CHAPTER 11

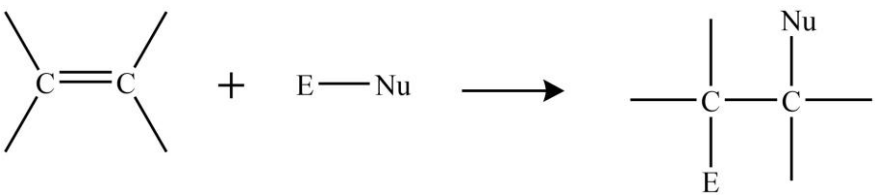
Addition to Carbon-Carbon Multiple Bonds

❖ Mechanistic and Stereochemical Aspects of Addition Reactions Involving Electrophiles, Nucleophiles and Free Radicals

We know that addition reactions in organic chemistry are the chemical transformations where two or more molecules combine to yield a usually single but bigger molecule called an adduct. Since these addition reactions are restricted to chemical compounds with multiple bonds, molecules with carbon-carbon multiple bonds (alkenes, alkynes, or many cyclic species like benzene derivatives or cyclo-alkene/alkynes), or with carbon-heteroatom multiple bonds (like carbonyl C=O or imine C=N derivatives) are suitable candidates. Furthermore, these addition reactions can be classified into polar addition (electrophilic and nucleophilic) and non-polar addition (free radical and cycloaddition) reactions. Nevertheless, in this section, we will only discuss the mechanistic and stereochemical aspects of electrophilic, nucleophilic, and free radical addition to the carbon-carbon multiple bonds.

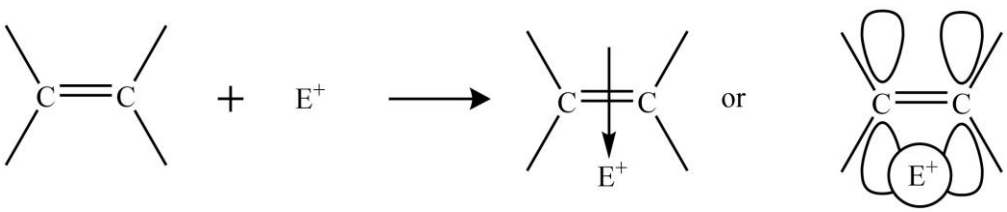
➢ *Electrophilic Addition to Carbon-Carbon Multiple Bond*

We know from the wave-mechanical treatment that space below and above the chemical bond is quite rich in electron density due to π-overlap; which makes the carbon-carbon multiple bonds very susceptible to electrophilic attacks. The general reaction showing the electrophilic attack on carbon-carbon multiple bonds is shown below.

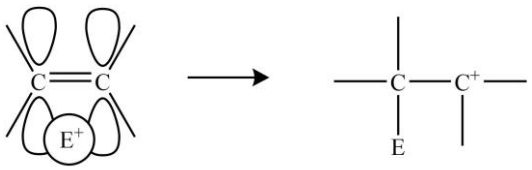


Now first we will discuss the mechanism responsible for this transformation and then we will study the stereochemical aspects of the same.

Mechanism: Since the reaction between the reagent and substrate requires them to get close to each other first, some attractive force is needed to do so. This can be achieved by considering the attacking reagent as a species that can be fragmented into electrophile (E^+) and nucleophile (Nu^-).



Now because the double bond is a Lewis base (and nucleophile), it will attract the electrophilic part of the attacking reagent towards itself, forming π-complex. One might ask the since we have a nucleophilic part too in the attacking reagent then why we don't call the nucleophilic addition; the answer would be that the electrophilic part attacks first, and therefore, dictates almost everything. Also, we can not assign the electrophile to any specific carbon because the empty orbital of the attacking electrophile is overlapping with π-bond and not with any particular atomic orbital. However, this π-complex so formed will get convert into carbocation with real sigma bonds as shown below.

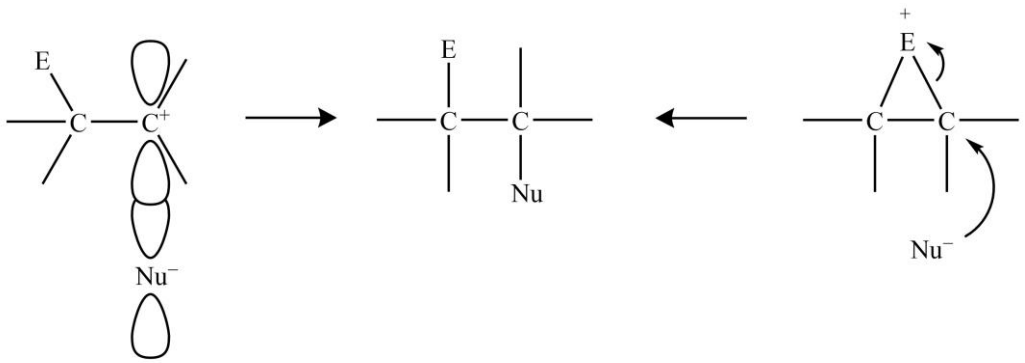


π-Complex Carbocation

Furthermore, if the attacking electrophile is having a lone pair of electrons, which can be donated to neighboring carbon, a three-membered cyclic cation will be obtained which can be represented via three resonating structures as shown below.

I II III

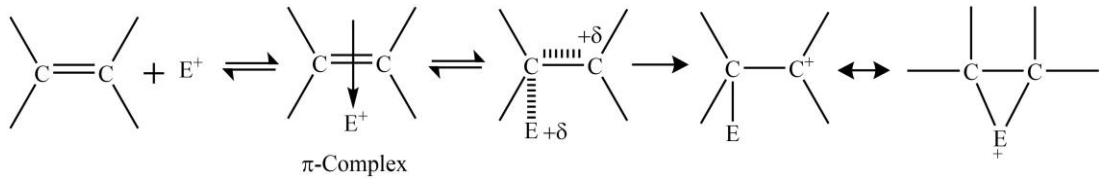
Now depending upon the relative stability of three resonating structures, the intermediatory carbocation becomes "more cyclic" or even acyclic at the extreme. In other words, the intermediate carbocation will be cyclic if structure II is more stable (and hence more contributing) and will be acyclic if the structure I and III are more stable (and hence more contributing). This cyclic (or acyclic) cation is then attacked by the nucleophilic part of the attacking reagent to give rise to the final product.



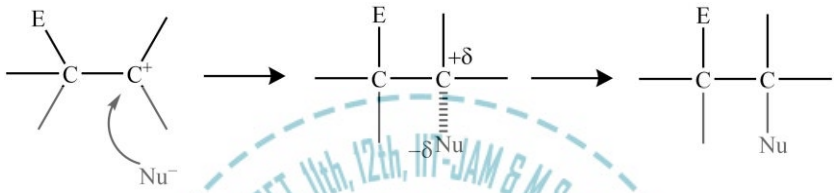
Attack on classical carbocation Attack on cyclic cation

The whole process of the electrophilic attack on the carbon-carbon multiple bonds can be fragmented into two steps as shown below.

1st Step:



2nd Step:

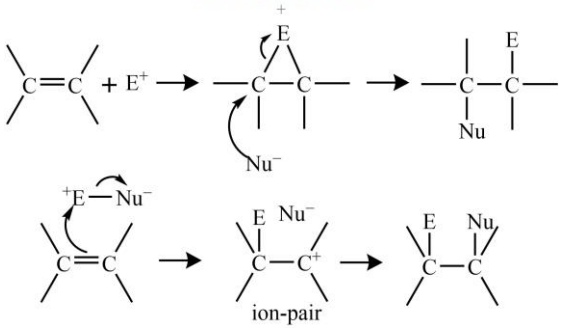


Stereochemistry: The stereochemistry of electrophilic addition to carbon-carbon multiple bonds is affected by two primary factors as discussed below.

i) The electrophile can attach itself to the double bond on the same or different side of the nucleophile i.e., syn- or anti-additions, respectively.

ii) In addition to the geometrical profile of addendum E^+ and Nu^-, the stereochemistry of the final product is also decided by the configuration of the addition product i.e., the orientation w.r.t rest of the molecule.

In other words, the electrophilic addition at the carbon-carbon multiple bonds can be cis- (syn) or trans- (anti), and may or may not be stereospecific. The only way for the nucleophile to attack is from backward if the intermediate is a cyclic cation; resulting in a syn addition product. Furthermore, if the reagent forms a 4-membered ring intermediate (instead of three), the addition will still be 'syn'.

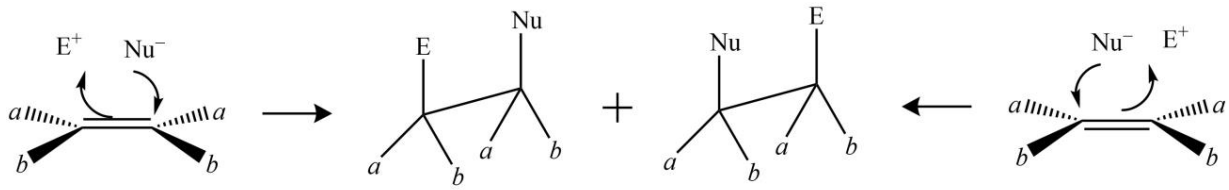


Conversely, if the classical carbocations dominate as intermediate and are having a sufficiently longer lifespan, they can show rotation about carbon-carbon single to yield a non-stereospecific product. However, if the classical carbocationic intermediate is short-lived, the nucleophile coming after the electrophilic attack may generate an ion-pair leading to a syn-addition product.

To find wheater the addition is syn or anti for a certain reagent (E–Nu), we need to use a substrate of form *ab*C=C*ab* where $a \neq b$ but E may or may not be the same as Nu. At this point, two scenarios can be realized, one when E ≠ Nu, and the other is when E = Nu; and we will discuss them one by one.

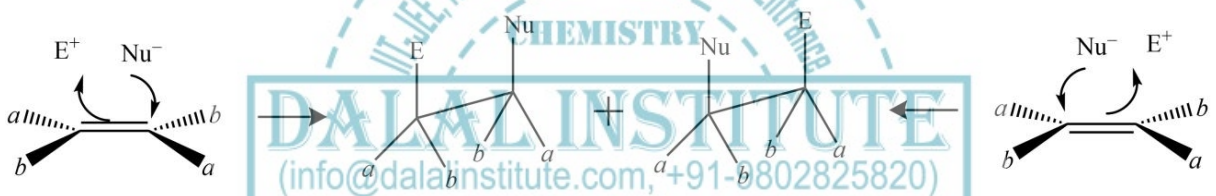
Case-I (E ≠ Nu):

If the addition is syn but on cis-compound, we will get a (*dl*)-erythro form via such type of transformation as shown below.



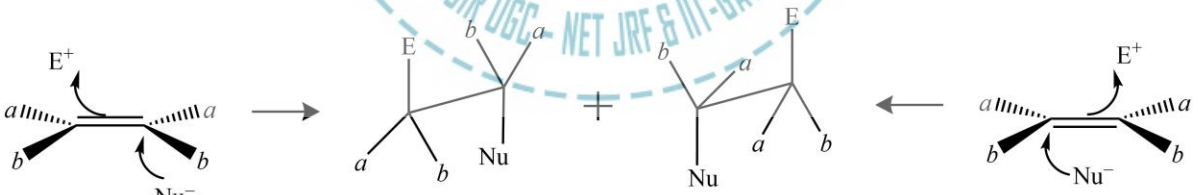
(*dl*)-erythro

On the other hand, if the addition is syn but on trans-compound, we will get a (dl)-threo form via such type of transformation as shown below.



(*dl*)-threo

Similarly, If the addition is anti but on cis-compound, we will get a (*dl*)-threo form via such type of transformation as shown below.



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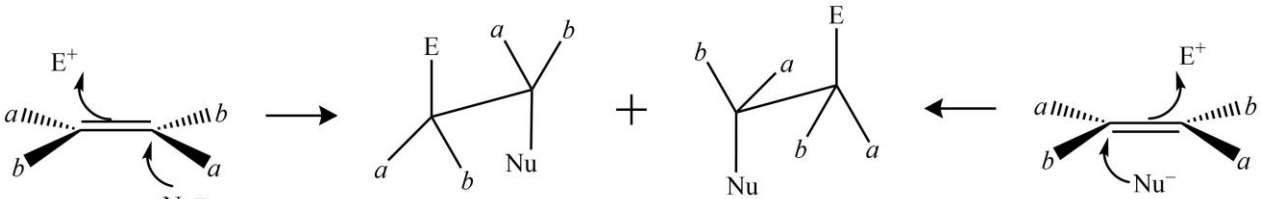
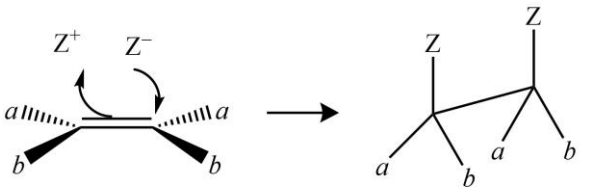


(*dl*)-erythro

Case-II (E = Nu):

In these types of cases, the (*dl*)-erythro forms will become meso-products; whereas the threo-forms will remain the same as shown below.



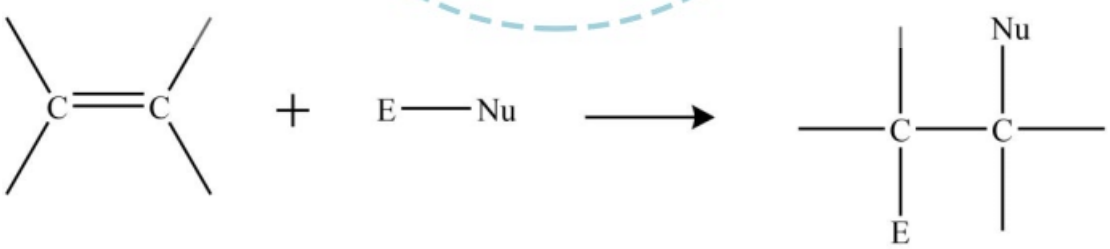
meso form

(*dl*)-threo form

Therefore, we may conclude that if the configuration of both the product and substrate are identified, the reaction pathway along with the addition mode can simply be predicted.

- ***Nucleophilic Addition to Carbon-Carbon Multiple Bond***

The nucleophilic addition in organic chemistry is an addition reaction where an organic compound with an electrophilic multiple bond reacts with an attacking nucleophile in such a way that the multiple bond is broken. It is different from the electrophilic additions because it involves the group, to which atoms are being attached, accepts electron pairs; whereas in electrophilic addition, the group, to which atoms are being attached, donates electron pairs. The reaction of nucleophilic attack on C-C multiple bonds is shown below.

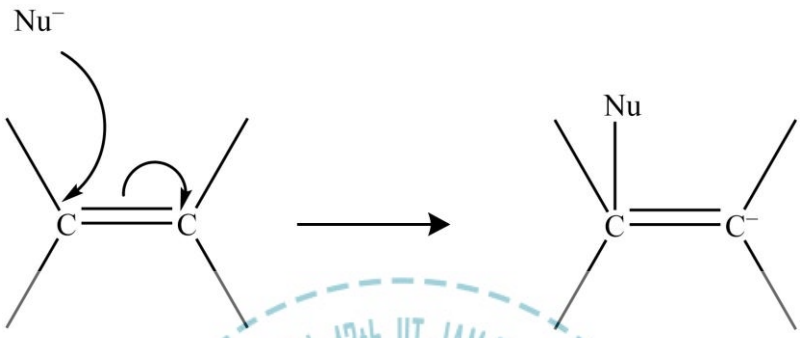


Substrate Reagent Product

Now first we will discuss the mechanism responsible for this transformation and then we will study the stereochemical aspects of the same.

Mechanism: The mechanism of nucleophilic addition to the carbon-carbon multiple bonds follows a two-step pathway as shown below.

Step I: The driving force for the addition to the alkenes is the generation of a nucleophile X^- that creates a covalent bond with an electron-deficient unsaturated system −C=C− (first step); and the negative charge on nucleophile is shifted to the C−C bond.



Step II: In the second step, the carbanion binds with the electrophilic part of the reagent (E^+) that is electron-deficient to form another covalent bond. Simple alkenes are not vulnerable to a nucleophilic attack due to the non-polar nature of the bond.

Stereochemistry: The stereochemistry of nucleophilic addition to carbon-carbon multiple bonds is affected by two primary factors as discussed below.

i) The nucleophile can attach itself to the double bond on the same or different side of the electrophile i.e., syn- or anti-additions, respectively.

ii) In addition to the geometrical profile of addendum Nu^- and E^+, the stereochemistry of the final product is also decided by the configuration of the addition product i.e., the orientation w.r.t rest of the molecule.

In other words, the nucleophilic addition at the carbon-carbon multiple bonds can be cis- (syn) or trans- (anti), and may or may not be stereospecific. The carbanion intermediate can be attacked in syn or anti mode to yield different products. To find wheater the addition is syn or anti for a certain reagent (E−Nu), we need to use a substrate of form *ab*C=C*ab* where $a \neq b$ but E may or may not be the same as Nu. At this point, two scenarios can be realized, one when E ≠ Nu, and the other is when E = Nu; and we will discuss them one by one.

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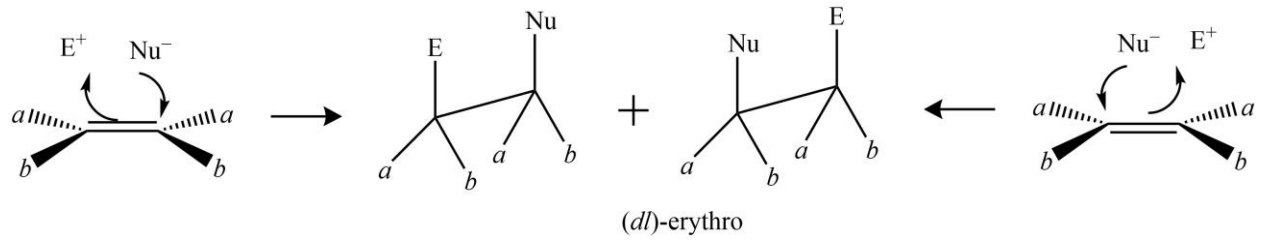

(*dl*)-erythro

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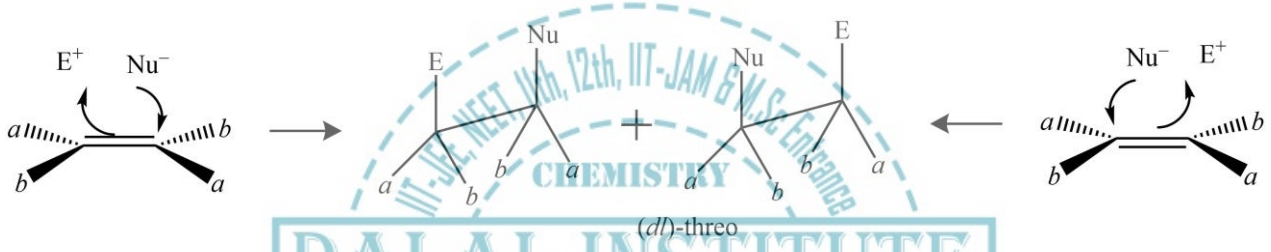
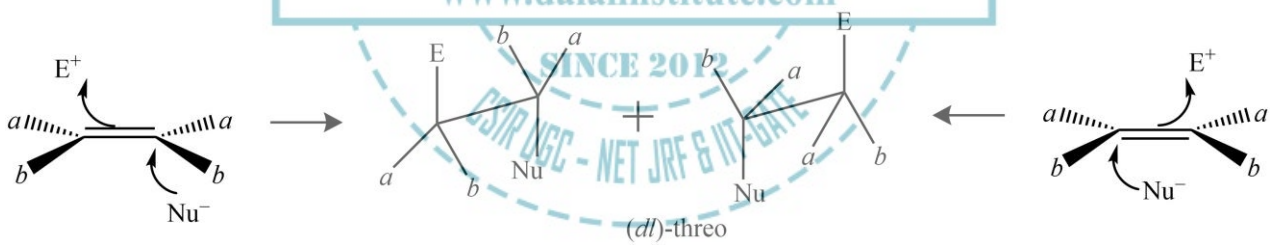


(*dl*)-threo

Similarly, If the addition is anti but on cis-compound, we will get a (*dl*)-threo form via such type of transformation as shown below.



(*dl*)-threo

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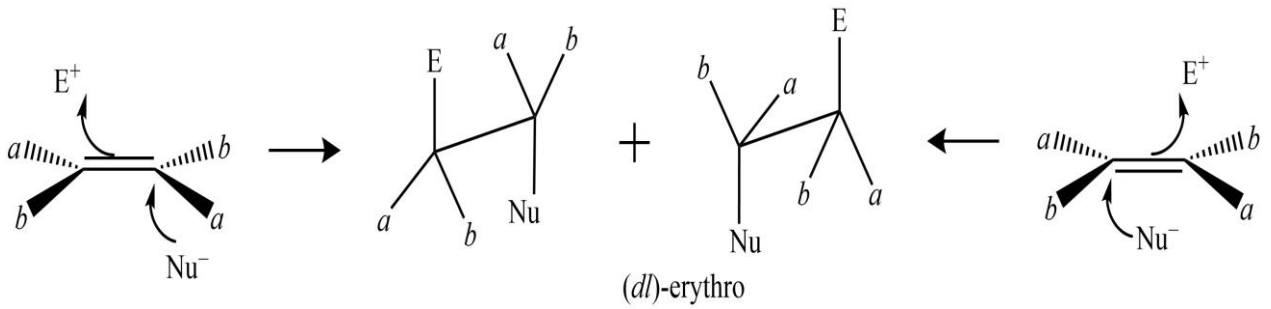
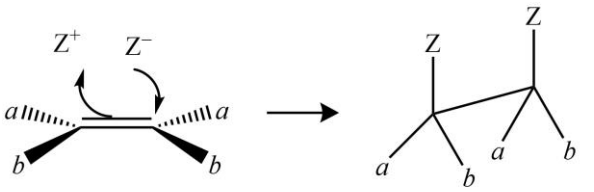


(*dl*)-erythro

Case-II (E = Nu):

In these types of cases, the (*dl*)-erythro forms will become meso-products; whereas the threo-forms will remain the same as shown below.



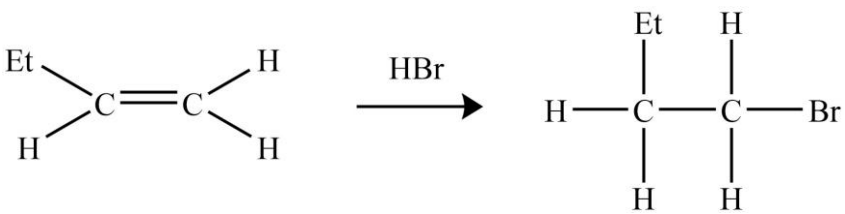
meso form

(*dl*)-threo form

Therefore, we may conclude that if the configuration of both the product and substrate are identified, the reaction pathway along with the addition mode can simply be predicted.

- ***Free Radical Addition to Carbon-Carbon Multiple Bond***

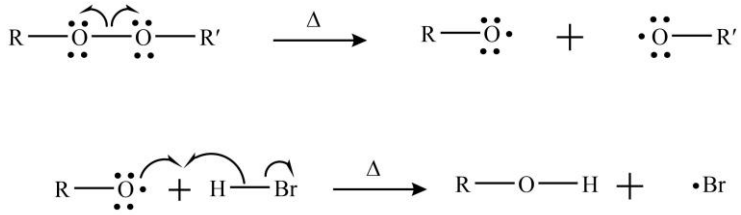
Besides electrophiles and nucleophiles, the reactive species that can initiate addition reactions to carbon-carbon multiple bonds are free radicals. All this started with the regioselectivity HBr additions where the product from Markovnikov Rule wasn't the 'major' product suggesting some other route than the normal electrophilic addition. Further research in this field showed that the reason for the anti-Markovnikov product is the contamination of the reactants by peroxide, which in turn initiated an entirely different pathway called the free-radical mechanism. Nevertheless, if extremely pure HBr is added to pure 1-butene, 1-bromobutane (Markovnikov product) was the main yield. The reaction of nucleophilic attack on carbon-carbon multiple bonds is shown below.



Free-radical reactions depend on a reagent having a (relatively) weak bond, allowing it to homolysis to form radicals (often with heat or light). Reagents without such a weak bond would likely proceed via a different mechanism.

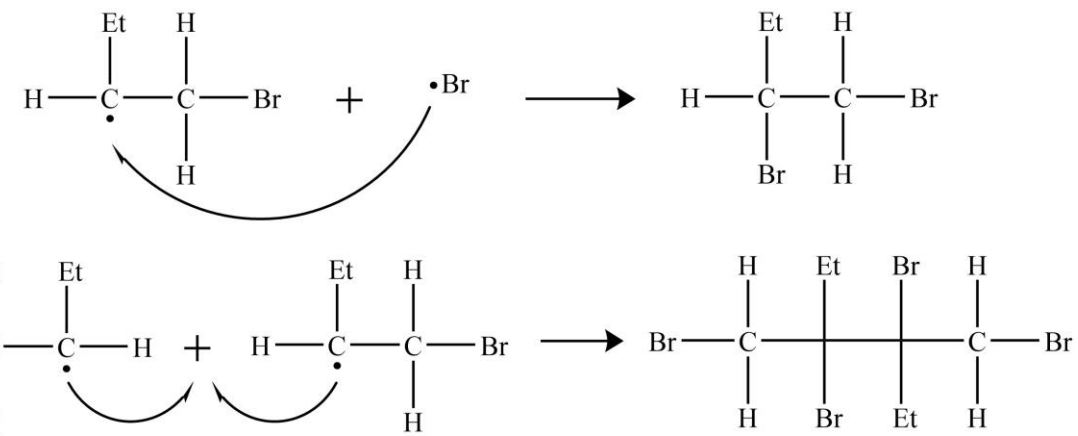
Mechanism: The mechanism of radical addition to the carbon-carbon multiple bonds follows a three-step pathway as shown below.

Initiation: In this step, a catalytic amount of organic peroxide is needed to abstract the acidic proton from HBr and generate the bromine radical.

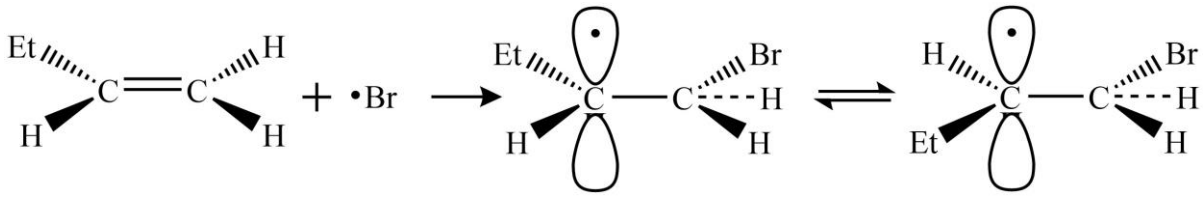


Propagation: In this step, the radical initiated addition to carbon-carbon multiple bonds propagates via the attack of free radicals on the substrate.

Termination: In this step, the radical initiated addition to carbon-carbon multiple bonds terminates via the attack of free radicals on the substrate.



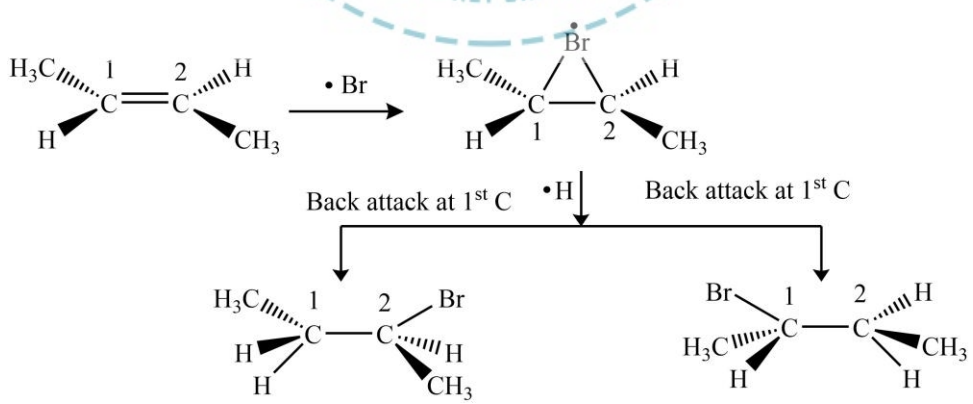
Stereochemistry: The addition of HBr to acyclic cis- or trans-olefins at room temperature results in 20% cis and 80% trans product, indicating that the radical addition of HBr to acyclic olefins is stereoselective but not stereospecific.



This can be rationalized in terms of rotation about C−C single bond in bromo-alkyl radical that can give rise to many conformations.

Conversely, if the reaction is carried out at −80°C, the trans addition resulted in 90% meso product whereas the cis addition resulted in 100% of (*dl*)-pair. All this can be rationalized in terms of a bridged molecular geometry. For cis-addition, we have

Similarly, for trans addition, we have



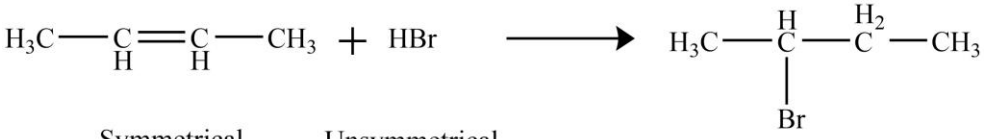
It is also worthy to note that the free-radical addition does not occur with the molecules HCl or HI because both reactions are extremely endothermic and are not chemically favored.

❖ Regio- and Chemoselectivity: Orientation and Reactivity

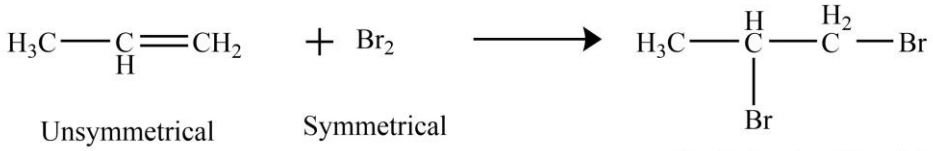
In this section, we will study the orientation (or regio-selectivity) and reactivity (chemo-selectivity) of addition to carbon-carbon multiple bonds.

➢ *Orientation of Addition to Carbon-Carbon Multiple Bonds*

The structural orientation will not affect the final product if either the regent or the alkene is symmetrical in nature. On the other hand, if the alkene and attacking reagent both are unsymmetrical, two different products can be obtained as shown below.



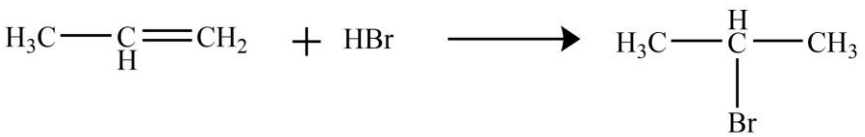
Symmetrical Unsymmetrical Single Product Possible



Unsymmetrical Symmetrical Single Product Possible

In such a case, one of the products will be major and the other one will be minor depending upon their relative yield. In other words, the structural orientation is nothing but the preference that the double gives during its shift to decide which carbon to bind electrophile and which one to the nucleophile. The regioselectivity of electrophilic addition can be rationalized via two different rules as given below.

1. Markovnikov's Rule: The problem of structural orientation or regioselectivity in electrophilic addition was solved by a Russian chemist, Vladimir Markovnikov, in 1870 by giving an empirical rule called Markovnikov's rule. This rule states that when a polar reagent (like protic acid HX) is added to unsymmetrical alkenes, the electronegative part (i.e., halide) binds to the carbon with more alkyl groups; whereas the electropositive part (i.e., hydrogen) binds to the carbon with more hydrogens.



Unsymmetrical Unsymmetrical Markovnikov Product

The theoretical basis for Markovnikov's Rule is the creation of a stable carbocation in the course of addition. The addition of the H^+ to one of the carbons in alkene gives rise to a positive charge on another carbon, yielding an intermediate carbocation.

If the carbocation is highly substituted, its stability will increase due to hyperconjugation and induction. The addition reaction's major product will be the one that is formed from the intermediate with the highest stability. So, the major product of the HX-addition (X is atom greater electronegativity than H) to an alkene has the H atom in the less substituted site and X in the more substituted site. Nonetheless, the other substituted product from less stable carbocation will still be yielded as minor having the opposite conjugate attachment of X.

2. Anti-Markovnikov's Rule: If the addition pathway carbon-carbon double bond doesn't involve an intermediatory carbocation, the regioselectivity will not be dictated by Markovnikov's rule; for instance, the free radical addition. Such additions are labeled as anti-Markovnikov additions because the halogen binds to the less substituted carbon (i.e., the reverse of Markovnikov addition).

The anti-Markovnikov rule can be demonstrated via the addition of HBr to isobutylene in the presence of hydrogen peroxide or benzoyl peroxide. The addition of hydrogen bromide to substituted alkenes was archetypal in the study of free-radical addition. Chemists in the early era found that the reason for the inconsistency in the ratio of Markovnikov to anti-Markovnikov products was because of the presence of peroxides (which are free radical ionizing substances). They thought that the O−O bond in the peroxide is comparatively weak; and therefore, light or heat, or sometimes even acting on its own, this bond gets broken to give two radicals species. These radicals can then interact with hydrogen bromide to give a Br radical, which in turn, reacts with the C−C double bond.

Now because the Br atom is comparatively bigger, more likely it will encounter and react with the least substituted carbon which can be attributed to less static interactions between the two. Additionally, just like a positively charged species, the radical will be more stable if the unpaired electron is in the more substituted site. The intermediary radical is then stabilized by the hyperconjugation effect. In the more substituted sites, a greater number of carbon-hydrogen bonds are aligned with the electron-deficient molecular orbital of the radical. All this implies that there are superior hyperconjugation effects, so that site will be more favorable. In such a case, the terminal carbon of the substrate will give rise to the primary addition product rather than the secondary one.

➢ ***Reactivity of Addition to Carbon-Carbon Multiple Bonds***

The double bond's reactivity towards the electrophilic addition increases with electron-donating groups and decreases with electron-withdrawing groups. For instance, consider the following order of reactivity.

$$CH_3CH{=}CH_2 > ClCH_2CH{=}CH_2 > Cl_2CHCH{=}CH_2 > CCl_3CH{=}CH_2$$

The above-given order gets revered if addition type becomes nucleophilic it will be supported by electron-withdrawing groups rather than electron-donating i.e.

$$CH_3CH{=}CH_2 < ClCH_2CH{=}CH_2 < Cl_2CHCH{=}CH_2 < CCl_3CH{=}CH_2$$

Also, the favourability of nucleophilic addition becomes significant only if three or four strongly electron-withdrawing groups like $F_2C{-}CF_2$ and $(NC)_2C{-}C(CN)_2$ are present. The substituents' effect is so dominant that polyhalo (or polycyano) alkenes almost always react via the nucleophilic pathway, whereas simple alkenes prefer to go via the electrophilic-addition route. Many reagents like ammonia which can only act as nucleophiles attack only react substrates vulnerable for such attacks. Conversely, the 'electrophilic only' type reagents simply refuse to add to the substrate like $F_2C{=}CF_2$. Furthermore, there are some reagents that add via electrophilic pathway if the substrate is simple alkene, but changes their mode of addition to nucleophilic if the substrate a polyhalo-alkene. For instance, HF and Cl_2 normally add via electrophilic attack, but it has been shown that Cl_2 and HF add to $(N{\equiv}C)_2C{=}CHC{\equiv}N$ and $F_2C{=}CClF$ via Cl^- and F^-, respectively.

Very fast Slow

Reactivity Toward Bromine in Acetic Acid

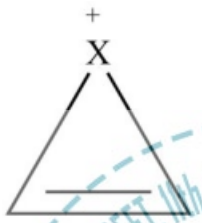
Substrates like the form $-C{=}C{-}Z-$ (Z = CHO, COR, etc.), where the substituent is conjugated with the double bond, almost always react via nucleophilic addition. The order of activation by the substituent Z is given below.

$$NO_2 > COAr > CHO > COR > SO_2Ar > CN > CO_2R > SOAr > CONH_2 > CONHR$$

The nucleophilic attack on substituted alkenes can be attributed to the reduced electron density which attracts the electron-rich species. Nevertheless, some alkenes do react via an electrophilic pathway even after substituted with electron-withdrawing groups.

The rationale given above isn't totally suitable when comparing addition to carbon-carbon double vs triple bonds. For instance, even though the triple bond is richer in electron density than the double bond, it is less susceptible to electrophilic attack, and usually prefers to react via nucleophilic addition. It has been observed that reagents that form bridged intermediate prefer to add to double bond the triple one. Also, the rate ratio of alkenes to alkyne is reduced when electron-withdrawing groups are attached.

The higher susceptibility of triple bonds to nucleophilic attack can be attributed to the firm attachment of electrons in the triple bond due to smaller carbon-carbon bond length, which in turn make the electron density less available for any such attack. Alternatively, the lower susceptibility of triple bonds to electrophilic attack can be explained in terms of the accessibility of the empty orbital in the alkyne. In other words, it has been shown theoretically that bent alkynes have a π^* orbital of lower energy than the π^* orbital of simple alkenes; and therefore, linear alkynes can get a bent during transition states (electrophile addition) but alkene cannot. Also, bridged-ion intermediates arising from electrophilic addition to triple bonds will be more strained than their double bond counterparts; and therefore, slowing the rate of electrophilic addition. Nevertheless, triple bonds conjugated to the Z group favor the nucleophilic addition more aggressively.



More Strain

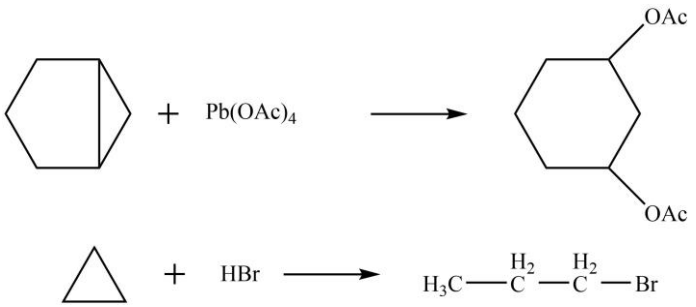
Less Strain

As expected, the attachment of alkyl groups typically increases the electrophilic addition's rates because of increased electron density; thought the order might change depending upon whether the intermediate formed is an open carbocation or a cyclic cation. If the first step is slowest (rate-determining) in electrophilic additions, like in the case of brominations, the rates for different substituted alkenes are dictated by the corresponding ionization potentials only and steric effects play little to no role.

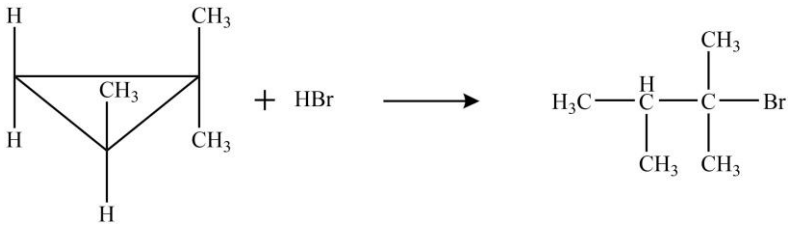
No special types of substrates are required for free radical additions and the presence of a reactive free radical species predominantly dictates the overall rate. In the absence of initiator, reagents HBr or RSH) prefer to attack via ionic pathway; however, the mechanism changes to free radical addition as the in the radical initiator is mixed. Nucleophilic and electrophilic radicals behave more or less like nucleophiles and electrophiles, respectively; and the rate is affected accordingly. Nevertheless, it isn't expected but The rate of reaction of nucleophilic radical attack is faster with alkenes than with alkynes. Finally, it is also worthy to note that the steric effect might get an important role in some particular cases like catalytic hydrogenation where substitution decreases the reaction rate due to adsorption on the catalyst surface.

❖ Addition to Cyclopropane Ring

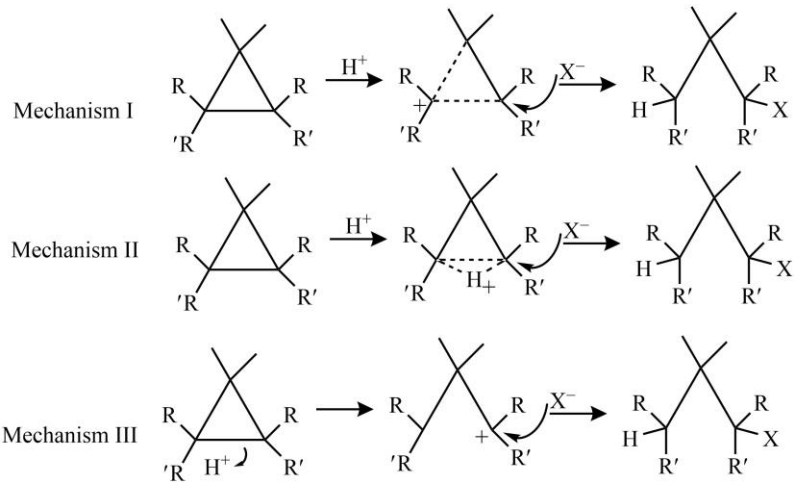
It is quite a well-known fact that cyclopropane rings behave in a similar manner as double bonds as far the reactivity is concerned. Therefore, like carbon-carbon multiple bonds, the cyclopropane ring can also undergo addition giving rise to open chain products as shown below.



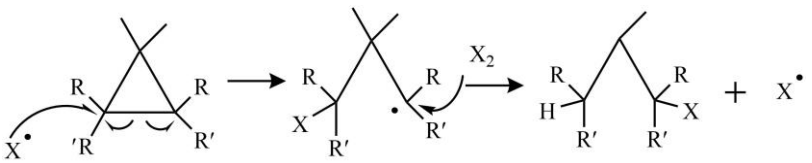
Now although the attack at cyclopropanes can occur via polar as well as non-polar additions, the electrophile type is the most important to discuss. The final product of electrophilic addition to substituted cyclopropanes is primarily dictated by Markovnikov's rule with rare exceptions.



The stereochemical configuration of the final product can be analyzed in terms of the electrophilic as well as nucleophilic part of the attacking reagent. The electrophilic position can give rise to retention, inversion, or a mixture of two; whereas the nucleophilic position almost always gives rise to inversion. Three primary mechanisms that the electrophilic addition can adapt are given below.



It is obvious that a cyclopropane ring system with one cornered carbon protonated is involved in the first mechanism; for instance, 7-norbornenyl and 2-norbornyl cations. On the other hand, the cyclopropane ring system with one protonate edge is involved in the second mechanism. The third mechanism involves an SE_2 type attack of H^+ to result in a classical cation, which subsequently reacts with the nucleophilic part of the attacking regent. It is also important to recall the fact that despite the depiction of configuration retention at carbon in all three cases, the 1st and 3rd routes are capable of giving inversion also. Since the cherry-picking of the mechanisms is not always possible, all or some of the cases take place at the same time. It has been found that Br^+ and Cl^+ react primarily via the second pathway; whereas D+ and Hg^{2+} react via the first pathway. Furthermore, density functional analysis has shown that edge-protonated is less stable than the corner-protonated; and the third pathway is usually opposed or less favorable. The reagents like Br_2 and Cl_2 can add to cyclopropanes via the free radical pathway (according to Markovnikov's rule) when the sample is irradiated with ultra-violet light. These free radical additions are stereospecific w.r.t only one carbon as shown below.

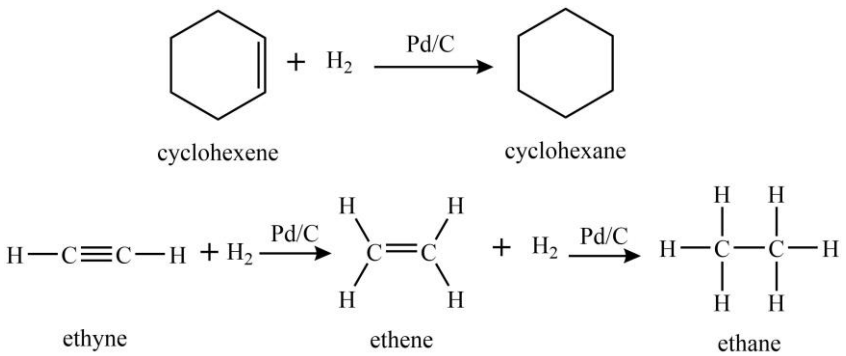


The addition to the cyclopropane ring may also occur in conjugated mode if the cyclopropyl ring is conjugated with a multiple bond.

❖ Hydrogenation of Double and Triple Bonds

The double and triple bonds in organic compounds can easily be reduced by heterogeneous catalysis. One of the most common examples of such type of addition to multiple bonds is the process of hydrogenation of alkene or alkyne. These reactions involve the attachment of two hydrogen atoms across the double or triple bond. Since a σ-bond is stronger than the π one, the hydrogenation of a multiple bond is thermodynamically favored (exothermic reaction). The molecule's stability can also be quantified in terms of its heat released during its hydrogenation.

Illustrative Reaction:



Mechanism Involved: It is also worth noting that the hydrogenation of multiple bonds does not proceed without the addition of a catalyst because the final product is thermodynamically favorable but the reactants are kinetically stable. To illustrate this, the reaction coordinate diagram for the hydrogenation of alkenes and alkynes is given below.

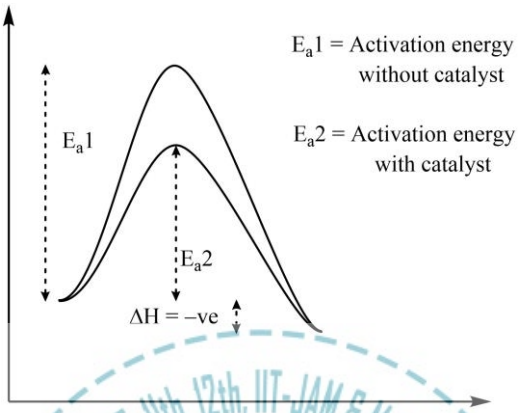
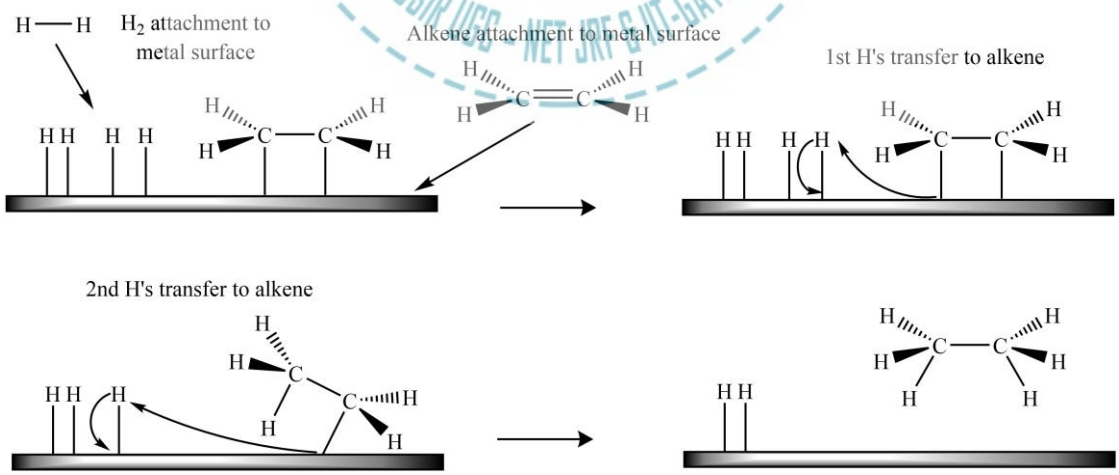


Figure 1: The reaction coordinate diagram for the catalytic hydrogenation of alkenes or alkynes.

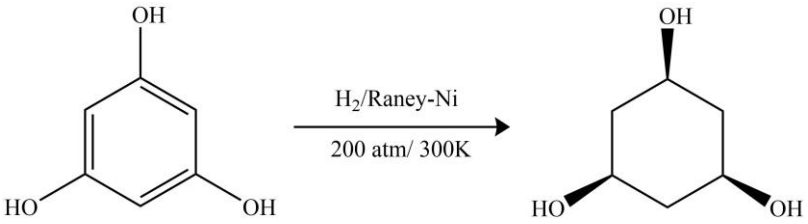
The H−H bond in dihydrogen breaks in the presence of a metal catalyst and each hydrogen atom gets attached to the surface heterogeneous metal catalyst via a metal-hydrogen bond. The participating alkene also gets absorbed on the catalyst's surface. At this stage, an H atom is moved to the participating alkene, via a new C−H bond, followed by the movement of the second hydrogen atom via another C−H bond. Furthermore, since the hydrogens and alkene are on a flat surface of the metal catalyst, the two hydrogens being attached must do so via syn addition (i.e., at the same face of the double bond).



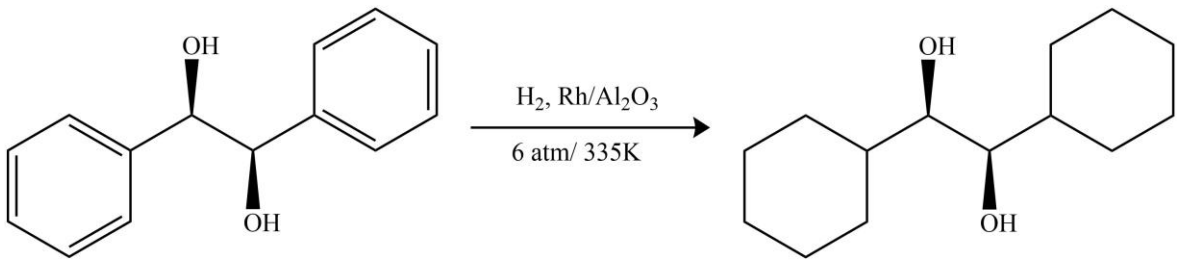
The most commonly used catalysts for alkene- or alkyne hydrogenation are platinum in the form of PtO_2, insoluble metals like palladium in the form of Pd-C, and Ni in the form of Ra-Ni.

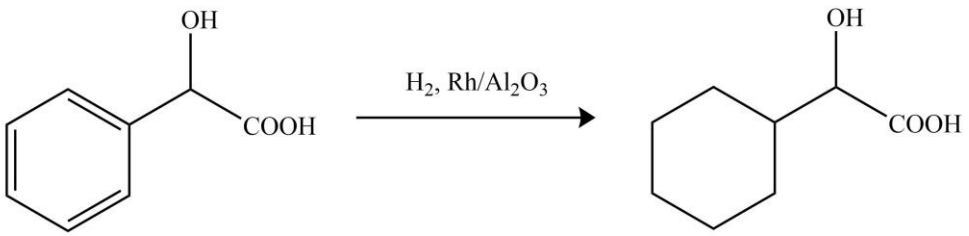
❖ Hydrogenation of Aromatic Rings

It is not an easy task to hydrogenate aromatic rings even If we use precious metal catalysts, and require higher pressures and temperatures will still be needed. Nonetheless, after initiating the hydrogenation of the benzene ring, it won't stop at partial hydrogenation and will give rise to cyclohexane. This can be attributed to the fact that once it is converted to cyclohexadiene, (endothermic step), the aromatic will be lost, and therefore, the subsequent hydrogenation-steps will become exothermic and will take place at a much faster transformation rate.



At normal temperatures, commonly used catalysts are Pt and Rh, while Ru catalysts or Raney-Nickel need much higher pressures and temperatures. Furthermore, the Raney-Nickel catalyst is used for mass-level hydrogenations including temperature and pressures of 150^{O}C and 100-200 atm, respectively. Another important catalyst is 'Rh over Alumina' which is needs very mild experimental conditions. It is also worthy to note that this catalyst does not make C−O bonds undergo hydrogenolysis, which is another useful aspect as far as practicality is concerned.



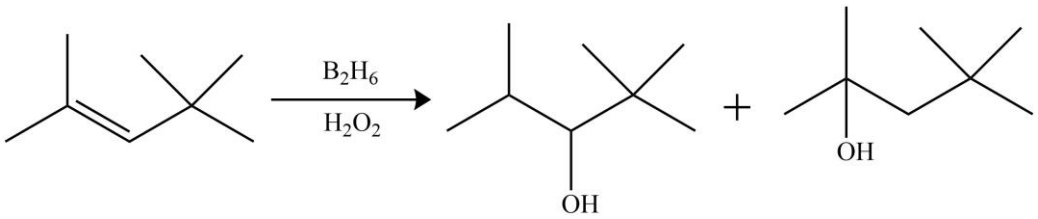


Polycyclic aromatic rings, like phenanthrenes and naphthalenes, can also undergo hydrogenation under suitable experimental conditions, and can fully- or partially be hydrogenated. For instance, decahydro- or tetrahydro-naphthalene can be obtained via Raney-Nickel catalyst under appropriate reaction conditions.

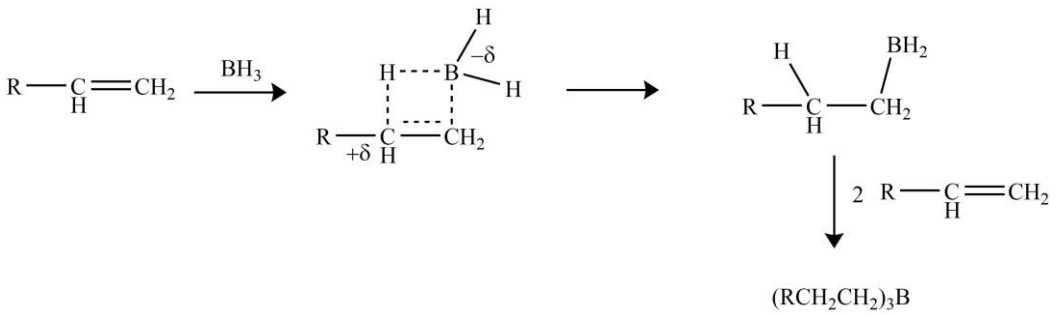
❖ Hydroboration

The hydroboration may simply be defined as the addition of a hydrogen-boron bond to C-N double bonds, and C-O double bonds, and C-C double or triple bonds. Hydroboration is extremely valuable in synthetic organic chemistry. Herbert C. Brown, who developed the conceptual and technological framework of hydroboration, received Nobel Prize in Chemistry for his work.

Illustrative reaction: A typical organic reaction hydroboration-type addition to carbon-carbon multiple reactions is given below.



Mechanism Involved: The hydroboration reactions are primarily dictated by anti-Markovnikov's rule, which means that the H gets attached to the most substituted carbon of the multiple bond. This reversal of regiochemistry indicates a polar $B^{\delta+}$–$H^{\delta-}$ bond. The hydroboration reaction occurs via a four-membered transition state where the H and the B atoms are attached to the same double bond's face. Since the mechanism is of concerted-type, the C-H bond is slightly slower than the formation of the C-B bond. Therefore, the B atom develops a somewhat negative charge in the transition state; whereas the partially positive charge resides on the more substituted carbon, which can be compensated via the +I effect from substituting groups. In other words, we may say that it is a case of group transfer reaction. Nevertheless, orbitals' investigation showed that the transformation is 'pseudopericyclic'; and therefore, the Woodward-Hoffmann rule cannot be implemented strictly for reactivity rationalization.

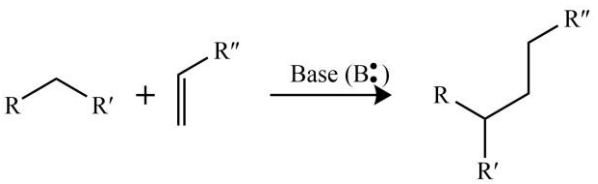


The hydroboration generally gives rise to compounds beyond monoalkyl borane if the reagent used is BH_3 (particularly in the case of alkenes with very small sterically hindrance). The hydroboration of trisubstituted alkenes can give rise to dialkyl boranes; though any subsequent alkylation of the organoboranes is discouraged due to increased steric hindrance. The difference of rate in the generation of di- and tri-alkyl boranes can be employed in the synthesis of bulky boranes to fine-tune the regioselectivity.

❖ Michael Reaction

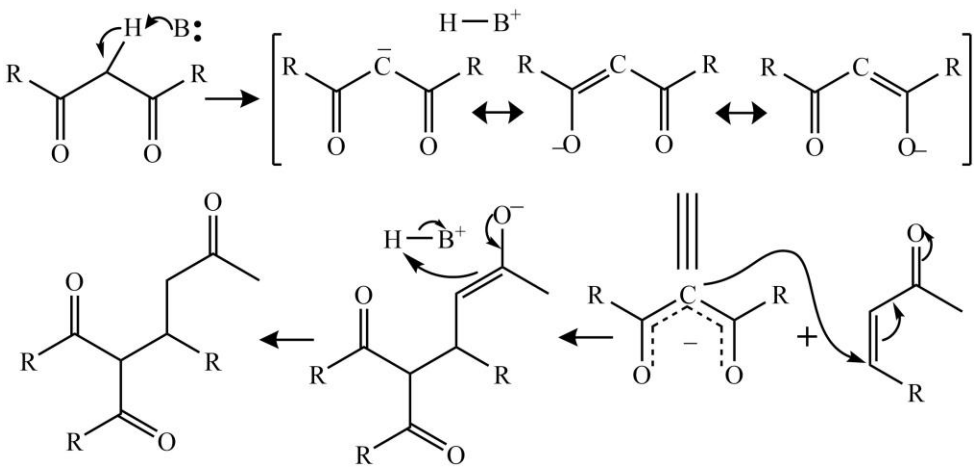
The Michael addition (or Michael reaction) may simply be defined as the addition of a nucleophile like a carbanion to an α, β-unsaturated carbonyl compound with an electron-withdrawing group. It is a type of conjugated addition, and this process is one of the most practical approaches for the formation of C-C bonds.

Illustrative Reaction: The typical organic reaction showing this type of addition is shown below.



Where R and R' on the nucleophile symbolize the electron-withdrawing groups such as cyano and acyl, making the nearby methylene H enough acidic to give rise to a carbanion when treated with a base (B). The R" group on the activated olefin (Michael acceptor) is generally a ketone to makes the molecule an enone; nevertheless, it can also be a sulfonyl fluoride or nitro group.

Mechanism Involved: In the first step, the carbanion is formed due to the deprotonation of the substates, which is stabilized by electron-withdrawing groups. Three resonating structures (2A, 2B, and 2C) can be drawn for this hybrid species with two enolate ion types. The electrophilic alkene reacts with this nucleophile via conjugated addition mode. Finally, the abstraction of a proton by the enolate from solvent (or protonated base) gives rise to the final product.

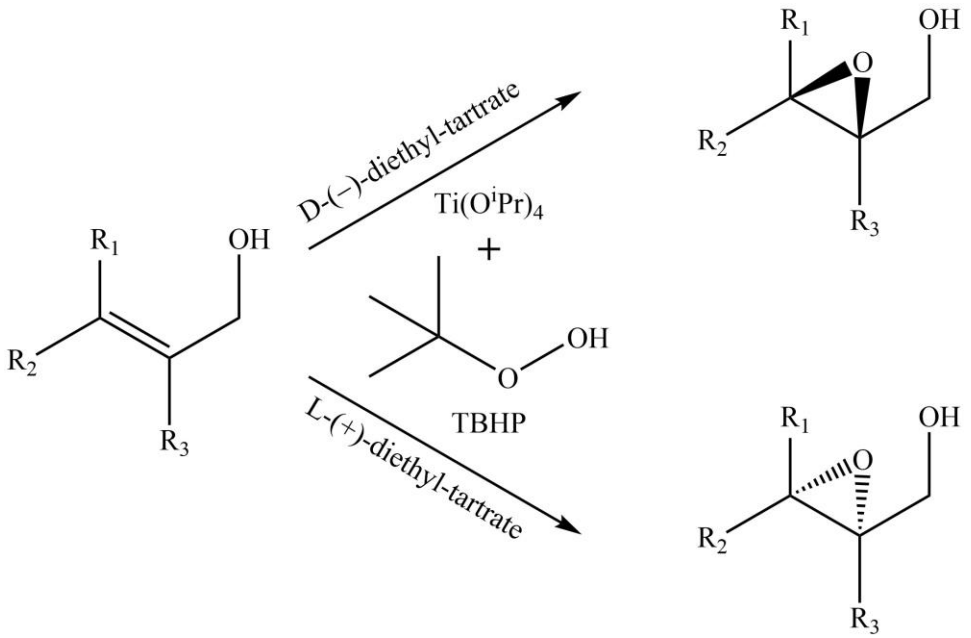


It is also worthy to note that the Michael addition is primarily dominated by the orbital picture rather than the electrostatic interactions. The lowest unoccupied molecular orbital (LUMO) of α-, β- unsaturated carbonyl systems have a hefty magnitude of the coefficient for β-carbon, whereas the HOMO of resonance stabilized enolates have a large magnitude of the coefficient for carbon. Therefore, owing to the similar-energy polarized frontier orbitals and softens, they are suitable for generating a good C–C bond.

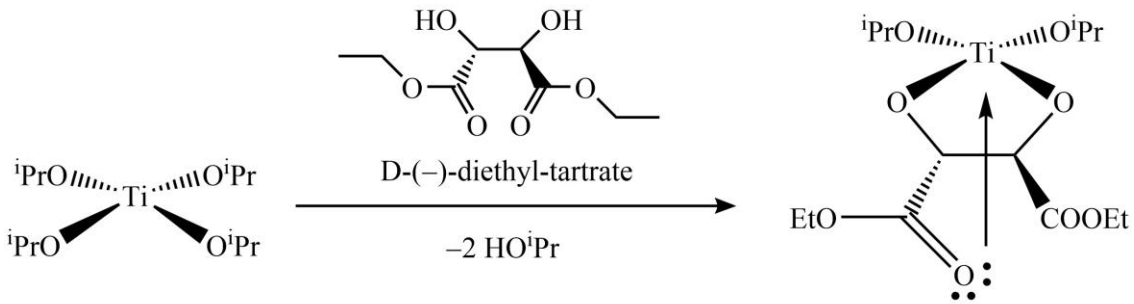
❖ Sharpless Asymmetric Epoxidation

The Sharpless asymmetric epoxidation may simply be defined as an enantioselective chemical reaction where primary and secondary allylic alcohols are converted into epoxy-alcohols using tert-butyl hydroperoxide (TBHP), chiral diethyl tartrate (DET), and titanium tetra(isopropoxide) as the catalyst.

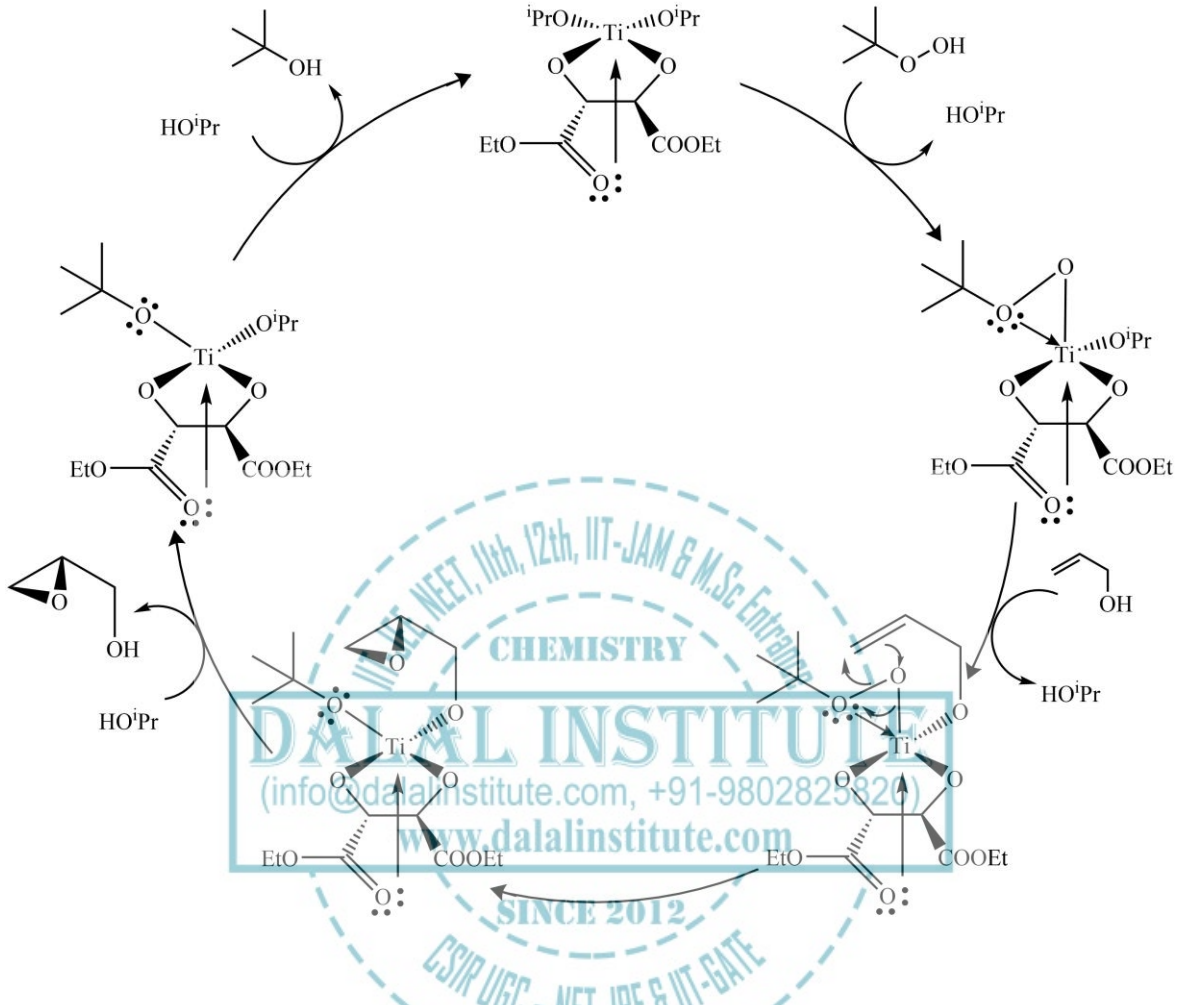
Illustrative Reaction: The typical organic chemical reaction showing Sharpless asymmetric epoxidation is given below.



Mechanism Involved: The mechanism for asymmetric epoxidation starts with the substitution of the isopropoxide ligands in titanium tetra(isopropoxide) catalyst by the chiral diethyl tartrate, which is followed by the further displacement via TBHP in the resulting complex.



In the last, the allylic alcohol reagent displaces the fourth isopropoxide ligand (the only remaining). Although the resulting titanium complex is supposed to be a dimer, the monomer unit is much easier to tackle as far as the mechanism is concerned. After that, the olefin part gets oxidized byTBHP with the face of attack dictated by the chiral DET resulting in the final product i.e., stereoselective epoxy-alcohol.



The Sharpless asymmetric epoxidation can be employed to synthesize different pheromones, leukotrienes, saccharides, terpenes, and antibiotics.

❖ Problems

Q 1. Discuss the mechanism and stereochemistry of electrophilic addition to carbon-carbon multiple bond.

Q 2. What is nucleophilic addition to carbon-carbon multiple bond? How is it different from free radical addition to carbon-carbon double bond?

Q 3. Define Markovnikov's rule.

Q 4. Discuss the chemoselectivity of electrophilic addition to carbon-carbon double bond.

Q 5. State and explain Michael reaction.

Q 6. Define hydroboration.

Q 7. Discuss the Sharpless asymmetric epoxidation.

Q 8. Write a short note the hydrogenation of aromatic rings.

Q 9. How does the hydrogenation of double bonds is different from the hydrogenation of carbon-carbon triple bonds?

❖ Bibliography

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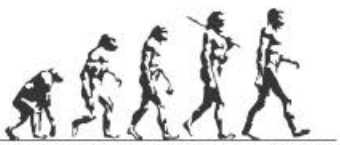

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