

1. Fundamentals & Nomenclature

Priority of Functional Groups: Carboxylic Acid > Anhydride > Ester > Acid Halide > Amide > Nitrile > Aldehyde > Ketone > Alcohol > Amine > Alkene > Alkyne.

Isomerism Summary:

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- **Enantiomers:** Non-superimposable mirror images (*R/S*). Equal physical props, opposite $[\alpha]_D$.
- **Diastereomers:** Non-mirror image stereoisomers. Diff. physical/chemical properties.
- **Meso Compounds:** Internal plane of symmetry (C_i/C_s), optically inactive despite chiral centers.

Degree of Unsaturation (DoU / IHD):

$$\text{DoU} = C + 1 - \frac{H}{2} - \frac{X}{2} + \frac{N}{2}$$

2. Reaction Intermediates

Carbocation Stability:

Benzylic $\approx$ Allylic > 3° > 2° > 1° > Methyl

Stabilized by +I (inductive) and hyperconjugation ($3 \times \alpha\text{-H}$ per methyl).

Carbanion Stability:

$\text{sp} > \text{sp}^2 > \text{sp}^3$ | Methyl > 1° > 2° > 3°

Stabilized by electron-withdrawing groups (-I, -M).

Radical Stability:

Allylic $\approx$ Benzylic > 3° > 2° > 1° > Methyl

3. Nucleophilic Substitution

Property	S_N1	S_N2	Hofmann
Kinetics	First Order: $r = k[RX]$	Second Order: $r = k[RX][Nu]$	(Less
Steps	2-step (C+ intermed.)	1-step (Concerted TS)	sub-
Substrate	3° > 2° $\gg$ 1°	Me > 1° > 2° $\gg$ 3°	sti-
Stereo	Racemization	Inversion (180° attack)	tuted
Solvent	Polar Protic	Polar Aprotic	alkene):

Solvents:

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- **Polar Protic (S_N1):** H₂O, MeOH, EtOH, AcOH.
- **Polar Aprotic (S_N2):** Acetone, DMSO, DMF, ACN, THF.

4. Elimination Reactions

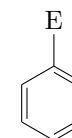
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- **E1:** 2-step via carbocation. Favored by weak bases, high temp, 3° substrates.
- **E2:** 1-step concerted. Requires **anti-periplanar** geometry of H and LG. Favored by strong bases.
- **Zaitsev vs. Hofmann:**

—
Zaitsev
 (More
 sub-
 sti-
 tuted
 alkene):
 Small
 un-
 hin-
 dered
 base
 (e.g.,
 NaOEt,
 NaOH).

5. Electrophilic Aromatic Substitution (EAS)

Basic mechanism involving arenium ion intermediate:



(Regioselectivity below)

Directing Groups:

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- **Ortho/Para Directors (Activating):**

$-\text{O}^-$, $-\text{NH}_2$, $-\text{OH}$, $-\text{OR}$, $-\text{NHCOR}$, $-\text{R}$

- **Ortho/Para Directors (Deactivating):**

$-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$ (Inductive -I ; Resonance +M)

- **Meta Directors (Deactivating):**

$-\text{NO}_2$, $-\text{CF}_3$, $-\text{CN}$, $-\text{SO}_3\text{H}$, $-\text{CHO}$, $-\text{COR}$, $-\text{COOH}$

6. Key Organic Reactions

Alkene Additions:

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- **Hydroboration-Oxidation:** 1. BH_3 · THF/2. $\text{H}_2\text{O}_2, \text{NaOH}$ *arrow* Anti-Markovnikov, Syn-addition alcohol.
- **Oxymercuration-Demercuration:** 1. $\text{Hg}(\text{OAc})_2, \text{H}_2\text{O}$ /2. NaBH_4 *arrow* Markovnikov, No rearrangement.
- **Ozonolysis:** 1. O_3 /2. Zn, AcOH (Reductive) *arrow* Aldehydes/Ketones.

Carbonyl Chemistry:

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- **Aldol Condensation:** Base-catalyzed enolate formation + addition to carbonyl *arrow* β -hydroxy carbonyl $\xrightarrow{\Delta}$ α, β -unsaturated carbonyl.
- **Grignard Reaction:** $\text{R-MgX} + \text{Carbonyl}$ *arrow* Alcohol ($1^\circ, 2^\circ, 3^\circ$ depending on formaldehyde, aldehyde, or ketone).
- **Fisher Esterification:** $\text{RCOOH} + \text{R}'\text{OH} \xrightarrow{\text{H}^+} \text{RCOOR}' + \text{H}_2\text{O}$.

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- **O–H (Alcohol):** 3200 – 3600 (Broad, strong)
- **N–H (Amine):** 3300 – 3500 (Medium, sharp)
- **C=O (Carbonyl):** 1700 – 1750 (Strong, sharp)
- **$\text{C}\equiv\text{N}$ (Nitrile):** **2200–2250** (Medium)
- **$\text{C}=\text{C}$ (Alkene):** 1620 – 1680 (Variable)

$^1\text{H-NMR}$ Chemical Shifts (ppm):

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- Alkyl (R-CH_3): 0.9 – 1.5
- Allylic/Alkynyl: 1.8 – 2.5
- Heteroatom-adjacent ($-\text{CH}_2-\text{O}-$): 3.3 – 4.5
- Vinylic ($\text{C}=\text{C-H}$): 4.5 – 6.5
- Aromatic (Ar-H): 6.5 – 8.5
- Aldehyde ($-\text{CHO}$): 9.5 – 10.0
- Carboxylic Acid ($-\text{COOH}$): 10.5 – 12.0

7. Reagent Reference Guide

Reagent	Primary Function
PCC	Mild oxidation (1° Alc <i>arrow</i> Aldehyde)
$\text{KMnO}_4/\text{CrO}_3$	Strong oxidation (1° Alc <i>arrow</i> Carboxylic Acid)
LiAlH_4	Strong reducer (Esters, Acids, Carbonyls <i>arrow</i> Alcohols)
NaBH_4	Mild reducer (Only Aldehydes/Ketones <i>arrow</i> Alcohols)
$\text{SOCl}_2/\text{PCl}_5$	Converts $-\text{OH}$ to $-\text{Cl}$ with inversion
DIBAL-H	Reduces Esters/Nitriles to Aldehydes (at low temp)

8. Spectroscopy Quick Guide

IR Absorptions (cm^{-1}):