Solution

HALOALKANES AND HALOARENES

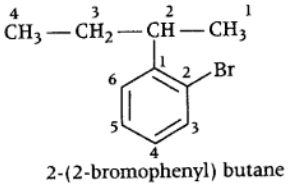
Class 12 - Chemistry

1. 2-chloro-3-ethyl-2-methylpentane
2. The structure of 1-bromo-4-chlorobut-2-ene is

$$\underset{Cl}{H_2C} - CH = CH - \underset{Br}{CH_2}$$

3. Ethyl chloride undergoes hydrolysis to form ethyl alcohol (through S_N2 nucleophilic substitution).

$$\underset{Ethylchloride}{C_2H_5Cl} + KOH(aq) \rightarrow \underset{Ethanol}{C_2H_5OH} + KCl$$

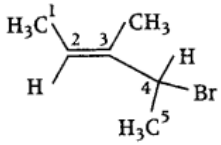
4. Plane polarised light is a light whose vibrations are confined, to one plane only.
5. 

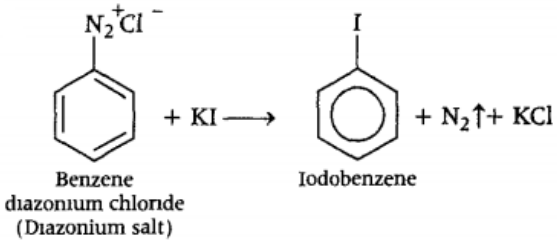
2-(2-bromophenyl) butane

6. Hydrocarbon which gives only one monochlorination product is

$$H_3C - \underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}} - CH_3$$

7. $\overset{4}{C}H_3 - \underset{CH_3}{\overset{3}{C}} = \underset{Br}{\overset{2}{C}} - \overset{1}{C}H_2OH$

   2 - bromo - 3 - methyl - but - 2 - en - 1 - ol
8. 

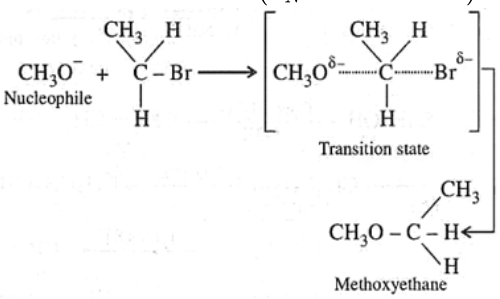
   4-bromo-3-methylpent-2-ene
9. 

   Benzene diazonium chloride (Diazonium salt)

   Iodobenzene
10. $\underset{3-bromo-2-methylprop-1-ene}{\overset{1}{C}H_2 = \underset{CH_3}{\overset{2}{C}} - \overset{3}{C}H_2Br}$
11. a. represents elimination because in this the anion attacks the H and simultaneously Br leaves leading to formation of a double bond.

    b. represents substitution as the nucleophile attacks the compound and simultaneously the leaving group leaves.
12. $CH_3CH_2Br + CH_3O^- \rightarrow CH_3CH_2OCH_3 + Br^-$

    $Mechanism(S_N2\ mechanism)$



Nucleophile

Transition state

Methoxyethane

13. In S_N2 reaction, steric factors determine the reactivity. more reactive alkyl halides have less steric hindrance. Hence, the decreasing order of the reactivity of alkyl halides is $1^o > 2^o > 3^o$. The order of reactivity as follows:
    i. 1-bromopentane > 2-bromopentane > 2-bromo-2-methylbutane
    ii. 1-bromo-3-methylbutane > 3-bromo-2-methylbutane > 2-bromo-2-methylbutane
    iii. 1-bromobutane > 1-bromo-3-methylbutane > 1-bromo-2-methylbutane> 1-bromo-2, 2 dimethylpropane

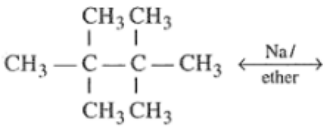
14. i. $CH_3CH_2CH_2CH_2Br < (CH_3)_2CHCH_2Br < CH_3CH_2CH(Br)CH_3 < (CH_3)_3CBr$ (S_N1) $CH_3CH_2CH_2CH_2Br > (CH_3)_2CHCH_2Br > CH_3CH_2CH(Br)CH_3 > (CH_3)_3CBr$ (S_N2)

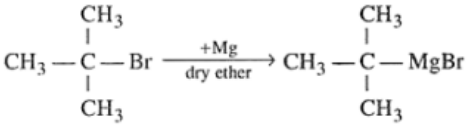
    Of the two primary bromides, the carbocation intermediate derived from $(CH_3)_2CHCH_2Br$ is more stable than derived from $CH_3CH_2CH_2CH_2Br$ because of greater electron-donating inductive effect of $(CH_3)_2CH$- group. Therefore, $(CH_3)_2CHCH_2Br$ is more reactive than $CH_3CH_2CH_2CH_2Br$ in S_N1 (unimolecular substitution) reactions. $CH_3CH_2CH(Br)CH_3$ is a secondary bromide and $(CH_3)_3CBr$ is a tertiary bromide. Hence the above order is followed in S_N1 unimolecular substitution reaction. The reactivity in S_N2 (bimolecular substitution) reactions follows the reverse order as the steric hindrance around the electrophilic carbon increases in that order.

    ii. $C_6H_5C(CH_3)(C_6H_5)Br > C_6H_5CH(C_6H_5)Br > C_6H_5CH(CH_3)Br > C_6H_5CH_2Br$ (S_N1) $C_6H_5C(CH_3)(C_6H_5)Br < C_6H_5CH(C_6H_5)Br < C_6H_5CH(CH_3)Br < C_6H_5CH_2Br$ (SN_2)

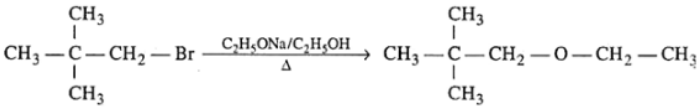
    Of the two secondary bromides, the carbocation intermediate obtained from $C_6H_5CH(C_6H_5)Br$ is more stable than obtained from $C_6H_5CH(CH_3)Br$ because it is stabilized by two phenyl groups due to resonance. Therefore, the former bromide is more reactive than the latter in $S_N1$unimolecular substitution reactions. A phenyl group is bulkier than a methyl group. Therefore, $C_6H_5CH(C_6H_5)Br$ is less reactive than $C_6H_5CH(CH_3)Br$ in S_N2 bimolecular substitution reactions.

15. i.

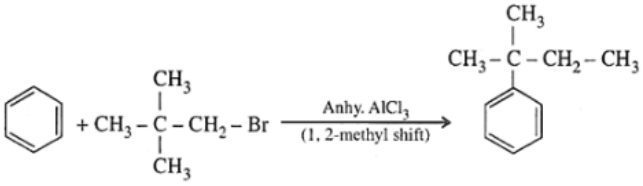




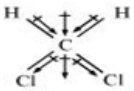
    ii.



    iii.



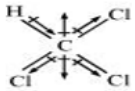
16. i.



Dichlormethane (CH_2Cl_2)

μ = 1.60D

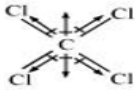
    ii.



Chloroform ($CHCl_3$)

μ = 1.08D

iii.



Carbon tetrachloride (CCl_4)

μ = 0D

CCl_4 is a symmetrical molecule. Therefore, the dipole moments of all four C-Cl bonds cancel each other. Hence, its resultant dipole moment is zero. As shown in the above figure, in $CHCl_3$,the resultant of dipole moments of two C-Cl bonds is opposed by the resultant of dipole moments of one C-H bond and one C-Cl bond. Since the resultant of one C-H bond and one C-Cl bond dipole moments is smaller than two C-Cl bonds, the opposition is to a small extent. As a result, has a smaller dipole moment of 1.08 D. On the other hand, in case of CH_2Cl_2, the resultant of the dipole moments of two C-Cl bonds is strengthened by the resultant of the dipole moments of two C-H bonds. As a result, CH_2Cl_2 has a higher dipole moment of 1.60 D than $CHCl_3$ i.e., CH_2Cl_2 has the highest dipole moment. Hence, the given compounds can be arranged in the increasing order of their dipole moments as:

$CCl_4 < CHCl_3 < CH_2Cl_2$

17. i. $\underset{1-Bromobutane(1^\circ)}{CH_3CH_2CH_2CH_2Br}, \underset{2-Bromobutane(2^\circ)}{CH_3CH_2\underset{Br}{\underset{|}{CH}}-CH_3}$

2-bromobutane is a 2°alkyl halide whereas 1-bromobutane is a 1°alkyl halide. The approaching of nucleophile is more hindered in 2-bromobutane than in 1-bromobutane. Therefore, 1-bromobutane reacts more rapidly than 2-bromobutane by an S_N2 mechanism.

ii. $\underset{2-\text{Bromobutane}(2^\circ)}{CH_3-CH_2-\underset{Br}{\underset{|}{CH}}-CH_3}$, $\underset{2-Bromo-2-methylpropane(3^\circ)}{CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-Br}$

2-Bromobutane is 2° alkylhalide whereas 2-bromo-2-methylpropane is 3°alkyl halide. Therefore, greater numbers of substituents are present in 3° alkyl halide than in 2°alkyl halide to hinder the approaching nucleophile. Hence, 2-bromobutane reacts more rapidly than 2-bromo-2-methylpropane by an S_N2 mechanism.

iii. $\underset{1-Bromo-3-\text{methylbutane}(1^\circ)}{CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_2-Br}$, $\underset{1-Bromo-2-\text{methylbutane}(1^\circ)}{CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-Br}$

Both the alkyl halides are primary. However, the substituent $-CH_3$ is at a greater distance from the carbon atom linked to -Br in 1-bromo-3-methylbutane than in 1-bromo-2-methylbutane. Therefore, the approaching nucleophile is less hindered in case of the former than in case of the latter. Hence, the former reacts faster than the latter by S_N2 mechanism.

18. There are four different dihalogen derivatives of propane. The structures of these derivatives are shown below.

i. $Br-\underset{Br}{\underset{|}{CH}}-CH_2-CH_3$

1, 1-Dibromopropane

ii. $CH_3-\overset{Br}{\overset{|}{\underset{Br}{\underset{|}{C}}}}-CH_3$

2,2-Dibromopropane

iii. $Br-CH_2-\overset{Br}{\overset{|}{CH}}-CH_3$

1, 2-Dibromopropane

iv. $Br-CH_2-CH_2-CH_2-Br$

1, 3-Dibromopropane

19. Two primary alkyl halides with molecular formula C_4H_9Br are possible. They are n-butyl bromide and isobutyl bromide.

When (a) is reacted with sodium metal it gives compound (d), C_8H_{18} which is different from the compound formed when n-butyl

bromide is reacted with sodium. Hence, compound a is isobutyl bromide and compound d is 2, 5-dimethylhexane.

$2CH_3CH_2CH_2CH_2Br + 2Na \xrightarrow{\text{Wurtz reaction}} CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ (n-octane)

$2CH_3CH(CH_3)CH_2Br + 2Na \xrightarrow{\text{wurtz reaction}} CH_3CH(CH_3)CH_2CH_2CH(CH_3)CH_3$(2, 5-dimethylhexane)

(a) reacted with alcoholic KOH to give compound (b).

$CH_3CH(CH_3)CH_2Br \xrightarrow{\text{alcKOH}} CH_3C(CH_3) = CH_2$(2 - methyl - 1 - propene)

Compound (b) is reacted with HBr to give (c) which is an isomer of (a).

$CH_3 - C(CH_3) = CH_2 \xrightarrow[\text{Markownikoff's rule}]{\text{HBr}} CH_3 - CBr(CH_3)\ CH_3$ (tert - butylbromide)