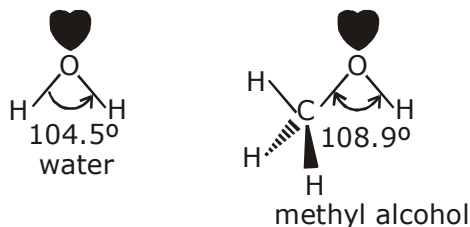


ALCOHOL

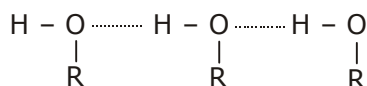
Introduction



Physical Properties

(1) Boiling point :

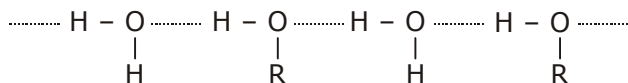
- Alcohols show increase in boiling point with increase in molecular weight amongst homologues.
- Alcohols have higher boiling point than hydrocarbons of the same molecular weight. The reason for higher boiling point is the intermolecular H-bonding present in alcohols.



Intermolecular H bonds in alcohol

(2) Solubility in water :

As molecular weight increases solubility in water decreases. The lower alcohols are miscible with water. This is due to intermolecular hydrogen bonding between alcohol and water molecules.

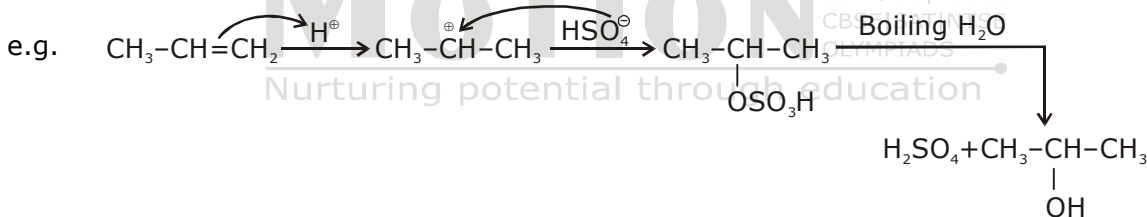
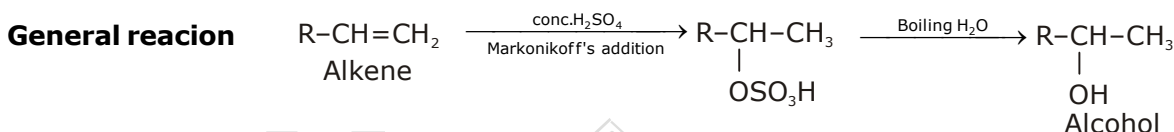


Intermolecular H bond between water & alcohol molecules

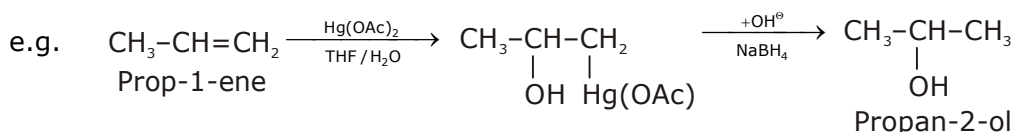
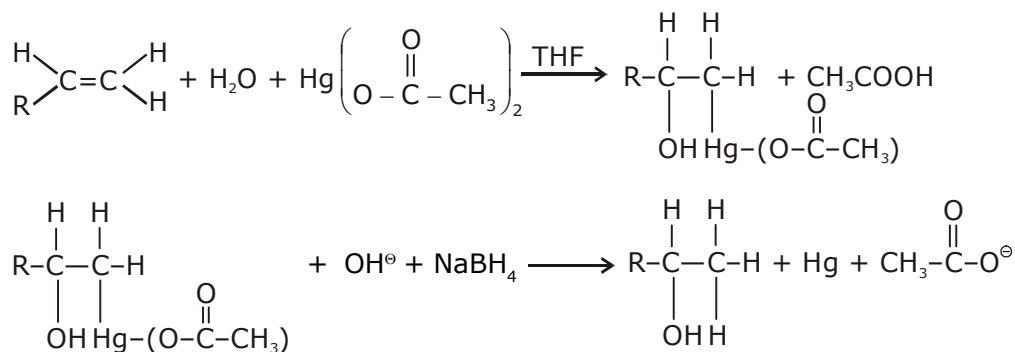
Preparation of alcohols

(1) From alkenes

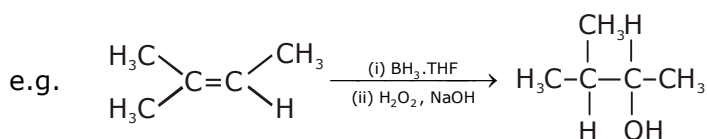
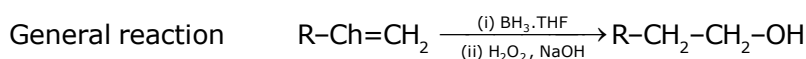
(a) By acid catalyzed hydration of alkenes : Formation of carbocation intermediate (Markovnikov addition, rearrangement possible)



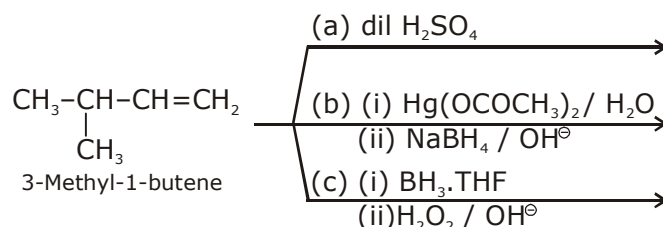
- By Oxymercuration - demercuration process :
 - Oxymercuration involves an electrophilic attack on the double bond by the positively charged mercury species. The product is a mercurinium ion, an organometallic cation containing a three-membered ring.
 - In the second step, water from the solvent attacks the mercurinium ion to give (after deprotonation) an organomercurial alcohol.
 - The third step is demercuration to remove the Hg. Sodium borohydride (NaBH_4 , a reducing agent) re-replaces the mercuric acetate fragment with hydrogen.

General reaction

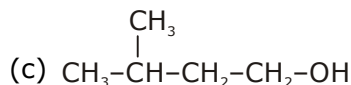
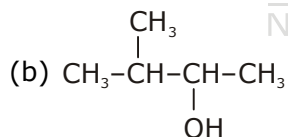
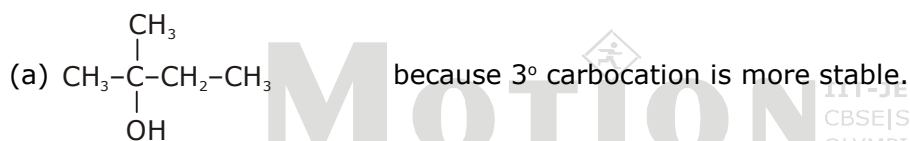
(c) By Hydroboration - oxidation process : (Forms anti-markovnikov alcohol, no rearrangement)



Ex. Give the major product of the following reaction

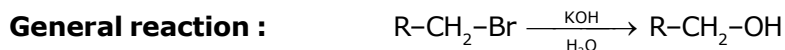


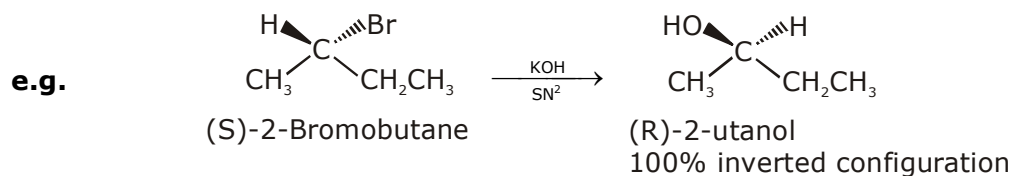
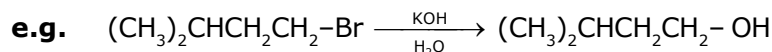
Ans. Major product is



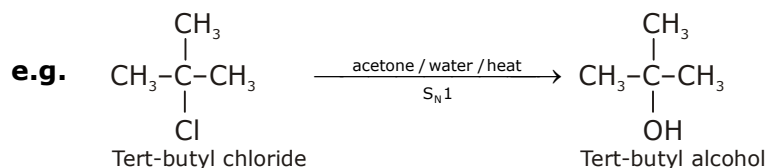
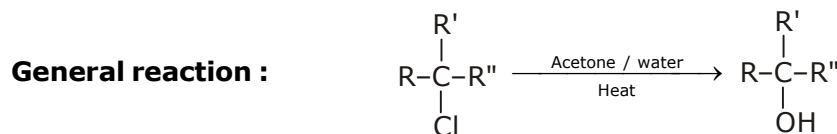
(2) From alkyl halides : By nucleophilic substitution reactions

(a) By S_N^2 mechanism (second-order substitution) : It is given by primary (and some secondary) halides





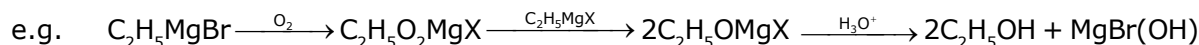
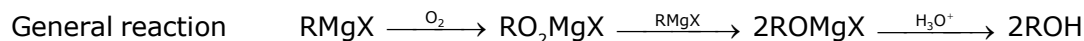
(b) By SN^1 mechanism : It is given by tertiary and some secondary halides



(3) From Grignard reagents

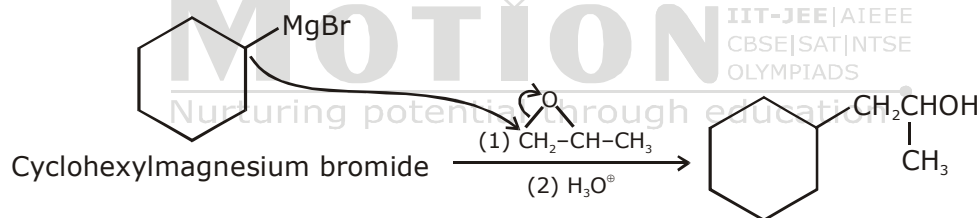
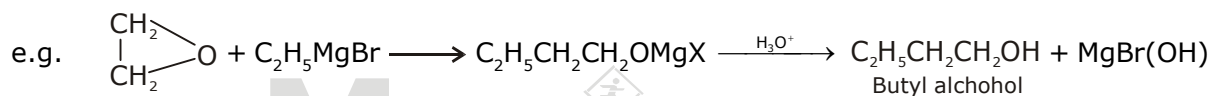
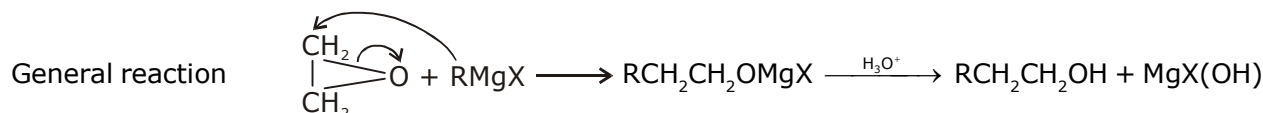
(a) From air

A Grignard reagent may be used to synthesize an alcohol by treating it with dry oxygen and decomposing the product with acid :

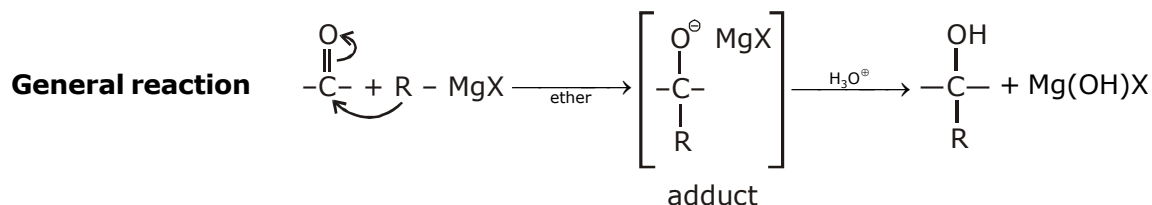


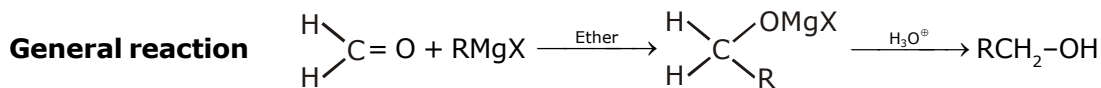
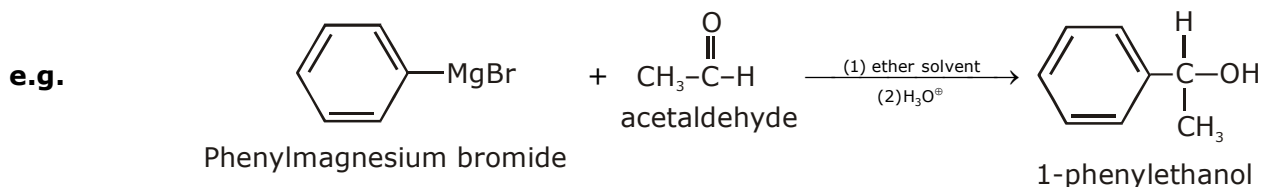
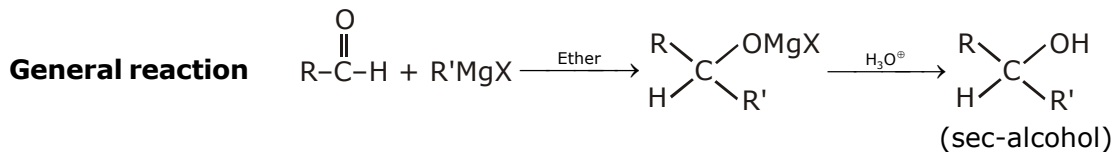
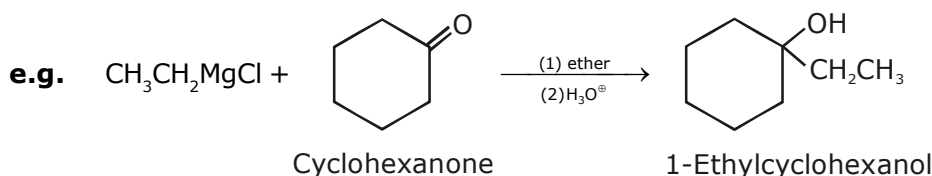
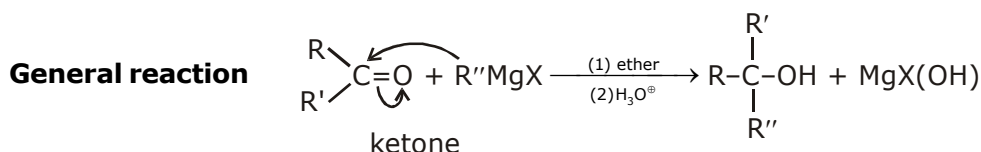
(b) From ethylene oxide

Addition of Grignard reagent to ethylene oxide gives a primary alcohol (with two carbon atoms added)

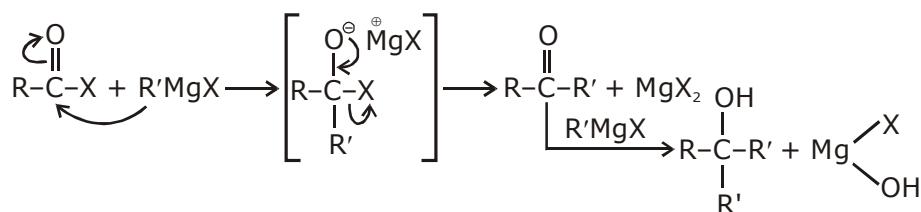
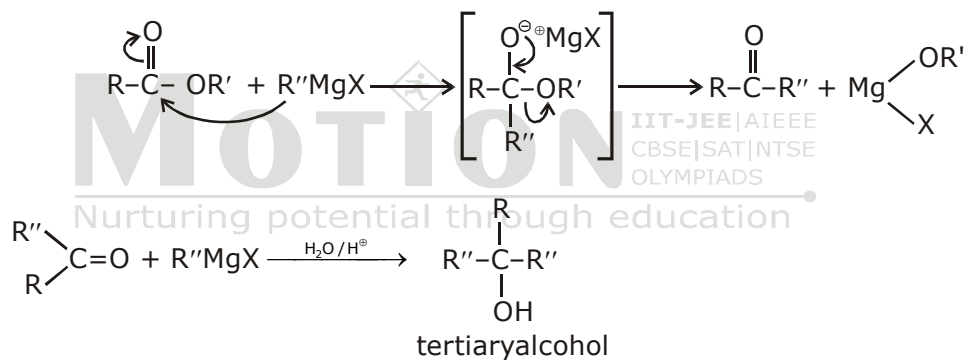


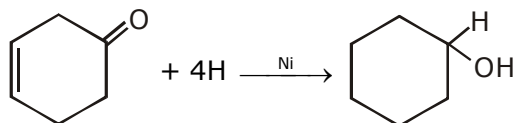
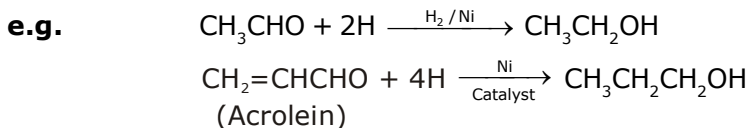
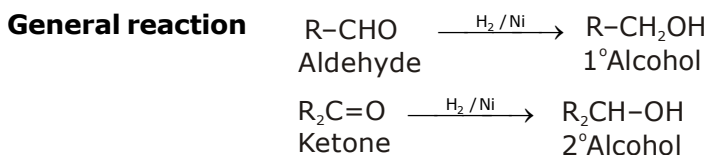
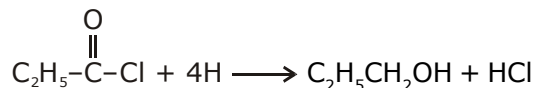
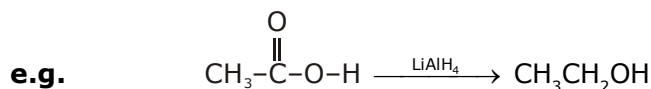
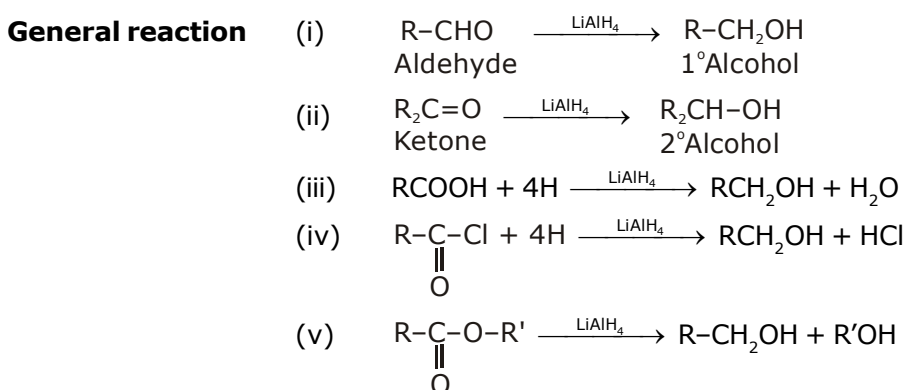
(c) From carbonyl compounds : Nucleophilic addition to the carbonyl groups by Grignard reagent



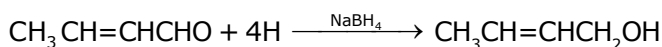
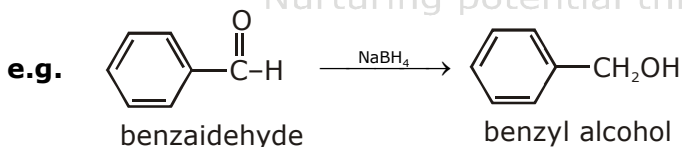
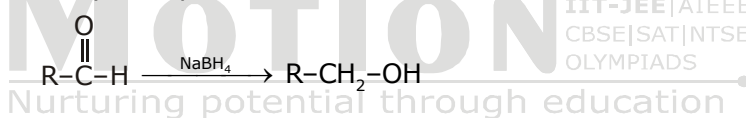
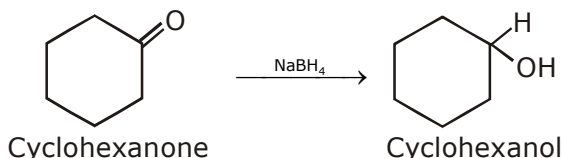
(i) Addition of formaldehyde gives a primary alcohol**(ii) Addition to an aldehyde (other than formaldehyde) gives a secondary alcohol****(iii) Addition to a ketone gives a tertiary alcohol****(iv) Addition to an acid halide or an ester gives a tertiary alcohol**

Esters on treatment with Grignard reagent first form ketones which then react with second molecule of Grignard reagent and form tertiary alcohol.

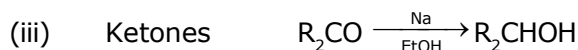
General reaction

(4) By reduction of carbonyl compounds**(a) Catalytic hydrogenation of aldehydes and ketones****(b) Lithium aluminium hydride reduction of aldehydes and ketones**

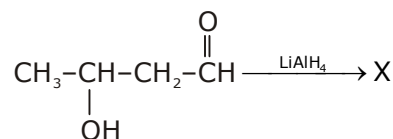
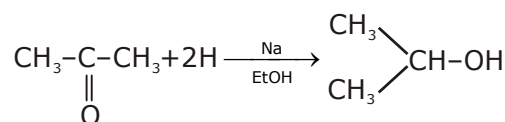
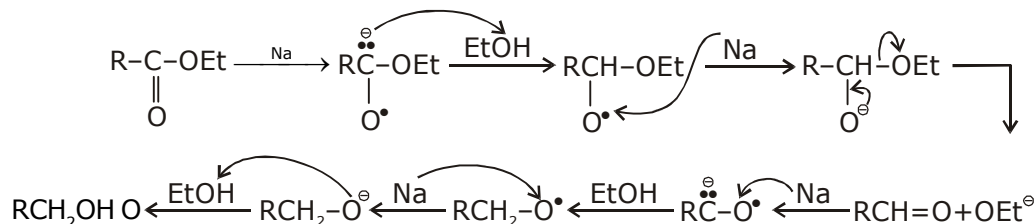
(c) By NaBH₄ (sodium borohydride) : It is insoluble in ether and is used in aqueous ethanolic solution to reduce carbonyl compounds. It does not reduce esters and acids.


**(ii) Reduction of a ketone gives a secondary alcohol**

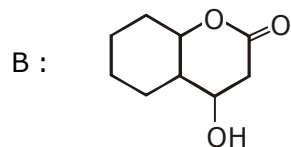
General reaction



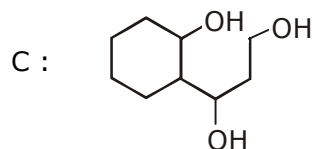
Mechanism



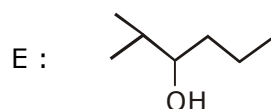
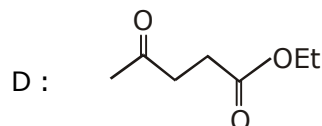
Ans. A :  + (EtOH)



Ester part is not affected by NaBH_4

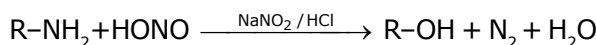


Ester part and keto parts are affected by LiAlH_4

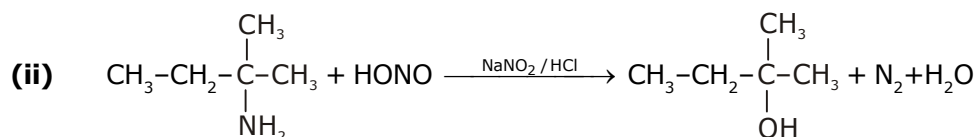
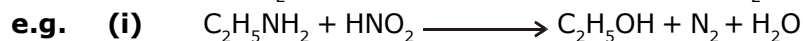
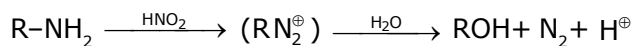


(5) By reaction of nitrous acid on aliphatic primary amines

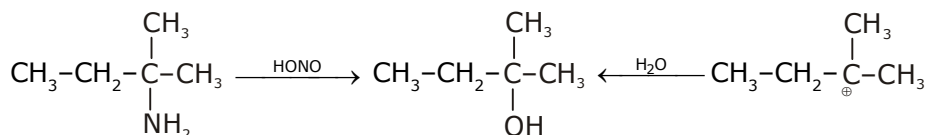
General reaction



Mech.



Mech.

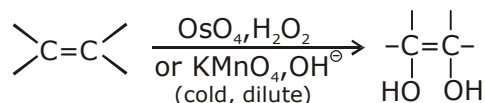


(6) Hydroxylation : Forms vicinal diols (glycols)

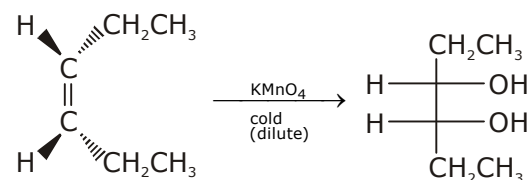
Converting an alkene to a glycol requires adding a hydroxy group to each end of the double bond. This addition is called hydroxylation of the double bond.

(a) Syn hydroxylation, using KMnO_4 / NaOH or using OsO_4 / H_2O_2

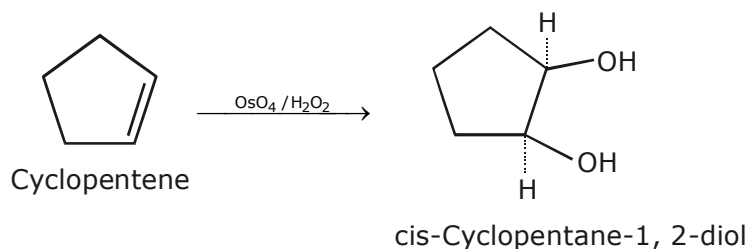
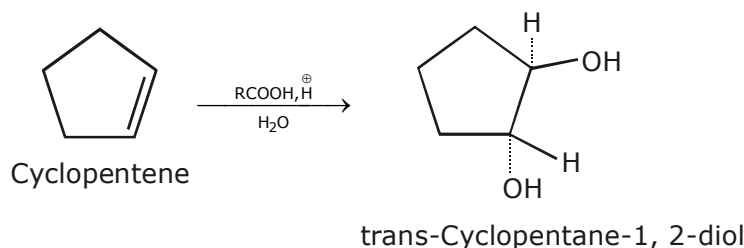
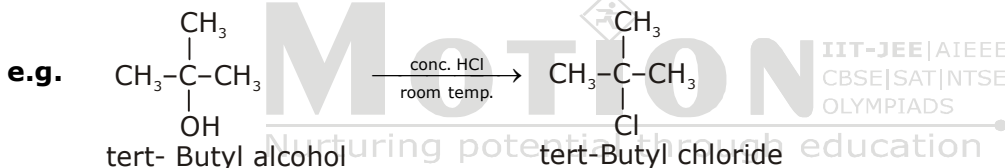
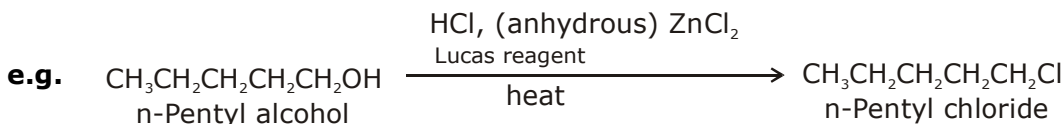
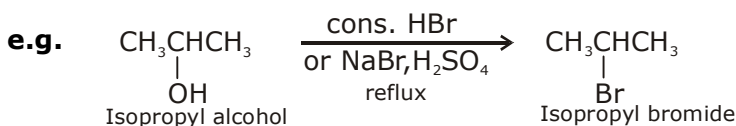
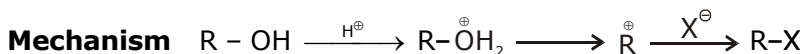
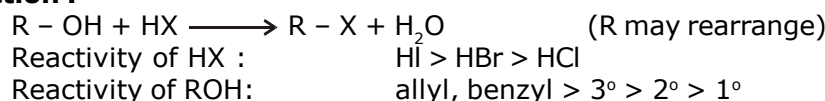
General reaction :



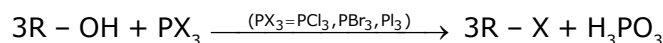
e.g.



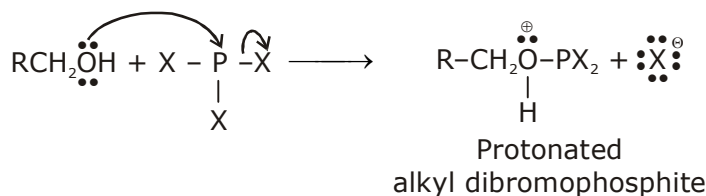
cis-3-hexene

**(b) Anti hydroxylation, using per acids****Chemical reactions of alcohols****1. Reaction with hydrogen halides****General reaction :****2. Reaction with Phosphorus trihalides**

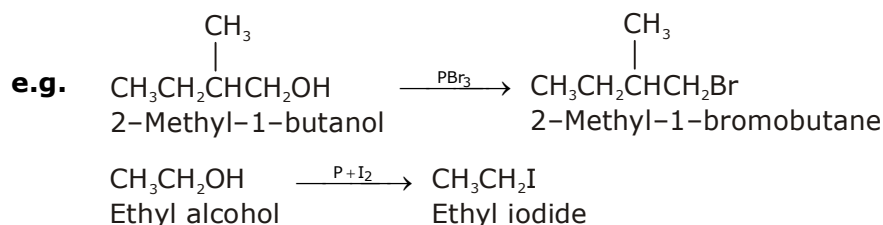
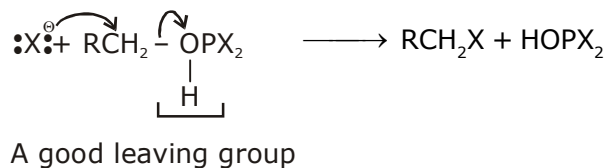
- (1) Several phosphorus halides are useful for converting alcohols to alkyl halides. PBr_3 , PCl_3 , & PCl_5 work well and are commercially available.
- (2) Phosphorus halides produce good yields of most primary and secondary alkyl halides, but none works well with ter. alcohols. The two phosphorus halides used most often are PBr_3 and the P_4/I_2 combination.

General reaction :**Mechanism**

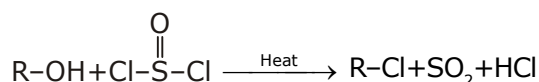
The mechanism for the reaction involves attach of the alcohol group on the phosphorus atom, displacing a bromide ion and forming a protonated alkyl dibromophosphite (see following reaction).



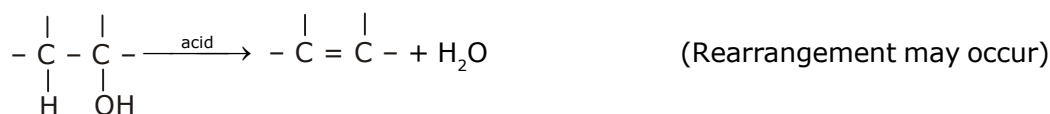
In second step a bromide ion acts as nucleophile to displace HOPBr_2 , a good leaving group due to the electronegative atoms bonded to the phosphorus.



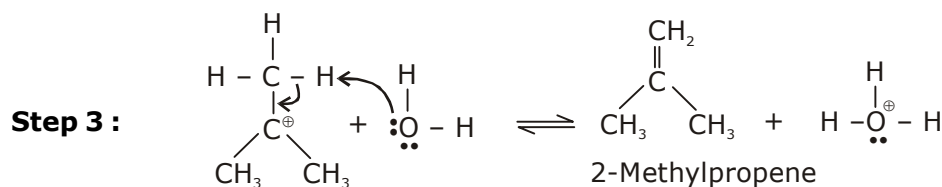
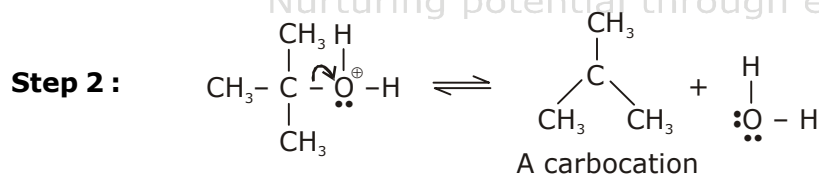
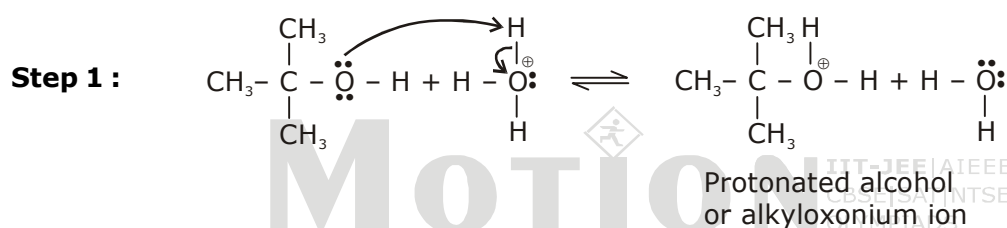
3. Reaction with thionyl chloride



4. Dehydration of alcohols

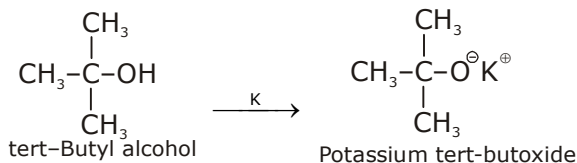
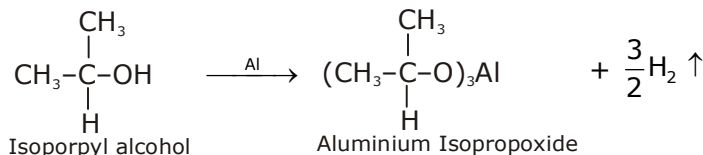
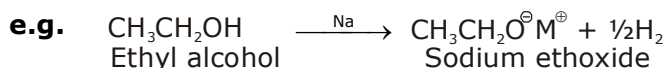
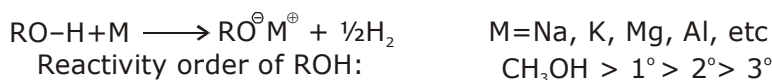


Mechanism



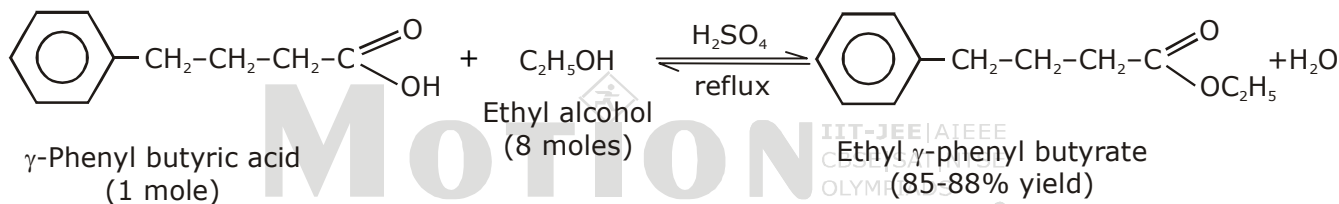
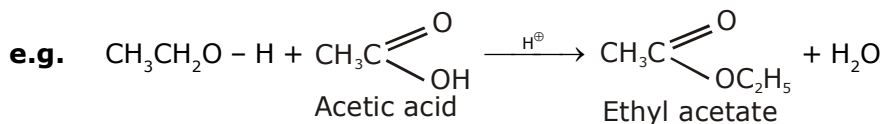
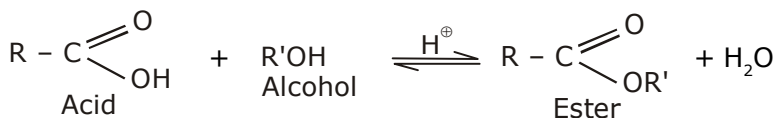
Reactivity of ROH : $3^\circ > 2^\circ > 1^\circ$

5. Reaction with metals



6. Ester formation

General reaction



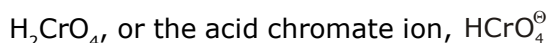
7. Oxidation reactions

(a) oxidation of primary alcohols

Oxidation of a primary alcohol initially forms an aldehyde. obtaining the aldehyde is often difficult, since most oxidizing agents are strong enough to oxidize the aldehydes formed. CrO_3 acid generally oxidizes a primary alcohol all the way upto the carboxylic acid

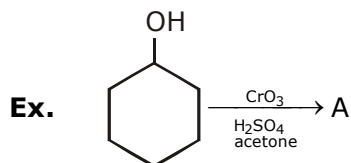
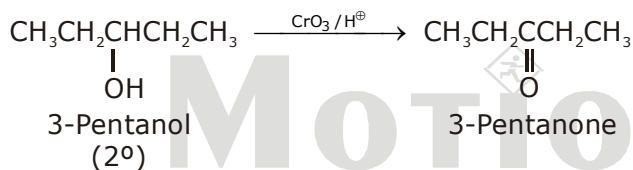
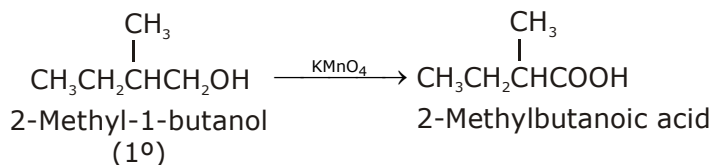
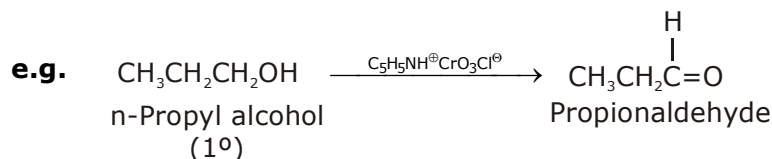
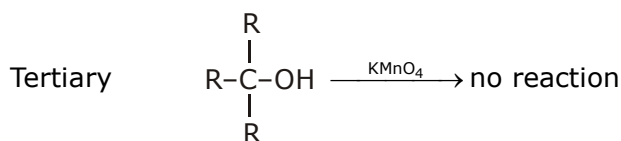
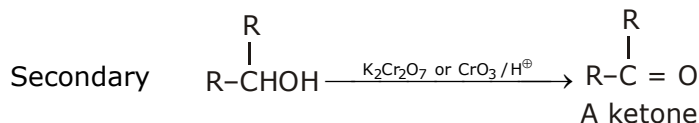
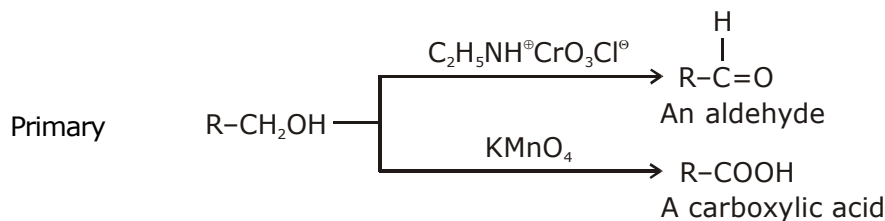
(b) oxidation of secondary alcohols

Sec. alcohols are easily oxidized to give excellent yields of ketones. The chromic acid reagent is often best for laboratory oxidations of secondary alcohols. The active species in the mixture is probably chromic acid,

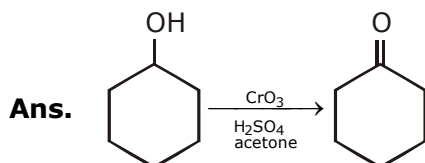


(c) Resistance of tertiary alcohols to oxidation

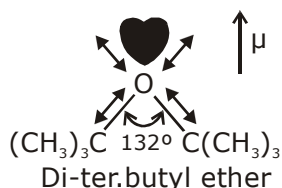
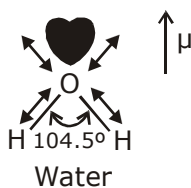
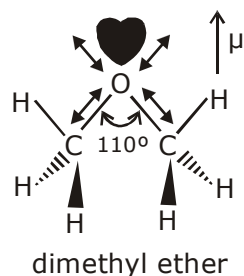
Oxidation of ter-alcohol is not an important reaction in organic chemistry. Ter-alcohols have hydrogen atoms on the carbinol carbon atom, so oxidation must take place by breaking C-C bonds. These oxidations require severe conditions and result in mixtures of products.



Identify A

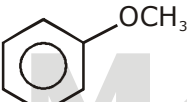
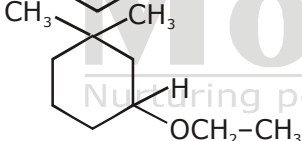
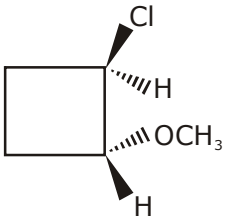


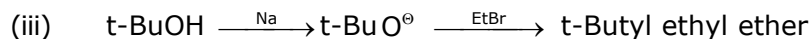
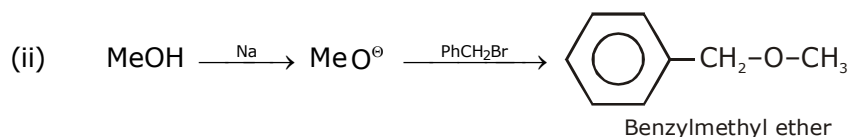
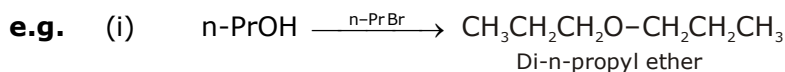
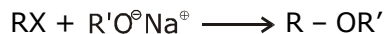
Structure of ether



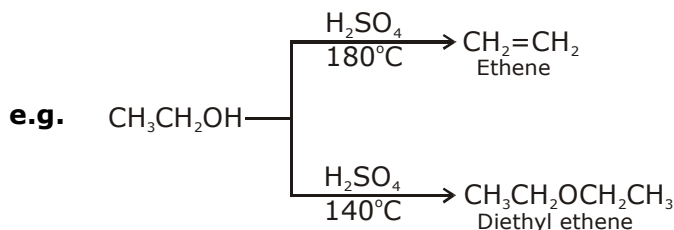
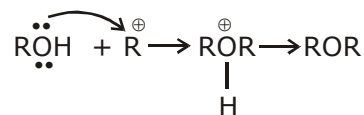
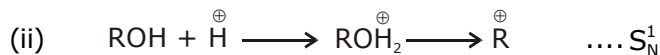
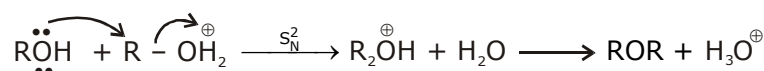
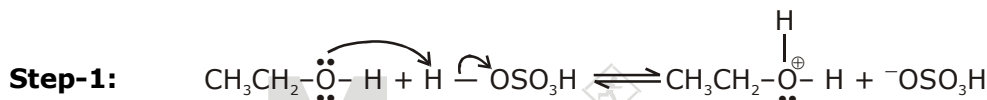
Classificaion of Acyclic ethers

IUPAC Nomenclature of ether "Alkoxy Alkane"

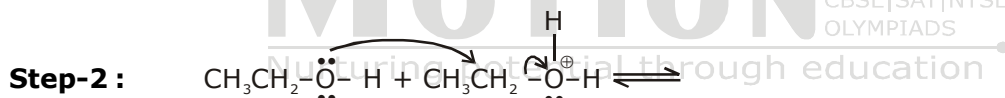
S.N.	Compound	IUPAC Name
1.	$\begin{array}{c} \text{CH}_3-\text{CH}-\text{O}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	2-Methoxy propane
2.	$\text{Cl}-\text{CH}_2-\text{O}-\text{CH}_3$	Chloromethoxy methane
3.		Methoxy benzene (Anisole)
4.		3-Ethoxy-1, 1-dimethyl cyclohexane
5.		trans-1-Chloro-2-methoxy cyclobutane
6.	$\begin{array}{c} \text{CH}_2-\text{OH} \\ \\ \text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_3 \end{array}$	2-Ethoxy ethan-1-ol

Method of Preparation of Ether**(1) Williamson synthesis****General reaction**

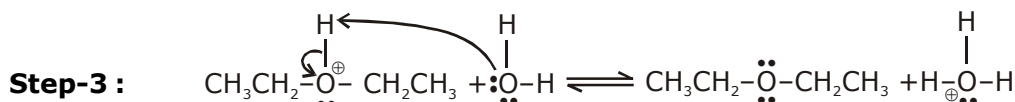
(This reaction produces a poor yield of ether because of the bulkiness of $t\text{-BuO}^{\ominus}$)

2. Williamson's Continuous Etherification process or by Dehydration of Alcohols**Mechanism**

This is an acid-base reaction in which the alcohol accepts a proton from the sulfuric acid



Another molecule of the alcohol acts as a nucleophile and attacks the protonated alcohol in an S_N^2 reaction.

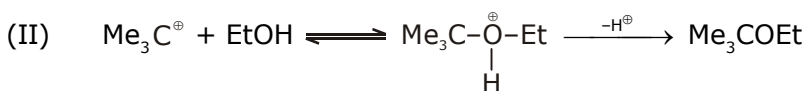
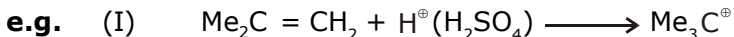
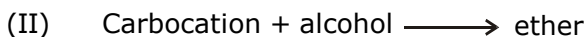
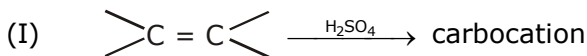
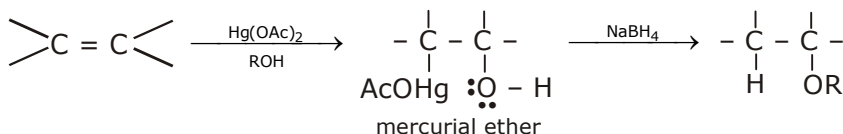


Another acid-base reaction converts the protonated ether to an ether by transferring a proton to a molecule of water (or to another molecule of the alcohol).

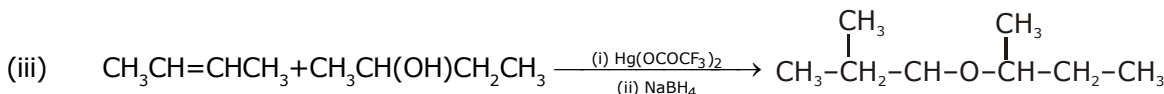
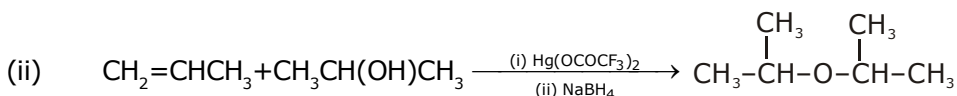
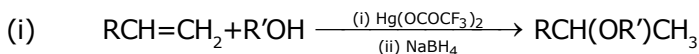
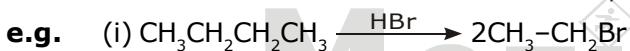
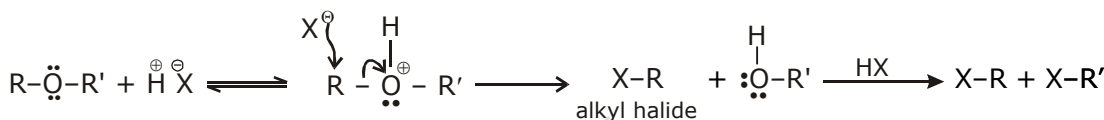
Only one combination of alkylhalide and alkoxide is appropriate for the preparation of each of the following ethers by Williamson ether synthesis. What is the correct combination in each case ?

3. Form alkenes**(a) By addition of alcohols in alkenes**

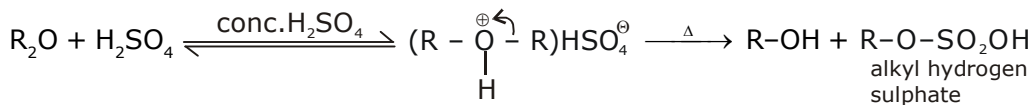
When alcohol is added to alkenes in presence of acid, we get ethers.

General reaction**(b) Alkoxymercuration - demercuration**

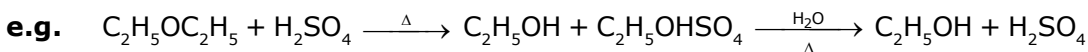
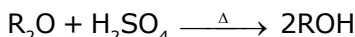
e.g.

**Reactions of ethers****1. With HX****General reaction****2. Reaction with sulphuric acid**

Ethers dissolve in concentrated solutions of strong inorganic acids to form oxonium salts, i.e. ether behave as bronsted Lowry bases.



When heated with dilute H_2SO_4

**3. Autoxidation of ethers :**

When ethers are stored in the presence of atmospheric oxygen, they slowly oxidize to produce hydroperoxides and dialkyl peroxides, both of which are explosive. Such a spontaneous oxidation by atmospheric oxygen is called an autoxidation.

