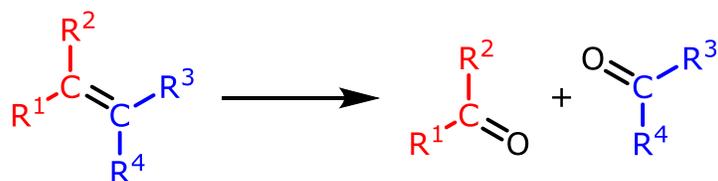


Oxidative Cleavage of Alkenes and Alkynes by Ozonolysis or Potassium Permanganate

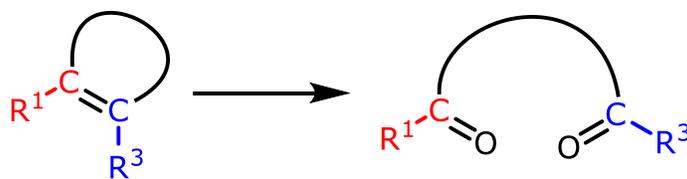
Klein's textbook gives only a short discussion of oxidative cleavage in Section 9.11. We will not go into great detail about the mechanisms of these reactions, because there are actually many pathways possible and which one dominates depends on the compound and the conditions. The outcomes are all the same, however, and you need to be able to use reactions of this type in "predict the product" questions and in designing multi-step syntheses. Here is a little more detail to help you understand these reactions.

The Basic Pattern of Oxidative Cleavage

In all cases the reaction follows a simple pattern: The C=C bond is broken, and each of the former alkene carbons becomes a carbonyl.



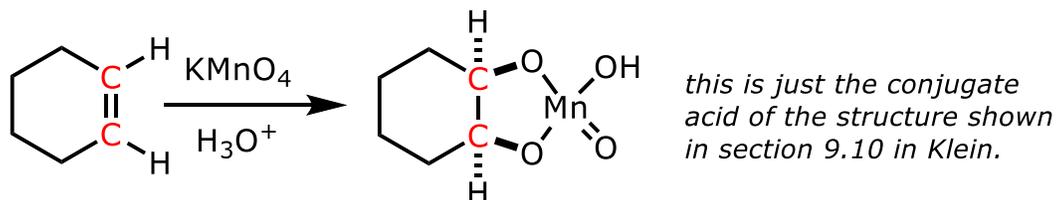
If the alkene is included in a ring in the starting material, the two carbonyl groups remain attached to one another in the product.



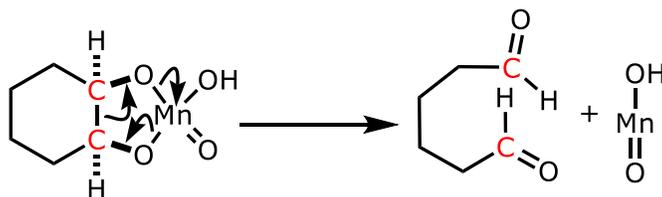
Acidic Potassium Permanganate – $\text{KMnO}_4/\text{H}_3\text{O}^+$

When KMnO_4 reacts with an alkene in **cold, alkaline (basic) conditions**, it is possible to obtain *cis*-diol products, as Klein points out in section 9.10. However, this reaction is not easy to control, and yields are typically low because permanganate is such a strong oxidizing agent that it readily oxidizes the diol product further. Nowadays chemists generally use OsO_4 instead.

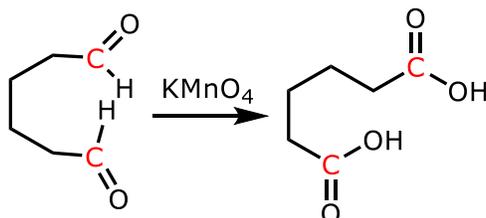
When alkenes are treated with KMnO_4 in acidic solutions, the diol is not formed. Instead, the alkene is cleaved. The reaction proceeds by the same mechanism at the start, forming a cyclic *manganate ester* (although since the reaction is under acidic conditions the structure is protonated). In the schemes below, the alkene carbons are highlighted throughout, so you can see where they end up in the product.



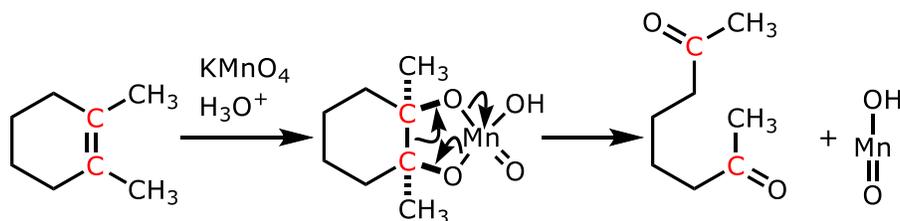
Now, under these conditions the manganate ester is not very stable and it undergoes a cyclic fragmentation process, which results in breaking the C-C bond between the two oxygens. Notice that in this case, since there was a hydrogen atom attached to each of the alkene carbons in the starting material, there is a hydrogen attached to the carbonyl carbon in the product and therefore the product that is initially formed is an aldehyde.



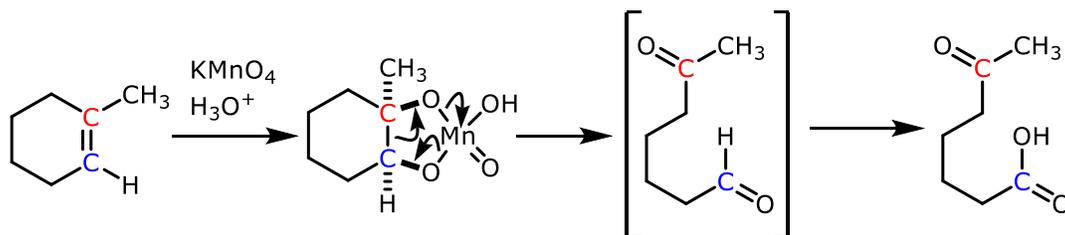
Aldehydes are very easily oxidized to carboxylic acids, and thus the aldehydes formed in the cleavage reaction do not survive. They are rapidly transformed into carboxylic acid groups, by a complex reaction whose mechanism you need not worry about.



Now, if the alkene had not had any hydrogens attached, the product in that case would have been a ketone rather than an aldehyde. Ketones are not easily oxidized further, and the reaction would have stopped at that stage.



If one of the alkene carbons had a hydrogen substituent, while the other did not, then we would get both acid and ketone groups in our product, as shown below.

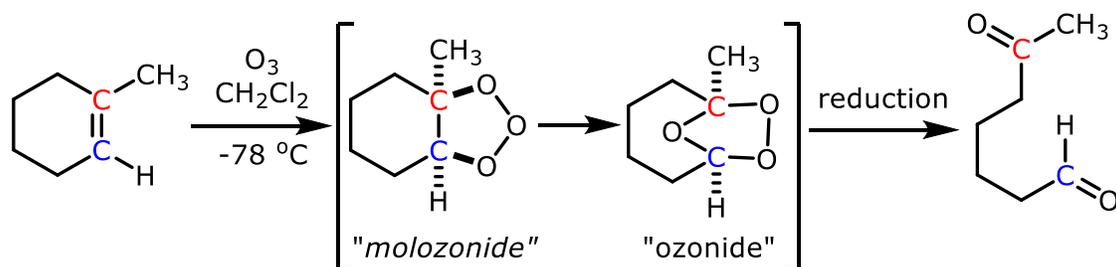


Ozonolysis

Ozone (O_3) is a gas that is easily prepared in the laboratory by exposing a stream of air or pure O_2 to a strong electric field. Commercial instruments to make ozone are relatively inexpensive and easy to operate. The electric field breaks down a certain amount of O_2 into highly reactive oxygen atoms, which go on to react with another molecule of O_2 to form O_3 . The gas emerging from the electric field is enriched in ozone, and can be bubbled through a solution of an alkene in a solvent like CH_2Cl_2 . The reaction is usually performed at $-78^\circ C$.

Ozone is a much better behaved reagent than permanganate, at least at low temperatures. The fundamental pattern is identical to that of the permanganate reaction, although the details of the reaction mechanism are quite different. Ozone cleaves alkenes, but it will not oxidize aldehyde groups to carboxylic acids. Klein shows a simple mechanism for the reaction of ozone with an alkene in section 9.11 on page 445 of your textbook. Notice that the first step is similar to that shown in section 9.1 for OsO_4 or $KMnO_4$ additions. The so-called

“molozonide” is unstable and it rapidly fragments and re-arranges to form a new structure referred to as the “ozonide”. The ozonide persists in solution at low temperatures.



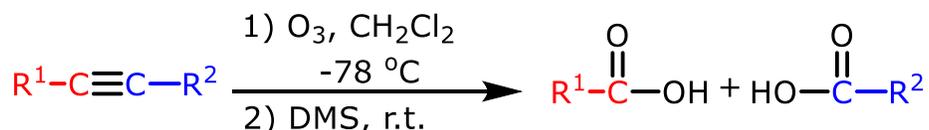
The reaction of ozone with most alkenes is very fast, so the ozone is consumed as quickly as it is added to the reaction solution and does not accumulate. However, once all the alkene has reacted, additional ozone does accumulate in the solution. Because ozone is bright blue, it is easy to see when the reaction is finished just by looking at the reaction!

To obtain the carbonyl cleavage product(s) from the ozonide, once the flow of O_3 has been stopped and excess O_3 in solution has been purged, a mild reducing agent is added to reduce the peroxide bonds in the ozonide. The details of how this occurs are not important, and depend on exactly what reducing agent is used. Most often *dimethylsulfide* (CH_3SCH_3) is added, and the solution is allowed to warm to room temperature before being worked up.

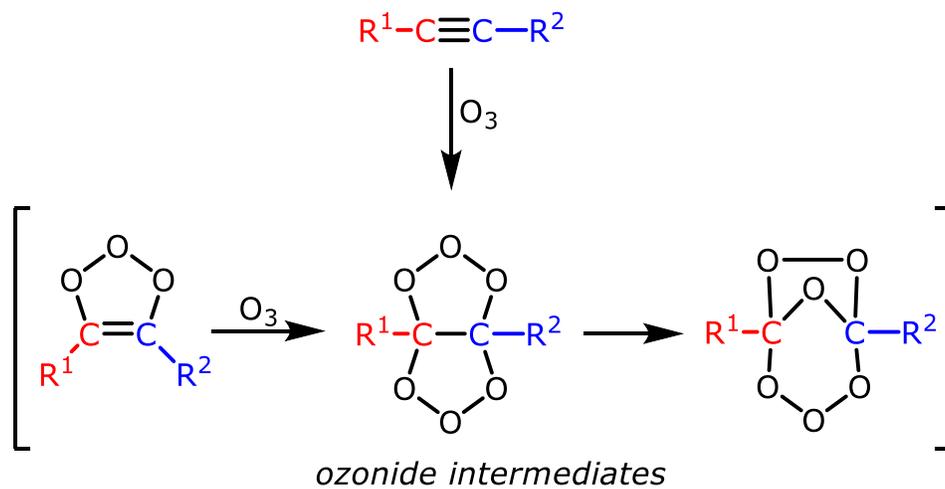


Solutions of ozone.
<http://www.ozonotech.com/sites/default/files2/images/news/ozone-treatment-polymer-solution.jpg>

Oxidative Cleavage Reactions of Alkynes



An alkyne is more highly oxidized than an alkene, so it should be no surprise that when it is oxidatively cleaved, the products obtained are also at a higher oxidation level. **Ozonolysis/reduction cleaves alkynes, forming carboxylic acid groups.**



The intermediate structures are similar to those formed in the ozonolysis of alkenes, but simply involve addition of a second molecule of ozone. Notice that the net result is to form 3 C-O bonds at each of the former alkyne carbons, and the result of reduction is to cleave the peroxidic bonds, just as before. You are not expected to be able to write detailed stepwise mechanisms for the rearrangement or reduction steps in this reaction.

About the Mechanisms

The addition of permanganate, or OsO_4 or O_3 to an alkene or alkyne is a concerted process known as a cycloaddition. The π -bond is broken and the new C-O bonds are formed simultaneously in one continuous flow of electron density. This type of reaction is called a pericyclic reaction, and we will discuss these reactions in more detail in Chapter 17 of Klein's text. It turns out that this mechanism has some very interesting and useful features, although in oxidative cleavages these features play little role.