St Andrew's Junior College

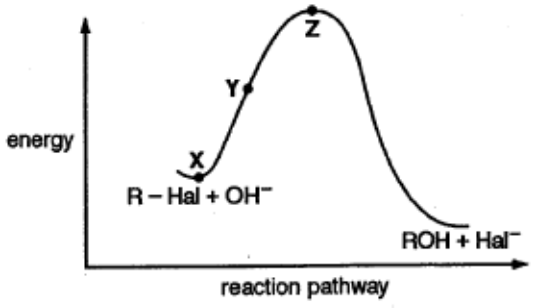
H2 Chemistry 2025

Tutorial 13: Halogen Derivatives

SELF-CHECK QUESTIONS

Mechanism

1. Halogenoalkanes react with aqueous alkali. One mechanism of this reaction has the reaction pathway diagram shown below.



Which statements are correct?

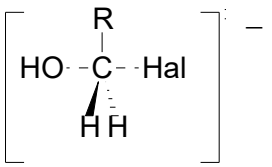
1 The reaction is an example of nucleophilic substitution.
2 Between **X** and **Y** the C-Hal bond will be lengthening.
3 The energy difference between **X** and **Z** represents the activation energy.

A **1, 2** and **3** **B** **1** and **2** **C** **2** and **3** **D** **1 only**

Ans: A (1, 2 and 3)

1. True. OH^- substitutes halogen in R-hal.

2. True. C−hal bond starts to break between **X** and **Y** and C−OH bond starts to form as well to reach the transition state in **Z** shown below:



3. True.

Reactions of Halogenoalkanes

2. Write balanced equations and the reagents and conditions for the following conversions.

(a) CH_3CH_2Br to $CH_3CH_2NH_2$ (1 step)

$CH_3CH_2Br + NH_3 \rightarrow CH_3CH_2NH_2 + HBr$
Reagent & Conditions: NH_3 in ethanol, heat under pressure

(b) CH_3CH_2Br to CH_3CH_2COOH (2 steps)

$CH_3CH_2Br + KCN \rightarrow CH_3CH_2CN + KBr$
Reagent & Conditions: KCN in ethanol, heat

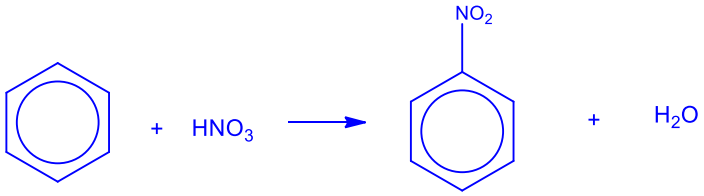
$CH_3CH_2CN + 2\ H_2O + H^+ \rightarrow CH_3CH_2COOH + NH_4^+$
Reagent & Conditions: H_2SO_4 (aq), heat

(c) CH_3CH_2Cl to $CH_2(OH)CH_2OH$ (2 steps)

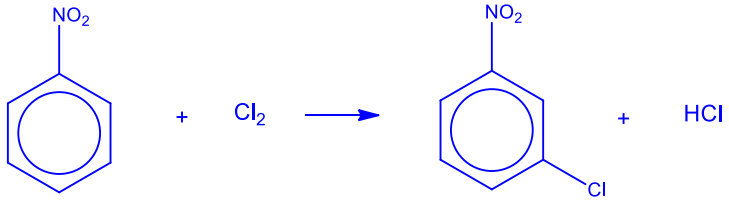
$CH_3CH_2Cl + NaOH \rightarrow CH_2{=}CH_2 + KCl + H_2O$
Reagent & Conditions: NaOH in ethanol, heat

$CH_2{=}CH_2 + H_2O + [O] \rightarrow CH_2(OH)CH_2OH$
Reagent & Conditions: $KMnO_4$(aq), NaOH(aq), cold

(d) Benzene to 3-chloronitrobenzene (2 steps)

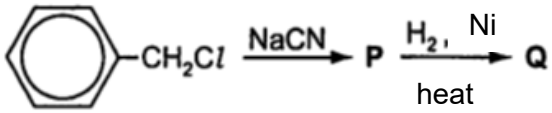


Reagent & Conditions: conc HNO_3, conc H_2SO_4, 50°C



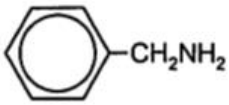
Reagent & Conditions: Cl_2, anhydrous $AlCl_3$, heat

3. The diagram shows a reaction sequence.

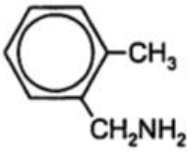


What would be the product **Q**?

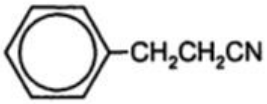
A



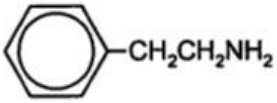
C



B



D



Ans: D

Nucleophilic substitution occurs to form a nitrile (the alkyl chain increases by 1 C).
Nitrile is reduced to a primary amine.

4. The reduction of a nitrile produced a compound of formula $C_3H_7NH_2$.

Which compound would be produced if the same nitrile was hydrolysed by heating with dilute hydrochloric acid?

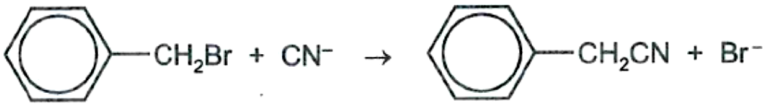
A $CH_3CH_2NH_2$
B CH_3CH_2OH
C $CH_3CH_2CO_2H$
D $(CH_3)_2CHCO_2H$

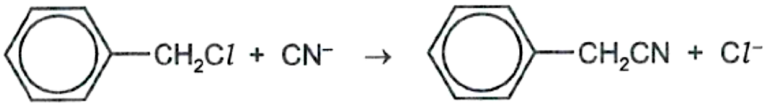
Ans: C

The primary amine produced is $CH_3CH_2CH_2NH_2$ which means the nitrile is CH_3CH_2CN.
When CH_3CH_2CN undergoes acidic hydrolysis, it will become CH_3CH_2COOH.

5. N16/1/25

The reactions below follow the same S_N1 mechanism.

reaction 1 

reaction 2 

Reaction 1 is faster than reaction 2, under identical conditions.

Which statement explains this difference?

A Bromine is more electronegative than chlorine.

B The bromide ion is a stronger electrophile than the chloride ion.

C The C–C*l* bond is more polar than the C–Br bond.

D The C–C*l* bond is stronger than the C–Br bond.

Ans: D

Rate of reaction 1 is higher than rate of reaction 2 because of the weaker C – Br bond.
Lecture notes 4.2.1 → Down the group, **size of the halogen atom increases** and the valence orbitals of the halogen atom become bigger and more diffuse. **Orbital overlap is less effective** and **C – X bond strength decreases**. Less energy is required to break the C – X bond.

Option A is wrong as C*l* is more electronegative (F > O > C*l* ~ N)
Option B is wrong as Br^- and Cl^- ions are not electrophiles
Although Option C is a correct statement, it cannot be used to explain the experimental results. If polarity were the main factor, a more polar C−C*l* bond means the C in C−C*l* has a larger δ+. This makes the chloroalkane more susceptible to nucleophilic attack and reaction 2 would be faster. Since this does not match the experimental results, bond strength is the main factor, not bond polarity.

6. *Use of the Data Booklet is relevant to this question.*

2-bromopropane reacts with the following.

- an aqueous solution of sodium hydroxide to form organic product **P**
- an ethanolic solution of sodium hydroxide to form organic product **Q**
- an ethanolic solution of sodium cyanide to form organic product **R**

What is the order of increasing relative molecular masses, lowest to highest, of the organic products?

A P Q R **B** Q P R **C** Q R P **D** R P Q

Ans: B

P is $CH_3CH(OH)CH_3$, **Q** is $CH_3CH{=}CH_2$ and **R** is $CH_3CH(CN)CH_3$

7. N17/1/24

During the preparation of many organic compounds, by-products are formed. This usually occurs because the reagent can react in more than one way depending on the conditions used or because the products formed may react with the reactants.

Propan-1-ol is produced by the reaction between 1-bromopropane and aqueous sodium hydroxide.

$CH_3CH_2CH_2Br + NaOH \rightarrow CH_3CH_2CH_2OH + NaBr$

What could be a by-product of this reaction?

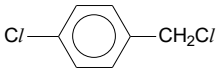
Hint: NaOH functions differently under aqueous and alcoholic (e.g. ethanolic) medium. This causes RX to undergo different types of reactions.

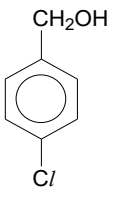
1 $CH_3CH{=}CH_2$
2 $CH_3CH_2CH_2ONa$
3 $CH_3CH(OH)CH_3$

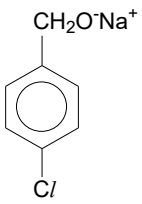
A **1, 2** and **3** **B** **1** and **2** **C** **2** and **3** **D** **1 only**

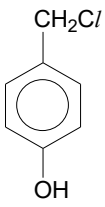
Ans: D (1 only)

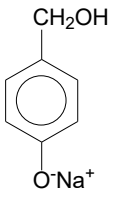
NaOH functions as a strong base in alcoholic medium (product formed in nucleophilic substitution is an alcohol) and hence elimination (of HBr) can occur to form alkene.

8. 4-chloro-1-(chloromethyl)benzene,  , is boiled under reflux with an excess of aqueous sodium hydroxide. What is the main product?

A


B


C


D


Ans: A

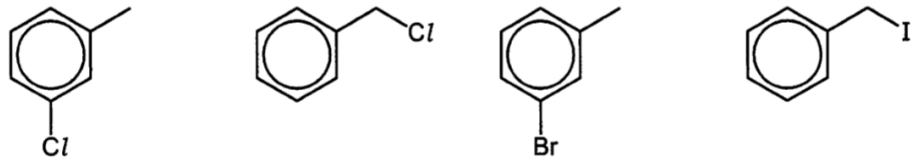
OH^- will only be able to substitute the C*l* on the side chain and not the C*l* directly bonded to benzene ring.

The lone pair of electrons on C*l* atom of chlorobenzene delocalises into the benzene ring.

This strengthens the C–C*l* bond (due to the partial double bond character), thus causing chlorobenzene to be resistant to nucleophilic substitution under the given conditions.

9. N17/1/23

Equal amounts of compounds **W**, **X**, **Y** and **Z** are added separately to four test-tubes containing equal concentrations of ethanolic silver nitrate solution in a heated water bath. No precipitate forms in two of the tubes. In the two other tubes, precipitates formed at different rates.



W X Y Z

Which row is correct?

	compounds which do **not** form a precipitate	colour of the precipitate which forms the fastest
A	**W** and **X**	cream
B	**W** and **X**	yellow
C	**W** and **Y**	white
D	**W** and **Y**	yellow

Ans: D

W and **Y** are halogenoarenes. They do not undergo hydrolysis.

Lecture notes 5.1 →

- The p orbital of the halogen atom overlaps with the π bond
- **Lone pair of electrons of the halogen atom delocalise into the benzene ring**.
- The C–X bond has **partial double bond** character (shortened and strengthened bond)
- **More energy** is required to break the **stronger C–X** bond
- Furthermore, the bulky benzene ring prevents the approach of nucleophiles.

The C−I bond in **Z** is weaker than C−Cl bond in **X** as I is larger and has less effective orbital overlap with C.

Uses of Halogen Derivatives

10. Chlorofluorocarbons (CFCs) have been widely used in aerosols sprays, refrigerators and in making foamed plastics, but are now widely known to destroy ozone in the upper atmosphere.

What will **not** destroy ozone, and therefore can be used as a replacement for CFCs?

A $CHBr_3$
B CCl_3CBr_3
C $CHClFCClF_2$
D $CH_3CH_2CH_2CH_3$

Ans: D

The C−Cl bond is relatively weaker than C−F or C−H bonds. It is the most likely to break and form Cl•. Cl• catalyses the destruction of ozone.
Any bond weaker than C−Cl will be broken by UV light even more readily to give radicals, e.g. C−Br bond in options A and B will also break to give Br•.
Option D which has only stronger C−H bonds will not break to give radicals.

Answers

1	3	4	5	6	7	8	9	10
A	D	C	D	B	D	A	D	D