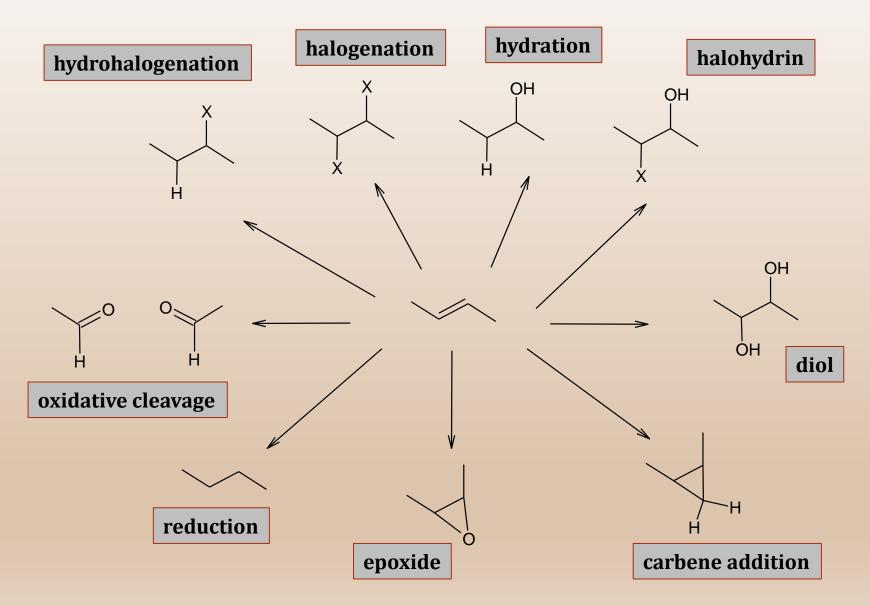
Alkene Reactions - 3- Oxidation Reactions

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All Reactions



Oxidation of Alkenes (oxidative cleavage) - O_3

 Cleavage of alkenes with ozone and workup with zinc in acetic acid (or dimethyl sulfide – Me₂S) leads to less highly oxidized carbons than products from cleavage with hot KMnO₄ (next slide)

$$\begin{array}{c} \textbf{CH}_{3} \\ \textbf{CH}_{3}\textbf{CH} - \textbf{CH} = \textbf{CH}_{2} \\ \textbf{3-Methyl-1-butene} \end{array} \xrightarrow{(1) \ O_{3}, \ CH_{2}Cl_{2}, \ -78^{\circ}C} \xrightarrow{\textbf{CH}_{3}\textbf{CH} - \textbf{CH}} + \begin{array}{c} \textbf{CH}_{3} \\ \textbf{CH}_{3}\textbf{CH} - \textbf{CH} + \\ \textbf{Isobutyraldehyde} \end{array} \xrightarrow{\textbf{Formaldehyde}}$$

$$\begin{array}{c} \textbf{CH}_{3} \\ \textbf{CH}_{3} \\ \textbf{CH}_{3}\textbf{C} = \textbf{CHCH}_{3} \xrightarrow{(1) \ O_{3}, \ CH_{2}Cl_{2}, \ -78^{\circ}C} \xrightarrow{\textbf{CH}_{3}\textbf{C}} \xrightarrow{\textbf{CH}_{3}\textbf{C}} \xrightarrow{\textbf{CH}_{3}\textbf{C}} \xrightarrow{\textbf{CH}_{3}\textbf{CH}} \\ \textbf{2-Methyl-2-butene} \end{array} \xrightarrow{\textbf{Acetone}} \begin{array}{c} \textbf{CH}_{3} \\ \textbf{CH}_{3} \\ \textbf{CH}_{3}\textbf{C} = \textbf{CHCH}_{3} \xrightarrow{\textbf{CH}_{3}\textbf{CH}} \xrightarrow{\textbf{CH}_{3}\textbf{CH}_{3}\textbf{CH}} \xrightarrow{\textbf{CH}_{3}\textbf{CH}_{3}\textbf{CH}} \xrightarrow{\textbf{CH}_{3}\textbf{CH}_{3}\textbf{CH}_{3}\textbf{CH}} \xrightarrow{\textbf{CH}_{3}\textbf{CH}_{3}\textbf{CH}_{3}\textbf{CH}} \xrightarrow{\textbf{CH}_{3}\textbf{CH}_{3}\textbf{CH}_{3}\textbf{CH}_{3}\textbf{CH}_{3}\textbf{CH}_{3}} \xrightarrow{\textbf{CH}_{3}\textbf{CH}_{3$$

Mechanism

Oxidation of Alkenes (oxidative cleavage) - KMnO₄

- KMnO₄ is a powerful oxidizing agent that cleaves (break) the double bond and oxidizing them in the process giving aldehydes (alkenes with hydrogens on it) and ketones (substituted alkenes) as products.
- Terminal alkenes give CO₂ with KMnO₄
- It is a useful technique in determining structure of molecule
- It is a also a good **QUALITATIVE TEST**

$$\begin{array}{c}
\mathbf{CH_3CH} \stackrel{!}{=} \mathbf{CHCH_3} \xrightarrow{\mathrm{KMnO_4, OH^-, H_2O}} & 2 & \mathbf{CH_3C} \\
\text{(cis or trans)} & \mathbf{Acetate ion} & \mathbf{Acetic acid}
\end{array}$$

$$\begin{array}{c}
\mathbf{CH_3} \\
\mathbf{CH_3CH_2C} \xrightarrow{\downarrow} \mathbf{CH_2} \xrightarrow{(1) \text{ KMnO}_4, \text{ OH}^-} \\
\downarrow \\
\mathbf{CH_3CH_2C} \xrightarrow{\downarrow} \mathbf{CH_2} \xrightarrow{(2) \text{ H}_3\text{O}^+} \mathbf{CH_3CH_2C} = \text{O} + \text{O} = \mathbf{C} = \text{O} + \text{H}_2\text{O}
\end{array}$$

Worked Example - 1

Question: An unknown alkene with formula C₇H₁₂ yields only the following product on oxidation with hot KMnO₄

$$C_7H_{12} \xrightarrow{(1) \text{ KMnO}_4, \text{ H}_2\text{O}, } CH_3CCH_2CH_2CH_2CH_2C-OH$$

Answer: Since no carbons are missing in the product, the alkene must be part of a ring in the original molecule

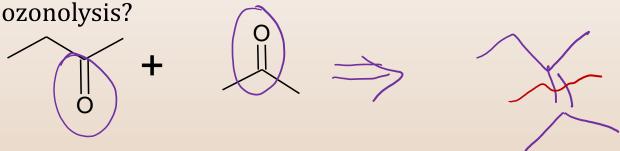
$$CH_{3} \xrightarrow{(1) \text{ KMnO}_{4}, \text{ H}_{2}\text{O}, \\ \text{OH}^{-}, \text{ heat}}} CH_{3}CCH_{2}CH_{2}CH_{2}CH_{2}C-OH$$

$$Unknown \text{ alkene}$$

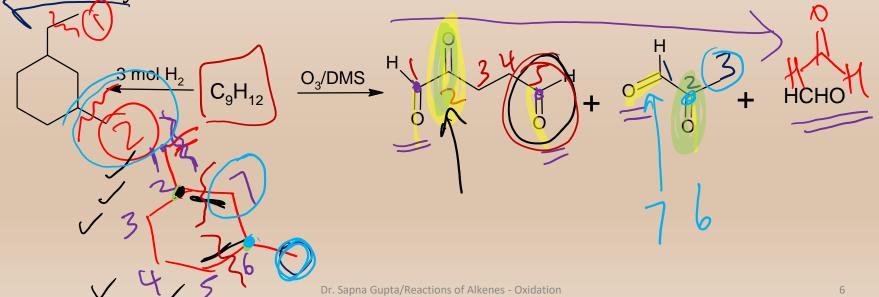
$$(1-methylcyclohexene)$$

Worked Example - 2

1) What is the alkene that gives the following two products on



2) An unknown alkene with formula C_9H_{12} reacts with 3 mols of hydrogen to give 1-ethyl-3-methylcyclohexane and the products below ∞ n ozonolysis. What is the structure of the alkene?



Qualitative Tests

- These tests are done to test for functional groups.
- Qualitative tests should be visual and as specific as possible for a functional group.

For alkenes:

- Addition of Bromine dark red Br₂ will add to alkene and as reaction progresses the color will disappear. So disappearance of red color is the positive test for alkenes.
- Addition of $KMnO_4$ $KMnO_4$ (aq) is a purple solution. Since it oxidizes the alkene, it itself gets reduced during the reaction to give MnO_2 , which is brown in color. So disappearance of purple color and appearance of brown ppt is positive for alkenes.

Key Words/Concepts

- Oxidative Cleavage
- Ozonolysis
- Qualitative Analysis