

EXAM  
DRILL

## Haloalkanes and Haloarenes

## ANSWERS

1. (i) **(b)** : An optically pure compound which has optical centre but shows no optical activity because of internal compensation is known as a meso compound. This internal compensation is possible only where there is an even balance of asymmetric centres in the compound.

(ii) **(b)** : Racemic mixture contains *d*- and *l*- isomers in equimolar amount.

(iii) **(b)**

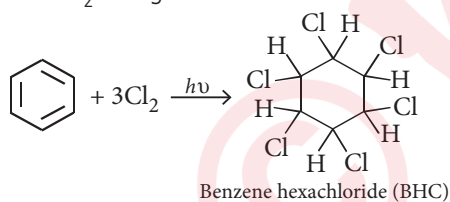
(iv) **(b)** :  $\text{CH}_3 - \overset{\text{Br}}{\underset{\text{H}}{\text{C}^*}} - \text{CH}_2\text{CH}_3$ ; 2-Bromobutane : optically active.

(v) **(d)** :  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{Br} - \text{C}^* - \text{H} \\ | \\ \text{Br} - \text{C}^* - \text{H} \\ | \\ \text{COOH} \end{array}$

The given compound is unsymmetrical with 2 chiral carbons.

$\therefore$  Number of optical isomers =  $2^2 = 4$ .

2.  $\text{Cl}_2/\text{Sunlight}$



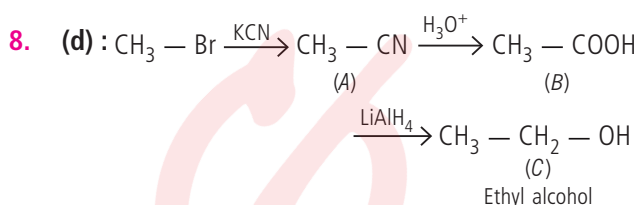
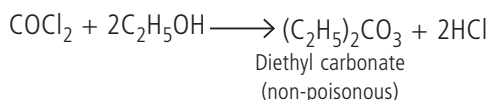
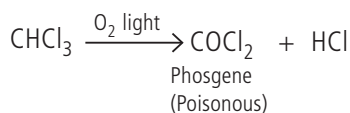
3. It is used as antiseptic.

4. Three isomers (*-o*, *-p* and *-m*) of dichlorobenzene are possible.

5. 1-Chloro-4-isopropylbenzene.

6. **(c)** : Rate of solvolysis directly proportional to stability of carbocation.

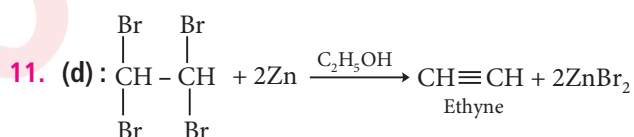
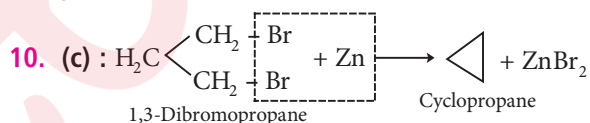
7. **(d)** :  $\text{CHCl}_3$  on exposure to air forms phosgene gas which is a poisonous gas and is removed by converting it into diethyl carbonate (which is non-poisonous substance).



OR

(a)

9. **(d)** :  $\text{S}_{\text{N}}2$  reaction is involved with inversion of configuration.



12. **(b)** :  $\text{CCl}_4$  is used as a fire extinguisher. The dense, non-combustible vapours cover the burning substance and prevents the availability of oxygen around burning material.

13. **(c)** : In electrophilic substitution reaction of toluene due to resonance the electron density increases more at *ortho*- and *para*-position that at *meta*-positions.

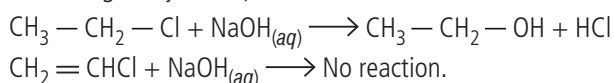
14. **(a)**

OR

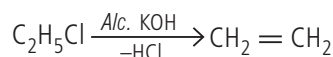
(b)

15. **(a)**

16. Chloroethane hydrolyses more readily than chloroethene because Cl is bonded to  $sp^3$  carbon atom which has less electronegativity than  $sp^2$  carbon atom of chloroethene.

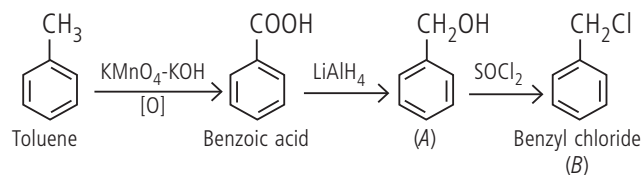


17. Alkyl halides react with alcoholic potassium hydroxide to form alkenes. The reaction involves the elimination of  $\text{HX}$  from the alkyl halide and is called dehydrohalogenation reaction.

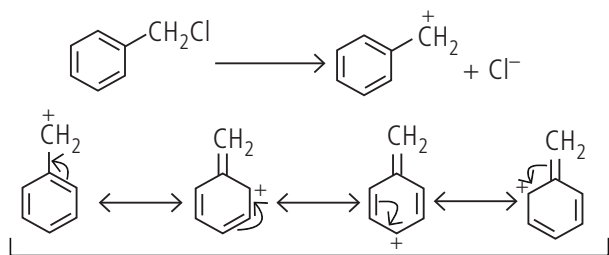


As H atom is removed from  $\beta$  carbon atom, its reaction is also called  $\beta$ -elimination reaction.

18.

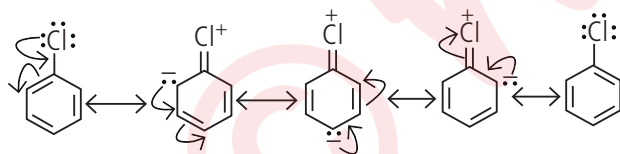


19.  $C_6H_5CH_2Cl$ ,  $S_N1$  reaction proceeds through the formation of carbocation intermediate.  $C_6H_5CH_2Cl$  readily breaks into  $C_6H_5CH_2^+$  carbocation which is stabilised by resonance.



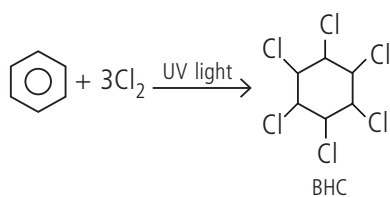
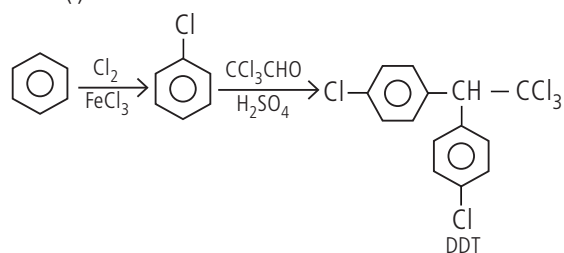
Benzyl carbocation is stabilised by resonance. On the other hand carbocation formed in case of  $CH_3CH_2Cl$  is not resonance stabilised. Therefore,  $C_6H_5CH_2Cl$  reacts faster than  $CH_3CH_2Cl$  with  $OH^-$  ion

20. Haloarenes (say chlorobenzene) is a resonance hybrid of the following five structures :

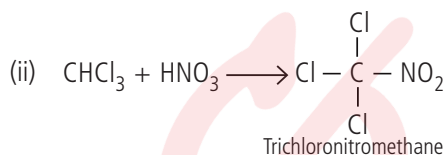
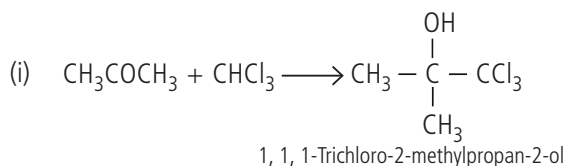


Resonance leads to lowering of energy and hence greater stability. On the other hand, no such resonance is possible in haloalkanes. Halogens directly attached to benzene ring are *ortho*, *para*-directing in electrophilic substitution reactions. This is due to greater electron density at these positions in resonance.

21. (i)



OR



22. (i) Chloroform in the presence of air gives a poisonous phosgene gas. The reaction is catalysed by light. To slow down this reaction, we store the  $CHCl_3$  in dark coloured bottles.

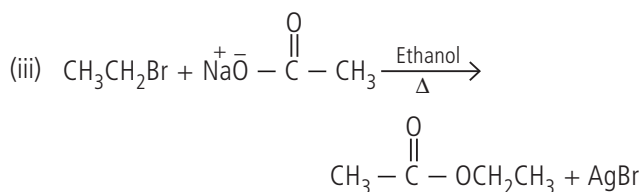


(ii) A small amount of ethanol is added to convert poisonous  $COCl_2$  (if any) into a non-poisonous diethyl carbonate.

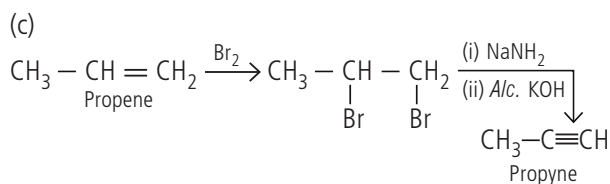
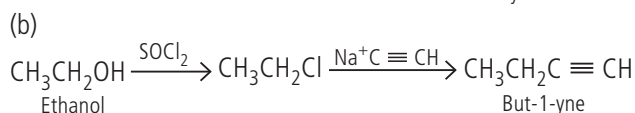
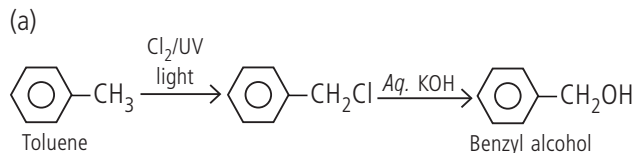


23. (i)  $CH_3 - \underset{\substack{| \\ H}}{CH} - \underset{\substack{| \\ Br}}{CH_2} + KOH \xrightarrow[\Delta]{Ethanol} CH_3 - CH = CH_2 + KBr + H_2O$

(ii)  $CH_3CH_2 - I + AgNO_2 \longrightarrow CH_3CH_2NO_2 + AgI$



OR



24.  $\text{CH}_2 = \text{CH} - \text{CH}_2\text{Cl}$  is an allylic chloride that reacts rapidly with  $\text{AgNO}_3$  in the cold to give a white precipitate of  $\text{AgCl}$ , insoluble in  $\text{HNO}_3$ .

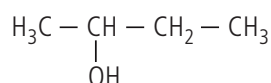
$\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$  give the same precipitate but after being warmed, because it is less reactive than  $\text{CH}_2 = \text{CHCH}_2\text{Cl}$ .

$\text{CH}_3\text{CH} = \text{CHCl}$ , a vinyl chloride is inert even when heated, as in hexane which lacks Cl.

The alkane and vinyl halide are distinguished by adding  $\text{Br}_2$  in  $\text{CCl}_4$  to each, the red brown  $\text{Br}_2$  colour persists in (does not react with) the alkane, but disappears in (react with) the alkene.

25. (i) The boiling points of isomeric haloalkanes decrease with increase in branching. Since, *tert*-butylbromide has a branched structure in comparison to *n*-butyl bromide, it has a lower boiling point.

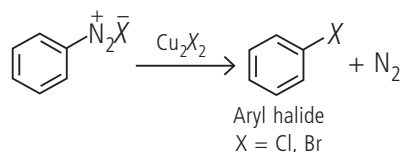
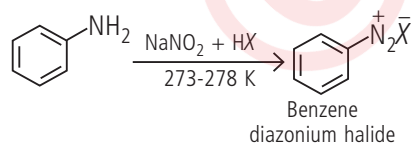
(ii) In a racemic mixture, one type of rotation is cancelled by another. Therefore,  $(\pm)$  butan-2-ol is optically inactive.



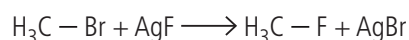
(iii) The C - Cl bond length in chlorobenzene is shorter than that in  $\text{CH}_3 - \text{Cl}$  as in haloalkanes, the halogen atom in chlorobenzene is attached to  $sp^2$  hybridised carbon atom which has more s-character than  $sp^3$  carbon atom in haloalkane. Thus C - X bond length in haloarene is shorter and stronger than  $sp^3$  carbon atom in haloalkanes.

OR

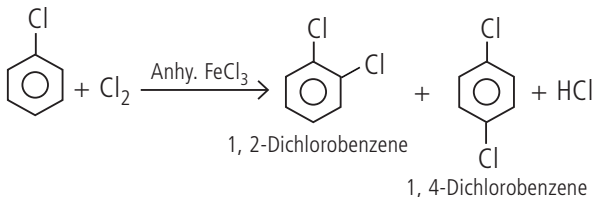
(i) When a primary aromatic amine, dissolved or suspended in cold aqueous mineral acid, is treated with sodium nitrite, a diazonium salt is formed. Mixing the solution of the freshly prepared diazonium salt with cuprous chloride or cuprous bromide results in the replacement of the diazonium group by -Cl or -Br.



(ii) Swarts reaction : The synthesis of alkyl fluorides is best accomplished by heating an alkyl chloride/bromide in the presence of metallic fluoride such as  $\text{AgF}$ ,  $\text{Hg}_2\text{F}_2$ ,  $\text{AsF}_3$  or  $\text{SbF}_3$ . This reaction is termed as Swarts reaction.



26. (i)

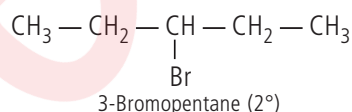
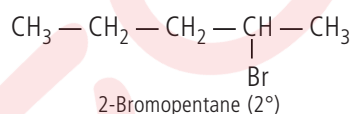
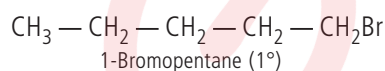


(ii)  $\text{CH}_3\text{CH}_2\text{Cl} + \text{AgNO}_2 \longrightarrow \text{CH}_3\text{CH}_2\text{NO}_2 + \text{AgCl}$   
Nitroethane

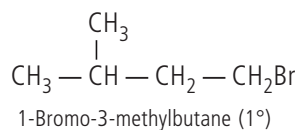
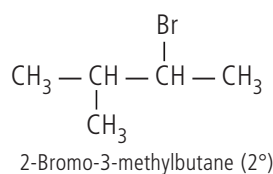
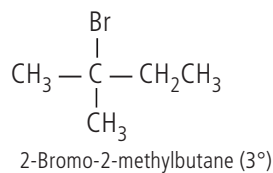
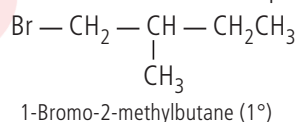
(iii)  $\text{CH}_3 - \overset{\text{Br}}{\underset{|}{\text{CH}}} - \text{CH}_2\text{CH}_2\text{CH}_3 + \text{KOH (Alic.)} \longrightarrow \text{CH}_3 - \overset{\text{CH}=\text{CH}}{\text{CH}} - \text{CH}_2\text{CH}_3$   
Pent-2-ene

27. (a) Total eight isomers.

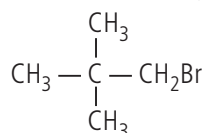
(i) Three isomers have the pentane skeleton.



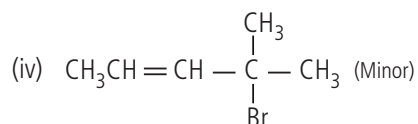
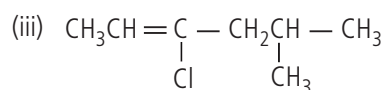
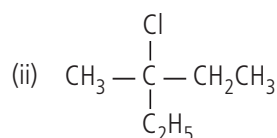
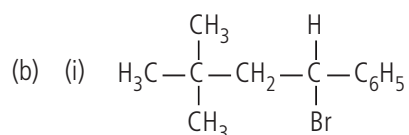
(ii) Four isomers have the isopentane skeleton :



(iii) One isomer has the neopentane skeleton :

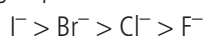


1-Bromo-2, 2-dimethylpropane ( $1^\circ$ )



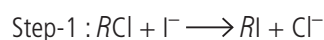
OR

(a) For any type of reaction, wherever the rate determining transition state involves breaking of the C — X bond, the rate is directly related to the leavability of X<sup>−</sup> which in turn, is indirectly related to its basicity. The weakest base is the best leaving group :



The order of reactivity is  $R-\text{I} > R-\text{Br} > R-\text{Cl} > R-\text{F}$

(b) With I<sup>−</sup>, the overall reaction occurs in two steps, each of which is faster than the uncatalysed reaction.

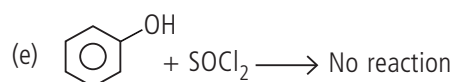
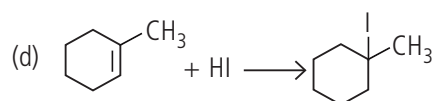
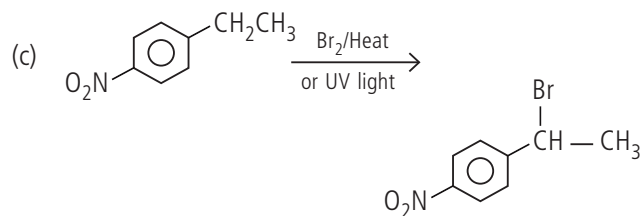
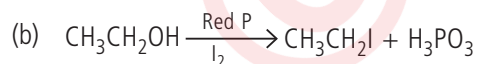
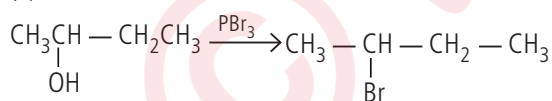


This step is faster because I<sup>−</sup> has more nucleophilicity than CH<sub>3</sub>COO<sup>−</sup>

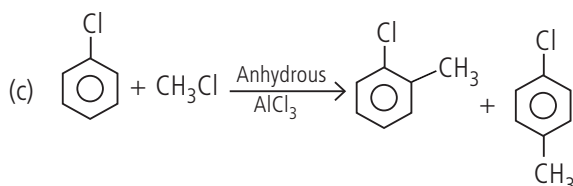
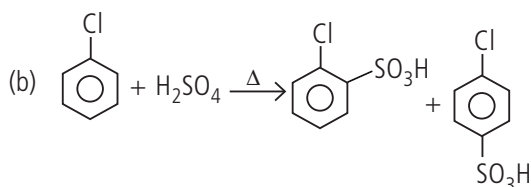
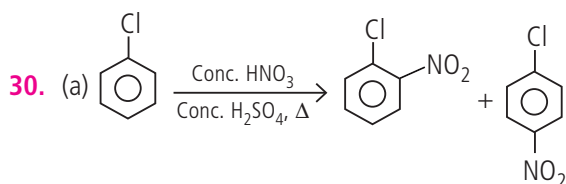
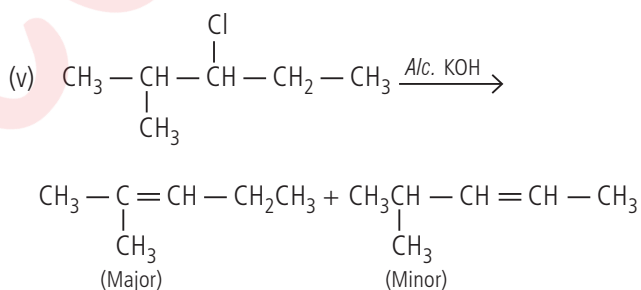
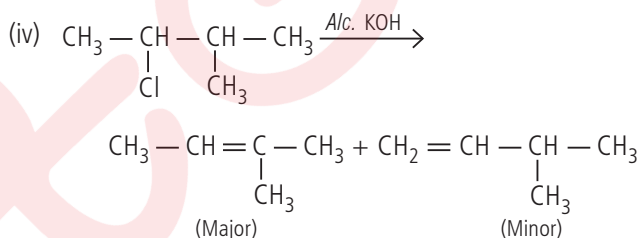
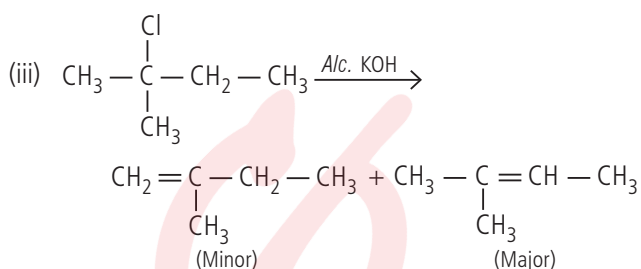
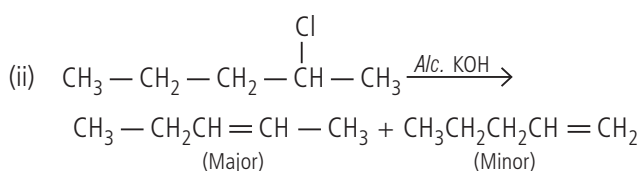
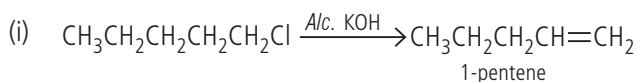


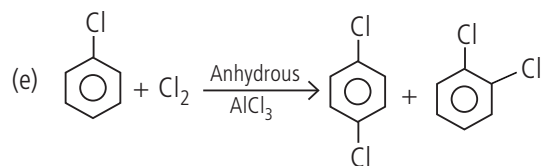
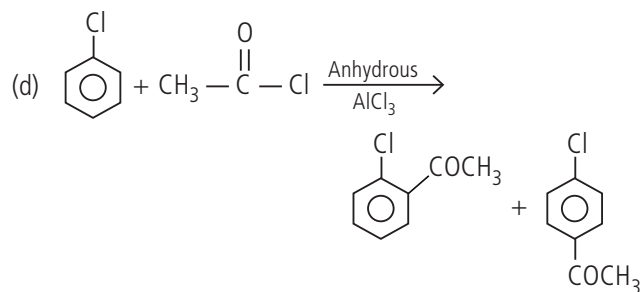
This step is faster because I<sup>−</sup> is a better leaving group than Cl<sup>−</sup>.

28. (a)



29.

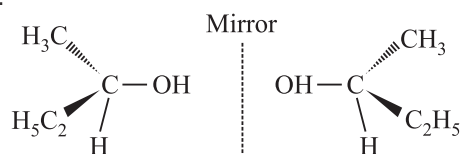




**OR**

(i) The molecules which are not superimposable on their mirror images are called chiral molecules. The property of non-


superimposability of a structure on its mirror image is called chirality.



Non-superimposable mirror image of 2-butanol

(ii)  $\text{CH}_3\text{CH}_2\underset{\text{Cl}}{\text{CH}}\text{CH}_3$  hydrolyses easily with KOH because it

is secondary halide.

(iii) As iodide is a better leaving group because of its large size, therefore,  undergoes  $\text{S}_{\text{N}}2$  reaction faster than

