



DISCUSSION QUESTIONS

Mechanism

1. 2017/P3/Q5(c) – Modified

The following scheme shows a synthesis of the beta-blocker drug, *metoprolol*. Study Fig 5.1 carefully and answer the questions that follow.

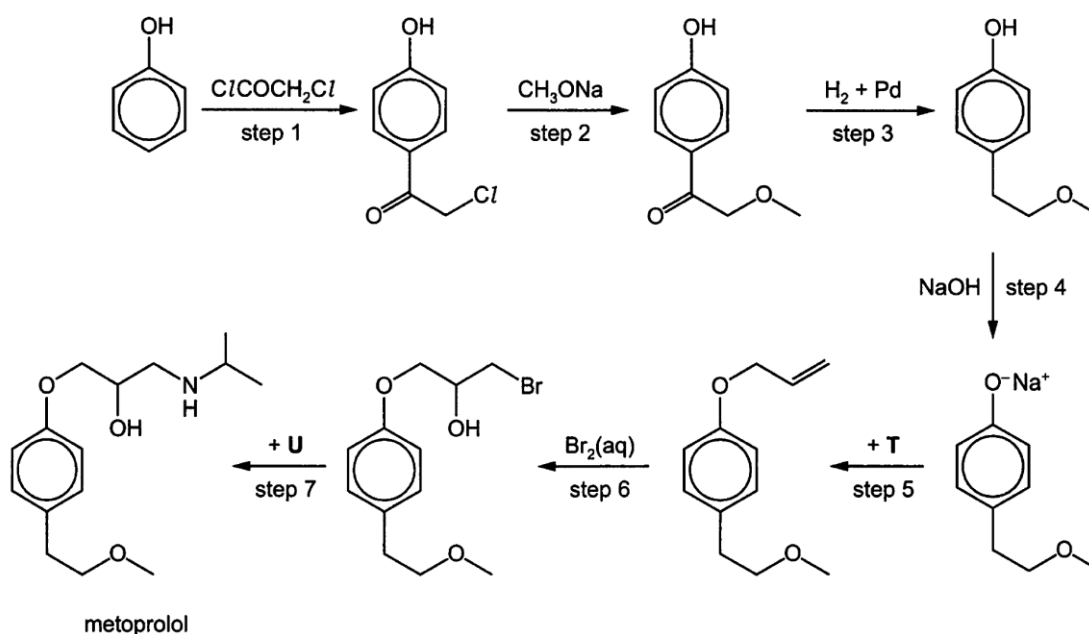
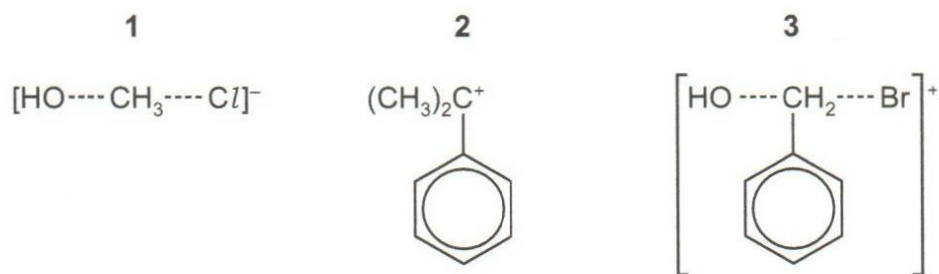


Fig. 5.1

- (a) Name the mechanism of the reaction in each of the steps 1, 2 and 6.
- (b) Suggest the identity of the reagent **T** in step 5.
- (c) Suggest the identity of the reagent **U** in step 7.

2. 2016/P1/Q38

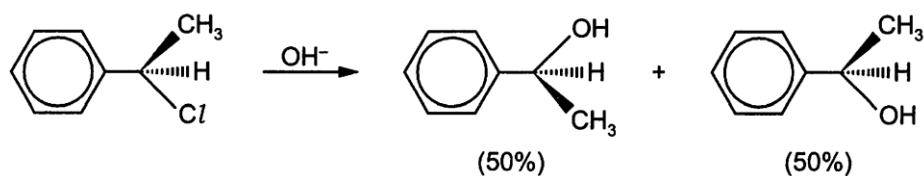
What could be formed during a nucleophilic substitution reaction?



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

3. 2022/P1/Q22

The following scheme represents the result of a hydrolysis reaction.



Which statements about this reaction are correct?

- 1 An intermediate in the reaction has a plane symmetry.
- 2 There are two intermediates in the reaction which are mirror images of each other.
- 3 The reaction proceeds via the $\text{S}_{\text{N}}2$ mechanism.

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

4. Describe the mechanism of the alkaline hydrolysis of $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{Br}$. Explain why the resulting organic product(s) would be optically inactive. In your answer, show any relevant charges, dipoles or lone pairs of electrons you consider to be important in this mechanism.

Criteria of Success for $\text{S}_{\text{N}}1$ mechanism:

- ☐ Name of mechanism: **Nucleophile Substitution, $\text{S}_{\text{N}}1$**
- ☐ $\delta+$ on C, $\delta-$ on X
- ☐ Curly arrows to show flow of a pair of electrons
- ☐ Lone pair of electrons on Nu^-
- ☐ Trigonal planar carbocation intermediate
- ☐ Nu^- attack from either side of the trigonal plane
- ☐ Label slow and fast steps
- ☐ If chiral C exists, a pair of optical isomers as products

5. 2019/P3/Q4(c)

When phenylethene reacts with $\text{HCl}(\text{g})$, only one of the two possible constitutional (structural) isomers with formula $\text{C}_8\text{H}_9\text{Cl}$ is formed. When this isomer, **E** is reacted with $\text{NaOH}(\text{aq})$, compound **F**, $\text{C}_8\text{H}_{10}\text{O}$, is produced in a reaction whose rate is independent of $[\text{OH}^-(\text{aq})]$.

- (a) Draw the structures of the two possible constitutional (structural) isomers of $\text{C}_8\text{H}_9\text{Cl}$ that could be formed from phenylethene. [1]

(b) Identify isomer **E**, and draw the structure of **F**.

[1]

(c) By referring to the mechanisms of these reactions, explain why both **E** and **F** are produced as a 50:50 mixture of enantiomers.

[2]

Reactions of Halogenoalkanes

6. 2022/3/4f

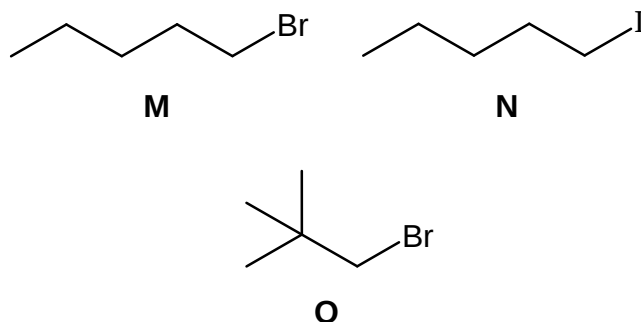
(a) Describe the mechanism for the reaction of 1-bromopropane with hot ethanolic NaCN. Show relevant lone pairs of electrons, dipoles and curly arrows. [3]

Criteria of Success for S_N2 mechanism:

- ☐ Name of mechanism: **Nucleophile Substitution, S_N2**
- ☐ 3D representation of reactant and product
- ☐ $\delta+$ on C, $\delta-$ on X
- ☐ Lone pair of electrons on Nu⁻
- ☐ Nu⁻ attack from the side opposite to X
- ☐ Curly arrows to show flow of a pair of electrons
- ☐ Bond breaking and bond forming in transition state
- ☐ Overall charge on transition state if Nu⁻ was used
- ☐ Inverted product

- (b) A small quantity of two organic by-products is formed in the reaction of 1-bromopropane with hot aqueous ethanolic NaCN. Suggest an identity for one of these two organic by-products. [1]

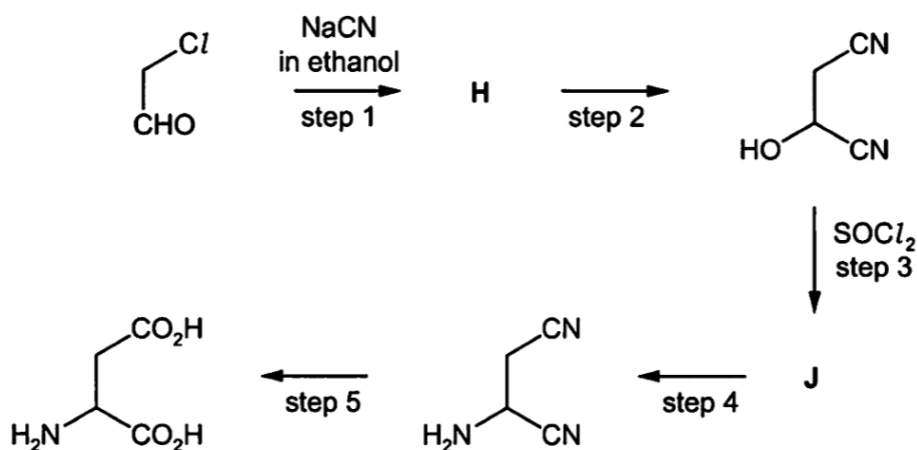
- (c) A kinetics investigation for the reaction of the halogenoalkanes **M**, **N**, and **O** with NaOH(aq) at a particular temperature is carried out.



State and explain the relative rate of reaction of **M**, **N** and **O** with NaOH(aq). [2]

7. 2015/3/3(d)

Aspartic acid can be synthesised from chloroethanal by the following route.

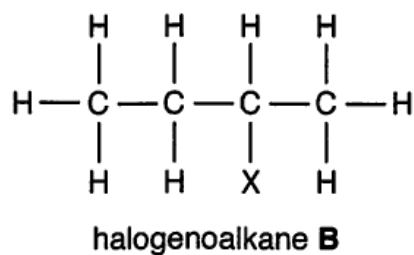


(a) Suggest structures for the intermediates for **H** and **J**.

(b) Suggest reagents and conditions for step 4 and for step 5.

8. 2018/P2/Q3

Halogenoalkanes **B** reacts with sodium hydroxide, under different conditions, to form 4 different organic products **C**, **D**, **E** and **F**.



C is the product formed when **B** is warmed with aqueous sodium hydroxide.

(a)(i) Name the *type of reaction* occurring when **C** is made from **B**.

(ii) Describe a chemical test, with appropriate observations, which would confirm the identity of **B** as a chloroalkane.

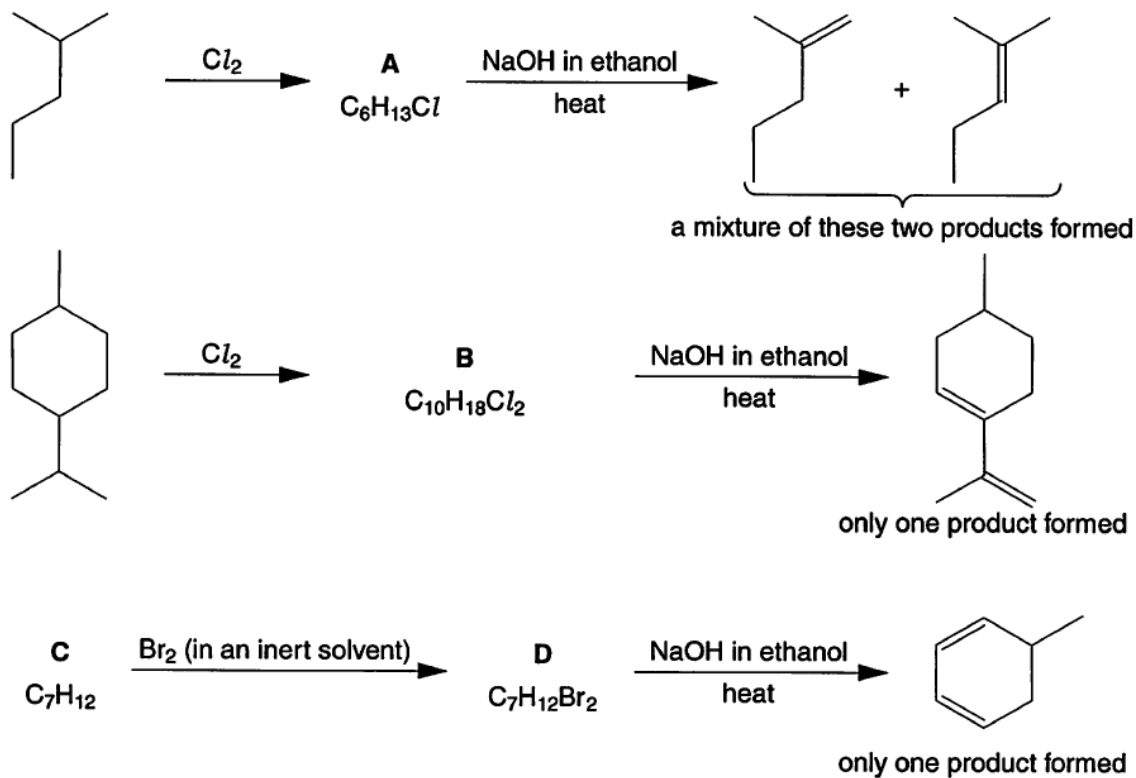
(b) Compounds **D**, **E**, and **F** are all hydrocarbons. **D** and **E** are stereoisomers of each other.

(i) Describe the reagents and conditions needed to favour the formation of a mixture of products of **D**, **E** and **F**, rather than product **C**.

(ii) Draw the skeletal diagram of **D**, **E** and **F** and name them.

9. 2010/P3/Q1(d)

Suggest a structural formula for each of the compounds **A** – **D** in the following schemes.



Reactivity of Halogen Derivatives

10. 2012/P1/Q39

Bromoethane, $\text{CH}_3\text{CH}_2\text{Br}$, is very unreactive to nucleophiles while 3-bromopropene is $\text{CH}_2=\text{CHCH}_2\text{Br}$, is very reactive by comparison.

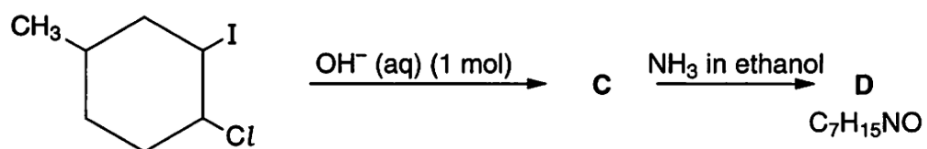
Which could be a reason for the lack of reactivity of $\text{CH}_3\text{CH}_2\text{Br}$?

- 1 The electrons of the bromine atom delocalise into the π bond.
- 2 The electrons of the π bond repel the attacking nucleophile.
- 3 The presence of the π bond prevents the free rotation of the C-Br bond thus decreasing the reactivity.

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

11. 2012/P3/Q2(d) – Modified

Predict the outcomes of the following transformation, drawing the structures of the intermediate **C** and the cyclic product **D**.



Chlorofluorocarbons

12. Chlorofluorocarbons, CFCs, were once used as refrigerant fluids and aerosol propellants. In many applications they have now been replaced by hydrofluoroalkanes (HFCs) or hydrochlorofluoroalkanes (HCFCs). This is because CFCs contribute to the destruction of the ozone layer.

(a) Suggest one reason why CFCs were originally used for these purposes.

(b) Explain how CFCs destroy the ozone layer.

(c) Suggest one problem with the use of HFCs and HCFCs.

Assessment Objectives	Questions
(a) recall the chemistry of halogenoalkanes as exemplified by	
(i) the following nucleophilic substitution reactions of bromoethane:	Q8a
• hydrolysis using NaOH(aq) and heat	
• formation of nitriles using KCN in ethanol and heat	Q6a, Q7a
• formation of primary amines by reaction with ammonia in ethanol heated under pressure	Q7b, Q11
(ii) the elimination of hydrogen bromide from 2-bromopropane using NaOH in ethanol and heat	Q8b, Q9
(b) describe and explain the mechanisms of nucleophilic substitutions in halogenoalkanes:	
(i) S _N 1, in terms of stability of the carbocation intermediates	Q4, Q5b
(ii) S _N 2, in terms of steric hindrance in the halogenoalkanes	Q6c
(c) explain the stereochemical outcome in nucleophilic substitution involving optically active substrates (see also (b)):	Q2, Q3
(i) inversion of configuration in S _N 2 mechanism	Q6a
(ii) racemisation in S _N 1 mechanism	Q4, Q5c
(d) interpret the different reactivities of halogenoalkanes, with particular reference to hydrolysis, and to the relative strengths of the carbon-halogen bonds	Q11
(e) explain the unreactivity of chlorobenzene compared to halogenoalkanes towards nucleophilic substitution, in terms of the delocalisation of the lone pair of electrons on the halogen and steric hindrance	Q10
(f) suggest characteristic reactions to differentiate between	
(i) different halogenalkanes (see also (d))	Q6c, Q8a
(ii) halogenalkanes and halogenoarenes (see also (e))	Q10
e.g. hydrolysis, followed by testing the halide ions	
(g) explain the uses of fluoroalkanes and fluorohalogenoalkanes in terms of their relative chemical inertness	Q12
(h) recognise the effect of chlorofluoroalkanes (CFCs) on the ozone layer, and that their proposed replacements, hydrofluoroalkanes (HFCs) and hydrochlorofluoroalkanes (HCFCs), have significant environmental impact too	Q12
[the mechanistic details of how CFCs and HCFCs deplete the ozone layer are not required]	