#### CHEM 261

### Review: Addition Reactions of Alkynes

- 1. H<sub>2</sub> addition (syn addition)
- 2. X<sub>2</sub> addition (anti addition)
- 3. HX (mostly syn addition) X=Cl, Br, I

### 3. HX Addition (mostly syn)

Addition of HCl to propyne (follows Markovnikov's rule)



#### Terms

Chemoselective:  $OsO_4$ , always stops at the di-hydroxyl product *Regioselective*: Where is the most stable carbocation (C<sup>+</sup>)? *Stereoselective*: Syn or anti

# **Substitution Patterns of Multiple Bonds**



#### Be aware: syn-additions not necessarily lead to cis-alkenes!

Deuterium (D, is an isotope of hydrogen) as it behaves similarly to hydrogen but it weights twice as much and is distinguishable from regular hydrogen, has higher priority.



## 4. Addition of Water (requires acid, follows Markovnikov's rule)

Tautomers (e.g. keto/enol) are rapidly equilibrating structural isomers. The process is called **tautomerization**.

Tautomerization is **NOT** the same as resonance. Resonance is the movement of *electrons only*, tautomerization is the movement of an *atom*.



Retro-synthesis question: How can you make this ketone?



## 5. Anti-Markovnikov Water Addition - Hydroboration-Oxidation



> Two possibilities for the reaction of organoboranes:

- 1. Water and acid to add H and give the alkene
- 2. NaOH and  $H_2O_2$  to give the enol tautomer that converts (equilibrium) primarily to the keto tautomer (aldehyde shown below)

$$H_{3}C-C \equiv C-H \xrightarrow{1) R_{2}BH} \longrightarrow H$$

$$H_{3}C-C \equiv C-H \xrightarrow{2) NaOH, HOOH} O$$

$$H_{2}OH \xrightarrow{1} H_{2}O$$

$$H_{3}C \xrightarrow{1} C = CH_{2}$$

### **Oxidation of Alkynes**

With potassium permanganate:



Example 1: 2-butyne



Recall the difference between resonance and tautomerization arrows





# How is acidity of organic compounds defined?

Alkanes

$$H_{3}C-C H = H_{3}C-CH_{2} + H^{\oplus}$$

$$Ka = \frac{[CH_{3}CH_{2}][H^{+}]}{[CH_{3}CH_{3}]} = 10^{-46}$$

Alkenes

$$H_2C = CH \longrightarrow H_2C = CH + H^{\oplus}$$

Ka = 
$$\frac{[CH_2CH^-][H^+]}{[CH_2CH_2]} = 10^{-36}$$

Alkynes

HCECH 
$$\longrightarrow$$
 HCEC + H <sup>$\oplus$</sup> 

Ka = 
$$\frac{[HC \equiv C] [H^+]}{[HC \equiv CH]}$$
 = 10<sup>-26</sup>

# How strong of a base is needed to deprotonate?

	acid	conjugate base
НС≡С−Н	H <sub>2</sub> N-H pKa ~ 36	H₂N <sup>-</sup>
рКа = 26	Н <sub>3</sub> С-Н рКа ~ 45	H <sub>3</sub> C <sup>-</sup>
	RO-H pKa ~17	RO
	HO-H pKa ~ 15.7	HO <sup>-</sup>

 $\rightarrow$  H<sub>2</sub>N<sup>-</sup> and H<sub>3</sub>C<sup>-</sup> are strong enough bases to deprotonate a terminal alkyne, but water is not a strong enough.