Raffles Institution
Year 5 H2 Chemistry 2024

Tutorial 14: Halogen Derivatives (Suggested Answers)

Discussion Questions – Suggested Answers

3a **Preparation of CH_3CH_2Cl**
Reagent: PCl_5
Condition: room temperature
Equation: $CH_3CH_2OH + PCl_5 \longrightarrow CH_3CH_2Cl + POCl_3 + HCl$

Preparation of CH_3CH_2Br
Reagent: PBr_3 or HBr(g)
Condition: heat under reflux if HBr is used
Equations: $3CH_3CH_2–OH + PBr_3 \longrightarrow 3CH_3CH_2–Br + H_3PO_3$
$CH_3CH_2OH + HBr \xrightarrow{\text{heat}} CH_3CH_2Br + H_2O$

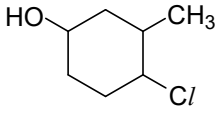
Preparation of CH_3CH_2I
Reagent: red P, I_2
Condition: room temperature
Equations: $2P + 3I_2 \longrightarrow 2PI_3$
$3CH_3CH_2OH + PI_3 \longrightarrow 3CH_3CH_2I + H_3PO_3$

3b From the Data Booklet:
BE(C–C*l*) = 340 kJ mol^{-1}; BE(C–Br) = 280 kJ mol^{-1}; BE(C–I) = 240 kJ mol^{-1}.

The reactivity towards nucleophilic reagents increases from CH_3CH_2Cl to CH_3CH_2Br to CH_3CH_2I. This is due to decreasing strength of the carbon–halogen bond in the following order: C–C*l* > C–Br > C–I.

3c

Q



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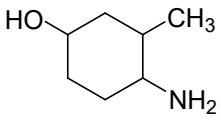


4a Compare expt. 1 and 2.
When [NaOH] is doubled, initial rate is doubled.
$\Rightarrow$ rate $\propto$ [NaOH]
$\Rightarrow$ order of reaction with respect to NaOH = 1

Compare expt. 2 and 3.
When [NaOH] and [(2-chloroethyl)benzene] is doubled, initial rate is quadrupled.
Since order of reaction with respect to NaOH =1,
$\Rightarrow$ rate $\propto$ [(2-chloroethyl)benzene]
$\Rightarrow$ order of reaction with respect to (2-chloroethyl)benzene = 1
OR
Let the rate equation be: rate = k [NaOH] [(2-chloroethyl)benzene]^n

Compare expt. 2 and 3

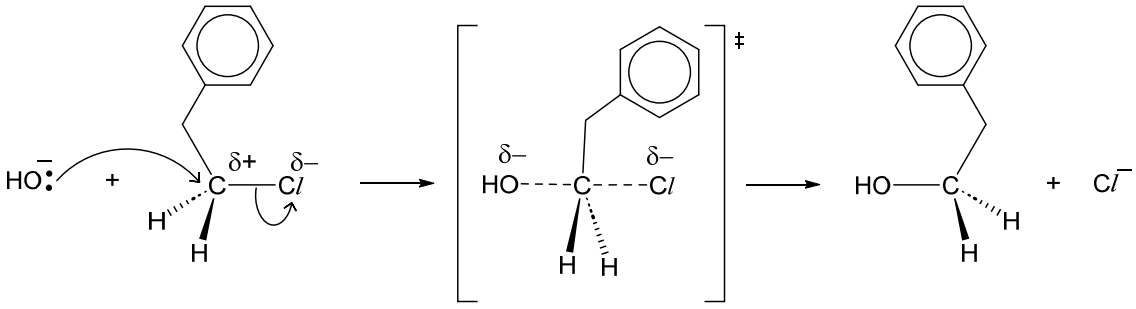
$$\frac{\text{rate 2}}{\text{rate 3}} = \frac{k\,(0.02)(0.01)^n}{k\,(0.04)(0.02)^n} = \frac{0.0050}{0.0200}$$

$$\Rightarrow 2^n = 2$$

$\Rightarrow$ n = 1
$\Rightarrow$ order of reaction with respect to (2-chloroethyl)benzene = 1

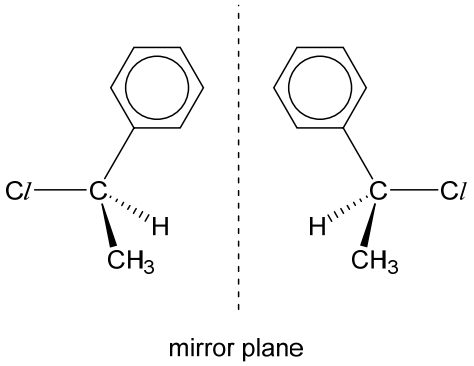
Hence the rate equation is: **rate = k [NaOH] [(2-chloroethyl)benzene]**

Since the overall order of the reaction is 2, the mechanism involved in the reaction is **S_N2**.



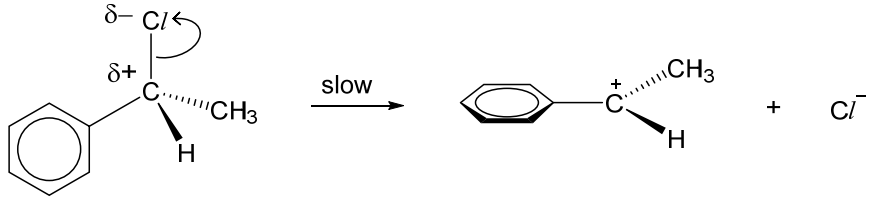
4b(i) (1-chloroethyl)benzene displays **enantiomerism**.

Stereoisomers of (1-chloroethyl)benzene:

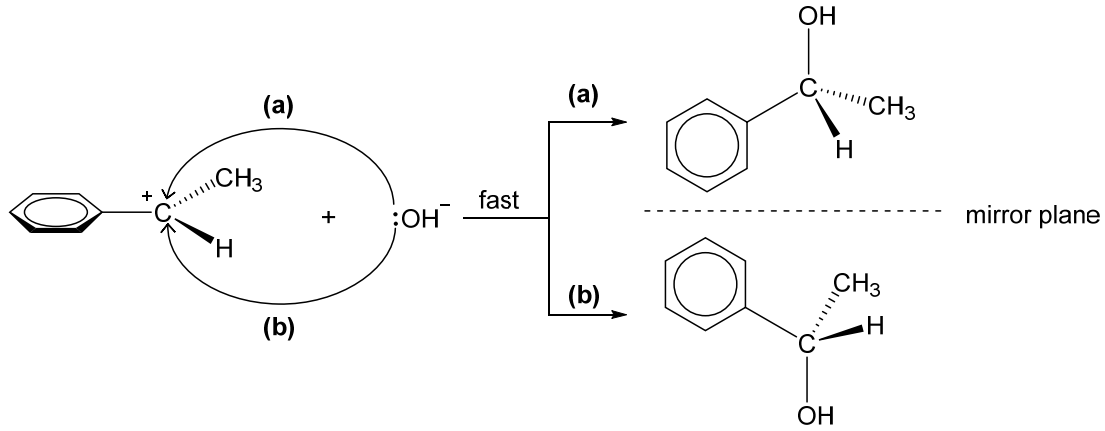


4b(ii) The mechanism is **S_N1**.

Step 1:



Step 2:



In step 1, the optically active (1-chloroethyl)benzene forms a carbocation via the heterolytic fission of the C–C*l* bond. This carbocation is trigonal planar with respect to the positively charged carbon.

In step 2, the OH^- nucleophile can attack this positively charged carbon from either side of the trigonal plane with equal likelihood.

This results in 50% of the product molecules formed with retention of configuration and the other 50% of the product molecules formed with inversion of configuration. Consequently, the product solution is a racemic mixture and hence is optically inactive.

4c In **(a)**, (2-chloroethyl)benzene undergoes hydrolysis via the S_N2 mechanism because it is a primary halogenoalkane with little steric hindrance for the OH^- nucleophile to attack the electron-deficient carbon from the side directly opposite the chlorine atom.

In this case, (2-chloroethyl)benzene forms a less stable carbocation and hence the S_N1 mechanism is not favoured.

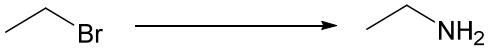
In **(b)(ii)**, (1-chloroethyl)benzene undergoes hydrolysis via the S_N1 mechanism because it can form a carbocation which is resonance-stabilised. In this carbocation, the empty p orbital of the positively charged carbon overlaps with the π electron cloud of the benzene ring. This allows the π electrons of the benzene ring to delocalise over the positively charged carbon and disperse the positive charge, thus stabilising the carbocation.

In this case, the S_N2 mechanism is less favoured because it is a 2° halogenoalkane with one methyl and one very bulky phenyl group attached to the electron deficient C atom, thus hindering the backside attack of the OH^- nucleophile.

5a A nucleophile is a species which can donate an electron pair to an electron-deficient atom to form a covalent bond.

5b

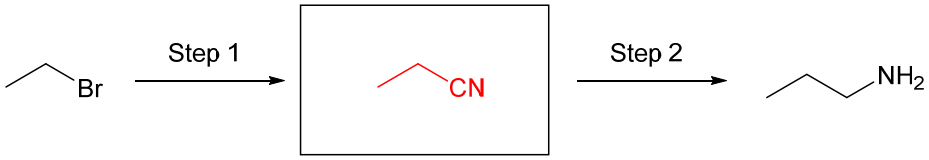
(i)



Reagents and conditions:

Excess conc NH_3 in ethanol, sealed tube and heat

(ii)

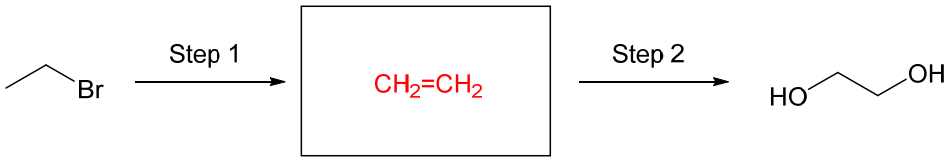


Reagents and conditions

Step 1: ethanolic KCN, heat (or heat under reflux)

Step 2: H_2, Ni catalyst, heat

(iii)

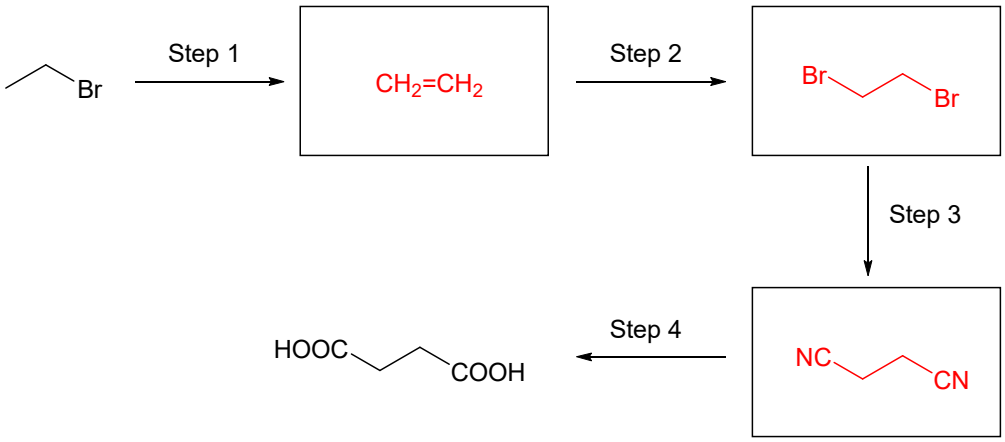


Reagents and conditions

Step 1: ethanolic KOH, heat (or heat under reflux)

Step 2: $KMnO_4$(aq), NaOH(aq), cold

(iv)



Reagents and conditions

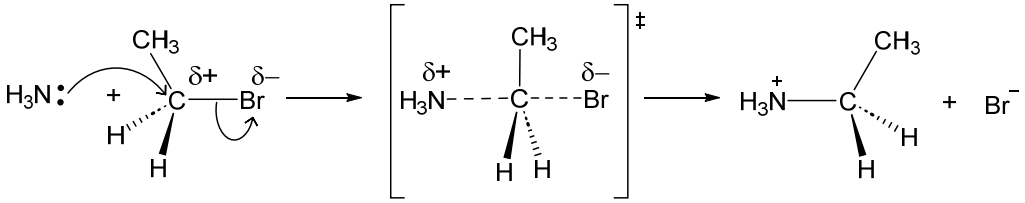
Step 1: ethanolic KOH, heat (or heat under reflux)

Step 2: Br_2 in CCl_4, room temperature, dark

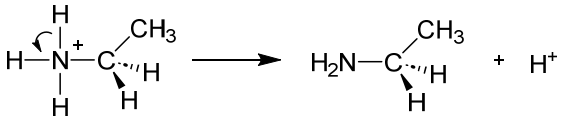
Step 3: ethanolic KCN, heat (or heat under reflux)

Step 4: H_2SO_4(aq), heat (or heat under reflux)

5c The mechanism is **S_N2**.
(followed by deprotonation)

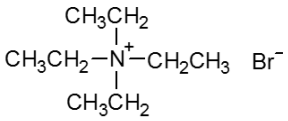


Then,



5d **S** gives an immediate precipitate with $AgNO_3(aq)$.
$\Rightarrow$ The precipitate is AgBr and **S** is an ionic compound containing $C_8H_{20}N^+$ and Br^- ions.

S is



S is formed from simplified nucleophilic substitution reactions as shown below.

$NH_3 + CH_3CH_2Br \longrightarrow CH_3CH_2NH_2 + HBr$

$CH_3CH_2NH_2 + CH_3CH_2Br \longrightarrow (CH_3CH_2)_2NH + HBr$

$(CH_3CH_2)_2NH + CH_3CH_2Br \longrightarrow (CH_3CH_2)_3N + HBr$

$(CH_3CH_2)_3N + CH_3CH_2Br \longrightarrow \mathbf{(CH_3CH_2)_4N^+\ Br^-}$

6a The rate of formation of precipitate decreases in the following order:

AgI (yellow) > AgBr (pale cream) > AgCl (white)

The rate of the nucleophilic substitution reaction of the halogenobutanes decreases in the following order:

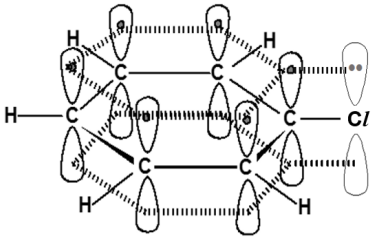
2-iodobutane > 2-bromobutane > 2-chlorobutane

The nucleophilic substitution reaction involves the cleavage of the carbon-halogen bond and the rate of the reaction depends on the strength of the carbon-halogen bond. The weaker the carbon-halogen bond, the easier it can be cleaved and the faster is the rate of the nucleophilic substitution reaction.

Hence the above order of rate of reaction arises because the strength of the carbon–halogen bond increases as follows:

C–I < C–Br < C–Cl

6b In clorobenzene molecule, the p orbital containing the lone pair of electrons on chlorine overlaps with the π electron cloud of the benzene ring. This allows the lone pair of electrons in the p orbital of chlorine to delocalise into the π electron cloud of the benzene ring.

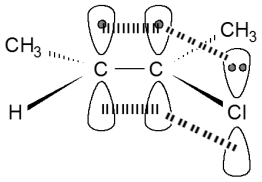


This results in partial double bond character in the C– C*l* bond.

This bond is strengthened and hence not easily broken

Note: In addition, the electron-rich benzene ring repels the electron-rich nucleophile and also hinders the backside attack by the nucleophile on the electron-deficient carbon. Consequently, chlorobenzene does not undergo any nucleophilic substitution reaction.

6c In 2-chlorobut-2-ene, the p orbital containing the lone pair of electrons on the C*l* atom overlaps with the π electron cloud of the C=C bond. This allows the lone pair of electrons in the p orbital of chlorine to delocalise into the π electron cloud of the C=C bond.

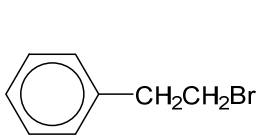


This results in partial double bond character in the C–C*l* bond.

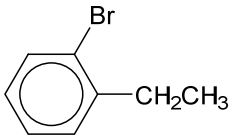
This bond is strengthened and hence not easily broken. Consequently, 2-chlorobut-2-ene is resistant to nucleophilic substitution under the given conditions. There will not be any Cl^- ions present to react with Ag^+ ions. Hence using 2-chlorobut-2-ene will lead to no obervable change in the experiment.

Note: In addition, the electron-rich C=C bond repels the electron-rich nucleophile and hinders the backside attack by the nucleophile on the electron-deficient carbon. Consequently, 2-chlorobut-2-ene does not undergo any nucleophilic substitution reaction.

7a



(2-bromoethyl)benzene



1-bromo-2-ethylbenzene

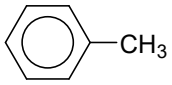
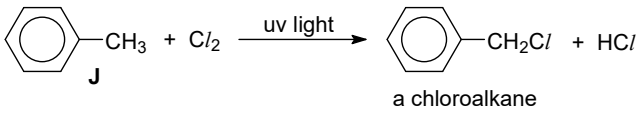
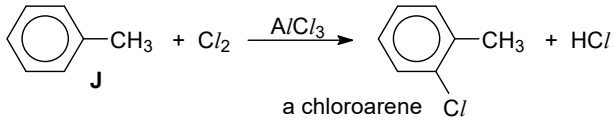
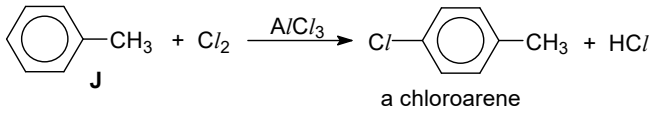
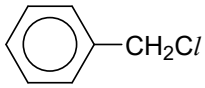
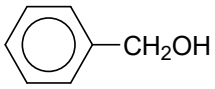
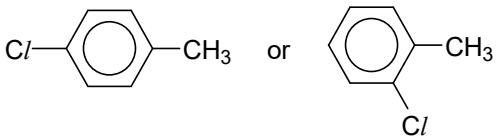
Add NaOH(aq) to each sample in a test-tube and heat each mixture in a hot water bath. Cool each mixture and acidify each one with dilute HNO_3. Then add $AgNO_3$(aq) to each mixture.

For (2-bromoethyl)benzene, a pale cream precipitate of AgBr will be observed.
For 1-bromo-2-ethylbenzene, a pale cream precipitate of AgBr will not be observed.

7b Add NaOH(aq) to each sample in a test-tube and heat each mixture in a hot water bath. Cool each mixture and acidify each one with dilute HNO_3. Then add $AgNO_3$(aq) to each mixture.

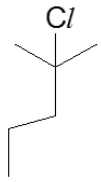
For chloroethane, a white precipitate of AgC*l* will be observed.
For iodoethane, a yellow precipitate of AgI will be observed.

8

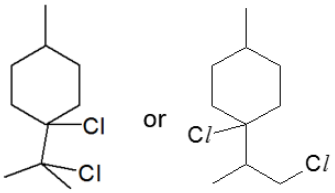
Information	Deduction and Explanation
Hydrocarbon **J** has M_r = 92.	• Let **J** be C_xH_y. • M_r of C_xH_y = 92 ⇒ 12x + y = 92 • By guess and check, a sensible set of x and y would be: x = 7 and y = 8. • Hence the molecular formula of **J** is C_7H_8. • With C: H ≈ 1:1, **J** is likely to contain a benzene ring. • Hence **J** is 
J reacts with Cl_2 under different conditions to give two isomeric chlorides, **K** and **L.**	• **J** has a $–CH_3$ side chain and hence can undergo **free-radical substitution** reaction with Cl_2 (limiting amount) in the presence of uv light to form a chloroalkane.  **J** a chloroalkane • **J** also has a benzene ring and hence can undergo **electrophilic substitution** reaction with Cl_2 in the presence of $AlCl_3$ to form a chloroarene.  **J** a chloroarene or  **J** a chloroarene • With the same molecular formula, the chloroalkane and chloroarene produced from **J** are structural isomers and are **K** and **L**.
On heating **K** with NaOH(aq), **M**, with molecular formula, C_7H_8O, is formed.	• **Nucleophilic substitution** occurs. • Hence **K** is the chloroalkane produced from J. • **K** is  • **M** is an alcohol and **M** is 
L is inert towards NaOH(aq)	• Nucleophilic substitution does **not** occur. • Hence **L** is the chloroarene produced from **J**. • **L** is 

9a

A



B



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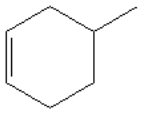

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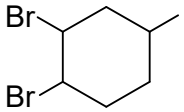

9b(i) CFCs were originally used because

- they were inert and non-toxic;
- and because they were compounds that liquefied under pressure and thus volatilised readily when that pressure was released.

9b(ii) In the stratosphere, ultraviolet radiation from the sun brings about homolytic fission of the C–C*l* bonds in the CFC molecules to generate chlorine radicals (not fluorine radicals). Each chlorine radical participates in a chain reaction resulting in destruction of ozone molecules.

9b(iii) Alkanes are readily flammable.