ALCOHOL & ETHERS

Hydroxy derivatives

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Aliphatic hydroxy derivatives | Aromatic hydroxy derivatives

(I) Aliphatic hydroxy derivatives :

Hydroxy derivatives in which —OH is directly attached to sp^3 C (Alcoholic compounds).

(II) Aromatic hydroxy derivatives :

Hydroxy derivatives in which —OH is directly attached to sp^2 C of benzene ring (Phenolic compounds).

Aliphatic hydroxy derivatives :

(a) Classification according to number of —OH groups :

(i) Monohydric [one –OH] ⟶ $CH_3CH_2—OH$

(ii) Dihydric [two –OH] ⟶ $CH_2(OH)—CH_2(OH)$ Glycol

(iiii) Trihydric [three –OH] ⟶ $CH_2(OH)—CH(OH)—CH_2(OH)$ Glycerol

(iv) Polyhydric [n –OH] ⟶ $CH_2(OH)-(CHOH)_4-CH_2(OH)$ Sorbitol

GENERAL METHODS OF PREPARATION

(1) From alkenes :

(i) By hydration :

$$CH_3—CH=CH_2 \xrightarrow[H_2O]{H^{\oplus}} CH_3—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_3$$

(ii) By hydroboration oxidation :

$$CH_3—CH=CH_2 \xrightarrow[(ii)H_2O_2/HO^{\ominus}]{(i)\ B_2H_6/THF} CH_3—CH_2—\underset{\displaystyle OH}{\underset{|}{CH_2}}$$ (1° alcohol)

Mechanism :

Takes place by Anti Markownikov Rule in presence of H_2O_2

Firstly formed trialkyl borane by Cis cyclic addition which convert in alcohol by oxidation with H_2O_2 /OH^-

(iii) By oxymercuration demercuration :

$$CH_3—CH=CH_2 \xrightarrow[(ii)\,NaBH_4,HO^{\ominus}]{(i)\,Hg(OAc)_2,H_2O} CH_3—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_3$$

(2) From alkyl halides (By hydrolysis) :

$$CH_3—CH_2—Cl \xrightarrow[\text{or Moist } Ag_2O]{\text{Aq. KOH}} CH_3CH_2—OH$$

(3) From ethers :

$$R—O—R \xrightarrow{dil.H_2SO_4} R—OH + R—OH$$

$$CH_3—O—CH_2CH_3 \xrightarrow{dil.H_2SO_4} CH_3—OH + CH_3CH_2—OH$$

(4) From carbonyl compounds (By reduction) :

$$>C=O \xrightarrow{\text{Reducing agent}} >CH—OH$$

◆ Reducing agents may be,

$LiAlH_4$/protic solvent, $NaBH_4$/protic solvent

Na + EtOH [Bouveault-blanc Reduction]

Ni/H_2

$$R—CHO \xrightarrow[\text{protic solvent}]{LiAlH_4} R—CH_2—OH$$

$$R—\underset{\displaystyle O}{\underset{\|}{C}}—R \xrightarrow[\text{protic solvent}]{NaBH_4} R—\underset{\displaystyle OH}{\underset{|}{CH}}—R$$

$$CH_3—\underset{\displaystyle O}{\underset{\|}{C}}—CH_3 \xrightarrow[\text{protic solvent}]{LiAlH_4} CH_3—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_3$$

(5) From acid and derivatives (By reduction) :

$$R—COOH \xrightarrow[H^{\oplus}]{LiAlH_4} R—CH_2—OH + H_2O$$

$$R—\underset{\displaystyle O}{\underset{\|}{C}}—Cl \xrightarrow[H^{\oplus}]{LiAlH_4} R—CH_2—OH + HCl$$

$$R—\underset{\displaystyle O}{\underset{\|}{C}}—OR \xrightarrow[H^{\oplus}]{LiAlH_4} R—CH_2—OH + R—OH$$

$$R—\underset{\displaystyle O}{\underset{\|}{C}}—O—\underset{\displaystyle O}{\underset{\|}{C}}—R \xrightarrow[H^{\oplus}]{LiAlH_4} R—CH_2—OH + R—CH_2—OH$$

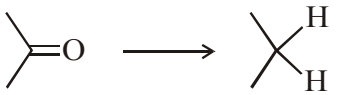
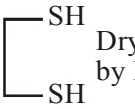
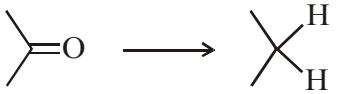
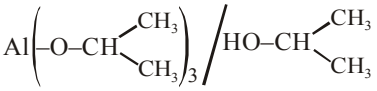
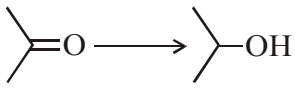
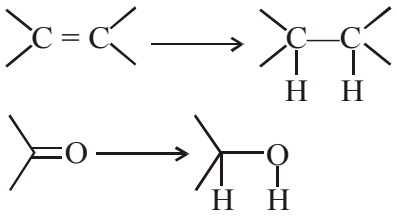
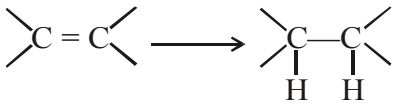
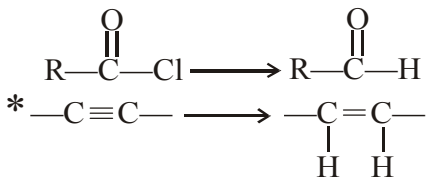
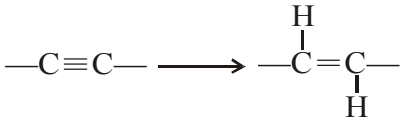
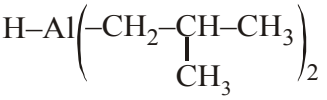
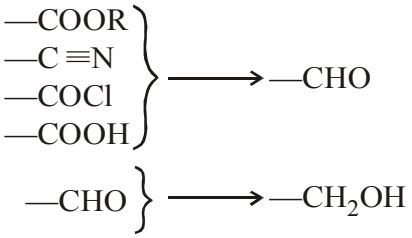
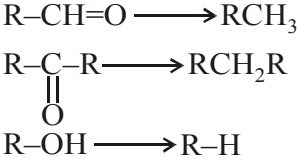
** $R—\underset{\displaystyle O}{\underset{\|}{C}}—NH_2 \xrightarrow[H^{\oplus}]{LiAlH_4} R—CH_2—NH_2 + H_2O$

** Amide gives amine (not alcohol) with $LiAlH_4$

Chart-1

REDUCING AGENTS AND THEIR ROLE

Group	Product	LAH in Ether	$NaBH_4$ in H_2O	B_2H_6 in THF	H_2 / Catalyst Δ
–CHO	$–CH_2OH$	+	+	+	+
>C = O	>CH – OH	+	+	+	+
$–CO_2H$	$–CH_2OH$	+	–	+	–
$–CO_2R$	$–CH_2OH$	+	–	+	+
–COCl	$–CH_2OH$	+	+	–	+
$–CONH_2$	$–CH_2NH_2$	+	–	+	+
$(RCO)_2O$	RCH_2OH	+	–	+	+
–CN	$–CH_2NH_2$	+	–	+	+
>C = NOH	$–CH_2NH_2$	+	–	–	+
>C = C<	>CH – CH<	–	–	+	+
–C ≡ C–	–CH = CH–	–	–	+	+
1° RX	RH	+	–	–	+

Name	Reagent	Function
Wolf Kishner Reduction	(i) N_2H_4 / (ii) KOH, Δ	
Clemenson Reduction	Zn–Hg / HCl	
Mozingo Reduction	 Dry HCl, followed by Raney Ni	
Stephen's Reduction	$SnCl_2$ / HCl followed by H_3O^+	$R–C\equiv N \longrightarrow R–CH=O$
MPV Reduction		
Hydroboration Reduction	B_2H_6 / AcOH, H_2O	
Bouvoult Blank Reduction	Na / EtOH	$R–COO–R \longrightarrow RCH_2OH + ROH$
Transfer Hydrogenation	N_2H_4 / H_2O_2	
Rosenmund Reduction	H_2, Pd–$BaSO_4$	
Birch Reduction	Na / Liq. NH_3	
DIBAL-H	 followed by $H_3O^{\oplus}$	
Red phosphorus in presence of HI	Red P + HI	

(6) From hydrolysis of ester

$$R-\underset{\underset{O}{\|}}{C}-OR' + H_2O \xrightarrow{\ominus OH} R-\underset{\underset{O}{\|}}{C}-O^{\ominus} + R'OH \quad \text{(irreversible)}$$

$$R-\underset{\underset{O}{\|}}{C}-OR' + H_2O \underset{}{\overset{H^+}{\rightleftharpoons}} R-\underset{\underset{O}{\|}}{C}-OH + R'OH \quad \text{(acidic hydrolysis is reversible)}$$

Note : (i) Hydrolysis of ester can be catalysed by acid/base.

(ii) Acid cataalysed hydrolysis of ester is reversible.

(iii) Base catalysed hydrolysis of ester is called saponification

(7) From primary amines :

$$R—NH_2 \xrightarrow[\text{or } HNO_2]{NaNO_2+HCl} R—OH + N_2 + H_2O$$

Example : $CH_3CH_2—NH_2 \xrightarrow{HNO_2} CH_3CH_2—OH + N_2 + H_2O$

Ex. $CH_3CH_2CH_2—NH_2 \xrightarrow{NaNO_2+HCl} CH_3—\underset{\underset{OH}{|}}{CH}—CH_3$

Exception : $CH_3-NH_2 \xrightarrow{HNO_2} CH_3-O-CH_3$

GRIGNARD REAGENT RMgX

(8) From Grignard reagent :

Now we need to learn chemistry of Grignard reagent

(A). Organometallic compounds

Organometallic compounds are the organic compounds in which a metal atom is directly attached to carbon of organic molecules through covalent bond or ionic bond. For example

$C-M$ or $\overset{\ominus}{C}\ \overset{\oplus}{M}$

(Where C is a carbon atom of an organic molecule and M is a metal atom)

If the metal atom is attached to oxygen, nitrogen. sulphur, etc., then such an organic compound is not regarded as an organometallic compound. The following structural formula do not belong to the family of organometallic compounds.

RONa (Sodium alkoxide). CH_3COONa (Sodium acetate), CH_3COOAg(Silveracetate),RSK (Potassium mercaptide) RNHK

(N-Alkylpotassamide), $(CH_3COO)_4Pb$ (Lead tetraacetate), etc.

Note : It should be noted that $(CH_3)_4Si$ (Tetramethylsilane, TMS) is also not an organometallic compound because silicon is a nonmetal.

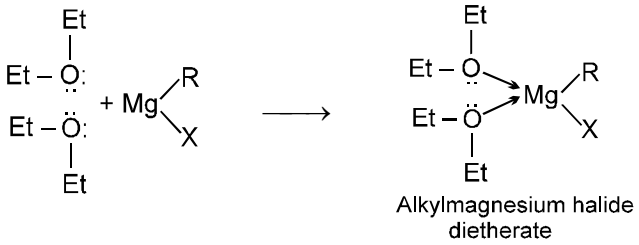
Most important examples of organometallic compounds are Grignard reagents. In Grignard reagent, the carbon and magnesium atoms are bonded with each other through polar covalent bond and magnesium atom is attached to halogen by ionic bond.

$>C-\overset{\oplus}{Mg}\ \overset{\ominus}{X}$ (Functional part of a Grignard reagent molecule)

(B) Preparation of Grignard Reagent

$$RX + Mg \xrightarrow[\text{Ether}]{\text{Dry and pure}} RMgX$$

Ether is used as a solvent because it is a Lewis base that donates its lone pair of electrons to electron-deficient magnesium atom, therefore providing stability to the Grignard reagent by completing the octet on magnesium atom.



(C) Reactions of Grignard reagents

It has been found out by estimation that there is 35% ionic character in carbon-magnesium bond of Grignard reagent. Therefore, there is a tendency of forming carbanion by heterolysis of this polar coordinate bond as follows.

$$R \leftarrow \overset{\oplus}{Mg}\overset{\ominus}{X} \longrightarrow \overset{\ominus}{R}: + \overset{2\oplus}{Mg}\overset{\ominus}{X}$$

The carbanion (a nucleophile) formed as shown above, attacks the positively charged electrophilic centre of other compound. Therefore. It can be said that if a Grignard reagent is regarded as the substrate, then electrophile displaces MgX, i.e. electrophilic substitution (S_E) reaction takes place.

$$R - MgX \longrightarrow \overset{\ominus}{R}: \xrightarrow{\overset{\oplus}{E}} R - E \ (S_E \text{ Product})$$

Grignard reagents form adducts by addition on the following types of pi bonds.

$$>C = O,\ >C = S,\ >C = N \text{ and } C \equiv N\ ,\ -N = O,\ >S = O$$

eg. $R - MgX + >C = O \longrightarrow R - \underset{\text{Adduct}}{\overset{|}{\underset{|}{C}}} - OMgX$

(D) Synthetic importance of Grignard reagents

(a) Synthesis of Alkanes

(i) With compounds having reactive hydrogen atom

General reaction :

$$R - MgX + H - Z \longrightarrow R - H + ZMgX$$

$$CH_3 - MgX + H - OH \longrightarrow CH_3 - H + Mg(OH)X$$

$$C_2H_5 - MgX + H - OR \longrightarrow C_2H_5 - H + Mg(OR)X$$

$$CH_3 - MgX + H - C \equiv CR \longrightarrow CH_3 - H + R - C \equiv C - MgX \text{ (Alkynylmagnesium halide)}$$

Methane gas is released on reacting methylmagnesium iodide with a compound containing reactive hydrogen atom. The reaction is used for estimation of reactive hydrogen atoms present in a molecule. This method is called **Zerewitinoff's** method of estimation of reactive hydrogen atoms.

(ii) With alkyl halide (coupling) :

$$R - MgX + X' - R' \longrightarrow R - R' + MgXX'$$

(b) Synthesis of alkenes

$$R - MgX + X' - \underset{\text{Allyl halide}}{CH_2 - CH = CH_2} \longrightarrow R - CH_2 - CH = CH_2 + MgXX'$$

(c) Synthesis of higher alkynes

Non-terminal alkynes

$$R' C \equiv C - H \xrightarrow[-RH]{RMgx} R' - C \equiv CMgX \xrightarrow[-MgX_2]{R''X} R' - C \equiv C - R''$$

(d) Synthesis of other organometallics

$$4R - MgCl + 2PbCl_2 \longrightarrow R_4Pb + Pb + 4MgCl_2$$

Two important antiknocking compounds, tetraethyllead (T.E.L.) and tetramethyllead (T.M.L.) are manufactured by the above reaction.

$$2R - MgCl + HgCl_2 \longrightarrow \underset{\text{Diallkylmercury}}{R - Hg - R} + 2MgCl_2$$

$$2R - MgCl + CdCl_2 \longrightarrow \underset{\text{Diallkylcadmium}}{R - Cd - R} + 2MgCl_2$$

$$4R - MgCl + SnCl_4 \longrightarrow \underset{\text{Tetraalkyltin}}{R_4Sn} + 4MgCl_2$$

(e) Synthesis of Alcohols

There are following methods to obtain alcohols from Grignard reagent.

(i) From carbonyl compounds

$$R - MgX + \diagdown\!\!\diagup C = O \longrightarrow R - \underset{|}{\overset{|}{C}} - OMgX \xrightarrow{HOH} \underset{\text{alcohol}}{R - \underset{|}{\overset{|}{C}} - OH}$$

This is nucleophilic addition reaction

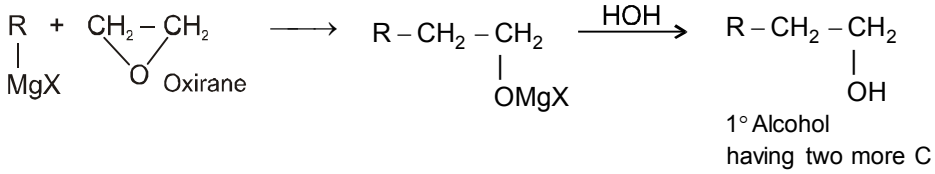
(ii) From Ester :

Tertiary alcohols are also obtained on hydrolysis of the product obtained by taking excess of Grignard reagent and an ester of a higher homologue of formic acid.

$$\underset{MgX}{\overset{R}{|}} + \underset{O}{\overset{R}{\underset{||}{C}}} - OEt \longrightarrow R - \underset{O^{-}MgX^{+}}{\overset{R}{\underset{|}{C}}} - OEt \xrightarrow{-Mg(OEt)X} R - \underset{O}{\overset{R}{\underset{||}{C}}} \xrightarrow[H_2O]{RMgX} R - \underset{OH}{\overset{R}{\underset{|}{C}}} - R$$

Various alcohols can be prepared by changing R in the above synthesis.

(iii) From Epoxides



(iv) From Oxygen

Synthesis of alcohol

$R - MgX + O = O \longrightarrow R - O - O - MgX$

$R - O - O - MgX + R - MgX \longrightarrow 2R - O - MgX$

$R - O - MgX + HOH \longrightarrow R - O - H + Mg(OH)X$

Primary, secondary and tertiary alcohols can be obtained by above reaction

From Alkyl Cyanides

A ketimine is formed on hydrolysis of the adduct obtained by the reaction of Grignard reagent and an alkyl cyanide, which gives ketone on further hydrolysis.

$$RMgX + RCN \longrightarrow \underset{}{R_2C = NMgX} \xrightarrow{HOH} \underset{\text{Ketimine}}{R_2C = NH} \xrightarrow{HOH} \underset{\text{Ketone}}{R_2C = O}$$

(g) Synthesis of Carboxylic acids

A carboxylic acid is formed on hydrolysis of the adduct formed by passing carbon dioxide in the ethereal solution of a Grignard reagent.

$$R - MgX + C(=O) \longrightarrow R - C(=O) - OMgX \xrightarrow[-Mg(OH)X]{HOH} R - C(=O) - OH$$

(h) Synthesis of Carboxylic acid esters

Esters are formed on reacting the ethylchloroformate with Grignard reagent.

$RMgCl + ClCOOEt \longrightarrow RCOOEt + MgCl_2$

Ex. Which of the following formula represents Grignard reagent ?

(A) H_2NMgX (B) $HC \equiv CMgX$

(C) RMg (D) $Mg(OH)Br$

Ex. Which of the following is not a Grignard reagent ?

(A) $(CH_3)_2CHMgCl$ (B) $CH_3COOMgI$

(C) $C_6H_{11}MgBr$ (D) C_2H_5MgCl

PHYSICAL PROPERTIES :

(i) C_1 to C_{11} are colourless liquids and higher alcohols are solids.

(ii) Density of monohydric alcohol is less than H_2O.

(iii) Density $\propto$ mol. wt. (for monohydric alcohol).

(iv) **Solubility :** C_1 to C_3 and t-butyl alcohol is completely soluble in H_2O due to H–bonding.

$$\text{solubility} \propto \text{No. of side chain} \propto \frac{1}{\text{molecular weight}}$$

Order of solubility :

$C_4H_9OH > C_5H_{11}OH > C_6H_{13}OH$

$CH_3CH_2CH_2CH_2OH < CH_3CH_2\underset{\displaystyle CH_3}{\overset{|}{C}}H-OH < CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OH$

$CH_3CH_2\underset{\displaystyle OH}{\overset{|}{C}}H_2 < CH_3-\underset{\displaystyle OH}{\overset{|}{C}}H-\underset{\displaystyle OH}{\overset{|}{C}}H_2 < CH_2(OH)-CH(OH)-CH_2(OH)$

[Number of —OH increases, H-bonding increases]

(v) **Boiling points :** B.P. $\propto$ molecular weignt

If molecular wt. is same then $\text{B.P.} \propto \frac{1}{\text{branching}}$

Order of BP : $C_4H_9OH < C_5H_{11}OH < C_6H_{13}OH$

$CH_3CH_2CH_2CH_2OH > CH_3CH_2\underset{\displaystyle CH_3}{\overset{|}{C}}H-OH > CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OH$

$CH_3CH_2\underset{\displaystyle OH}{\overset{|}{C}}H_2 < CH_3-\underset{\displaystyle OH}{\overset{|}{C}}H-\underset{\displaystyle OH}{\overset{|}{C}}H_2 < CH_2(OH)-CH(OH)-CH_2(OH)$

[Number of OH increases, H-bonding increases]

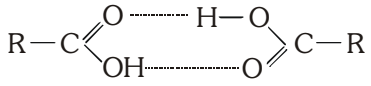
Ex. Boiling point of alcohol is more than corresponding ether. Why ?

Sol. **Reason :** H-bonding in alcohol.

$$O(R)-H\cdots\cdots O(R)-H\cdots\cdots O(R)-H\cdots\cdots O(R)-H\cdots\cdots$$

Ex. Boiling point of alcohol is less than corresponding carboxylic acid. Why ?

Sol. **Reason :** Dimer formation in carboxylic acid.



KEY POINT

1. Diols and triols have higher b.p's and are more water soluble

2. In Thiols ,Hydrogen bonding is much weaker than that in alcohols.

3. Thiols have Lower boiling points than similar alcohols.

4. Thiols are much more acidic than similar alcohols

CHEMICAL PROPERTIES :

Monohydric alcohol show following reactions

(A) Reaction involving cleavage of $O\dashv H$

(B) Reaction involving cleavage of $C\dashv OH$

(C) Reaction involving complete molecule of alcohol

(A) Reaction involving cleavage of $O\dashv H$: Reactivity order (Acidic nature) is

$CH_3—OH > CH_3CH_2—OH > (CH_3)_2CH—OH > (CH_3)_3C—OH$

(i) Acidic nature :

$H_2O >$ R—OH > $CH\equiv CH >$ NH_3 (Acidic strength)

Alcohols are less acidic than H_2O and neutral for litmus paper and gives H_2 with active metals (Na, K)

$$R—OH + Na \longrightarrow R—ONa + \frac{1}{2}H_2$$

$$R—OH + K \longrightarrow R—OK + \frac{1}{2}H_2$$

(ii) Reaction with CS_2 :

$$R—OH + Na \longrightarrow R—ONa + \frac{1}{2}H_2$$

$$R—ONa + S=C=S \longrightarrow R-O-\underset{\underset{S}{\|}}{C}-S-Na$$

Sodium alkyl xanthate (Used as floating agent)

(iii) Alkylation :

$$R—OH \xrightarrow{CH_2N_2/\Delta} R—O—CH_2—H \text{ (Chain insertion)}$$

$$R—OH \xrightarrow{Na} R—ONa \xrightarrow{R-X} R—O—R$$

(Williamson synthesis)

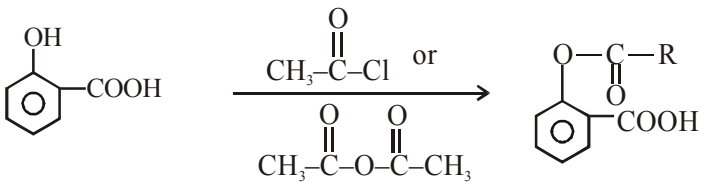
(iv) Acylation :

$$R-OH + Cl-\underset{\underset{O}{\|}}{C}-R \longrightarrow R-O-\underset{\underset{O}{\|}}{C}-R$$

(Acylation)

$$R—OH + Cl-\underset{\underset{O}{\|}}{C}-CH_3 \longrightarrow R—O-\underset{\underset{O}{\|}}{C}-CH_3$$

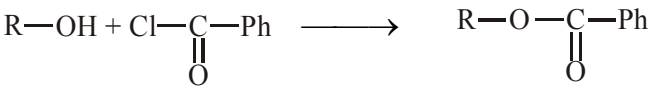
(Acetylation)



Salicylic acid

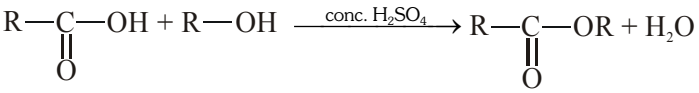
Acetoxy benzoic acid
or Acetyl salicylic acid
or Aspirin [Used as analgesic] pain killer

(v) Benzoylation : (Schotten Baumann's Reaction) :

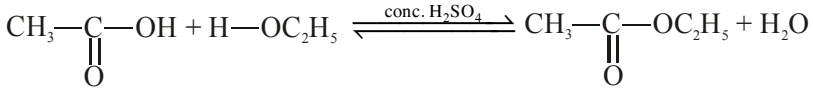


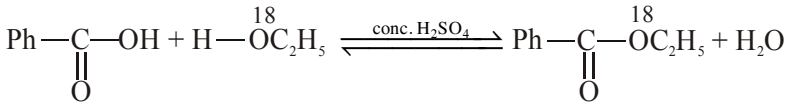
(Benzoylation)

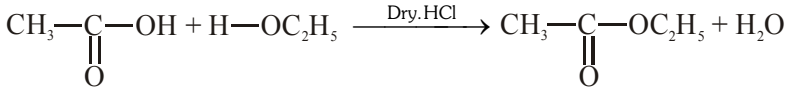
(vi) Esterification : Conc. H_2SO_4 is used as catalyst and dehydrating agent.



Note : This is a laboratory method to prepare ester i.e. esterification.

Ex. 

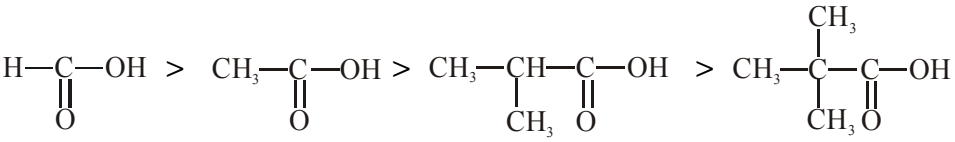
Ex. 

Ex. 

(i) Reactivity for esterification $\propto \frac{1}{\text{Steric hinderence}}$.

(ii) Reactivity of R – OH [If acid is same] : $CH_3 - OH > 1^\circ > 2^\circ > 3^\circ$ alcohol

(iii) Reactivity of RCOOH [If alcohol is same] :



KEY POINT

1. Esters are obtained by refluxing the parent carboxylic acid with the appropriate alcohol with an acid catalyst.

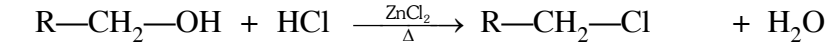
2. The equilibrium can be driven to completion by using an excess of either the alcohol or the carboxylic acid, or by removing the water as it forms.

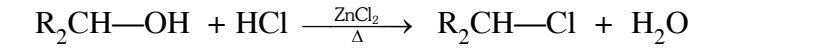
3. Esters can also be made from other carboxylic acid derivatives, especially acyl halides and anhydrides, by reacting them with the appropriate alcohol in the presence of a weak base

(B) Reaction involving cleavage of C ⁞ OH **:** Reactivity order or basic nature is

$CH_3—OH < CH_3CH_2—OH < (CH_3)_2CH—OH < (CH_3)_3\ C—OH$

(i) Reaction with halogen acid :





2^0 alcohol

Reactivity of the acids is HI > HBr > HCl > HF

(C) Reaction involving complete molecule of alcohol :

(i) Dehydration : Removal of H_2O by two type

(a) Intermolecularly removal of H_2O [form ether]

(b) Intramolecularly removal of H_2O [form alkene]

Ease of dehydration follow the order : **3° ROH > 2° ROH > 1° ROH > CH_3OH**

(ii) Catalytic Dehydrogenation : This reaction is useful in distinction of 1°, 2° and 3° alcohols.

$$CH_3CH_2OH \xrightarrow[300°C]{Cu} CH_3CHO + H_2$$

(p- alcohol) (Acetaldehyde)

$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow[300°C]{Cu} CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + H_2$$

(s- alcohol) (acetone)

$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH \xrightarrow[300°C]{Cu} CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 + H_2O \text{ [dehydration]}$$

(tertiary butyl alcohol) (Iso - butylene)

(II) <u>OXIDATION OF ALCOHOLS</u>

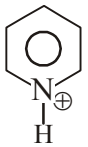
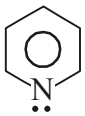
<u>Oxidising agents</u>

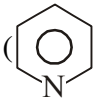
(1) $H^{\oplus}/K_2Cr_2O_7$, Δ (Strong oxidising agent)

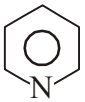
(2) $H^{\oplus}/KMnO_4$, Δ (Strong oxidising agent)

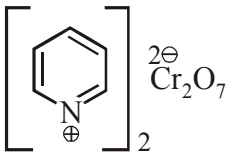
(3) **Jones reagent :** CrO_3 / H_2SO_4 treated with alcohol usually taken in acetone (strong oxidising agent)

(4) Cu / 300°C (or Red hot Cu tube)

(5) PCC (Pyridinium chloro chromate)  CrO_3 $Cl^{\bullet}$ or  CrO_3 + HCl

(6) Collin's reagent ( (2 mol) + CrO_3 + CH_2Cl_2)

(7) Sarett reagent (i.e. PCC in CH_2Cl_2)  + CrO_3 + HCl + CH_2Cl_2

(8) PDC (Pyridinium dichromate) 

(9) $TsCl + DMSO + NaHCO_3$

$RCH_2OH \xrightarrow{Ts-Cl} RCH_2OTs \xrightarrow[NaHCO_3]{DMSO} RCHO$

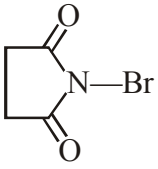
$R_2CHOH \xrightarrow{Ts-Cl} R_2CH-OTs \xrightarrow[NaHCO_3]{DMSO} R_2CO$

$R_3COH \xrightarrow{Ts-Cl} R_3C-OTs \xrightarrow[NaHCO_3]{DMSO} \times$

(10) MnO_2-Oxidises only allylic or benzylic– OH. 1° Allylic or benzylic OH $\xrightarrow{MnO_2}$ Aldehyde

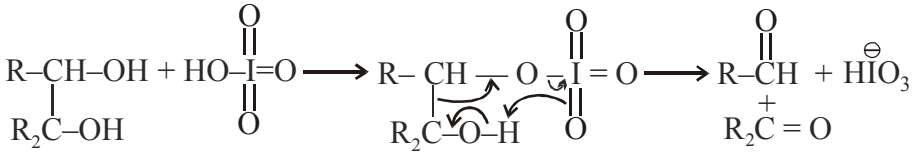
2° Allylic or benzylic OH $\xrightarrow{MnO_2}$ Ketone

No effect on 3° ROH and on Carbon-Carbon multiple bond.

(11) NBS (N-Bromosuccinamide) 

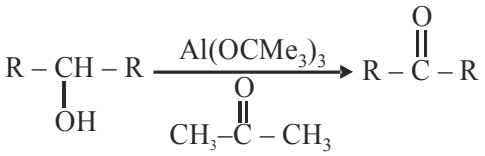
(12) **Periodic cleavage**

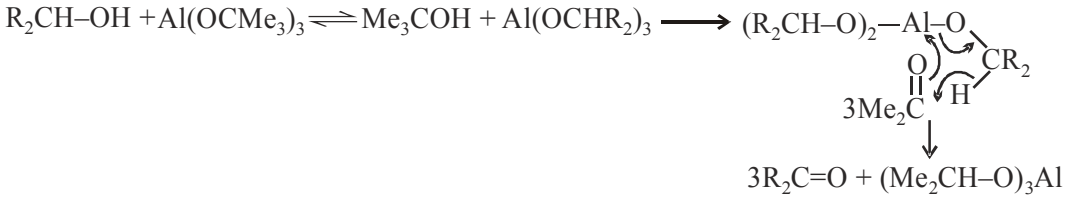
A similar oxidation is obtained in case of HIO_4 known as periodic cleavage.



But reaction is observed for Vic-diols.

(13) **Openaur oxidation**





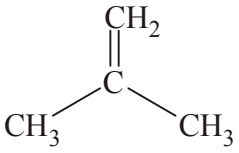
Oxidation of alcohol with aluminium tertiary butoxide is Openaur oxidation.

Ex. Different oxidising agents are used to oxidise alcohols in corresponding carbonyl compounds and carboxylic acids.

e.g. (I) $\underset{1°\text{alcohol}}{R-CH_2-OH} \xrightarrow{1,2,3,} R-\underset{\underset{O}{\|}}{C}-OH$

(II) $\underset{1°\text{alcohol}}{R-CH_2-OH} \xrightarrow{4,5,6,7,8,9,10,11} R-\underset{\underset{O}{\|}}{C}-H\,(\text{Aldehyde})$

(III) $\underset{2°\,\text{Alcohol}}{R-\underset{\underset{OH}{|}}{CH}-R'} \xrightarrow{1,2,3,4,5,6,7,8,8,9,10,11} R-\overset{\overset{O}{\|}}{C}-R'\,(\text{Ketone})$

(IV) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH \xrightarrow{Cu\ 300°C}$  Dehydration takes place.

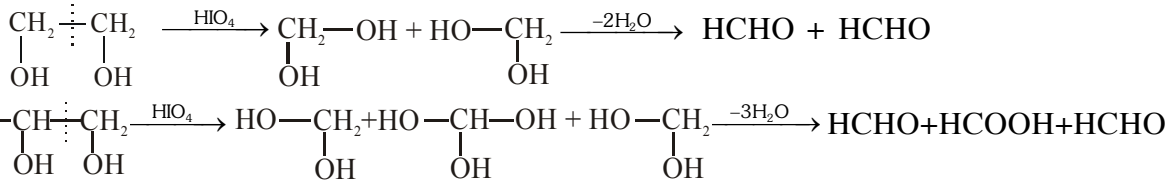
(V) Double bond or Tripple bond is not affected by 4,5,6,7,8,9,10

(VI) No effect on 3° alcohol by 1,2,3,5,6,7,8,9,10,12,13

(a) Oxidation by HIO_4 [per iodic acid] :

When diols reacts with HIO_4 [Periodic acid]. Those diols/ Polyols in which –OH group attached to vic C-atom after reaction with HIO_4 forms aldehyde and ketone.

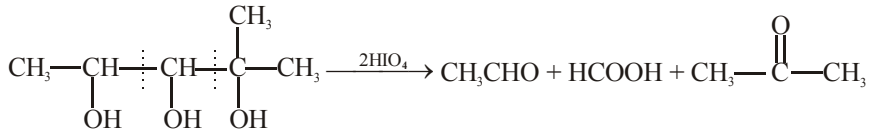
This reaction is also used in identification of no. of OH group in polyol.

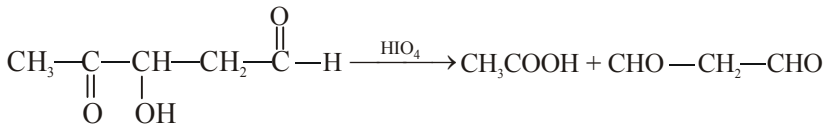


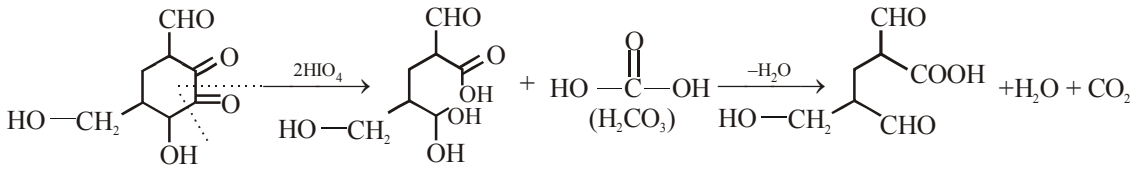
(Glycerol)

Condition for oxidation by HIO_4 :

At least 2 —OH or 2 >C=O or 1 —OH and 1 >C=O should be at adjacent carbons.

Ex. 

Ex. 

Ex. 

Ex. $\mathrm{R-\underset{\displaystyle CH_2-OH}{\overset{\displaystyle |}{CH}}-OH} + HIO_4 \xrightarrow[\text{oxidation}]{\text{strong}} R-\overset{\displaystyle O}{\overset{\displaystyle ||}{C}}-H + H-\overset{\displaystyle O}{\overset{\displaystyle ||}{C}}-H + 2H_2O$

Ex. $\mathrm{\underset{\displaystyle R-C-OH}{\overset{\displaystyle R}{\overset{\displaystyle |}{\overset{\displaystyle |}{R-C-OH}}}}} \xrightarrow[\text{oxidation}]{\text{strong}} 2\left[R-\overset{\displaystyle O}{\overset{\displaystyle ||}{C}}=O\right] + 2H_2O$

Ex. $\mathrm{R-\underset{\displaystyle R-CH-OH}{\overset{\displaystyle |}{\underset{\displaystyle CH_2}{|}}}-CH-OH} + HIO_4 \xrightarrow[\text{oxidation}]{\text{strong}}$ No reaction (due to absence of vic diols.)

KEY POINT

1. 1,2- or vicinal diols are cleaved by periodic acid, HIO_4, into two carbonyl compounds.

2. The reaction is selective for 1,2-diols.

3. The reaction occurs via the formation of a cyclic periodate ester .

4. This can be used as a functional group test for 1,2-diols.

5. The products are determined by the substituents on the diol

6. The product of alcohol oxidation depends on whether the starting alcohol is a primary, secondary or tertiary alcohol.

7. Oxidation of methanol is unique amongst alcohols as the eventual products of methanol oxidation are water and carbon dioxide.

8. A common reagent that selectively oxidizes a primary alcohol to an aldehyde (and no further) is pyridinium chlorochromate, PCC.

9. 3º alcohol are resistant to oxidation because they have no hydrogen atoms attached to the oxygen bearing carbon (carbinol carbon).

10. Potassium permanganate is a cheaper but stronger oxidizing agent, and conditions must be controlled carefully.

(b) Pinacole - Pinacolone Rearrangement :

$\mathrm{CH_3-\overset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}-\overset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}-CH_3} \xrightarrow[-H_2O]{\text{conc. } H_2SO_4} \mathrm{CH_3-\overset{\displaystyle O}{\overset{\displaystyle ||}{C}}-\overset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}-CH_3}$

Pinacole Pinacolone

TEST OF ALCOHOLS :

(1) Lucas test : A mixture of HCl(conc.) and anhydrous $ZnCl_2$ is called Lucas reagent.

p-alcohol $\xrightarrow{ZnCl_2+HCl}$ No turbidity at room temp. [On heating within 30 minutes.]

s-alcohol $\xrightarrow{ZnCl_2+HCl}$ Turbidity appears within 5 minutes.

t-alcohol $\xrightarrow{ZnCl_2+HCl}$ Turbidity appears within 1 minute.

This test is used to differentiate 1°, 2° and 3° alcohols,

(2) Victor - Meyer test : This is colour test for alcohol (primary, secondary & tertiary) .

p-alcohol $\longrightarrow$ Red colour

s-alcohol $\longrightarrow$ Blue colour

t-alcohol $\longrightarrow$ No colour

This test is used to differentiate 1°, 2° and 3° alcohols,

$R—CH_2—OH$ [1°]	$R_2CH—OH$ [2°]	$R_3C—OH$ [3°]
$\downarrow P + I_2$	$\downarrow P + I_2$	$\downarrow P + I_2$
$R—CH_2—I$	$R_2CH—I$	$R_3C—I$
$\downarrow AgNO_2$	$\downarrow AgNO_2$	$\downarrow AgNO_2$
$RCH_2—NO_2$	$R_2CH—NO_2$	$R_3C—NO_2$
$\downarrow HNO_2$	$\downarrow HNO_2$	$\downarrow HNO_2$
$R—\underset{\underset{N—OH}{\|}}{C}—NO_2$	$R_2\underset{\underset{N=O}{\|}}{C}—NO_2$	No reaction
$\downarrow NaOH$	$\downarrow NaOH$	$\downarrow NaOH$
Soluble (Red)	Insoluble (Blue)	Colourless (White)

(3) Other test of alcohols :

(a) Dichromate test :

1° Alcohol $\xrightarrow[\text{orange}\,[Cr^{+6}]]{H^{\oplus}/K_2Cr_2O_7}$ Acid + Cr^{+3} [green]

2° Alcohol $\xrightarrow[\text{orange}\,[Cr^{+6}]]{H^{\oplus}/K_2Cr_2O_7}$ Ketone + Cr^{+3} [green]

3° Alcohol $\xrightarrow[\text{orange}\,[Cr^{+6}]]{H^{\oplus}/K_2Cr_2O_7}$ No oxidation, No green

(b) Test of alcholic group :

$R—OH \xrightarrow{Na} R—ONa + \frac{1}{2}H_2$ [effervesence of H_2]

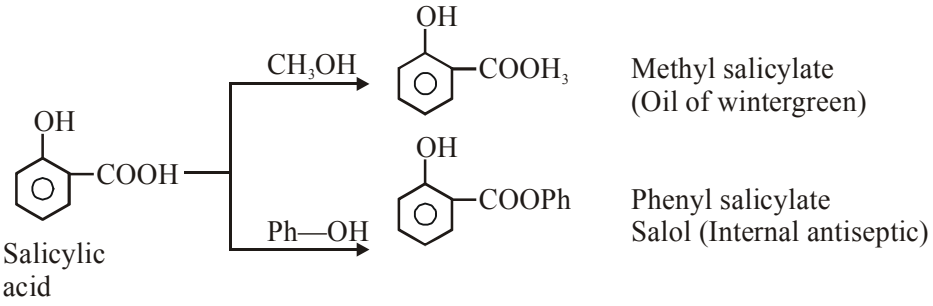
$R—OH \xrightarrow{PCl_5} R—Cl + POCl_3 + HCl \xrightarrow{NH_3} NH_4Cl$ [White fumes]

$R—OH \xrightarrow{\text{Cerric ammonium nitrate}}$ Red colour

(c) Distinction between $CH_3 - OH$ and C_2H_5OH

	CH_3OH	CH_3CH_2OH
I_2 + NaOH	No ppt	Yellow ppt of CHI_3
Cu/300°C	Smell of formalin [HCHO]	No smell
Salicylic acid	Smell of oil of wintergreen	No smell

Synthesis of oil of wintergreen and other related reactions are as following :



KEY POINT

1. Alcohols are very weak acids (somewhat weaker than water) but may loose H^+ from the OH group if sodium or a sufficiently strong base is present
2. Phenol is more acidic than alcohols and H^+ may be removed with sodium hydroxide solution. It is less acidic than carboxylic acids.
3. Normally an alcohol cannot be directly reduced to an alkane in one step. The –OH group is a poor leaving group so hydride displacement is not a good option - however the hydroxyl group is easily converted into other groups that are superior leaving groups, and allow reactions to proceed.
4. The -OH is a poor leaving group, but $-OH_2^+$ is an excellent leaving group, and once the –OH is protonated, the molecule may take part in a variety of substitution and/or elimination reactions.
5. The $ZnCl_2$ coordinates to the hydroxyl oxygen, and this generates a far superior leaving group.

ETHER

GENERAL METHODS OF PREPARATION :

From alkyl halides :

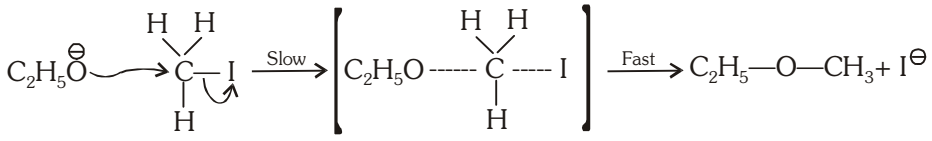
(i) By Williamson's synthesis :

$$R—X + Na—O—R \longrightarrow R—O—R + NaX \ [S_{N^2} \text{ Reaction}]$$

Ex. $CH_3—I + C_2H_5\ O^-\ Na^+ \longrightarrow CH_3—CH_2O—CH_3 + NaI$

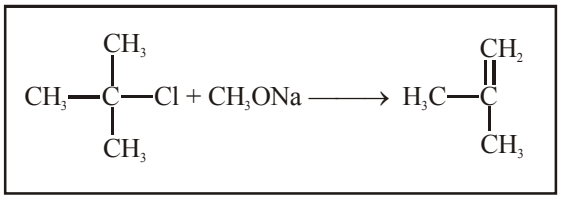
Mechanism : $[S_{N^2}$ Reaction]

$$C_2H_5\overset{\ominus}{O}Na^{\oplus} \rightleftharpoons C_2H_5O^{\ominus} + Na^{\oplus}$$

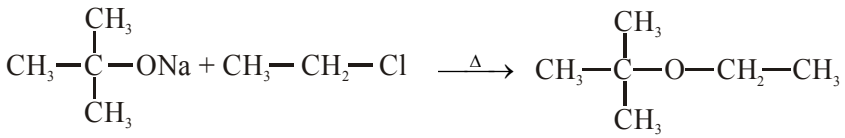


$$Na^{\oplus} + I^{\ominus} \longrightarrow NaI$$

Ex.



Ex.



Ex. $CH_2=CH-Cl + CH_3CH_2-ONa \longrightarrow$ No reaction

[Stable by Resonance]

(ii) Reaction with Dry Ag_2O :

$$2RX + Ag_2O \xrightarrow{\Delta} R-O-R + 2AgX$$

Ex. $2CH_3-CH_2-Cl + Ag_2O \xrightarrow{\Delta} CH_3CH_2OCH_2CH_3 + 2AgCl$

PHYSICAL PROPERTIES :

(i) CH_3OCH_3 , $CH_3OCH_2CH_3$ are gases and higher are volatile liquids.

(ii) Ether are less polar [μ=1.18D].

(iii) Ethers are less soluble in H_2O.

(iv) Ethers have less BP then corresponding alcohol.

Ex. Ethers are less soluble in H_2O . Why ?

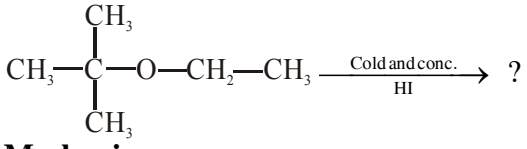
Sol. **Reason :** Due to less polar, it forms weaker H–Bonding with H_2O.

Ex. Ethers have less BP then corresponding alcohol. Why ?

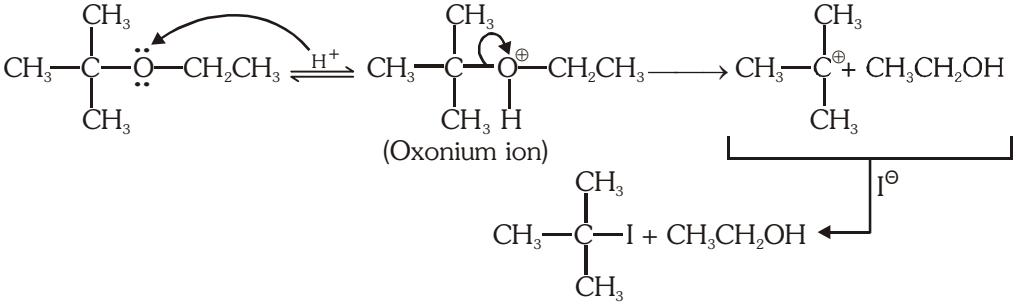
Sol. **Reason :** No H–Bonding in ether molecules.

CHEMICAL PROPERTIES :

Ex.



Sol. **Mechanism**



- If oxonium ion gives more stable carbocation [$Ph\overset{\oplus}{C}H_2$, $CH_2=CH-\overset{\oplus}{C}H_2$, $(CH_3)_3\overset{\oplus}{C}$] then SN^1 reaction occurs.
- If oxonium ion gives less stable carbocation [$P\overset{\oplus}{h}$, $CH_2=\overset{\oplus}{C}H$, $CH_3\overset{\oplus}{C}H_2$] then SN^2 reaction occurs, and $X^{\ominus}$ attacks at less hindered carbon.

Ex. $CH_3CH_2—O—CH_2Ph \xrightarrow[HI]{\text{Cold con.}} CH_3CH_2—OH + PhCH_2—I$, write mechanism of given reaction.

Ex. $CH_3CH_2—O—CH_3 \xrightarrow{\text{anhy.HI}} ?$

Sol. $CH_3CH_2—\ddot{O}—CH_3 \overset{HI}{\rightleftharpoons} CH_3CH_2—\overset{\oplus}{O}(H)—CH_3 \xrightarrow{I^{\ominus}} CH_3I + CH_3CH_2OH$

Oxonium ion gives less stable carbocation

SN^2 reaction $I^{\ominus}$ attacks at less hinderd carbon.

Ex. $CH_3—CH_2—O—Ph \xrightarrow{\text{(aq.)HBr}} ?$

Sol. **Mechanism :** $CH_3—CH_2—\ddot{O}—Ph \xrightarrow{H^+} CH_3—\overset{\oplus}{O}H(CH_2)—Ph \xrightarrow{Br^{\ominus}} CH_3CH_2Br + PhOH$

- If excess of HI is used then two moles of alkyl hallides are formed.
- $CH_3CH_2—O—CH_2Ph \xrightarrow{HI} CH_3CH_2OH + PhCH_2I \xrightarrow{HI} CH_3CH_2—I + PhCH_2—I$

(B) Reaction with hot and conc. HX :

$$CH_3CH_2—O—CH_3 \xrightarrow{\text{hot and conc HI}} CH_3CH_2—I + CH_3—I$$

Ex. $C_2H_5—O—C_2H_5 \xrightarrow{\text{hot and conc. HBr}} ? + ?$

Sol. $C_2H_5—Br + C_2H_5—Br$

USES OF ETHER :

(i) General anaesthetics agent.

(ii) Refrigerant a mixture of ether and dry ice gives temperature as low 110°C.

(iii) Solvent for oil, fats, resins, Grignard reagent.

(iv) For providing inert & moist free medium to organic reaction example : Wurtz reactions.

(v) In perfumery.

(vi) Mixture of alcohol and ether is used as a substitute of petrol. Trade name **"Natalite"**

(vii) Halothane ($CF_3CHClBr$) used as an anaesthetic because it produces unconsciousness without affecting lung and heat.

EPOXIDES :

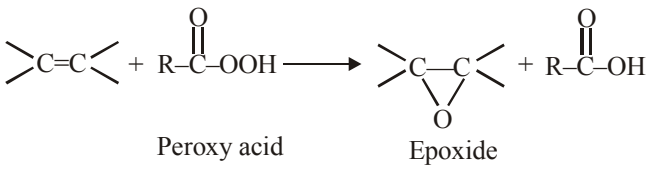
Preparation of Epoxides :

(i) Epoxidation of alkenes by reaction with peroxy acids

(ii) Base-promoted ring closure of vicinal halohydrins

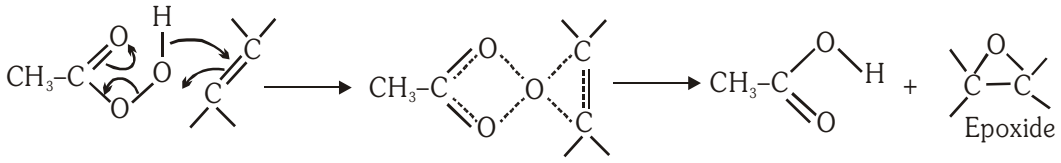
(iii) Epoxidation of alkenes by reaction with peroxy acids

- **Epoxidation of alkenes by reaction with peroxy acids :**

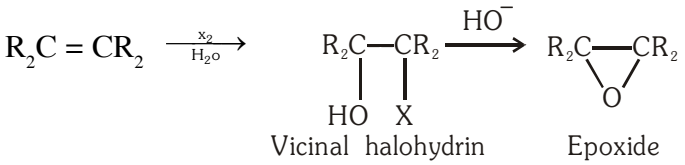


Peroxy acid Epoxide

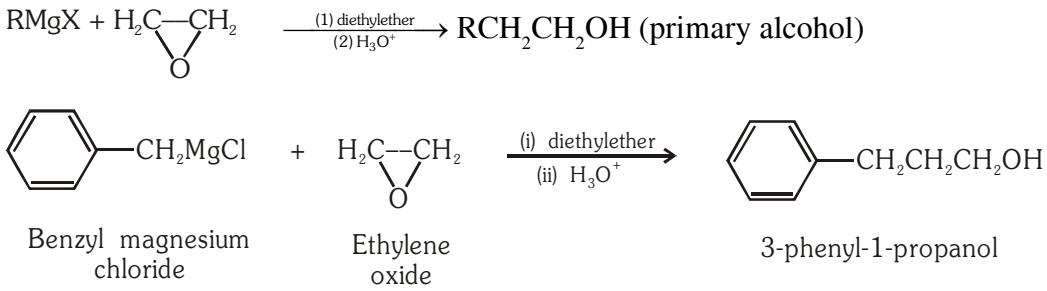
Mechanism :



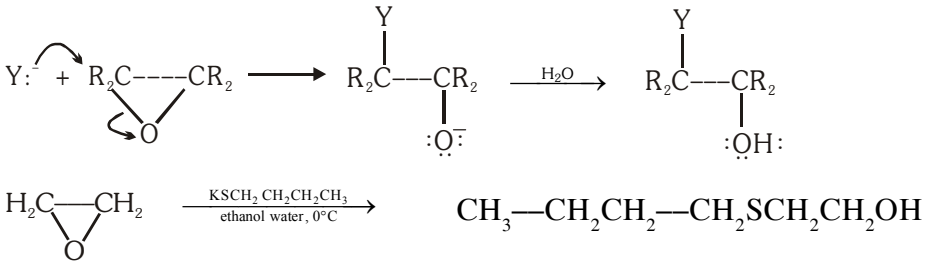
- **Base-promoted ring closure of vicinal halohydrins :**



- **Reaction of Epoxides :**
- **With Grignard reagent :**



- **Nucleophilic ring opening reactions of epoxides :**



Problems :

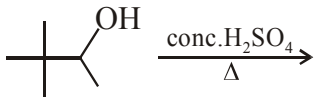
Ex. Which of the following is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene and why ?

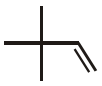
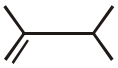
Ex. Write the equation of the reaction of hydrogen iodide with :

(i) 1-propoxypropane (ii) Methoxybenezene and (iii) Benzyl ethyl ether

ALCOHOLS AND ETHERS

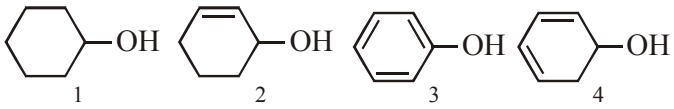
EXERCISE # O-1

1.  Major product :

(A)  (B)  (C)  (D) None of these

AE0001

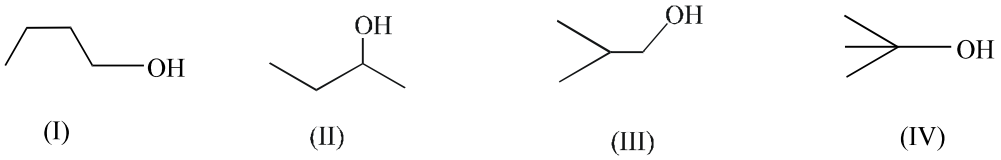
2. Correct order of dehydration of following alcohols will be :



(A) 1 < 2 < 3 < 4 (B) 4 > 3 > 1 > 2 (C) 4 > 2 > 1 > 3 (D) 1 > 3 > 4 > 2

AE0002

3. Dehydration of the isomeric alcohols

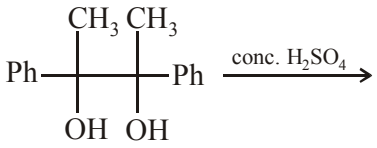


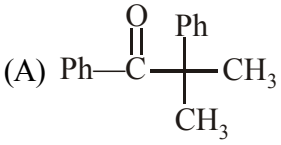
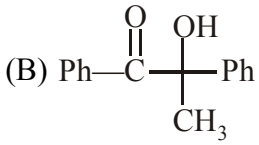
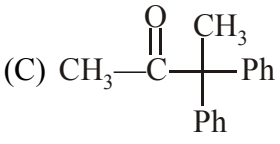
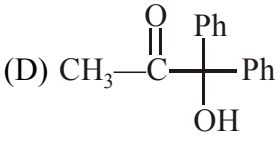
What will be the order of rate of reaction ?

(A) IV > III > II > I (B) I > II > III > IV (C) IV > II > III > I (D) II > IV > I > III

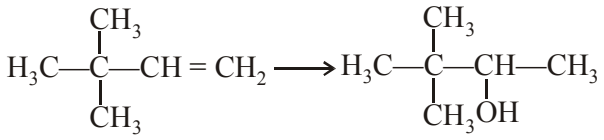
AE0003

4. Find out major product of following reaction.



(A)  (B)  (C)  (D) 

AE0004

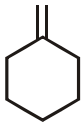
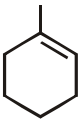
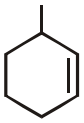
5.  , This interconversion can be achieved by :

(A) Acid catalysed hydration (B) Oxymercuration-demercuration

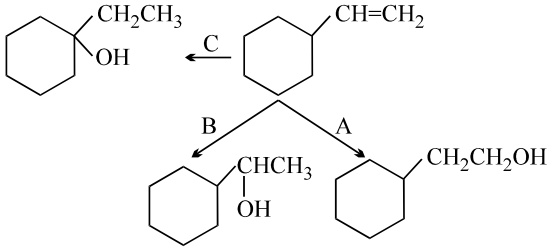
(C) Hydroboration - oxidation (D) Any method mentioned above

AE0005

6. A $\xrightarrow[\text{(ii) } NaBH_4\text{, } \bar{O}H]{\text{(i) } Hg(OAc)_2\text{, HOH}}$ 1–Methylcyclohexanol. Here A is :

(A)  (B)  (C)  (D) (A) or (B)

AE0006

7. 

Select schemes A, B, C out of

(I) Acid catalysed hydration

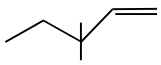
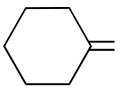
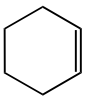
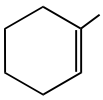
(II) HBO

(III) Oxymercuration-demercuration

(A) I in all cases (B) I, II, III (C) II, III, I (D) III, I, II

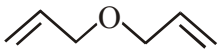
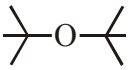
AE0007

8. HBO, oxymercuration-demercuration and acid catalysed hydration will give same product in

(A)  (B)  (C)  (D) 

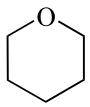
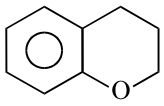
AE0008

9. Which of the following ethers is least reactive to cleavage with conc. HBr ?

(A) Ph—CH_2—O—CH_3 (B) Ph—O—Ph (C)  (D) 

AE0009

10. Consider the reaction of HI with the following:

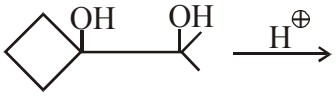
I.  II 

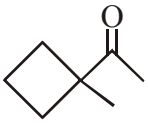
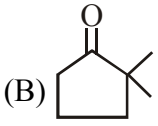
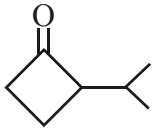
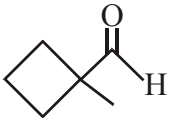
Which forms di-iodide on reaction with HI (excess)?

(A) I and II both (B) II only (C) I only (D) none

AE0010

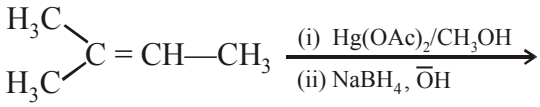
11. Find out major product of following reaction.



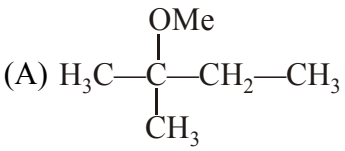
(A)  (B)  (C)  (D) 

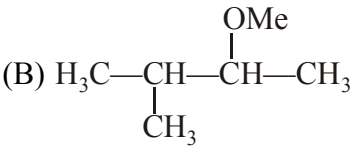
AE0011

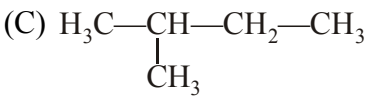
12. In the given reaction

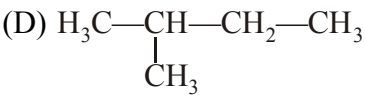


[X] , [X] will be :

(A) 

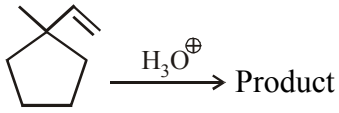
(B) 

(C) 

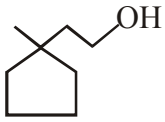
(D) 

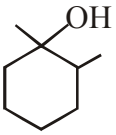
AE0012

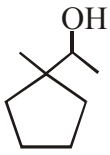
13. In the following reaction

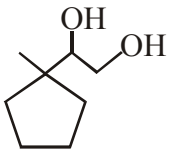


The major product is :

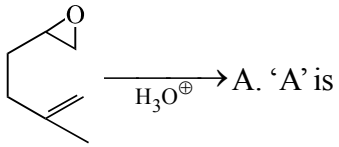
(A) 

(B) 

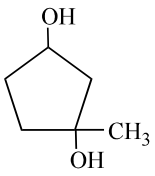
(C) 

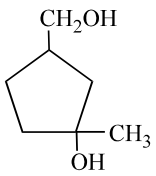
(D) 

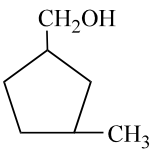
AE0013

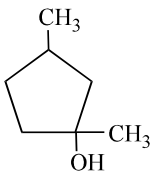
14. 

A. 'A' is

(A) 

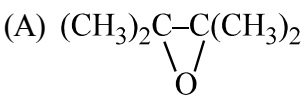
(B) 

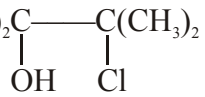
(C) 

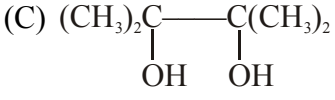
(D) 

AE0014

15. $(CH_3)_2C=C(CH_3)_2 \xrightarrow[H_2O]{X_2} A \xrightarrow[\text{limited amount}]{OH^-} B$, Product 'B' is :

(A) 

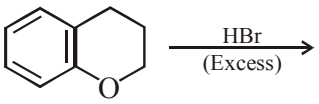
(B) 

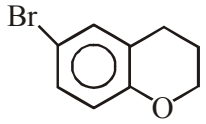
(C) 

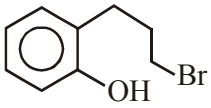
(D) None

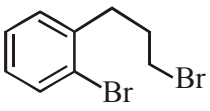
AE0015

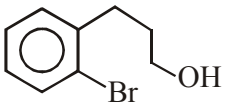
16. Find out correct product of reaction :



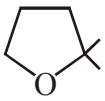
(A) 

(B) 

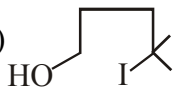
(C) 

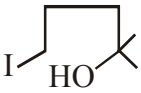
(D) 

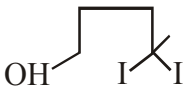
AE0016

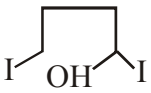
17. 

$+ \underset{(1\ eq.)}{HI} \longrightarrow$ Product, Product is :

(A) 

(B) 

(C) 

(D) 

AE0017

18. $Z \xrightarrow{PCl_5} X \xrightarrow[\Delta]{Alc.KOH} Y \xrightarrow{dil.\ H_2SO_4} Z$; Z is :

(A) $CH_3–CH_2–CH_2–OH$ (B) $H_3C-\underset{\underset{OH}{|}}{CH}-CH_3$ (C) $\begin{matrix} CH_3 \\ \diagdown \\ \quad CH-CH_2-OH \\ \diagup \\ CH_3 \end{matrix}$ (D) $CH_3-CH=CH_2$

AE0018

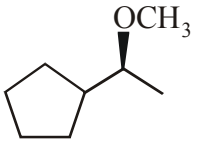
19. When 2-chloroethanol is warmed slightly with dilute NaOH, the major product formed is :

(A) $CH_3–CH_2–CH_2–O–CH_2–CH_2–Cl$ (B) $HO–CH_2–CH_2–CH_2–CH_2–OH$

(C) $HO–CH_2–CH_2–OH$ (D) 

AE0019

20. How many total alcohols are form by acidic hydrolysis of following ether.



(A) 5 (B) 6 (C) 7 (D) 8

AE0020

21. Which of the following test can be used to differentiate methyl alcohol and iso-propyl alcohol.

(A) Litmus paper test (B) Bromine water test

(C) Lucas test (D) All of these

AE0021

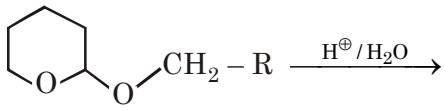
22. On reaction of ether with BF_3, ether acts as :

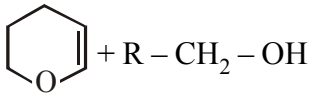
(A) Electrophile (B) Nucleeophile

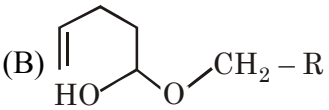
(C) Ambiphile (D) None

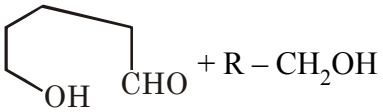
AE0022

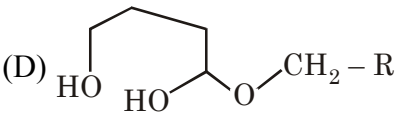
23. Give suitable major product for following reaction



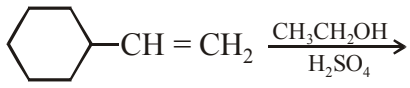
(A) 

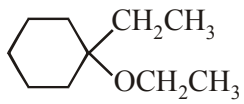
(B) 

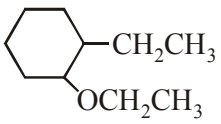
(C) 

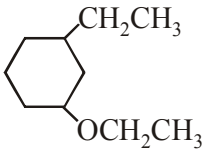
(D) 

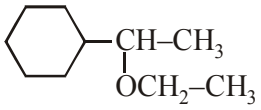
AE0023

24. 

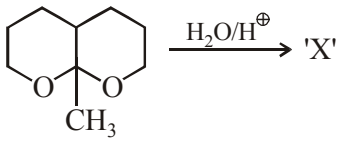
(A) 

(B) 

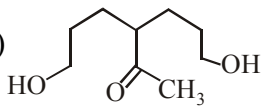
(C) 

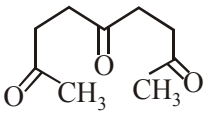
(D) 

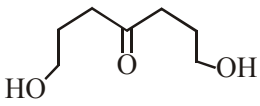
AE0024

25. 

Product 'X' will be :

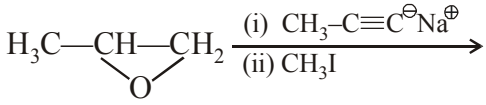
(A) 

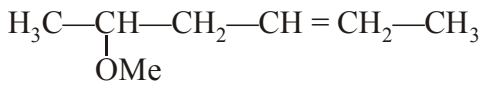
(B) 

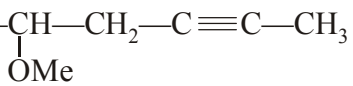
(C) 

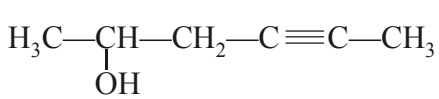
(D) All of these

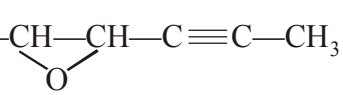
AE0025

26. 

(A) 

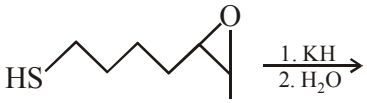
(B) 

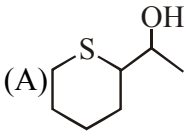
(C) 

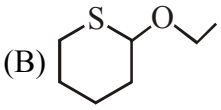
(D) 

AE0026

27. The product of the reaction is :



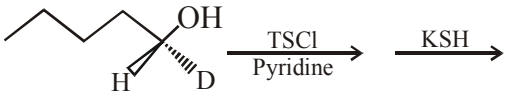
(A) 

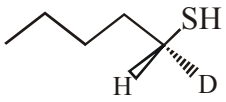
(B) 

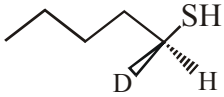
(C) $HS-(CH_2)_5-O-Et$ (D) $HS-(CH_2)_4-CH(OH)-CH_2OH$

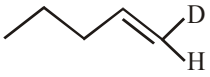
AE0027

28. Identify the major product of reaction :



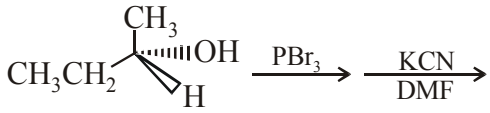
(A) 

(B) 

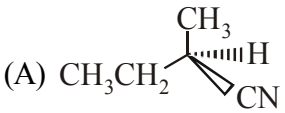
(C) 

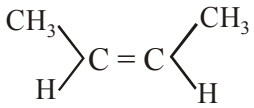
(D) No reaction

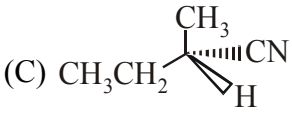
AE0028

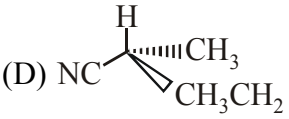
29. 

Final product is ?

(A) 

(B) 

(C) 

(D) 

AE0029

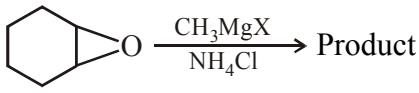
30. Diethyl ether on prolong exposure to air gives :

(A) Ethanol (B) Diethyl peroxide

(C) Diethyl hydroxy peroxide (D) Ethanoic acid

AE0030

EXERCISE # O-2

1.  Product

What is the product ?

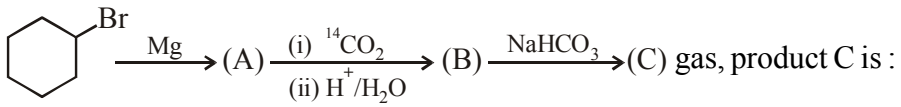
(A) Enantiomer (B) Diastereisomer (C) Meso (D) Achiral

AE0031

2. $RMgX \xrightarrow[(ii)\ HOH / H^+]{(i)\ CH_3CN} (A) \xrightarrow[NH_4Cl]{RMgX} (B)$, (B) will be :

(A) 1° ROH (B) 2° ROH (C) 3° ROH (D) Alkene

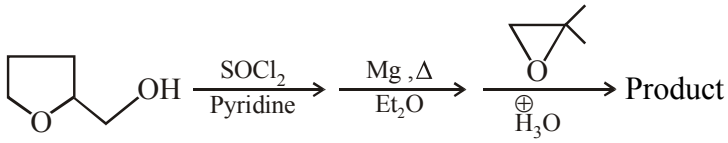
AE0032

3. 

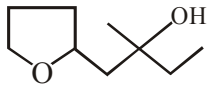
(A) CO (B) $^{14}CO_2$

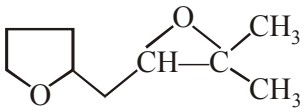
(C) CO_2 (D) A mixture $^{14}CO_2$ and CO_2

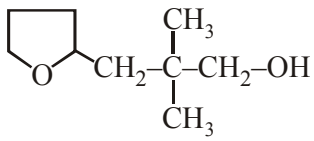
AE0033

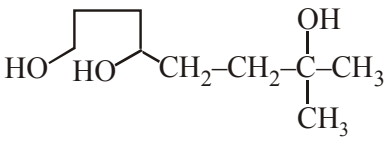
4. 

Product of reaction is :

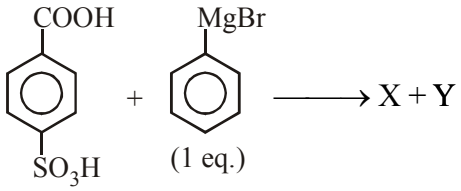
(A) 

(B) 

(C) 

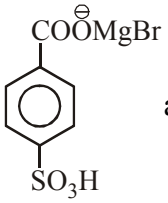
(D) 

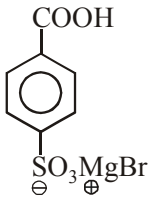
AE0034

5. 

X and Y are respectively :

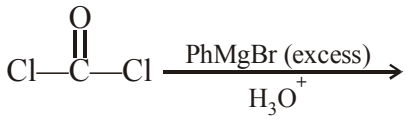
(A)  only

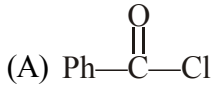
(B)  and 

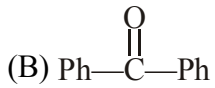
(C)  and 

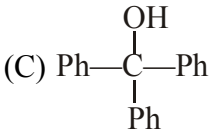
(D) None of these

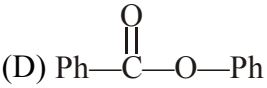
AE0035

6.  ; Product (X) is :

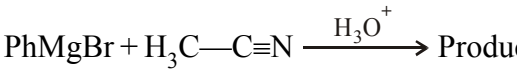
(A) 

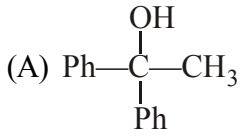
(B) 

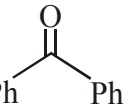
(C) 

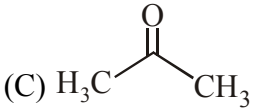
(D) 

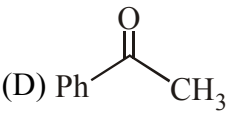
AE0036

7. 

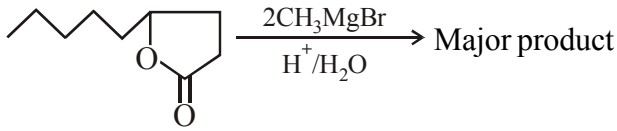
(A) 

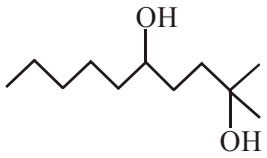
(B) 

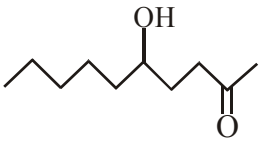
(C) 

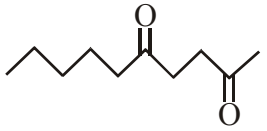
(D) 

AE0037

8. 

(A) 

(B) 

(C) 

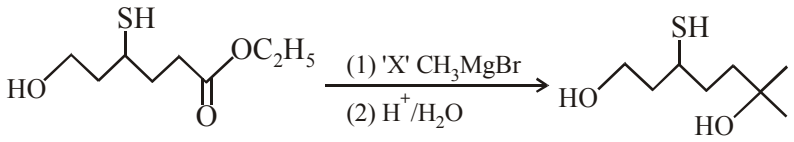
(D) No reaction

AE0038

9. $Cl-\overset{\overset{O}{\|}}{C}-OC_2H_5 \xrightarrow[(2)\ NH_4Cl]{(1)\ 'X'RMgX} 3^{o}$ Alcohol. Find out value of 'X'.

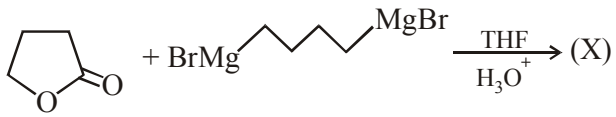
(A) 2 (B) 3 (C) 4 (D) 1

AE0039

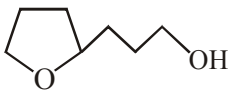
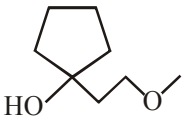
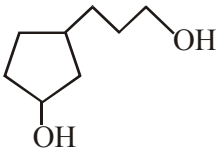
10. 

(A) 2 (B) 3 (C) 4 (D) 5

AE0040

11. 

Identify (X) :

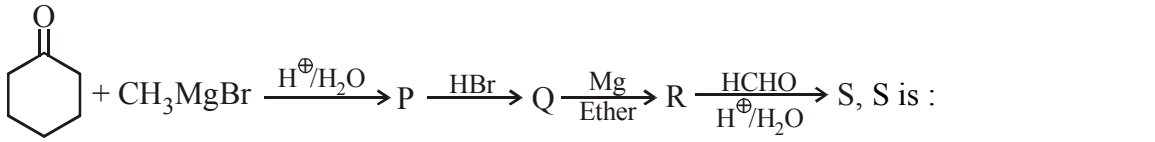
(A)  (B)  (C)  (D) 

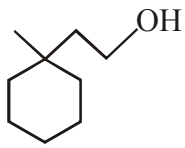
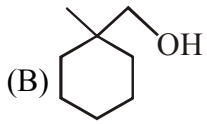
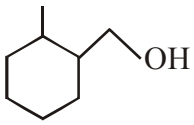
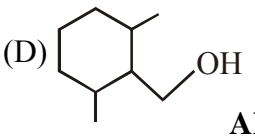
AE0041

12. If phenyl magnesium bromide and acetaldehyde are the reactants, the product formed after hydrolysis would be :

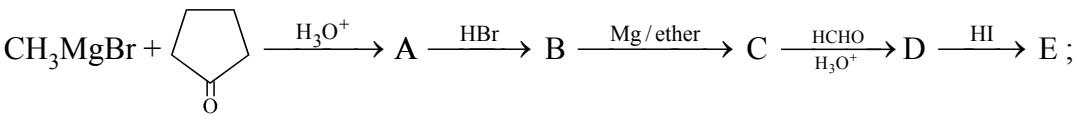
(A) Benzyl alcohol (B) 1-Phenylethanol (C) 2-Phenylethanol (D) Acetone

AE0042

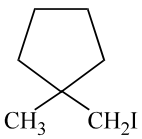
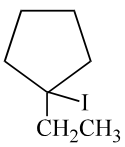
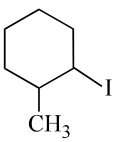
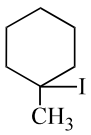
13. 

(A)  (B)  (C)  (D) 

AE0043

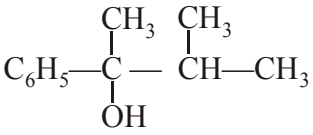
14. 

Product E is

(A)  (B)  (C)  (D) 

AE0044

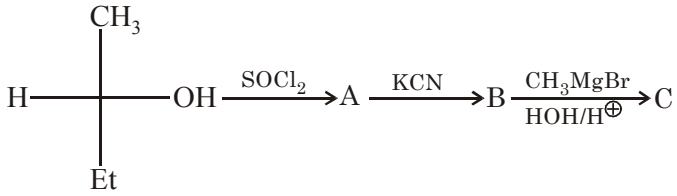
15. Which of the following reagents (A to D) would you not select to convert $C_6H_5COCH_3$ (acetophenone) to the following alcohol ?



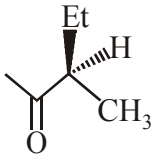
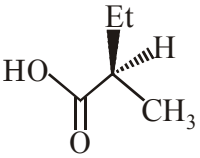
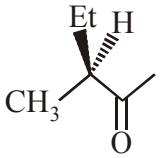
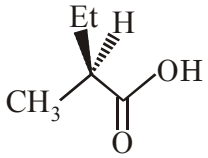
(A) $CH_3CH_2CH_2MgBr$ and hydrolysis
(B) CH_3MgBr and acid hydrolysis
(C) $(CH_3)_2CHMgBr$ and acid hydrolysis
(D) PhMgBr and acid hydrolysis

AE0045

16.

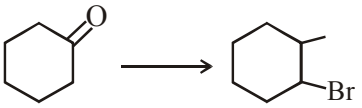


the final product C is :

(A) 
(B) 
(C) 
(D) 

AE0046

17. Which combination of reagents will not bring about the following conversion ?

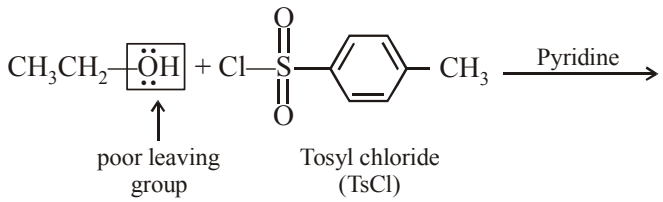


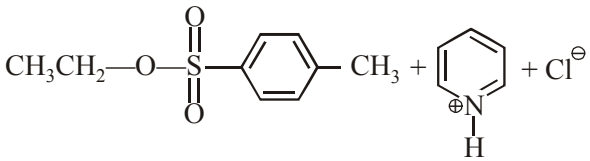
(A) $MeMgBr/H^{\oplus}$, H_2SO_4/Δ, HBr/H_2O_2, hν
(B) $MeMgBr/H^{\oplus}$, H_2SO_4/Δ, HBr
(C) $MeMgBr/H^{\oplus}$, HBr/CCl_4
(D) MeMgBr, NH_4Cl

AE0047

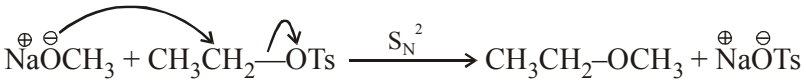
Paragraph for Q.No. 18 to 19

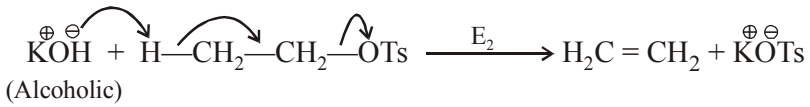
Alcohols are converted to tosylates by treatment with p-toluene sulfonyl chloride (TsCl) in presence of pyridine. This overall process converts a poor leaving group ($\overset{\ominus}{O}H$) into better one ($\overset{\ominus}{O}Ts$). A tosylate is a better leaving group because its conjugated acid p-toluene sulfonic acid is strong acid.
Because alkyl tosylates have better leaving tendency they undergo both nucleophilic substitution and β-elimination.



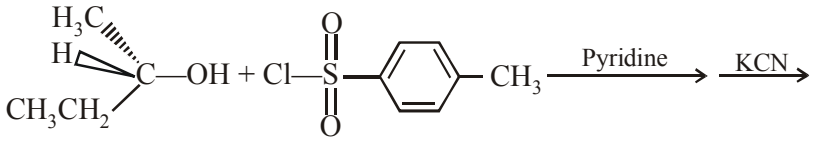


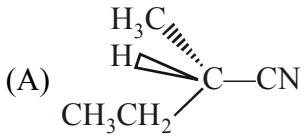
Or

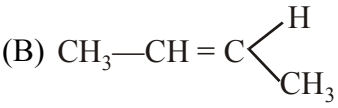


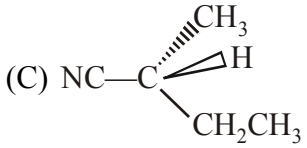


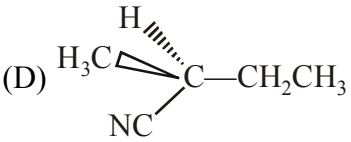
18. Find the major product of following reaction :



(A) 

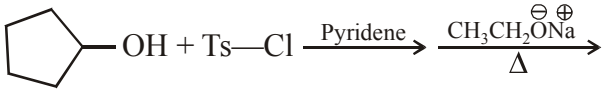
(B) 

(C) 

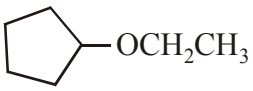
(D) 

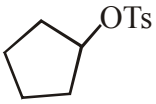
AE0048

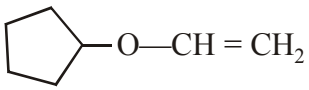
19. What would be the major product of following reactions ?



(A) 

(B) 

(C) 

(D) 

AE0049

20. Which of the following order is incorrect ?

(A) $CH_3–CH_2–OH > CH_3–CH_2–CH_2–OH > CH_3–CH_2–CH_2–CH_2–OH$ (Solubility in H_2O)

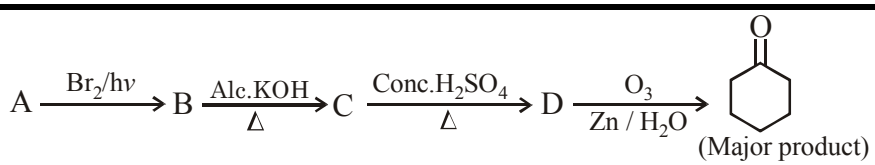
(B) $CH_3–CH_2–OH > CH_3–O–CH_3 > CH_3–CH_2–CH_3$ (Boiling point)

(C) Pentan-1-ol > Pentanal > Ethoxy ethane (Boiling point)

(D) $CH_3–OH > CH_3–CH_2–OH > CH_3–CH_2–CH_2–OH$ (Boiling point)

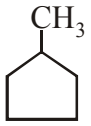
AE0050

EXERCISE # S-1

1. 

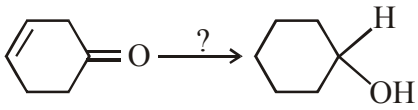
(Major product)

Find out the structure of 'A' :

(A)  (B)  (C)  (D) 

AE0051

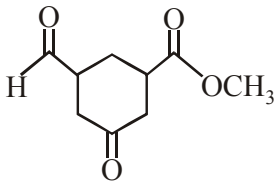
2. Predict the reducing agents in following reaction.

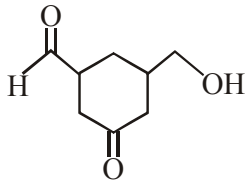


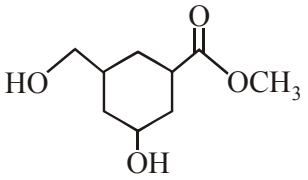
(A) $LiAlH_4$ (B) $NaBH_4$ (C) H_2 / Pt, Δ (D) Both (A) and (B)

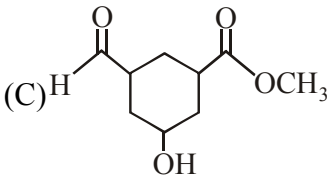
AE0052

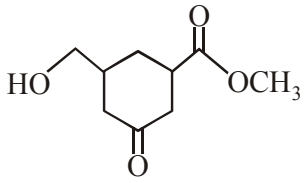
3. Find out the product when the following compound react with $NaBH_4$:



(A) 

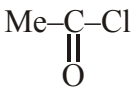
(B) 

(C) 

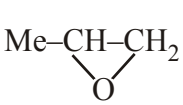
(D) 

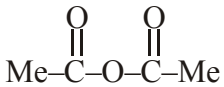
AE0053

4. Compound which does not give alcohol on reduction by $LiAlH_4$ is/are ?

(A) 

(B) 

(C) 

(D) 

AE0054

5. Choose the incorrect option ?

(A) Boiling point increases with increase in carbon due to increase in vander wall forces

(B) Branching in carbon decreases the boiling point

(C) High boiling point of alcohols are mainly due to pressure of intermolecular H-bonding

(D) Methoxymethane has higher boiling point than ethanol & propane

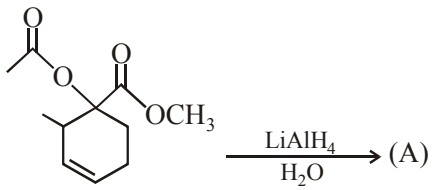
AE0055

6. Ethoxyethane & butan-1-ol are miscible to almost same extent (7.5 & 9 gm per 100 ml water respectively because of :

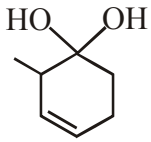
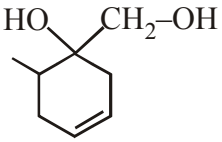
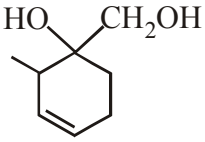
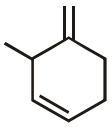
(A) Same molecular mass (B) They are isomers

(C) Both can form hydrogen bond with water (D) Water is universal solvent

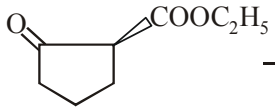
AE0056

7. 

Find out 'A' of the reaction

(A)  (B)  (C)  (D) 

AE0057

8.  ; Products of the reaction are :

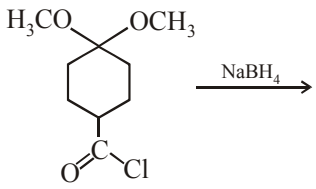
(A) Racemic (B) Diastereomers (C) Meso (D) Optically pure

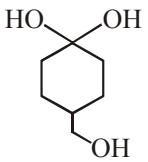
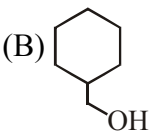
AE0058

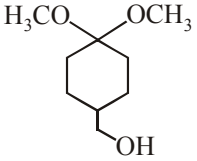
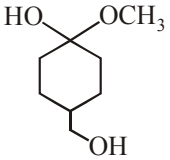
9. Reduction of $R—CH_2OH \longrightarrow RCH_3$ can be carried out by :

(A) $LiAlH_4$ (B) H_2 / Ni (C) Red P + HI (D) $NaBH_4$ / $AlCl_3$

AE0059

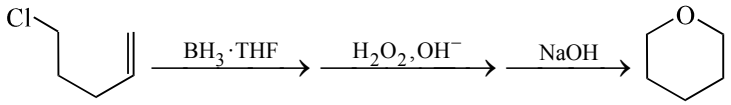
10.  (X), Product (X) is :

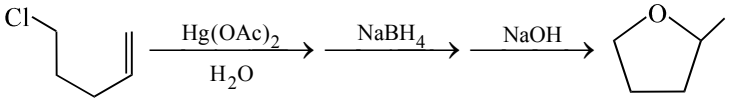
(A)  (B) 

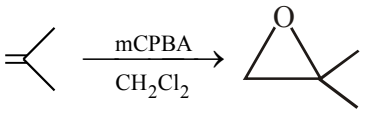
(C)  (D) 

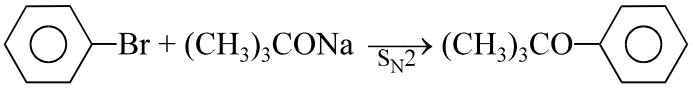
AE0060

11. Select the correct synthesis

(A) 

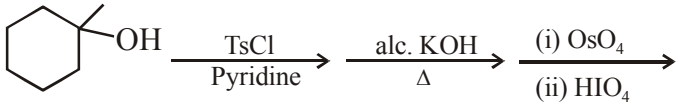
(B) 

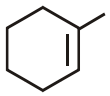
(C) 

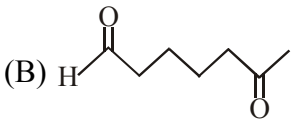
(D) 

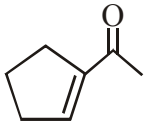
AE0061

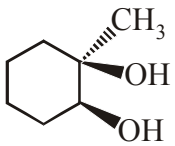
12. Identify the final product of following sequence of reactions :



(A) 

(B) 

(C) 

(D) 

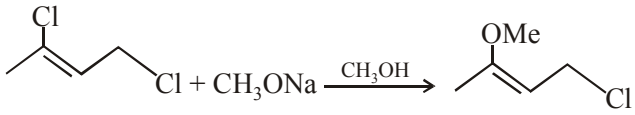
and its enantiomer

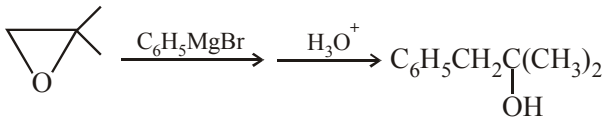
AE0062

13. Which of the following reaction is not possible ?

(A) $C_6H_5OH + HBr \longrightarrow C_6H_5Br + H_2O$

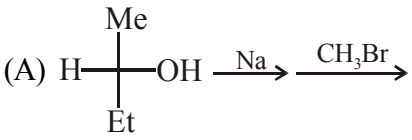
(B) $(CH_3)_3CCl + NaOCH_3 \longrightarrow (CH_3)_3COCH_3 + NaCl$

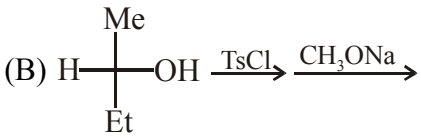
(C) 

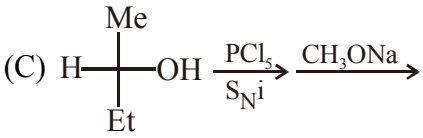
(D) 

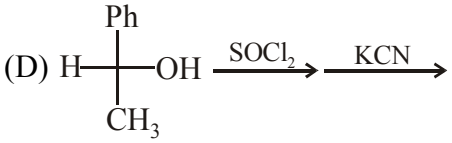
AE0063

14. Which of the following reactions proceeds with inversion of configuration ?

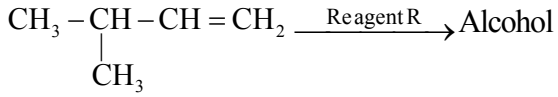
(A) 

(B) 

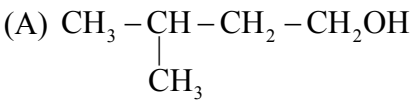
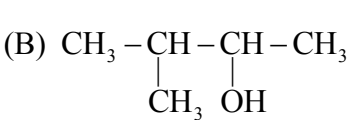
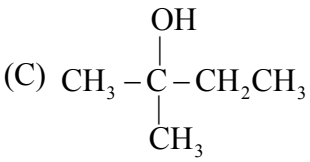
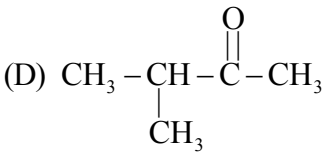
(C) 

(D) 

AE0064

15. 

which is true about alcohol and Reagent ?

List-I **(Alcohol)**	**List-II** **(Reagent)**
(A) 	(P) B_2H_6 , H_2O_2 / NaOH
(B) 	(Q) $Hg(OAc)_2$, H_2O / $NaBH_4$ followed by P.C.C.
(C) 	(R) $Hg(OAc)_2$, H_2O / $NaBH_4$
(D) 	(S) dil. H_2SO_4

AE0065

EXERCISE (J-MAIN)

1. In the following sequence of reactions $CH_3CH_2OH \xrightarrow{P + I_2} A \xrightarrow[Ether]{Mg} B \xrightarrow{HCHO} C \xrightarrow{H_2O} D$, then compound 'D' is - **[AIEEE-2007]**

(1) Butanal (2) n–Butyl alcohol (3) n–Propyl alcohol (4) Propanal

AE0066

2. A liquid was mixed with ethanol and a drop of concentrated H_2SO_4 was added. A compound with a fruity smell was formed. The liquid was :- **[AIEEE-2009]**

(1) CH_3COCH_3 (2) CH_3COOH (3) CH_3OH (4) HCHO

AE0067

3. From amongst the following alcohols the one that would react fastest with conc. HCl and anhydrous $ZnCl_2$, is :- **[AIEEE-2010]**

(1) 1–Butanol (2) 2–Butanol

(3) 2–Methylpropan–2–ol (4) 2–Methylpropanol

AE0068

4. Consider the following reaction : **[AIEEE-2011]**

$C_2H_5OH + H_2SO_4 \rightarrow$ Produce

Among the following, which one cannot be formed as a product under any conditions ?

(1) Ethyl-hydrogen sulphate (2) Ethylene (3) Acetylene (4) Diethyl ether

AE0069

5. An unknown alcohol is treated with the "Lucas reagent' to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts fastest and by what mechanism :- **[AIEEE-2013]**

(1) secondary alcohol by SN^1 (2) tertiary alcohol by SN^1

(3) secondary alcohol by SN^2 (4) tertiary alcohol by SN^2

AE0070

6. Allyl phenyl ether can be prepared by heating: **(JEE-MAIN-2014)**

(1) CH_2=CH–CH_2–Br + C_6H_5ONa (2) C_6H_5–CH=CH–Br + CH_3–ONa

(3) C_6H_5Br + CH_2=CH–CH_2–ONa (4) CH_2=CH–Br + C_6H_5–CH_2–ONa

AE0071

7. In the Victor-Meyer's test, the colour given by 1°, 2° and 3° alcohols are respectively :-

(1) Red, blue, colourless (2) Colourless, red, blue **(JEE-MAIN-2014)**

(3) Red, blue, violet (4) Red, colourless, blue

AE0072

8. Williamson synthesis of ether is an example of **(JEE-MAIN-2014)**

(1) Nucleophilic addition (2) Electrophilic substitution

(3) Nucleophilic substitution (4) Electrophilic addition

AE0073

9. The gas evolved on heating CH_3MgBr in methanol is : **[JEE-MAIN-On-line-2016]**

(1) Ethane (2) Propane (3) Methane (4) HBr

AE0074

10. Bouveault–Blanc reduction reaction involves: **[JEE-MAIN-On-line-2016]**

(1) Reduction of an ester with Na/C_2H_5OH

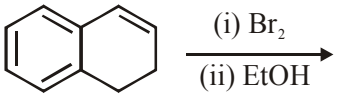
(2) Reduction of an ester with H_2/Pd

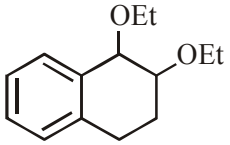
(3) Reduction of a carbonyl compound with Na/Hg and HCl

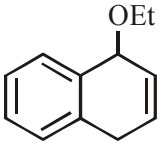
(4) Reduction of an anhydride with $LiAlH_4$

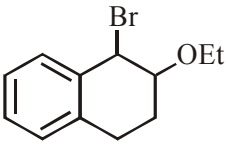
AE0075

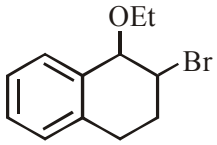
11. The major product the following reaction is : **[JEE-MAIN-On-line-(Jan)-2019]**



(1) 

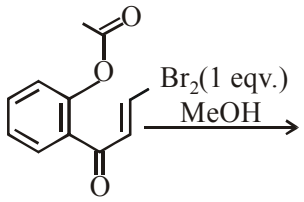
(2) 

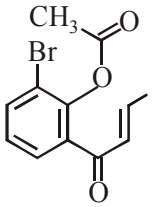
(3) 

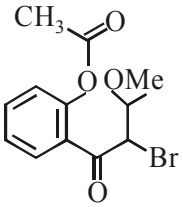
(4) 

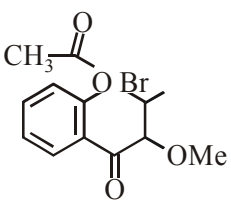
AE0076

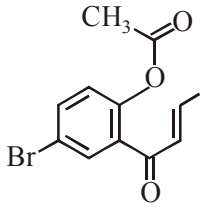
12. The major product obtained in the following conversion is :- **[JEE-MAIN-On-line-(Jan)-2019]**



(1) 

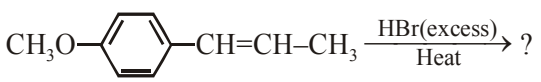
(2) 

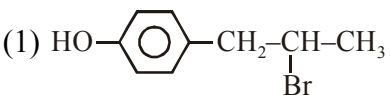
(3) 

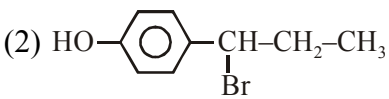
(4) 

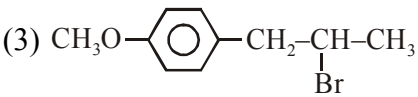
AE0077

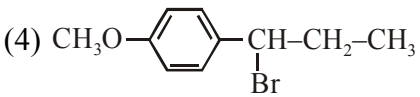
13. The major product in the following conversion is : **[JEE-MAIN-On-line-(Jan)-2019]**



(1) 

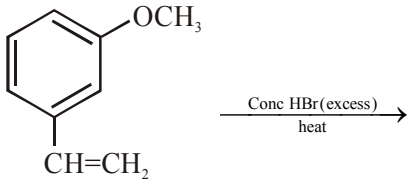
(2) 

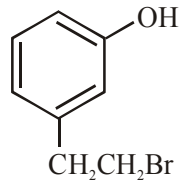
(3) 

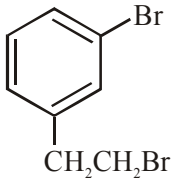
(4) 

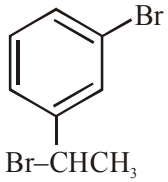
AE0078

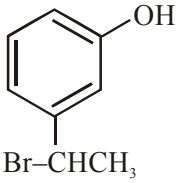
14. The major product of the following reactions: **[JEE-MAIN-On-line-(April)-2019]**



(1) 

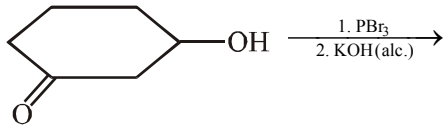
(2) 

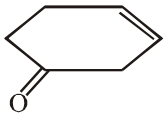
(3) 

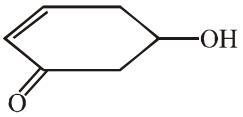
(4) 

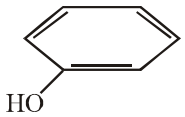
AE0079

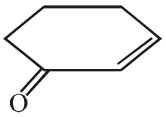
15. The mojor product of the following reaction is : **[JEE-MAIN-On-line-(April)-2019]**



(1) 

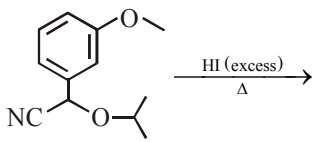
(2) 

(3) 

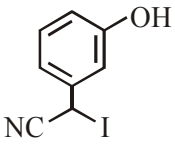
(4) 

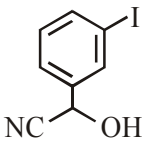
AE0080

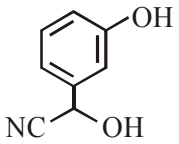
16. The major product of the following reaction is :

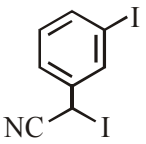


[JEE-MAIN-On-line-(April)-2019]

(1) 

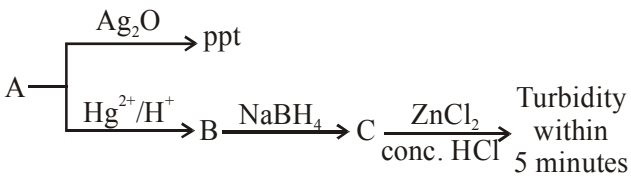
(2) 

(3) 

(4) 

AE0081

17. Consider the following reactions : **[JEE-MAIN-On-line-(April)-2019]**



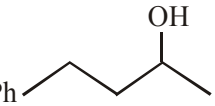
'A' is :

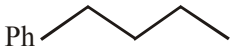
(1) CH≡CH (2) CH_3–C≡CH (3) CH_2=CH_2 (4) CH_3–C≡C–CH_3

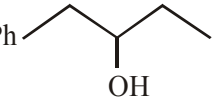
AE0082

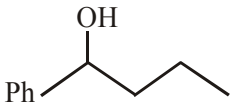
18. Heating of 2-chloro-1-phenylbutane with EtOK/EtOH gives X as the major product. Reaction of X with $Hg(OAc)_2/H_2O$ followed by $NaBH_4$ gives Y as the major product. Y is :

[JEE-MAIN-On-line-(April)-2019]

(1) 

(2) 

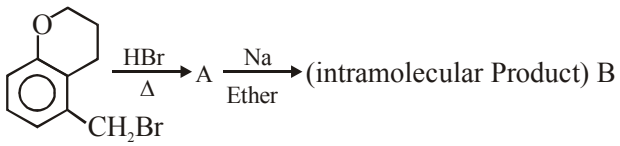
(3) 

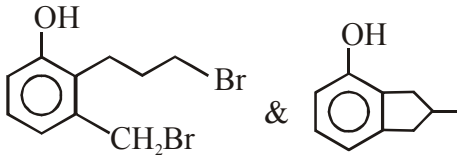
(4) 

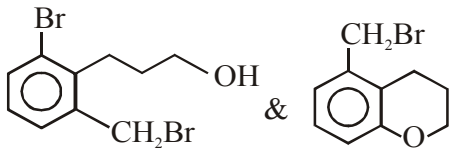
AE0083

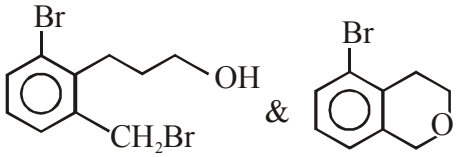
19. In the following reaction squence, structures of A and B, respectively will be :

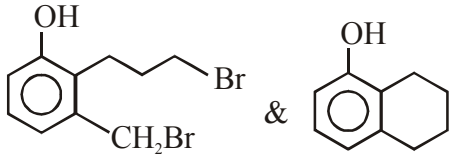
[JEE-MAIN-(Jan)-2020]



(1) 

(2) 

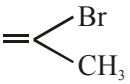
(3) 

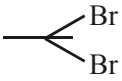
(4) 

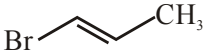
AE0084

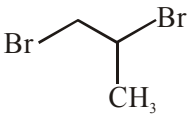
20. 1-methyl ethylene oxide when treated with an excess of HBr produces :

[JEE-MAIN-(Jan)-2020]

(1) 

(2) 

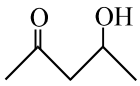
(3) 

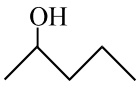
(4) 

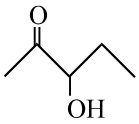
AE0085

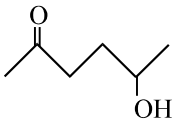
EXERCISE-(J-ADVANCE)

1. Which one of the following will most readily be dehydrated in acidic condition: **[JEE 2000]**

(A) 

(B) 

(C) 

(D) 

AE0086

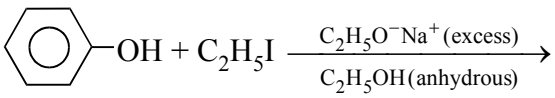
2. Identify the correct order of boiling point of the following compounds: **[JEE 2002]**

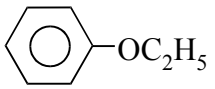
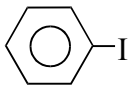
$CH_3CH_2CH_2CH_2OH$ $CH_3CH_2CH_2CHO$ $CH_3CH_2CH_2COOH$

1 2 3

(A) 1 > 2 > 3 (B) 3 > 1 > 2 (C) 1 > 3 > 2 (D) 3 > 2 >1

AE0087

3.  **[JEE 2003]**

(A)  (B)  (C) $C_6H_5OC_6H_5$ (D) $C_2H_5OC_2H_5$

AE0088

4. Reaction of entainomerically pure acid with 1 chiral carbon and racemic alcohol with 1 chiral carbon gives an ester which is: **[JEE 2003]**

(A) Meso (B) Optically active mixture

(C) Racemic mixture (D) Enantionmerically pure

AE0089

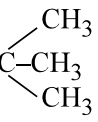
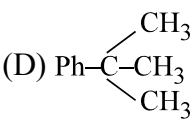
5. On acid catalysed hydration, 2-phenyl propene gives: **[JEE 2004]**

(A) 3-phenyl-2-propanol (B) 2-phenyl-1-propanol

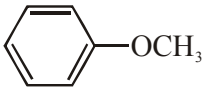
(C) 1-phenyl-3-propanol (D) 2-phenyl-2-propanol

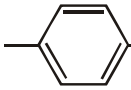
AE0090

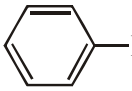
6. Phenyl magnesium bromide reacting with t-Butyl alcohol gives **[JEE 2005]**

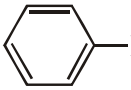
(A) Ph – OH (B) Ph – H (C)  (D) 

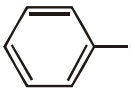
AE0091

7. In the reaction  the products are **[JEE 2010]**

(A) Br  and H_2

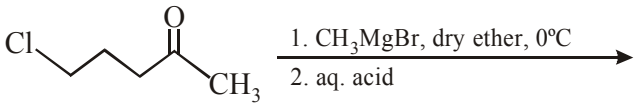
(B)  and CH_3Br

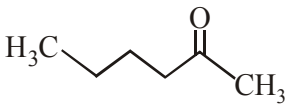
(C)  and CH_3OH

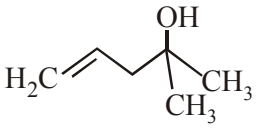
(D)  and CH_3Br

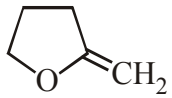
AE0092

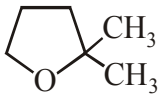
8. The major product in the following reaction is



A) 

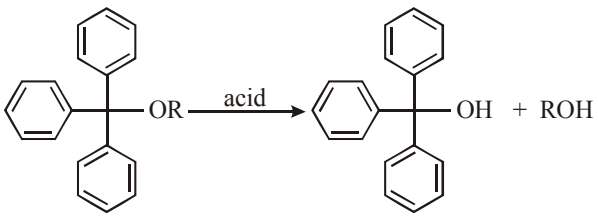
(B) 

(C) 

(D) 

AE0093

9. The acidic hydrolysis of ether (X) shown below is fastest when **[JEE 2014]**



[X]

(A) one phenyl group is replaced by a methyl group
(B) one phenyl group is replaced by a para-methoxyphenyl group
(C) two phenyl groups are replaced by two para-methoxyphenyl group
(D) no structural change is made to X

AE0094

10. The correct combination of names for isomeric alcohols with molecular formula $C_4H_{10}O$ is/are- **[JEE 2014]**

(A) *tert*-butanol and 2-methylpropan-2-ol
(B) *tert*-butanol and 1, 1-dimethylethan-1-ol
(C) *n*-butanol and butan-1-ol
(D) isobutyl alcohol and 2-methylpropan-1-ol

AE0095

ANSWER KEY

EXERCISE # O-1

1.	**Ans.** (B)	**2.**	**Ans.** (C)	**3.**	**Ans.** (C)	**4.**	**Ans.** (C)
5.	**Ans. (B)**	**6.**	**Ans.** (D)	**7.**	**Ans.** (C)	**8.**	**Ans.** (C)
9.	**Ans.** (B)	**10.**	**Ans.** (C)	**11.**	**Ans. (B)**	**12.**	**Ans.** (A)
13.	**Ans.** (B)	**14.**	**Ans. (B)**	**15.**	**Ans.** (A)	**16.**	**Ans.** (B)
17.	**Ans.** (A)	**18.**	**Ans.** (B)	**19.**	**Ans.** (D)	**20.**	**Ans.** (D)
21.	**Ans. (C)**	**22.**	**Ans.(B)**	**23.**	**Ans. (C)**	**24.**	**Ans. (A)**
25.	**Ans. (A)**	**26.**	**Ans.** (B)	**27.**	**Ans. (A)**	**28.**	**Ans.** (B)
29.	**Ans. (C)**	**30.**	**Ans.(C)**				

EXERCISE # O-2

1.	**Ans. (A)**	**2.**	**Ans. (C)**	**3.**	**Ans. (C)**	**4.**	**Ans. (D)**
5.	**Ans. (C)**	**6.**	**Ans. (C)**	**7.**	**Ans. (D)**	**8.**	**Ans. (A)**
9.	**Ans. (B)**	**10.**	**Ans. (C)**	**11.**	**Ans. (A)**	**12.**	**Ans. (B)**
13.	**Ans. (B)**	**14.**	**Ans.(D)**	**15.**	**Ans.(A,B,D)**	**16.**	**Ans.** (A)
17.	**Ans.** (B,C,D)	**18.**	**Ans.** (C)	**19.**	**Ans.** (A)	**20.**	**Ans. (D)**

EXERCISE # S-1

1.	**Ans. (B)**	**2.**	**Ans.** (C)	**3.**	**Ans. (B)**	**4.**	**Ans.** (B)
5.	**Ans. (D)**	**6.**	**Ans (C)**	**7.**	**Ans.** (C)	**8.**	**Ans.**(B)
9.	**Ans.** (C)	**10**	**Ans. (C)**	**11.**	**Ans. (A,B,C)**	**12.**	**Ans.** (B)
13.	**Ans. (A,B,C)**	**14.**	**Ans. (B,C,D)**	**15.**	**Ans.(A)→P; (B)→R; (C)→S; (D)→Q**		

EXERCISE # (J-MAIN)

1. **Ans.(3)** **2.** **Ans. (2)** **3.** **Ans. (3)** **4.** **Ans. (3)** **5.** **Ans. (2)**
6. **Ans. (1)**

Sol. $C_6H_5\overset{\ominus\ \oplus}{O}Na + CH_2=CH-CH_2-Br \longrightarrow$

$C_6H_5O-CH_2-CH=CH_2$
Allyl phenyl ether

7. **Ans.** (1)

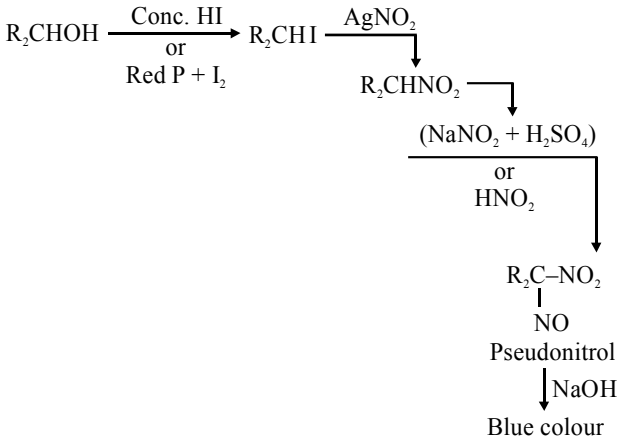
Sol. Victor Meyer's Test :

1°Alcohol

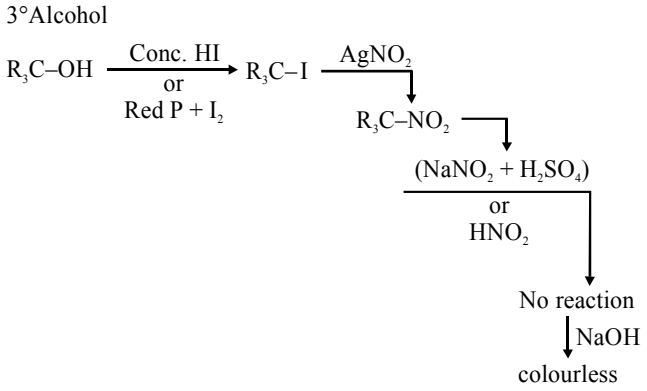
$RCH_2OH \xrightarrow[\text{or}\ \text{Red P} + I_2]{\text{Conc. HI}} RCH_2I \xrightarrow{AgNO_2} RCH_2NO_2 \xrightarrow[\text{or}\ HNO_2]{(NaNO_2 + H_2SO_4)}$

$R-\underset{\underset{N-OH}{\|}}{C}-NO_2$
Nitrolic acid
$\xrightarrow{NaOH}$
Blood Red colour

2°Alcohol

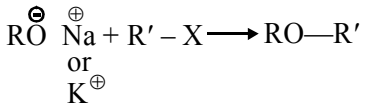


3°Alcohol



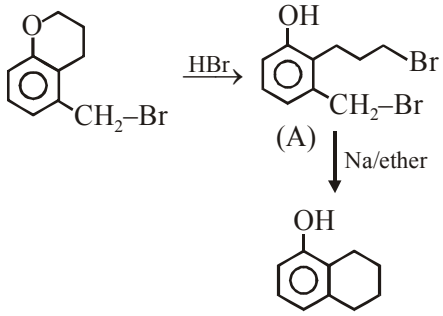
8. Ans.(3)

Sol. Nucleophilic substitution

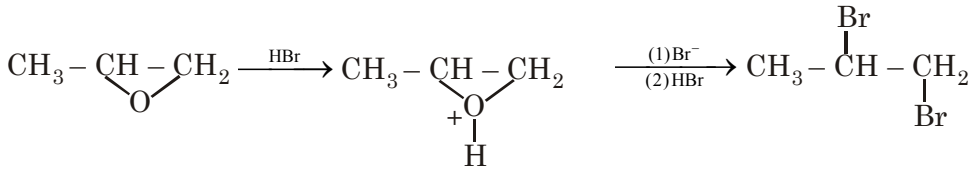


9. Ans. (3) **10. Ans. (1)** **11. Ans.(4)** **12. Ans. (2)** **13. Ans. (2)**
14. Ans. (4) **15. Ans.(4)** **16. Ans. (1)** **17. Ans. (2)** **18. Ans. (4)**
19. Ans.(4)

Sol.

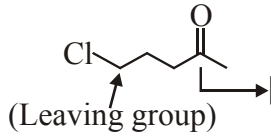


20. Ans.(4)

Sol. 

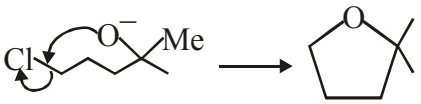
EXERCISE-(J-ADVANCE)

1. Ans. (A) **2. Ans.(B)** **3. Ans.**(D) **4. Ans.** (B)
5. Ans. (D) **6. Ans. (B)** **7. Ans.** (D)
8. Ans. (D)

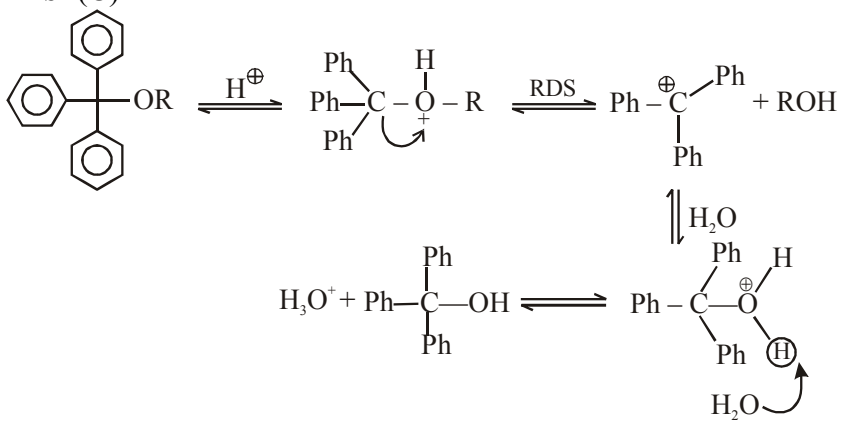
Sol. 
[Polar π-bond give nucleophilic addition reaction]
(Leaving group)
give substitution

(i) Grignard prefer to give nucleophilic addition on polar π-bond and form anion intermediate.

(ii) In next step anion give intramolecular nucleophilic substitution reaction & form 5 membered ring.



9. Ans. (C)

Sol. 

If 2 Ph groups are substituted by 2 MeO— ⬡ — groups then carbocation formed in above sequence is more stable and rate of above hydrolysis increases

10. **Ans.** (A,C,D)

The combination of names for isomeric alcohols with molecular formula $C_4H_{10}O$ is/are

Formula	Names
$CH_3CH_2CH_2CH_2OH$	n-butyl alcohol / n-butanol / butan-1-ol
$CH_3–\underset{\displaystyle CH_3}{\underset{\vert}{CH}}–CH_2–OH$	isobutyl alcohol / 2-methyl propan-1-ol
$CH_3–CH_2–\underset{\displaystyle CH_3}{\underset{\vert}{CH}}–OH$	Secondary butyl alcohol / butan-2-ol
$CH_3–\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{\vert}{\underset{\vert}{C}}}}–OH$	Tertiary butyl alcohol / tert butanol / 2-methyl propan-2-ol / 1,1-dimethyl ethan-1-ol

Reference : National Institute of standards and technology (NIST)