

10.7: Oxidation Reactions of Alkenes

Alkenes undergo a number of reactions in which the C=C double bond is oxidized. For organic compounds, a conventional way to tell whether the oxidation or reduction occur is to check the number of C–O bonds or the C–H bonds. An **oxidation reaction** increase the number of C–O bonds or decrease the number of C–H bonds. On the other side a **reduction reaction** increase the number of C–H bonds or decrease the number of C–O bonds. The relative oxidation state of some common organic functional groups are listed here based on the trend.

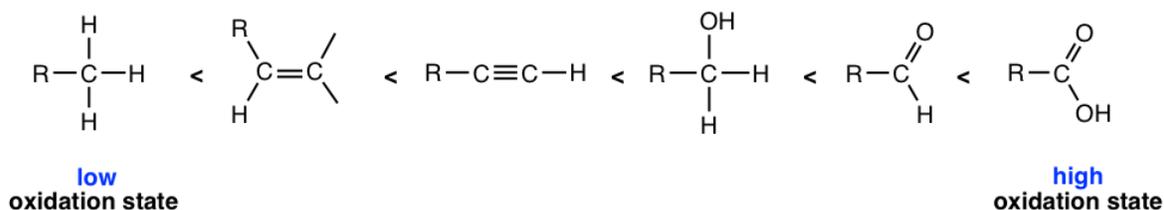


Figure 10.7a The relative oxidation state of some common organic functional groups

10.7.1 Syn 1,2-Dihydroxylation

1,2-Dihydroxylation, the conversion of the C=C double bond to 1,2-diol, is an oxidative addition reaction of alkene. Osmium tetroxide (OsO₄) is a widely used oxidizing agent for such purpose. Potassium permanganate can be used as well, although further oxidation is prone to occur to cleave the diol because it is a stronger oxidizing agent (**10.7.2**).

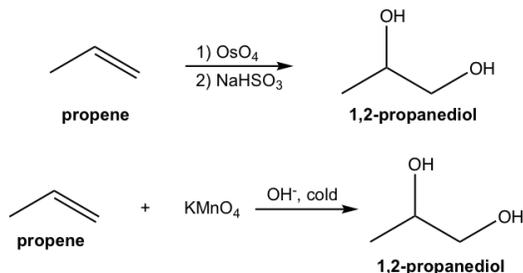


Figure 10.7b Example of 1,2-Dihydroxylation

The traditional method of 1,2-dihydroxylation with osmium tetroxide is a **two-step procedure**. Osmium tetroxide first reacts with alkene to form a cyclic osmate ester intermediate and this cyclic intermediate involves the **syn addition** of OsO₄ to the double bond. The cleavage of the O–Os bond of the intermediate then takes place in the second step with reducing agent NaHSO₃, without modifying the stereochemistry of the C–O bond. The diol formed therefore has the **syn** stereochemistry property.

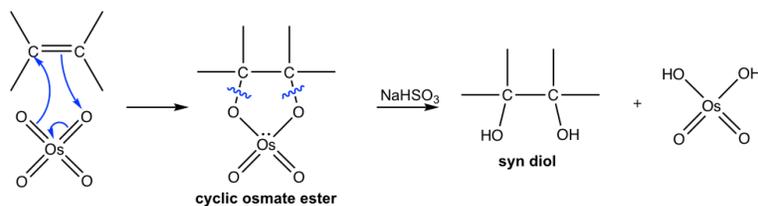
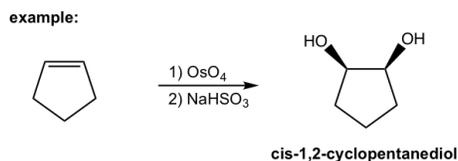


Figure 10.7c 1,2-dihydroxylation mechanism



Catalytic OsO₄ 1,2-Dihydroxylation

The 1,2-dihydroxylation with osmium tetroxide is an effective reaction that is used very often in the labs for the preparation of diol from alkene. However, this method has major drawbacks because osmium tetroxide is a highly toxic, volatile and expensive reagent. Improved methods have been developed that allow only a catalytic amount of OsO₄ being used in conjunction with a co-oxidant in a stoichiometric amount. *N*-methylmorpholine *N*-oxide (NMO) is one of the most commonly employed co-oxidants. In such

condition, osmium compounds are re-oxidized by NMO and can be reused to react with more alkenes, so only small molar percentage of OsO_4 is necessary in the reaction mixture. The reaction proceeds smoothly with syn diols produced in good yield.

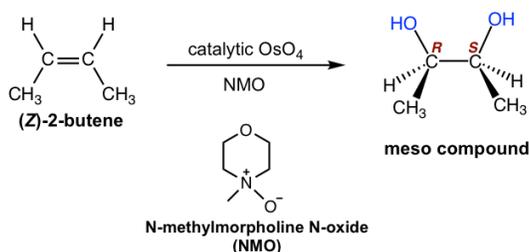
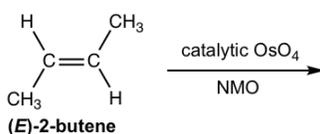


Figure 10.7d Example of a Catalytic OsO_4 1,2-Dihydroxylation

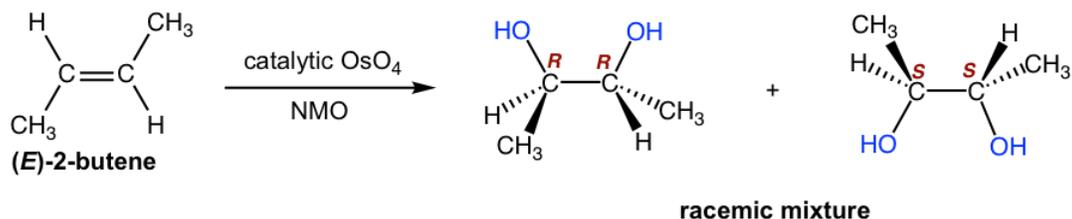
In terms of the stereochemistry of the product, although the syn addition could occur on either side of the alkene plane, that gives the same product which is the meso compound. This can be identified by either looking for the plane of symmetry of the product, or by assigning the absolute configuration on the chirality centers. Review the stereochemistry knowledge.

Examples Show product of following reaction:



Solution:

The syn addition occurs on either side of the alkene plane, so both enantiomers are obtained with same amount as racemic mixture.



10.7.2 Oxidative Cleavage of Alkenes

Cleavage with Ozone

With stronger oxidizing agent being applied, the $\text{C}=\text{C}$ double bond of alkenes can be oxidatively cleaved, and the alkene molecule is cleaved to smaller molecules.

The most effective way for cleaving alkene is to use ozone, O_3 , by a two-step process. Alkene is first reacted with ozone at very low temperature (-78°C) and then treated with dimethyl sulfide, $(\text{CH}_3)_2\text{S}$, (or $\text{Zn}/\text{CH}_3\text{COOH}$) to give the cleavage products. The whole process is called **ozonolysis**.

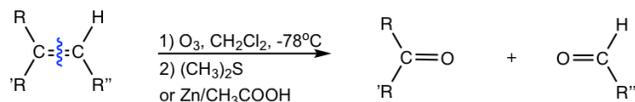


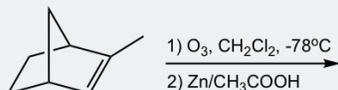
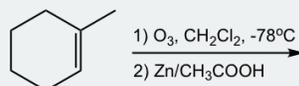
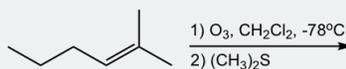
Figure 10.7e The process of Cleavage with Ozone

Ozonolysis results in the cleavage of the double bond, and each double bond carbon get bonded to an oxygen atom with a new double bond. The products of ozonolysis are aldehyde(s) and/or ketone(s), and the exact structures of the products depends on the structure of the initial alkene:

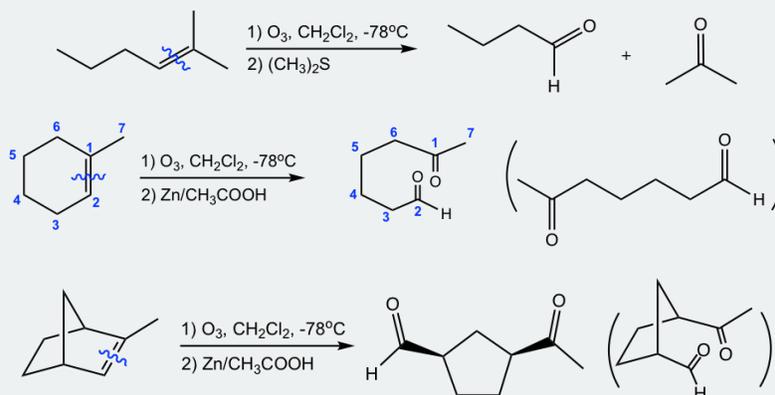
- Disubstituted alkene carbons are oxidatively cleaved to ketone;
- Monosubstituted alkene carbons are oxidatively cleaved to aldehyde;
- Unsubstituted alkene carbons are oxidatively cleaved to formaldehyde (HCHO).

Examples

Show ozonolysis products of following reactions:



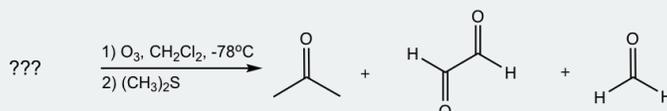
Hint: To figure out the structure of ozonolysis product(s), “cut” the double bond, then “add” a “=O” (double bonded oxygen) to each carbon.



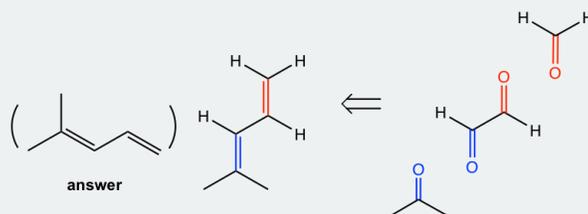
As shown with above examples, ozonolysis reaction is useful as a synthetic tool for certain aldehyde and ketone. Meanwhile, it is also a method for determining the position of double bonds in an alkene by working backward from the structure of the products.

Examples

Determine the structure of the alkene:



Approach: To determine the structure of initial alkene, we can work backwards by connecting two C=O bonds in the products together. The two C=O bonds are “connected” to give a C=C bond with all oxygen atoms “removed”. In this example, the two blue C=O bonds gives the blue C=C bond, and the two red C=O bonds gives the red C=C bond.



Mechanism for Ozonolysis

The hints mentioned earlier is to help us solving the problems with ozonolysis reaction, not the reaction mechanism. The mechanism of ozonolysis reaction is rather complicated that involves the formation of initial cyclic ozonide that decompose to

fragments, and the fragment recombine to form a new cyclic ozonide, which is reduced to give products.

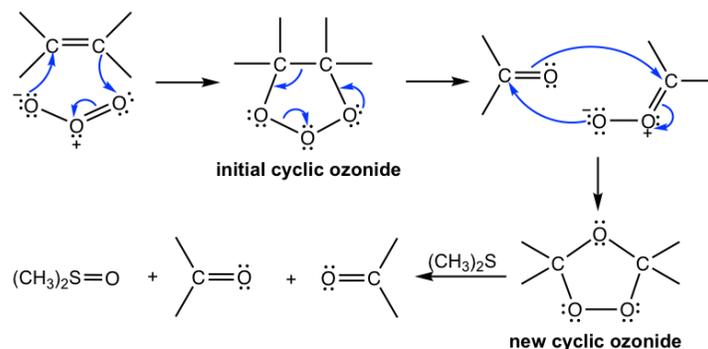


Figure 10.7f Mechanism for Ozonolysis

Cleavage with Potassium Permanganate KMnO₄

Potassium permanganate, **KMnO₄**, is another oxidizing agent that cleaves the C=C double bond of an alkene. Under hot basic condition, the oxidative cleavage products of alkenes could involve ketone, salt of carboxylic acid or carbon dioxide depends on the different substituent patterns on the alkene:

- Disubstituted alkene carbons are oxidatively cleaved to ketone;
- Monosubstituted alkene carbons are oxidatively cleaved to the carboxylic acid (in salt format);
- Unsubstituted alkene carbons are oxidatively cleaved to CO₂ and H₂O.

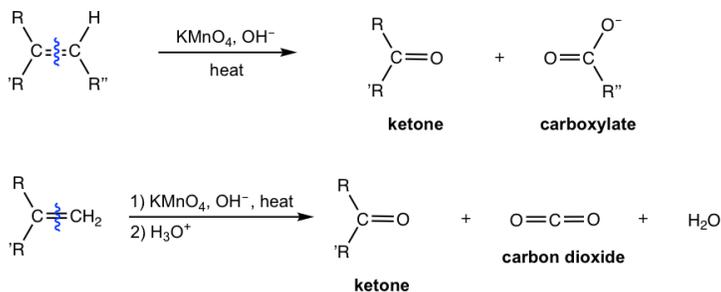


Figure 10.7g Cleavage with Potassium Permanganate KMnO₄

KMnO₄ is a stronger oxidizing agent that further oxidize the initial cleavage products, therefore aldehyde is further oxidized to carboxylic acid (in salt format under basic condition). For terminal unsubstituted alkene carbons, the initial product is HCHO, which is then further oxidized to carboxylate CO₃²⁻ in basic condition. Acidification of CO₃²⁻ produces H₂CO₃ that decomposes to CO₂ and H₂O. Because of over oxidation, KMnO₄ is not the useful reagent for the synthesis of aldehyde/ketone from alkenes.

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