

Starting Material → Alkene					
Name	Reagents	Regiochemistry	Stereochemistry	Functional Outcome	Mechanism
Hydrohalogenation (HX Addition)	HX (HCl, HBr, HI)	Markovnikov (X attaches to more substituted carbon)	Racemic	Alkyl Halide	*
Hydrohalogenation (HX Addition with Peroxide)	HBr, ROOR (peroxide)	Anti-Markovnikov (X attaches to less substituted carbon)	Racemic	Alkyl Halide	*
Acid-Catalyzed Hydration	H ₂ SO ₄ , H ₂ O (or H ₃ O ⁺)	Markovnikov	Racemic	Alcohol	
Oxymercuration-Demercuration	1. Hg(OAc) ₂ , H ₂ O 2. NaBH ₄	Markovnikov	Anti-Addition	Alcohol	
Hydroboration-Oxidation	1. BH ₃ , THF 2. H ₂ O, NaOH	Anti-Markovnikov	Syn-Addition	Alcohol	



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Starting Material → Alkene (cont)				
Halogenation (X ₂ Addition)	X ₂ (Br ₂ , Cl ₂)	None	Anti-Addition	Vicinal Dihalide
Halohydrin Formation	X ₂ , H ₂ O	Markovnikov	Anti-Addition	Halohydrin
Hydrogenation	H ₂ , Pt/Pd/Ni	None	Syn-Addition	Alkane
Dihydroxylation (Syn)	OsO ₄ or KMnO ₄ (cold, dilute), NaHSO ₃	None	Syn-Addition	Vicinal Diol
Dihydroxylation (Anti)	1. mCPBA 2. H ₃ O ⁺	None	Anti-Addition	Vicinal Diol
Ozonolysis	1. O ₃ 2. Me ₂ S (DMS) or Zn/H ₂ O	None	None	Aldehyde/Ketone

Ranking Radical Stability

1. Benzylic/Allylic Radicals [**MOST STABLE**]
2. Tertiary (3°) Radicals
3. Secondary (2°) Radicals
4. Primary (1°) Radicals
5. Methyl Radicals

Key Factors Affecting Stability:

Resonance Stabilization (Allylic & Benzylic > Non-resonance stabilized)

Hyperconjugation

(More alkyl groups donate electron density)

Inductive Effects

(Electron-withdrawing groups destabilize)

Number of Unique Products

NBS
(Allylic Bromination)

Cl₂/hν
(Radical Chlorination)

Selective
Only abstracts the **allylic hydrogen**

Less selective
attacks **all possible C-H bonds**

Favors one major product due to resonance stabilization

More radical products due to no preference

Highly Selective → Major product at most stable radical site

Non-selective → Multiple products

Arrow Pushing in Radical Reactions

Fishhook Arrows → movement of 1 electron

Initiation → arrows depict homolytic cleavage

Propagation → 1 radical reacts to form another

Termination → 2 radicals combine to form a stable molecule

Terms to Know

Markovnikov's Rule → *addition reactions* proton added to the **carbon** with the **most hydrogen** atoms attached

Geminal → 2 atoms bonded to the **same side** of the carbon

Anti-Markovnikov's Rule → *addition reactions* proton added to the **carbon** with the **least hydrogen** atoms attached

Vicinal → 2 atoms bonded to **same carbon**

Zaitsev's Rule → *elimination reaction*, major product is the **more stable** alkene with the **highly substituted** double bond

Syn-Addition → added to **same side** of compound

Terms to Know (cont)

E/Z System → Prioritize the 2 groups attached to each carbon relative to one another.

Higher priority groups are:

cis/same side → Z

trans/opposite sides → E

Anti-Addition → added to **different sides** of compounds

Oxidation State of Carbons

C-H bond → carbon gains **-1** per hydrogen

C-C bond → no change (**0**)

C-X bond → carbon loses **+1** per electronegative atom

The **oxidation state** of a carbon atom depends on its **bonds** to atoms of different electronegativities

NMR

¹H NMR

Chemical Shift Trends

0-2 ppm → Alkane

2-3 ppm → Allylic, benzylic, alkynyl

4-6 ppm → Alkene

¹³C NMR

Chemical Shift Trends

0-50 ppm → Alkane

50-100 ppm → Alcohol, ether, alkynes

100-150 ppm → Aromatic, alkene

C

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NMR (cont)

6-8 ppm → **150-200 ppm** Carbonyl
(ketone, aldehyde, carboxylic acid)
Aromatic

9-10 ppm →

Aldehyde

10-12 ppm →

Carboxylic acid (broad)

Splitting Patterns ^(n+1 rule)

Singlet → no adjacent protons

Doublet → 1 adjacent proton

Triplet → 2 adjacent protons

IR Spectroscopy

Key Peaks

O-H (Alcohol) → 3200-3600 cm⁻¹ (broad)

C-H (Alkanes) → 2800-3000 cm⁻¹

C=O (Carbonyls) → ~1700 cm⁻¹

C=C (Alkene) → ~1650 cm⁻¹

C≡C, C≡N → ~2100-2200 cm⁻¹

Starting Material → Alkyne

Substitution Reactions

S_N1 (Unimolecular)

S_N2 (Bimolecular)

Mechanism → Two-step; carbocation formation, nucleophilic attack

Mechanism → One-step; backside attack

Substitution Reactions (cont)

Rate → Dependent *only* on substrate
rate=k[R-X]

Stereochemistry → Racemic mixture

Preferred Conditions → Weak nucleophile, polar protic solvent

Tertiary >
Secondary >
Primary

Rate → Dependent on *both* substrate & nucleophile
rate=k[R-X][Nu-]

Stereochemistry → Inversion of configuration

Preferred Conditions → Strong nucleophile, polar aprotic solvent

Methyl > Primary >
Secondary >
Tertiary

Elimination Reactions

E1 (Unimolecular)

E2 (Bimolecular)

Mechanism → Two-step; carbocation intermediate, base deprotonates

Rate → Dependent *only* on substrate

Mechanism → One-step; concerted β-H abstraction

Rate → Dependent on *both* substrate and base

Elimination Reactions (cont)

Regiochemistry → Zaitsev's Rule (more substituted alkene favored)

Stereochemistry → Forms most stable alkene

Preferred Conditions → Weak base, polar protic solvent

Tertiary > Secondary > *Primary*

Regiochemistry → Zaitsev's Rule (unless bulky base → Hofmann product)

Stereochemistry → Anti-periplanar elimination

Preferred Conditions → Strong base required

Primary >
Secondary >
Tertiary (as long as β-H is anti-periplanar)



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