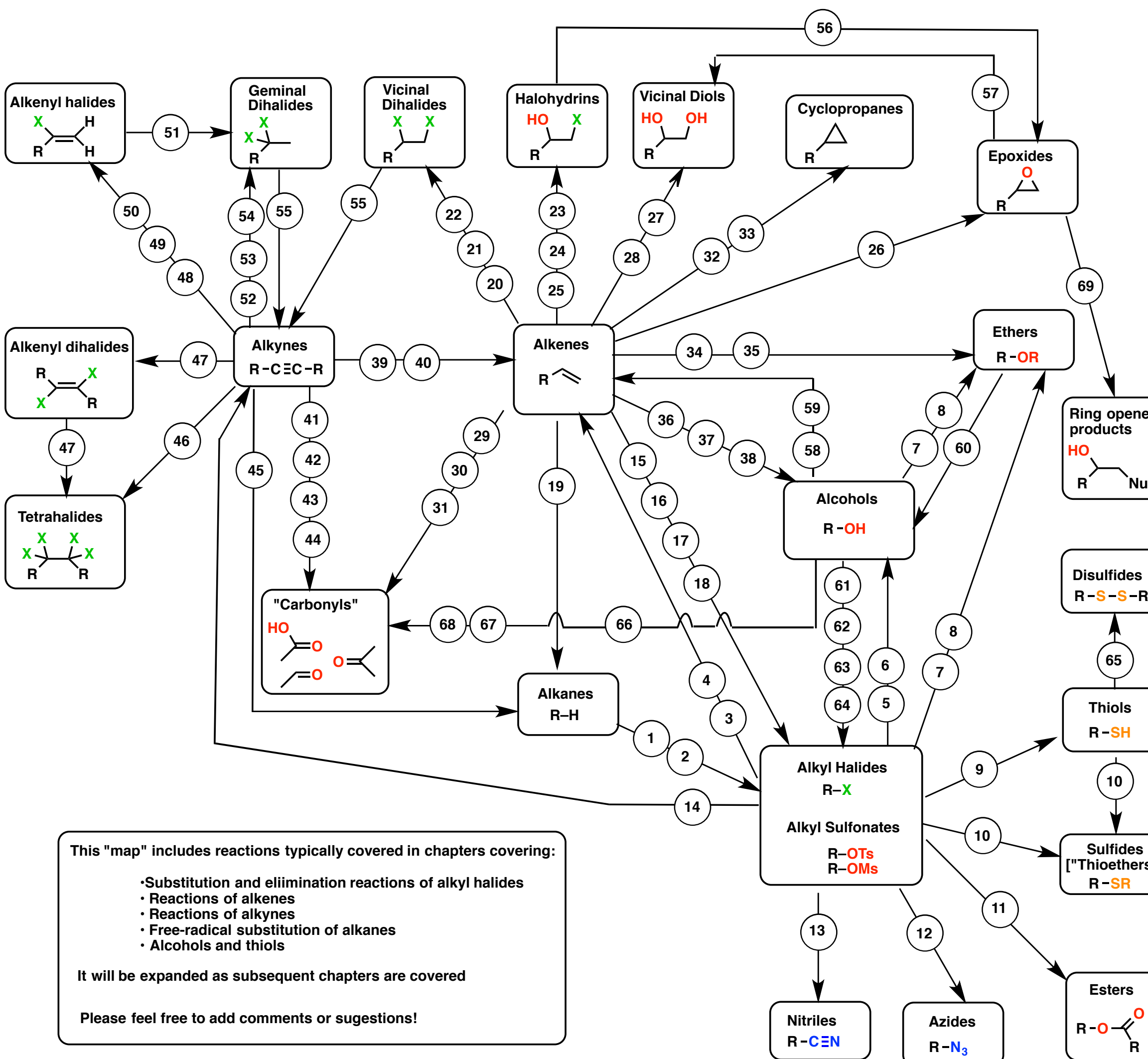


Reaction Map: Reactions of Alkanes, Alkyl Halides, Alkenes, Alkynes and Alcohols



This "map" includes reactions typically covered in chapters covering:

- Substitution and elimination reactions of alkyl halides
- Reactions of alkenes
- Reactions of alkynes
- Free-radical substitution of alkanes
- Alcohols and thiols

It will be expanded as subsequent chapters are covered

Please feel free to add comments or suggestions!

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] "Solvolysis"	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] "Solvolysis"	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	<i>anti</i> -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	<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)
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 $\text{C}=\text{C}$ to give two carbonyls. Alkenyl $\text{C}-\text{H}$ bonds oxidized to $\text{C}-\text{OH}$	56	Formation of epoxides from halohydrins	NaH (strong base)	Internal $\text{S}_{\text{N}}2$ reaction: inversion of configuration at carbon
32	Cyclopropanation (Simmons-Smith)	Cu/Zn , CH_2I_2	<i>syn</i> -selective	57	Opening of epoxides with aqueous acid	H_3O^+ (or $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$)	Protonation of epoxide, then attack of H_2O at most substituted carbon
33	Dichlorocyclopropanation	CHCl_3 , KOH	<i>syn</i> -selective	58	Elimination of alcohols to form alkenes (acidic)	H_2SO_4 , heat	Follows Zaitsev's rule (most sub. alkene formed). Rearrangements can occur
34	Acid-catalyzed ether formation	H_2SO_4 , ROH	Markovnikov selective, rearr. possible	59	POCl_3 elimination of alcohols to alkenes	POCl_3 , pyridine	E2 reaction
35	Oxymercuration	$\text{Hg}(\text{OAc})_2$, ROH , then NaBH_4	Markovnikov selective, alcohol is solvent	60	Acidic cleavage of ethers	HI , heat	Can proceed through $\text{S}_{\text{N}}2$ or $\text{S}_{\text{N}}1$ depending on type of alcohol
36	Oxymercuration	$\text{Hg}(\text{OAc})_2$, H_2O , then NaBH_4	Markovnikov selective, water is solvent	61	Conversion of alcohols to alkyl halides with PBr_3	PBr_3	$\text{S}_{\text{N}}2$ reaction. PCl_3 can also be used to make alkyl chlorides
37	Hydroboration	BH_3 , then NaOH , H_2O_2	anti-Markovnikov selective, <i>syn</i> -selective	62	SOCl_2 conversion of alcohols to alkyl chlorides	SOCl_2	Usually taught as $\text{S}_{\text{N}}2$. Pyridine can be used as base.
38	Acid-catalyzed hydration	H_2SO_4 , H_2O (" H_3O^+ ")	Markovnikov selective; rearr possible	63	Alcohols to alkyl halides with HX	HCl , HBr , HI	Can go through $\text{S}_{\text{N}}1$ or $\text{S}_{\text{N}}2$ depending on type of alcohol
39	Partial hydrogenation (Lindlar)	Lindlar, H_2	<i>syn</i> -selective	64	Tosylate and mesylate formation	TsCl or MsCl	Does not affect stereochemistry. Can use a base such as pyridine.
40	Partial hydrogenation (sodium reduction)	Na/NH_3	anti-selective	65	Disulfide formation	I_2 (oxidant)	Can use other oxidants but I_2 is most common
41	Alkyne hydroboration	BH_3 , then NaOH , H_2O_2	anti-Markovnikov selective; tautomerization	66	Alcohol oxidation with PCC	PCC	1° alcohols to aldehydes; 2° alcohols to ketones
42	Alkyne Oxymercuration	HgSO_4 , H_2O , H_2SO_4	Markovnikov selective; tautomerization	67	Alcohol oxidation with H_2CrO_4	$\text{K}_2\text{Cr}_2\text{O}_7$ + acid	1° alcohols to carboxylic acids, 2° alcohols to ketones.
43	Alkyne Ozonolysis	O_3	Carboxylic acids formed; terminal alkynes give CO_2	68	Dess Martin oxidation	Dess Martin Periodinane	1° alcohols to aldehydes; 2° alcohols to ketones
44	Alkyne Ox. Cleavage [KMnO_4]	KMnO_4 , H^+	same as ozonolysis	69	Basic ring opening of epoxides	Grignards, $-\text{OH}$, LiAlH_4	Add to least substituted position of epoxides
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 $\text{H}-\text{Cl}$ to Alkynes	$\text{H}-\text{Cl}$	Markovnikov selective				
49	Addition of $\text{H}-\text{Br}$ to Alkynes	$\text{H}-\text{Br}$	Markovnikov selective				
50	Addition of $\text{H}-\text{I}$ to Alkynes	$\text{H}-\text{I}$	Markovnikov selective				
51	Addition of $\text{H}-\text{X}$ to haloalkenes	$\text{H}-\text{Cl}$, $\text{H}-\text{Br}$, or $\text{H}-\text{I}$	Markovnikov selective				
52	Double addition of $\text{H}-\text{Cl}$ to Alkynes	$\text{H}-\text{Cl}$ [2 equiv]	Adds twice to alkyne; Markovnikov selective				
53	Double addition of $\text{H}-\text{Br}$ to Alkynes	$\text{H}-\text{Br}$ [2 equiv]	Adds twice to alkyne; Markovnikov selective				
54	Double addition of $\text{H}-\text{I}$ to Alkynes	$\text{H}-\text{I}$ [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				