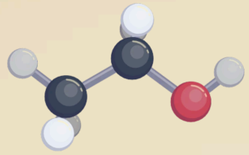
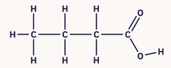
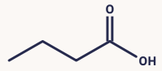
11.1 Introduction to Organic Chemistry



1 Formulae of Organic Compounds

Carbon forms many compounds: strong C–C bonds allow long chains and rings (catenation), C is tetravalent, allowing branching and multiple bonds.

Formula	Shows	Butanoic acid
Empirical	simplest _____ of atoms of each element	C_2H_4O
Molecular	_____ of atoms of each element in one molecule	$C_4H_8O_2$
Structural	how the atoms are joined, with minimal detail	$CH_3CH_2CH_2CO_2H$
Displayed	all atoms and _____. Bent (–O–H) and trigonal planar (C=O) groups must be drawn out with their shapes	
Skeletal	carbon skeleton and functional groups only, C and H on C not shown	
Stereochemical	3D arrangement: wedge = _____ the plane, dash = _____ the plane	

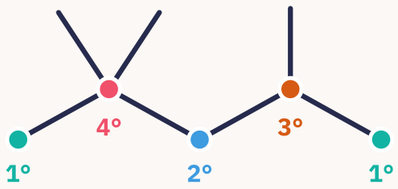
2 Terminology

DEFINITION **Hydrocarbon**: a compound containing _____

- **Functional group**: an atom or group of atoms responsible for the _____ of a compound
- **Alkyl group**, R: C_nH_{2n+1}, e.g. CH_3– methyl, C_2H_5– ethyl
- **Saturated**: only single bonds. **Unsaturated**: contains multiple bonds. Each π bond removes 2 H.
- **Homologous series**: a series of compounds with the same functional group, each member differing by $–CH_2–$. Its members have:
  - similar _____ reactions
  - similar methods of preparation
  - M_r increasing by _____ from one member to the next
  - a gradual change in _____ properties

2.1 Degree of substitution

A carbon bonded to _____ other carbons is primary (1°), secondary (2°), tertiary (3°) or quaternary (4°).



2,2,4-trimethylpentane

2 Terminology (continued)

2.2 Classes of compounds, in order of priority

Class	General	Group	Suffix	Prefix
carboxylic acid	RCO_2H	$–CO_2H$	**-oic acid**	–
ester	RCO_2R'	$–CO_2–$	**-oate**	alkoxy-carbonyl-
acyl chloride	RCOCl	–COCl	**-oyl chloride**	chloro-carbonyl-
amide	$RCONH_2$	–CONH–	**-amide**	–
nitrile	RCN	–C≡N	**-nitrile**	cyano-
aldehyde	RCHO	–CHO	**-al**	–
ketone	RCOR′	C=O	**-one**	–

Class	General	Group	Suffix	Prefix
alcohol	ROH	–OH	**-ol**	hydroxy-
phenol	ArOH	–OH	**phenol**	hydroxy-
amine	RNH_2, R_2NH, R_3N	–N	**-amine**	amino-
alkene	C_nH_{2n}	C=C	**-ene**	–
alkane	C_nH_{2n+2}	–	**-ane**	alkyl-
arene	$C_6H_5–R$	$C_6H_5–$	**-benzene**	phenyl-
halogeno-alkane	RX	–X	–	chloro-, bromo-, iodo-
amino acid	$RCH(NH_2)CO_2H$	$–NH_2$, $–CO_2H$	**-oic acid**	amino-

The highest group in the order gives the **suffix**, and every other group becomes a **prefix**: $HOCH_2CH_2CHO$ is 3-hydroxypropanal, $H_2NCH_2CO_2H$ is aminoethanoic acid. Halogens and alkyl groups are always prefixes, and C=C stays in the stem, as in but-3-en-1-ol.

An ester is named alkyl first, as in ethyl ethanoate: R′ (on O) must be an alkyl group, R may be H. The carbon of –C≡N and of –CHO counts in the stem, as in ethanenitrile, CH_3CN.

2.3 Naming organic compounds

No. of C	1	2	3	4	5	6	7	8	9	10
Stem	meth	eth	prop	but	pent	hex	hept	oct	non	dec

Steps

1. Find the **longest carbon chain** that contains the functional group: this gives the stem
2. **Number** the chain from the end that gives the functional group the lowest number
3. Name the **substituents** (methyl, chloro …) as prefixes with their positions, in alphabetical order (di-, tri- for repeats)
4. Add the **suffix** of the highest-priority functional group (table 2.2) with its position

Example: $CH_3CH(CH_3)CH_2OH$

1. Longest chain with the –OH: 3 C → _____
2. –OH on C1 → propan-1-ol
3. $–CH_3$ on C2 → _____

3 Types of Organic Reactions

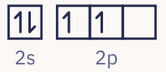
Type	What happens	Example
Addition	two molecules combine to form _____ product, π bond broken	$CH_2=CH_2 + Br_2 \rightarrow CH_2BrCH_2Br$
Substitution	an atom or group is _____ by another	$CH_3CH_2Cl + OH^- \rightarrow CH_3CH_2OH + Cl^-$
Elimination	atoms removed from two _____ atoms to form a π bond	$CH_3CH_2OH \rightarrow CH_2=CH_2 + H_2O$
Condensation	two molecules join with loss of a _____ (H_2O, HCl)	$RCO_2H + R'OH \rightleftharpoons RCO_2R' + H_2O$
Hydrolysis	breaking of a bond by reaction with _____	$RCO_2R' + H_2O \rightleftharpoons RCO_2H + R'OH$
Oxidation	gain of O or loss of H, [O]	$CH_3CH_2OH + 2[O] \rightarrow CH_3CO_2H + H_2O$
Reduction	gain of H or loss of O, [H]	$CH_3COCH_3 + 2[H] \rightarrow CH_3CH(OH)CH_3$

4 Hybridisation

DEFINITION **Hybridisation**: the mixing of atomic orbitals in various combinations to give a set of _____ of equivalent energy for covalent bonding with other atoms.

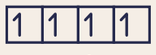
Why hybridise? In its ground state C has only **two** unpaired electrons, yet in CH_4 it forms **four identical** bonds at 109.5°. So: one 2s electron is promoted, then the orbitals are mixed.

1. ground state C → 2. promote one 2s e⁻ → 3. mix: sp³, sp² or sp





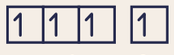
sp³

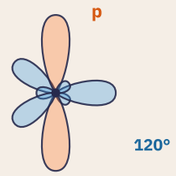




2s + three 2p mixed → 4 sp³ orbitals
tetrahedral, _____, 4σ, 25% s
e.g. CH_4, ethane

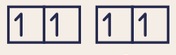
sp²

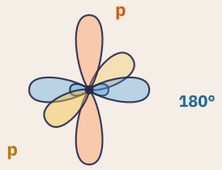




2s + two 2p mixed → 3 sp² + ____
trigonal planar, _____, 3σ + 1π, 33% s
e.g. ethene, benzene

sp





2s + one 2p mixed → 2 sp + ____
linear, _____, 2σ + 2π, 50% s
e.g. ethyne, CO_2

Each hybrid orbital has one large and one small lobe, the large lobe is used in bonding. Hybrid orbitals form σ bonds, unhybridised p orbitals form π bonds.

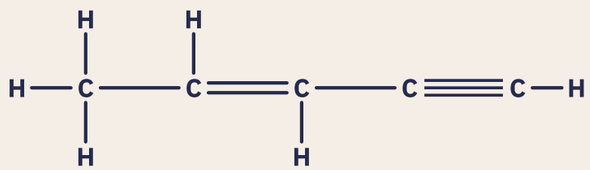
4.1 Hybridisation of each carbon atom

Count the regions of electron density around the C atom (a double or triple bond counts as _____ region):

Regions around C	Hybridisation	Shape
4 (all single bonds)	_____	tetrahedral
3 (one C=C or C=O)	_____	trigonal planar
2 (C≡C, or two C=C)	_____	linear

- Every single bond is **one σ** bond
- A double bond is **1σ + 1π**, a triple bond is **1σ + 2π**

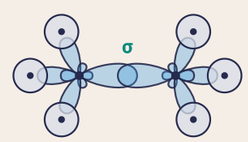
WORKED EXAMPLE For pent-3-en-1-yne, $CH_3CH{=}CHC{\equiv}CH$, state the hybridisation of each carbon atom and the number of σ and π bonds in one molecule.



C5 C4 C3 C2 C1
sp³ sp² sp² sp sp

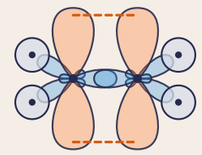
1. C5 has 4 single bonds → sp³, C4 and C3 each have one C=C → _____, C2 and C1 each have one C≡C → _____
2. σ bonds: 6 C–H + 4 C–C = ____
3. π bonds: 1 in C=C + 2 in C≡C = ____

5 Shapes and Bonding in Organic Molecules



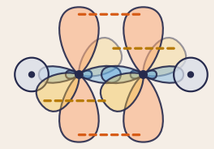
ethane (sp^3)

Ethane: each C is _____, tetrahedral, 109.5°, 4σ bonds
- C–H: head-on overlap of an **sp^3** orbital of C with the 1s orbital of H
- C–C: head-on overlap of an sp^3 orbital of each C



ethene (sp^2)

Ethene: each C is _____, trigonal planar, 120°, 3σ + 1π
- σ bonds: head-on overlap of sp^2 orbitals (and H 1s)
- π bond: _____ overlap of the unhybridised 2p orbital of each C, above and below the plane



ethyne (sp): two π bonds at 90°

Ethyne: each C is _____, linear, 180°, 2σ + 2π
- σ bonds: head-on overlap of sp orbitals (and H 1s)
- 2 π bonds: side-on overlap of the $2p_y$ orbitals and of the $2p_z$ orbitals, at _____ _____ to each other

Benzene: each C is sp^2, 120°, planar, the delocalised π system is covered in Arenes.

- **σ bond**: _____ overlap of hybrid orbitals (C–C) or of a hybrid orbital with H 1s (C–H)
- **π bond**: _____ overlap of unhybridised p orbitals, electron density above and below the plane

Why is C–H in ethene stronger than in ethane?
1. sp^2 orbital has more _____ than sp^3
2. → smaller orbital, electrons _____ _____
3. → more effective overlap, shorter and stronger bond

6 Reagents and Bond Fission

6.1 Types of reagent

Reagent	DEFINITION	Examples	Attacks
Nucleophile (Lewis base)	an _____, with a lone pair of electrons	OH^-, CN^-, Cl^-, NH_3, H_2O, ROH	an electron-poor centre, e.g. a $C^{\delta+}$ atom bonded to a halogen
Electrophile (Lewis acid)	an _____, electron deficient	H^+, NO_2^+, $Br^{\delta+}$–$Br^{\delta-}$, $H^{\delta+}$–Cl	an electron-rich centre, e.g. C=C or a benzene ring
Free radical	a species with an _____	Cl•, Br•, •CH_3	C–H bonds, e.g. in alkanes

NOTE A free radical is electron poor but is **not** an electrophile: an electrophile carries a partial or full positive charge.

6 Reagents and Bond Fission (continued)

6.2 Homolytic fission

The two bonding electrons are shared _____ : each atom takes one → two _____.



6.3 Heterolytic fission

The more electronegative atom takes _____ electrons → a cation and an anion. C^+ is a _____, C^- is a carbanion.



6.4 Drawing curly arrows

Where it starts and ends

An arrow starts at a **bond** or a **lone pair** and points to where the electrons go

Which way electrons flow

From _____ to _____ sites

The arrowhead

Full: a _____ of electrons moves. **Half** (fish-hook): _____ electron moves

What else to show

δ+ / δ−, lone pairs and charges on the species involved

7 Naming a Mechanism

ANSWER STRUCTURE mechanism name = attacking species + type of reaction

1. Look at the **first step**: what attacks the organic molecule? (nucleophile, electrophile or free radical)
2. Compare the **starting reactant** with the **final product** (ignore intermediates): is a group _____ (substitution) or are two molecules _____ (addition)?

Reaction	Attacked by	Mechanism
$CH_2{=}CH_2 + Br_2 \rightarrow CH_2BrCH_2Br$	$Br^{\delta+}$ attacks electron-rich C=C	_____
$CH_3CH_2Cl + OH^- \rightarrow CH_3CH_2OH + Cl^-$	OH^- attacks $C^{\delta+}$	_____
$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$ (UV)	Cl• attacks C–H	_____
$C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr$ ($FeBr_3$)	Br^+ attacks the benzene ring	electrophilic substitution

8 Factors Affecting Reactivity

8.1 Inductive effect

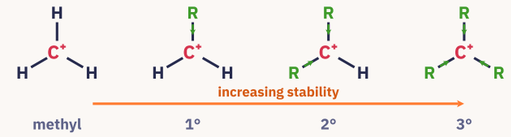
- **Electron-donating**: alkyl groups, increasing with size: $-CH_3 < -C_2H_5 < -CH(CH_3)_2 < -C(CH_3)_3$
- **Electron-withdrawing**: groups more electronegative than H, e.g. $-NO_2$, –Cl, –Br, –I
- The effect is stronger with **more** groups, and weaker the **further** the group is from the charge

	cation (+)	anion (–)
electron-donating	charge _____ → stabilised	charge intensified → destabilised
electron-withdrawing	charge intensified → destabilised	charge _____ → stabilised

8.2 Stability of carbocations

Why is a 3° carbocation more stable than a 1°?

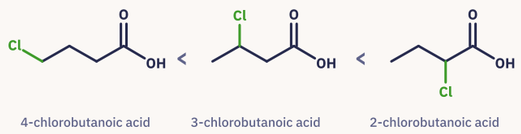
1. Alkyl groups are _____
2. → three alkyl groups _____ the positive charge on C^+ to a greater extent than one



8.3 Stability of anions and acid strength

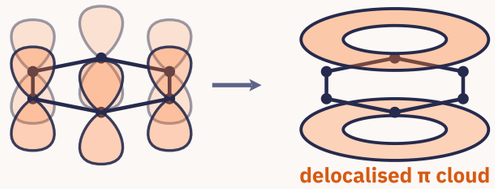
Arrange in increasing K_a:

1. –Cl is _____: it disperses the negative charge on the carboxylate ion
2. The _____ Cl is to $-CO_2^-$, the stronger the effect → more stable anion
3. → the acid dissociates more readily → larger K_a



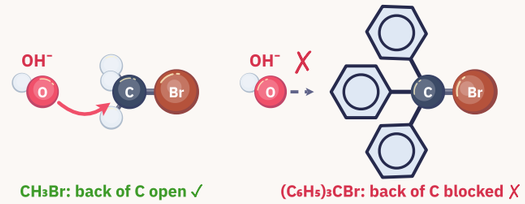
8.4 Delocalisation

When three or more adjacent p orbitals overlap, the π electrons spread over a _____ → the molecule gains extra _____, e.g. benzene.



8.5 Steric hindrance

Bulky groups near the reacting site _____ of the attacking species and slow the reaction. E.g. OH^- must attack the C of C–Br from the side opposite Br: easy in CH_3Br with its small H atoms, but the three bulky benzene rings in $(C_6H_5)_3CBr$ block it.



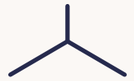
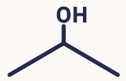
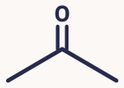
9 Isomerism

Isomers: compounds with the _____ but a different arrangement of atoms.

DEFINITION **Constitutional (structural) isomers**: molecules that have the same molecular formula but _____ _____. Types: chain, position and functional group.

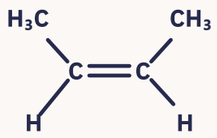
DEFINITION **Stereoisomers**: compounds that have the same molecular and structural formula, but differ in the _____ _____ of their atoms. Types: cis–trans isomers and enantiomers.

9.1 Constitutional (structural) isomerism

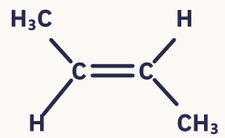
Type	The isomers differ in	Example
Chain	the _____ (branching)	 butane  2-methylpropane
Position	the _____ of the same functional group	 propan-1-ol  propan-2-ol
Functional group	the _____, e.g. an aldehyde and a ketone	 propanal  propanone

Each pair has one molecular formula: C_4H_{10}, C_3H_8O and C_3H_6O.

9.2 Cis–trans isomerism



cis-but-2-ene



trans-but-2-ene

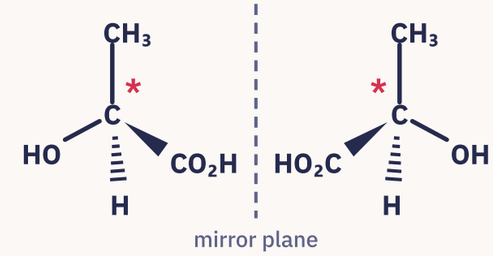
- Arises from _____ about the C=C bond: rotation would break the π bond, formed by side-on overlap of p orbitals
- Each C of the C=C must have _____ groups attached to it
- **cis**: the groups are on the same side of the C=C. **trans**: they are on opposite sides.

Physical properties of cis and trans isomers are in Topic 11.3.

9 Isomerism (continued)

9.3 Enantiomerism

- **Chiral centre**: a carbon atom bonded to _____ _____ atoms or groups, marked *
- **Chiral molecule**: a molecule that is not superimposable on its mirror image
- **Enantiomers**: a pair of molecules that are non-superimposable _____ of each other
- A molecule with a _____ is superimposable on its mirror image, so it is not chiral, even if it has chiral centres



EXAM TIP Draw a pair of enantiomers as mirror images on either side of a mirror plane, with two bonds in the plane, one wedge and one dash.

9.4 Properties of enantiomers

Property	Enantiomers are
Physical	_____, except the direction in which they rotate plane-polarised light (equal extent, opposite directions)
Chemical	_____, except in their interactions with another chiral molecule, e.g. an enzyme
Biological	often _____, e.g. in drug action, one enantiomer may treat the illness while the other is inactive or harmful

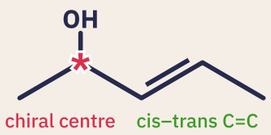
- **Optically active**: a sample that rotates plane-polarised light. It contains chiral molecules.
- **Racemic mixture**: equal proportions of both enantiomers. As each enantiomer rotates plane-polarised light to equal extents but in opposite directions, optical activity cancels out in the racemic mixture.

9.5 Deducing isomers

Steps

1. **Constitutional**: vary the _____, the _____ or the _____
2. **Cis–trans**: look for a C=C with _____ _____ groups on each C
3. **Enantiomers**: look for carbons with _____ _____ groups, the chiral centres
4. **Count**: stereoisomers = _____, n = chiral centres + C=C showing cis–trans (fewer if there is a plane of symmetry)

Worked example: pent-3-en-2-ol



$CH_3CH{=}CHCH(OH)CH_3$ has one chiral centre and one C=C that shows cis–trans isomerism. n = 1 + 1 = 2, so 2^2 = **4** stereoisomers.

EXAM TIP To find chiral centres in a skeletal formula, ignore the bends and the ends, as they cannot carry four different groups. Only look at the intersections.