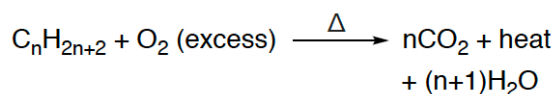


Know the mechanism for all reactions marked with an asterisk (\*)

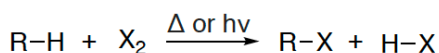
Reactions of Alkanes	General Characteristics
----------------------	-------------------------

Combustion



No heat, no reaction

\*Radical Halogenation



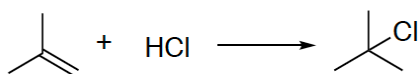
R = Alkyl

X = Cl, Br (only)

(Cl is more reactive & less chemoselective)

Reactions of Alkenes	General Characteristics
----------------------	-------------------------

\*Addition of HX

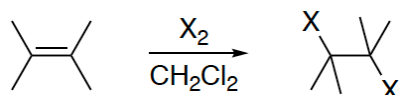


X = Cl, Br, I

Carbocation rearrangements possible

Markovnikov orientation

\*Addition of Halogens (X<sub>2</sub>)



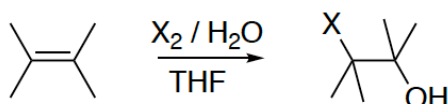
X=Br<sub>2</sub>, Cl<sub>2</sub>, also ICl or BrCl

Halonium ion intermediate

No rearrangements

Anti-addition

\*Halohydrin Formation



X=Br<sub>2</sub>, Cl<sub>2</sub>, I<sub>2</sub>

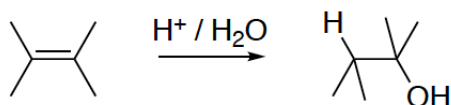
Anti-addition

Modification: NBS/H<sub>2</sub>O/Solvent (NCS or NIS)

Can use non H<sub>2</sub>O nucleophiles (ROH, RCO<sub>2</sub>H)

Halonium Ion (no rearrangements)

\*Addition of Water

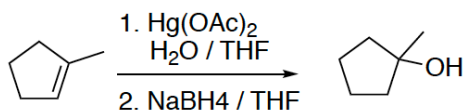


Acid catalyst

Nucleophiles besides H<sub>2</sub>O (ROH, RSH, etc.)

Carbocation rearrangements possible

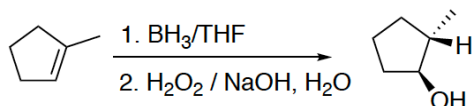
### \*Oxymercuration-Demercuration



*\*Know mechanism for step 1 only*

Mercurinium ion intermediate  
No carbocation rearrangements  
Can use ROH instead of  $\text{H}_2\text{O}$

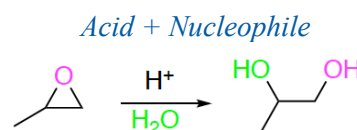
### \*Hydroboration



*\*Know mechanism for step 1 only*

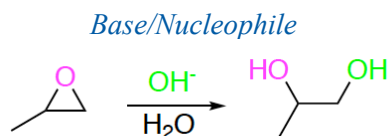
Also with **9-BBN** ( $\text{H}-\text{BR}_2$ ) and deuterated versions (**D-9-BBN**)  
Anti-Markovnikov orientation  
Syn addition of  $\text{H}_2\text{O}$   
No carbocation rearrangement

### \*Ring-Opening of Epoxides



*Mechanism summary:*

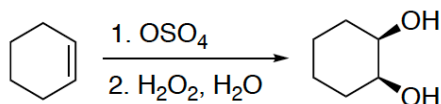
1) *protonate oxygen*  
2) *nucleophilic attack*  
Diol product – anti-addition  
Can also use  $\text{H}_2\text{S}$ , ROH, RSH



*Mechanism summary:*

1) *nucleophilic attack at less hindered carbon*  
2) *protonate oxygen*  
Diol product – anti-addition  
Also  $\text{OR}^-$ ,  $\text{SR}^-$

### Hydroxylation



Mild oxidation

Syn addition

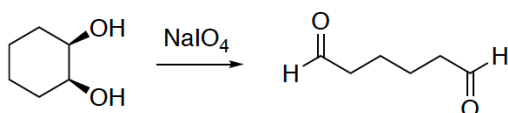
Variations:

Step 2.  $\text{NaHSO}_4, \text{H}_2\text{O}$

or

Step 2. N-methylmorpholine oxide (NMO)

### Oxydative Cleavage

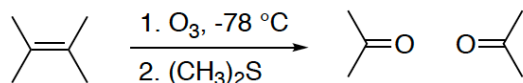


*Cis* diols only!

Aldehyde product

Mild oxidative cleavage

## Ozonolysis



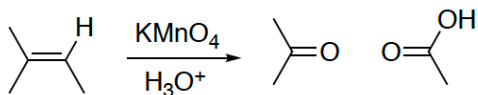
Mild Oxidation

Break double bond

End groups stay the same

May lead to mixtures with asymmetric alkenes









## Permanganate Oxidation



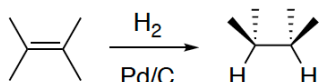
Vigorous Oxidation

Complete oxidation, does not stop at the aldehyde

## Comparisons:

	Ozonolysis	Vigorous Oxidation
	 formaldehyde	$\text{O}=\text{C}=\text{O}$ carbon dioxide
	 aldehyde	 carboxylic acid
	 ketone	 ketone

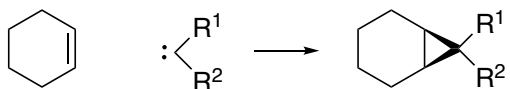
## Hydrogenation



Reduction to alkane

Syn addition of  $\text{H}_2$  (or  $\text{D}_2$ )

## Addition of Carbenes

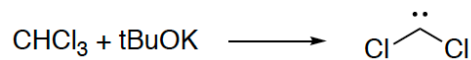


Highly reactive

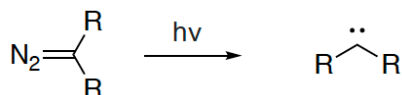
Unfilled octet

Formal charge on carbene carbon = 0

## Generation of Carbenes

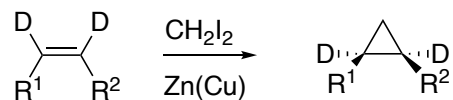


Dichlorocarbene only



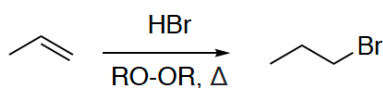
R = H, alkyl

### Simmons-Smith Cyclopropanation



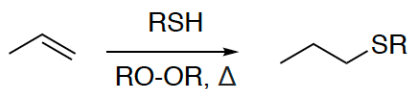
No carbene intermediate

### Radical Addition of HBr



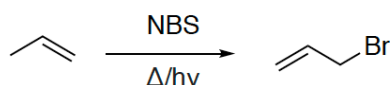
Anti-Markovnikov orientation  
Only HBr (or DBr), *no HI or HCl*  
Radical mechanism

### Thiol-ene Reaction



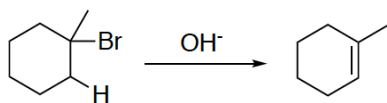
Anti-Markovnikov addition of SR  
Radical mechanism

### Allylic Bromination

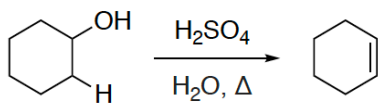


Radical mechanism *via* resonance stabilized allyl radical

### Synthesis of Alkenes (an introduction)



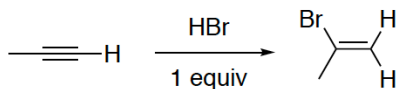
Elimination of HBr  
More substituted C=C (Saytzeff orientation)



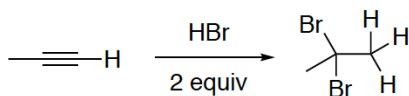
Elimination of H<sub>2</sub>O  
Need heat

## Reactions of Alkynes

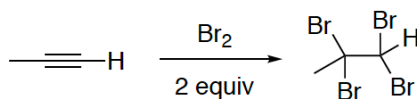
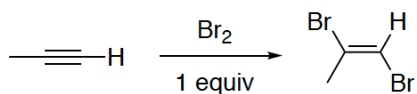
### \*Addition of HX



Markovnikov orientation  
Similar to alkenes  
Via 2° vinylic carbocation first



### \*Addition of X<sub>2</sub>

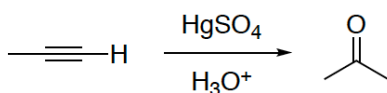


*Anti*-addition

Similar to alkenes

Via 2° vinylic carbocation first

### \*Oxymercuration



Ketone product

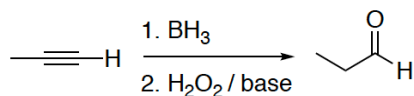
No analogous demercuration step



Via acid tautomerization

(know *tautomerism mechanism separately*)

### \*Hydroboration



9-BBN (H-BR<sub>2</sub>) and **deuterated** variations

Aldehyde generation

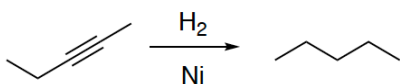
Skip mechanism for step 2



Via base tautomerization

(know *tautomerism mechanism separately*)

### Full Reduction



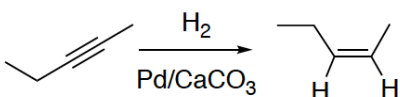
Also with D<sub>2</sub>

Other catalysts: Ni, Pt, Pd, PtO

Full reduction to alkane

No reaction without catalyst

### Partial Reduction

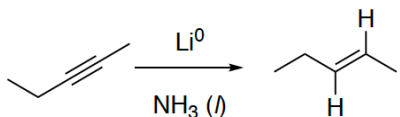


Lindlar's catalyst

Syn - addition (Z isomer)

D<sub>2</sub> also

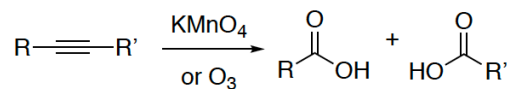
### Dissolving Metal Reduction



Anti – addition

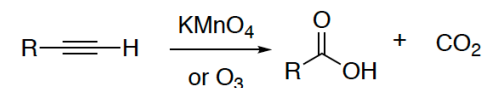
Also  $\text{ND}_3$  instead of  $\text{NH}_3$

### Oxidative Cleavage



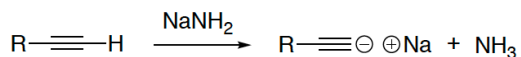
May lead to mixtures if asymmetric alkyne is used

Break alkyne to form carboxylic acids

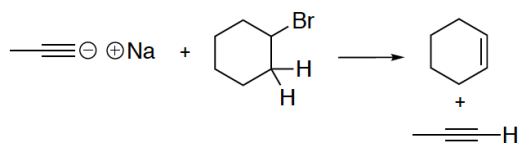
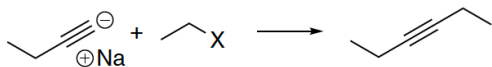


One product +  $\text{CO}_2(g)$

### Acetylides as Nucleophiles

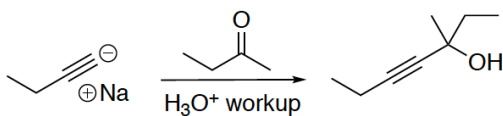


Acetylide can act as a nucleophile with  $1^\circ \text{RX}$  only



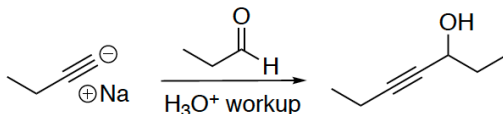
Acetylides can act as a base with  $2^\circ$  and  $3^\circ \text{R-X}$

### Addition of Acetylides to Carbonyls

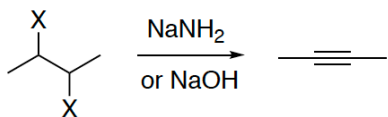


First, form acetylide

Need acidic workup

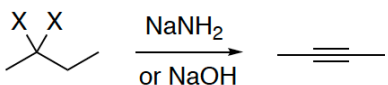


### Synthesis of Alkynes



$\text{X} = \text{Cl}, \text{Br}, \text{I}$

Dehydrohalogenation of vicinal dihalides



$\text{X} = \text{Cl}, \text{Br}, \text{I}$

Dehydrohalogenation of geminal dihalides

