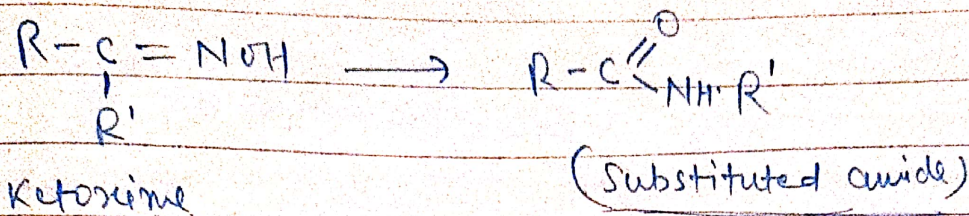


Beckmann Rearrangement :->

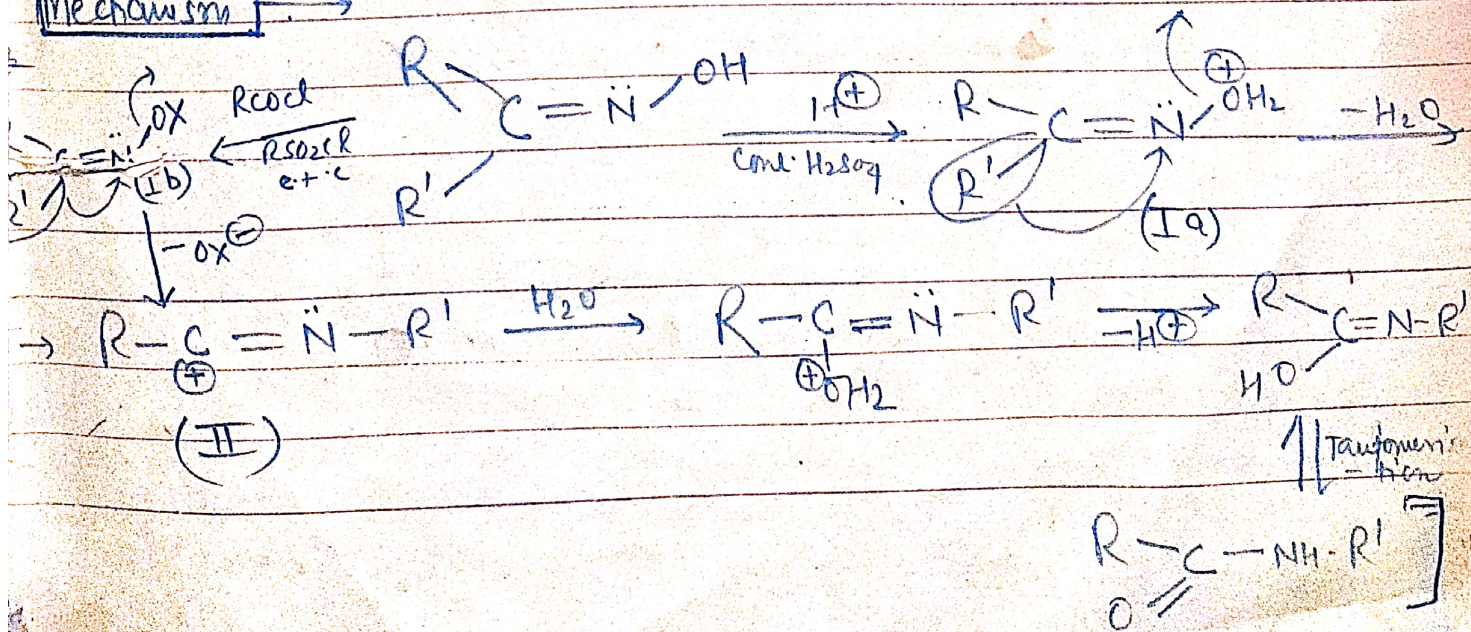
(Stereospecific)

It is the transformation of ketoximes to N-substituted amide and takes place under the catalytic influence of acid reagents such as POCl_3 , PCl_5 , H_2SO_4 , HCl , TsCl , $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$, $p\text{-CH}_3\text{-C}_6\text{H}_4\text{-SO}_2\text{Cl}$ (Tosyl chloride), P.P.A etc.



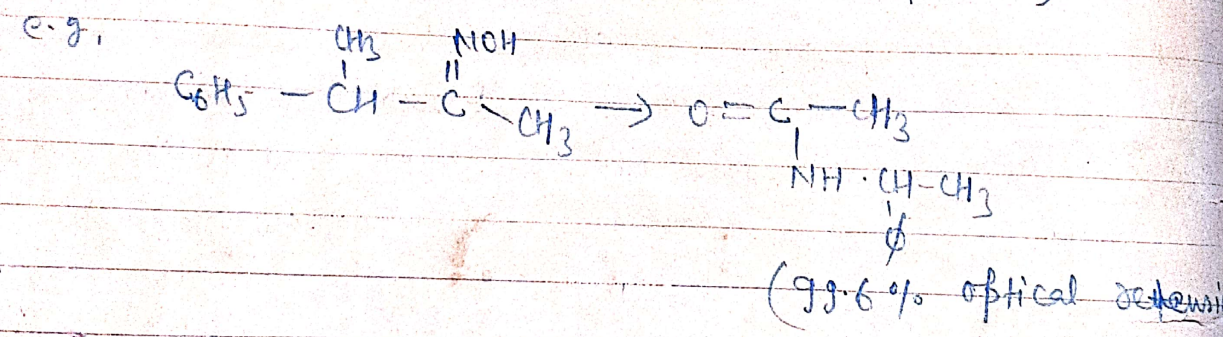
It is a highly stereospecific reaction in that ~~the~~ group trans (anti) to the hydroxyl group ^(always) generally migrates & hence this is often used as a method of determining the configuration of the oxime. However it is not unequivocal. It is known that with some oximes the cis group migrates and that with others, especially where R and R' both are alkyl, mixtures of the two possible amides are obtained. However this behavior does not necessarily mean that the cis group is actually undergoing the migration. In some cases it may be that the oxime undergoes isomerisation under the reaction conditions, before the migration takes place.)

Mechanism :->



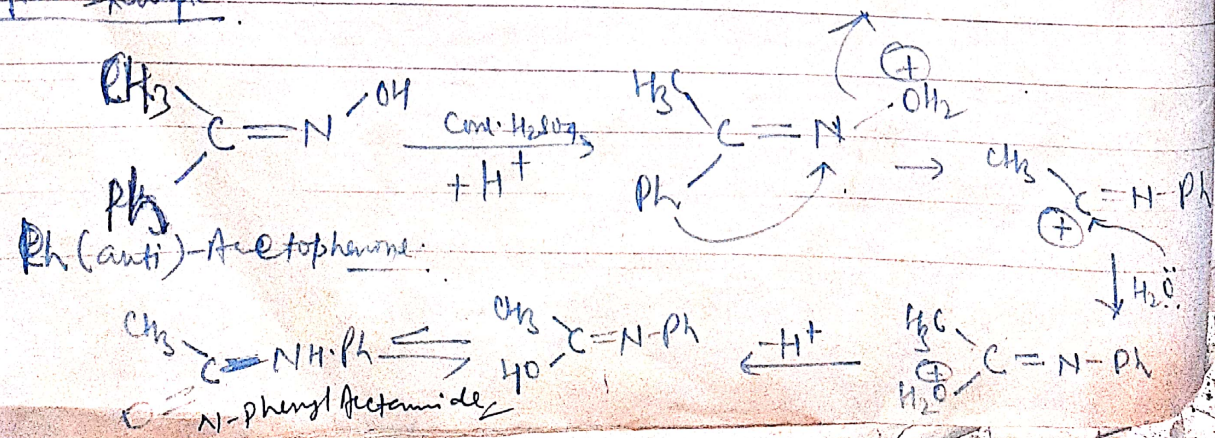
In strong acids (e.g. H_2SO_4) the rearrangement involves O-protonation to yield (Ia) followed by loss of water to (II), while with the acid chlorides, PCl_5 , PCOCl , etc. the intermediate ester (Ib) is formed; the anion OX^\ominus constitutes a good leaving group so that, again (II) is obtained. (The stronger the acid XOH , i.e. the more capable the anion is of independent existence, the better leaving group XO^\ominus should be & hence faster the rearrangement should occur. This is observed in the series where XO^\ominus is $\text{CH}_3\text{CO}_2^\ominus < \text{ClCH}_2\text{CO}_2^\ominus < \text{PhCO}_2^\ominus$. That such ionisation is the rate-limiting step in the rearrangement is also suggested by the observation that the rate of reaction increases as the solvent polarity increases.)

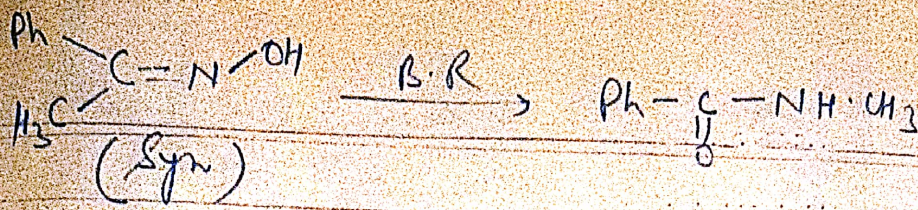
If the migrating group contains an asymmetric carbon centre, then it retains its configuration on migration (i.e. its configuration is retained in the product).



This indicated concerted-ness and intramolecular state of affair for the reaction. (It is also supported by the fact that it leads no mixed products having cross-over experiment.)

Other example:

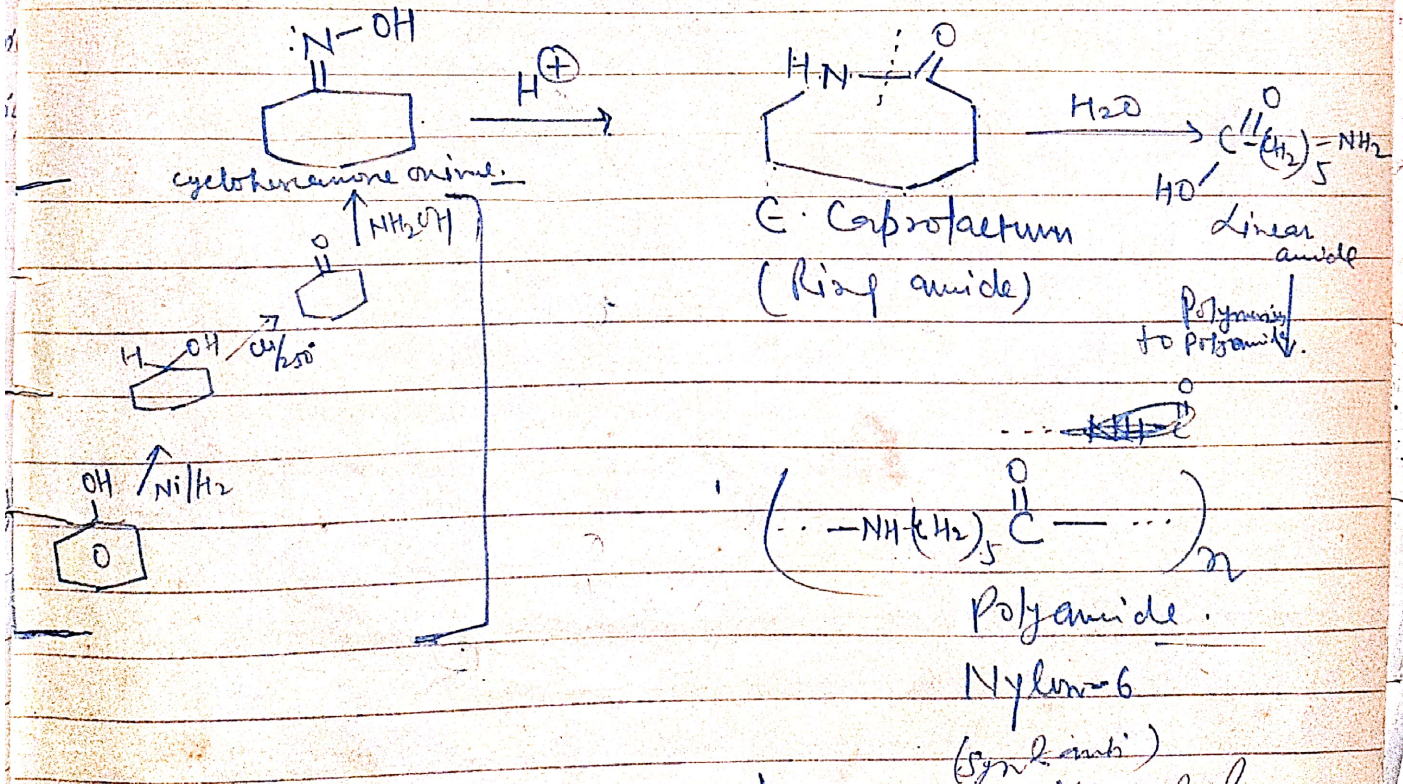




∴ Thus the migratory aptitude of the group is immaterial, it is the geometry of the group which is the deciding factor.

Application. (i) → The stereochemical use of the Beckmann rearrangement is the assignment of configuration of ketoximes (as shown above).

(ii) Industrial application → B.R. has a large scale application in the synthesis of textile polymer Nylon-6 from cyclohexanone oxime via the cyclic amide (lactam).



∴ because the isomeric ketoximes after B.R. give different amides, which can be identified by their hydrolysis products.

