Unit 9

Answers: Organic Compounds

Quick checks

1 c In cyclobutane the four carbon atoms are joined in a ring. The others are open chains: a branch (2-methylpropane) or a double bond (but-1-ene) doesn't close the chain.

2 c In ethyne, HC≡CH, each carbon has only two things bonded to it (the other carbon and a hydrogen), so they are 180° apart and all four atoms are in a line. Ethene is flat but not straight (about 120° angles); ethane and butane are tetrahedral at each carbon.

3 c Two atoms are always joined by exactly one σ bond, along the line between them; any second and third bond is a π bond. So a triple bond is one σ and two π.

4 b A cycloalkane is C_nH_{2n}: with n = 5, C_5H_{10}. C_5H_{12} is pentane, the open chain; closing the ring takes off two hydrogens.

5 c If the double bonds were fixed, three bonds would be 134 pm and three 154 pm. Equal bonds, between the two, show that the six π electrons are delocalized over the whole ring. That is what makes benzene aromatic, not alicyclic.

6 c 4n + 2 with n = 2 is 4 × 2 + 2 = 10, as in naphthalene. 4 and 8 are 4n numbers (antiaromatic if the ring is flat and conjugated); 12 is also 4n (n = 3).

7 b It meets the first two conditions, but 4 π electrons would need n = ½. With 4n electrons (n = 1) it is antiaromatic, and so unstable that it can only be kept far below −200 °C or trapped inside another molecule. It has no CH_2: each carbon carries one hydrogen.

8 c Both are C_3H_6O, but one is an aldehyde (–CHO) and the other a ketone (C=O inside the chain): different functional groups, so functional isomers.

9 d Four alcohols (butan-1-ol, butan-2-ol, 2-methylpropan-1-ol, 2-methylpropan-2-ol) and three ethers (1-methoxypropane, 2-methoxypropane, ethoxyethane). Try them in the widget above.

10 c Addition needs a double or triple bond. Propene, $CH_2{=}CHCH_3$, has a C=C and adds H_2 to give propane. Ethane, propane and cyclohexane are saturated: every carbon already has four single bonds.

11 b Methane has no double bond to add to. One of its hydrogens is replaced by chlorine, and the hydrogen leaves with the other chlorine atom as HCl: a substitution reaction. Two products form, where an addition reaction gives one.

1 a. **c** Propan-2-ol, $CH_3CH(OH)CH_3$, is an open chain. Cyclohexane is alicyclic and benzene and naphthalene are aromatic: all three are closed chains.

1 b. **b** Closing an alkane's chain into a ring removes two hydrogens: $C_nH_{2n+2} - 2H = C_nH_{2n}$, the same general formula as the alkenes.

1 c. **c** All six are 139 pm, between a double bond (134 pm) and a single bond (154 pm), because benzene's π electrons are spread evenly round the ring. 120 pm is a triple bond.

1 d. **b** A flat, completely conjugated ring is aromatic with $4n + 2$ π electrons ($n = 0, 1, 2\ldots$). A ring with $4n$ π electrons would be antiaromatic.

1 e. **c** $C_5H_5^-$ is flat and every ring carbon takes part, with $2 \times 2 + 2 = 6$ π electrons ($n = 1$). Cyclobutadiene has 4 and cyclooctatetraene 8 (and is tub-shaped); cyclohexane has none.

1 f. **b** Same formula ($C_4H_{10}O$), same chain, same group (–OH), but the –OH is on carbon 1 in one and carbon 2 in the other: position isomers.

1 g. **c** Both are C_2H_6O; ethanol has –OH (an alcohol) and methoxymethane –O– between two carbons (an ether).

1 h. **c** HBr is removed from neighboring carbons and a double bond forms: elimination. The first is addition, the second and fourth substitution.

1 i. **b** A hydrogen atom of methane is replaced by a chlorine atom: substitution. Methane is saturated, so it can't add anything.

1 j. **c** The bromine adds across the C=C bond and is used up, so its orange or red-brown color disappears: the test for unsaturation.

2 a. Benzene's six π electrons are delocalized evenly round its flat ring, which makes the ring unusually stable (by about 150 kJ/mol). Addition of bromine would break up this ring of π electrons and lose that stability, so benzene doesn't add bromine as an alkene does, and the bromine water keeps its color. Benzene instead reacts by substitution (with bromine and an iron(III) bromide catalyst), which keeps the aromatic ring.

2 b. Cyclohexane, C_6H_{12}, has only single bonds: it has no π electrons, and its ring is puckered, not flat, so it can't be aromatic; its ring behaves like an alkane's (an aliphatic cyclic compound, alicyclic). Benzene, C_6H_6, is flat, every ring carbon is in a double bond (completely conjugated), and it has 6 π electrons, $4n + 2$ with $n = 1$: it obeys Hückel's rule, so it is aromatic.

2 c. Both are C_4H_{10}, so they are isomers, but their atoms are joined differently: butane is an unbranched chain, 2-methylpropane a branched one. They are different compounds with different properties. The branched molecule is more compact, so it has less surface in contact with its neighbors and they attract each other more weakly; less energy is needed to separate them, and it boils lower (−12 °C against −0.5 °C).

2 d. Addition happens at a double or triple bond: the π bond opens and the new atoms add to its carbons. Alkanes are saturated: every carbon already has four single bonds and no π bond to open. So an alkane can react only by having one of its atoms (a hydrogen) replaced by another, which is substitution, as in $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$.

2 e. The –CHO group contains a carbon that has a hydrogen and a double bond to oxygen, so it can only be at the end of a chain: its carbon is always carbon 1. The group can't move to another position without becoming a different group (a C=O inside the chain is a ketone). So aldehydes have chain isomers (butanal and 2-methylpropanal) but no position isomers of the –CHO group.

2 f. Light gives chlorine molecules the energy to split into atoms, which start the reaction: in the dark, methane and chlorine don't react. In bright direct sunlight the reaction can run out of control, even explosively, giving carbon and hydrogen chloride ($CH_4 + 2Cl_2 \rightarrow C + 4HCl$). Diffused sunlight starts the reaction and keeps it steady.

3 i.

Open-chain compounds	Closed-chain compounds
Carbon atoms joined in chains, straight or branched, with no ring.	Some atoms joined in a ring.
Also called acyclic or aliphatic compounds.	Also called cyclic compounds.
Alkanes C_nH_{2n+2}, alkenes C_nH_{2n}, alkynes C_nH_{2n-2}.	Cycloalkanes C_nH_{2n}; aromatic rings such as C_6H_6.
Examples: butane, ethanol, ethanoic acid.	Examples: cyclohexane, benzene, pyridine.

3 ii.

Alicyclic compounds	Aromatic compounds
Rings that behave like aliphatic (open-chain) compounds.	Rings with special stability, like benzene's.
The ring is often puckered, not flat (cyclohexane).	The ring is flat.
No delocalized ring of π electrons (any double bonds stay separate).	Delocalized π electrons all round the ring, $4n + 2$ of them (Hückel's rule).
Saturated ones react by substitution; unsaturated ones (cyclohexene) by addition, like alkenes.	Resist addition; react by substitution, keeping the ring.
Examples: cyclopropane, cyclohexane, cyclohexene.	Examples: benzene, methylbenzene, naphthalene.

3 iii.

Chain isomerism	Position isomerism
The isomers have different carbon skeletons (a longer chain, or a shorter one with branches).	The isomers have the same carbon skeleton.
The functional group, if any, is the same.	The same functional group, double bond or substituent is in a different position.
Example: butane and 2-methylpropane (C_4H_{10}).	Example: propan-1-ol and propan-2-ol (C_3H_8O).

3 iv.

Addition reaction	Substitution reaction
Two molecules join to form one product.	An atom or group in a molecule is replaced by another.
Shown by unsaturated compounds (alkenes, alkynes).	Shown by saturated compounds (alkanes) and others with a replaceable atom or group.
A double or triple bond becomes single (or double).	The bonds between carbons don't change.
One product.	Two products.
Example: $CH_2{=}CH_2 + Cl_2 \rightarrow CH_2ClCH_2Cl$.	Example: $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$.

3 v.

Addition reaction	Elimination reaction
Atoms are added to the two carbons of a multiple bond.	Atoms are removed from two neighboring carbons.
A double bond becomes single: the product is more saturated.	A single bond becomes double: the product is unsaturated.
Two reactants give one product.	One reactant gives two products (one a small molecule such as H_2O or HBr).
Example: $CH_2{=}CH_2 + H_2 \rightarrow CH_3CH_3$ (Ni, heat).	Example: $C_2H_5OH \rightarrow CH_2{=}CH_2 + H_2O$ (conc. H_2SO_4, 170 °C).

4 a. Aliphatic (open-chain or acyclic) compounds are organic compounds whose carbon atoms are joined in straight or branched chains, not in rings. Saturated aliphatic compounds have only single bonds between carbon atoms: for example ethane, CH_3CH_3, and propane, $CH_3CH_2CH_3$. Unsaturated aliphatic compounds have at least one double or triple bond between carbon atoms: for example ethene, $CH_2{=}CH_2$, and ethyne, CH≡CH.

4 b. Closed-chain (cyclic) compounds are organic compounds in which atoms are joined in a ring. They are classified as:

- **Homocyclic (carbocyclic):** the ring is made of carbon atoms only. These are **alicyclic** compounds, rings that behave like aliphatic compounds, such as cyclohexane, C_6H_{12}, and **aromatic** compounds, flat rings with delocalized π electrons, such as benzene, C_6H_6.
- **Heterocyclic:** the ring contains at least one atom other than carbon, such as pyridine, C_5H_5N (a nitrogen in the ring).

4 c. **Hückel's rule:** a cyclic, planar molecule in which every ring atom takes part in a continuous ring of π electrons is aromatic if it contains $(4n + 2)$ π electrons, where $n = 0, 1, 2, 3\ldots$

Benzene, C_6H_6: a flat ring of six carbons, each in a double bond; 3 double bonds give 6 π electrons. $4n + 2 = 6$ gives $n = 1$, a whole number: aromatic.

Naphthalene, $C_{10}H_8$: two flat fused rings, all ten carbons in double bonds; 5 double bonds give 10 π electrons. $4n + 2 = 10$ gives $n = 2$, a whole number: aromatic.

4 d. Kekulé's structure draws benzene with three single and three double bonds, but there are two ways to place them, and neither matches the real molecule: all six C–C bonds are the same length, 139 pm, between a single (154 pm) and a double bond (134 pm). The six π electrons are not fixed in three bonds but delocalized evenly round the ring, above and below it. The circle inside the hexagon stands for these six delocalized π electrons, and the hexagon for the ring of six carbons, each with one hydrogen.

4 e. Isomerism is the existence of two or more compounds with the same molecular formula but different structural formulas, and so different properties; such compounds are isomers.

- **Chain isomerism:** the isomers have different carbon skeletons. Example: butane, $CH_3CH_2CH_2CH_3$, and 2-methylpropane, $CH_3CH(CH_3)CH_3$, both C_4H_{10}.
- **Position isomerism:** the same skeleton and the same functional group (or multiple bond), in different positions. Example: but-1-ene, $CH_2{=}CHCH_2CH_3$, and but-2-ene, $CH_3CH{=}CHCH_3$, both C_4H_8.
- **Functional isomerism:** the same molecular formula but different functional groups. Example: ethanol, CH_3CH_2OH (an alcohol), and methoxymethane, CH_3OCH_3 (an ether), both C_2H_6O.

4 f. At 170 °C, with excess concentrated sulphuric acid, each ethanol molecule loses water from neighboring carbons and gives ethene: $CH_3CH_2OH \rightarrow CH_2{=}CH_2 + H_2O$. This is an **elimination** reaction (dehydration).
At about 140 °C, with excess ethanol, one water molecule is removed between two ethanol molecules, giving ethoxyethane (diethyl ether): $2C_2H_5OH \rightarrow C_2H_5OC_2H_5 + H_2O$.

4 g. X is **ethene**, $CH_2{=}CH_2$ (it decolorizes bromine water, so it has a double bond). $CH_2{=}CH_2 + H_2 \rightarrow CH_3CH_3$ (Ni, heat): **addition**; Y is **ethane**. $CH_3CH_3 + Cl_2 \rightarrow CH_3CH_2Cl + HCl$ (diffused sunlight): **substitution**; Z is **chloroethane**.

5 a. **Pentane**, $CH_3CH_2CH_2CH_2CH_3$; **2-methylbutane**, $CH_3CH(CH_3)CH_2CH_3$; **2,2-dimethylpropane**, $C(CH_3)_4$ (or $CH_3C(CH_3)_2CH_3$). Three isomers, all chain isomers of each other.

5 b. **But-1-ene**, $CH_2{=}CH{-}CH_2{-}CH_3$, and **but-2-ene**, $CH_3{-}CH{=}CH{-}CH_3$. The double bond is between carbons 1 and 2 in one and carbons 2 and 3 in the other.

5 c.

a. **Methoxymethane**, CH_3OCH_3 (an ether; both C_2H_6O).

b. **Propanal**, CH_3CH_2CHO (an aldehyde; both C_3H_6O).

c. **Cyclopropane**, a ring of three CH_2 groups (a cycloalkane; both C_3H_6).

5 d.

- **Butan-1-ol**, $CH_3CH_2CH_2CH_2OH$
- **Butan-2-ol**, $CH_3CH_2CH(OH)CH_3$
- **2-methylpropan-1-ol**, $(CH_3)_2CHCH_2OH$
- **2-methylpropan-2-ol**, $(CH_3)_3COH$

Chain isomers: butan-1-ol and 2-methylpropan-1-ol (both with the –OH on an end carbon, different skeletons). Position isomers: butan-1-ol and butan-2-ol (same chain, –OH on carbon 1 or 2); also 2-methylpropan-1-ol and 2-methylpropan-2-ol.

5 e. **Cyclohexane, C_6H_{12}:** a ring of six CH_2 groups joined by single bonds (drawn as a hexagon, each corner a CH_2). **Benzene, C_6H_6:** a flat ring of six CH groups with alternate single and double bonds in a Kekulé structure, or a hexagon with a circle inside (each corner a CH). See Figure 9.3 and Figure 9.4.

6 a.

i. $CH_2{=}CH_2 + Cl_2 \rightarrow$ **CH_2ClCH_2Cl** (1,2-dichloroethane): addition.

ii. $CH{\equiv}CH + 2H_2 \rightarrow$ **CH_3CH_3** (ethane): addition.

iii. $CH_4 + Cl_2 \rightarrow$ **$CH_3Cl + HCl$** (chloromethane): substitution.

iv. $CH_3CH_2Br + KOH\ (aq) \rightarrow$ **$CH_3CH_2OH + KBr$** (ethanol): substitution.

v. $CH_3CH_2Br + KOH\ (alc) \rightarrow$ **$CH_2{=}CH_2 + KBr + H_2O$** (ethene): elimination.

vi. $CH_3CH_2OH \rightarrow$ **$CH_2{=}CH_2 + H_2O$** (ethene): elimination.

6 b. $CH_2{=}CHCH_3 + Br_2 \rightarrow$ **$CH_2BrCHBrCH_3$**, **1,2-dibromopropane**. It is an addition reaction: the red-brown color of the bromine disappears as it adds across the C=C bond.

7 a. π electrons $= 7 \times 2 =$ **14**. $4n + 2 = 14$ gives $4n = 12$, **$n = 3$**, a whole number. Anthracene is flat and completely conjugated, so it is **aromatic**.

7 b. π electrons $= 3 \times 2 + 0 =$ **6**. Every ring carbon takes part (the charged carbon's empty orbital completes the ring), the ring is flat, and $4n + 2 = 6$ gives **$n = 1$**: **aromatic**.

7 c. $14n = 84$, so $n = 6$: **C_6H_{12}**, **cyclohexane**. Check: $6 \times 12 + 12 \times 1 = 84$.

7 d. Molar mass of $C_2H_4 = 28$ g/mol, so 14 g is 0.5 mol. It needs 0.5 mol of H_2, and H_2 is 2 g/mol: $0.5 \times 2 =$ **1 g** of hydrogen.

7 e. Molar mass of $CH_4 = 16$ g/mol, so 8 g is 0.5 mol.
$CH_3Cl = 12 + 3 + 35.5 = 50.5$ g/mol: $0.5 \times 50.5 =$ **25.25 g** of chloromethane.
HCl: 0.5 mol, which at STP is $0.5 \times 22.4 =$ **11.2 L**.

7 f. Three separate double bonds: $3 \times 120 = 360$ kJ/mol. Benzene gives out only 208 kJ/mol, so it is more stable by about $360 - 208 =$ **152 kJ/mol** (about 150 kJ/mol, its resonance energy), because its π electrons are delocalized round the ring.

7 g. $14n - 2 = 40$, so $n = 3$: **C_3H_4, propyne**, $CH{\equiv}C{-}CH_3$.
Bonds: the C≡C is 1 σ + 2 π; the C–C single bond is 1 σ; the four C–H bonds are 4 σ.
Total **6 σ and 2 π** bonds.