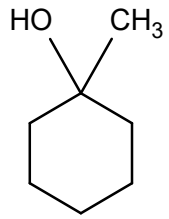
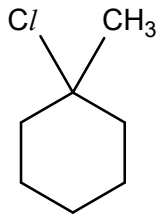
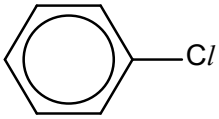
VICTORIA JUNIOR COLLEGE
CHEMISTRY DEPARTMENT
Halogen Derivatives (Halogenoalkanes and Halogenoarenes)
Tutorial Questions

Complete the following tables:

(1) Preparation of halogen derivatives

Preparation of halogenoalkanes		
Starting compound	Reagents and conditions	Product
		
	HCl(g)	
Preparation of halogenoarenes		
	Cl_2, anhydrous $AlCl_3$	

(2) Reactions of halogen derivatives

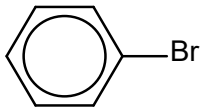
(a) Halogenoalkanes

Starting compound	Reaction type	Reagents and conditions	Product
$CH_3CHClCH_3$		NaOH(aq), heat	
			$CH_3CH(NH_2)CH_3$
		Limited NH_3 in ethanol, heat in sealed tube	

Starting compound	Reaction type	Reagents and conditions	Intermediate	Reaction type, reagents and conditions	Final product
CH_3CHC/CH_3			$CH_3CH(CN)CH_3$	Hydrolysis H_2SO_4(aq), heat	
					CH_3CHCH_3 CH_2NH_2

Starting compound	Reaction type	Reagents and conditions	Product
$(CH_3)_2CC/CH_2CH_3$		NaOH in ethanol, heat	

(b) Halogenoarenes and vinyl halides

Compound	Reactivity
	No reaction under normal laboratory conditions.
$CH_3CI=CH_2$	

Preparation of Halogenoalkanes

1 State the reagents and conditions needed for the conversion of $CH_3CH_2CH_2CH_2OH$ into

(a) 1–bromobutane

……..

……..

(b) 2–bromobutane (in two steps)

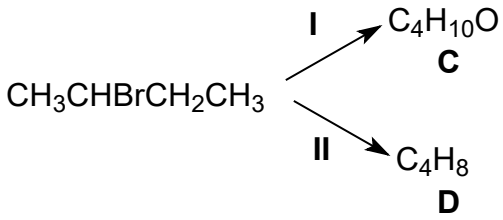
……..

……..

……..

Reactions of halogenoalkanes

2 2–bromobutane can react under two different sets of reaction conditions to give two different product mixtures **C** and **D**.



(a) State the reagents and conditions necessary for each of the reactions **I** and **II**.

……..

……..

……..

(b) Product **D** is a mixture of isomers, all of which decolourise bromine water. Draw displayed formulae of these isomers and explain the reaction with $Br_2(aq)$.

……..

……..

……..

(c) State the reagents and conditions for the conversion of $CH_3CH(Br)CH_2CH_3$ into $CH_3CH(NH_2)CH_2CH_3$.

……..

……..

……..

3 A monocarboxylic acid **R** occurs in goat's milk. **R** has the following composition by mass:

C, 62.1%; H, 10.3%; O, 27.6%.

Neutralisation of a sample of 0.10 g of **R** requires 8.6 cm^3 of 0.10 mol dm^{-3} sodium hydroxide.

(a) Determine the molecular formula of **R**.

……..

……..

……..

……..

(b) **R** can be synthesized in the laboratory from 1–bromo–2,2–dimethylpropane by a 2–stage reaction sequence:

1–bromo–2,2–dimethylpropane → **Q** → **R**

(i) Draw the skeletal formula of 1–bromo–2,2–dimethylpropane.

……..

……..

……..

(ii) Suggest the reagents and conditions necessary for each step of the synthesis.

……..

……..

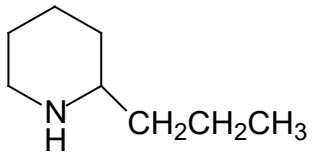
……..

(iii) Predict from this synthesis the structural formulae of **Q** and **R**.

……..

……..

4 The alkaloid *coniine* is the major constituent of oil of hemlock, the poison taken by Socrates when he committed suicide in 399 BCE.



coniine

Coniine can be synthesized by reacting ammonia with a dibromo compound **J**.

$$NH_3 + C_8H_{16}Br_2 \rightarrow \text{coniine} + 2HBr$$
J

(a) What *type of reaction* is occurring here?

……..

(b) Suggest the structure and name of compound **J**.

……..

……

Nucleophilic substitution mechanisms

5 **(a)** A sample of (2–chloroethyl)benzene, $C_6H_5CH_2CH_2Cl$, underwent hydrolysis when heated with dilute aqueous NaOH. The kinetics of the study show that the reaction is overall second order. By showing relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs, describe the mechanism for the hydrolysis of (2–chloromethyl)benzene.

(b) (1–chloroethyl)benzene, $C_6H_5CH(Cl)CH_3$, is a positional isomer of (2–chloroethyl)benzene.

(i) State the type of stereoisomerism exhibited by (1–chloroethyl)benzene and draw its stereoisomers.

……..

……..

……..

(ii) When a sample containing purely one of the stereoisomers of (1–chloroethyl)benzene underwent hydrolysis in NaOH(aq), the product was found to be optically inactive.

By showing relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs, describe the mechanism for the hydrolysis of (1–chloroethyl)benzene. Explain why the product was optically inactive.

……..

……..

……..

……..

……..

……..

……..

……..

(iii) Suggest reasons for the difference in mechanisms in **(a)** and **(b)(ii).**

……...

……..

……..

……...

Effect of different halogen atoms on reactivity of halogenoalkanes

6 Why does the reaction $C_2H_5X + OH^- \rightarrow C_2H_5OH + X^-$ take place more rapidly in aqueous solution when *X* is I than when *X* is Br?

A The I^- ion is a stronger nucleophile than the Br^- ion.
B The I^- ion is less hydrated in solution than the Br^- ion.
C The C–Br bond is more polar than the C–I bond.
D The C–Br bond is stronger than the C–I bond. ( )

Additional notes:

……...

……..

Fluoroalkanes and fluorohalogenoalkanes

7 Which of the following would be suitable for use in a fire extinguisher?

1 $CBrF_3$
2 $CH_3(CH_2)_5CBr_3$
3 HF

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

Additional notes:

……...

……..

8 Ozone depletion potential (ODP) is a measure of the effectiveness of chlorofluoroalkanes in destroying stratospheric ozone. In which sequence are compounds listed in increasing order of their ODPs?

A $CHCl F_2 < CH_3CCl_2F < CCl_2FCCl F_2$
B $CHCl F_2 < CCl_2FCCl F_2 < CH_3CCl_2F$
C $CCl_2FCCl F_2 < CHCl F_2 < CH_3CCl_2F$
D $CH_3CCl_2F < CCl_2FCCl F_2 < CHCl F_2$ ( )

Additional notes:

……...

Halogenoarenes

9 A mixture of 1 mol of bromobenzene and 1 mol of 2–bromopropane is heated under reflux for several hours with 2 mol of sodium hydroxide in aqueous solution.

(a) How many moles of bromobenzene and 2–bromopropane are likely to remain?

……..

(b) Give 2 reasons to explain the low reactivity of bromobenzene towards nucleophilic substitution.

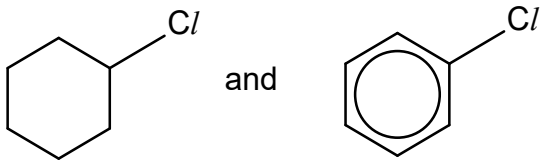
……..

……..

……..

……..

10 Describe how you would distinguish between the following pair of compounds. Indicate clearly in your answer the reagents, conditions and observations for each compound.



……..

……..

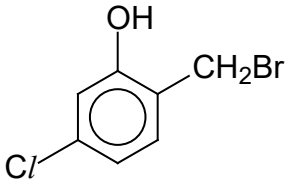
……..

……

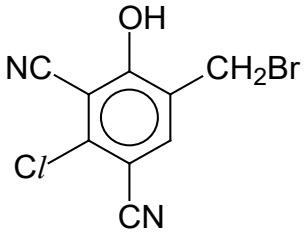
……

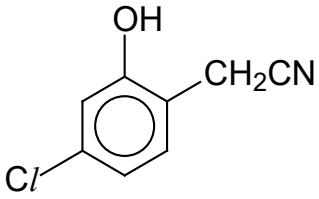
VICTORIA JUNIOR COLLEGE
CHEMISTRY DEPARTMENT
Halogen Derivatives (Halogenoalkanes and Halogenoarenes)
Supplementary Questions

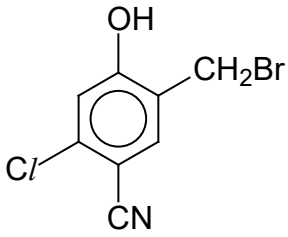
1 A compound has the following structure.

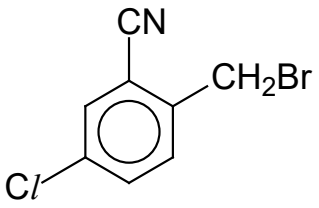


Which compound is obtained by nucleophilic substitution when a cyanide ion reacts with this compound?

A


C


B


D


2 Some chlorobutanes were separately treated with hot ethanolic sodium hydroxide. Two of these gave the same hydrocarbon C_4H_6. From which pair of chlorobutanes was this hydrocarbon obtained?

A $CH_3CH_2CH_2CH_2Cl$ and $CH_3CH_2CH_2CHCl_2$
B $CH_3CHClCHClCH_3$ and $ClCH_2CH_2CH_2CH_2Cl$
C $CH_3CH_2CH_2CH_2Cl$ and $ClCH_2CH_2CH_2CH_2Cl$
D $CH_3CH_2CH_2CH_2Cl$ and $CH_3CH_2CHClCH_3$

3 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 $(CH_3)_2CHCO_2H$

4 **(a)** Suggest reagents, and conditions necessary to convert bromoethane into **(i)** $CH_3CH_2NH_2$ **(ii)** $CH_3CH_2CH_2NH_2$.

(b) A by–product in the formation of $CH_3CH_2NH_2$ in **(a)(i)** above has the formula $C_8H_{20}NBr$ and it gives an immediate precipitate with aqueous silver nitrate. Suggest a structure for this compound.

5 2–iodooctane, $CH_3CHI(CH_2)_5CH_3$, exists as two optical isomers, **A** and **B** which rotate polarized light in opposite direction.

An optically pure sample containing only isomer **A** rotates polarised light by an angle of +33.3°. It reacts with a solution of radioactive iodide, $^{131}I^-$, dissolved in acetone until 1.5% of the original 2–iodooctane is incorporated with radioactive iodide. The product mixture at this point in time is found to rotate polarized light by an angle of +32.3°.

(a) Calculate the percentage composition of **A** and **B** present in the product mixture.

(b) Hence, deduce whether the mechanism proceeds via S_N1 or S_N2.

(c) Describe, with the aid of curly arrows, the stereochemistry of the mechanism stated in **(b)**.

In your answer, indicate clearly the presence of any radioactive iodine, ^{131}I, and the relative spatial configuration of the organic reactant and product.

(d) 3–iodo–3–methylhexane exists as a pair of enantiomers. When an enantiomerically pure sample of 3–iodo–3–methylhexane was reacted with excess radioactive iodide, $^{131}I^-$, a racemic mixture was obtained. Describe the mechanism of the reaction, and explain why it results in a racemic mixture.

6 Explain the following observations as fully as you can. (Use of the *Data Booklet* is recommended.)

Compound	*Observations after adding $AgNO_3$ (aq)*
$CH_3CHICH_2CH_3$	Ppt forms almost immediately
$CH_3CHBrCH_2CH_3$	Ppt forms after 2 minutes
$CH_3CHCl CH_2CH_3$	Ppt slowly forms after 10 minutes
$CH_3CHFCH_2CH_3$	No ppt forms
C_6H_5Cl	No ppt forms

7 The halogenoethanes C_2H_5Cl, C_2H_5Br and C_2H_5I differ in their physical properties and reactivities.

(a) Suggest and explain how the boiling points of these three compounds differ.

(b) Suggest and explain how the C–*X* bond polarities in these three compounds differ.

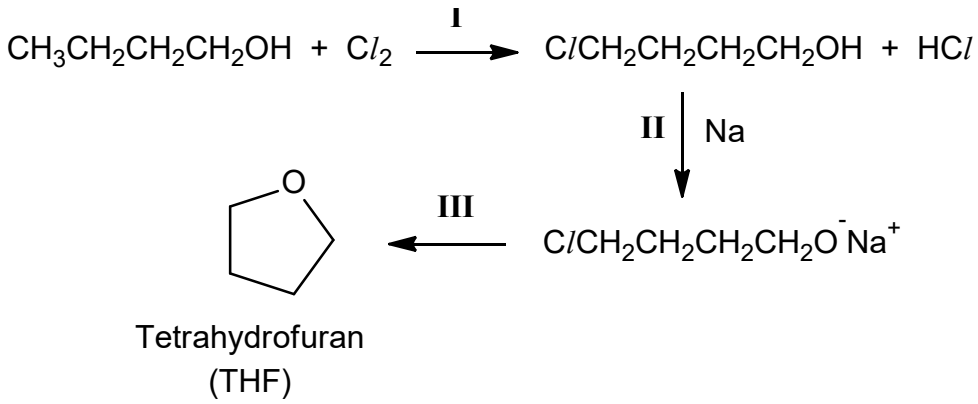
(c) Describe and explain how the reactivities of the three compounds differ towards nucleophilic reagents.

8 When a mixture of beryllium hydroxide pellets and ethanol is added to 2–chlorobutane, **P**, **Q** and **R** are formed. Although **P**, **Q** and **R** do not react with PCl_5, they decolourise potassium manganate (VII), with only **R** giving effervescence.

Suggest the identities of **P**, **Q** and **R**, explaining your reasoning.

9 The common industrial solvent, tetrahydrofuran (THF) is widely used to degrease metal parts.

It can be synthesized from butan–1–ol as shown below.



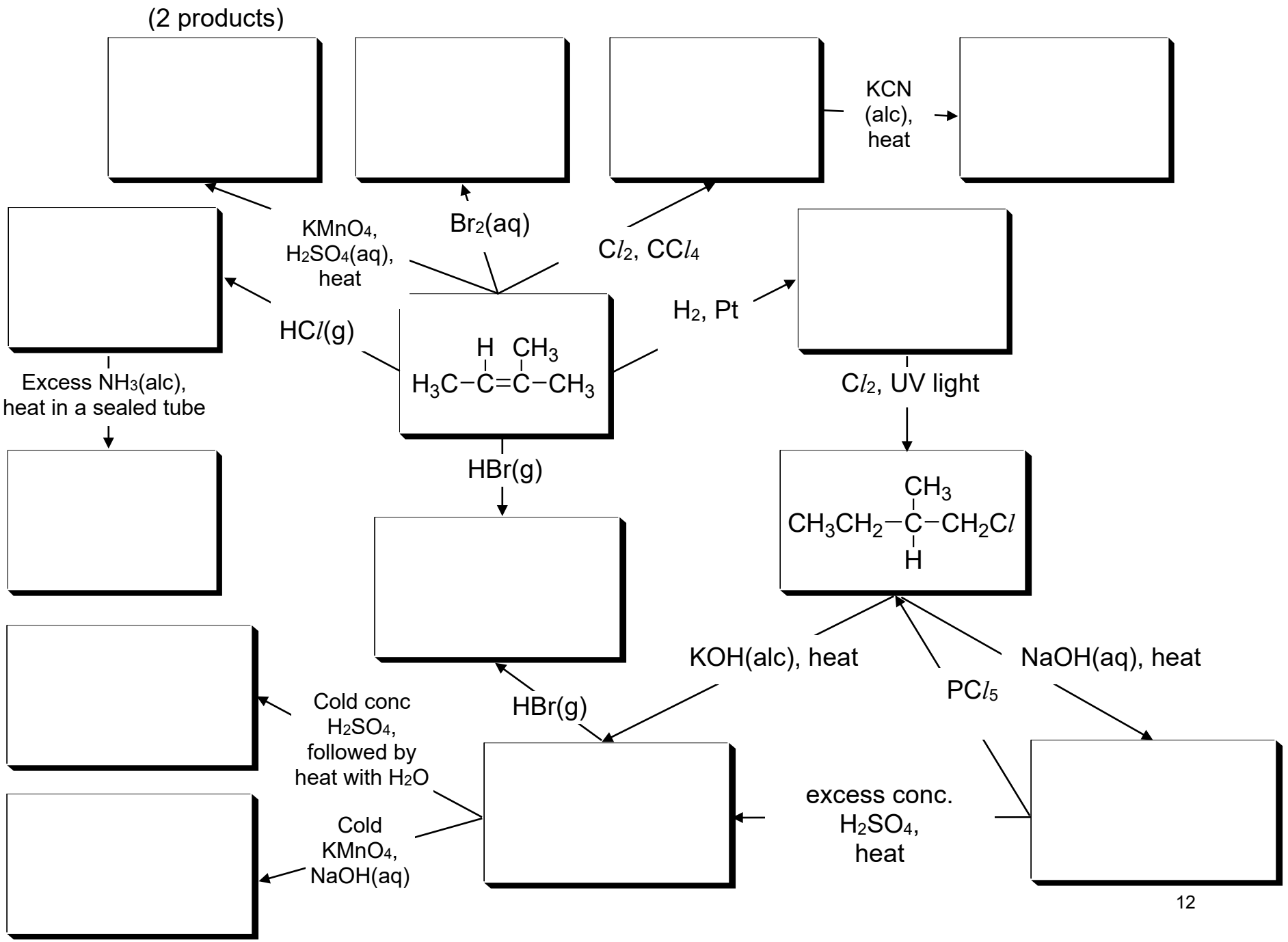
Tetrahydrofuran
(THF)

(a) What types of reaction are steps **I** and **III**?

(b) Draw a mechanism for step **III**. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons.

(c) Comment on the yield of THF in this synthesis. Briefly explain your reasoning.

Alkanes / Alkenes / Halogenoalkanes



Arenes and RX