

SUMMARY OF REACTIONS BY TYPE

CHAPTERS 1-13

I. SUBSTITUTION REACTIONS

Type	Stereochemical Result	Favoring Conditions
S_N2 Chapter 6 See Section 6.14 for a summary of nucleophiles mentioned in early chapters	inversion	1° , 2° , benzylic (1° or 2°), or allylic (1° or 2°) leaving group (e.g., halide, tosylate, mesylate); strong nucleophile; polar aprotic solvent
S_N1 Chapter 6	racemization (via carbocation)	3° , benzylic, or allylic leaving group
Radical substitution Chapter 10 Section 13.2	racemization (via radical)	3° , benzylic, or allylic hydrogen; peroxide, heat/light

II. ELIMINATION REACTIONS

Type	Stereochemical/Regiochemical Result	Favoring Conditions
E2 (dehydrohalogenation) Section 7.6	elimination to form the most substituted alkene (Zaitsev elimination) with small bases formation of the less substituted alkene with use of a bulky base (e.g., <i>tert</i> -BuOK/ <i>tert</i> -BuOH)	strong base (e.g., NaOEt/EtOH, KOH/EtOH, <i>tert</i> -BuOK/ <i>tert</i> -BuOH); 2° or 3° leaving group (e.g., halide, tosylate, mesylate, etc.); heat
E1 (dehydrohalogenation) Sections 6.17 and 7.8	formation of most substituted alkene; may occur with carbocation rearrangement	3° leaving group; weak base; heat
Dehydration Section 7.7	formation of most substituted alkene; may occur with carbocation rearrangement	catalytic acid (H^+ , e.g., concd H_2SO_4 , H_3PO_4); heat

III. MECHANISTIC SUMMARY OF ALKENE AND ALKYNE ADDITION REACTIONS

Reactant	Stereochemical Result		Regiochemical Result	
Alkenes	syn $H_2/Pt, Pd$ or Ni (Sections 4.17A, 7.13, 7.14)	anti $*X_2/CCl_4$ (Section 8.12)	Markovnikov $*H_2O, H^+$ (hydration) (Section 8.5)	anti-Markovnikov (i) $BH_3:THF$ (ii) OH^-, H_2O_2 (Section 8.7)
	(i) OsO_4 , (ii) $NaHSO_3$ (Section 8.16)	$*X_2, H_2O$ (Section 8.14)	$* (i) Hg(OAc)_2, H_2O, THF$ $(ii) NaBH_4, OH^-$ (Section 8.6)	
	RCO_3H (e.g., MMPP) (Section 11.13)	(i) RCO_3H , (ii) H_3O^+ or OH^- (Section 11.14)	$*HX$ (no peroxides) (Section 8.2)	HBr (w/peroxides) (Section 10.9)
	$* (i) BH_3:THF$ $(ii) H_2O_2, OH^-$ (Sections 8.7 and 8.8)	$*X_2/ROH$ (Section 8.14)	$* addition of other alkenes$	
		$*X_2$, Nucleophile (e.g., RO^- , $RMgX$) (Section 8.14)		
	$:C$ \ Addition of carbenes (Section 8.15)			

*Shares mechanistic themes with other reactions denoted by the same symbol.

Alkynes	H_2, Pd on $BaCO_3$ w/quinoline (Lindlar's cat.) (Section 7.15A)	(i) $Li, EtNH_2, -78^\circ C$ (ii) $NH_4^+ Cl^-$ (Section 7.15B)	HX (one or two molar equivalents) (Section 8.19)
	H_2, Ni_2B (P-2) (Section 7.15A)	X_2 (2 equiv.)/ CCl_4 (Section 8.18)	
	H_2 (2 equiv.), Pt or Ni (complete hydrogenation) (Sections 4.17A, 7.14)		

IV. ALKENE AND ALKYNE CLEAVAGE WITH OXIDATION

Conditions	Reactant	Product(s)
Alkenes		
(i) $\text{KMnO}_4/\text{OH}^-$, heat; (ii) H_3O^+ (Section 8.17A)	tetrasubstituted alkene	→ two ketones
	trisubstituted alkene	→ one ketone, one carboxylic acid
	monosubstituted alkene	→ one carboxylic acid and CO_2
(i) O_3 , (ii) Zn, HOAc (Section 8.17B)	tetrasubstituted alkene	→ two ketones
	trisubstituted alkene	→ one ketone, one aldehyde
	monosubstituted alkene	→ one aldehyde and formaldehyde
Alkynes		
(i) $\text{KMnO}_4/\text{OH}^-$, heat; (ii) H_3O^+ (Section 8.20)	terminal alkyne	→ a carboxylic acid and formic acid
	internal alkyne	→ two carboxylic acids
(i) O_3 , (ii) HOAc (Section 8.20)	terminal alkyne	→ a carboxylic acid and formic acid
	internal alkyne	→ two carboxylic acids

V. CARBON—CARBON BOND-FORMING REACTIONS

- Alkylation of alkynide anions (with 1° alkyl halides, epoxides, and aldehydes or ketones) (Sections 7.12, 8.21 and 12.8D)
- Grignard reaction (with aldehydes and ketones, or epoxides) (Sections 12.7B, C, and 12.8)
- Carbocation addition to alkenes (e.g., polymerization) (Special Topic A)
- Diels-Alder reaction (Section 13.11)
- Addition of a carbene to an alkene (Section 8.15)

VI. REDUCTIONS/OXIDATIONS (NOT INCLUDING ALKENES/ALKYNES)

- $2 \text{R-X} \xrightarrow{\text{w/Zn/H}_3\text{O}^+} 2 \text{R-H} + \text{ZnX}_2$ (Section 5.15)
- $\text{R-X} \xrightarrow[\text{ether}]{\text{Mg}} \text{R-MgX} \xrightarrow{\text{H}_3\text{O}^+} \text{R-H}$ (Section 12.8B)
- Lithium aluminum hydride (LiAlH_4) and sodium borohydride (NaBH_4) reduction of carbonyl compounds (Section 12.3)
- Oxidation of alcohols with chromic acid, pyridinium chlorochromate (PCC), or hot potassium permanganate (Section 12.4)

VII. MISCELLANEOUS

- (a) $R-CO-R' + PCl_5 \rightarrow R-CCl_2-R' \rightarrow$ alkynes (Section 7.9)
- (b) $R-COOH + SOCl_2$ or $PCl_5 \rightarrow R-COCl \rightarrow$ acyl chlorides for Friedel-Crafts reactions, esters, amides, etc. (Sections 15.7 and 18.5)
- (c) Terminal alkynes + $NaNH_2$ in liq. $NH_3 \rightarrow$ alkynide anions (Sections 8.21, 12.8D)
- (d) $ROH + TsCl$, $MsCl$, or $TfCl$ (with pyridine) $\rightarrow R-OTs$, $R-OMs$, or $R-OTf$ (Section 11.10)
- (e) $R-OH + Na$ (or NaH) $\rightarrow R-O^-Na^+ + H_2$ (Section 6.15B, 11.11B)

VIII. CHEMICAL TESTS

- (a) Alkenes/Alkynes: Br_2/CCl_4 (Section 8.12)
- (b) Rings/Unsaturation/etc.: Index of Hydrogen Deficiency (Section 4.18)
- (c) Position of Unsaturation: $KMnO_4$ (Section 8.17A); O_3 (Section 8.17B)