Chem Factsheet

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Isomerism in Organic Chemistry

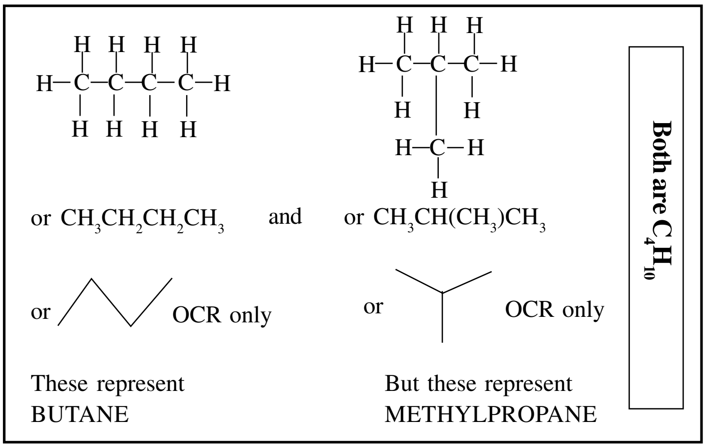
To succeed in this topic you need to understand:
- homologous series (covered in Factsheet 15);
- functional groups (covered in Factsheet 15);
- empirical formulae (covered in Factsheet 02);
- molecular formulae (covered in Factsheet 02);
- structural (including displayed) formulae (covered in Factsheet 15);
- tetrahedral bonding shapes (covered in Factsheet 04);
- naming organic molecules by I.U.P.A.C. rules (covered in Factsheet 15).

After working through this Factsheet you will be able to:
- explain what is meant by isomerism;
- explain the different sub-groups of isomers;
- draw structures of isomers from their molecular formula;
- recognise different types of isomer from their structural formulae.

Organic molecules number many millions. Carbon, hydrogen, oxygen, nitrogen and halogen atoms form the few basic building units of most organic molecules but, by varying their numbers and how they are bonded relative to each other, these millions of different molecules are possible. One of the reasons for this diversity is the occurrence of *isomerism* which is concerned with the "how the atoms are bonded relative to each other", rather than how many are present.

C_4H_{10} is a *molecular formula*; it relates to *all* molecules composed of four carbon atoms and ten hydrogen atoms. However, if all possible structural formulae with this *same* molecular formula are drawn (Fig1)

Fig 1. Structural formulas of C_4H_{10}



Note: they may take more time and effort but, unless specified otherwise, *full displayed structures* are usually the best ones to use, especially in this context.

This example illustrates what is meant by isomerism. Butane and methylpropane are said to be "isomers of each other" or "isomeric" or "isomers of C_4H_{10}".

This leads to the first important definition:

Isomers are molecules with the same molecular formula, but different arrangements of atoms.

Isomers may have significant differences in chemical properties only, in physical properties only or in both. Butane and methylpropane, for example have very similar chemical properties but quite different physical properties. Mostly as a result of this, isomerism is sub-divided into various types (Fig 2).

Fig 2.

Isomers
(molecules with the same molecular formula, but different arrangements of atoms)

- **Structural Isomers** (isomers resulting from different **bonding patterns between the atoms)**
  - **Chain Isomers** are isomers resulting from the atoms being bonded to form **different arrangements of the carbon atoms.**
  - **Positional Isomers** are isomers resulting from the atoms being bonded so that the **functional groups are in different positions on the same carbon chain.**
  - **Functional Group Isomers** are isomers resulting from the atoms being bonded to form **different functional groups.**
- **Stereoisomers** (isomers resulting from different **spatial arrangements** of the atoms in the same structural formula)
  - **Geometrical Isomers** are isomers resulting from the atoms being bonded to form **different arrangements of same groups around a planar group such as the C=C group.**
  - **Optical Isomers (A2)** are isomers resulting from the atoms being bonded to form **different 3D arrangements, around a central carbon atom, which are non-identical mirror images of each other.**

Structural Isomers 1: Chain Isomers

> ***Remember:*** Isomers resulting from the atoms being bonded to form ***different arrangements of the carbon atoms***

Our first example showed chain isomers. Butane and methylpropane differ only in the bonding pattern of the four carbon atoms; the former is a *straight-chain isomer* but the latter is a *branched-chain isomer*. If only chain isomerism applies (as here), the isomers will belong to the *same homologous series* and have very similar chemistry but different physical properties. For example, methylpropane has a noticeably lower boiling point.

> **Note:** the petrochemical industry converts a lot of straight chain isomers into branched chain isomers because the latter act as better fuels in petrol engines. Not surprisingly, they call the process "isomerisation"!

Another example of chain isomerism is C_5H_{12}.

pentane	**2-methylbutane**	**2-2dimethylpropane**
$CH_3CH_2CH_2CH_2CH_3$	$CH_3CH(CH_3)CH_2CH_3$	$CH_3C(CH_3)_2CH_3$

> ***Exam Hint:*** *Examine all the possible carbon chains in a systematic fashion. Draw the maximum number of carbons in one continuous chain first (e.g. 6 in the following question). Then consider all possible variations of a 5C chain with a 1C side-chain. Then consider all possible variations of a 4C chain with two 1C side-chains etc. If you have time, naming each will show whether you have repeated a structure because each should have a unique name.*

Q1 Draw and name the structures of the five chain isomers of C_6H_{14}.

Structural Isomers 2: Positional Isomers

> ***Remember:*** *Isomers resulting from the atoms being bonded so that the* ***functional groups are in different positions on the same carbon chain***.

C_3H_7Br illustrates this type of isomerism. The three carbon atoms form a chain but the bromine atom may be bonded to either the end (at C1) or middle (at C2) of the chain. Hence, the positional isomers of C_3H_7Br are:

1-bromopropane	and	**2-bromopropane**
$CH_3CH_2CH_2Br$		$CH_3CHBrCH_3$

If *only* positional isomerism applies, the isomers will again belong to the *same homologous series* and have very similar chemistry but different physical properties. However, for some examples, the reaction products may vary from positional isomer to positional isomer. For example, as you will encounter when you study the halogenoalkanes, elimination of hydrogen bromide from 1-bromobutane produces only one alkene type product whereas its positional isomer, 2-bromobutane, produces three.

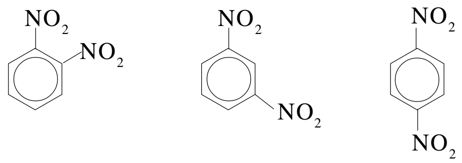
Here are some more examples.

(a)	butan-1-ol [$CH_3CH_2CH_2CH_2OH$]	and	butan-2-ol [$CH_3CH_2CH(OH)CH_3$]
(b)	1,1-dicloroethane [$CHCl_2CH_3$]	and	1,2-dicloroethane [CH_2ClCH_2Cl]
(c)	pentan-2-one [$CH_3CO.CH_2CH_2CH_3$]	and	pentan-3-one [$CH_3CH_2CO. CH_2CH_3$]

> *Exam Hint: If positional isomerism only is occurring, the names vary only in the numbering pattern. Try naming your isomers to check they are genuine positional isomers.*

A2 Only: Benzene derivatives (C_6H_6; )commonly show positional isomerism.

Di-substituted benzene derivatives occur as three positional isomers. For example:



1,2-dinitrobenzene 1,3-dinitrobenzene 1,4-dinitrobenzene

One last point! Chain and positional isomerism can occur *together*. For example, there are four isomers of $C_4H_{10}F$. These are:

(a) 1-fluorobutane [$CH_3CH_2CH_2CH_2F$]

(b) 2-fluorobutane [$CH_3CH_2CHFCH_3$]

(c) 1-fluoro-2-methylpropane [$CH_3CH(CH_3)CH_2F$]

(d) 2-fluoro-2-methylpropane [$CH_3CF(CH_3)CH_3$]

> (a) and (b) are positional isomers
> (c) and (d) are positional isomers
> (a) and (c) are chain isomers
> (b) and (d) are chain isomers
> but (a) and (d) and (b) and (c) are a mixture of both!

A similar pattern is shown by the isomeric alcohols with molecular formula $C_4H_{10}O$. The straight chain positional isomers have already been considered but the full set of isomers is:

(a) butan-1-ol [$CH_3CH_2CH_2CH_2OH$]

(b) butan-2-ol [$CH_3CH_2CH(OH)CH_3$]

(c) 2-methylpropan-1-ol [$CH_3CH(CH_3)CH_2OH$]

(d) 2-methylpropan-2-ol [$CH_3C(OH)(CH_3)CH_3$].

> **Note:** Isomers (a) and (c) are called *primary* alcohols because both contain a $–CH_2OH$ group. (b) is a *secondary* alcohol since it contains a -CH(OH)- group and (d) is a *tertiary* alcohol since it contains a >C(OH)- group. As you will see when you study alcohols, these different types have some significantly different chemical reactions.

> ***Exam Hint:*** *Examine all the positional variations in a systematic fashion. First draw the basic carbon chain (e.g. C-C-C in the following question). Then consider all possible positional variations of the additional functional groups.*

Q2 Draw and name the structures of the four positional isomers of $C_3H_6Cl_2$.

Structural Isomers 3 : Functional Group Isomers

> ***Remember:*** *Isomers resulting from the atoms being bonded to form* ***different functional groups****.*

For molecules with three or more carbon atoms, aldehydes and ketones can show functional group isomerism. Similarly, carboxylic acids and esters can show functional group isomerism whilst, in A2, you will also encounter primary, secondary and tertiary amine functional group isomers. Of course, since organic molecules' chemical properties are controlled by their functional groups, functional group isomers are extremely different in their chemistry. Also, since different functional groups often result in different inter-molecular forces, physical properties can be very different.

Aldehydes and ketones

C_3H_6O could be propanal [CH_3CH_2CHO – an aldehyde] or propanone [$CH_3CO.CH_3$ – a ketone].

Similarly, C_4H_8O could be butanal [$CH_3CH_2CH_2CHO$] or butanone [$CH_3CH_2CO.CH_3$].

Linked to these, there is also a chain isomer of butanal. This is methylpropanal, [$CH_3CH(CH_3)CHO$].

> ***Exam Hint:*** *Draw the functional group first and then add the remaining atoms in all their possible chain and positional variations.*

Q3 Draw and name the structures of the seven isomers of $C_5H_{10}O$. Restrict your answers to aldehydes or ketones but remember to include chain and positional variations.

Carboxylic acids and esters

$C_2H_4O_2$ could be: ethanoic acid [$CH_3CO.OH$ – an acid] or methyl methanoate [$HCO.OCH_3$ – an ester].

Similarly, $C_3H_6O_2$ could be: propanoic acid [$CH_3CH_2CO.OH$], methyl ethanoate [$CH_3CO.OCH_3$] or ethyl methanoate [$HCO.OCH_2CH_3$]

Q4 Draw and name the structures of the six isomers of $C_4H_8O_2$. Restrict your answers to acids or esters but remember to include chain and positional variations.

Primary, secondary and tertiary amines (A2 only):

C_2H_7N could be:
aminoethane (ethylamine) [$CH_3CH_2NH_2$ – a primary amine] or *N*-methylaminomethane (*N*-methylmethylamine) [$(CH_3)_2NH$ – a secondary amine].

Similarly, C_3H_9N could be:
1-aminopropane [$CH_3CH_2CH_2NH_2$], 2-aminopropane [$CH_3CH(NH_2)CH_3$], *N*-methylaminoethane [$CH_3NHCH_2CH_3$] or *N,N*-dimethylaminomethane [$(CH_3)_3N$ – a tertiary amine]. Note again how positional isomerism also occurs.

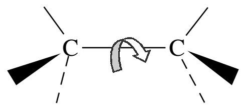
Q5 Draw and name the structures of the eight isomers of $C_4H_{11}N$. Restrict your answers to amines but remember to include chain and positional variations.

Stereoisomers 1 : Geometrical Isomers

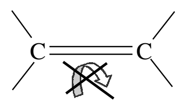
> ***Remember****: Isomers resulting from the atoms being bonded to form* ***different arrangements of same groups around a planar group such as the C=C group.***

Geometrical isomerism (also known as cis-trans isomerism) can occur in many types of molecules but you should concentrate on examples involving alkenes. Such isomerism tends to cause the isomers to have very different physical properties but, since the functional groups have not changed, very similar chemical properties.

Single covalent C-C bonds (sigma bonds) are free to rotate about their axis. However, when the Pi bond is added to form a double covalent C=C bond, this ability to rotate is lost. Also the C=C atoms and the four atoms directly bonded to them are forced to lie in the same plane.

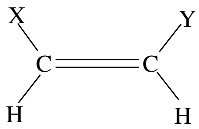


Free rotation; non-planar

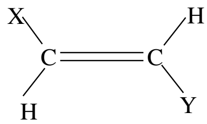


No free rotation;planar

Consider the following general structures where X and Y represent various atoms or groups *other than H* that may be bonded to the C=C carbons. Because of the planar and non-rotating nature of the C=C bond, these structures have the same molecular formula but are non-identical; in other words they are isomers. In fact they are *geometrical isomers*. As shown, the isomer with X and Y on the same side of the C=C bond is referred to as the *cis* isomer whereas the other is called the *trans* isomer.



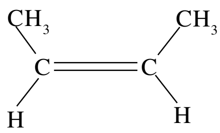
cis-isomer



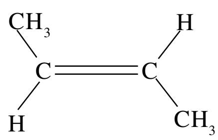
trans-isomer

Some examples of this type of isomerism include:

1. Geometrical isomers of but-2-ene

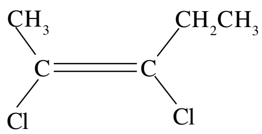


cis-but-2-ene

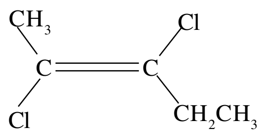


trans-but-2-ene

2. Geometrical isomers of 2,3-dichloropent-2-ene

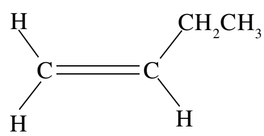


cis-2,3-dichloropent-2-ene



trans-2,3-dichloropent-2-ene

> **Note:** Example 2 shows that the "similar" atoms bonded to C=C do not have to be H atoms. However, the two groups bonded to any particular C=C carbon *must* not be the same. This occurs in but-1-ene, resulting in no geometrical isomers. Similar examples would be 1,2-difluoroethene which *does* have geometrical isomers whereas 1,1-difluoroethene *does not*.



but-1-ene

> ***Exam Hint:*** *Draw the C=C bond with it's four other bonds and then fit in the other atoms or groups. Remember, neither C of the C=C bond can be bonded to the same group.*

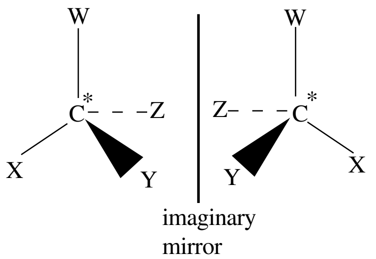
Q6 (a) Draw and name the structures of geometrical isomers of (a) hex-3-ene
(b) 1,2-dibromoethene
(c) 2-chlorobut-2-ene.

Stereoisomers 2 : Optical Isomers (A2 only)

Remember.:** Isomers resulting from the atoms being bonded to form **different 3D arrangements, around a central carbon atom, which are non-identical mirror images of each other.

Optical isomers (also known as enantiomers) always occur in pairs and have identical chemical and physical properties, except that one structure rotates the plane of plane-polarized light (p.p.l.) clockwise and the other rotates it anti-clockwise. This is referred to as their *optical activity*.

Optical isomers can occur if there is an *asymmetric* (also called chiral) carbon atom (marked *). This is a carbon atom which is bonded (tetrahedrally) to *four different groups*. Consider the general structures shown, where W-Z represent these four different groups.

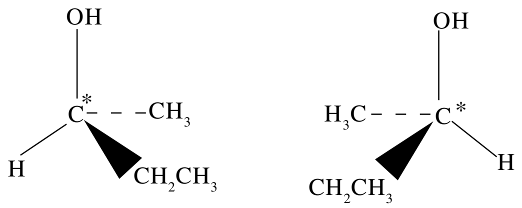


These are *mirror images of each other*, yet they are *non-identical*. "Chiral" is term used to describe such molecules. Hence, they are optical isomers of each other. The "non-identicality" can be seen by imagining looking down on the molecules from above group W. The remaining groups in clockwise order would be Z-Y-X for isomer A but Z-X-Y for B.

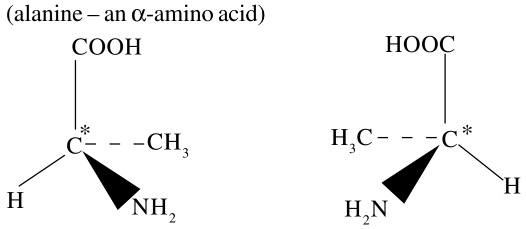
Notes: (a) Inter-changing any two groups in isomer A produces isomer B, and vice-versa.
(b) The direction of rotation of p.p.l. *cannot* be predicted from the structure.

Some examples of optical isomers are:

(1) Optical isomers of butan-2-ol



(2) optical isomers of 2-aminopropanoic acid
(alanine – an α-amino acid)



***Exam Hint**: When drawing optical isomers, 3D diagrams are essential. CLEARLY draw the 3D representation for the tetrahedral carbon atom with it's four bonds and then fit in the four different atoms or groups. Finally, copy your first structure in an imaginary mirror (or exchange any two groups) to obtain the second isomer.*

Q7 Marking the asymmetric carbon with an asterisk, draw structures of the optical isomers of:
(a) 2-methylhexane (b) 2-chlorobutan-1-ol (c) 1-chloro-1-fluoroethane.

Answers to questions in text

Q1 $CH_3CH_2CH_2CH_2CH_2CH_3$ – hexane ;
$CH_3CH(CH_3)CH_2CH_2CH_3$ – 2-methylpentane ;
$CH_3CH_2CH(CH_3)CH_2CH_3$–3-methylpentane;
$CH_3C(CH_3)_2CH_2CH_3$ – 2,2-dimethylbutane ;
$CH_3CH(CH_3)CH(CH_3)CH_3$ – 2,3-dimethylbutane.

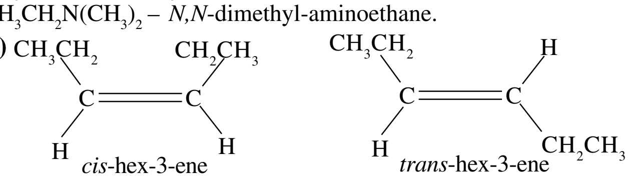
Q2 $CH_3CH_2CHCl_2$ – 1,1-dichloropropane ;
$CH_3CCl_2CH_3$ – 2,2-dichloropropane ;
$CH_3CHClCH_2Cl$ – 1,2-dichloropropane
$CH_2ClCH_2ICH_2Cl$ - 1,3-dichloropropane

Q3 $CH_3CH_2CH_2CH_2CHO$ – pentanal ;
$CH_3CO.CH_2CH_2CH_3$ – pentan-2-one ;
CH_3 $CH_2CO.CH_2CH_3$ – pentan-3-one ;
$CH_3CH_2CH(CH_3)CHO$ – 2-methylbutananal ;
$CH_3CH(CH_3)CH_2CHO$– 3-methylbutananal ;
$CH_3CO.CH(CH_3)CH_3$ – 3-methylbutan-2-one ;
$CH_3C(CH_3)_2CHO$ – 2,2-dimethylpropanal

Q4 $CH_3CH_2CH_2COOH$ – butanoic acid ;
$CH_3CH(CH_3)COOH$ – 2-methylpropanoic acid ;
$CH_3CH_2COOCH_3$ – methyl propanaote ;
$CH_3COOCH_2CH_3$ – ethyl ethanoate ;
$HCOOCH_2CH_2CH_3$ – (1-propyl) methanoate ;
$HCOOCH(CH_3)CH_3$ – (2-propyl) methanoate ;

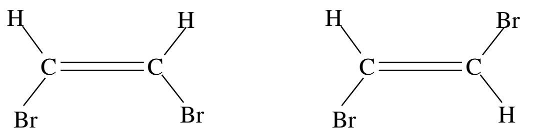
Q5 $CH_3CH_2CH_2CH_2NH_2$ – 1-aminobutane ;
$CH_3CH_2CH(NH_2)CH_3$ – 2-aminobutane ;
$CH_3CH(CH_3)CH_2NH_2$ – 1-amino-2-methylpropane ;
$CH_3C(CH_3)_2NH_2$ – 2-amino-2-methylpropane ;
$CH_3CH_2CH_2NHCH_3$ – *N*-methyl-1-aminopropane ;
$CH_3CH(CH_3)NHCH_3$ – *N*-methyl-2-aminopropane ;
$CH_3CH_2NHCH_2CH_3$ – *N*-ethyl-aminoethane ;
$CH_3CH_2N(CH_3)_2$ – *N,N*-dimethyl-aminoethane.

Q6 (a)



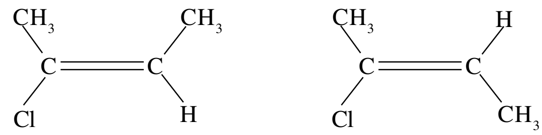
cis-hex-3-ene *trans*-hex-3-ene

(b)



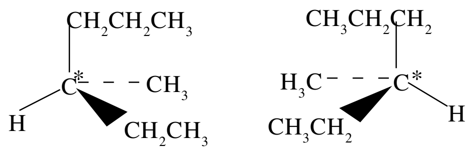
cis-1,2-dibromethane *trans*-1,2-dibromethane

(C)

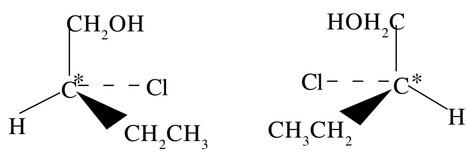


cis-2-chloro-but-2-ene *trans*--2-chloro-but-2-ene

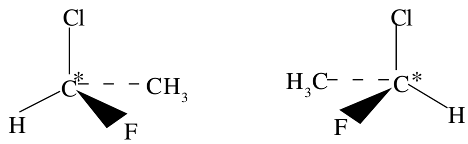
Q7 (a)



(b)



(c)



Practice Questions

1. Which of the following isomers of $C_4H_{11}N$ can exist as optical isomers?
   $CH_3CH_2CH_2CH_2NH_2$ – 1-aminobutane
   $CH_3CH_2CH(NH_2)CH_3$ – 2-aminobutane
   $CH_3CH(CH_3)CH_2NH_2$ – 1-amino-2-methylpropane
   $CH_3C(CH_3)_2NH_2$ – 2-amino-2-methylpropane
   $CH_3CH_2CH_2NHCH_3$ – *N*-methyl-1-aminopropane
   $CH_3CH(CH_3)NHCH_3$ – *N*-methyl-2-aminopropane
   $CH_3CH_2NHCH_2CH_3$ – *N*-ethyl-aminoethane
   $CH_3CH_2N(CH_3)_2$ – *N,N*-dimethyl-aminoethane

   Illustrate your answer with appropriate structures and mark the chiral centre with an asterisk.

2. Draw and name all the isomers of C_3H_5Cl. State the types of isomerism that occur.

3. Draw and name
   (a) a chain isomer of 1-bromobutane

   (b) a positional isomer of 2-bromo-2-methylbutane

   (c) a functional straight-chain isomer (containing a single functional group) of pentanoic acid

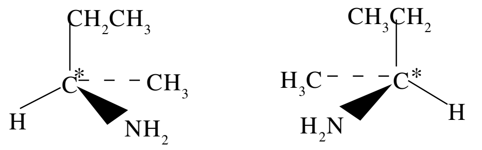
4. Write down the formulae and names of the four alcohols, corresponding to the formula C_4H_9OH, which are structural isomers of one another.

5. Compounds of molecular formula $C_4H_{10}O$ can exhibit skeletal isomerism, positional isomerism, functional group isomerism and stereoisomerism.
   (a) Write down the structural formulae of suitable pairs of compounds that show:
   (i) skeletal isomerism
   (ii) positional isomerism
   (iii) stereoisomerism

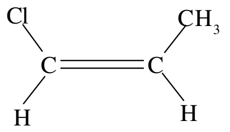
   (b) Explain why it is that compounds of molecular formula $C_4H_{10}O$ can exhibit one kind of stereoisomerism but not another.

Answers

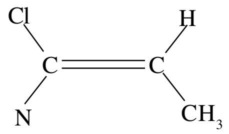
1. $CH_3CH_2CH(NH_2)CH_3$ – 2-aminobutane



2. CH_2=$CHCH_2Cl$ – 3-chloropropene ; CH_2=$CClCH_3$ – 2-chloropropene;



cis-1-chloro-propene



trans-1-chloro-propene

All four are positional isomers of each other but 1-chloroproene also shows geometrical isomerism.

3. (a) $CH_3CH(CH_3)CH_2Br$ – 1-bromo-2-methylbutane

   (b) $CH_3CH(CH_3)CH_2CH_2Br$ - 1-bromo-3-methylbutane
   or $CH_3CH(CH_3)CHBrCH_3$ - 2-bromo-3-methylbutane
   or $CH_2BrCH(CH_3)CH_2CH_3$ - 1-bromo-2-methylbutane

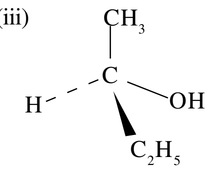
   (c) $CH_3CH_2CH_2CO.OCH_3$ - methyl butanoate
   or $CH_3CH_2CO.OCH_2CH_3$ - ethyl propanoate
   or $CH_3CO.OCH_2CH_2CH_3$ - propyl ethanoate
   or $HCO.OCH_2CH_2CH_2CH_3$ - butyl methanoate

4. $CH_3CH_2CH_2CH_2OH$ - butan-1-ol
   $(CH_3)_2CHCH_2OH$ - 2-methylpropan-1-ol
   $CH_3CH(OH)CH_2CH_3$ - butan-2-ol
   $(CH_3)_3COH$ - 2-methylpropan-2-ol

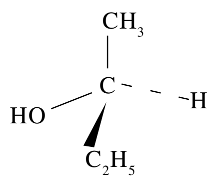
5. (a) (i) $CH_3CH_2CH_2CH_2OH$ and $(CH_3)_2CHCH_2OH$
   or $(CH_3)_3COH$ and $CH_3CH(OH)CH_2CH_3$

   (ii) $CH_3CH_2CH_2CH_2OH$ and $CH_3CH(OH)CH_2CH_3$
   or $(CH_3)_2CHCH_2OH$ and $(CH_3)_3COH$

   (iii)



and



   (b) Butan-2-ol has a chiral centre / asymmetric C atom ∴ can exhibit optical isomerism / exist in two non-superimposable forms
   but none of the compounds has a C = C bond (or other structural feature) which can cause restricted rotation of atoms
   ∴ there is no possibility of geometrical isomerism / existence of *cis* and *trans* isomers

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