Unit 13 · Fundamental Principles of Organic Chemistry

STUDY NOTES

WHAT NEB'S GRADE 11 EXAM ASKS

- **CDC's grid (2077):** Organic Chemistry (Units 12–15 together): 18 of 75 marks
- **The paper:** 11 MCQs × 1 · 8 short × 5 · 3 long × 8; 3 hours; 1 mark per expected point
- **CDC's model paper:** short: IUPAC names of given compounds and a position isomer; long: two functional isomers Y and Z of C_3H_6O (with Unit 14)
- **MCQ (1 mark)**: prefix + root + primary + secondary suffix; match group and class; NO_2^+ electrophile, CN^- nucleophile; longest chain; tartaric acid's name; $Na^+ + SCN^-$ means N and S; $2C^{-4} + 1$ (C_4–C_7 only); Lassaigne makes ionic compounds; blood red $Fe(SCN)_3$; functional isomer pairs; chiral carbon (four different groups); Cl–CH_2CH_2COOH the stronger acid (−I); C_nH_{2n+2}
- **Short (5 marks, in parts)**
  - terms of a name; a compound for each group; why IUPAC beats common names
  - Lassaigne: sodium extract (why, how); N in urea; N and S in thiourea; Cl in $CHCl_3$
  - isomers of C_5H_{12} with names; structural isomerism, each kind; nucleophile vs electrophile; chain vs position
  - optical isomers and the chiral carbon; geometrical isomers and E–Z
  - homolytic fission, free radical, inductive effect; resonance of benzene; +R vs −R
- **Long (8 marks)**: IUPAC names of eight compounds; Lassaigne report (which has S, which Br); types of isomerism with examples; optical vs inactive, +I vs −I, the two fissions; benzene resonance, geometrical vs optical, is $CH_3CH_2CCl(CH_3)CH_3$ optically active (no); naming rules

Naming (IUPAC)

prefix + word root + primary suffix + secondary suffix: 5-methylhex-3-en-2-ol

- **word root**: carbons in the parent chain: meth, eth, prop, but, pent, hex, hept, oct, non, dec
- **primary suffix**: -ane (all single), -ene (C=C), -yne (C≡C)
- **secondary suffix**: the main functional group; the group's own C counted in -al, -oic acid, -amide, -nitrile, -oyl halide

Group	Class	Suffix	Name
–OH	alcohol	-ol	alkanol
–CHO	aldehyde	-al	alkanal
>C=O	ketone	-one	alkanone
–COOH	acid	-oic acid	alkanoic acid
–COOR′	ester	-oate	alkyl alkanoate
$–CONH_2$	amide	-amide	alkanamide
–CN	nitrile	-nitrile	alkanenitrile
–COX	acyl halide	-oyl halide	alkanoyl halide
–CO–O–CO–	anhydride	-oic anhydride	alkanoic anhydride
$–NH_2$	amine	-amine	alkanamine
–O–	ether	(prefix alkoxy)	alkoxyalkane

- **prefixes** (substituents): methyl, ethyl…; fluoro, chloro, bromo, iodo; nitro; amino; cyano; methoxy, ethoxy; never suffixes: halogens, $–NO_2$, –OR
- **seniority** (the suffix): –COOH > $–SO_3H$ > anhydride > ester > acyl halide > amide > –CN > –CHO > >C=O > –OH > $–NH_2$; the rest as prefixes: hydroxy, amino, oxo, formyl, carboxy, cyano, carbamoyl
- IUPAC better: one name per compound, built by rules, tells the structure; common names (acetone, formic acid) must be learned one by one

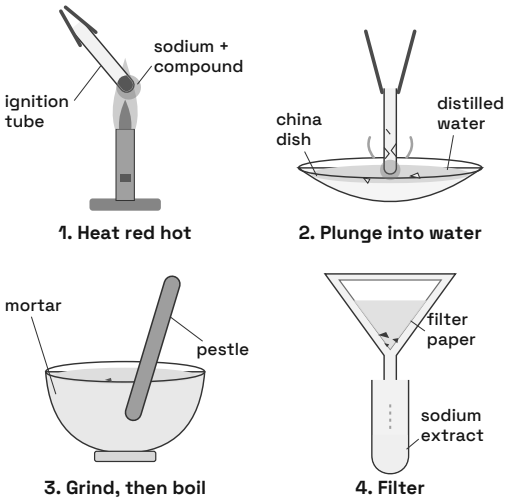
Rules

1. **parent chain**: longest continuous chain (holding the functional group and both C of a multiple bond); equal length → more substituents
2. number from the end that gives the **functional group**, then the multiple bond, then substituents the **lowest locants** (first point of difference; "lowest sum" usually agrees)
3. a tie: the substituent first in the **alphabet** gets the lower number
4. prefixes written in **alphabetical order** (di, tri ignored): 3-ethyl-2-methylhexane, 2-amino-3-hydroxybutanoic acid
5. di, tri, tetra with every locant: 2,2,3-trimethyl; numbers–numbers commas, numbers–letters hyphens
6. rings: **cyclo** + alkane; two multiple bonds: buta-1,3-diene (a added); C=C and C≡C: -en-…-yne, a tie → C=C lower: pent-1-en-4-yne
7. –CHO, –COOH always C-1 (number not written); diol, triol keep the e: ethane-1,2-diol, propane-1,2,3-triol

Compound	Name
$(CH_3)_2CHCH_2CH_3$	2-methylbutane
$(CH_3)_2CH–CH_2–C(CH_3)_3$	2,2,4-trimethylpentane
$CH_3CH(OH)CH_2CH_3$	butan-2-ol
$CH_3CH(OH)CH_2COCH_3$	4-hydroxypentan-2-one
$CH_2=C(C_3H_7)CH_2CH_2CH_3$	2-propylpent-1-ene
$Cl–CH_2CH_2COOH$	3-chloropropanoic acid
HOOC–CH(OH)–CH(OH)–COOH	2,3-dihydroxybutanedioic acid
$CH_3CH_2–O–CH_2CH_2CH_3$	1-ethoxypropane
$CH_3COOC_2H_5$	ethyl ethanoate
$CH_3CO–CH(OH)–CH(NH_2)–COOH$	2-amino-3-hydroxy-4-oxopentanoic acid

Lassaigne's test (N, S, halogens)

- covalent N, S, X give no ions: **fuse with sodium** → ionic NaCN, Na_2S, NaX, soluble in water
- $Na + C + N \longrightarrow NaCN$; $2\,Na + S \longrightarrow Na_2S$; $Na + X \longrightarrow NaX$
- **sodium extract**: rice-grain of Na melted in an ignition tube, compound added, heated **red hot**, plunged into distilled water, ground, boiled, filtered (behind a screen)



Preparing the sodium extract: fuse, break the red-hot tube in water, grind, boil, filter; the filtrate is the extract.

Nitrogen: extract (alkaline) + fresh **$FeSO_4$**, boil; + $FeCl_3$, conc. HCl → **Prussian blue**

- $FeSO_4 + 2\,NaOH \longrightarrow Fe(OH)_2 + Na_2SO_4$
- $Fe(OH)_2 + 6\,NaCN \longrightarrow Na_4[Fe(CN)_6] + 2\,NaOH$
- $3\,Na_4[Fe(CN)_6] + 4\,FeCl_3 \longrightarrow Fe_4[Fe(CN)_6]_3\downarrow + 12\,NaCl$ (iron(III) hexacyanoferrate(II))
- HCl dissolves the green $Fe(OH)_2$: $Fe(OH)_2 + 2\,HCl \longrightarrow FeCl_2 + 2\,H_2O$

Sulphur

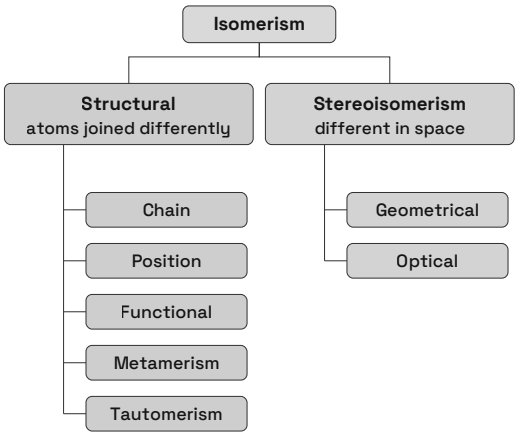
- with **sodium nitroprusside** → **violet**: $Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow Na_4[Fe(CN)_5NOS]$
- with ethanoic acid and **lead acetate** → **black** PbS: $Na_2S + (CH_3COO)_2Pb \longrightarrow PbS\downarrow + 2\,CH_3COONa$

N and S together (too little Na): NaSCN; with $FeCl_3$ **blood red**: $3\,NaSCN + FeCl_3 \longrightarrow Fe(SCN)_3 + 3\,NaCl$; excess Na: $NaSCN + 2\,Na \longrightarrow NaCN + Na_2S$

Halogens: boil with dil. HNO_3 (fume cupboard), then $AgNO_3$

- HNO_3 drives off CN^- and S^{2-} as HCN, H_2S (else white AgCN, black Ag_2S)
- $NaX + AgNO_3 \longrightarrow AgX\downarrow + NaNO_3$
- AgCl **white**, soluble in dil. NH_3: $AgCl + 2\,NH_4OH \longrightarrow [Ag(NH_3)_2]Cl + 2\,H_2O$; AgBr **pale yellow**, sparingly soluble (soluble in conc. NH_3); AgI **yellow**, insoluble

Isomerism



The kinds of isomerism in this unit.

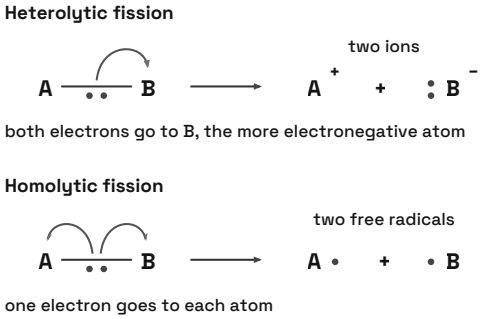
- **isomers**: same molecular formula, different structures (term coined by **Berzelius**, 1830)
- **structural** (atoms joined in another order)
  - **chain**: different carbon chain: butane / 2-methylpropane; C_5H_{12}: pentane, 2-methylbutane, 2,2-dimethylpropane (3); C_6 5, C_7 9, C_{10} 75
  - **position**: same chain, group or bond elsewhere: 1- / 2-chlorobutane; propan-1-ol / propan-2-ol; but-1-ene / but-2-ene
  - **functional**: different functional groups: alcohol / ether ($C_nH_{2n+2}O$), aldehyde / ketone ($C_nH_{2n}O$: **propanal / propanone, C_3H_6O**), acid / ester ($C_nH_{2n}O_2$)
  - **metamerism**: same group, carbons shared differently on its two sides: 1-methoxypropane / ethoxyethane; pentan-2-one / pentan-3-one; N-ethylethanamine / N-methylpropan-1-amine
  - **tautomerism**: an H (and a double bond) moves; both in **dynamic equilibrium**: keto ⇌ enol, CH_3COCH_3 ⇌ $CH_2=C(OH)CH_3$ (over 99.99% keto)
- **stereo** (same order, different arrangement in space)
  - **geometrical** (cis–trans): needs a C=C (no rotation) and **each** C of it holding **two different** groups: cis- (same side, b.p. 4 °C) and trans-but-2-ene (1 °C); cis/trans-1,2-dichloroethene; not propene
  - **E–Z**: priority by atomic number (Br > Cl > O > N > C > H; then the next atoms out); higher ones same side **Z** (zusammen), opposite **E** (entgegen)
  - **optical**: a **chiral carbon** (four different groups) → two **non-superimposable mirror images**

(**enantiomers**); same m.p., b.p.; turn **plane-polarized light** equally, opposite ways: **d (+)** clockwise, **l (−)** anticlockwise (polarimeter); 1 : 1 = **racemic** (±), inactive
  - lactic acid $CH_3CH(OH)COOH$, CHBrClF, butan-2-ol: chiral; propan-2-ol, $CH_3CH_2CCl(CH_3)CH_3$ (two CH_3): not
  - tartaric acid: 2 chiral C → d, l and **meso** (mirror plane inside, inactive)

Geometrical	Optical
C=C (or ring) with two different groups on each C	chiral carbon (four different groups)
cis / trans differ in physical properties	enantiomers alike except for light
not mirror images	mirror images

Reaction mechanism

- substrate + reagent → [intermediate] → products; curly arrows: full → a pair, half (fish-hook) → one electron

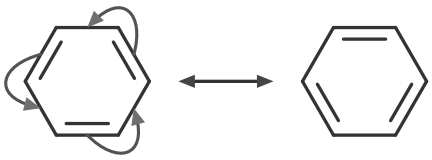


Bond fission: homolytic, one electron each (free radicals); heterolytic, both to the more electronegative atom (ions).

- **homolytic**: even split, **free radicals** Cl−Cl ⟶ 2 $Cl^{\bullet}$, CH_3−CH_3 ⟶ 2 $CH_3^{\bullet}$; non-polar bonds, gas phase, heat, UV light, peroxides
- **heterolytic**: uneven, ions: CH_3−Cl ⟶ $CH_3^+ + Cl^-$; polar bonds, polar solvents; **carbocation** (6 outer e^-, +), **carbanion** (8, −), **free radical** (7, neutral, very reactive)

	Electrophile	Nucleophile
meaning	electron-loving	nucleus-loving
has	too few electrons	a lone pair
new bond	accepts a pair	gives a pair
kind	+ ions; neutral, incomplete octet	− ions; neutral with lone pairs
attacks	electron-rich (C=C, ring)	δ+ carbon
examples	NO_2^+, CH_3^+, H^+, Br^+, BF_3, $AlCl_3$, SO_3	OH^-, CN^-, Cl^-, RO^-, NH_3, H_2O, ROH
	Lewis acid	Lewis base

- **inductive effect**: permanent shift of σ electrons along a chain by an electronegative atom; fades along the chain ($\delta+ > \delta\delta+ > \delta\delta\delta+$)
  - **+I** (push electrons, vs H): alkyls, $(CH_3)_3C- > (CH_3)_2CH- > C_2H_5- > CH_3-$
  - **−I** (pull): $-NO_2 > -CN > -F > -Cl > -Br > -I > -COOH > -OH > -C_6H_5$
  - −I **strengthens** acids (spreads the COO^- charge): $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH > CH_3COOH$; Cl nearer the COOH helps more; +I weakens: HCOOH > CH_3COOH
- **resonance**: same atoms, π electrons or lone pairs placed differently; ↔; real molecule a **hybrid**, more stable; benzene's six C–C bonds all 139 pm
- **+R** (lone pair given to the ring; o, p richer): –OH, –OR, $-NH_2$, –SH (phenol brominates at once)
- **−R** (π electrons pulled out onto O or N; o, p poorer): $-NO_2$, –CHO, –COOH, –CN



The two Kekulé structures of benzene, joined by ↔; curly arrows move the π electrons round.

COMMON MISTAKES

✗ 2-methyl-3-ethylhexane
✓ **3-ethyl-2-methylhexane** (prefixes alphabetical).

✗ propan-1,2,3-tri-ol, ethan-1,2-diol
✓ propane-1,2,3-triol, ethane-1,2-diol.

✗ –N=N– is diazo
✓ **azo**; diazo is $=N_2$ on one carbon.

✗ ether's group written as alcohol's
✓ **–O–**, alkoxyalkane.

✗ Ag_2S is white
✓ **black** (the reason HNO_3 boils off S^{2-} first).

✗ AgBr dissolves in dilute NH_3
✓ only **sparingly**; it dissolves in concentrated NH_3.

✗ $CH_3CH_2CCl(CH_3)CH_3$ is optically active
✓ its C–Cl carbon holds two CH_3: **not chiral**.

✗ $2C^{n-4} + 1$ gives the isomers of any alkane
✓ fits only C_4–C_7 (C_8 has 18, not 17).

✗ resonance structures with ⇌
✓ ↔; they are not in equilibrium, the molecule is a hybrid.