Reactions of Alkenes

Typical type: addition

$$\text{C=C} \quad + \quad \text{Y—Z} \quad \longrightarrow \quad \overset{|}{\underset{Y}{\text{C}}}\overset{|}{\underset{Z}{\text{C}}}$$

substrate   reagent   product
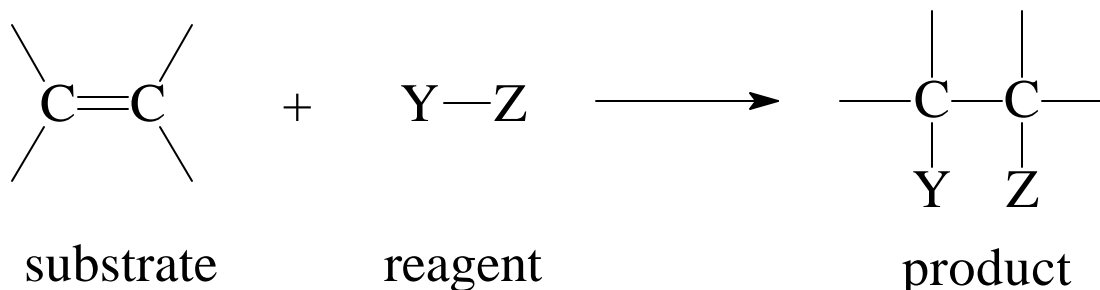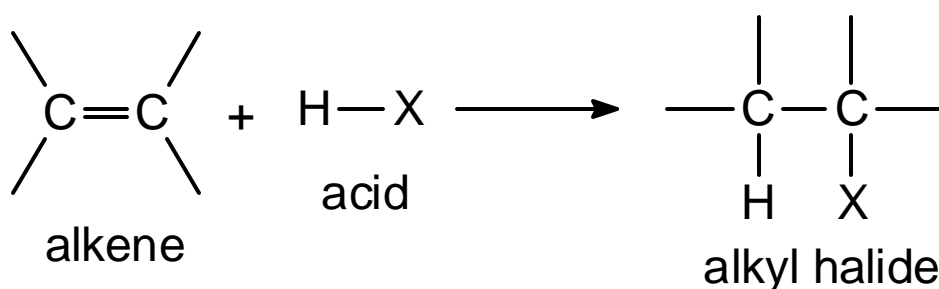
Mechanism: Usually <u>not</u> one simple step.

Weaker π-bond broken, also Y - Z bond. Energy provided by formation of C - Y and C - Z bonds.

π-bond: source of electrons.
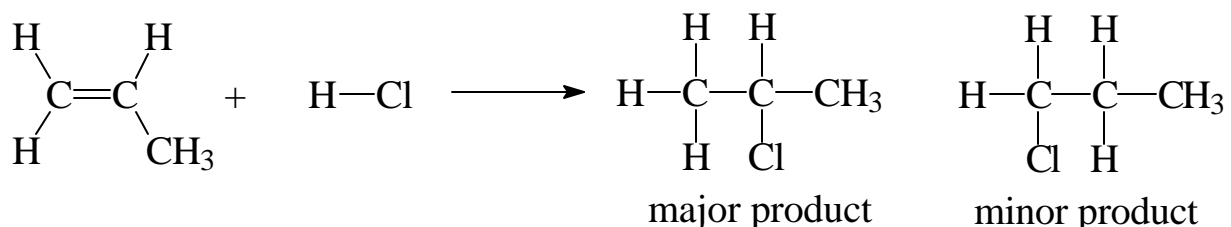Reagent: typically electrophile or free radical.
Therefore, electrophilic or free radical addition.

Addition of Acids & Markovnikov's Rule

$$\text{C=C} \quad + \quad \text{H—X} \quad \longrightarrow \quad \overset{|}{\underset{H}{\text{C}}}\overset{|}{\underset{X}{\text{C}}}$$

    alkene   acid   alkyl halide

HX = HCl, HBr, HI (or KI + H_3PO_4), HOH (with H_3O^+)

Markovnikov rule: Polar (ionic) addition of an acid to a double bond — the hydrogen preferentially attaches itself to the carbon which already has the greater number of hydrogens <u>directly</u> attached. This preference is strong; we say these are highly *regioselective* or *regiospecific* reactions.
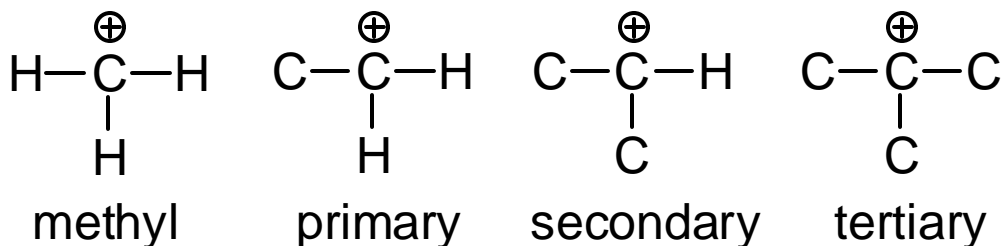
$$H_2C=CH-CH_3 \quad + \quad H-Cl \quad \longrightarrow \quad H-CH_2-CHCl-CH_3 \qquad H-CH_2-CHCl-CH_3$$

major product   minor product

HCl, HBr, HI (or KI + H_3PO_4) and H_2O (with H_3O^+; water by itself is not acidic enough to react) follow this rule.

<u>Reaction Mechanism</u>

Addition of Bronsted-Lowry acids to alkenes takes place in two steps. In the first step the proton grabs the electrons in the π bond [electrophilic attack by the proton], and in so doing, forms a bond between itself and one of the carbons. The other carbon develops a positive charge – a *carbocation* is formed. This is the slower of the two steps.
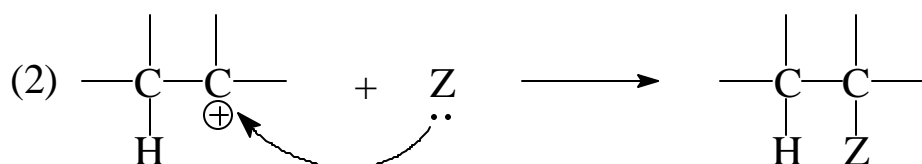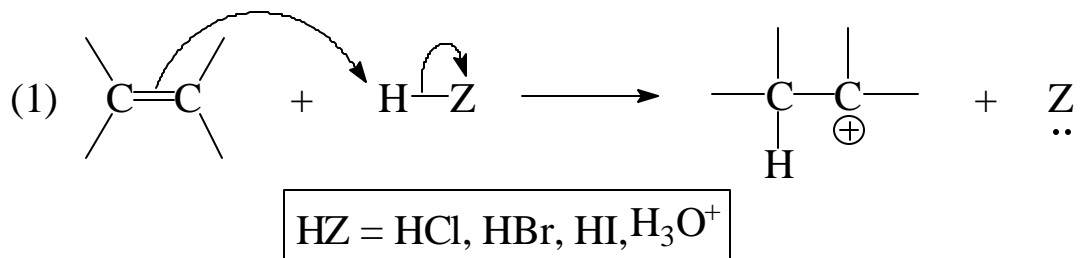
In the second step, the positively charged carbon [electrophile] in the carbocation unites with the conjugate base [nucleophile] of the Bronsted-Lowry acid, to produce the final product.

In the examples below, note that if each of the doubly bonded carbons of the alkene does not have the same number of carbon atoms attached, a different class of carbocation will result, depending on which carbon becomes attached to the incoming hydrogen ion. By "class" of carbocation we mean methyl, primary (1º), secondary (2º), or tertiary (3º).

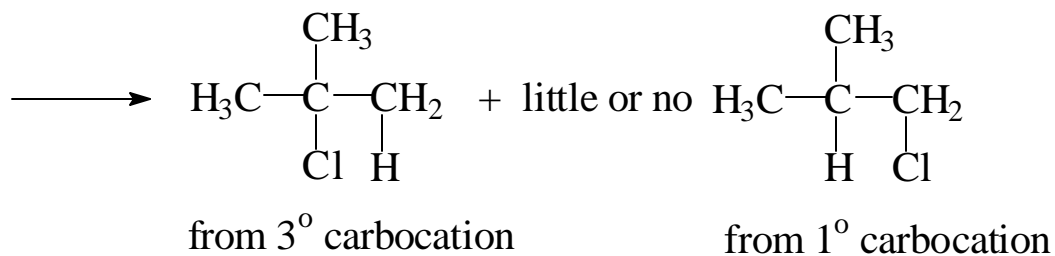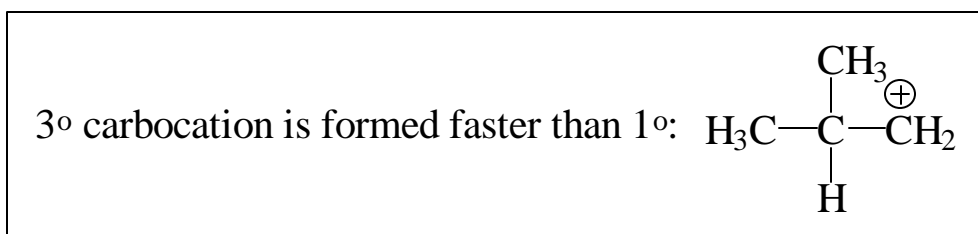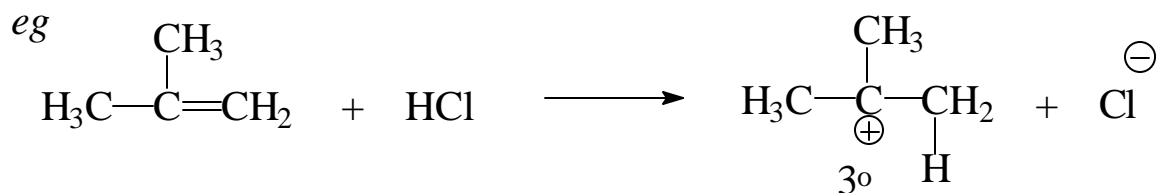$$\overset{\oplus}{\underset{\underset{\displaystyle H}{|}}{H-C-H}} \qquad \overset{\oplus}{\underset{\underset{\displaystyle H}{|}}{C-C-H}} \qquad \overset{\oplus}{\underset{\underset{\displaystyle C}{|}}{C-C-H}} \qquad \overset{\oplus}{\underset{\underset{\displaystyle C}{|}}{C-C-C}}$$

methyl   primary   secondary   tertiary

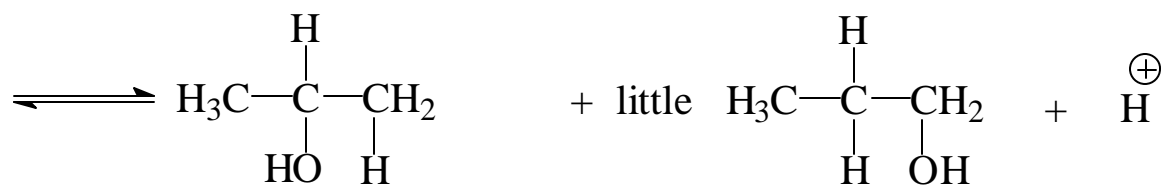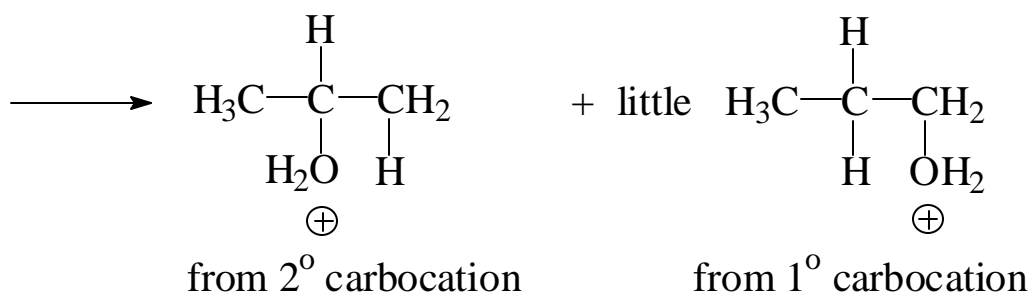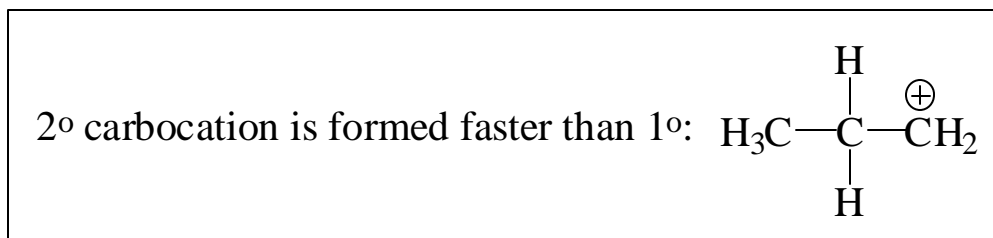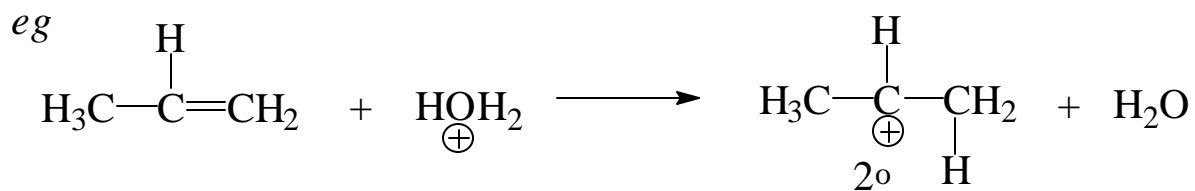(Methyl carbocation cannot form by attachment of a proton to an alkene, since the smallest alkene has two carbons.)

Also, note that when we say a step in a mechanism is "rate limiting" we mean that it is the slowest step and that the reaction cannot proceed faster than this step. In the examples that follow, the rate limiting step involves the formation of an unstable (high energy) intermediate carbocation.

(1) $C=C$ + $H-Z$ $\longrightarrow$ $-\overset{|}{\underset{H}{C}}-\overset{|}{\underset{\oplus}{C}}-$ + Z

$$\boxed{HZ = HCl, HBr, HI, H_3O^+}$$

(2) $-\overset{|}{\underset{H}{C}}-\overset{|}{\underset{\oplus}{C}}-$ + Z $\longrightarrow$ $-\overset{|}{\underset{H}{C}}-\overset{|}{\underset{Z}{C}}-$

Step 1 is rate limiting.

eg

$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2$ + HCl $\longrightarrow$ $H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{3o}{\overset{\oplus}{C}}}-\overset{|}{\underset{H}{C}H_2}$ + $Cl^{\ominus}$

$\boxed{3^o \text{ carbocation is formed faster than } 1^o: \quad H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{H}{C}}-\overset{\oplus}{C}H_2}$

$\longrightarrow$ $H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{Cl}{C}}-\overset{|}{\underset{H}{C}H_2}$ + little or no $H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{H}{C}}-\overset{|}{\underset{Cl}{C}H_2}$

from 3° carbocation   from 1° carbocation

eg

$$H_3C-\overset{\overset{\displaystyle H}{|}}{C}=CH_2 \quad + \quad H\overset{\oplus}{O}H_2 \quad \longrightarrow \quad H_3C-\overset{\overset{\displaystyle H}{|}}{\underset{\oplus}{C}}-\overset{|}{\underset{H}{C}H_2} \quad + \quad H_2O$$

2o

2o carbocation is formed faster than 1o: $H_3C-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\oplus}{C}H_2$

$$\longrightarrow \quad H_3C-\overset{\overset{\displaystyle H}{|}}{C}-CH_2 \quad + \text{ little } \quad H_3C-\overset{\overset{\displaystyle H}{|}}{C}-CH_2$$

$\underset{\oplus}{H_2O}$ H   H $\underset{\oplus}{OH_2}$

from 2° carbocation   from 1° carbocation

$$\rightleftharpoons \quad H_3C-\overset{\overset{\displaystyle H}{|}}{C}-CH_2 \quad + \text{ little } \quad H_3C-\overset{\overset{\displaystyle H}{|}}{C}-CH_2 \quad + \quad \overset{\oplus}{H}$$

HO H   H OH

A fact about carbocations:

The order of stability of carbocations is:

3° (tertiary) > 2° (secondary) > 1° (primary) > methyl
most stable   least stable

Reason –   Charge and electrons are most *delocalized* in 3° and most *localized* in methyl, with 2° being more delocalized than 1°. [It can be shown by quantum mechanics that spreading electrons over a larger volume of space — delocalization — leads to lower energy.]

Thus, orientation of addition (regioselectivity) seems to depend on the formation of the more stable carbocation; in other words the more stable carbocation is formed (much) faster.

Why?

It is usually the case when a high energy intermediate is formed that the energy barrier (E_{act}) that must be overcome for its formation is lower for more stable intermediates and higher for less stable ones. This is because the transition state is similar in structure to the intermediate and, so, whatever structural features make the intermediate lower in energy will also make the transition state lower in energy and, hence, lower the E_{act}. If the E_{act} is lower the intermediate will form faster.

It is also usually true that the relative reactivity of two different alkenes will depend on which forms the more stable carbocation – the one forming the more stable carbocation will react faster.

Electrophilic Addition with Electrophiles Other Than H⁺

Halogenation —

$$X_2 = Br_2 \text{ or } Cl_2$$

eg
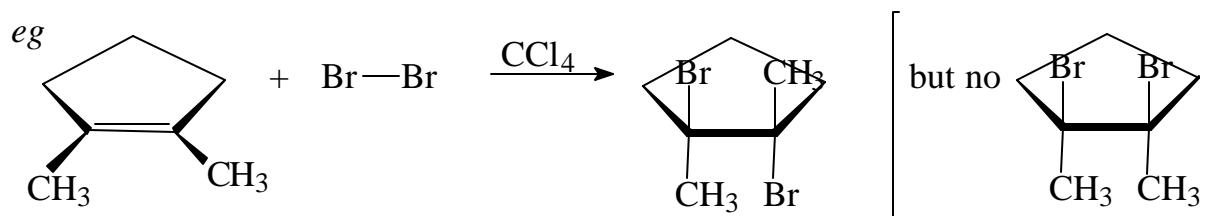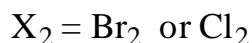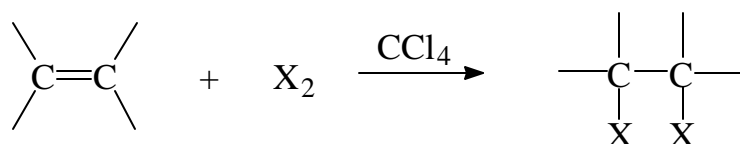
ANTI ADDITION ONLY

[By *anti* addition we mean that the two halves of the electrophilic reagent (in this case the two bromine atoms) attach on opposite faces of the molecule. So, in the product the bromines are *trans* to each other. Why don't we say trans addition rather than anti? Because an anti addition can lead to a cis product as shown below.]

Anti addition ...   ...but a *cis* product.
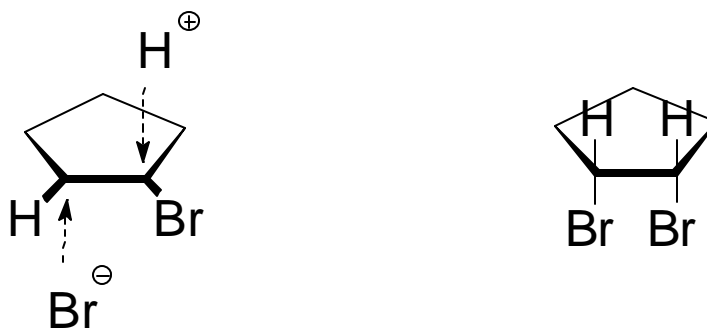
This exclusive anti addition may be contrasted with the addition of HX to an alkene where syn and anti addition are observed —

eg

+ H—Br ⟶

ANTI AND SYN ADDITION
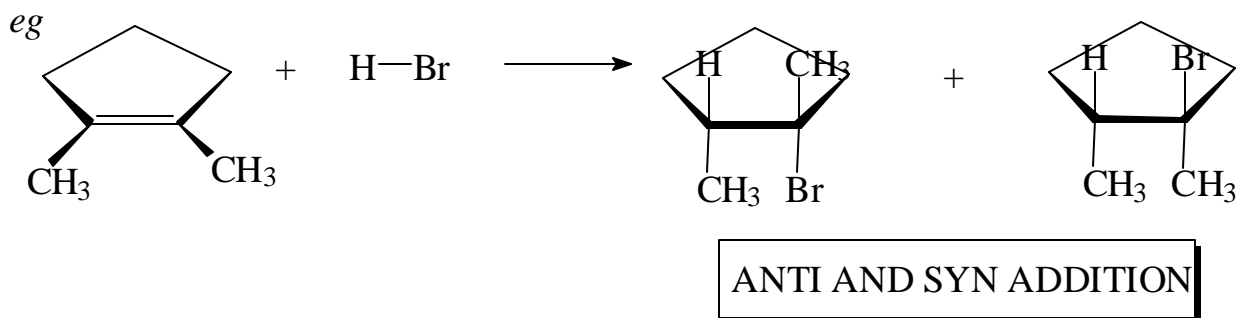
Since bromination gives a different stereochemical result from acid addition the mechanism for bromination must, somehow, be different from that of acid addition.

As we can see below, the intermediate that is formed in bromination is not a carbocation, as was the case in Bronsted-Lowry acid addition, but rather a *bromonium ion* is formed. Once this intermediate is formed the second bromine must attach itself in anti fashion because of steric interference – it cannot approach one of the carbons attached to the first bromine on the same side (syn) as that bromine because it is blocked by that bromine.

Mechanism —

:Br: δ −   bromine:
:Br: δ +   polarized by π bond

π bond

a bromonium ion
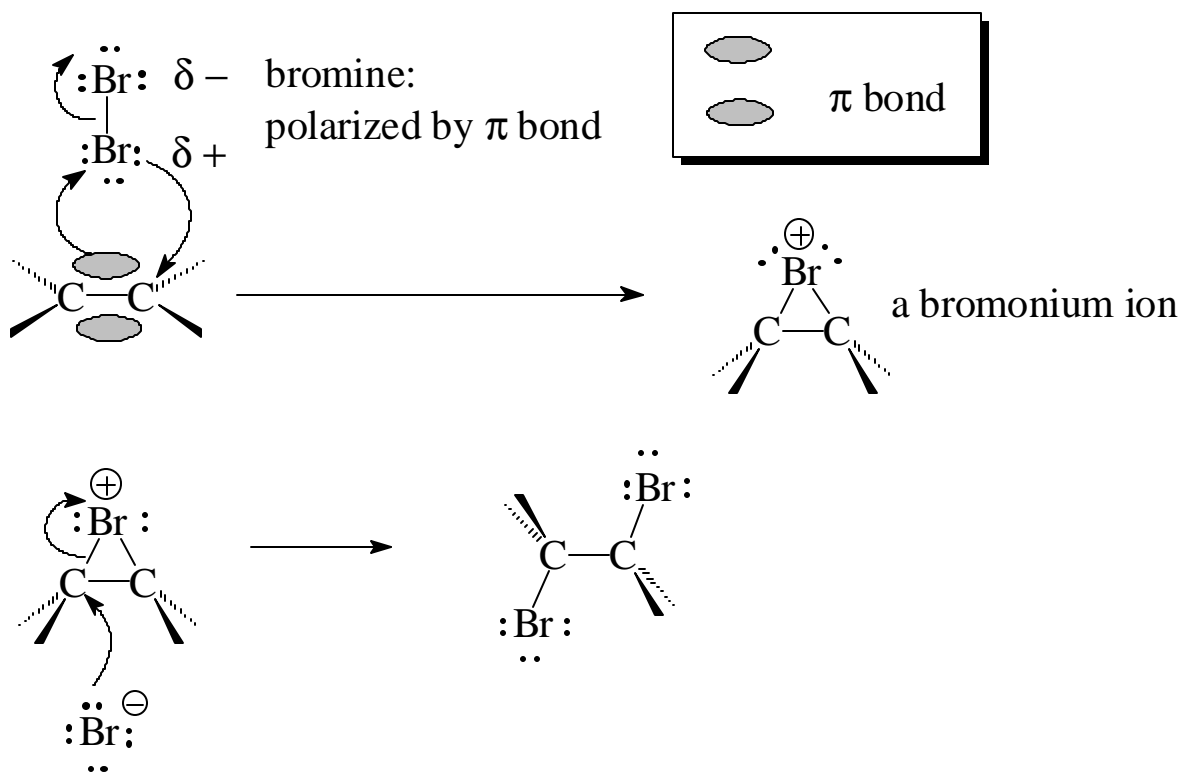
A proton, unlike bromine, is not large enough to form a 3-membered ring intermediate; it forms an open carbocation.

Hydrogenation of Alkenes –

The double bond of an alkene will react with hydrogen gas, H_2, in the presence of certain metal catalysts (usually platinum or palladium) in such a way that one hydrogen is added to each of the carbons that had been joined by the double bond. The addition in this case is syn.
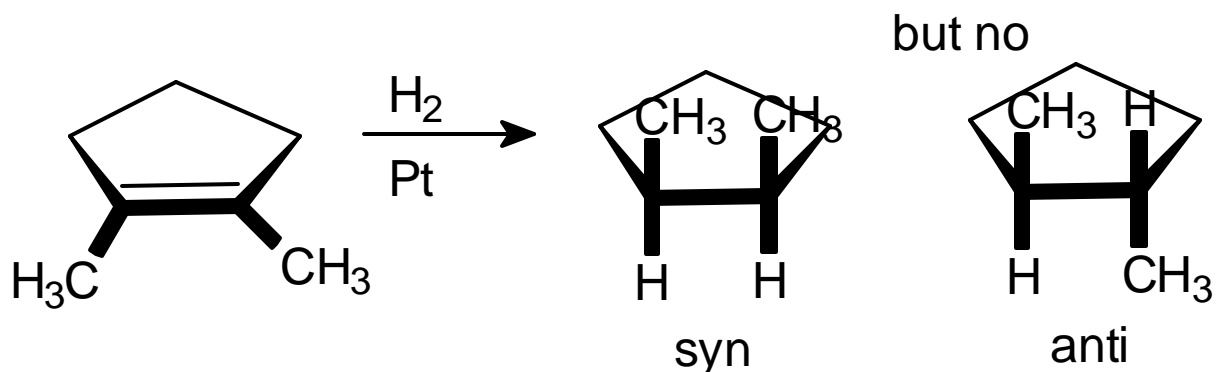
Oxidation of Alkenes with Potassium Permanganate –

When reacted with potassium permanganate under "mild conditions" – basic solution and moderate temperature – alkenes undergo *hydroxylation*. In this reaction an OH group adds to each of the doubly bonded carbons and the double bond, as usual, becomes a single bond. The addition is syn.
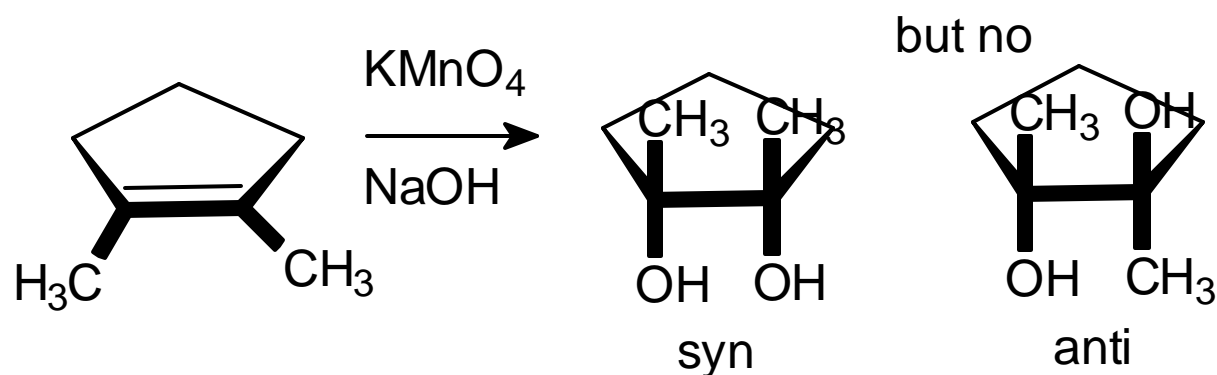
When conditions are more vigorous – acidic and heating – the double bond is completely cleaved – the molecule is split into two molecules. The exact outcome depends on how many hydrogens are attached to the carbons that are doubly bonded. If a carbon has two hydrogens, it will become carbon dioxide, CO_2. If a carbon has one hydrogen attached, it will become a carboxylic acid. If a carbon has no hydrogens attached, it will become a ketone. Examples are shown below.