Cheatography

Organic Chemistry Exam 1 Cheat Sheet

by teganski via cheatography.com/211266/cs/45736/

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_2SO_4 (strong), $KMnO_4$
	Ozonolysis	Cleaves Alkenes → Aldehydes/Ketones	2. O_3 2. $(CH_3)_2S$ or Zn/H_2O
	Benzylic Oxidation	Benzylic carbon → Carboxylic acid	$KMnO_4$, heat
Reduction			
	Catalytic Hydrogenation	Alkene/Alkyne → Alkane	H_2, Pt/Pd/Ni
	Poisioned 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_2O, H_1SO_4
	Hydroboration-Oxidation	Anti-Markovnikov addition of OH	1. BH_3, THF 2. H_2O_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
	Halohdrin Cyclization	Halohydrin → Epoxide	X_2, H_2O to NaOH
Substitution			
	S_N1	Forms Carbocation; Racemic	Weak nucleophile, Polar protic solvent
	S_N2	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)
C-C Bond Formation		
Grignard Reaction	Adds R group to carbonyl	RMgX
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 *allylic position* (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 $Na_2Cr_2O_7$ 2. H_2SO_4, heat	Oxidation occurs **only** at the *benzylic carbon*	None	Carboxylic acid	

Starting Material → Alkene

Name	Reagents	Regiochemistry	Stereochemistry	Functional Outcome	Mechanism
Hydrohalogenation (HX Addition)	HX $^{\text{(HCl, HBr, HI)}}$	Markovnikov (X attaches to more substituted carbon)	Racemic	Alkyl Halide	*

Starting Material → Alkene (cont)

Hydrodrohalogenation (HX Addition with Peroxide)	HBr, ROOR $^{\text{(peroxide)}}$	Anti-Markovnikov (X attaches to less substituted carbon)	Racemic	Aklyl Halide	*
Acid-Catalyzed Hydration	H_2SO_4, H_2O (or H_3O^+)	Markovnikov	Racemic	Alcohol	
Oxymercuration-Demurcuration	1. $Hg(OAc)_2$, H_2O 2. $NaBH_4$	Markovnikov	Anti	Alcohol	
Hydroboration-Oxidation	1. BH_3, THF 2. H_2O, NaOH	Anti-Markovnikov	Syn	Alcohol	
Halogenation (X_2 Addition)	X_2 $^{(Br_2,\ Cl_2)}$	None	Anti	Vicinal Dihalide	
Halohydrin Formation	X_2, H_2O	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_3O^+	None	Anti	Vicinal Diol	

Starting Material → Alkene (cont)

Ozonlysis	1. O_3 2. Me_2S (DMS) or Zn/H_2O	None	None	Aldehyde/Ketone	

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_2SO_4, H_2O	Markovnikov	None	Enol → Ketone (tautomerization)	*
Hydroboration-Oxidation	1. 9-BBN or BH_3, THF 2. H_2O_2, NaOH	Anti-Markovnikov	Syn	Enol → Aldehyde (tautomerization)	
Hydrogenation	H_2, Pt/Pd/Ni	None	Syn	Alkane	
Poisioned 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_2O	None	None	Carboxylic acid (CO_2 if terminal)	

Starting Material → Alcohol

Name	Reagents	Regiochemistry	Stereochemistry	Functional Outcome	Mechanism

Starting Material → Alcohol (cont)

Oxidation **(Primary → Aldehyde)**	PCC/PDC, CH_2Cl_2 or $(COCl_2)$, DMSO; Et_3N, CH_2Cl_2 (-78 to 22°C)	N/A	N/A	Aldehyde	*
Oxidation **(Primary → Carboxylic Acid)**	1. $Na_2Cr_2O_7$ 2. H_2SO_4, H_2O	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_3N (or Pyridine)	None	Retained	Converts **-OH** to **-OTMS**	
Deprotecting Alcohols	TBAF or H_3O^+	Removes silly group from OH	Retained	Restores **-OH**	

Starting Material → Alcohol (cont)

Intramolecular Williamson Ether Synthesis	1. $X_2^{(Br_2 \text{ or } Cl_2)}$, H_2O 2. NaOH $^{(\text{or } NaH,\ NaNH_2,\ KOH)}$	1. Markovnivkov 2. None	1. Anti 2. Inversion	Converts halohydrin → Epoxide

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

Starting Material → Epoxide

Name	Reagents	Regiochemistry	Stereochemistry	Functional Outcome	Mechanism
Acidic Opening	HX H_2O, H_2SO_4 ROH (or RSH), H_2SO_4	More substituted carbon attack	Anti	Vicinal Diol	*
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 stablized)

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)	**Cl$_2$/hv** (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

Synthesis

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

Starting Material → Ether

Name	Reagents	Functional Outcome
Acidic Cleavage	xsHX $^{(\text{HBr or HI})}$ 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 *Chemical Shift Trends*	**^{13}C NMR** *Chemical Shift Trends*
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 → *addition reactions* proton added to the *carbon* with the **most** *hydrogen* atoms attached	**Geminal** → 2 atoms bonded to the *same side* of the carbon

Terms to Know (cont)

Anti-Markovnivkov'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
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

Formation of Grignard Reagent

Mg(0); THF (or Et_2O)

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