

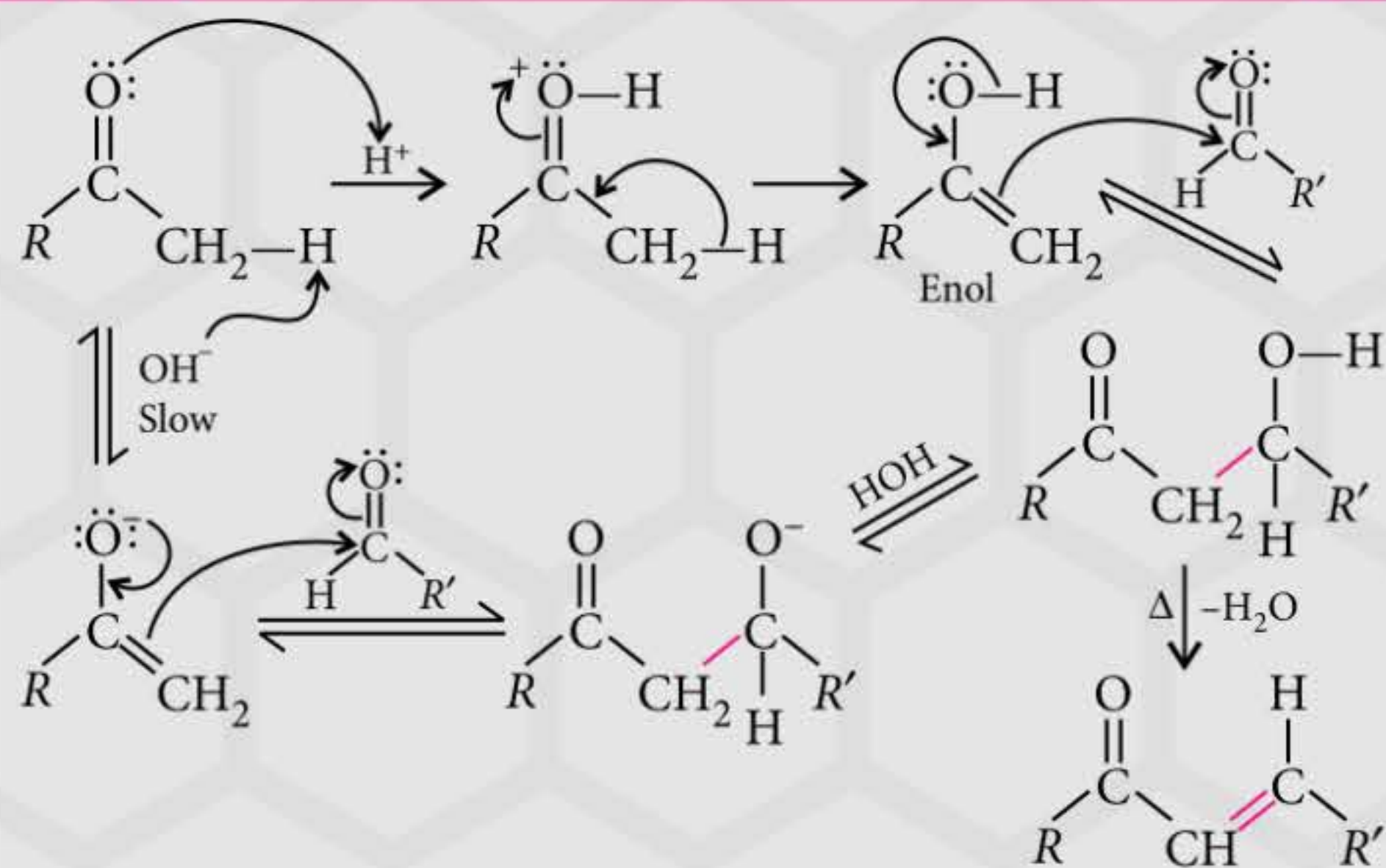
# Mechanistic Approach to Some Name Reactions

## CONCEPT MAP

### CLASS XII

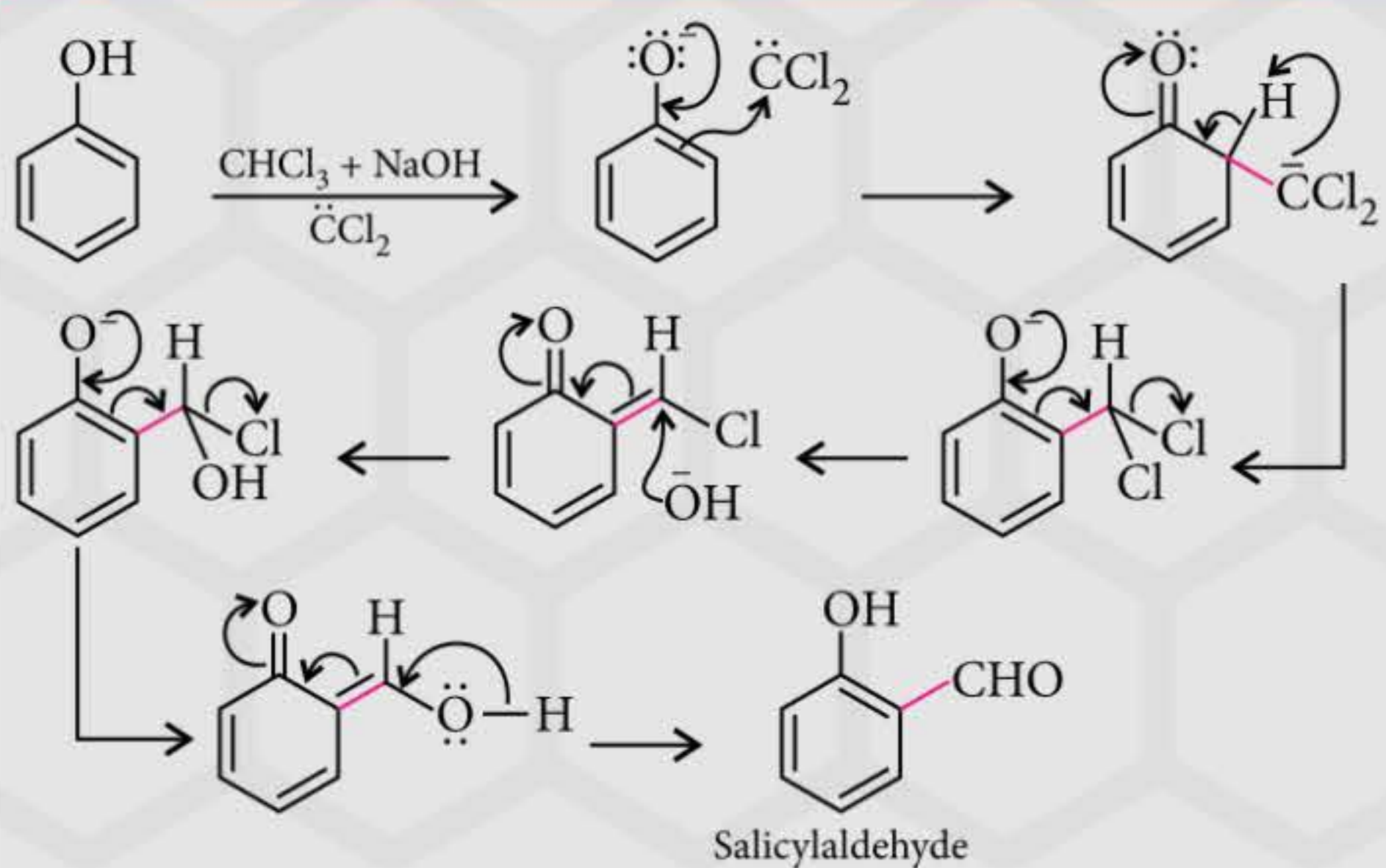
A mechanistic approach to any reaction classifies the reaction according to mechanism rather than by functional group. It explains the stereochemistry involved in a particular reaction, which can either be regioselective, stereoselective or stereospecific.

#### I Aldol Condensation



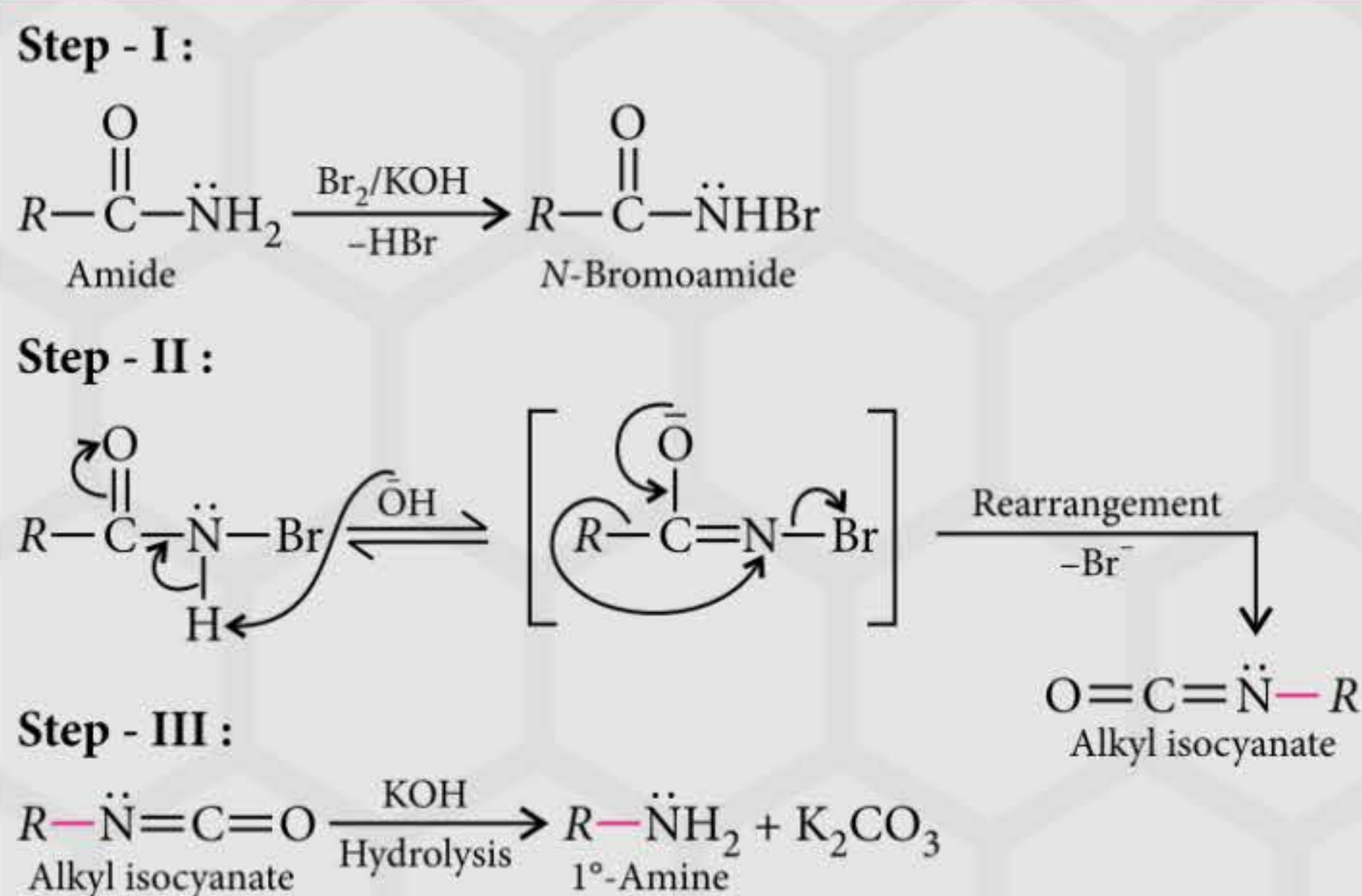
- In this reaction, an enolate ion (strong nucleophile) reacts with a carbonyl compound to form  $\beta$ -hydroxyaldehyde (aldol) or  $\beta$ -hydroxyketone (ketol) followed by dehydration to give a conjugated enone.
- Aldol condensation provides a good way to form carbon-carbon bond.
- This reaction 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  $:\text{CCl}_2$ , (dichlorocarbene) which does not add to benzene, but does attack the electron rich aromatic ring of phenol.
- If  $\text{CCl}_4$  is used instead of  $\text{CHCl}_3$ , 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  $\text{Br}_2$  and  $\text{KOH}$  /  $\text{NaOH}$ .
- 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  $\text{RCONH}_2$ .
- 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.