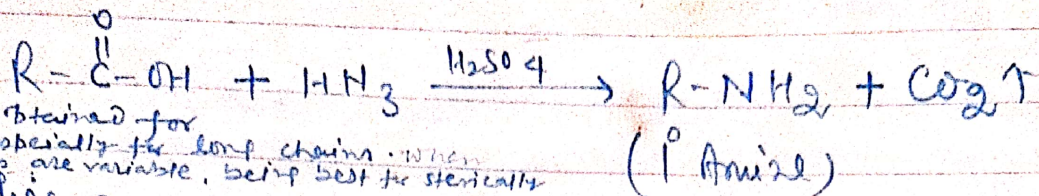


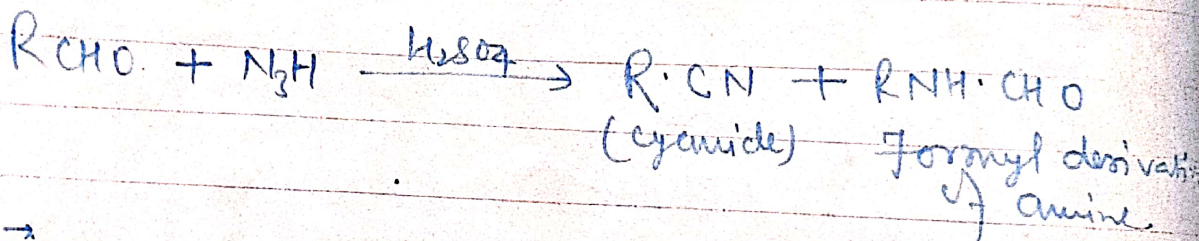
IV SCHMIDT REARRANGEMENT : \rightarrow Carboxylic Acids react with hydrazoic acid (HN_3) in presence of conc. H_2SO_4 (cat) to give amines directly. This rxn is known as Schmidt reaction.



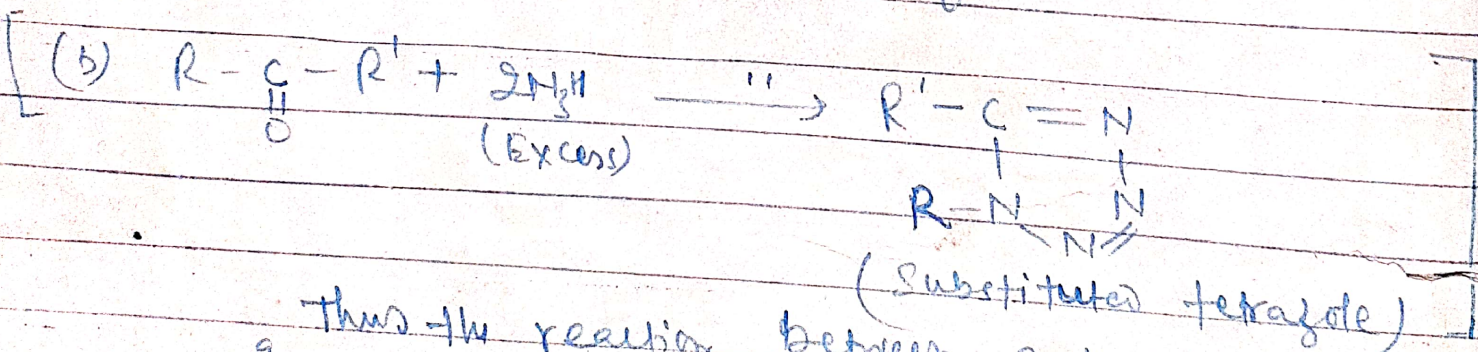
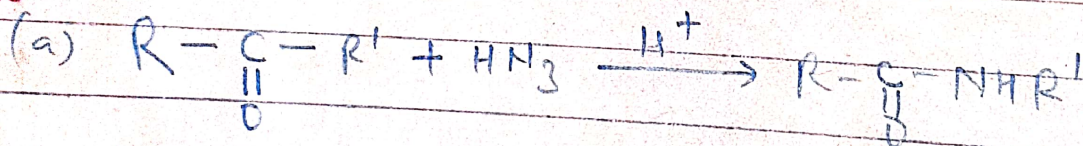
(Good yields are obtained for aliphatic R, especially for long chains. When R is aryl, the yields are variable, being best for sterically hindered compounds like p-nitrobenzoyl.)

This reaction also takes place between aldehydes, ketones and hydrazoic acid to form a mixture of cyanides and formyl derivatives of primary amines, and amides (substituted) respectively.

(i) Reaction of aldehyde.



(ii) ketone : \rightarrow

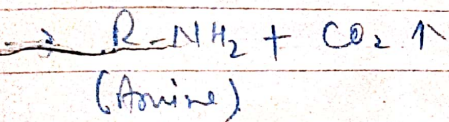
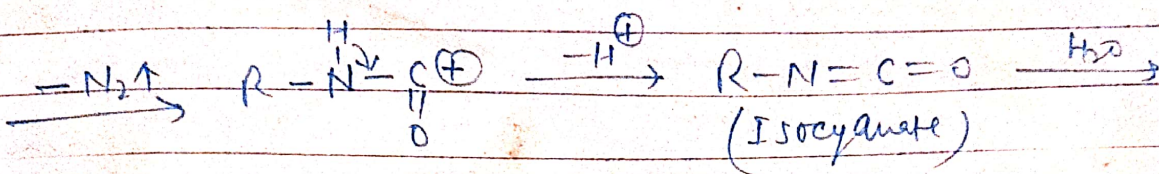
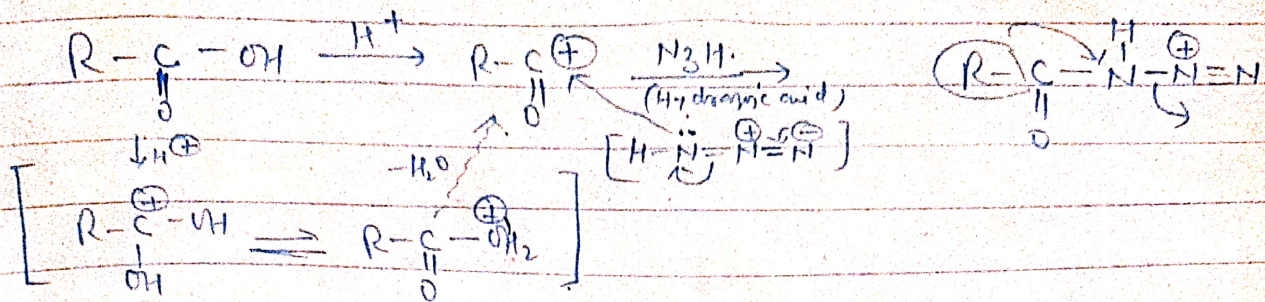


Thus the reaction between a ketone & hydrazoic acid is a method for "insertion" of NH between the carbonyl group and one R group, (thus converting the ketone into an amide (substituted))

However, the most common reaction is the reaction with carboxylic acids as, illustrated above.

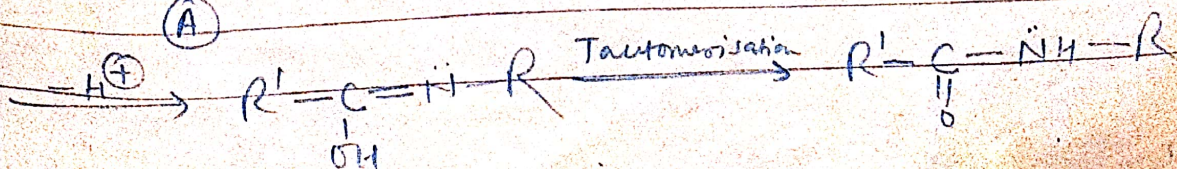
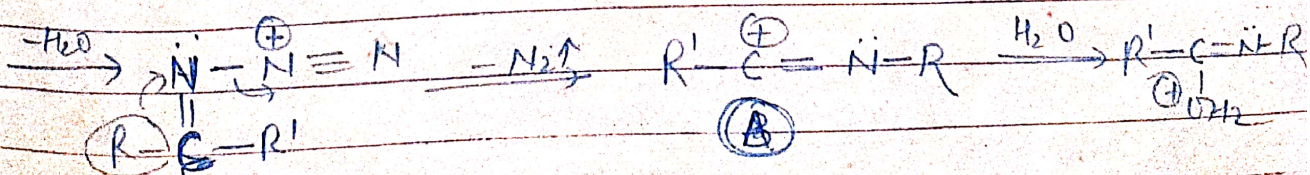
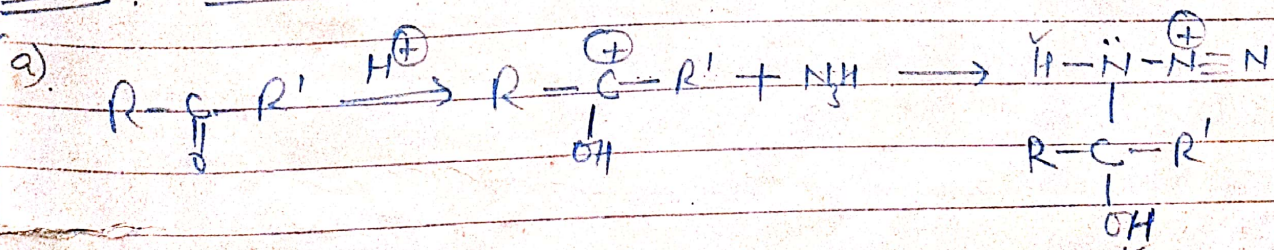
Mechanism.

(i) Reaction with Acids: The mechanism with carboxylic acids is similar to that of Curtius rearrangement, except it is the protonated anide which undergoes the rearrangement.

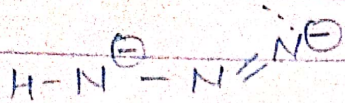
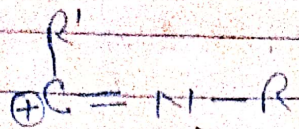


Evidently the first step of the reaction (i.e. the formation of $\text{R}-\text{C}^{\oplus}$) is as that of Ac^{\oplus} mechanism. Hence in the case of sterically hindered compounds (when R is very bulky) ~~the~~ good yields are obtained. (As in that case rate of formation of $\text{R}-\text{C}^{\oplus}$ is rapid.)

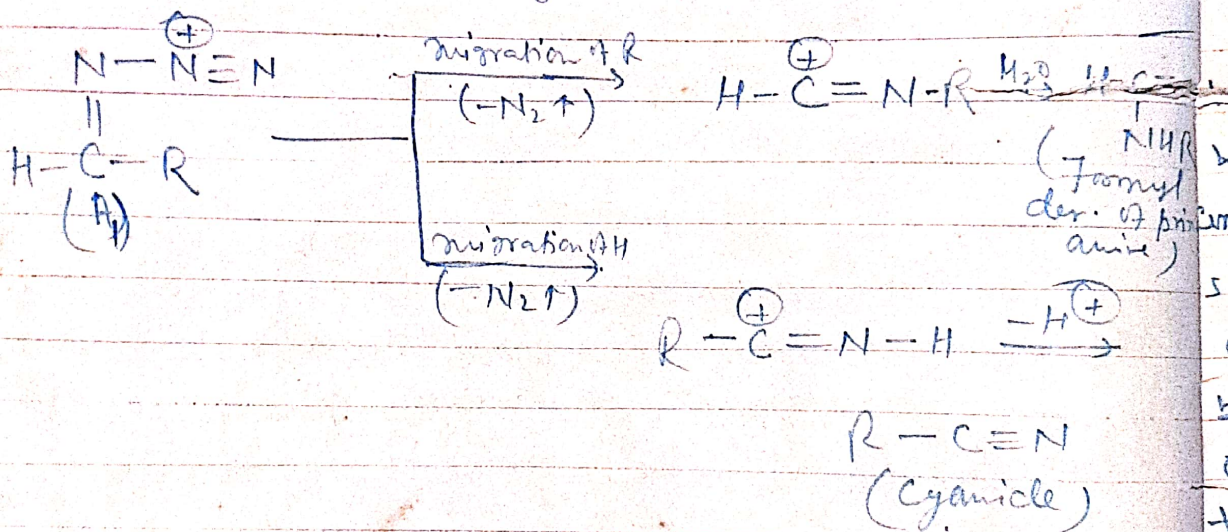
(ii) With Ketones.



(b) In cases of excess of NH_3 .



(ii) with Aldehydes: \rightarrow For aldehydes the mechanism is same, except that the ion (A) in the above case is now (A₁) & hence R or H can migrate to form a mixture of formyl derivative of primary amine and cyanide respectively.



Application \rightarrow

The Schmidt reaction has the advantage over Hofmann or Curtius rxn, that it is just a direct method for preparation of primary amine from carboxylic acids, but conditions are more drastic. Moreover it is important to note that the rxn is applicable only when the carboxylic acid used does not contain any group sensitive to conc. H_2SO_4 .

(1) Preparation of α -amino acids: \rightarrow this rxn can be applied for the synthesis of α -amino acids from aceto-acetic esters.

