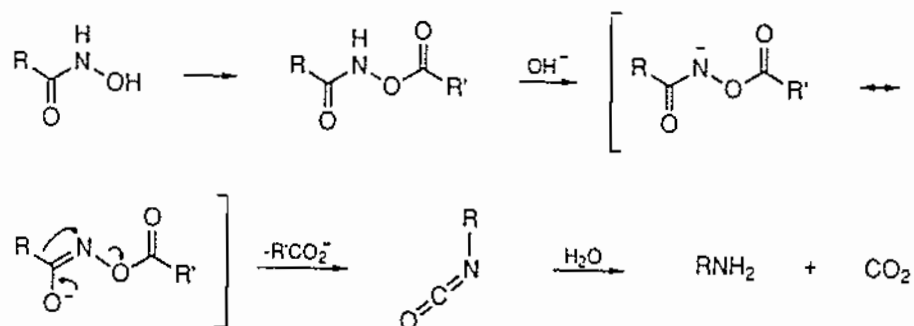


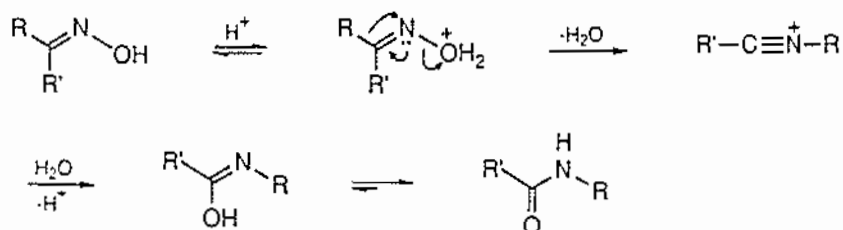
(iv) *Lossen rearrangement.* This differs from the Hofmann rearrangement only in that the leaving group is a carboxylate anion rather than bromide ion. The starting material is the ester of a hydroxamic acid:



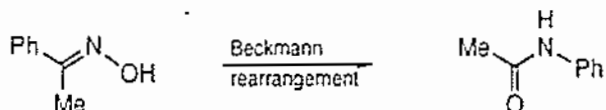
Of these four related processes the Lossen rearrangement is the least useful in the synthesis of amines because hydroxamic acids are not readily available. The Schmidt reaction is the most direct method but is only applicable if the acid does not contain groups which are sensitive to concentrated sulfuric acid. The Curtius rearrangement involves the mildest conditions but requires the preparation of the azide. The Hofmann rearrangement is convenient providing that other functional groups in the molecule do not react with bromine and alkali.

### (b) The Beckmann rearrangement

Oximes undergo a rearrangement in acidic conditions to give substituted amides:

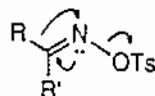


The Beckmann rearrangement is stereospecific: the group *trans* to the leaving group migrates. For example, acetophenone oxime, which has the stereochemistry shown, gives only acetanilide.

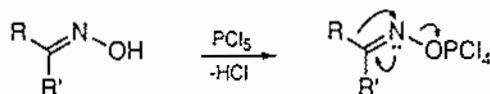


As in other intramolecular rearrangements, if the carbon atom which migrates is asymmetric, it retains its configuration during the reaction.

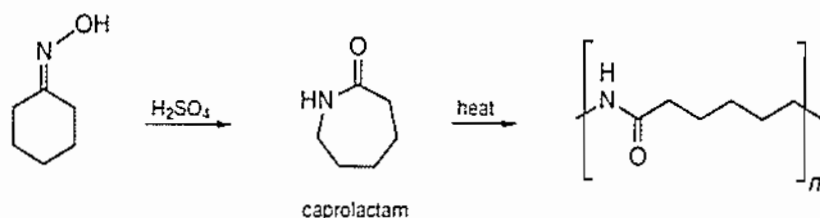
The rearrangement is also induced by reagents other than proton acids. Boron trifluoride removes the hydroxyl group as  $\text{HO}-\text{BF}_3$ , toluene-*p*-sulfonyl chloride forms the oxime tosylate which eliminates the stable tosylate anion,



and phosphorus pentachloride, normally used in ether, induces rearrangement by providing a phosphate as leaving group,

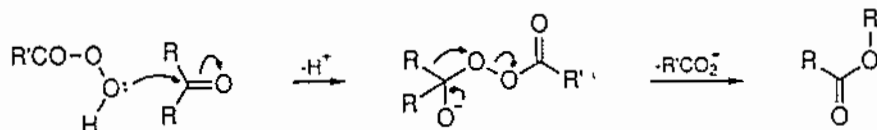


An interesting application of the rearrangement is the synthesis of caprolactam (70%) from cyclohexanone oxime and concentrated sulfuric acid [2], a ring expansion of analogous type to the formation of cycloheptanone from cyclohexanone (p. 435). Caprolactam gives a polymer of the nylon group when heated:



#### 14.4 Rearrangement to electron- deficient oxygen

The most general rearrangement of this type is the *Baeyer-Villiger reaction* in which ketones are converted into esters and cyclic ketones into lactones, by treatment with a peroxyacid. The mechanism is closely related to that of the pinacol rearrangement: nucleophilic attack by the peroxyacid on the carbonyl group gives an intermediate which rearranges with the expulsion of the anion of an acid.



Acids catalyze the reaction by facilitating both the addition to carbonyl and the expulsion of the carboxylate.

A number of peroxyacids, including peroxyacetic, monoperoxyphthalic, and