# ELECTROPHILIC ADDITIONS OF ALKENES AS THE
# COUNTERPART OF ELIMINATIONS

INTRODUCTION - Chapter 8 is mostly about alkene reactions. That is, how one can transform alkenes into other functional groups. Most of these reactons are **electrophilic additions**, or the addition of electrophiles across the double bond. Several of these reactions amount to addition of water to the π-bond. The result is the transformation of alkenes into alcohols. We now look at the generalities of this type of reaction (electrophilic addition) and then we look at each reaction individually.

The C=C π-bond of alkenes is a source of electrons. It is considered a **weak** base or nucleophile. As such, it can react with **strong electrophiles**. We have already learned how to identify electrophiles, but the π-bond requires strong electrophiles to react with. These can be strong proton acids, or species containing atoms with incomplete octets (Lewis acids). Examples of strong proton acids are HBr and H_2SO_4. Examples of Lewis acids are BH_3, transition metal salts such as $HgSO_4$, and carbocations.

The addition of strong electrophiles to the C=C π-bond can be viewed as the opposite of the elimination reaction, as illustrated below.
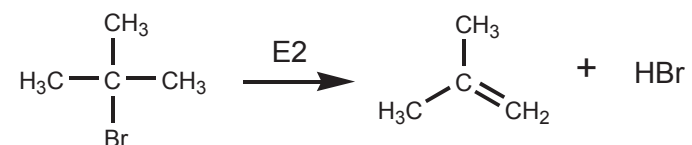

Elimination results in net loss of HBr to form a new C=C bond.
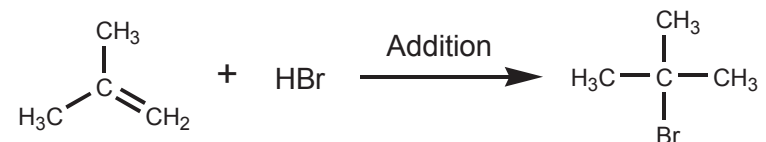
Addition of HBr (a strong electrophile) across the π-bond
forms a new functional group, in this case an alkyl halide.

According to **Saytzeff's rule**, in elimination reactions where formation of several alkenes is possible, the most highly substituted alkene predominates as a product.

E1 or E2

Saytzeff's product

Br
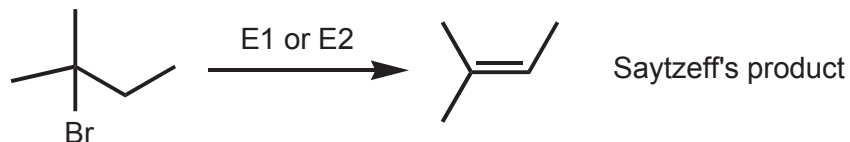
Conversely, **Markovnikov's rule** says that *in addition reactions of proton acids to alkenes, the proton of the strong acid preferentially bonds to the carbon in the π-bond that already holds the greater number of hydrogens on it*. In the alkene shown below, C-2 has more protons attached to it (one) than C-1 (none). Accordingly, the hydrogen from HBr bonds to C-2 and the bromine bonds to C-1.

HBr

1 2

Markovnikov's product,
a tertiary bromide

1 2

Br
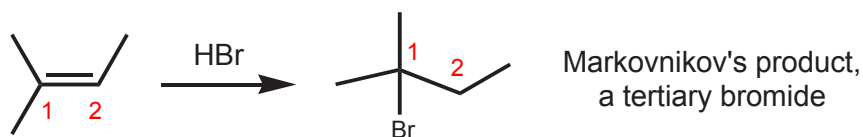
This preferred orientation is referred to as **Markovnikov orientation**. This suggests the possibility that another product with opposite orientation, called the **anti-Markovnikov product**, might form. Given that this product does not normally form under ordinary conditions, the question then is, are there special conditions under which it could form? The answer is yes, but with a very limited scope. We'll address that point later.

HBr

?

1 2

1 2

Br

Anti-Markovnikov's product,
a secondary bromide
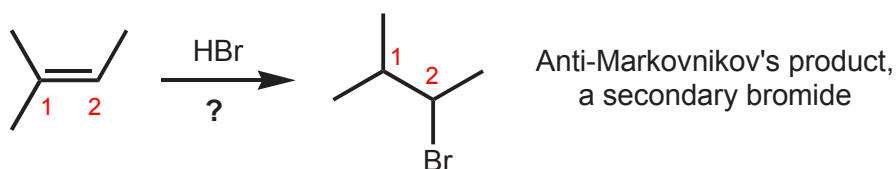
Another way to state Markovnikov's rule, in this case, is to say the the tertiary bromide will form preferentially over the secondary bromide. If the electrophilic part of the reactant (H⁺) adds to the least substituted carbon (C-2), then the nucleophilic part (Br⁻) adds to the most substituted carbon (C-1). The degree of substitution in this case refers to the number of alkyl groups originally attached to the π-bond. This is another way by which Markovnikov's rule becomes the counterpart of Saytzeff's rule. The two statements are complementary.

Modern understanding of ionic mechanisms provides the key to Markovnikov's rule. In the first step of the reaction, which is protonation of the π-bond, the most stable carbocation forms. This leads directly to formation of the tertiary bromide, i.e. Markovnikov's product.


3° cation

3° bromide
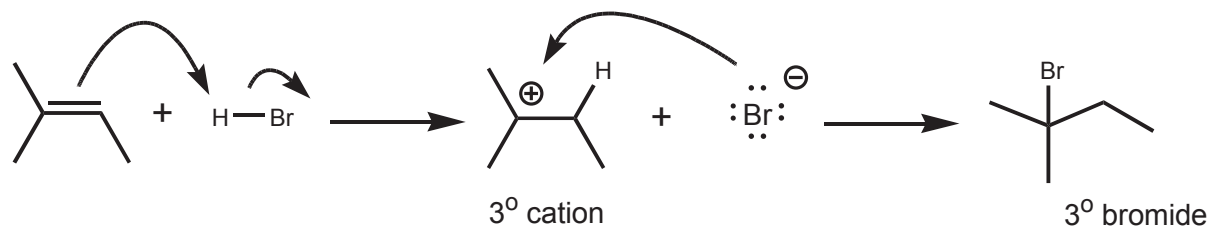
Here is another example involving a cyclic alkene:
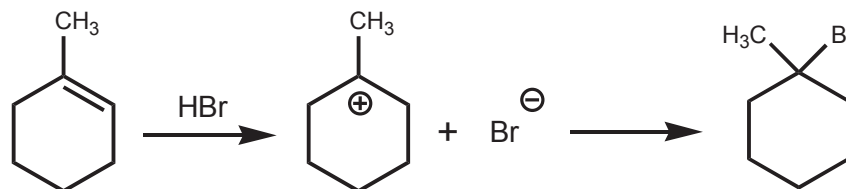
REGIOSELECTIVITY - A reaction such as the above that leads to **preferential formation of one of several possible structural isomers** is said to be *regioselective*. The addition of proton acids to alkenes, which follows an **ionic mechanism**, is an example of a regioselective reaction.

FORMATION OF ANTI-MARKOVNIKOV PRODUCTS VIA FREE RADICAL MECHANISMS. Ionic mechanisms favor formation of the Markovnikov product through formation of the most stable carbocation. However, one can manipulate conditions to favor formation of the anti-Markovnikov product through a different mechanism, or a different series of steps. This is the case in the addition of HBr to alkenes **in the presence of peroxides**. Peroxides are well known *free radical initiators*. This promotes a reaction where the reactants add in a different order and by a different mechanism, in this case with formation of the most stable free radical.

2° bromide, anti-Markovnikov product.
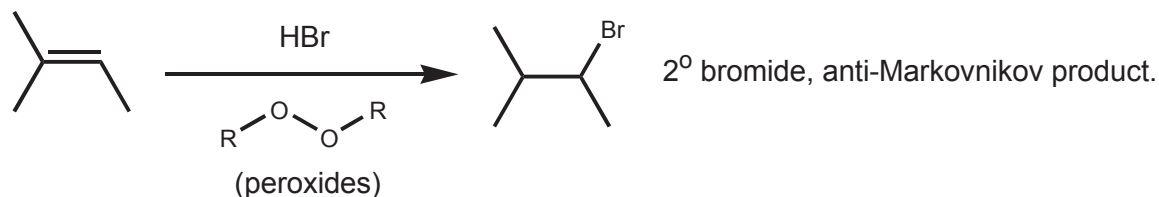
(peroxides)

Another example:
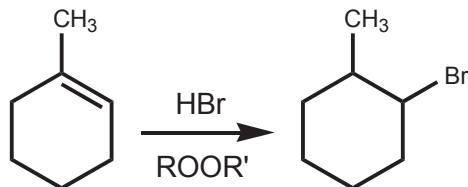
Refer to section 8-3B of the Wade textbook (p. 319 of the 5th ed.) and remember the following points.

a) The anti-Markovnikov addition of proton acids to alkenes **works only with HBr**.
b) It requires the presence of peroxides, which are **free radical** initiators.
c) The reaction follows a free radical mechanism, where the bromine is first to add to the alkene with formation of the **most stable free radical**, which eventually leads to the anti-Markovnikov product.

Other proton acids that follow Markovnikov's rule include HCl. HI, and H_2O (acid-catalyzed) to form alcohols. We now summarize all the important addition reactions of alkenes, including the markovnikov addition of proton acids and water. Then we address some concepts and mechanistic considerations relevant to these reactions.

Alkenes are primarily prepared by elimination reactions of molecules that contain good leaving groups attached to sp^3 carbons. Examples of such reactions are dehydrohalogenations with strong base, and acid-catalyzed dehydrations of alcohols. The opposite of an elimination is an addition reaction. **In an addition reaction an alkene adds elements to each of the carbons involved in the π-bond, resulting in formation of sp^3 carbons from sp^2 carbons.** This is one of the most important types of reactions that alkenes undergo.

Another important type of reaction involving alkenes is oxidative cleavage. In such reactions the carbon-carbon π-bond is completely broken by the action of an oxidizing agent, resulting in more oxidized forms of carbon, such as aldehydes, ketones, and carboxylic acids. All these reactions are covered in chapter 8 of the Wade text, 4th ed.

The following is a summary of the most important representative types of these reactions. For full details, please refer to the textbook.

1. ADDITION OF HBr, HCl, and HI. The addition of these substances to an alkene proceeds by an ionic mechanism, with formation of the most stable carbocation. Therefore, it follows Markovnikov's Rule.
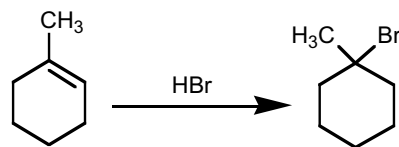

An Anti-Markovnikov variation requires the presence of peroxides as free radical initiators, and can only be performed with HBr. The mechanism proceeds with formation of the most stable free radical, which results in formation of the Anti-Markovnikov product.
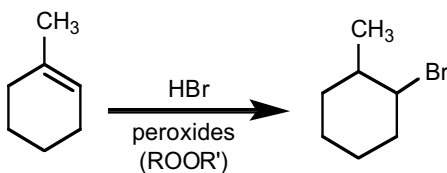
## THE NEXT THREE REACTIONS ADD THE ELEMENTS OF WATER (H/OH) ACROSS THE DOUBLE BOND

2. ACID-CATALYZED ADDITION OF WATER. Produces Markovnikov alcohols, it is an equilibrium reaction, and proceeds with formation of carbocations in the rate-determining step.
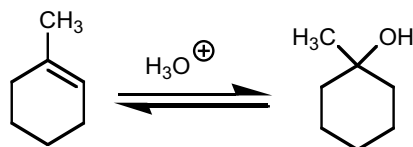

3. OXYMERCURATION-DEMERCURATION SEQUENCE. This sequence consists of two steps. It is the most effective way to prepare Markovnikov alcohols from alkenes.
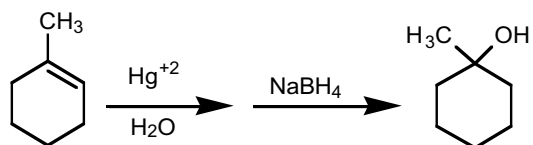

4. HYDROBORATION-OXIDATION SEQUENCE. This sequence also consists of two steps. It is the most effective way to prepare anti-Markovnikov alcohols from alkenes. The components of water (H/OH) add to the π-bond with *syn*-stereochemistry. If chiral centers result from this reaction, the product is obtained as an enantiomeric mixture.

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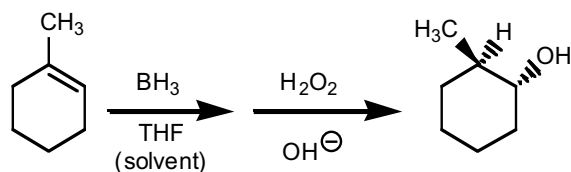
5. HALOGEN ADDITION. This reaction is performed most frequently with bromine and chlorine. It adds a halogen atom to each of the two carbons comprising the π-bond with *anti*-stereochemistry. If chiral centers result from this reaction, the product is obtained as an enantiomeric mixture.
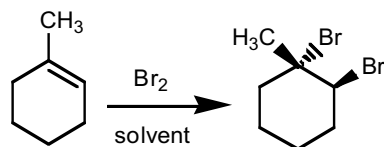
6. HALOGEN ADDITION IN THE PRESENCE OF WATER (halohydrin formation). Produces Markovnikov alcohols with a neighboring halogen. The OH and the halogen add with *anti*-stereochemistry. If chiral centers result from this reaction, the product is obtained as an enantiomeric mixture.
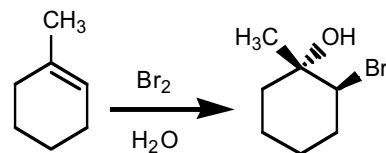

## THE NEXT TWO REACTIONS ADD TWO HYDROXYL GROUPS (OH) ACROSS THE DOUBLE BOND

7. SYN HYDROXYLATION. Adds two hydroxyl groups accross the π-bond with *syn*-stereochemistry. It can be performed with two reagent mixtures: pot assium permanganate in basic medium, or osmium tetroxide in the presence of hydrogen peroxide. If chiral centers result from this reaction, the product is obtained as an enantiomeric mixture.
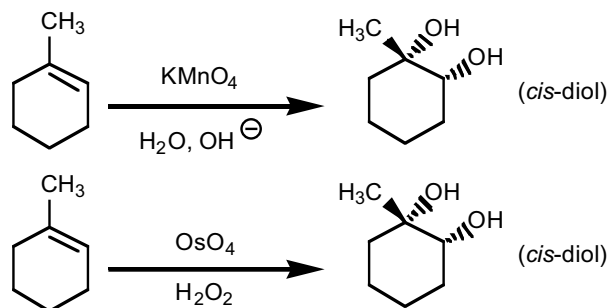
8. ANTI-HYDROXYLATION SEQUENCE. Adds two hydroxyl groups accross the π-bond with *anti*-stereochemistry. It proceeds in two steps via an epoxide (three-membered ring ether). If chiral centers result from this reaction, the product is obtained as an enantiomeric mixture.
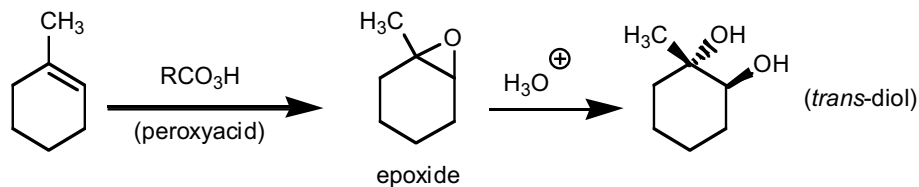
9. CATALYTIC HYDROGENATION. Adds hydrogen accross the π-bond with *syn*-stereochemistry. It basically transforms an akene into an alkane.
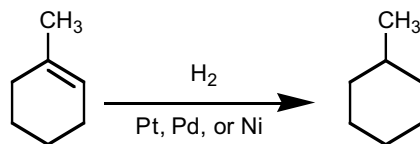
MAIN OXIDATIVE CLEAVAGE REACTIONS

1. CLEAVAGE WITH HOT, CONCENTRATED POTASSIUM PERMANGANATE yields ketones and/or carboxylic acids, depending on whether the carbon in question is in the middle of a chain or at the end of a chain in the product.
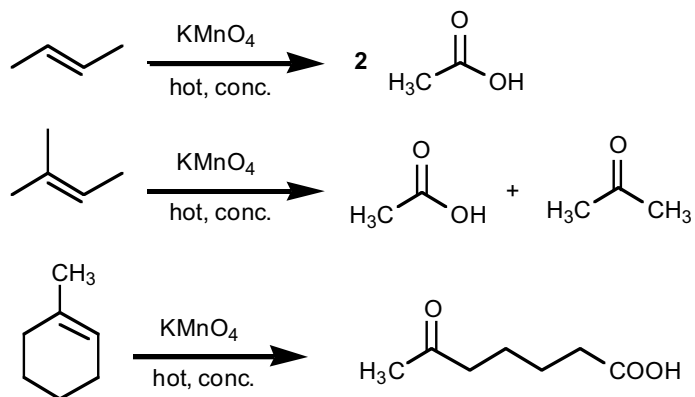
2. OZONOLYSIS. Similar to the above, but it yields only carbonyl compounds (aldehydes or ketones). Ozone is required for the reaction, but the other reagent may vary from one context to another.