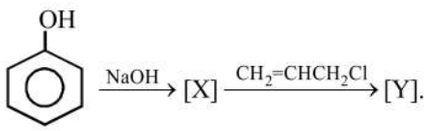
Alcohols, Phenols and Ethers

1. Among the given hydroxyl compound how many will give precipitate immediately when treated with concentrated hydrochloric acid and anhydrous zinc chloride.
3-methyl-2-butanol; 3-methyl-1-butanol; 1-butanol; 2-methyl-2-butanol; 2, 3-dimethyl-2-butanol, 2, 3-dimethyl-1-butanol

2. 

How many products are formed in above reaction?

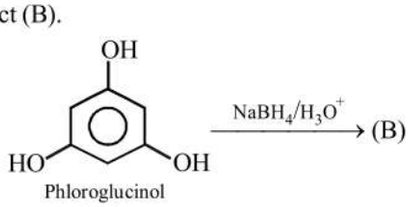
3. An ether (A), $C_5H_{12}O$, when heated with excess of hot concentrated HI produced two alkyl halides which when treated with NaOH yielded compounds (B) and (C). Oxidation of (B) and (C) gave a propanone and an ethanoic acid respectively.
In the compound A, at which carbon of alkane is the ether group attached?

4. How many of the given reaction will form *tert*-Butyl ethyl ether?

(I) *tert* – Butanol + Ethanol $\xrightarrow{H^+}$
(II) *tert*-Butyl bromide + Sodium ethoxide $\longrightarrow$
(III) Sodium *tert*-butoxide + Ethyl bromide $\longrightarrow$
(IV) Isobutene + Ethanol $\xrightarrow{H^+}$

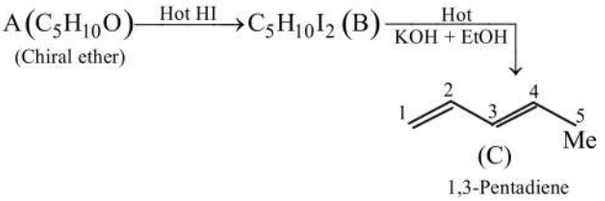
5. Which of the following statements is/ are true?
(I) Ethers are soluble in conc. H_2SO_4 but separate out on addition of water.
(II) Ethers are used as solvents for BF_3 and Grignard reagent.
(III) Mononitration of *p*-methylanisole gives 2-nitro-4-methylanisole
(IV) Monobromination of *p*-ethoxyphenol gives 2-bromo-4-ethoxyphenol
(V) 4-Chlorophenol (I) will dissolve in NaOH but 4-chloro-1-methyl benzene (II) will not.
(VI) 4-Methyl benzoic (III) acid will dissolve in aq. $NaHCO_3$ but 4-methyl phenol (IV) will not.
(VII) 2,4,6-Trinitrophenol (V) will dissolve in aq. $NaHCO_3$ but 4-methyl phenol (VI) will not.
(VIII) 4-Ethyl phenol (VII) will dissolve in aq. NaOH but ethyl phenyl ether (VIII) will not.

6. Generally, phenols, 1,3,1,4-benzenediols and 1,3,5-benzenetriols do not react with $NaBH_4/H_3O^+$. However, 1,3,5-benzenetriol (phloroglucinol) gives a high yield of product (B).



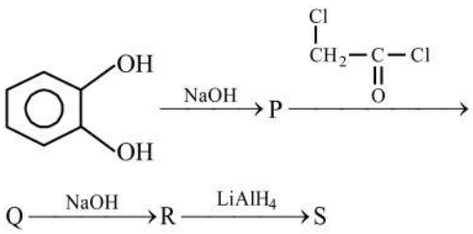
Phloroglucinol
(A)

The compound (B) has how many functional groups on benzene ring?

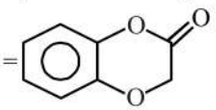
7. 

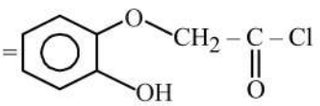
(C)
1,3-Pentadiene

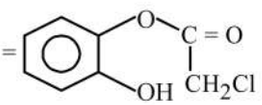
How many members are there in the ring of structure of A?

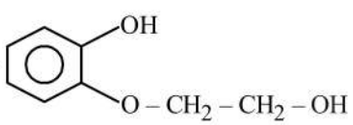
8. 

How many among the below given compounds correctly match the products of the given reaction sequence?

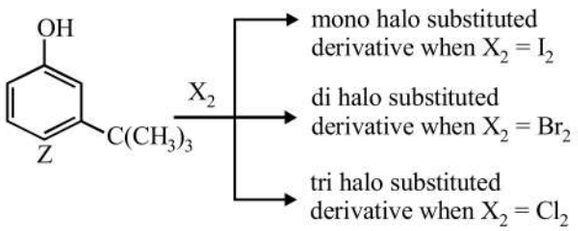
(I) R = 

(II) Q = 

(III) Q = 

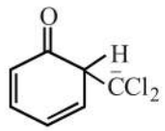
(IV) S = 

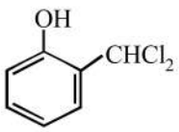
9. The reactivity of compound Z with different halogens under appropriate conditions is given below:

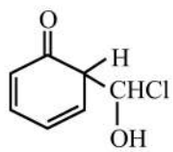


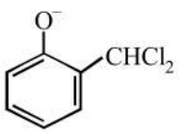
How many among the below given statements correctly explains pattern of elctrophilic substitution?
(I) The steric effect of the halogen.
(II) The steric effect of the *tert*-butyl group.
(III) The electronic effect of the phenolic group.
(IV) The electronic effect of the *tert*-butyl group.
(V) The mesomeric effect of *tert*-butyl group.

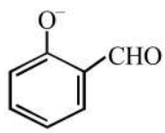
10. When phenol is reacted with $CHCl_3$ and NaOH followed by acidification, salicylaldehyde is obtained. How many among following species are involved in the above mentioned reaction as intermediates?

(I) 

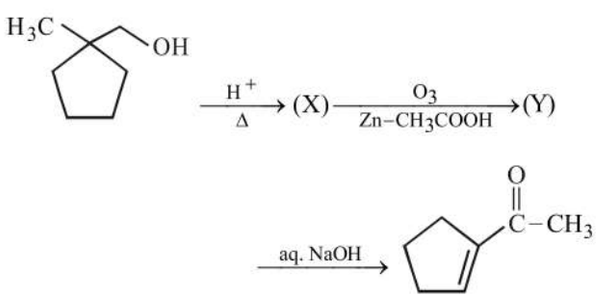
(II) 

(III) 

(IV) 

(V) 

11. How many total number of carbon has sp^2 hybridization in the compound *X* and *Y*?



12. Total number of isomers, considering only structural isomers of cyclic ethers with the molecular formula C_4H_8O is____

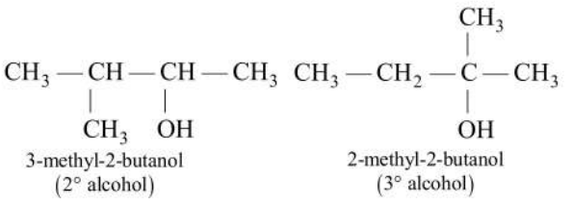
13. What amount of bromine will be required to convert 2 g of phenol into 2, 4, 6 – tribromophenol?

14. Calculate the number of metamers represented by molecular formula $C_4H_{10}O$.

15. How many number of dihydric phenols possible with the molecular formula $C_6H_6O_2$.

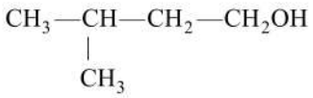
SOLUTIONS

1. **(2)** Structure of given alcohols

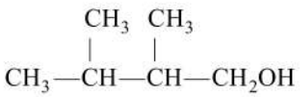


3-methyl-2-butanol (2° alcohol)

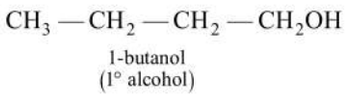
2-methyl-2-butanol (3° alcohol)



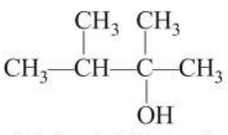
3-methyl-1-butanol (1° alcohol)



2,3-dimethyl-1-butanol (1° alcohol)



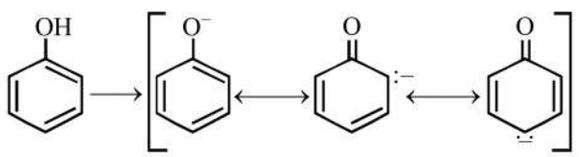
1-butanol (1° alcohol)

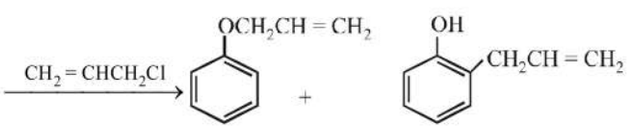


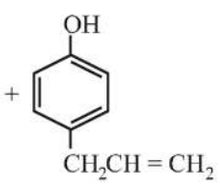
(2,3-dimethyl-2-butanol) (3° alcohol)

2, 3-dimethyl -2-butanol and 2-methyl-2-butanol being tertiary alcohol gives precipitate immediately with conc. HCl and anhydrous $ZnCl_2$.

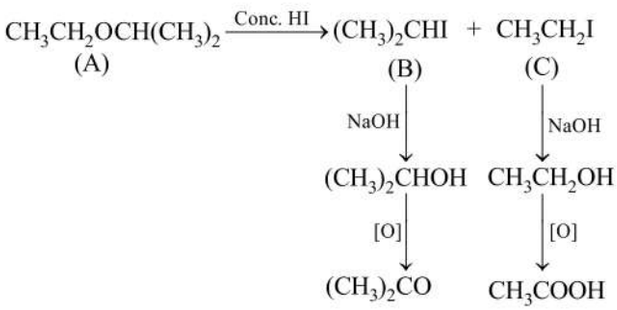
2. **(3)**



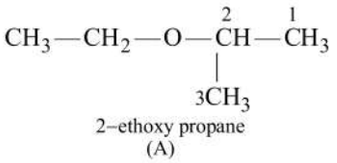




3. **(2)**



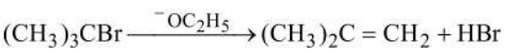
Hence,



2–ethoxy propane (A)

Therefore, ether group is attached at the 2nd carbon of carbon chain.

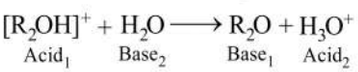
4. **(3)** $(CH_3)_3CBr + NaOC_2H_5$ can't be applied for synthesising the ether because sod. ethoxide, being a strong base, will preferentially cause elimination reaction.



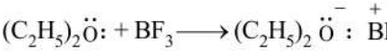
Rest other forms *tert*-Butyl ethyl ether.

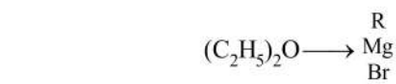
5. **(8)**

(I) Water is stronger base than ether and removes proton from protonated ether, R_2OH^+



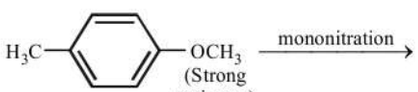
(II) Due to unshared electron pairs, ethers act as Lewis bases and hence easily react with Lewis acids like BF_3 and RMgBr to form coordinated compounds.



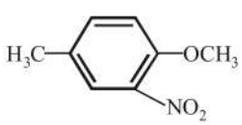


Note that two molecules of ether coordinate tetrahedrally with one Mg^{2+}.

(III)

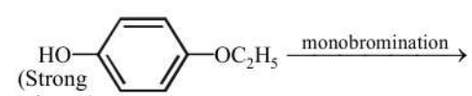


p-Methylanisole

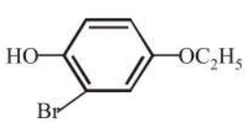


2 Nitro-4-methylanisole

(IV)



p-Ethoxyphenol



2-Bromo-4-ethoxyphenol

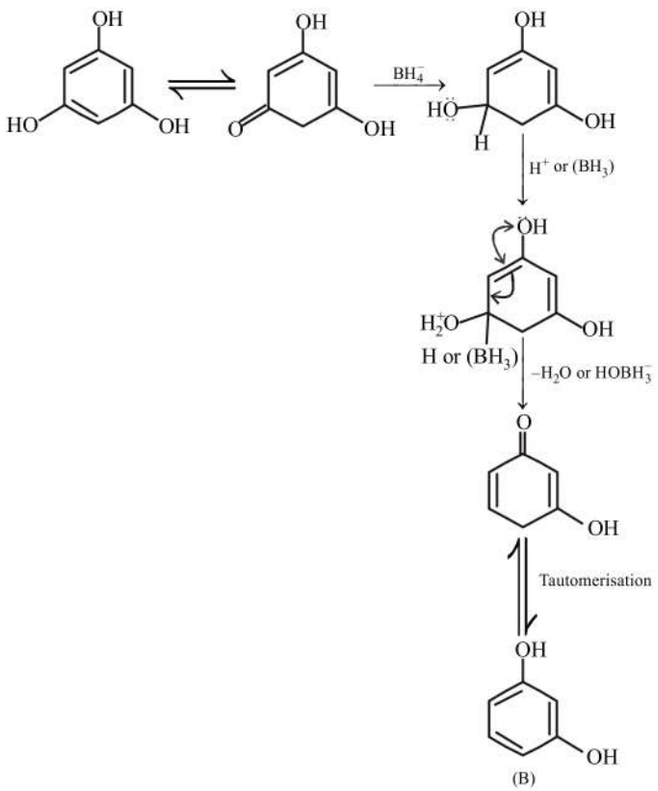
(V) Due to –I effect of Cl, 4-chlorophenol is acidic and dissolves in NaOH, but (II) is an aryl halide and does not dissolve.

(VI) (III) is an acid and dissolves in $NaHCO_3$ but (IV) is a phenol and does not dissolve.

(VII) Although (V) is a phenol, because of the presence of $(3NO_2)$ group, it is exceptionally acidic ($pK_a = 0.38$). So it dissolves in $NaHCO_3$, but (VI) is a phenol ($pK_a = 10.17$) and will not dissolve.

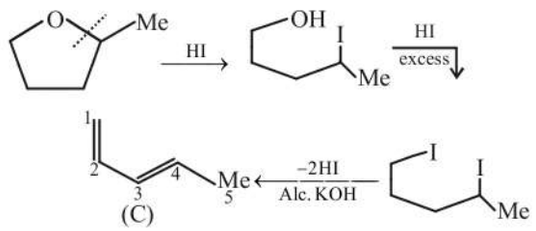
(VIII) (VII) is a phenol and dissolves in NaOH, but (VIII) is an ether; and does not dissolve.

6. (2)

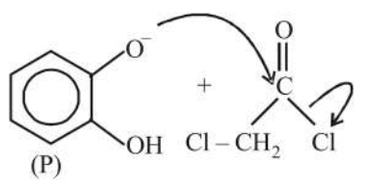


(B)

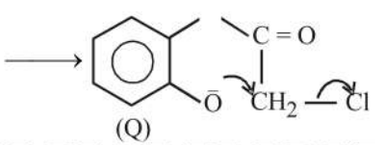
7. (5) One degree of unsaturation in (A) and formation of (B) with two I atoms suggest that (A) is a ring. The formation of (C) (five C atoms) suggest that (A) is a five-membered ring ether.



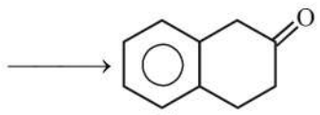
8. (3)



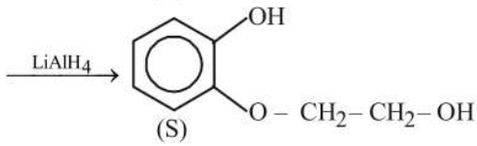
(P)



(Q)

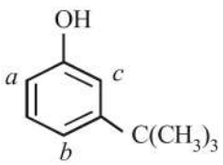


(R)



(S)

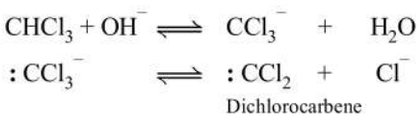
9. (3) —OH group is strongly activating and *o*, *p*-directing due to +M effect. Thus positions *a*, *b* and *c* are the sites for attack by an electrophile. However, sites *b* and *c* are not preferred by bulky electrophile due to steric crowding. Thus more bulky electrophile (like I_2) can attack only site *a*, which is least sterically hindered, a bit smaller electrophile (Br_2) can attack at sites *a* and also *b* (relatively less sterically hindered site) and the smallest electrophile (Cl_2) can attack all the three sites, viz., *a*, *b* and *c* (most sterically hindered site).



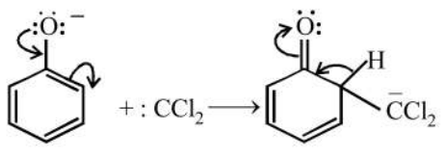
Statements 1, 2 and 3 correctly explains the pattern of electrophilic substitution.

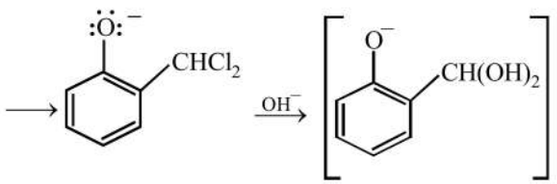
10. (2) The given reaction involves electrophilic substitution on the highly reactive phenoxide ion.

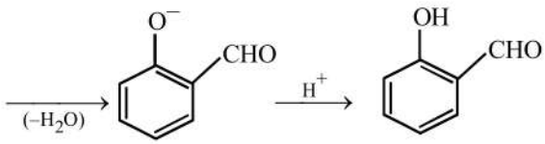
Here the electrophile is dichlorocarbene formed by the action of strong alkali on chloroform.



Dichlorocarbene

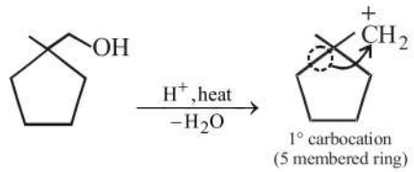




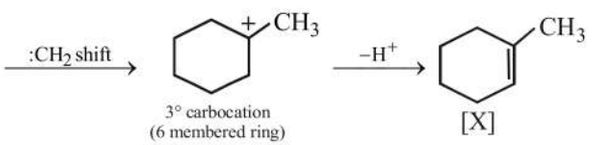


Salicylaldehyde
(*o*-Hydroxybenzaldehyde)

11. (4)

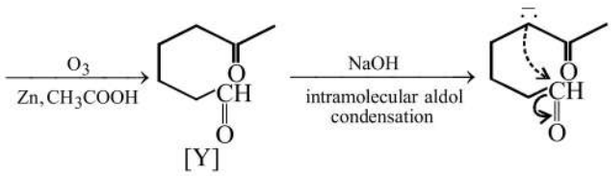


1° carbocation
(5 membered ring)

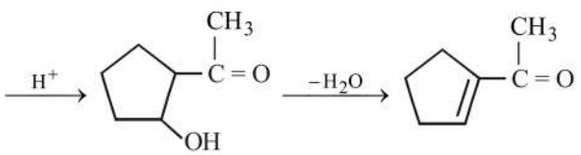


3° carbocation
(6 membered ring)

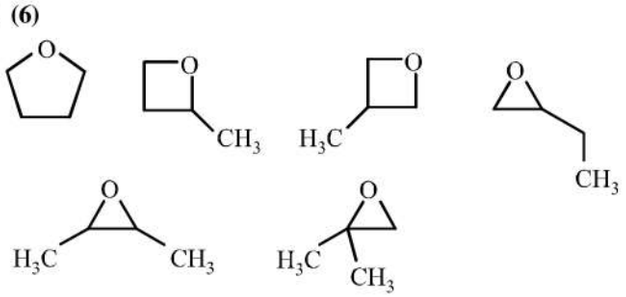
[X]



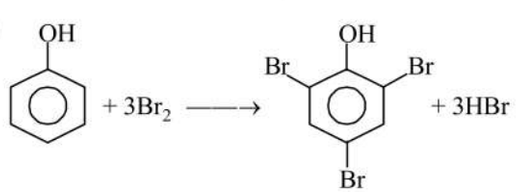
[Y]



12. (6)



13. (10.22)



1 mole 3 moles 1 mole

94 g of phenol reacts with 480 g of Br_2.

2 g of phenol — $\frac{480}{94} \times 2 = 10.22$ g.

14. (3) Three, these are $CH_3CH_2OCH_2CH_3$ (I), $CH_3OCH_2CH_2CH_3$ (II) and $CH_3OCH(CH_3)_2$ (III). Here I and II, I and III are pairs of metamers.

15. (3)