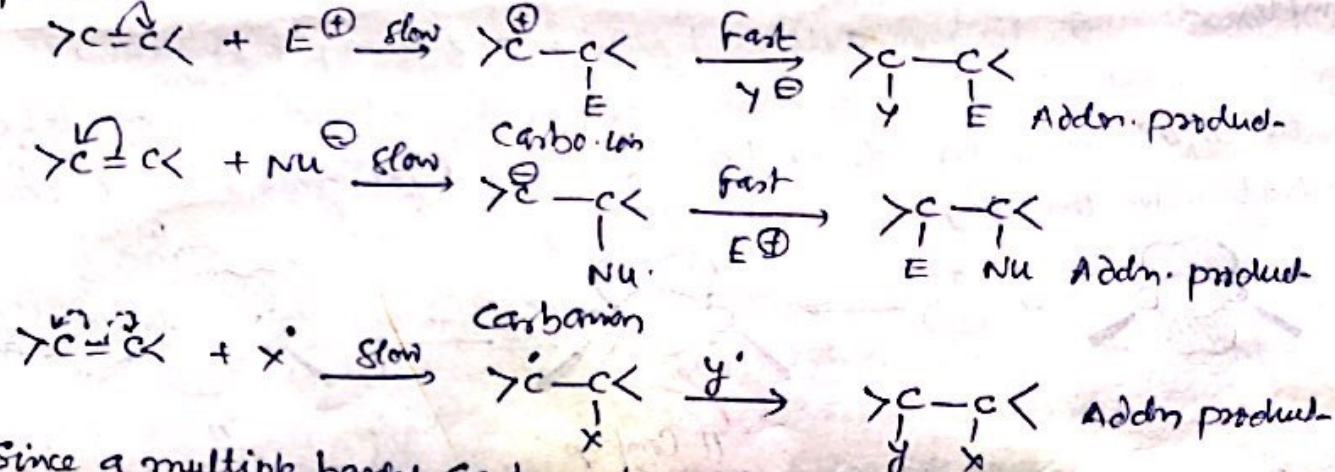


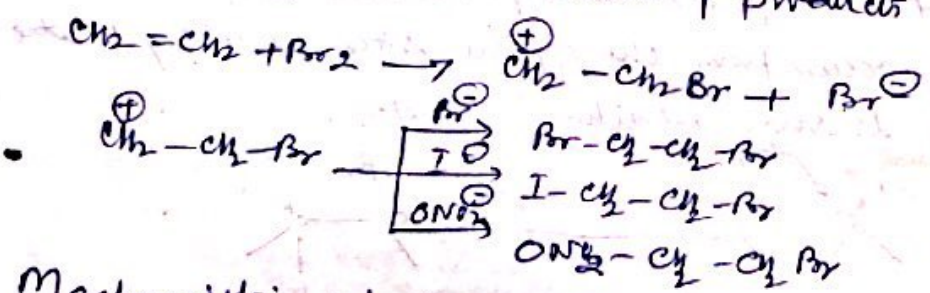
Addition to a carbon-carbon multiple bond may be initiated by an electrophile, nucleophile or a free radical. All these reactions occur by a two step mechanism. In the first step carbonium ion or carbanion or free radical is formed which is then attacked by a nucleophile, electrophile or a free radical, to form the addition product.



Since a multiple bonded carbon atom can readily supply the loosely held  $\pi$  electrons to the electrophile, electrophilic addition is the characteristic reaction of the alkene. On the other hand the  $\pi$  electron cloud tends to shield the molecule from nucleophilic attack, therefore these reactions are likely to occur only if the molecule has strongly electron withdrawing groups present in it.

Electrophilic Additions.

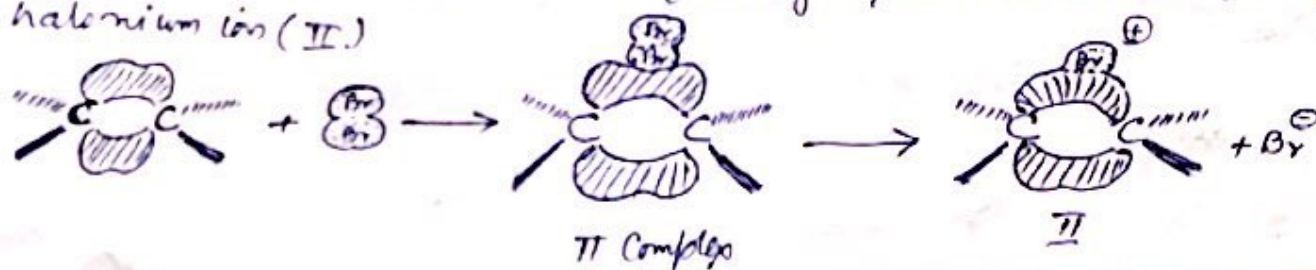
Addition of halogen. It provides a typical example of such type of reaction. The best evidence for the mechanism comes from the observation that when ethylene is treated with Br<sub>2</sub> in presence of other nucleophiles, a mixture of products is obtained.



Mechanistic details of the reaction can be summarised as—

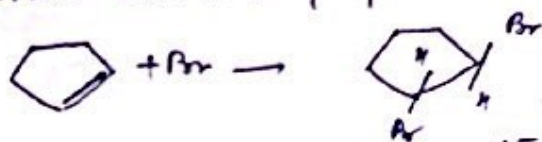
(A) The formation of a  $\pi$  complex (B) The stereochemical consequences of the reaction and the choice of addition of the electrophile to an unsymmetrically substituted alkene and (C) the side of the double bond attacked by the electrophile in case of cyclic alkenes.

(A) Formation of the  $\pi$ -Complex. The initial step of an electrophilic addition is the forming a  $\pi$ -Complex formed by the attack of  $\pi$ -electron cloud of alkene on the vacant orbital of an electrophile. This complex does not involve actual bonding and may be regarded as an association in which halogen molecule is embedded in one lobe of the  $\pi$  orbital of the double bond forming cyclic intermediate, known as halonium ion (II).

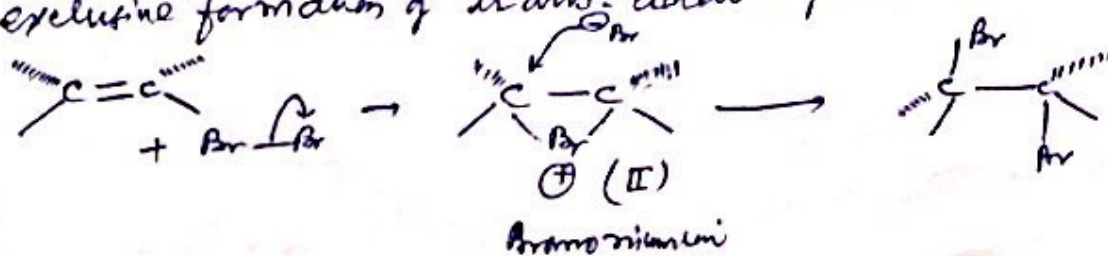


(B) Stereochemical Consequences.

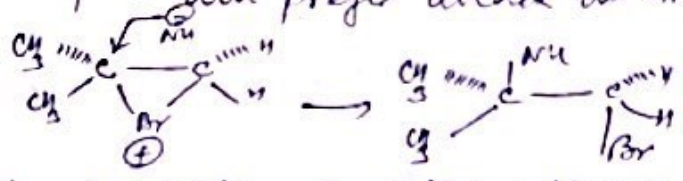
Stereochemistry of polar addition occurs across the double bond in a trans and anti parallel manner. Addition of  $Br_2$  to cyclopentene yields trans-dibromocyclopentane.



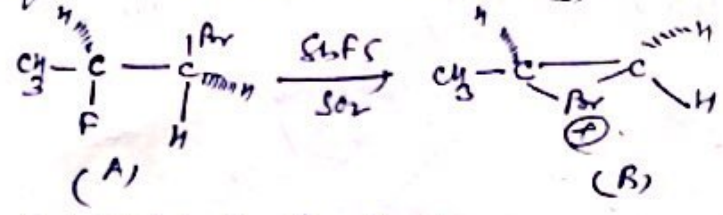
Carbocation is a planar structure which can be attacked on either side giving a mixture of cis and trans product but this does not happen as it appears that free carbocation is not formed and instead the participation of bromonium ion is involved. Bromonium ion is a cyclic intermediate in which bromine is bonded to both carbons of the double bond and carries the +ve charge. Attack of bromide ion, as this intermediate can only occur from the opposite side resulting in the exclusive formation of trans-addition product.



94 If  $\pi$  is symmetrically substituted attack by the nucleophile can occur at either carbon, but if it is derived from an unsymmetrical alkene. The nucleophile will prefer attack at more substituted carbon.



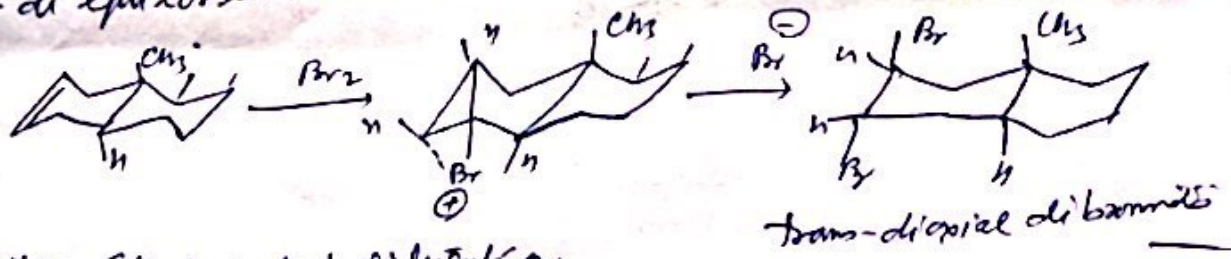
Direct evidence for intermediacy of bromonium ion has been provided by low temp NMR studies of product obtained on treatment of 1-bromo-2-fluoropropane (A) with  $\text{SbF}_5$  in  $\text{SO}_2$ . NMR spectrum of the product was found to be identical with (B).



(c) Addition to cycloalkenes.

Since all the four substituents attached to the two carbons of a double bond are coplanar, the  $\pi$  electrons do not hinder the approach of electrophile from above or below the plane in an alicyclic system.

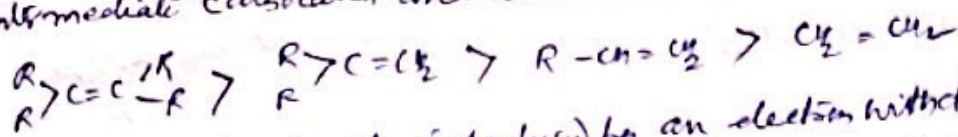
Cyclic alkenes do not possess this property, due to large quasi-axial groups, which sterically hinder the approach of electrophile on its side, because of the intervention of a halonium ion intermediate the nucleophile then attacks from the back side of the ring producing a trans-di axial product. In many cases trans-di axial dibromide undergoes rearrangement to the thermodynamically more stable trans-di equatorial dibromide. eg. Bromination of 2-chlorocyclohexene



Reactivity or Effect of substituents on

rate of addition. Electrophilic attack depends on the availability of  $\pi$  electrons, any effect which increases electron density of double bond will enhance its reactivity towards electrophilic reagents.

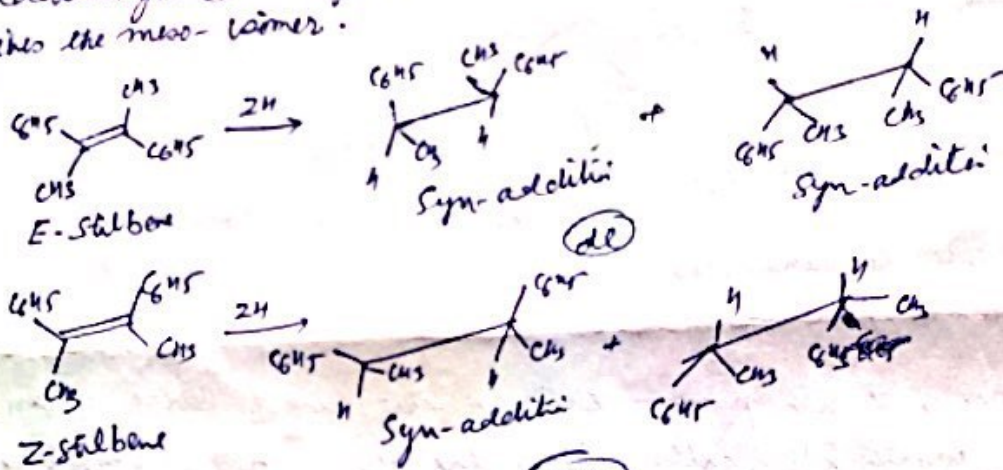
These substituents increase the rate of addition by stabilising the intermediate carbocation and thus lowering the activation energy.



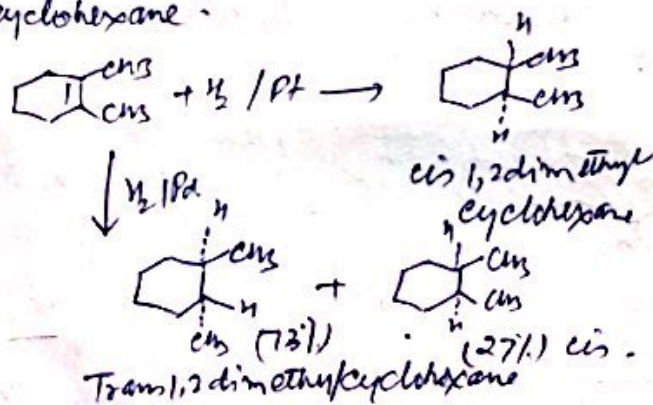
If the electron density is reduced by an electron withdrawing group such as NO<sub>2</sub>, CN or a halogen, the cation will be destabilized and rate of reaction will retard.

Hydrogenation of alkenes and alkynes.

Stereochemically the hydrogenation of an olefine occurs in syn-fashion. When we consider the hydrogenation of E-stilbene derivative, the syn-addition gives the meso- isomer. While syn addition to the Z-isomer gives the racemic isomer.



Although syn-addition of hydrogen to an alkene is the general rule, but anti addition is observed with Pt catalyst. Thus 1,2 dimethyl cyclohexene gives variable mixture of cis and Trans 1,2 dimethyl cyclohexane.



Anti-addition has been explained due to migration of methyl substituted double bond.

Hydrogenation of alkynes.