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HOMEWORK

DATE	PARTICULARS

DATE	PARTICULARS

NOTES

NOTES

NOTES

NOTES

14 Introduction to organic chemistry

Organic chemistry involves the study of a large class of chemical compounds containing carbon. This topic introduces naming conventions, organic reaction terminology and structures of organic molecules.

14.1	Formulae, functional groups and the naming of organic compounds	☐
14.2	Characteristic organic reactions	☐
14.3	Shapes of organic molecules; σ and π bonds	☐
14.4	Isomerism: structural and stereoisomerism	☐

INTRO TO ORGANIC

14 An introduction to organic chemistry

Organic chemistry involves the study of a large class of chemical compounds containing carbon. This topic introduces naming conventions, organic reaction terminology and structures of organic molecules.

	Learning outcomes Candidates should be able to:
14.1 Formulae, functional groups and the naming of organic compounds	a) interpret and use the general, structural, displayed and skeletal formulae of the following classes of compound: (i) alkanes, alkenes **and arenes** (ii) halogenoalkanes **and halogenoarenes** (iii) alcohols (including primary, secondary and tertiary) **and phenols** (iv) aldehydes and ketones (v) carboxylic acids, esters **and acyl chlorides** (vi) amines (primary only), nitriles, **amides and amino acids** (Candidates will be expected to recognise the shape of the benzene ring when it is present in organic compounds. Knowledge of benzene or its compounds is *not* required for AS Level.) b) understand and use systematic nomenclature of simple aliphatic organic molecules with functional groups detailed in 14.1(a), up to six carbon atoms (six plus six for esters and amides, straight chains only) **c) understand and use systematic nomenclature of simple aromatic molecules with one benzene ring and one or more simple substituents, for example 3-nitrobenzoic acid, 2,4,6-tribromophenol** d) deduce the possible isomers for an organic molecule of known molecular formula e) deduce the molecular formula of a compound, given its structural, displayed or skeletal formula
14.2 Characteristic organic reactions	a) interpret and use the following terminology associated with organic reactions: (i) functional group (ii) homolytic and heterolytic fission (iii) free radical, initiation, propagation, termination (iv) nucleophile, electrophile (v) addition, substitution, elimination, hydrolysis, condensation (vi) oxidation and reduction (in equations for organic redox reactions, the symbols [O] and [H] are acceptable for oxidising and reducing agents)

ORGANIC COMPOUNDS

Today, organic chemicals (artificially made or naturally occurring) number well over 10 million. Hundreds of thousands of new compounds are being made each year. Why are there so many of them? There are two main reasons:

In general, organic compounds are **kinetically stable**. Even exothermic organic reactions have an unusually high activation energy.

Carbon atoms have an exceptional ability to form chains, branched chains and rings of varying sizes. No other element can form long chains of its atoms in the same way as carbon. This process of carbon-carbon bond formation is called **catenation.**

1

CATENATION

Carbon–carbon bonding allows chains and rings of carbon atoms to be produced by a process called catenation. Other elements don't make such strong single bonds.

What is more, the ability of carbon to make 4 single bonds allows branched chains to occur, and the attachment of other atoms, increasing further the number of structures possible.

Bond	Bond enthalpy/kJ mol^{-1}
C — C	350
Si — Si	222
N—N	160
O—O	150

2

CATENATION

There are four different ways in which we can arrange four linked carbon atoms:



3

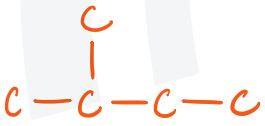
CATENATION

With five carbon atoms there are ten different arrangements. Some of them are shown below.

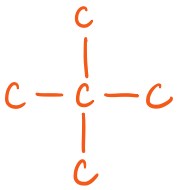
One structure will contain a chain of **five** carbon atoms:



If we **take one carbon atom** from the end and **join it** to the middle of the chain, we produce another structure:

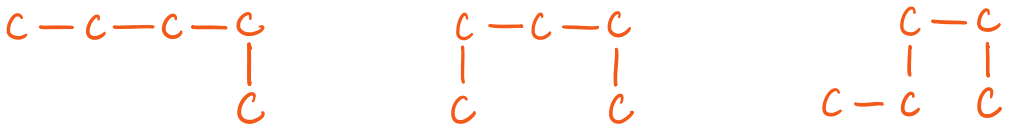


If we do this once more, we get a **three**-carbon chain structure:



4

CATENATION



All of the above are imperfect ways of drawing the five-carbon chain in the two dimensions of a page, but each shows that there is a chain of five carbon atoms. Merely 'bending' the shape of the chain does not alter it.

This is because the carbon atoms in a chain are not arranged in a straight line, but are in fact positioned in a zig-zag manner, with each C—C—C angle being 109.5°.

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CHEMICAL STABILITY OF ORGANIC COMPOUNDS

In general, organic compounds are kinetically stable. This is due to the strong bonding that occurs between carbon atoms.

Consequently, organic reactions require a **high activation energy** and the rate of reaction may be slow under normal conditions.

With the **right conditions and catalysts**, it is possible to convert one 'stable' organic compound into another 'stable' compound. It is even possible to use the same reagent (e.g. hydroxide ions) on the same compound (e.g. a bromoalkane) to produce two different products, depending on the conditions of solvent used.

6

CHEMICAL STABILITY OF ORGANIC COMPOUNDS

Consider the reaction of 2-bromopropane with Sodium Hydroxide under 2 different conditions:

- **When warmed in water:**

$CH_3CHBrCH_3$ (l) + NaOH (aq) ⟶ NaBr + $CH_3CH(OH)CH_3$ (**Reaction 1**)

- **When heated in ethanol:**

$CH_3CHBrCH_3$ (l) + NaOH (in ethanol) ⟶ NaBr + H_2O + $CH_2{=}{=}CHCH_3$

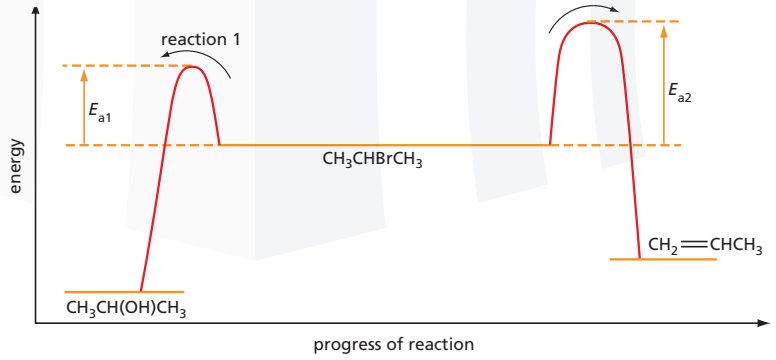
(**Reaction 2**)

7

CHEMICAL STABILITY OF ORGANIC COMPOUNDS

Take a look at the energy profile for reactions 1 and 2:

Organic compounds occupy 'low energy' valleys with 'high energy' hills in between them. The right conditions can allow for conversion from one to another.



8

SHAPES OF ORGANIC COMPOUNDS

We have learned before how atomic orbitals overlap to create **molecular orbitals**. These orbitals generally follow the same orientation (in the x, y or z-plane) as the parent atomic orbitals.

For compounds that have trigonal planar or tetrahedral geometry, these orbitals are insufficient. Suitable orbitals, 'pointing' in the right direction, can be obtained by **hybridising** (mixing) *s* and *p* orbitals in different ways.

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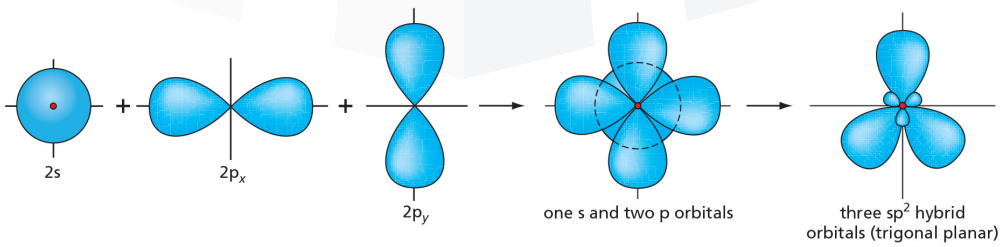
SHAPES OF ORGANIC COMPOUNDS

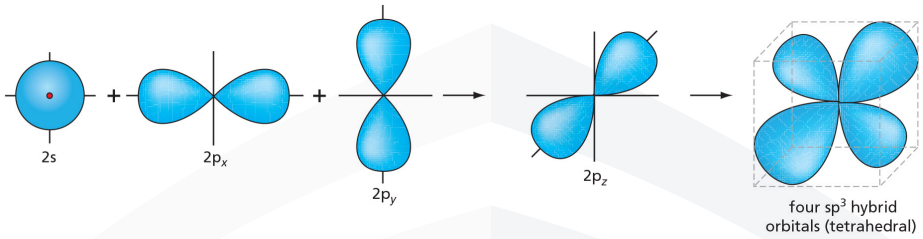
The following figures show 2 different types of hybridisation. When one *s* orbital combines with the p_x and p_y orbitals, the result is three identical orbitals pointing 120 degrees away from one another. This is called **sp^2 hybridisation**.



10

SHAPES OF ORGANIC COMPOUNDS

When one *s* orbital combines with all three *p* orbitals, the result is four identical orbitals pointing 109.5 degrees away from one another. This is called **sp³ hybridisation**.

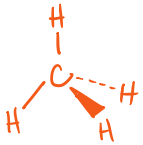


11

SHAPES OF ORGANIC COMPOUNDS

Take a look at the bond angles in some organic compounds:

The shapes of organic compounds depend upon bond lengths and angles, which are subject to the repulsive force between electron pairs. This is where hybridisation comes into play.

Bond angle	Examples	Hybridisation
180°	O=C=O H–C≡N	sp
120°		sp^2
109.5°		sp^3

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REPRESENTING ORGANIC COMPOUNDS

There are 6 different ways of representing organic compounds. Some of these formulae you are familiar with, and some may be new to you. They are:

Empirical Formula: this shows the simplest ratio in which atoms in an organic molecule combine, and so many different molecules can have the same empirical formula. For example, the empirical formula for all alkenes is CH_2!

Molecular Formula: this is a whole number multiple of the empirical formula and tells us the exact number of atoms in any organic molecule. For instance, the molecular formula of ethanoic acid is $C_2H_4O_2$, while that of propene is C_3H_6 (obtained by multiplying the empirical formula by 3).

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REPRESENTING ORGANIC COMPOUNDS

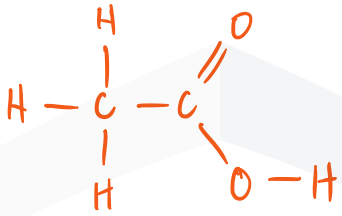
Structural Formula: this shows *how* the atoms are joined together in an organic compound. Carbon-carbon double bonds are always shown in a structural formula, carbon-carbon single bonds (if needed to make the structure clearer). Here are some examples:

$(CH_3CH_2)_2CHCH=CHCl$ $(CH_3)_2C(OH)CH_2CH(CH_3)CO_2H$ $ClCH_2CH_2CH(CO_2H)_2$

14

REPRESENTING ORGANIC COMPOUNDS

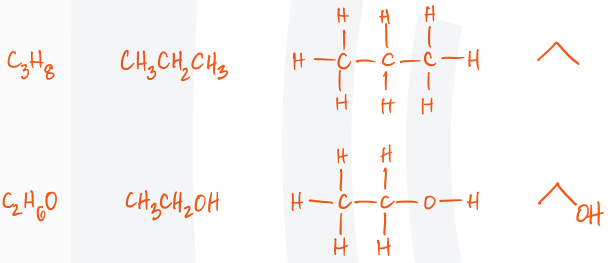
Displayed Formula: this is an 'expanded' form of the structural formula, showing the location and type of every bond in an organic molecule. The displayed formula for ethanoic acid is:

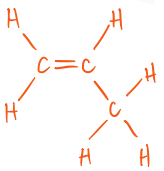


15

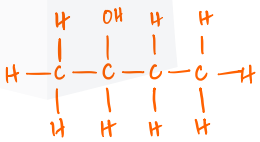
DISPLAYED & SKELETAL FORMULAE

Here are some examples of displayed and skeletal formulae:











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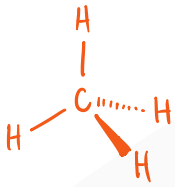
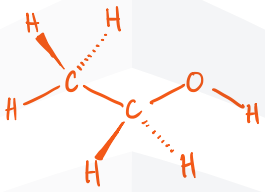
REPRESENTING ORGANIC COMPOUNDS

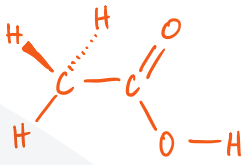
Stereochemical Formula: this shows the positions of molecular bonds in 3 dimensions. 'Wedges' represents bonds coming out of the plane of the paper and 'dotted lines' represents bonds to atoms behind the plane of the paper. Here are some compounds and their stereochemical formulae:



Methane, CH_4



Ethanol, C_2H_5OH



Ethanoic Acid, CH_3CO_2H

17

REPRESENTING ORGANIC COMPOUNDS

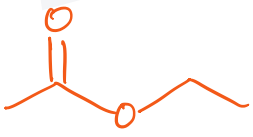
Skeletal Formula: this is the simplest way of representing larger or more complex organic compounds. Every 'corner' represents a carbon atom, and the lines between carbon atoms show the type of bonding that exists. Side chains or functional groups can be easily 'added on' to illustrate important features of the compound. Here are some examples:



CH_3COCH_3



$CH_3CH_2CH(CH_3)2$



$CH_3\ CO_2CH_2CH_3$

18

SKILL CHECK 1

Find the molecular and skeletal formulae for the following compounds:

a. Propane, $CH_3CH_2CH_3$

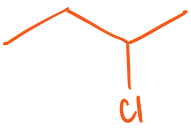
b. Ethane-1,2-diol (glycol), $HOCH_2CH_2OH$

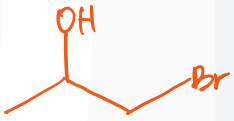
c. Dicholoroethanoic acid, $CHCl_2CO_2H$

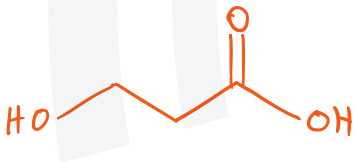
19

SKILL CHECK 2

Work out the structural, molecular and empirical formulae of the following compounds:



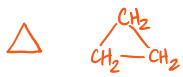




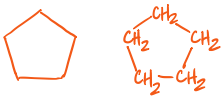
20

REPRESENTING ORGANIC COMPOUNDS

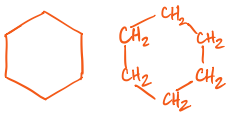
Skeletal formulae are very useful for representing 'rings' of carbon atoms. Take a look at the following:



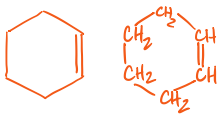
Cyclopropane



Cyclopentane



Cyclohexane

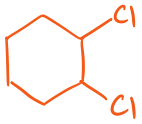


Cyclohexene

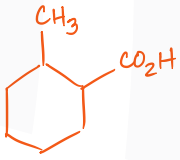
21

SKILL CHECK 3

Find the molecular formulae for the following compounds:



A



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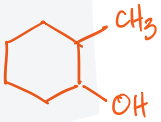

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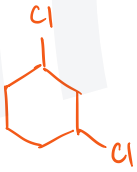

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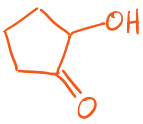
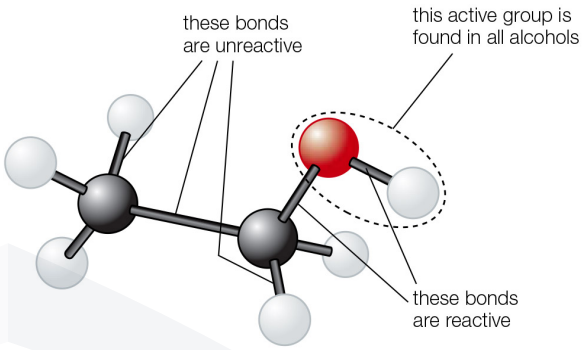


E

22

FUNCTIONAL GROUP & HOMOLOGOUS SERIES

A **functional group** is the atom (or group of atoms) that gives an organic compound its characteristic properties. For example, the –OH group is responsible for most of the reactions of alcohols, while the rest of the molecule remains relatively unreactive (due to stable carbon-carbon bonds).

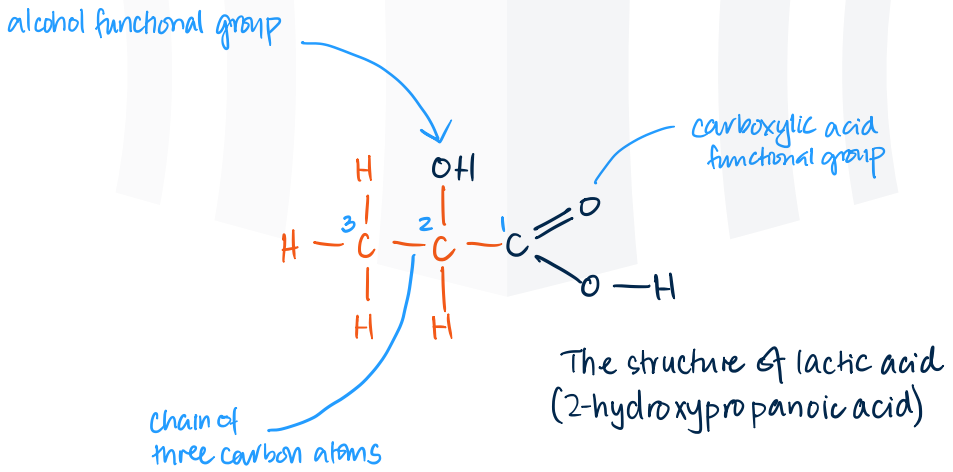


the number of carbon and hydrogen atoms does not have much effect on the chemistry of alcohols

23

FUNCTIONAL GROUP & HOMOLOGOUS SERIES

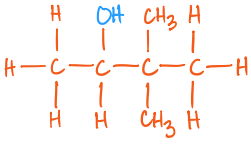
Some compounds have more than one **functional group:**



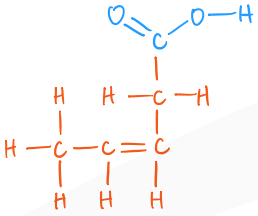
24

SKILL CHECK: FUNCTIONAL GROUPS

Q1: Name the functional group in the following compounds:



A



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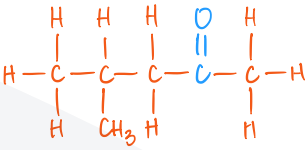

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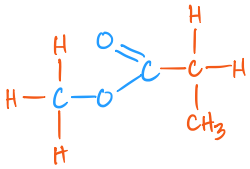

D

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FUNCTIONAL GROUP & HOMOLOGOUS SERIES

A **homologous series** is a way to classify organic compounds that have the same functional group in which the formula of each successive member differs by CH_2.

The features of a **homologous series** are:

They can usually be described by a general molecular formula, e.g. C_nH_{2n+2} for alkanes (non-cyclic) or C_nH_{2n} for alkenes.

Members of the series show similar chemical properties.

Members of the series show a gradation in physical properties such as boiling point.

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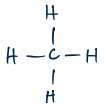
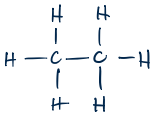
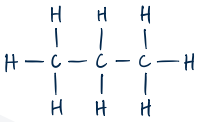
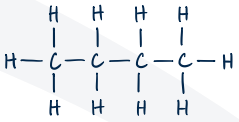
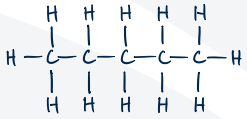
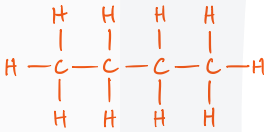
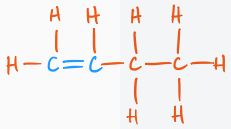
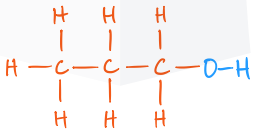
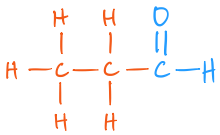
EXAMPLE OF A HOMOLOGOUS SERIES

methane	CH_4	CH_4	
ethane	C_2H_6	CH_3CH_3	
propane	C_3H_8	$CH_3CH_2CH_3$	
butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$	
pentane	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	

27

TYPES OF HOMOLOGOUS SERIES

alkane			butane
alkene	C=C		but-1-ene
alcohol	–OH		propan-1-ol
aldehyde			propanal

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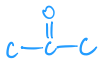
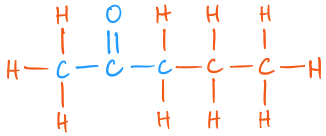
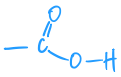
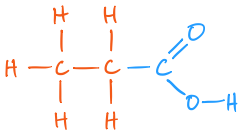
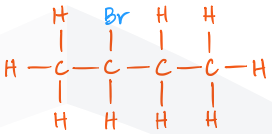
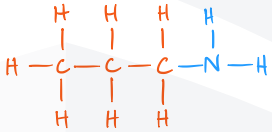
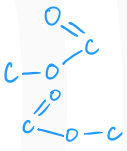
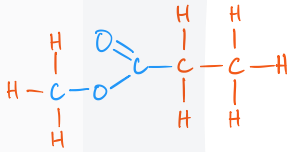
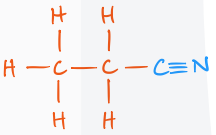
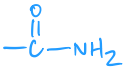
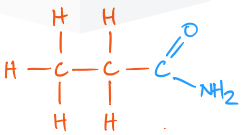
TYPES OF HOMOLOGOUS SERIES

Ketone			pentan-2-one
carboxylic acid			propanoic acid
halogenoalkane			2-bromobutane
amine			propylamine

29

TYPES OF HOMOLOGOUS SERIES

ester			methyl propanoate
nitrile			propanenitrile
amide			propanamide

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HOMOLOGOUS SERIES: PHYSICAL PROPERTIES

Homologous series	Polarity	Intermolecular forces	Boiling point	Solubility in water
alkane	non-polar	van der Waals'	low	insoluble
alkene	non-polar	van der Waals'	low	insoluble
alcohol	polar	hydrogen bonding	high	lower members soluble; hydrogen bonding to water
aldehydes/ketones	polar	dipole–dipole	higher than alkanes; lower than alcohols	lower members soluble; polar and water can hydrogen bond to them
carboxylic acid	polar	hydrogen bonding	high: higher than alcohols; more hydrogen bonding	lower members soluble; hydrogen bonding to water
halogenoalkane	polar	dipole–dipole	For same number of C atoms: iodo > bromo > chloro; van der Waals' forces stronger if M_r higher	insoluble

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SKILL CHECK 4

The first and third members of a homologous series have the molecular formulae C_2H_2 and C_4H_6.

- What is the formula of the **fourth** member of the series?
- What is the **general formula** of the series?

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SKILL CHECK 5

The formulae of the first two members of 3 homologous series are shown below. For each, state the molecular formula of the 5th member and the general formula of the series:

1. CH_2O, C_2H_4O

2. C_2H_3N, C_3H_5N

3. C_6H_6, C_7H_8

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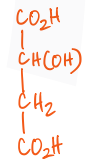
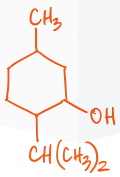
NAMING ORGANIC COMPOUNDS

Before the **International Union of Pure and Applied Chemists** (IUPAC) adopted a systematic set of naming rules, organic compounds (like their inorganic counterparts) were derived from Latin words. Here are some examples of compounds where the non-standard names are still used:



malic acid



menthol



oxalic acid
(ethandioc acid)

However, the rapidly increasing number of man-made organic compounds made it necessary to have a standardised way to name organic compounds.

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NAMING ORGANIC COMPOUNDS

A **systematic name** for an organic compound is often based on the 'parent' hydrocarbon (the hydrocarbon that resembles the compound most closely). Each name consists of the components listed below (not all may be present, however - it depends on the complexity of the compound):

1. A **stem**: this specifies the number of carbon atoms in the longest carbon chain. If the carbon atoms are joined in a ring, the prefix 'cyclo' is added.
2. A **stem-suffix:** this indicates the type of carbon-carbon bonds that occur in the compound.
3. A **suffix**: this indicates any oxygen-containing groups that might be present.
4. One or more **prefixes**: these indicate non-oxygen-containing groups, which may be other carbon (alkyl) groups, or halogen atoms which are substituted for hydrogen along the carbon chain.

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ORGANIC NAMING: THE STEM

stem name	# of carbon atoms.
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8

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ORGANIC NAMING: THE STEM-SUFFIX

Stem-suffix	Meaning
-an	all C–C single bonds
-en	one C=C double bond
-dien	two C=C double bonds
-trien	three C=C double bonds
-yn	one C≡C triple bond

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ORGANIC NAMING: THE STEM-SUFFIX

CH_3-CH_3 ethane
$CH_3-CH=CH_2$ propene
$CH_2=CH-CH=CH_2$ is butadiene.

are added before the stem suffix to show position of any double bond. Eg.

$CH_2=CH-CH=CH_2$ is buta-1,3-diene
$CH_2=C=CH-CH_3$ is buta-1,2-diene

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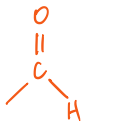
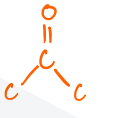
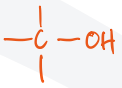
ORGANIC NAMING: THE SUFFIX

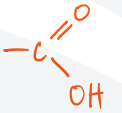
3 A suffix – the functional group

Suffix	Functional group
-al	an aldehyde group
-one	a ketone group
-ol	an alcohol group
-oic acid	a carboxylic acid group









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ORGANIC NAMING: THE SUFFIX

CH_3-CHO is ethanal

$CH_3-CH_2-CO_2H$ is propanoic acid

$CH_3-CO-CH_2-CH_3$ is butanone

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ORGANIC NAMING: THE PREFIX

Prefix	Meaning
methyl-	CH_3-
ethyl-	CH_3CH_2-
propyl-	$CH_3CH_2CH_2-$
chloro-	$Cl-$
bromo-	$Br-$
hydroxy-	$HO-$

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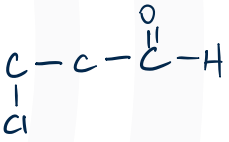
ORGANIC NAMING EXAMPLES

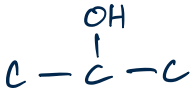
$Cl-CH_2-CH_2-CHO$



3-chloropropanal

prefix — stem — stem-suffix — suffix

$CH_3-CH(OH)-CH_3$



propan-2-ol

stem — stem-suffix — suffix

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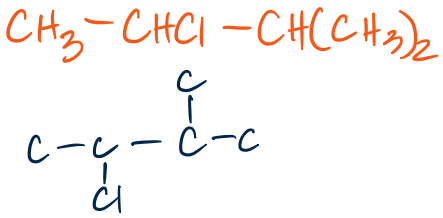
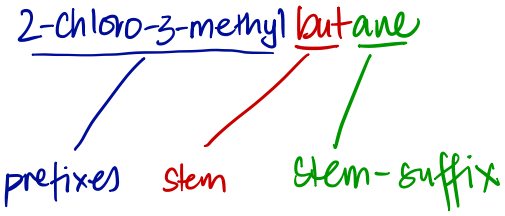
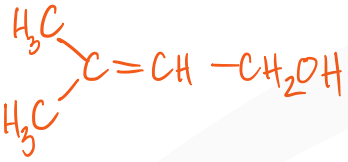
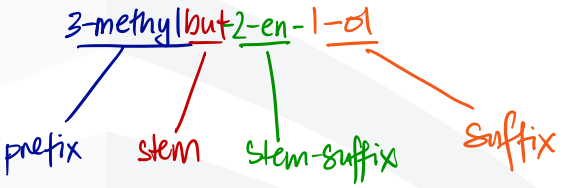
ORGANIC NAMING EXAMPLES









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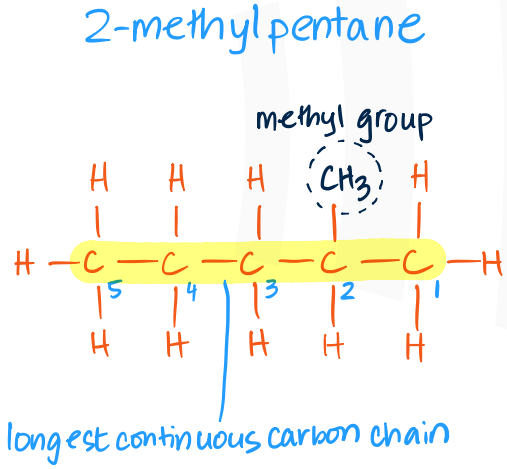
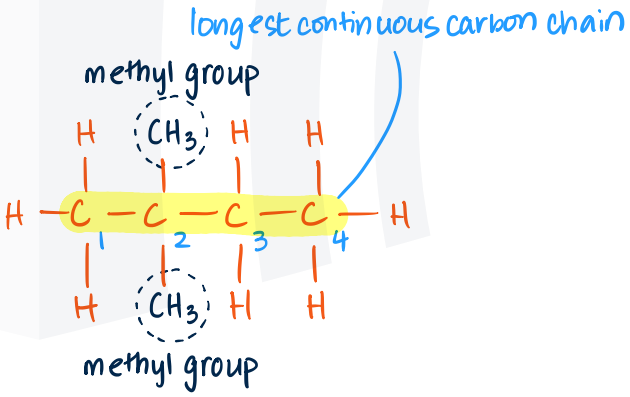
ORGANIC NAMING EXAMPLES





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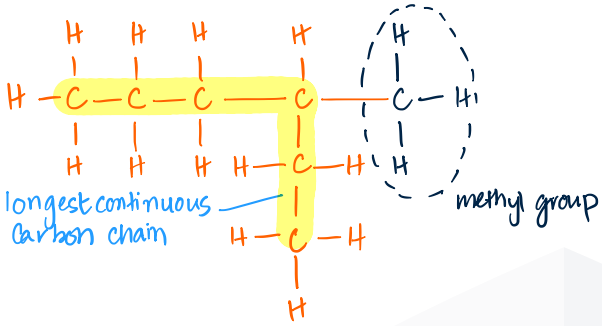
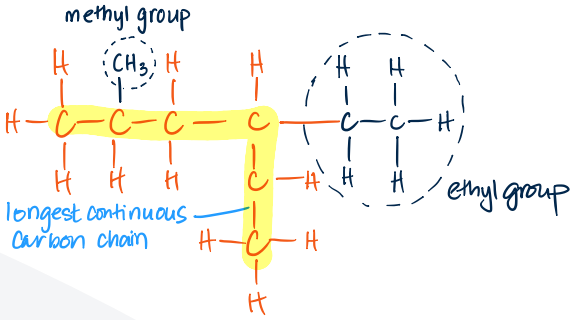
ORGANIC NAMING EXAMPLES



3-methylhexane



4-ethyl-2-methylhexane

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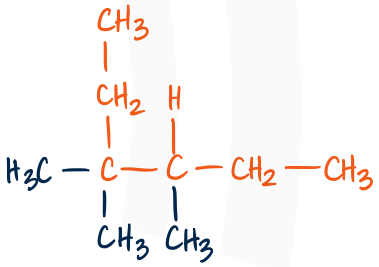
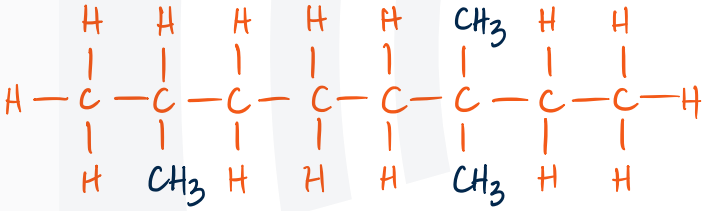
ORGANIC NAMING EXAMPLES



3,3,4-trimethylhexane



2,6,6-trimethyloctane

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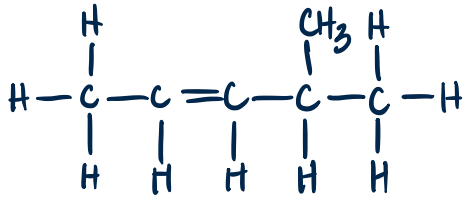
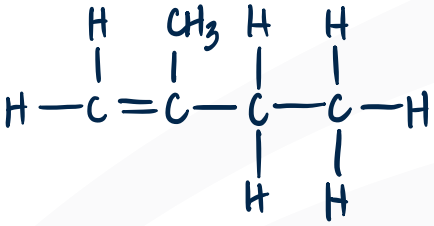
ORGANIC NAMING EXAMPLES

4-methylpent-2-ene





2-methylbut-1-ene

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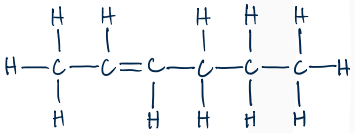
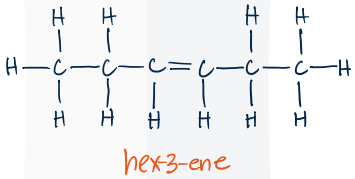
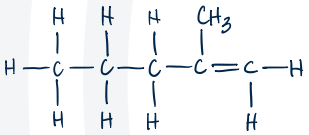
ORGANIC NAMING EXAMPLES



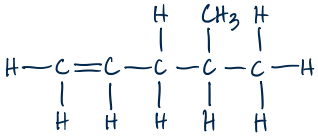
hex-2-ene



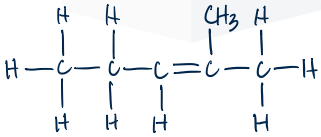
hex-3-ene



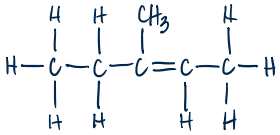
2-methylpent-1-ene



4-methylpent-1-ene



2-methylpent-2-ene



3-methylpent-2-ene

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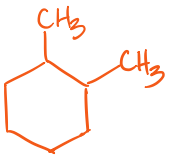
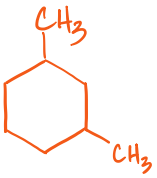
ORGANIC NAMING EXAMPLES



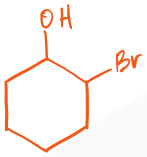
1,2-dimethyl cyclohexane



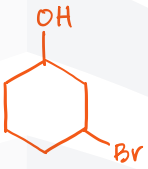
1,3-dimethyl cyclohexane



1,4-dimethyl cyclohexane



2-bromocyclohexanol



3-bromocyclohexanol

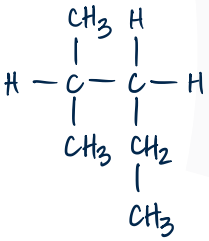


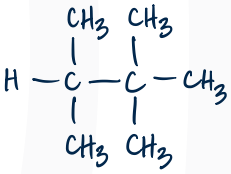
4-bromocyclohexanol

49

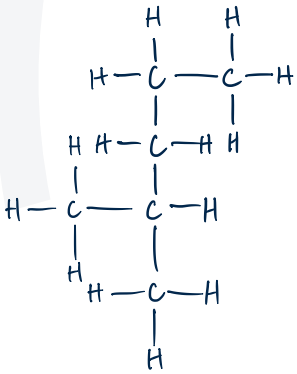
SKILL CHECK 6

Name the following compounds:





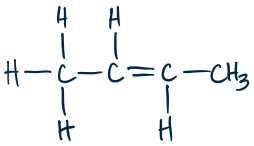
$CH_3(CH_2)_2C(CH_3)_3$

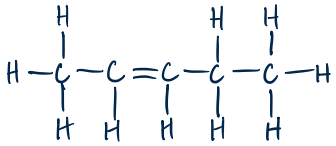


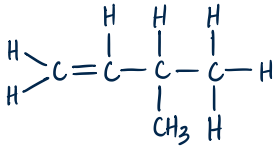
50

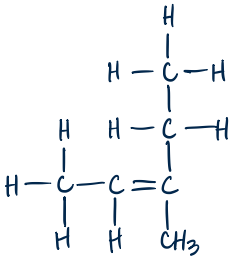
SKILL CHECK 7

Name the following compounds:









51

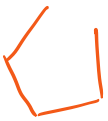
SKILL CHECK 8

Name the following compounds:



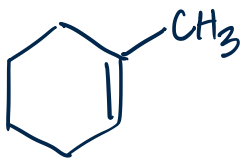






$(CH_3)_3CCH(OH)CH_2CH_3$

$CH_3CH=CHCH_3$

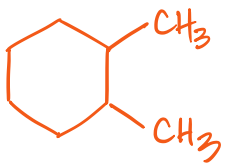


52

SKILL CHECK 9

Name the following compounds:

$C(CH_3)_3OH$



$H_3C-CH_2-CH(OH)-CH_3$

$(CH_3)_2CHCH_2CH_2OH$

$ClCH_2CH_2CH_2Cl$

53

SKILL CHECK 10

Draw the following compounds:

2-methylpropan-2-ol

1,2-dimethylcyclohexane

butan-2-ol

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SKILL CHECK 11

Draw the following compounds:

3-methyl butan-1-ol

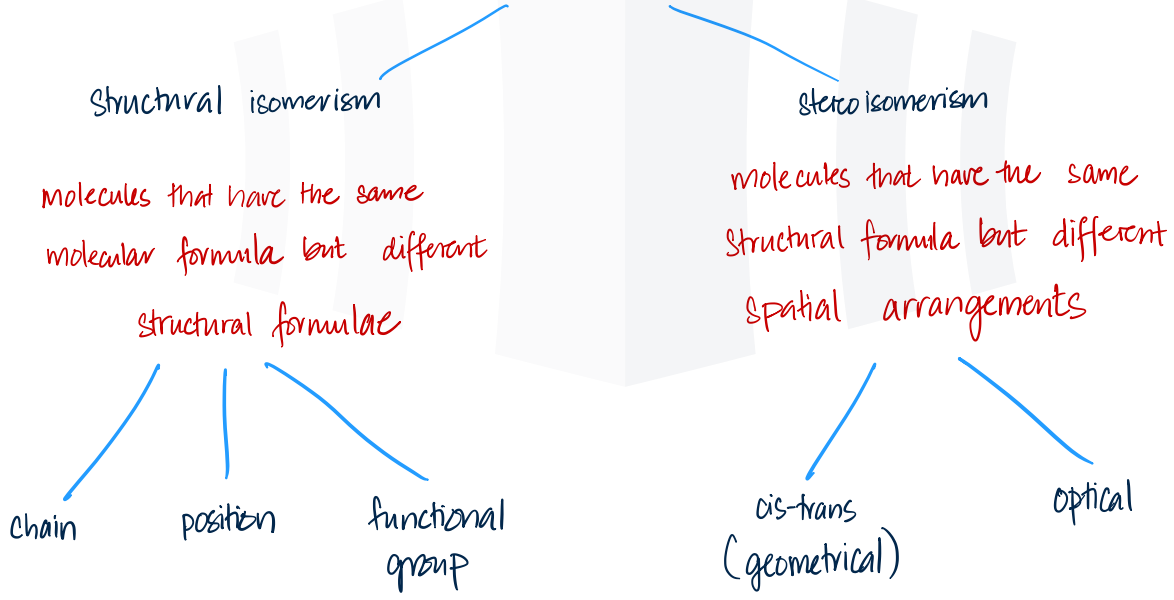
1,3-dichloro propane

2-methyl-2,3-dibro mopentane

2,2-dimethyl propane

55

ISOMERISM

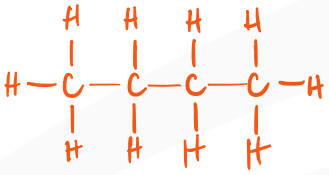


56

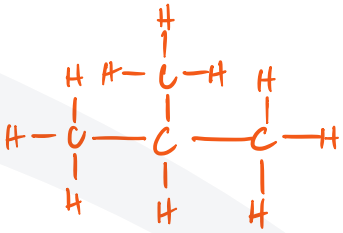
STRUCTURAL ISOMERS

Structural isomers are compounds with the same molecular formula but different structural formulae**.**

Chain isomers have different chains of carbon atoms. For instance, look at the following isomers of C_4H_{10}:



butane



2-methylpropane

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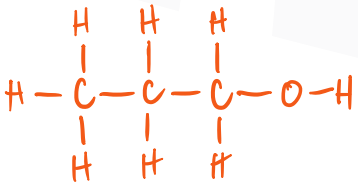
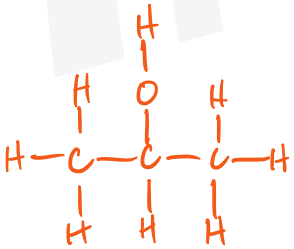
STRUCTURAL ISOMERS

Position isomers have different positions of the same functional group.

Consider the case of *propan-1-ol* and *propan-2-ol*. All alcohols contain the –OH functional group, but in these compounds the –OH group is in different positions on the carbon chain:



propan-1-ol



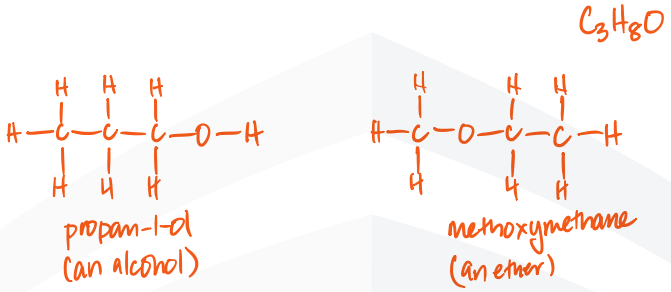
propan-2-ol

58

STRUCTURAL ISOMERS

Functional group isomers have different functional groups

Propan-1-ol is an alcohol with the –OH functional group. *Methoxyethane* is an ether with the C–O–C functional group. Both of these compounds have the same molecular formula, C_3H_8O:



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SKILL CHECK 12

Draw and name structural isomers of the following:

A. Alkenes with the formula C_5H_{10}

B. Alcohols with the formula C_4H_9OH

C. Halogenoalkenes with the formula $C_2H_2Cl_2$

D. Alkanes with the formula C_6H_{14}

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SKILL CHECK 13

Draw and name structural isomers of the following:

A. Halogenoalkanes with the formula C_4H_9Cl

B. Alkenes with the formula C_6H_{12}

C. Alcohols with the formula $C_5H_{11}OH$

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STEREOISOMERS

Stereoisomers are molecules with the same molecular formula and the same structural formula but with a different arrangement in space.

There are two types of stereoisomerism:

1. **Geometric** isomerism (**cis–trans** isomerism).
2. **Optical** isomerism.

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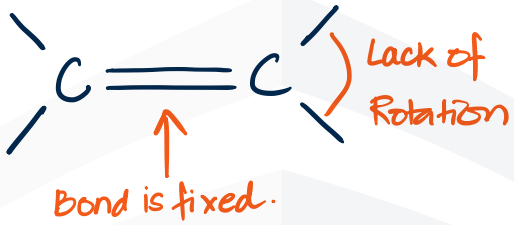
CIS-TRANS ISOMERISM

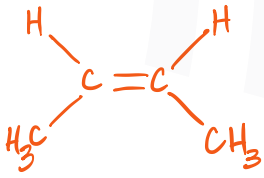
Geometric isomerism occurs with alkenes that **do not have two identical groups on both ends** of the C–C double bond. It arises because, unlike the case of a C–C single bond, it is not possible to rotate one end of a C–C double bond with respect to the other.



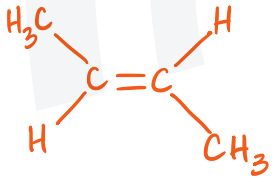
63

CIS-TRANS ISOMERISM

The following two forms of *but-2-ene* are therefore distinct and separate isomers:



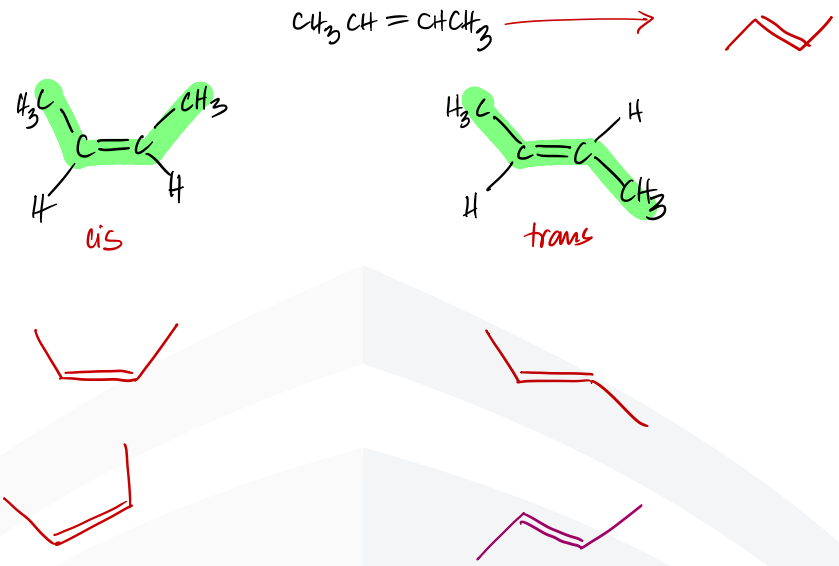
cis but-2-ene



trans but-2-ene

64

CIS-TRANS ISOMERISM

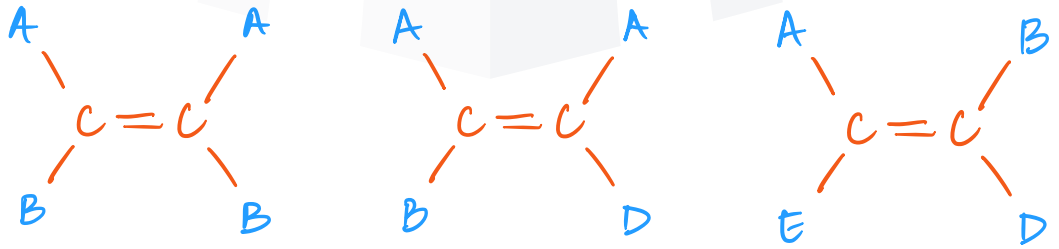


65

CIS-TRANS ISOMERISM

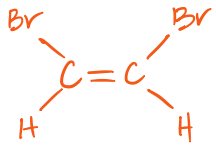
The isomer with both methyl groups on the same side of the double bond is called the **cis isomer**, and that with the methyl groups on opposite sides is called the **trans isomer**.

Note that the carbon atoms on both ends of the double bond must each be bonded to two non-identical groups. These three arrangements can result in cis–trans isomerism because there is restricted rotation about the C–C double bond:

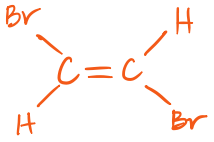


66

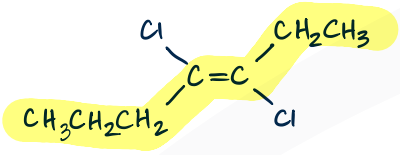
CIS-TRANS EXAMPLES



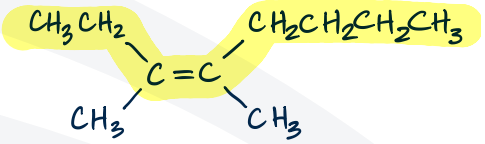
cis-1,2-dibromoethene



trans-1,2-dibromoethene



trans-3,4-dichlorohept-3-ene

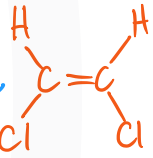


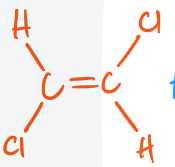
cis-3,4-dimethyl oct-3-ene

67

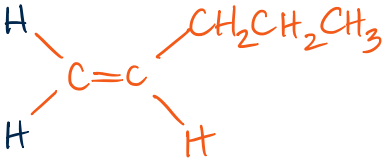
CIS-TRANS EXAMPLES

cis-1,2-dichloroethene

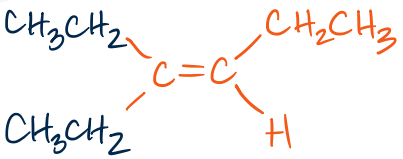




trans-1,2-dichloroethene



no cis-trans isomer



no cis-trans isomer

68

CIS-TRANS EXAMPLES

How many cis–trans isomers does the compound C_8H_{12} have?

Consider the structure of C_8H_{12}:



In order to calculate the number of geometric isomers it has, we have to first discover which of the three C–C double bonds exhibit cis–trans isomerism.

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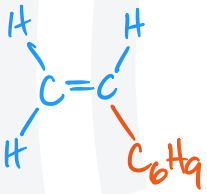
CIS-TRANS EXAMPLES

Let us look at the first carbon–carbon double bond from the left:





The first carbon from the left is bonded to 2 hydrogen atoms, as shown above. Overall, at this point there are three-of-a-kind atoms around the two carbon atoms on either side of the double bond, so this site **does not** exhibit cis–trans isomerism.

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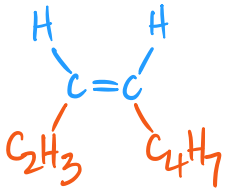
CIS-TRANS EXAMPLES

Let us look at the second carbon–carbon double bond from the left:





Both carbon atoms around the double bond are bonded to 2 different atoms, as shown above. So this site **will exhibit** cis–trans isomerism.

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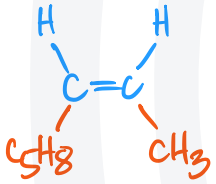
CIS-TRANS EXAMPLES

Let us look at the third carbon–carbon double bond from the left:





Both carbon atoms around the double bond are bonded to 2 different atoms, as shown above. So this site **will exhibit** cis–trans isomerism.

The entire molecule has **2 cis–trans sites**. So, the total number of geometric isomers, which are calculated using the formula 2^n (where 'n' is the number of cis–trans sites), is $2^2 = 4$ cis–trans isomers.

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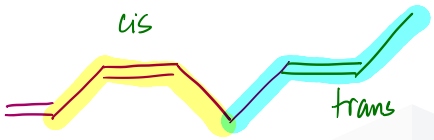
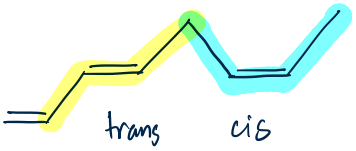
CIS-TRANS EXAMPLES

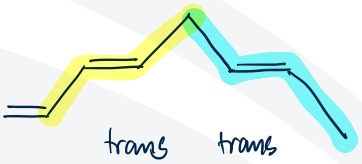
$H_2C{=}CHCH{=}CHCH_2CH{=}CHCH_3$











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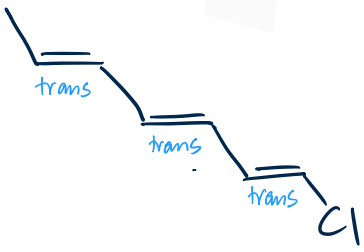
CIS-TRANS EXAMPLES

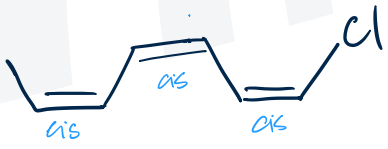
Look at the following molecule. Three of its 8 cis-trans isomers are drawn for you as an example.

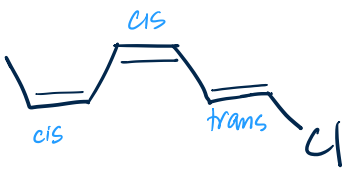
$CH_3CH{=}CHCH{=}CHCH{=}CHCl$

#of cis trans sites = 3

#of optical isomers for this structure $= 2^3 = 8$







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SKILL CHECK 14

Which of the following will exhibit cis–trans isomerism? If the molecule exhibits cis–trans isomerism, draw out the isomers.

A. 2,3-dimethylpent-2-ene

B. 3,4-dimethylpent-2-ene

C. 1,2,3-trimethylcyclopropane

D. 1,3-dimethylcyclobutane

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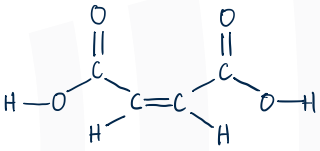
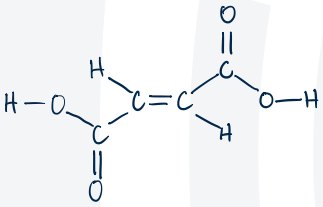
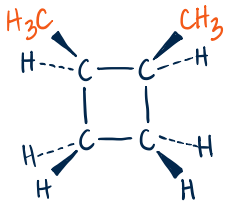
STEREOISOMERISM EXAMPLES



cis-but-2-ene-1,4-dioic acid
(maleic acid)
melting point: 130 °C

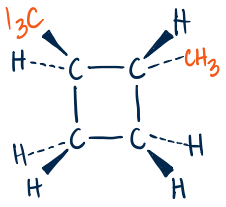


trans-but-2-ene-1,4-dioic acid
(fumaric acid)
melting point: 287 °C



cis-1,2-dimethylcyclobutane

76



trans-1,2-dimethylcyclobutane

OPTICAL ISOMERISM

Optical isomerism arises out of the three-dimension symmetry (or asymmetry) of certain organic molecules.

If a molecule can exist as two non-superimposable mirror images, it is said to have two **enantiomers**, or optical isomers.

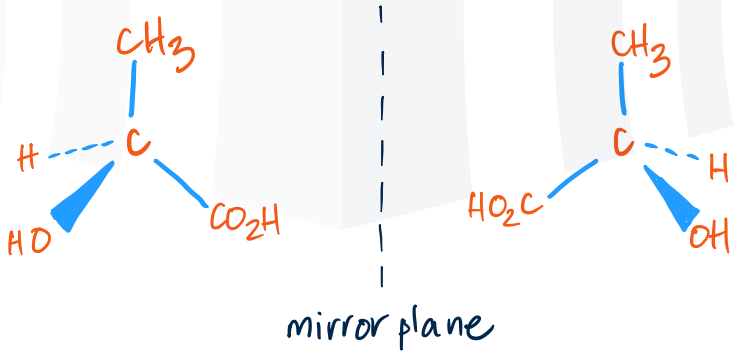
The most common kind of optical isomerism arises when a carbon atom is singly bonded to 4 different atoms or groups of atoms. This kind of a carbon atom is called a **chiral center**.

Chiral molecules have **no** plane of symmetry.

77

STEREOISOMERS

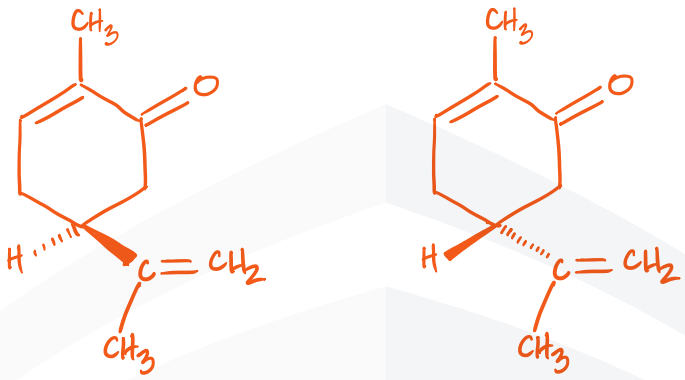
Below is an example of **chirality** due to the presence of 4 different groups around a carbon atom:



78

STEREOISOMERS

Below is an example of **chirality** in ring compounds. Notice the placement of the C–H bond at the base of the ring (going *behind the plane of the paper* on the left and coming *out of the plane of the paper* on the right):



79

STEREOISOMERS

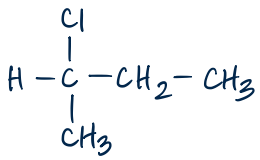
Physical properties such as melting point, boiling point and solubility are identical in enantiomers.The only difference in physical properties is in the direction of rotation of the plane of plane-polarised light.

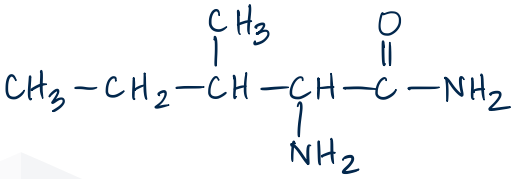
Chemical properties of enantiomers are identical for reactions with compounds that are not optically active. Enantiomers may, however, react differently with other optically active compounds.

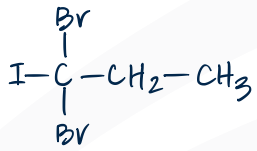
80

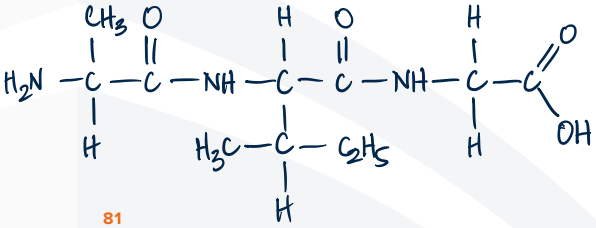
SKILL CHECK 15

Which of the following molecules have chiral centers? Find the chiral carbon (if one exists) for each of these:









81

SKILL CHECK 16

Which of the following molecules has a chiral centre correctly labelled with an asterisk?

A $CH_3C^*HClCH_3$

B $CH_3C^*HClCH_2Br$

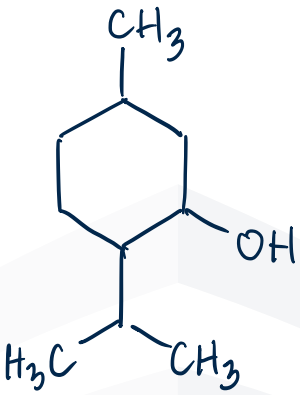
C $HOCH_2C^*H(OH)CH_2OH$

D $CH_3C^*Br_2CH_3$

82

SKILL CHECK 17

Find the chiral centers in the following molecule:

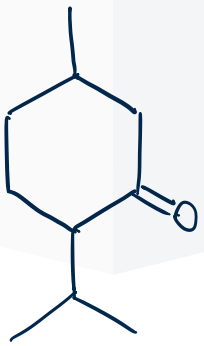


menthol

83

SKILL CHECK 18

Find the chiral centers in the following molecule:



menthone

84

SKILL CHECK 19

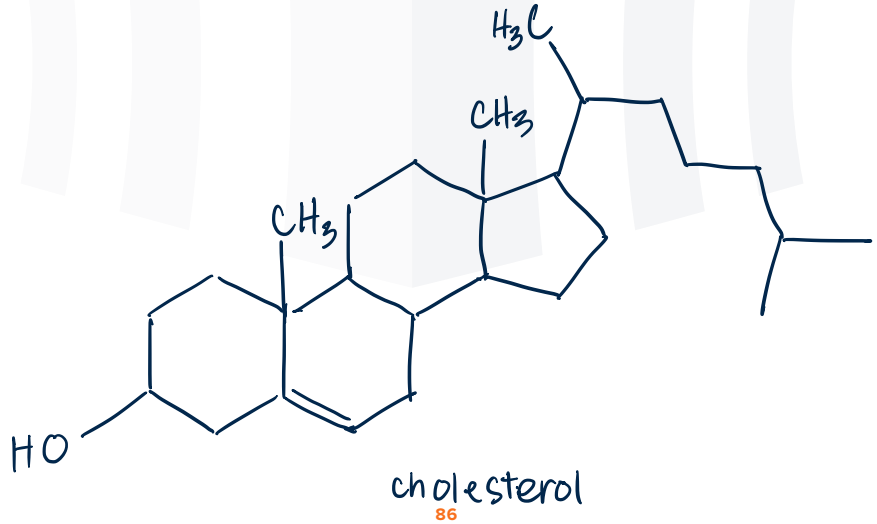
Find the chiral centers in the following molecule:



85

SKILL CHECK 20

Find the chiral centers in the following molecule:

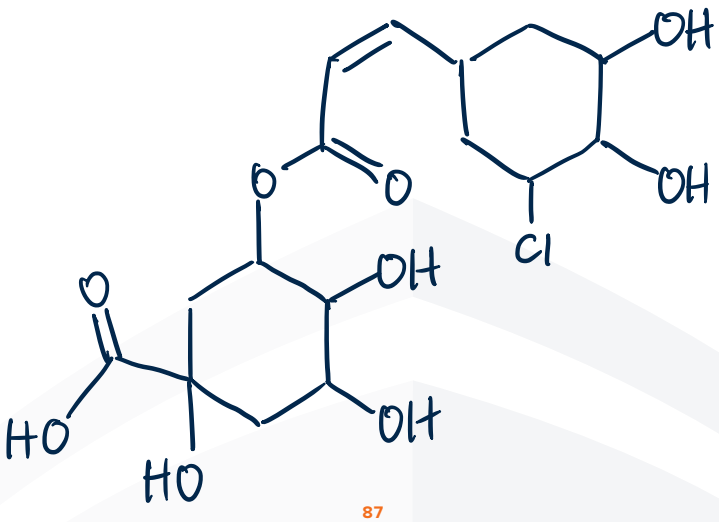


cholesterol

86

SKILL CHECK 21

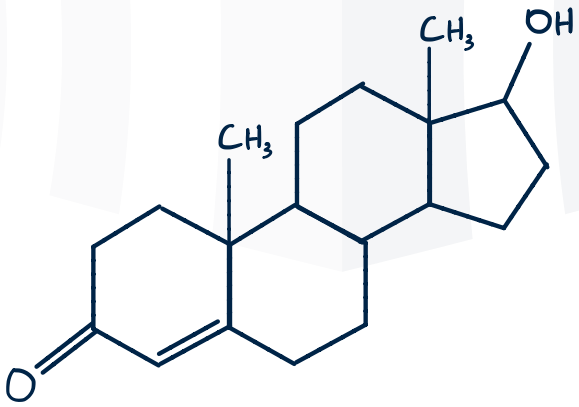
Find the chiral centers in the following molecule:



87

SKILL CHECK 22

Find the chiral centers in the following molecule:



testosterone

88

REACTIONS OF ORGANIC COMPOUNDS

Most organic compounds can be represented as **R–Fg**, where Fg represents the functional group and R represents the rest of the molecule.

Most organic reactions are those of functional groups. **The rest of the molecule does not change under the conditions of the reaction that changes the functional group**. *If it did change, it would have become a functional group itself!*

Many functional groups have characteristic reactions.

89

REACTIONS OF ORGANIC COMPOUNDS

An **addition reaction** is a reaction in which an organic molecule (usually containing a double bond) reacts with another molecule to give only one product: A + B $\longrightarrow$ C only.

A **substitution reaction** is a reaction in which one functional group in an organic compound is replaced by another functional group.

90

TYPES OF PARTICLES IN ORGANIC CHEMISTRY

A **radical** is an atom or a group of atoms that has an unpaired electron *Examples include the hydroxyl radical (HO•) and the triplet carbene radical (:CH_2).*

An **electrophile** is an atom or group of atoms that is attracted to regions of high electron density and accepts a pair of electrons to form a covalent bond. *Examples include cations or positive end of a dipole such as H^+, NO^+ and* the $H^{\delta+}$ in $H^{\delta+}$–$Cl^{\delta-}$.

A **nucleophile** is an atom or group of atoms that is attracted to electron-deficient regions in molecules and donates a pair of electrons to form a covalent bond. *Examples include anions or compounds with lone pairs such as I^- or F^- and :NH_3.*

91

FREE RADICAL SUBSTITUTION

Radicals (sometimes called **free radicals**) are highly reactive and are intermediates in many of the reactions of alkanes. They have the same number of protons as electrons, so are electrically neutral (unlike cations or anions).

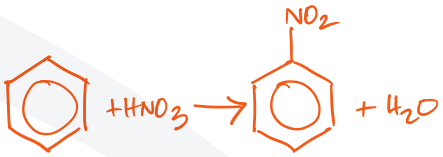
free radical substitution alkane $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$

92

ELECTROPHILIC SUBSTITUTION

Electrophiles possess **either a positive charge or an empty orbital in their valence shell**, or they contain a polar bond producing an atom with a partial charge, shown as **δ+.**

electrophilic substitution arene



93

NUCLEOPHILIC SUBSTITUTION

All nucleophiles possess a lone pair of electrons, and many are anions. Nucleophiles are called *ligands* when they react with transition metals.

nucleophilic substitution haloalkane alcohol

$OH^- + CH_3Br \rightarrow CH_3OH + Br^-$

$CH_3OH + HBr \rightarrow CH_3Br + H_2O$

94

ELECTROPHILIC ADDITION

An example of an **electrophilic addition** reaction is the bromination of alkenes.

electrophilic addition alkene $CH_2=CH_2 + Br_2 \rightarrow BrCH_2CH_2Br + H_2O$

95

NUCLEOPHILIC ADDITION

An example of a **nucleophilic addition** reaction is the addition of hydrogen cyanide to carbonyl compounds such as aldehydes and ketones.

nucleophilic addition aldehyde or ketone



96

HYDROLYSIS

Hydrolysis is a reaction in which a molecule is split into two by the action of water (often helped by OH^- or H^+ as a catalyst).

An example of a hydrolysis reaction is the dissociation of an ester into its parent carboxylic acid and alcohol.

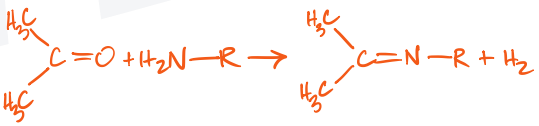
hydrolysis ester $CH_3CO_2CH_3 + H_2O \rightarrow CH_3CO_2H + CH_3OH$

97

CONDENSATION

Condensation is the opposite of hydrolysis. Two molecules come together to form a bigger molecule, with the elimination of a molecule of water (or other small molecule, such as HCl).

condensation aldehyde or ketone



98

ELIMINATION

Elimination is a reaction that forms an alkene by the removal of a molecule of H_2O from a molecule of an alcohol, or a molecule of H-X from a molecule of a halogenoalkane.

elimination

halogenoalkane



alcohol



99

REDUCTION AND OXIDATION

Reduction and oxidation – these have their usual meanings. Reduction addition hydrogen and Oxidation is the addition of oxygen.

reduction

aldehyde or ketone



oxidation

alcohol



aldehyde



100

BREAKING BONDS

Chemical reactions involve the breaking of bonds and the formation of new bonds.

A detailed description of which bonds break and which form, and in what order these processes occur is called a **mechanism**.

A mechanism also includes a description of how any catalyst that might be involved in a reaction works. There are two different ways in which a covalent bond to a carbon atom may break. Each way produces a different carbon species. These are:

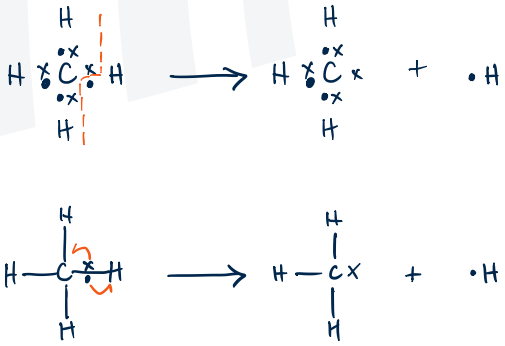
- Bond Homolysis (Homolytical Fission).
- Bond Heterolysis forming carbocations.

101

BREAKING BONDS

Homolysis, often called homolytic fission, results in carbon radicals. It is the splitting of a bond giving an equal share of bonding electrons to each particle. In the figure below, the carbon and hydrogen atoms take one electron each. The curly arrows with only half a head represent how each electron in the bond moves when the bond breaks.

The carbon atom in the methyl radical CH_3 has only seven electrons around it. Methyl radicals are highly reactive, and readily form bonds with other atoms or molecules to regain their full octet of electrons.

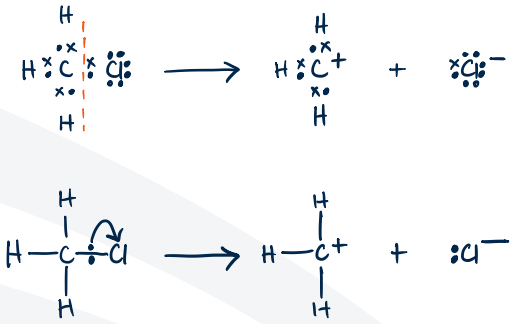


102

BREAKING BONDS

Heterolysis involves the splitting of a bond giving an unequal share of bonding electrons to each particle. In the figure below, the chlorine atom has taken both the bonding electrons, leaving the carbon atom with none. The curly arrow describes the movement of the bonded pair of electrons to the chlorine atom.

Chlorine, being more electronegative than carbon, has already attracted the bonding electrons partially, forming a bond dipole $^{\delta+}C–Cl^{\delta-}$. This movement of the electron pair results in the carbon atom in the methyl carbocation having only six electrons in its outer shell, and a single positive charge. It is a strong electrophile.



103

SKILL CHECK 23

Use curly arrows to describe what happens to the electrons when (ionic) ammonium chloride is made from ammonia and hydrogen chloride:

$$NH_3 + HCl \longrightarrow NH_4Cl$$

104

INTRO TO ORGANIC WS 1

SECTION A

1 There are three structural isomers with the formula C_5H_{12}.

Which formulae correctly represent these three structural isomers?

A $CH_3CH_2CH_2CH_2CH_3$ $CH_3CH_2CHCH_3CH_3$ $CH_3CH_3CCH_3CH_3$

B $CH_3CH_2CH_2CH_2CH_3$ $CH_3CH_2(CH)CH_3CH_3$ $C(CH_3)_4$

C $CH_3CH_2CH_2CH_2CH_3$ $CH_3CH(CH_3)CH_2CH_3$ $CH_3C(CH_3)_2CH_3$

D $CH_3CH_2CH_2CH_2CH_3$ $CH_3CH(CH_3)CH_2CH_3$ $CH_3CH_2CH(CH_3)CH_3$

[J'14 11 Q24]

2 How many geometrical (cis-trans) isomers are there of hex-2,4-diene, $CH_3CH=CHCH=CHCH_3$?

A none; hex-2,4-diene does not show geometric isomerism

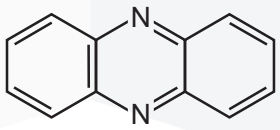
B 2

C 3

D 4

[J'14 11 Q29]

3 The diagram shows the skeletal formula of phenazine.



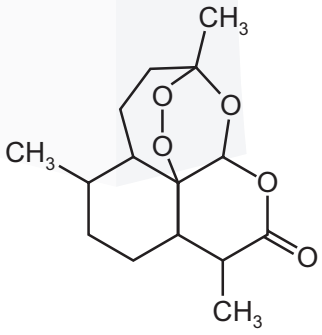
phenazine

What is the empirical formula of phenazine?

A C_6H_4N **B** C_6H_6N **C** $C_{12}H_8N_2$ **D** $C_{12}H_{12}N_2$

[J'14 12 Q20]

4 Artemisinin is a powerful anti-malarial drug.



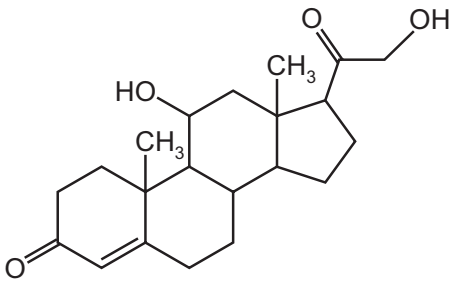
artemisinin

How many chiral centres are there in each molecule of artemisinin?

A 4 **B** 6 **C** 7 **D** 8

[J'14 12 Q30]

5 Corticosterone is a hormone involved in the metabolism of carbohydrates and proteins.



corticosterone

How many chiral centres are there in one molecule of corticosterone?

A 5 **B** 6 **C** 7 **D** 8

[N'14 11 Q26]

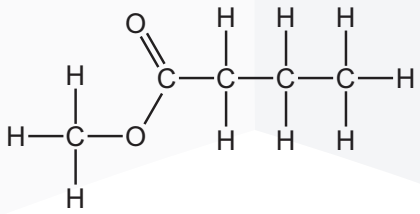
6 In this question, structural isomerism **and** stereoisomerism should be considered.

How many isomeric aldehydes have the formula $C_5H_{10}O$?

A 3 **B** 4 **C** 5 **D** 6

[N'14 13 Q21]

7 Methyl butanoate, $C_5H_{10}O_2$, is an ester used in the food industry to give products the flavour of apples.



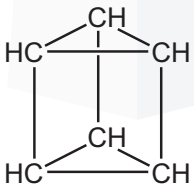
methyl butanoate

Including methyl butanoate, how many **structural** isomers are there of $C_5H_{10}O_2$ that are esters?

A 6 **B** 8 **C** 9 **D** 10

[N'14 13 Q30]

8 In 1869 Ladenburg suggested a structure for benzene, C_6H_6, in which one hydrogen atom is attached to each carbon atom.



Ladenburg structure

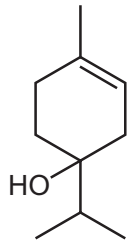
A compound $C_6H_4Cl_2$ could be formed with **the same** carbon skeleton as the Ladenburg structure.

How many **structural** isomers would this compound have?

A 3 **B** 4 **C** 5 **D** 6

[J'15 11 Q28]

9 Terpinen-4-ol is one of the active ingredients in tea tree oil.



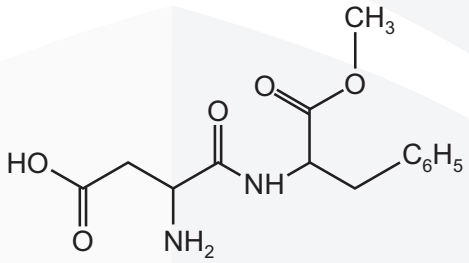
terpinen-4-ol

What is the molecular formula of terpinen-4-ol?

A $C_7H_{11}O$ **B** $C_{10}H_{16}O$ **C** $C_{10}H_{17}O$ **D** $C_{10}H_{18}O$

[J'15 12 Q25]

10 The compound *aspartame* is widely used as a sweetener in 'diet' soft drinks.



aspartame

Aspartame is chiral. (There are no chiral carbon atoms in C_6H_5.)

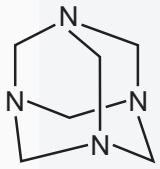
How many chiral carbon atoms are present in a molecule of *aspartame*?

A 1 **B** 2 **C** 3 **D** 4

[J'15 13 Q27]

11 Hexamine is a crystalline solid used as a fuel in portable stoves.

The diagram shows its skeletal structure.



What is the empirical formula of hexamine?

A CH_2N **B** $C_3H_6N_2$ **C** $C_4H_8N_4$ **D** $C_6H_{12}N_4$

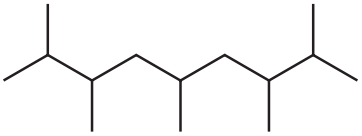
[N'15 11 Q9]

12 How many isomeric esters have the molecular formula $C_4H_8O_2$?

A 2 **B** 3 **C** 4 **D** 5

[N'15 11 Q20]

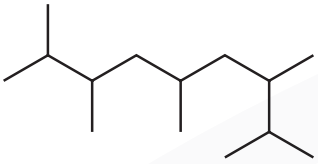
13 A new jet fuel has been produced that is a mixture of different structural isomers of compound Q.



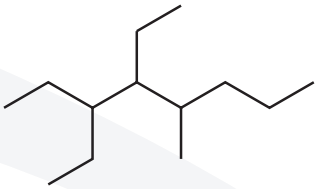
Q

Which skeletal formula represents a **structural isomer** of Q?

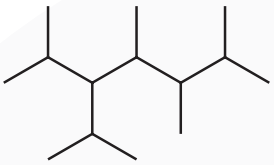
A



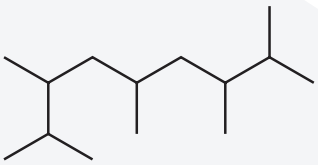
B



C



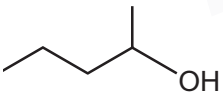
D



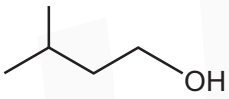
[N'15 11 Q21]

14 What is the skeletal formula of 2-methylpentan-1-ol?

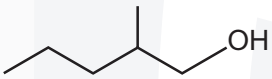
A



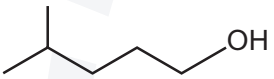
B



C



D



[N'15 12 Q29]

15 Which compound shows optical isomerism?

A 2-chloropropane

B 1,2-dichloropropane

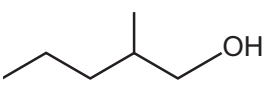
C 1,3-dichloropropane

D 2,2-dichloropropane

[N'15 12 Q21]

16 What is the skeletal formula of 2-methylpentan-1-ol?

A



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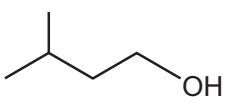

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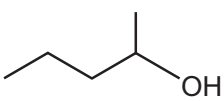

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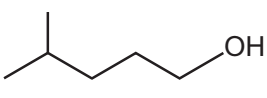
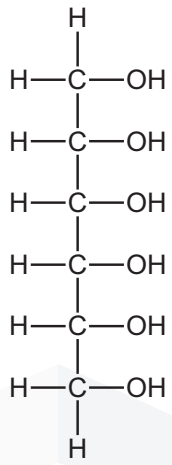


[N'15 12 Q29]

17 Sorbitol is a naturally-occurring compound with a sweet taste. It is often used as a substitute for sucrose by the food industry.



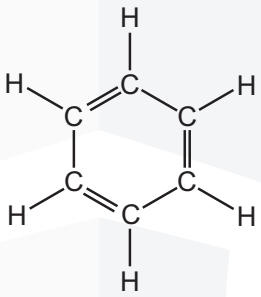
sorbitol

How many chiral centres are present in sorbitol?

A 3 **B** 4 **C** 5 **D** 6

[N'15 13 Q29]

18 In 1865 Kekulé suggested a ring structure for benzene, C_6H_6, in which a hydrogen atom is attached to each carbon atom.



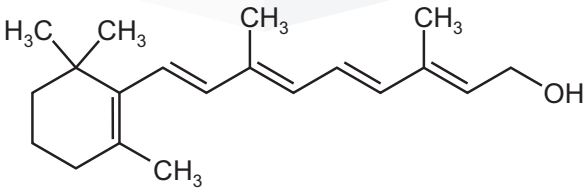
Kekulé structure

In this structure all of the bonds remain in the places shown. Assuming this is the structure of benzene, how many isomers of dichlorobenzene, $C_6H_4Cl_2$, would exist?

A 3 **B** 4 **C** 5 **D** 6

[N'16 11 Q20]

19 The diagram shows the structure of vitamin A.



vitamin A

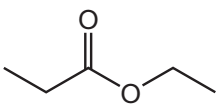
How many chiral centres are present in one vitamin A molecule?

A 0 **B** 1 **C** 2 **D** 3

[N'16 11 Q21]

20 Which formula represents an ester that will form propanoic acid on hydrolysis with dilute sulfuric acid?

A



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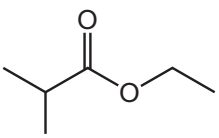

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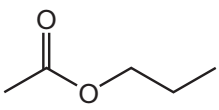
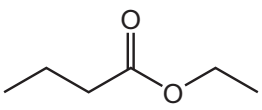


D



[N'16 11 Q29]

21 Which statement about stereoisomers is correct?

A Cis-trans isomers are mirror images of each other.

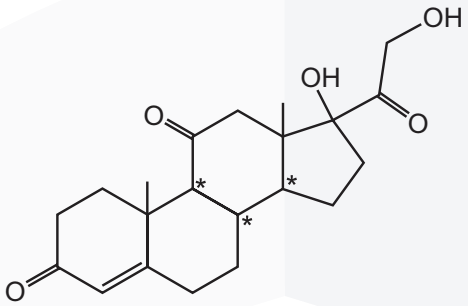
B Optical isomers must contain a double bond that restricts rotation.

C Stereoisomers have the same structural formula as each other.

D Stereoisomers must contain a chiral centre.

[N'16 12 Q24]

22 The drug cortisone has the formula shown.



In addition to those chiral centres marked by an asterisk (*), how many **other** chiral centres are present in the cortisone molecule?

A 0 **B** 1 **C** 2 **D** 3

[J'17 11 Q21]

23 Structural isomerism and stereoisomerism should be considered when answering this question.

If a molecule contains two non-identical chiral carbon atoms, four optical isomers exist.

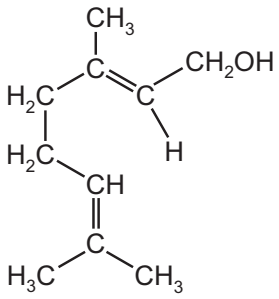
How many isomers are there with

- molecular formula $C_7H_{14}O$ **and**
- a five-membered ring **and**
- a tertiary alcohol group?

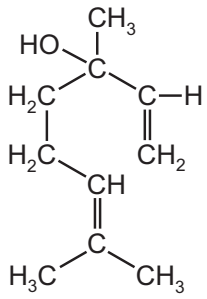
A 4 **B** 5 **C** 9 **D** 13

[J'17 11 Q21]

24 Geraniol and linalool are compounds found in some flower fragrances.



geraniol



linalool

Which statement is correct?

A They are chain isomers of each other.

B They are geometrical isomers of each other.

C They are optical isomers of each other.

D They are positional isomers of each other.

[J'17 12 Q21]

25 Structural isomerism and stereoisomerism should be considered when answering this question.

Which formula identifies a **single** substance?

A $CH_3CHClCH_2CHO$

B $CH_3CHCHCH_3$

C $CH_2ClCH_2CHCl_2$

D C_4H_{10}

[J'17 13 Q20]

26 Which compound does **not** exhibit stereoisomerism?

A $CH_3CHClCH_2CHO$

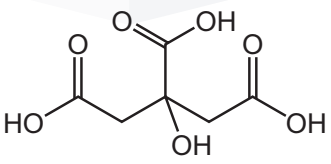
B $CH_3CHCHCH_3$

C $CH_2ClCH_2CCl_2H$

D $CHClCHCl$

[N'17 12 Q20]

27 The diagram shows the skeletal formula of citric acid.



citric acid

What is the molecular formula of citric acid?

A $C_6H_8O_7$ **B** $C_6H_4O_7$ **C** $C_8H_8O_7$ **D** $C_{10}H_8O_7$

[N'17 12 Q21]

28 Which types of stereoisomerism are shown by 2,4-dimethylhex-2-ene?

A both cis-trans isomerism and optical isomerism

B cis-trans isomerism only

C neither cis-trans isomerism nor optical isomerism

D optical isomerism only

[M'18 12 Q20]

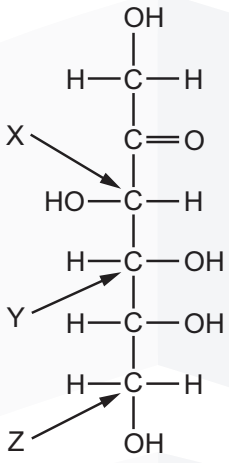
29 X has the molecular formula $C_5H_{12}O$. X has a branched carbon skeleton and a secondary alcohol functional group.

How many **structural** isomers fit this description of X?

A 1 **B** 2 **C** 3 **D** 4

[N'18 11 Q21]

30 Fructose is a sugar with more than one chiral centre. The fructose molecule is shown with X, Y and Z indicating three carbon atoms.



fructose

Which carbon atoms are chiral centres?

A X, Y and Z **B** X and Y only **C** X only **D** Y only

[J'18 11 Q20]

31 Which pair of alcohols are isomers of each other?

A butan-1-ol and 2,2-dimethylpropan-1-ol

B butan-2-ol and 2-methylpropan-2-ol

C pentan-1-ol and 2-methylpropan-2-ol

D propan-2-ol and 2-methylpropan-2-ol

[J'18 11 Q21]

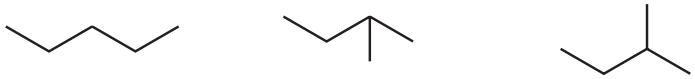
32 There are three structural isomers with the formula C_5H_{12}.

Which formulae correctly represent these three structural isomers?

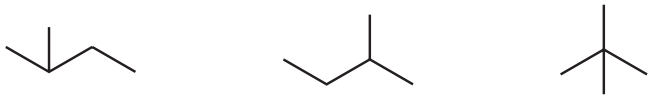
A $CH_3CH_2CH_2CH_2CH_3$ $CH_3CH(CH_3)CH_2CH_3$ $C(CH_3)_4$

B $CH_3CH_2CH_2CH_2CH_3$ $CH_3CH(CH_3)CH_2CH_3$ $CH_3CH_2CH(CH_3)CH_3$

C

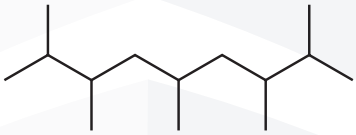


D



[N'18 12 Q20]

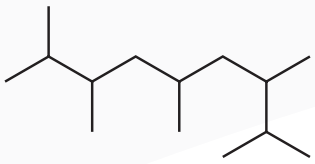
33 A new jet fuel has been produced that is a mixture of different structural isomers of compound Q.



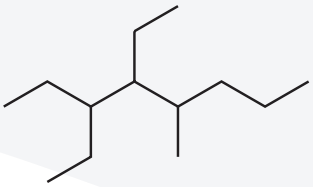
Q

Which skeletal formula represents a **structural isomer** of Q?

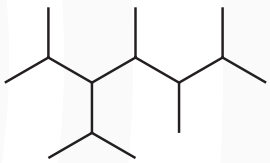
A



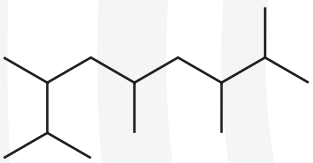
B



C



D



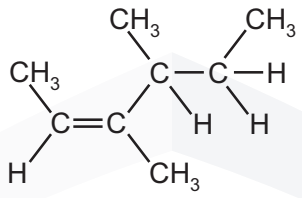
[N'18 11 Q22]

SECTION B

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

1 The diagram shows the structure of an alkene molecule.



Which statements about this molecule are correct?

1 All the carbon atoms are in the same plane.

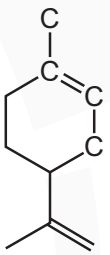
2 It has geometrical isomers.

3 It is optically active.

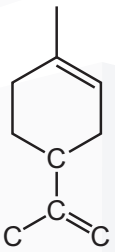
[J'15 11 Q37]

2 In which structures do the four carbon atoms labelled C lie in the same plane?

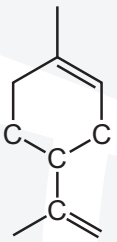
1



2

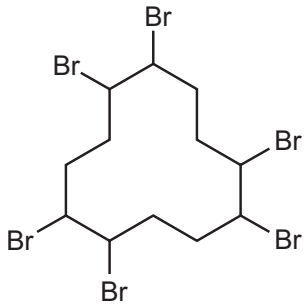


3



[J'15 12 Q37]

3 The diagram shows a molecule of a compound used as a flame retardant.



Which statements about this structure are correct?

1 Each brominated C atom is chiral.

2 The molecular formula is $C_{12}H_{20}Br_6$.

3 The C–C–C bond angles are all 120°.

[J'15 13 Q37]

4 Several structural isomers of $C_3H_6O_3$ are listed below.

$HOCH_2COCH_2OH$

$HOCH_2CH(OH)CHO$

$HOCH_2CH_2CO_2H$

$CH_3CH(OH)CO_2H$

Which statements about these structural isomers are correct?

1 One mole of each reacts with two moles of sodium.

2 Only one of the isomers contains a tertiary alcohol group.

3 They all contain a primary alcohol group.

[N'16 11 Q39]

5 P and Q are a pair of cis-trans isomers.

What **must** be the same for P and Q?

1 their empirical formula

2 their functional groups

3 their skeletal formula

[J'17 11 Q37]

6 Which compounds contain a chiral centre?

1 2-hydroxybutanoic acid

2 3-hydroxybutanoic acid

3 4-hydroxybutanoic acid

[J'17 12 Q37]

7 Which compounds show geometrical (cis-trans) isomerism?

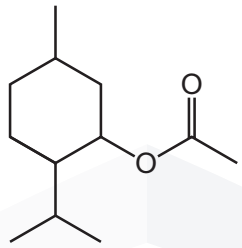
1 $CH_3CH=C(CH_3)C_2H_5$

2 $CH_3CH=CHCH_2CH_2CH_3$

3 $C_2H_5CH=CHC_2H_5$

[J'18 12 Q37]

8 Molecule G is shown.



G

How many chiral centres are present in each molecule of G?

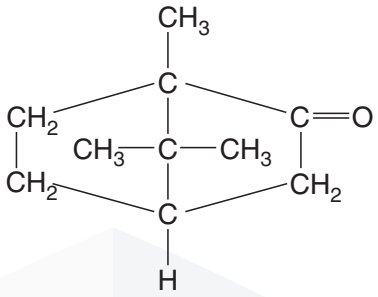
A 1 **B** 2 **C** 3 **D** 4

[J'18 13 Q20]

INTRO TO ORGANIC WS 2

SECTION A

1 Camphor is used for medical purposes, the diagram shows its structure.



How many chiral centres are present in one molecule of camphor?

A 0 **B** 1 **C** 2 **D** 3

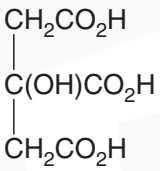
[N'02 Q21]

2 How many structural and *cis-trans* isomers are there for dichloropropene, $C_3H_4Cl_2$?

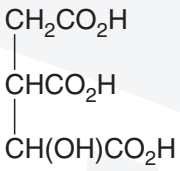
A 3 **B** 5 **C** 6 **D** 7

[J'03 Q20]

3 The isomers, citric acid and isocitric acid, are intermediates in the Krebs cycle of the oxidation of glucose in living cells.



citric acid



isocitric acid

How many chiral centres does each acid possess?

	citric acid	isocitric acid
A	0	1
B	0	2
C	1	1
D	1	2

[J'03 Q21]

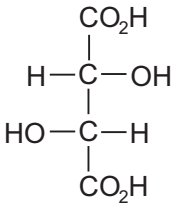
4 How many alcohols (including both structural isomers and stereoisomers) can have the molecular formula $C_4H_{10}O$?

A 3 **B** 4 **C** 5 **D** 6

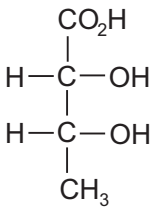
[N'03 Q20]

5 Which molecule does not have a chiral centre?

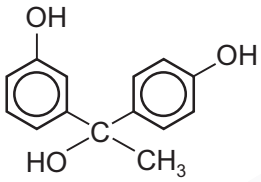
A



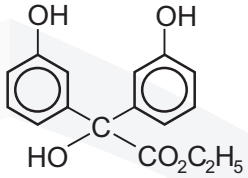
B



C



D



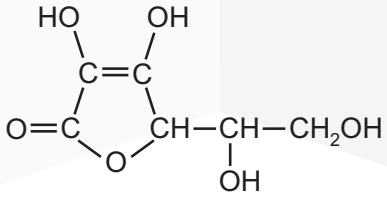
[N'04 Q21]

6 What is the number of isomers of $C_2H_2Cl_2$ including *cis-trans* isomers?

A 2 **B** 3 **C** 4 **D** 5

[N'05 Q20]

7 The diagram shows the structure of vitamin C.

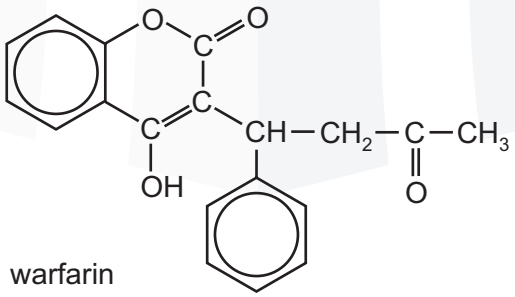


How many chiral centres are there in one molecule?

A 1 **B** 2 **C** 3 **D** 4

[N'05 Q19]

8 Warfarin is used as a rat poison.



warfarin

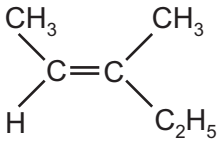
How many chiral centres are present in the warfarin molecule?

A 0 **B** 1 **C** 2 **D** 3

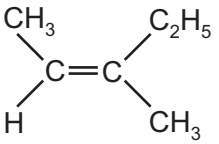
[J'06 Q21]

9 The structures below show isomers of C_6H_{12}.

1



2



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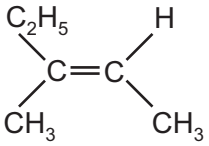

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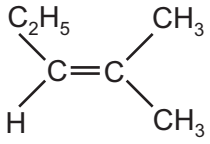


In which pair are the members *cis-trans* isomers of each other?

A 1 and 2 **B** 1 and 3 **C** 1 and 4 **D** 2 and 4

[J'06 Q22]

10 What is the total number of different chloroethanes, formula $C_2H_{6-n}Cl_n$, where n can be any integer from 1 to 4?

A 4 **B** 6 **C** 7 **D** 8

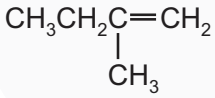
[N'06 Q21]

11 Which alkene could exist in *cis* and *trans* forms?

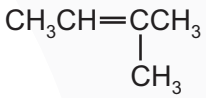
A $CH_3CH_2CH_2CH{=}CH_2$

B $CH_3CH_2CH{=}CHCH_3$

C



D



[N'06 Q23]

12 Which molecules, each with a linear carbon chain, can have an optically active isomer?

I	II	III	IV
C_3H_6BrI	C_3H_4BrI	$C_3H_6I_2$	$C_3H_4Br_2$

A I and II only

B I, II and III only

C II and III only

D I, II and IV only

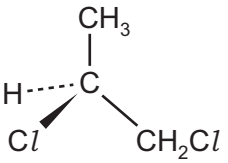
[N'07 Q19]

13 In which pair do the isomers have identical boiling points?

A $CH_3CH_2CH_2CH_2OH$ and $(CH_3)_2CHCH_2OH$

B $CH_3(CH_2)_4CH_3$ and $(CH_3)_2CHCH(CH_3)_2$

C



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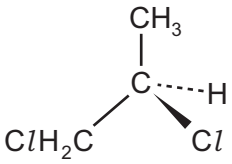

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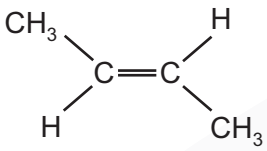

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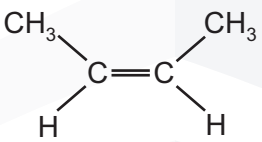
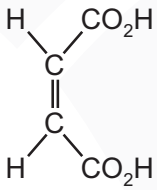


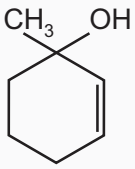
[N'07 Q20]

14 Which compound is both chiral and acidic?

A



B



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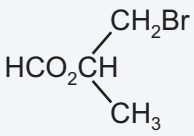

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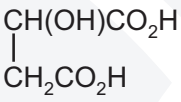
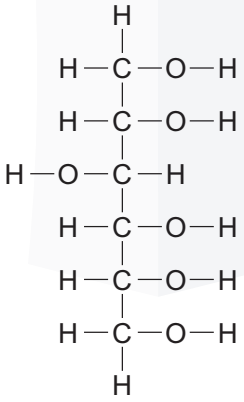


[J'08 Q29]

15 Sorbitol is a naturally-occurring compound with a sweet taste. It is often used as a substitute for sucrose by the food industry.

The diagram shows its structure.

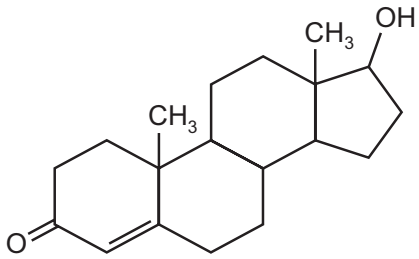


How many chiral centres are present in sorbitol?

A 1 **B** 2 **C** 3 **D** 4

[N'08 Q20]

16 In recent years a number of athletes have been banned from sports because of their illegal use of synthetic testosterone, a naturally occurring hormone in the body.



testosterone

How many chiral centres are present in a testosterone molecule?

A 1 **B** 2 **C** 3 **D** 6

[J'09 Q19]

17 The compound known as 'gamma-linolenic acid' is found in significant amounts in the seeds of the Evening Primrose plant. There is evidence that the compound may help patients with diabetes.

$$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_4CO_2H$$

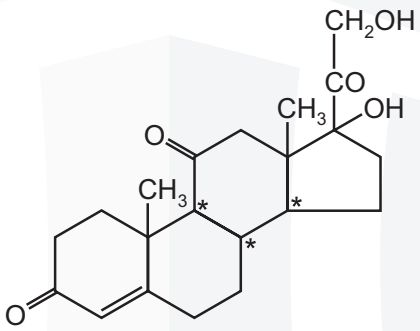
gamma-linolenic acid

How many *cis-trans* isomers does gamma-linolenic acid have?

A 3 **B** 6 **C** 8 **D** 12

[J'09 Q20]

18 The drug cortisone has the formula shown.



In addition to those chiral centres marked by an asterisk (*), how many other chiral centres are present in the cortisone molecule?

A 0 **B** 1 **C** 2 **D** 3

[N'09 11 Q20]

19 What is the least number of carbon atoms in a non-cyclic alkane molecule that has a chiral centre?

A 7 **B** 8 **C** 9 **D** 10

[N'09 12 Q21]

20 Which compound exhibits both *cis-trans* and optical isomerism?

A $CH_3CH=CHCH_2CH_3$

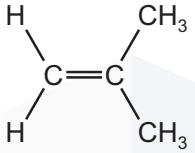
B $CH_3CHBrCH=CH_2$

C $CH_3CBr=CBrCH_3$

D $CH_3CH_2CHBrCH=CHBr$

[J'10 11 Q30]

21 The compound 2-methylpropene, C_4H_8, is a monomer used in the production of synthetic rubber.



In addition to 2-methylpropene there are x other isomers of C_4H_8, structural or otherwise, which contain a double bond.

What is the value of x?

A 1 **B** 2 **C** 3 **D** 4

[N'10 1 Q29]

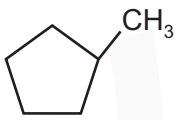
22 How many structural isomers are there of trichloropropane, $C_3H_5Cl_3$?

A 3 **B** 4 **C** 5 **D** 6

[N'10 12 Q20]

23 Which of the compounds shown have chiral carbon atoms?

1



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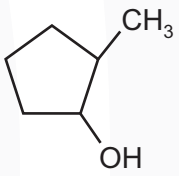

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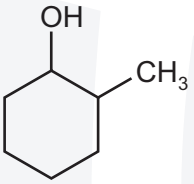
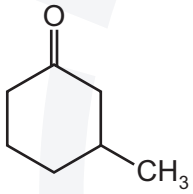


4



A 1, 2, 3 and 4

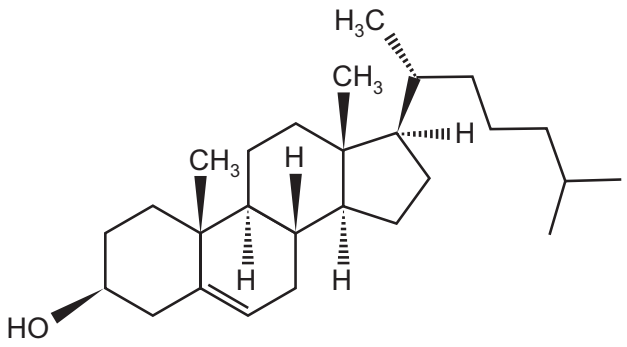
B 1 and 4 only

C 2 and 3 only

D 2, 3 and 4 only

[N'10 12 Q30]

24 The diagram shows the structure of the naturally-occurring molecule cholesterol.



cholesterol

Student X claimed that the seventeen carbon atoms in the four rings all lie in the same plane.

Student Y claimed that this molecule displays *cis-trans* isomerism at the C=C double bond.

Which of the students are correct?

A both X and Y

B neither X nor Y

C X only

D Y only

[J'11 11 Q24]

25 Which compound does **not** show cis-trans isomerism?

A 2-methylpent-2-ene

B 3-methylpent-2-ene

C 3,4-dimethylhex-3-ene

D pent-2-ene

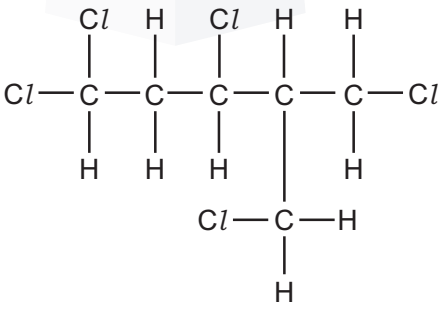
[J'11 12 Q24]

26 How many isomers with the formula C_5H_{10} have structures that involve π bonding?

A 3 **B** 4 **C** 5 **D** 6

[J'11 12 Q26]

27 The molecule shown is optically active.



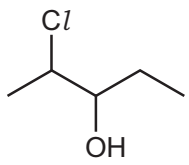
How many chiral carbon atoms are present in this molecule?

A 1 **B** 2 **C** 3 **D** 4

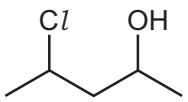
[N'11 12 Q27]

28 Which diagram gives the skeletal formula of 2-chloropentan-3-ol?

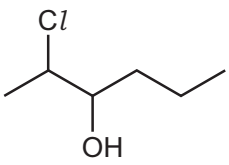
A



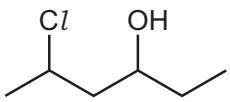
B



C



D



[J'12 12 Q21]

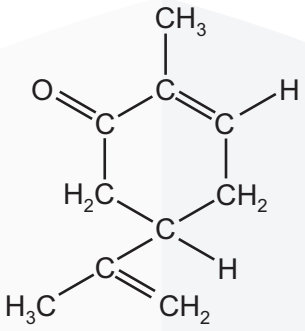
29 An alkene has the formula $CH_3CH{=}CRCH_2CH_3$ and does **not** possess *cis-trans* isomers.

What is *R*?

A H **B** Cl **C** CH_3 **D** C_2H_5

[N'12 11 Q21]

30 Carvone is found in spearmint.



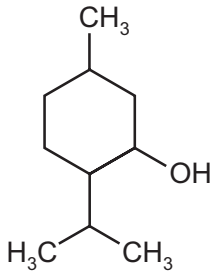
carvone

How many σ and π bonds are present in this molecule?

	σ	π
A	13	3
B	22	3
C	22	6
D	25	3

[N'12 11 Q20]

31 Menthol is an important compound extracted from the peppermint plant.



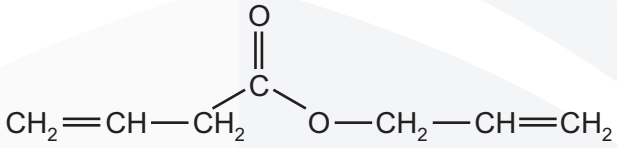
menthol

How many chiral centres are there in one molecule of menthol?

A 1 **B** 2 **C** 3 **D** 4

[N'12 11 Q22]

32 The diagram shows a molecule that has σ bonds and π bonds.



How many σ bonds are present in this molecule?

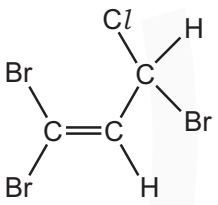
A 15 **B** 17 **C** 18 **D** 21

[N'12 13 Q21]

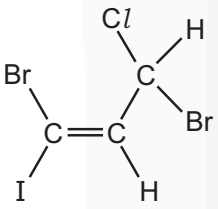
33 The following compounds are found in the seaweed *Asparagopsis taxiformis*.

Which compound could show **both** *cis-trans* isomerism and optical isomerism?

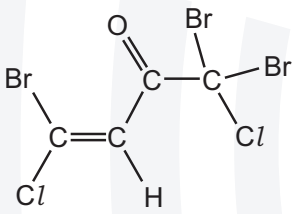
A



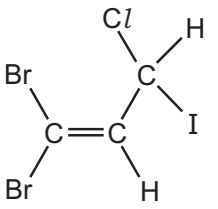
B



C



D



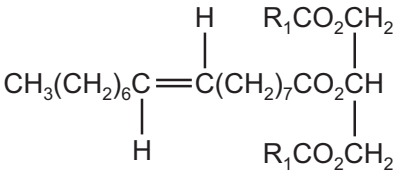
[J'13 11 Q20]

34 Some vegetable oils contain 'trans fats' that are associated with undesirable increases in the amount of cholesterol in the blood.

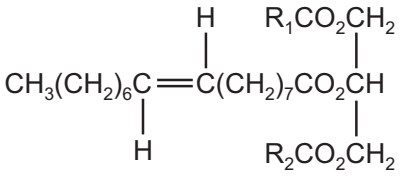
In the diagrams below, R_1 and R_2 are different hydrocarbon chains.

Which diagram correctly illustrates an optically active 'trans fat'?

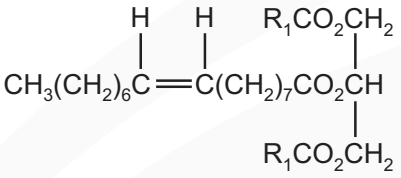
A



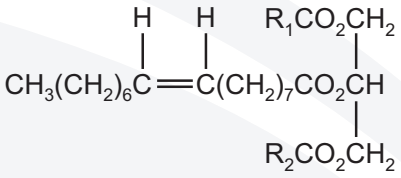
B



C



D



[J'13 11 Q30]

35 How many isomers, including structural and stereoisomers, with the formula C_4H_8 have structures that involve π bonding?

A 1 **B** 2 **C** 3 **D** 4

[J'13 13 Q22]

36 Which compound exhibits stereoisomerism?

A $CH_3CHClCH_3$

B $CH_3CHClCH_2Cl$

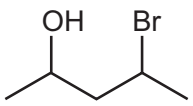
C $CH_3CCl_2CH_3$

D $CH_2ClCH_2CH_2Cl$

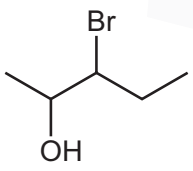
[N'13 11 Q23]

37 Which diagram gives the skeletal formula of 2-bromopentan-4-ol?

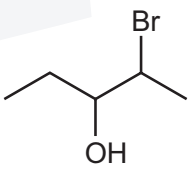
A



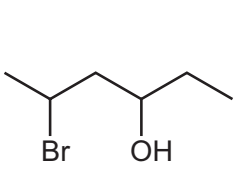
B



C



D



[N'13 13 Q20]

38 Including structural and stereoisomers, how many isomers are there of $C_2H_2Br_2$?

A 2 **B** 3 **C** 4 **D** 5

[N'13 13 Q21]

SECTION B

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

1 Which pairs of compounds have the same empirical formula?

1 ethane and ethene

2 ethene and cyclohexane

3 cyclohexane and oct-1-ene

[J'02 Q31]

2 Which compounds have the empirical formula CH_2O?

1 methanal

2 ethanoic acid

3 methyl methanoate

[N'2 Q31]

3 Which compounds show *cis-trans* isomerism?

1 but-2-ene

2 but-1-ene

3 2-methylpropene

[N'02 Q37]

4 What will always be a characteristic of a compound containing a single carbon atom with four different groups bonded to it?

1 It will have an optical isomer.

2 It will have a chiral centre.

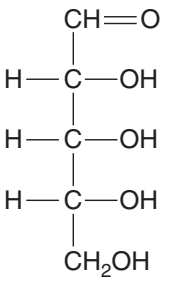
3 It will have a structural isomer.

[J'03 Q37]

5 The taste buds on the tongue are chiral and can distinguish one optical isomer from another.

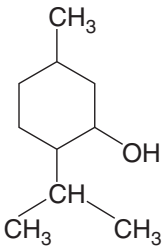
Which naturally-occurring compounds will have optical isomers that may be distinguished by taste?

1



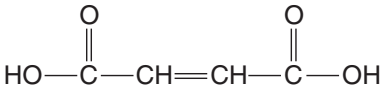
ribose

2



menthol

3



maleic acid

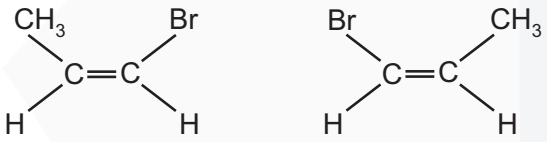
[N'03 Q38]

6 In which pairs are the members stereoisomers of each other?

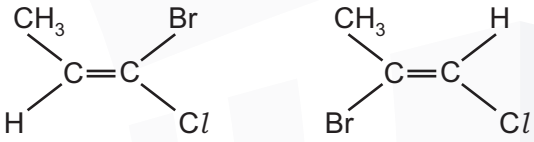
1



2



3



[J'06 Q37]

7 Which structural formulae represent 2,2-dimethylpentane?

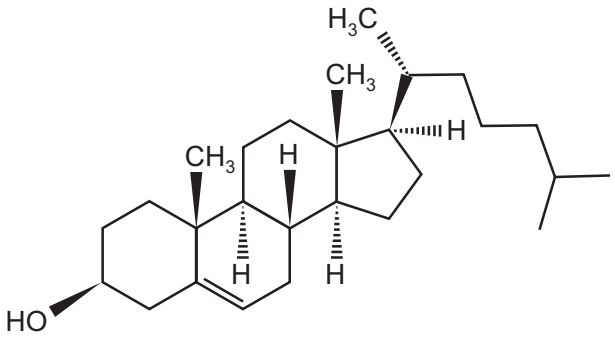
1 $(CH_3)_2CHCH_2CH(CH_3)_2$

2 $(CH_3)_3CCH_2CH_2CH_3$

3 $CH_3CH_2CH_2C(CH_3)_3$

[J'10 11 Q38]

8 The diagram shows the structure of the naturally-occurring molecule cholesterol.



cholesterol

Which statements about cholesterol are correct?

1 The molecule contains a secondary alcohol group.

2 The molecule contains two π bonds.

3 All carbon atoms in the four rings lie in the same plane.

[N'10 11 Q37]

9 What are the same for a pair of optical isomers?

1 their empirical formula

2 their functional groups

3 their structural formula

[J'12 12 Q38]

10 What is **always** involved in a carbon-carbon π bond?

1 a shared pair of electrons

2 a sideways overlap of p orbitals

3 delocalised electrons

[J'12 13 Q38]

11 Which substances contain delocalised electrons?

1 cyclohexene

2 graphite

3 sodium

[J'13 12 Q33]

12 The structural formulae of two compounds are shown below.



Which statements about these compounds are correct?

1 The two compounds are structural isomers of each other.

2 The empirical formula of both compounds is C_3H_6O.

3 Both compounds are carboxylic acids.

[N'13 13 Q40]

15.1 Alkanes

a Compounds containing only carbon and hydrogen are called hydrocarbons. This class of compound can be sub-divided into alkanes, alkenes and arenes.

b understand the general unreactivity of alkanes, including towards polar reagents ☐

c describe the chemistry of alkanes as exemplified by the following reactions of ethane:

(i) combustion ☐

(ii) substitution by chlorine and by bromine ☐

d describe the mechanism of free-radical substitution at methyl groups with particular reference to the initiation, propagation and termination reactions ☐

e explain the use of crude oil as a source of both aliphatic and aromatic hydrocarbons ☐

f suggest how cracking can be used to obtain more useful alkanes and alkenes of lower Mr from larger hydrocarbon molecules ☐

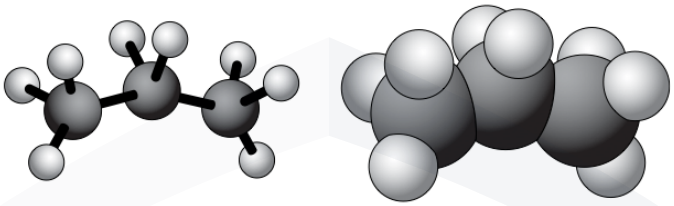
ALKANES

15.1 Alkanes	a) understand the general unreactivity of alkanes, including towards polar reagents b) describe the chemistry of alkanes as exemplified by the following reactions of ethane: (i) combustion (ii) substitution by chlorine and by bromine c) describe the mechanism of free-radical substitution at methyl groups with particular reference to the initiation, propagation and termination reactions d) explain the use of crude oil as a source of both aliphatic and aromatic hydrocarbons e) suggest how cracking can be used to obtain more useful alkanes and alkenes of lower M_r from larger hydrocarbon molecules

ALKANES

Alkanes are the hydrocarbons that make up most of crude oil and natural gas.

In alkane molecules, every carbon atom forms four single covalent bonds.The electrons in these four bonds repel each other to tetrahedral positions around each carbon atom.



structure of propane showing the tetrahedral shape around each carbon atom.

1

PROPERTIES

The alkanes are non-polar molecules with only van der Waals' forces between molecules. This means that they are volatile (evaporate easily), with the first four members being gases at room temperature. Due to their non-polar nature, they are also insoluble in water.

As the molecules get longer and larger, the intermolecular forces increase, so the melting and boiling points rise as the number of carbon atoms per molecule increases.

Because of the weak intermolecular forces they are highly volatile. As the series is ascended due to the increase in the number of electrons the strength of the van der Waals' forces increases.

Consequently the melting and boiling point, density and viscosity increases, while volatility and vapour pressure decreases.

2

PROPERTIES

For any one set of isomers the boiling point decreases as branching increases.

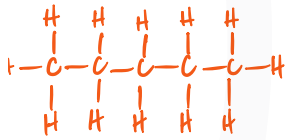
This is because as branching increases the molecules become more nearly spherical and expose less surface area.

Hence less intermolecular forces are exerted. The melting point also depends on the packing of the molecules.

Closer packing leads to higher melting point.

3

STRUCTURES



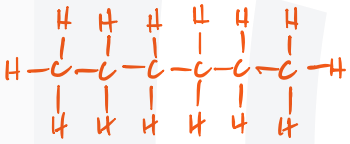
displayed formula of pentane

$CH_3CH_2CH_2CH_2CH_3$

structural formula of pentane



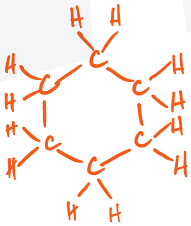
skeletal formula of pentane



displayed formula of hexane



skeletal formula of hexane



displayed formula of cyclohexane



skeletal formula of cyclohexane

4

REACTIVITY

The bond enthalpies of C–C and C–H bonds are relatively high, so the bonds in alkanes are difficult to break.

In addition, these bonds in alkanes are non- polar. This means that alkanes are very unreactive with ionic reagents in water, such as acids, alkalis, oxidising agents and reducing agents.

There are, however, three important reactions of alkanes involving combustion, halogenation and cracking.

5

COMBUSTION

In air or oxygen, alkanes are completely oxidised to carbon dioxide and water, and the reaction is highly exothermic. e.g.

$$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$$

In a limited supply of air or oxygen, alkanes burn incompletely forming highly toxic carbon monoxide, as well as carbon dioxide and water.

If the supply of air or oxygen is even more restricted, the major products will be soot (carbon) and water.

$$C_3H_8 + 3.5O_2 \longrightarrow 3CO + 4H_2O$$
$$C_3H_8 + 2O_2 \longrightarrow 3C + 4H_2O$$

6

COMBUSTION

The exothermic nature of the combustion of alkanes has led to their widespread use as fuels.

Combustion is an exothermic reaction. The greater the number of carbon atoms, the more energy produced and the greater the amount of oxygen needed for complete combustion.

$$C_xH_{y\,(g)} + (x + y/4)O_{2\,(g)} \longrightarrow xCO_{2\,(g)} + y/2\,H_2O_{(l)}$$

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)} \qquad \Delta H^{\ominus} = -890\ kJ\,mol^{-1}$$

$$C_{20}H_{42(l)} + 30.5O_{2(g)} \longrightarrow 20CO_{2(g)} + 21H_2O_{(l)} \qquad \Delta H = -13368\ kJ\,mol^{-1}$$

7

POLLUTION

Motor vehicles are generally the main source of air pollutants. Engines that burn petrol or diesel fuels can pollute the air for three main reasons:

- they do not burn the fuel completely
- the fuel contains impurities
- they run at such a high temperature that nitrogen and oxygen in the air can react.

8

POLLUTION

POLLUTANT	PROBLEMS
Carbon monoxide	A toxic gas that combines strongly with haemoglobin, which means that the blood can carry less oxygen. In low doses, this can put a strain on the heart. In higher doses, it kills
Oxides of nitrogen: NO & NO_2	Reacts with moist air to make nitric acid in acid rain. Affects the lungs and can cause breathing problems
Unburned hydrocarbons	Some of the hydrocarbons, such as benzene, are carcinogenic. Others react with ozone to form harmful pollutants

9

CATALYTIC CONVERTERS

Catalytic converters have done a great deal to improve air quality.

The catalyst speeds up reactions that remove pollutants from motor vehicle exhausts.

The reactions convert oxides of nitrogen to nitrogen and oxygen.

They also convert carbon monoxide to carbon dioxide and unburned hydrocarbons to carbon dioxide and steam.

$$2CO + 2NO \longrightarrow 2CO_2 + N_2$$

$$NO \longrightarrow N_2 + O_2$$

10

GREENHOUSE EFFECT

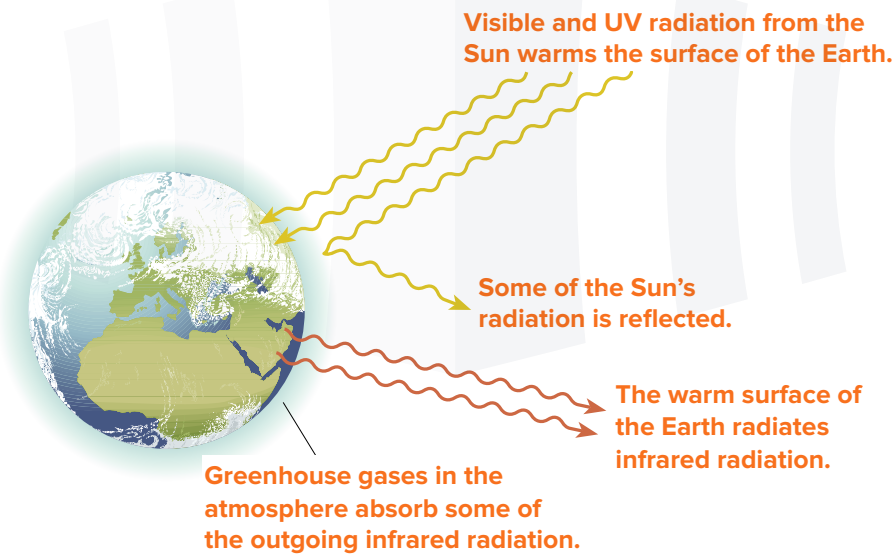
Without the atmosphere, the whole Earth would be colder than Antarctica. The greenhouse effect keeps the surface of the Earth about 30 °C warmer than it would be if there were no atmosphere. With no greenhouse effect, there would be no life on Earth.

When the Sun's radiation reaches the Earth's atmosphere, about 30% is reflected into space, 20% is absorbed by gases in the air and about 50% reaches the surface of the Earth.

The surface of the Earth is very much cooler than the Sun. This means that it radiates most of its energy back into space. Some of this infrared radiation is absorbed by molecules in the air and warms up the atmosphere. This is the greenhouse effect.

11

GREENHOUSE EFFECT



ENHANCED GREENHOUSE EFFECT

The Earth's average temperature stays the same if the energy input from the Sun is balanced by the re-radiation of energy back into space. Anything that changes this steady state gradually leads to global warming or global cooling.

The gases in the air that do absorb infrared radiation are called greenhouse gases. The natural greenhouse gases that help keep the Earth warm are water vapour, carbon dioxide and methane. Water vapour makes the biggest contribution.

Since the Industrial Revolution, human activity has led to a marked increase in the concentrations of greenhouse gases in the atmosphere. This enhances the greenhouse effect. As a result, the Earth warms up more than it would naturally, and as the Earth warms up, its climate changes.

13

GREENHOUSE GASES

This increase in temperature could cause rising sea levels, resulting in the flooding of low-lying areas of land. The climate will also change around the world, with more extreme weather predicted.

Unfortunately, catalytic converters can do nothing to reduce the amount of carbon dioxide (a greenhouse gas) given off in the exhaust gases of cars.

Carbon dioxide is not a toxic gas but it is still considered a pollutant because of its contribution to enhanced global warming.

14

FRACTIONAL DISTILLATION OF CRUDE OIL

B.P / °C	# of C atoms	Name of fraction	Uses
< 25	1 - 4	LPG	Camping Gas
40-100	6 - 12	GASOLINE	Petrol
100-150	7 - 14	NAPHTHA	Petrochemicals
150-200	11 - 15	KEROSINE	Aviation Fuel
220-350	15 - 19	GAS OIL (DIESEL)	Central Heating Fuel
>350	20 - 30	LUBRICATING OIL	Lubrication Oil
> 400	30 - 40	FUEL OIL	Power Station Fuel
> 400	40 - 50	WAX, GREASE	Candles
> 400	> 50	BITUMEN	Road surfaces

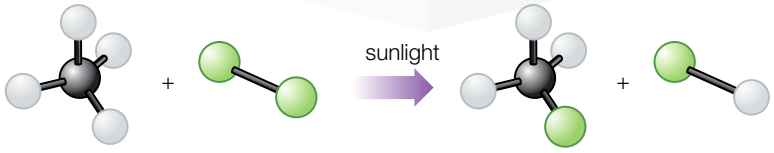
15

REACTION WITH HALOGENS

Alkanes react with chlorine and bromine on exposure to ultraviolet light.

During the reactions, hydrogen atoms in the alkane molecules are replaced (substituted) by halogen atoms. These are described as substitution reactions.

Any or all of the hydrogen atoms in an alkane may be replaced and the reaction can continue until all of the hydrogen atoms have been substituted by halogen atoms.



$CH_4(g) + Cl_2(g) \xrightarrow{\text{sunlight}} CH_3Cl(g) + HCl(g)$

16

FREE RADICAL FORMATION

In the presence of u.v light chlorine undergoes homolysis to give Cl free radicals.



FREE RADICALS are reactive species (atoms or groups) which possess an unpaired electron. However, they are neutral.

Their reactivity is due to them wanting to pair up the single electron.

Formed by homolytic fission (homolysis) of covalent bonds.

17

FREE RADICAL FORMATION

During initiation, the **WEAKEST BOND IS BROKEN** as it requires less energy.

There are three possible bonds in a mixture of alkanes and chlorine.

C — H	C — C	Cl — Cl
410	**350**	**242**

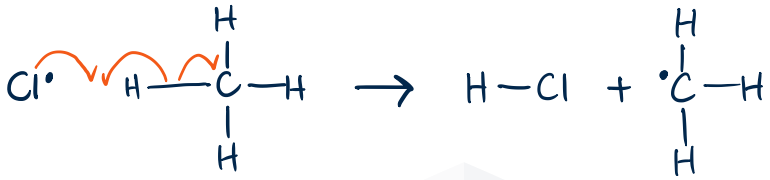
The Cl-Cl bond is broken in preference to the others as it is the weakest and requires requires less energy to separate the atoms.



18

PROPAGATION

The free radicals then attack the methane molecules abstracting a hydrogen atom to form hydrogen chloride and a methyl $CH_3\bullet$ free radical.





19

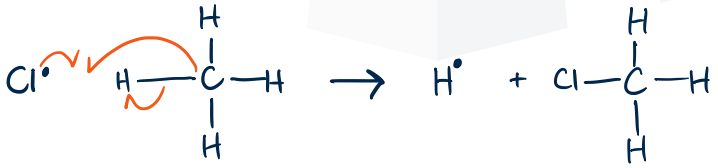
PROPAGATION

Reaction with methane could occur in one of two ways. In the previous reaction, a C—H bond has been broken, and a H—Cl bond has been formed, an exothermic reaction.

C—H = 413 KJ mol^{-1}
H—Cl = 431 KJ mol^{-1}

$\Delta H = 413 - 431 = -18$ KJ mol^{-1}

IF the Cl were to combine with the C atom, a C—H bond would be broken, and a C—Cl bond form and would result in an endothermic reaction.



C—Cl = 338 KJ mol^{-1}

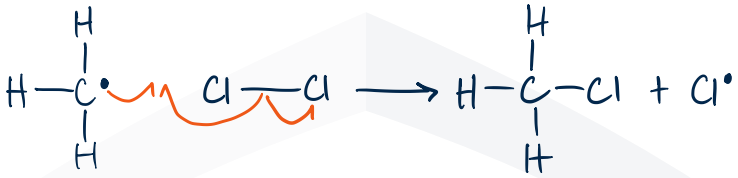
$\Delta H = 413 - 338 = +75$ KJ mol^{-1}

20

PROPAGATION

The methyl radical formed in the first step of propagation is equally as reactive as a chlorine radical.

It is likely to react with the first molecule it collides with. If it collides with a chlorine molecule, the following highly exothermic reaction occurs:



$Cl-Cl = 242$
$C-Cl = 338$

$\Delta H = 242 - 338 = -96\ kJmol^{-1}$

21

PROPAGATION SO FAR

In the initiation reaction, we had produced two reactive chlorine atoms and the following two reactions occur.

$$Cl^{\bullet} + CH_4 \longrightarrow CH_3^{\bullet} + HCl$$

$$CH_3^{\bullet} + Cl_2 \longrightarrow CH_3Cl + Cl^{\bullet}$$

After these two reactions have taken place we have:

- used up one molecule of methane, and one molecule of chlorine
- produced one molecule of chloromethane, and one molecule of hydrogen chloride
- used up a chlorine atom, but regenerated another one.

22

TERMINATION

$Cl^{\bullet} + CH_4 \longrightarrow CH_3^{\bullet} + HCl$ $CH_3^{\bullet} + Cl_2 \longrightarrow CH_3Cl + Cl^{\bullet}$

The above two reactions together constitute a never-ending chain reaction. They could, in theory, continue until all the methane and chlorine had been converted into chloromethane and hydrogen chloride.

This situation does not occur in practice, however. UV light initiates the production of many thousands of molecules of chloromethane.

Eventually the chain reaction comprising the above two reactions stops, because there is a (small) chance that two radicals could collide with each other, to form a stable molecule.

$Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl_2$

$CH_3^{\bullet} + Cl^{\bullet} \longrightarrow CH_3Cl$

$CH_3^{\bullet} + CH_3^{\bullet} \longrightarrow CH_3CH_3$

23

OVERALL

Any of these reactions would use up the free radicals Cl· and CH·3, and so stop the chain reaction.

It would require another chlorine molecule to slit in order to restart the chain.

Overall, the chlorination of methane is an example of a radical substitution reaction.

The different stages of the chain reaction are named as **initiation**, **propagation** and **termination**.

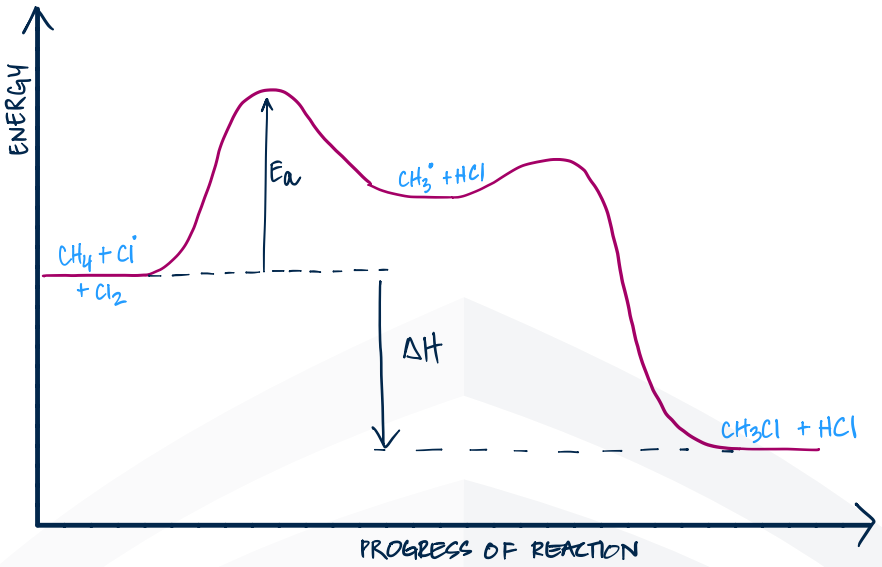
$Cl_2 \longrightarrow 2Cl^{\bullet}$ initiation

$Cl^{\bullet} + CH_4 \longrightarrow CH_3^{\bullet} + HCl$
$CH_3^{\bullet} + Cl_2 \longrightarrow CH_3Cl + Cl^{\bullet}$
} propagation

$Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl_2$
$CH_3^{\bullet} + Cl^{\bullet} \longrightarrow CH_3Cl$
$CH_3^{\bullet} + CH_3^{\bullet} \longrightarrow CH_3CH_3$
} termination

24

CHLORINATION OF METHANE: ENERGY CHANGES



25

FURTHER SUBSTITUTION

As the reaction takes place, the concentration of methane is being reduced, and the concentration of chloromethane is increasing.

Chlorine atoms are therefore increasingly likely to collide with molecules of chloromethane, causing the following reactions to take place:

$$Cl^{\bullet} + CH_3Cl \longrightarrow HCl + {}^{\bullet}CH_2Cl$$
$${}^{\bullet}CH_2Cl + Cl_2 \longrightarrow CH_2Cl_2 + Cl^{\bullet}$$

26

FURTHER SUBSTITUTION

Further substitution gives dichloromethane, trichloromethane and eventually tetrachloromethane. A mixture is formed.

dichloromethane

$$Cl^{\bullet} + CH_3Cl \longrightarrow CH_2Cl^{\bullet} + HCl$$
$$Cl_2 + CH_2Cl^{\bullet} \longrightarrow CH_2Cl_2 + Cl^{\bullet}$$

trichloromethane

$$Cl^{\bullet} + CH_2Cl_2 \longrightarrow CHCl_2^{\bullet} + HCl$$
$$Cl_2 + CHCl_2^{\bullet} \longrightarrow CHCl_3 + Cl^{\bullet}$$

tetrachloromethane

$$Cl^{\bullet} + CHCl_3 \longrightarrow CCl_3^{\bullet} + HCl$$
$$Cl_2 + CCl_3^{\bullet} \longrightarrow CCl_4 + Cl^{\bullet}$$

27

BY PRODUCTS

A set of by-products are chlorinated ethanes.

These arise from the ethane produced in termination) undergoing a similar set of substitution reactions, or chloromethyl radicals combining at termination stages.

28

BROMINATION OF ETHANE

Bromine reacts with ethane to produce bromoethane, C_2H_5Br. The reaction is a free radical substitution reaction.

Initiation: Bromine splits by homolytic fission using UV light.

$$Br_2(g) \longrightarrow 2Br^{\bullet}$$

Propagation: The Br• radical removes a hydrogen atom from ethane.

$$Br^{\bullet} + C_2H_6 \longrightarrow C_2H_5^{\bullet} + HBr$$

$$C_2H_5^{\bullet} + Br_2 \longrightarrow C_2H_5Br + Br^{\bullet}$$

Termination: Two radicals join to form a molecule.

$$Br^{\bullet} + C_2H_5^{\bullet} \longrightarrow C_2H_5Br$$

29

HALOGENATION OF HIGHER ALKANES

There are two monochloropropane isomers: 1-chloropropane, $CH_3CH_2CH_2Cl$, and 2-chloropropane, $CH_3CHClCH_3$.

When propane reacts with chlorine, a mixture of the two monochloro- compounds is produced.

This is because the chlorine atom can abstract either one of the end-carbon hydrogens or one of the middle-carbon hydrogens, the former resulting in $CH_3CH_2CH_2Cl$ and the latter $CH_3CHClCH_3$.

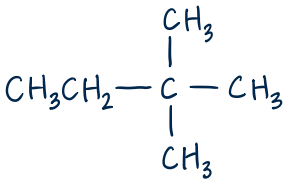
$$Cl^{\bullet} + CH_3-CH_2-CH_3 \longrightarrow CH_3-CH_2-CH_2^{\bullet} + H-Cl$$

$$Cl^{\bullet} + CH_3-CH_2-CH_3 \longrightarrow CH_3-\dot{C}H-CH_3 + H-Cl$$

30

SKILL CHECK

Draw the structures of all possible free radicals in the mono-chloro substitution of:



31

HALOGENATION OF HIGHER ALKANES

The above reaction can produce organic by-products, in addition to C_2H_5Cl. Draw the structural formulae of four possible organic by-products. Two of your by-products should contain 4 carbon atoms per molecule and write the equation of the formation of each of your four products.

32

SKILL CHECK

Predict the major organic products formed during the monobromination of:

(a) $CH_3CH_2CH_2CH_3$

(b) $(CH_3)_2CH—CH_3$

33

CRACKING

Cracking is the decomposition of hydrocarbons by heat and pressure with or without a catalyst to produce lighter hydrocarbons, specially in oil refining. It is the breakdown of a large alkane into smaller, more useful alkenes and an alkane.

The larger hydrocarbon molecules are fed into a steel chamber which contains no oxygen, so combustion does not take place. The larger hydrocarbon molecules are heated to a high temperature and are passed over a catalyst.

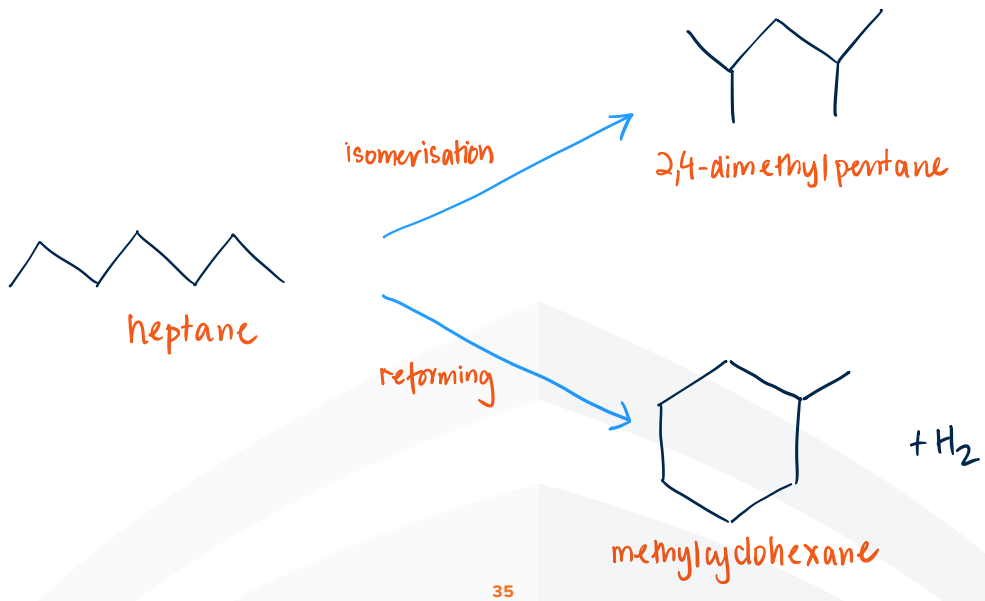
When large alkane molecules are cracked they form smaller alkane molecules and alkene molecules. Possible examples of a cracking reaction are:

$$C_{10}H_{22} \longrightarrow C_6H_{14} + C_4H_8$$

$$C_{10}H_{22} \longrightarrow C_3H_8 + C_2H_4 + C_5H_{10}$$

34

OTHER REACTIONS



35

ALKANES WS 1

SECTION A

1 The hydrocarbon $C_{17}H_{36}$ can be cracked.

Which compound is the **least** likely to be produced in this reaction?

A C_3H_8 **B** C_4H_8 **C** C_8H_{16} **D** $C_{16}H_{34}$

[S'14 11 Q27]

2 In the presence of ultraviolet light, ethane and chlorine react to give a mixture of products.

Which compound could be present in the mixture of products?

A CH_3Cl

B $CH_3CH_2CH_2Cl$

C $CH_3CH_2CH_2CH_3$

D $CH_3CH_2CH_2CH_2CH_3$

[S'14 13 Q21]

3 Which molecule could **not** be obtained from the cracking of a molecule of nonane, $CH_3(CH_2)_7CH_3$?

A $CH_2=CHCH=CH_2$

B $CH_3CH_2CH_2CH_2CH_3$

C $CH_3CH_2CH_2CH_2CH_2CH=CH_2$

D $(CH_3CH_2CH_2)_3CH$

[S'14 13 Q23]

4 The free radical substitution reaction between methane and chlorine involves initiation, propagation and termination stages.

Which row is correct?

	involved in initiation stage	radical produced in a propagation stage
A	heterolytic fission	H•
B	heterolytic fission	CH_3•
C	homolytic fission	H•
D	homolytic fission	CH_3•

[S'14 13 Q30]

5 Which equation correctly represents the balanced equation for the complete combustion of a hydrocarbon with the formula C_xH_y?

A $C_xH_y + (x + \frac{y}{2})O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$

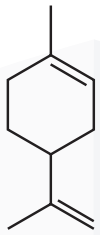
B $C_xH_y + (x + \frac{y}{4})O_2 \rightarrow xCO_2 + yH_2O$

C $C_xH_y + (x + \frac{y}{4})O_2 \rightarrow xCO_2 + \frac{y}{4}H_2O$

D $C_xH_y + (x + \frac{y}{4})O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$

[W'14 11 Q29]

6 The citrus flavour of lemons is due to the compound limonene, present in both the peel and the juice.



limonene

What is the mole ratio of carbon dioxide to water produced when limonene is completely burnt in oxygen?

	number of moles carbon dioxide	number of moles water
A	4	3
B	5	4
C	5	8
D	9	7

[S'15 11 Q29]

7 Crude oil is a mixture of many hydrocarbons ranging in size from 1 to 40 carbon atoms per molecule. The alkanes in crude oil can be separated because they have different boiling points.

The table below shows the boiling points of some alkanes.

alkane	boiling point / °C	M_r
butane	0	58
pentane	36	72
hexane	69	86
2-methylbutane	28	72
dimethylpropane	10	72
2,3-dimethylbutane	58	86

What is the correct explanation for the difference in the boiling points of the three isomers with M_r = 72?

A Boiling point is dependent upon the length of the carbon chain **only**.

B Increased branching on a carbon chain increases the boiling point.

C Increased branching reduces the strength of the intermolecular hydrogen bonding.

D Increased branching reduces the strength of the intermolecular van der Waals' forces.

[W'15 11 Q22]

8 Which equation represents a valid propagation step in the chlorination of ethane?

A $C_2H_6 + Cl\bullet \rightarrow C_2H_5Cl + H\bullet$

B $C_2H_5Cl + Cl\bullet \rightarrow C_2H_4Cl\bullet + HCl$

C $C_2H_5Cl + H\bullet \rightarrow C_2H_5\bullet + HCl$

D $C_2H_5\bullet + Cl\bullet \rightarrow C_2H_5Cl$

[J'18 12 Q21]

SECTION B

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

1 A car has a catalytic converter fitted to its exhaust. On analysis its exhaust gases are shown to contain small quantities of nitrogen oxides.

Which modifications would result in lower exhaust concentrations of nitrogen oxides?

1 an increase in the surface area of the catalyst in the converter

2 an increase in the rate of flow of the exhaust gases through the converter

3 a much higher temperature of combustion in the engine

[J'14 12 Q36]

2 The chlorine oxide free radical, $Cl O\bullet$, is produced by the reaction between chlorine atoms and ozone.

$$Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$$

Which features are present in the chlorine oxide free radical?

1 an odd number of electrons

2 a single covalent bond

3 a dative covalent bond from oxygen to chlorine

[N'17 12 Q32]

ALKANES WS 2

1 **(a)** Define the term *mole*.

.....

..... [1]

(b) 10 cm^3 of a gaseous hydrocarbon, C_xH_y, was reacted with 100 cm^3 of oxygen gas, an excess.

The final volume of the gaseous mixture was 95 cm^3.

This gaseous mixture was treated with concentrated, aqueous sodium hydroxide to absorb the carbon dioxide present. This reduced the gas volume to 75 cm^3.

All gas volumes were measured at 298 K and 100 kPa.

(i) Write an equation for the reaction between sodium hydroxide and carbon dioxide.

..... [1]

(ii) Calculate the volume of carbon dioxide produced by the combustion of the hydrocarbon.

volume of CO_2 produced = ... cm^3 [1]

(iii) Calculate the volume of oxygen used up in the reaction with the hydrocarbon.

volume of O_2 used = ... cm^3 [1]

(iv) Use your answers to **(b)(ii)** and **(b)(iii)**, together with the initial volume of hydrocarbon, to balance the equation below.

$$\text{.....}C_xH_y + \text{.....}O_2 \rightarrow \text{.....}CO_2 + zH_2O \quad [2]$$

(v) Deduce the values of *x*, *y* and *z* in the equation in **(iv)**.

x = ...

y = ...

z = ...

[3]

[S'14 23 Q1]

2 Ethane reacts with chlorine to form chloroethane.

$$C_2H_6(g) + Cl_2(g) \rightarrow C_2H_5Cl(g) + HCl(g)$$

(a) (i) Use bond energies from the *Data Booklet* to calculate the enthalpy change for this reaction. Include a sign in your answer.

enthalpy change = ... $kJ\,mol^{-1}$ [3]

(ii) State the conditions needed for this reaction to occur.

..... [1]

(iii) Use a series of equations to describe the mechanism of this reaction including the names of each stage and an indication of how butane can be produced as a minor by-product.

.....

.....

.....

.....

.....

..... [5]

(b) Chloroethane can be converted back into ethane by a two-stage process via an intermediate compound, **X**.

$$C_2H_5Cl \xrightarrow{\text{reaction 1}} \mathbf{X} \xrightarrow{\text{reaction 2}} C_2H_6$$

(i) Give the name of **X**.

..... [1]

(ii) Suggest the reagent and conditions needed for reaction 1.

..... [2]

(iii) Suggest the reagent and conditions needed for reaction 2.

..... [1]

[S'15 22 Q3]

3 Heptane, C_7H_{16}, is an undesirable component of petrol as it burns explosively causing 'knocking' in an engine.

(a) There are nine structural isomers with the formula C_7H_{16}, only two of which contain chiral centres.

(i) Explain the meanings of the terms *structural isomers* and *chiral*.

structural isomers .....

.....

.....

chiral .....

.....

.....

[2]

(ii) Give the structures and names of the two structural isomers of C_7H_{16} which contain a chiral centre.

[4]

(b) **(i)** Write an equation for the complete combustion of heptane.

..... [1]

(ii) Write an equation for the incomplete combustion of heptane leading to the production of a solid pollutant.

..... [1]

(iii) Incomplete combustion can also lead to emission of unburnt hydrocarbons.

State one environmental consequence of this.

..... [1]

(c) The reaction of heptane with chlorine in the presence of UV light produces a wide variety of products.

Formation of the monochloroheptanes can be represented by the following equation.

$$C_7H_{16} + Cl_2 \rightarrow C_7H_{15}Cl + HCl$$

(i) Name the mechanism of the reaction between heptane and chlorine in the presence of UV light.

..... [1]

(ii) Describe this mechanism, using suitable equations and including the names of each stage in the process.

.....

.....

.....

.....

.....

.....

.....

.....

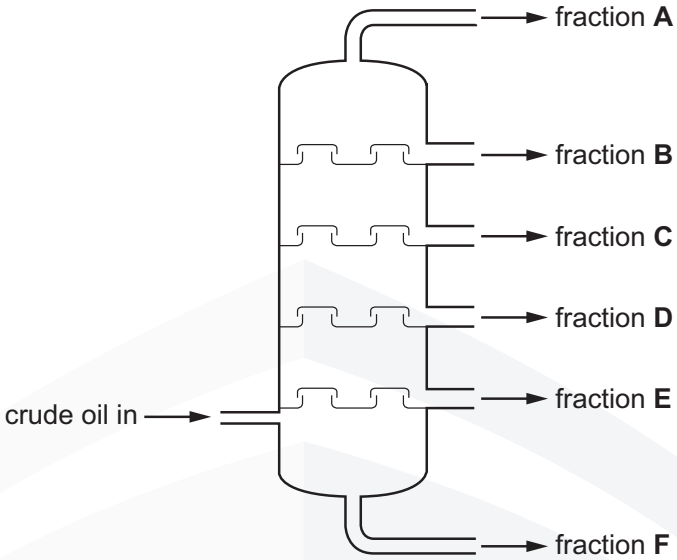
..... [5]

[W'15 21 Q3]

4 Crude oil is a mixture of hydrocarbons and provides many useful chemicals when processed.

Two of the stages involved in the processing of crude oil are fractional distillation and cracking.

(a) The diagram is a simplified representation of a fractional distillation column.



(i) What has to be done to the crude oil before it enters the column?

..... [1]

(ii) What trend in **structure** is there from fraction **A** to fraction **F**?

.....

..... [1]

(iii) State the trends in **two** properties of the fractions from **A** to **F**.

.....

.....

..... [2]

(b) The naphtha fraction from fractional distillation of crude oil is used as a starting material for cracking.

(i) Write an equation for the cracking of $C_{12}H_{26}$ to form the products ethene and one other hydrocarbon in a 2 : 1 mole ratio.

..... [1]

(ii) Suggest a use for each of the products from your equation in **(i)**. Explain what makes each product from **(i)** suitable for the use you suggest.

use of ethene .....

.....

explanation .....

.....

use of other product .....

.....

explanation .....

.....

[4]

(c) Burning hydrocarbons can cause a number of environmental problems.

The products of internal combustion engines can include oxides of nitrogen and oxides of carbon.

Sulfur dioxide is a by-product of burning coal in power stations.

(i) Explain how and why oxides of nitrogen are produced in internal combustion engines.

.....

.....

..... [2]

(ii) Write an equation for the reaction between nitrogen monoxide and carbon monoxide in a catalytic converter.

..... [1]

(iii) Write equations to show the involvement of nitrogen monoxide in the formation of acid rain from atmospheric sulfur dioxide.

.....

.....

..... [3]

(iv) Describe two of the problems associated with acid rain.

.....

.....

..... [2]

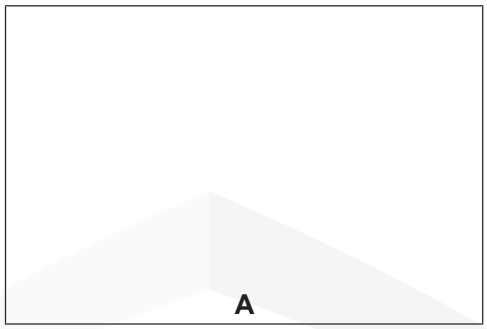
[S'16 23 Q3]

5 **(a)** The hydrocarbons **A**, C_4H_{10}, and **B**, C_4H_8, are both unbranched.

A does **not** decolourise bromine.

B decolourises bromine and shows geometrical isomerism.

(i) Draw the skeletal formula of **A**.



[1]

(ii) The hydrocarbon **A**, C_4H_{10}, has a branched isomer.

Suggest why unbranched **A** has a higher boiling point than its branched isomer.

.....

.....

.....

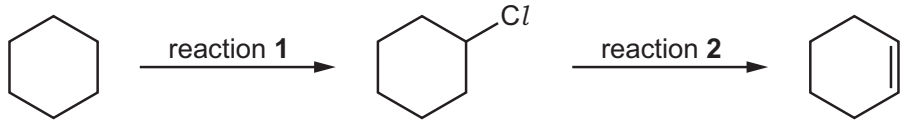
.....

..... [2]

[S'17 22 Q4]

6 Cyclohexane is a colourless liquid used in industry to produce synthetic fibres.

A reaction scheme involving cyclohexane is shown.

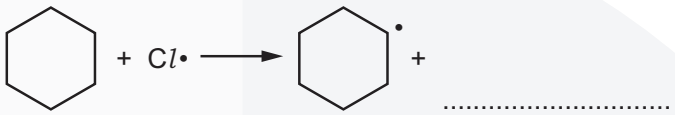
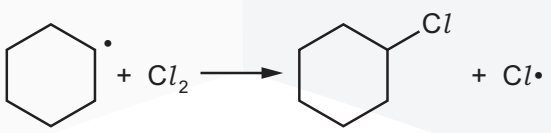


(a) Reaction **1** involves a free radical substitution mechanism.

(i) State the essential condition required for reaction **1** to occur.

..... [1]

(ii) Complete the table to give details of the mechanism in reaction **1**.

name of step	reaction
.....	$Cl_2 \longrightarrow 2Cl\bullet$
propagation	
.....	
termination	

[4]

(b) Name the type of reaction that occurs in reaction **2**.

..... [1]

[M'18 22 Q4]

7 Crude oil is a complex mixture of hydrocarbon molecules.

The hydrocarbon molecules in crude oil are separated by fractional distillation. Fractional distillation is used because the different hydrocarbon molecules in crude oil have different boiling points.

(a) Explain why the hydrocarbon molecules in crude oil have different boiling points.

.....

.....

.....

.....

.....

.....

..... [2]

(b) Some of the hydrocarbon molecules obtained from crude oil are processed further by cracking.

Suggest why some hydrocarbon molecules are processed further by cracking.

.....

.....

..... [1]

[J'18 21 Q2]

8 Most vehicle fuels contain hydrocarbons obtained from crude oil.

(a) (i) State the name of the type of reaction that hydrocarbons undergo when being used as fuels.

..... [1]

(ii) Write an equation for the reaction of octane, C_8H_{18}, as a fuel, as in **(a)(i)**.

..... [2]

(b) The supply of material suitable for use as fuels directly from crude oil is **not** sufficient to meet demand. A process is carried out to make some of the larger hydrocarbon molecules more useful.

(i) Name this process.

..... [1]

[J'18 22 Q3]

ALKANES WS 3

SECTION A

1 What is the total number of different chloroethanes (formula $C_2H_{6-n}Cl_n$, where n can be any integer from 1 to 6)?

A 6 **B** 8 **C** 9 **D** 10

[S'02 Q21]

2 As a simplification, an adult human can be considered to have a daily diet of 1.80 kg of carbohydrate (empirical formula CH_2O).

Which mass of carbon dioxide does a person produce each day if all the carbohydrate eaten is digested and oxidised?

A 0.267 kg **B** 0.800 kg **C** 1.32 kg **D** 2.64 kg

[S'02 Q2]

3 Which substance in a vehicle exhaust results from incomplete combustion of a hydrocarbon fuel?

A CO **B** H_2O **C** N_2 **D** NO

[S'02 Q24]

4 Which gas is present in the exhaust fumes of a car engine in a much greater amount than any other gas?

A carbon dioxide

B carbon monoxide

C nitrogen

D water vapour

[W'02 Q19]

5 Chloroethane is used as a starting material for the production of 'time-release capsules' in pharmaceutical products. One way of preparing chloroethane is to react chlorine and ethane in the presence of ultraviolet light.

Which statement is correct about the **first** stage of the mechanism of this reaction?

A The C*l* – C*l* bond is split homolytically.

B The C*l* – C*l* bond is split heterolytically.

C The C – H bond is split homolytically.

D The C – H bond is split heterolytically.

[W'02 Q22]

6 One of the most important chemical species responsible for the removal of ozone from the stratosphere is a free radical of chlorine, $^{35}Cl^{\bullet}$.

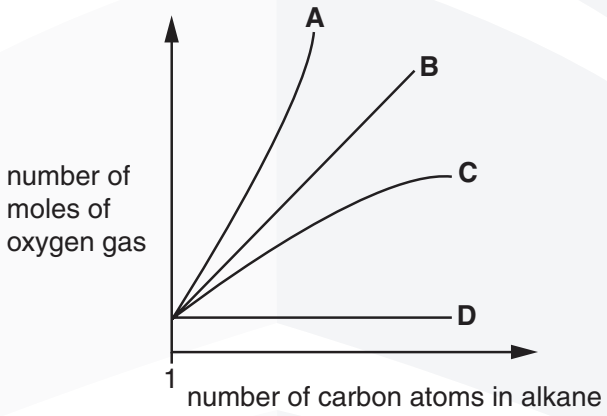
What does $^{35}Cl^{\bullet}$ contain?

	protons	neutrons	electrons
A	17	18	16
B	17	18	17
C	18	17	17
D	18	17	18

[W'02 Q2]

7 The complete combustion of alkanes to produce carbon dioxide and water is an important exothermic reaction.

Which line on the graph shows the relationship between the number of carbon atoms in the alkane and the number of moles of oxygen gas needed for complete combustion of the alkane?



[S'03 Q23]

8 Which pollutant is formed in the internal combustion engine and, if not removed by the catalytic converter, may become involved in the formation of acid rain?

A C **B** C_8H_{18} **C** CO **D** NO

[S'03 Q19]

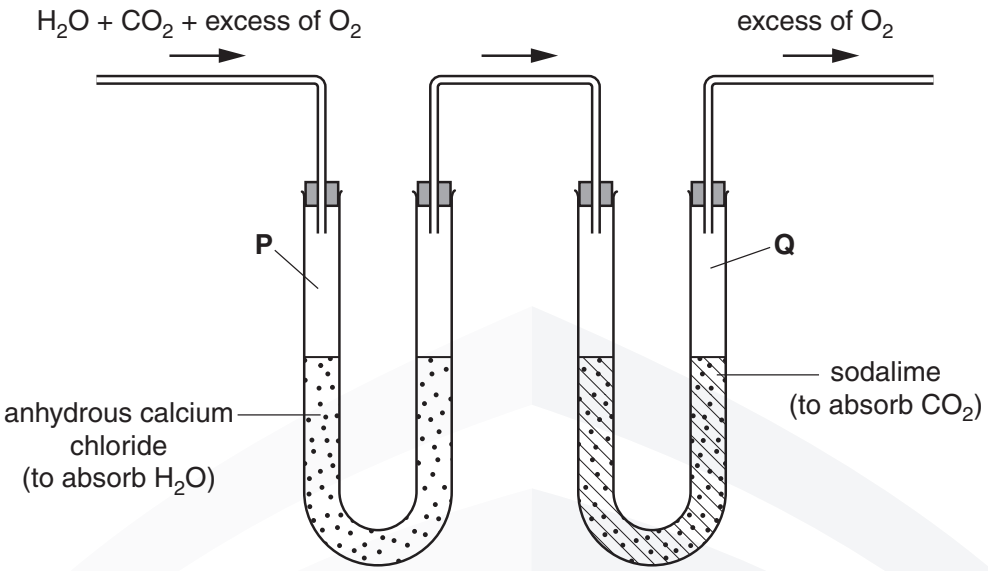
9 On strong heating a hydrocarbon produces ethene, propane and but-1-ene in the mole ratio 5 : 1 : 1.

What is the molecular formula of the hydrocarbon?

A $C_{17}H_{34}$ **B** $C_{17}H_{36}$ **C** $C_{19}H_{38}$ **D** $C_{19}H_{40}$

[W'03 Q22]

10 A sample of the hydrocarbon C_6H_{12} is completely burned in dry oxygen and the product gases are collected as shown.
[A_r : H, 1 ; C, 12 ; O, 16.]



The increases in mass of the collecting vessels **P** and **Q** of the apparatus are M_P and M_Q, respectively.

What is the ratio M_P / M_Q?

A 0.41 **B** 0.82 **C** 1.2 **D** 2.4

[W'03 Q3]

11 Which compound could **not** be obtained from cracking a sample of nonane, $CH_3(CH_2)_7CH_3$?

A $CH_3CH{=}CHCH{=}CHCH_2CH_2CH_2CH_3$

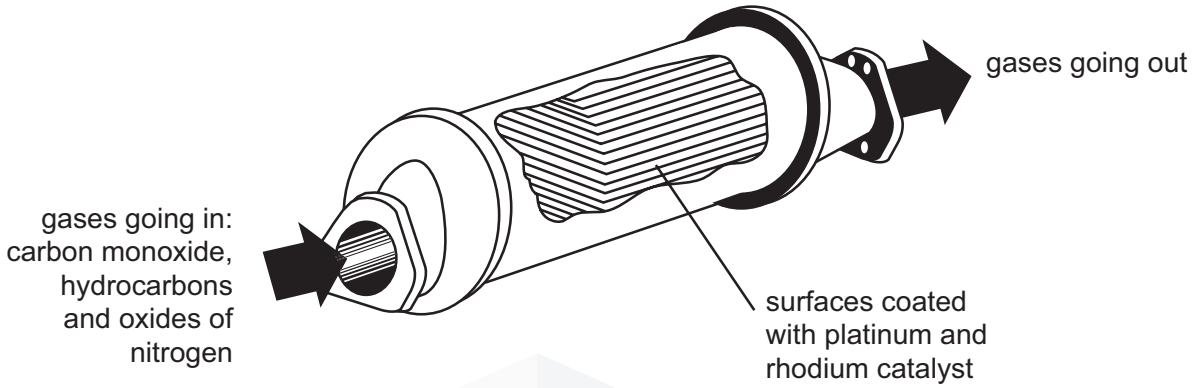
B $CH_3CH_2CH_2CH_2CH_3$

C $CH_3CH_2CH_2CH_2CH_2CH{=}CH_2$

D $(CH_3CH_2CH_2)_3CH$

[S'04 Q23]

12 Which reaction in the catalytic converter does **not** remove hazardous and polluting gases from the exhaust fumes of a motor car?



These equations are qualitative and unbalanced.
[HC = unburnt hydrocarbons; NO_x = oxides of nitrogen]

A $HC + NO_x \rightarrow H_2O + CO + N_2$

B $CO + NO_x \rightarrow CO_2 + N_2$

C $HC + NO_x \rightarrow H_2O + CO_2 + N_2$

D $CO + O_2 \rightarrow CO_2$

[S'04 Q25]

13 Granular urea, CON_2H_4, can be used to remove NO_2 from the flue gases of power stations, converting it into harmless nitrogen.

$$2CON_2H_4 + x\,NO_2 \rightarrow 2CO_2 + y\,H_2O + z\,N_2$$

What are the values of *x*, *y* and *z* in a balanced equation?

	x	*y*	*z*
A	1½	2	1¼
B	2	4	3
C	3	4	3½
D	3	4	3

[W'04 Q1]

14 The foul smell that skunks spray is due to a number of thiols, one of which is methanethiol, CH_3SH, which burns as follows.

$$CH_3SH + 3O_2 \rightarrow CO_2 + SO_2 + 2H_2O$$

A sample of 10 cm^3 of methanethiol was exploded with 60 cm^3 of oxygen.

What would be the final volume of the resultant mixture of gases when cooled to room temperature?

A 20 cm^3 **B** 30 cm^3 **C** 50 cm^3 **D** 70 cm^3

[W'04 Q3]

15 Which of these compounds, on complete combustion of one mole, will release the greatest amount of energy?

A $CH_3CH_2CH_2OH$

B $CH_3CH_2CH_3$

C $CH_3CH_2CO_2H$

D CH_3COCH_3

[W'04 Q9]

16 How many different substitution products are possible, in principle, when a mixture of bromine and ethane is allowed to react?

A 3 **B** 5 **C** 7 **D** 9

[W'04 Q23]

17 Which reaction occurs with saturated hydrocarbons?

A catalytic hydrogenation

B ready decolourisation of aqueous bromine

C polymerisation

D thermal cracking

[W'04 Q25]

18 The reaction of chlorine with methane is carried out in the presence of light.

What is the function of the light?

A to break the C – H bonds in methane

B to break up the chlorine molecules into atoms

C to break up the chlorine molecules into ions

D to heat up the mixture

[W'04 Q26]

19 A pure hydrocarbon is used in bottled gas for cooking and heating.

When 10 cm^3 of the hydrocarbon is burned in 70 cm^3 of oxygen (an excess), the final gaseous mixture contains 30 cm^3 of carbon dioxide and 20 cm^3 of unreacted oxygen. All gaseous volumes were measured under identical conditions.

What is the formula of the hydrocarbon?

A C_2H_6 **B** C_3H_6 **C** C_3H_8 **D** C_4H_{10}

[S'05 Q1]

20 The petrol additive tetraethyl-lead(IV), $Pb(C_2H_5)_4$, is now banned in many countries. When it is completely burned in air, lead(II) oxide, CO_2 and H_2O are formed.

How many moles of oxygen are required to burn one mole of $Pb(C_2H_5)_4$?

A 9.5 **B** 11 **C** 13.5 **D** 27

[W'05 Q1]

21 Light initiates the following reaction.

alkane + chlorine → chloroalkane + hydrogen chloride

What happens to chlorine in this photochemical reaction?

A heterolytic fission to give an electrophile

B homolytic fission to give an electrophile

C heterolytic fission to give a free radical

D homolytic fission to give a free radical

[S'06 Q24]

22 When gaseous chemicals are transported by road or by rail they are classified as follows.

flammable non-flammable poisonous

Which commonly transported gas is non-flammable?

A butane

B hydrogen

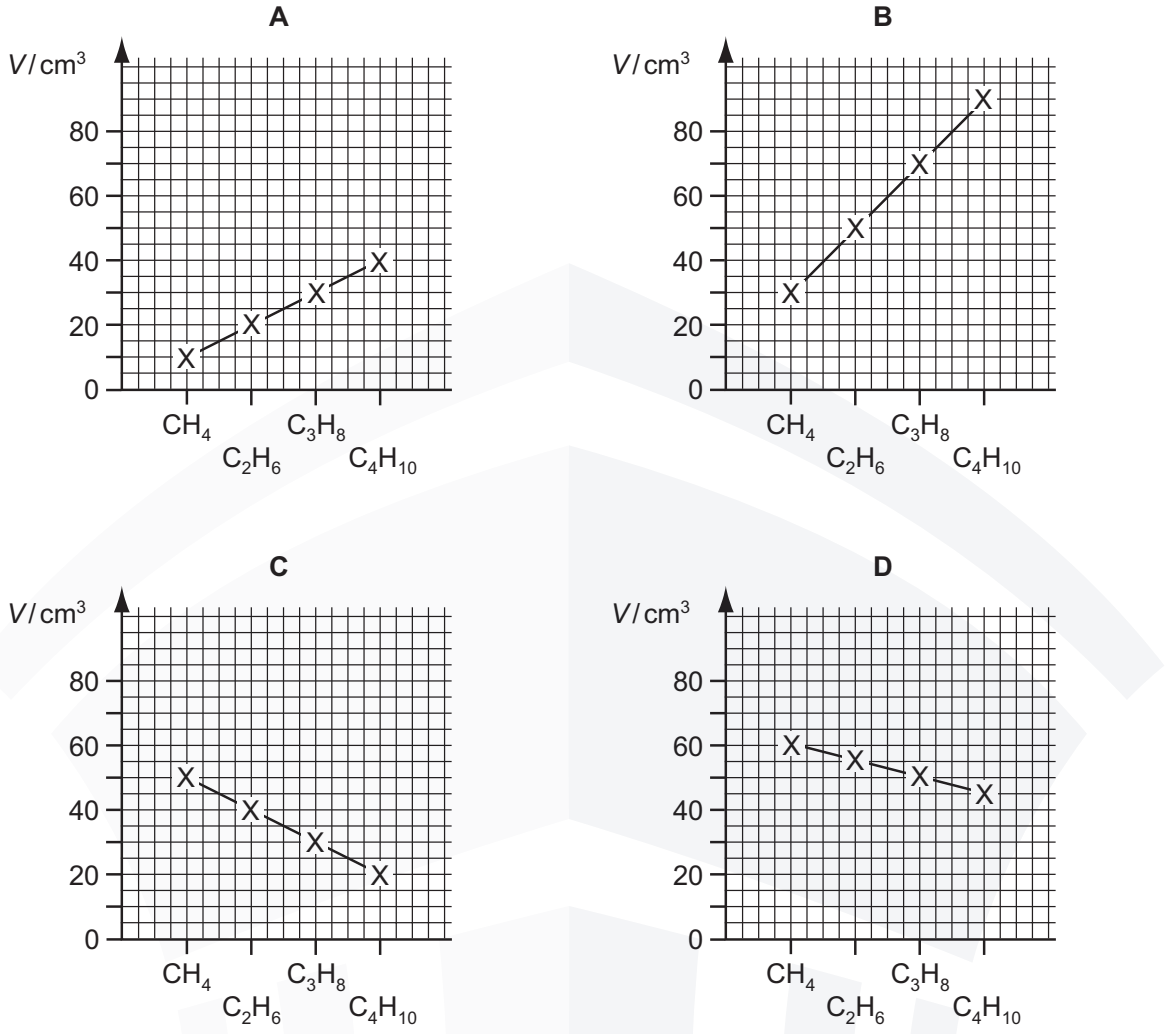
C oxygen

D propene

[W'06 Q24]

23 Samples of 10 cm^3 of each of the first four members of the alkane series are separately mixed with 70 cm^3 of oxygen. Each is then burned and the total volume, *V*, of residual gas measured again at room temperature and pressure.

Which graph represents the results that would be obtained?



[W'06 Q4]

24 Tetramethyl-lead(IV), $(CH_3)_4Pb$, increases the rate of the reaction of methane with chlorine.

$$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$$

Why can tetramethyl-lead(IV) behave in this way?

A It is a source of methyl radicals.

B It releases $CH_3^+(g)$.

C It reacts with chloromethane and prevents equilibrium being established.

D Metal ions catalyse the reaction.

[W'07 Q21]

25 Which reaction occurs when ethane and chlorine are mixed in diffused sunlight?

A a free-radical substitution with hydrogen given off

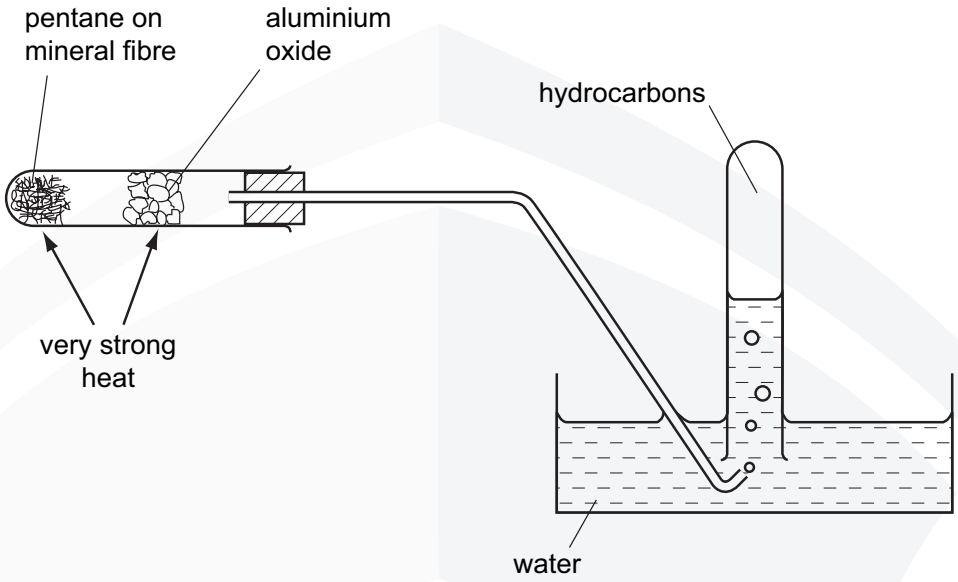
B a free-radical substitution with hydrogen chloride given off

C a free-radical substitution with no gas given off

D a nucleophilic substitution with hydrogen chloride given off

[W'07 Q22]

26 Which hydrocarbon would **not** be collected in the inverted tube by heating pentane, $CH_3(CH_2)_3CH_3$, in the apparatus shown?



A CH_4

B CH_3CH_3

C $CH_3CH_2CH=CH_2$

D $CH_3(CH_2)_8CH_3$

[S'08 Q23]

27 Which hydrocarbon can form a monochloro-substitution derivative which shows **both** chirality **and** *cis-trans* isomerism?

A $CH_3CH=CH_2$

B $(CH_3)_2C=CH_2$

C $CH_3CH=C(CH_3)_2$

D $CH_3CH=CHCH_2CH_3$

[W'08 Q22]

28 Carbon disulphide vapour burns in oxygen according to the following equation.

$$CS_2(g) + 3O_2(g) \rightarrow CO_2(g) + 2SO_2(g)$$

A sample of 10 cm^3 of carbon disulphide was burned in 50 cm^3 of oxygen. After measuring the volume of gas remaining, the product was treated with an excess of aqueous sodium hydroxide and the volume of gas measured again. All measurements were made at the same temperature and pressure, under such conditions that carbon disulphide was gaseous.

What were the measured volumes?

	volume of gas after burning / cm^3	volume of gas after adding NaOH(aq) / cm^3
A	30	0
B	30	20
C	50	20
D	50	40

[W'08 Q2]

29 In leaded petrol there is an additive composed of lead, carbon and hydrogen only. This compound contains 29.7 % carbon and 6.19 % hydrogen by mass.

What is the value of **x** in the empirical formula PbC_8H_x?

A 5 **B** 6 **C** 16 **D** 20

[S'09 Q1]

30 0.200 mol of a hydrocarbon undergo complete combustion to give 35.2 g of carbon dioxide and 14.4 g of water as the only products.

What is the molecular formula of the hydrocarbon?

A C_2H_4 **B** C_2H_6 **C** C_4H_4 **D** C_4H_8

[W'09 11 Q2]

31 Which equation represents a valid propagation step in the free radical reaction between ethane and chlorine?

A $C_2H_6 + Cl^{\bullet} \rightarrow C_2H_5Cl + H^{\bullet}$

B $C_2H_5Cl + Cl^{\bullet} \rightarrow C_2H_4Cl^{\bullet} + HCl$

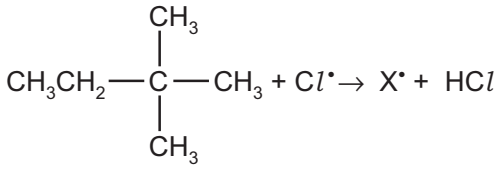
C $C_2H_6 + H^{\bullet} \rightarrow C_2H_5^{\bullet} + HCl$

D $C_2H_5^{\bullet} + Cl^{\bullet} \rightarrow C_2H_5Cl$

[W'09 12 Q25]

32 When heated with chlorine, the hydrocarbon 2,2-dimethylbutane undergoes free radical substitution.

In a propagation step the free radical X• is formed.



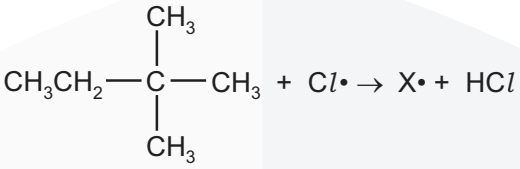
How many different forms of X• are possible?

A 1 **B** 2 **C** 3 **D** 4

[S'10 11 Q21]

33 When heated with chlorine, the hydrocarbon 2,2-dimethylbutane undergoes free radical substitution.

In a propagation step a free radical X• is formed.



How many different forms of X• are possible?

A 1 **B** 2 **C** 3 **D** 4

[S'10 11 Q21]

34 Which environmental problem is **not** made worse by the release of oxides of nitrogen from car engines?

A acidification of lakes

B corrosion of buildings

C photochemical smog

D the hole in the ozone layer

[W'10 11 Q30]

35 The formula CH_3 can represent an anion, a cation or a free radical. Species with the molecular formula CH_3 can act as an electrophile, a free radical or a nucleophile depending on the number of outer shell electrons on the central carbon atom.

How many outer shell electrons must be present for CH_3 to act in these different ways?

	CH_3 as an electrophile	CH_3 as a free radical	CH_3 as a nucleophile
A	6	7	8
B	6	8	7
C	7	6	8
D	8	7	6

[S'11 11 Q22]

36 The products obtained by cracking an alkane, **X**, are methane, ethene and propene.

The mole fraction of ethene in the products is 0.5.

What is the identity of **X**?

A C_6H_{14} **B** C_8H_{18} **C** C_9H_{20} **D** $C_{11}H_{24}$

[S'11 12 Q23]

37 Carbon monoxide, CO, nitrogen monoxide, NO, and sulfur dioxide, SO_2, may all be present in the exhaust fumes from a car engine.

Which reaction concerning these compounds occurs in the atmosphere?

A CO is spontaneously oxidised to CO_2

B NO_2 is reduced to NO by CO

C NO_2 is reduced to NO by SO_2

D SO_2 is oxidised to SO_3 by CO_2

[S'12 11 Q19]

38 Oct-1-ene, $CH_3(CH_2)_5CH{=}CH_2$, is subjected to thermal cracking.

Which combination of compounds W, X, Y and Z can be obtained?

$CH_2{=}CH_2$	$CH_3CH{=}CH_2$	$CH_3CH_2CH_3$	$CH_2{=}CHCH{=}CH_2$
W	X	Y	Z

A W, X, Y and Z

B W, X and Y only

C W, X and Z only

D W and X only

[S'12 12 Q24]

39 The cracking of a single hydrocarbon molecule, C_nH_{2n+2}, produces two hydrocarbon molecules only. Each hydrocarbon product contains the same number of carbon atoms in one molecule. Each hydrocarbon product has non-cyclic structural isomers.

What is the value of n?

A 4 **B** 6 **C** 8 **D** 9

[W'12 11 Q23]

40 One of the reactions taking place in a catalytic converter in a car exhaust system is between nitrogen oxide and octane (unburned petrol). The products of this reaction are non-toxic.

Which is the correct equation for the reaction?

A $C_8H_{16} + 16NO \rightarrow 8CO + 8N_2 + 8H_2O$

B $C_8H_{16} + 24NO \rightarrow 8CO_2 + 12N_2 + 8H_2O$

C $C_8H_{18} + 17NO \rightarrow 8CO + 8\frac{1}{2}N_2 + 9H_2O$

D $C_8H_{18} + 25NO \rightarrow 8CO_2 + 12\frac{1}{2}N_2 + 9H_2O$

[W'12 11 Q25]

41 A mixture of 10 cm^3 of methane and 10 cm^3 of ethane was sparked with an excess of oxygen. After cooling to room temperature, the residual gas was passed through aqueous potassium hydroxide.

What volume of gas was absorbed by the alkali?

A 15 cm^3

B 20 cm^3

C 30 cm^3

D 40 cm^3

[S'13 11 Q2]

42 Pentane, C_5H_{12}, is reacted with chlorine in the presence of ultraviolet light. A compound R is found in the products. R has molecular formula $C_5H_{10}Cl_2$. Each molecule of R contains **one** chiral carbon atom.

Which two atoms of the pentane chain could be bonded to chlorine atoms in this isomer?

A 1 and 3 **B** 1 and 5 **C** 2 and 3 **D** 2 and 4

[S'13 11 Q25]

43 Which volume of oxygen measured at room temperature and pressure is needed for complete combustion of 0.1 mol of propan-1-ol?

A 10.8 dm^3 **B** 12.0 dm^3 **C** 21.6 dm^3 **D** 24.0 dm^3

[S'13 12 Q26]

44 Which volume of oxygen, at room temperature and pressure, is needed for complete combustion of 0.1 mol of ethanol?

A 7.2 dm^3 **B** 8.4 dm^3 **C** 14.4 dm^3 **D** 16.8 dm^3

[S'13 13 Q27]

45 Which stage in the free radical substitution of methane by chlorine will have the lowest activation energy?

A $CH_3\bullet + Cl_2 \rightarrow CH_3Cl + Cl\bullet$

B $Cl\bullet + Cl\bullet \rightarrow Cl_2$

C $Cl\bullet + CH_4 \rightarrow CH_3\bullet + HCl$

D $Cl_2 \rightarrow Cl\bullet + Cl\bullet$

[W'13 12 Q7]

SECTION B

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

1 When octane is subjected to catalytic cracking, which compounds can be obtained?

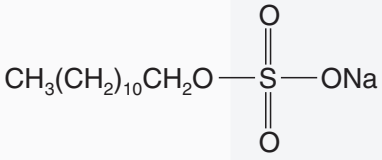
1 $CH_2=CH_2$

2 $CH_3CH_2CH=CH_2$

3 $CH_3(CH_2)_4CH_3$

[N'02 Q38]

2 Long-chain alkanes are converted on an industrial scale into alkylsulphates for use as detergents, e.g. sodium lauryl sulphate.



sodium lauryl sulphate

What deductions about the properties of this substance can be made from this structure?

1 Part of the structure is polar and is water–attracting.

2 The alkyl chain is soluble in oil droplets.

3 All the C-C-C bond angles are tetrahedral.

[J'03 Q32]

3 Modern cars are fitted with catalytic converters. These remove carbon monoxide, unburnt hydrocarbons and oxides of nitrogen from exhaust gases.

Which of these pollutant gases are removed by oxidation?

1 carbon monoxide

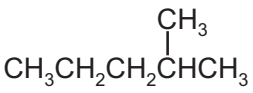
2 hydrocarbons

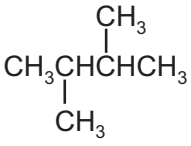
3 nitrogen oxides

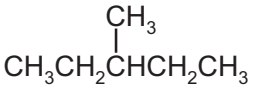
[N'05 Q39]

4 During the bromination of methane, the free radical $CH_3\bullet$ is generated. A possible terminati step of this reaction is the formation of C_2H_6 by the combination of two free radicals.

What could be produced in a terminating step during the bromination of **propane**?

1 

2 

3 

[N'08 Q39]

5 Which compounds may result from mixing ethane and chlorine in the presence of sunlight?

1 CH_3CH_2Cl

2 $CH_3CH_2CH_2CH_3$

3 $CH_3CHClCHClCH_3$

[N'04 Q37]

6 For complete combustion, 1 mol of an organic compound **X** was found to require 2.5 mol of molecular oxygen.

Which compounds could be **X**?

1 C_2H_5OH

2 C_2H_2

3 CH_3CHO

[J'08 Q31]

7 A fraction of distilled crude oil contains molecules with between 15 and 19 carbon atoms. This fraction is cracked by strong heating.

Why is this done?

1 To produce alkenes.

2 To produce smaller molecules which are in higher demand.

3 To insert oxygen atoms into the hydrocarbons.

[J'09 Q37]

8 In a car engine pollutant oxide **Y**, which contains non-metallic element **X**, is formed.

Further oxidation of **Y** to **Z** occurs in the atmosphere. In this further oxidation, 1 mol of **Y** reacts with 0.5 mol of gaseous oxygen.

X could be either nitrogen or sulfur.

Which statements about **X**, **Y** and **Z** can be correct?

1 The oxidation number of **X** increases by two from **Y** to **Z**.

2 **Y** may have an unpaired electron in its molecule.

3 **Y** is a polar molecule.

[J'11 12 Q36]

9 In a car engine, non-metallic element X forms a pollutant oxide Y.

Further oxidation of Y to Z occurs spontaneously in the atmosphere. In this further oxidation, 1 mol of Y reacts with 0.5 mol of gaseous oxygen.

Which statements about X, Y and Z are correct?

1 X forms a basic hydride.

2 Y is a diatomic molecule.

3 Z is a polar molecule.

[N'11 11 Q36]

10 In a car engine, non-metallic element ***X*** forms a pollutant oxide ***Y***.

Further oxidation of ***Y*** to ***Z*** occurs spontaneously in the atmosphere. In this further oxidation, 1 mol of ***Y*** reacts with 0.5 mol of gaseous oxygen.

Which statements about ***X***, ***Y*** and ***Z*** are correct?

1 The oxidation number of ***X*** increases by 2 from ***Y*** to ***Z***.

2 The molecule of ***Y*** has no unpaired electrons.

3 The molecule of ***Z*** contains three oxygen atoms.

[N'11 12 Q36]

11 Which statements about the photochemical chlorination of ethane are correct?

1 Hydrogen gas is one of the products.

2 A propagation step in the mechanism is $C_2H_6 + Cl\bullet \rightarrow C_2H_5\bullet + HCl$.

3 The initiation step is the homolytic fission of chlorine.

[J'12 12 Q39]

12 Which molecules would be present in the mixture produced by the photochemical chlorination of methane?

1 hydrogen

2 hydrogen chloride

3 dichloromethane

[J'13 11 Q37]

ALKANES WS 4

SECTION A

1 A car can be considered to run on octane, C_8H_{18}.

(a) Write an equation for the complete combustion of octane.

.....[1]

The composition of the exhaust gases (fumes) from a petrol (gasoline) engine is given below.

Gas	Percentage by volume
carbon dioxide	9
water vapour	8
oxygen	4
hydrogen	2
carbon monoxide	3–6
hydrocarbons	0.2
nitrogen oxides	0.4–0.05

(b) **(i)** What gas, omitted from the table, makes up most of the remainder of the exhaust fumes?

.....

(ii) Explain why there is always water vapour in the exhaust fumes.

.....

.....

[2]

(c) **(i)** State two gases in the exhaust fumes which are poisonous to humans. Also state briefly for each the particular effect on humans.

gas I .....

effect .....

gas II .....

effect .....

(ii) The two gases you have given in **(c)(i)** can be removed by reaction in a platinised catalytic converter. The products of the reaction in the converter are not hazardous. For each of your gases in **(c)(i)** give an equation which shows how it is removed to form less harmful substances.

I .....

II .....

(iii) Suggest **one** reason why the exhaust fumes from a car fitted with a catalytic converter are still hazardous to human health to some degree.

.....

.....

.....[5]

[W'03 Q2]

2 Most submarines travel under water using electrical power from batteries. The German engineer Helmut Walter designed a diesel engine that could be used to propel a submarine beneath the surface of the sea. Instead of taking air from above the surface of the sea, Walter's engine used hydrogen peroxide, H_2O_2, to provide oxygen for a conventional diesel engine.

Hydrogen peroxide may be catalytically decomposed to give water and oxygen.

(a) (i) What is meant by the term *catalyst*?

.....

.....

(ii) Construct a balanced equation for the decomposition of H_2O_2.

..... [3]

Diesel fuel may be considered to consist of the hydrocarbon $C_{15}H_{32}$ which reacts completely with oxygen according to the following equation.

$$C_{15}H_{32} + 23O_2 \rightarrow 15CO_2 + 16H_2O$$

(b) (i) To which homologous series does $C_{15}H_{32}$ belong?

.....

(ii) Use the equation above and your answer to **(a)(ii)** to calculate the amount, in moles, of H_2O_2, that will provide sufficient oxygen for the complete oxidation of one mole of $C_{15}H_{32}$.

amount of H_2O_2 = ... mol

[3]

A submarine equipped with a Walter engine used 212 tonnes of diesel fuel during an underwater voyage. The submarine also carried concentrated aqueous H_2O_2.
[1 tonne = 10^6 g]

(c) **(i)** Calculate the amount, in moles, of diesel fuel used during the underwater voyage.

amount of diesel fuel = ... mol

(ii) Use your answers to **(b)(ii)** and **(c)(i)** to calculate the mass, in tonnes, of hydrogen peroxide used during the underwater voyage.

mass of H_2O_2 = ... tonnes
[4]

(d) The exhaust products of the Walter engine were passed into the sea.

What would happen to them?

..... [1]

[W'08 Q1]

3 **(b)** **(i)** By using equations, describe the mechanism of the reaction between chlorine and methane to form chloromethane, CH_3Cl.

Identify, by name, the separate steps of the overall reaction.

.....

.....

.....

.....

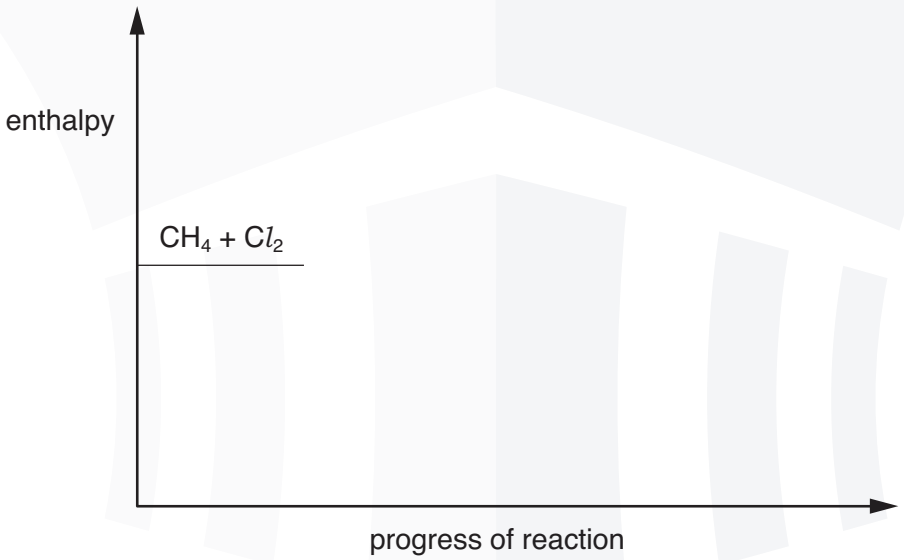
.....

.....

(ii) What is the intermediate organic species in this reaction?

..... [7]

(c) The energy of activation for the formation of CH_3Cl is 16 kJ mol^{-1}.
Use this figure and your answer to **(a)(i)** to complete the reaction pathway diagram below showing the formation of CH_3Cl from CH_4 and Cl_2.
Show clearly the intermediate organic species and the final products.
Indicate on your sketch the relevant enthalpy changes and their values.



[4]

[W'09 21 Q3]

4 In 1814, Sir Humphrey Davy and Michael Faraday collected samples of a flammable gas, **A**, from the ground near Florence in Italy.
They analysed **A** which they found to be a hydrocarbon. Further experiments were then carried out to determine the molecular formula of **A**.

(a) What is meant by the term *molecular formula*?

.....

.....

.....[2]

Davy and Faraday deduced the formula of **A** by exploding it with an excess of oxygen and analysing the products of combustion.

(b) Complete and balance the following equation for the complete combustion of a hydrocarbon with the formula C_xH_y.

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \rightarrow \text{.....} + \text{.....}$$

[2]

(c) When 10 cm^3 of **A** was mixed at room temperature with 50 cm^3 of oxygen (an excess) and exploded, 40 cm^3 of gas remained after cooling the apparatus to room temperature and pressure.
When this 40 cm^3 of gas was shaken with an excess of aqueous potassium hydroxide, KOH, 30 cm^3 of gas still remained.

(i) What is the identity of the 30 cm^3 of gas that remained at the end of the experiment?

.....

(ii) The combustion of **A** produced a gas that reacted with the KOH(aq).

What is the identity of this gas?

.....

(iii) What volume of the gas you have identified in **(ii)** was produced by the combustion of **A**?

.....cm^3

(iv) What volume of oxygen was used up in the combustion of **A**?

.....cm^3 [4]

(d) Use your equation in **(b)** and your results from **(c)(iii)** and **(c)(iv)** to calculate the molecular formula of **A**.
Show all of your working.

[3]

[W'10 21 Q1]

5 Crude oil is a naturally occurring flammable liquid which consists of a complex mixture of hydrocarbons. In order to separate the hydrocarbons the crude oil is subjected to fractional distillation.

(a) Explain what is meant by the following terms.

(i) *hydrocarbon* .....

.....

(ii) *fractional distillation* .....

.....[2]

(b) Undecane, $C_{11}H_{24}$, is a long chain hydrocarbon which is present in crude oil.
Such long chain hydrocarbons are 'cracked' to produce alkanes and alkenes which have smaller molecules.

(i) Give the conditions for **two different** processes by which long chain molecules may be cracked.

process 1 .....

.....

process 2 .....

.....

(ii) Undecane, $C_{11}H_{24}$, can be cracked to form pentane, C_5H_{12}, and an alkene.
Construct a balanced equation for this reaction.

.....[3]

Pentane, C_5H_{12}, exhibits structural isomerism.

(c) **(i)** Draw the three structural isomers of pentane.

isomer **B**	isomer **C**	isomer **D**

(ii) The three isomers of pentane have different boiling points.

Which of your isomers has the highest boiling point?

isomer .....

Suggest an explanation for your answer.

.....

.....

.....[6]

(e) The boiling points of methane, ethane, propane, and butane are given below.

compound	CH_4	CH_3CH_3	$CH_3CH_2CH_3$	$CH_3(CH_2)_2CH_3$
boiling point / K	112	185	231	273

(i) Suggest an explanation for the increase in boiling points from methane to butane.

.....

.....

.....

(ii) The isomer of butane, 2-methylpropane, $(CH_3)_3CH$, has a boiling point of 261 K. Suggest an explanation for the difference between this value and that for butane in the table above.

.....

.....

.....

[4]

[W'10 22 Q3]

6 Crude oil contains a mixture of hydrocarbons together with other organic compounds which may contain nitrogen, oxygen or sulfur in their molecules.

At an oil refinery, after the fractional distillation of crude oil, a number of other processes may be used including 'cracking', 'isomerisation', and 'reforming'.

(a) (i) What is meant by the term '*cracking*' and why is it carried out?

.....

.....

.....

.....

(ii) Outline briefly how the cracking of hydrocarbons would be carried out.

.....

.....

(iii) Construct a balanced equation for the formation of heptane, C_7H_{16}, by cracking tetradecane, $C_{14}H_{30}$.

.....

[4]

One of the sulfur-containing compounds present in crude oil is ethanethiol, C_2H_5SH, the sulfur-containing equivalent of ethanol. Ethanethiol is toxic and is regarded as one of the smelliest compounds in existence.

(b) The boiling point of ethanol, C_2H_5OH, is higher than that of C_2H_5SH.
Suggest a reason for this difference.

.....

.....[1]

When ethanethiol is burned in an excess of air, three oxides of different elements are formed.

(c) (i) Construct a balanced equation for this reaction.

.....

(ii) **Two** of the oxides formed cause serious environmental damage.

For **each** of these oxides, identify the type of pollution caused and describe one consequence of this pollution.

.....

.....

.....

.....

.....

[6]

(d) A small amount of ethanethiol is added to liquefied gases such as butane that are widely used in portable cooking stoves.

Suggest a reason for this.

.....[1]

Sulfur-containing compounds are removed from oil products at the refinery. The sulfur is recovered and converted into SO_2, which is then used in the Contact process.

(e) State the main operating details of the formation of SO_3 in the Contact process.

.....

.....

.....

.....

.....[3]

[Total: 15]

[S'11 21 Q2]

7 Propane, C_3H_8, and butane, C_4H_{10}, are components of Liquefied Petroleum Gas (LPG) which is widely used as a fuel for domestic cooking and heating.

(a) **(i)** To which class of compounds do these two hydrocarbons belong?

.....

(ii) Write a balanced equation for the complete combustion of butane.

.....
[2]

(b) When propane or butane is used in cooking, the saucepan may become covered by a solid black deposit.

(i) What is the chemical name for this black solid?

.....

(ii) Write a balanced equation for its formation from butane.

.....
[2]

[W'13 21 Q5]

8 Petrol and diesel fuel are both used in internal combustion engines.
Petrol may be regarded as having the formula C_9H_{20} and diesel fuel as having the formula $C_{14}H_{30}$.

(a) (i) To which class of compounds do these two hydrocarbons belong?

.....

(ii) Write a balanced equation for the complete combustion of petrol.

.....
[2]

(b) When petrol or diesel fuel are used in internal combustion engines, several different products of the incomplete combustion of the fuel may be formed.

(i) Name **two** of these products that do not contain hydrogen.

..... and .....

(ii) Choose one of these and state a hazard it causes.

product .....

hazard .....

(iii) Write a balanced equation for the formation of **one** of the products in **(i)** from diesel fuel.

.....
[4]

[W'13 23 Q2]

Alkenes

a describe the chemistry of alkenes as exemplified, where relevant, by the following reactions of ethene and propene (including the Markovnikov addition of asymmetric electrophiles to alkenes using propene as an example): ☐

(i) addition of hydrogen, steam, hydrogen halides and halogens

(ii) oxidation by cold, dilute, acidified manganate(VII) ions to form the diol

(iii) oxidation by hot, concentrated, acidified manganate(VII) ions leading to the rupture of the carbon–carbon double bond in order to determine the position of alkene linkages in larger molecules

(iv) polymerisation

b describe the mechanism of electrophilic addition in alkenes, using bromine/ethene and hydrogen bromide/propene as examples ☐

c describe and explain the inductive effects of alkyl groups on the stability of cations formed during electrophilic addition ☐

d describe the characteristics of addition polymerisation as exemplified by poly(ethene) and PVC ☐

e deduce the repeat unit of an addition polymer obtained from a given monomer ☐

f identify the monomer(s) present in a given section of an addition polymer molecule ☐

g recognise the difficulty of the disposal of poly(alkene)s, i.e. non- biodegradability and harmful combustion products ☐

ALKENES

15.2 Alkenes	a) describe the chemistry of alkenes as exemplified, where relevant, by the following reactions of ethene and propene (including the Markovnikov addition of asymmetric electrophiles to alkenes using propene as an example): (i) addition of hydrogen, steam, hydrogen halides and halogens (ii) oxidation by cold, dilute, acidified manganate(VII) ions to form the diol (iii) oxidation by hot, concentrated, acidified manganate(VII) ions leading to the rupture of the carbon–carbon double bond in order to determine the position of alkene linkages in larger molecules (iv) polymerisation (see also Section 21) b) describe the mechanism of electrophilic addition in alkenes, using bromine/ethene and hydrogen bromide/propene as examples c) describe and explain the inductive effects of alkyl groups on the stability of cations formed during electrophilic addition d) describe the characteristics of addition polymerisation as exemplified by poly(ethene) and PVC e) deduce the repeat unit of an addition polymer obtained from a given monomer f) identify the monomer(s) present in a given section of an addition polymer molecule g) recognise the difficulty of the disposal of poly(alkene)s, i.e. non-biodegradability and harmful combustion products

ALKENES

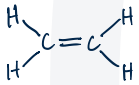
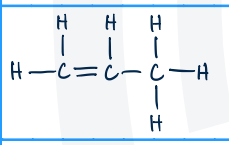
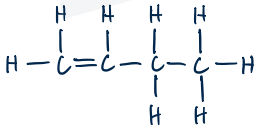
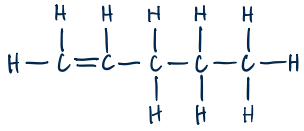
Alkenes contain a C=C double bond. Another way of saying this is that the functional group present in alkenes is C=C.

Noncyclic alkenes containing just one C=C all have the same empirical formula: CH_2 and a general formula C_nH_{2n}

This has two fewer hydrogen atoms than the alkane with the same number of C atoms.

Alkenes are **unsaturated hydrocarbons** – they can still have hydrogen or halogen atoms added to their formula.

1

Name	Molecular formula	Empirical formula	Structural formula	
			Condensed	Full
ethene	C_2H_4	CH_2	$CH_2=CH_2$	
prop-1-ene	C_3H_6	CH_2	$CH_2=CHCH_3$	
but-1-ene	C_4H_8	CH_2	$CH_2=CHCH_2CH_3$	
pent-1-ene	C_5H_{10}	CH_2	$CH_2=CHCH_2CH_2CH_3$	

2

ALKENES

Carbon atoms with a double bond are surrounded by 3 groups of electrons.

The three bonds form a flat trigonal plane with a bond angle of 120°.

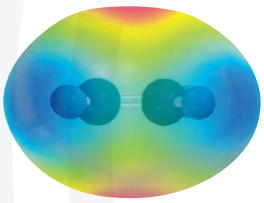
The alkenes, like alkanes, are non-polar molecules with only van der Waals' forces between them.

This means that they are volatile, with the first four members being gases at room temperature. Owing to their non- polar nature, they are also insoluble in water.

3

REACTIVITY OF ALKENES

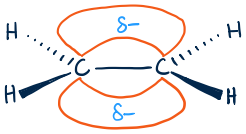
Alkenes are more reactive than alkanes.



The double bond in alkenes is made of a strong sigma bond and a weak pi bond.

In order to attain more stability the pi bond tends to get replaced by two stable sigma bonds. **Thus alkenes undergo addition reactions.**

Due to the presence of the double bond there is a layer of negative charge above and below the carbon atoms and hence alkenes are susceptible to electrophilic attack.



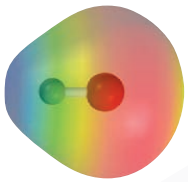
Thus the majority of the reactions of alkenes are **electrophilic addition reactions**.

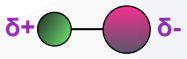
4

ELECTROPHILES

An electrophile is a reagent (a positively charged ion or the positive end of a dipole)

that is attracted to regions of high electron density and accepts a pair of electrons to form a covalent bond.





δ+ H — Br δ-

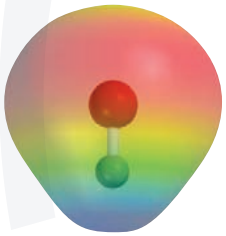
δ+ Br — Br δ-

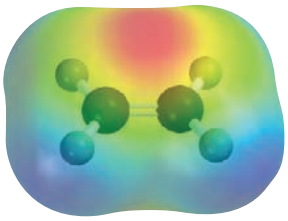
5

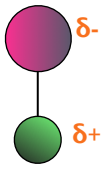
ELECTROPHILIC ATTACK

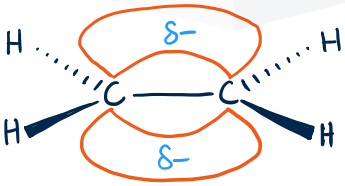
The C=C contains four electrons and is thus a region of very high electron density.

Electrophiles will be attracted to the electron density in the double bond.









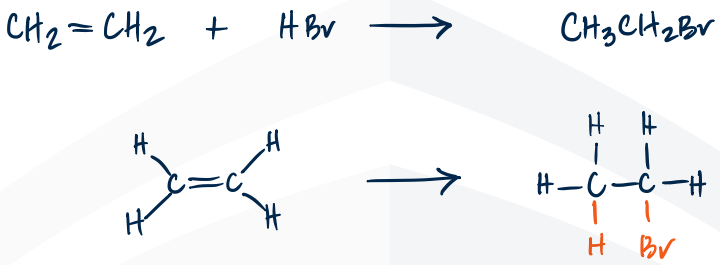
6

ELECTROPHILIC ADDITION OF HBr

The hydrogen halides HCl, HBr and HI all react with alkenes to give halogenoalkanes.

For example HBr with ethene gives 1-bromoethane.

The overall equation is:

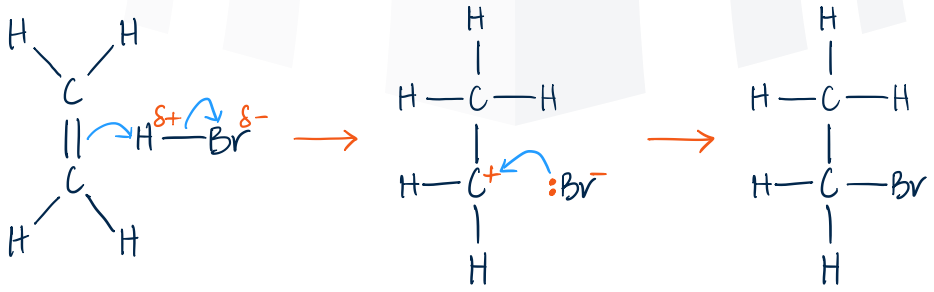


7

ELECTROPHILIC ADDITION OF HBr

H–Br is polar, with the $H^{\delta+}$ and the $Br^{\delta-}$.

The H is thus attracted to the high electron density in the C=C.

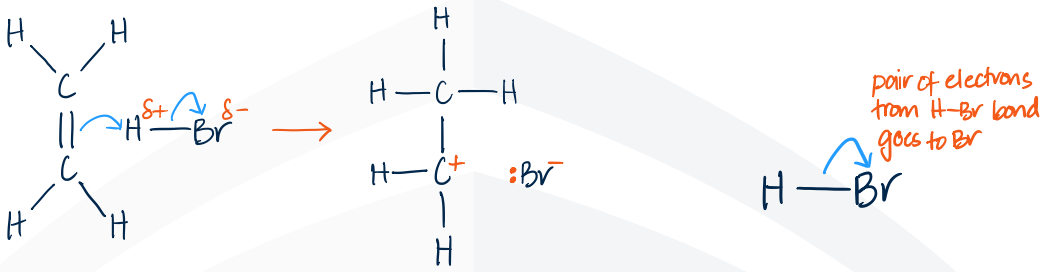


8

ELECTROPHILIC ADDITION: STEP 1

In the first stage, a pair of electrons is donated from the C=C to form a bond between one C and the H of the H–Br.

At the same time the H–Br bond breaks (heterolytic fission), and the pair of electrons from the bond goes to the Br.



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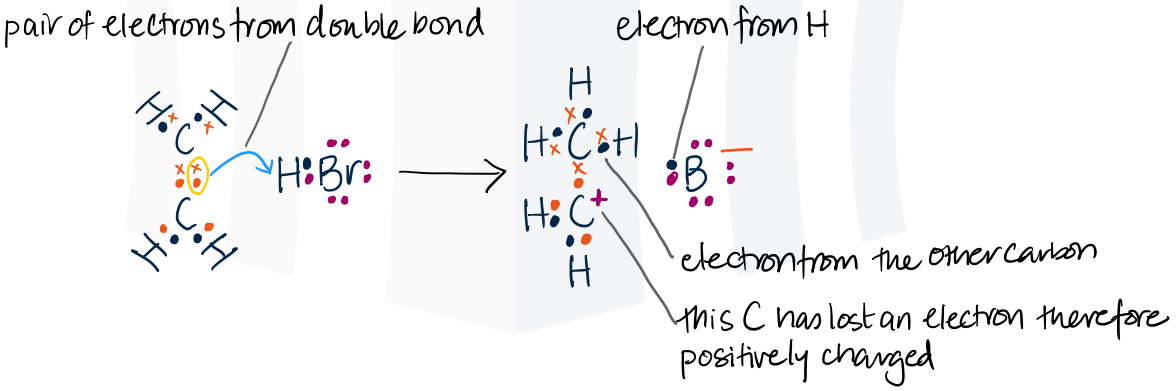
ELECTROPHILIC ADDITION: STEP 1



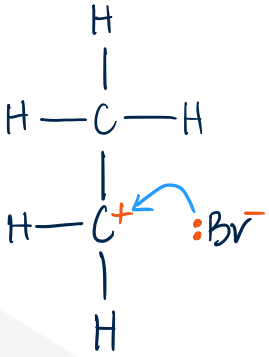
10

ELECTROPHILIC ADDITION: INTERMEDIATE

The other carbon has lost an electron (this electron is now in the C–H bond) and thus this carbon atom has a positive charge.

The intermediate formed is called a carbocation (a positively charged organic ion with a positive charge on C).

The Br atom has gained an electron from the H–Br bond and is therefore a negatively charged bromide ion.

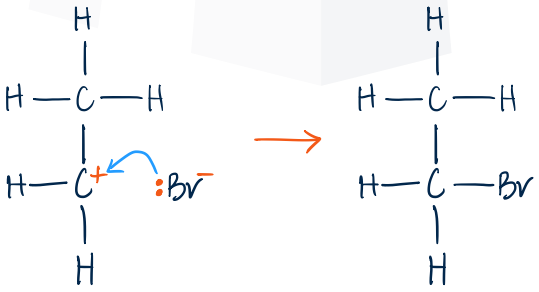


11

ELECTROPHILIC ADDITION: STEP 2

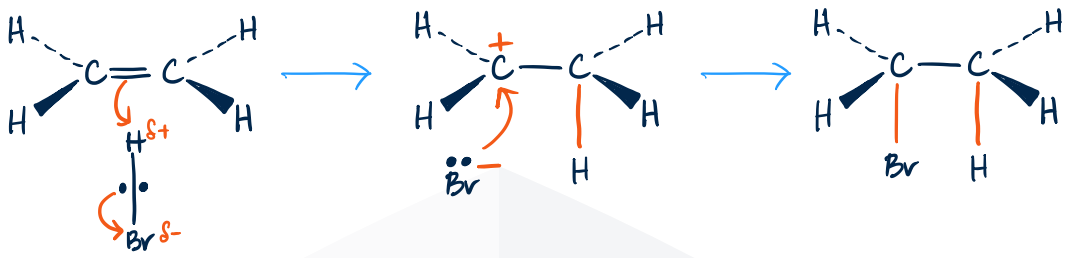
In the second stage the Br^- ion is attracted to the C^+ and donates a pair of electrons to form a bond.

The electrons in the final compound are also shown below.



12

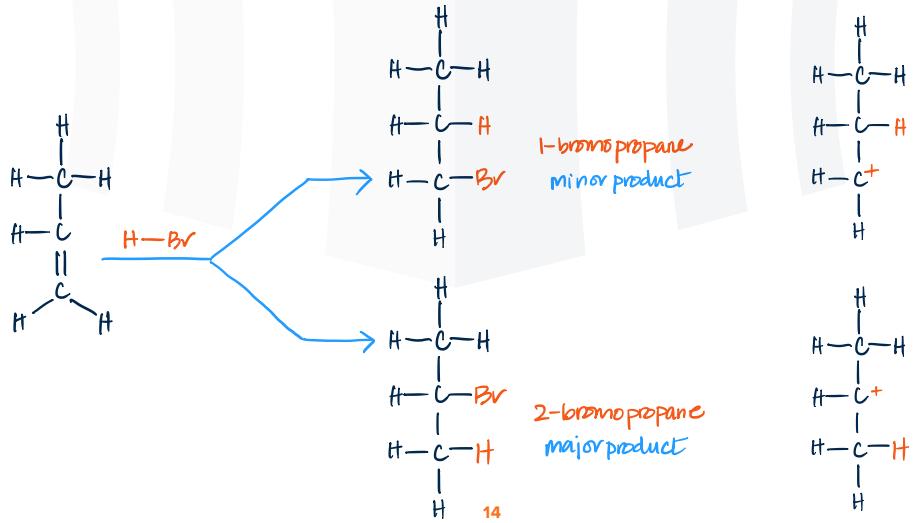
ELECTROPHILIC ADDITION OF HBr



13

REACTION OF HBr WITH PROPENE

When HBr adds to propene, two products are possible:

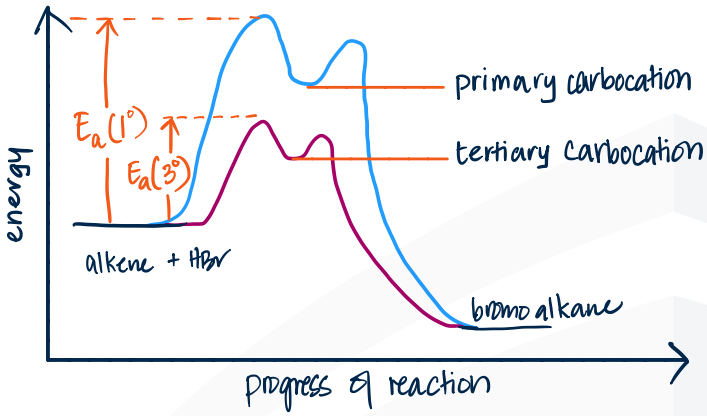


14

REACTION OF HBr WITH PROPENE

This is because when the electrophile $H^{\delta+}$ attacks the double bond either a secondary or a primary carbocation ion can form.

The major product that forms depends on the stability of the intermediate carbocation.

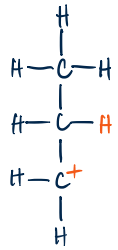


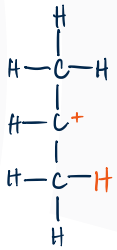
An electrophile adds on to an unsymmetrical alkene so that the most stable carbocation forms as the intermediate.

15

REACTION OF HBr WITH PROPENE

The two possible carbocations that can be formed when propene reacts with H–Br are:


primary carbocation


secondary carbocation

The secondary carbocation is more stable than the primary carbocation.

This is due to the electron-releasing effect of alkyl groups.

There are two alkyl groups next to the positively charged C in the secondary carbocation but only one in the primary carbocation.

Two alkyl groups reduce the positive charge on the C more than one alkyl group and thus stabilise the ion more.

Since the secondary carbocation is more stable, it is more likely to be formed.

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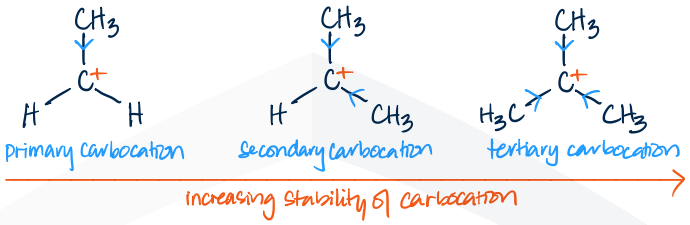
CARBOCATIONS

In general, the more alkyl groups there are attached to C^+, the more stable the carbocation.

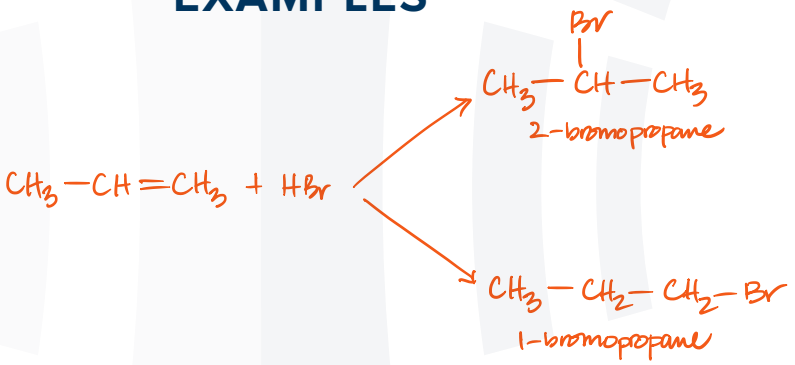
The electron-releasing effect is roughly independent of the size of the alkyl group, i.e. a methyl group donates approximately the same amount of electron density as an ethyl group.

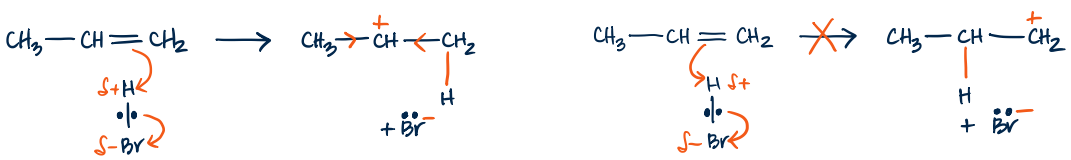


Stability of carbocations is useful in determining the products of the reaction between unsymmetrical alkenes and halogen halides.

17

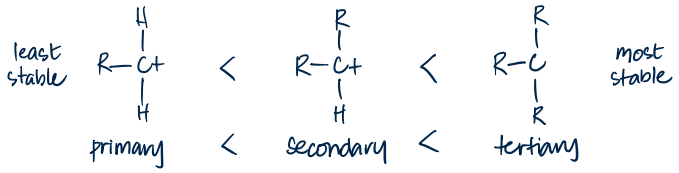
EXAMPLES



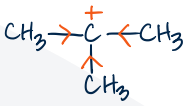


18

REACTION OF HBr WITH METHYLPROPENE

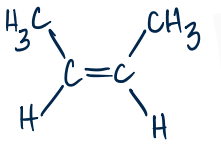






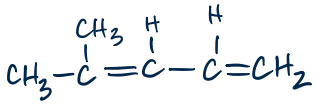
19

SKILL CHECK 1



+ HBr ⟶

$CH_3CH=CHCH_3$

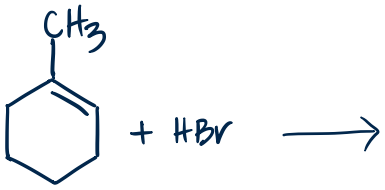


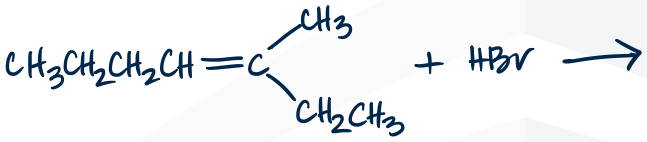
+ HBr ⟶

$(CH_3)_2C=CHCH=CH_2$

20

SKILL CHECK 2

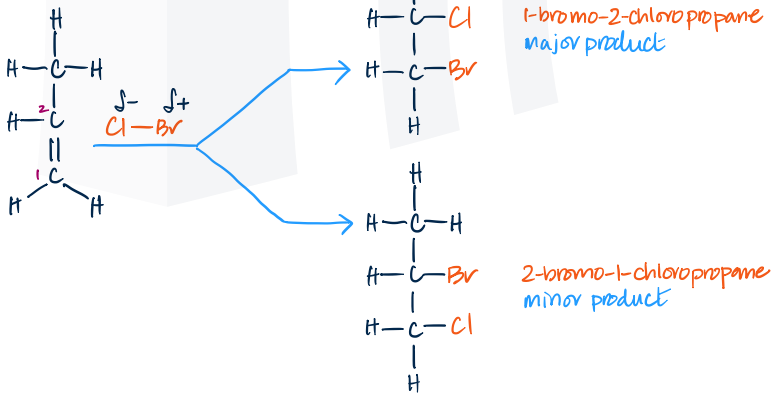




21

PROPENE WITH BrCl

Br is less electronegative than Cl and becomes attached to C1, which has two H atoms already attached, rather than C2, which only has one H atom already attached.



22

ETHENE WITH BROMINE

$$CH_2{=}CH_2 + Br_2 \longrightarrow CH_2BrCH_2Br$$

Although the bromine is not originally polar, as it approaches the high electron density in the C=C it becomes polarised (there is an induced dipole).

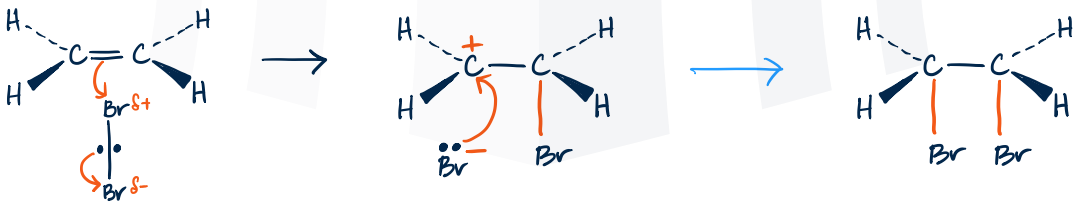
The electrons are repelled in the Br_2 molecule so that the Br closest to the C=C has a slight positive charge and the Br further away has a slight negative charge.



23

ALKENES WITH BROMINE

The mechanism is exactly analogous to the reaction of H–Br with ethene, i.e. via a carbocation intermediate.

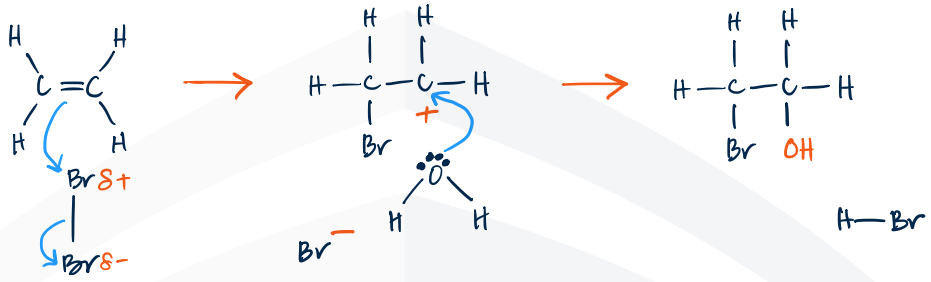


24

ALKENES WITH AQUEOUS BROMINE

Alkenes react with bromine water to form mainly bromoalcohols with a negligible amount of dibromoalkanes.

The reaction is similar to that of liquid bromine but the carbocation attacks the water molecule instead as it is found in large concentration. Small amounts of dibromoalkanes are formed.

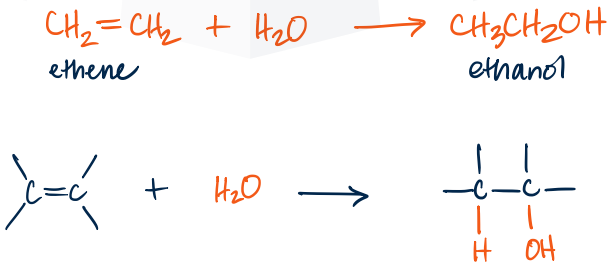


25

ALKENES WITH STEAM

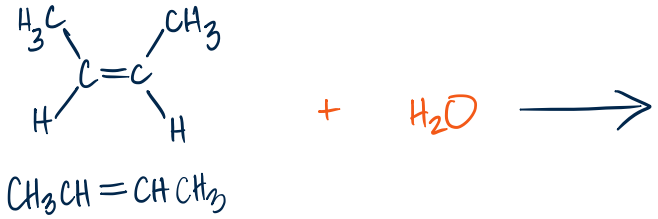
Alkenes react with acid catalyst and steam at temperatures of around 350°C and pressures over 100 atm to form alcohols.

Reagent	Steam and dil phosphoric acid (H_3PO_4)
Condition	350 °C and 100 atm
Type	Electrophilic addition



26

ETHENE WITH STEAM



$CH_3CH=CHCH_3$



$(CH_3)_2C=CHCH=CH_2$

27

ALKENES WITH HYDROGEN

When a mixture of alkene and hydrogen is passed over Ni catalyst at 200°C to 300°C, an alkane is formed.

Reagent	Hydrogen (H_2) and Nickel (Ni)
Condition	200 °C to 300 °C
Type	Reduction

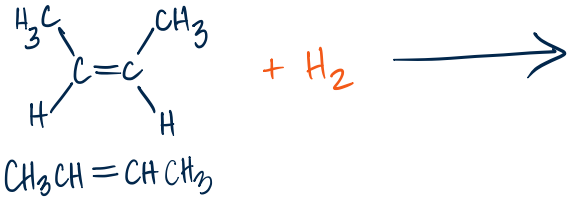
$CH_3CH_2=CH_2$ + H_2 → $CH_3CH_2CH_3$

propene → propane



28

ALKENES WITH HYDROGEN



$CH_3CH=CHCH_3$



$(CH_3)_2C=CHCH=CH_2$

29

MILD OXIDATION OF ALKENES

When an alkene is passed through cold dilute alkaline manganate (VII), a diol is formed. During the reaction the purple colour of manganate (VII) is removed.

Reagent	cold dilute alkaline (or acidic) potassium manganate ($KMnO_4$)
Condition	cold (room temperature)
Type	Oxidation

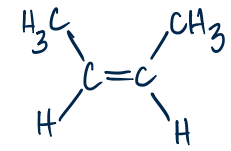
$CH_2=CH_2 + H_2O + [O] \longrightarrow CH_2(OH)CH_2OH$

ethene — ethan-1,2-diol



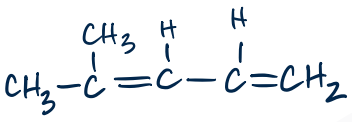
30

MILD OXIDATION OF ALKENES



OH^- OR $H^+/KMnO_4$ → cold (room temp.)

$CH_3CH=CHCH_3$



OH^- OR $H^+/KMnO_4$ → cold (room temp.)

$(CH_3)_2C=CHCH=CH_2$

31

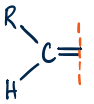
STRONG OXIDATION OF ALKENES

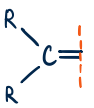
When an alkene is passed through hot concentrated acidified manganate (VII) the double bonds rupture giving two carbonyl compounds.

If the carbonyl compound is an aldehyde it is further oxidised to the corresponding acid.

If the double bond carbon is:

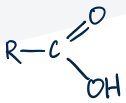


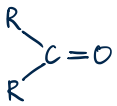




Then the oxidised product will be:

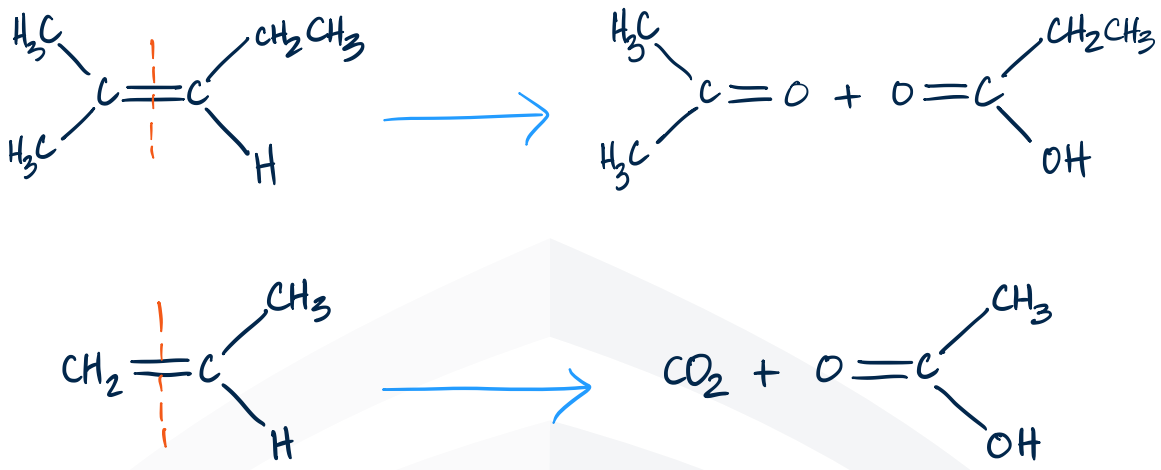
$CO_2 + H_2O$





32

STRONG OXIDATION OF ALKENES



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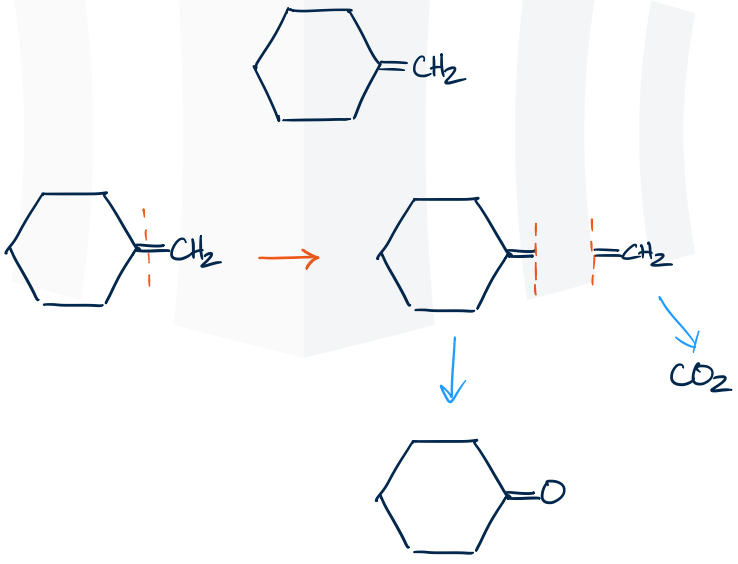
STRONG OXIDATION OF ALKENES



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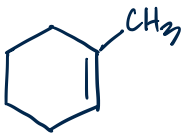
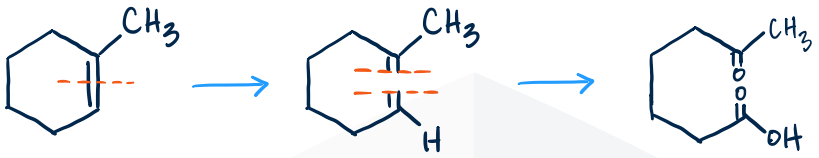
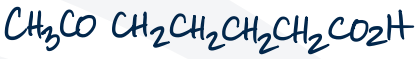
STRONG OXIDATION OF ALKENES

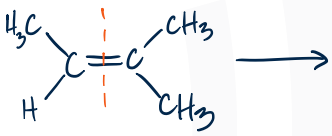


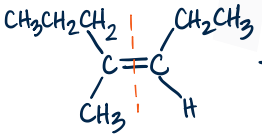


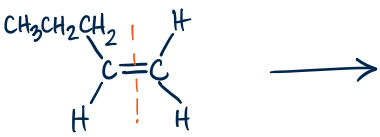


35

STRONG OXIDATION OF ALKENES

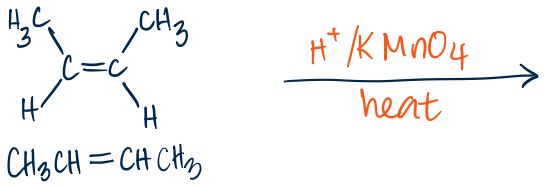


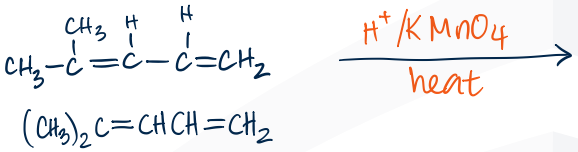




36

STRONG OXIDATION OF ALKENES





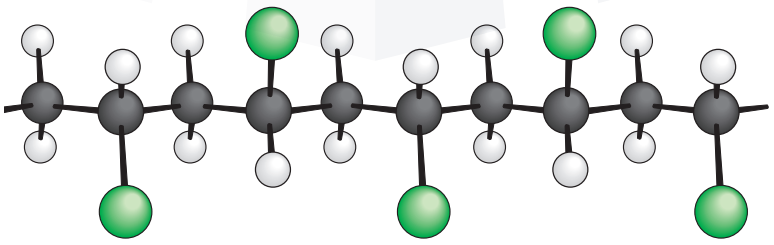
37

ADDITION POLYMERISATION

Alkenes undergo addition polymerisation, in which a large number of monomers are joined together into a polymer chain.

It is important to realise from this reaction that it is only the C=C group that reacts when the polymerisation reaction occurs – all the other groups attached to the C=C are unaffected.

A 3D displayed formula of part of the poly(chloroethene) molecule

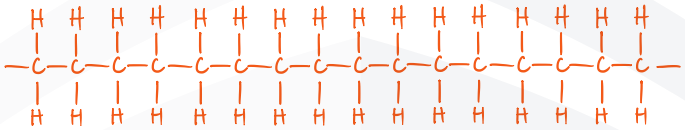


38

POLY(ETHENE)

Poly(ethene), commonly called polythene, is termed an addition polymer because one molecule is made from many ethene units. Poly(ethene) is used to make bags, electrical insulation, dustbin liners, bottles, etc.

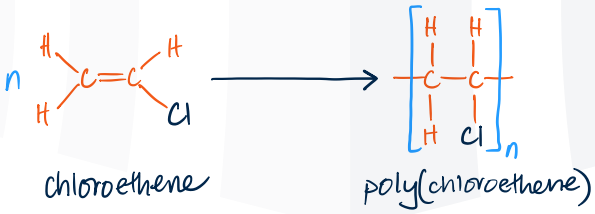


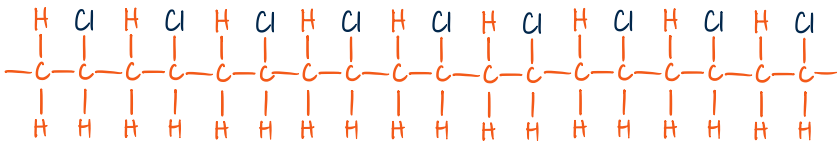


39

POLY(CHLOROETHENE)

poly(chloroethene), commonly called PVC [poly(vinylchloride)], is used to make guttering, water pipes, window frames, floor coverings.

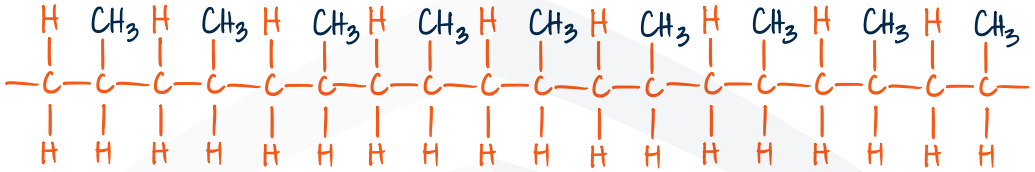




40

POLY(PROPENE)





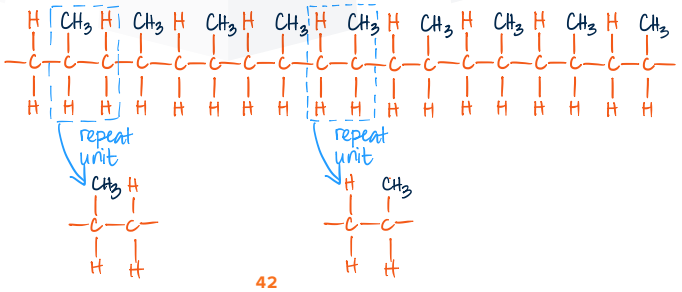
41

REPEAT UNITS

The repeat unit or repeating unit of a polymer is the basic unit from which the whole polymer chain can be made up.

In each of the equations seen so far, this has been shown in brackets.

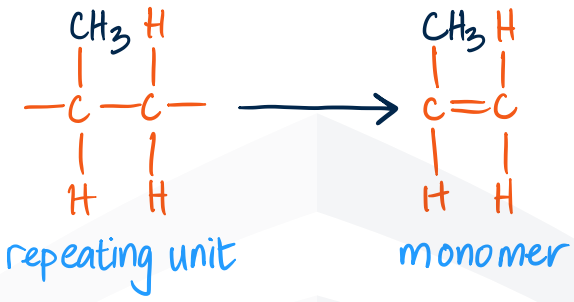
The repeat unit for a polymer may be obtained simply by taking any two adjacent carbon atoms in the main polymer chain.



42

REPEAT UNITS

The monomer for a polymer can be derived by simply placing a double bond between the carbons of the repeat unit.



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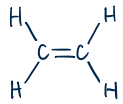
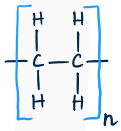
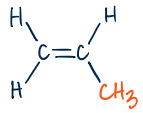
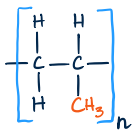
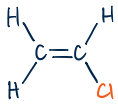
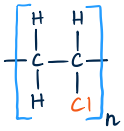
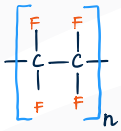
POLYMERS

Monomer	Polymer repeat unit	Properties	Uses
ethene 	poly(ethehe) 	Light Flexible Easily moulded Transparent Good insulator Resistant to water, acids and alkalis	Plastic bags and bottles Insulation for cables
propene 	poly(propene) 	Tough Easily moulded Easily coloured Very resistant to water, acids and alkalis	Fibre for ropes and carpets Crates Toys

44

POLYMERS

Monomer	Polymer repeat unit	Properties	Uses
chloroethene 	poly(chloroethene) [PVC] 	Tough Rigid or flexible Very resistant to water, acids and alkalis	Clingfilm Guttering and window frames Insulation for cables Waterproof clothing Flooring
tetrafluoroethene 	poly(tetrafluoroethene) (ptfe) 	Tough Rigid Low friction solid Resistant to water, acids and alkalis	Coating for non-stick pans and skis Low friction surfaces for bridges to move as metals expand and contract

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ALKENES FROM ALCOHOLS

When an alcohol is heated with excess concentrated sulphuric acid at around 200 °C an alkene is formed. (Refer to the notes on Alkenes).

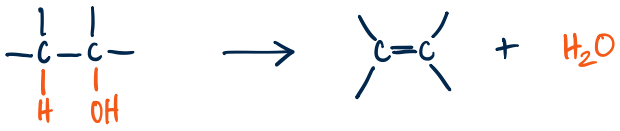
Dehydration of the alcohol can also be carried out by passing the alcohol vapour over alumina at 350 °C.

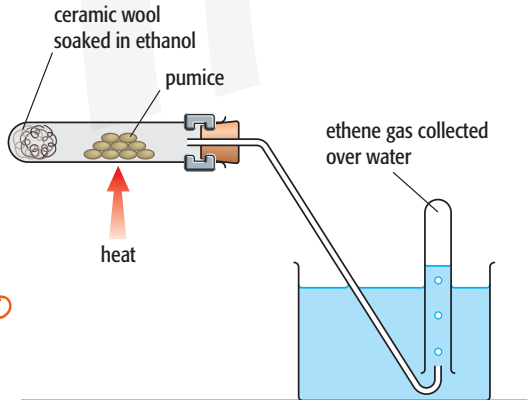
Reagent conc H_2SO_4

Condition 200 °C

Alternatively Alumina at 350°C.

Type elimination





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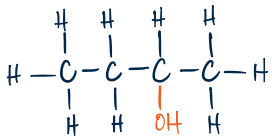
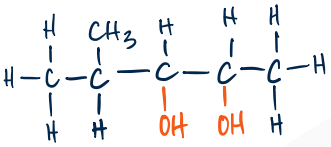
ALKENES FROM ALCOHOLS



conc. H_2SO_4 and heat

$CH_3CH_2CH(OH)CH_3$

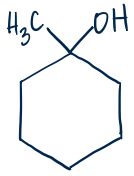


Al_2O_3 and heat

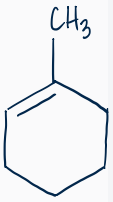
$(CH_3)_2CHCH(OH)CH(OH)CH_3$

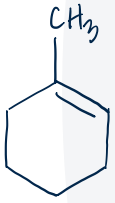
47

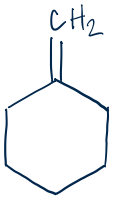
ALKENES FROM ALCOHOLS



conc. H_2SO_4 and heat







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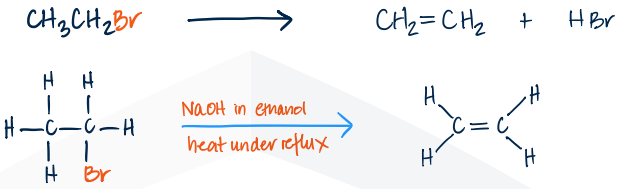
ALKENES FROM HALOGENOALKANES

Reagent	sodium (or potassium) hydroxide dissolved in ethanol
Condition	heat under reflux
Product	Alkene
Type	elimination

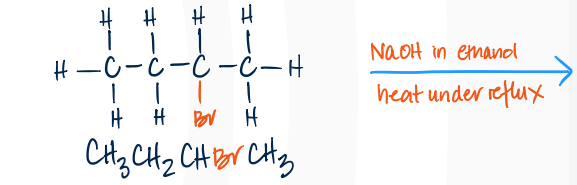


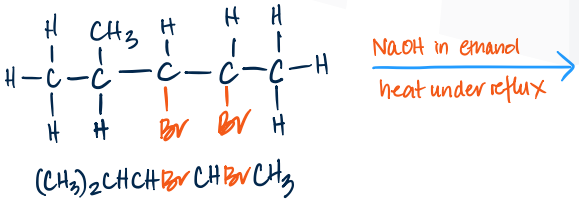
The OH^- removes a proton from a carbon atom adjacent the C bearing the halogen.

If the haloalkane is unsymmetrical (e.g. 2-bromobutane) a mixture of isomeric alkene products is obtained.

49

ALKENES FROM HALOGENOALKANES





50

ALKENES WS 1

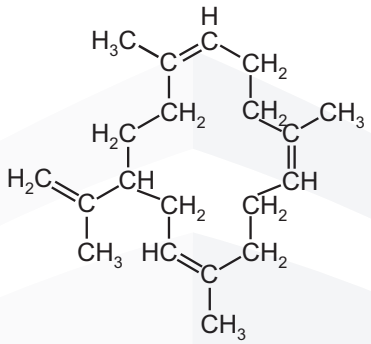
SECTION A

1 How many moles of oxygen molecules are needed for the complete combustion of one mole of 3-methylpent-2-ene?

A 9 **B** $9\frac{1}{2}$ **C** 18 **D** 19

[J'14 P11 Q26]

2 The naturally-occurring molecule shown below can be made by the addition of four identical monomer molecules.



What could be the structural formula of the monomer?

A $CH_3CH_2CH_2CH=CH_2$

B $CH_3CH=CHCH=CH_2$

C $CH_2=C(CH_3)CH_2CH_3$

D $CH_2=C(CH_3)CH=CH_2$

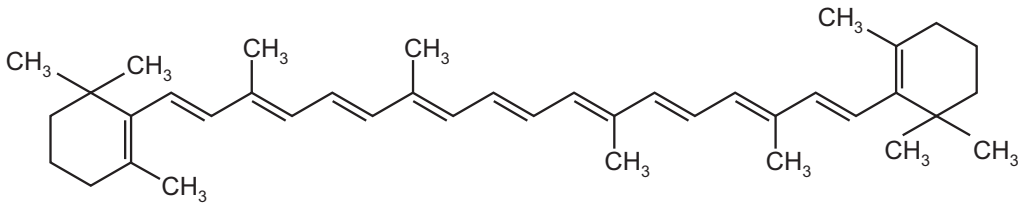
[J'14 P13 Q27]

3 Which row correctly describes the reaction between propene and bromine, $Br_2(l)$?

	reaction mechanism	organic product
A	electrophilic addition	$CH_3CHBrCH_2Br$
B	electrophilic addition	$CH_3CH_2CH_2Br$
C	nucleophilic substitution	$CH_3CH_2CH_2Br$
D	nucleophilic substitution	$CH_3CHBrCH_2Br$

[N'14 P11 Q20]

4 β-carotene is responsible for the orange colour of carrots.



β-carotene

β-carotene is oxidised by hot, concentrated, acidified $KMnO_4$.

When an individual molecule of β-carotene is oxidised in this way, many product molecules are formed.

How many of these product molecules contain a ketone functional group?

A 4 **B** 6 **C** 9 **D** 11

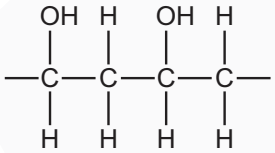
[N'14 P11 Q30]

5 Poly(ethenol) can be used to make plastic bags that dissolve in water.

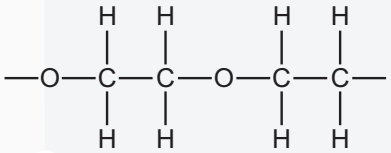
It may be considered to be made by addition polymerisation of CH_2=CH(OH).

Which structure represents a length of the polymer chain consisting of two monomer residues?

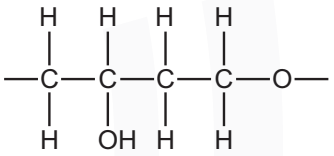
A



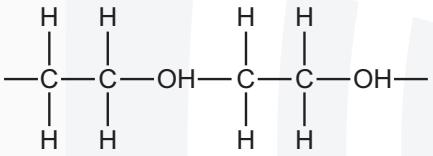
B



C



D



[N'14 P13 Q28]

6 Cottonseed oil contains large amounts of polyunsaturated carboxylic acids. When this oil is used to make margarine, the C=C double bonds in the unsaturated carboxylic acids are hydrogenated.

What reagents and conditions would be suitable to bring about this hydrogenation reaction?

A H_2 gas, nickel catalyst, 400 °C

B $LiAlH_4$ in dry ether

C $NaBH_4$, aqueous solution

D steam, concentrated H_2SO_4, 300 °C and 60 atm pressure

[J'15 P11 Q22]

7 Which intermediate ion forms in the greatest amount during the addition of HBr to propene?

A $CH_3CH^+CH_3$

B $CH_3CH_2CH_2^+$

C $CH_3CH^-CH_2Br$

D $CH_3CHBrCH_2^-$

[J'15 P11 Q23]

8 Four students, W, X, Y and Z, made the following statements about alkanes and alkenes.

W 'Bromine reacts with alkanes by electrophilic substitution.'

X 'Bromine reacts with alkenes by a free-radical addition mechanism.'

Y 'Alkenes can be oxidised by acidified manganate(VII) ions.'

Z 'Alkenes are formed from alkanes by cracking.'

Which two students are correct?

A W and X **B** W and Z **C** X and Y **D** Y and Z

[J'15 P12 Q22]

9 Alkane X has molecular formula C_4H_{10}.

X reacts with Cl_2(g) in the presence of sunlight to produce only two different monochloroalkanes, C_4H_9Cl. Both of these monochloroalkanes produce the same alkene Y, and no other organic products, when they are treated with hot ethanolic KOH.

What is produced when Y is treated with hot concentrated acidified $KMnO_4$?

A CO_2 and $CH_3CH_2CO_2H$

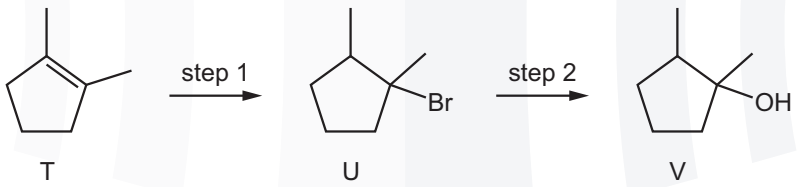
B CO_2 and CH_3COCH_3

C HCO_2H and CH_3COCH_3

D CH_3CO_2H only

[J'15 P13 Q26]

10 Hydrogen bromide can be added to T to give compound U. Compound U can be hydrolysed to compound V.



Four students, W, X, Y and Z, made the following statements.

W All the atoms in a molecule of compound T lie in the same plane.

X Compound V contains only one chiral centre.

Y Step 1 is an electrophilic addition reaction.

Z Step 2 is a nucleophilic substitution reaction.

Which two students are correct?

A W and Y **B** W and Z **C** X and Y **D** Y and Z

[M'16 P12 Q24]

11 Which statement about poly(chloroethene) is correct?

A The polymer can be cracked to produce chlorinated alkenes.

B The polymer has harmless combustion products.

C The polymer is readily biodegradable when buried.

D The repeat unit of the polymer has an M_r of 97.

[M'16 P12 Q29]

12 Oct-1-ene, $CH_3(CH_2)_5CH{=}CH_2$, can be thermally cracked.

Which combination of compounds W, X, Y and Z can be obtained by thermally cracking oct-1-ene?

$CH_2{=}CH_2$	$CH_3CH{=}CH_2$	$CH_3CH_2CH_3$	$CH_2{=}CHCH{=}CH_2$
W	X	Y	Z

A W, X, Y and Z

B W, X and Y only

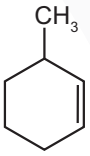
C W, X and Z only

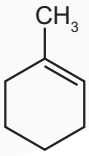
D W and X only

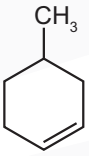
[J'16 P12 Q22]

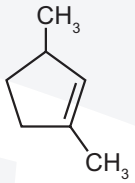
13 A cycloalkene with the molecular formula C_7H_{12} was oxidised by hot concentrated acidified MnO_4^-. The only organic product was 2-methylhexane-1,6-dioic acid.

What is the identity of the cycloalkene?

A 

B 

C 

D 

[J'16 P12 Q23]

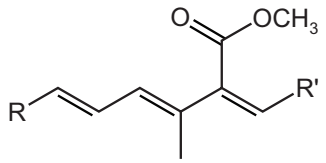
14 PVC is difficult to dispose of. Two possible methods are burying it in landfill sites and disposal by combustion.

Which row of the table is correct?

	rate of biodegradation of PVC in landfill sites	gases produced when PVC combusts
A	fast	CO_2, H_2O, HCl
B	fast	CO_2, H_2O, Cl_2
C	slow	CO_2, H_2O, Cl_2
D	slow	CO_2, H_2O, HCl

[N'16 P11 Q22]

15 Part of the structure of a fungicide, strobilurin, is shown. R and R' are inert groups.

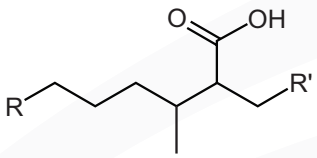


strobilurin

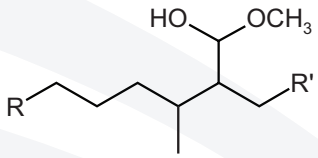
In this reaction, strobilurin is warmed with aqueous sulfuric acid producing compound X. Compound X is then treated with hydrogen in the presence of a nickel catalyst producing compound Y.

What could be the structure of compound Y?

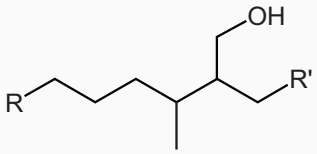
A



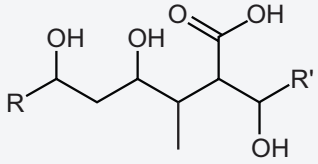
B



C

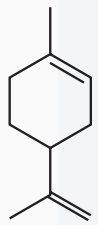


D



[N'16 P11 Q23]

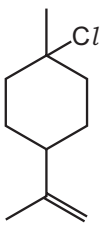
16 Limonene is found in lemon and orange oils.



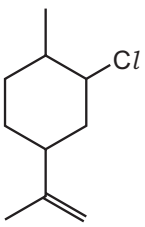
limonene

What will be the major product when limonene is reacted with an excess of dry hydrogen chloride?

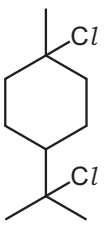
A



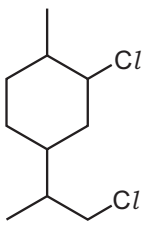
B



C



D



[N'16 P12 Q20]

17 Propene undergoes a variety of reactions.

Which row is correct?

	reagent added to propene	products include
A	$Br_2(aq)$	1-bromopropane
B	cold, dilute, acidified $KMnO_4(aq)$	propanoic acid
C	HBr(g)	2-bromopropane
D	hot, concentrated, acidified $KMnO_4(aq)$	propanoic acid

[M'17 P12 Q23]

18 Polymerisation of ethene gives poly(ethene).

How does the bonding between carbon atoms in poly(ethene) compare with that in ethene?

A longer and stronger in poly(ethene)

B longer and weaker in poly(ethene)

C shorter and stronger in poly(ethene)

D shorter and weaker in poly(ethene)

[M'17 P12 Q24]

19 An alkene is reacted with acidified manganate(VII) ions, MnO_4^-. The desired organic product has a relative molecular mass greater than that of the alkene by 34.

What conditions should be used?

A cold, concentrated MnO_4^-

B cold, dilute MnO_4^-

C hot, concentrated MnO_4^-

D hot, dilute MnO_4^-

[J'17 P11 Q22]

20 An alkene is reacted with acidified manganate(VII) ions, MnO_4^-. The desired organic product has a relative molecular mass greater than that of the alkene by 34.

What conditions should be used?

A cold, concentrated MnO_4^-

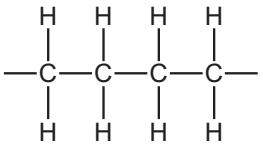
B cold, dilute MnO_4^-

C hot, concentrated MnO_4^-

D hot, dilute MnO_4^-

[J'17 P11 Q22]

21 The diagram shows a short length of an addition polymer chain.



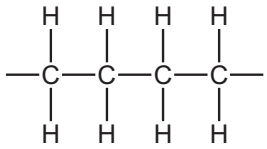
The polymer has a relative molecular mass of approximately 10 000.

Approximately how many monomer units are joined together in each polymer molecule?

A 180 **B** 360 **C** 625 **D** 710

[J'17 P11 Q23]

22 The diagram shows a short length of an addition polymer chain.



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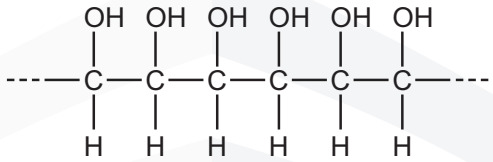
[J'17 P11 Q23]

23 The diagram represents the structure of a polymer.



By which method might this polymer be made?

A polymerise ethene followed by hydration

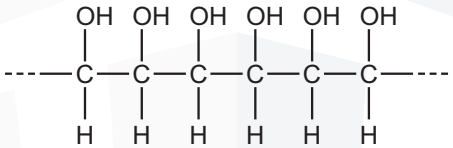
B polymerise ethene followed by oxidation with cold, acidified $KMnO_4$

C polymerise 1,2-dichloroethene followed by hydrolysis

D polymerise 1,2-dichloroethene followed by oxidation with cold, acidified $KMnO_4$

[J'17 P13 Q24]

24 The diagram represents the structure of a polymer.



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C polymerise 1,2-dichloroethene followed by hydrolysis

D polymerise 1,2-dichloroethene followed by oxidation with cold, acidified $KMnO_4$

[J'17 P13 Q24]

25 Bromine reacts with ethene in the dark.

Which description of the organic intermediate in this reaction is correct?

A It has a negative charge.

B It is a free radical.

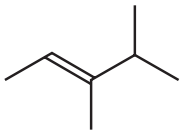
C It is a nucleophile.

D It is an electrophile.

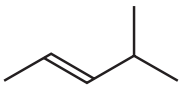
[J'17 P13 Q25]

26 Which compound would produce two different carboxylic acids when treated with hot, concentrated, acidified manganate(VII) ions?

A



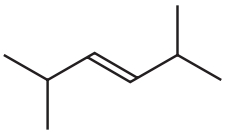
B



C



D



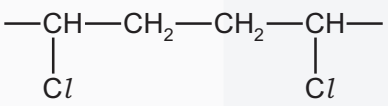
[N'17 P12 Q22]

27 Which types of bond are broken and formed in the addition polymerisation of alkenes?

	type of bond broken	type of bond formed
A	π only	σ only
B	π only	σ and π
C	σ and π	σ only
D	σ and π	σ and π

[N'17 P12 Q23]

28 A section of an addition polymer chain is shown.



Which monomer could be used to make this polymer?

A CH_2CHCH_2Cl

B CH_2CHCl

C $CH_3CHCHCl$

D $CHClCHCH_2CH_2Cl$

[N'17 P11 Q23]

29 Maleic acid is used in the food industry and for stabilising drugs. It is the cis-isomer of butenedioic acid and has the structural formula $HO_2CCH{=}CHCO_2H$.

What is the product formed from the reaction of maleic acid with cold, dilute, acidified manganate(VII) ions?

A $HO_2CCH(OH)CH(OH)CO_2H$

B HO_2CCO_2H

C $HO_2CCH_2CH(OH)CO_2H$

D $HO_2CCOCOCO_2H$

[J'18 P12 Q22]

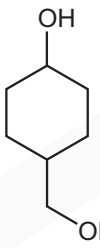
SECTION B

The responses **A** to **D** should be selected on the basis of

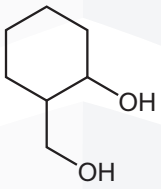
A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

1 Which compounds, on heating with excess concentrated sulfuric acid, produce **only one** product with molecular formula C_7H_{10}?

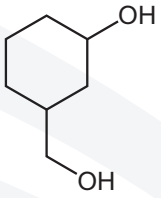
1



2



3

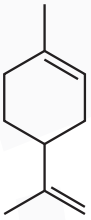


[N'15 P12 Q39]

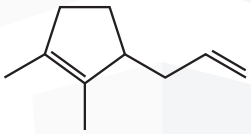
2 Compound **Z** is heated with concentrated acidified potassium manganate(VII). This produces an equimolar mixture of CO_2 and $CH_3COCH_2CH_2CH(COCH_3)CH_2CO_2H$.

What could be the structural formula of **Z**?

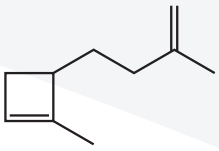
1



2

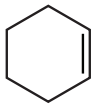


3



[N'15 P12 Q40]

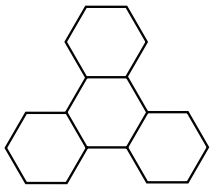
3 The diagram shows the structure of cyclohexene.



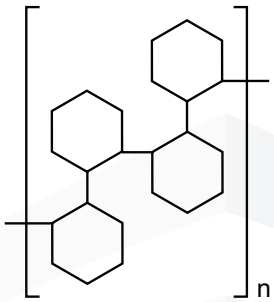
cyclohexene

Which structures could be formed by addition reactions with cyclohexene as the only reactant?

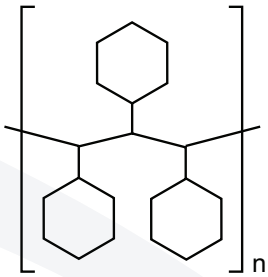
1



2

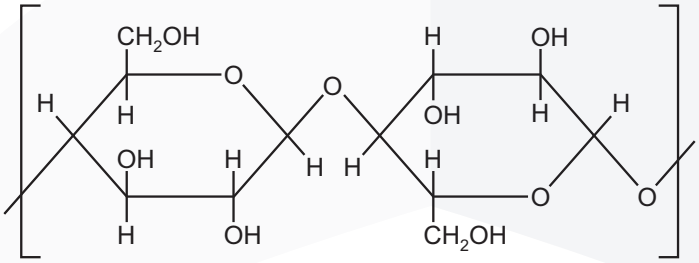


3



[J'16 P11 Q38]

4 A cathedral in New Zealand has been constructed from cardboard. Cardboard contains polymer molecules. Part of one such polymer molecule is shown below.



Which statements about this polymer are correct?

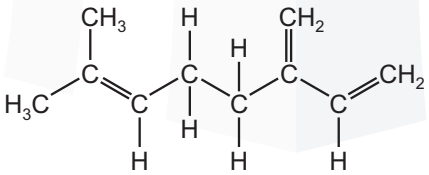
1 The polymer molecules can form hydrogen bonds with each other.

2 The polymer can form intermolecular forces with water molecules.

3 The polymer will not burn easily because it is a secondary alcohol.

[N'16 P12 Q32]

5 A species of termite produces a chemical defence secretion which contains the molecule shown.



To help determine the structure of this compound, it is treated with hot, concentrated, acidified manganate(VII) ions.

Which compounds are produced in this reaction?

1 CO_2

2 CH_3COCH_3

3 CH_3CO_2H

[N'16 P12 Q37]

6 Which mechanisms are represented in this sequence of reactions?

$CH_3CH_2CH_3 \rightarrow CH_3CH_2CH_2Cl \rightarrow CH_3CH_2CH_2OH \rightarrow CH_3CHCH_2 \rightarrow CH_3CHBrCH_2Br$

1 electrophilic addition

2 nucleophilic substitution

3 free radical substitution

[J'17 P13 Q37]

7 Limonene is found in lemons.



limonene

Limonene is heated with concentrated acidified potassium manganate(VII).

Which compounds are produced?

1 $CH_3COCH_2CH_2CH(CH_2CO_2H)_2$

2 CO_2

3 $CH_3COCH_2CH_2CH(COCH_3)CH_2CO_2H$

[J'18 P11 Q38]

ALKENES WS 2

SECTION A

1 Alkanes and alkenes both react with bromine.

(a) Explain how and why bromine can be used to distinguish between an alkene and an alkane.

.....

.....

..... [2]

(b) The reaction of ethane with bromine forms a mixture of products.

(i) State the essential conditions for this reaction to occur.

..... [1]

(ii) Give the full name of the mechanism of this reaction.

..... [2]

(iii) Give the equation for a **termination** step that could occur, producing a **hydrocarbon**.

..... [1]

(iv) Give the equation for one **propagation** step involved in the formation of dibromoethane from bromoethane during this reaction.

..... [1]

(c) The reaction of ethene with bromine forms a single product.

(i) Give the full name of the mechanism of this reaction.

..... [2]

(ii) Complete the diagram below to illustrate this mechanism.
Include all relevant charges, partial charges, curly arrows and lone pairs.



[4]

[J'14 P21 Q4]

2 (b) $(CH_3)_2C=C(CH_3)_2$

(i) name ..... [1]

(ii) Draw the **skeletal** formula of the organic product of the reaction of this compound with cold, dilute, acidified manganate(VII) ions.

[1]

(iii) Name the organic product of the reaction of this compound with hot, concentrated, acidified manganate(VII) ions.

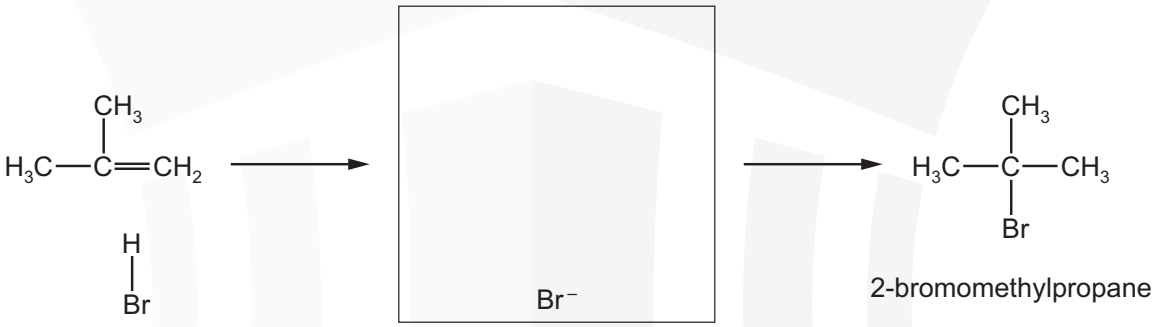
..... [1]

(iv) Draw the structure of part of a molecule of the addition polymer formed from this compound, showing exactly **three** repeat units.

(c) $(CH_3)_2C=CH_2$

(i) name ..... [1]

(ii) Complete the mechanism for the reaction of this compound with hydrogen bromide. Include all necessary curly arrows, lone pairs, charges and partial charges.



[4]

(iii) Explain fully why 2-bromomethylpropane is the major product of this reaction while only relatively small amounts of 1-bromomethylpropane are produced.

.....

.....

.....

.....

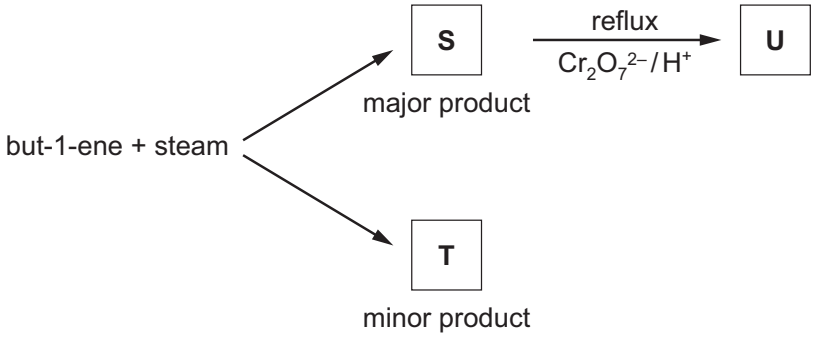
.....

.....

..... [3]

[N'16 P21 Q4]

3 **(c)** But-1-ene reacts with steam as shown to form a mixture of two structural isomers, **S** and **T**.



S can be oxidised with acidified potassium dichromate(VI) to form compound **U**.
S and **U** both react with alkaline aqueous iodine.

(i) Identify the *type of reaction* that occurs when but-1-ene reacts with steam.

..... [1]

(ii) State what can be deduced about the structure of **S** from its reaction with alkaline aqueous iodine.

..... [1]

(iii) Explain why **S** is the major product of the reaction of but-1-ene with steam.

.....

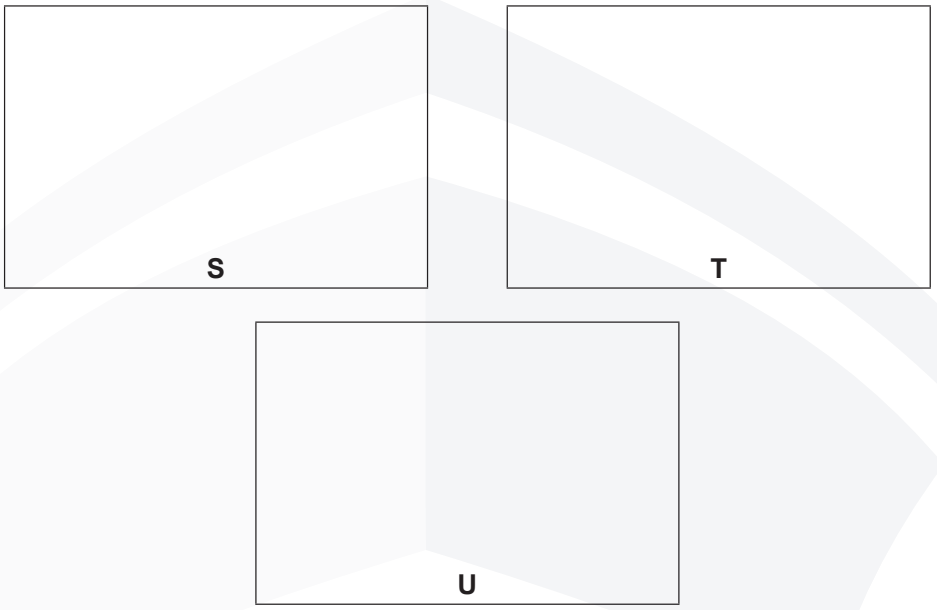
.....

.....

.....

..... [2]

(iv) Draw the **skeletal** formulae of **S**, **T** and **U**.



[3]

(v) Write an equation to represent the oxidation of **S** to **U** by acidified potassium dichromate(VI).

You should use [O] to represent the oxidising agent.

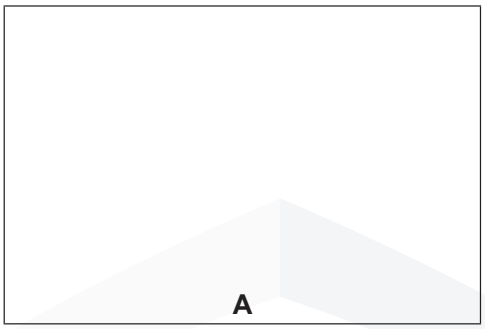
..... [1]

4 **(a)** The hydrocarbons **A**, C_4H_{10}, and **B**, C_4H_8, are both unbranched.

A does **not** decolourise bromine.

B decolourises bromine and shows geometrical isomerism.

(i) Draw the skeletal formula of **A**.



[1]

(ii) The hydrocarbon **A**, C_4H_{10}, has a branched isomer.

Suggest why unbranched **A** has a higher boiling point than its branched isomer.

.....

.....

.....

.....

..... [2]

(iii) Give the structural formula of **B**.

..... [1]

(iv) Explain why **B** shows geometrical isomerism.

.....

.....

.....

..... [2]

(v) Draw the mechanism of the reaction of **B** with bromine, Br_2.
Include all necessary charges, dipoles, lone pairs and curly arrows.

[4]

(vi) Explain the origin of the dipole on Br_2 in this mechanism.

.....

.....

..... [1]

[J'17 P22 Q4]

5 **A**, **B** and **C** all have the formula C_4H_8. They all decolourise bromine and are structural isomers of each other.

(a) State the name of the process by which **A**, **B** and **C** could be obtained from $C_{10}H_{22}$.

..... [1]

(b) Draw the structures of these three **structural** isomers.

[1]

(c) Only **A** shows geometrical isomerism.

(i) Explain the meaning of the term *geometrical isomerism*.

.....

.....

.....

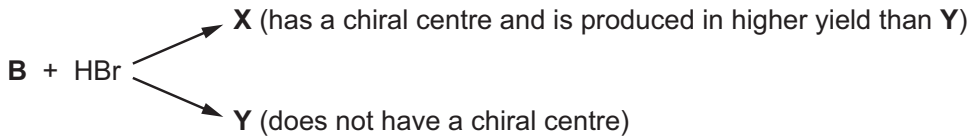
..... [2]

(ii) Draw the displayed formula of **A** and use it to show the mechanism of the reaction of **A** with HBr. Include all necessary charges, dipoles, lone pairs and curly arrows.

[4]

(d) **B** does **not** show geometrical isomerism.

B reacts with HBr to form a mixture of two structural isomers, **X** and **Y**.



(i) State the meaning of the term *chiral centre*.

.....

.....

.....

..... [1]

(ii) Name **B**.

..... [1]

(iii) **X** exists as a pair of optical isomers.

Draw these isomers using the conventional three-dimensional representation.

[2]

(iv) Explain why **X** is produced in higher yield than **Y**.

.....

.....

.....

..... [2]

(e) **C** does **not** show geometrical isomerism.

C reacts with HBr to form a mixture of two structural isomers, neither of which has a chiral centre.

(i) Name **C**.

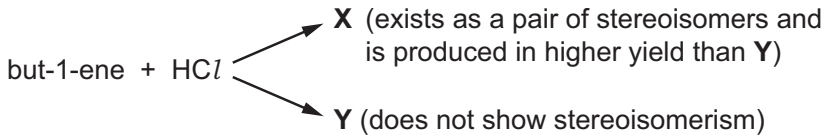
..... [1]

(ii) Draw the **displayed** formula of each of the structural isomers produced by the reaction of **C** with HBr.

[2]

[J'17 P23 Q4]

6 (d) The product of reaction 2, but-1-ene, does **not** show stereoisomerism. However, but-1-ene reacts with HC*l* to form a mixture of structural isomers **X** and **Y**.



(i) Explain the meaning of the term *stereoisomers*.

.....

.....

..... [2]

(ii) Give **two** reasons why but-1-ene does **not** show stereoisomerism.

.....

.....

..... [2]

(iii) Name **X** and **Y**.

X .....

Y .....
[2]

(iv) Name the type of stereoisomerism shown by **X**.

..... [1]

(v) Use the conventional representation to draw the two stereoisomers of **X**.

[2]

[J'17 P23 Q4]

7 **(b)** $CHCl F_2$ was used as an alternative to chlorofluorocarbons (CFCs). $CHCl F_2$ should no longer be used because it was found to contribute to the *enhanced greenhouse effect*.

(i) Give the meaning of the term *enhanced greenhouse effect*.

.....

..... [1]

(ii) Explain how $CHCl F_2(g)$ may contribute to this effect.

.....

.....

..... [2]

(iii) Suggest another environmental problem associated with the use of $CHCl F_2$.

..... [1]

(c) $CHCl F_2$ is also used to produce the monomer tetrafluoroethene, C_2F_4.

This monomer can be used to produce poly(tetrafluoroethene), PTFE.

(i) State the type of polymerisation that occurs during the production of PTFE.

..... [1]

(ii) Draw the repeat unit of PTFE.

[1]

(iii) Suggest why PTFE is used as a coating for cooking pans.

.....

.....

.....

..... [1]

(iv) Waste disposal can cause litter problems.

State two **other** difficulties associated with the disposal of PTFE.

1 .....

.....

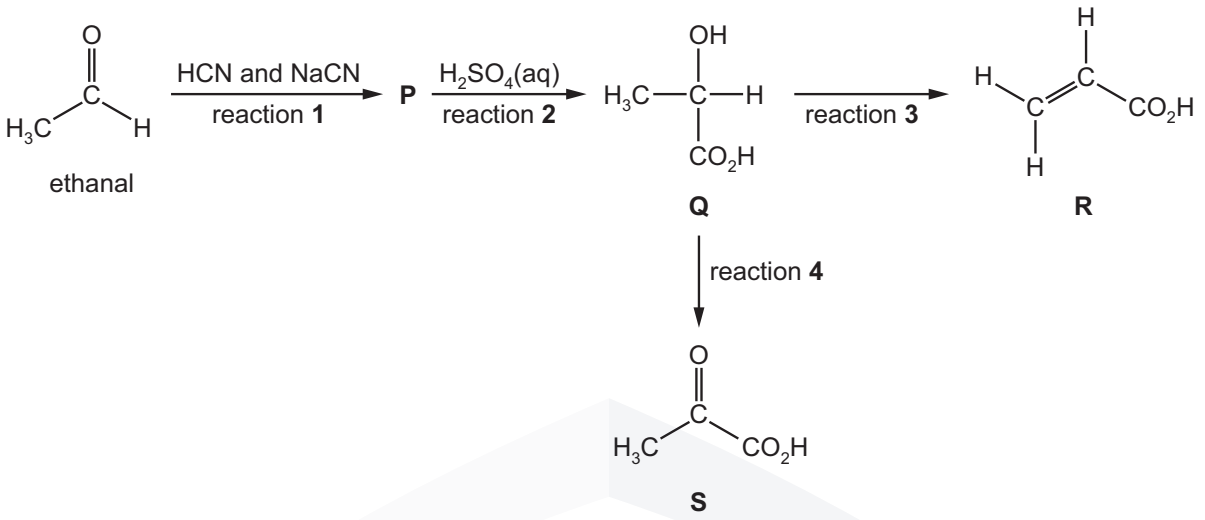
2 .....

.....

[2]

[J'18 P21 Q3]

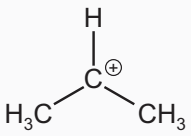
8 The diagram shows a reaction sequence starting from ethanal.



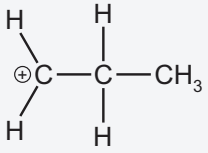
(d) Compound **Z**, $H_2C{=}CHCH_3$, is produced from **R**.

Z can be used in a two-step process to produce 2-aminopropane.

(i) In the first step, **Z** reacts with HBr to form two products. The structure of the product depends on which intermediate is formed, intermediate **I** or intermediate **II**.



intermediate **I**



intermediate **II**

Explain why intermediate **I** is more likely to form than intermediate **II**.

.....

.....

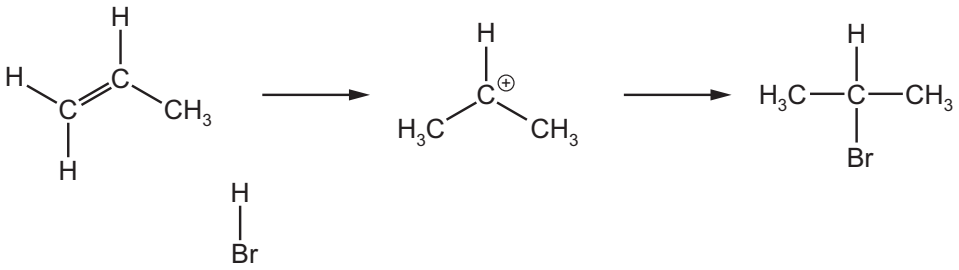
.....

..... [2]

(ii) When intermediate **I** forms, the product of the first step is **T**.

Complete the diagram to show the mechanism for the conversion of **Z** to **T**.
Include all relevant charges, partial charges, curly arrows and lone pairs.

Z



T

[3]

ALKENES WS 3

SECTION A

1 Polymerisation of chloroethene gives pvc.

How does the carbon-carbon bond in pvc compare with that in chloroethene?

A longer stronger

B longer weaker

C shorter stronger

D shorter weaker

[J'02 Q22]

2 Chloroethene, CH_2=CHC*l*, is the monomer of pvc.

What are the C–C–C bond angles along the polymeric chain in pvc?

A They are all 109 °.

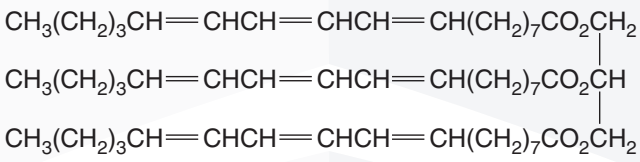
B Half are 109 ° and half are 120 °.

C They are all 120 °.

D They are all 180 °.

[N'02 Q23]

3 In the preparation of soft margarine, glyceryl trieleostearate



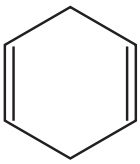
is suitably hydrogenated so that, on average, one of its side-chains is converted into the $CH_3(CH_2)_4CH$=$CHCH_2CH$=$CH(CH_2)_7CO_2$ residue and two side-chains are converted into the $CH_3(CH_2)_7CH$=$CH(CH_2)_7CO_2$ residue.

How many moles of hydrogen are required to convert one mole of glyceryl trieleostearate into the soft margarine?

A 4 **B** 5 **C** 6 **D** 9

[J'03 Q2]

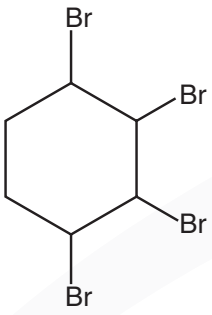
4 Cyclohexa-1,4–diene is treated with a solution of bromine in tetrachloromethane.



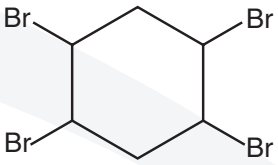
cyclohexa-1,4-diene

Which product is formed?

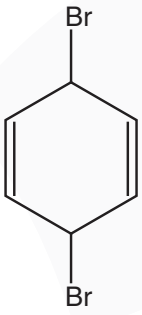
A



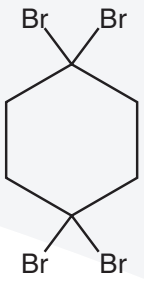
B



C



D



[J'03 Q24]

5 Which reaction is **not** an electrophilic addition?

A $CH_2{=}CH_2 + HI \longrightarrow CH_3CH_2I$

B $CH_3CH{=}CH_2 + Br_2 \longrightarrow CH_3CHBrCH_2Br$

C $CH_3CH{=}CH_2 + H_2O \xrightarrow{\text{conc } H_2SO_4} CH_3CH(OH)CH_3$

D $CH_3CHO + HCN \longrightarrow CH_3CH(OH)CN$

[J'03 Q25]

6 Hydrogen bromide reacts with ethene to form bromoethane.

What is the best description of the organic intermediate in this reaction?

A It contains carbon, hydrogen and bromine.

B It has a negative charge.

C It is an electrophile.

D It is a free radical.

[N'03 Q21]

7 In which way are ethene and propane similar?

$CH_2=CH_2$	$CH_3CH_2CH_3$
ethene	propane

A They are both obtained by the dehydration of alcohols.

B They are both neutral to an indicator solution.

C They can both be hydrogenated using a suitable catalyst.

D They can both undergo polymerisation under suitable conditions.

[J'04 Q24]

8 Ethene reacts with aqueous bromine to give two products, CH_2BrCH_2Br and CH_2BrCH_2OH.

Which statement is correct for these products?

A Both products are obtained in this reaction by electrophilic substitution.

B Both products are obtained in this reaction by nucleophilic addition.

C Both products can be hydrolysed to form the same diol.

D Both products can form hydrogen bonds with water.

[J'04 Q27]

9 What can behave as an electrophilic reagent?

A Br_2

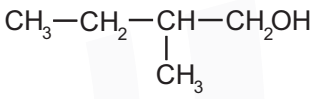
B Na

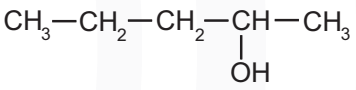
C NH_3

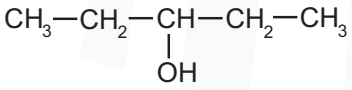
D CN^-

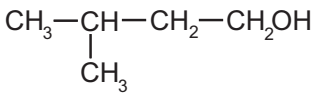
[N'04 Q20]

10 Which isomer of $C_5H_{11}OH$ gives, on dehydration, the greatest number of different alkenes?

A 

B 

C 

D 

[N'04 Q27]

11 When bromine reacts with propene in an organic solvent at room temperature, what is the mechanism by which the bromine attacks the propene?

A electrophilic addition

B electrophilic substitution

C nucleophilic addition

D nucleophilic substitution

[J'05 Q22]

12 In many countries plastic waste is collected separately and sorted. Some of this is incinerated to provide heat for power stations.

Why is pvc, polyvinylchloride, removed from any waste that is to be incinerated?

A It can be melted down and re-used.

B Its combustion products are harmful.

C It destroys the ozone layer.

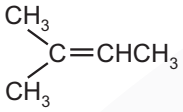
D It does not burn easily.

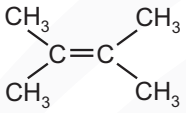
[J'05 Q30]

13 Which hydrocarbon, on treatment with hot acidified potassium manganate(VII), would give ethanoic acid only?

A $CH_3CH=CH_2$

B $CH_3CH=CHCH_3$

C


D


[N'05 Q21]

14 Compound **X** on reaction with hot concentrated sulphuric acid gave a mixture of **three** alkenes.

What could **X** be?

A butan-2-ol

B propan-2-ol

C 2-methylbutan-2-ol

D 2-methylpropan-2-ol

[N'05 Q24]

15 Which equation or statement describes what happens when poly(propene) is burned in an excess of air?

A $(C_3H_6)_n + 1\frac{1}{2}\,nO_2 \rightarrow 3nC + 3nH_2O$

B $(C_3H_6)_n + 4\frac{1}{2}\,nO_2 \rightarrow 3nCO_2 + 3nH_2O$

C $(C_3H_6)_n + 6nO_2 \rightarrow 3nCO_2 + 3nH_2O$

D Poly(propene) does not burn.

[N'06 Q25]

16 In which reaction is a carbocation (carbonium ion) an intermediate?

A $CH_2{=}CH_2 + Br_2 \longrightarrow CH_2BrCH_2Br$

B $CH_3CH_2Br + NaOH \longrightarrow CH_3CH_2OH + NaBr$

C $CH_3CH_3 + Cl_2 \longrightarrow CH_3CH_2Cl + HCl$

D $CH_3CHO + HCN \xrightarrow{CN^-} CH_3CH(OH)CN$

[J'07 Q22]

17 The compound 1,2-dichloroethene, $C_2H_2Cl_2$, has been used as an industrial solvent for a number of compounds including fats, camphor and caffeine.

Which statement about this compound is **incorrect**?

A The compound can be catalytically hydrogenated.

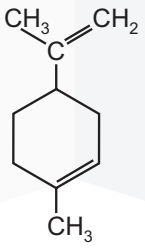
B The compound is a planar molecule.

C The compound shows *cis-trans* isomerism.

D The compound shows optical isomerism.

[J'07 Q23]

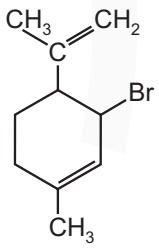
18 Limonene is an oil formed in the peel of citrus fruits.



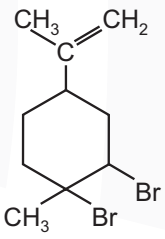
limonene

Which product is formed when molecular bromine reacts with limonene at room temperature in the dark?

A



B



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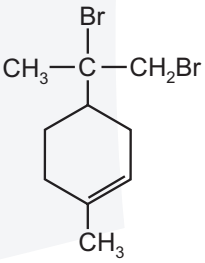
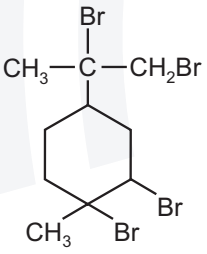
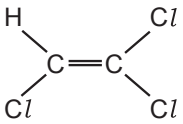


D



[N'07 Q23]

19 Trichloroethene is widely used as a dry-cleaning agent.



With which of the following does trichloroethene react to give a chiral product?

A Br_2 **B** HCl **C** NaCN(aq) **D** NaOH(aq)

[J'08 Q21]

20 Which reaction would **not** give propene as one product?

A adding an excess of concentrated sulfuric acid to propan-1-ol

B adding warm aqueous sodium hydroxide to 2-bromopropane

C adding warm ethanolic sodium hydroxide to 1-bromopropane

D passing propan-2-ol vapour over heated aluminium oxide

[J'09 Q25]

21 2-Methylbuta-1,3-diene, $CH_2=C(CH_3)–CH=CH_2$, is used as a monomer in the manufacture of synthetic rubbers.

Which compound would **not** produce this monomer on treatment with concentrated sulfuric acid at 170 °C?

A $(CH_3)_2C(OH)CH(OH)CH_3$

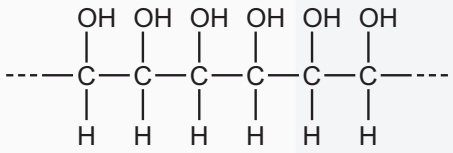
B $HOCH_2CH(CH_3)CH_2CH_2OH$

C $HOCH_2CH(CH_3)CH(OH)CH_3$

D $HOCH_2C(CH_3)(OH)CH_2CH_3$

[J'09 Q29]

22 The following diagram represents the structure of a possible polymer.



By which method might this polymer be made?

A polymerise ethene followed by hydration

B polymerise ethene followed by oxidation with cold acidified $KMnO_4$

C polymerise 1,2-dichloroethene followed by hydrolysis

D polymerise 1,2-dichloroethene followed by oxidation with cold acidified $KMnO_4$

[N'09 P11 Q23]

23 Polymerisation of 1,1-dichloroethene produces a dense, high melting point substance that does not allow gases to pass through. It is used as cling wrapping.

Which sequence appears in a short length of the polymer chain?

A $\{CH_2CCl_2CH_2CCl_2CH_2CCl_2\}$

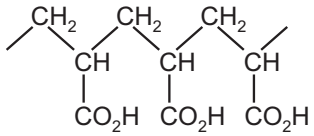
B $\{CHClCHClCHClCHClCHClCHCl\}$

C $\{CCl_2CCl_2CCl_2CCl_2CCl_2CCl_2\}$

D $\{CH_2CCl_2CHClCHClCH_2CCl_2\}$

[J'10 P11 Q27]

24 One of the characteristics of addition polymerisation is that the empirical formulae of the polymer and of its monomer are the same. The absorbent material in babies' disposable nappies is made from the addition polymer shown.



From which monomer could this addition polymer be obtained?

A $CH_3CH(OH)CO_2H$

B $HOCH_2CH_2CO_2H$

C $H_2C{=}CHCO_2H$

D $HO_2CCH{=}CHCO_2H$

[N'10 P11 Q20]

25 Which alcohol gives only **one** possible oxidation product when warmed with dilute acidified potassium dichromate(VI)?

A butan-1-ol

B butan-2-ol

C 2-methylpropan-1-ol

D 2-methylpropan-2-ol

[N'10 P11 Q24]

26 Nine compounds have molecular formula $C_4H_8Br_2$.

Which compound may be synthesised from an alkene by an addition reaction?

A 1,1-dibromobutane

B 1,2-dibromobutane

C 1,3-dibromobutane

D 1,3-dibromomethylpropane

[N'10 P12 Q21]

27 Which sequence of reagents may be used in the laboratory to convert propan-1-ol into 2-bromopropane?

A concentrated sulfuric acid, followed by bromine

B concentrated sulfuric acid, followed by hydrogen bromide

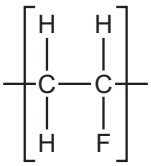
C ethanolic sodium hydroxide, followed by bromine

D ethanolic sodium hydroxide, followed by hydrogen bromide

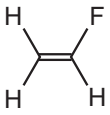
[N'10 P12 Q23]

28 Fluoroalkenes are used to make polymers such as poly(vinyl)fluoride (PVF).

PVF is used to make non-flammable interiors for aircraft. The diagram shows the repeat unit of the polymer PVF.



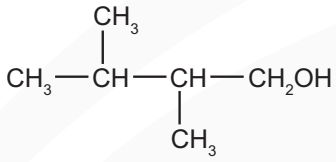
What is the skeletal formula of the monomer of PVF?

A  **B**  **C**  **D** 

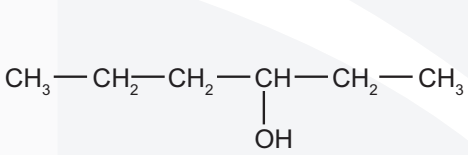
[N'10 P12 Q28]

29 Which isomer of $C_6H_{13}OH$ gives the greatest number of different alkenes when it is dehydrated?

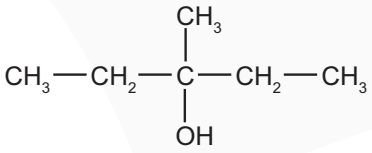
A



B



C



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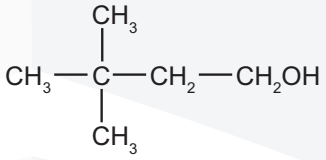
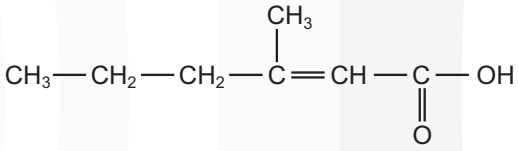


[J'11 P11 Q25]

30 An unpleasant smelling chemical produced in the human armpit is 3-methylhex-2-enoic acid.



If this compound is reacted with a cold, dilute, acidified solution of potassium manganate(VII), how many chiral centres will be produced?

A 0 **B** 1 **C** 2 **D** 3

[N'11 P11 Q28]

31 Bromine and propene undergo an addition reaction.

Which is a property of the product?

A It exists in *cis-trans* isomers.

B It is more volatile than propene.

C It possesses a chiral centre.

D It possesses hydrogen bonding.

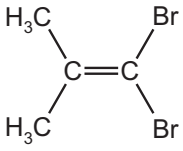
[N'11 P12 Q20]

32 How many of the isomeric alcohols with the formula C_4H_9OH will produce an alkene that has cis and trans isomers, on treatment with conc. H_2SO_4?

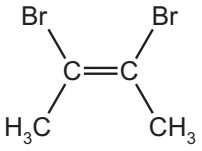
A 1 **B** 2 **C** 3 **D** 4

[N'11 P12 Q30]

33 Isomers **X** and **Y** both react with HBr.



X



Y

A mixture of **X** and **Y** is reacted with HBr.

Which three structures represent three **different** possible products of this reaction?

A $(CH_3)_2CHCBr_3$ $(CH_3)_2CBrCHBr_2$ $CH_3CHBrCHBrCH_3$

B $(CH_3)_2CHCBr_3$ $(CH_3)_2CBrCHBr_2$ $CH_3CBr_2CHBrCH_3$

C $(CH_3)_2CBrCBr_3$ $(CH_3)_2CHCBr_3$ $CH_3CBr_2CHBrCH_3$

D $(CH_3)_2CBrCHBr_2$ $CHBr_2CBr(CH_3)CH_3$ $CH_3CHBrCBr_2CH_3$

[J'12 P12 Q23]

34 Which statement does **not** correctly describe the polymer PVC?

A Combustion of PVC waste produces a highly acidic gas.

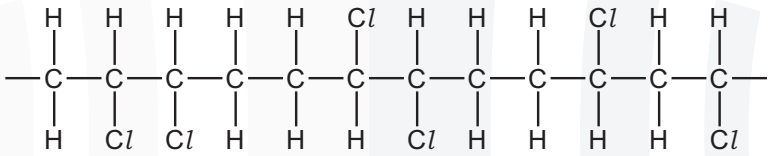
B PVC molecules are saturated.

C The empirical formula of PVC is the same as the empirical formula of its monomer.

D The repeat unit of PVC is $-(CHClCHCl)-$.

[J'12 P13 Q30]

35 A molecule of a polymer contained the sequence shown.



Which monomer could produce this polymer by addition polymerisation?

A $CHCl=CHCl$

B $CH_2=CHCl$

C $CH_3CCl=CHCl$

D $CH_3CCl=CH_2$

[N'12 P13 Q22]

36 Bromine reacts with ethene to form 1,2-dibromoethane.

What is the correct description of the organic intermediate in this reaction?

A It has a negative charge.

B It is a free radical.

C It is a nucleophile.

D It is an electrophile.

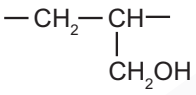
[J'13 P11 Q22]

37 Synthetic resins, plasticisers and many other chemicals can be made by polymerisation of a variety of monomers including prop-2-en-1-ol, $CH_2{=}CHCH_2OH$.

Which structure represents the repeat unit in poly(prop-2-en-1-ol)?

A $-CH_2-CH-CH_2-OH-$

B



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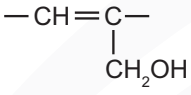

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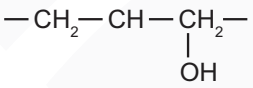
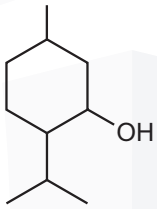


[J'13 P11 Q29]

38 The compound shown is menthol, a naturally-occurring alcohol found in peppermint oil.

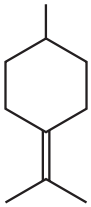


menthol

When menthol is heated with concentrated sulfuric acid it reacts. The products that form include compound **T**.

What could be the structure of compound **T**?

A



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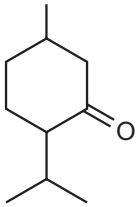

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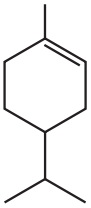

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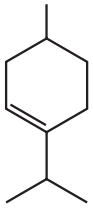


[J'13 P12 Q25]

39 Polymerisation of ethene gives poly(ethene).

How does the carbon-carbon bond in poly(ethene) compare with that in ethene?

A The carbon-carbon bond is longer and stronger in poly(ethene).

B The carbon-carbon bond is longer and weaker in poly(ethene).

C The carbon-carbon bond is shorter and stronger in poly(ethene).

D The carbon-carbon bond is shorter and weaker in poly(ethene).

[J'13 P12 Q30]

40 Ethene reacts with steam in the presence of sulfuric acid.

$$C_2H_4 + H_2O \rightarrow CH_3CH_2OH$$

What type of reaction is this?

A acid / base

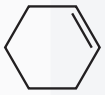
B addition

C hydrolysis

D substitution

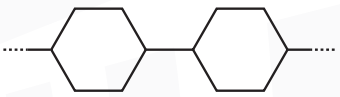
[J'13 P13 Q20]

41 Cyclohexene, shown below, can form an addition polymer.



Which structure represents a section of the polymer including two cyclohexene residues?

A



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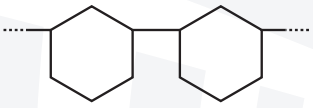

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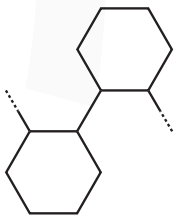


D



[J'13 P13 Q28]

42 The compound 'leaf alcohol' is partly responsible for the smell of new-mown grass.

$CH_3CH_2CH{=}CHCH_2CH_2OH$

leaf alcohol

What will be formed when 'leaf alcohol' is oxidised using an excess of hot, acidified $K_2Cr_2O_7(aq)$?

A $CH_3CH_2CH(OH)CH(OH)CH_2CO_2H$

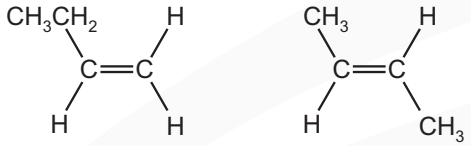
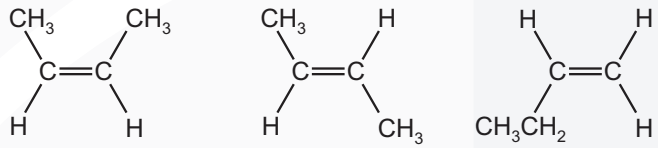
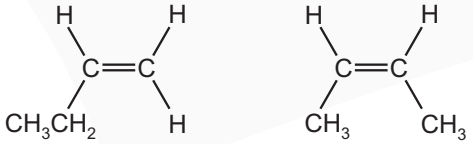
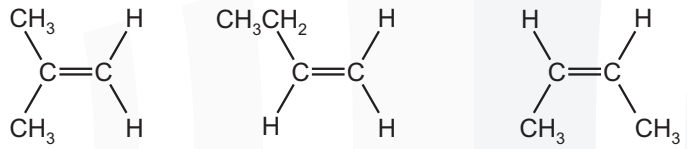
B $CH_3CH_2COCOCH_2CO_2H$

C $CH_3CH_2CH{=}CHCH_2CO_2H$

D $CH_3CH_2CO_2H$ and $HO_2CCH_2CO_2H$

[N'13 P11 Q22]

43 What are the only structures formed when butan-2-ol is heated with concentrated H_2SO_4?

A	
B	
C	
D	

[N'13 P11 Q25]

44 Which types of bond breakage and bond formation occur in the addition polymerisation of alkenes?

	bond breakage	bond formation
A	π only	σ only
B	π only	σ and π
C	σ and π	σ only
D	σ and π	σ and π

[N'13 P11 Q30]

45 Pent-2-ene, $CH_3CH_2CH{=}CHCH_3$, reacts in a similar way to ethene.

Pent-2-ene is reacted with cold, dilute, acidified manganate(VII) ions.

What will be produced in the greatest amount?

A $CH_3CH_2CH(OH)CH(OH)CH_3$

B $CH_3CH_2COCOCH_3$

C a mixture of $CH_3CH_2CH(OH)CH_2CH_3$ and $CH_3CH_2CH_2CH(OH)CH_3$

D CH_3CH_2COOH and CH_3COOH

[N'13 P13 Q23]

46 Which fragment could appear in the chain produced by polymerising 1,1-dichloroethene?

A $-CH_2-CH_2-CCl_2-CCl_2-CH_2-CH_2-$

B $-CHCl-CHCl-CHCl-CHCl-CHCl-CHCl-$

C $-CH_2-CCl_2-CH_2-CH_2-CH_2-CCl_2-$

D $-CCl_2-CCl_2-CH_2-CH_2-CH_2-CCl_2-$

[N'13 P13 Q30]

SECTION B

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

1 Which compounds would be formed in the reaction of ethene with aqueous bromine in the presence of sodium chloride?

1 CH_2ClCH_2Cl

2 CH_2BrCH_2Cl

3 CH_2BrCH_2Br

[J'02 Q40]

2 Which properties of poly(alkenes) and of pvc can cause their disposal to be difficult?

1 Poly(alkenes) are highly flammable.

2 Poly(alkenes) are non–biodegradable.

3 pvc produces harmful combustion products.

[J'04 Q40]

3 Which compounds can be obtained from ethene in a **single** reaction?

1 CH_3CH_3

2 $-(-CH_2CH_2-)_n-$

3 $HOCH_2CH_2OH$

[J'05 Q38]

4 The sex-attractant of the house-fly is muscalure, with the following formula.

$$CH_3(CH_2)_7CH=CH(CH_2)_{12}CH_3$$

Which statements about muscalure are correct?

1 It will decolourise aqueous bromine.

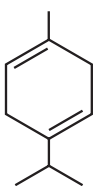
2 It will be oxidised by cold aqueous alkaline $KMnO_4$ to give a diol.

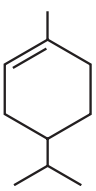
3 It will be optically active.

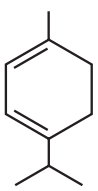
[N'05 Q40]

5 The following three hydrocarbons all occur naturally.

Which of these will be split into two organic compounds, both containing a ketone group, when treated with hot acidified potassium manganate(VII)?

1 

2 

3 

[N'06 Q37]

6 Which structures show a primary alcohol that **cannot** be dehydrated to form an alkene?

1 CH_3OH

2 CH_3CH_2OH

3 $CH_3CH(OH)CH_3$

[N'07 Q38]

7 Which statements about alkenes are correct?

1 They are formed when higher alkanes are cracked.

2 They are used as monomers for polymerisation.

3 They are less reactive than alkanes towards electrophiles.

[N'08 Q37]

8 Which alkenes, on reaction with steam at 600 K and 6 x 10^6 Pa pressure in the presence of a phosphoric acid catalyst, could produce an alcohol containing a chiral carbon atom?

1 $(CH_3)_2C=CH_2$

2 $CH_3CH=CHCH_3$

3 $CH_3CH_2CH=CH_2$

[J'11 P11 Q38]

9 Which compounds can be obtained from propene in a **single** reaction?

1 $CH_2OHCHOHCH_3$

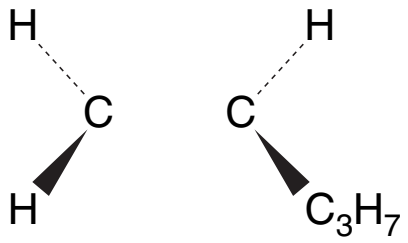
2 $-(-CH_2CH(CH_3)-)_n-$

3 $CH_2BrCH_2CH_2Br$

[J'12 P12 Q37]

ALKENES WS 4

1 Dehydration of pentan-1-ol produces pent-1-ene. Sketch on the diagram below the orbital overlap between the two carbon atoms. Label the bonds.



[2]

[N'02 Q6]

2 Oleic acid is the *cis* isomer and elaidic acid the *trans* isomer of

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H.$$

By using this formula, draw the structural formula of elaidic acid, clearly showing the stereochemistry.

[1]

[J'11 P22 Q5]

3 When ethene is reacted with HC*l*, C_2H_5Cl is the only product.

(i) Using structural formulae, give an equation for the reaction between ethene and HC*l*.

(ii) What type of reaction occurs between HC*l* and ethene?

.....

(iii) Explain why there is no further reaction between C_2H_5Cl and HC*l*.

.....

[3]

[J'08 Q4]

4 Two types of isomerism found in organic compounds are structural isomerism and *cis-trans* isomerism.

(a) Draw displayed formulae for

(i) **two** structural isomers of $C_2H_4Br_2$,

D	**E**

(ii) the *cis-* and the *trans-* isomers of $C_2H_2Br_2$.

cis	*trans*

[4]

(b) **(i)** The *cis-* isomer of $C_2H_2Br_2$ can be converted into **one** of the structural isomers of $C_2H_4Br_2$. State the reagent(s) and conditions you would use to do this.

.....

.....

(ii) Which of your structural isomers, **D** or **E**, would be formed? Explain your answer.

isomer formed is .....

reason .....

[3]

[J'08 Q4]

5 Octadecane, $C_{18}H_{38}$, is a long chain hydrocarbon which is present in crude oil. Such long chain hydrocarbons are 'cracked' to produce alkanes and alkenes which have smaller molecules.

(a) Give **two** different conditions under which long chain molecules may be cracked.

.....

.....

..... [2]

(b) Octadecane, $C_{18}H_{38}$, can be cracked to form hexane and an alkene.

Write a balanced equation for this reaction.

..... [1]

Alkenes are important industrially because the C=C bond makes them very reactive.

(c) Ethene reacts with bromine to give 1,2-dibromoethane.

(i) What type of reaction is this?

.....

(ii) Outline the mechanism of this reaction, giving the structure of the intermediate.

Show clearly any relevant dipoles, charges and lone pairs of electrons.



[4]

[N'06 Q4]

6 Dodec-1-ene has the structure shown.

$$CH_3(CH_2)_9CH = CH_2$$

(a) Draw the structures of the organic molecules produced when dodec-1-ene reacts with each of the following.

(i) bromine	**(ii)** hydrogen bromide
(iii) hot, concentrated manganate(VII) ions	**(iv)** steam

[4]

(b) **(i)** What type of isomerism is shown by the organic products in **(i)**, **(ii)** and **(iv)**?

.....

(ii) Draw structures to represent these isomers, choosing any **one** of these products.

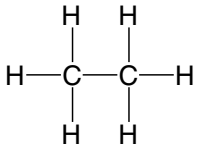
[3]

(c) Dodec-2-ene shows another type of isomerism. Draw and label diagrams which show these two isomers.

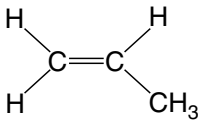
[2]

[N'01 Q5]

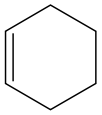
7 Crude oil is the principal source of hydrocarbons. The following are examples of such hydrocarbons.



ethane



propene



cyclohexene

(a) Give the structural formulae of the organic products in the following reactions.

(i) The reaction of ethane with bromine in the presence of u.v. light.

(ii) The polymerisation of propene.

(iii) The oxidation of propene with cold, acidified potassium manganate(VII).

(iv) The reaction of cyclohexene with hydrogen bromide.

(v) The reaction of cyclohexene with hot acidified potassium manganate(VII).

[5]

(b) Write equations for the following reactions.

(i) The complete combustion of ethane.

(ii) The action of steam on propene in the presence of a catalyst.

(iii) The reaction of cyclohexene with hydrogen in the presence of a catalyst.

[3]

(c) The process of cracking produces useful substances from oil.

(i) Explain why cracking is useful.

.....

.....

.....

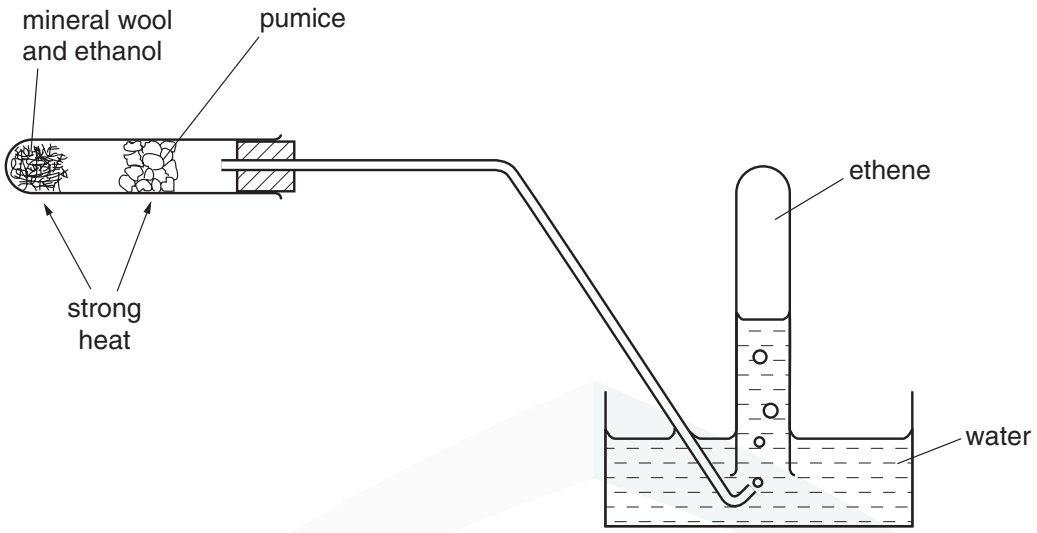
.....

(ii) Suggest an equation for the cracking of $C_{16}H_{34}$ into at least three fragments.

[3]

[J'02 Q5]

8 The apparatus shown can be used to prepare ethene from ethanol.



(a) **(i)** State what type of reaction takes place on the hot pumice.

.....

(ii) Write an equation for this preparation.

.....

[2]

(b) Describe the colour changes which are observed and write equations for the reaction of ethene with the following two reagents.

(i) bromine

colour change from ..... to .....

equation .....

(ii) cold, dilute, acidified manganate(VII) ions

colour change from ..... to .....

equation .....

[4]

(c) Draw structures for each of the following polymers showing **two** repeat units.

(i) poly(ethene)

(ii) pvc [poly(chloroethene)]

[2]

(d) The formula of the alkene cyclohexene can be written as shown.



(i) State the molecular formula of cyclohexene. .....

(ii) Calculate the percentage of carbon by mass in cyclohexene.

[3]

[N'03 Q4]

9 The molecular formula of a compound states the number of atoms of each element that are present in one molecule. It contains no information about the structure of the molecule. Hydrocarbons with the molecular formula C_5H_{10} may be branched chain, straight chain or cyclic.

(a) Draw a displayed formula of C_5H_{10} as a branched chain hydrocarbon.

[1]

Pent-2-ene is one straight chain hydrocarbon with formula C_5H_{10}.

(b) Pent-2-ene exhibits *cis-trans* isomerism. Draw and label the structural formulae of the two *cis-trans* isomers of pent-2-ene.

[2]

(c) In the spaces below draw the structural formulae of **two** alcohols which would **each** produce pent-2-ene on dehydration.



[2]

(d) One of these alcohols exhibits optical isomerism. Draw the structural formulae of the two isomers of this alcohol. Your structures should clearly indicate the three-dimensional nature of the structures.

[2]

(e) Pent-2-ene decolourises aqueous bromine. Suggest the structural formula of an isomer of C_5H_{10} which does **not** decolourise aqueous bromine.

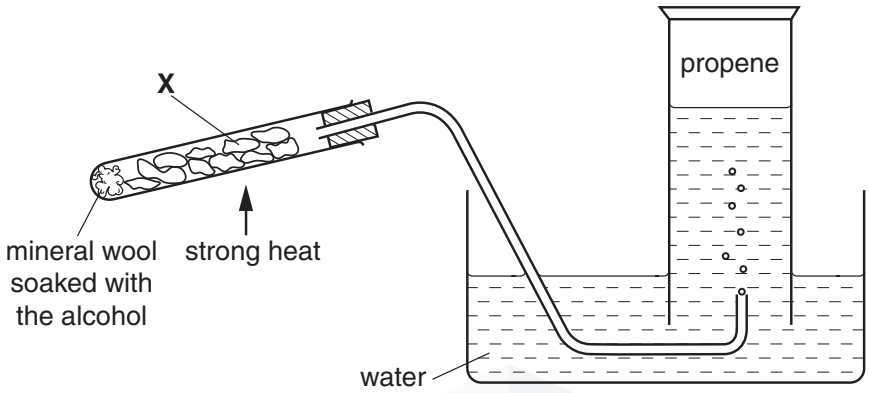
[1]

(f) Pent-2-ene can be polymerised. Draw a section of the polymer chain produced showing **two** repeat units.

[1]

[N'07 Q4]

10 Alkenes such as propene can be readily prepared from alcohols in a school or college laboratory by using the apparatus below.



(a) (i) Give the **name** of an alcohol that can be used in this apparatus to prepare propene.

.....

(ii) Draw the **skeletal** formula of the alcohol you have named in **(i)**.

(iii) What type of reaction occurs in this case?

.....

[3]

(b) (i) During the reaction, the material **X** becomes black in colour.
Suggest the identity of the black substance and suggest how it is produced during the reaction.

.....

.....

.....

(ii) At the end of the experiment, when no more propene is being produced, the delivery tube is removed from the water before the apparatus is allowed to cool.

Suggest why this done.

.....

.....

.....

(iii) The material labelled **X** can be broken crockery, broken brick or pumice.

Give the chemical formula of a compound that is present in one of these materials.

.....

(iv) State another reagent that could be used to produce propene from an alcohol.

.....

[5]

(c) Give the structural formula of the organic product formed when propene reacts separately with **each** of the following substances.

(i) bromine

(ii) cold, dilute manganate(VII) ions

(iii) hot, concentrated manganate(VII) ions

[3]

[J'10 P22 Q5]

11 The gas ethyne, C_2H_2, more commonly known as acetylene, is manufactured for use in the synthesis of organic compounds. It is also used, in combination with oxygen, in 'oxy-acetylene' torches for the cutting and welding of metals.

Industrially, ethyne is made from calcium carbide, CaC_2, or by cracking liquid hydrocarbons.

(a) When calcium carbide is reacted with water, ethyne and calcium hydroxide are formed.

Construct a balanced equation for this reaction.

.....[1]

Ethyne can also be obtained from ethene by using the following sequence of reactions.

$$CH_2CH_2 \xrightarrow{\text{step 1}} ClCH_2CH_2Cl \xrightarrow{\text{step 2}} HC{\equiv}CH$$

(b) (i) What types of reaction are step 1 and step 2?

step 1 .....

step 2 .....

(ii) Suggest what reagent and conditions would be used in a laboratory in step 2.

reagent .....

conditions ..... [5]

[J'11 P21 Q5]

12 **(a)** Draw a section of poly(propene), showing three repeat units.

[1]

(b) To what homologous series does poly(propene) belong?

.....[1]

(c) When a rupture (hernia) or a deep wound, e.g. as a result of a sports accident, is repaired by surgery, a mesh is inserted below the muscle tissue so that on healing the wound is less likely to reopen and the repair is stronger.

Poly(propene) is the recommended material for the mesh.

(i) Suggest **two** reasons why poly(propene) is used rather than a natural fibre such as cotton.

.....

.....

.....

(ii) Members of the homologous series you have given in **(b)** are considered to have two different kinds of reactions. Explain why neither of them can take place in a poly(propene) mesh inserted in living body tissues.

.....

.....

.....

.....[4]

[J'03 Q5]

13 Astronomers using modern spectroscopic techniques of various types have found evidence of many molecules, ions and free radicals in the dust clouds in Space. Many of the species concerned have also been produced in laboratories on Earth.

Two such species are the dicarbon monoxide molecule, C_2O, and the amino free radical, NH_2.

(a) (i) Dicarbon monoxide can be produced in a laboratory and analysis of it shows that the sequence of atoms in this molecule is carbon-carbon-oxygen and there are no unpaired electrons, but one of the atoms is only surrounded by six electrons.

Draw a 'dot-and-cross' diagram of C_2O and suggest the shape of the molecule.

shape .....

(ii) What is meant by the term *free radical*?

.....

.....

(iii) Explain why NH_2 is described as a 'free radical'.

.....

.....[5]

Two derivatives of ethene which have been detected in dust clouds in Space are acrylonitrile (2-propenenitrile), CH_2=CHCN, and vinyl alcohol (ethenol), CH_2=CHOH.

(b) Like ethene, acrylonitrile can be polymerised. The resulting polymer can be used to make carbon fibres.

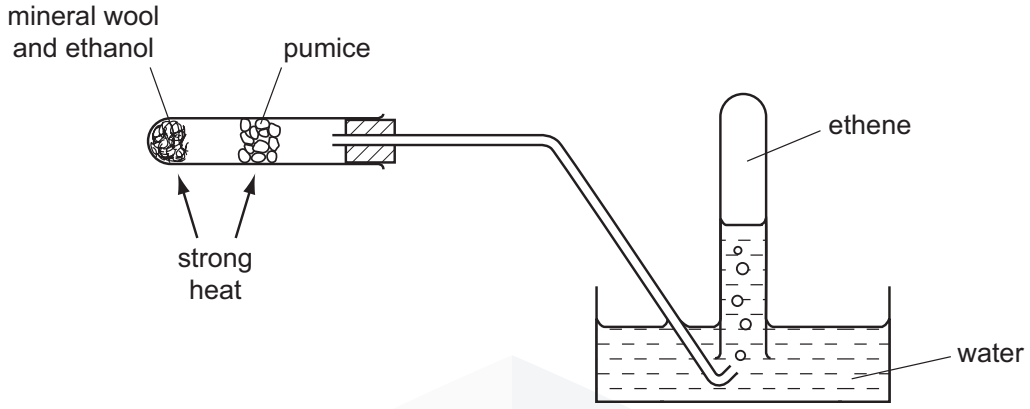
(i) Draw the structural formula of the polymer made from acrylonitrile, showing **two** repeat units.

(ii) What type of polymerisation is this reaction?

.....[2]

[N'10 P23 Q3]

14 One method of preparing ethene in a school or college laboratory is from ethanol by using the apparatus shown below.



(a) (i) Write a balanced equation for this reaction.

.....

(ii) What *type of reaction* is this?

.....

(iii) Give the chemical name of a reagent other than pumice that could be used to carry out this reaction. It is not necessary to use the same apparatus.

.....

[3]

(b) Ethene is bubbled into two separate test-tubes, one containing aqueous hydrogen bromide and the other containing cold, dilute acidified potassium manganate(VII).

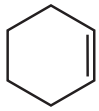
In **each** case, describe any colour changes you would see and give the structural formula of the organic product.

	aqueous hydrogen bromide	cold, dilute acidified potassium manganate(VII)
colour at start		
colour after reaction		
structural formula of organic product		

[4]

[J'03 Q5]

(c) Cyclohexene has the following structural formula.



(i) What is the molecular formula of cyclohexene?

.....

(ii) Draw the structural formula of the compound formed when cyclohexene is reacted with bromine.

(iii) State as fully as you can what *type of reaction* this is.

.....

(iv) Draw the structural formula of the compound formed when cyclohexene is reacted with hot concentrated acidified potassium manganate(VII).

[5]

[N'10 P23 Q3]

15 But-2-ene, $CH_3CH{=}CHCH_3$, is an important compound which is obtained from the cracking of hydrocarbons present in crude oil.

(a) Give **two** different conditions under which long chain hydrocarbons may be cracked.

.....

.....

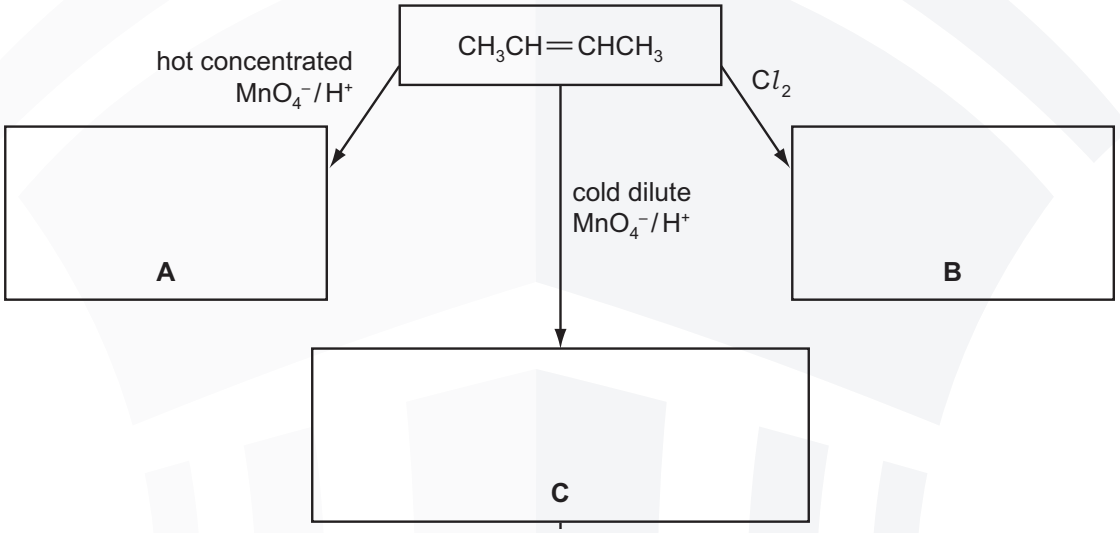
..... [2]

(b) Dodecane, $C_{12}H_{26}$, is a long chain hydrocarbon which is present in crude oil and which can be cracked to form but-2-ene and an alkane.

Write a balanced equation for this reaction.

..... [1]

(c) Some reactions of but-2-ene are shown below.
In the boxes below, give the **structural** formulae of the organic compounds **A** to **D**.



[J'12 P21 Q4]

(e) But-2-ene can be polymerised to give poly(butene).

Draw the **structural** formula of a portion of the polymer chain in poly(butene) showing **two** repeat units.

[1]

(f) Compound **C** is a liquid which can be reacted with concentrated sulfuric acid to give a gas, **E**, which will decolourise aqueous bromine when passed through it.

(i) Suggest the **structural** formula of **E**.

(ii) Suggest the **structural** formula of the product of the reaction between **E** and an excess of bromine.

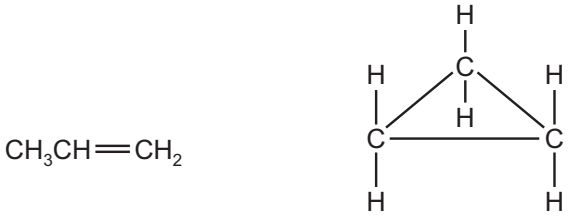
(iii) What *type of reaction* occurs between **E** and an excess of bromine?

.....

[3]

[J'12 P23 Q4]

16 The molecular formula C_3H_6 represents the compounds propene and cyclopropane.



propene

cyclopropane

(a) What is the H–C–H bond angle at the terminal $=CH_2$ group in propene?

..... [1]

(b) Under suitable conditions, propene and cyclopropane each react with chlorine.

(i) With propene, 1,2-dichloropropane, $CH_3CHCl CH_2Cl$ is formed.

State fully what type of reaction this is.

..... [1]

(ii) When cyclopropane reacts with chlorine, three different compounds with the molecular formula $C_3H_4Cl_2$ can be formed.

Draw displayed structures of **each** of these three compounds.

[3]

[N'13 P21 Q2]

Halogenoalkanes

The inclusion of a halogen atom within an organic molecule affects its reactivity. The reactions of halogenoalkanes and halogenoarenes are very important in organic chemistry.

a recall the chemistry of halogenoalkanes as exemplified by: ☐

(i) the following nucleophilic substitution reactions of bromoethane: hydrolysis, formation of nitriles, formation of primary amines by reaction with ammonia

(ii) the elimination of hydrogen bromide from 2-bromopropane

b describe the SN1 and SN2 mechanisms of nucleophilic substitution in halogenoalkanes including the inductive effects of alkyl groups ☐

c recall that primary halogenoalkanes tend to react via the SN2 mechanism; tertiary halogenoalkanes via the SN1 mechanism and secondary halogenoalkanes by a mixture of the two, depending on structure ☐

HALOGENOALKANES

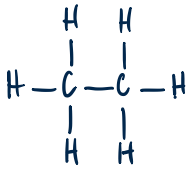
16 Halogen derivatives

The inclusion of a halogen atom within an organic molecule affects its reactivity. The reactions of halogenoalkanes and halogenoarenes are very important in organic chemistry.

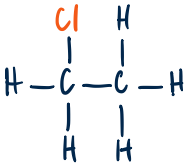
	Learning outcomes Candidates should be able to:
16.1 Halogenoalkanes and halogenoarenes	a) recall the chemistry of halogenoalkanes as exemplified by: (i) the following nucleophilic substitution reactions of bromoethane: hydrolysis, formation of nitriles, formation of primary amines by reaction with ammonia (ii) the elimination of hydrogen bromide from 2-bromopropane b) describe the S_N1 and S_N2 mechanisms of nucleophilic substitution in halogenoalkanes including the inductive effects of alkyl groups (see Section 15.2(c)) c) 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 structure
16.2 Relative strength of the C-Hal bond	a) interpret the different reactivities of halogenoalkanes (with particular reference to hydrolysis and to the relative strengths of the C-Hal bonds) b) explain the uses of fluoroalkanes and fluorohalogenoalkanes in terms of their relative chemical inertness c) recognise the concern about the effect of chlorofluoroalkanes on the ozone layer

HALOGENOALKANES

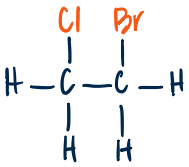
Halogenoalkanes are alkane molecules with one or more hydrogen atoms replaced with halogen atoms. For example:



ethane

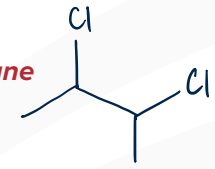


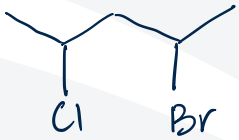
chloroethane



1-bromo-2-chloroethane

2,3-dichlorobutane

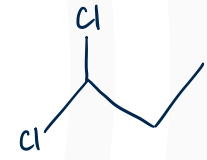


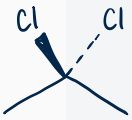


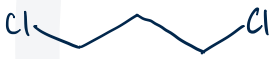
2-bromo-4-chloropentane

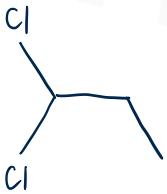
1

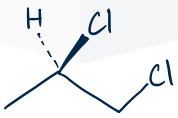
ISOMERS OF DICHLOROPROPANE

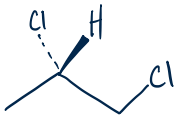






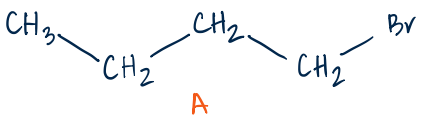




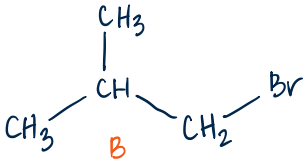


2

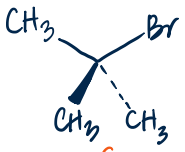
ISOMERS OF C_4H_9Br



A



B



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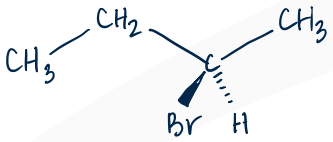

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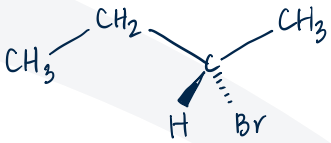


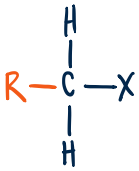
E

3

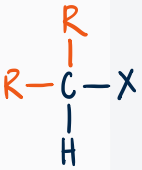
HALOGENOALKANES

They contain the functional group C-X where X is a halogen (F, Cl, Br or I).

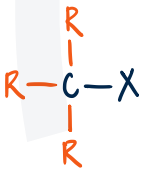
They are classified according to what is attached to the C-X functional group.



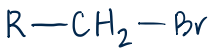
primary 1°

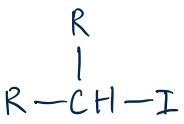


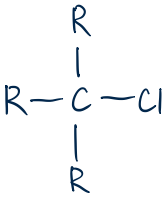
secondary 2°



tertiary 3°







4

PROPERTIES

Halogenoalkanes are generally colourless liquids, immiscible with and heavier than water, with pleasant odours (Chloromethane, chloroethane and bromomethane are gases at room temperature.)

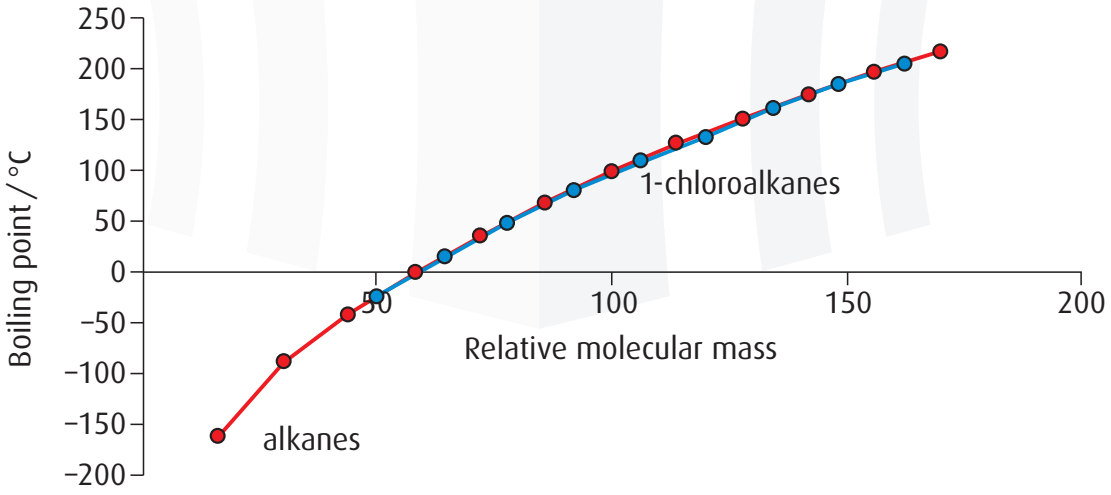
Compared with the alkanes, their boiling points are higher, with the boiling point rising from each chloroalkane to the corresponding iodoalkane.

The main intermolecular force in halogenoalkanes is the van der Waals' induced dipole force, the dipole - dipole attractions being not very effective in monohalogen derivatives.



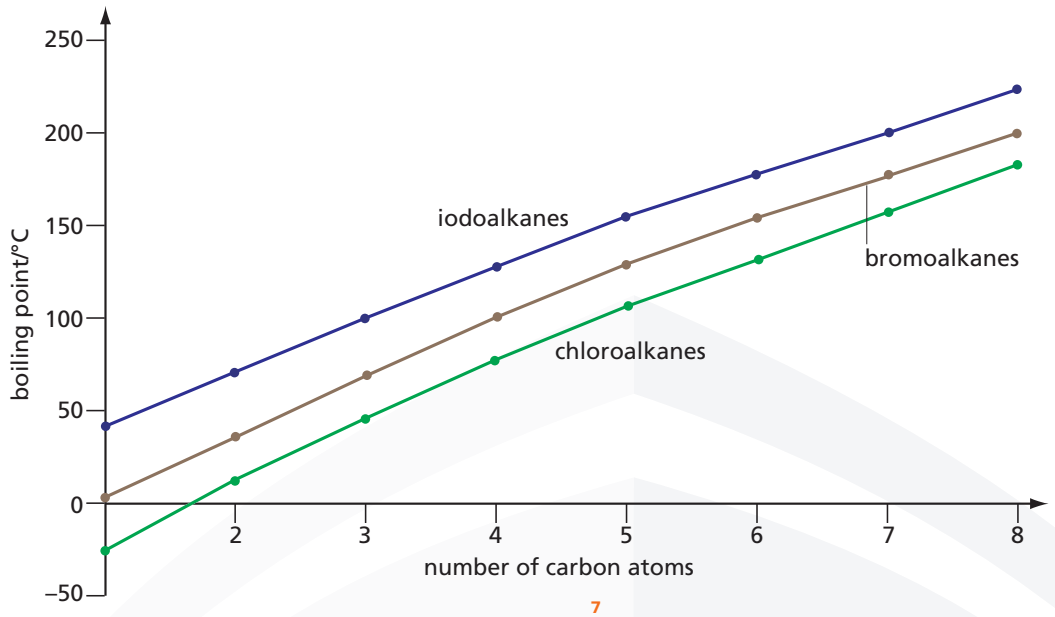
5

BOILING POINTS



6

BOILING POINTS



7

SOLUBILITY

Although slightly more soluble than alkanes, halogenoalkanes are still only either sparingly soluble or insoluble in water as they cannot form hydrogen bonding with water.

For all intents and purposes, they may be regarded as insoluble in water but soluble in organic solvents.

They are good solvents for organic compounds.

8

REACTIVITY

Halogens are very electronegative, and so the **C—Halogen** (C—X) bond is strongly polarised. C(δ+) —Br(δ−)

During the reactions of halogenoalkanes, this bond breaks heterolytically to give the halide ion:

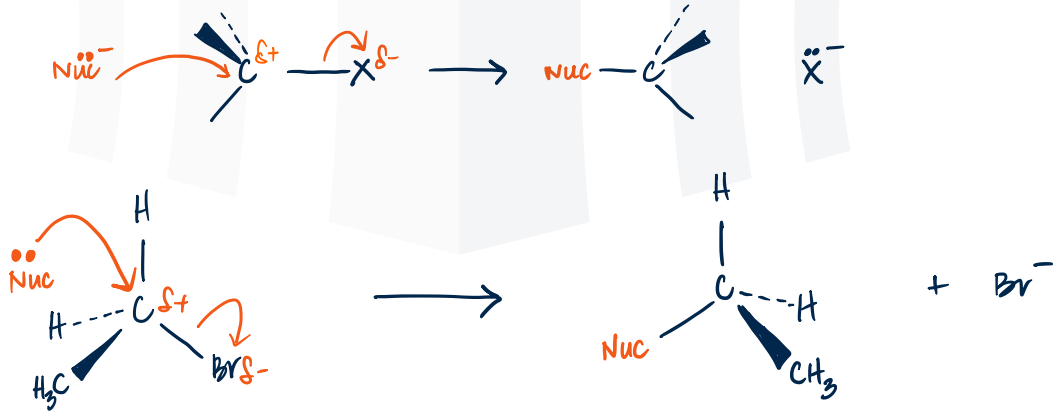
The type of mechanism by which halogenoalkane reactions occurs is nucleophilic substitution: **the halogenoalkane is attacked by a nucleophile and the nucleophile replaces the halogen atom.**

The exact nature of the nucleophilic substitution reaction depends on which type (primary, secondary or tertiary) of halogenoalkane reacts.

9

NUCLEOPHILIC SUBSTITUTION

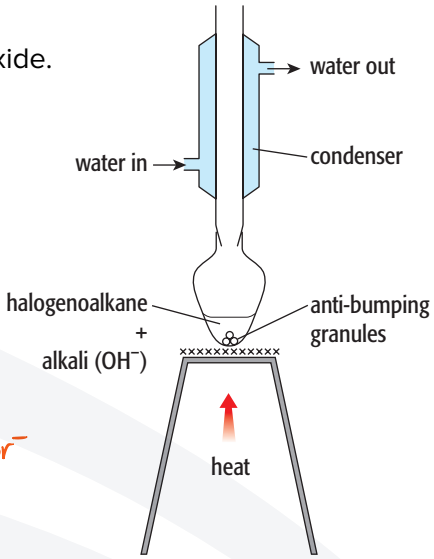
The halogenoalkane is attacked by a nucleophile and the nucleophile replaces the halogen atom.

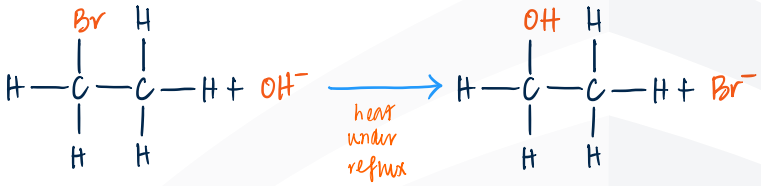


10

REACTION WITH ALKALIS

Reagent	**Aqueous** sodium (or potassium) hydroxide.
Condition	heat under reflux in **aqueous** solution
Product	Alcohol
Type	nucleophilic substitution





11

REACTION WITH ALKALIS

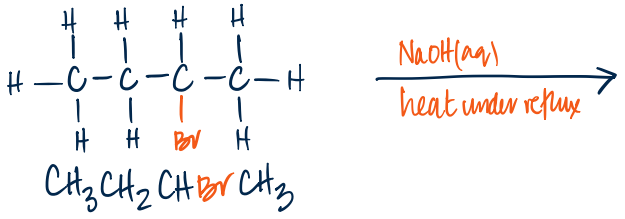
$CH_3CH_2Br + NaOH \longrightarrow CH_3CH_2OH + NaBr$

$CH_3CH_2Br + OH^- \longrightarrow CH_3CH_2OH + Br^-$

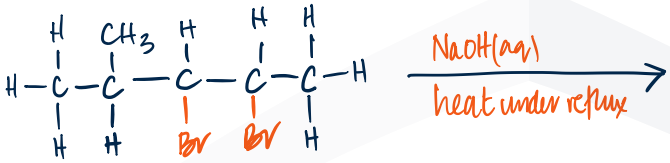


12

REACTION WITH ALKALIS



$CH_3CH_2CHBrCH_3$



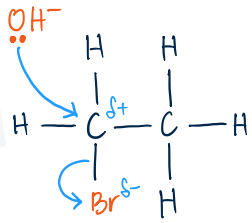
$(CH_3)_2CHCHBrCHBrCH_3$

13

NUCLEOPHILIC SUBSTITUTION OF PRIMARY HALOGENOALKANES

The exact nature of the nucleophilic substitution reaction depends on which type (primary, secondary or tertiary) of halogenoalkane reacts.

The initial part of the mechanism is the attack of the OH^- on the C attached to the Br.



As the Br is more electronegative than the C, the C atom is slightly positive and the OH^- is attracted to it.

The OH^- is the nucleophile and donates a lone pair of electrons to the C to form a (dative) covalent bond.

The curly arrow shows the lone pair on OH^- becoming a bonding pair of electrons between the O and C.

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NUCLEOPHILIC SUBSTITUTION OF PRIMARY HALOGENOALKANES

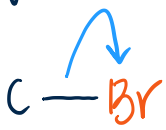
C can have a maximum of only eight electrons in its outer shell, and therefore as the C–O bond forms the C–Br bond must break.

The curly arrow shown indicates that the C–Br bond breaks.

Both electrons from the C–Br bond go back to the bromine atom to form a bromide ion.

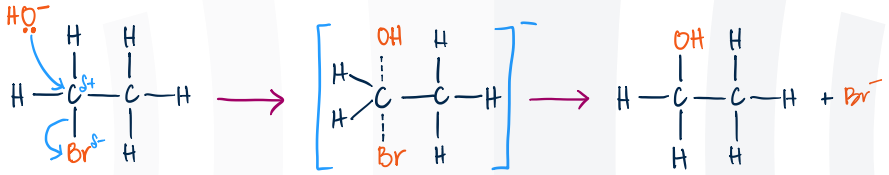
This is called **heterolytic fission** – the bond breaks so that both electrons go to the same atom (Br).

pair of electrons from C–Br bond goes to Br



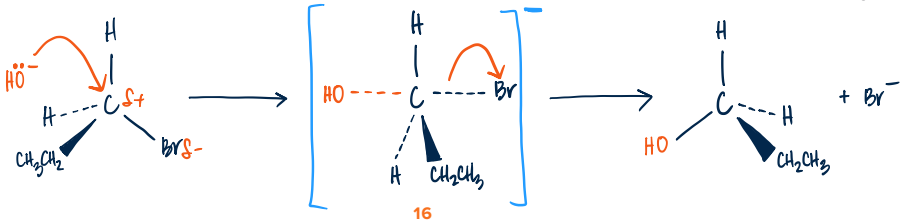
15

NUCLEOPHILIC SUBSTITUTION OF PRIMARY HALOGENOALKANES



Part of the way through the process, the OH and Br are both partially joined to the C, and this is often shown in the mechanism.

This is not an intermediate in the reaction but is the highest point on the reaction energy profile, which is often called the transition state or activated complex.

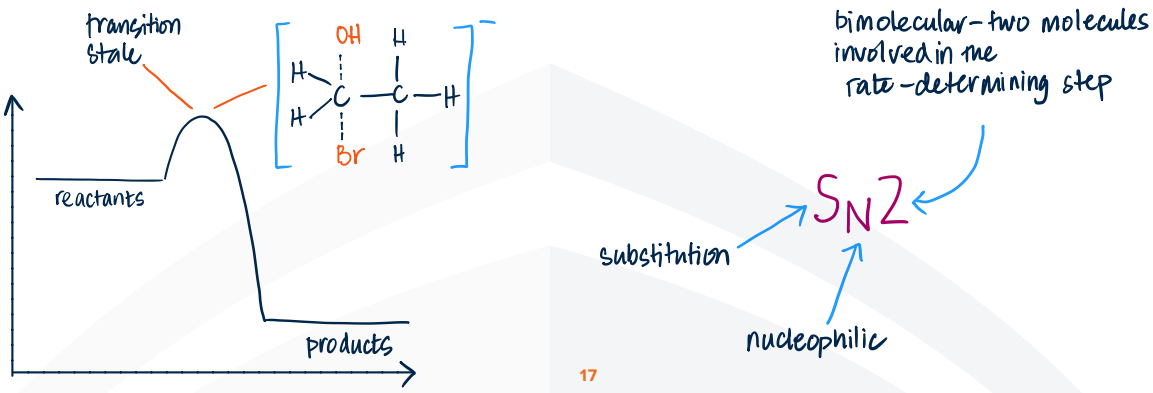


16

NUCLEOPHILIC SUBSTITUTION OF PRIMARY HALOGENOALKANES

This is a single-step mechanism, and the formation of the transition state is just part of the way along this step.

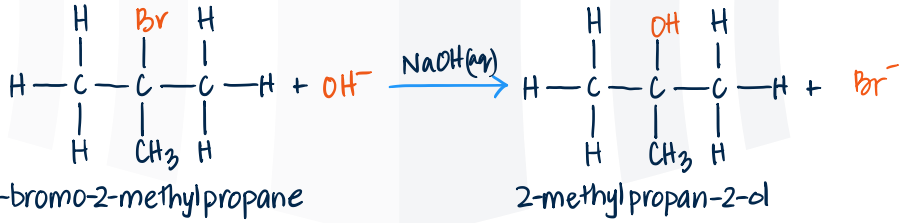
This mechanism is known as an **S_N2 mechanism** where the rate is determined by the concentrations of the primary haloalkane and the sodium hydroxide.



17

NUCLEOPHILIC SUBSTITUTION OF TERTIARY HALOGENOALKANES

Consider the reaction of 2-bromo-2-methylpropane with sodium hydroxide. This occurs fairly rapidly at room temperature.



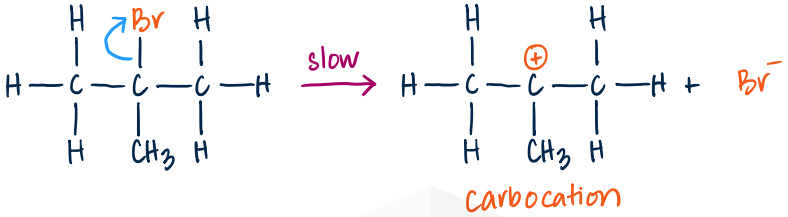
Studies of the rate of this reaction determined that the rate of reaction does not seem to depend on the concentration of the sodium hydroxide.

This reaction must, therefore, occur via a different mechanism.

18

NUCLEOPHILIC SUBSTITUTION OF TERTIARY HALOGENOALKANES

This mechanism is described as S_N1, i.e. substitution nucleophilic unimolecular.



In the first step, the C–Br bond breaks to form a positively charged carbocation. This is the rate-determining step in the mechanism and hydroxide ions do not take part in it.

19

NUCLEOPHILIC SUBSTITUTION OF TERTIARY HALOGENOALKANES

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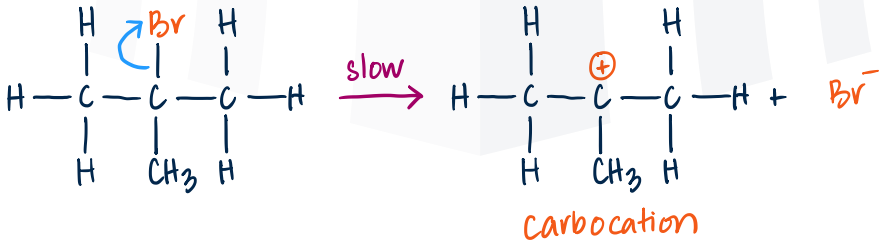
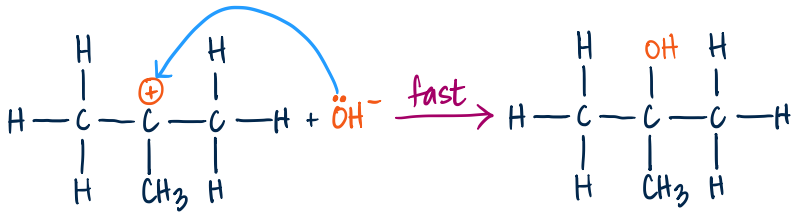


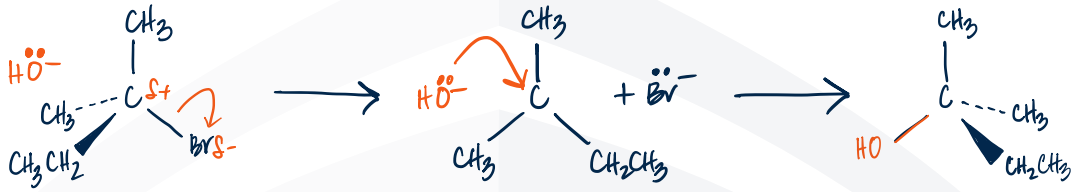
20

NUCLEOPHILIC SUBSTITUTION OF TERTIARY HALOGENOALKANES

The carbocation formed is attacked by the OH− ion.



Overall:



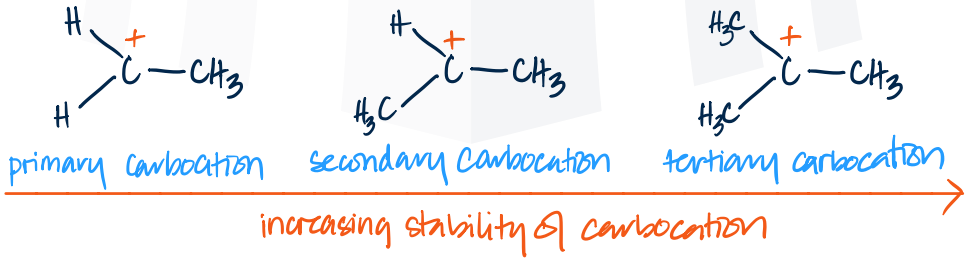
21

WHY TWO DIFFERENT MECHANISMS

S_N1 is more favourable for tertiary halogenoalkanes.

Alkyl groups donate electrons to carbocations and radicals by the inductive effect.

The stability of carbocations increases in the order primary < secondary < tertiary.



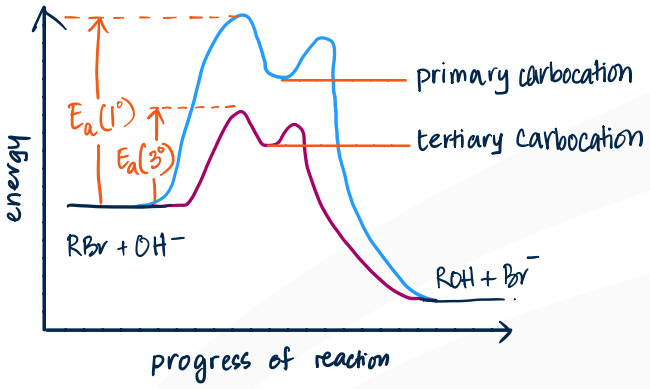
22

WHY IS S_N1 MORE FAVOURABLE FOR TERTIARY HALOGENOALKANES

As the carbocation becomes more stable, the activation energy for the reaction leading to it also decreases.

We therefore expect that the rate of the S_N1 reaction will increase in the order:

primary < secondary < tertiary.



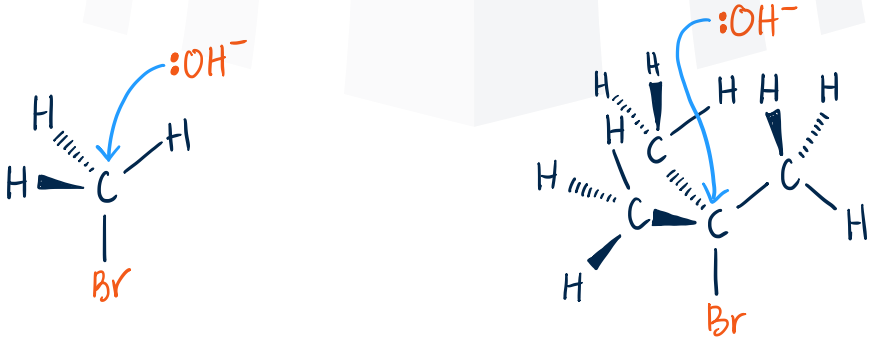
Compound	Type	Relative rate of S_N1 reaction
CH_3CH_2Br	primary	1
$(CH_3)_2CHBr$	secondary	26
$(CH_3)_3CBr$	tertiary	60000000

23

WHY IS S_N2 MORE FAVOURABLE FOR PRIMARY HALOGENOALKANES

S_N2 is more favourable for primary halogenoalkanes.

This is mainly because of steric effects. The methyl groups surrounding the central C in a tertiary halogenoalkane make it much more difficult for the nucleophile to get in to attack the central C.



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WHY IS S_N2 MORE FAVOURABLE FOR PRIMARY HALOGENOALKANES

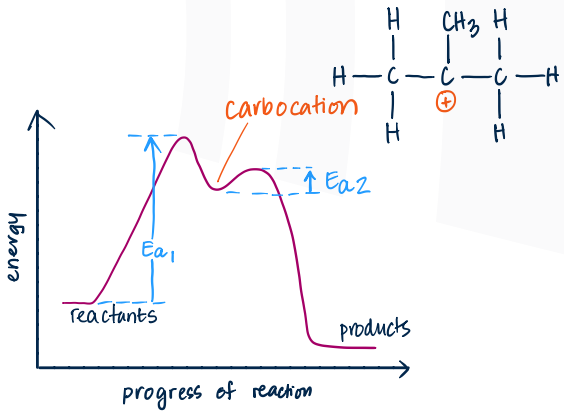
Another way of explaining this is that, if the OH^- did get in to attack the C in a tertiary halogenoalkanes, there would be five large groups surrounding the central C in the transition state, which would make this very unstable.

The activation energy would therefore be very high. This will slow down the reaction.

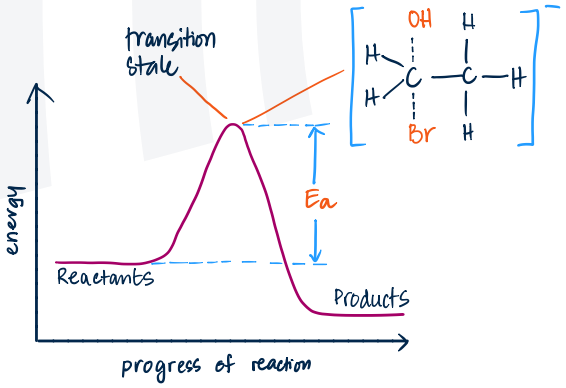


S_N1 VS S_N2

S_N1

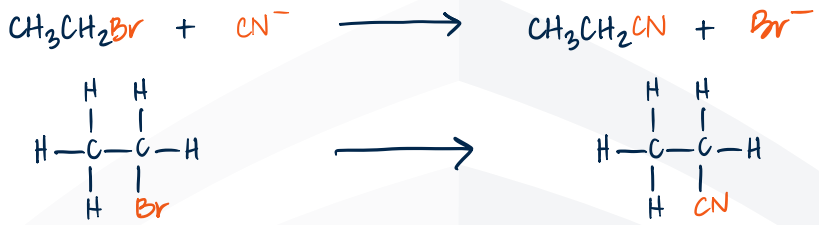


S_N2



REACTION WITH CN⁻

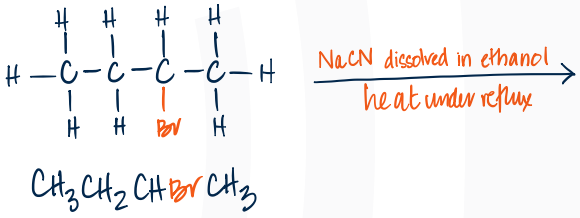
Reagent	potassium cyanide, KCN, (or sodium cyanide, NaCN) dissolved in ethanol
Condition	heat under reflux in **ethanolic** solution
Product	Nitrile
Type	nucleophilic substitution



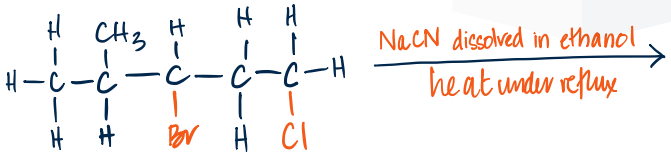
Importance of the reaction with CN^- is that it extends the carbon chain by one carbon atom.

27

REACTION WITH CN⁻



$CH_3CH_2CHBrCH_3$



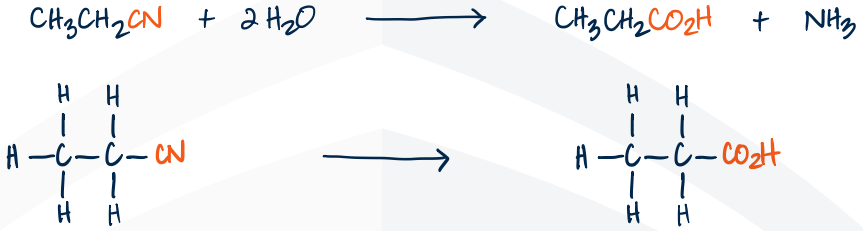
$(CH_3)_2CHCHBrCH_2CH_2Cl$

28

REACTION WITH CN⁻

Hydrolysis of nitriles formed after the reaction of halogenoalkanes with CN⁻ produces carboxylic acids.

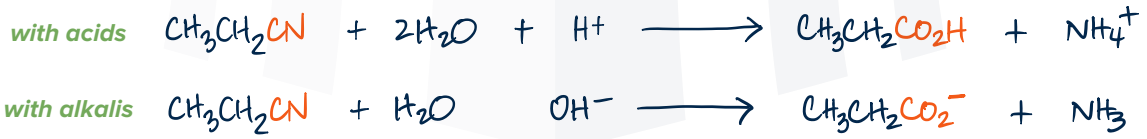
Reagent	dilute HCl or NaOH (aq)
Condition	heat under reflux
Type	hydrolysis



29

REACTION WITH CN⁻

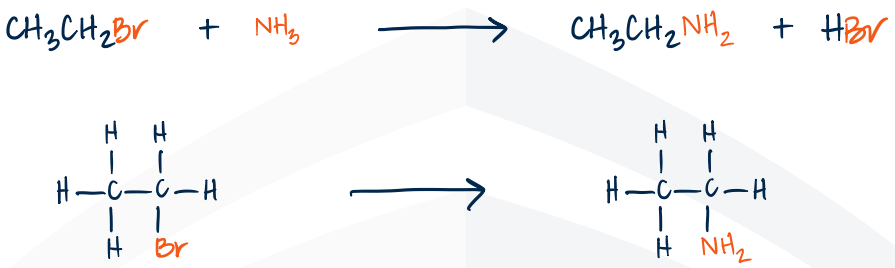
Hydrolysis of nitriles formed after the reaction of halogenoalkanes with CN⁻ produces carboxylic acids.



30

REACTION WITH AMMONIA

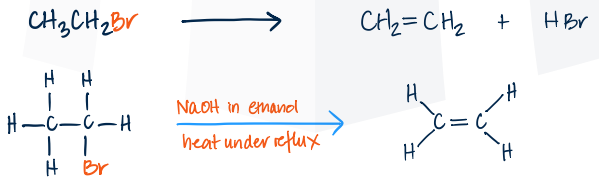
Reagent	Ammonia, NH_3 (conc. or dissolved in ethanol)
Condition	heat under reflux
Product	Amine
Type	nucleophilic substitution



31

ELIMINATION REACTION

Reagent	sodium (or potassium) hydroxide dissolved in ethanol
Condition	heat under reflux
Product	Alkene
Type	Elimination

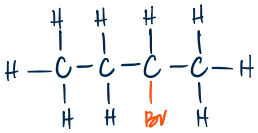


The OH^- removes a hydrogen from a carbon atom adjacent the C bearing the halogen.

If the haloalkane is unsymmetrical (e.g. 2-bromobutane) a mixture of isomeric alkene products is obtained.

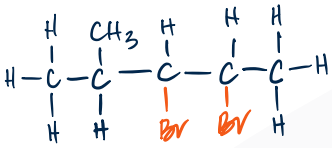
32

ELIMINATION REACTION



$CH_3CH_2CHBrCH_3$

NaOH in ethanol
heat under reflux

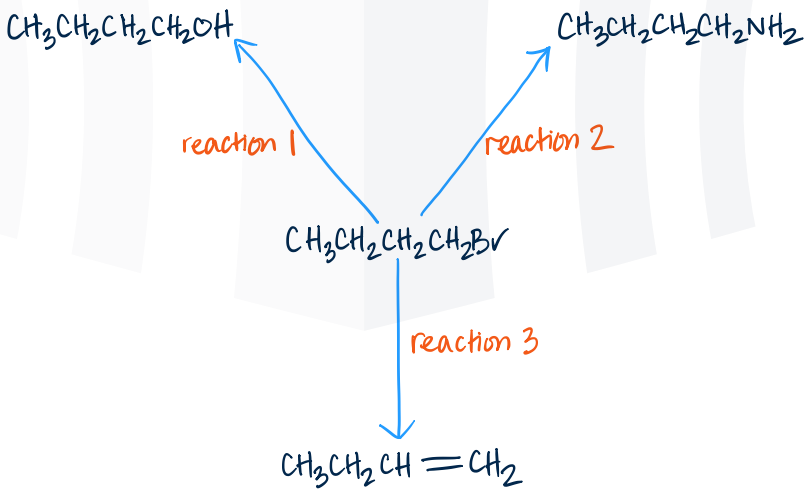


$(CH_3)_2CHCHBrCHBrCH_3$

NaOH in ethanol
heat under reflux

33

REACTIONS



34

REACTIVITY OF HALOGENOALKANES

Bond	C – I	C – Br	C – Cl	C – F
Bond energies / kJ mol^{-1}	240	280	340	485

The rate of nucleophilic substitution of the different halides containing the same alkyl group with differing halogen is as follows: RI > RBr > RCl .

This is because the rate of hydrolysis depends on the ease with which the heterolysis of the C—X bond occurs.

As the atom becomes smaller bond length decreases, bond strength increases and heterolysis becomes more difficult. Hence, the rate of reaction decreases.

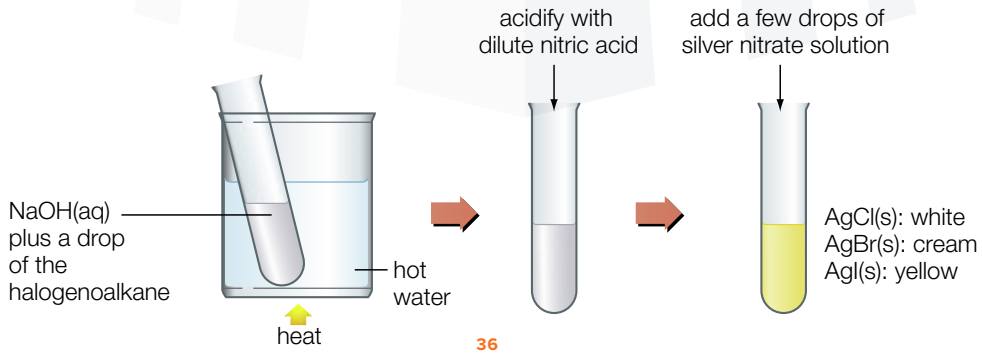
Fluorocarbons are almost inert.

35

REACTIVITY OF HALOGENOALKANES

Hydrolysis of halogenoalkanes makes it possible to distinguish between chloro-, bromo- and iodo-compounds.

Heating the compound with an alkali releases halide ions. Acidifying with nitric acid and then adding silver nitrate produces a precipitate of the silver halide.



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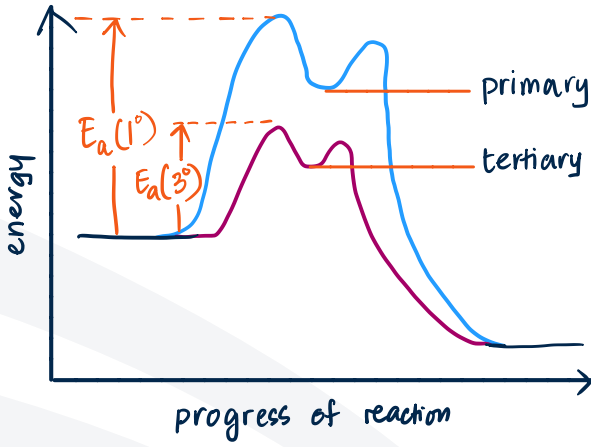
REACTIVITY OF HALOGENOALKANES

For a given set of isomers the reaction rate is in the order:

tertiary > secondary > primary

The chances for forming the carbocation increases with increasing number of alkyl groups due to the electron releasing effect of the alkyl group stabilizing the carbocation.

Therefore activation energy decreases as the number of alkyl groups increases.



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USES OF HALOGENOALKANES

USES	COMPOUND	PROPERTY	SUSTITUTE
SOLVENT	CCl_4	non-polar liquid	hexane
NON-STICK PANS	PTFE	non-toxic, resistant to & low coefficient of friction.	
AEROSOL SPRAYS	CFCs	volatile & odourless	butane
REFRIGERANTS	CFCs	volatile & odourless	
PIPES	PVC	hard polymer & non-polar	poly(propene)
ANAESTHETIC	chloroalkanes		

38

POLLUTION

The main pollutants responsible for depletion of ozone are chlorofluorocarbons (CFCs) and nitrogen oxides (NO_x).

CFCs (chlorofluorocarbons), also called Freons, were developed and used from the first half of the 20th century as non-toxic, non-flammable substances useful as refrigerants, aerosol propellants and foaming agents for plastics and fire extinguishers and also as solvents for cleaning.

Examples are: CCl_3F (CFC-11, trichlorofluoromethane) and CCl_2F_2 (CFC-12, dichlorodifluoromethane).

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POLLUTION

CFCs are so unreactive that they can pass through the troposphere and up into the stratosphere without reacting.

In the stratosphere UV light causes the C–Cl bond to break (it is weaker than the C–F bond) to produce chlorine free radicals, which catalyse the depletion of ozone.

One chlorine free radical can destroy thousands of ozone molecules.

$$CF_3Cl \rightarrow CF_3^{\bullet} + Cl^{\bullet}$$

$$CF_2Cl_2 \rightarrow CF_2Cl^{\bullet} + Cl^{\bullet}$$

$$Cl^{\bullet} + O_3 \rightarrow O_2 + ClO^{\bullet}$$

40

FLOUROALKANES

Fluoroalkanes are very inert. This corresponds to the trend in their bond strengths.

Bond	C – I	C – Br	C – Cl	C – F
Bond energies / kJ mol^{-1}	240	280	340	485

Chlorofluoroalkanes (CFCs) have been responsible for damaging the Earth's ozone layer, but alternative inert compounds, such as fluoroalkanes and hydrofluoroalkanes (hydrofluorocarbons, HFCs), are now replacing the use of CFCs.

Because these HFCs don't contain any chlorine, they have zero effect on the ozone layer. The C—F bond isn't broken by uv radiation.

HFE's are hydrofluoroethers, which are solvents used for cleaning and drying, these are far more stable due to C—F being stronger than C—Cl.

41

HALOGENOALKANES WS 1

SECTION A

1 The hydrolysis of 1-chloropropane to produce propan-1-ol is much slower than the corresponding hydrolysis of 1-iodopropane.

Which statement explains this observation?

A Chlorine is more electronegative than iodine.

B The bond strength of the C – I bond is less than that of the C – C*l* bond.

C The carbon atom in the C – C*l* bond is more δ+ than that in the C – I bond.

D The hydrolysis involves a nucleophilic addition reaction.

[S'14 P11 Q23]

2 Butanoic acid can be produced from 1-bromopropane using reagents X and Y as shown below.

1-bromopropane $\xrightarrow{\text{reagent X}}$ compound Q $\xrightarrow{\text{reagent Y}}$ butanoic acid

What could be reagents X and Y?

	X	Y
A	KCN in ethanol	HC*l*(aq)
B	KCN in ethanol	NaOH(aq)
C	NH_3 in ethanol	HC*l*(aq)
D	NaOH(aq)	$H^+ / Cr_2O_7^{2-}$(aq)

[S'17 P13 Q29]

3 Halogenoalkanes undergo a range of nucleophilic substitution reactions.

Which reaction proceeds **only** by an S_N1 mechanism?

A $CH_3CH_2Br + NH_3$

B $CH_3CH_2CH_2I + OH^-$

C $CH_3CHBrCH_3 + NH_3$

D $(CH_3)_3CI + OH^-$

[S'14 P12 Q21]

4 Which statement does **not** correctly describe a problem related to the disposal of PVC?

A PVC is slowly degraded in the environment by bacteria and fungi.

B PVC is slowly degraded in the environment by sunlight.

C When PVC is burnt, a significant amount of ethene gas is present in the products.

D When PVC is burnt, a significant amount of HC*l* gas is present in the products.

[S'14 P12 Q25]

5 Dichlorodifluoromethane, CCl_2F_2, has been used in aerosol propellants and as a refrigerant.

Which statement helps to explain why dichlorodifluoromethane is chemically inert?

A All fluorine compounds are non-flammable.

B Fluorine is highly electronegative.

C The carbon-fluorine bond energy is large.

D The carbon-fluorine bond has a low polarity.

[S'14 P12 Q27]

6 A compound **Y**, C_4H_9Br, undergoes hydrolysis in aqueous alkali to form an alcohol, C_4H_9OH. The rate of this reaction is found to be unaffected by changes in the concentration of OH^- ions present.

Which is the most likely molecular structure of **Y**?

A $CH_3CH_2CH_2CH_2Br$

B $CH_3CH_2CHBrCH_3$

C $(CH_3)_2CHCH_2Br$

D $(CH_3)_3CBr$

[W'14 P13 Q23]

7 2-bromopropane reacts with a hot concentrated solution of sodium hydroxide in ethanol.

Which substance is the major product of this reaction?

A propan-1-ol

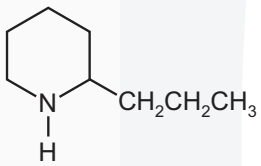
B propan-2-ol

C 2-hydroxypropene

D propene

[S'15 P11 Q25]

8 Coniine is the major constituent of the poison 'oil of hemlock'.



coniine

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

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

X

What is the name of compound **X**?

A 1,1-dibromo-2-propylcyclopentane

B 1,2-dibromo-2-propylcyclopentane

C 1,4-dibromooctane

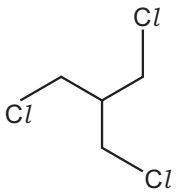
D 1,5-dibromooctane

[S'15 P11 Q24]

9 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



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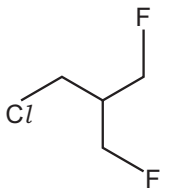

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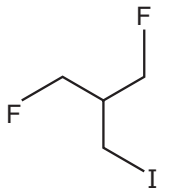

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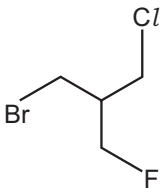


[S'15 P11 Q26]

10 Butanedioic acid may be synthesised in two steps from 1,2-dibromoethane.

$$BrCH_2CH_2Br \xrightarrow{\text{step 1}} X \xrightarrow{\text{step 2}} HO_2CCH_2CH_2CO_2H$$

Which reagents could be used for this synthesis?

	step 1	step 2
A	HCN(g)	HCl(aq)
B	HCO_2Na(aq)	HCl(aq)
C	KCN(alcoholic)	H_2SO_4(aq)
D	NaOH(aq)	$K_2Cr_2O_7/H_2SO_4$(aq)

[S'15 P12 Q23]

11 Which reaction would **not** give propene?

A adding excess hot concentrated sulfuric acid to propan-1-ol

B adding warm aqueous sodium hydroxide to 2-bromopropane

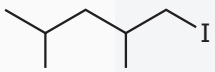
C adding warm ethanolic sodium hydroxide to 1-bromopropane

D passing propan-2-ol vapour over heated aluminium oxide

[S'15 P12 Q24]

12 The Finkelstein reaction occurs when NaI in propanone reacts with a chloroalkane or bromoalkane. The halogen is directly replaced by I and the reaction only works for primary halogenoalkanes.

Which halogenoalkane would produce compound X?



compound X

A $(CH_3)_2CHCH(CH_3)CH_2CH_2Br$

B $(CH_3)_2CHCH(CH_3)CH_2Br$

C $(CH_3)_2CHCH_2CH_2CH(CH_3)Cl$

D $(CH_3)_2CHCH_2CH(CH_3)CH_2Cl$

[S'15 P13 Q22]

13 A student prepares pentan-1-ol by the alkaline hydrolysis of 1-iodopentane. She gently warms the reaction mixture for 20 minutes.

$$CH_3CH_2CH_2CH_2CH_2I + OH^- \rightarrow CH_3CH_2CH_2CH_2CH_2OH + I^-$$

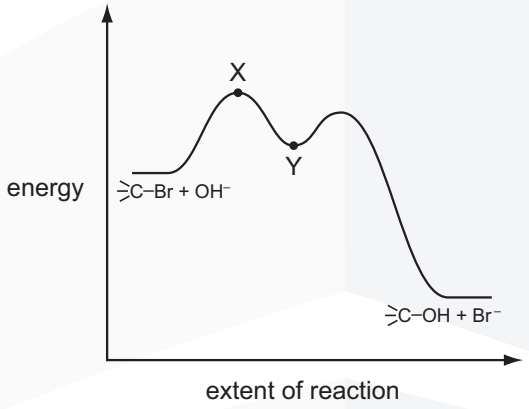
When the student uses 1-chloropentane to prepare the same alcohol she has to change the condition of the reaction.

Which change in condition should she use and what is the correct reason for its use?

	change in condition	reason
A	heat under reflux	C–C*l* bond is more polar than the C–I bond
B	heat under reflux	C–C*l* bond is stronger than the C–I bond
C	room temperature	C–C*l* bond is more polar than the C–I bond
D	room temperature	C–C*l* bond is shorter than the C–I bond

[S'16 P11 Q25]

14 A tertiary bromoalkane, indicated here by $\geq C–Br$, reacts with aqueous NaOH. The mechanism has the reaction pathway below.



Which point in the diagram is correctly identified?

A X is $\geq C^+$

B X is

C Y is $\geq C^+$

D Y is

[S'15 P13 Q28]

15 Four drops of 1-chlorobutane, 1-bromobutane and 1-iodobutane were put separately into three test-tubes containing 1.0 cm^3 of aqueous silver nitrate at 60 °C.

In each case, a hydrolysis reaction occurred. R represents the butane chain C_4H_9 and X the halogen atom.

$$H_2O(l) + R–X(l) + Ag^+(aq) \rightarrow R–OH(aq) + AgX(s) + H^+(aq)$$

The rate of formation of cloudiness in the test-tubes was in the order RCl < RBr < RI.

Why is this?

A The bond energy of R–X decreases from RCl to RI.

B The first ionisation energy of the halogen decreases from Cl to I.

C The solubility of AgX(s) decreases from AgCl to AgI.

D The R–X bond polarity decreases from RCl to RI.

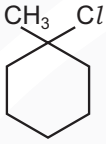
[S'15 P13 Q29]

16 Which compound undergoes an S_N1 substitution reaction with NaOH(aq)?

A $CH_3CH_2CH_2Br$

B $(CH_3)_3CCH_2I$

C



D $CH_2=CHCl$

[W'15 P13 Q24]

17 If the starting material is iodoethane, which sequence of reactions will produce propanoic acid as the main final product in good yield?

A add NaOH(aq), isolate the organic product, add acidified $K_2Cr_2O_7$ and boil under reflux

B add NaOH(aq), isolate the organic product, add H_2SO_4(aq) and boil under reflux

C heat with HCN in ethanol, isolate the organic product, add H_2SO_4(aq) and boil under reflux

D heat with KCN in ethanol, isolate the organic product, add H_2SO_4(aq) and boil under reflux

[W'15 P13 Q25]

18 The depletion of the ozone layer in the upper atmosphere reduces the Earth's natural protection from harmful ultraviolet radiation.

Which compound would cause the most depletion of the ozone layer?

A CCl_3F **B** CF_4 **C** CO_2 **D** SO_2

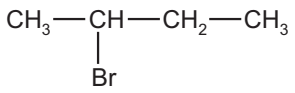
[W'15 P12 Q24]

19 Structural isomerism and stereoisomerism should be considered in answering this question.

Compound J is reacted with KOH dissolved in ethanol. Three isomeric alkenes with molecular formula C_4H_8 are formed.

What is J?

A $CH_3—CH_2—CH_2—CH_2—Br$

B


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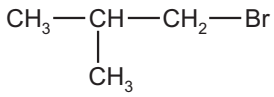

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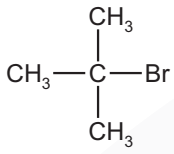


[M'16 P12 Q25]

20 An unknown organic compound reacts with sodium to give a combustible gas as one product but does **not** give a yellow precipitate with alkaline aqueous iodine.

What is a possible identity of the unknown organic compound?

A propanal

B propan-1-ol

C propan-2-ol

D propanone

[S'16 P13 Q28]

21 An unknown organic compound reacts with sodium to give a combustible gas as one product but does **not** give a yellow precipitate with alkaline aqueous iodine.

What is a possible identity of the unknown organic compound?

A propanal

B propan-1-ol

C propan-2-ol

D propanone

[S'16 P13 Q27]

22 The reaction $CH_3CH_2CH_2CH_2Br + OH^- \rightarrow CH_3CH_2CH_2CH_2OH + Br^-$ proceeds via an S_N2 mechanism.

The reaction $(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$ proceeds via an S_N1 mechanism.

Which statement about these two reactions is correct?

A Both reactions involve homolytic bond fission.

B Both reactions involve hydroxide ions acting as electron pair donors.

C Both reactions involve the formation of a positively-charged intermediate.

D Both reactions occur in a single step.

[W'16 P12 Q22]

23 Chloroethane can be used to make sodium propanoate.

chloroethane → Q → sodium propanoate

The intermediate, Q, is hydrolysed with boiling aqueous sodium hydroxide to give sodium propanoate.

Which reagent would produce the intermediate, Q, from chloroethane?

A concentrated ammonia solution

B dilute sulfuric acid

C hydrogen cyanide in water

D potassium cyanide in ethanol

[W'16 P11 Q24]

24 Aqueous sodium hydroxide 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

[S'17 P12 Q23]

25 2-bromo-2-methylpropane undergoes nucleophilic substitution when heated under reflux with an aqueous solution of sodium hydroxide.

Which row is correct?

	mechanism for this reaction	reason
A	S_N1	the hydroxide ion is helped in its approach to the central carbon atom by the methyl groups
B	S_N1	the intermediate carbocation is stabilised by the inductive effect of the methyl groups
C	S_N2	the hydroxide ion is hindered in its approach to the central carbon atom by the methyl groups
D	S_N2	the intermediate carbocation is destabilised by the inductive effect of the methyl groups

[S'17 P12 Q26]

26 Equal volumes of aqueous silver nitrate were added to separate small volumes of bromoethane and iodoethane in two test-tubes. The test-tubes were shaken.

Which row about the observations made for **bromoethane** is correct?

	colour of precipitate	rate of reaction
A	cream	faster than for iodoethane
B	cream	slower than for iodoethane
C	yellow	faster than for iodoethane
D	yellow	slower than for iodoethane

[W'17 P12 Q25]

27 Which organic reaction is an example of nucleophilic substitution?

A $CH_3CH_2Br + NaOH \rightarrow CH_2CH_2 + H_2O + NaBr$

B $CH_3CH_2Br + NaOH \rightarrow CH_3CH_2OH + NaBr$

C $CH_2CH_2 + HCl \rightarrow C_2H_5Cl$

D $C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$

[W'17 P13 Q24]

28 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 aqueous sodium hydroxide and 1-bromobutane proceeds by an S_N2 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

[M'18 P12 Q21]

29 A reaction occurs when a sample of 1-chloropropane is heated under reflux with sodium hydroxide dissolved in ethanol.

Which row is correct?

	type of reaction	name of product
A	elimination	propan-1-ol
B	elimination	propene
C	substitution	propan-1-ol
D	substitution	propene

[M'18 P12 Q27]

30 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	$[HOCH_2\text{- - -}C(CH_3)_3\text{- - -}Cl]^-$	$HOCH_2C(CH_3)_3$
D	$[H_3CO\text{- - -}C(CH_3)_3\text{- - -}Cl]^-$	$H_3COC(CH_3)_3$

[S'18 P11 Q22]

31 Primary halogenoalkanes undergo hydrolysis reactions.

Which reaction would occur most rapidly if they are all warmed to the same temperature?

A C_2H_5Br with H_2O

B C_2H_5Br with NaOH(aq)

C C_2H_5Cl with H_2O

D C_2H_5Cl with NaOH(aq)

[S'18 P12 Q23]

32 Structural isomerism and stereoisomerism should be considered when answering this question.

A colourless liquid, $C_5H_{11}Cl$, exists as a mixture of two optical isomers.

When heated with sodium hydroxide in ethanol, a mixture of **only** two alkenes is formed.

What could the colourless liquid be?

A $(CH_3CH_2)_2CHCl$

B $CH_3CH_2CH_2CHClCH_3$

C $(CH_3)_2CHCHClCH_3$

D $CH_3CH_2CCl(CH_3)_2$

[S'18 P12 Q24]

33 When warm water is added to halogenoalkane X, an S_N1 reaction occurs.

$AgNO_3$(aq) is then added; a yellow precipitate is formed.

What could be X?

A 1-chlorobutane

B 1-iodobutane

C 2-chloro-2-methylpropane

D 2-iodo-2-methylpropane

[S'18 P12 Q25]

34 Which statement is **not** correct?

A Combustion of PVC produces a highly acidic gas.

B PVC molecules are saturated.

C The empirical formula of PVC is the same as the empirical formula of its monomer.

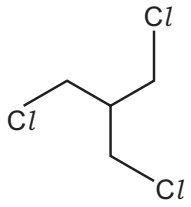
D The repeat unit of PVC is ~~(~~$CHClCHCl$~~)~~.

[S'18 P13 Q22]

35 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



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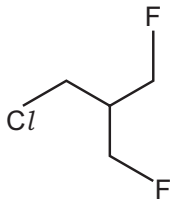

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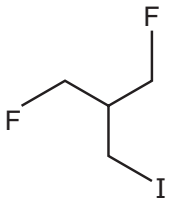

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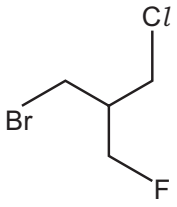


[S'18 P13 Q23]

36 Halogenoalkanes react with NaOH(aq) either by an S_N1 mechanism or by an S_N2 mechanism. The mechanism followed by the reaction depends on the structure of the halogenoalkane.

This question is about the reaction of 3-bromo-3-ethylpentane, $(C_2H_5)_3CBr$.

Which statement is correct?

A The mechanism is S_N1, due to the stabilisation of an intermediate anion by three alkyl groups.

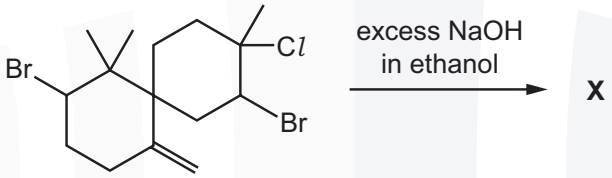
B The mechanism is S_N1, due to the stabilisation of an intermediate cation by three alkyl groups.

C The mechanism is S_N2, due to the stabilisation of an intermediate anion by three alkyl groups.

D The mechanism is S_N2, due to the stabilisation of an intermediate cation by three alkyl groups.

[S'18 P13 Q23]

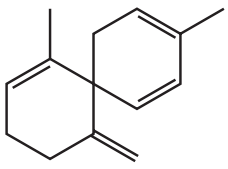
37 Compound J, $C_{15}H_{23}Br_2Cl$, is reacted with an excess of a hot concentrated solution of sodium hydroxide in ethanol. One of the products is **X**.



compound J

What could be the skeletal formula of **X**?

A



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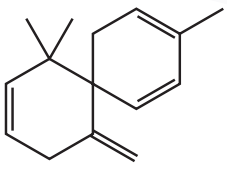

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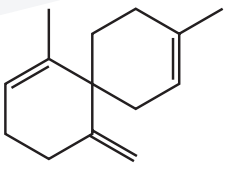

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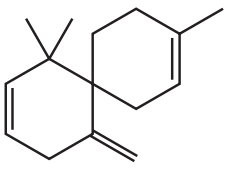


[W'18 P11 Q25]

38 A halogenoalkane has the molecular formula $C_5H_{11}Br$. The halogenoalkane does **not** form an alkene when treated with ethanolic sodium hydroxide.

What could be the halogenoalkane?

A 1-bromo-2-methylbutane

B 2-bromo-2-methylbutane

C 3-bromopentane

D bromodimethylpropane

[W'18 P12 Q25]

SECTION B

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

1 **X** is an organic compound that gives a precipitate with aqueous silver nitrate. This precipitate remains undissolved when concentrated aqueous ammonia is added.

What is a possible identity for **X**?

1 iodomethane

2 2-bromobutane

3 2-chlorobutane

[W'14 P11 Q38]

2 Which compounds produce pent-2-ene as either one of the products, or as the only product, on heating with potassium hydroxide in ethanol?

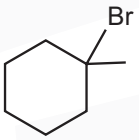
1 $CH_3CH_2CH_2CH_2CH_2Br$

2 $CH_3CHBrCH_2CH_2CH_3$

3 $CH_3CH_2CHBrCH_2CH_3$

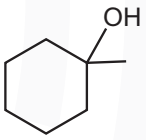
[W'14 P13 Q38]

3 Which compounds will react with HBr to give the compound R?



R

1



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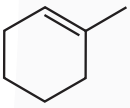

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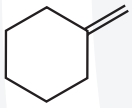


[S'15 P11 Q9]

4 Which types of reaction are undergone by $CH_2BrCHCH_2$?

1 hydrolysis

2 free radical substitution

3 nucleophilic addition

[S'15 P13 Q40]

5 **X** is an organic compound. **X** gives a precipitate with aqueous silver nitrate. Some or all of this precipitate remains undissolved when excess dilute aqueous ammonia is added.

What could be the identity of **X**?

1 2-chlorobutane

2 2-bromobutane

3 iodomethane

[W'15 P12 Q38]

6 Which types of reaction can occur with 1-bromobutane?

1 elimination

2 hydrolysis

3 free radical substitution

[S'16 P11 Q36]

7 Halogenoalkanes show trends in their physical and chemical properties.

Which properties steadily increase from C_2H_5Cl to C_2H_5Br to C_2H_5I ?

1 the polarity of the carbon-halogen bond

2 the boiling point of the halogenoalkane

3 the rate of reaction of the halogenoalkane with nucleophiles

[S'16 P13 Q37]

8 Bromoethane reacts with NaOH in different ways depending on the solvent used.

Which statements about these reactions are correct?

	solvent used	main organic product
1	water	ethane-1,2-diol
2	ethanol	ethene
3	water	ethanol

[W'16 P11 Q38]

9 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 statements are correct?

1 $(CH_3)_2CHCH_2Cl$ reacts with NaOH(aq) by an S_N2 mechanism.

2 The tertiary chloroalkane reacts more quickly than the others because the carbon atom bonded to the Cl atom is more positive in this molecule.

3 The Cl atoms in the three chloroalkanes are attacked by OH^-.

[S'17 P11 Q38]

10 Which statements help to explain the mechanism of the reaction between 1-chloropropane and ammonia?

1 1-chloropropane has a $\delta-$ chlorine atom that forms hydrogen bonds with a $\delta+$ hydrogen atom in ammonia.

2 1-chloropropane is a polar compound with a $\delta+$ carbon atom.

3 There is a lone pair of electrons on the nitrogen atom in ammonia.

[M'17 P12 Q38]

11 Which compounds react with alkaline aqueous iodine to give a pale yellow precipitate of tri-iodomethane?

1 butanone

2 ethanal

3 propan-2-ol

[M'17 P12 Q39]

12 Which compounds, on heating with ethanolic NaOH, produce more than one product with molecular formula C_4H_8?

1 2-bromobutane

2 2-bromo-2-methylpropane

3 1-bromo-2-methylpropane

[S'17 P13 Q38]

13 Which statements are correct for an S_N2 mechanism?

1 One bond is being broken at the same time as another bond is being formed.

2 The formation of the intermediate involves the collision of two molecules or ions.

3 A carbon atom in the transition state is bonded, either fully or partially, to five atoms.

[W'17 P12 Q37]

14 Bromoethane is heated under reflux with concentrated aqueous NaOH.

Which statements are correct?

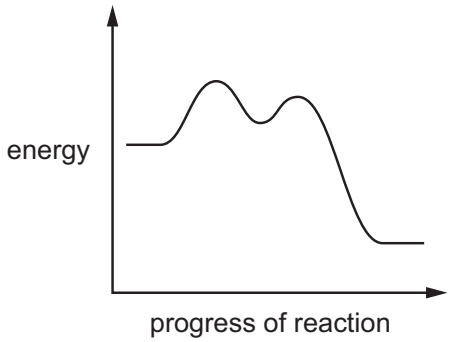
1 The major product is a primary alcohol.

2 The major reaction is hydrolysis by an S_N2 mechanism.

3 The major product would be the same if the NaOH is dissolved in ethanol.

[W'17 P12 Q38]

15 A reaction pathway diagram is shown.



Which reactions would have this reaction pathway diagram?

1 $(CH_3)_3CBr + NaOH \rightarrow (CH_3)_3COH + NaBr$

2 $CH_3CH_2CH_2Br + NaOH \rightarrow CH_3CH_2CH_2OH + NaBr$

3 $(CH_3)_3CCH_2CH_2Cl + 2NH_3 \rightarrow (CH_3)_3CCH_2CH_2NH_2 + NH_4Cl$

[W'17 P13 Q38]

16 Organic compound X gives a precipitate when warmed with aqueous silver nitrate. This precipitate dissolves when concentrated aqueous ammonia is added.

What could X be?

1 1-bromopropane

2 2-chlorobutane

3 2-iodo-2-methylpropane

[M'18 P12 Q38]

17 Chlorofluoroalkanes have been used as the refrigerant in refrigerators but care has to be taken in disposing of old refrigerators.

Which statements about chlorofluoroalkanes are correct?

1 C–Cl bonds more readily undergo homolytic fission than C–F bonds.

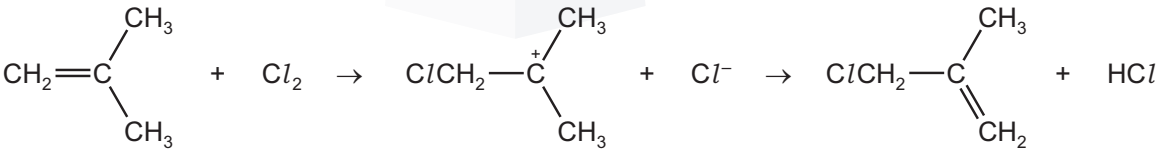
2 Care is taken in the disposal of old refrigerators because of possible ozone depletion.

3 C_2H_4ClF is more volatile than C_2H_6.

[S'17 P11 Q39]

18 2-methylpropene can react in more than one way with chlorine.

One of the reactions follows the pathway shown.



2-methylpropene intermediate product

Which statements about this mechanism are correct?

1 The intermediate has all carbon atoms in the same plane.

2 There is an electrophilic attack on the double bond.

3 It is a free radical mechanism.

[S'18 P11 Q37]

19 The halogenoalkanes listed below all react with NaOH(aq).

Which reactions proceed mainly by an S_N1 mechanism?

1 1-iodopropane

2 2-iodo-2-methylpropane

3 2-bromo-2-methylbutane

[S'18 P11 Q38]

20 Halogenoalkanes can undergo reaction with hydroxide ions.

$$RBr + OH^- \rightarrow ROH + Br^-$$

The reaction of some halogenoalkanes proceeds by the S_N1 mechanism.

Which statements about the S_N1 mechanism are correct?

1 A carbocation is formed which is stabilised by the inductive effect of the alkyl groups present.

2 Only tertiary halogenoalkanes are hydrolysed in this way.

3 The intermediate formed includes a carbon atom with five bonds attached to it.

[S'18 P12 Q38]

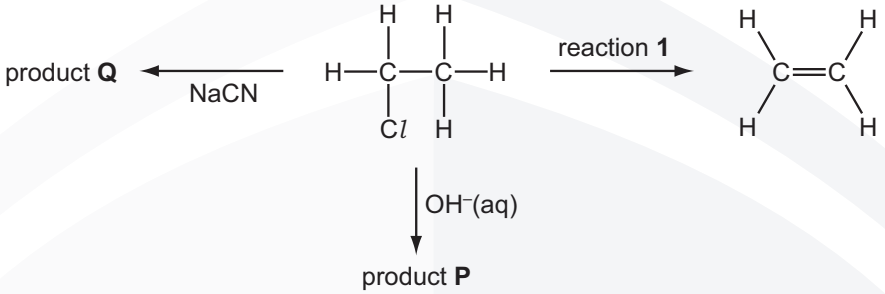
HALOGENOALKANES WS 2

SECTION A

1 **(d)** Chloroethene can be polymerised to form a polymer commonly known as PVC.
Draw a diagram of the structure of PVC including **three** repeat units.

[2]

(e) Chloroethane undergoes a series of reactions as shown in the diagram below.



(i) Give the reagent and conditions necessary for reaction **1**.

.....

..... [2]

(ii) Give the **skeletal** formula of product **P**.

[1]

(iii) Give the **displayed** formula and the name of product **Q**.

..... [2]

[S'14 P21 Q4]

2 **(c)** **(i)** Give the structures of the four structural isomers of C_4H_9Br **and** identify each as primary, secondary or tertiary.

....

....

[4]

(ii) Name the isomer of C_4H_9Br that contains a chiral centre and draw the three-dimensional structures of the two optical isomers.

name .....

structures

[3]

(d) Aqueous silver nitrate solution was added to separate tubes containing chloroethane, bromoethane and iodoethane. The tubes were heated in a water bath.

A yellow precipitate appeared first in the tube containing iodoethane, followed by a cream precipitate in the tube containing bromoethane and finally a white precipitate appeared in the tube containing chloroethane.

Explain these observations.

.....

.....

.....

.....

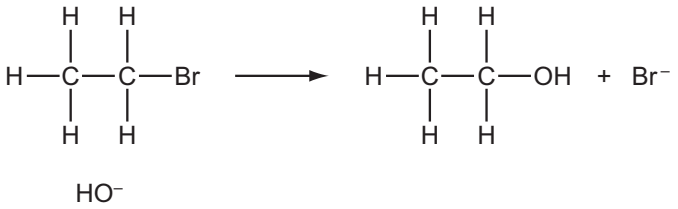
.....

..... [2]

(e) **(i)** Give the full name of the mechanism for the reaction between aqueous sodium hydroxide and bromoethane.

..... [2]

(ii) Complete the diagram below to represent this mechanism. Include all necessary curly arrows, partial charges and lone pairs.



[2]

(f) In the past, CFCs such as CF_3Cl were widely used as refrigerants.

(i) State a property of CFCs which makes them suitable for use as refrigerants.

..... [1]

(ii) State the damaging effect of CFCs in the upper atmosphere.

.....

Explain your answer.

.....

.....

.....

[2]

[S'14 P23 Q4]

3 Halogenoalkanes are useful intermediates in the synthesis of a wide variety of compounds.

(a) 2-bromobutane reacts in two different ways with sodium hydroxide depending on the conditions.

When warmed with aqueous sodium hydroxide, 2-bromobutane produces an alcohol that exists as a pair of optical isomers.

(i) Give the name of the mechanism of the reaction between 2-bromobutane and aqueous sodium hydroxide.

..... [1]

(ii) Explain why the alcohol produced exists as a pair of optical isomers.

.....

..... [1]

(iii) Draw the three-dimensional structure of the two optical isomers of the alcohol produced in **(ii)**.

[2]

Heating 2-bromobutane with ethanolic sodium hydroxide produces a mixture of three alkenes, two of which are a pair of geometrical isomers.

(iv) Give the name of the mechanism of the reaction between 2-bromobutane and ethanolic sodium hydroxide.

..... [1]

(v) Draw and name the structures of the pair of geometrical isomers formed by reaction of 2-bromobutane with ethanolic sodium hydroxide.

name .....

name .....

[2]

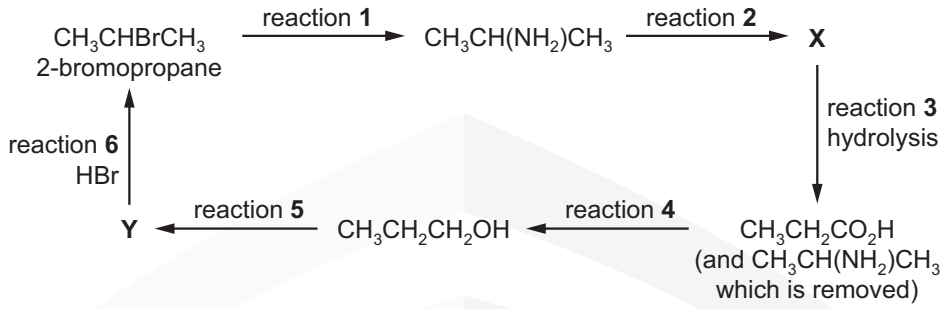
(vi) Name the third alkene produced by reaction of 2-bromobutane with ethanolic sodium hydroxide and explain why it does **not** show geometrical isomerism.

.....

.....

..... [2]

(b) Some reactions involving 2-bromopropane are shown.



(i) State the reagent needed for reaction **1**.

..... [1]

(iv) Name the type of reaction involved in reaction **4** and suggest a suitable reagent.

.....

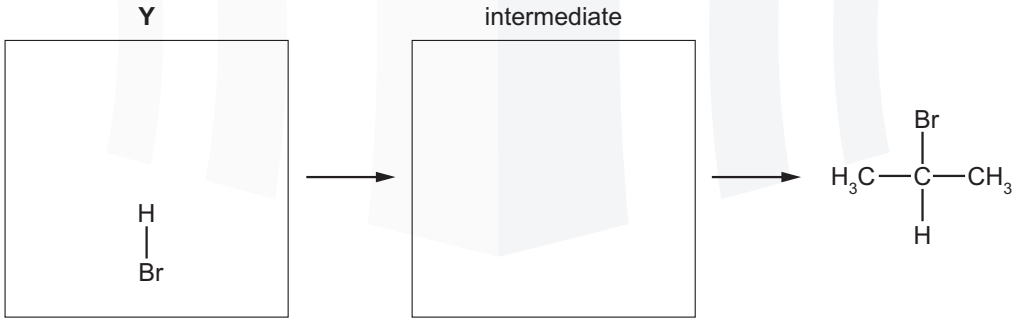
..... [2]

(v) State the name of a solid catalyst for reaction **5**.

..... [1]

(vi) Complete the mechanism for the production of 2-bromopropane from **Y** in reaction **6** shown below.

Include the structure of **Y** and any necessary lone pairs, curly arrows, charges and partial charges.



[4]

(vii) Give the name of the mechanism in **(vi)**.

..... [1]

(viii) 1-bromopropane is a minor product of reaction **6**.

Explain why 2-bromopropane is the major product of reaction **6**.

.....

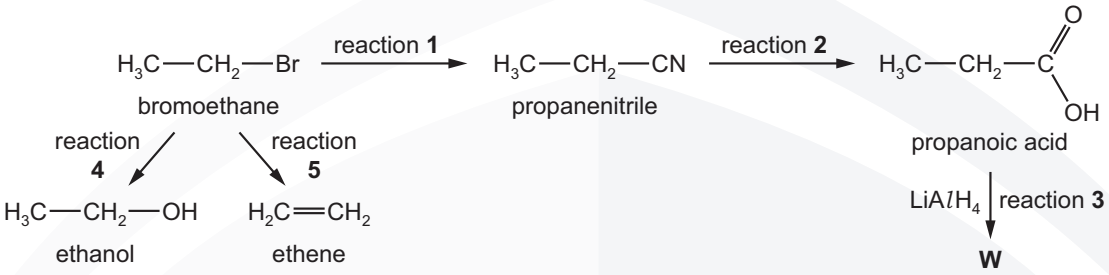
.....

.....

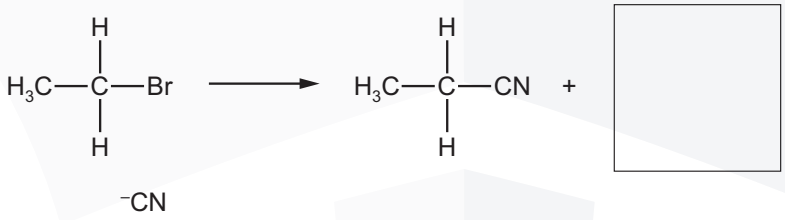
..... [2]

[W'15 P22 Q4]

4 A reaction sequence is shown.



(a) Complete the diagram to show the mechanism of reaction **1**. Include all necessary charges, partial charges, lone pairs and curly arrows.



[2]

(b) **(i)** Give the name of the type of reaction involved in reaction **3**.

..... [1]

[S'16 P21 Q5]

5 **(c)** **(i)** Reactions **4** and **5** use the same reagent.

Give the reagent and conditions needed for reaction **4**.

reagent .....

conditions ..... [2]

(ii) Give the conditions needed for reaction **5**.

..... [1]

(d) Under appropriate conditions, ethanol and propanoic acid undergo a condensation reaction.

(i) State the condition necessary for the reaction.

..... [1]

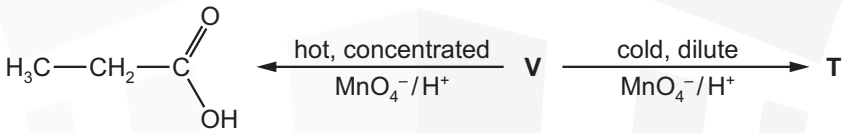
(ii) Draw the skeletal formula of the organic product of this reaction.

[1]

(iii) Name the organic product of this reaction.

..... [1]

(e) **V** reacts with acidified manganate(VII) ions in two different ways depending on the conditions, as shown in the reaction sequence below.



propanoic acid

V decolourises bromine water.

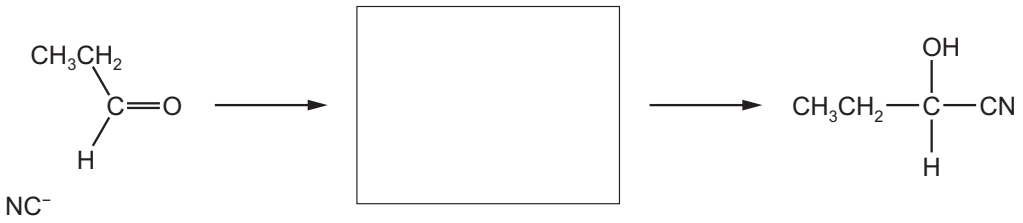
When the acidified manganate(VII) is hot and concentrated, propanoic acid is the only organic product.

When the acidified manganate(VII) is cold and dilute, the organic product is **T** which has two chiral centres.

(i) Give the structural formulae of **V** and **T**.

V ..... **T** .....

(c) **(i)** Complete the reaction mechanism for reaction **5**. Include all relevant lone pairs, curly arrows, charges and partial charges.



[4]

The product of reaction **5** exhibits stereoisomerism.

(ii) Draw the two stereoisomers in the conventional way.

[2]

(iii) Suggest why a mixture of the two stereoisomers is formed by reaction **5**.

.....

.....

..... [2]

[Total: 13]

[S'16 P21 Q5]

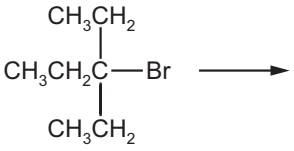
6 **(b)** $(C_2H_5)_3CBr$

(i) Name this compound.

..... [1]

(ii) $(C_2H_5)_3CBr$ reacts with aqueous OH^-.

Complete the mechanism for this reaction including all necessary curly arrows, charges, partial charges and lone pairs.



[3]

(iii) What *type of mechanism* occurs in **(ii)**?

..... [1]

(c) $CH_3CH_2CH_2CHBrCH_3$

(i) Give the reagents and conditions necessary for the conversion of this compound into a mixture of alkenes.

.....

..... [2]

(ii) Give the name of the mechanism for the conversion in **(i)**.

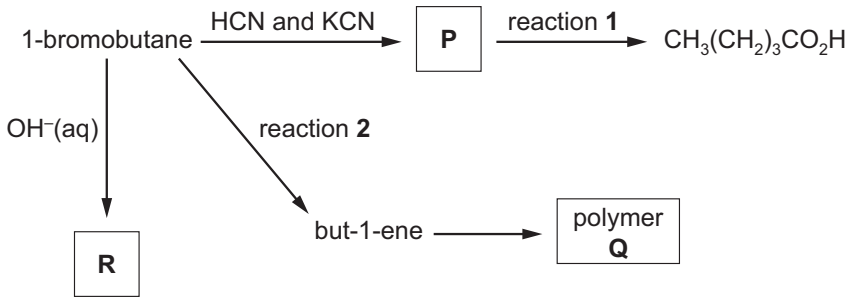
..... [1]

(iii) Draw the skeletal formulae of the three alkenes produced by the conversion in **(i)**.

[3]

[W'16 P22 Q4]

7 **(a)** A series of reactions starting from 1-bromobutane is shown.



(i) Draw the **displayed** formula of compound **P**.

[1]

(ii) Identify the reagent(s) and conditions for reactions **1** and **2**.

reaction **1** .....

reaction **2** .....

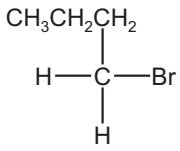
[2]

(iii) Draw the structure of the repeat unit of polymer **Q**.

[2]

(b) Complete the reaction scheme to show the mechanism of the reaction of 1-bromobutane with OH^-(aq) to produce **R**.

Include all necessary charges, dipoles, lone pairs and curly arrows and the structure of **R**.

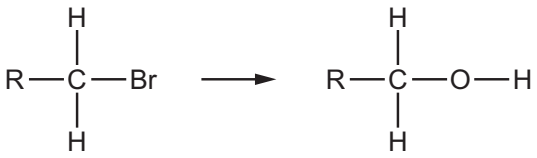


^{-}OH

[3]

[M'17 P22 Q3]

8 **(b)** Complete the diagram to show the S_N2 mechanism of reaction 1. R represents the $CH_3(CH_2)_2$ group.
Include all necessary charges, dipoles, lone pairs and curly arrows.



[2]

(c) 2-bromo-2-methylpropane is a tertiary halogenoalkane that is a structural isomer of 1-bromobutane.

(i) Define the term *structural isomer* and name the three different types of structural isomerism.

definition .....

.....

.....

.....

types of structural isomerism

1 .....

2 .....

3 .....

[4]

(ii) 2-bromo-2-methylpropane is treated with the same reagents as in reaction 1.
Methylpropan-2-ol is formed.

Identify the mechanism for this reaction.
Explain why this reaction proceeds via a different mechanism from that of reaction 1.

mechanism .....

explanation .....

.....

.....

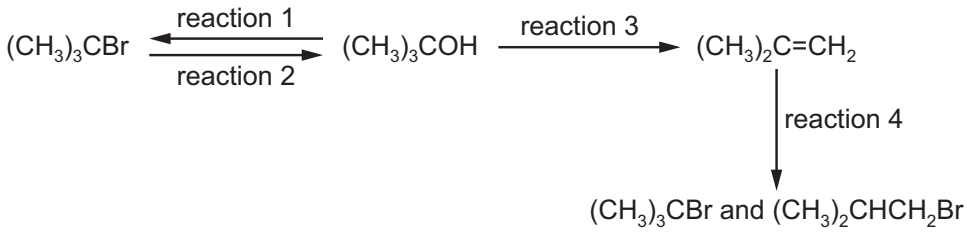
.....

.....

[3]

[W'17 P21 Q3]

9 Some reactions are shown, based on methylpropan-2-ol, $(CH_3)_3COH$.



(a) For each of the reactions state the reagent(s), the particular conditions required, if any, and the type of reaction.

For the type of reaction choose from the list.
Each type may be used once, more than once or not at all.
Each reaction may be described by one or more than one type.

hydrolysis dehydration substitution

oxidation addition condensation

reaction	reagent(s) and conditions	type(s) of reaction
1		
2		
3		
4		

[5]

(b) Draw a diagram to show the S_N1 mechanism of reaction 2.
Include all necessary charges, dipoles, lone pairs and curly arrows.

[3]

(ii) 1-bromobutane is treated with the same reagents as in reaction 2. Butan-1-ol is formed.

Identify the mechanism of this reaction.
Explain why this reaction proceeds via a different mechanism from that of reaction 2.

mechanism .....

explanation .....

.....

.....

.....

.....

[3]

(d) The product of reaction 3, methylpropene, does **not** show stereoisomerism.

(i) Give **two** reasons why methylpropene does **not** show stereoisomerism.

.....

.....

..... [2]

[N'17 P22 Q4]

HALOGENOALKANES WS 3

SECTION A

1 The anaesthetic *halothane,* $CF_3CHBrCl$, is made industrially as shown below.

$$CCl_2{=}CHCl \xrightarrow[\text{stage 1}]{HF} CF_3CH_2Cl \xrightarrow[\text{stage 2}]{Br_2} CF_3CHBrCl$$

What type of reaction is occurring in stage 2?

A electrophilic addition

B electrophilic substitution

C free radical substitution

D nucleophilic addition

[S'02 Q19]

2 2-Bromopropane, $(CH_3)_2CHBr$, may be used as the starting point for making $(CH_3)_2CHCO_2H$.

Which of the following sequences would be most suitable?

A $(CH_3)_2CHBr \rightarrow (CH_3)_2CHOH \rightarrow (CH_3)_2CHCO_2H$

B $(CH_3)_2CHBr \rightarrow (CH_3)_2CHCN \rightarrow (CH_3)_2CHCO_2H$

C $(CH_3)_2CHBr \rightarrow (CH_3)_2CHOH \rightarrow (CH_3)_2CHCN \rightarrow (CH_3)_2CHCO_2H$

D $(CH_3)_2CHBr \rightarrow (CH_3)_2CHCN \rightarrow (CH_3)_2CHOH \rightarrow (CH_3)_2CHCO_2H$

[S'02 Q23]

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

Which of the following will not destroy ozone, and therefore can be used safely as a replacement for CFCs?

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

[W'02 Q25]

4 Chlorofluoroalkanes, commonly known as CFCs, undergo homolytic fission by ultraviolet irradiation in the stratosphere.

Which radical could result from this irradiation of $CHFClCF_2Cl$?

A $CHFCl\dot{C}FCl$

B $\dot{C}HClCF_2Cl$

C $\dot{C}HFCF_2Cl$

D $\dot{C}FClCF_2Cl$

[S'03 Q27]

5 1,2-Dibromo-3-chloropropane (DBCP) has been used in the control of earthworms in agricultural land.

What would be the best synthesis of this compound?

A $CH_3CH_2CH_2Cl + 2Br_2 \rightarrow DBCP + 2HBr$

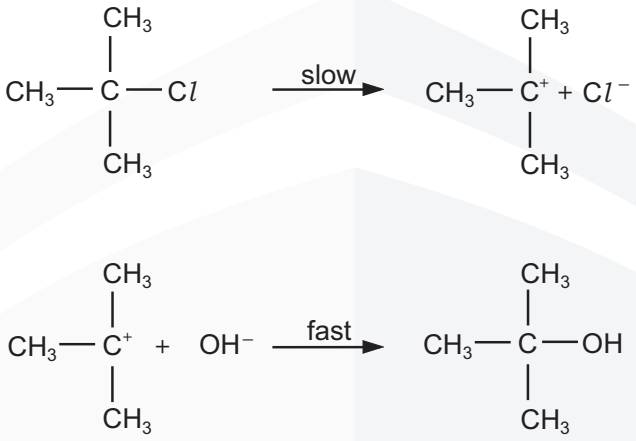
B $CH_3CHBrCH_2Br + Cl_2 \rightarrow DBCP + HCl$

C $CH_2{=}CHCH_2Cl + Br_2 \rightarrow DBCP$

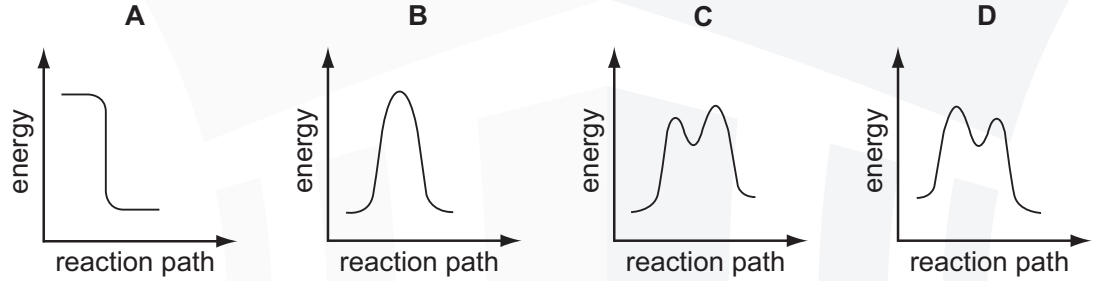
D $ClCH_2CH{=}CH_2 + PBr_5 \rightarrow DBCP + PBr_3$

[W'03 Q23]

6 A possible mechanism of the hydrolysis of 2-chloro-2-methylpropane is shown.

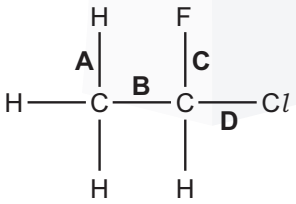


Which diagram represents the reaction profile for this mechanism?



[S'04 Q26]

7 Which bond in the structure below has the lowest bond energy?



[W'04 Q27]

8 Which of these always applies to a nucleophile?

A It attacks a double bond.

B It has a lone pair of electrons.

C It is a single atom.

D It is negatively charged.

[S'04 Q21]

9 Under the Montreal Protocol the use of chlorofluorocarbons is to be phased out. Fluorocarbons are often used to replace them. One chlorofluorocarbon which was widely used as a solvent is CCl_2FCClF_2 and large stocks of it remain. One process to use up these stocks is to convert it into the fluorocarbon CH_2FCF_3 by the following route.

$$CCl_2FCClF_2 \xrightarrow{\text{step 1}} CCl_3CF_3 \xrightarrow{\text{step 2}} CCl_2FCF_3 \xrightarrow{\text{step 3}} CH_2FCF_3$$

What type of reaction is step 1?

A elimination

B free radical substitution

C isomerisation

D nucleophilic substitution

[S'05 Q21]

10 Dichlorodifluoromethane, CCl_2F_2, has been used in aerosol propellants and as a refrigerant.

Which statement helps to explain why dichlorodifluoromethane is chemically inert?

A The carbon-fluorine bond energy is large.

B The carbon-fluorine bond has a low polarity.

C Fluorine is highly electronegative.

D Fluorine compounds are non-flammable.

[S'05 Q23]

11 In the upper atmosphere chlorofluoroalkanes (CFCs) are broken down to give chlorine radicals but not fluorine radicals.

What is the best explanation for this?

A Fluorine is more electronegative than chlorine.

B Fluorine radicals are less stable than chlorine radicals.

C The C–F bond is stronger than the C–Cl bond.

D The chlorine atom is larger than the fluorine atom.

[W'05 Q22]

12 Which reaction is an example of nucleophilic substitution?

A $CH_3CH_2Br \rightarrow CH_2{=}CH_2 + HBr$

B $CH_2{=}CH_2 + HBr \rightarrow CH_3CH_2Br$

C $C_3H_7Br + H_2O \rightarrow C_3H_7OH + HBr$

D $C_2H_6 + Br_2 \rightarrow C_2H_5Br + HBr$

[W'06 Q22]

13 An amine is produced in the following reaction.

$$C_2H_5I + 2NH_3 \rightarrow C_2H_5NH_2 + NH_4I$$

What is the mechanism?

A electrophilic addition

B electrophilic substitution

C nucleophilic addition

D nucleophilic substitution

[W'05 Q23]

14 High-energy irradiation in the stratosphere produces radicals from chlorofluoroalkanes, commonly known as CFCs.

Which radical could result from this irradiation of $CHFCl CF_2Cl$?

A $CHFCl\dot{C}FCl$

B $\dot{C}HCl CF_2Cl$

C $\dot{C}HFCF_2Cl$

D $\dot{C}FCl CF_2Cl$

[S'06 Q25]

15 Under the Montreal Protocol, the manufacture of chlorofluorocarbons has been phased out, and they are being replaced by fluorocarbons.

One chlorofluorocarbon which was widely used as a solvent is CCl_2FCClF_2. Large stocks of it remain. One process to use up these stocks is to convert it into the fluorocarbon CH_2FCF_3 by the following route.

$$CCl_2FCClF_2 \xrightarrow{\text{step 1}} CCl_3CF_3 \xrightarrow{\text{step 2}} CCl_2FCF_3 \xrightarrow{\text{step 3}} CH_2FCF_3$$

What type of reaction is step 2?

A electrophilic substitution

B free radical reduction

C isomerisation

D nucleophilic substitution

[S'05 Q20]

16 Which term describes the action of NaOH(aq) on a bromoalkane?

A acid-base reaction

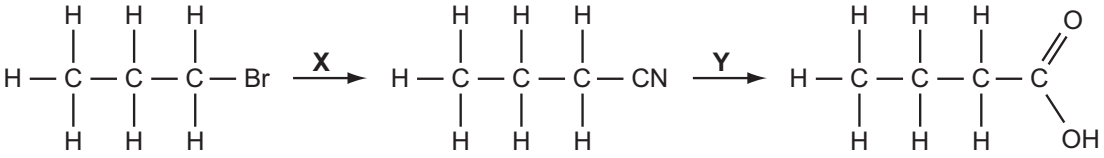
B electrophilic substitution

C elimination of HBr

D nucleophilic substitution

[S'07 Q24]

17 **X** and **Y** are the reagents required to convert 1-bromopropane into butanoic acid.



What are the correct identities of **X** and **Y**?

	X	Y
A	NH_3	HCl(aq)
B	KCN in C_2H_5OH	NaOH(aq)
C	KCN in C_2H_5OH	HCl(aq)
D	HCN	NaOH(aq)

[S'07 Q25]

18 Chlorofluoroalkanes, CFCs, can be used as refrigerants, aerosol propellants and fire extinguishers.

CFCs such as CCl_3F and CCl_2F$_2$ are more stable than chloroalkanes such as CCl_4.

What is the reason for their greater stability?

A Fluorine has a higher first ionisation energy than chlorine.

B Fluorine radicals are more stable than chlorine radicals.

C The C–F bond energy is larger than the C–Cl bond energy.

D The C–F bond is more polar than the C–Cl bond.

[W'07 Q25]

19 Butanedioic acid occurs in amber, algae, lichens, sugar cane and beets. It may be synthesised in two steps from 1,2-dibromoethane.

$$BrCH_2CH_2Br \xrightarrow{\text{step 1}} \mathbf{X} \xrightarrow{\text{step 2}} HO_2CCH_2CH_2CO_2H$$

Which reagents could be used for this synthesis?

	step 1	step 2
A	HCN(g)	HCl(aq)
B	HCO_2Na(aq)	HCl(aq)
C	KCN(aq/alcoholic)	H_2SO_4(aq)
D	NaOH(aq)	$K_2Cr_2O_7$ / H_2SO_4(aq)

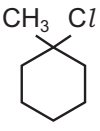
[S'11 P11 Q21]

20 Which compound undergoes an S_N1 substitution reaction?

A $CH_3CH_2CH_2Br$

B $(CH_3)_3CCH_2I$

C



D CH_2=CHCl

[W'10 P11 Q28]

21 Which pair of reaction types is illustrated by the reaction sequence below?

$$CH_3CH{=}CHCH_3 \xrightarrow{HI \text{ in } CH_3CO_2H} CH_3CH_2CHICH_3 \xrightarrow{NaOH(aq)} CH_3CH_2CH(OH)CH_3$$

A electrophilic addition and electrophilic substitution

B electrophilic addition and nucleophilic substitution

C nucleophilic addition and electrophilic substitution

D nucleophilic addition and nucleophilic substitution

[S'08 Q20]

22 Halogenoalkanes are important molecules in organic synthetic reactions. In particular they undergo a range of nucleophilic reactions.

Which reaction proceeds **only** by an S_N1 mechanism?

A $CH_3CH_2Br + NH_3$

B $CH_3CH_2CH_2I + OH^-$

C $CH_3CHBrCH_3 + NH_3$

D $(CH_3)_3CI + OH^-$

[S'08 Q25]

23 Four drops of 1-chlorobutane, 1-bromobutane and 1-iodobutane were put separately into three test-tubes containing 1.0 cm^3 of aqueous silver nitrate at 60 °C.

A hydrolysis reaction occurred. (R represents the butane chain C_4H_9– and *X* the halogen atom.)

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

The rate of formation of cloudiness in the tubes was in the order RC*l* < RBr < RI.

Why is this?

A The R–*X* bond polarity decreases from RC*l* to RI.

B The solubility of Ag*X*(s) decreases from AgC*l* to AgI.

C The ionisation energy of the halogen decreases from C*l* to I.

D The bond energy of R–*X* decreases from RC*l* to RI.

[W'08 Q23]

24 In the hydrolysis of bromoethane by aqueous sodium hydroxide, 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

[S'09 Q24]

25 Which halogenoalkane will undergo an S_N1 reaction and produce a yellow precipitate when $AgNO_3(aq)$ is added to it?

A 1-chlorobutane

B 1-iodobutane

C 2-chloro-2-methylpropane

D 2-iodo-2-methylpropane

[S'11 P12 Q21]

26 Which reaction will give 2-chloropropane in the best yield?

A propane gas with chlorine gas in the presence of ultraviolet light

B propan-2-ol with dilute $NaCl(aq)$

C propan-2-ol with $SOCl_2$

D propene with dilute $HCl(aq)$

[S'11 P12 Q22]

27 Many different compounds have been used in aerosol sprays, refrigerators and in making foamed plastics.

Which compound will cause the **most** ozone depletion?

A CCl_3F

B $CH_2FCHClF$

C $CH_3CH_2CH_2CH_3$

D N_2O

[W'11 P11 Q21]

28 What is involved in the mechanism of the reaction between aqueous sodium hydroxide 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

[W'11 P11 Q24]

29 The depletion of the ozone layer in the upper atmosphere reduces the Earth's natural protection from harmful ultraviolet radiation.

Which compound would cause the most depletion of the ozone layer?

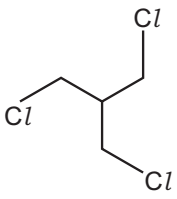
A CCl_3F **B** CF_4 **C** $CHClF_2$ **D** CH_2F_2

[S'12 P11 Q29]

30 The presence of halogen in an organic compound may be detected by warming the organic compound with aqueous silver nitrate.

Which compound would produce a precipitate quickest?

A



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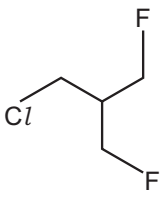

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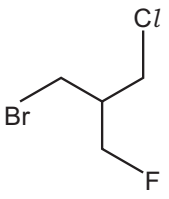

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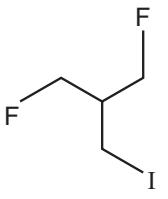
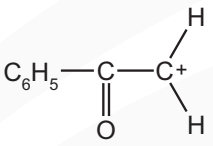


[S'12 P11 Q27]

31 When phenacyl chloride, $C_6H_5COCH_2Cl$, is reacted with aqueous NaOH, the substitution reaction follows an S_N2 mechanism.

Which structure represents a species formed during the reaction?

A



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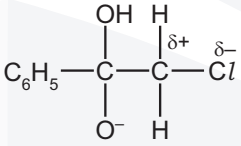

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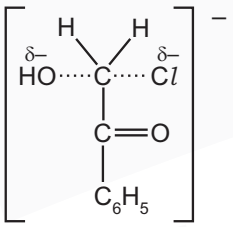

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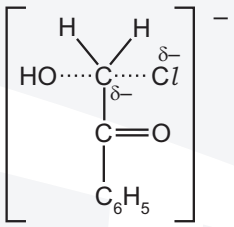


[S'12 P12 Q25]

32 Chloroethane can be used to make sodium propanoate.

chloroethane → Q → sodium propanoate

The intermediate, Q, is hydrolysed with boiling aqueous sodium hydroxide, to give sodium propanoate.

Which reagent would produce the intermediate, Q, from chloroethane?

A concentrated ammonia solution

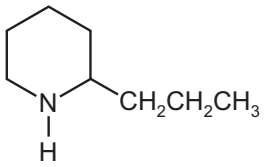
B dilute sulfuric acid

C hydrogen cyanide

D potassium cyanide

[S'13 P11 Q23]

33 Coniine is the major constituent of the poison 'oil of hemlock'.



coniine

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

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

X

What is the name of compound **X**?

A 1,1-dibromo-2-propylcyclopentane

B 1,2-dibromo-2-propylcyclopentane

C 1,4-dibromooctane

D 1,5-dibromooctane

[S'12 P12 Q28]

34 Aqueous sodium hydroxide reacts with 1-bromopropane to give propan-1-ol.

How should the first step in the mechanism be described?

A by a curly arrow from a lone pair on the OH^- ion to the $C^{\delta+}$ atom of 1-bromopropane

B by a curly arrow from the $C^{\delta+}$ atom of 1-bromopropane to the OH^- ion

C by a curly arrow from the C–Br bond to the C atom

D by the homolytic fission of the C–Br bond

[S'13 P11 Q24]

35 Aqueous sodium hydroxide reacts with 2-bromo-2-methylpropane to give 2-methylpropan-2-ol.

The reaction proceeds by an S_N1 mechanism.

How should the first step in the mechanism be described?

A by a curly arrow from a lone pair on the OH^- ion to the $C^{\delta+}$ atom of 2-bromopropane

B by a curly arrow from the C–Br bond to the Br atom

C by a curly arrow from the C–Br bond to the C atom

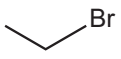
D by the homolytic fission of the C–Br bond

[S'13 P12 Q23]

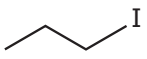
36 Compound **Y** can be hydrolysed by warm aqueous silver nitrate to form a precipitate that is soluble in dilute aqueous ammonia. Compound **Y** can undergo an elimination reaction to form an alkene.

What could be the skeletal formula of compound **Y**?

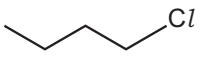
A



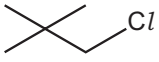
B



C



D



[S'13 P12 Q24]

37 A carbanion is an organic ion in which a carbon atom has a negative charge. A carbocation is an organic ion in which a carbon atom has a positive charge.

What is involved in the mechanism of the reaction between aqueous sodium hydroxide and 2-bromo-2-methylbutane?

A heterolytic bond fission followed by an attack by an electrophile on a carbanion

B heterolytic bond fission followed by an attack by a nucleophile on a carbocation

C homolytic bond fission followed by an attack by an electrophile on a carbanion

D homolytic bond fission followed by an attack by a nucleophile on a carbocation

[S'13 P13 Q25]

38 CCl_2FCClF_2 can be converted into CH_2FCF_3 by the following route.

$$CCl_2FCClF_2 \xrightarrow{\text{step 1}} CCl_3CF_3 \xrightarrow{\text{step 2}} CCl_2FCF_3 \xrightarrow{\text{step 3}} CH_2FCF_3$$

What type of reaction is step 1?

A addition

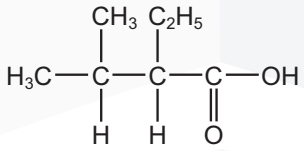
B elimination

C isomerisation

D oxidation

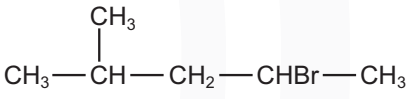
[S'13 P13 Q30]

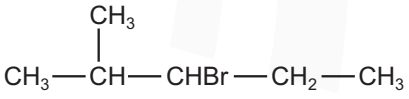
39 The characteristic odour of rum is attributed to the compound 2-ethyl-3-methylbutanoic acid.

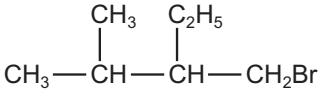


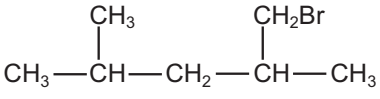
2-ethyl-3-methylbutanoic acid

Which compound will produce 2-ethyl-3-methylbutanoic acid by heating under reflux with alcoholic sodium cyanide and subsequent acid hydrolysis of the reaction product?

A 

B 

C 

D 

[W'09 P11 Q29]

40 Each of the following compounds is effective as a refrigerant.

The release of which one of these causes the greatest depletion of the ozone layer?

A CCl_2F_2 **B** CH_3OCH_3 **C** CH_3CHF_2 **D** $CH_3CH_2CH_3$

[W'03 Q24]

41 Under identical conditions, even though it proceeds by the same mechanism, reaction 1 is faster than reaction 2.

reaction 1 $CH_3CHBrCH_3 + NaCN \rightarrow CH_3CH(CN)CH_3 + NaBr$

reaction 2 $CH_3CHBrCH_3 + NaI \rightarrow CH_3CHICH_3 + NaBr$

What factor will explain this result?

A The C — I bond is a stronger bond than the C — Br bond.

B The C — N bond is a stronger bond than the C — I bond.

C The cyanide ion is a stronger nucleophile than the iodide ion.

D The cyanide ion is a weaker nucleophile than the iodide ion.

[S'05 Q24]

42 When an isomer Y of molecular formula C_4H_9Br undergoes hydrolysis in aqueous alkali to form an alcohol C_4H_9OH, the rate of reaction is found to be unaffected by changes in the concentration of OH^- ions present.

Which is the most likely molecular structure of Y?

A $CH_3CH_2CH_2CH_2Br$

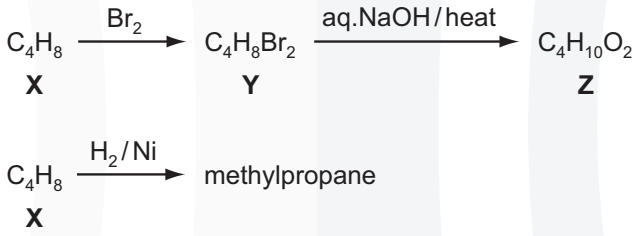
B $CH_3CH_2CHBrCH_3$

C $(CH_3)_2CHCH_2Br$

D $(CH_3)_3CBr$

[S'10 P11 Q28]

43 Compound X, molecular formula C_4H_8, undergoes the following reactions.



What is the formula of compound Z?

A $CH_3CH_2CH(OH)CH_2OH$

B $CH_3CH(OH)CH(OH)CH_3$

C $CH_3CH(CH_2OH)CH_2OH$

D $(CH_3)_2C(OH)CH_2OH$

[W'11 P12 Q29]

44 The reaction scheme outlines the production of one of the monomers of nylon 66 from compound **X**.

$$\text{compound X} \xrightarrow[\text{in ethanol}]{\text{KCN}} \text{NCCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CN} \xrightarrow{\text{reduction}} \text{H}_2\text{N(CH}_2\text{)}_6\text{NH}_2$$

Which compound could be **X**?

A $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$

B $\text{CH}_2\text{=CHCH=CH}_2$

C $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$

D $\text{HO}_2\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$

[S'03 Q26]

45 A carbanion is an organic ion in which a carbon atom has a negative charge. A carbocation is an organic ion in which a carbon atom has a positive charge.

The reaction between aqueous sodium hydroxide and 1-bromobutane proceeds by an S_N2 mechanism.

How should the first step in the mechanism be described?

A attack by a nucleophile on a carbon atom with a partial positive charge

B heterolytic bond fission followed by an attack by an electrophile on a carbanion

C heterolytic bond fission followed by an attack by a nucleophile on a carbocation

D homolytic bond fission followed by an attack by a nucleophile on a carbocation

[W'13 P11 Q24]

46 Including structural and stereoisomers, how many isomeric products are produced when alcoholic KOH reacts with 2-chlorobutane?

A 1 **B** 2 **C** 3 **D** 4

[W'13 P13 Q24]

47 Chlorofluorocarbons, CFCs, can be used as refrigerants, aerosol propellants and fire extinguishers.

CFCs such as $\text{CC}l_3\text{F}$ and $\text{CC}l_2\text{F}_2$ are more stable than chloroalkanes such as $\text{CC}l_4$.

What is the reason for their greater stability?

A Fluorine has a higher first ionisation energy than chlorine.

B Fluorine radicals are more stable than chlorine radicals.

C The C–F bond energy is larger than the C–Cl bond energy.

D The C–F bond is more polar than the C–Cl bond.

[W'07 Q25]

48 Halogenoalkanes react with aqueous NaOH to give alcohols. The mechanism involved is either S_N1 or S_N2.

Which halogenoalkane produces the highest percentage of product by an S_N1 mechanism, when treated with aqueous NaOH?

A 2-bromopropane

B 2-chloropropane

C 1-iodo-2-methylpropane

D 2-iodo-2-methylpropane

[W'13 P13 Q26]

49 Which reaction will give 2-chloropropane in the best yield?

A propane gas with chlorine gas in the presence of ultraviolet light

B propan-2-ol with dilute NaCl(aq)

C propan-2-ol with SOCl_2(l)

D propene with dilute HCl(aq)

[S'11 P12 Q22]

SECTION B

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

1 Chloroethane can be formed from bromoethane in two steps.

$$C_2H_5Br \xrightarrow{\text{step X}} C_2H_5OH \xrightarrow{\text{step Y}} C_2H_5Cl$$

Which statements about these steps are correct?

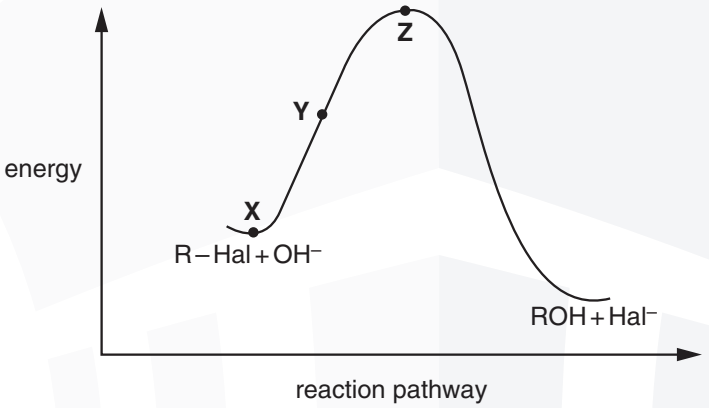
1 Step **X** involves a nucleophilic substitution.

2 Hot aqueous sodium hydroxide is the reagent in step **X**.

3 Hot aqueous sodium chloride is the reagent in step **Y**.

[W'12 P12 Q38]

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



Which of the following statements are correct?

1 The reaction is an example of nucleophilic substitution.

2 Between **X** and **Y** the C-Hal bond will be lengthening.

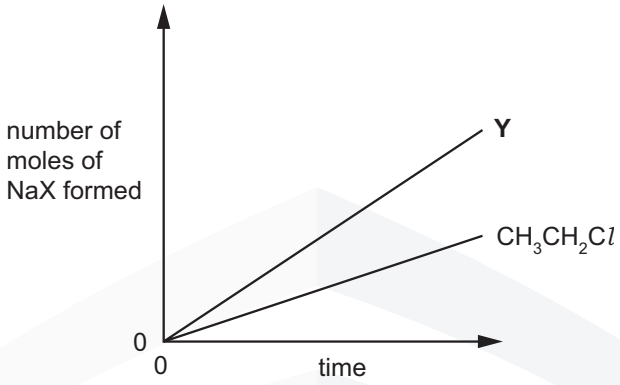
3 The energy difference between **X** and **Z** represents the activation energy.

[S'02 Q39]

3 When halogenoalkanes, RX, are hydrolysed with NaOH, the corresponding sodium halide, NaX, is produced.

$$RX + NaOH \rightarrow ROH + NaX$$

A student investigated the amount of NaX produced by hydrolysing CH_3CH_2Cl and another halogenoalkane, **Y**. In a given time the amount of sodium halide formed was greater with **Y** than with CH_3CH_2Cl.



Which compound could be **Y**?

1 $ClCH_2CH_2Cl$

2 CH_3CH_2Br

3 CH_3CH_2I

[W'04 Q38]

4 Fabrics for use in aircraft seating are treated with a coating containing a halogenoalkane.

Why is this coating used?

1 The treated fabric burns less easily, improving safety.

2 The treated fabric forms hydrogen bonds to water more readily, so it is easier to wash.

3 The halogenoalkane undergoes addition polymerisation, stiffening the fabric.

[S'13 P13 Q38]

5 For the reaction

$$(CH_3)_3SiCl + C_2H_5O^- \rightarrow (CH_3)_3SiOC_2H_5 + Cl^-$$

which statements are likely to be true?

1 It involves nucleophilic attack by $C_2H_5O^-$.

2 Cl^- is displaced by $C_2H_5O^-$.

3 The oxygen-carbon bond is not broken.

[W'05 Q38]

6 Which are properties of fluoroalkanes?

1 They are less reactive than the corresponding chloroalkanes.

2 They are non-flammable.

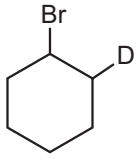
3 The C-F bond is stronger than a C-Cl bond.

[S'13 P12 Q37]

7 Deuterium, D, is the $^{2}_{1}H$ isotope of hydrogen. DBr has the same chemical properties as HBr.

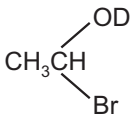
Which compounds could be made by the reaction of DBr with another compound in a single reaction?

1



2 $CHBr_2CHDBr$

3



[S'06 Q38]

8 The chlorine oxide free radical, $ClO^{\bullet}$, is formed during the depletion of the ozone layer by chlorofluoroalkanes (CFCs).

$$Cl^{\bullet} + O_3 \rightarrow ClO^{\bullet} + O_2$$

Which features are present in the chlorine oxide free radical?

1 an odd number of electrons

2 a single covalent bond

3 a dative covalent bond from oxygen to chlorine

[W'06 Q31]

9 What types of reaction are undergone by 2-bromopropane?

1 elimination

2 free radical substitution

3 nucleophilic substitution

[S'07 Q38]

10 Which statements are true for an S_N2 reaction?

1 One bond is broken as another bond is formed.

2 The formation of a transition state involves the collision of two molecules or ions.

3 A carbon atom in the transition state is bonded, either fully or partially, to five other atoms.

[W'09 P12 Q36]

11 The chlorine free radical takes part in the destruction of the ozone layer.

Which statements about this free radical are correct?

1 It is formed by the heterolytic fission of the covalent bond in a chlorine-containing molecule.

2 It has a single unpaired electron.

3 It has the same electron arrangement as a chlorine atom.

[W'09 P12 Q37]

12 Which reactions are examples of nucleophilic substitution?

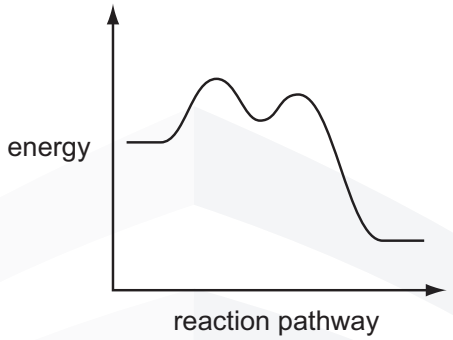
1 $CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$

2 $CH_3I + H_2O \xrightarrow{H^+} CH_3OH + HI$

3 $CH_3CH_2CH_2Cl + NH_3 \rightarrow CH_3CH_2CH_2NH_2 + HCl$

[S'10 P11 Q39]

13 A reaction pathway diagram is shown.



Which reactions would have such a profile?

1 $(CH_3)_3CBr + NaOH \rightarrow (CH_3)_3COH + NaBr$

2 $CH_3CH_2Br + NaOH \rightarrow CH_3CH_2OH + NaBr$

3 $(CH_3)_3CCH_2CH_2Cl + 2NH_3 \rightarrow (CH_3)_3CCH_2CH_2NH_2 + NH_4Cl$

[W'10 P12 Q40]

14 Bromoethane undergoes all of the conversions shown.

Which conversions are examples of nucleophilic substitution?

1 $C_2H_5Br \rightarrow C_2H_5CN$

2 $C_2H_5Br \rightarrow C_2H_5OH$

3 $C_2H_5Br \rightarrow C_2H_5NH_2$

[S'11 P11 Q39]

15 **X** is an organic compound. **X** gives a precipitate with aqueous silver nitrate. Some or all of this precipitate remains undissolved when an excess of dilute aqueous ammonia is added.

What could be the identity of **X**?

1 2-chlorobutane

2 2-bromobutane

3 iodomethane

[W'11 P13 Q37]

16 **Y** is an organic compound. **Y** gives a precipitate with aqueous silver nitrate. All of this precipitate dissolves when concentrated aqueous ammonia is added.

What is a possible identity for **Y**?

1 1-bromopropane

2 chloroethane

3 2-iodo-2-methylpropane

[W'11 P12 Q38]

17 How can a good yield of ethylamine be made using bromoethane as starting material?

1 by heating bromoethane with an excess of ammonia gas in a sealed tube

2 by adding dilute aqueous ammonia to bromoethane at room temperature

3 by heating bromoethane under reflux with aqueous ammonium chloride

[S'12 P13 Q39]

18 Chloroethane can be formed from bromoethane in two steps.

$$C_2H_5Br \xrightarrow{\text{step X}} C_2H_5OH \xrightarrow{\text{step Y}} C_2H_5Cl$$

Which statements about these steps are correct?

1 Hot aqueous sodium hydroxide is the reagent in step X.

2 $SOCl_2$ is the reagent in step Y.

3 Step X is a substitution reaction.

[W'12 P13 Q37]

19 Free-radicals play an important part in reactions involving the destruction of the ozone layer and the substitution of alkanes by chlorine.

Some free-radicals contain two unpaired electrons. Such species are called diradicals.

Which species are diradicals?

1 O

2 Cl

3 CH_3

[S'13 P11 Q31]

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

1 $CBrF_3$

2 $CH_3(CH_2)_5CH_2Br$

3 HCl

[W'08 Q38]

21 The organic compound **X** gives a precipitate when warmed with aqueous silver nitrate. This precipitate dissolves when concentrated aqueous ammonia is added.

What is a possible identity for **X**?

1 1-bromopropane

2 2-chlorobutane

3 2-iodo,2-methylpropane

[W'13 P11 Q37]

HALOGENOALKANES WS 4

SECTION A

1 Chlorofluorocarbons, CFCs, are small alkane molecules in which some of the hydrogen atoms have been replaced by atoms of chlorine and fluorine.

(a) (i) State **two** uses of CFCs.

.....

.....

(ii) What property of CFCs causes them to be useful?

.....

[2]

(b) A typical CFC is $CHF_2CHCl F$.

(i) Which covalent bond in this CFC is the weakest?

.....

(ii) Why does this CFC present an environmental concern?

.....

.....

.....

.....

[3]

(c) Another CFC contains the following elements by mass. The value of its M_r is 135.

C, 17.8%; H, 1.5%; Cl, 52.6%; F, 28.1%

Use these data to determine the molecular formula of the CFC.

[3]

[Total : 8]

[S'02 Q6]

2



$CH_3CH_2CH_2CH_2Br$ — 1-bromobutane

2-bromo-2-methylpropane

(a) 1-Bromobutane reacts with **aqueous** sodium hydroxide to form butan-1-ol.

(i) Give a balanced equation for this reaction.

.....

(ii) Name the type of reaction. .....

(iii) Describe the mechanism of this reaction.

[5]

(b) 1-Bromobutane and 2-bromo-2-methylpropane both react with an **ethanolic** (**alcoholic**) solution of sodium hydroxide to form alkenes.

(i) Name the type of reaction. .....

(ii) Identify, by means of the structural formula, the alkene formed from

I 1-bromobutane,

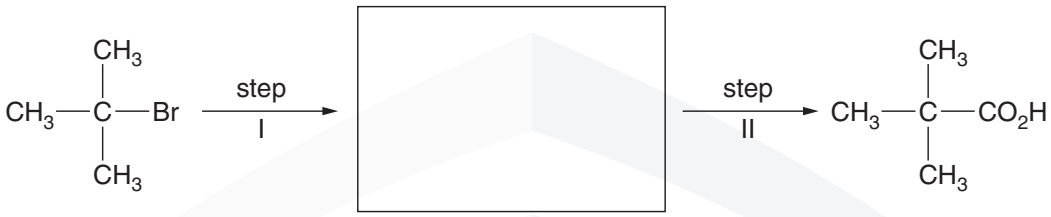
II 2-bromo-2-methylpropane.

(iii) Hot, concentrated manganate(VII) ions break the double bond in alkenes. Each of the two alkenes in **(b)(ii)** gives CO_2 and H_2O from the terminal group, but the rest of the molecule remains as an organic oxidation product. Suggest the formula of each of these products.

from I .....

from II .....
[5]

(c) Complete the reaction sequence giving the intermediate, the reagents and the conditions for the synthesis of 2,2-dimethylpropanoic acid.



Step I: reagent .....

conditions .....

Step II: reagent .....

conditions .....
[3]

[Total : 13]

[W'03 Q5]

3 A number of organic compounds containing the halogens fluorine and/or chlorine are commercially important because of their chemical inertness.

(a) Name **three** such compounds, and for each state a use where its inertness is important.

(i) .....

.....

(ii) .....

.....

(iii) .....

.....[6]

(b) Under certain conditions in the upper atmosphere, some of these compounds break down.

(i) Explain how this happens and what effects this has, in chemical terms.

.....

.....

.....

.....

(ii) Suggest alternative compounds, which do not contain a halogen, for **two** of the uses you have given in **(a)**.

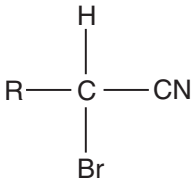
.....

.....[5]

[Total : 11]

[S'04 Q5]

4 Compound **G**, in which R– represents the rest of the molecule, was made for use as a tear gas in World War 2.



compound **G**

Compound **G** was made by the following sequence of reactions.

$$R\text{–}CH_3 \xrightarrow{\text{stage I}} R\text{–}CH_2Cl \xrightarrow{\text{stage II}} R\text{–}CH_2CN \xrightarrow{\text{stage III}} R\text{–}CHBrCN$$

(a) (i) For stage I **and** for stage II, state the reagent(s) and condition(s) used to carry out **each** change.

stage I reagent(s) .....

condition(s) .....

stage II reagent(s) .....

condition(s) .....

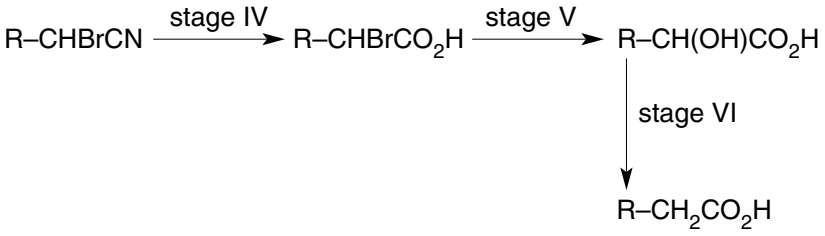
(ii) Suggest the reagent(s) and condition(s) necessary to carry out stage III.

reagent(s) .....

condition(s) .....

[6]

Compound **G** was not actually used in World War 2 and stocks of it had to be destroyed safely. The following sequence of reactions was used in this process.



(b) For stage IV **and** for stage V state the reagent(s) and condition(s) necessary to bring about **each** reaction.

stage IV reagent(s) .....

condition(s) .....

stage V reagent(s) .....

condition(s) ..... [4]

(c) The full sequence of stages I to VI involves some compounds which contain chiral centres.

(i) Explain what is meant by the term *chiral centre*.

.....

.....

(ii) Draw displayed formulae for the isomers of **one** compound in the full sequence of stages I to VI which you consider to be chiral.

[3]

[Total: 13]

[S'05 Q4]

5 Many organic reactions are substitution reactions in which the number of carbon atoms in the organic compound is unchanged.

(a) What is meant by the term *substitution reaction*?

.....

.....[1]

(b) One example of a substitution reaction is the formation of an alcohol from a halogenoalkane.

(i) Write a balanced equation for the formation of ethanol from bromoethane.

.....

(ii) State the conditions for this reaction.

.....[2]

(c) In a few organic reactions, the product contains **one** more carbon atom than the starting material.

(i) Write the equation for a reaction in which the organic compound bromoethane, which contains **two** carbon atoms, is converted into an organic compound which contains **three** carbon atoms.

.....

(ii) State the conditions for this reaction.

.....[2]

(d) Ethanol may be converted into propanoic acid in a three-stage process which uses ethanol as the only organic compound.

$$C_2H_5OH \xrightarrow{\text{step I}} \mathbf{K} \xrightarrow{\text{step II}} \mathbf{L} \xrightarrow{\text{step III}} C_2H_5CO_2H$$

(i) Give the structural formulae of the intermediate compounds **K** and **L**.

K .....

L .....

(ii) State the reagent(s) used and give the essential condition(s) for step I and for step III.

step I

reagent(s) .....

condition(s) .....

step III

reagent(s) .....

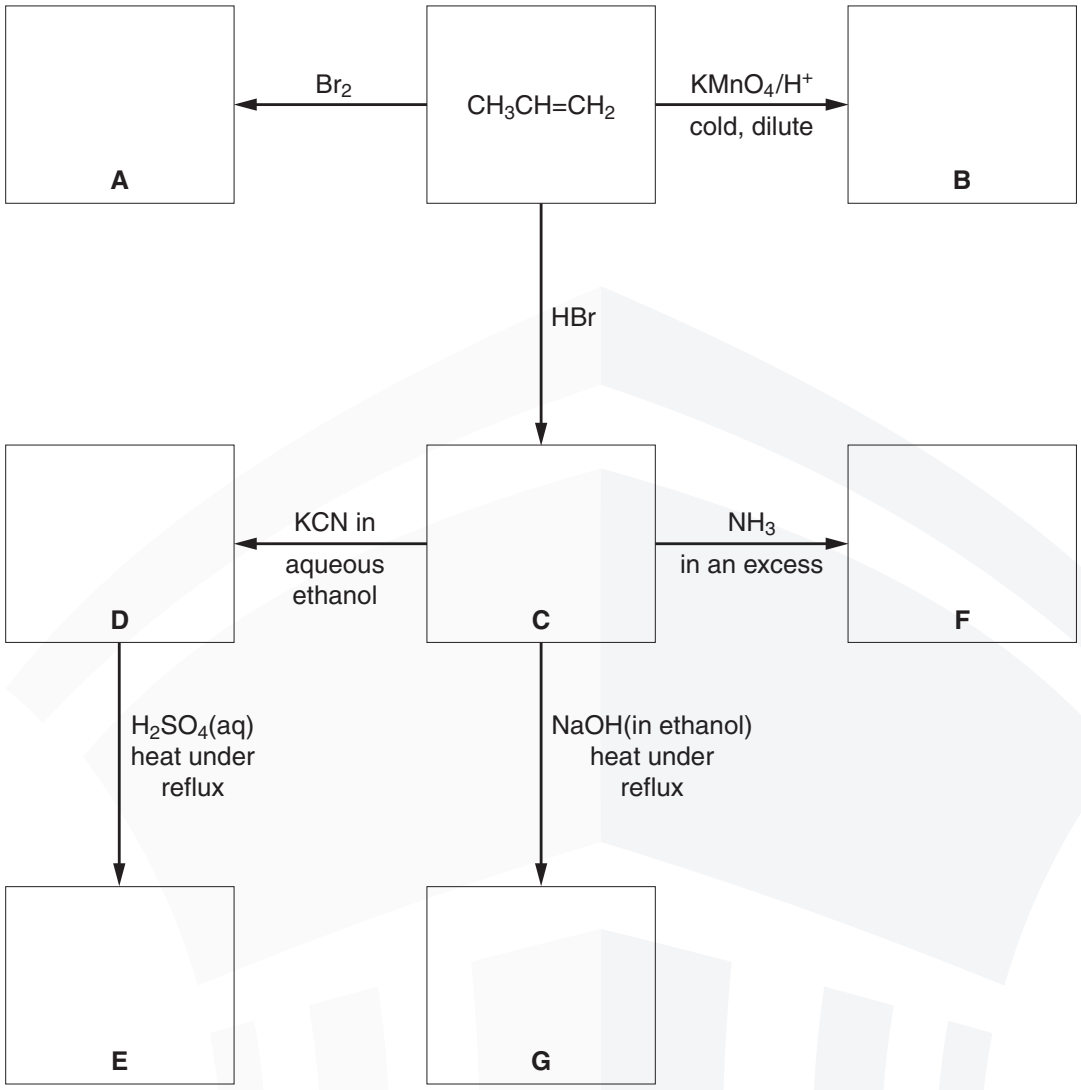
condition(s).....

[6]

[Total: 11]

[S'06 Q5]

6 **(a)** Complete the following reaction scheme which starts with propene.
In **each empty** box, write the **structural formula** of the organic compound that would be formed.



[7]

(b) Under suitable conditions, compound **E** will react with compound **B**.

(i) What functional group is produced in this reaction?

.....

(ii) How is this reaction carried out in a school or college laboratory?

.....

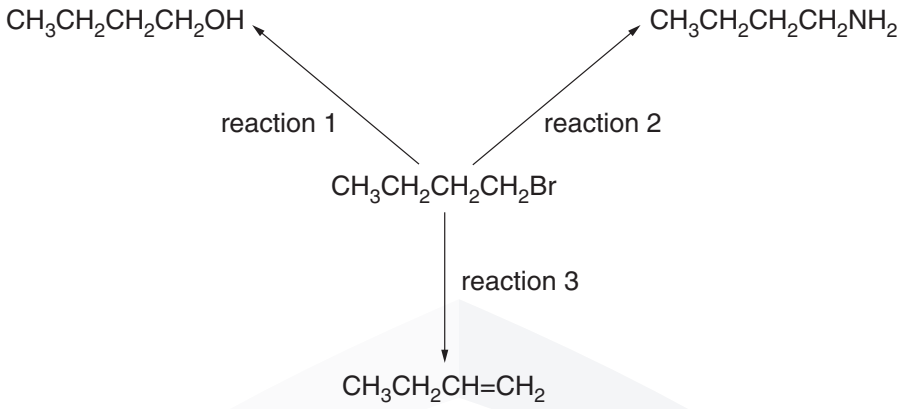
.....

[3]

[S'10 P21 Q4]

7 Halogenoalkanes have many chemical uses, particularly as intermediates in organic reactions.

Three reactions of 1-bromobutane, $CH_3CH_2CH_2CH_2Br$, are shown below.



(a) For **each** reaction, state the reagent and solvent used.

reaction 1 reagent .....

solvent .....

reaction 2 reagent .....

solvent .....

reaction 3 reagent .....

solvent ..... [6]

(b) When 1-iodobutane, $CH_3CH_2CH_2CH_2I$, is reacted under the same conditions as those used in reaction 1, butan-1-ol is formed.

What difference, if any, would there be in the rate of this reaction compared to the reaction of 1-bromobutane?

Use appropriate data from the *Data Booklet* to explain your answer.

.....

.....

.....

.....[3]

Dichlorodifluoromethane, CCl_2F_2, is an example of a chlorofluorocarbon (CFC) that was formerly used as an aerosol propellant. In September 2007, at the Montreal summit, approximately 200 countries agreed to phase out the use of CFCs by 2020.

(c) State two properties of CFCs that made them suitable as aerosol propellants.

1. .....

2. ..... [2]

(d) When CFCs are present in the upper atmosphere, homolytic fission takes place in the presence of ultraviolet light.

(i) What is meant by the term *homolytic fission*?

.....

.....

(ii) Suggest an equation for the homolytic fission of CCl_2F_2.

.....[2]

(e) The most common replacements for CFCs as aerosol propellants are hydrocarbons such as propane and butane.

Suggest **one** disadvantage of these compounds as aerosol propellants.

.....[1]

[W'10 P21 Q4]

8 Although few halogenoalkanes exist naturally, such compounds are important as intermediates in organic reactions and as solvents.

The bromoalkane **B** has the following composition by mass: C, 29.3%; H, 5.7%; Br, 65.0%. The relative molecular mass of **B** is 123.

(a) Calculate the molecular formula of **B**.

[3]

Halogenoalkanes such as bromoethane, C_2H_5Br, have two different reactions with sodium hydroxide, NaOH, depending on the conditions used.

(b) (i) When hot aqueous NaOH is used, the C_2H_5Br is hydrolysed to ethanol, C_2H_5OH.

Describe the mechanism of this reaction. In your answer, show any relevant charges, dipoles, lone pairs of electrons and movement of electron pairs by curly arrows.

(ii) What will be formed when C_2H_5Br is reacted with NaOH under different conditions?

.....

(iii) What are the conditions used?

.....

(iv) What type of reaction is this?

.....[7]

When 1,4-dichlorobutane, $Cl CH_2CH_2CH_2CH_2Cl$, is reacted with NaOH, two different reactions can occur, depending on the conditions used.

(c) (i) Draw the **displayed** formula of the product formed when 1,4-dichlorobutane is reacted with hot aqueous NaOH as in **(b)(i)**.

(ii) Draw the **skeletal** formula of the product formed when 1,4-dichlorobutane is reacted with NaOH in the way you have described in **(b)(ii)** and **(b)(iii)**.

[2]

[W'10 P23 Q4]

9 Halogenoalkanes have been widely used as aerosol propellants, refrigerants and solvents for many years.

Fluoroethane, CH_3CH_2F, has been used as a refrigerant. It may be made by reacting ethene with hydrogen fluoride.

You are to calculate a value for the C–F bond energy in fluoroethane.

(a) Use relevant bond energies from the *Data Booklet*, and the equation below to calculate a value for the bond energy of the C–F bond.

$$CH_2 = CH_2(g) \quad + \quad HF(g) \quad \rightarrow \quad CH_3CH_2F(g) \qquad \Delta H^{\ominus} = -73\,kJ\,mol^{-1}$$

C–F bond energy = ... $kJ\,mol^{-1}$ [4]

(b) Another halogenoalkane which was used as a refrigerant, and also as an aerosol propellant, is dichlorodifluoromethane, CCl_2F_2.

State **two** reasons why compounds such as CH_3CH_2F and CCl_2F_2 have been used as aerosol propellants and refrigerants.

.....

..... [2]

CCl_2F_2 is one of many chlorofluorocarbon compounds responsible for damage to the ozone layer in the stratosphere.

(c) By using relevant data from the *Data Booklet*, and your answer to **(a)** suggest why CCl_2F_2 is responsible for damage to the ozone layer in the stratosphere whereas CH_3CH_2F is not.

.....

.....

..... [2]

Both CH_3CH_2F and CCl_2F_2 are greenhouse gases.

The 'enhanced greenhouse effect' is of great concern to the international community.

(d) (i) What is meant by the term *enhanced greenhouse effect*?

.....

.....

.....

(ii) Water vapour is the most abundant greenhouse gas.

What is the second most abundant greenhouse gas?

..... [3]

A greenhouse gas which is present in very small amounts in the atmosphere is sulfur hexafluoride, SF_6, which is used in high voltage electrical switchgear.

(e) What shape is the SF_6 molecule?

..... [1]

[S'11 P22 Q2]

DATA BOOKLET

1 Important values, constants and standards

molar gas constant	$R = 8.31\ \text{J K}^{-1}\ \text{mol}^{-1}$
the Faraday constant	$F = 9.65 \times 10^{4}\ \text{C mol}^{-1}$
the Avogadro constant	$L = 6.02 \times 10^{23}\ \text{mol}^{-1}$
the Planck constant	$h = 6.63 \times 10^{-34}\ \text{J s}$
speed of light in a vacuum	$c = 3.00 \times 10^{8}\ \text{m s}^{-1}$
rest mass of proton, $^{1}_{1}\text{H}$	$m_p = 1.67 \times 10^{-27}\ \text{kg}$
rest mass of neutron, $^{1}_{0}\text{n}$	$m_n = 1.67 \times 10^{-27}\ \text{kg}$
rest mass of electron, $^{0}_{-1}\text{e}$	$m_e = 9.11 \times 10^{-31}\ \text{kg}$
electronic charge	$e = -1.60 \times 10^{-19}\ \text{C}$
molar volume of gas	$V_m = 22.4\ \text{dm}^3\ \text{mol}^{-1}$ at s.t.p $V_m = 24.0\ \text{dm}^3\ \text{mol}^{-1}$ under room conditions (where s.t.p. is expressed as 101 kPa, approximately, and 273 K (0 °C))
ionic product of water	$K_w = 1.00 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}$ (at 298 K (25 °C))
specific heat capacity of water	= 4.18 kJ $\text{kg}^{-1}\ \text{K}^{-1}$ (= 4.18 J $\text{g}^{-1}\ \text{K}^{-1}$)

2 Ionisation energies (1st, 2nd, 3rd and 4th) of selected elements, in kJ mol^{-1}

	Proton number	First	Second	Third	Fourth
H	1	1310	–	–	–
He	2	2370	5250	–	–
Li	3	519	7300	11800	–
Be	4	900	1760	14800	21000
B	5	799	2420	3660	25000
C	6	1090	2350	4610	6220
N	7	1400	2860	4590	7480
O	8	1310	3390	5320	7450
F	9	1680	3370	6040	8410
Ne	10	2080	3950	6150	9290
Na	11	494	4560	6940	9540
Mg	12	736	1450	7740	10500
Al	13	577	1820	2740	11600
Si	14	786	1580	3230	4360
P	15	1060	1900	2920	4960
S	16	1000	2260	3390	4540
Cl	17	1260	2300	3850	5150
Ar	18	1520	2660	3950	5770
K	19	418	3070	4600	5860
Ca	20	590	1150	4940	6480
Sc	21	632	1240	2390	7110
Ti	22	661	1310	2720	4170
V	23	648	1370	2870	4600
Cr	24	653	1590	2990	4770
Mn	25	716	1510	3250	5190
Fe	26	762	1560	2960	5400
Co	27	757	1640	3230	5100
Ni	28	736	1750	3390	5400
Cu	29	745	1960	3350	5690
Zn	30	908	1730	3828	5980
Ga	31	577	1980	2960	6190

	Proton number	First	Second	Third	Fourth
Br	35	1140	2080	3460	4850
Rb	37	403	2632	3900	5080
Sr	38	548	1060	4120	5440
Ag	47	731	2074	3361	–
I	53	1010	1840	2040	4030
Cs	55	376	2420	3300	–
Ba	56	502	966	3390	–

3 Bond energies

3(a) Bond energies in diatomic molecules (these are exact values)

Homonuclear

Bond	Energy/kJ mol^{-1}
H–H	436
D–D	442
N≡N	944
O=O	496
P≡P	485
S=S	425
F–F	158
Cl–Cl	242
Br–Br	193
I–I	151

Heteronuclear

Bond	Energy/kJ mol^{-1}
H–F	562
H–Cl	431
H–Br	366
H–I	299
C≡O	1077

3(b) Bond energies in polyatomic molecules (these are average values)

Homonuclear

Bond	Energy/kJ mol^{-1}
C–C	350
C=C	610
C≡C	840
C⋯⋯C (benzene)	520
N–N	160
N=N	410
O–O	150
Si–Si	222
P–P	200
S–S	264

Heteronuclear

Bond	Energy/kJ mol^{-1}
C–H	410
C–Cl	340
C–Br	280
C–I	240
C–N	305
C=N	610
C≡N	890
C–O	360
C=O	740
C=O in CO_2	805
N–H	390
N–Cl	310
O–H	460
Si–Cl	359
Si–H	320
Si–O (in SiO_2(s))	460
Si=O (in SiO_2(g))	640
P–H	320
P–Cl	330
P–O	340
P=O	540
S–H	347
S–Cl	250
S–O	360
S=O	500

4 Standard electrode potential and redox potentials, $E^{\ominus}$ at 298 K (25 °C)

For ease of reference, two tables are given:

(a) an extended list in alphabetical order

(b) a shorter list in decreasing order of magnitude, i.e. a redox series.

(a) $E^{\ominus}$ in alphabetical order

Electrode reaction	$E^{\ominus}/V$
$Ag^+ + e^- \rightleftharpoons Ag$	+0.80
$Al^{3+} + 3e^- \rightleftharpoons Al$	–1.66
$Ba^{2+} + 2e^- \rightleftharpoons Ba$	–2.90
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.07
$Ca^{2+} + 2e^- \rightleftharpoons Ca$	–2.87
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$2HOCl + 2H^+ + 2e^- \rightleftharpoons Cl_2 + 2H_2O$	+1.64
$ClO^- + H_2O + 2e^- \rightleftharpoons Cl^- + 2OH^-$	+0.89
$Co^{2+} + 2e^- \rightleftharpoons Co$	–0.28
$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	+1.82
$[Co(NH_3)_6]^{2+} + 2e^- \rightleftharpoons Co + 6NH_3$	–0.43
$Cr^{2+} + 2e^- \rightleftharpoons Cr$	–0.91
$Cr^{3+} + 3e^- \rightleftharpoons Cr$	–0.74
$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$	–0.41
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33
$Cu^+ + e^- \rightleftharpoons Cu$	+0.52
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
$Cu^{2+} + e^- \rightleftharpoons Cu^+$	+0.15
$[Cu(NH_3)_4]^{2+} + 2e^- \rightleftharpoons Cu + 4NH_3$	–0.05
$F_2 + 2e^- \rightleftharpoons 2F^-$	+2.87
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	–0.44
$Fe^{3+} + 3e^- \rightleftharpoons Fe$	–0.04
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77
$[Fe(CN)_6]^{3-} + e^- \rightleftharpoons [Fe(CN)_6]^{4-}$	+0.36
$Fe(OH)_3 + e^- \rightleftharpoons Fe(OH)_2 + OH^-$	–0.56
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	–0.83
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54

Electrode reaction	$E^{\ominus}$ / V
$K^+ + e^- \rightleftharpoons K$	–2.92
$Li^+ + e^- \rightleftharpoons Li$	–3.04
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	–2.38
$Mn^{2+} + 2e^- \rightleftharpoons Mn$	–1.18
$Mn^{3+} + e^- \rightleftharpoons Mn^{2+}$	+1.49
$MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O$	+1.23
$MnO_4^- + e^- \rightleftharpoons MnO_4^{2-}$	+0.56
$MnO_4^- + 4H^+ + 3e^- \rightleftharpoons MnO_2 + 2H_2O$	+1.67
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+1.52
$NO_3^- + 2H^+ + e^- \rightleftharpoons NO_2 + H_2O$	+0.81
$NO_3^- + 3H^+ + 2e^- \rightleftharpoons HNO_2 + H_2O$	+0.94
$NO_3^- + 10H^+ + 8e^- \rightleftharpoons NH_4^+ + 3H_2O$	+0.87
$Na^+ + e^- \rightleftharpoons Na$	–2.71
$Ni^{2+} + 2e^- \rightleftharpoons Ni$	–0.25
$[Ni(NH_3)_6]^{2+} + 2e^- \rightleftharpoons Ni + 6NH_3$	–0.51
$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	+1.77
$HO_2^- + H_2O + 2e^- \rightleftharpoons 3OH^-$	+0.88
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23
$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$	+0.40
$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	+0.68
$O_2 + H_2O + 2e^- \rightleftharpoons HO_2^- + OH^-$	–0.08
$Pb^{2+} + 2e^- \rightleftharpoons Pb$	–0.13
$Pb^{4+} + 2e^- \rightleftharpoons Pb^{2+}$	+1.69
$PbO_2 + 4H^+ + 2e^- \rightleftharpoons Pb^{2+} + 2H_2O$	+1.47
$SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons SO_2 + 2H_2O$	+0.17
$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$	+2.01
$S_4O_6^{2-} + 2e^- \rightleftharpoons 2S_2O_3^{2-}$	+0.09
$Sn^{2+} + 2e^- \rightleftharpoons Sn$	–0.14
$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$	+0.15
$V^{2+} + 2e^- \rightleftharpoons V$	–1.20
$V^{3+} + e^- \rightleftharpoons V^{2+}$	–0.26
$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O$	+0.34
$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$	+1.00
$VO_3^- + 4H^+ + e^- \rightleftharpoons VO^{2+} + 2H_2O$	+1.00
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	–0.76

(b) $E^{\ominus}$ in decreasing order of oxidising power

(a selection only – see also the extended alphabetical list on the previous pages)

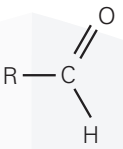
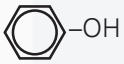
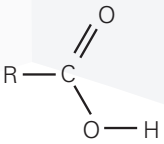
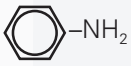
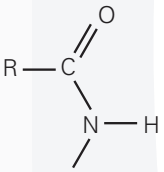
Electrode reaction	$E^{\ominus}/V$
$F_2 + 2e^- \rightleftharpoons 2F^-$	+2.87
$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$	+2.01
$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	+1.77
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+1.52
$PbO_2 + 4H^+ + 2e^- \rightleftharpoons Pb^{2+} + 2H_2O$	+1.47
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.07
$ClO^- + H_2O + 2e^- \rightleftharpoons Cl^- + 2OH^-$	+0.89
$NO_3^- + 10H^+ + 8e^- \rightleftharpoons NH_4^+ + 3H_2O$	+0.87
$NO_3^- + 2H^+ + e^- \rightleftharpoons NO_2 + H_2O$	+0.81
$Ag^+ + e^- \rightleftharpoons Ag$	+0.80
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54
$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$	+0.40
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
$SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons SO_2 + 2H_2O$	+0.17
$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$	+0.15
$S_4O_6^{2-} + 2e^- \rightleftharpoons 2S_2O_3^{2-}$	+0.09
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$Pb^{2+} + 2e^- \rightleftharpoons Pb$	–0.13
$Sn^{2+} + 2e^- \rightleftharpoons Sn$	–0.14
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	–0.44
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	–0.76
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	–0.83
$V^{2+} + 2e^- \rightleftharpoons V$	–1.20
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	–2.38
$Ca^{2+} + 2e^- \rightleftharpoons Ca$	–2.87
$K^+ + e^- \rightleftharpoons K$	–2.92

5 Atomic and ionic radii

(a) Period 1	atomic/nm		ionic/nm			
single covalent	H	0.037	H^+	0.208		
van der Waals	He	0.140				
(b) Period 2						
metallic	Li	0.152	Li^+	0.060		
	Be	0.112	Be^{2+}	0.031		
single covalent	B	0.080	B^{3+}	0.020		
	C	0.077	C^{4+}	0.015	C^{4-}	0.260
	N	0.074			N^{3-}	0.171
	O	0.073			O^{2-}	0.140
	F	0.072			F^-	0.136
van der Waals	Ne	0.160				
(c) Period 3						
metallic	Na	0.186	Na^+	0.095		
	Mg	0.160	Mg^{2+}	0.065		
	Al	0.143	Al^{3+}	0.050		
single covalent	Si	0.117	Si^{4+}	0.041		
	P	0.110			P^{3-}	0.212
	S	0.104			S^{2-}	0.184
	Cl	0.099			Cl^-	0.181
van der Waals	Ar	0.190				
(d) Group 2						
metallic	Be	0.112	Be^{2+}	0.031		
	Mg	0.160	Mg^{2+}	0.065		
	Ca	0.197	Ca^{2+}	0.099		
	Sr	0.215	Sr^{2+}	0.113		
	Ba	0.217	Ba^{2+}	0.135		
	Ra	0.220	Ra^{2+}	0.140		

(e) Group 14	atomic/nm		ionic/nm			
single covalent	C	0.077				
	Si	0.117	Si^{4+}	0.041		
	Ge	0.122	Ge^{2+}	0.093		
metallic	Sn	0.162	Sn^{2+}	0.112		
	Pb	0.175	Pb^{2+}	0.120		
(f) Group 17						
single covalent	F	0.072	F^-	0.136		
	Cl	0.099	Cl^-	0.181		
	Br	0.114	Br^-	0.195		
	I	0.133	I^-	0.216		
	At	0.140				
(g) First row transition elements						
metallic	Sc	0.164			Sc^{3+}	0.081
	Ti	0.146	Ti^{2+}	0.090	Ti^{3+}	0.067
	V	0.135	V^{2+}	0.079	V^{3+}	0.064
	Cr	0.129	Cr^{2+}	0.073	Cr^{3+}	0.062
	Mn	0.132	Mn^{2+}	0.067	Mn^{3+}	0.062
	Fe	0.126	Fe^{2+}	0.061	Fe^{3+}	0.055
	Co	0.125	Co^{2+}	0.078	Co^{3+}	0.053
	Ni	0.124	Ni^{2+}	0.070	Ni^{3+}	0.056
	Cu	0.128	Cu^{2+}	0.073		
	Zn	0.135	Zn^{2+}	0.075		

6 Typical proton (^{1}H) chemical shift values (δ) relative to TMS = 0

Type of proton	Environment of proton	Example structures	Chemical shift range (δ)
C–H	alkane	$-CH_3$, $-CH_2-$, >CH–	0.9–1.7
	alkyl next to C=O	$CH_3-C=O$, $-CH_2-C=O$, >CH–C=O	2.2–3.0
	alkyl next to aromatic ring	CH_3-Ar, $-CH_2-Ar$, > CH–Ar	2.3–3.0
	alkyl next to electronegative atom	CH_3-O, $-CH_2-O$, $-CH_2-Cl$, >CH–Br	3.2–4.0
	attached to alkyne	≡C–H	1.8–3.1
	attached to alkene	$=CH_2$, =CH–	4.5–6.0
	attached to aromatic ring		6.0–9.0
	aldehyde		9.3–10.5
O–H (see note below)	alcohol	RO–H	0.5–6.0
	phenol		4.5–7.0
	carboxylic acid		9.0–13.0
N–H (see note below)	alkyl amine	R–NH–	1.0–5.0
	aryl amine		3.0–6.0
	amide		5.0–12.0

Note: δ values for –O–H and –N–H protons can vary depending on solvent and concentration.

7 Typical carbon (^{13}C) chemical shift values (δ) relative to TMS = 0

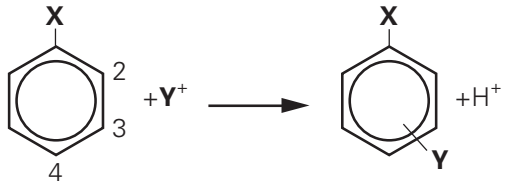
Hybridisation of the carbon atom	Environment of carbon atom	Example structures	Chemical shift range (δ)
sp^3	alkyl	**C**H_3–, **C**H_2–, –**C**H<	0–50
sp^3	next to alkene/arene	–**C**H_2–C=C, –**C**H_2– 	10–40
sp^3	next to carbonyl/carboxyl	–**C**H_2–COR, –**C**H_2–CO_2R	25–50
sp^3	next to nitrogen	–**C**H_2–NH_2, –**C**H_2–NR_2, –**C**H_2–NHCO	30–65
sp^3	next to chlorine (–CH_2–Br and –CH_2–I are in the same range as alkyl)	–**C**H_2–C*l*	30–60
sp^3	next to oxygen	–**C**H_2–OH, –**C**H_2–O–CO–	50–70
sp^2	alkene or arene	>**C**=**C**<, 	110–160
sp^2	carboxyl	R–**C**O_2H, R–**C**O_2R	160–185
sp^2	carbonyl	R–**C**HO, R–**C**O–R	190–220
sp	alkyne	R–**C**≡**C**–	65–85
sp	nitrile	R–**C**≡N	100–125

8 Characteristic infra-red absorption frequencies for some selected bonds

Bond	Functional groups containing the bond	Absorption range (in wavenumbers)/cm^{-1}	Appearance of peak (*s = strong, w = weak)*
C–O	alcohols, ethers, esters	1040–1300	***s***
C=C	aromatic compounds, alkenes	1500–1680	***w*** unless conjugated
C=O	amides ketones and aldehydes esters	1640–1690 1670–1740 1710–1750	***s*** ***s*** ***s***
C≡C	alkynes	2150–2250	***w*** unless conjugated
C≡N	nitriles	2200–2250	***w***
C–H	alkanes, CH_2–H alkenes/arenes, =C–H	2850–2950 3000–3100	***s*** ***w***
N–H	amines, amides	3300–3500	***w***
O–H	carboxylic acids, RCO_2–H H-bonded alcohol, RO–H free alcohol, RO–H	2500–3000 3200–3600 3580–3650	***s*** and very broad ***s*** ***s*** and sharp

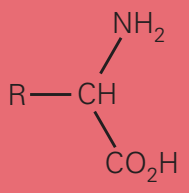
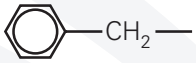
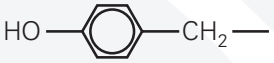
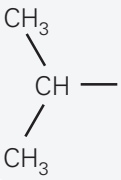
9 The orientating effect of groups in aromatic substitution reactions.

The position of the incoming group, **Y**, is determined by the nature of the group, **X**, already bonded to the ring, and not by the nature of the incoming group **Y**.



X– groups that direct the incoming Y group to the 2– or 4– positions	X– groups that direct the incoming Y group to the 3– position
$-NH_2$, –NHR or $-NR_2$	$-NO_2$
–OH or –OR	$-NH_3$
–NHCOR	–CN
$-CH_2$, –alkyl	–CHO, –COR
$-Cl$	$-CO_2H$, $-CO_2R$

10 Names, structures and abbreviations of some amino acids

Name	3-letter abbreviation	1-letter symbol	structure of side chain R– in 
alanine	Ala	A	CH_3–
aspartic acid	Asp	D	HO_2CCH_2–
cysteine	Cys	C	$HSCH_2$–
glutamic acid	Glu	E	$HO_2CCH_2CH_2$–
glycine	Gly	G	H–
lysine	Lys	K	$H_2NCH_2CH_2CH_2CH_2$–
phenylalanine	Phe	F	
serine	Ser	S	$HOCH_2$–
tyrosine	Tyr	Y	
valine	Val	V	

Group																	
1	2											13	14	15	16	17	18
							1 H hydrogen 1.0										2 He helium 4.0
3 Li lithium 6.9	4 Be beryllium 9.0		Key atomic number atomic symbol name relative atomic mass									5 B boron 10.8	6 C carbon 12.0	7 N nitrogen 14.0	8 O oxygen 16.0	9 F fluorine 19.0	10 Ne neon 20.2
11 Na sodium 23.0	12 Mg magnesium 24.3	3	4	5	6	7	8	9	10	11	12	13 Al aluminium 27.0	14 Si silicon 28.1	15 P phosphorus 31.0	16 S sulfur 32.1	17 Cl chlorine 35.5	18 Ar argon 39.9
19 K potassium 39.1	20 Ca calcium 40.1	21 Sc scandium 45.0	22 Ti titanium 47.9	23 V vanadium 50.9	24 Cr chromium 52.0	25 Mn manganese 54.9	26 Fe iron 55.8	27 Co cobalt 58.9	28 Ni nickel 58.7	29 Cu copper 63.5	30 Zn zinc 65.4	31 Ga gallium 69.7	32 Ge germanium 72.6	33 As arsenic 74.9	34 Se selenium 79.0	35 Br bromine 79.9	36 Kr krypton 83.8
37 Rb rubidium 85.5	38 Sr strontium 87.6	39 Y yttrium 88.9	40 Zr zirconium 91.2	41 Nb niobium 92.9	42 Mo molybdenum 95.9	43 Tc technetium –	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
55 Cs caesium 132.9	56 Ba barium 137.3	57–71 lanthanoids	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.6	81 Tl thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium –	85 At astatine –	86 Rn radon –
87 Fr francium –	88 Ra radium –	89–103 actinoids	104 Rf rutherfordium –	105 Db dubnium –	106 Sg seaborgium –	107 Bh bohrium –	108 Hs hassium –	109 Mt meitnerium –	110 Ds darmstadtium –	111 Rg roentgenium –	112 Cn copernicium –		114 Fl flerovium –		116 Lv livermorium –		

lanthanoids	57 La lanthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.4	61 Pm promethium –	62 Sm samarium 150.4	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.1	71 Lu lutetium 175.0
actinoids	89 Ac actinium –	90 Th thorium 232.0	91 Pa protactinium 231.0	92 U uranium 238.0	93 Np neptunium –	94 Pu plutonium –	95 Am americium –	96 Cm curium –	97 Bk berkelium –	98 Cf californium –	99 Es einsteinium –	100 Fm fermium –	101 Md mendelevium –	102 No nobelium –	103 Lr lawrencium –