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Application of different catalysts in Beckmann Rearrangement

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ABSTRACT

Many catalysts for the Beckmann rearrangement has attracted researchers attention for their efficiency in catalytic activity and easy to handle during the rearrangement. Efforts are continued for developing new environment friendly catalytic system for the Beckmann rearrangement. In this article, we are going to present some catalysts used for Beckmann rearrangement of ketoximes to corresponding amides.

Keywords: Beckmann rearrangement, catalysts, ε-caprolactam ionic liquids, solid acid catalyst.

INTRODUCTION

The Beckmann rearrangement is a well-known transformation of keto-oximes to N-substituted amides in the presence of an acid. [1,2] More than a century ago, Beckmann first carried out in 1886 the conversion of an oxime into an amide since then, this reaction has been called after his name, the Beckmann rearrangement. With the test of time the Beckmann rearrangement (designated hereafter as BR) has proven to constitute one of the most widely employed transformations of oximes in organic synthesis [3] and is one of the most important methods in organic synthesis.

The most prominent example of its industrial use is probably the large-scale production of the Nylon 6 precursor ε-caprolactam from cyclohexanone oxime. [4]

The Beckmann rearrangement is a typical acid catalyzed reaction. Many attempts to replace sulphuric acid with a solid acid catalyst have been done. Most commonly, the Beckmann rearrangement is carried out in strongly acidic and dehydrating media such as phosphorus pentachloride, concentrated sulphuric acid, or the so-called 'Beckmann's mixture' which contains acetic acid, acetic anhydride and hydrogen chloride. [5] Since these reagents are not suitable for a large number of sensitive substrates, several attempts have been made to achieve the Beckmann rearrangement under significantly milder conditions. In these studies, thionyl chloride, [6] silica gel, [7] molybdenum trioxide on silica gel, [8] montmorillonite KSF, [9] bismuth(III) chloride, [10] 2,4,6-trichloro-1,3,5-triazine, [11] and gallium(III) triflate, [12] P_2O_5, [13] HSO_3Cl, [14] PCl_5, [15] metallic Lewis acid $[RhCl(cod)]_2$, [16] $Yb(OTf)_3$, [17] $RuCl_3$, [18] $HgCl_2$, [19] several liquid-phase catalysis systems, such as sulphamic acid, [20] chlorosulphonic acid, [21] anhydrous oxalic acid, [22] ethyl chloroformate/boron trifluoride etherate, [23] bis(2-oxo-3-oxazolidinyl) phosphoric chloride [24] and diethyl chlorophosphate [25] potential solid acid catalysts such as TS-1, [26] SAPO-11, [27] FSM-16, [28] Y, [29] ZSM-5, [30] ZSM-11, [31] TiO_2-ZrO_2, [32] and mordenite, [33] have been evaluated as substitutes for the traditionally employed reagents. Recently, several lanthanide-containing catalysts [with Ce(III), La(III), and Sm(III) among others] have also been found to effect the rearrangement. [34, 35] The reaction could be performed in the vapor phase, process which has been shown to be applicable even on an industrial scale with the use of a high-silica MFI zeolite as catalyst. [36] It is also possible to initiate the Beckmann rearrangement in supercritical water [37] or ionic liquids. [38]

Recently, organocatalyst for the Beckmann rearrangement has attracted researchers' attention for its efficiency in catalytic activity and easy to handle during the rearrangement. Cyanuric chloride (CNC), [39] as the first organocatalyst, was reported to be a highly efficient catalyst for the Beckmann rearrangement by Ishihara and his co-workers.

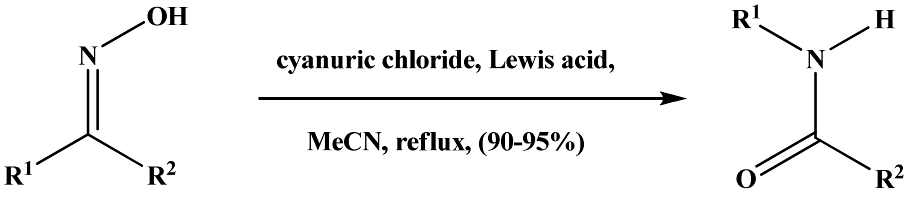
The environmental regulations and process safety continue to drive the industry to develop solid acids to replace liquid acid processes. In the past two decades, various solid catalysts have been applied to the Beckmann rearrangement of cyclohexanone oxime, [39] especially the zeolite catalysts for vapor-phase reactions.

Under mild conditions and without any additional organic solvents, Beckmann rearrangements of several ketoximes were performed in the catalytic media consisting of room temperature ionic liquid. [40]

Catalysts applied in Beckmann rearrangement-

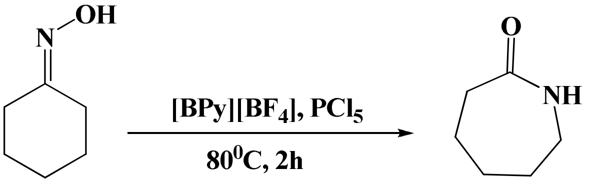
Cyanuric chloride:

Cyanuric chloride is a highly effective catalyst for the organocatalytic Beckmann rearrangement under reflux in acetonitrile or nitromethane. [41]



1,3-dialkylimidazolium or alkylpyridinium salts:

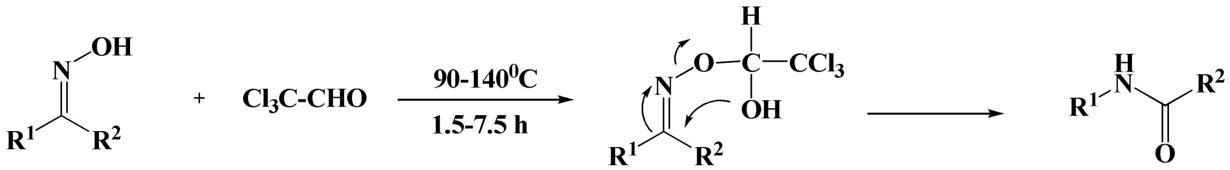
In a recent study by Peng and Deng [42] the catalytic Beckmann rearrangement of several ketoximes was achieved with satisfactory conversion and selectivity in 1,3-dialkylimidazolium or alkylpyridinium salts and phosphorated compounds (PCl_5, $POCl_3$, or P_2O_5)



BPy= N-butylpyridinium

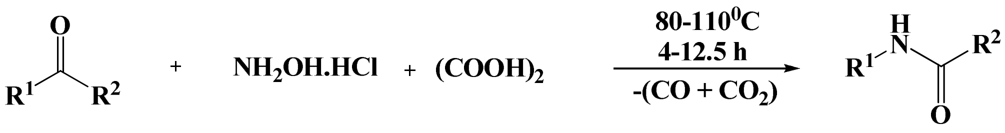
Chloral:

Ketoximes on treatment with chloral underwent rearrangement to the corresponding amides, presumably vi*a* the formation of the oxime hemi-acetal intermediate and aldoximes underwent dehydration to the corresponding nitriles by Beckmann rearrangement. [43]

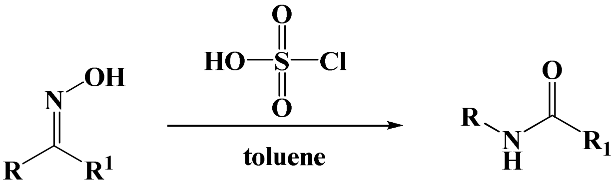


Oxalic acid:

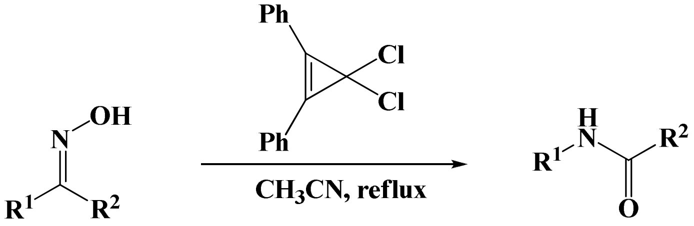
The possible formation of oximes as intermediates in the reaction prompted a study of the Beckmann rearrangement of oximes with $(COOH)_2$ which were successful. [44]



Chlorosulphonic acid:
Under mild conditions, Beckmann rearrangement of a variety of ketoximes could proceed in the presence of chlorosulphonic acid using toluene as a solvent with excellent conversion and selectivity. This procedure could also be applied in the dehydration of aldoximes for obtaining the corresponding nitriles. [45]



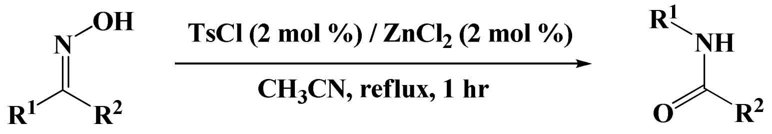
1-Chloro-2,3-diphenylcyclopropenium ion:
1-Chloro-2,3-diphenylcyclopropenium ion was found to be a very efficient organocatalyst for liquid phase Beckmann rearrangement of various ketoximes to the corresponding amides/lactams within 2 h in acetonitrile at reflux temperature. This is the first example of the application of the cyclopropenium ion as a catalyst, which opens up a new aspect of the synthetic utility of aromatic cation based catalysis. [46]



Hexamethylphosphoric triamide (HMPT):
Hexamethylphosphoric triamide (HMPT), in addition to its well known uses as a reaction medium (shows promise of becoming a useful reagent in several dehydration and substitution reactions. [47] Continuing our studies on the uses of this versatile reagent, we now report that the Beckmann rearrangement of ketoximes can be successfully carried out in HMPT.

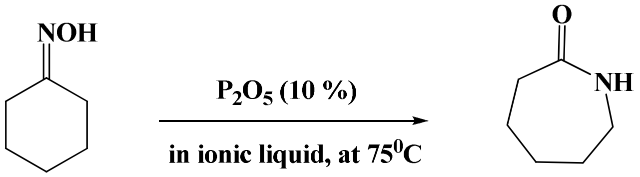
TsCl (p-toluenesulfonyl chloride):
TsCl (p-toluenesulfonyl chloride), a commercially available organosulfonyl chloride, has been widely used as a stoichiometric dehydrogenation reagent in the transformation of ketoximes into corresponding amides via the Beckmann rearrangement. It has been now found to catalyze the Beckmann rearrangement with high catalytic efficiency, converting a wide range of ketoximes into their corresponding amides under mild condition with good to excellent yields (up to 99% of yield with 1-5 mol % of catalyst loading). [48]

TsCl/ZnCl$_2$:
The Beckmann Rearrangement of ketoximes to amides catalyzed by TsCl or TsCl/ZnCl$_2$ catalyst systems had investigated. It is obvious that excellent yields were obtained for most of oximes, aromatic oximes in particular, in acetonitrile under reflux condition for 1 h with TsCl/ZnCl$_2$ thanTsCl. [48]



Phosphorous pentoxide:
Catalytic Beckmann rearrangement of cyclohexanone oxime using catalytic amount of P_2O_5 or Eaton's reagent has been successfully carried out in bmiPF$_6$.

When catalytic amount (20 mol %) of phosphorous pentoxide (P_2O_5) was used in ionic liquid bmiBF$_4$, conversion to ε-caprolactam was low (32%), and hydrolysis to cyclohexanone reached to 66%. [49]



B_2O_3:

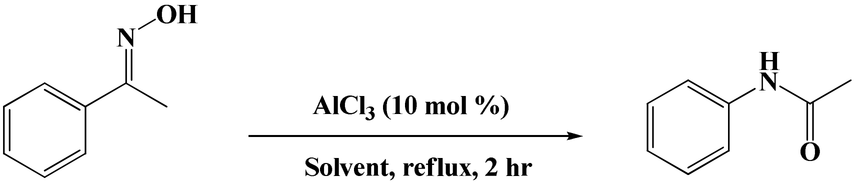
Dawydoff (Leunawerke) [50] verified that the catalysts mainly composed of B_2O_3 gave an excellent selectivity to ε-caprolactam with a very good conversion of cyclohexanone oxime. According to the patents [51, 52] ε-caprolactam was produced in >95% yield. The conversion and selectivity were very high however, the vapor phase Beckmann rearrangement process based on the B_2O_3 catalysts has not yet been commercialized.

$BF_3{\cdot}OEt_2$:

$BF_3{\cdot}OEt_2$ (Boron trifluoride etherate) in presence hydroxylamine hydrochloride is an inexpensive and commercially easily available Lewis acid stoichiometrically employed for Beckamann rearrangement in general, was now found to efficiently catalyse Beckmann rearrangement of ketoximes into their corresponding amides (up to 99% yield) in anhydrous acetonitrile under reflux temperature. [53]

Aluminum chloride:

Aluminum chloride, an inexpensive and commercially available Lewis acid traditionally employed for Beckmann rearrangement with stoichiometric amounts, has been now found to smoothly promote the Beckmann rearrangement of various ketoximes to the corresponding amides (up to 99% of yield) with 10 mol% catalyst loading in anhydrous acetonitrile under reflux temperature. [54]



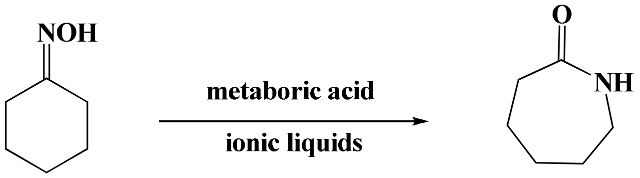
Sulphonyl chloride:

Under mild conditions and without any additional organic solvents, Beckmann rearrangement of ketoximes was performed in a novel task-specific ionic liquid consisting sulphonyl chloride. Especially for the conversion of cyclohexanone oxime to ε-caprolactam, ε-caprolactam has good solubility in water while the task-specific ionic liquid is immiscible with water, therefore, ε-caprolactam could be easily separated from the reaction system by water extraction. [55]

Metaboric acid:

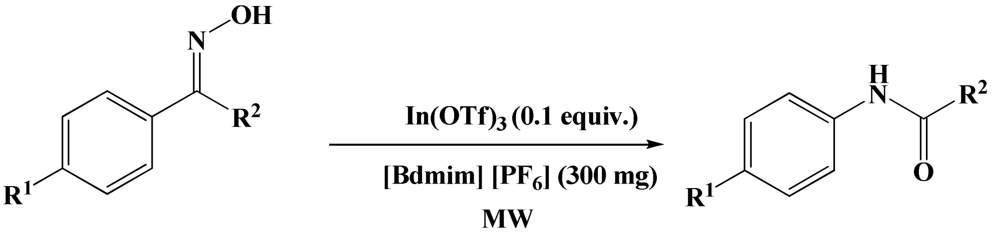
Chandrasekhar and Gopalaiah [56] investigated solid metaboric acid catalyzed Beckmann rearrangement of ketoximes. Beckmann rearrangement of several oximes catalyzed by metaboric acid was studied in room temperature ionic liquids. Especially for conversion of cyclohexanone oxime into ε-caprolactam, excellent conversion and selectivity were obtained.

$$n\ B(OH)_3\ \text{(Boric Acid)} \xrightarrow[-n(H_2O)]{120^0C} (HBO_2)_n$$



Aluminium orthophosphates:
The Aluminium orthophosphates systems used in this study show promising catalytic activity for this process. The acidity of the catalyst is the main variable to be considered, but at the same time such an increase in acidity adds to the secondary process of fragmentation that disagrees with the proposal of rearrangement. [57]

In(OTf)$_3$:
Beckmann rearrangement of aryl ketoximes catalyzed by In(OTf)$_3$ gave amides in ionic liquid under microwave irradiation. Aryl ketoximes were converted to corresponding amides in good yield within very short times (10-270 s). The catalyst and the ionic liquid were easily recovered and reused. [58]



Tungstated zirconia catalysts:
Tungstated zirconia catalysts are employed for liquid-phase Beckmann rearrangement of 4-hydroxyacetophenone oxime to N-acetyl-p-aminophenol. Tungstated zirconia possesses some advantages such as higher stability under high-temperature treatments and reductive atmospheres, lower deactivation rates and easier regeneration. [59]

Titanium silicalite (TS-1):
Titanium silicalite, TS-1 belong to the MFI type of zeolites. TS-1 is found to be the better catalyst for the transformation of cyclohexanone oxime into ε-caprolactam than the other MFI zeolites, viz., ZSM-5 and Silicalite-1. The incorporation of Ti increases the yield of ε-caprolactam, besides lowering the deactivation rate. Both oxime conversion and selectivity for the lactam increase with increasing Ti content in the zeolite. [60]

Tantalum pillared-ilerite:
The vapor phase Beckmann rearrangement of cyclohexanone oxime has been studied using a novel tantalum pillared-ilerite as catalyst: the cyclohexanone oxime conversion rate reaches 97.1% and the selectivity for ε-caprolactam is up to 89.1% at 350°C. [61]

Nano-Ordered Zn-MCM-41:
Nano-Ordered Zn-MCM-41 materials were synthesized using different zinc sources and applied for liquid phase Beckman rearrangement of 4-hydroxyacetophenone oxime to acetaminophenone. The reaction conditions such as amount of the catalyst and solvent were optimized to afford acetaminophenone in high yields. It was found that aprotic solvents with high dielectric constant are preferred for this transformation. [62]

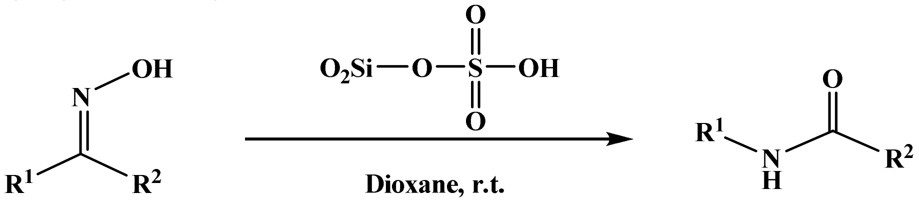
Silferc (anhydrous FeCl$_3$ supported on silica-gel by co-grinding method):
Beckmann rearrangement of substituted benzophenone and acetophenone oximes had been done using 'silferc' under milder conditions. The catalyst could effectively bring about the rearrangement of substituted benzophenone oximes in catalytic amount and it also gave reusability for atleast one run. Although the yields of corresponding rearrangement product in case of substituted acetophenone oximes are low, the method eliminates the use of various hazardous reagents which are otherwise used to bring about the reaction, thereby reducing the amount of toxic by-products generated at the end of the process. [63]

Silanol:
Recently, H¨olderich and co-workers [64] investigated the contribution of different kinds of silanols- terminal (3740 cm^{-1}), vicinal (3680 cm^{-1}) and nests (around 3500 cm^{-1}) to the catalytic activity and selectivity. They concluded that the silanol nests were most suitable for the reaction and that the vicinal silanol groups were more favourable than the terminal silanols.

Layered silicates:
Layered silicates, such as kanemite ($NaHSi_2O_5{\cdot}3H_2O$), magadiite ($Na_2Si_{14}O_{29}{\cdot}11H_2O$), kenyaite ($K_2Si_{20}O_4{\cdot}11H_2O$), makatite ($Na_2Si_4O_9{\cdot}5H_2O$) and ilerite ($Na_2Si_8O_{17}{\cdot}xH_2O$) are composed of tetrahedral silicate sheets only and the each silicate sheet is terminated by hydroxy groups. Layered silicates, therefore, possess abundant hydroxy groups oriented in a crystallographically regular manner, and have a great potential to act as new catalysts for the vapor phase Beckmann rearrangement reaction. [65]

H-USY zeolite with different SiO_2/Al_2O_3:
Dai et al. [66] studied the catalysis of H-USY zeolite with different SiO_2/Al_2O_3 ratios in the co-presence of 1-hexanol. They showed that an appropriate amount of relatively weak acid sites of H-USY were effective for a high selectivity.

Silica sulphuric acid:
Silica sulphuric acid in which sulphuric acid is immobilized on the surface of silica gel *via* covalent bond has been proved to be green catalyst for liquid-phase Beckmann rearrangement of oximes in dried dioxane at room temperature. Excellent conversion and selectivity were acquired in the Beckmann rearrangement of cyclohexanone oxime. The catalyst system was recycled and reused. [67]



WO_3/SiO_2 gel:
Kob et al. [68] performed the vapor phase Beckmann rearrangement reaction using WO_3/SiO_2 gel catalysts and revealed that the acid property of the catalyst affected the activity and selectivity. They concluded that strong acid sites were more favorable to the reaction than weak acid ones.

Silica supported molybdenum (VI) oxide:
Silica supported molybdenum (VI) oxide (20%) has been explored as a new solid catalyst for the Beckmann rearrangement and the results are compared in parallel with the known b-zeolite as a catalyst for the same transformation. Both catalysts were found to facilitate the rearrangement under mild conditions and the conditions employed were tolerable for protecting groups such as isopropylidene, cyclohexylidene and PMB are commonly employed in carbohydrate chemistry.

Among the supported oxides, V_2O_5/SiO_2, ZrO_2/SiO_2, PbO/SiO_2 and MoO_3/SiO_2, MoO_3 /SiO_2 had revealed the highest activity and selectivity. [69]

High silica MFI zeolite catalysts:
Aucejo et al. [70] studied the vapor phase Beckmann rearrangement with some MFI zeolites (equivalent to ZSM-5) as a catalyst. The zeolites of large external surface area gave high conversion of cyclohexanone oxime. They strongly suggested that the vapor phase Beckmann reaction took place on the outer surface of the catalyst and the active sites might be different from the acid sites caused by Al.

MCM-22:
There are several reasons which indicate, that the MCM-22 could be a good catalyst for the Beckmann rearrangement of cyclohexanone oxime. MCM-22 has according to [71] a large and good accessible external surface, which should be ideal for a fast external surface reaction like the Beckmann rearrangement. In particular, owing to its extraordinarily large extra crystalline surface area compared to its zeolite counterparts, MCM-22 is more preferable in Beckmann rearrangement.

SBA-15 (SBA-or-SO_3H):
Beckmann rearrangement of cyclohexanone oxime to *ε*-caprolactam was performed in liquid phase for the first time on arenesulphonic acidfunctionalized SBA-15 (SBA-or-SO_3H) mesoporous silica with different loadings of the acid. The catalytic activity of SBA-or-SO_3H was also compared with the activities of other solid acid catalysts such as propylenesulphonic acid-functionalized SBA-15, H-ZSM-5, H-mordernite, Al-MCM-41 and Al-SBA-15. The results revealed that SBA-ar-SO_3H has higher catalytic activity and lactam selectivity. [72]

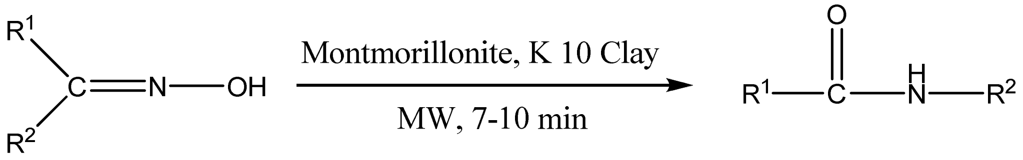
H-ZSM-5:
Fois et al. [73] studied the vapor phase of the Beckmann rearrangement in H-Faujasite, H-ZSM-5, and silicalite-1 by using IR spectroscopy and found that (a) both internal silanols and strong acid sites in zeolite can catalyze the Beckmann rearrangement of cyclohexanone oxime, (b) a stable protonated intermediate is formed on a strong acid site, and (c) the reaction at weak acid sites has a higher activation energy through a mechanism not involving a protonated intermediate.

M41S:
The discovery of mesoporous molecular sieves of M41S family has attracted much attention of many research groups because these materials are likely to offer improved reaction activity in the conversion of larger substrate molecules in their well defined channels with narrow pore size distribution. [74]

Al-MCM-41 and Al-SBA-15:
The acidity of mesoporous materials like Al-MCM-41 and Al-SBA-15 is much weaker than that of microporous zeolites. [75] In order to overcome this drawback, ordered sulphonic-acid modified mesoporous silica has been prepared either via post-grafting technique or through one-pot synthesis. [76]

BOP-Cl15 (bis(2-oxo-3-oxazolidinyl)phosphinic chloride) and triphosphazene (TAPC):
BOP-Cl15 (bis(2-oxo-3-oxazolidinyl)phosphinic chloride) as the first highly efficient organophosphorus catalyst for the Beckmann rearrangement, then the second generation of organophosphorus catalyst triphosphazene (TAPC). [77]

Montmorillonite K 10:
Bosch *et al.* have achieved the Beckmann rearrangement of ketoximes with montmorillonite K 10 clay in ‘dry’ media in good yields. [78]



Activated Fly ash:
Activated Fly ash, an industrial waste (pollutant) is found to be well suited for catalyzing reactions which are having industrial, pharmacological and therapeutic importance, e.g. Knoevenagel condensation, ‘One-Pot’ conversions of ketones to amides, via, Beckmann rearrangement, Schiff Bases formation, Biginelli and Hantzsch reactions under microwave irradiation in solvent-free conditions. Moreover, this catalyst shows a promising future in that it can provide environmentally clean processes for the chemical industry. [79]

Supercritical water:
Recently, the Beckmann rearrangement in supercritical water has been reported, in which, although there were no serious corrosion problems and excellent selectivity for *ε*-caprolactam was obtained, very low conversion and rigorous reaction conditions make the above approach utilisable only in research. [80]

Ionic liquids:
Six Bronsted acidic ionic liquids (ILs) 1a-1f were synthesized and used as the dual solvent catalyst systems for Beckmann rearrangement reactions. Among ILs 1a-1f, IL 1a exhibited the highest catalytic activity and successfully catalyzed the Beckmann rearrangement of ketoximes and the corresponding amides were obtained in good to excellent yields (74%-92%). In addition, IL 1a could be recovered easily and reused at least three times without any loss of catalytic activity. [81]

Deng *et al*. [82] have carried out the Beckmann rearrangements of oximes into amides using RTILs based on *N,N*-dialkylimidazolium salts or *n*-butylpyridinium tetrafluoroborate in the presence of PCl_5, P_2O_5 or H_3BO_3 as a catalyst, which showed high conversion and selectivity, especially for *ε*-caprolactam.

Beckmann rearrangement catalyzed by the combined use of tetrabutylammonium perrhenate(VII) and trifluoromethanesulfonic acid has been studied. [83] Arisawa and Yamaguchi found that a small amount of rhodium complex could promote the reaction of ketoxime and trifluoromethanesulfonic acid. [84]

CONCLUSION

The rearrangement generally requires high reaction temperatures and a large amount of a strong Bronsted acid and dehydrating media, causing large numbers of by-products and serious corrosion problems. Hence, over the past half century, extensive efforts have been devoted to the optimization of the catalytic reaction system. Many catalytic systems such as liquid-phase system, vapor-phase system, supercritical water system and ionic liquid system have been developed so far. Liquid-phase catalytic Beckmann rearrangement under mild conditions has become a topic of current interest because of its advantages such as easy workup and industrial practicability. As a consequence, various catalysts such as inorganic catalysts, organocatalysts, and metallic Lewis acid systems were developed.

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