A solvent-free one step conversion of ketones to amides *via* Beckmann rearrangement catalysed by $FeCl_3.6H_2O$ in presence of hydroxylamine hydrochloride

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A solvent-free one step conversion of ketones to amides *via* Beckmann rearrangement catalysed by $FeCl_3.6H_2O$ in presence of hydroxylamine hydrochloride

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Abstract

$FeCl_3.6H_2O$ catalyses the direct conversion of ketones to amides *via* Beckmann rearrangement in presence of hydroxylamine hydrochloride in good to excellent yields. No additional organic solvent is required. This solid phase reaction involves *in situ* formation of oxime, cleavage of C-C bond and formation of C-N bond. $FeCl_3.6H_2O$ is inexpensive, stable, easy to handle and eco-friendly.

Keywords: Beckmann rearrangement, Ferric chloride, eco-friendly, amides, solid phase, solvent-free reaction.

The Beckmann rearrangement (BKR) is a powerful method in organic synthesis for the preparation of amides or lactams from ketones and is often employed in chemical industry especially for the preparation of ε-caprolactam.[1] The conventional BKR of ketoximes occurs in presence of strong Bronsted or Lewis acids such as conc. sulfuric acid, PCl_5 in diethyl ether, hydrogen chloride in acetic anhydride and it results in large amount of by-products, environmental hazards and serious corrosion problems.[2] This rearrangement in vapour phase[3] suffers from low selectivity of ε-caprolactam formed and rapid decay in catalytic activity due to high reaction temperatures.[4] In the liquid phase processes, BKR has been mediated by small organic molecules[5] such as bis(2-oxo-3-oxazolidinyl)phosphinic chloride (BOP-Cl),[5a] 1,3,5-triazo-2,4,6-triphosphorine-2,2,4,4,6,6-chloride (TAPC),[5b] *p*-toluenesulfonyl chloride (TsCl),[5c] 1-chloro-2,3-diphenylcyclo-propenium ion,[5d] bromodimethyl sulfonium bromide-zinc chloride (BDMS-$ZnCl_2$),[5e] propylphosphonic anhydride (T3P),[5f] triphenylphosphine/iodine (Ph_3P/I_2),[5g] 2,4,6-trichloro[1.3.5]triazine[5h] and chloral[5i] as well as by metallic Lewis acids[6] such as[$RhCl(cod)]_2$,[6a] $Yb(OTf)_3$,[6b] $RuCl_3$,[6c] $HgCl_2$,[6d] bismuth(III) chloride,[6e] copper salts,[6f] copper(II)acetate,[6g] indium and zinc salts.[6h] However the reaction conditions became milder in liquid phase but the usage of large amount of organic solvent rendered these methods as less popular due to environmental threats.[7] This reaction has also been reported in supercritical H_2O,[8] ionic liquids[9] and solid phase systems.[10]

It is pertinent to mention here that only few methods have been developed for the single-step conversion[11] of ketones into amides in presence of hydroxylamine hydrochloride *via* Beckmann rearrangement and therefore there still exists a need to find new methodologies which are simpler, cheaper, faster and eco-friendly to facilitate this rearrangement.

In view of this context and also our ongoing efforts[12] to develop newer methodologies, we conceived a solvent free one-pot conversion of ketones to amides using $FeCl_3.6H_2O$ as an environmentally benign catalyst involving *in situ* formation of ketoximes followed by Beckmann rearrangement to the corresponding amides.

To begin with, benzophenone oxime was treated with 1 eq. of various transition metal Lewis acids in dry toluene and 1,2- dichloroethane at their respective refluxing temperature for 3 hrs. and the results are shown in Table 1.