15. HALOGEN COMPOUNDS

Learning outcomes

Candidates should be able to:

1. recall the reactions (reagents and conditions) by which halogenoalkanes can be produced:
   (a) the free-radical substitution of alkanes by Cl_2 or Br_2 in the presence of ultraviolet light, as exemplified by the reactions of ethane
   (b) electrophilic addition of an alkene with a halogen, X_2, or hydrogen halide, HX(g), at room temperature
   (c) substitution of an alcohol, e.g. by reaction with HX or KBr with H_2SO_4 or H_3PO_4; or with PCl_3 and heat; or with PCl_5; or with $SOCl_2$
2. classify halogenoalkanes into primary, secondary and tertiary
3. describe the following nucleophilic substitution reactions:
   (a) the reaction with NaOH(aq) and heat to produce an alcohol
   (b) the reaction with KCN in ethanol and heat to produce a nitrile
   (c) the reaction with NH_3 in ethanol heated under pressure to produce an amine
   (d) the reaction with aqueous silver nitrate in ethanol as a method of identifying the halogen present as exemplified by Bromoethane
4. describe the elimination reaction with NaOH in ethanol and heat to produce an alkene as exemplified by Bromoethane
5. describe the S_N1 and S_N2 mechanisms of nucleophilic substitution in halogenoalkanes including the inductive effects of alkyl groups
6. recall that primary halogenoalkanes tend to react via the S_N2 mechanism; tertiary halogenoalkanes via the S_N1 mechanism; and secondary halogenoalkanes by a mixture of the two, depending on the structure
7. describe and explain the different reactivities of halogenoalkanes (with particular reference to the relative strengths of the C–X bonds as exemplified by the reactions of halogenoalkanes with aqueous silver nitrates)

Introduction

1. 2-bromo-2-methylpropane is a tertiary bromoalkane.
   Define tertiary bromoalkane. [1]

1. Which row shows the correct name and classification of the halogenoalkane shown?
   $CH_3(CH_2)_2CBr(CH_3)CH_2CH_3$

	Name	classification of halogenoalkane
A	3-bromo-3-methylhexane	secondary
B	3-bromo-3-methylhexane	tertiary
C	3-bromo-4-methylhexane	tertiary
D	4-bromo-5-methylhexane	secondary

2. Structural isomerism only should be considered when answering this question.
How many compounds with molecular formula $C_5H_{11}Br$ are **primary** halogenoalkanes?

A 4 **B** 5 **C** 7 **D** 8

3. A few drops of 2-bromopropane were placed in a test-tube. An equal volume of aqueous silver nitrate was added. A precipitate was formed.
The experiment was repeated with 2-iodopropane.
Which row is correct?

	colour of precipitate from **2-bromopropane** + $AgNO_3(aq)$	faster rate of reaction
A	cream	2-bromopropane + $AgNO_3$ (aq)
B	yellow	2-bromopropane + $AgNO_3$ (aq)
C	cream	2-iodopropane + $AgNO_3$ (aq)
D	yellow	2-iodopropane + $AgNO_3$ (aq)

Look at the different structures of 1^0, 2^0 and 3^0 haloalkanes in MolView website as 3D structures.

Preparation

substitution of an alcohol

by reaction with HX or KBr with H_2SO_4 or H_3PO_4

with PCl_3 and heat

with PCl_5

with $SOCl_2$

$$CH_3CH_2OH + HCl \xrightarrow{\text{conc. } HCl + ZnCl_2 + \text{heat}} CH_3CH_2Cl + H_2O$$

$$CH_3CH_2OH + PCl_5 \xrightarrow{\text{warm}} CH_3CH_2Cl + HCl + POCl_3$$

$$CH_3CH_2OH + SOCl_2 \xrightarrow{\text{warm}} CH_3CH_2Cl + HCl + SO_2$$

$$CH_3CH_2OH + HBr \xrightarrow{\text{conc. } H_2SO_4 + NaBr + \text{heat}} CH_3CH_2Br + H_2O$$

$$3CH_3CH_2OH + PI_3 \xrightarrow{\text{heat with } P + I_2} 3CH_3CH_2I + H_3PO_3$$

- Tertiary alcohols react easily with concentrated hydrochloric acid on shaking at room temperature. The reaction proceeds via the S_N1 mechanism.
- Secondary and primary alcohols also react with concentrated hydrochloric acid, but at a slower rate. Anhydrous zinc chloride needs to be added as a catalyst, and the mixture requires heating.
- Reaction with phosphorus(V) chloride or sulfur dichloride oxide hydrogen chloride is evolved. This fizzing with PCl_5, and the production of misty fumes, can be used as a test for the presence of an alcohol (as long as water is absent).
- Alcohols can be converted into bromoalkanes by reaction with either concentrated hydrobromic acid or a mixture of sodium bromide, concentrated sulfuric acid and water (50%). These react to give hydrogen bromide:
$2NaBr + H_2SO_4 \rightarrow Na_2SO_4 + 2HBr$

- Halogens react with phosphorus to give the phosphorus trihalides:
  $2P + 3Br_2 \rightarrow 2PBr_3$
  $2P\ 3I_2 \rightarrow 2PI_3$
- The phosphorus trihalides, for example phosphorus triiodide, then react with alcohols to form iodoalkanes.

2. PCl_5 reacts with alcohols to form chloroalkanes.
   (i) Identify this type of reaction. [1]

   (ii) Draw the structure of the organic product formed in the reaction of an excess of PCl_5 with butane-1,3-diol.[2]

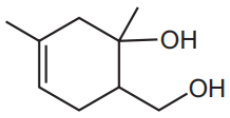
3. Pentan-3-ol, $C_2H_5CH(OH)C_2H_5$, reacts slowly with HCl to form a secondary halogenoalkane.
   Complete the equation for this reaction using structural formulae.

   $C_2H_5CH(OH)C_2H_5$ +…….. [1]

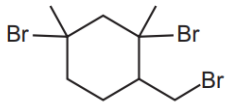
4. Construct an equation for the reaction of $(CH_2OH)_2$ with $SOCl_2$ to form G, $(CH_2Cl)_2$. [1]

4. What is the major product formed when compound R is warmed with an excess of HBr?

R



A



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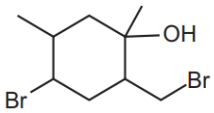

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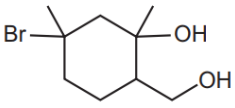
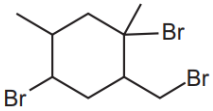


D



5. The table shows three sets of reagents and reaction conditions.

	reagents	reaction conditions
1	$CH_2C(CH_3)CH_3$ and HCl(g)	room temperature
2	$CH_3C(CH_3)(OH)CH_3$ and $SOCl_2$	room temperature
3	$CH_3CH(CH_3)CH_3$ and Cl_2	the presence of ultraviolet light

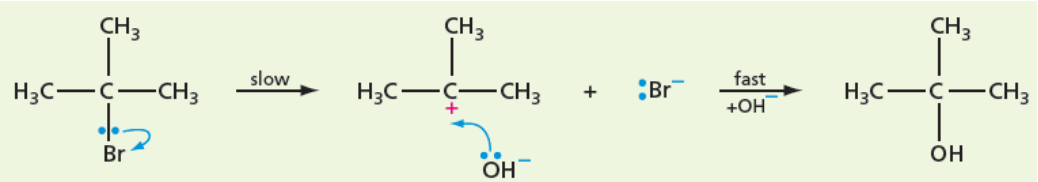
Which sets of reagents and conditions can be used to produce 2-chloro-2-methylpropane as one of the organic products?

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

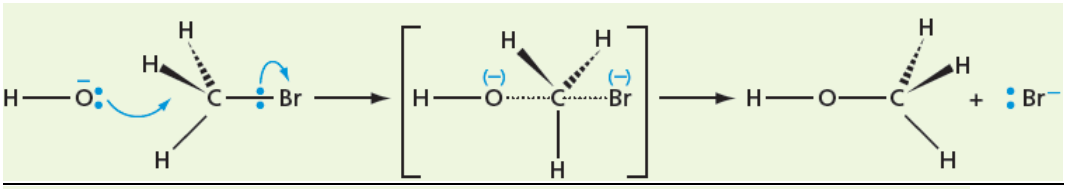
Properties

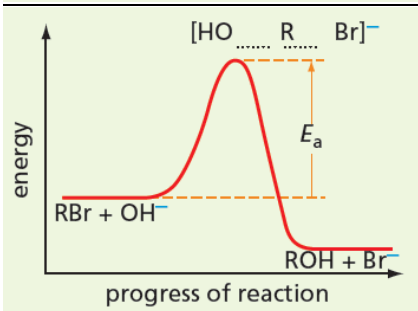
With aqueous NaOH

SN1

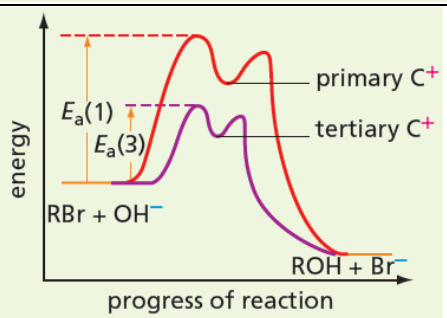


SN2





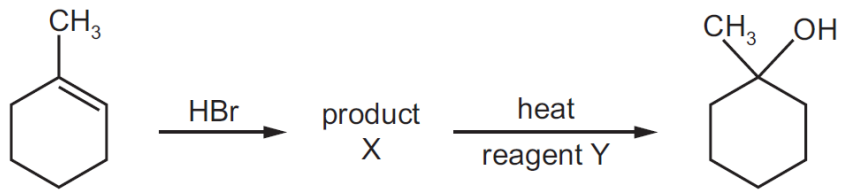
▲ Figure 16.10 Reaction profile for the S_N2 hydrolysis of bromomethane



▲ Figure 16.11 Reaction profiles for the S_N1 hydrolysis of primary and tertiary bromoalkanes

www.youtube.com/watch?v=Bg3c5c9b1BQ&t=117s
An Animated Explanation of Nucleophilic Substitution

6. The diagram shows a synthetic route to produce 1-methylcyclohexanol.



What is reagent Y?

A aqueous NaOH
B cold dilute $KMnO_4$
C ethanolic NaOH
D hot concentrated $KMnO_4$

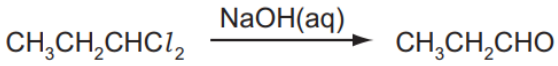
5. The reaction of $CH_3CH_2CH_2Br$ and NaOH is different depending on whether water or ethanol is used as a solvent. Complete the following table to identify the organic and inorganic products of the reaction of $CH_3CH_2CH_2Br$ and NaOH in each solvent. [2]

Solvent	Organic product(s)	Inorganic product(s)
Ethanol		
Water		

1. Which type of reaction happens during the hydrolysis of 2-bromopropane?

A electrophilic addition
B free radical substitution
C nucleophilic addition
D nucleophilic substitution

2. 1,1-dichloropropane reacts with aqueous sodium hydroxide in a series of steps to give propanal.



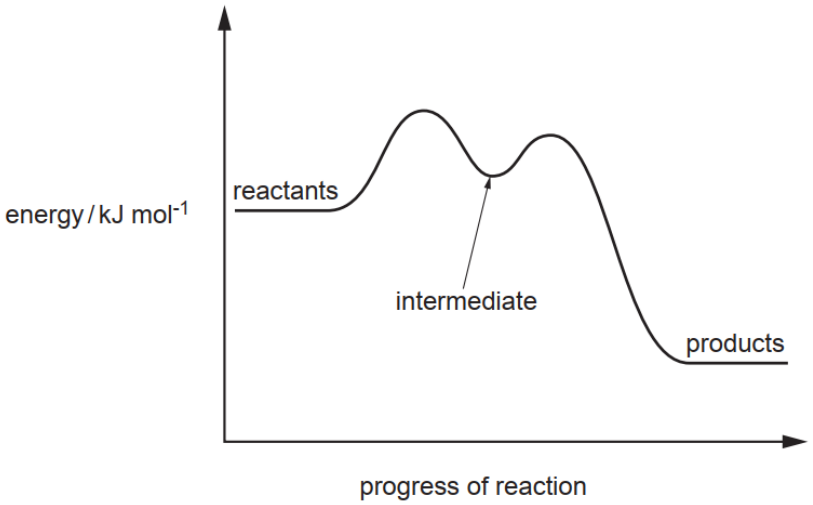
Which term describes the first step of this reaction?

A addition
B elimination
C oxidation
D substitution

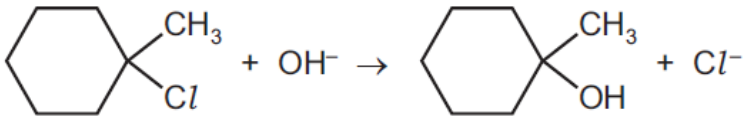
3. What is true of **every** nucleophile?

A It attacks a double bond.
B It donates a lone pair of electrons.
C It is a single atom.
D It is negatively charged.

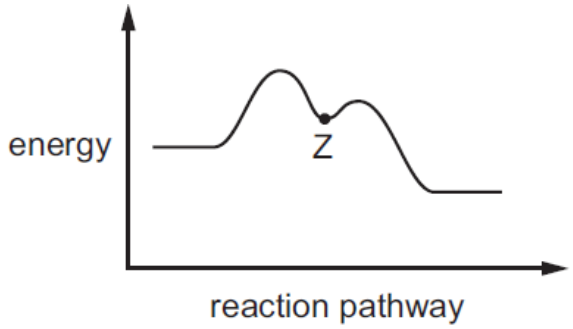
6. When 2-bromo-2-methylpropane reacts with OH^-, two mechanisms, SN1 and SN2, both occur. The SN2 mechanism has a slower rate.
Fig. 4.1 shows the reaction pathway diagram for the SN1 mechanism.
Sketch a graph on Fig. 4.1 to show the reaction pathway for the SN2 mechanism.



4. 1-chloro-1-methylcyclohexane is hydrolysed by heating with NaOH(aq).



The reaction pathway is shown.

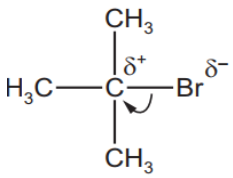


One carbon atom in 1-chloro-1-methylcyclohexane is bonded to three other carbon atoms.
What is the charge on this carbon atom at point Z?

A 1– B – C + D 1+

5. When 2-bromo-2-methylpropane reacts with aqueous sodium hydroxide, an alcohol is formed.
Which diagram describes the first step in the reaction mechanism?

A



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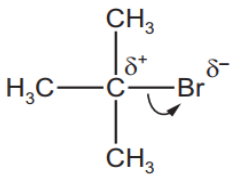

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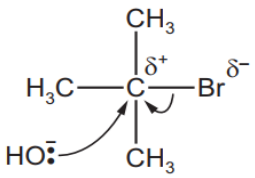

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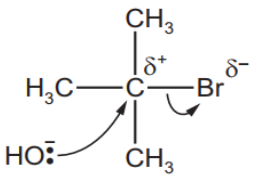
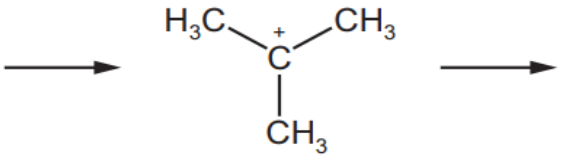
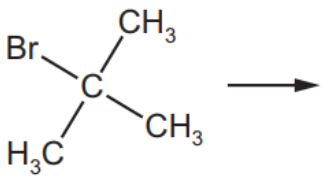


7. OH^-(aq) reacts with 2-bromo-2-methylpropane in an S_N1 reaction.
The molecular ion $(CH_3)_3C^+$ forms as the intermediate in this reaction.
Draw the mechanism for the S_N1 reaction of OH^- with 2-bromo-2-methylpropane.
Include charges, dipoles, lone pairs of electrons and curly arrows as appropriate.
Draw the structures of the organic reactant and organic product.



[3]

8. A large excess of 2-bromo-2-methylpropane is added to 0.0010mol of NaOH(aq), which contains a few drops of phenolphthalein indicator. A stopwatch is started as soon as the substances are mixed. The time taken for the pink colour to disappear is recorded.
The experiment is repeated at different temperatures, keeping all concentrations and volumes of reagents constant.
(i) Draw the mechanism to show the reaction of 2-bromo-2-methylpropane with OH^-(aq).
Show the intermediate formed in this reaction.
Include all charges, partial charges, lone pairs and curly arrows as appropriate.

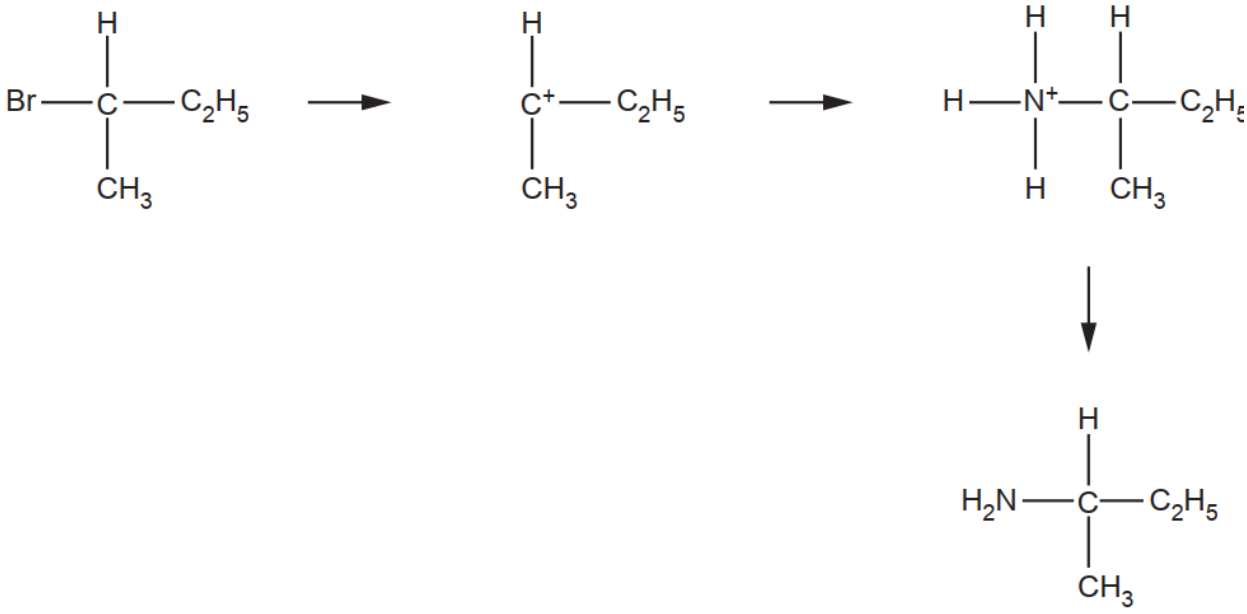


(ii) Name the mechanism for this reaction.

(iii) The original experiment is repeated at 25°C with 2-chloro-2-methylpropane instead of 2-bromo-2-methylpropane. All other variables remain constant.
Predict the effect of using 2-chloro-2-methylpropane compared to 2-bromo-2-methylpropane on the time taken for the pink colour to disappear. Explain your answer. [2]

9. A sample of $CH_3(CH_2)_5CHBrCH_3$ reacts with NaOH to make $CH_3(CH_2)_5CH(OH)CH_3$ in an SN1 mechanism.
Complete Fig. 4.1 to show the mechanism for the reaction of $CH_3(CH_2)_5CHBrCH_3$ and NaOH.
Include charges, dipoles, lone pairs of electrons and curly arrows, as appropriate.

10. Complete Fig. 4.2 to show the mechanism for the SN1 reaction that occurs when $CH_3CHBrC_2H_5$ reacts with NH_3 to produce $CH_3CH(NH_2)C_2H_5$.
Include charges, dipoles, lone pairs of electrons and curly arrows, as appropriate.



6. The following statements are about the reaction of NaOH(aq) with the three chloroalkanes shown.
$CH_3CH_2CHClCH_3$ $(CH_3)_2CHCH_2Cl$ $(CH_3)_3CCl$
Which statement is correct?

A $(CH_3)_2CHCH_2Cl$ reacts with NaOH(aq) by an SN^2 mechanism.
B The tertiary chloroalkane reacts more quickly than the others because the carbon atom bonded to the Cl atom is more positive in this molecule.
C The Cl atoms in the three chloroalkanes are attacked by OH–.
D The molecular formula of the major product is C_4H_8 for each reaction.

7. Which statement describes what happens when 2-chloro-2-methylpropane is warmed with NaOH(aq)?

A This secondary halogenoalkane reacts by a mixture of an SN^1 and an SN^2 mechanism.
B This secondary halogenoalkane reacts only by an SN^2 mechanism.
C This tertiary halogenoalkane reacts mostly by an SN^1 mechanism.
D This tertiary halogenoalkane does not react with hydroxide ions under these conditions.

8. Q is either a primary or a tertiary halogenoalkane. Q undergoes hydrolysis with aqueous sodium hydroxide.
The first step in the mechanism of this reaction involves two species reacting together.
Which row is correct?

	Q	behaviour of hydroxide ion
A	primary halogenoalkane	electrophile
B	primary halogenoalkane	nucleophile
C	tertiary halogenoalkane	electrophile
D	tertiary halogenoalkane	nucleophile

9. Which statement concerning the hydrolysis of 1-bromopropane with water is correct?

A The hydrolysis reaction between water and 1-iodopropane is faster because the C–Br bond is less polar than the C–I bond.
B The hydrolysis reaction with water is very slow because water is a weak electrophile.
C The mechanism of the reaction involves the formation of a stable carbocation.
D The reaction is slower with 1-chloropropane because the C–C*l* bond is stronger than the C–Br bond.

10. C_4H_9Cl reacts with warm dilute aqueous sodium hydroxide solution.
Which isomer of C_4H_9Cl will form the most stable cation intermediate?

A 1-chlorobutane

B 2-chlorobutane

C 1-chloro-2-methylpropane

D 2-chloro-2-methylpropane

11. Which statement is correct?

A Bromoethane reacts with NaOH(aq) to form ethene as a major product.
B 1-chlorobutane reacts more rapidly than 1-bromobutane with NaOH(aq) at the same temperature.
C Hydrolysis of $(C_2H_5)_3CBr$ occurs mostly by the S_N2 mechanism.
D The $CH_3CH_2CH_2CH_2^+$ ion is less stable than the $(CH_3)_3C^+$ ion.

12. In the hydrolysis of bromoethane by aqueous NaOH, what is the nature of the attacking group and of the leaving group?

	attacking group	leaving group
A	electrophile	electrophile
B	electrophile	nucleophile
C	nucleophile	electrophile
D	nucleophile	nucleophile

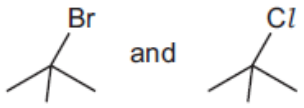
13. Aqueous NaOH reacts with 1-bromopropane to give propan-1-ol.
What should be included in a diagram of the first step in the mechanism?

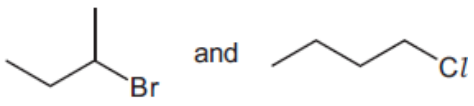
A a curly arrow from a lone pair on the OH^- ion to the $C\delta+$ atom of 1-bromopropane
B a curly arrow from the $C\delta+$ atom of 1-bromopropane to the OH^- ion
C a curly arrow from the C–Br bond to the C atom
D the homolytic fission of the C–Br bond

14. What is involved in the mechanism of the reaction between aqueous NaOH and 1-bromobutane?

A attack by a nucleophile on a carbon atom with a partial positive charge
B heterolytic bond fission and attack by a nucleophile on a carbocation
C homolytic bond fission and attack by an electrophile on a carbanion
D homolytic bond fission and attack by a nucleophile on a carbocation

15. Halogenoalkanes react with nucleophiles such as OH^-.
Which pair of halogenoalkanes **both** react via an S_N1 mechanism?

A


B


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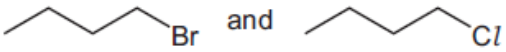

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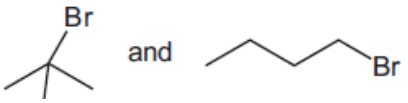
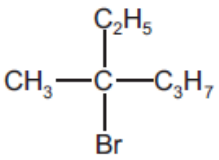
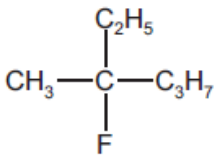


16. 1-chlorobutane and 1-iodobutane react separately with aqueous sodium hydroxide by a nucleophilic substitution mechanism.
Which reaction has the greatest rate under the same conditions, and which mechanism is followed by this reaction?

	greatest rate	mechanism
A	1-chlorobutane	S_N1
B	1-chlorobutane	S_N2
C	1-iodobutane	S_N1
D	1-iodobutane	S_N2

17. The diagram shows the structures of two halogenoalkanes, P and Q.

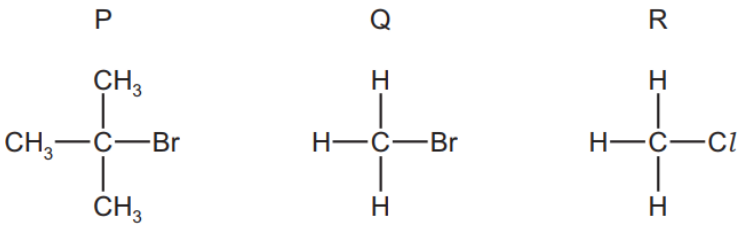
P


Q


Both compounds can be hydrolysed.
Which row is correct?

	compound more readily hydrolysed	reaction mechanism
A	P	S_N1
B	P	S_N2
C	Q	S_N1
D	Q	S_N2

18. The diagram shows the structures of three halogenoalkanes.



P, Q and R can all be hydrolysed.
Which row is correct?

	relative speed of hydrolysis		mechanism of hydrolysis	
	Q	R	P	Q
A	fast	slow	SN1	SN2
B	fast	slow	SN2	SN1
C	slow	fast	SN1	SN2
D	slow	fast	SN2	SN1

19. When bromoethane, C_2H_5Br, is heated with NaOH in ethanol, which type of reaction occurs?

A electrophilic substitution
B elimination
C nucleophilic substitution, mainly via an SN^1 mechanism
D nucleophilic substitution, mainly via an SN^2 mechanism

20. 2-chloropropane and 2-bromopropane react separately with aqueous NaOH.

Which row is correct?

	comparison of rates of reaction	explanation of the difference in reaction rates
A	2-chloropropane reacts faster	chlorine is more reactive than bromine
B	2-chloropropane reacts faster	the C–C*l* bond is more polar than the C–Br bond
C	2-bromopropane reacts faster	the first ionisation energy of bromine is lower than chlorine's
D	2-bromopropane reacts faster	the C–Br bond is weaker than the C–C*l* bond

21. An organic ion containing a carbon atom with a negative charge is called a carbanion.
An organic ion containing a carbon atom with a positive charge is called a carbocation.
The reaction between NaOH(aq) and 1-bromobutane proceeds by an SN2 mechanism.
What is the first step in the mechanism?

A attack by a nucleophile on a carbon atom with a partial positive charge
B heterolytic bond fission followed by attack by an electrophile on a carbanion
C heterolytic bond fission followed by attack by a nucleophile on a carbocation
D homolytic bond fission followed by attack by a nucleophile on a carbocation

22. Structural and stereoisomerism should be considered when answering this question.
A mixture of 1-chlorobutane and 2-chlorobutane is heated with an excess of NaOH in ethanol.
How many different organic molecules will be produced?

A 1 B 2 C 3 D 4

The reaction with ethanolic KCN

23. Halogenoalkanes react with hot ethanolic potassium cyanide.
The reaction mechanism is either SN^1 or SN^2.
Which statement is correct?

A All secondary halogenoalkanes react by the SN^2 mechanism only.
B Both the halogenoalkane and the cyanide ion are involved in the initial step of the SN^1 mechanism.
C Chloroethane reacts with cyanide ions by the SN^1 mechanism only.
D The SN^2 mechanism involves a short-lived negatively charged transition state.

24. Which reagents and conditions would result in the formation of butanenitrile, $CH_3CH_2CH_2CN$?

A 1-bromobutane heated under pressure with ammonia in ethanol
B 1-bromopropane heated with potassium cyanide in ethanol
C propanal heated with hydrogen cyanide in the presence of potassium cyanide
D propanone heated with hydrogen cyanide in the presence of potassium cyanide

25. Ethanol can be used to make propanenitrile in two steps.

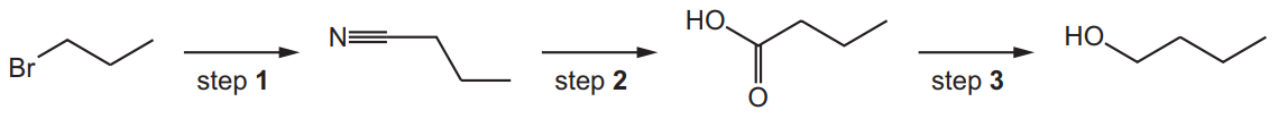
$$CH_3CH_2OH \xrightarrow{X} CH_3CH_2Br \xrightarrow{Y} CH_3CH_2CN$$

	X	Y
A	free-radical substitution	electrophilic substitution
B	free-radical substitution	nucleophilic substitution
C	nucleophilic substitution	nucleophilic substitution
D	nucleophilic substitution	electrophilic substitution

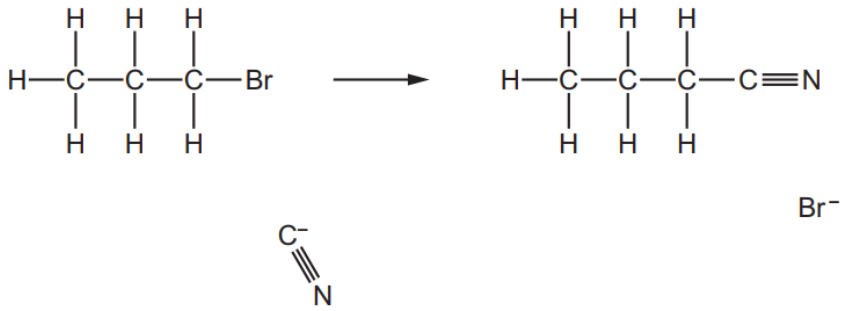
26. For which reaction will the major organic product have the lowest relative molecular mass?

A Bromoethane is heated under reflux with an aqueous solution of sodium hydroxide.
B Bromoethane is heated under reflux with a solution of sodium cyanide in ethanol.
C 2-bromopropane is heated under reflux with an aqueous solution of sodium hydroxide.
D 2-bromopropane is heated under reflux with concentrated ethanolic sodium hydroxide.

11. Fig. 5.2 shows how butan-1-ol can be made from 1-bromopropane in three steps.



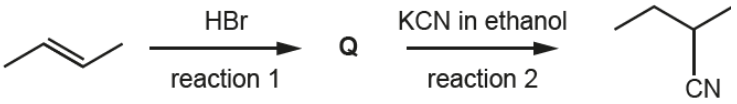
(i) In step **1**, 1-bromopropane reacts with CN^- to form butanenitrile.
Complete Fig. 5.3 to show the mechanism for step **1**. Include charges, dipoles, lone pairs of electrons and curly arrows as appropriate.



27. Bromoethane reacts with cyanide ions, producing propanenitrile.
Which statement about the S_N2 mechanism of this reaction is correct?

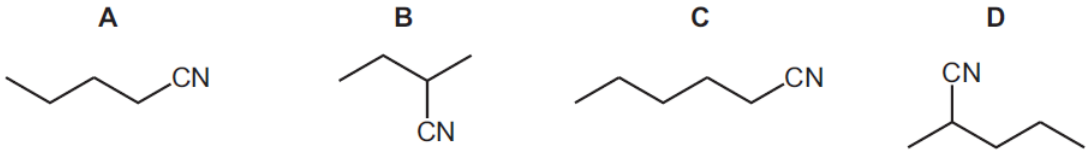
A The lone pair of electrons on C of CN^- attacks the carbon atom of the C–Br bond.
B The lone pair of electrons on C of CN^- attacks the carbocation formed when the C–Br bond breaks.
C The lone pair of electrons on N of CN^- attacks the carbon atom of the C–Br bond.
D The lone pair of electrons on N of CN^- attacks the carbocation formed when the C–Br bond breaks.

12. Name the mechanism in reaction 2.



[1]

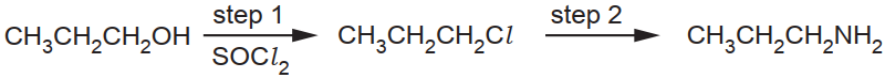
28. When X is added to NaOH(aq) and heated under reflux, pentan-2-ol is made.
Which organic product is made when X is heated with a solution of KCN dissolved in ethanol?



The reaction with NH_3 in ethanol heated under pressure

13. Propanenitrile is heated with hydrogen gas and a platinum catalyst. The only product is propylamine.
(i) Construct an equation for this reaction. [1]

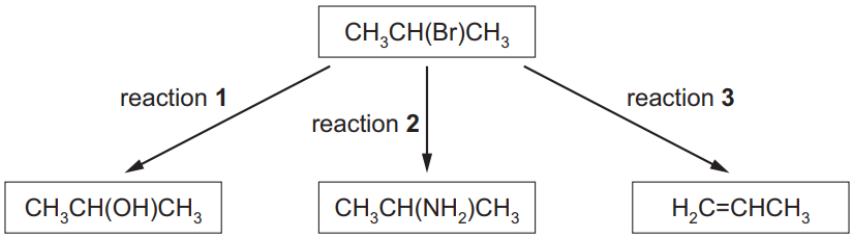
(ii) Propylamine can also be formed in a two-step synthesis from propan-1-ol, as shown below



a) Name the type of reaction in step 1. [1]

b) Identify the reagent and conditions for step 2. [1]

14. Fig. 5.1 shows three reactions of 2-bromopropane, $CH_3CH(Br)CH_3$.



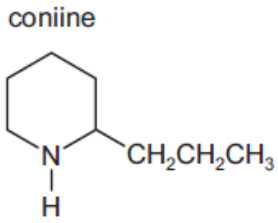
(i) Complete Table 5.1 for each reaction, by:
- stating the reagent and conditions used
- identifying the type of reaction that occurs. [6]

(ii)

reaction	reagent and conditions	type of reaction
1		
2		
3		

(ii) A sample of 2-iodopropane, $CH_3CH(\mathbf{I})CH_3$, reacts under the same conditions as reaction 1 to produce $CH_3CH(OH)CH_3$.
Explain why 2-iodopropane reacts at a faster rate than 2-bromopropane. [1]

29. The structure of coniine is shown.



Coniine can be synthesised by reacting ammonia with a dibromo compound, X.

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

What is compound X?

A 1,1-dibromo-2-propylcyclopentane
B 1,2-dibromo-2-propylcyclopentane
C $Br(CH_2)_3CHBr(CH_2)_3CH_3$
D $Br(CH_2)_4CHBr(CH_2)_2CH_3$

30. Which reaction is classified as S_N1?

A the reaction of 1-chloropropane with ammonia in ethanol
B the reaction of 1-chloropropane with potassium hydroxide in ethanol
C the reaction of 2-chloro-2-methylpropane with potassium cyanide in ethanol
D the reaction of 2-chloro-2-methylpropane with potassium hydroxide in ethanol

15. Substitution reactions of NH_3 and OH^- with halogenoalkanes both involve a lone pair of electrons.

(i) Name the role of NH_3 and OH^- in these reactions.

..... [1]

(ii) Suggest which species, NH_3 or OH^-, is more reactive during these reactions. Explain your answer.

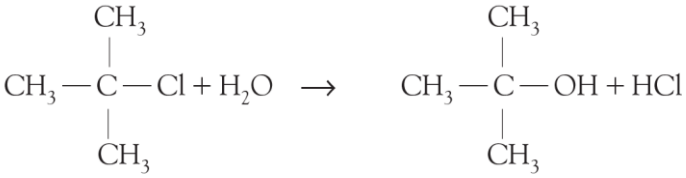
.....

.....

..... [1]

The reaction with aqueous silver nitrate in ethanol

Some halogenoalkanes are reactive enough to be hydrolysed to form alcohols just by heating with water (in practice, a mixed ethanol–water solvent is used because halogenoalkanes are immiscible with water, but the ethanol is miscible with both):



The hydrolysis is quicker if it is carried out in hot aqueous sodium hydroxide:

$$CH_3CH_2Br + NaOH(aq) \xrightarrow{\text{boil under reflux}} CH_3CH_2OH + NaBr(aq)$$

The relative rates of hydrolysis of chloro-, bromo- and iodoalkanes can be studied by dissolving the halogenoalkane in ethanol and adding aqueous silver nitrate. As the halogenoalkane slowly hydrolyses, the halide ion is released, and forms a precipitate of silver halide:

$$R{-}X + H_2O + Ag^+ \rightarrow R{-}OH + H^+ + AgX(s)$$

The following table shows the results obtained.

Aqueous silver nitrate can be used to distinguish between organic chlorides, bromides and iodides.

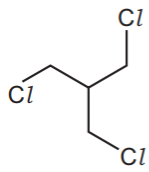
Compound	Observation on reaction with $AgNO_3 + H_2O$ in ethanol	Colour of precipitate
$(CH_3)_2CH—Cl$	slight cloudiness after 1 hour	white
$(CH_3)_2CH—Br$	cloudiness appears after a few minutes	pale cream
$(CH_3)_2CH—I$	thick precipitate appears within a minute	pale yellow

31. Which compound reacts most rapidly with aqueous silver nitrate by an S_N1 mechanism?

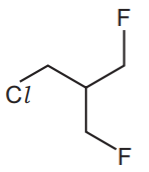
A 1-chloromethylpropane
B 2-chloromethylpropane
C 1-iodomethylpropane
D 2-iodomethylpropane

32. The presence of a halogen in an organic compound may be detected by warming the organic compound with aqueous silver nitrate.
Which compound would be the quickest to produce a precipitate?

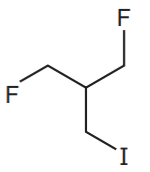
A



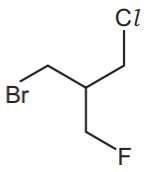
B



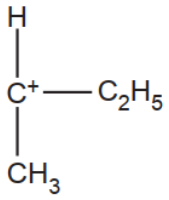
C



D



16. Complete Table 4.1 by drawing the structural formula of the intermediate that is formed when 2-bromo-2-methylpropane reacts in an S_N1 reaction.

	2-bromobutane	2-bromo-2-methylpropane
structural formula of intermediate in S_N1 reaction		

17. Identify the halogenoalkane in Table 4.1 that has the greater tendency to react using the S_N1 mechanism. Explain your answer.

.....

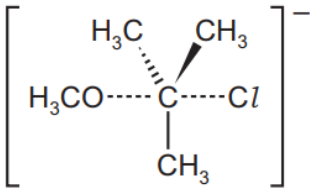
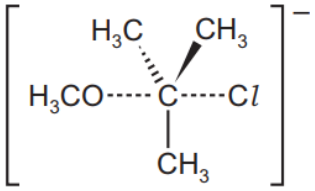
.....

..... [2]

18. Separate samples of $CH_3(CH_2)_5CHBrCH_3$, $CH_3(CH_2)_5CH(OH)CH_3$ and $CH_3(CH_2)_5CHCH_2$ are tested with different reagents.
Complete Table 4.1. If no reaction occurs, write × in the relevant box.

reagent added	observation with $CH_3(CH_2)_5CHBrCH_3$	observation with $CH_3(CH_2)_5CH(OH)CH_3$	observation with $CH_3(CH_2)_5CHCH_2$
$Br_2(l)$ in the dark			
$PCl_5(s)$			
$AgNO_3(aq)$			

33. Sodium methoxide, $Na^+CH_3O^-$, reacts with 2-chloro-2-methylpropane in a nucleophilic substitution reaction.
The nucleophile is the CH_3O^- ion.
Which row is correct?

	intermediate or transition state	product
A	$(CH_3)_3C^+$	$(CH_3)_3COCH_3$
B	$(CH_3)_3C^+$	$(CH_3)_3CCH_2OH$
C		$HOCH_2C(CH_3)_3$
D		$H_3COC(CH_3)_3$

19. An unlabelled bottle contains a straight-chain halogenoalkane, **Q**. The molecular formula of **Q** is $C_5H_{11}\mathbf{X}$, where **X** is a halogen; bromine, chlorine or iodine.
A test is carried out to identify the halogen present in **Q**.
A sample of **Q** is added to NaOH(aq) and warmed. Dilute nitric acid is then added followed by a few drops of aqueous silver nitrate. A cream precipitate is observed.
(i) Suggest the identity of **X**.

..... [1]

(ii) Write an ionic equation to describe the formation of the cream precipitate. Include state symbols.

..... [1]

(iii) Describe a further test which would confirm the identity of **X**.

test .....

expected result ..... [2]

The reaction of **Q** with NaOH(aq) tends to proceed via an S_N2 mechanism.

(iv) Suggest the structural formula of the straight-chain halogenoalkane **Q**. [1]

(ii) Explain why the reaction tends to proceed via an S_N2 mechanism rather than an S_N1 mechanism.

.....

.....

..... [2]

20. Name an organic functional group which tends to react with a nucleophile in an S_N1 substitution mechanism.

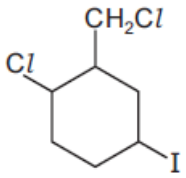
..... [1]

34. Iodoethane, CH3CH2I, reacts with aqueous silver nitrate at 50 °C. A precipitate forms during this reaction.
Which row of the table is correct about this reaction?

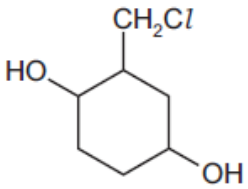
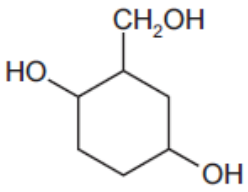
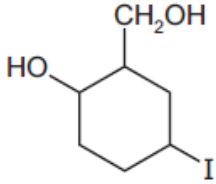
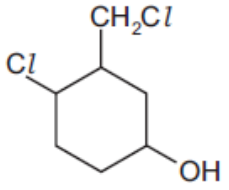
	type of organic reaction	colour of precipitate
A	electrophilic substitution	cream
B	electrophilic substitution	yellow
C	nucleophilic substitution	cream
D	nucleophilic substitution	yellow

35. Compound X, $C_7H_{11}IC\mathit{l}_2$, is dissolved in ethanol and the solution mixed with warm aqueous silver nitrate.
A precipitate is seen immediately.

compound X



What is the colour of this precipitate and what is the structural formula of the first organic product?

	colour of the precipitate	structural formula of the **first** organic product
A	cream	
B	cream	
C	white	
D	yellow	

Elimination reaction

21. Two different halogenoalkanes, **P** and **R**, both with the molecular formula C_4H_9Cl, are separately dissolved in ethanol and heated under reflux with sodium hydroxide.
The major organic product of each of these reactions is methylpropene.
(i) Name the type of reaction occurring.

..... [1]

(ii) Write an equation, using molecular formulae, to represent the reaction occurring.

..... [1]

(iii) Give the names of **P** and **R**.

..... [2]

22. Tertiary alcohols tend to react with Lucas's reagent using the same mechanism as in their reaction with HCl. Suggest the type of reaction shown by tertiary alcohols with Lucas's reagent. [1]

36. In which reactions is the major product formed by a nucleophilic substitution reaction?

1 bromoethane + potassium cyanide in ethanol
2 bromoethane + ammonia in ethanol under pressure
3 bromoethane + hot concentrated sodium hydroxide in ethanol

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

*****This is not a complete note. It is to guide you. It is recommended to study the prescribed textbooks along with this material. *****