



WELCOME



ADDITION REACTION

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M PHARM PART 1



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INTRODUCTION

Addition reaction is defined as that reaction in which all the reagent atoms are added to the reactant and thus the product contains all the atoms of the reactant as well as that of the reagent.

Characteristic feature of unsaturated compounds



Types of addition reaction

Electrophilic addition

Nucleophilic addition

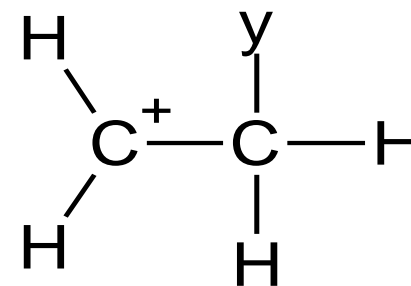
Free radical addition

Addition to conjugated system

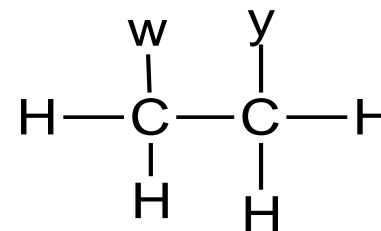
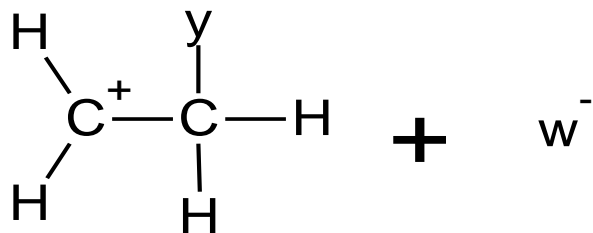


ELECTROPHILIC ADDITION

Step 1

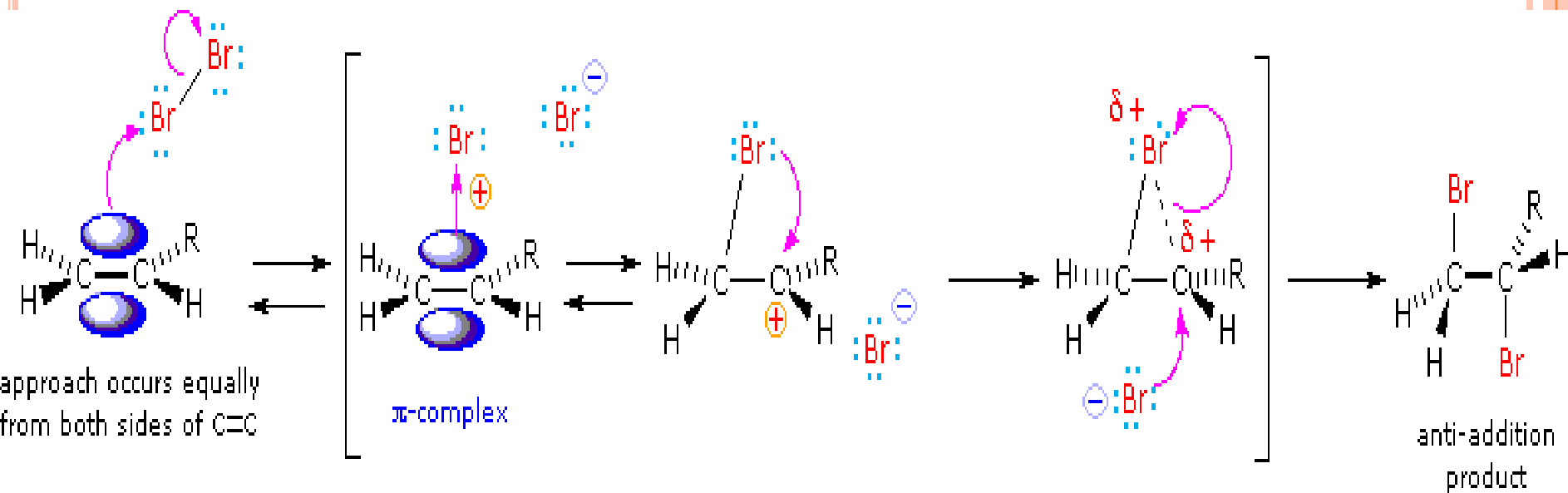
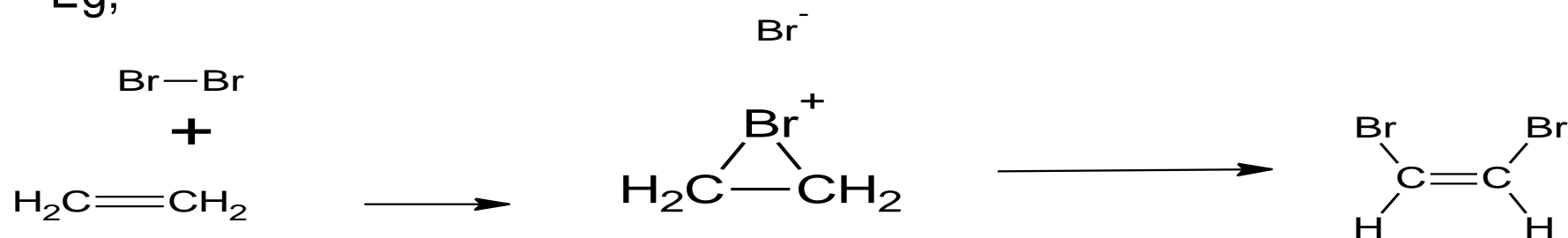


Step 2



- The second step is similar to SN1 mechanism
- Not all additions follow the simple mechanism

Eg;



STEREO CHEMISTRY

Three possibilities.

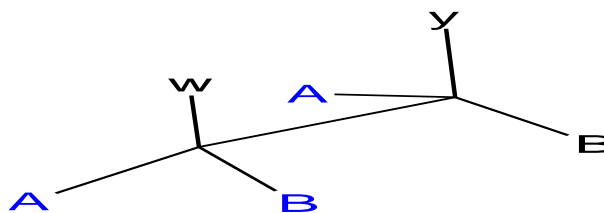
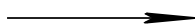
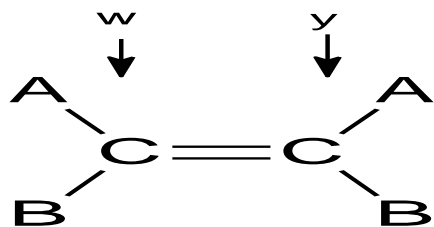
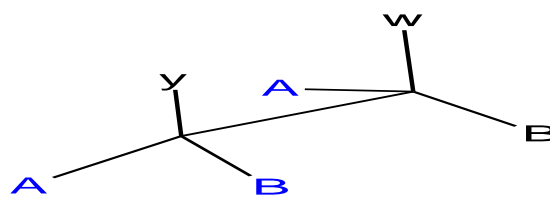
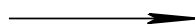
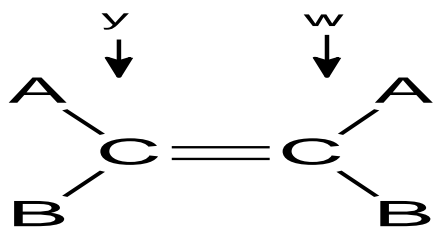
- Y and W enter on same side of the plane, addition is stereospecific and syn
- May enter on the opposite sides, stereospecific anti addition
And may be Not stereospecific
- YW is added to cis and trans of an olefin $ABC=CBA$ Cis olefin is an eg;

If the addition is syn the product will be erythro

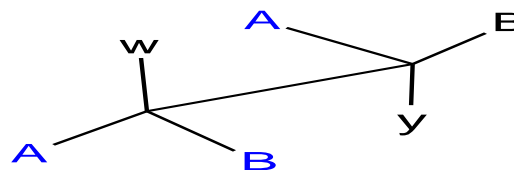
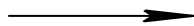
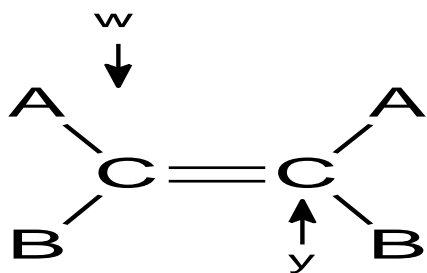
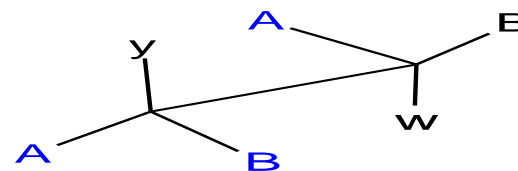
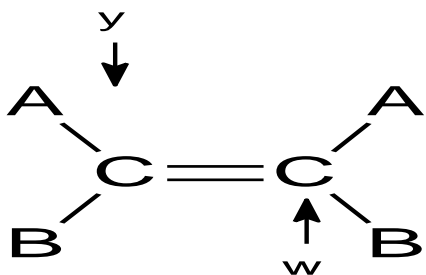
If the addition is anti the product is threo



Erythro



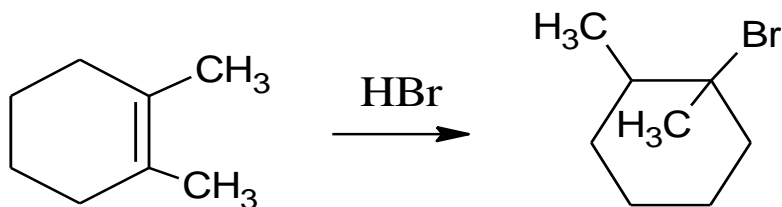
Threo



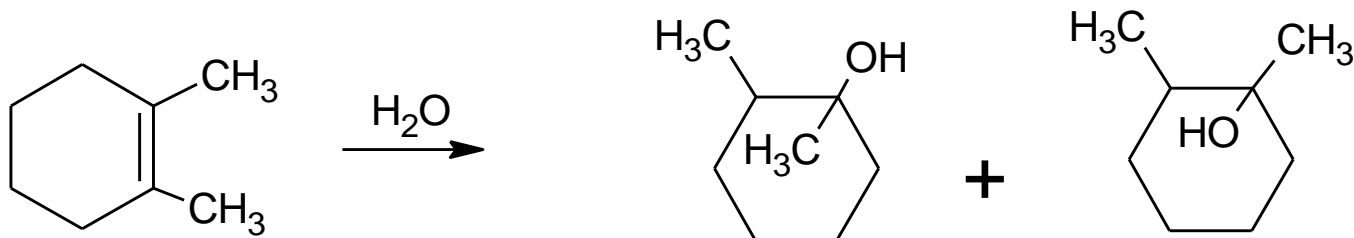
If $Y=W$ (Br_2) the erythro pair is meso compound.

STEREOCHEMISTRY OF HX

- The stereochemistry of HX is varied
- Treatment of 1,2, dimethyl cyclohexene with HBr gave predominant antiaddition

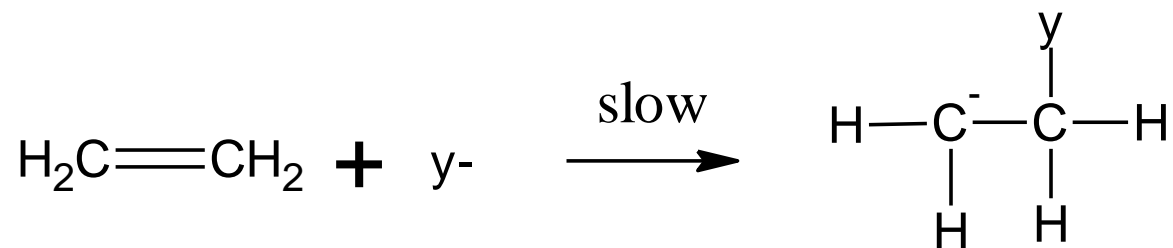


While addition of water to 1,2- dimethyl cyclohexene gave equal amount of the cis and trans alcohols.

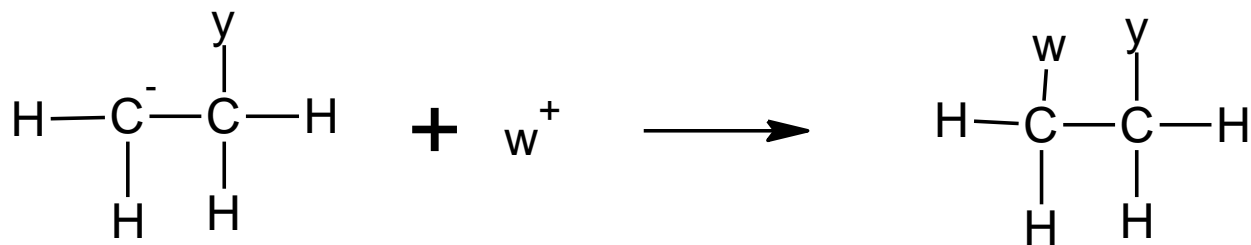


NUCLEOPHILIC ADDITION

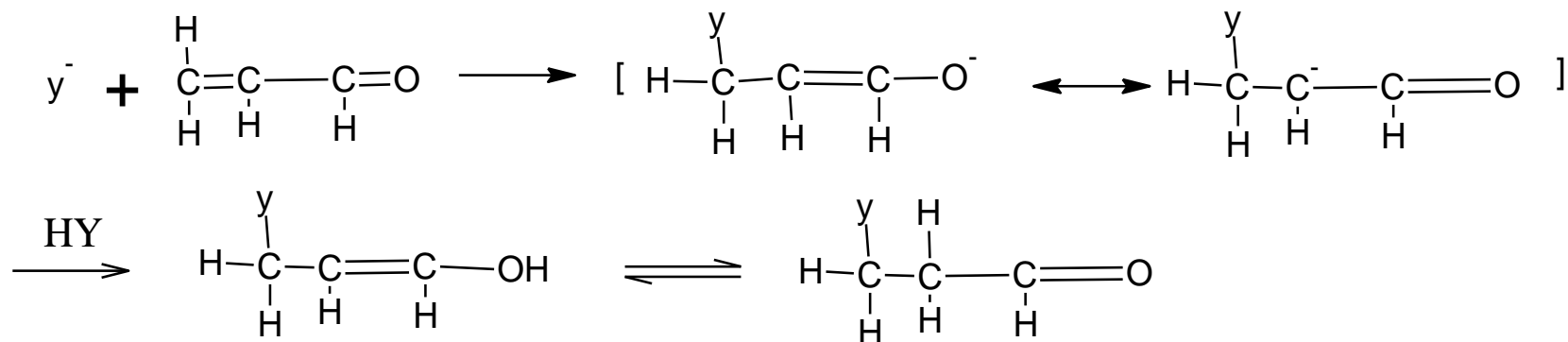
step 1



step 2



Addition of HY to a substrate of the form $-\text{C}=\text{C}-\text{Z}$, where $\text{Z} = \text{CHO}, \text{COR}, \text{COOR}, \text{CONH}_2, \text{SOR}, \text{SO}_2\text{R}$ etc.



Protonation occur at oxygen

The mechanism is 1,4 nucleophilic addition.

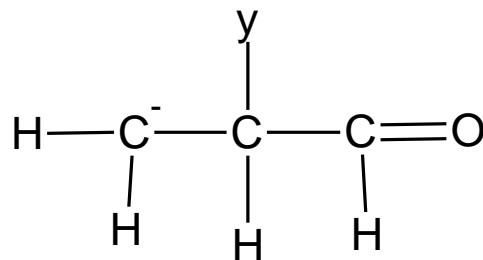
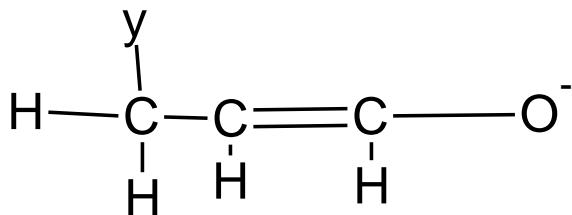


When Z = CN or CO

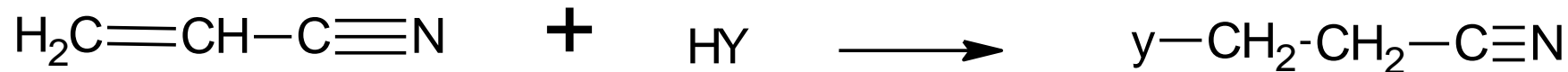
Y⁻ attack to the carbon, similar to the above

Mechanism may be 1,2 or 1,4 addition .

Y⁻ never attack at 3 position



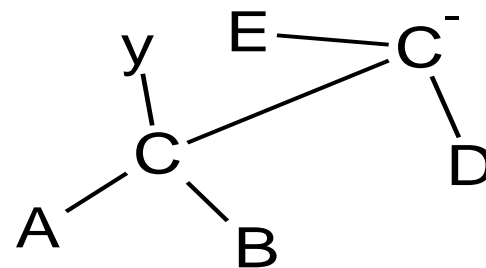
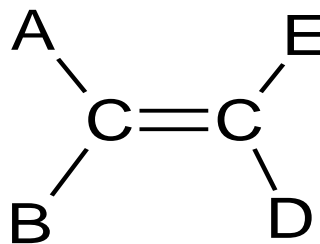
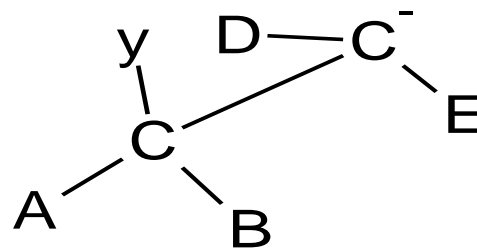
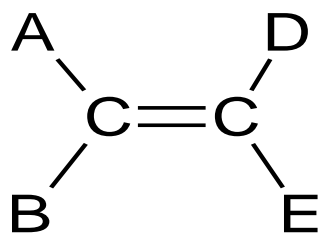
An important substrate of this type is acrylonitrile and 1,4 addition to is called cyanoethylation, because the Y is cyanoethylated



STEREO CHEMISTRY

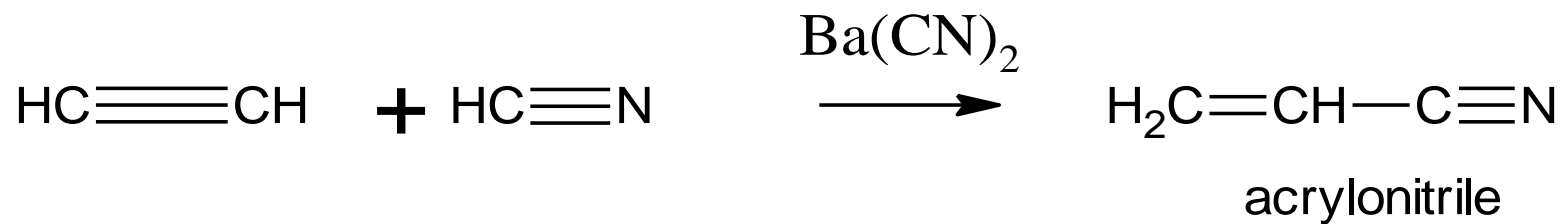
- Nucleophilic addition is a carbanion mechanism
- Addition should be nonstereospecific and stereoselective.

Eg ; E and Z from of an olefin ABC=CDE

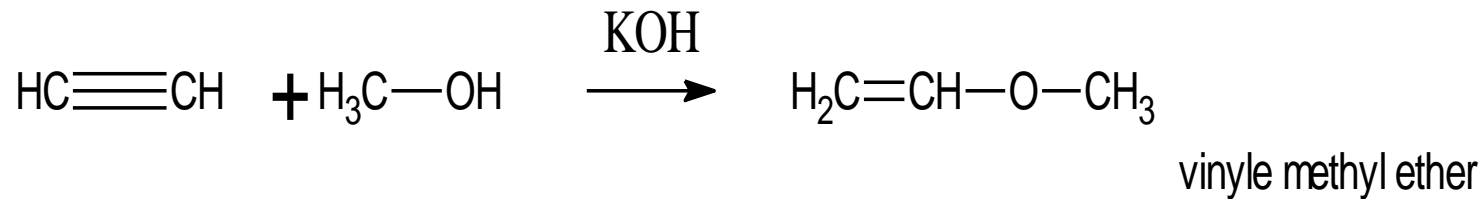


Eg ; addition of HCN, addition of alcohols

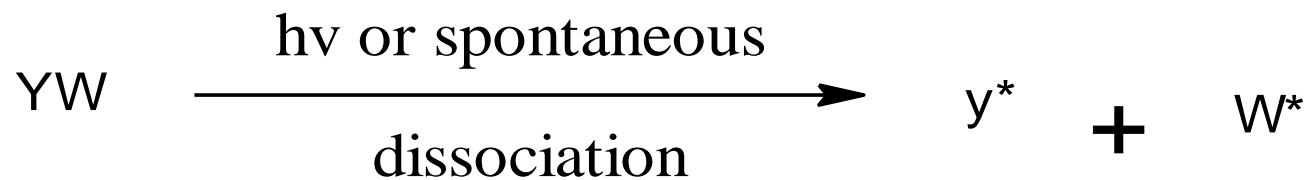
Addition of HCN



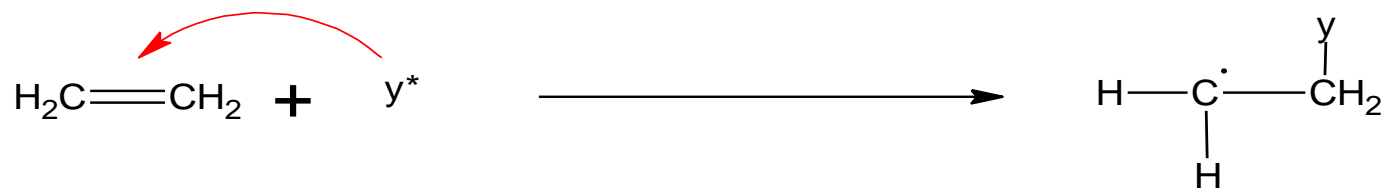
Addition of alcohols



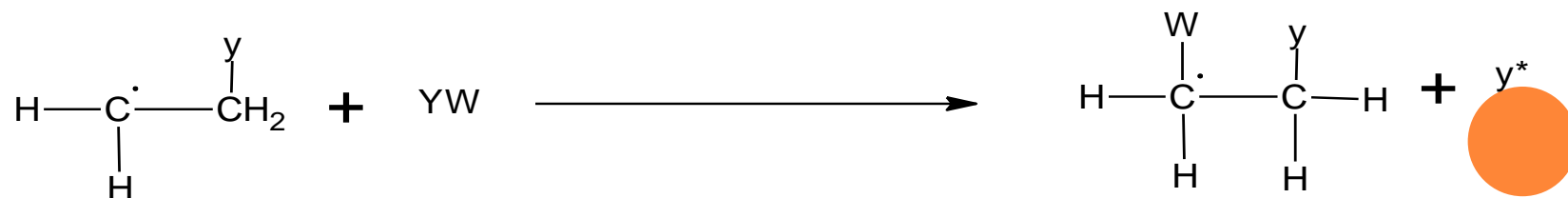
FREE RADICAL ADDITION



step 1

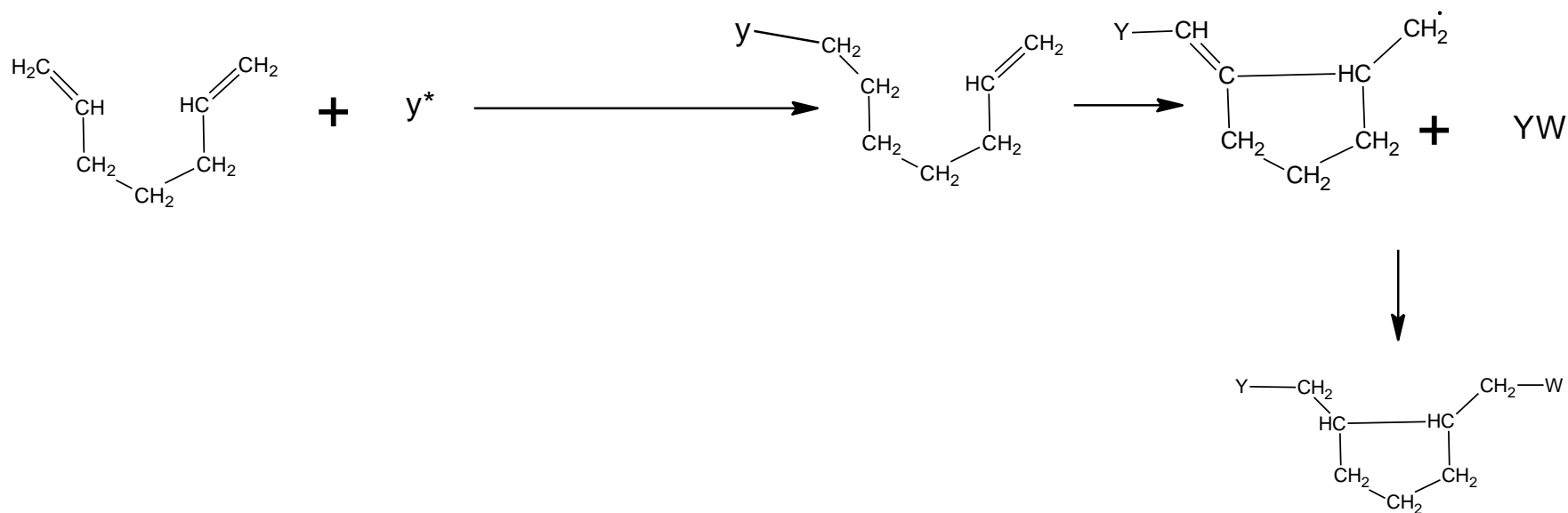


step 2



When free radicals are added to 1,5 or 1,6 dienes, the initially formed radical can add intramolecularly to the other bond leading to a cyclic product.

Eg;

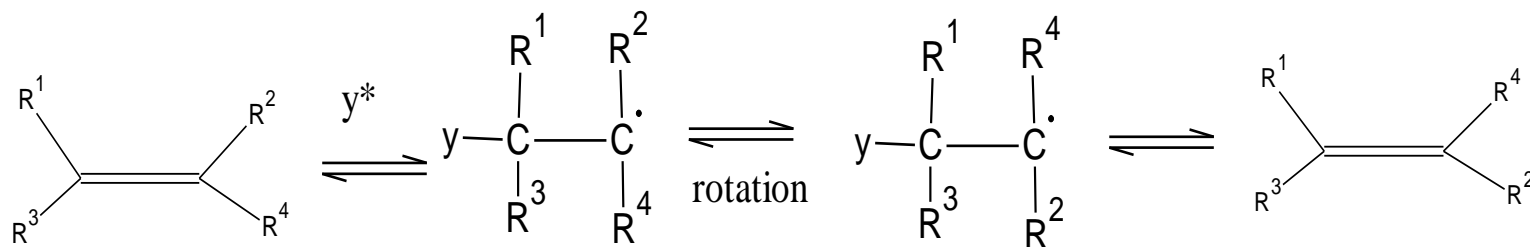


☐ It should be non stereospecific, may stereoselective,

☐ Not all free radical additions are stereoselective

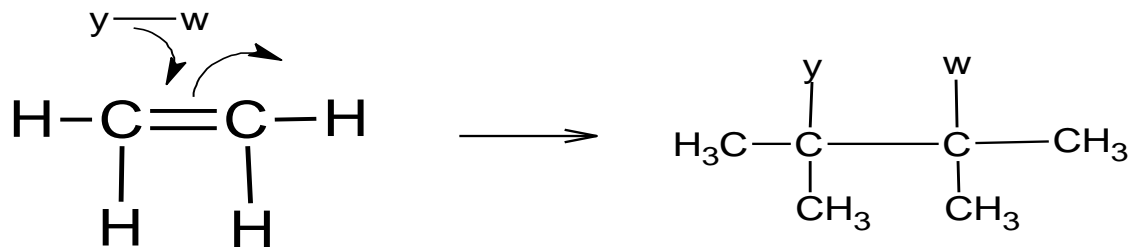


For many radicals step 1 is reversible.
Causes cis – trans isomerization.



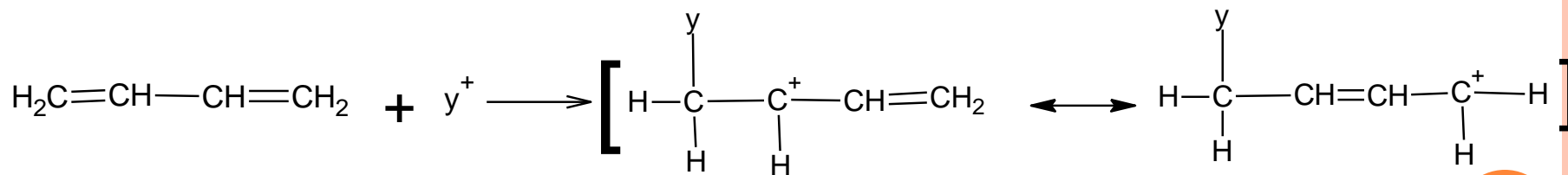
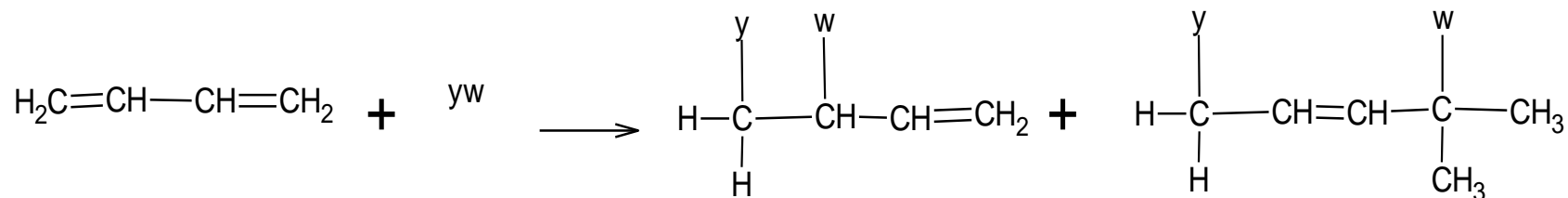
CYCLIC MECHANISMS

- Initial attack is not at one carbon
- Both carbon are attacked simultaneously



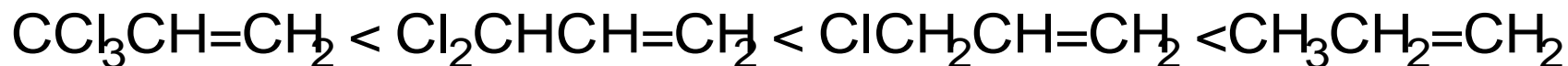
ADDITION TO CONJUGATED SYSTEM

Electrophillic addition on a compound with two double bonds in conjugation 1,2 addition product is often obtained, but in most cases there is also a 1,4 addition product often in larger yield.



ORIENTATION AND REACTIVITY

- ❖ Electron donating groups increase the reactivity of a double bond towards electrophilic addition.
- ❖ Electron withdrawing groups decrease it.
- ❖ The reactivity toward electrophilic addition of a group of olefins increased in the order.



- ❖ Simple olefins do not react by the nucleophilic mechanism
- ❖ Compounds that have a double bond conjugated with a Z-group always react by a nucleophilic mechanism

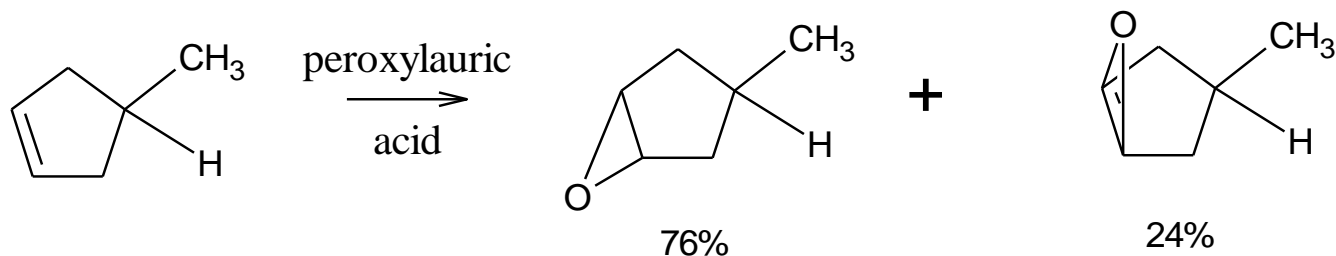


- ❖ Electron withdrawing groups enhance nucleophilic addition and inhibit electrophilic addition
- ❖ In compounds containing both double and triple bonds, bromine, an electrophilic reagent, always adds to the double bond
- ❖ Bridged intermediates react faster with double than with triple bonds
- ❖ The presence of electron withdrawing groups lowers the alkene/alkyne rate ratio
- ❖ Triple bonds are more susceptible to nucleophilic & less to electrophilic attack than double bonds
- ❖ Alkyl groups in general increase the rates of electrophilic addition
- ❖ In free radical addition the main effect seems to be steric
- ❖ Stability order of the free radical intermediates $3^\circ > 2^\circ > 1^\circ$



STEREOCHEMICAL ORIENTATION

The syn addition of an unsymmetrical cyclic olefin, the two groups can come in from the more hinderd face or from the less hinderd face of the double bond.

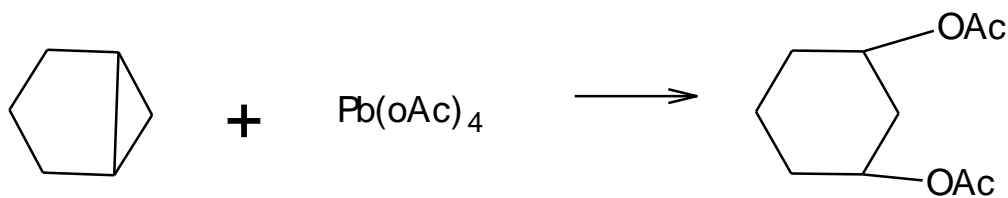
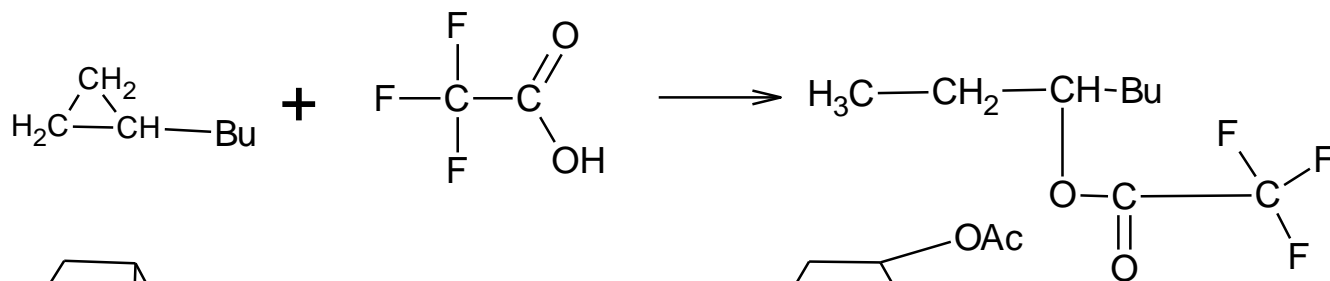
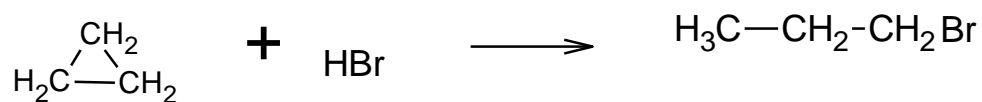


In anti addition the initial attack by the electrophile is from less hindered face.

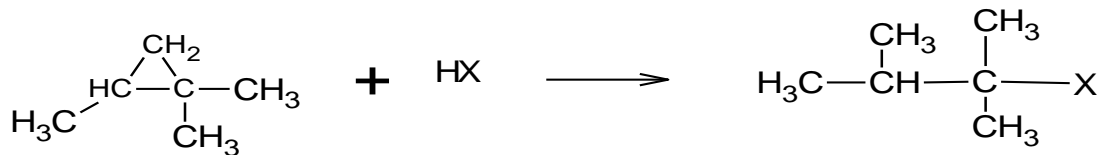


Addition to cyclopropane rings

Addition to cyclopropane ring results in the opening of 3 membered ring.



Addition of cyclopropane involves electrophilic addition.
Substituted cyclopropane follow markonikov's rule.

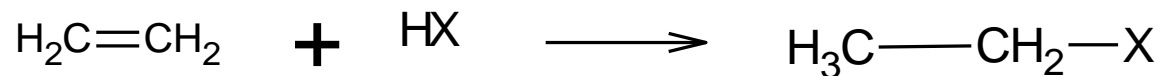
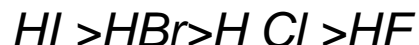


REACTIONS

Addition of hydrogen halides

Alkenes reacts with hydrogen halides form alkyl halides

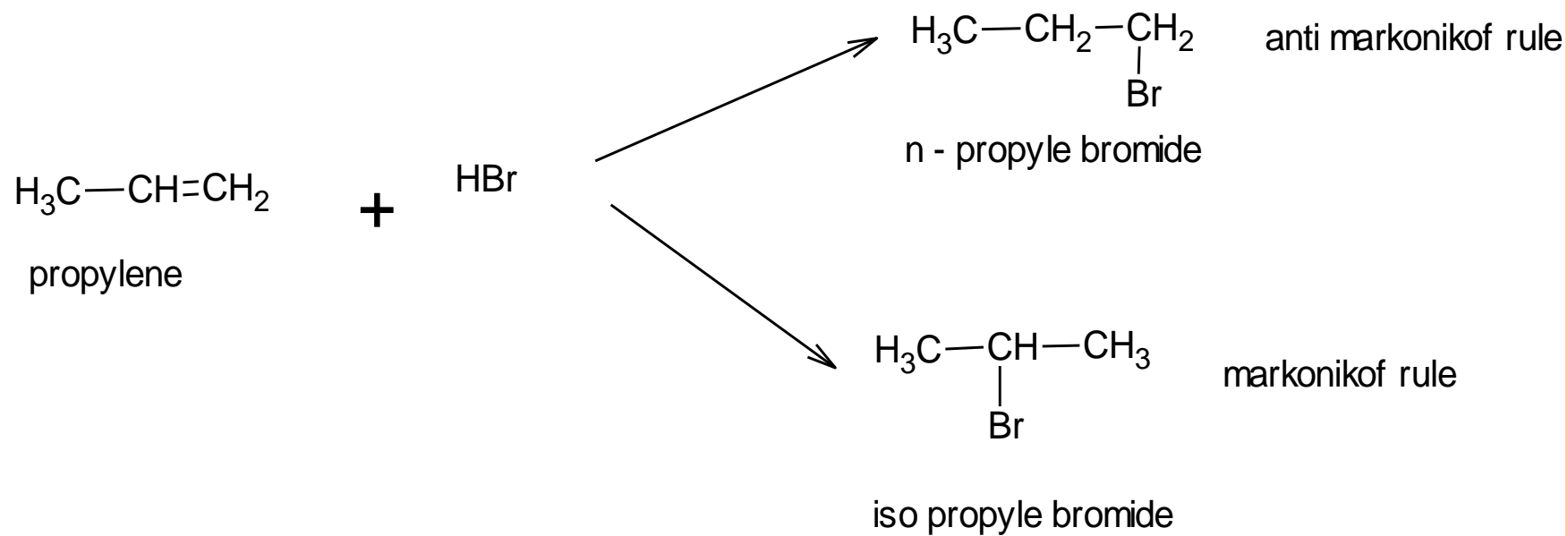
Order of reactivity



If olefin is symmetrical alkyl halide is formed.

If it is unsymmetrical two different alkyl halides are possible.



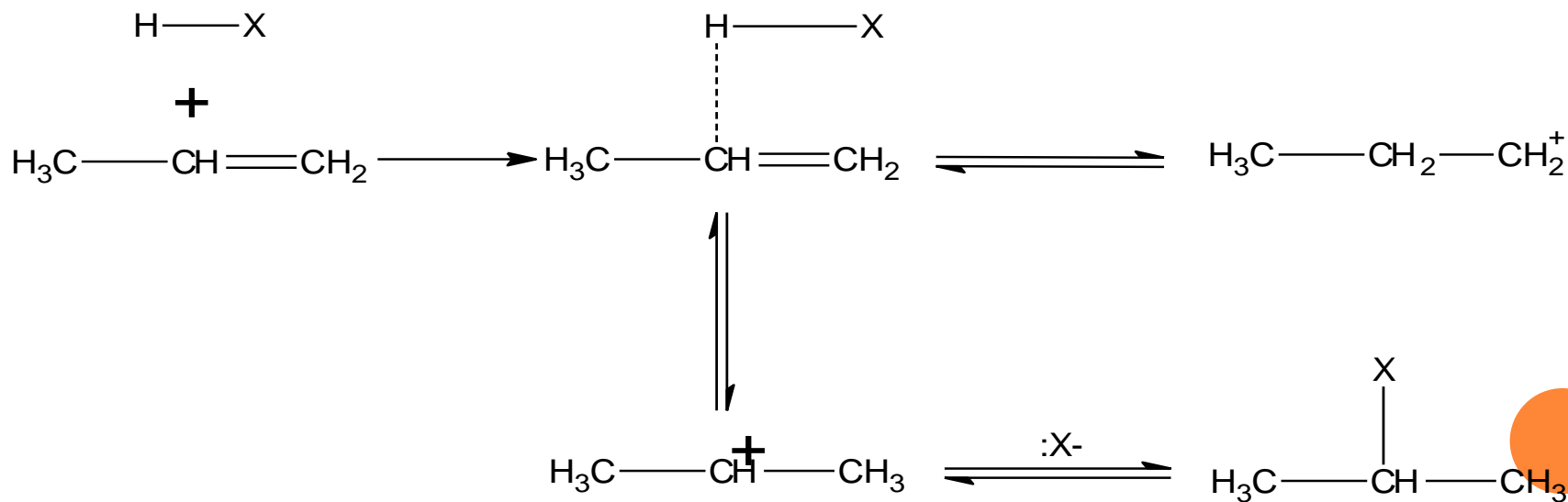


MARKOWNIKOFF RULE

The positive portion of the reagent goes to the side of the double or triple bond that has more number of hydrogen atom.

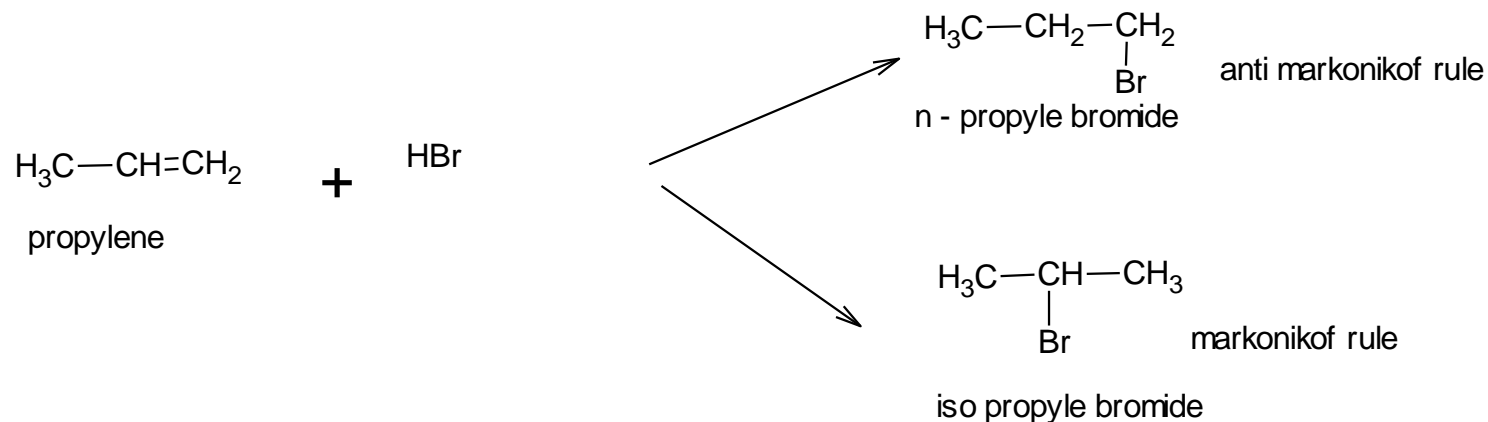
The negative (or more negative) part of unsymmetrical addendum attaches to that carbon atom of the double bond which bears the least number of hydrogen atoms.

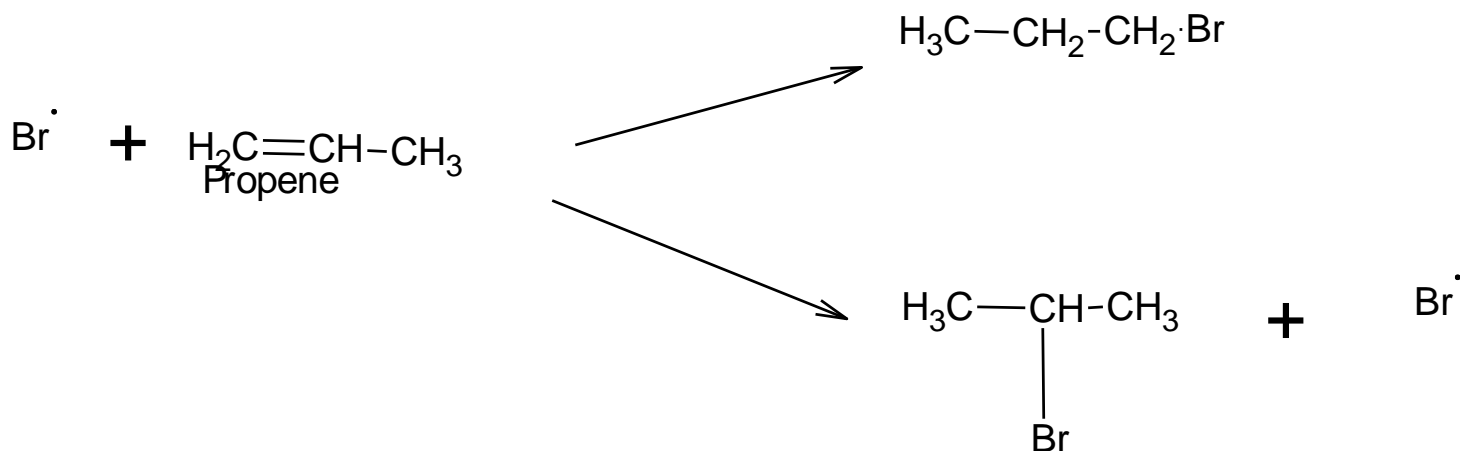
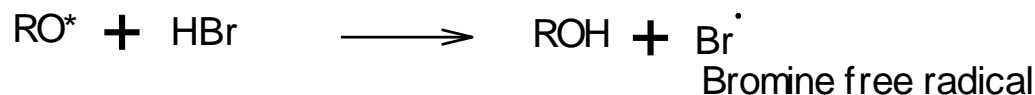
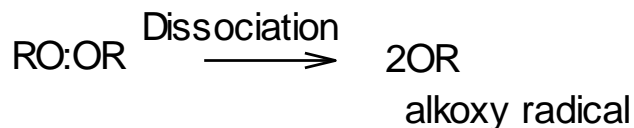
MECHANISM



The peroxide effect (anti-Markownikoff's addition)

Addition of hydrogen bromide to propene in presence of air, peroxide or light yields predominantly n-bromo pentane i.e, the reagent adds on the olefin in a manner contrary to Markownikoff's rule.





HCl and HI do not give peroxide effect.

HCl bond is stronger than H-Br bond it is not broken by free radicals easily.

HI is weaker than H-Br it is broken easily but the Iodine atoms combine readily and yield iodine molecule.



REFERENCES

- ✓ Jerry March , Advanced Organic Chemistry,Wiley Student Edition, 734
- ✓ O.P. Agarwal, Organic Chemistry, Goel Publishing House, 409
- ✓ Morrison Boyd , Organic Chemistry, Prentice Hall of India Private Limited , 317



Thank You

