

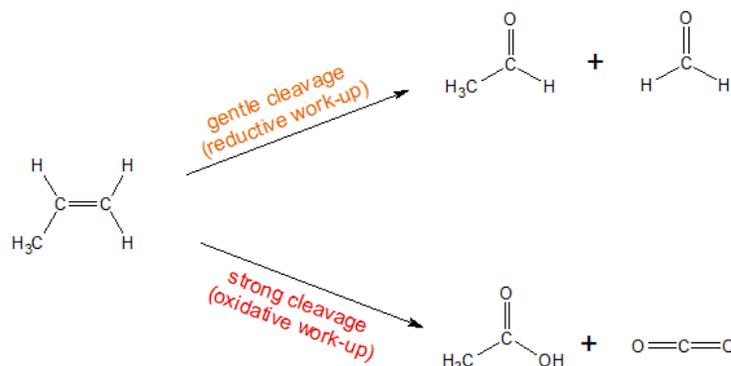
9.15: OXIDATIVE CLEAVAGE OF ALKENES

Learning Objective

- predict the products/specify the reagents for oxidative cleavage of alkenes

OVERVIEW

Oxidative cleavage can occur by several different reaction pathways. The cleavage can be strong or gentle depending on the reaction conditions and/or the work-up of the initial reaction product. Both alkenes and alkynes can undergo cleavage reactions. This section will focus on alkenes.



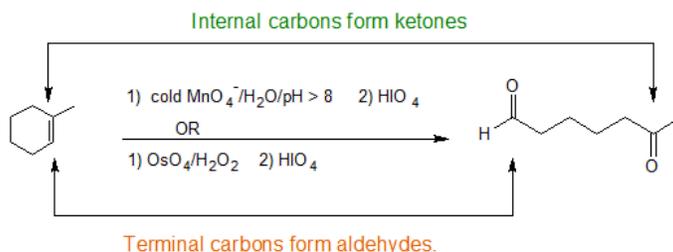
Gentle cleavage of alkenes occurs by two primary reaction pathways: ozolysis with a reductive work-up or syn-dihydroxylation followed by oxidation with periodic acid. Gentle cleavage will leave terminal carbons partially oxidized to aldehydes. Strong cleavage of alkenes will fully oxidize terminal carbons to carboxylic acids. Internal carbons become ketones by either reaction pathway.

WHY SO MANY REACTIONS?

At first glance, it may seem silly to have more than more reaction pathway for the same functional group conversion. As this course proceeds, it will become necessary to target reactions to a single functional group of an organic compound with multiple functional groups. A particular reaction pathway can be advantageous when the reactivity of the entire molecule is considered, not just a single functional group.

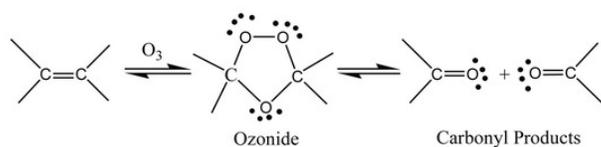
GENTLE CLEAVAGE: SYN-DIHYDROXYLATION FOLLOWED BY PERIODIC ACID

Alkenes can also be gently cleavage in a two-step reaction sequence in which the alkene first undergoes syn-dihydroxylation using cold, slightly basic KMnO_4 or $\text{OsO}_4/\text{H}_2\text{O}_2$ followed by oxidation with periodic acid (HIO_4). Both reaction sequences are shown below using 1-methylcyclohexene as an example.



GENTLE CLEAVAGE: OZONOLYSIS WITH A REDUCTION WORK-UP

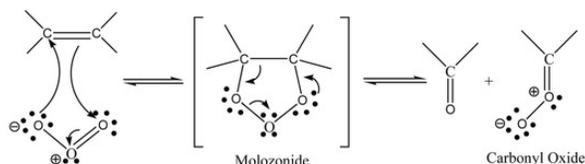
Ozonolysis is a method of oxidatively cleaving **alkenes** or **alkynes** using **ozone** (O_3), a reactive allotrope of oxygen. The process allows for carbon-carbon double or triple bonds to be replaced by double bonds with oxygen. This reaction is often used to identify the structure of unknown alkenes by breaking them down into smaller, more easily identifiable pieces. Ozonolysis also occurs naturally and would break down repeated units used in rubber and other polymers. On an industrial scale, azelaic acid and pelargonic acids are produced from ozonolysis.



OZONOLYSIS REACTION MECHANISM

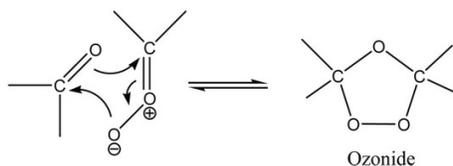
The gaseous ozone is first passed through the desired alkene solution in either methanol or dichloromethane. The first intermediate product is an ozonide molecule which is then further reduced to carbonyl products. This results in the breaking of the carbon-carbon double bond and is replaced by a carbon-oxygen double bond instead.

Step 1:



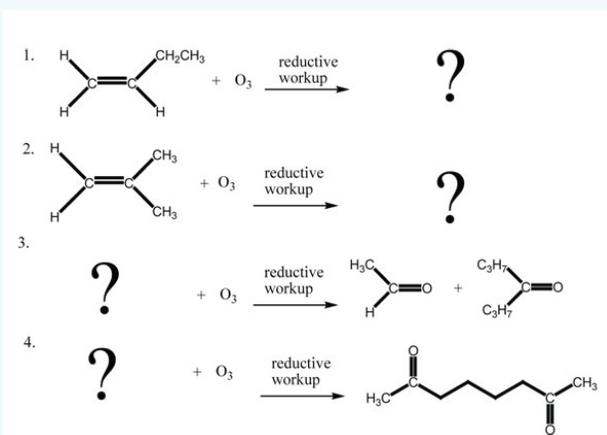
The first step in the mechanism of ozonolysis is the initial electrophilic addition of ozone to the carbon-carbon double bond to form the molozonide intermediate. Due to low stability of molozonide, it continues reacting and breaks apart to form a carbonyl and a carbonyl oxide molecule.

Step 2:

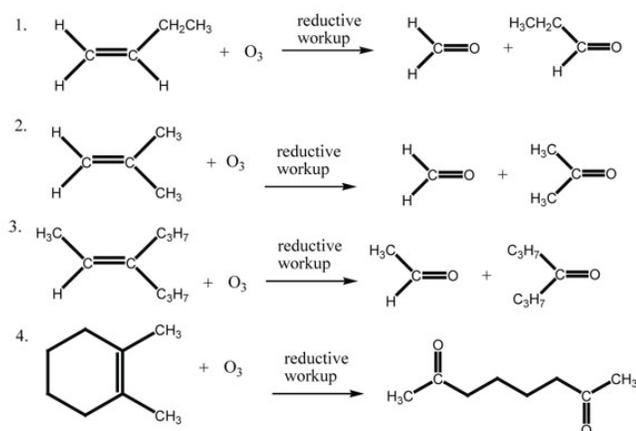


The electrons of the carbonyl and the carbonyl oxide form the stable ozonide intermediate which can then undergo an oxidative or reductive work-up to form the products of interest. A reductive workup converts the ozonide molecule into the desired carbonyl products with aldehyde on terminal carbons. An oxidative workup converts the ozonide molecule into the desired carbonyl products with carboxylic acids on terminal carbons. The two reaction workup conditions are summarized below.

Exercises

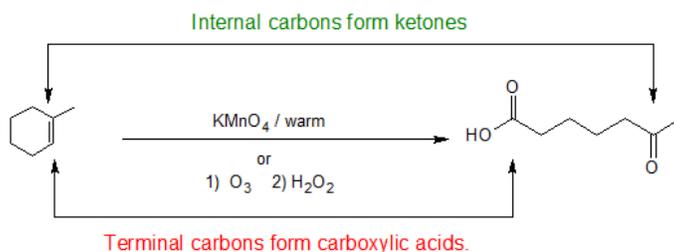


Answers



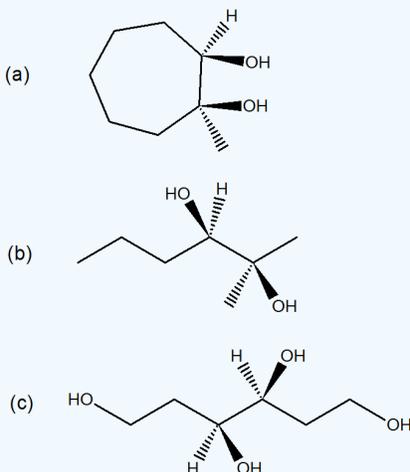
STRONG CLEAVAGE FROM STRONG OXIDATIVE REACTIONS

When the reaction conditions for potassium permanganate are warm, then the oxidation reaction is stronger and cleavage occurs at the alkene with any terminal carbons fully oxidizing to carboxylic acids. When the ozonolysis reaction is followed by an oxidative work-up, then any terminal carbons will oxidize fully to the carboxylic acid as shown in the example below. The example for 1-methylcyclohexene is shown below.



Exercise

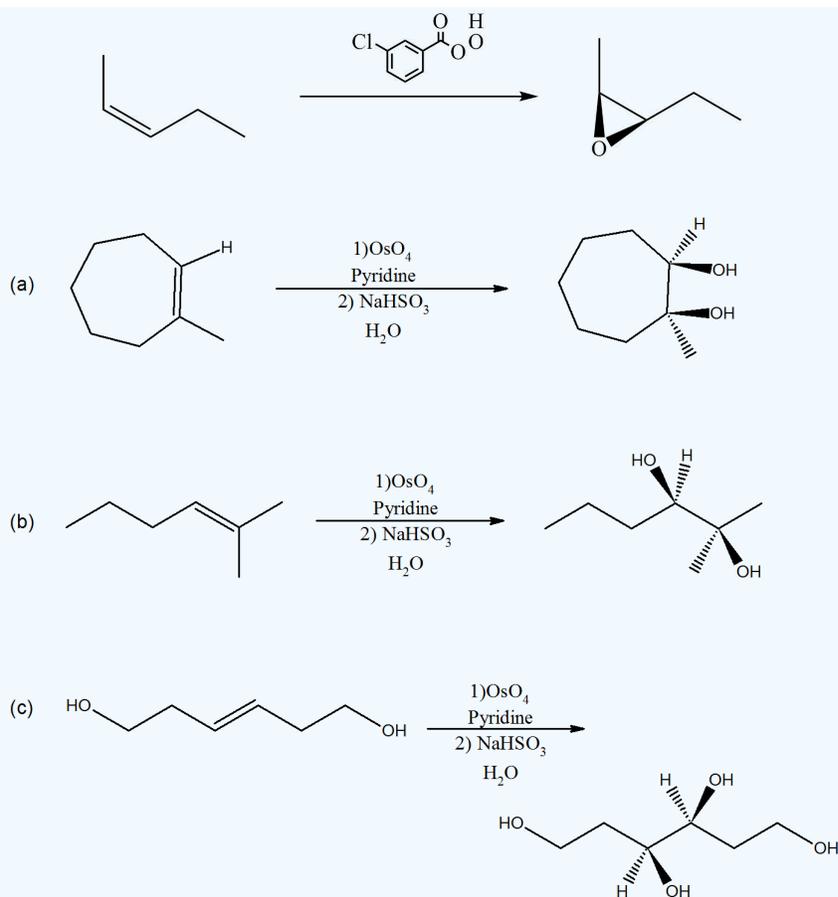
5. What would you expect the products to be from the reaction of *cis*-2-pentene with *m*-chloro-peroxybenzoic acid? Show the stereochemistry of the final product.
6. Give a reaction scheme with starting alkenes and required reagents to produce the following compounds.



Answer

5.

6.



REFERENCES

1. Vollhardt, K., Schore, N. *Organic Chemistry: Structure and Function*. 5th ed. New York, NY: W. H. Freeman and Company, 2007.
2. Shore, N. *Study Guide and Solutions Manual for Organic Chemistry*. 5th ed. New York, NY: W.H. Freeman and Company, 2007.

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