

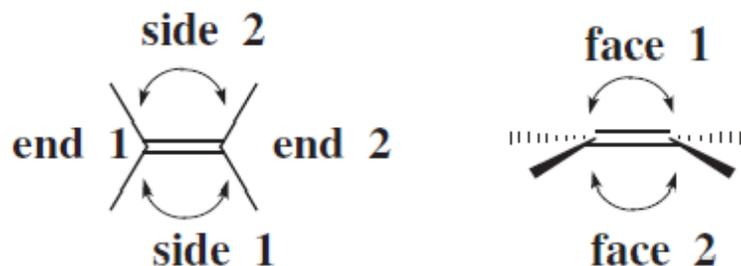
**M.SC-Sem-II, CC-VIII , Organic Chemistry II**  
**UNIT - I Addition to Carbon-Carbon Multiple Bonds**  
**Mechanistic and stereochemical aspects of addition reactions involving nucleophile**

**The case of nucleophilic addition reactions**

For nucleophilic addition the situation is reversed. These reactions are best carried out on substrates containing three or four electron-withdrawing groups, two of the most common being  $\text{F}_2\text{C}=\text{CF}_2$  and  $(\text{NC})_2\text{C}=\text{C}(\text{CN})_2$ . The effect of substituents is so great that it is possible to make the statement that simple alkenes do not react by the nucleophilic mechanism, and polyhalo or polycyano alkenes do not generally react by the electrophilic mechanism.

## Orientation

When an unsymmetrical reagent is added to an unsymmetrical substrate, the question arises: Which side of the reagent goes to which side of the double or triple bond?



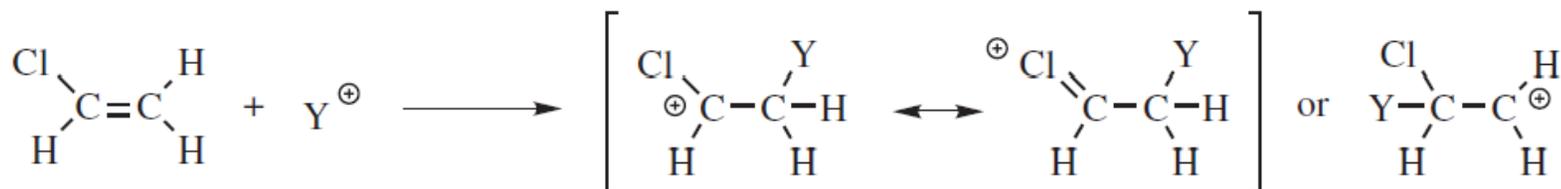
## Markovnikov's rule

## ELECTROPHILIC ADDITION REACTION

When an unsymmetrical reagent is added to an unsymmetrical substrate, the question arises: Which side of the reagent goes to which side of the double or triple bond. Electrophile attack, to Carbon–Carbon Multiple Bonds that has more hydrogens. A number of explanations have been suggested for this regioselectivity, but the most probable is that  $Y^+$  adds to that side which can give the more stable carbocation



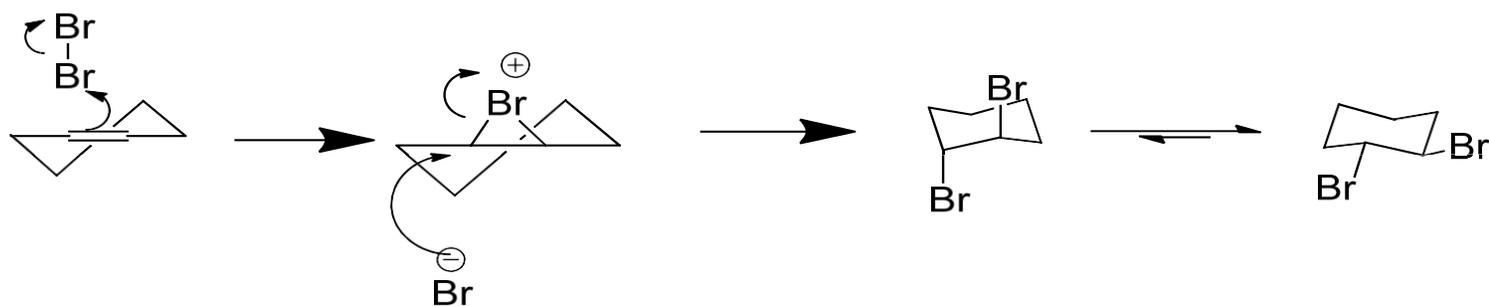
More stable



More stable

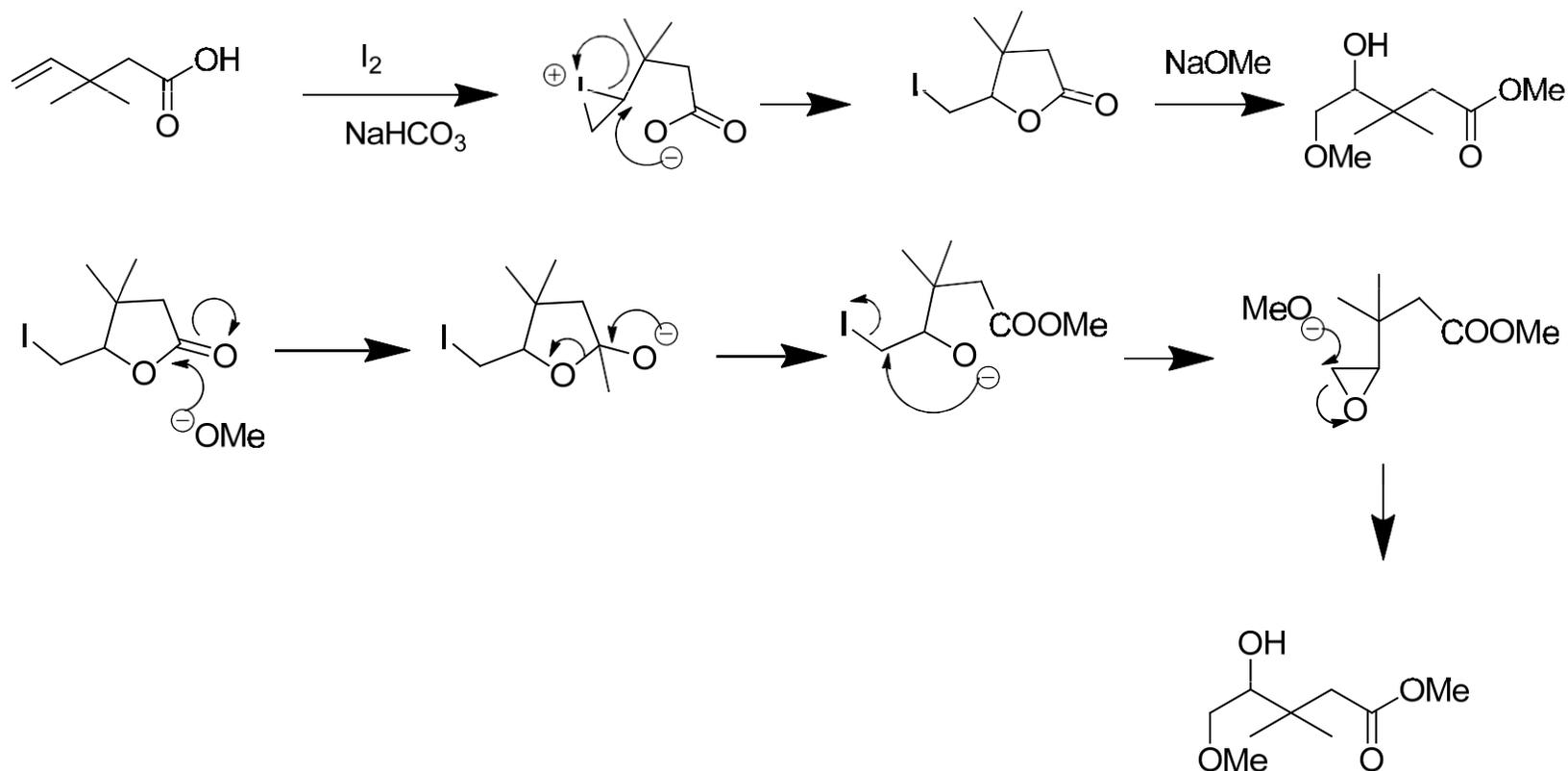
## BROMINATION OF CYCLOHEXENE

For the formation of epoxide ring closure is possible only when the compound is diaxially substituted and thus ring opening also takes place leading the formation of diaxial product. Similarly bromonium ion also open with the formation of diaxial product which easily flip to diequatorial conformation.



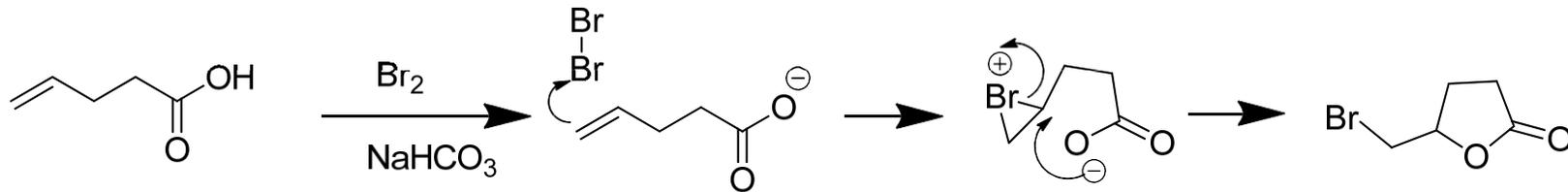
### IDO LACTONIZATION

Alkene is undergoing electrophilic addition reaction. Iodonium ion is opened by intramolecular reaction leading the formation of epoxide. As the second step of the reaction has been carried out in presence of sodium methoxide ring opening takes place.



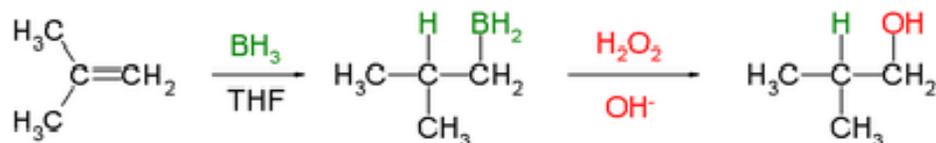
## BROMO LACTONIZATION

The reaction is cyclisation of unsaturated carboxylic acid. The nucleophile is carboxylate anion. The reaction is known as bromolactonization.



### Hydroboration oxidation reaction

The hydroboration oxidation reaction is an organic chemical reaction which is employed for the conversion of alkenes into alcohols that are neutral. This is done via a ***two-step process which includes a hydroboration step and an oxidation step.*** This is done by a net addition (across the entire double bond) of water.

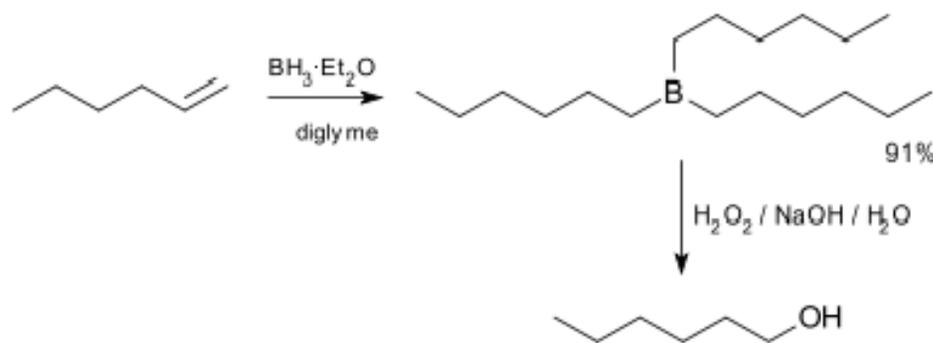


Hydroboration oxidation reaction mechanism can be considered as an anti-Markovnikov reaction where a hydroxyl group attaches itself to the carbon which is less substituted. The first time the hydroboration oxidation reaction was reported was in the second half of the 1950s by the *English born American chemist Herbert Charles Brown*. He went on to win the Nobel Prize in Chemistry in the year 1979 for this work.

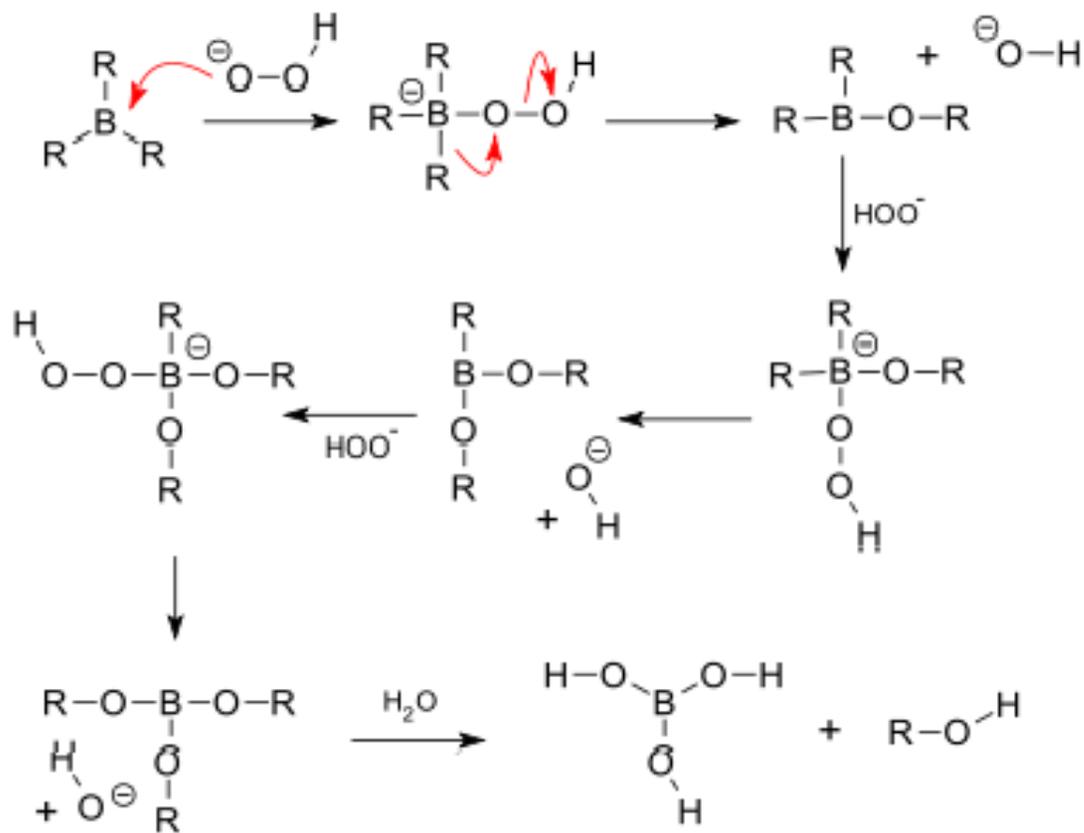
## The Hydroboration Step

This step begins with the addition of borane in the form of  $\text{BH}_3$  to the given double bond. This leads to the transfer of a hydrogen atom to the carbon atom that is adjacent to the carbon bonded with the boron atom. The hydroboration step described is now repeated twice, giving three alkenes that are attached to the boron atom from the initial  $\text{BH}_3$ .

The compound that results from the addition of three alkenes to the borane is referred to as trialkyl borane. This trialkyl borane is now treated with a base (or water) and hydrogen peroxide. Thus, the boron-carbon bonds are replaced with carbon-OH group bonds. The conversion of boron into boric acid is also observed. 1-hexene can be converted into 1-hexanol using this method as shown below.

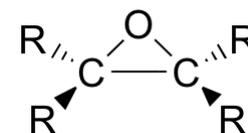


In the second step of the hydroboration process the boron atom comes under attack by the hydroperoxide ion which is nucleophilic in nature. Now, the R group is rearranged along with its bond pair of electrons to the adjacent oxygen atom



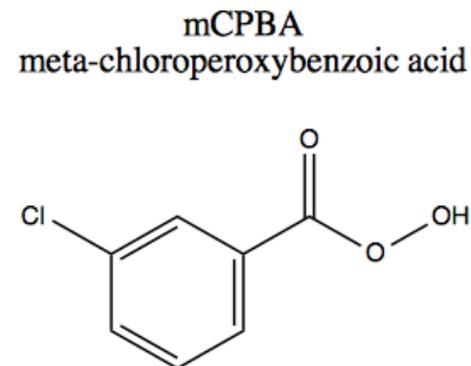
## EPOXIDATION

An epoxide is a 3-membered ring containing two carbon atoms and one oxygen atom (a cyclic ether). It is interesting because it is easily opened due to small ring strain and due to the electronegativity of the oxygen atom.



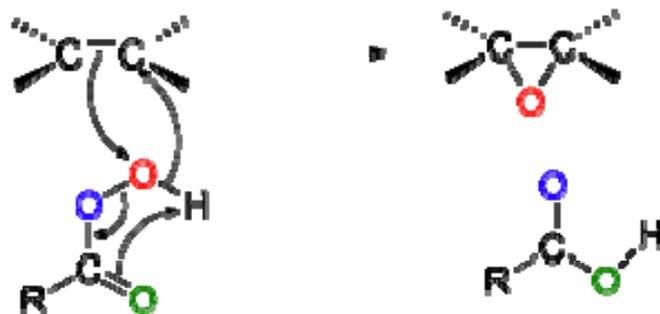
In epoxidation reactions an alkene is subjected to a peroxyacid to convert it into an epoxide. Another way to say that epoxidation is the electrophilic addition of oxygen to the double bond of the alkene.

There are several types of commonly used peroxyacid such as peroxy trifluoroacetic acid, peroxyacetic acid, hydrogen peroxide, and mCPBA, which is the most common of all.



## MECHANISM

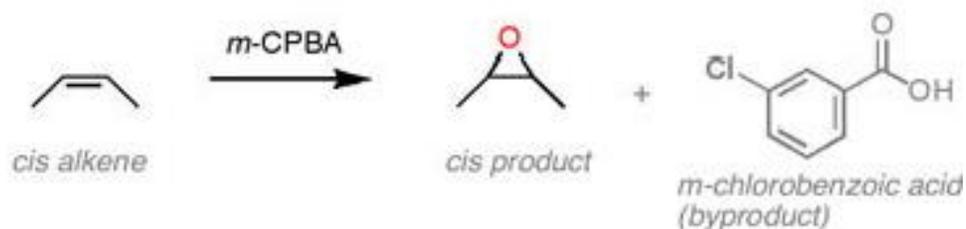
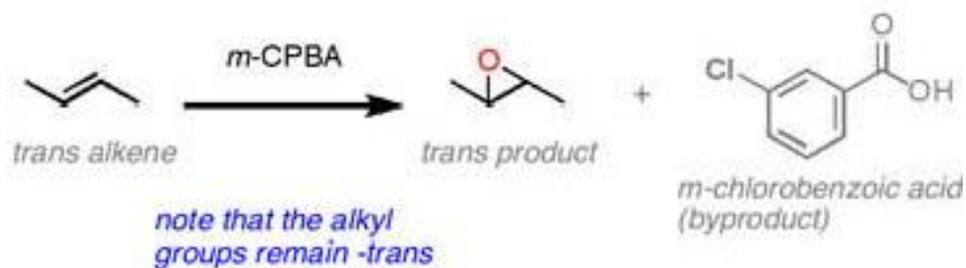
The double bond is electron rich and attacks the more electrophilic oxygen. This breaks the weak oxygen-oxygen bond and creates a new carbonyl. Once this carbonyl is formed, rearrangement occurs and the more electrophilic oxygen is released to become the oxygen of the epoxide.



## STEREOCHEMISTRY

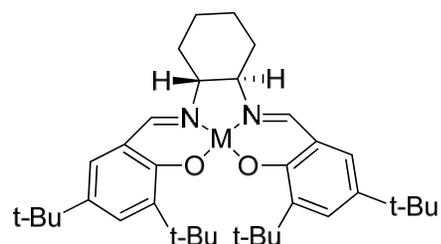
The stereochemistry associated with this reaction is interesting and important. As the reaction can occur on a cis or trans alkene, we see the two different products come from these two different starting materials. The oxygen can only attack from one face of the alkene. This means that the stereochemistry of the alkene is retained.

### Epoxidation of alkenes

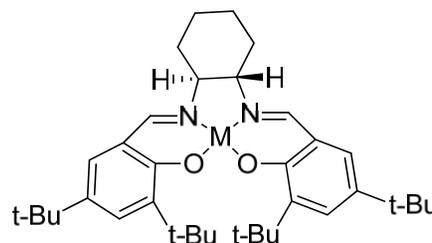


## HYDROLYTIC KINETIC RESOLUTION (HKR)

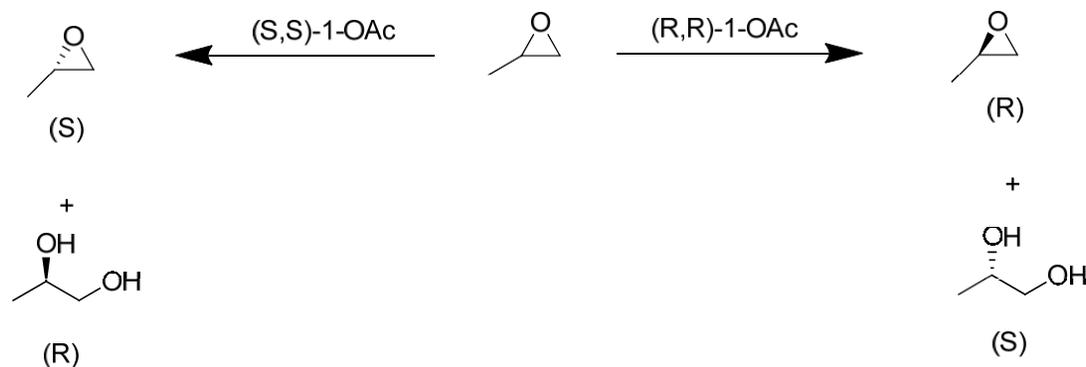
Jacobsen discovered the (salen)Co complex catalyzed efficient hydrolytic kinetic resolution (HKR) of a variety of terminal epoxides allowing efficient kinetic resolution of virtually any type of terminal epoxide.



M= Co: (R,R)  
M= Co-OAc: (R,R)-5-OAc



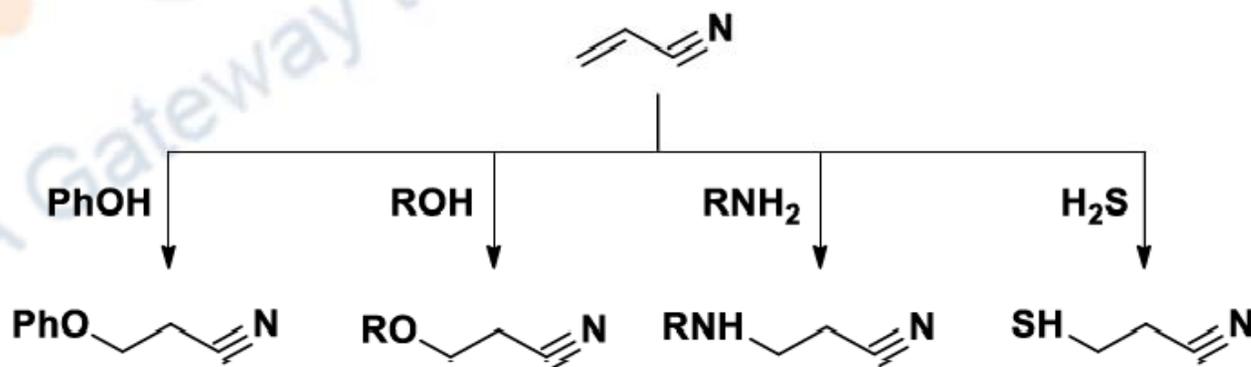
M= Co: (S,S)  
M= Co-OAc: (S,S)-5-OAc



## NUCLEOPHILIC ADDITION REACTION

### Cyanoethylation

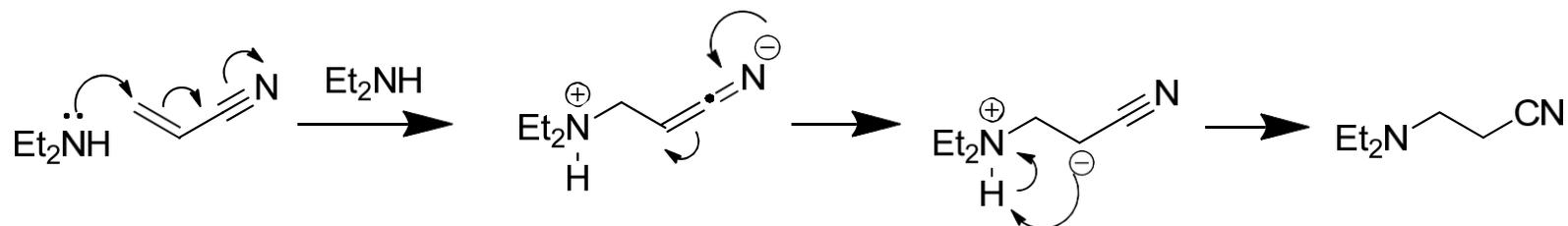
With alkenes containing a -CN substituent, the most common being acrylonitrile, a variety of nucleophiles such as phenols, alcohols, amines or sulfides may easily add to the unsubstituted carbon of the double bond. Thus, on abstraction of a proton from the solvent, the original nucleophile now has an attached 2-cyanoethyl group and this process is termed as cyanoethylation.



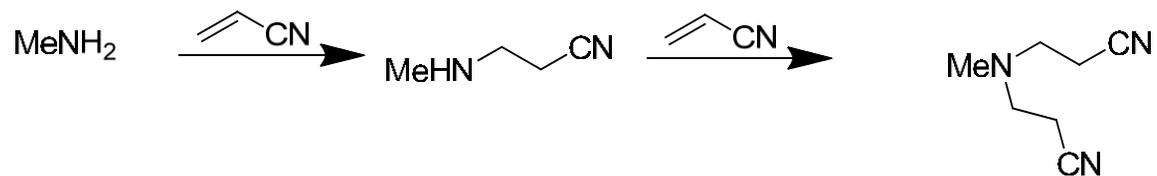
## Reaction of acryl nitrile with diethylamine



### MECHANISM



## Reaction of acryl nitrile with ethyl amine



To be continued .....