

9.12: OXIDATION OF ALKENES - EPOXIDATION

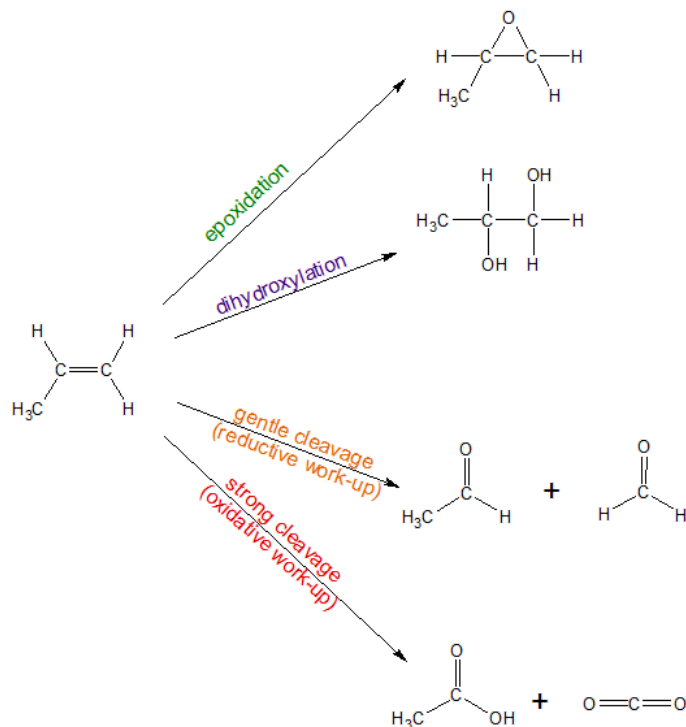
Learning Objective

- recognize organic oxidation and reduction reactions
- predict the products/specify the reagents for epoxidation of alkenes

OXIDATION - A CLOSER LOOK

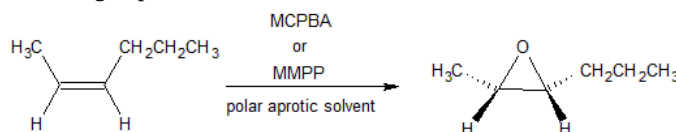
There are a variety of oxidative reagents that can react with alkenes. These reagents oxidize the alkene to different degrees and have different synthetic applications. It can be helpful to describe the relative oxidative strength of the reagents. Some reagents are so strong that the carbon chain will be cleaved at the alkene. This reactivity can also be a useful distinction. Before we explore the specific details of these different reaction pathways, let's look at the overall patterns of functional group reactivity.

There are four levels of oxidation for alkenes. The gentlest and least oxidative is epoxide (oxacyclopropane) formation in which the vinyl carbons share a single oxygen atom as a three membered ring. Moderate oxidation will convert the alkene into a vicinal diol in which each vinyl carbon is bonded to an independent oxygen atom. The stronger oxidative reactions cleave the carbon chain at the alkene. While the overall chemical process is an oxidation reaction, the work-up (second step) of the reaction can be performed under reductive or gentle conditions or a strong, oxidative cleavage reaction can occur with the strongest reagents. These four reaction pathways are summarized below.



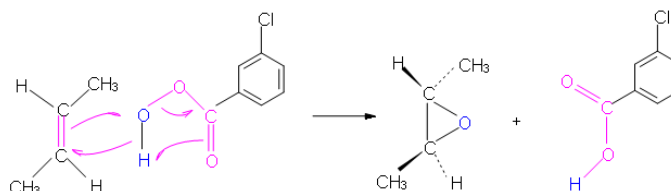
EPOXIDE (OXACYCLOPROPANE) SYNTHESIS BY PEROXYCARBOXYLIC ACID

Oxacyclopropane rings, also called epoxide rings, are useful reagents that may be opened by further reaction to form anti vicinal diols. One way to synthesize oxacyclopropane rings is through the reaction of an alkene with a peroxycarboxylic acid, such as MCPBA (m-chloroperoxybenzoic acid). Oxacyclopropane synthesis by peroxycarboxylic acid requires an alkene and a peroxycarboxylic acid as well as an appropriate solvent. The peroxycarboxylic acid has the unique property of having an electropositive oxygen atom on the COOH group. The reaction is initiated by the electrophilic oxygen atom reacting with the nucleophilic carbon-carbon double bond. The mechanism involves a concerted reaction with a four-part, circular transition state. The result is that the originally electropositive oxygen atom ends up in the oxacyclopropane ring and the COOH group becomes COH .



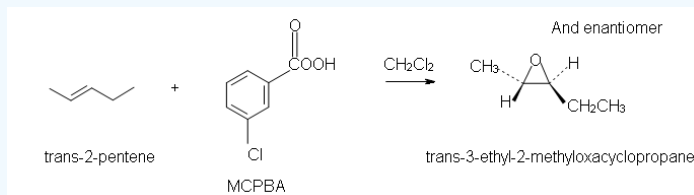
MECHANISM

The mechanism is a concerted reaction between the alkene and peroxyacid. As seen with other concerted reactions, it is stereospecific: a cis-alkene will produce a cis-epoxide and a trans alkene will produce a trans-epoxide.



Peroxydicarboxylic acids are generally unstable. An exception is MCPBA, shown in the mechanism above. Often abbreviated MCPBA, it is a stable crystalline solid. Consequently, MCPBA is popular for laboratory use. However, MCPBA can be explosive under some conditions. Peroxydicarboxylic acids are sometimes replaced in industrial applications by monoperphthalic acid, or the monoperoxyphthalate ion bound to magnesium, which gives magnesium monoperoxyphthalate (MMPP). In either case, a nonaqueous solvent such as chloroform, ether, acetone, or dioxane is used. This is because in an aqueous medium with any acid or base catalyst present, the epoxide ring is hydrolyzed to form a vicinal diol, a molecule with two OH groups on neighboring carbons. (For more explanation of how this reaction leads to vicinal diols, see below.) However, in a nonaqueous solvent, the hydrolysis is prevented and the epoxide ring can be isolated as the product. Reaction yields from this reaction are usually about 75%. The reaction rate is affected by the nature of the alkene, with more nucleophilic double bonds resulting in faster reactions.

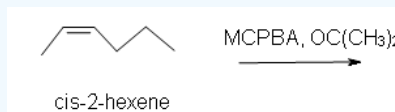
Example 9.12.1



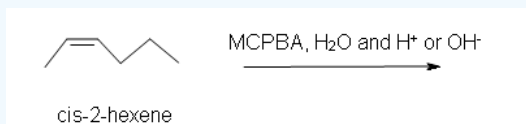
Since the transfer of oxygen is to the same side of the double bond, the resulting oxacyclopentane ring will have the same stereochemistry as the starting alkene. A good way to think of this is that the alkene is rotated so that some constituents are coming forward and some are behind. Then, the oxygen is inserted on top. (See the product of the above reaction.) One way the epoxide ring can be opened is by an acid catalyzed oxidation-hydrolysis. Oxidation-hydrolysis gives a vicinal diol, a molecule with OH groups on neighboring carbons. For this reaction, the dihydroxylation is *anti* since, due to steric hindrance, the ring is attacked from the side opposite the existing oxygen atom. Thus, if the starting alkene is trans, the resulting vicinal diol will have one S and one R stereocenter. But, if the starting alkene is cis, the resulting vicinal diol will have a racemic mixture of S, S and R, R enantiomers.

Exercise 9.12.1

1. Predict the product of the reaction of cis-2-hexene with MCPBA (meta-chloroperoxybenzoic acid) a) in acetone solvent.



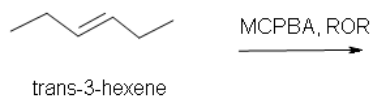
- b) in an aqueous medium with acid or base catalyst present.



2. Predict the product of the reaction of trans-2-pentene with magnesium monoperoxyphthalate (MMPP) in a chloroform solvent.



3. Predict the product of the reaction of trans-3-hexene with MCPBA in ether solvent.

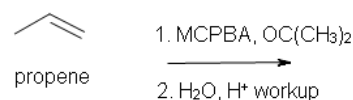


4. Predict the reaction of propene with MCPBA.

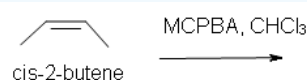
a) in acetone solvent



b) after aqueous work-up.

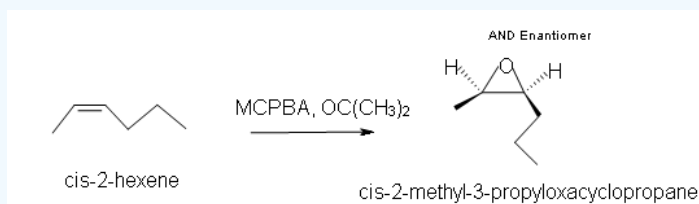


5. Predict the reaction of cis-2-butene in chloroform solvent.

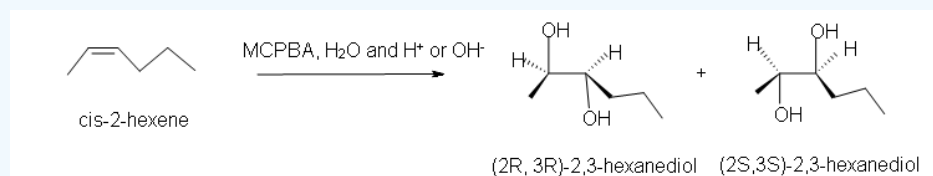


Answer

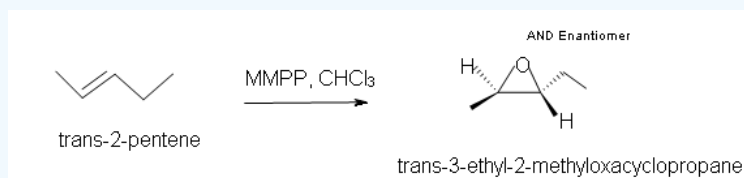
1. a) Cis-2-methyl-3-propyloxacyclopropane



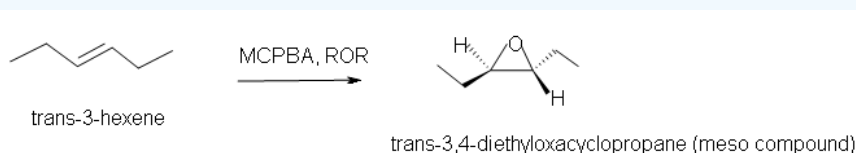
b) Racemic (2R,3R)-2,3-hexanediol and (2S,3S)-2,3-hexanediol



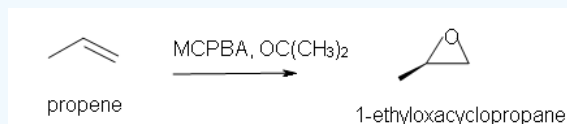
2. Trans-3-ethyl-2-methyloxacyclopropane.



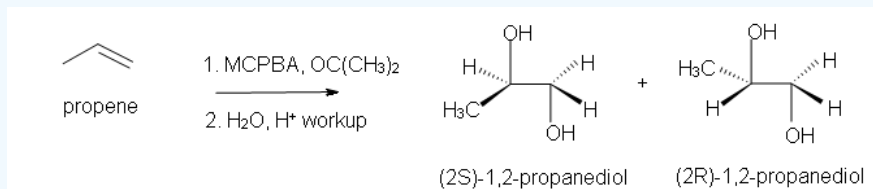
3. Trans-3,4-diethyloxacyclopropane.



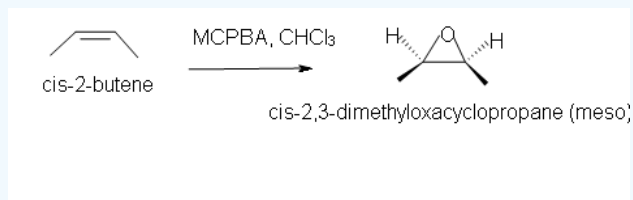
4. a) 1-ethyloxacyclopropane



b) Racemic (2S)-1,2-propanediol and (2R)-1,2-propanediol



5. Cis-2,3-dimethyloxacyclopropane



CONTRIBUTORS AND ATTRIBUTIONS

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- Shivam Nand
- [Organic Chemistry With a Biological Emphasis](#) by Tim Soderberg (University of Minnesota, Morris)
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