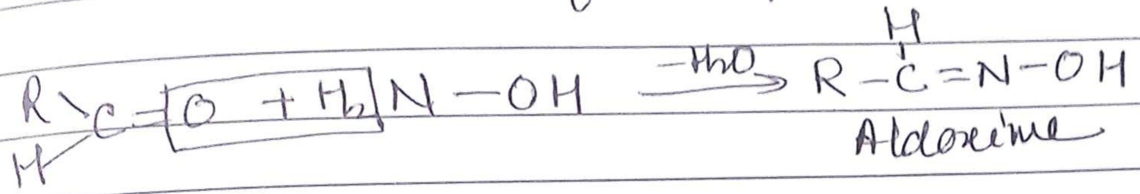
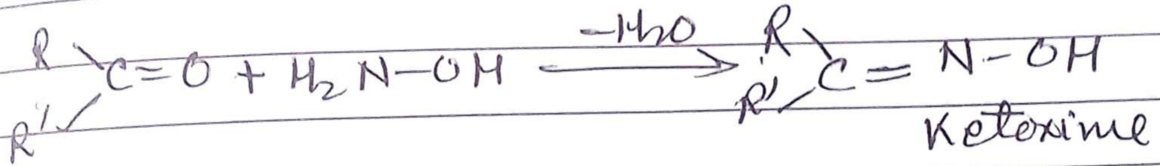
Beckmann rearrangment

When an aldehyde or ketone is treated with hydroxylamine (or oxime) NH_2OH respective oxime derivative is form upon condensation.



$$\overset{R}{\underset{H}{}}\!\!>C=\boxed{O + H_2}N-OH \xrightarrow{-H_2O} R-\overset{H}{\overset{|}{C}}=N-OH$$

Aldoxime

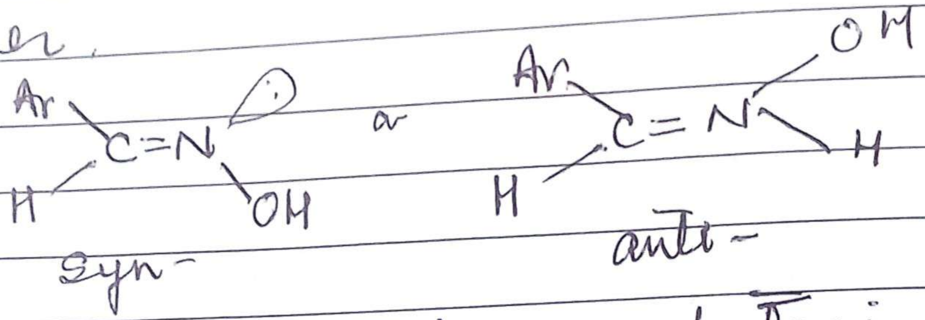


$$\overset{R}{\underset{R'}{}}\!\!>C=O + H_2N-OH \xrightarrow{-H_2O} \overset{R}{\underset{R'}{}}\!\!>C=N-OH$$

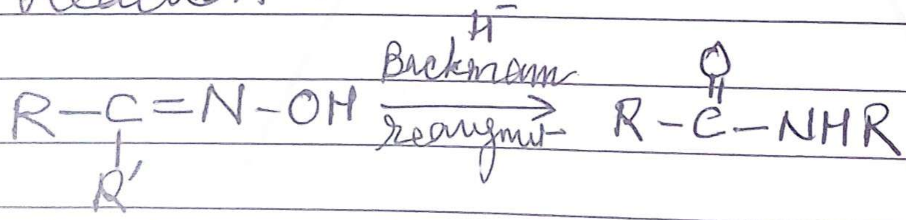
Ketoxime

Molecules containg $-C=N$ double are also capable of cis-trans isomer. The position of the lone pair of $\bar{e}$ of N-atom is fixed comparable to the second group of C-atom of the $C=N$ bond. The isomer in which $-H$ and $-OH$ groups are on the same side is called

Syn isomer and the another which they are on opposite side is anti-isomer.

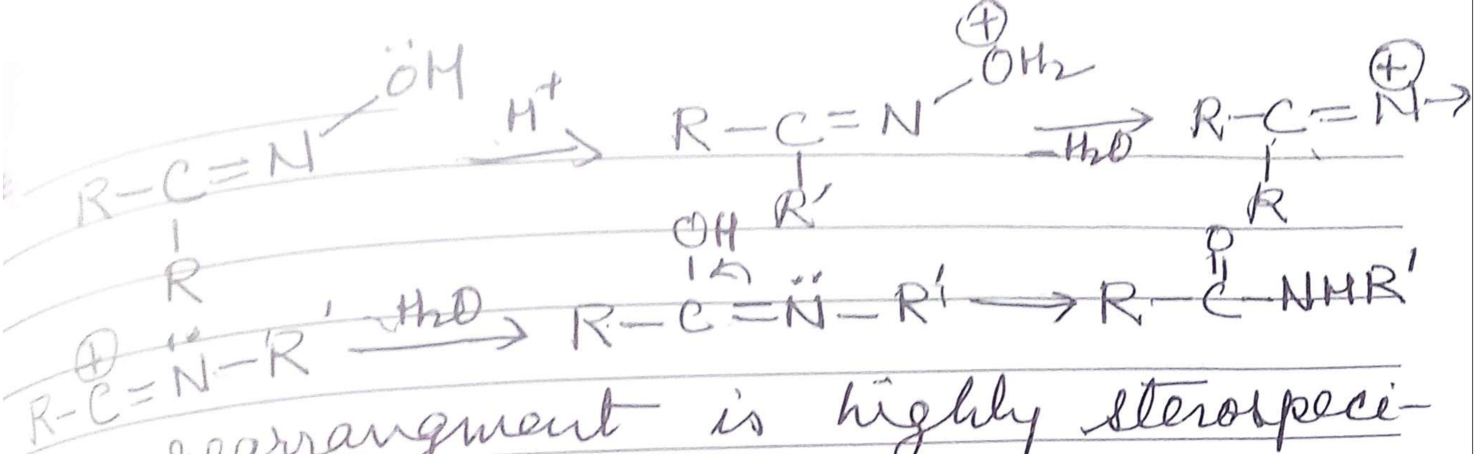


When an aldoxime or ketoxime is treated with an acidic reagent like H_2SO_4, P_2O_5 etc, It rearranges itself to form a substituted amide. This rearrangment is called Backmann rearrangment. The acidic ~~rearrangment~~ reagent catalyses the reaction.

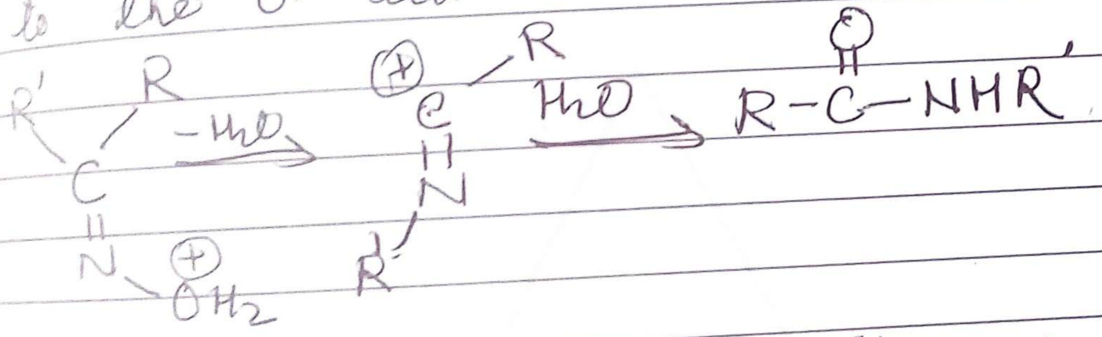


$$R-\underset{R'}{\underset{|}{C}}=N-OH \xrightarrow[\text{rearrgmnt}]{\overset{H^+}{\text{Backmann}}} R-\overset{O}{\overset{\|}{C}}-NHR$$

Mechanism :- It involves an intermediate with positive charge on N-atom.



The rearrangment is highly sterospecific as the migrating group attached itself to N- atom on the side opposite to the O- atom.



Application :- (1) Determination of the configuration of ketoxime :- Syn and anti isomers gives different amides when subjected to Beckmann reamgment. these amide can be ~~d~~ identified by the hydrolysis products.

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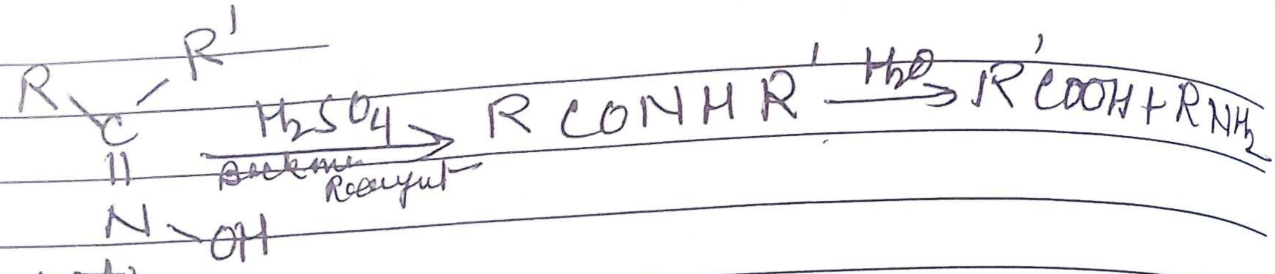
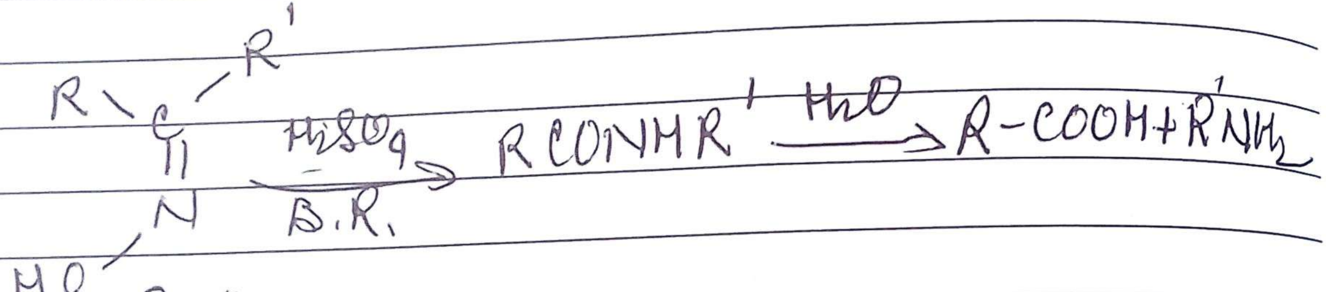
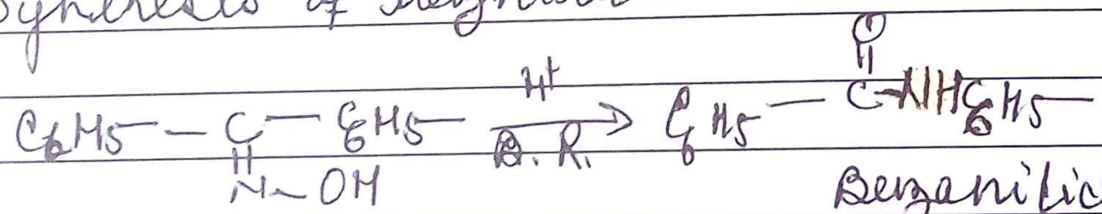


Anti



Syn

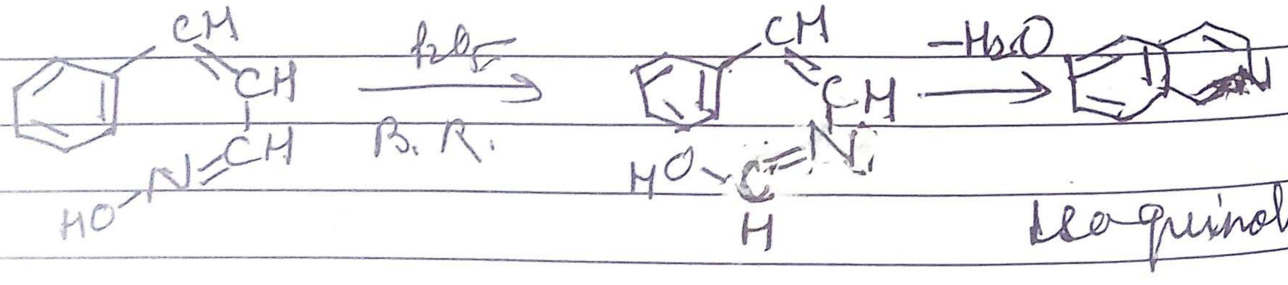
② Synthesis of beznilide—



Benzanilide

Benzophenone oxime

③



Iso quinoline