CHAPTER 11

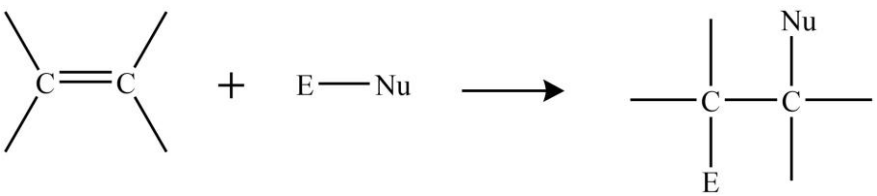
Addition to Carbon-Carbon Multiple Bonds

❖ 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.

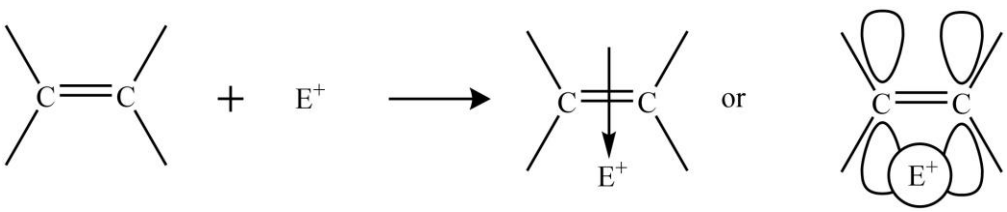
➢ *Electrophilic Addition to Carbon-Carbon Multiple Bond*

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.

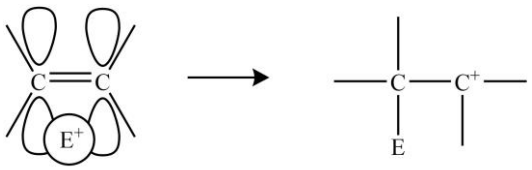


Now first we will discuss the mechanism responsible for this transformation and then we will study the stereochemical aspects of the same.

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.

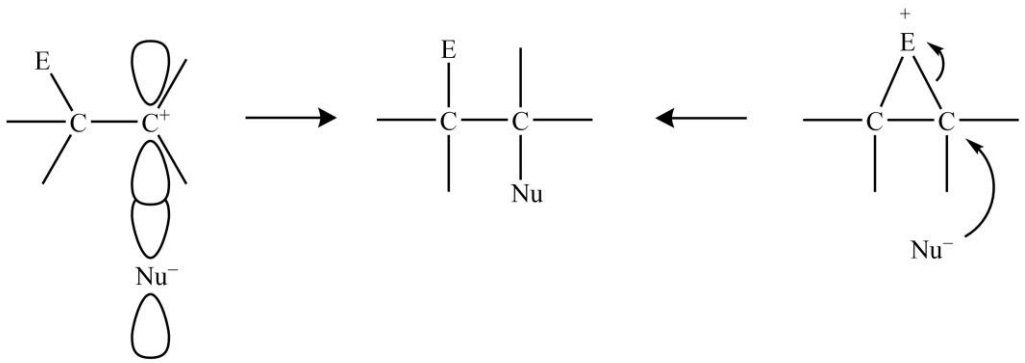


π-Complex Carbocation

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

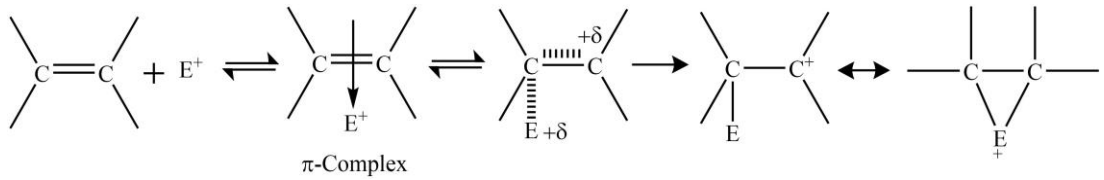
Now depending upon the relative stability of three resonating structures, the intermediatory carbocation becomes "more cyclic" or even acyclic at the extreme. In other words, the intermediate carbocation will be cyclic if structure II is more stable (and hence more contributing) and will be acyclic if 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.



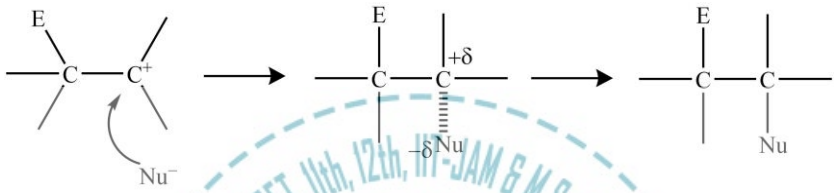
Attack on classical carbocation Attack on cyclic cation

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:

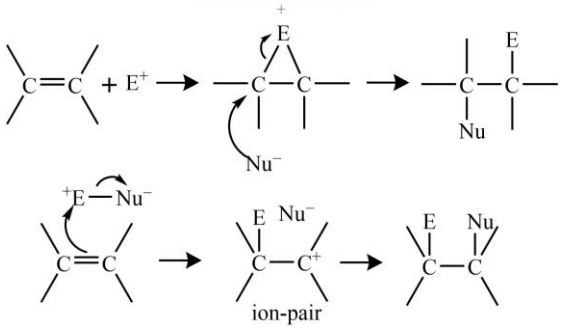


Stereochemistry: The stereochemistry of electrophilic addition to carbon-carbon multiple bonds is affected by two primary factors as discussed below.

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'.

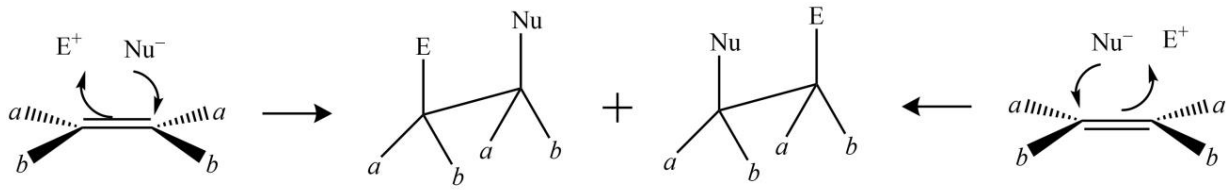


Conversely, if the classical carbocations dominate as intermediate and are having a sufficiently longer lifespan, they can show rotation about carbon-carbon single to yield a non-stereospecific product. However, if the classical carbocationic intermediate is short-lived, the nucleophile coming after 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.

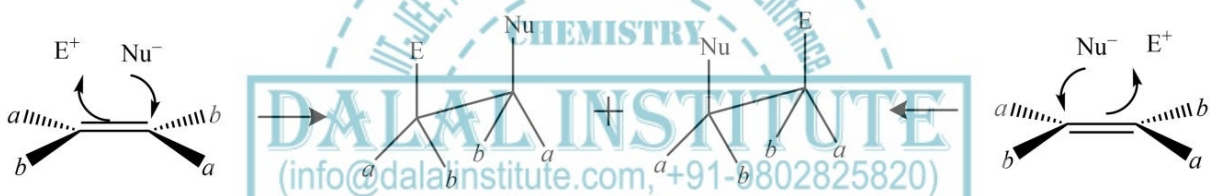
Case-I (E ≠ Nu):

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



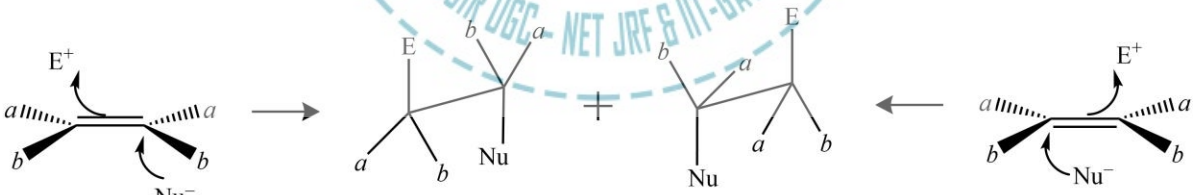
(*dl*)-erythro

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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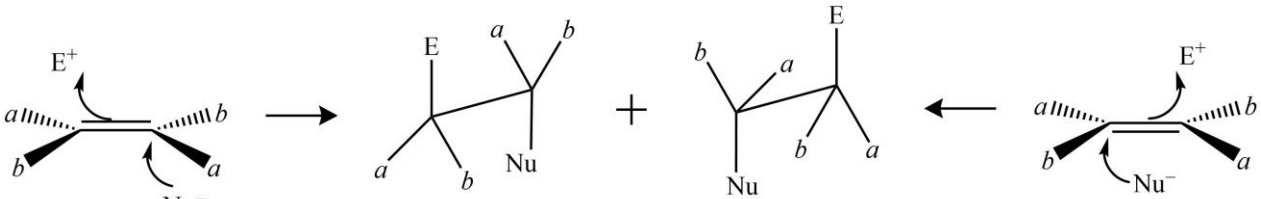
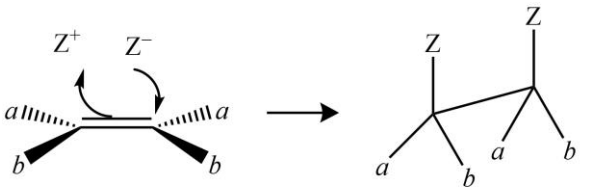


(*dl*)-erythro

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.



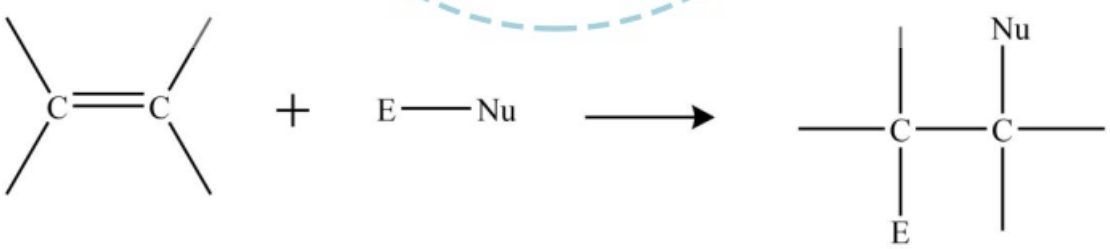
meso form

(*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.

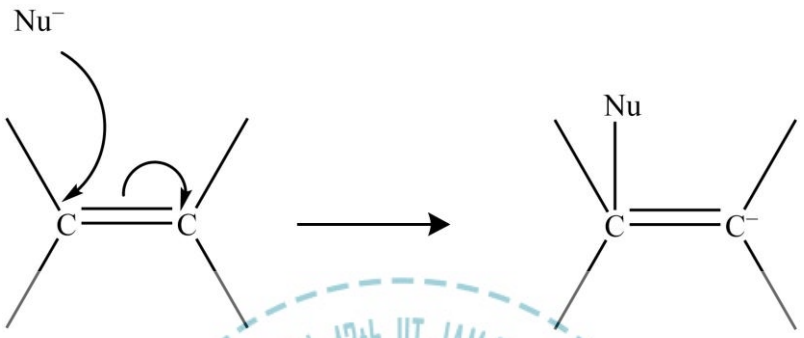


Substrate Reagent Product

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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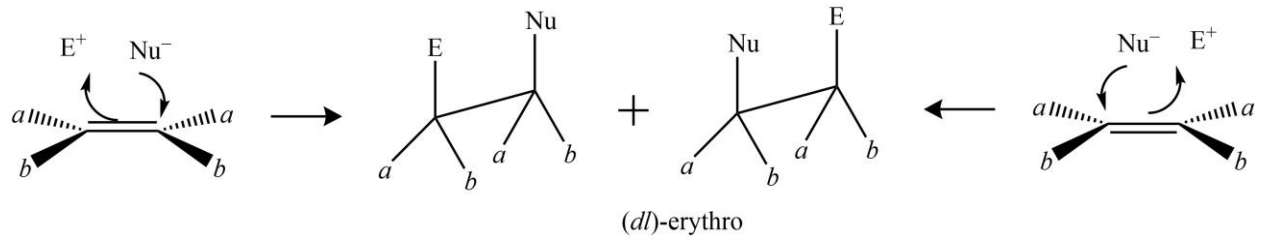
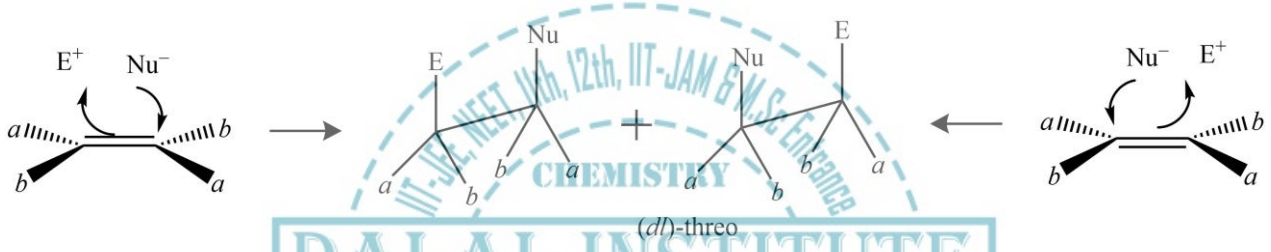


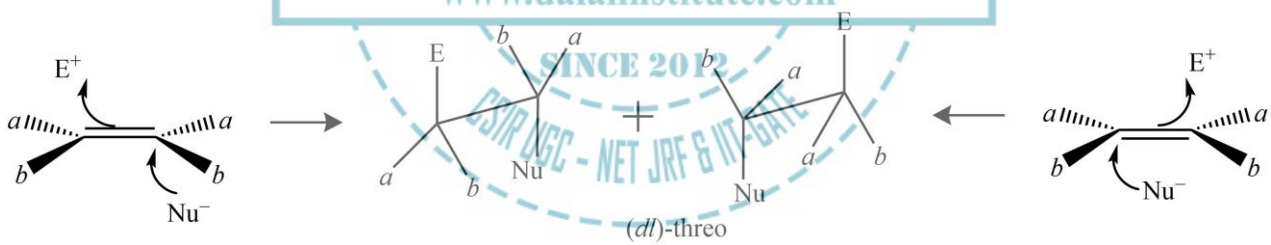
(*dl*)-erythro

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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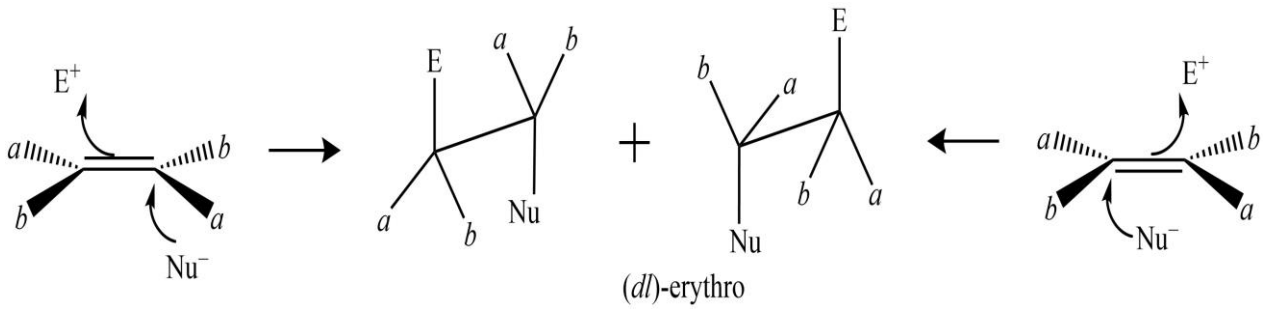
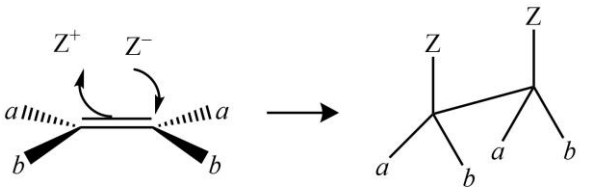


(*dl*)-erythro

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.



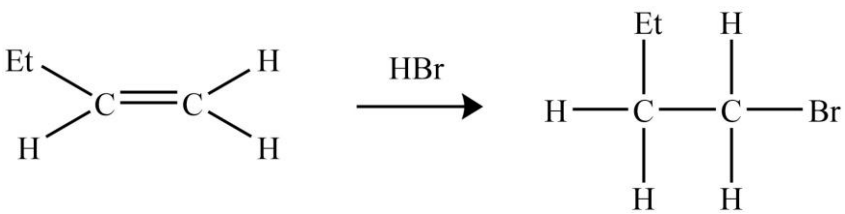
meso form

(*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.

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

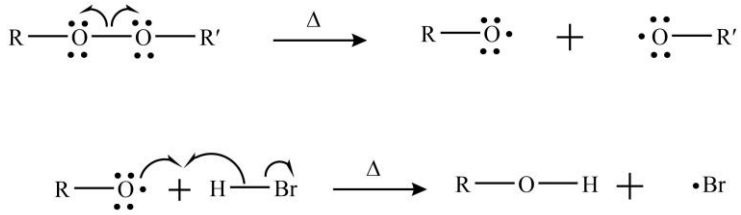
Besides electrophiles and nucleophiles, the reactive species that can initiate addition reactions to carbon-carbon multiple bonds are free radicals. All this started with the regioselectivity HBr additions where the product from Markovnikov Rule wasn't the 'major' product suggesting some other route 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.

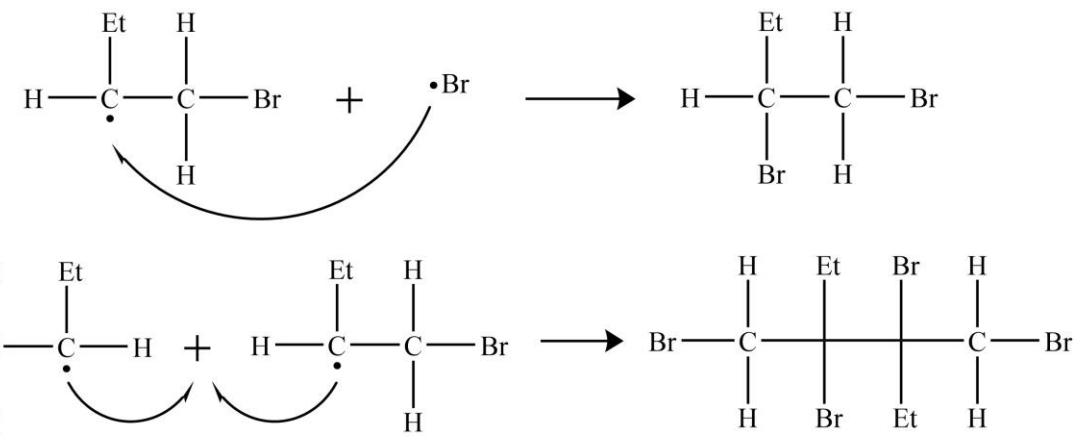
Mechanism: The mechanism of radical addition to the carbon-carbon multiple bonds follows a three-step pathway as shown below.

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

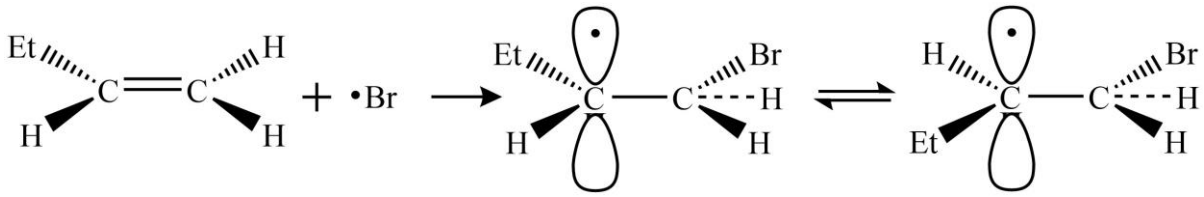


Propagation: In this step, the radical initiated addition to carbon-carbon multiple bonds propagates via the attack of free radicals on the substrate.

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



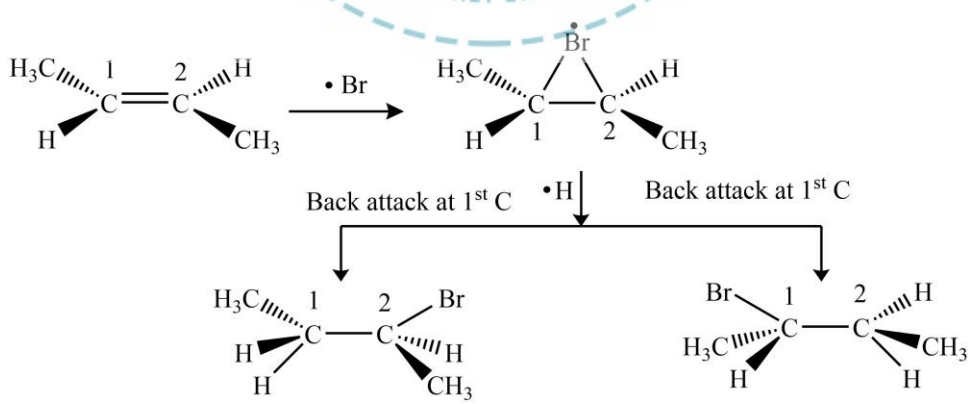
Stereochemistry: The addition of HBr to acyclic cis- or trans-olefins at room temperature results in 20% cis and 80% trans product, indicating that the radical addition of HBr to acyclic olefins is stereoselective but not stereospecific.



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.

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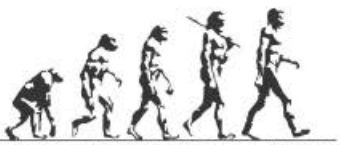

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Mandeep Dalal is an Indian research scholar who is primarily working in the field of Science and Philosophy. He received his Ph.D in Chemistry from Maharshi Dayanand University, Rohtak, in 2018. He is also the Founder of "Dalal Institute" (India's best coaching centre for academic and competitive chemistry exams), the organization that is committed to revolutionize the field of school-level and higher education in Chemistry across the globe. He has published more than 40 research papers in various international scientific journals, including mostly from Elsevier (USA), IOP (UK), and Springer (Netherlands).

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