

AS Organic Chemistry Notes

Typed version of Fahad Hameed's handwritten AS Organic Chemistry notes for Cambridge International AS Level Chemistry (9701). Every page of the original is typed in the same order, with drawn structures named and written as formulae, and drawn mechanisms written as numbered steps, so the notes can be searched and copied. The handwritten original is on the same page of megalecture.com.

Organic Chemistry

Carbon compounds → living organisms (plants / animals).

Arrows lead from here to:

- food
- fossil fuels
- pharmaceutical
- agriculture

Formulas

1. Molecular formula

Total number of atoms of elements in a compound.

$C_4H_8O_2$, $C_6H_{12}O_6$. No information about structure.

2. Structural formula

Provides information about the **structure**.

(a) Full displayed formula

Every single atom / bond is shown.

- C: 4 bonds
- N: 3 bonds
- O: 2 bonds
- H: 1 bond
- halogens: 1 bond

Example drawn in full, with every C, H and O and every bond shown: 4-hydroxybutan-2-one, $CH_3COCH_2CH_2OH$.

A displayed formula is not the actual shape. Two small sketches show the real shapes: a carbon with four single bonds (one drawn as a wedge, one as a dashed line) with a bond angle of 109.5° , and a carbon with a double bond ($C=$) with a bond angle of 120° .

Two displayed formulas joined by a double-headed arrow labelled "same": 2-fluoropropenoic acid, $CH_2=CFCOOH$, drawn once starting from the COOH end ($HOOC-CF=CH_2$) and once starting from the



CH₂ end with the chain bent downwards (CH₂=CF-COOH). Both drawings are the same molecule.

A ring drawn as a full displayed formula: a six-membered carbon ring containing two C=C double bonds (four CH groups), one CH₂ group and one carbon that is double bonded to N-H outside the ring. This is cyclohexa-2,4-dien-1-imine, C₆H₇N.

(b) Condensed structural formula

Running out of space.

First example, drawn three ways:

- Skeletal: 3-methylpentan-2-ol.
- Displayed: a chain of four carbons drawn in a straight line with an arrow along it. The O-H group on the second carbon (drawn above the chain) and the CH₂CH₃ group on the third carbon (drawn below the chain) are circled.
- Condensed: CH₃CH(OH)CH(CH₂CH₃)CH₃. The carbons of the chain are underlined and the circled groups go in brackets.

Second example, drawn three ways:

- Skeletal: prop-1-en-2-yl 2-oxopropanoate.
- Displayed: H₃C-C(=O)-C(=O)-O-C(CH₃)=CH₂, drawn in a straight line with an arrow along it. The CH₃ group above the chain is circled.
- Condensed: CH₃COCOO C(CH₃)=CH₂. The carbons of the chain are underlined.

R-C(=O)-H, aldehyde.

Condensed: RCHO

Displayed + condensed

4-methylcyclohexene drawn as a ring of condensed groups: CH=CH, CH₂, CH(CH₃), CH₂ and CH₂ joined in a six-membered ring. Next to it is the same molecule as a skeletal formula: a cyclohexene ring with one methyl branch.

(c) Skeletal formula

Only C-C bonds shown and any functional group (no C / H atoms are shown).

CH₃-CH₂-CH₂-CH₂-CH₃ (pentane) is drawn as a zigzag of four lines. Each dot on a carbon in the formula matches a corner or an end of the zigzag. The lines are the C-C bonds.

CH₃-CH₂-CH(CH₃)-CH(CH₂CH₃)-CH=CH₂, drawn with an arrow along the main chain and the two branches (CH₃ above, CH₂CH₃ below) circled.

Condensed: CH₃CH₂CH(CH₃)CH(CH₂CH₃)CH=CH₂

Skeletal: 3-ethyl-4-methylhex-1-ene.

CH₃-CH₂-C(=O)-CH(CH₂CH₃)-C(=O)-OH, with the skeletal formula drawn below it: 2-ethyl-3-oxopentanoic acid. The skeletal formula shows the two C=O groups and the OH.

A skeletal formula showing O, two C=O groups and NH₂, with its full displayed formula drawn below it: ethyl 2-carbamoylbutanoate, CH₃CH₂OCOCH(CH₂CH₃)CONH₂.

Naming

Homologous series

Family of organic molecules having:

1. Similar chemical properties.
2. Show trends in physical properties. As molecule size increases:
 - melting point / boiling point higher
 - more viscosity
 - less flammability

Reason: bigger molecule / more electrons / stronger temporary / induced dipoles, more van der Waals forces.

Sketch: two $\text{CH}_3\text{--CH}_3$ molecules (18 electrons each) side by side. The electrons shift in one molecule so that one end is δ^+ and the other δ^- , and this induces a matching δ^+ and δ^- in the molecule next to it, with a dotted line of attraction between them. A second pair shows the same thing with the dipoles the other way round. Label: instantaneous - induced dipole.

3. Same functional group: group of atoms / structure that determines chemical properties.

$\text{CH}_2=\text{CH--CH}_2\text{--CH}_3$, with an arrow to the $\text{C}=\text{C}$: all reactions.

4. Same general formula: only applicable for simple molecules.

C_nH_{2n}

$\text{CH}_3\text{--CH=CH}_2$ is C_3H_6 : general formula works.

$\text{CH}_2=\text{CH--CH}_2\text{--CH=CH--CH}_3$ is C_6H_{10} : general formula does not work.

5. Successive members differ by CH_2 .

$\text{CH}_4 \rightarrow \text{C}_2\text{H}_6 \rightarrow \text{C}_3\text{H}_8 \rightarrow \text{C}_4\text{H}_{10}$, each step adding CH_2 .

Prefix = number of carbon atoms

Prefix	meth	eth	prop	but
Carbons	1C	2C	3C	4C

Prefix	pent	hex	hept	oct
Carbons	5C	6C	7C	8C

Prefix	non	dec
Carbons	9C	10C

Suffix

The suffix gives the homologous series.

No.	Homologous series	Suffix	Notes
1	Alkane	-ane	saturated hydrocarbon
2	Alkene	-ene	unsaturated hydrocarbon, $\text{C}=\text{C}$
3	Alcohol	-ol	--OH , hydroxy group (hydroxyl)
4	Carboxylic acid	-oic acid	--C(=O)--OH

5	Carbonyl compounds		
5 (a)	Aldehyde	-al	-C(=O)-H , at the end of the carbon chain
5 (b)	Ketone	-one	-C(=O)- , in the middle of the carbon chain
6	Nitriles	-nitrile	$\text{-C}\equiv\text{N}$, at the end of a carbon chain
7	Amines	-amine	-NH_2

A name has three parts:

Prefix	an / en	Suffix
number of C	saturated or unsaturated	homologous series

Alkanes

$\text{CH}_3\text{CH}_2\text{CH}_3$ (drawn as a displayed formula): **propane**

Alkenes

$\text{CH}_3\text{CH}=\text{CH}_2$ (displayed formula): **propene**

$\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_3$ (displayed formula, carbons numbered 5 to 1 from left to right so the $\text{C}=\text{C}$ is between carbons 2 and 3): **pent-2-ene**

$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$ (displayed formula, carbons numbered 1 to 5 from left to right): **pent-1,3-diene**. The numbers 1,3 give the position of $\text{C}=\text{C}$.

Number (smaller number should be given to higher precedence group):

1. carboxylic acid
2. nitrile
3. aldehyde
4. ketones
5. alcohols (hydroxy)
6. amines (amino)

Alcohols

$\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{OH}$ (displayed formula, the three OH groups circled, numbering starts from the right-hand end): **pentan-1,2,3-triol**. The "an" shows a saturated carbon chain.

$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}(\text{OH})-\text{CH}_2\text{OH}$ (displayed formula, the two OH groups circled, carbons numbered 6 to 1 from left to right): **hex-3,5-dien-1,2-diol**

Aldehyde

Suffix -al, group -C(=O)-H

$\text{CH}_3\text{CH}_2\text{CHO}$ (displayed formula): **propan-1-al**, the same as propanal. It is unnecessary to write the 1.

$\text{CH}_2=\text{CH}-\text{CH}_2-\text{CHO}$ (carbons numbered 4 to 1 from left to right, starting from the CHO carbon): **but-3-en(-1-)al**

Ketones

–C(=O)– in the middle of the chain. Suffix -one.

CH₂=CH–CH₂–CO–CH₃ (carbons numbered 5 to 1 from left to right): pent-4-en-2-one

CH₃–CO–CH₂–CO–CH₃ (numbered from the right): pentan-2,4-dione

Nitriles

Group –C≡N

CH₃–CH₂–CH₂–CH₂–C≡N: pentanenitrile

CH₂=CH–CH₂–C≡N (carbons numbered 4 to 1 from left to right, the C of C≡N is carbon 1): but-3-enenitrile

Amines

CH₃–CH₂–CH₂–NH₂: propanamine

Branched molecules and multiple functional groups

- number, number → comma
- number - letter → dash

Structure drawn with the main chain highlighted and numbered 1 to 6: CH₃CH(NH₂)C(OH)(CH₃)CH=C(CH₃)CHO. Carbon 1 is the CHO carbon. The branches are circled and labelled: methyl on carbon 2, hydroxy and methyl on carbon 4, amino on carbon 5.

Name: 5-amino-4-hydroxy-2,4-dimethylhex-2-enal

Position - branches, alphabetically.

Main chain: longest possible / continuous carbon atom chain, containing:

- suffix functional group
- maximum C=C, C≡C
- maximum groups attached to it

Number (smaller number should be given to higher precedence group). The name used when the group is a branch is in brackets:

1. carboxylic acid
2. nitrile (cyano)
3. aldehyde (formyl)
4. ketones (oxo)
5. alcohols (hydroxy)
6. amines (amino)

Structure drawn with the chain highlighted: OHC–CH(OH)–CH(CH₂CH₃)–COOH. The COOH carbon is carbon 1 (carboxylic acid). The circled groups are labelled formyl (the H–C=O at the left-hand end), hydroxy (the OH on carbon 3) and ethyl (the CH₂CH₃ on carbon 2).

Name: 2-ethyl-3-formyl-3-hydroxypropanoic acid

- Halogen branches: chloro, bromo, iodo
- Carbon branches: alkyl, methyl etc.

$\text{CH}_3\text{--CO--CHCl--CHO}$ (displayed formula, carbons numbered 4 to 1 from left to right, the Cl circled, an arrow pointing at the CHO carbon as carbon 1): 2-chlorobutan-3-one-1-al

Isomers

$\text{C}_2\text{H}_4\text{O}_2$. Six different displayed formulas are drawn for this one molecular formula:

- ethanoic acid, CH_3COOH
- hydroxyethanal, HOCH_2CHO
- ethene-1,2-diol, HOCH=CHOH
- methyl methanoate, HCOOCH_3
- ethene-1,1-diol, $\text{CH}_2=\text{C}(\text{OH})_2$
- oxiran-2-ol, a three-membered ring of two carbons and one oxygen, with an OH group on one of the carbons

Structural isomers

Molecules having same molecular formula and different structural formulas.

Methyl methanoate drawn twice, once in a straight line as $\text{CH}_3\text{--O--CHO}$ and once bent round as OHC--O--CH_3 , joined by a double-headed arrow labelled "same". These are not isomers, they are the same molecule.

Types of structural isomers

(a) Chain isomer

Four displayed formulas of carboxylic acids with five carbons, with the carbon chain highlighted in each:

- pentanoic acid, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$ (straight chain of five carbons)
- 2-methylbutanoic acid, $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{COOH}$ (chain of four with one branch)
- 3-methylbutanoic acid, $(\text{CH}_3)_2\text{CHCH}_2\text{COOH}$ (chain of four with one branch)
- 2,2-dimethylpropanoic acid, $(\text{CH}_3)_3\text{CCOOH}$ (chain of three with two branches, drawn as a cross)

(b) Positional isomers

Three displayed formulas of a five-carbon chain with the OH group circled in a different position each time:

- pentan-1-ol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
- pentan-3-ol, $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$
- pentan-2-ol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$

An arrow leads from pentan-2-ol to a three-dimensional drawing of it: a central carbon marked with a star (C^*) bonded to H (up), CH_3 (dashed bond), OH (wedge bond) and $\text{CH}_3\text{CH}_2\text{CH}_2$. A vertical line is drawn beside it.

3. Functional group isomer

Change the functional group.

Functional group	Example drawn	Isomer with a different functional group	Example drawn
alkenes	propene, $\text{CH}_2=\text{CHCH}_3$	cycloalkanes	cyclopropane, a ring of three CH_2 groups
aldehydes	propanal, $\text{CH}_3\text{CH}_2\text{CHO}$	ketones	propanone, CH_3COCH_3
carboxylic acid	ethanoic acid, CH_3COOH	ester	methyl methanoate, HCOOCH_3

Stereoisomer

Molecules having same molecular formula, same structural formula but different 3-dimensional geometry (shape is different).

Picture: a left hand and a right hand on either side of a mirror. They are mirror images and cannot be superimposed.

1. Geometric isomer

- $\text{C}=\text{C}$ must be present, each C in $\text{C}=\text{C}$ must be bonded to two different groups.

Each C of the $\text{C}=\text{C}$ is sp^2 hybridised: 120° , trigonal planar. Sketch: a carbon atom with three sp^2 orbitals pointing outwards in one plane, each holding one electron, and one p orbital drawn above and below the plane.

Sketch: $\text{C}=\text{C}$ with H and Cl on each carbon and the π bond drawn as two shaded regions, one above and one below the line joining the carbons. Independent rotation is restricted.

Sketch for comparison: two carbons joined by a single bond, one carrying Cl, Cl and H and the other carrying H, Cl and H. Rotation possible around a σ bond.

The two arrangements of $\text{CHCl}=\text{CHCl}$ (1,2-dichloroethene), each drawn first with its π bond and again as a plain structure with the Cl atoms circled:

Isomer	Arrangement
cis (same side)	both H on the top, both Cl on the bottom
trans (opposite sides)	one Cl on the bottom left and the other Cl on the top right, H on the top left and bottom right

Examples

(a) $\text{CH}_3-\text{CH}=\text{CH}_2$, propene. Redrawn around the $\text{C}=\text{C}$: the left carbon has H and CH_3 (different groups), the right carbon has H and H (same groups). No geometric isomers.

(b) but-2-ene, $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$

- cis but-2-ene: both CH_3 groups on the same side (both drawn at the bottom), both H at the top
- trans but-2-ene: CH_3 groups on opposite sides (one bottom left, one top right)

Unsymmetric molecules

Multiple cis / trans.

$\text{Cl}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$. Each of the two $\text{C}=\text{C}$ can be cis / trans.

First $\text{C}=\text{C}$	Second $\text{C}=\text{C}$
cis	cis
cis	trans
trans	cis
trans	trans

The cis, trans and trans, cis rows are the same if the molecule is symmetric.

The isomers are drawn out as structures with each $\text{C}=\text{C}$ labelled. On this page: cis, cis and cis, trans.

Continued at the top of the next page: trans, trans and trans, cis.

$\text{Cl}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$. With three $\text{C}=\text{C}$ there are 8 combinations:

First $\text{C}=\text{C}$	Second $\text{C}=\text{C}$	Third $\text{C}=\text{C}$
cis	cis	cis
cis	cis	trans
cis	trans	cis
cis	trans	trans
trans	cis	cis
trans	cis	trans
trans	trans	cis
trans	trans	trans

Arrows pair up rows that are the same if the molecule is symmetric: cis, cis, trans with trans, cis, cis, and cis, trans, trans with trans, trans, cis (each pair is the same order read from the other end).

Number of geometric isomers

$$2^n$$

n is the number of $\text{C}=\text{C}$ that make cis / trans isomers in unsymmetric molecules (also add chiral centres).

Can't form geometric isomers in cyclic structures

Cyclohexene drawn as a ring, $-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$, with the two H atoms on the $\text{C}=\text{C}$ marked. Can't make the trans version as the cyclic structure needs to be broken.

2. Optical isomers

Enantiomers. Mixture of enantiomers → racemic mixture.

Chiral centre needed: C atom that is making 4 single bonds with 4 different groups.

- tetrahedral, 109.5° bond angles, sp^3 hybridised

Sketch: a carbon with four H atoms in a tetrahedral arrangement, one bond up, one to the side, one dashed and one wedge.

Two three-dimensional drawings of 2-chlorobutan-2-ol, $\text{CH}_3\text{CH}_2\text{C}(\text{OH})(\text{Cl})\text{CH}_3$, on either side of a vertical mirror line. The chiral carbon is marked C^* and carries Cl (up), OH, CH_2CH_3 (dashed bond) and CH_3 (wedge bond). The left drawing is labelled (+) and the right drawing, its reflection, is labelled (-). These are non-superimposable mirror images.

A third drawing below shows the molecule turned upside down (CH_3 on a wedge at the top, Cl at the bottom, HO on the left, CH_2CH_3 on a dashed bond). A curved arrow labelled "same" joins it to one of the two drawings above: turning the molecule over does not make a new isomer.

Enantiomers have almost identical physical / chemical properties.

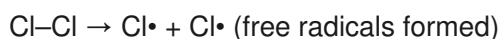
- Shape specific functionality varies a lot, e.g. biology / enzyme.

Differentiate between enantiomers

Both enantiomers rotate plane polarised monochromatic light in opposite directions, clockwise (+) and anticlockwise (-).

Homolytic bond fission

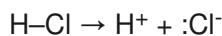
Bond breaks equally.



Two half arrows start from the Cl-Cl bond, one going to each chlorine atom.

Heterolytic bond fission

Bond breaks unequally.



One full arrow starts from the H-Cl bond and goes to the chlorine atom.

Curly arrows

Represent movements of electrons.

- Half arrow: movement of 1 electron.
- Full arrow: movement of 2 electrons.

Free radical

A species (atom or molecule) with an unpaired electron. Very reactive.



Dot-and-cross diagrams are drawn for the hydroxyl radical, $\cdot\text{OH}$, and the methyl radical, $\cdot\text{CH}_3$. In each one the central atom has one unpaired electron.

Nucleophile (attracted to +ve charge)

Species which can donate a pair of electrons and is attracted to +ve charge.

Diagram: curly arrows go to X^+ from the lone pair of each of these nucleophiles, and from the double bond of ethene:

- NC^-
- :OH^-
- :NH_3
- H_2O
- ethene, $\text{CH}_2=\text{CH}_2$

Electrophile

Species which can accept a pair of electrons and is attracted to -ve charge.

Types of reactions

Type of reaction	Example
(a) Addition	$\text{CH}_2=\text{CH}_2 + \text{Br}_2 \rightarrow \text{CH}_2\text{BrCH}_2\text{Br}$
(b) Substitution	$\text{CH}_3\text{CH}_3 + \text{Cl}_2 \rightarrow \text{CH}_3\text{CH}_2\text{Cl} + \text{HCl}$
(c) Elimination	$\text{CH}_3\text{CH}_2\text{Cl} \rightarrow \text{CH}_2=\text{CH}_2 + \text{HCl}$

Source of organic compounds

Source of organic compounds → fossil fuel.

Printed diagram: fractionating column. Crude oil passes through a heater and enters the bottom of the column.

Fraction	Temperature	Use
Refinery gas	20 °C	Bottled gas
Petrol	70 °C	Petrol for vehicles
Naphtha	120 °C	Chemicals
Kerosene	170 °C	Jet fuel, paraffin for lighting and heating
Diesel	270 °C	Diesel fuels
Lubricating oil		Lubricating oils, waxes, polishes
Fuel oil		Fuel for ships, factories and central heating
Bitumen	340 °C	Roads and roofing

Small molecules (top of the column)	Large molecules (bottom of the column)
Low boiling point	High boiling point
Light in colour	Dark in colour
Easy to light	Hard to light
Runny	Thick

Alkanes

Saturated hydrocarbons. C_nH_{2n+2}

Structures drawn: 2-methylpropane, $(CH_3)_3CH$; cyclopropane, C_3H_6 (a ring of three CH_2 groups); methane, CH_4 .

Physical properties

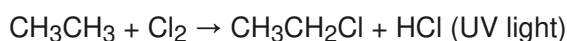
- Non-polar, van der Waals (weak).
- Not soluble in water.

When size of molecule increases:

- more van der Waals
- higher MP, BP
- more viscous
- less flammable

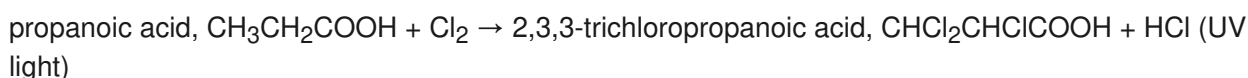
Free radical substitution

Halogenation / chlorination / bromination (for I_2 reaction is very slow, F_2 reaction is very uncontrolled).



Also drawn below the product: 1,1,2-trichloroethane, $CH_2ClCHCl_2$. Many random substitution products.

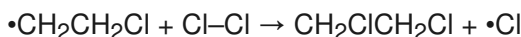
Reaction can happen with any alkyl chain:



The alkyl chain of the propanoic acid (the CH_3CH_2 part) is underlined.

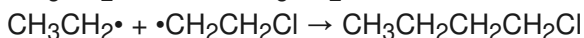
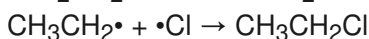
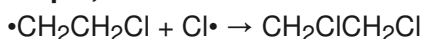
Mechanism

- Step 1, Initiation:** free radicals formed, homolytic bond fission because of UV light.
 $Cl-Cl \rightarrow Cl\cdot + Cl\cdot$ (free radicals formed)
 UV light falls on the $Cl-Cl$ bond. Two half arrows start from the $Cl-Cl$ bond, one going to each chlorine atom.
- Step 2, Propagation:** total number of free radicals remains constant.
 $CH_3CH_3 + \cdot Cl \rightarrow CH_3CH_2\cdot + HCl$ (ethyl radical formed)
 One half arrow goes from the $C-H$ bond to the carbon atom. A second half arrow from the $C-H$ bond and a half arrow from the unpaired electron of $\cdot Cl$ meet between H and Cl to form the $H-Cl$ bond.
 $CH_3CH_2\cdot + Cl-Cl \rightarrow CH_3CH_2Cl + \cdot Cl$
 A half arrow from the unpaired electron of the ethyl radical and a half arrow from the $Cl-Cl$ bond meet to form the $C-Cl$ bond. The other half arrow from the $Cl-Cl$ bond goes to the second chlorine atom, which leaves as $\cdot Cl$.
- Propagation (continued, further substitution):**
 $CH_3CH_2Cl + \cdot Cl \rightarrow \cdot CH_2CH_2Cl + HCl$ (chloroethyl radical)
 The $\cdot Cl$ takes a hydrogen atom from the carbon that does not carry the chlorine. Half arrows go from the $C-H$ bond and from the unpaired electron of $\cdot Cl$.



A half arrow from the unpaired electron on carbon and a half arrow from the Cl-Cl bond form the new C-Cl bond, giving 1,2-dichloroethane, and $\bullet\text{Cl}$ is regenerated.

4. **Step 3, Termination:** two free radicals join, no more free radicals $\rightarrow$ reaction stops.



In each case a half arrow from the unpaired electron of each radical meets to form the new bond. In the last product the new C-C bond in the middle of the chain is marked.

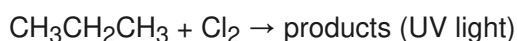
Bigger molecules are produced than the original molecule, because two radicals join.

(H_2 gas molecules are never produced as there are no $\text{H}\bullet$ radicals.)

Speed up free radical: higher concentration of free radicals.



Free radical substitution of propane



Products drawn:

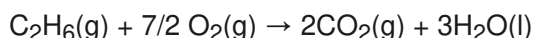
- 1,2,2-trichloropropane, $\text{CH}_2\text{ClCCl}_2\text{CH}_3$ (ticked)
- 1,1,1,2,2-pentachloropropane, $\text{CH}_3\text{CCl}_2\text{CCl}_3$ (ticked)
- 2-chlorohexane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHClCH}_3$

How the bigger molecules form (two radicals join):

From	To
propyl radical, $\text{CH}_3\text{CH}_2\text{CH}_2\bullet$ + 2-chloropropyl radical, $\bullet\text{CH}_2\text{CHClCH}_3$	2-chlorohexane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHClCH}_3$
3-chloropropyl radical, $\text{CH}_2\text{ClCH}_2\text{CH}_2\bullet$ + secondary radical $\text{CHCl}_2\text{-}\bullet\text{CH-CH}_2\text{Cl}$	$\text{CH}_2\text{ClCH}_2\text{CH}_2\text{CH}(\text{CHCl}_2)\text{CH}_2\text{Cl}$

Not formed (arrow crossed out): $\text{CH}_3\text{CHClCH}(\text{CH}_3)\text{CCl}_2\text{CCl}_3$ (as drawn). Can't split it into two propyl radicals.

All hydrocarbons (or most organic compounds): combustion



O_2 in "excess": complete combustion.

In incomplete combustion C (soot) and CO are produced.

CO: deadly poisonous gas, causes choking, combines irreversibly with haemoglobin.

Cracking of long chain hydrocarbons

From	Reagents and conditions	To

Fossil fuel → large molecules (not useful) high MP/BP, more van der Waals solid, semi-solid, wax very viscous less flammable	Catalytic cracking $T > 450\text{ }^{\circ}\text{C}$ catalyst: Al_2O_3 / SiO_2 pumice / zeolite	Small molecules (alkanes / alkenes) + hydrogen gas low MP/BP, less van der Waals less viscous very flammable
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Drawn example: octane, $\text{CH}_3(\text{CH}_2)_6\text{CH}_3$, with the chain broken between the sixth and seventh carbon atoms → hex-1-ene, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ + $\text{H}_2(\text{g})$ + ethene, $\text{CH}_2=\text{CH}_2$

C_8H_{18} can crack in different ways:

- $\text{C}_8\text{H}_{18} \rightarrow \text{C}_2\text{H}_6$ (ethane) + C_6H_{12} (hexene)
- $\text{C}_8\text{H}_{18} \rightarrow \text{CH}_4$ (alkane) + C_3H_6 (alkene) + C_4H_8 (alkene)
- $\text{C}_8\text{H}_{18} \rightarrow \text{C}_3\text{H}_6$ + C_5H_{10} + H_2

Alkenes

C_nH_{2n}

Ethene, $\text{CH}_2=\text{CH}_2$. Each carbon atom of the double bond is sp^2 .

Diagram of ethene with the π electron cloud above and below the C–C bond: high charge density π electron cloud.

An arrow points to the cloud from: electrophiles (+ve ions, δ^+ charge, electron deficient).

Electrophilic addition reactions

$\text{CH}_3\text{CH}=\text{CH}_2 + \text{X}-\text{Y}$ (electrophile) → $\text{CH}_3\text{CHXCH}_2\text{Y}$

A curly arrow goes from the C=C double bond to X–Y.

1. Bromination reaction

$\text{CH}_3\text{CH}=\text{CH}_2 + \text{Br}-\text{Br}$ (electrophile) → $\text{CH}_3\text{CHBrCH}_2\text{Br}$ (r.t.p., solvent: aqueous or inert (CCl_4))

A curly arrow goes from the C=C double bond to Br–Br.

If aqueous: the product is $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{Br}$.

Test for identification of unsaturated compounds: +ve test → red / orange / brown Br_2 decolourises.

Electrophilic addition mechanism

Drawn first with the π cloud of ethene, then with displayed formulae (boxed):

1. Step 1: a curly arrow goes from the C=C double bond (the π electron cloud) of ethene, $\text{CH}_2=\text{CH}_2$, to the $\text{Br}^{\delta+}$ of $\text{Br}^{\delta+}-\text{Br}^{\delta-}$. A second curly arrow goes from the Br–Br bond to the $\text{Br}^{\delta-}$. This forms the carbocation intermediate, $^+\text{CH}_2\text{CH}_2\text{Br}$, and $:\text{Br}^-$.
2. Step 2: a curly arrow goes from the lone pair of $:\text{Br}^-$ to the C^+ of the carbocation. The product is 1,2-dibromoethane, $\text{CH}_2\text{BrCH}_2\text{Br}$.

2. Hydration of alkenes (electrophilic addition)

$\text{CH}_3\text{CH}=\text{CH}_2$ (unsymmetric) + $\text{H}_2\text{O} \rightarrow$ products (300 °C, 60 atm, H_3PO_4 catalyst)

- $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, propan-1-ol, minor product
- or $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$, propan-2-ol, major product

Markovnikov's Rule

H likes to be bonded to C in $\text{C}=\text{C}$ which is already bonded to more H-atoms.

$(\text{CH}_3)_2\text{C}=\text{CH}_2 + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_3$ (major product)

In $(\text{CH}_3)_2\text{C}=\text{CH}_2$ the left carbon of the double bond has 0 × H and the right carbon has 2 × H.

Mechanism for the major product:

1. A curly arrow goes from the $\text{C}=\text{C}$ double bond of $(\text{CH}_3)_2\text{C}=\text{CH}_2$ to the $\text{H}^{\delta+}$ of $\text{H}^{\delta+}-\text{OH}^{\delta-}$. A second curly arrow goes from the $\text{H}-\text{O}$ bond to the $\text{O}^{\delta-}$. The H joins the CH_2 carbon, forming the 3° carbocation $(\text{CH}_3)_2\text{C}^+\text{CH}_3$ and $:\text{OH}^-$.
2. A curly arrow goes from the lone pair of $:\text{OH}^-$ to the C^+ . The product is $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_3$, the major product.

Mechanism for the minor product:

1. A curly arrow goes from the $\text{C}=\text{C}$ double bond of $(\text{CH}_3)_2\text{C}=\text{CH}_2$ to the $\text{H}^{\delta+}$ of $\text{H}^{\delta+}-\text{OH}^{\delta-}$. A second curly arrow goes from the $\text{H}-\text{O}$ bond to the $\text{O}^{\delta-}$. This time the H joins the carbon carrying the two CH_3 groups, forming the 1° carbocation $(\text{CH}_3)_2\text{CHCH}_2^+$ and $:\text{OH}^-$.
2. A curly arrow goes from the lone pair of $:\text{OH}^-$ to the C^+ . The product is $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$, the minor product.

Carbocations with more alkyl chains, which are electron donating, are more stable, as they have lower charge density.

1° carbocation	2° carbocation	3° carbocation
CH_3CH_2^+	$(\text{CH}_3)_2\text{CH}^+$	$(\text{CH}_3)_3\text{C}^+$
CH_3 (9 electrons) and two H (1 electron each) around C^+ high charge density		three CH_3 (9 electrons each) around C^+ low charge density
unstable	→	stable

3. Hydrogenation

$\text{CH}_3\text{CH}=\text{CH}_2$ (unsaturated) + $\text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_3$ (saturated) (Ni / Pt catalyst, 150 °C)

Molecule size slightly increases, van der Waals increase, higher MP/BP.

Printed diagram: unsaturated vegetable oil (a triglyceride with linoleic, linoleic and oleic chains) → margarine (a triglyceride with stearic, oleic and oleic chains) (H_2 , Ni).

Heterogeneous catalyst → drawn as ethene, $\text{CH}_2=\text{CH}_2$, and $\text{H}-\text{H}$ above a nickel surface, in three stages:

1. Ethene and $\text{H}-\text{H}$ approach the Ni surface.

2. Adsorption: catalyst and reactants form very weak bonds.
3. Desorption: weak bonds between catalyst / reactants break, now new bonds can form. The H atoms join the carbon atoms and the product leaves the Ni surface.

4. Hydrogen halides (electrophilic addition)



Mechanism (boxed):

1. A curly arrow goes from the C=C double bond of $\text{CH}_3\text{CH}=\text{CH}_2$ to the $\text{H}^{\delta+}$ of $\text{H}^{\delta+}-\text{Cl}^{\delta-}$. A second curly arrow goes from the H-Cl bond to the $\text{Cl}^{\delta-}$. This forms the carbocation $\text{CH}_3\text{C}^+\text{HCH}_3$ and $:\text{Cl}^-$.
2. A curly arrow goes from the lone pair of $:\text{Cl}^-$ to the C^+ . The product is $\text{CH}_3\text{CHClCH}_3$.

Oxidation of alkenes

1. Mild oxidation

Cold / dilute KMnO_4



Diols formed. Propane-1,2-diol.

Skeletal example: 4-(prop-1-enyl)cyclohexene (a cyclohexene ring with a $-\text{CH}=\text{CHCH}_3$ side chain) $\rightarrow$ 4-(1,2-dihydroxypropyl)cyclohexane-1,2-diol. An OH group is added to each of the four carbon atoms that were in the two double bonds.

2. Strong oxidation

Hot, concentrated, acidified KMnO_4 (potassium manganate(VII)).

* Double bond breaks completely.

From (each end of C=C)	To
1. $=\text{CH}_2$	$\text{CO}_2 + \text{H}_2\text{O}$
2. $=\text{CHR}$	RCHO (aldehyde) $\rightarrow$ RCOOH (carboxylic acid)
3. $=\text{CR}_2$	$\text{R}_2\text{C}=\text{O}$ (ketone)

Example: 2-methylpent-1-ene, $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)=\text{CH}_2$. The double bond is broken:

- $=\text{CH}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)= \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)=\text{O}$ (ketone)

Skeletal example: 2-methylbut-2-ene, $(\text{CH}_3)_2\text{C}=\text{CHCH}_3$, with the double bond broken $\rightarrow$ ethanoic acid, CH_3COOH (from the $=\text{CHCH}_3$ end) + propanone, $(\text{CH}_3)_2\text{C}=\text{O}$ (from the $=\text{C}(\text{CH}_3)_2$ end).

Assignment

Draw products for both mild and strong oxidation.

1. 2,3-dimethylpent-2-ene

2. 2-methylbut-1-ene
3. Skeletal structure: 4-methylcyclohexene
4. Skeletal structure: 1-methylcyclohexa-1,4-diene (as read from the sketch)
5. Skeletal structure: 2,3,5-trimethylhexa-2,4-diene, $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)\text{CH}=\text{C}(\text{CH}_3)_2$ (as read from the sketch)
6. penta-1,3-diene

Alkenes, addition polymers

Polymer: a very large macromolecule formed when hundreds of monomers join together.

Monomer: ethene, $\text{CH}_2=\text{CH}_2$ (six ethene molecules drawn side by side)

→ polyethene: $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ with continuation bonds at each end.

Polyethene: plastic bags etc.

Repeat unit: $-(\text{CH}_2-\text{CH}_2)-_n$

2-methylpropene

2-methylpropene, $(\text{CH}_3)_2\text{C}=\text{CH}_2$. The $\text{C}=\text{C}$ is highlighted. The CH_3 group and the H drawn in line with the double bond are circled, with arrows showing them being moved to above and below the carbon atoms, so the monomer is redrawn with the $\text{C}=\text{C}$ horizontal and the four groups above and below it.

Five 2-methylpropene monomers drawn side by side → polymer chain $-\text{C}(\text{CH}_3)_2-\text{CH}_2-\text{C}(\text{CH}_3)_2-\text{CH}_2-\text{C}(\text{CH}_3)_2-\text{CH}_2-\text{C}(\text{CH}_3)_2-\text{CH}_2-$ with continuation bonds at each end.

Repeat unit: $-(\text{C}(\text{CH}_3)_2-\text{CH}_2)-_n$

Two unlabelled sketches at the side: many long polymer chains tangled across each other, and two long chains joined by short links between them.

PVC

Polyvinyl chloride: pipes, tiles, doors, windows.

Monomer: chloroethene, $\text{CH}_2=\text{CHCl}$ (five drawn side by side) → polymer chain $-\text{CH}_2-\text{CHCl}-\text{CH}_2-\text{CHCl}-\text{CH}_2-\text{CHCl}-\text{CH}_2-\text{CHCl}-$ with continuation bonds at each end. The Cl atoms are marked δ^- and an H atom is marked δ^+ .

Dipoles, stronger attraction between polymer chains.

PTFE

Teflon.

Monomer: tetrafluoroethene, $\text{CF}_2=\text{CF}_2$. Repeat unit: $-(\text{CF}_2-\text{CF}_2)-_n$

- No dipoles, less intermolecular, non-stick in cooking.
- C-F strong, heat resistant.

* **Addition polymers:** non-biodegradable. C-C bonds are strong and unreactive / non-polar.

Halogenoalkanes

Structure drawn: 2-bromo-1-chlorobutane, $\text{CH}_3\text{CH}_2\text{CHBrCH}_2\text{Cl}$, with the Br and the Cl circled.

- Higher (slightly) melting and boiling points. Polar molecules: chloromethane, CH_3Cl , drawn with $\text{C}^{\delta+}-\text{Cl}^{\delta-}$. Strength of dipoles decreases down the group, electronegativity of halogen decreases (bigger molecules have more van der Waals).
- Very slightly soluble in water.

Formation of halogenoalkanes

1. Free radical substitution (see alkanes)



2. Electrophilic addition of alkenes (see alkenes)



3. Alcohols (nucleophilic substitution)

From	Reagents and conditions	To
$\text{CH}_3\text{CH}_2\text{OH}$	1. PCl_3 + heat 2. PCl_5 , vigorous at r.t.p. 3. SOCl_2 + heat (thionyl chloride) 4. HCl + heat (NaCl + conc. H_2SO_4)	$\text{CH}_3\text{CH}_2\text{Cl}$
$\text{CH}_3\text{CH}_2\text{OH}$	1. HBr + heat 2. PBr_3 + heat ($\text{P} + \text{Br}_2$)	$\text{CH}_3\text{CH}_2\text{Br}$
$\text{CH}_3\text{CH}_2\text{OH}$	1. HI + heat 2. PI_3 + heat ($\text{P} + \text{I}_2$)	$\text{CH}_3\text{CH}_2\text{I}$

Printed diagram: Heating under Reflux. Labels, from the top: stopper, condenser (water outlet at the top, water inlet at the bottom), round bottom flask, Bunsen burner.

Primary halogenoalkane	RCH_2Cl
Secondary halogenoalkane	R_2CHCl
Tertiary halogenoalkane	R_3CCl

Skeletal example with each halogen labelled: $\text{CH}_2\text{Cl}-\text{CHBr}-\text{CCl}(\text{CH}_3)-\text{CH}_2\text{Cl}$ (as read from the sketch). The Cl at each end is primary, the Br is secondary and the Cl on the carbon with the methyl branch is tertiary.

Nucleophilic substitution, S_N

From	Reagents and conditions	Nucleophile	To
$\text{CH}_3\text{CH}_2\text{Cl}$	NaOH(aq) + reflux	$:\text{OH}^-$	$\text{CH}_3\text{CH}_2\text{OH}$
$\text{CH}_3\text{CH}_2\text{Cl}$	NaCN (ethanolic), reflux	$:\text{CN}^-$	$\text{CH}_3\text{CH}_2\text{CN}$
$\text{CH}_3\text{CH}_2\text{Cl}$	NH_3 (ethanolic) + reflux or $\text{NH}_3(\text{g})$ in a sealed container + heat	$":\text{NH}_3"$	$\text{CH}_3\text{CH}_2\text{NH}_2$

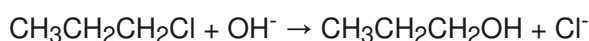
Nucleophile: species which is attracted to +ve charge, donates a pair of electrons.

S_N2 Reaction Mechanism: Primary Halogenoalkanes

1-chloropropane, CH₃CH₂CH₂Cl, reacting with the hydroxide ion, HO⁻. The carbon bonded to chlorine is δ⁺ and the chlorine is δ⁻.

Other nucleophiles (boxed): NC⁻ and H₃N, each with a lone pair.

1. A curly arrow starts from the lone pair on the oxygen of HO⁻ and goes to the δ⁺ carbon. At the same time a curly arrow starts from the C–Cl bond and goes to the chlorine.
2. Transition state: [HO...C(H)(H)(CH₂CH₃)...Cl]⁻, with partial bonds from carbon to both HO and Cl. C is partially bonded to 5 groups.
3. The C–Cl bond breaks completely, giving propan-1-ol, CH₃CH₂CH₂OH, and a chloride ion, Cl⁻.



Rate depends on both reactants. Rate ∝ [R–Cl][OH⁻]

S_N2: One Step Mechanism.

S_N1 Reaction Mechanism: Tertiary Halogenoalkanes

2-chloro-2-methylbutane, CH₃C(CH₃)(Cl)CH₂CH₃. The carbon bonded to chlorine is δ⁺ and the chlorine is δ⁻.

1. Slow step: a curly arrow starts from the C–Cl bond and goes to the chlorine. The bond breaks to give an intermediate carbocation, CH₃C⁺(CH₃)CH₂CH₃, and a chloride ion, Cl⁻. Intermediate carbocation formed.
2. Fast step: a curly arrow starts from the lone pair on OH⁻ (or CN⁻, NH₃) and goes to the positive carbon, giving 2-methylbutan-2-ol, CH₃C(CH₃)(OH)CH₂CH₃.

Rate ∝ [R–Cl] ([OH⁻] is crossed out). Rate depends on only one reactant.

2 step reaction.

Why do primary halogenoalkanes undergo S_N2 and tertiary halogenoalkanes undergo S_N1?

Primary	Tertiary
Chloroethane, CH ₃ CH ₂ Cl. If the C–Cl bond broke (curly arrow from the C–Cl bond to Cl) it would give CH ₃ CH ₂ ⁺ and Cl ⁻ . The positive charge on the carbon is large.	2-chloro-2-methylpropane, (CH ₃) ₃ CCl. The C–Cl bond breaks (curly arrow from the C–Cl bond to Cl) to give (CH ₃) ₃ C ⁺ and Cl ⁻ . Each of the three CH ₃ groups donates electrons to the positive carbon, so the positive charge is small.
Primary carbocations have less electron donating alkyl chains, which increases charge density on the carbocation, making it very unstable, hence S _N 2 mechanism.	Tertiary carbocations have more electron donating alkyl chains, which decreases charge density on the carbocation, making it very stable, hence S _N 1 mechanism.

Secondary: both S_N1 / S_N2, depends on conditions.

Reactivity of Halogenoalkanes

$R-I > R-Br > R-Cl$
 $R-I$: very reactive.

 $R-Cl$: least reactive.

- smaller atoms, make stronger bonds
- shorter bond length
- more orbital overlap
- less shielded nuclei

Elimination Reactions

2-chlorobutane, $CH_3CH_2CHClCH_3$. The Cl is underlined, and a hydrogen on each of the two carbons next to the C-Cl carbon is underlined with a question mark (either one can be lost with the Cl).

From	Reagents and conditions	To
2-chlorobutane, $CH_3CH_2CHClCH_3$	NaOH (ethanolic), reflux	but-1-ene, $CH_3CH_2CH=CH_2$ + HCl
2-chlorobutane, $CH_3CH_2CHClCH_3$	NaOH (ethanolic), reflux	but-2-ene, $CH_3CH=CHCH_3$ + HCl

Identification of halogen in halogenoalkane

 $R-X \rightleftharpoons R^+ + X^-$
 $X = Cl, Br, I$

Ion	Add aqueous $AgNO_3$	Dissolve in NH_3
Cl^-	$AgCl(s)$, white ppt	dissolves in aqueous NH_3
Br^-	$AgBr(s)$, cream ppt	dissolves in conc. NH_3
I^-	$AgI(s)$, yellow ppt	does not dissolve

Uses of Halogenoalkanes

1. CFCs, chlorofluorocarbons. Example drawn: 1,1,2-trichloro-1,2,2-trifluoroethane, $CF_2ClCFCl_2$.
Inert solvents, volatile.
 - solvents, coolants, freons, anaesthetics, aerosols
2. Fire retardants: bromine related compounds.
3. Polymers → PVC: pipes, tiles. Teflon, PTFE: non stick in cooking utensils.

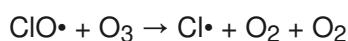
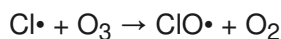
Harmful effect of CFC

Destroy ozone. Free radicals in upper atmosphere / strong UV rays.

Trichlorofluoromethane, $CFCl_3$: the C-Cl bond breaks, with one electron of the bond going to each atom.

 $CFCl_3 \rightarrow \cdot CFCl_2 + \cdot Cl$

$Cl\cdot$ radicals attack O_3 , ozone.



Ozone reflects harmful UV rays.

Alcohols

Ethanol, $\text{CH}_3\text{--CH}_2\text{--OH}$. The --OH group is the hydroxy group.

1. high melting / boiling points
2. soluble in water

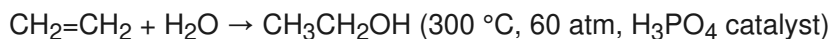
→ form hydrogen bonds.

Diagram: methanol, $\text{CH}_3\text{--O--H}$, with two lone pairs on the oxygen (δ^-) and δ^+ on the hydrogen. A dotted line (hydrogen bond) runs from the δ^+ hydrogen of the alcohol to a lone pair on the δ^- oxygen of a water molecule, H--O--H , whose hydrogens are δ^+ .

Primary alcohol	Secondary alcohol	Tertiary alcohol
propan-1-ol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	pentan-3-ol, $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$	3-ethylpentan-3-ol, $(\text{CH}_3\text{CH}_2)_3\text{COH}$

Formation of Alcohols

1. Hydration of alkenes (see Alkenes)

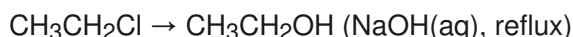


Dehydration of alcohols

Butan-2-ol, $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$. The OH is crossed out, and a hydrogen on each of the two carbons next to the C–OH carbon is underlined (either one can be lost with the OH).

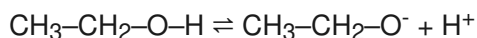
From	Reagents and conditions	To
butan-2-ol, $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$	concentrated H_2SO_4 (dehydrating agent), or heat with Al_2O_3 / SiO_2 (pumice, zeolite)	but-2-ene, $\text{CH}_3\text{CH}=\text{CHCH}_3$
butan-2-ol, $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$	concentrated H_2SO_4 (dehydrating agent), or heat with Al_2O_3 / SiO_2 (pumice, zeolite)	but-1-ene, $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$

2. S_N nucleophilic substitution of halogenoalkanes (see Halogenoalkanes)



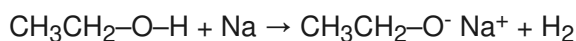
Alcohols are extremely weak acids (not acids, no acid-base reactions)

Ionization is even weaker compared to H_2O .

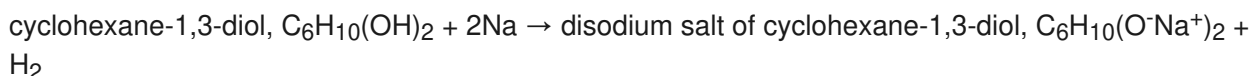


An arrow from the $\text{CH}_3\text{--CH}_2$ group points towards the O^- , and the charge on the oxygen is labelled large. Almost no ionization.

Alcohols do react with Group 1 reactive metals, very slow.



The H of the O–H gains an electron. Na loses an electron. Slight effervescence.



Oxidation of Alcohols

Primary alcohols → aldehydes → carboxylic acids

From	Reagents and conditions	To
primary alcohol, R–CH ₂ –OH	1. K ₂ Cr ₂ O ₇ / H ⁺ , heat with reflux (orange to green) 2. KMnO ₄ / H ⁺ , heat with reflux (purple to colourless)	aldehyde, R–CHO
aldehyde, R–CHO	1. K ₂ Cr ₂ O ₇ / H ⁺ , heat with reflux (orange to green) 2. KMnO ₄ / H ⁺ , heat with reflux (purple to colourless) 3. Tollens reagent, [Ag(NH ₃) ₂] ⁺ (mix NH ₃ (aq) + AgNO ₃ (aq)). Silver mirror formed, black ppt. Ag ⁺ + 1e [–] → Ag 4. Fehling solution + heat. Cu ²⁺ gets reduced to a brick red ppt of Cu ₂ O	carboxylic acid, R–COOH

Stopping the reaction at the aldehyde: use distillation + heat instead of heat with reflux.

Aldehydes have a lower boiling point compared to alcohols, carboxylic acid, so they will immediately evaporate once they are formed.

Secondary alcohols → ketone (no further oxidation)

From	Reagents and conditions	To
secondary alcohol, R–CH(OH)–R	1. K ₂ Cr ₂ O ₇ / H ⁺ , heat with reflux (orange to green) 2. KMnO ₄ / H ⁺ , heat with reflux (purple to colourless)	ketone, R–CO–R

* Tertiary alcohols are not oxidized.

Examples: Oxidation of alcohols

Skeletal structure of the starting compound: a cyclohexane ring carrying four alcohol groups.

- One ring carbon carries a methyl group and an –OH group, labelled tertiary.
- The next ring carbon carries a –CH₂OH group, labelled primary.
- The ring carbon opposite the tertiary one carries a methyl group and a side chain –CH(OH)–CH(OH)–CH₃. Both –OH groups on the side chain are labelled secondary.

Reagents and conditions: K₂Cr₂O₇ / H⁺, reflux.

Product: the tertiary –OH is unchanged, the primary –CH₂OH becomes –COOH, and the two secondary –CH(OH)– groups become C=O, giving the side chain –CO–CO–CH₃.

Reduction

Gain of H / loss of O.

From	Reagents and conditions	To
carboxylic acid: ethanoic acid, CH_3COOH	LiAlH_4	aldehyde: ethanal, CH_3CHO
aldehyde: ethanal, CH_3CHO	LiAlH_4 or NaBH_4	primary alcohol: ethanol, $\text{CH}_3\text{CH}_2\text{OH}$
ketone: propanone, CH_3COCH_3	LiAlH_4 or NaBH_4	secondary alcohol: propan-2-ol, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$

LiAlH_4 , reducing agent. Lithium aluminium hydride. AlH_4^- is drawn as AlH_3 with a fourth H^- (carrying a lone pair) bonded to the Al. It is a source of H^- ions.

In $\text{R}-\text{CO}-\text{R}$ the carbonyl carbon is δ^+ . The lone pair on H^- attacks the δ^+ carbon and the $\text{C}=\text{O}$ bond pair moves to the oxygen. H^- ions are nucleophiles.

Example: the product of the oxidation example above (cyclohexane ring with a tertiary $-\text{OH}$ and methyl on one carbon, $-\text{COOH}$ on the next carbon, and a methyl and $-\text{CO}-\text{CO}-\text{CH}_3$ side chain on the opposite carbon) + $\text{LiAlH}_4 \rightarrow$ the $-\text{COOH}$ becomes $-\text{CH}_2\text{OH}$ and the two $\text{C}=\text{O}$ groups become $-\text{CH}(\text{OH})-$, giving the side chain $-\text{CH}(\text{OH})-\text{CH}(\text{OH})-\text{CH}_3$. The tertiary $-\text{OH}$ is unchanged.

Uses of Alcohols

- Alcoholic drinks.
- Industrial methylated spirits.
- Use of ethanol as a fuel.
- Ethanol as a solvent.
- Methanol as a fuel.
- Methanol as an industrial feedstock.

Aldehyde and Ketones

Aldehyde: $\text{R}-\text{CHO}$ ($\text{R}-\text{C}(=\text{O})-\text{H}$). Ketone: $\text{R}-\text{CO}-\text{R}$ ($\text{R}-\text{C}(=\text{O})-\text{R}$).

Carbonyl compound: $\text{C}=\text{O}$, with O δ^- and C δ^+ . Polar molecule. Permanent dipole - permanent dipole attraction.

Example

- $\text{CH}_3\text{CH}_2\text{CHO}$, propanal
- $\text{CH}_3\text{COCH}_2\text{CH}_3$, butan-2-one

Identification of Carbonyl Compounds

Add 2,4-DNPH (2,4-dinitrophenylhydrazine), $\text{H}_2\text{NNHC}_6\text{H}_3(\text{NO}_2)_2 \rightarrow$ orange precipitate.

$\text{R}-\text{CO}-\text{R} + \text{H}_2\text{N}-\text{NH}-\text{C}_6\text{H}_3(\text{NO}_2)_2 \rightarrow \text{H}_2\text{O} + \text{R}-\text{C}(\text{R})=\text{N}-\text{NH}-\text{C}_6\text{H}_3(\text{NO}_2)_2$ (condensation)

The O of the $\text{C}=\text{O}$ and the two H atoms of the $-\text{NH}_2$ group are circled together. They leave as H_2O . The product, with a $\text{C}=\text{N}$ bond, is the orange precipitate.

How to differentiate between aldehyde / ketone

Aldehydes get oxidized, ketones don't.

aldehydes → carboxylic acids, $R-COOH$ ("oxidation")

1. $K_2Cr_2O_7 / H^+$, heat with reflux (orange to green)
2. $KMnO_4 / H^+$, heat with reflux (purple to colourless)
3. Tollens reagent, $[Ag(NH_3)_2]^+$ (mix $NH_3(aq) + AgNO_3(aq)$). Silver mirror formed, black ppt. $Ag^+ + 1e^- \rightarrow Ag$
4. Fehling solution + heat. Cu^{2+} gets reduced to a brick red ppt of Cu_2O

Carbonyl Compounds, nucleophilic addition (mechanism, 2 step reaction)

$R-CO-R$, with the carbonyl carbon δ^+ and the oxygen δ^- .

1. A curly arrow starts from the lone pair on CN^- (from catalyst) and goes to the δ^+ carbon. A second curly arrow starts from the $C=O$ double bond and goes to the oxygen. Intermediate formed: $R-C(O^-)(CN)-R$, with a lone pair and a negative charge on the oxygen.
2. A curly arrow starts from the lone pair on the O^- of the intermediate and goes to H^+ . Product: cyanohydrin, $R-C(OH)(CN)-R$.

$R-CO-R \rightarrow R-C(OH)(CN)-R$ (HCN, NaCN catalyst)

Iodoform Test ($NaOH(aq) + I_2$)

Identifies a specific structure.

- $H/R-CO-CH_3$ (a $C=O$ with a CH_3 group attached)
- $H/R-CH(OH)-CH_3$ (a $CH(OH)$ with a CH_3 group attached)

Not carboxylic acid or esters. R represents an alkyl chain.

The bond between the carbon and the CH_3 group is marked as the bond that breaks. Two products:

- CHI_3 , triiodomethane, yellow ppt
- $H/R-COO^- Na^+$

Alkaline condition: $RCOOH \rightarrow RCOO^- Na^+$

Further acidification can form $RCOOH$.

Carboxylic Acids

$R-COOH$ ($R-C(=O)-OH$)

- hydrogen bonds
- high melting / boiling points
- very soluble in water

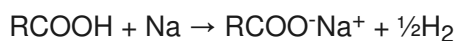
Weak acids

$pH = 3 - 7$

Partially dissociate and produce fewer H^+ ions.

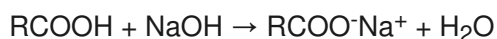
$R-COOH \rightleftharpoons R-COO^- + H^+$

Acid + Metal → Salt + H_2



Redox reaction. Na loses an electron, H^+ gains an electron.

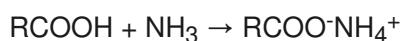
Acid + Metal oxide / hydroxide $\rightarrow$ Salt + H_2O



Acid + Metal carbonate $\rightarrow$ Salt + H_2O + CO_2



Acid + $\text{NH}_3 \rightarrow$ Ammonium salt



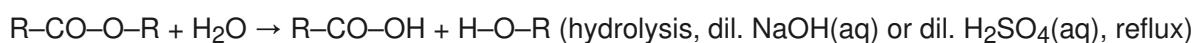
Esterification

Formation of esters



The OH of the acid and the H of the alcohol's O-H are crossed out. They leave as H_2O . The carbonyl carbon of the acid is δ^+ and the alcohol oxygen has lone pairs.

Hydrolysis of esters



An arrow from H_2O points to the C-O single bond of the ester, the bond that breaks.

In alkaline hydrolysis the acid reacts with the alkali: RCOO^-Na^+

Naming of esters

$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CO}-\text{O}-\text{CH}_3$, split by a line between the C=O carbon and the -O-.

- $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CO}$: 4C, butanoate
- $\text{O}-\text{CH}_3$: 1C, methyl

Hydrolysis of Nitriles



In alkaline conditions: RCOO^-Na^+



Infrared Spectroscopy

Diagram: propanone, CH_3COCH_3 , drawn in three dimensions. Infrared radiation (labelled infrared spectrum) is shown arriving at the C=O bond. Double-headed arrows on the C=O bond and on a C-H bond are labelled vibrate.

Each bond will vibrate / stretch at a very specific frequency.

Table 4.2 ($1/\lambda \propto$ frequency)

bond	functional group containing the bond	characteristic infrared absorption range (in wavenumbers) / cm^{-1}
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C—O	hydroxy, ester	1040–1300
C=C	aromatic compound, alkene	1500–1680
C=O (circled)	amide carbonyl, carboxyl ester	1640–1690 1670–1740 1710–1750 (all three circled)
C≡N	nitrile	2200–2250
C—H	alkane	2850–3100
N—H	amine, amide	3300–3500
O—H (circled)	carboxyl hydroxy (alcohol)	2500–3000 3200–3650

40 Which diagram shows the infrared spectrum of a compound that contains both a C=O and an O—H group?

Four infrared spectra, A to D, each plotted as transmittance / % (0 to 100) against wavenumber / cm^{-1} (from above 3000 down to below 1000). The teacher's markings:

Spectrum	What the spectrum shows	Teacher's marking
A	A sharp absorption just below 3000 and a strong sharp absorption near 1700.	The absorption near 3000 is marked with a cross. The absorption near 1700 is marked C=O. The region below about 1500 is marked hard to identify.
B	A broad absorption around 3000 to 3500 and a strong sharp absorption near 1700.	The broad absorption is marked alcohol. The absorption near 1700 is marked C=O. B is circled as the answer.
C	A strong sharp absorption just below 3000 and a sharp absorption near 1400.	The absorption near 1400 is marked probably not C=O.
D	A broad, strong absorption around 3300 and absorptions below about 1500.	The broad absorption is marked alcohol. Marked no C=O.

Checked by Mega Lecture

Typed from the handwritten original, page by page. Drawn structures are given as names and formulae, and mechanisms as numbered steps; names for structures the original leaves unnamed were added by us, and a few small skeletal sketches are marked "as read from the sketch". Slips of the pen put right: a missing subscript in a condensed formula (page 5); the primary carbocation in the minor-product mechanism (page 18); water shown as a reactant in the mild oxidation of propene (page 19); the heading "Dehydration of alcohols" (page 26); $\text{NH}_3(\text{aq})$ in Tollens' reagent (pages 27 and 29); the formula of 2,4-DNPH (page 29); and the equations for a carboxylic acid with a metal carbonate and with ammonia (page 31). The four printed infrared spectra on the last page are summarised by their main absorptions, not reproduced. Spotted a mistake? Tell us on WhatsApp: +92 336 780 1123.