

Isomerism in Alcohols

This Factsheet is designed to cover all aspects of the isomerism of alcohols across both AS and A2 syllabuses. As a consequence, parts of the factsheet would not be examined at AS level but may prove of interest to those AS students wishing for a more complete understanding of chemistry.

In general, AS questions will concern themselves with the drawing and naming of structural isomers and E-Z isomers. Optical isomers (enantiomers) are introduced at A2.

Nomenclature

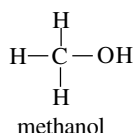
An alcohol must contain an **-OH** group (its functional group – the part of a molecule responsible for its reactions) and its name will end with the suffix **-ol**. (However, when further functional groups are introduced at A2 it is sometimes necessary to name the **-OH** group as though it were a side-group. In this case the presence of an alcohol is denoted by the prefix **hydroxy-**).

Simple alcohols

The naming of all organic substances under the IUPAC system is based on the method of naming **alkanes**. You should, therefore, know the prefixes **meth-**, **eth-**, **prop-** and **but-** which indicate the presence of 1, 2, 3 and 4 carbon atoms respectively in the chain. After this the prefixes continue as **pent-**, **hex-**, **hept-**, **oct-**, **non-** and **dec-** much as they would when naming polygons in mathematics. In general, however, A level questions rarely stray into chains longer than 6 carbon atoms.

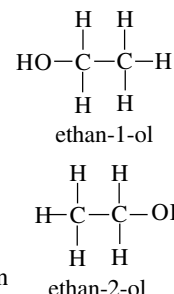
methane CH ₄	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$	
ethane C ₂ H ₆	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	
propane C ₃ H ₈	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	
butane C ₄ H ₁₀	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	

An alcohol of five carbon atoms in length is therefore pentan(e)-ol but the **e** is dropped to make the name less awkward to say.

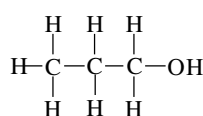


The general rule for isomers is that the shorter the carbon chain, the fewer isomers there can be. The simplest alcohol is methanol and it clearly has no possible isomers. It is unnecessary to write methan-1-ol as there is only one carbon atom that the **-OH** group could be bonded to. It is tempting (but incorrect) to think that there could be two isomers of ethanol since there are two carbon atoms to which the **-OH** group could be bonded.

In practice these molecules are merely rotations of each other. Since whichever carbon atom the **-OH** group is bonded to should be considered to be carbon 1 it is unnecessary to number them and the correct name would simply be ethanol. There are no isomers of ethanol **that are also alcohols**.

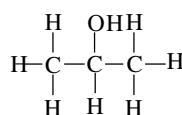


However, alcohols with carbon chains longer than two will always have isomers.



propan-1-ol

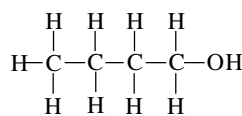
There are only two alcohol isomers with 3 carbons since carbon 1 and carbon 3 are equivalent.



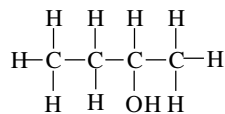
propan-2-ol

Both these isomers are propanol and so to distinguish between them we name the position of the functional group. Therefore, if the **-OH** group is bonded at either end of the chain it is propan-1-ol, but in the centre it is propan-2-ol.

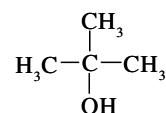
Examination questions are likely to ask you to distinguish between **primary, secondary and tertiary alcohols**. Since the **-OH** group can bond to only one carbon atom, we must look at exactly how many carbon atoms are bonded to the carbon atom bearing the **-OH** group. This can be illustrated using the isomers of butanol.



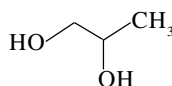
Butan-1-ol is **primary** because C1 is bonded to **only one** other carbon atom (C2). (Methanol is also primary, although in this case C1 is bonded to no other carbon atoms).



Butan-2-ol is **secondary** because C2 is bonded to **two** other carbon atoms (C1 and C3).



Methylpropan-2-ol is **tertiary** because C2 is bonded to **three** other carbon atoms (C1, C3 and the methyl group).



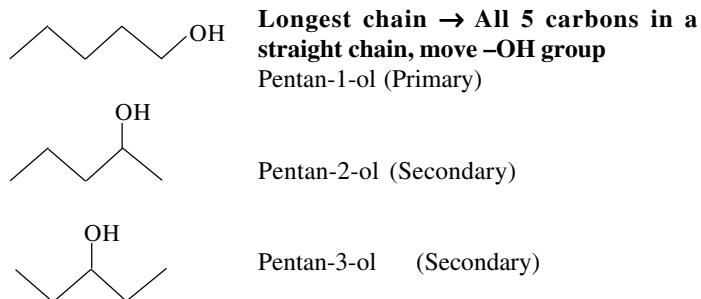
Isomers could also have more than one alcohol group. The example shown would be propan-1,2-diol (note the "e" is usually included in the cases of diols and triols).

There would also be propan-1,1-diol, propan-1,3-diol and propan-2,2-diol. Once the carbon chain is made longer the number of isomers increases dramatically and so it is unlikely that you would be expected to find all the diols (or triols) of a five or six membered chain.

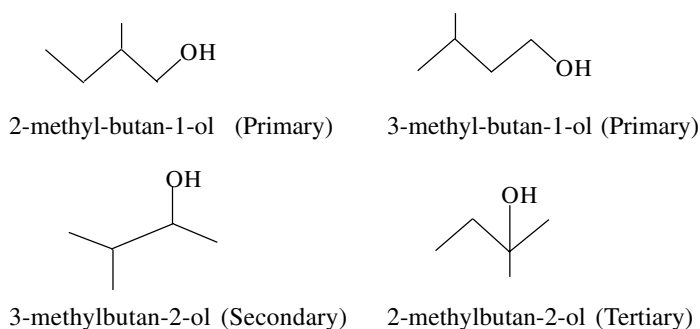
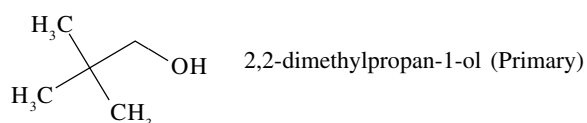
Working out structural isomers.

- To find **all** the structural isomers you must be systematic and it can be quicker to draw *skeletal* formulae, even if you then have to draw the full *displayed* formulae to satisfy the question.
- Start with the longest chain and move the functional group from carbon atom 1 to every other *non-equivalent* carbon atom. **Take care not to accidentally draw the same isomer twice.** (Count carbon atoms from the end closest to the –OH group – make sure you identify the longest chain)
- Shorten the chain by one carbon atom and move the methyl group **and** –OH group
- Shorten the chain again. If the chain is long enough it may be that you need to consider possible *ethyl* side-groups as well as *methyl* groups

Note: You are very unlikely to be asked to do this for alcohols longer than 5 because there are too many possible isomers.

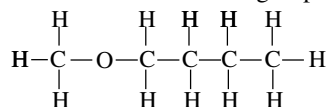
Isomeric e.g the Alcohols of Pentanol**Note:**

There are no further straight chain isomers because pentan-4-ol = pentan-2-ol and pentan-5-ol = pentan-1-ol

Shorten the chain → 4 carbon atoms in chain with 1 methyl group. Move both groups systematically.**Shorten the chain again → 3 carbon atoms in chain with 2 methyl groups.**

These are the only isomers of $C_5H_{11}OH$ that are alcohols that you would expect to be able to name at AS. There will also be isomers that are not alcohols (*functional group isomers*) and it is possible that you might be asked to draw them but not to name them. There are also optical isomers (enantiomers) of $C_5H_{11}OH$ but these would only be required at A2.

The functional group isomers of alcohols are called ethers and contain a C-O-C functional group.

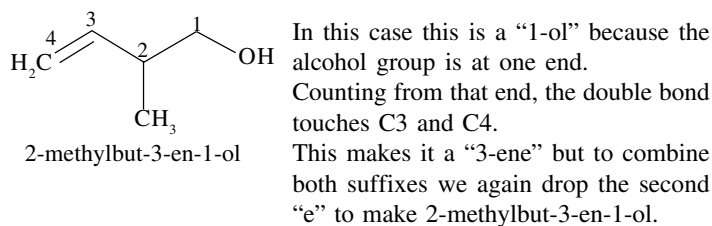


It is not impossible to draw such molecules at AS but, as ethers are not on AS syllabuses you would not need to be able to name them. In fact the one shown is called 1-methoxybutane. There would be several other isomers of this kind so questions will generally ask you only to draw isomers that **are** alcohols.

Stereoisomers

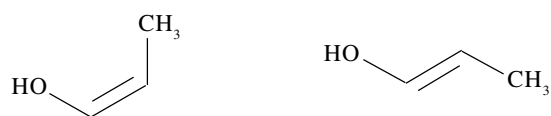
Isomers which have their atoms bonded in a different order are structural isomers. If their order is the same, but the only difference is the spatial orientation of the bonds they are stereoisomers. For alcohols there can be two types; *E-Z isomerism* and *optical isomerism*.

At AS we study E-Z isomerism of alkenes. It is perfectly possible for a molecule to be both an alkene **and** an alcohol. To name these we would have to give the position of both the alcohol functional group and the double bond. It is usual to start counting carbon atoms from the end bonded to the –OH group. The number ascribed to the double bond is the lower of the two carbon atoms it touches



The molecular formula of 2-methylbut-3-en-1-ol is $C_5H_{10}O$ so, as well as other structural isomers, it also has isomers such as pentanal and pentan-2-one as well as other carbonyls. It is unlikely that you would be asked to draw many isomers of unsaturated alcohols for this reason. This particular unsaturated alcohol would not show EZ isomerism because both groups bonded to C4 are hydrogen atoms.

However, A level questions concerning unsaturated alcohols are likely to concern E-Z isomerism and to ask you to name them.

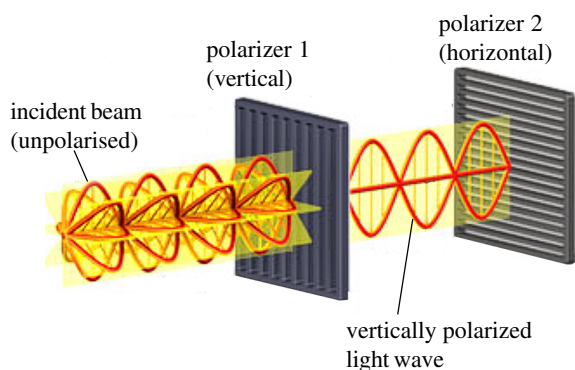


Both these molecules are prop-1-en-1-ol. Which one is the E and which one is the Z isomer?

The way to work this out is to look at the atomic mass of the groups on each carbon of the C=C bond. On both C1 and C2 the hydrogen atoms are the lighter groups. They have a lower priority. So the molecule on the left has the high priority groups on the same side of the double bond and is therefore Z-prop-1-en-1-ol whereas on the right the higher priority groups are across the double bond making this molecule E-prop-1-en-1-ol.

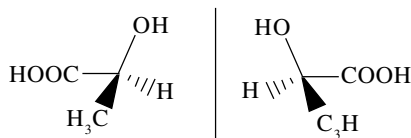
Older textbooks may still refer to these as *cis-trans isomers* but this is not the required nomenclature in this context for A level and it should be avoided. The terms “cis” and “trans” is now used only for transition metal complexes.

Optical Isomers (A2 only)



Optical isomers (enantiomers) are mirror images of each other. They are non-superimposable in much the same way as your left and right hand. There are few differences in their chemistry but, if separated, one will rotate plane-polarised light in a clockwise direction and the other anticlockwise – hence optical. For non-physics students, normal light is emitted with waves at every possible angle to the vertical plane. But passing it through a polaroid will cut out all angles except one – this is now plane-polarised light. This angle will be changed when the polarised light passes through a single enantiomer. But mixed together the two enantiomers form a **racemic** mixture (50/50 mix) and light would appear to pass through unchanged.

Due to the different spatial arrangement of bonds one enantiomer may have a positive effect on the human body (perhaps by binding to an active site on a protein), the different shape of the second enantiomer means it will not fit this site. Famously, one enantiomer of Thalidomide reduces nausea, the other enantiomer causes severe birth defects, though more usually the second enantiomer of an optically active drug is simply inactive.

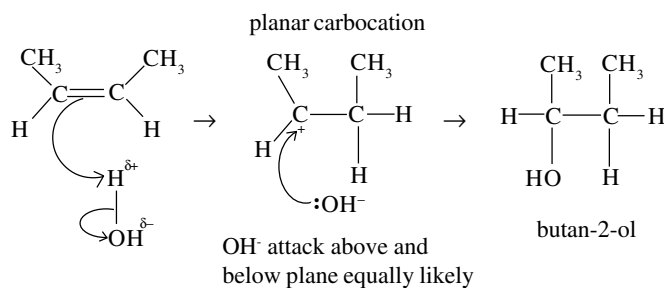


These two alcohols are enantiomers of each other. Both are also carboxylic acids and so the alcohol group would be named as a hydroxy side group. The wedges and dots show bonds out of and into the plane of the paper respectively. You would not be expected to know which isomer rotates light in which direction but might be expected to name either (or both) as 2-hydroxypropanoic acid. You would certainly be expected to be able to draw one isomer given the structure of the first, and to be able to indicate the chiral carbon atom – the central carbon atom responsible for this type of isomerism. To find a chiral carbon atom you simply need to find a carbon atom bonded to 4 different groups. In this case to a methyl group, a hydrogen atom, an acid group and the -OH group.

To draw the other enantiomer quickly you can simply swap over the groups bonded at the wedge and dots.

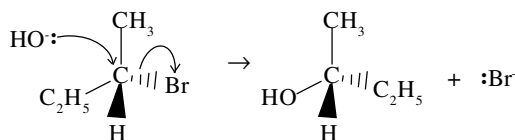
How do Optically Active Alcohol Isomers Form?

One way is **electrophilic addition to alkenes**. You should know that the intermediate carbocation has trigonal planar symmetry (120° bond angle). The attacking OH^- has a 50% chance of attacking from above the plane or below.



The answer to an AS question “Name the isomers made when but-2-ene undergoes electrophilic addition with steam” would be butan-1-ol and butan-2-ol. However, the same question at A2 would require both these answers and also an explanation that there are two enantiomers of butan-2-ol that should form in a racemic mixture.

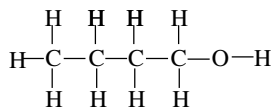
The same two optically active alcohols could also form from but-2-ene if it were to react with hydrogen bromide to form two enantiomers of 2-bromobutane which could then undergo nucleophilic substitution with OH^- . However, if one were to start with a single enantiomer of 2-bromobutane a single enantiomer of butan-2-ol would form.



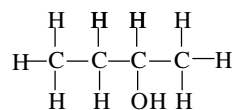
Differences between Isomeric Alcohols

Physical Differences

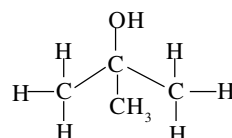
In an examination the main physical difference between alcohols which are structural isomers is likely to concern boiling points. An example would be the alcohol isomers of $\text{C}_4\text{H}_9\text{OH}$.



Butan-1-ol has a boiling point of 180°C . As with all alcohols this is higher than the equivalent alkane of the same mass due to the presence of hydrogen bonds between molecules.



Butan-2-ol has the same molecular mass so we can assume it should form Van der Waals forces of similar strength. It can also hydrogen bond but boils at only 98°C .



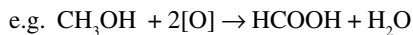
Methylpropan-2-ol should also form Van der Waals forces and hydrogen bonds in the same way but boils at an even lower 83°C .

The only way to account for the differences in boiling point is some sort of decrease in the strength of intermolecular force. In this case it is because the more branched the structure the further apart the molecules are forced to stay. Electrostatic forces become weaker over greater distances (as do gravity and magnetic forces) so the higher boiling point in butan-1-ol is entirely due to the smaller space between its molecules compared to that of other isomers. Straight-chain isomers will always have the higher boiling point.

Chemical Differences

You should know that different classes of alcohol have different chemistry with *oxidising agents*.

At A level the oxidising agent of choice is usually acidified potassium dichromate solution ($K_2Cr_2O_7$) or potassium manganate VII ($KMnO_4$). In either case, AS and A2 questions will tend to use the [O] notation to represent the oxidising agent, and you should be able to balance such equations, remembering that water is always produced.



You should know:

- Tertiary alcohols cannot be oxidised
- Secondary alcohols can be oxidised but only as far as ketones.
- Primary alcohols may be oxidised to aldehydes and on to carboxylic acids.

In this way it is possible to distinguish between primary, secondary and tertiary alcohols by their effect on the oxidising agent. To do so you should also recall

- The colour changes associated with the oxidising agent
- How it is possible to stop the oxidation of primary alcohols at the aldehyde stage.

Example

Three isomers of $C_4H_{10}OH$ that are isomers are refluxed with acidified potassium dichromate solution. After ten minutes the reaction mixture containing isomer A is orange. The mixtures containing isomers B and C are both green. After distillation to isolate the organic product, sodium carbonate solution is added to both and bubbles are observed in isomer C. Identify the three isomeric alcohols.

A is not oxidised since the solution remains orange. Hence, A is a tertiary alcohol.

B is oxidised since the solution turns green but the product is non-acidic even though it has been refluxed for 10 minutes. Hence, B is a secondary alcohol.

C is also oxidised and an acid is produced since the product displaces CO_2 from carbonate. Hence, C is a primary alcohol.

Acknowledgements: This Factsheet was researched and written by Paul Swainson.

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