

## Alkene Reaction Comparisons

### Addition of Water

Reaction Name	Reagents	Markovnikov	Carbocation	Notes
Acid Catalyzed Hydration	H <sub>2</sub> SO <sub>4</sub> , H <sub>2</sub> O	Yes	Yes	<ul style="list-style-type: none"> <li>Rearrangements possible</li> <li>Adds an OH</li> </ul>
Oxymercuration	1) Hg(OAc) <sub>2</sub> , H <sub>2</sub> O, THF 2) NaBH <sub>4</sub>	Yes	No	<ul style="list-style-type: none"> <li>Racemic (enantiomers)</li> <li>No possible rearrangements</li> <li>Adds an OH</li> </ul>
Hydroboration	1) BH <sub>3</sub> , THF 2) NaOH, H <sub>2</sub> O <sub>2</sub> , H <sub>2</sub> O	Anti	No	<ul style="list-style-type: none"> <li>No possible rearrangements</li> <li>Adds an OH</li> </ul>
Hydroxylation	1) OsO <sub>4</sub> , pyr, 2) NaHSO <sub>3</sub> , H <sub>2</sub> O	--	No	<ul style="list-style-type: none"> <li>Syn</li> <li>Adds 2 OHs</li> <li>NMO (catalyst)</li> </ul>

### Halide (X) Additions

Reaction Name	Reagents	Markovnikov	Carbocation	Notes
H-X Additions	H-X	Yes	Yes	<ul style="list-style-type: none"> <li>Rearrangements possible</li> </ul>
Halogenation	X <sub>2</sub> , DCM	--	No	<ul style="list-style-type: none"> <li>Adds 2 X</li> <li>Racemic, anti</li> </ul>
Radical H-X Additions	H-X, ROOR	Anti	--	<ul style="list-style-type: none"> <li>Radical mechanism</li> </ul>
Halohydrin	X <sub>2</sub> , H <sub>2</sub> O	X as the H, Yes	--	<ul style="list-style-type: none"> <li>Adds OH &amp; X</li> <li>Racemic, anti</li> </ul>

### Ring Formations

Reaction Name	Reagents	Adds	Notes
Cyclopropanation	CH <sub>2</sub> I <sub>2</sub> , Zn(Cu)	C ring	<ul style="list-style-type: none"> <li>Trans alkene -&gt; anti</li> <li>Cis alkene -&gt; syn</li> <li>New C-C bonds</li> </ul>
Epoxidation	MCPBA, DCM	O ring	<ul style="list-style-type: none"> <li>Trans alkene -&gt; anti</li> <li>Cis alkene -&gt; syn</li> <li>Forms epoxide</li> </ul>

## Bond Cleavage

Reaction Name	Reagents	Notes
Ozonolysis	1) O <sub>3</sub> , MeOH 2) DMS or Zn, AcOH	<ul style="list-style-type: none"><li>• Oxidizes alkene Cs to carbonyls</li><li>• Cuts alkene</li><li>• Forms aldehydes and/or ketones</li></ul>
Oxidative Cleavage of Syn-1,2-diol	HIO <sub>4</sub> , H <sub>2</sub> O	<ul style="list-style-type: none"><li>• Oxidizes OHs to carbonyls</li><li>• Must be syn</li><li>• Cuts alkane</li><li>• Forms aldehydes</li></ul>

## New C-C Bond Reaction Comparisons

Reaction Name	Reagents	Reactant	Notes
Acetylide Substitution Reaction	1) NaNH <sub>2</sub> , NH <sub>3</sub> 2) 1° alkyl halide	Terminal Alkyne	<ul style="list-style-type: none"><li>• SN2 Mechanism</li></ul>
Grignard Reagent (Alkyne)	1) CH <sub>3</sub> MgBr, THF 2) 1° alkyl halide	Terminal Alkyne	<ul style="list-style-type: none"><li>• Must be done anhydrous</li><li>• Acts as a strong base then nucleophile</li><li>• Will attack carbonyls</li><li>• SN2 Mechanism</li></ul>
Gilman Reagent	1) (Alkyl) <sub>2</sub> -CuLi, THF	Haloalkene (Halogen directly on alkene)	<ul style="list-style-type: none"><li>• Cannot attack carbonyls</li></ul>
Organolithium	a) 2 Li, hexanes b) Substitution group	Alkyl Halide	<ul style="list-style-type: none"><li>• Acts as a strong base then nucleophile</li></ul>

## Alkyne Reaction Comparisons

### $\pi$ Bond Reductions

Reaction Name	Reagents	Alkyne to...	Notes
Complete Reductive Hydrogenation	H <sub>2</sub> , Pd/C	Alkane	<ul style="list-style-type: none"> <li>Will remove present halides</li> <li>Will keep reacting in excess</li> </ul>
Incomplete Reductive Hydrogenation	H <sub>2</sub> , Lindlar's Cat.	Cis Alkene	<ul style="list-style-type: none"> <li>Only makes cis alkene on internal alkynes</li> </ul>
Dissolving Metal Reduction	2 Na, NH <sub>3</sub>	Trans Alkene	<ul style="list-style-type: none"> <li>Uses radical like mechanism</li> </ul>

### Formation of Aldehydes/Ketones

Reaction Names	Reagents	Forms	Notes
Acid Catalyzed Hydration (Internal)	H <sub>2</sub> SO <sub>4</sub> , H <sub>2</sub> O	Ketone	<ul style="list-style-type: none"> <li>Internal alkyne</li> <li>Can form on either alkyne C (mixture)</li> </ul>
Acid Catalyzed Hydration (Terminal)	HgSO <sub>4</sub> , H <sub>2</sub> SO <sub>4</sub> , H <sub>2</sub> O	Ketone	<ul style="list-style-type: none"> <li>Terminal alkyne</li> <li>Forms on <b>more</b> substituted C</li> </ul>
Hydroboration	a) HB(Sia) <sub>2</sub> , THF b) NaOH, H <sub>2</sub> O <sub>2</sub> , H <sub>2</sub> O	Aldehyde / Ketone	<ul style="list-style-type: none"> <li>Terminal alkyne (Ald)</li> <li>Internal alkyne (Ket)</li> <li>Forms on <b>less</b> substituted C for terminal alkyne</li> <li>Can form on either alkyne C (mixture) for internal alkyne</li> </ul>

### Halide (X) Addition

Reaction Name	Reagents	Notes
H-X Addition (Terminal)	H-X	<ul style="list-style-type: none"> <li>If in excess, will react until it is an alkane</li> <li>Can be stopped at alkene with 1 mol equivalent</li> <li>Follows Markovnikov's</li> </ul>
H-X Addition (Internal)	H-X	<ul style="list-style-type: none"> <li>If stopped at alkene with 1 mol equivalent, forms cis alkene</li> <li>Follows Markovnikov's</li> </ul>
Halogenation	X <sub>2</sub> , DCM	<ul style="list-style-type: none"> <li>Halides are added to both ends, and can react in excess or 1 mol equivalent</li> </ul>