenol, which is more volatile? Explain.

A.6 The o-nitrophenol is more volatile because of the presence of intramolecular hydrogen bonding between NO_2 and OH group.

Q.7 Out of o-nitrophenol and o-cresol which is more acidic?

A.7 In orth-nitrophenol due to the presence of an electron-withdrawing group NO_2 at ortho position, the acidic strength is enhanced and becomes more acidic. There is decrease in acidic strength due to the presence of an electron releasing group in o-cresol.

Q.8 Arrange the following compounds in increasing order of acidity and give a suitable explanation. Phenol, o-nitrophenol, o-cresol

A.8 o-cresol < Phenol < o-nitrophenol is the increasing order of the acidity of the given compounds. Due to the presence of the electron-withdrawing group, NO_2 o-nitrophenol becomes more acidic. Remaining has an electron releasing group which de- creases the acidic strength.

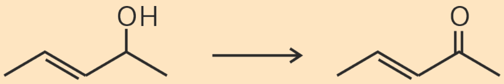
Q.9 Alcohols react with active metals e.g. Na, K etc. to give corresponding alkoxides.
Write down the decreasing order of reactivity of sodium metal towards primary, secondary and tertiary alcohols

A.9 Due to the steric hindrance property of the alkyl groups and for the hydroxyl bond there is increase in the electron density on an oxygen atom, the reactivity of sodium metal towards tertiary alcohols is lowest.
Primary alcohols > secondary alcohols > tertiary alcohols is the decreasing order of reactivity of sodium metal towards alcohols.

Q.10 What happens when benzene diazonium chloride is heated with water?

A.10 When benzene diazonium chloride is heated with H_2O, Phenol is formed along with the hydrochloric acid, nitrogen gas and by-products.

Q.11 Suggest a reagent for the following conversion.



A.11 The oxidation of secondary alcohol in a ketone is shown by above chemical reaction. It can be easily achieved by using oxidizing agents like Pyridinium chlorochromate (PCC), chromic anhydride (CrO_3), etc.

Q.12 Name the enzymes and write the reactions involved in the preparation of ethanol from sucrose by fermentation.

A.12 Invertase and zymase are the names of the enzymes involved in the preparation of ethanol from sucrose by fermentation. Invertase converts sucrose into glucose and fructose. Then, glucose and fructose undergo fermentation in the presence of zymase and ethanol is produced.

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

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

Q.13 How can propane-2-one be converted into tert-butyl alcohol?

A.13 In the presence of Grignard reagent, propane-2-one is treated with CH3MgBr, followed by the hydrolysis to yield tert- butyl alcohol.

Q.14 Explain why the OH group in phenols is more strongly held as compared to OH group in alcohols.

A.14 In phenol the –OH group is directly attached to the sp2-hybridized carbon atom of the benzene ring. The carbon-oxygen bond length in alkyl alcohol is greater as compared to the carbon-oxygen bond length in phenol and this is due to the partial double bond character or due to the resonance and charge distribution in phenol.

Q.15 Explain why nucleophilic substitution reactions are not very common in phenols.

A.15 The o- and p-positions in the benzene ring becomes electron-rich due to the presence of resonance and therefore, activates it towards electrophilic substitution reaction. Therefore, nucleophilic substitution reactions are not very common in phenols.

Q.16 Explain why is O=C=O nonpolar while R—O—R is polar.

A.16 O=C=O is nonpolar because in C=O bonds the dipole moment of the two is exactly equal and opposite of each other. Hence, they cancel each other and so, the net dipole moment of O=C=O is zero.

Q.17 Why is the reactivity of all the three classes of alcohols with conc. HCl and $ZnCl_2$ (Lucas reagent) different?

A.17 Due to steric hindrance of the alkyl group and the stability of carbocation, the reactivity of all three classes of alcohols with conc. HCl and $ZnCl^2$ (Lucas reagent) differed.

Due to least stability of 1° carbocation the primary alcohol does not show any reaction at room temperature.

On heating, turbidity appears in secondary alcohol which is not shown at room temperature.

Higher stability of the carbocation causes tertiary alcohol to show turbidity after addition of Lucas reagent .

Q.18 Write steps to carry out the conversion of phenol to aspirin.

A.18 Phenoxide ion is prodused when phenol is treated with NaOH. It is then undergoes electrophilic substitution with CO_2 to yield salicylic acid as the major product. This is called Kolbe's reaction.

Q.19 In Kolbe's reaction, instead of phenol, phenoxide ion is treated with carbon dioxide. Why?

A.19 Due to high reactivity of electrophilic aromatic substitution towards phenoxide ion, phenoxide ion is treated with carbon dioxide, instead of phenol, in Kolbe's reaction.

Q.20 The dipole moment of phenol is smaller than that of methanol. Why?

A.20 Due to the electron-withdrawing effect of the phenyl ring, so by resonance, the polarity of the C—O bond in phenol decreases, the dipole moment of phenol is smaller than that of methanol.

Q.21 Ethers can be prepared by Williamson synthesis in which an alkyl halide is reacted with sodium alkoxide. Di-tert-butyl ether can't be prepared by this method. Explain.

A.21 Di-tert-butyl ether can't be prepared by the above given method because in this case, elimination is more favoured over substitution.

Q.22 Why is the C—O—H bond angle in alcohols slightly less than the tetrahedral angle whereas the C—O—C bond angle in ether is slightly greater?

A.22 Due to the repulsion between the unshared pair of electrons or the lone pair of electrons on the oxygen atom, the C—O—H bond angle in alcohols is slightly less than the tetrahedral angle.

Summary

- $LiAlH_4$ and $NaBH_4$ are highly specific reducing agents which reduce different organic compounds (e.g.-acid, aldehyde, ketone, ester) to correspondign alcohol without attacking double bond. But if double bond is present in conjugation with benzene ring aldehyde group is also reduced along with —C=C— group.
- C_2H_5OH (or grain alcohol) is present in beverages. 100% ethyl alcohol is called absolute alcohol. It is drinking alcohol.
- Rectified spirit is C_2H_5OH (95.87%) + H_2O (4.13%).
- Denatured spirit is C_2H_5OH + 5-10% CH_3OH (it is not fit for drinking). In place of CH_3OH pyridinie or $CuSO_4$ is also used to denature C_2H_5OH.
- Power alcohol is mixture of absolute alcohol and petrol in 1 : 4 ratio with cosolvent benzene. It is used for running automobiles.
- Test for alcohols : Alcohol + ceric ammonium nitrate → Pink/red colouration.
- 3° alcohols are resistant to oxidation.
- Alcohols can't be dried over $CaCl_2$ because they form addition compound, $CaCl_2.4CH_3OH$ with it.
- Order of acidity $H_2O > 1°$ alcohol > 2° alcohol > 3° alcohol > $RCH \equiv CH > RCH_3$.
- CH_3OH is obtained by destructive distillation of wood. It is poisonous and causes permanent blindness.
- Pyroligneous acid has 10% CH_3COOH + CH_3OH 2.5%, and CH_3COCH_3 0.5%.
- Fusel oil is last fraction obtained during distillation of fermented alcohol. It mainly contains n-propyl alcohol, isobutyl aocohol and isoamyl alcohol.
- Aqueous solution of phenol is called carbolic acid.
- Phenol is obtained from middle oil fraction of coal-tar distillation.
- Acidic strengths of isomeric phenols :

  (i) Phenols having electron withdrawing groups p > o > m.

  (ii) Phenols having electron donating group m > p > o.
- $:CCl_2$ is reaction intermediate o Reimer Tiemann reaction.
- Crown ethers are condensation polymers of eethylene glycol. They are in fact heterocyclic ethers having at least 4 oxygen atoms.
- Dynamite is glyceryl trinitrate absorbed on keiselguhr.
- Glycerol trinitrate also known as Nobel’s oil, is a colourless, oily liquid and an inorganic ester. It is used in the treatment of asthma and pectoris.