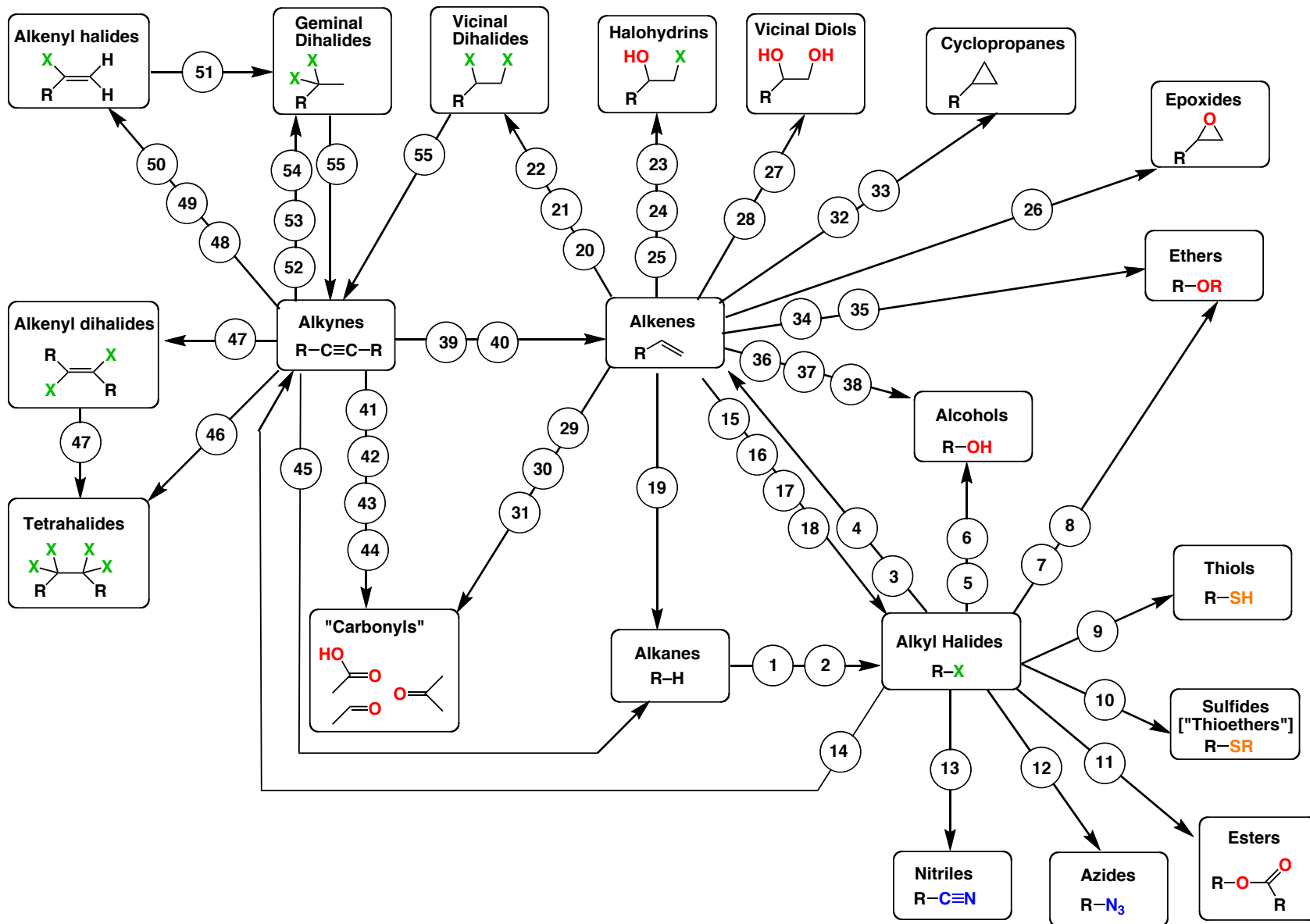


Reaction Map: Reactions of Alkanes, Alkyl Halides, Alkenes, and Alkynes



Reaction	Name	Typical Conditions	Notes [1°, 2° and 3° refers to primary, secondary, tertiary]
1	Free radical chlorination	Cl ₂ , hν	Not highly selective
2	Free radical bromination	Br ₂ , hν	Highly selective for tertiary C-H
3	Elimination [E2]	RO [⊖] /ROH	Best for 2° and 3°, <i>anti</i> stereochemistry
4	Elimination [E1]	polar solvent, heat	Competes with S _N 1
5	Alcohol Formation [S _N 2]	OH [⊖] / H ₂ O	Best for 1° alkyl halides; 2° can compete w/ E2
6	Alcohol Formation [S _N 1] "Solvolytic"	H ₂ O	Best for 3° alkyl halides; rearr possible w/ 2°
7	Ether Formation [S _N 2] ["Williamson Ether Synthesis"]	RO [⊖] /ROH	Best for 1° alkyl halides; 2° can compete w/ E2
8	Ether Formation [S _N 1] "Solvolytic"	ROH	Best for 3° alkyl halides; rearr possible w/ 2°
9	Thiol formation [S _N 2]	SH [⊖]	S _N 2; best for 1° alkyl halides, 2° OK
10	Sulfide formation [S _N 2]	SR [⊖]	S _N 2; best for 1° alkyl halides, 2° OK
11	Ester formation [S _N 2]	RCO ₂ [⊖]	S _N 2; best for 1° alkyl halides, 2° OK
12	Azide formation [S _N 2]	N ₃ [⊖]	S _N 2; best for 1° alkyl halides, 2° OK
13	Nitrile formation [S _N 2]	CN [⊖]	S _N 2; best for 1° alkyl halides, 2° OK
14	Alkyne formation [S _N 2]	R-C≡C [⊖]	Best for 1° alkyl halides; 2° can compete w/ E2
15	Addition of H-Cl To Alkenes	H-Cl	Markovnikov-selective; rearr. possible
16	Addition of H-Br To Alkenes	H-Br	Markovnikov-selective; rearr. possible
17	Addition of H-I To Alkenes	H-I	Markovnikov-selective; rearr. possible
18	Radical addition of H-Br to alkenes	HBr, hν	anti-Markovnikov-selective; radical process
19	Hydrogenation of alkenes	Pd/C, H ₂	<i>syn</i> -selective
20	Alkene chlorination	Cl ₂ , CCl ₄	<i>anti</i> -selective
21	Alkene bromination	Br ₂ , CCl ₄	<i>anti</i> -selective
22	Alkene iodination	I ₂ , CCl ₄	<i>anti</i> -selective
23	Chlorohydrin formation	Cl ₂ , H ₂ O or NCS	<i>anti</i> -selective; Markovnikov selective, water is solvent. Alcohol solvent gives ether
24	Bromohydrin formation	Br ₂ , H ₂ O or NBS	<i>anti</i> -selective; Markovnikov selective, water is solvent. Alcohol solvent gives ether
25	Iodohydrin formation	Cl ₂ , H ₂ O or NIS	<i>anti</i> -selective; Markovnikov selective, water is solvent. Alcohol solvent gives ether
26	Epoxidation of alkenes	RCO ₃ H (e.g. <i>m</i> -CPBA)	<i>anti</i> -selective; Markovnikov selective, water is solvent. Alcohol solvent gives ether
27	Dihydroxylation of alkenes with OsO ₄	OsO ₄ , KHSO ₃ (e.g. <i>m</i> -CPBA)	<i>syn</i> -selective. KHSO ₃ helps remove Os
28	Dihydroxylation of alkenes (cold KMnO ₄)	KMnO ₄ , NaOH (cold, dilute)	<i>syn</i> -selective. Important to keep cold, otherwise oxidative cleavage occurs (see 31)

Reaction	Name	Typical Conditions	Notes [1°, 2° and 3° refers to primary, secondary, tertiary]
29	Ozonolysis (reductive workup)	O ₃ , then Zn/H ⁺ or (CH ₃) ₂ S	cleaves C=C to give two carbonyls. Alkenyl C-H bonds remain
30	Ozonolysis (oxidative workup)	O ₃ , then H ₂ O ₂	cleaves C=C to give two carbonyls. Alkenyl C-H bonds oxidized to C-OH
31	Oxidative cleavage with KMnO ₄	KMnO ₄ , acid, heat	cleaves C=C to give two carbonyls. Alkenyl C-H bonds oxidized to C-OH
32	Cyclopropanation (Simmons-Smith)	Cu/Zn, CH ₂ I ₂	<i>syn</i> -selective
33	Dichlorocyclopropanation	CHCl ₃ , KOH	<i>syn</i> -selective
34	Acid-catalyzed ether formation	H ₂ SO ₄ , ROH	Markovnikov selective, rearr. possible
35	Oxymercuration	Hg(OAc) ₂ , ROH, then NaBH ₄	Markovnikov selective, alcohol is solvent
36	Oxymercuration	Hg(OAc) ₂ , H ₂ O, then NaBH ₄	Markovnikov selective, water is solvent
37	Hydroboration	BH ₃ , then NaOH, H ₂ O ₂	anti-Markovnikov selective, <i>syn</i> -selective
38	Acid-catalyzed hydration	H ₂ SO ₄ , H ₂ O ("H ₃ O ⁺ ")	Markovnikov selective; rearr possible
39	Partial hydrogenation (Lindlar)	Lindlar, H ₂	<i>syn</i> -selective
40	Partial hydrogenation (sodium reduction)	Na/NH ₃	anti-selective
41	Alkyne hydroboration	BH ₃ , then NaOH, H ₂ O ₂	anti-Markovnikov selective; tautomerization
42	Alkyne Oxymercuration	HgSO ₄ , H ₂ O, H ₂ SO ₄	Markovnikov selective; tautomerization
43	Alkyne Ozonolysis	O ₃	Carboxylic acids formed; terminal alkynes give CO ₂
44	Alkyne Ox. Cleavage [KMnO ₄]	KMnO ₄ , H ⁺	same as ozonolysis
45	Hydrogenation	Pd/C, H ₂	Adds twice to alkynes
46	Alkyne double halogenation	Cl ₂ , Br ₂ , or I ₂ (2 equiv)	Each individual reaction is <i>anti</i> -selective
47	Halogenation	Cl ₂ , Br ₂ , or I ₂ (1 equiv)	<i>anti</i> -selective
48	Addition of H-Cl to Alkynes	H-Cl	Markovnikov selective
49	Addition of H-Br to Alkynes	H-Br	Markovnikov selective
50	Addition of H-I to Alkynes	H-I	Markovnikov selective
51	Addition of H-X to haloalkenes	H-Cl, H-Br, or H-I	Markovnikov selective
52	Double addition of H-Cl to Alkynes	H-Cl [2 equiv]	Adds twice to alkyne; Markovnikov selective
53	Double addition of H-Br to Alkynes	H-Br [2 equiv]	Adds twice to alkyne; Markovnikov selective
54	Double addition of H-I to Alkynes	H-I [2 equiv]	Adds twice to alkyne; Markovnikov selective
55	Elimination of dihalides to give alkynes	NaNH ₂ [2 equiv]	vicinal or geminal dihalides; for terminal alkynes, 3 equiv NaNH ₂ required