Organic Chemistry 1 Study Guide

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Rules, trends, reaction tables and worked examples for a first-semester university organic chemistry course.

Abbreviations: Nu = nucleophile · LG = leaving group · R = alkyl · X = halogen · Δ = heat · hν = light · equiv = equivalents · cat. = catalytic · Ts/Ms/Tf = tosyl/mesyl/triflyl (sulfonate LGs) · DMS = $(CH_3)_2S$ · NMO = N-methylmorpholine N-oxide (reoxidant) · NBS = N-bromosuccinimide · DBU/DBN = bulky amidine bases.
≈ marks approximate textbook values; books differ slightly, so use your instructor's numbers on exams.

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1 Structure and bonding

Lewis structures and formal charge

- **Formal charge** = valence electrons − nonbonding electrons − bonds. Formal charges add up to the overall charge.
- C, N, O and F never exceed an octet. In skeletal structures each carbon carries implied H up to 4 bonds; lone pairs are often omitted.

Bonding patterns and formal charge

Atom	+1	0	−1
C	3 bonds, no lone pair (carbocation)	4 bonds	3 bonds + 1 lone pair (carbanion)
N	4 bonds	3 bonds + 1 lone pair	2 bonds + 2 lone pairs
O	3 bonds + 1 lone pair	2 bonds + 2 lone pairs	1 bond + 3 lone pairs
Cl, Br, I	2 bonds + 2 lone pairs	1 bond + 3 lone pairs	4 lone pairs (halide)

Hybridization and geometry

Steric number = σ bonds + lone pairs. Single bond = 1 σ; double = 1 σ + 1 π; triple = 1 σ + 2 π.

Steric number, hybridization and shape

Steric no.	Hybrid, geometry	Examples
4	sp^3, tetrahedral, 109.5°	CH_4; NH_3 pyramidal (≈107°); H_2O bent (≈104.5°)
3	sp^2, trigonal planar, 120°	C=C, C=O, carbocation C^+
2	sp, linear, 180°	C≡C, C≡N, the C of CO_2

A lone pair next to a π bond is usually delocalized in a p orbital, so that atom is sp^2 (e.g. the N of an amide).

Resonance

- Move only π electrons and lone pairs. Never move atoms, break a σ bond, exceed an octet on C/N/O, or change the overall charge.
- Patterns: lone pair next to a π bond; + charge next to a π bond (allylic cation; **allylic** = on the sp^3 carbon next to a C=C, **benzylic** = next to a benzene ring); lone pair next to a + charge; polar π bond (C=O ↔ C^+–O^-); alternating π bonds in a ring.
- Contributors are joined by ↔ (not ⇌); the real molecule is the hybrid. Equivalent contributors give extra stability (both C–O bonds of a carboxylate are the same length).

Major contributor (criteria in order):

1. Most atoms with full octets.
2. Fewest formal charges.
3. Negative charge on the more electronegative atom (positive on the less).

Example: in CH_3–O–CH_2^+ ↔ CH_3–O^+=CH_2, the second form is major: every atom has an octet (rule 1), even with + on O.

Intermolecular forces (strongest first)

1. **Ion–dipole**: ion + polar molecule (Na^+ in water).
2. **Hydrogen bonding**: H on N, O or F (donor) to a lone pair on N, O or F (acceptor).
3. **Dipole–dipole**: permanent dipoles (acetone, CH_3Cl).
4. **London dispersion**: all molecules; grows with surface area and polarizability.

Ethanol (H-bond donor, bp ≈78 °C) vs dimethyl ether (same formula, bp ≈−24 °C). Longer chains raise bp; branching lowers it. Like dissolves like: water solubility of alcohols falls as the carbon chain grows.

1°, 2°, 3° (primary, secondary, tertiary): a carbon bonded to one, two or three other carbons. An alkyl halide or alcohol takes the degree of the carbon bearing –X or –OH; for amines the degree counts the carbons on N instead.

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2 Acids and bases

- **Brønsted** acid donates H^+, base accepts H^+. **Lewis** acid accepts an electron pair, base donates one.
- **Lower pKa = stronger acid** = weaker conjugate base. Each pKa unit is a factor of 10 in Ka.

Approximate pKa values (sources differ by about ±1)

Acid → conjugate base	pKa ≈
HI → I^-	−10
HBr → Br^-	−9
HCl → Cl^-	−7
H_2SO_4 → HSO_4^-	−3 (some tables −9)
ROH_2^+ → ROH (protonated alcohol)	−2
H_3O^+ → H_2O	−1.7
RCOOH → $RCOO^-$ (acetic acid)	4.8
NH_4^+ → NH_3	9.2
PhOH → PhO^- (phenol)	10
R_3NH^+ → R_3N (alkylammonium)	10–11
H_2O → HO^-	15.7
ROH → RO^- (ethanol; t-BuOH)	16; 18
Ketone α-C–H → enolate	19–20
RC≡CH → $RC{\equiv}C^-$ (acetylide)	25
H_2 → H^- (NaH); $(i\text{-}Pr)_2NH$ → LDA; NH_3 → NH_2^-	35; 36; 38
Alkene C–H; alkane C–H	44; 50

ARIO: what stabilizes the conjugate base

More stable A^- = stronger acid. Usual order of importance (when factors disagree, trust measured pKa values):

1. **Atom.** Across a row, electronegativity: $CH_4 < NH_3 < H_2O < HF$. Down a group, size wins over electronegativity: HF < HCl < HBr < HI (the large, polarizable I^- spreads the charge); likewise thiols RSH (≈10) are more acidic than alcohols.
2. **Resonance.** Delocalized charge: acetic acid (≈4.8) vs ethanol (≈16).
3. **Induction.** Nearby electron-withdrawing groups, fading with distance: $ClCH_2COOH$ (≈2.9) vs CH_3COOH (≈4.8).
4. **Orbital.** More s-character holds the lone pair closer: sp C–H (≈25) > sp^2 (≈44) > sp^3 (≈50) in acidity.

Equilibrium direction

> The **equilibrium favors the side with the weaker acid (higher pKa)**, which is also the weaker-base side. log K ≈ pKa(acid formed) − pKa(acid consumed).

> **Example:** $HC{\equiv}CH + NH_2^- \rightleftharpoons HC{\equiv}C^- + NH_3$. Acid consumed HC≡CH (≈25), acid formed NH_3 (≈38): log K ≈ 38 − 25 = 13, so it lies right. With HO^- the acid formed is H_2O (≈15.7): log K ≈ −9, so NaOH can't deprotonate an alkyne.

Curved arrows for proton transfer

Two arrows: (1) base lone pair → H; (2) H–A bond → A. For $CH_3COOH + HO^- \rightarrow CH_3COO^- + H_2O$: HO^- lone pair → acidic H, and O–H bond → carboxylate O. Never start an arrow at H^+ (it has no electrons).

3 Functional groups and IUPAC naming

Functional group priority for naming (highest first)

Group	Suffix	Prefix
Carboxylic acid RCOOH	-oic acid	carboxy-
Ester RCOOR′	alkyl -oate	—
Amide $RCONH_2$	-amide	—
Nitrile $RC{\equiv}N$	-nitrile	cyano-
Aldehyde RCHO	-al	oxo-, formyl-
Ketone RCOR′	-one	oxo-
Alcohol ROH	-ol	hydroxy-
Amine RNH_2	-amine	amino-
Alkene, alkyne	-ene, -yne	(in parent name)
Halide, ether, nitro	—	halo- (chloro- …), alkoxy-, nitro-

Naming steps

1. The highest-priority group gives the suffix.
2. **Parent chain:** the longest chain containing that group. Most Ochem 1 textbooks also make it include the C=C/C≡C; the 2013 IUPAC rules prefer chain length, so follow your course.
3. **Number** for lowest locants, in order: (a) the suffix group; (b) C=C/C≡C (on an ene/yne tie, the double bond gets the lower number); (c) all substituents at the first point of difference; (d) alphabetical order.
4. **Alphabetize** substituents, ignoring di-, tri-, sec- and tert-, but not iso (isopropyl files under "i").
5. **Assemble:** stereodescriptors (in locant order, in parentheses) + substituents + parent + suffix: (2*E*,4*R*)-4-chloropent-2-ene; (*R*)-butan-2-ol, older style (*R*)-2-butanol.

Rings: the carbon bearing the suffix group is C1 (3-methylcyclohexan-1-ol); in a cycloalkene the C=C carbons are C1 and C2. Roots C1–C10: meth, eth, prop, but, pent, hex, hept, oct, non, dec.

4 Conformations

Newman projections

- Looking down one C–C bond: front carbon = where three bonds meet, back carbon = circle. **Staggered** (60°) is lower in energy than **eclipsed** (0°).
- **Torsional strain** comes from eclipsed bonds; **steric strain** from crowded groups (gauche, eclipsed).

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- **Ethane:** eclipsed lies ≈12 kJ/mol (≈2.9 kcal/mol) above staggered, ≈4 kJ/mol per H/H eclipsing.

Butane about C2–C3 (approximate energy above anti)

Conformation (CH_3/CH_3 dihedral)	Energy ≈
Anti, staggered (180°)	0, lowest
Gauche, staggered (60°)	3.8 kJ/mol (0.9 kcal/mol)
Eclipsed, CH_3 over H (120°)	16 kJ/mol (3.8 kcal/mol)
Totally eclipsed, CH_3 over CH_3 (0°)	19 kJ/mol (4.5 kcal/mol), highest

Ring strain: cyclopropane > cyclobutane > cyclopentane > cyclohexane (≈0 in the chair).

Cyclohexane chairs

- Each carbon has one **axial** bond (parallel to the ring axis, alternating up/down) and one **equatorial** bond (pointing outward).
- **Ring flip:** axial ↔ equatorial for every group, but up stays up (a wedged group stays on the top face).
- Groups prefer equatorial to avoid **1,3-diaxial** interactions (methylcyclohexane ≈95% equatorial at 25 °C). The best chair puts the largest groups equatorial; A-values are roughly additive, and t-Bu effectively locks the ring.

Approximate A-values (cost of axial vs equatorial)

Group	kJ/mol ≈	kcal/mol ≈
–Cl, –Br	2	0.4–0.5
–OH (solvent-dependent)	2.5–4	0.6–0.9
$-CH_3$	7.1	1.7
$-CH(CH_3)_2$	9.2	2.2
$-C(CH_3)_3$	≈20	≈4.9

cis/trans on rings

cis = same face (both wedges or both dashes); **trans** = opposite faces. A ring flip never converts cis into trans: they are diastereomers.

Disubstituted cyclohexanes: chair options (a = axial, e = equatorial)

Pattern	cis	trans	More stable
1,2-	a,e ↔ e,a	e,e ↔ a,a	trans
1,3-	e,e ↔ a,a	a,e ↔ e,a	cis
1,4-	a,e ↔ e,a	e,e ↔ a,a	trans

5 Stereochemistry

CIP priority rules

1. Higher atomic number of the attached atom wins: I > Br > Cl > S > F > O > N > C > H. Isotopes: higher mass wins (D > H).
2. Tie: list the three atoms on each tied atom (highest first) and compare pair by pair; the first point of difference decides. Move outward one sphere at a time.
3. Multiple bonds count as duplicated atoms: C=O counts as C bonded to (O, O); C≡C as C bonded to (C, C, C).

> **Example:** $-CH_2OH$ (O, H, H) outranks $-C(CH_3)_3$ (C, C, C): O beats C at the first comparison.

Assigning R/S

1. Rank groups 1–4 and point group 4 away from you (dash).
2. Trace 1 → 2 → 3: clockwise = ***R***, counterclockwise = ***S***.

- **Group 4 on a wedge:** read the direction, then reverse it.
- **Swap trick:** any one swap of two groups inverts the configuration. Swap group 4 onto the dash, assign, then reverse. Two swaps return the original.
- *R*/*S* does not predict the sign of rotation (+/−).

E/Z for alkenes

- Rank the two groups on each alkene carbon. Higher-priority groups on the same side = ***Z***; opposite sides = ***E***.
- cis/trans can disagree with *Z*/*E*: 2-bromobut-2-ene with its two CH_3 groups trans is *Z*, because Br outranks CH_3.
- A C=C in a ring of fewer than eight atoms must be cis.

Isomer relationships

- Different connectivity → **constitutional isomers**. Same connectivity, different 3-D arrangement → **stereoisomers**: mirror images → **enantiomers**; not mirror images → **diastereomers** (includes cis/trans, E/Z).
- Comparing descriptors: all centers inverted → enantiomers (unless meso: then the same compound); some inverted → diastereomers; none → same compound.
- **Chiral** = not superimposable on its mirror image. An internal mirror plane makes a molecule achiral.
- **Meso** = has stereocenters but is achiral (internal mirror plane): (2*R*,3*S*)-butane-2,3-diol, cis-1,2-dimethylcyclopentane.
- **2^n rule:** n stereocenters (count stereogenic C=C too) give at most 2^n stereoisomers, fewer with meso forms. Tartaric acid: 2 centers, 3 stereoisomers (enantiomer pair + meso).

Optical activity

- Enantiomers: same mp, bp and solubility; equal but opposite rotation of plane-polarized light. Diastereomers differ in all physical properties.
- $[\alpha] = \alpha / (c \cdot l)$, c in g/mL, l in dm. Racemic (50:50) mixtures and meso compounds: $[\alpha] = 0$.
- **ee** = % major − % minor = observed $[\alpha] / [\alpha]$ of pure enantiomer × 100%. 75% *R* + 25% *S* = 50% ee.

Fischer projections

- Each cross point is a stereocenter. **Horizontal** bonds point toward you (wedges), **vertical** bonds away (dashes); the carbon chain runs vertically.
- A 180° rotation in the plane keeps the molecule; a 90° rotation gives the enantiomer. One swap of two groups inverts that stereocenter only (enantiomer for a single center, diastereomer if other centers are present); two swaps restore it.
- R/S: group 4 vertical → read 1 → 2 → 3 directly; group 4 horizontal → read, then reverse.
- A horizontal mirror line through the middle reveals a meso compound.

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6 Arrow pushing

- Arrows move electrons. **Tail** on a lone pair or bond; **head** on an atom (new lone pair) or between atoms (new bond). Full head = 2 electrons; fishhook (half head) = 1 electron.
- Electrons flow from Nu/base (lone pair, π bond) to electrophile/acid (C^+, δ+ C bearing a LG, C=O carbon, acidic H).
- A new bond to an atom that already has an octet means another bond to it must break. Never start at H^+ or a + charge. Each step keeps the total charge.

The four electron-flow patterns

Pattern	Arrows	Example
Nucleophilic attack	1: Nu → electrophilic atom	$Br^- + (CH_3)_3C^+ \rightarrow (CH_3)_3CBr$
Loss of LG	1: C–LG bond → LG	$(CH_3)_3C{-}OH_2^+ \rightarrow (CH_3)_3C^+ + H_2O$
Proton transfer	2: base → H; H–A bond → A	$ROH + H_3O^+ \rightarrow ROH_2^+ + H_2O$
Rearrangement	1: C–H or C–C bond next to C^+ → C^+	1,2-hydride or 1,2-methyl shift

Concerted steps combine patterns: SN2 = attack + loss of LG (2 arrows); E2 = proton transfer + loss of LG (3 arrows).

Carbocation stability and 1,2-shifts

- 3° > 2° > 1° > methyl (alkyl donation: hyperconjugation, induction). Resonance (allylic, benzylic, or next to an O or N lone pair) adds strong stabilization. Vinyl and aryl cations are too unstable to form here, so no SN1/E1 at sp^2 carbons.
- A **1,2-hydride or 1,2-alkyl shift** occurs when it gives a more stable cation (2° → 3°, or → resonance-stabilized). A strained ring next to C^+ can expand by a 1,2-alkyl shift (4- → 5-, 5- → 6-membered) when that relieves strain or gives a more stable cation.
- Expect shifts wherever a free C^+ forms: SN1, E1, HX addition, acid-catalyzed hydration, 2°/3° ROH + HX. None in SN2, E2, oxymercuration, hydroboration or X_2 addition.

Example: 3-methylbutan-2-ol + HBr: protonate OH, lose H_2O (2° C^+), 1,2-hydride shift (3° C^+), add Br^-. Major product: 2-bromo-2-methylbutane.

Energy diagrams

- **Transition state** (‡) = energy maximum with partial bonds, never isolable; **intermediate** = a valley between steps (C^+, radical). SN2/E2 show one hump; SN1/E1 show two or more (a small extra hump when a neutral Nu like H_2O must lose H^+), and the first (C^+ formation) has the highest barrier: it is the **rate-determining step**, so only [RX] appears in the rate law.
- Rate depends on the barrier ΔG‡, not on ΔG; a catalyst lowers ΔG‡ only. **$\Delta G = \Delta H - T\Delta S$**; ΔG < 0 means products are favored (K > 1). Elimination makes more molecules (ΔS > 0), so heat (larger TΔS) favors E over S.
- **Hammond postulate:** a transition state resembles the species closest to it in energy, so endothermic steps have late, product-like transition states. That is why carbocation stability controls SN1/E1 rates.

7 Substitution and elimination

SN2, SN1, E2 and E1 compared

Feature	SN2	SN1	E2	E1
Steps	1, concerted backside attack	2: C^+ forms, then Nu adds	1, concerted (β-H and LG leave together)	2: C^+ forms, then β-H lost
Rate law	k[RX][Nu]	k[RX]	k[RX][base]	k[RX]
Substrate	methyl > 1° > 2°; never 3°	3° > 2°; allylic, benzylic	3° > 2° > 1° (needs β-H)	3° > 2°
Reagent	good Nu, often anionic	weak Nu (H_2O, ROH)	strong base	weak base; or acid + Δ
Solvent	polar aprotic (DMSO, DMF)	polar protic (H_2O, ROH)	less decisive	polar protic
Stereo	inversion	mostly racemization	anti-periplanar; stereospecific	more stable (E) alkene favored
Regio	—	—	Zaitsev (more substituted alkene); Hofmann (less substituted) if bulky base	Zaitsev
Rearrangement	no	possible	no	possible

Decision flow

1. **Leaving group on an sp^3 carbon?** –OH and –OR must first be protonated or converted; vinyl and aryl halides don't do SN1 or SN2.
2. **Classify the reagent:** *Nu only* (strong Nu, weak base): I^-, Br^-, Cl^-, HS^-, RS^-, H_2S, RSH, N_3^-, CN^-. *Base only* (strong base, poor Nu): t-BuOK, DBU, DBN, LDA, NaH. *Strong base + strong Nu:* HO^-, CH_3O^-, EtO^-, acetylides. *Weak Nu + weak base:* H_2O, ROH.
3. **Classify the substrate** and read the table below.
4. **Adjust:** heat favors elimination; polar aprotic solvent boosts SN2; polar protic supports SN1/E1; branching near the reacting carbon (e.g. neopentyl) slows SN2.

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Usual major pathway by substrate and reagent (real reactions often give mixtures)

Substrate	Nu only	Strong base/Nu (HO^-, RO^-)	Bulky base (t-BuOK)	Weak (H_2O, ROH)
Methyl	SN2	SN2	SN2 (no β-H)	no reaction
1°	SN2	SN2 major, E2 minor	E2	no reaction (allylic/benzylic: SN1)
2°	SN2	E2 major, SN2 minor	E2	SN1 + E1 (slow)
3°	SN1 (protic)	E2	E2 (Hofmann)	SN1 + E1 (Δ favors E1)

Leaving groups and nucleophiles

- Good LGs are **weak bases**: sulfonates (TsO^-, MsO^-, TfO^-), $I^- > Br^- > Cl^-$, and H_2O from a protonated alcohol. Poor: F^-, HO^-, RO^-, NH_2^-, H^-. Turn –OH into a LG by protonating it or converting it to OTs, Br or Cl (section 11).
- Nucleophilicity: an anion beats its conjugate acid ($HO^- > H_2O$). **Protic** solvents (O–H or N–H: H_2O, ROH) H-bond to and cage small anions, so in them nucleophilicity rises down a group ($I^- > Br^- > Cl^- > F^-$; $RS^- > RO^-$). **Polar aprotic** solvents (DMSO, DMF, acetone, CH_3CN: no O–H) leave anions bare, so the order follows basicity ($F^- > Cl^- > Br^- > I^-$) and SN2 is much faster. Bulk lowers nucleophilicity far more than basicity.

- **E2 needs H and LG anti-periplanar** (180°). On a cyclohexane both must be **axial** (trans-diaxial): use the chair with the LG axial. If the only anti-periplanar β-H is on the less substituted carbon, that alkene forms even with a small base.
- E2 is stereospecific: when the β-carbon has one H, the anti-periplanar geometry decides E vs Z.

Example: cis-1-chloro-2-methylcyclohexane (Cl axial, CH_3 equatorial) has an axial H on C2, so NaOEt gives 1-methylcyclohexene (Zaitsev). In the trans isomer, putting Cl axial also puts CH_3 axial and the C2–H equatorial; only C6 has an axial H, so it gives 3-methylcyclohexene, and reacts more slowly.

8 Alkene reactions

- **Markovnikov:** the electrophile (H^+, Br^+, ^+HgOAc) adds first, and the nucleophile ends up on the carbon that best bears positive charge, the more substituted one, because that gives the more stable carbocation (or the more δ^+ end of a bridged ion). Anti-Markovnikov happens when the first species to add is not H^+: Br• (radical HBr) or boron (hydroboration) goes to the less substituted carbon.
- **Syn** = same face, **anti** = opposite faces (visible only when both carbons become stereocenters). Achiral alkene + achiral reagents → optically inactive products (achiral, racemic or meso).
- **Stereospecific** = each stereoisomer of the starting material gives a different stereoisomer of product (cis-but-2-ene + Br_2 → racemic, trans → meso). **Stereoselective** = one stereoisomer is simply preferred (E over Z in E1).
- **Alkene stability** (from heats of hydrogenation): tetrasubstituted > tri- > disubstituted (trans > cis) > monosubstituted. More alkyl groups mean more hyperconjugation; this is why Zaitsev and E1 favor the most substituted, E alkene.

Alkene addition and cleavage reactions

Reaction	Reagents	Regiochemistry	Stereochemistry	Intermediate, notes
Hydrohalogenation	HCl, HBr, HI	Markovnikov	syn + anti mixture	carbocation; shifts possible
Radical HBr addition	HBr, ROOR (hν or Δ)	anti-Markovnikov	syn + anti mixture	Br• adds → more stable C•; HBr only
Acid-catalyzed hydration	H_2O, cat. H_2SO_4	Markovnikov	syn + anti mixture	carbocation; shifts possible
Oxymercuration	1) $Hg(OAc)_2$, H_2O; 2) $NaBH_4$	Markovnikov	step 1 anti; the $NaBH_4$ step is radical, so overall stereochemistry is lost	mercurinium ion; no shifts; ROH gives ether
Hydroboration	1) BH_3·THF; 2) H_2O_2, NaOH	anti-Markovnikov	syn (H and OH)	concerted; no shifts; H_2O_2/NaOH swaps B for OH with retention, so H and OH end up syn
Halogenation	Br_2 or Cl_2 (CH_2Cl_2)	—	anti	bridged halonium ion
Halohydrin	Br_2 or Cl_2, H_2O	OH on more substituted C	anti	halonium ion; H_2O attacks its more δ^+ end, as in acid epoxide opening
Epoxidation	mCPBA (RCO_3H)	—	syn; cis → cis epoxide	concerted
Anti dihydroxylation	1) mCPBA; 2) H_3O^+	—	anti (trans diol)	epoxide opened by H_2O
Syn dihydroxylation	OsO_4 (cat.), NMO; or cold $KMnO_4$, NaOH	—	syn (cis diol)	cyclic osmate/manganate ester
Hydrogenation	H_2; Pt, Pd/C or Ni	—	syn	metal surface → alkane

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Reaction	Reagents	Regiochemistry	Stereochemistry	Intermediate, notes
Cyclopropanation (some courses)	CH_2I_2, Zn(Cu) (Simmons–Smith); or $CHCl_3$, KOH (→ dichlorocyclopropane)	—	syn, stereospecific (cis → cis)	carbenoid or carbene adds in one step
Ozonolysis	1) O_3; 2) DMS or Zn/H_2O	C=C → two C=O	—	$R_2C=$ → ketone; RCH= → aldehyde. Hot acidic $KMnO_4$ also cleaves but over-oxidizes: RCH= → RCOOH, $=CH_2$ → CO_2

Worked mini-examples: 1-methylcyclohexene + reagents

Reagents	Major product
HBr	1-bromo-1-methylcyclohexane
HBr, ROOR	1-bromo-2-methylcyclohexane (cis + trans)
H_3O^+; or 1) $Hg(OAc)_2$, H_2O; 2) $NaBH_4$	1-methylcyclohexan-1-ol
1) BH_3·THF; 2) H_2O_2, NaOH	trans-2-methylcyclohexan-1-ol (racemic)
Br_2	trans-1,2-dibromo-1-methylcyclohexane (racemic)
Br_2, H_2O	trans-2-bromo-1-methylcyclohexan-1-ol (racemic)
OsO_4, NMO	cis-1-methylcyclohexane-1,2-diol (racemic)
1) O_3; 2) DMS	6-oxoheptanal (ring opens to one chain)

Stereospecific pairs: Br_2 (anti) + trans-but-2-ene → meso-2,3-dibromobutane; + cis-but-2-ene → racemic (2*R*,3*R*) + (2*S*,3*S*). OsO_4 (syn) is the reverse: cis → meso diol, trans → racemic diol.

9 Alkyne reactions

Alkyne reactions

Reagents	Product, selectivity
H_2 (excess), Pt, Pd/C or Ni	alkane
H_2, Lindlar's catalyst (poisoned Pd)	**cis (Z) alkene** (syn addition; stops at the alkene)
Na or Li, NH_3(l)	**trans (E) alkene** from an internal alkyne (dissolving metal; terminal alkynes are deprotonated instead and reduce slowly)
H_2O, H_2SO_4, $HgSO_4$	Markovnikov enol → **ketone** (terminal alkyne → methyl ketone)
1) R_2BH (disiamylborane or 9-BBN); 2) H_2O_2, NaOH	anti-Markovnikov enol → **aldehyde** from a terminal alkyne (bulky borane adds once)
HX: 1 equiv; 2 equiv	Markovnikov vinyl halide; then a **geminal** dihalide (both X on one C)
HBr, ROOR (terminal)	anti-Markovnikov vinyl bromide (E/Z mixture)
X_2: 1 equiv; 2 equiv	mainly (E)-dihaloalkene (anti); then tetrahalide

- **Tautomerization:** the enol converts (acid or base catalysis) to the more stable C=O form. Unsymmetrical internal alkynes give ketone mixtures.
- **Terminal alkyne acidity (pKa ≈25):** deprotonate with $NaNH_2$ (NH_3 ≈38) or NaH, not NaOH or NaOEt.
- **Alkylation:** $RC{\equiv}C^-$ + CH_3X or 1° RX → $RC{\equiv}CR'$ by SN2 (new C–C bond). With 2°/3° halides the acetylide acts as a base (E2).
- **Making alkynes:** vicinal or geminal dihalide + excess $NaNH_2$ (double E2; 3 equiv for a terminal alkyne), then H_2O.

Example: acetylene → (*Z*)-hex-3-ene: 1) $NaNH_2$; 2) CH_3CH_2Br; 3) $NaNH_2$; 4) CH_3CH_2Br; 5) H_2, Lindlar. Na, NH_3(l) in step 5 gives (*E*)-hex-3-ene.

10 Radical reactions

Radicals form by **homolysis** and are drawn with fishhook arrows. Stability: allylic/benzylic > 3° > 2° > 1° > methyl.

Halogenation mechanism (CH_4 + Cl_2, hν)

1. **Initiation** (makes radicals): Cl_2 → 2 Cl• (light or heat).
2. **Propagation** (chain; radical count unchanged): Cl• + CH_4 → HCl + •CH_3; then •CH_3 + Cl_2 → CH_3Cl + Cl•.
3. **Termination** (uses up radicals): any two combine, e.g. Cl• + •CH_3 → CH_3Cl; 2 •CH_3 → ethane.

Selectivity: Cl_2 vs Br_2

- **Chlorination:** exothermic H-abstraction (≈thermoneutral for CH_4), early transition state, **poorly selective**: ≈1 : 4 : 5 per H (1° : 2° : 3°, 25 °C). Propane → ≈45% 1-chloro + ≈55% 2-chloropropane.

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- **Bromination:** endothermic H-abstraction, so the transition state is late and radical-like (Hammond postulate, section 6) and the full 3° > 2° > 1° radical stability difference shows up in the rates: **highly selective**, ≈1 : 80 : 1600. Propane → ≈97% 2-bromopropane. Use Br_2, hν to target the most substituted C–H.
- F_2 is too violent, I_2 too unreactive. A new stereocenter formed at a planar radical carbon comes out racemic.

Allylic bromination with NBS

NBS, hν (or ROOR), CCl_4 swaps an allylic H for Br. NBS keeps [Br_2] low, so Br_2 doesn't add to the C=C. The allylic radical is delocalized, so Br can end up at either end: cyclohexene → 3-bromocyclohexene; but-1-ene → 3-bromobut-1-ene + 1-bromobut-2-ene (E/Z).

11 Alcohols, ethers and epoxides

Turning –OH into a leaving group or a halide

Reagent → product	Mechanism, stereochemistry (substrates)
HBr, HCl (+ $ZnCl_2$), HI → R–X	3°/2°: SN1 (racemization, shifts possible); 1°: SN2
PBr_3 → R–Br	SN2: inversion, no shifts (1°, 2°)
$SOCl_2$, pyridine → R–Cl	SN2: inversion, no shifts (1°, 2°)
TsCl (or MsCl), pyridine → R–OTs	C–O bond untouched: **retention**; a later SN2 on R–OTs inverts (1°, 2°)

- **Dehydration:** conc. H_2SO_4 or H_3PO_4, Δ → alkene. Ease 3° > 2° > 1°; 2°/3° by E1 (Zaitsev, shifts possible). For control: TsCl, pyridine; then t-BuOK (E2).
- **Alkoxides:** ROH + NaH (or Na) → $RO^-\ Na^+ + H_2$ (irreversible).

Alcohol oxidation

Alcohol	PCC, CH_2Cl_2 (also DMP, Swern)	Chromic acid or Jones ($Na_2Cr_2O_7$ or CrO_3, H_2SO_4, H_2O)
1°	aldehyde	carboxylic acid
2°	ketone	ketone
3°	no reaction	no reaction

Making alcohols from C=O and epoxides (the last Ochem 1 chapter in many courses)

Reagents	Result
$NaBH_4$, CH_3OH	aldehyde → 1° alcohol; ketone → 2° alcohol (esters and acids untouched)
1) $LiAlH_4$, dry ether; 2) H_3O^+	same, and also reduces esters and carboxylic acids to 1° alcohols
1) RMgBr or RLi; 2) H_3O^+	new C–C bond: formaldehyde → 1°; other aldehydes → 2°; ketone → 3°; ester (2 R add) → 3° alcohol
1) RMgBr + epoxide; 2) H_3O^+	R attacks the less substituted C (SN2-like); ethylene oxide adds a $–CH_2CH_2OH$ unit

Grignard reagents (RBr + Mg, dry ether) and RLi are strong bases: no O–H, N–H or COOH in the substrate or solvent (they would protonate R^- to R–H). RMgBr + CO_2, then H_3O^+ → RCOOH.

Ethers

- **Williamson:** $RO^- + R'X$ → ROR′ by SN2, so R′X must be methyl or 1°; put the bulky part on the alkoxide. $(CH_3)_3CO^-\ K^+ + CH_3I$ → t-BuOCH$_3$ works; $CH_3O^- + (CH_3)_3CBr$ gives E2 (2-methylpropene).
- Cleavage: excess HBr or HI, Δ → two R–X (SN2 at methyl/1°, SN1 at 3°); an aryl alkyl ether gives phenol + RX.

Epoxides

- Made by alkene + mCPBA (syn, stereospecific), or halohydrin + NaOH (intramolecular SN2; O^- and X must be anti).
- **Base or strong Nu** (HO^-, RO^-, RS^-, CN^-, N_3^-, acetylide; then a proton source): SN2 at the **less substituted** carbon.
- **Acid** (H_3O^+, ROH/H^+, HX): protonate O, then Nu attacks the **more substituted** carbon (more δ+, SN1-like transition state). Clear-cut when that carbon is 3°.
- Both modes attack from the back side (inversion there): anti opening, so cyclic epoxides give trans-1,2-products.

> **Example:** 2,2-dimethyloxirane + CH_3O^-/CH_3OH → 1-methoxy-2-methylpropan-2-ol. With CH_3OH, cat. H_2SO_4 → 2-methoxy-2-methylpropan-1-ol.

12 Spectroscopy basics

Degrees of unsaturation = (2C + 2 + N − H − X)/2 (ignore O, S). Each ring or π bond = 1; C≡C = 2; benzene ring = 4. C_6H_{12} → (12 + 2 − 12)/2 = 1: one ring or one C=C.

- **^{1}H NMR signals** = sets of chemically distinct H (use symmetry). **Integration** = relative number of H.
- **n + 1 rule:** n equivalent neighboring H split a signal into n + 1 peaks (Pascal's triangle). Equivalent H don't split each other; O–H usually doesn't (fast exchange).
- Ethyl = triplet (3H) + quartet (2H); isopropyl = doublet (6H) + septet (1H); tert-butyl = singlet (9H). J ≈ 7 Hz in alkyl chains; vinyl trans (≈12–18 Hz) > cis (≈6–12 Hz).
- **^{13}C** (one line per distinct C; heights not quantitative): sp^3 C 0–50; C–O 50–90; C≡C 65–90; C=C and aromatic 100–160; C≡N 115–125; C=O 160–220.
- **Mass spec:** M^+ = molecular mass (an odd M^+ means an odd number of N). An M+2 peak about equal to M^+ → one Br; about ⅓ of M^+ → one Cl. Common losses: 15 (CH_3), 29 (C_2H_5), 18 (H_2O from alcohols).

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Key IR absorptions (approximate)

Bond	cm^{-1} ≈	Appearance
O–H alcohol	3200–3600	strong, broad
O–H acid	2500–3300	very broad
N–H	3300–3500	1° amine 2 peaks, 2° one
C–H: sp; sp^2; sp^3	≈3300; 3000–3100; 2850–3000	sp strong, sharp; sp^2 just above 3000, sp^3 just below
Aldehyde C–H	≈2720, 2820	two weak peaks
C≡N; C≡C	≈2250; 2100–2260	C≡C weak or absent if symmetric
C=O	1650–1750	strong (ketone ≈1715, ester ≈1740)
C=C	1600–1680	medium to weak
C–O	1000–1300	strong

^{1}H NMR chemical shifts (approximate)

Proton type	δ ≈ (ppm)
Alkyl C–H (CH_3 < CH_2 < CH)	0.9–1.8
Allylic, benzylic, α to C=O	1.7–2.6
Alkyne ≡C–H	2–3
H–C–O, H–C–X	3–4.5
Vinyl =C–H	4.5–6.5
Aromatic Ar–H	6.5–8.5
Aldehyde –CHO	9–10
Carboxylic acid –COOH	10–13, broad
O–H, N–H	1–5, variable

13 Synthesis strategy

Reaction map: interconverting Ochem 1 functional groups

From → to	Reagents (notes)
Alkane → alkyl bromide	Br_2, hν (most substituted C)
Alkyl halide → alkene	NaOEt (Zaitsev) or t-BuOK (Hofmann), E2
Alkyl halide → SN2 products	NaOH, NaOR, NaCN, NaN_3, NaSR, $RC{\equiv}C^-\ Na^+$ (methyl or 1° halide best); 3° RX + H_2O → alcohol (SN1)
Alkene → alkyl halide	HX (Markovnikov); HBr, ROOR (anti-Markovnikov)
Alkene → alcohol	H_3O^+, or $Hg(OAc)_2/H_2O$ then $NaBH_4$ (Markovnikov); BH_3 then H_2O_2/NaOH (anti-Markovnikov, syn)
Alkene → alkane; X_2 adducts	H_2, Pd/C; X_2 (dihalide); X_2/H_2O (halohydrin)
Alkene → epoxide; diol; carbonyls	mCPBA; OsO_4/NMO (syn) or mCPBA then H_3O^+ (anti); O_3 then DMS
Alkene → allylic bromide; alkyne	NBS, hν; 1) Br_2, 2) excess $NaNH_2$, 3) H_2O
Alkyne → cis/trans alkene; alkane	H_2, Lindlar (cis); Na, NH_3(l) (trans); H_2, Pd/C (alkane)
Alkyne → ketone; aldehyde	$HgSO_4$, H_2SO_4, H_2O; R_2BH then H_2O_2/NaOH (terminal alkyne)
Alcohol → alkyl halide; tosylate	PBr_3, $SOCl_2$/pyridine or HX; TsCl/pyridine
Alcohol → alkene	H_2SO_4, Δ (E1, Zaitsev); or TsCl/pyridine then t-BuOK (E2)
Alcohol → aldehyde; ketone; acid	PCC (1°); PCC or chromic acid (2°); chromic acid (1°)
Alcohol → ether	NaH, then CH_3X or 1° RX (Williamson)
Epoxide → alcohol	Nu^- then H_2O (less substituted C); H_3O^+ or ROH/H^+ (more substituted C)
Aldehyde, ketone, ester → alcohol	$NaBH_4$ (not esters), or $LiAlH_4$ then H_3O^+; RMgBr or RLi, then H_3O^+ (new C–C bond)

Retrosynthesis tips

- Work backward (⇒) and compare carbon counts. New C–C bonds: acetylide + methyl or 1° halide, or Grignard (RMgBr/RLi) + C=O or epoxide.
- **Move a functional group:** eliminate, then add with the opposite regiochemistry. Propan-2-ol → (TsCl, pyridine; t-BuOK) → propene → (BH_3; H_2O_2/NaOH) → propan-1-ol.

Common exam pitfalls

- SN2 or Williamson at a 3°, vinyl or aryl C (E2 or no reaction).
- Missing C^+ shifts (SN1, E1, HX, H_3O^+); none in oxymercuration or hydroboration.
- Chromic acid on a 1° alcohol when you want the aldehyde (use PCC).
- Ring E2 without a trans-diaxial H and LG.
- Grignard with an O–H or N–H elsewhere in the molecule.
- Dropping stereochemistry; arrows from H^+ or a + charge; five-bonded C.

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