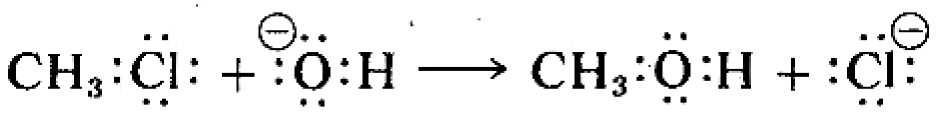
a) Nucleophilic substitution and elimination reactions of this type proceed by radical-chain mechanisms in which the bonds are broken and formed by atoms or radicals as reactive intermediates. This mode of bond-breaking, in which one electron goes with R and the other with X, is called homolytic bond cleavage:

$$R{:}X + Y\cdot \longrightarrow X\cdot + R{:}Y \qquad \text{a } \textit{homolytic} \text{ substitution reaction}$$

There are a large number of Nucleophilic substitution and elimination reactions, usually occurring in solution, that do not involve atoms or radicals but rather involve ions. They occur by heterolytic cleavage as opposed to homolytic cleavage of electron-pair bonds. In heterolytic bond cleavage, the electron pair can be considered to go with one or the other of the groups R and X when the bond is broken. As one example, Y is a group such that it has an unshared electron pair and also is a negative ion. A heterolytic substitution reaction in which the R:X bonding pair goes with X would lead to RY and $:X^{(-)}$

$$R{:}X + {:}Y^{\ominus} \longrightarrow {:}X^{\ominus} + R{:}Y \qquad \text{a } \textit{heterolytic} \text{ substitution reaction}$$

A specific substitution reaction of this type is that of chloromethane with hydroxide ion to form methanol:



$$CH_3{:}\ddot{\underset{..}{Cl}}{:} + {}^{\ominus}{:}\ddot{\underset{..}{O}}{:}H \longrightarrow CH_3{:}\ddot{\underset{..}{O}}{:}H + {:}\ddot{\underset{..}{Cl}}{:}^{\ominus}$$

b) Halogens can act as electrophiles to attack a double bond in alkene. Double bond represents a region of electron density and therefore functions as a nucleophile.

As halogen molecule, for example Br2, approaches a double bond of the alkene, electrons in the double bond repel electrons in bromine molecule causing polarization of the halogen bond.

In other words this creates a dipolar moment in the halogen molecule bond. Heterolytic bond cleavage occurs and one of the halogens obtains positive charge and reacts as an electrophile. The reaction of the addition is not regioselective but stereoselective. Stereochemistry of this addition can be explained by the mechanism of the reaction. In the first step electrophilic halogen with a positive charge approaches the double carbon bond and 2 p orbitals of the halogen, bond with two carbon atoms and create a cyclic ion with a halogen as the intermediate step. In the second step, halogen with the negative charge attacks any of the two carbons in the cyclic ion from the back side of the cycle as in the SN2 reaction.Therefore stereochemistry of the product is vicinial dihalides through anti addition.

$$R_2C=CR_2 \ + \ X_2 \rightarrow R_2CX\text{-}CR_2X$$

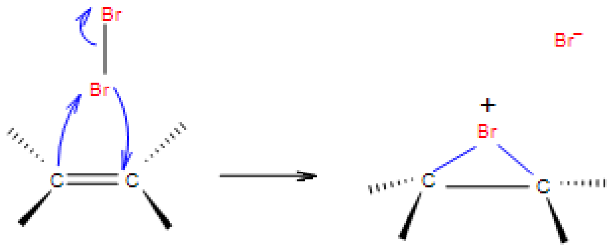
Halogens that are commonly used in this type of the reaction are: Br and Cl.In thermodynamical terms I is too slow for this reaction because of the size of its atom, and F is too vigorous and explosive.

Solvents that are used for this type of electrophilic halogenation are inert. For example CCl4 can be used in this reaction.

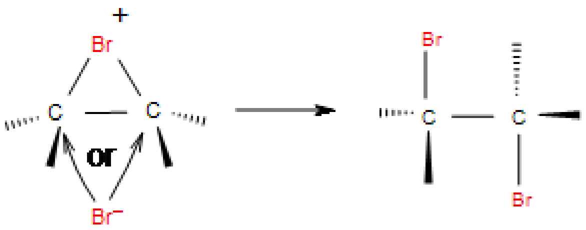
Because halogen with negative charge can attack any carbon from the opposite side of the cycle it creates a mixture of steric products. Optically inactive starting material produce optically inactive achiral products (meso) or a racemic mixture.

Electrophilic addition mechanism consists of two steps.

Step 1 In the first step of the addition the Br-Br bond polarizes, heterolytic cleavage occurs and Br with the positive charge forms a intermediate cycle with the double bond.



Step 2 In the second step, bromide anion attacks any carbon of the bridged bromonium ion from the back side of the cycle. Cycle opens up and two halogens are in the position anti.



Summary. Hallogens can act as electrophiles due to polarizability of their covalent bond. Addition of halogens is stereospecific and produces vicinial dihalides with anti addition. Cis starting material will give mixture of enantiomers and trans produces a meso compound.