

9

HALOALKANES AND HALOARENES

PREVIOUS YEARS' QUESTIONS

2019

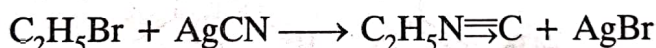
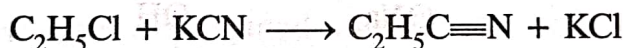
Very Short Answer Type Questions [1 Mark]

1. Why is *t*-butyl bromide more reactive towards S_N1 reaction as compared to *n*-butyl bromide? [AI Uttarakhand]

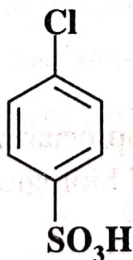
Ans. It is because *t*-butyl carbocation is more stable than *n*-butyl carbocation.

2. Define ambident nucleophile with an example. [Delhi]

Ans. **Ambident nucleophiles:** Those nucleophiles which can form bond through either of the two atoms are called ambident nucleophiles, e.g. CN^- can link through 'C' or 'N' to form cyanide or isocyanide as follows:



3. Write IUPAC name of the given compound: [Delhi]



Ans. 4-Chlorobenzene sulphonic acid.

4. Write one stereochemical difference between S_N1 and S_N2 reactions. [Delhi]

Ans. In S_N1 , racemisation takes place, whereas in S_N2 mechanism stereochemical inversion (optical inversion) takes place.

5. Why is $CH_2=CH-CH_2-Cl$ more easily hydrolysed than $CH_3-CH_2-CH_2-Cl$? [AI Chennai]

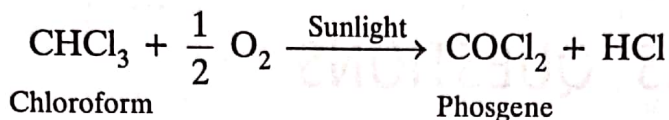
Ans. It is because $CH_2=CH-\overset{\oplus}{C}H_2 \longleftrightarrow \overset{\oplus}{C}H_2-CH=CH_2$, allyl carbocation is stabilized by resonance more than $CH_3-CH_2-\overset{\oplus}{C}H_2$ by inductive effect.

6. Why is cyclohexyl chloride is more reactive than chlorobenzene? [CBSE]

Ans. It is because in chlorobenzene there is double bond character between C—Cl bond which has higher bond dissociation energy than C—Cl, in cyclohexyl chloride, 'C' is sp^3 hybridised whereas 'C' is sp^2 hybridised in chlorobenzene.

7. Why is chloroform stored in dark coloured bottle? [AI Panchkula]

Ans. It is because chloroform reacts with oxygen in the presence of sunlight to form phosgene gas which is poisonous.



8. What are the products of exhaustive ammonolysis of alkyl halide? [AI Chandigarh]

Ans. $\text{CH}_3\text{Cl} \xrightarrow{\text{NH}_3} \text{CH}_3\text{NH}_2 \xrightarrow{\text{CH}_3\text{Cl}} (\text{CH}_3)_2\text{NH} \xrightarrow{\text{CH}_3\text{Cl}} (\text{CH}_3)_3\text{N} \xrightarrow{\text{CH}_3\text{Cl}} (\text{CH}_3)_4\text{N}^+\text{Cl}^-$.

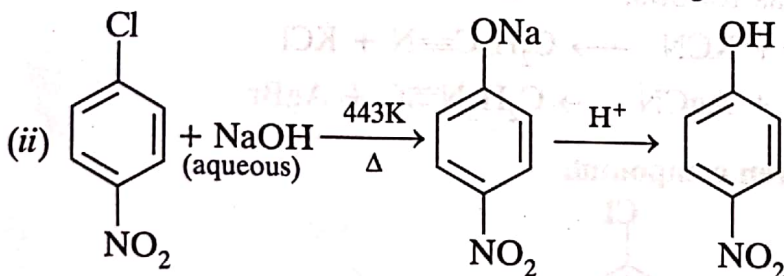
Long Answer Type [I] Questions [3 Marks]

9. (i) Out of $(\text{CH}_3)_3\text{C—Br}$ and $(\text{CH}_3)_3\text{C—I}$, which one is more reactive towards $\text{S}_\text{N}1$ and why?

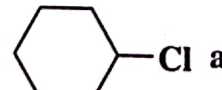
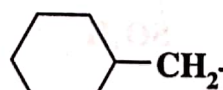
(ii) Write the product formed when *p*-nitrochlorobenzene is heated with aqueous NaOH at 443 K followed by acidification.

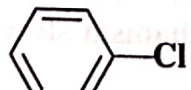
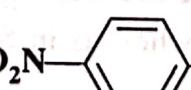
(iii) Why *dextro* and *laevo* – rotatory isomers of Butan-2-ol are difficult to separate by fractional distillation? [Delhi]

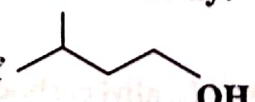
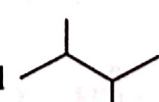
Ans. (i) $(\text{CH}_3)_3\text{C—I}$ will be more reactive because C—I has lower bond dissociation enthalpy than C—Br bond, due to longer bond length.



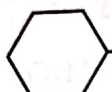
(iii) It is because they do not differ appreciably in their boiling points (physical properties), but differ in optical rotation and biological properties.

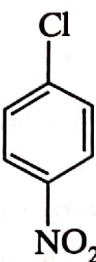
10. (i) Out of  and , which one is more reactive towards $\text{S}_\text{N}2$ reaction and why?

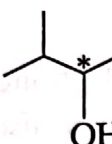
(ii) Out of  and , which one is more reactive towards $\text{S}_\text{N}2$ reaction and why?

(iii) Out of  and , which one is optically active and why?

[AI Chennai]

Ans. (i)  because it is primary halide and has less steric hindrance.

(ii)  is more reactive because $-\text{NO}_2$ being electron withdrawing stabilizes intermediate negatively charged ion.

(iii)  is optically active because it has chiral 'C' atom (asymmetric carbon).

11. Give reasons for the following:

- The presence of $-\text{NO}_2$ group at ortho or para position increases the reactivity of haloarenes towards nucleophilic substitution reactions.
- p*-dichlorobenzene has higher melting point than that of ortho or meta isomer.
- Thionyl chloride method is preferred for preparing alkyl chloride from alcohols.

[AI Uttarakhand]

Ans. (a) $-\text{NO}_2$ group stabilises intermediate having $-ve$ charge, therefore, increases rate of nucleophilic substitution reactions.

(b) It is because *p*-isomer is symmetrical and fits into crystal lattice readily.

(c) It is because side products formed are SO_2 and HCl gases, which can be easily removed to get pure alkyl halide.

12. Among all the isomers of molecular formula $\text{C}_4\text{H}_9\text{Br}$, identify:

- the one isomer which is optically active.
- the one isomer which is highly reactive towards $\text{S}_{\text{N}}2$.
- the two isomers which give same product on dehydrohalogenation with alcoholic KOH .

[CBSE]

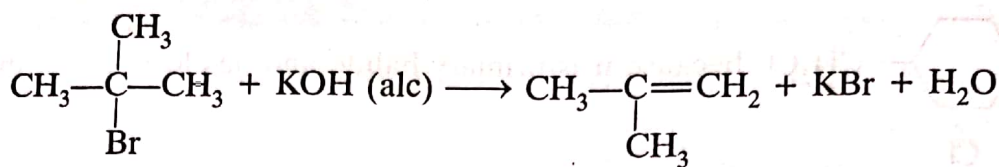
Ans. (a) $\text{CH}_3-\underset{\text{Br}}{\overset{*}{\text{C}}}-\text{CH}_2-\text{CH}_3$ is optically active due to presence of chiral 'C' atom.

(b) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{Br}$ is highly reactive towards $\text{S}_{\text{N}}2$ because it is primary halide and it has less steric hindrance.

(c) $\text{CH}_3-\underset{\text{CH}_3}{\text{C}}-\text{CH}_2\text{Br} + \text{KOH (alc.)} \longrightarrow \text{CH}_3-\underset{\text{CH}_3}{\text{C}}=\text{CH}_2 + \text{KBr} + \text{H}_2\text{O}$

1-Bromo-2-methyl propane

2-Methyl propene

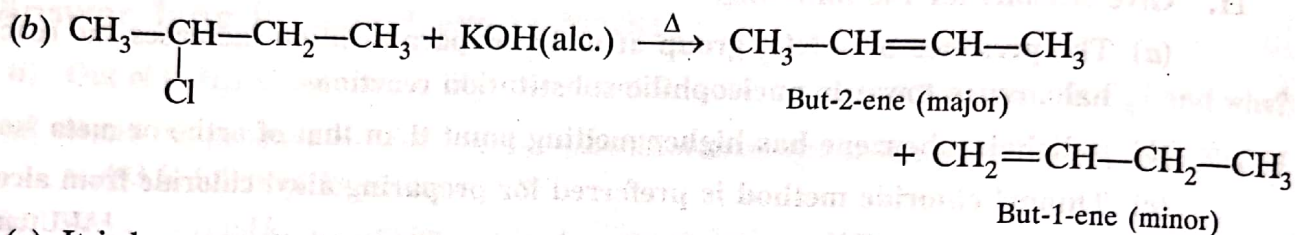


2-Bromo-2-methyl propane

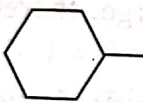
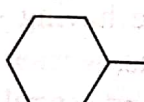
2-Methyl propene

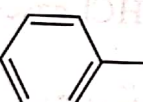
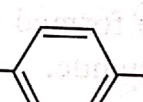
13. (a) Out of chloro cyclohexane and chlorobenzene which one is more reactive towards nucleophilic substitution reaction and why?
 (b) Predict all the alkenes that would be formed by dehydrohalogenation of 2-bromobutane.
 (c) Chloroform contains chlorine but it does not give white ppt with AgNO_3 solution, why? [CBSE]

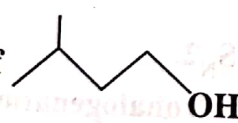
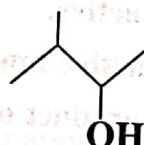
Ans. (a) Cyclohexyl chloride is more reactive due to partial double bond character of $\text{C}=\text{Cl}$ bond in chlorobenzene due to resonance, it is sp^2 hybridised where as in cyclo hexyl chloride, there is single bond, sp^3 hybridised.



(c) It is because all chlorine atoms are bonded to carbon atom by covalent bond.

14. (a) Out of -Cl and -CH₂Cl, which one is more reactive towards S_N2 reaction and why?

- (b) Out of -Cl and -Cl, which one is more reactive towards nucleophilic substitution reaction and why?

- (c) Out of -OH and -OH, which one is optically active and why?

Ans. (a) Refer Ans. to Q.10 (i). (b) Refer Ans. to Q.10 (ii) (c) Refer Ans. to Q.10 (iii). [CBSE]

15. (a) Define the following:

(i) Enantiomers (ii) Racemic mixture

- (b) Why is chlorobenzene resistant to nucleophilic substitution reaction?

Ans. (a) (i) Those stereoisomers which are non-super imposable but not mirror images of each other are called enantiomers. [AI Chandigarh]

(ii) Racemic mixture: Equimolar mixture of 'd' and 'l' form is known as racemic mixture.

- (b) It is due to double bond character between $\text{C}=\text{Cl}$ bond which is difficult to break and phenyl cation is unstable.