

17

Beckmann Rearrangement

Introduction

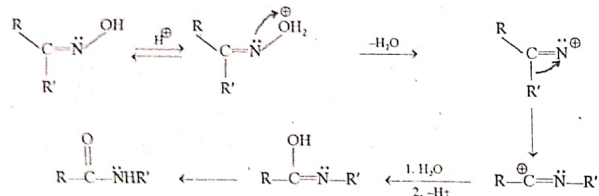
The acid-catalysed rearrangement involving the conversion of ketoximes into amides is known as the Beckmann rearrangement.



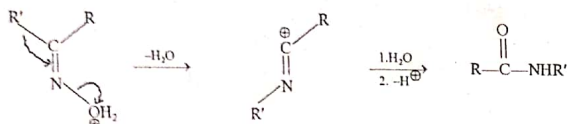
A variety of acidic reagents such as H_3PO_4 , H_2SO_4 , P_2O_5 , SOCl_2 and PCl_5 have been found to catalyse this rearrangement.

Mechanism

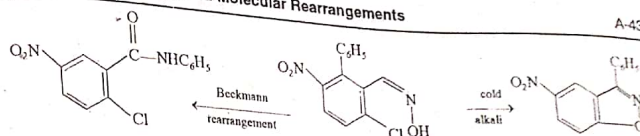
The simplified mechanism of Beckmann rearrangement is as follow :



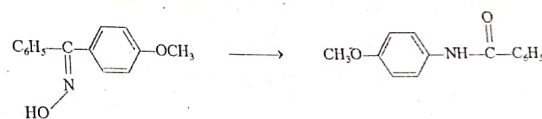
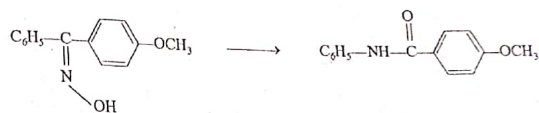
As the migrating group is always approaching the nitrogen atom on the side opposite to the oxygen atom, this rearrangement is highly stereo specific.



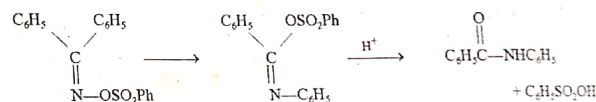
In the above example, there occurs the migration of the R' group to the electron-deficient nitrogen, which is *anti* or *trans* to the hydroxyl group. In a number of cases, there occurs the migration of the *anti* group which has been confirmed in the conversion of 2-chloro-5-nitro-benzophenone oxime to a chloronitrobenzamide. In earlier studies the configuration of this particular oxime was established by its ready conversion to a nitro-substituted phenylbenzoxazole, thereby revealing that the nitrated benzene ring lies on the same side of the $\text{C}=\text{N}$ linkage as the $-\text{OH}$ group. When this oxime is subjected to undergo Beckmann rearrangement, the phenyl group, rather than the nitrated benzene ring, gets migrated to the nitrogen.



As the *anti* group always migrates, it is evident that either the breakage of the $\text{N}-\text{O}$ bond and the group migration are synchronous or these two steps may be following each other quickly. There is so much certainty in the migration of the *anti* group in the Beckmann rearrangement that it is normally the configuration of a particular oxime which can be established readily by identifying its rearrangement products.



It was first found by Kuhara and later by Chapman who ascertained that the rearrangement does not occur in the oxime itself, but in its acyl derivative which gets ionised and then undergoes rearrangement. The ionization of the acyl derivative is the rate-controlling step of the rearrangement. Typically, the benzene sulphonic ester of benzophenone oxime undergoes rearrangement without involving any acid catalyst.



In the Beckmann rearrangement the carbon atom of the migrating group retains its configuration. By carrying out the various series of reactions, Kenyon proved retention of configuration as well as correlated Beckmann and Hofmann rearrangements. In the series of experiments optically active 3-heptylcarboxylic acid after converting into amide was subjected to Hofmann rearrangement. In another series of experiments the same acid was first converted into 3-heptylmethyl ketone and then the oxime of this ketone was subjected to the Beckmann method. Both these rearrangements gave the same optical isomer of 3-heptylamine.