Class XII

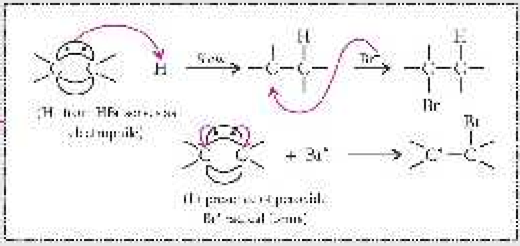
REACTION MECHANISM

describes the stepwise elementary reactions take place in the complex chemical process.

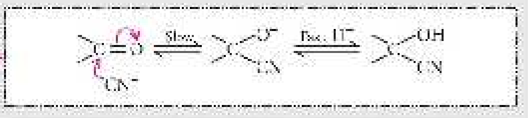
CONCEPT MAP

Addition Reaction

Addition of a substituent to a multiple bonded atom is addition reaction which can be electrophilic, nucleophilic or radical in character depending upon the attacking species. Addition to a simple carbon-carbon double bond is generally either electrophilic or radical induced depending on the conditions, *e.g.*, addition of HBr to an alkene.

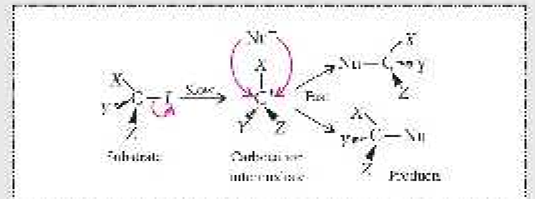


Addition to carbon oxygen double bond in aldehydes and ketones are generally nucleophilic.



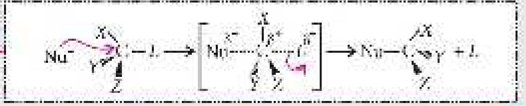
Substitution Reaction

Substitution of one atom or group attached to the reactant molecule by another atom or group is substitution reaction which further can be electrophilic, nucleophilic or radical induced depending on attacking species. The most common among these is nucleophilic which is further divided into S_N1 and S_N2 reactions.



S_N1 (substitution nucleophilic unimolecular) is a two steps reaction. In first step, a carbocation is formed and in second step, nucleophile attacks on it.

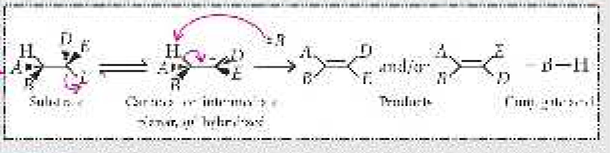
S_N2 (substitution nucleophilic bimolecular) is a concerted, one step reaction which gives stereochemical inversion product.



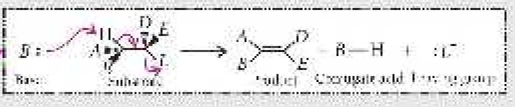
Elimination Reaction

Elimination of two atoms or groups from reactant molecule to form a multiple bond is elimination reaction. It is just reverse of addition reaction. Similar to substitution, it is divided into E1 and E2 reactions.

E1 (Elimination unimolecular) has two steps, first is the formation of carbonium ion which is the rate determining step. Second step is formation of multiple bond by another elimination from carbonium ion. It is non-stereospecific - follows Saytzeff rule.



E2 (Elimination bimolecular) is a concerted, single step reaction in which elimination of both the atoms or groups and multiple bond formation takes place simultaneously. It is stereospecific.



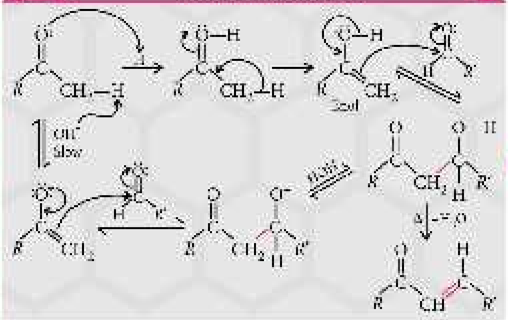
Mechanistic Approach to Some Name Reactions

A mechanistic approach to any reaction classifies the reaction according to mechanism rather than by functional group. It explains the stereochemistry involved in a particular reaction, which can either be regioselective, stereoselective or stereospecific.

CONCEPT MAP

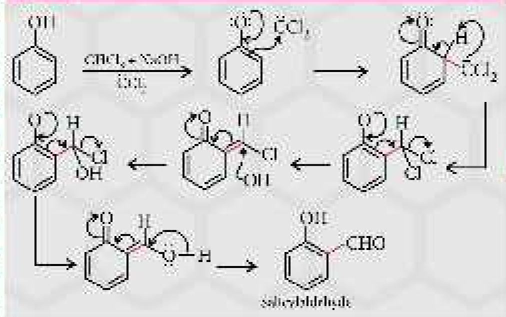
CLASS XII

I Aldol Condensation



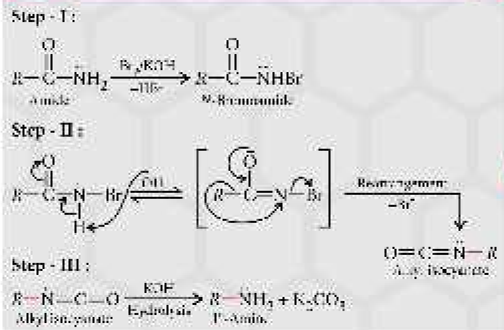
- In this reaction, an enolate ion (strong nucleophile) reacts with a carbonyl compound to form β-hydroxyaldehyde (aldol) or β-hydroxyketone (ketol) followed by dehydration to give a conjugated enone.
- Aldol condensation provides a good way to form carbon-carbon bond.
- This reaction is diastereoselective because of the way in which two prochiral reagents come together.
- Enolate is an important factor controlling the diastereoselectivity, in many examples *cis*-enolates give *syn*-aldols and *trans*-enolates give *anti*-aldols preferentially.
- Some enolates can only exist as *trans*-enolate because they are derived from cyclic ketones.

II Reimer—Tiemann Reaction



- Phenol on refluxing with chloroform and aqueous sodium hydroxide at 340 K followed by acid hydrolysis yields salicylaldehyde.
- This reaction is an example of carbene based reactions where it is also considered to be an electrophilic attack on benzene.
- The electrophile is :CCl_2 (dichlorocarbene) which does not add to benzene, but does attack the electron rich aromatic ring of phenol.
- If CCl_4 is used instead of $CHCl_3$, salicylic acid is formed.
- The Reimer—Tiemann reaction is an important way of making *ortho*-substituted phenols, but the yields are often poor.

III Hoffmann Bromamide Degradation Method



- In this reaction, amide gets converted to primary amine by the action of Br_2 and KOH / NaOH.
- This method is used for stepping down the series as the amine formed contains one carbon atom less than the parent amide.
- This reaction involves the migration of alkyl group from carbonyl in the precursor to nitrogen with the elimination of carbon dioxide.
- This method is limited to amides of the type $RCONH_2$.
- The step that leads to the formation of isocyanate through rearrangement is the slow and the rate determining step.
- The rearrangement proceeds with complete retention of configuration in the migrating group. The migrating group is never completely detached from the substance.