BECKMANNS REARRANGEMENT

Oximes on reaction with PCl_5 or any other such reagents gets rearranged to form substituted amides. This rearrangement is known as Beckmanns rearrangement.

Examples of other reagents are conc. H₂SO₄, formic acid, liquid SO₂, polyphosphoric acid, thionyl chloride etc.

Stereochemistry of this rearrangement is that the group which is anti to the hydroxyl group migrates. Oxime undergoes isomerisation before migration takes place. R and R' may

be alkyl, aryl or hydrogen. The oximes of cyclic ketones gives ring enlargement. For example,

Mechanism: Initially the –OH group gets converted into a better leaving group i.e. – OH gets converted into $OH_2^{(+)}$. Then the mechanism is just similar to Schmidt reaction.

Beckmann rearrangement can also be carried out photochemically. If the oxime rearrangement is induced by organoaluminium reagents, the intermediate gets captured by the nucleophile originally attached to the aluminium. So, oxime can be converted into an imine, an imino thio ether or an imino nitrile.

$$R^{1}-C-R^{2} \longrightarrow \begin{bmatrix} R^{1}-C=N-R^{2} \end{bmatrix} \xrightarrow{AIR_{3}^{3}} R^{2}-C=N-R^{1} \text{ (Imine)}$$

$$R_{3} \longrightarrow R^{2}-C=N-R^{1} \text{ (Iminothioether)}$$

$$R^{2}-C=N-R^{1} \text{ (Iminothioether)}$$

$$R^{2}-C=N-R^{1} \text{ (Imino nitrite)}$$