

Known Reaction Pathways

Reaction Type	Name	Functional Outcome	Key Reagents
Oxidation			
	Alcohol Oxidation	1° OH → Aldehyde/Carboxylic acid 2° OH → Ketone	PCC (mild), CrO ₃ /H ₂ SO ₄ (strong), KMnO ₄
	Ozonolysis	Cleaves Alkenes → Aldehydes/Ketones	2. O ₃ 2. (CH ₃) ₂ S or Zn/H ₂ O
	Benzylic Oxidation	Benzylic carbon → Carboxylic acid	KMnO ₄ , heat
Reduction			
	Catalytic Hydrogenation	Alkene/Alkyne → Alkane	H ₂ , Pt/Pd/Ni
	Poisoned Hydrogenation	Alkyne → Cis-Alkene	H ₂ , Lindlar's Catalyst
	Dissolving Metal Reduction	Alkyne → Trans-Alkene	Na, NH ₃
	Carbonyl Reduction	Aldehyde → 1° OH Ketone → 2° OH	NaBH ₄ or LiAlH ₄
Addition			
	Hydrohalogenation	Markovnikov addition of X	HX
	Hydration	Markovnikov addition of OH	H ₂ O, H ₁ SO ₄
	Hydroboration-Oxidation	Anti-Markovnikov addition of OH	1. BH ₃ , THF 2. H ₂ O ₂ , NaOH
	Halogenation	Anti-Addition of X-X	X ₂
	Hydrogenation	Syn-Addition of H-H	H ₂ , Pd/Pt
Cyclization			
	Epoxidation	Alkene → Epoxide	mCPBA
	Halohydrin Cyclization	Halohydrin → Epoxide	X ₂ , H ₂ O to NaOH
Substitution			
	S _N 1	Forms Carbocation; Racemic	Weak nucleophile, Polar protic solvent
	S _N 2	Inversion of Configuration	Strong nucleophile, polar aprotic solvent
Elimination			
	E1	Carbocation intermediate, Zaitsev's Rule	Weak base, polar protic solvent



Known Reaction Pathways (cont)

E2	Concerted, anti-periplanar	Strong base (NaOEt, NaOMe, tBuOK)
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C-C Bond Formation

Grignard Reaction	Adds R group to carbonyl	RMgX
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Protecting Groups

Alcohol Protection	ROH → ROTMS	TMSCl, pyridine
Alcohol Deprotection	ROTMS → ROH	TBAF

Starting Material → Alkane

Name	Reagents	Regiochemistry	Stereochemistry	Functional Outcome	Mechanism
Radical Halogenation	X ₂ , hv or heat	Tertiary > Secondary > Primary Selectivity	Racemic (if chiral)	Alkyl Halide	*
Allylic Bromination	NBS, hv (or heat), CCl ₄	Selective for <i>allylic position</i> (next to a C=C bond)	Mixture if allylic radical is symmetric	Allylic Bromide	*
Benzylic Bromination	NBS, hv (or heat), CCl ₄	Selective for *benzylic	None, unless chiral center formed	Benzylic Bromide	*
Benzylic Oxidation	1. KMnO ₄ or Na ₂ Cr ₂ O ₇ 2. H ₂ SO ₄ , heat	Oxidation occurs only at the <i>benzylic carbon</i>	None	Carboxylic acid	

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	*



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Starting Material → Alkene (cont)				
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	Alcohol
Hydroboration-Oxidation	1. BH ₃ , THF 2. H ₂ O, NaOH	Anti-Markovnikov	Syn	Alcohol
Halogenation (X ₂ Addition)	X ₂ (Br ₂ , Cl ₂)	None	Anti	Vicinal Dihalide
Halohydrin Formation	X ₂ , H ₂ O	Markovnikov	Anti	Halohydrin
Hydrogenation	H ₂ , Pt/Pd/Ni	None	Syn	Alkane
Dihydroxylation (Syn)	OsO ₄ or KMnO ₄ (cold, dilute), NaHSO ₃	None	Syn	Vicinal Diol
Dihydroxylation (Anti)	1. mCPBA 2. H ₃ O ⁺	None	Anti	Vicinal Diol



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Starting Material → Alkene (cont)

Ozonolysis	1. O ₃ 2. Me ₂ S (DMS) or Zn/H ₂ O	None	None	Aldehyde/Ketone
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Starting Material → Alkyne

Name	Reagents	Regiochemistry	Stereochemistry	Functional Outcome	Mechanism
Hydrohalogenation (HX Addition)	HX (HCl, HBr, HI) (1 or 2 equivalents)	Markovnikov	None	Alkyl Dihalide	*
Halogenation (H ₂ Addition)	X ₂ (Br ₂ , Cl ₂) (1 or 2 equivalents)	None	Anti	Vicinal Tetrahalide	*
Acid-Catalyzed Hydration	HgSO ₄ ; H ₂ SO ₄ , H ₂ O	Markovnikov	None	Enol → Ketone (tautomerization)	*
Hydroboration-Oxidation	1. 9-BBN or BH ₃ , THF 2. H ₂ O ₂ , NaOH	Anti-Markovnikov	Syn	Enol → Aldehyde (tautomerization)	
Hydrogenation	H ₂ , Pt/Pd/Ni	None	Syn	Alkane	
Poisoned Hydrogenation	H ₂ , Lindlar's catalyst	None	Syn	Cis-alkan	
Dissolving Metal Reduction	Na ⁰ or Li ⁰ ; NH ₃	None	Anti	Trans-alkene	
Ozonolysis	1. O ₃ 2. H ₂ O	None	None	Carboxylic acid (CO ₂ if terminal)	

Starting Material → Alcohol

Name	Reagents	Regiochemistry	Stereochemistry	Functional Outcome	Mechanism
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Starting Material → Alcohol (cont)					
Oxidation (Primary → Aldehyde)	PCC/PDC, CH ₂ Cl ₂ or (COCl ₂), DMSO; Et ₃ N, CH ₂ Cl ₂ (-78 to 22°C)	N/A	N/A	Aldehyde	*
Oxidation (Primary → Carboxylic Acid)	1. Na ₂ Cr ₂ O ₇ 2. H ₂ SO ₄ , H ₂ O	N/A	N/A	Carboxylic acid	*
Williamson Ether Synthesis	1. NaH (or KH), 15-Crown-5 (or 18-C-6) 2. RX	N/A	N/A	Ether	*
Protecting Alcohol	TMSCl in Et ₃ N (or Pyridine)	None	Retained	Converts -OH to -OTMS	
Deprotecting Alcohols	TBAF or H ₃ O ⁺	Removes silly group from OH	Retained	Restores -OH	



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Starting Material → Alcohol (cont)

Intramolecular Williamson Ether Synthesis	1. X_2 (Br_2 or Cl_2), H_2O	1. Markovnikov	1. Anti	Converts halohydrin → Epoxide
	2. $NaOH$ (or NaH , $NaNH_2$, KOH)	2. None	2. Inversion	

Secondary → Ketone PCC/PDC, Swern, or Jones Oxidation

Starting Material → Epoxide

Name	Reagents	Regiochemistry	Stereochemistry	Functional Outcome	Mechanism
Acidic Opening	HX	More substituted carbon attack	Anti	Vicinal Diol	*
	H_2O , H_2SO_4				
	ROH (or RSH), H_2SO_4				
Basic Opening	1. $NaCN$ (or $NaSR$, $RMgBr$, $LiAlH_4$, NaN_3) 2. H_2O (or $NaOH$)	Less substituted carbon attack	Anti	Vicinal Diol	*

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)

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

Number of Unique Products	
NBS (Allylic Bromination)	Cl₂/hν (Radical Chlorination)
<i>Selective</i> Only abstracts the allylic hydrogen	<i>Less selective</i> 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

Synthesis		
1. Identify Target Molecule	Determine functional groups & backbone	<i>What is the most complex feature?</i>
2. Work Backward	Identify possible precursors	<i>What reactions introduce those functional groups?</i>
3. Select Key Transformations	Use known reaction pathways	<i>Oxidation, Reduction, Substitution, Addition, Elimination</i>
4. Consider Stereo- & Regio-Chemistry	Identify selective pathways	<i>Anti vs Syn, Markovnikov vs Anti-Markovnikov</i>
5. Check for Side Reactions	Minimize unwanted byproducts	<i>Use protecting groups if necessary</i>
6. Verify Pathway	Double check feasibility & efficiency	<i>Are reagents compatible? Do steps make sense?</i>

Starting Material → Ether		
Name	Reagents	Functional Outcome
Acidic Cleavage	xsHX (HBr or HI) in heat	Alkyl Halide

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	
¹ H NMR	¹³ C NMR
<i>Chemical Shift Trends</i>	<i>Chemical Shift Trends</i>
0-2 ppm → Alkane	0-50 ppm → Alkane
2-3 ppm → Allylic, benzylic, alkynyl	50-100 ppm → Alcohol, ether, alkynes
4-6 ppm → Alkene	100-150 ppm → Aromatic, alkene
6-8 ppm → Aromatic	150-200 ppm Carbonyl (ketone, aldehyde, carboxylic acid)
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

Terms to Know	
Markovnikov's Rule → <i>addition reactions</i> proton added to the <i>carbon</i> with the most <i>hydrogen</i> atoms attached	Geminal → 2 atoms bonded to the <i>same side</i> of the carbon



Terms to Know (cont)

Anti-Markovnikov's Rule → <i>addition reactions</i> proton added to the <i>carbon</i> with the least hydrogen atoms attached	Vicinal → 2 atoms bonded to <i>same</i> carbon
Zaitsev's Rule → <i>elimination reaction</i> , major product is the more stable alkene with the highly substituted double bond	Syn-Addition → added to <i>same side</i> of compound
E/Z System → Prioritize the 2 groups attached to each carbon relative to one another. <i>Higher</i> priority groups are: cis/same side → Z trans/opposite sides → E	Anti-Addition → added to <i>different sides</i> of compounds

Formation of Grignard Reagent

Mg(0); THF (or Et₂O)

Forms Gignard Reagent (**RMgX**)
Can be used to form C-C bonds

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 <i>only</i> on substrate rate=k[R-X]	Rate → Dependent on <i>both</i> substrate & nucleophile rate=k[R-X][Nu-]
Stereochemistry → Racemic mixture	Stereochemistry → Inversion of configuration
Preferred Conditions → Weak nucleophile, polar protic solvent	Preferred Conditions → Strong nucleophile, polar aprotic solvent
Tertiary > Secondary > ~~Primary~~	Methyl > Primary > Secondary > ~~Tertiary~~

Elimination Reactions

E1 (Unimolecular)	E2 (Bimolecular)
Mechanism → Two-step; carbocation intermediate, base deprotonates	Mechanism → One-step; concerted β-H abstraction
Rate → Dependent <i>only</i> on substrate	Rate → Dependent on <i>both</i> substrate and base
Regiochemistry → Zaitsev's Rule (more substituted alkene favored)	Regiochemistry → Zaitsev's Rule (unless bulky base → Hofmann product)
Stereochemistry → Forms most stable alkene	Stereochemistry → Anti-periplanar elimination

Elimination Reactions (cont)

Preferred Conditions → Weak base, polar protic solvent	Preferred Conditions → Strong base required
Tertiary > Secondary > ~~Primary~~	Primary > Secondary > Tertiary (as long as β-H is anti-periplanar)

Nomenclature

Functional Group	Suffix (Highest Priority)	Prefix (Lowest Priority)
Alcohol (-OH)	-ol	hydroxy-
Alkyne	-yne	alkynyl-
Ether (R-O-R')	uses parent name	alkoxy-
Epoxide	oxirane (cyclic naming)	epoxy-
Key Naming Rules →		
Number the longest chain to give OH the lowest number		
Number to give triple bond the lowest number, unless -OH is present		

C

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