HL Paper 3

A polarimeter can be used to determine the optical rotation of an optically active substance.

a. Describe what happens to plane-polarized light when it passes through a solution of an optically active compound. [1]

b. A mixture of enantiomers shows optical rotation. [1]

Suggest a conclusion you can draw from this data.

Markscheme

a. plane of polarization is rotated

Award zero if answer refers to plane-polarized light being bent.

[1 mark]

b. not a racemic mixture

OR

two enantiomers not equimolar

OR

mixture contains optically active impurity

OR

relative proportions of enantiomers in mixture can be determined

[1 mark]

Examiners report

a. [N/A]
b. [N/A]

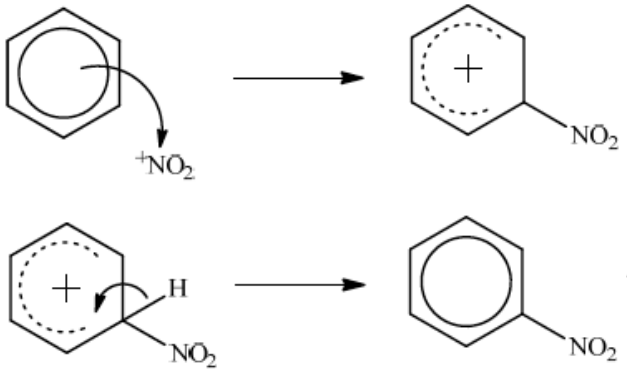
(i) Identify the **two** reagents used to form the electrophile in the nitration of benzene.

(ii) Explain, using curly arrows to represent the movement of electrons, the mechanism for this reaction.

Markscheme

(i) H_2SO_4/sulfuric acid **and** HNO_3/nitric acid;

(ii)



curly arrow going from delocalized electrons in benzene to $^+NO_2$;

Do not penalize if NO_2^+ is written.

representation of carbocation with correct formula **and** positive charge on ring;

curly arrow going from CH bond to benzene ring cation;

formation of organic product nitrobenzene **and** H^+;

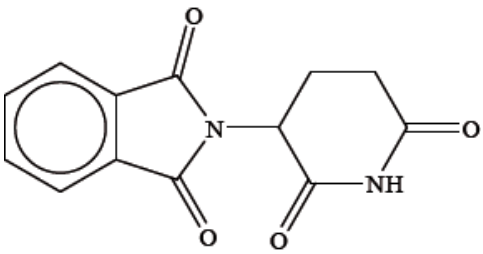
Allow mechanism with corresponding Kekulé structures.

Examiners report

Q27 was well answered by most candidates although some need to take care with the placement of the delocalized positive charge in the intermediate.

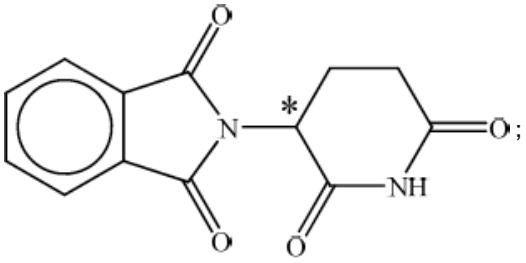
Chirality plays an important role in the action of drugs.

a. Using an asterisk (*), identify the chiral carbon atom in the structure of thalidomide. [1]



b. Describe the composition of a racemic mixture. [1]

Markscheme

a.  ;

b. equimolar/50:50 mixture (of a pair) of enantiomers/both isomers;

Examiners report

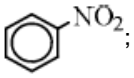
a. Identification of the chiral carbon atom was generally well done.

b. Some were not able to describe the composition of a racemic mixture correctly by not mentioning an equimolar (50:50) mixture.

Identify the organic product in the following reaction.

$$C_6H_6 + HNO_3 \xrightarrow{H_2SO_4}$$

Markscheme

nitrobenzene / $C_6H_5NO_2$ /  ;

Accept multiple substitution products.

Examiners report

Nitrobenzene was usually easily identified in (d).

Vision is dependent on retinol (vitamin A) present in retina cells. Retinol is oxidized to the photosensitive chemical 11-*cis*-retinal and isomerizes to 11-*trans*-retinal on absorption of light.

Outline how the formation of 11-*trans*-retinal results in the generation of nerve signals to the brain.

Markscheme

11-*trans* retinal no longer fits into the rhodopsin/protein

OR

11-*trans* retinal is ejected from the rhodopsin/protein

leads to conformational change in rhodopsin/protein «to opsin generating signals»

[2 marks]

Examiners report

[N/A]

The action of a drug molecule often depends on its shape. Discuss a specific example of a drug where one stereoisomer has a different physiological activity to the other.

Markscheme

one enantiomer/isomer of thalidomide relieves nausea/morning sickness;

other enantiomer/isomer of thalidomide causes foetal deformities;

OR

one enantiomer/isomer of taxol is an anti-cancer drug;

other enantiomer/isomer of taxol is ineffective;

OR

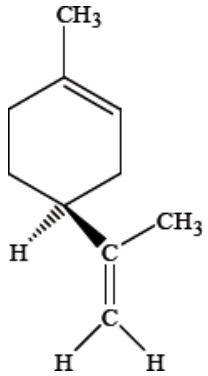
cis-isomer of diamminedichloroplatinum(II)/cisplatin is an anti-cancer drug;

trans-isomer is ineffective;

Examiners report

Whilst a drug in which stereochemistry was important was well known (usually Thalidomide), the other two parts of the question were poorly answered in very vague terms. Few seemed to realize the importance of the 3D modelling of the drug and its active site or to have grasped the concept that combinatorial chemistry involved the random ordering of specific chemical building blocks.

Different conventions are used to classify enantiomers. Orange and lemon peel each contain different enantiomers of the compound limonene. One of the enantiomers is represented below.

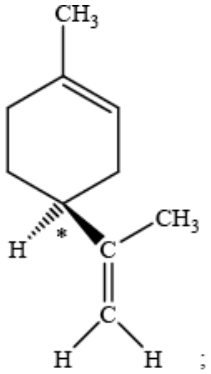


a. Identify the chiral centre in this enantiomer with an asterisk, *. [1]

b. The $(+)d$-enantiomer has the characteristic smell of oranges and the $(-)l$-enantiomer has the characteristic smell of lemons. Explain the meaning of the $(+)d$ and $(-)l$ symbols used in this notation. [1]

c. The R, S notation is also used. The $(+)d$-enantiomer is often described as R-limonene and the $(-)l$-enantiomer as S-limonene. Explain what is meant by the R, S notation and state whether the structure shown is R or S. [2]

Markscheme

a. 

;

b. dextro/d and levo/l refer to right and left-handed / clockwise and anti-clockwise rotation of plane polarized light;

c. clockwise and anti-clockwise sequence of prioritized atoms (working from high to low atomic numbers) / *OWTTE*;

Allow absolute configuration of enantiomers.

Allow convention for labelling chiral carbon atoms using the Cahn-Ingold-Prelog notation.

S;

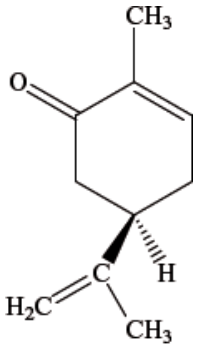
Examiners report

a. In (a), surprisingly a number of students were not able to identify the chiral centre.

b. Although some knew what d and l referred to, a number did not refer to plane-polarized light.

c. R and S notation was not understood and only the best candidates were able to determine the structure as S. Some simple class exercises on chiral centres, d and d notation and R and S notation using a number of simple molecules would greatly improve student understanding of this topic.

The structure below shows –(*l*)-carvone.



–(*l*)-carvone has another optical isomer.

a. State its name and, by means of a diagram, predict its structure. [2]

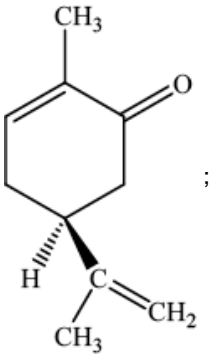
b. Describe the structural feature of the carvone molecule that allows it to exist as optical isomers. [1]

Markscheme

a. *Name*:

+(*d*)-carvone/s-carvone/(+)-(S)-carvone / dextro-carvone;

Structure:



;

b. asymmetric/chiral carbon / *OWTTE*;

Examiners report

a. This question was reasonably well answered.

b. This question was reasonably well answered

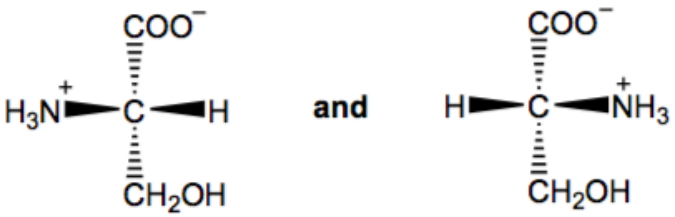
Amino acids, shown in section 33 of the data booklet, can be combined to form polypeptides and proteins.

(i) Serine is a chiral amino acid. Draw both enantiomers of serine.

(ii) State the enantiomeric form of serine found in proteins.

Markscheme

(i)



Accept un-ionized or zwitterionic forms.

Accept any other correct representation which clearly indicates 3-dimensional structure at chiral centre.

Accept Fischer projections with the chiral carbon atom represented by crossing lines or shown as C.

(ii)
L

Examiners report

[N/A]

Methylbenzene can be prepared from benzene and iodomethane.

Methylbenzene reacts when heated with a mixture of concentrated sulfuric acid and concentrated nitric acid.

(i) Name the major organic products formed.

(ii) Identify the electrophile in this reaction and explain how it is formed.

Markscheme

(i) 1-methyl-2-nitrobenzene **and** 1-methyl-4-nitrobenzene;

*Accept 2-methylnitrobenzene **and** 4-methylnitrobenzene.*

*Accept 2-nitromethylbenzene **and** 4-nitromethylbenzene*.

*Accept o-methylnitrobenzene **and** p-methylnitrobenzene.*

(ii) NO_2^+ / nitronium ion;

the (concentrated) sulfuric acid protonates the nitric acid /

$HNO_3 + H_2SO_4 \rightarrow H_2NO_3^+ + HSO_4^-$;

the $H_2NO_3^+$ formed loses water / $H_2NO_2^+ \rightarrow H_2O + NO_2^+$;

Accept $HNO_3 + H_2SO_4 \rightarrow NO_2^+H_2O + H_2SO_4^-$ for the second and third points.

Examiners report

Candidates often named the products but had difficulty in the formation of the electrophile. The charge for NO_2^+ was often omitted.

Amino acids are the building blocks of proteins.

c. Draw the structures of the main form of glycine in buffer solutions of pH 1.0 and 6.0. [2]

The pK_a of glycine is 2.34.

pH = 1.0	pH = 6.0

d. Calculate the pH of a buffer system with a concentration of 1.25×10^{-3} mol dm^{-3} carbonic acid and 2.50×10^{-2} mol dm^{-3} sodium hydrogen carbonate. Use section 1 of the data booklet. [1]

pK_a (carbonic acid) = 6.36

e. Sketch the wedge and dash (3-D) representations of alanine enantiomers. [1]

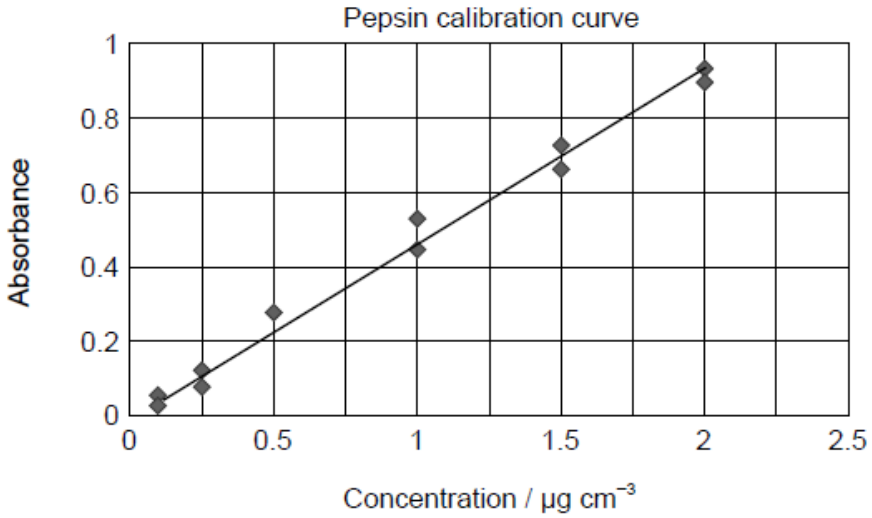
f. UV-Vis spectroscopy can be used to determine the unknown concentration of a substance in a solution. [1]

Calculate the concentration of an unknown sample of pepsin with an absorbance of 0.725 using section 1 of the data booklet.

Cell length = 1.00 cm

Molar absorptivity (extinction coefficient) of the sample = 49650 dm^3 cm^{-1} mol^{-1}

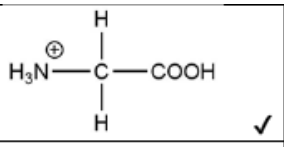
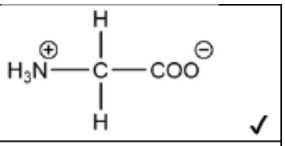
g. A different series of pepsin samples is used to develop a calibration curve. [1]



Estimate the concentration of an unknown sample of pepsin with an absorbance of 0.30 from the graph.

Markscheme

c.

 ✓	 ✓
pH = 1.0	pH = 6.0

Penalize charge on incorrect atom once only.

Penalize missing hydrogens or incorrect bond connectivities once only in Option B.

Accept condensed structural formulas.

Accept skeletal structures.

[2 marks]

d. ***ALTERNATIVE 1***

«pH = 6.36 + log $\left(\frac{2.50\times10^{-2}}{1.25\times10^{-3}}\right)$ =»

7.66

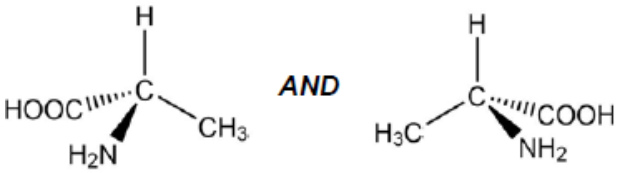
ALTERNATIVE 2

«K_a = 4.4 × 10^{-7} = [H^+] $\left(\frac{2.50\times10^{-2}}{1.25\times10^{-3}}\right)$, [$H^+$] = 2.2 × 10^{-8} mol dm^{-3}»

«pH =» 7.66

*Do **not** accept "«pH =» 8".*

[1 mark]

e. 

Penalize missing hydrogens or incorrect bond connectivities once only in Option B.

*Wedges **AND** dashes must be used.*

[1 mark]

f. «$\frac{0.725}{49650\ \mathrm{dm^3\ cm^{-1}\ mol^{-1}}\times1.00\ \mathrm{cm}}$ =» 1.46 × 10^{-5} «mol dm^{-3}»

[1 mark]

g. 0.65 «μg cm^{-3}»

Accept any value in the range 0.60–0.70 «μg cm^{-3}»

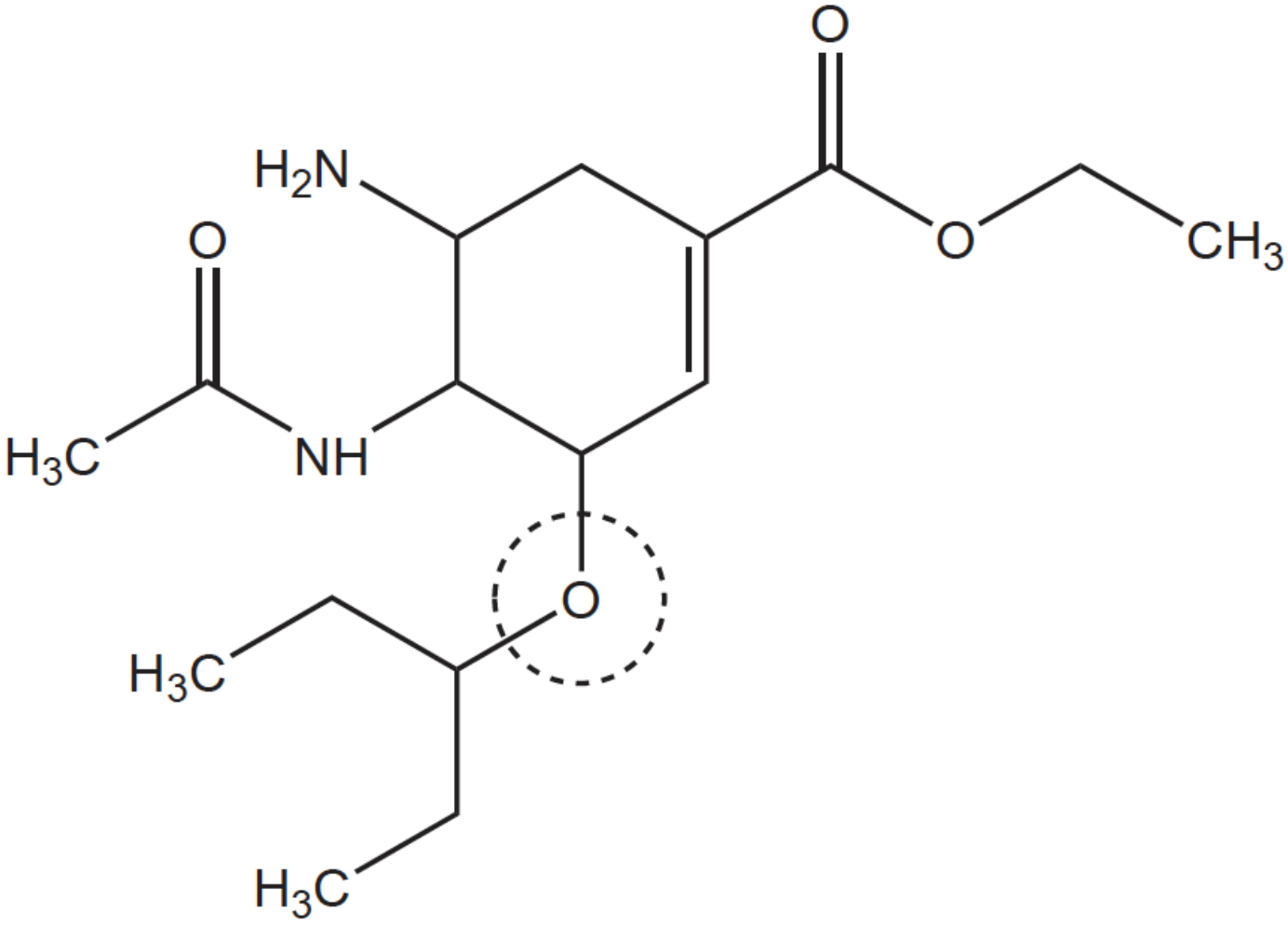
[1 mark]

Examiners report

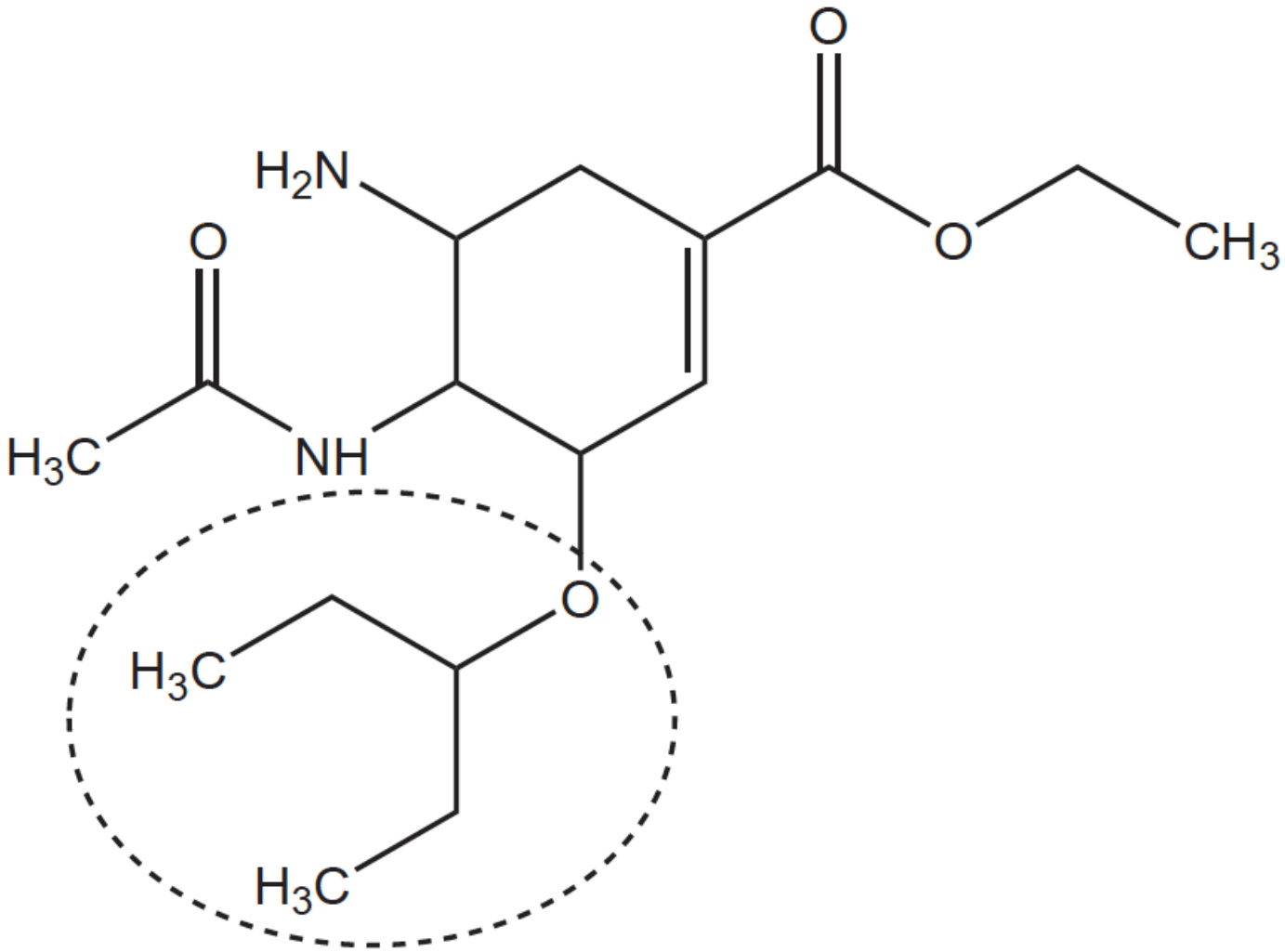
c. [N/A]
d. [N/A]
e. [N/A]
f. [N/A]
g. [N/A]

In recent years several antiviral medications have been produced. One of these medications is oseltamivir (Tamiflu).

a. Identify the functional group circled in the structure of oseltamivir. [1]



b. Predict the number of signals and relative integration you would expect to see in the nuclear magnetic resonance spectroscopy (^{1}H NMR) spectrum for the circled portion in the structure. [2]



Number of signals:

Relative integration:

c. Oseltamivir is a chiral compound. [3]

(i) Identify an apparatus that can be used to distinguish between its enantiomers.

(ii) Explain how the differentiation between the enantiomers is obtained using this apparatus.

Markscheme

a. ether

*Do **not** accept "C-O-C".*

b. *Number of signals:* 3 «signals»

Relative integration: 6:4:1

Accept any correct ratio order.

c. (i)

polarimeter

Accept other alternative techniques such as “GC/HLPC/chromatography using a chiral column”.

*Do **not** accept just “polarizer”.*

(ii)
«plane-»polarized light passed through sample

analyzer/second polarizer determines the angle of rotation of the plane of polarized light
OR
each enantiomer will rotate plane «of plane-»polarized light in opposite directions «by the same angle»

Accept explanation related to other alternative techniques such as GC/ HLPC/chromatography using a chiral column.

*Award **[2]** for “(+)/d rotates plane of polarization to the right* **AND** *(-)/l rotates plane of polarization to the left”.*

Examiners report

a. [N/A]
b. [N/A]
c. [N/A]