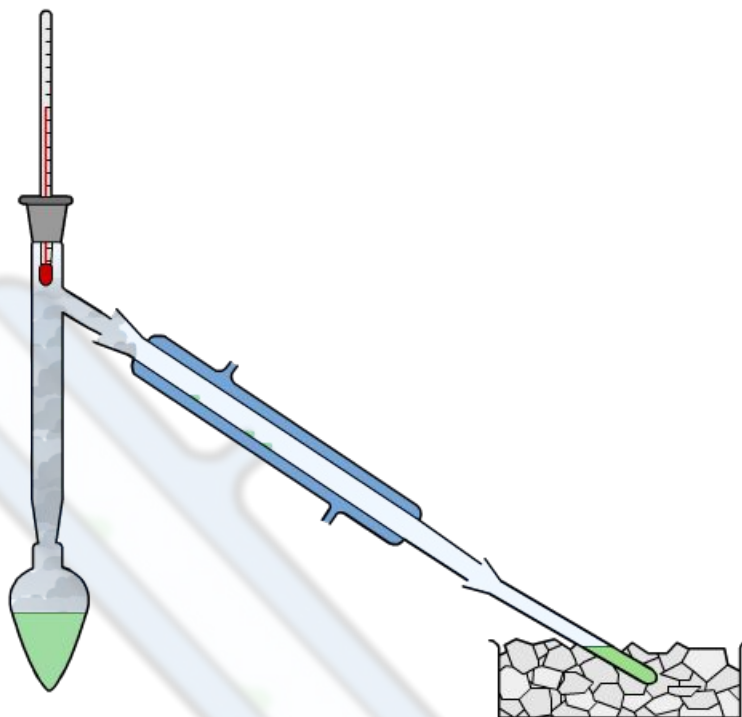


Alcohols



Alcohols

Nomenclature and production

Oxidation

Other reactions

Summary activities



What are alcohols?

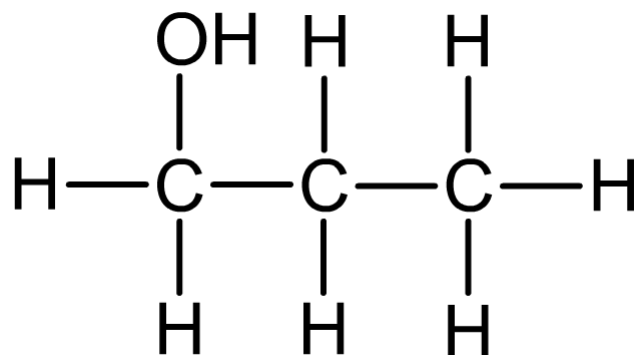
Alcohols are a **homologous series** of organic compounds with the general formula $C_nH_{2n+1}OH$ and names ending **-ol**.

The functional group in alcohols is the **hydroxyl group**: $-OH$.

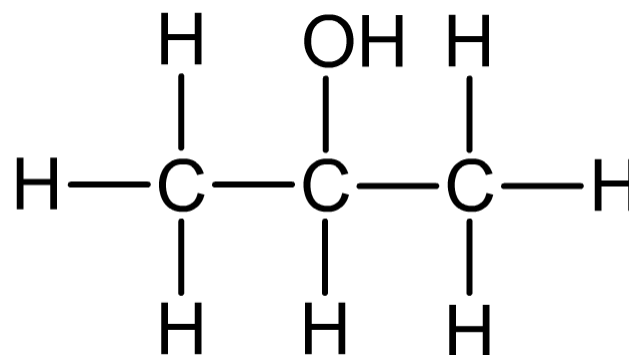
No. of carbon atoms	Molecular formula	Name
1	CH_3OH	methanol
2	C_2H_5OH	ethanol
3	C_3H_7OH	propanol
4	C_4H_9OH	butanol
5	$C_5H_{11}OH$	pentanol
6	$C_6H_{13}OH$	hexanol

Naming alcohols

Alcohols with three or more carbon atoms display **positional isomerism**. The number of the carbon to which the hydroxyl groups is attached is written before the *-ol*.



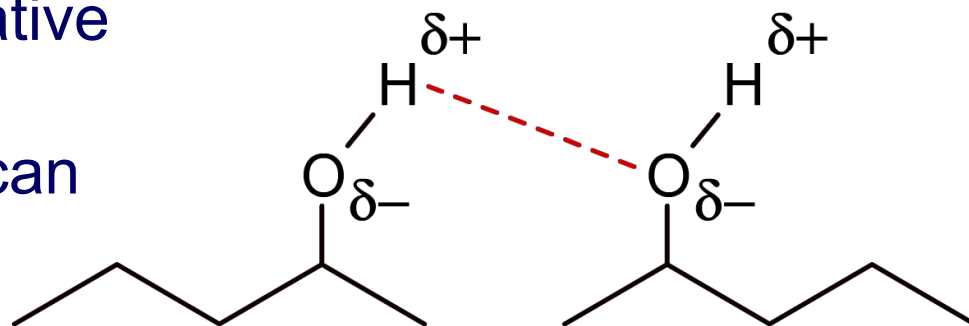
propan-1-ol



propan-2-ol



The presence of the hydroxyl group with its electronegative oxygen atom means that alcohols are polar. They can therefore take part in hydrogen bonding.



Hydrogen bonding between alcohol molecules means that an alcohol's boiling point is higher than that of an alkane of similar molecular mass. For example, methanol ($M_r = 32$) boils at 64.7°C but ethane ($M_r = 30$) boils at -88.6°C .

Alcohols can mix with water because their molecules can form hydrogen bonds with water molecules.



Alcohol has been produced by fermentation of sugars for thousands of years.

Sugar from fruit or grains such as wheat and barley is mixed with yeast and water, which produces ethanol and other compounds.



Industrially, sugar cane, molasses (a product of refining sugar cane) or starch (from potatoes or corn) can be used for fermentation.

The product is a mixture of water and about 15% ethanol by volume. No more alcohol is produced because the yeast is denatured by the alcohol.

Distillation can be used to remove most of the water from the ethanol.



Production of ethanol from ethene



Fermentation vs. hydration



Alcohols

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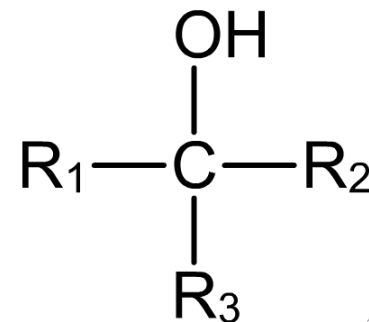
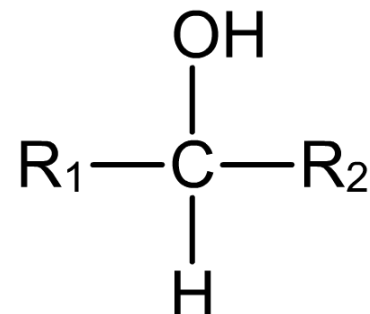
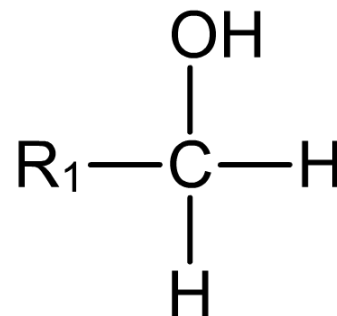
Summary activities



Primary, secondary and tertiary

A chain of carbon atoms can be represented by R when drawing the structure. This is referred to as an **R group**.

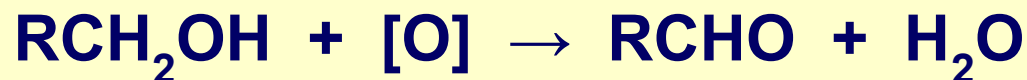
- **Primary (1°) alcohols** have one R group attached to the carbon to which the OH group is attached.
- **Secondary (2°) alcohols** have two R groups attached to the carbon to which the OH group is attached.
- **Tertiary (3°) alcohols** have three R groups attached to the carbon to which the OH group is attached.



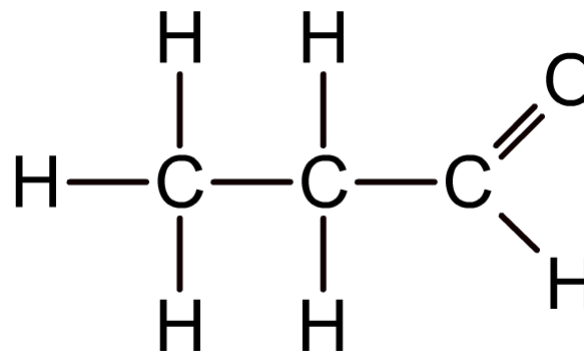
Oxidation of 1° alcohols: aldehydes

Primary alcohols can be oxidized to **aldehydes** by an oxidizing agent such as an aqueous solution of acidified potassium dichromate(VI).

When the symbol equation is written, the oxidizing agent is represented by [O]:



Aldehydes contain a carbonyl group (C=O) at the end of the carbon chain, and are named using the suffix *-al*.



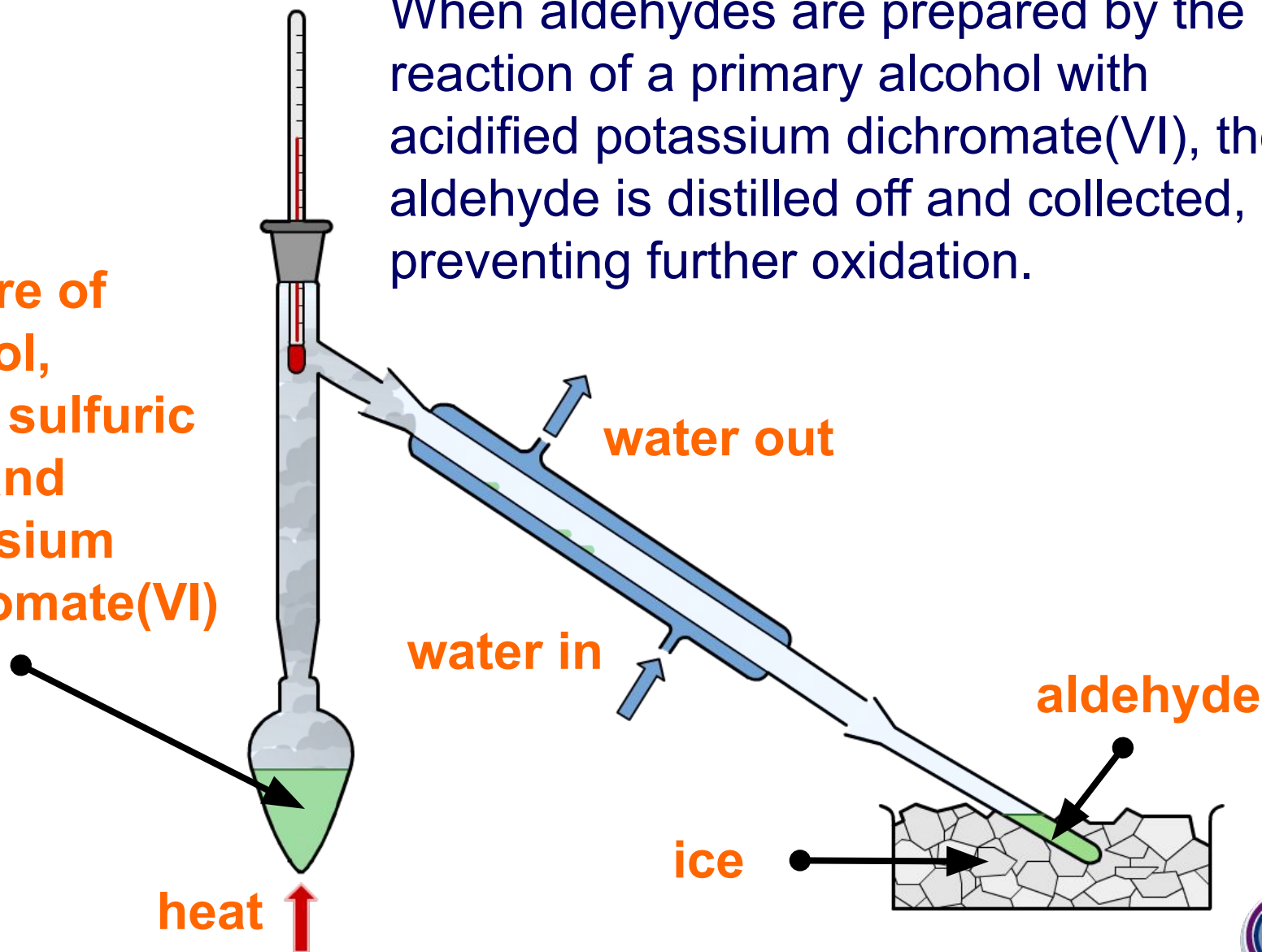
propanal



Synthesis of aldehydes

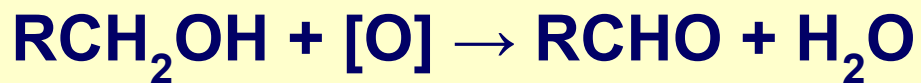
When aldehydes are prepared by the reaction of a primary alcohol with acidified potassium dichromate(VI), the aldehyde is distilled off and collected, preventing further oxidation.

mixture of alcohol, dilute sulfuric acid and potassium dichromate(VI)



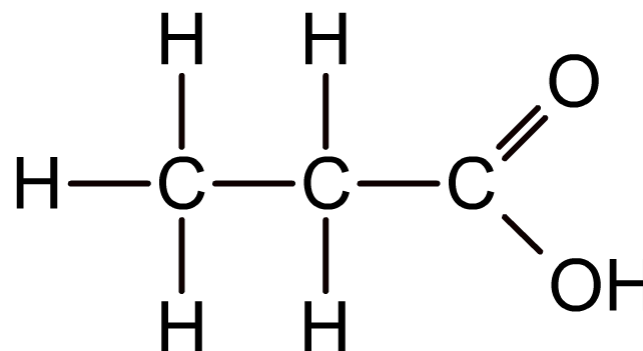
Oxidation of 1° alcohols: carboxylic acids

If primary alcohols are reacted with an excess of oxidizing agent and **refluxed**, they can be oxidized to aldehydes and then oxidised further to **carboxylic acids**.



Carboxylic acids contain a carbonyl group ($\text{C}=\text{O}$) at the end of the carbon chain, with a hydroxyl group (OH) attached to the carbonyl carbon.

Carboxylic acid are named using the suffix *-oic acid*.



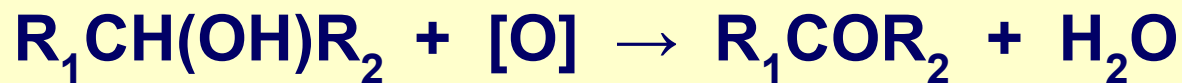
propanoic acid



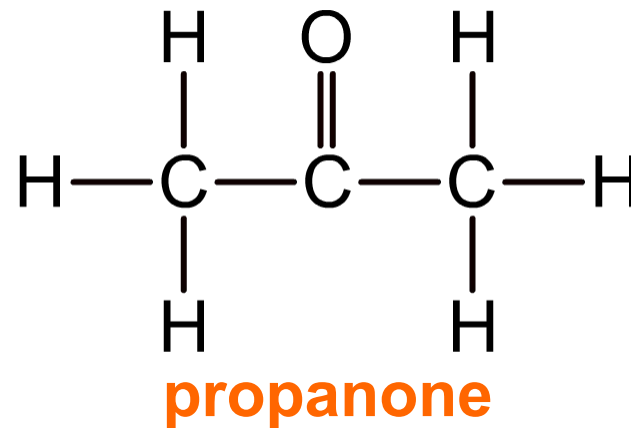
Synthesis of carboxylic acids



Secondary alcohols can be oxidized to **ketones** by an oxidizing agent such as an aqueous solution of acidified potassium dichromate(VI).



Ketones contain a carbonyl group (C=O) attached to any carbon in the chain except a terminal carbon atom, and are named using the suffix *-one*.



Tertiary alcohols are resistant to oxidation due to the lack of hydrogen atoms on the carbon atom to which the hydroxyl group is attached.

Aldehyde, ketone or carboxylic acid?



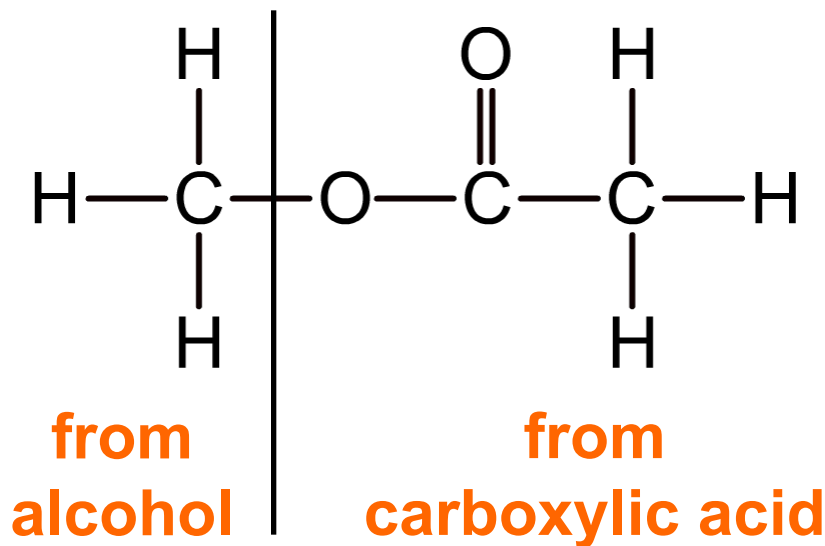
Distinguishing aldehydes and ketones



Esterification involves refluxing a carboxylic acid and an alcohol with a concentrated sulfuric acid catalyst.



The names of esters have two parts: the first is an alkyl group (from the alcohol) and the second is a carboxylate group (from the carboxylic acid).



For example, methanol and ethanoic acid react to form methyl ethanoate.



Oxidation of alcohols

Alcohols

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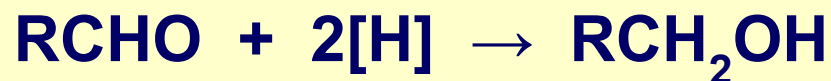
Summary activities

Making alcohols from aldehydes/ketones

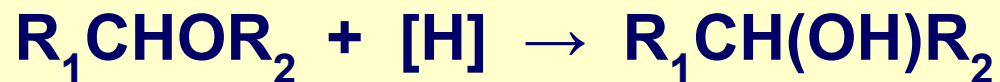
Aldehydes and ketones can be reduced by a reducing agent, such as sodium borohydride (NaBH_4), to form alcohols.

When the symbol equation is written, the reducing agent is represented by $[\text{H}]$.

Aldehydes are reduced to primary alcohols:



Ketones are reduced to secondary alcohols:



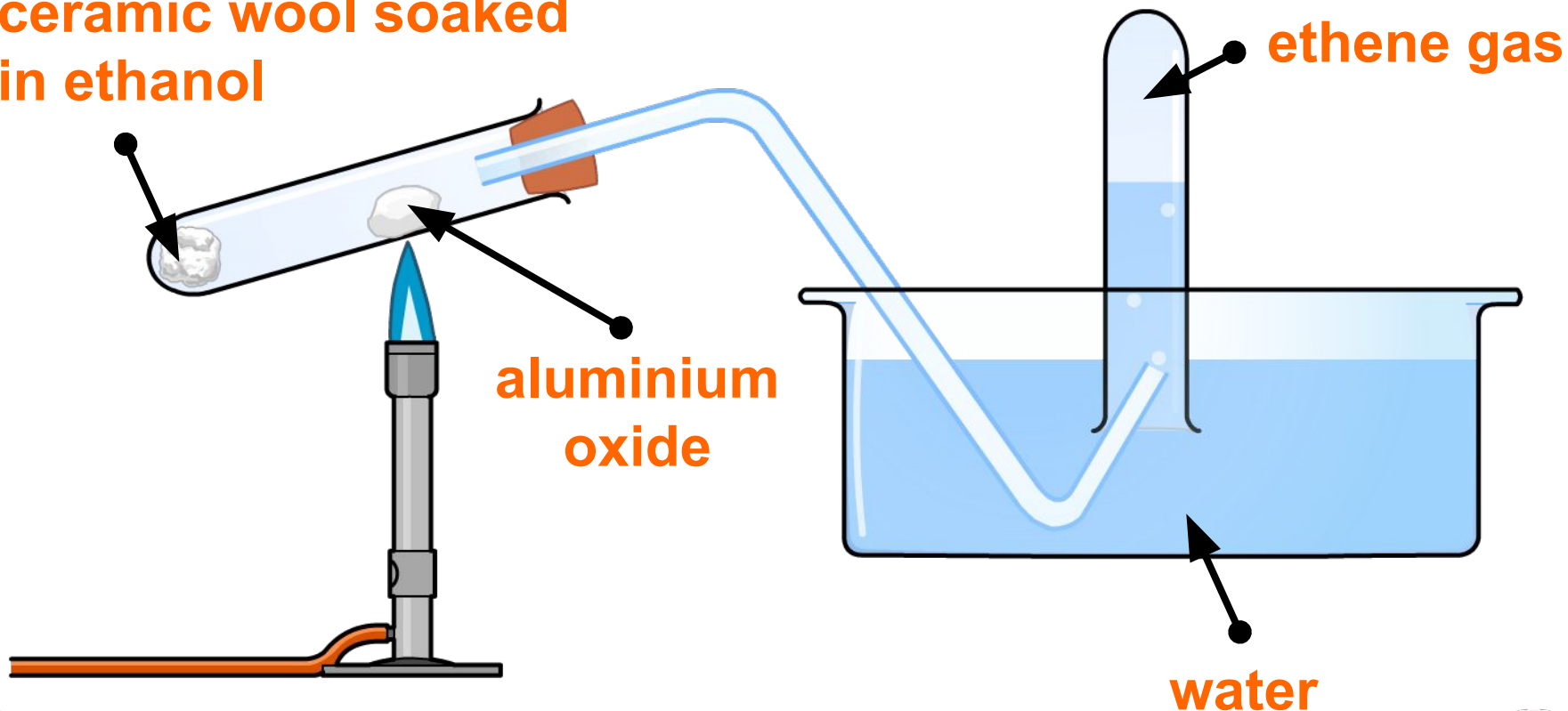
Synthesis of ethene from ethanol



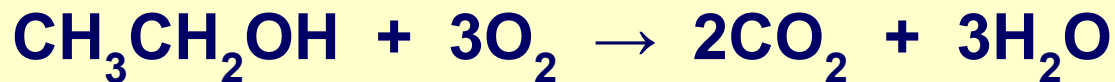
Dehydration of ethanol in the lab

In the lab, dehydration of ethanol can be achieved by passing ethanol over a hot aluminium oxide catalyst. Ethene gas is collected by displacement.

ceramic wool soaked
in ethanol



Alcohols undergo complete combustion to form carbon dioxide and water.



Denatured alcohol is ethanol that has been made toxic and undrinkable by the addition of other chemical additives. A traditional additive was methanol, which formed **methyated spirits** (meths): 90% ethanol and 10% methanol.

Denatured alcohol is a useful portable fuel (e.g. for camping stoves) as, unlike LPG, it does not need to be transported in heavy, specialized containers. It is also used as a solvent.

Reaction with sodium



Forming halogenoalkanes from alcohols

Primary, secondary and tertiary alcohols all react with phosphorus(V) chloride to form a chloroalkane. For example:



Adding solid phosphorous(V) chloride to an alcohol at room temperature produces white HCl fumes, as well as the chloroalkane.

This reaction can be used as a test for alcohols (the OH group), as well as a method of producing halogenoalkanes.



Alcohols

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What's the keyword?



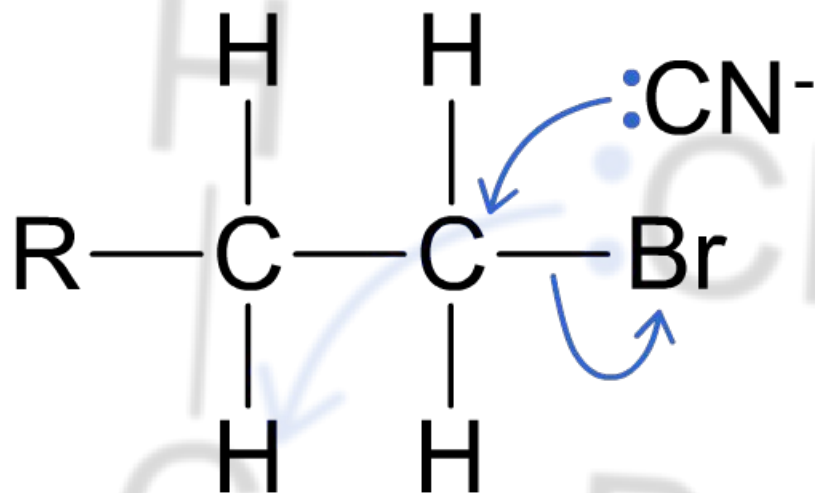
What's the structure?



Multiple-choice quiz



Halogenoalkanes



Halogenoalkanes

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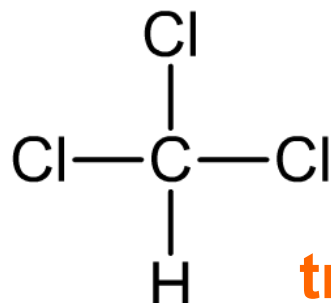
Nucleophilic substitution reactions

Elimination reactions

Summary activities

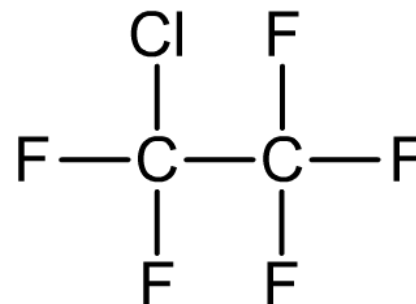
What are halogenoalkanes?

Halogenoalkanes are similar to alkanes but with one or more of the hydrogen atoms replaced by a halogen.



trichloromethane

Halogenoalkanes can contain more than one type of halogen. For example, **CFCs (chlorofluorocarbons)** contain both chlorine and fluorine atoms.



chloro-pentafluoroethane

Some halogenoalkanes are useful themselves, but many are valuable intermediates in the production of other molecules.

Naming halogenoalkanes

A prefix is added to the name of the alkane depending on what halogens are attached.

halogen	prefix
fluorine	fluoro-
chlorine	chloro-
bromine	bromo-
iodine	iodo-

no. halogen atoms	prefix
one	—
two	di-
three	tri-
four	tetra-
five	penta-

Another prefix is used to indicate how many atoms of each halogen is present.

Numbers are used, where necessary, to indicate to which carbon atom(s) each halogen is attached.

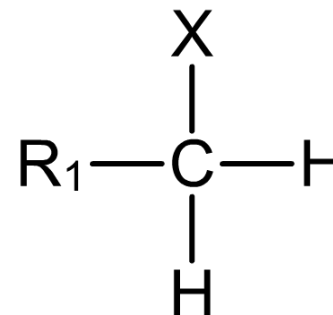
What's the halogenoalkane?



A chain of carbon atoms can be represented by R when drawing the structure. This is referred to as an **R group**.

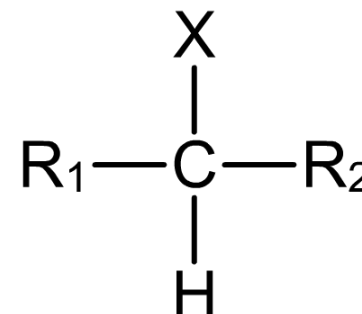
- **Primary (1°) halogenoalkanes**

have one R group attached to the carbon linked to the halogen.



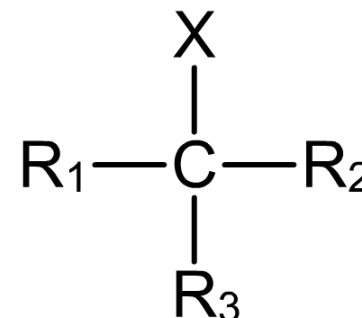
- **Secondary (2°) halogenoalkanes**

have two R groups attached to the carbon linked to the halogen.



- **Tertiary (3°) halogenoalkanes**

have three R groups attached to the carbon linked to the halogen.



Primary, secondary or tertiary?



Halogenoalkanes

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Nucleophilic substitution reactions

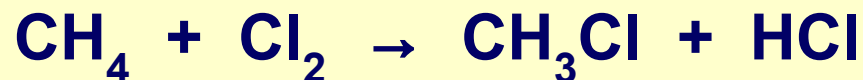
Elimination reactions

Summary activities

How are halogenoalkanes made?

There are several ways by which halogenoalkanes can be made, including:

- **free radical substitution** of an alkane:



- **electrophilic addition** of HX or X₂ to an alkene:

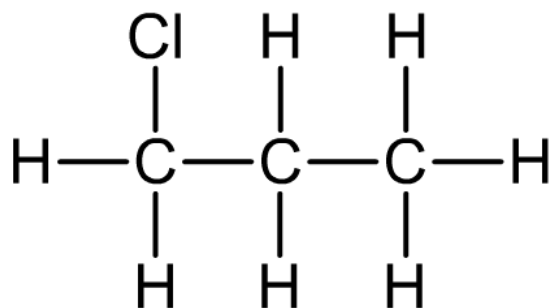


Free radical substitution: $\text{Cl}_2 + \text{CH}_4$

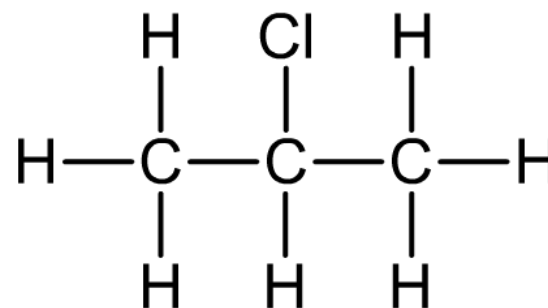


Other products of chain reactions

If an alkane is more than two carbons in length then any of the hydrogen atoms may be substituted, leading to a mixture of different isomers. For example:



1-chloropropane

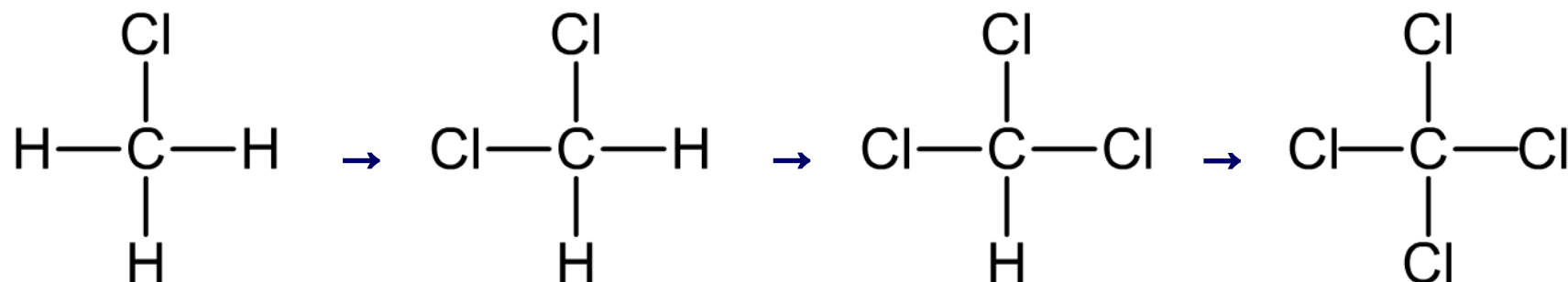


2-chloropropane

The mixture of products is difficult to separate, and this is one reason why chain reactions are not a good method of preparing halogenoalkanes.

Further substitution in chain reactions

Some chloromethane molecules formed during free radical substitution between methane and chlorine will undergo further substitution to form dichloromethane. Further substitution can occur until all hydrogens are substituted.



The further substituted chloroalkanes are impurities that must be removed. The amount of these molecules can be decreased by reducing the proportion of chlorine in the reaction mixture.

Chain reactions and ozone



Free radical reactions: true or false?



Halogenoalkanes

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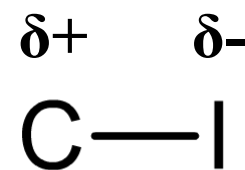
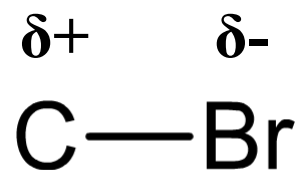
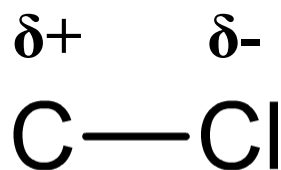
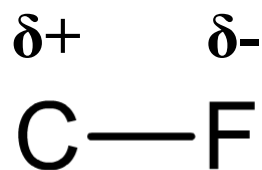
Nucleophilic substitution reactions

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Summary activities

Polar bonds and nucleophiles

The carbon–halogen bond in halogenoalkanes is polar because all halogens are more electronegative than carbon.



The polar bond means that the carbon atom has a small positive charge ($\delta+$), which attracts substances with a lone pair of electrons. These are **nucleophiles**, meaning ‘nucleus (positive charge) loving’. Examples include:



ammonia



cyanide



hydroxide

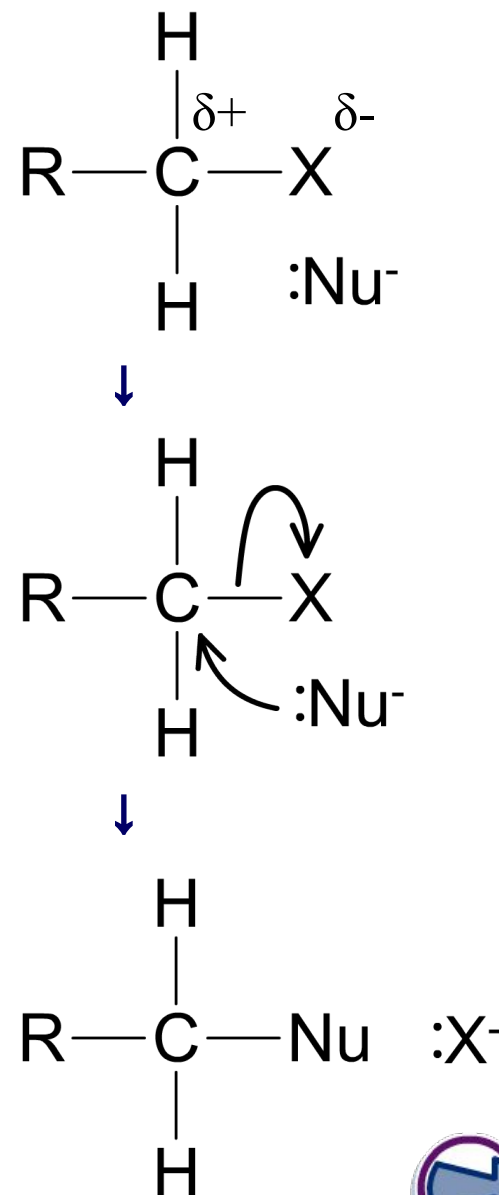
Reaction with nucleophiles

Nucleophiles (Nu^-) attack the carbon of a carbon–halogen ($\text{C}-\text{X}$) bond, because the electron pair on the nucleophile is attracted towards the small positive charge on the carbon.

The electrons in the $\text{C}-\text{X}$ bond are repelled as the Nu^- approaches the carbon atom.

The Nu^- bonds to the carbon and the $\text{C}-\text{X}$ bond breaks. The two electrons move to the halogen, forming a halide ion.

The halide is substituted, so this is a **nucleophilic substitution reaction**.



Nucleophilic substitution reactions



Rate of nucleophilic substitution

The rate of a nucleophilic substitution reaction depends on the strength of the carbon–halogen bond rather than the degree of polarization in the bond.

Bond	Strength (kJ mol ⁻¹)
C–F	484
C–Cl	338
C–Br	276
C–I	238

The C–I bond is the weakest and so most readily undergoes nucleophilic substitution. The rate of reactions involving iodoalkanes is the highest.

Nucleophilic substitution



Halogenoalkanes

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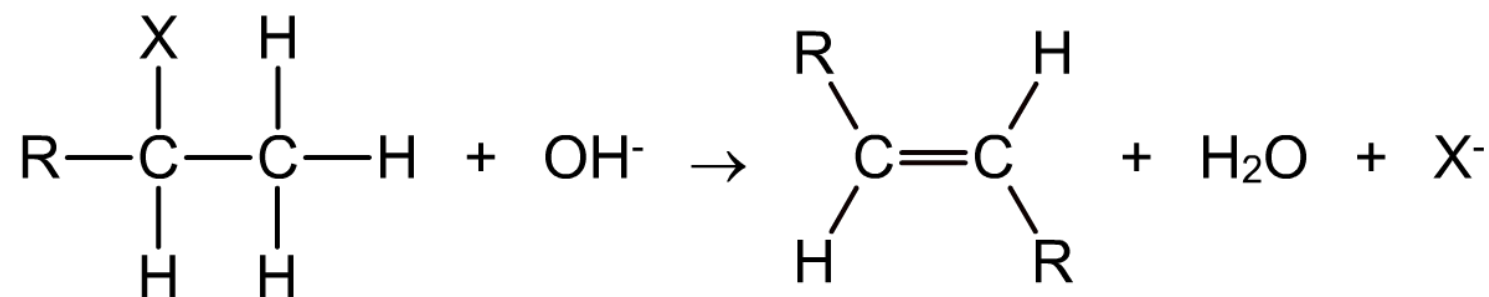
Nucleophilic substitution reactions

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Elimination in halogenoalkanes

In the reaction with a strong base, halogenoalkanes will undergo not only nucleophilic substitution but also **elimination reactions**, forming alkenes and water.



The OH^- acts as both a base and a nucleophile. When acting as a base, the OH^- removes H^+ from the halogenoalkane, which also results in the formation of a halide ion.

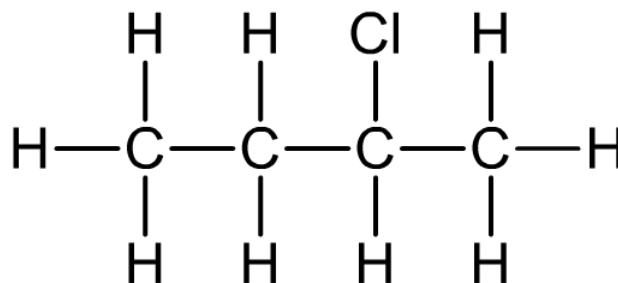
The reaction between a halogenoalkane and a strong base usually results in the formation of a mixture of substitution and elimination products.

Elimination mechanism



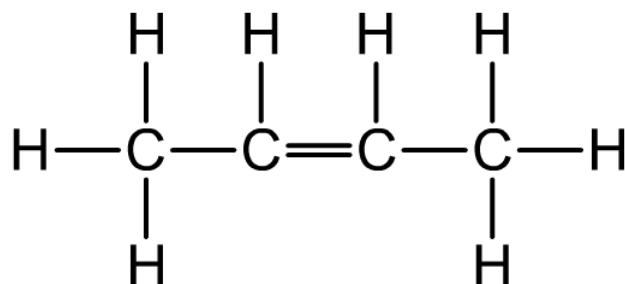
Mixture of elimination products

If the carbon chain is four or more carbons in length and the halogen is not attached to a terminal carbon, a mixture of positional isomers may be formed.



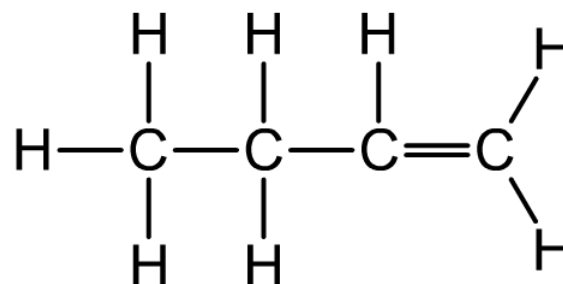
A **B**

attack at A



but-2-ene

attack at B



but-1-ene

The conditions for the reaction that favour substitution or elimination are different.

- **Base strength:** the stronger the base used, the more elimination is favoured. Sodium hydroxide in aqueous solution contains OH^- , but when dissolved in ethanol, $\text{CH}_3\text{CH}_2\text{O}^-$ is also present, which is a stronger base.

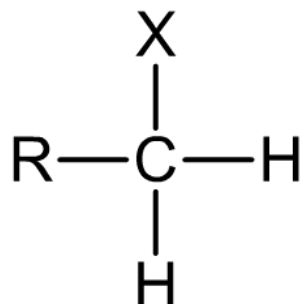
Therefore elimination is favoured by NaOH in ethanolic solution, and substitution is favoured by NaOH in aqueous solution.

- **Temperature:** elimination is favoured at hotter temperatures whereas substitution is favoured by warm conditions.

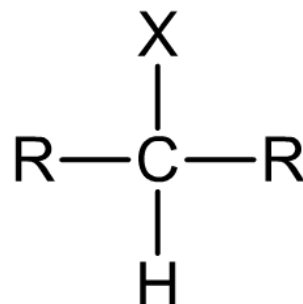


Primary, secondary or tertiary?

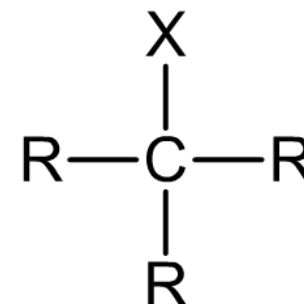
Primary halogenoalkanes favour substitution whereas tertiary halogenoalkanes favour elimination.



primary



secondary



tertiary

substitution more likely

elimination more likely

Elimination or substitution?



Halogenoalkanes

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What's the keyword?



Multiple-choice quiz

