Unit 9

Organic Compounds

This unit online, with its interactives:
science-playground.com/s/10a9

Open a packet of naphthalene balls, the white mothballs sold in every Nepali bazaar to keep insects out of wool clothes, and you smell them at once. Leave one in a drawer and, over a few months, it shrinks to nothing: the solid turns straight into vapor without melting. Its molecule, $C_{10}H_8$, is two rings of carbon atoms joined side by side. Compare it with the butane in an LPG cylinder, C_4H_{10}, a short open chain of carbon atoms. Both are hydrocarbons, compounds of only carbon and hydrogen, yet one is a gas that burns in your stove and the other is a smelly solid made of rings.

And here is a stranger fact. The cylinder's butane gas is often mixed with another gas that has exactly the same formula, C_4H_{10}, but boils at a different temperature: same atoms, a different compound. In Grade 9 you learned to name organic compounds. This unit goes further: how organic compounds are sorted by the shape of their carbon skeleton, open chains and rings; why some rings, like benzene's, are unusually stable; how the same atoms can make different compounds; and how organic molecules react.



Figure 9.1 *Naphthalene balls (mothballs). Naphthalene, $C_{10}H_8$, is an aromatic hydrocarbon: two rings of carbon atoms sharing one side. It sublimes, turning straight from solid to vapor, which is why a mothball slowly disappears.*
Photo: Wiki Farazi, CC0

9.1 Organic compounds

Introduction

You met organic compounds in Grade 9: the compounds of carbon, mostly with hydrogen, and the compounds made from them by putting other atoms (oxygen, nitrogen, a halogen) in place of hydrogen. Carbon can form so many of them because of its three unique properties: it makes four bonds (**tetracovalency**), it bonds to itself in chains and rings (**catenation**), and it makes double and triple bonds (**multiple bonding**). With millions of compounds, chemists sort them in two ways at once:

- by their **functional group**, the atom or group that decides how they react (alcohols, aldehydes, acids…), which you met in Grade 9;
- by the **shape of their carbon skeleton**: whether the carbon atoms form an open chain or close up into a ring. That is the sorting this unit begins with.

Examples

Compound	Formula	Skeleton	Where you meet it
butane	C_4H_{10}	open chain	LPG (cooking gas)
ethanol	C_2H_5OH	open chain	hand sanitizer, spirit lamps
ethanoic acid	CH_3COOH	open chain	vinegar, achar
cyclohexane	C_6H_{12}	ring of carbon atoms	a solvent; making nylon
benzene	C_6H_6	ring of carbon atoms	in petrol (a little); making plastics, dyes and medicines
naphthalene	$C_{10}H_8$	two rings of carbon atoms	mothballs
glucose	$C_6H_{12}O_6$	in water, mostly a ring of five carbons and one oxygen	fruit, honey, your blood
pyridine	C_5H_5N	ring of five carbons and one nitrogen	a solvent; making medicines

Classification of organic compounds

Chemists divide organic compounds into two big groups by their carbon skeleton, and divide the second group again.

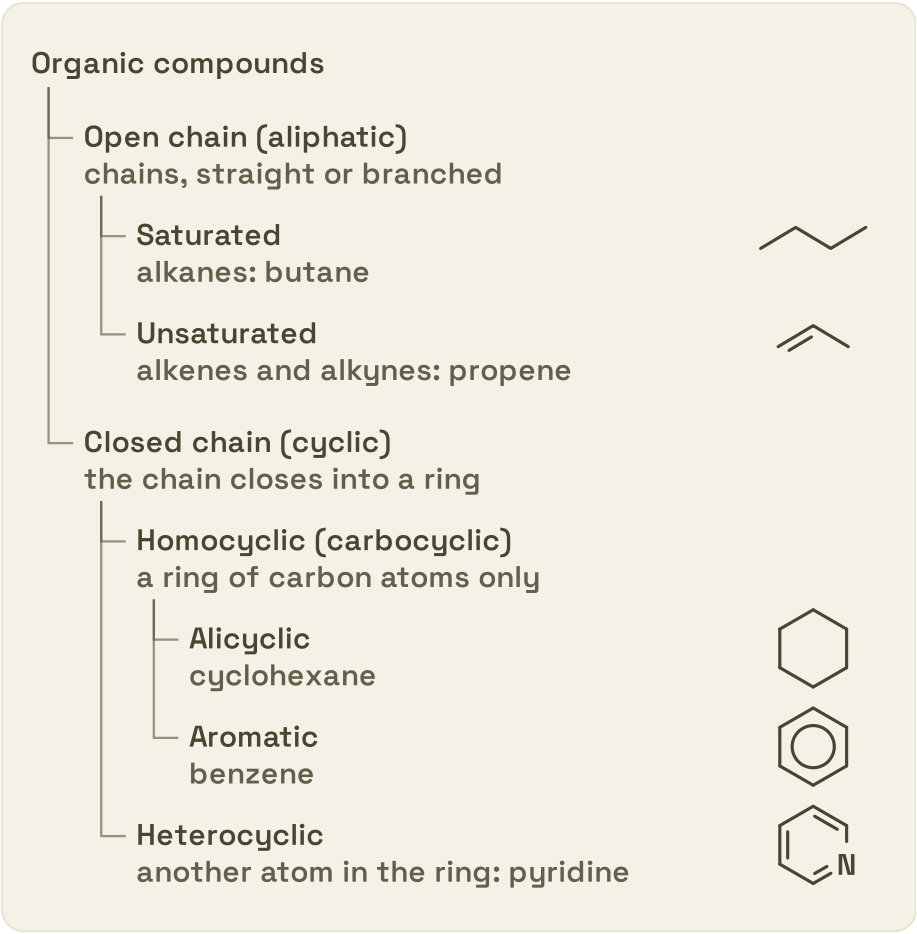


Figure 9.2 *Organic compounds sorted by the shape of their carbon skeleton. In the small drawings on the right, each corner and end of a line is a carbon atom with its hydrogens, which are not written (unless another atom is lettered there, like pyridine's N); a ring is drawn as a polygon.*

Each kind is explained in the sections that follow: open-chain compounds in 9.2; closed-chain compounds, alicyclic and aromatic, in 9.3; and how to tell an aromatic compound by Hückel's rule in 9.4.

Check 1

Which of these is a closed-chain compound?

a propane, $CH_3CH_2CH_3$

b 2-methylpropane, $CH_3CH(CH_3)CH_3$

c cyclobutane, C_4H_8

d but-1-ene, $CH_2{=}CHCH_2CH_3$

9.2 Open chain organic compounds

Statement and examples

Open-chain (acyclic) compounds are organic compounds whose carbon atoms are joined in chains, straight or branched, with no ring. They are also called **aliphatic compounds**, from the Greek *aleiphar*, oil or fat, because the first ones studied came from fats and oils.

Every family you named in Grade 9 is a family of open-chain compounds: alkanes, alkenes, alkynes, alcohols, ethers, aldehydes, ketones and carboxylic acids, as long as their carbons form a chain and not a ring.

- **Straight (unbranched) chain:** every carbon is joined to at most two others, in one line of bonds: butane, $CH_3CH_2CH_2CH_3$; propan-1-ol, $CH_3CH_2CH_2OH$; ethanoic acid, CH_3COOH.
- **Branched chain:** at least one carbon is joined to three or four others: 2-methylpropane, $CH_3CH(CH_3)CH_3$; 2-methylpropan-2-ol, $(CH_3)_3COH$.

Open-chain compounds are also sorted by their bonds:

- **Saturated:** only single bonds between carbon atoms, each carbon holding as many hydrogens as it can. The alkanes, C_nH_{2n+2}: methane, ethane, propane.
- **Unsaturated:** at least one double or triple bond between carbon atoms. The alkenes, C_nH_{2n} (ethene, $CH_2{=}CH_2$), and the alkynes, C_nH_{2n-2} (ethyne, $CH{\equiv}CH$). They are called unsaturated because they can still take on more atoms, hydrogen or a halogen, at the multiple bond (you will see how in 9.6).

> CAREFUL
> **“Straight” chains are not straight**
>
> A “straight chain” means unbranched, not a straight line. At every carbon with four single bonds, the bonds are 109.5° apart, so a real chain zigzags (turn the butane model below and see). The condensed formula $CH_3CH_2CH_2CH_3$ is written in a line only for convenience.

Bonds and shapes: single, double and triple

Each kind of carbon–carbon bond gives the molecule its own shape:

	Single bond (alkane)	Double bond (alkene)	Triple bond (alkyne)
Example	ethane, CH_3–CH_3	ethene, CH_2=CH_2	ethyne, CH≡CH
Electron pairs shared between the two carbons	1	2	3
Shape round each carbon	tetrahedral	flat (planar)	straight (linear)
Angle between bonds	109.5°	about 120°	180°
C–C bond length	154 pm	134 pm	120 pm
Can the two ends spin about the bond?	yes	no	(a straight line: spinning changes nothing)

A double bond is not two identical bonds. One of its two shared pairs lies along the line joining the carbons, like a single bond: a **sigma (σ) bond**. The other lies above and below that line: a **pi (π) bond**, weaker and more easily broken. A triple bond is one σ bond and two π bonds. You meet how σ and π bonds form in Unit 7 (Chemical Bonding). What matters here is that π bonds are where unsaturated compounds react, and that the π electrons are the ones Hückel's rule counts in 9.4.

Check 2

In which molecule do all the atoms lie in one straight line?

a ethane **b** ethene
c ethyne **d** butane

Check 3

How many σ and π bonds join the two carbon atoms in ethyne?

a three σ bonds **b** two σ and one π
c one σ and two π **d** three π bonds

9.3 Closed chain organic compounds

Statement

Closed-chain (cyclic) compounds are organic compounds in which some of the atoms are joined in a ring. When the ring is made of carbon atoms only, the compound is **homocyclic** (or **carbocyclic**). Homocyclic compounds are of two kinds: **alicyclic** and **aromatic**.

To close a chain into a ring, its two end carbons must bond to each other. Each gives up one hydrogen to free a bond, so a ring has two hydrogens fewer than the open chain with the same carbons: hexane is C_6H_{14}, cyclohexane C_6H_{12}.

Alicyclic compounds

Alicyclic compounds are closed-chain compounds whose ring of carbon atoms behaves like an aliphatic (open-chain) compound: the name is short for *aliphatic cyclic*. The simplest are the **cycloalkanes**, rings of CH_2 groups joined by single bonds. Their general formula is $\mathbf{C_nH_{2n}}$ (from $n = 3$), and each is named by putting **cyclo-** before the alkane with the same number of carbons.

Other examples: **cyclohexene**, C_6H_{10}, a six-carbon ring with one double bond, which behaves like an alkene; **methylcyclohexane**, a cyclohexane ring with a CH_3 in place of one hydrogen. Many natural compounds have alicyclic rings: menthol, the cooling compound of pudina (mint), has a cyclohexane ring, and so do the steroids, including cholesterol.

Cycloalkanes behave much like alkanes. Cyclohexane, like hexane, is a colorless liquid that burns, doesn't mix with water and reacts with chlorine in light by substitution. Small rings are the exception: in cyclopropane the angle between the ring's bonds is forced to 60°, far from the 109.5° that carbon's bonds prefer, so the ring is strained and breaks open more easily. Larger rings avoid strain by not being flat: cyclohexane puckers into a "chair" shape in which every angle is close to 109.5° (turn its model in the widget above).

Aromatic compounds

In 1825 Michael Faraday, in London, studied an oily liquid left behind in the containers of a gas sold for lighting, and found it was made of carbon and hydrogen alone, in the proportion that we now know means equal numbers of the two atoms. It was later named **benzene**, C_6H_6. Six carbons and only six hydrogens: if benzene were an open chain it would need several double or triple bonds, and should react like an alkene,

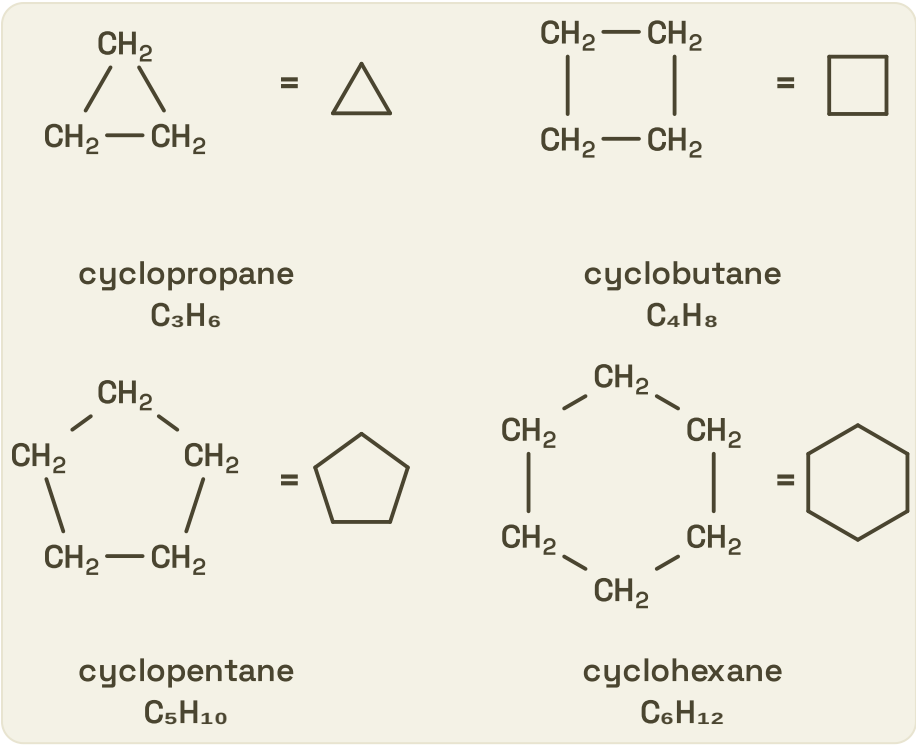


Figure 9.3 *The first four cycloalkanes. Each corner is a carbon with two hydrogens (CH_2), joined to its two neighbors by single bonds. Chemists usually draw such a ring as a bare polygon, as on the right of each: every corner is a carbon, and the hydrogens are left unwritten.*

DID YOU KNOW?

The same formula as an alkene

Cyclohexane, C_6H_{12}, has the same formula as hex-1-ene, $CH_2{=}CH(CH_2)_3CH_3$, since both are C_nH_{2n}: a ring and a double bond each cost two hydrogens. Cyclopropane and propene are both C_3H_6. A cycloalkane and the alkene with the same formula are isomers (you will meet isomers in 9.5), but different kinds of compound: shake each with bromine solution and only the alkene takes the color away at once.

taking the color from bromine at once. It doesn't. Benzene is strangely unreactive for such an unsaturated formula.

Kekulé's ring has a problem. If the bonds really took turns, single and double, three of the six bonds would be long (154 pm) and three short (134 pm), and the hexagon

A STORY FROM SCIENCE

The ring of benzene

In 1865 the German chemist August Kekulé proposed that benzene's six carbons form a ring, with single and double bonds taking turns, and each carbon holding one hydrogen. Twenty-five years later, at a celebration of the idea in Berlin in 1890, he told the story that it came to him while dozing by the fire, when he saw a chain of atoms twist round like a snake seizing its own tail. Historians still argue over whether the dream really happened as he told it. The ring itself was proved beyond doubt: in 1929 the Irish-born crystallographer Kathleen Lonsdale used X-rays to show that the ring in hexamethylbenzene (a benzene ring carrying six methyl groups) is a flat, regular hexagon. She became one of the first two women elected to the Royal Society, in 1945.

would be lopsided. In fact all six carbon–carbon bonds in benzene are the same length, **139 pm**, between the two. Benzene is not either of Kekulé's two structures but something in between: its six π electrons are not fixed in three double bonds but spread evenly round the whole ring, above and below it. Chemists call this **delocalization**, and draw benzene either as one Kekulé structure (knowing it stands for the real molecule) or as a hexagon with a circle inside, the circle standing for the six shared π electrons.

Aromatic compounds are cyclic compounds containing one or more flat rings in which the π electrons are delocalized all round the ring, like benzene's, which makes them unusually stable. Most aromatic compounds contain one or more benzene rings. They were first called "aromatic" because many of the early ones had strong pleasant smells: benzaldehyde (bitter almonds), vanillin (vanilla) and cinnamaldehyde (dalchini, cinnamon) all contain a benzene ring. Today the word means only the special, stable ring; many aromatic compounds have no smell at all, and plenty of compounds with a smell are not aromatic.

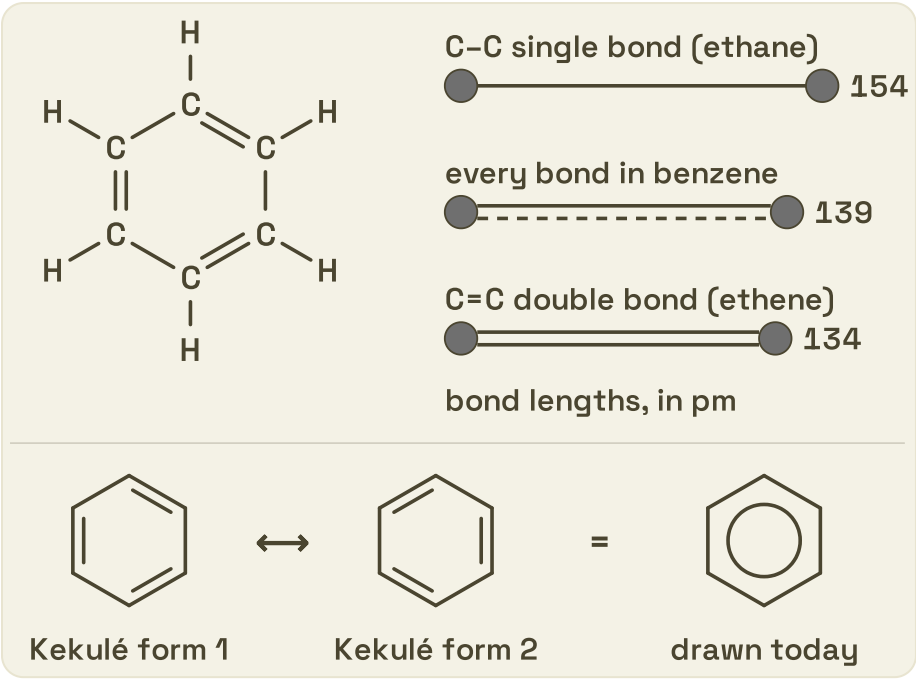


Figure 9.4 *Benzene, C_6H_6. Top left: every atom, in one Kekulé structure: a flat hexagon of carbon atoms, each with one hydrogen. Top right: its carbon–carbon bonds, all 139 pm long, between a single bond and a double bond (the dashed line stands for the half-shared π electrons). Below: the two Kekulé structures, which differ only in where the double bonds are drawn, and the hexagon with a circle that stands for the real molecule.*

Aromatic hydrocarbon	Formula	Where it is found or used
benzene	C_6H_6	coal tar and petroleum; making plastics (polystyrene), nylon, dyes, detergents and medicines
methylbenzene (toluene)	$C_6H_5CH_3$	a solvent in paints and glues; making explosives (TNT)
naphthalene	$C_{10}H_8$	mothballs; making dyes and plastics
anthracene	$C_{14}H_{10}$	coal tar; making dyes

Aromatic rings behave very differently from alkenes. Their delocalized π electrons are so stable that they resist **addition** (which would break up the ring of π electrons) and instead take part in **substitution**: a hydrogen on the ring is replaced, and the ring survives. Benzene doesn't take the color from bromine water; with bromine and

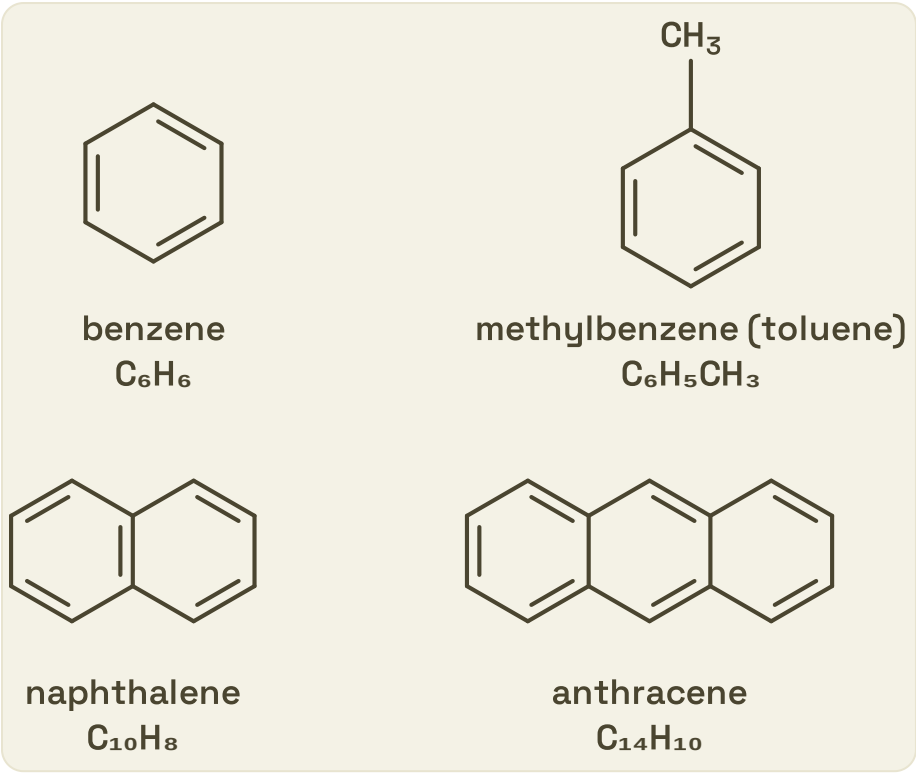


Figure 9.5 *Four aromatic hydrocarbons, drawn as hexagons with one Kekulé structure. Each corner is a carbon; a corner with only two ring bonds also holds one hydrogen, not written. Methylbenzene (toluene) has a CH_3 in place of one hydrogen of benzene. Naphthalene has two rings sharing one side, anthracene three in a row.*

an iron(III) bromide catalyst it gives bromobenzene, C_6H_5Br, and hydrogen bromide, replacing one hydrogen.

Heterocyclic compounds

The rings of a few cyclic compounds contain an atom other than carbon, usually nitrogen, oxygen or sulphur. These are **heterocyclic compounds** (Greek *heteros*, other): **pyridine**, C_5H_5N, has a nitrogen in a benzene-like ring, **furan**, C_4H_4O, an oxygen in a five-membered ring. They are everywhere in living things: the bases of DNA, adenine, guanine, cytosine and thymine, are heterocyclic rings, and so are caffeine (in tea and coffee) and nicotine (in tobacco).

CAREFUL

Benzene is dangerous

Benzene causes leukemia, a cancer of the blood, in people who breathe its vapor for long periods; the World Health Organization's cancer agency lists it among the substances known to cause cancer. It is no longer used as a solvent in school labs. Petrol contains a little (in many countries, by law no more than 1%), which is one more reason not to breathe petrol fumes. Naphthalene is poisonous if swallowed, and a mothball can look like a sweet to a small child: keep them out of reach.

Check 4

What is the molecular formula of cyclopentane?

a C_5H_{12}
b C_5H_{10}
c C_5H_8
d C_5H_5

Check 5

All six carbon–carbon bonds in benzene are 139 pm long. This shows that:

a benzene has three single and three double bonds
b benzene is not flat
c its π electrons are shared evenly round the whole ring
d benzene is an alicyclic compound

9.4 Huckel's rule

Statement

Benzene is not the only aromatic ring. In 1931 the German physicist Erich Hückel worked out, from the quantum theory of electrons, which rings share their π electrons in the special stable way that benzene does. The answer came down to a count.

Hückel's rule: a cyclic molecule (or ion) is **aromatic** if

1. it is **cyclic** and **planar** (flat), so that the electrons above and below the ring can join up all the way round;
2. every atom of the ring takes part in the ring of π electrons (**completely conjugated**): each ring atom is part of a double bond, or has a lone pair or an empty orbital to share, with no CH_2 or other atom with four single bonds in the ring;

3. the ring holds **(4n + 2) π electrons**, where n = 0, 1, 2, 3… : that is, 2, 6, 10, 14, 18… π electrons.

A ring that is cyclic, planar and conjugated but has **4n** π electrons (4, 8, 12…) is not aromatic; it is unusually *unstable*, and is called **antiaromatic**. A ring that fails conditions 1 or 2 is simply **non-aromatic**.

Counting π electrons

- Each **double bond** in the ring gives **2** π electrons.
- A ring carbon with a negative charge (a **lone pair**) that can join the ring gives **2**.
- A ring carbon with a positive charge (an **empty** orbital) gives **0**, but still completes the ring.
- A CH_2 (or any carbon with four single bonds) in the ring gives nothing and **breaks** the ring of π electrons.

Then solve 4n + 2 = (number of π electrons) for n. If n comes out as a whole number (0, 1, 2…), the count fits.

WORKED EXAMPLE

Is benzene aromatic?

Apply Hückel's rule to benzene, C_6H_6.

Answer

1. Benzene is a ring of six carbons, and it is flat.
2. Every ring carbon is in a double bond (in either Kekulé structure): the ring is completely conjugated.
3. It has 3 double bonds, so $3 \times 2 = \mathbf{6\ \pi\ electrons}$. 4n + 2 = 6 gives 4n = 4, $\mathbf{n = 1}$, a whole number.

All three conditions hold: **benzene is aromatic.**

WORKED EXAMPLE

Naphthalene and cyclooctatetraene

Use Hückel's rule on a. naphthalene, $C_{10}H_8$ (two flat rings sharing a side, five double bonds), and b. cyclooctatetraene, C_8H_8 (a ring of eight carbons with four double bonds, shaped like a tub).

Answer

a. Naphthalene is flat and every one of its ten ring carbons is in a double bond. π electrons: $5 \times 2 = \mathbf{10}$. $4n + 2 = 10$ gives $4n = 8$, $\mathbf{n = 2}$, a whole number: **aromatic.**

b. Cyclooctatetraene has $4 \times 2 = \mathbf{8}$ π electrons. $4n + 2 = 8$ gives $4n = 6$, $n = 1.5$, not a whole number: the count fails. (8 is a 4n number, $n = 2$.) A flat ring with 8 π electrons would be antiaromatic, so the molecule avoids being flat: it folds into a tub, its double bonds stay separate and react like an alkene's. **Not aromatic.**

WORKED EXAMPLE

Cyclopentadiene and its anion

a. Cyclopenta-1,3-diene, C_5H_6, is a flat ring of five carbons with two double bonds and one CH_2. Is it aromatic? b. It easily loses an H^+ from the CH_2 to form the cyclopentadienyl anion, $C_5H_5^-$, in which that carbon keeps a lone pair. Is the anion aromatic?

Answer

a. The CH_2 carbon has four single bonds and no π electrons to share, so the ring of π electrons is broken (condition 2 fails). **Not aromatic.** (Its 4 π electrons wouldn't fit the count either: $4n + 2 = 4$ gives $n = ½$.)

b. Now the fifth carbon's lone pair joins the ring: every ring atom takes part. π electrons: 2×2 (double bonds) $+ 2$ (lone pair) $= \mathbf{6}$. $4n + 2 = 6$, $\mathbf{n = 1}$: **aromatic.** This is why cyclopentadiene gives up that H^+ unusually easily for a hydrocarbon: the anion it leaves is stabilized by becoming aromatic.

CAREFUL

Fused rings and the limits of the rule

Hückel worked his rule out for a single ring. For fused rings, like naphthalene (10 π electrons, $n = 2$) and anthracene (14, $n = 3$), counting all the π electrons gives the right answer, and that is how exams use the rule. For some larger fused rings it doesn't work (pyrene, $C_{16}H_{10}$, has 16 π electrons, a 4n number, yet is aromatic), so for those chemists look at each ring or at the outer ring of atoms. For your exam: check the three conditions, count the π electrons, and find n.

DID YOU KNOW?

Measuring benzene's extra stability

Adding hydrogen to cyclohexene's one double bond gives out about 120 kJ per mole. If benzene had three ordinary double bonds, adding hydrogen to all three would give out about $3 \times 120 = 360$ kJ/mol. Measured, it gives out only about 208 kJ/mol. The missing $360 - 208 \approx 150$ kJ/mol is energy benzene doesn't have to start with: its delocalized ring is that much more stable than three separate double bonds. Chemists call it benzene's **resonance energy**.

Check 6

How many π electrons does an aromatic ring with $n = 2$ in Hückel's rule have?

a 4
b 8
c 10
d 12

Check 7

Cyclobutadiene, C_4H_4, is a flat ring of four carbons with two double bonds. By Hückel's rule it is:

a aromatic, because it is flat and cyclic
b not aromatic, because it has 4 π electrons, which is not $4n + 2$
c aromatic, because every carbon is in a double bond
d not aromatic, because it has a CH_2 in its ring

9.5 Description of isomerism

What isomers are

In Grade 9 you saw that butane, $CH_3CH_2CH_2CH_3$, and 2-methylpropane, $CH_3CH(CH_3)CH_3$, are both C_4H_{10}. They are not two drawings of one compound: butane boils at −0.5 °C and 2-methylpropane at −12 °C; they are two different substances. Compounds like these are called isomers (Greek *isos*, equal, and *meros*, part: made of equal parts).

Isomers are compounds that have the same molecular formula but different structural formulas, and so different properties. The existence of such compounds is called **isomerism**.

Isomers have the same molecular mass and the same percentage of each element, but their atoms are joined differently. When the difference is in the order in which the atoms are joined, it is **structural isomerism**, which has three kinds: chain, position and functional.

> CAREFUL
> **The same molecule, drawn twice, is not an isomer**
>
> A chain drawn bent is the same chain: $CH_3CH_2CH_2CH_3$ and a butane drawn with a corner, or turned round, are one compound. Before calling two structures isomers, follow the longest chain and see what is joined to what. If the atoms are joined in the same order, it is the same molecule however it is drawn: give both the IUPAC name, and if the names are the same, so are the compounds.

Chain isomerism

Chain isomers have the same molecular formula but different carbon skeletons: a longer chain, or a shorter one with branches. The functional group (if any) is the same.

Pentane, C_5H_{12}, has three chain isomers: pentane (boils at 36 °C), 2-methylbutane (28 °C) and 2,2-dimethylpropane (9.5 °C). The more branched the molecule, the more nearly round it is, the less surface it has to touch its neighbors, and the lower it boils.

Chain isomerism happens in other families too: butan-1-ol, $CH_3CH_2CH_2CH_2OH$, and 2-methylpropan-1-ol, $(CH_3)_2CHCH_2OH$, are chain isomers ($C_4H_{10}O$, both with the –OH on an end carbon); so are butanoic acid, $CH_3CH_2CH_2COOH$, and 2-methylpropanoic acid, $(CH_3)_2CHCOOH$.

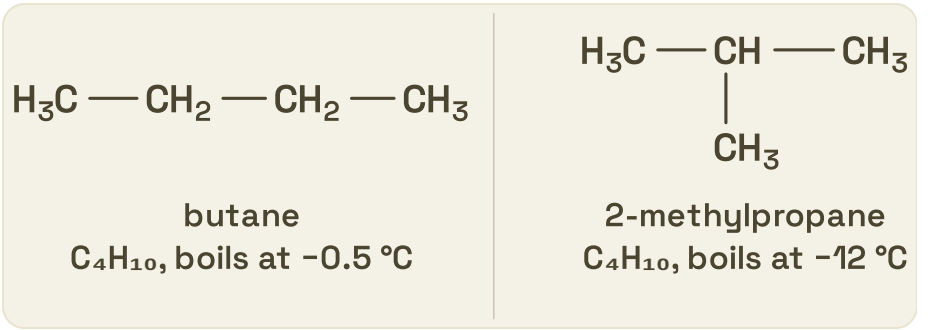


Figure 9.6 *The two chain isomers of C_4H_{10}. A branched chain packs less closely to its neighbors than a straight one, so its molecules hold each other more weakly, and it boils lower.*

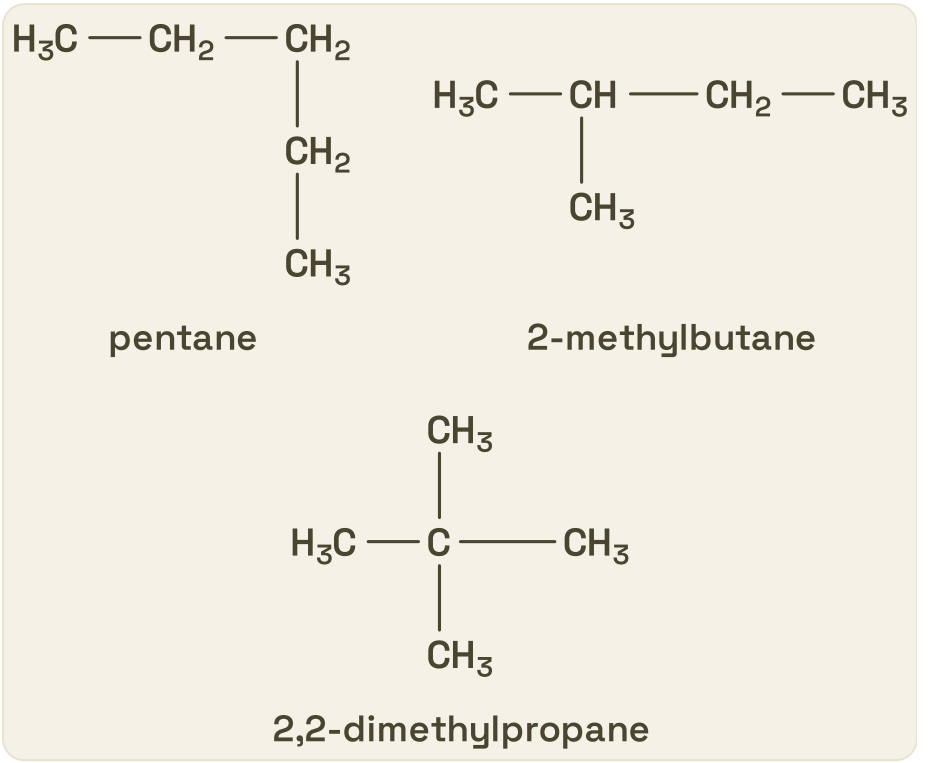


Figure 9.7 *The three chain isomers of C_5H_{12}, drawn as condensed structural formulas. The first is pentane, an unbranched chain drawn with a corner; the others have one and two methyl branches.*

Position isomerism

Position isomers have the same molecular formula, the same carbon skeleton and the same functional group, but the functional group (or a double or triple bond, or a

substituent such as a halogen) is in a different position on the chain.

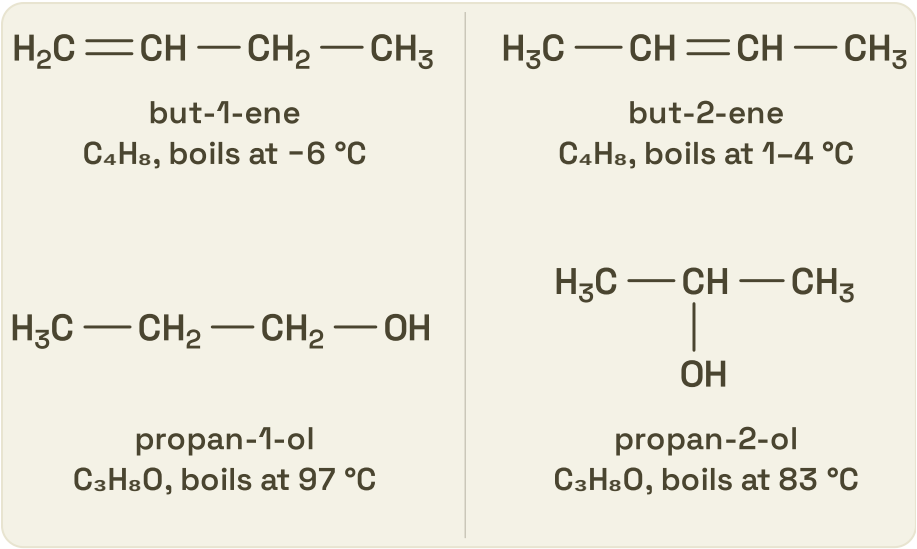


Figure 9.8 *Two pairs of position isomers. In but-1-ene and but-2-ene the double bond is in a different place; in propan-1-ol and propan-2-ol, the –OH. (But-2-ene comes in two forms, with slightly different boiling points; that is another kind of isomerism, which you meet in Grade 11.)*

More examples:

- pent-1-ene, $CH_2{=}CHCH_2CH_2CH_3$, and pent-2-ene, $CH_3CH{=}CHCH_2CH_3$ (C_5H_{10});
- but-1-yne, $CH{\equiv}CCH_2CH_3$, and but-2-yne, $CH_3C{\equiv}CCH_3$ (C_4H_6);
- pentan-2-one, $CH_3COCH_2CH_2CH_3$, and pentan-3-one, $CH_3CH_2COCH_2CH_3$ ($C_5H_{10}O$);
- 1-chloropropane, $CH_3CH_2CH_2Cl$, and 2-chloropropane, $CH_3CHClCH_3$ (C_3H_7Cl).

Aldehydes and carboxylic acids have no position isomers of this kind: their group is always on carbon 1, at the end of the chain.

Functional isomerism

Functional isomers have the same molecular formula but different functional groups, so they belong to different families and have different chemical properties.

The common pairs follow from the general formulas you learned in Grade 9:

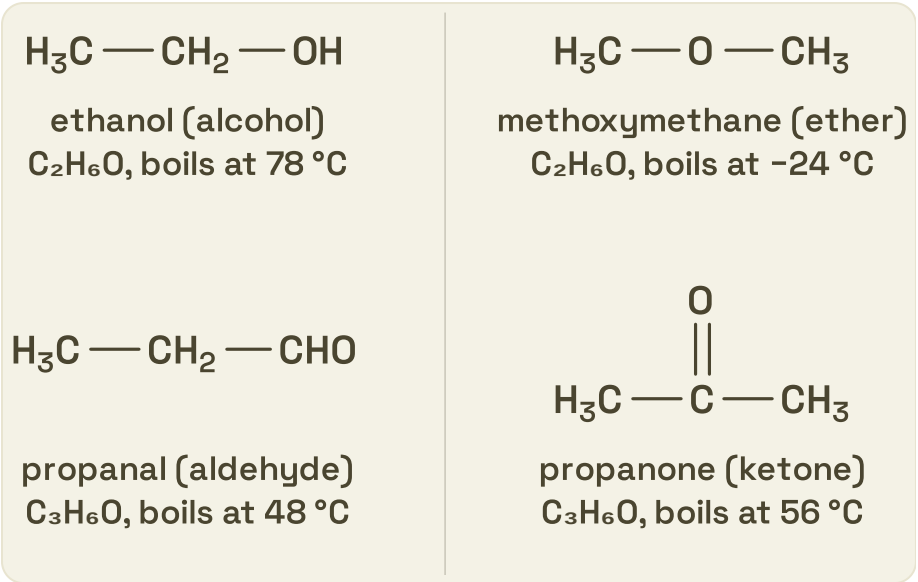


Figure 9.9 *Two pairs of functional isomers. Ethanol is an alcohol and methoxymethane an ether, both C_2H_6O; propanal is an aldehyde and propanone a ketone, both C_3H_6O.*

General formula	Functional isomers	Example (same formula)
$C_nH_{2n+2}O$	alcohols and ethers	ethanol, CH_3CH_2OH, and methoxymethane, CH_3OCH_3 (C_2H_6O)
$C_nH_{2n}O$	aldehydes and ketones	propanal, CH_3CH_2CHO, and propanone, CH_3COCH_3 (C_3H_6O)
C_nH_{2n}	alkenes and cycloalkanes	propene, $CH_2{=}CHCH_3$, and cyclopropane (C_3H_6)

Functional isomers differ far more than chain or position isomers do. Ethanol, with its –OH, is a liquid that mixes with water and reacts with sodium to give hydrogen; methoxymethane is a gas (it boils at −24 °C) that doesn't react with sodium at all.

Finding every isomer

To write all the isomers of a formula without missing any or writing one twice, work step by step:

1. **Decide the family or families** the formula allows from the general formulas: C_nH_{2n+2} is an alkane only; $C_nH_{2n+2}O$ an alcohol or an ether; $C_nH_{2n}O$ an aldehyde

CAREFUL

Metamerism

Some books add a fourth kind, **metamerism**: isomers of the same family that differ in the groups on either side of a functional group, like the ethers ethoxyethane, $C_2H_5OC_2H_5$, and 1-methoxypropane, $CH_3OC_3H_7$ (both $C_4H_{10}O$). These are often counted as position isomers, the oxygen being in a different place in the chain. If an exam asks for chain, position and functional isomers only, describe a pair like this as position isomers.

or ketone.

2. **Chain:** write the longest possible chain of carbons first, then chains one carbon shorter with the missing carbon as a methyl branch at each different place, then two carbons shorter, and so on.
3. **Position:** on each skeleton, put the functional group (or double bond) at each different place.
4. **Name each one.** Two structures with the same IUPAC name are the same compound: cross one out.

WORKED EXAMPLE

The isomers of C_6H_{14}

Write and name all the isomers of C_6H_{14}.

Answer

C_6H_{14} is C_nH_{2n+2} with $n = 6$: only alkanes.
Six carbons in a chain: **hexane**, $CH_3CH_2CH_2CH_2CH_2CH_3$.
Five in the chain, one methyl branch: on carbon 2, **2-methylpentane**, $CH_3CH(CH_3)CH_2CH_2CH_3$; on carbon 3, **3-methylpentane**, $CH_3CH_2CH(CH_3)CH_2CH_3$. (On carbon 4 is 2-methylpentane again, counted from the other end; on carbon 1 it would lengthen the chain to hexane.)
Four in the chain, two methyl branches: both on carbon 2, **2,2-dimethylbutane**, $CH_3C(CH_3)_2CH_2CH_3$; on carbons 2 and 3, **2,3-dimethylbutane**, $CH_3CH(CH_3)CH(CH_3)CH_3$.
Three in the chain would need three methyls on carbon 2, which then has five bonds: impossible.
So C_6H_{14} has **5** isomers, all chain isomers of each other.

WORKED EXAMPLE

The isomers of C_3H_8O

Write and name all the isomers of C_3H_8O, and say which kind each pair is.

Answer

C_3H_8O fits $C_nH_{2n+2}O$: alcohols and ethers.
Alcohols: **propan-1-ol**, $CH_3CH_2CH_2OH$, and **propan-2-ol**, $CH_3CH(OH)CH_3$.
Ether: **methoxyethane**, $CH_3OCH_2CH_3$.
Propan-1-ol and propan-2-ol are position isomers; each of them and methoxyethane are functional isomers. **3** isomers in all.

YOUR TURN

The ketones of $C_5H_{10}O$

Write and name the ketones with the formula $C_5H_{10}O$, and say how they are related.

Hint

A ketone's C=O can't be on an end carbon. Try a five-carbon chain with the C=O on carbon 2 and on carbon 3, then a four-carbon chain with a methyl branch.

Answer

Pentan-2-one, $CH_3COCH_2CH_2CH_3$; **pentan-3-one**, $CH_3CH_2COCH_2CH_3$; **3-methylbutan-2-one**, $CH_3COCH(CH_3)CH_3$. Pentan-2-one and pentan-3-one are position isomers; 3-methylbutan-2-one is a chain isomer of both. ($C_5H_{10}O$ also has aldehydes, functional isomers of these ketones.)

Check 8

Propanal, CH_3CH_2CHO, and propanone, CH_3COCH_3, are:

a chain isomers
b position isomers
c functional isomers
d not isomers

Check 9

How many structural isomers does $C_4H_{10}O$ have?

a 4
b 5
c 6
d 7

9.6 Introduction to some organic reactions

An organic reaction usually happens at the functional group, or at a double or triple bond, while the rest of the molecule stays as it is. Three kinds of reaction are met again and again in aliphatic compounds, sorted by what happens to the molecule.

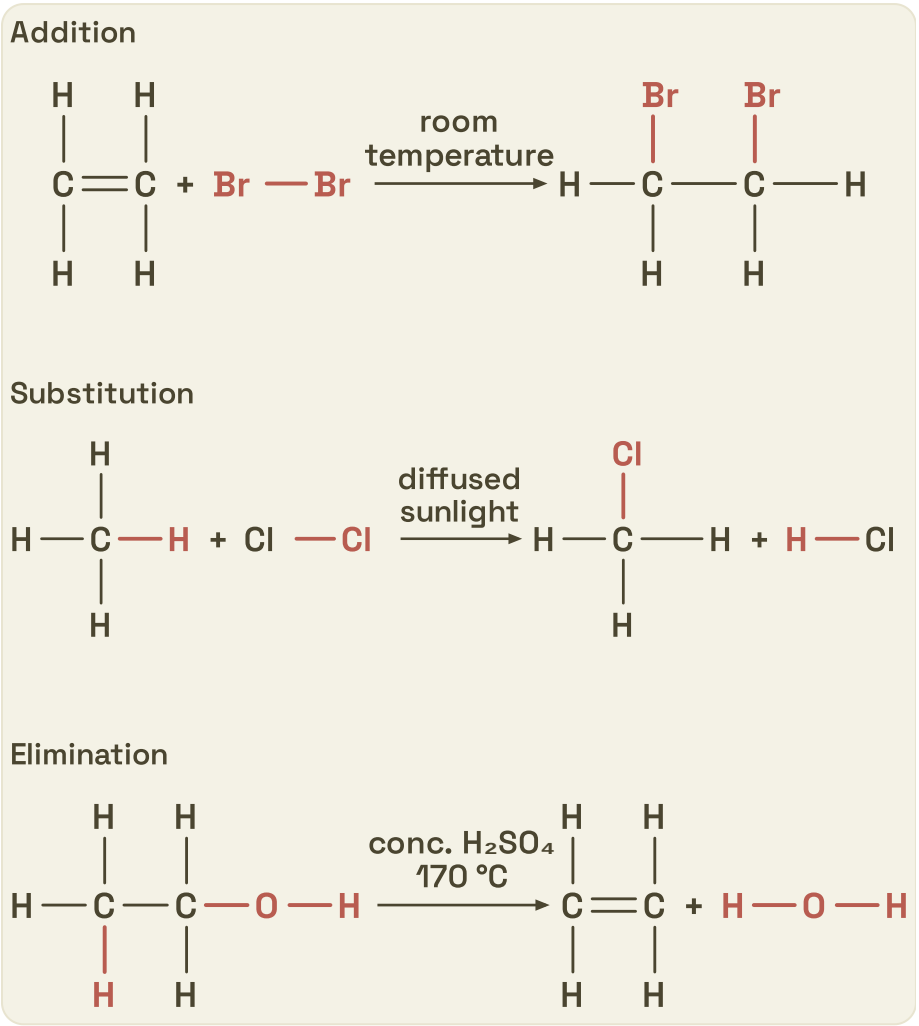


Figure 9.10 *One example of each kind of reaction, every atom drawn. The atoms that come in or go out are red.* ***Addition:*** *two bromine atoms add on at the double bond.* ***Substitution:*** *a chlorine atom takes the place of a hydrogen atom.* ***Elimination:*** *an –OH and an H leave from neighboring carbons, which then form a double bond.*

Addition reaction

An **addition reaction** is a reaction in which two molecules join to form a single product, with nothing left over. In organic chemistry it happens at a double or triple bond: the π bond opens, and an atom or group adds to each of its two carbons. So only **unsaturated** compounds (alkenes, alkynes) take part in addition; the product is more saturated than what you started with.

Here we take addition of **homoatomic molecules**, molecules made of two atoms of the same element: hydrogen (H_2), chlorine (Cl_2) and bromine (Br_2). The molecule splits, and one atom joins each carbon of the double bond.

Addition of hydrogen (hydrogenation). Ethene and hydrogen, passed over heated, finely divided nickel (or with platinum or palladium at room temperature), give ethane:

$$CH_2{=}CH_2 + H_2 \xrightarrow{Ni,\ heat} CH_3{-}CH_3$$

An alkyne adds hydrogen twice: first to an alkene, then to an alkane.

$$CH{\equiv}CH + H_2 \xrightarrow{Ni} CH_2{=}CH_2 \qquad CH_2{=}CH_2 + H_2 \xrightarrow{Ni} CH_3{-}CH_3$$

The same reaction turns liquid vegetable oils, whose molecules have C=C double bonds, into solid fat: this is how vanaspati ghee is made.

Addition of chlorine (chlorination). Ethene and chlorine react at room temperature to give 1,2-dichloroethane, each carbon taking one chlorine atom:

$$CH_2{=}CH_2 + Cl_2 \longrightarrow CH_2Cl{-}CH_2Cl$$

1,2-Dichloroethane is made in huge amounts: it is the first step in making PVC, the plastic of water pipes and electric cable covers.

Addition of bromine (bromination). Ethene and bromine (in an organic solvent) react at room temperature to give 1,2-dibromoethane. The red-brown color of the bromine disappears as it is used up:

$$CH_2{=}CH_2 + Br_2 \longrightarrow CH_2Br{-}CH_2Br$$

Ethyne adds two molecules of bromine, one to each of its π bonds, giving 1,1,2,2-tetrabromoethane:

$$CH{\equiv}CH + 2Br_2 \longrightarrow CHBr_2{-}CHBr_2$$

CAREFUL

Bromine water: the test for unsaturation

Shake a few drops of orange bromine water with a liquid alkene, or bubble ethene through it, and the color disappears within seconds. An alkane (or benzene) leaves the color as it is. This decolorization is the test for a C=C or C≡C bond. In exams, write the product as 1,2-dibromoethane, which is what forms with bromine in an organic solvent. In bromine water itself, water molecules join in and the main product is 2-bromoethanol, CH_2BrCH_2OH; the color goes either way, so the test is the same.

Check 10

Which of these will take part in an addition reaction with hydrogen?

a ethane
b propane
c propene
d cyclohexane

Substitution reaction

A **substitution reaction** is a reaction in which an atom or group in a molecule is replaced by another atom or group. Saturated compounds, which can't add anything, react this way.

Chlorination of methane. Methane and chlorine don't react in the dark. In diffused sunlight (or ultraviolet light) one hydrogen atom of methane is replaced by a chlorine atom, giving chloromethane and hydrogen chloride:

$$CH_4 + Cl_2 \xrightarrow{\text{diffused sunlight}} CH_3Cl + HCl$$

With more chlorine, the other hydrogens are replaced one by one:

$$CH_3Cl + Cl_2 \longrightarrow CH_2Cl_2 + HCl \qquad CH_2Cl_2 + Cl_2 \longrightarrow CHCl_3 + HCl \qquad CHCl_3 +$$

The products are chloromethane, dichloromethane, trichloromethane (chloroform, once used to put patients to sleep for surgery) and tetrachloromethane (carbon tetrachloride, once used in fire extinguishers and now banned in most uses because it destroys the ozone layer). Ethane reacts the same way: $C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$.

Replacing a halogen. A halogen atom on a carbon chain can itself be replaced. Boiling bromoethane with **aqueous** potassium hydroxide replaces its bromine by –OH, giving ethanol:

$$C_2H_5Br + KOH\,(aq) \xrightarrow{\text{boil}} C_2H_5OH + KBr$$

CAREFUL

Diffused sunlight, not bright sunlight

Light is needed to split the chlorine molecules into atoms, which start the reaction. In bright direct sunlight the reaction can run out of control, even explosively, and strips the methane bare, giving black carbon (soot) and hydrogen chloride ($CH_4 + 2Cl_2 \rightarrow C + 4HCl$). That is why the condition is written "diffused sunlight".

Check 11

In the reaction $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$, the chlorine atom:

a adds on at a double bond
b takes the place of a hydrogen atom
c removes two atoms to make a double bond
d joins two molecules into one

Elimination reaction

An **elimination reaction** is a reaction in which atoms or groups are removed from two neighboring carbon atoms of a molecule, and a double (or triple) bond forms between those carbons. It is the reverse of addition: a saturated compound becomes an unsaturated one, and a small molecule (water, a hydrogen halide, hydrogen) is given off.

Removing water (dehydration) from an alcohol. Ethanol heated to 170 °C with excess concentrated sulphuric acid loses an –OH from one carbon and an H from the next, which leave as water:

$$CH_3{-}CH_2{-}OH \xrightarrow{\text{conc. } H_2SO_4,\ 170\ ^\circ C} CH_2{=}CH_2 + H_2O$$

Concentrated sulphuric acid takes up water strongly, which is why it is used. (Passing ethanol vapor over hot aluminium oxide, at about 350–400 °C, does the same.)

Removing a hydrogen halide (dehydrohalogenation). Bromoethane heated with potassium hydroxide dissolved in **alcohol** (alcoholic KOH) loses HBr and gives ethene:

$$CH_3{-}CH_2Br + KOH\ (alc) \xrightarrow{\text{heat}} CH_2{=}CH_2 + KBr + H_2O$$

Removing hydrogen (dehydrogenation). Heated briefly with steam to about 850 °C, ethane loses hydrogen and gives ethene. This "steam cracking", of ethane from natural gas and of naphtha from petroleum, is where most of the world's ethene comes from:

$$CH_3{-}CH_3 \xrightarrow{\text{high temperature}} CH_2{=}CH_2 + H_2$$

CAREFUL

Two exam traps

Temperature decides the product of ethanol and sulphuric acid. At 170 °C, with excess acid, the product is ethene (elimination). At about 140 °C, with excess ethanol, two ethanol molecules lose one water molecule between them and the product is ethoxyethane, $C_2H_5OC_2H_5$, an ether. **The solvent decides what KOH does to bromoethane.** Aqueous KOH gives ethanol (substitution); alcoholic KOH gives ethene (elimination). Always write the conditions on the arrow.

The three kinds compared

	Addition	Substitution	Elimination
What happens	two molecules join into one	one atom or group replaces another	atoms leave from neighboring carbons
Compounds that do it	unsaturated (alkenes, alkynes)	saturated (alkanes), and compounds with a group that can be replaced	saturated (alcohols, haloalkanes)
Change in the bonds	a double or triple bond becomes single (or double)	no change in the bonds between carbons	a single bond becomes double
Number of products	one	two	two (the organic product and a small molecule)
Example	$CH_2{=}CH_2 + Br_2 \rightarrow CH_2BrCH_2Br$	$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$	$C_2H_5OH \rightarrow CH_2{=}CH_2 + H_2O$

WORKED EXAMPLE

Name the reaction

Say whether each is addition, substitution or elimination, and name the organic product.

a. $CH_3CH{=}CH_2 + H_2 \rightarrow CH_3CH_2CH_3$ (Ni, heat)

b. $CH_3CH_2CH_2OH \rightarrow CH_3CH{=}CH_2 + H_2O$ (conc. H_2SO_4, heat)

c. $C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$ (diffused sunlight)

Answer

a. Two molecules give one, and the C=C becomes single: **addition** (hydrogenation). The product is **propane**.

b. –OH and H leave from neighboring carbons as water, and a C=C forms: **elimination** (dehydration). The product is **propene**.

c. A hydrogen of ethane is replaced by chlorine: **substitution**. The product is **chloroethane**.

WORKED EXAMPLE

How much bromine?

What mass of bromine is decolorized by 7 g of ethene, and what mass of 1,2-dibromoethane forms? (C = 12, H = 1, Br = 80)

Answer

$CH_2{=}CH_2 + Br_2 \rightarrow CH_2BrCH_2Br$: 1 mole of ethene reacts with 1 mole of bromine and gives 1 mole of product.
Molar masses: ethene $C_2H_4 = 2 \times 12 + 4 \times 1 = 28$ g/mol; bromine $Br_2 = 2 \times 80 = 160$ g/mol; $C_2H_4Br_2 = 28 + 160 = 188$ g/mol.
Moles of ethene $= 7\text{ g} \div 28\text{ g/mol} = 0.25$ mol.
Bromine: $0.25\text{ mol} \times 160\text{ g/mol} =$ **40 g**. Product: $0.25\text{ mol} \times 188\text{ g/mol} =$ **47 g** (check: 7 + 40 = 47 g, as mass is conserved).

WORKED EXAMPLE

Hydrogen for an alkyne

What volume of hydrogen at STP is needed to turn 13 g of ethyne completely into ethane? (C = 12, H = 1; 1 mole of gas at STP = 22.4 L)

Answer

$CH{\equiv}CH + 2H_2 \rightarrow CH_3CH_3$: 1 mole of ethyne needs 2 moles of hydrogen. Molar mass of $C_2H_2 = 2 \times 12 + 2 \times 1 = 26$ g/mol, so 13 g is $13 \div 26 = 0.5$ mol. Hydrogen needed: $2 \times 0.5 = 1$ mol, which at STP is $1 \times 22.4 =$ **22.4 L**.

YOUR TURN

Ethene from ethanol

What volume of ethene at STP can be made by dehydrating 23 g of ethanol completely? (C = 12, H = 1, O = 16)

Hint

$C_2H_5OH \rightarrow C_2H_4 + H_2O$: one mole of ethanol gives one mole of ethene. Find the moles of ethanol first.

Answer

Molar mass of $C_2H_5OH = 2 \times 12 + 6 \times 1 + 16 = 46$ g/mol, so 23 g is 0.5 mol. It gives 0.5 mol of ethene: $0.5 \times 22.4 =$ **11.2 L** at STP.

IN SHORT

- Organic compounds are sorted by their skeleton: **open chain (aliphatic)**, straight or branched, saturated or unsaturated; and **closed chain (cyclic)**: **homocyclic** (alicyclic or aromatic) or **heterocyclic** (another atom in the ring).
- Single bond: tetrahedral, 109.5°, 154 pm, free to spin. Double bond ($\sigma + \pi$): flat, about 120°, 134 pm. Triple bond ($\sigma + 2\pi$): straight, 180°, 120 pm.
- **Alicyclic** compounds are rings that behave like aliphatic ones; cycloalkanes are C_nH_{2n} (cyclopropane, cyclohexane).
- **Aromatic** compounds have flat rings of delocalized π electrons, like benzene, C_6H_6 (all six C–C bonds 139 pm); they prefer substitution to addition.
- **Hückel's rule:** a ring that is planar and completely conjugated is aromatic if it has **$4n + 2$** π electrons (2, 6, 10, 14…): benzene 6 ($n = 1$), naphthalene 10 ($n = 2$), anthracene 14 ($n = 3$), $C_5H_5^-$ 6. Cyclobutadiene (4) and cyclooctatetraene (8, a tub) are not aromatic.
- **Isomers** have the same molecular formula and different structural formulas. **Chain:** different skeletons (butane, 2-methylpropane). **Position:** the group or multiple bond in a different place (propan-1-ol, propan-2-ol). **Functional:** different functional groups (ethanol, methoxymethane; propanal, propanone).
- **Addition:** two molecules give one at a multiple bond ($CH_2{=}CH_2 + Br_2 \rightarrow CH_2BrCH_2Br$). **Substitution:** an atom is replaced ($CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$, diffused sunlight). **Elimination:** atoms leave from neighboring carbons to form a multiple bond ($C_2H_5OH \rightarrow C_2H_4 + H_2O$, conc. H_2SO_4 at 170 °C).

Exercise

1. Choose the correct option

a. Which of these is an aliphatic compound?

- **a** benzene
- **b** cyclohexane
- **c** propan-2-ol
- **d** naphthalene

b. The general formula of the cycloalkanes is:

- **a** C_nH_{2n+2}
- **b** C_nH_{2n}
- **c** C_nH_{2n-2}
- **d** C_nH_n

c. The length of each carbon–carbon bond in benzene is:

a 120 pm
b 134 pm
c 139 pm
d 154 pm

d. According to Hückel's rule, an aromatic ring contains:

a 4n π electrons
b (4n + 2) π electrons
c (4n + 1) π electrons
d (2n + 4) π electrons

e. Which of these is aromatic?

a cyclobutadiene, C_4H_4
b cyclooctatetraene, C_8H_8
c the cyclopentadienyl anion, $C_5H_5^-$
d cyclohexane, C_6H_{12}

f. Butan-1-ol and butan-2-ol are:

a chain isomers
b position isomers
c functional isomers
d the same compound

g. Ethanol and methoxymethane are functional isomers because they have:

a different molecular formulas
b different numbers of carbon atoms
c the same molecular formula but different functional groups
d the same functional group in different positions

h. Which reaction is an elimination?

a $CH_2{=}CH_2 + H_2 \rightarrow CH_3CH_3$
b $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$
c $CH_3CH_2Br + KOH\,(alc) \rightarrow CH_2{=}CH_2 + KBr + H_2O$
d $CH_3CH_2Br + KOH\,(aq) \rightarrow CH_3CH_2OH + KBr$

i. Methane reacts with chlorine in diffused sunlight to give chloromethane. This is an example of:

a addition
b substitution
c elimination
d polymerization

j. When ethene is passed through bromine water, the solution:

a turns blue
b turns red-brown
c loses its color
d gives off a gas

2. Give reasons

a. Benzene is an unsaturated compound, yet it doesn't decolorize bromine water.

b. Cyclohexane is alicyclic, while benzene is aromatic.

c. Butane and 2-methylpropane are isomers, but they have different boiling points.

d. Alkanes undergo substitution reactions, but not addition reactions.

e. Aldehydes don't show position isomerism of the functional group.

f. Chlorination of methane is carried out in diffused sunlight, not in the dark or in bright sunlight.

3. Differentiate between

i. Open-chain and closed-chain compounds

ii. Alicyclic and aromatic compounds

iii. Chain isomerism and position isomerism

iv. Addition reaction and substitution reaction

v. Addition reaction and elimination reaction

4. Answer the following questions

a. What are aliphatic compounds? Give two examples each of saturated and unsaturated aliphatic compounds.

b. What are closed-chain compounds? How are they classified? Give an example of each kind.

c. State Hückel's rule. Use it to show that benzene and naphthalene are aromatic.

d. Why is benzene drawn as a hexagon with a circle inside? What does the circle show?

e. What is isomerism? Describe chain, position and functional isomerism with one example each.

f. How does ethanol react with concentrated sulphuric acid at 170 °C and at 140 °C? Name the kind of reaction in the first case.

g. A hydrocarbon X, C_2H_4, decolorizes bromine water. X adds hydrogen in the presence of nickel to give Y. Y reacts with chlorine in diffused sunlight to give Z and hydrogen chloride. Identify X, Y and Z, write the equations, and name the kind of each reaction.

5. Write the structures and names

a. Write the condensed formulas and IUPAC names of all the isomers of C_5H_{12}, and name the kind of isomerism they show.

b. Write the structures and IUPAC names of two position isomers of C_4H_8 that have an unbranched chain.

c. Write a functional isomer of each, with its IUPAC name: a. ethanol, CH_3CH_2OH; b. propanone, CH_3COCH_3; c. propene, $CH_2{=}CHCH_3$.

d. Write the structures and IUPAC names of the four alcohols with the formula $C_4H_{10}O$. Pick out one pair of chain isomers and one pair of position isomers among them.

e. Draw the structure of cyclohexane and of benzene, and write the molecular formula of each.

6. Complete the reactions

a. Complete and name the kind of each reaction:

i. $CH_2{=}CH_2 + Cl_2 \rightarrow$

ii. $CH{\equiv}CH + 2H_2 \rightarrow$ (Ni)

iii. $CH_4 + Cl_2 \rightarrow$ (diffused sunlight)

iv. $CH_3CH_2Br + KOH$ (aq) $\rightarrow$

v. $CH_3CH_2Br + KOH$ (alc) $\rightarrow$

vi. $CH_3CH_2OH \rightarrow$ (conc. H_2SO_4, 170 °C)

b. Propene, $CH_2{=}CHCH_3$, reacts with bromine. Write the equation, name the product and the kind of reaction, and say what you would see.

7. Numerical problems

a. How many π electrons does the anthracene molecule, $C_{14}H_{10}$, have (seven double bonds in its Kekulé structure)? Find n in Hückel's rule and say whether it is aromatic. It is flat.

b. The cycloheptatrienyl cation, $C_7H_7^+$, is a flat ring of seven carbons with three double bonds; the seventh carbon carries the positive charge (an empty orbital). Count its π electrons and decide whether it is aromatic.

c. A cycloalkane has a molecular mass of 84. Find its molecular formula and name it. (C = 12, H = 1)

d. What mass of hydrogen is needed to change 14 g of ethene into ethane? (C = 12, H = 1)

e. When 8 g of methane reacts with chlorine in diffused sunlight to give chloromethane only, what mass of chloromethane and what volume of hydrogen chloride at STP form? (C = 12, H = 1, Cl = 35.5; 1 mole of gas at STP = 22.4 L)

f. Adding hydrogen to one mole of cyclohexene gives out about 120 kJ, and to one mole of benzene about 208 kJ. Estimate how much more stable benzene is than a ring of three separate double bonds would be.

g. An alkyne has a molecular mass of 40. Find its formula, draw its structure and name it. How many σ and π bonds does it contain? (C = 12, H = 1)

Found a mistake? Please tell us.