## Solution

## PHENOLS, ALCOHOLS AND ETHERS

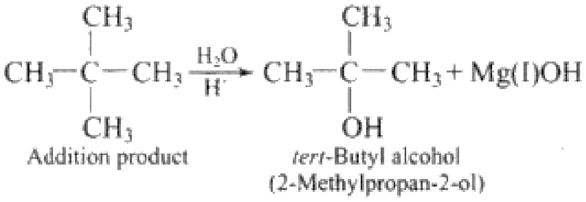
## Class 12 - Chemistry

1. Industrial alcohol (ethyl alcohol) is made unfit for drinking purpose by addition of a small quantity of poisonous substance, methanol. This is called denatured alcohol. For denaturation, copper sulphate or pyridine can also be added.
2. The process of breaking down large molecules into smaller one in the presence of biological catalysts is called fermentation we can prepare ethyl alcohol from molasses or starch by fermentation.
3. The conversions are achieved as under:

   (i) Ethanol to 2-propanol

   $$\underset{Ethanol}{CH_3CH_2OH}\xrightarrow[573K]{Cu}\underset{Ethanal}{CH_3-\overset{\overset{O}{||}}{C}-H}\xrightarrow[(ii)H_2O/H^+]{(i)CH_3MgBr}\underset{2-\text{Propanol}}{CH_3-\overset{\overset{OH}{|}}{C}H-CH_3}$$
4. $HO-CH_2-CH_2-\underset{\underset{CH_2Cl}{|}}{CH}-CH_2-CH_3$
5. $\overset{5}{CH_3}\,\overset{4}{CH_2}-\overset{3}{\underset{\underset{CH_2Cl}{|}}{CH}}-\overset{2}{\underset{\underset{\overset{1}{CH_2OH}}{|}}{CH}}-\underset{\underset{CH_3}{|}}{CH}-CH_3$

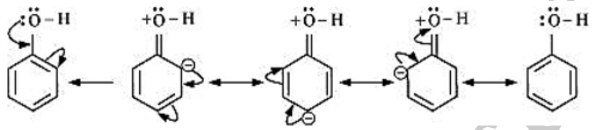
   $3-chloromethyl-2-isopropylpentan-1-ol$
6. $CH_3CH_2CH_2OH+HBr\xrightarrow{reflux}CH_3CH_2CH_2Br+H_2O$
7. $CH_3-\overset{\overset{O}{||}}{C}-CH_3+CH_3MgI\xrightarrow{\text{Ether}}$

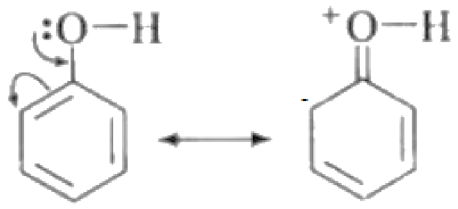
   Addition product

   *tert*-Butyl alcohol (2-Methylpropan-2-ol)

   The action of Grignard reagent on ketones give tertiary alcohols.
8. The -OH group is an electron-donating group. Thus, it increases the electron density in the benzene ring as shown in the given resonance structure of phenol.

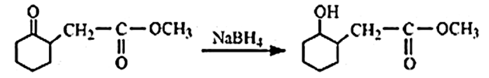
   

   As a result, the benzene ring is activated towards electrophilic substitution.
9. This can be explained as under:
   1. In phenol, the conjugation of unshared electron pairs over oxygen with the aromatic ring shows the +M effect that results in partial double bond character in C - O bond.

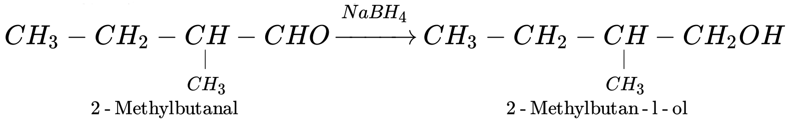
      

      In methanol, no such conjugation (resonance) is possible.
   2. In phenol, oxygen is attached to sp$^2$ hybridized carbon while in methanol, oxygen attached to sp$^3$ hybridized carbon. An sp$^2$ hybridized carbon is more electronegative (because of greater s -character than sp$^3$ hybridized carbon atom. Therefore, the bond between oxygen and sp$^2$ hybridized carbon is more stable than the bond between oxygen and sp$^3$, hybridized orbital.

   Due to these reasons, the bond strength of carbon and oxygen in phenol is high.
10. i. $\underset{\text{Propene}}{CH_3-CH=CH_2}\xrightarrow{H_2O/H^+}\underset{\text{Propane - 2 - ol}}{CH_3-\underset{\underset{OH}{|}}{C}H-CH_3}$

ii. 

Methyl (2 – oxocyclohexyl) ethanoate → Methyl (2 – hydroxycyclohexyl) ethanoate

iii. 

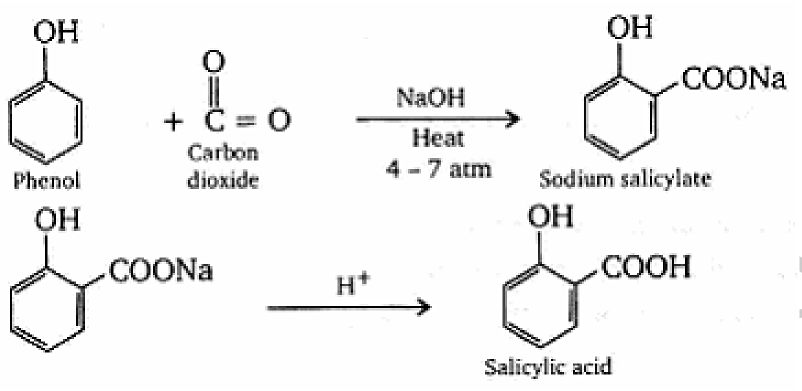
$\underset{\text{2 - Methylbutanal}}{CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-CHO} \xrightarrow{NaBH_4} \underset{\text{2 - Methylbutan - 1 - ol}}{CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2OH}$

11. The addition of borane followed by oxidation is known as the hydroboration-oxidation reaction.

For example, propan-1-ol is produced by the hydroboration-oxidation reaction of propene. In this reaction, propene reacts with diborane $(BH_3)^2$ to form trialkyl borane as an addition product. This addition product is oxidized to alcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide.

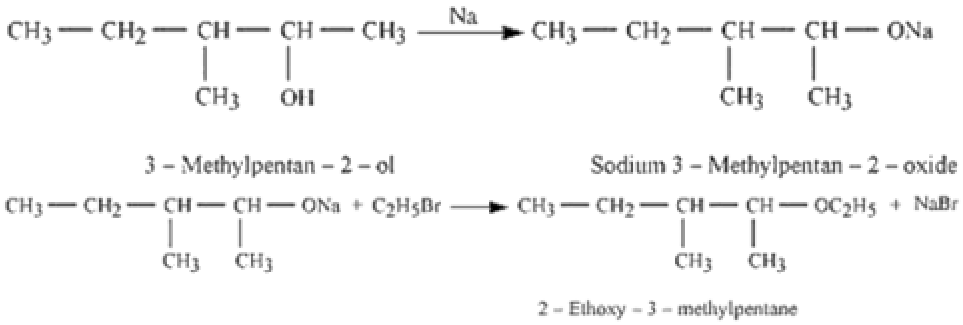
12. i. $\mathrm{CH_3CH = CH_2} \xrightarrow[\text{(ii) } H_2O_2\ /\ OH]{\text{(i) } R_2H_2} \underset{\text{1 - Propanol}}{\mathrm{CH_3CH_2CH_2OH}}$

ii.



13. In Williamson synthesis, an alkyl halide reacts with an alkoxide ion. Also, it is an $S_N^2$ reaction. In the reaction, alkyl halides should be primary having the least steric hindrance. Hence, an alkyl halide is obtained from ethanol and alkoxide ion from 3-methylpentan-2-ol.

$\underset{\text{Ethanol}}{\mathrm{C_2H_5OH}} \xrightarrow{\text{HBr}} \underset{\text{Bromoethane}}{\mathrm{C_2H_5Br}}$



14. Oxidation of phenol with Zn given Benzene(A).

Nitration of Benzene give Nitro Benzene (B).

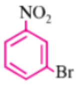
Bromination of nitrobenzene gives Bromonitrobenzene(C).

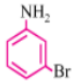
Reduction of Bromonitrobenzene give Bromaniline(D).

Treatment with sandmeyer's reaction, D gives Benzenediazonium salt(E).

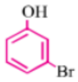
Finally, hydrolysis of E gives Bromophenol (F).

A = $C_6H_6$, B = $C_6H_5NO_2$

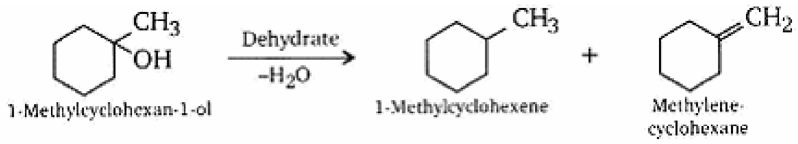
C = 

D = 

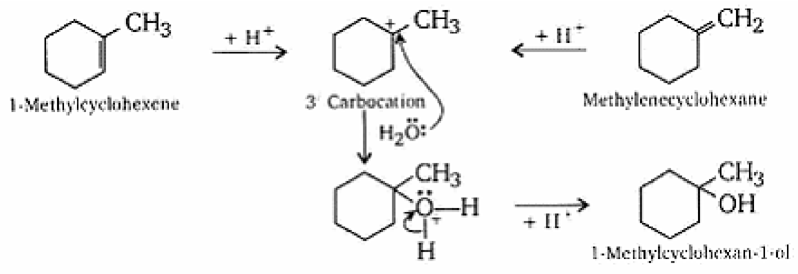
E = 

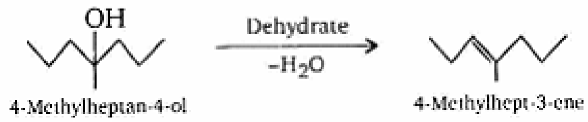
F = 

15. Since addition and elimination are reverse of each other, therefore, the general strategy is to first dehydrate a suitable alcohol to give either a single alkene or a mixture of alkenes. If a mixture of alkenes is possible, then find out which of the alkenes will give the desired alcohol. Please note that acid catalysed addition of $H_2O$ to alkenes occurs in accordance with Markovnikov's rule.

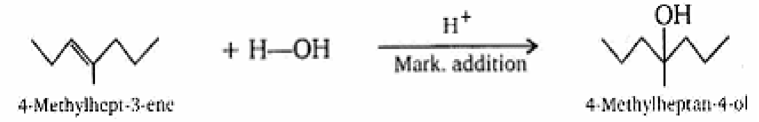
i. 

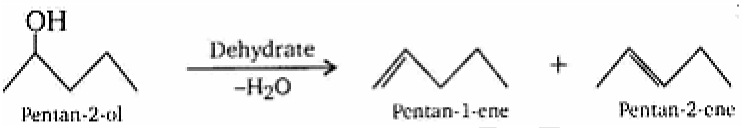
Addition of $H_2O$ to both these alkenes give the desired alcohol.



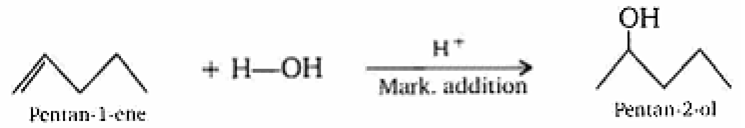
ii. 

Addition of $H_2O$ to 4-methylhept-3-ene in presence of an acid gives the desired alcohol.

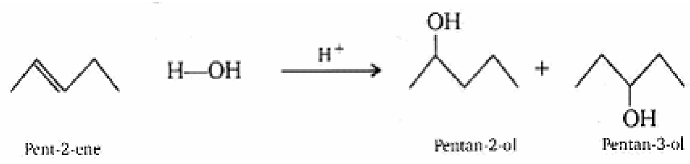


iii. 

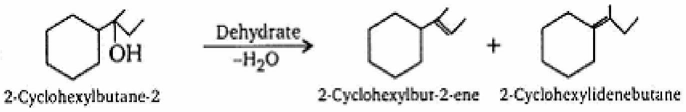
Now addition of $H_2O$ to pent-l-ene gives the desired alcohol.



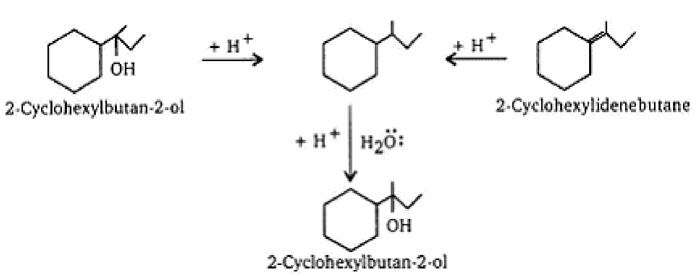
However, addition of $H_2O$ to pent-2-ene gives a mixture of two alcohols i.e. pentan-2-ol and pentan-3-ol.



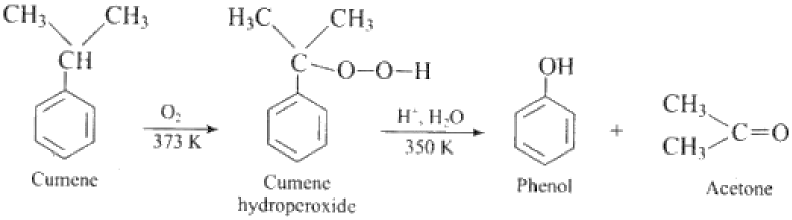
Thus, the desired alkene is pent-l-ene and not pent-2-ene.

iv. 

Now addition of $H_2O$ to both 2-cyclohexylbut-2-ene and 2-cyclohexylidenebutane in presence of an acid gives the desired alcohol.

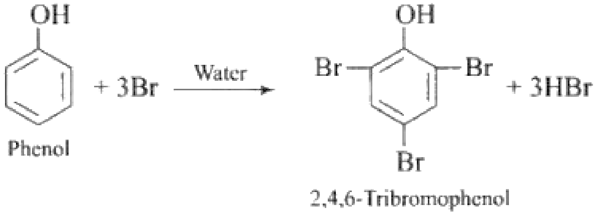


16. a. Cumene (Isopropyl benzene) is the starting material used in industrial preparation of phenol.

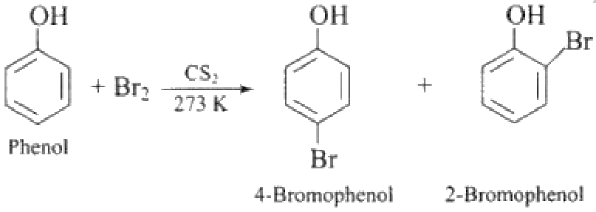


b. Bromination of phenol

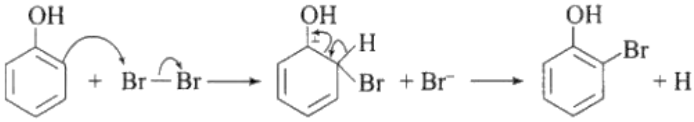
i. in aqueous medium



ii. in non-aqueous medium



c. Usual halogenation is carried out in the presence of Lewis acid, $FeBr_3$ which polarises the halogen molecule. In the case of phenol, the polarisation of bromine occurs even in the absence of Lewis acid. This is because of the highly activating effect of -OH group on the benzene ring. The reaction follows:



Note: In an aqueous solution, phenol ionizes to give phenoxide ion. Due to the presence of the negative charge, the oxygen atom of the phenoxide ion donates electrons to the benzene ring to a large extent. As a result, the ring gets highly activated leading to the formation of the trisubstituted product. On the other hand, in the non-polar solvents, the ionization of phenol does not occur to a large extent. As a result, the -OH group donates electrons to the benzene ring only to a small extent. Consequently, the ring is activated slightly and, therefore, only mono substitution occurs.

17. On adding neutral $FCl_3$ solution phenol will give violet colour whereas benzoic acid does not exist.