

Sulfonic Acid Modified MCM-41 Mesoporous Silica as an Efficient Nano-Catalyst for Synthesis of amides and lactams from Oximes Via Beckman Rearrangement

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Abstract

Mesoporous MCM-41 silicas anchored with sulfonic acid ($-\text{SO}_3\text{H}$) groups (denoted MSN-SA) via postsynthesis modification are very effective for the Beckman rearrangement. A simple and convenient procedure for conversion of a variety oximes to their corresponding amides and lactams has been developed. The reaction was carried out in the presence of MSN-SA as the catalyst. The best results for conversion of oximes to amides and lactams were obtained in the presence of MSN-SA and solvent free condition at 110 °C. Excellent yields were obtained from oximes with electron-donating and electron-withdrawing groups. The system also worked well with polynuclear aromatic, heterocyclic and aliphatic oximes.

Keywords: Oxime, MCM-4; Sulfonic acid; Beckman rearrangement.

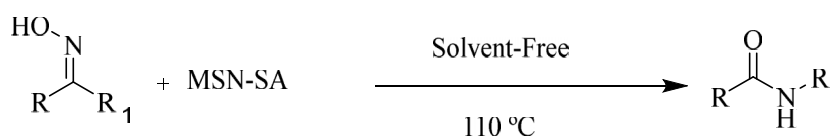
Introduction

Amides and lactams are an important class of organic compounds. Amids and lactames are useful precursors for the synthesis of amines, amides, ketones, carboxylic acids and esters which are useful raw materials for pharmaceuticals, agrochemicals and dyes [1].

Numerous methods to synthesize amids and lactames have been documented in the literature, such as the Sandmeyer reaction [2], metal-catalyzed cyanation of aryl halides, oxidation of amines, [3] and dehydration of amides and oximes [4]. Dehydration of oximes into amids and lactames is one of the most attractive procedures for the synthesis of amids and lactames as

the availability of starting material and the avoidance of very toxic cyanide ion. In recent years a number of efficient reagents and conditions have been reported for the dehydration of oximes to amids and lactames such as $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}/\text{KI}/\text{H}_2\text{O}/\text{CH}_3\text{CN}$ [5], 1H-benzotriazol-1-yl-oxo-tris(dimethylamino)phosphonium hexafluorophosphate (BOP) [6], N-chlorosuccinimide/pyridine [7], diethylchlorophosphate [8], $\text{ZnO}/\text{CH}_3\text{COCl}$, N-triflylimidazole [9], N,N,N',N'-Tetrabromobenzene-1,3-disulfonamide (TBBDA)/triphenylphosphine and N,N,N',N'-tetra-chlorobenzene-1,3-disulfonamide (TCBDA)/triphenylphosphine [10], $\text{Ac}_2\text{O}/\text{K}_2\text{CO}_3/\text{DMSO}$ [11] and O-sulfonate esters of oxyma [12] as a dehydrating agent, and Tungsten-tin

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R= Aliphatics, Aromatics, Polynuclear Aromatics, Heterocyclics

Scheme 1. MSN-SA catalysed Beckman rearrangement

mixed hydroxide [13], Pd(OAc)₂/PPh₃ [14], melamine-formaldehyde resin supported sulfuric acid [15], Cobalt(II) chloride [16], Copper(II) acetate [17], propylphosphonic anhydride [18] and PEG-SO₃H [19] as a catalyst.

However, some of these modifications suffer from drawbacks such as toxicity, the use of toxic solvents, expensive reagents, production of considerable amounts of by-products, long reaction times and low yields. Therefore, to improve the mentioned limitations, we decided to apply a new reaction media for the conversion of oximes to amids and lactames.

Herein we report a simple and efficient process for rearrangement of oximes to amids and lactames in the presence of MSN-SA in solvent free conditions under heating (Scheme 1). The method is simple, isolation of the product from reaction mixture is easy and the yields are high.

Materials and Methods

All products were known and their physical and spectroscopic data were compared to those of authentic samples. Chemicals were either prepared in our laboratories or were purchased from Fluka or Merck. MSN-SA was purchased from Sigma-Aldrich. The purity of the products was determined by TLC on silica gel polygram SIL G/UV 254 plates. IR spectra were obtained using a Shimadzu FT-IR 8300 spectrophotometer. NMR spectra were recorded on a Bruker Avance DPX-250 (¹H-NMR 250 MHz and ¹³C NMR 62.9 MHz) spectrometer in pure deuterated solvents with tetramethylsilane as an internal standard. Melting points were recorded on a Büchi B-545 (Swiss) apparatus in open capillary tubes.

2-1 Preparation of sulfonic acid functionalized MCM-41

Pure silica MCM-41 was synthesized according to the method described earlier [20]. Surface functionalization with sulfonic acid groups was carried out according to the method described in the literature. [21,22] For this, freshly prepared MCM-41 (1 g) and

dry dichloromethane (20 ml) was charged in a round flask equipped with a heater and magnetic stirrer. 1,4-butanediol (0.5 g) was added and stirred for 24 hours at room temperature. The product was filtrated and washed with dichloromethane (3 × 5 ml) and then with 5 ml of concentrated sulfuric acid. The solid product was dried at reduced pressure and used as catalyst in the reactions.

2-2- General Procedure for rearrangement of Oximes to Amids and lactames

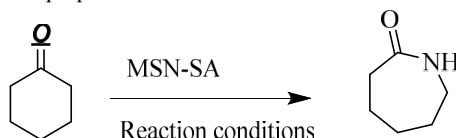
Oxime (2mmol) and MSN-SA (1 gr) were charged into a 25 ml round-bottom flask equipped with a magnetic stirrer and condenser. The reaction was heated in an oil bath to 119 °C. The progress of reactions was monitored by TLC. After completion of reaction the mixture was cooled to room temperature. The crude mixture was neutralized with 10 ml of an aqueous solution of HCl (5%) and then extracted with diethyl ether (10 ml), dried over anhydrous sodium sulfate and was evaporated. The crud product was purified by column chromatography on silica gel with petroleum ether and ethyl acetate (70:30) to give the pure product.

Results and Discussion

At the first stage of research, the transformation of 4-nitrobenzoxime to 4-nitrobenzamide and lactame in the presence MSN-SA in various solvents and also under solvent-free conditions was investigated. The results were summarized in Table 1.

According to Table 1, the best results for dehydration of oximes to amids and lactames were obtained in the presence of MSN-SA and solvent free condition at 110 °C, where the molar ratio of MSN-SA and oxime is 1.2:1 (Table 1, entrie 8)

The reaction is carried out on a series of the prepared oximes with different substituents (hydroxyl, methyl, chloro, nitro, and dimethylamino groups in *ortho*-, *para*-, and *meta*-positions (Table 2, entries 1–8 and 14), polynuclear aromatic (Table 2, entries 9–11), heterocyclic (Table 2, entries 12 and 13) and aliphatic oximes (Table 2, entrie 15) under similar reaction

Table 1. Effect of solvent on the preparation of 4-nitrobenzamide and lactame in the presence MSN-SA.

Entry	Reaction Conditions	Equivalent of reagent	Yield (%) ^a
1	CH ₂ Cl ₂ / Reflux /2 hrs	1	-
2	Toluene/Reflux/5 hrs	1	55
3	CH ₃ CN/Reflux/ 2 hrs	1	-
4	DMF/Reflux/5 hrs	1	30
5	H ₂ O/Reflux/2 hrs	1	-
6	EtOH/Reflux/2 hrs	1	-
7	Solvent free/110 °C/25 min	1	80
8	Solvent free/110 °C/10 min	1.2	92
9	Solvent free/110 °C/10 min	1.5	93

^a Isolated Yield**Table 2.** Dehydration of Oximes to Amids and lactames in the Presence of MSN-SA under Solvent Free Conditions 110 °C.^a


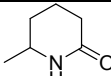

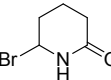
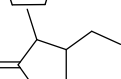
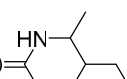

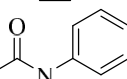
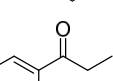
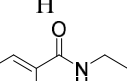

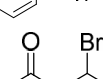

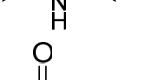

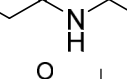
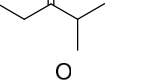
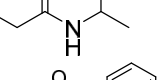
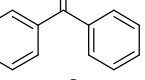
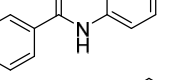

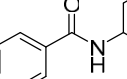
Entry	Starting material	Amids and lactame	Yield (%) ^b	m.p. (°C)	Ref.
1			92	66-69	15
2			89	101-103	13
3			90	71-74	13
4			85	79-81	6
5			89	147-149	6

conditions.

According to Table 2, excellent to good yields were

obtained from benzoximes with electron-donating, electron-withdrawing groups, polynuclear aromatic,

Table 2. Cntd

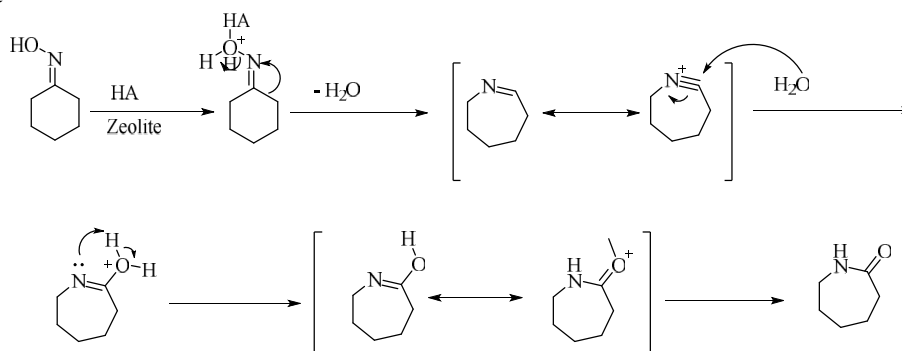
6			91	64-65	6
7			87		7
8			83	94-96	14
9 ^c			94	111-114	7
10			92	91-92	14
11			89	99-102	
12			90	oily	14
13			91	42-44	14
14			93	136-137	14
15			94	156-158	7
16			90	103-105	14

^a All the products are known and characterized by spectroscopic data (IR, ¹H and ¹³C NMR).

^b Isolated yield.

^c Reaction carried out with 2eq of sulfur trioxide pyridine.

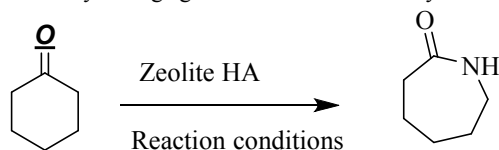
^d Boiling point



Scheme 2. Proposed mechanism for MSN-SA catalyzed Beckman rearrangement

heterocyclic and aliphatic oximes. Proposed mechanism

can be seen in Scheme 2.

Table 3. Comparison between different dehydrating agents with MSN-SA for synthesis of 4-Nitrobenzoamids and lactame.

Entry	Reagents	Reaction conditions	Yield[%]	Ref.
1	N-triflylimidazole	CH ₂ Cl ₂ , N ₂ , RT, 12 h	76	10
2	diethylchlorophosphate	Toluene, reflux, 35 min	92	9
3	TBBDA/PPh ₃	CH ₃ CN, RT, 10 min	92	11
4	Ac ₂ O/K ₂ CO ₃	DMSO, 50 °C, 10 min	91	12
5	sulfonate esters of oxim	CH ₂ Cl ₂ , DBU, N ₂ , RT, 10 min	89	13
6	MSN-SA	Solvent free, 110 °C, 10 min	92	This work

To show the advantage of MSN-SA over some of the reported reagents in the literature, we have tabulated some of the results in Table 3. As evident from the results, in comparison with the other reported reagents in literature, MSN-SA is comparable with some of these reagents and gives better yield in shorter reaction time than others. Solvent free condition is the most important advantage of this reagent in comparison with all of them.

References

- Miller J. S., Manson J. L., Designer magnets containing cyanides and amids and lactames. *Acc Chem Res.* **34(7)**:563-570 (2001).
- Sundermeier M., Zapf A., Beller J., MPalladium-Catalyzed Cyanation of Aryl Halides: Recent Developments and Perspectives. *Eur. J. Inorg. Chem.* **19**:3513–3526 (2003).
- Fatiadi A. J., Preparation and Synthetic Applications of Cyano Compounds. *Triple-Bonded Functional Groups.* **2**:1057-1303 (1983).
- (a) Narsaiah A. V., Nagaiah K., An Efficient and Improved Method for the Preparation of Amids and lactames from Primary Amides and Oximes. *Adv. Synth. Catal.* **346(11)**:1271–1274 (2004); (b) Ishihara K., Furuya Y., Yamamoto H., Rhenium(VII) Oxo Complexes as Extremely Active Catalysts in the Dehydration of Primary Amides and Oximes to Amids and lactames. *Angew. Chem.* **114(16)**:3109–3112 (2002); (c) Khalili S. B., Sardarian A. R., KF/Al₂O₃: an efficient solid heterogeneous base catalyst in one-pot synthesis of benzimidazoles and bis-benzimidazoles at room temperature. *Monatsh Chem* **143**:841–846 (2012); (d) Bahadorikhalili S., Ma'mani L., Mahdavi H., Shafiee A., Palladium catalyst supported on PEGylated imidazolium based phosphinite ionic liquidmodified magnetic silica core-shell nanoparticles: a worthy and highly water-dispersible catalyst for organic reactions in water. *RSC Adv.* **5**:71297-71305 (2015).
- (a) Boruah M., Konwar D. AlCl₃.6H₂O/KI/H₂O/CHCN: a new alternate system for dehydration of oximes and amides in hydrated media. *J Org Chem.* **67 (20)**:7138-7139 (2002); (b) Saboury A. A., Poorakbar E., Rezaei-Behbahani G, A calorimetric study of the interaction of silver ions with jack bean urease. *Turk J Chem* **34 (4)**:631-638 (2010).
- Singh M. K., Lakshman M. K., A Simple Synthesis of Amids and lactames from Oximes. *J Org Chem.* **74(8)**:3079–3084 (2009).
- Gucma M., Golebiewski W. M., Convenient Conversion of Oximes into Amids and lactames with N-Chlorosuccinimide and Pyridine. *Synthesis*, 1997-1999 (2008).
- Sardarian A. R., Shahsavari-Fard Z., Shahsavari H. R., Ebrahimi Z. Efficient Beckmann rearrangement and dehydration of oximes via phosphonate intermediates. *Tet Lett.* **48(14)**:2639–2643 (2007).
- Kalkhambkar R. G., Bunge S. D., Laali K. K., Reaction of triflyl-imidazole with oximes: facile synthesis of amids and lactames and formation of novel oxime-bis(N-triflyl)-imidazole adducts. *Tet Lett.* **52(40)**:5184–5187 (2011).
- Ghorbani-Vaghei R., Shiri L., Ghorbani-Choghamarani A., An efficient, rapid and facile procedure for conversion of oximes to amids and lactames using triphenylphosphine and N-halo sulfonamides. *Chinese Chem Lett.* **24(12)**:1123–1126 (2013).
- Song Y., Shen D., Zhang Q., Chen B., Xu G., Ac₂O/K₂CO₃/DMSO: an efficient and practical reagent system for the synthesis of amids and lactames from oximes. *Tet Lett.* **55(2)**:639–641 (2014).
- Dev D., Palakurthy N. B., Kumar N., Mandal B., An unexpected involvement of ethyl-2-cyano-2-(hydroxyimino) acetate cleaved product in the promotion of the synthesis of amids and lactames from oximes: mechanistic perception. *Tet Lett.* **54(33)**:4397–4400 (2013).
- Yamaguchi K., Fujiwara H., Ogasawara Y., Kotani M., Mizuno N., A Tungsten-Tin Mixed Hydroxide as an Efficient Heterogeneous Catalyst for Dehydration of Oximes to Amids and lactames. *Angew. Chem Int Ed.* **46(21)**:3922-3925 (2007).
- Kim H. S., Kim S. H., Kim S. H. Highly efficient Pd-catalyzed synthesis of amids and lactames from oximes. *Tet Lett.* **50(15)**:1717–1719 (2009).
- Rezaei R., Karami M. Microwave promoted rapid dehydration of oximes to amids and lactames using melamine-formaldehyde resin supported sulphuric acid in dry media. *Chin Chem Lett.* **22 (7)**:815-818 (2011).
- Tamilselvan P., Basavaraju Y. B., Sampathkumar E.,

- Murugesan R. Cobalt(II) catalyzed dehydration of oximes: A highly efficient practical procedure for the synthesis of amids and lactames. *Catal Comm.* **10(5)**:716-719 (2009).
17. Jiang N., Ragauskas A. J., Ultrasound-promoted synthesis of amids and lactames from oximes under ambient conditions. *Tet Lett.* **51(34)**:4479-4481 (2010).
 18. Augustine J. K., Kumar R., Bombrun A., Mandal A. B., An efficient catalytic method for the Beckmann rearrangement of ketoximes to amides and oximes to amids and lactames mediated by propylphosphonic anhydride (T3P). *Tet Lett.* **52(10)**:1074-1077 (2011).
 19. Wang X. C., Li L., Quan Z., Gong H. P., Ye, L., Cao, X. F. PEG-SO₃H as catalyst for the Beckmann rearrangement and dehydration of oximes. *Chin Chem Lett.* **20(6)**:651-655 (2009).
 20. Das D., Tsai C.M., Cheng S. Improvement of hydrothermal stability of MCM-41 mesoporous molecular sieve. *Chem. Commun.*, **5**:473-474 (1999).
 21. Bossert W. D., De vos D. E., Van Rhijn W. M., Bullen J., Grobet P. J., Jacobs P. A. Mesoporous sulfonic acids as selective heterogeneous catalysts for the synthesis of monoglycerides. *J. Catal.*, **182**:156-164 (1999).
 22. Lim M. H., Blanford C. F., Stein A., Synthesis of ordered microporous silicates with organosulfur surface groups and their applications as solid acid catalysts. *Chem. Mater.*, **10**:467-470 (1998).