

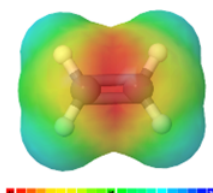
4.7: Electrophilic addition reactions

Learning Objectives

- Draw an electrophilic addition mechanism with curly arrows showing the movement of electrons.
- Apply the electrophilic addition to reactions of alkenes and alkynes with halogen acids and water.
- Define the concepts: regioselectivity, stereoselective and stereospecific reactions, and tautomerism with examples of electrophilic addition reactions of alkenes and alkynes.

Electrophilic addition mechanism

The π -bond of alkenes distributes electrons above and below the σ -bond that creates a local electron-rich (δ^-) region, as shown by red color region in the following electrostatic potential map of ethene.



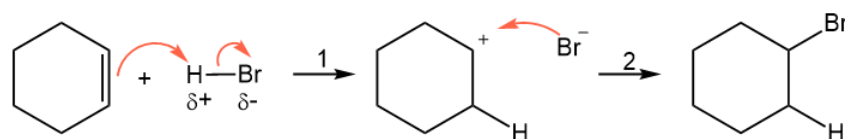
Therefore, the alkenes are nucleophiles (δ^-) attracted to electrophiles (δ^+) and capable of donating their π -electrons to make a bond with them, as shown in the following reaction mechanism.



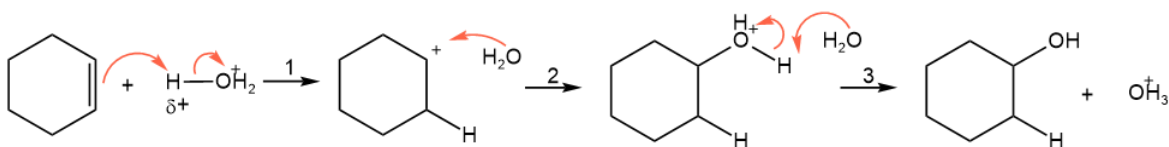
In first step of this mechanism, π -bond acts as an incoming nucleophile making a σ -bond with the electrophilic δ^+ end of the polar reagent $A-B$ while the (B) acts as a leaving group, leaving as a nucleophile B^- . One of the π -bonded carbon that receives the electrophile A becomes sp^3 hybridized, and the other carbon stays sp^2 hybridized with an empty p-orbital as a carbocation. In the second step, the nucleophile (B^-) attacks the electrophilic carbocation and makes a new bond. As a result, the reagent $A-B$ adds to the $C=C$ -bond. Since the process begins with the addition of an electrophile A , it is called an electrophilic addition reaction.

Examples of electrophilic addition reactions of alkenes

Halogen acids ($H-Cl$, $H-Br$, and $H-I$) are among many reagents that add to alkenes by electrophilic addition mechanism, as shown in the following example.



Water (H_2O) has more polar $H-O$ bonds than the halogen acids, but $-OH$ is a bad leaving group and usually do not act as a leaving group. The bad leaving $-OH$ is first converted to a good leaving $-OH_2^+$ by adding stronger acid like sulfuric acid (H_2SO_4) in the water. Then, the hydronium ion ($H-OH_2^+$) enters the first step of the electrophilic addition reaction, as shown below.



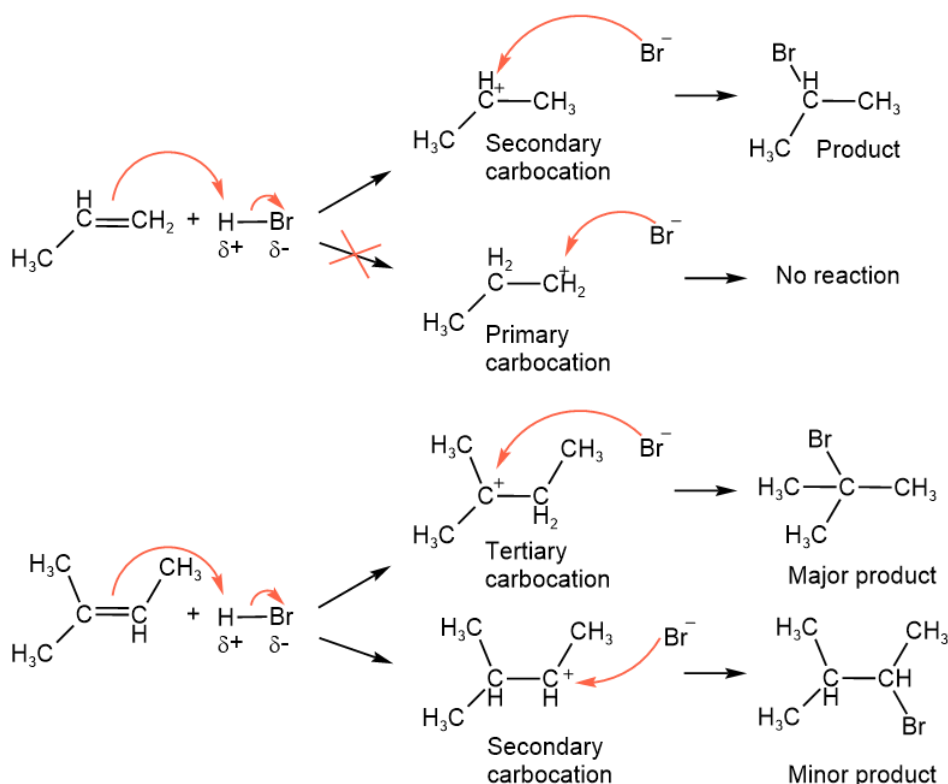
H_2O acts as an incoming nucleophile in step#2, another water molecule removes its acidic proton in step#3. This reaction is called hydration of alkene because the result is the addition of a water molecule $\text{H}^{\delta+}-\text{OH}^{\delta-}$ to a $\text{C}=\text{C}$ -bond of an alkene.

Sulfuric acid is used as an acid catalyst because its conjugate base HSO_4^- is a poor nucleophile. H_2O is also a poor nucleophile, but being in higher concentration wins the competition in step#2. Even if HSO_4^- add to the carbocation in the second step, it is substituted by H_2O under the reaction conditions.

Regioselectivity of electrophilic addition reactions

In the cases of unsymmetrical alkenes, two constitutional isomers are possible, but one is produced exclusively or as a major product. The reason is that the two potential carbonation intermediates have unequal stability. The stability of carbocations

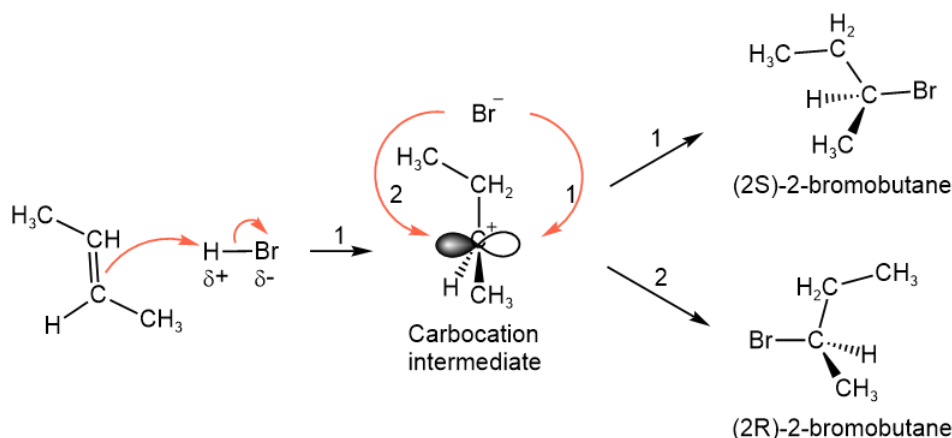
increases in this order: primary (RCH_2^+) < secondary (R_2CH^+) < tertiary (R_3C^+). The following examples show that the more stable carbocation is formed exclusively or predominantly when there is a choice.



Chemical reactions in which two constitutional isomers are possible, but one is formed exclusively or predominantly are called **regioselective reactions**. Electrophilic additions are regioselective reactions.

Stereoselectivity of electrophilic addition reactions

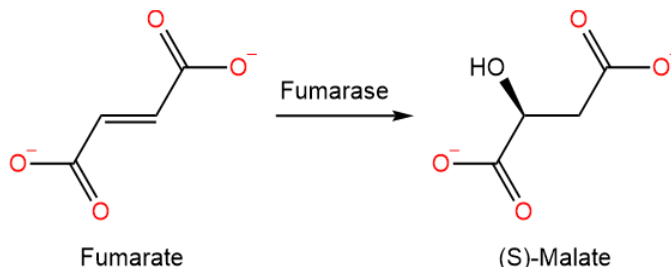
When reactants and catalysts are achiral, but the product is chiral, it is produced equally in both (R) and (S) configurations. For example, the carbocation intermediate in electrophilic addition reactions is trigonal planar. The nucleophile can attack it from either side with about equal probability resulting in a racemic mixture, as illustrated in the following example.



However, suppose one of the reactants or the catalyst is chiral and a pure enantiomer. In that case, one of the enantiomers (R or S) is usually formed exclusively or as a major product. Enzymes in biochemical systems are chiral catalysts that usually produce one enantiomer exclusively.

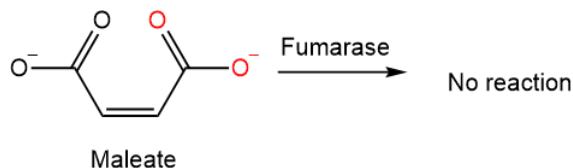
Chemical reactions that produce one stereoisomer exclusively or preferentially relative to the others are called **stereoselective reactions**.

Enzyme-catalyzed reactions are stereoselective reactions. For example, hydration fumarate, catalyzed by an enzyme fumarase, produces (S)-malate, as shown below.



The R-enantiomer is not produced in the above reaction.

Enzymes usually also react with one stereoisomer in the reactant exclusively. For example, fumarase catalyzes the hydration of fumarate but does not react with its enantiomer maleate, as illustrated below.

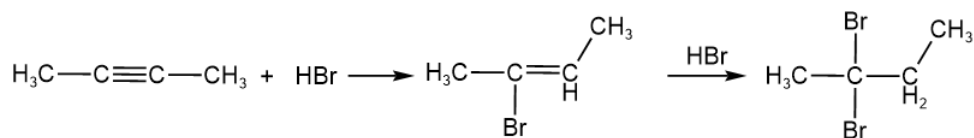


Chemical reactions that preferentially react with one stereoisomer among reactant and preferentially produce one stereoisomer in the products are called **stereospecific reactions**.

Enzyme-catalyzed reactions are often stereospecific reactions. For example, the fumarase enzyme selectively reacts with fumarate (and not with its stereoisomer maleate) and selectively produces (S)-malate (and not its stereoisomer (R)-malate).

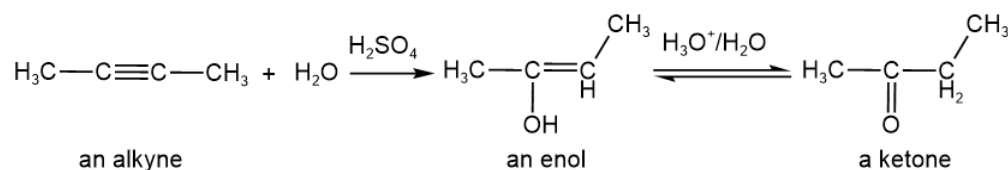
Electrophilic addition reactions of alkynes

Alkynes have a triple $\text{C} \equiv \text{C}$ -bond, i.e., one σ -bond and two π -bonds. The electrophilic addition reactions happen on π -bonds of alkynes. If the reagent is in a one-to-one mole ratio, it adds to one of the π -bonds. If the reagent is in excess, a second addition reaction happens on the product of the first addition, as shown below.



In step#2, the nucleophile (Br^- in this case) adds to the carbon carrying the nucleophile of step#1. This is because the carbocation intermediate of step#2 is stabilized by resonance with the lone pair of electrons on the nucleophile added in the first step.

Hydration of alkyne follows the same step#1 as for alkenes, but the intermediate enol containing $\text{C}=\text{C}$ and $-\text{OH}$ together exists in equilibrium with its structural isomer ketone, as shown in the following example.



Tautomers are constitutional isomers that are readily interconvertible. **Tautomerization** is the chemical reaction that interconverts the tautomers.

Enol and its isomer ketone, e.g., but-2-ene-2-ol and but-2-one in the above example, are called **tautomers**, and the equilibrium between the two in step#2 of the above reaction is **tautomerization**.

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