Unit 9 · Organic Compounds

STUDY NOTES

Key terms

Open-chain (acyclic, aliphatic): carbons in chains, straight or branched, no ring.

Saturated: only single C–C bonds. **Unsaturated**: at least one double or triple bond.

Closed-chain (cyclic): some atoms joined in a ring.

Homocyclic (carbocyclic): a ring of carbon only: alicyclic or aromatic.

Alicyclic: a carbon ring that behaves like an aliphatic compound.

Aromatic: one or more flat rings with π electrons delocalized all round; unusually stable.

Heterocyclic: another atom in the ring (N, O, S).

Delocalization: π electrons spread round the ring, not fixed in bonds.

Isomers: same molecular formula, different structural formulas, different properties.

Addition: two molecules give one product, at a multiple bond.

Substitution: an atom or group is replaced by another.

Elimination: atoms leave two neighboring carbons; a multiple bond forms.

Formulas

$4n + 2$ π electrons	$n = 0, 1, 2...$: 2, 6, 10, 14, 18 **Use:** aromatic (with the other two conditions)
$4n$ π electrons	4, 8, 12... **Use:** antiaromatic if flat and conjugated

Family	Formula	Mass
alkanes	C_nH_{2n+2}	$14n + 2$
alkenes, cycloalkanes	C_nH_{2n}	$14n$
alkynes	C_nH_{2n-2}	$14n - 2$

Sorting by skeleton

- **open chain**: saturated (alkanes: butane); unsaturated (alkenes, alkynes: propene)
- **closed chain**: homocyclic, alicyclic (cyclohexane) or aromatic (benzene); heterocyclic (pyridine)
- carbon's three:
  - tetracovalency
  - multiple bonding
  - catenation
- ring: 2 H fewer than the chain (hexane C_6H_{14}, cyclohexane C_6H_{12})
- "straight" = unbranched; a real chain zigzags (109.5°)

Bonds and shapes

	Single	Double	Triple
example	ethane	ethene	ethyne
shape	tetrahedral	flat	straight
angle	109.5°	about 120°	180°
C–C length	154 pm	134 pm	120 pm
spins?	yes	no	no change
bonds	σ	$\sigma + \pi$	$\sigma + 2\pi$

- σ along the line between the carbons; π above and below, weaker; π is where unsaturated compounds react

Rings

- cycloalkanes C_nH_{2n}, from $n = 3$; cyclo- + alkane name. Behave like alkanes
- cyclopropane: 60°, strained, breaks open more easily; cyclohexane puckers into a chair, near 109.5°
- others:
  - cyclohexene C_6H_{10} (like an alkene)
  - menthol
  - steroids, cholesterol
- **benzene** C_6H_6: Faraday 1825; Kekulé's ring 1865; Lonsdale's X-rays 1929, a regular hexagon
- all six C–C **139 pm**, between 134 and 154; six π electrons delocalized; the circle stands for them
- resists addition, prefers substitution: $C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr$ ($FeBr_3$); leaves bromine water's color
- stability: $3 \times 120 = 360$ kJ/mol predicted, about 208 measured; about 150 kJ/mol more stable (**resonance energy**)
- aromatic:
  - benzene C_6H_6
  - methylbenzene (toluene) $C_6H_5CH_3$
  - naphthalene $C_{10}H_8$
  - anthracene $C_{14}H_{10}$
- the word no longer means a smell: many have none
- benzene causes leukemia; naphthalene poisonous if swallowed
- heterocyclic:
  - pyridine C_5H_5N
  - furan C_4H_4O
  - DNA bases, caffeine, nicotine

Hückel's rule (1931)

Aromatic if all three:

1. cyclic and planar
2. every ring atom takes part (completely conjugated); no CH_2
3. $4n + 2$ π electrons

Count:

- double bond 2

- lone pair (−) 2
- empty orbital (+) 0, but completes the ring
- CH_2 nothing and **breaks** the ring

Ring	π electrons	Result
benzene C_6H_6	6 ($n = 1$)	aromatic
naphthalene $C_{10}H_8$	10 ($n = 2$)	aromatic
anthracene $C_{14}H_{10}$	14 ($n = 3$)	aromatic
$C_5H_5^-$	$2 \times 2 + 2 = 6$	aromatic
$C_7H_7^+$	$3 \times 2 + 0 = 6$	aromatic
C_5H_6	has a CH_2	not aromatic
C_4H_4	4	antiaromatic
C_8H_8	8, a tub	not aromatic

- fails 1 or 2: non-aromatic
- fused rings: count all; pyrene, 16, is an exception

Isomerism

Kind	What differs	Example
chain	skeleton	butane (−0.5 °C), 2-methylpropane (−12 °C)
position	place of group or multiple bond	propan-1-ol, propan-2-ol; but-1-ene, but-2-ene
functional	functional group	ethanol, methoxymethane

General formula	Functional isomers
$C_nH_{2n+2}O$	alcohols, ethers
$C_nH_{2n}O$	aldehydes, ketones
C_nH_{2n}	alkenes, cycloalkanes

- more branched: rounder, less surface, boils lower
  - pentane 36 °C
  - 2-methylbutane 28 °C
  - 2,2-dimethylpropane 9.5 °C
- aldehydes and acids have no position isomers: group always on carbon 1
- metamers (ethoxyethane, 1-methoxypropane) count as position isomers
- **to find all**:
  - family
  - longest chain, then shorter with branches
  - group at each place
  - name each, cross out repeats
- C_5H_{12}: 3
- C_6H_{14}: 5 (hexane, 2- and 3-methylpentane, 2,2- and 2,3-dimethylbutane)
- C_3H_8O: 3
- $C_4H_{10}O$: 7 (4 alcohols, 3 ethers)
- ketones $C_5H_{10}O$:
  - pentan-2-one
  - pentan-3-one
  - 3-methylbutan-2-one

Reactions

	Addition	Substitution	Elimination
done by	unsaturated	saturated	alcohols, haloalkanes
bonds	multiple → single (or double)	C–C unchanged	single → double
products	one	two	two

Addition

- $CH_2{=}CH_2 + H_2 \rightarrow CH_3CH_3$ (Ni, heat); vanaspati ghee
- $CH{\equiv}CH + 2H_2 \rightarrow CH_3CH_3$ (Ni), by way of ethene
- $CH_2{=}CH_2 + Cl_2 \rightarrow CH_2ClCH_2Cl$ (toward PVC)
- $CH_2{=}CH_2 + Br_2 \rightarrow CH_2BrCH_2Br$
- $CH{\equiv}CH + 2Br_2 \rightarrow CHBr_2CHBr_2$
- **test**: bromine water loses its color (alkene, alkyne); alkane, benzene keep it

Substitution

- $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$ (diffused sunlight)
- then CH_2Cl_2, $CHCl_3$ (chloroform), CCl_4
- dark: none. Bright sun: $CH_4 + 2Cl_2 \rightarrow C + 4HCl$
- $C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$
- $C_2H_5Br + KOH\ (aq) \rightarrow C_2H_5OH + KBr$ (boil)

Elimination

- $CH_3CH_2OH \rightarrow CH_2{=}CH_2 + H_2O$ (conc. H_2SO_4, 170 °C; or hot Al_2O_3)
- $CH_3CH_2Br + KOH\ (alc) \rightarrow CH_2{=}CH_2 + KBr + H_2O$
- $CH_3CH_3 \rightarrow CH_2{=}CH_2 + H_2$ (steam cracking, about 850 °C)

Amounts

- 7 g ethene + 40 g Br_2 → 47 g $C_2H_4Br_2$
- 13 g ethyne needs 22.4 L H_2 at STP
- 23 g ethanol gives 11.2 L ethene at STP

COMMON MISTAKES

✗ ethanol + H_2SO_4 always gives ethene
✓ 170 °C ethene; about 140 °C (excess ethanol) ethoxyethane.

✗ KOH on bromoethane, any solvent, same result
✓ aqueous: ethanol; alcoholic: ethene.

✗ benzene decolorizes bromine water
✓ no; only substitution, with $FeBr_3$.

✗ aromatic means it smells
✓ flat, delocalized ring.

✗ a chain drawn bent is an isomer
✓ same name, same compound.

✗ 4-methylpentane is a new isomer
✓ it's 2-methylpentane.

✗ flat and cyclic is enough
✓ count the electrons; check for CH_2.

✗ CH_4 reacts in bright sunlight to give CH_3Cl
✓ diffused; bright strips it to carbon.