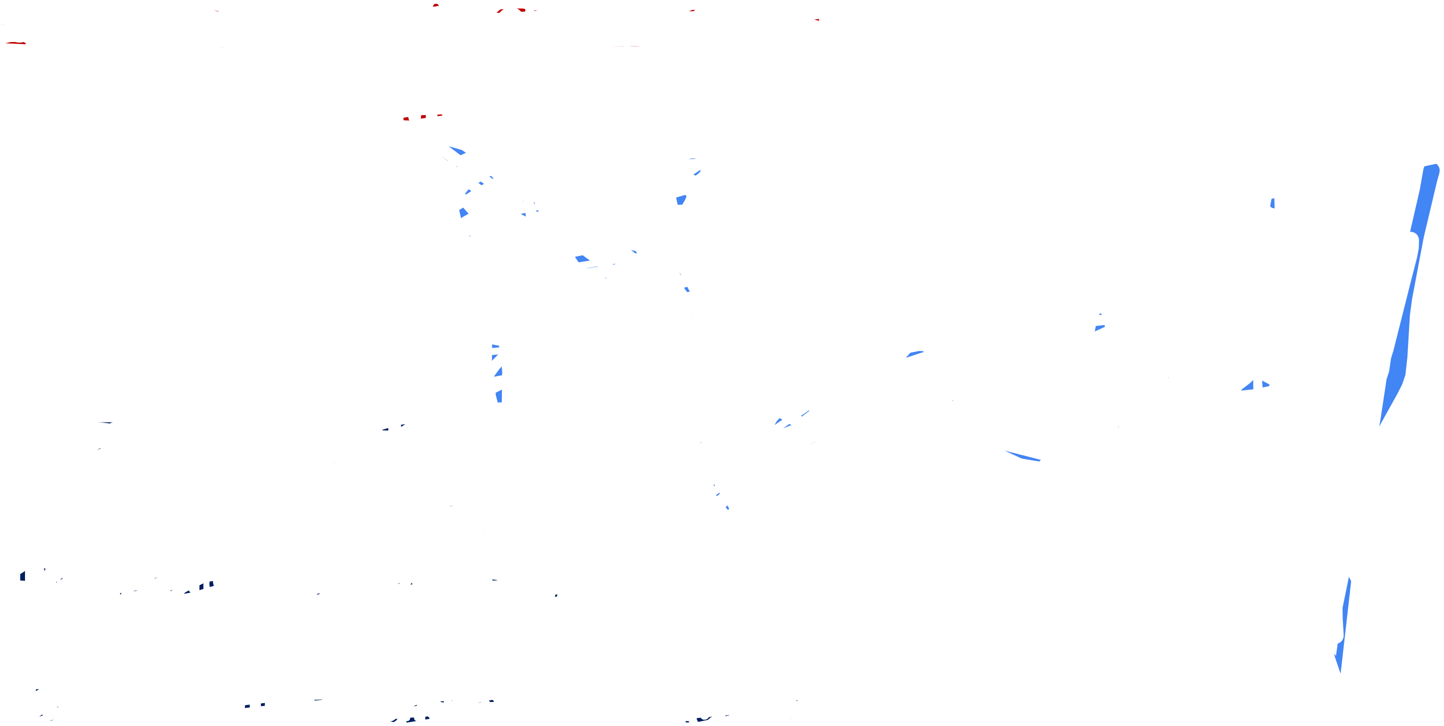
Addition to Carbon–Carbon Multiple Bonds



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,

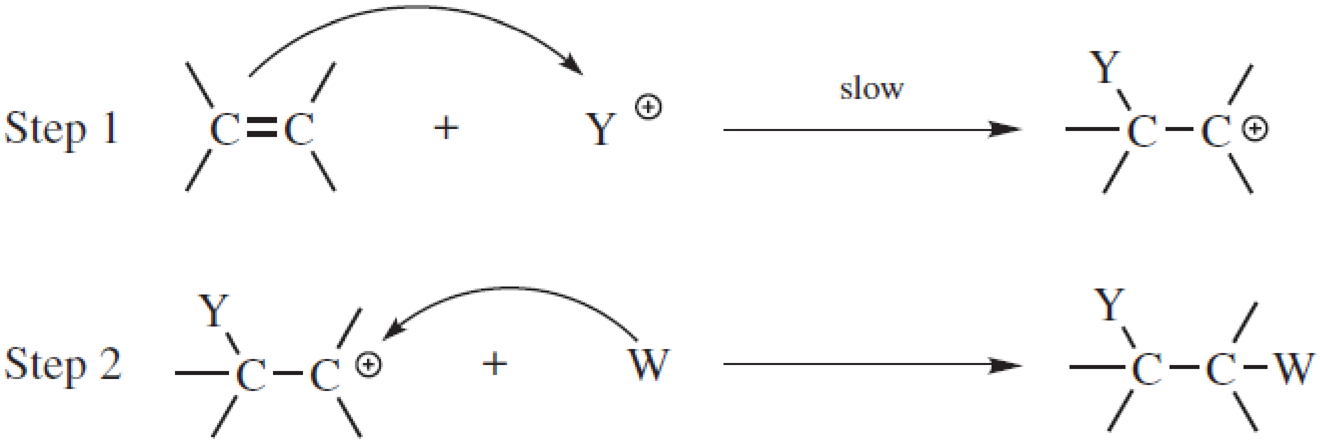
2. Two-step processes, with initial attack upon an electrophile

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

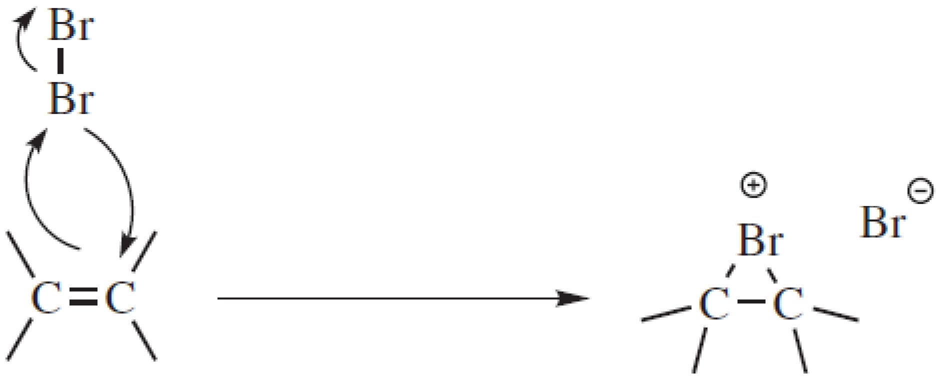
Mechanism and stereochemical aspects of the addition reactions involving electrophiles

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

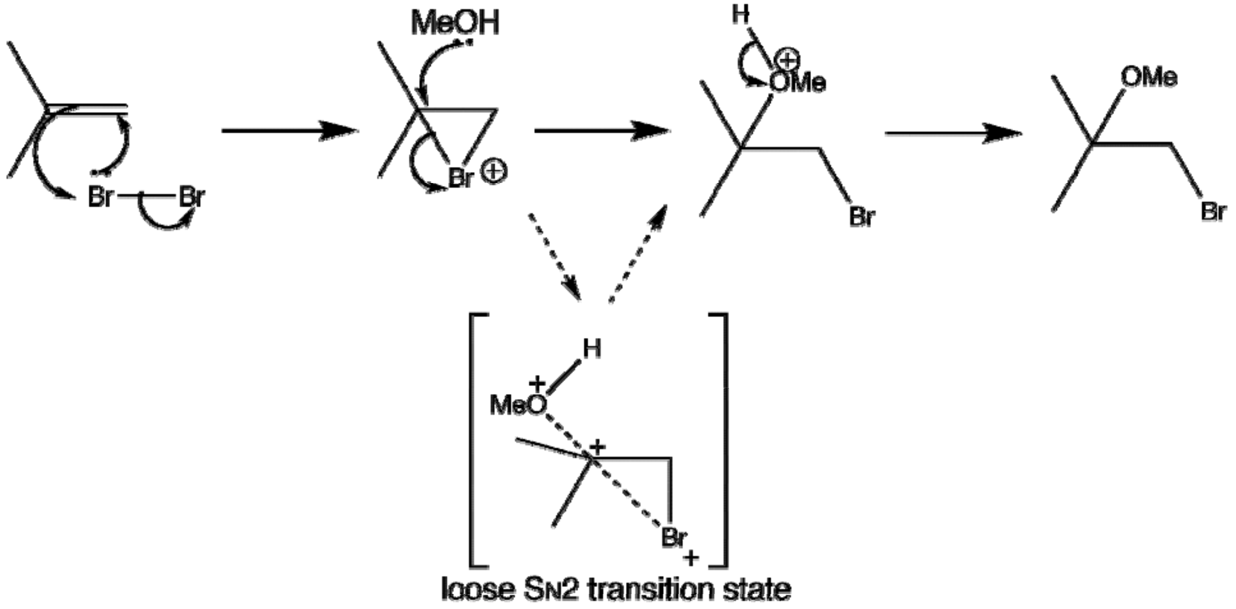


In the second step intermediate formed in the first step combines with the species (W) carrying an electron pair, generally, it is negatively charged

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

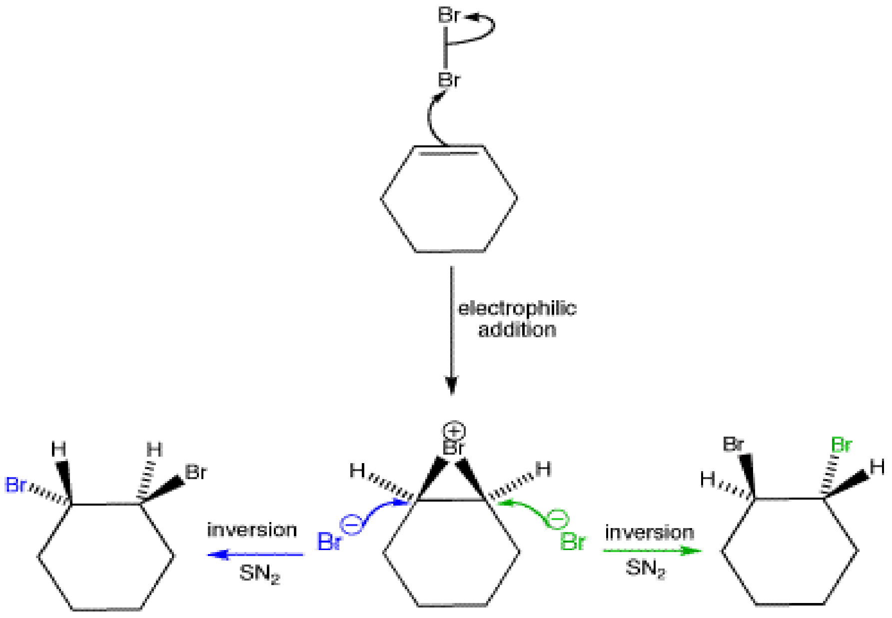


Unsymmetrical bromonium ion open regioselectively



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.

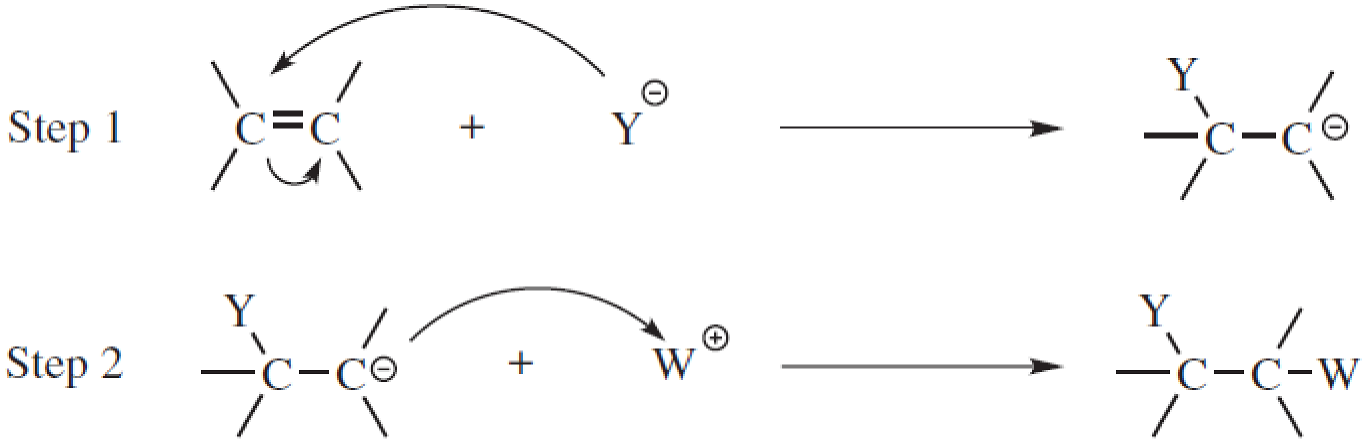
Formation of sterioisomers



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

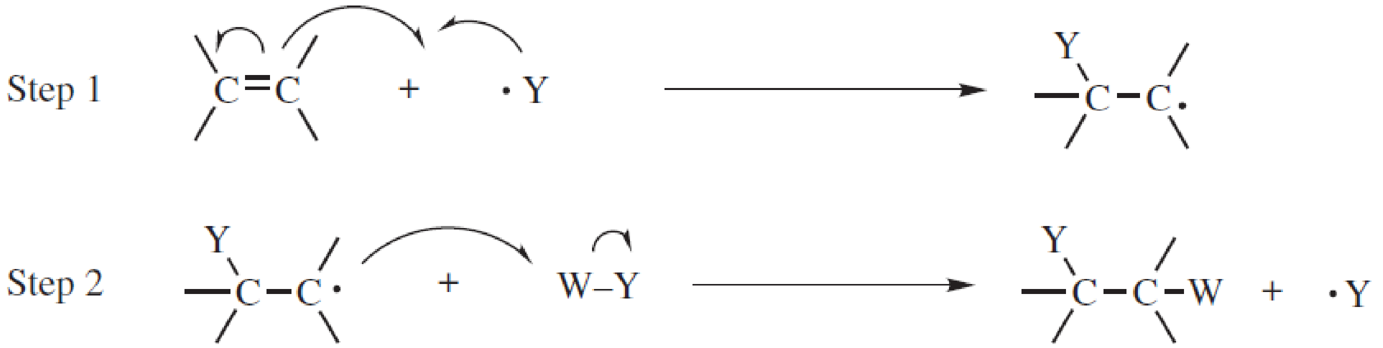
INITIATION STEP

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

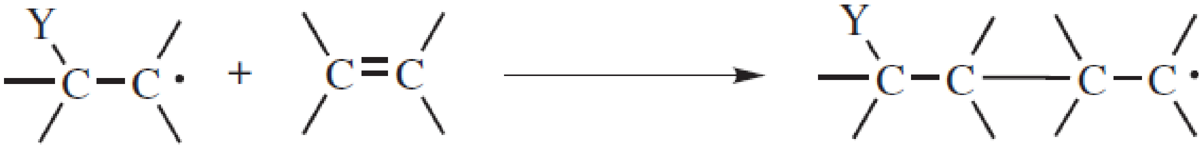
or

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

PROPAGATION STEP



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

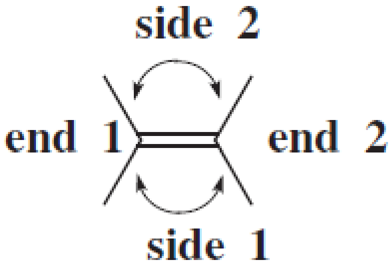
$$CCl_3CH{=}CH_2 < Cl_2CHCH{=}CH_2 < ClCH_2CH{=}CH_2 < CH_3CH_2{=}CH_2$$

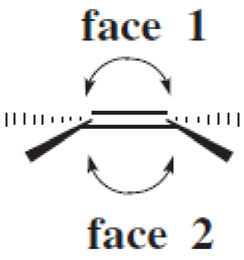
The case of nucleophilic addition reactions

For nucleophilic addition the situation is reversed. These reactions are best carried out on substrates containing three or four electron-withdrawing groups, two of the most common being $F_2C=CF_2$ and $(NC)_2C=C(CN)_2$. The effect of substituents is so great that it is possible to make the statement that simple alkenes do not react by the nucleophilic mechanism, and polyhalo or polycyano alkenes do not generally react by the electrophilic mechanism.

Orientation

When an unsymmetrical reagent is added to an unsymmetrical substrate, the question arises: Which side of the reagent goes to which side of the double or triple bond?

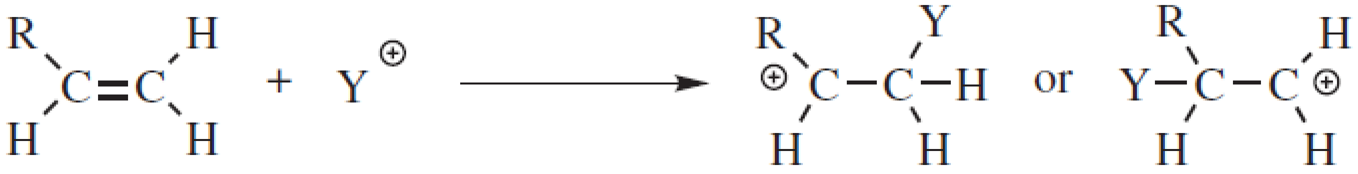




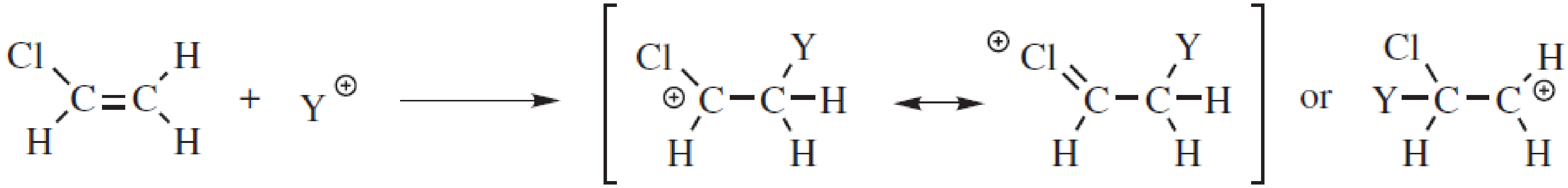
Markovnikov’s rule

ELECTROPHILIC ADDITION REACTION

When an unsymmetrical reagent is added to an unsymmetrical substrate, the question arises: Which side of the reagent goes to which side of the double or triple bond. Electrophile attack, to Carbon–Carbon Multiple Bonds that has more hydrogens. A number of explanations have been suggested for this regioselectivity, but the most probable is that Y+ adds to that side which can give the more stable carbocation



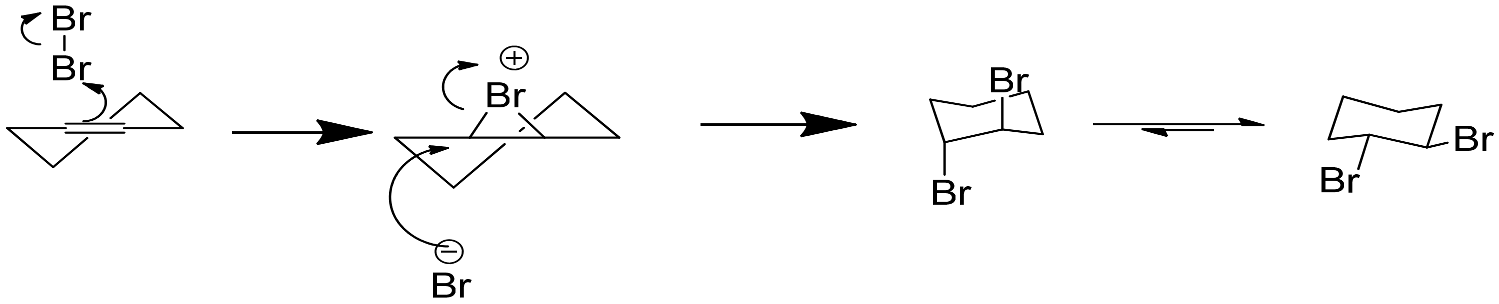
More stable



More stable

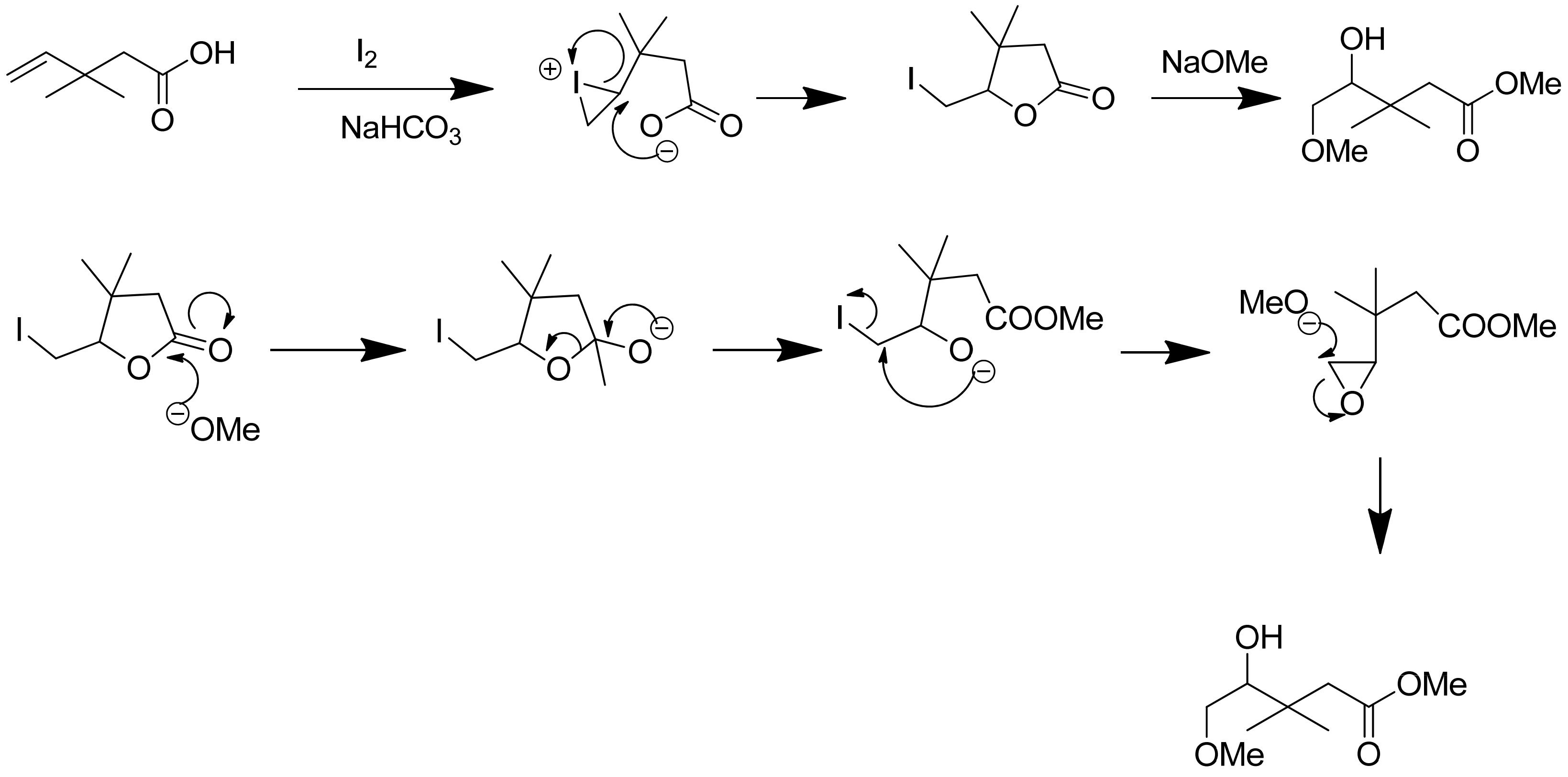
BROMINATION OF CYCLOHEXENE

For the formation of epoxide ring closure is possible only when the compound is diaxially substitutes and thus ring opening also takes place leading the formation of diaxial product. Similarly bromonium ion also open with the formation of diaxial product which easily flip to di equatorial conformation.



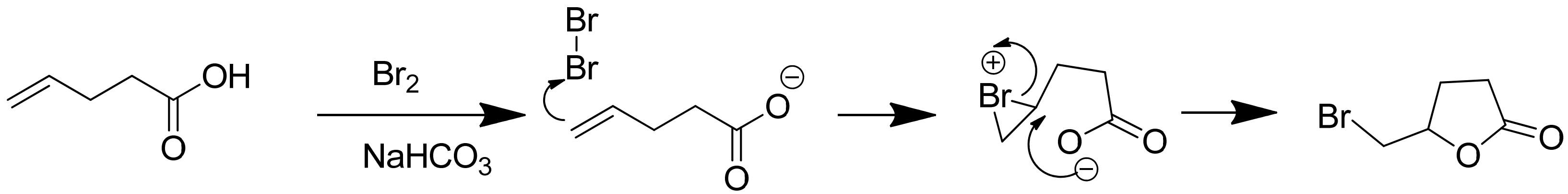
IODO LACTONIZATION

Alkene is undergoing electrophilic addition reaction. Iodonium ion is opened by intramolecular reaction leading the formation of epoxide. As the second step of the reaction has been carried out in presence of sodium methoxide ring opening takes place.



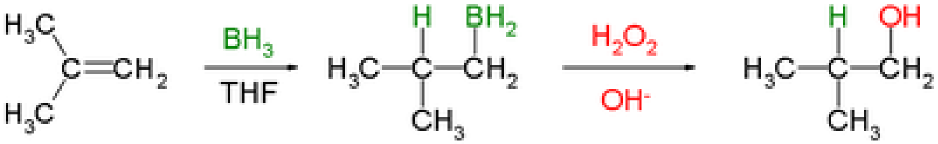
BROMO LACTONIZATION

The reaction is cyclisation of unsaturated carboxylic acid. The nucleophile is carboxylate anion. The reaction is known as bromolactonization.



Hydroboration oxidation reaction

The hydroboration oxidation reaction is an organic chemical reaction which is employed for the conversion of alkenes into alcohols that are neutral. This is done via a ***two-step process which includes a hydroboration step and an oxidation step.*** This is done by a net addition (across the entire double bond) of water.

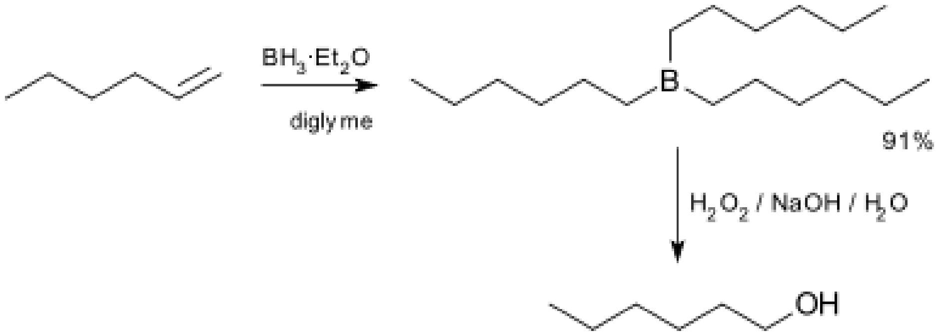


Hydroboration oxidation reaction mechanism can be considered as an anti-Markovnikov reaction where a hydroxyl group attaches itself to the carbon which is less substituted. The first time the hydroboration oxidation reaction was reported was in the second half of the 1950s by the *English born American chemist Herbert Charles Brown.* He went on to win the Nobel Prize in Chemistry in the year 1979 for this work.

The Hydroboration Step

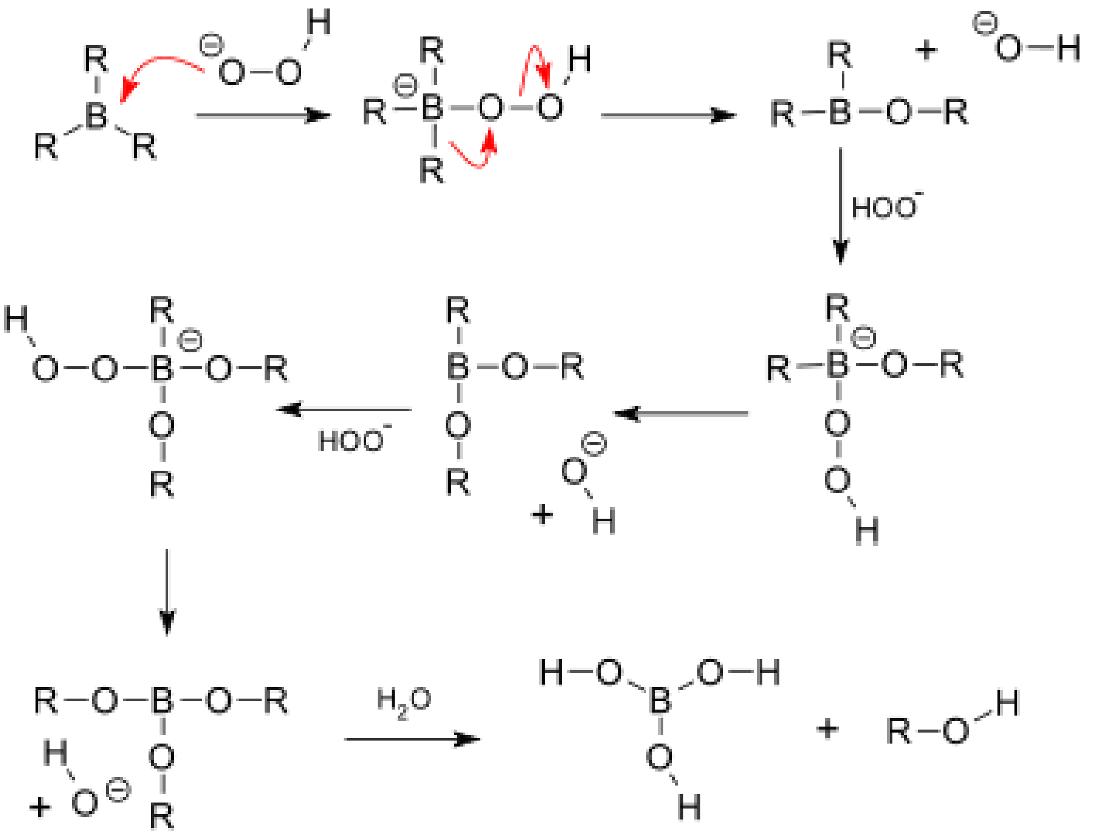
This step begins with the addition of borane in the form of BH_3 to the given double bond. This leads to the transfer of a hydrogen atom to the carbon atom that is adjacent to the carbon bonded with the boron atom. The hydroboration step described is now repeated twice, giving three alkenes that are attached to the boron atom from the initial BH_3.

The compound that results from the addition of three alkenes to the borane is referred to as trialkyl borane. This trialkyl borane is now treated with a base (or water) and hydrogen peroxide. Thus, the boron-carbon bonds are replaced with carbon-OH group bonds. The conversion of boron into boric acid is also observed. 1-hexene can be converted into 1-hexanol using this method as shown below.



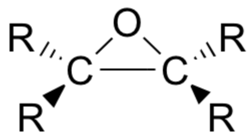
THE OXIDATION STEP

In the second step of the hydroboration process the boron atom comes under attack by the hydroperoxide ion which is nucleophilic in nature. Now, the R group is rearranged along with its bond pair of electrons to the adjacent oxygen atom



EPOXIDATION

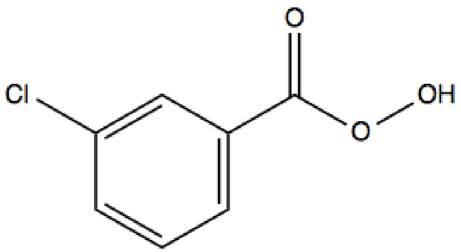
An epoxide is a 3-membered ring containing two carbon atoms and one oxygen atom (a cyclic ether). It is interesting because it is easily opened due to small ring strain and due to the electronegativity of the oxygen atom.



In epoxidation reactions an alkene is subjected to a peroxyacid to convert it into an epoxide. Another way to say that epoxidation is the electrophilic addition of oxygen to the double bond of the alkene.

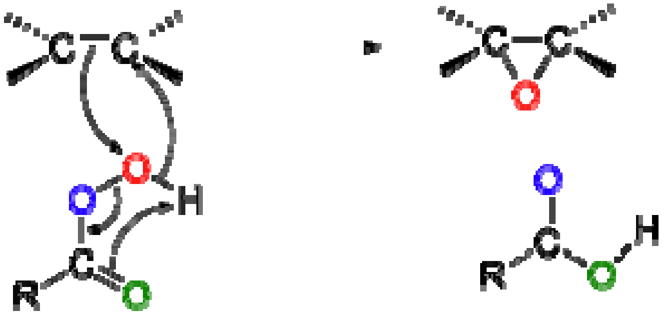
There are several types of commonly used peroxyacid such as proxy trifluoroacetic acid, peroxyacetic acid, hydrogen peroxide, and mCPBA, which is the most common of all.

mCPBA
meta-chloroperoxybenzoic acid



MECHANISM

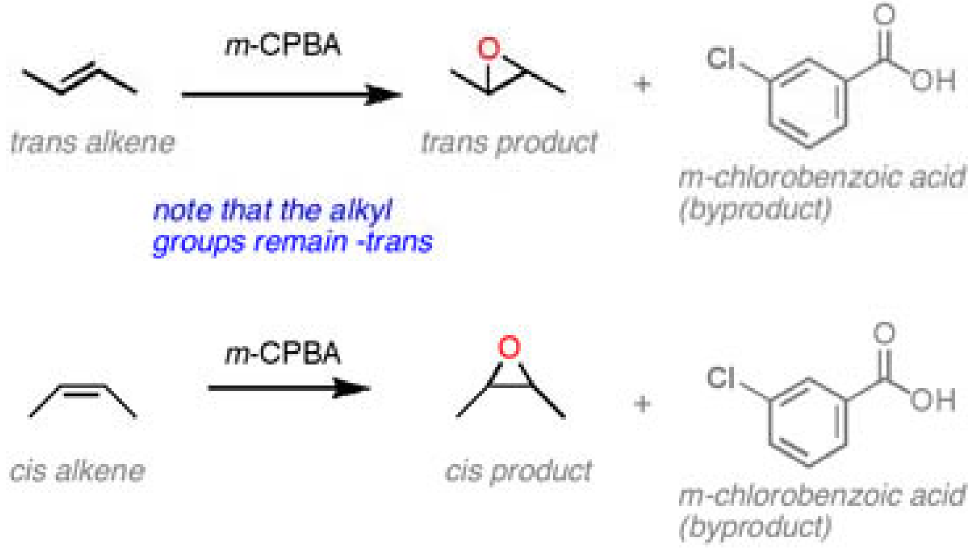
The double bond is electron rich and attacks the more electrophilic oxygen. This breaks the weak oxygen-oxygen bond and creates a new carbonyl. Once this carbonyl is formed, rearrangement occurs and the more electrophilic oxygen is released to become the oxygen of the epoxide.



STEREOCHEMISTRY

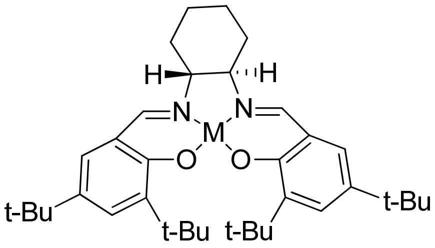
The stereochemistry associated with this reaction is interesting and important. As the reaction can occur on a cis or trans alkene, we see the two different products come from these two different starting materials. The oxygen can only attack from one face of the alkene. This means that the stereochemistry of the alkene is retained.

Epoxidation of alkenes

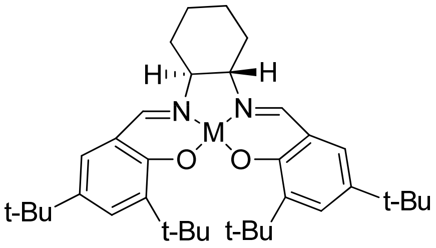


HYDROLYTIC KINETIC RESOLUTION (HKR)

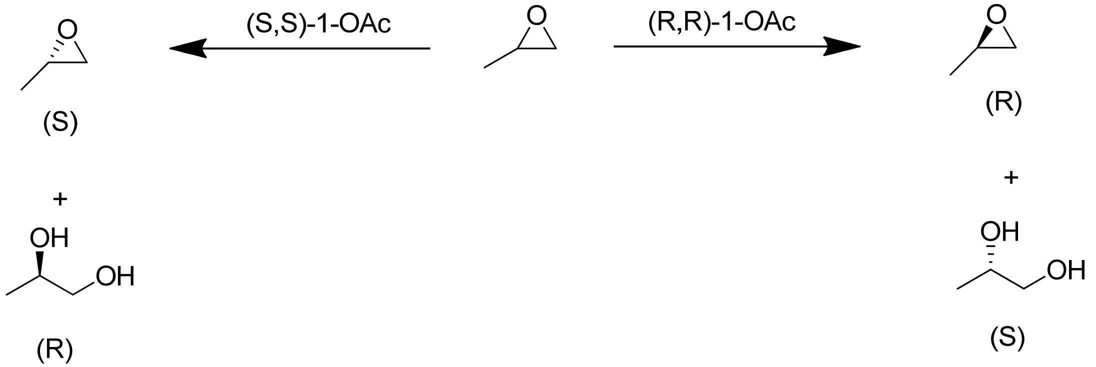
Jacobsen discovered the (salen)Co complex catalyzed efficient hydrolytic kinetic resolution (HKR) of a variety of terminal epoxides allowing efficient kinetic resolution of virtually any type of terminal epoxide.



M= Co: (R,R)
M= Co-OAc: (R,R)-5-OAc



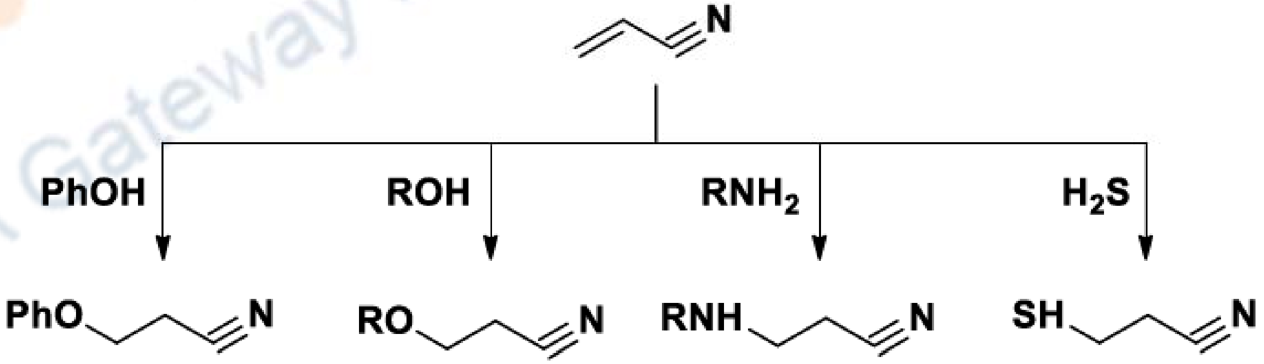
M= Co: (S,S)
M= Co-OAc: (S,S)-5-OAc



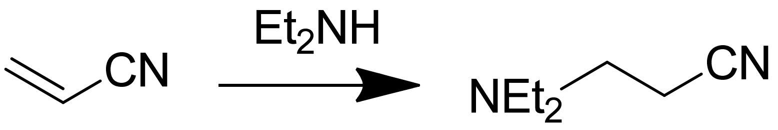
NUCLEOPHILIC ADDITION REACTION

Cyanoethylation

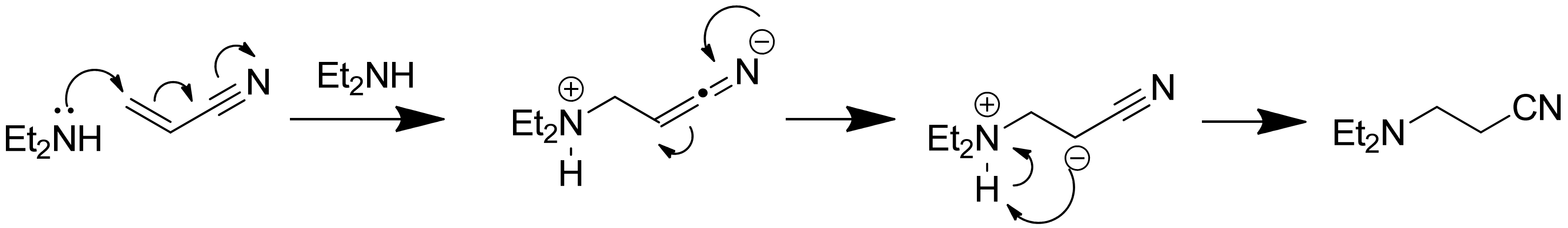
With alkenes containing a -CN substituent, the most common being acrylonitrile, a variety of nucleophiles such as phenols, alcohols, amines or sulfides may easily add to the unsubstituted carbon of the double bond. Thus, on abstraction of a proton from the solvent, the original nucleophile now has an attached 2-cyanoethyl group and this process is termed as **cyanoethylation.**



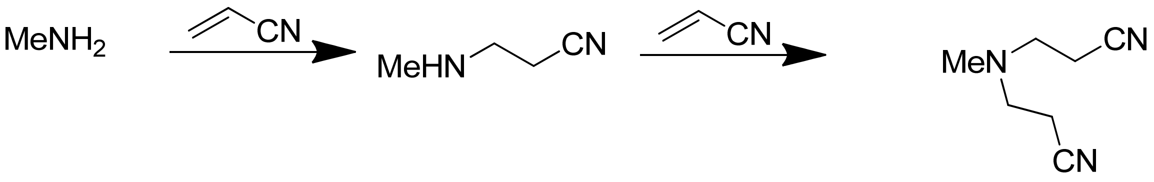
Reaction of acryl nitrile with diethylamine



MECHANISM

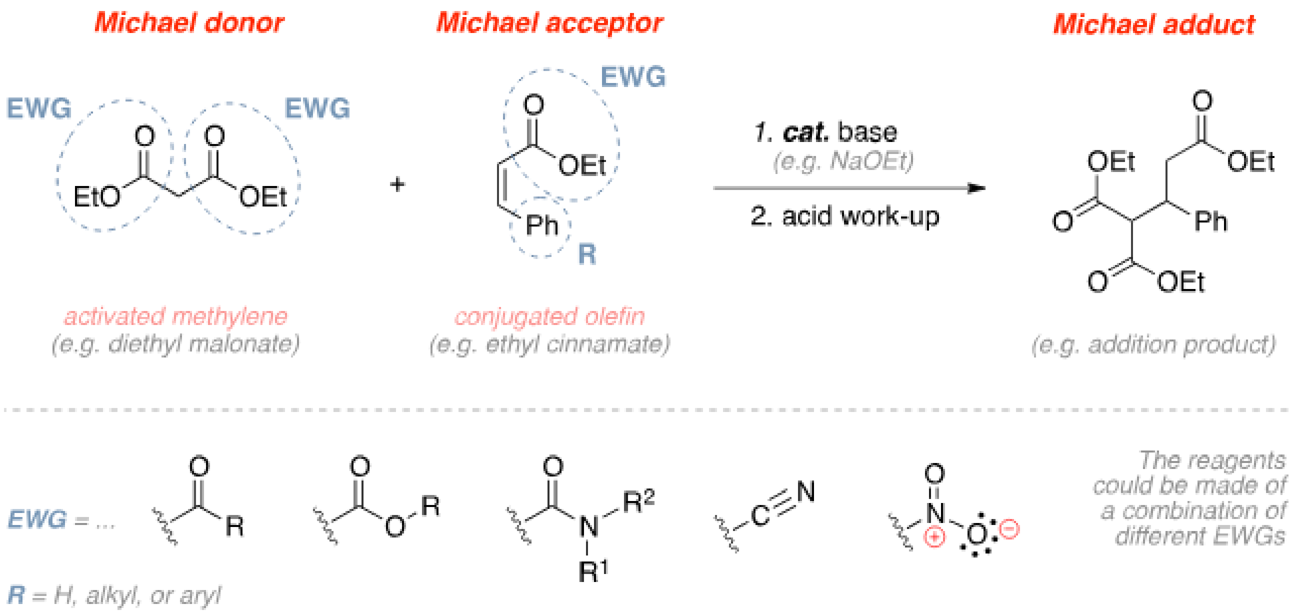


Reaction of acryl nitrile with ethyl amine

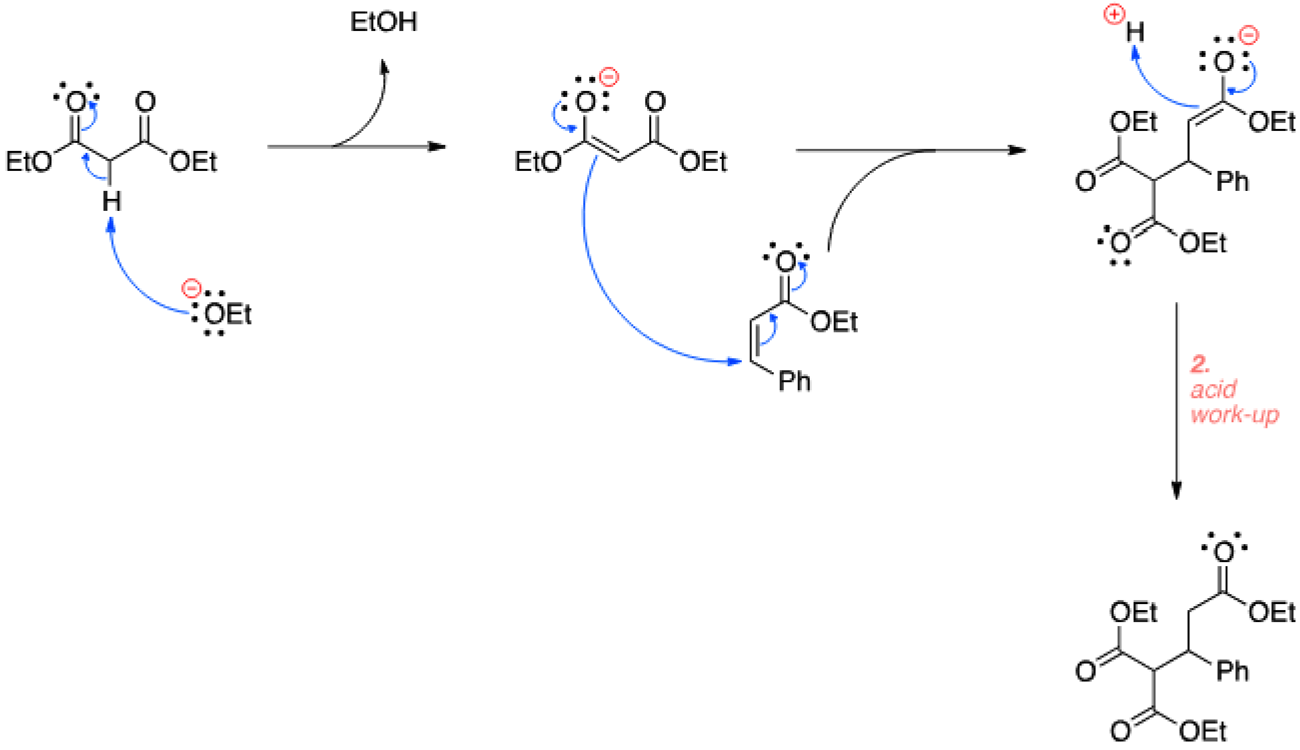


MICHAEL REACTION

The Michael reaction or Michael addition is the nucleophilic addition of a carbanion or another nucleophile to an α,β-unsaturated



MECHANISM

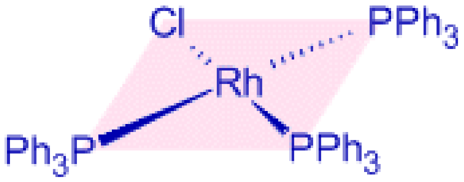


WILKINSON'S CATALYST

Homogeneous Catalysis

A homogeneous catalyst is a catalyst which is in the same phase as the substrate. Homogeneous hydrogenation involves two phases; hydrogen is in the gas phase and the catalyst and substrate (an olefin) are in the liquid phase. Therefore, although the system is technically heterogeneous, the catalyst is a homogeneous catalyst.

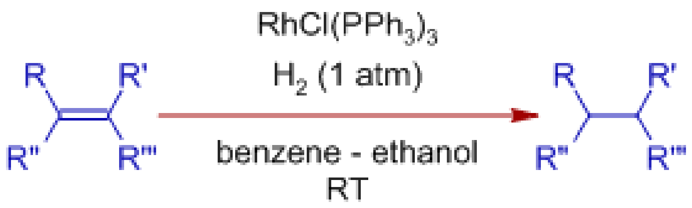
$RhCl(PPh_3)_3$ - Chlorotris(triphenylphosphine)rhodium(I), is known as Wilkinson's catalyst. It is used as a homogeneous hydrogenation catalyst. It is a square planar 16-electron complex. The oxidation state of Rhodium in it is +1



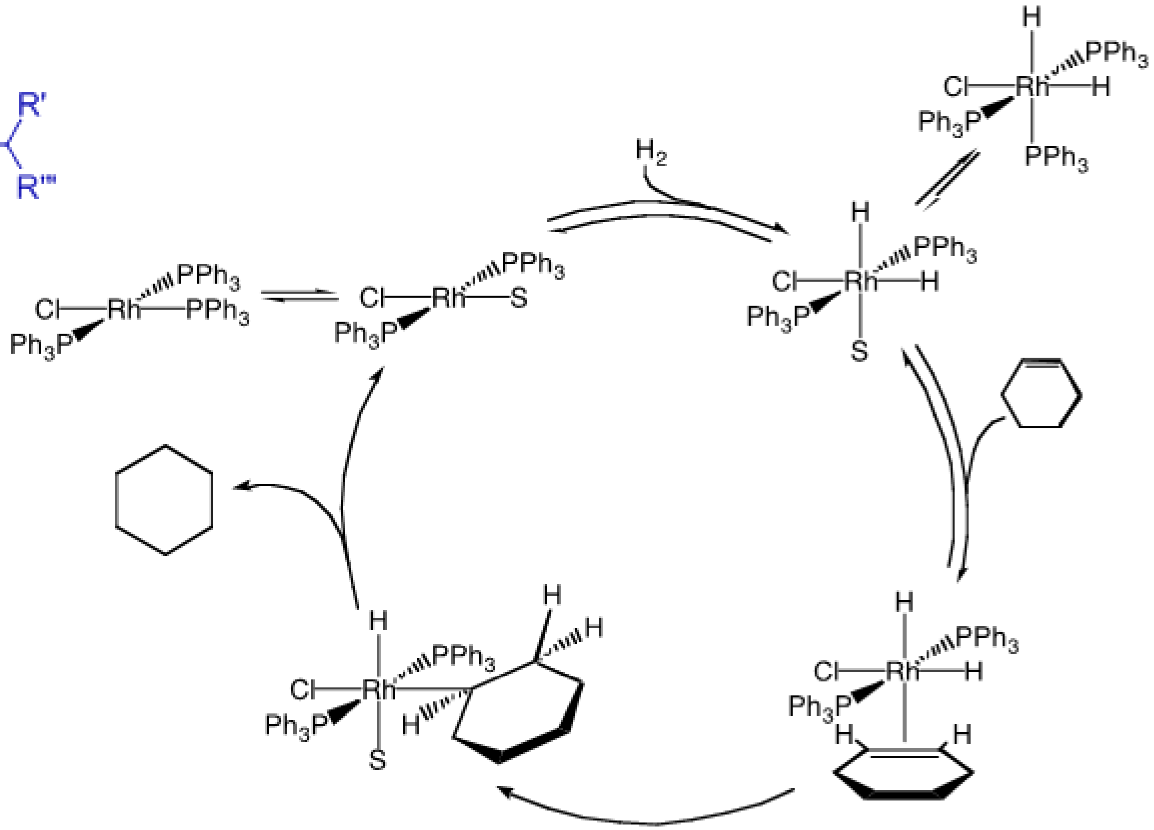
Wilkinson's catalyst can be prepared by reacting $RhCl_3.3H_2O$ with excess PPh_3 in EtOH

$$RhCl_3 \cdot H_2O + \text{excess } PPh_3 \xrightarrow{EtOH} RhCl(PPh_3)_3 + Ph_3P{=}O + \text{oxidized solvent}$$

It is used in the selective hydrogenation of alkenes and alkynes without affecting the functional groups like: C=O, CN, NO_2, Aryl, CO_2R etc

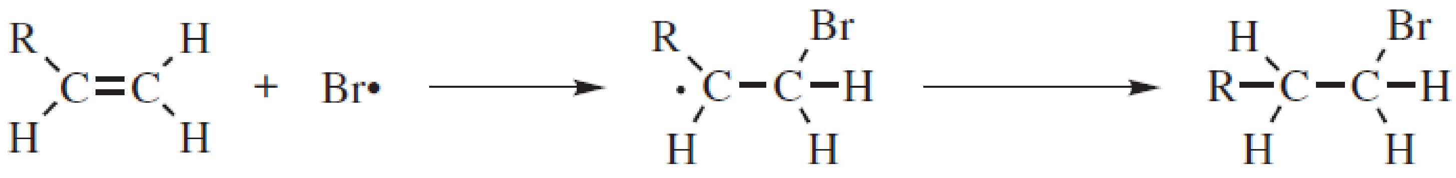


MECHANISM



FREE RADICAL ADDITION REACTION

In free-radical addition the main effect seems to be steric. All substrates CH_2=CHX preferentially react at the CH_2, regardless of the identity of X or of the radical. With a reagent such as HBr, this means that the addition is anti-Markovnikov



Thus the observed orientation in both kinds of HBr addition (Markovnikov electrophilic and anti-Markovnikov free radical) is caused by formation of the secondary intermediate. In the electrophilic case it forms because it is more stable than the primary; in the free-radical case because it is sterically preferred

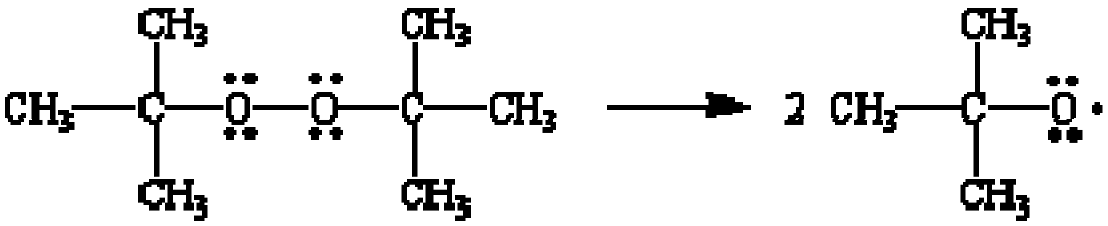
FREE-RADICAL POLYMERIZATION REACTIONS

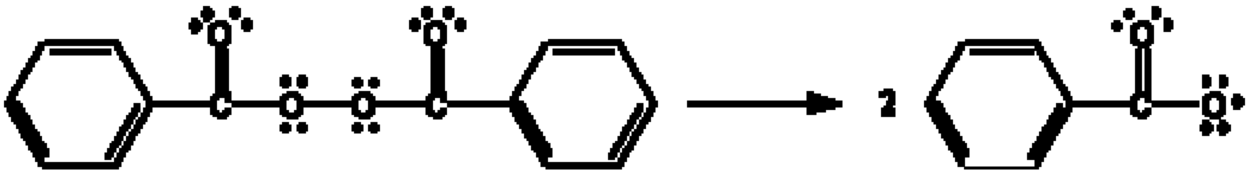
Formation of addition polymers from monomers containing C=C double bonds; many of these compounds polymerize spontaneously unless polymerization is actively inhibited.

The simplest way to catalyze the polymerization reaction that leads to an addition polymer is to add a source of a **free radical** to the monomer. In the presence of a free radical, addition polymers form by a chain-reaction mechanism that contains chain-initiation, chain-propagation, and chain-termination steps.

Chain Initiation

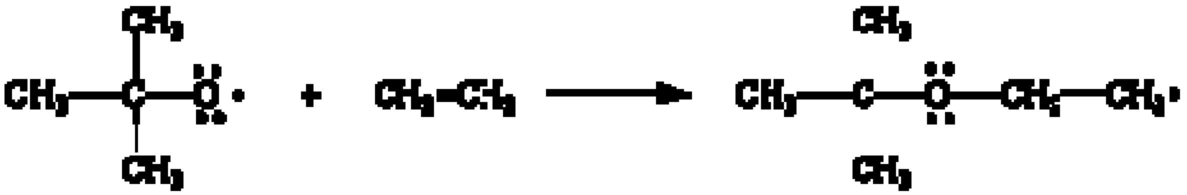
A source of free radicals is needed to initiate the chain reaction. These free radicals are usually produced by decomposing a peroxide such as di-*tert*-butyl peroxide or benzoyl peroxide, shown below. In the presence of either heat or light, these peroxides decompose to form a pair of free radicals that contain an unpaired electron.



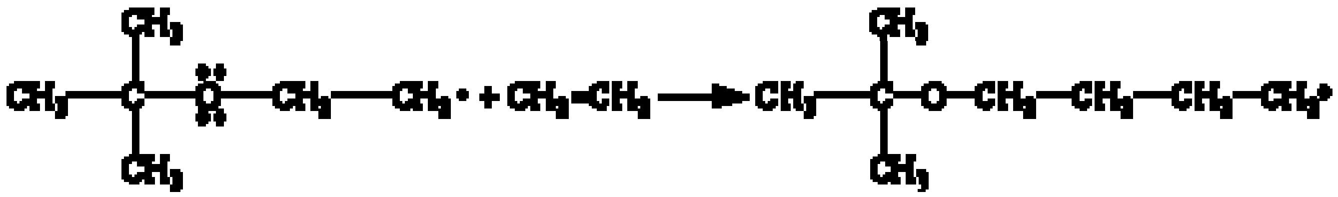


CHAIN PROPAGATION

The free radical produced in the chain-initiation step adds to an alkene to form a new free radical

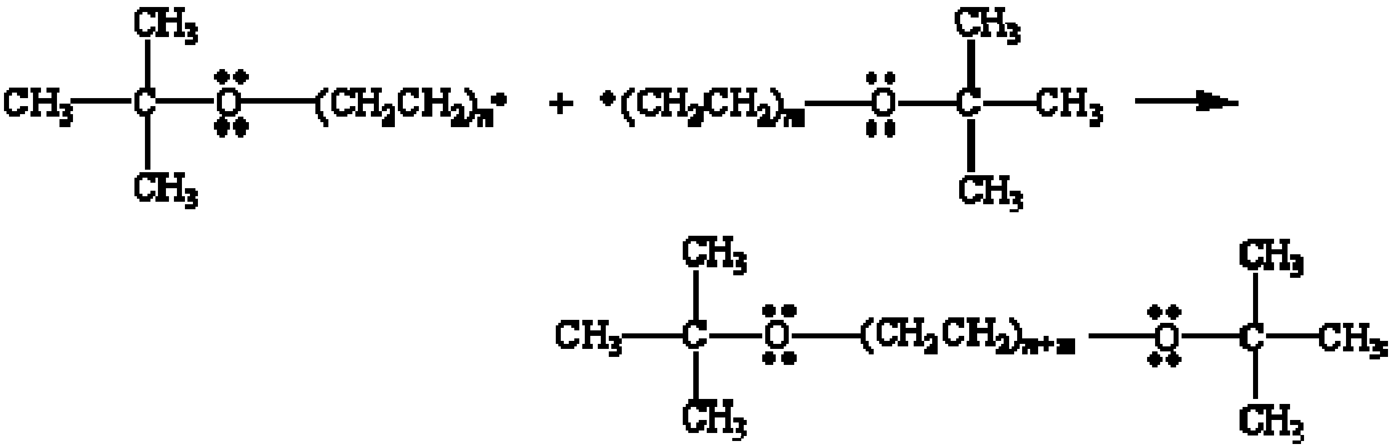


The product of this reaction can then add additional monomers in a chain reaction.



CHAIN TERMINATION

Whenever pairs of radicals combine to form a covalent bond, the chain reactions carried by these radicals are terminated.



$$(CH_3)_3C-\ddot{O}-(CH_2CH_2)_n^{\bullet} + {}^{\bullet}(CH_2CH_2)_m-\ddot{O}-C(CH_3)_3 \longrightarrow (CH_3)_3C-\ddot{O}-(CH_2CH_2)_{n+m}-\ddot{O}-C(CH_3)_3$$

BOOKS TO BE CONSULTED