Learning Objective

• predict the products and specify the reagents for the oxidation of alkynes

Alkynes, similar to alkenes, can be oxidized gently or strongly depending on the reaction environment. Since alkynes are less stable than alkenes, the reactions conditions can be gentler. For examples, alkynes form vicinal dicarbonyls in neutral permanganate solution. For the alkene reaction to vicinal dialcohols, the permanganate reaction requires a lightly basic environment for the reaction to occur. During strong oxidation with ozone or basic potassium permanganate, the alkyne is cleaved into two products. Because at least one of the reaction products is a carboxylic acid, it is important to consider the acid-base chemistry of the product in the reaction solution. Carboxylic acids are deprotonated in basic solutions to carboxylates. A second reaction step is required to protonate the carboxylate to the neutral form of the carboxylic acid. The generic reactions are summarized below for the different oxidative conditions - gentle or strong.

Gentle Alkyne Oxidation

\[
\text{R} = \text{C} \equiv \text{C} = \text{R}' \text{ or H} \quad \xrightarrow{\text{K}\text{MnO}_4 / \text{H}_2\text{O} \text{ neutral}} \quad \text{R} = \text{C} \equiv \text{C} = \text{R}' \text{ or H} \quad \text{vicinal dicarbonyl}
\]

Strong Alkyne Oxidation - Oxidative Cleavage

\[
\text{R} = \text{C} \equiv \text{C} = \text{R} \quad \xrightarrow{\text{1) K}\text{MnO}_4 / \text{H}_2\text{O}^+} \quad \text{R} = \text{C} \equiv \text{C} = \text{R} \quad \xrightarrow{\text{2) H}_2\text{O}^+} \quad \text{R} = \text{C} \equiv \text{C} = \text{H} \quad \xrightarrow{\text{1) O}_2} \quad \text{R} = \text{C} \equiv \text{C} = \text{H} \quad \xrightarrow{\text{2) H}_2\text{O}}
\]

Exercise

1. Draw the bond-line structures for the product(s) of the following reactions.
a) $\text{C} \equiv \text{C} \xrightarrow{1) \text{KMnO}_4 / \text{HO}^-} \text{C} \equiv \text{C} \xrightarrow{2) \text{H}_2\text{O}}$

b) $\text{C} \equiv \text{C} \xrightarrow{1) \text{O}_3} \xrightarrow{2) \text{H}_2\text{O}}$

c) $\text{C} \equiv \text{C} \equiv \text{H} \xrightarrow{1) \text{KMnO}_4 / \text{HO}^-} \xrightarrow{2) \text{H}_3\text{O}^+}$

d) $\text{C} \equiv \text{C} \equiv \text{H} \xrightarrow{1) \text{O}_3} \xrightarrow{2) \text{H}_2\text{O}}$

Answer

1.

a) $\text{C} \equiv \text{C} \xrightarrow{1) \text{KMnO}_4 / \text{HO}^-} \xrightarrow{2) \text{H}_2\text{O}}$

b) $\text{C} \equiv \text{C} \xrightarrow{1) \text{O}_3} \xrightarrow{2) \text{H}_2\text{O}}$

c) $\text{C} \equiv \text{C} \equiv \text{H} \xrightarrow{1) \text{KMnO}_4 / \text{HO}^-} \xrightarrow{2) \text{H}_3\text{O}^+}$

d) $\text{C} \equiv \text{C} \equiv \text{H} \xrightarrow{1) \text{O}_3} \xrightarrow{2) \text{H}_2\text{O}}$

Oxidative cleavage of alkenes produces carboxylic acids and/or carbon dioxide. Aldo/hydes are not produced.

Contributors and Attributions

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