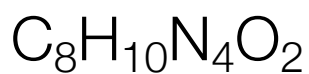
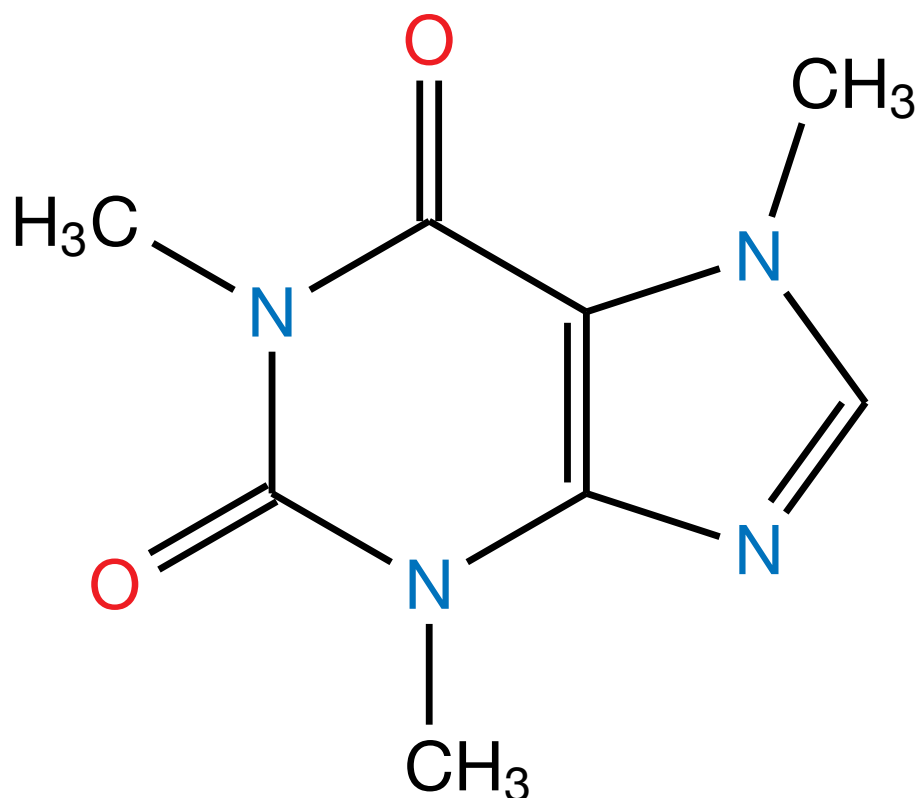


# Organic Chemistry



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

*or*

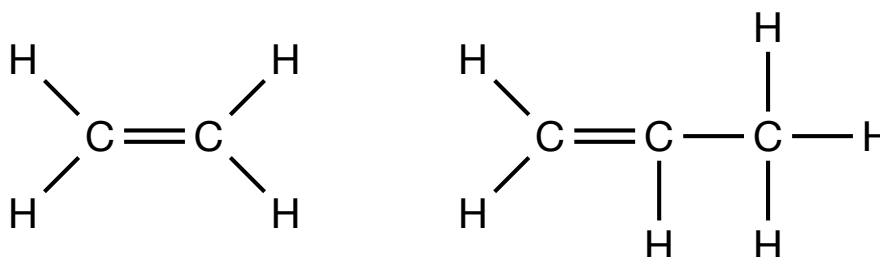
Caffeine

Chapters 8 to 12

# 1 Alkenes

## 1.1 Open Chain

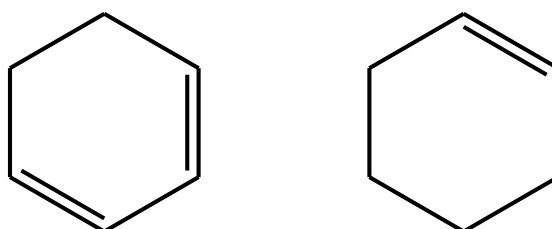
Alkenes are simply unsaturated hydrocarbons, with one or more double bonds. They have the general form of  $C_nH_{2n}$



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

## 1.2 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.

## 1.3 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.

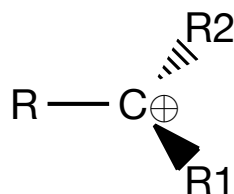
## 1.4 Stability of Carbocations

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.

### 1.4.1 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.

### 1.4.2 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 ( $F_2$ ,  $Cl_2$  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.

## 1.5 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.

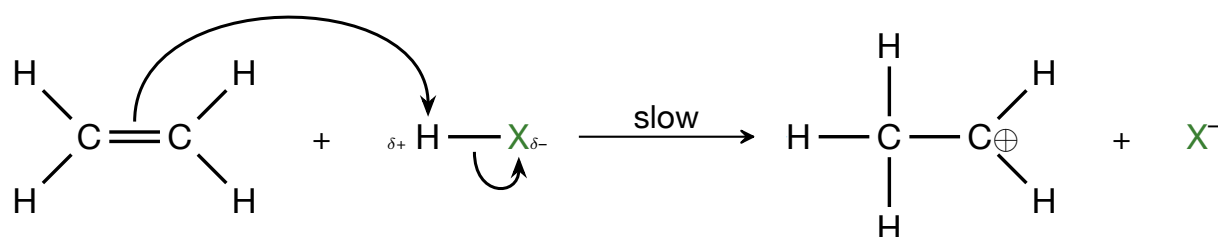
During a reaction, the comparatively weaker  $\pi$ -bond is preferentially broken over the stronger  $\sigma$ -bond; only a C–C bond remains, and atoms are *added* to the carbons, since they are now able to form an additional bond each. Hence, electrophilic *addition*.

### 1.5.1 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).

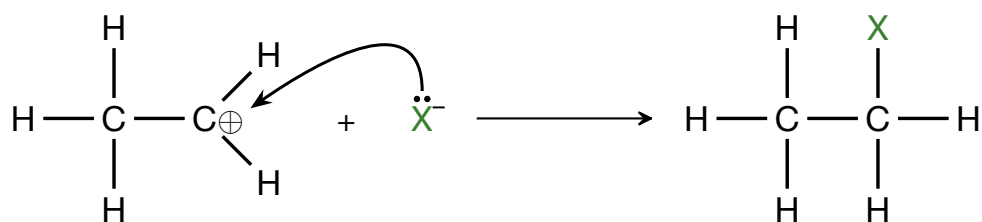
#### Step 1



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,  $\delta^+$  H atom.

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

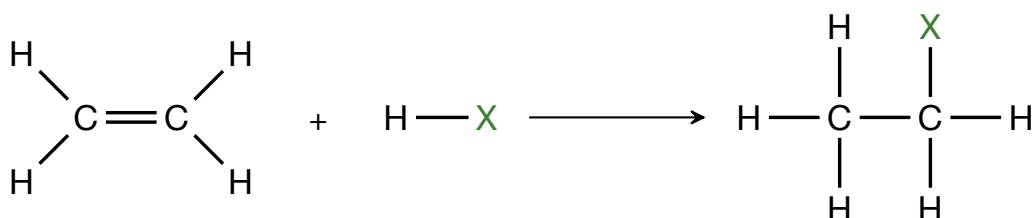
## Step 2



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



### 1.5.2 Markovnikov's Rule

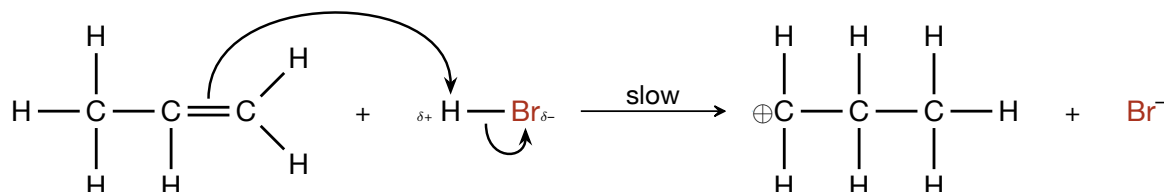
This rule governs the major product that is formed when asymmetrical compounds are electrophilically added to alkenes, such as hydrogen halides. It does not apply to symmetrical reactants like  $\text{Cl}_2$  or  $\text{Br}_2$ .

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.

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

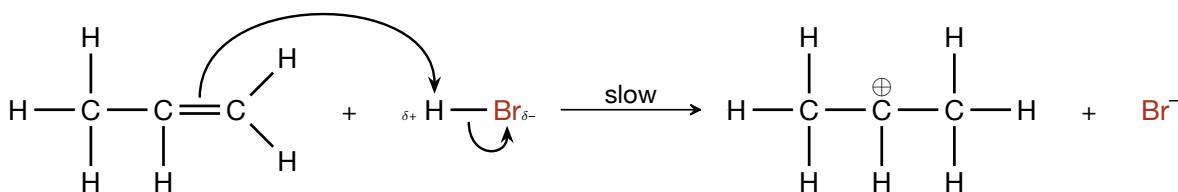
The behaviour that Markovnikov's rule predicts can be derived from the fact that adding the non-hydrogen species to the least substituted carbon would result in a less stable intermediate being formed. This can be illustrated using the electrophilic addition of HBr to prop-1-ene ( $\text{C}_3\text{H}_6$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

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*.

### 1.5.4 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 high-electron-density  $\pi$ -bond, it is polarised, forming  $\delta^+$  and  $\delta^-$  partial charges.

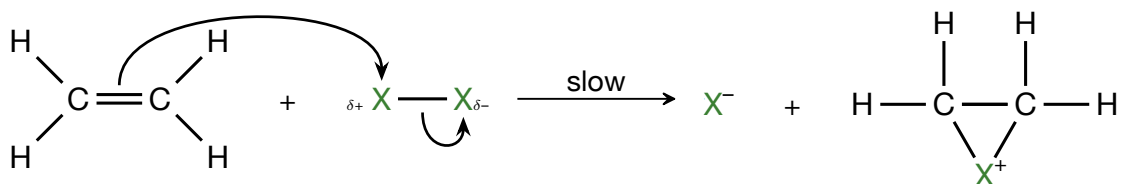
Note that the halogens used are usually either  $\text{Br}_2$  or  $\text{Cl}_2$ , since  $\text{F}_2$  is too reactive, and  $\text{I}_2$  is too *unreactive*.

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  $\text{X}_2$ .

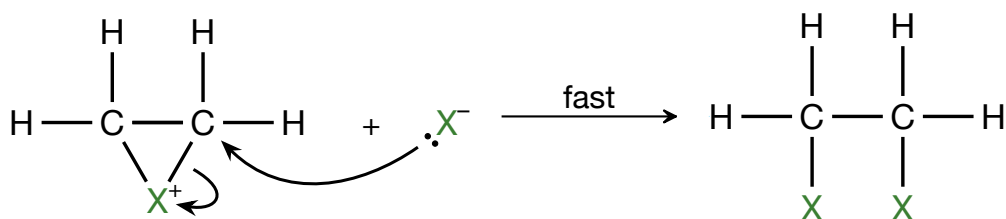
## Step 1

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



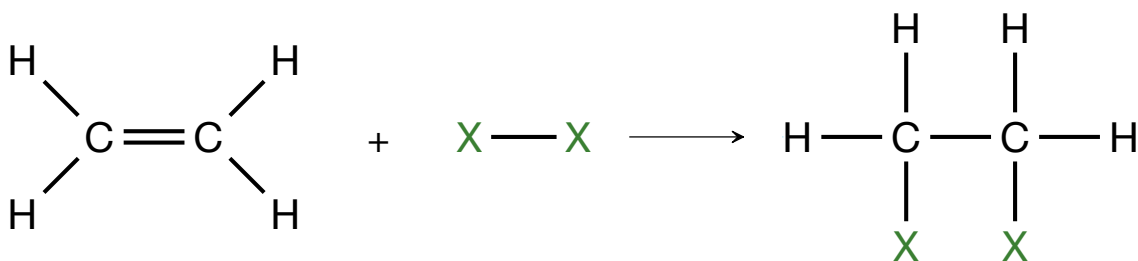
## Step 2

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.



The observable change for this reaction would be the decolourisation of the respective halogen; *reddish-brown* for bromine, and *yellowish-green* for chlorine.

## Overall Reaction



- 1.5.5 Electrophilic Addition of Aqueous  $\text{Br}_2$
- 1.5.6 Electrophilic Addition of Steam (Hydration)
- 1.6 Hydrogenation of Alkenes (Non-electrophilic Addition)
- 1.7 Oxidation of Alkenes
  - 1.7.1 Mild Oxidation in an Acidic Medium
  - 1.7.2 Mild Oxidation in an Alkaline Medium
  - 1.7.3 Oxidative Cleavage (Strong Oxidation)
  - 1.7.4 Uses of Oxidative Cleavage



## 2 Arenes

## 3 Halogen Derivatives