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Halogenation of Alkynes

Eg.

HX Addition (syn)

$$H_3C-C=C-CH_3$$
  $\xrightarrow{syn}$   $H_3C$   $C=C$ 
 $H-X$ 

Eg. Propyne (follows markovnikov's rule)

Addition Reactions of Alkynes – Addition of water (requires acid)

Remember

$$H_2O + H_2SO_4 \longrightarrow H_3O + HSO_4$$

# 2. Anti-Markovnikov Water Addn – Hydroboration-Oxidation

Two possibilities for addition of water

# 3. Oxidation of alkynes:

$$R-C \equiv C-R' \qquad \xrightarrow{KMnO_4} \qquad \qquad R \qquad \qquad + \qquad O \qquad \qquad + \qquad \qquad R' \qquad \qquad \\ & \qquad \qquad CO_2 \text{ is formed} \qquad \qquad CO_2 \text{ is formed} \qquad \qquad \\$$

eg. i. 
$$H_3C-C \equiv C-CH_3 \xrightarrow{KMnO_4} H_3C \xrightarrow{O} H_3C \xrightarrow{O} CH_3$$
 acetic acid (vinegar) "carboxylic acid"

NOTE: do not need to worry about the mechanism of this reaction

## 4. Ozonolysis of alkynes:

$$R-C\equiv C-R'$$
  $\xrightarrow{O_3}$   $Z_n$   $Q_n$   $Q$ 

i. 
$$H_3C-C \equiv C-H \qquad \begin{array}{c} O_3 \\ \hline Zn \end{array} \qquad \begin{array}{c} H_3C \longrightarrow O \\ \hline OH \\ acetic \ acid \end{array} \qquad \begin{array}{c} O \\ \hline HO \\ \hline \\ no \ CO_2 \ is \ formed \end{array}$$

5. Reactions of terminal alkynes:  $\{R-C \equiv C-H \}$  eg.

### - acidity of alkane / alkene / alkyne:

i.
$$H_{3}C-C \cdot H \longrightarrow H_{3}C-CH_{2} + H^{+}$$

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

$$pKa = 46$$

ii.

$$H_{2}C = CH$$
 $H_{2}C = CH$ 
 $H^{\oplus}$ 
 $H_{2}C = CH$ 
 $H_{2}C = CH$ 
 $H^{\oplus}$ 
 $H^{\oplus}$ 

- How strong a base needed?

acid conjugate base 
$$HC = C - H \qquad H_2N - H \quad pKa \sim 36 \qquad H_2N^-$$
 
$$pKa = 26 \qquad H_3C - H \quad pKa \sim 45 \qquad H_3C^-$$
 
$$HO - H \quad pKa \sim 15.7 \qquad HO^-$$

- only  $H_2N^-$  and  $H_3C^-$  are strong enough bases to deprotonate the proton of the alkyne.

### Reactions of terminal acetylenes:

H-C=C: Na 
$$\xrightarrow{B_3}$$
  $\xrightarrow{B_3}$   $\xrightarrow{B_3}$   $\xrightarrow{H_3}$   $\xrightarrow{H_3}$ 

Acetylenes are key intermediates for making other types of compounds:

$$H_3C$$
 $CH_2$ 
 $CH_3$ 
 $H^+$ ,  $H_2O$  or  $R_2BH$  then NaOH and  $H_2O_2$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_4$ 
 $CH_5$ 
 $CH_5$ 
 $CH_5$ 
 $CH_5$ 
 $CH_6$ 
 $CH_7$ 
 $CH_8$ 
 $CH_8$ 

**Problem:** How to convert acetylene (ethyne) to hexanal (6 carbon aldehyde) using any other necessary reagents

Approach:

$$H \longrightarrow H$$
 $+ Na NH_2$ 
 $H \longrightarrow H$ 
 $+ NH_3$ 
 $+ NH_3$ 
 $+ NH_3$ 
 $+ NH_4$ 
 $+ NH_5$ 
 $+ NH_5$