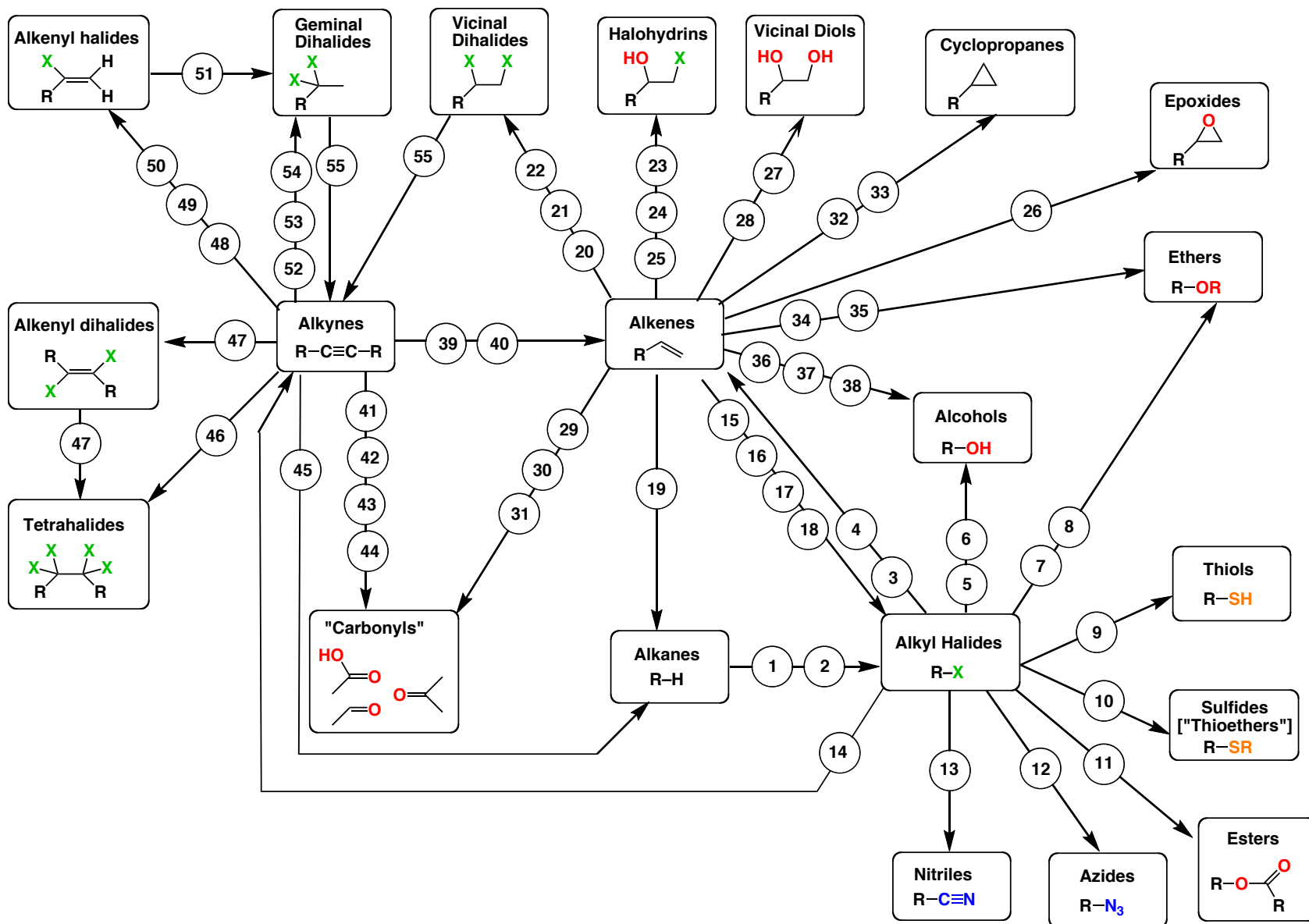


Reaction Map: Reactions of Alkanes, Alkyl Halides, Alkenes, and Alkynes



Reaction	Name	Typical Conditions	Notes [1°, 2° and 3° refers to primary, secondary, tertiary]	
1	Free radical chlorination	Cl <sub>2</sub> , hν	Not highly selective	
2	Free radical bromination	Br <sub>2</sub> , hν	Highly selective for tertiary C-H	
3	Elimination [E2]	RO <sup>⊖</sup> /ROH	Best for 2° and 3°, <i>anti</i> stereochemistry	
4	Elimination [E1]	polar solvent, heat	Competes with S <sub>N</sub> 1	
5	Alcohol Formation [S <sub>N</sub> 2]	OH <sup>⊖</sup> / H <sub>2</sub> O	Best for 1° alkyl halides; 2° can compete w/ E2	
6	Alcohol Formation [S <sub>N</sub> 1] "Solvolysis"	H <sub>2</sub> O	Best for 3° alkyl halides; rearr possible w/ 2°	
7	Ether Formation [S <sub>N</sub> 2] ["Williamson Ether Synthesis"]	RO <sup>⊖</sup> /ROH	Best for 1° alkyl halides; 2° can compete w/ E2	
8	Ether Formation [S <sub>N</sub> 1] "Solvolysis"	ROH	Best for 3° alkyl halides; rearr possible w/ 2°	
9	Thiol formation [S <sub>N</sub> 2]	SH <sup>⊖</sup>	in polar aprotic solvent	S <sub>N</sub> 2; best for 1° alkyl halides, 2° OK
10	Sulfide formation [S <sub>N</sub> 2]	SR <sup>⊖</sup>		S <sub>N</sub> 2; best for 1° alkyl halides, 2° OK
11	Ester formation [S <sub>N</sub> 2]	RCO <sub>2</sub> <sup>⊖</sup>		S <sub>N</sub> 2; best for 1° alkyl halides, 2° OK
12	Azide formation [S <sub>N</sub> 2]	N <sub>3</sub> <sup>⊖</sup>		S <sub>N</sub> 2; best for 1° alkyl halides, 2° OK
13	Nitrile formation [S <sub>N</sub> 2]	CN <sup>⊖</sup>		S <sub>N</sub> 2; best for 1° alkyl halides, 2° OK
14	Alkyne formation [S <sub>N</sub> 2]	R-C≡C <sup>⊖</sup>	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 <sub>2</sub>	<i>syn</i> -selective	
20	Alkene chlorination	Cl <sub>2</sub> , CCl <sub>4</sub>	<i>anti</i> -selective	
21	Alkene bromination	Br <sub>2</sub> , CCl <sub>4</sub>	<i>anti</i> -selective	
22	Alkene iodination	I <sub>2</sub> , CCl <sub>4</sub>	<i>anti</i> -selective	
23	Chlorohydrin formation	Cl <sub>2</sub> , H <sub>2</sub> O or NCS	<i>anti</i> -selective; Markovnikov selective, water is solvent. Alcohol solvent gives ether	
24	Bromohydrin formation	Br <sub>2</sub> , H <sub>2</sub> O or NBS	<i>anti</i> -selective; Markovnikov selective, water is solvent. Alcohol solvent gives ether	
25	Iodohydrin formation	Cl <sub>2</sub> , H <sub>2</sub> O or NIS	<i>anti</i> -selective; Markovnikov selective, water is solvent. Alcohol solvent gives ether	
26	Epoxidation of alkenes	RCO <sub>3</sub> 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 <sub>4</sub>	OsO <sub>4</sub> , KHSO <sub>3</sub> (e.g. <i>m</i> -CPBA)	<i>syn</i> -selective. KHSO <sub>3</sub> helps remove Os	
28	Dihydroxylation of alkenes (cold KMnO <sub>4</sub> )	KMnO <sub>4</sub> , 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 <sub>3</sub> , then Zn/H <sup>+</sup> or (CH <sub>3</sub> ) <sub>2</sub> S	cleaves C=C to give two carbonyls. Alkenyl C-H bonds remain
30	Ozonolysis (oxidative workup)	O <sub>3</sub> , then H <sub>2</sub> O <sub>2</sub>	cleaves C=C to give two carbonyls. Alkenyl C-H bonds oxidized to C-OH
31	Oxidative cleavage with KMnO <sub>4</sub>	KMnO <sub>4</sub> , acid, heat	cleaves C=C to give two carbonyls. Alkenyl C-H bonds oxidized to C-OH
32	Cyclopropanation (Simmons-Smith)	Cu/Zn, CH <sub>2</sub> I <sub>2</sub>	<i>syn</i> -selective
33	Dichlorocyclopropanation	CHCl <sub>3</sub> , KOH	<i>syn</i> -selective
34	Acid-catalyzed ether formation	H <sub>2</sub> SO <sub>4</sub> , ROH	Markovnikov selective, rearr. possible
35	Oxymercuration	Hg(OAc) <sub>2</sub> , ROH, then NaBH <sub>4</sub>	Markovnikov selective, alcohol is solvent
36	Oxymercuration	Hg(OAc) <sub>2</sub> , H <sub>2</sub> O, then NaBH <sub>4</sub>	Markovnikov selective, water is solvent
37	Hydroboration	BH <sub>3</sub> , then NaOH, H <sub>2</sub> O <sub>2</sub>	anti-Markovnikov selective, <i>syn</i> -selective
38	Acid-catalyzed hydration	H <sub>2</sub> SO <sub>4</sub> , H <sub>2</sub> O ("H <sub>3</sub> O <sup>+</sup> ")	Markovnikov selective; rearr possible
39	Partial hydrogenation (Lindlar)	Lindlar, H <sub>2</sub>	<i>syn</i> -selective
40	Partial hydrogenation (sodium reduction)	Na/NH <sub>3</sub>	anti-selective
41	Alkyne hydroboration	BH <sub>3</sub> , then NaOH, H <sub>2</sub> O <sub>2</sub>	anti-Markovnikov selective; tautomerization
42	Alkyne Oxymercuration	HgSO <sub>4</sub> , H <sub>2</sub> O, H <sub>2</sub> SO <sub>4</sub>	Markovnikov selective; tautomerization
43	Alkyne Ozonolysis	O <sub>3</sub>	Carboxylic acids formed; terminal alkynes give CO <sub>2</sub>
44	Alkyne Ox. Cleavage [KMnO <sub>4</sub> ]	KMnO <sub>4</sub> , H <sup>+</sup>	same as ozonolysis
45	Hydrogenation	Pd/C, H <sub>2</sub>	Adds twice to alkynes
46	Alkyne double halogenation	Cl <sub>2</sub> , Br <sub>2</sub> , or I <sub>2</sub> (2 equiv)	Each individual reaction is <i>anti</i> -selective
47	Halogenation	Cl <sub>2</sub> , Br <sub>2</sub> , or I <sub>2</sub> (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 <sub>2</sub> [2 equiv]	vicinal or geminal dihalides; for terminal alkynes, 3 equiv NaNH <sub>2</sub> required