# Chapter 9:

#### Alkynes and Reactions with Alkynes

- Today (9.5-9.10) Reactions with Alkynes
- Friday (End Chapter 9)
  - ✓ Preparation of Alkynes
  - ✓ Acetylide Formation
  - ✓ Hydrohalogenation
  - ✓ Anti Markovnikov Hydrohalogenation
  - Addition of Halogens
  - Reduction of Alkynes
  - Acid Catalyzed Addition of Water
  - Hydroboration/Oxidation
  - Oxidative Cleavage

### Hydrohalogenation of Alkynes

$$H_3C$$
 $H_2C-C\equiv C-CH_3+H-CI$ 
excess

**Anti- Markovnikov Addition** 

## Halogenation of Alkynes

$$CH_3CH_2C = CCH_3 \xrightarrow{Cl_2} CH_2Cl_2$$

$$CH_3C \equiv CH \xrightarrow{Br_2} CH_2Cl_2$$



# Halogenation of Alkynes

$$R = R \xrightarrow{\frac{X_2 \text{ (one equivalent)}}{CCI_4}}$$

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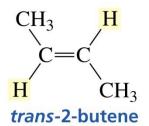
# Addition of Hydrogen Formation of Cis Alkene

Like alkenes, alkynes can readily undergo hydrogenation.

$$CH_3CH_2$$
  $C = CH$   $H_2$   $Pt/C$ 

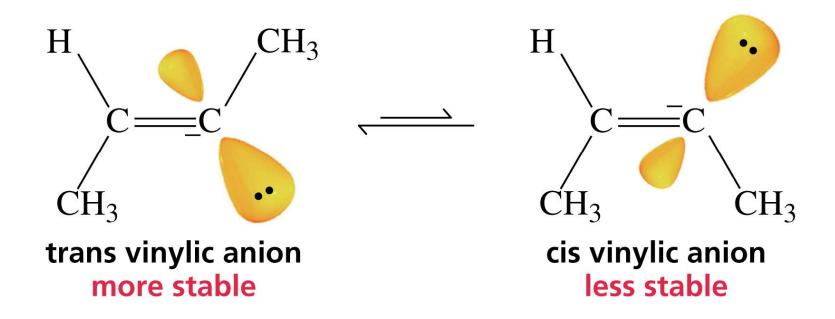
# Chemical Reduction of Internal Alkynes to form Trans Alkenes

 $CH_3C \equiv CCH_3$  **2-butyne** 



#### Reason for trans addition:

The radical anion adopts a trans configuration to reduce repulsion.



# Reduction of Alkynes – Summary

 Two equivalents of H₂ are consumed for each alkyne → alkane conversion.



# **New Functional Groups**

### Acid-Catalyzed Addition of Water to Alkynes

Like alkenes, alkynes can also undergo acid catalyzed Markovnikov hydration.

$$CH_3C \equiv CCH_3 + H_2O \xrightarrow{H_2SO_4}$$

# Hydroboration — Internal Alkynes

$$3 \text{ CH}_{3}\text{C} \equiv \text{CCH}_{3} + \text{BH}_{3} \xrightarrow{\text{THF}} \overset{\text{CH}_{3}}{\text{H}} \overset{\text{CH}_{3}}{\text{C}} = \overset{\text{CH}_{3}}{\text{H}} \xrightarrow{\text{HO}^{-}, \text{ H}_{2}\text{O}_{2}} \xrightarrow{\text{H}_{2}\text{O}}$$

boron-substituted alkene

Internal alkynes react easily with  $BH_3$  to form a trialkenylborane. The addition is comparable to treatment of an alkene with  $BH_3$ . The reaction involves <u>syn</u> addition of hydrogen and boron.

## Formation of Ketone versus Aldehyde

$$H_2O, H_2SO_4$$
 $HgSO_4$ 
 $CH_3C \equiv CH$ 

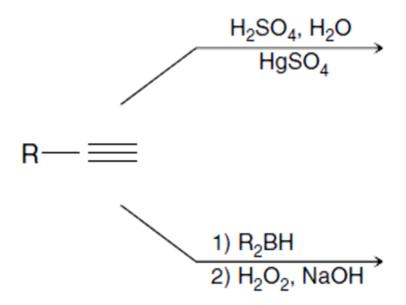
1. disiamylborane
2.  $HO^-, H_2O_2, H_2O$ 

# Hydroboration—Oxidation of Terminal Alkynes

$$HO^-$$
,  $H_2O_2$   $H$   $C=C$   $H$   $CH_2CH_3$   $CH_3CH_2CH_2CH$ 

# Hydration Regioselectivity

- Markovnikov hydration leads to a ketone.
- Anti-Markovnikov hydration leads to an aldehyde.



#### Suggested Homework Problems Chapter 9

# 1,7,9,13,18,20,32-37, 41,44,52,57