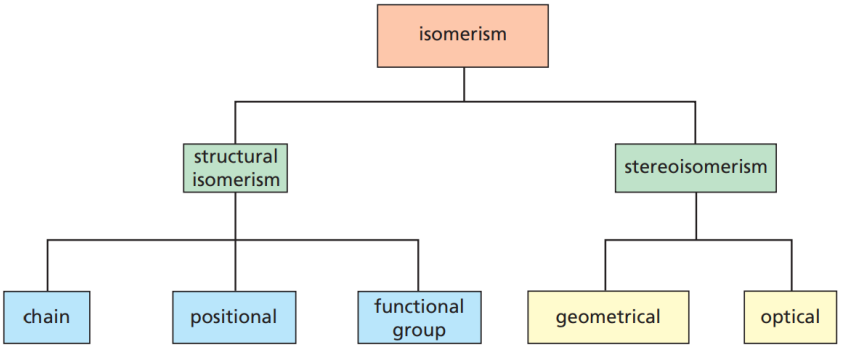
13.4 ISOMERISM

Learning outcomes

Candidates should be able to:

1. describe structural isomerism and its division into chain, positional and functional group isomerism
2. describe stereoisomerism and its division into geometrical (cis/trans) and optical isomerism (use of E, Z nomenclature is acceptable but is not required)
3. describe geometrical (cis/trans) isomerism in alkenes, and explain its origin in terms of restricted rotation due to the presence of π bonds
4. explain what is meant by a chiral centre and that such a centre gives rise to two optical isomers (enantiomers) (Candidates should appreciate that compounds can contain more than one chiral centre, but knowledge of meso compounds, or nomenclature such as diastereoisomers is **not** required)
5. identify chiral centres and geometrical (cis/trans) isomerism in a molecule of given structural formula including cyclic compounds
6. deduce the possible isomers for an organic molecule of known molecular formula

Introduction



Structural isomerism

Structural isomers **differ as to which atoms in the molecule are bonded to which.**

1. Describe structural isomerism. [1]

2. Define Structural isomers. [1]
3. Define structural isomerism. [1]
4. Explain what is meant by **structural isomer**. [1]

There are three types of structural isomerism.

Chain isomerism

Chain isomers have the same number of carbon atoms as one another, but **their carbon backbones are different.** E.g., pentane and 2-methylbutane are isomers with the molecular formula C_5H_{12}.

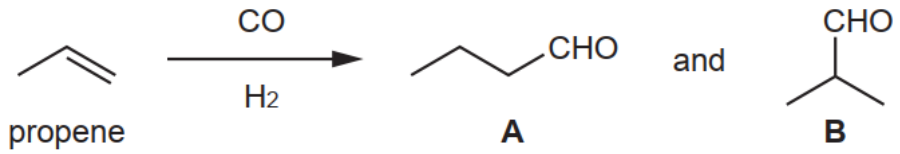
Positional isomers have the same carbon backbone, but the **positions of their functional group(s) differ**.

In, **Functional group isomerism** there are different functional groups present. E.g., the carboxylic acid $CH_3CH_2CO_2H$ (propanoic acid), the ester $CH_3CO_2CH_3$ (methyl ethanoate)

5. Bromine reacts with butane in the presence of ultraviolet light to form bromobutane.
Two structural isomers with the molecular formula C_4H_9Br are produced during this reaction.
(i) Draw the two structural isomers and state the systematic name of each isomer. [2]

(ii) Identify the type of structural isomerism shown in **(i).** **[1]**

6. Alkenes undergo an addition reaction with a 1:1 mixture of CO and H_2 to form aldehydes.
Fig. 3.1 shows the reaction of propene with a 1:1 mixture of CO and H_2.



Aldehydes **A** and **B** are structural isomers.
(i) State the type of structural isomerism shown by **A** and **B**. [1]

(ii) Name **A**. [1]

(iii) The complete reaction of propene with a 1:1 mixture of CO and H_2 produces **A** and **B** only. The product mixture contains 96% **A** and 4% **B**.
Calculate the mass of **A** produced in this reaction when 5.00×10^3 kg of propene is used.

mass of **A** = (ans = 6857)..... kg [1]

1. In this question, alkenes and cyclic alkanes should be considered.
How many structural isomers of C_4H_8 are there?

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

2. Which two formulae correctly represent a pair of structural isomers?

A	$CH_3CH(CH_3)COOH$ and $(CH_3)_2CHCOOH$
B	$CH_3CH(COOH)CH_3$ and $(CH_3)_2CHCOOH$
C	$CH_3CHCOOH$ and $CH_3CH_2CH_2COOH$
D	$CH_3CH_2CH_2COOH$ and $(CH_3)_2CHCOOH$

3. Which pair of alcohols are isomers of each other?

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

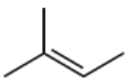
B butan-2-ol and 2-methylpropan-2-ol

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

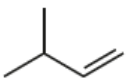
D propan-2-ol and 2-methylpropan-2-ol

7. Draw the structure of a molecule that is a positional isomer of **C** and **D**.

C



D



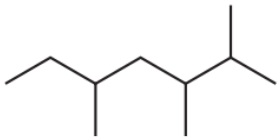
[1]

4. How many esters have the molecular formula $C_4H_8O_2$?

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

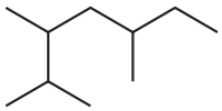
5. Compound T has the skeletal formula shown.

compound T

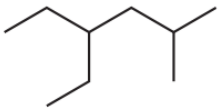


Which structure is a structural isomer of compound T?

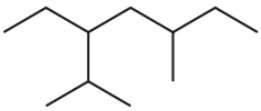
A



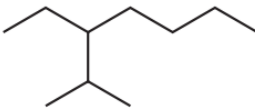
B



C



D



6. Structural isomerism **only** should be considered when answering this question.
How many straight-chain isomers are there with molecular formula $C_4H_8Cl_2$?

A 6 **B** 7 **C** 8 **D** 9

7. Which statement is correct?

A 2,2-dimethylpropanoic acid is an isomer of propyl methanoate.

B 2-methylbutan-2-ol is an isomer of hexan-3-ol.

C 3-methylbutan-2-one is an isomer of pentanal.

D 3,3-dimethylbutan-2-one is an isomer of pentan-3-one.

8. Which pair of compounds are functional group isomers of each other?

A butan-1-ol and butanal

B ethylpropanoate and pentanoic acid

C hex-1-ene and hex-2-ene

D propylamine and propanenitrile

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

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

10. The general formula for a non-cyclic alcohol is $C_nH_{2n+1}OH$.
How many different structural isomers are there for $n = 3$ and $n = 4$?

	$n = 3$	$n = 4$
A	2	2
B	2	4
C	3	4
D	3	8

8. Hexane, C_6H_{14}, has four structural isomers.
Fig. 3.1 shows hexane and two of its structural isomers.

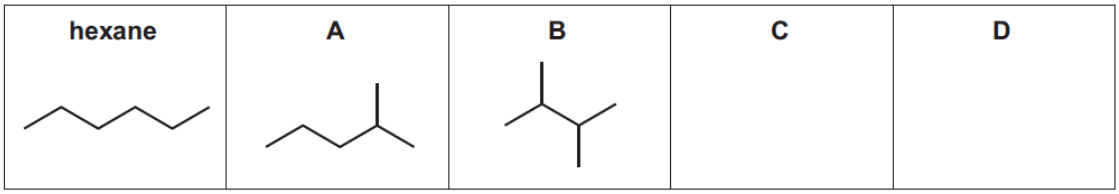
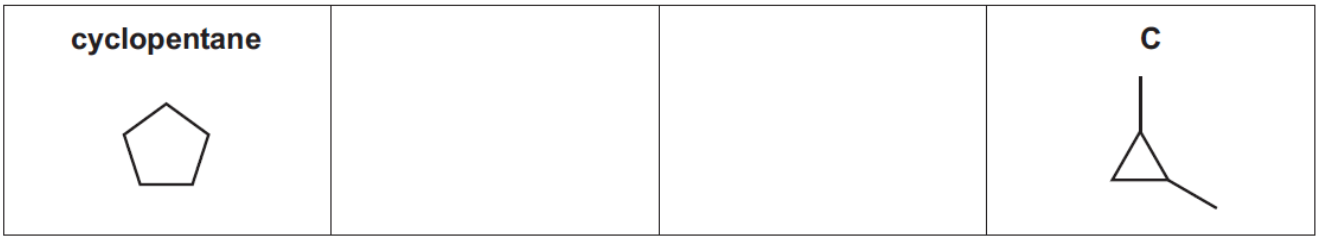


Fig. 3.1

Complete Fig. 3.1 by drawing structures for C and D, the other two structural isomers of hexane. [2]

9. Cyclopentane, C_5H_{10}, has four cyclic structural isomers. One of these isomers is C, shown in the figure below.
Complete the figure below to show two other cyclic structural isomers of C_5H_{10}. [2]



Stereoisomers are compounds whose molecules have the same atoms bonded to each other but with different arrangements of the atoms in space.

10. Describe stereoisomerism. [1]
11. Explain what is meant by **stereoisomerism**. [1]

There are two types of stereoisomerism:

Geometrical (cis/trans) isomerism

Unlike a C─C single bond, there is **no free rotation** about a C═C double bond. This can result in a different type of isomerism in unsaturated organic compounds.

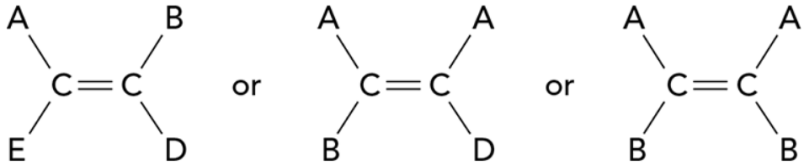
In **cis**-1,2-dibromoethene, both the Br atoms remain fixed on the same side of the C═C double bond as there is no free rotation about this bond because of the presence of a **π** (pi) bond. However, in **trans**-1,2-dibromoethene, the Br atoms are positioned across the C═C double bond. (Remember that the prefix 'trans-' means **across**.)

cis-1,2-dibromoethene *trans*-1,2-dibromoethene

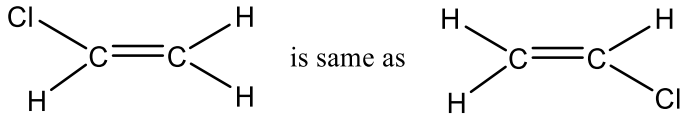
These two stereoisomers have different arrangements of atoms in space, so they are different compounds with different physical properties. Stereoisomers can also have some different chemical properties. E.g., they may react at different rates for the same reaction.

trans-but-2-ene cis-but-2-ene

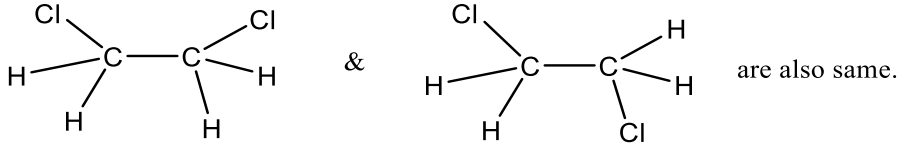
Whenever we have unsaturated compounds with the structures shown in Figure below, we can have this geometrical (cis/trans) type of isomerism.



But



Chloroethene Chloroethene



1,2-dicholoethane 1,2-dicholoethane

are also same.

There is also geometrical (**cis/trans**) isomerism possible in **substituted cyclic compounds**. This is because of the limited rotation about C─C single bonds that make up the rings. We usually show the **cis**- and **trans**-isomers using a combination of skeletal and 3D formulae. E.g., **cis**-3-methylcyclopentanol and **trans**-3-methylcyclopentanol:

cis-3-methylcyclopentanol *trans*-3-methylcyclopentanol

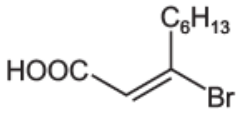
12. Describe the **two** essential features of an alkene molecule that cause it to show geometrical stereoisomerism. [2]

13. Draw the structure of the cis isomer of **C2**.

C2

14. **T** is one of a pair of geometrical (*cis-trans*) isomers.

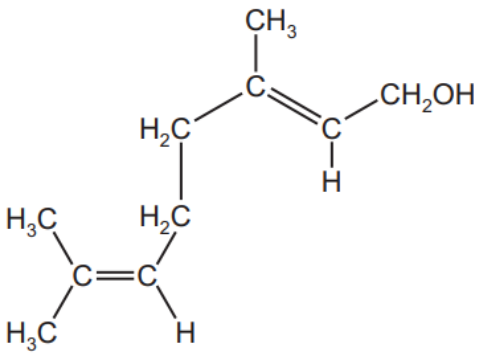
T



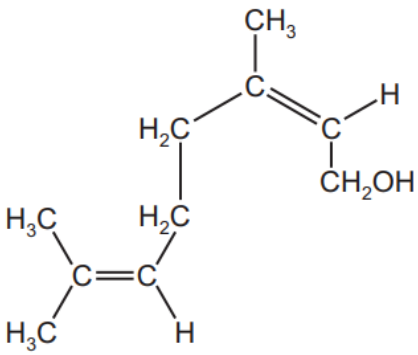
Draw the other geometrical isomer of **T** and explain why the molecules exhibit this form of isomerism. [3]

11. Geraniol and nerol are isomers of each other.

geraniol



nerol



Which type of isomerism is shown here?

A chain B geometrical (cis /trans) C optical D positional

15. Draw the two stereoisomers of but-2-ene. [2]

12. Which alkene shows geometric isomerism?

A $CH_3CH_2CH_2CH{=}CH_2$

B $CH_3CH_2CH{=}CHCH_3$

C $CH_3CH_2C(CH_3){=}CH_2$

D $CH_3CH{=}C(CH_3)CH_3$

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

A 4
B 2
C 3
D none; hex-2,4-diene does **not** show geometric isomerism

14. The unsaturated hydrocarbon octa-1,3,5,7-tetraene, C_8H_{10}, can display geometric isomerism.

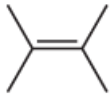
octa-1,3,5,7-tetraene
$CH_2{=}CHCH{=}CHCH{=}CHCH_2$

How many isomers exist?

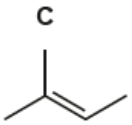
A 2 **B** *3* **C** 4 **D** 8

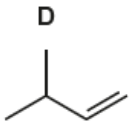
16. Draw the skeletal formula of a structural isomer of **T** that shows *cis-trans* (geometrical) isomerism.

T



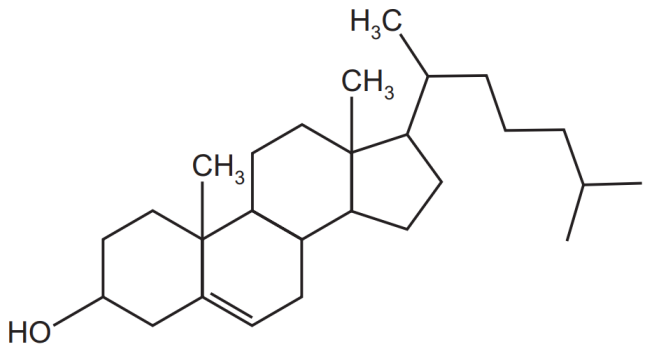
17. Explain why C and D do not show geometrical (cis/trans) isomerism. [1]





15. The diagram shows the structure of the naturally occurring molecule cholesterol.

cholesterol



Student X stated that the 17 carbon atoms in the 4 rings all lie in the same plane.
Student Y stated that this molecule displays cis/trans isomerism at the C=C double bond.
Which students are correct?

A both student X and student Y
B neither student X nor student Y
C student X only
D student Y only

18. Compounds P and Q are structural isomers.

Fig. 4.1

(ii) P shows geometrical isomerism.
Draw the geometrical isomer of P. Explain why the two isomers are not identical.

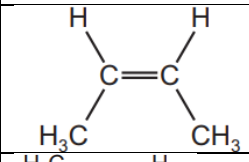
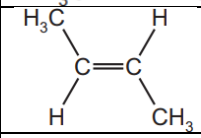
geometrical isomer of **P**

explanation .....

.....

..... [2]

19. The table shows the structural formulae of four compounds, **A**, **B**, **C** and **D**, with molecular formula C_4H_8.
Complete the table by giving the systematic name of **A**, **B**, **C** and **D**. [4]

	structural formula	Name
A	$CH_3CH_2CH{=}CH_2$	
B		
C		
D	$CH_2{=}C(CH_3)_2$	

20. The skeletal formula of W is shown in Fig. 5.1.

W

(a) W has two positional isomers. Only one shows stereoisomerism.
Draw the structures of the two positional isomers of W in the boxes. [2]

(b) (i) Describe the origin of stereoisomerism in W.

.....

..... [1]

(ii) State why W shows stereoisomerism but one of the positional isomers in (a) does not.

.....

.....

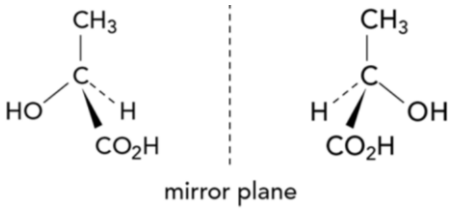
..... [1]

(c) Draw the skeletal structure of the stereoisomer of W.

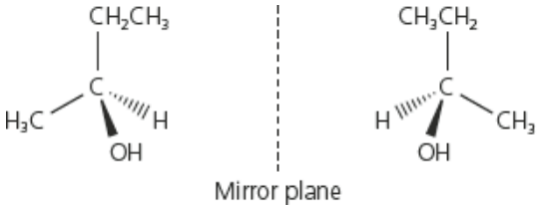
Optical isomerism

www.youtube.com/watch?v=JS-iAuCIexk

- If a molecule contains a carbon atom that is bonded to four different atoms or groups of atoms, it can form two optical isomers.
- We can describe this carbon atom as an '**asymmetric**' carbon atom because there is no plane of symmetry in its molecule.
- The two different optical isomers, called **enantiomers**, are mirror images of each other, and they cannot be superimposed (Figure below).
- The carbon atom with the four different groups attached to it is called the **chiral centre** of the molecule.



- Organic molecules can contain more than one asymmetric carbon atom, i.e., more than one chiral centre. If there are two asymmetric carbon atoms, then each of its chiral centres will rotate the plane of polarised light. In this case, there will be four possible optical isomers.
- To decide where the chiral centres are, we have to find any carbon atoms that are bonded to four different atoms or groups of atoms.



21. 2-hydroxypropanoic acid has a chiral centre.
State what is meant by chiral centre. [1]

22. Stereoisomerism occurs when a molecule has at least one of two key features.
State the two key features that give rise to stereoisomerism. [2]

23. Describe the essential feature of an unbranched hydrocarbon that causes its molecules to show stereoisomerism.
Explain how this feature leads to stereoisomerism.

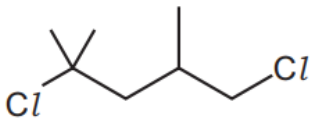
.....

.....

..... [3]

24. T exhibits optical isomerism.
Explain what is meant by the term optical isomer and circle any atom(s) in T that give rise to optical isomerism.

T



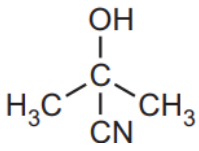
……

……

……..[2]

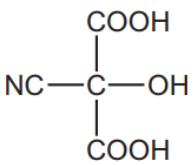
25. Explain why A does not show optical isomerism. [1]

A



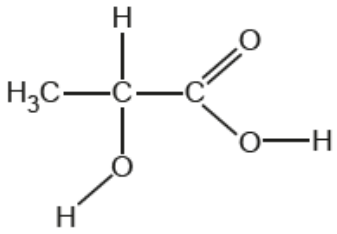
26. **Q** does **not** show optical isomerism. Explain why. **[1]**

Q

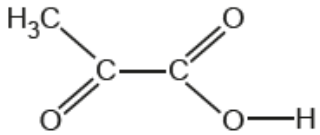


27. Lactic acid, $CH_3CH(OH)COOH$, and pyruvic acid, $CH_3COCOOH$, both contain two functional groups.

lactic acid



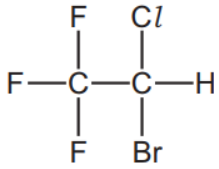
pyruvic acid



Explain why lactic acid exists as optical isomers. [1]

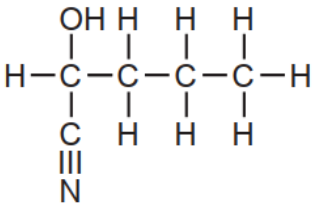
28. Halothane is an anaesthetic.

halothane

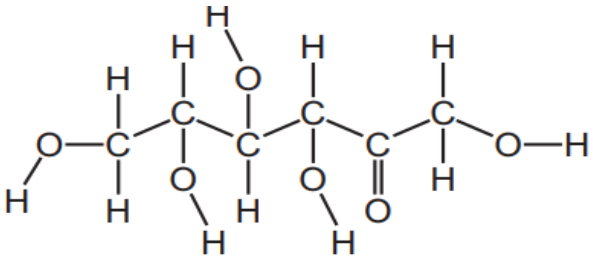


Identify the chiral centre in halothane and mark it with an asterisk (*). [1]

29. **C** is a chiral molecule.
Circle any chiral centres in the structure of **C** shown in Fig. 3.2.



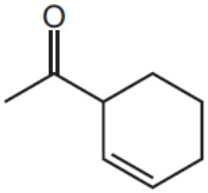
16. On the diagram of the fructose molecule, label all the chiral centres with an asterisk (*).



[1]

17. Compound X has the structure shown.
Which type of carbonyl group is present and how many chiral centres are there in one molecule of X?

compound X



	carbonyl group	chiral centres
A	aldehyde	0
B	aldehyde	1
C	ketone	0
D	ketone	1

18. How many chiral carbon atoms are there in one molecule of 2,2,4,5-tetramethylhexan-3-ol?

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

19. Structural isomerism and stereoisomerism should be considered when answering this question.
How many non-cyclic isomers have the molecular formula C_5H_{10}?

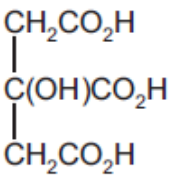
A 3 **B** 4 **C** 5 **D** 6

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

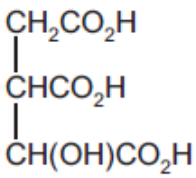
A 7 **B** 8 **C** 9 **D** 10

21. The structures of citric acid and isocitric acid are shown.
How many chiral centres does each acid possess?

citric acid

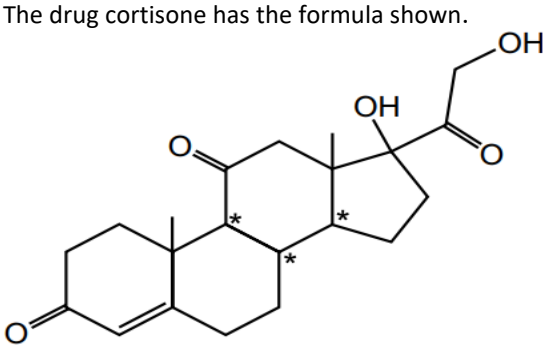


isocitric acid



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

22. The drug cortisone has the formula shown.

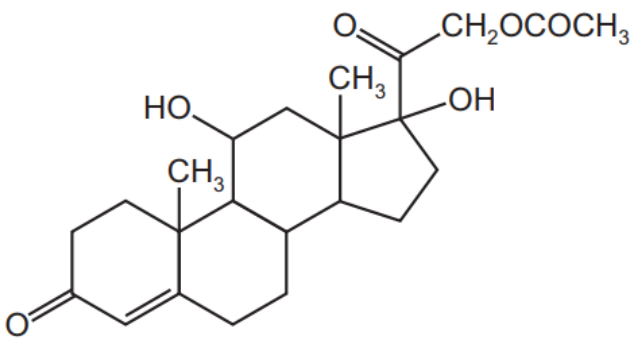


In addition to those chiral centres marked by an asterisk (*), how many other chiral centres are present in the cortisone molecule?

A 0 B 1 C 2 D 3

23. The formula of hydrocortisone acetate is shown.

hydrocortisone acetate

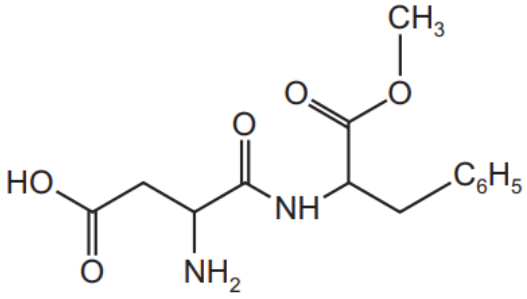


Which row is correct?

	number of C atoms in one molecule	number of chiral atoms in one molecule
A	22	7
B	22	8
C	23	7
D	23	8

24. The compound **aspartame** is widely used as a sweetener in 'diet' soft drinks. Aspartame is chiral. (There are no chiral carbon atoms in C_6H_5.)

aspartame

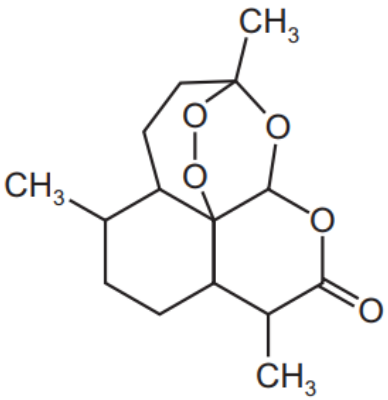


How many chiral carbon atoms are present in a molecule of **aspartame**?

A 1 B 2 C 3 D 4

25. Artemisinin is a powerful anti-malarial drug.

artemisinin

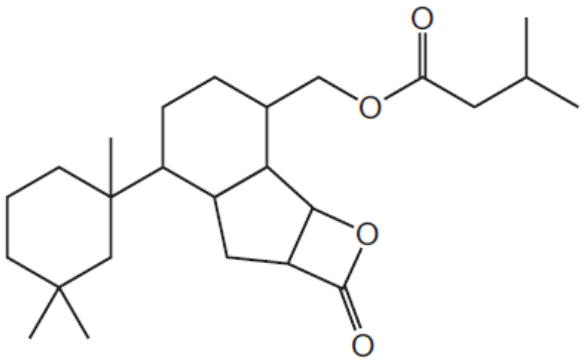


How many chiral centres are there in each molecule of artemisinin?

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

26. The structure of compound Q is shown.

compound Q

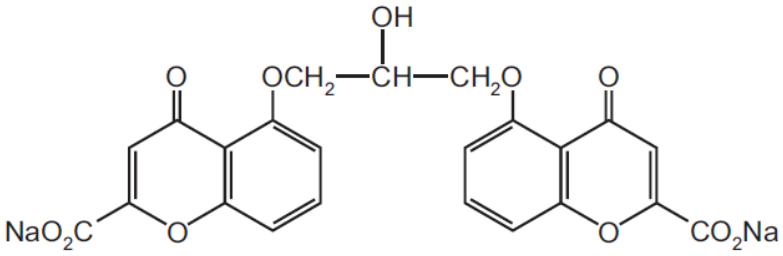


How many chiral centres are present in a molecule of Q?

A 4 B 5 C 6 D 7

27. The structure of disodium cromoglycate is shown.

disodium cromoglycate



How many chiral centres are there in this molecule?

A 0 B 1 C 2 D 3

28. Which pair includes a hydrocarbon without a chiral centre?

A $CH_3CH_2CH_2CH(CH_3)CH_2CH_3$ $CH_3CH(CH_3)CH(CH_3)CH_2CH_3$

B $CH_3CH_2CH_2CH(CH_2CH_3)CH_3$ $CH_3CH_2CH_2CH(CH_3)CH_2CH_3$

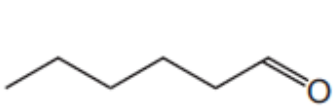
C $CH_3CH_2CH_2CH(CH_3)CH_2CH_3$ $CH_3CH_2CH(CH_3)CH(CH_3)_2$

D $CH_3CH(CH_2CH_3)CH(CH_3)CH_3$ $CH_3CH(CH_3)CH_2CH(CH_3)_2$

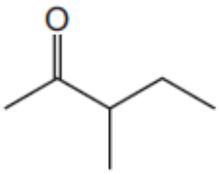
29. Which compound shows stereoisomerism?

A 2-methylbut-2-ene
B 2-chloropropan-1-ol
C difluorochlorobromomethane
D pent-1-ene

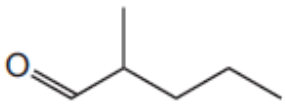
30. The diagrams show skeletal formulas of some isomers of $C_6H_{12}O$.



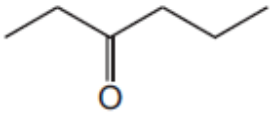
1



2



3



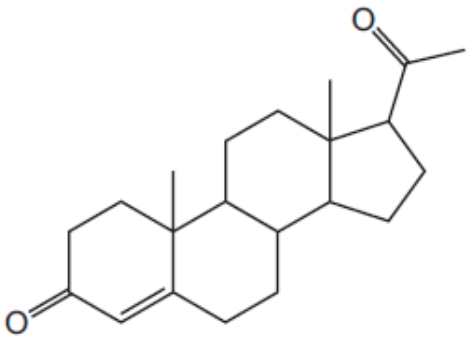
4

Which statement is correct?

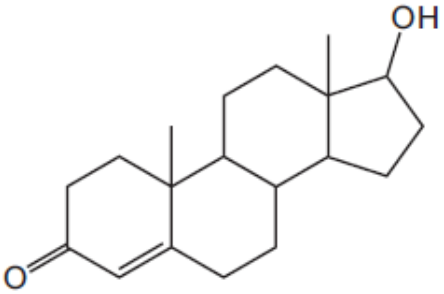
A 1 and 3 are chain isomers of each other and positional isomers of each other.
B 2 and 3 are functional group isomers of each other and both have a chiral centre.
C 1 and 4 are functional group isomers of each other and both have a chiral centre.
D 2 and 4 are positional isomers of each other and functional group isomers of each other.

31. The skeletal formulas of two compounds are shown.

progesterone



testosterone

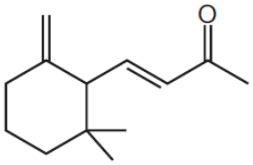


Which statements about progesterone and testosterone are correct?

A They both contain a ketone group, and they both have geometrical isomers due to the C=C bond.
B They have the same molecular formula, and they both have geometrical isomers.
C They have the same number of chiral carbons, and they have the same molecular formula.
D They have the same number of chiral carbons, and they both contain a ketone group.

32. The structure of the compound γ-ionone is shown.

γ-ionone

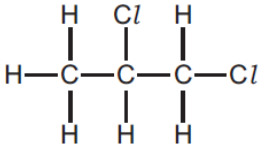


Including γ-ionone, how many stereoisomers exist with this molecular formula?

A 1 B 2 C 4 D 8

30. Compound Q is a by-product of reaction 1.

Q



The molecular formula of Q is $C_3H_6Cl_2$.
Identify the types of structural isomerism and stereoisomerism that a molecule with molecular formula $C_3H_6Cl_2$ can show.

type of structural isomerism .....

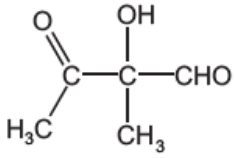
type of stereoisomerism ..... [2]

31. $CH_3(CH_2)_5CHBrCH_3$ exists as a pair of stereoisomers.
Draw the three-dimensional structures of the **two** stereoisomers of $CH_3(CH_2)_5CHBrCH_3$.
R can be used to represent $CH_3(CH_2)_5$. [2]

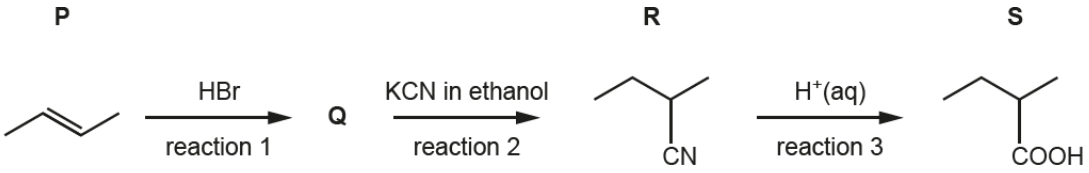
32. Molecules of $CH_3CH(OH)CN$ exist as a pair of optical isomers.
Draw three-dimensional diagrams in the boxes to show the optical isomers of $CH_3CH(OH)CN$. [2]

33. **J** has **two** optical isomers.
Draw the three-dimensional structures of the **two** optical isomers of **J**. [2]

J



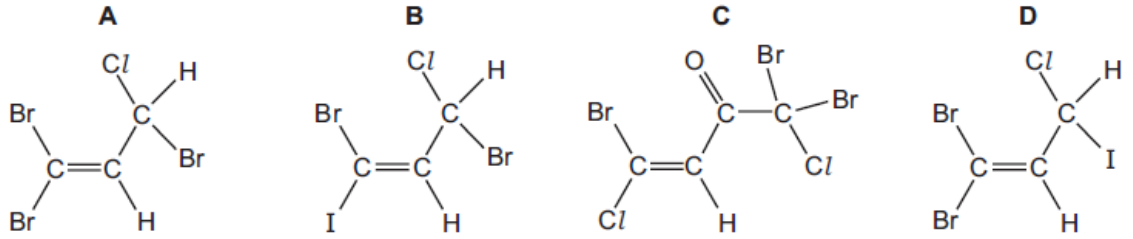
34. Compound S is used in food flavourings. A possible synthesis of S is shown in Fig.



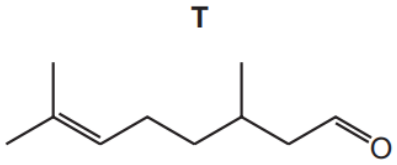
P, Q, R and S show stereoisomerism.
Complete the following table by identifying with a tick (√) the type of stereoisomerism that each molecule shows.
The type of stereoisomerism shown by Q is given.

	P	Q	R	S
geometrical isomerism				
optical isomerism		✓		

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

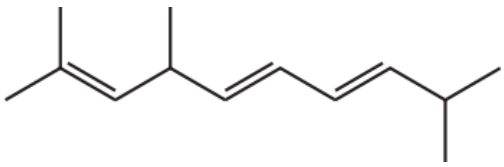


35. Liquids that contain molecules of **T** smell like lemons.



Molecules of **T** exist as a pair of stereoisomers.
Name the type of stereoisomerism shown by molecules of **T**. Explain your answer. [2]

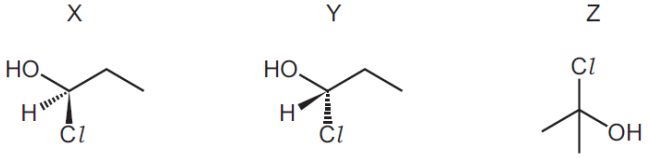
34. A skeletal formula is shown.



What is the total number of stereoisomers including the one shown?

A 4 **B** 6 **C** 8 **D** 16

35. Structural and stereoisomerism should be considered when answering this question.
Compounds X, Y and Z are shown.



How many other isomers of C_3H_7ClO are there that are alcohols?

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

36. A sample of pent-2-en-4-ol, $C_5H_{10}O$, contains all the possible stereoisomers of this compound.
How many stereoisomers are there in the sample?

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

37. Structural isomerism and stereoisomerism should be considered when answering this question.
How many isomeric compounds with molecular formula $C_5H_6O_4$ contain two $–CO_2H$ groups and one C=C double bond?

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

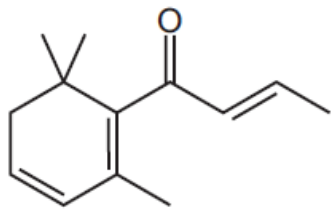
38. Compound X is found in cell walls of some bacteria. Its structural formula is shown.

$CH_3(CH_2)_{17}CH{=}CH(CH_2)_{17}CH(OH)CH(CH_3)CO_2H$
How many stereoisomers are there with this structural formula?

A 2 **B** 4 **C** 6 **D** 8

39. The structure of damascenone is shown.

damascenone



Including damascenone, how many stereoisomers exist with this structural formula?

A 1 B 2 C 4 D 8

40. How many isomeric esters have the molecular formula $C_4H_8O_2$?

A 2 B 3 C 4 D 5

41. Which compound has the greatest number of stereoisomers?

A 2-methylhex-2-ene

B 3-methylhex-2-ene

C 4-methylhex-2-ene

D 5-methylhex-2-ene

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