

Addition Reactions

Conversion of multiple bonds, such as a double or a triple bond, into other functional groups are usually achieved using addition reactions. The reaction of multiple bonds will convert an unsaturated compound to more saturated and functionalized species. In this module, a number of examples of electrophilic addition to electron rich double bonds are presented. When a double bond is activated by attaching it with electron withdrawing groups, conjugated addition is observed.

These reactions are characteristic of compounds containing multiple bonds. The alkene (=), alkynes (\equiv), C=O, C \equiv N react by addition to multiple bond Thus in addition reaction there is increase in the number of groups attached to the substrate and decrease in its unsaturation.

Addition reactions are of four type namely

- electrophilic,
- nucleophilic,
- free radical
- concerted (Cyclic)

The first three are the two-step processes, with initial attack by electrophile, nucleophile or a free radical.

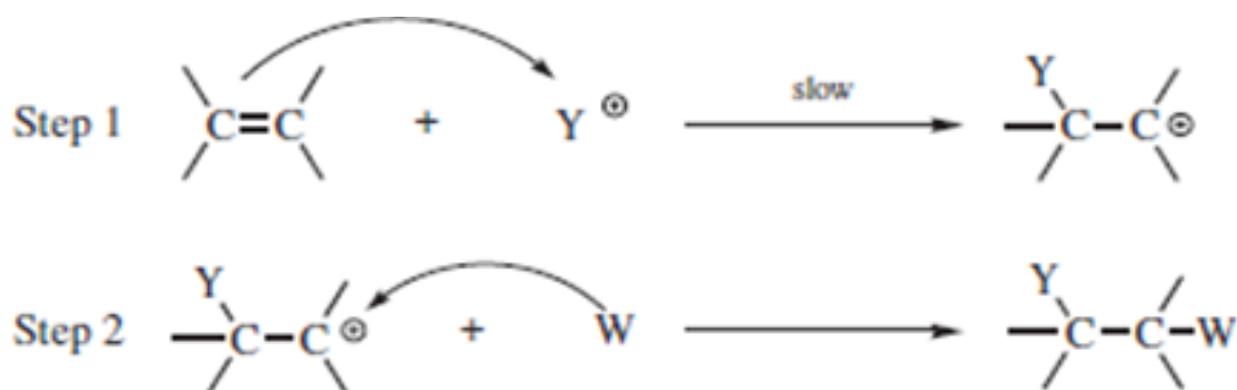
The second step consists of a combination of the resulting intermediate with a negative species, a positive species or a neutral entity. In addition, attack at the two carbon atoms of the double or triple bond is simultaneous.

Electrophilic Addition Reactions

The first step is addition of electrophile by formation of σ bond through donation of π electrons to the electrophile and carbocation is formed. The next step is reaction of the positively charged intermediate (carbocation) with a species carrying lone pair or negative charge i.e nucleophiles.

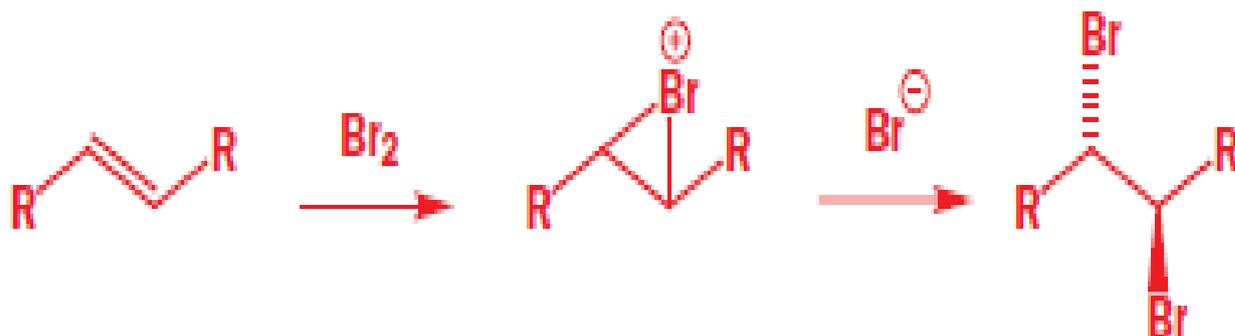
Eg: Carbon carbon multiple bond (Alkene & alkynes)

This step is the same as the second step of the SN1 mechanism



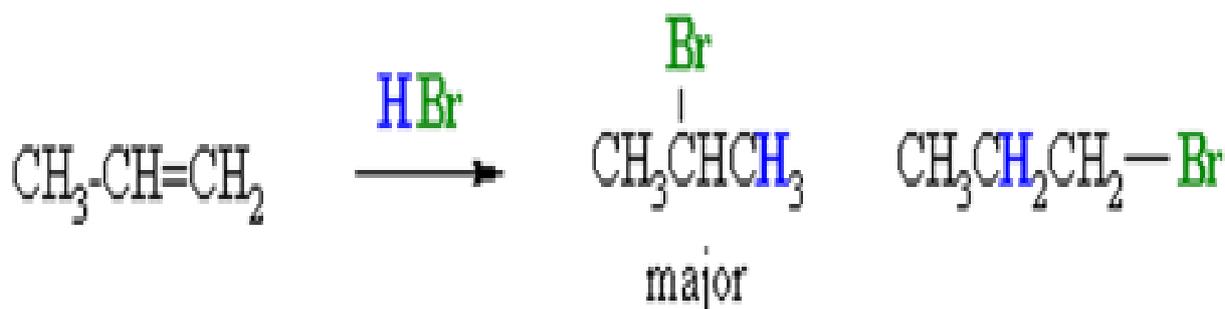
Examples of electrophilic addition reactions:

(a) Addition of bromine to alkenes: The addition reaction of bromine to alkenes proceeds via a cyclic bromonium ion intermediate. This intermediate is similar to those



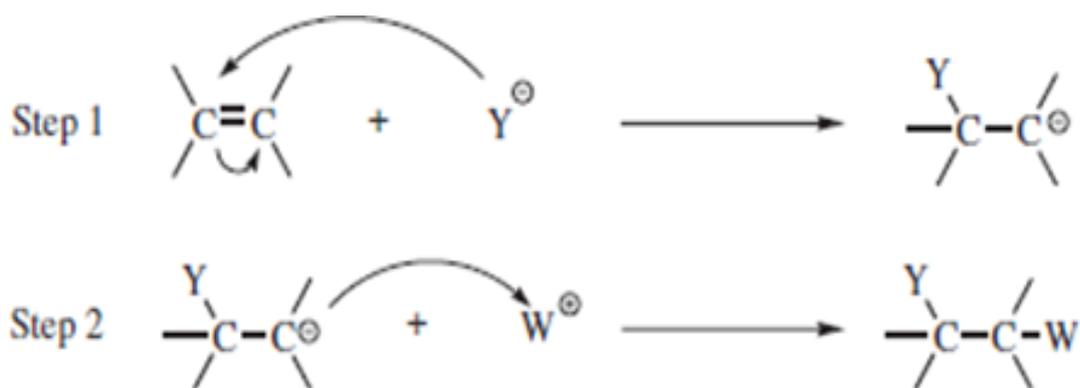
encountered in the neighbouring-group mechanism of nucleophilic substitution. This reaction is used as a colour test to detect the presence of multiple bonds. The brown colour of bromine disappears when it is added to a compound with double or triple bonds.

(b) Addition of unsymmetrical reagents to unsymmetrical alkenes (Markownikoff rule): For example in the reaction of propene with HBr, H⁺ acts as an electrophile which is added to the carbon bearing double bond followed by attack of bromide ion (Br⁻).



Nucleophilic Addition Reactions

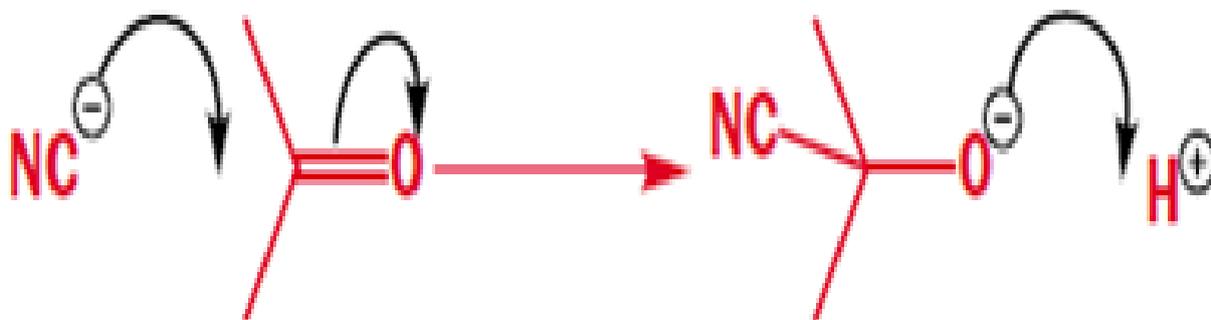
Such reactions are encountered in compounds containing polar functional groups (C=O, C≡N, C=S). In the first step a nucleophile with its pair of electrons attacks the carbon atom of a double or triple bond, forming a carbanion. It is followed by a second step in which this carbanion reacts with a positive species.



When the olefin contains a good leaving group (as defined for nucleophilic substitution), substitution is a side reaction. (i.e. a nucleophilic substitution at a vinylic substrate).

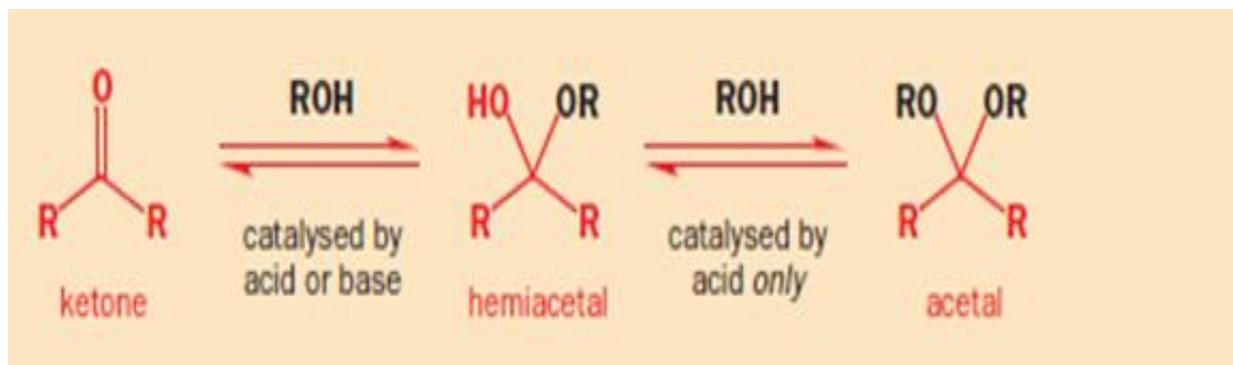
Examples of nucleophilic addition reactions:

- a) Addition of HCN to carbonyl group: In this reaction cyanide ion (CN⁻) acts as a nucleophile which attacks the carbon of carbonyl group, the carbon-oxygen double bond breaks followed by capture of proton and a cyanohydrin is formed.



- b) Addition of alcohol to carbonyl compounds: Aldehydes or ketone react with one mole of alcohol to form hemiacetal or hemiketal, respectively. Reaction with second mole of alcohol gives acetal or ketal. In this reaction the alcohol with lone pair of electrons of oxygen atom acts as a nucleophile

Hemoacetal, Acetal and ketal (Addition products of alcohol with aldehyde and ketones, respectively).



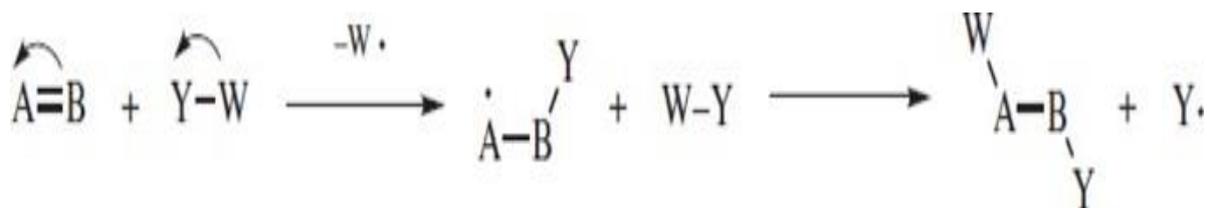
c) Nucleophilic addition to carbon-carbon double bond (Michael reaction):

In Michael reaction a nucleophile adds on to the β -carbon of an α,β -unsaturated system having electron withdrawing group. HY added to substrate having groups such as CHO, COR, COOR, CONH₂, CN, NO₂, SOR, SOOR etc. always give a product with Y- bonding with the carbon away from the Z group and follows nucleophilic mechanism.



Free Radical Addition Reactions

Free radicals add to an unsaturated molecule to give a new radical intermediate which further reacts to give final product. The radical is generated by photo light or spontaneous dissociation



Example of free radical addition reaction:

Addition of HBr to alkene in presence of peroxide (Anti-Markownikoff addition) is a type of free radical addition reaction. The peroxide acts as radical initiator. This is a stereoselective free- radical addition reaction.

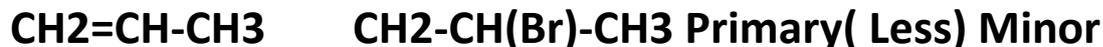


Benzoyl free Radical

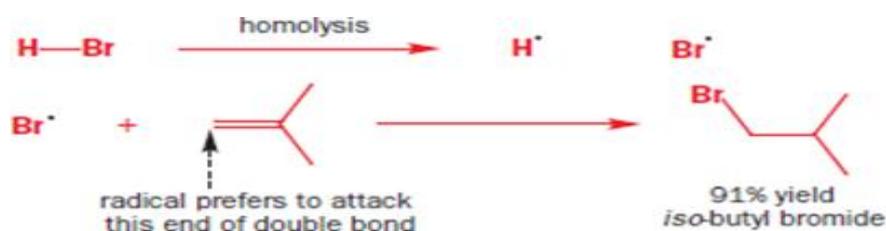


Reagent

Bromine free radical



... Radical (More stable)



Concerted Addition Reactions: (Cyclic Intermediate)

Concerted addition reactions occur by simultaneous attack at both the carbons. The initial attack is not at one carbon of the double bond, but both carbons are attacked

simultaneously. Most of these reactions involve four-membered transition state but in few cases, there is a five- or six-membered transition state. In these cases, the addition to the double or triple bond must be syn. The most important reaction of this type is Diels-Alder reaction

Reactant and reagent both are unsaturated (Lone pair)

Addition of alkene Dienophile with diene = Adduct (cyclic)

