Addition to Carbon–Carbon Multiple Bonds

Semester – II
CC – VIII
Organic Chemistry-II
Unit 1

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What are addition reactions

❖An addition reaction, in organic chemistry, is in its simplest terms, an organic reaction where two or more molecules combine to form a larger one; the adduct.

❖Addition reactions are limited to chemical compounds that have multiple bonds, such as molecules with carbon–carbon double or triple bond.

❖Molecules containing carbon—hetero double bonds like (C=O) groups, or (C=N) groups, can also undergo addition, as they too have double-bond character.

❖There are two main types of polar addition reactions electrophilic and nucleophilic addition reactions .

❖Free radical addition reaction is non-polar addition reaction.

Basically addition to a double or triple bond can takes place in following three different ways.

1. Two-step processes, with initial attack by a nucleophile,

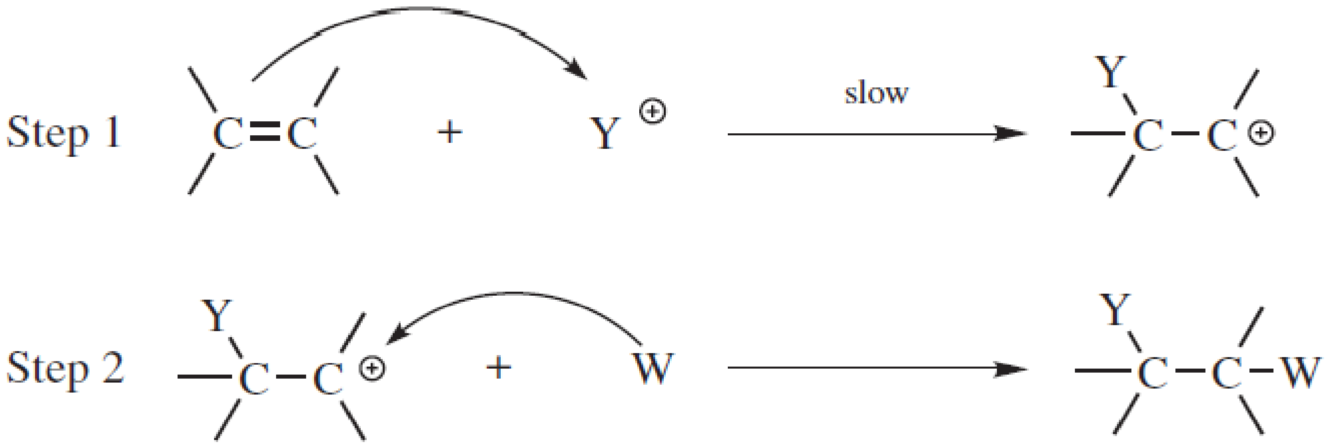
2. Two-step processes, with initial attack upon an electrophile

3. Two-step processes, with initial attack upon a free radical.

The second step of the reaction will consists of combination of thus formed intermediate with, a positive species, a negative species, or a neutral entity respectively

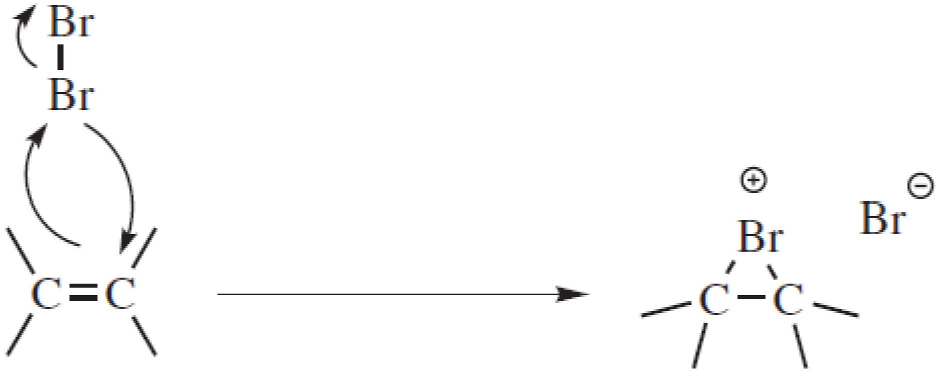
Mechanism and stereochemical aspects of the addition reactions involving electrophiles

In this type of mechanism, a positive species (electrophile) approaches the double or triple bond (as it is electron rich) and in the first step forms a bond by donation of the pair of π electrons to the electrophilic species to form a sigma pair as follows

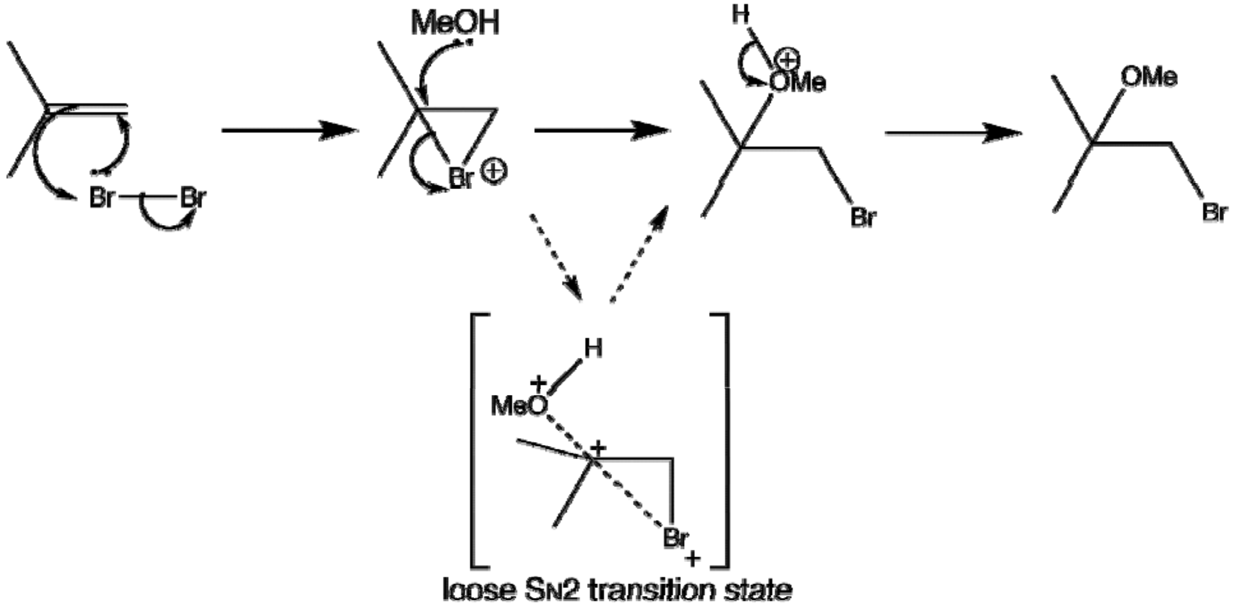


In the second step intermediate formed in the first step combines with the species (W) carrying an electron pair, generally, it is negatively charged

Not all electrophilic additions follow the simple mechanism of electrophilic addition reactions. In bromination the intermidiate formed in first step, very rapidly cyclizes to a bromonium ion

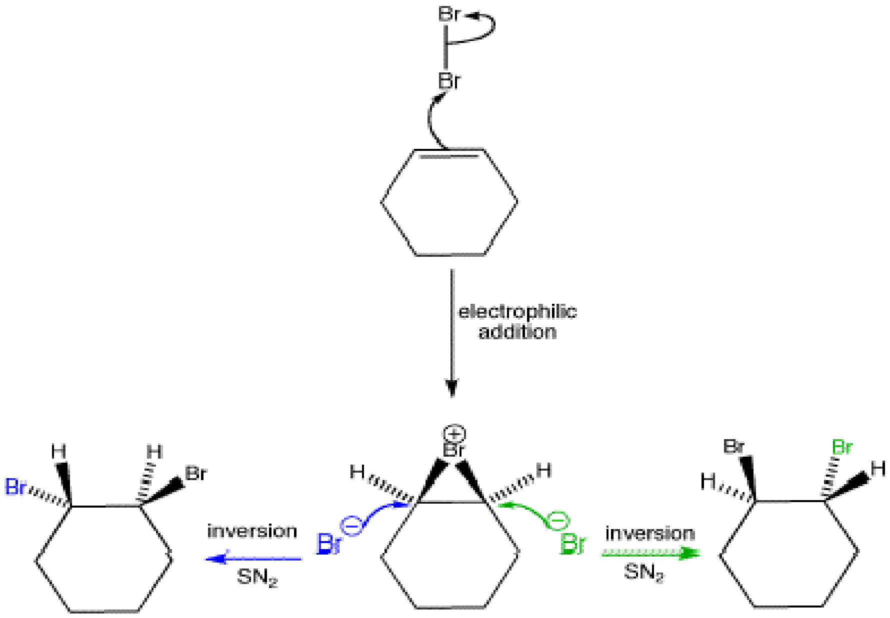


Unsymmetrical bromonium ion open regioselectively



When a bromination reaction is done in a nucleophilic solvent, such as water or methanol, the solvent molecules compete with the bromide to open the bromonium ion. When isobutene is treated with bromine in methanol, an ether is formed by attack of methanol only at the more substituted end of the bromonium ion. Methanol is attacking the bromonium ion where it is most hindered, so there must be some effect at work more powerful than steric hindrance.

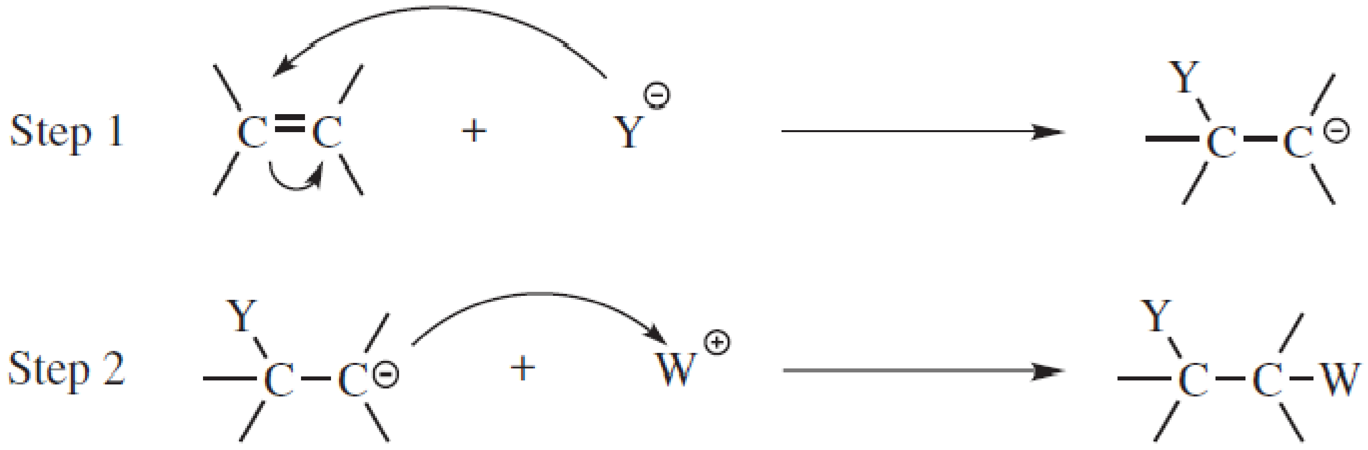
Formation of sterioisomers



When cyclohexene is treated with bromine in carbon tetrachloride, the racemic *anti*-1,2-dibromocyclohexane is obtained exclusively. The bromonium ion is opened with inversion in an S_N2 reaction. As the bromine can attack from either side we get both stereoisomers and a racemic mixture.

Mechanism and stereochemical aspects of the addition reactions involving nucleophiles

In the first step of nucleophilic addition, a nucleophile donates its pair of electrons to one of the doubly/ triply bonded carbon atom, which generates a carbanion. The second step is a combination of this carbanion with a positive species



This mechanism is the similar as the electrophilic addition, except that the charges are reversed. When the alkene contains a good leaving group, substitution is a side reaction

Mechanism and stereochemical aspects of the addition reactions involving free radicals

INITIATION STEP

$$\mathrm{YW} \xrightarrow[\text{dissociation}]{h\nu \text{ or spontaneous}} \mathrm{Y}\bullet + \mathrm{W}\bullet$$

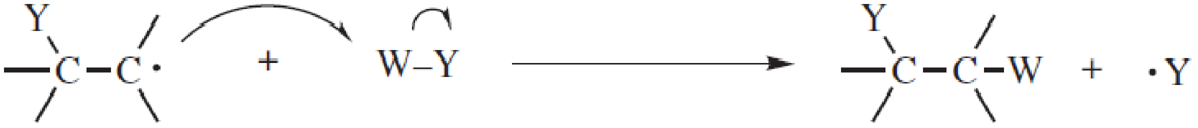
or

$$\mathrm{R}\bullet \ \text{(from some other source)} + \mathrm{YW} \longrightarrow \mathrm{RW} + \mathrm{Y}\bullet$$

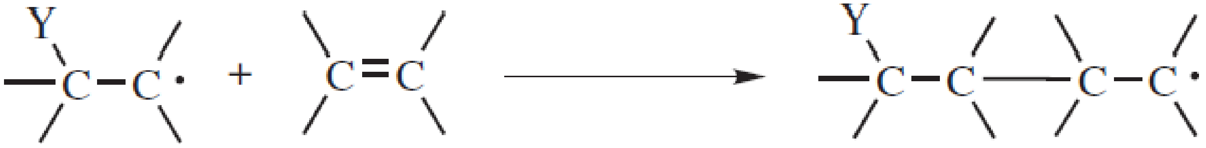
PROPAGATION STEP

Step 1

Step 2



TERMINATION STEP



Regioselectivity chemoselectivity reactivity and orientation of addition reaction

Reactivity

The case of electrophilic addition reactions

As in electrophilic aromatic substitution electron-donating groups increase the reactivity of a double bond toward electrophilic addition and electron-withdrawing groups decrease it. Similarly the reactivity toward electrophilic addition of a group of alkenes increased in the order

$$CCl_3CH{=}CH_2 < Cl_2CHCH{=}CH_2 < ClCH_2CH{=}CH_2 < CH_3CH_2{=}CH_2$$