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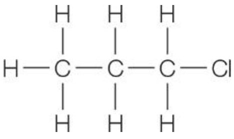
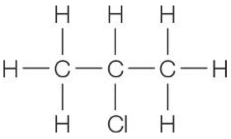
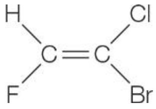
1 a) Two structural isomers with the same functional group [1]; structures of 1-chloropropane and 2-chloropropane. [1]

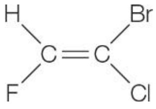

1-chloropropane


2-chloropropane

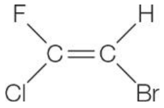
b) Six isomers in total: three structural isomers, each of which have *E*/*Z* forms.

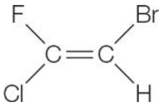
- F and H on the same C atom [2]


Z-1-bromo-1-chloro-2-fluoroethene

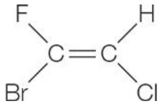

E-1-bromo-1-chloro-2-fluoroethene

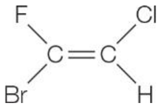
- F and Cl on the same C atom [2]


Z-2-bromo-1-chloro-1-fluoroethene

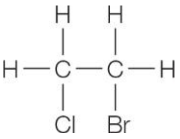

E-2-bromo-1-chloro-1-fluoroethene

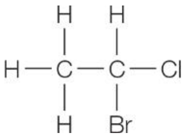
- F and Br on the same C atom [2]


Z-1-bromo-2-chloro-1-fluoroethene

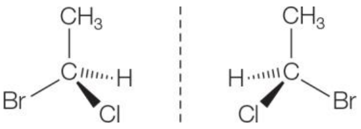

E-1-bromo-2-chloro-1-fluoroethene

c) Structural isomerism (position) and optical isomerism.


1-bromo-2-chloroethane [1]


1-bromo-1-chloroethane [1]

1-Bromo-1-chloroethane exists as a pair of optical isomers:


[1]

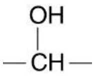
2 a) A chiral centre is typically a carbon atom with four different groups around it [1]; in general a molecule is chiral if it is asymmetric.

b) The mirror-image forms of a chiral molecule cannot be superimposed on one another [1]; they have opposite effects as they rotate the plane of plane-polarised light. [1]

c) Only $CH_3CHOHCOOH$ is chiral and can exist as two optical isomers [1]; the other two compounds both have two hydrogen atoms on the central carbon atom.

d) A racemic mixture contains equal amounts of the two optical isomers [1]; the two isomers rotate the plane of plane-polarised light equally but in opposite directions, so their effects cancel. [1]

e) i) $C_{13}H_{21}O_3N$ [1]

ii) There is one chiral carbon atom:  $\overset{\text{OH}}{\overset{|}{-\text{CH}-}}$ [1]

3 Stereoisomerism involves molecules with the same molecular formula [1]; and the same structural formula [1]; but different three-dimensional shapes [1]; in which their atoms occupy different positions in space. [1]

There are two forms of stereoisomerism.

E/Z (*cis/trans*) isomerism [1]; which occurs principally in alkenes and other compounds with C=C double bonds. [1]

In *E/Z* isomerism, the *Z*-isomer has atoms, attached to the C atoms of the double bond, with higher atomic number [1] on the same side of the double bond. [1]

In the *E*-isomer, atoms attached to the C atoms of the double bond with higher atomic number are on opposite sides of the double bond. [1] An example of *E/Z* isomerism is 1,2-dibromoethene.

Named structures of the *E*- and *Z*-isomers. [2]

Optical isomerism [1] involves non-superimposable mirror images. [1] In most cases, this requires the molecules to possess a C atom with four different atoms or groups attached to it. [1]

These mirror images are labelled (+) and (–) forms. [1]

The (+) form rotates plane-polarised light clockwise [1] and the (–) form rotates plane-polarised light anticlockwise. [1]

A named example of optical isomerism [1]; e.g. alanine or bromochlorofluoromethane.

Diagram showing structures of the optical isomers of the example suggested as mirror images. [1]

(*Any 15 of these or other legitimate points*)

4 a) There is a chiral centre in $C_2H_5CHBrCH_3$. This means that the molecule is asymmetric and has distinct mirror-image forms. [1]

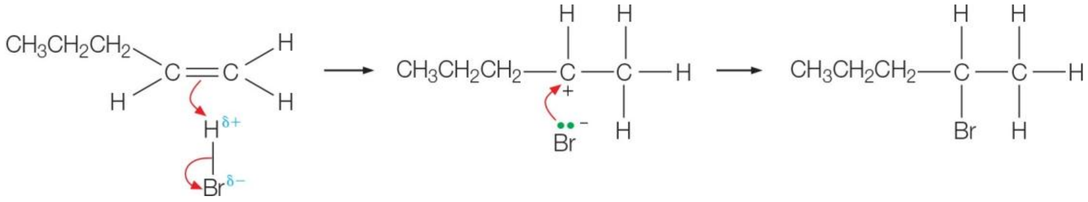
b) At a lower temperature the main mechanism for the hydrolysis is S_N2. [1] The molecule inverts in the one continuous step of this process. [1] So an optically active reactant gives rise to an optically active product. [1]

c) At the higher temperature there is more energy in the collisions between molecules. [1] The energy is sufficient to break the C–Br bond and permit the S_N1 mechanism. [1] The first step of this process gives rise to a planar carbocation intermediate with a positive charge on the central carbon atom. [1] In the second step, hydroxide ions can attack from either side of the plane, giving rise to a roughly equal mixture of the two optical isomers. [1] The result is the optically inactive racemic mixture. [1]

d) $H_2C{=}CHCH_2CH_3$; but-1-ene [1]

$CH_3CH{=}CHCH_3$; but-2-ene [1]; both *E*- and *Z*-isomers. [1]

5 **a)** Electrophilic addition [1]



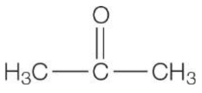
[4] for the diagram: [1] for each of the three curly arrows and [1] for the structure of the intermediate ion.

b) HBr can add across the double bond in two ways via different carbocations. [1]

The secondary carbocation is more stable than the primary because of the extra inductive effect [1], so 2-bromopentane is the major product. [1]

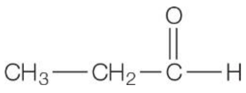
c) In the mechanism, the planar carbocation [1] can be attacked by the bromide ion from above or below [1] with equal probability [1] so an optically inactive racemic mixture is formed. [1]

6 **a)**



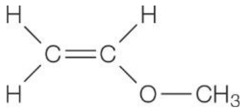
A

[1]



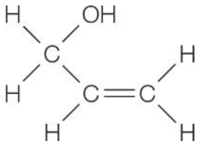
B

[1]



C

[1]



D

[1]

b) **i)** Call the isomers A, B, C & D as shown. A possible method is:

Add bromine water to all four [1]: C & D decolourise it [1]; no change with A & B. [1]

Add acidified potassium dichromate(VI) to C & D [1]: D turns it from orange to green [1]; no change with C. [1]

Add acidified potassium dichromate(VI) to A & B. [1]: B turns it from orange to green [1]; no change with A. [1]

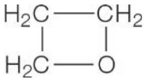
ii) A – absorption at 1720–1700 cm^{-1} for a ketone C=O. [1]

B – absorption at 1740–1720 cm^{-1} for an aldehyde C=O. [1]

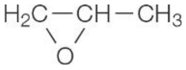
C – absorption at 1669–1645 cm^{-1} for an alkene C=C but no absorption for an O–H alcohol around 3750–3200 cm^{-1}. [1]

D – absorption at 1669–1645 cm^{-1} for an alkene C=C and also an absorption for an O–H alcohol around 3750–3200 cm^{-1}. [1]

c)



and



Four-membered ring is strained as the bond angle is 90° [1] compared with the tetrahedral 109.5°. [1]

Three-membered ring is even more strained as the bond angle is only 60°. [1]

The four-membered ring is likely to be more stable. [1]

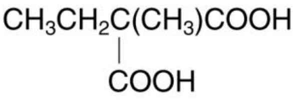
7 The final step gives equal amounts of two optical isomers. [1]

The molecules of R must have a chiral centre: $CH_3CH_2CH(CH_3)COOH$. [1]

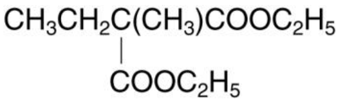
The change from P to Q suggests the hydrolysis of the double ethyl ester of a carboxylic acid. [1]

So Q must have two carboxylic acid groups. [1]

Q decomposes to R by losing CO_2. [1] Acids with two carboxylic acid groups attached to the same carbon atom lose a carboxylic acid group relatively easily. [1]

Q:  [1]

$$\mathrm{CH_3CH_2}\underset{\substack{|\\ \mathrm{COOH}}}{\mathrm{C}}\mathrm{(CH_3)COOH}$$

P:  [1]

$$\mathrm{CH_3CH_2}\underset{\substack{|\\ \mathrm{COOC_2H_5}}}{\mathrm{C}}\mathrm{(CH_3)COOC_2H_5}$$