

8.8: OXIDATION OF ALKENES - CLEAVAGE TO CARBONYL COMPOUNDS

OBJECTIVE

After completing this section, you should be able to

- write an equation to describe the cleavage of an alkene by ozone, followed by reduction of the ozonide so formed with either sodium borohydride or zinc and acetic acid.
- predict the products formed from the ozonolysis-reduction of a given alkene.
- write an equation to describe the cleavage of an alkene by potassium permanganate.
- predict the products from the oxidative cleavage of a given alkene by potassium permanganate.
- use the results of ozonolysis-reduction, or cleavage with permanganate, to deduce the structure of an unknown alkene.
- identify the reagents that should be used in the oxidative cleavage of an alkene to obtain a given product or products.
- write the equation for the cleavage of a 1,2-diol by periodic acid, and draw the structure of the probable intermediate.
- predict the product or products that will be formed from the treatment of a given 1,2-diol with periodic acid.
- use the results of hydroxylation/1,2-diol cleavage to deduce the structure of an unknown alkene.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

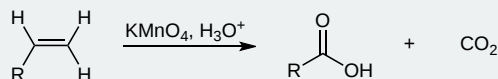
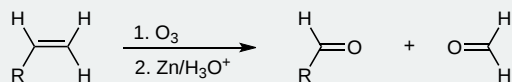
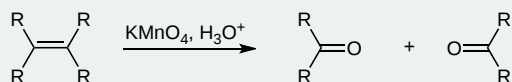
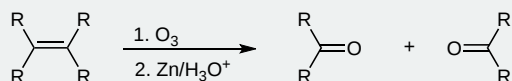
- molozonide
- ozonide
- ozonolysis

STUDY NOTES

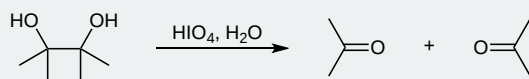
Ozonolysis, or ozonolysis-reduction, refers to the treatment of an alkene with ozone followed by a suitable reducing agent to break down complex double-bond-containing compounds into smaller, more easily identified products. From the identity of the products formed, it may be possible to deduce the structure of the original double-bond-containing substance. Ozonolysis will feature prominently in many of the road-map problems that you will encounter in this course.

A *molozonide* is an unstable, cyclic intermediate that is initially formed when an alkene reacts with ozone.

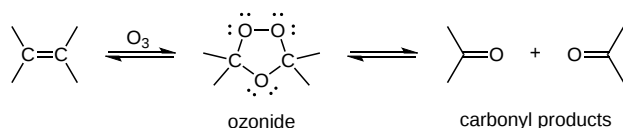
Alkenes can also be cleaved by other oxidizing agents such as potassium permanganate. However, KMnO_4 will carry the oxidation further than ozonolysis, so products can be slightly different. Note within the summary of the following reactions that ozonolysis produces aldehydes and ketones, while KMnO_4 can oxidize all the way to carbon dioxide and carboxylic acid.



Diol cleavage is another example of a redox reaction; periodic acid, HIO_4 , is reduced to iodic acid, HIO_3 .



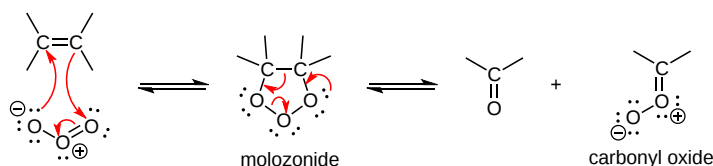
Ozonolysis is a method of oxidatively cleaving **alkenes** or **alkynes** using **ozone** (O_3), a reactive allotrope of oxygen. The process allows for carbon-carbon double or triple bonds to be replaced by double bonds with oxygen. This reaction is often used to identify the structure of unknown alkenes, 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.



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.

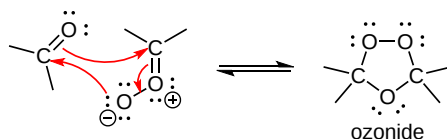
REACTION MECHANISM

Step 1:



The first step in the mechanism of ozonolysis is the initial electrophilic addition of ozone to the Carbon-Carbon double bond, which then form the molozonide intermediate. Due to the unstable molozonide molecule, it continues further with the reaction and breaks apart to form a carbonyl and a carbonyl oxide molecule.

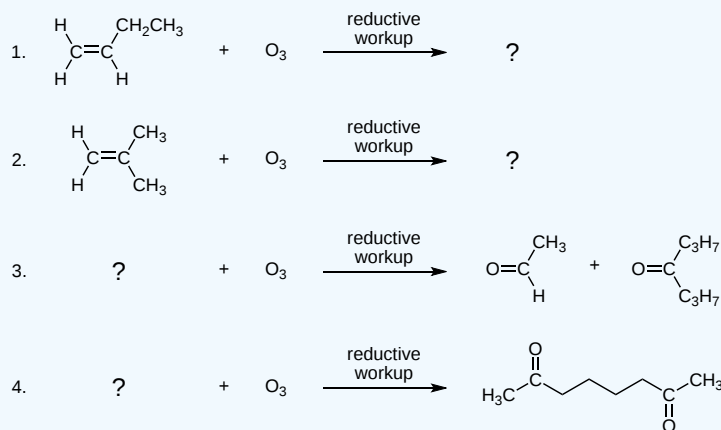
Step 2:



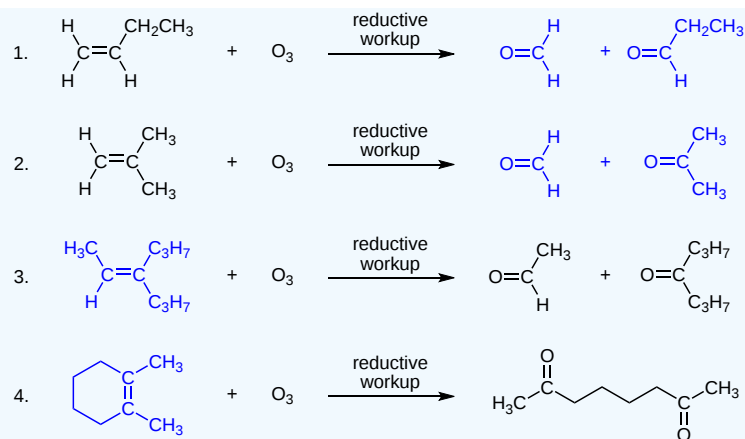
The carbonyl and the carbonyl oxide rearranges itself and reforms to create the stable ozonide intermediate. Since some ozonides are explosive, it is immediately reacted with a reductive workup to then convert the ozonide molecule into the desired carbonyl products. A typical reductive workup is zinc metal in acetic acid. A variety of carbonyl products could result depending on the starting alkene. For example, a tetrasubstituted alkene would yield two ketone products, while a trisubstituted alkene would yield one ketone product and one aldehyde product.

While there are other options for oxidative cleavage of the double bond, this is the most commonly used reaction.

? EXERCISE 8.8.1

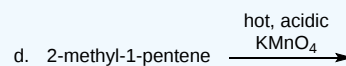
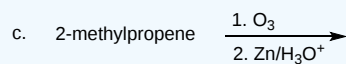


Answer

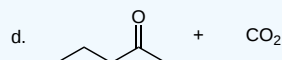
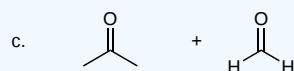
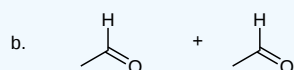
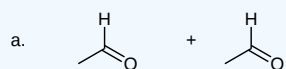


? EXERCISE 8.8.2

Draw the structure of the product or products obtained in each of the following reactions:



Answer



? EXERCISE 8.8.3

Exercises 1(a) and 1(b), above, indicate that it is not possible to distinguish between *cis* and *trans* isomers of alkenes using oxidative cleavage.

Answer

Both isomers give the same product or products.

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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