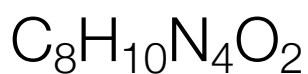
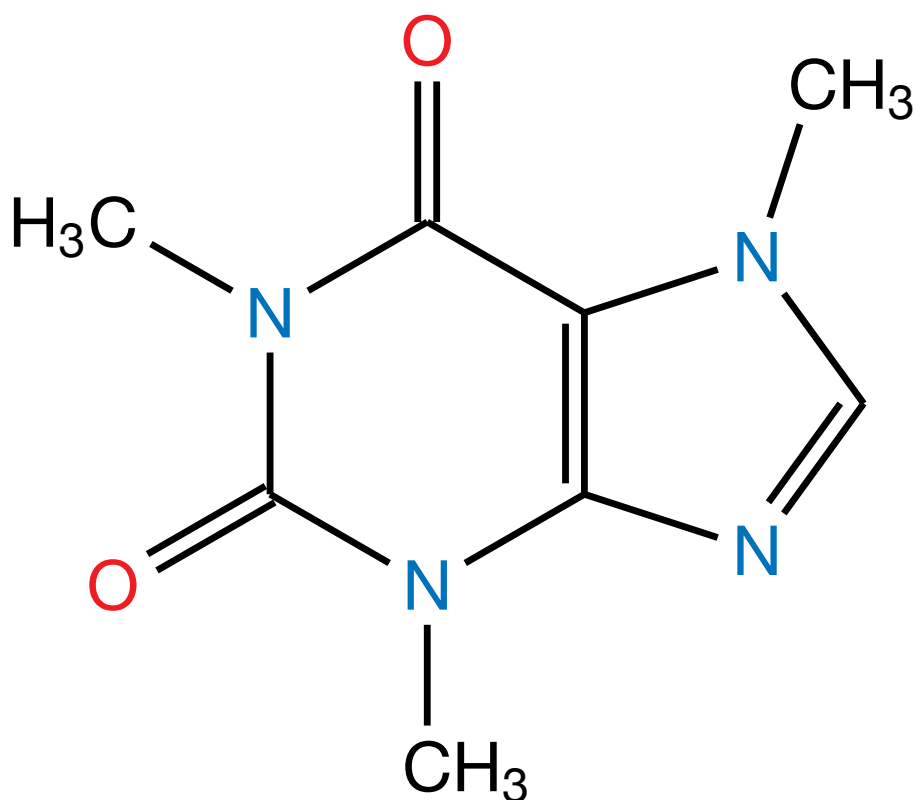


# Organic Chemistry



1,3,7-trimethylpurine-2,6-dione

-

Caffeine

Chapters 8 to 12

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## A. List of Reaction Mechanisms

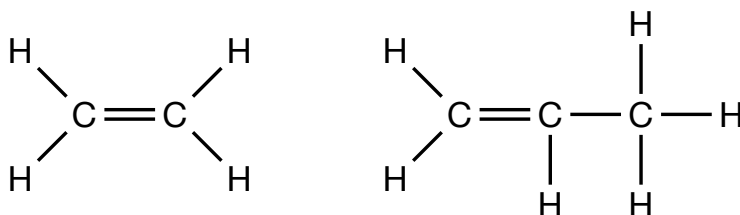
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# I Alkenes

## 1 Open Chain

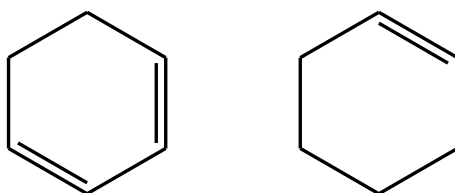
Alkenes are simply unsaturated hydrocarbons, with one or more double bonds. They have the general form of  $C_nH_{2n}$



Ethene (C<sub>2</sub>H<sub>4</sub>) and propene (C<sub>3</sub>H<sub>6</sub>) are examples of alkenes.

## 2 Cycloalkenes

Cycloalkenes are simply cycloalkanes where one or more of the C–C bonds have been replaced with a C=C double bond.



Cyclohex-1,3-diene and cyclohexene are examples of cycloalkenes.

## 3 Physical Properties

The physical properties of alkenes, including melting and boiling points, density and solubility follow the same trends as alkanes. Larger molecules have higher melting and boiling points, and higher densities, and alkenes are generally only soluble in non-polar solvents.

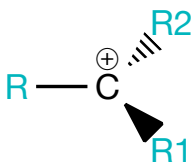
## 4 Stability of Carbocations

Before reactions and mechanisms of alkenes can be discussed, it is important to note the rules governing the formation of products, and the behaviour of molecules during the reaction.

All physical systems have a tendency to move to the lowest energy state — this state is characterised by the formation of the most stable molecules. As such, ions and radicals are inherently unstable.

### 4.1 Structure

One of the important intermediate products are carbocations, which are alkyl groups with an  $sp^2$  hybridised central carbon atom, and carries a positive charge on that atom.



The 3 substituent groups are arranged in a trigonal planar fashion, with the p-orbitals above and below this plane. As such, nucleophiles can attack the carbocation from either the top or bottom.

### 4.2 Stability

Charged ions are inherently more unstable than their neutral molecule counterparts; any species that stabilises the charge on the carbon ion would in turn increase the stability of the entire molecule. The primary reason for this is that molecules that are created from a more stable intermediate product have a higher chance to form. Thus, the probability of formation of a given product of a reaction can be estimated by looking at the stability of the intermediate compound leading to its creation.

For carbocations, the carbon atom has a positive charge, thus electron-donating substituents such as alkyl groups ( $-CH_3$ ), would stabilise the ion, as the donated electrons partially disperse the positive charge on the central atom.

Conversely, electron-withdrawing species such as halogens (F, Cl etc.) would further destabilise the carbocation, and as such products that involve the formation of these intermediates would have constitute much lower proportion of the final products.

## 5 Creation of Alkenes

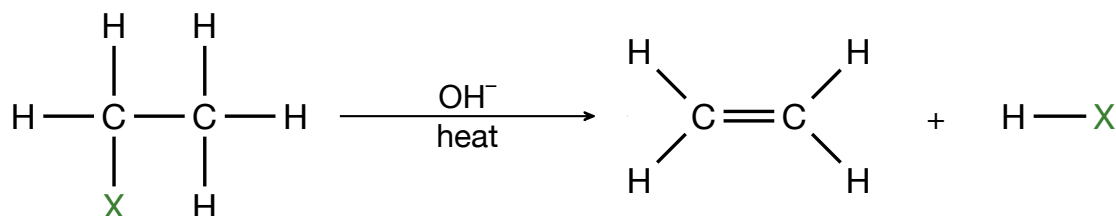
There are two methods of creating alkenes that are covered here, both of which involve elimination reactions, where a small molecule is *eliminated* along an alkane, and a double bond formed in its place.

For brevity, only the conditions and overall reaction will be covered.

### 5.1 Elimination of Hydrogen Halide

The main section that elaborates on this reaction can be found *here*, in the chapter on halogenoalkanes.

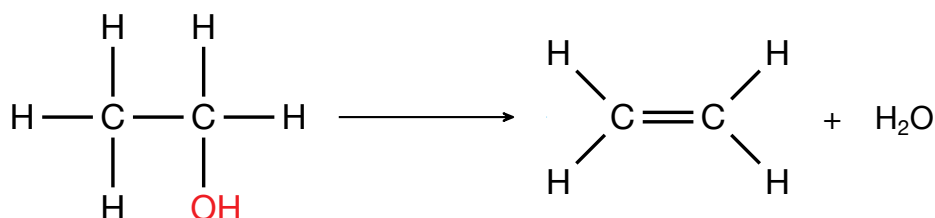
**Conditions:** Ethanolic KOH or NaOH, heat.



### 5.2 Dehydration (Elimination of Water)

Detail on this reaction, including the handling of isomers via Zaitsev's rule, can be found *here*, in the chapter on alcohols.

**Conditions:** Excess concentrated  $\text{H}_2\text{SO}_4$ ,  $170^\circ\text{C}$ , OR  $\text{Al}_2\text{O}_3$ , heat.



## 6 Alkene Reactions

### 6.1 Electrophilic Addition

The primary reaction mechanism of alkenes is electrophilic addition. Due to the high electron density of the  $\pi$ -bonds, electrophiles are readily attracted — thus alkenes are far more reactive than alkanes.

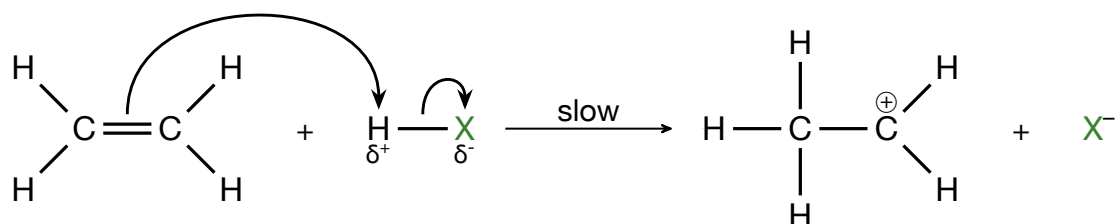
During a reaction, the comparatively weaker  $\pi$ -bond is preferentially broken over the stronger  $\sigma$ -bond; only a C–C bond remains, and atoms are *added* to the carbons, since they are now able to form an additional bond each. Hence, electrophilic *addition*.

#### 6.1.1 Electrophilic Addition of Hydrogen Halides

In this reaction, the hydrogen and halogen atom are added across the double bond of the alkene. The hydrogen halide should be in a gaseous state for this reaction.

**Conditions:** Gaseous HX (usually HCl or HBr).

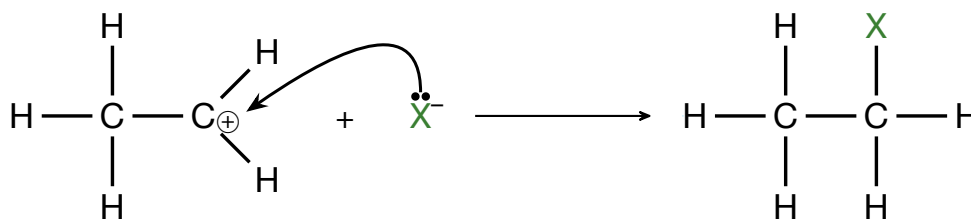
Step 1



This is the rate-determining step, which involves the breaking of the  $\pi$ -bond. The polar HX molecule has to approach the electron cloud of the  $\pi$ -bond in the correct orientation (hydrogen-facing), where the  $\pi$ -bond electrons attack the electron deficient,  $\text{H}^{\delta+}$  atom.

The H–X bond then undergoes heterolytic fission, producing a carbocation intermediate and a halide ion.

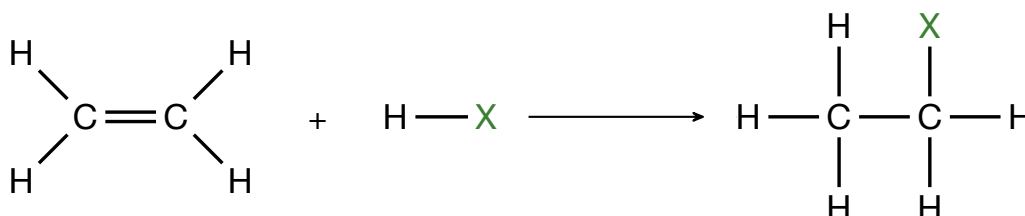
## Step 2



Note that the electron pair arrow points to the plus charge on the carbon, *not* the carbon atom itself.

This is the fast step; the bromide anion acts as a nucleophile, attacking the positively-charged carbocation. Since this step involves the reaction of two oppositely-charged species, it is a fast step.

## Overall Reaction



### 6.1.2 Markovnikov's Rule

This rule governs the major product that is formed when asymmetrical compounds are electrophilically added to alkenes, such as hydrogen halides. It does not apply to symmetrical reactants like  $\text{Cl}_2$  or  $\text{Br}_2$ .

The rule states basically states that when a hydrogen compound with the general form  $\text{H-X}$  is added to an alkene that is asymmetrical about the double-bond, the hydrogen atom will be added to the carbon with *more* existing hydrogen atoms. Note that  $\text{X}$  can be a halogen, a hydroxide (ie.  $\text{H-X}$  is  $\text{H}_2\text{O}$ ) or some other electronegative species.

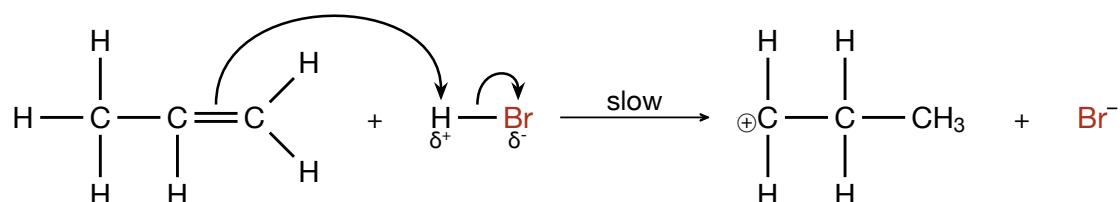
The mirror of the rule, used more with the cyclic halonium ion, is that the nucleophile will be added to the more substituted carbon atom.



### 6.1.3 Addition of H-X to Unsymmetrical Alkenes

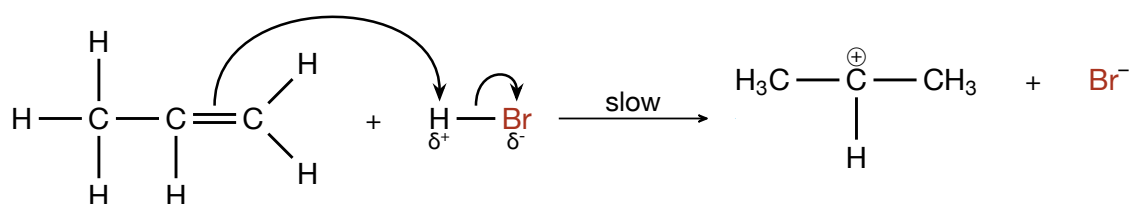
The behaviour that Markovnikov's rule predicts can be derived from the fact that adding the non-hydrogen species to the least substituted carbon would result in a less stable intermediate being formed. This can be illustrated using the electrophilic addition of HBr to prop-1-ene ( $\text{C}_3\text{H}_6$ ).

If the Markovnikov's rule is *not* followed, the following will take place:



The hydrogen was added to the centre carbon, in violation of Markovnikov's rule.

Notice that the positively-charged carbon on the intermediate only has 1 electron-donating alkyl group to stabilise its charge. Conversely, if Markovnikov's rule is followed below, the outcome would be different.



The hydrogen was added to the terminal carbon, following Markovnikov's rule.

In this case, the carbon atom containing the positive charge has 2 electron-donating alkyl groups attached to it, making this intermediate molecule more stable than the one above it.

As such, it is more likely to form, and hence 2-bromopropane will be the *major product*, and 1-bromopropane will be the *minor product*.

### 6.1.4 Electrophilic Addition of Halogens

The electrophilic addition of halogens to alkenes does not involve Markovnikov's rule, since it is symmetrical. As the non-polar halogen molecule approaches the electron-rich  $\pi$ -bond, it is polarised, forming  $\delta^+$  and  $\delta^-$  partial charges.

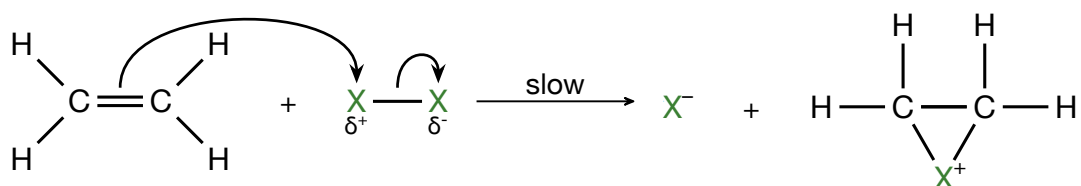
Note that the halogens used are usually either  $\text{Br}_2$  or  $\text{Cl}_2$ , since  $\text{F}_2$  is too reactive, and  $\text{I}_2$  is too *unreactive*. The reaction mechanism involves the formation of a *cyclic halonium ion* (bromonium or chloronium) — the double bond breaks, and each carbon forms a single bond with one positive halide ion (both carbons bond to the same atom).

**Conditions:** No UV Light, gaseous  $\text{X}_2$ .

**Observations:** *Reddish-brown*  $\text{Br}_2$  / *yellowish-green*  $\text{Cl}_2$  decolourises.

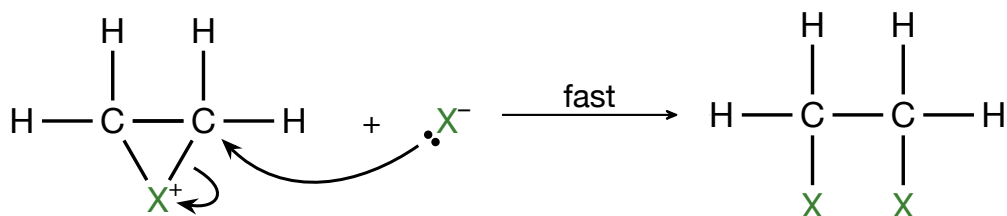
#### Step 1

This initial step is the slow, rate-determining one. It involves breaking of the  $\pi$ -bond, as well as the  $\text{X}-\text{X}$  bond. Note that the resulting cyclic halonium ion is highly unstable, due to the inherent strain of having a three-membered ring.

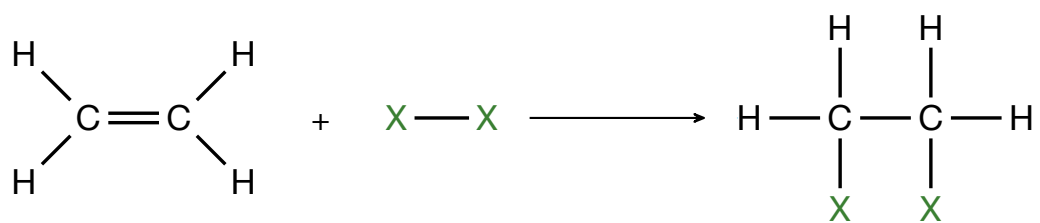


#### Step 2

In the second, fast step, the negatively-charged bromide ion from the first step attacks the overall positively-charged cyclic bromonium ion, resulting in the final product. Note that the bromide ion attacks one of the carbons attached to the positive bromide ion, breaking that bond. This is the fast step as it involves the reaction of two oppositely-charged species.



## Overall Reaction



### 6.1.5 Electrophilic Addition of Aqueous Br<sub>2</sub>

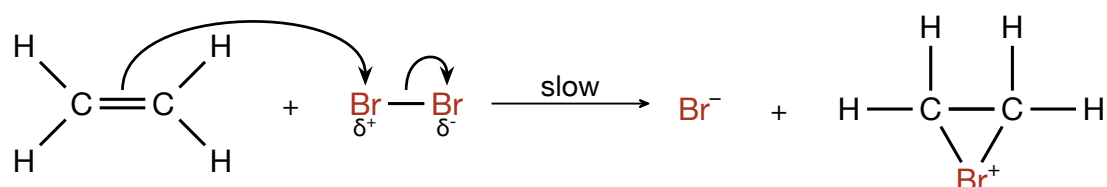
The mechanics of this reaction are basically the same as that of the electrophilic addition of Br<sub>2</sub>. The conditions and observations are fairly similar as well, except for the colour change — aqueous Br<sub>2</sub> is **yellow**, not reddish-brown.

Also, since the Br atoms are not both added across the double bond in a symmetrical manner, Markovnikov's Rule applies — the OH group will preferentially attack the carbon that has more stabilising alkyl groups.

**Conditions:** No UV Light, aqueous Br<sub>2</sub>.

**Observations:** **Yellow** Br<sub>2</sub> (aq) decolourises.

#### Step 1

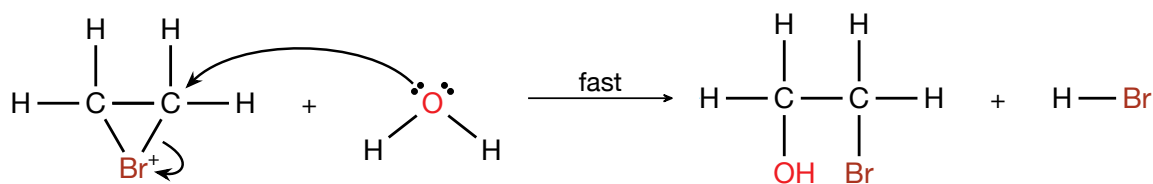


The cyclic bromonium ion is formed.

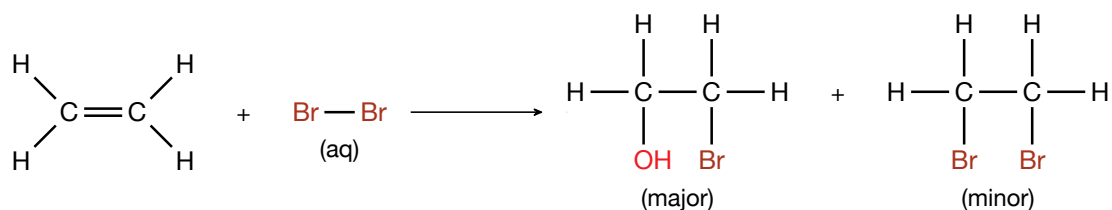
#### Step 2

Once the cyclic bromonium ion is formed however, it is susceptible to attack from any and all nucleophiles — including water, which has lone pairs and is a stronger nucleophile Br<sup>-</sup>. Since it is in much higher concentrations than Br<sup>-</sup>, the primary product will now have an OH group.

Note that the OH<sup>-</sup> group will attach to the more substituted carbon — it is the same mechanism as Markovnikov's Rule.



#### Overall Reaction



Both products are formed, except 1,2-dibromoethane is in much lower proportions.

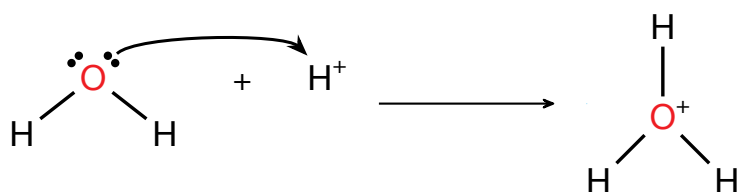
### 6.1.6 Electrophilic Addition of Steam (Hydration)

Under certain (usually industrial) conditions, alkenes can react with steam to form alcohols. Since this reaction involves the formation of a carbocation intermediate, the proportion of products will be governed by Markovnikov's Rule.

**Conditions:** 300 °C, at 70 atm,  $\text{H}_3\text{PO}_4$  catalyst, *OR*  
Concentrated  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}$ , warming.

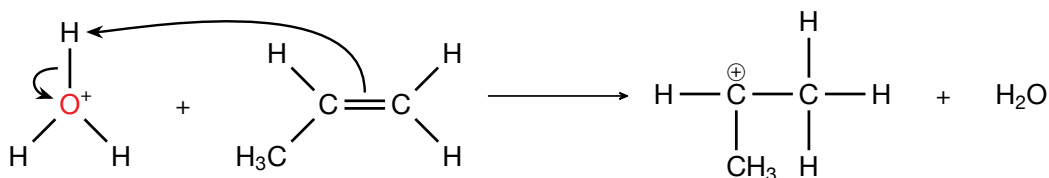
#### Step 0

The first step is to form  $\text{H}_3\text{O}^+$  (aq). Simply put, it is aqueous  $\text{H}^+$ .



#### Step 1

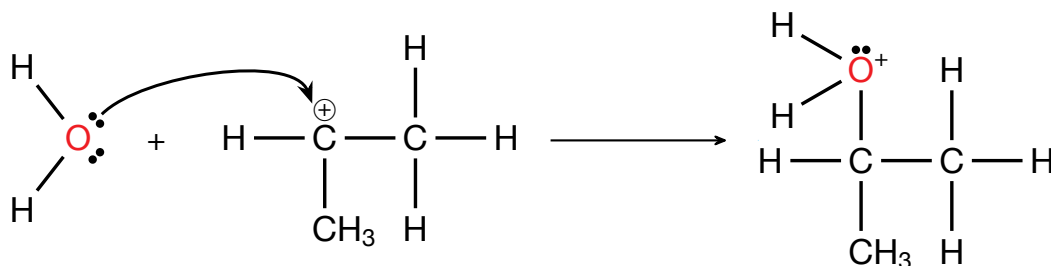
The electron-rich double-bond ( $\text{C}=\text{C}$ ) is then attacked by one of the H atoms on the  $\text{H}_3\text{O}^+$ , acting as an electrophile.



Since the alkene is not symmetrical, there are two product possibilities; hence, the positive charge will be on the carbon atom with more electron donating alkyl groups, in this case carbon 2.

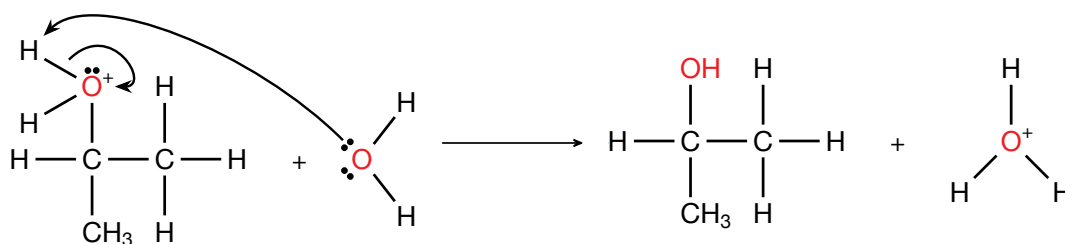
## Step 2

One of the lone pairs on the oxygen atom of a water molecule acts as a nucleophile, attacking the newly-formed carbocation. This results in a protonated alcohol, which is basically an alcohol with an extra H atom on the OH group.

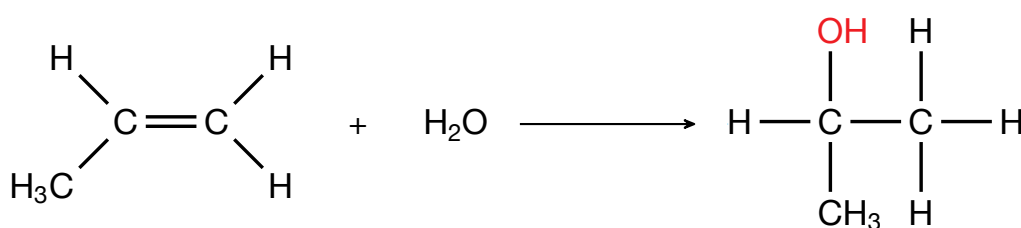


## Step 3

The acid catalyst is regenerated as a lone pair on another water molecule's O atom attacks the extra H of the OH group. This forms the alcohol proper, and the H<sub>3</sub>O<sup>+</sup> ion.



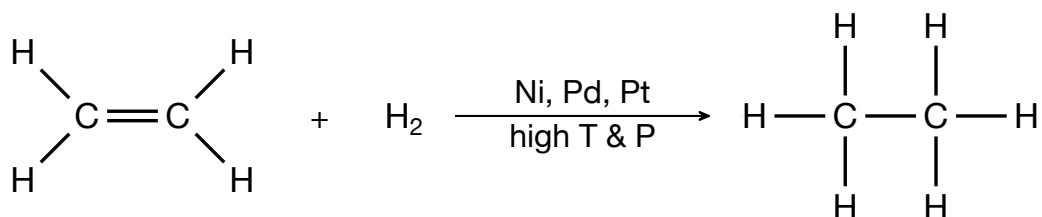
## Overall Reaction



## 6.2 Hydrogenation of Alkenes

Hydrogen gas can be used to saturate alkenes, through the use of an insoluble metal catalyst such as nickel, palladium or platinum, as well as sufficiently high temperatures and pressures.

It was commonly used in the food industry to produce margarine from unsaturated plant oils. However, the resulting dense fats were found to be hazardous to human health, and subsequent usage was discontinued.



## 6.3 Mild Oxidation of Alkenes

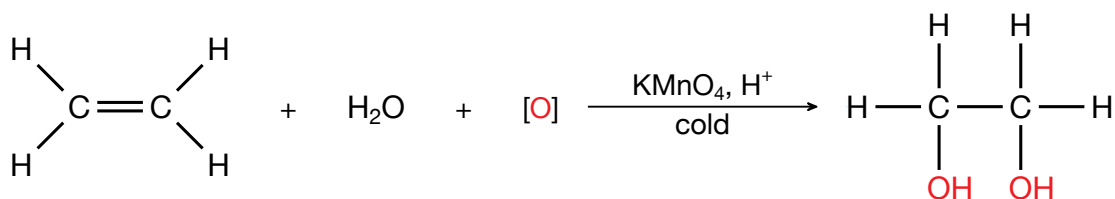
Alkenes can be mildly oxidised with potassium manganate (VII),  $\text{KMnO}_4$ , forming *diols*. This requires a cold environment, and either an acidic or alkaline medium (for  $\text{MnO}_4^-$  to function).

On a side note, balancing redox reactions involving organic molecules simply involves adding  $\text{H}_2\text{O}$  to balance the H or O (for oxidation and reduction respectively), and adding an appropriate number of  $[\text{O}]$  or  $[\text{H}]$  to balance the remaining oxygen or water.

### 6.3.1 Acidic Medium

A dilute acid is used to provide the acidic medium, in the form of  $\text{H}^+$  ions. Typically, this is  $\text{H}_2\text{SO}_4$ . The oxidising agent,  $\text{MnO}_4^-$ , is reduced, forming  $\text{Mn}^{2+}$ .

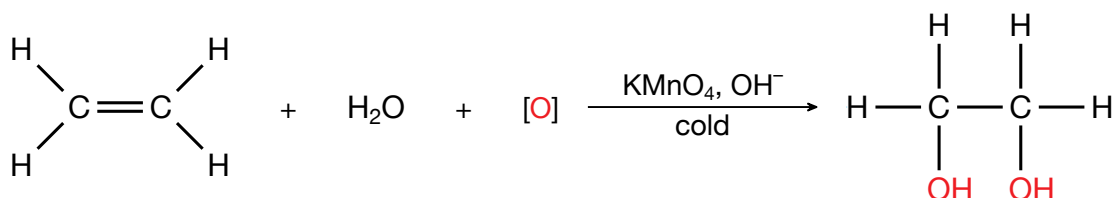
**Conditions:** Cold  $\text{KMnO}_4$ , acid ( $\text{H}_2\text{SO}_4$ ).  
**Observations:** **Purple**  $\text{KMnO}_4$  decolourises.



### 6.3.2 Alkaline Medium

An aqueous base, such as  $\text{NaOH}$ , is used to provide the  $\text{OH}^-$  ions. The oxidising agent  $\text{MnO}_4^-$  is reduced to  $\text{MnO}_2$ .

**Conditions:** Cold  $\text{KMnO}_4$ , aqueous base ( $\text{NaOH}$ ).  
**Observations:** **Purple**  $\text{KMnO}_4$  decolourises, forming a **brown** precipitate of  $\text{MnO}_2$ .





## 6.4 Oxidative Cleavage (Strong Oxidation) of Alkenes

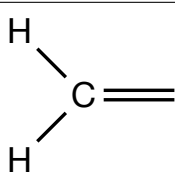
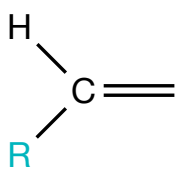
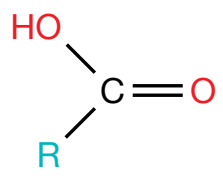
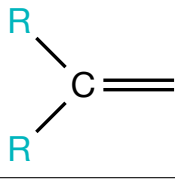
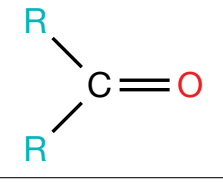
When the  $\text{KMnO}_4$  solution containing an alkene is heated, *strong oxidation* will take place. The double bond is *cleaved* instead of added to, and each side of the double bond forms its own fragment. In the case of cycloalkenes however, the end product might still only be one molecule.

Furthermore, only a strong oxidising agent like  $\text{MnO}_4^-$  can be used. The difference between mild and strong oxidation also depends *only* on the temperature of the reacting solution. Only heated solutions will result in oxidative cleavage.

**Conditions:** Cold  $\text{KMnO}_4$ , dilute  $\text{H}_2\text{SO}_4$ , heat.

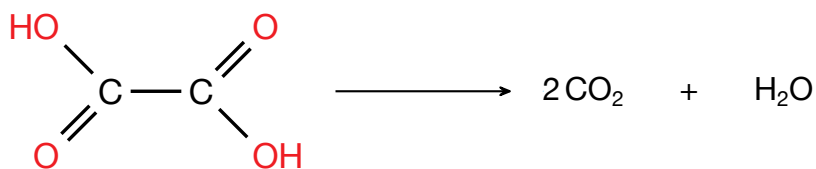
**Observations:** *Purple*  $\text{KMnO}_4$  decolourises, forming colourless  $\text{Mn}^{2+}$ .

Depending on the number of substituents (or inversely, the number of hydrogen atoms) attached to the carbon with the double bond, there are 3 possible products. Again, a table is the best way to present this, unfortunately.

Substituents	Structure	Product
0		$\text{CO}_2 + \text{H}_2\text{O}$
1		
2		

### 6.4.1 Further Oxidation of Ethanedioic Acid

The sole special case that must be noted is that if the oxidative cleavage results in the formation of ethanedioic acid ( $\text{C}_2\text{H}_2\text{O}_4$ ), it is further oxidised to form  $2\text{CO}_2$  and  $\text{H}_2\text{O}$ .



Ethanedioic acid, or oxalic acid.

### 6.4.2 Uses of Oxidative Cleavage

Oxidative cleavage can be used to determine the position of the double bond in carbon chains and cycloalkenes, given the products (fragments) of the cleavage reaction.

Most importantly, if  $\text{CO}_2$  is one of the products (gas evolved), then there are 2 possibilities — either the original molecule has a terminal  $\text{C}=\text{C}$  double bond, or the cleavage involved the formation of ethanedioic acid that further decomposed to form  $\text{CO}_2$ .

# Addendums

Herein lie things that *must* be known, but for brevity are excluded from the main text.

# A List of Reaction Mechanisms

## 1 Electrophilic Addition

Electrophilic Addition the main reaction mechanism for alkenes, and involves an electrophile attacking the electron-rich  $\pi$ -bond of the alkene.

### 1.1 Markovnikov's Rule

This rule governs the major product that is formed when asymmetrical compounds are electrophilically added to alkenes, such as hydrogen halides. It does not apply to symmetrical reactants like  $\text{Cl}_2$  or  $\text{Br}_2$ .

The rule states basically states that when a hydrogen compound with the general form  $\text{H-X}$  is added to an alkene that is asymmetrical about the double-bond, the hydrogen atom will be added to the carbon with *more* existing hydrogen atoms. Note that  $X$  can be a halogen, a hydroxide (ie.  $\text{H-X}$  is  $\text{H}_2\text{O}$ ) or some other electronegative species.

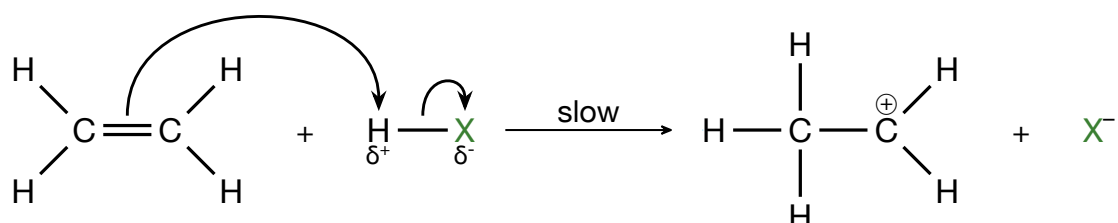
The mirror of the rule, used more with the cyclic halonium ion, is that the nucleophile will be added to the more substituted carbon atom.

## 1.2 Electrophilic Addition of HX

In this reaction, the hydrogen and halogen atom are added across the double bond of the alkene. The hydrogen halide should be in a gaseous state for this reaction.

**Conditions:** Gaseous HX (usually HCl or HBr).

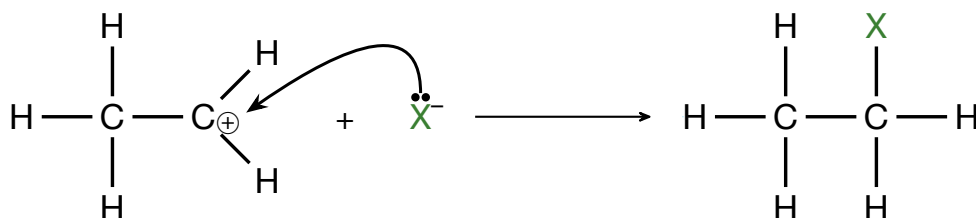
### Step 1



This is the rate-determining step, which involves the breaking of the  $\pi$ -bond. The polar HX molecule has to approach the electron cloud of the  $\pi$ -bond in the correct orientation (hydrogen-facing), where the  $\pi$ -bond electrons attack the electron deficient, H $^{\delta+}$  atom.

The H-X bond then undergoes heterolytic fission, producing a carbocation intermediate and a halide ion.

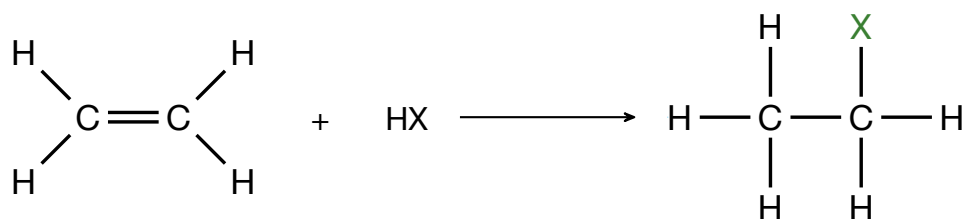
### Step 2



The electron pair arrow points to the plus charge on the carbon, *not* the carbon atom itself.

This is the fast step; the bromide anion acts as a nucleophile, attacking the positively-charged carbocation.

### Overall Reaction



## 1.3 Electrophilic Addition of $X_2$

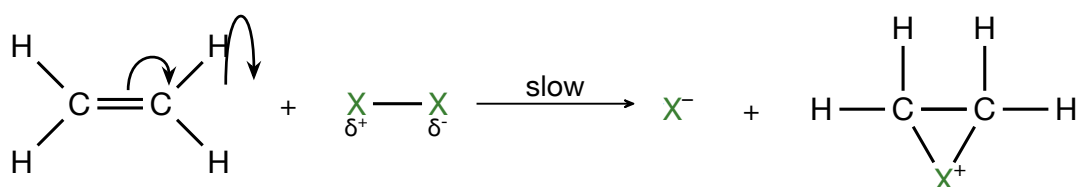
The electrophilic addition of halogens to alkenes does not involve Markovnikov's rule, since it is symmetrical. As the non-polar halogen molecule approaches the high-electron-density  $\pi$ -bond, it is polarised, forming  $\delta^+$  and  $\delta^-$  partial charges. The reaction mechanism involves the formation of a *cyclic halonium ion* — the double bond breaks, and each carbon forms a single bond with one positive halide ion.

**Conditions:** No UV Light, gaseous  $X_2$ .

**Observations:** **Reddish-brown**  $Br_2$  / **yellowish-green**  $Cl_2$  decolourises.

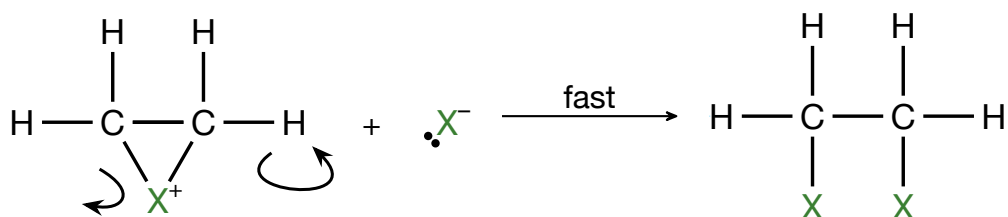
### Step 1

This initial step is the slow, rate-determining one. The resulting cyclic halonium ion is highly unstable, due to the geometric constraints of having a three-membered ring.

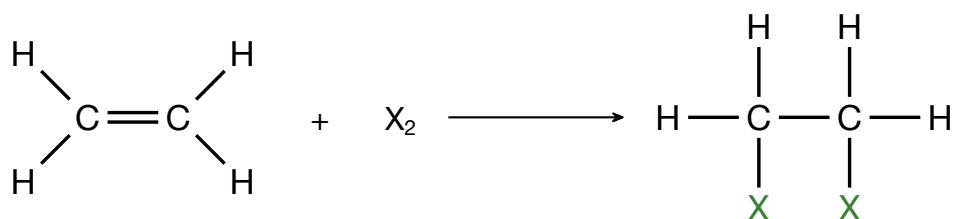


### Step 2

In the second, fast step, the negatively-charged bromide ion from the first step attacks the overall positively-charged cyclic bromonium ion. The bromide ion attacks one of the carbons attached to the positive bromide ion, breaking that bond.



### Overall Reaction



## 1.4 Electrophilic Addition of Aqueous $X_2$

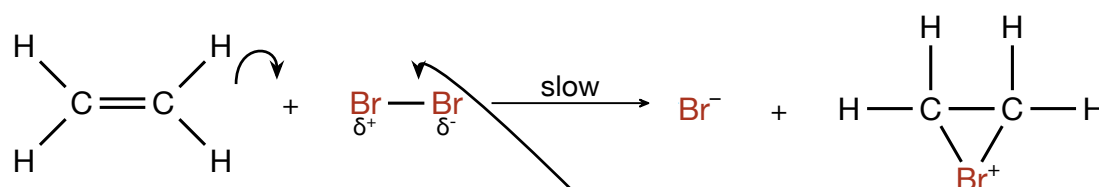
The mechanics of this reaction are basically the same as that of the electrophilic addition of  $Br_2$ , and the conditions and observations are fairly similar as well.

Also, since the Br atoms are not both added across the double bond in a symmetrical manner, Markovnikov's Rule applies — the OH group will preferentially attack the carbon that has more stabilising alkyl groups.

**Conditions:** No UV Light, aqueous  $Br_2$ .

**Observations:** **Yellow**  $Br_2$  (aq) decolourises.

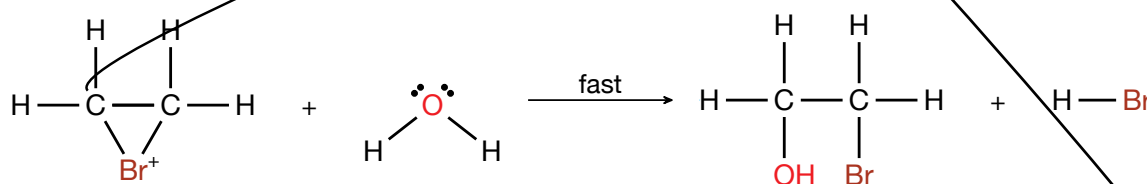
### Step 1



The cyclic bromonium ion is formed.

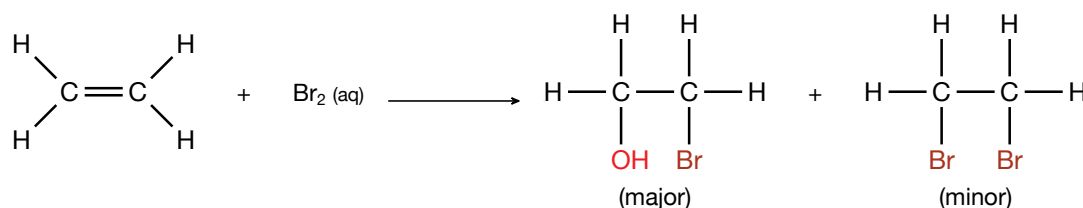
### Step 2

Once the cyclic bromonium ion is formed however, it is susceptible to attack from any and all nucleophiles — including water, which has lone pairs and is a stronger nucleophile  $Br^-$ . Since it is in much higher concentrations than  $Br^-$ , the primary product will now have an OH group.



Following Markovnikov's Rule, the  $OH^-$  group will attach to the more substituted carbon.

### Overall Reaction



- 2 Electrophilic Substitution
- 3 Nucleophilic Addition
- 4 Nucleophilic Substitution ( $S_N1$ )
- 5 Nucleophilic Substitution ( $S_N2$ )