CHEMISTRY · UNITS 4 & 8 · QUICK REFERENCE

Organic Chemistry

Grades 11–12+ · 8 pages

Bonding and structure drawing, functional groups and IUPAC names, isomers and stereochemistry, acids and bases, resonance, curly-arrow mechanisms, alcohols, carbonyls and aromatic rings, IR, NMR and mass spectra, polymers and biomolecules.

1 Bonding · 2 Structures · 3 Functional groups · 4 IUPAC names · 5 Isomers · 6 R/S · 7 E/Z · 8 Acids & bases · 9 Resonance · 10 Curly arrows · 11 SN1, SN2 · 12 E1, E2 · 13 Alkenes · 14 Alcohols · 15 Carbonyls · 16 Aromaticity · 17 IR · 18 1H NMR · 19 Mass spec · 20 Polymers · 21 Biomolecules · 22 Roadmap · 23 Practice

1 BONDING & HYBRIDIZATION

carbon makes four bonds

Why carbon

Carbon has 4 valence electrons and forms 4 covalent bonds: chains, branches and rings. Organic chemistry is the chemistry of carbon compounds. Wöhler made urea from an inorganic salt in 1828.

Count bonds in CH_2=CH–C≡N WORKED

Draw every bond, H included

C=C: 1 σ + 1 π; C≡N: 1 σ + 2 π; plus 4 single bonds

σ / π

6 σ, 3 π; carbons sp^2, sp^2, sp; N is sp *groups*

Formal charge

FC = V − (lone-pair e⁻) − ½(bonding e⁻)

Polar bonds

Electronegativity C 2.5, O 3.5: in C–O and C=O the oxygen is δ− and the carbon δ+. Electron-poor carbon is where nucleophiles attack (§10).

Count groups, read the hybrid

Groups on C	Hybrid	Shape, angle	Example
4	sp^3	tetrahedral, 109.5°	ethane
3	sp^2	trigonal planar, 120°	ethene
2	sp	linear, 180°	ethyne

Sigma and pi

- Every single bond is one **σ** (end-on overlap).
- A double bond is 1 σ + 1 **π**; a triple bond is 1 σ + 2 π.
- π bonds block rotation and hold the reactive electrons.

Hybrids in ethanal, CH_3CHO WORKED

CH_3 carbon: 4 groups — *sp^3*

C=O carbon: 3 groups — *sp^2*

O: C=O plus 2 lone pairs — *sp^2*

Lone pairs count as groups

Atom in	Groups	Shape at atom
alcohol O (C–O–H)	4 (2 lone pairs)	bent, about 104.5°
amine N	4 (1 lone pair)	pyramidal, about 107°
carbonyl O (C=O)	3 (2 lone pairs)	sp^2, trigonal

Bond patterns to know

Atom	Neutral	−1	+1
C	4 bonds	3 bonds + 1 pair	3 bonds, no pair
N	3 bonds + 1 pair	2 bonds + 2 pairs	4 bonds
O	2 bonds + 2 pairs	1 bond + 3 pairs	3 bonds + 1 pair

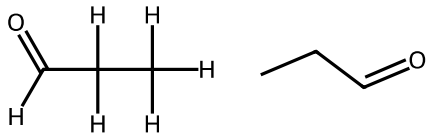
MEMORY TRICK

Groups give the hybrid

Four groups: sp^3. Three: sp^2. Two: sp. Count lone pairs as groups.

2 DRAWING STRUCTURES

Lewis, condensed, skeletal



all bonds shown **skeletal**

Propanal, two ways

Skeletal to formula WORKED

$(CH_3)_2CHCH_2CH_2OH$

5 carbons, 1 O; fill each C to 4 bonds *count*

$C_5H_{12}O$ *formula*

⚠ Common slips

- Five bonds to a carbon.
- Leaving off the H on O or N.
- Straight chains that hide carbons: draw zigzags.

Same molecule, four forms

Style	Propanal
Condensed	CH_3CH_2CHO
Molecular	C_3H_6O
Lewis	every bond and lone pair (O has 2 pairs)

Skeletal rules

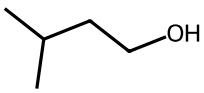
- Each line end and corner is a **carbon**.
- Hydrogens on carbon are not drawn: add H until each C has 4 bonds.
- Draw every heteroatom (O, N, halogen) and the H on it.
- Draw chains as zigzags.

Degrees of unsaturation

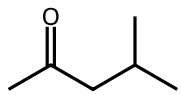
DoU = (2C + 2 + N − H − X) ÷ 2

Condensed shorthand

$(CH_3)_2CH$– isopropyl; $(CH_3)_3C$– tert-butyl; –CHO aldehyde; –COOH acid; –COOR ester; –CN nitrile.



3-methylbutan-1-ol
$(CH_3)_2CHCH_2CH_2OH$



4-methylpentan-2-one
$CH_3COCH_2CH(CH_3)_2$

Condensed to skeletal

Reading a DoU WORKED

C_6H_6: (14 − 6) ÷ 2 = **4** *ring + 3 C=C*

$C_6H_{12}O$: (14 − 12) ÷ 2 = **1** *one C=O, C=C or ring*

C_2H_5Br: halogen counts as H, DoU **0** *saturated*

MEMORY TRICK **Corners are carbons**

Every corner and end is C. Fill each carbon to four with hidden H.

3 FUNCTIONAL GROUPS — the reactive part



alkane propane · **alkene** propene · **alkyne** propyne · **arene** benzene · **haloalkane** 1-chloropropane · **alcohol** propan-1-ol · **ether** methoxyethane

amine propan-1-amine · **aldehyde** propanal · **ketone** propan-2-one · **carboxylic acid** propanoic acid · **ester** methyl ethanoate · **amide** propanamide · **nitrile** propanenitrile

Hydrocarbons and singles

Group	Pattern	Name ending
alkene	C=C	-ene
alkyne	C≡C	-yne
haloalkane	C–X	halo- (prefix)
alcohol	C–OH	-ol

Oxygen and nitrogen

Group	Pattern	Name ending
ether	C–O–C	alkoxy- (prefix)
amine	C–NH_2	-amine
aldehyde	R–CHO	-al
ketone	R–CO–R	-one

Acid family

Group	Pattern	Name ending
carboxylic acid	R–COOH	-oic acid
ester	R–COO–R	-oate
amide	R–$CONH_2$	-amide
nitrile	R–C≡N	-nitrile

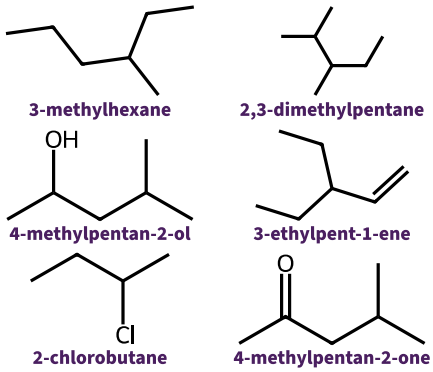
4 IUPAC NAMING — parent, numbers, prefixes

Chain roots

C	Root	C	Root
1	meth-	6	hex-
2	eth-	7	hept-
3	prop-	8	oct-
4	but-	9	non-
5	pent-	10	dec-

Five steps

- **Parent**: the longest chain that holds the main group (and C=C).
- **Number** from the end that gives the main group the lowest locant.
- **Substituents** (methyl, ethyl, chloro) get locants too.
- **Alphabetize** prefixes; di-, tri- do not count.
- **Write**: locants, prefixes, root, ending.



3-methylhexane · **2,3-dimethylpentane** · **4-methylpentan-2-ol** · **3-ethylpent-1-ene** · **2-chlorobutane** · **4-methylpentan-2-one**

Each name checked against its structure

Ester names WORKED

$CH_3CH_2COOCH_2CH_3$

alcohol part first (ethyl), acid part second (propanoate)

two words

ethyl propanoate *name*

Name $CH_3CH(OH)CH_2CH(CH_3)_2$ WORKED

Longest chain with C–OH: 5 C, pentan-…-ol *parent*

Number from the OH end: OH on C2, methyl on C4 *lowest locant*

4-methylpentan-2-ol *name*

Main group wins the suffix

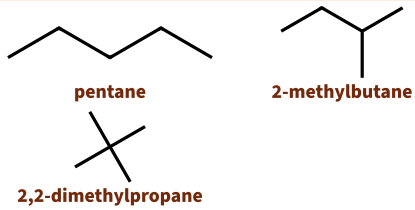
Priority	Suffix
carboxylic acid	-oic acid
ester	-oate
aldehyde	-al
ketone	-one
alcohol	-ol

MEMORY TRICK **Lowest numbers win**
Number from the end nearer the main group; ties go to the first point of difference.

5 ISOMERS — same formula, different molecule

Types of isomer

Kind	What differs	Example
Constitutional	which atoms connect	butane vs 2-methylpropane
Enantiomers	mirror images that cannot be stacked	(R)- vs (S)-butan-2-ol
Diastereomers	stereoisomers, not mirror images	(E)- vs (Z)-but-2-ene
Conformers	rotation about σ bonds	not isomers you can isolate



pentane · **2-methylbutane** · **2,2-dimethylpropane**

Three isomers of C_5H_{12}

MEMORY TRICK **Connect, then space**
Different connections: constitutional. Same connections, different 3-D: stereo.

Functional-group isomers, C_2H_6O WORKED

CH_3CH_2OH: an alcohol, H-bonds, a liquid *ethanol*

CH_3OCH_3: an ether, no O–H, a gas *methoxymethane*

same formula, different groups and properties *constitutional*

History

Wöhler and Liebig found two compounds with the same formula but different structures: isomers.

6 CHIRALITY & R/S

handedness at carbon



(R)-butan-2-ol **(S)-butan-2-ol**

Wedge: toward you. Dashes: away.

Vocabulary

Term	Meaning
Enantiomers	mirror images; same properties except rotating light (equal, opposite)
Racemic mixture	50:50 R and S; no net rotation
Meso	has stereocenters but an internal mirror plane; not chiral
Count	n stereocenters: at most 2^n stereoisomers

Spotting a stereocenter

- An sp^3 carbon with **four different groups**.
- CH_2, CH_3 and C=C carbons are never stereocenters.
- A molecule with one stereocenter is **chiral**.

Butan-2-ol, wedge drawing WORKED

$OH > CH_2CH_3 > CH_3 > H$ — *rank by atomic number, then the next atoms*

H points back; 1 → 2 → 3 runs clockwise — *trace*

R — *answer*

Fischer projections

Horizontal lines come toward you, vertical lines go back. Sugars and amino acids are often drawn this way (D, L).

Assigning R or S

- **Rank** the four groups by atomic number at the first point of difference (CIP rules).
- Put the **lowest** (often H) pointing away.
- Trace 1 → 2 → 3: clockwise is **R**, counterclockwise is **S**.
- If the lowest group points toward you, reverse the answer.

Life is one-handed

Natural amino acids are the L form; L-alanine is (S). Tartaric acid has 2 stereocenters but only 3 stereoisomers, because one is meso.

MEMORY TRICK **Hand on the wheel**

H in back, steer 1 to 2 to 3: turning right is R.

7 ALKENES: E/Z

no rotation about C=C



(E)-but-2-ene **(Z)-but-2-ene**

E or Z

- On each alkene carbon, rank the two groups (CIP).
- Higher groups on the **same** side: **Z** (zusammen, together).
- Opposite sides: **E** (entgegen, opposite).
- If one alkene carbon has two identical groups, there is no E/Z.

$ClBrC{=}CHCH_3$, Cl trans to CH_3 WORKED

C1: Br > Cl; C2: $CH_3 > H$ — *rank*

Br and CH_3 on the same side — *compare*

(Z)-1-bromo-1-chloroprop-1-ene — *name*

Name $CH_3CH{=}C(CH_3)CH_2CH_3$ WORKED

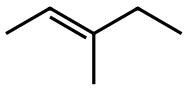
C2: $CH_3 > H$; C3: $CH_2CH_3 > CH_3$ — *rank each end*

CH_3 (on C2) and CH_2CH_3 opposite, as drawn — *compare*

(E)-3-methylpent-2-ene — *name*

⚠ Cis is not always Z

- Cis/trans compares like groups; E/Z compares ranks. In the example Cl is trans to CH_3, yet the alkene is Z.



(E)-3-methylpent-2-ene

Rings

Rings block rotation too: cis-1,2-dimethylcyclohexane has both CH_3 on one face; trans has one up, one down.

8 ACIDS & BASES

pKa: lower is stronger

Brønsted–Lowry (1923)

An acid is a proton donor; a base is a proton acceptor. pKa = −log Ka: each pKa unit is a factor of 10.

Typical pKa values

Acid	pKa	Acid	pKa
HCl	−7	ethanol	16
acetic acid	4.76	acetone (α-H)	19
NH_4^+	9.25	ethyne	25
phenol	10	ammonia	38
water	14	ethane	50

MEMORY TRICK

Stable base, strong acid

The more stable the conjugate base, the stronger the acid.

Why one acid is stronger: ARIO

- **Atom**: across a row, more electronegative is more acidic (C–H < N–H < O–H); down a group, larger is more acidic.
- **Resonance**: a delocalized conjugate base is stable (acetate).
- **Induction**: nearby electronegative atoms pull charge away.
- **Orbital**: more s character holds the pair closer ($sp > sp^2 > sp^3$).

Induction in action WORKED

CH_3COOH 4.76 → $ClCH_2COOH$ 2.86 → CF_3COOH 0.23 — *more pull, lower pKa*

each F or Cl spreads the negative charge of the anion — *why*

Which way does it go? WORKED

$CH_3COOH + NH_3 \rightleftharpoons CH_3COO^- + NH_4^+$

pKa 4.76 on the left, 9.25 on the right — *compare acids*

equilibrium favors the **weaker acid**: goes right — *answer*

Phenol vs ethanol WORKED

phenoxide spreads its − charge into the ring — *resonance*

ethoxide holds it on one O — *no resonance*

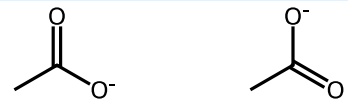
phenol (10) is about 1,000,000 times more acidic than ethanol (16) — *pKa*

Size of the gap

Ka of acetic acid ≈ 1.7×10^{-5}. Acetic acid (4.76) is about 100,000 times stronger than phenol (10).

9 RESONANCE

electrons spread, atoms stay



acetate, form 1 — form 2

Form 1 ↔ form 2: the real ion is their average

Rules

- Move **electrons only** (π bonds and lone pairs); never move atoms or break σ bonds.
- Keep the same total charge and the octet on C, N, O.
- Join forms with a double-headed arrow ↔, not ⇌.
- The real molecule is a **hybrid**; it does not flip between forms.

Ranking contributors

Better form has	Why
more full octets	stability first
fewer charges	less separation
− on the more electronegative atom	O holds − better than C

Why acetate is stable WORKED

the −1 charge is shared by two O atoms — *two equal forms*

both C–O bonds are the same length, between single and double — *evidence*

stable base: acetic acid is a far stronger acid than ethanol — *pKa 4.76 vs 16*

Where to look for resonance

Pattern	Example
lone pair next to a π bond	acetate, amide
+ charge next to a π bond	allyl cation
π bond in a ring of p orbitals	benzene
π bond to a more electronegative atom	C=O ↔ C^+–O^-

Benzene

6 π electrons spread evenly over 6 carbons; every C–C bond is the same length (§16).

MEMORY TRICK **Arrows move pairs**

In resonance, only electrons move. If an atom moves, it is a different molecule.

10 CURLY ARROWS

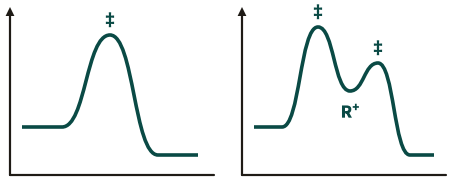
follow the electron pairs

Arrow rules

- An arrow shows a **pair** of electrons moving; a fishhook (half head) moves one.
- Start at a **lone pair** or a **bond**; end at an atom or a new bond position.
- Electrons flow from electron-rich to electron-poor.
- Check charges and octets after every step.

Good leaving groups are weak bases

Leaving group	Quality
I^-, Br^-, TsO^-, H_2O	good (weak bases)
Cl^-	fair
OH^-, OR^-, NH_2^-	poor: protonate OH first



SN2: one step — SN1: two steps

Energy (up) against reaction progress

Alkyl groups donate electrons

Carbocation	Stability
3° (R_3C^+)	most stable
2° (R_2CH^+)	moderate
1° (RCH_2^+)	poor
CH_3^+	least

Reading the diagram

Each hump is a transition state (‡); a dip between humps is an intermediate. The highest hump sets the rate.

Who attacks whom

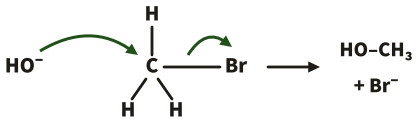
Nucleophile (Nu)	Electrophile (E)
electron-rich: lone pair, π bond, − charge	electron-poor: δ+, + charge, empty orbital
OH^-, CN^-, NH_3, H_2O, Br^-, C=C	C–X carbon, C=O carbon, H^+, carbocations

MEMORY TRICK **Rich to poor**

Arrows run from the electron-rich tail to the electron-poor head.

11 SUBSTITUTION: SN2 & SN1

Nu replaces a leaving group



one step: backside attack, inversion

SN2: bond forms as bond breaks

SN2

- One step; rate = k[RX][Nu]: both in the rate law.
- Backside attack: **inversion** of configuration.
- Fastest at CH_3 and 1° carbons; blocked at 3°.
- Strong nucleophile; polar aprotic solvent (acetone, DMSO).

Nucleophiles by strength

Nucleophile	Strength
HS^-, CN^-, I^-, OH^-, RO^-	strong
Br^-, NH_3, Cl^-	fair
H_2O, ROH	weak

(S)-2-bromobutane + OH^- (SN2) WORKED

2° carbon, strong Nu, one step — *mechanism*

OH enters opposite Br: geometry inverts — *inversion*

(R)-butan-2-ol — *product*

⚠ Watch the substrate

- Vinyl and aryl halides (Br on C=C or a ring) do not do SN1 or SN2.
- Neopentyl carbons are too crowded for SN2.

SN1

- Two steps: the leaving group leaves, then Nu adds to the **carbocation**.
- Rate = k[RX]: only the substrate.
- Best at 3°; flat cation gives a mix of R and S (racemic).
- Weak nucleophile, polar protic solvent (water, alcohol).

$(CH_3)_3CBr$ in water (SN1) WORKED

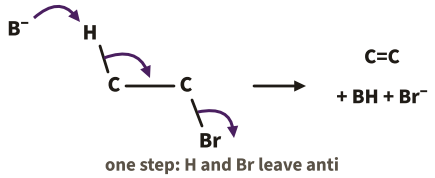
3° carbon, weak Nu

Br^- leaves: $(CH_3)_3C^+$ — *slow step*

water adds, loses H^+: **2-methylpropan-2-ol** — *product*

12 ELIMINATION & CHOOSING

E2, E1, and which wins



one step: H and Br leave anti

E2: base, C–H and C–Br act together

2-bromobutane + strong base, heat WORKED

remove H from C1 or C3	*two choices*
but-2-ene (disubstituted) vs but-1-ene	*compare*
but-2-ene major (Zaitsev)	*product*

E2 and E1

- **E2**: one step, strong base; H and leaving group **anti**; rate = k[RX][B].
- **E1**: carbocation first (like SN1), then loss of H^+; rate = k[RX].
- **Zaitsev**: the more substituted alkene is the major product.
- Heat favors elimination over substitution.

Quick decision guide

Substrate	Strong Nu, weak base	Strong bulky base	Weak Nu, heat
1°	SN2	E2	slow
2°	SN2	E2	SN1 / E1
3°	SN1	E2	SN1 / E1

SN1, SN2, E1, E2 side by side

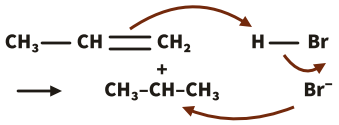
	SN2	SN1	E2	E1
Steps	1	2	1	2
Rate law	[RX][Nu]	[RX]	[RX][B]	[RX]
Substrate	1°, CH_3	3°	3°, 2°	3°
Reagent	strong Nu	weak Nu	strong base	weak base
Stereo	inversion	racemic	anti H, X	mix

MEMORY TRICK **Strong or weak first**

Strong reagent: one step (SN2, E2). Weak reagent: cation first (SN1, E1).

13 ADDITION TO ALKENES

the π bond attacks



H went to CH_2: 2° cation

→ $CH_3CHBrCH_3$ 2-bromopropane

Br ends on the carbon with fewer H

Propene + HBr: through the more stable cation

Cyclohexene + Br_2 WORKED

Br_2 forms a 3-membered bromonium ion	*step 1*
Br^- attacks from the back face	*step 2*
trans-**1,2-dibromocyclohexane** (anti addition)	*product*

Markovnikov's rule

H adds to the alkene carbon that already has **more H**; the other group goes to the carbon that forms the more stable cation.

Common additions

Reagent	Adds	Product from propene
HBr	H, Br (Markovnikov)	2-bromopropane
H_2O, H^+	H, OH (Markovnikov)	propan-2-ol
Br_2	Br, Br (anti)	1,2-dibromopropane
H_2, Pt	H, H (syn)	propane
BH_3 then H_2O_2, OH^-	H, OH (anti-Markovnikov)	propan-1-ol

Why the 2° cation WORKED

H^+ on C1 gives CH_3–C^+H–CH_3 (2°)	*path A*
H^+ on C2 gives $^+CH_2$–CH_2–CH_3 (1°)	*path B*
2° is more stable, so Br bonds to C2	*answer*

More alkyl groups, more stable

Alkene	Stability
tetrasubstituted $R_2C{=}CR_2$	most stable
trisubstituted	↓
disubstituted (trans > cis)	↓
monosubstituted $RCH{=}CH_2$	least

MEMORY TRICK

H joins the H-rich carbon

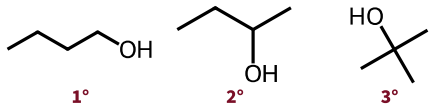
The alkene carbon with more H gets the new H (Markovnikov).

14 ALCOHOLS

the O–H group

Classify, then predict

Class	C bearing OH has	Oxidized (Cr(VI) or PCC)
methanol	no C neighbor	methanal, then methanoic acid
1°	one C neighbor	aldehyde (PCC); acid (Cr(VI), H^+)
2°	two C neighbors	ketone
3°	three C neighbors	no reaction



Butan-1-ol, butan-2-ol, 2-methylpropan-2-ol

Same mass, different boiling point WORKED

ethanol, methoxymethane: both 46.1 g/mol	
ethanol 78 °C; methoxymethane −25 °C; propane (44.1) −42 °C	*bp*
only ethanol has O–H: **hydrogen bonds** hold its molecules together	*why*

Oxidation ladder WORKED

ethanol → ethanal → ethanoic acid	*1°*
butan-2-ol → butan-2-one, then stops	*2°*
each step loses 2 H or gains 1 O	*pattern*

Key reactions

Reaction	Reagent	Product
oxidation 1°	PCC	aldehyde
dehydration	H_2SO_4, heat	alkene (E1, Zaitsev)
to alkyl halide	HBr	R–Br (via $R–OH_2^+$)
as acid	Na	alkoxide RO^- + H_2

MEMORY TRICK **Count C on the C–OH**

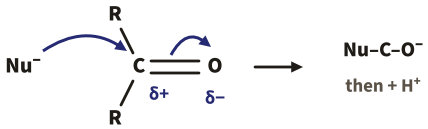
One neighbor: 1°. Two: 2°. Three: 3° (will not oxidize).

Phenols

An OH on a benzene ring is a phenol, not an alcohol: it is far more acidic (pKa 10) and does not oxidize like a 1° or 2° alcohol.

15 CARBONYL CHEMISTRY

the C=O group



Nu attacks the δ+ carbon; π electrons go to O

Nucleophilic addition to C=O

Acyl substitution: add, then kick out

Derivative	Leaving group	Reactivity
acid chloride	Cl^-	highest
anhydride	$RCOO^-$	high
ester	RO^-	moderate
amide	NH_2^-	lowest

Keto–enol

Propanone ⇌ prop-1-en-2-ol (keto form dominates). An α-H is weakly acidic (pKa 19) because the enolate is resonance-stabilized.

Aldehydes and ketones

- C=O is polar: C δ+, O δ−; the flat sp^2 carbon is open to attack from either face.
- Nu adds to C; O^- picks up H^+. The carbon becomes sp^3.
- Aldehydes react faster than ketones (less crowded, more δ+).

Fischer esterification WORKED

$CH_3COOH + CH_3CH_2OH \rightleftharpoons CH_3COOCH_2CH_3 + H_2O$

acid catalyst

ethyl ethanoate, 88.11 g/mol: fruity smell

ester

reverse it with water and acid or base: hydrolysis

reverse

Additions to C=O

Reagent	With a ketone gives
$NaBH_4$ or $LiAlH_4$, then H^+	2° alcohol (aldehyde: 1°)
R–MgBr (Grignard), then H_3O^+	new C–C bond; 3° alcohol
HCN	cyanohydrin

Build propan-2-ol WORKED

CH_3MgBr + ethanal (CH_3CHO)

Nu: CH_3^- adds to C=O

then H_3O^+ — *$O^- \rightarrow OH$*

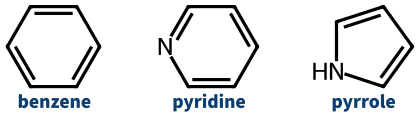
$(CH_3)_2CHOH$, propan-2-ol — *product*

MEMORY TRICK **Nucleophiles love δ+**

Nucleophiles hit the C of C=O; the O takes the electrons.

16 AROMATICITY

extra-stable rings



Each has 6 π electrons

Substitution keeps the ring

Reaction	Reagents	Product
nitration	HNO_3, H_2SO_4	nitrobenzene
bromination	Br_2, $FeBr_3$	bromobenzene
Friedel–Crafts	RCl, $AlCl_3$	alkylbenzene

MEMORY TRICK **Two more than four**

Aromatic rings hold 4n + 2 π electrons: 2, 6, 10.

Hückel's rule

- Cyclic, planar and fully conjugated (a p orbital on every ring atom).
- **4n + 2** π electrons: 2, 6, 10 … is aromatic.
- 4n π electrons in a flat ring: **antiaromatic** (unstable).
- Fails the shape test: nonaromatic.

Second substituent

Group on ring	Directs to
–OH, $–NH_2$, $–CH_3$ (activate)	ortho, para
–F, –Cl, –Br (deactivate)	ortho, para
$–NO_2$, –CN, –C=O (deactivate)	meta

Test the rule

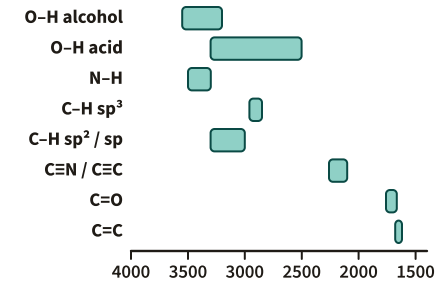
Ring	π e^-	Verdict
benzene	6	aromatic
pyrrole (N lone pair counts)	6	aromatic
cyclopentadienyl anion	6	aromatic
cyclobutadiene	4	antiaromatic
cyclooctatetraene (tub shape)	8	nonaromatic

⚠ Rings that fail

- Cyclohexane: no π electrons.
- Cyclooctatetraene: 8 π e^- and a tub shape, so it is not flat: nonaromatic.

17 IR SPECTROSCOPY

bonds absorb by type



Key bands, in cm^{-1}

MEMORY TRICK **Three zones**

X–H above 2500; triple bonds 2100–2260; C=O 1665–1760.

Band table

Bond	cm^{-1}	Look
O–H alcohol	3200–3550	broad, strong
O–H acid	2500–3300	very broad
N–H	3300–3500	medium
C–H sp^3	2850–2960	just below 3000
C–H sp^2, sp	3000–3300	just above 3000
C≡N, C≡C	2100–2260	sharp
C=O	1665–1760	strong, sharp
C=C	1620–1680	medium

Fingerprint

Below 1500 cm^{-1} the pattern is unique to each compound; use it to match, not to assign.

C_3H_6O: strong 1715, nothing above 3000 WORKED

strong 1715: C=O — *carbonyl*

no broad O–H; no aldehyde C–H pair — *rule out*

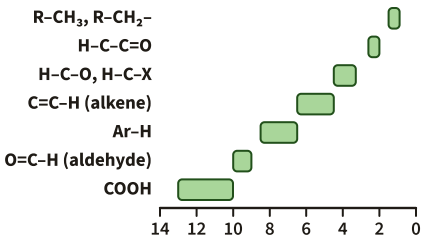
propanone (a ketone) — *answer*

Alcohol, acid, ketone or ester?

Bands seen	Points to
broad 3300 only	alcohol
very broad 2500–3300 + 1710	carboxylic acid
1715, no O–H	ketone
1740, no O–H	ester

18 ^{1}H NMR

environments, area, splitting



Chemical shift δ (ppm); TMS = 0

Ethyl ethanoate, $CH_3COOCH_2CH_3$ WORKED

δ 2.0, 3H, singlet: CH_3–C=O (no H neighbors)	*signal 1*
δ 4.1, 2H, quartet: O–CH_2, next to CH_3	*signal 2*
δ 1.2, 3H, triplet: CH_3, next to CH_2	*signal 3*

Read four things

Feature	Tells you
Number of signals	different H environments
Shift δ	neighbors: O, C=O, rings pull downfield
Integration	ratio of H in each signal
Splitting	n neighboring H give **n + 1** peaks

O–H and N–H

Usually a broad singlet that does not split its neighbors (it exchanges); ethanol shows singlet, quartet, triplet.

^{13}C NMR

One peak per carbon environment, no splitting: ethanol 2, ethyl ethanoate 4, benzene 1. C=O carbons sit far downfield.

Patterns to recognize

Group	Pattern
ethyl, –CH_2CH_3	2H quartet + 3H triplet
isopropyl, –$CH(CH_3)_2$	1H septet + 6H doublet
tert-butyl, –$C(CH_3)_3$	9H singlet
methyl ester, –$COOCH_3$	3H singlet

C_3H_6O: one singlet, 6H WORKED

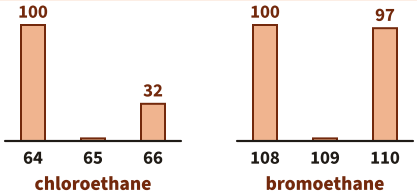
propanal would give 3 signals	*rule out*
two identical CH_3 next to C=O	*symmetry*
propanone; its ^{13}C shows 2 signals	*answer*

MEMORY TRICK **Neighbors plus one**

Count H on the next carbons, add one: that many peaks.

19 MASS SPECTROMETRY

weigh the ion



Computed M and M+2 peaks

Bromoethane WORKED

peaks at 108 and 110, nearly equal	*M, M+2*
equal pair: one Br	*isotopes*
108 − 79 = 29: C_2H_5	*rest*

History

Aston's mass spectrograph (1919) split chlorine into masses 35 and 37. Bromine is about 51% bromine-79 and 49% bromine-81.

Reading a spectrum

- **M^+**, the molecular ion, gives the molar mass (lightest isotopes).
- Cl: M and M+2 about **3 : 1**. Br: about **1 : 1**.
- M+1 is about 1.1% per carbon (carbon-13).
- **Nitrogen rule**: an odd M^+ means an odd number of N (propan-1-amine, 59).

Common fragments

m/z	Ion	Hint
M − 15	lost CH_3	methyl branch
29	$C_2H_5^+$	ethyl
43	CH_3CO^+	methyl ketone
77	$C_6H_5^+$	phenyl
91	$C_7H_7^+$	benzyl

Isotope and mass clues

Clue	Means
M+2 ≈ ⅓ of M	one Cl
M+2 ≈ M	one Br
M+2 ≈ 4.5% of M	one S
odd M^+	odd number of N

Peaks at 78 and 80, about 3 : 1 WORKED

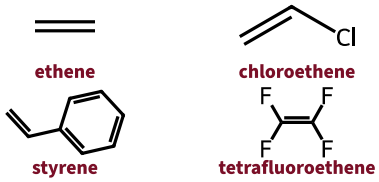
M+2 a third as tall: one Cl	*isotopes*
78 − 35 = 43: C_3H_7	*rest*
C_3H_7Cl, e.g. **2-chloropropane**	*answer*

Honest weights

"A just weight and balance are the LORD's: all the weights of the bag are his work" (Proverbs 16:11, KJV).

20 POLYMERS

many small units joined



Addition-polymer monomers

Two ways to build

- **Addition**: the π bond of each alkene opens; no atoms are lost; repeat unit –[CH_2–CHX]–.
- **Condensation**: two functional groups join and give off a small molecule (H_2O).

Addition polymers: C=C opens

Monomer	Polymer	Use
ethene	polyethylene	bags, bottles
chloroethene	PVC	pipes
ethenylbenzene (styrene)	polystyrene	foam cups
tetrafluoroethene	PTFE	nonstick coating

Size

Polyethylene of 1,000 ethene units has a molar mass near 28,000 g/mol. PET (bottles) joins benzene-1,4-dicarboxylic acid and ethane-1,2-diol by ester links.

Condensation polymers

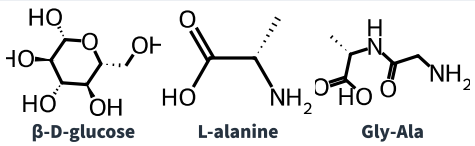
Polymer	Link	Lost
nylon-6,6	amide	H_2O
PET (polyester)	ester	H_2O
protein	peptide (amide)	H_2O
starch, cellulose	glycosidic	H_2O

Nylon-6,6 WORKED

hexanedioic acid + hexane-1,6-diamine	*monomers*
–COOH + H_2N– → –CO–NH– + H_2O	*amide link*
repeat; the same bond as in proteins	*polyamide*

21 BIOMOLECULES

organic chemistry of life



Functional groups in the molecules of life

Molecule	Groups it carries
glucose	–OH ×5, aldehyde (open chain) or ring hemiacetal
amino acid	$–NH_2$, –COOH, side chain R
fat	ester ×3, long C chains
DNA, RNA	phosphate esters, nitrogen bases (amines, amides)

Ring and chain

Open-chain glucose has 4 stereocenters; closing the ring at C1 adds a fifth, giving α and β forms.

Four families

Family	Monomer	Link
carbohydrate	glucose, $C_6H_{12}O_6$	glycosidic (ether)
protein	20 amino acids	peptide (amide)
lipid (fat)	glycerol + 3 fatty acids	ester
nucleic acid	nucleotide	phosphate ester

Dehydration synthesis WORKED

$2\ C_6H_{12}O_6 \rightarrow C_{12}H_{22}O_{11} + H_2O$	*maltose*
glycine + alanine → Gly-Ala + H_2O	*peptide bond*
hydrolysis adds the water back	*digestion*

Stereo in life

Cells build with D-sugars and L-amino acids only. Glucose, 180.16 g/mol, has 5 stereocenters in its ring form.

Saturated or not

Saturated fatty acids have only C–C single bonds and pack tightly (solid fats); a cis C=C makes a kink, so oils stay liquid.

Classic lab tests

Test	Positive for
iodine turns blue-black	starch
Benedict's, heat: brick red	reducing sugar (glucose)
biuret turns violet	protein (peptide bonds)
translucent spot on paper	fat

22 REACTION ROADMAP

from one group to another

Alkenes and halides

From	Reagent	To
alkene	H_2O, H^+	alcohol (Markovnikov)
alkene	HBr	alkyl bromide
alkyl halide	OH^- (SN2 or SN1)	alcohol
alkyl halide	strong base, heat (E2)	alkene

Plan: propene to propanone WORKED

propene + H_2O, H^+ → propan-2-ol	*Markovnikov*
propan-2-ol + Cr(VI) → **propanone**	*2° to ketone*

Alcohols up the ladder

From	Reagent	To
alcohol	H_2SO_4, heat	alkene
1° alcohol	PCC	aldehyde
2° alcohol	Cr(VI), H^+	ketone
aldehyde	Cr(VI), H^+	carboxylic acid

Carbonyls

From	Reagent	To
ketone	$NaBH_4$, then H^+	2° alcohol
acid + alcohol	H^+, heat	ester
ester	H_2O with H^+ or OH^-	acid + alcohol
acid chloride	NH_3	amide

Plan: bromoethane to ethyl ethanoate WORKED

$CH_3CH_2Br + OH^- \rightarrow$ ethanol	*SN2*
ethanol + ethanoic acid, H^+ → **ethyl ethanoate**	*esterify*

MEMORY TRICK **Work backward**

Start from the target; ask which group it came from one step before.

Count carbons

If the product has more carbons than the start, you need a C–C bond: a Grignard reagent on C=O (§15) is the classic choice.

23 PRACTICE

answers on the right

Structure and reactions

Question	Answer
Hybridization of each C in $CH_3CH{=}CH_2$?	sp^3, sp^2, sp^2
Hybridization of N in $CH_3C{\equiv}N$?	sp
Name $CH_3CH_2CH(CH_3)CH_2CH_2OH$.	3-methylpentan-1-ol
DoU of C_5H_8?	2: two π bonds, or a ring + π
Stereocenters in 3-methylhexane?	1 (C3)
2-methylpropene + HBr gives?	2-bromo-2-methylpropane (via 3° cation)
More acidic: ethanol or acetic acid?	acetic acid (4.76 vs 16): resonance

Mechanisms and spectra

Question	Answer
$(CH_3)_3CBr + H_2O$, warm: which mechanism?	SN1 (3°, weak Nu)
$CH_3Br + OH^-$: which mechanism?	SN2 (methyl, strong Nu)
C_3H_6O, IR 1715, one ^1H singlet?	propanone
M^+ at 59 with no Cl or Br pattern?	odd: one N (e.g. propan-1-amine)
Is cyclobutadiene aromatic?	no: 4 π e^-, antiaromatic
^1H NMR of CH_3CH_2Br?	2H quartet, 3H triplet
IR 1740, no O–H?	ester
Br_2 + cyclohexene: syn or anti?	anti (bromonium ion)

Quick checks

Question	Answer
Is L-alanine R or S?	S
^1H NMR signals in ethanol?	3 (triplet, quartet, singlet)
Butan-2-ol + H_2SO_4, heat: major product?	but-2-ene (Zaitsev)
Propan-1-ol + PCC?	propanal
Peaks at M and M+2, equal height?	one Br

Stretch

Question	Answer
DoU of C_6H_{10}: name one structure.	2: cyclohexene
Is pyridine aromatic?	yes: 6 π e^-, flat ring
Ethanol → ethanoic acid needs?	Cr(VI), H^+ (oxidation)