CHAPTER
5

Reaction Mechanism

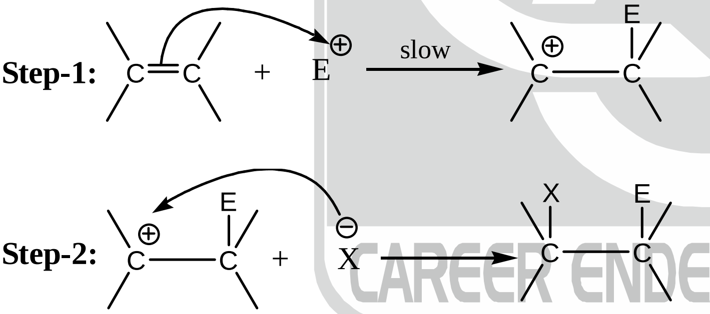
5.1 Addition Reactions:

5.1. (A) Addition to Carbon-Carbon multiple bond

Addition to a Carbon-carbon multiple bond may be initiated by an electrophile, a nucleophile or a free radical. All the three reaction takes place by a two-step mechanism, the second step consisting of the combination of the resultant intermediate with a negative species, a positive species or a neutral entity.

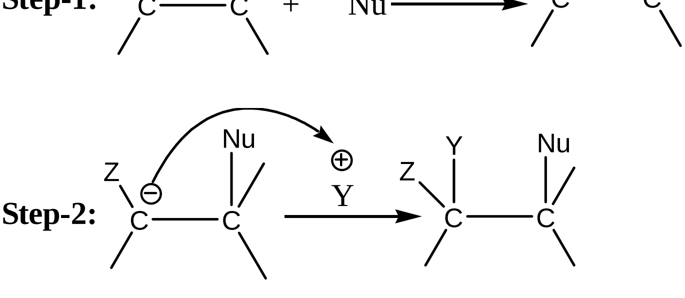
Electrophilic Addition:

In this mechanism a positive species approaches the double or triple bond and in the first step forms a bond by converting the π-pair of electrons into a σ-pair.



Nucleophilic Addition:

In the first step of Nucleophilic addition a nucleophile brings its pair of electrons to one carbon atom of the double or triple bond, creating a carbanion. The second step is combination of this carbanion with a positive species.



Z = Electron withdrawing group
Example: CHO, COOH, COOEt, CN, etc

Free Radical Addition :

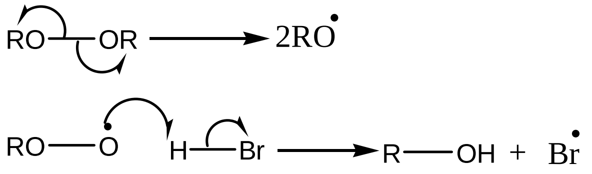
The mechanism of free-radical addition occur in two steps. Free radicals are generated by homolytic cleavage in the inition steps. Reactions occur through propagation steps.

$$XY \xrightarrow[\text{dissociation}]{h\nu \text{ or spontaneous}} \dot{X} + \dot{Y}$$

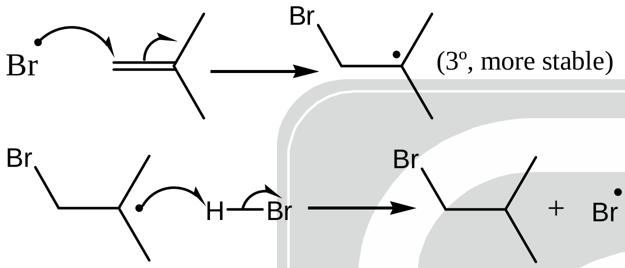
$$R^{\bullet}\text{(from other source)} + XY \longrightarrow RX + Y^{\bullet}$$

Radical chain reaction consist of

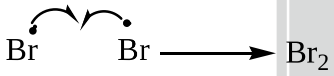
- Initiation Steps:



- **Propagation Steps:**



- **Termination Step:**

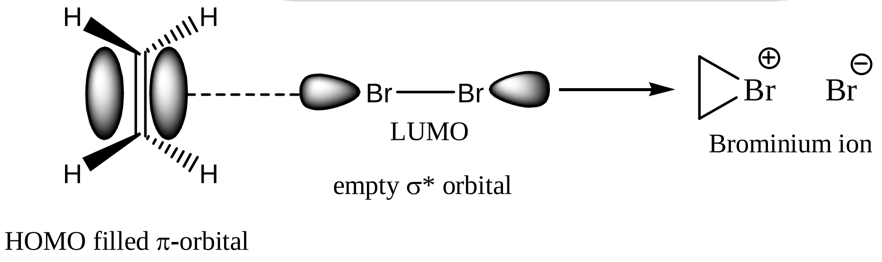


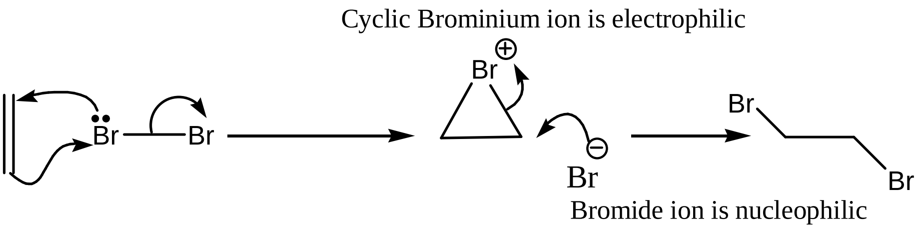
5.1. (B) Addition of halogen to alkenes

In the reaction with ethylene, the alkene must be nucleophile and its HOMO is the C=C π-bond. Other simple alkenes are similarly electron rich and they typically act as Nucleophile and attack electrophiles.

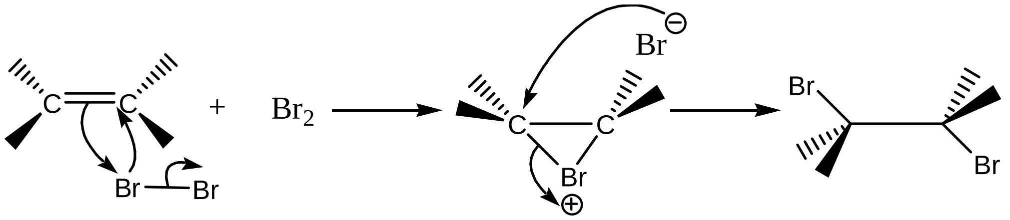
Simple unconjugated alkenes are nucleophilic and react with electrophiles.

Alkene's filled π-orbital (the HOMO) will interact with the bromines empty σ* orbitals to give a product. π-HOMO can interact in a bonding manner with σ* LUMO is if the Br_2 approaches end on.

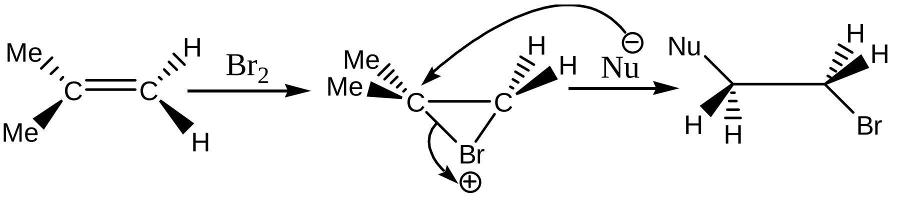


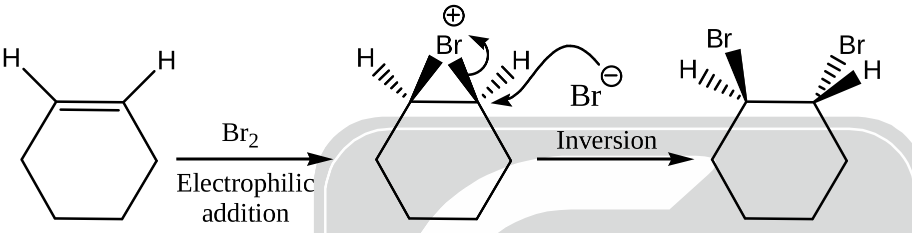


Electrophilic Addition to Symmetrical Alkene:

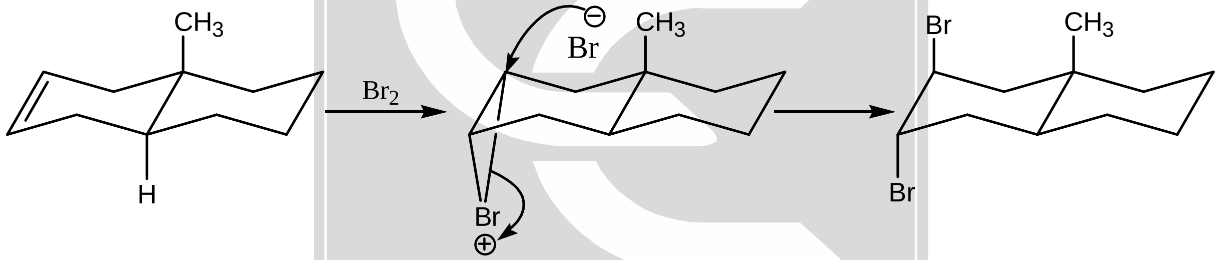


In case of unsymmetrical alkene, nucleophile preferably attacks the more substituted carbon.





(±)-anti-1, 2-dibromo-cyclohexane

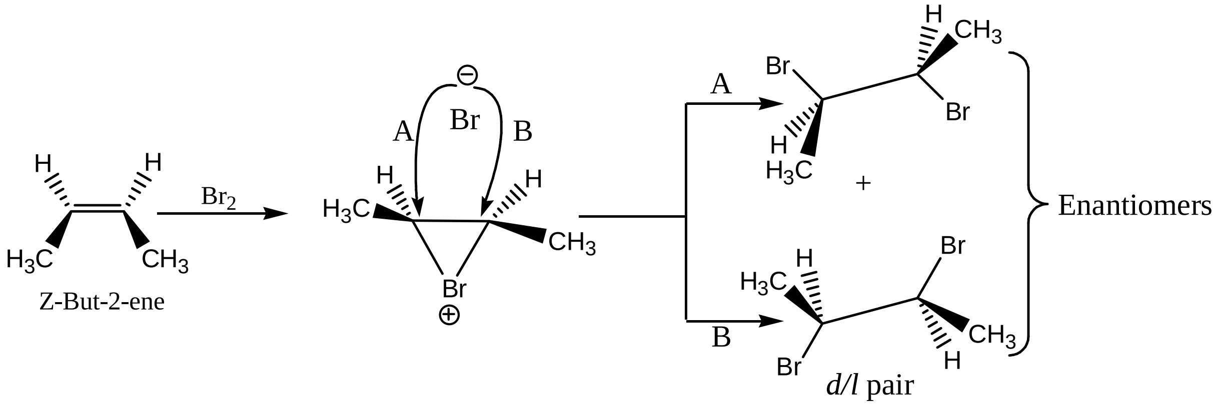


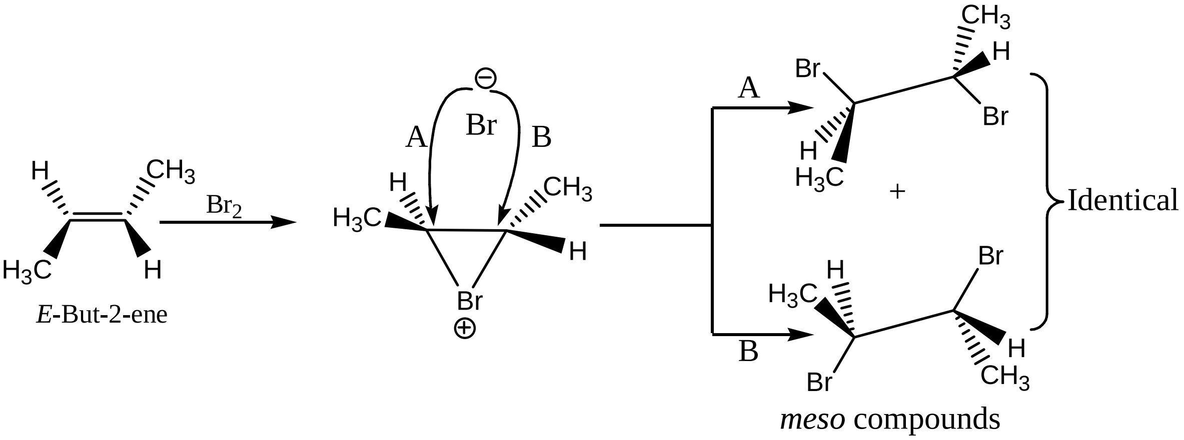
Halogenation involves elecrophilic attack, substituents on the double bond that increases electron density increases the rate of reaction, whereas electron withdrawing group substituents decreases the rate of reaction. Most simple alkenes add bromine in a stereospecific manner, giving the product of anti-addition. Cyclic positively charged brominium ion intermediate provide an explanation for the observed anti-stereospecific.

Electrophilic addition to alkenes can be stereospecific.

Bromination of alkenes is a stereospecific process as the geometry of the starting alkene determines which diastereoisomer is obtained.

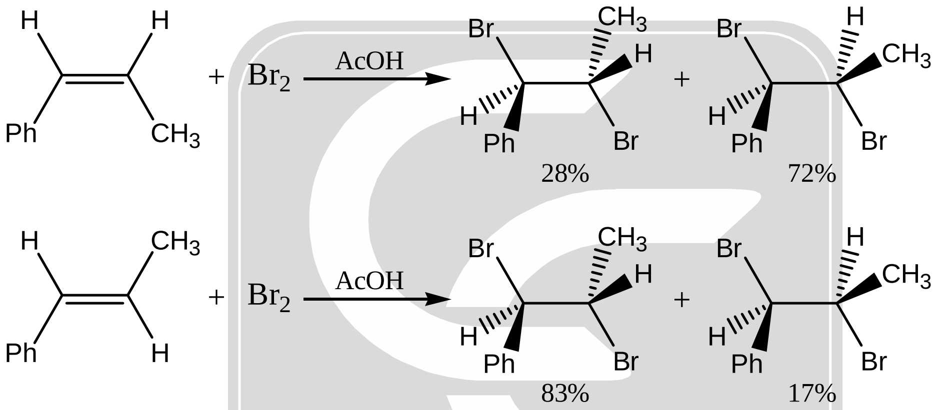
On bromination *Z* but-2-ene gives *d/l* pair and *E*-but-2-ene gives *meso* compound.





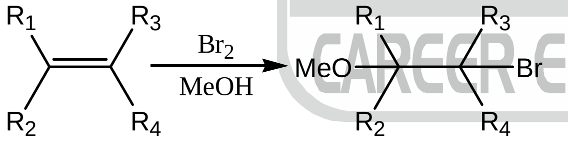
The bridging by bromine prevents rotation about the remaining bond and backside nucleophilic opening of the brominium ion leads to the observed anti-addition.

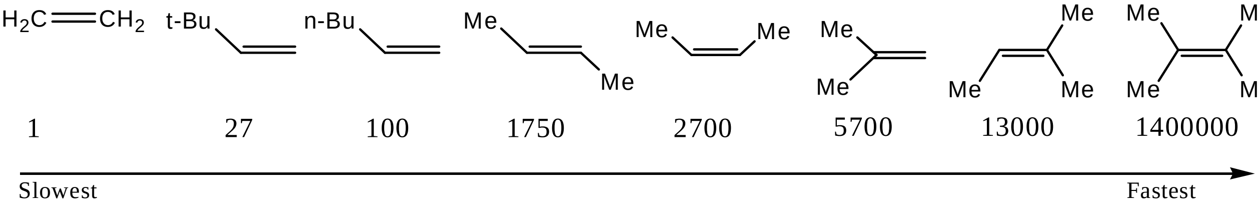
A substantial amount of syn addition is oberved for Z-1-phenylpropene (27–30% syn addition), E-1-phenylpropene (17–29% syn addition), and cis-stilbene (upto 90% syn addition in polar solvents).



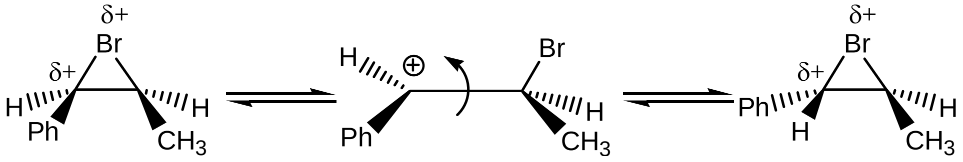
Rates of bromination of alkene:

Relative rates of reaction of alkenes with bromine in methanol.

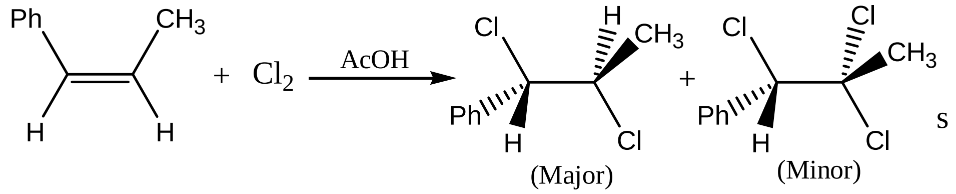




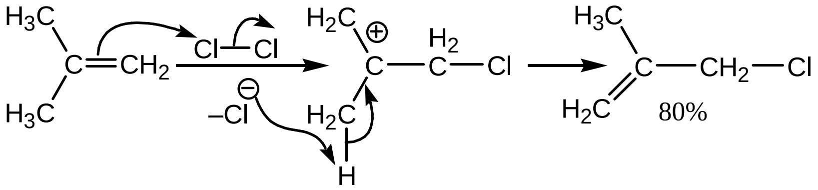
Phenyl substituted double bond gives syn addition on bromination. The presence of phenyl substituent diminshes the strength of bromine bridging by stabilizing the cationic center.



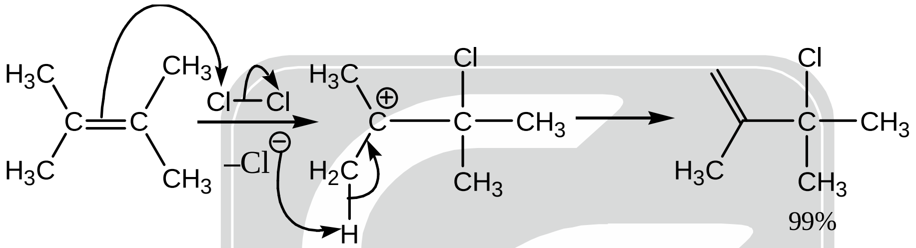
Chlorination of aliphatic alkenes usually gives anti-addition. Syn addition is often dominant for phenyl-substituted alkenes.

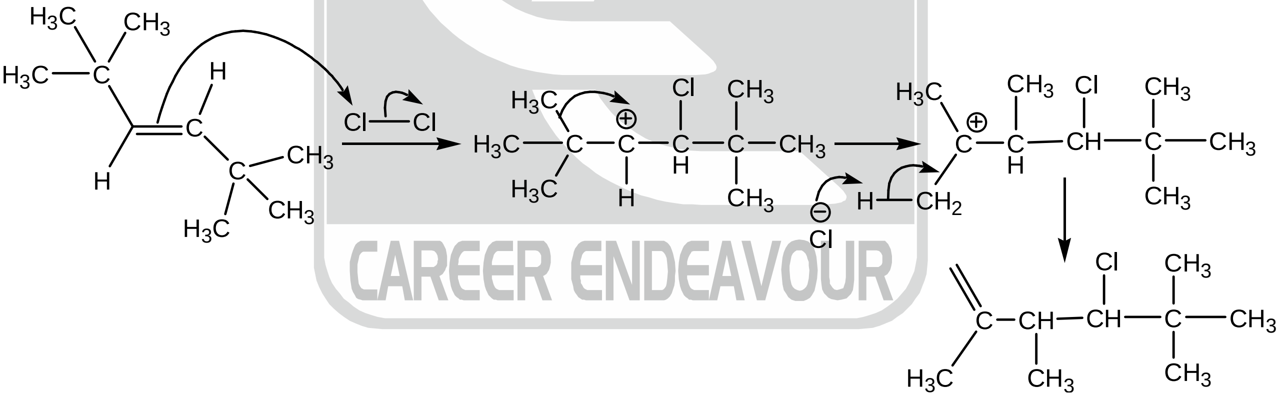


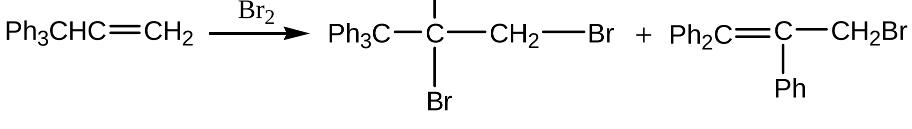
Phenyl substituted leads to cationic character at the benzylic site, and there is more syn addition.
Bromination therefore, generally gives a higher degree of anti-addition than chlorination.
Chlorination can be accompanied by other reactions that are indicative of carbocation intermediate branched alkenes can give products that are the result of elimination of a proton from a cationic intermediate.



Note: Cl^- is a hard base and perfer the H^+ i.e. hard acid abstraction from 3° cation.

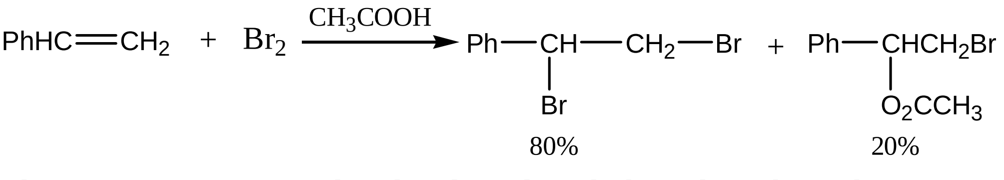






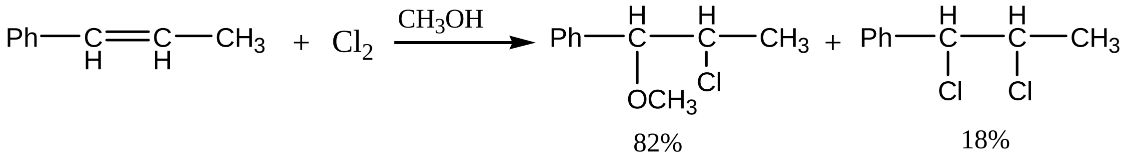
$$Ph_3CHC{=}CH_2 \xrightarrow{Br_2} Ph_3C\text{–}\overset{H}{\underset{Br}{C}}\text{–}CH_2\text{–}Br + Ph_2C{=}\underset{Ph}{C}\text{–}CH_2Br$$

Nucleophilic solvent can complete with halide ion for the cationic intermediate.



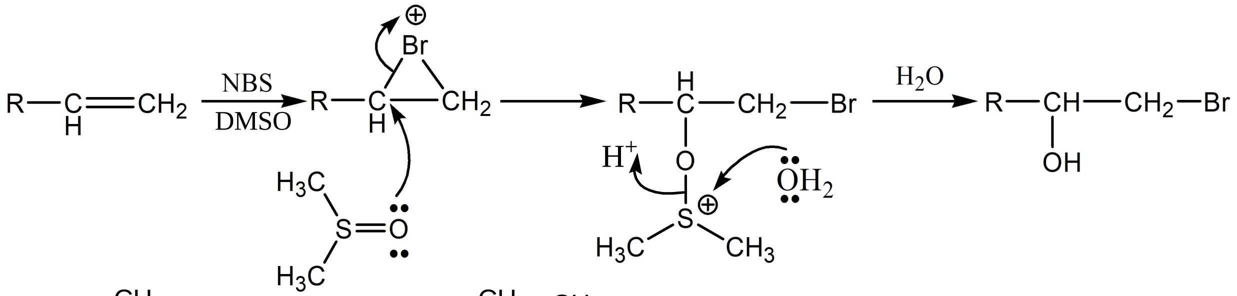
$$PhHC{=}CH_2 + Br_2 \xrightarrow{CH_3COOH} Ph\text{–}\underset{Br}{CH}\text{–}CH_2\text{–}Br + Ph\text{–}\underset{O_2CCH_3}{CH}CH_2Br$$

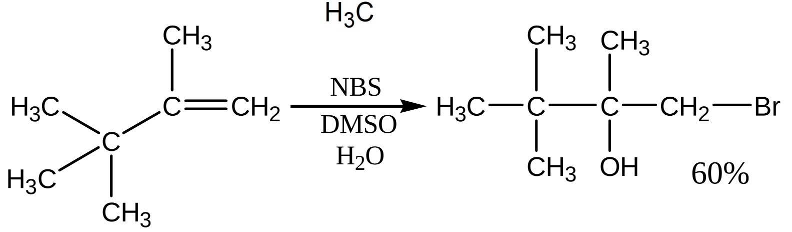
The acetoxy group is introduced exclusively at the benzylic carbon. This is in accord with the intermediate being a weakly bridged species or a benzylic cation.



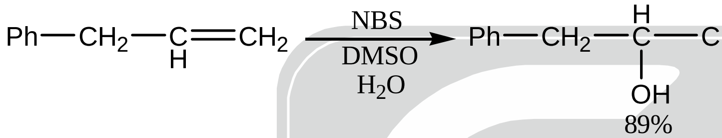
$$\text{Ph}-\underset{H}{C}=\underset{H}{C}-CH_3 + Cl_2 \xrightarrow{CH_3OH} \text{Ph}-\overset{H}{\underset{OCH_3}{C}}-\overset{H}{\underset{Cl}{C}}-CH_3 + \text{Ph}-\overset{H}{\underset{Cl}{C}}-\overset{H}{\underset{Cl}{C}}-CH_3$$

82% 18%





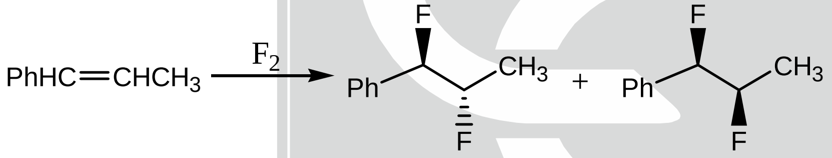
60%

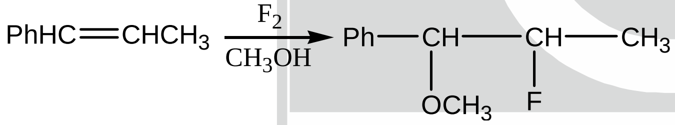


$$\text{Ph}-CH_2-\underset{H}{C}=CH_2 \xrightarrow[\text{DMSO, } H_2O]{\text{NBS}} \text{Ph}-CH_2-\overset{H}{\underset{OH}{C}}-CH_2-Br_2$$

89%

Because of high reactivity, special precautions must be taken with reactions of fluorine and its use some what specialized. There is some basis for comparison with the less reactive halogen. Addition of fluorine to Z- and E-1-propenyl benzene is not stereosepecific.

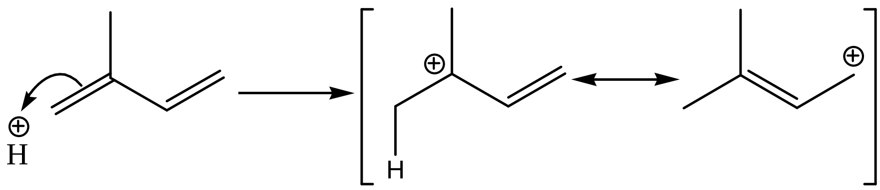




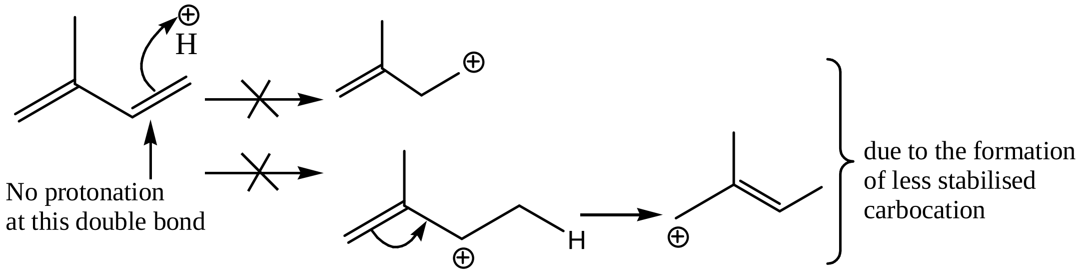
$$\text{PhHC}=\text{CHCH}_3 \xrightarrow[CH_3OH]{F_2} \text{Ph}-\underset{OCH_3}{CH}-\underset{F}{CH}-CH_3$$

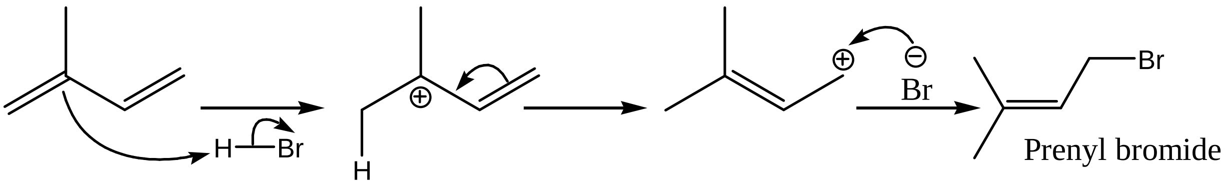
5.1. (C) Electrophilic addition to dienes

Dienes are more nucleophilic than isolated alkenes. Dienes react with electrophile in such a way that, formation of more stabilised carbocation.

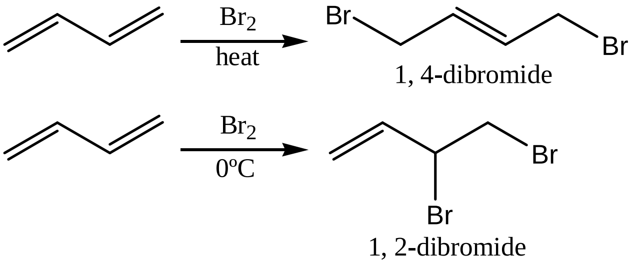


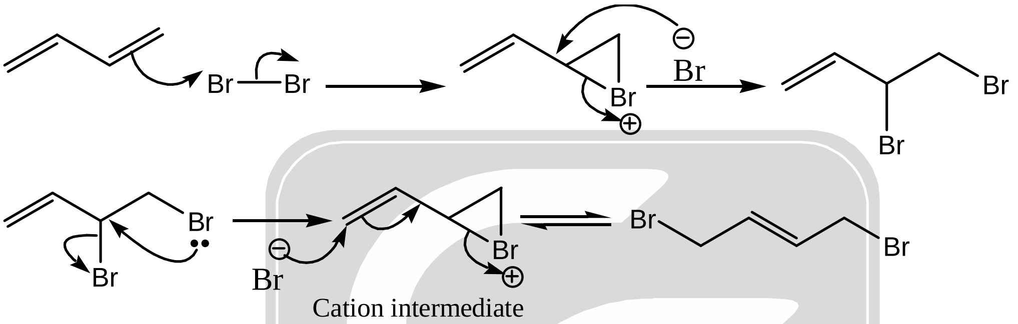
More stabilised carbocation





Addition of Br_2 with 1, 3-butadiene depends upon condition. At high temperature more stable alkene(product) is favoured (major) and at low temperature, less stable alkene (product) is favoured (major)



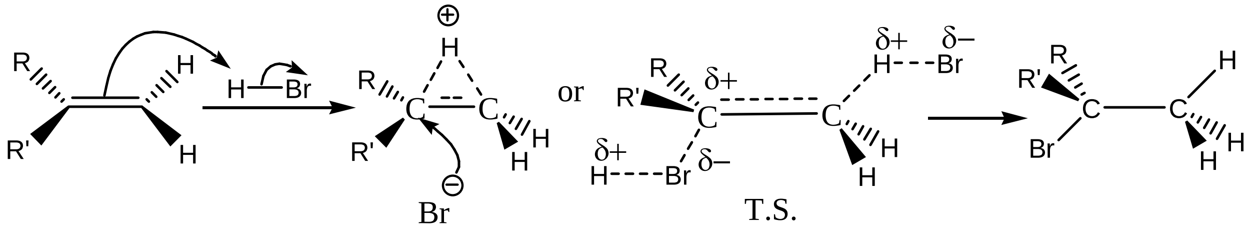


Changing the conditions slightly gives a different outcome. If the reaction is done at lower temperature, the bromine just adds across one of the double bonds to give a 1, 2-dibromide. This compound turn out to be the kinetic product of the bromination reaction. The 1, 4-dibromide is formed only when the reaction is heated and is the thermodynamic product. The 1, 2-dibromide can still react further because it can undergo nucleophilic substitution. At high temperature all steps are reversible so the fact that 1, 4-dibromide is formed under these conditions must mean it is more stable than the 1, 2-dibromide.

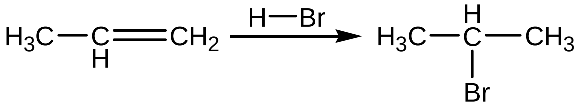
5.1. (D) Addition of hydrogen halide:

Electrophilic addition to unsymmetrical alkenes is regioselective:

In the addition of hydrogen halides to a carbon-carbon double bond, proton is electrophilic and forms a hydrogen-bridged intermediate called a protium ion which is subsequently attacked from backside by the halide ion resulting in the trans addition.



According to Markovnikov's rule: Addition of unsymmetrical alkene to unsymmetrical reagent, negative part of reagent goes to more substituted carbon atom of alkene.



$$H_3C-\underset{H}{C}=CH_2 \xrightarrow{H-Br} H_3C-\underset{Br}{\overset{H}{C}}-CH_3$$

But actual addition of unsymmetrical reagent to unsymmetrical alkene, negative part of reagent goes to more stabilised carbocation of alkene.